Environmental Pollution 230 (2017) 405–412

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Emissions of fine particulate nitrated phenols from the burning of five common types of biomass☆

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ARTICLE INFO

Article history:
Received 18 February 2017
Received in revised form
21 June 2017
Accepted 21 June 2017

Keywords:
Nitrated phenols
Emission
Biomass burning
Fine particulate matter
Smoke

ABSTRACT

Nitrated phenols are among the major constituents of brown carbon and affect both climates and ecosystems. However, emissions from biomass burning, which comprise one of the most important primary sources of atmospheric nitrated phenols, are not well understood. In this study, the concentrations and proportions of 10 nitrated phenols, including nitrophenols, nitrocatechols, nitrosalicylic acids, and dinitrophenol, in fine particles from biomass smoke were determined under three different burning conditions (flaming, weakly flaming, and smoldering) with five common types of biomass (leaves, branches, corncob, corn stalk, and wheat straw). The total abundances of fine nitrated phenols produced by biomass burning ranged from 2.0 to 99.5 μg m^{-3}. The compositions of nitrated phenols varied with biomass types and burning conditions. 4-nitrocatechol and methyl nitrocatechols were generally most abundant, accounting for up to 88–95% of total nitrated phenols in flaming burning condition. The emission ratios of nitrated phenols to $PM_{2.5}$ increased with the completeness of combustion and ranged from 7 to 45 ppmm and from 239 to 1081 ppmm for smoldering and flaming burning, respectively. The ratios of fine nitrated phenols to organic matter in biomass burning aerosols were comparable to or lower than those in ambient aerosols affected by biomass burning, indicating that secondary formation contributed to ambient levels of fine nitrated phenols. The emission factors of fine nitrated phenols from flaming biomass burning were estimated based on the measured mass fractions and the $PM_{2.5}$ emission factors from literature and were approximately 0.75–11.1 mg kg^{-1}. According to calculations based on corn and wheat production in 31 Chinese provinces in 2013, the total estimated emission of fine nitrated phenols from the burning of corncobs, corn stalks, and wheat straw was 670 t. This work highlights the apparent emission of methyl nitrocatechols from biomass burning and provides basic data for modeling studies.

1. Introduction

Nitrated phenols have adverse effects on organisms and the environment. Nitrated phenols in the atmosphere originate not only from the emissions of various anthropogenic activities, including the combustion of biomass and fossil fuels and production and use of pesticides, insecticides, herbicides, and dyes (Nojima et al., 1983; Tremp, 1992; Tremp et al., 1993; Harrison et al., 2005a), but also from the secondary transformation of phenolic compounds and aromatic hydrocarbons in the presence of reactive nitrogen oxides and oxidants (Harrison et al., 2005a; 2005b; Yuan et al., 2016). Most nitrated phenols are toxic and therefore harm human health and ecosystem productivity (Rippen et al., 1987). In addition, nitrated phenols can absorb sunlight at wavelengths near UV and visible light and serve as a major component of brown carbon, thus affecting global radiative forcing and regional climates (Mohr et al., 2013).

Biomass burning is considered to be one of the most important sources of nitrated phenols both regionally and globally. In recent years, several field studies have identified atmospheric nitrated phenols in diverse locations affected by biomass burning. For example, Iinuma et al. (2010) identified 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-5-nitrocatechol (3M5NC), and 3-methyl-6-nitrocatechol (3M6NC) in PM_{10} samples from a rural residential area in Seiffen, Saxony, Germany in the winter of 2007. There, good

☆ This paper has been recommended for acceptance by B. Nowack.
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http://dx.doi.org/10.1016/j.envpol.2017.06.072
0269-7491/

correlations between nitrated phenols and levoglucosan strongly suggested that the former originated primarily from biomass burning. Desyaterik et al. (2013) detected abundant 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), and 4-nitrocatechol (4NC) in cloud water collected at Mount Tai in North China during the burning of wheat straw in June 2008. In Brazil, Claeys et al. (2012) also identified 4-NC, 4M5NC, and 3M5NC in particles associated with biomass burning. Mohr et al. (2013) observed high levels of nitrophenol (NP), methylnitrophenols (MNPs), NC, methylnitrocatechols (MNCs), and dinitrophenol (DNP) in Detlig, UK during the winter of 2012, when domestic wood burning was prevalent. Furthermore, Chow et al. (2015) suggested an association of elevated nitrated phenols in Hong Kong during autumn and winter with biomass burning in the west and northeast, following a 3-year quantification analysis of 4NC, 4M5NC, 4NP, MNPs, and 2,6-dimethyl-4-nitrophenol (26DM4NP).

In the past decade, several studies have been conducted to identify specific nitrated phenolic compounds and determine emission factors. Early measurements of emission profiles from wood combustion identified phenol and substituted phenols, guaiacol and substituted guaiacols, and syringol and substituted syringols which were primarily produced via wood lignin pyrolysis (Schauer et al., 2001; Simoneit, 2002). The 4NC and MNCs detected in ambient PM_{10} samples were initially attributed to the secondary transformation of phenol and cresols produced from biomass burning (Iinuma et al., 2010; Iinuma and Herrmann, 2013). Through later laboratory experiments involving wood and grass combustion, Hoffmann et al. (2007) successfully identified the nitrated phenols NC, 4NP, MNPs, and 2,4DNP in emitted particles, with total emission factors of 0.8–8.1 mg per kg biomass fuel, and observed that flaming combustion produced more nitrated phenols compared to smoldering combustion. Iinuma et al. (2007) also detected 4NC in size-resolved burning particles of wood, grass and peat, with emission factors of 0.4–4.3 mg kg^{-1}, as well as 2-nitroguaiacol (2NG) and 4-methyl-2-nitroguaiacol (4M2NG) at levels several times higher than those of 4NC. Despite the above efforts, the scientific community lacks a comprehensive understanding of the direct emission of recognizable nitrated phenols from the burning of common types of biomass.

In this study, laboratory experiments involving the combustion of five types of common biomass were conducted, and 10 nitrated phenols were analyzed in $PM_{2.5}$ samples using high performance liquid chromatography–mass spectrometry (HPLC-MS). Here, we present the concentration and fraction of each nitrated phenol in fine particles from biomass smoke, calculate the ratios of nitrated phenols to $PM_{2.5}$ and organic matter (OM), estimate the emission factors associated with fine nitrated phenols, and quantify emissions from the burning of wheat straw, corn stalks and corncobs in China during 2013.

2. Experimental methods

2.1. Biomass selection

Five types of biomass from Shandong Province, China were selected for combustion experiments: wheat straw (rural Liaocheng), corn stalks and corncobs (Tai'an countryside), and dead wood branches and yellow fallen *Platanus hispanica* leaves (urban Ji'nan). These types of biomass are commonly subjected to domestic and open burning in northern China. Specifically, wheat straw and corn stalks are often burned on or near harvested farmlands, thus leaving plant ashes in the fields, and are occasionally burned for domestic cooking and heating in rural areas. Corncobs and wood branches are usually burned for cooking and heating. Fallen leaves are occasionally burned near wooded areas in late autumn and winter.

2.2. Experimental apparatus

The experimental combustion and sampling device comprised a burning stove, buffering tunnel, sampling chamber, and $PM_{2.5}$ sampler (as shown in Fig. 1). Five types of biomasses were burned individually in the stove. Once the $PM_{2.5}$ sampler was activated, biomass smoke traveled through the buffering tunnel without additional dilution, cooled to near room temperature, and was drawn into the sampler. Smoke samples were collected under stable burning conditions involving flames (flaming), small flames (weakly flaming), and no flames (smoldering). The flaming states of the three burning conditions for corn stalk are shown in Fig. 2a. The weakly flaming condition was notably difficult to control, and occasionally varied between near-flaming and near-smoldering. The chamber and tunnel were cleaned for 20 min with particle-free air before sampling smoke for each burning condition.

2.3. $PM_{2.5}$ sampling

A medium-volume $PM_{2.5}$ sampler (*TH-150, Wuhan Tianhong, China*) was used to collect fine particulate matters from biomass smoke on quartz-fiber filters in the sampling chamber during an approximately 60-s period at a flow rate of 100 L min^{-1}. The particulate matters collected on the filters for flaming, weakly flaming, and smoldering burning generally appeared brown black, brown, and tawny, respectively (see Fig. 2b). Before and after sampling, the filters were equilibrated at a constant temperature (20 ± 0.5 °C) and humidity (50± 2%) and weighed on an electronic microbalance (*ME5, Sartorius, Germany*). Two $PM_{2.5}$ samples were collected successively for each biomass type and burning condition, and the average values of these samples were recorded. Three additional $PM_{2.5}$ samples were collected from the open-field burning of wheat straw on two different farmlands in the Liaocheng countryside on June 18, 2015.

2.4. Sample pretreatment

Each filter sample was cut into two halves, and one half was pretreated for a chemical nitrated phenol analysis. Organic matters including nitrated phenols were extracted via three 20-minute sonification in an ultrasonic bath with 20 mL methanol. The resulting extract was concentrated to an approximate 1-mL volume using a non-heated rotary evaporator with a vacuum pressure >95 mbar. After PTFE filtration (0.45 μm), the concentrate was nearly dried using a high-purity nitrogen flow. Finally, the residue was re-dissolved in a 300-μL volume of methanol containing 200 μg L^{-1} 2,4,6-trinitrophenol as internal standard or further diluted to 600–3000 μL. Each sample solution was then transferred to an insert-pipe in a screw vial for subsequent HPLC-MS analysis. Additionally, a small area (2 cm^2) of the filter sample was cut and used to directly determine the organic carbon (OC) and element carbon (EC) contents via a thermal-optical method with the protocol of NOISH 5040 (*Sunset, OCEC analyzer, USA*). The OM concentration was calculated based on OC concentration by being multiplied by a factor of 1.6 (Aiken et al., 2008, 2009).

2.5. Analysis of nitrated phenols

Nitrated phenols in the sample solutions were separated by HPLC (*Dionex, UltiMate 3000, USA*) and detected by a trap mass spectrometer equipped with an ESI source (*Thermo Scientific, LCQ Fleet, USA*). High-purity nitrogen was used as the curtain, nebulizer,

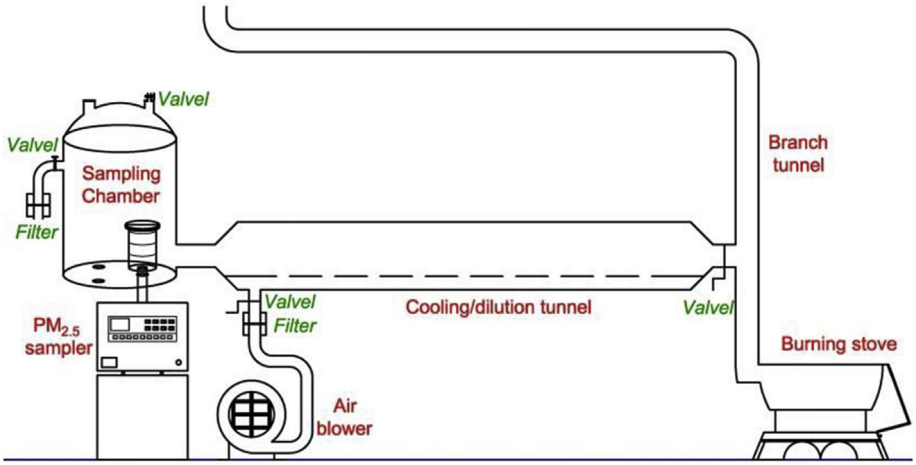

Fig. 1. Schematic diagraph of the combustion and sampling device.

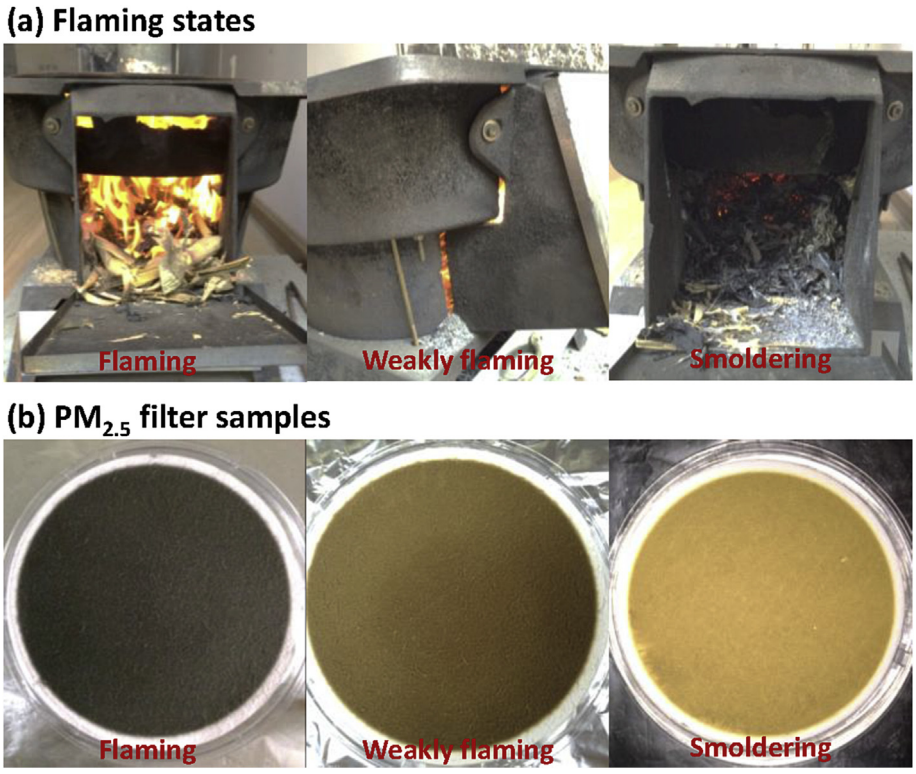

Fig. 2. Examples of photographs of (a) flaming states and (b) $PM_{2.5}$ filter samples for flaming, weakly flaming, and smoldering burning of corn stalk.

auxiliary, and collision gas. An Atlantis T3 C18 column (100 Å, 3 μm, 2.1 mm × 150 mm) was used to separate nitrated phenols and other organic compounds at a temperature of 30 °C with an injection volume of 10 μL. HPLC was performed for 30 min, with a mobile phase flow rate of 0.2 mL min^{-1}. The mixture of water/methanol (v/v) in the mobile phase changed gradually from 66/34 at 0 min to 44/56 at 19 min, was maintained at this ratio from 19 to 22 min, and returned to 66/34 from 22 to 30 min. Ten nitrated phenols in the sample solutions, including 4NP, 3M4NP, 2M4NP, 4NC, 4M5NC, 3M5NC, 3M6NC, 5-nitrosalicylic acid (5NSA), 3-nitrosalicylic acid (3NSA), and 2,4DNP, were detected in negative polarity in the selected ion monitoring (SIM) mode. These nitrated phenols were further verified using separate standards (*Sigma-Aldrich, USA*) and quantified using corresponding multi-point standard curves. Detailed information about the analysis of nitrated phenols has been described in previous studies by Kitanovski et al. (2012a and 2012b).

2.6. Calculation and estimation

In this study, the emission factor of fine nitrated phenols (EF_{NPs}) was calculated using the product of the emission ratio of nitrated phenols to $PM_{2.5}$ and the emission factor of $PM_{2.5}$ (see Eq. (1)), as the $PM_{2.5}$ sampler only collected a fraction of each type of biomass smoke.

$$EF_{NPs} = ER_{NPs/PM2.5} \cdot EF_{PM2.5} \quad (1)$$

here, $ER_{NPs/PM2.5}$ represents the emission ratio of nitrated phenols to $PM_{2.5}$, and $EF_{PM2.5}$ represents the emission factor of $PM_{2.5}$ from each biomass, as per the existing literature.

The emission factor of total fine nitrated phenols ($EF_{\Sigma NPs}$) was then used to estimate the emission quantity of fine nitrated phenols from domestic and open biomass burning ($Q_{\Sigma NPs}$), according to Eq. (2).

$$Q_{\Sigma NPs} = EF_{\Sigma NPs} \cdot P \cdot N \cdot (F_f \cdot \eta_f + F_o \cdot \eta_o) \quad (2)$$

here, P and N represent the grain production and ratio of grain to straw, respectively, F_f and F_o represent the proportions of straw burned as domestic fuel and in open fields, respectively, and η_f *and* $\cdot\eta_o$ represent the efficiencies of biomass burned as domestic fuel and in open fields, respectively.

3. Results and discussion

3.1. Concentrations and compositions of fine nitrated phenols in biomass smoke

The concentrations of fine nitrated phenols, fine OC, and $PM_{2.5}$ in fresh biomass smoke samples are listed in Table 1. The concentrations of individual nitrated phenols ranged from below the detection limit to dozens of μg m^{-3}. Among the 10 evaluated nitrated phenols, 4NP, 3M4NP, 4NC, 3M6NC, and 3M5NC were detected in smoke samples from all five types of biomass subjected to all three burning conditions, and 2M4NP, 4M5NC, 3NSA, and 2,4DNP were detected in some or most smoke samples. In contrast, 5NSA was never detected. The total nitrated phenol (ΣNP) concentrations in these samples ranged from 2.0 to 99.5 μg m^{-3}, and the OC and $PM_{2.5}$ ranged from 5.8 to 353 mg m^{-3} and from 34.8 to 729 mg m^{-3}, respectively. Notably, smoke samples from openly burned wheat straw (also listed in Table 1) contained significantly lower levels of nitrated phenols, OC, and $PM_{2.5}$ than did samples from laboratory stove burning, possibly due to the effects of ambient air diffusion and dilution. Generally, the nitrated phenol concentrations were higher and the OC and $PM_{2.5}$ concentrations were lower in samples from completely burned biomass (*i.e.*, flaming), compared to those subjected to incomplete burning (*i.e.*, weakly flaming and smoldering).

The proportions of each nitrated phenol in freshly emitted biomass smoke samples are shown in Fig. 3 (rows indicate biomass types, columns indicate burning conditions). As illustrated, 4NC and methyl nitrocatechols (*i.e.*, 4M5NC, 3M6NC, and 3M5NC; red) were the most abundant nitrated phenols detected in freshly emitted fine particles in most cases. In samples from flaming burning, 4NC and methyl-substituted nitrocatechols accounted for 88–95% of the total nitrated phenols (4NC > 3M5NC > 4M5NC > 3M6NC). Incomplete burning conditions led to the increased emission of 4NP, methyl nitrophenols (*i.e.*, 3M4NP and 2M4NP), and 3NSA and decreased emission of 4NC and methyl nitrocatechols, compared to complete burning. Particularly, incompletely burned leaves emitted much higher proportions of 4-NP and methyl nitrophenols (~60%), compared to other biomass types. Fig. 3 also presents the proportions of individual nitrated phenols in samples from wheat straw burned in open fields (last grey shaded column), which were similar to those in laboratory samples subjected to flaming and weakly flaming burning.

The above results strongly indicate that nitrated phenols can be directly emitted via common biomass burning. In contrast to previous studies by Hoffmann et al. (2007) and Iinuma et al. (2007), methyl nitrocatechols and 3NSA were also observed in fresh biomass smoke samples in this study. The burning condition-related changes in the fractions of nitrated phenols were primarily attributed to changes in reaction pathways at different burning temperatures (Yang et al., 2007). During biomass burning, emitted nitrated phenols are mainly produced from the pyrolysis of lignin, which contains aromatic groups (Simoneit, 2002), and subsequent chemical reactions. Notably, 4-nitrocatechol and methyl nitrocatechols were the predominant nitrated phenols in samples subjected to flaming burning at relatively high temperatures. In contrast, weakly flaming and smoldering burning at relatively low temperatures predominantly yielded 4NP, methyl nitrophenols, and 3NSA.

An examination of the boiling points (BP) and vapor pressures (VP) of these nitrated phenols (Table S1) found that all the most abundant 4-nitrocatechol and methyl nitrocatechols had high BPs and low VPs, whereas most minor species (*i.e.*, nitrophenol, methylnitrophenols, and dinitrophenols) had lower BPs and higher VPs. These results suggest that in fresh biomass smoke, a large fraction of these semi-volatile species might exist in the gas phase (Cecinato et al., 2005).

Table 1
Concentrations of fine nitrated phenols, OC, and $PM_{2.5}$ in fresh biomass burning smokes under different burning conditions (unit in μg m^{-3} except OC and $PM_{2.5}$ in mg m^{-3}).

Condition	Biomass	4NP	3M4NP	2M4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA	2,4DNP	∑NPs	OC	$PM_{2.5}$
Flaming	Leaves	0.68	0.22	0.29	9.32	1.89	0.83	2.16	N.D.	0.00	N.D.	15.4	5.8	34.8
	Branches	0.88	0.28	0.13	8.85	4.90	3.77	8.61	N.D.	0.03	0.02	27.5	11.7	45.9
	Corncob	5.14	1.60	0.91	35.2	17.0	9.92	29.6	N.D.	0.01	0.10	99.5	19.5	85.8
	Corn Stalk	1.30	0.23	0.08	6.68	2.63	1.93	4.14	N.D.	0.02	0.42	17.4	21.2	72.6
	Wheat Straw	2.01	0.89	0.49	15.2	8.49	6.14	24.9	N.D.	0.01	N.D.	58.1	41.6	152
Weakly flaming	Leaves	16.8	3.21	4.97	7.55	2.48	1.48	2.02	N.D.	2.55	1.71	42.8	147	373
	Branches	1.98	0.65	0.02	3.05	0.92	1.12	2.13	N.D.	1.77	0.73	12.4	278	726
	Corncob	1.60	1.05	0.88	17.4	5.45	6.08	18.2	N.D.	0.12	N.D.	50.7	16.0	56.0
	Corn Stalk	0.35	0.21	0.07	2.26	0.47	0.91	1.78	N.D.	0.13	0.17	6.3	85.6	238
	Wheat Straw	1.56	1.33	0.39	9.64	4.69	4.62	14.4	N.D.	0.35	N.D.	37.0	247	627
Smoldering	Leaves	1.62	0.33	0.47	0.69	0.32	0.11	0.28	N.D.	0.12	0.05	4.0	39.8	91.5
	Branches	0.22	0.09	0.07	0.54	N.D.	0.57	0.39	N.D.	0.04	0.10	2.0	47.2	107
	Corncob	0.19	0.23	N.D.	0.32	N.D.	0.44	0.56	N.D.	3.74	N.D.	5.5	95.1	216
	Corn Stalk	0.37	0.19	0.01	1.10	0.01	0.68	0.41	N.D.	0.55	0.50	3.8	353	729
	Wheat Straw	0.44	0.23	0.04	0.63	0.04	0.58	0.48	N.D.	0.75	0.02	3.2	198	440
Open burning	Wheat Straw	0.10	0.08	0.02	0.53	0.18	0.16	0.43	N.D.	0.00	N.D.	1.5	3.2	7.8
	Wheat Straw	0.12	0.11	0.04	0.85	0.24	0.29	0.73	N.D.	0.02	N.D.	2.4	3.8	12.2
	Wheat Straw	0.08	0.06	0.01	0.24	0.17	0.07	0.22	N.D.	N.D.	N.D.	0.8	1.1	4.1

N.D.: not detected.

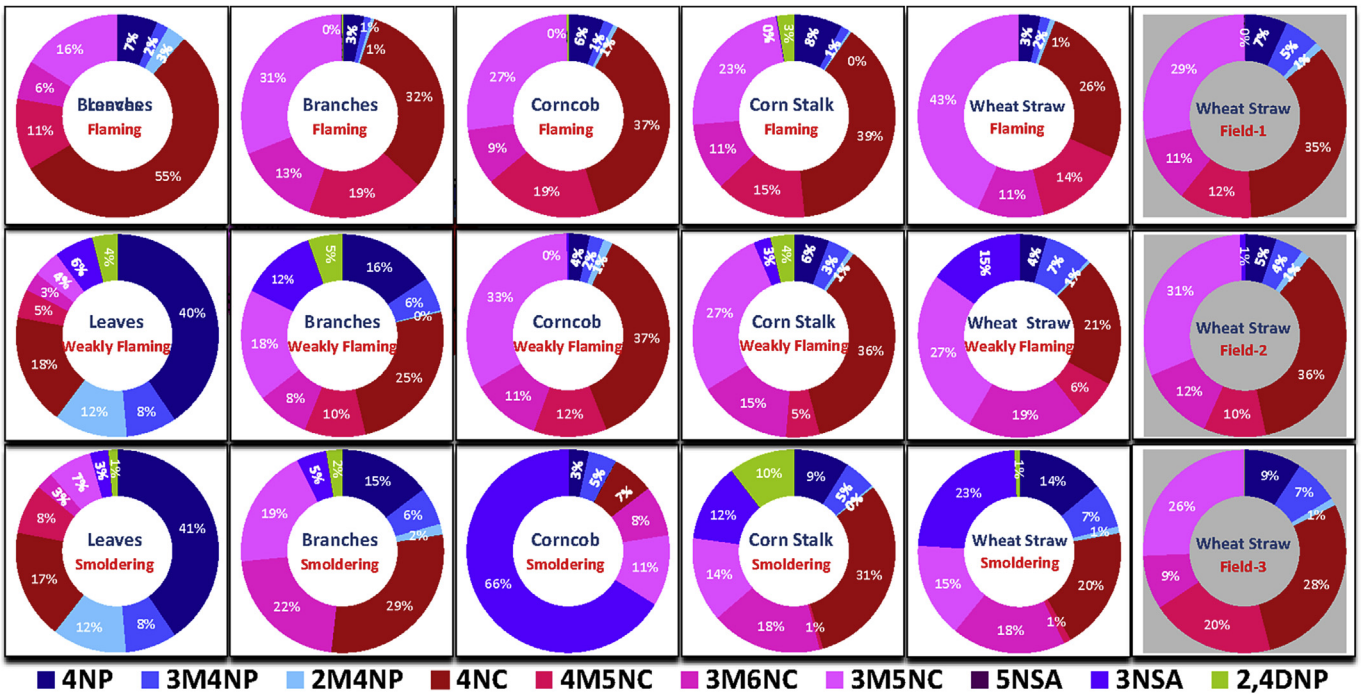

Fig. 3. Proportions of individual nitrated phenols in $PM_{2.5}$ emitted from biomass burning.

3.2. Emission ratios of nitrated phenols in fine particulate matter

Following biomass burning, the emission ratios (*ER*) of nitrated phenols in fine particulate matter were calculated based on the mass concentration ratio of the nitrated phenols to $PM_{2.5}$. As listed in Table 2, the *ER*s of individual nitrated phenols varied widely according to burning condition, ranging from zero (below detection limit) for nitrosalicylic acids and 2,4DNP to hundreds of ppmm for 4-NC and methyl nitrocatechols. The *ER*s of total nitrated phenols ranged from 7 to 1081 ppmm. The highest nitrated phenol *ER*s were recorded for flaming burning (239–1081 ppmm), followed by weakly flaming burning (19–988 ppmm), and smoldering (7–45 ppmm). The *ER*s of nitrated phenols also differed significantly according to biomass type. Generally, corncobs, branches, and leaves emitted more nitrated phenols, compared to wheat straw and corn stalks. Regarding wheat straw, the *ER*s of open field-burned samples (Table 2) were lower than of laboratory flaming-burned samples but higher than that of weakly flaming-burned samples. The observed higher emission of nitrated phenols from completely biomass burning aerosols was consistent with the findings of a previous study by Hoffmann et al. (2007). The *ER*s of nitrated phenols to $PM_{2.5}$ obtained herein could provide basic data for emission estimations and modeling simulations.

The mass ratios of nitrated phenols to OM (ΣNPs/OM ratio) in fresh biomass smoke were also calculated (Table 3). Similar to the *ER*s of nitrated phenols to $PM_{2.5}$, the highest and lowest ΣNPs/OM ratios were observed with flaming burning (0.51–3.02‰), and smoldering (0.01–0.07‰). In general, corncobs, branches, and

Table 2
Emission ratios of nitrated phenols to $PM_{2.5}$ from biomass burning under different burning conditions (unit in ppmm).

Condition	Biomass	4NP	3M4NP	2M4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA	2,4DNP	∑NPs
Flaming	Leaves	20.2	6.5	8.7	252	51.2	23.3	60.7	N.D.	0.0	N.D.	423
	Branches	21.5	6.9	2.9	228	123	97.3	223	N.D.	0.5	0.6	703
	Corncob	57.5	17.4	9.6	388	190	105	312	N.D.	0.1	1.5	1081
	Corn Stalk	18.7	3.3	0.9	92.7	34.9	25.9	56.3	N.D.	0.3	6.4	239
	Wheat Straw	13.1	5.9	3.3	99.0	55.0	40.4	165	N.D.	0.1	N.D.	382
Weakly flaming	Leaves	49.3	9.1	14.8	22.7	8.6	4.8	6.4	N.D.	7.4	5.2	128
	Branches	3.0	1.1	0.1	4.9	2.1	1.5	3.5	N.D.	2.1	1.0	19.4
	Corncob	35.5	22.5	14.5	367	117	107	323	N.D.	1.3	N.D.	988
	Corn Stalk	1.6	0.9	0.4	10.3	2.4	4.1	8.3	N.D.	0.5	0.7	29.1
	Wheat Straw	4.1	3.4	1.0	25.5	12.5	11.9	38.2	N.D.	0.5	N.D.	97.0
Smoldering	Leaves	18.4	3.7	5.4	7.4	3.5	1.2	3.2	N.D.	1.3	0.7	44.7
	Branches	2.0	0.8	0.3	4.3	0.0	3.6	2.9	N.D.	0.6	0.5	15.1
	Corncob	0.9	1.1	0.0	1.6	0.0	2.0	2.8	N.D.	16.7	N.D.	25.2
	Corn Stalk	0.6	0.4	0.0	2.8	0.1	1.4	1.4	N.D.	0.8	0.5	8.1
	Wheat Straw	1.0	0.5	0.1	1.4	0.1	1.3	1.1	N.D.	1.7	0.1	7.3
Open burning	Wheat Straw	13.0	10.6	2.5	67.6	22.4	20.2	54.6	N.D.	0.1	N.D.	191
	Wheat Straw	10.0	8.7	2.9	70.1	19.5	23.6	60.1	N.D.	1.5	N.D.	196
	Wheat Straw	18.9	14.8	2.5	58.3	40.6	17.7	52.5	N.D.	N.D.	0.1	205

N.D.: not detected.

Table 3
Mass ratios of fine nitrated phenols to OM in fresh biomass burning smokes under different burning conditions (unit in ‰).

ΣNPs/OM	Leaves	Branches	Corncob	Corn stalk	Wheat straw
Flaming	1.60	2.07	3.02	0.51	0.90
Weakly flaming	0.23	0.04	2.70	0.05	0.24
Smoldering	0.07	0.02	0.04	0.01	0.01

leaves yielded higher ΣNPs/OM ratios, compared to wheat straw and corn stalks. Among freshly emitted biomass smoke samples, the largest ΣNPs/OM ratio was only 3.02% from corncobs subjected to flaming burning. The ΣNPs/OM ratios of fresh biomass burning aerosols in this study were comparable to or lower than those observed in ambient aerosols influenced by domestic wood combustion in Europe during the winter (~5‰ average at a site downwind of London (Mohr et al., 2013) and ~4.3‰ in an urban background site in Ljubljana (Kitanovski et al., 2012a,b)). These findings suggest that a large fraction of nitrated phenols in atmospheric particles possibly originate from the secondary transformation of precursors such as aromatics, phenol, and substituted phenols (Harrison et al., 2005b; Iinuma and Herrmann, 2013; Jenkin et al., 2003; Yuan et al., 2016), in addition to partitioning and aging of gas-phase nitrated phenols (Cecinato et al., 2005; Harrison et al., 2005a; Vione et al., 2005, 2009). The difference in the ΣNPs/OM ratio between fresh biomass burning particles and ambient aerosols could also resulted from systematic repartitioning of semi-volatile nitrated phenols and other semi-volatile organic matters during the dilution into ambient air or the different fuels and stoves deployed.

3.3. Estimated emission factors and amounts of nitrated phenols from biomass burning

The EF_{NPs} values from each type of biomass subjected to flaming burning were estimated in this study, and each value is expressed as the mass of nitrated phenols emitted per mass unit of combusted biomass (listed in Table 4). The $EF_{PM2.5}$ values of the five biomasses were not determined in this study and values from previous studies of flaming burning were thereby adopted (Li et al., 2009; Wardoyo et al., 2006; Xu et al., 2016) (Table 4). Insufficient $EF_{PM2.5}$ data of incomplete biomass burning were available in the literature, and therefore these samples were excluded from the analysis. The estimated $EF_{\Sigma NPs}$ values under flaming burning condition were 11.1, 2.14, 1.23, 1.09, and 0.75 mg kg^{-1} for corncobs, branches, wheat straw, corn stalks, and leaves, respectively. Overall, the emission factors of 4NC, 4M5NC, 3M6NC, and 3M5NC were relatively high, ranging from 0.1 to 5.4 mg kg^{-1}. The emission factors of 4NP, 3M4NP, and 2M4NP were moderate (0.01–0.81 mg kg^{-1}), whereas those of 2,4DNP, 3NSA, and 5NSA were very low (<0.1 mg kg^{-1}). Note that due to the differences in biomass fuel, burning stove, burning condition, and experiment setup between pre-existing literature and the present work, large uncertainty possibly exists in the above emission factors of nitrated phenols estimated from measured mass fractions and literature values of $EF_{PM2.5}$.

Table 4
Estimated emission factors of fine nitrated phenols from flaming biomass burning (unit in mg kg^{-1} except $PM_{2.5}$ emission factor in g kg^{-1}).

Emission factor	Leaves	Branches	Corncob	Corn stalk	Wheat straw
$PM_{2.5}$	1.77[a]	3.04[b]	10.24[c]	4.54[b]	3.21 [b]
4NP	0.04	0.07	0.59	0.08	0.04
3M4NP	0.01	0.02	0.18	0.02	0.02
2M4NP	0.02	0.01	0.10	0.00	0.01
4NC	0.45	0.69	3.97	0.42	0.32
4M5NC	0.09	0.37	1.95	0.16	0.18
3M6NC	0.04	0.30	1.07	0.12	0.13
3M5NC	0.11	0.68	3.20	0.26	0.53
5NSA	N.D.	N.D.	N.D.	N.D.	N.D.
3NSA	0.00	0.002	0.001	0.002	0.00
2,4DNP	N.D.	0.002	0.02	0.03	N.D.
ΣNPs	0.75	2.14	11.1	1.09	1.23

N.D.: not detected.
[a, b,c]Data of $PM_{2.5}$ emission factor for common biomass burning in stoves are adopted from Li et al. (2009), Wardoyo et al., 2006, and Xu et al. (2016), respectively.

The findings that corncobs and wood emitted the highest levels of fine nitrated phenols were primarily ascribed to differences in lignin contents. Generally, wood and corncobs contain approximately 25.2% (Azeez et al., 2010) and 22.0% (Flores-Sánchez et al., 2013) lignin, respectively, whereas wheat straw and corn stalks contain approximately 20.4% (Niu et al., 2013) and 15.4% (Wang et al., 2015) lignin, respectively. In contrast to previous studies by Hoffmann et al. (2007) and Iinuma et al. (2007), this study presented and highlighted the large emission factors of methyl nitrocatechols associated with common biomass burning.

Further, an estimation of fine nitrated phenols emitted from the burning of major crop straws in China in 2013 was conducted based on the obtained emission factors, grain production from the China Statistical Yearbook 2014 (National Bureau of Statistics, 2014), and straw-to-grain ratios, burning proportions, and burning efficiencies from the literature. As shown in Table S2, wheat and corn production in each of 31 Chinese provinces ranged from 0.3×10^4 to 3226×10^4 t. The respective straw-to-grain ratios for wheat straw, corn stalks, and corncobs were 1.1, 1.2, and 0.25 (Niu and Liu, 1986; Bi et al., 2009). The respective proportions of the biomass burned as domestic fuel and in open fields ranged from 20% to 80% and from 10% to 30%, (Wang and Zhang, 2008; Tian et al., 2011), with respective burning efficiencies of 100% and 88.9% (Zhang et al., 2008; Tian et al., 2011; Sun et al., 2016). Finally, a total of 670 t of fine nitrated phenols were estimated to have been emitted from biomass burning throughout China in 2013. However, this estimate is relatively uncertain, given the assumptions regarding identical emission factors for household stove and open field burning and changes in burning proportions in recent years. Among the 31 provinces, Heilongjiang exhibited the highest emission of fine nitrated phenols, followed by Shandong, Jilin, Henan, and Hebei (see Fig. 4). These provinces are all located in the Northeast and North China Plains, thus highlighting the urgent need to improve biomass utilization and to ban biomass burning without smoke removal devices.

4. Conclusions

This laboratory combustion study was conducted in combination with the HPLC-MS analysis of smoke $PM_{2.5}$ to understand the emission of fine nitrated phenols from biomass burning. Using five common types of biomass (leaves, branches, corncobs, corn stalks, and wheat straw) and three different burning conditions (flaming, weakly flaming, and smoldering) to produce smoke samples, 10 major nitrated phenols were assessed in the resulting fine particulate matter, yielding total concentrations ranging from 2.0 to 99.5 μg m^{-3}. The predominant nitrated phenol species and their proportions varied with biomass type and burning condition. In most cases, 4NC, 4M5NC, 3M5NC, and 3M6NC were the predominant fine nitrated phenols and were present at levels as high as 88–95% in flaming-burned samples. In contrast, the proportions of 4NP, 3M4NP, 2M4NP, and 3NSA were significantly higher in incompletely burned samples, and exceeded 50% in some cases. The *ER*s of total nitrated phenols to $PM_{2.5}$ varied from 7 to 1081 ppmm, and higher values were achieved with flaming burning relative to incomplete burning. In biomass smoke, the ratios of fine nitrated

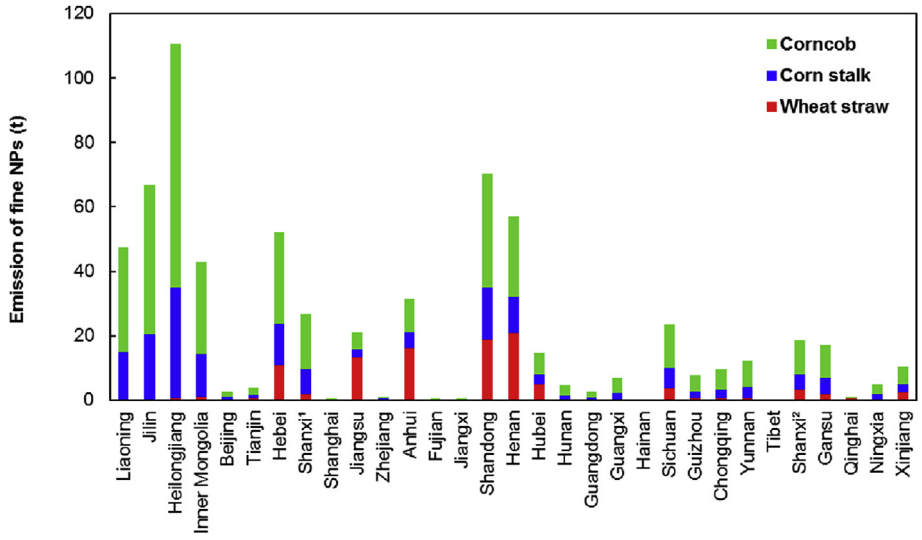

Fig. 4. Estimated emission amounts of fine nitrated phenols from burning of wheat straw, corn stalk, and corncob in China in 2013.

phenols to OM (0.01–3.02‰) were comparable to or lower than those observed in ambient aerosols affected by domestic biomass burning, suggesting that a large proportion of fine nitrated phenols originate from chemical reactions involving precursors and the partitioning and aging of gas-phase nitrated phenols. The EF_{NPs} were approximated according to *ER*s of nitrated phenols to $PM_{2.5}$ and literature values of $EF_{PM2.5}$ and ranged from 0.75 to 11.1 mg kg^{-1} for five types of biomass for flaming burning. Corncob was associated with a higher *ER* and EF_{NPs} relative to other tested biomass types. Finally, this study estimated that 670 t of fine nitrated phenols were emitted from the domestic and open burning of corncobs, corn stalks, and wheat straw in China in 2013.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21407094, 91544213, 91644214), the National Key Research and Development Program of China (No. 2016YFC0200503), and the Natural Science Foundation of Shandong Province (No. ZR2014BQ031).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.06.072.

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