



# Emissions of fine particulate nitrated phenols from the burning of five common types of biomass<sup>☆</sup>



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## 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  $\mu\text{g m}^{-3}$ . 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  $\text{PM}_{2.5}$  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  $\text{PM}_{2.5}$  emission factors from literature and were approximately 0.75–11.1  $\text{mg kg}^{-1}$ . 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.

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## 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  $\text{PM}_{10}$  samples from a rural residential area in Seiffen, Saxony, Germany in the winter of 2007. There, good

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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), methyl-nitrophenols (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<sub>10</sub> 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<sup>-1</sup>, 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> sampler (as shown in Fig. 1). Five types of biomasses were burned individually in the stove. Once the PM<sub>2.5</sub> 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<sub>2.5</sub> sampling

A medium-volume PM<sub>2.5</sub> 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<sup>-1</sup>. 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<sub>2.5</sub> samples were collected successively for each biomass type and burning condition, and the average values of these samples were recorded. Three additional PM<sub>2.5</sub> 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<sup>-1</sup> 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<sup>2</sup>) 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,

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