



Particulate nitrated aromatic compounds from corn straw burning: Compositions, optical properties and potential health risks[☆]

Runqi Zhang^{a,c}, Wei Song^a, Yanli Zhang^{a,b}, Xinming Wang^{a,b,c,*}, Xuewei Fu^{a,c}, Sheng Li^{a,c}

^a State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

^b Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China

^c University of Chinese Academy of Sciences, Beijing, 100049, China

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ABSTRACT

Nitrated aromatic compounds (NACs) are important components of brown carbon (BrC), and their health and climate effects are of wide concern. Biomass burning is a major contributor to NACs in the atmosphere, yet NACs emitted from biomass burning are poorly constrained. In this study particulate NACs from open burning of corn straws were characterized in terms of their compositions, light absorption and toxic equivalents. 1, 6-dinitropyrene was the most abundant species among the measured nitropolycyclic aromatic hydrocarbons (NPAHs) with a share of 13.4% in total NPAHs, while 4-nitrocatechol was the most abundant nitrophenol (NP) species and accounted for 25.4% of measured NPs. 2-nitropyrene, widely used as a marker of secondary formation of NPAHs, was found to be the second most abundant NPAHs (13.3% of the total NPAHs) in the particulate matter (PM) primarily emitted from corn straw burning, and thus is inappropriate to be an indicator of the secondary formation. The measured primary NACs could only explain a negligible part (0.2%) of the light absorption by BrC. Although the concentrations of 9 toxic NACs were less than one-third of the 16 USEPA priority PAHs, their benzo(a)pyrene toxic equivalency quotients however were approximately 10 times that of the 16 PAHs. This study suggests that in comparison of PAHs from straw burning, NACs should be given greater attention due to their potentially higher toxic effects.

1. Introduction

Nitrated aromatic compounds (NACs), containing one or more benzene rings in their molecular structures, are widely detected nitrogen-containing organic compounds in atmospheric particulate matter (PM) and in gas phase. PM-bound NACs in ambient air can be both primarily emitted from nitrification during fossil and biofuel combustion processes (Shen et al., 2012; Yang et al., 2017; Zhang et al., 2022b) and secondarily formed via the reactions of the precursor aromatic hydrocarbons in the gas phase with OH radicals under light conditions and with NO₃ radicals under dark conditions, or via the heterogeneous reaction of precursors on the surface of PM with N₂O₅ (Arey et al., 1986; Atkinson and Arey, 1994; Chen and Bond, 2010; Lin et al., 2014). Although the concentration of NACs in ambient air is extremely low in particulate organic matter (OM) (Liu et al., 2017; Zhang et al., 2019;

Yuan et al., 2021), their toxicity and light-absorption property make them a growing source of concern in terms of health and climate effects.

Previous studies have demonstrated that NACs may pose great harm to human health. Kawanaka et al. (2008) found that, based on the Ames test, five nitropolycyclic aromatic hydrocarbons (NPAHs), which are a class of highly toxic NACs, could account for more than 10% of the mutagenicity of fine particles. Studies have also revealed the critical role played by NACs in PM-induced oxidative stress effects (Ovrevik et al., 2013). Park and Park (2009) and Andersson et al. (2009) showed that even low doses of NACs can significantly induce an increase in intracellular levels of reactive oxygen clusters, which has been suggested to be a key mechanism for inflammatory injury induced by PM (Gonzalez-Flecha, 2004; Vinzents et al., 2005). Therefore, a thorough investigation into the highly toxic compounds within PM, such as NACs, is imperative in order to better comprehend and lessen the health risks

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* Corresponding author. State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China.

E-mail address: wangxm@gig.ac.cn (X. Wang).

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posed by PM.

NACs have a highly unsaturated or conjugated structure that allows them to effectively absorb light radiation at near ultraviolet (UV) wavelengths, and are therefore considered important constituents of brown carbon (BrC), which refers to a class of organic matter in atmospheric PM that has the ability to absorb light. Feng et al. (2013) estimated that the enhanced absorption of solar radiation due to BrC might be more than a quarter of the global radiative effect of black carbon. Laskin et al. (2015) also found significant differences in emission levels and absorption properties of BrC from different regions, with BrC in the Asian region having a higher absorption Ångström exponent (AAE). Mohr et al. (2013) determined five NACs in a forest environment and found that they could contribute 4% of the light absorption of BrC at 370 nm. Lin et al. (2017) determined more than 60 nitrogen-containing aromatic compounds during the Israeli bonfire festival and found that they could contribute 50–80% of the BrC light absorption at 400 nm. Therefore, investigating the sources, compositions and light absorption properties of NACs is critical for gaining an in-depth insight into BrC on a molecular level.

Biomass burning is one of the most important sources of NACs, emitting not only NACs but also significant amounts of aromatic compounds as precursors to NACs secondarily formed via atmospheric oxidation (Iinuma et al., 2010; Wang et al., 2017). Field observations have revealed a significant positive correlation between NACs and the biomass burning marker levoglucosan (Iinuma et al., 2010), and PM-bound NACs were found to increase substantially in regions and periods under significant influence of biomass burning (Claeys et al., 2012; Desyaterik et al., 2013; Chuesaard et al., 2014; Chow et al., 2016; Orakij et al., 2017). Lin et al. (2017) found that a larger amounts of BrC occurred in ambient air during a biomass burning event, and that NACs could contribute more than 50% of the BrC light absorption in the near-UV wavelengths. Since emission of NACs from biomass burning are influenced by many factors, such as combustion conditions, wood type and measurement methods, there are significant differences in reported source characterization results. For example, Shen et al. (2012) characterized NACs from combustion of 27 kinds of wood using actual cookstoves and found that 9-nitroanthracene (9-NAnt) was the abundant NAC species while 5-nitroacenaphthene (5-NAce) was not detected in most combustion emissions. However, Vicente et al. (2016) showed the opposite results, with 5-NAce being the dominant species while 9-NAnt and other NACs were negligible. Similarly, Iinuma et al. (2007) found that the emission of PM-bound nitroguaiacol (NG) and its methyl derivatives from biomass burning is one to two orders of magnitude higher than that of 4-nitrocatechol (4-NC); however, NG and its methyl derivatives was not measured by Hoffmann et al. (2007) and they instead detected 4-NC as the dominant species. Therefore, characterizing NACs from biomass burning is far from enough for a comprehensive understanding of their source contribution by biomass burning. Interestingly, recent field studies have suggested that the ratios between individual NACs could potentially help evaluate and distinguish between the contribution of coal combustion and biomass burning (Zhang et al., 2022a), and between primary emissions and secondary formations (Iinuma et al., 2007), as well as between liquid-phase and gas-phase secondary formation reactions (Frka et al., 2016; Vidovic et al., 2018; Wang et al., 2019). Nevertheless, the applicability of these ratios needs to be verified by more source characterization studies and field observations.

The open burning of straw accounts for 60% of the total biomass burning in China each year (Streets et al., 2003; Zhou et al., 2017). Li et al. (2016) estimated that crop residue burning in China could reach 160 million tons in 2012, accounting for 40% of global straw burning, and corn straw was among the most commonly burned crop biomasses with 33 Tg corn straws burned annually in China. Moreover, BrC emitted from corn straw burning was reported to have higher AAE, when compared to those from burning other straws (Wang et al., 2017; Tian et al., 2019). In this study, emissions from open burning of corn straw

were investigated to (1) characterize the compositions of PM-bound NACs in the open burning plume, (2) quantify the contribution of PM-bound NACs in the light absorption of BrC from the biomass burning, and (3) assess the toxicity equivalence of PM-bound NACs and compared them with those of PAHs from the biomass burning.

2. Experimental

2.1. Open-burning sampling

In this study, corn straw was selected as a typical biomass material for the open burning experiment mainly for two main reasons: 1) corn straw is widely used in relatively larger quantities in China: previous survey in China's 31 provinces/municipalities indicated that the annual use of corn straw-related biomass fuels is 2.0×10^8 tons, accounting for more than 20% open-burning in China (Wang et al., 2017); 2) the PM from the burning of corn straw show stronger light-absorbing properties: a previous study revealed that PM from the burning of corn straw has a higher AAE than that from the burning of other types of straw (wheat, rice, cotton, sesame, soybean and sugarcane) (Tian et al., 2019). The corn straw used for the experiments in this study was collected from the southern provinces of China, and was dried at 80 °C for 24 h (Fang et al., 2017).

As shown in Fig. S1, the plume of corn straw open burning was introduced into the $\sim 30 \text{ m}^3$ Teflon reactor of the GIG indoor chamber (Wang et al., 2014) under the dark condition to ensure near-ambient dilution with purified air (Fang et al., 2017; Fang et al., 2022), and PM diluted inside the chamber was collected onto a 47 mm diameter quartz filter at a flow rate of 25 L min^{-1} by using an oil-free vacuum pump (Gast Manufacturing, Inc, USA) for the analysis of PM-bound NACs. Six parallel burning experiments were conducted in this study (Table S1). Before each experiment, the Teflon reactor used as the dilution room was cleaned with purified air for at least 48 h. Purified air was prepared by compressing ambient air with an air compressor (FXe1, Atlas Copco, Sweden) and purifying it with activated carbon, an oxidizing agent (Purafil), an absorbent (Hopcalite) and a filter to ensure that the NO_x and O_3 concentrations in the incoming pure air were less than 1 ppbv, the total non-methane hydrocarbon concentration was less than 2 ppbv, the particle number concentration was less than 10 particles cm^{-3} and the relative humidity was less than 5%.

2.2. Chemical analysis

Organic carbon (OC) and elemental carbon (EC) in the PM samples were analyzed by a DRI 2015 multi-wavelength thermal/optical carbon analyzer (Desert Research Institute, Nevada, USA). The IMPROVE_A protocol was used for the OC/EC analysis in this study. The analyzer is equipped with seven diode lasers (405, 455, 532, 635, 780, 808 and 980 nm) for determining the spectral reflectance and transmittance of filter samples. The stability and reliability of the instrument was tested daily with a standard sucrose solution during sample analysis (Li et al., 2018; Zhang et al., 2021).

A wide range of NACs, including highly light-absorbing nitrophenols (NPs) and highly toxic nitrated polycyclic aromatic hydrocarbons (NPAHs), were selected as the target compounds in this study. The target NACs and polycyclic aromatic hydrocarbons (PAHs) were ultrasonically extracted from the quartz filters, and mixed recovery indicators (2-nitrobiphenyl-d9, 1-nitropyrene-d9, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) were added to the filter samples prior to sonication. To ensure good recovery and extraction efficiency, each sample was extracted for 4 times and each time for 15 min. A mixture of hexane and dichloromethane (1:1 vol ratio) was used for the first two times of extraction, and a mixture of dichloromethane and methanol (1:1 vol ratio) was used for the last two times of extraction. The temperature of the water bath was maintained below 20 °C during the ultrasonic extraction. The extracts were then

filtered, concentrated, purified and concentrated to ~0.2 mL using an anhydrous sodium sulfate column, a cold rotary evaporator, a silica gel chromatography column and a nitrogen blowing apparatus. More details about the analysis can be found in our previous study (Zhang et al., 2022b). After blown to near dryness, the extract was added with 200 μ L of BSTFA/TMCS solution and 100 μ L of pyridine for silylation at 70 $^{\circ}$ C for 1 h. The silylated derivatization pretreatment was to improve measurement sensitivity. Finally, hexane was added to fix the volume to 500 μ L.

NACs in the extracts were analyzed using an Agilent 7890/5975C gas chromatography-mass selective detector (GC-MSD) with negative chemical ionization (NCI) in selected ion monitoring (SIM) mode, with high purity helium (>99.999%) as the carrier gas. The GC column was an Agilent HP-5MS (30 m length \times 0.25 mm I.D. \times 0.25 μ m film thickness) with a constant flow rate of 1.2 mL min⁻¹. The oven temperature was initially set at 60 $^{\circ}$ C for 1 min, increased to 150 $^{\circ}$ C at 10 $^{\circ}$ C min⁻¹, and then to 300 $^{\circ}$ C at 5 $^{\circ}$ C min⁻¹ with a final hold time of 4 min. The target ions, retention times and method detection limits are shown in Table S2. In this study, the recoveries of the mixed standards (23 nitro-polycyclic aromatic compounds and 18 nitro-phenolic compounds) were tested to range from 86.0 \pm 19.9% to 102.5 \pm 17.2% (Table S3). The details about the PAH analysis have been described in our previous studies (Yu et al., 2016; Yu et al., 2018) and are not presented here.

2.3. Light absorption calculation

Based on measurements by the DRI 2015 multi-wavelength thermal/optical carbon analyzer, the light absorption coefficient (b_{abs}) of the particles can be calculated as (Li et al., 2018):

$$b_{\text{abs}} = [A_{\lambda} \times \ln\left(\frac{FT_{\lambda,i}}{FT_{\lambda,f}}\right)]^2 + B_{\lambda} \times \ln\left(\frac{FT_{\lambda,i}}{FT_{\lambda,f}}\right) \times \frac{A}{V} \quad (1)$$

where A_{λ} and B_{λ} are coefficients for specific multiple scattering and loading effects at wavelength λ nm. The values of A_{λ} and parameter B_{λ} reported by Chen et al. (2015) were used in this study for different wavelengths based on the DRI 2015 analyzer. $FT_{\lambda,i}$ and $FT_{\lambda,f}$ are the measured filter transmittance values before and after the thermal analysis, respectively. A is the filter area, and V is the sampling volume.

As black carbon (BC) and brown carbon (BrC) are the light-absorbing components in aerosol samples, this study uses a simplified two-component model to distinguish their relative contributions in the particles (Chen et al., 2015; Li et al., 2018):

$$b_{\text{abs}} = (K_{\text{BC}} \times \lambda^{-\text{AAE}_{\text{BC}}} + K_{\text{BrC}} \times \lambda^{-\text{AAE}_{\text{BrC}}}) \times \frac{A}{V} \quad (2)$$

where K_{BC} and K_{BrC} are the fitting coefficients for BC and BrC; AAE_{BC} and AAE_{BrC} are the AAE for BC and BrC, respectively. Previous studies have shown that when particulate matter is emitted mainly from biomass combustion processes, the corresponding AAE_{BC} value is close to 1.2 (Lack and Langridge, 2013). Therefore, the AAE_{BC} value in equation (2) is assumed to be 1.2 for the calculation in this study.

The absorbance mass absorption efficiency (MAE) can be calculated as:

$$\text{MAE} = \frac{b_{\text{abs}}}{C} \quad (3)$$

where C is the concentration of the corresponding absorbent substance, and BrC corresponds to the mass concentration of OC.

In this study, a DU-8200 single beam ultraviolet/visible spectrophotometer (DRAWELL) was used to determine the light absorption of the individual NAC standards (Abs_{λ}). More details were reported in our previous study (Zhang et al., 2022b). According to the Beer-Lambert law, the light absorption of a solution is defined as (Hecobian et al., 2010)

$$A_{i,j} = l \times C_i \times \varepsilon_{i,j} \quad (4)$$

where $A_{i,j}$ is the light absorption of the i -th NAC at j nm, C_i is the concentration of the i -th NAC in the solution (methanol solution was used in this study), and $\varepsilon_{i,j}$ is the molar extinction coefficient of the i -th NAC at j nm.

The MAE of NACs can be calculated as (Hecobian et al., 2010; Teich et al., 2017):

$$\text{MAE}_{i,j} = \frac{b_{\text{liq}}}{10000 \times M_i} \times N_A = \frac{1000 \times \ln(10) \times \varepsilon_{i,j} / N_A}{10000 \times M_i} \times N_A \quad (5)$$

where $\text{MAE}_{i,j}$ is the MAE of the i -th NAC at j nm, M_i is the molecular mass of the i -th NAC, N_A is Avogadro's constant, and b_{liq} is the molecular absorption cross section in the liquid phase. The MAE at 365 nm for the 44 NAC standards calculated based on the above equations are shown in Fig. S2. The solvent used in this study was methanol. Many studies on the light absorption of BrC have been conducted by extracting with solvents for the convenience of scanning broad-band light absorption properties. Initially, water was widely used as an extraction solvent. However, the extraction efficiency of water was found to be not high since a large proportion of BrC was insoluble in water. Instead, methanol as an extraction solvent could significantly improve the extraction efficiency (Xie et al., 2017), and therefore methanol has been increasingly chosen as the solvent for studying the light absorption of BrC. It is worth noting that the solvent effect should be considered in the BrC measurement of solvent method. Under the influence of solvent polarity, the absorption peak and wavelength will change considerably. As shown in Fig. S3, the light absorption of toluene dissolved in n-hexane varies with that dissolved in methanol. However, researchers argued that the fluctuation was within 20%, which was acceptable. We admit that there are uncertainties in solvent-based approaches in understanding the light absorption of BrC constituents, although the methanol extraction method has been widely used and seems to be a kind of best available approach.

3. Results and discussion

3.1. Compositions of PM-bound NPAHs

On average, the 26 NPAHs and 18 NPs measured from corn straw burning contributed 0.22 \pm 0.08‰ of the total organic matter (OM=OC \times 1.8; Andreae et al., 2008; Fu et al., 2015). Fig. 1 shows the mean mass contribution percentages of individual NPAHs in the total measured NPAHs (The data points of Fig. 1 were shown in Table S in supplementary material). 1,6-dinitropyrene was the most abundant with a share of 13.4 \pm 4.0%, followed by 2-nitropyrene (13.3 \pm 4.4%) and 1,8-dinitropyrene (9.6 \pm 2.6%), all being nitrated pyrenes. The composition profiles of NPAHs from biomass burning varied greatly in different studies. Shen et al. (2012) burned 27 common woods with cookstoves in rural China and found that 9-nitroanthracene was the most abundant (12.4 \pm 4.6%) among the 9 p.m.-bound NPAHs, while 5-nitroacenaphthene was not detected or negligible. However, Vicente et al. (2016) found that 5-nitroacenaphthene was the dominant species (91.3 \pm 9.4%) among the 15 measured NPAHs in the plumes of burning common biomass composite fuels and wood, while 9-nitroanthracene was not detected. In this study, 9-nitroanthracene and 5-nitroacenaphthene were both detected, but were not dominant among the measured NPAH species. Substantial discrepancies between studies call for a more thorough characterization.

Previous studies have proposed using ratios between specific NPAH compounds to distinguish their different sources. Chuesaard et al. (2014) and Orakij et al. (2017) proposed that a ratio of 9-nitroanthracene/1-nitropyrene greater than 10 could indicate biomass combustion as the major contributor. However, Shen et al. (2012) found that the 9-nitroanthracene/1-nitropyrene ratio varied considerably between

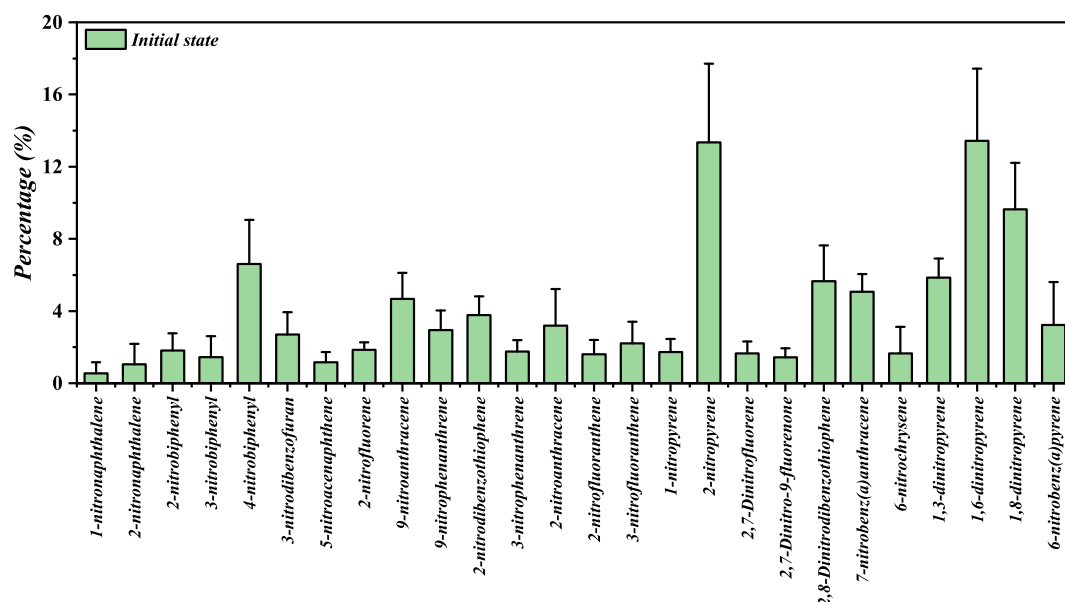


Fig. 1. Profiles of the 26 particulate NPAHs emitted from the open burning of corn straws.

different wood burnings, and it was only 0.62 for lespedeza burning. The results from this study showed that the 9-nitroanthracene/1-nitropyrene ratio was 3.3 ± 1.7 . Therefore, the suitability of a 9-nitroanthracene/1-nitropyrene ratio greater than 10 as a marker of biomass burning has yet to be fully explored.

2-nitropyrene has been widely used to indicate secondary formation in various field observations (Arey et al., 1986; Arey et al., 1988; Atkinson and Arey, 1994; Arey, 1998; Zhang et al., 2018, 2019). Assuming that 2-nitropyrene is mainly generated by the photochemical reaction of pyrene with OH radicals, 2-nitrofluoranthene is generated by the photochemical reaction of pyrene with both OH radicals and NO_3 radicals, and 1-nitropyrene is mainly primarily emitted from combustion sources, Arey et al. (1988) first proposed the 2-nitrofluoranthene/1-nitropyrene ratio as an indicator for the relative contribution of primary emission and secondary formation, and the 2-nitrofluoranthene/2-nitropyrene ratio as an indicator for the relative contribution of reaction pathways involving OH or NO_3 radicals. Orakij et al. (2017) observed a significant increase in indoor PM-bound 2-nitropyrene during cooking with biomass fuels. Chuesaard et al. (2014) also found

higher levels of 2-nitropyrene in ambient PM in a region in Thailand with dominant biomass burning contributions. In this study, high levels of 2-nitropyrene among NPAHs were also detected in the PM from corn straw burning. By further comparing with other emission sources, Zhao et al. (2019) found that 2-nitropyrene shared mass percentages of 2.0–48.5% in the 12 p.m.-bound NPAHs emitted by inland ships, 21.9–53.7% in the 12 p.m.-bound NPAHs emitted by ocean ships, and reached as high as 50% for both inland ships and ocean-going vessels at berth (Zhao et al., 2019). Nevertheless, both Orakij et al. (2017) and Zhao et al. (2019) insisted that the detected 2-nitropyrene should be secondarily formed during sampling and should not be regarded as directly emitted. More recently, Zhang et al. (2022b) reported that 2-nitropyrene ranked 6th with a share of 5.1% among the 26 measured NPAHs in vehicle emissions based on a tunnel test. Therefore, it might be inappropriate to use 2-nitropyrene as an indicator of the secondary formation pathway.

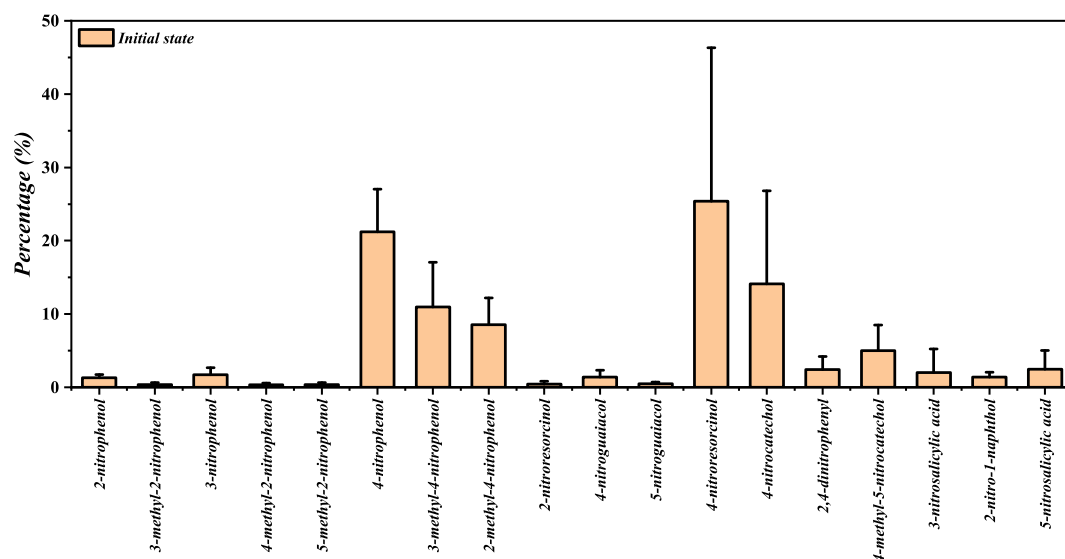


Fig. 2. Composition profiles of the 18 particulate NPs emitted from the open burning of corn straws.

3.2. Compositions of PM-bound NPs

Measured 18 NP species accounted for an average percentage of $0.16 \pm 0.07\%$ in OM. Fig. 2 shows the compositions of PM-bound NPs emitted from the corn straw burning (The data points of Fig. 2 were shown in Table S in supplementary material). 4-nitroresorcinol showed the highest average proportion of 25.4%, followed by 4-nitrophenol ($21.2 \pm 6.2\%$), 4-nitrocatechol ($14.1 \pm 12.7\%$), 3-methyl-4-nitrophenol ($11.0 \pm 6.1\%$) and 2-methyl-4-nitrophenol ($8.5 \pm 3.7\%$). These top 5 NPs were responsible for 80.2% of the total measured NPs. Previous studies also found that 4-nitrophenol/4-nitroresorcinol and their methyl derivatives were major NP species that could account for over 60% of the total measured NACs (Mohr et al., 2013; Lin et al., 2016; Wang et al., 2017; Xie et al., 2019). NPs are mainly derived from the pyrolysis of lignin during biomass burning (Simoneit, 2002) and their emissions are influenced by combustion conditions. Wang et al. (2017) found that 4-nitroresorcinol and 4-nitrocatechol and their methyl derivatives were more abundant under complete combustion while 4-nitrophenol and its methyl derivatives were more abundant under incomplete combustion. The open burning of corn straw in this study was a mixture of flaming and smoldering, so the NP emissions showed a high proportion of both 4-nitroresorcinols/4-nitrocatechols and 4-nitrophenols.

Linuma et al. (2010) indicated that methyl-nitrocatechols are mainly derived from the secondary formation in ambient air while 4-nitrocatechol can be both primarily emitted and secondarily formed. Therefore, methyl-nitrocatechols are proposed to be a tracer to differentiate secondary formation from primary emissions. In this study, 4-nitrocatechol had a higher proportion ($14.1 \pm 12.7\%$) and 4-methyl-5-nitrocatechol was also detected although it had a lower proportion ($5.0 \pm 3.4\%$) in the straw burning aerosols. This was consistent with the study by Wang et al. (2017) in which they found a higher proportion of PM-bound 4-nitrocatechol (18–55%) and a lower proportion of 4-methyl-5-nitrocatechol (1–14%) in the biomass burning aerosols.

Recently, Wang et al. (2019) observed significantly enhanced correlation between NACs and relative humidity at night, and suggested that liquid-phase oxidation might be an important pathway to form NACs at night. Ren et al. (2022) also found that 4-nitroguaiacol and 2,4-dinitrophenol, mainly from secondary formation, showed a more significant correlation with relative humidity based on field observations. Moreover, Ren et al. (2022) found that either during the daytime or at nighttime, when the relative humidity (RH) was below 40%, the (4-nitroguaiacol + 2,4-dinitrophenol)/NACs ratio was overall less than 0.4, and when RH was above 40%, the ratio increased with the increase of RH, and finally stabilized at about 0.6. Therefore, Ren et al. (2022) proposed using the (4-nitroguaiacol + 2,4-dinitrophenol)/NPs ratio to indicate the importance of the liquid-phase oxidation pathway in the NAC formation. The (4-nitroguaiacol + 2,4-dinitrophenol)/NPs ratio was 0.3 in this study, consistent with the results by Ren et al. (2022) that the ratio was below 0.4 when RH was below 40%. Zhang et al. (2022a) found that the 2-nitro-1-naphthol/4-nitrocatechol ratio was around 15 in coal combustion aerosols, while it was only 2–3 in biomass burning aerosols, and therefore they suggested that this ratio may help distinguish between coal combustion and biomass burning, both of which give off levoglucosan and thus are hard to be differentiate when using levoglucosan as a tracer. In this study, an even lower 2-nitro-1-naphthol/4-nitrocatechol ratio of 0.3 ± 0.3 was observed for corn straw burning aerosols, which is still greatly lower than that reported by Zhang et al. (2022a) for coal combustion aerosols.

3.3. Light absorption of BrC and PM-bound NACs

The light absorption by the straw burning aerosols at 365 nm and 635 nm was $819.0 \pm 259.8 \text{ Mm}^{-1}$ and $53.2 \pm 25.4 \text{ Mm}^{-1}$, respectively, and the AAE for the corn straw burning aerosol was 4.1 ± 0.7 . A significant AAE greater than 1 indicated a large amount of BrC in corn straw burning PM (Tian et al., 2019). Tian et al. (2019) also observed

brown carbon emitted from corn straw open burning has stronger light dependence than those from burning other 6 types of biomasses. In this study, the light absorption by black carbon (BC) and BrC was separated based on non-linear regression. According to previous studies, a wavelength of 365 nm was chosen to characterize the optical properties of BrC (Hecobian et al., 2010). As shown in Fig. 3, the light absorption of BrC at 365 nm was $738.8 \pm 319.7 \text{ Mm}^{-1}$, responsible for $96.5 \pm 3.2\%$ of the total light absorption by carbonaceous aerosols at 365 nm, and the mass absorption efficiency ($\text{MAE}_{365 \text{ nm}}$) of organic carbon (OC) was $1.9 \pm 0.6 \text{ m}^2 \text{ g}^{-1} \text{C}$ with an AAE of 5.4 ± 0.6 . Compared to the previous solution-based MAE_{OC} of $0.62\text{--}2.09 \text{ m}^2 \text{ g}^{-1} \text{C}$ for biomass burning aerosols (Table 1), the higher MAE_{OC} in this study may come from two reasons: first, the extraction efficiency of the solvent extraction method to characterize MAE has a large uncertainty, and previous studies have shown that the extraction efficiency, even with methanol as solvent, is around 90% for the PM from biomass burning (Xie et al., 2017). The light absorption of unextracted OC may bring about a lower MAE; second, different combustion conditions and different wood types bring about great uncertainties in the characterization of PM from biomass burning. Previous studies have shown that the composition of OC from biomass burning changes significantly under different combustion conditions (Wang et al., 2017). This difference in the compositions of organic aerosols would certainly results in different light absorption properties.

In this study, the total light absorption of the 44 NACs at 365 nm was $1.2 \pm 0.6 \text{ Mm}^{-1}$, and their contribution to the light absorption of BrC was $1.6 \pm 0.4\%$, which is a relatively negligible small portion. As total concentrations of NPs were about one order of magnitude higher than that of NPAHs, NPs contributed over 80% of the light absorption by the NACs. As shown in Fig. 4 (The data points of Fig. 4 were shown in Table S in supplementary material), 1,8-dinitropyrene had the highest light absorption contribution ($18.2 \pm 6.6\%$) among the NPAHs, followed by 1,3-dinitropyrene ($9.4 \pm 3.8\%$), 6-nitrobenzo [a]pyrene ($8.8 \pm 12.0\%$) and 1, 6-dinitropyrene ($7.6 \pm 1.3\%$). 4-nitroresorcinol alone accounted for $42.6 \pm 34.2\%$ of the light absorption contribution by the measured NPs, followed by 4-nitrocatechol ($16.6 \pm 19.5\%$), 4-nitrophenol ($12.0 \pm 3.8\%$) and 3-methyl-4-nitrophenol ($6.3 \pm 3.5\%$).

Observations in a forest area revealed that the light absorption of 5 NACs at 370 nm could contribute 4% of the total light absorption of BrC (Mohr et al., 2013). More recently, Huang et al. (2020) found that the light absorption of 17 NACs at 365 nm was responsible for 10%–13% that of the humic-like substances (HULIS) in urban areas. Li et al.

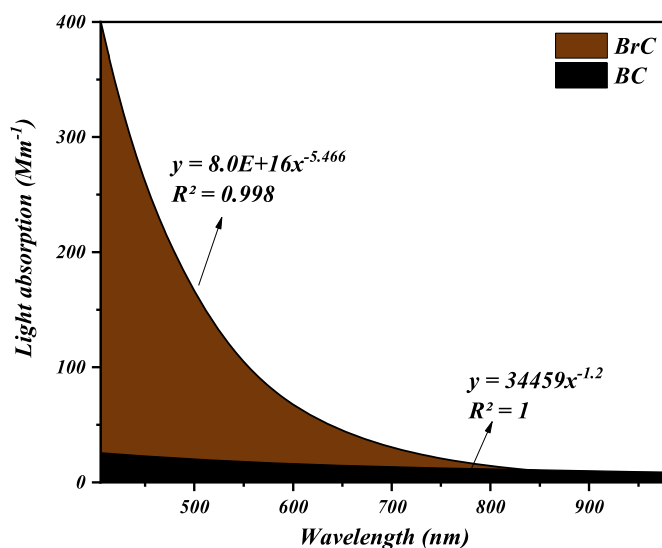


Fig. 3. Average light absorption of BrC and BC from the open burning of corn straws.

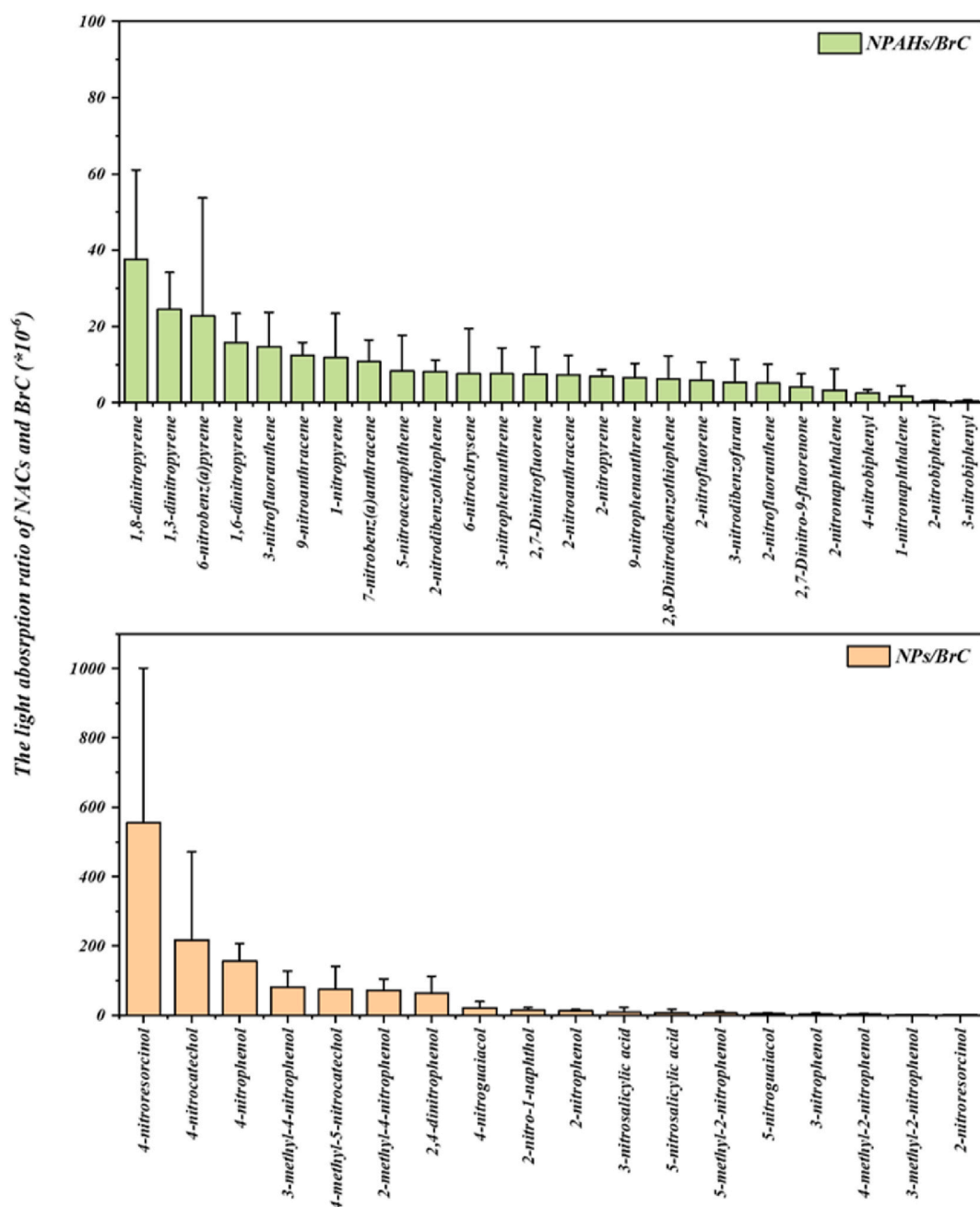
Table 1

Comparison of MAE of BrC from biomass burning sources.

	Type	MAE _{365 nm} (m ² g ⁻¹ C)	References
Biomass burning	WSOC	1.6 ± 0.6	Tang et al. (2020)
	WSOC	0.7	Hecobian et al., 2010
	WSOC	1.2	Cheng et al. (2016)
	MSOC	1.5	
	WSOC	1.3	Satish et al. (2017)
	MSOC	0.9–1.8	Xie et al. (2017)
	HULIS	0.6–0.8	Hoffer et al. (2006)
	HULIS	1.0–2.1	Fan et al. (2016)
	HULIS	0.9–1.5	Huo et al. (2021)

WSOC: Water-soluble organic carbon; HULIS: humic-like substances.

(2020a) found that the light absorption of 8 NACs at 365 nm contributed 1.6–3.2% to methanol-soluble BrC (MSBrC) in urban areas. Studies have also demonstrated that there were highly significant correlations between BrC/NPs and levoglucosan, a biomass burning tracer (Yang et al., 2020; Yuan et al., 2021). Therefore, Yan et al. (2020) considered NACs as important components of BrC from biomass burning. However, our results showed that the contribution of NACs to the light absorption of BrC from corn straw burning at 365 nm was not significant and can be neglected. Nevertheless, due to substantially secondary formation of the NACs from biomass burning related precursors (Li et al., 2020b), the overall contribution of biomass burning to NACs and their light absorption of BrC might not be negligible. As observed by Lin et al. (2017), 60 nitrogen-containing aromatic compounds measured by high-resolution mass spectrometry could contribute 50–80% of the total light absorption of BrC at 400 nm during the bonfire festival in Israel. In fact, combinedly using high performance liquid chromatography

**Fig. 4.** Characterization of the light absorption contribution of 44 measured NACs to BrC in this study.

(HPLC), photodiode array spectrophotometer (PDA) and high resolution mass spectrometry (HRMS), Lin et al. (2016) determined hundreds of chromophores in emissions from open burning of biomasses (sawgrass, peat, ponderosa pine and black spruce), and found the main light absorption contributors at 365 nm were nitrogen-containing high-carbon oxygenated substances. Xie et al. (2019) also pointed out that the chromophore might include nitrogen-containing compounds other than nitro-containing substances, such as compounds with the nitrile functional group.

3.4. Health risks of PM-bound NACs

NACs are highly lipophilic and thus can accumulate in plants and animals, causing harms to human health and plant growth (Kawanaka et al., 2008). Although many studies have been conducted on the toxicity of NACs, at present benzo [a]pyrene toxicity equivalent factors (TEFs) are available only for only a few NACs (Table S4). In this study, 9 NACs with TEFs are considered for the potential health risks of NACs. While the average concentration of the 16 USEPA priority PAHs was 3.1 times that of the 9 NACs (Fig. 5), the benzo(a)pyrene toxic equivalency quotients (TEQ_{BaP}) of the 16 priority PAHs were only about 10% that of the 9 NACs. Zhao et al. (2020) characterized the emission of ocean-going ships under different operating conditions and found that the average concentration of the 16 PAHs was 3.6 times that of the 8 NACs (5-nitroacenaphthene not measured), but their TEQ_{BaP} was only about 20% of the 8 NACs. Zhang et al. (2022b) found that the average concentration of the 16 PAHs were 27 times that of 9 NACs in vehicle emissions based on tunnel tests, and the average TEQ_{BaP} of the PAHs was still 1.5 times that of the 9 NACs. While people's exposure to PAHs from burning biomasses or solid biofuels is of wide concern, this study highlights that higher health risks may induced by NACs than PAHs.

Benzo [a]pyrene and dibenzo [a,h]anthracene were the main toxic contributors in the 16 PAHs in terms of TEQ_{BaP} , together accounting for $82.4 \pm 3.6\%$ of the total TEQ_{BaP} of 16 PAHs. 1, 6-dinitropyrene was the main toxic contributor to the TEQ_{BaP} of the 9 NACs, and it alone was responsible for 81.6% of the total TEQ_{BaP} of 9 NACs.

4. Conclusions

In this study PM-bound NACs from corn straw open burning were characterized by near-ambient dilution using a large indoor chamber followed by filter-based sampling and GC-MSD analysis. The composition profiles of measured 26 NPAHs and 18 NPs were obtained. Nitropyrene and dinitropyrene are abundant NPAH species while nitrophenols/methylnitrophenols and nitrobenzenediols/methyl nitrobenzenediols were abundant among NPs. The results may also help assess the applicability of some source indicators. 2-nitropyrene, for example, was widely used as an indicator of the secondary formation pathway, but in this study it was detected in the PM from corn straw burning, signaling that it might be inappropriate to use as an indicator of secondary formation. This study also found that while BrC emitted from the straw burning contributed more than 90% of the total light absorption of PM at 365 nm, the measured NACs were only responsible for a negligible share of 0.2% in BrC. More importantly, this study implied that the 9 NACs in the PM from corn straw burning were about 10 times more toxic than the 16 USEPA priority PAHs in terms of calculated TEQ_{BaP} although their average total concentration was only about one-third of the 16 PAHs. The results of this study suggest that while PAHs are among the main focuses when considering health risks associated with biomass fuels, special attention should also be paid to toxic NAC species, like 1, 6-dinitropyrene as revealed in this study.

Credit author statement

Runqi Zhang: Investigation, Methodology, Formal analysis, Writing – original draft. **Sheng Li:** Investigation, Formal analysis. **Xuewei Fu:**

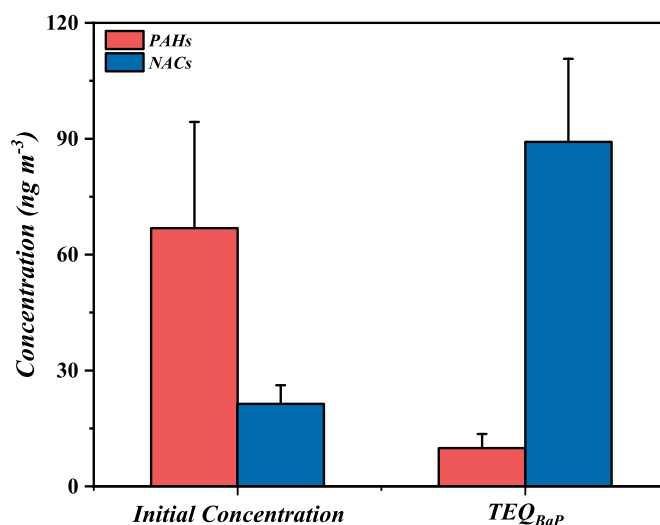


Fig. 5. Comparison of TEQ_{BaP} of PAHs and NACs in this study.

Investigation, Formal analysis. **Wei Song:** Data curation, Writing – review & editing. **Yanli Zhang:** Writing – review & editing. **Xinming Wang:** Data curation, Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.121332>.

References

- Andersson, H., Piras, E., Demma, J., Hellman, B., Brittebo, E., 2009. Low levels of the air pollutant 1-nitropyrene induce DNA damage, increased levels of reactive oxygen species and endoplasmic reticulum stress in human endothelial cells. *Toxicology* 262, 57–64.
- Andreae, M.O., Schmid, O., Yang, H., Chand, D., Zhen Yu, J., Zeng, L.M., Zhang, Y.H., 2008. Optical properties and chemical composition of the atmospheric aerosol in urban Guangzhou, China. *Atmos. Environ. Times* 42, 6335–6350.
- Arey, J., Zielinska, B., Atkinson, R., Winer, A.M., Ramdahl, T., Pitts, J.N., 1986. The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x. *Atmos. Environ.* 20, 2339–2345.
- Arey, J., Zielinska, B., Harger, W.P., Atkinson, R., Winer, A.M., 1988. The contribution of nitrofluoranthenes and nitropyrenes to the mutagenic in southern-California. *Mutat. Res.* 207, 45–51.
- Arey, J., 1998. Atmospheric reactions of PAHs including formation of nitroarenes. In: Neilson, A.H. (Ed.), *PAHs and Related Compounds: Chemistry*. Springer Berlin Heidelberg, pp. 347–385.

- Atkinson, R., Arey, J., 1994. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons - formation of atmospheric mutagens. *Environ. Health Perspect.* 102, 117–126.
- Chen, L.W.A., Chow, J.C., Wang, X.L., Robles, J.A., Sumlin, B.J., Lowenthal, D.H., Zimmermann, R., Watson, J.G., 2015. Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol. *Atmos. Meas. Tech.* 8, 451–461.
- Chen, Y., Bond, T.C., 2010. Light absorption by organic carbon from wood combustion. *Atmos. Chem. Phys.* 10, 1773–1787.
- Cheng, Y., He, K.B., Du, Z.Y., Huang, G., Liu, J.M., Ma, Y.L., Zheng, M., Weber, R.J., 2016. The characteristics of brown carbon aerosol during winter in Beijing. *Atmos. Environ.* 127, 355–364.
- Chow, K.S., Huang, X.H.H., Yu, J.Z., 2016. Quantification of nitroaromatic compounds in atmospheric fine particulate matter in Hong Kong over 3 years: field measurement evidence for secondary formation derived from biomass burning emissions. *Environ. Chem.* 13, 665–673.
- Chuesaard, T., Chetianukornkul, T., Kameda, T., Hayakawa, K., Toriba, A., 2014. Influence of biomass burning on the levels of atmospheric polycyclic aromatic hydrocarbons and their nitro derivatives in Chiang Mai, Thailand. *Aerosol Air Qual. Res.* 14, 1247–1257.
- Claeys, M., Vermeylen, R., Yasmineen, F., Gomez-Gonzalez, Y., Chi, X., Maenhaut, W., Meszaros, T., Salma, I., 2012. Chemical characterisation of humic-like substances from urban, rural and tropical biomass burning environments using liquid chromatography with UV/vis photodiode array detection and electrospray ionisation mass spectrometry. *Environ. Chem.* 9, 273–284.
- Desyaterik, Y., Sun, Y., Shen, X., Lee, T., Wang, X., Wang, T., Collett Jr., J.L., 2013. Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China. *J. Geophys. Res. Atmos.* 118, 7389–7399.
- Fan, X.J., Wei, S.Y., Zhu, M.B., Song, J.Z., Peng, P.A., 2016. Comprehensive characterization of humic-like substances in smoke PM_{2.5} emitted from the combustion of biomass materials and fossil fuels. *Atmos. Chem. Phys.* 16, 13321–13340.
- Fang, Z., Deng, W., Zhang, Y.L., Ding, X., Tang, M.J., Liu, T.Y., Hu, Q.H., Zhu, M., Wang, Z.Y., Yang, W.Q., Huang, Z.H., Song, W., Bi, X.H., Chen, J.M., Sun, Y.L., George, C., Wang, X.M., 2017. Open burning of rice, corn and wheat straws: primary emissions, photochemical aging, and secondary organic aerosol formation. *Atmos. Chem. Phys.* 17, 14821–14839.
- Fang, Z., Deng, W., Wang, X.M., He, Q.F., Zhang, Y.L., Hu, W.W., Song, W., Zhu, M., Lowther, S., Wang, Z.Y., Fu, X.W., Hu, Q.H., Bi, X.H., George, C., Rudich, Y., 2022. Evolution of light absorption properties during photochemical aging of straw open burning aerosols. *Sci. Total Environ.* 838, 156431.
- Feng, Y., Ramanathan, V., Kotamarthi, V.R., 2013. Brown carbon: a significant atmospheric absorber of solar radiation? *Atmos. Chem. Phys.* 13, 8607–8621.
- Frka, S., Sala, M., Kroflic, A., Hus, M., Cusak, A., Grgic, I., 2016. Quantum chemical calculations resolved identification of methylnitrocatechols in atmospheric aerosols. *Environ. Sci. Technol.* 50, 5526–5535.
- Fu, X.X., Guo, H., Wang, X.M., Ding, X., He, Q.F., Liu, T.Y., Zhang, Z., 2015. PM_{2.5} acidity at a background site in the Pearl River Delta region in fall-winter of 2007–2012. *J. Hazard Mater.* 286, 484–492.
- Gonzalez-Flecha, B., 2004. Oxidant mechanisms in response to ambient air particles. *Mol. Aspect. Med.* 25, 169–182.
- Hecobian, A., Zhang, X., Zheng, M., Frank, N., Edgerton, E.S., Weber, R.J., 2010. Water-soluble organic aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States. *Atmos. Chem. Phys.* 10, 5965–5977.
- Hoffer, A., Gelencser, A., Guyon, P., Kiss, G., Schmid, O., Frank, G.P., Artaxo, P., Andreae, M.O., 2006. Optical properties of humic-like substances (HULIS) in biomass-burning aerosols. *Atmos. Chem. Phys.* 6, 3563–3570.
- Hoffmann, D., Iinuma, Y., Herrmann, H., 2007. Development of a method for fast analysis of phenolic molecular markers in biomass burning particles using high performance liquid chromatography/atmospheric pressure chemical ionisation mass spectrometry. *J. Chromatogr. A* 1143, 168–175.
- Huang, R.J., Yang, L., Shen, J., Yuan, W., Gong, Y., Guo, J., Cao, W., Duan, J., Ni, H., Zhu, C., Dai, W., Li, Y., Chen, Y., Chen, Q., Wu, Y., Zhang, R., Dusek, U., O'Dowd, C., Hoffmann, T., 2020. Water-insoluble organics dominate brown carbon in wintertime urban aerosol of China: chemical characteristics and optical properties. *Environ. Sci. Technol.* 54, 7836–7847.
- Huo, Y.Q., Wang, Y., Qi, W.M., Jiang, M.H., Li, M., 2021. Comprehensive characterizations of HULIS in fresh and secondary emissions of crop straw burning. *Atmos. Environ.* 248, 118220.
- Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M.O., Helas, G., Parmar, R., Herrmann, H., 2007. Source characterization of biomass burning particles: the combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat. *J. Geophys. Res.* 112, D08209.
- Iinuma, Y., Boege, O., Graefe, R., Herrmann, H., 2010. Methyl-Nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols. *Environ. Sci. Technol.* 44, 8453–8459.
- Kawanaka, Y., Matsumoto, E., Wang, N., Yun, S.-J., Sakamoto, K., 2008. Contribution of nitrated polycyclic aromatic hydrocarbons to the mutagenicity of ultrafine particles in the roadside atmosphere. *Atmos. Environ.* 42, 7423–7428.
- Lack, D.A., Langridge, J.M., 2013. On the attribution of black and brown carbon light absorption using the Ångström exponent. *Atmos. Chem. Phys.* 13, 10535–10543.
- Laskin, A., Laskin, J., Nizkorodov, S.A., 2015. Chemistry of atmospheric brown carbon. *Chem. Rev.* 115, 4335–4382.
- Li, J., Bo, Y., Xie, S., 2016. Estimating emissions from crop residue open burning in China based on statistics and MODIS fire products. *J. Environ. Sci.* 44, 158–170.
- Li, S., Zhu, M., Yang, W., Tang, M., Huang, X., Yu, Y., Fang, H., Yu, X., Yu, Q., Fu, X., Song, W., Zhang, Y., Bi, X., Wang, X., 2018. Filter-based measurement of light absorption by brown carbon in PM_{2.5} in a megacity in South China. *Sci. Total Environ.* 633, 1360–1369.
- Li, X., Yang, Y., Liu, S., Zhao, Q., Wang, G., Wang, Y., 2020a. Light absorption properties of brown carbon (BrC) in autumn and winter in Beijing: composition, formation and contribution of nitrated aromatic compounds. *Atmos. Environ.* 223, 117289.
- Li, M., Wang, X., Lu, C., Li, R., Zhang, J., Dong, S., Yang, L., Xue, L., Chen, J., Wang, W., 2020b. Nitrated phenols and the phenolic precursors in the atmosphere in urban Jinan, China. *Sci. Total Environ.* 714, 136760.
- Lin, Y.H., Budisulistiorini, H., Chu, K., Siejack, R.A., Zhang, H., Riva, M., Zhang, Z., Gold, A., Kautzman, K.E., Surratt, J.D., 2014. Light-absorbing oligomer formation in secondary organic aerosol from reactive uptake of isoprene epoxydiols. *Environ. Sci. Technol.* 48, 12012–12021.
- Lin, P., Aiona, P.K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S.A., Laskin, A., 2016. Molecular characterization of brown carbon in biomass burning aerosol particles. *Environ. Sci. Technol.* 50, 11815–11824.
- Lin, P., Bluvstein, N., Rudich, Y., Nizkorodov, S.A., Laskin, J., Laskin, A., 2017. Molecular chemistry of atmospheric brown carbon inferred from a nationwide biomass burning event. *Environ. Sci. Technol.* 51, 11561–11570.
- Liu, D., Lin, T., Syed, J.H., Cheng, Z., Xu, Y., Li, K., Zhang, G., Li, J., 2017. Concentration, source identification, and exposure risk assessment of PM_{2.5}-bound parent PAHs and nitro-PAHs in atmosphere from typical Chinese cities. *Sci. Rep.* 7, 10398.
- Mohr, C., Lopez-Hilfiker, F.D., Zotter, P., Prevot, A.S., Xu, L., Ng, N.L., Herndon, S.C., Williams, L.R., Franklin, J.P., Zahniser, M.S., Worsnop, D.R., Knighton, W.B., Aiken, A.C., Gorkowski, K.J., Dube, M.K., Allan, J.D., Thornton, J.A., 2013. Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time. *Environ. Sci. Technol.* 47, 6316–6324.
- Orakij, W., Chetianukornkul, T., Kasahara, C., Boongla, Y., Chuesaard, T., Furuchi, M., Hata, M., Tang, N., Hayakawa, K., Toriba, A., 2017. Polycyclic aromatic hydrocarbons and their nitro derivatives from indoor biomass-fueled cooking in two rural areas of Thailand: a case study. *Air Qual. Atmos. Health* 10, 747–761.
- Ovrevik, J., Refsnes, M., Holme, J.A., Schwarze, P.E., Lag, M., 2013. Mechanisms of chemokine responses by polycyclic aromatic hydrocarbons in bronchial epithelial cells: sensitization through toll-like receptor-3 priming. *Toxicol. Lett.* 219, 125–132.
- Park, E.J., Park, K., 2009. Induction of pro-inflammatory signals by 1-nitropyrene in cultured BEAS-2B cells. *Toxicol. Lett.* 184, 126–133.
- Ren, Y., Wei, J., Wang, G., Wu, Z., Ji, Y., Li, H., 2022. Evolution of aerosol chemistry in Beijing under strong influence of anthropogenic pollutants: composition, sources, and secondary formation of fine particulate nitrated aromatic compounds. *Environ. Res.* 204, 111982.
- Satish, R., Shamjad, P., Thamban, N., Tripathi, S., Rastogi, N., 2017. Temporal characteristics of brown carbon over the central Indo-Gangetic Plain. *Environ. Sci. Technol.* 51, 6765–6772.
- Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., Li, W., Shen, H., Huang, Y., Chen, Y., Chen, H., Yang, Y., Wang, W., Wang, X., Liu, W., Simonich, S.L.M., 2012. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons from residential wood combustion in rural China. *Environ. Sci. Technol.* 46, 8123–8130.
- Simoneit, B.R.T., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 17, 129–162.
- Streets, D.G., Yarbber, K.F., Woo, J.H., Carmichael, G.R., 2003. Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions. *Global Biogeochem. Cycles* 17, 1099.
- Tang, J., Li, J., Su, T., Han, Y., Mo, Y.Z., Jiang, H.X., Cui, M., Jiang, B., Chen, Y.J., Tang, J.H., Song, J.Z., Peng, P.A., Zhang, G., 2020. Molecular compositions and optical properties of dissolved brown carbon in biomass burning, coal combustion, and vehicle emission aerosols illuminated by excitation-emission matrix spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry analysis. *Atmos. Chem. Phys.* 20, 2513–2532.
- Teich, M., van Pinxteren, D., Wang, M., Kecorius, S., Wang, Z., Müller, T., Močnik, G., Herrmann, H., 2017. Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments in Germany and China. *Atmos. Chem. Phys.* 17, 1653–1672.
- Tian, J., Wang, Q., Ni, H., Wang, M., Zhou, Y., Han, Y., Shen, Z., Pongpiachan, S., Zhang, N., Zhao, Z., Zhang, Q., Zhang, Y., Long, X., Cao, J., 2019. Emission characteristics of primary brown carbon absorption from biomass and coal burning: development of an optical emission inventory for China. *J. Geophys. Res. Atmos.* 124, 1879–1893.
- Vicente, E.D., Vicente, A.M., Bandowe, B.A.M., Alves, C.A., 2016. Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azarenes and nitrated PAHs) from manually and automatically fired combustion appliances. *Air Qual. Atmos. Health* 9, 653–668.
- Vidovic, K., Jurkovic, D.L., Sala, M., Kroflic, A., Grgic, I., 2018. Nighttime aqueous-phase formation of nitrocatechols in the atmospheric condensed phase. *Environ. Sci. Technol.* 52, 9722–9730.
- Vinzents, P.S., Moller, P., Sorensen, M., Knudsen, L.E., Hertel, O., Jensen, F.P., Schibye, B., Loft, S., 2005. Personal exposure to ultrafine particles and oxidative DNA damage. *Environ. Health Perspect.* 113, 1485–1490.
- Wang, X., Liu, T., Bernard, F., Ding, X., Wen, S., Zhang, Y., Zhang, Z., He, Q., Lu, S., Chen, J., Saunders, S., Yu, J., 2014. Design and characterization of a smog chamber for studying gas-phase chemical mechanisms and aerosol formation. *Atmos. Meas. Tech.* 7, 301–313.
- Wang, X., Gu, R., Wang, L., Xu, W., Zhang, Y., Chen, B., Li, W., Xue, L., Chen, J., Wang, W., 2017. Emissions of fine particulate nitrated phenols from the burning of five common types of biomass. *Environ. Pollut.* 230, 405–412.

- Wang, Y., Hu, M., Wang, Y., Zheng, J., Shang, D., Yang, Y., Liu, Y., Li, X., Tang, R., Zhu, W., Du, Z., Wu, Y., Guo, S., Wu, Z., Lou, S., Hallquist, M., Yu, J.Z., 2019. The formation of nitro-aromatic compounds under high NO_x and anthropogenic VOC conditions in urban Beijing, China. *Atmos. Chem. Phys.* 19, 7649–7665.
- Xie, M., Hays, M.D., Holder, A.L., 2017. Light-absorbing organic carbon from prescribed and laboratory biomass burning and gasoline vehicle emissions. *Sci. Rep.* 7, 7318.
- Xie, M., Chen, X., Hays, M.D., Holder, A.L., 2019. Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning. *Atmos. Chem. Phys.* 19, 2899–2915.
- Yan, J., Wang, X., Gong, P., Wang, C., 2020. Nitratated polycyclic aromatic compounds in the atmospheric environment: a review. *Crit. Rev. Environ. Sci. Technol.* 51, 1159–1185.
- Yang, X., Liu, S., Xu, Y., Liu, Y., Chen, L., Tang, N., Hayakawa, K., 2017. Emission factors of polycyclic and nitro-polycyclic aromatic hydrocarbons from residential combustion of coal and crop residue pellets. *Environ. Pollut.* 231, 1265–1273.
- Yang, Y., Li, X., Shen, R., Liu, Z., Ji, D., Wang, Y., 2020. Seasonal variation and sources of derivatized phenols in atmospheric fine particulate matter in North China Plain. *J. Environ. Sci.* 89, 136–144.
- Yu, Q.Q., Gao, B., Li, G.H., Zhang, Y.L., He, Q.F., Deng, W., Huang, Z.H., Ding, X., Hu, Q. H., Huang, Z.Z., Wang, Y.J., Bi, X.H., Wang, X.M., 2016. Attributing risk burden of PM_{2.5}-bound polycyclic aromatic hydrocarbons to major emission sources: case study in Guangzhou, south China. *Atmos. Environ.* 142, 313–323.
- Yu, Q.Q., Yang, W.Q., Zhu, M., Gao, B., Li, S., Li, G.H., Fang, H., Zhou, H.S., Zhang, H.N., Wu, Z.F., Song, W., Tan, J.H., Zhang, Y.L., Bi, X.H., Chen, L.G., Wang, X.M., 2018. Ambient PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) in rural Beijing: unabated with enhanced temporary emission control during the 2014 APEC summit and largely aggravated after the start of wintertime heating. *Environ. Pollut.* 238, 532–542.
- Yuan, W., Huang, R.-J., Yang, L., Wang, T., Duan, J., Guo, J., Ni, H., Chen, Y., Chen, Q., Li, Y., Dusek, U., O'Dowd, C., Hoffmann, T., 2021. Measurement report: PM_{2.5}-bound nitratated aromatic compounds in Xi'an, Northwest China - seasonal variations and contributions to optical properties of brown carbon. *Atmos. Chem. Phys.* 21, 3685–3697.
- Zhao, J., Zhang, Y., Wang, T., Sun, L., Yang, Z., Lin, Y., Chen, Y., Mao, H., 2019. Characterization of PM_{2.5}-bound polycyclic aromatic hydrocarbons and their derivatives (nitro-and oxy-PAHs) emissions from two ship engines under different operating conditions. *Chemosphere* 225, 43–52.
- Zhao, J., Zhang, Y., Chang, J., Peng, S., Hong, N., Hu, J., Lv, J., Wang, T., Mao, H., 2020. Emission characteristics and temporal variation of PAHs and their derivatives from an ocean-going cargo vessel. *Chemosphere* 249, 126194.
- Zhang, J., Yang, L., Mellouki, A., Chen, J., Chen, X., Gao, Y., Jiang, P., Li, Y., Yu, H., Wang, W., 2018. Atmospheric PAHs, NPAHs, and OPAHs at an urban, mountainous, and marine sites in Northern China: molecular composition, sources, and ageing. *Atmos. Environ.* 173, 256–264.
- Zhang, J., Yang, L., Ledoux, F., Courcot, D., Mellouki, A., Gao, Y., Jiang, P., Li, Y., Wang, W., 2019. PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) and nitratated PAHs (NPAHs) in rural and suburban areas in Shandong and Henan Provinces during the 2016 Chinese New Year's holiday. *Environ. Pollut.* 250, 782–791.
- Zhang, R., Li, S., Fu, X., Pei, C., Huang, Z., Wang, Y., Chen, Y., Yan, J., Wang, J., Yu, Q., Luo, S., Zhu, M., Wu, Z., Fang, H., Xiao, S., Huang, X., Zeng, J., Zhang, H., Song, W., Zhang, Y., Bi, X., Wang, X., 2021. Emissions and light absorption of carbonaceous aerosols from on-road vehicles in an urban tunnel in south China. *Sci. Total Environ.* 790, 148220.
- Zhang, L., Hu, B., Liu, X.L., Luo, Z.H., Xing, R., Li, Y.J., Xiong, R., Li, G., Cheng, H.F., Lu, Q., Shen, G.F., Tao, S., 2022a. Variabilities in primary N-containing aromatic compound Emissions from residential solid fuel combustion and implications for source tracers. *Environ. Sci. Technol.* 56, 13622–13633.
- Zhang, R., Li, S., Fu, X., Pei, C., Wang, J., Wu, Z., Xiao, S., Huang, X., Zeng, J., Song, W., Zhang, Y., Bi, X., Wang, X., 2022b. Emissions and light absorption of PM_{2.5}-bound nitratated aromatic compounds from on-road vehicle fleets. *Environ. Pollut.* 312, 120070.
- Zhou, Y., Xing, X.F., Lang, J.L., Chen, D.S., Cheng, S.Y., Wei, L., Wei, X., Liu, C., 2017. A comprehensive biomass burning emission inventory with high spatial and temporal resolution in China. *Atmos. Chem. Phys.* 17, 2839–2864.