PM$_{2.5}$ Associated Phenols, Phthalates, and Water Soluble Ions from Five Stationary Combustion Sources

Zhiyong Li$^{1,2}$*, Songtao Guo$^1$, Zhenxin Li$^1$, Yutong Wang$^1$, Yao Hu$^1$, Yiran Xing$^1$, Guoqing Liu$^1$, Rui Fang$^1$, Hongtao Zhu$^1$

$^1$A Hebei Key Lab of Power Plant Flue Gas Multi-Pollutants Control, Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China

$^2$MOE Key Laboratory of Resources and Environmental Systems Optimization, Ministry of Education, Beijing 102206, China

ABSTRACT

Phenols and phthalates (PAEs) are always linked with the formation of secondary organic aerosols (SOA), while the water soluble ions (WSIs) are connected to the formation of secondary inorganic aerosols (SIA). A total of PM$_{2.5}$ associated 20 phenols, 6 phthalates, and 9 WSIs were detected using GC-MS, ICS-1100, ICP-OES, and UV-VIS spectrophotometer for 5 stationary incineration sources including the domestic garbage (DG), garbage-fired power plant (GFPP), workshop of cable combustion for metal reclamation (WCC), peanut straw (PS), and wheat straw (WS). The anion equivalent (AE) and cation equivalent (CE) concentrations indicated that the emitted PM$_{2.5}$ was alkaline for all the 5 combustion sources. Cl$^-$ possessed high contents among all the 5 burning sources and the highest value occurred at WCC due to the high Cl content in PVC. The WSI profiles were different from each other for the 5 incineration sources on the basis of high coefficients of divergence (CDs). The mass contributions of 9 WSIs in PM$_{2.5}$ from 5 sources were far lower than those of atmospheric PM$_{2.5}$. DEHP and DBP dominated in PM$_{2.5}$ from 4 sources, while WCC possessed high levels of DEHP, DNOP, and DBP. WCC possessed the highest daily intakes of PAEs due to its highest $\Sigma$6PAEs of 32000 ng g$^{-1}$ resulted from the high usage of plasticizers in PVC. The PAE profile similarities were found for both GFPP vs. DG and PS vs. WS based on low CDs. Only 11 phenols were detected for the 5 sources and WCC possessed the highest level of phenols although only phenol was detected. WS had the high levels of phenols due to the using of phenolic pesticides during wheat growth process.

Keywords: Phenols; Phthalates; Water soluble ions; Combustion source; Daily intake

*Corresponding author.

Tel.:+86 312 7525506; Fax: +86 312 7525506

Email address: lzy6566@126.com
INTRODUCTION

Fine particle matte (PM), especially PM with aerodynamic diameter less than 2.5 µm (PM$_{2.5}$), which impact human health and visibility negatively, and promote the formation of serious haze (Li et al., 2017a, 2017b, 2018a, 2018b, 2019a, 2019b; Masekameni et al., 2018; Wang et al., 2018a; Begum and Hopke, 2019; Ding et al., 2019; Hu et al., 2019; Zhang et al., 2019). The PM$_{2.5}$ characteristics including hygroscopicity, solubility and the particle light extinction efficiency were mainly determined by its chemical compositions (Wang et al., 2015; Yue et al., 2018; Zhao et al., 2018). Atmospheric PM$_{2.5}$ consists of primary and secondary pollutants such as volatile, semi-volatile, and non-volatile components derived from different emission sources (Sharma et al., 2018). The 60–70% of PM mass is attributed to the water soluble ions and this value fluctuates from 30% to 80% due to the industrialization and urbanization in China (Wang et al., 2015). The corresponding values for PM$_{2.5}$ were 79.2% for Shanghai (Huang et al., 2012), and 64.4% for Beijing (Sun et al., 2010).

Phenols, with at least one or more hydroxyl attached to the aromatic group, have unavoidable effects on environment and human health (Wang et al., 2018b). Previous research reported the secondary organic aerosol (SOA) could formed by oxidation of phenol, guaiacol (2-methoxyphenol), and syringol (2,6-dimethoxyphenol) from biomass burning (Yee et al., 2013). Chemical species emitted from biomass burning relied heavily on the fuel sources and combustion conditions. The pyrolysis of lignin within natural wood can result in the emission of methoxyphenols such as guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol), and their derivatives, which are identified as the potential tracers for wood burning (Liu et al., 2019). Wang et al. (2018) indicated that the coal and biomass burning, traffic, secondary formation, and aged coal combustion flumes were important contributors of nitrate phenols in air of northern China. The emitted phenolic compounds from these sources also can result in the formation of SOA by atmospheric aqueous phases associated reactions between the phenols and triplet excited state of carbonyl and hydroxyl radical (Yee et al., 2013; Smith et al., 2014). The O/C values of phenol associated aqueous SOA were similar to those of low-volatility oxygenated organic aerosol observed in ambient air, which are all in the range of 0.83–1.25 (Yu et al., 2014). Nakao et al. (2011) suggested that during the formation process of aromatic SOA, phenolic compounds could act as important intermediate species.

As a group of well known plasticizers or softening agents, phthalates are produced in large volumes and used in numerous consumer products mainly including PVC plastics, personal care products, food packaging, children's toys, and building materials, which can damage human endocrine or reproductive systems (Ji et al., 2014; Ma et al., 2014). They are physically bound to the polymer instead of covalent bonding and escape of PAEs from these materials after a long time use may be an important contributor to PAEs in different environmental media (Wang et al., 2016; Ji et al., 2014). Also the incineration of these PAEs containing products can result in the release of atmospheric PAEs (Ji et al., 2014).
1990s, PAEs had been suspected to be linked with human endocrine disruption (Sultan et al., 2001). Also high loadings of DEHP and DBP have been verified to play a significant side effect on fetus in decreasing testicular testosterone production (Takahashi et al., 2006). Parallel to aforementioned adverse effects, an increased rate of diagnosed allergy and asthma among children was found to be related to PAEs (Kolarik, et al., 2008). Previous research efforts were to investigate the concentrations and evaluate the exposure risks of PAEs in indoor and outdoor air particles (Ji et al., 2014; Ma et al., 2014; Subedi et al., 2017), while few studies about PAEs from combustion sources were conducted.

The incineration processes in DG, BB, WCC, and GFPP can result in the emission of various pollutants such as heavy metals, organic compounds, SO₂, PAHs, PCBs, WSIs, and NOₓ (Li et al., 2017a, 2017b, 2018a, 2018b, 2019a, 2019b; Lang et al., 2017; Liu et al., 2017; Tiwari et al., 2017; Chen et al., 2018; Dat et al., 2018; Mario et al., 2018; Hu et al., 2019). A comprehensive study about emission characteristics of WSIs, phenols, and PAEs from 5 combustion sources including PS, WS, GFPP, DG, and WCC was conducted and aimed to investigate the contents and profiles of these pollutants, and evaluate the daily intakes of PAEs.

METHODOLOGY

Re-suspension of Ash for Obtainment of PM₂.₅ for the 5 Sources

The ash samples were collected from the combustion of biomass, cable wrapping for metal reclamation, domestic waste for its reduction, garbage for power generation during January to May, 2015. The same sampling and analysis methods as our research in Li et al. (2017a, 2019a) were adopted in this study. The samples were collected from the electrostatic precipitators (ESP) of garbage-fired power plants, ash outlet at bottom of the stoves, and outdoor combustion residue using a stainless shovel. A total of 18 samples including ashes derived from 4 of DG, 4 of PS, 4 of WS, 3 of WCC, and 3 of GFPP. Finally, 1 kg of ash was obtained and dried using a vacuum freeze dryer, and subsequently stored in brown glass bottles before re-suspended for PM₂.₅ fractions. The re-suspension of ashes for collection of PM₂.₅ was entirely conducted according to our study of Li et al. (2019a). The every ash sample experienced two repeated re-suspension and finally the ash intercepted in 8 quartz filters (diameter 47 mm; Pall Co. USA) was used for the analysis of 6 PAEs and 20 phenols to ensure the detection of as many PAE and phenols isomers as possible. The ash intercepted in 2 Teflon filter (diameter 47 mm; Pall Co. USA) was used to analyze the 9 WSIs within PM₂.₅.

PAEs Extraction and Analysis

A total of 6 PAEs (DMP, DEP, DBP, DEHP, DOP, and BBP) were analyzed in this study and the corresponding PAE standards were all purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The 4-bromo-2-fluorobiphenyl and deuterated terphenyl
(Accustandard, USA) were used as surrogate standards. D₈-NaP, D₁₀-Ace D₁₀-Phe, D₁₂-Chr, and D₁₂-Pyr supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany) were used as internal standards in analysis process. The splitless injection was adopted and Helium was used as the carrier gas with the constant flow keeping at 1.1 mL min⁻¹. The oven temperature program was as follows: 70 °C held for 4 min, ramped to 300 °C at 10 °C min⁻¹ and held for 2 min, and then ramped to 340 °C at 5 °C min⁻¹.

The limited m/z values and quantitative m/z values (in bracket) were 68 and 137 (136) for D₈-NaP, 162 and 165 (164) for D₁₀-Ace, 94 and 189 (188) for D₁₀-Phe, 120 and 241 (240) for D₁₂-Chr, and 260 and 265 (264) for D₁₂-Pyr, respectively. The surrogate standards 4-bromo-2-fluorobiphenyl and deuterated terphenyl possessed the corresponding values as 170 and 151 (250), and 122 (244). In regard to 6 PAEs, they were 194 and 164 (163) for DMP, 177 and 150 (149) for DEP, 104 (149) for DBP, 167 and 279 (149) for DEHP, 91 and 206 (149) for BBP, and 167 and 43 (149) for DOP, respectively.

The pre-treatment and analysis of PAEs were entirely conducted according to the strict quality assurance (QA) and quality control (QC) procedures. The experiments linked with sample and procedure blank, sample duplication, and recoveries of matrix spiked and internal standards were carried on schedule every 6 samples. Sample and procedure blank experiments showed that no target chemicals were detected. The recovery rates ranged from 72.5 to 121% for 4-bromo-2-fluorobiphenyl and from 75.3 to 122% for deuterated terphenyl, and the mean values were 96.3% and 90.9%, respectively. The 6 PAEs in 3 matrix injected samples possessed the recovery fluctuated from 72.5% of DMP to 106% of DEHP with the mean value as 86.3±12.6%. The mass concentrations of 16 PAHs and 6 PAEs corresponding to triple signal to noise ratio were identified as the method detection limits (MDLs) of them. The MDLs (in ng g⁻¹) for 6 PAEs were 0.060 for DMP, 0.530 for DEP, 0.340 for DBP, 0.221 for BBP, 0.101 for DOP, and 0.112 for DEHP, respectively.

**Phenols Analysis**

A total of 20 phenols were detected for each sample (contain 4 quartz filters) in this study using HP6890 GC equipped with a flame ion detector. The samples were ultrasonic extracted by dichloromethane mixed with n-hexane (v:v =4:1) for 20 mins. The NaOH were added into extractions for the conversion of phenols to salts (pH=8) and the extractions were adjusted to acidity by HCl (pH=5). Finally the extractions were ultrasonic extracted once again by dichloromethane and ethyl acetate (v:v=4:1), and the extractions were subjected to the subsequent dehydration, condensation, and volume fixation by a constant N₂ stream before analysis. A total of 20 phenols such as phenol, 2-chlorophenol (2-CP), 2-methylphenol (2-MP), 3/4-methylphenol (3/4-MP), 2-nitrophenol (2-NP), 2,4-xylene (2,4-DMP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 4-chloro-3-methylphenol (4-C-3-MP), 2,4,6-trichlorophenol (2,4,6-TRCP), 2,4,5-trichlorophenol (2,4,5-TRCP), 2,4-
dinitrophenol (2,4-DNP), 4-nitrophenol (4-NP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TECP),
2,3,4,5- tetrachlorophenol (2,3,4,5-TECP), 2,3,5,6-tetrachlorophenol (2,3,5,6-TECP), 2-
methyl-4,6-dinitrophenol (2-M-4,6-DNP), pentachlorophenol (PCP), 2-(1-methyl-butyl) -4,6-
dinitrophenol (2-(1MB)-4,6-DNP), and 2-cyclohexyl-4,6-dinitrophenol (2-CY-4,6-DNP)
were involved in this study. A mixed standard solution contain these phenols was supplied by
AccuStandard, USA. Also the strict QA/QC measures such as field and procedure blank,
sample duplication, and matrix injection were conducted for the phenols analysis. The MDLs,
retention times, and recovery rates of 20 phenols were listed in Table 1S. The MDLs ranged
from 0.021 to 0.072 µg kg\(^{-1}\) with a mean as 0.030±0.020. The matrix standards of 2 and 10
µg kg\(^{-1}\) were added into the samples to calculate the recoveries of 20 phenols, which were in
the ranges of 77.7 – 102%.

**Analysis of Water Soluble Ions**

In regard to WSIs, a Teflon filter membrane was firstly put into the centrifuge tube and
extracted with 10 mL ultra-pure de-ionized water (18.25 MΩ·cm). Secondly the tube was
ultrasonically extracted 3 times and each lasted 20 mins. Finally, the extract was filtered by a
PTFE membrane with pore size as 0.22 µm (Whatman, Middlesex, UK) and transferred into a
plastic bottle, and stored at 4 °C before analysis. Four anions SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\), and F\(^-\) were
detected by ICS-1100 (Thermo Scientific, USA) with method detection limits (MDLs) ranged
from 0.006 to 0.010 µg mL\(^{-1}\). K\(^+\), Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) were analyzed by ICP-OES (Agilent
725, Agilent Co. USA) with the MDLs as 0.003-0.022 µg mL\(^{-1}\). NH\(_4^+\) was measured by the
sodium reagent spectrophotometer using the ultraviolet-visible spectrophotometer (UV-VIS,
T6, Beijing General Instruments Co., Ltd) with MDL as 0.010 µg mL\(^{-1}\). Standard reference
solutions were purchased from the Research Center of China National Standard Reference
Materials.

**RESULTS AND DISCUSSIONS**

**PAE Contents, Profiles, and Exposure Risks of PAEs from Emission Sources**

(Fig. 1)

Fig. 1 showed the contents of PM\(_{2.5}\) bounded PAEs from 5 emission sources. The \(\Sigma 6\)PAEs
(in ng g\(^{-1}\)) varied significantly from 2030 of WS to 32000 of WCC and they followed the
order WCC > GFPP > DG > PS > WS. The maximum value occurred at WCC might be
closely related to the application of high content of plasticizer in cable wrapping. Higher PAE levels were found for GFPP and DG compared with PS and WS, which was attributed to the plastic materials contained in GFPP and DG. The PAEs derived from burning of PS and WS were possibly resulted from the plant root absorption of soil PAEs. Compared with the PAE contents in other environmental media and food, the PAE contents within 5 emission sources were much higher than 19.35 ng g$^{-1}$ of fish, 13.73 ng g$^{-1}$ of chicken, 11.95 ng g$^{-1}$ of meat, 11.20 ng g$^{-1}$ of steamed bun, 2.70–10.91 ng g$^{-1}$ of milk, 3.98–11.88 ng g$^{-1}$ of fruit, and 198.62 ng g$^{-1}$ of soil in Tianjin, while the PAE contents among all the emission sources except for WCC were lower than that of outdoor dust (4927 ng g$^{-1}$) in Tianjin (Ji et al., 2014). The PAE levels for all the 5 combustion sources were far lower than those of indoor dust in Chinese and American cities including Beijing (255000 ng g$^{-1}$), Jinan (151000 ng g$^{-1}$), Guangzhou (173000 ng g$^{-1}$), Qiqihaer (428000 ng g$^{-1}$), Shanghai (401000 ng g$^{-1}$), and Urumchi (765000 ng g$^{-1}$), and Albany (396000 ng g$^{-1}$) (Guo and Kannan, 2011).

In regard to the contents of individual PAE, they varied significantly within one source or among different sources. DEPH and DBP dominated in the 4 burning sources including PS, WS, GFPP, and DG, which was similar to the reported pattern in soil of Tianjin and Denmark, and indoor dust in Jinan, Guangzhou, Beijing, Qiqihaer, Shanghai, and Urumchi (Vikelsøe et al., 2002; Guo and Kannan, 2011; Ji et al., 2014), might be ascribed to their high usage in China (Xu et al., 2008). WCC possessed high levels of DEPH, DNOP, and DBP, which was attributed to the application of DEPH, DNOP, and DBP as plasticizers in PVC. For the rest 4 PAEs from 4 sources, they were BBP > DNOP > DEP > DMP for GFPP, DEP > DMP > DNOP > BBP for both PS and WS, and BBP > DNOP > DEP > DMP for DG, respectively.

As a widely used parameter, coefficient of divergence (CD) documented elsewhere was applied to distinguish the similarity of WSI profiles between two emission sources (Hu et al., 2019; Li et al., 2019). CD value was calculated using eq. (1).

$$CD_{jk} = \frac{1}{p} \times \sum \left( \frac{x_{jk} - x_{jl}}{x_{jk} + x_{jl}} \right)^2$$  \hspace{1cm} (1)

The implications of abovementioned parameters were same as the reported results in Hu et al. (2019) and Li et al. (2019). The critical CD value of 0.30 used in identification of source profile similarity was documented frequently in recent studies (Kong et al., 2011; Li et al., 2016, 2017b, 2018a, 2018b).

Table 2S showed the CD values between any two emission sources. Except for GFPP vs. DG and PS vs. WS, the CD values for the other pairs of sources were higher than 0.3, which implied the similarity of PAE profiles between GFPP and DG, and PS and WS. GFPP and DG possessed the plastic containing fuels might be the explanation of similarity of PAE profiles between them. The PAE profile similarity between WS and PS was possibly attributed to the similarity of soil PAEs within Beijing-Hebei-Tianjin region.
Exposure of humans to PAEs via inhalation, ingestion, dermal adsorption, and dietary intake can result in significant adverse health effects (Guo and Kannan, 2011; Xia et al., 2011; Ji et al., 2014; Zhang et al., 2014; Li et al., 2016). The CalTOX model developed by researchers from the University of California campuses and national laboratories in the United States was extensively used to estimate the chemical fate and human exposure (USEPA, 1989; Xia et al., 2011). Also the daily intake (DI) was another well known method to evaluate the exposure risks of PAEs (Guo and Kannan, 2011; Ji et al., 2014; Zhang et al., 2014; Li et al., 2016). In this study, DI had priority over CalTOX model as the evaluation method due the data lack of parameters for CalTOX model. Only two exposure pathways ingestion (ING) and dermal adsorption (DERM) were involved in this study ascribe to the lack of PM$_{2.5}$ concentration in air. DI of phthalate posed by ING and DERM were calculated as the same method adopted by Guo and Kannan. (2011).

$$DI_{\text{ING}} = \frac{C_{\text{PM}_{2.5}} f_1 f_2}{BW}$$

(2)

Where, $C_{\text{PM}_{2.5}}$ is the PAE content in PM$_{2.5}$ measured in this study ($\mu g \ g^{-1}$), $f_1$ is the outdoor exposure fraction (hours spent over a day), $f_2$ is the dust ingestion rate, and BW is the body weight (kg). The parameter $f_1$ was set to 0.88 by Guo and Kannan. (2011) for the infants, teenagers, and adults based on 21 of 24h indoor stay per day, and 0.79 for toddler and children according to their 19 of 24 h spent outdoor per day. However, $f_1$ was defined as 0.12 in this study for the infants, teenagers, and adults, and 0.21 for the toddler and children on the basis their time spent outdoor per day. Values of $f_2$ are 0.02 g day$^{-1}$ for infants, 0.1 g day$^{-1}$ for toddlers and 0.05 g day$^{-1}$ for others, respectively. BW values for infants (INF), toddlers (TOD), children (CHI), teenagers (TEE) and adults (ADU) in China are 5, 19, 29, 53 and 63 kg from Chinese provincial government.

Table 1 listed the DI values via ING of PM$_{2.5}$ associated PAEs originated from 5 emission sources. The total DI values (reported in ng kg-bw$^{-1}$ day$^{-1}$) posed by 6 PAE from the same source varied significantly among different age groups. The same order as WCC > GFPP > DG > PS > WS was found for the total DIs among all the age groups, which was attributed to the same parameters for different sources within one age group. Due to the difference of values of parameters in eq. (1) among different age group, TOD had the highest DIs and the rest age groups followed the order INF > CHI > TEE > ADU. The DIs posed by ING of the individual PAE were determined by their contents from emission sources and they were DEHP > DBP > BBP > DNOP > DEP > DMP for GFPP and DG, DEHP > DBP > DEP > DMP > DNOP > BBP for PS and WS, and DEHP > DNOP > DBP > BBP > DEP > DMP for WCC, respectively.

(Table 1)
\[ \text{DI}_{\text{DERM}} = \frac{C_{\text{PM}_{2.5}} \times A \times M_2 \times f_3 \times f_5}{\text{BW}} \]  

(3)

Where, \( A \) is the skin surface area available for contact (cm\(^2\) day\(^{-1}\)), \( M_2 \) is the dust to skin adherence factor (0.096 mg cm\(^{-2}\)), and \( f_3 \) is the fraction of phthalate absorbed in the skin. \( A \) representing 25% of the total skin including hands, legs and arms are 801, 2564, 3067, 3692 and 4615 cm\(^2\) day\(^{-1}\) for infants, toddlers, children, teenagers and adults, respectively. \( f_3 \) values of infants, toddlers, children and teenagers are the mean value of child, which are two times to those of adults and they were 0.000955 for DMP, 0.002051 for DEP, 0.001556 for DBP, 0.000707 for BBP, and 0.000106 for DEHP, respectively. The same \( f_3 \) value of DEHP was adopted for DNOT due to the same molecular formula and similar chemical properties between them, which were 0.000053 and 0.000106 for adults and others.

(Table 2)

Table 2 listed the DI values for different age groups posed by DERM of PM\(_{2.5}\) bounded PAEs from five sources. WCC possessed the highest DIs followed by DG, GFPP, PS, and WS, which were different with those of DIs posed by ING due to the differences of \( f_3 \) among 6 PAE. DBP possessed the highest DI values among all the 5 sources due to its high contents and \( f_3 \) value.

The sum of DIs for the individual PAE and 5 emission sources via both ING and DERM adsorption were shown in Fig. 2. The individual PAE including DMP from DG, DEP from PS, DBP, BBP, DNOP, and DEHP from WCC possessed the highest DIs for all the 5 age groups. For the DIs posed by the 5 emission sources, WCC > GFPP > DG > PS > WS was found for all the age groups and TOD possessed the highest DIs.

(Fig. 2)

**Water Soluble Ion Contents and Profiles**

(Fig. 3)

Fig. 3 showed the contents (µg g\(^{-1}\)) of 9 WSIs for 5 emission sources. The sum of 9 WSIs contributed 3.91%, 9.56%, 10.0%, 11.5%, and 19.7% to the total PM\(_{2.5}\) mass for DG, GFPP, WCC, PS, and WS, respectively. The mass contributions of WSIs to PM\(_{2.5}\) for 5 sources were
far lower than those of the atmospheric PM$_{2.5}$ in Taiyuan (32.86%) (He et al., 2017), Xi’an (39.16%) (Zhang et al., 2011), Chengdu (42%) (Tao et al., 2014), Beijing (60%) (Zhang et al., 2016), and Hefei (54%) (Deng et al., 2016). The PM$_{2.5}$ associated SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ (SNN) had great impact on atmospheric quality and visibility (He et al., 2017; Xu et al., 2017). As the secondary inorganic aerosol contributors, SNN (in mg g$^{-1}$) varied from 1.95 of WCC to 42.4 of WS, and the corresponding values were 19.8, 18.1, and 3.18 for GFPP, PS, and DG, respectively. The 21.6%, 20.8%, 15.7%, 8.12%, and 1.94% of total WSIs in WS, GFPP, PS, DG, WCC were ascribed to the contribution of SNN.

Cl$^-$ had high contents among all the 5 burning sources, which followed the order WCC (59.7 mg g$^{-1}$) > WS (39.1 mg g$^{-1}$) > GFPP (32.5 mg g$^{-1}$) > DG (18.5 mg g$^{-1}$) > PS (13.0 mg g$^{-1}$). The fine particle associated Cl$^-$ could be derived from burning of coal, biomass, and waste (He et al., 2017; Zhang et al., 2018). The highest Cl$^-$ level occurred at WCC might be resulted from the high Cl content in PVC.

NH$_4^+$ possessed the lowest content (in µg g$^{-1}$) compared with the other 8 WSIs for all the 5 burning sources, which was PS (62.5) > DG (39.3) > WS (16.0). NH$_4^+$ was not detectable in both WCC and GFPP due to their fuel composition and combustion condition.

WSI balance was estimated by anion equivalent (AE) and cation equivalent (CE) to evaluate aerosol acidity (He et al., 2017).

\[
AE = \frac{\sigma^-}{35.5} + \frac{SO_4^{2-}}{48} + \frac{NO_3^-}{62} + \frac{F^-}{19}
\]

\[
CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39} + \frac{Mg^{2+}}{12} + \frac{Ca^{2+}}{20}
\]

The AE (meq) was correlated well with CE (meq) with the linear relationship described as

CE=4.60AE+0.060 ($R^2=0.98$, n=4) for PS, CE=1.46AE+0.062 ($R^2=0.99$, n=4) for WS, CE=1.27AE+0.023 ($R^2=0.97$, n=3) for WCC, CE=1.10AE+0.067 ($R^2=0.94$, n=4) for GFPP, and CE=1.20AE+0.034 ($R^2=0.94$, n=3) for DG, respectively (Fig. 4). The slope values higher than 1 were found for all the 5 emission sources implying the anion deficiencies and indicating that the discharged PM$_{2.5}$ was strongly alkaline (Zhang et al., 2011; He et al., 2017). The most alkaline PM$_{2.5}$ was originated from PS and the rest combustion sources followed the order of WS > WCC > DG > GFPP.

(Fig. 4)
The ratio of NO₃⁻/SO₄²⁻ (N/S) is widely used as indicator to access the relative importance of vehicle source and stationary coal combustion source. The ratio of 13/1 or 8/1 is found during combustion of gasoline or diesel fuel, while 1/2 is found for coal combustion (Kong et al., 2010). In this study, the N/S values were 0.033, 0.009, 0.248, 0.008, and 0.037 for PS, WS, WCC, GFPP, and DG, which were far lower than the 1/2 of coal.

CD values of WSI profiles were calculated for any 2 of 5 sources to distinguish the WSI profiles similarities. The WSI profiles were different from each other for all the 5 sources based on higher CD values than 0.3 (Fig. 1S).

**Contents of Phenols for Five Stationary Combustion Sources**

(Fig. 5)

The phenols varied significantly among different sources. Only 11 phenols were detected in PM₂.₅ originated from the 5 emission sources, which were 3/4-MP (182 ng g⁻¹) for GFPP, 2,4-DCP (3.90 ng g⁻¹), 2,4,5-TRCP (3.90 ng g⁻¹), and 2-M-4,6-DNP (16.9 ng g⁻¹) for PS, 3/4-MP (913 ng g⁻¹), 2-MP (913 ng g⁻¹), 3/4-MP (1020 ng g⁻¹) and 2,4-DMP (575 ng g⁻¹) for WS, phenol (9010 ng g⁻¹) for WCC, and 2,4-DMP (13.0 ng g⁻¹), 4-C-3-MP (13.0 ng g⁻¹), 2,4-DNP (117 ng g⁻¹), 4-NP (267 ng g⁻¹), and 2-M-4,6-DNP (182 ng g⁻¹) for DG, respectively (Fig. 5).

The total contents of 20 phenols for the 5 emission sources were WCC (9010 ng g⁻¹) > WS (2930 ng g⁻¹) > DG (599 ng g⁻¹) > GFPP (182 ng g⁻¹) > PS (24.7 ng g⁻¹). WCC possessed the highest phenols content although only phenol was detected, which should be paid more attention. High levels of phenol in PM₂.₅ from WS might be resulted from the using of phenolic pesticides during wheat growth process.

**CONCLUSIONS**

In this study, PM₂.₅ bounded 6 PAEs, 9 WSIs, and 20 phenols were analyzed for the 5 combustion sources including garbage-fired power plant (GFPP, n=4), peanut straw (PS, n=4), wheat straw (WS, n=4), domestic garbage fired for volume reduction (DG, n=3), and workshop of cable combustion for metal reclamation (WCC, n=3) to obtain the information about: 1) contents of these pollutants for the 5 incineration sources; 2) daily intakes of PAEs through ingestion and dermal adsorption; and 3) PAE, phenols, and WSI profile similarities between any 2 of 5 emission sources.

The Σ₆PAEs (in ng g⁻¹) varied significantly among the 5 sources and they were WCC (32000) > GFPP (3680) > DG (2990) > PS (2340) > WS (2030). DEHP and DBP were top PAEs among 4 sources except for WCC, and DEHP, DNOP, and DBP were the predominant PAEs for WCC. Both GFPP vs. DG and PS vs. WS had the similar PAE profiles based on lower CD values than 0.30, which were 0.122 and 0.086, respectively. The DI of PAEs by
ING of emission sources were WCC > GFPP > DG > PS > WS for all age groups, which was attributed to the same parameters for different sources within one age group. Unlike DIs by ING, the DIs by PAE DERM from the 5 sources showed the different trend due to the differences of $f_3$ values among different PAE, which were TOD > CHI > INF > TEE > ADU. DBP possessed the highest DIs by DERM among all the 5 sources due to its high content and $f_3$ value. The integrated DIs by both ING and DERM showed the same trend with those by DERM.

The sum of 9 WSIs contributed 3.91%, 9.56%, 10.0%, 11.5%, and 19.7% to the total PM$_{2.5}$ mass for DG, GFPP, WCC, PS, and WS, respectively, which were far lower than those of atmospheric PM$_{2.5}$ reported elsewhere. All the 5 burning sources possessed high level of Cl$^-$ and they were WCC (59.7 mg g$^{-1}$) > WS (39.1 mg g$^{-1}$) > GFPP (32.5 mg g$^{-1}$) > DG (18.5 mg g$^{-1}$) > PS (13.0 mg g$^{-1}$). The highest Cl$^-$ level of WCC might be ascribed to high Cl content in PVC. NH$_4^+$ possessed the lowest content (in µg g$^{-1}$) compared with the other 8 WSIs for all the 5 burning sources, which was PS (62.5) > DG (39.3) > WS (16.0). The AE (meq) was correlated well with CE (meq) and the regression equations were CE=4.60AE+0.060 for PS, CE=1.46AE+0.062 for WS, CE=1.27AE+0.023 for WCC, CE=1.10AE+0.067 for GFPP, and CE=1.20AE+0.034 for DG, respectively, indicating that the discharged PM$_{2.5}$ was strongly alkaline. The CD values higher than 0.30 were found for WSI profiles of any 2 sources indicated the WSI profiles were different from each other.

Only 11 phenols were detected for all the 5 sources. The sum of the 20 phenols for the 5 emission sources were WCC (9010 ng g$^{-1}$) > WS (2930 ng g$^{-1}$) > DG (599 ng g$^{-1}$) > GFPP (182 ng g$^{-1}$) > PS (24.7 ng g$^{-1}$). Phenol in WCC should be paid more attention and phenolic pesticides using in wheat growth process might be the reason of high levels of phenols in WS.

ACKNOWLEDGEMENTS
This study was supported by the Fundamental Research Funds for the Central Universities (2017MS142), the National Natural Science Foundation of China (21407048), and Prime Minister Fund (DQGG-05-13).

REFERENCES


within PM$_{2.5}$ and PM$_{10}$ fractions of fly ashes from coal-fired power plants. Aerosol Air Qual. Res. 17: 1105–1116.


Table Captions

Table 1. Daily intakes (ng kg-bw\(^{-1}\) day\(^{-1}\)) via ingestion of PM\(_{2.5}\) bounded PAEs from 5 exposure sources

Table 2. Daily intakes (ng kg-bw\(^{-1}\) day\(^{-1}\)) via dermal adsorption of PM\(_{2.5}\) bounded PAEs from 5 exposure sources
Table 1 Daily intakes (ng kg bw\(^{-1}\) day\(^{-1}\)) via ingestion of PM\(_{2.5}\) bounded PAEs from 5 exposure sources

<table>
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<td>0.032</td>
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Table 2 Daily intakes (ng kg-bw\(^{-1}\) day\(^{-1}\)) via dermal adsorption of PM\(_{2.5}\) bounded PAEs from 5 exposure sources

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<th>Age groups</th>
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Figure Captions

Fig. 1. Contents of the individual PAE, and (b) sum of the 6 PAEs for the 5 stationary sources
Fig. 2. Integrated daily intakes posed by both ingestion and dermal adsorption of PAEs
Fig. 3. Contents of 9 water soluble ions for the 5 stationary combustion sources
Fig. 4. Regression equations between CE and AE for the 5 stationary combustion sources
Fig. 5. Phenols contents for the 5 emission sources
Fig. 1(a). Contents of the individual PAE, and (b) sum of the 6 PAEs for the 5 stationary sources
Fig. 2. Integrated daily intakes posed by both ingestion and dermal adsorption of PAEs
Fig. 3. Contents of 9 water soluble ions for the 5 stationary combustion sources
Fig. 4. Regression equations between CE and AE for the 5 stationary combustion sources

- PS: $CE = 4.60AE + 0.060$, $R^2 = 0.99$
- DG: $CE = 1.20AE + 0.034$, $R^2 = 0.94$
- GFPP: $CE = 1.10AE + 0.067$, $R^2 = 0.94$
- WCC: $CE = 1.27AE + 0.034$, $R^2 = 0.97$
- WS: $CE = 1.46AE + 0.062$, $R^2 = 0.99$
Fig. 5. Phenols contents for the 5 emission sources