



Nitrated phenols and the phenolic precursors in the atmosphere in urban Jinan, China

Min Li^a, Xinfeng Wang^{a,*}, Chunying Lu^a, Rui Li^{a,b,c}, Jun Zhang^a, Shuwei Dong^a, Lingxiao Yang^a, Likun Xue^a, Jianmin Chen^d, Wenxing Wang^a

^a Environment Research Institute, Shandong University, Qingdao 266237, China

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

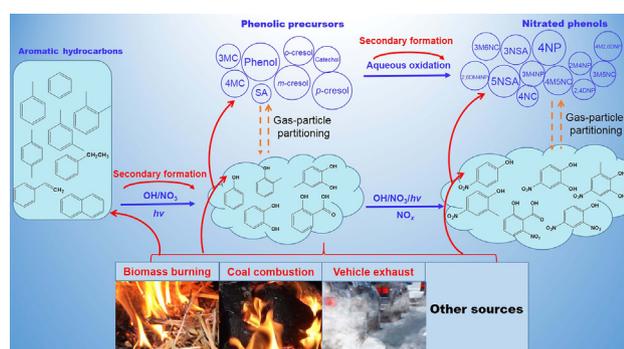
^c University of Chinese Academy of Sciences, Beijing 100049, China

^d Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Institute of Atmospheric Sciences, Fudan University, Shanghai 200438, China

HIGHLIGHTS

- Gas- and particle-phase phenols and nitrated phenols were measured in three seasons.
- Phenol, salicylic acid, 4-nitrophenol, and 4-nitrocatechol were dominant species.
- More phenols and nitrated phenols appeared in fine particles and gas phase in summer.
- Four sources were identified and the contributions varied with species and seasons.
- Phenolic precursors promoted the formation of nitrated phenols especially in summer.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrated phenols are a major class of brown carbon in the atmosphere and have adverse effects on human and plants health. They are emitted from combustion sources or produced by oxidation of phenolic precursors. In this study, fine particulates, total suspended particulates, and gas-phase samples were collected in urban Jinan in winter, spring, and summer, and UHPLC-MS analysis was used to determine 8 phenolic compounds and 12 nitrated phenols in these samples. The seasonal average concentrations of total phenolic compounds and total nitrated phenols were in the ranges of 2.6–18.7 ng m⁻³ and 13.5–105.4 ng m⁻³, respectively. The concentrations of phenolic compounds and nitrated phenols were highest in winter, followed (in decreasing order) by spring, and summer. Phenol and salicylic acid were the most abundant phenolic species in both gaseous and particulate samples. 4-Nitrophenol was the most abundant nitrated phenols in particulate matters, followed by 4-nitrocatechol and 5-nitrosalicylic acid, while 4-nitrophenol and 2,4-dinitrophenol were the dominant species in the gas phase. The distributions of phenolic compounds and nitrated phenols in fine and coarse particles and in gas and particle phases were largely dependent on the aerosol size distribution, the ambient temperature, and the compound volatility. More of them were distributed in fine particles and gas-phase in summer than in spring. It was found that phenol, catechol, methyl-catechols, 4-nitrophenol, and methyl-nitrophenols mainly derived from coal combustion, while biomass burning was the main source of cresols, 2,6-dimethyl-4-nitrophenol,

* Corresponding author.

E-mail address: xinfengwang@sdu.edu.cn (X. Wang).

4-nitrocatechol, and methyl-nitrocatechols. In addition, secondary formation contributed the largest fraction of nitrosalicylic acids and vehicle exhaust was the major source of cresols, 2,6-dimethyl-4-nitrophenol, and 4-methyl-2,6-dinitrophenol. Further correlation analysis revealed positive correlations between nitrated phenols and corresponding phenolic precursors, indicating the important roles that phenolic precursors played in the secondary formation and abundance of nitrated phenols in the atmosphere.

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1. Introduction

Environmental levels of nitrated phenols, which are compounds comprising hydroxyl- and nitro- functionalized benzene rings, have been under close scrutiny in the past decades because they are harmful to human and plants health, leading to genotoxicity and forest decline, respectively (Blank, 1985; Grosjean, 1991; Huang et al., 1995). Nitrated phenols are widespread pollutants in the atmosphere, with compounds such as nitrophenol, methyl-nitrophenols, dimethyl-nitrophenol, nitrocatechol, methyl-nitrocatechols, nitrosalicylic acids, dinitrophenol and methyl-dinitrophenol present in the gas phase (Morville et al., 2006), aqueous phase (Richartz et al., 1990) and particle phase (Belloli et al., 1999). They are a primary component of brown carbon (BrC), and the absorption properties of nitrated phenols in near-UV light can affect solar radiation and perturb photochemistry, air quality, and regional climate (Andreae and Gelencsér, 2006; Desyaterik et al., 2013; Feng et al., 2013). These compounds also form organic aerosols in the atmosphere (Chow et al., 2016; Mohr et al., 2013), which have serious effects on visibility (Eldering and Cass, 1996), climate change (Kanakidou et al., 2005), and human health (Chow, 2006).

Concentrations of nitrated phenols in the ambient atmosphere are not only the results of primary emissions from anthropogenic activities such as coal combustion, biomass burning and vehicle exhaust (Lu et al., 2019a; Lu et al., 2019b; Wang et al., 2017a) but are also secondary formation products from phenolic precursors (Borrás and Tortajada-Genaro, 2012; Lin et al., 2015). The increasing attention given to phenolic compounds is primarily due to their toxicity to humans (Allen and Allen, 1997) and their participation in the formation of secondary organic aerosols (SOAs) (Nakao et al., 2011). They are primary pollutants in emissions from combustion processes and motor vehicles (Lüttke et al., 1999; Tremp et al., 1993) and are secondary products derived from the oxidations of aromatic hydrocarbons (Atkinson et al., 1989; Volkamer et al., 2002). Previous studies have shown that nitrophenol and its derivatives can originate from the oxidation reactions of phenol and cresols (i.e., *m*-cresol, *p*-cresol, and *o*-cresol) in the presence of NO₂ (Harrison et al., 2005; Olariu et al., 2002). Nitrocatechol and its derivatives can be formed by the photo-oxidation of cresols that are emitted from biomass burning (Iinuma et al., 2010). In addition, the nitration of salicylic acid has been shown to be the dominant formation pathway of 3-nitrosalicylic acid and 5-nitrosalicylic acid in the aqueous phase (Andreozzi et al., 2006; Hummel et al., 2010). Therefore, to gain a comprehensive understanding of nitrated phenols in the atmosphere, it is essential to determine the concentrations, chemical compositions, and origins of their phenolic precursors in addition to the derivatives of nitrated phenols.

Due to the semi-volatile properties of nitrated phenols and phenolic compounds (Bannan et al., 2017), gas-particle partitioning and their distribution in fine and coarse particles govern the fate, long-distance transport, and biological toxicity of these compounds (Bidleman, 1988). The high deposition rate of coarse particles means that they can be easily removed from the atmosphere, while fine particles and gaseous pollutants can be inhaled into the body or remain for a long period in the ambient air (Asmi et al., 2016). Furthermore, the distribution of these compounds in the gas phase and in fine and coarse particles can reveal their origins and pathways of formation (Gao et al., 2016). However, there has until now been little known of the partitioning and distribution of phenolic compounds and nitrated phenols.

In this study, the identity and concentrations of 8 phenolic compounds and 12 nitrated phenols in both gas- and particle-phase samples from winter, spring and summer in urban Jinan were determined to reveal characteristic variations and distribution patterns. Source apportionment was then performed to determine the origins of phenolic compounds and nitrated phenols, and the relationships between these were also investigated via correlation analyses.

2. Experimental methods

2.1. Sampling site

Samples were collected at the Atmospheric Environment Observation Station of Shandong University (AEOS-SDU) (36°40'N, 117°03'E) in Jinan, an urban site situated in the central area of the North China Plain. The sampling site was located approximately 20 m above the ground and the surrounding areas were mainly educational and residential districts. There were several urban roads nearby and a dozen of large factories, such as thermal power plants, cement plants, petrochemical plants, and oil refineries in urban and suburban areas. More information on the location of the sampling site and the surrounding areas can be seen in our previous studies (Wang et al., 2017b). The sample collection was conducted in three different seasons in 2016, i.e., from February 19 to March 7 (winter), April 12 to 27 (spring), and June 27 to July 11 (summer). Only fine particulate (PM_{2.5}) samples were collected in winter, while PM_{2.5}, total suspended particles (TSP), and semi-volatile samples were collected in both spring and summer.

2.2. Sample collection and other online measurements

PM_{2.5} samples were collected with a medium-volume sampler (TH-150A, Wuhan Tianhong, China) on quartz filters (Pall, USA) at a flow rate of 100 L min⁻¹. TSP and gas-phase semi-volatile organic compounds (SVOCs) were collected by a high-volume sampler (TE-1000, Tisch, USA) at an average flow rate of 204 L min⁻¹. Particulate matter was blocked and sampled when it passed through the quartz-fiber filter, and the gas-phase SVOCs were then enriched in the polyurethane foams (PUF, Tisch) situated below. The sampling period lasted for 11.5 h, with the daytime samples collected from 08:00 to 19:30 (local time) and the nighttime samples from 20:00 to 07:30 the next day. Prior to sampling, quartz-fiber filters were pre-heated at 600 °C for 2 h to remove any adsorbed organic contaminants. The PUF were cleaned via sonication extraction in *n*-hexane and de-ionized water before use to remove the residuals. The filter and PUF samples were stored at -20 °C in a freezer until analysis. PM_{2.5} and TSP filters were weighed before and after the sampling by using electronic microbalance (ME5-F, Sartorius, Germany) under constant temperature (20 ± 0.5 °C) and humidity (50 ± 2%). Two field blanks of filters and PUF were collected before and after the sampling experiment with the pump not working.

During the sampling periods, several real-time instruments were deployed to measure the trace gases, as follows: NO_x (Model 42C, Thermo Electron Instruments, TEI, USA), SO₂ (Model 43C, TEI) and O₃ (Model 49C, TEI). Real-time monitoring of PM_{2.5} was also performed with a SHARP 5030 (synchronized hybrid ambient real-time particulate monitor, Thermo Scientific, USA). Detailed

information on these instruments was given by Wang et al. (2018). Meteorological data covering temperature, humidity, wind direction and wind speed during sampling were obtained from an automatic meteorological station (CAWS600, Huayun, China).

2.3. Sample extraction and chemical analysis

PM_{2.5} and TSP filter samples were cut in half, and each half was treated with three successive 15 mL portions of methanol for 40 min on a thermostatic orbital shaker to extract organic compounds, including phenolic compounds and nitrated phenols. The extracted solution (45 mL) was concentrated on rotary evaporator at room temperature. The extract was passed through a syringe filter (PTFE, 0.45 μm), and the resulting filtrate was evaporated to near-dryness under a gentle stream of high-purity nitrogen. Finally, the residue was re-dissolved in 300 μL methanol containing 200 μg L⁻¹ 2,4,6-trinitrophenol as an internal standard. The PUF sample was cut into small pieces and extracted with 55 mL methanol on an orbital shaker for 2 h. The remaining PUF sample-processing steps were the same as those used for the particulate matter samples.

Nitrated phenols and phenolic compounds in sample solutions were analyzed and quantified on an ultra-high performance liquid chromatography (UHPLC, Thermo Scientific) coupled with an ion-trap mass spectrometer (MS, LCQ Fleet, Thermo Scientific) equipped with an electrospray ionization (ESI) source. Chromatographic separation of nitrated phenols and phenolic compounds was achieved on an Atlantis T3 C18 column (2.1 mm × 150 mm, 2.1 μm particle size, Waters, USA) at a flow rate of 0.2 mL min⁻¹. The mobile phase contained (A) 11% acetonitrile in methanol and (B) 11% acetonitrile and 0.1% formic acid in deionized water. The applied gradient elution for the analyses was: initial conditions 66% B, and then decreased to 44% B within 19 min, maintained at 44% for 4 min, and then returned to 66% from 23 to 30 min. The following 8 phenolic compounds and 12 nitrated phenols were detected by negative polarity in selected ion monitoring (SIM) mode: phenol, *o*-cresol, *m*-cresol, *p*-cresol, catechol, 3-methylcatechol (3MC), 4-methylcatechol (4MC), salicylic acid (SA), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 4-nitrocatechol (4NC), 3-methyl-5-nitrocatechol (3M5NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC), 3-nitrosalicylic acid (3NSA), 5-nitrosalicylic acid (5NSA), 2,4-dinitrophenol (2,4DNP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP), and 4-methyl-2,6-dinitrophenol (4M2,6DNP). Target compounds were identified based on the retention time and mass spectra of the standard samples (Sigma-Aldrich, USA). Further quantification with internal standards and multi-standard curves were conducted for phenolic compounds and nitrated phenols. In addition, recovery rates were determined for filter and PUF samples. The recovery rates for PUF samples, a little lower than those for filter samples, were acceptable with the average value of 80.3%. Note that only a few target compounds were detected in very low levels in the filed blank samples. The background signals have been taken into account in the subsequent concentration calculation.

2.4. Source appointment by positive matrix factorization (PMF) model

As a useful factorization methodology tool, the US EPA PMF v5.0 model was used to determine the source profiles and the contributions to the target species. The two files required for the input are: (1) the concentration data of nitrated phenols, phenolic compounds and trace gases and (2) the corresponding uncertainty data. The above values were determined as follows (Arruti et al., 2011; Polissar et al., 1998):

For the concentration values below the detection limits:

$$x_{ij} = \frac{DL_i}{2}, \sigma_{ij} = \frac{5DL_i}{6} \quad (1)$$

For the concentration values beyond the detection limits:

$$x_{ij} = c_{ij} \quad (2)$$

$$\text{If } x_{ij} \leq 3DL_i, \sigma_{ij} = \frac{DL_i}{3} + 0.2 \times c_{ij}; \quad (3)$$

$$\text{If } x_{ij} > 3DL_i, \sigma_{ij} = \frac{DL_i}{3} + 0.1 \times c_{ij}; \quad (4)$$

where x_{ij} is the concentration value of the species i for the sample j , DL_i is the detection limit of the species i , σ_{ij} is the uncertainty value corresponding to the concentration x_{ij} , and c_{ij} is the measured concentration. Note that the data with missing values were not included in the input data file.

The bootstrap error estimation was determined by minimum Q/Qexp value and more information can be seen in Zhang et al. (2018).

3. Results and discussion

3.1. Concentrations and compositions

Table 1 lists the average concentrations of phenolic compounds and nitrated phenols in PM_{2.5}, TSP, and gas-phase samples from different seasons. The atmospheric concentrations of nitrated phenols were relatively high, with the average total concentrations in PM_{2.5} being 105.4 ± 59.8, 34.0 ± 12.7, and 13.5 ± 1.7 ng m⁻³ in winter, spring, and summer, respectively. The average total concentrations of nitrated phenols in TSP were almost twice those in PM_{2.5}. The total concentration of gas-phase nitrated phenols was between the concentrations in PM_{2.5} and in TSP in spring but higher than that in the particle phase in summer. Nevertheless, the concentrations of phenolic compounds were much lower than those of nitrated phenols. The concentrations of phenolic compounds in PM_{2.5} were 16.7 ± 3.7, 7.1 ± 2.6, and 2.6 ± 0.4 ng m⁻³ in winter, spring, and summer, respectively, which was approximately 20% of the concentration of nitrated phenols. Both nitrated phenols and phenolic precursors were present in the highest concentrations in PM_{2.5} in winter and the lowest in summer. The distinct increases in the concentrations of nitrated phenols and phenolic compounds in winter are attributable to the intensified combustion of coal and biomass for heating during this season (Wang et al., 2018).

When compared with other locations, the concentrations of fine particulate nitrated phenols in urban Jinan in 2016 were substantially higher than the observed average concentrations of 9.8–48.4 ng m⁻³ in Jinan in 2014 (Wang et al., 2018) and the average concentrations of 1.99–11.63 ng m⁻³ in Hong Kong from 2009 to 2012 (Chow et al., 2016). Moreover, the summertime concentrations of fine particulate nitrated phenols in Jinan in this study were significantly higher than those observed in the rural sites of Xianghe (1.45 ng m⁻³ on average) and Yucheng (5.7 ng m⁻³), and in the urban site of Beijing (6.62 ng m⁻³) on the North China Plain, in the past several years (Teich et al., 2017; Wang et al., 2018; Wang et al., 2019). These 2016 concentrations of fine particulate phenolic compounds in urban Jinan were comparable with those in urban Strasbourg, France, at the beginning of the 21st century (16.4 ng m⁻³, gas and particle phases) (Delhomme et al., 2010), but the gaseous concentrations in this study were much lower than those observed more than twenty years before at an urban site in Poland in 1984 (521 ng m⁻³) (Leuenberger et al., 1985), rural Great Dun Fell in England in 1993 (13.8–70.5 ng m⁻³) (Lüttke et al., 1997), and Bicocca University in urban Milan in 1998 (400 ng m⁻³) (Belloli et al., 1999).

Table 1
Average concentrations (average \pm standard deviation, ng m^{-3}) of total phenolic compounds and total nitrated phenols in $\text{PM}_{2.5}$, TSP and gas phase in urban Jinan.

Season	$\text{PM}_{2.5}$		TSP		Gas	
	Phenols	Nitrated phenols	Phenols	Nitrated phenols	Phenols	Nitrated phenols
Winter	16.7 \pm 3.7	105.4 \pm 59.8				
Spring	7.1 \pm 2.6	34.0 \pm 12.7	18.7 \pm 5.1	87.9 \pm 33.4	9.1 \pm 2.6	52.1 \pm 20.9
Summer	2.6 \pm 0.4	13.5 \pm 1.7	5.2 \pm 0.8	23.1 \pm 3.5	11.3 \pm 3.1	36.7 \pm 6.0

The fractional compositions of phenolic compounds differed according to the sample types and seasons. The proportions of 8 phenolic compounds in $\text{PM}_{2.5}$, TSP, and gas-phase samples are shown in Fig. 1. Phenol was the most abundant phenolic compound in $\text{PM}_{2.5}$, accounting for 26%–34% of the measured phenolic precursors in winter, spring, and summer. $\text{PM}_{2.5}$ was also rich in salicylic acid, with a proportion of 14%–22%. Each of the three cresols isomers (i.e., *m*-cresol, *p*-cresol, and *o*-cresol) comprised ~10% of the detected phenolic compounds, with the total contribution being up to ~30%. In addition, 4-methylcatechol comprised a significant proportion (7%–14%) of the detected phenolic compounds, higher than that of catechol (6%–11%) and 3-methylcatechol (4%–5%). When compared with winter and spring, the proportion of phenol in $\text{PM}_{2.5}$ in summer decreased, while that of catechol increased. The phenolic compounds fractional compositions in TSP and their seasonal variations were similar to those in $\text{PM}_{2.5}$. As one would expect, in the gas-phase samples, the proportions of the highly volatile phenolic compounds of salicylic acid and phenol were higher, at 33%–34% and 38%–41%, respectively, whereas the fractions of low-volatile cresols and methylcatechols were significantly lower.

The relative proportions of nitrated phenols also varied greatly with sample types and seasons. As shown in Fig. 2, 4-nitrophenol and 4-nitrocatechol were the predominant species among the 12 detectable nitrated phenols in $\text{PM}_{2.5}$ during the three seasons, accounting for 26%–41% and 15%–29%, respectively. Methyl-nitrophenols and dimethyl-nitrophenol (i.e., 2M4NP, 3M4NP, and 2,6DM4NP) comprised 8%–22% and were also the most prevalent of the 12 nitrated phenols, followed by nitrosalicylic acids (i.e., 3NSA and 5NSA) (6%–20%), methyl-nitrocatechols (i.e., 3M5NC, 3M6NC, and 4M5NC) (7%–10%), and dinitrophenols (i.e., 2,4DNP and 4 M2,6DNP) (4%–10%). Recent studies have reported that 4-nitrophenol and 4-nitrocatechol were the most abundant species in total nitrated phenols in urban Jinan and

Beijing (Wang et al., 2018; Wang et al., 2019). The dominance of 4-nitrophenol and 4-nitrocatechol may arise from primary emissions such as combustion activities and secondary formations from precursors. Compared with winter and spring, the contributions of 5-nitrosalicylic acid and 2,4-dinitrophenol in $\text{PM}_{2.5}$ in summer in Jinan increased while the proportions of 4-nitrophenol and methyl-nitrophenols decreased, which indicated that there was intense secondary formation of 5-nitrosalicylic acid and 2,4-dinitrophenol in the hottest season. Similar variations in the proportions of nitrated phenols also occurred in TSP samples across different seasons, but the proportion of 5-nitrosalicylic acid in TSP (9%–20%) was higher than that in $\text{PM}_{2.5}$ (3%–14%). Significant increases in the proportions of 4-nitrophenol, methyl-nitrophenols, and 2,4-dinitrophenol were observed in gas-phase samples, while there were only very small fractions of methyl-nitrocatechols and nitrosalicylic acids present in these samples.

3.2. Fractions in fine particles and gas-particle partitioning

3.2.1. Fractions in fine particles

The results showed that phenolic compounds and nitrated phenols were distributed both in fine particles and coarse particles in urban Jinan, and their respective fractions varied with the season. As shown in Fig. 3(a), most phenolic compounds were mainly distributed in coarse particles in spring, with an average fraction of <40% in fine particles, except for *m*-cresol and *o*-cresol, about half of which was present in fine particles. Compared with spring, the fractions of phenolic compounds in fine particles showed an overall upward trend in summer, when these comprised almost half of the compounds in fine particles. In particular, the fraction of catechol in fine particles in summer increased from 22% to 63%. Similar to phenolic compounds, in spring,

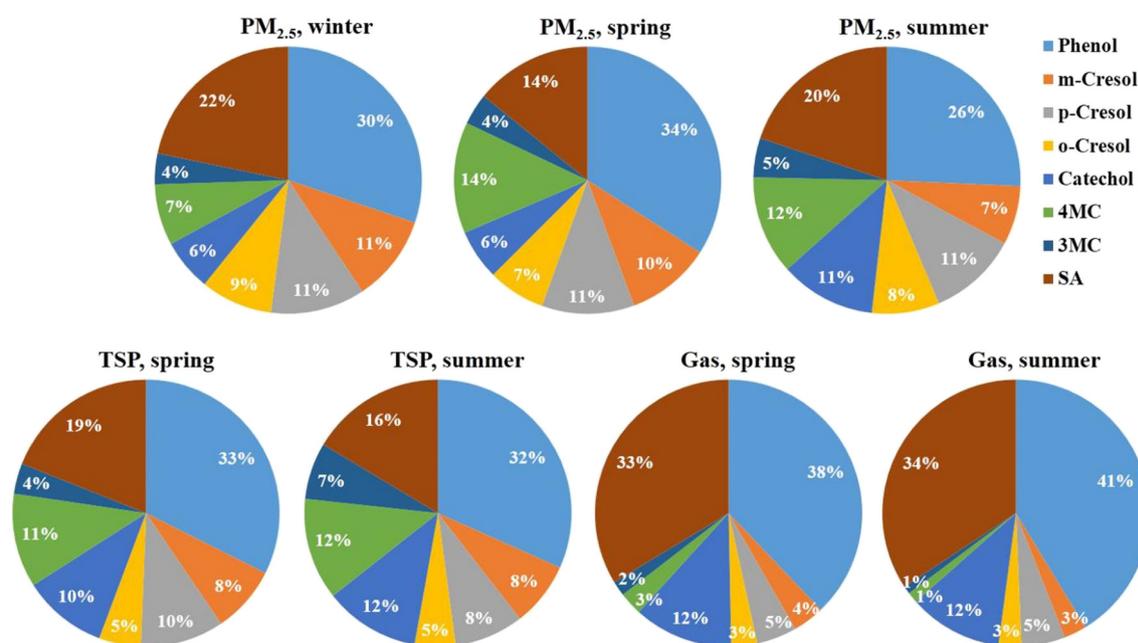


Fig. 1. Proportions of individual phenolic compounds in $\text{PM}_{2.5}$, TSP and gas phase in winter, spring, and summer.

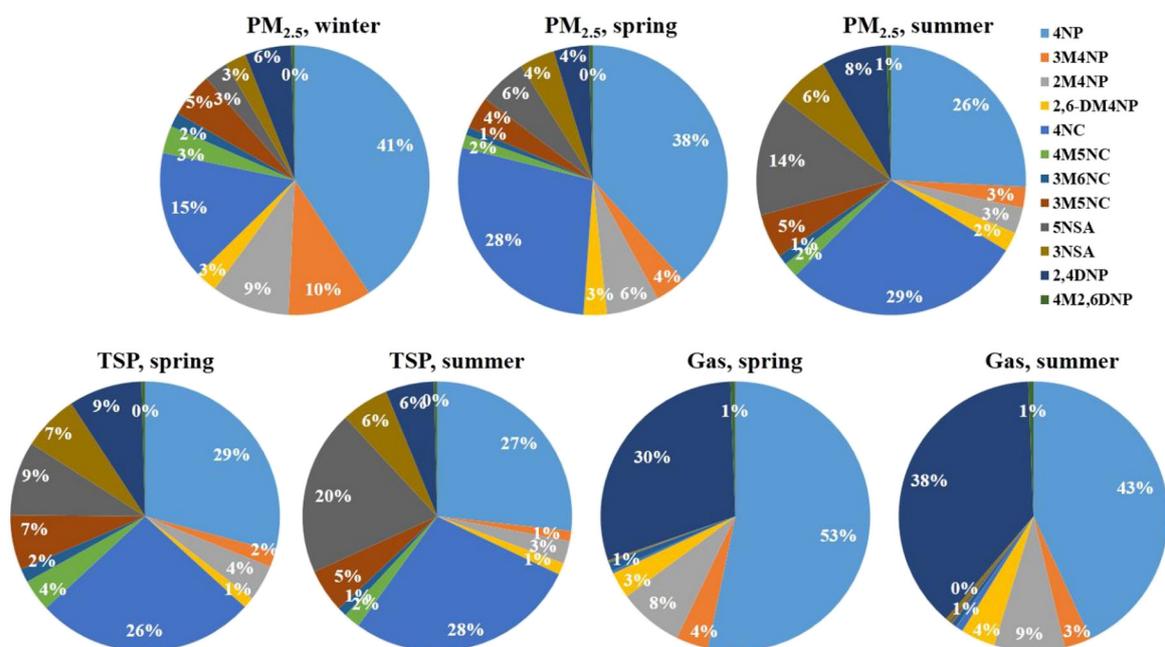


Fig. 2. Proportions of individual nitrated phenols in $PM_{2.5}$, TSP and gas phase in winter, spring, and summer.

most nitrated phenols were primarily distributed in coarse particles, except methyl-nitrophenols and 2,6-dimethyl-4-nitrophenol, with average fractions in fine particles of 55%–74% (see Fig. 3(b)). In summer, however, approximately 65% of the nitrated phenols existed in fine particles. In particular, >80% of 3-methyl-4-nitrophenol and 2,4-dinitrophenol were found in fine particles in summer.

The relatively low fractions of phenolic compounds and nitrated phenols in fine particles in spring were primarily attributed to the emission of dusts from local bare-soil areas and remote deserts at high wind speeds, and the high proportions of coarse particles (the average $PM_{2.5}/PM_{10}$ ratios in spring and summer were 0.45 and 0.57, respectively, based on the reported data from the nearest air quality monitoring station). In the moderate temperatures (20.1 ± 2.8 °C on average) of spring, a large fraction of the emitted and produced gas-phase phenolic compounds and nitrated phenols condensed onto coarse particles due to the vast surface areas of such particles. Nevertheless, in summer, due to high temperature, intense photochemical reactions, and a large quantity of fine particles produced from secondary formation, phenolic compounds and nitrated phenols were mostly distributed in fine particles. The small differences in the fractions of the 8 phenolic compounds

and the 12 nitrated phenols in fine particles in the same season were believed to be associated with their differing source emissions, formation pathways, and the condensation and uptake on pre-existing particles.

3.2.2. Gas-particle partitioning

The gas-particle partitioning of phenolic compounds and nitrated phenols greatly changed with species and seasons. Fig. 4(a) compares the fraction of measured phenolic compounds in the particle phase (F_p). As depicted, in spring, the F_p of phenolic compounds was 58%–86%, indicating that more phenolic compounds were distributed in the particle phase during the moderate spring temperatures of urban Jinan. In contrast, in summer, the F_p for most phenolic compounds decreased significantly. Especially, the F_p values of phenol, catechol, and salicylic acid were below 40%, suggesting that these mainly existed in the gas phase at this time.

A dramatic difference was found in the F_p among different species of nitrated phenols, as shown in Fig. 4(b). In spring, 4-nitrophenol, methyl-nitrophenols, 2,6-dimethyl-4-nitrophenol, and 4-methyl-2,6-dinitrophenol were almost evenly distributed between the gas and particle phases, but 4-nitrocatechol, 4-methyl-5-nitrocatechol, 3-methyl-

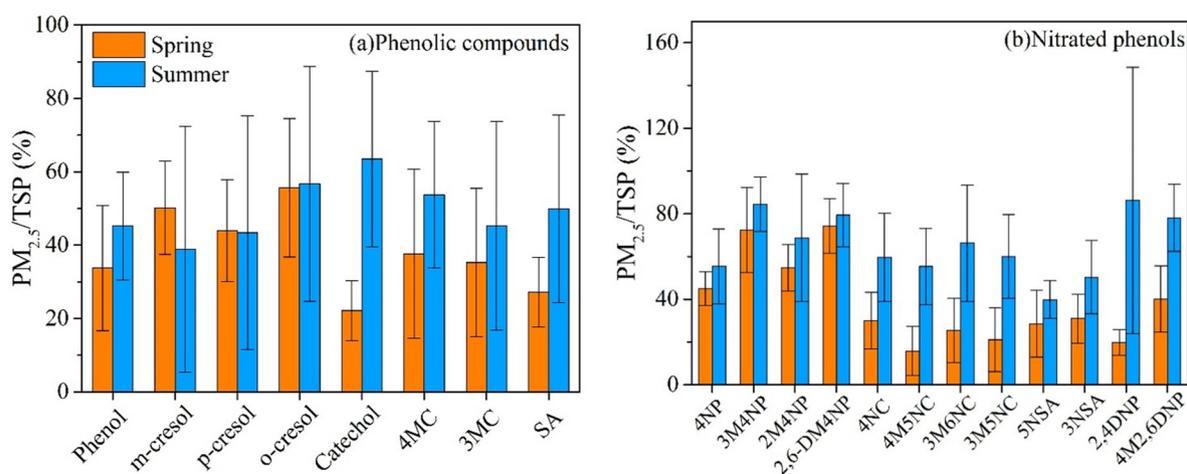


Fig. 3. The fractions of phenolic compounds and nitrated phenols in fine particles in spring and summer.

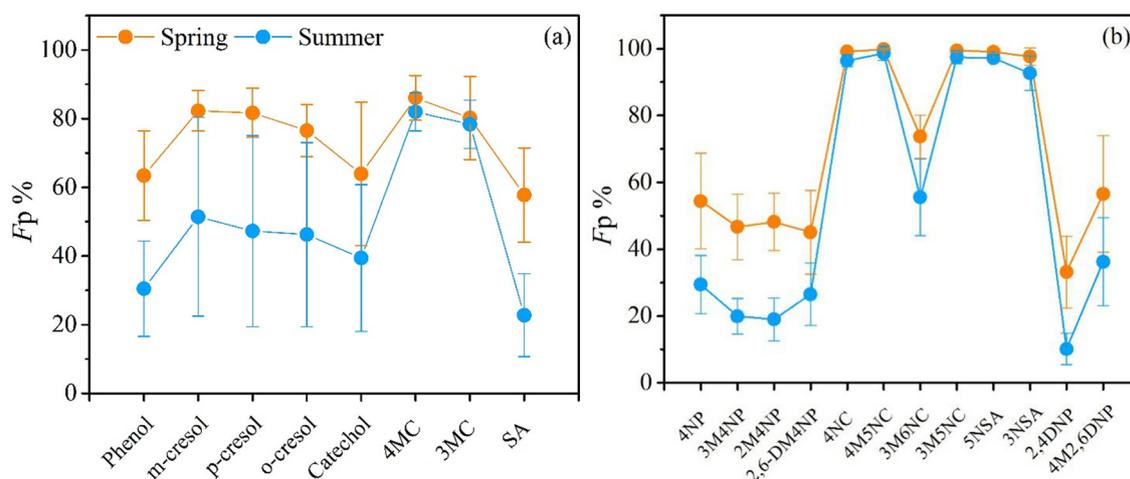


Fig. 4. The fractions of phenolic compounds and nitrated phenols in particle phase in spring and summer.

5-nitrocatechol, and nitrosalicylic acids were almost entirely in the particle phase. In addition, most of the 3-methyl-6-nitrocatechol was distributed in the particle phase, while 2,4-dinitrophenol was mostly present in the gas phase. The F_p for nitrated phenols reduced from spring to summer: >70% of 4-nitrophenol, methyl-nitrophenols, 2,6-dimethyl-4-nitrophenol, and 2,4-dinitrophenol and nearly half of 3-methyl-6-nitrocatechol were distributed in the gas phase at the relatively higher summer temperatures. Nevertheless, >90% of 4-nitrocatechol, 4-methyl-5-nitrocatechol, 3-methyl-5-nitrocatechol, and nitrosalicylic acids still existed in the particle phase in summer.

The large variations in the measured F_p among different phenolic compounds and nitrated phenols were generally consistent with the results and findings in other studies, and were largely attributable to the difference in the saturated vapor pressures of compounds. That is, higher fractions were in the gas phase in summer than in spring due to the higher saturated vapor pressures the compounds had in the warmer summer conditions (Chandramouli et al., 2003).

In previous studies, Herterich and Herrmann (2008) demonstrated that 4-nitrophenol and dinitrophenols mainly existed in the gaseous phase at two hill sites in Germany during summer. In cold season in downtown Rome, Italy, the fractions of 4-nitrophenol, 3-methyl-4-nitrophenol, and 2,6-dimethyl-4-nitrophenol in the particle phase were 82%, 78% and 75%, respectively (Cecinato et al., 2005). In addition, more than half of phenol and cresols were detected in the gas phase, while most 2,4-dinitrophenol was present in the particle phase in Strasbourg during spring and autumn (Morville et al., 2006). Overall, low saturated vapor pressures favored the partitioning of organic compounds from the gas phase to the particle phase, and the species with higher saturated vapor pressures showed greater increases in gas-phase fractions.

As reported by Leuenberger et al. (1985), the saturated vapor pressures of phenol, *o*-cresol, *m*-cresol, and *p*-cresol at 298 K were 45.3, 38.7, 18.7, and 16.0 Pa, respectively, which means that more phenol existed in the gas phase than did cresols in urban Jinan in this study. According to Wang et al. (2019), the estimated saturation pressures of 4-nitrocatechol and methyl-nitrocatechols ranged from 3.1×10^{-6} to 3.4×10^{-5} Pa (296 K), which were much lower than those for 4-nitrophenol, methyl-nitrophenols, and 2,4-dinitrophenol (Yuan et al., 2016), and therefore most 4-nitrocatechol and methyl-nitrocatechols were distributed in the particle phase in both spring and summer in urban Jinan. Similarly, the low saturated vapor pressures of nitrosalicylic acids meant that these mostly existed in the particle phase rather than the gas phase (Kitanovski et al., 2012). 4-Nitrocatechol is highly water-soluble and thus easily accumulates in the aqueous phase (Desyaterik et al., 2013). In addition, methyl-nitrocatechols have been produced from precursors of cresols in the

aqueous phase (Vidovic et al., 2018). Thus, the moderately high ambient humidity ($57.7 \pm 12.2\%$) in summer in urban Jinan facilitated the aqueous formation of methyl-nitrocatechols and led to their distribution into the particle phase. Similar processes also accounted for the distribution of nitrosalicylic acids, which could form by aqueous-phase oxidation of salicylic acid (Andreozzi et al., 2006). Nevertheless, 3-methyl-6-nitrocatechol presented lower fractions in particle phase than 3-methyl-5-nitrocatechol and 4-methyl-5-nitrocatechol, which may suggest different formation pathways for 3-methyl-6-nitrocatechol (Wang et al., 2019). As reported by Frka et al. (2016), electrophilic substitution reactions under acidic conditions and nitration by NO_2^+ in aqueous phase at night-time were proposed to produce methyl-nitrocatechols. Further theoretical predictions of nitration products of 3-methylcatechol in aqueous phase indicated higher activation barriers on 3-methyl-6-nitrocatechol, so a smaller fraction of 3-methyl-6-nitrocatechol was produced and distributed in particle phase than other two methyl-nitrocatechols.

In summary, the differences in the saturated vapor pressures of different phenolic compounds and nitrated phenols led to their great diversity of F_p , and the seasonal changes in ambient temperature caused the seasonal variations of F_p values for these species.

3.3. Source appointment by receptor model

3.3.1. Source identification

To elucidate the primary origins of phenolic compounds and nitrated phenols in urban Jinan, the positive matrix factorization (PMF) receptor model was applied to concentrations of 8 phenolic compounds and 12 nitrated phenols in $\text{PM}_{2.5}$ and concentrations of gaseous tracer (i.e., NO_x , SO_2 , O_3). Four source contributors were identified based on the PMF outputs (as shown in Fig. 5).

Factor 1 (F1) was recognized as secondary formation given the reasonably high concentration of ozone and the fact that it was one of the major sources of OH radicals, which dominate the gas-phase formation of nitrated phenols (Harrison et al., 2005). Factor 2 (F2) was considered to be biomass burning due to the high concentrations of 4-nitrocatechol and methyl-nitrocatechols and given that methyl-nitrocatechols were identified as a good atmospheric tracer for biomass burning-derived secondary organic aerosols (Iinuma et al., 2010; Wang et al., 2017a). Factor 3 (F3) was ascribed to coal combustion because of the high concentration of SO_2 and the fact that SO_2 can be used as a tracer for direct emissions of coal combustion from nearby thermal power plants, industry, and residential cooking and heating use (Ross et al., 2002). In particular, the combustion of anthracite has been shown to emit a large amount of particulate 4-nitrophenol, and more 5-nitrosalicylic acid than 3-nitrosalicylic acid (Lu et al., 2019b). Finally, Factor 4 (F4) was

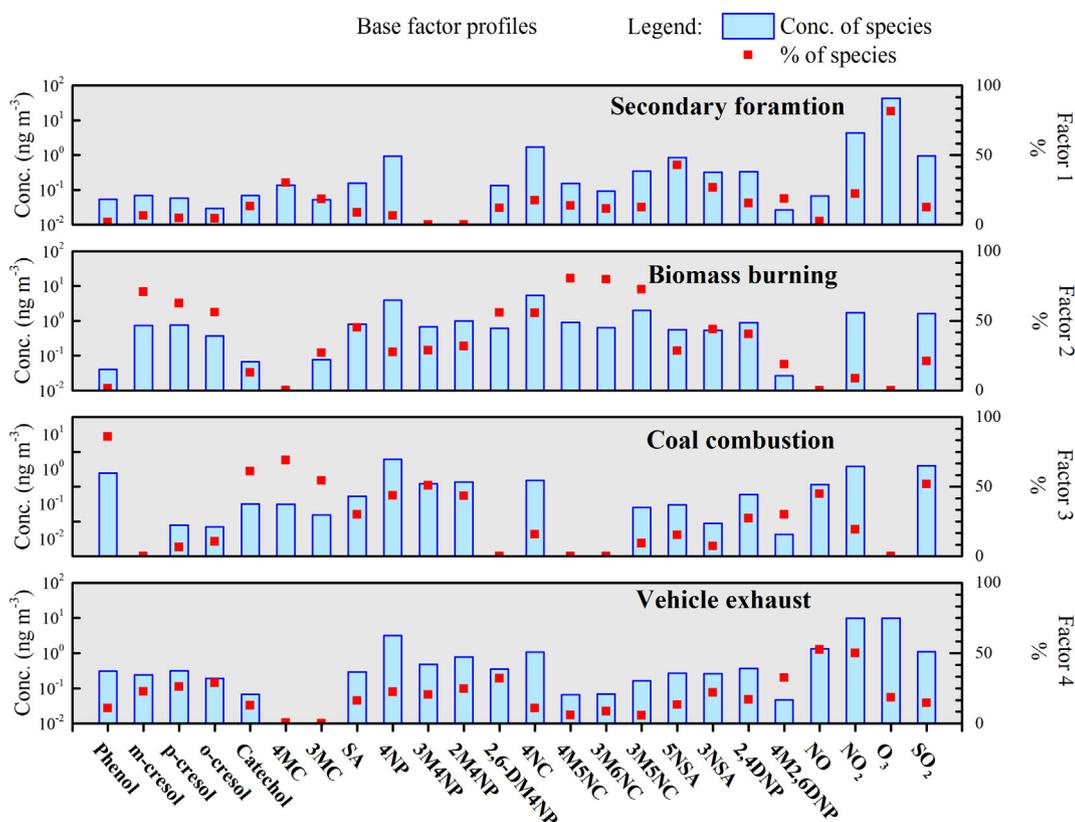


Fig. 5. The source profiles of phenolic compounds and nitrated phenols in PM_{2.5} and associated air pollutants by PMF analysis in urban Jinan.

identified as vehicle exhaust given the high concentrations of NO and NO₂ but relatively low concentration of SO₂. Vehicle exhaust directly has recently been shown to release nitrated phenols, mostly comprising 4-nitrophenol and with methyl-nitrophenols accounting for almost half (Lu et al., 2019a).

3.3.2. Source contributions

The contributions from different source factors changed with species and seasons. Overall, as shown in Table 2, biomass burning

served as the biggest source of *m*- and *p*-cresols, 4-nitrocatechol, and methyl-nitrocatechols in fine particles, contributing >30% of these species found in urban Jinan. It also contributed ~35% of *o*-cresol and 2,6-dimethyl-4-nitrophenol. Coal combustion was the largest source of phenol, catechol, methylcatechols, 4-nitrophenol, and methyl-nitrophenols, with a contribution larger than 35%. In addition, vehicle exhaust contributed 33%–39% of the determined cresols, 2,6-dimethyl-4-nitrophenol, and 4-methyl-2,6-dinitrophenol. Secondary formation contributed a large fraction (35%–47%) of

Table 2

Contributions of four source factors to the phenolic precursors and nitrated phenols in winter, spring and summer. (F: Factor, F1 = secondary formation, F2 = biomass burning, F3 = coal combustion, F4 = vehicle exhaust.)

	Winter				Spring				Summer				All			
	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
Phenol	1%	8%	76%	15%	4%	1%	66%	29%	14%	1%	66%	19%	5%	3%	69%	22%
<i>m</i> -Cresol	2%	71%	0%	28%	12%	37%	0%	50%	56%	18%	0%	25%	19%	44%	0%	37%
<i>p</i> -Cresol	1%	64%	9%	26%	9%	32%	7%	52%	46%	18%	7%	30%	15%	39%	8%	38%
<i>o</i> -Cresol	1%	59%	14%	26%	8%	29%	11%	52%	41%	16%	11%	31%	13%	36%	12%	39%
Catechol	3%	21%	61%	16%	23%	7%	44%	27%	56%	4%	28%	13%	24%	10%	46%	20%
4MC	1%	1%	90%	8%	52%	0%	47%	2%	81%	0%	18%	1%	42%	0%	54%	3%
3MC	0%	40%	60%	0%	43%	12%	45%	0%	70%	9%	21%	0%	35%	20%	45%	0%
SA	2%	48%	33%	17%	16%	22%	27%	36%	52%	12%	20%	16%	20%	28%	27%	25%
4NP	1%	33%	45%	20%	11%	14%	34%	40%	41%	8%	30%	22%	15%	19%	37%	29%
3M4NP	0%	33%	49%	18%	0%	16%	41%	43%	0%	11%	61%	28%	0%	21%	48%	31%
2M4NP	0%	36%	43%	21%	0%	18%	36%	46%	0%	12%	55%	32%	0%	23%	43%	35%
2,6-DM4NP	4%	64%	0%	33%	18%	30%	0%	51%	64%	11%	0%	24%	24%	37%	0%	39%
4NC	4%	60%	21%	15%	32%	25%	16%	27%	72%	11%	7%	9%	32%	33%	16%	19%
4M5NC	5%	79%	0%	16%	36%	39%	0%	25%	76%	18%	0%	6%	35%	47%	0%	17%
3M6NC	4%	77%	0%	19%	29%	39%	0%	32%	73%	18%	0%	9%	31%	47%	0%	22%
3M5NC	3%	72%	15%	11%	31%	33%	13%	23%	71%	17%	6%	6%	31%	42%	12%	15%
5NSA	11%	43%	24%	21%	54%	12%	13%	21%	86%	4%	3%	7%	47%	20%	15%	18%
3NSA	7%	55%	11%	26%	37%	20%	8%	35%	78%	7%	2%	13%	37%	29%	8%	27%
2,4DNP	3%	46%	32%	19%	25%	19%	23%	33%	65%	9%	13%	14%	27%	26%	24%	24%
4M2,6DNP	5%	29%	38%	29%	25%	10%	23%	42%	65%	3%	12%	20%	28%	14%	25%	33%

The bold number indicates the largest contribution to each species in each season and only the values higher than 30% are marked.

methylcatechols and nitrosalicylic acids and served as the largest contributor of nitrosalicylic acids. It also made a significant contribution (~30%) to 4-nitrocatechol, methyl-nitrocatechols and 4-methyl-2,6-dinitrophenol. As for salicylic acid and 2,4-dinitrophenol, the above four source factors provided almost even contributions. The source contributions in different seasons in urban Jinan are shown in Table 2 and are described in detail below.

In winter, coal combustion (F3) was the largest source of phenol, catechol, methyl-catechols, 4-nitrophenol, methyl-nitrophenols, and 4-methyl-2,6-dinitrophenol, contributing >60% to phenol, catechol, methyl-catechols and >35% to 4-nitrophenol, methyl-nitrophenols, and 4-methyl-2,6-dinitrophenol. Our recent study has found that coal combustion serves as the major source of nitrated phenols in urban Jinan during winter (Wang et al., 2018). Coal combustion for industrial processes and residential heating and cooking was not only found to directly emit nitrated phenols and phenolic compounds (Lu et al., 2019b), but also to release aromatic precursors that further yielded phenolic compounds and nitrated phenols in the presence of oxidants and NO₂ (Bi et al., 2008; Harrison et al., 2005).

Biomass burning was the greatest source of cresols, salicylic acid, 2,6-dimethyl-4-nitrophenol, 4-nitrocatechol, methyl-nitrocatechols, nitrosalicylic acids, and 2,4-dinitrophenol, responsible for more than half of cresols, 2,6-dimethyl-4-nitrophenol, 4-nitrocatechol, methyl-nitrocatechols, and 3-nitrosalicylic acid. It also contributed more than two-thirds of the methyl-nitrocatechols. In biomass burning plumes, 4-nitrocatechol and methyl-nitrocatechols were recognized as the most abundant nitrated phenols (Wang et al., 2017a), which could be produced by the released benzene and cresols from the pyrolysis of lignin in the presence of NO_x (Kahnt et al., 2013). In addition, vehicle exhaust contributed to a significant fraction (<40%) of most phenolic compounds and nitrated phenols, but the contributions from secondary formation were relatively small (<15%) in winter in urban Jinan.

During the sampling period in spring, vehicle exhaust served as the largest source for some phenolic compounds and nitrated phenols, including cresols, salicylic acid, 4-nitrophenol, methyl-nitrophenols, 2,6-dimethyl-4-nitrophenol, 2,4-dinitrophenol, and 4-methyl-2,6-dinitrophenol. In particular, the contributions to cresols from vehicle exhaust were >50%. Vehicle exhaust was recently identified as a major emission source of nitrated phenols (Lu et al., 2019a), which comprised abundant 4-nitrophenol and methyl-nitrophenols. Moreover, toluene emitted from vehicle exhaust could be oxidized to yield cresols, and further oxidized to methyl-nitrophenols in the presence of NO_x (Schauer et al., 2002; Tremper et al., 1993; Wang et al., 2019). In addition, the contributions from secondary formation rose significantly in spring due to the increased solar radiation compared with winter, and this secondary formation acted as the largest source of 4-methylcatechol, 4-nitrocatechol, and nitrosalicylic acids. Similar to winter, biomass burning remained the largest source of methyl-nitrocatechols and coal combustion was the dominant source of phenol, catechol and 3-methylcatechol in spring.

In summer in urban Jinan, secondary formation was the largest contributor of most phenolic compounds and nitrated phenols. For example, more than two-thirds of methylcatechols, 2,6-dimethyl-4-nitrophenol, 4-nitrocatechol, methyl-nitrocatechols, nitrosalicylic acids, 2,4-dinitrophenol, and 4-methyl-2,6-dinitrophenol were produced via secondary formation pathways. The conditions of high temperature, intensive solar radiation, and moderately high humidity in summer facilitated the photochemical reactions, enhanced the atmospheric oxidation capacity, and promoted the aqueous reactions, and thus led to the rapid formation of phenolic compounds and nitrated phenols (Wang et al., 2019). However, coal combustion still served as the biggest source in summer of phenol and methyl-nitrophenols, indicating that coal-fired industries were the probable source of phenolic compounds and nitrated phenols in the particulate matter samples from urban Jinan.

3.4. Correlations between phenolic precursors and nitrated phenols

Understanding the relationships between nitrated phenols and their phenolic precursors helps to delineate their origins and transformations and the influence of phenolic compounds on the abundances of nitrated phenols. Table 3 shows the correlations between nitrated phenols and phenolic compounds in semi-volatile samples during spring and summer in urban Jinan. The correlation coefficients for different nitrated phenols varied from 0.20 to 0.92 in spring and from 0.14 to 0.91 in summer. The moderately and very good correlations between nitrosalicylic acids and their salicylic acid precursor demonstrated the key role played by salicylic acids in the secondary formation of nitrosalicylic acids.

However, there was an obvious difference between the correlation coefficients in spring and summer, suggesting that a discrepancy existed between emission sources or formation pathways in these seasons. In spring, nitrated phenols and phenolic precursors were mainly derived from primary sources such as vehicles. Hence, the strong linear correlations between 2-methyl-4-nitrophenol and *o*-cresol ($r = 0.73, p < 0.01$) and 3-methyl-4-nitrophenol and *m*-cresol ($r = 0.92, p < 0.01$) confirm the same emission source, i.e., vehicle exhaust, and the relatively high linear slopes between these (11.51 and 5.84, respectively) approximate their corresponding emission ratios. The moderate correlation between 4-nitrocatechol and catechol ($r = 0.63, p = 0.06$) and strong correlations between methyl-nitrocatechols and the corresponding methylcatechols in spring ($r = 0.69-0.83, p < 0.05$) were attributable to their same origins, i.e., both primary emission sources and secondary formation. Nevertheless, 4-nitrophenol and 2,4-dinitrophenol only presented very weak correlations with phenol in spring, which was ascribed to the dominant emission source for 4-nitrophenol and 2,4-dinitrophenol in this season being vehicle exhaust, while coal combustion was the primary contributor of phenol.

In contrast with spring, secondary formation was the major source of the nitrated phenols and the phenolic precursors in summer, with strong correlations observed. As shown in Table 3, the correlation coefficients between 4-nitrophenol and phenol ($r = 0.80, p < 0.01$), 2,4-dinitrophenol and phenol ($r = 0.67, p < 0.01$), and 4-nitrocatechol and catechol ($r = 0.79, p < 0.01$) in summer were much higher than those in spring, which indicated that the secondary formation of 4-nitrophenol, 2,4-dinitrophenol, and 4-nitrocatechol was dependent on their phenol and catechol precursors. The linear slopes partly reflected the conversion ratios of these nitrated phenols from their corresponding phenolic precursors. Previous studies have shown that phenol, a product of the gas-phase reactions of OH radical with benzene, can be oxidized by OH radicals (during the daytime) or NO₃ radicals (during the nighttime) to produce 4-nitrophenol and 2,4-dinitrophenol in the presence of NO₂ (Harrison et al., 2005; Yuan et al., 2016). In addition, the reactions of catechol initiated by OH/NO₃ radicals in the presence of NO_x are the major source of 4-nitrocatechol (Finewax et al., 2018). Nevertheless, lower correlation coefficients were found between methyl-nitrocatechols and the methylcatechols precursors in summer than in spring, which was possibly because most methyl-nitrocatechols were produced from aqueous-phase oxidation during the relatively high humidity of summer. Overall, the secondary formation in summer of nitrosalicylic acids, 4-nitrophenol, methyl-nitrophenols, 4-nitrocatechol and 2,4-dinitrophenol strongly depended on the abundances of their respective precursor phenolic compounds.

4. Conclusions

In this study, 12 nitrated phenols and 8 phenolic precursors were determined in both the gas phase and the particle phase (PM_{2.5} and TSP) in samples from collected in winter, spring, and summer of 2016 in urban Jinan, China. During the sampling period, the concentrations of total phenolic compounds and total nitrated phenols typically varied from several to >100 ng m⁻³, with the highest values observed in winter and the lowest in summer. The compositions of phenolic compounds

Table 3The linear correlation coefficients (*r*) and slopes (*k*) between gas-phase nitrated phenols and phenolic precursors in spring and summer.

Y		4NP	2,4DNP	2M4NP	3M4NP	4NC	3M5NC	3M6NC	3NSA	5NSA
X		Phenol	Phenol	<i>o</i> -Cresol	<i>m</i> -Cresol	Catechol	3MC	3MC	SA	SA
Spring	<i>r</i>	0.20	0.26	0.73	0.92	0.63	0.83	0.69	0.69	0.78
	<i>k</i>	4.64	0.91	11.51	5.84	0.04	0.17	1.85	0.007	0.009
Summer	<i>r</i>	0.80	0.67	0.77	0.6	0.79	0.43	0.14	0.91	0.62
	<i>k</i>	1.57	1.46	8.67	1.44	0.22	0.22	0.14	0.06	0.02

and nitrated phenols also varied with sample types and seasons. Phenol and salicylic acid were the dominant phenolic compounds in both gas and particle phases. 4-Nitrophenol was the dominant species in the particle phase, while 4-nitrophenol and 2,4-dinitrophenol were most abundant in the gas phase. Further analysis on the fractions of phenolic compounds and nitrated phenols in fine particles suggested that high wind-speed and dust particles in spring promoted the distribution of these compounds in coarse particles. Nevertheless, the high temperature in summer was also favorable for these pollutants' partitioning into the gas phase, in particular those with relatively high vapor pressures (e.g., phenol, catechol, salicylic acid, 4-nitrophenol, methyl-nitrophenols and 2,4-dinitrophenol). The outputs of the PMF model suggested that coal combustion was the dominant contributor of phenol, catechol, methylcatechols, 4-nitrophenol, and methyl-nitrophenols, whereas biomass burning contributed the largest proportions of *m*- and *p*-cresols, 4-nitrocatechol, and methyl-nitrocatechols. Nitrosalicylic acids were mainly derived from secondary formation, and vehicle exhaust was the biggest source of *o*-cresol, 2,6-dimethyl-4-nitrophenol, and 4-methyl-2,6-dinitrophenol. Furthermore, primary emissions from coal combustion and biomass burning contributed significant amounts of phenolic compounds and nitrated phenols in winter, vehicle exhaust was a key source in spring, and secondary formation was identified as the highest contributor in summer. In addition, strong correlations were observed between some nitrated phenols and their corresponding phenolic precursors, particularly in summer, which showed the dependence of the formation and abundances of nitrated phenols on their phenolic precursors.

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.

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