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Observations of fine particulate nitrated phenols in four sites in northern China: concentrations, source apportionment, and secondary formation

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Abstract. Filter samples of fine particulate matters were collected at four sites in northern China (urban, rural, and mountain) in summer and winter, and the contents of nine nitrated phenols were quantified in the laboratory with the use of ultra-high-performance liquid chromatography coupled with mass spectrometry. During the sampling periods, the concentrations of particulate nitrated phenols exhibited distinct temporal and spatial variation. On average, the total concentration of particulate nitrated phenols in urban Jinan in the wintertime reached 48.4 ng m^{-3}, and those in the summertime were 9.8, 5.7, 5.9, and 2.5 ng m^{-3} in urban Jinan, rural Yucheng and Wangdu, and Mt. Tai, respectively. The elevated concentrations of nitrated phenols in wintertime and in urban areas demonstrate the apparent influences of anthropogenic sources. The positive matrix factorization receptor model was then applied to determine the origins of particulate nitrated phenols in northern China. The five major source factors were traffic, coal combustion, biomass burning, secondary formation, and aged coal combustion plume. Among them, coal combustion played a vital role, especially at the urban site in the wintertime, with a contribution of around 55 %. In the summertime, the observed nitrated phenols were highly influenced by aged coal combustion plumes at all of the sampling sites. Meanwhile, in remote areas, contributions

from secondary formation were significant. Further correlation analysis indicates that nitrosalicylic acids were produced mostly from secondary formation that was dominated by NO$_2$ nitration.

1 Introduction

Nitrated phenols, with at least one nitro and one hydroxyl group attached to the aromatic group, have undeniable effects on the environment and on living beings. Due to their strong absorption in the near-ultraviolet and visible regions, nitrated phenols are classified as poorly characterized brown carbon (BrC) (Desyaterik et al., 2013; Teich et al., 2017). Though the absorption of BrC is weak compared to that of black carbon (BC), it can enhance the absorption of solar radiation and may have an indirect effect on regional climate (Feng et al., 2013; Mohr et al., 2013; Laskin et al., 2015; Lu et al., 2015; Zhao et al., 2015). Recent studies have shown that several semivolatile nitrated phenols, including nitrophenol, nitrocatechol, and methyl-nitrocatechol (NC), are important photochemical oxidation products of gas-phase precursors, which may play a part in the formation of secondary organic

aerosols (SOAs; Pereira et al., 2015). Via photo-oxidation and aqueous-phase reactions, nitrated phenols could alter the tropospheric photochemistry and influence SOA formation, thus affecting regional air quality and atmospheric visibility (Mohr et al., 2013; Laskin et al., 2015; Chow et al., 2016; Yuan et al., 2016). In addition, nitrated phenols are hazardous to plants, animals, aquatic life, and humans (Natangelo et al., 1999; Schüssler and Nitschke, 2001; Harrison et al., 2005a; Ganranoo et al., 2010). The significant roles of nitrated phenols in the atmosphere and their adverse effects on living things have triggered the need to understand their pollution characteristics and their origins.

Nitrated phenols in the troposphere largely originate from primary emissions of anthropogenic activities. In recent decades, nitrated phenols have drawn attention because of their prevalence in biomass burning plumes (Kahnt et al., 2013; Mohr et al., 2013). Due to the good correlation with levoglucosan, Iinuma et al. (2010) pointed out that NCs could be a reasonable tracer for biomass burning events. In addition to biomass burning, other combustion activities (e.g., coal, gasoline) are possible sources of nitrated phenols (Nojima et al., 1983; Tremp et al., 1993; Yan et al., 2015); their contributions, however, have not yet been well evaluated. Furthermore, nitrated phenols have been used as pesticides in some farmlands and are widely used as raw materials in industrial processes (Harrison et al., 2005a).

Secondary formation also plays an important role in the atmospheric abundance of nitrated phenols (Grosjean, 1985). Various atmospheric processes are responsible for the formation of nitrated phenols, including photochemical oxidation of benzenes in the presence of NO_x (NO and NO_2) and ultraviolet rays (Nojima et al., 1975, 1976), oxidation of phenols by OH and NO_3 radicals in the presence of NO_x (Atkinson et al., 1992; Bolzacchini, et al., 2001), and nitration of phenols in aqueous solutions (Lüttke et al., 1997; Vione et al., 2005; Frka et al., 2016). However, the formation pathways of nitrated phenols from the condensed phase remains more uncertain than those for the gas phase (Harrison et al., 2005a). Once formed in the gas phase, the phenols and nitrated phenols partition between the gas and particle phases according to their saturated vapor pressure (Nojima et al., 1975; Bolzacchini et al., 2001; Harrison et al., 2005b; Xu and Wang, 2013). Chow et al. (2016) found evidence from field measurements that high levels of nitrated phenols in Hong Kong were associated with high concentrations of NO_2.

As an important economic and industrial center of East Asia, northern China experiences severe $PM_{2.5}$ pollution and high levels of NO_x (Wang et al., 2014; Y. Q. Wang et al., 2015; Zhang et al., 2015). In recent years, several field studies related to concentrations, size distributions, and light absorption of particulate nitrated phenols have been conducted in and near the region, showing the large influences of anthropogenic sources such as biomass burning and other combustion activities (Li et al., 2016; Teich et al., 2017). In this study, we present the concentrations, compositions, and tem-

poral and spatial differences of nine nitrated phenols in samples of $PM_{2.5}$ collected from four different sites in northern China. Positive matrix factorization (PMF) model and correlation analysis are then applied to understand the primary sources and secondary formation of particulate nitrated phenols in this region.

2 Experiments and methods

2.1 Sampling sites and online instruments

$PM_{2.5}$ filter sampling and related online measurements were conducted in five field campaigns at four sampling sites in northern China, which are illustrated in detail in Table 1. As shown, two field campaigns were conducted in urban Jinan in winter 2013 and summer 2014, whereas the measurements at the rural and mountain sites took place in summer 2014.

The sampling site in urban Jinan was the Atmospheric Environment Observation Station of Shandong University (AEOS-SDU) (36°40′ N, 117°03′ E). The urban Jinan site is surrounded by education, commercial, and residential districts, with several heavily trafficked roads nearby. Therefore, it is frequently influenced by vehicle emissions, urban plumes, and industrial plumes from suburban areas. The NO_x concentration was measured by a chemiluminescence method equipped with the model 42C molybdenum oxide converter (Thermo Electronic Corporation, TEC, USA). The O_3 concentration was analyzed with an ultraviolet absorption method (model 49C, TEC). The SO_2 concentration was measured with the pulsed fluorescence method (model 43C, TEC). Water-soluble ions, including Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, and Ca^{2+}, were detected with the online Monitor for AeRosols and GAses in ambient air (MARGA, ADI20801, Applikon-ECN, the Netherlands). The online instruments and methods used for the winter field campaign were described in detail by L. Wang et al. (2015). In the summer campaign, due to logistical issues, water-soluble ions were determined from quartz-filtered samples of $PM_{2.5}$ by ion chromatography (Wang et al., 2017a).

The second sampling site was located in an open field in rural Yucheng (36°52′ N, 116°34′ E), Dezhou, Shandong Province, about 50 km northwest of the city of Jinan (see Fig. 1). During summer, polluted urban plumes arrived with the assistance of prevailing winds from the southeast. The rural Yucheng site was surrounded by farmland, but there was a national road 1.5 km away to the south and a few small-scale factories nearby. Trace gases of NO_x and O_3 were measured with model 42C and model 49C analyzers, respectively. Water-soluble ions were detected with the MARGA. Details about the site and the instruments deployed were described by Yao et al. (2016).

The third sampling site was located in rural Wangdu (38°42′ N, 115°08′ E), Baoding, Hebei Province, near grasslands and farms. Although located in a rural area, it could be
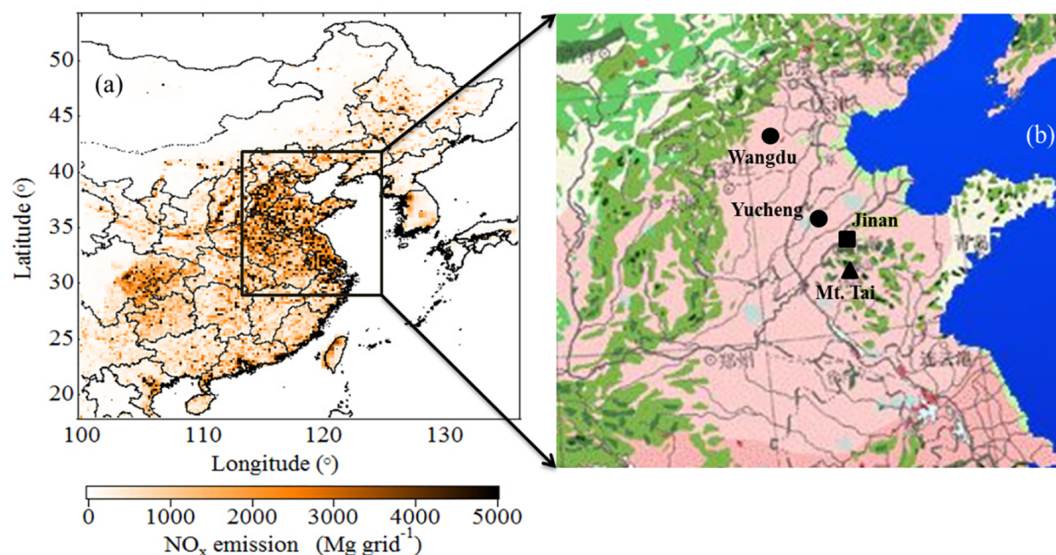
Figure 1. Maps of the study region show **(a)** the NO_x emission intensity and **(b)** the four sampling sites.

Table 1. Sampling sites and sampling periods involved in this study.

Sampling site	Type	Altitude	Sampling period	Season
Jinan	urban	$\sim 50\,m$	2013.11.26–2014.01.05	winter
	urban		2014.09.04–2014.09.21	summer
Yucheng	rural	$\sim 23\,m$	2014.06.09–2014.06.20	summer
Wangdu	rural	$\sim 14\,m$	2014.06.19–2014.06.29	summer
Mt. Tai	mountain	$\sim 1465\,m$	2014.07.27–2014.08.06	summer

easily influenced by industrial and urban plumes from large cities like Beijing, Tianjin, and Shijiazhuang. Trace gases of NO_x and O_3 were measured with a model 42i analyzer coupled with a blue light convertor and a model 49i analyzer (TEC). Water-soluble ions were analyzed by a gas aerosol collector–ion chromatography (GAC-IC) system. More information on the site and instruments may be found in Tham et al. (2016).

The fourth sampling site was located near the summit of Mt. Tai ($36°15'$ N, $117°06'$ E), Tai'an, Shandong Province. It was infrequently influenced by incense burning and restaurants at the popular tourism areas on Mt. Tai. Notably, with an altitude of about 1465 m above sea level, the Mt. Tai site is an ideal place to understand the transport, sources, and formation processes of air pollution in northern China. Trace gases of NO_x and O_3 were measured with a model 42i analyzer coupled with a blue light converter and a model 49i analyzer, respectively. Water-soluble ions were analyzed with the MARGA. Detailed information of this site and the instruments deployed was given by Z. Wang et al. (2017).

2.2 PM$_{2.5}$ sampling

$PM_{2.5}$ filter samples were collected using the mid-volume sampler (TH-150A, Wuhan Tianhong, China) with a flow rate of $100\,L\,min^{-1}$ (LPM). The sampler was fixed in the open fields with the $PM_{2.5}$ cutting head 1.5 m above the ground or station. Two filter samples were collected each day, with the daytime samples from 07:00 to 18:30 (local time) and the nocturnal samples from 19:00 to 06:30 the next day. The filter samples were stored at $-20\,°C$ until subsequent mass weighing and chemical analysis of nitrated phenols, organic carbons, and water-soluble ions. The fine particulate matter collected was weighed with a microbalance (ME5, Sartorius, Germany) for calculation of the $PM_{2.5}$ concentration. The organic carbon concentration was determined by a thermal–optical method with the protocol of NIOSH 5040 (Sunset, OCEC analyzer, USA) and was further used to estimate the concentration of organic matter. According to the ratios of organic matter to organic carbon (OM / OC) reported in previous studies, organic matter concentrations were calculated from the organic carbon concentrations by multiplying by a factor of 1.8 at the urban Jinan site and by a factor of 2.0 at the remote sites of Yucheng and Mt. Tai as an estimation (Aiken et al., 2008; Yao et al., 2016).

2.3 Analytical method of nitrated phenols

The preparation procedure and analytical method of nitrated phenols used in this study were adopted from those developed by Kitanovski et al. (2012) and Chow et al. (2016). First, the $PM_{2.5}$ filter sample was extracted with 20 mL methanol (containing a small amount of ethylenediaminetetraacetic acid) twice for 10 min. The extracts were evaporated with a rotary evaporator to near dryness. After they were re-dissolved to about 2 mL, the extracts were filtered through a polytetrafluoroethylene syringe filter (0.45 μm; 3 mm). The sample solution was then dried with a gentle stream of nitrogen and re-dissolved to 300 μL with methanol containing 200 μg L^{-1} 2,4,6-trinitrophenol as an internal standard.

The determination of nitrated phenols was performed with an Ultimate 3000 ultra-high-performance liquid chromatography system coupled with an LCQ Fleet mass spectrometer (UHPLC-MS, Thermo Scientific, USA) and equipped with an electrospray ionization source. The nitrated phenols were separated with an Atlantis T3 C18 column (2.1 × 150 mm, 3 μm particle size, Waters, USA) with am Atlantis T3 guard column (2.1 × 10 mm, 3 μm particle size). The mobile phase contained 11 % acetonitrile in methanol (A) and 11 % acetonitrile and 0.1 % acetic acid in water (B). The proportion of elution A started at 34 % and gradually increased to 66 % within 19 min. It was then kept at 66 % for 4 min and then decreased to 34 % for the last 8 min.

The mass signals at six mass-to-charge ratios (138, 152, 154, 168, 182, and 228 amu) were monitored under the selective ion mode, and the standards of the target compounds and isomers were applied for identification. As shown in Supplement Fig. S1, nine species of nitrated phenols were identified: 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-5-nitrocatechol (3M5NC), 3-methyl-6-nitrocatechol (3M6NC), 3-nitro-salicylic acid (3NSA), and 5-nitro-salicylic acid (5NSA). With the analysis of gradient concentrations of the standard mixtures, standard curves were applied for quantification of the nine nitrated phenols.

3 Results and discussion

3.1 Temporal and spatial variations

During the sampling periods, the concentrations of nitrated phenols in $PM_{2.5}$ presented distinct seasonal and diurnal variations. As shown in Table 2, in urban Jinan, the concentrations of total nitrated phenols (ΣNPs) in the wintertime were much higher than those in the summertime. The mean concentration in the wintertime in urban Jinan reached 48.4 ng m^{-3}, about 5 times the mean concentration at this site in the summertime (9.8 ng m^{-3}). Meanwhile, the proportion of ΣNPs in $PM_{2.5}$ and the ratio of ΣNPs to organic

matter were both high in the wintertime (average, 0.28 and 1.69‰, respectively), more than 3 times those in the summertime. In addition, the diurnal pattern of nitrated phenols differed in winter and summer. During the winter campaign, both the concentration and the proportion of nitrated phenols in $PM_{2.5}$ at night largely outweighed those during the day. In the summertime, however, no significant difference was observed. The above differences in the concentration and proportion of particulate nitrated phenols with seasonal and diurnal changes were possibly associated with the emission sources, formation pathways, and with meteorological factors (e.g., solar radiation, temperature, and relative humidity).

The abundance of nitrated phenols also exhibited large variations among locations and site types. In the summertime, the concentrations of nitrated phenols in urban Jinan, rural Yucheng, rural Wangdu, and Mt. Tai were 9.8 ± 4.2, 5.7 ± 2.8, 5.9 ± 3.8, and 2.5 ± 1.6 ng m^{-3}, respectively (also shown in Table 2). The higher concentration of ΣNPs in the urban site than those measured at the rural and mountain sites indicates significant contributions from anthropogenic activities. The concentrations of particulate nitrated phenols observed in northern China in this study were comparable with those measured in northern and eastern China in previous studies and substantially higher than those found in Germany (Li et al., 2016; Teich et al., 2017).

Spatial differences were also observed in the proportions of the various species of nitrated phenols (shown in Fig. 2). For instance, nitrated phenols that are abundant in biomass burning smoke (Wang et al., 2017b), nitrocatechols and NCs, appeared in lower concentrations than the other nitrated phenols in this study. Nitrophenols and methyl-nitrophenols (NPs), however, were predominant in the measurements at the Jinan (40 %) and Wangdu sites (56 %). The domination of NPs instead of NCs in particulate nitrated phenols at the urban site indicates that a large fraction of the nitrated phenols originated from sources other than biomass burning. The strong correlations between NPs and NCs (see Table 3) suggest that they might have similar sources. At the rural and mountain sites, the proportions of nitrosalicylic acids (NSAs) were much higher than that in urban Jinan. Specifically, in Yucheng and Mt. Tai, NSAs contributed to about half of the concentration of ΣNPs. The NSAs, which contain carboxyl groups, are naturally more oxidized than the other nitrated phenols measured in this study. They exhibited lower correlation coefficients (lower than 0.6) than most other nitrated phenols (also shown in Table 3). It is notable that 5NSA does not correlate well with 3NSA (correlation coefficient, 0.57), indicating that these two components might have different origins or experience different formation processes.

Overall, obvious temporal and spatial variations were observed in the concentrations and compositions of nitrated phenols in northern China. The implied differences in the primary sources and the secondary formation pathways are analyzed in detail in the following sections.

Table 2. Average concentration levels of total particulate nitrated phenols (ΣNPs) and the proportions in $PM_{2.5}$ and fine organic matters.

Site	Season	Concentrations (ng m^{-3})			ΣNPs / $PM_{2.5}$ (‰)	ΣNPs / OM (‰)
		daytime	nighttime	average		
Jinan	winter	38.0 ± 26.3	55.8 ± 24.0	48.4 ± 25.5	0.28 ± 0.09	1.69 ± 0.64
Jinan	summer	10.3 ± 4.9	9.3 ± 3.6	9.8 ± 4.2	0.09 ± 0.04	0.41 ± 0.16
Yucheng	summer	5.2 ± 2.3	6.3 ± 3.2	5.7 ± 2.8	0.05 ± 0.02	0.23 ± 0.09
Wangdu	summer	6.0 ± 4.3	5.7 ± 3.3	5.9 ± 3.8	0.07 ± 0.04	
Mt. Tai	summer	2.8 ± 1.5	2.3 ± 1.8	2.5 ± 1.6	0.06 ± 0.09	0.17 ± 0.14

Table 3. Linear correlation coefficients (r) between individual nitrated phenols measured in $PM_{2.5}$ samples in five measurements.

|	4NP	3M4NP	2M4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA
4NP	1.00								
3M4NP	0.95	1.00							
2M4NP	0.95	0.96	1.00						
4NC	0.77	0.64	0.70	1.00					
4M5NC	0.86	0.81	0.82	0.82	1.00				
3M6NC	0.85	0.78	0.81	0.85	0.94	1.00			
3M5NC	0.85	0.79	0.80	0.92	0.90	0.90	1.00		
5NSA	0.27	0.16	0.29	0.48	0.38	0.43	0.41	1.00	
3NSA	0.58	0.57	0.61	0.52	0.58	0.63	0.57	0.53	1.00

3.2 Source apportionment

3.2.1 Source identification

To obtain a comprehensive understanding of the sources of nitrated phenols observed in northern China, the PMF receptor model (Paatero and Tapper, 1994) was applied with the measurement data from the nine nitrated phenols and from nine additional tracer species. Ninety-one sets of input data were used and the model was run 40 times to choose the optimal solution. Based on the results of the PMF model, we evaluated the solutions with four, five, and six factors. The four-factor solution did not distinguish the factor of coal combustion from those of traffic and biomass burning, failing to provide reasonably separated sources. The six-factor result, however, exhibited two factors with high levels of both SO_2 and O_3, which indicated splitting from one factor. Therefore, five major factors were finally identified and are shown in Fig. 3.

The first source factor, traffic, had the highest concentration of NO and contributed an average of 17 % of the total nitrated phenols. This source mainly comes from the heavily trafficked urban areas of Jinan and major roads near the Yucheng and Wangdu sites. The direct emission of nitrated phenols from car engines was confirmed in a laboratory study by Tremp et al. (1993), which gave an emission factor of 9 to 36 nmol L^{-1}.

The second source factor, which is featured with the highest loading of SO_2 and particulate sulfate, was identified as coal combustion, which accounted for 15 % of the ni-
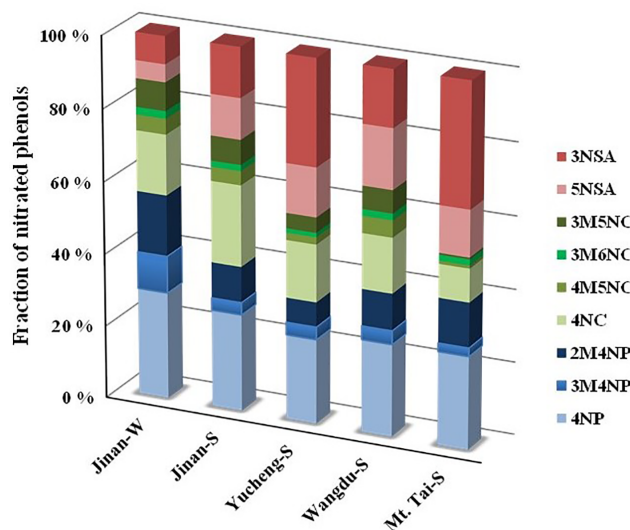
Figure 2. Fractions of individual nitrated phenols in the total particulate nitrated phenols at four sampling sites in wintertime and summertime. W represents the winter measurement and S represents the summer measurements.

trated phenol concentrations and included direct emissions from coal combustion from industrial and residential usage. Despite a lack of verification of the direct emission of nitrated phenols from coal combustion at this time, previous field studies provided evidence that coal combustion activities could be an important contributor to the observed el-
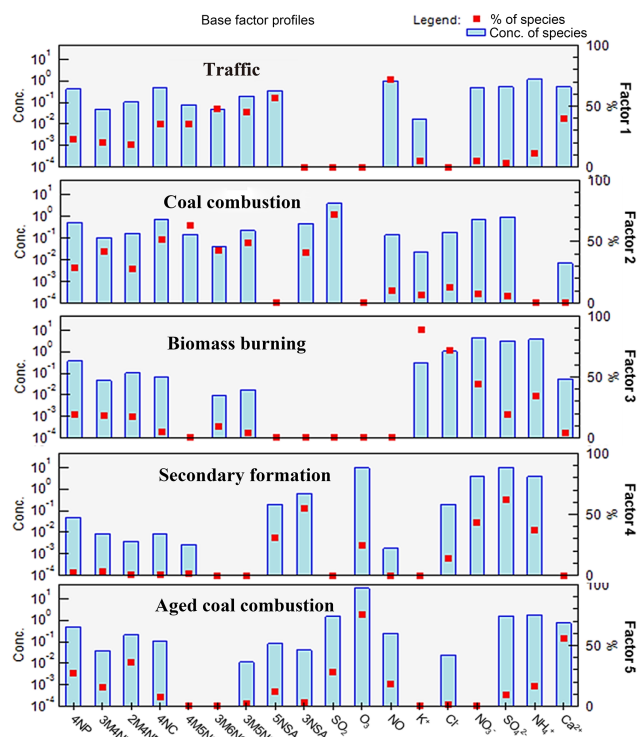
Figure 3. Source profiles of nitrated phenols and related air pollutants obtained from PMF analysis.

evated levels of particulate nitrated phenols. In field measurements at the summit of Great Dun Fell, UK, coal combustion was considered to be associated with the relatively high levels of nitrated phenols in clouds (Lüttke et al., 1997). In addition, the large proportion of nitroaromatic compounds in $PM_{2.5}$ observed in urban Cork, Ireland, was attributed to intensive anthropogenic activities including domestic solid fuel burning (peat, coal, and wood) and vehicle emissions (Kourtchev et al., 2014).

The third source factor, biomass burning, was identified with highest concentrations of potassium and chloride and high levels of particulate nitrate in $PM_{2.5}$. This source constituted 18 % of the total particulate nitrated phenols. It mainly included biomass burning in nearby farmlands and rural areas and smoke from restaurants and residential kitchens. The direct emission of nitrated phenols from biomass burning was confirmed and determined by several previous studies, with emission factors ranging from 0.4 to 11.1 mg kg^{-1} (Hoffmann et al., 2007; Iinuma et al., 2007; Wang et al., 2017b).

The fourth source factor, secondary formation, showed high concentrations of O_3 (one of the major oxidants in the troposphere) coupled with fine particulate nitrate, sulfate, and ammonium. It contributed 23 % to the concentrations of nitrated phenols. Secondary nitrated phenols were produced from precursors along with the formation of O_3 and secondary inorganic aerosols. Secondary formation was shown

to be an important source of nitrated phenols in atmosphere in recent field and modeling studies (Harrison et al., 2005b; Iinuma et al., 2010; Yuan et al., 2016).

The last source factor, aged coal combustion plume, showed relatively high levels of both SO_2 and O_3 and accounted for 27 % of the nitrated phenol concentration. This source, which was also related to coal combustion, was ascribed to the aging processes of coal combustion products. The contribution of aged coal combustion plumes to the particulate nitrated phenols requires further confirmation and evaluation via chamber simulation and field measurements.

3.2.2 Contributions of primary sources at different sites and in different seasons

Figure 4 compared the average contributions of the five source factors to the concentrations of total particulate nitrated phenols in summertime and wintertime. This clarifies the difference in the sources of particulate nitrated phenols at the four sampling sites in northern China.

Biomass burning, which, in previous studies, was usually regarded as the most important source of nitrated phenols, was identified in all five field measurements in this study. However, it was not the dominant contributor at any site, which was attributed to the very strict control measures on open biomass burning activities, comprehensive utilization of biomass, and improved biomass burning techniques in household stoves in recent years (Lin et al., 2015). As shown in Fig. 4, the average contributions of biomass burning in the summertime followed the order Jinan (21 %) > Yucheng (18 %) ≈ Wangdu (18 %) > Mt. Tai (10 %), which are comparable with the contribution of 17 % in the wintertime in Jinan.

The influence of traffic on the concentrations of particulate nitrated phenols was observed during all sampling periods and played an important role in the summertime. In particular, traffic contributed the most (27 %) in urban Jinan in the summertime, possibly because of the heavy traffic load nearby. In rural Yucheng and Wangdu, traffic contributed 12 and 20 %, respectively, mainly due to the national and high-speed roads nearby, which could be busy at nighttime with more diesel vehicles. The nitrated phenol levels at Mt. Tai were seldom affected by traffic transportation, with an average contribution of only 3 %.

Surprisingly, coal combustion emissions and its aged plumes, which received little attention in previous studies, were identified in all five field measurements and often dominated the sources of nitrated phenols. In the wintertime in urban Jinan, ∼ 55 % of the particulate nitrated phenols originated from coal combustion. This contribution was approximately 3 times that in the summertime in Jinan. Among all the species of nitrated phenols, NC and its derivations contributed most to the coal combustion factor. As shown in Fig. 5, the concentration of NCs in urban Jinan increased with high concentrations of SO_2, which originates from coal
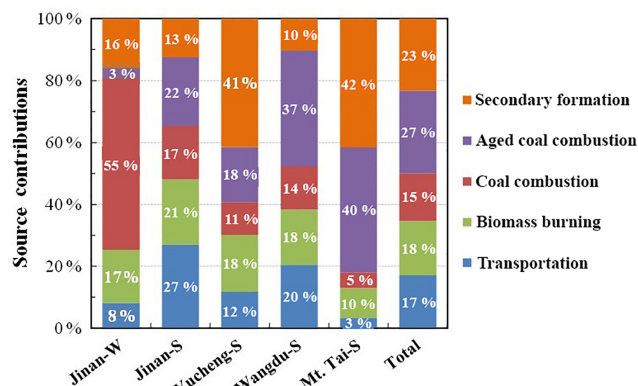
Figure 4. Contributions of the five source factors to the concentrations of particulate nitrated phenols at four sampling sites in wintertime and summertime. *Total* represents the average contributions of the five field measurements.
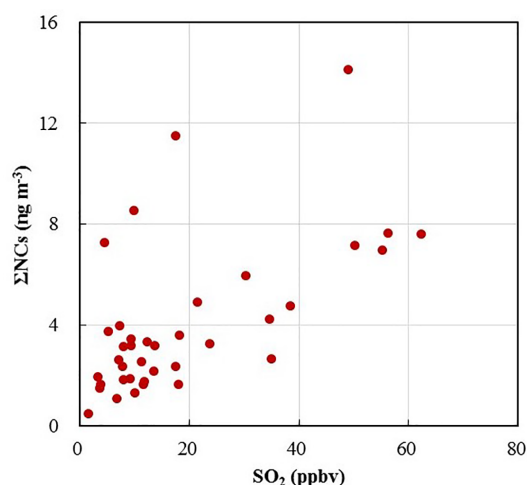

Figure 6. Scatter plot of particulate nitrated phenols with fine inorganic nitrate at the rural and mountain sites. A and B indicate daytime and nighttime samples, respectively.

Figure 5. Scatter plot of particulate nitrated phenols with SO_2 in urban Jinan.

combustion. Therefore, the large contribution of coal combustion may be the main cause of the elevated nitrated phenol concentrations in the urban areas in wintertime. The high demand of residential heating at nighttime might lead to the elevated nocturnal concentrations of nitrated phenols in $PM_{2.5}$ during winter. In addition, the contribution of aged coal combustion to nitrated phenols was more important in the summertime than in wintertime and reached 37 % in Wangdu and 40 % at Mt. Tai. The large contribution of aged coal combustion at rural sites in the summertime was likely linked to the rapid oxidation processes of gas-phase products of coal combustion from nearby industries with high atmospheric oxidation capacity in the summertime in northern China.

Though there was evidence that coal combustion served as a primary source of nitrated phenols in atmosphere (Lüttke et al., 1997; Kourtchev et al., 2014), it was not identified as a major contributor in eastern China and eastern Germany
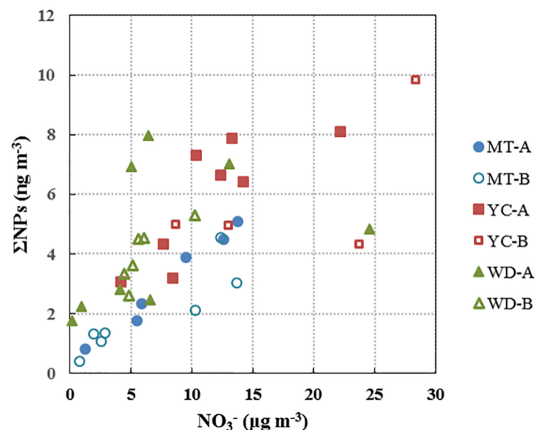
in previous studies (Li et al., 2016; Teich et al., 2017). It is probably due to the fact that coal combustion was not an important source contributor in those regions during the measurement periods. In northern China, however, as coal still serves as the dominant energy resource and the demand from residential heating increases dramatically during the winter, it is possible that significant consumption of coal resulted in elevated levels of nitrated phenols in this region. Although a series of regulations have been introduced and strict emission reduction measures have been implemented in the past decade, coal combustion remains a major source of air pollution in northern China. Therefore, pertinent strategies and control techniques on coal combustion are still needed to reduce the concentrations of nitrated phenols as well as their precursors and consequently to mitigate their effects on the climate, environment, and human health.

3.3 Secondary formation of nitrated phenols

As mentioned above, secondary formation was recognized as an important source of particulate nitrated phenols in northern China, especially in the summertime. It was identified as the dominant contributor in the field measurements in rural Yucheng (41 %) and Mt. Tai (42 %). To clarify the secondary formation of nitrated phenols and to understand the underlying chemical processes, the relationships between nitrated phenols and the related pollutants (including nitrate, NO_2, and O_3) were analyzed in detail by discarding the samples with high contributions (> 40 %) from primary emission sources (including biomass burning, traffic, and coal combustion) based on the results of the PMF model.

Fine inorganic nitrates, which are mainly produced via homogeneous and heterogeneous oxidations of NO_x, are among the most important secondary formed nitrogen-containing constitutes (Wen et al., 2015). A scatter plot of the concentrations of fine nitrates and nitrated phenols is pre-
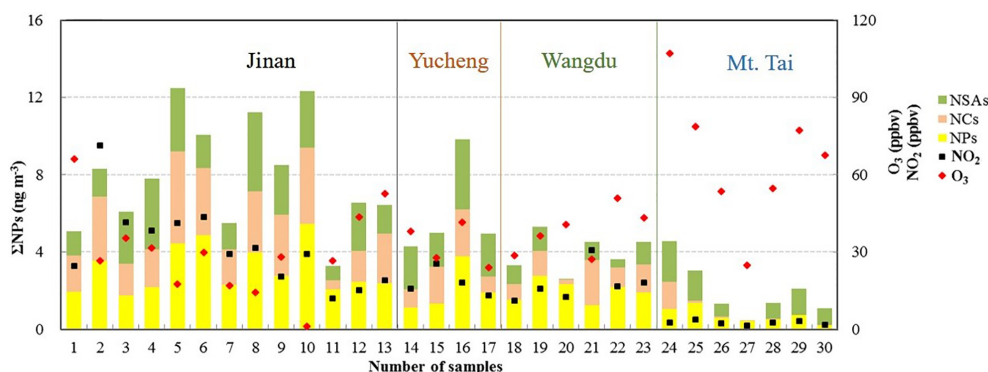
Figure 7. Time series of concentrations of three kinds of nitrated phenols in the nocturnal samples collected in the summertime and the corresponding mixing ratios of NO_2 and O_3.
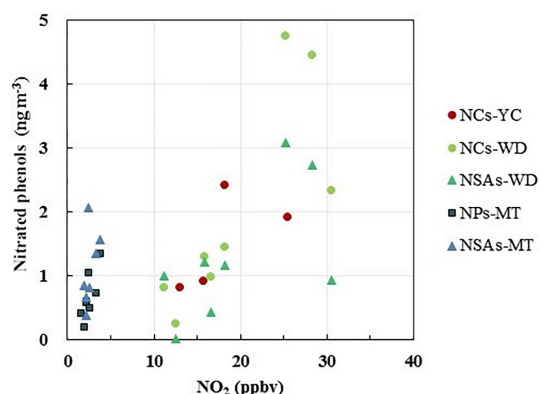

Figure 8. Scatter plot of nocturnal concentrations of nitrated phenols with NO_2. NPs-MT and NSAs-MT indicate samples collected at Mt. Tai, NCs-WD and NSAs-WD samples were collected in Wangdu and NCs-YC samples were collected in Yucheng.

sented in Fig. 6. The concentrations of nitrated phenols increased with the increasing nitrate content at the three remote sites. The good correlations and trends between them indicate that the nitrated phenols in the selected $PM_{2.5}$ samples in the rural and mountain areas of northern China in the summertime originated mainly from secondary formation rather than primary emissions.

To further understand the dominant factors that influence secondary formation of particulate nitrated phenols, we examined the variations of precursors of NO_2 and available oxidants of O_3. Figure 7 illustrates the concentrations of nitrated phenols and the averaged mixing ratio of NO_2 and O_3 at nighttime in the summer campaigns. Only data from nocturnal samples were analyzed here regarding the photolysis of nitrated phenols in the daytime. In general, higher concentrations of ΣNPs correlated with higher mixing ratio of NO_2 at all four sites in the summertime, and better correlations were found at the three remote sites than in urban Jinan. The relevance of nitrated phenols to NO_2 in the rural and mountain areas suggests that NO_2 played an important role in the

secondary formation of nitrated phenols in northern China, and that nitration of phenolic compounds was thus very likely the dominant production process. Concurrent variation of nitrated phenols with O_3 was also observed in rural Yucheng and at Mt. Tai. Nevertheless, little correlation was found between the concentration of nitrated phenols and the O_3 mixing ratio in urban Jinan and rural Wangdu, indicating that the oxidant level only acted as a limiting factor to the abundance of nitrated phenols in certain conditions. Further studies are required to obtain a reasonable explanation. However, the daytime samples exhibited no apparent relationship between nitrated phenols and NO_2 or O_3 (not shown here), due to the influence of photolysis.

Figure 7 shows that distinct differences exist in the concentrations and variations of three kinds of nitrated phenols in the five field measurements. To understand the discrepancy in the formation mechanism among them, we further inspected the correlations of the nocturnal abundances of NPs, NCs, and NSAs with the NO_2 concentrations. As shown in Fig. 8, NSAs, which increase with the mixing ratio of NO_2, showed a high correlation coefficient at the remote site of Mt. Tai, and they exhibited a moderately good correlation in rural Wangdu. The similar variation trend and strong correlation between NSAs and NO_2 at the remote sites and the high proportions of NSAs in the source factor of secondary formation are good evidence that most of the NSAs came from secondary transformation of aromatic precursors. However, only weak correlation was identified between NSAs and NO_2 in rural Yucheng (not shown here), where nitration may not be the prevailing aging process in the formation of NSAs. NCs exhibited moderately good correlations with NO_2 at the Yucheng and Wangdu sites rather than at the Mt. Tai site, indicating that the secondary produced NCs were also largely associated with anthropogenic emissions and that the formations were probably associated with emissions of precursor volatile organic compounds from combustion of biomasses and fossil fuels. Furthermore, NPs were found to have good correlation with NO_2 only at the Mt. Tai site, suggesting that

secondary formation of NPs was controlled by NO_2 in conditions of low NO_x. With consideration of the better correlations of nitrated phenols with inorganic nitrates than with NO_2, for the selected nocturnal samples mainly from secondary formation, multiphase reactions of precursors on the surfaces of and/or within particles might be the dominant formation pathways of nitrated phenols. Concurrent measurements of gas- and particle-phase nitrated phenols, aromatic precursors, oxidants, and aerosol physical and chemical properties are needed to clarify the major formation processes.

In summary, NO_2 played a major role in the formation of nitrated phenols in rural and mountainous areas in northern China. On the other hand, because of diverse sources and aging processes, the origins of the three kinds of nitrated phenols were distinguished at different types of sites. Further comprehensive field measurements on nitrated phenols, their precursors, and oxidants are required to understand the formation mechanisms in various atmospheric conditions.

4 Summary and conclusions

Nine nitrated phenols in fine particulate matters were measured in four different types of sites in northern China. Much higher concentrations of nitrated phenols were observed in the wintertime and in the urban site, indicating strong influences of anthropogenic activities. To clarify the sources of nitrated phenols in this region, the PMF receptor model was applied and five major sources were identified, including traffic, biomass burning, coal combustion, secondary formation, and aged coal combustion plume. Surprisingly, coal combustion contributed significantly to the total concentration of nitrated phenols. It was recognized as the dominant source at the urban site in the wintertime, and aged coal combustion contributed a large fraction at the rural and mountain sites in the summertime. In addition, secondary formation was the most important source of nitrated phenols in the summertime in remote areas and the majority of nitrosalicylic acids are suggested to come from secondary formation of the precursor aromatic compounds with the participation of NO_x. Further, the strong correlation between nitrated phenols and NO_2 at the rural and mountain sites suggests that the nitration process is the control process of the secondary formation.

This work highlights the crucial roles that anthropogenic sources play in the pollution levels and variation characteristics of nitrated phenols in the atmosphere in northern China. Further control measures for emissions reduction in both particulate-phase and gas-phase pollutants from coal combustion are needed to mitigate the pollution and the environmental impacts of nitrated phenols in this region. Concurrent measurements of nitrated phenols, the aromatic precursors, and oxidants are required in the future to obtain a comprehensive understanding of the formation mechanisms in various conditions.

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