

# Observations of fine particulate nitrated phenols in four sites in North China: Concentrations, source apportionment, and secondary formation

Liwei Wang<sup>1,a</sup>, Xinfeng Wang<sup>1</sup>, Rongrong Gu<sup>1</sup>, Hao Wang<sup>1</sup>, Lan Yao<sup>1</sup>, Liang Wen<sup>1</sup>, Fanping Zhu<sup>2</sup>,  
5 Weihao Wang<sup>3</sup>, Likun Xue<sup>1</sup>, Lingxiao Yang<sup>1,2</sup>, Keding Lu<sup>4</sup>, Jianmin Chen<sup>1,2,5</sup>, Tao Wang<sup>3</sup>, Yuanghang  
Zhang<sup>4</sup>, and Wenxing Wang<sup>1</sup>

<sup>1</sup>Environment Research Institute, Shandong University, Ji'nan, Shandong 250100, China

<sup>2</sup>School of Environmental Science and Engineering, Shandong University, Ji'nan, Shandong 250100,  
China

10 <sup>3</sup>Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong,  
China

<sup>4</sup>State Key Laboratory for Environment Simulation and Pollution Control, College of Environmental  
Sciences and Engineering, Peking University, Beijing 100871, China

15 <sup>5</sup>Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of  
Environmental Science and Engineering, Institute of Atmospheric Sciences, Fudan University,  
Shanghai 200433, China

<sup>a</sup> Now at Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI, 5232, Switzerland

*Correspondence to:* Xinfeng Wang (xinfengwang@sdu.edu.cn)

**Abstract.** Filter samples of fine particulate matters were collected at four sites in North China (urban,  
20 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 Ji'nan in the wintertime reached 48.4 ng m<sup>-3</sup>, and those in the summertime were 9.8,  
25 5.7, 5.9, and 2.5 ng m<sup>-3</sup> in urban Ji'nan, rural Yucheng and Wangdu, and Mt. Tai, respectively. The  
elevated concentrations of nitrated phenols in wintertime and in urban areas demonstrate the apparent  
influences from anthropogenic sources. The positive matrix factorization receptor model was then  
applied to determine the origins of particulate nitrated phenols in North China. The five major source  
factors were traffic, coal combustion, biomass burning, secondary formation, and aged coal combustion  
30 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<sub>2</sub> 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 methylnitrocatechol, are important photochemical oxidation products of gas phase precursors, which may play a part in the formation of secondary organic aerosols (SOA) (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 methylnitrocatechols could be a reasonable tracer for biomass burning events. In addition to biomass burning, other combustion activities (e.g., coal, gasoline,

etc.) 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).

5     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  $\text{NO}_x$  (NO and  $\text{NO}_2$ ) and ultraviolet rays (Nojima et al., 1975, 1976), oxidation of phenols by OH and  $\text{NO}_3$  radicals in the presence of  $\text{NO}_x$  (Atkinson et al., 1992; Bolzacchini, et al., 2001), and nitration of phenols in aqueous solutions (Lüttke  
10 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  
15 measurements that high levels of nitrated phenols in Hong Kong were associated with high concentrations of  $\text{NO}_2$ .

As an important economic and industrial center of East Asia, North China experiences severe  $\text{PM}_{2.5}$  pollution and high levels of  $\text{NO}_x$  (Wang et al., 2014; Wang et al., 2015a; Zhang et al., 2015). In recent years, several field studies related to concentrations, size distributions, and light absorption of  
20 particulate nitrated phenols have been conducted in and near the region, showing the large influences from 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 temporal and spatial differences of nine nitrated phenols in samples of  $\text{PM}_{2.5}$  collected from four different sites in North China. PMF model and correlation analysis are then applied to understand the primary sources and  
25 secondary formation of particulate nitrated phenols in this region.

## 2 Experiments and methods

### 2.1 Sampling sites and on-line instruments

PM<sub>2.5</sub> filter sampling and related online measurements were conducted in five field campaigns at four sampling sites in North China, which are illustrated in detail in Table 1. As shown, two field campaigns  
5 were conducted in urban Ji'nan 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 Ji'nan was the Atmospheric Environment Observation Station of Shandong University (AEOS-SDU) (N 36°40', E 117°03'). The urban Ji'nan site is surrounded by education, commercial, and residential districts, with several **heavily trafficked roads** nearby. Therefore,  
10 it is frequently influenced by vehicle emissions, urban plumes, and industrial plumes from suburban areas. The NO<sub>x</sub> concentration was measured by a chemiluminescence method equipped with a molybdenum oxide **converter** (Model 42C, **Thermo Electronic Corporation (TEC)**, USA). The O<sub>3</sub> concentration was analyzed with an ultraviolet absorption method (Model 49C, TEC). The SO<sub>2</sub> concentration was measured by the pulsed fluorescence method (Model 43C, TEC). Water-soluble ions,  
15 including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>, were detected with the online Monitor for AeRosols and GAses in ambient air (MARGA, ADI20801, Applikon-ECN, Netherlands). The online instruments and methods used for the winter field campaign were described in detail by Wang et al. (2015b). In the summer campaign, due to logistical issues, water-soluble ions were determined from quartz-filtered samples of PM<sub>2.5</sub> by ion chromatography (Wang et al., 2017a).

20 The second sampling site **was** located in an open field in rural Yucheng (N 36°52', E 116°34'), Dezhou, Shandong Province, about 50 km northwest from the city of Ji'nan (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<sub>x</sub> and O<sub>3</sub> were measured with Model 42C and  
25 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 (N 38°42', E 115°08'), Baoding, Hebei Province, near grasslands and gardens. **Although it was in a rural area**, it **could** be easily influenced by industrial

and urban plumes from large cities like Beijing, Tianjin, and Shijiazhuang. Trace gases of  $\text{NO}_x$  and  $\text{O}_3$  were measured with Model 42i analyzer coupled with a blue light convertor and 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).

5 The fourth sampling site was located near the summit of Mt. Tai (N 36°15', E 117°06'), Tai'an, Shandong Province. It was infrequently influenced by incense burning and restaurants from the famous tourism spots at 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 North China. Trace gases of  $\text{NO}_x$  and  $\text{O}_3$  were measured with a Model 42i analyzer coupled with a blue light  
10 converter and a Model 49i analyzer, respectively. Water-soluble ions were analyzed with the MARGA. Detailed information of this site and the deployed instruments was given by Wang et al., (2017b).

## 2.2 $\text{PM}_{2.5}$ sampling

$\text{PM}_{2.5}$  filter samples were collected using the mid-volume sampler (TH-150A, Wuhan Tianhong, China) with a flow rate of 100 liters per minute (LPM). The sampler was fixed in the open fields with the  
15  $\text{PM}_{2.5}$  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  $-20\text{ }^\circ\text{C}$  until subsequent mass weighing and chemical analysis of nitrated phenols, organic carbons, and water-soluble ions. The collected fine particulate matter was weighed with a microbalance (ME5, Sartorius, Germany) for calculation of the  $\text{PM}_{2.5}$   
20 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 OM/OC ratios 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 Ji'nan site and by a factor of 2.0 at the remote sites of Yucheng and Mt. Tai as an  
25 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<sub>2.5</sub> filter sample was extracted with 20 ml methanol (containing a small amount of EDTA) twice for 10 minutes. 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<sup>-1</sup> 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 a guard column Atlantis T3 (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 minutes and then decreased to 34% for the last 8 minutes.

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 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<sub>2.5</sub> presented distinct seasonal and diurnal variations. As shown in Table 2, in urban Ji'nan, 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 Ji'nan reached 48.4 ng m<sup>-3</sup>, about five times the mean concentration at this site in the summertime (9.8 ng m<sup>-3</sup>). Meanwhile, the proportion of ΣNPs in PM<sub>2.5</sub> and the ratio of ΣNPs to organic matter were both high in the wintertime (average, 0.28‰ and 1.69‰, respectively), more than three 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<sub>2.5</sub> 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 Ji'nan, 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<sup>-3</sup>, 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 North China in this study were comparable with those measured in North and East 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. 2017c), nitrocatechols and methylnitrocatechols (NCs), appeared in lower concentrations than the other nitrated phenols in this study. Nitrophenols and methylnitrophenols (NPs), however, were predominant in the measurements at the Ji'nan (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 Ji'nan. **Specifically**, in Yucheng and Mt. Tai, NSAs contributed about half of the concentration of  $\Sigma$ NPs. 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 North China. The implied differences in the primary sources and the secondary formation pathways are analyzed in detail in the following sections.

## 3.2 Source apportionment

### 3.2.1 Source identification

To obtain a comprehensive understanding of the sources of nitrated phenols observed in North China, the positive matrix factorization (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, which failed to provide reasonable separated sources. The six-factor result, however, exhibited two factors with high levels of both SO<sub>2</sub> and O<sub>3</sub>, 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 Ji'nan 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.

The second source factor, which is featured with the highest loading of SO<sub>2</sub> and particulate sulfate, was identified as coal combustion, which accounted for 15% of the nitrated phenol concentrations and included direct emissions from coal combustion from industries and residential usage. Despite a lack of verification on 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 elevated 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 (Lütke et al., 1997). In addition, the large proportion of nitroaromatic compounds in PM<sub>2.5</sub> 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 level of particulate nitrate in PM<sub>2.5</sub>. This source contributed 18% to 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 0.4–11.1 mg kg<sup>-1</sup> (Hoffmann et al., 2007; Iinuma et al., 2007; Wang et al., 2017c).

The fourth source factor, secondary formation, showed high concentrations of O<sub>3</sub> (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<sub>3</sub> 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<sub>2</sub> and O<sub>3</sub> 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 North 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 Ji'nan (21%) > Yucheng (18%) ≈ Wangdu (18%) > Mt. Tai (10%), which are comparable with the contribution of 17% in the wintertime in Ji'nan.

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 Ji'nan 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 Ji'nan, ~55% of the particulate nitrated phenols originated from coal combustion. This contribution was approximately three times that in the summertime in Ji'nan. 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 Ji'nan increased with high

concentrations of SO<sub>2</sub>, which originates from coal 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<sub>2.5</sub> during winter. In addition, the contribution of aged coal combustion to nitrated phenols was more important in the summertime than in wintertime and reached 5 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 North China.

10 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 East 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 North China, however, as coal still serves as the dominant energy resource and 15 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 published and strict emission reduction measures have been implemented in the past decade, coal combustion remains a major source of air pollution in North China. Therefore, pertinent strategies and control techniques against coal combustion are still needed to reduce 20 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 North China, especially in the summertime. It was identified as the dominant contributor in 25 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<sub>2</sub>, and O<sub>3</sub>) 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  $\text{NO}_x$ , are among the most important secondary formed nitrogen-containing constituents (Wen et al., 2015). Scatter plots of the concentrations of fine nitrates and nitrated phenols are presented in Fig. 6. The concentrations of nitrated phenols increased with the increasing nitrate contents at the three remote sites. The good correlations and trends between them indicate that the nitrated phenols in the selected  $\text{PM}_{2.5}$  samples in the rural and mountain areas of North 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  $\text{NO}_2$  and available oxidants of  $\text{O}_3$ . Figure 7 illustrates the concentrations of nitrated phenols and the averaged mixing ratio of  $\text{NO}_2$  and  $\text{O}_3$  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  $\Sigma\text{NPs}$  correlated with higher mixing ratio of  $\text{NO}_2$  at all four sites in the summertime, and better correlations were found at the three remote sites than in urban Ji'nan. The relevance of nitrated phenols to  $\text{NO}_2$  in the rural and mountain areas suggests that  $\text{NO}_2$  played an important role in the secondary formation of nitrated phenols in North China, and that nitration of phenolic compounds was thus the probable dominant production process. Concurrent variation of nitrated phenols with  $\text{O}_3$  was also observed in rural Yucheng and at Mt. Tai. Nevertheless, little correlation was found between the concentration of nitrated phenols and the  $\text{O}_3$  mixing ratio in urban Ji'nan 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  $\text{NO}_2$  or  $\text{O}_3$  (not shown here), due to the influence of photolysis.

Fig. 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<sub>2</sub> concentrations. As shown in Fig. 8, NSAs, which increase with the mixing ratio of NO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> only at the Mt. Tai site, suggesting that secondary formation of NPs was controlled by NO<sub>2</sub> in conditions of low NO<sub>x</sub>. With consideration of the better correlations of nitrated phenols with inorganic nitrates than with NO<sub>2</sub>, 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<sub>2</sub> played a major role in the formation of nitrated phenols in rural and mountainous areas in North 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 North China. Much higher concentrations of nitrated phenols were observed in the wintertime and in the urban site, indicating strong influences from 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<sub>x</sub>. [Further, the](#) strong correlation between nitrated phenols and NO<sub>2</sub> at the rural and mountain sites suggest that the nitration process [is the control process of the secondary formation](#).

This work highlights the crucial roles of anthropogenic sources playing in the pollution levels and variation characteristics of nitrated phenols in the atmosphere in North China. Further control measures on emission 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 on the formation mechanisms in various conditions.

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**Tables:**

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

Sampling site	Type	Altitude	Sampling time	Season
Ji'nan	Urban	~50 m	2013.11.26 - 2014.01.05	Winter
	Urban		2014.09.04 - 2014.09.21	Summer
Yucheng	Rural	~23 m	2014.06.09 - 2014.06.20	Summer
Wangdu	Rural	~14 m	2014.06.19 - 2014.06.29	Summer
Mt. Tai	Mountain	~1465 m	2014.07.27 - 2014.08.06	Summer

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

Site	Season	Concentrations (ng m <sup>-3</sup> )			$\Sigma$ NPs/ $PM_{2.5}$ (%)	$\Sigma$ NPs/OM (%)
		Daytime	Nighttime	Average		
Ji'nan	Winter	38.0±26.3	55.8±24.0	48.4±25.5	0.28±0.09	1.69±0.64
Ji'nan	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

## Figure captions:

**Figure 1.** Maps of the study region show (a) the  $\text{NO}_x$  emission intensity and (b) the four sampling sites. Squares ■ represent urban site, circles ● represent rural sites, and the triangles ▲ represent mountain site.

5 **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 measurement.

**Figure 3.** Source profiles of nitrated phenols and related air pollutants obtained from PMF analysis.

**Figure 4.** Contributions of the five source factors to the concentrations of particulate nitrated phenols at  
10 four sampling sites in wintertime and summertime. *Total* represents the average contributions of the five field measurements.

**Figure 5.** Scatter plots of particulate nitrated phenols with  $\text{SO}_2$  in urban Ji'nan.

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

15 **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  $\text{NO}_2$  and  $\text{O}_3$ .

**Figure 8.** Scatter plots of nocturnal concentrations of nitrated phenols with  $\text{NO}_2$ . 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.

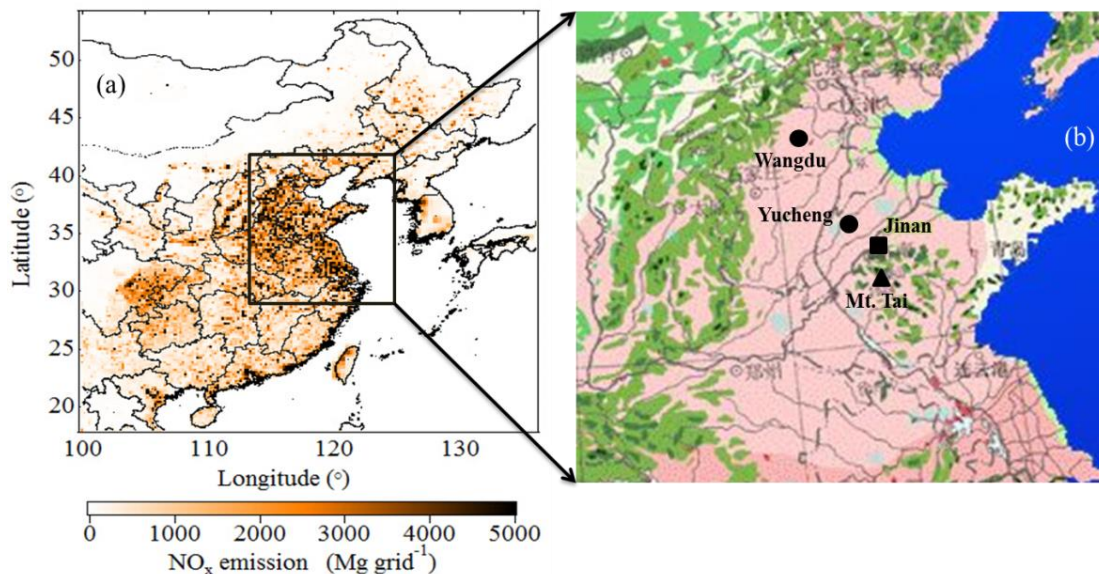
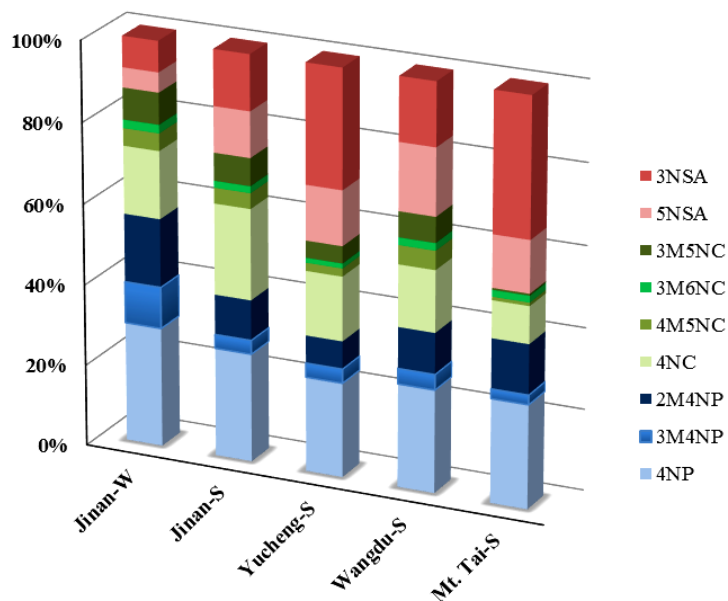


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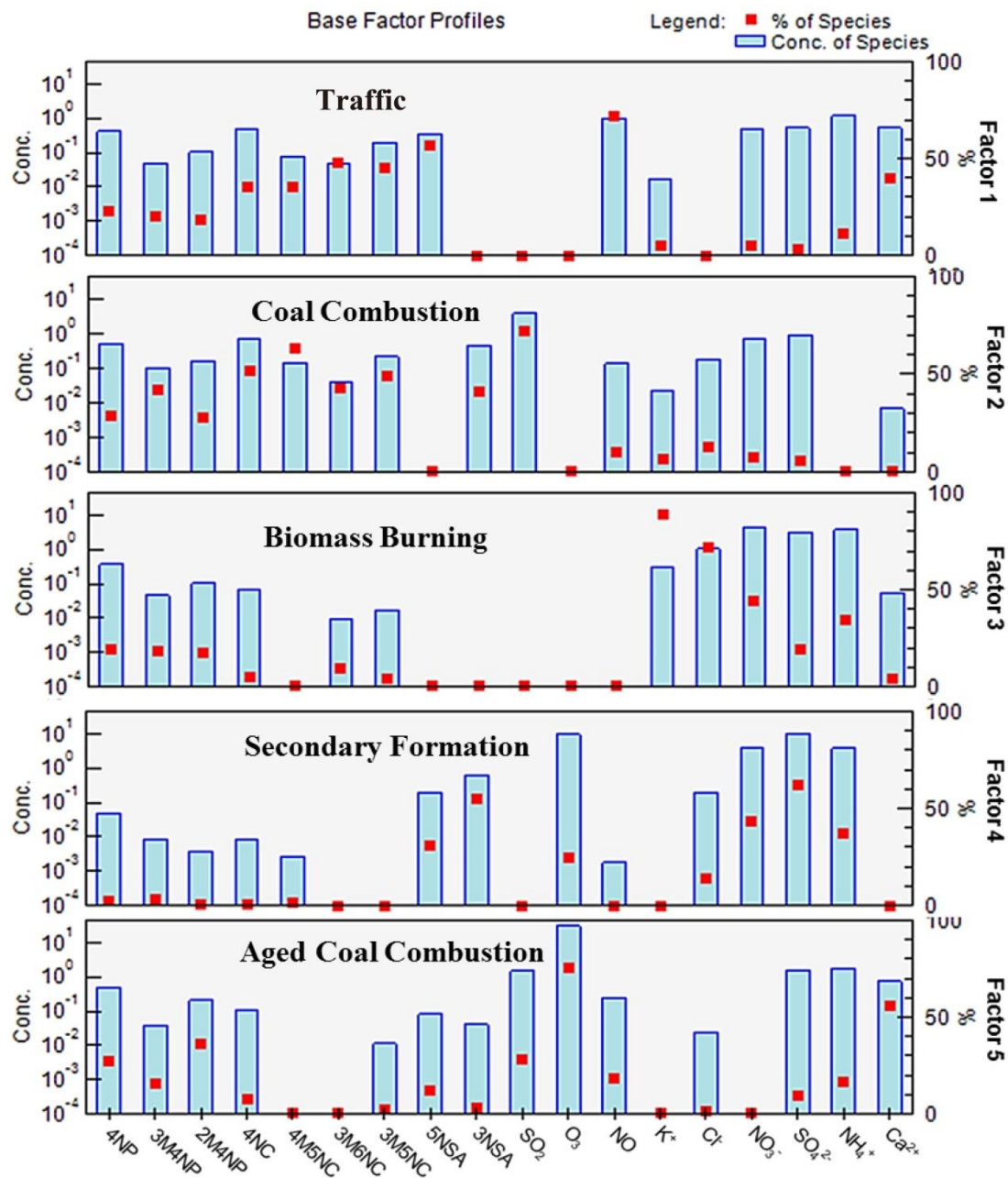


Figure 3. Source profiles of nitrated phenols and related air pollutants obtained from PMF analysis.



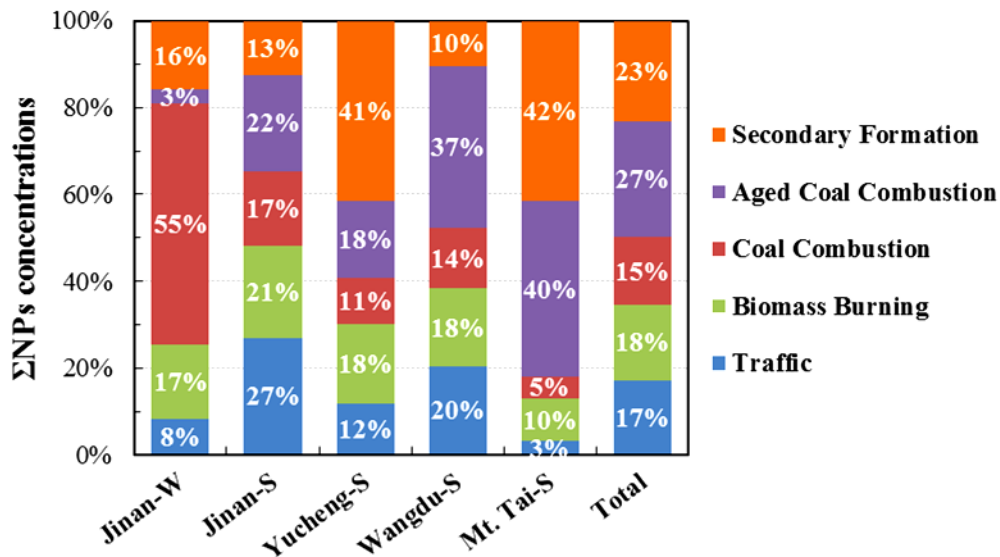
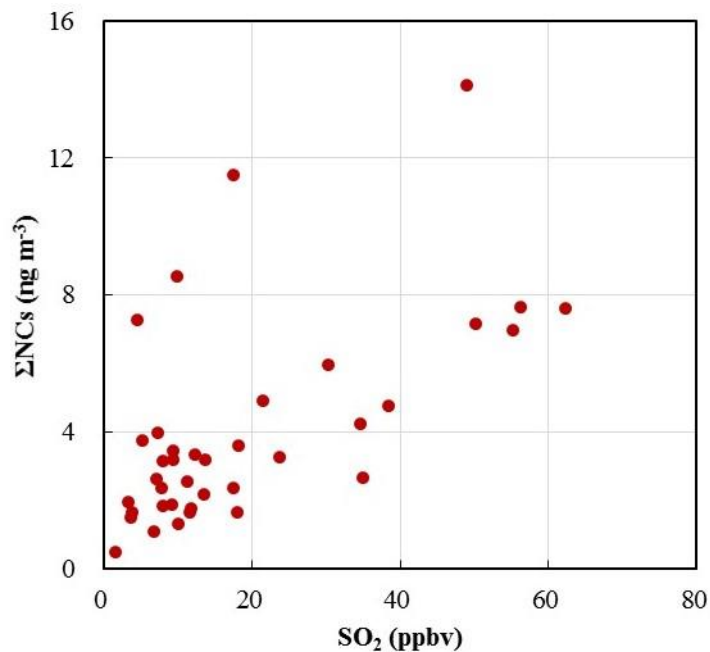


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Figure 5. Scatter plots of particulate nitrated phenols with  $\text{SO}_2$  in urban Ji'nan.

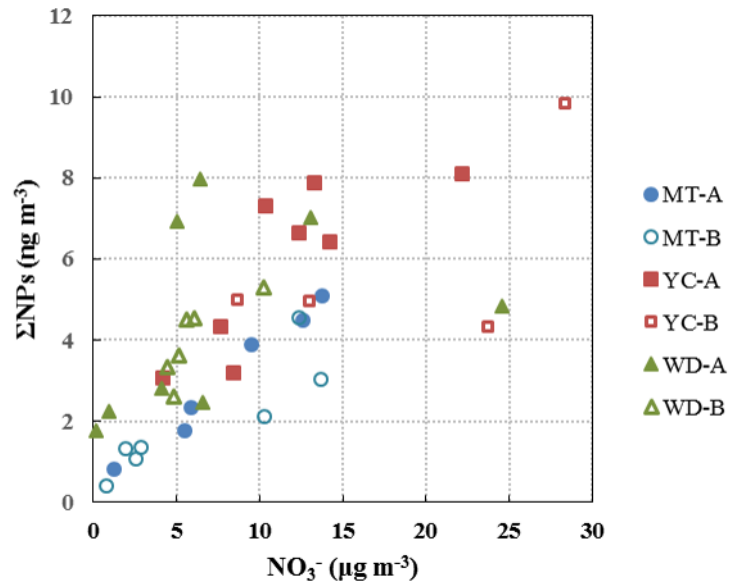
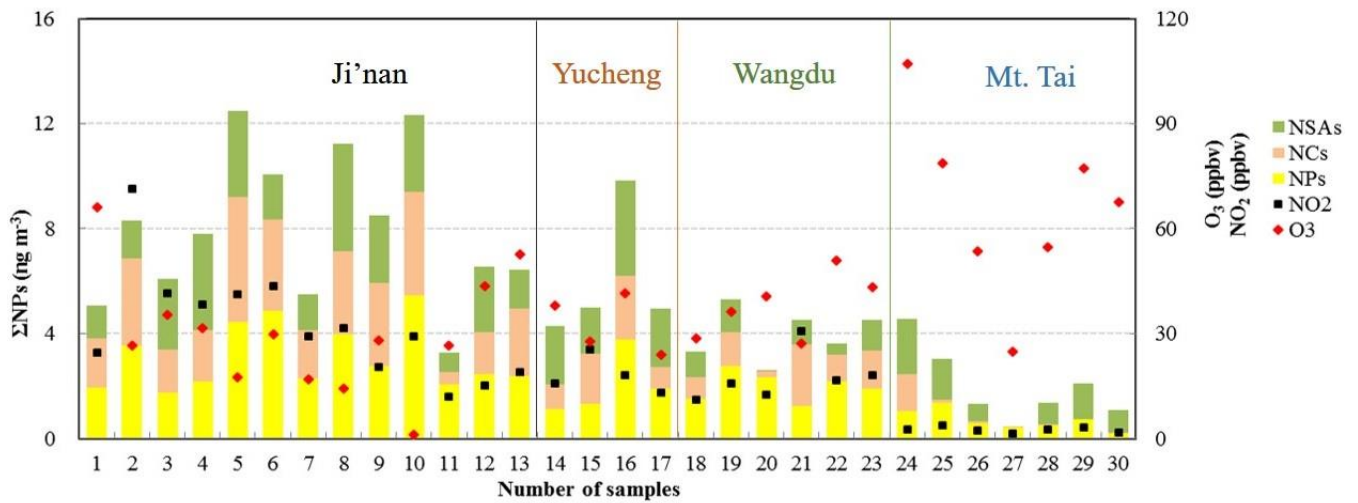
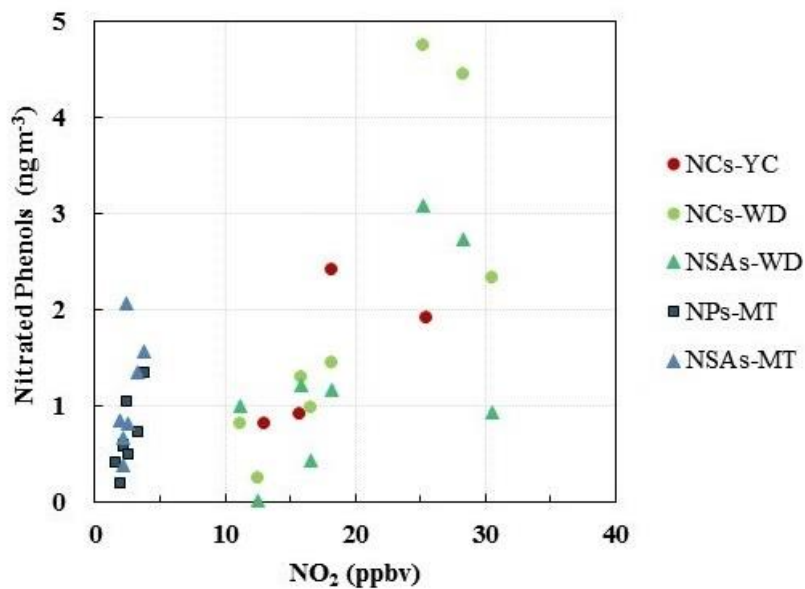


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