



Substantial emissions of nitrated aromatic compounds in the particle and gas phases in the waste gases from eight industries[☆]



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ABSTRACT

Nitrated aromatic compounds, the ubiquitous nitrogen-containing organic pollutants, impact the environment and organisms adversely. As industrial raw materials and intermediates, nitrated aromatic compounds and their aromatic precursors are widely employed in the industrial production activities. Nevertheless, their emission from industrial waste gases has so far not been studied extensively. In this study, the concentrations of 12 nitrated aromatic compounds in the particle and gas phases downwind of 16 factories encompassing eight industries (*i.e.*, pharmaceutical, weaving and dyeing, herbicide, explosive, painting, phenolic resin, paper pulp and polystyrene foam industries), were determined by ultra-high-performance liquid chromatography-mass spectrometry. Their concentrations in the particle and gas phases from different factories ranged from 114.7 ± 63.5 to 296.6 ± 62.5 ng m⁻³ and 148.7 ± 7.4 to 309.8 ± 26.2 ng m⁻³, respectively, thus, exhibiting significantly high concentrations as compared to the background sites. Among the 12 detected species, 4-nitrophenol, 5-nitrosalicylic acid, 3-nitrosalicylic acid and 4-methyl-2,6-dinitrophenol were observed to be the predominant species, with total fractions up to 47.9–72.3% and 63.1–70.3% in the particle and gas phases, respectively. Their emission profiles with respect to the industrial activities exhibited large discrepancies as compared to the combustion sources, thus, indicating different formation mechanisms. The emission ratios of particulate nitrated aromatic compounds owing to the industrial activities were estimated between 0.5 ± 0.2 and 4.3 ± 1.5 ng μg⁻¹, which were higher than or comparable to those from various combustion sources. The findings from this study confirm the industrial emission to be an important source of nitrated aromatic compounds in the atmosphere. The substantial emissions of nitrated aromatic compounds from various industries reported in this study provide the fundamental basis for further emission estimation and pollution control.

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1. Introduction

Nitrated aromatic compounds, comprising of an aromatic ring with nitro- and hydroxyl-groups, are widespread in the atmosphere (Rubio et al., 2012). As one of the major components of brown carbon, these compounds can strongly absorb in the near-UV and visible light wavelength range, thus, affecting the radiation balance, air quality and local climate (Desyaterik et al., 2013; Mohr et al., 2013; Teich et al., 2017; Zhang et al., 2011). Nitrated

aromatic compounds are also regarded as hazardous materials due to their detrimental effects on human health and plant growth. Their inhalation can cause allergies, headache and breathing difficulties, along with inducing gene mutation, chromosome aberrations, oxidative damage to DNA and cancer (Dai et al., 2020; Fernandez et al., 1992; Harrison et al., 2005; Huang et al., 1995; She et al., 2012; Wang et al., 2021; Wu et al., 2016). Nitrated aromatic compounds may also lead to the plant damage and forest decline (Rippen et al., 1987; Shafer and Schönherr, 1985). Among the major nitrated aromatic compounds, 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol have been listed as the priority toxicity pollutants by the U.S. Environmental Protection Agency (EPA, 1980).

As raw materials and intermediates, nitrated aromatic compounds and their aromatic precursors are widely utilized for the

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production of pesticides, herbicides, disinfectants, dyes, phenol-formaldehyde resins, pharmaceuticals, and explosives (Harrison et al., 2005). For instance, 4-nitrophenol is commonly used to synthesize parathion and methyl parathion, whereas 2,6-dinitrophenol is used to produce various herbicides and fungicides (Dere et al., 2007; Ju and Parales, 2010). In addition nitrated aromatic compounds, such as 2-nitrophenol, 2,4-dinitrophenol, 2,5-dinitrophenol and 2,4,6-trinitrophenol are used to synthesize dyes, chemicals, and explosives (ATSDR, 1995; ATSDR, 1992; Egerer, 1918). Nitrated aromatic compounds are also used as raw materials to synthesize various pharmaceuticals, such as paracetamol (Arora et al., 2014; Ju and Parales, 2010). Therefore, it can be envisaged that the numerous industrial activities associated with nitrated aromatic compounds serve as their potential emission sources in the environment.

Nitrated aromatic compounds in the atmosphere partly originate from the primary emission sources, including burning of biomass (Hoffmann et al., 2007; Iinuma et al., 2010; Wang et al., 2017), coal combustion (Lüttke et al., 1997; Lu et al., 2019b), and vehicle exhausts (Lu et al., 2019a; Nojima et al., 1983; Tremp et al., 1993). The secondary transformation of aromatic compounds taking place in both gas and aqueous phases in the presence of nitrogen oxides and oxidants also serves as the source of nitrated aromatic compounds (Al-Naiema et al., 2020; Harrison et al., 2005; Ikemori et al., 2019; Sato et al., 2007; Xie et al., 2017). Recently, it is speculated that nitrated aromatic compounds can enter into the atmospheric environment through industrial activities (Harrison et al., 2005). Delhomme et al. (2010) observed relatively high concentrations of phenol and 4-methyl-2-nitrophenol in the urban areas of Strasbourg (France) probably due to the local industrial activities. Industrial emissions have already been recognized as an important source of nitrated aromatic compounds in the industrial wastewater owing to their significant concentration (Liu et al., 2017; Romas et al., 2020). For instance, several nitrophenols, dinitrophenols, methyl-dinitrophenols and picric acid have been identified in the ammunition wastewater in Elsnig (Saxony, Germany), with the maximum concentration of the individual species reaching up to $540 \mu\text{g L}^{-1}$ (Preiss et al., 1997). However, the emissions of nitrated aromatic compounds from the waste gases in the process industries have not been confirmed and systematically characterized so far.

To verify and characterize nitrated aromatic compounds in the waste gases generated from the relevant industrial activities, both particle- and gas-phase samples were collected downwind of 16 factories (comprising of pharmaceutical, weaving and dyeing, herbicide, explosive, painting, phenolic resin, paper pulp and polystyrene foam factories) as well as at their background sites. Twelve species of nitrated aromatic compounds were detected and quantified by ultra-high-performance liquid chromatography-mass spectrometry (UHPLC-MS). The concentration levels, emission profiles and emission ratios (ERs) of the detected nitrated aromatic compounds in the particle and gas phases were subsequently compared. In addition, the formation mechanisms of nitrated aromatic compounds during industrial processes were discussed, along with their implication on air pollution control. To our knowledge, this is the first attempt to verify and quantify the nitrated aromatic compounds in the industrial waste gases.

2. Experimental methods

2.1. Factory selection

Based on raw materials, primary products and production processes related to nitrated aromatic compounds, industrial samples were collected from 16 large factories in Jinan (the capital of

Shandong province), Weifang (Shandong province) and Bengbu (Anhui province). The selected factories encompassed eight large industrial sectors. Among the selected factories, five were pharmaceutical factories and two each were weaving and dyeing, herbicide, explosive and painting factories. A single phenolic resin, paper pulp and polystyrene foam factory was also chosen. Detailed information about the selected factories, including locations, main products, production processes and meteorological parameters during the sampling periods, is presented in Table 1. In addition, the background sites were selected mostly in the upwind directions for the three cities for comparison. The locations of the selected factories and corresponding background sites as well as the wind rose plots with hourly values during the sampling periods are presented in Fig. 1. The wind directions and wind speeds were obtained from the Weather Underground (<http://www.wunderground.com>).

2.2. Sample collection

Due to the difficulty in accessing the factory premises to collect the samples from the chimney under normal production conditions, the downwind sampling method was selected to collect the waste gas samples. Although the downwind sampling may not enable the quantitative analyses of emissions from a single production process, however, this method can reflect the overall emissions from the factory and their influences on the ambient air quality. The downwind sampling method has been recently applied to explore the emissions of particulate matter from steel factories and a petroleum and oil refinery industrial area (Than et al., 2019; Sylvestre et al., 2017), thus, demonstrating the applicability of this method in assessing the industrial emissions.

For each of the selected factories in this study, fine particulate matter with an aerodynamic diameter less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) and semi-volatile organic compounds (SVOCs) were collected by a modified portable particle sampler (DPS, SKC, USA) in the downwind areas within a distance of 150–450 m. The sampling distances and number of sample sets are also presented in Table 1. The $\text{PM}_{2.5}$ samples were collected using the 47-mm quartz-fiber filter situated at the top of the sampler at a flow rate of 10 L min^{-1} , whereas SVOCs were enriched using the small polyurethane foam (PUF, Tisch, USA; 38 mm diameter, 80 mm length) situated at the bottom of the sampler. The sampling period for each sample lasted 3 h, and three sets of samples were collected during the time periods 10:00–13:00, 14:00–17:00 and 17:30–20:30 (Beijing time). It should be noted that the sample collection was carried out in winter, i.e., from mid-November to mid-January, and the sunset occurred before 17:30. Therefore, the samples collected in the first two time periods were classified as daytime samples, whereas the samples in the third time period were denoted as nighttime samples. $\text{PM}_{2.5}$ and SVOCs were also collected at the background sites during the same time periods with a medium-volume sampler (TH-150 A, Wuhan Tianhong, China) on the 88-mm quartz-fiber filter and in the large PUF (Tisch, USA; 65 mm diameter, 76 mm length), respectively, with a flow rate of 100 L min^{-1} . The above sample collection was performed in winter, from November 2019 to January 2020. The field blank filters and PUF were obtained with the pump in the switched off mode. Comparisons were made between the portable and medium-volume samplers, and the measured concentrations of both $\text{PM}_{2.5}$ and nitrated aromatic compounds in the particle and gas phases exhibited differences of less than 30% (Table S1). It confirmed that the data was reliable and comparable, as also indicated in the previous studies by Peters et al. (2000) and Wilson et al. (1991). According to our previous study, the proportion of the fine particulate nitrated aromatic compounds in the total suspended particles is usually higher than 89% (Liang et al., 2020). Therefore, in this study the determined

Table 1
Summary of information on the 16 factories involving in sample collection of waste gases.

Classification	Sampling factories	Locations	Main products or production process	N ^a	Temperature (°C)	Prevailing wind direction	Wind speed (m s ⁻¹)	Distance (m)
Pharmaceutical	Pharm.1	Jinan, Shandong Province	Antitumor drugs such as seratinib toluene sulfonate tablets	4	15.0 ± 2.3	SE	1.5 ± 1.0	400
	Pharm.2	Jinan, Shandong Province	Carboplatin, cisplatin, terbinaphthol, etc	4	4.6 ± 2.5	NNE	1.7 ± 0.9	300
	Pharm.3	Jinan, Shandong Province	Cefotaxime sodium, cefoperazone sodium, cefuroxime sodium, ceftriaxone sodium	4	4.7 ± 2.3	ENE	2.3 ± 1.8	250
	Pharm.4	Bengbu, Anhui Province	Paracetamol, paracetamol hydrochloride	3	2.5 ± 0.3	W/WNW	8.4 ± 1.2	200
	Pharm.5	Bengbu, Anhui Province	Paracetamol, glucuronolactone, acetylacetone	3	2.8 ± 1.1	E/N	2.1 ± 1.0	150
Weaving and dyeing	Dye.	Weifang, Shandong Province	Sulfide dyes	3	3.7 ± 4.9	S/W	1.5 ± 0.5	200
	Weave. D.	Jinan, Shandong Province	Dyeing and finishing, coating and digital printing of nylon, polyester and polyester cotton	3	13.0 ± 3.6	ENE	1.5 ± 0.4	200
Herbicide	Herbi.1	Jinan, Shandong Province	Herbicide, insecticide, fungicide, pyrimidine	5	6.3 ± 5.7	ENE	2.1 ± 0.8	250
	Herbi.2	Jinan, Shandong Province	Herbicide, insecticide	3	6.3 ± 2.1	NE	2.3 ± 1.0	300
Explosive	Explo.1	Weifang, Shandong Province	Colloidal emulsion explosive, modified ANFO explosive, expanded ammonium nitrate explosive	4	6.5 ± 5.4	S	2.7 ± 1.6	200
	Explo.2	Jinan, Shandong Province	Expanded ammonium nitrate explosive, emulsion explosive, seismic charge, ground station mixed explosive	3	4.0 ± 3.1	N/NW	1.9 ± 1.0	450
Painting	Paint. 1	Jinan, Shandong Province	Painting, processing and cutting of steel products	3	12.8 ± 3.4	SW	3.5 ± 3.5	100
	Paint. 2	Jinan, Shandong Province	Painting	3	9.3 ± 6.6	NNE	5.7 ± 1.7	100
Phenolic resin	Phenol.	Jinan, Shandong Province	Furan resin, phenolic resin, special epoxy resin, fuel ethanol, foam ceramics	4	5.7 ± 4.8	W	2.6 ± 1.7	300
Paper pulp	Paper. P.	Jinan, Shandong Province	Production of paper products	4	3.4 ± 1.9	ENE/W	3.6 ± 1.6	150
Polystyrene foam	Polys. F.	Jinan, Shandong Province	Production of polystyrene foam (EPS) sheet	4	1.5 ± 3.1	NE	1.7 ± 0.7	100

^a Number of sets of samples.

concentrations in the PM_{2.5} samples represented the particle-phase abundances. In addition, the determined concentrations in the PUF samples were regarded as the gas-phase abundances.

Before sampling, the quartz-fiber filters were heated at 600 °C for 120 min to remove the adsorbed organic pollutants. PUF was first cleaned in n-hexane for 90 min by using an orbital shaker to remove the residual non-polar compounds. After drying, it was subsequently cleaned in ultra-pure water for 90 min to remove the polar compounds, including nitrated aromatic compounds. The filters were weighed prior to and after sampling by using an electronic microbalance (ME5, Sartorius, Germany) at constant temperature and humidity (T = 20 °C, RH = 50%). After sampling, the filter and PUF samples were stored at -20 °C for subsequent chemical analysis.

2.3. Sample treatment and analysis

The organic (OC) and elemental (EC) carbon contents in the filter samples were determined using a thermal-optical carbon analyzer (Model 3, Sunset Lab, USA), which complied with the NIOSH 5040 protocol. The OC concentration was multiplied by a factor of 1.8 (f_{OM/OC}) to estimate the organic matter (OM) content in the industrial and background samples (Genga et al., 2017). Subsequently, one-half of the 88-mm filters and the rest of the 47-mm filters were cut into small pieces for determination of nitrated aromatic compounds. The organic matter on the filters was extracted with 15 mL methanol by using an ultrasonic bath for 15 min, and the extraction process was repeated thrice. The extracted solution was concentrated to approximately 1 mL by using rotary

evaporation at room temperature, followed by filtration using 0.22 μm pore-size PTFE syringe filters. The filtrate solution was blown to the near dry state with a gentle stream of high purity nitrogen, so as to avoid the potential volatilization of semi-volatile compounds. Finally, the residue was re-dissolved in 300 μL methanol, which also contained 200 ng mL⁻¹ 2,4,6-trinitrophenol as the internal standard. Likewise, the PUF samples were cut into small pieces and extracted with 55 mL methanol by using an ultrasonic bath for 45 min. The extracted solutions were concentrated to 1 mL with rotary evaporation, followed by filtration and drying using high purity nitrogen. Finally, 20 μL methanol containing 10 μg mL⁻¹ 2,4,6-trinitrophenol was added to ensure the final concentration of the internal standard in the PUF solution to be 200 ng mL⁻¹.

The concentration of nitrated aromatic compounds in the filter and PUF samples was determined by UHPLC (Ultimate 3000, Thermo Scientific, USA) coupled with a mass spectrometer (ISQ EC, Thermo Scientific, USA) processing with an electrospray ionization source. The compounds were separated by using an Atlantis T3 C18 column (2.1 mm × 150 mm, 3 μm particle size, 100 Å) at a flow rate of 0.2 mL min⁻¹. The mobile phase consisted of 11% acetonitrile in methanol (A) and 11% acetonitrile and 0.1% formic acid in ultra-pure water (B). The gradient elution program was configured as follows: initialization with 34% A; increment to 66% A within 19 min; steady at 66% A for 4 min and finally reduction to 34% A within 8 min. The details of the operational procedure can be found in our previous study (Wang et al., 2018). Twelve nitrated aromatic compounds were detected under negative mode (with selective ion mode), including 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 4-nitrocatechol

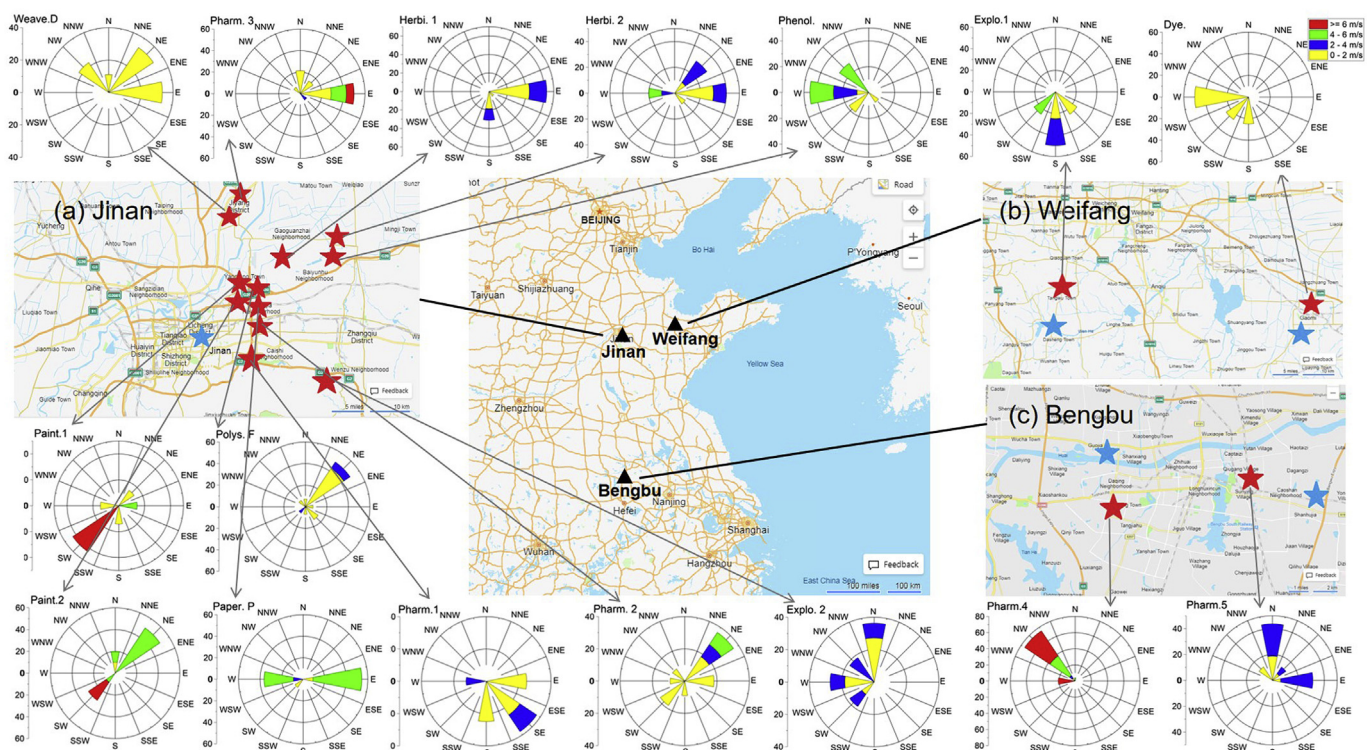


Fig. 1. The locations of the 16 factories and the background sites and the wind rose plots during sampling periods in (a) Jinan, (b) Weifang, and (c) Bengbu. The red stars represent the factories and the blue stars represent the background sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(4NC), 2,6-dimethyl-4-nitrophenol (2,6-DM-4NP), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC), 3-methyl-5-nitrocatechol (3M5NC), 5-nitrosalicylic acid (5NSA), 3-nitrosalicylic acid (3NSA), 2,4-dinitrophenol (2,4-DNP) and 4-methyl-2,6-dinitrophenol (4M-2,6-DNP). The chemicals employed in this study were purchased from Sigma-Aldrich (St. Louis, USA), Merck (Darmstadt, Germany), J&K Chemical (Beijing, China) and Atomax Chemicals (Shenzhen, China).

2.4. Quality assurance and quality control

As mentioned earlier, 12 nitrated aromatic compounds were quantified on the basis of retention time and mass signals. An internal standard and standard curves were employed to quantify the concentration of nitrated aromatic compounds in the sample solutions. Different linear standard curves, with the concentrations in the range of 0–0.2 and 0.2–2.5 $\mu\text{g mL}^{-1}$, respectively, were applied for the low and high levels of samples (Table S2). The mean recovery rates for the filter and PUF samples were determined to be 82.4% and 101.4%, respectively. Further, the concentrations of individual nitrated aromatic compounds in the field blank samples for 47-mm and 88-mm quartz-fiber filter samples lied in the ranges 0.00–9.42 and 0.00–85.51 ng mL^{-1} , respectively. On the other hand, the concentrations in the small and large PUF samples were in the ranges 0.76–7.85 and 2.11–62.47 ng mL^{-1} , respectively (Table S3). The field blank values accounted for <22.6% of the concentrations in the waste gases and ambient air for the quartz-fiber filter and <32.0% for PUF. The sampling materials (particular PUF) generally exhibited high blank values, which could be primarily attributed to the adsorption of semi-volatile compounds (such as nitrated aromatic compounds) as these materials were placed in the atmosphere of the sampling sites. The blank values were deducted in the subsequent calculations.

2.5. Calculation of ERs

In this study, the relative ERs of nitrated aromatic compounds generated from different industries were calculated from the ratios of their mass concentration in the particle and gas phases to $\text{PM}_{2.5}$, after subtracting the ambient background concentration, as shown in Equation (1). Overall, the calculation of emission ratio aims to compare the emissions of nitrated aromatic compounds from different industrial activities with other primary sources.

$$\text{ER}_i = \frac{\text{CNACs} - \text{IND}_i - \text{CNACs} - \text{BG}_i}{\text{CPM}_{2.5} - \text{IND} - \text{CPM}_{2.5} - \text{BG}} \quad (1)$$

Here, i represents particle or gas phase. For ERs of particulate nitrated aromatic compounds ($\text{ER}_{\text{particle}}$), $\text{CNACs} - \text{IND}_i$ represents their concentrations in the particle phase in the waste gases from different industries, $\text{CNACs} - \text{BG}_i$ represents their concentrations in the particle phase at the background sites, $\text{CPM}_{2.5} - \text{IND}$ denotes the $\text{PM}_{2.5}$ concentrations from different industries and $\text{CPM}_{2.5} - \text{BG}$ indicates the $\text{PM}_{2.5}$ concentrations at the background sites. Similarly, ERs of nitrated aromatic compounds in the gas phase to $\text{PM}_{2.5}$ (ER_{gas}) were also calculated on the basis of Equation (1).

3. Results and discussion

3.1. Concentrations and variation patterns

The concentrations of $\text{PM}_{2.5}$, OM and nitrated aromatic compounds in the particle and the gas phases in the gases from different factories and background sites are illustrated in Figs. 2 and 3. As can be observed, the concentrations of $\text{PM}_{2.5}$ and OM in the naturally diluted waste gases emitted from various factories ranged between 96.2 ± 10.7 and 246.5 ± 6.1 (\pm indicates standard deviation) $\mu\text{g m}^{-3}$ and between 29.9 ± 7.0 and 73.2 ± 13.5 $\mu\text{g m}^{-3}$,

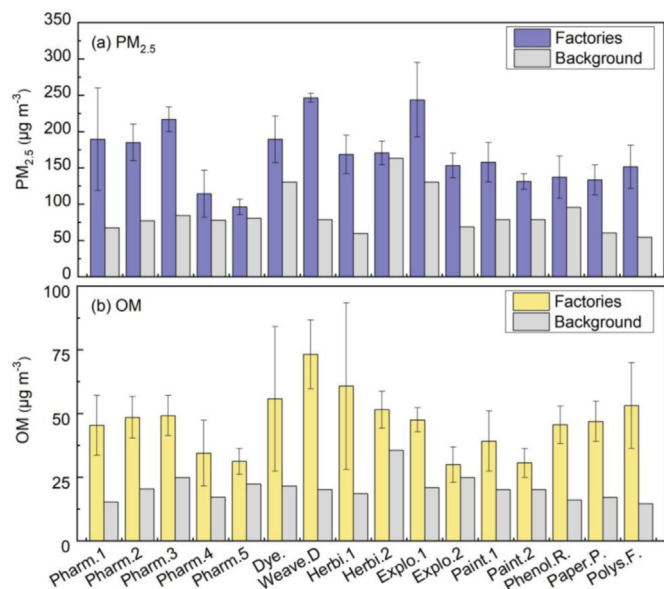


Fig. 2. Concentrations of PM_{2.5} and organic matter from different factories and background sites (units in $\mu\text{g m}^{-3}$).

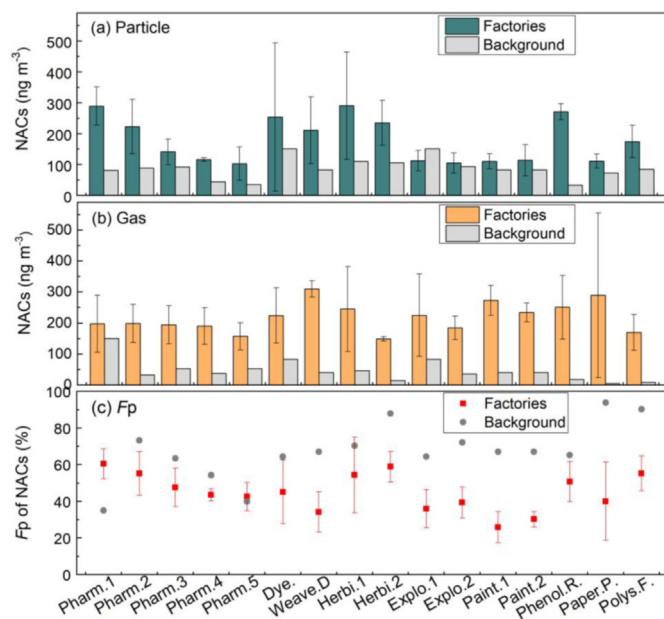


Fig. 3. Concentrations of nitrated aromatic compounds in the (a) particle phase (units in ng m^{-3}) and (b) gas phase (units in ng m^{-3}) and (c) their fraction in the particle phase from different factories and background sites (units in %).

respectively. These concentrations were observed to be substantially higher than those at the background sites (with the values for PM_{2.5} and OM in the ranges 54.8–163.3 $\mu\text{g m}^{-3}$ and 14.5–35.6 $\mu\text{g m}^{-3}$, respectively) ($p < 0.01$ for PM_{2.5} and OM, t -test; the same hereinafter). The EC concentrations in the waste gases were noted to be generally low (between 1.70 \pm 0.49 and 7.26 \pm 4.91 $\mu\text{g m}^{-3}$), with the OC/EC ratios similar to those at the background sites. It indicated that the collected waste gases were mainly emitted from industrial processes, instead of combustion processes. Further, the concentrations of nitrated aromatic compounds in the particle and gas phases in the gases emitted from various factories were determined to be in the ranges between

114.7 \pm 63.5 and 296.6 \pm 62.5 ng m^{-3} and between 148.7 \pm 7.4 and 309.8 \pm 26.2 ng m^{-3} , respectively. The observed values were significantly higher than those at the background sites (with the values for nitrated aromatic compounds in the particle and the gas phases in the ranges 33.8–151.0 ng m^{-3} and 4.8–150.8 ng m^{-3} , respectively) ($p < 0.01$). The high concentrations of nitrated aromatic compounds in the naturally diluted waste gases from various factories demonstrated that industrial activities significantly influenced their abundances in the atmosphere, thus, enhancing their concentrations in the downwind areas.

As shown in Fig. 3a and b, the total concentrations of nitrated aromatic compounds varied with the type of industry. Among the eight industries, the phenolic resin (282.0 \pm 32.3 ng m^{-3} and 250.9 \pm 102.6 ng m^{-3} for the particle and the gas phases, respectively; the same hereinafter), weaving and dyeing (between 217.7 \pm 107.7 and 262.2 \pm 241.6 ng m^{-3} and between 224.5 \pm 88.9 and 309.8 \pm 26.2 ng m^{-3}), and herbicide (between 236.2 \pm 72.3 and 295.0 \pm 164.3 ng m^{-3} and between 148.7 \pm 7.4 and 245.4 \pm 137.1 ng m^{-3}) industries were observed to yield the highest concentrations of nitrated aromatic compounds. It was followed by the paper pulp (123.6 \pm 27.4 ng m^{-3} and 289.7 \pm 266.0 ng m^{-3}), pharmaceutical (between 114.7 \pm 63.5 and 296.6 \pm 62.5 ng m^{-3} and between 157.6 \pm 43.8 and 198.5 \pm 61.5 ng m^{-3}) and painting (between 116.6 \pm 25.4 and 121.8 \pm 50.2 ng m^{-3} and between 234.1 \pm 30.1 and 273.0 \pm 48.3 ng m^{-3}) industries. Finally, the explosive (between 115.0 \pm 31.3 and 121.7 \pm 34.9 ng m^{-3} and between 184.6 \pm 38.2 and 225.1 \pm 133.2 ng m^{-3}) and polystyrene foam (182.3 \pm 43.2 ng m^{-3} and 169.8 \pm 57.6 ng m^{-3}) industries exhibited comparatively low concentrations. Even for the same type of industry, the total concentrations of nitrated aromatic compounds were noted to vary from factory to factory. The discrepancies in the concentrations of nitrated aromatic compounds for various industries and different factories belonging to the same industry type could be largely attributed to the consumption of raw and auxiliary materials, product types and outputs, mechanisms of product formation, production conditions, waste gas treatment devices and atmospheric conditions. For instance, based on the production information obtained from the factories and local environmental protection agencies, Pharm.1 and Pharm.2 consumed a higher extent of raw and auxiliary materials and yielded more products as compared to the other pharmaceutical factories, thus, leading to relatively high concentrations of the detected species in their waste gas streams. The concentration of nitrated aromatic compounds in the waste gas from Herbi.1 was higher than Herbi.2, owing to the large production volumes of herbicides and pesticides in Herbi.1 as compared with Herbi.2, thus, requiring a large amount of nitrated aromatic compounds as raw materials. The formation mechanisms of nitrated aromatic compounds in the different industries are also discussed in the later sections.

Generally, a higher fraction of nitrated aromatic compounds in the waste gases is distributed in the gas phase as compared to the ambient air. As shown in Fig. 3c, the fraction of nitrated aromatic compounds in the particle phase (Fp) in the waste gases ranged between 30.3 \pm 8.1 and 61.0 \pm 7.4%, with a mean value of 45.5 \pm 9.6% for the selected factories. The Fp value of nitrated aromatic compounds varied from industry to industry, with low values (<50%) observed for the weaving and dyeing, explosive, painting and paper pulp industries. The observed variation might be attributed to the differences in the temperature of working fluid/gas media during the production processes and waste gases released to the atmosphere. In contrast, the Fp values of nitrated aromatic compounds in the ambient air at the background sites were observed to be relatively high (ranging between 35.1 and 93.9%, with a mean value of 68.6 \pm 21.3%). For most factories (except

for two pharmaceutical factories), the F_p values in the waste gases were lower than those in the ambient air ($p < 0.01$). It indicated that nitrated aromatic compounds emitted from the industrial processes were largely enriched in the gas phase as compared with the background sites (Table S4, S5 and S6), which was attributed to the heating process during the industrial production activities.

In addition, some differences in the concentrations of nitrated aromatic compounds from industrial production processes were also observed between the daytime and nighttime samples. As shown in Fig. 4, for the weaving and dyeing and herbicide industries, the particle-phase concentrations of nitrated aromatic compounds in the nighttime samples were substantially higher than the daytime samples ($p < 0.01$). On increasing the boundary layer height after sunset, the $PM_{2.5}$ concentration in the nighttime samples exhibited a slight increase as compared to the daytime samples ($p < 0.05$). However, the increment in the concentrations of particulate nitrated aromatic compounds for the two industries (210% and 119%, respectively) was substantially higher than the observed enhancement in the $PM_{2.5}$ concentration (15.8% and 23.8%, respectively) ($p < 0.05$). It implied that the weaving and dyeing as well as herbicide factories possibly emitted more nitrated aromatic compounds at night. As depicted in Fig. 4c, the high particle-phase concentrations in the nighttime samples for the weaving and dyeing and herbicide industries as well as the high gas-phase concentrations in the daytime samples for the paper pulp industry resulted in higher F_p values at night than during the day in these three industries ($p < 0.05$). For most of other industries, including pharmaceutical, explosive, painting and phenolic resin industries, the F_p values of nitrated aromatic compounds in the daytime samples were similar to the nighttime samples.

3.2. Emission profiles of nitrated aromatic compounds from different industries

Fig. 5 depicts the fractions of various nitrated aromatic compounds in the particle and gas phases in the gas streams from different industries and background sites. Overall, the emission profiles of nitrated aromatic compounds in the waste gases emitted

from different industries were noted to be similar. In the particle phase, 4NP, 3NSA, 5NSA and 4-M-2,6-DNP were the most abundant species, with the individual fractions in the range 6.0–31.2% and aggregated fraction up to 47.9–72.3%. The fractions of 4NC, 4M5NC, 3M6NC, and 3M5NC were observed to be moderate, with the individual contributions in the range 0–15.8%. Other nitrated aromatic compounds were present in small fractions, with the individual contributions ranging from 0.7 to 9.7%. Further, the emission profiles of nitrated aromatic compounds in the gas phase were similar to those in the particle phase. 4NP, 3NSA, 5NSA and 4-M-2,6-DNP were still noted to be the predominant species, with the aggregated fraction in the range 63.1–70.3%. In contrast with the particle phase, the fractions of 4NP and 5NSA in the gas phase were observed to decrease (9.3–24.2%), while the fractions of 3NSA and 4-M-2,6-DNP increased (12.1–31.7%). Moreover, the fractions of 4M5NC, 3M6NC, and 3M5NC in the gas phase were moderate, with each species accounting for 2.8–12.3% of the total nitrated aromatic compounds. Other compounds were present in small fractions in the range 0.9–8.9%.

The fractions of nitrated aromatic compounds in the waste gases from various industries were quite different from those at the background sites. In ambient air, 2,4-DNP was the dominant species in the gas phase, whereas 4NP and 4NC were observed to be the primary species in the particle phase, which was consistent with our previous observations in urban Jinan (Li et al., 2020). However, in the waste gases from industries, 4NP, NSAs and 4-M-2,6-DNP were the most abundant species. The high fractions of 4NP and 4-M-2,6-DNP in the industrial waste gases could be attributed to the extensive use of related nitrated aromatic compounds for industrial production. The high percentage of nitrosalicylic acids in industrial waste gases can also be credited to the use of acidic solutions in production processes (Andreozzi et al., 2006). For instance, the phenolic resin industry employs acidic solvents as catalysts during production (Hirano and Asami, 2013). Further, the emission profiles of particulate nitrated aromatic compounds generated during industrial activities are different from the profiles observed for other anthropogenic emission sources, such as burning of biomass, coal combustion and vehicle exhausts. In the fine particles emitted during burning of biomass and coal

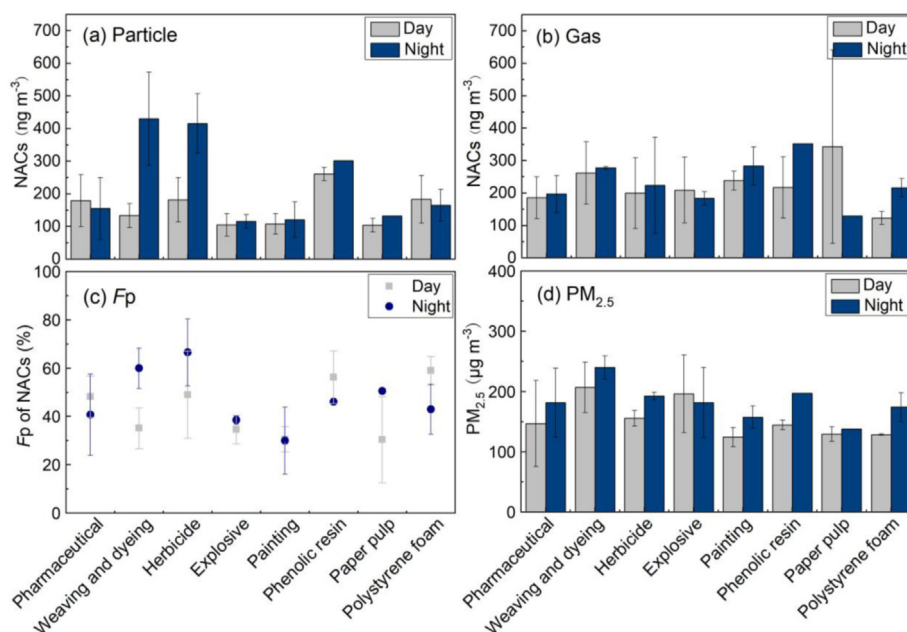


Fig. 4. Differences in the concentrations of nitrated aromatic compounds in the (a) particle phase and (b) gas phase, (c) their fractions in the particle phase, and (d) $PM_{2.5}$ concentrations in waste gases from different industrial factories.

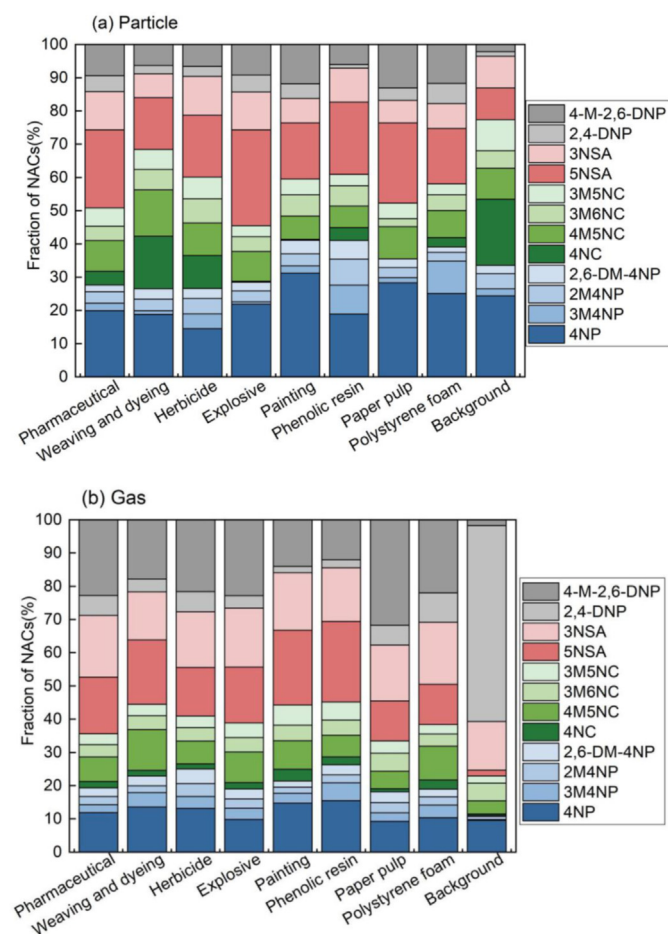


Fig. 5. Fractions of each nitrated aromatic compound in the (a) particle phase and (b) gas phase from different industries and background sites.

combustion, 4NC and methyl nitrocatechols are observed to be the prevalent nitrated aromatic compounds (Hoffmann et al., 2007; Iinuma et al., 2010; Kitanovski et al., 2012; Lu et al., 2019b; Wang et al., 2017), whereas 4NP and methyl nitrophenols account for the largest fractions in the vehicle exhausts (Lu et al., 2019a; Tremp et al., 1993). The large fractions of nitrosalicylic acids and 4-M-2,6-DNP in the waste gases from industrial sites indicate that these compounds can be emitted from primary sources. Thus, industrial emissions represent an important source of nitrosalicylic acids and 4-M-2,6-DNP in the atmosphere.

Despite the similarity in the emission profiles of nitrated aromatic compounds from different industries in both particle and gas phases, some differences in the particle phase were still observed. For pharmaceutical, herbicide, explosive and phenolic resin industries, nitrosalicylic acids were observed to be the most dominant compounds. 4NP demonstrated the largest fractions in painting, paper pulp and polystyrene foam industries. On the other hand, 4NC contributed a high fraction in weaving and dyeing industry. Such differences in the emission profiles of nitrated aromatic compounds could be related to the different formation mechanisms and reaction conditions during the production processes. Overall, the emission profiles determined in this study are beneficial for identifying the sources of nitrated aromatic compounds in industrial and urban regions.

During industrial activities, nitrated aromatic compounds are speculated to be released due to the volatilization of nitrated aromatic raw materials or reactions of aromatic raw materials with

nitrogen oxides and oxidants at high temperatures. In pharmaceutical and pesticide industries, 4NP is often used as a raw material (Arora et al., 2014; Ju and Parales, 2010). A fraction of 4NP can easily volatilize to the atmosphere, with other nitrated aromatic compounds also forming during the production processes at high temperatures. In the weaving and dyeing, herbicide, painting, phenolic resin and polystyrene foam industries, the aromatic compounds such as benzene, toluene, xylene, nitrobenzene and phenol, are commonly used as raw or auxiliary materials for industrial production (Hirano and Asami, 2013; Mamutova and Balashov, 2009; Mohammadyan and Baharfar, 2015; Teli et al., 2001; Tong et al., 2019; Zheng et al., 2013). During the baking, boiling, drying and heating processes, the aromatic compounds can readily react with nitrogen oxides and oxidants to form nitrated aromatic compounds at high-temperature conditions. In addition, in explosive and paper pulp industries, raw and auxiliary materials containing benzene ring structures (e.g., lignin, emulsifier) are used (Laftah and Rahman, 2016; Mishra et al., 2019), which can react in the presence of nitrates or nitrogen oxides in heated conditions to produce nitrated aromatic compounds. In summary, the use of aromatic raw or auxiliary materials at high temperatures possibly leads to the formation of nitrated aromatic compounds during industrial activities, thus, leading to their subsequent release to the atmospheric environment. It should be noted that nitrated aromatic compounds can also form secondarily from their precursors during the dilution and ageing processes immediately after the waste gases are emitted from the factories. However, the secondary formation after leaving the factories is limited, as the air temperature decreased rapidly, and the residence time is rather short within a distance of hundreds of meters.

3.3. Emission ratios of nitrated aromatic compounds from different industries

The relative ERs of particle-phase nitrated aromatic compounds to PM_{2.5} for different industries were calculated, as listed in Table 2. As can be observed, the ER values ranged between 0.5 ± 0.2 and $4.3 \pm 1.5 \text{ ng } \mu\text{g}^{-1}$. Among the detected species, the ERs of 4NP, nitrosalicylic acids and 4-M-2,6-DNP were the highest (between 0.05 ± 0.07 and $1.04 \pm 0.38 \text{ ng } \mu\text{g}^{-1}$), followed by methyl nitrophenols and methyl nitrocatechols (between 0 and $0.53 \pm 0.69 \text{ ng } \mu\text{g}^{-1}$). On the other hand, 4NC and 2,4-DNP (between 0 and $0.30 \pm 0.45 \text{ ng } \mu\text{g}^{-1}$) exhibited low ER values. The ERs obtained in this study can be used to further quantify the emissions of nitrated aromatics compounds in industrial waste gases. The fundamental data obtained in this study can be helpful in establishing the emission inventory of nitrated aromatic compounds, simulating the atmospheric concentrations with regional chemical models and evaluating the effects on climate and environment.

Further, ERs of particulate nitrated aromatic compounds exhibited large discrepancies among different industries. In general, the phenolic resin, herbicide and pharmaceutical industries exhibited the highest emission ratios, with the values of 4.3 ± 1.5 , 3.9 ± 4.5 and $2.8 \pm 3.4 \text{ ng } \mu\text{g}^{-1}$, respectively. The weaving and dyeing, polystyrene foam, painting and paper pulp industries demonstrated moderate ERs, with the values of 1.4 ± 1.3 , 1.3 ± 0.6 , 1.2 ± 0.6 and $1.1 \pm 0.3 \text{ ng } \mu\text{g}^{-1}$, respectively. These were followed by explosive industry with ER value of $0.5 \pm 0.2 \text{ ng } \mu\text{g}^{-1}$.

The previous studies have reported ERs of particulate aromatic compounds from different emission sources, as presented in Table 2. Generally, the emissions from the industrial sources are noted to be higher than or comparable to the combustion sources, including biomass burning ($0.01\text{--}1.08 \text{ ng } \mu\text{g}^{-1}$), coal combustion ($0.1\text{--}1.1 \text{ ng } \mu\text{g}^{-1}$) and vehicle exhausts ($0.07\text{--}1.83 \text{ ng } \mu\text{g}^{-1}$) (Lu et al., 2019a, 2019b; Wang et al., 2017). The high ERs of

Table 2

Emission ratios of nitrated aromatic compounds in the particle phase from different industries obtained in this study and those from biomass burning, coal combustion and vehicle exhaust reported in previous studies. (units in $\text{ng } \mu\text{g}^{-1}$).

Species	Pharmaceutical	Weaving and dyeing	Herbicide	Explosive	Painting	Phenolic Resin	Paper Pulp	Polystyrene Foam	Biomass burning ^a	Coal combustion ^b	Vehicle exhaust ^c
4NP	0.64 ± 1.38	0.20 ± 0.27	0.25 ± 0.20	0.07 ± 0.10	0.42 ± 0.39	0.69 ± 0.33	0.25 ± 0.05	0.26 ± 0.26	0.00–0.06	0.01–0.13	0.02–0.66
3M4NP	0.06 ± 0.07	0.05 ± 0.11	0.39 ± 0.77	0 ± 0	0.03 ± 0.06	0.40 ± 0.07	0.01 ± 0.02	0.16 ± 0.19	0.00–0.02	0.00–0.04	0.01–0.28
2M4NP	0.14 ± 0.36	0.04 ± 0.06	0.32 ± 0.55	0 ± 0	0.02 ± 0.02	0.36 ± 0.16	0.01 ± 0.02	0.01 ± 0.01	0.00–0.02	0.00–0.05	0.00–0.13
2,6-DM-4NP	0.03 ± 0.05	0.03 ± 0.05	0.12 ± 0.20	0.01 ± 0.01	0.05 ± 0.05	0.25 ± 0.11	0.02 ± 0.03	0.01 ± 0.01	–	–	0.00–0.11
4NC	0.03 ± 0.07	0.30 ± 0.45	0.22 ± 0.26	0 ± 0	0 ± 0	0.07 ± 0.11	0 ± 0	0 ± 0	0.00–0.39	0.00–0.27	0.00–0.22
4M5NC	0.20 ± 0.19	0.30 ± 0.40	0.53 ± 0.69	0 ± 0	0.05 ± 0.12	0.31 ± 0.27	0.06 ± 0.09	0.03 ± 0.06	0.00–0.19	0.00–0.24	0.00–0.05
3M6NC	0.16 ± 0.25	0.06 ± 0.12	0.25 ± 0.34	0.01 ± 0.02	0.03 ± 0.04	0.29 ± 0.12	0.02 ± 0.04	0.08 ± 0.09	0.00–0.11	0.01–0.23	0.00–0.06
3M5NC	0.10 ± 0.09	0.05 ± 0.09	0.17 ± 0.24	0 ± 0	0.03 ± 0.08	0.14 ± 0.09	0.05 ± 0.06	0.02 ± 0.02	0.00–0.32	0.00–0.22	0.00–0.07
5NSA	0.82 ± 1.02	0.27 ± 0.24	0.65 ± 0.70	0.27 ± 0.16	0.24 ± 0.13	1.04 ± 0.38	0.38 ± 0.15	0.30 ± 0.30	N.D.	0.01–0.07	0.00–0.16
3NSA	0.17 ± 0.26	0.05 ± 0.07	0.61 ± 0.83	0.05 ± 0.08	0.05 ± 0.08	0.45 ± 0.17	0.08 ± 0.06	0.10 ± 0.02	0.00–0.02	0.00–0.04	0.00–0.25
2,4-DNP	0.02 ± 0.07	0 ± 0	0.08 ± 0.09	0.02 ± 0.03	0 ± 0	0.04 ± 0.03	0.05 ± 0.02	0.12 ± 0.07	0.00–0.01	0.00–0.05	0.00–0.12
4-M-2,6-DNP	0.40 ± 0.53	0.09 ± 0.07	0.32 ± 0.65	0.08 ± 0.09	0.24 ± 0.10	0.31 ± 0.3	0.19 ± 0.06	0.24 ± 0.11	–	–	0.00–0.45
Total NACs	2.8 ± 3.4	1.4 ± 1.3	3.9 ± 4.5	0.5 ± 0.2	1.2 ± 0.6	4.3 ± 1.5	1.1 ± 0.3	1.3 ± 0.6	0.01–1.08	0.1–1.1	0.07–1.83

N.D.: not detected.

^a Wang et al. (2017).

^b Lu et al. (2019b).

^c Lu et al. (2019a).

particulate nitrated aromatic compounds from industrial activities further indicate that industrial emission is a significant source of such compounds in particulate matter in the atmosphere.

Additionally, the relative ERs of gas-phase nitrated aromatic compounds to $\text{PM}_{2.5}$ from industrial activities were noted to be rather high, ranging between 1.5 ± 0.2 and $4.8 \pm 8.8 \text{ ng } \mu\text{g}^{-1}$ (see Table S7). Further, the observed values were higher than those in the particle phase ($p < 0.05$), even for the samples collected in winter. In summer, a high fraction of nitrated aromatic compounds is expected to distribute in the gas phase, thus, enhancing the emission ratios of the gaseous compounds. Moreover, the species and industries with the highest emission ratios were observed to be similar to the particle phase. The obtained results confirm that industrial emission is a primary source of the gaseous nitrated aromatic compounds in the atmosphere. To mitigate the environmental pollution associated with nitrated aromatic compounds in industrial areas and to reduce their effect on the regional climate and air quality, it is necessary to reduce their emissions from industrial activities. The industries with relatively high emission ratios must take effective control measures based on their production processes, e.g., sealing devices, reducing the volatilization of raw materials, accelerating the cooling process, lowering the production temperature and upgrading waste gas treatment devices. Further, the governments need to formulate targeted management policies for different industries and strengthen the supervision of pollutant emissions.

4. Conclusion

The concentrations of nitrated aromatic compounds in both particle and gas phases in the naturally diluted waste gases from 16 factories are substantially higher than those at the background sites. In the waste gases, nitrated aromatic compounds are noted to largely distribute in the gas phase as compared to the ambient air, which is attributed to the relatively high temperatures used during the production processes. 4NP, NSAs and 4-M-2,6-DNP are determined to be the dominant species in the waste gases, which is obviously different with combustion sources. Further, the relative emission ratios of particulate nitrated aromatic compounds to $\text{PM}_{2.5}$ are higher than or comparable to the combustion sources, thus, confirming that industrial emission is an important source of such compounds in the atmosphere. Overall, the emission profiles

and emission ratios of nitrated aromatic compounds obtained in this study provide fundamental data for emission estimation, source identification and atmospheric pollution control.

Credit author statement

Chunying Lu: Investigation, Formal analysis, Writing-original draft. **Xinfeng Wang:** Conceptualization, Supervision, Writing-review & editing, Funding acquisition. **Jun Zhang:** Investigation. **Zhiyi Liu:** Investigation. **Yiheng Liang:** Investigation. **Shuwei Dong:** Investigation. **Min Li:** Investigation. **Jing Chen:** Investigation. **Haibiao Chen:** Investigation. **Huijun Xie:** Resources. **Likun Xue:** Resources. **Wenxing Wang:** Resources.

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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Appendix B. Supplementary data

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