Environmental Research 179 (2019) 108709

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Emissions of fine particulate nitrated phenols from various on-road vehicles in China

Chunying Lu, Xinfeng Wang*, Shuwei Dong, Jun Zhang, Juan Li, Yanan Zhao, Yiheng Liang, Likun Xue, Huijun Xie, Qingzhu Zhang, Wenxing Wang

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

ARTICLE INFO

Keywords:
Nitrated phenols
Vehicle exhaust
Emission profiles
Emission factors
Total emission

ABSTRACT:

Nitrated phenols are receiving increasing attention due to their adverse impacts on the environment and human health. Previous measurements have revealed the non-ignorable contribution of vehicle exhaust to atmospheric nitrated phenols in urban areas. However, there is a lack of comprehensive understanding of the emission characteristics and the total emission of nitrated phenols from current on-road traffic. This study investigated the emissions from eight passenger vehicles, eight trucks, and two taxis, with fuel types including diesel, gasoline, and compressed natural gas. Exhaust emissions were collected and measured using a mobile measurement system on two testing routes. Twelve nitrated phenols in the collected fine particulate matter were detected using ultrahigh performance liquid chromatography-mass spectrometry. Overall, the emission profiles of fine particulate nitrated phenols varied with vehicle load and fuel type. The 4-nitrophenol and its methyl derivatives were dominant nitrated phenol species emitted by the vehicles with proportions of 38.4%–68.0%, which is significantly different from the proportions of nitrated phenols emitted from biomass burning and coal combustion. The emission factors also exhibited large variations across vehicle type, fuel type, and emission standards, with relatively low values for gasoline vehicles and taxis fueled by compressed natural gas and high values for diesel vehicles. Based on the emission factors of nitrated phenols from different vehicles, the estimated total emission of nitrated phenols from on-road vehicles in China was 58.9 Mg (−86%–85% within 95% confidence interval), with diesel trucks contributing the most substantial fractions. This work highlights the very high level of emissions of nitrated phenols from diesel vehicles and provides an essential basis for atmospheric modeling and effective pollution control.

1. Introduction

Nitrated phenols are among the major nitrogen-containing atmospheric pollutants from anthropogenic sources and have detrimental impacts on the environment and human health. Atmospheric nitrated phenols mainly include nitrophenols and their methyl derivatives, nitrocatechols and their methyl derivatives, nitrosalicylic acid, dinitrophenols and their methyl derivatives, etc (Mohr et al., 2013; Teich et al., 2017). A large fraction of nitrated phenols in the atmosphere originate from primary anthropogenic emissions sources such as biomass burning (Chow et al., 2016; Hoffmann et al., 2007), coal combustion (Lüttke et al., 1997), vehicle exhaust (Nojima et al., 1983; Tremp et al., 1993), and the production and use of pesticides and herbicides (Shafer and Schönherr, 1985). They are also generated from secondary transformations of benzenes and phenols in the presence of nitrogen oxides and oxidants, particularly in remote areas (Harrison et al., 2005; Yuan et al., 2016). The nitrated phenols in particulate matter are regarded as important contributors to brown carbons (BrC) because of the strong absorption efficiency of near-UV light and visible light (Chen et al., 2018; Mohr et al., 2013; Teich et al., 2017; Zhang et al., 2011). Nitrated phenols are harmful to the growth and production of plants (Shafer and Schönherr, 1985) and led to forest decline in central Europe and North America in 1970s (Rippen et al., 1987). In addition, nitrated phenols have genotoxic effects on humans and animals and can cause respiratory diseases and skin disorders (Fernandez et al., 1992; Harrison et al., 2005; Huang et al., 1995; Still et al., 2005; Vo et al., 2019). The 4-nitrophenol can disturb the cardiovascular system, and the analogues may affect the reproductive functions (Li et al., 2009; Mori et al., 2003).

The direct emission of nitrated phenols from motor vehicles has been confirmed and vehicle exhaust has been identified as one of the major sources of nitrated phenols in atmospheric particulate matter in

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

https://doi.org/10.1016/j.envres.2019.108709
Received 3 July 2019; Received in revised form 25 August 2019; Accepted 27 August 2019
Available online 28 August 2019
0013-9351/

urban areas (Sjögren et al., 1995). Nitrophenols and dinitrophenols have been directly measured in the ranged of 0–13 ppbv in automobile exhaust gas (Nojima et al., 1983). Nitrophenols and methyl nitrophenols ranged from 9 to 36 nmol L^{-1} in motor exhaust gas without a regulated three-way catalytic converter (Tremp et al., 1993). In addition, measurements of nitrated phenols in particulate matters in the urban atmosphere, including in Yokohama, Japan (Nojima et al., 1983), Rome, Italy (Cecinato et al., 2005), Mainz, Germany (Zhang et al., 2010), Strasbourg, France (Delhomme et al., 2010), and Jinan, China (Wang et al., 2018), suggest the large contributions from direct vehicle emissions and the subsequent aging processes. Furthermore, even at the mountain site of Mount Brocken, Germany, a significant portion of nitrated phenols in gas and cloud samples was attributed to vehicle exhaust (Lüttke et al., 1999). Although it is well recognized that vehicle emissions are an important source of nitrated phenols in the atmosphere, there is a lack of comprehensive research that characterizes the direct emissions of nitrated phenols from the various kinds of vehicle that are currently used on the road.

To date and to the best of our knowledge, only one innovative research study by Inomata et al. (2015) has determined the emission factors of particulate nitrated phenols from vehicle exhausts. They analyzed the 4-nitrophenol in exhaust particles emitted from diesel and gasoline vehicles by using a chassis dynamometer system equipped with a constant-volume sampler followed by subsequent analysis with liquid chromatography-mass spectrometry (LC/MS). The emission factors of particulate 4-nitrophenol with and without after-treatment systems were in the range of 0.2–21 μg km^{-1} and showed that the after-treatments could significantly reduce the emissions levels. In recent years, portable emission measurement systems (PEMS) have been widely deployed to investigate the emission characteristics of various pollutants (e. g., CO, NO_x, hydrocarbons, polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons) emitted from different kinds of motor vehicles because of their ability to capture emissions under real-life operational conditions (Cao et al., 2017; Giechaskiel et al., 2018; Huang et al., 2013; Huo et al., 2012; Mahesh et al., 2018; Zheng et al., 2017). Mobile measurement systems have the necessary requirements for determining the emission characteristics and emission factors of nitrated phenols from on-road vehicles.

The number of vehicles in China increased from 2.5 million in 1995 to 185 million in 2017 with the rapid development of both the economy and society (National Bureau of Statistic of China (NBSC), 2018). These vehicles released numerous pollutants into the atmosphere and worsened air quality, particularly in urban areas. In this study, to understand the emission characteristics, emission profiles and emission factors of nitrated phenols from the exhausts of different vehicles, we designed a mobile measurement system to collect fine particulate emission samples from eight passenger vehicles, eight trucks, and two taxis under real driving conditions. We then characterized the emissions of twelve nitrated phenols using ultrahigh performance liquid chromatography-mass spectrometry (UHPLC-MS). The concentrations and the emission profiles of particulate nitrated phenols from various vehicle exhausts were then presented. The emission factors of nitrated phenols were calculated and subsequently used to estimate the total emission of nitrated phenols from various vehicles in China in 2017.

2. Methods

2.1. Choice of vehicles and on-road testing routes

In total, eighteen vehicles were recruited in this study, including eight passenger vehicles, eight trucks, and two taxis. The passenger vehicles were divided according to vehicle size and fuel type into four categories: light-duty gasoline vehicles (LDGVs), medium-duty gasoline vehicles (MDGVs), medium-duty diesel vehicles (MDDVs), and heavy-duty diesel vehicles (HDDVs). The trucks were divided into four categories: light-duty gasoline trucks (LDGTs), light-duty diesel trucks (LDDTs), medium-duty diesel trucks (MDDTs), and heavy-duty diesel trucks (HDDTs). The two taxis were fueled by compressed natural gas (CNG). The on-road tests were performed in Jinan city, the capital of Shandong province in China, where China III to China V emission standards are currently implemented for passenger vehicles and China III and China IV emission standards apply to trucks. Therefore, the test vehicles were selected to conform to the emission standards from China III to China V. The model year of the test vehicles ranged from 2010 to 2017, which generally correlated well with the odometer reading. A three-way catalytic converter was used in passenger vehicles and light-duty gasoline trucks, and a selective catalytic reduction system was used in the diesel trucks. More detailed information on the vehicles involved in this study can be found in Tables S1 and S2. The vehicles that were selected for this study are also very common in other provinces and account for a large proportion of the vehicle fleet in China (Chinese Statistical Yearbook, 2017). During sampling, the selected vehicles were operated by professional drivers who have driving licenses that corresponded to the vehicle type that they drove. Before each test, they knew the testing routes and drove the vehicles as normal in real traffic circumstances.

Two road types were selected for passenger vehicles and trucks according to the typical activity characteristics of the vehicles, which are similar in different provinces. As shown in Fig. S1 and Table S3, the testing routes included urban roads for the eight passenger vehicles, two taxis, and two light-duty trucks, and suburban roads for the two light-duty trucks, two medium-duty trucks, and two heavy-duty trucks because medium-duty trucks and heavy-duty trucks are prohibited from entering urban areas from 07:00 to 23:00. The total length of the urban route was approximately 14.9 km, starting from Shandong University (Central Campus) and then travelling along Minghu North Road, Jing'er Road, and Luoyuan Street before returning to Shandong University (Central Campus). The passenger vehicles, taxis, and light-duty trucks were operated for one or two cycles along the urban route to collect enough particulate matter for subsequent chemical analysis. The total length of the suburban route was about 19.6 km, beginning from Meihu Road and then travelling along Jingshi West Road before going back to Meihu Road. The test vehicles completed one cycle on the suburban route. The urban roads were more congested when compared to suburban roads with an average speed on the urban roads of 16.0 ± 2.7 km h^{-1} compared to 24.4 ± 3.0 km h^{-1} on the suburban roads, as shown in Table S3. The sampling periods lasted for between 47 min and 2.5 h, depending on route and traffic circumstances. The measurement results obtained in Shandong province in this study can be expected to generally reflect the emission characteristics in real-world circumstances in China.

2.2. On-road measurements and filter sampling

In this study, a mobile measurement system was designed and used to measure the emissions of pollutants from vehicle exhausts under real driving conditions, as shown in Fig. S2 (Li et al., 2019). The sampling system consisted of three major parts: an exhaust flow meter, a gaseous pollutants measurement system, and a $PM_{2.5}$ sampling system. The exhaust flow meter was used to determine the flow velocity of vehicle exhaust based on the pitot tube method at a 1-s time resolution. The diameter of the automobile exhaust pipe was measured with a caliper and then used to calculate the vehicle exhaust flow rate. An exhaust gas analyzer (Auto 5-2, UK) was used to determine the concentrations of CO, CO_2, and NO with a time resolution of 1 min. An SKC Deployable Particulate Sampler System was used to collect fine particulate matter onto a 47-mm quartz-fiber filter at a flow rate of 10 L min^{-1}. To avoid potential influences on particle collection, water vapor was removed from the exhaust by passing the gas through a hollow silica-gel drying tube (40 cm in length) before passing it through the particulate sampler. Before sampling, the quartz-fiber filters were baked in a muffle furnace at 600 °C for 2.5 h to remove any organic compounds that had

been absorbed. The weight of each sample filter was determined before and after sampling with an electronic microbalance (ME5, Sartorius, Germany) at a constant temperature and humidity to obtain the mass concentrations of $PM_{2.5}$. During both the on-road measurements and filter sampling, a GPS application was used to record the vehicle's path and the driving speeds to calculate the driving distances and average speeds of the test vehicles.

2.3. Chemical analysis of particulate samples

The collected particulate samples were pretreated before chemical analysis. First, an area of 2 cm^2 of the filter samples was cut out to determine the contents of organic carbon (OC) and elemental carbon (EC) using a thermal-optical carbon analyzer (Sunset, USA), which used the thermal-optical transmittance (TOT) method and complied with the NIOSH 5040 protocol. Then, the organic matter in the rest of the filter samples was extracted using an ultrasonic bath with 15 mL methanol for three 15-min periods. The extracts were concentrated using non-heated rotary evaporation under vacuum (> 95 mbar) to approximately 1 mL, followed by filtration with polytetrafluoroethylene (PTFE, 0.45 μm) and blowing to near dryness using a gentle stream of high-purity nitrogen. Finally, the residue was re-dissolved in 300 μL methanol containing 200 μg L^{-1} 2, 4, 6-trinitrophenol as an internal standard and the final sample solution was analyzed using UHPLC-MS.

The concentrations of nitrated phenols in vehicle exhaust particles were detected using ultrahigh performance liquid chromatography-mass spectrometry (UHPLC-MS, Thermo Scientific). The separation of nitrated phenols was performed by using an Atlantis T3 C18 column (100 Å, 3 μm particle size, 2.1 mm × 150 mm) with an Atlantis T3 guard column (3 μm particle size, 2.1 mm ×10 mm). The column temperature was 30 °C and the injection volume was 10 μL. The mobile phases were (A) methanol containing 11% acetonitrile and (B) water containing 11% acetonitrile and 0.1% formic acid. The mobile phases started with 34% A, increased linearly to 66% A within 19 min, then held at 66% A for 4 min, and finally returned to 34% A for 8 min. More detailed information on the sample pretreatment and the analysis of nitrated phenols can be found in our previous studies (Wang et al., 2018). The mass signals of 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 4-nitrocatechol (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) were monitored in negative polarity mode by using the selective ion monitoring (SIM) mode. The chemicals used in this study were ordered from Sigma-Aldrich (St. Louis, MO, USA), J&K Chemical (Beijing, China), and Atomax Chemicals (Shenzhen, China). Internal standards and standard curves were used to quantify the concentrations of the twelve target nitrated phenols.

2.4. Calculations of emission factors and total emissions

The emission factors of nitrated phenols were calculated according to the nitrated phenols species (i) and vehicle type (j) on the basis of the testing distances, as illustrated in Eq (1).

$$EF_{i,j} = \frac{C_{i,j} \times V_j \times S_j \times T_{i,j}}{D_j} \quad (1)$$

Here, $EF_{i,j}$ is the distance-based emission factor of the nitrated phenols species i for the vehicle type j in μg km^{-1}; $C_{i,j}$ is the concentration of particulate nitrated phenols species i in the exhaust for vehicle type j in μg m^{-3}; V_j is the average exhaust velocity for vehicle type j in m s^{-1}; S_j is the cross-sectional area of exhaust pipe for vehicle type j in m^2; $T_{i,j}$ is the sampling time of nitrated phenols species i for vehicle type j in s^{-1}; D_j is the effective testing distance for vehicle type j in km.

The $EF_{i,j}$ of nitrated phenols and the vehicle kilometers travelled (VKT) were used to calculate the amount of emission of nitrated phenols from different types of vehicle in China, as shown in Eq (2).

$$\text{Emission} = \sum_{i,j,k,m} EF_{i,j} \times VKT_{j,k} \times P_{j,k} \times R_{j,m} \quad (2)$$

In Eq (2), the Emission is the total estimated emission of particulate nitrated phenols in China; $VKT_{j,k}$ is the average annual VKT for vehicle type j in province k in km yr^{-1}; $P_{j,k}$ is the populations of vehicle type j in province k; $R_{j,m}$ is the ratio of different fuel types m for vehicle type j (m includes gasoline, diesel, and alternative fuels).

In this study, the amounts of emissions of fine particulate nitrated phenols from different vehicles in 28 provinces in China in 2017 were estimated based on the measured emission factors, the numbers of different kinds of vehicles, the percentages of different vehicles with different fuels, and the average annual VKT for different vehicles. The total number of vehicles in each province was acquired from the Chinese Statistical Yearbook and ranged from 374,800 to 17,233,400. Fuel types were mainly gasoline and diesel, and the proportions of alternative fuels (e.g., CNG) for vehicles were not taken into consideration because the shares are relatively low in China and there are no available data. Specifically, light-duty passenger vehicles use gasoline, while the heavy-duty passenger vehicles, medium-duty trucks and heavy-duty trucks use diesel. Gasoline was reportedly used by 56.5% of medium-duty passenger vehicles and 41.5% of light-duty trucks, and the others used diesel (Liu et al., 2017). The China III and China IV emission standards were the dominant standards implemented in vehicles in 2015 (Liu et al., 2017). Therefore, the average VKTs for vehicles with China IV emission standard were used in this study. The annual VKTs for LDGTs, LDDTs, MDDTs, HDDTs, MDGVs, MDDVs, and HDDVs for all provinces were adopted as 34,165, 45,237, 60,308, 98,206, 31,300, 31,300 and 58,000 km yr^{-1} (Liu et al., 2017; Wu et al., 2016). Province-specific values of average VKT for LDGVs were applied, ranging from 13,169 to 25,460 km yr^{-1} (Liu et al., 2017).

2.5. Uncertainty analysis

The uncertainty of the estimated emissions of nitrated phenols in this study mainly came from three sources: emission factors, vehicle kilometers travelled, and the number of vehicles. The uncertainty of the total emission of fine particulate nitrated phenols was quantified using Monte Carlo simulation based on the coefficients of variation (CV) of the above three factors. The CVs of the emission factors for different vehicles were calculated using the on-road measurements. The VKTs for different vehicles followed a normal distribution, with a CV of 10%, as reported by previous studies (Kioutsioukis et al., 2004). The total number of vehicles of each type in different provinces was assumed to have a normal distribution, with a CV of 5% (Zhao et al., 2011). Average values and ranges were used to quantify the uncertainty of the total emissions of nitrated phenols.

3. Results and discussion

3.1. Concentrations and compositions of nitrated phenols

In general, the concentrations of fine particulate nitrated phenols in freshly emitted vehicle exhausts varied significantly with species and fuel type. Table 1 and Table S4 show the concentrations of fine particulate nitrated phenols, $PM_{2.5}$, and gaseous pollutants (CO_2, CO and NO) in the on-road vehicle exhausts. The total concentrations of the twelve nitrated phenols varied from 0.17 to 10.73 μg m^{-3} and the concentrations of individual nitrated phenols ranged from zero to 2.11 μg m^{-3}. Among the twelve detected nitrated phenols, 4NP, 3M4NP, 2M4NP, 4M5NC, 5NSA, and 2, 4-DNP were found in all of the vehicle exhaust samples, while other species were only identified in a

Table 1
Concentrations of nitrated phenols, $PM_{2.5}$, CO_2, CO, and NO from vehicle emissions (in μg m^{-3} for nitrated phenols, mg m^{-3} for $PM_{2.5}$, % for CO_2 and CO, and in ppm for NO).

Types	Taxis	LDGVs	MDGVs	LDGTs	MDDVs	HDDVs	LDDTs	MDDTs	HDDTs
4NP	0.05	0.04	0.05	0.10	1.45	1.18	1.38	2.11	0.67
3M4NP	0.02	0.01	0.01	0.02	0.72	0.23	0.45	0.85	0.52
2M4NP	0.01	0.01	0.01	0.02	0.33	0.11	0.31	0.59	0.24
2, 6-DM-4NP	0.01	0.01	0.00	0.00	0.11	0.03	0.49	0.89	0.22
4NC	0.01	0.01	0.00	0.00	0.57	0.20	0.79	1.98	0.06
4M5NC	0.01	0.01	0.01	0.01	0.30	0.08	0.33	0.58	0.22
3M6NC	0.01	0.01	0.00	0.00	0.09	0.05	0.19	0.31	0.04
3M5NC	0.01	0.01	0.00	0.00	0.10	0.02	0.43	0.77	0.20
5NSA	0.01	0.01	0.02	0.02	0.42	0.09	0.17	0.39	0.16
3NSA	0.00	0.01	0.01	0.00	0.64	0.09	0.28	0.61	0.15
2, 4-DNP	0.02	0.05	0.05	0.04	0.07	0.18	0.11	0.21	0.04
4M-2, 6-DNP	0.01	0.01	0.01	0.01	0.00	0.04	0.60	1.44	1.38
ΣNPs	0.17	0.17	0.18	0.23	4.79	2.30	5.52	10.73	3.91
$PM_{2.5}$	0.35	0.42	2.41	1.13	2.62	1.68	29.93	87.69	2.91
CO_2	4.16	7.06	10.04	5.60	2.16	3.18	2.18	2.33	2.90
CO	0.06	0.04	0.13	0.25	0.03	0.03	0.03	0.03	0.03
NO	137.67	2.88	2.68	153.34	153.53	377.67	323.29	350.52	457.76

portion of the samples. The concentration of nitrated phenols for taxis and gasoline vehicles (i.e., LDGVs, MDGVs, and LDGTs, ranging from 0.17 to 0.23 μg m^{-3}) were much lower than those for diesel vehicles (i.e., MDDVs, HDDVs, LDDTs, MDDTs, and HDDTs, in the range of 2.30–10.73 μg m^{-3}). For $PM_{2.5}$, CO_2, CO, and NO, the emission concentrations for all types of vehicle exhausts were within the ranges of 0.35–87.69 mg m^{-3}, 2.16–10.04%, 0.03–0.25%, and 2.68–457.76 ppm, respectively.

To understand the differences in the composition of nitrated phenols in the emitted $PM_{2.5}$, we compared the proportions of individual nitrated phenols from different vehicles (see Fig. 1). The twelve nitrated phenols that were detected were grouped into four categories: 4NP and MNPs (3M4NP, 2M4NP, and 2, 6-DM-4NP), 4NC and MNCs (4M5NC, 3M6NC and 3M5NC), NSAs (5NSA and 3NSA), and DNP and MDNP (2, 4-DNP and 4M-2, 6-DNP). As shown in Fig. 1, the fractions of different nitrated phenols also varied with vehicle type and fuel type. Among all the 12 species, 4NP and MNPs were dominant in most cases, with the contribution ranging from 38.4% to 68.0%. Specifically, 4NP accounted for the largest proportion (17.0%–48.9%). The percentage of 4NP increased with load capacity for passenger vehicles, but decreased with load capacity for diesel trucks (i.e., LDDTs, MDDTs, and HDDTs). The fraction of MNPs was comparable for different vehicles (17.9%–28.2%). As for DNP and MDNP, 2, 4-DNP accounted for a higher fraction in taxis and gasoline vehicles (13.3%–26.6%) than in diesel vehicles (1.5%–9.3%), while the proportion of 4M-2, 6-DNP was large for diesel trucks (particularly HDDTs, with a proportion of 39.1%). Therefore, DNP and MDNP may be good trace species for gasoline vehicles and diesel trucks, respectively, due to their remarkable variations in different vehicles. In addition, the proportion of 4NC and MNCs was higher for diesel vehicles and taxis (12.1%–37.8%) than gasoline vehicles (5.1%–15.3%). The fraction of NSAs was highest for medium-duty diesel trucks (22.1%), with relatively consistent values in other types of vehicle (5.7%–13.9%). These results indicate that vehicle type, fuel type, and load capacity significantly influence the formation mechanism of nitrated phenols in vehicle exhaust.

The predominance of 4NP and MNPs in the vehicle exhausts that were sampled in this study is in accordance with previous studies. For examples, 4-nitrophenol, 2-nitrophenol and MNPs were the most prevalent species in motor exhausts under different operating conditions (Tremp et al., 1993) and 4-nitrophenol may be the predominant nitroaromatic compound in diesel emission particles (Inomata et al., 2015). Furthermore, the proportions of individual nitrated phenols in fine particulate matter from vehicle exhausts were distinctly dissimilar to those from biomass burning and coal combustion, in which 4NC and MNCs are the most common species (Lu et al., 2019; Wang et al., 2017).

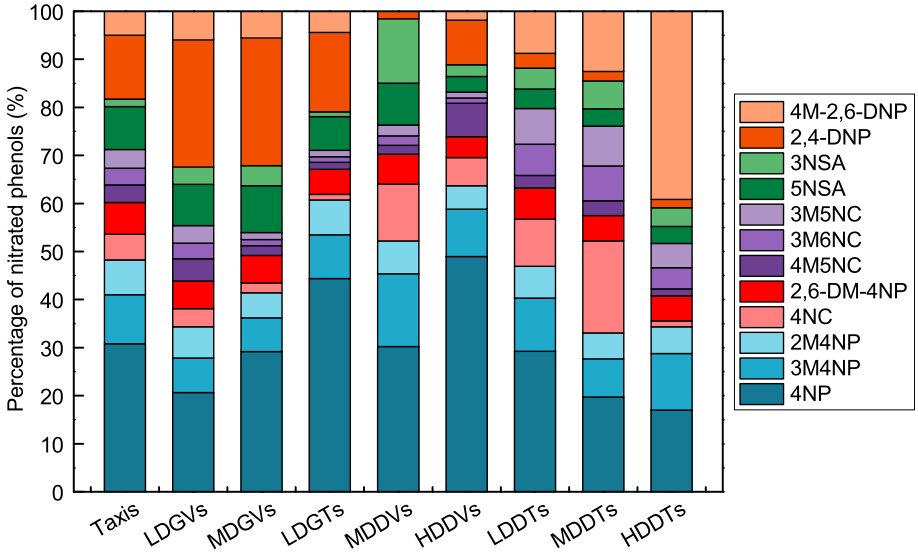

Fig. 1. Emissions fractions of nitrated phenols from vehicle emissions.

Table 2
Emission ratios of NPs/$PM_{2.5}$ from vehicle emissions (in μg mg^{-1}).

Types	4NP	3M4NP	2M4NP	2, 6-DM-4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA	2, 4-DNP	4M-2, 6-DNP	ΣNPs
Taxis	0.15	0.05	0.04	0.03	0.02	0.02	0.02	0.02	0.04	0.01	0.07	0.02	0.48
LDGVs	0.09	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.04	0.02	0.12	0.03	0.44
MDGVs	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.00	0.07
LDGTs	0.35	0.03	0.02	0.02	0.01	0.01	0.01	0.01	0.03	0.01	0.07	0.02	0.56
MDDVs	0.55	0.28	0.13	0.11	0.22	0.03	0.04	0.04	0.16	0.25	0.03	0.00	1.83
HDDVs	0.66	0.14	0.06	0.05	0.10	0.05	0.01	0.01	0.05	0.04	0.10	0.02	1.31
LDDTs	0.07	0.03	0.01	0.01	0.02	0.00	0.01	0.02	0.01	0.01	0.01	0.02	0.21
MDDTs	0.03	0.01	0.01	0.01	0.03	0.00	0.01	0.01	0.00	0.01	0.00	0.02	0.14
HDDTs	0.21	0.16	0.07	0.07	0.02	0.01	0.06	0.07	0.05	0.05	0.02	0.45	1.24

3.2. Emission factors of nitrated phenols

The emission ratios of fine particulate nitrated phenols to $PM_{2.5}$ ($ER_{NPs/PM2.5}$) from different vehicle exhausts were obtained according to their mass concentrations (as shown in Table 2). Overall, the $ER_{NPs/PM2.5}$ exhibited large discrepancies among fuel type and vehicle type, with the total ratios in the range of 0.07–1.83 μg mg^{-1} and individual ratios in the level of 0–0.66 μg mg^{-1}. The ranking of the total $ER_{NPs/PM2.5}$ from high to low was as follows: diesel passenger vehicles (1.31–1.83 μg mg^{-1}), diesel trucks (0.14–1.24 μg mg^{-1}), and taxis and gasoline vehicles (0.07–0.56 μg mg^{-1}). Interestingly, the medium-duty diesel passenger vehicle (MDDV) exhibited the highest value of $ER_{NPs/PM2.5}$ (1.83 μg mg^{-1}) while the medium-duty gasoline passenger vehicle (MDGV) showed the lowest value (0.07 μg mg^{-1}). This phenomenon is not a coincidence because unlike MDDV, MDGV is fueled by gasoline, with stricter emission standard and lower waste, as indicated by the vehicle's driving range.

The emission ratios of nitrated phenols to organic matter (OM, estimated based on the OC concentration multiplied by a factor of 1.25) ($ER_{NPs/OM}$) were also calculated and are shown in Table 3 (Aiken et al., 2008). The $ER_{NPs/OM}$ for different vehicle exhausts ranged from 0.20 to 7.31 μg mg^{-1}, also varying with fuel type and vehicle type. Similar to the $ER_{NPs/PM2.5}$, the highest $ER_{NPs/OM}$ appeared in diesel passenger vehicles (4.70–5.85 μg mg^{-1}), the ratios for taxis and gasoline vehicles were moderate (0.75–2.27 μg mg^{-1}), and the values for diesel trucks were lowest (0.16–1.56 μg mg^{-1}). The $ER_{NPs/OM}$ from the exhausts of various vehicles is not only affected by fuel types, but also influenced by emission standards and after-treatment techniques.

The emission factors of fine particulate nitrated phenols from the exhausts of taxis, passenger vehicles and trucks were calculated based on the measured concentrations of nitrated phenols, total exhaust volumes and driving ranges. As shown in Fig. 2, the average emission factors of nitrated phenols were 0.68, 1.18, 0.87, 46.35, and 52.92 μg km^{-1} for taxis, LDGVs, MDGVs, MDDVs, and HDDVs, respectively, and 0.77, 57.15, 89.61, and 47.38 μg km^{-1} for LDGTs, LDDTs, MDDTs, and HDDTs, respectively. Overall, the emission factors for nitrated phenols varied significantly across fuel types, with higher values for diesel vehicles and lower values for gasoline and CNG vehicles (i. e., taxis). Furthermore, the EF_{NPs} increased with the vehicle load for both passenger vehicles and trucks. The emission standard, after-treatment technique, displacement, driving range, engine type, and road condition also influenced the emission factors for nitrated phenols. The emission factors for nitrated phenols in diesel trucks, diesel passenger vehicles, and gasoline passenger vehicles with different emission standards are displayed in Fig. 3. The EF_{NPs} decreased by 58.6% and 12.4% for diesel trucks and diesel passenger vehicles, respectively, when the emission standard changed from China III to China IV. For gasoline passenger vehicles, the value decreased by 56.5% when the emission standard improved from China IV to China V. Therefore, the improvement of emission standards effectively reduced the emissions of nitrated phenols from the exhausts of vehicles through the upgrade of the vehicle engine and after-treatment technique.

The emission factors of individual nitrated phenols emitted from vehicle exhausts are listed in Table 4. Overall, the individual EF_{NPs} for taxis and gasoline vehicles (0.01–0.36 μg km^{-1}) were much lower than those for diesel vehicles (0–26.69 μg km^{-1}). For taxis and gasoline vehicles, 4NP had the largest values (0.21–0.36 μg km^{-1}), followed by 2, 4-DNP (0.09–0.35 μg km^{-1}), and other species had relatively lower values (0.01–0.10 μg km^{-1}). For diesel vehicles, 4NP and MNPs had the highest levels (1.72–26.69 μg km^{-1}), followed by 4NC and MNCs (0.48–15.81 μg km^{-1}) and NSAs (1.65–6.22 μg km^{-1}). The values of 4M-2, 6-DNP for diesel passenger vehicles (0–0.68 μg km^{-1}) were much lower than that for diesel trucks (6.31–16.69 μg km^{-1}). The emission factors of 4NP were comparable to a previous study by Inomata et al. (2015), which reported emission factors of 4NP with values of 0.2–21 μg km^{-1}.

In addition, the emission factors of nitrated phenols from vehicle exhaust also varied with driving speed and traffic circumstances. As shown in Tables S3 and S4, the on-road tests for the same vehicles at different driving speeds (e.g., 7-1, 7-2, 8-1, and 8-2) indicated that the emission factors of nitrated phenols at high speeds are lower than those at low speeds. Generally, the emission factors of nitrated phenols obtained in this study can be considered representative valves for other cities with similar traffic circumstances. However, the values could be somewhat different in the cities with more congested or smoother traffic than Jinan.

Table 3
Emission ratios of NPs/OM from vehicle emissions (in μg mg^{-1}).

Types	4NP	3M4NP	2M4NP	2, 6-DM-4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA	2, 4-DNP	4M-2, 6-DNP	ΣNPs
Taxis	0.32	0.11	0.08	0.05	0.07	0.04	0.04	0.04	0.09	0.02	0.15	0.05	1.06
LDGVs	0.29	0.10	0.09	0.07	0.08	0.07	0.05	0.06	0.13	0.06	0.43	0.10	1.53
MDGVs	0.22	0.05	0.04	0.02	0.04	0.02	0.01	0.01	0.07	0.03	0.20	0.04	0.75
LDGTs	1.22	0.17	0.12	0.03	0.10	0.03	0.02	0.03	0.13	0.02	0.31	0.09	2.27
MDDVs	1.77	0.88	0.40	0.69	0.36	0.11	0.12	0.13	0.51	0.78	0.09	0.00	5.85
HDDVs	2.35	0.48	0.23	0.36	0.18	0.22	0.05	0.05	0.17	0.15	0.38	0.08	4.70
LDDTs	0.10	0.04	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.02	0.30
MDDTs	0.03	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.02	0.16
HDDTs	0.27	0.19	0.09	0.02	0.08	0.02	0.07	0.08	0.06	0.06	0.02	0.59	1.56

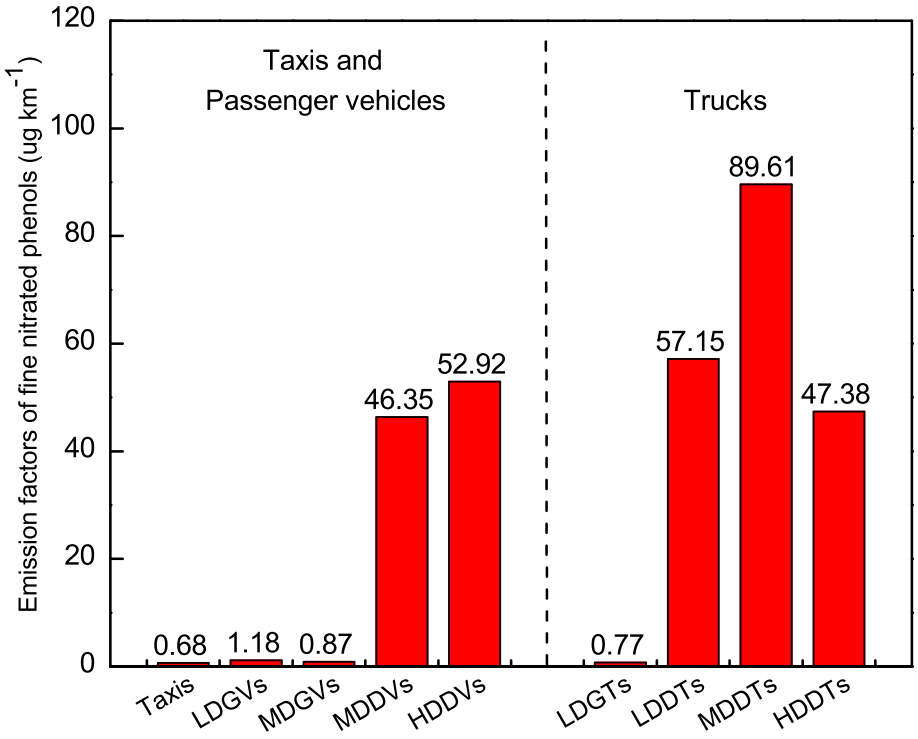

Fig. 2. Emission factors of fine particulate nitrated phenols from vehicle emissions according to the sub-classification of vehicle type.

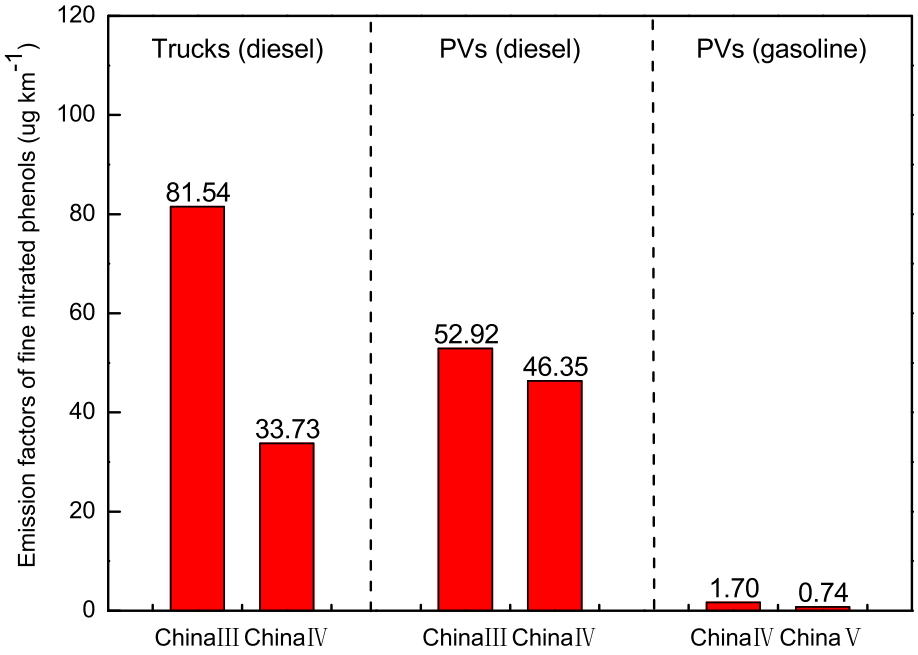

Fig. 3. Emission factors of nitrated phenols from vehicle emissions according to emission standards (PVs refers to passenger vehicles).

3.3. Influences of fuel type on the emissions of nitrated phenols

As demonstrated above, the concentrations, composition, emission ratios, and emission factors of nitrated phenols in the exhaust from different vehicles varied remarkably with fuel type. Gasoline and diesel fuels that are used in vehicles contain a large fraction of aromatic components. When the fuel is combusted in the engine, benzenes in the fuel can react with OH radicals by H-abstractions to generate phenyl radicals or with O-atoms to generate phenols or resonance stabilized phenoxy radicals (Nicovich et al., 1982). Toluene in these fuels primarily reacts by H-abstractions to form benzyl radicals, with O-atoms to produce cresols or cresoxy radicals, or by ipso-addition of H-atoms to generate benzenes (Nicovich and Ravishankara, 1984). The substances that are produced (i. e., phenols or phenyl radicals, cresols or cresoxy radicals) can readily react with nitrogen oxides to generate various species of nitrated phenol (Zhang et al., 2014). Therefore, the emissions of nitrated phenols from vehicle exhaust are likely to be affected by the aromatic compound content in the fuel and the level of emission of nitrogen oxides during fuel combustion.

A number of previous studies have indicated that the aromatic hydrocarbons content in diesel fuel (in the range of 1.5%–30%) is substantially lower than that in gasoline fuel (30%–50%) (Guibet and

Table 4
Emission factors of fine nitrated phenols from vehicle emissions (in μg km^{-1}).

Types	4NP	3M4NP	2M4NP	2, 6-DM-4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA	2, 4-DNP	4M-2, 6-DNP	ΣNPs
Taxis	0.21	0.07	0.05	0.05	0.03	0.02	0.02	0.03	0.06	0.01	0.09	0.03	0.68
LDGVs	0.22	0.07	0.06	0.06	0.06	0.06	0.04	0.05	0.10	0.05	0.35	0.08	1.18
MDGVs	0.25	0.06	0.05	0.05	0.02	0.02	0.01	0.01	0.08	0.04	0.23	0.05	0.87
LDGTs	0.36	0.07	0.05	0.04	0.01	0.01	0.01	0.01	0.05	0.01	0.12	0.03	0.77
MDDVs	14.01	7.01	3.17	2.87	5.49	0.87	0.93	1.05	4.04	6.22	0.71	0.00	46.35
HDDVs	26.69	5.17	2.07	1.72	6.21	1.26	0.48	0.54	2.36	2.38	3.36	0.68	52.92
LDDTs	15.65	4.82	3.40	3.51	6.64	1.70	4.52	5.19	1.65	2.71	1.07	6.31	57.15
MDDTs	17.64	7.16	5.02	4.89	15.81	2.34	6.39	7.41	3.25	4.95	1.78	12.98	89.61
HDDTs	8.09	6.32	2.91	2.63	0.79	0.50	2.41	2.72	1.97	1.84	0.51	16.69	47.38

Faure-Birchem, 1999; Liang et al., 2005; Marchal et al., 2006; Sjögren et al., 1995). Therefore, the aromatics content in diesel and gasoline fuels cannot explain the discrepancy in emission factors of nitrated phenols.

The other factor in producing nitrated phenols is the presence of nitrogen oxides. The on-road emissions factors of NO, $PM_{2.5}$, CO, CO_2, and nitrated phenols were simultaneously measured from the exhausts of eighteen vehicles in our study by using a mobile measurement platform. Fig. S3 presents the correlations between the emission factors of nitrated phenols and other pollutants for the eighteen vehicles with different fuels. Generally, the emission factors of nitrated phenols were relatively strongly correlated with NO emission factors (R = 0.75), moderately correlated with $PM_{2.5}$ (R = 0.60), and weakly correlated with CO (R = 0.20) and CO_2 (R = 0.44). The NO emission factors from the exhaust of the gasoline vehicle and taxis fueled with CNG ranged from 0 to 1.97 g km^{-1}, which were much lower than those from diesel vehicle exhausts (2.10–21.91 g km^{-1}). Strong correlations between NO and nitrated phenols (R = 0.972 and 0.971 for 4NP and 2M4NP, respectively) were also previously found in suspended particulate matter affected by vehicle exhausts (Nojima et al., 1983). The higher emission factors of NO_x from diesel vehicles compared to gasoline vehicles observed in this study are consistent with the results of previous studies (Dallmann et al., 2013; Fontaras et al., 2014; Park et al., 2011). Therefore, the much higher emission factors of nitrated phenols from diesel vehicles compared to gasoline and CNG vehicles in this study were mainly attributed to the higher level of nitrogen oxide emissions from the diesel vehicles.

3.4. The estimated emissions of nitrated phenols

The emissions of fine nitrated phenols from vehicle exhausts in 28 provinces in China in 2017 were estimated to be 58.9 Mg (−86%–85% within 95% confidence interval), based on the measured emission factors, the number of different kinds of vehicle, the percentages of different vehicles with different fuels, and the average annual VKTs for different vehicles (see Tables S5–S8). The emission of nitrated phenols from vehicle exhausts is lower than that from residential coal combustion and biomass burning (Lu et al., 2019; Wang et al., 2017), which may be related to the tightened emission standards and the improved after-treatments techniques that have been adopted in on-road vehicles.

Fig. 4 presents the provincial emissions of fine particulate nitrated phenols from different kinds of vehicle in China in 2017. In terms of the total emissions in different provinces, the highest value appeared in Shandong (5.69 Mg), followed by Guangdong, Hebei, Henan and Jiangsu (all above 3.00 Mg). Trucks were the predominant contributor to the emissions of nitrated phenols, with a percentage of 86.8%. The emissions from diesel vehicles (94.1%) were much higher than those from gasoline vehicles (5.9%), which can be ascribed to the very high emission factors of nitrated phenols from diesel vehicles. Among subcategories of vehicles, LDDTs and HDDTs accounted for the largest proportion (75.0%) of the total nitrated phenol emission. In brief, the variation in the estimated emissions of nitrated phenols across different provinces was mainly linked to differences in the shares of vehicle and fuel type. Therefore, to control the emissions of fine particulate nitrated phenols from vehicle exhaust, governments should focus on the clean use of diesel vehicles (in particular light-duty and heavy-duty diesel trucks), further improve emission standards and fuel quality, and strengthen the monitoring of motor vehicle emissions in urban regions.

Note that the uncertainty analysis of the total emissions of nitrated phenols considered the uncertainties in the on-road emission factors, vehicle kilometers travelled, and number of vehicles. The large uncertainty range of the total emissions (−86%–85% within 95% confidence interval) was mainly attributed to the higher variations of the on-road emission factors due to the limited number of vehicles that were studied. Furthermore, there are inevitable uncertainties in the on-road emission factors of fine particulate nitrated phenols that were used in this study. For example, discrepancies exist in emission standards, age of the engine, manufacturer, and after-treatment technique between the test vehicles and the massive vehicle fleet in China. The operational conditions of the test vehicles and real vehicles (e.g., vehicle speed, ignition, brake, and road types) may vary significantly. In addition, several nitrated phenols, such as 4NP and 2, 4-DNP, are moderately volatile and a large fraction of them exist in the gas phase in atmospheric conditions. Due to the evaporation of gaseous nitrated phenols from the collected particles and the adsorption of gaseous nitrated phenols on the quartz fiber filters, some additional uncertainties are introduced in the determined emission factors and the estimated emission of fine particulate nitrated phenols. Despite these uncertainties, the emissions of nitrated phenols from the exhausts of vehicles in this study provide important evidence for understanding the source of nitrated phenols, basic data for relevant atmospheric models, and a scientific basis for targeted pollution control with the use of clean fuels.

4. Summary and conclusions

In-situ measurements and fine particulate matter collection from eighteen vehicles followed by chemical analysis were conducted to understand the emission characteristics, factors, and amounts of nitrated phenols from various types of vehicle used in China. Overall, the concentrations and composition of nitrated phenols in freshly emitted vehicle exhaust exhibited large variations across the fuel and vehicle type. The concentrations of particulate nitrated phenols for taxis that used CNG and gasoline vehicles were in the range of 0.17–0.23 μg m^{-3}, while the levels for diesel vehicles were much higher (2.30–10.73 μg m^{-3}). Among the twelve detected nitrated phenols, 4-NP and its methyl-derivatives (2M4NP, 3M4NP, and 2, 6-DM-4NP) accounted for the highest proportions in most cases, while the proportions of 4M-2, 6-DNP, 4NC and MNCs were higher for diesel vehicles than gasoline and CNG vehicles, with the reverse being true for 2, 4-DNP. The proportions of NSAs were relatively consistent for different vehicles. The emission factors of nitrated phenols ranged from 0.68 to 1.18 μg km^{-1} for gasoline vehicles and taxis, and ranged from 46.35 to 89.61 μg km^{-1} for diesel vehicles, increasing with rising vehicle size

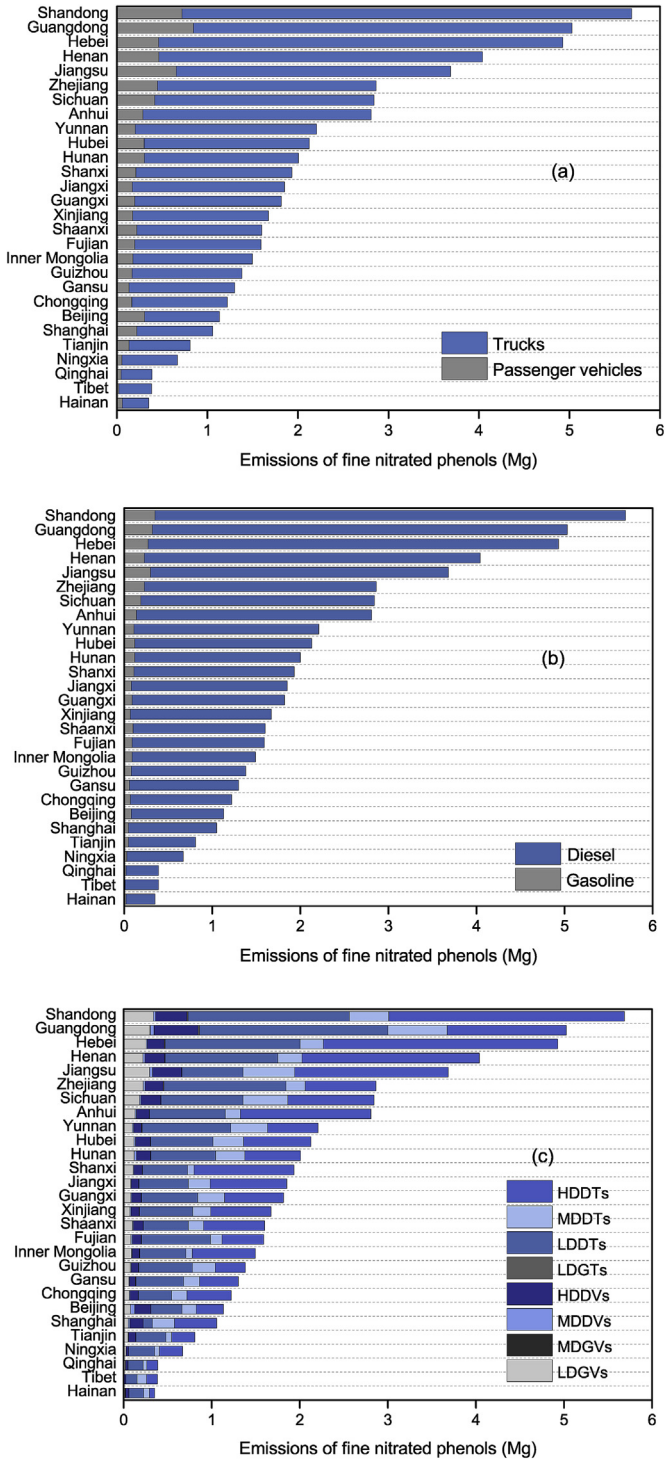

Fig. 4. Provincial nitrated phenol emissions from vehicles in 2017: (a) total emission by vehicle type; (b) total emission by fuel type; (c) total emission by the sub-categories of vehicle type.

and when the fuel changed from gasoline to diesel, while decreasing with tightened emission standards. The significant discrepancy in emission factors of nitrated phenols between gasoline vehicles and diesel vehicles was mainly attributed to the nitrogen oxides emissions. The emission of fine particulate nitrated phenols from motor vehicle exhausts in China in 2017 was estimated to be 58.9 Mg (−86%–85% within 95% confidence interval), among which light-duty and heavy-duty diesel trucks contributed the most part with fractions of 34.5% and 40.5%, respectively.

Funding

This work was supported by National Natural Science Foundation of China (grant numbers 41775118, 91644214, 91544213), the National Key Research and Development Program of China (grant number 2016YFC0200500), and the Taishan Scholar (grant number ts201712003).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2019.108709.

References

Aiken, A.C., DeCarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K.S., Ulbrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P.J., Canagaratna, M.R., Onasch, T.B., Alfarra, M.R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., Jimenez, J.L., 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. Environ. Sci. Technol. 42, 4478–4485. https://doi.org/10.1021/es703009q.

Cao, X., Hao, X., Shen, X., Xi, J., Wu, B., Yao, Z., 2017. Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from diesel trucks based on on-road measurements. Atmos. Environ. 148, 190–196. https://doi.org/10.1016/j.atmosenv.2016.10.040.

Cecinato, A., Palo, V.D., Pomata, D., Scianò, M.C.T., Possanzini, M., 2005. Measurement of phase-distributed nitrophenols in Rome ambient air. Chemosphere 59 (5), 679–683. https://doi.org/10.1016/j.chemosphere.2004.10.045.

Chen, Y., Ge, X., Chen, H., Xie, X., Chen, Y., Wang, J., Ye, Z., Bao, M., Zhang, Y., Chen, M., 2018. Seasonal light absorption properties of water-soluble brown carbon in atmospheric fine particles in Nanjing, China. Atmos. Environ. Times 187, 230–240. https://doi.org/10.1016/j.atmosenv.2018.06.002.

Chow, K.S., Huang, X.H.H., Yu, J.Z., 2016. Quantification of nitroaromatic compounds in atmospheric fine particulate matter in Hong Kong over 3 years: field measurement evidence for secondary formation derived from biomass burning emissions. Environ. Chem. 13 (4), 665–673. https://doi.org/10.1071/en15174.

Dallmann, T.R., Kirchstetter, T.W., Demartini, S.J., Harley, R.A., 2013. Quantifying on-road emissions from gasoline-powered motor vehicles: accounting for the presence of medium- and heavy-duty diesel trucks. Environ. Sci. Technol. 47 (23), 13873–13881. https://doi.org/10.1021/es402875u.

Delhomme, O., Morville, S., Millet, M., 2010. Seasonal and diurnal variations of atmospheric concentrations of phenols and nitrophenols measured in the Strasbourg area. France. Atmos. Pollut. Res. 1 (1), 16–22. https://doi.org/10.5094/apr.2010.003.

Fernandez, P., Grifoll, M., Solanas, A.M., Bayona, J.M., Albaiges, J., 1992. Bioassay-directed chemical analysis of genotoxic components in coastal sediments. Environ. Sci. Technol. 26 (4), 817–829. https://doi.org/10.1021/es00028a024.

Fontaras, G., Franco, V., Dilara, P., Martini, G., Manfredi, U., 2014. Development and review of Euro 5 passenger car emission factors based on experimental results over various driving cycles. Sci. Total Environ. 468–469, 1034–1042. https://doi.org/10.1016/j.scitotenv.2013.09.043.

Giechaskiel, B., Clairotte, M., Valverde-Morales, V., Bonnel, P., Kregar, Z., Franco, V., Dilara, P., 2018. Framework for the assessment of PEMS (portable emission measurement systems) uncertainty. Environ. Res. 166, 251–260. https://doi.org/10.1016/j.envres.2018.06.012.

Guibet, J., Faure-Birchem, E., 1999. Fuels and Engines, vol. 1 Editions Technip, Paris.

Harrison, M.A.J., Barra, S., Borghesi, D., Vione, D., Arsene, C., Iulian Olariu, R., 2005. Nitrated phenols in the atmosphere: a review. Atmos. Environ. 39 (2), 231–248. https://doi.org/10.1016/j.atmosenv.2004.09.044.

Hoffmann, D., Iinuma, Y., Herrmann, H., 2007. Development of a method for fast analysis of phenolic molecular markers in biomass burning particles using high performance liquid chromatography/atmospheric pressure chemical ionisation mass spectrometry. J. Chromatogr., A 1143 (1–2), 168–175. https://doi.org/10.1016/j.chroma.2007.01.035.

Huang, Q., Wang, L., Han, S., 1995. The genotoxicity of substituted nitrobenzenes and the quantitative structure-activity relationship studies. Chemosphere 30 (1), 915–923. https://doi.org/10.1016/0045-6535(94)00450-9.

Huang, C., Lou, D., Hu, Z., Feng, Q., Chen, Y., Chen, C., Tan, P., Yao, D., 2013. A PEMS study of the emissions of gaseous pollutants and ultrafine particles from gasoline- and diesel-fueled vehicles. Atmos. Environ. 77, 703–710. https://doi.org/10.1016/j.atmosenv.2013.05.059.

Huo, H., Yao, Z., Zhang, Y., Shen, X., Zhang, Q., Ding, Y., He, K., 2012. On-board measurements of emissions from light-duty gasoline vehicles in three mega-cities of China. Atmos. Environ. 49, 371–377. https://doi.org/10.1016/j.atmosenv.2011.11.005.

Inomata, S., Fushimi, A., Sato, K., Fujitani, Y., Yamada, H., 2015. 4-Nitrophenol, 1-nitropyrene, and 9-nitroanthracene emissions in exhaust particles from diesel vehicles with different exhaust gas treatments. Atmos. Environ. 110, 93–102. https://doi.org/10.1016/j.atmosenv.2015.03.043.

Kioutsioukis, I., Tarantola, S., Saltelli, A., Debora, G., 2004. Uncertainty and global sensitivity analysis of road transport emission estimation. Atmos. Environ. 38,

6609–6620. https://doi.org/10.1016/j.atmosenv.2004.08.006.
Li, X.Z., Li, C.M., Suzuki, A.K., Taneda, S., Watanabe, G., Taya, K., 2009. 4-Nitrophenol isolated from diesel exhaust particles disrupts regulation of reproductive hormones in immature male rats. Endocrine 36 (1), 98–102. https://doi.org/10.1007/s12020-009-9192-0.
Li, J., Wang, X., Xue, L., Gao, X., Sun, L., Wang, W., 2019. Study on pollution characteristics and the influencing factors of exhaust particles from typical vehicles in Jinan. Acta Sci. Circumstantiae 39 (1), 35–43. (In Chinese). https://doi.org/10.13671/j.hjkxxb.2018.0323.
Liang, F., Lu, M., Keener, T.C., Liu, Z., Khang, S.-J., 2005. The organic composition of diesel particulate matter, diesel fuel and engine oil of a non-road diesel generator. J. Environ. Monit. 7 (10), 983–988. https://doi.org/10.1039/b504728e.
Liu, H., Man, H., Cui, H., Wang, Y., Deng, F., Wang, Y., Yang, X., Xiao, Q., Zhang, Q., Ding, Y., He, K., 2017. An updated emission inventory of vehicular VOCs and IVOCs in China. Atmos. Chem. Phys. 17 (20), 12709–12724. https://doi.org/10.5194/acp-17-12709-2017.
Lu, C., Wang, X., Li, R., Gu, R., Zhang, Y., Li, W., Gao, R., Chen, B., Xue, L., Wang, W., 2019. Emissions of fine particulate nitrated phenols from residential coal combustion in China. Atmos. Environ. 203, 10–17. https://doi.org/10.1016/j.atmosenv.2019.01.047.
Lüttke, J., Scheer, V., Levsen, K., Wünsch, G., Cape, J.N., Hargreaves, K.J., Storeton-West, R.L., Acker, K., Wieprecht, W., Jones, B., 1997. Occurrence and formation of nitrated phenols in and out of cloud. Atmos. Environ. 31 (16), 2637–2648. https://doi.org/10.1016/s1352-2310(96)00229-4.
Lüttke, J., Levsen, K., Acker, K., Wieprecht, W., Möller, D., 1999. Phenols and nitrated phenols in clouds at Mount Brocken. Int. J. Environ. Anal. Chem. 74 (1–4), 69–89. https://doi.org/10.1080/03067319908031417.
Mahesh, S., Ramadurai, G., Nagendra, S.M.S., 2018. Real-world emissions of gaseous pollutants from diesel passenger cars using portable emission measurement systems. Sustain. Cities. Soc. 41, 104–113. https://doi.org/10.1016/j.scs.2018.05.025.
Marchal, R., Penet, S., Solano-Serena, F., Vandecasteele, J.P., 2006. Gasoline and diesel oil biodegradation. Oil Gas Sci. Technol. 58 (4), 441–448. https://doi.org/10.2516/ogst:2003027.
Mohr, C., Lopez-Hilfiker, F.D., Zotter, P., Prévoˆt, A.S., Xu, L., Ng, N.L., Herndon, S.C., Williams, L.R., Franklin, J.P., Zahniser, M.S., Worsnop, D.R., Knighton, W.B., Aiken, A.C., Gorkowski, K.J., Dubey, M.K., Allan, J.D., Thornton, J.A., 2013. Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time. Environ. Sci. Technol. 47 (12), 6316–6324. https://doi.org/10.1021/es400683v.
Mori, Y., Kamata, K., Toda, N., Hayashi, H., Seki, K., Taneda, S., Yoshino, S., Sakushima, A., Sakata, M., Suzuki, A.K., 2003. Isolation of nitrophenols from diesel exhaust particles (DEP) as vasodilatation compounds. Biol. Pharm. Bull. 26 (3), 394–395. https://doi.org/10.1248/bpb.26.394.
National Bureau of Statistic of China (NBSC), 2018. Chinese statistical Yearbook 2017. http://www.stats.gov.cn/tjsj/ndsj/2018/indexch.htm.
Nicovich, J.M., Ravishankara, A.R., 1984. Reaction of hydrogen atom with benzene. Kinetics and mechanism. J. Phys. Chem. 88 (12), 2534–2541. https://doi.org/10.1021/j150656a021.
Nicovich, J.M., Gump, C.A., Ravishankara, A.R., 1982. Rates of reactions of atomic (3p) with benzene and toluene. J. Phys. Chem. 86 (9), 1684–1690. https://doi.org/10.1021/j100206a040.
Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M., 1983. Studies on photochemical reaction of air pollutants. X. Identification of nitrophenols in suspended particulates. Chem. Pharm. Bull. 31 (3), 1047–1051. https://doi.org/10.1248/cpb.31.1047.
Park, S.S., Kozawa, K., Fruin, S., Mara, S., Hsu, Y.K., Jacober, C., Winer, A., Herner, J., 2011. Emission factors for high-emitting vehicles based on on-road measurements of individual vehicle exhaust with a mobile measurement platform. J. Air Waste Manag. Assoc. 61 (10), 1046–1056. https://doi.org/10.1080/10473289.2011.595981.
Rippen, G., Zietz, E., Frank, R., Knacker, T., Klöpffer, W., 1987. Do airborne nitrophenols contribute to forest decline? Environ. Technol. Lett. 8 (1–12), 475–482. https://doi.org/10.1080/09593338709384508.
Shafer, W.E., Schönherr, J., 1985. Accumulation and transport of phenol, 2-nitrophenol, and 4-nitrophenol in plant cuticles. Ecotoxicol. Environ. Saf. 10 (2), 239–252. https://doi.org/10.1016/0147-6513(85)90071-5.
Sjögren, M., Hang, L., Rannug, U., Westerholm, R., 1995. A multivariate statistical analysis of chemical composition and physical characteristics of ten diesel fuels. Fuel 74 (7), 983–989. https://doi.org/10.1016/0016-2361(95)00056-b.
Still, K.R., Jung, A.E., Ritchie, G.D., Jederberg, W.W., Wilfong, E.R., Briggsy, G.B., Arfsten, D.P., 2005. Disposition of 2, 6-di-tert-butyl-4-nitrophenol (DBNP), a submarine atmosphere contaminant, in male Sprague-Dawley rats. Environ. Res. 98 (3), 363–367. https://doi.org/10.1016/j.envres.2018.12.060.
Teich, M., van Pinxteren, D., Wang, M., Kecorius, S., Wang, Z., Müller, T., Močnik, G., Herrmann, H., 2017. Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments. Atmos. Chem. Phys. 17 (3), 1653–1672. https://doi.org/10.5194/acp-17-1653-2017.
Tremp, J., Mattrel, P., Fingler, S., Giger, W., 1993. Phenols and nitrophenols as tropospheric pollutants: emissions from automobile exhausts and phase transfer in the atmosphere. Water Air Soil Pollut. 68 (1–2), 113–123. https://doi.org/10.1007/bf00479396.
Vo, N.T., Seymour, C.B., Mothersill, C.E., 2019. The common field lampricide 3-trifluoromethyl-4-nitrophenol is a potential radiosensitizer in fish cells. Environ. Res. 170, 383–388. https://doi.org/10.1016/j.envres.2018.06.012.
Wang, X., Gu, R., Wang, L., Xu, W., Zhang, Y., Chen, B., Li, W., Xue, L., Chen, J., Wang, W., 2017. Emissions of fine particulate nitrated phenols from the burning of five common types of biomass. Environ. Pollut. 230, 405–412. https://doi.org/10.1016/j.envpol.2017.06.072.
Wang, L., Wang, X., Gu, R., Wang, H., Yao, L., Wen, L., Zhu, F., Wang, W., Xue, L., Yang, L., Lu, K., Chen, J., Wang, T., Zhang, Y., Wang, W., 2018. Observations of fine particulate nitrated phenols in four sites in northern China: concentrations, source apportionment, and secondary formation. Atmos. Chem. Phys. 18 (6), 4349–4359. https://doi.org/10.5194/acp-18-4349-2018.
Wu, X., Wu, Y., Zhang, S., Liu, H., Fu, L., Hao, J., 2016. Assessment of vehicle emission programs in China during 1998–2013: achievement, challenges and implications. Environ. Pollut. 214, 556–567. https://doi.org/10.1016/j.envpol.2016.04.042.
Yuan, B., Liggio, J., Wentzell, J., Li, S.-M., Stark, H., Roberts, J.M., Gilman, J., Lerner, B., Warneke, C., Li, R., Leithead, A., Osthoff, H.D., Wild, R., Brown, S.S., Gouw, J.A., 2016. Secondary formation of nitrated phenols: insights from observations during the uintah basin winter ozone study (UBWOS) 2014. Atmos. Chem. Phys. 16 (4), 2139–2153. https://doi.org/10.5194/acp-16-2139-2016.
Zhang, Y.Y., Müller, L., Winterhalter, R., Moortgat, G.K., 2010. Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter. Atmos. Chem. Phys. 10 (16), 7859–7873. https://doi.org/10.5194/acp-10-7859-2010.
Zhang, X., Lin, Y.H., Surratt, J.D., Zotter, P., Prevot, A.S.H., Weber, R.J., 2011. Light-absorbing soluble organic aerosol in los angeles and atlanta: a contrast in secondary organic aerosol. Geophys. Res. Lett. 38 (21), L21810. https://doi.org/10.1029/2011gl049385.
Zhang, Q.Z., Gao, R., Xu, F., Zhou, Q., Jiang, G., Wang, T., Chen, J., Hu, J., Jiang, W., Wang, W.X., 2014. Role of water molecule in the gas-phase formation process of nitrated polycyclic aromatic hydrocarbons in the atmosphere: a computational study. Environ. Sci. Technol. 48 (9), 5051–5057. https://doi.org/10.1021/es500453g.
Zhao, Y., Nielsen, C.P., Lei, Y., McElroy, M.B., Hao, J., 2011. Quantifying the uncertainties of a bottom-up emission inventory of anthropogenic atmospheric pollutants in China. Atmos. Chem. Phys. 11 (5), 2295–2308. https://doi.org/10.5194/acp-11-2295-2011.
Zheng, X., Wu, Y., Zhang, S., Hu, J., Zhang, K.M., Li, Z., He, L., Hao, J., 2017. Characterizing particulate polycyclic aromatic hydrocarbon emissions from diesel vehicles using a portable emissions measurement system. Sci. Rep. 7 (1), 10058. https://doi.org/10.1038/s41598-017-09822-w.