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# Characterization and carcinogenic risk assessment of polycyclic aromatic and nitro-polycyclic aromatic hydrocarbons in exhaust emission from gasoline passenger cars using on-road measurements in Beijing, China

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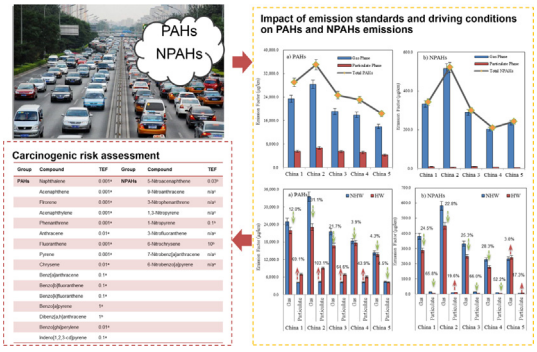
## HIGHLIGHTS

- PAH and NPAH emissions from 16 gasoline passenger cars were tested using a PEMS.
- The EFs and $TEQ_{BaP}$ of PAHs and NPAHs decreased with improved emission standards.
- The $TEQ_{BaP}$ of particulate-phase PAHs was 4.2 times higher than that of gas-phase PAHs.
- Further studies should be conducted to identify unknown NPAHs in the future.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The polycyclic aromatic hydrocarbon (PAH) and nitro-polycyclic aromatic hydrocarbon (NPAH) emissions from 16 gasoline passenger cars, encompassing five emission standards and two driving conditions, were tested using a portable emission measurement system (PEMS) in Beijing under on-road conditions. In total, 16 PAHs and 9 NPAHs were quantified in both the gaseous and particulate phases by high-performance liquid chromatography (HPLC). The results indicated that lower PAH and NPAH emissions were observed with improved emission standards, especially for China 3 to China 5 vehicles ($P < 0.05$). Higher emission factors (EFs) were detected on nonhighway roads than on highway roads due to incomplete combustion. Although most PAHs and NPAHs were in the gas-phase, the $TEQ_{BaP}$ of the particulate-phase PAHs was 4.2 times higher than that of the gas-phase PAHs, whereas the opposite pattern was observed for NPAHs. The $TEQ_{BaP}$ EFs on nonhighway roads were 1.0–2.3 times higher than those on highway roads. The results of this study will be valuable for estimating the emissions and performing carcinogenic risk assessment of PAHs and NPAHs from urban gasoline passenger cars on roads. Formulating more stringent regulations and emission control technologies for PAHs and NPAHs is important.



## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous, semivolatile organic pollutants in the environment (Chen et al., 2013; Huang et al., 2015; Li et al., 2018). Certain PAHs are highly carcinogenic

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and have been implicated in various types of human cancers, including breast, lung, and colon cancers. These PAHs cause metabolic activation in mammalian cells via dioepoxides, which results in errors in deoxyribonucleic acid (DNA) replication and mutation (Abramsson-Zetterberg and Maurer, 2015; Armstrong et al., 2004; USEPA, 2002; Yoon et al., 2007) and initiates the carcinogenic process (Ke et al., 2018; Farhadian et al., 2010). Nitro-polycyclic aromatic hydrocarbons (NPAHs) are derived from the reaction of parent PAHs with hydroxyl (OH) and nitrate ($NO_3$) radicals in the presence of $NO_x$ or via nitration during combustion processes (Alves et al., 2017; Cochran et al., 2016), and NPAHs have toxicological significance even though they are present at much lower concentrations than their parent compounds (Bandowe and Meusel, 2017; Huang et al., 2013). Because of their toxicity and potential to harm human health and the environment, PAHs and NPAHs have aroused the concern of scholars in recent decades (Ali et al., 2017; Karavalakis et al., 2010a, 2010b; Shen et al., 2012).

In recent years, with the rapid increase in the number of vehicles in urban areas, vehicles have been reported as one of the most important emission sources of urban PAH and NPAH pollutants in source apportionment studies (Jamhari et al., 2014; Khairy and Lohmann, 2013; Perez et al., 2010; Wang et al., 2016). Fang et al. (2018) determined that vehicles exhaust emissions contributed 61.66% and 62.22% of the total PAHs for $PM_{10}$ and $PM_{2.5}$. Wada et al. (2001) found that the NPAH concentration in particulate matter in the atmosphere in Nagasaki, Japan was positively correlated with the traffic volume. Traffic-related pollution from PAHs and NPAHs occurs via mixed emissions, including gasoline and diesel exhausts, vapors from fuel evaporation, spilled fuel and lube oil, brake, tire and road surface material particulates, resuspended road dust, and condensation (Lawrence et al., 2013; Liu et al., 2015; Wu et al., 2014). The contributions from gasoline and diesel exhausts are predominant. Previous studies have focused on PAHs and NPAHs in diesel vehicle exhaust, but only a few studies focused on gasoline vehicle exhaust (Cao et al., 2017; Souza and Corrêa, 2015; Zwirner-Baier and Neumann, 1999). Riddle et al. (2007) confirmed that heavy PAHs could also be derived from gasoline. Additionally, the number of gasoline passenger cars in urban areas is much larger than that of diesel vehicles in China. By the end of 2016, China had 158,528,000 small passenger cars (with most using gasoline as fuel), which accounted for 86.0% of all vehicles. Therefore, the PAH and NPAH exhaust emissions from urban gasoline passenger cars in China cannot be ignored.

In recent decades, many researchers have conducted studies on the emission characteristics of PAHs and NPAHs from motor vehicles via chassis dynamometer tests (Bikas and Zervas, 2007; Hu et al., 2013; Huang et al., 2013; Karavalakis et al., 2010a, 2010b) and tunnel experiments (Chen et al., 2013; Lawrence et al., 2016). However, dynamometer tests do not necessarily reflect the real on-road driving conditions and emission performance of vehicles (Palmgren et al., 2001; Weiss et al., 2011). In tunnel measurements, the measured PAH and NPAH compositions broadly represent a large number of vehicles and fuel types used in a certain area (Kwangsam, 2006), but the measured emissions may be a mixture of ambient and tunnel PAH and NPAH concentrations. Moreover, the characteristics of emissions from a single vehicle cannot be tested. In recent years, with the development of the portable emission measurement system (PEMS), more on-road studies have been carried out on vehicular emissions using this technology. The data collected by a PEMS can reflect real driving conditions. The PEMS has been proven to be a reliable, inexpensive and relatively simple system, and it can be installed on a wide variety of vehicles. However, at present, studies using a PEMS to measure on-road PAH and NPAH emissions are very limited. Therefore, in this study, the emissions of 16 PAHs and 9 NPAHs from 16 in-use gasoline passenger cars were tested in Beijing using a PEMS for on-road measurements. The test encompassed vehicles meeting five emission standards (China 1 to China 5) and two driving conditions, highway and nonhighway roads. The objectives of this study were 1) to quantify the emissions of 16 PAHs and 9 NPAHs from 16 gasoline passenger cars and to analyze the emission characteristics of these compounds along with the impacts of several factors. 2) to evaluate the carcinogenic risk of 16 PAHs and 9 NPAHs from 16 gasoline passenger cars along with the impacts of several factors.

## 2. Experimental

### 2.1. PEMS

A combined PEMS (Sensors Inc., USA) was utilized for the test, mainly consisting of four parts. A Semtech-DS was employed to measure gaseous pollutant emissions with a 1-s resolution. An exhaust flow meter (EFM-2) was used to measure the instantaneous mass flow of the exhaust. A microproportional sampling system (MPS) was applied to dilute the exhaust sample. A sample-collection unit was used to collect the samples. The vehicle speed, latitude, and longitude were continuously logged by a GPS unit. Detailed information related to the PEMS was described in our previous study (Wu et al., 2016; Yao et al., 2015).

### 2.2. Test vehicles and routes

The on-road experiments were conducted in Beijing. In total, 16 vehicles were selected from the most common in-use gasoline passenger cars, including vehicles that met five different emission standards (China 1 to China 5). The specifications of the test vehicles are listed in Table 1. All tested vehicles were rented from a local car rental company and were operated under normal operation conditions. The gasoline fuel used in the test was commercially available in Beijing and met the 10 mg/kg sulfur limit of the Chinese phase V gasoline standard. The driving route for the onboard measurement was designed to simulate real traffic conditions in Beijing and included highway and nonhighway roads. The total length of the route was approximately 35 km, consisting of 15 km of nonhighway roads and 20 km of highways in northwest Beijing, mainly Lianhuachi Road, west 5th Ring Road and Fushi Road. All of the tested vehicles were tested in parallel two times on the two types of roads.

### 2.3. Sampling, extraction and composition analysis

The particulate phase was collected on a 47 mm quartz filter (QF, 2500QAT-UP, PALL Corp., USA), and the gas phase was sampled by three-stage polyurethane foam (PUF) cartridges. The exhaust was first passed through the QF, followed by passage through the three-stage PUF. The dilution ratios were approximately 8:1. The flow rate of the sampling was controlled at approximately 3 L/min, and the flow meter used in this work was calibrated with a BIOS Defender 530 (Drycal Technology Inc., USA) before each test. To ensure that the PAH and NPAH contents measured in the laboratory were within the detection limits of the instruments, the sampling time was set at 30–40 min. All samples were collected under hot, stabilized conditions. An assistant was onboard the tested vehicles to check the emissions equipment. The test was carried out in October 2014, and the atmospheric temperature, which was measured by an atmospheric temperature device, ranged from approximately 293–303 K. The samples were stored at −10 °C in a refrigerator before analysis.

Sample extraction and analysis were identical to the procedures used in our tests of diesel truck emission characteristics and were previously described in detail (Cao et al., 2017). The PAHs and NPAHs were analyzed using an HPLC system (Agilent 1200, Santa Clara, CA, USA) equipped with a UV detector (Agilent G1314A, Santa Clara, CA, USA) to detect at 220 nm, 230 nm, 254 nm and 290 nm. In total, 16 PAHs and 9 NPAHs were quantified.