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Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from diesel trucks based on on-road measurements

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HIGHLIGHTS

- PAHs and NPAHs from 18 diesel trucks were tested in Beijing using a PEMS.
- No significant reduction was observed for PAHs or NPAHs from diesel trucks with China 3 to 4 emission standards.
- The gaseous-phase compounds had important contributions to the total PAHs and NPAHs.
- Large gaps were found in the PAH and NPAH emissions from diesel vehicles when comparing the results of different studies.

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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH) and nitro-polycyclic aromatic hydrocarbon (NPAH) emissions from 18 diesel trucks of different sizes and with different emission standards were tested in Beijing using a portable emission measurement system (PEMS). Both the gaseous- and particulate-phase PAHs and NPAHs were quantified by high-performance liquid chromatography (HPLC) in the laboratory. The emission factors (EFs) of the total PAHs from light-duty diesel trucks (LDDTs), medium-duty diesel trucks (MDDTs) and heavy-duty diesel trucks (HDDTs) were 82229.11 ± 41906.06, 52867.43 ± 18946.47 and 93837.35 ± 32193.14 μg/km, respectively, much higher than the respective values of total NPAHs from their counterpart vehicles. The gaseous phase had an important contribution to the total PAHs and NPAHs, with a share rate of approximately 69% and 97% on average, respectively. The driving cycle had important impacts on the emissions of PAHs and NPAHs, especially for LDDTs and HDDTs. Higher emissions of PAHs and NPAHs were detected on non-highway roads compared to that on highways for these two types of vehicles. Compared to the results of different studies, the difference in the EFs of PAHs and NPAHs can reach several orders of magnitudes, which would introduce errors in the development of an emission inventory of PAHs and NPAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and nitro-polycyclic aromatic hydrocarbons (NPAHs) have attracted considerable concerns due to their toxicity, mutagenicity and carcinogenicity (Bamford and Baker, 2003; Albinet et al., 2007; Casal et al., 2014). NPAHs are derived from the reaction of the parent PAHs with hydroxyl (OH) and nitrate (NO_3) radicals in the presence of NOx or through nitration during combustion processes (Tsapakis and Stephanou, 2007), which have toxicological significance even if present at much lower concentrations than their parent compound (Grimmer et al., 1987; Durant et al., 1996; Shen et al., 2012).

Both PAHs and NPAHs can form through the incomplete combustion of organic matter such as coal, oil and wood (Chetwittayachan et al., 2002; Thuy et al., 2012). Shen et al. (2013) estimated that on-road motor vehicles were the fourth important major source and contributed approximately 12.8% of the global total annual atmospheric emissions of 16 PAHs in 2007. In urban cities, vehicle exhaust is one of the most important sources of PAHs and NPAHs, especially diesel engine exhaust (Wada et al., 2001; Chen et al., 2004; Chang et al., 2006; Ravindra et al., 2006; Logan, 2007). Zhang et al. (2009) found that motor vehicles and heating were the most important sources of PAHs in Beijing. Zhou et al. (2005) reported that the total concentration of 17 PAHs in an

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urban area was 1.1–6.6 times higher than that measured in a suburban area of Beijing. Fromme et al. (2004) inferred that motor vehicles were the main source of PAHs in urban residential areas of Berlin, Germany. Wada et al. (2001) found that the concentration of NPAHs in particulate matter was positively correlated with the traffic volume and concluded that diesel vehicles were the main source of NPAHs in the atmosphere in Nagasaki, Japan. Although the contribution of motor vehicles to global PAH emissions is less than that of biomass burning and wildfires (Shen et al., 2013), the relative contribution of PAHs from motor vehicles to the human exposure risk is much higher than its contribution to the emissions themselves because motor vehicle emissions occur mostly in urban areas where population densities are much higher than the global average. The inhalation intake fraction, defined as the fraction of the emission that is eventually inhaled, of benzo(a)pyrene from motor vehicles in China was estimated to be 4 times greater than the mean inhalation intake fraction from all other sources (Zhang et al., 2009).

In recent decades, many researchers have conducted studies of the emission characteristics of PAHs and NPAHs from motor vehicles via chassis dynamometer tests (Deabrantes et al., 2004; Bikas and Zervas, 2007; Karavalakis et al., 2010; Huang et al., 2013; Hu et al., 2013) and tunnel experiments (Benner et al., 1989; Fraser et al., 1998; Ho et al., 2009; Chen et al., 2013). The emission factors (EFs), gas-particle partitioning, isomer distribution, impact factors, etc. for PAHs and NPAHs from motor vehicles have been widely studied. However, the existing studies mainly focused on PAHs, especially on particulate-phase PAHs, which have been investigated for decades (Heeb et al., 2010). Studies on NPAHs and gaseous-phase PAHs are relatively few. More research on the emission characteristics of NPAHs and gaseous-phase PAHs is necessary.

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 technique. The emission characteristics of CO_2, CO, HC, PM, and the chemical constituents of PM and VOCs have been widely studied using this method because the results reflect real emissions from vehicles. However, studies reporting the on-road emissions of PAHs and NPAHs using the PEMS are very limited. Shah et al. (2005) presented the emission rates of PAHs from on-road emissions testing of nine heavy-duty diesel (HDD) vehicles tested using CE-CERT's Mobile Emissions Laboratory (MEL) over the California Air Resources Board (ARB) Four-Phase Cycle. This is the only paper related to the on-road emission characteristics of PAHs or NPAHs published to date.

In this study, the main purpose is to understand the real emissions of gaseous- and particulate-phase PAHs and NPAHs and the impact of several factors on the emissions of PAHs and NPAHs. To achieve this objective, PAH and NPAH emissions from nine China III and nine China IV diesel trucks of different sizes (light, medium, and heavy duty) in Beijing were tested using a PEMS. Both the gaseous- and particulate-phase PAHs and NPAHs were collected and then quantified by high-performance liquid chromatography (HPLC) in the laboratory. Based on the measured data, the EFs and distributions of PAHs and NPAHs and the impact factors were characterized. The results of this study will be helpful for understanding the real emission levels of PAHs and NPAHs from diesel trucks on roads.

2. Experimental section

2.1. Portable emission measurement system (PEMS)

A combined PEMS was developed based on our previous studies (Yao et al., 2011; Huo et al., 2012) that mainly consisted of a SEMTECH-DS (Sensors Inc., USA), exhaust flow meter (EFM-2, Sensors Inc., USA), micro-proportional sampling system (MPS, Sensors Inc., USA) and PAH-collection unit. The SEMTECH-DS was used to analyze the emissions of gaseous pollutants at a 1 s resolution. The EFM-2 was employed to measure the instantaneous mass flow of the exhaust, which can be used to calculate the EF of the pollutants. The MPS was applied to dilute the exhaust sample before it was passed through the PAH-collection unit. The dilution ratios were approximately 8:1. The PAH-collection unit included quartz filters (QFs, 47 mm in diameter) followed by two-stage polyurethane foam (PUF) cartridges. In addition, a GPS unit was used to record the instantaneous speed and driving distance. More information related to the PEMS can be found in our previous studies (Yao et al., 2015a; Wu et al., 2016).

2.2. On-road experiments

The on-road experiments were carried out in southwest Beijing. In total, 18 vehicles, including six types of diesel trucks of different sizes (light, medium and heavy) and different emission standards (China 3 and China 4), were tested, and three vehicles were tested for each type of truck. For all the tested China IV light-duty diesel trucks (LDDTs) and medium-duty diesel trucks (MDDTs), particulate oxidation catalyst (POC), diesel oxidation catalyst (DOC) and exhaust gas recirculation (EGR) control devices were installed. Selected catalytic reduction (SCR) control devices were installed on all the tested China 4 heavy-duty diesel trucks (HDDTs). No aftertreatment control device was installed on any of the China 3 diesel trucks tested. All of the test vehicles have manual transmissions. Detailed information on the tested trucks is listed in Table S1 in the Supplemental Materials. The measurements were taken when the test vehicles were driven repeatedly on a predesigned test route. The length of the test route was 47 km for the LDDTs and MDDTs and 63 km for the HDDTs. Both of test routes included highway and non-highway roads. In addition, the diesel trucks were fueled with commercially available diesel fuel from Beijing that met the 10 mg/kg sulfur limit of the Chinese phase V diesel standard. During the measurements, the trucks were not in service and were under hot stabilized conditions, and an assistant was onboard the trucks to check the emissions equipment. The total weight of the emissions equipment was approximately 200 kg. More information on the test route and measurements can be found in our previous studies (Yao et al., 2015a; Wu et al., 2016).

2.3. Sample collection

Particle-phase PAHs and NPAHs were collected on a 47 mm QF (2500QAT-UP, PALL Corp., USA) the QFs. Gas-phase PAHs were sampled by two-stage PUF cartridges. 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. The samples were collected when the tested trucks were driven on highway and non-highway roads, respectively. Each type of road was tested twice. The sampling time for each test was approximately 30–40 min. After sampling, the samples were stored at −10 °C before analysis. Before sampling, a PUF was pre-cleaned in an ultrasonic cleaner with dichloromethane three times, with each time lasting 30 min. The QFs were pre-combusted at 550 °C for 12 h in a muffle furnace.

2.4. PAH and NPAH analysis

Sample pretreatment followed standardized internal procedures (Yao et al., 2015b; Hao et al., 2016). Firstly, the samples were