



Contents lists available at ScienceDirect

Atmospheric Environment

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

4-Nitrophenol, 1-nitropyrene, and 9-nitroanthracene emissions in exhaust particles from diesel vehicles with different exhaust gas treatments

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H I G H L I G H T S

- 4-Nitrophenol probably dominates nitro-organics in diesel emission particles.
- The DPNR system decreased emissions of nitro-PAHs but probably not 4-nitrophenol.
- Nitro-PAH and 4-nitrophenol emissions were suppressed by the urea-SCR system.
- Oxidation catalysts are sources of nitro-PAHs and possibly 4-nitrophenol.
- Nitro-organic compounds are mainly produced by engines under load.

A R T I C L E I N F O

Article history:

Received 9 September 2014

Received in revised form

13 March 2015

Accepted 19 March 2015

Available online 23 March 2015

Keywords:

Diesel exhaust particles (DEPs)

Nitro-PAH

Nitrophenol

TD-GC/MS

LC/MS

A B S T R A C T

The dependence of nitro-organic compound emissions in automotive exhaust particles on the type of aftertreatment used was investigated. Three diesel vehicles with different aftertreatment systems (an oxidation catalyst, vehicle-DOC; a particulate matter and NO_x reduction system, vehicle-DPNR; and a urea-based selective catalytic reduction system, vehicle-SCR) and a gasoline car with a three-way catalyst were tested. Nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) and nitrophenols in the particles emitted were analyzed by thermal desorption gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry. The secondary production of nitro-organic compounds on the filters used to collect particles and the adsorption of gaseous nitro-organic compounds by the filters were evaluated. Emissions of 1-nitropyrene, 9-nitroanthracene, and 4-nitrophenol in the diesel exhaust particles were then quantified. The NO_x reduction process in vehicle-DPNR appeared to remove nitro-hydrocarbons efficiently but not to remove nitro-oxygenated hydrocarbons efficiently. The nitro-PAH emission factors were lower for vehicle-DOC when it was not fitted with a catalyst than when it was fitted with a catalyst. The 4-nitrophenol emission factors were also lower for vehicle-DOC with a catalyst than vehicle-DOC without a catalyst, suggesting that the oxidation catalyst was a source of both nitro-PAHs and 4-nitrophenol. The time-resolved aerosol mass spectrometry data suggested that nitro-organic compounds are mainly produced when an engine is working under load. The presence of 4-nitrophenol in the particles was not confirmed statistically because of interference from gaseous 4-nitrophenol. Systematic errors in the estimated amounts of gaseous 1-nitropyrene and 9-nitroanthracene adsorbed onto the filters and the estimated amounts of volatile nitro-organic compounds that evaporated during sampling and during post-sampling conditioning could not be excluded.

Abbreviations: 1NP, 1-nitropyrene; 9NA, 9-nitroanthracene; DEP, diesel exhaust particle; DOC, diesel oxidation catalyst; DPF, diesel particulate filter; DPNR, diesel PM-NO_x reduction; EC, elemental carbon; EF, emission factor; HC, hydrocarbon; LC/MS, liquid chromatography/mass spectrometry; LNT, lean NO_x trap; NO_x, nitrogen oxides; NSR, NO_x storage reduction; OC, organic carbon; PAH, polycyclic aromatic hydrocarbon; PM, particulate matter; PNM, 3-methyl-4-nitrophenol; PNO, 2-methyl-4-nitrophenol; PNP, 4-nitrophenol; SCR, selective catalytic reduction; TC, total carbon; TD-GC/MS, thermal desorption gas chromatography/mass spectrometry; vehicle-DOC, diesel truck with an oxidation catalyst; vehicle-DPNR, diesel truck with a PM-NO_x reduction system; vehicle-GASOLINE, compact gasoline passenger car with a three-way catalyst; vehicle-SCR, diesel truck with a urea-selective catalytic reduction system; VOC, volatile organic compound.

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An analytical method in which all gaseous compounds are absorbed before particles are collected, and in which the volatile compounds are derivatized, would improve the precision and the accuracy of the data.
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1. Introduction

Diesel engines are important sources of nitrogen oxides (NO_x), volatile organic compounds (VOCs), and fine particulate matter (PM) to the urban atmosphere (Lloyd and Cackette, 2001). These pollutants negatively affect air quality and, therefore, negatively affect human health (HEI, 2010). NO_x and VOCs are precursors of photochemical ozone and PM, which contribute to urban and regional haze (Atkinson, 2000; Jenkin and Clmitshaw, 2000; Monks et al., 2009). Diesel exhaust particles (DEPs) contain various organic compounds, including polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (oxy-PAHs), and nitro-PAHs (Levsen, 1988). Some types of VOC and DEP emissions are toxic and cause adverse health effects in humans (IARC, 2010, 2013). Nitro-PAHs, thought to be produced by the nitration of PAHs during combustion (Pitts et al., 1978), account for large proportions of the direct-acting mutagens in DEPs (Hayakawa et al., 1997; Schuetzle, 1983). Several types of nitrophenol have also been found in DEPs (Nojima et al., 1983; Taneda et al., 2004a), and these have vasodilatory effects and estrogenic and anti-androgenic activities (Taneda et al., 2004b).

New technologies for treating exhaust gases (i.e., aftertreatments) have been developed to decrease NO_x and DEP emissions from diesel vehicles (Hammerle et al., 1994; Johnson, 2009; Knecht, 2008; Maricq, 2007). Selective catalytic reduction (SCR) and lean NO_x traps (LNTs) can be used to control NO_x emissions. SCR works by reducing NO_x on a selective catalyst using an ammonia-based reductant (e.g., urea, $(\text{NH}_2)_2\text{CO}$). LNTs store NO_x as nitrates on alkaline earth materials under lean conditions and allow the nitrates to dissociate under slightly rich conditions every minute or so, releasing the NO_x , which are then converted by an integrated three-way catalyst (Johnson, 2009). A diesel particulate filter (DPF) has been developed to control PM, and all new diesel vehicles in Europe, Japan, and the United States have or will shortly have DPFs (Johnson, 2009). A DPF is usually coupled with a diesel oxidation catalyst (DOC), which oxidizes hydrocarbons (HCs) to CO_2 , burning the fuel to actively regenerate the filter and generating NO_2 to passively regenerate the DPF (Johnson, 2009). It has been reported that DPFs very effectively convert gaseous HCs and PM-associated PAHs (Ratcliff et al., 2010). However, the secondary production of some nitro-PAHs during catalytic aftertreatments has been found in several recent studies (Heeb et al., 2008, 2010). Locating a DOC upstream of a DPF allows the intentional conversion of NO to NO_2 , to accelerate the oxidation of accumulated PM in the DPF (Kobayashi et al., 2008).

We have previously investigated emissions of gaseous nitro-organic compounds in automotive exhausts during transient cycles using a chassis dynamometer system, and we determined the effects of various aftertreatments on nitro-organic compound emissions (Inomata et al., 2013; Sekimoto et al., 2013). We tested three diesel trucks (one each fitted with a DOC, a PM- NO_x reduction system, and a urea-based SCR system) and a gasoline passenger car. Of the mononitro-organic compounds determined, nitromethane was commonly found in the automotive exhausts. Nitromethane emissions were suppressed when a NO_x -reduction catalyst using HCs was used (Sekimoto et al., 2013). Other nitro-organic compounds (e.g., nitrophenols and

dihydroxynitrobenzenes) were emitted in the gaseous phase, but their emissions appeared to depend on the vehicle and, particularly, the type of aftertreatment used. Indeed, the results of our study suggested that gaseous nitrophenols and dihydroxynitrobenzenes, along with acetic acid, phenol, and acetonitrile, were formed by the oxidation catalyst (Sekimoto et al., 2013). The emission of nitromethane in automotive exhausts was confirmed by measurements at a busy intersection (Inomata et al., 2014).

In the study presented here, we used thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) and liquid chromatography/mass spectrometry (LC/MS) to analyze nitro-PAHs and nitrophenols in DEPs collected on filters during transient cycles of a chassis dynamometer system. When quantifying nitro-organic compounds in diesel vehicle exhausts, it should be noted that organic compounds can easily be nitrated on the sampling filter, resulting in sampling “artifacts” (Levsen et al., 1988). Therefore, we conducted some experiments to investigate the influences of such artifacts and then assessed the dependence of nitro-organic compound emissions in DEPs on the aftertreatment used.

2. Materials and methods

2.1. Experiments using the chassis dynamometer

Experiments were performed using a chassis dynamometer system equipped with a constant-volume sampler (later called a “dilution tunnel”; DLT-1860 ($40 \text{ m}^3 \text{ min}^{-1}$) or CVS-7400T ($120 \text{ m}^3 \text{ min}^{-1}$); Horiba, Kyoto, Japan) at the National Traffic Safety and Environment Laboratory, Japan (Inomata et al., 2013; Yamada et al., 2011). Three diesel trucks, one fitted with an oxidation catalyst (DOC; the vehicle is later called vehicle-DOC), one with a PM- NO_x reduction system (DPNR; vehicle-DPNR), and one with a urea-based SCR system (vehicle-SCR), and a compact gasoline passenger car (vehicle-GASOLINE) (Sekimoto et al., 2013) were tested. The specifications of the vehicles are given in Table 1. The DPNR system consisted of a NO_x storage reduction (NSR) catalyst, a wall-flow-type-DPF coated with the NSR catalyst, and a DOC. A fuel injector was mounted upstream of the system. The NO_x was trapped by the NSR and converted into N_2 under fuel-rich conditions (fuel being added using a fuel injector). PM trapped by the DPF was mainly oxidized during a regeneration period initiated by heat released by fuel being oxidized on the NSR catalyst (Shoji et al., 2004). A three-way catalyst was used to aftertreat the vehicle-GASOLINE exhaust gas. The exhaust gas from each vehicle was diluted with filtered (through a high-efficiency-particulate-air filter and a charcoal filter) air (later called “background air”) by an average factor of 57 for vehicle-DOC, 15 for vehicle-DPNR, 68 for vehicle-SCR, and 39 for vehicle-GASOLINE. The background air was kept at 298 K and 50% relative humidity. Each vehicle was set on the chassis dynamometer and driven according to the appropriate Japanese transient emission test cycle, JE05 for the diesel trucks and JC08 for the vehicle-GASOLINE (Sekimoto et al., 2013). Each vehicle was warmed by performing the test cycle before starting a hot-start experiment (referred to as JE05H for the diesel trucks and JC08H for vehicle-GASOLINE). Each vehicle was left for 8–48 h in a

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