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Emissions of particulate associated oxygenated and native polycyclic aromatic hydrocarbons from vehicles powered by ethanol/gasoline fuel blends

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ABSTRACT

Emission factors for oxygenated polycyclic aromatic hydrocarbons (OPAHs) and PAHs have been determined from two different fuel flexible light duty vehicles operated at −7 °C in the New European Driving Cycle (NEDC) and at +22 °C in the Artemis Driving Cycle (ADC). Three different gasoline/ethanol blends, commercially available in Sweden, were tested i.e., gasoline E5, with 5% v/v ethanol and ethanol fuel E85 with 85% v/v ethanol and winter time quality E70 with 70% v/v ethanol, respectively.

The results showed greatly increased emissions of both OPAHs and PAHs at cold engine start conditions (−7 °C in the NEDC) compared to warm engine start (+22 °C in the ADC). For the OPAHs, higher average total emission factors were obtained when running on E85 compared to E5 at both cold 2.72 μg/km vs 1.11 μg/km and warm 0.19 μg/km vs 0.11 μg/km starting conditions with the highest emissions when using E70 at −7 °C 4.12 μg/km. The same trend was found for the PAHs at cold engine start with higher average total emission factors when using ethanol fuel 71.5 μg/km and 60.0 μg/km for E70 and E85, respectively compared to gasoline E5 (20.2 μg/km). Slightly higher average total PAH emissions were obtained when operating at +22 °C with E5 compared to with E85 1.23 μg/km vs 0.72 μg/km.

1. Introduction

Particulate matter (PM) in air has a negative health impact on humans and accounts as one of the most important outdoor air pollutants [1,2]. Air PM is generated from both natural and anthropogenic sources and exposure to respirable PM can cause various health problems like cardiovascular disease, lung cancer and asthma [3–7]. Air PM is a very chemically complex matrix and contains toxic organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs (OPAHs). PAHs and OPAHs are directly formed during incomplete combustion of organic material in air and emitted from both natural and anthropogenic sources e.g. fossil automotive fuels, coal/wood burning and forest fires [8,9]. A second formation process of OPAHs is photochemical reactions of PAHs in the presence of NO and NO_2 or ozone radicals in the atmosphere [10,11]. OPAHs are suspected to be more toxic than the parent PAHs and to cause adverse biological effects due to their direct mutagenic activity [12,13]. Anthraquionone (AQ) has been classified by the International Agency for Research on Cancer (IARC) as a possible carcinogen to humans (Group 2B) [12]. Meanwhile, numerous PAHs are classified as probably or possibly carcinogenic to humans (groups 2A and 2B) by the IARC [14]. Benzo[a]pyrene (B[a]P), is the most studied PAH and is the only PAH that has been classified as a human carcinogen (Group 1) by IARC [15]. Furthermore, a group of PAHs with a molecular weight of 302 Da i.e., the dibenzopyrene isomers (DBPs) have demonstrated high carcinogenic potencies in animal tests [16,17]. Four of these DBPs: dibenzo[a,l]pyrene (DB[a,l]P), dibenzo[a,e]pyrene (DB[a,e]P), dibenzo[a,i]pyrene (DB[a,i]P) and dibenzo[a,h]pyrene (DB[a,h]P) have been listed as expected human carcinogens by the US Department of Health and Human Services [18]. DB[a,l]P has been reported as the most potent carcinogen of all PAHs tested in rodents [13]. The formation and emission of OPAHs and PAHs into the environment is of high concern and in urban areas traffic could be a significant contributor to air levels of OPAHs and PAHs [19–21].

Interest in bio fuels with a non-petroleum carbon source has increased with increasing number of vehicles globally [22]. In 2003, the European Union (EU) passed a directive with the aim to substitute 5,75% of petrol and diesel fuels with biofuels (on energy basis) before year 2010 [23]. Sweden has taken this challenge seriously and has set this level as a national target. Several other measures have been made

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to remove barriers (e.g. legislative and economic) to facilitate this development. In Sweden, a national specification for E85 i.e. 15% gasoline and 85% ethanol (v/v) including a winter quality, E70, 30% gasoline and 70% ethanol was adopted in 2006. This fuel has been introduced on the market by the oil companies in the autumn of 2007. Presently in Sweden, all regular gasoline contains at least 5% ethanol. Exhaust emissions from vehicles in general are defined as regulated and unregulated, regulated exhaust emissions are unburned fuel hydrocarbons (HC), nitrogen oxides (NOx), carbon monoxide (CO) and for diesel cars particulate matter (PM) [24].

Unregulated emissions of PAHs and in particular OPAHs from flex fuel vehicles running on gasoline/ethanol fuel blends are not well studied. We have previously reported the emissions of PAHs from vehicles running on E5, E70 and E85 at cold and warm ambient conditions for two passenger cars operated in two different real world driving cycles [25]. A selection of these samples has in the present study been analyzed for OPAHs and PAHs using a recently developed and validated method.

2. Experimental and material

2.1. Sampling

Exhaust particles from two flex fuel passenger cars a Saab 95 (FFV1) and a Volvo V50 (FFV2) (both Euro 4) operated in two different driving cycles were analyzed in the present study. The New European Driving Cycle (NEDC) is the test cycle used for emission certification of light duty vehicles. The NEDC tests were performed at cold ambient temperature (−7 °C). The second driving cycle used was the Artemis Driving Cycle (ADC), which includes three cycles referred to as Artemis Urban, Artemis Road and Artemis Motorway [25]. The ADC tests were performed at +22 °C. Three gasoline/ethanol fuel blends were tested: Swedish commercial petrol (5% ethanol in gasoline (E5) and ethanol fuels (E85 and winter quality E70 with 85% and 70%) ethanol in gasoline, respectively. The sampling was performed using a constant volume sampling system (CVS) with a dilution of the exhaust applied; this step is important in-order to simulate the dilution of the exhaust in the atmosphere [25]. Particulate exhaust samples were collected on Teflon coated glass fiber filters (Pallflex Inc T60A20, Putnam, USA). After sampling the filters were stored in a freezer until chemical analysis. Detailed description of the driving cycles, vehicles, fuels and sampling procedures used as well as of analysis of regulated and unregulated exhaust emissions can be found elsewhere [25].

2.2. Chemical analysis of OPAHs and PAHs

The solvents used in this study were methyl *tert*-butyl ether (MTBE), hexane, toluene and methanol (MeOH) all were of HPLC-grade from Rathburn Chemicals Ltd, UK. Ethanol was from Kemetyl AB (Haninge, Sweden) and anhydrous dodecane (> 99%) from Sigma Aldrich (St. Louis, MO, USA).

A complete list of the PAH and OPAH standards and surrogate internal standards, with supplier information, purity and abbreviations used in this study can be found in detail elsewhere [26].

Filter parts (about one quarter of each filter) were spiked with a mixture of six perdeuterated surrogate internal standards: phenanthrene-D_{10}, pyrene-D_{10}, benz[a]anthracene-D_{12}, B[a]P-D_{12}, benzo[ghi]perylene-D_{12} and anthraquinone-D_8 prior to extraction. The samples were extracted using an accelerated solvent extraction system (ASE 200, Dionex Corporation, Sunnyvale, CA, USA) with toluene: methanol (Tol: MeOH, 9:1) as extraction solvent. The extract was evaporated to approximately 5 ml under a gentle gas stream of nitrogen in a water bath heated to about 60 °C. The extracts were then transferred to disposable test tubes and further evaporated to 0.5 ml. Clean-up was performed using silica solid phase extraction (SPE) cartridges (100 mg, Isolute, IST, UK) with toluene as mobile phase. A detailed description of the extraction procedure and the SPE clean-up method can be found in detail elsewhere [26,27]. Furthermore, blank filters were processed in the same manner as the samples to check for contaminations.

2.3. Instrumental analysis

A hyphenated High Performance Liquid Chromatography Gas Chromatography/Mass Spectrometry (LC-GC/MS) system was used for the analysis of OPAHs and PAHs. This system consists of an auto sampler (CMA/200 micro sampler, CMA Microdialysis AB, Sweden), a HPLC pump (Varian Inc, Palo Alto, CA, USA), an UV detector (SPD-6A, Shimadzu, Japan) and a normal phase LC column (Nucleosil 100-5NO2 124 × 4.6 mm, 5 μm) which was coupled to an Agilent 6890 N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) fitted with a DB-17MS column (60 m × 0.25 mm i.d. x 0.1 μm film thickness) and interfaced with an Agilent 5973 N MSD (Agilent Technologies). A description of the setup of this online system and the parameters used for the determination of OPAHs and PAHs are described in detail elsewhere [27,28].

3. Results and discussion

Emission factors in ng/km were derived for the two vehicles operated in five different driving conditions as described in Table 1. Average emission factors for 4 OPAHs and 23 PAHs are shown in Tables 2 and 3 respectively.

3.1. OPAHs

More than ten times higher average total OPAH emission factors were obtained when driving the vehicles at cold ambient temperature −7 °C compared to running the vehicles at a temperature of + 22 °C, Table 2. However, the difference might to some extent be caused by the different driving cycles used: NEDC at −7 °C and ADC at +22 °C. At both warm and cold engine start conditions higher average total OPAH emissions were obtained when driving the vehicles with E85 (0.19 μg/km at +22 °C and 2.72 μg/km at −7 °C) compared to when operating with E5 (0.11 μg/km at +22 °C and 1.11 μg/km at −7 °C). Highest average total OPAH emissions were obtained with the winter quality ethanol fuel E70 at −7 °C with almost four times higher values compared to running on gasoline (E5), Table 2. The most abundant OPAH in almost all the samples was AQ. This is in agreement with previous studies on OPAHs in outdoor air particulate matter from traffic sites [29–31].

To our knowledge there is no data in the literature on emission factors of OPAHs from vehicles fueled with gasoline/ethanol blends and studies on the emission factors of OPAHs from motorized vehicles. Significantly higher emission factors of AQ compared to those obtained in the present study have previously been reported from heavy duty vehicles fueled with diesel. Rogge and co-workers determined an emission factor of 23.5 μg/km [32], while another study reported emission factors of 9.1 μg/km and 10.4 μg/km [8].

Table 1
Driving modes used.

Fuel	E5	E70	E85	E5	E85
Temperature	−7 °C	−7 °C	−7 °C	+22 °C	+22 °C
Driving cycle	NEDC	NEDC	NEDC	ADC	ADC
Replicates FFV1	2	0	2	2	1
Replicates FFV2	1	2	2	1	2

NEDC = New European Driving Cycle.
ADC = Artemis Driving Cycle.
E5 = 5% ethanol blend.
E70 = 70% ethanol blend.
E85 = 85% ethanol blend.