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Emission of polycyclic aromatic hydrocarbons from gasohol and ethanol vehicles

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ABSTRACT

The exhaust emission of the polycyclic aromatic hydrocarbons (PAHs) considered toxic to human health were investigated on two spark ignition light duty vehicles, one being gasohol (Gasohol, in Brazil, is the generic denomination for mixtures of pure gasoline plus 20–25% of anhydrous ethyl alcohol fuel (AEAF).)-fuelled and the other a flexible-fuel vehicle fuelled with hydrated ethanol. The influence of fuel type and quality, aged lubricant oil type and use of fuel additives on the formation of these compounds was tested using standardized tests identical to US FTP-75 cycle. PAH sampling and chemical analysis followed the basic recommendations of method TO-13 (United States. Environmental Protection Agency, 1999. Compendium Method TO-13A – Determination of polycyclic Aromatic hydrocarbons (PAH) in Ambient Air Using Gas Chromatography/Mass Spectrometry (CG/MS). Center for environmental research information, Cincinnati, p. 78), with the necessary modification for this particular application.

Results showed that the total PAH emission factor varied from 41.9 $\mu g\,km^{-1}$ to 612 $\mu g\,km^{-1}$ in the gasohol vehicle, and from 11.7 $\mu g\,km^{-1}$ to 27.4 $\mu g\,km^{-1}$ in the ethanol-fuelled vehicle, a significant difference in favor of the ethanol vehicle. Generally, emission of light molecular weight PAHs was predominant, while high molecular weights PAHs were not detected. In terms of benzo(*a*)pyrene toxicity equivalence, emission factors varied from 0.00984 μg TEQ km^{-1} to 4.61 μg TEQ km^{-1} for the gasohol vehicle and from 0.0117 μg TEQ km^{-1} to 0.0218 μg TEQ km^{-1} in the ethanol vehicle.

For the gasohol vehicle, results showed that the use of fuel additive causes a significant increase in the emission of naphthalene and phenanthrene at a confidence level of 90% or higher; the use of rubber solvent on gasohol showed a reduction in the emission of naphthalene and phenanthrene at the same confidence level; the use of synthetic oil instead of mineral oil also contributed significantly to a decrease in the emission of naphthalene and fluorene. In relation to the ethanol vehicle, the same factors were tested and showed no statistically significant influence on PAH emission.

1. Introduction

The world fleet of motorized vehicles launches millions of tons of pollutants into the Earth's atmosphere daily, frequently leading to poor air quality conditions, mainly in large urbanized areas, causing, among other effects, human health deterioration and climate change.

The profile of pollutants emitted from light-duty vehicles can be considered unique in Brazil due to the use of: (i) a mixture of gasoline and ethanol (gasohol), (ii) plain hydrated ethanol in vehicles that account for approximately 11% of the vehicle fleet at this time, and (iii) flexible-fuel vehicles (FFV) that can use either gasohol or HEAF[1], or any mixture of them. The FFV fleet currently represents about 5% of the total Brazilian fleet, and is rapidly growing.

Apart from regulated pollutants, vehicles are also responsible for the emission of other pollutants, such as polycyclic aromatic hydrocarbons (PAHs), some of them already recognized as being carcinogenic to mammals, and also leading to an increase in human morbidity and mortality rates (WHO, 1998; Saldiva et al., 2001).

Sixteen PAHs are considered priority pollutants in terms of health effects: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, dibenz(*a*,*h*)anthracene and benzo(*g*,*h*,*i*)perylene (WHO, 1998).

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[1] HEAF: Hydrated ethyl alcohol fuel.

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Table 1
CAS number, molecular weight and equivalent toxicity factors of 16 PAHs.

PAH	CAS number	Molecular weight ($g\ mol^{-1}$)	ATSDR (2001)
Naphthalene	91-20-3	128.18	0
Acenaphthylene	208-96-8	152.20	0.001
Acenaphthene	83-29-9	154.20	0.001
Fluorene	86-73-7	166.23	0.001
Phenanthrene	85-01-8	178.24	0.001
Anthracene	120-12-7	178.24	0.01
Fluoranthene	206-44-0	202.26	0.001
Pyrene	129-00-00	202.26	0.001
Benzo(*a*)anthracene	56-55-3	228.30	0.1
Triphenylene	217-59-4	228.30	<0.001
Chrysene	218-01-9	228.30	0.001
Benzo(*b*)fluoranthene	205-99-2	252.32	0.1
Benzo(*k*)fluoranthene	207-08-9	252.32	0.01
Benzo(*a*)pyrene	50-32-8	252.32	1
Indeno(1,2,3-*cd*) pyrene	193-39-5	276.32	0.1
Dibenz(*a*,*h*)anthracene	53-70-3	276.32	1
Benzo(*g*,*h*,*i*)perylene	191-24-2	278.35	0.01

Extracted from: ATSDR (2001).

Some authors consider benzo(*a*)pyrene the most toxic, and recommend its use as a reference with a toxicity factor of 1 on an equivalent toxicity scale. These authors also suggest that the other 15 compounds should receive relative values regarding their respective carcinogenic potencies (toxicity factors), determined by comparative assays. Table 1 shows the equivalent toxicity factors recommended by the Agency for Toxic Substances and Disease Registry (ATSDR, 2001). In this paper all results expressed in TEQ refer to the ASTDR's benzo(*a*)pyrene equivalent toxicity factors. Nitro- or oxy-PAHs were not within the scope of this study.

Incomplete combustion plays an important role in PAH emissions. Studies have shown that the higher the amount of aromatics in the fuel the greater the emission of these compounds in the exhaust of vehicles (Westerholm and Li, 1994; Mi et al., 2000).

Some fuel additive manufacturers claim that its use helps to reduce pollutant emission (Silva, 2003). Although important for the analysis of its contribution to emission, the chemical compositions of fuel additives are not disclosed. The chemical composition of fuel additives is only reported in a generic way, for example: phenolic compounds, polyether-amines, polymethacrylates, copolymers, polyisobutileno-amines, among others. However, in Brazil, product constituents that can cause damage to human health must be reported to the Brazilian Federal Administration (ANP, 1999).

Vehicle aging can also cause an increase in PAH emissions, due to the burning of lubricant oil vapors in the combustion chamber. This is caused by the enlargement of gaps in the engine's moving parts, which usually leads to an increase in lubricant oil consumption (Lee et al., 1995; Sher, 1998).

Lee et al. (1995) and Sher (1998) also showed that PAH emissions increase in moments of vehicle acceleration, due to the richer air/fuel ratio, and during the initial minutes of vehicle operation, when the catalytic converter is still not so effective because its working temperature is below the ideal one.

PAH emissions from gasohol vehicles compared to PAH emissions from ethanol vehicles, and the extent to which several factors influence these emissions, were the objectives of this study, which is part of a bigger project on toxic substances in air and pollution sources being developed by the toxic pollutants research group of the Department of Environmental Health, University of São Paulo, Brazil.

2. Materials and methods

Experiments were carried out at the CETESB's vehicle testing laboratory (Vehicular Emission Laboratory of the São Paulo State Environment Agency) in São Paulo, Brazil. Standardized assays were performed in a chassis dynamometer using the standardized driving cycle (ABNT, 2005), which simulates the urban driving condition and is identical to the US FTP-75 cycle. This testing cycle was adopted by Brazil for legal certification of emissions of new light-duty vehicles. The influence of fuel type and quality, aged lubricant oil type and the use of fuel additives on the formation of PAHs was tested.

2.1. Vehicles

Two vehicles were used, one gasohol fuelled and one a flexible-fuelled type vehicle. Both are similar to the most frequently used vehicles in São Paulo in terms of average mileage and age (ANFAVEA, 2006). The vehicles were at half-life, with at least 50 000 km traveled, equipped with catalytic converters and electronic fuel injection systems. The catalytic converters were still in good working condition, in which, according to Brazilian legislation, new vehicles should be under their respective emission limits until at least 80 000 km (CONAMA, 1986, 2002).

The gasohol vehicle was manufactured in 1998, had 1111 kg mass, and was equipped with an engine of 1.6 L volumetric capacity, with a torque of 15.1 kg m at 4500 rpm and 78 kW of power at 5500 rpm. The vehicle was received for the assays with an odometer reading of 67 546 km.

The flexible-fuel vehicle was manufactured in 2004, had 1111 kg mass, a 1.6 L volumetric capacity, 14.4 kg m of torque at 3000 rpm and 73 kW of power at 5750 rpm. The vehicle was received for assays with an odometer reading of 56 908 Km. Tests were conducted using only hydrated ethanol as a fuel in this car.

2.2. Assay planning and conditions

Experiments were planned according to a statistical factorial design. This approach reduces the number of assays while extracting the maximum amount of information on the effects of tested factors on changes in the results of the system being studied (Box et al., 2005; Bruns et al., 2006).

Nine assays with the gasohol vehicle were planned as follows:

- 1 assay with commercial gasohol and mineral oil lubricant, without fuel additive;
- 1 assay with premium[2] gasohol and mineral oil lubricant, without fuel additive;
- 3 assays with standard gasohol for emission assay and synthetic oil lubricant, without fuel additive;
- 1 assay with standard gasohol for emission assay with fuel additive and mineral oil lubricant;
- 1 assay with adulterated gasohol and mineral oil lubricant, without fuel additive;
- 2 assays with adulterated gasohol with fuel additive and synthetic oil lubricant.

These configurations compose a 2^{3-1} fractional factorial design that allows the simultaneous determination of the influence of several variables (Bruns et al., 2006).

Before use in the tests, oil lubricants were aged in a vehicle fuelled with just gasohol until reaching their operational half-lives. The mineral oil lubricant was aged for about 2500 km and the synthetic oil was aged for about 5000 km. All gasohol fuel used in these assays contained 22% hydrated ethanol in volume. The adulterated standard gasohol was obtained mixing 80% of standard

[2] Premium gasohol has a minimum anti-knocking Index of 91 and is suitable for high performance vehicles.