Correlations between the exhaust emission of dioxins, furans and PAH in gasohol and ethanol vehicles

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Abstract

The emissions of seventeen 2,3,7,8 substituted Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans (PCDD/Fs) and sixteen Polycyclic Aromatic Hydrocarbons (PAH) [14] in the exhaust pipes of spark ignition light duty vehicles considered toxic to human health were investigated. The formations of these compounds were evaluated under the influence of variations of fuels and fuel additives.

Standard tests in a gasohol (gasohol is pure gasoline plus 20% to 25% of anhydrous ethyl alcohol fuel (AEAF)) vehicle and in an ethanol vehicle were performed with variations in the quality of fuels. The sampling of the PCDD/Fs followed the recommendations of a modified 23 method and the analysis basically followed the 8290 method. The recommendations of the TO-13 method were followed for the PAH analysis, with the necessary modifications for a vehicular emission laboratory.

The emission factors of the total PCDD/Fs varied between undetected and 0.157 pg I-TEQ/km. The emission factors of the total PAH varied from 0.01 μg TEQ/km to 4.61 μg TEQ/km.

Significant and positive correlations were observed between the emissions of naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene and fluoranthene and significant and negative correlations were observed between the emissions of CO_2 and fluoranthene in the gasohol vehicle. Significant and positive correlations between carbon monoxide and phenanthrene and between acenaphthylene, fluorene and fluoranthene in the alcohol vehicle were also observed, apart from significant and negative correlations between NOx and phenanthrene. In general way, significant correlations between PAH and PCDD/Fs were not observed, except in the ethanol vehicle considering phenanthrene.

Keywords: vehicular emissions, PCDD/Fs, PAH, air pollution, toxic pollutants, gasohol, ethanol.

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1 Introduction

Vehicles are responsible for some pollutants that, due to their toxicities, can alter the morbidity and mortality rates of populations. The emissions of some pollutants, such as the PCDD/Fs and PAH from vehicles have the potential to cause damage to human health [9]. Some of these pollutants are carcinogenic to mammalians, even at very low concentrations [5, 16].

PCDD/Fs are formed in combustion process where chlorine atoms are present. The chlorine sources for PCDD/Fs formation can be fuels and fuels additives. Small amounts of chlorine may not be removed from the fuels during refining process. Moreover, chlorine compounds can also be added to premium gasoline to improve engine performance [15].

Information about chemical composition of fuel additives is furnished in just a generic way, but it is possible that organic chlorides can be mixed with fuels additives to improve engine performance [6, 7]; however the Brazilian Federal Administration must be informed about substances that can cause damage to human health [3].

In vehicles, PAH can be formed from incomplete fuel burning and from annealing aromatics rings. PAH emissions can also increase with vehicle aging, due to rising of lubricant oil consumption in the combustion chamber, caused by enlargement of the gaps in the engine's moving parts [10].

Considering the importance of these compounds in relation to human health, the aim of this work was to study the relations between PCDD/Fs and PAH, considered toxic to human health, in the exhaust pipe of spark ignition light duty gasohol and ethanol vehicles.

2 Materials and methods

2.1 Vehicle testing conditions

To carry out this study, two spark ignition light duty vehicles, equipped with catalytic converters and electronic injection systems, have been used, a gasohol vehicle (GV) and a flexible fuel vehicle (EV) fuelled just with hydrated ethyl alcohol fuel (HEAF). They were representative of the vehicle fleet in the State of São Paulo, which corresponds to 36% of the Brazilian fleet [2]. The vehicles characteristics are shown in Table 1.

The assays were carried out in the vehicular emission laboratory of the State Environment Agency (Cetesb) in São Paulo, Brazil. A standardized driving cycle in a chassis dynamometer was performed [1] that simulates the urban conditions. It is identical to the American driving cycle FTP-75 procedure (USEPA).

With the purpose of establishing possible correlations between PCDD/Fs and PAH, factors that could influence the emission of these pollutants, like rate of aromatics in the fuels and fuel additives, were varied under controlled conditions, in nine assays in the GV (from G1 to G9) and six assays in the EV (from A1 to A6). All these variations compose a 2^{3-1} fractional factorial design, which allows determination of the influence of each variable [4].

Table 1: Vehicle characteristics.

	Year	Mass (kg)	Motor (L)	Torque (k/gm at rpm)	Power (kW at rpm)	Odometer reading (km)
GV	1998	1111	1.6	15.1 at 4500	78 at 5500	67 546
EV	2004	1111	1.6	14.4 at 3000	73 at 5750	56 908

2.2 Collection and analysis

Sampling of the exhaust gas was performed during the entire working time of the vehicle. The collection of PCDD/Fs was carried out based on a modified 23 method [13] and in the work developed by RYAN and GULLETT [8].

Raw gas was sampled through a heated line, in order to collect PCDD/Fs. Solid phase was collected in two heated 70 mm diameter quartz fibre filters (120 ºC), while the gaseous phase was collected in a cooled at 7 ºC 60 mm diameter polyurethane foam (PUF), all of them assembled in series. The condensed material collected upstream the PUF was also sent for analysis. The extraction and analysis were done based in an adapted and validated 8290 method [12]. The PCDD/Fs were identified and quantified by HRGC/HRMS.

Diluted gas was sampled through a simple line, in order to collect PAH. The PAH were identified and quantified by GC/MS according an adapted TO-13 method [14]. The retention of solid phase was done by filtration; two quartz fibre filters with 47 mm in diameter were used, while a 22 mm diameter pre-washed PUF was used for retention of the gaseous phase, all of them assembled in series. Regulated pollutants were also quantified, according Brazilian legislation [1].

3 Results and discussion

The emissions rates of regulated pollutants obtained according Brazilian legislation, and CO_2, are shown in Figure 1. The values obtained are typical of vehicles with these mileages and technology of pollutants control. In the GV, the average emissions rates were 3.3 g/km of carbon monoxide (CO), 0.3 g/km of total hydrocarbons (HC), 0.5 g/km of nitrogen oxides (NOx) and 215.8 g/km of carbon dioxide (CO_2). In the EV, the average emissions rates were 0.7 g/km of CO, 0.3 g/km of HC, 0,3 g/km of NOx and 201.2 g/km of CO_2. In general way, EV emitted less regulated pollutants than GV.

The PAH emissions rates per distance travelled in the GV are shown in Figure 2. The average emissions rates were: 153.1 µg/km of naphthalene, 32.0 µg/km of acenaphthylene, 3.5 µg/km of acenaphthene, 5.3 µg/km of fluorene, 16.3 µg/km of phenanthrene, 3.5 µg/km of anthracene, 5.9 µg/km of

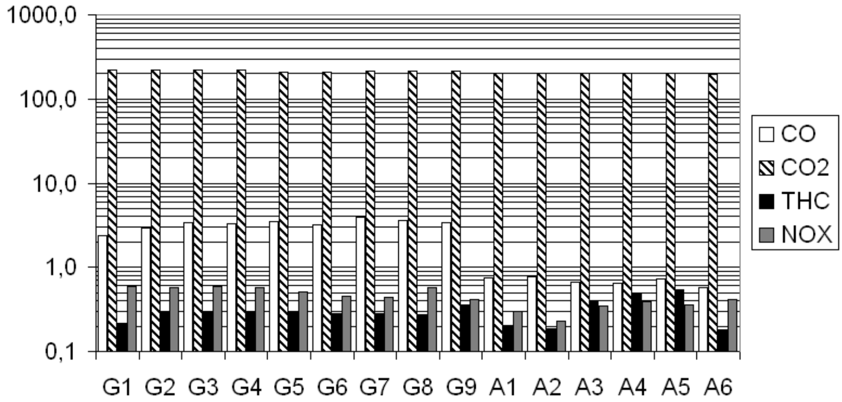

Figure 1: Regulated pollutants emission in the vehicles, in g/km.

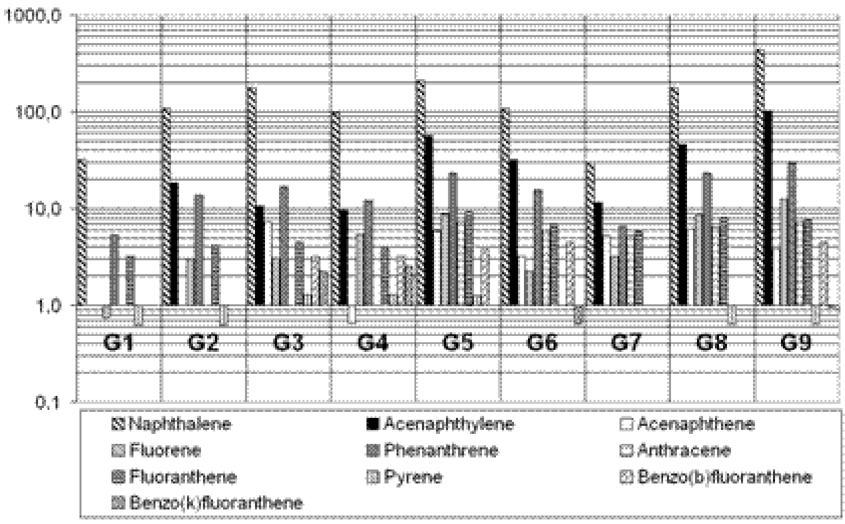

Figure 2: PAH Emission in the GV, in μg/km.

fluoranthene, 0.7μg/km of pyrene, 0.8 μg/km of benzo(a)anthracene, 2.1 μg/km of benzo(b)fluoranthene, 0.7 μg/km of benzo(k)fluoranthene. Benzo(a)pyrene was quantified in just one assay. chrysene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene were not detected. In general way, the higher PAH molecular weight represented lower emissions rates.

The PAH emissions rates per distance travelled in the EV are shown in Figure 3. The average emissions rates were 3.0 μg/km of naphthalene, 2.8 μg/km of acenaphthylene, 0.9 μg/km of acenaphthene, 0.6 μg/km of fluorene, 7.7 μg/km of phenanthrene, 4.0 μg/km of fluoranthene. Others PAH were not detected. The emission rates of PAH from EV are far lower than GV, in average 92% lesser. The PCDD/Fs emissions rates per distance travelled are shown in Figure 4. In the GV, the average emissions rates were 2.4 pg/km of 1,2,3,4,6,7,8 Hepta Chlorinated Dibenzo-p-Dioxins (HpCDD), 16.5 pg/km of Octa Chlorinated Dibenzo-p-Dioxins (OCDD). 1,2,3,4,6,7,8 Hepta Polychlorinated Dibenzofurans (HpCDF) was quantified in just one assay. Others PCDD/Fs were not quantified, and none of the 17 PCDD/Fs studied were detected in the G8 and G9 assays. In the EV, average emissions rates were 21.2 pg/km of OCDD. HpCDD was quantified in just one assay. Others PCDD/Fs were not detected. The emissions of PCDD/Fs showed large dispersions and non-regular behaviour.

3.1 Hierarchical cluster analysis

This procedure attempts to identify relatively homogeneous groups of variables based on selected characteristics, using an algorithm that starts with each variable in a separate cluster and combines clusters until only one is left.

The results of samples were submitted to Hierarchical Cluster Analysis (HCA) with the intention of determine the relations between the compounds. The variables were standardized by z-score method, before computing the proximities, because the magnitudes of results are very different. The association levels between the pollutants were defined using the Ward’s method (method of minimum variance) as measure of similarity combined with Euclidean distance.

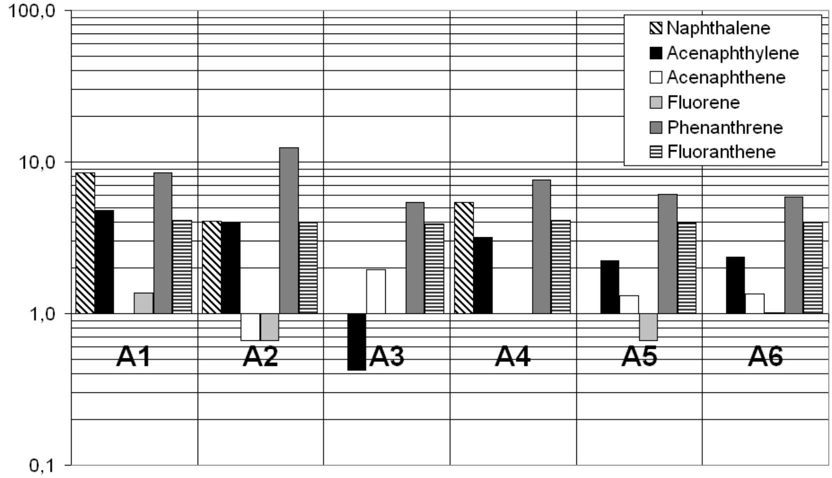

Figure 3: PAH emission in the EV, in μg/km.

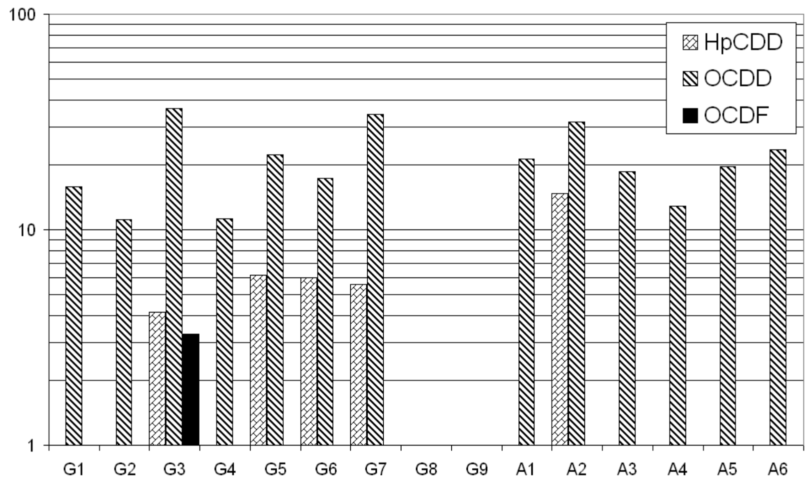

Figure 4: PCDD/Fs emission in the vehicles, in pg/km.

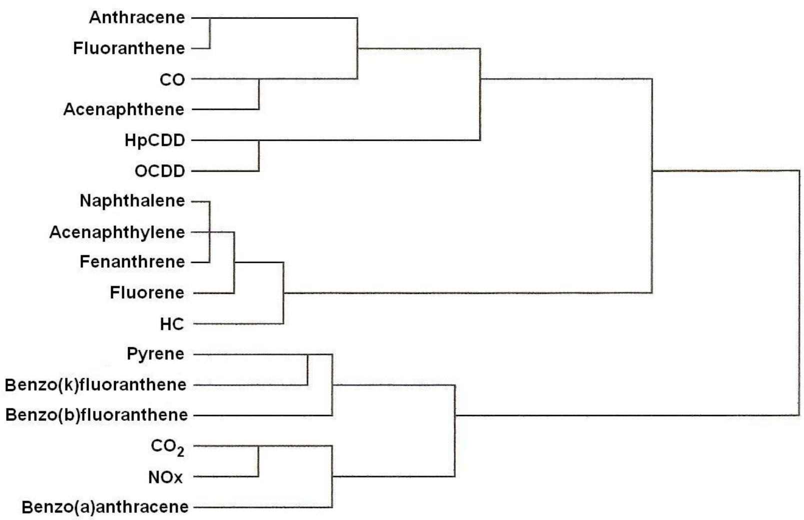

Figure 5: Dendrogram of GV obtained by Ward's method, using Euclidean distance.

The dendrogram in Figure 5 shows the results of HCA and the similarities level between the pollutants from GV. There are five groups of pollutants, the first one characterized by anthracene, fluoranthene, CO and acenaphthene, the correlation coefficient between them is not significant, except between anthracene and fluoranthene, which is 0.94. The second is the PCDD/Fs group that does not show similarities with others compounds.

The third group shows a relationship between HC and naphthalene, acenaphthylene, phenanthrene and fluorene, the correlation coefficients between all of them are very significant, above 0.7. The fourth group shows a relationship between pyrene, benzo(k)fluoranthene and benzo(b)fluoranthene, which were not detected in all assays, and the correlation coefficients are not significant. In the fifth group benzo(a)anthracene are related with CO_2 and NOx, however the correlation coefficients are also not significant. Significant and negative correlation coefficients of –0.87 are observed between the emissions of CO_2 and fluoranthene.

The dendrogram in Figure 6 shows the results of HCA and the similarities level between the pollutants from EV. There are three groups of pollutants, the first one characterized by CO_2, HC and NOx and acenaphthene, the correlation coefficients between them are not significant. In EV, HC not belongs to the light PAH group, because the main part of HC is not burned ethanol, different than occurred with GV, where the main part of HC is not burned gasoline.

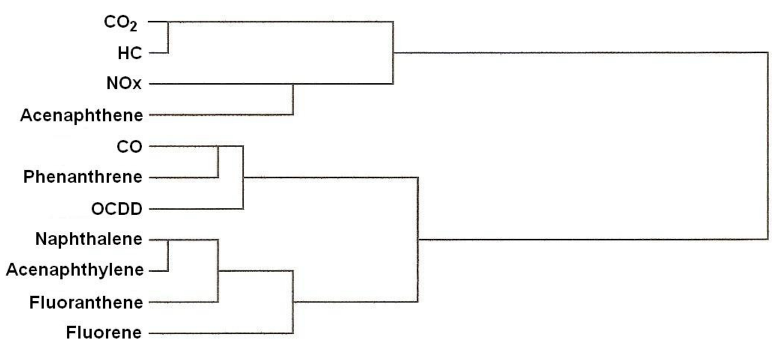

Figure 6: Dendrogram of EV obtained by Ward's method, using Euclidean distance.

Second group relates CO, phenanthrene and OCDD. The correlation coefficients between CO and phenanthrene is 0.71, and the correlation coefficients between phenanthrene and OCDD is 0.68, indicating some relationship between then, and in certain way shows the opposite than proposed by Stanmore [11], that suggests that "de novo" formation process of PCDD/Fs was mainly proportional to the number of phenanthrene skeletons, instead annealing of aromatic rings.

The main part of HC in GV is not burned fuel, what means a phenanthrene skeletons source, however, in GV, phenanthrene and PCDD/Fs correlation is not significant, even belong the same group, according Figure 5. On the other hand, PAH in EV are formed predominantly by annealing process, once there are no aromatics in the fuel, as there is correlation between phenanthrene and OCDD, exists the possibility that PCDD/Fs are also formed mainly by annealing of aromatic rings in ethanol combustion process.

Moreover, in the second group, the correlation coefficient between CO_2 and OCDD is -0.72, and the correlation coefficient between HC and OCDD is -0.72. The correlation coefficient between NOx and phenanthrene is -0.85.

Third group shows a relationship between light and medium molecular weights PAH, the correlation coefficient between acenaphthylene and fluoranthene is 0.73 and the correlation coefficient between fluorene and fluoranthene is 0.98.

The correlation coefficient between acenaphthene and acenaphthylene is -0.98, between acenaphthene and acenaphthylene is -0.98 and between acenaphthene and fluoranthene is -0.87, probably the reason by acenaphthene belongs another group, according Figure 6.

4 Conclusions

The two light duty vehicles used in these experiments were sources of PCDD/Fs, mainly OCDD, and PAH of light and medium molecular weight, high molecular weights PAH were not detected. In general way, with some exceptions, Hierarchical Cluster Analysis grouped the pollutants by their respective families, except in the case of ethanol vehicle where phenanthrene and OCDD have significant correlation coefficients, different than occurred in GV, what suggests that, in vehicles, PCDD/Fs are formed mainly by annealing of aromatic rings.

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