Exhaust emissions of PAHs of passenger cars

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Abstract: Exhaust emissions of 16 PAHs referenced by the U.S. Environmental Protection Agency (USEPA) are measured using a vehicle bench on a sample of passenger cars. 13 gasoline vehicles and 17 diesel vehicles are tested, complying with ECE 1504 to Euro 3 emission standards, according to to 3 real-world driving cycles based on European driving behaviour (2 urban and 1 motorway. The quantification of the 16 PAHs is carried out by HPLC with fluorometric detection.
The effect of cold or hot start is carried out with the short urban INRETS cycle.
The PAH distribution in particulate and gaseous phases is studied for all of the vehicles for the four types of driving.

The influence of the successive emission standards on the emission factors is very positive in most of the cases. Diesel vehicles are more polluting for PAH. The majority of volatile PAH is observed in the gas phase, but the less volatile and the carcinogenic PAH are more adsorbed in particle phase.

Keywords: driving cycle, PAH, HPLC, passenger cars, gasoline, diesel.

1. Introduction

Transport activities contribute significantly to air pollution in Europe. Reliable and credible emission estimates are a central prerequisite. Some of the priority research topics in atmospheric transport emissions (Joumard, 1999a) are the estimation of non regulated pollutants (NRP), the impact of cold engine start (Joumard, 1996) and the database updating of unitary emission for recent vehicles.
Previous studies have been achieved on this topic (Combet, 1993), (Paturel, 1996), (Miguel, 1998), (Schauer, 2002) and the different PAH results obtained need to be completed.

Thirty vehicles (gasoline and diesel) have been tested over three driving cycles representative of real-world driving conditions (Joumard, 1999b). These results have been obtained as part of ARTEMIS "Assessment and reliability of transport emission models and inventory systems" and ADEME projects. These projects will first result in the determination of the transport emission factors for regulated and non regulated pollutants.

2. Methods

Driving cycles

The cycles were carried out on a controlled bracking chassis dynanometer. Each vehicle was tested over two types of driving cycles (André, 2002):

- two cycles which are representative of the actual driving conditions in Europe, called *urban and motorway VP low/high motorisation*, under hot engine start conditions.
- one short cycle, called Inrets short urban free-flow, repeated 15 times with the first cycle being carried out under cold or hot engine start condition.

Vehicle characteristics

Thirty passenger cars (17 diesel and 13 gasoline) registered from 1990 to 2002 and representative of european fleet have been tested. Table 1 shows the number of vehicles for each reglementation.

Reglementation	Gasoline	Diesel	
Euro 1	2	4	6
Euro 2	6	12	18
Euro 3	5	1	6
	13	17	

Table 1 : Vehicle repartition.

Sample collecting and processing

A classical Constant Volume Sampling (CVS) system is used. In parallel to the emissions of regulated pollutants, PAHs are collected at the end of the dilution tunnel at ambient temperature by means of a filter and an adsorber as described previously (Paturel, 1996). The system consists of two stainless steel cartridges separated by a stainless steel grid and filled with 15g of Teflon wool and 20g of XAD2 Amberlite polymer which are well suitable respectively for particulate and gaseous PAH sampling.

All PAHs were extracted by cyclohexane ultrasonic method performed over 30min at 37°C. After evaporation near to dryness, extracts were dissolved in n-octane. To eliminate polar compounds a clean-up was performed on silica cartridges with an elution by n-hexane. After evaporation, residues were dissolved in acetonitrile. All solvents used were of spectrometric grade.

HPLC analysis

The study was carried out on a Merck-Hitachi chromatograph equipped with a LiChroCart column, fed by an injection loop with a volume fixed at 20µl and coupled with adsorption and fluorescence spectrometers. Elution was performed using ACN/H2O in mobile phase at a flow of 1ml/mn.

Average recovery factors for the whole procedure are calculated for each PAH using spiked Teflon wool and XAD2 Amberlite resin.

Only Acenaphthylene (Acy) is detected with UV absorption at 254 nm . Unit emissions (µg km^{-1}) are corrected for analytical blanks, air dilution and recovery factors.

3. Results and Discussion

PAH distribution profile

An example of total PAH distributions for gasoline and diesel vehicles is presented in Fig. 1.
Acy is rarely quantified in emissions due to high limit of detection and poor selectivity.
Very similar PAH distributions are observed for these two gasoline and diesel vehicles. A relation between the values of unit emissions and the volatility of the PAHs appears : N with 2 rings is predominant (~50/90% of the sums expressed in mass) and then a decrease is pointed out for the 3 rings (Ace, Flu, An, Phe), the 4 rings (Fla, Pyr, BaA, Chr) and the 5 and 6 rings (BbF, BkF, BaP, BghiP, IP, DbahA) with respectively 25, 5 and 1% of the total. This distribution is similar to the one obtained by Mi et al. (1998).
All patterns of results are quite similar for all driving cycles and all cars.

Very low recovery factors (5 to 40%) and important errors are observed for N, Ace, Flu due to their volatility (Boiling point < 300 °C, Henry constant : about 1.10^{-4} atm m^3 mol^{-1}) responsible of important losses during extraction processes. So, results will be expressed per individual PAH, as sums of the 12 less volatile PAHs, and sums of the 6 most carcinogenic PAHs (BaA, BbF, BkF, BaP, DBahA, IP) (IARC, 1983), (IARC, 1987).

Figure 1: Mean distribution of PAHs for Euro 2 vehicles (gasoline and diesel) according to VP low/high motorisation hot emissions.

Reglementation influence

The means of the 12 PAH sums for gasoline (13) and diesel (17) are presented for the 4 driving cycles in Fig. 2.

Figure 2 : Means of the 12 PAH sums according to the reglementation.
Confidence interval deviation is calculated as 2 times the standard deviation.

Gasoline Euro1 and diesel Euro3 reglementations concern respectively 2 and 1 vehicles ; consequently, the evolution observed needs a confirmation. Furthermore, emission values for Inrets urban fluid cycle with cold engine start and Artemis european motorway cycle are not available for gasoline Euro1. The histogram highlights from Euro1 to Euro3 that reglementation has a positive influence on the diesel emissions (decrease of 5 to 20 times according to cycle) and that at the opposite the gasoline classes show a negative evolution in their emissions.
For the both technologies in the case of hot cycles the two urban (INRETS and VP) lead to similar mean values.

In the case of cold engine start, the PAH emission increase is especially enhanced for gasoline vehicles: the ratios of emissions between cold and hot engine starts are respectively 10 to 2 and 1.4 for gasoline and diesel vehicles.

Gaseous and particulate distribution

For the two technologies, Table 2 shows the gaseous and particulate distribution for the more volatile, the less volatile and the 6 carcinogenic PAHs.

PAH sums	Gasoline	Diesel
3 PAHs (volatile : N, Ace, Flu)	89/11	49/51
12 PAHs (less volatile)	45/55	12/88
6 PAHs (carcinogenic)	32 / 68	28/72

Table 2 : Average gaseous and particulate distribution (%) for hot cycles.

The majority of volatile PAHs are principally in the gaseous phase (50/90 %) while the less volatile or the carcinogenic PAHs are more adsorbed on particulates (55/90%). The distribution of PAHs on particulates is more important for diesel vehicles.

Conclusion

This work shows that the unit emissions of the 12 less volatile PAHs are very similar according to hot driving cycles. For gasoline cars an important over emission is observed for the INRETS urban free-flow cycle with cold engine start.

Sampling of PAHs both in particulate and gaseous phases is indispensable to have a good quantification of these non regulated pollutants (NRP) in the vehicular emissions particularly for volatile PAHs (two to four rings).

Finally, for all hot cycles, a large decrease is observed for the emissions of PAHs according to the evolution of reglementation for the diesels. In the case of gasoline vehicles, a weak decrease is only obtained for the cold engine start cycle.

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