

# COMPARISON OF PAH LEVELS AND MUTAGENICITY OF GDI- AND DIESEL VEHICLE EXHAUSTS AND IMPACT OF (BIO)ETHANOL

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## BACKGROUND

GDI vehicles appear to be a promising technology for reducing exhaust emissions and fuel consumption. However, several sources reported high emissions of particles exceeding the Euro 6 limit of  $6 \times 10^{11}$  particles/km. In addition, increased emissions of genotoxic pollutants (e.g. Polycyclic aromatic hydrocarbons or PAHs) are produced. PAHs are known to induce genotoxic responses inside cells causing mutations, which may lead to cancer. The WHO also classified several PAHs as carcinogenic, like benzo(a)pyrene, a group 1 carcinogen.

## METHODOLOGY

Complete exhaust samples sampled from a CVS tunnel (Fig. 1.A), including solid, condensed and gaseous fractions were collected from 5 GDI vehicles. Vehicles were driven following the WLTC (World Harmonized Light Vehicles Test Cycle) under hot (WLTC-H) and cold (WLTC-C) start conditions. Vehicle 1 was also tested with two ethanol blends (E10 and E85). In addition, an Euro-5 diesel vehicle equipped with a filter was tested. Samples went through extraction and cleanup procedures and were analyzed by HRGC-HRMS. Concentrations of the genotoxic PAHs were determined (Fig. 2).

To evaluate the mutagenicity, aliquots of the exhaust extracts (5%) of vehicle 1 in WLTC-H, with E0, E10, E85 and the diesel vehicle were tested for mutagenicity using the bacterial Ames test (Xenometrix, *S. typhimurium*, strains TA98 and TA100). Different concentrations (C1-C6, two fold dilutions, C1 low to C6 high) of the extracts were directly exposed to the bacteria for 1.5 h, then dispersed in histidine-free medium and incubated for a 48-h period at 37 °C. Exhaust extracts collected in the WLTC-C, for all vehicles were also tested with the mutagenicity Ames test in order to compare the whole GDI fleet with the diesel vehicle.

## RESULTS

Fig. 3. shows the effect of the ethanol blends on PAH concentrations ( $\text{ng}/\text{Nm}^3$ ) and respective patterns for the WLTC-C and WLTC-H. There is a significant decrease on the emissions when ethanol is used. WLTC-H is also decreasing compared to WLTC-C, when ethanol is used. Except for E10, patterns are similar but differ with respect to absolute values. Fig. 4 shows the concentrations in  $\text{ng}/\text{Nm}^3$  and patterns of genotoxic PAHs for all GDI-vehicles and diesel vehicle with filter. Patterns and PAH emission levels differ from vehicle to vehicle. Fig. 5 displays the fold-increase of revertants over the negative control for the samples E0, E10, E85 and diesel in WLTC-H, with the strain TA 98. There were no signs of mutagenicity in the TA100 strain. A three-fold or higher increase in the number of revertants relative to the negative control or a clear dose response suggests mutagenicity. This is the case for E0 at the concentration C6. Regarding the fleet, no significant differences were found in the Ames test.

## CONCLUSIONS

**Ethanol effect.** The concentrations of genotoxic PAHs decrease with increased ethanol contents. This decrease is in accordance with the particle number, which is also reduced.

**GDI fleet emissions.** All GDI vehicles tested emit more genotoxic PAHs than the diesel vehicle (which included a particle filter), some emitted even 1 order of magnitude higher concentrations.

**Ames test results.** From all dose-tests performed, only the gasoline sample (E0, WLTC-H) at C6 showed a significant response with TA 98 strain, meaning “probably mutagenic” and being in accordance with the PAH concentration (the highest also in WLTC-H with E0). No significant results were found for other samples. However, these experiments should be reconfirmed with higher doses.

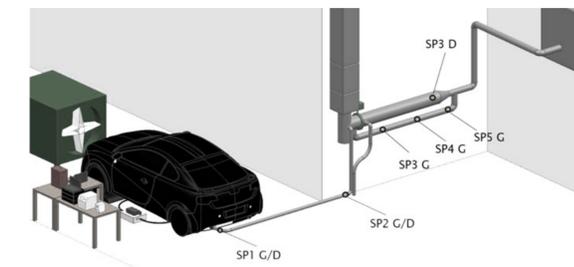
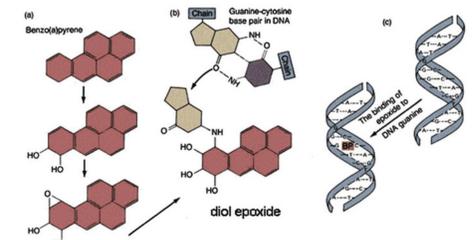
## ACKNOWLEDGEMENTS

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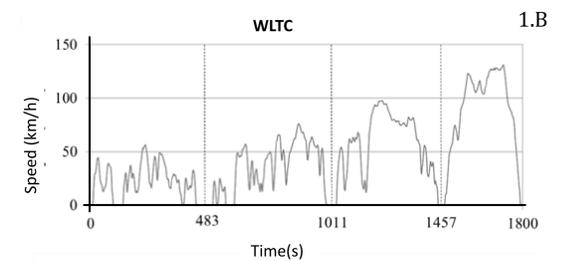
## GENOTOXIC EXHAUST ?



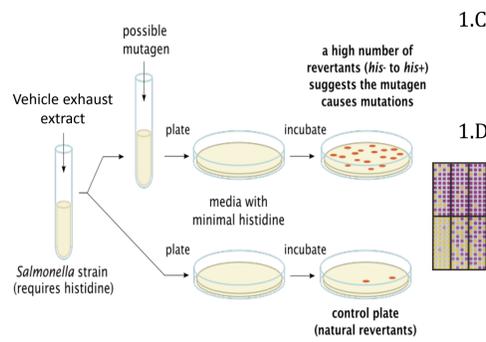
## Genotoxic effect of benzo(a)pyrene



1.A



1.B



1.C

1.D

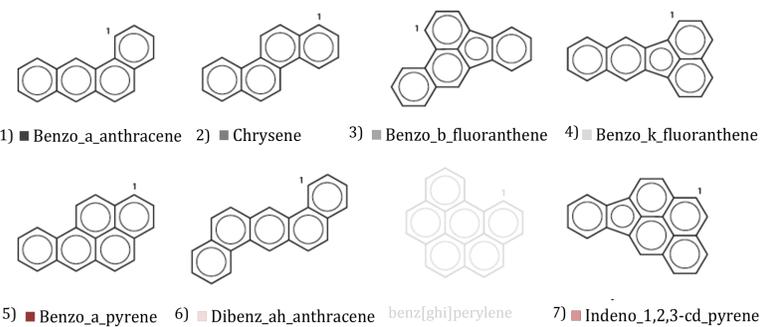


Fig.1. Sampling setup (1.A), driving cycles (1.B) and scheme of Ames test with an example of a mutagenicity test plate (1.C and 1.D)

Fig. 2. The 7 genotoxic PAH. According to the WHO, these PAHs are genotoxic, with benzo(a)pyrene being a class 1 carcinogen.

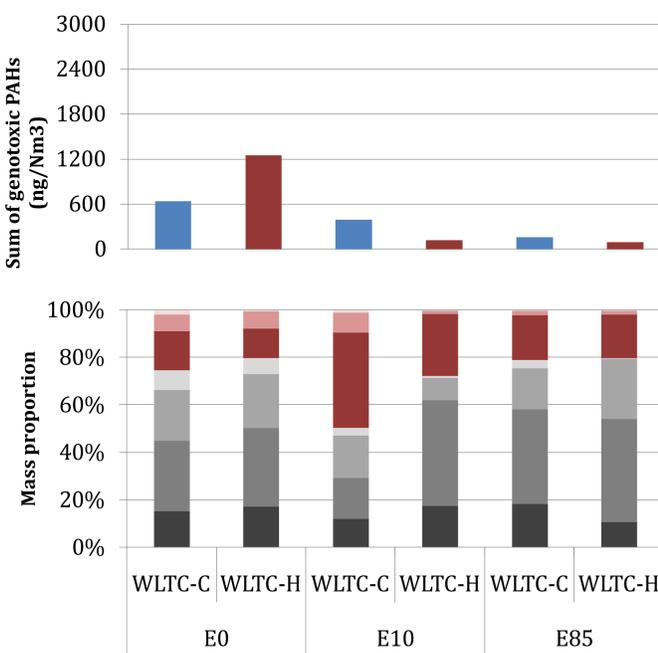


Fig. 3. Ethanol effect on PAH emissions. Concentration of genotoxic PAHs in  $\text{ng}/\text{Nm}^3$  (top, WLTC-C in blue, WLTC-H in red) and respective patterns (bottom, color code in Fig.2).

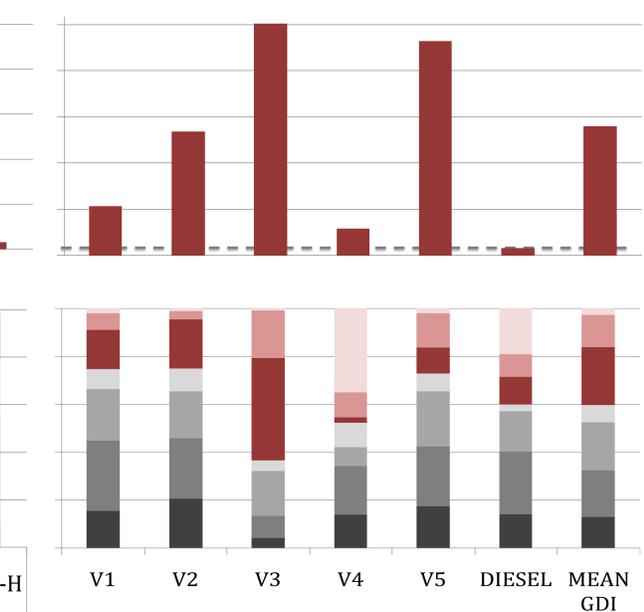


Fig. 4. Emissions of PAHs of the GDI fleet and comparison with the diesel vehicle. Concentration of genotoxic PAHs in  $\text{ng}/\text{Nm}^3$  (top) and respective patterns (bottom).

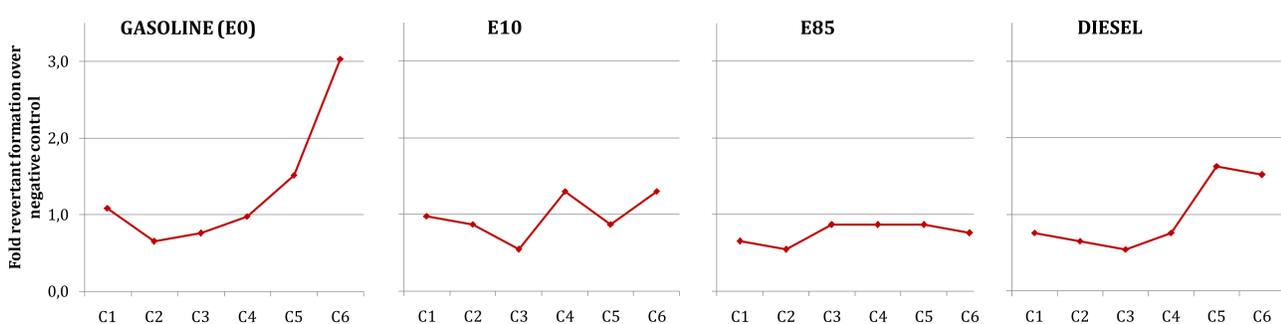


Fig. 5. Exhaust mutagenicity (Ames test, strain TA98, WLTC-H). Fold revertant is obtained by dividing the number of revertants in the sample by the number in the negative control (untreated sample) indicating mutagenicity if higher or equal to 3. C1-C6 correspond to the different concentrations tested, C6 being the highest.