PAH and Nitro-PAH emissions from GDI vehicles

Dr. Maria Muñoz Fernandez

Coauthors: Dr. Norbert Heeb and GASOMEP Team

Postdoctoral Researcher at the GasOMep Project

Laboratory for Advanced Analytical Technologies, EMPA

maria.munozfernandez@empa.ch
Are GDI vehicle exhausts as genotoxic as those of diesel engines?

GENOTOXIC EMISSIONS?

GasOMeP
Chemical characterization
OVERVIEW

Introduction

• Energy data and diesel case
• Polycyclic aromatic hydrocarbons
• Genotoxicity

Sampling and Laboratory analysis

• Detailed HRGC-HRMS analysis

Results

Conclusions
Swiss energy consumption

Energy consumption traffic (313.220 TJ, 35% in 2013)

Energy consumption 2013

Total: 896 000 TJ

Transportation: 313 220 TJ

- Transportation: 35%
- Household: 18%
- Services: 17%
- Manufacturing: 29%
- Gasoline: 38%
- Diesel: 22%
- Kerosene: 4%
- Electricity: 36%
- Gas and others: 1%

Statistic differences including agriculture

Quelle: BFE – Gesamtenergiestatistik

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Swiss Federal Office for Statistics
GDI vehicles on the rise

Gasoline/diesel production in EU:
- 50/50 in **2010** (18 mio vehicles/y)
- 60/40 in **2020** (22 mio vehicles/y)
  half of the gasoline vehicles are GDI

**30% of EU fleet** will be GDI in **2020** with

**53 mio cumulated in 2010-2020**
DIESEL ENGINE EXHAUST
Carcinogenic to humans (Group 1)

Miners study, Silverman et al.
JNCI, 104(11), 2011

Particulate matter (PM)
Particles exceed those of diesel with filter
(Mohr et al., Environ. Sci. Technol., 40 2375-2383, 2006)

1000x more than other gasoline vehicles
10x more than new diesel vehicles

New pollutants
DIESEL
GDI

Particle filters?
PAHs (Polycyclic Aromatic Hydrocarbons)

1) naphthalene
2) acenaphthylene
3) acenaphthene
4) fluorene
5) phenanthrene
6) anthracene
7) fluoranthene
8) pyrene
9) benzo(a)anthracene
10) chrysene
11) benzo[b]fluoranthene
12) benzo[k]fluoranthene
13) benzo[a]pyrene
14) dibenz[ah]anthracene
15) benz[ghi]perylene
16) indeno(1,2,cd)pyrene
# AGENTS CLASSIFIED BY THE IARC MONOGRAPHS, VOLUMES 1–112

<table>
<thead>
<tr>
<th>Group</th>
<th>Classification</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>Carcinogenic to humans</td>
<td>116</td>
</tr>
<tr>
<td>Group 2A</td>
<td>Probably carcinogenic to humans</td>
<td>73</td>
</tr>
<tr>
<td>Group 2B</td>
<td>Possibly carcinogenic to humans</td>
<td>287</td>
</tr>
<tr>
<td>Group 3</td>
<td>Not classifiable as to its carcinogenicity to humans</td>
<td>503</td>
</tr>
<tr>
<td>Group 4</td>
<td>Probably not carcinogenic to humans</td>
<td>1</td>
</tr>
</tbody>
</table>
PAHs (Polycyclic Aromatic Hydrocarbons)

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Group 1
Group 2A
Group 2B
Nitro- and alkyl- PAHs

**Nitro-PAHs**
- 3,9-dinitro-fluoranthene
- 3,7-dinitro-fluoranthene
- 7) fluoranthene
- 8) pyrene

**Alkyl-PAHs**
- 5-methyl-chrysene
- 10) chrysene

**Group 2A**
- 6-nitro-chrysene
- 1-nitro-pyrene

**Group 2B**
- 4-nitro-pyrene
- 1,3-dinitro-pyrene
- 1,6-dinitropyrene
- 1,8-dinitropyrene

**Nitro-PAHs**
- 1-nitro-pyrene
- 4-nitro-pyrene
- 1,3-dinitro-pyrene
- 1,6-dinitropyrene
- 1,8-dinitropyrene
**GENOTOXICITY: The Benzo[a]pyrene example**

<table>
<thead>
<tr>
<th>Carcinogen</th>
<th>Environmental source</th>
<th>Major active metabolite</th>
<th>Sites of modification</th>
<th>Major type of mutation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[a]pyrene</td>
<td>Tobacco smoking Combustion processes</td>
<td>B[a]P-7,8-dihydrodiol 9,10-epoxide (BPDE)</td>
<td>N(^2)-Guanine N(^6)-Adenine</td>
<td>GC → TA</td>
</tr>
</tbody>
</table>

Pathway of metabolic activation and DNA adduct formation of benzo[a]pyrene
SAMPLING PROCEDURE

Several GDI vehicles:
- 3 different brands
A non-catalytic filter

- Chassis dynamometer, UASB, Nidau

WLTC
- HOT start

SSC
- COLD start

From J. Czerwinski Group, Berner Fachhochschule
LABORATORY ANALYSIS

- Diluted exhaust - CVS tunnel: solid + condensed + gaseous phases

 ASE/Soxhlet extraction  Concentration  Cleanup and fractionation  HRGC/HRMS analysis
DIFFERENT VEHICLES

2-3 RINGS and PYRENE

Boiling point

Naphthalene

Phenanthrene

Pyrene

218 °C

404 °C
CONCLUSIONS

- Emissions decrease under hot start conditions (vehicles without filter)
- The higher the boiling point the better the FILTRATION EFFICIENCY

- The higher the boiling point the higher the emissions on hot start conditions

\[ \text{COLD start conditions} \]

- PAH storage/release ??
- PAH formation ??

- Nitro-PAHs in ambient levels
THANK YOU VERY MUCH FOR YOUR ATTENTION

Maria Muñoz-Fernandez
Postdoctoral Researcher, EMPA
maria.munozfernandez@empa.ch