

PAH and Nitro-PAH emissions from GDI vehicles

Dr. Maria Muñoz Fernandez

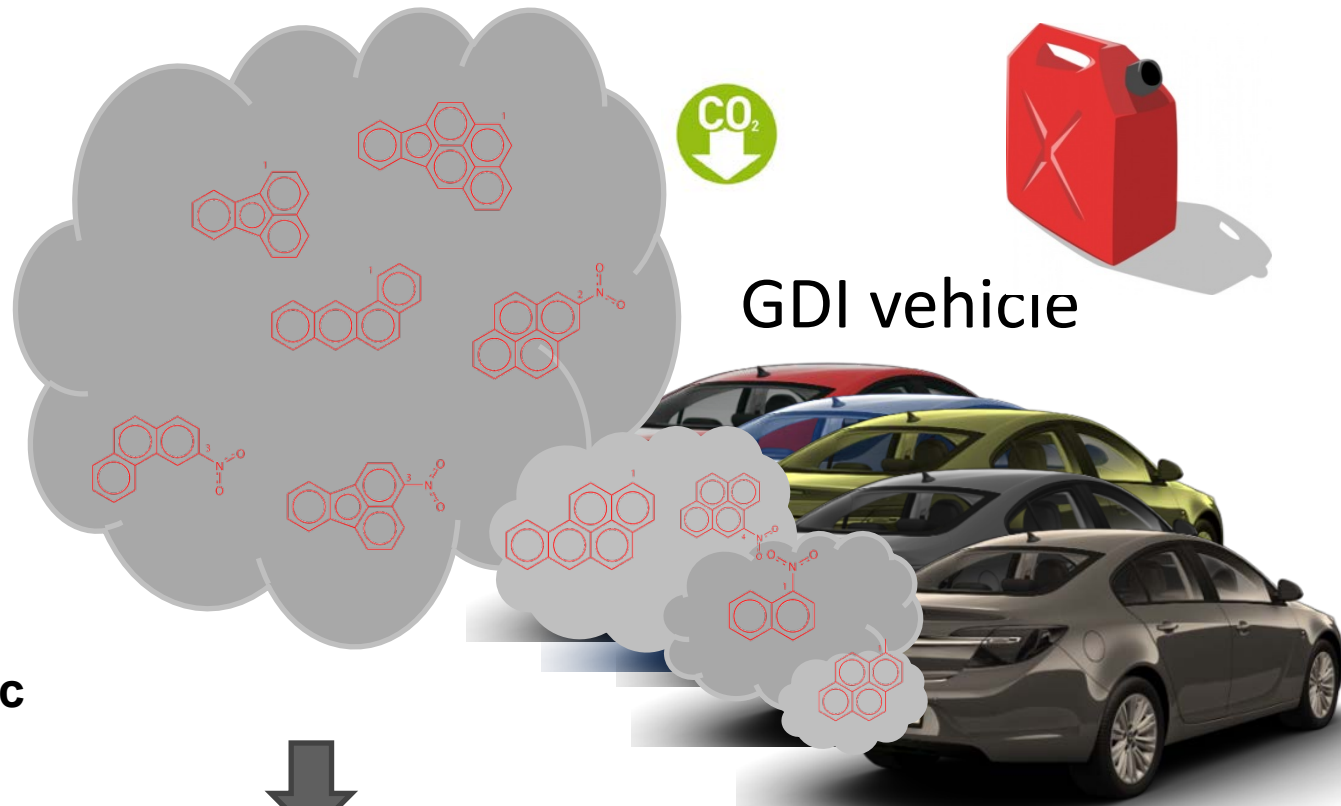
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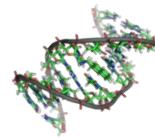


**Are GDI vehicle
exhausts as genotoxic
as those of diesel
engines?**

GENOTOXIC EMISSIONS ?

GasOMeP

Chemical characterization



OVERVIEW

Introduction

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

Sampling and Laboratory analysis

- Detailed HRGC-HRMS analysis

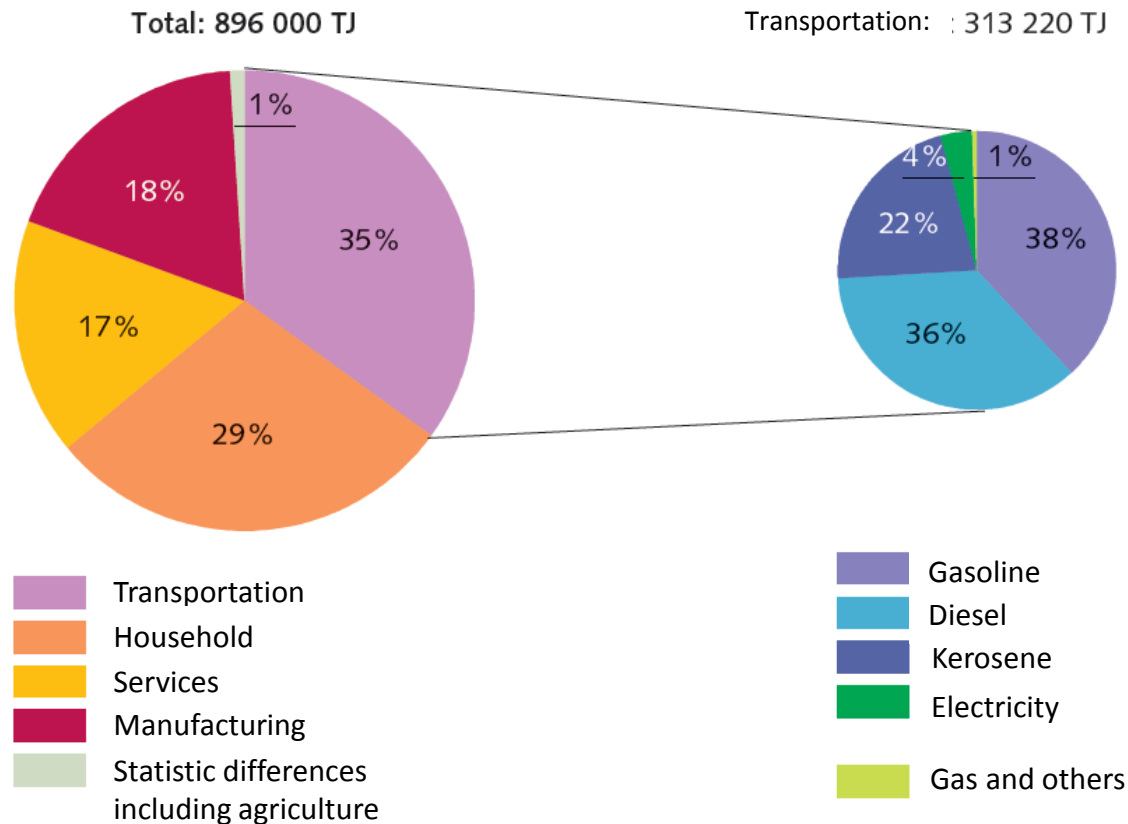
Results

Conclusions

Swiss energy consumption

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

Energy consumption 2013



Quelle: BFE – Gesamtenergiestatistik

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Swiss Federal Office for Statistics

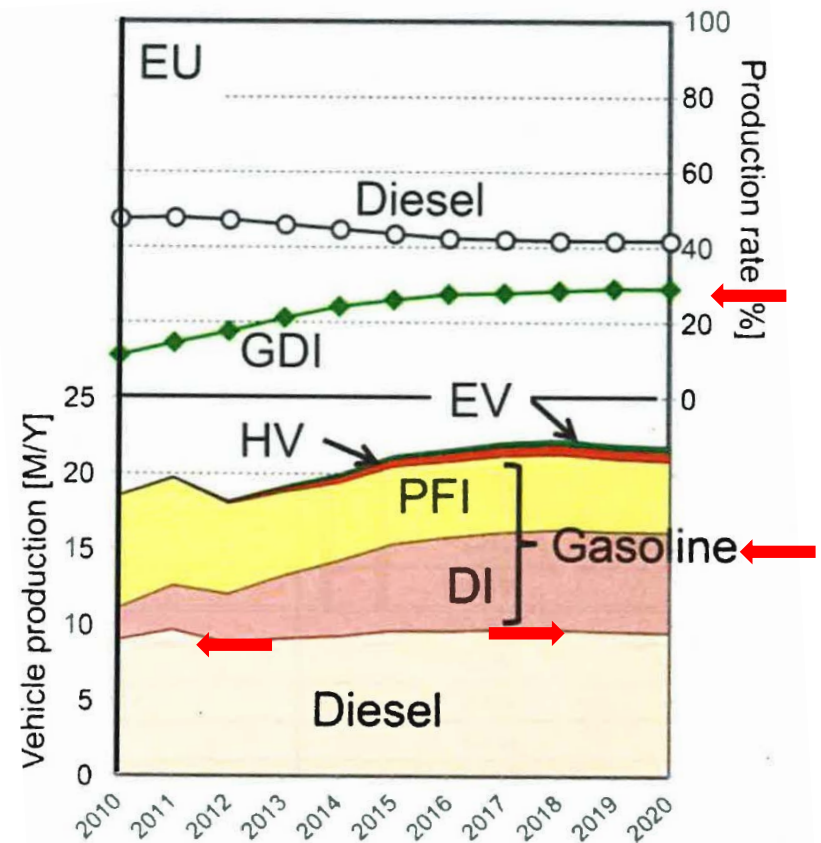
GDI vehicles on the rise

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





International Agency for Research on Cancer



DIESEL ENGINE EXHAUST
Carcinogenic to humans
(Group 1)

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

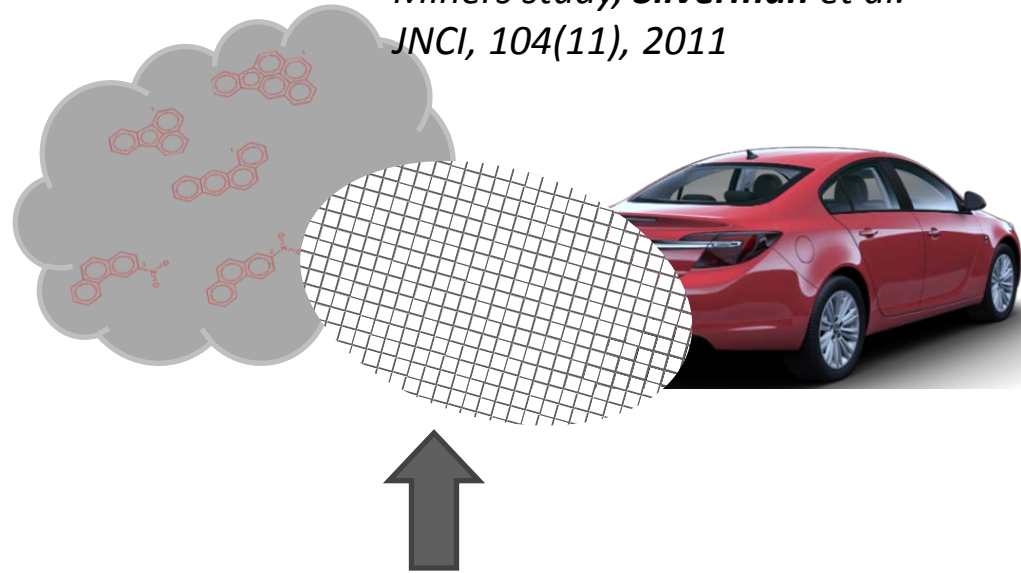
DIESEL

New pollutants

GDI

***Particles exceed those
of diesel with filter***

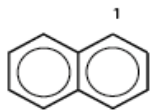
(Mohr et al., Environ. Sci. Technol., 40 2375-2383, 2006)



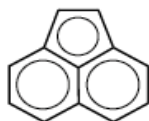
Particle filters ?

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

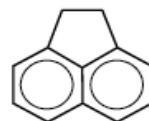
PAHs (Polycyclic Aromatic Hydrocarbons)



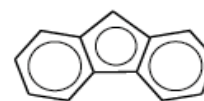
1) naphthalene



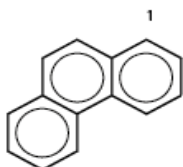
2) acenaphthylene



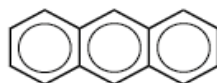
3) acenaphthene



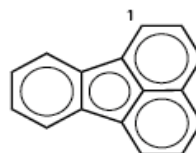
4) fluorene



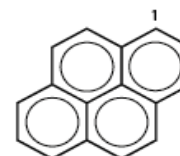
5) phenanthrene



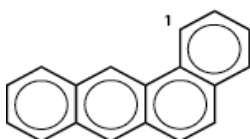
6) anthracene



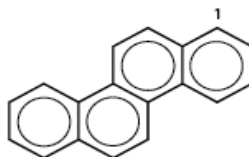
7) fluoranthene



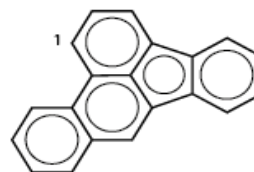
8) pyrene



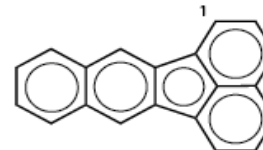
9) benzo(a)anthracene



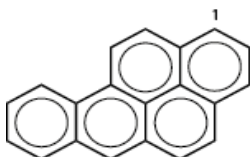
10) chrysene



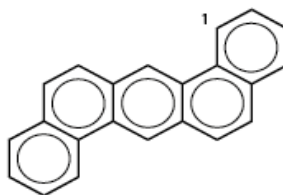
11) benzo[b]fluoranthene



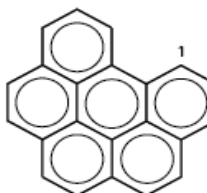
12) benzo[k]fluoranthene



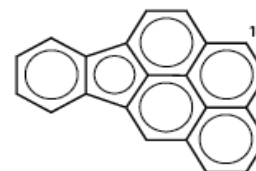
13) benzo[a]pyrene



14) dibenz[ah]anthracene



15) benz[ghi]perylene



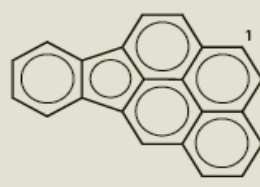
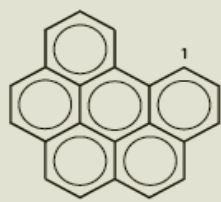
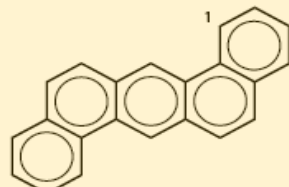
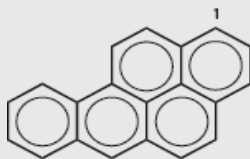
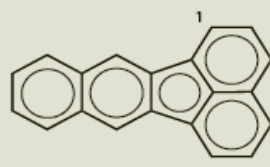
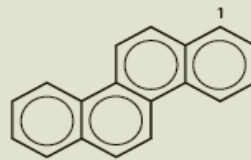
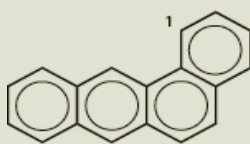
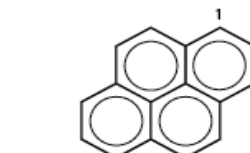
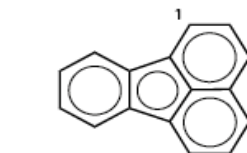
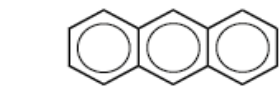
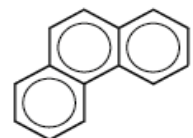
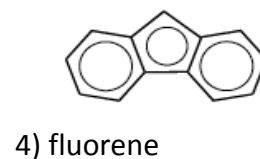
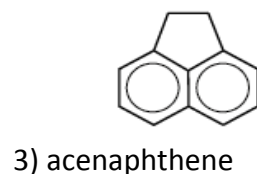
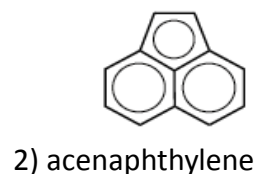
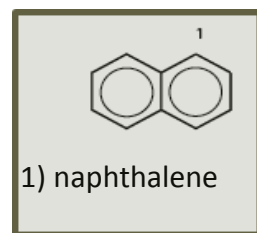
16) indeno(1,2,cd)pyrene

AGENTS CLASSIFIED BY THE *IARC MONOGRAPHS*, VOLUMES 1–112

Group 1	<i>Carcinogenic to humans</i>	116 agents
Group 2A	<i>Probably carcinogenic to humans</i>	73
Group 2B	<i>Possibly carcinogenic to humans</i>	287
Group 3	<i>Not classifiable as to its carcinogenicity to humans</i>	503
Group 4	<i>Probably not carcinogenic to humans</i>	1

Last update: 3 June 2015

PAHs (Polycyclic Aromatic Hydrocarbons)



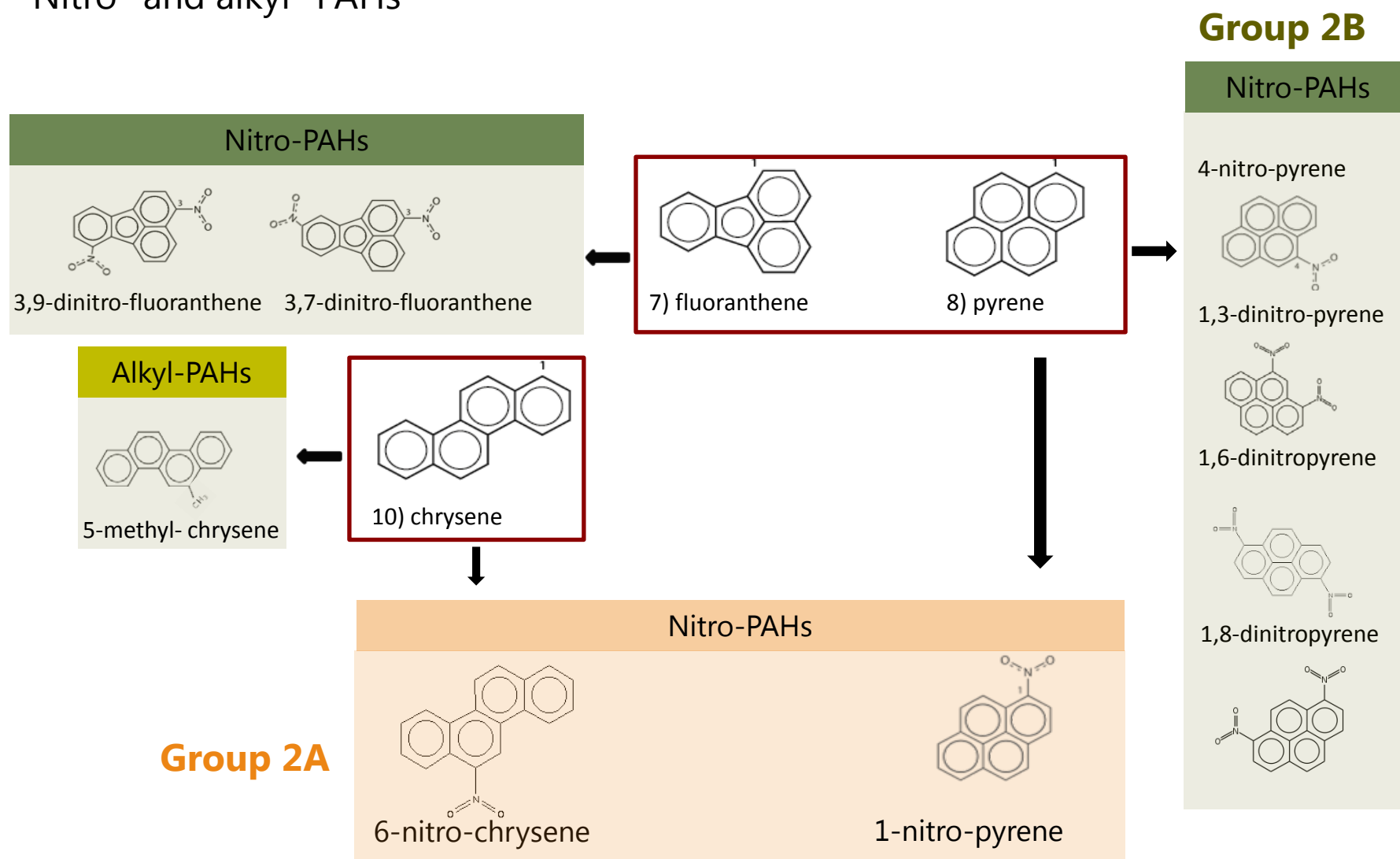
Group 1

Group 2A

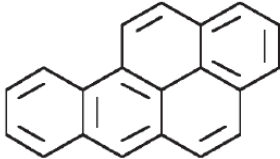
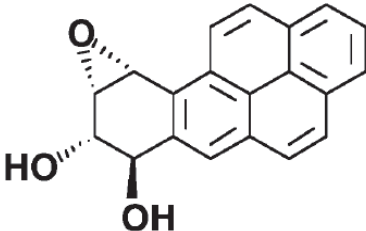
Group 2B

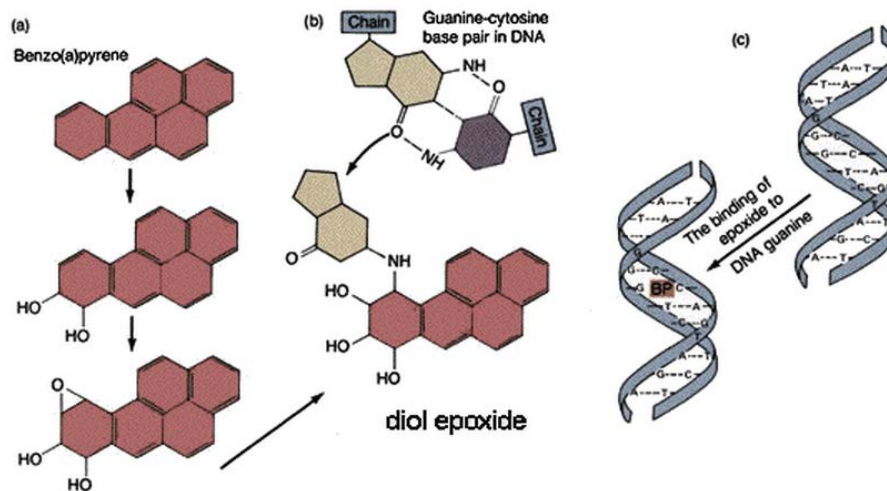
↑ MW
↓ vapor pres.
and solubility

Nitro- and alkyl- PAHs



GENOTOXICITY: The Benzo[a]pyrene example

Carcinogen	Environmental source	Major active metabolite	Sites of modification	Major type of mutation
 Benzo[a]pyrene (B[a]P)	<div style="border: 1px solid black; padding: 5px; display: inline-block;">Tobacco smoking Combustion processes</div>	 B[a]P-7,8-dihydrodiol 9,10-epoxide (BPDE)	<div style="border: 1px solid black; padding: 5px; display: inline-block;">N²-Guanine N⁶-Adenine</div>	<div style="border: 1px solid black; padding: 5px; display: inline-block;">GC → TA</div>



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

SAMPLING PROCEDURE

Several GDI vehicles:

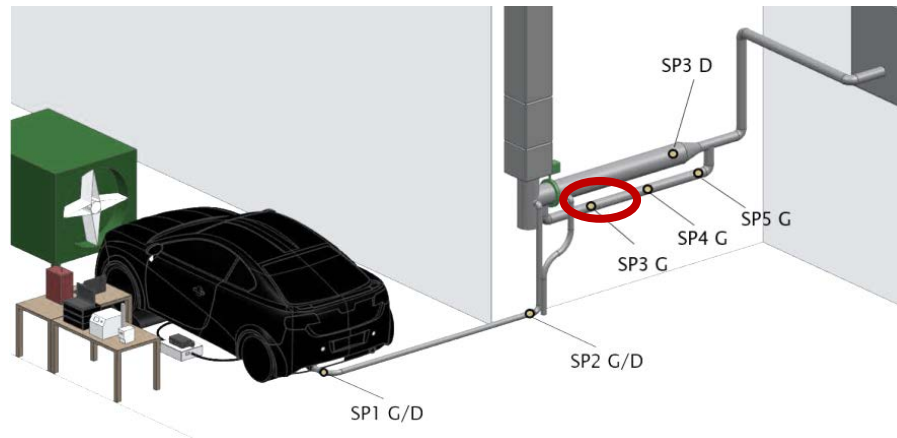
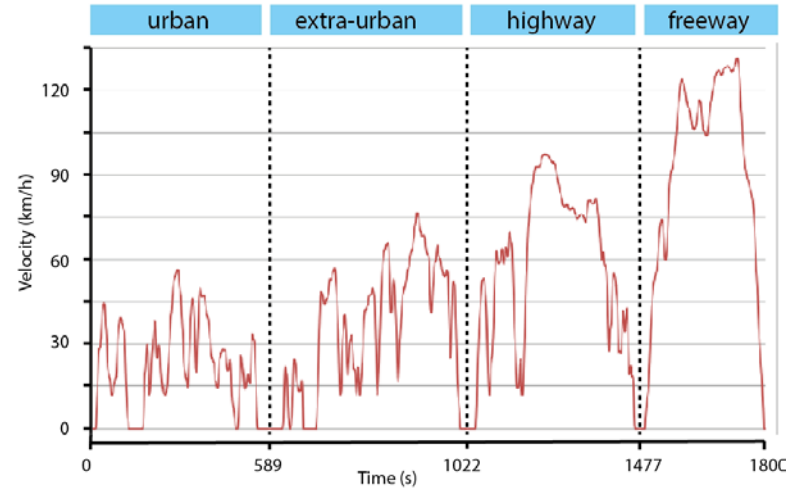
3 different brands

A non-catalytic filter

- Chassis dynamometer, UASB, **Nidau**

WLTC → **HOT start**
→ **COLD start**

SSC



From J. Czerwinski Group, Berner Fachhochschule

LABORATORY ANALYSIS

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

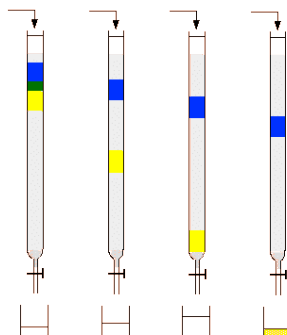


ASE/Soxhlet
extraction

Concentration

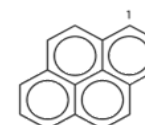
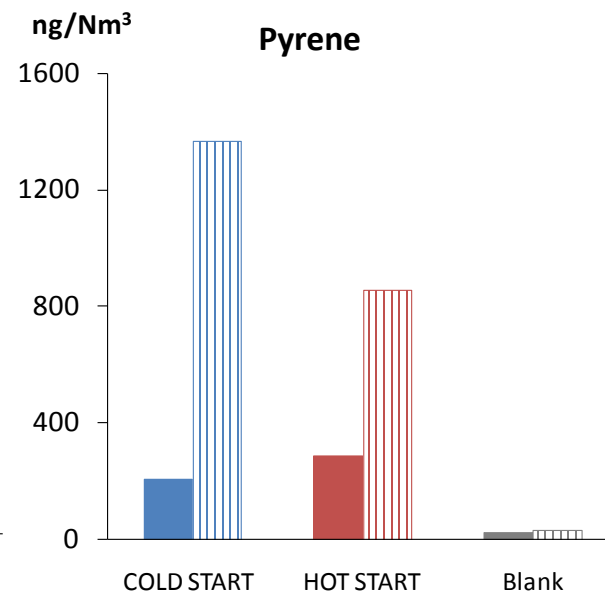
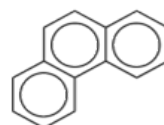
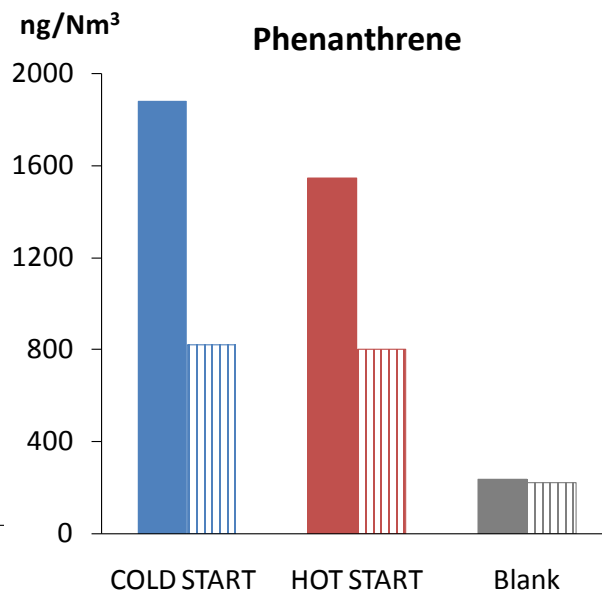
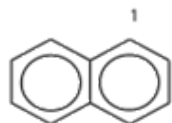
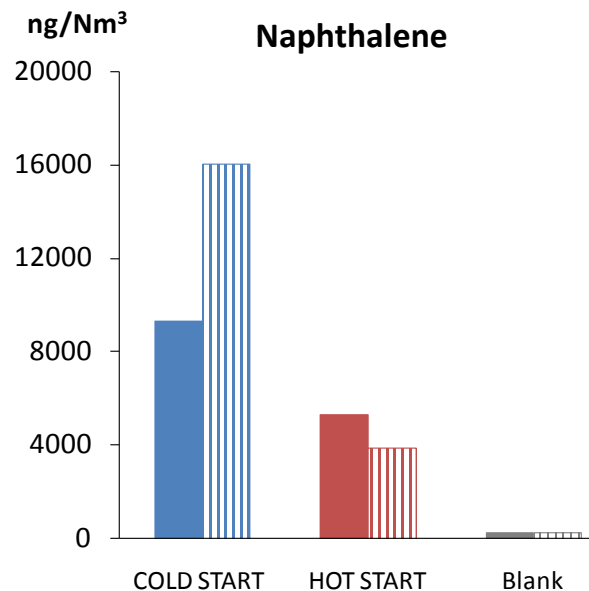
Cleanup and
fractionation

HRGC/HRMS
analysis



DIFFERENT VEHICLES

2-3 RINGS and PYRENE



218 °C

Boiling point

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 **COLD** start conditions **hot** start conditions



PAH storage/release ??
PAH formation ??

- Nitro-PAHs in ambient levels

THANK YOU VERY MUCH FOR YOUR ATTENTION



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