Emissions of Particle-bound Polyaromatic Hydrocarbons of 2-Stroke Scooters with different combinations of oil/ fuel/ engine technology.

C. Astorga, M. Rey, K. Douglas, G. Martini, G. de Santi and B. Larsen*

EC- JRC, Institute for Environment and Sustainability- Emissions and Health Unit –
TP 441- Via Enrico Fermi, 1- 21020 Ispra (Va) Italy
Phone +390332786110; Fax +390332786671; covadonga.astorga-llorens@jrc.it

In view of the preparation of an amendment to the European directive 97/24/EC on "Characteristics of two or three-wheel motor vehicles", particulate matter (PM) from motorcycles has become an urgent matter of interest for the EC. Concern about potential health effects of particulate matter (PM) necessitates improved knowledge, not only the physical characteristics of PM, but also on the chemical composition and its content of toxic compounds. The Commission-Joint Research Center (EC-JRC) at the Emissions and Health Unit is presently working on the characterization of PM emitted by motorcycles with the aim of obtaining estimates of the impact of these emission sources on air quality. Numerous measurements programs on O_3 precursors have clearly showed that traffic emission is the may source in urban areas. If we take into account that in some Southern European regions and developing countries the percentage of two wheels, mainly mopeds, can raise 60-80% in some urban areas, we can easily conclude that the contribution of these vehicles is extremely important.
The work presented here is a part of the contribution from the EC-JRC to an international project network namely "Two-Stroke Scooters: Particle emissions, toxicology and environmental impacts" mandated by the Swiss Agency of Environment Forests and Landscape (SAEFL, BUWAL) and by the Swiss Associations of Oils and Lubricants (EV and VSS). This program was started at the end of last year and it is involving a number of prestigious research groups.

A key asset of this work is the development of advanced analytical methods for the characterization of non-regulated toxic compounds. Method and results of the chemical analysis are summarized below. Results have been presented on the influence by engine technology/conditions and fuel/oil quality on the emissions of the group of non-regulated pollutants, polyaromatic hydrocarbons (PAHs).

Unregulated emissions: chemical composition of particulate from Moped exhaust (Particulate-Associated PAH).

Very recently, a new European Directive (2004/107/EC) regarding air quality came out. This new directive is guidance for member states that bear directly on either emissions or air quality objectives of PAHs. The 2004/107/EC directive covers the remaining pollutants listed in Annex I of Air quality directive 96/62/EC, including PAHs. One of the first chemicals of this family which has been recognized as carcinogenic is the Benzo[a]pyrene (BaP). B(a)P has been considered in this directive as a suitable marker due to its stability and relatively constant contribution to the carcinogenic activity of particle-bound PAHs.
For this work, sixteen priority Polycyclic Aromatic Hydrocarbons (PAH) recommended by EPA because of their mutagenic and, in some cases, carcinogenic properties have been analyzed in particulate matter from moped engine exhaust emissions.
Total particulate mass collected using Pallflex 70 mm T60A20 filters generally consist of agglomerates of very small carbon particles (soot fraction) and heavy hydrocarbons adsorbed on

them (soluble organic fraction). Chemical composition of the soluble organic fraction is important due to its relevance for human health. In particular, what is grabbing our attention is the amount of potentially harmful organic compounds adsorbed on the particles. Data presented in this paper demonstrate the potential for reducing the possible toxicity of the PM emissions from existing mopeds by optimizing the two-stroke engine technology.

A total of 21 filters from the first test round of the Scooter-Projects were analyzed for their content of particulate-associated polyaromatic hydrocarbons (PAH) and the fraction of volatile organic components (VOF). The methods and results of the chemical analysis are described in this document. In Phase 1 of this test series, the 2-stroke motorbikes were tested at constant speed (45 km/h). In Phase 2, the used Test cycle was initiated both at cold-start engine conditions and at hot-start engine conditions. The particle-bound PAHs were analysed by gas-chromatography mass spectrometry in the emitted particulate and varied in a broad range from 50 to 1500 ng/g (sum of 12 EPA priority PAH + coronene and benzo(e)pyrene). The PAH emitted with the particles consisted mainly of the most toxic isomers containing 5 to 6 aromatic rings. The corresponding emissions of PAH per driven km pointed to the same conclusions than the results on particulate emissions, namely that the far lowest PAH emissions were obtained for the 2-stroke vehicle with carburetor + secondary air injection run with Aspen fuel and Panolin Synth Aqua oil at stationary warm operating condition. These emission factors, which are due to the very strong oxidation potential of the exhaust gas in this vehicle type, are below the level previously found in our laboratories for EURO 3 Diesel vehicles.
For data reduction the toxicity equivalency factor (TEF) approach was used, in which each individual PAH is assigned a toxicity rating relative to benzo(a)pyrene that is set to unity. The benzo(a)pyrene toxicity equivalents (TEQ) of a given sample are calculated as the sum of the concentrations multiplied by TEF over all the measured compounds (*3*). This approach it is based on vast toxicological data and represents a convenient way to reduce a multidimensional data set in a meaningful way. The TEF approach has found widespread use for chlorinated dibenzodioxins and dibenzofurans. In the present study we have quantified the following PAH (TEF value): fluorene (F, 0.001), phenanthrene (Phen, 0.001), fluoranthene (Fl, 0.01), pyrene (P, 0.01), benzo[a]anthracene (B(a)A, 0.1), chrysene (Chr, 0.01), benzo[b]fluoranthene (B(b)Fl, 0.1), benzo[k]fluoranthene (B(k)Fl, 0.1), benzo[a]pyrene (B(e)P, 0.1), benzo[a]pyrene (B(a)P, 1), indeno[1,2,3-cd]pyrene (Ind(123cd)P, 0.1), dibenzo[a,h]anthracene (diB(ah)A, 1), benzo[ghi]perylene (B(ghi)Per, 0.01), coronene (COR, 0.01).

References:
Astorga, C.; Suurballe, A.; Bech Olsen, M.; Vialaton, D.; Dilara, P.; De Santi, G.; Larsen, B.R. *Development of a protocol for the analysis of toxic PAH, azarenes, and their nitro-, hydroxyl-, and oxo-derivatives in emission exhaust and ambient PM.* EUR 20560 EN. European Communities, Brussels, 2003.
Larsen, B.R.; Astorga, C.; Baglio, D.; Brussol, C.; Duane, M.; Kotzias, D. *Characterisation of engine exhaust particulate fingerprints and the contribution to air quality.* EUR 19047 EN. European Communities, Brussels, 2000.
EPA. *Provisional guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons,* U.S. Environmental Protection Agency, Washington, 1989.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Emissions & Health Unit

Institute for Environment and Sustainability (IES)
EC-JRC Ispra, Italy

Emissions of Particle-bound Polyaromatic Hydrocarbons of 2-Stroke Scooters with different combinations of oil/ fuel/ engine technology

C. Astorga, M. Rey, K. Douglas, G. Martini and B. Larsen*

http://ies.jrc.cec.eu.int
http://ies.jrc.cec.eu.int/Units/eh/

Joint Research Centre

Institute for Environment and Sustainability

2 STROKE SCOOTERS
INTERNATIONAL PROJECT NETWORK:

Particle emissions, toxicology & environmental impacts

Ordered by:

Swiss Agency of Envoronment, Forests and Landscape, SAEFL Bern, CH

Bundesamt fur Umwelt, Wald und Landschaft, BUWAL Bern

Swiss Association of Oil Industry, Erdol-Vereinigung, Zurich, CH

Report by: Dr Czerwinski *et al.*

University of Applied Sciences. Laboratory IC-Engines & exhaust emission Control, Nidau, CH

Network Leading:

TTM, Technik Thermische Maschinen, Niedorrohrdorf, CH

Partnerships:

EMPA (CH), EC-JRC (IT), VVT (FIN), SUVA (CH), Peugeot Motorcycles (F), Piaggio Motorcycles (IT), Panolin AG oil (CH), Motorex (CH), Lubrizol (GB), Matter Eng. AG (CH), TTM (CH)

Joint Research Centre

LAYOUT OF THE PROJECT

a/ PM, PC emissions, basics, technology for reduction, inputs for legislation

b/ JRC Analysis of toxic compounds, PAHs (complementary Time, independent)

c/ VTT, complementary time synchron & coordinated

d/ Toxicity Network, France Prof Morin

e/ EMPA: Environmental impacts, Analysis of VOCs, GH gases & O3 potentials

f/ India (complementary Time, independent)

g/ IEA implementing agreement, Coordination AFHB…

VELA Laboratory

Emissions & Health Unit

(Action 2113: Emissions Characterization and inventories)

Key Objective: to reduce exposure to priority/TOXIC Environmental pollutants

EU Legislation

Challenges arising from TWO main Directives Regarding motorcycles

2002/51/EC

On the reduction of the level of pollutant emissions from two- and three-wheel vehicles and amending Directive 97/24/EC

2003/77/EC

Amending Directives 97/24/EC and 2002/24/EC of the European Parliament and of the Council relating the type-approval of two- or three-wheel motor vehicles

EU Directive 97/24/EC

Emissions limits values for MOPEDS

	CO (g/km)	HC+NOx (g/km)
EURO 1	**6**	**3**
EURO 2	**1**	**1.2**

Emissions limits values for MOTORCYCLES

	CO (g/km)	HC (g/km)	NOx (g/km)
EURO 1 (two stroke)	**8**	**4**	**0.1**
EURO 2 (four stroke)	**13**	**3**	**0.3**

Folie 6

a1 astorco; 22.09.2004

EU Directive 2002/51/EC

EURO 3_Emissions limits values for MOPEDS (<150cm^3)

	CO (g/km)	HC (g/km)	NOx (g/km)
A (2003)	5.5	1.2	0.3
B (2006)	2.0	0.8	0.15

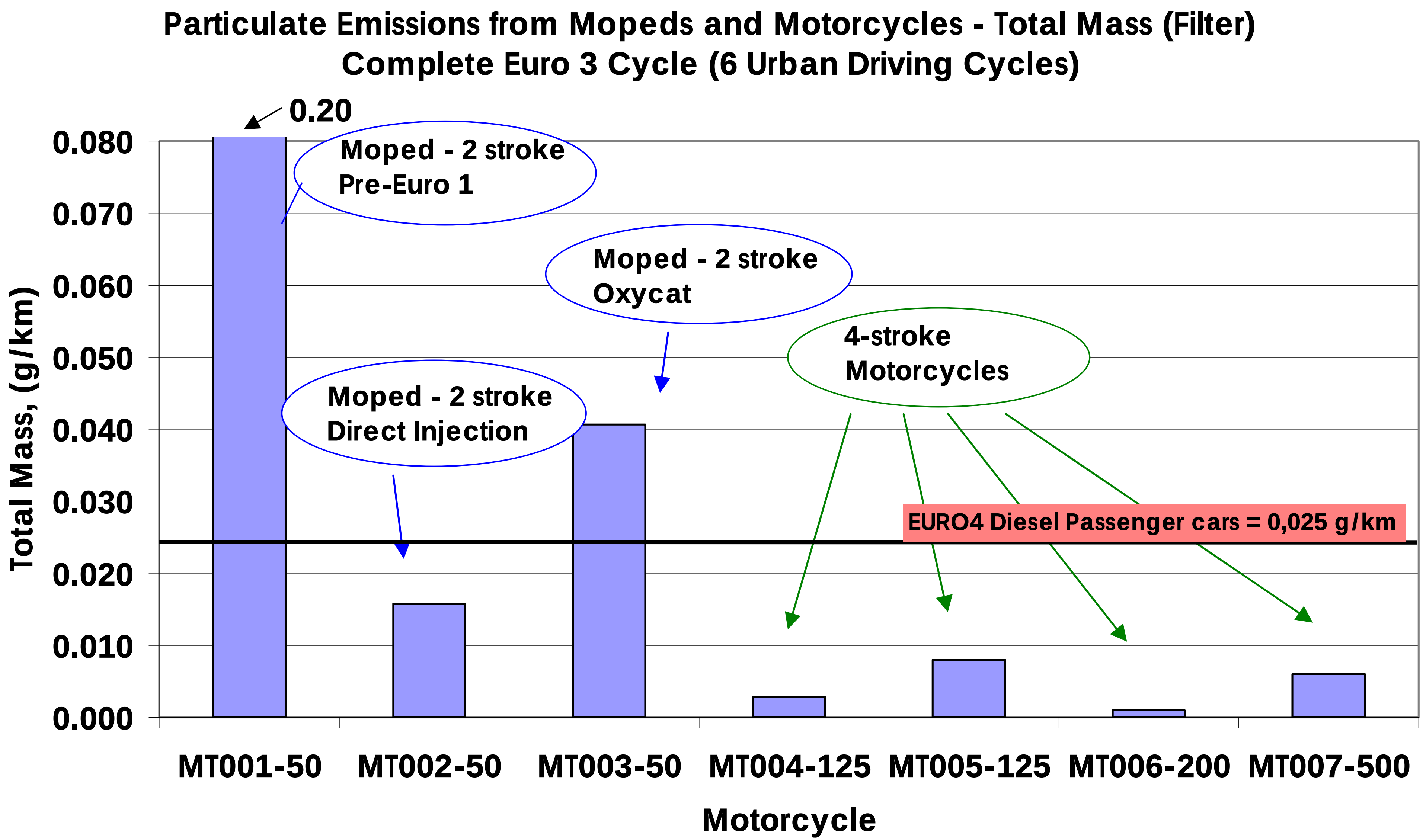
EURO 3_Emissions limits values for MOTORCYCLES (<150cm^3)

	CO (g/km)	HC (g/km)	NOx (g/km)
A (2003)	5.5	1.0	0.3
B (2006)	2.0	0.3	0.15

Folie 7

a2 astorco; 22.09.2004

Motorcycle Emissions: Particulates



Set of Experiments

- Phase 1: the 2-stroke motorbikes were tested at constant speed (45 km/h)

- In Phase 2, the used Swiss Test cycle was initiated both at cold-start engine conditions and at hot-start engine conditions

Analysis Performed

1st_ Content of particulate associated polyaromatic hydrocargbons (PAH)

and

2nd_ Fraction of volatile organic components (VOF)

Joint Research Centre

Analytical procedure

- extraction (soxhlet 2h, ultrasonic)
- SPE
- Evaporation (TurboVap)
- GC/MS

Why these compounds?

- Very recently the European Commission came out with a new for a Directive (2004/107/EC) which is guidance for member states that bear directly on either emissions or air quality objectives of PAHs.

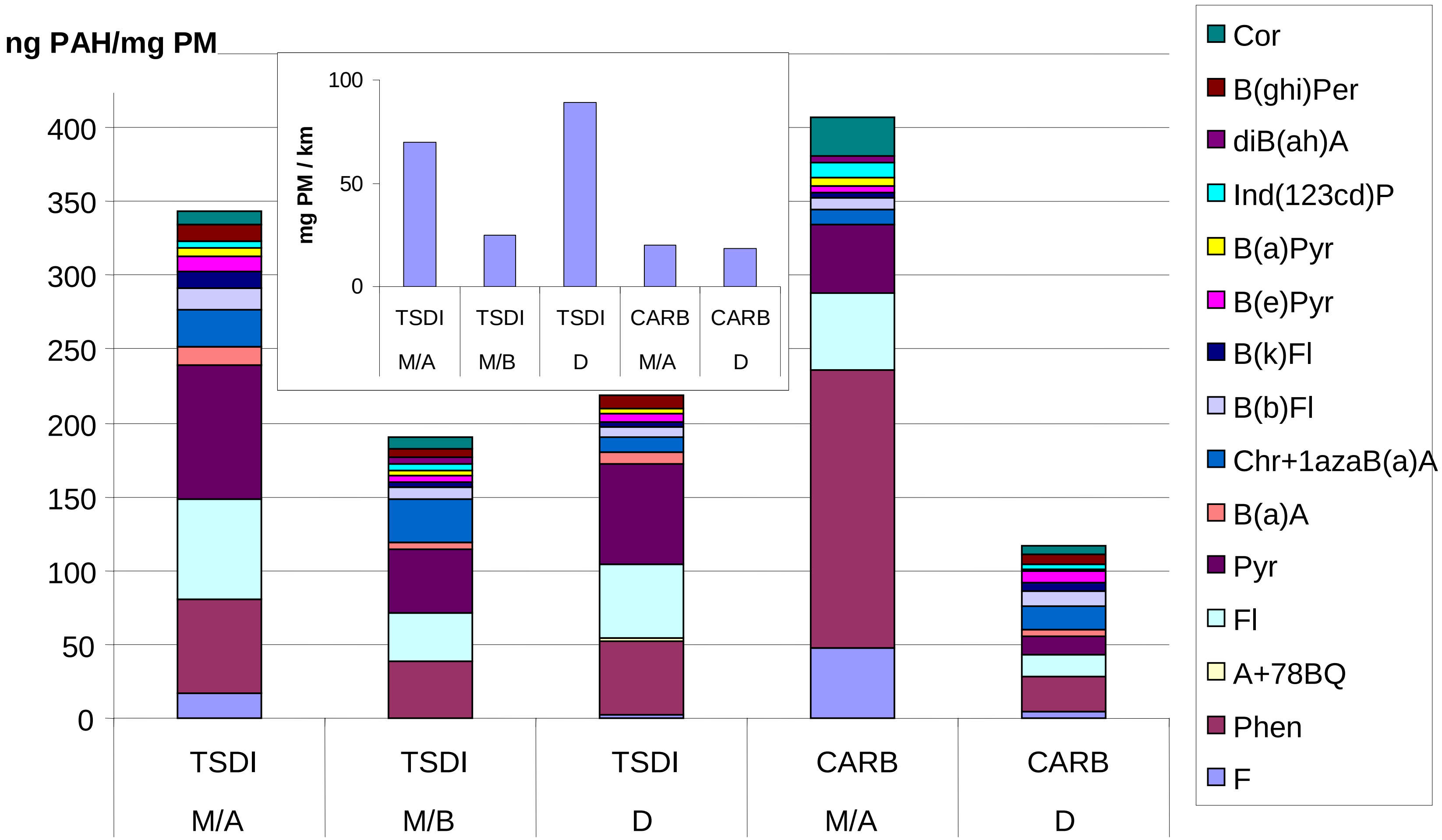
- This directive covers the remaining pollutants listed in Annex I of Air quality Directive (96/62/EC), including PAHs. One of the first chemicals of this family which has been recognized as carcinogenic is the Benzo[a]pyrene (BaP). B(a)P has been considered in this directive as a suitable marker due to its stability and relatively constant contribution to the carcinogenic activity of particle-bound PAHs.

Main objective of Directive

- *"To take all the necessary measures, not entailing disproportionate cost, to ensure that, as from 31 December 2012, concentration of B(a)P used as marker for carcinogenic risk of polycyclic aromatic hydrocarbons, in ambient air… do not exceed that target value of 1ng/m3(laid down in Annex I), for the total content in PM10 fraction averaged over a calendar year."*

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

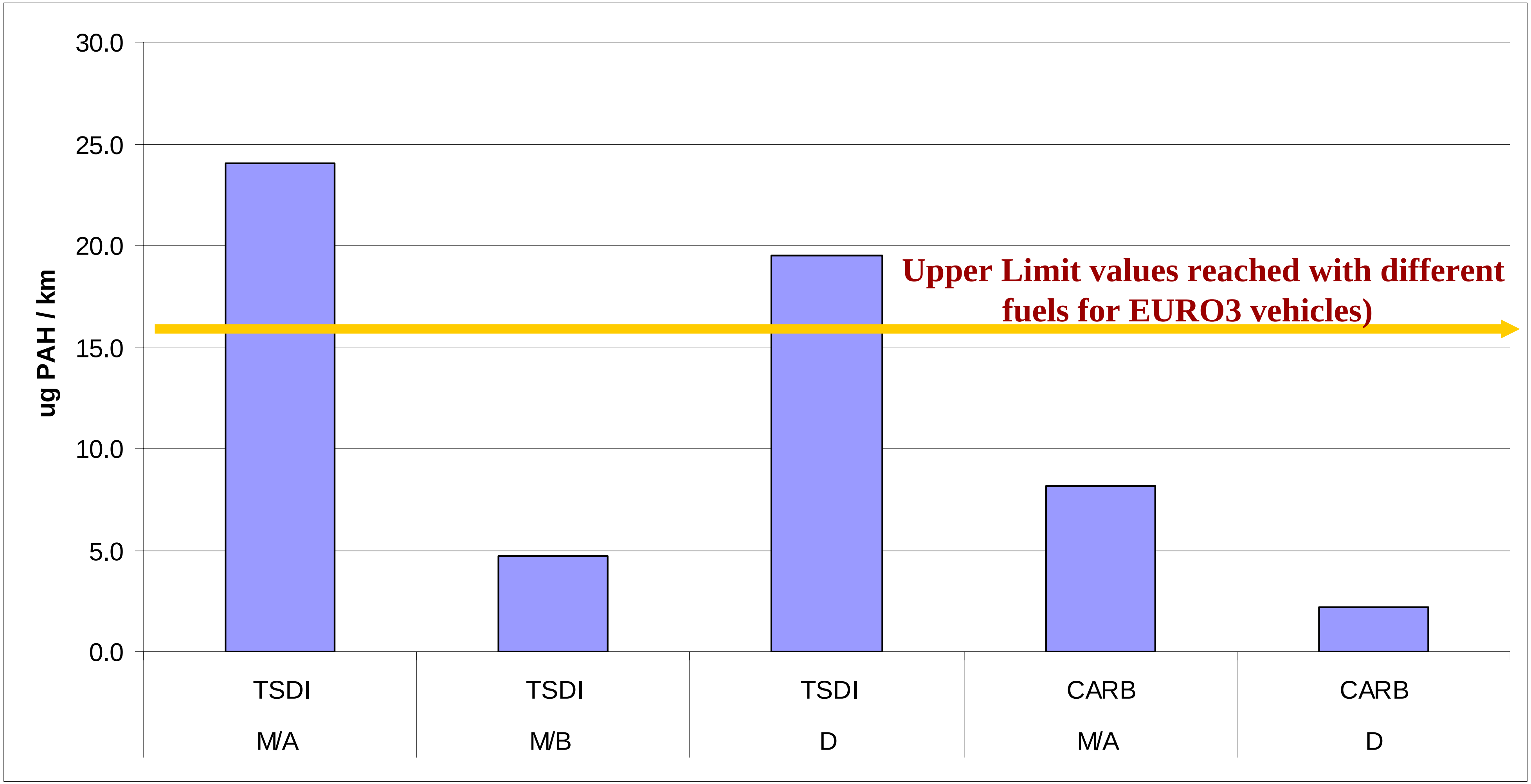
Distribution of the individual PAH compounds in PM (ng PAH / mg PM) from 2-strokers



M = after partial dilution tunnel "Metas" (only 1 filter),
A = without thermo-conditioner / B = with thermo-conditioner
D = after dilution tunnel "CVS' 2 filters (primary and secondary)
Running statically at a constant speed of 45 km/h with "Panolin TS" as oil and unleaded fuel, 96 oct.

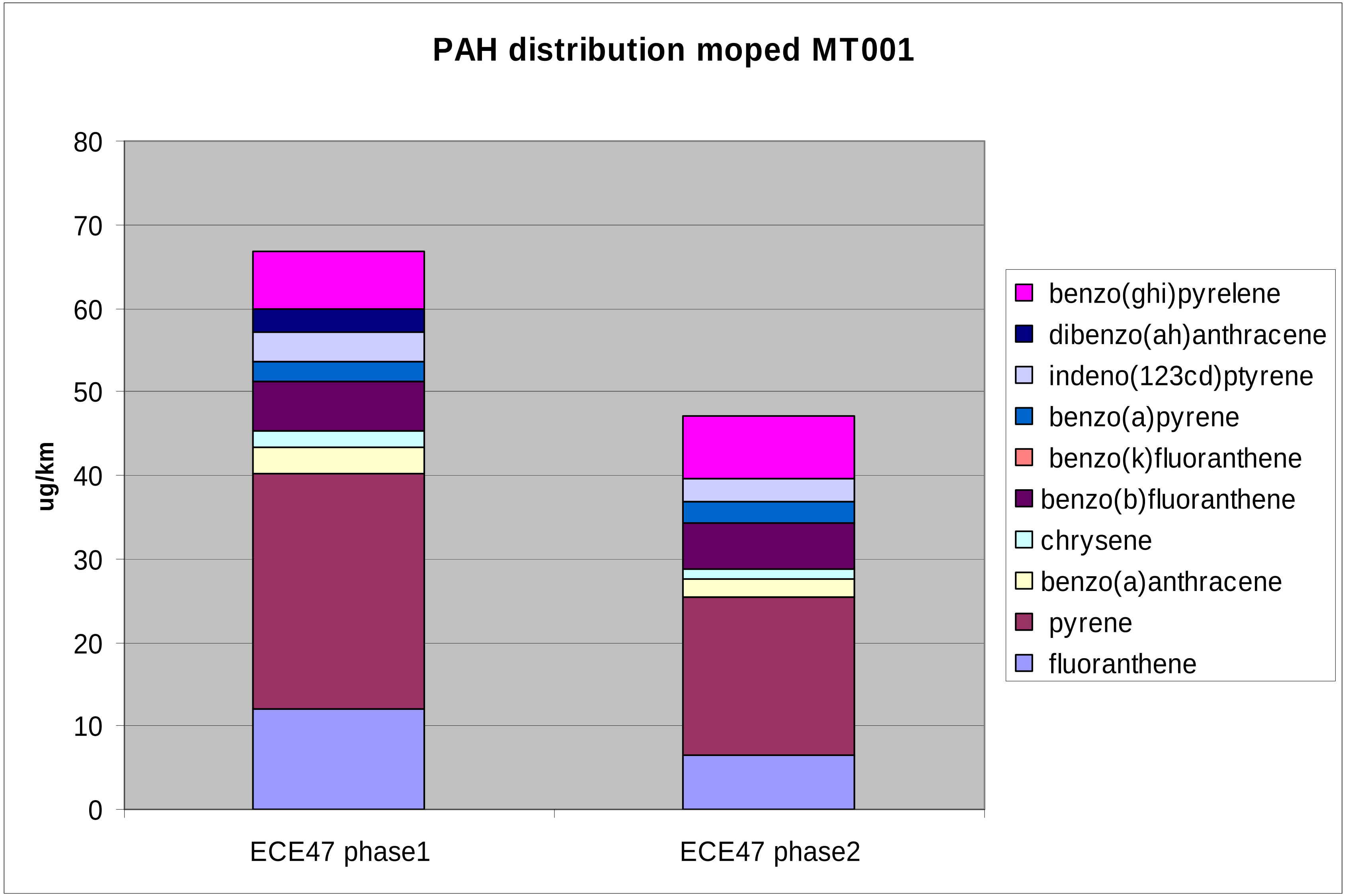
Joint Research Centre

Variation of PAH Emissions in the static tests; Phase 1



M = after partial dilution tunnel "Metas" (only 1 filter)
A = without thermo-conditioner,
B = with thermo-conditioner
D = after dilution tunnel "CVS' 2 filters (primary and secondary)

In house results for a pre-EURO 1 Moped



TEF is a measure of relative toxicological potency of a chemical compared to a well characterized reference compound

TEFs can be used to sum the toxicological potency of a mixture of chemicals which are all members of the same chemical class, having common structural, toxicological and biochemical properties.

TEQ = S [Ci] x TEF i

TEF for PAC

PAH	TEF	PAH-derivative	TEF
benzo[*a*]pyrene	=1		
dibenzo[*a,l*]pyrene	10	7,12-dimethylbenzanthracene	65
dibenzo[*a,h*]pyrene	10	1,6-dinitropyrene	10
dibenzo[*a,i*]pyrene	10	6-nitrochrysene	10
dibenz[*a*,h]anthracene	1.1	3-methylcholanthrene	5.7
7H-dibenzo[*c,g*]carbazole	1	5-methylchrysene	1
dibenzo[*a,e*]pyrene	1	1,8-dinitropyrene	1
indeno[1,2,3-*cd*]pyrene	0.1	4-nitropyrene	0.1
benzo[*a*]anthracene	0.1	1-nitropyrene	0.1
benzo[*b*]fluoranthene	0.1	5-nitroacenaphthene	0.034
benzo[*j*]fluoranthene	0.1	2-nitrofluorene	0.01
benzo[*k*]fluoranthene	0.1		
dibenz[*a,j*]acridine	0.1		
dibenz[*a,h*]acridine	0.1		

$$\text{Total TEQ} = \sum TEF_i \times CONC_i$$

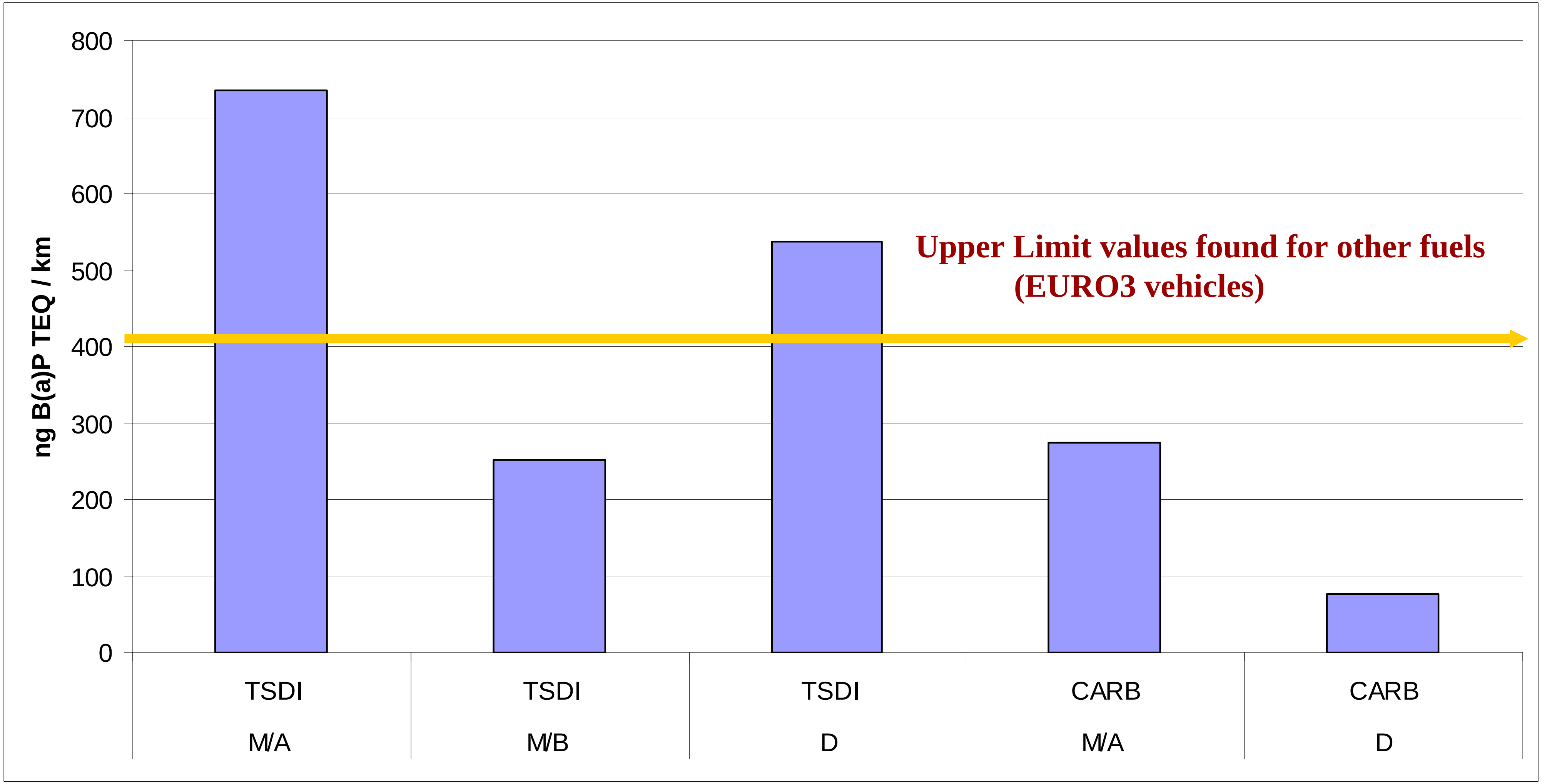
EPA Revision, 1994; OEHHA,Children's Environmental Health Protection Act, California 2001

The TEF approach has been extensively used for hazard assessment of different mixtures of for chlorinated dibenzodioxins and dibenzofurans and for polycylic aromatic hydrocarbons.

It is based on vast toxicological data and represents a convenient way to reduce a multidimensional data set in a meaningful way.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Variation of B(a)P toxicity equivalents For Emissions in the static tests/ Phase 1

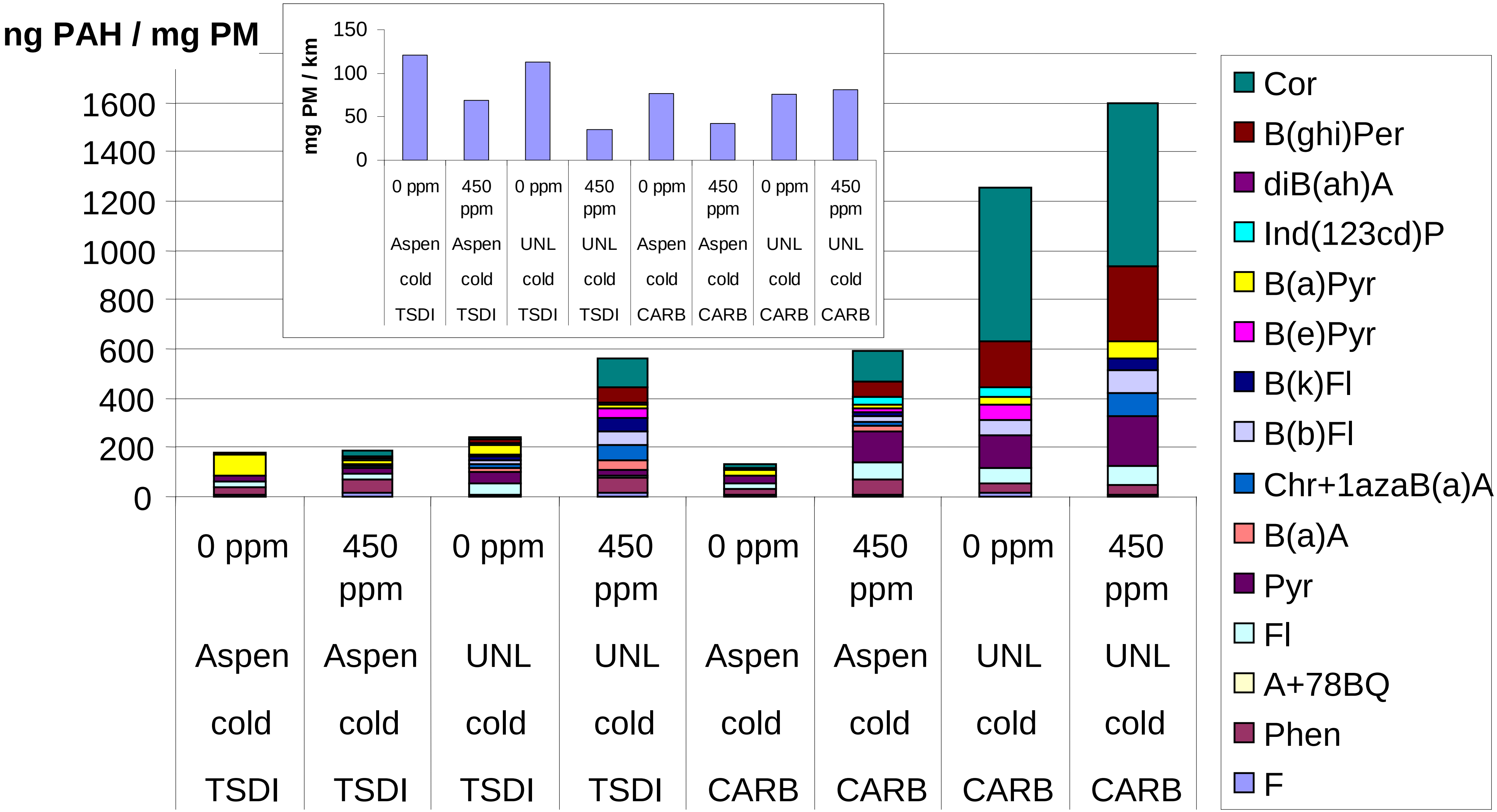


M = after partial dilution tunnel "Metas" (only 1 filter)
A = without thermo-conditioner,
B = with thermo-conditioner
D = after dilution tunnel "CVS' 2 filters (primary and secondary)

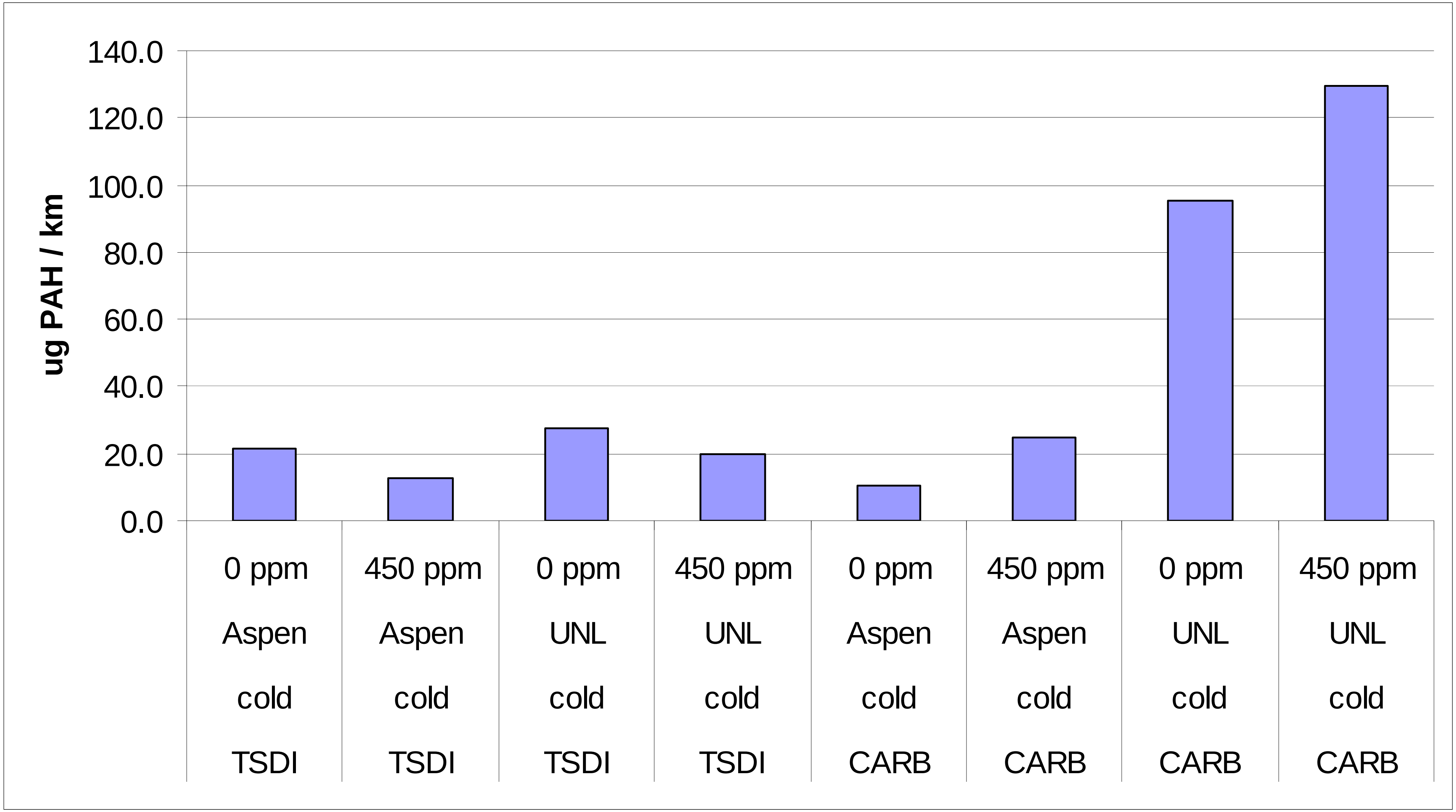
Joint Research Centre

Institute for Environment and Sustainability

Distribution of the individual PAH compounds in particulate matter (ng PAH / mg PM) from 2-strokers (phase 2)

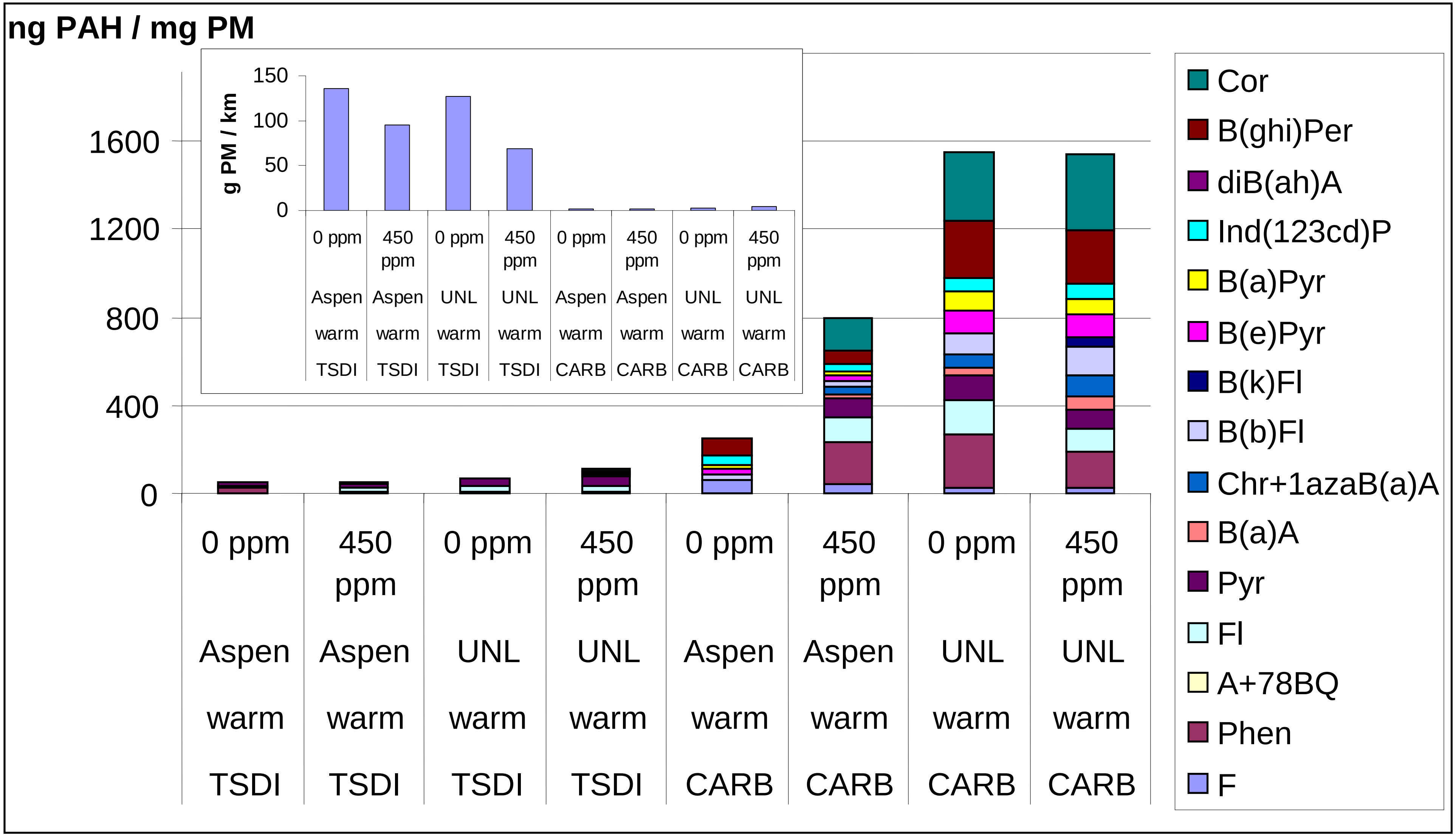


Variation of PAH emissions from 2-stroke in particulate matter from 2-strokers (phase 2)_ Cold-start

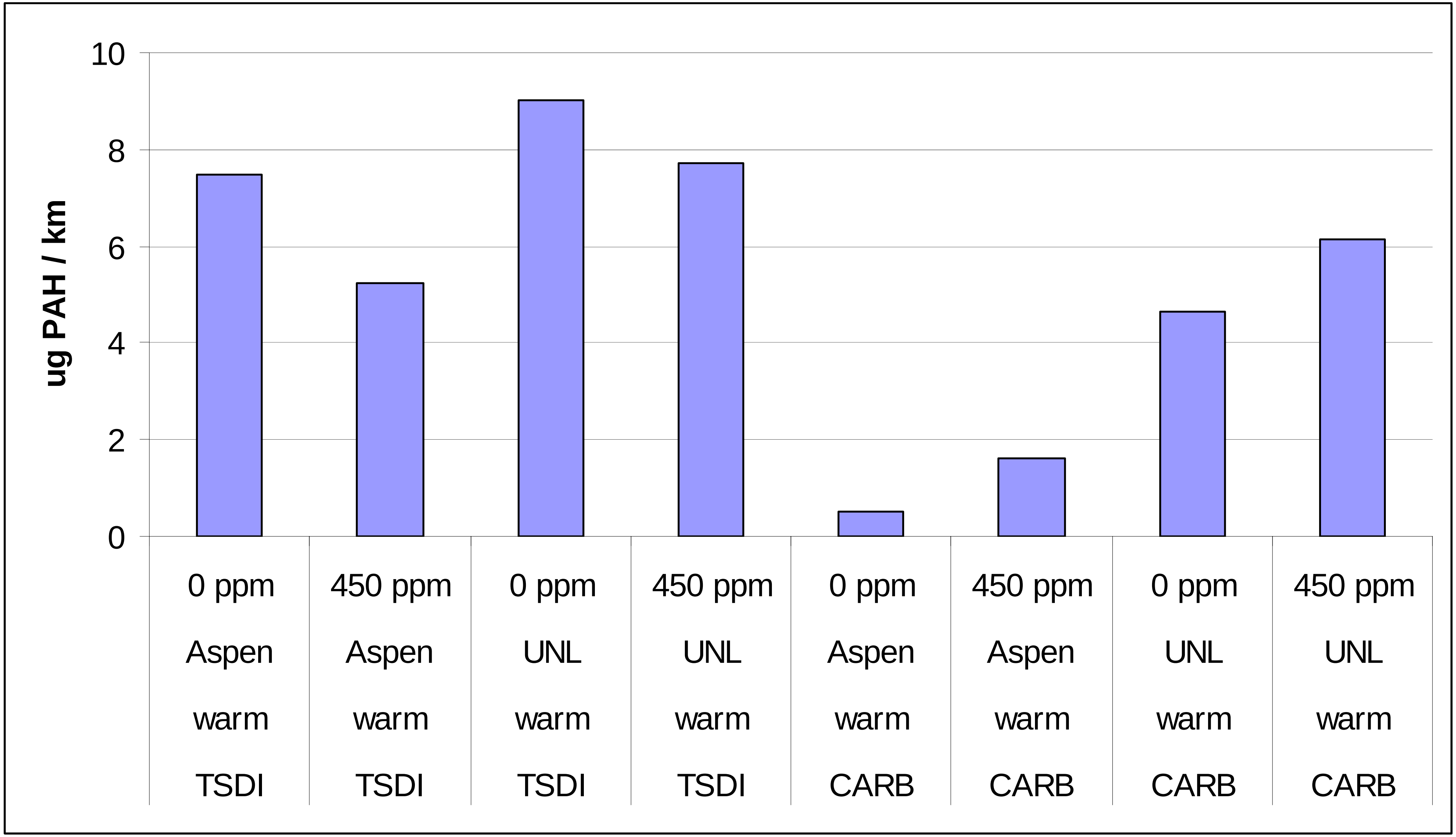


The variation of PAH emissions from 2-strokers (phase 2) including cold-start using Aspen or (UNL) unleaded fuel, and Panolin Synth Aqua (0 ppm sulfur) or Panolin Synth (450 ppm sulfur as oil).

The distribution of the individual PAH compounds in particulate matter (ng PAH / mg PM) from 2-strokers (phase 2)_ warm-start



Variation of PAH emissions from 2-stroke in particulate matter from 2-strokers (phase 2)_ warm-start



The variation of PAH emissions from 2-strokers (phase 2) including warm-start using Aspen or (UNL) unleaded fuel, and Panolin Synth Aqua (0 ppm sulfur) or Panolin Synth (450 ppm sulfur as oil).

Conclusions, PAHs

The far lowest PAH emissions were obtained for the vehicle with carburetor plus secondary air injection **including warm-start** run with Aspen fuel and Panolin Synth Aqua (0 ppm sulfur) oil, which is at the level or even below EURO 3 Diesel vehicles tested in our laboratories.

Thus not only for the PM emissions, but also from the PAH point of view it seems to be the most promising combination of technology, fuel and oil to further optimization.