POPs & HM emission results for vehicles – Nordic study

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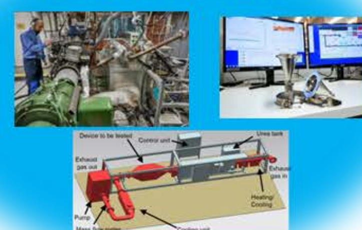
Our group at VTT: Engine and vehicle emissions
Focus areas

Large engines


Fuels


High speed engines


Heavy duty vehicles


Aftertreatment


Light duty vehicles


Support for administration


Field studies

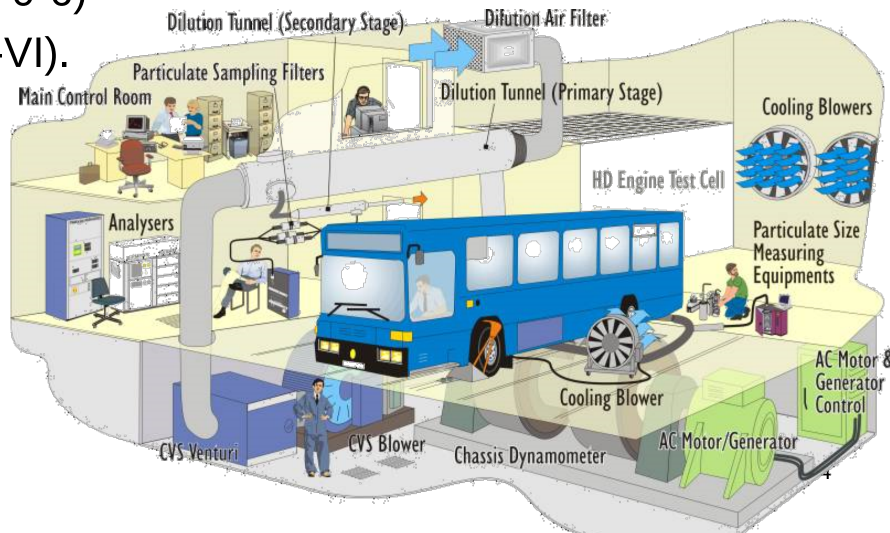

Monitoring R&D


Nordic study on POPs & HM

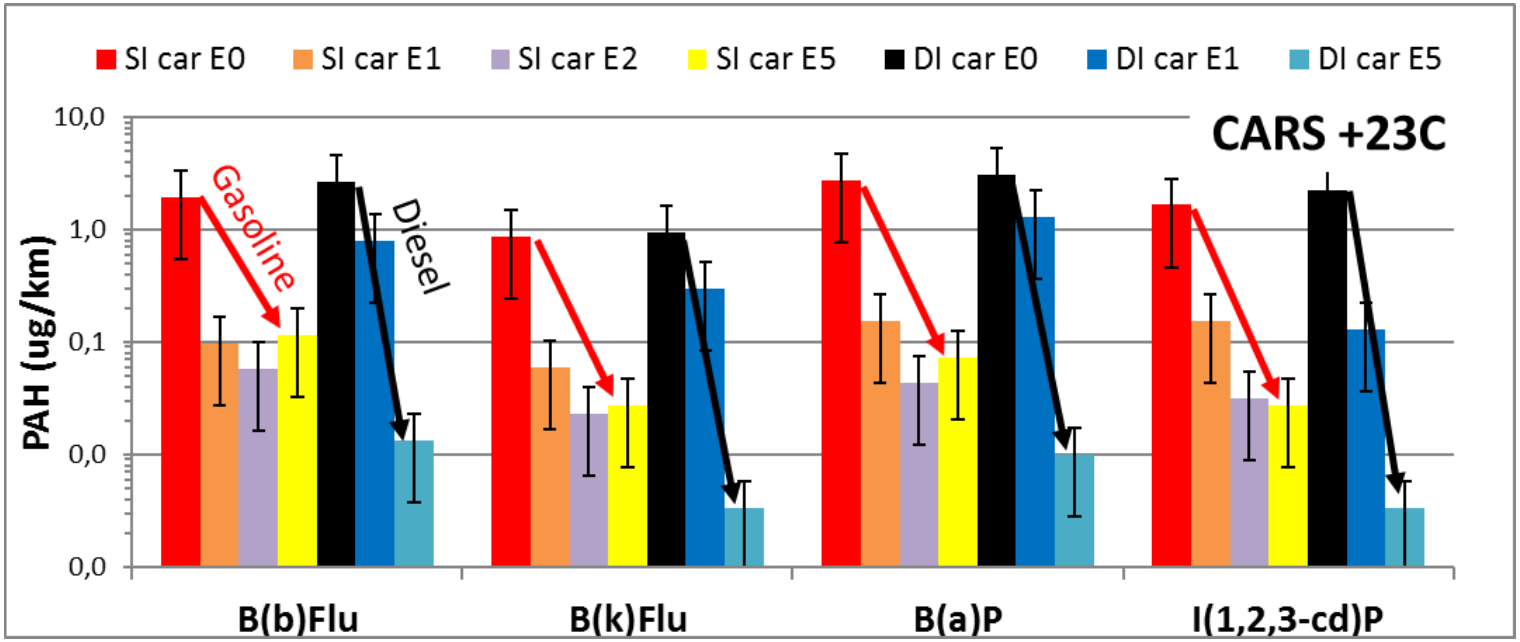
- Nordic programme on developing air pollutant emission inventories, especially POP and heavy metal emissions
- Project duration 1/1 /2016-31/12 /2018
- Participants/project group:
  - Ole-Kenneth Nielsen, Denmark
  - Tomas Gustafsson, Sweden
  - Britta Hoem, Norway
  - Vanda Hellsing, Iceland
  - Kristina Saarinen, Finland; EF work: Päivi Aakko-Saksa, VTT

Nordic study on POPs & HM

- Emission factors (EF) for vehicle types in Nordic Countries.
  - **Heavy metals (HM):** As, Cd, Cr, Cu, Ni, Pb, Se, Zn
  - **Four polyaromatic hydrocarbons (PAHs):** Benzo(a)pyrene, benzo(b) fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene.
- EFs based on the existing data at VTT from public projects since early 1990's.
- Substantial amount of PAH data is available at VTT:
  - Gasoline (SI) and diesel (DI) cars (Euro 0-6)
  - Heavy-duty (HD) trucks&buses (Euro 0-VI).
  - Data for cars at cold temp., e.g. -7 °C → EFs at real-life conditions in Norden.
- Limited data on HMs available at VTT
  - One passenger car (Euro 2)
  - One bus engine (Euro II)

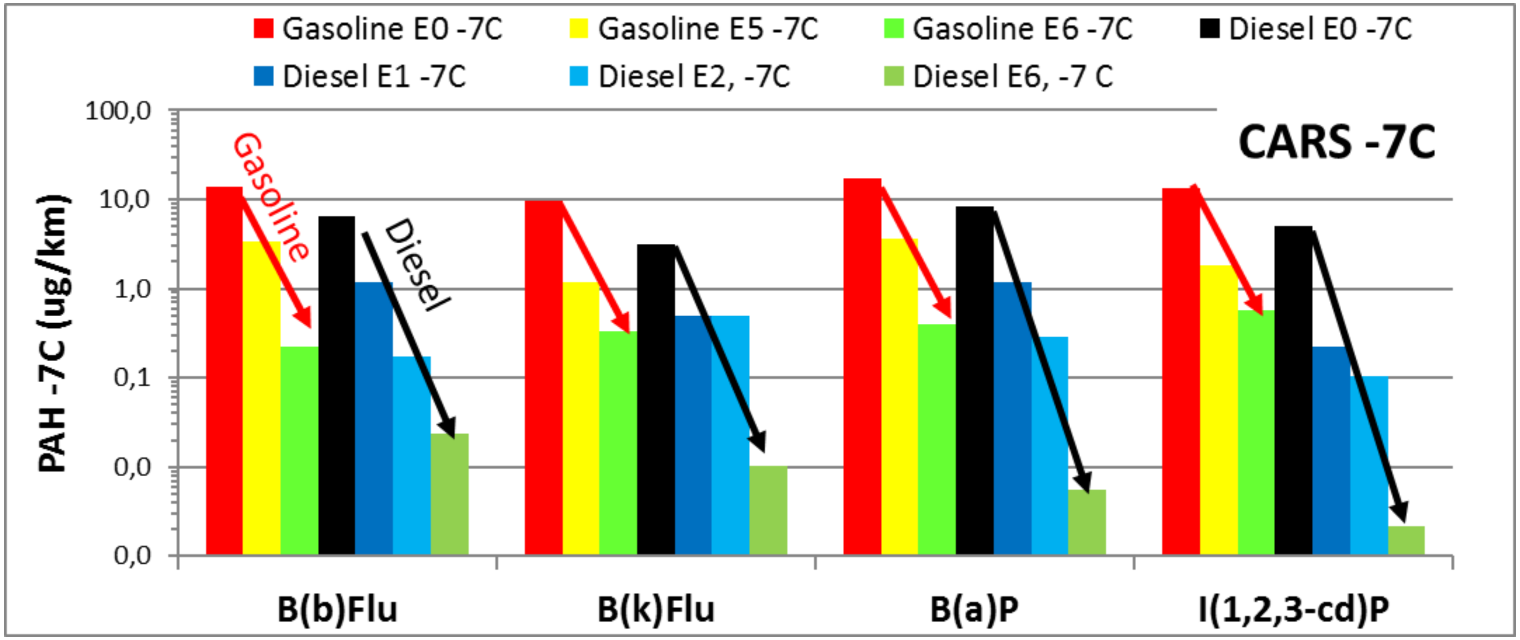


PAHs for cars at +23 °C test temperature

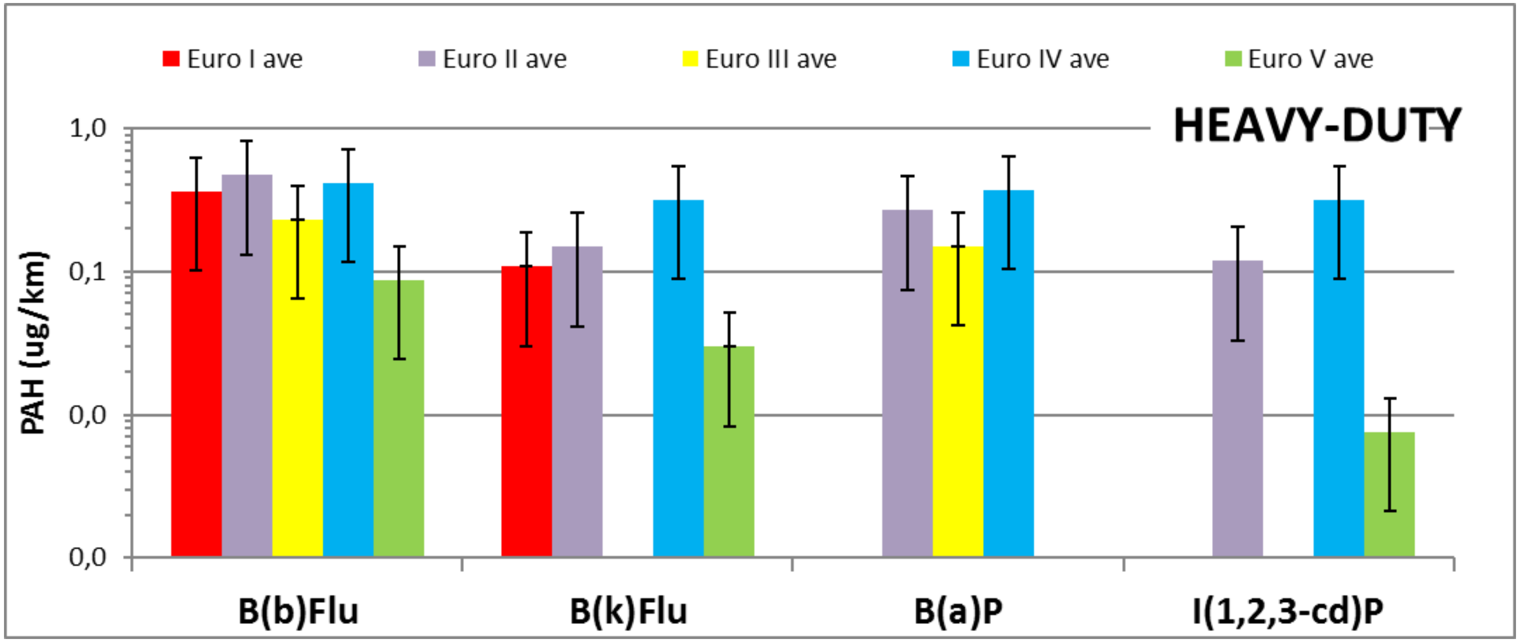


PAH emissions at -7 °C test temperature

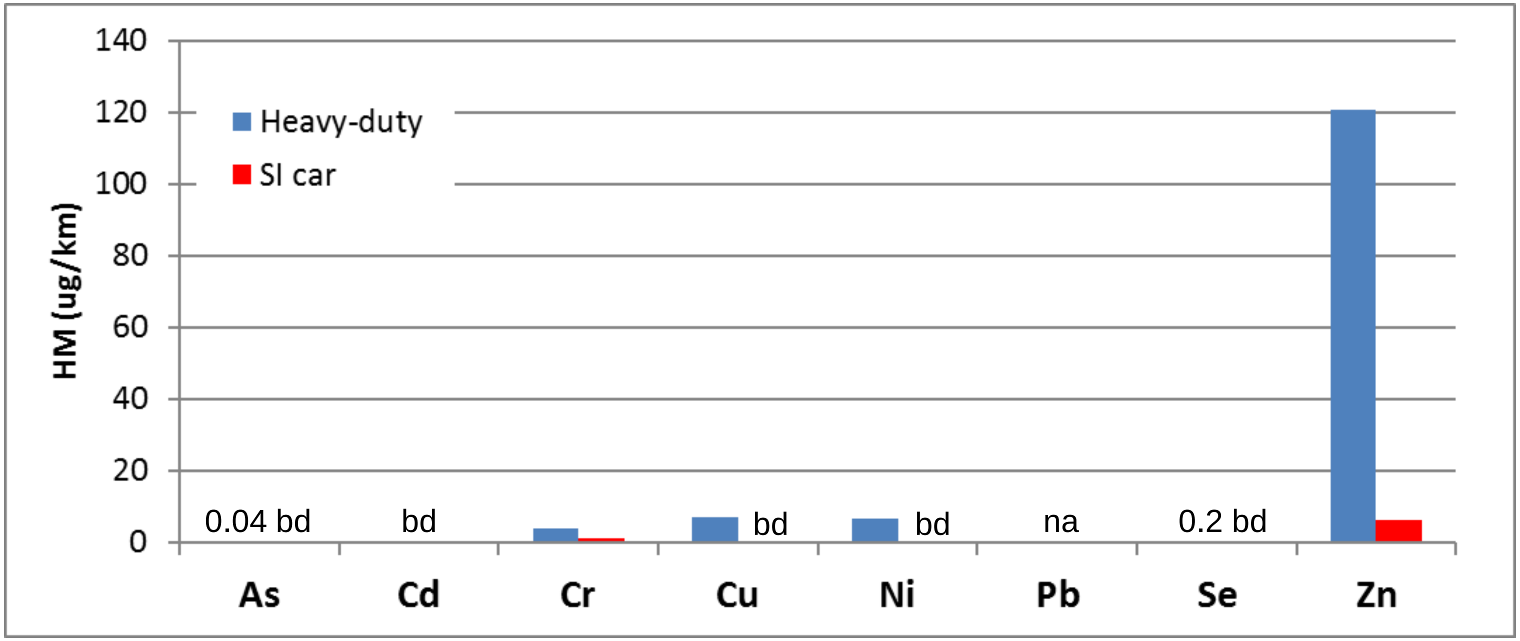
- Non-catalyst gasoline car: 3-5 x higher PAHs at -7 °C vs +23 °C
- Gasoline cars, Euro 5: 60-70 x higher PAHs at -7 °C vs +23 °C
- Diesel cars: no substantial effect of test temperature on PAHs



PAHs for HD engines and vehicles



HM for HD bus engine (Euro II) and a gasoline car (Euro 2)



EFs in Nordic study 2017 (*µg/km)*

	PAH7	B(b)Flu	B(k)Flu	B(a)P	I(1,2,3-cd)P	As	Cd	Cr	Cu	Ni	Pb	Se	Zn
Heavy-duty vehicles													
Euro 0	na	na	na	na	na	na	na	na	na	na	na	na	na
Euro I-IV	3,8	0,6	0,6	0,7	0,6	0,04	bd	3,6	7,0	6,5	na	0,2	121
Euro V-VI	0,2	0,2	0,05	0,00	0,02	na	na	na	na	na	na	na	na
Gasoline cars													
Euro 0	31	3,6	1,7	4,9	2,8	na	na	na	na	na	na	na	na
Euro 1-4	0,7	0,10	0,06	0,15	0,15	bd	bd	1,1	bd	bd	na	bd	6,0
Euro 5-6	0,7	0,20	0,04	0,14	0,08	na	na	na	na	na	na	na	na
Diesel cars													
Euro 0	31	4,9	2,2	5,8	4,7	na	na	na	na	na	na	na	na
Euro 1-4	6,0	0,8	0,3	1,3	0,13	na	na	na	na	na	na	na	na
Euro 5-6	0,1	0,02	0,01	0,02	0,01	na	na	na	na	na	na	na	na
Detection limit	*0,04*	*0,04*	*0,04*	*0,04*	*0,04*	*0,01*	*0,2*	*0,1*	*0,6*	*0,4*		*0,01*	

bd = Below detection limit. na = Not analysed

Analytical uncertainty for PAHs and metals appr. ±30%. These are analysed from particulate mass (PM) samples, for which uncertainty appr. ±42%. **Total uncertainty is estimated as ±72%.**

		No of data	PAH7 µg/km	Benzo(b) fluorantene µg/km	Benzo(k) fluorantene µg/km	Benzo(a) pyrene µg/km	Indeno(1,2,3-cd)pyrene µg/km	No of data	As µg/km	Cd µg/km	Cr µg/km	Cu µg/km	Ni µg/km	Pb µg/km	Se µg/km	Zn µg/km
Heavy-duty vehicles																
Euro I	max	2	1,9	0,4	0,1	0,0	0,0									
	average		1,9	0,4	0,1	0,0	0,0									
Euro II	max	2	3,2	0,5	0,2	0,4	0,2	2	0,04	bd	3,6	7,0	6,5	na	0,2	121
	average		3,0	0,5	0,1	0,3	0,1									
Euro III	max	1	1,9	0,2	0,0	0,2	0,0									
	average		1,9	0,2	0,0	0,2	0,0									
Euro IV	max	4	3,8	0,6	0,6	0,7	0,6									
	average		2,3	0,4	0,3	0,4	0,3									
Euro V&EEV	max	2	0,20	0,17	0,05	0,00	0,02									
	average		0,10	0,09	0,03	0,00	0,01									
Euro VI	max	0	na	na	na	na	na									
	average		na	na	na	na	na									
Gasoline cars																
Euro 0	max at +23 °C	8	31,4	3,6	1,7	4,9	2,8									
	average at +23 °C		16,5	1,9	0,9	2,7	1,7									
	max at -7 °C	8	96,9	13,6	9,5	17,2	13,5									
Euro 1	max at +23 °C	1	0,7	0,1	0,1	0,2	0,2									
	average at +23 °C															
Euro 2	max at +23 °C	3	0,3	0,08	0,03	0,08	0,07	2	bd	bd	1,1	bd	bd	na	bd	6,0
	average at +23 °C		0,2	0,06	0,02	0,04	0,03				0,6					3,8
Euro 3	max	0														
	average															
Euro 4	max	0														
	(average)															
Euro 5	max at +23 °C	4	0,7	0,20	0,04	0,14	0,08									
	average at +23 °C		0,5	0,12	0,03	0,07	0,03									
	max at -7 °C	4	14,3	3,4	1,2	3,6	1,9									
Euro 6	max at -7 °C	1	2,3	0,2	0,3	0,4	0,6									
Diesel cars																
Euro 0	max at +23 °C	4	31	4,9	2,2	5,8	4,7									
	average at +23 °C		17	3	1	3	2									
	max at -7 °C		38	6,4	3,1	8,3	5,1									
Euro 1	max at +23 °C	1	6,0	0,8	0,3	1,3	0,1									
	max at -7 °C	1	8,7	1,2	0,5	1,2	0,2									
Euro 2	max at -7 °C	1	1,6	0,2	0,5	0,3	0,1									
Euro 3	max	0														
	average															
Euro 4	max	0														
	average															
Euro 5	max at +23 °C	3	0,10	0,02	0,01	0,02	0,01									
	average at +23 °C		0,07	0,01	0,00	0,01	0,00									
Euro 6	max at -7 °C	1	0,06	0,02	0,01	0,01	0,00									

EF also at -7 °C test temperature.

Consideration of cold temperature EFs → real-life emissions?

Other considerations

Origin of exhaust PAH and HM

- PAHs found in the exhaust gas originate mainly from fuel (unburned and partially combusted fuel).

- Metals in the exhaust gas may originate from different sources.
  - Zn is typically present in the engine oil.
  - Cr, Ni and Cu originate typically from engine wear.
  - Development of engines towards lower engine oil consumption and engine wear reduce metal tailpipe emissions.

- Note: Intake air in lab measurements is filtered. In outdoor measurements (intake) air and other contaminations to be considered.

Exhaust species originate from fuel and lube mainly

CO_2, H_2O, HCs, NOx...
SO_2

[SVOC?]

Fuel, lube
Hydrocarbons (fuel mainly)

Sulphur (fuel &lube) → SO_3

Ash (not important for on-road)
marine fuel V, Ni, Na; lube Ca, Zn, P; engine wear Fe, Cu, Cr, Al etc.

PM raw exhaust *
Liquid HCs
Oxidation products

Black carbon (BC, soot)

H_2SO_4

Metalsulphates
Metal anions
Metal oxides (V_2O_5…)
Metals etc.

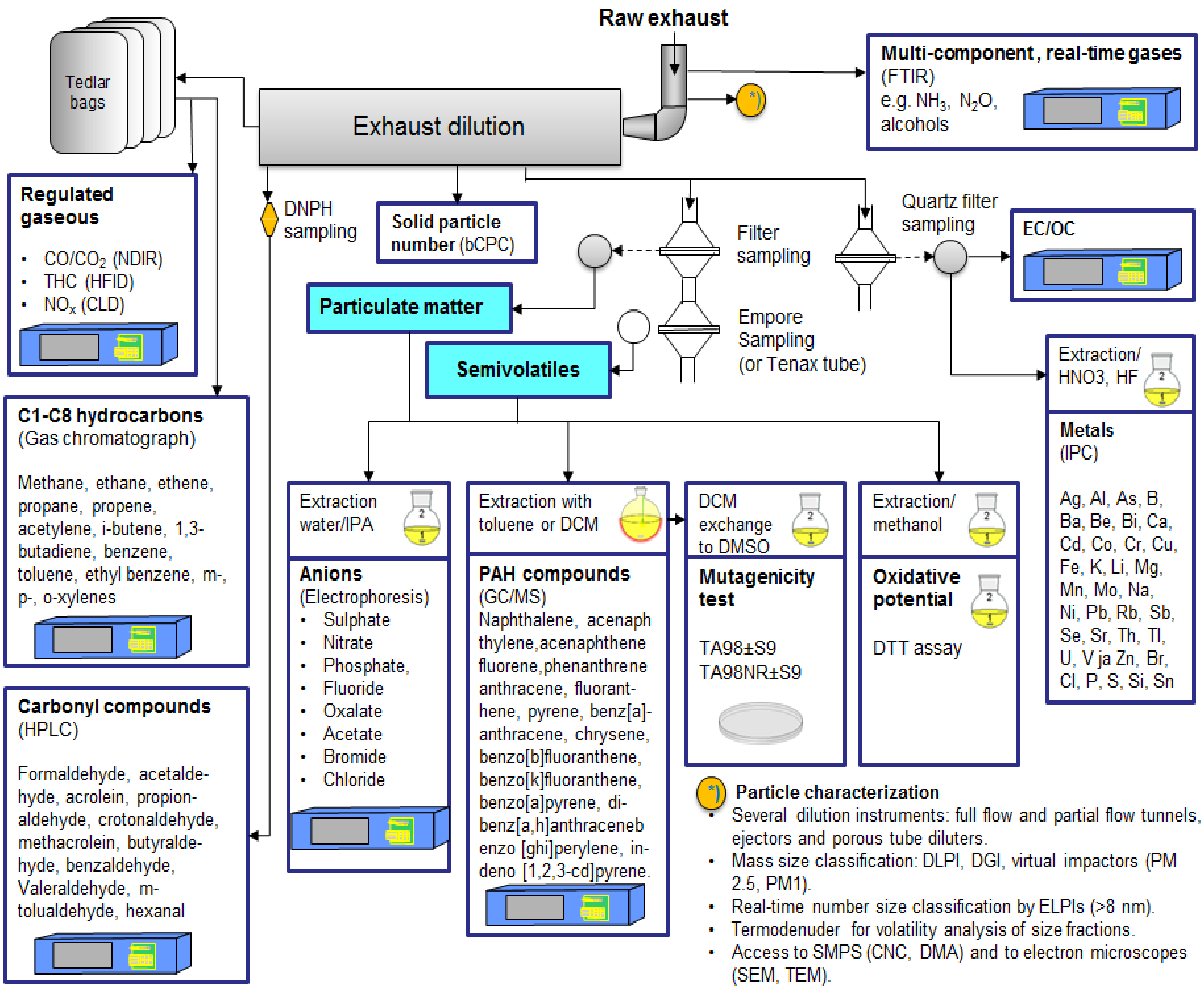
Dilution and ageing **
Further oxidation (larger molecules). Partly attach to soot.

BC carbon particles agglomerate and adsorb other species

Hydrated sulphuric acid $H_2SO_4 \cdot H_2O$, sulphates, metalsulphates, metal oxides (V_2O_5…), metals etc..
Partly attach to soot

* Hot sampling 120-180 °C
** Standardised lab dilution <52°C, typical dilution ratio 3:1 - 20:1 vs atmospheric dilution 500:1 -1000:1.

Emission measurements at VTT

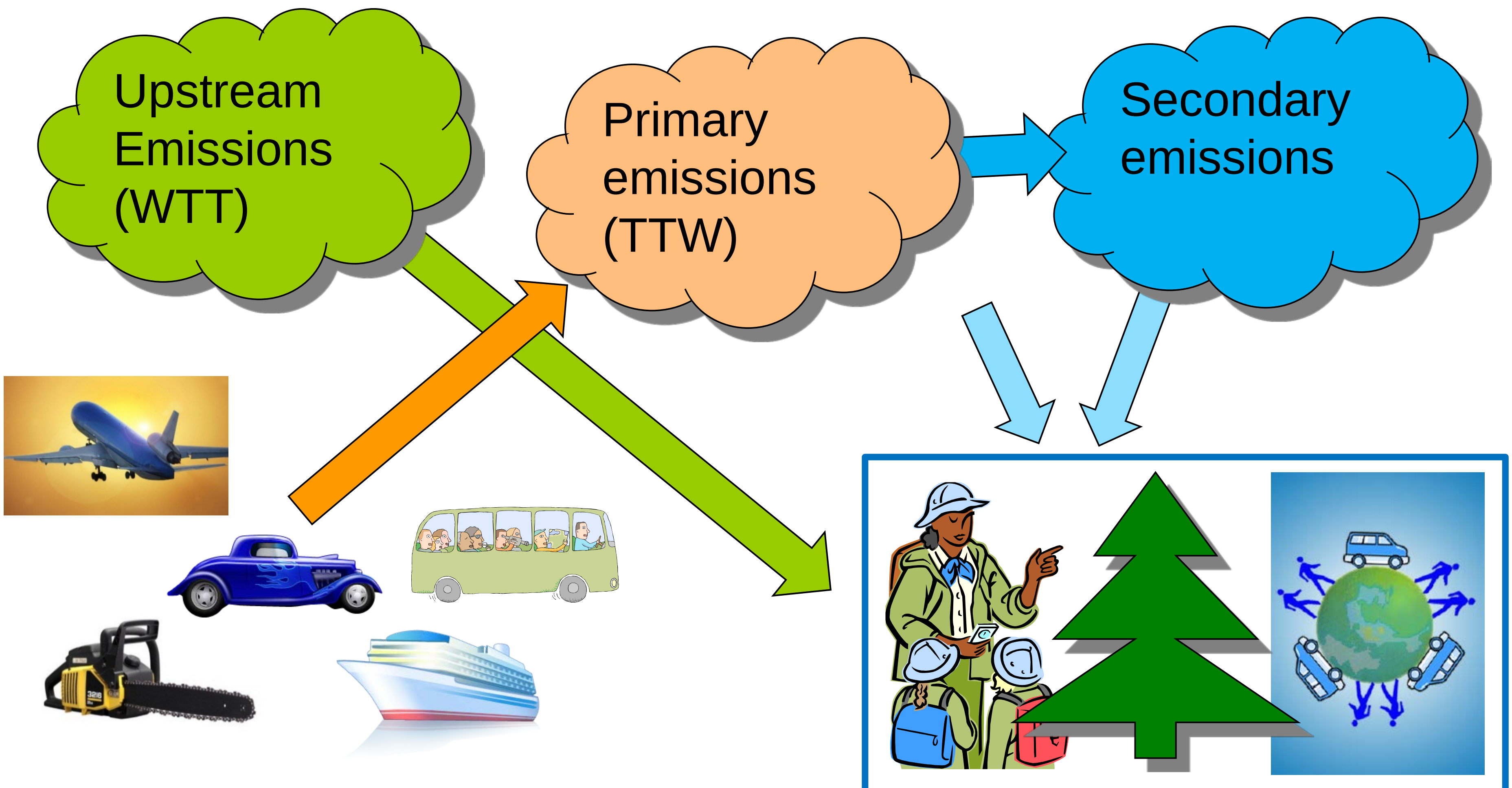


Significance of emissions

	Health effects	Environmental effects			Global warming
		Vegetation	Acidifi-cation	Eutrophi-cation	
CO	X	X			
NO_x/NO_2	X	X	X	X	
PM and SOA	X				
PN	X				
BC	X				X
SO_2	X		X		
Priority PAHs	X				
Aldehydes: formaldehyde, acetaldehyde, acrolein	X	X			
1,3-Butadiene	X	X			
Aromatics: benzenes, toluene, xylenes	X	X			
Methane					X
NH_3	X		X	X	
N_2O					X
Ozone, ground-level troposphere caused by VOCs[a], CO, NO_x	X	X			X
Ozone depletion in stratosphere caused by N_2O	X				X
CO_2					X

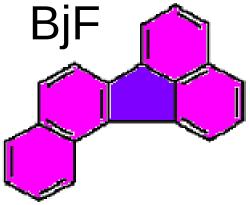
Aakko-Saksa et al. (2016) VTT Report VTT-R-04494-16

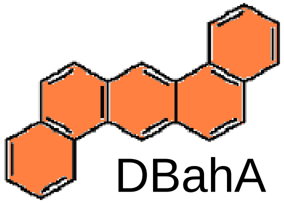
It is not enough to work piece by piece… wholeness need to be understood



Priority PAHs are carcinogenic

BjF





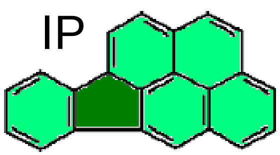
DBahA

	N	Ace	Acy	Flu	Phe	An	F	P	**BaA**	DMBA	**Chr**	**BbF**	**BjF**	**BkF**	**BaP**	**BeP**	**IP**	**DBahA**	BghiP
IARC[6]	2B	3		3	3	3	3	3	2B		2B	2B	2B	2B	1	3	2B	2A	3
Ring [a]	2/2	3/2	3/2	3/2	3/3	3/3	4/3	4/4	4/4	4/4	4/4	5/4	5/4	5/4	5/5	5/5	6/5	5/5	6/5
TEF EU (2001)				0.001[b]	0.0005 **–0.01**	0– **0.01**	0– **0.06**	0– **0.081**	0.005– **0.145**	(10[b])	0.001– **0.89**	0.06– **0.14**	0.045– **0.061**	0.03– **0.1**	1		0– **0.232**	0.69–**5**	0.01– **0.03**
a (16)	x	x	x	x	x	x	x	x	X		X	X		X	X		X	X	x
b (14)				x	x	x	x	x	X		X	X		X	X	x	X	X	x
c (US 7)									X	X	X	X		X	X		X		
d (EU7)									X			X	X	X	X		X	X	

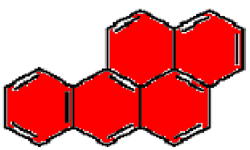
[a] No. of rings/aromatic rings [b] Collins et al. (1998)

a) 16 PAHs[5] defined by the US EPA (1998)
b) 14 PAHs reported e.g. by Kokko et al. (2000).
c) 7 PAHs defined by the US EPA (2007)
d) 7 PAHs defined in European Directive 2004/107/EC.

IP

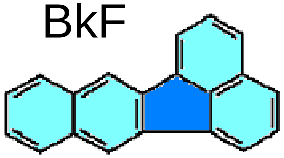


BaP



NMR2017 (yellow): Benzo(a) pyrene, benzo(b) fluoranthene, benzo(k) fluoranthene and indeno (1,2,3-cd)pyrene.

BkF



Cancer potency of engine exhaust can be calculated using risk factors e.g. OEHHA (2009), US EPA IRIS (2010) and Nordic Ecolabelling (2008)

Substance	Unit Risk Factor $(\mu g/m^3)^{-1}$			Normalized[7]
	Nordic Ecolabelling	OEHHA 2009	US EPA IRIS 2010	
Particulate matter[8]	7×10^{-5}	30×10^{-5}	insuff. Data	177
Benzene	0.8×10^{-5}	2.9×10^{-5}	$(0.22\text{-}0.78) \times 10^{-5}$	17
Formaldehyde	10×10^{-5}	0.6×10^{-5}	1.3×10^{-5}	4
Acetaldehyde	0.2×10^{-5}	0.27×10^{-5}	0.22×10^{-5}	2
Ethene	5×10^{-5}			17
Propene	1×10^{-5}			3
1,3-Butadiene	30×10^{-5}	17×10^{-5}	3×10^{-5}	100
PAH (including benzo(a)pyrene)	2800×10^{-5}			9333

Not only CO_2 warms climate: Short-lived climate forcers (SLCF): CH_4, BC, O_3

- Cutting the SLCF emissions reduce the warming rate in short-term, while their long-term impact is limited (driven mainly by CO_2).
- CH_4 impact is well understood, while BC is more uncertain (co-emitted species have cooling effects).
- SLCF reductions have impact on climate change and possible co-benefits for air pollution.

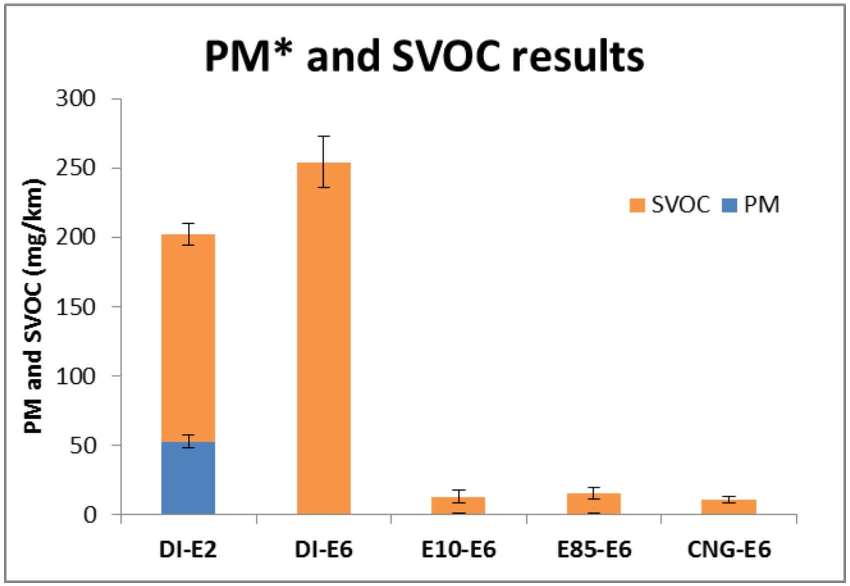
Global warming potential (GWP) values relative to CO_2

Industrial designation or common name	Chemical formula	GWP values for 100-year time horizon		
		Second Assessment Report (SAR)	Fourth Assessment Report (AR4)	Fifth Assessment Report (AR5)
Carbon dioxide	CO_2	1	1	1
Methane	CH_4	21	25	28
Nitrous oxide	N_2O	310	298	265

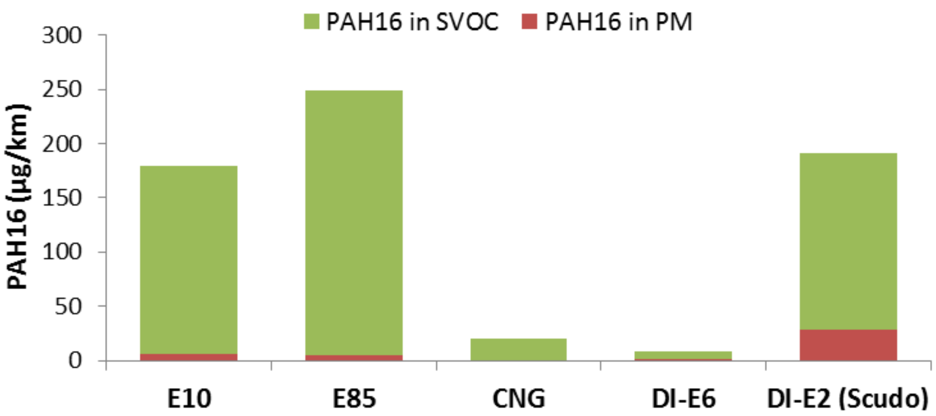
Note also N_2O →

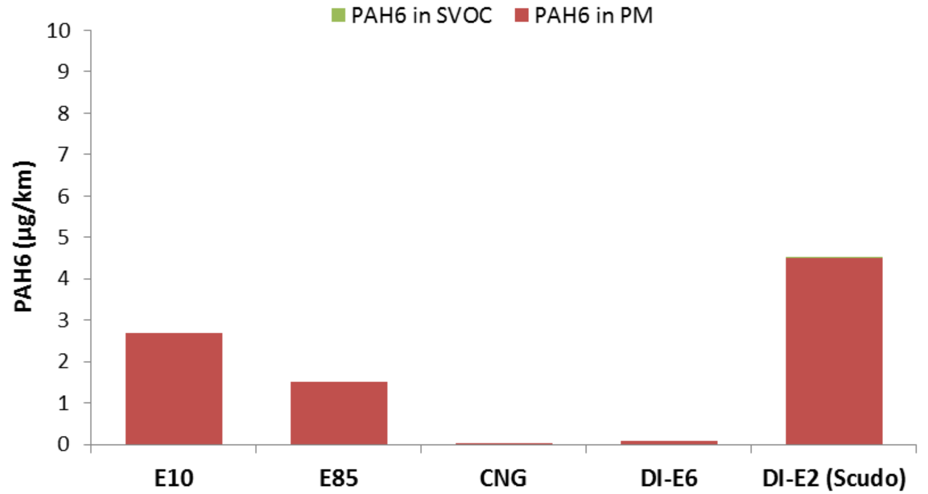
Source: IPCC Climate Change 2014 Synthesis Report

Recent project example with compherensive analytics (tests at -7 °C): SVOCs



We seldom measure semivolatiles (SVOCs), although their role may be significant.

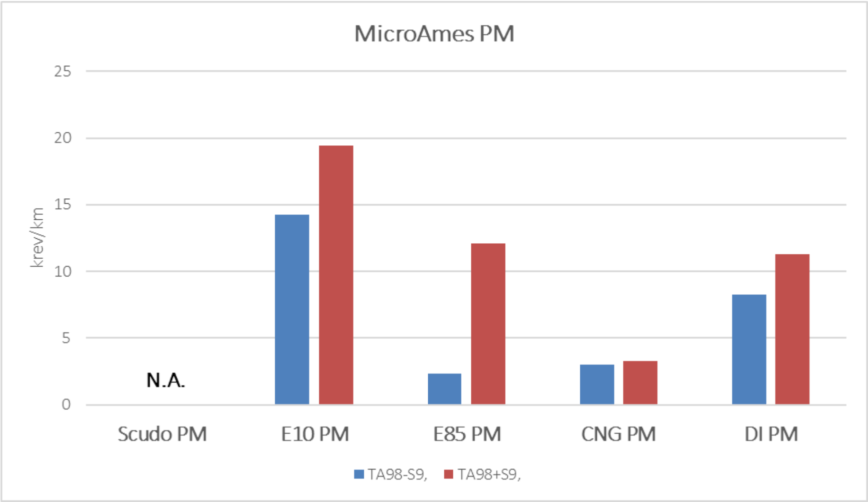


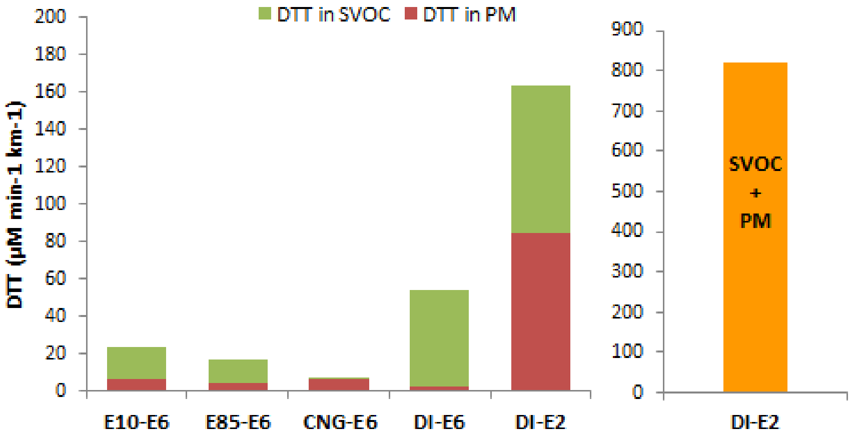


Aakko-Saksa et al. (2016) VTT Report VTT-R-04494-16

Recent project example with compherensive analytics (tests at -7 °C): SVOCs

- All PM samples were mutagenic in the Ames test, while SVOC samples only from diesel cars were mutagenic.
- SVOC showed substantial oxidative potential for all cars except NGV. Oxidative potential was low for new cars compared to Euro 2 diesel car.

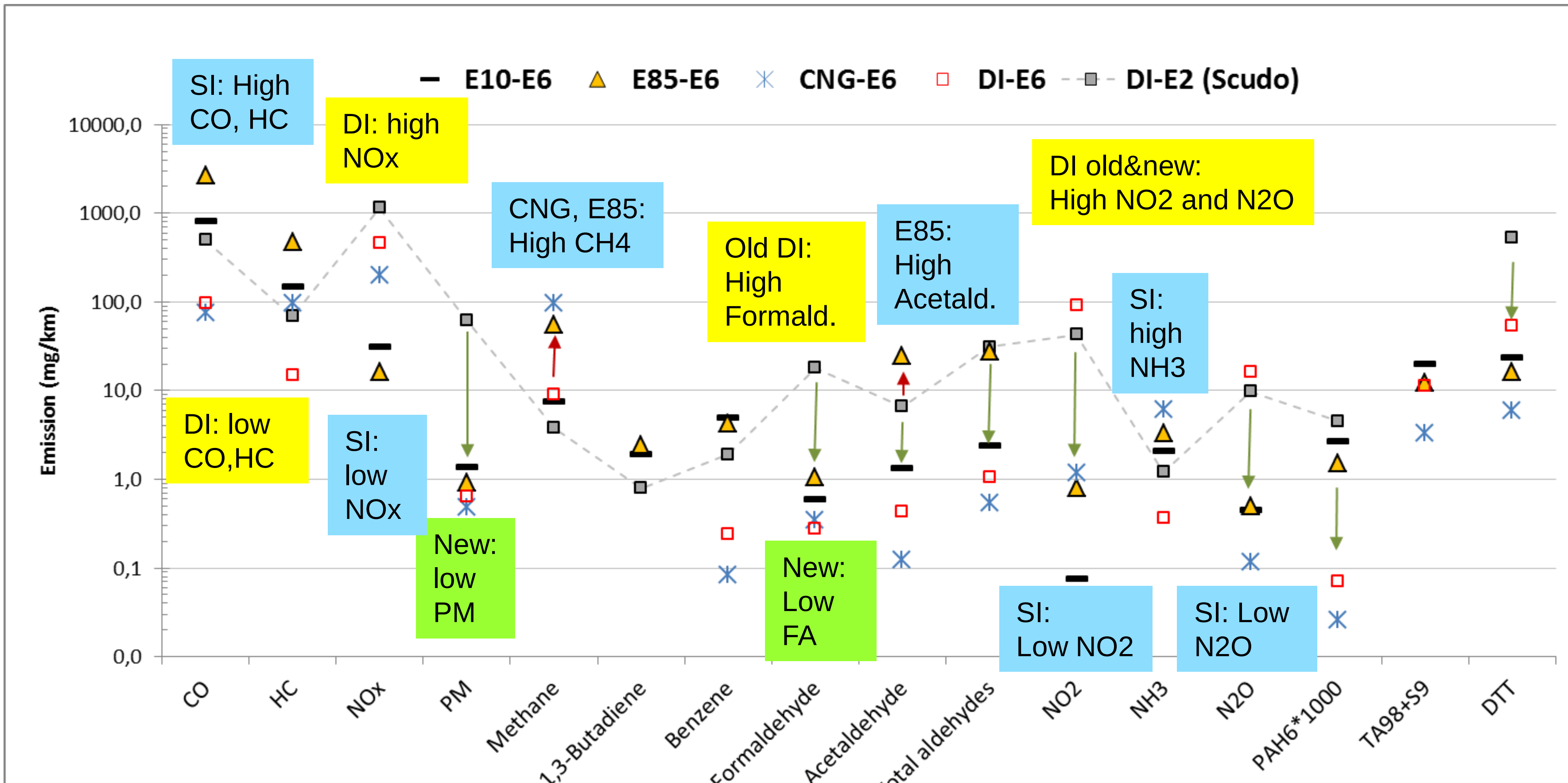




Aakko-Saksa et al. (2016) VTT Report VTT-R-04494-16

Recent project example with compherensive analytics for cars (tests at -7 °C)

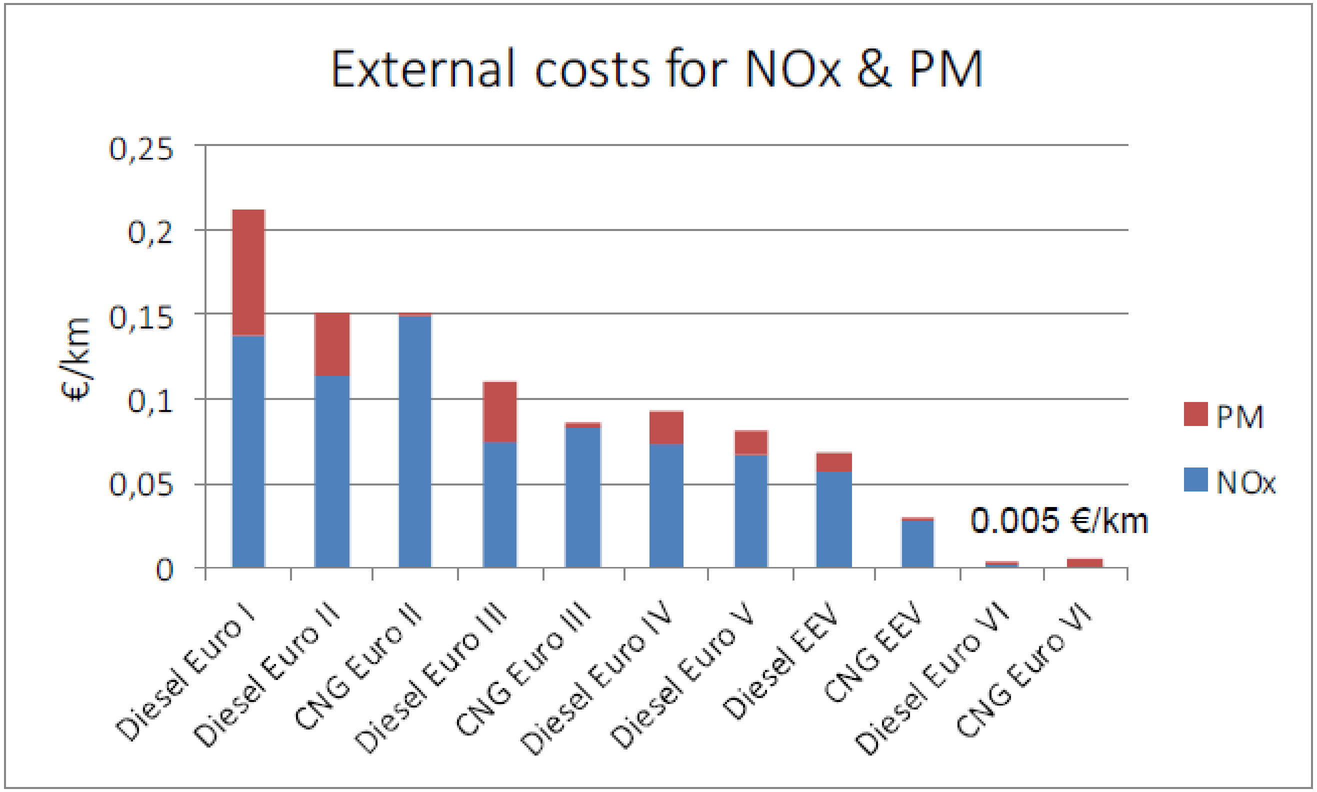
DI-E2 = Euro 2 diesel car ; DI-E6 = Euro 6 diesel car ; E10-E6 = Euro 6 gasoline car using E10 fuel ;
E85-E6 = Euro 6 FFV using E85 fuel ; CNG-E6 = Euro 6 bi-fuel car using CNG fuel



Aldehydes: No limits in Europe.
US LEV III formald. max. 4 mg/mi

Euro VI: **THC 160 mg/kWh for HD (WTHC)**
Euro 6: **THC max 100 mg/km for cars**

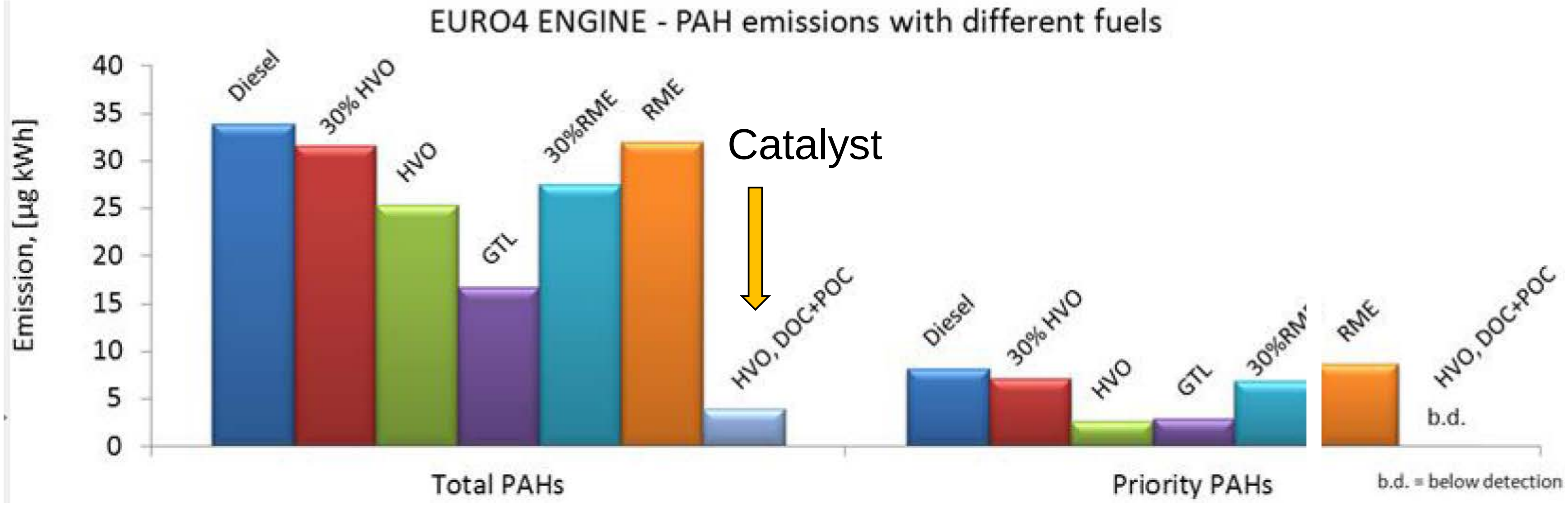
Euro VI heavy-duty is very clean: emission control devices benefit from warm engines



VTT data & Directive 2009/33/EC

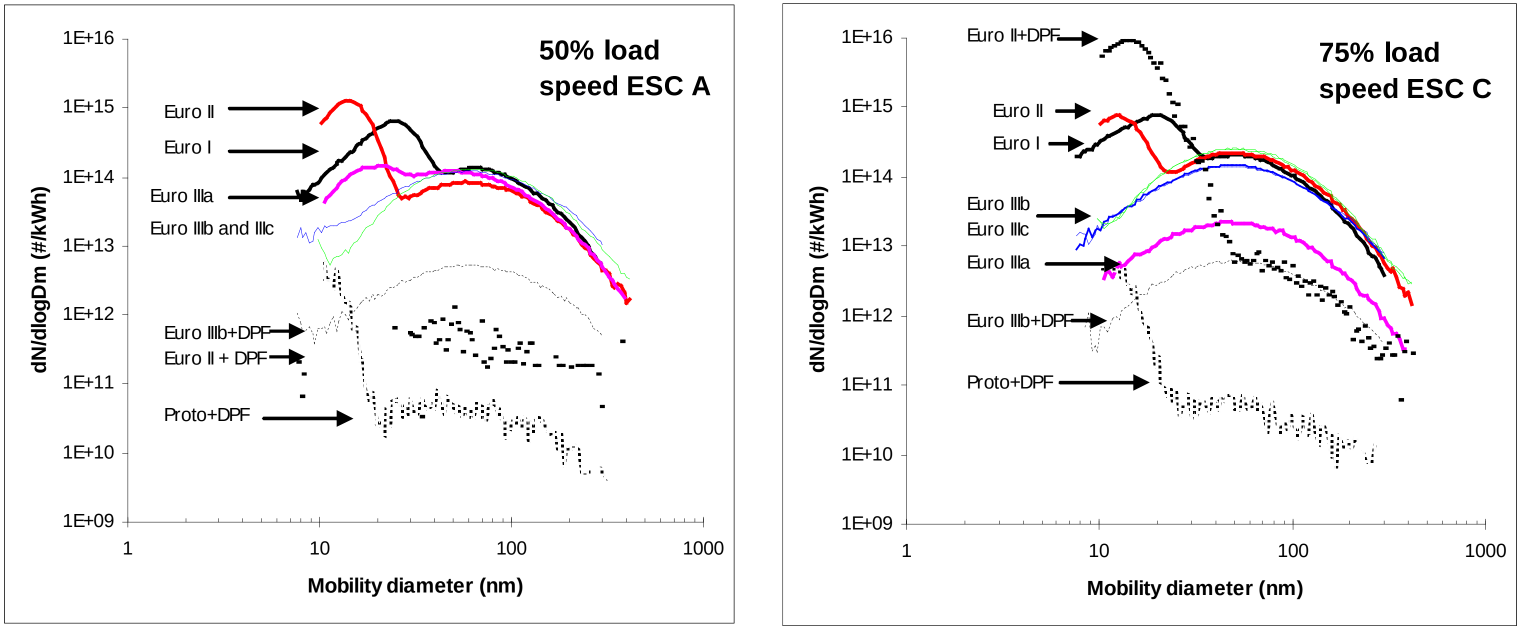
Heavy-duty PAHs

- Heavy-duty PAH emissions reduced with paraffinic fuels and **particularly with exhaust aftertreatment technology**.



Murtonen et al. SAE 2009-01-2693

Particle size distributions with HD engines



- Fairly consistent accumulation mode for the conventional diesel
- Nucleation mode at high load conditions (even on the low sulphur fuel), especially on the CRT-equipped Euro-II engine

Thompson, Aakko et al. SAE 2004-01-1986. ("EU Particulates project")

Conclusions

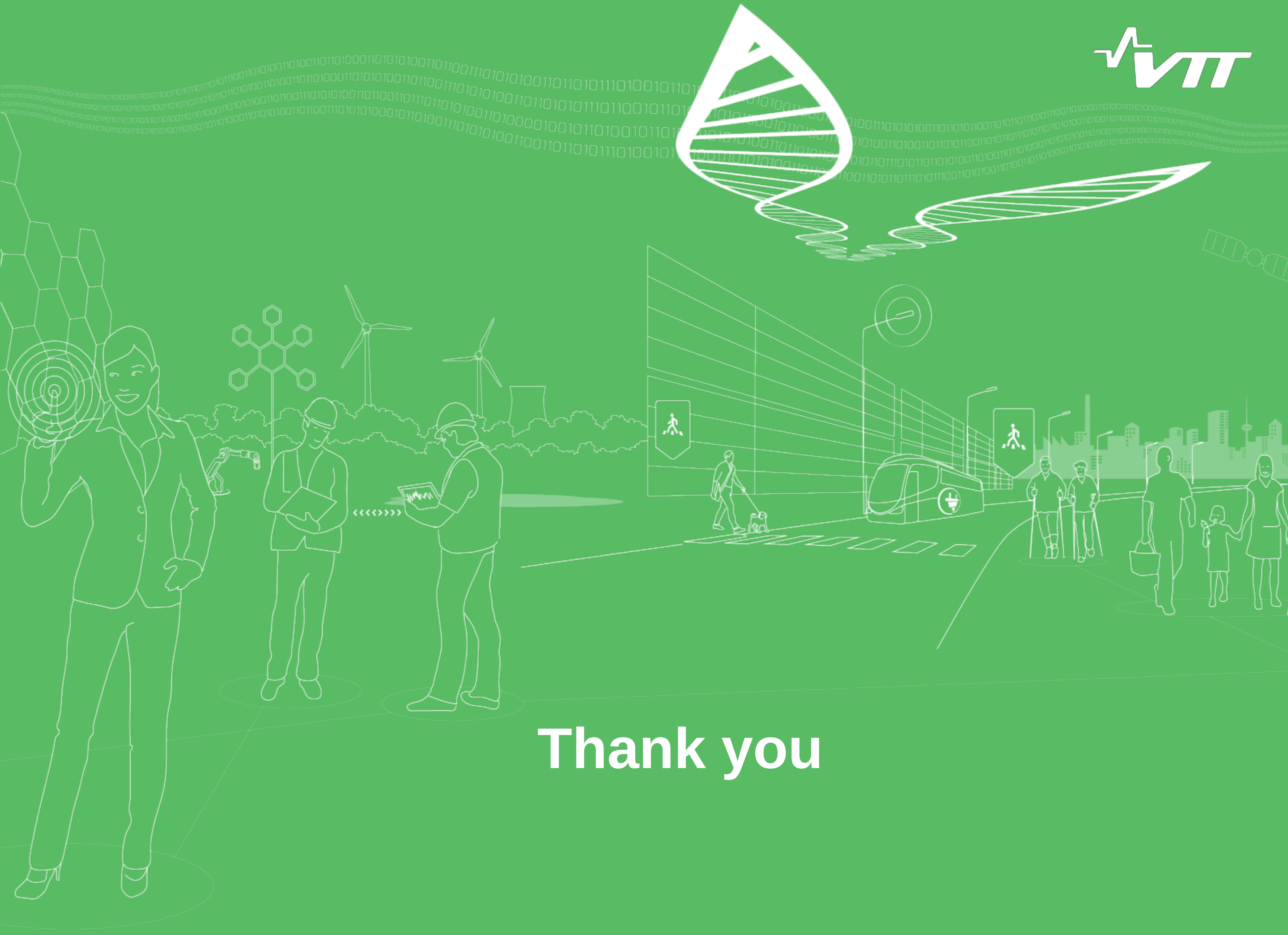
EF evaluation in Nordic stydy

- PAHs for cars (Euro 0-6) and for HD trucks and buses (Euro 0-VI)
    - Besides normal test temperature (+23 °C) also sub-zero (-7 °C) temperature
- Heavy metals for Euro 2 car and Euro II bus.

Low EFs in general for new engine and emission control technology.

EFs can be higher at low temperatures.

EFs of Nordic study presented to EMEP/EEA.



Thank you

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