Experiences in semivolatile (SVOC) emission measurements at VTT

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Contents

- SVOC definitions
- Measurements at VTT
- Recent research elsewhere
- US legislation
- Conclusions

SVOC definition

- SVOCs are **sufficiently volatile to be in vapor form at the temperature of engine-out exhaust, but condensable under atmospheric conditions**.

- Most SVOC molecules have **at least 14 carbon atoms and boiling points 240-400 °C.** SVOCs may contain PAHs, dioxins and nitro-PAHs (US EPA 40 CFR 1065.1103–1111). Analysed SVOC species are typically PAHs or n-alkanes, but majority of SVOC mass is challenging to identify.

- SVOC concentrations depend on the **gas particle partitioning** of the emissions, which vary depending on **concentration and saturation pressure, other constituents of exhaust gas and sampling parameters**.

SVOC definition

- SVOC emissions from cars are not well-known.

- Exhaust emission measurements cover:
  - THC (<C12), which is measured using FID
  - Particulate matter (PM) associated primary organic aerosol (POA).

➢ **Exhaust emission measurements do no cover SVOCs**, although regulatory test conditions favor condensing of the lightest SVOCs (or IVOCs) in PM.

- Note: SVOCs potentially form secondary organic aerosol (SOA).

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Atmospheric Chemistry and Physics
EGU

Organic emission profiles (Lu et al. 2018)

- Lu et al. classified
  - IVOCs **C12 to C22**
  - SVOCs **C23 to C32**
  - LVOCs C33 to C36 (respective to n-alkanes)

- Volatility basis set (VBS) framework lumps organics into logarithmically spaced bins of saturation concentrations (C*) at 298 K. Designed for C12 and larger.

Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions

Quanyang Lu[1,2], Yunliang Zhao[1,2,a], and Allen L. Robinson[1,2]

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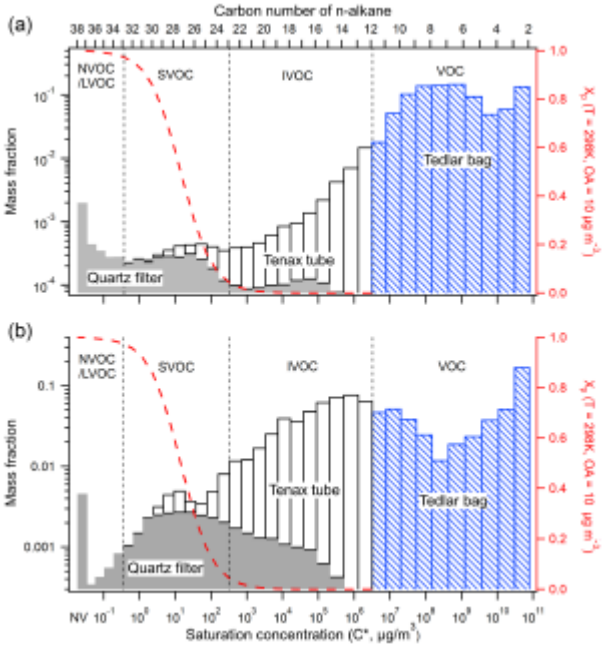

Volatility distribution a) gasoline b) diesel.
Red dashed line = the particle fraction.

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Atmospheric Chemistry and Physics

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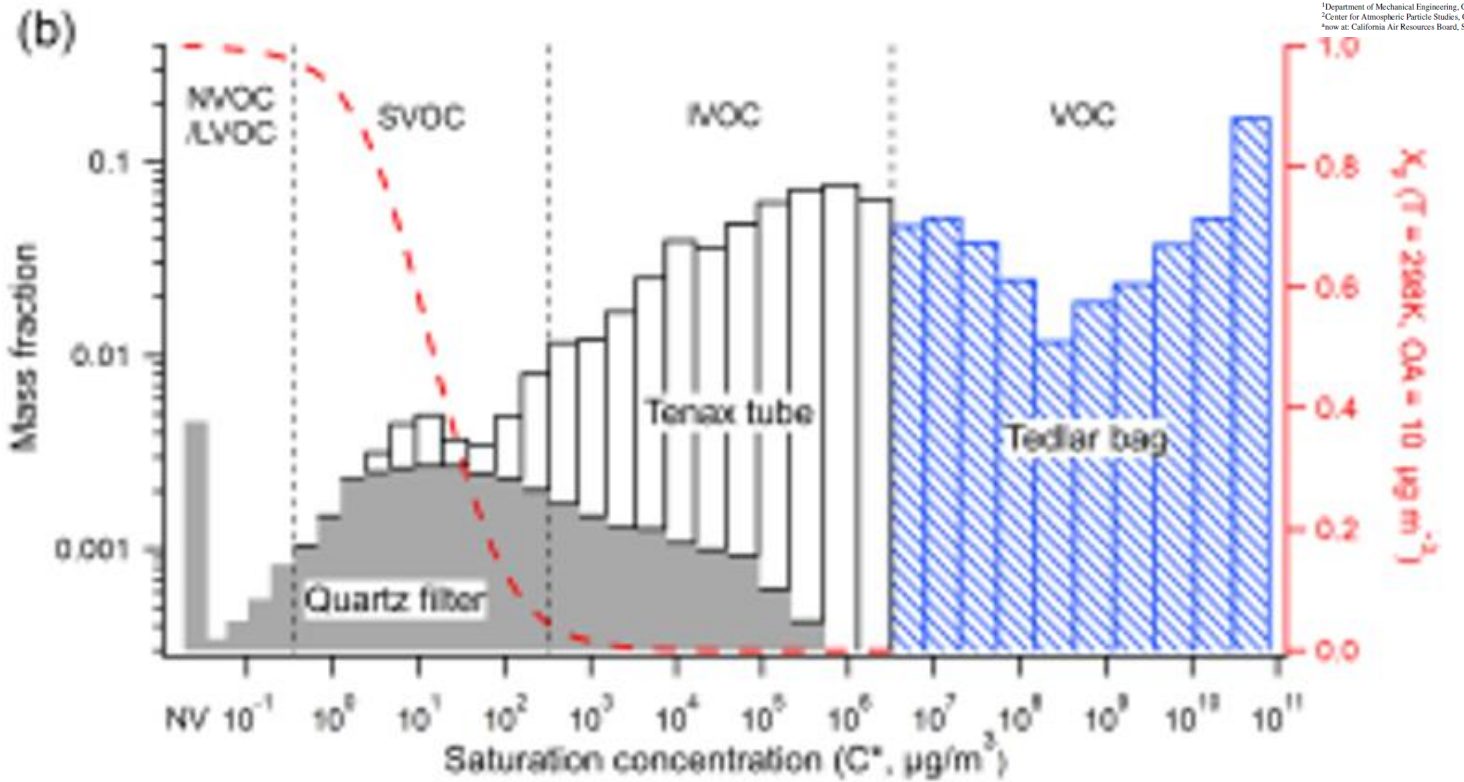


SVOC measurements at VTT

- In 90's at VTT, SVOCs were collected using PUF material for PAH analyses and Ames tests
  - Demanding, expensive pre-purification of PUF material
  - Filter face velocity and temperature affect the SVOC/PAH emissions

- SVOC sampling (US §1065.1103-1065.1111) with XAD–2 resin with or without PUF plugs.

- XAD and Empore materials were tested in late 90's at VTT, and Empore materials again in 2015.

SVOC measurements at VTT in 2015

Raw exhaust

Exhaust dilution

VOCs
- e.g. CO, THC
- C1-C8 hydrocarbons, e.g. methane, acetylene, benzene, toluene, ethyl benzene, xylenes
- C1-C6 carbonyls e.g. formaldehyde, acetaldehyde, hexanal

PM sampling
e.g. PTFE filters

SVOC sampling
e.g. Empore disks
(or Tenax tube etc.)

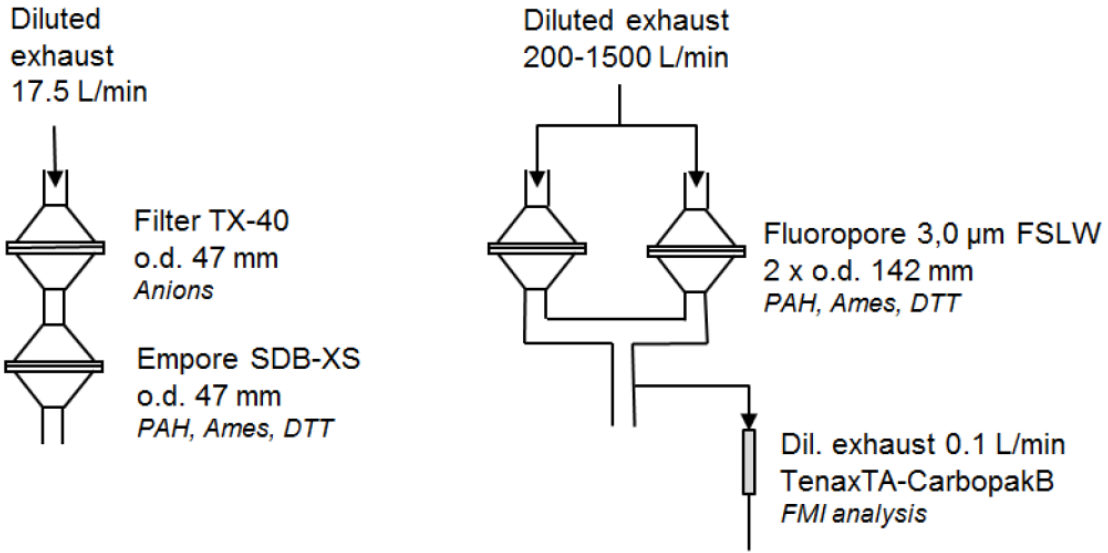
PM Quartz filter sampling

EC/OC
Metals

PAH compounds e.g. benz[a]pyrene
Mutagenicity e.g. Ames test
Oxidative potential e.g. DTT
Anions e.g. sulphates

Particle characterization, many dilution systems, mass and number size classification, thermodenuder for volatility analysis, access to SMPS, SEM and TEM.

Details of sampling



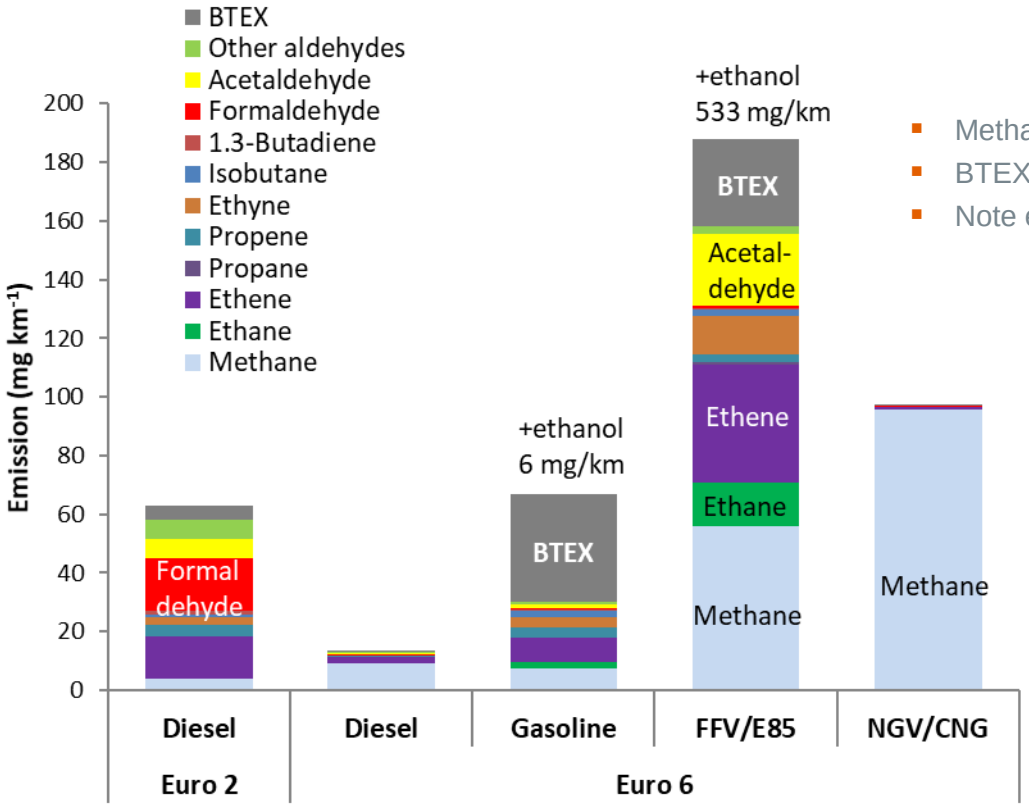
Empore sampling

- Empore disks are developed for water and air sampling (e.g. for PAH analysis).

- At VTT, Empore disks were tested for SVOC sampling in late 90's.
  - Two types of Empore disks a) nonpolar C18 (activated) and b) slightly polar SDB
  - Results with both Empore types gave comparable results with PUF sampling,
  - Extraction of heavy PAHs from Empore was more challenging than from PUF.

- In 2015 testing, Empore SDB-XC disks (poly(styrenedivinylbenzene) copolymer) were used for SVOC sampling. Similar Empore products as in 90's were not available.

VOCs in 2015 measurements



- Methane emission highest from NGV/CNG and FFV/E85.
- BTEX aromatics highest from FFV/E85 and gasoline.
- Note ethene emission from FFV/E85.

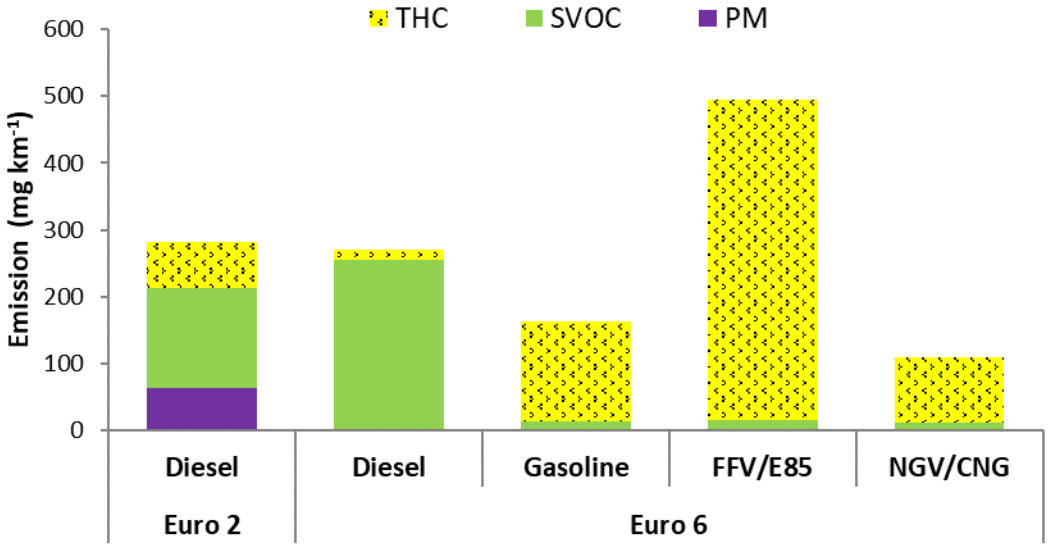
VOCs: ~15 E6 diesel, ~ 150 mg/km gasoline, ~ 700 mg/km FFV/E85, ~100 mg/km NGV/CNG

Ref. Aakko-Saksa et al. TAP 2019 presentation

SVOC emissions

- Higher SVOC than PM emissions for all cars tested. **Very high SVOC emission for Euro 6 diesel** car. Chemical composition was not analysed (except PAHs).

- SVOCs were collected after PM filters using Empore disks. Back-up filter of PM sampling captures some SVOCs, but not substantially.

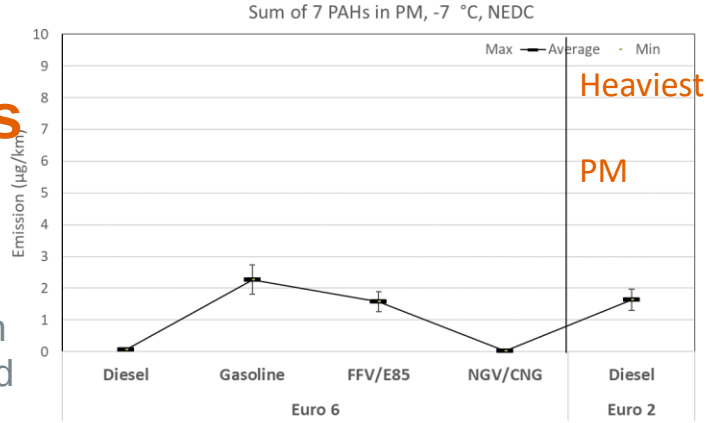


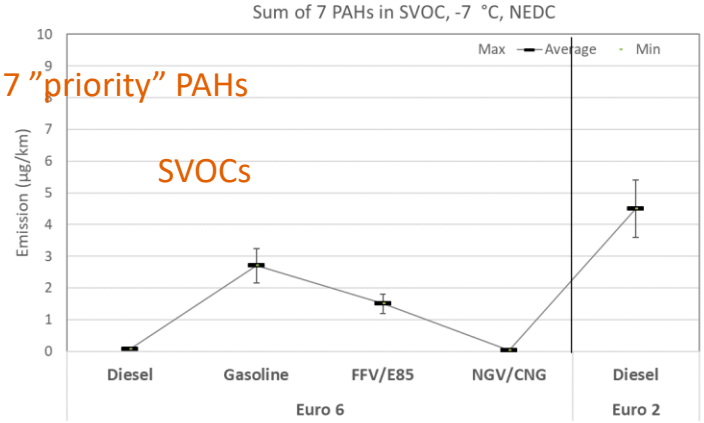
Sum of PM, SVOC and THC mass emissions are surprisingly similar for different cars.

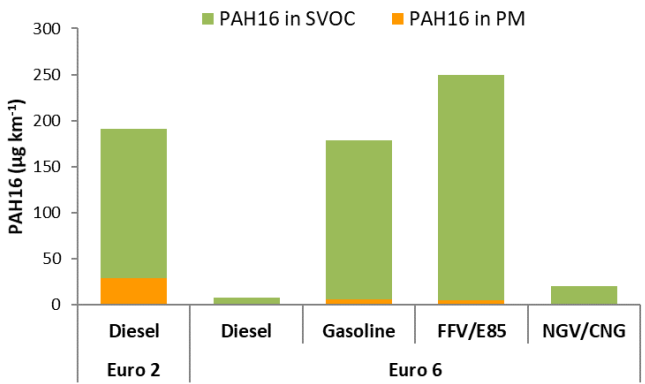
Ref. Aakko-Saksa et al. TAP 2019 presentation

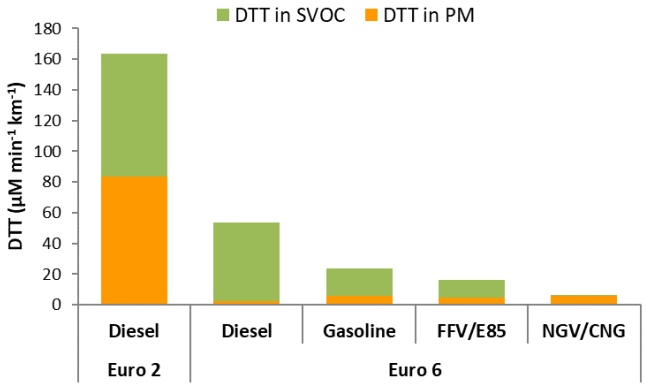
PAHs in SVOCs and in PM

- Sum of 16 PAHs high in SVOCs when comapred with PM.
- Sum of 7 PAHs at the same level in PM and SVOCs for Euro 6.
- High PAH emissions from gasoline car and FFV/E85.









Secondary organic aerosol (SOA)

In 2015 measurements, SOA formation decreased as ethanol content of the fuel increased and aromatics content decresed.

BTEX compounds had a large impact on SOA formation. Also Nordin et al. (2013) found C6–C9 aromatics as SOA precursors.

SVOCs as SOA formers?

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www.atmos-chem-phys.net/17/5311/2017/
doi:10.5194/acp-17-5311-2017

Atmospheric Chemistry and Physics

Influence of fuel ethanol content on primary emissions and secondary aerosol formation potential for a modern flex-fuel gasoline vehicle

Hilkka Timonen[1], Panu Karjalainen[2], Erkka Saukko[2,a], Sanna Saarikoski[1], Päivi Aakko-Saksa[3], Pauli Simonen[2], Timo Murtonen[3], Miikka Dal Maso[2], Heino Kuuluvainen[2], Matthew Bloss[1], Erik Ahlberg[4,5], Birgitta Svenningsson[5], Joakim Pagels[6], William H. Brune[7], Jorma Keskinen[2], Douglas R. Worsnop[8], Risto Hillamo[1], and Topi Rönkkö[2]

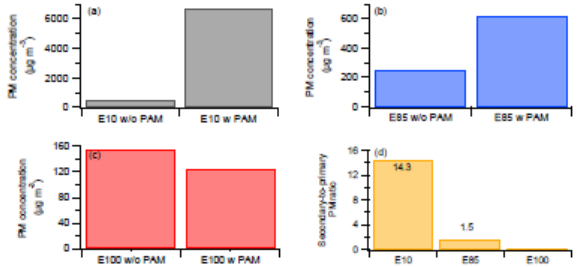


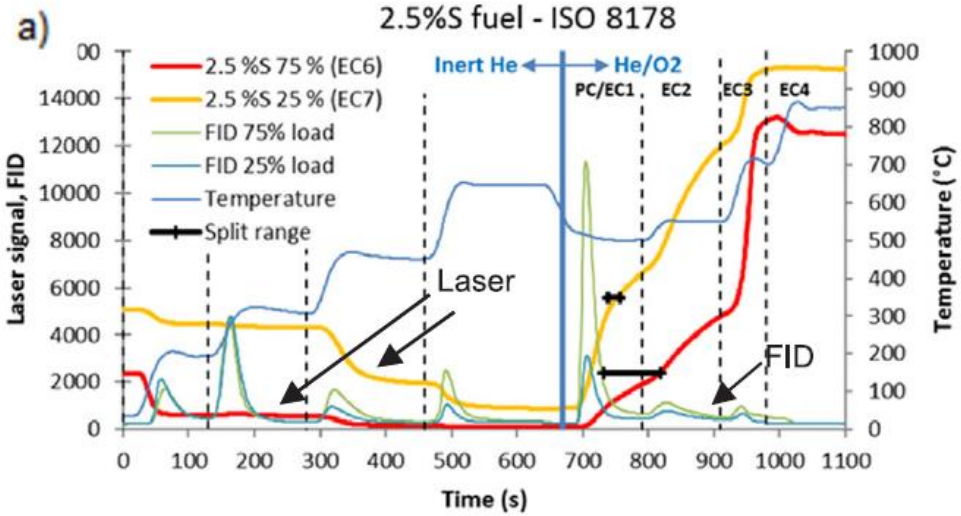
Figure 6. The primary submicron PM concentrations in the exhaust emissions measured without the PAM chamber and the submicron PM concentrations measured with the PAM chamber for E10 (**a**), E85 (**b**) and E100 (**c**). The secondary-to-primary PM ratio for the submicron PM mass in the exhaust calculated from the SP-AMS measurements (**d**). The concentration of the secondary particulate emissions was calculated by subtracting the concentration of the primary PM from the PM measured after the PAM chamber.

Organic fraction of POA could also give valuable information

EC/OC analysis

- The thermal-optical technique based on the evolution of carbon species in different temperatures.
- Temperature and gas atmosphere adjusted while monitoring a laser signal reflectance or transmission through the sample matrix.

Heating in steps up to 550–900 °C in inert He to remove OC. The organics may be pyrolysed (PC) inducing decrease in the laser signal. Oxygen introduced and temperature elevated step-wise. Carbon oxidised to CO_2, converted to methane and detected by FID. PC formed compensated by determining the point (split) when the laser signal achieves its original value.



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Considerations in analysing elemental carbon from marine engine exhaust using residual, distillate and biofuels

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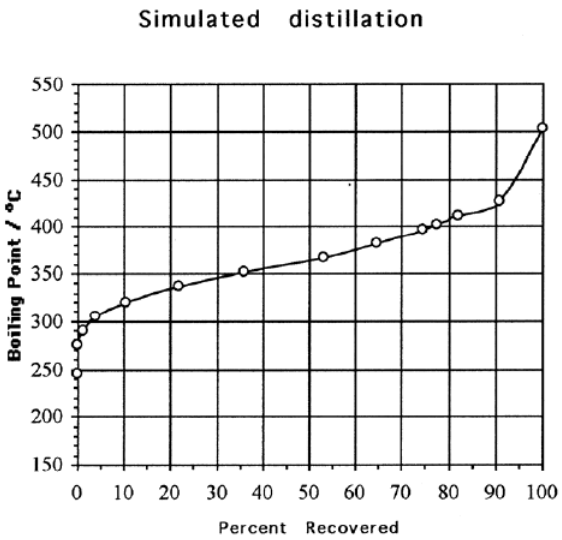
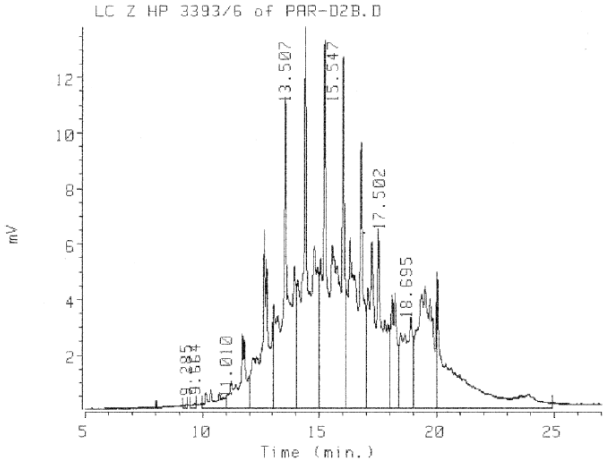
Simulated distillation

- PM extracted with DCM and analysed with GC.
- Distillation range of PM SOF in sample was 250-500 °C.

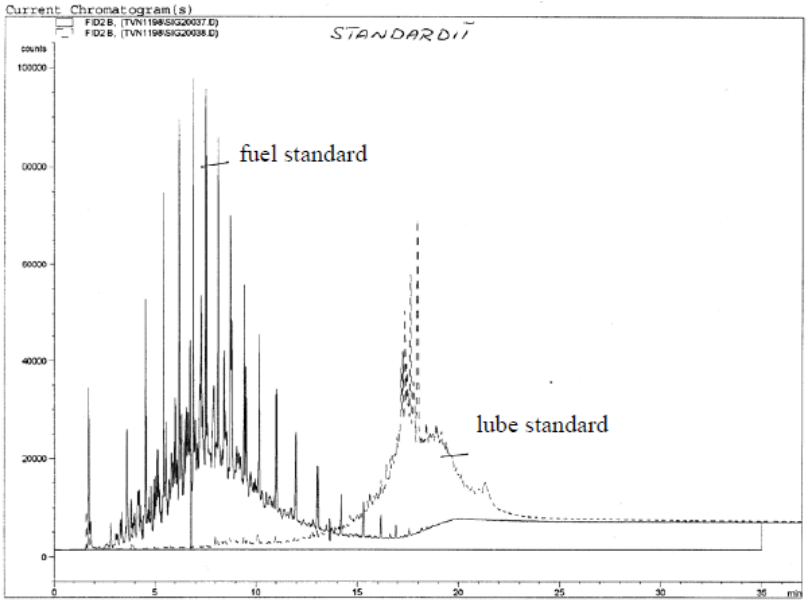




Aakko-Saksa et al., EU PARFIN project report.

Fuel/lube

The fuel/lube analysis was used in 90’s, which part of PM SOF originates from the lube oil and which part from the fuel. Fuel/lube analysis was carried out with GC / solid injection method by Neste using standard chromatograms of lube oil and 10 % distillation residue of the fuel. For gasoline particulates it is assumed that compounds other than those found in the boiling area of the lube standard originate from the fuel.



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Thank you

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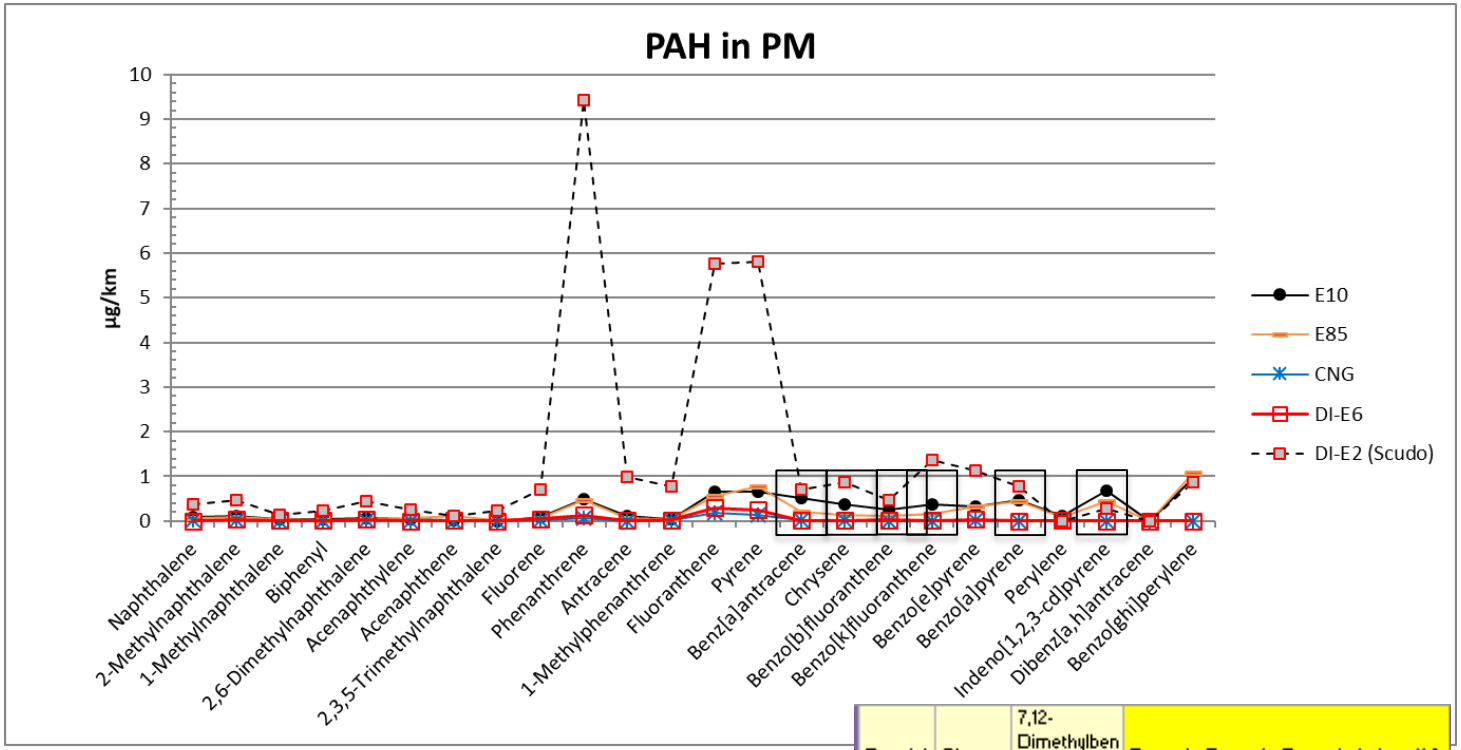
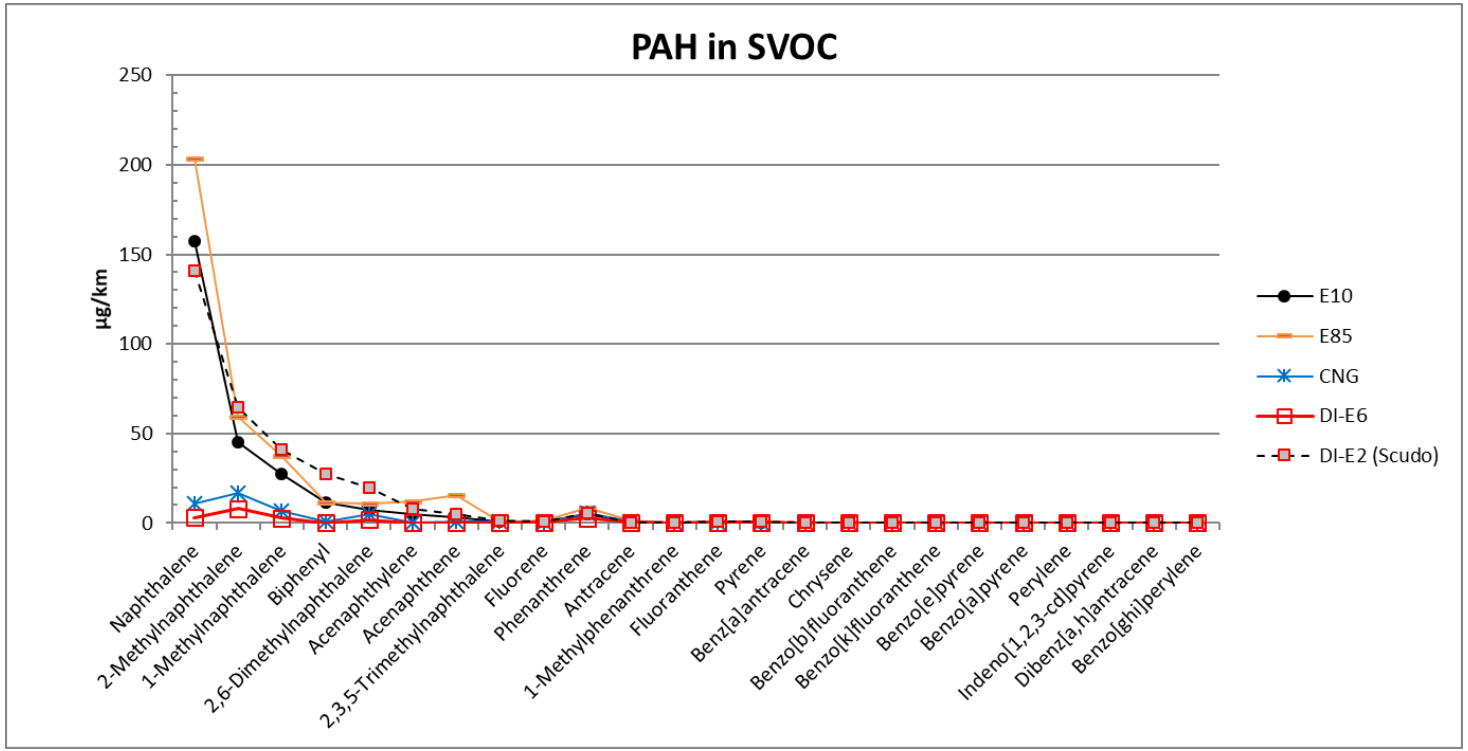
Introduction

- New renewable and alternative transport fuels are introduced, and engine and exhaust aftertreatment technologies develop. Valid and comparable data is needed both on the direct and indirect effects of these new technologies.
- Real-world emissions are increasingly important (transient driving, cold temperatures), particularly unregulated emissions that are less studied than regulated emissions.
- Goal was to investigate emissions from Euro 5/6 cars (Euro 2 as reference), i.a. methane, aromatics, aldehydes, nitrogen dioxide, nitrous oxide, ammonia, semivolatile organic compound (SVOC), PAH, mutagenicity and oxidative potential. Test temperature -7 °C.



Benz(a)antrase eni	Chrysene/triphenylene	7,12-Dimethylbenzo(a)anthracene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km

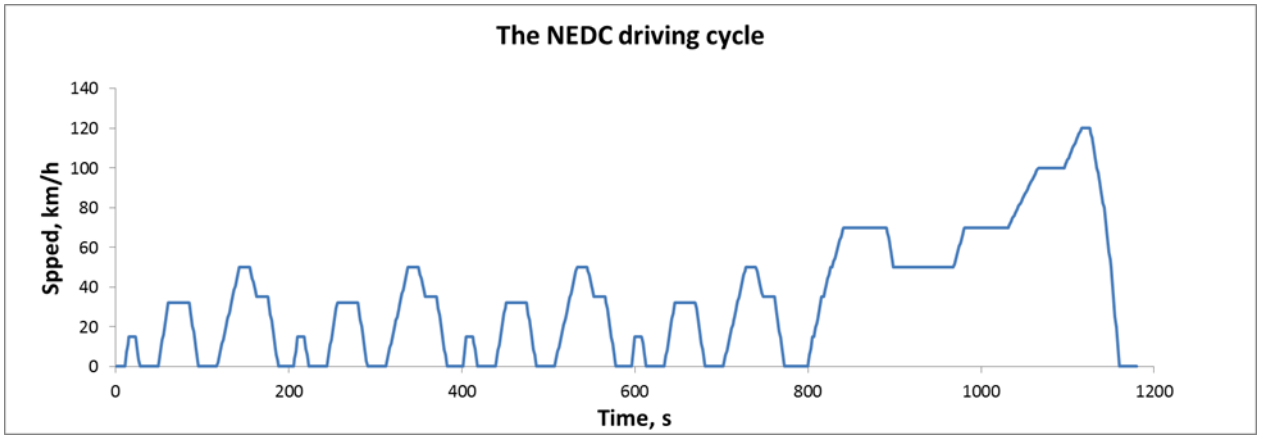

PAH in SVOC
µg/km
250
200
150
100
50
0
E10
E85
CNG
DI-E6
DI-E2 (Scudo)
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Biphenyl
2,6-Dimethylnaphthalene
Acenaphthylene
Acenaphthene
2,3,5-Trimethylnaphthalene
Fluorene
Phenanthrene
Antracene
1-Methylphenanthrene
Fluoranthene
Pyrene
Benz[a]antracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene
Perylene
Indeno[1,2,3-cd]pyrene
Dibenz[a, h]antracene
Benzo[ghi]perylene

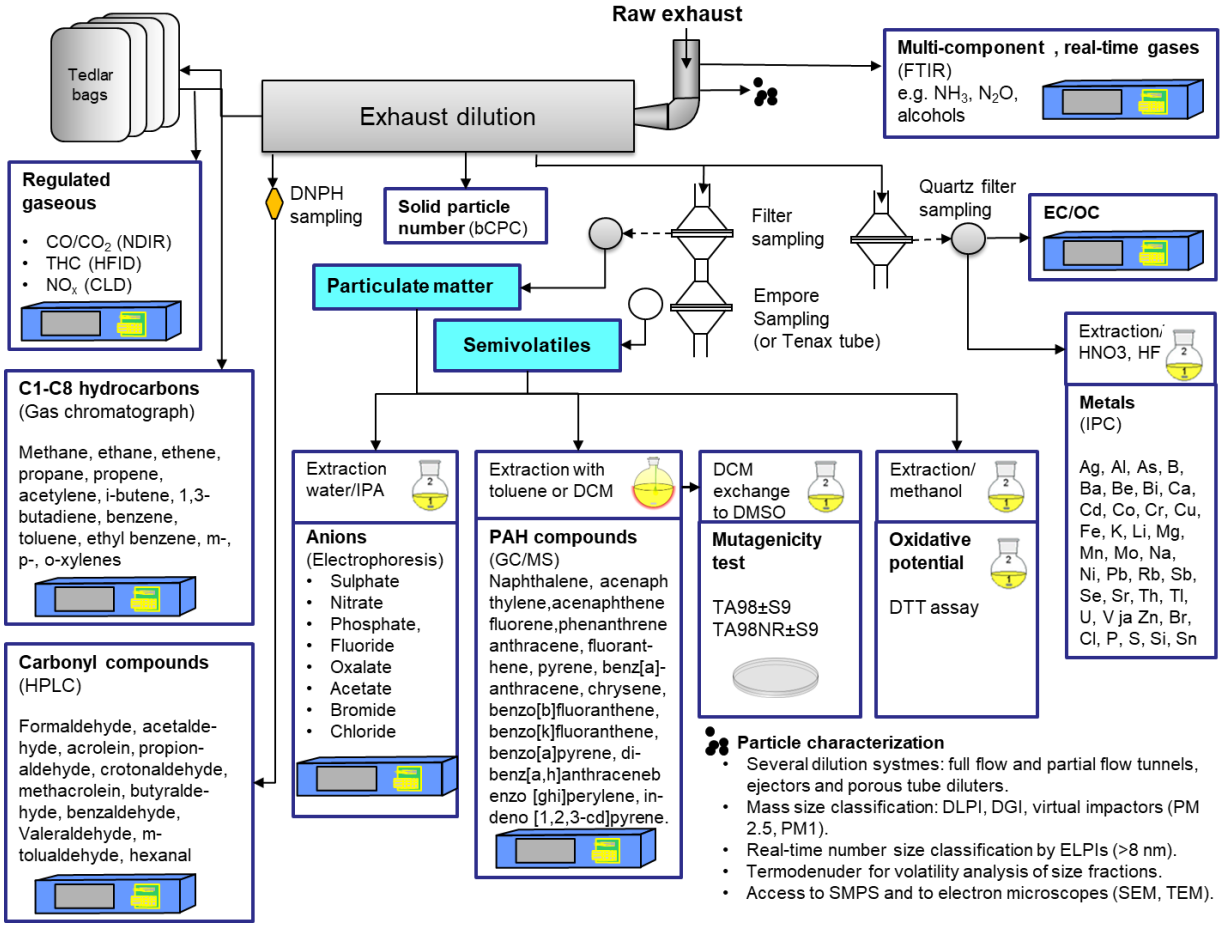
Priority PAHs

	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)

An example of driving cycle




Raw exhaust
Tedlar bags
Exhaust dilution
Multi-component , real-time gases (FTIR)
e.g. NH3, N2O, alcohols
Regulated gaseous
CO/CO2 (NDIR)
THC (HFID)
NOx (CLD)
DNPH sampling
Solid particle number (bCPC)
Filter sampling
Quartz filter sampling
EC/OC
Particulate matter
Empore Sampling (or Tenax tube)
Semivolatiles
Extraction/ HNO3, HF
Metals (IPC)
Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Tl, U, V ja Zn, Br, Cl, P, S, Si, Sn
C1-C8 hydrocarbons (Gas chromatograph)
Methane, ethane, ethene, propane, propene, acetylene, i-butene, 1,3-butadiene, benzene, toluene, ethyl benzene, m-, p-, o-xylenes
Extraction water/IPA
Anions (Electrophoresis)
Sulphate
Nitrate
Phosphate,
Fluoride
Oxalate
Acetate
Bromide
Chloride
Extraction with toluene or DCM
PAH compounds (GC/MS)
Naphthalene, acenaphthylene,acenaphthene fluorene,phenanthrene anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthraceneb enzo [ghi]perylene, indeno [1,2,3-cd]pyrene.
DCM exchange to DMSO
Mutagenicity test
TA98±S9
TA98NR±S9
Extraction/ methanol
Oxidative potential
DTT assay
Carbonyl compounds (HPLC)
Formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, Valeraldehyde, m-tolualdehyde, hexanal
Particle characterization
Several dilution systmes: full flow and partial flow tunnels, ejectors and porous tube diluters.
Mass size classification: DLPI, DGI, virtual impactors (PM 2.5, PM1).
Real-time number size classification by ELPIs (>8 nm).
Termodenuder for volatility analysis of size fractions.
Access to SMPS and to electron microscopes (SEM, TEM).