Nanosize Metal Oxide Particles

emitted by Diesel- and Petrol-Engines

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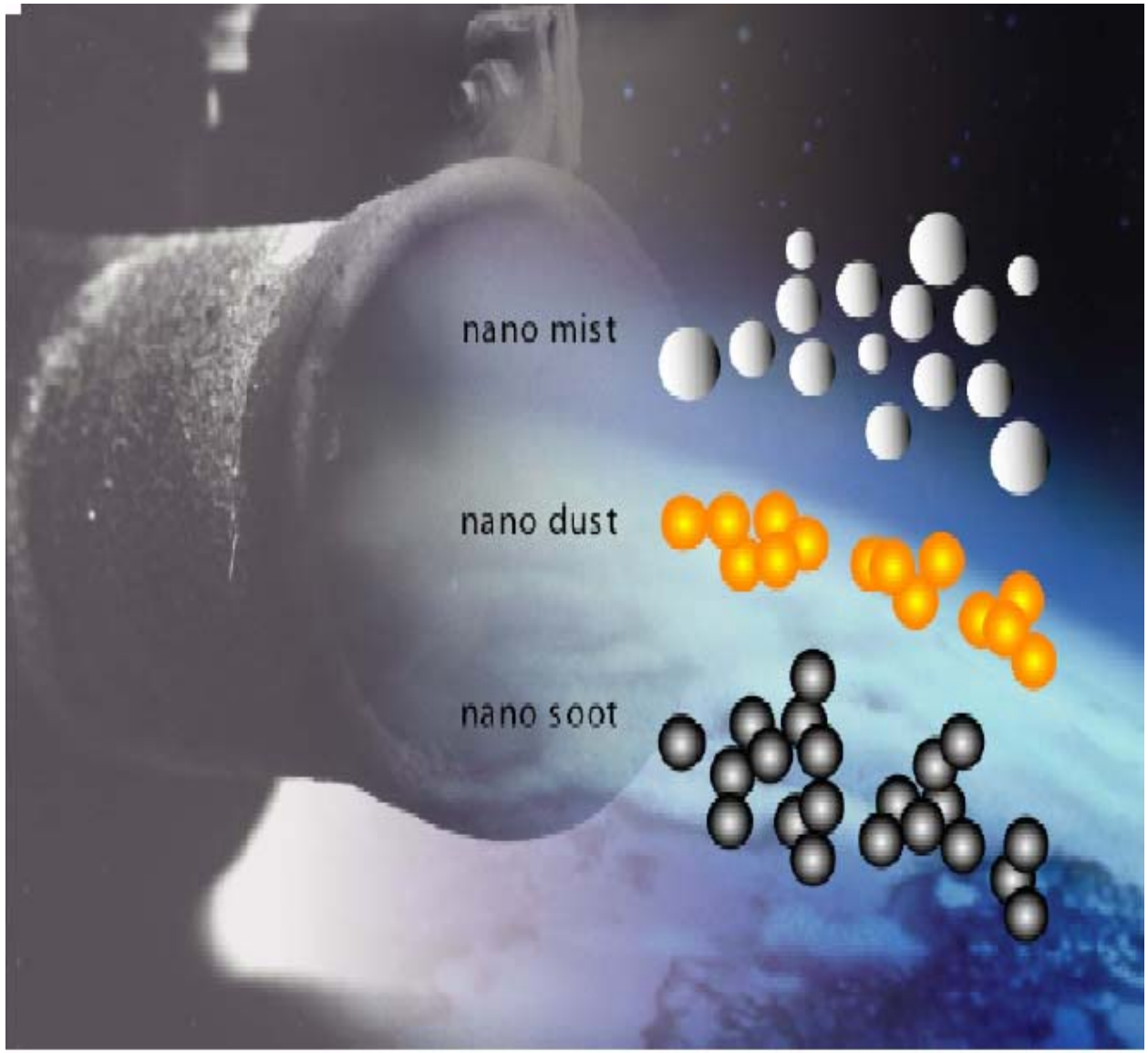
ICE Exhaust Gas Contains

Soot Particles
Ash Particles
Condensates

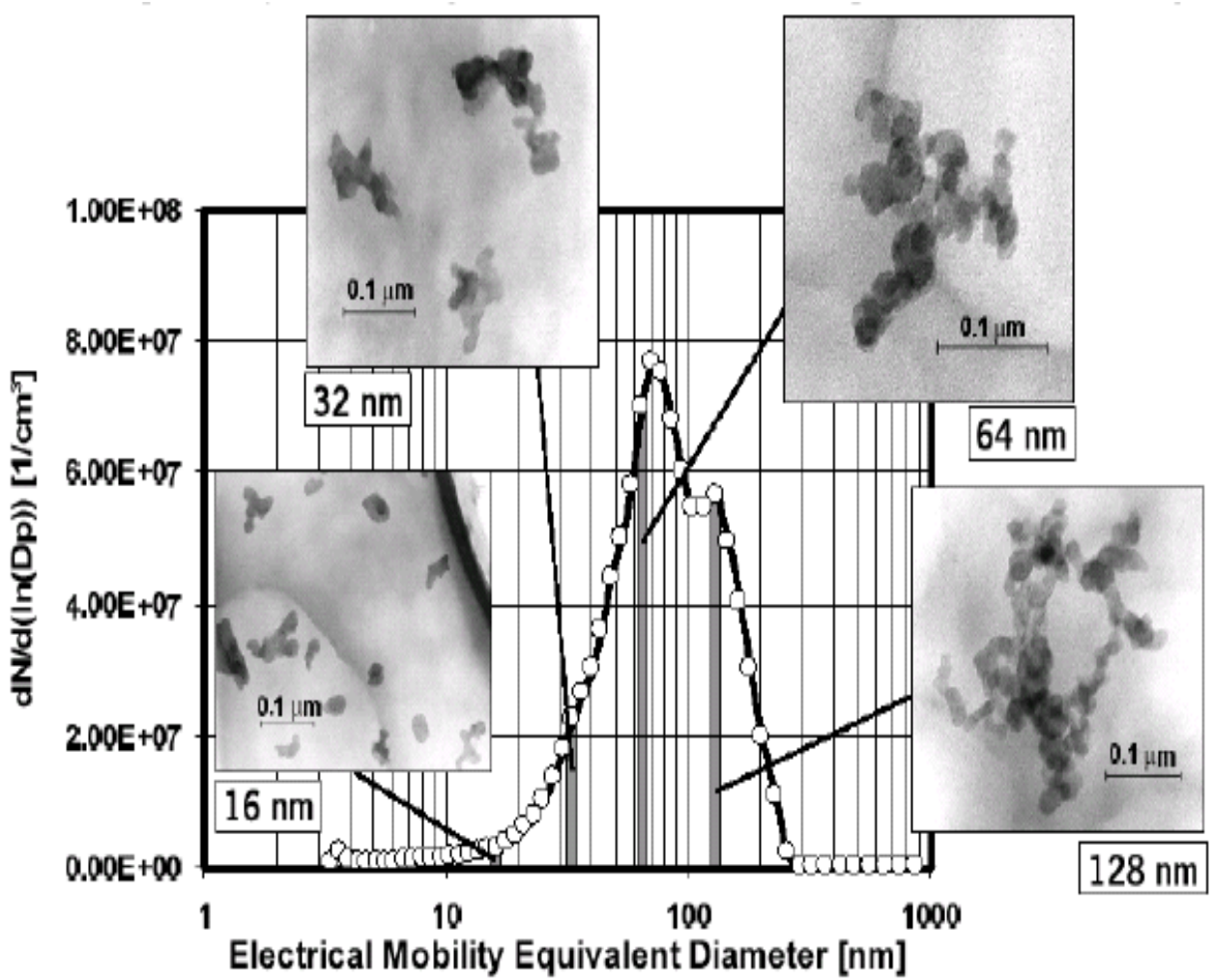
internally or
externally mixed

which of them are of highest concern with respect to human health ?



Diesel Particles

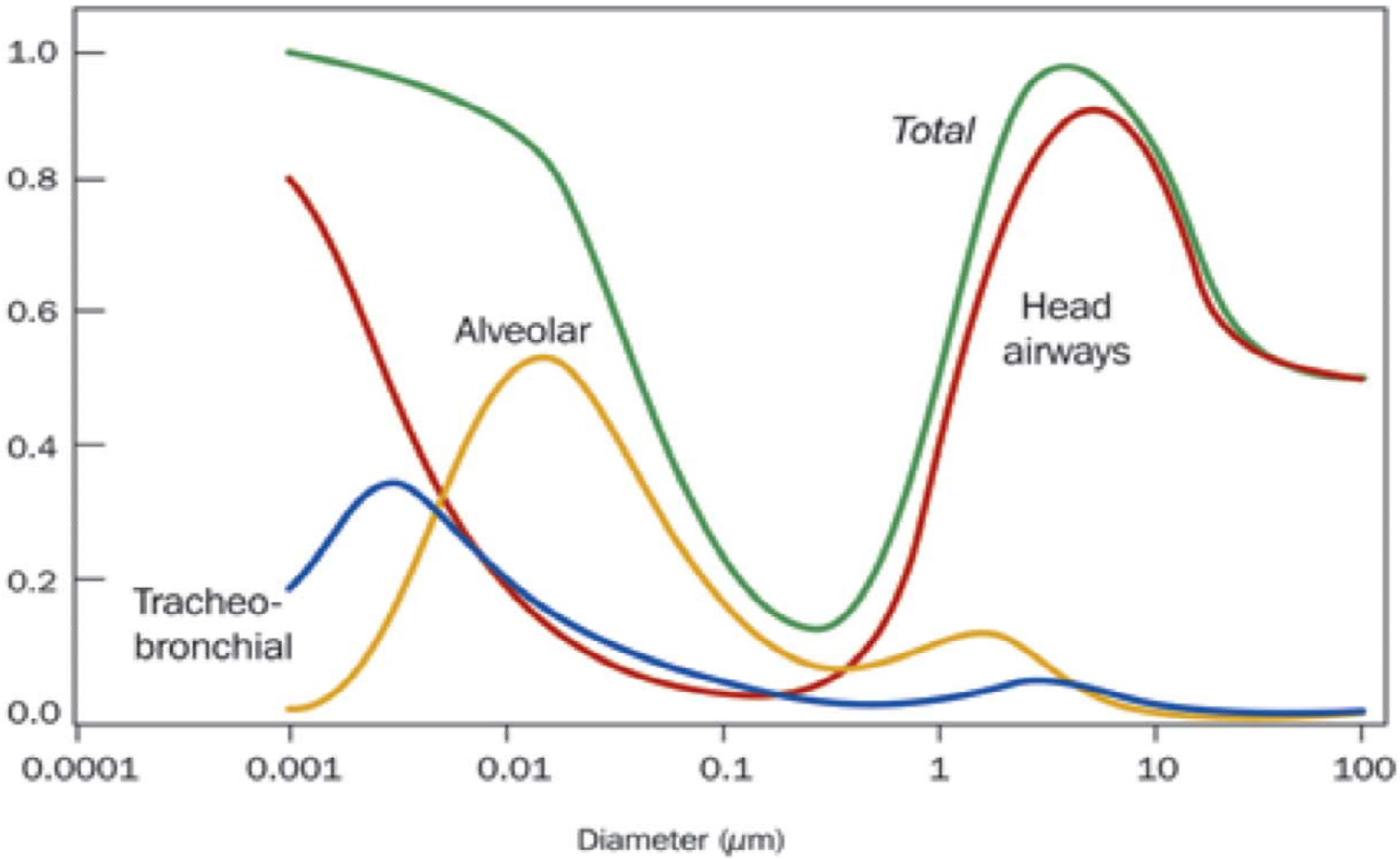
maybe “decorated” with metal oxic particles ?



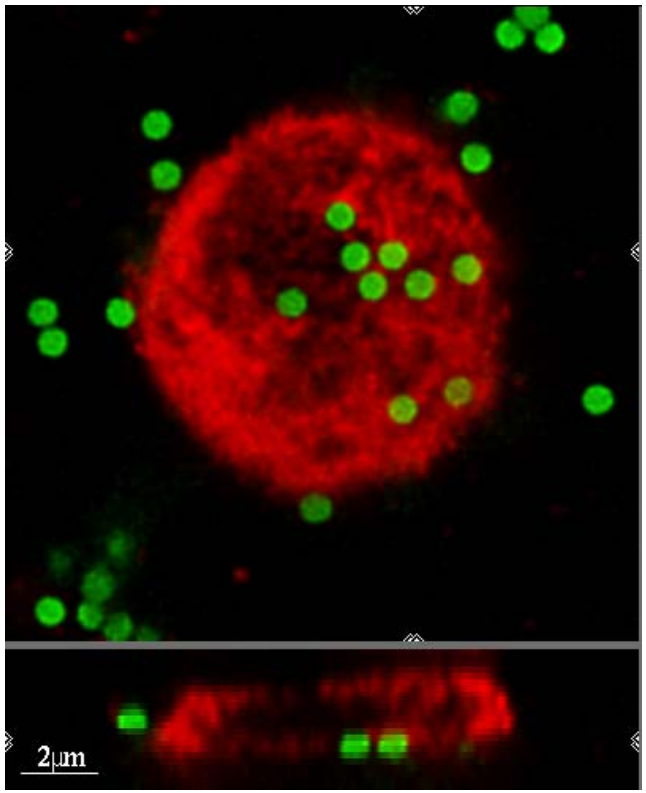
Quelle: METZ, BMW

Predicted deposition of inhaled particles

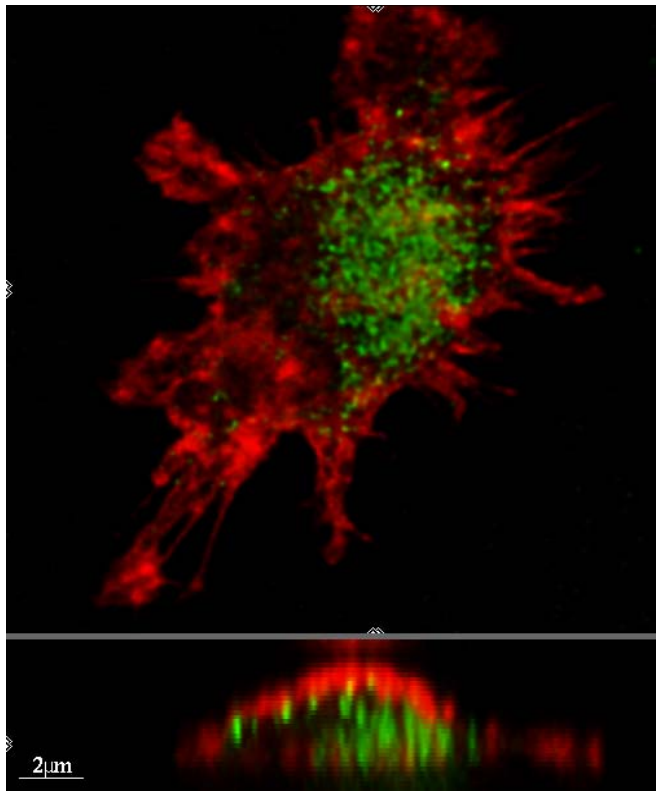
in the human respiratory tract – ICRP [1994] model: light exercise, nose breathing (Source Oberdörster)



Macrophages *in vitro*: Laser Scanning Microscopy



1-µm
Polystyrene particles

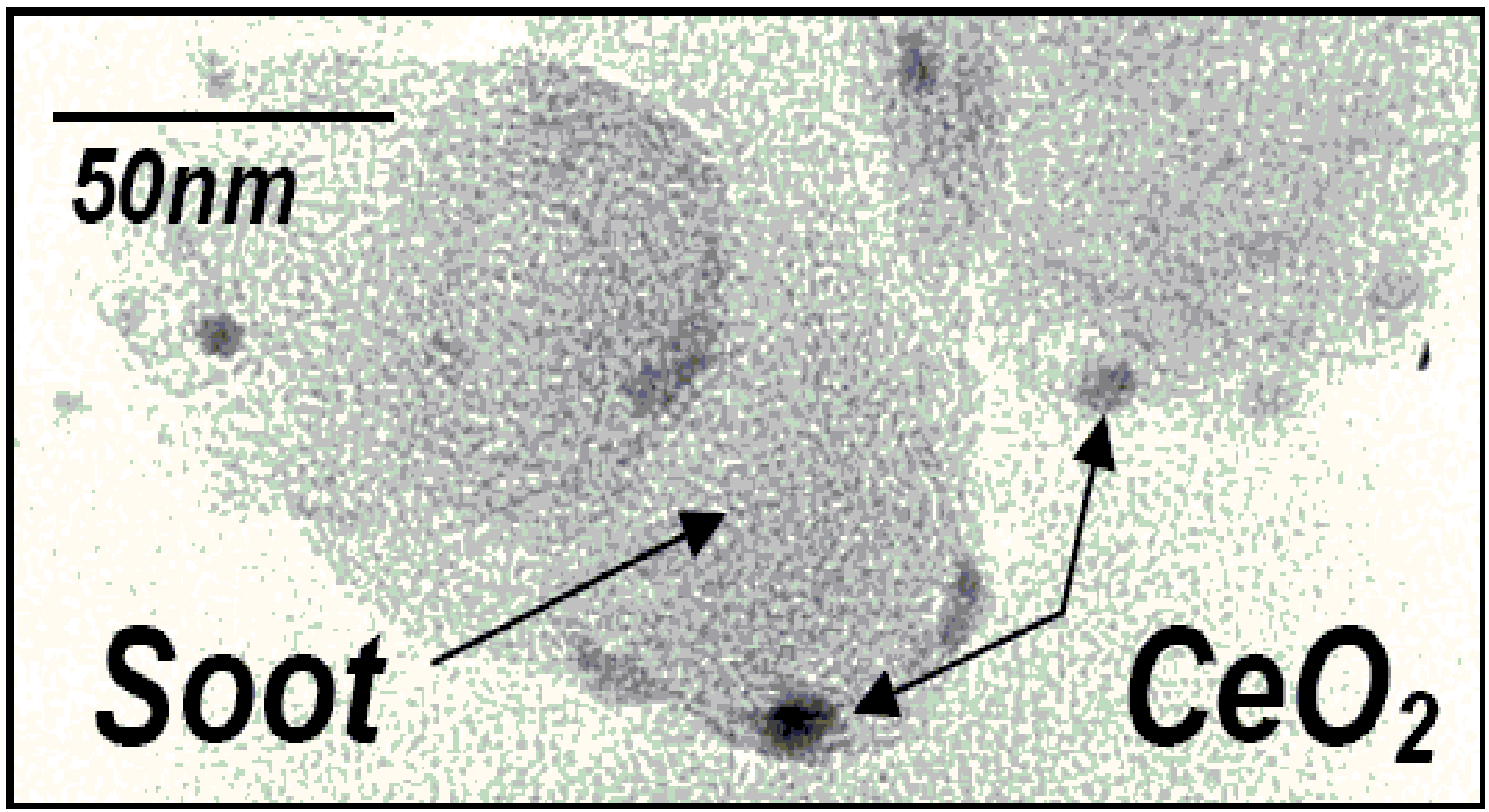


78-nm
Polystyrene particles

Source:
B. Rothen-Rutishauser
Uni Bern

Cerium oxide FBC on soot particles

source:Rhodia



What makes Particles harmful ?

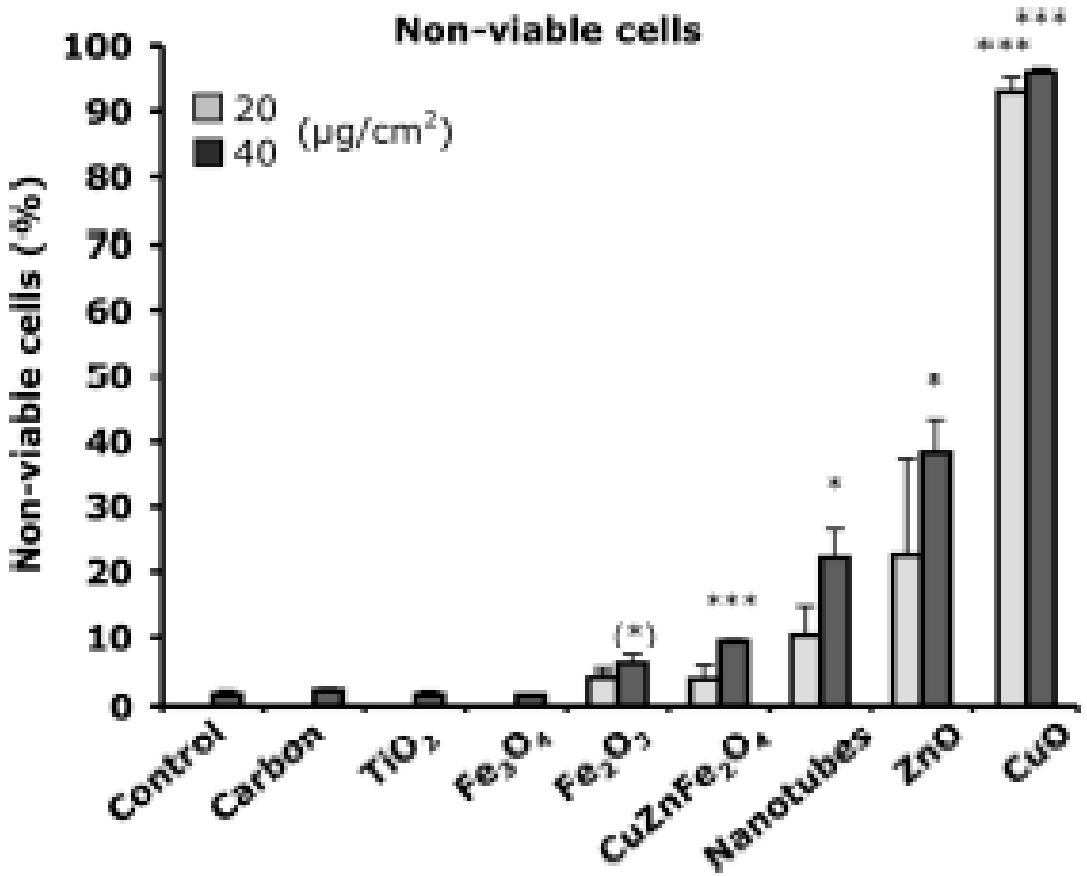
Concentration, Size and Substance

Particulate Substances

have very different toxicity

% cells not surviving

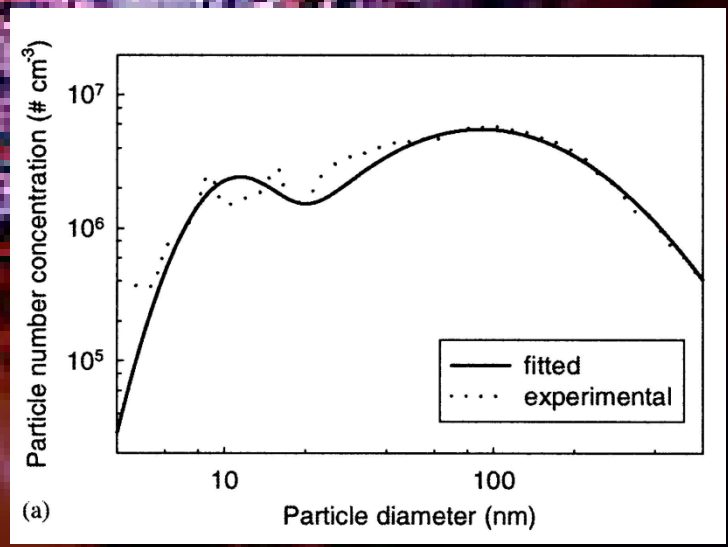
Karlsson, Chem, Res.Tox 1998



Racette et al., 2001:
Welding-related Parkinsonism

Metal Welders develop Parkinson Desease 20 years before average population

Zimmer et al., 2002



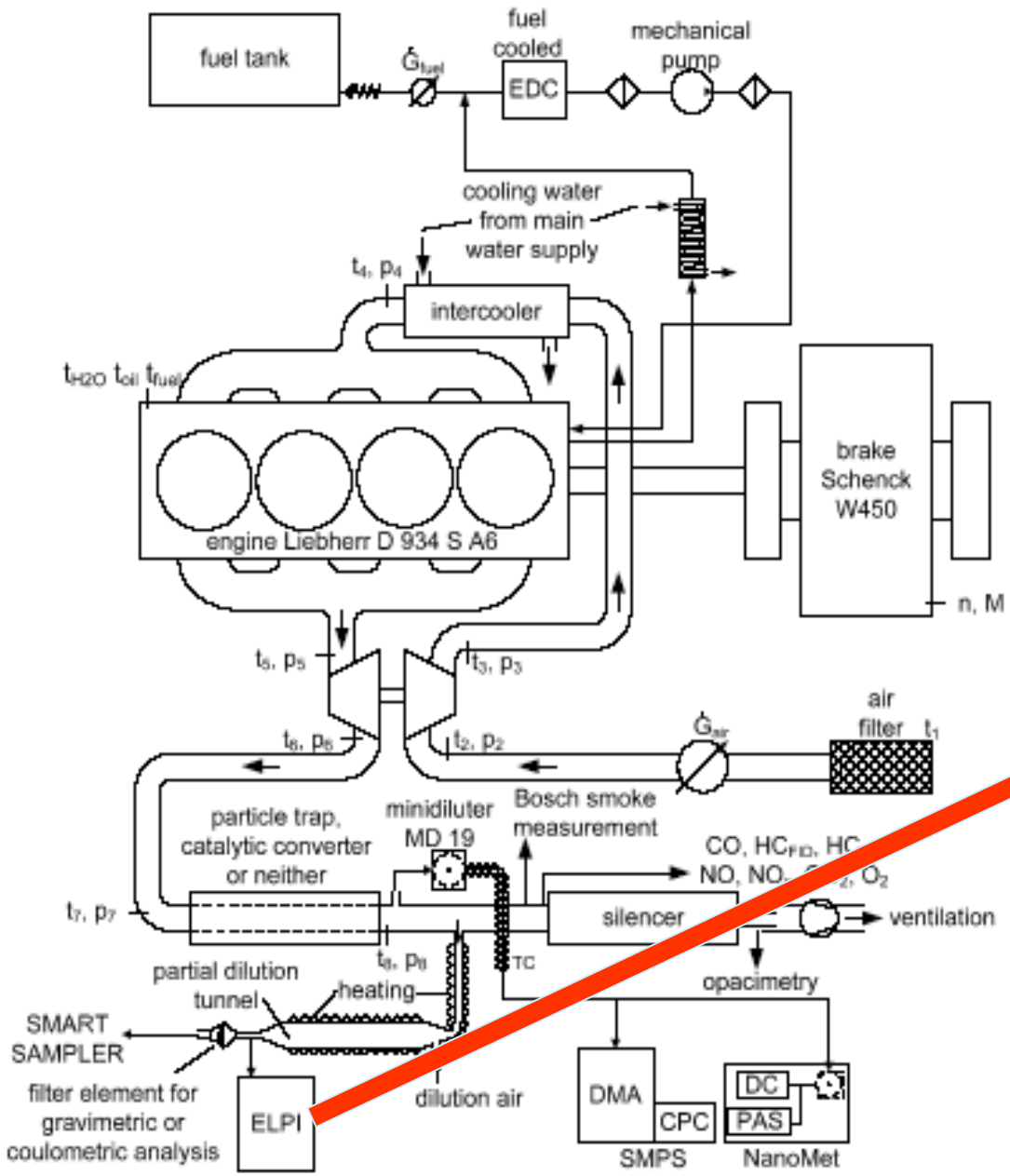
Sources of Metals

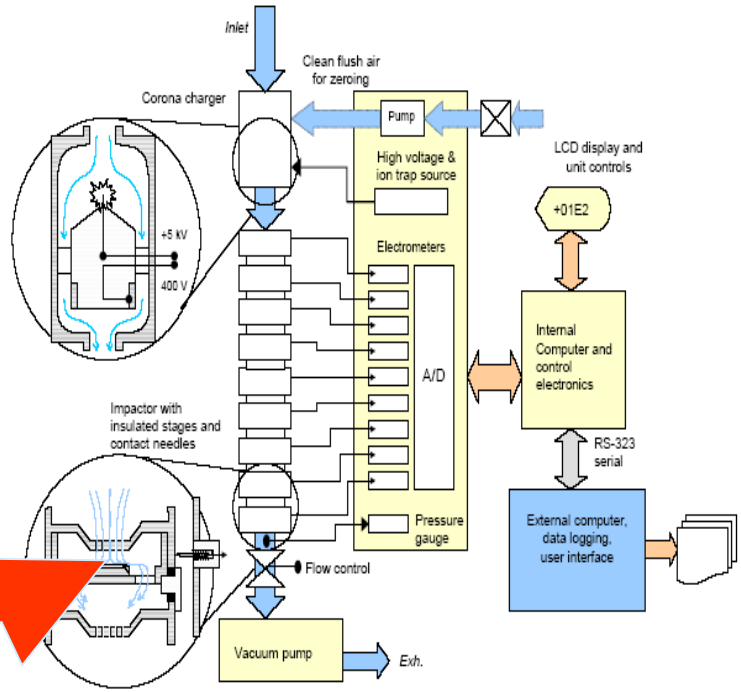
Engine Wear:	Fe, Ni, Cr, Al, Si
Bearing Wear:	Cu, Sn
Lube Oil:	Zn, Ca, P
Cat.Coatings:	Pt, Pd, V, Cu, Ce
FBC:	Fe, Ce, Pt, Cu

VERT-DPF-certification protocol

looks at metal emissions size-specific –
part of the secondary emissions test VSET

Test Setup



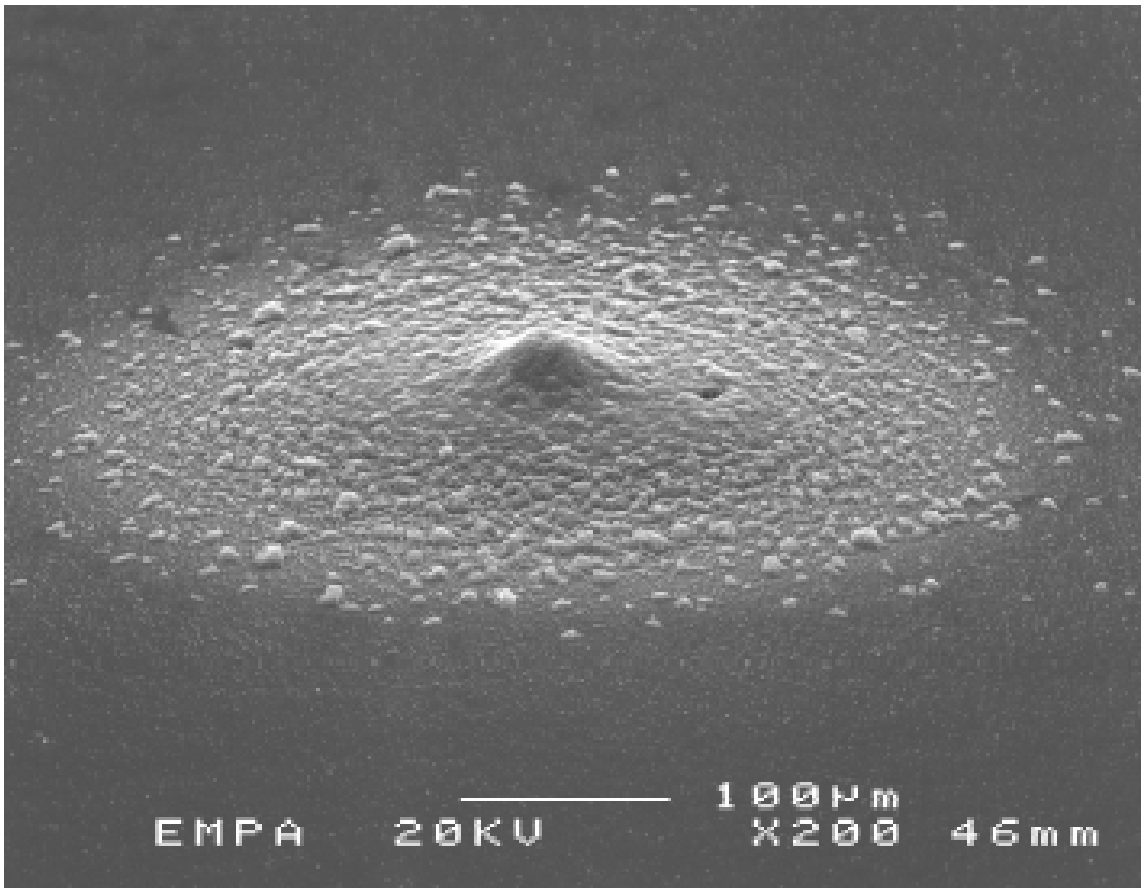


ELPI – Impactor

13 size classes

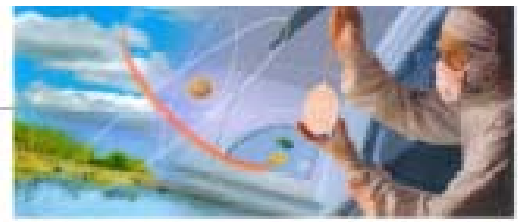
30 nm – 10 µm

ELPI-sample



Plasma Mass Spectrometry ICP-MS

Fast Multi-Element Technique: 75 Elements in 2 min.
High Sensitivity ppt Levels (ng)

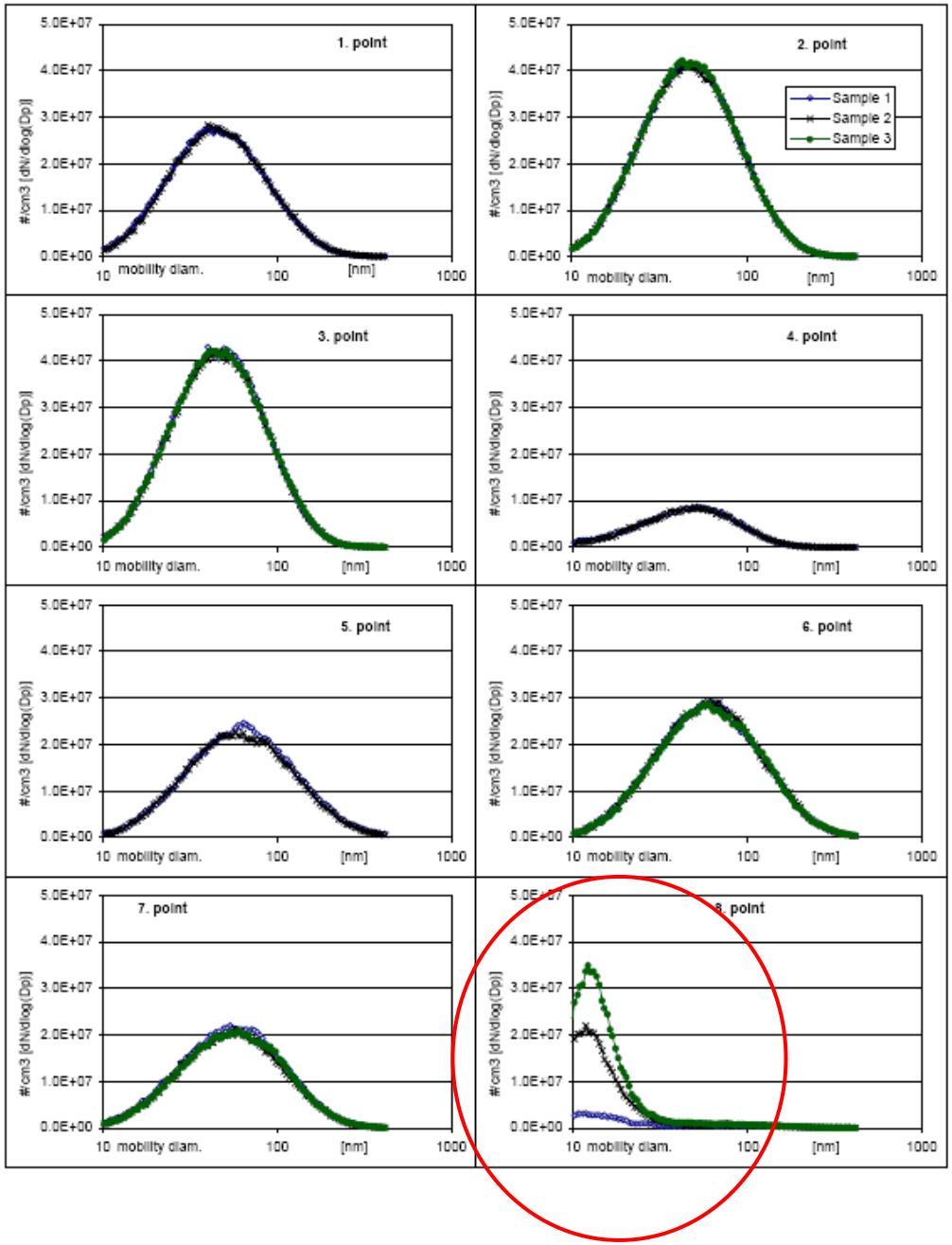


The **ELAN® Series** of ICP-Mass Spectrometers

Simplifying Ultratrace Analysis

DIESEL – Emission

- Particle Mass Emission of Diesels is limited since 1982
- Size and number PN were first adressed
  - for retrofit in Swiss Tunneling in 1994
  - for OE with EURO 5/6 in 2007
- Both regulations focus on solid particles
- Substance is not adressed yet



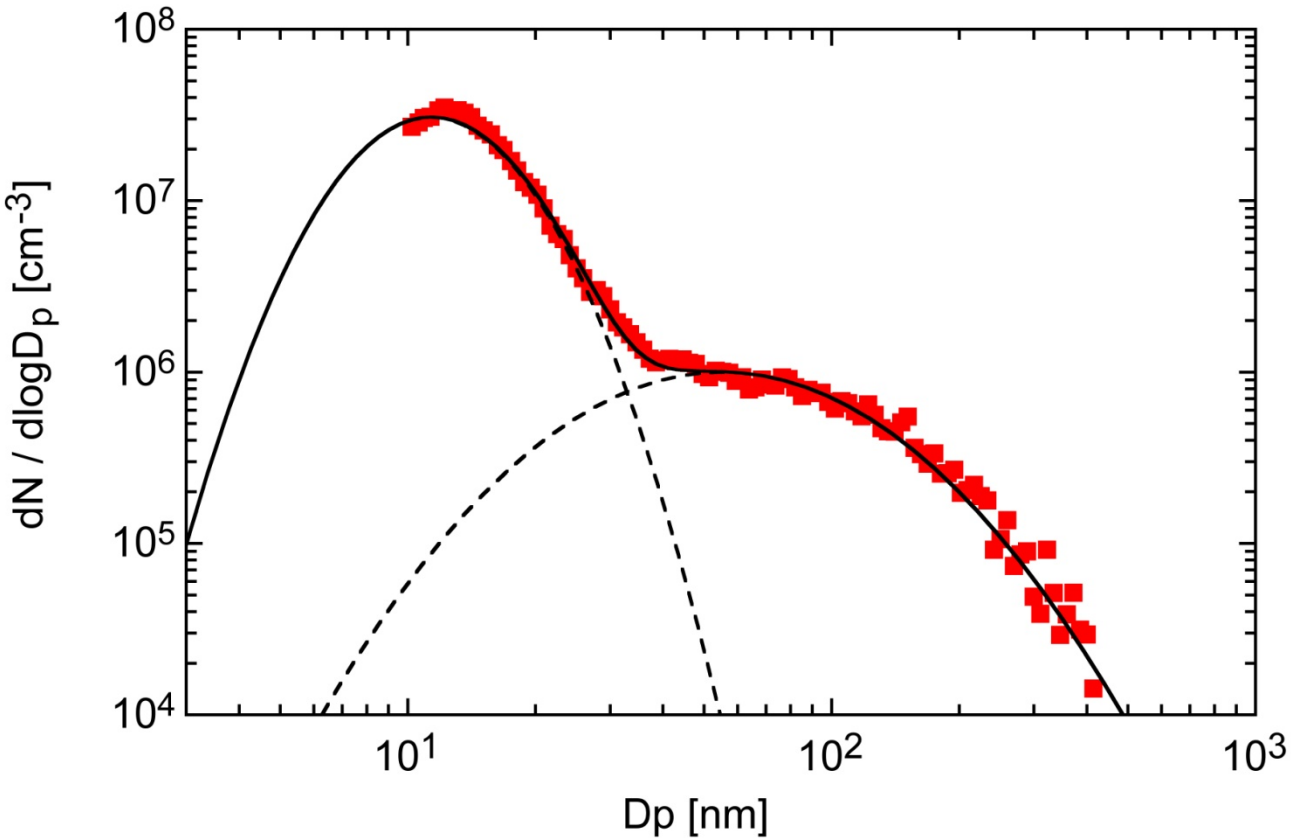
Baseline Diesel

Liebherr Construction
6.1 ltr, 110 kW
64 mg/kWh

Size distributions
without DPF
ISO 8178/4-C1 – 8 pts

OP 8 = idle
Sampling: 300°C,
DR=100

Analysis for Idle OP8 without DPF
Double-LogNormal Fit of a Bimodal Distribution



Double-LNDF Fit of Bimodal Particle Distribution OP8 (idle) compared to 50%load without DPF

	OP 8 = Idle	OP 5 = 50% load
N tot [1/cc]	1.46E+07	1.80E+07
N ash [1/cc]	1.37E+07	-
N soot [1/cc]	8.56E+05	1.80E+07
D ash [nm]	11.8	-
D soot [nm]	48.3	61.1

Size Specific Metal Analysis without DPF – Idle

ELPI Stages	Size class D50%	Fe	Ni	Zn	Ca	Rh	Pt
	[µm]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]
Backup stage	<0.03	1.5	0.030	1.36	5.7	<DL	0.00007
1	0.03	<DL	0.007	0.27	2.4	<DL	0.00008
2	0.06	<DL	0.007	0.21	2.2	<DL	0.00005
3	0.11	0.04	0.023	0.07	1.5	0.00008	0.00003
4	0.17	<DL	0.004	0.28	5.9	0.00001	0.00002
5	0.27	0.05	0.010	0.16	4.0	0.00001	0.00006
6	0.41	0.03	0.008	0.06	1.0	0.00001	0.00002
7	0.66	0.02	0.012	0.12	2.5	0.00004	0.00032
8	1.02	0.06	0.010	0.23	5.1	0.00001	<DL
9	1.65	0.08	0.009	0.19	3.4	<DL	0.00002
10	2.52	0.10	0.015	0.25	4.4	<DL	0.00003
11	4.08	0.32	0.014	0.33	5.8	0.00001	0.00001
12	6.56	0.22	0.014	0.18	2.8	<DL	<DL
Sum with blanks		**2.42**	**0.136**	**3.69**	**46.7**	**0.00016**	**0.00071**

Metal analysis corrected for blanks

with and without Fe-FBC added 20mg/kg fuel

blue: all sizes

red: < 60 nm

mg/kWh – ISO 8178	Fe	
Baseline w/o FBC	0.078	
< 60 nm	0.023	
Baseline with FBC	2.48	
< 60 nm	1.34	
with DPF and FBC	0.091	
Penetration %	*3.6*	
< 60nm	0.016	
Penetration %	*1.22*	

Particle Mass converted to Particle Number

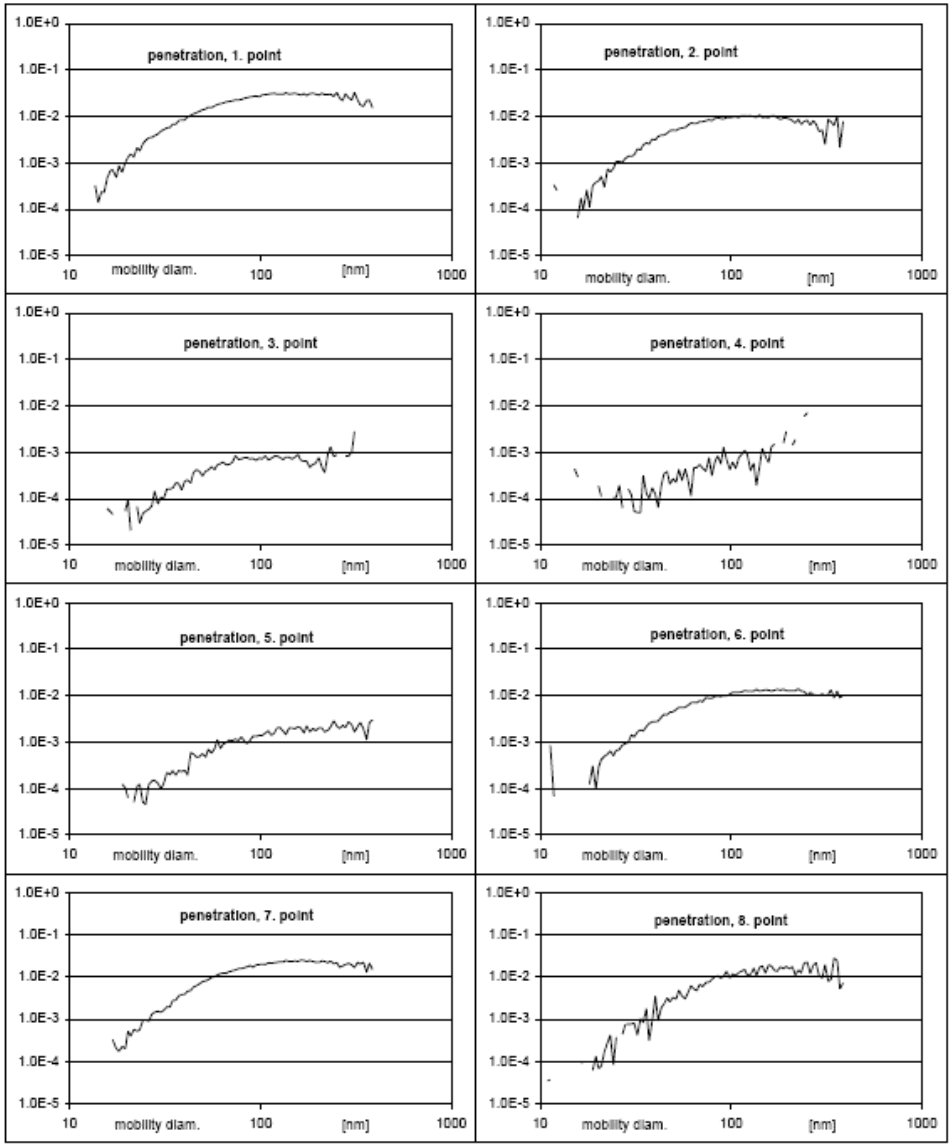
Assuming spherical particles

1 Particle 100 nm has a mass of 10^{-15} g = 1 Femtogramm

1 Particle 20 nm has a mass of 10^{-17} g

	1mg / kWh	**0.1mg / kWh**
100 nm	10^{12}/ kWh	**10^{11}/ kWh**
20 nm	10^{14}/ kWh	**10^{13}/ kWh**

Compare to : EURO VI : < 6 x10^{11} / kWh of > 23 nm



VERT-certified DPF

Penetration at
the 8 operating points of
the coated filter

→ Filtration is excellent
even for metal oxide
particles < 30 nm

Filter-Ash of 3 DPF - an overall balance analysed after 1000 operation hours

%	Vehicle A + DOC (Pt)	Vehicle B Pt-coated	Vehicle C no catalyst
S	9.5	12.9	1.8
Ca	11	17	4.5
Zn	4.7 → 0.2 mg/kWh	4.9	1.2
Fe	0.3	0.24	1.33
Cu	0.14	0.05	0.11
Al	1.0	0.1	0.3
Cr	0.12	0.03	0.15
Ni	0.08	0.002	0.03
Pt	0.005 → 200 ng/kWh	0.0003	0.00001

Petrol – Engines

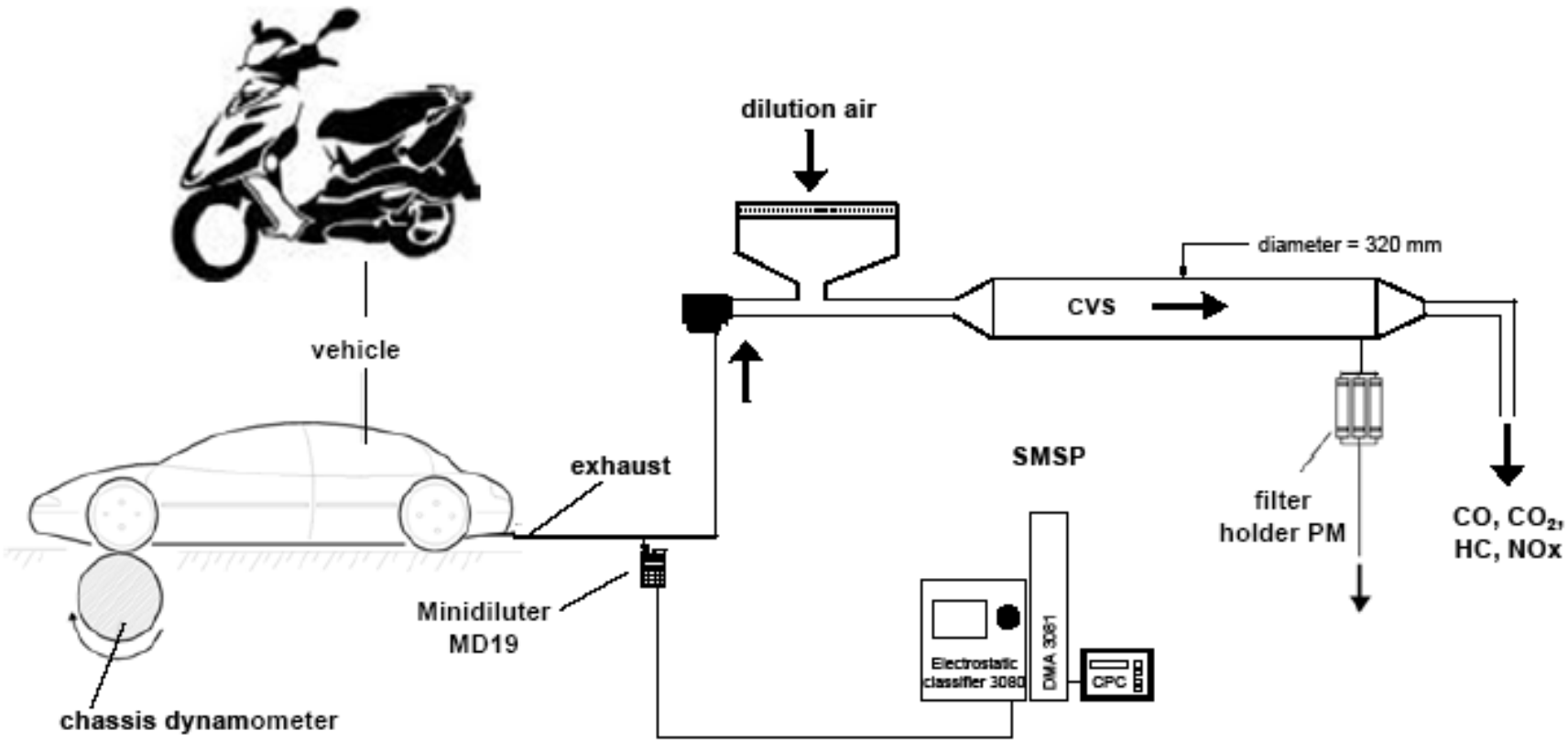
- Particle Emissions of Petrol Engines were long neglected because mass is so small
- Size and number first adressed with EURO 5/6
- Substance is still not adressed

4 Vehicles selected

Vehicle Type	Car old	Motorbike old	Car new	Scooter new
Manufacturer/ brand	**Renault R18**	**Honda 450 CBR**	**Nissan Qashqai**	**Piaggio**
Engine Volume [cc]	2165	447	1997	124
	4 Cyl. 4 Stroke	2 Cyl. 4 Stroke	4 Cyl. 4 Stroke	1 Cyl. 4 Stroke
Engine RPM [1/min]	5000	8800	6000	8500
Rated power [kW]	79	24.7	104	11

Renault R18	Honda 450 CBR	Nissan Qashqai	Scooter Piaggio
Idling • 120 min.	Idling • 120 min.	Idling • 120 min.	Idling • 120 min.
50 km/h • 20 min.	50 km/h • 20 min.	50 km/h • 20 min.	50 km/h • 20 min.
NEDC • 1187 sec. • 11.028 km • 33.6 km/h	Euro 3 • 1568 sec • 13.065 km • 30.0 km/h	NEDC • 1187 sec • 11.028 km • 33.6 km/h	Euro 3-C1 • 1170 sec • 6.110 km • 18.8 km/h

Test Set-up AFHB / Biel



Overall Particle Mass PM is very small

Vehicle	Renault R18		Honda 450 CBR		Nissan Qashqai		Scooter Piaggio	
Cycle	NEDC	Idling	Euro 3	Idling	NEDC	Idling	Euro3-C1	Idling
Time [3]	3540	7200	4710	7200	3540	7200	3510	7200
PM total								
• mg/km	0.531		0.277		0.639		0.492	
• mg/hr		8.800		2.079		3.520		4.33

Diesel-Car:

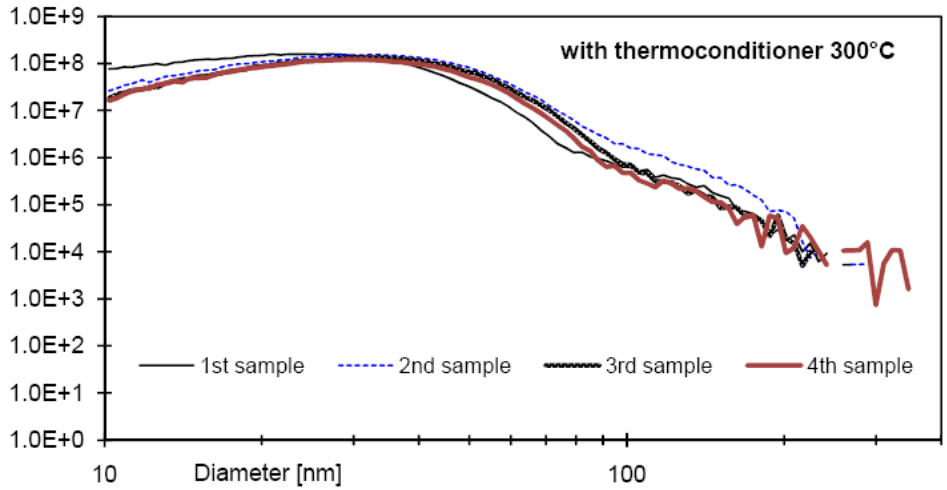
Euro 3: PM < 50 mg/km

Euro 4: PM < 25 mg/km

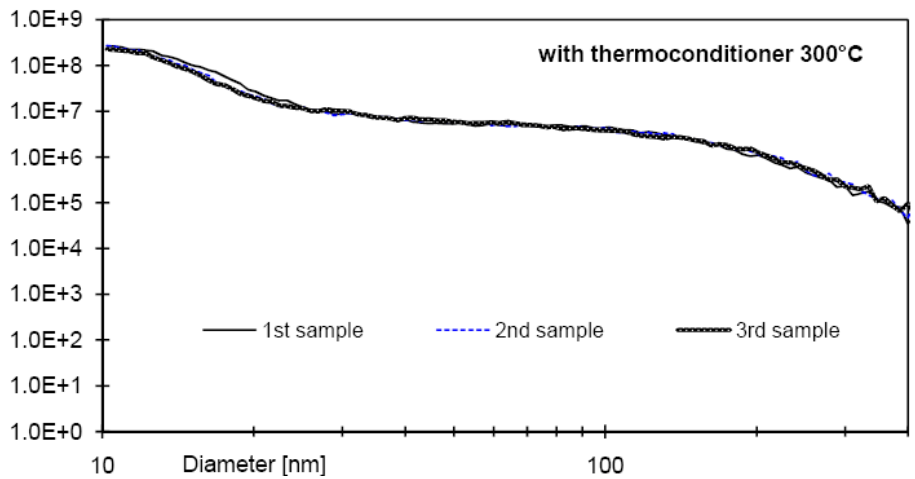
Euro 6: PM < 10 mg/km ; PN < 6×10^{11} #/km

Renault 18 (162‘000 km)
Size Distribution at Idle and 50 km/h

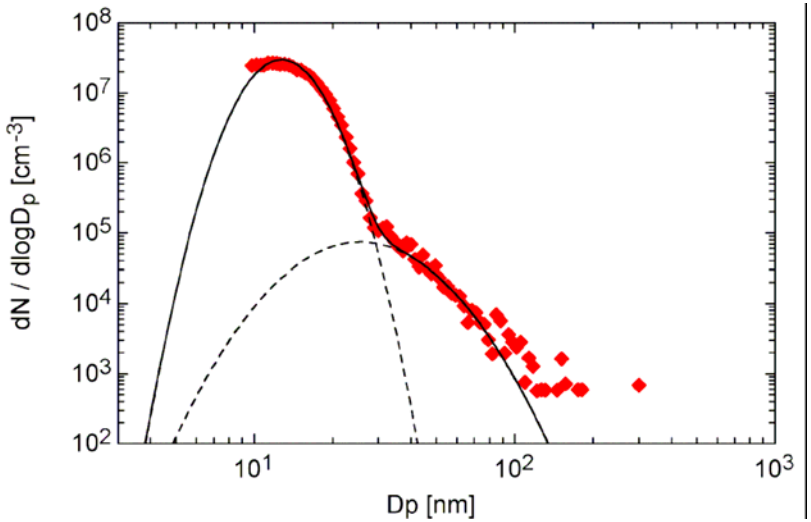
Idle

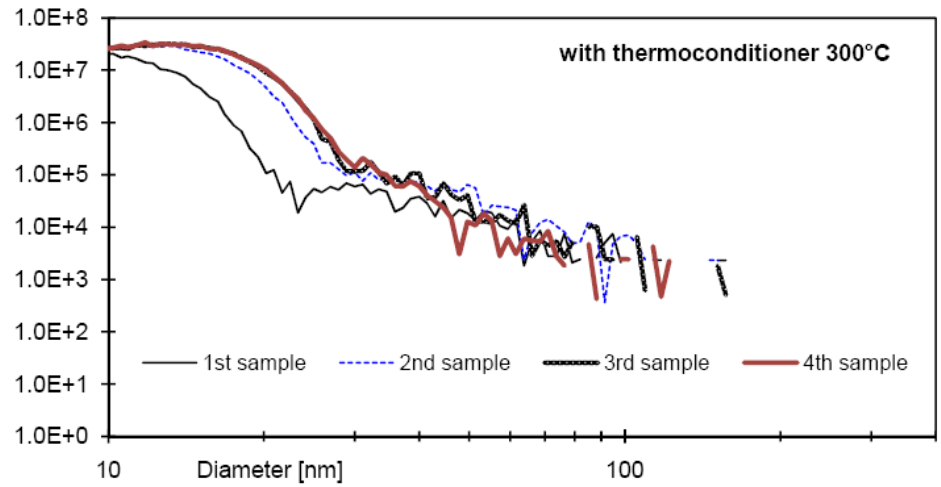


50 km/h

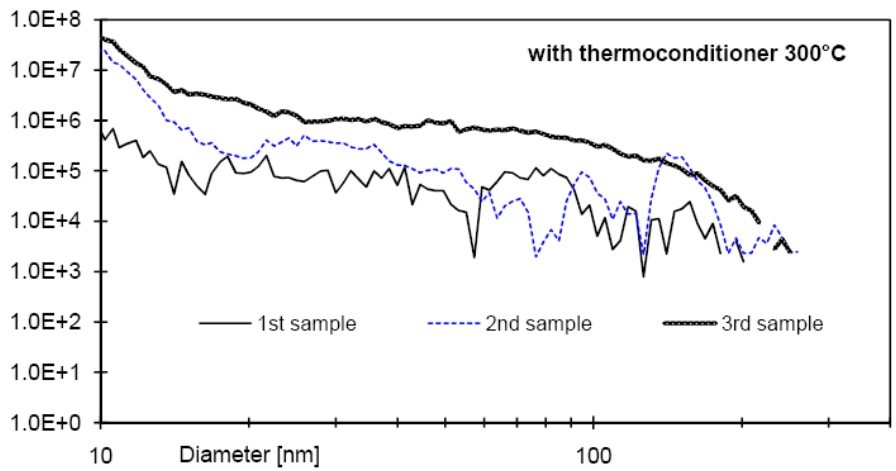


Honda 450 Motorbike (10‘000 km)
Size Distribution at Idle and 50 km/h





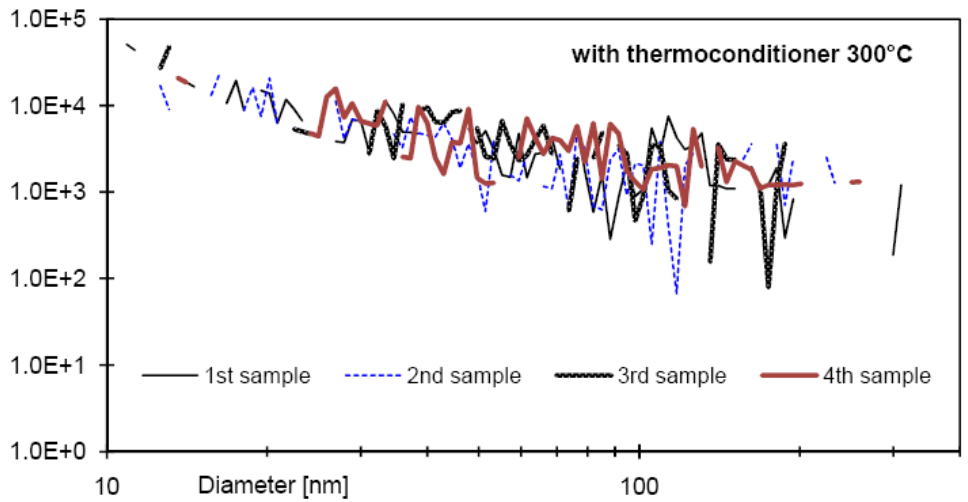
Idle



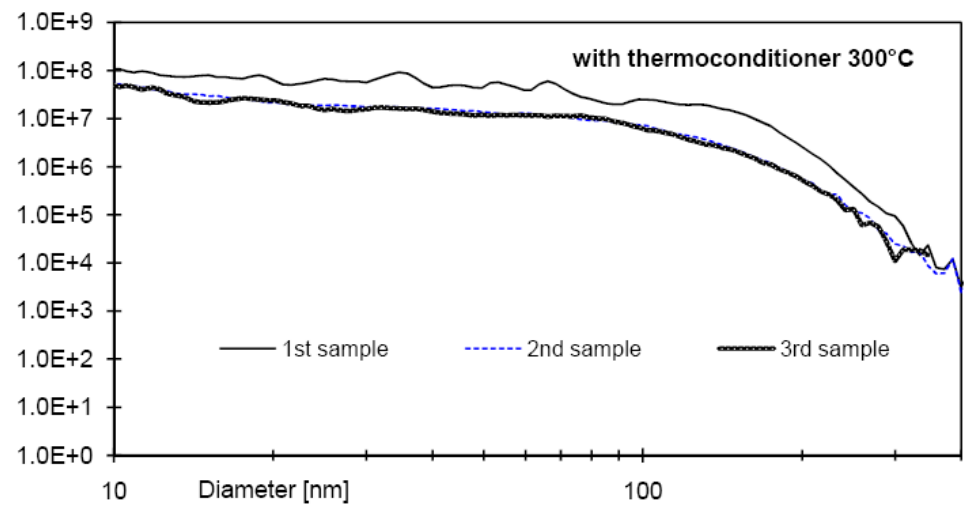
50 km/h

Piaggio Scooter (1000 km)
Size Distribution at Idle and 50 km/h

Idle

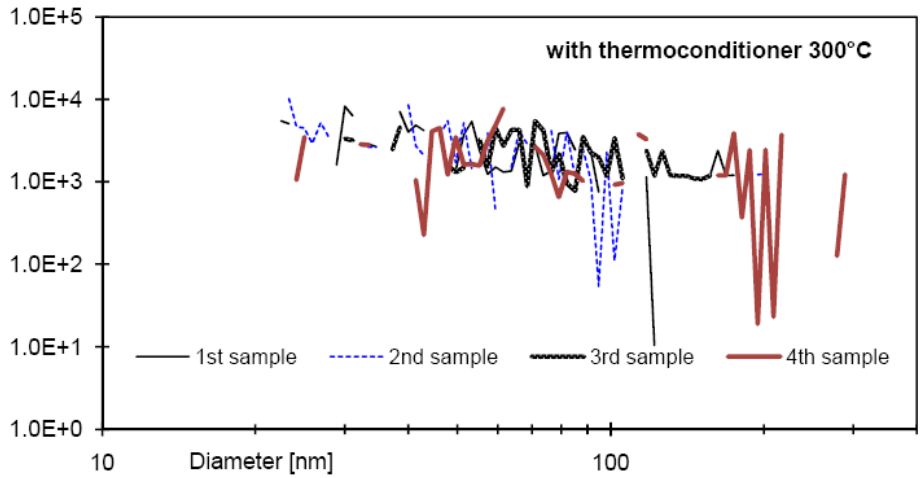


50 km/h

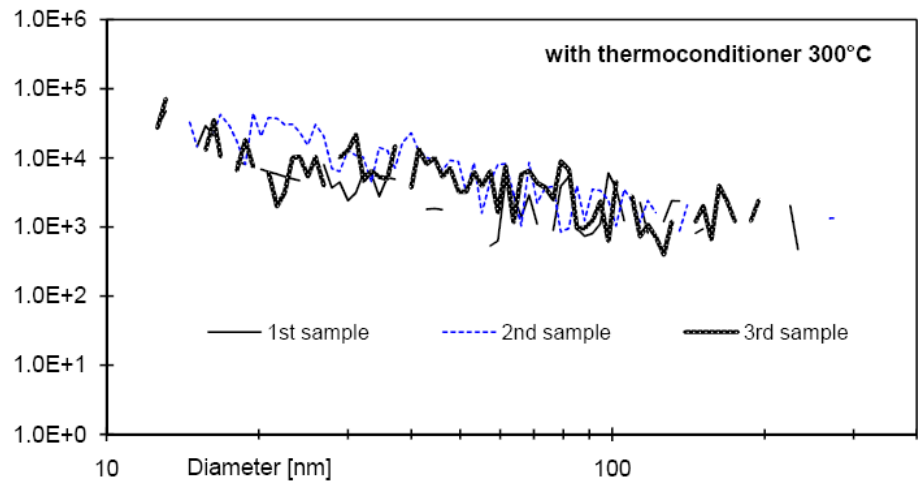


Nissan Qashqai (25‘000 km)
Size Distribution at Idle and 50 km/h

Idle



50 km/h



Metal-Emissions of Petrol Engines

unfortunaltely not size-specific

Vehicle	Renault R18		Honda 450 CBR		Nissan Qashqai		Scooter Piaggio	
Cycle	NEDC	Idling	Euro 3	Idling	NEDC	Idling	Euro 3-Cl	Idling
Tune (s)	3540	7200	4710	7200	3540	7200	3510	7200
Metal content	µg/100 kg	µg/hr	µg/100 kg	µg/hr	µg/100 kg	µg/hr	µg/100 kg	µg/hr
▪ Sulfur	2.15	1.42	1.77	0.98	3.97	2.44	3.9	1.25
▪ Calcium	448	195	375	205	393	216	815	176
▪ Zinc	1234	500	965	616	1096	575	1445	488
▪ Magnesium	36.8	16	31	22	39.7	26	71	16.5
▪ Iron	20.6	6.6	10.3	5	25.4	5.8	21.1	5.1
▪ Nickel	0.1	0.05	0.08	0.04	0.07	0.03	0.12	0.03
▪ Cromium	0.53	0.17	0.48	0.22	0.52	0.30	0.85	0.20
▪ Copper	0.2	0.08	0.15	0.06	1.77	0.05	0.25	0.09

not corrected for blanks

PN Emissions of Petrol Engines

can be very high
both overall and in the Metal Ash Peak
and comparable to Diesel particle emissions

Vehicle		Renault R18		Honda 450 CBR		Nissan Qashqai		Piaggio		Diesel
Cycle		50 km/h	Idling	50 km/h	Idling	50 km/h	Idling	50 km/h	Idling	Idling
N_{total}	[P/cm^3]	$4.1 \cdot 10^7$	$7.1 \cdot 10^7$	$2.2 \cdot 10^6$	$6.8 \cdot 10^6$	$9.1 \cdot 10^3$	$1.86 \cdot 10^3$	$3.6 \cdot 10^7$	$6.2 \cdot 10^3$	$1.5 \cdot 10^7$
N_{ash}	[P/cm^3]	$3.8 \cdot 10^7$	$7.1 \cdot 10^7$	n.d.	$6.8 \cdot 10^6$	n.d.	n.d.	n.d.	n.d.	$1.4 \cdot 10^7$
N_{soot}	[P/cm^3]	$3.1 \cdot 10^6$	$7.1 \cdot 10^4$	n.d.	$3.7 \cdot 10^4$	n.d.	n.d.	n.d.	n.d.	$8.6 \cdot 10^5$
D_{ash}	[nm]	7.9	24.4	n.d.	12.7	n.d.	n.d.	n.d.	n.d.	11.8
D_{soot}	[nm]	69.6	131.6	n.d.	25.6	n.d.	n.d.	n.d.	n.d.	48.1

Conclusions

- Internal combustion engines emit metal oxide particles from engine wear and lubrication oil
- metal oxides are probably more toxic than EC (soot)
- PM can be 0.1-1 mg/km → PN >10^8 #/cc → 10^{14} #/kWh
- Size around 20 nm, insoluble and toxic
- → **health concern is justified**

Measures:

- deploy efficient Particle Filter Systems on all ICE
- reduce the metal content of the lubrication oil
- extend PN-measurement to particle sizes < 23 nm