Nano-sized Metal Oxide Emissions from IC-Engines

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Internal combustion engines can emit metal oxides originating from various sources such as engine wear, lubrication oil, fuel ashes, fuel additives or coatings from exhaust gas after-treatment systems. Conventional on-road fuels usually contain relatively low metal contents, whereas most of the lubrication oils often contain much higher metal concentrations. Engine wear metals are usually present in all internal combustion engines. Metal compounds collected in lubrication oil can be re-entrained into the cylinder and then oxidized during combustion. Some metals can even be vaporized and re-nucleide as very small particles in a size range typically below 30 nm. These metal oxide particles might be present in the exhaust aerosol either as free metal oxide particles or attached to soot particles.

Introduction

Toxicological effects of nanoparticles

Particle emissions of diesel vehicles can cause acute and chronic harm at lung and cardiovascular system. The biological impact depends on the particles' ability to defeat the human body defense. Crucial factors are particle size and solubility. Almost insoluble particles are hazardous especially in small size ranges. Toxicological studies have shown increased toxicity of nanoparticles compared to micrometer particles of the same composition, which has raised concern about the impact on human health. Nanoparticles can enter alveoli in the lungs, pass biological barriers including placenta and blood–brain barrier, and enter cells. The high surface area and chemical composition of the nanoparticles (NPs) play an important role in biological activity and toxicology, but toxicology depends also on cell types. The binding of NPs to bacterial proteins can inhibit enzymatic activity. Epidemiological studies on ultrafine particles have shown increased cancer risk after long-term exposure of diesel vehicle drivers enhanced allergy tendency at traffic burdened sites and enhanced risk of heart attack.[1-14]

Figure 1 shows that particles < 10 µm can intrude deep into the lung. Particles smaller than 100 nm show a high deposition rate in the alveoli, which increase with decreasing particle diameter. Tissue penetration from alveoli to the blood vessels, too, is highly dependent on particle size. Therefore, the particle dosage should be weighted with this size influence.

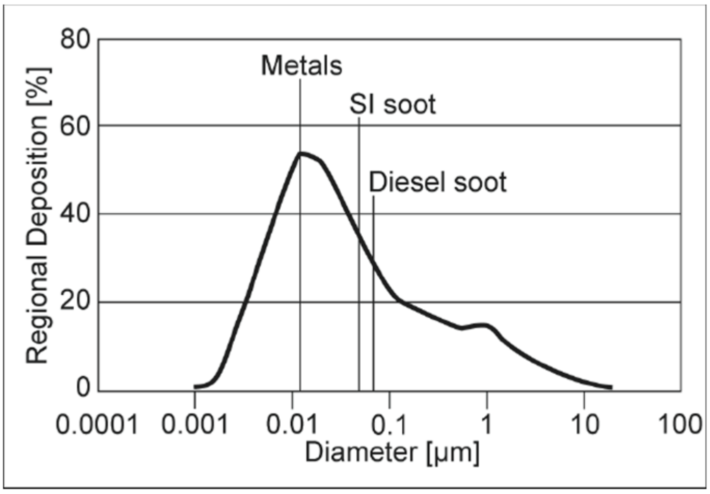


Fig. 1: Deposition of inhaled particles in the alveoli [14] The mean particle sizes are: Diesel soot about 100 nm; SI soot about 50 nm and metal oxides about 15 nm.

Particulate emissions of different Vehicle types

Not only diesel vehicles show high particulate emissions, but also direct injection (DI) gasoline vehicles have a tendency to increasing emission of particulate matter compared to *multi-port injection (MPI) vehicles*.[15] The following graphic compares particle number concentration (PN) for different vehicle types i.e. multiport injection (MPI) and direct injection (DI) gasoline vehicles, diesel vehicles without and with diesel particle filter (DPF) in the loading (load) and regeneration phase and vehicles fueled by compressed natural gas (CNG)

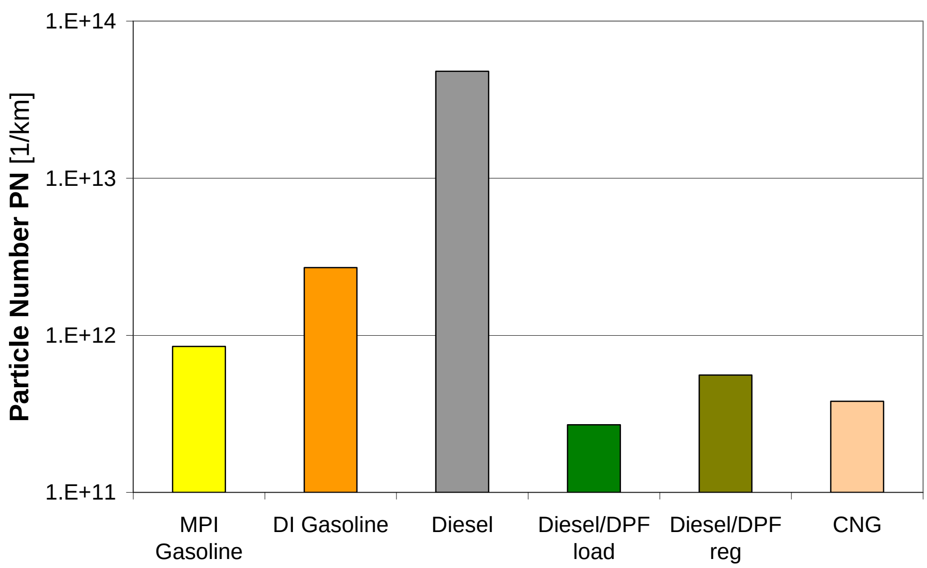


Fig. 2: Particle number concentration (PN) for different vehicle types

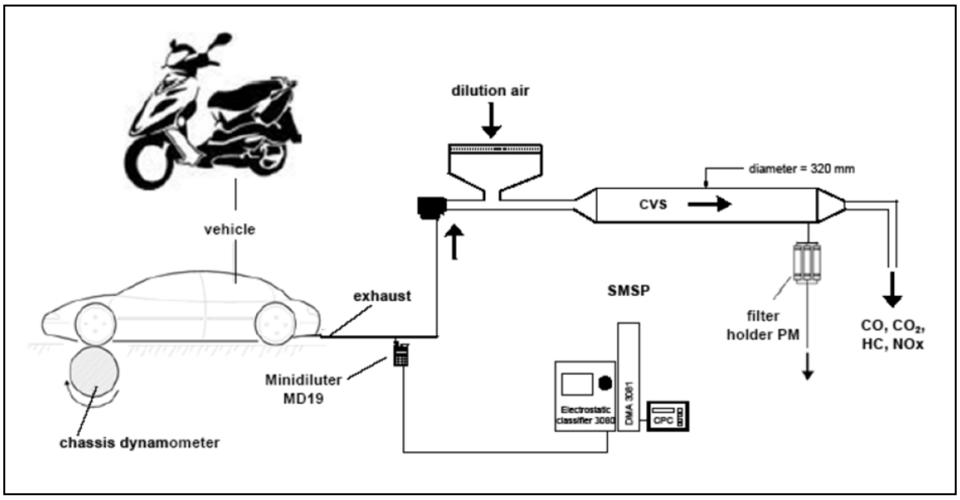
The following table summarizes the potential sources for metallic particles in vehicle emissions. Further details can be found elsewhere.[2,16,17]

Tab. 1: Potential sources for metallic particles in vehicle emissions

Sources for metal emissions	Metals	Estimated amount
Abrasion from piston ring, cylinder liner, valve cams, valves, bearings	e.g. Fe, Al, Cr, Ni, Cu, Pb ...	abraded metal mass ca. 0.1 to 1 mg/km
Lubrication oil	e.g. Zn, Ca, B, Mg	Zn: 0.1 – 0.2 %, Ca: 0.5 %, B: 0.09 %. Mg: 0.002-0.004 % ,.. old vehicles: up to 1 % oil of fuel consumption
Fuel	several metals in traces, Heavy metals like Pb and Mn are limited by law (e.g. in Germany BzBIG 1971: Pb <150 mg/kg fuel)	

Experimental

The vehicle characteristics as well as the sampling procedures and analysis are displayed in the following graphs and tables. Online particle analysis has been performed with SMPS. Size fractionated chemical analysis of nanoparticles in vehicle emissions were carried out by sampling with an electrical low pressure multi-stage impactor ELPI with subsequent acid digestion in a microwave system and chemical analysis with plasma mass spectrometry ICPMS. Further details can be found elsewhere.[2,16,17]



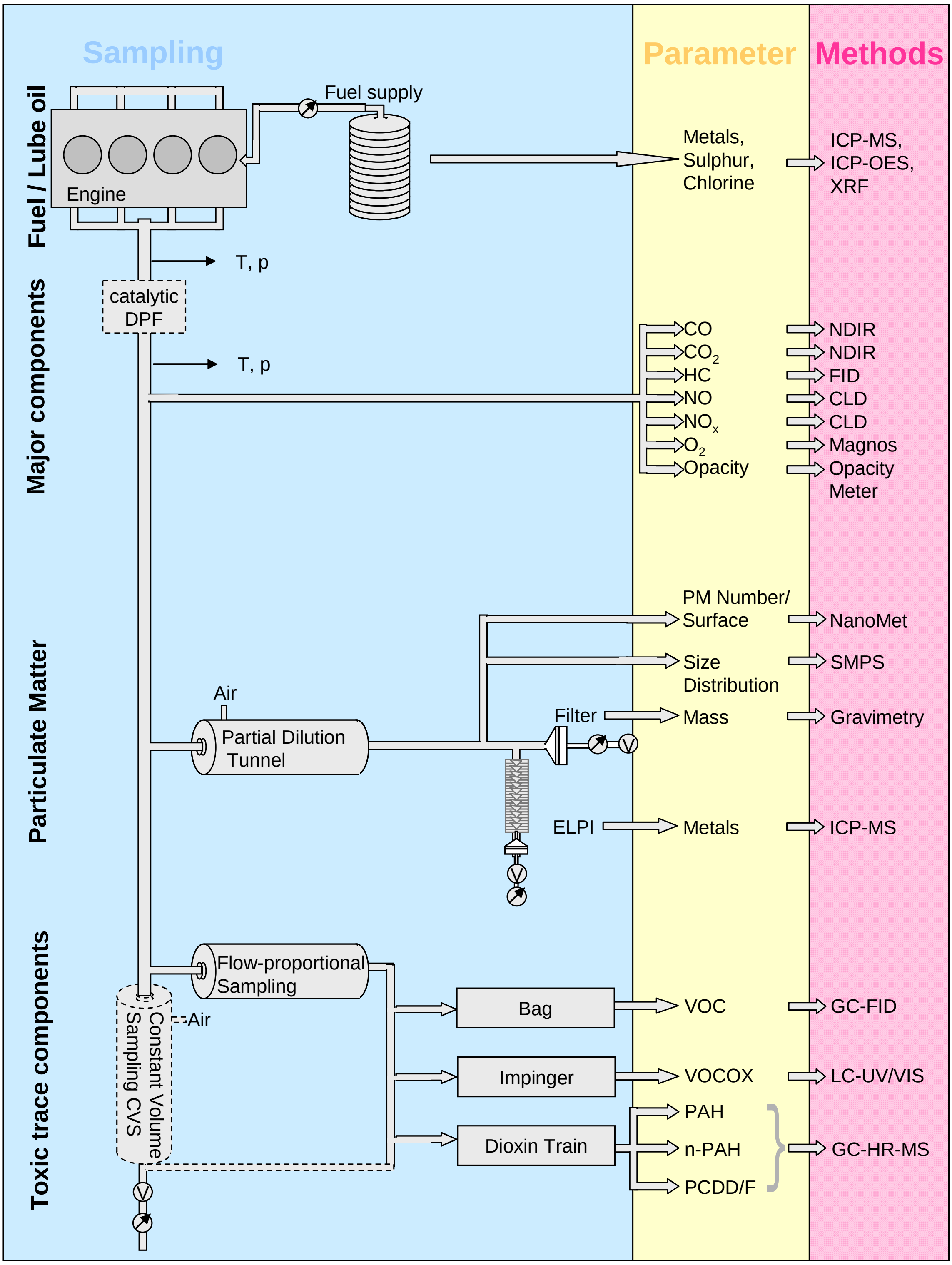


Fig. 3: *Test and sampling setup*

(A) for passenger cars and 2-wheelers

(B) for diesel engine tests

__Tab. 2:__ Operation points for vehicle and diesel engine tests

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

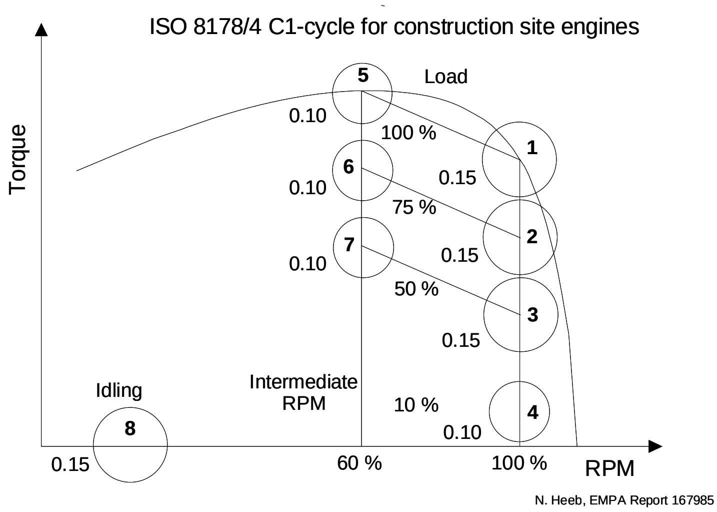


__Fig. 4:__ Used Test cycle ISO 8178/4 C1

__Tab. 3:__ Characteristics of lubrication oils for cars and 2-wheelers

Lubrication oil	Renault / Honda		Quashqai		Piaggio	
	Used	Fresh	Used	Fresh	Used	Fresh
Oil Ash content [%}		SAE 15W-40 1.8		SAE 5W-40 1.6		SAE 5W-40 1.6
[mg/kg]						
Sulfur	6439/3170	3011	2490	2725	5000	4800
Calcium	2100/1600	1700	1438	1584	2200	2200
Phosphorous	886/797	869	753	895	1200	1100
Zinc	1016/934	967	893	984	1300	1200
Iron	6.2/7.9	1.5	32	0.9	14	0.9
Nickel	DL	DL	0.03	0.02	DL	0.11
Copper	0.77/ 3.78	0.01	0.04	0.03	33	0.0001
Operating time since oil change	1000/4000 km/		25000 km		1000 km	

__Tab. 4:__ Lubrication oil 15 W/40 and fuel for Liebherr D934S and D914T diesel engine

Viscosity kin 40°C	-	mm^2/s
Viscosity kin 100°C	13.98	mm^2/s
Viscosity index	-	(--)
Density 20°C	-	kg/m^3
Pour point	- 25	°C
Flame point	-	°C
TBN	8.4	mg KOH/g
Sulfur ashes	10 770	mg/kg
Sulfur	3 360	mg/kg
Mg	< 10	mg/kg
Zn	1 200	mg/kg
Ca	2 630	mg/kg
P	1 110	mg/kg

Density (at 40°C)	0.820 - 0.845 g/ml
Viscosity (at 20°C)	2.0 – 3.2 mm^2/s
Flame point: min	62°C
Cloud point :max	- 10°C
Filtering limit	CFPP max. - 20°C
Coke residue	max. 0.02 g/100g
Ash	Traces
Sulfur	max. 0.001 g/100g
Cetane index	min. 52 – 54
Boiling analysis	min. 98 vol %
Calorific value (lower)	min. 42.5 MJ/kg

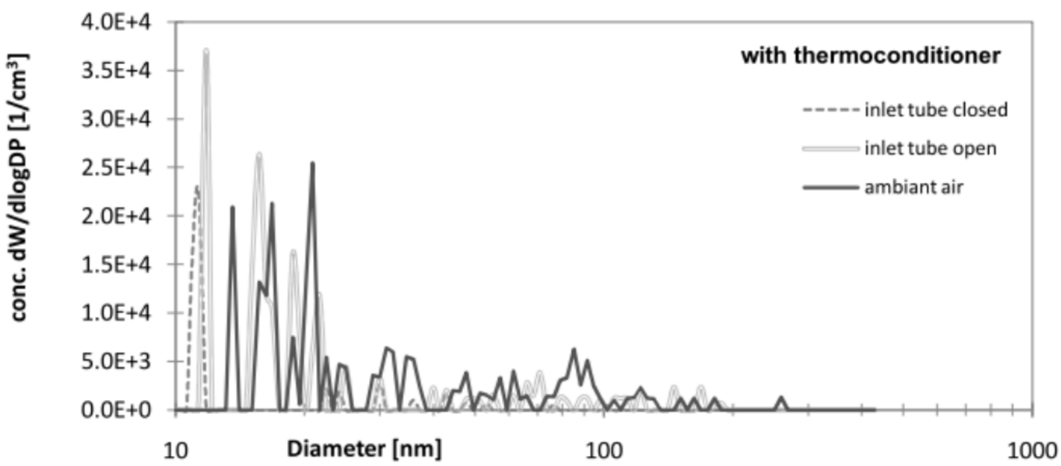


__Fig. 5:__ CVS Background: Lab air and CVS tunnel only

Results

The investigation within this study focused on the particle emissions. Gaseous emissions are not reported. The particle mass emissions and their composition are summarized in table 5. Figure 6 shows the particle size distribution (measured by scanning mobility particle sizer SMPS) for Liebherr 924 engine without DPF and with DPF at the 8 tested operation points. At the point 8, i.e. idling at 800 RPM, the particle number concentration in the smaller size range is relatively low. A possible explanation for this fact might be the lower soot generation at idling point 8. Therefore, possibly emitted metal species are emitted as free metal oxides, whereas at the other operating points the concentration of soot particles is much higher that the metals can be bounded to the soot particles like shown as an example in Fig. 8.

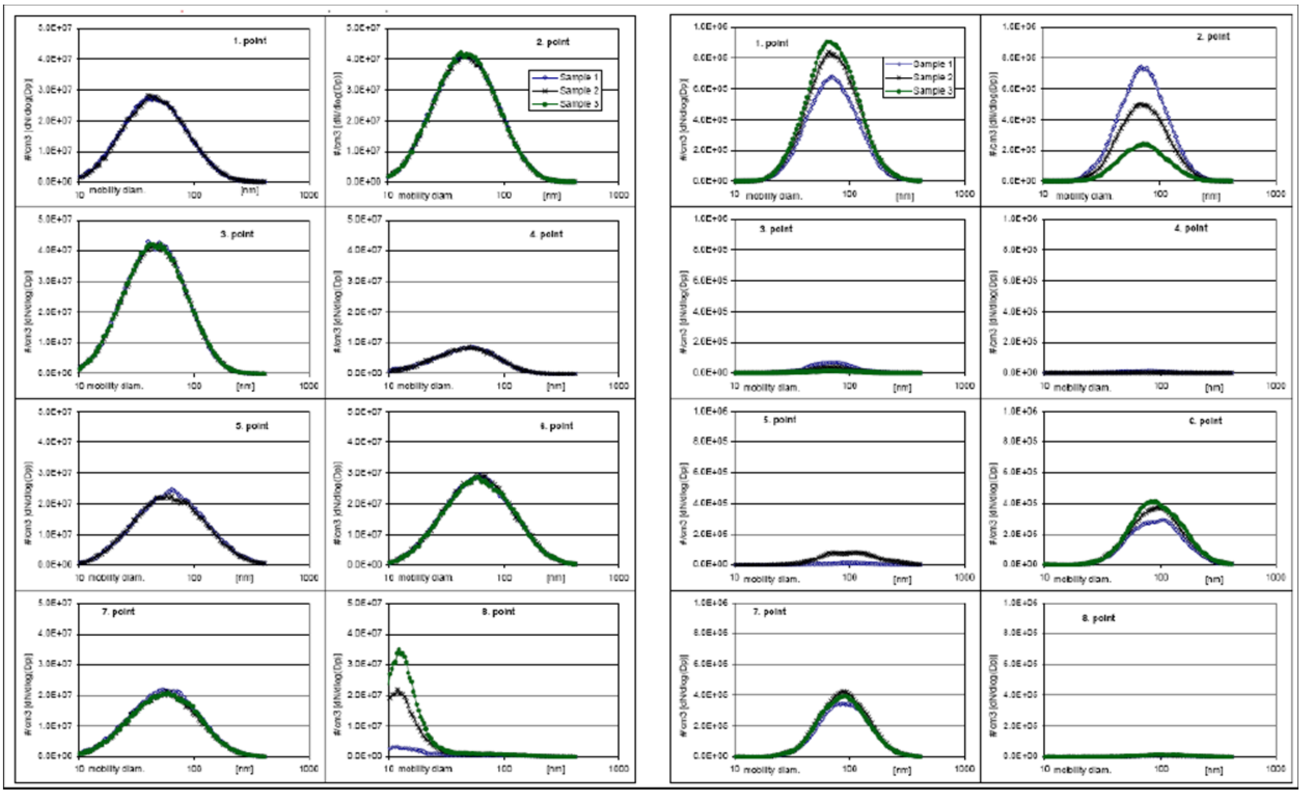


Fig. 6: *Particle size distribution (SMPS) for Liebherr 924 engine (A) without DPF and (B) with DPF at 8 operation points. Point 8 is idling at 800 RPM.*

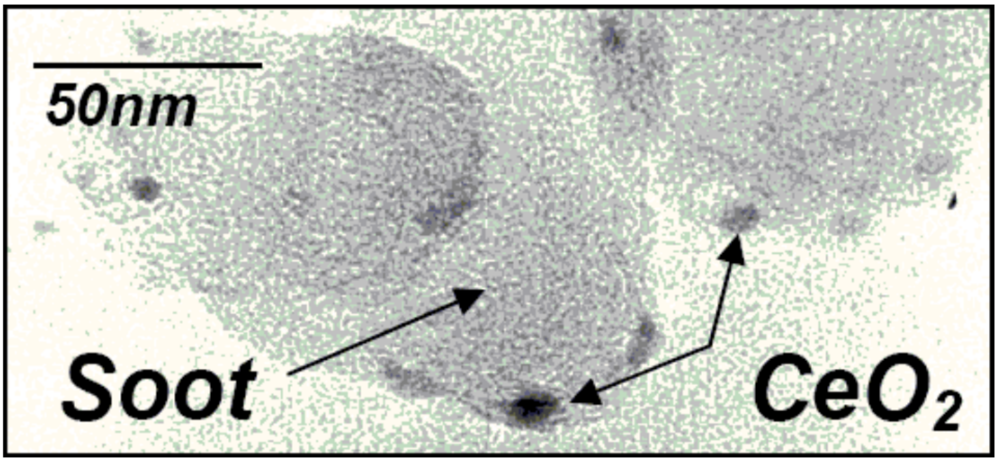


Fig. 7: *SEM image of metal NPs, here cerium oxide, bound to soot particles*

Tab 5: *Particle mass emissions of filter samples for vehicles*

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

If metal emissions lead to nanoparticulate emissions at very low size ranges, it was suspected that the phenomenon is also visible for petrol engines. The following graph shows the size distribution measured by SMPS for measurement of two cars and two 2 weelers. All measurements were carried out at two different steady-state conditions, i.e. at a constant speed of 50 km/h and at idling. The Renault R18 car has, both at the medium load point and at idling, relatively high particle emissions. A bimodal distribution was observed at part load. For the Honda 450 CWR Motorbike modality of the size distribution is clearly evident and the emissions are relatively high. Also the 1-cylinder/4-stroke scooter engine of the Piaggio Scooter showed significant particle emissions at 50 km/h which were even higher than for the Honda motorbike. However, the bimodal distribution is less evident. The .particle emission at idling operation was lower than expected. The second car Nissan Qashqai, which was of newer engine technique showed relatively low particle emissions which hardly exceed the background, neither at 50 km/h nor at idling. Further investigations on metal oxide emissions of different vehicle types have been already published[16,18].

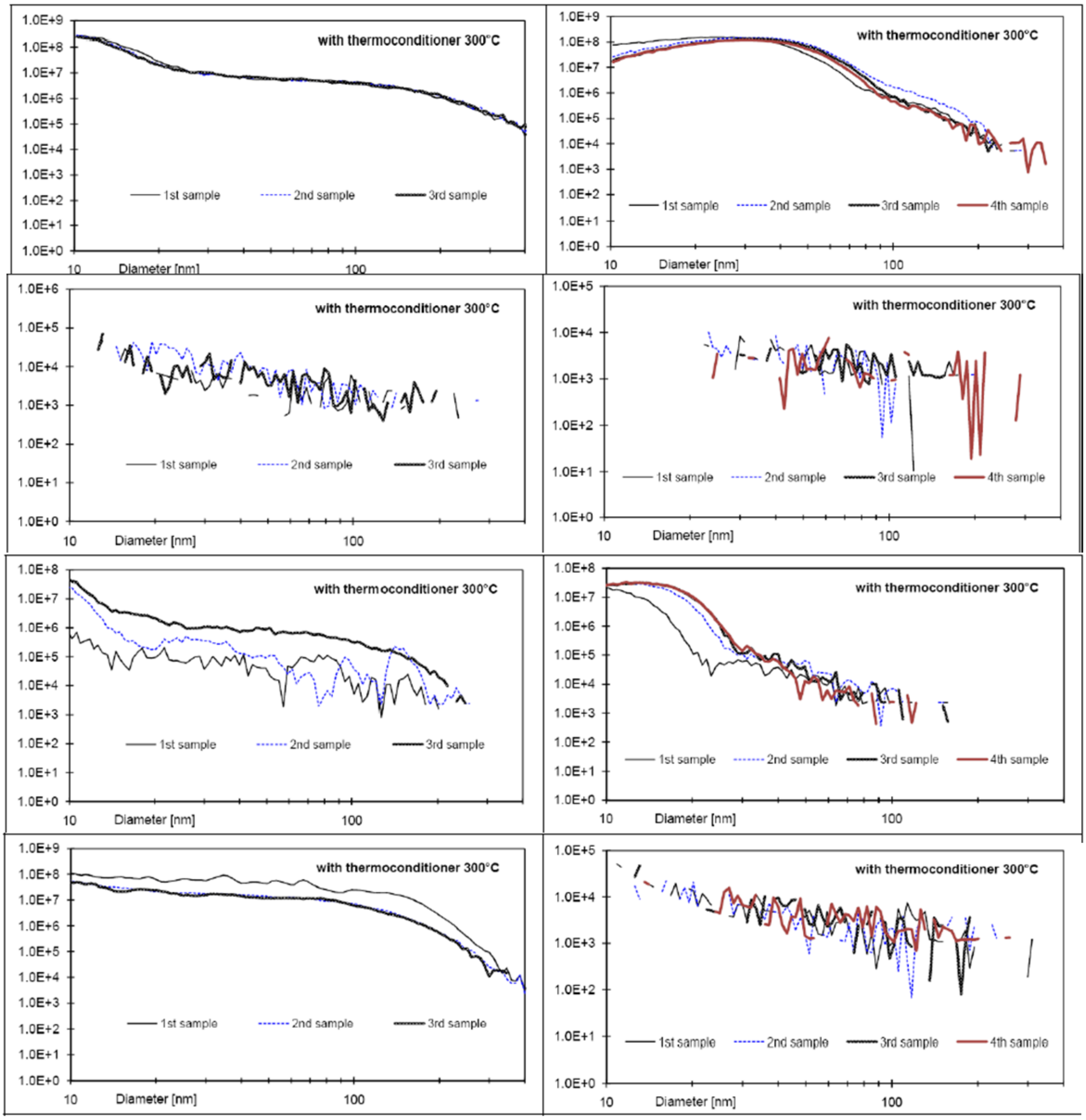


Fig. 8: *Particle distribution (SMPS) at 50 km/h and idle for cars: (A) Renault R18 and (B) Nissang Quahqai motorbikes: (A) Honda 450 and (B) Scooter Piaggio*

Conclusion

Emissions of metal oxide particles can occur for all types of internal combustion engines. Even if clean fuels are used, lubrication oil remains as a potential source for metal oxide particles. Full-wall-flow particle filter systems show high filtration efficiency in diesel exhaust gas after-treatment, but this study will demonstrate that they can be also useful to remove not only soot but also metal oxide emissions from exhaust gas. This makes filtration technology promising not only for diesel engines (soot filtration) but also for exhaust gas cleaning of other engine types.

Acknowledgements:

The authors like to thank the Swiss Federal Office for Environment BAFU for financial support.

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