Effect of Organometallic Fuel Additives on Nanoparticle Emissions from a Gasoline Passenger Car

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Outline

- Introduction
- Experimental
- Total particle measurements
- Solid particle measurements
- Conclusions

Introduction

- Paper submitted to EST
  - Jeremy T. Gidney, Martyn V. Twigg, and David B. Kittelson, 2009. Effect of Organometallic Fuel Additives on Nanoparticle Emissions from a Gasoline Passenger Car
- Investigates the influence of inorganic fuel additives (Mn, Fe, Pb) on nanoparticle emissions from a PFI gasoline vehicle
- Issues
  - Health impacts
    - Solid nanoparticles
    - Rapid translocation in body
  - Catalyst plugging and engine deposits
  - Iron and manganese octane boosters still used in Eastern Europe, China, and developing countries
    - Mn used at 30, 50, and 55 mg/liter in China, Russia, and Lithuania, respectively
    - Mn allowed but not used at levels up to 8 and 18 mg/liter in US and Canada, respectively
    - Fe allowed at levels up to 37 mg/liter in Russia

Health

- Correlations between fine particles and excess deaths
- Increased asthma and respiratory problems in children living near roadways
- Special concerns about ultrafine and nanoparticles
  - More surface area and number per unit mass
  - Increased deep lung deposition efficiency
  - Very small particles may pass through cell membranes and along neurons
  - Effects of solid particles clear, volatile particles uncertain

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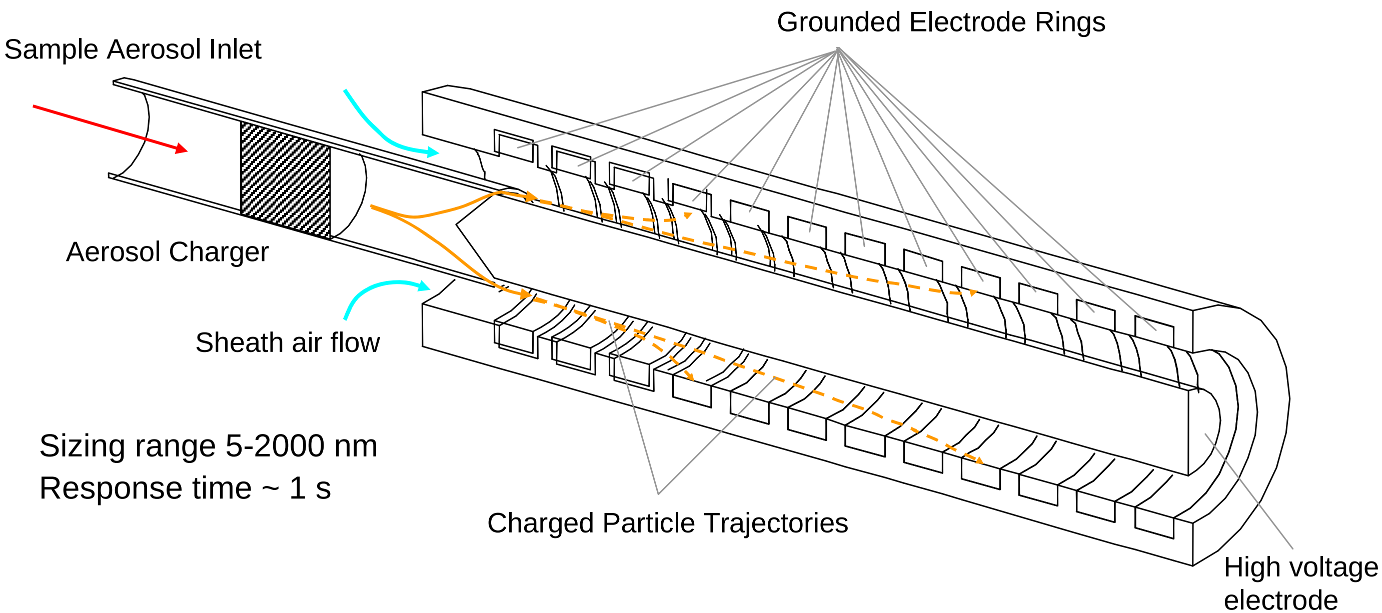
Vehicle and fuels used in study

Table 1: Vehicle, catalyst and other details	
Vehicle	Subcompact car
Model year	2000
Engine type	Gasoline spark ignition
Fuel system	Multi point injection
Engine	4 cylinder, 1.6 litre displacement
Catalyst volume	1.66 litre
Emissions conformance	European Stage 3
Vehicle age	11,000 miles
Catalyst age	4,000 miles
Catalyst cell density	400 cpsi, 6 mil wall thickness
Catalyst formulation	Palladium/rhodium
Lubrication oil	Fully synthetic 5 - 30 SAE

Table 2. Details of additive concentrations used in the present study			
Batch	Additive	Metal concentration	Additive concentration
code		mg/l	g/20 litre
Mn-8	$(CH_3C_5H_4)Mn(CO)_3$	8.3	0.658
Mn-18	$(CH_3C_5H_4)Mn(CO)_3$	18	1.429
Fe-8	$Fe(C_6H_5)_2$	8.4	0.562
Pb-30	$Pb(C_2H_5)_4$	31.3	0.626

Particle measurement and sampling



Sizing range 5-2000 nm
Response time ~ 1 s

- Cambustion DMS500* used for particle measurements
- Samples taken at engine out, catalyst out, and tailpipe using short sampling lines
- Integrated DMS diluter used for engine and catalyst out measurements
- Dekati ejector dilutor used for tailpipe measurements
- Catalytic stripper used to remove volatiles for solid particle measurements

*Reavell, K., T. Hands, and N. Collings, 2002. “A Fast Response Particulate Spectrometer for Combustion Aerosols,” SAE paper 2002-01-2714
Kittelson, David, Tim Hands, Chris Nickolaus, Nick Collings, Ville Niemelä, and Martyn Twigg, 2004. “Mass Correlation of Engine Emissions with Spectral Instruments,” JSAE paper number 20045462

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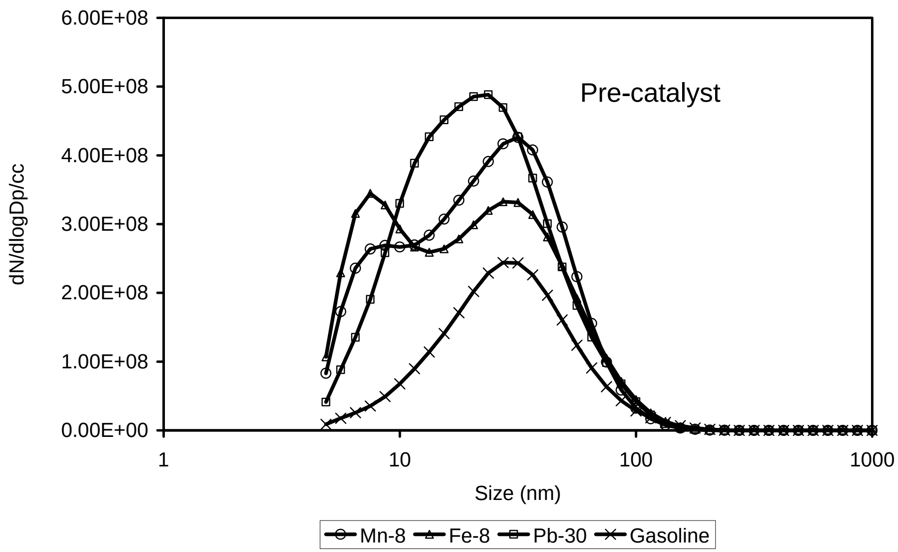
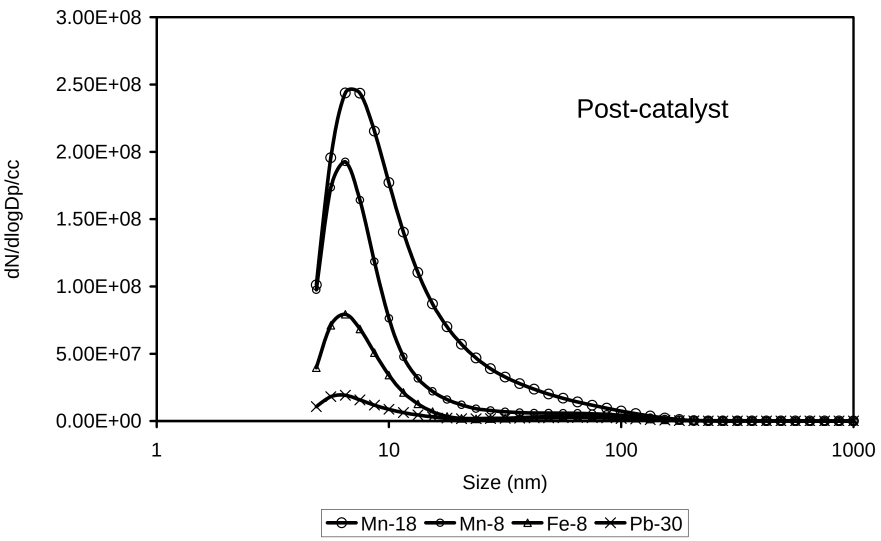
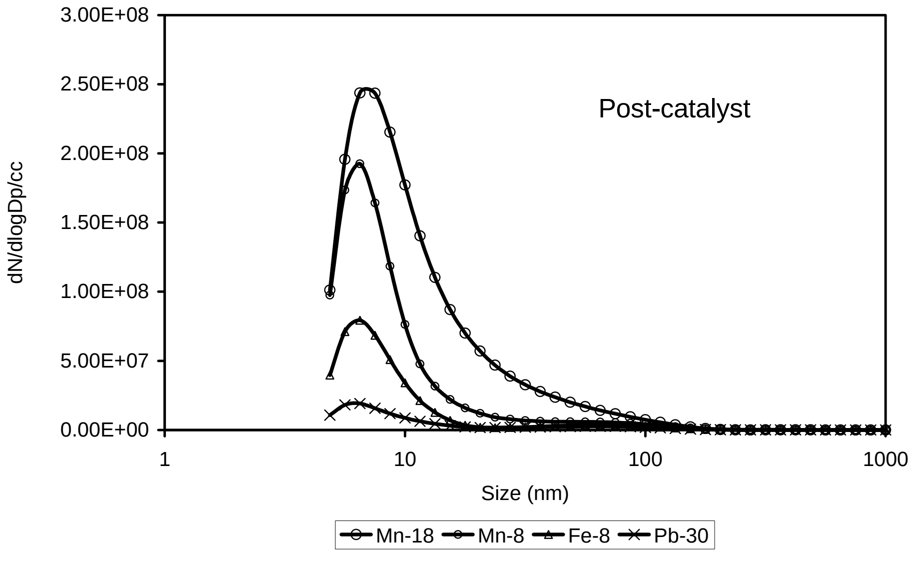
Cycle average pre and post catalyst size distributions for high speed EUDC test cycle.

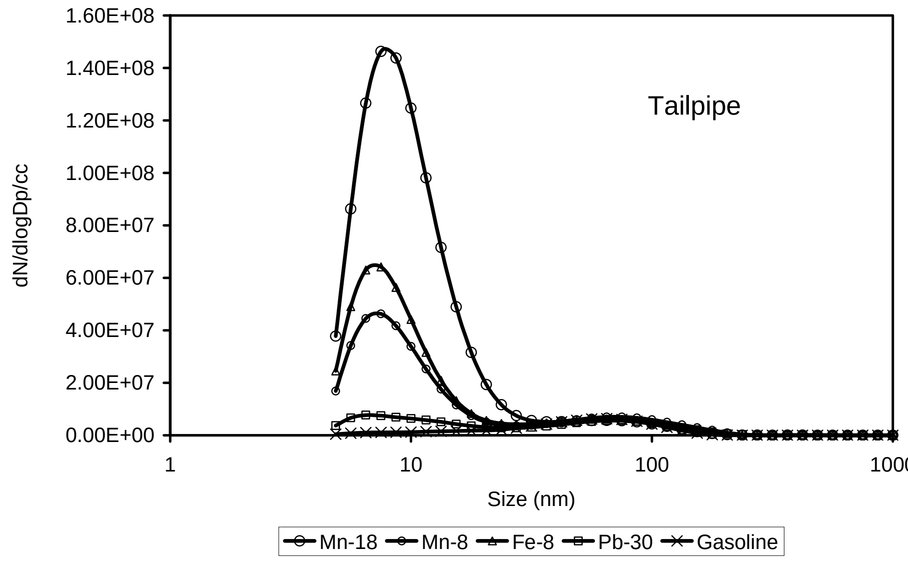




- Engine out measurements (pre-catalyst) show large accumulation mode
  - All three metals increase particle emissions
  - Iron and manganese show clear nucleation mode
- Post-catalyst measurements show large reductions in accumulation mode region indicating efficient removal of organic carbon by three-way catalyst
- Post-catalyst measurements show a distinct nucleation mode for all three metals

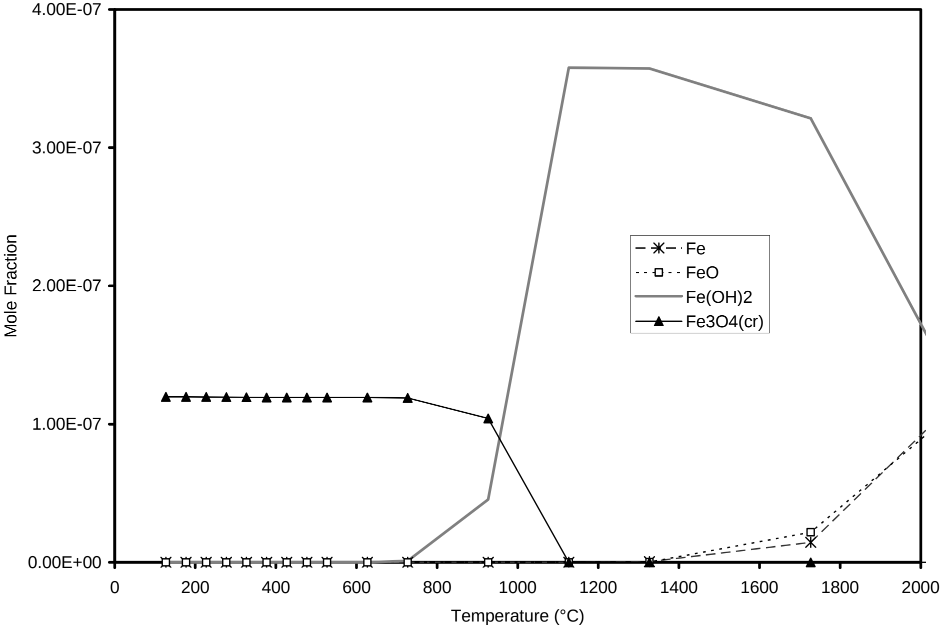
Cycle average post catalyst and tailpipe size distributions for high speed EUDC test cycle.

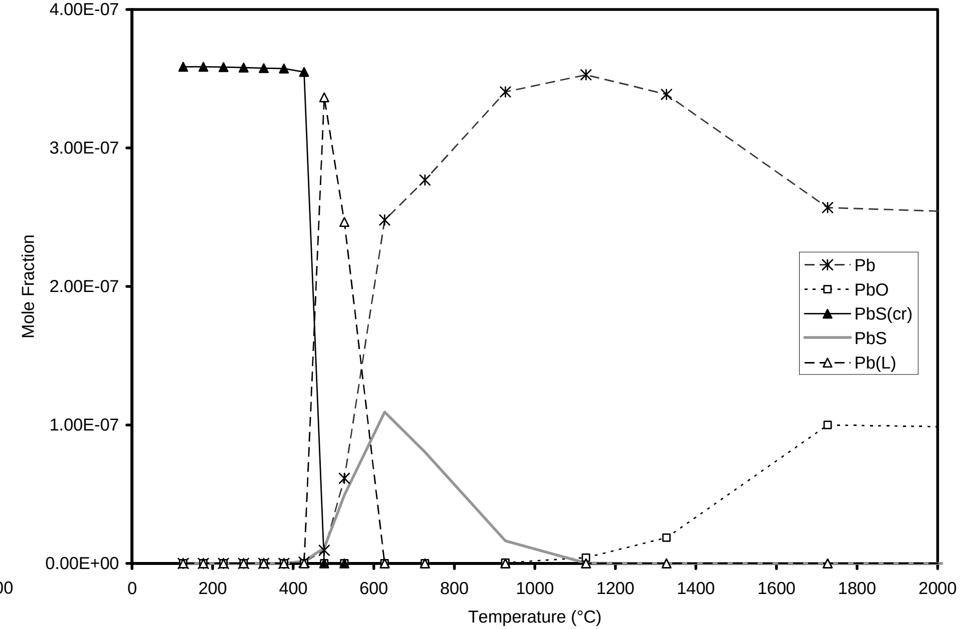




- Tailpipe out concentrations roughly a factor of two lower than post catalyst due to diffusion and thermophoresis losses in exhaust system
- Clear, large nucleation mode for Mn and Fe, smaller mode for Pb, no significant mode for standard gasoline
- Why does lead make such a small nucleation mode?

Chemical equilibrium calculations suggest lead compounds are more likely to be lost to walls





- Calculations were done using the NASA CEAgui chemical equilibrium program
  - Gasoline containing sulphur (50 ppm S)
  - 8.4 and 31.3mg/l iron or lead, respectively
  - Excess air factor of 0.98
  - Calculations are based on bulk phase properties, nanoscale and kinetic factors not included
- Iron forms stable solid compound below about 900 C, Mn expected to behave in similar manner
- Lead compounds are volatile above about 600 C.
  - This temperature is often exceeded at the catalyst inlet
  - Temperatures at the exhaust valve are even higher
- Volatile compounds are more likely to be lost by mass transfer to the walls of the exhaust system than solid particles because of much higher diffusion coefficients
- Some of the deposited material likely to blow off in larger particles

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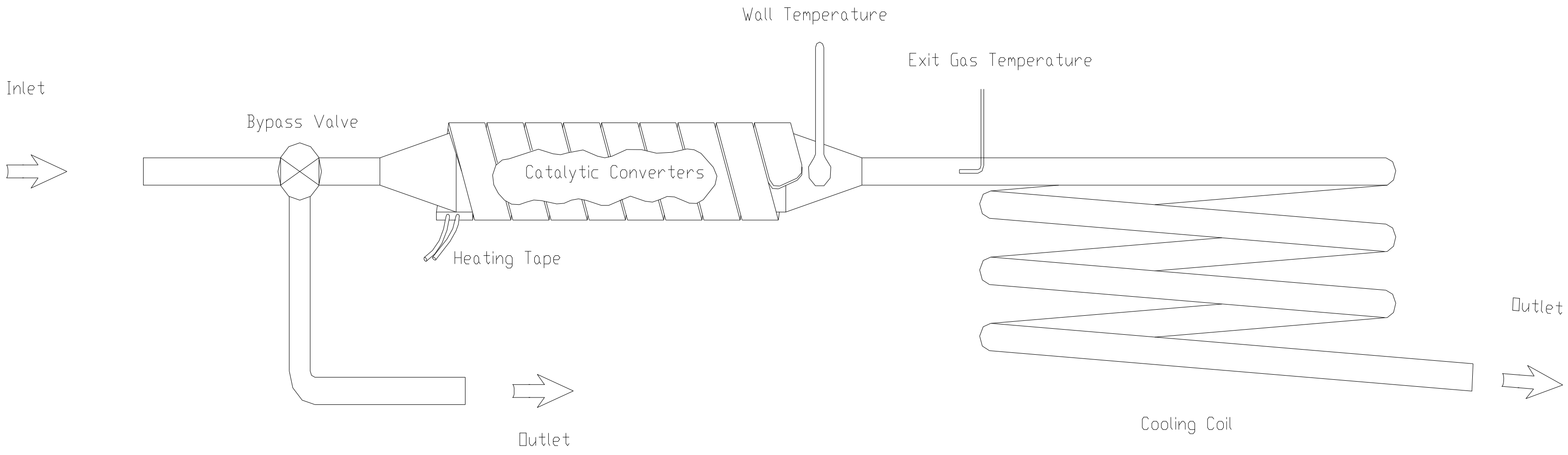
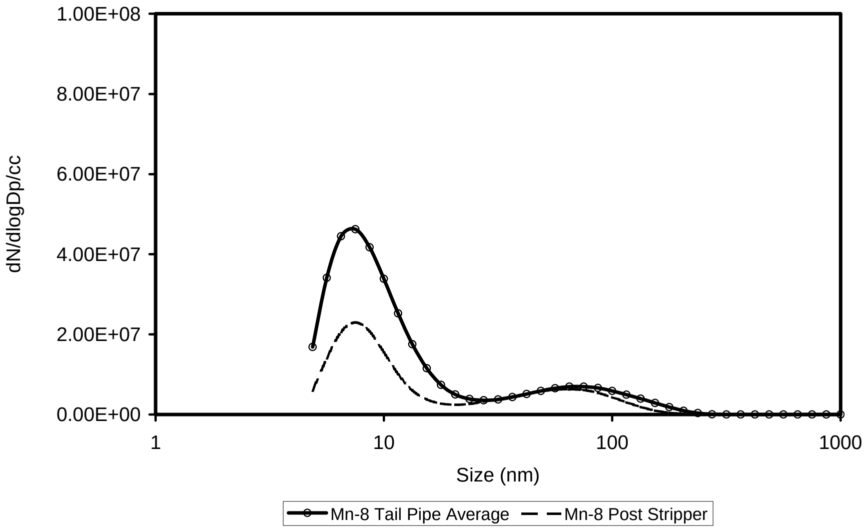
A catalytic stripper was used to remove volatile particles with little loss of solid particles

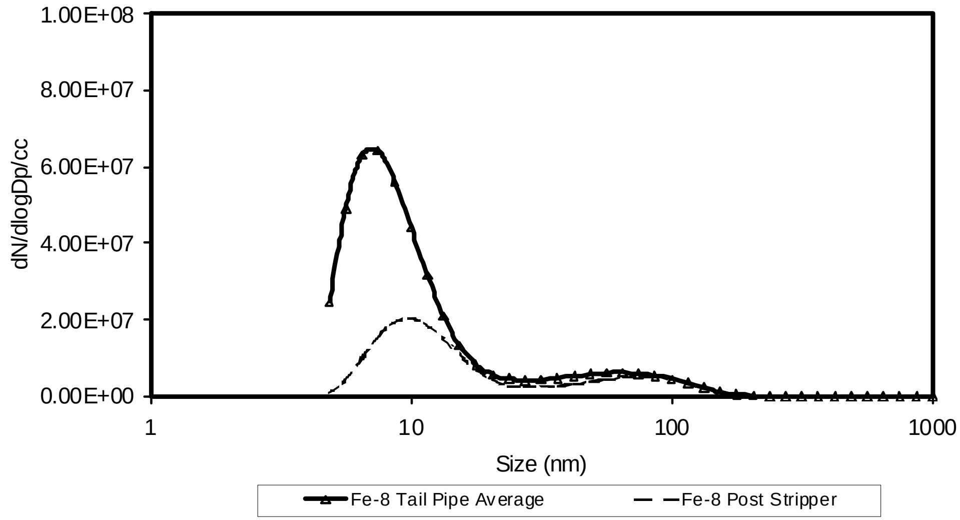


- Recent stripper design
  - Stripper consists of a 2 substrate catalyst* followed by a cooling coil
  - The first substrate removes sulfur compounds
  - The second substrate is an oxidizing catalyst
  - Diffusion and thermophoretic losses present but well defined

*Catalysts were provided by Johnson-Matthey

Both manganese and iron led to significant solid nanoparticle emissions

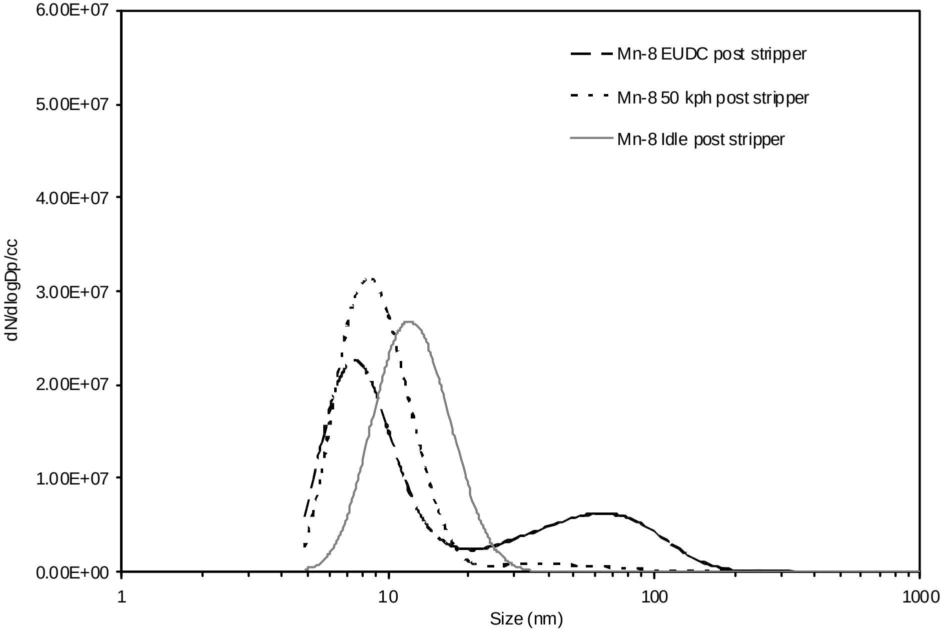


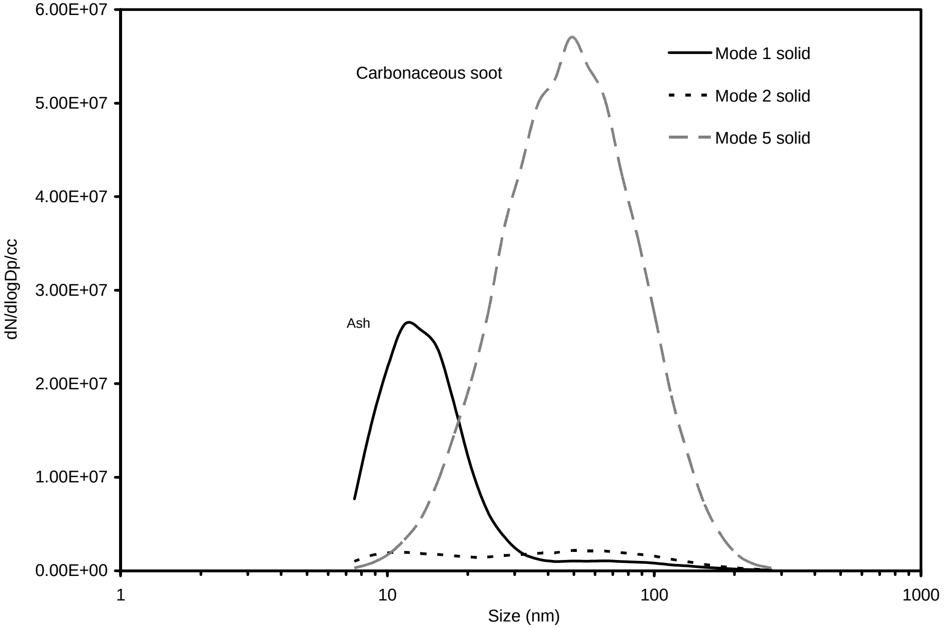


- These results are not corrected for diffusion and thermophoresis losses, which are about 60% at 7.5 nm and 30% at 200 nm
- These results show that the nucleation mode consists mainly of solid particles, most likely iron and manganese oxides
- These are the types of particles that have been shown to translocate along the olfactory nervous system to the brain in rats*

*Translocation of inhaled ultrafine manganese oxide particles on the central nervous system. Alison Elder, Robert Gerlein, Vanessa Silva, Tessa Feikert, Lisa Opanashuk, Janet Carter, Russell Potter, Andrew Maynard, Yasuo Ito, Jacob Finkelstein and Gunter Oberdorster. Environmental Health Perspectives, Volume 114, Number 8, August 2006.

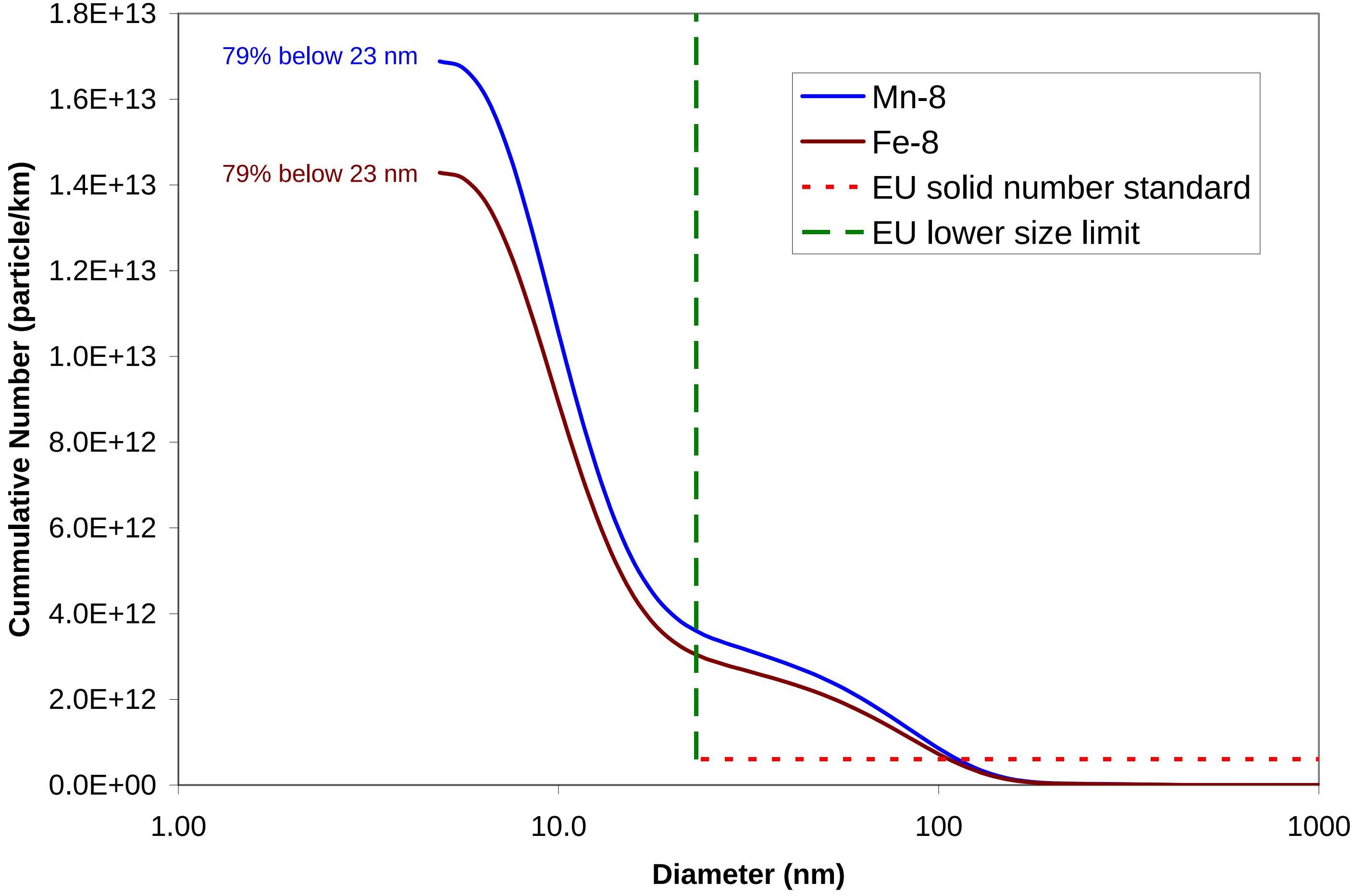
Solid nucleation mode emissions with metal doped gasoline are remarkably similar to idling Diesel





- All measurements made downstream of a catalytic stripper
- Diesel results are for a heavy-duty engine without after treatment complying with US 2004 standards
  - Measurements made with an SMPS
  - BP50 fuel
  - Solid ash particles mainly from additives in the lube oil, Ca, Zn, Mg, P

Here the results for the EUDC measurements of solid number emissions and the EU number standard



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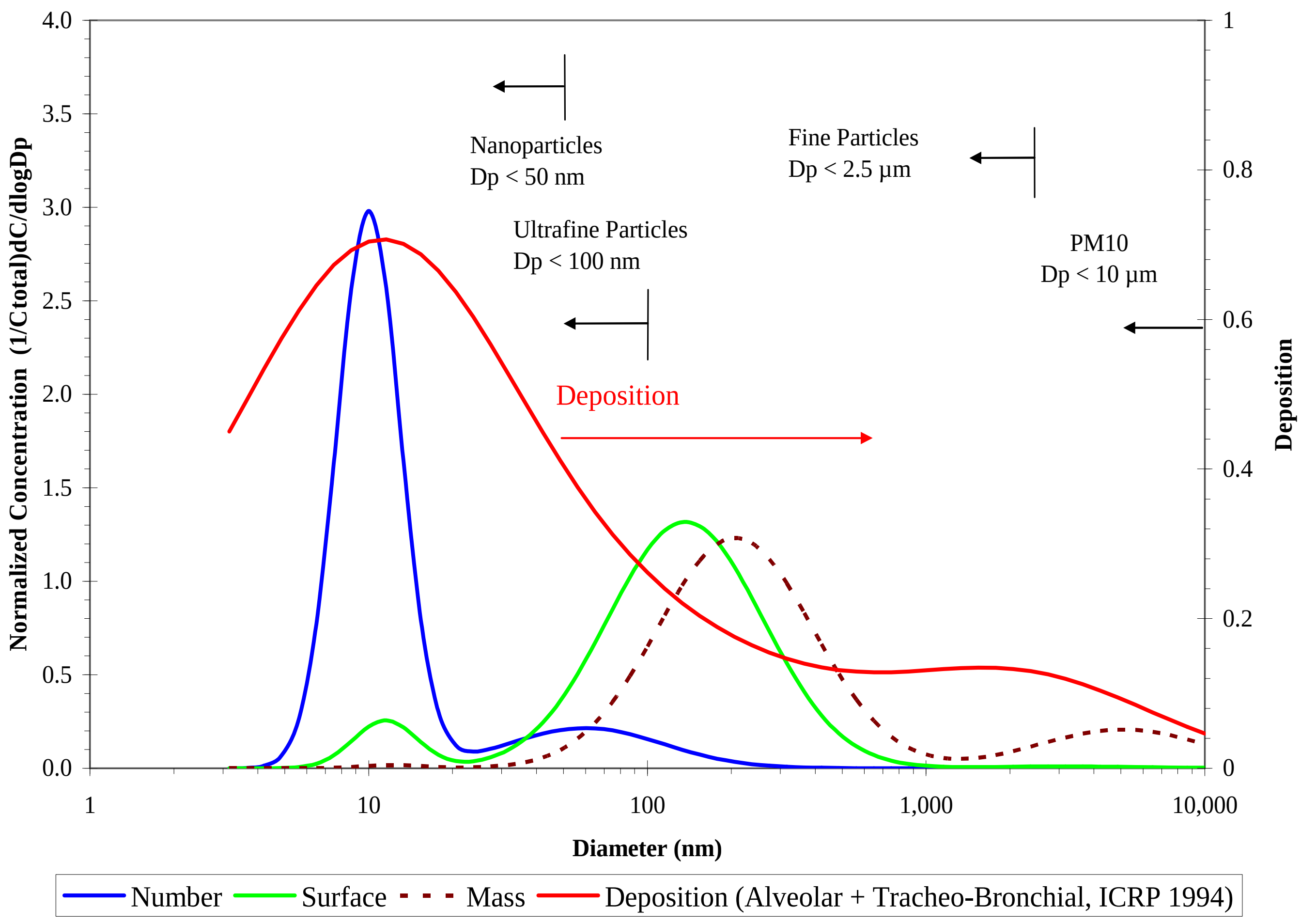
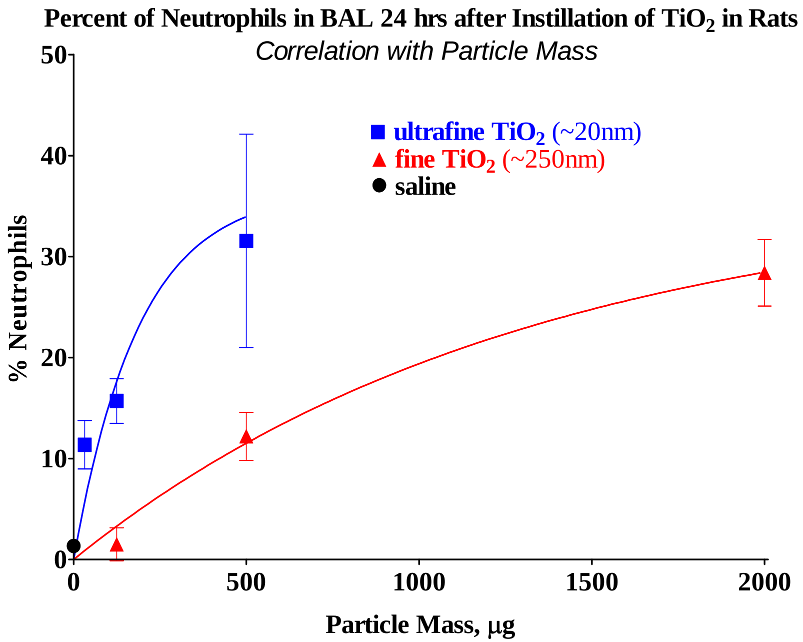
Conclusions

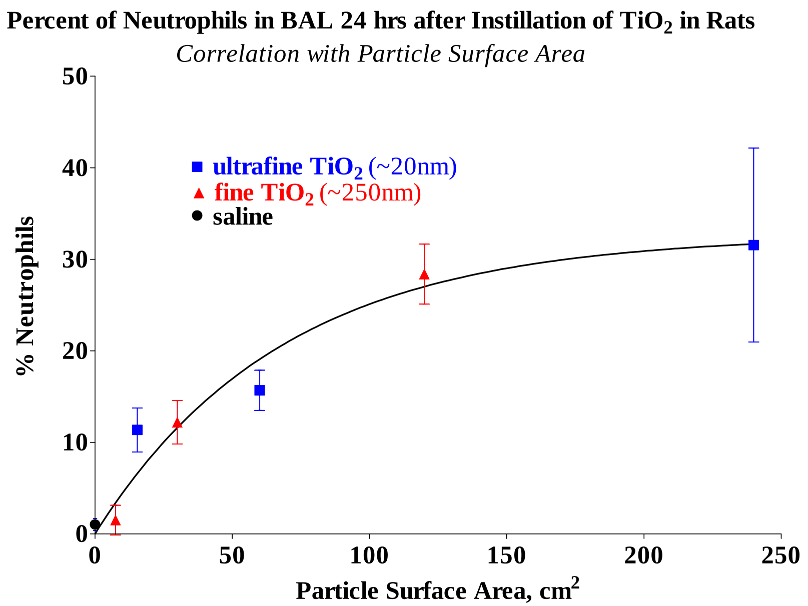
- Mn and Fe additives are used many areas outside the EU, Japan, and US
- Mn and Fe additives resulted in the formation of a distinct nucleation mode
  - The particles in this mode were nearly all solid, likely metal oxides
  - Particles in this mode were nearly all below the current lower size limit of EU number regulations
  - With Mn-8 and Fe-8
    - Total solid number emissions were 25-30 times current EU standard
    - Only about 20% of the solid particle emissions were in the EU measurement range above 23 nm
  - Dosing rates of up to 55 mg/liter used in some countries would lead much higher emissions

Health – Ultrafine particles are deposited on the deep lung regions more efficiently than fine particles



Which is the relevant measure of biological impact of particles, number, surface, or mass?

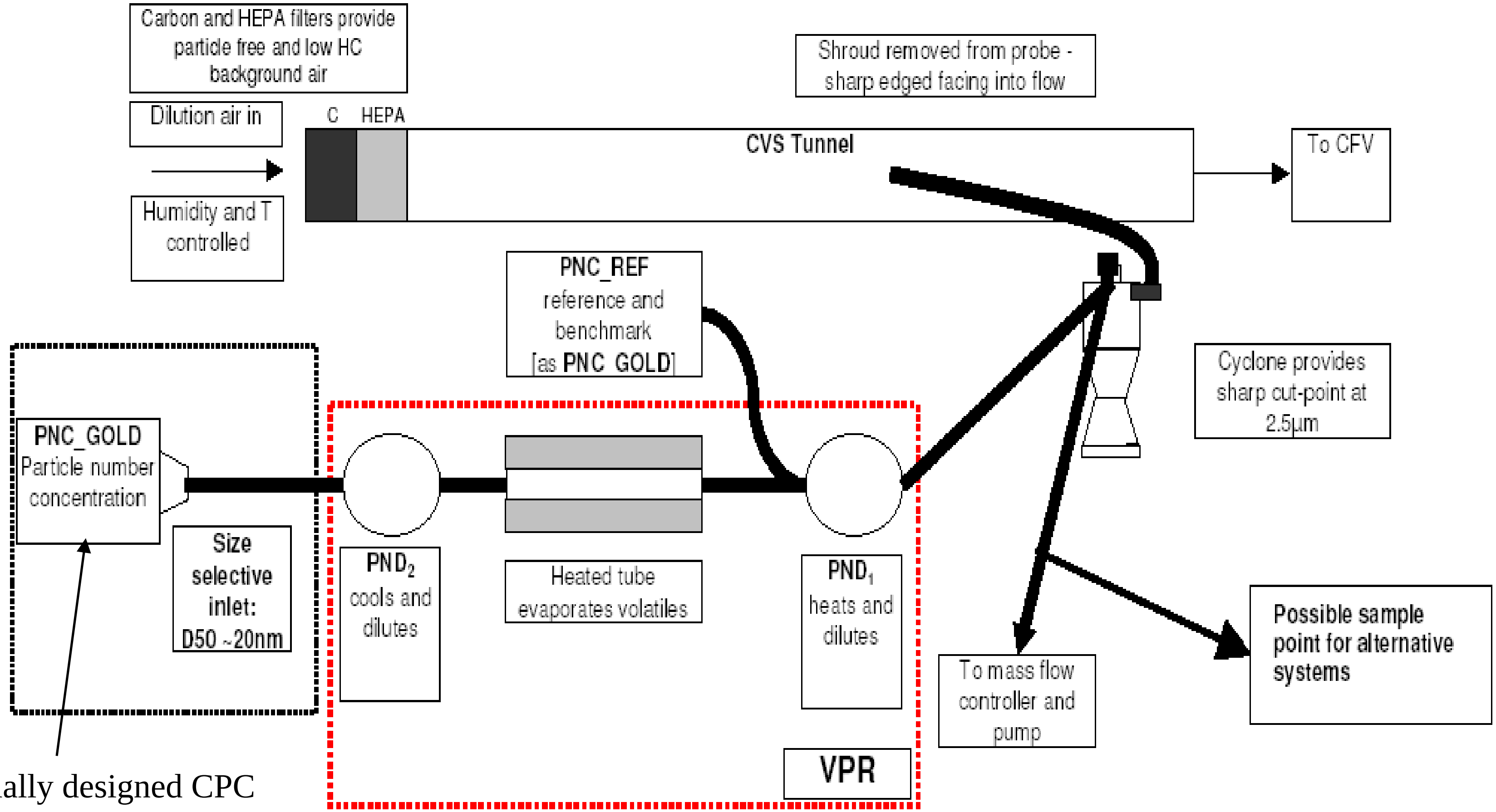




Oberdorster's work suggests best correlation of biological impact is with surface area

Oberdorster, G., Pulmonary effects of inhaled ultrafine particles, *Int. Arch. Occup. Environ. Health* **74**:1-8 (2001).

Proposed PMP number measurement system



A specially designed CPC with a lower size cutoff of 23 nm is used