How are emissions of nuclei mode particles affected by new PM control technologies and fuels?

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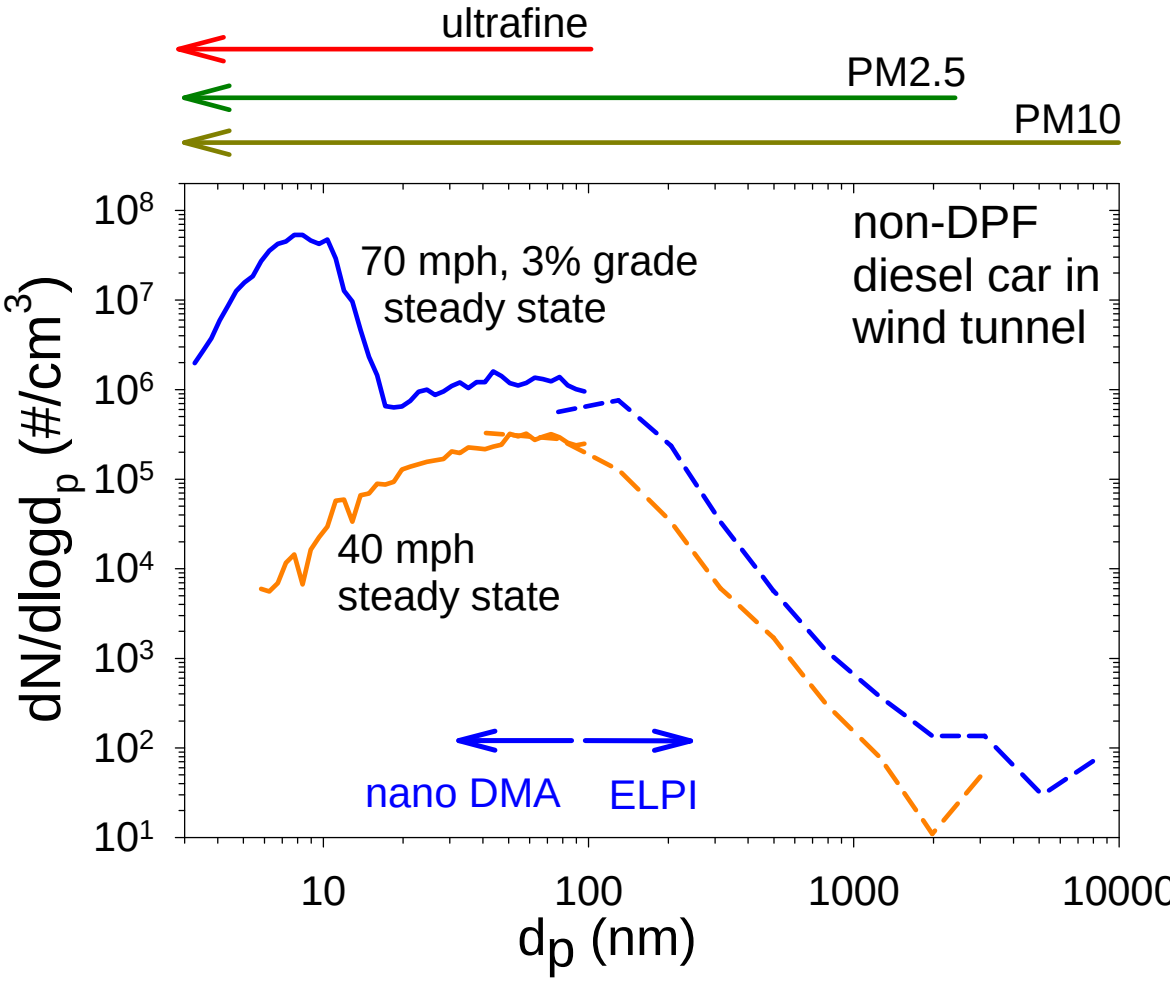
Outline

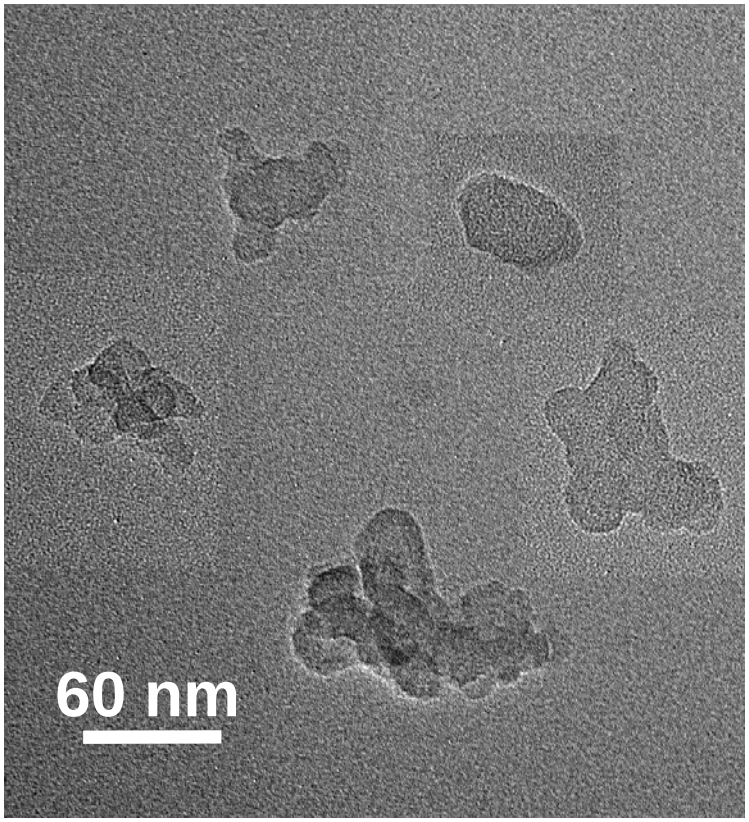
- What are diesel ultrafine particles?
- How do DPFs, DOCs, and fuel affect diesel PM?
- How do GDI PM emissions differ from conventional gasoline vehicles?
- What does particle number measurement mean in the PMP method?

What does “ultrafine” mean with respect to engine exhaust PM?

- **Definition**: ultrafine particle diam < 100 nm
- This occurs near peak of diesel “accumulation mode” (20-300 nm)
- Second type of diesel particle is “nucleation mode” (3 – 10 nm)
- Two modes generally have very different chemistry



What is the nature of diesel PM?

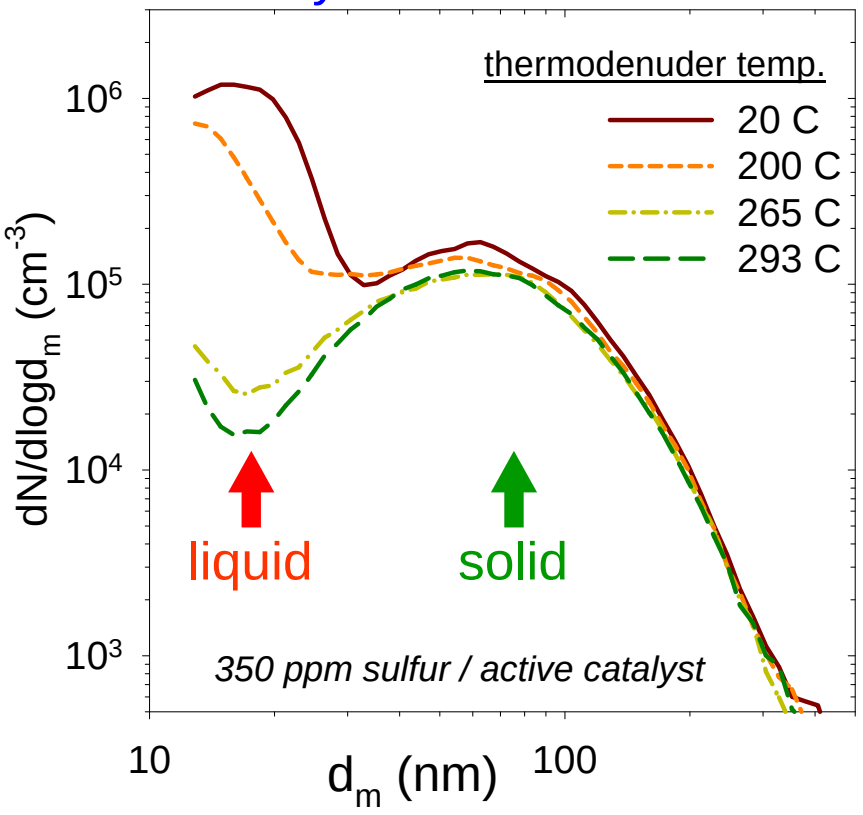


Accumulation mode particles at engine idle

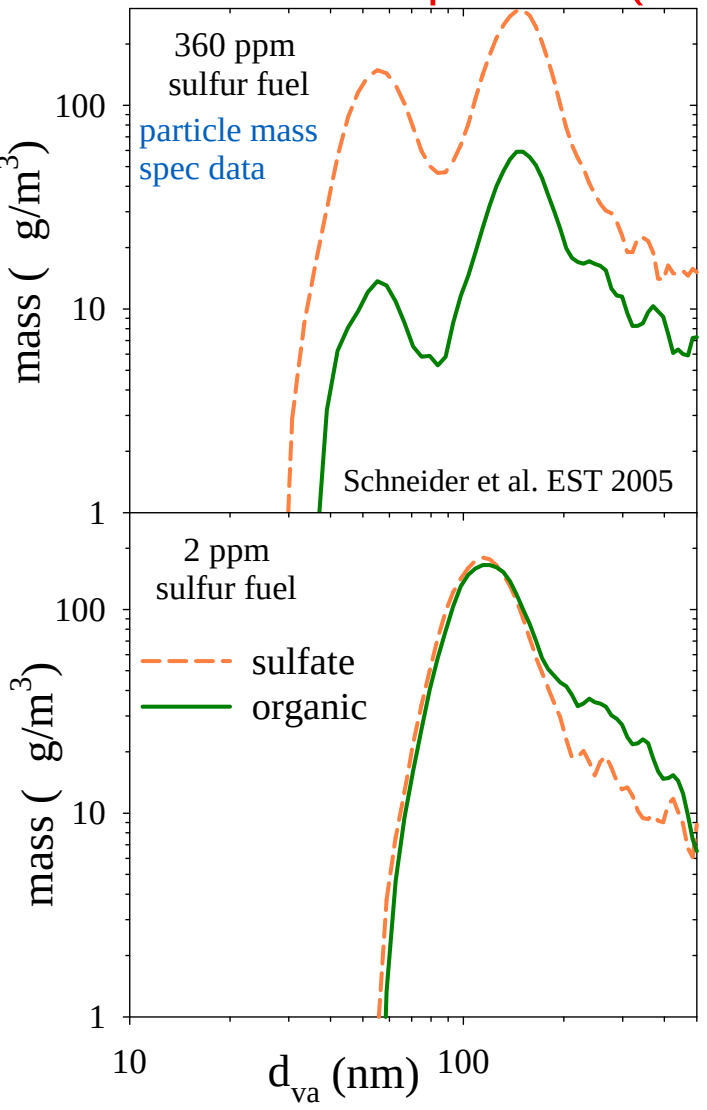
- Particles are size selected by DMA at 60 nm, near peak of “accumulation (soot)” mode
- Includes larger, multiply charged particle
- Range from spheroidal to aggregates

What is the nature of diesel PM?

Volatility size distributions

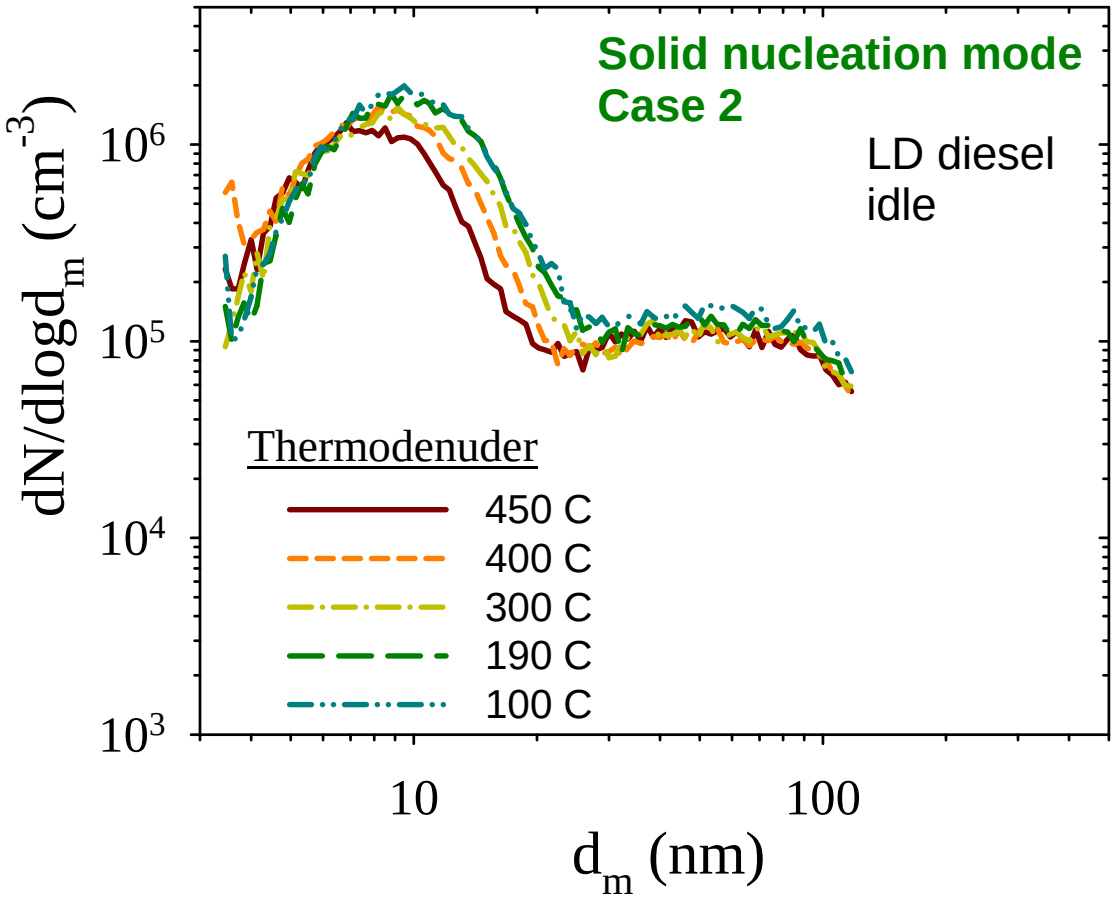


Semivolatile composition (LDV)



- nuclei mode is usually semivolatile and disappears upon heating
- Light duty diesel – high fraction sulfate
- Heavy duty diesel – mostly lube oil (likely from higher oil consumption)

Is nucleation mode always semivolatile?



Sometimes find particles not removed by heat → Solid

Also, they are electrically charged → formed in engine

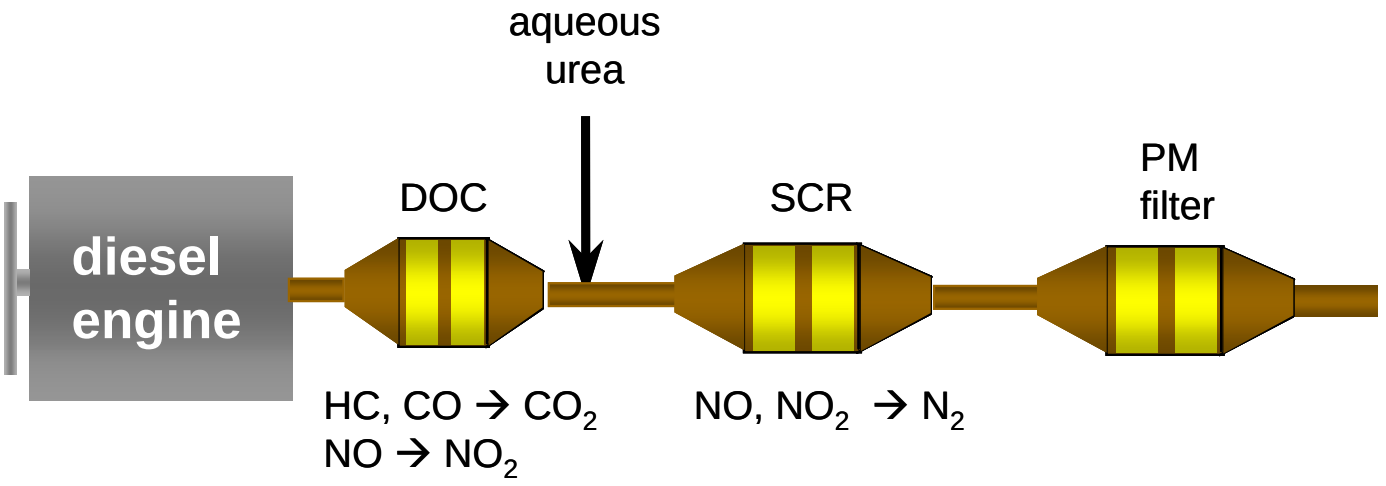
Main lessons

I. 100 nm is not a natural cutpoint for engine exhaust PM
II. But neither is PM2.5
III. 2 kinds of exhaust particles
    I. accumulation mode – solid (soot & ash formed in engine) coated with organics and sulfate, 20 – 300 nm
    II. nucleation mode – usually liquid mixture of sulfate and organic that form in atmosphere, but sometimes solid particles from engine, 3 – 30 nm

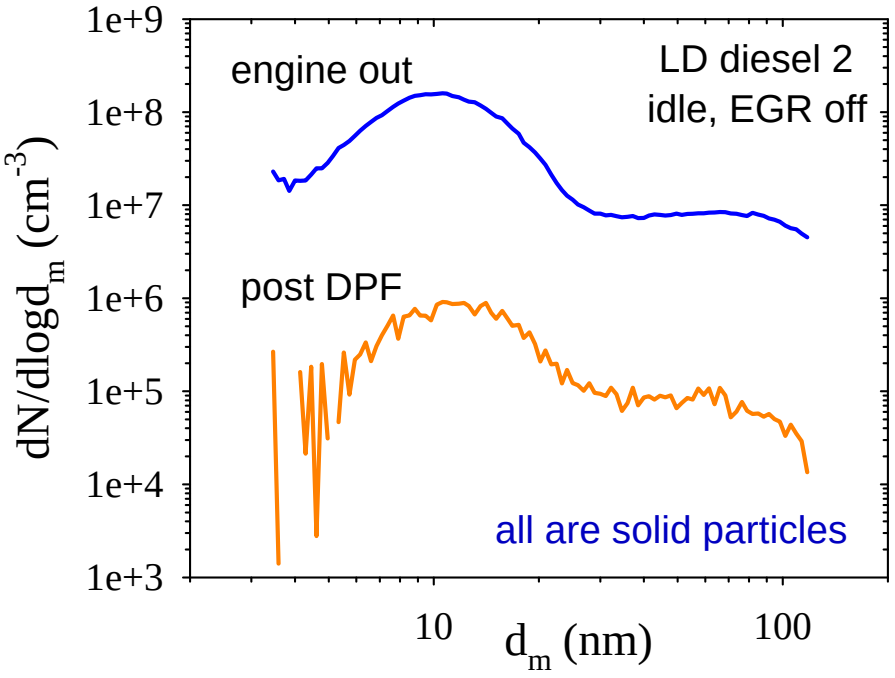
Complexity of exhaust aftertreatment

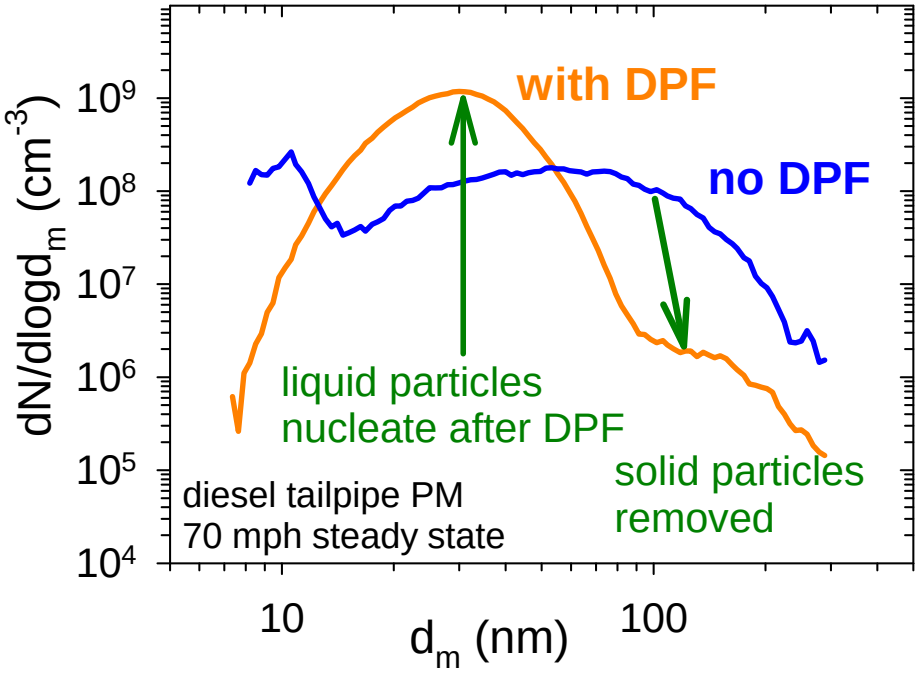
Four factors affect PM: 1) engine, 2) fuel, 3) DOC, and 4) DPF

- Fuel injection and EGR control PM – NOx tradeoff
- DPF traps soot (solid) particles
- DOC removes HCs that are precursors to nucleation. But it also oxidizes SO_2 to SO_3 leading to sulfate nucleation
- Low sulfur fuel lowers sulfate formation



What does diesel particulate filter (DPF) do to PM?



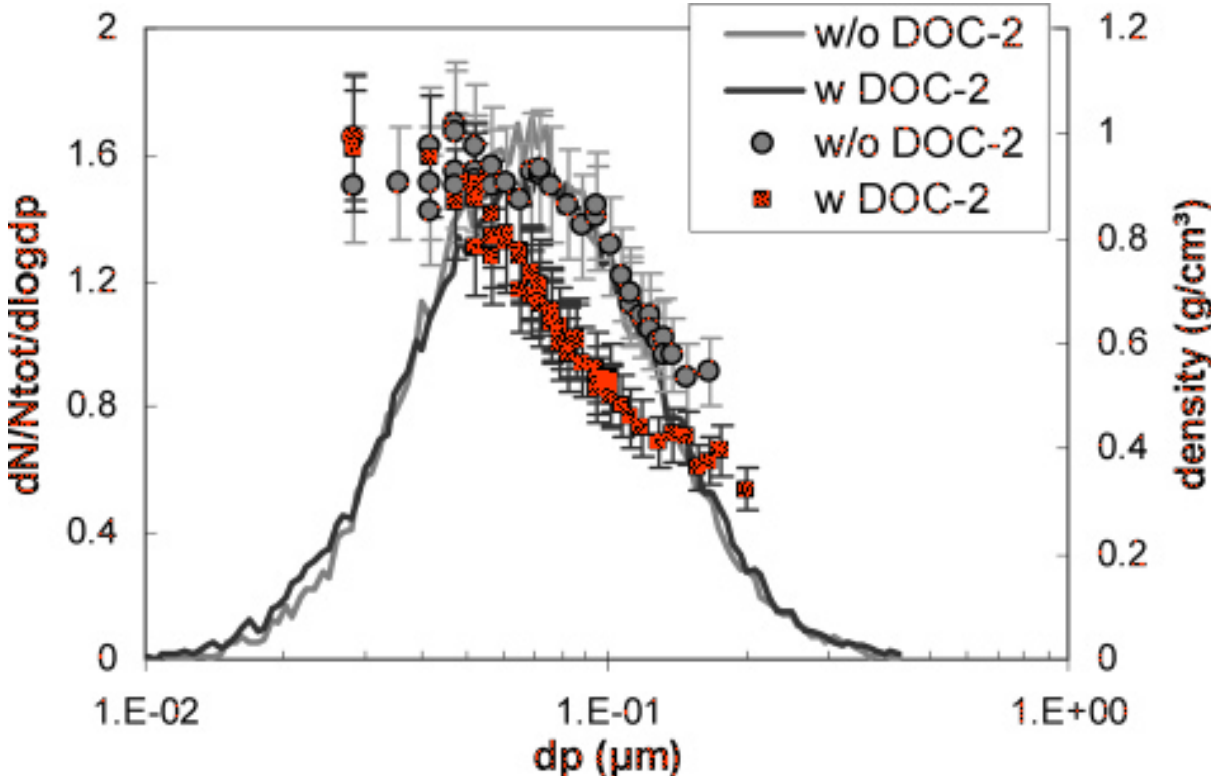


- DPFs can be >99% efficient by particle #
- Efficiency is nearly independent of particle size

- With high sulfur fuel (and lube oil) can form liquid nuclei particles after DPF
- Depends on many factors: dilution ratio, dilution rate, engine catalyst, humidity, …

What effect does the catalyst (DOC) have?

- DOC does not affect solid particles – they diffuse too slowly to reach catalyst surface
- DOC removes hydro-carbons – less condenses on particles, so their density decreases
- When DPF is present, DOC reduces nucleation from HCs, but can increase it from sulfate



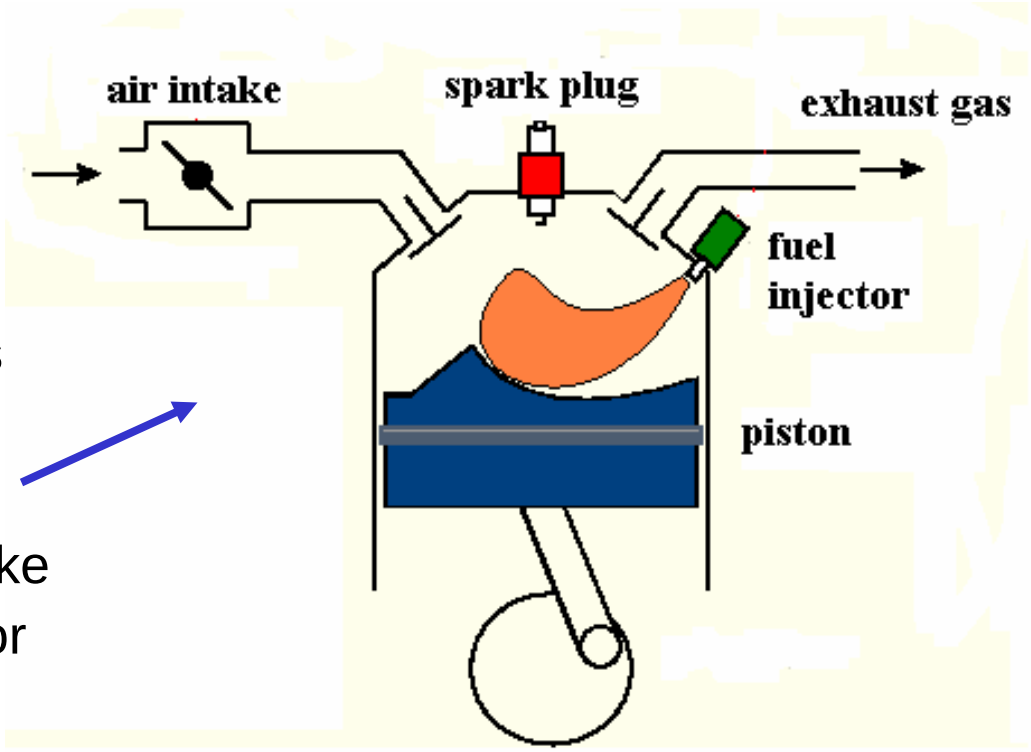
Vaaraslahti et al. EST 2006
Heavy duty diesel, very low sulfur fuel

Impact of diesel aftertreatment

I. Current wall-flow DPFs ~99% efficient from 3 – 500 nm solid particles
II. Oxidation catalyst reduces HCs
    I. Particle size not affected
    II. Density decreased – mass decreased
III. Effect of fuel sulfur
    I. Normal sulfur – DOC oxidizes to sulfate, exacerbates nucleation mode
    II. Low sulfur – less chance of nucleation mode, may occur at high load as stored sulfur is released from catalyst

How GDI differs from conventional gasoline engine

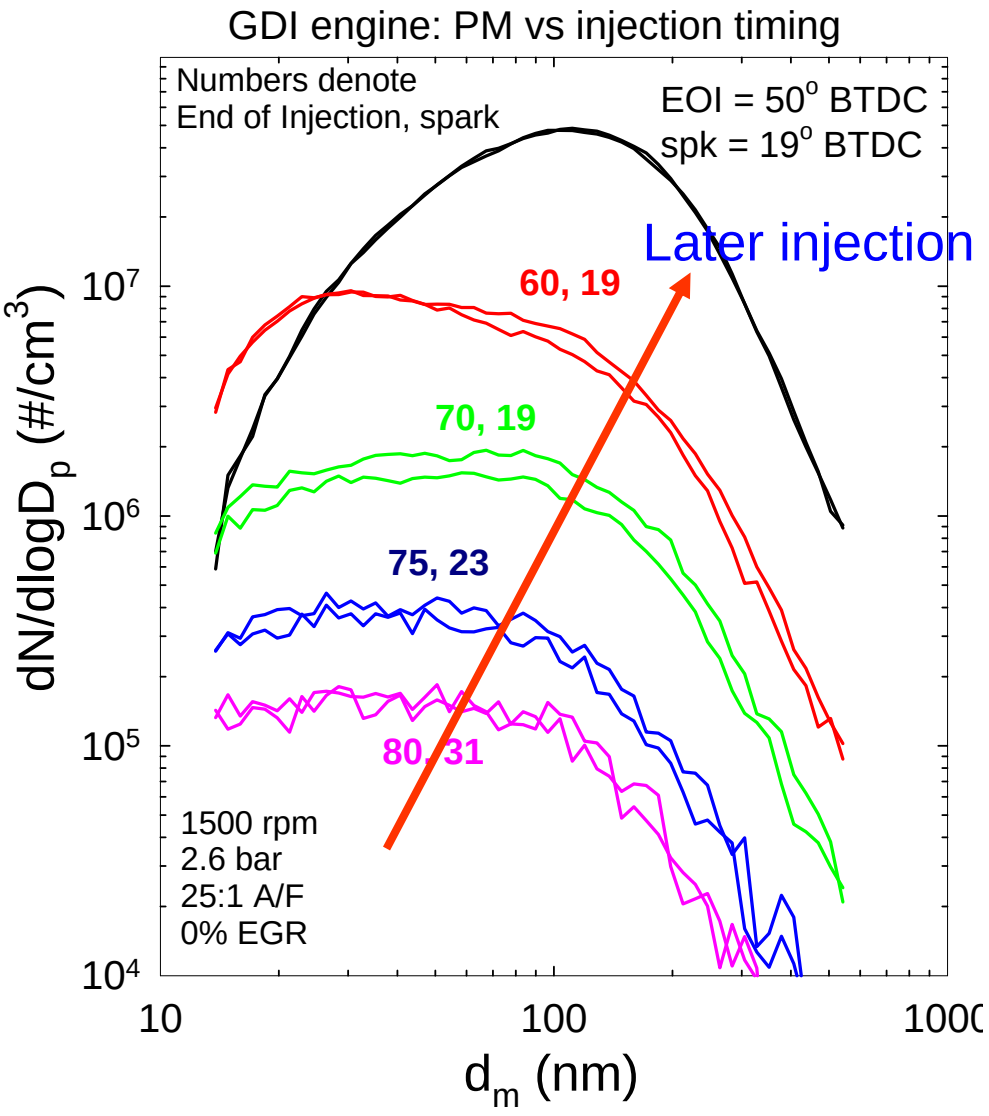
- Port fuel injection
  - Stoichiometric A/F mixture enters during intake stroke
  - Mixture compressed
  - Spark ignites homogeneous mixture
- Gasoline direct injection
  - Air enters during intake stroke
  - Fuel injected during intake or during compression
  - Spark ignites homogeneous or stratified mixture



Particle size from GDI engines

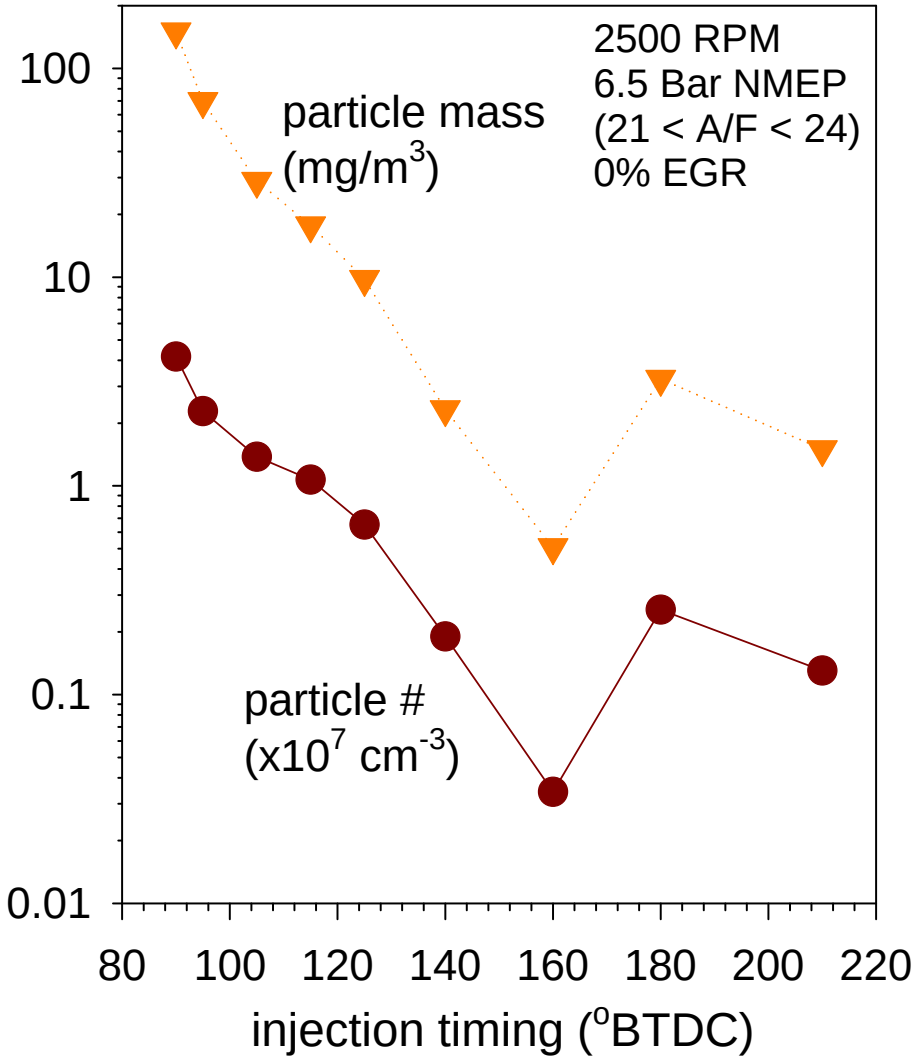
Two modes of operation

- Stratified
  - Late fuel injection
  - Lean operation
  - Lower pumping losses
  - Fuel impingement, lack of mixing → higher PM
- Homogeneous
  - Early fuel injection
  - Stoichiometric A/F
  - PM closer to conventional gasoline engine



How PM varies with GDI engine operation

- Particle number and mass both show increase with late fuel injection
- Mass emissions meet 2007 standards
- Number emissions are on borderline for upcoming EU particle number standard

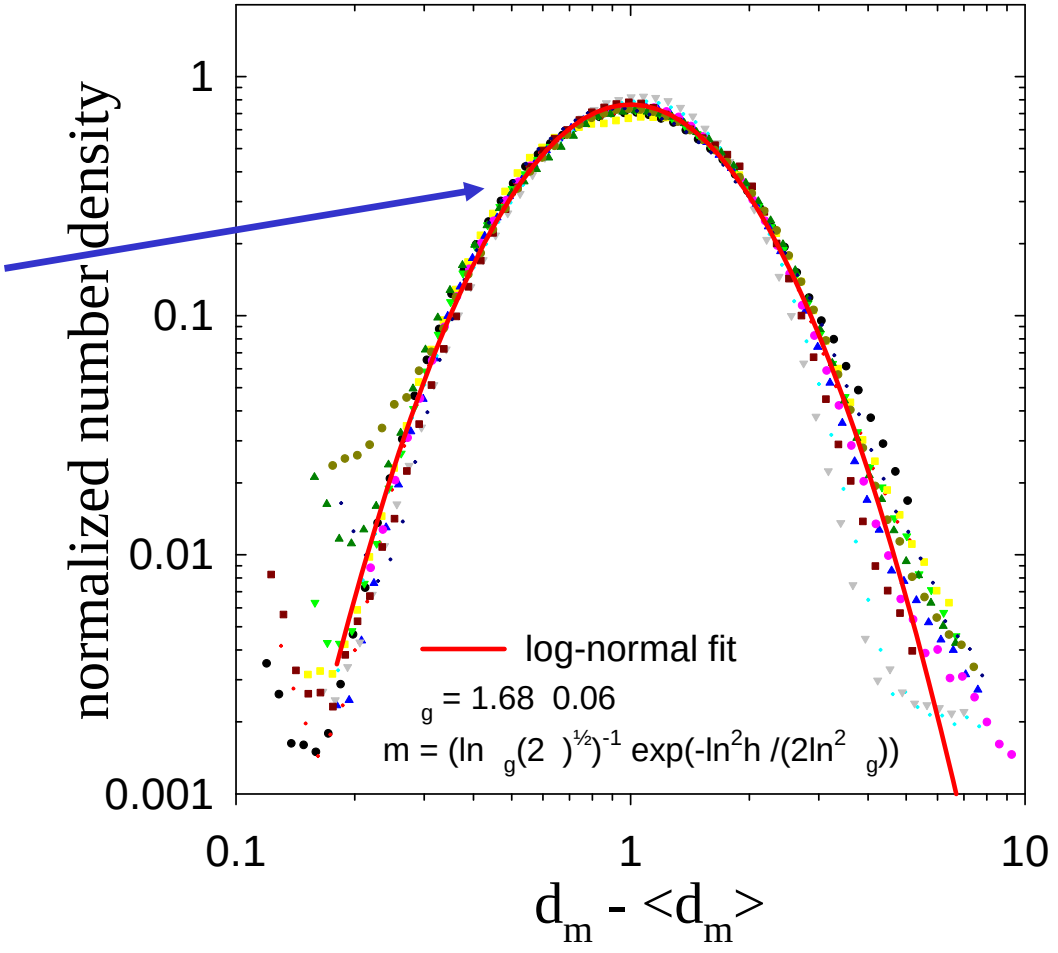


Impact of direct injection gasoline engines

I. Direct injection operates in two modes
   I. Stratified – more fuel economy benefit, higher emissions
   II. homogeneous – uses turbocharging to get fuel economy, emissions similar to conventional gasoline engines

Relationship between PM mass and solid particle number

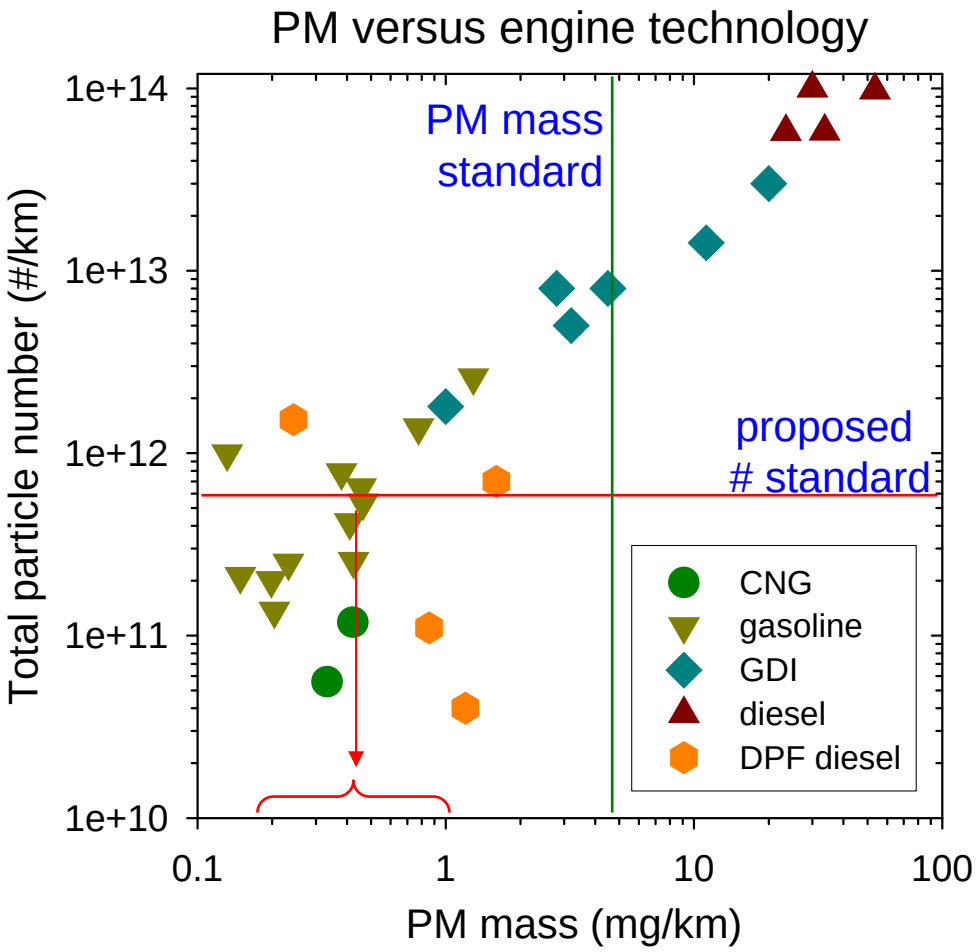
- PMP method removes nuclei particles
- Remaining solid particles follow lognormal distribution with 2 free parameters
  - Number
  - Mean diameter
- Mean diameter between ~40 – 80 nm
- To fulfill number standard of 5×10^{11} #/km → PM mass must be < 1 mg/km



$$\text{Mass} = \mathbf{N}\ \pi/6\ \rho_0\ d_0^{(3-df)}\ \mu_g^{df}\ \exp(df^2\ (\ln\sigma_g)^2/2)$$

PM mass versus solid number

Are these independent measures of particle emissions?



- This comparison is for modern light duty vehicles, relatively independent of drive cycle
- These tend to have no, or small, nucleation modes
- Tests are done in laboratory – may not reflect ambient PM release, where more extensive nucleation may sometimes occur
- Also observed by Ricardo

PMP number method versus PM mass

I. PMP number method counts solid particles >23 nm diameter & < 2500 nm
II. Nature of diesel PM size distribution → solid number and mass are correlated
III. Number count method is arguably as reproducible as PM mass
IV. Has sensitivity and lack of artifact advantage
V. PMP measures soot, but in different way than the mass method
VI. Measuring total PM number is different because it would include the nucleation mode (and very difficult)