Defining ultrafine particles, let's agree on what they are, a discussion

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MOVING TARGETS IN NANOPARTICLE ABATEMENT
VERT Forum 24 March 2022

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Acknowledgement

- This presentation is largely based on our recent paper

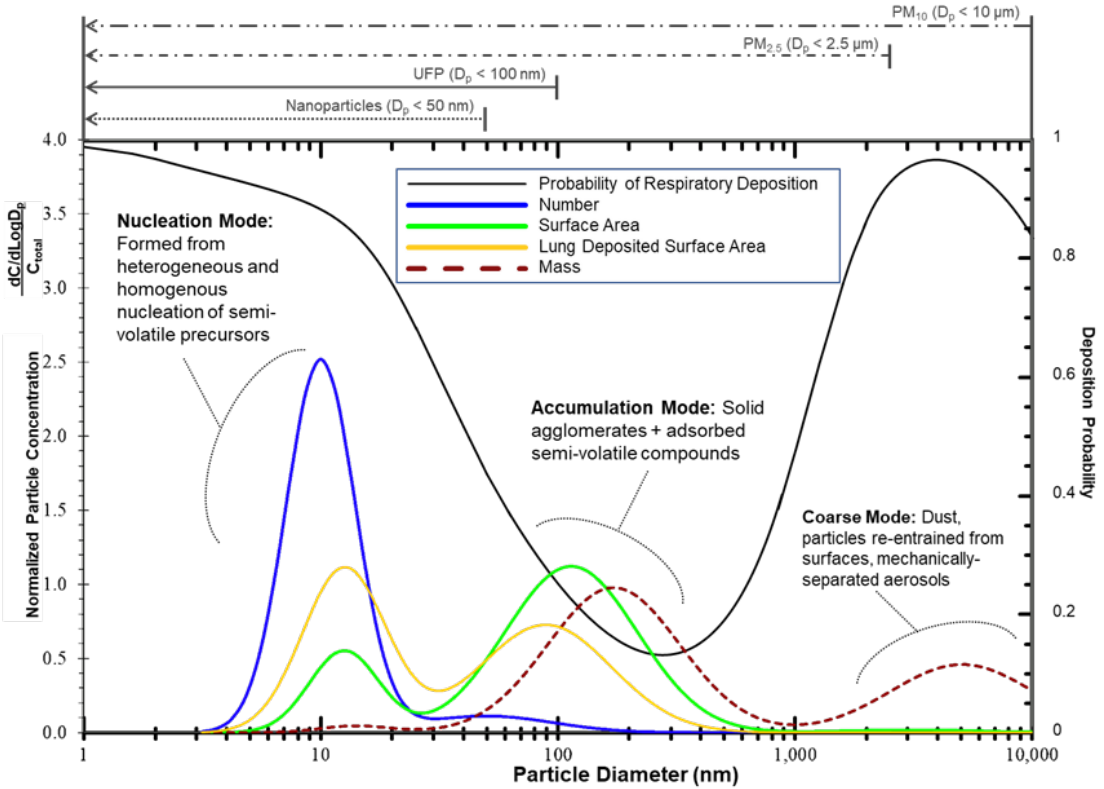
  - Kittelson, D., Khalek, I., McDonald, J, Stevens, J., and Giannelli, R. (2022). Particle emissions from mobile sources: Discussion of ultrafine particle emissions and definition, Journal of Aerosol Science, Volume 159, 105881, ISSN 0021-8502, https://doi.org/10.1016/j.jaerosci.2021.105881.

- I want to thank my co-authors for all the hard work put into this paper.
- This work was supported by USEPA but does not reflect their official position

Current UFP measurement approaches

- PM2.5 and UFP epidemiological impacts at present are indistinguishable.
- UFP are ill-defined in the literature, typically number based and do not capture the surface area and mass metrics.
- Common metrics
  - Number below 100 nm, sometimes total particle number. Lower cut point, 10 nm, 3 nm, …?
  - Mass with an upper aerodynamic diameter cut point, no agreement on cut point 100 nm, 200 nm, , 300 nm, etc. ?
  - Surface area or lung deposited surface area (LDSA), surface area weighted on lung deposition fraction.
- Sometimes these metrics are well correlated, sometimes not.

Traditional size boundaries

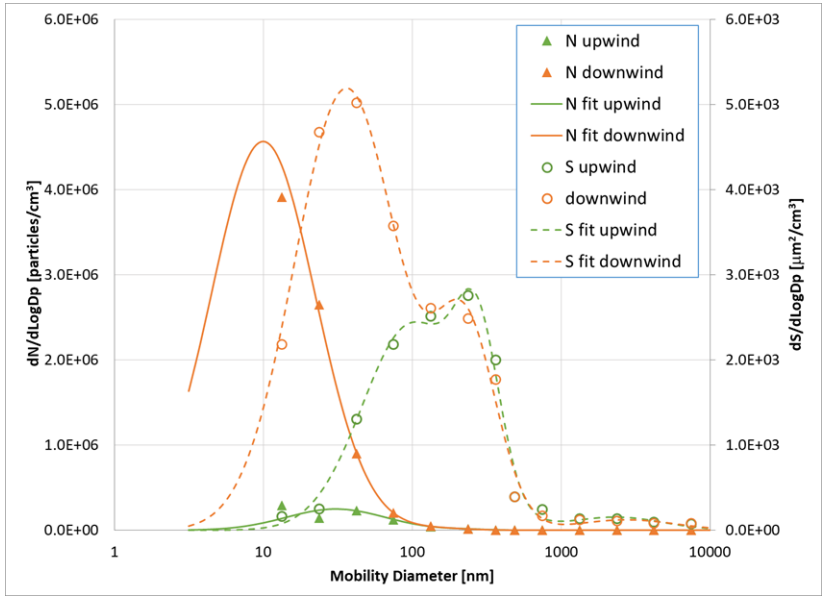


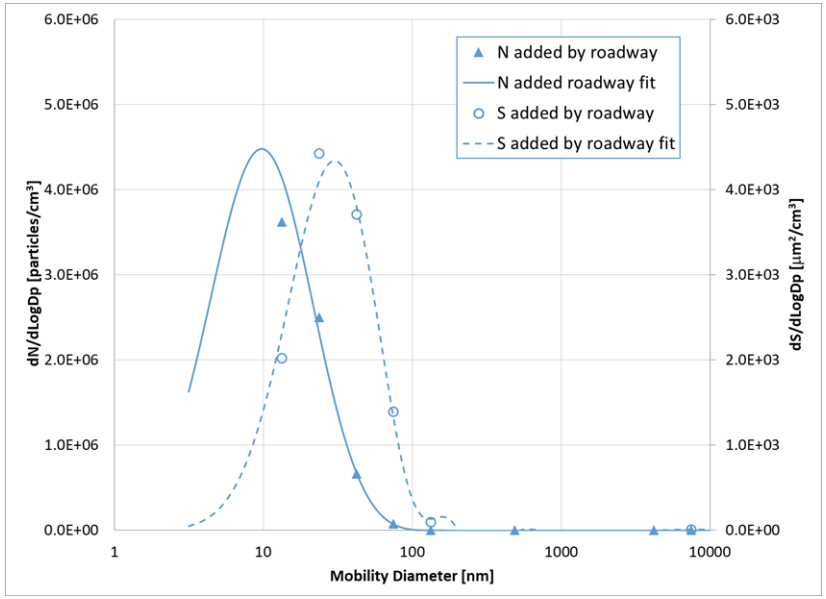
- PM10 and PM2.5 are unambiguous regulatory definitions based on particle mass and aerodynamic classification
- Ultrafine particles typically are defined as particles smaller than 100 nm
  - Based on number, surface, or mass, or all?
  - Classification by aerodynamic or mobility diameter?
- Nanoparticles typically are defined as particles smaller than 50 nm, but sometimes 10 or 100 nm
  - Based on number, surface, or mass, or all?
  - Classification by aerodynamic or mobility diameter?

New metrics for UFP

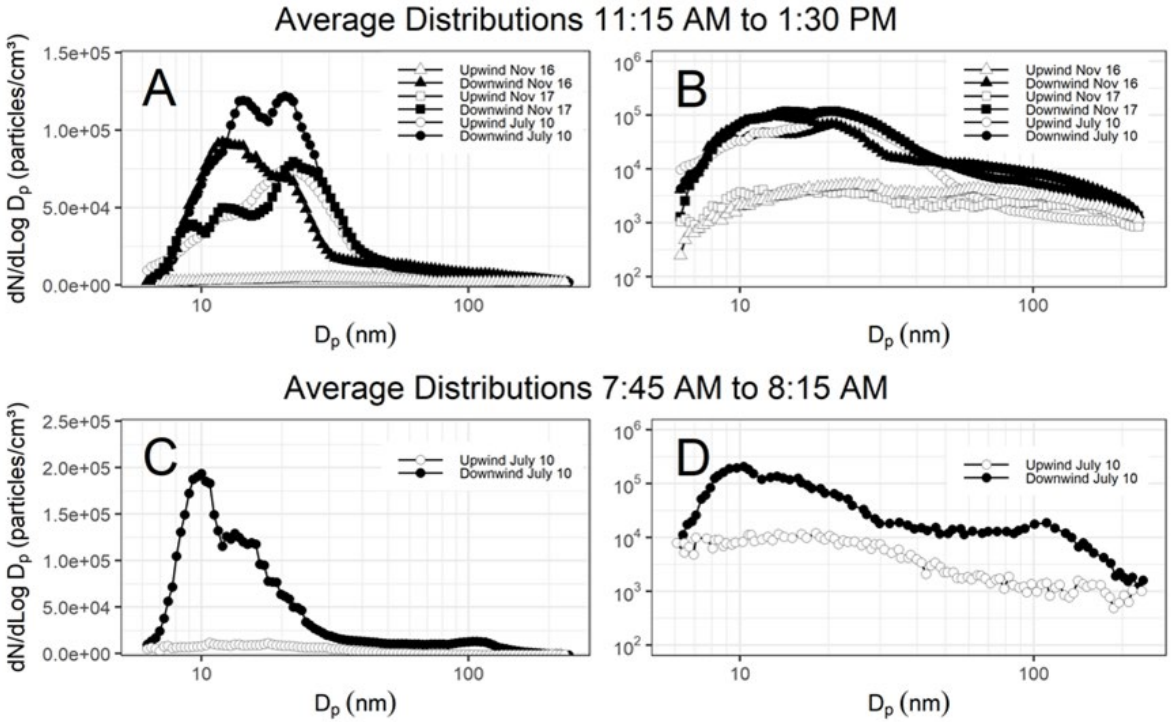
- We suggest three exposure metrics: UFP-N, UFP-M, and UFP-S, total number, mass, and surface area below 500 nm, respectively.
- Highest human exposure to Ultrafine particles (UFP) is on-road and near-road.
- The characteristics of on-road and near-road tailpipe emissions have guided the formulation of these new metrics
  - As tailpipe emissions have decreased the relative importance of particles from brake and tire wear has increased.
  - These particles cover a wide size range and consist of both larger particles (PM2.5, PM10) and UFP

Particle size distributions measured upwind and downwind of an CA freeway (adapted from Whitby et al., 1975).



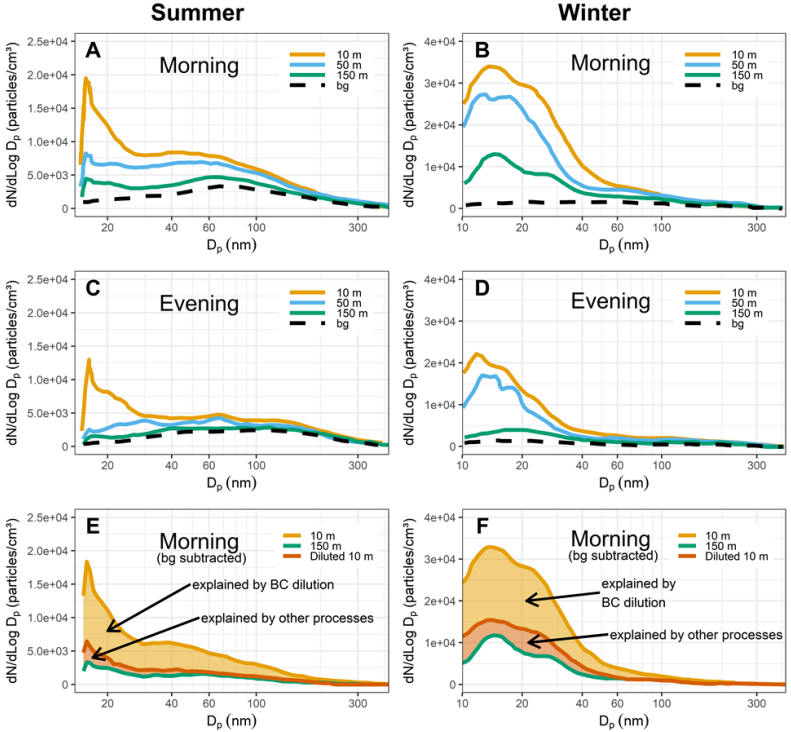


Roadside size distributions CA freeway, 2004



Adapted from Nanzetta and Holmén (2004).

Roadside and downwind size distributions , 2018, same structure



(a–d) Average particle number size distributions at different distances from the roadway edge. Downwind measurements are not background-subtracted.

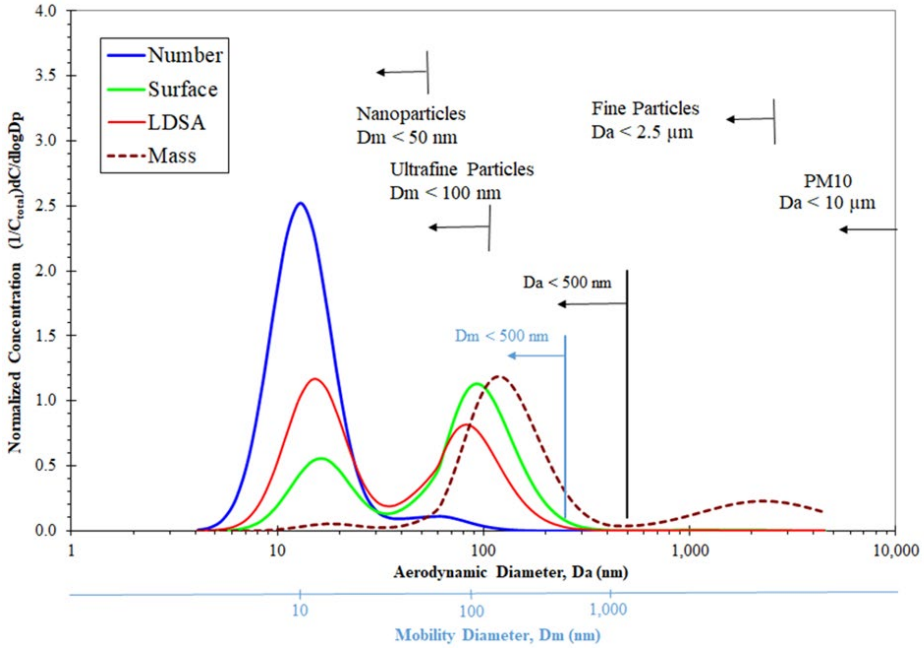
(e–f) Background-subtracted average particle number size distributions at 10m (red) and 150m (purple) downwind distances.

Figure adapted from (Saha et al., 2018)

Compare with previous slides
Falling dN/dLogDp, rough measure
1975 4.5 x 10^6
2004 2 x 10^5
2018 3.5 x 10^4
But modal structure remains

New measures for ultrafine particles?

- For discussion we suggest 3 new metrics: N500, M500, and S500
- These metrics represent total number, mass, and surface area below 500 nm, respectively. Aerodynamic of mobility based depending on instrument
- Captures all metrics, N, S, m
- N500 very similar to current UFP but lower cut point should be clearly stated and in the 3 to 6 nm range depending on instrument
- These new metrics
  - Intended for characterization of ambient exposures
  - Not necessarily intended to be used for regulatory tailpipe measurements



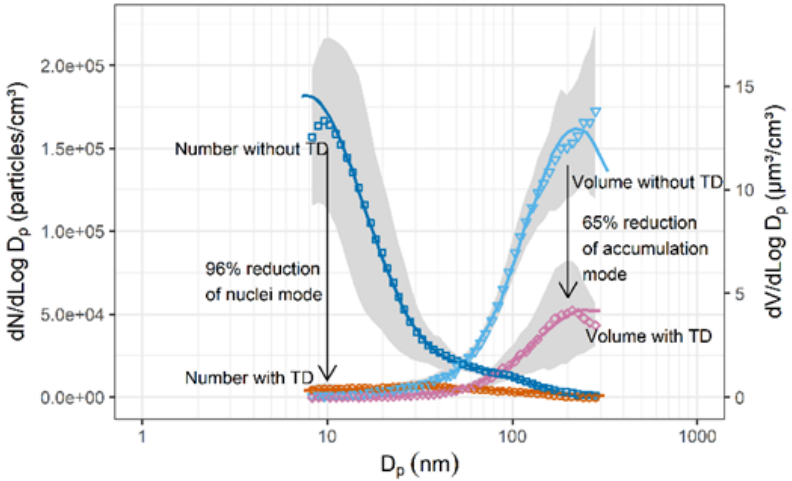
Measurement recommendations – on-road, near-road, neighborhood

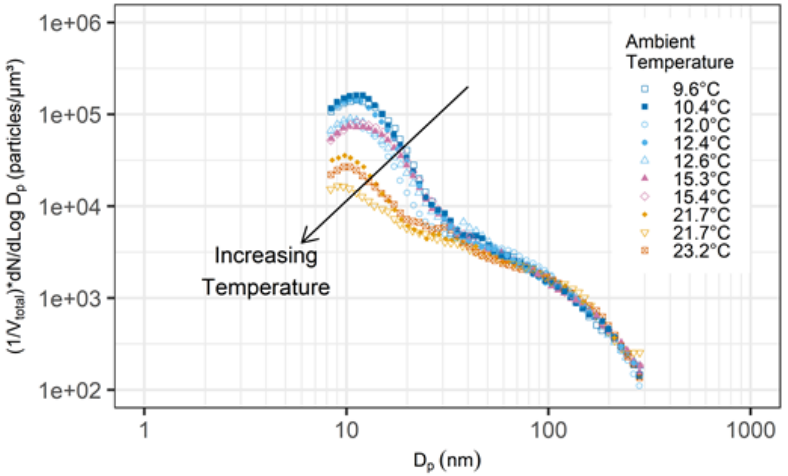
- Need wide deployment of instruments
  - For association immediate health effects, hospital emissions, asthma, etc.
  - For association with epidemiological studies
- Size distribution measurement preferred to capture all metrics
  - DMS500, FMPS, SMPS, ELPI, etc.
  - New lower cost sizers
  - Likely still too expensive for wide deployment
- Single metrics, usually lower cost
  - Number – CPC, diffusion charger
  - Surface or LDSA – diffusion charger
  - Mass
    - Instruments like Dekati mass monitor for real time
    - Filter mass M500 like current PM2.5 method with 500 nm instead of 2.5 μm cut size

Sampling and dilution

- The EU has developed a robust and effective method for **regulatory measurements** of non-volatile particle number
  - By design it **excludes** semi-volatile particles
  - It is not intended to simulate on-road and near-road aerosols
- On-road and near-road aerosols – that we breathe – consist of both solid and semi-volatile components
  - Formation of semi-volatile particles is very sensitive to dilution and sampling conditions
  - No laboratory sampling and dilution system can simulate all real-world dilution conditions – **but** it might predict the potential of an engine/vehicle to form semi-volatile particles

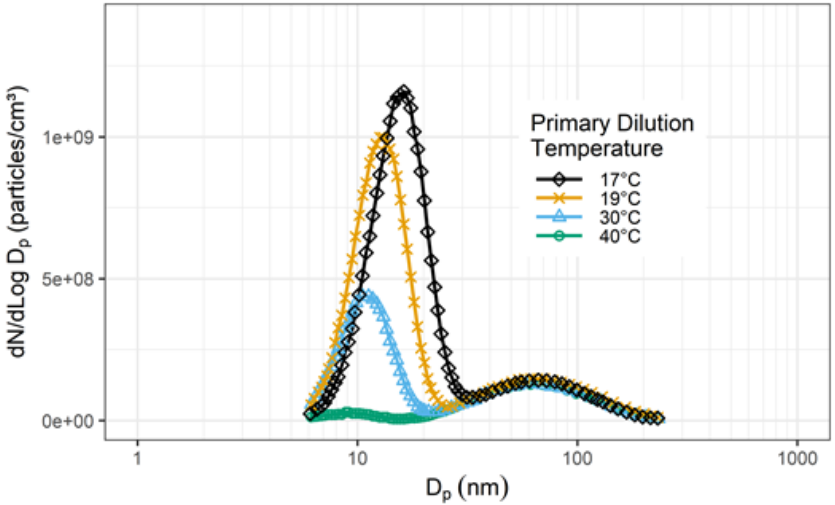
On-road size distributions, 2004, lots of semi-volatile material



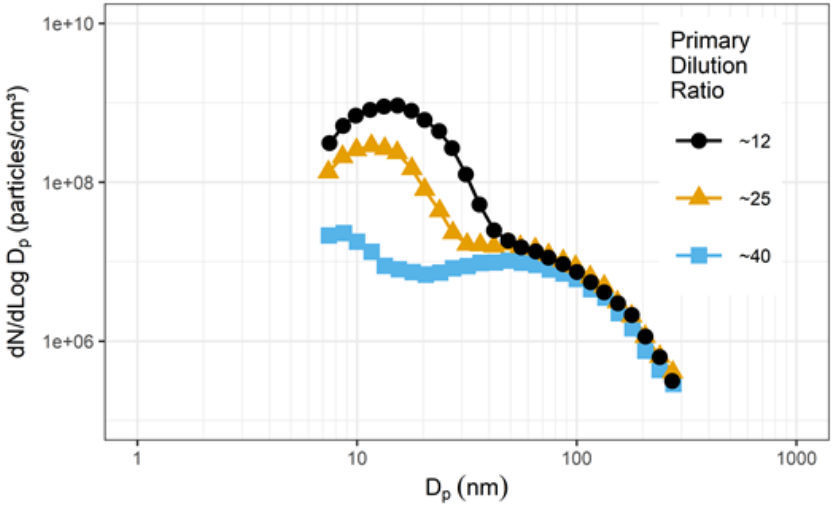


Based on 60 hours of on-road measurements in truck convoys rural NY freeway. Adapted from Kittelson et al. (2004).

Lab measurements, semi-volatile nucleation mode particles very sensitive to dilution conditions

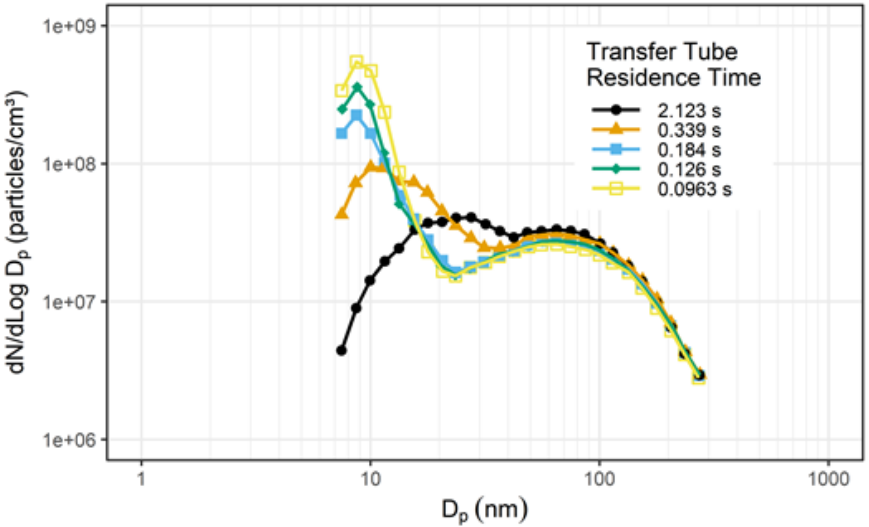


Influence of primary dilution temperature (PDT) on nanoparticle formation. Adapted with permission (Mathis et al., 2004).

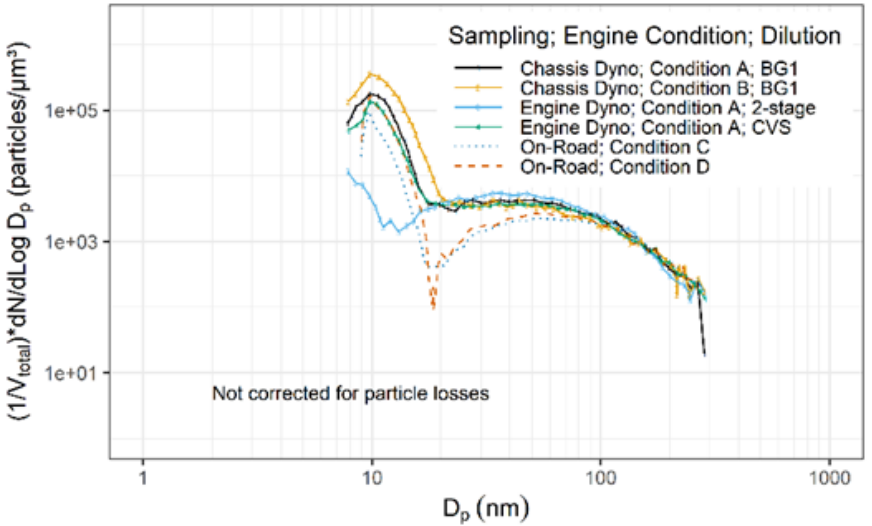


The effect of primary dilution ratio (PDR) on nanoparticle formation. Adapted with permission (Khalek et al., 1999).

Sample lines, even heated, lead to loss of semi-volatile nucleation mode precursors



The effect of Sample Transfer Tube Residence Time on Nanoparticle Emissions for uncatalyzed diesel exhaust. Adapted with permission (Wei et al., 2001).



Influence of dilution system design on nucleation mode formation. Engine dyno + 2 stage suppressed nucleation mode formation. Very similar to that used by Khalek et al., 1999 (previous slide) **except for transfer tube length 70 cm vs 20 cm.** Adapted with permission (Kittelson, et al. 2002)

Possible Non-regulatory sampling and dilution – for semi-volatile

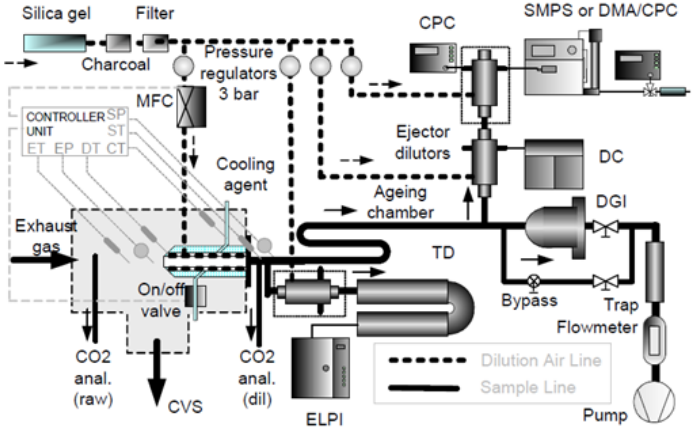


Figure 3: Sampling system used for characterization of exhaust aerosol.

Samaras, et al. (2005), Characterisation of Exhaust Particulate Emissions from Road Vehicles

- European "Particulates" Project developed a unique dilution system designed for optimized sampling of semi-volatile particles
- Features
  - Partial flow
  - No transfer line from exhaust to primary dilution
  - Porous wall dilution
  - Aging chamber
  - Designed for near ambient temperature dilution – simulating ambient dilution
- **Commercial systems with similar features available today**

Non-regulatory sampling and dilution – for semi-volatile particles

- Partial flow sampling
- Porous tube dilution
- Short heated exhaust transfer line, 350° C, residence time < 100 ms
- Primary dilution ratio of 12, secondary dilution as necessary
- Dilution air temperature of 25° C
- Aging chamber residence time 2 s
- Dry, < 5% RH dilution air (water in diluted exhaust sufficient)
- ***We do not recommend the use of heated dilution, either primary or secondary, it suppresses the formation of semi-volatile particles***

Alternative approach for prediction of potential to form semi-volatile particles

- Measure semi-volatile precursors, e.g., sulfuric acid, heavy HC, organic acids
- Possible long-term solution but more research needed
  - Which precursors?
  - Influence of solid particles
    - Homogenous vs heterogeneous nucleation
    - Gas-particle phase partitioning among modes

Summary

We propose ***for discussion***

- Three new metrics for UFP, N500, S500 (or LDSA), and M500
- A method for tailpipe sampling total UFP including semi-volatile particles
- Possible development methods to predict formation semi-volatile based on precursor measurement

Thank you for listening
Questions?
Suggestions?

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