Brake-wear PN

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- Our experience with brake-wear PN measurements.

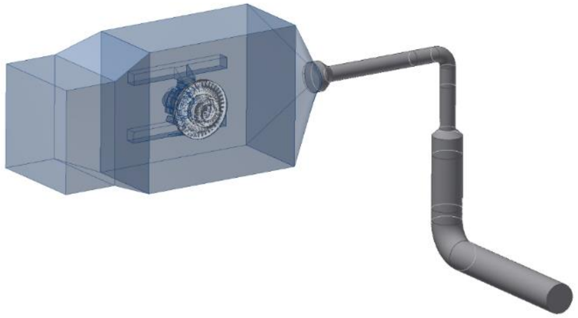
- Nature of volatile PN and nucleation theory.

- Simulations to assess relevance of:
  - Classifiers
  - Transport loss mechanisms

- Calibration

- Recommendations

Brake-wear particle odyssey



tunnel

nozzle

probe

tubing

Cyclone

Transport & extraction

Pre-classifier

Dilution (Treatment)

Detection

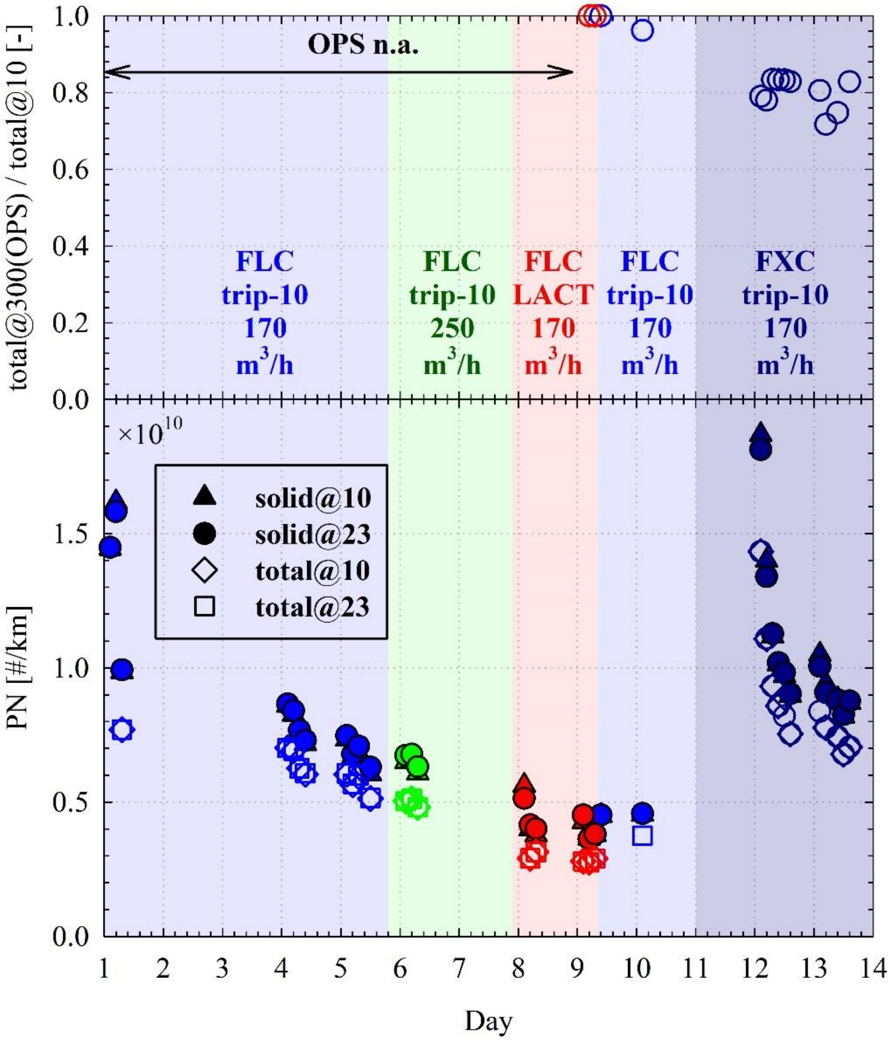
Setup employed by AVL for BW-PN measurements

- Our focus in recent research activities thus far was based on provisional recommendations of TF2:
  - Solid PN as described in GTR15 regulation (APC xApp):
    - Full flow CPC with cut-off size at 10 nm → augmented with a full flow CPC at 23 nm in selected tests
    - Primary dilution of >10:1 at 150°C. A 10:1 dilution was always sufficient
    - Catalytic Stripper at 350°C
    - Secondary diluter at 10:1 at ambient temperature.
    - Calibration of Particle Concentration Reduction Factors at 15, 30, 50 and 100 nm and use of the average at 30, 50 and 100 nm as representative for particle losses.
    - CPCs calibrated in a ISO27891-accredited laboratory using emery oil.
  - Untreated PN by means of directly sampling from CVS using a full flow CPC at 10 or 23 nm:
    - CPCs calibrated in a ISO27891-accredited laboratory using emery oil.
    - No dilution or ejector diluter, depending on concentrations.

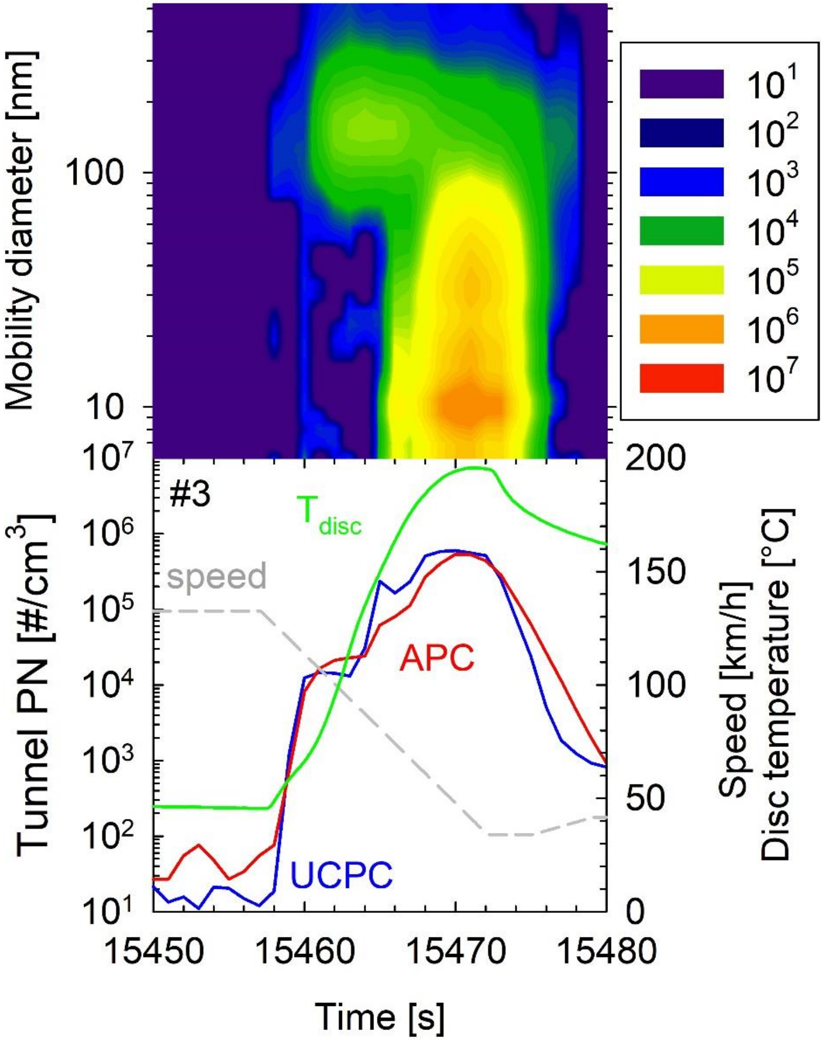
Nature of brake-wear PN – our experience

- In most of our experimental campaigns following the WLTP procedure, we observed no difference between SPN and untreated samples, as well as no difference between 23 and 10 nm CPCs.

- However, in our latest joint campaign with BMW we observed a distinct nucleation mode when braking from top cruising speed that was detected both with GTR15 method and a CPC sampling directly from tunnel → thermally stable nucleation mode. This release lasted ~20 s but led to ~1 order of magnitude increase in PN over the cycle.



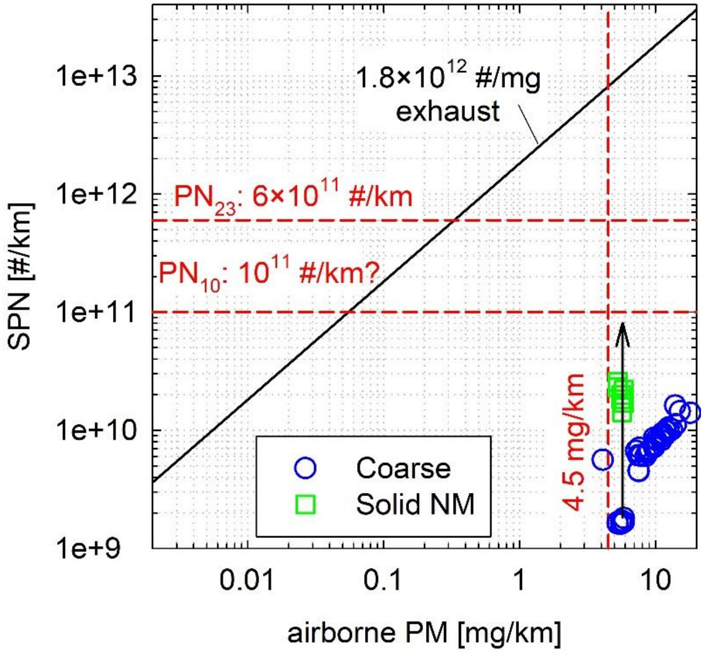
Mamakos et al.2019
Mamakos et al. 2020

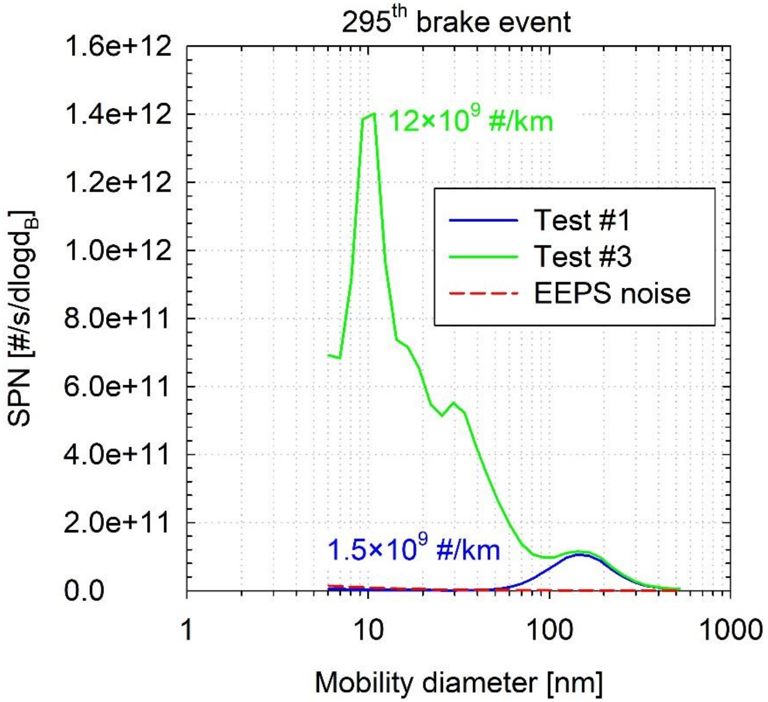


Mamakos et al. 2021

PN levels and distributions

- The coarse mode (CM) of brake-wear particles dominate the PM emissions, as reflected in the much smaller PN/PM ratios compared to exhaust (Vogt et al. 14th, 2010).
- When solid nucleation mode (NM) is present, it can increase PN emissions by more than an order of magnitude.
- Brake-wear PN becomes relevant in the presence of NM (solid or volatile) → PN instrumentation performance at NM size (~10 nm) is most critical.





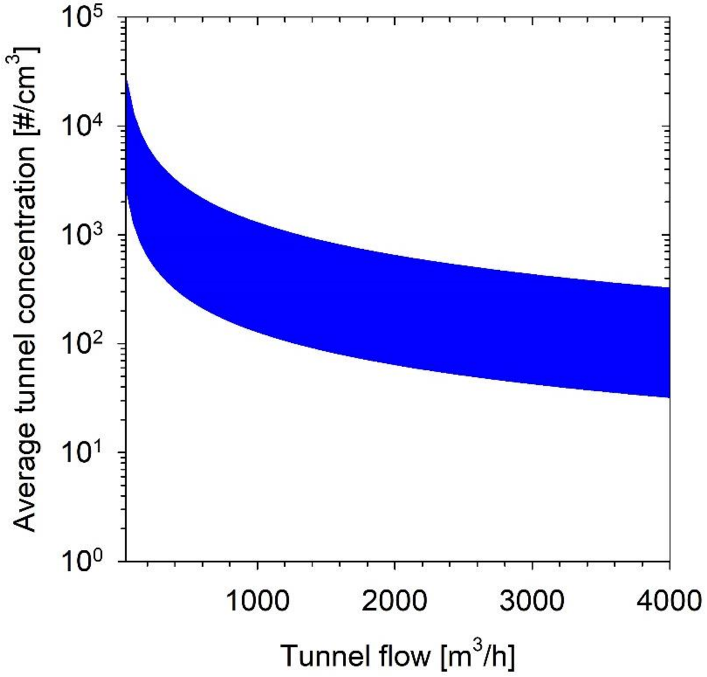
Tunnel concentrations: average and background levels

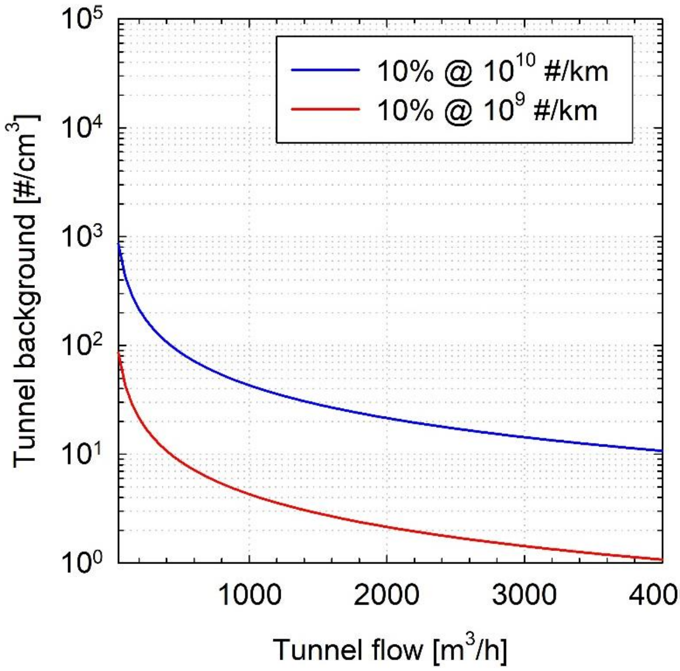
- Average PN concentrations in the tunnel depend on the operating flow. We extrapolated the range of average concentrations we measured in various campaigns over the reported ranges of tunnel flows.

- At these levels, background can be important but eventually background contributions should be considered in relation to the emission levels. We accordingly, calculated the background levels that would lead to 10% contribution at emission levels 1 and 2 orders of magnitude below the proposed Euro 7 exhaust level (10^{11} #/km).

➔ Given that the contribution of the same background levels strongly depends on tunnel flow, we recommend that a threshold is set in #/km units derived as:

$$PN_{bck} = \frac{PN_{bck}\left[\frac{\#}{m^3}\right] Q_{tunnel}\left[\frac{m^3}{s}\right]}{12.14\left[\frac{m}{s}\right]} < 10^9 \left[\frac{\#}{km}\right]$$





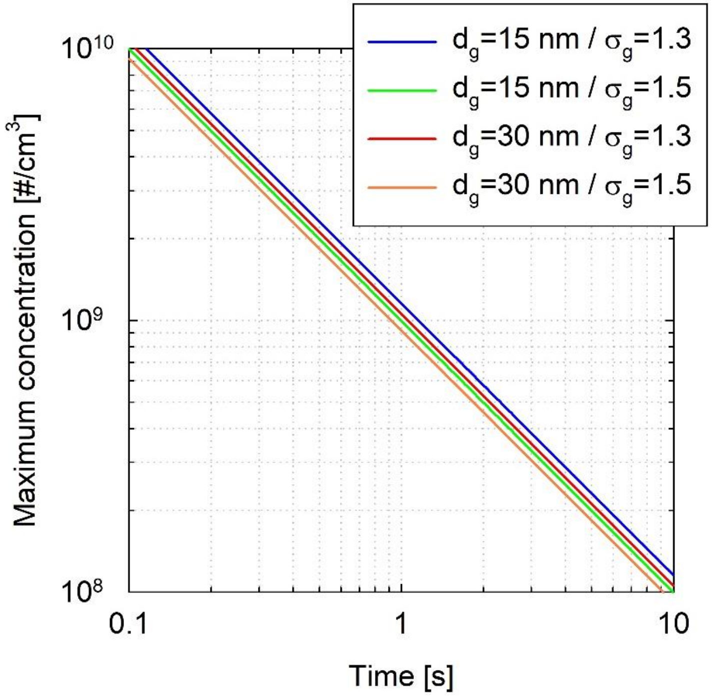
Tunnel concentrations: dilution requirements

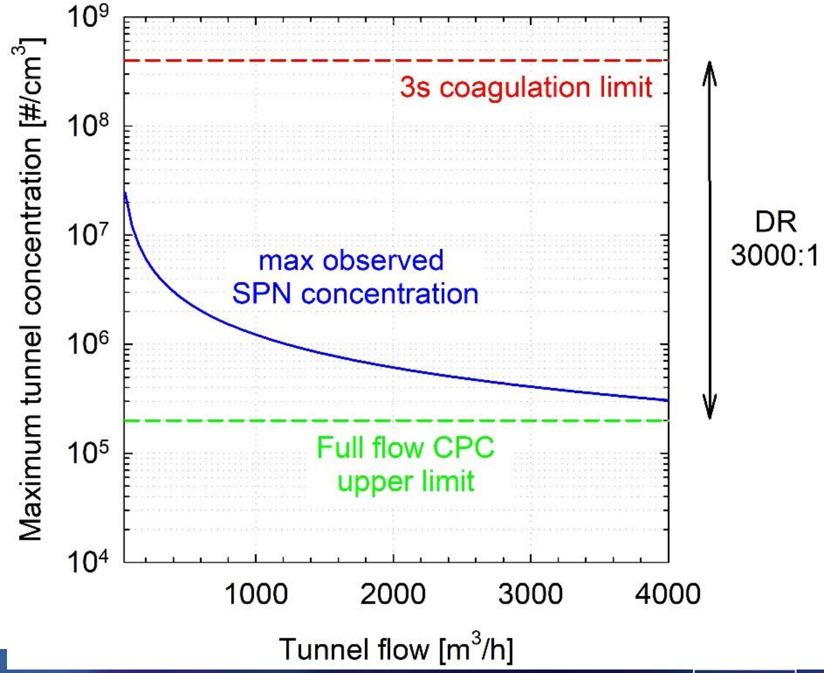
- The maximum SPN concentration we observed was ~10^6 #/cm^3 at a tunnel flow of 1200 m^3/h, following braking from top cruising speed over the WLTP-Brake. However, the upper number concentration limit, especially if total PN is to be considered, is only dictated by the coagulation limits.

- Particle number is not a conservative property, so maximum concentration will depend on residence time. Assuming a 3 s maximum residence time until any additional dilution one would expect potential concentration levels up to ~3×10^8 #/cm^3.

- Full flow CPCs measure in single count mode up to 5×10^4 #/cm^3 with a potential extension to 2×10^5 #/cm^3. This would imply a requirement for a dilution capable of reaching 3000:1. Even for SPN a dilution of 100:1 will be required for low tunnel flows.

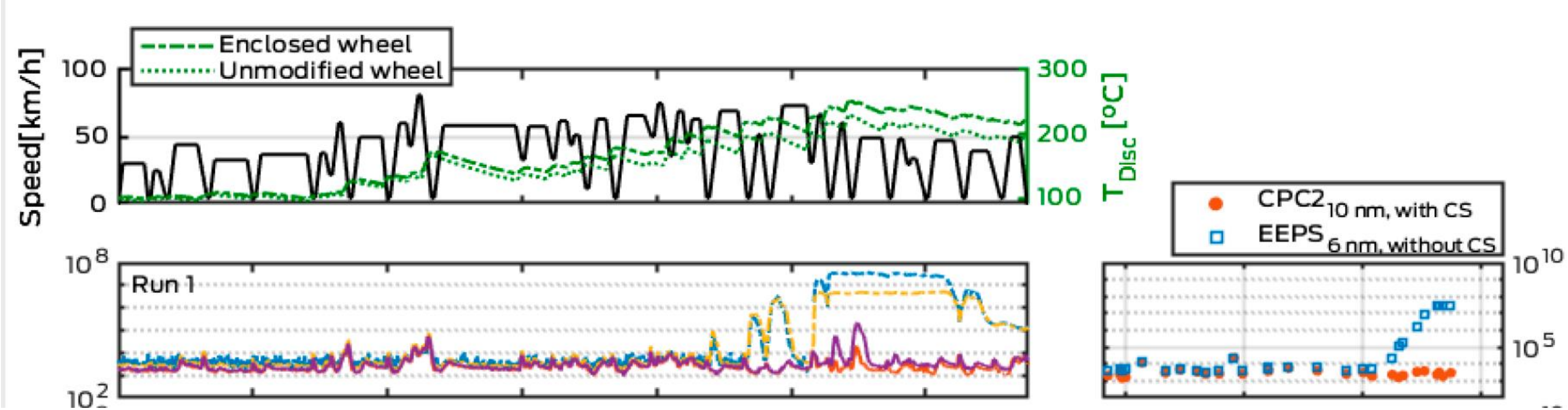
➔ Since dilution can freeze coagulation, ideally dilutor should be installed close to extraction point, and a limit on residence time up to dilutor should be defined. If nucleation occurs at different tunnel flows leading to coagulation-limited concentrations the effect on PN emissions can be vastly different.





Tunnel concentrations: Saturation effects

- Excessive concentrations outside the measurement range of the CPC lead to saturation of the signal, manifested in a flat response at a level where even the detector is not linear. True levels are then unclear.
- Several such cases have been presented within PMP but also published, also verifying that maximum concentration level of total PN can exceed 10^8 #/cm^3.



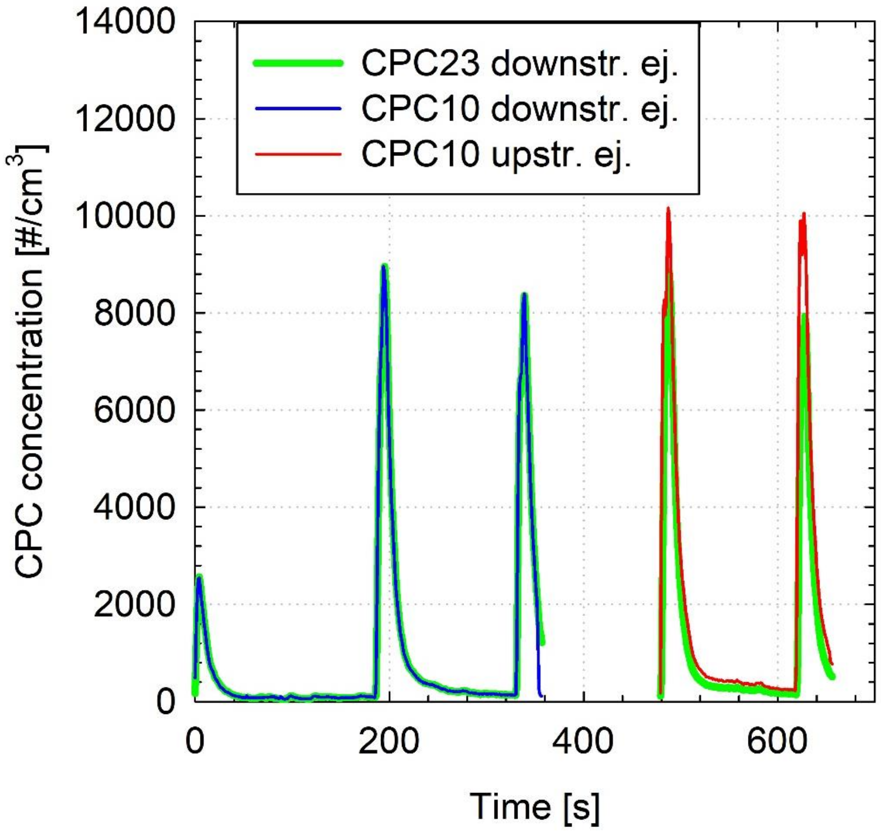
Mathissen et al. 2019
https://doi.org/10.3390/atmos10090556

PN instrumentation – Dilution status monitoring

- Diluter is also susceptible to drifts due to contamination. We have observed large reductions in the dilution ratio of an ejector used at a campaign at TUI.

- Nominal dilution should be ~7:1 but was experimentally found to be around 1.5!

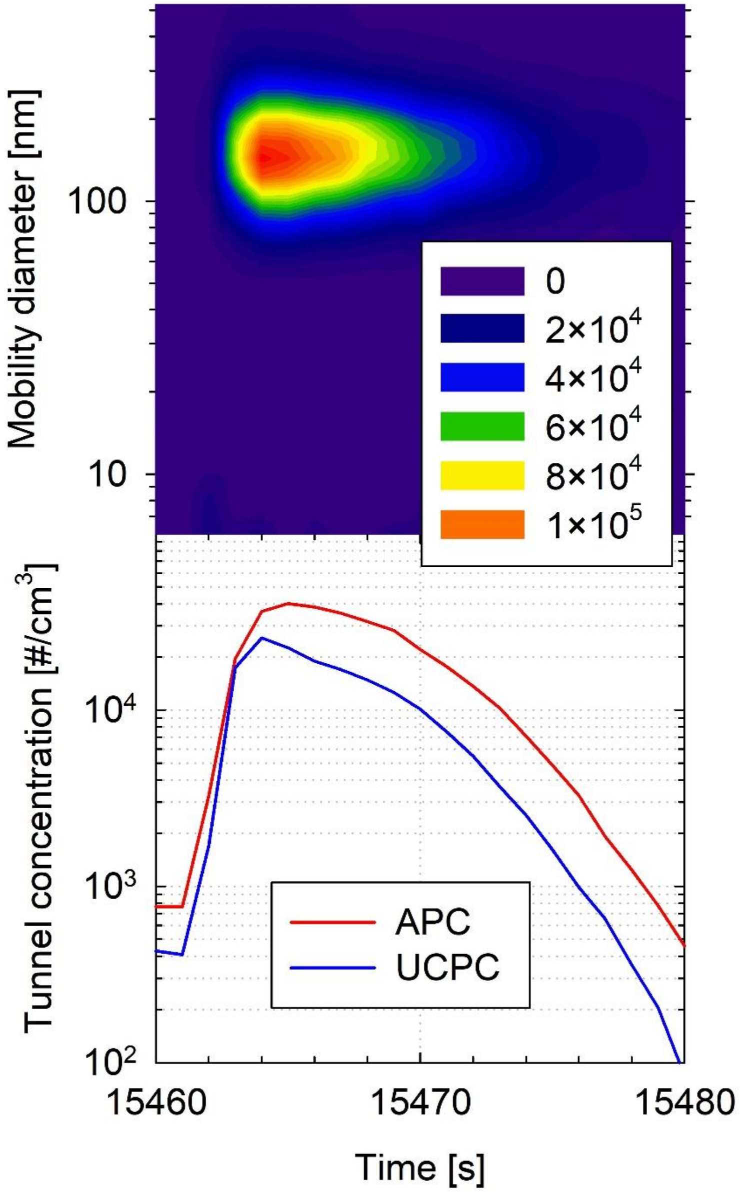
➔ Real time monitoring of the dilution ratio should be mandated, while regular checks of the dilution ratio are strongly recommended.



PN instrumentation – CPC status monitoring

- One important effect we show in some campaigns was underestimation of CPC counts due to flow changes caused by clogging. In our joint campaign with BMW (Mamakos et al. 2021), the CPC employed for total PN was systematically measuring 40% lower (i.e. half…). Maintenance by the supplier after the campaign verified a change in the capillary flow (it uses internal flow splitting).

➔ Full flow CPCs should be mandated, allowing for regular monitoring of the sample flow (using external flowmeter) which is directly used for the reported number concentrations from measured counts. While clogging may also eventually affect their performance, it would be easy to verify on-site.



What is the nature of the volatile PN?

- There seems to be a consensus that the precursors for volatile nano-particles are organic compounds released from brake pads at the elevated temperatures developed during braking.

- These are most probably originating from phenolic resins used as binders (Kukutschová et al., 2011), that can further decompose to lighter chemical components.

- These organic compounds originally in vapour phase at the elevated temperatures at the contact surface can subsequently form nanosized particles via homogeneous nucleation.

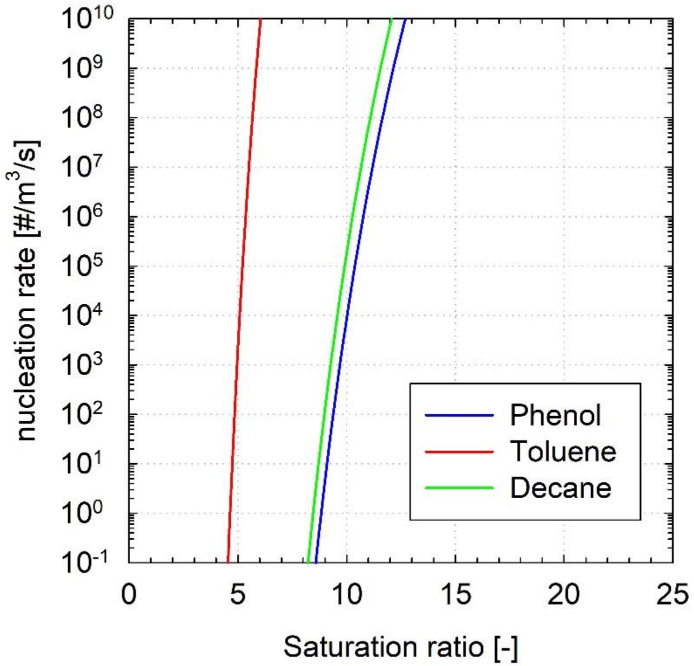
- Limited studies addressing volatility suggest that a thermodenuder (Perricone et al. 2019, Mamakos et al. 2019) or a catalytic stripper (Mathissen et al. 2019, Mamakos et al. 2019) at 300°C efficiently removed them, with a large fraction of them being removed by thermodilution at 200°C (Perricone et al. 2019, Mamakos et al. 2019).

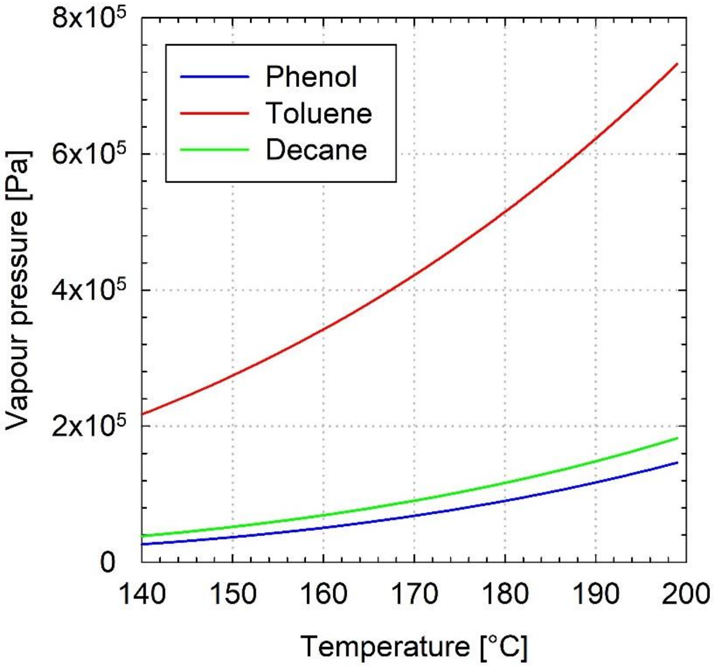
Volatile PN: Homogeneous nucleation theory

- Classical nucleation theory allows for calculation of nucleation rates (concentration of nuclei formed per unit time) and initial nuclei size as a function of species thermophysical properties and saturation ratio S.

- S is defined as the ratio of species partial pressure to species vapour pressure:

$$S = \frac{P_{precursor}(DR, T_{disc})}{P_{vapour,precursor}(T_{air})}$$



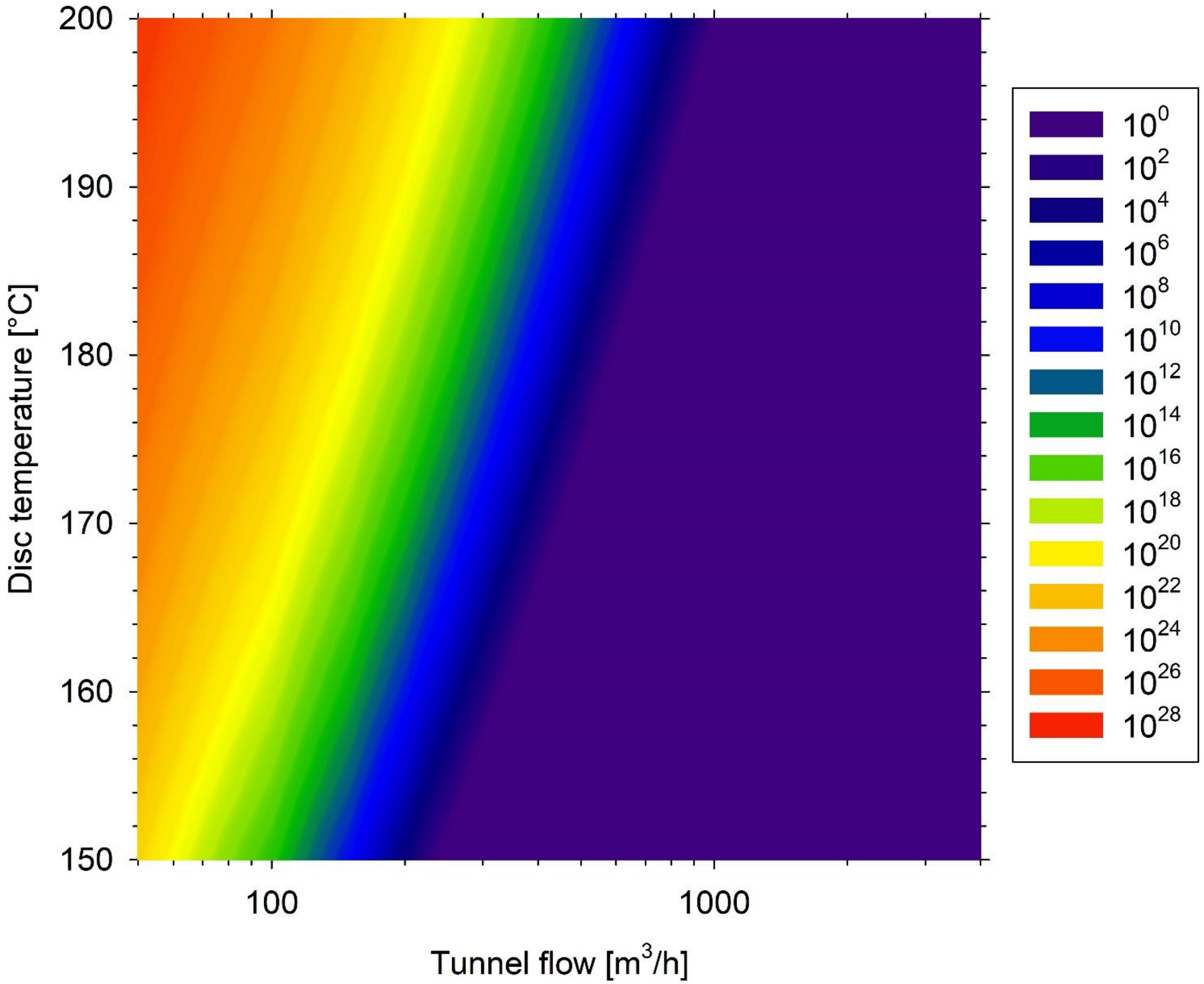


How would tunnel flow adjustment affect the nucleation potential?

➔ Amount of released vapours is not expected to change much by adjusting cooling. Even a 10°C reduction of pad temperature would correspond for example to a modest 15 to 40 % reduction in vapour pressure and thus the amount of released precursors.

➔ A change of the tunnel flow, however, will imply a similar change (approximately owing to complex velocity profiles and thus non-uniform dilution ratios) in the dilution of the precursors and therefore in their partial pressure, and thus saturation ratio.

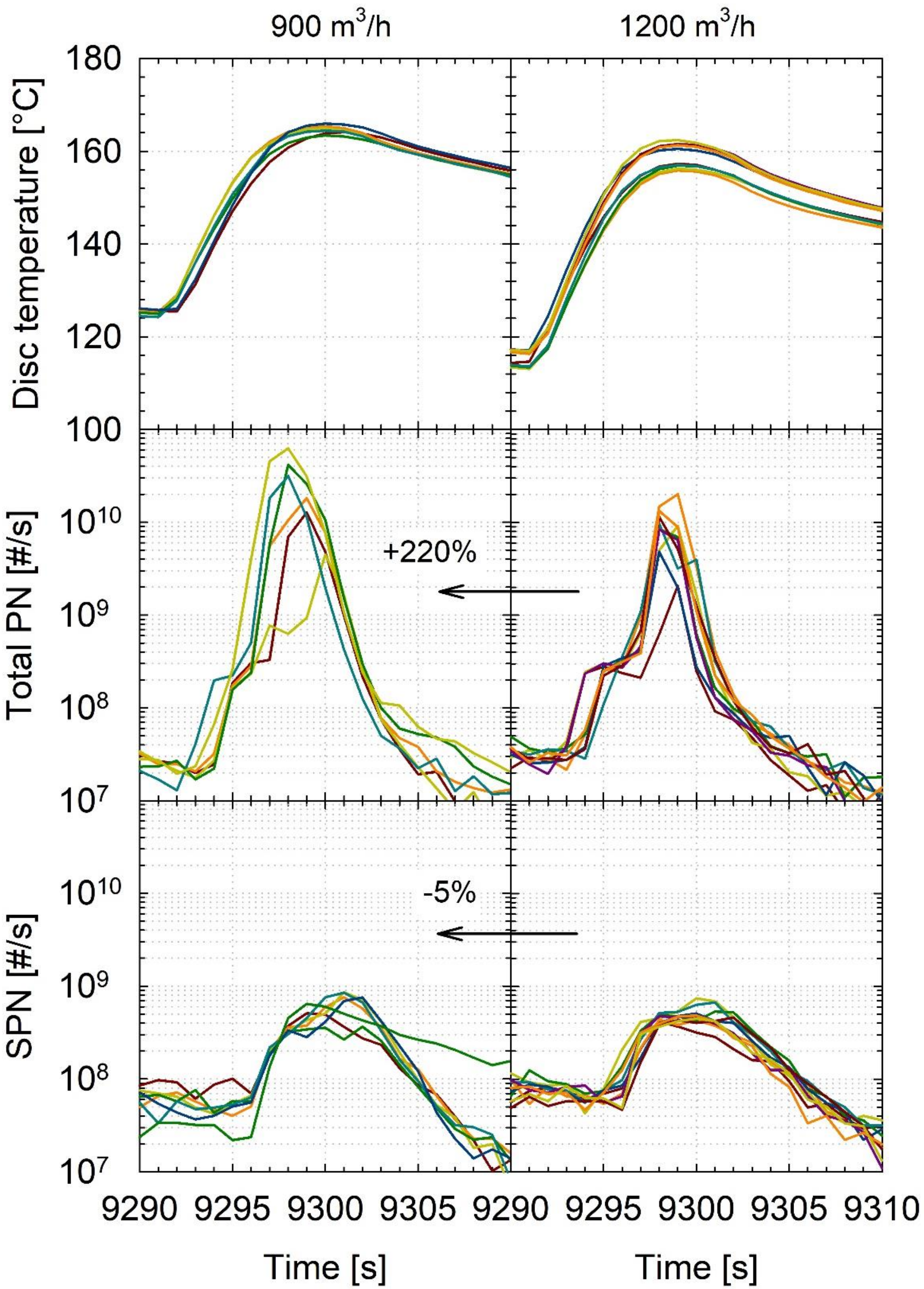
➔ Tunnel flow adjustments do not significantly change the amount of precursors but can suppress the formation process simply by dilution.



Example homogeneous nucleation rates [#/cm^3/s] based on phenol

Experimental verification of nucleation suppression

- We have not observed volatile nanoparticle formation over WLTP-Brake in our campaigns, although scope was limited on two brake systems and the same pad formulation.
- We have only observed volatile nanoparticles over LACT and this to significantly less levels than what previously reported.
- Event under such restricted formation of volatile nanoparticles, 25% reduction in tunnel flow and thus dilution was sufficient to increase their number concentrations by 220%, with no visible effect on SPN.
- Effect on peak disc temperature was minor, and recorded temperature was below the presumed threshold of 170°C.



How to measure total PN?

- The strong sensitivity of volatile PN on dilution conditions is well established in the exhaust aerosol community. More than 2 decades ago, Khalek I. and Kittelson D. (Khalek et al. 1998, Khalek et al. 1999) showed using specialized sampling equipment that one can in principle obtain any distribution for exhaust nucleation mode particles, by just modifying the conditioning parameters within the range permitted in an exhaust dilution tunnel.

- Given the strong sensitivity of volatile nucleation mode on dilution conditions, maintaining a fixed dilution is imperative to allow for repeatable and reproducible measurements (particulates.pdf (europa.eu)). Considering that the brake is enclosed in the brake dyno tunnel, this would effectively require fixing the operating tunnel flow at all laboratories and is inconsistent with the concept developed within TF1.

- Would it make sense to consider a dedicated setup for the evaluation of the volatile particle formation potential of brake pads?

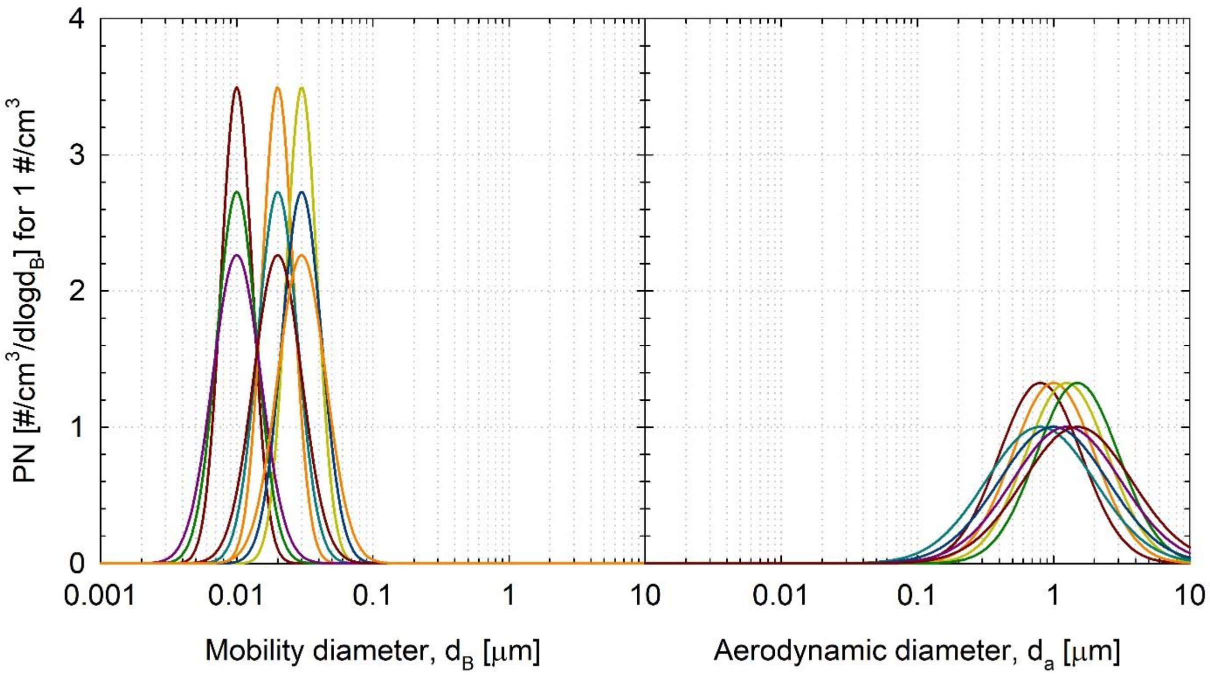
Simulations: Assumed size distributions

- For the assessment of the effect of loss mechanisms in PN measurements, the bimodal nature of brake-wear is of relevance. Losses of small particles are better described by mobility diameter while losses of large particles are linked to aerodynamic size ➔ No attempt was made to combine the two different modes (i.e. by effective density assumptions).

- Calculations were performed for the cases of:
  - No NM
  - NM leading to 1 order of magnitude higher average concentration over the cycle.

- It is assumed that a 2.5 µm pre-classifier is used.

- Mode parameters:
  - Coarse: d_g = 0.8 – 1.5 µm, σ_g = 2-2.5
  - NM: d_g = 10 – 30 nm, σ_g = 1.3-1.5



2.5 µm cut-off: Undetected fraction

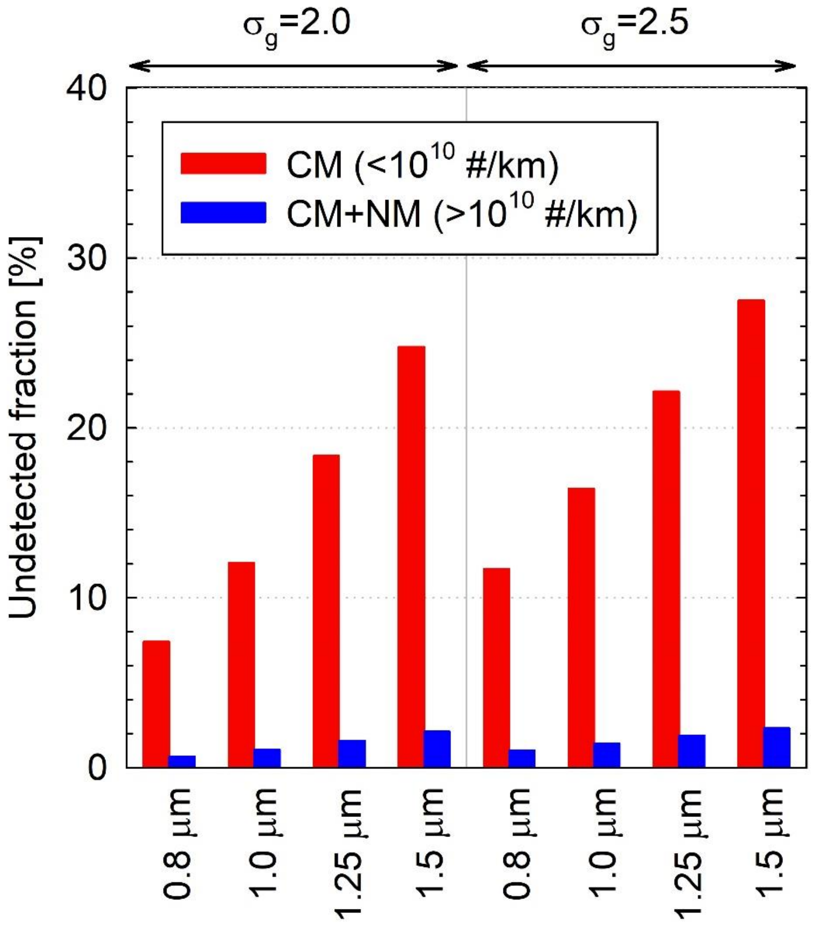
- The undetected fraction imposed by an ideal (ISO7708) 2.5 µm cyclone can range from 10 to 25% in the absence of a NM, but in these cases the PN emission rates are expected to lie below 10^{10} #/km where tunnel background concentration can have equal or stronger effect.

- Future developments in reducing PM, are expected to either further reduce number concentration of coarse particles or their size.

- It should be stressed as well that the above assume that all emitted >2.5 µm particles reach the optical detector which is demanding itself.

➔ Restriction of PN to <2.5 µm is justifiable.

➔ Might worth it though foreseeing a pre-classifier at 2.5 µm (perhaps lower?), at least to protect instrumentation.

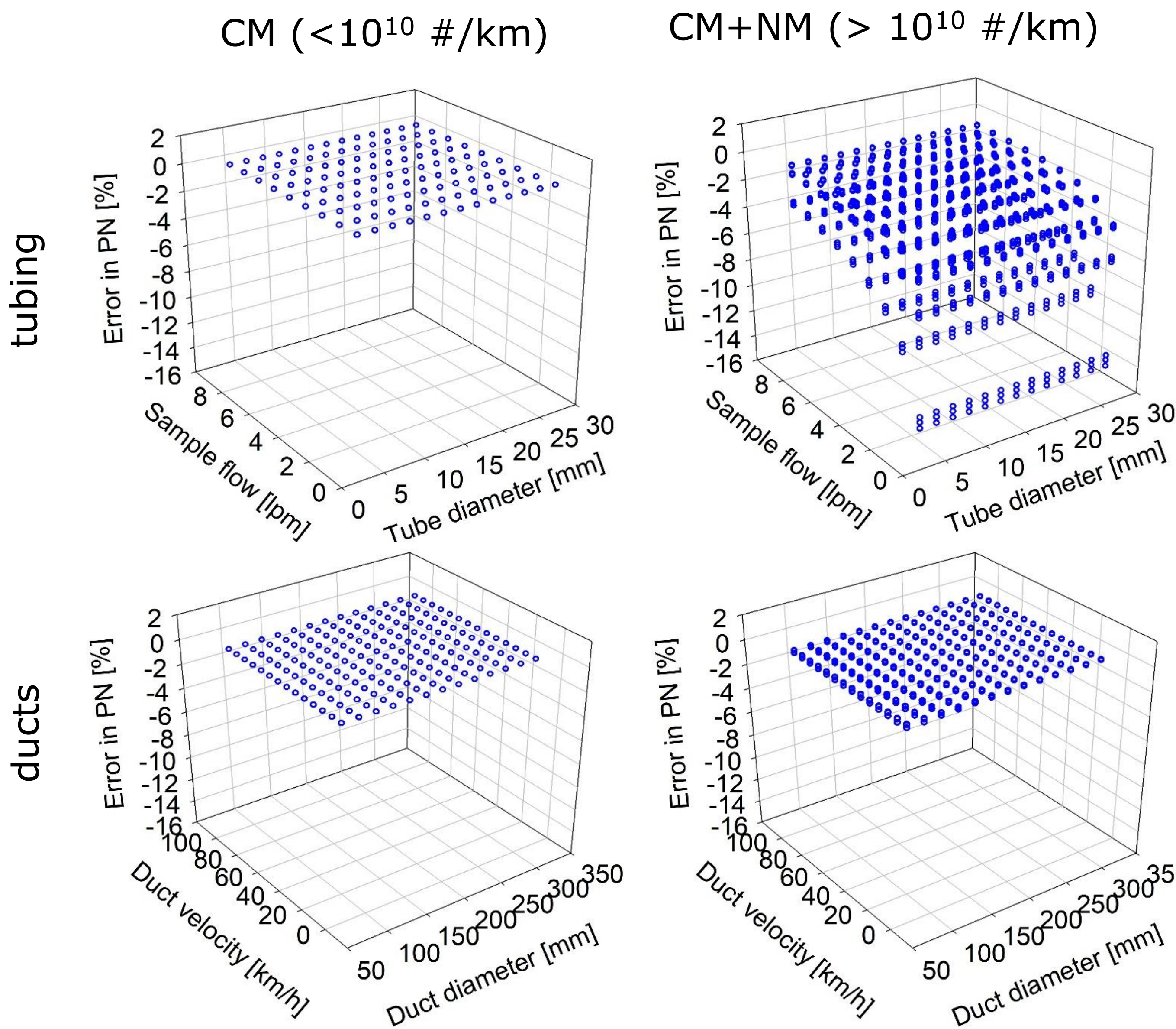


Diffusional losses per meter

- Diffusional deposition can become a relevant loss mechanism in the presence of nucleation mode, but only on tubes.

➔ Diffusional losses depend on length, L, over sample flow, Q_{sam}, ratio. There should be a provision to limit L/Q_{sam} or the tubing up to the diluter/CPC → 60000 s/m² (1 m at 1 lpm)?

➔ Losses in diluter (mostly diffusional) in the exact configuration used (i.e. if flow splitting is employed) should be well characterized and documented.



Calibration requirements

- Despite all its shortcomings, the PMP methodology allowed for the first ever standardization of calibration procedures for both CPC and dilutors.

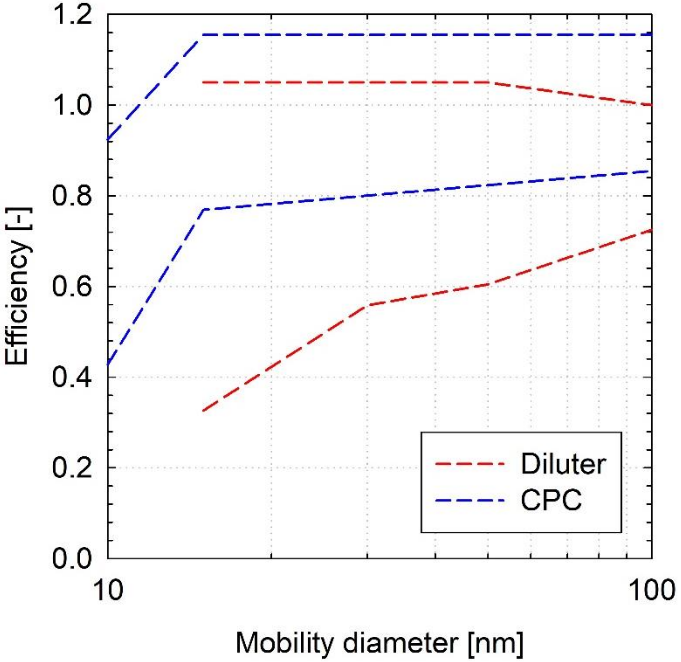
- Losses in dilution system and uncertainties in dilution ratios were not consistently (or even properly) considered before.

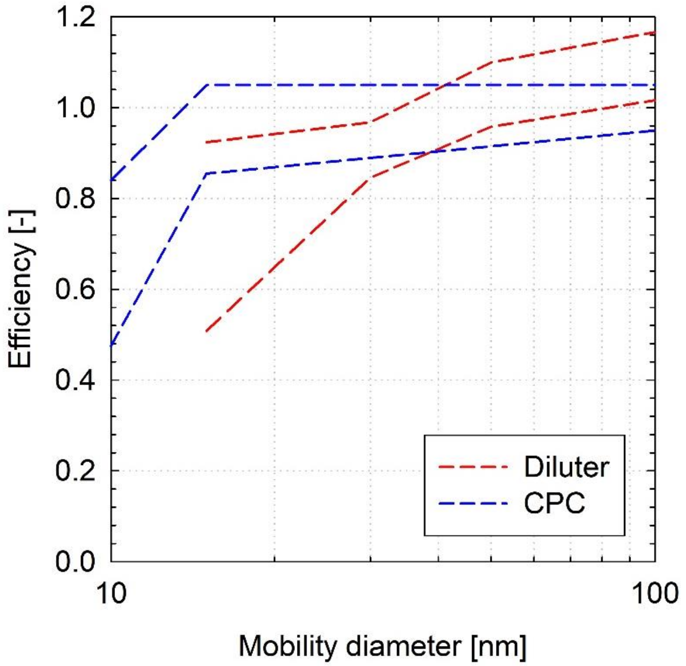
- Losses and dilution were addressed collectively with the Particle Concentration Reduction Factor (PCRF) defined as the ratio of upstream to downstream concentration and linked to dilution factor, DF, and penetration, P, via: $PCRF = \frac{DF}{P}$

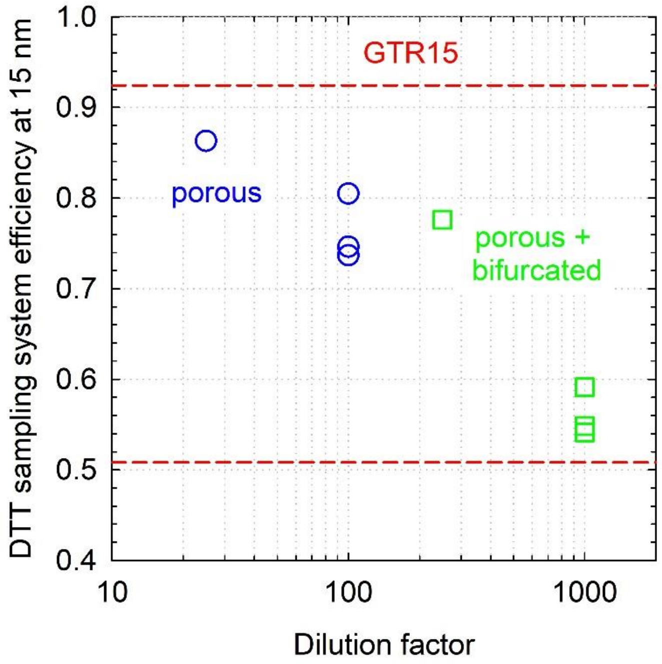
- Currently, there are discussion on harmonization of calibration procedures, including discussions on calibration material, PCRF vs calibration of the whole device (dilution + CPC) as a black box. We should try to align with these efforts as much as possible so that we minimize efforts for all upcoming calibration facilities/requirements (i.e. ISO certifications).

Calibration requirements GTR15

- The specifications on particle losses and CPC detection efficiencies as laid down in latest GTR15 reflect the challenges in measurement of nanosized particles. Note that calibration uncertainties are not considered!
- However, the CPC linearity requirements and PCRF approach for particle losses, help improve the comparability of different systems in the field.
- Diffusional losses are present even in highly optimized systems, like the Horizon 2020 DTT system, especially at high dilutions (in the specific case due to the need for a ternary bifurcated diluter).







Recommendations for minimum PN requirements #1

- Brake-wear nanoparticles are not necessarily volatile. BW PN is expected to become relevant only in the presence of either solid or volatile nucleation mode. The effort necessary to properly transfer particles larger than 2.5 µm is not justified from their anticipated number concentration → Focus should be made on the characterization and the definition of specifications for small mobility sizes. Still is 2.5 µm necessary or could we even reduce cut-off size to smaller sizes to protect instrumentation?
- PN background should be reported both in $\#/cm^3$ and #/km (using average speed over WLTP-Brake and tunnel flow).
- Full flow CPC should be used and sample flowrate should be measured before each test with external calibrated flowmeter. The measured flows should be reported at normal conditions (0°C, 1 atm). Sample pressure and temperature should also be reported.
- A maximum residence time (1s? - coagulation) and length over sample flow (60000 s/m^2?- diffusion) should be defined for the transport of particles from probe tip to PN instrumentation. This transport tube should not include any flow splitting.
- The entire path from the end of the transport tube to the inlet of the CPC shall constitute the PN conditioning unit and can include, dilution, (thermal treatment only for solid PN) and any flow splitting. The Particle Concentration Reduction Factors (PCRF) at 15, 30, 50 and 100 nm should be experimentally determined for each operating conditions employed and reported. We recommend that these fulfil the GTR15 requirements.

Recommendations for minimum PN requirements #2

- We recommend that the CPC is in accordance to the specifications of GTR15 for 10 nm measurements.
- A copy of a calibration certificate of both diluters and CPC, issued no more than 1 year before the campaign (ideally sooner) should be supplied.
- CPC concentrations during tests should not exceed the maximum concentration employed during linearity calibration by more than 10% → Labs should ensure that sufficient dilution is employed to avoid saturation of the CPC. This would require a dilutor capable of reaching 3000:1 dilution.
- In addition to number concentration real time recordings of dilution/PCRF should be reported.
- It is highly recommended that a provision for simple PCRF checks is considered (i.e. PN instrumentation sampling in parallel to a stand-alone CPC from the tunnel as in TUI).
- A pre-classifier at or above 2.5μm is highly recommended at least to protect instrumentation.

Points for clarifications

- Total PN measurements
  - Is the full-flow dilution tunnel suitable for such measurements? Should we consider complementary tests to assess the volatile release potential of brake pads?
  - Are there pads of poor performance that can be evaluated in the RR? If a completely new methodology is to be established, it is imperative that we verify it is robust in detecting those and discriminating them from good quality pads in a reproducible and unequivocal manner. This is similar to the original PMP RR in which the Solid PN methodology was use din different labs to measure the same golden vehicle but also different technologies allowing for an assessment of the discrimination capabilities and eventually the regulatory limits.
    - If such pads are not available would it make sense to include few LACT-20 tests at the end of the WLTP sequence?

Thank you

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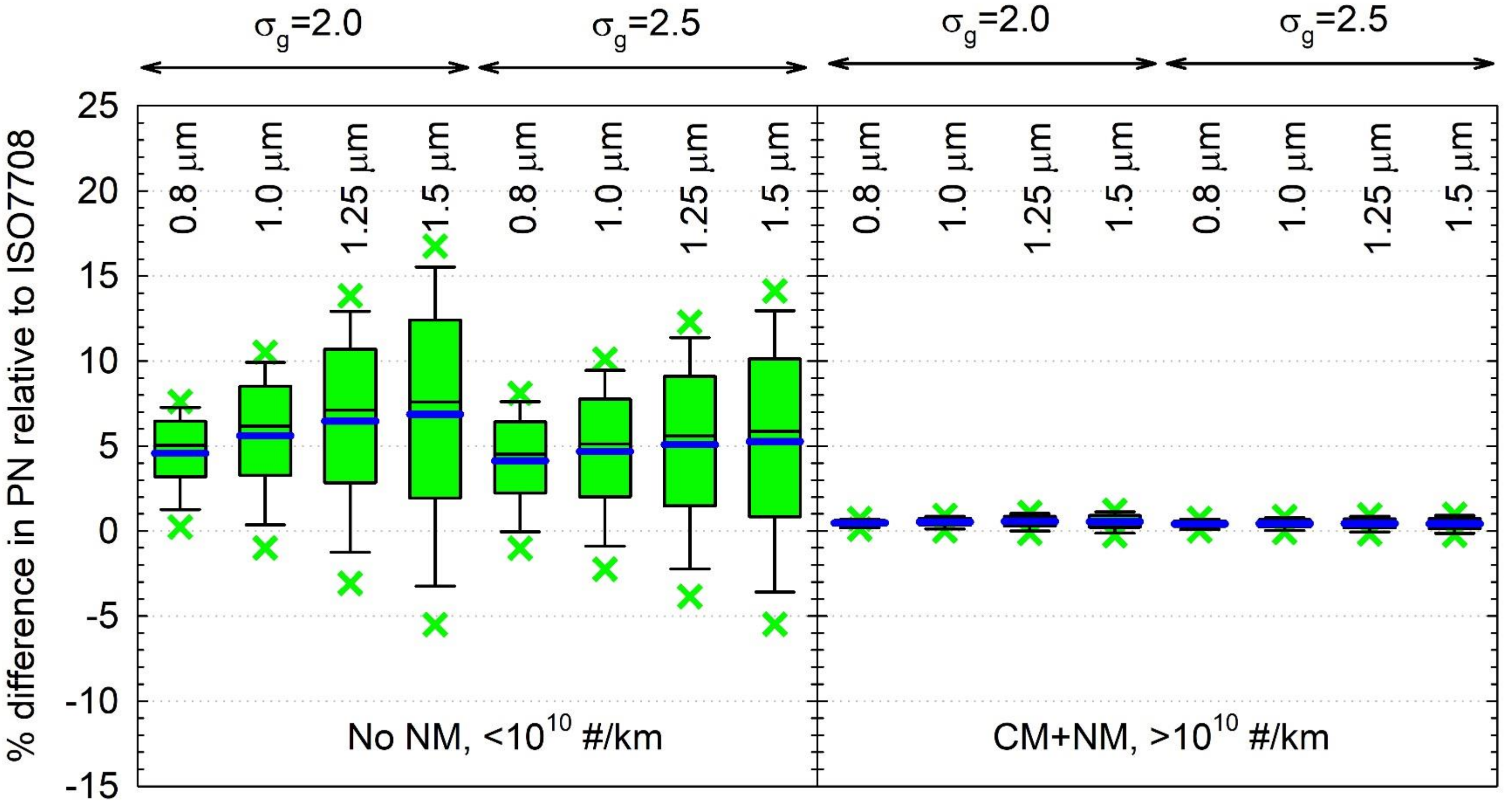
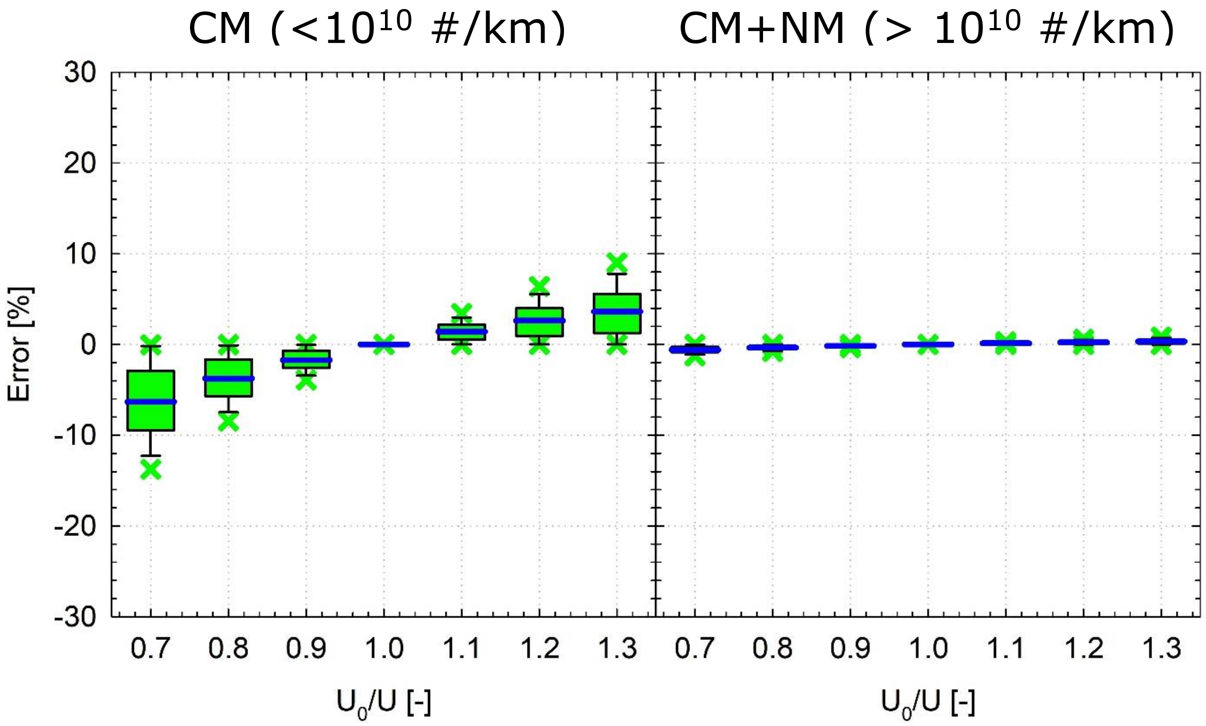
Effect of 2.5 µm pre-classifier

- The uncertainties in PN introduced by differences in the efficiencies of ISO25597-compliant 2.5 µm cyclones is considerably smaller than for $PM_{2.5}$ (-50% to +30%) and only relevant in the absence of NM, (emission levels below ~10^{10} #/km).



Anisokinetic sampling effect

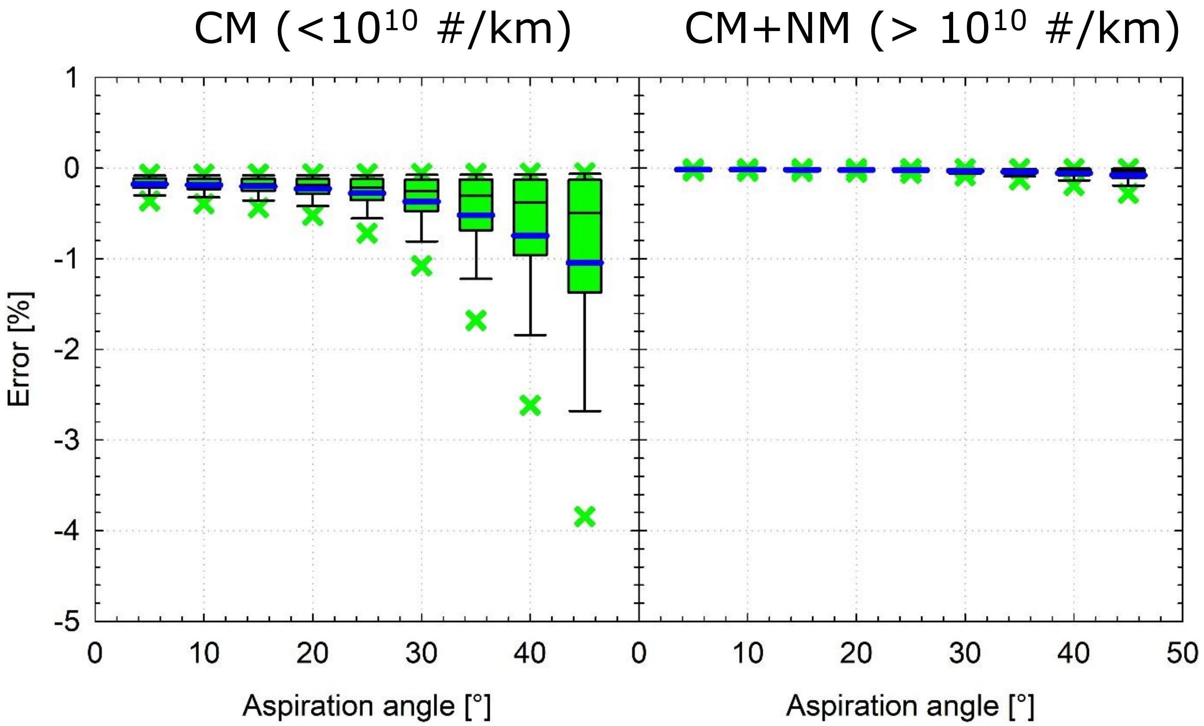
- Effect of anisokinetic sampling is relevant only in the case of brakewear aerosol with no nucleation mode.
- We do not see though a reason to still confine the isokinetic ratios to similar levels for PM.



Anisoaxial sampling effect

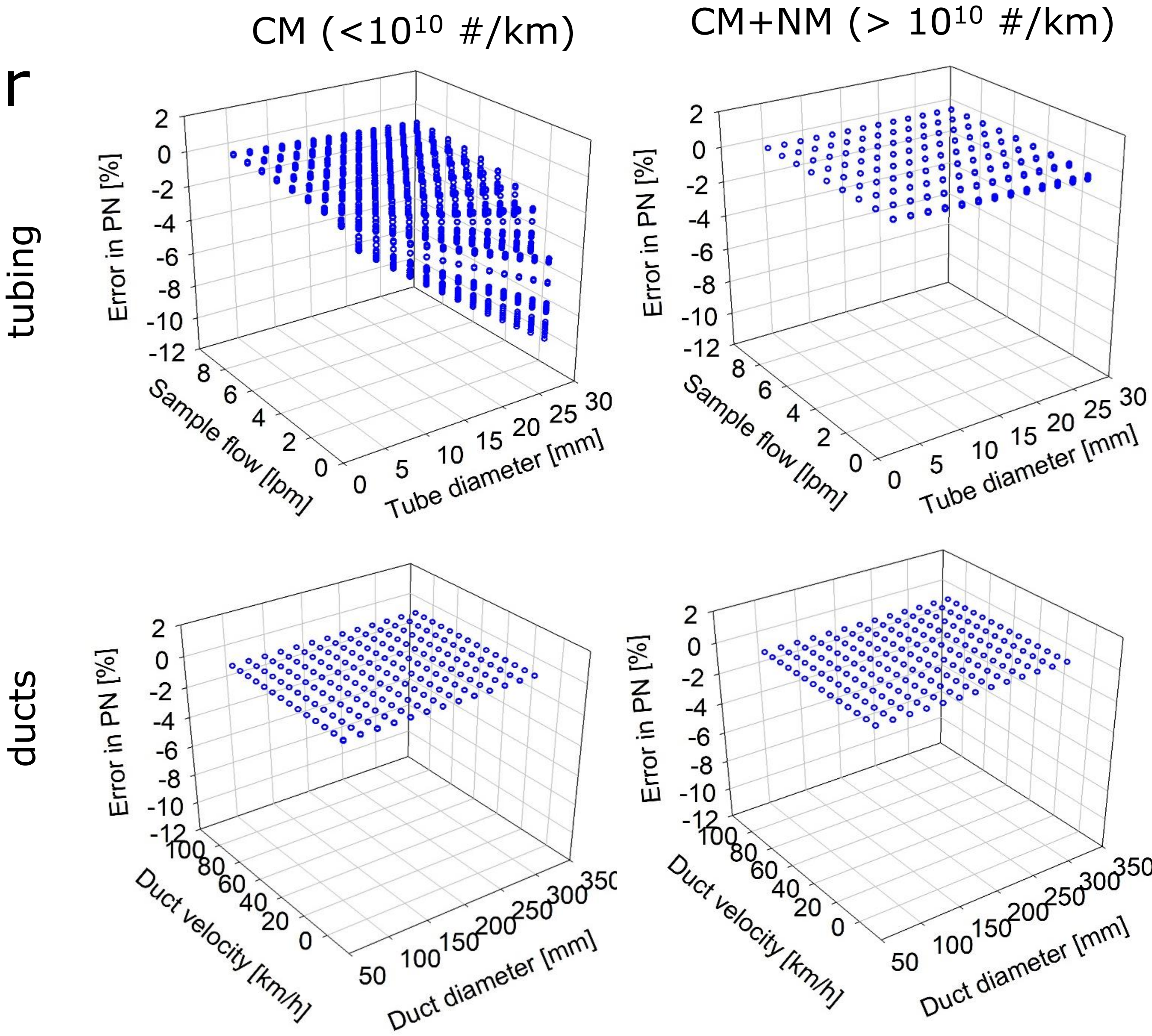
- Effect of anisoaxial sampling was evaluated for isokinetic conditions.
- Effect is generally expected to be negligible even in the absence of nucleation mode.

➔ Still we do not see a reason to relax the threshold for the aspiration angle for the case of PN.



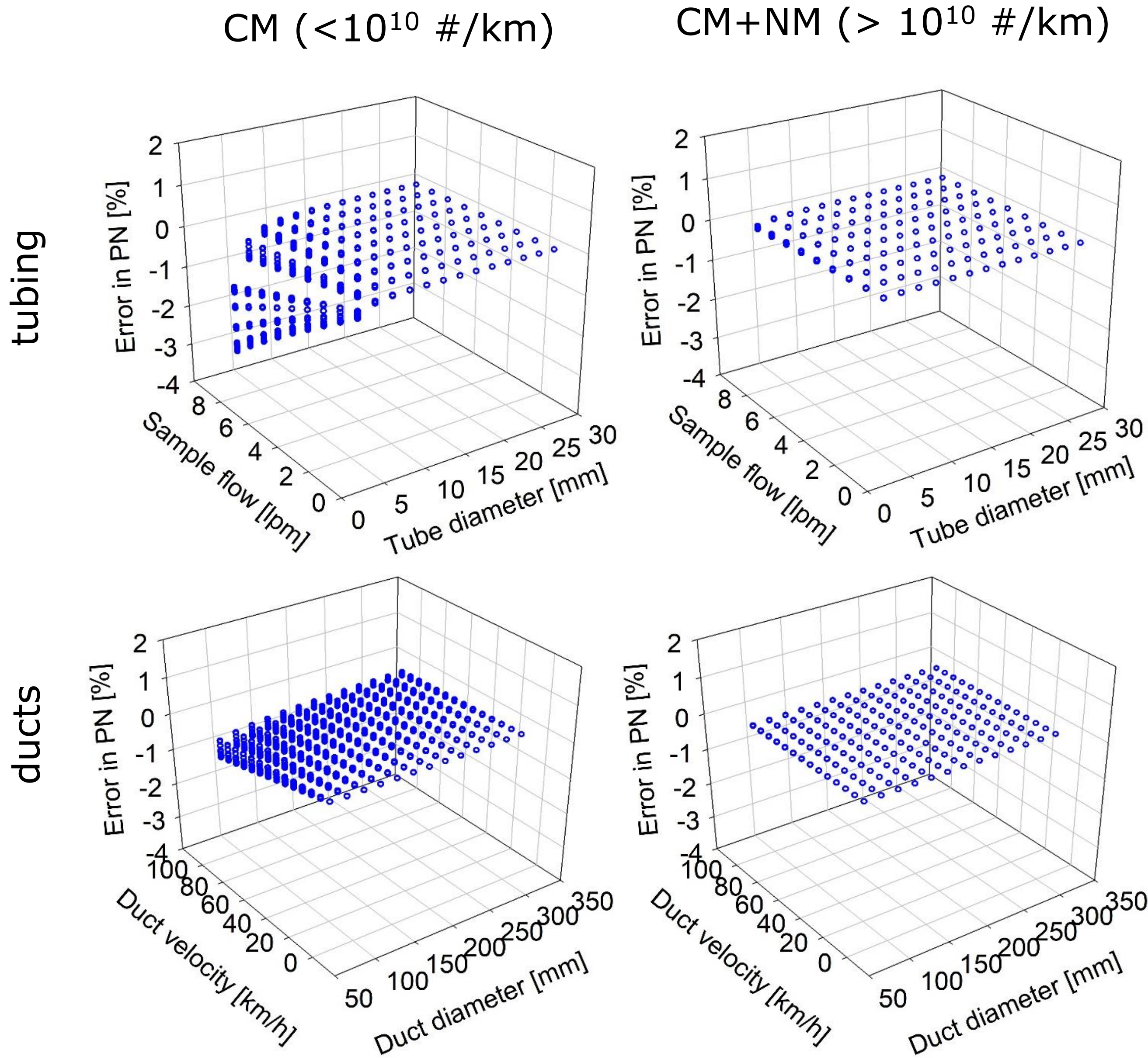
Gravitational losses per meter

- Gravitational losses are not critical for PN, especially considering that typical tubing employed for PN has small diameters.
- Once again, tubing is more critical than ducts.



Inertial deposition on bends

- The effect of inertial deposition on 90° bends is negligible for PN measurements.



How is the tunnel design affecting homogeneous nucleation?

- The effect of tunnel flow on peak disc temperatures is inconsistent as reflected from the recent decision to remove peak temperatures from TF1 requirements.

- This is not surprising considering the orders of magnitude higher friction power (10^6 W/m^2) compared to convection heat rates (maximum in the order of 10^4 W/m^2), also manifested in the much slower temperature drops compared to temperature rises during braking.