

Engine Exhaust Solid Sub-23 nm Particles: II. Feasibility Study for Particle Number Measurement Systems

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ABSTRACT

In the current heavy-duty engine and light-duty diesel vehicle exhaust emission legislation Particle Number (PN) limits for solid particles >23 nm are prescribed. The legislation was extended to include Gasoline Direct Injection (G-DI) vehicles since September 2014 and will be applied to Non-Road Mobile Machinery engines in the future. However there are concerns transferring the same methodology to other engine technologies, where higher concentration of sub-23 nm particles might exist. This paper focuses on the capabilities of existing PN measurement equipment on measuring solid particles smaller than 23 nm. More specifically, it is investigated: 1) whether it is feasible to easily modify existing systems to measure lower particle sizes, 2) whether all volatile particles can be removed efficiently in the PN measurement systems, 3) whether any artifacts happen in the PN systems (e.g. formation of non-volatile particles due to pyrolysis), and 4) whether by lowering the lower size the measurement uncertainty increases significantly. The main conclusions are: 1) It is relatively easy to modify the systems to measure from 10 nm. 2) The volatiles are not always removed efficiently in the PN measurement systems. The major issue is re-nucleation of sulfuric acid downstream of the evaporation tube. However, these particles typically do not grow to 23 nm or to 10 nm with high dilution. 3) There are indications of formation of 10 nm solid particles from hydrocarbons and sulfuric acid in the PN systems. 4) With lower size of the PN equipment, the measurement uncertainty will increase due to differences in the losses between the PN systems. However the increase of uncertainty is estimated to be <5% for measurements >10 nm, when no separate solid sub-23 nm core mode exists. Recommendations for proper measurements below 23 nm are given. The main conclusion of this study is that, in case that it is proven that there is a need for solid sub-23 nm particle measurements, the existing PN systems could be relatively easily adjusted to measure from 10 nm without increasing significantly the measurement uncertainty. Sub-10 nm measurements need major changes of the PN systems.

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INTRODUCTION

A Particle Number (PN) standard was introduced for diesel light duty vehicles in September 2011 (Euro 5b) limiting the number of solid¹ particles emitted over the legislated test cycle to 6×10^{11} p/km. The new standard effectively necessitated the installation of high-efficient wall-flow Diesel Particulate Filters (DPFs) in all diesel vehicles. The PN standard has also been introduced for heavy-duty engines since beginning of 2014 (Euro VI). The same standard was introduced to gasoline vehicles utilizing direct injection (G-DIs) at Euro 6 stage (September 2014) initially with a limit of 6×10^{12} p/km and from September 2017 with 6×10^{11} p/km. This 3 year delay was decided in order to allow the manufacturers sufficient time to investigate the possibility of compliance through improvements in the combustion process without the need of Gasoline Particulate Filter (GPF). A PN limit will also be introduced in the Non-Road Mobile Machinery (NRMM) engines regulation probably from 2017.

European legislation requires the measurement of solid particles >23 nm in order to avoid the uncertainties that measurements of volatile particles have. However, there were concerns whether the methodology applied to diesel engines can be applied to gasoline engines and other technologies. A literature survey showed that solid particles <23 nm can be emitted and sometimes in high concentrations ([1] and references therein). In general, a lot of studies have found a solid core mode with older and modern diesel engines, both at low and high loads. Solid core mode is often observed at gasoline engines with port fuel injection (G-PFI) and it is assumed to originate from the metals of the lube oil or from fuel additives. At G-DIs a shoulder at 10-20 nm appears quite often. The percentage of solid particles not measured (i.e. <23 nm) is 30-40% for G-DIs; similar to diesels. Higher percentages can be measured at low ambient temperatures or high ethanol fuels. It should be mentioned that in many studies it was recognized that the 'solid' core mode was re-nucleation artifact of the PMP method and the dilution factors employed.

1. In this paper particles after thermal pre-treatment at approximately 350°C are called 'solid'.

Note that it is important to distinguish solid particles < 23 nm that are part of the lognormal soot accumulation mode from a separate small solid core particle mode. Sub-23 nm accumulation mode particles are already regulated with the current 23 nm cut-off size, at least to an extent, even if they are not explicitly counted. For example for typical size distributions with means around 50-70 nm, approximately 5-15% of the total particles are not counted and this was taken indirectly into account with the current PN emission limits. However, one could theoretically manipulate the size distribution to lower sizes and thus avoid part of the emitted particles to be measured (e.g. with a mean 30 nm, 40% of the particles will not be counted). Lowering the cut-off size ensures that most particles will be counted and it is necessary when a separate solid core particle mode² exists (e.g. from additives). However, at the same time the measurement uncertainty can increase due to different particle losses in the commercial systems.

Thus, before reducing the lower size of the PN instruments for regulatory purposes it is important to investigate whether this is possible. Target of this report is to investigate:

- whether all volatile particles can be removed efficiently in existing PN systems,
- whether any artifacts happen in the PN systems (e.g. formation of non-volatile particles due to pyrolysis) and
- whether a lower than 23 nm size increases significantly the measurement uncertainty.

Initially the current PN systems will be described and the feasibility of sub-23 nm measurements with existing PN systems will be followed. Then the possibility of artifacts from the existing systems will be investigated experimentally. Recommendations for proper sub-23 nm measurements will also be given.

PARTICLE NUMBER (PN) METHOD

The PN method is based on the findings of the Particle Measurement Program (PMP) (Figure 1) [2, 3]. According to PMP and current regulations, the PN system should consist of a Volatile Particle Remover (VPR) and a Particle Number Counter (PNC) [4].

The VPR removes volatile particles and dilutes the sample. The PNC measures the number concentration of particles >23 nm in order to exclude possible confounding of measurements by low volatility species present as nucleation mode particles, while including the primary soot (spherule) size of 23 nm. The VPR should be connected to the full dilution tunnel (CVS) with a particle transfer tube (PTS) (laminar flow). The residence time (RT) to the primary diluter (PND₁) of the VPR should be ≤3 s. The primary dilution should be ≥10 (actually Particle Concentration Reduction Factor, PCRF) and the temperature of the diluted sample ≥150°C. In the VPR, after the PND₁, a heated tube with wall temperature between 300 and 400°C

should exist. A secondary diluter (PND₂) is not required but the temperature at the inlet of the particle number counter (PNC) should be <35°C. The residence time from the VPR to the PNC should be ≤0.8 s and the diameter of the tube ≥4 mm. The PNC should be full flow (no internal splitting) with a response time of <5 s and counting efficiencies (CE) of 50%±12% and >90% at 23 and 41 nm respectively. The slope of the PNC during calibration should be 1±0.1. The total residence time in the VPR and PNC should be ≤20 s.

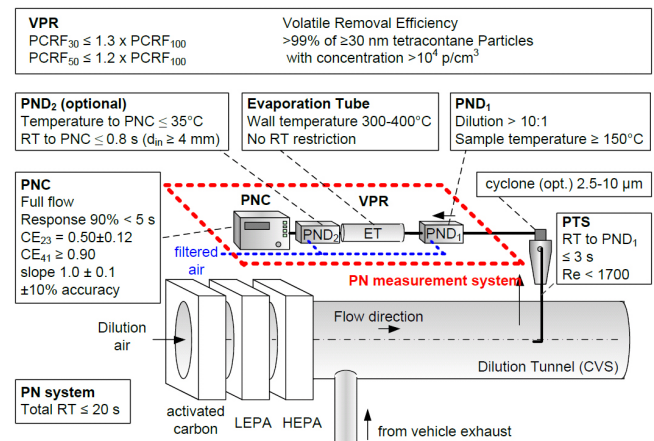


Figure 1. Particle Number (PN) system requirements. The PN system consists of a volatile particle remover (VPR) and a particle number counter (PNC). The VPR removes volatile particles and dilutes the sample. The PNC measures the number concentration of particles >23 nm. For details, see text and abbreviations.

FEASIBILITY OF SUB-23 NM MEASUREMENT FOR PNCs

The cut-off size ($d_{50\%}$) of a PN system is mainly determined by the PNC. Replacing the existing PNCs with PNCs with lower than 23 nm cut-off size is possible. Various full flow (no internal splitting or dilution) models exist in the market with cut-off sizes down to 5 nm.

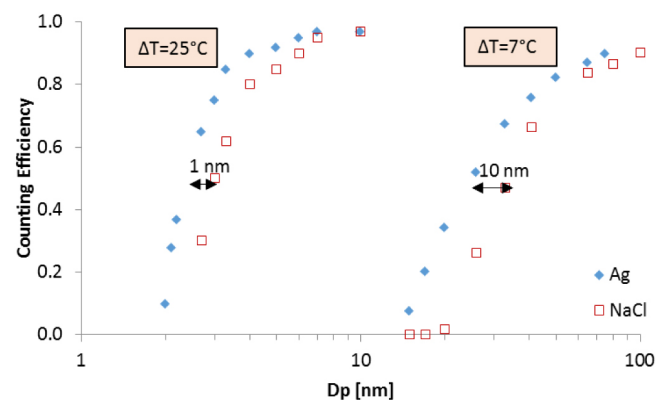


Figure 2. Counting efficiencies of PNCs with different temperature differences between saturator and condenser (from [7] and [8]).

The cut-off of a PNC is usually determined by adjusting the super-saturation ratio inside the device by adjusting the temperature difference ΔT between the saturator of the working fluid and the condenser. The higher the ΔT , the higher the

2. The term *core mode* is used for a separate solid size distribution with peak <23 nm to avoid confusion with the nucleation mode which is typically volatile.

super-saturation ratio and smaller particles can be activated, grow and be detected. For PNCs with working fluid n-butanol a cut-off of 23 nm is achieved with $\Delta T = 7.5^\circ\text{C}$. However, the cut-off size of the PMP PNCs with low temperature difference between saturator and condenser ($\Delta T = 7.5^\circ\text{C}$) depends strongly on the particle material (e.g. structure, surface properties etc.) [5, 6, 7]. For example, for the same ΔT , the $d_{50\%}$ for emery oil and NaCl particles have a difference of 12.5 nm and the difference between oxidized Ag and NaCl $d_{50\%}$ is around 9 nm [7]. However, for high ΔT (lower cut-off) smaller differences are noticed (in absolute values); note however that in relative terms the effect is quite similar. For example, in [8] they found only 0.7 nm difference between the Ag and NaCl cut-off diameters, for a PNC with $\Delta T = 25^\circ\text{C}$. In [9] smaller effect of the material (Ag and NaCl in this case) with decreasing $d_{50\%}$ was found for different PNC models. Figure 2 shows an example the effect of the material (Ag and NaCl) on the counting efficiencies of two PNCs with different temperature difference between the saturator and the condenser.

The commercial PNCs inside the PN systems can easily change the cut-off size down to 7-10 nm by adjusting the ΔT and without any major hardware modifications. Thus, in case of a change of the legislation the existing systems can be modified without a need for investment. Note however, that adjusting the temperature of a PNC will lead to non-linearity issues at high concentrations, unless internal software parameters also change to take into account the different growth of particles and thus the coincidence correction that is applied [10].

One point that needs attention is the calibration material. The most commonly used aerosol for automotive PNCs (emery oil) can be used for 10 nm, but not for 5 nm because it's extremely difficult to produce high concentration at such low size. Atomized NaCl, CAST (Combustion Aerosol STandard) and spark discharge graphite with N_2 do not produce such small particles. Materials that can be used are Ag and NaCl from the evaporation-condensation technique, spark-discharge with argon and soot from diffusion flame (e.g. mini CAST generator). All these materials need investigation. For example, NaCl is sensitive to humidity and Ag can form spheres or fractals depending on the thermal pre-treatment. The mini CAST that can produce size distributions with means down to 7-10 nm has to be investigated, because the properties of such small soot particles and their effect on the counting efficiency of the PNCs is not well understood [11, 12].

The second point is the verification of the PNCs. While in the current legislation validation (or even calibration) is allowed with another reference PNC, if the lower size is reduced to 5 nm then the possibilities for a reference PNC with even lower cut-off size are reduced. On the other hand, the charging efficiencies of small particles are very low and the electrometers will measure low currents, close to their background level, increasing thus the calibration uncertainty.

FEASIBILITY OF SUB-23 NM MEASUREMENT FOR VPRs

This section will examine the issues for VPRs if the lower detectable size will be decreased; more specifically the losses in the VPRs (penetrations), formation of particles in the VPR (e.g. pyrolysis) and the volatile removal efficiency of the VPR.

Penetration (Losses In The VPR)

Ideally a VPR should have no particle losses. In this case the measured concentration is determined only by the PNC counting efficiency. However due to diffusion all VPRs have losses that increase with decreasing particle size. Different VPRs might also have different diffusion and thermophoretic losses and thus different penetrations curves. Typical penetration curves of VPRs are shown in Figure 3. Two of them are based on the minimum requirements of the World Harmonized Light Duty Test Procedures (WLTP) and the Air Recommended Practice (ARP) for sampling exhaust gas of aircraft turbines [13, 14]³. The PMP curve shows a typical curve for commercial VPRs with evaporation tubes (ET). The fourth curve is based on a prototype system based on ejector diluters. The prototype was the VPR that was used for the Round Robin exercise for the determination of the calibration procedures of the VPRs [15]. Approximately 10% losses were found down to 30 nm and diffusion losses were added for a case of a tube with 3 s residence time as allowed in the current legislation.

Figure 3 shows that for particles <23 nm the losses increase rapidly. Penetrations of 10 nm particles at the VPRs are between 15% and 40%, but could be 70% at prototype systems. Below 5 nm the penetration could practically be 0 for some systems. These results indicate that measurements below 10 nm are difficult and will have high uncertainty, because high correction factors are needed. For example, the measurement of a solid core mode with the existing systems will need a correction factor of at least 2.

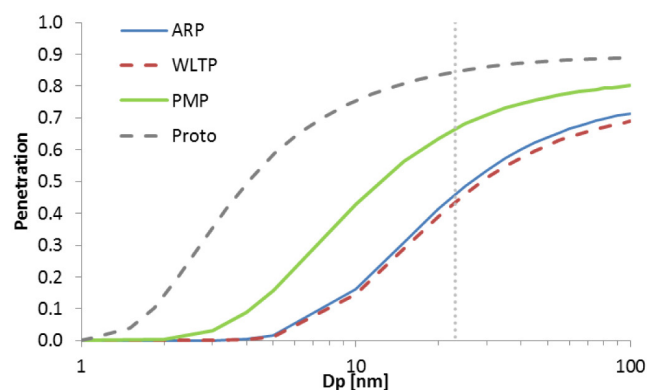


Figure 3. Typical penetration curves of VPRs and minimum requirements based on WLTP and ARP.

In order to take into account particle losses inside the VPR, legislation corrects the PNC measurements with a mean Particle number Concentration Reduction Factor (PCRF). This

3. Although not studied in detail, the aviation sector introduced a non-volatile particle number standard with lower cut-off size at 10 nm [13, 14]. However, the calibration procedures for the VPRs are different.

mean PCRF is determined by calibration of the VPRs with monodisperse solid particles of 30, 50 and 100 nm and concentration $>5000 \text{ p/cm}^3$. The ratios of 30 nm and 50 nm particles PCRFs have to be <1.3 and 1.2 times the 100 nm PCRF (see [Figure 1](#)). [Table A1](#) in the [Appendix](#) shows what a system reports compared to the true inlet concentration for different cases:

- **PMP-23:** PNC with $d_{50\%}$ at 23 nm and VPR with ratio 1.30 (30 to 100 nm) and 1.12 (50 to 100 nm). The 15 nm to 100 nm ratio is 2.21. The mean PCRF is calculated from the 30, 50 and 100 nm PCRFs.
- **Proto-23:** PNC with $d_{50\%}$ at 23 nm and VPR with ratio 1.28 (30 to 100 nm) and 1.09 (50 to 100 nm). In this case the 15 to 100 nm ratio is 1.55. The mean PCRF is calculated from the 30, 50 and 100 nm PCRFs.
- **PMP-10:** PNC with $d_{50\%}$ at 10 nm and VPR with ratio 1.30 (30 to 100 nm) and 1.12 (50 to 100 nm). The 15 nm to 100 nm ratio is 2.21. The mean PCRF is calculated from the 30, 50 and 100 nm PCRFs.
- **Proto-10:** PNC with $d_{50\%}$ at 10 nm and VPR with ratio 1.28 (30 to 100 nm) and 1.09 (50 to 100 nm). In this case the 15 to 100 nm ratio is 1.55. The mean PCRF is calculated from the 30, 50 and 100 nm PCRFs.
- **PMP-10,4x:** PNC with $d_{50\%}$ at 10 nm and VPR with ratio 1.30 (30 to 100 nm) and 1.12 (50 to 100 nm). The 15 nm to 100 nm ratio is 2.21. The mean PCRF is calculated from the 15, 30, 50 and 100 nm PCRFs.

PMP-23 and Proto-23 are systems with different VPR penetration curves (the 'Proto' and the 'PMP' in [Figure 3](#)). PMP-10 and Proto-10 are the two PMP systems with PNCs at 10 nm instead of 23 nm. PMP-10,4x is the PMP-10 system using the PCRF of 15, 30, 50 and 100 nm (extra 15 nm size for the PCRF determination).

As it can be seen in [Table A1](#) in the [Appendix](#), for systems with PNCs of 23 nm, the mean 30, 50 and 100 nm PCRF correction generally slightly (5-10%) underestimates the 'true' upstream emissions for typical vehicle size distributions with Count Median Diameter (CMD) between 50 and 70 nm but can slightly overestimate for bigger sizes (see PMP-23 and Proto-23 columns for 50-90 nm mean sizes). However, when the CMD of the size distributions is $<50 \text{ nm}$, the final result can be much lower compared to the actual PN concentration entering the VPR. Furthermore, different PN systems can exhibit around 5% differences in the PN results, even if they comply with the legislation requirements, due to the different VPR penetrations (compare PMP-23 and Proto-23 percentages). For more details see [\[16\]](#).

Considering the systems with 10 nm PNCs it can be observed (see PMP-10 and Proto-10 columns):

- For means 50-90 nm, the measured emissions are 5-10% higher compared to the 23 nm PN systems.
- The measured values are close to the true (inlet)

emissions, thus there is a small improvement compared to the 23 nm PNCs.

- The difference between different commercial systems remains around 5%.
- For means $<50 \text{ nm}$ higher percentage of the inlet distribution is measured compared to the PMP systems. The percentage is still low (18%-35% for a peak at 10 nm) but at least part of the core mode will be measured.
- However, the commercial systems will have higher differences between them and thus the measurement variability (reproducibility) will increase for cases with solid core modes.

If a lower cut-off size will be included in the legislation the main question that arises is whether the mean PCRF should also include a lower size. It can be observed from [Table A1](#) that the mean PCRF that includes the 15 nm results in $>50\%$ overestimation of the true PN emissions, assuming that the typical size distribution remain between 50 and 90 nm (see column PMP-10,4x). Thus, even when the lower cut-off size is reduced the mean PCRF determination should remain the same (i.e. it should be determined only at 30, 50 and 100 nm). This would also help keeping the same calibration procedures as in the past. A requirement for e.g. the 15 nm PCRF compared to the PCRF of 100 nm should be added nevertheless to ensure systems with minimum losses. Ideally this value should be <2 but a value of 2.2 seems also acceptable.

One other issue with the introduction of lower sizes is the aerosol that can be used for the calibration of the VPRs. Generally it is difficult to produce 10-15 nm (e.g. with atomized NaCl, CAST and spark discharge graphite generators) at adequate concentrations. Silver generators could be used, but with these generators it's very difficult to generate bigger particles (e.g. 100 nm). One generator that could be used for such wide range is the mini CAST generator. The thermal stability of the small nanoparticles however has to be ensured. It should be also realized that such small particles do not necessarily have the same properties as soot but are more PAH like due to the short residence time in the flame [\[17, 18\]](#).

Formation of Particles in the VPR

Some researchers [\[19, 20\]](#) suggested pyrolysis and/or charring of semi-volatiles in the evaporation tubes or the thermodenuders. This actually means formation of a solid core particle mode artifact, i.e. hydrocarbons will be counted as solid particles. The pyrolysis or charring of organic carbon that occurs during elemental carbon/organic carbon analysis depends on many factors, especially temperature, but also composition and amount; however at 300°C should be minimum [\[21\]](#). Alternatively, dehydration may be occurring where the sulfuric acid is removing hydrogens from the organic carbon, leaving just solid carbon that is measured in the particle phase. In this case, an analogous reaction is the well-known reaction of sucrose with strong sulfuric acid [\[22\]](#).

Another hypothesis is that n-alkanes are oxidized on the hot metal tube walls heterogeneously and then react with sulfuric acid to produce a non-volatile salt [20]. The explanation that sulfate is a precursor to solid particles is supported by the fact that experiments with pure hydrocarbon particles showed no solid particles and that formation of solid particles was only observed in the thermodenuder and not the catalytic stripper (CS) with sulfur trap [19]. The sulfur trap in the CS probably removed the sulfuric acid precursors that may be required for the solid particles to form. More studies are needed to thoroughly understand the mechanism of particle formation in the heated tubes and no conclusions can be drawn by the limited number of studies that mentioned this issue.

Volatile Removal Efficiency of the VPR

European regulations require hot (150°C) dilution at least 10:1 followed by an evaporation tube at 350°C. The volatile removal efficiency is checked at the lowest dilution setting with >30 nm tetracontane particles with concentration >10⁴ p/cm³. The volatile removal efficiency should be >99%.

Evaporation Tube (ET)

The following sections will discuss the following topics (theoretically and experimentally):

- Volatile removal efficiency of an evaporation tube (incomplete evaporation).
- Re-nucleation after an evaporation tube.

Evaporation

The residence time and the volatile particle concentration affect the removal efficiency, thus this method should be used downstream of a dilutor to avoid supersaturation and re-nucleation as the aerosol exits the evaporation tube and cools [23]. Experiments showed that 30 nm heavy alkane (tetracontane) particles can be removed with >99% efficiency in a heated tube with aerosol temperature >200°C, with decreasing efficiency for larger particles [23]. The evaporation is extremely fast (ms) thus the residence time in most evaporation tubes (>0.2 s) is enough. Experimentally it was shown that mass of 0.1 mg/m³ tetracontane could be removed [23] or even higher [24] for various PMP systems. Limited number of tests at different evaporation tube temperatures (300°C and 500°C) with real exhaust aerosol haven't shown any difference in the results of PNCs with d_{50%} at 3 nm indicating that the incomplete evaporation of the nucleation mode is not likely for diesel vehicles [25].

Re-Nucleation of Hydrocarbons

It was estimated that homogeneous nucleation of evaporated hydrocarbons (tetracontane) vapor at the evaporation tube exit can only occur at extremely high concentrations (>10⁷ p/cm³ 30 nm or 3 mg/m³) [23]. At lower concentrations, some condensation may occur onto the solid particles, but this will not affect the solid PN concentration.

A diesel vehicle without an oxidation catalyst could emit concentrations of organics up to 70 mg/m³ (e.g., [26]) although usually much lower concentrations are measured (e.g., 5 mg/m³ in [27]). Lower volatile emissions are expected for diesel engines with oxidation catalyst (<1 mg/m³) but can be much higher at higher speeds probably due to desorption of volatile material from the exhaust pipe walls (>4 mg/m³) [28]. During regeneration of Diesel Particulate Filters (DPF) high emissions of nucleation mode particles are observed. Hydrocarbons and sulfur compounds from fuel and lube oil that accumulate in the soot layer in a DPF are released during the high regeneration temperatures. Measurements of the emitted number distribution from the full dilution tunnel (CVS) during regeneration showed that the mean nucleation mode diameter can be up to 40 nm [29]. Estimates of the mass concentration of nucleation mode particles (assuming a density of 1 g/cm³) give >5 mg/m³.

From the previously mentioned values, the maximum value of 70 mg/m³ translates to a maximum mass concentration of 1.5 mg/m³ entering the evaporation tube (considering a dilution ratio of 5 at the full dilution tunnel and 10 at the primary diluter). This mass concentration is lower than the necessary for re-nucleation.

Mopeds (2-stroke) have much higher emissions of organics that can reach 700 mg/m³ [28]. This translates to >10 mg/m³ at the outlet of the evaporation tube. Such a high concentration can result in re-nucleation. Thus for mopeds a higher primary dilution is necessary (e.g. >100:1).

Re-Nucleation of Sulfuric Acid

An empirical equation can be used to determine the critical concentration C_{crit} (μg/m³) of gas-phase sulfuric acid that produces a binary H₂SO₄-H₂O nucleation rate of 1 p/cm³s [30]:

$$C_{crit} = 0.16 \exp(0.1 T - 3.5 RH - 27.7)$$

Where RH is the relative humidity (0 to 1) and T is the temperature in K. The empirical equation which fits the H₂SO₄-H₂O binary nucleation rate, predicts a critical mass concentration of the order of 0.7-3.5 μg/m³.

Emitted sulfate concentrations can reach 10 mg/m³ at high speeds when an oxidation catalyst is present and high sulfur fuel is used (280 ppm) [26]. If there is no oxidation catalyst sulfate emissions will be lower, e.g., a heavy-duty engine could emit 200 μg/m³ [31]. Thus, the maximum mass concentration at the evaporation tube inlet (after a dilution at the CVS and the primary diluter of the VPR of 5×10) should be less than 200 μg/m³ (with catalyst) or 4 μg/m³ (without catalyst) for vehicles with high sulfur contents. So re-nucleation of sulfuric acid is highly likely.

Assuming a sulfur content of 3-10 ppm for the fuel and 2000-10000 ppm for the lubricant, as well as an oil consumption equivalent to 0.1-0.2% of fuel, one estimates an engine-out SO₂ concentration in the range of 0.5-3 ppm.