

Sampling of Non-Volatile Vehicle Exhaust Particles: A Simplified Guide

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ABSTRACT

Recently, a particle number (PN) limit was introduced in the European light-duty vehicles legislation. The legislation requires measurement of PN, and particulate mass (PM), from the full dilution tunnel with constant volume sampling (CVS). Furthermore, PN measurements will be introduced in the next stage of the European Heavy-Duty regulation. Heavy-duty engine certification can be done either from the CVS or from a partial flow dilution system (PFDS). For research and development purposes, though, measurements are often conducted from the raw exhaust, thereby avoiding the high installation costs of CVS and PFDS. Although for legislative measurements requirements exist regarding sampling and transport of the aerosol sample, such requirements do not necessarily apply for raw exhaust measurements. Thus, measurement differences are often observed depending on where in the experimental set up sampling occurs.

The objective of this paper is to summarize and discuss particle loss mechanisms. Simple equations are given for the most important mechanisms. Topics like isokinetic sampling and agglomeration are discussed for various typical cases. Special emphasis is placed on thermophoretic losses since thermophoresis is the most important particle removal mechanism for raw exhaust sampling from modern engines. Sampling from high pressure exhaust gas is also mentioned, and comparisons of the effect of tubing materials on particle removal are carried out. Finally, expected losses for typical cases are shown.

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INTRODUCTION

The health effects of vehicle exhaust particles is a topic of great public concern and current multi-disciplinary investigations. Epidemiological (e.g., [1]) and toxicological studies (e.g., [2]) have associated urban air quality and air pollution, specifically particulate matter, with adverse health effects. Since vehicle exhaust particles constitute a significant percentage of anthropogenically emitted particles, legislation is in place worldwide to enforce a decrease of particle emissions from vehicles. Until recently, vehicles legislation required the determination of particulate mass (PM) emission over a specific test cycle, as measured from the filter weight increase when diluted vehicle exhaust was passed through a paper filter. However, this method reached its detection limit with the introduction of diesel particulate filters (DPF) [3, 4,

5]. Based on the studies of the Particle Measurement Programme (PMP) group (a programme that lasted approximately from 2001 until 2009) a new methodology was introduced in the European legislation to count non-volatile particles of diameter >23 nm [3, 6, 7]. As an immediate consequence, particle number (PN) concentration measurements became widespread in the automotive industry.

Light-duty vehicles legislation requires measurement of PN (and PM) from the full dilution tunnel with constant volume sampling (CVS). Heavy-duty engine certification can be done either from the CVS or from a partial flow dilution system (PFDS). For research and development purposes PN measurements have become an additional routine measurement. However, to avoid the high installation costs of

CVS and PFDS, measurements are frequently conducted from the raw exhaust. Although for legislative measurements certain requirements regarding the sampling and transport of the aerosol sample are specified (laminar flow, residence time until the PN system <3 s), no specifications exist for sampling from the raw exhaust. Inaccurate sampling and transport of the aerosol from the sampling location to the measurement instrument may lead to high particle losses [8] and incorrect results. Additionally, intrinsic aerosol processes (e.g., agglomeration) render the comparison of results obtained at different sampling locations (e.g., CVS and tailpipe) difficult.

The aim of this paper is to summarize, discuss, and quantify via simple equations the most important loss mechanisms associated with sampling particle emissions from modern engines. Special emphasis is given to thermophoretic losses. Topics like isokinetic sampling are discussed for various typical sampling layouts. Sampling from high pressure exhaust gas, other transport losses, and the effect of tubing are discussed. Finally, expected losses for typical cases are described. By applying the equations given herein it is possible to select the most appropriate sampling setup, and to estimate the emissions that would be measured from a CVS, based on tailpipe measurements.

THEORETICAL CONSIDERATIONS

The literature on the aerosol processes that lead to particle deposition is large, covering almost all cases that can be observed in practice [9, 10, 11]. In this brief report, a short summary of the main processes will be given, accompanied by simple equations that can be easily applied to most cases. Although particle losses calculators exist (e.g., [10, 12, 13, 14]), their application is not always straightforward. This section discusses the particle loss mechanisms that may modify PN and PM concentrations from the emission location to the inlet of the measurement instrument. They may be divided in two categories:

- *Sampling*, which includes losses due to anisoaxial and anisokinetic extraction of the aerosol at the sampling location,
- *Transport*, which includes losses due to internal processes (like agglomeration) and external processes (like diffusion and thermophoresis) that may occur from the sampling location to the measuring instrument.

The effect of each process is given in terms of the penetration fraction; i.e., the percentage of the inlet concentration that passes through a fixed element (e.g., sampling probe, tube), or, the ratio of the particle number concentration before and after the element. The total penetration fraction through the sampling system P is the product of the penetration fractions for each deposition mechanism.

$$P = P_{\text{sampling}} P_{\text{transport}} = P_{\text{anisok}} P_{\text{anisoaxial}} P_{\text{pressure}} P_{\text{agglom}} P_{\text{diff}} P_{\text{bend}} P_{\text{therm}} \quad (1)$$

Simple equations that can be used to calculate the total penetration will be given in the following sections. Mechanisms that do not contribute significantly (e.g. gravitational) or could result to extremely high losses (e.g. electrostatic losses) will be only discussed and not analyzed. Particle losses are generally a function of the aerodynamic particle diameter for mechanisms that depend on the inertia of the particles (sampling and bends), but mechanisms like diffusion, thermophoresis and electrostatic deposition depend on the mobility diameter: henceforth, particle diameter will refer to the appropriate particle diameter for each mechanism.

SAMPLING

Sampling penetration describes the fraction of particles that enter the sampling probe from the air surrounding it and successfully reach the transport tubing. In ideal situations sampling is isoaxial and isokinetic. Anisokinetic sampling is examined first, followed by anisoaxial sampling, and, finally, sampling at high pressures.

Anisokinetic Sampling

Sampling is isokinetic when the inlet axis of the probe is aligned parallel to the gas streamlines and the gas velocity entering the probe equals the gas free-stream velocity approaching the inlet [9]. The stream velocity has to be measured (or estimated) before the inlet of the probe; here for simplicity we use the mean velocity v of the stream. Details for more accurate calculations can be found in [Appendix A](#) [15, 16, 17]. Anisokinetic sampling occurs when the velocity in the probe differs from the free-stream velocity. If sampling is not done isokinetically (i.e., anisokinetic sampling), the concentration may not be determined accurately and the size distribution may be distorted. The penetration (over- or underestimation) may be calculated from [9]:

$$P_{\text{anisok}} = 1 + \left(\frac{v_o}{v_s} - 1 \right) \left(1 - \frac{1}{1 + (2 + 0.62 v_s / v_o) Stk} \right) \quad (2a)$$

where v_o [m/s] is the free-stream velocity, v_s [m/s] is the sampling probe velocity and Stk [-] is the Stokes number given by:

$$Stk = \frac{\rho_p d_p^2 v_o C_c}{18 \eta D_s} \quad (2b)$$

where ρ_p [kg/m³] is the particle material density, d_p [m] is the particle diameter, D_s [m] is the sampling probe diameter and C_c [-] is the Cunningham slip correction factor (see Eq. C4 in

Appendix C). Henceforth, the notation [...] refers to a variable's units; [–] refers to a dimensionless variable. Note that the calculated Stokes number is based on the free-stream flow velocity. The range of validity of this formula is: $0.18 < Stk < 2.03$ and $0.17 < v_o/v_s < 5.6$, although we will use it beyond its validity range, and more specifically for lower Stk numbers. Sampling is considered subisokinetic when $v_o/v_s > 1$ and superisokinetic when $v_o/v_s < 1$.

Table 1a gives typical dimensions of full dilution tunnels (CVS) for light-duty (LD) vehicles and heavy-duty (HD) engines. Based on typical temperatures and flows for the CVS and sampling probe, the mean velocities v were calculated. Penetrations for typical PN and PM cases for LD vehicles and HD engines were determined using the mean velocities. Accordingly, sampling is typically done subisokinetically with ratios $v_o/v_s = 1.4$ – 4.1 for PN, whereas it is superisokinetic for PM (ratios 0.3 – 0.9). However, based on the calculated Stokes numbers ($Stk \sim 10^{-3}$ – 10^{-4}) the over- or underestimation of PN or PM penetrations is negligible, even for particles up to $1 \mu\text{m}$ diameter (within 2% for all cases).

Table 1b gives typical velocities and penetrations for raw exhaust sampling for typical LD and HD exhaust flow rates and for some extreme cases (i.e., accelerations). They were also calculated using the mean velocities. Sampling is subisokinetic with ratios $v_o/v_s = 2.2$ – 12.5 , leading to penetrations up to 140% (for $1 \mu\text{m}$ particles). However, for 100 nm particles even the extreme case leads to a penetration of only 102%; thus, the effect of anisokinetic sampling is negligible. These results are in agreement with previous findings. Reference [18] estimated that deviations from isokinetic sampling are insignificant for number concentrations during the cycle for light duty vehicles (only ~4% higher number concentration was recorded at maximum deviation, ratio 1.32). However, these deviations may still be important for volume concentrations because they relate mainly to large particles (~25% higher volume concentration recorded at maximum deviation). References [19] and [20] calculated that significant sampling errors still arise for small Stokes numbers when the velocity mismatch is large (up to 30% for $1 \mu\text{m}$ particles). The key message is that anisokinetic sampling has negligible effect on PN when sampling is conducted from the CVS. For PM measurements it seems that tailpipe measurements overestimate emissions with respect to measurements in full flow dilution systems, unless there is a pre-classifier (hat or cyclone), a topic that is examined in the following subsection. Note, also, that this discussion is based on a probe with elbow that is placed in the main stream (see Figure A2 in Appendix A). If a probe with a 45° cut at the end is placed, then, based on simulations, sampling is conducted from the top 45° cut and has a significant recirculation zone [21]. In this case penetration might be different.

Table 1a. Typical velocities and penetrations of $d_p = 1 \mu\text{m}$ particles (density 1000 kg/m^3) due to anisokinetic and anisoaxial ($\Theta = 90^\circ$) sampling in the full dilution tunnel (CVS). Q is the flow rate, D is the diameter, t is the temperature, v is the mean velocity, and Re is the Reynolds number. The subscript “o” refers to the CVS and the subscript “s” refers to the sampling probe.

CVS	Light-Duty		Heavy-Duty	
	PM	PN	PM	PN
Q_o [m^3/min]	10	10	80	80
D_o [mm]	300	300	500	500
t_o [$^\circ\text{C}$]	47	47	47	47
v_o [m/s]	2.6	2.6	7.4	7.4
Re_o	44000	44000	211000	211000
Q_s [L/min]	50	5	50	5
D_s [mm]	12	8	12	8
t_s [$^\circ\text{C}$]	47	47	47	47
v_s [m/s]	8	1.8	8	1.8
Re_s	5500	820	5500	550
$Stk \times 10^{-3}$	0.7	1.0	2.1	3.1
v_o / v_s	0.3	1.4	0.9	4.1
P_{anisok}	99.8%	100.1%	100.0%	102.1%
$P_{anisoaxial}$	99.7%	99.6%	99.2%	98.8%

Table 1b. Typical velocities and penetrations of $d_p = 1 \mu\text{m}$ particles (density 1000 kg/m^3) due to anisokinetic and anisoaxial ($\Theta = 90^\circ$) sampling from the raw exhaust. Q is the flow rate, D is the diameter, t is the temperature, v is the mean velocity, V is the max velocity and Re is the Reynolds number. The subscript “o” refers to the raw exhaust and the subscript “s” refers to the sampling probe.

Raw	Light Duty		Heavy Duty	
	mean	max	mean	max
Q_o [m^3/min]	0.85	2.5	4.5	22
D_o [mm]	70	70	150	150
T_o [$^\circ\text{C}$]	200	350	300	550
v_o [m/s]	5.9	23.0	8.3	58.1
Re_o	12000	29000	26000	100000
Q_s [L/min]	5	5	5	5
D_s [mm]	8	8	8	8
t_s [$^\circ\text{C}$]	200	350	300	550
v_s [m/s]	2.7	3.5	3.2	4.6
Re_s	620	510	540	430
$Stk \times 10^{-3}$	2.0	7.2	2.7	17.0
v_o / v_s	2.2	6.5	2.6	12.5
P_{anisok}	100.6%	108.2%	100.9%	138.8%
$P_{anisoaxial}$	99.2%	97.2%	98.9%	93.5%

Anisoaxial Sampling

Anisoaxial sampling occurs when the velocity direction is different from stream velocity. For misaligned probe ($0^\circ < \Theta < 90^\circ$) and sampling conditions such that $0.01 < Stk < 6$ and correct (isokinetic) flow rate (we will use this equation also beyond its validity range) [9]:

$$P_{anisoaxial} = 1 + (\cos \Theta - 1)Z \quad (3a)$$

$$Z = \left(1 - \frac{1}{1 + 0.55Stk' \exp(0.25Stk')} \right) \quad (3b)$$

$$Stk' = Stk \exp(0.022\Theta) \quad (3c)$$

Tables 1a&b give the penetration (over- or underestimation) due to anisoaxial sampling and a probe at 90° for $1 \mu\text{m}$ particles. The underestimation is negligible for the typical CVS cases (Table 1a) and can be up to 7% for raw exhaust sampling during accelerations (Table 1b).

Tee Sampling

Anisoaxial sampling is sometimes done due to space restrictions. For example, PN sampling from some proportional partial flow dilution systems (PFDS) is conducted without a probe in the mini tunnel at a 90° angle (anisoaxial) because there is not enough space for a separate probe inside the mini tunnel (this sampling is typically called tee sampling, see Figure A2 of Appendix A). As the above equations show, the effect is negligible for particles $< 1 \mu\text{m}$. It should be noted, however, that simulations show that when there is no probe, the sample is taken from very near the wall of the mini tunnel, and thus it has to be ensured that the aerosol is spatially homogeneously mixed (see next section). In addition, there is a large re-circulation zone just inside the entrance of the sample tube [21]. If a straight (blind) pipe is used (see Figure A2 of Appendix A), the flow is similar to a tee, namely there is a smaller re-circulation zone and the sampled flow comes from slightly above the end of the sample tube [21].

Hat Sampling

Anisoaxial sampling is sometimes deliberately done in order to remove large particles from the flow or to alleviate effects due to backpressure and pressure pulsations. This can be achieved with a covered sampling probe (hat) or a probe not facing the flow. According to Eqs. 3, the 50% cut-point of the PM measurements with a hatted probe from the CVS with a sampling flow rate of 50 L/min, a 12 mm diameter tube and four $\Theta=90^\circ$ bends is estimated to be $5 \mu\text{m}$. In [22] they found 5% lower PM emissions from a Euro 3 LD vehicle for tests conducted in a CVS when the CVS sampling probe had a hat (the differences, however, were not statistically significant).

The pre-classifier is important for DPF engines, where emissions are very low, and re-entrainment of large particles (in the range of $20 \mu\text{m}$, [22, 23]) can result in higher deposited mass on the filter, thus affecting results and repeatability.

When the sampling flow rate is 5 L/min (e.g., a PN measurement system connected to the CVS) the 50% cut-point of the hatted probe is $15 \mu\text{m}$, instead of $5 \mu\text{m}$ with a 50 L/min flow rate. The 50% cut-point could decrease to $< 10 \mu\text{m}$ if a 8 mm diameter tube were used. As shown experimentally in [24] for a LD vehicle and in [25] for a HD engine, a pre-classifier (hat or cyclone) doesn't affect PN measurements. However, it protects measurement systems from contamination, especially those PN systems using orifices to control flows or dilution ratios.

For a HD engine with PM emission levels around 50 mg/kWh no statistically significant differences were found for a PFDS connected to the tailpipe with an open 45° probe, a probe not facing the flow, a probe with hat and a multihole probe (see Figure A2 in Appendix A for probe schematics). The open probe tests, however, gave slightly higher results [26], in agreement with the subsokinetic sampling typically done from raw exhaust as discussed in the previous section.

Note that similar results and conclusions would be drawn by using the penetration equations for bends (see Eqs. 6) or other equations for anisokinetic sampling (see e.g. [26]). The differences of the calculated 50% cut-points are 2-5 μm depending on the equation used.

Cyclone

An alternative instrument to remove larger particles is the cyclone. Air flows in a spiral pattern, beginning at the top (wide end) of the cyclone and ending at the bottom (narrow) end (Figure B1 in Appendix B). Then it exits from the top of the cyclone in a straight stream through the center. Larger (denser) particles in the rotating stream have too much inertia to follow the tight curve of the streamlines and strike the outside wall, falling to the bottom of the cyclone where they can be removed. Figure 1 shows typical penetration curves for a cyclone at different flow rates based on the theory given in [28, 29, 30] (see Appendix B for equations). This theory was chosen for its simplicity. Other theories give slightly different results, but the trends are always the same: The higher the flow rate, the lower the 50% cut-point (Figure 1). When an aerosol with higher temperature (than the design nominal cyclone temperature) enters the cyclone, the 50% cut-point moves to higher sizes due to the different gas viscosity.

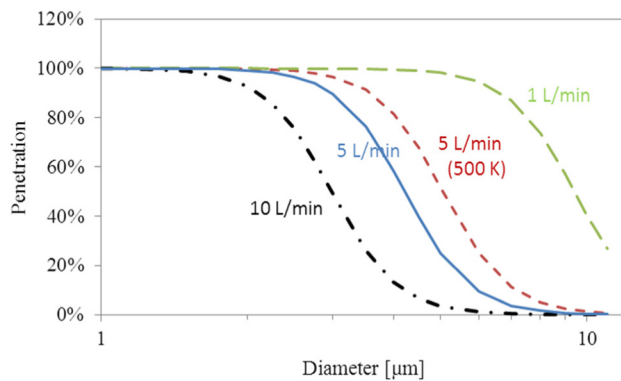


Figure 1. Typical penetration curves of a cyclone for different inlet flow rates at 300 K (unless otherwise specified).

Inhomogeneous Aerosol Concentration

One basic assumption when sampling is conducted from the centerline of the tube is that the concentration of the aerosol is (spatially) homogeneous. This is typically the case when sampling is conducted 10 diameters downstream of bends or obstructions and the flow is turbulent (for small Stokes-number particles). In the short exhaust duct section between the turbo charger and the first oxidation catalyst or diesel particulate filter (DPF), which usually has several bends and no straight sections, it is possible that the flow is not yet fully mixed and the particulate concentration is not (spatially) homogeneous across the cross section of the duct. In that case, the PN concentration at different points of the same cross section might be different. For example, sampling with two standard probes at a distance of only ~ 3 cm and at the same cross section of a 90° bend (of inner diameter ~ 11 cm) approximately 15 cm behind the turbo charger showed 30-50% differences of soot mass concentrations (AVL internal data measured with a Micro Soot Sensor [31]). In such cases, sampling from many points of the duct cross section is recommended [32] (e.g., using many probes or a multihole probe, see Figure A2 in Appendix A). This topic has to be taken seriously into account for measurements upstream or downstream of aftertreatment devices, since the results might not be representative due to spatially inhomogeneous aerosol concentration.

Sampling Exhaust Gas at High Pressure

Most measurement systems have an inlet pressure margin of the order of ± 200 mbar. However, upstream of DPFs higher pressures can be encountered. For such cases, devices that reduce the pressure to ambient levels are recommended. Figure 2 shows a diagram of the AVL Pressure Reducing Unit [31]. Pressure reduction and/or conditioning of the exhaust gas are carried out by routing the exhaust gas into an expansion pipe (where approximately ambient pressure prevails) through a flow restriction. In order to blow off enough exhaust gas even with lower exhaust gas

backpressures (typically >10 mbar), a plate with angled sides and with a central orifice is elastically supported on a matching truncated cone. At lower pressures the inlet channels between the sides of the plate with the orifice and the outer surface of the truncated cone are open. When the exhaust gas backpressure is increased, the inlet channels are reduced. If the exhaust gas backpressure reaches a certain value (typically >200 mbar relative), the inlet channels around the plate close and the exhaust gas can only flow into the expansion pipe through the central orifice of the plate. The instruments sample from the expansion chamber. Typically the pressure reducing unit is connected to the raw exhaust with a sampling probe (e.g., a multihole probe is preferred because an inhomogeneous particle concentration is likely in high pressure exhaust regions due to the restricted space and non-ideal geometry).

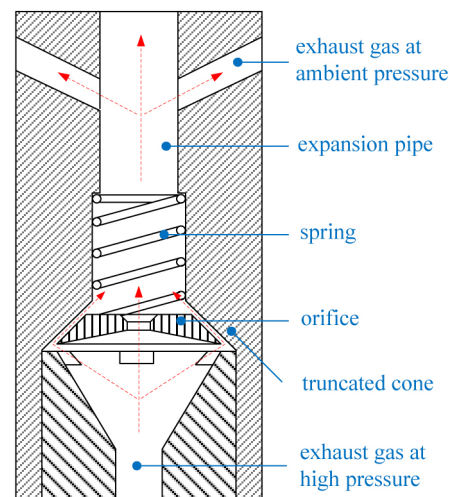


Figure 2. Diagram of the Pressure Reducing Unit [31].

Figure 3 shows measured particle losses in the Pressure Reducing Unit for up to 1 bar exhaust gas overpressure. They were determined as follows: One PN measurement system was connected to the Pressure Reducing Unit with a heated line at 150°C and another to the CVS, the latter being the reference instrument. The tests were conducted with a 1.6 L, Gasoline Direct Injection engine (#2) and a 1.9 L, four cylinder, light-duty diesel engine (#1) with different exhaust gas pressures (throttling the exhaust gases). For each test the difference between the two PN systems was calculated. Mean losses were around 15%, and almost independent of the exhaust gas pressure (Figure 3). The exhaust gas temperature was $<300^\circ\text{C}$, and therefore these losses include thermophoretic losses of ~ 5 -10% (see below). The thermophoretic losses were also determined experimentally for the low overpressure points by connecting the PN system directly (with the heated line at 150°C) to the tailpipe and comparing it to the PN system connected to the CVS. They were in good agreement with theoretical predictions (see section that discusses about thermophoresis).

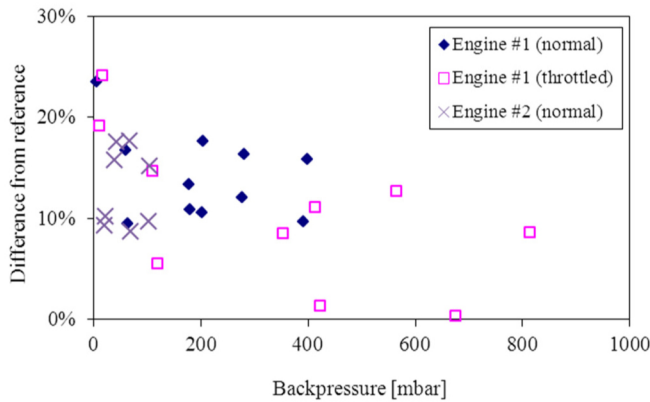


Figure 3. Losses with the Pressure Reducing Unit over a higher range of overpressures at the exhaust.

TRANSPORT LOSSES

The characteristics of aerosols flowing in a duct, in particular in sampling tubes of measuring instruments, change due to internal processes like coagulation/agglomeration, fragmentation, and gas-to-particle conversion, processes that also occur in stationary aerosols, or due to external processes like convective diffusion and thermophoresis, etc. [33].

Particle Dynamics (Internal Processes)

Figure 4 summarizes the most important particle transformation mechanisms that can affect the particle number or the mass concentration. Recommendations for better sampling and transport approaches are also given [11]. A short explanation follows.

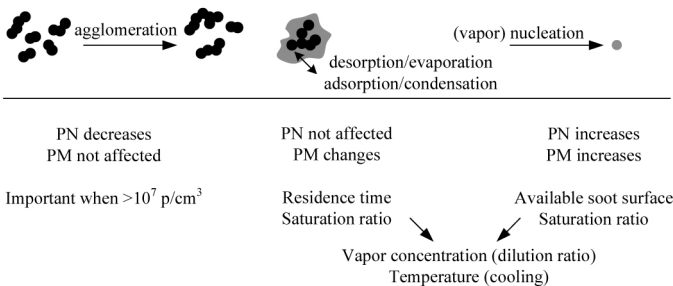


Figure 4. Particle dynamics and transformation (internal processes).

Agglomeration is a coagulation process arising from particle-particle collisions where the colliding particles retain their identity and shape. Agglomeration (and coagulation) changes the number concentration and size of particles (Eqs. 4), but it does not change the total particle mass concentration. Thus, it does not modify directly the results of certification tests that measure PM emissions. As agglomeration changes the particle size, it influences indirectly size dependent loss mechanisms (see next section).

The extend of agglomeration depends on the initial particle concentration and, to a smaller degree, on particle size.

The number concentration $N(\tau)$ [p/cm³] of an initially monodisperse distribution of spherical particles that coagulate thermally (due to their Brownian motion) with a constant coagulation kernel (coefficient) K [m³/s] changes with time as [9]

$$N(\tau) = \frac{N_o}{1 + N_o K \tau} \quad (4a)$$

and the particle diameter $d_p(\tau)$ [nm] as

$$d_p(\tau) = d_{p,o} (1 + N_o K \tau)^{1/3} \quad (4b)$$

at time τ [s]. N_o [p/cm³] and $d_{p,o}$ [nm] are the initial particle concentration and diameter, respectively. For Brownian coagulation of arbitrary size particles, the continuum kernel K is modified by the dimensionless Fuchs interpolation factor β [–] [9, 34]:

$$K = 4\pi d_p D_{diff} \beta \quad (5)$$

where D_{diff} [m²/s] is the particle diffusion coefficient (see Eq. C3 in Appendix C). The coagulation kernel is approximately 1×10^{-15} m³/s for 10-100 nm particles. Table 2 gives the coagulation kernel K_{mono} for monodisperse distributions, and an approximate expression K_{poly} for polydisperse distributions. The latter was obtained by averaging the kernel over the initial polydisperse distribution. In [35] it was shown that K_{poly} provides a reasonable approximation of the time evolution of the total number concentration of an initially polydisperse distribution, especially at short times.

Table 2. Coagulation coefficients for monodisperse aerosol of size d_p , polydisperse aerosol with Count Median Diameter (CMD) and standard deviation σ assuming spheres of density 1 g/cm³.

Monodisperse		Polydisperse		
d_p [nm]	K_{mono} [m ³ /s]	CMD [nm]	σ	K_{poly} [m ³ /s]
10	9.56×10^{-16}	10	1.3	9.60×10^{-16}
20	1.17×10^{-15}	20	1.4	1.14×10^{-15}
30	1.17×10^{-15}	30	1.6	1.10×10^{-15}
40	1.10×10^{-15}	40	1.7	1.04×10^{-15}
50	1.01×10^{-15}	50	1.8	9.67×10^{-16}
70	8.70×10^{-16}	70	1.9	8.59×10^{-16}
90	7.66×10^{-16}	90	2.0	7.79×10^{-16}

Figure 5 shows the variation of the fraction of final to initial particle concentration ($N(\tau)/N_o$, a quantity akin to the penetration fraction P_{agglom}) with time, parameterized by

various initial concentrations. The concentration remains almost constant at low initial concentrations ($<10^7$ p/cm³) but it may reduce significantly at higher concentrations. Legislation permits residence time between the CVS and the PN system up to 3 s. A concentration of 10^8 p/cm³ for 50 nm particles decreases by 23% in 3 s, and the particle diameter increases by 4.6 nm. Agglomeration was found to be important for vehicles without DPF, but negligible for the modern DPF equipped vehicles [35]. For example, even during cold start, where a number concentration of $<10^6$ p/cm³ is expected, the decrease of the 50 nm concentration is 0.3% (in 3 s).

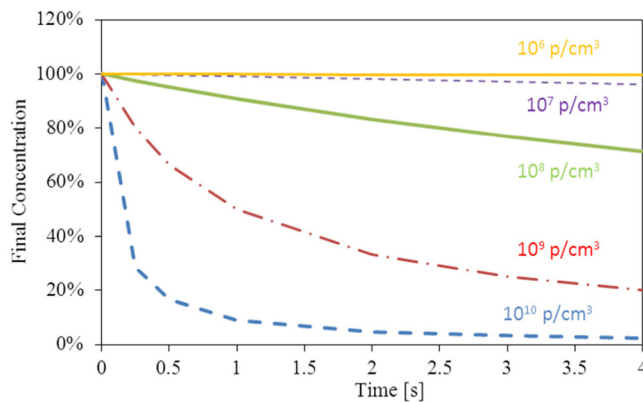


Figure 5. Effect of agglomeration on particle number concentration ($K=10^{-15}$ m³/s).

Adsorption is the transfer of gas or vapor molecules from the surrounding gas by sticking to a solid surface, while *condensation* is the growth of a particle due to the net accumulation of vapor molecules at a particle's surface. *Heterogeneous nucleation* is the formation of a liquid or solid coating on pre-existing particles (condensation nuclei). While condensation requires ambient supersaturation to occur, adsorption can occur even at pressures of the volatile material well below saturation. *Desorption* and *evaporation* are the opposite processes. The amount of organics adsorbed or condensed on diesel particles depends mainly on their saturation ratios (thus, their concentrations and ambient temperature), the amount of aerosol surface area available for adsorption, and the time available to adsorb. These phenomena do not affect PN number concentration. They can, however, affect PN measurements indirectly because they modify the particle size and, consequently, particle removal processes (see next section). The mass of the adsorbed and condensed material can affect PM measurements. For modern vehicles with oxidation catalysts the condensed material forms a thin layer of 0.5 nm approximately and it consists $<10\%$ of the total mass of the particles [36].

Adsorption of gas molecules can also occur on the fibers of the paper filter, the well-known 'filter artifact' [37]. Although not a particle effect in the strict sense, it can affect

the PM results. The filter artifact can be up to 2 mg/km or mg/kWh and depends, among others, on the filter material, teflon giving smaller artifact. In the past, the effect was negligible. For modern DPF equipped engines the filter artifact is higher than the true emissions of the engines [3, 5].

Finally, re-vaporization or desorption of semi-volatile species from the surfaces of the tubing due to hot exhaust gas may occur, affecting the mass results. The effect is usually of the order of a few $\mu\text{g}/\text{km}$, but an effect of up to 0.5 mg/km has been reported [38]. Desorption and re-vaporisation can also affect the number concentration through homogeneous nucleation after cooling and dilution.

Homogeneous nucleation is the formation of droplets in the absence of condensation nuclei. High saturation ratios (and insufficient available particle surface area) are necessary for homogeneous nucleation to occur. Nucleation shouldn't affect the legislated PN measurement of non-volatile particles because a PN measurement system conforming to the European legislation is designed to evaporate and possibly desorb all volatile and semi-volatile species below the 50% cut-point diameter of the Condensation Particle Counter (CPC) of 23 nm. The contribution of nucleation mode mass on PM results can be important. For example, for DPF-equipped vehicles it can be about 0.5 mg/km during regenerating cycles, a value that is similar to typical PM emissions of this category of vehicles [39].

Particle Losses (External Processes)

Figure 6 summarizes the most important loss mechanisms that affect both particle number and mass concentration. Recommendations for sampling approaches to avoid or reduce these loss mechanisms have been published [11, 40]. Moreover, losses calculators can be found in the literature (e.g., [10, 12, 13]). A short explanation follows.

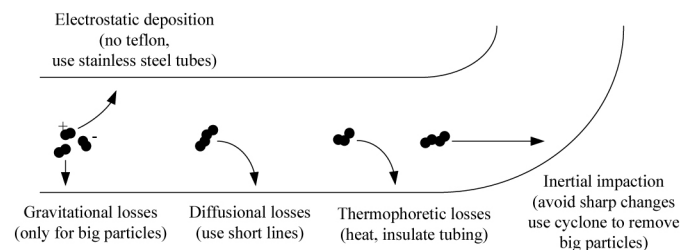


Figure 6. Mechanisms of particle loss (external processes).

Electrophoresis is the motion of a charged particle induced by an electric field. Electrostatic deposition can occur in sampling systems whose sample transfer lines are made of a material where electric charge can build up. Combustion generated exhaust gas particles of 100 nm size are approximately 20% positively charged, 30% negatively, and 50% neutral (these values depend on particle size, [41]). If a sampling line carrying particles is charged, the resulting electric field will deposit a portion of them, thereby removing them from the gas stream. It is, thus, highly recommended