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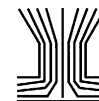
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Measurement of Automotive Nonvolatile Particle Number Emissions within the European Legislative Framework: A Review

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In 2011, the European Commission introduced a limit for non-volatile particle number (PN) emissions > 23 nm from light-duty (LD) vehicles and the stated intent is to implement similar legislation for on-road heavy-duty (HD) engines at the next legislative stage. This paper reviews the recent literature regarding the operation-dependent emission of PN from LD vehicles and HD engines, and the measurement procedure used for regulatory purposes. The repeatability of the PN method is of the order of 5% and higher scatter of the results can easily be explained by the effect of the vehicles or the aftertreatment devices on the PN emissions (e.g., the fill state of the diesel particulate filters). Reproducibility remains an issue since it may exceed 30%. These high-variability levels are mainly associated with calibration uncertainties of the PN instruments. Correlation measurements between the full-flow dilution tunnels (constant-volume samplers, CVS) and the proportional partial-flow dilution systems (PFDS) showed agreement within 15% for the PN method down to 1×10^{11} p/kWh. At lower concentrations, the PN background of the CVS and/or the PFDS can result in larger inconsistencies. The filter-based particulate matter (PM) mass and the PN emissions correlate well down to 1–2 mg/km for LD vehicles and to 2–3 mg/kWh for HD applications. The correlation improves when only elemental carbon mass is considered: it is relatively good down to 0.1–0.3 mg/km or mg/kWh.

ACRONYMS AND ABBREVIATIONS

ACEA	Association des Constructeurs Européens d'Automobiles (European Automobile Manufacturers' Association)
AM	Accumulation mode
APC	AVL particle counter

ASTRA	Bundesamt für Strassen (Swiss Federal Office for Roads)
AUVA	Allgemeine Unfallversicherungsanstalt (Austrian Social Insurance for Occupational Risks)
BUWAL	Bundesamt für Umwelt, Wald und Landschaft (Swiss Federal Office for Environment, Forests and Landscape)
CARB	California Air Resources Board
CAST	Combustion Aerosol Standard
CE	Counting efficiency
CMD	Count median diameter
CNC	Condensation nucleus counter
CO	Carbon monoxide
CoV	Coefficient of variance
CPC	Condensation particle counter
CVS	Constant-volume sampler
d_{50}	50% cut-point
D	Diesel
DEED	Dekati engine exhaust diluter
DF	Dilution factor
DI	Direct injection
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
E	Filtration efficiency
EEPS	Engine Exhaust Particle Sizer
EPA	Environmental Protection Agency
ESC	European Steady Cycle
ETC	European Transient Cycle
EU	European Union
FA	Filter artifact
G	Gasoline
GPF	Gasoline particulate filter
HC	Hydrocarbons
HD	Heavy duty
HEPA	High-efficiency particle filter

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LD	Light duty
LEV	Low-emission vehicles
LNC	Lean NO _x catalyst
LNT	Lean NO _x trap
MAAP	Multiangle absorption photometer
MFC	Mass flow controller
MSS	Micro soot sensor
NEDC	New European Driving Cycle
NIST	National Institute of Standards and Technology
NM	Nucleation mode
NO _x	(Mono)-nitrogen oxides
N ₂ O	Nitrous oxide
OM	Organic matter
P	Penetration
PCRF	Particle concentration reduction factor
PFDS	Partial-flow dilution system
PFI	Port fuel injection
PM	Particulate matter
PMP	Particle Measurement Program
PN	Particle number
PNC	Particle number counter
PND	Particle number diluter
POC	Particle oxidation catalyst
PTS	Particle transfer system
RT	Residence time
SCR	Selective catalytic reduction of NO _x
SO ₂	Sulfur dioxide
SO ₃	Sulfur trioxide
SMPS	Scanning mobility particle sizer
SPC	Solid particle counter
SPCS	Solid particle counting system
SUVA	Schweizerische Unfallversicherungsanstalt (Swiss Accident Insurance Fund)
TBG	Tiefbau – Berufsgenossenschaft (German Association of Construction Engineers)
UBA	Umweltbundesamt (German Federal Environmental Agency)
UNECE	United Nations Economic Commission for Europe
VERT	Verification of Emission Reduction Technologies
VPR	Volatile particle remover
WHSC	World Harmonized Steady Cycle
WHTC	World Harmonized Transient Cycle

1. INTRODUCTION

The health effects of vehicle exhaust particles is a topic of great public concern and of current multidisciplinary investigations, as epidemiological (Pope, 2000) and toxicological studies (Oberdörster, 2000) have associated urban air quality and air pollution, and specifically particulate¹ matter (PM), with ad-

verse health effects. Vehicle exhaust particles have long been considered as a significant source of anthropogenically generated particles, stimulating regulation authorities across the globe to control the levels of emitted particles. Past legislation was initially based upon black smoke levels and, over the last 30 years or so, by gravimetric quantification of PM deposited on to a filter, from a diluted exhaust sample extracted over a specific test cycle driven on a chassis dynamometer (Berg 2003).

Pioneering studies by Oberdörster (1996) and Donaldson et al. (1998) suggested that the inflammatory response to particles from nontoxic materials correlates better with the particle surface area rather than the mass. Thus, over the years, the interest has gradually shifted to other metrics than mass, driven by a number of health effect studies, suggesting that ultrafine particles, particles whose diameter is <100 nm, are potentially more hazardous than fine particles, particles whose diameter < ~2.5 µm (Ferin et al. 1992; Seaton et al. 2010). However, up to date, the available and rather limited information is still inadequate for a clear causality determination of ultrafine particles and adverse health effects (Environmental Protection Agency [EPA] 2009). In the most extensive and current review of the literature (EPA 2009), EPA found that for short-term and long-term exposures to PM, the determination of causality for adverse health outcomes is still best linked to PM size <2.5 µm.

The concerns on the potential size-dependent toxicity of particles have stimulated a significant research work since the mid-90s on the characterization of the particle number (PN)-weighted size distributions of internal combustion engines' exhausts. The spark however was given by a 1996 study indicating that newer engine technologies designed for low-mass emissions might generate higher-number emissions than older engines (Bagley et al. 1996). This observation was supported from tests with even newer engines equipped with diesel particulate filters (DPFs) (Vaaraslahti et al. 2004a), but not always (Kittelson et al. 2002; 2006a; Herner et al. 2011).

The main reason for these controversial findings relates to the sensitivity of the secondary particles forming from gaseous precursors on the sampling and dilution approach. The nucleation rate of these secondary, volatile particles was found to depend strongly on the dilution conditions (Khalek et al. 1998; 1999; Mathis et al. 2004), adsorption/desorption phenomena in the sampling lines (Maricq et al. 1999c), the amount of soot core that could promote condensation instead of nucleation (Khalek et al. 1998; Vouitsis et al. 2004), the aftertreatment devices (Herner et al. 2011), their preconditioning and pre-history (Giechaskiel et al. 2007a; Swanson et al. 2009), and the fuel and the lubricant (Kittelson et al. 2008), among others. Under favorable conditions, the number concentration of these secondary particles can exceed that of solid, primary particles by several orders of magnitude (Kittelson 1998). Chase study tests (i.e., following the exhaust of a vehicle) (Giechaskiel et al. 2005; Rönkkö et al. 2006; Casati et al. 2007; Sogawa et al. 2007) verified that these particles are also formed in the atmosphere under real-world driving conditions, while the use of appropriate sampling conditions in the laboratory (i.e., dilution air temperature 18–32°C

¹The term *particle* is conventionally used for the matter being characterized (measured) in the airborne phase (suspended matter), and the term *particulate* for the deposited matter, according to the definitions in the European regulation. The letter 'p' will be used to refer to 'particles' in the graphs.

and dilution factor [DF] 10–25:1; Mathis et al. 2004; Rönkkö et al. 2006; Sogawa et al. 2007) allows for a quantification of the nucleation mode (NM) formation potential and the size distribution characteristics.

A number of studies evaluated the effect of driving cycles and fuels on the PN emissions and size distributions from engines and vehicles (CONCAWE 1998; Association des Constructeurs Européens d'Automobiles [ACEA] 1999; Wedekind et al. 2000; Andersson et al. 2001; Mohr et al. 2003a; Kittelson et al. 2006a). The lack of standard measurement procedures, however, resulted in high variability, complicating at the same time any comparisons of data from different laboratories. Various reviews followed: evaluating dilution systems, measurement instruments, and best sampling practices (Kittelson et al. 2002; Bertscher 2005).

A limited number of studies have investigated the possibility of standardizing the measurement procedure. One is the "Particulates" project, where a partial-flow sampling system was used to measure directly from the tailpipe under constant "cold" sampling conditions (dilution ratio 12:1 and temperature 32°C) appropriately selected to promote the formation of volatile NM particles (Particulates 2003). The measurement setup consisted of two branches that allowed for the concurrent characterization of both the volatile and the nonvolatile (thermally pre-treated) fraction of the particle population (Ntziachristos et al. 2004a). The measured properties included number- and mass-weighted size distributions as well as active surface area. This standard protocol was successfully implemented in 22 different laboratories and the collected data provided the means to establish emission factors for a range of exhaust aerosol properties (Ntziachristos et al. 2004b; Thompson et al. 2004; Copert 2007).

The "VERT" (Verification of Emission Reduction Technologies) project (1994–2000) also aimed at the definition of a test protocol for the measurement of the particle removal efficiency of DPFs (Mayer et al. 1998; 1999). "VERT" was a collaborative effort of the Swiss (SUVA) and Austrian (AUVA) occupational health agencies, the German Association of Construction Engineers (TBG), and the Swiss (BUWAL) and German (UBA) environmental protection agencies, together with several engine and DPF manufacturers. Since DPFs only predictably control the solid core of the emitted particles, the protocol is based on the measurement of nonvolatile PN size distributions. Swiss authorities have not established a formal filter approval or certification program. Rather, a reference list of acceptable filter systems and/or suppliers is maintained by BUWAL/SUVA, known as the "VERT Filter List." DPF systems on the list are accepted for all BUWAL and SUVA retrofit programs. DPFs on the "VERT" list are also accepted by ASTRA (Swiss Federal Office for Roads) for retrofitting highway vehicles, although the "VERT" performance criteria (95% efficiency for number, 90% for soot, no secondary emissions) are not mandatory in road applications (DieselNet 2003).

The "Particulates" and the "VERT" studies showed that it is possible to achieve repeatable measurements of the nonvolatile

particle population, but also highlighted the sensitivity limitations imposed by the regulated gravimetric procedure that hinder the quantitative assessment of different particle emission reduction technologies (e.g., flow-through vs. wall-flow DPFs). Both studies aimed at a detailed characterization of the automotive exhaust and, as such, considered advanced measurement equipment (such as scanning mobility particle sizers, SMPS; Wang and Flagan 1990). The possibility to develop a more sensitive and accurate methodology that would replace or complement the regulated gravimetric procedure, requiring low investment costs, has been the objective of the Particle Measurement Program (PMP). The program was launched in 2001 on the initiative of several member states, and since then, it has evolved into an international group comprising governments, international institutions (European Commission), industry (associations of car and engine manufacturers, instrument manufacturers), and national vehicle emission laboratories and research institutions (Martini et al. 2009).

The proposed PN measurement method, based upon counting solid (nonvolatile) particles >23 nm, was rapidly integrated within European legislation (UNECE Regulation 83, Commission Regulation 692/2008; details of the protocol in the next section). Close involvement of the automotive industry and instrument manufacturers in PMP discussions enabled the PN measurement procedures to become rapidly accessible to legislators, test houses, and the automotive industry.

The objective of this paper is to summarize the status of the new nonvolatile particle counting method. Following a short historical background (Section 2), the PN and PM measurement methods are explained (Section 3). Next, topics such as traceability, uncertainty, repeatability, and reproducibility of the PN measurement are discussed (Section 4). Then, the effect of the aftertreatment devices on PN emissions is discussed (Section 5), typical real-time patterns are shown (Section 6), the emission levels of different technologies are given and the number, mass, and soot correlation is explained (Section 7). Finally, the differences between different sampling approaches (full-flow and proportional partial-flow dilution systems [PFDS]), and raw exhaust are discussed (Section 8).

2. HISTORICAL BACKGROUND OF THE LEGISLATED PN METHOD

The established method to measure particle emissions for type approval testing is the gravimetric analysis of filter samples, drawn from a full-flow constant-volume sampler (CVS) or a proportional (to the exhaust gas flow rate) partial-flow dilution tunnel (Berg 2003). However, some studies have raised concerns regarding the suitability of the mass method at low emission levels. For example, Chase et al. (2004) showed that a major part of the collected mass consists of gas compounds adsorbed on the filter media (volatile artifacts) and is not particle-bound volatile material. Inter-laboratory tests have

shown high variability (repeatability and reproducibility) for the mass method when using DPFs (Andersson et al. 2001; Zervas et al. 2005). Most importantly, the mass collected on the filter was found to be at the same level with the dilution tunnel background (Zervas et al. 2005), an indication that the true emission levels are below the detection limit of the gravimetric procedure.

2.1. PMP

The PMP Working Group of the UNECE GRPE (Working Party on Pollution and Energy) was formed from representatives from different countries (France, Germany, Greece, Japan, Korea, Sweden, Switzerland, the UK, etc.), the European Commission, laboratories and instrument manufacturers, and industrial associations from the automotive field to address the issues of the legislated filter method. The main target of the group was to develop new particle measurement techniques to complement or replace the existing filter-based PM measurement method, with special consideration given to measuring particle emissions at very low levels. These methods should include a detailed specification of test procedures and equipment, be suitable for light-duty (LD) vehicle and heavy-duty (HD) engine type approval testing, and allow measurements under transient engine operation. Since, within the European Union (EU), type approval testing to demonstrate compliance with emissions standards involves a limited number of tests, which take place in many laboratories, good repeatability and reproducibility between laboratories are key requirements for regulatory measurement techniques. PMP has therefore also sought to investigate and demonstrate the repeatability and reproducibility of the proposed methods. Important requirements also included robustness and low investments in equipment. PMP was also tasked with accumulating data on the particle emissions performance of a range of engine/vehicle technologies when tested according to the proposed procedures.

In the first two phases of the program, a wide range of measurement techniques and sampling systems were assessed over standard regulatory tests. During the first phase of the PMP study, a number of instruments measuring different properties, such as mass, number, surface, and chemistry, were evaluated along with appropriate dilution methods and sample conditioning. Phase 2 subjected the best-performing systems (also considering cost and logistical aspects) from Phase 1 to more rigorous evaluations in order to confirm the results of Phase 1 and determine fundamental levels of repeatability within a single laboratory during a variety of steady-state and transient tests on both engine-out and post-DPF exhausts (Mohr et al. 2005). The testing from Phase 2 concluded that a revised filter mass measurement method and a PN method met the original objective of the program. The two recommended systems were (PMP 2003):

- A filter method for the determination of the PM mass, based broadly upon those methods currently used in Europe and that proposed in the US for 2007 type approvals (Andersson et al. 2004).

- A nonvolatile (solid) PN² method using a sample preconditioning to remove volatile particles (volatile particle remover, VPR), a selected size range (23 nm–2.5 μm), and a PN counter (PNC).

Phase 3 consisted of inter-laboratory exercises for the evaluation of the repeatability and reproducibility of the recommended PMP systems for vehicles and HD engines. In the first LD inter-laboratory study (2004–2006), a DPF-equipped diesel passenger car utilizing fuel-borne catalyst and a reference “golden” PN measurement system from Matter Engineering (based on the rotating-disk principle for measuring nonvolatile particles) were circulated to nine laboratories, with one laboratory testing at the first, last, and intermediate stage. The work followed a prescribed guide (Andersson and Clarke 2004), which specified a draft measurement “PMP protocol.” The results obtained with the revised PM method exhibited a repeatability of 55%. Most importantly, the measured PM emissions were at the background levels (~0.5 mg/km) even from dilution tunnels equipped with very high-efficiency dilution air filters (high-efficiency particle filter [HEPA] filters) for the dilution air. Most of the mass collected on the filter consisted of volatiles, with soot (elemental carbon) constituting <10% of the collected mass (Andersson et al. 2007; Giechaskiel et al. 2008a). In contrast, the new nonvolatile PN measurement method showed intra-laboratory (40%) and inter-laboratory (25%) variability similar to other gaseous pollutants (CO and HC) and better than the revised mass method (55% and 35%, respectively). The variability in the PN results reflected to a large extent the variability in the vehicle particle emissions, since the method was sensitive enough to identify different DPF fill states and the effect of different preconditioning approaches. The method proved extremely repeatable when applied to conventional diesel vehicles (<5%; Andersson et al. 2007) with stable exhaust emissions. Different PN systems showed differences within ±30% (2 standard deviations of the differences between the systems) (Giechaskiel et al. 2008b). Following the successful implementation of the LD inter-laboratory study, which verified the superior performance of the PN methodology compared to the existing and revised PMP mass metric, the PN method was introduced in the LD European legislation (UNECE Regulation 83, Commission Regulation 692/2008) (Table 1).

²The sample preconditioning includes hot dilution at 150°C, followed by an evaporation tube at 300°C. Any surviving particles large enough to be detected with a PNC having a 50% counting efficiency at 23 nm are defined as *solids* in the PMP protocol. Accordingly, these operationally defined solid particles may also include semivolatile material not evaporating at 300°C (e.g., heavy molecular hydrocarbons) or at least not shrinking to a sufficiently small size that would not activate inside the PNC. In this paper, we use the term *nonvolatile* material instead. Similarly, we use the term *volatile* for particles that evaporate below 300°C, even though semivolatiles are also included. The term *PN method* refers to the measurement procedure defined by the PMP for the measurement of nonvolatile particles larger than 23 nm. Similarly, the term *PN (measurement) system* refers to PMP compliant system, unless otherwise specified.

TABLE 1
Limits of PM emissions in Europe since 2000 (compression ignition [diesel] engine)

Light-duty engines		Heavy-duty engines	
Cycle	NEDC (mg/km)	Cycles	ESC/ETC (mg/kWh)
Euro 3 (2000)	50	Euro III (2000)	100/160
Euro 4 (2005)	25	Euro IV (2005)	20/30
Euro 5 (2009)	5	Euro V (2008)	20/30
Euro 5b (2011) [†]	4.5*		
Euro 6 (2014) [‡]	4.5**	Euro VI (2014) [§]	10/10 [§]

*PM limit with the PMP method (one filter for the whole cycle).

**PM limit applicable to gasoline direct injection (G-DI) vehicles as well.

[†]PN introduction in Euro 5b (2011) 6×10^{11} p/km.

[‡]PN limit applicable to G-DI vehicles as well. The limit proposed is 6×10^{11} p/km, but with a footnote allowing a 3-year derogation to 6×10^{12} p/km at the request of the manufacturer.

[§]Euro VI limits apply for the World Harmonised Transient Cycle (WHTC) and World Harmonised Steady Cycle (WHSC). PN limits are introduced with values 6×10^{11} and 8×10^{11} p/kWh for WHTC and WHSC, respectively.

A similar exercise (2007–2009) was conducted for the assessment of the PN method for the HD type approval regulation (Giechaskiel et al. 2009a; Andersson et al. 2010). In this exercise, a Euro III HD engine retrofitted with a diesel oxidation catalyst (DOC) and a DPF was circulated to five European laboratories, with one laboratory testing the first and last stage. Two reference “golden” nonvolatile PN measurement systems from Horiba, based on dilution using mass flow controllers (MFCs), were also circulated for use in parallel; one connected to the CVS and the other to a (proportional) PFDS. The PM emissions of the engine were close to the background levels of the CVS and the PFDS and consisted mainly of volatiles (Andersson et al. 2010). The PM emissions determined from the CVS systems were typically double those derived from the PFDS due to the higher background in the CVS tunnels. The nonvolatile PN measurement method showed better repeatability, and the difference in emission levels measured via the CVS and PFDS was generally <20%. The PN methodology was proven to be extremely sensitive, revealing differences of up to two orders of magnitude in the emission levels from different test cycles (e.g., due to cold-start operation or passive regeneration) when the PM result differences were statistically insignificant. Extreme differences between CVS and PFDS PN levels were observed when the backgrounds of some CVS were higher than the emissions of the DPF engine (CVS background >100 p/cm³). Based on these results, the PN method will also be introduced in the HD regulation (UNECE Regulation 49, Commission Regulation 715/2007) (Table 1). Homologation of an engine has been permitted either from the CVS or the PFDS since Euro IV.

Since 2008, a Round Robin inter-laboratory exercise is under way. In this exercise, a different Euro III engine with an alternative, less-efficient DPF is being circulated to more than 10 different laboratories around the world. Each laboratory uses its own commercially available PN system, with the repeatability and reproducibility of the measurements to be determined following completion of the work. The Round Robin is expected to conclude in 2012.

It should be mentioned that the PMP protocol used in the inter-laboratory studies was not transferred unmodified to the legislation.³ For example, PMP required a cyclone with 50% cut-point at 2.5 μ m, but in the legislation, it is only recommended, based on the results of dedicated testing, suggesting that the use of a cyclone had no effect on the PN results (Giechaskiel et al. 2009a). The PMP used dilution factors (based on flow measurements or gas measurements) for the PN systems and expected particle losses to be <20%. The diameters of the counter with 10%, 25%, 50%, and 90% counting (detection) efficiencies (CE) had to be 16 ± 1 nm, 18 ± 2 nm, 23 ± 3 nm, and 37 ± 4 nm, respectively. The PMP calibration procedures of the PN systems proved complex and costly, and the penetration criteria were not always met. Thus, in order to control the penetration curve (i.e., losses) and simplify the calibration procedures, a “particle” DF was introduced (see “PCRF” in Section 3.3.2) for the PN systems in the legislation (Giechaskiel et al. 2008b). The counter’s cutoff sizes are checked only at 23 nm (CE: $50 \pm 12\%$) and 41 nm (CE > 90%). Details of the PN method will be given in Section 3.3.

2.2. Criticism of PMP

One of the main criticisms of the PMP approach is that it regulates only the nonvolatile fraction of the particles. There is no general consensus on whether the solid particle core or the chemical compounds adsorbed onto the diesel exhaust particles are responsible for the adverse health effects. Some authors suggest that the soot core is the component that stimulates the most adverse reaction (Lovik et al. 1997), while others suggest that the main toxicity arises from particle-bound organic compounds (Yang et al., 1999). Recent studies show that the volatile fraction might be equally or more important than the nonvolatile part for human health impacts (Biswas et al. 2009), or could even act synergistically (Stone et al. 2003). However, the PMP had no medical expertise and did not seek to pre-judge the advice from medical experts with respect to the most crucial particle characteristics affecting human health. Actually, the PN method was rather introduced to force the installation of the best-available technology at that time (i.e., wall-flow DPFs) without the uncertainties of the volatile NM and without the need of large investment for purchasing the equipment. Effectively, the introduction of the PN limit forced the use of wall-flow DPF systems, which are the only aftertreatment devices proven to effectively

³Nevertheless, the terms *PMP* or *Regulation 83* for LD (or *Regulation 49* for HD)-compliant PN measurement systems are used interchangeably.

control PM emissions under all driving conditions (in contrast to flow-through DPFs). Furthermore, the PN measurement is not replacing but rather complementing the gravimetric procedure that is still in force.

The quantification of the volatile part (either mass or number concentration) is not straightforward. The introduction of a wall-flow DPF has significantly altered the chemistry of the emitted particulates, mostly volatiles. This shift in the chemical composition has put into challenge the accurate quantification of the PM emissions, which were found to be strongly affected by adsorption artifacts, sometimes not originating from the engine but from the background of the installation. Elevated emissions of volatile nanoparticles downstream DPF-equipped diesel vehicles have also been reported, to a certain extent associated with the lack of soot core onto which vapors can condense. Yet, high-number concentrations of volatile nanoparticles were reported for other low PM emission technologies, including gasoline (Kittelson et al. 2006b) and homogeneous charge compression ignition (HCCI) (Kittelson and Franklin 2010) engines. Since generally the contribution of such nanoparticles to PM is insignificant, they rather qualify as unregulated pollutants. Their quantification is a rather challenging task that requires well-defined sampling conditions (dilution factor, dilution temperature, residence time [RT], etc.). This means that a completely different approach might be necessary: sampling directly from the tailpipe with well-defined sampling conditions (see "Particulates" project; Ntziachristos and Samaras 2010a).

One other concern regarding the PMP procedure is the relatively large nominal cutoff size of the PNC (23 nm). This relatively large size was selected as an additional safeguard against volatile NM particle interference in the measurements. Given that the whole procedure was designed around the assessment of the filtration efficiency (E) of particulate filters, this should not really be an issue, given that wall-flow DPFs have shown to be equally or even more efficient in removing nonvolatile sub-23-nm particles than in removing the carbonaceous accumulation mode (AM) (Yang et al. 2009; Tandon et al. 2010). Obviously, the limit value was based on measurements of nonvolatile particles >23 nm, but if a different cutoff size were selected, the limit value would be different, given the polydispersity of the diesel exhaust aerosol.

However, the main concern regarding the 23-nm cutoff size is that in some cases, there might be a distinct nonvolatile nanoparticle mode of size <23 nm that the PMP approach does not measure, especially considering the intention to extend the PN methodology to gasoline vehicles. Measurements of size distributions of a car fuelled with gasoline containing organometallic additives showed a solid NM of size <23 nm (Gidney et al. 2010; Mayer et al. 2010). But even measurements with HD diesel engines and vehicles without DPFs (Kittelson et al. 2006a; Rönkkö et al. 2007; Lähde et al. 2009) and LD diesel vehicles (Kirchner et al. 2009) suggest that sub-23-nm NM particles may have a nonvolatile core. Recent studies show that nonvolatile sub-23-nm NM particles might remain downstream

of DPF-equipped LD vehicles despite the >99% reduction of the engine-out NM (De Fillipo and Maricq 2008). Nonvolatile particles <23 nm have also been found in DPF-equipped HD engines at idle or low speeds (Johnson et al. 2009) or during regeneration (Giechaskiel et al. 2009a).

However, direct application of the PMP methodology for the measurement of sub-23-nm particles is not straightforward. Some studies showed that the European (PMP) approach might not be completely efficient in removing the volatile aerosol in some cases (Giechaskiel et al. 2010a; Mamakos et al. 2011a), while others (Swanson and Kittelson 2010) even suggested pyrolysis and/or charring of volatiles to form a solid NM artifact. The introduction of a different volatile organics removal approach, such as a catalytic stripper (Khalek and Kittelson 1995), may be necessary if the determination of solid particles <23 nm should be a regulatory or research objective. While the European approach relies on dilution and heating to remove the volatiles (physical approach) (Collings and Graskow 2000; Kasper 2004; Burtscher 2005), the catalytic stripper uses an oxidation catalyst that oxidizes volatile hydrocarbons (HCs) into carbon dioxide and water, while partially binding sulfates (chemical approach) (Swanson and Kittelson 2010). Note that the replacement of the evaporation tube with a catalytic stripper or other alternatives still retains PMP compliance as long as the temperature is above 300°C and the other regulatory requirements are met (Section 3.3). Finally, note that if there is no NM (i.e., if it is efficiently removed by the evaporation tube or the catalytic stripper), then the repeatability of the measurements is not affected—as shown by Herner et al. (2007), who found similar repeatability for PNCs of different cutoff sizes downstream of a PMP system. However, this needs further investigation, especially for cases where a distinct nonvolatile NM is formed.

Although there are still some concerns whether the PMP was the best approach, most studies so far have shown that the method presents a very robust methodology, because even in cases of re-nucleation or nonefficient removal of the NM, the 50% cut-point at 23 nm of the counter ensures minimal contribution of these particles to the final PN result (Kasper 2004). The accuracy of the PN method and the contribution of NM particles (volatile or nonvolatile) <23 nm will be discussed in more detail in Section 4.

2.3. Future Perspectives

In the US state of California, the introduction of a PN measurement approach has been under discussion for LEV III (low-emission vehicles), permitting either PM or PN certification, with the PN limit based upon the assumption that 1 mg/mile is equivalent to 10^{12} (nonvolatile) p/mile. Since time is required to agree the precise measurement method and limit value, it is unlikely that the PN option for certification will be available before 2017 (California Air Resources Board [CARB] 2010), and more recent discussions seem to have postponed this for 2025.

The possible application of the PN method is not restricted just to the automotive field. Switzerland has a PN limit for off-road engines (>18 kW). Aviation also is planning to introduce the PN method, probably with small modifications (e.g., lower cutoff size of the PNC and/or a catalytic stripper) for jet engines. The PN method is under discussion for use in conformity of HD engines and possibly LD vehicles in the future (Giechaskiel et al. 2011a). It could also be an alternative for inspection and maintenance procedures, considering that the currently employed opacimeters are not sensitive enough to quantify the emission levels of the current late-technology vehicles. In line with that, a solid PN limit, using a simplified measurement procedure, is investigated in Switzerland for the periodic inspection of DPF-equipped engines employed in construction machineries (VAMV 2006).

3. MEASUREMENT OF PM AND PN

In this section, the PM and PN measurement methods will be described. Emphasis will be given to the legislation requirements, i.e., measurement from the full-flow dilution tunnel (CVS).

3.1. From the Engine to the Measurement Location

Figure 1 gives a simplified overview of the processes, starting from combustion in the cylinder of the engine (or vehicle) to the measurement instrument connected to the full-flow dilution tunnel CVS (or the secondary dilution tunnel if there is one) for the determination of PM and PN emissions (Amann et al. 1980; Eastwood 2008). In the combustion chamber, primary particles (spherules or spherulites, 10–30 nm) form via the pyrolysis of fuel (and lubricant) molecules (when there is not sufficient oxygen for complete oxidation). In this stage, fuel (and lubricant) molecules can completely escape combustion and/or be partly modified.

In the exhaust tailpipe and the transfer tube from the engine to the full-dilution tunnel, the exhaust gas temperature is still high and spherules usually only coagulate, resulting in agglomerates (or aggregates or clusters) of the primary particles (spherules) (Bérubé et al. (1999) for terms like aggregates, clusters, etc.). An examination of the signature size distributions of the exhaust suggests that some fragmentation may also occur in the oxygen-rich diesel exhaust (Harris and Maricq 2001; 2002). Agglomerates are an impure form of elemental carbon possessing a graphite-like structure but can also contain minor amounts of bound heteroelements, especially hydrogen and oxygen. The agglomerates are quite often named (carbonaceous) *soot*.

In the full-flow dilution tunnel, the exhaust gas is mixed with the dilution air. During this process, some volatile material (from unburned fuel and/or lubricant, or H_2SO_4) can adsorb or condense on the agglomerates and/or nucleate to form a distinct volatile NM (droplets). Thus, at the end of the dilution tunnel, there is usually a tri-modal distribution of particles (see upper-left panel of Figure 1): the NM, which contains mainly

volatile droplets; the AM, which consists mainly of carbonaceous agglomerates with condensed/adsorbed hydrocarbon (fuel and lubricant); and the coarse mode, which consists of reentrained deposited particles or wear materials (Kittelson et al. 1991; Kittelson and Johnson 1991). While most of the mass resides in the AM, the NM can dominate number concentration under certain dilution conditions (Kittelson 1998). Sometimes, the agglomerates and the condensed material are called *soot*, but this definition will not be followed here, i.e., for the purpose of this study, soot is considered to be the agglomerates without any condensed material on them.

To overcome the cost and size problems of the full-flow dilution method, in HD applications proportional mini (or micro) dilution tunnels have been employed for the measurement of particulates. These systems were first developed in early 1980s and were applied to both HD engines and LD vehicles (MacDonald et al. 1984). In Europe, they are currently allowed only in the HD legislation, initially for steady-state tests, but since 2005 (Euro IV stage), also for transient tests. Mini tunnels are also allowed since 2011 for on-road approvals in the US (EPA CFR 40 1065; EPA 2011). In such systems, a small (but proportional to the total flow), fraction of the exhaust is sampled and used for the determination of the PM emissions. Consequently, the term (proportional) *partial flow dilution systems* (PFDS) is used to characterize such techniques (Vouitsis et al. 2003) (Figure 1). After sampling, the proportional sample flow rate may be conditioned accordingly, avoiding the limitation of full-flow systems imposed by the high flow rate of the total exhaust. Clearly, the maintenance of a proportional sample during extremely dynamic transients is critical for the precision of the measurement. The proportionality ratio is often called “split ratio” (r), and this needs to be kept nearly constant throughout the measurement. The extraction of a portion of the diluted exhaust from the PFDS using the PN system introduces some difficulties: if the extracted flow rate is not accurately reported to the PFDS and a correction is made, the proportionality is affected. The PFDS cannot check this flow because legislation requires the checks of the PFDS to be done independently from the PN system. Thus, the reported extracted flow rate depends on the accuracy and consistency of the PN system’s mass flow meter. Another point that needs to be considered is the correction of the PM result for the extracted flow using the PN system. For more detailed discussion on these topics, see Giechaskiel et al. (2011b).

CVS systems are bulky and expensive and PFDS also present considerable cost. For research and development, a common approach is to directly measure the raw gaseous exhaust emissions by connecting to the tailpipe upstream or downstream of aftertreatment devices. Various particle instruments have been used for raw exhaust sampling in the past (e.g., smoke meters, opacimeters, etc.), with a preference to real-time instruments (e.g., photoacoustic sensors) that give more information to the researchers. Most of these instruments reached their detection limits with modern engines and aftertreatment systems (Mohr et al. 2005). The introduction of the PN method resulted in the

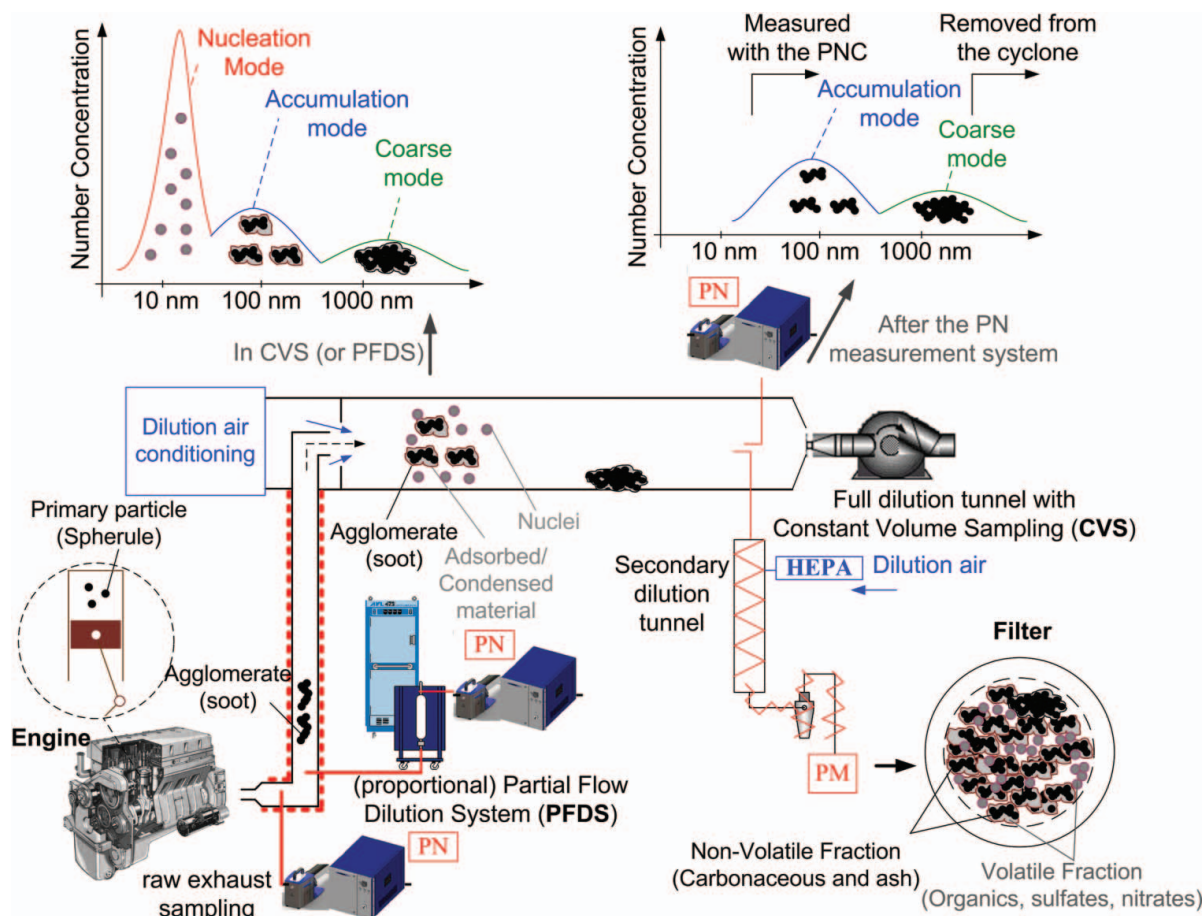


FIG. 1. Typical sequence of particle transformation from the engine to the measurement location. (Color figure available online.)

use of PN systems for raw exhaust measurements (Figure 1). Systems that can withstand the high exhaust gas temperatures are connected directly to the tailpipe, while others are used with a heated line that decreases the exhaust gas temperature to below 200°C, the maximum temperature for most instruments. Preliminary tests have shown that this approach gives results very close to the legislated procedures with the CVS or the PFDS (Giechaskiel et al. 2010b). However, special attention has to be given to the proper conditioning of the chemically “aggressive” exhaust aerosol. The correlation between PN results from different sampling locations (CVS, PFDS, or tailpipe) will be covered in Section 8.

3.2. Gravimetric Method and Chemical Analysis

The PM mass is determined by collecting the particles on a filter (bottom-right panel of Figure 1) after dilution of the whole exhaust gas (CVS) or part of it (PFDS). The difference in the filter weight after a test cycle (Table 1) is used to calculate the PM emissions of the specific engine or vehicle. The filter collects all particles (from nucleation, accumulation, and coarse modes, unless there is a cyclone to remove coarse particles). The nonvolatile fraction of the filter is the summed

weight of the agglomerates and any ash or wear particles, while the volatile fraction comes from the unburned fuel, lubricant, sulfates, and nitrates (Eastwood 2008). Note that due to the physicochemical complexity of PM, it is impossible to provide a precise definition of its chemical or physical properties. PM in automotive applications is rather defined by the measurement procedure, i.e., the mass of collected material on a filter at a temperature <52°C (or $47 \pm 5^\circ\text{C}$ in recent HD legislation) after exhaust sampling and dilution at specific conditions (regarding dilution air temperature, minimum DF, and RT). Species that are adsorbed on the particles are also part of the PM definition. Species (other than particles) that are adsorbed on the filter material are termed as *filter artifacts* (FA) but still considered as PM since there is no easy way of separating them out.

Two methods are commonly used to chemically characterize the PM on the filter: (i) gasification (evaporation and oxidation) and (ii) dissolution (extraction into solvents) (Maricq 2007; Eastwood 2008). In the first method, the particulate deposit is initially heated in an inert atmosphere so that volatile organic and anionic fractions evaporate. Then, an oxidizing atmosphere is introduced so that the carbonaceous fraction (agglomerates) is oxidized. What remains is the ash fraction. In the second

method, the particulate deposit is subjected to an organic solvent and water, which remove the organic and sulphate fractions, respectively. The ash and carbonaceous fractions remain. Based on the above, it is commonly accepted that the PM consists of the following fractions: carbonaceous (or carbon soot or agglomerates), ash, organics, sulfates, and nitrates. The first two fractions are nonvolatiles, the others volatiles (Eastwood 2008). Typical PM chemical composition for different engine technologies and the importance of the filter artifact for newer technologies are discussed in Sections 7.2 and 7.3, respectively.

3.3. Nonvolatile PN Measurement

According to UNECE Regulations 83 (LD) and 49 (HD), the PN system should consist of a volatile particle remover (VPR) and a particle number counter (PNC). When the (CVS) exhaust gas enters the VPR of the PN measurement system, it is diluted and heated; consequently, most of the volatiles compounds desorb and evaporate. This generally affects the PN distribution (Figure 1, top-right panel) and only the AM remains.

The PNC has a cutoff at 23 nm in order to exclude possible confounding of measurements by low-volatility HCs present as NM particles, while including the primary soot (spherule) size of ~ 20 nm (Wentzel et al. 2003). This means that the PN systems practically measure only the AM and (depending on whether there is a cyclone or not) the coarse mode. The contribution of the coarse mode in the number concentration results is insignificant. Desorption or evaporation from the AM no effect on the total number concentration. On the other hand, insufficient evaporation of the NM will have a profound effect on the total number concentration. The 23-nm cut-point of the PNC ensures that this effect will be small. The validity of these assumptions and the quantification of the effect of the different size distributions (NM and AM) on the PN results will be examined in Section 4.4.

Note that instead of a full-flow dilution tunnel, a partial-flow system can also be used. In this case, similar particle transformations are expected. However, since the NM is very sensitive to the sampling conditions (e.g., dilution factor, temperature, etc.), differences are often observed (for PM or total PN emissions). However, a robust nonvolatile PN measurement procedure should not be affected, because all volatiles would be removed. The following sections (3.3.1 and 3.3.2) describe the legislation PN requirements. Section 4 will discuss the accuracy of the PN method, and Sections 5 and 6 will discuss typical PN emissions for different aftertreatment devices and engine technologies, respectively.

3.3.1. Detailed description of PN systems

The PN system for LD certification purposes has to be connected to the full-flow dilution tunnel (CVS) with a particle transfer (tube) system (PTS) of inner diameter ≥ 8 mm (the diameter requirement will not be included in the future). The flow has to be laminar (Re number < 1700) (Figure 2). The RT to the primary dilution (particle number diluter, PND₁) of

the PN system has to be ≤ 3 s. These requirements were introduced to limit the particle losses during sampling, which are not included in the calibration of the PN systems. Upstream of the PN system, a cyclone or a probe with hat with 50% cut-point between 2.5 and 10 μm to protect the PN system is recommended, but not obligatory, because it has been shown that it does not affect the PN results. The primary dilution factor has to be ≥ 10 and the temperature of the diluted sample $\geq 150^\circ\text{C}$. After PND₁, a heated tube (evaporation tube) with wall temperature maintained at a constant value between 300 and 400°C is placed. Currently, no RT requirement is included, but in the future (World Harmonized procedures), the target is to require a RT between 0.25 and 0.4 s. The temperature of the evaporation tube will also need to be confined to 350°C ($\pm 10^\circ\text{C}$). A secondary diluter (PND₂) is not required (though recommended), but the temperature at the inlet of the PNC has to be $< 35^\circ\text{C}$. These parts comprise the sample preconditioning system or VPR for the evaporation of the volatile NM. The removal efficiency of the VPR is checked with 30-nm n-tetracontane ($\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$) particles (see next section). The losses of the system are controlled at 30, 50, and 100 nm (see next section). The RT from the VPR to the PNC should be ≤ 0.8 s and the diameter of the tube ≥ 4 mm. The requirement of the minimum diameter was introduced to avoid using smaller tubes that could easily become blocked, restricting the flow. The PNC has to be full flow (no internal mixing or splitting) with a response time 90% of < 5 s. The CEs of the PNC have to be 0.5 ± 0.12 ($50 \pm 12\%$) at 23 nm and > 0.9 ($> 90\%$) at 41 nm. The 10% CE is not required, but typically is around 16.5 nm. These CEs were chosen in order to include the primary soot particles (around 20 nm), while maximizing the opportunity of excluding any volatile NM that has not been removed completely. The PNC must have a linear response, and the slope of the linear regression against a traceable standard has to be 1 ± 0.1 . The total RT from the CVS to the PNC (including the response time of the PNC) has to be ≤ 20 s.

Currently, commercial VPRs are available from Dekati (DEED; Dekati 2010), Ecomasure (RS-PMP; Ecomasure 2010), Matter Aerosol (ViPR; Kasper 2008), AVL (APC [AVL particle counter] 489; Giechaskiel et al. 2010c), Maha (SPC 8000 [solid particle counter]; Maha 2010), Sokken (PMS-M2; Sokken 2010) and Horiba (SPCS 2000 [solid particle counting system]; Wei et al. 2006). The first two consist of ejector diluters (Koch et al. 1988; Giechaskiel et al. 2004), with an evaporation chamber in between. The next four systems use a rotating-disk diluter (Hueglin et al. 1997) with cavities or holes that transport the raw exhaust to the dilution air-line, followed by an evaporation tube and a simple mixer as secondary diluter. The dilution of the last system is controlled by pumps and MFCs. Commercial PNCs are always condensation nucleus counters (CNCs; also called condensation particle counters, CPCs) using *n*-butanol as working fluid, and these are currently available from TSI (model 3790; TSI 2007) or Grimm (model 5.430; Grimm 2010). A comparison of the most commonly used systems is presented in Section 4.3.1.

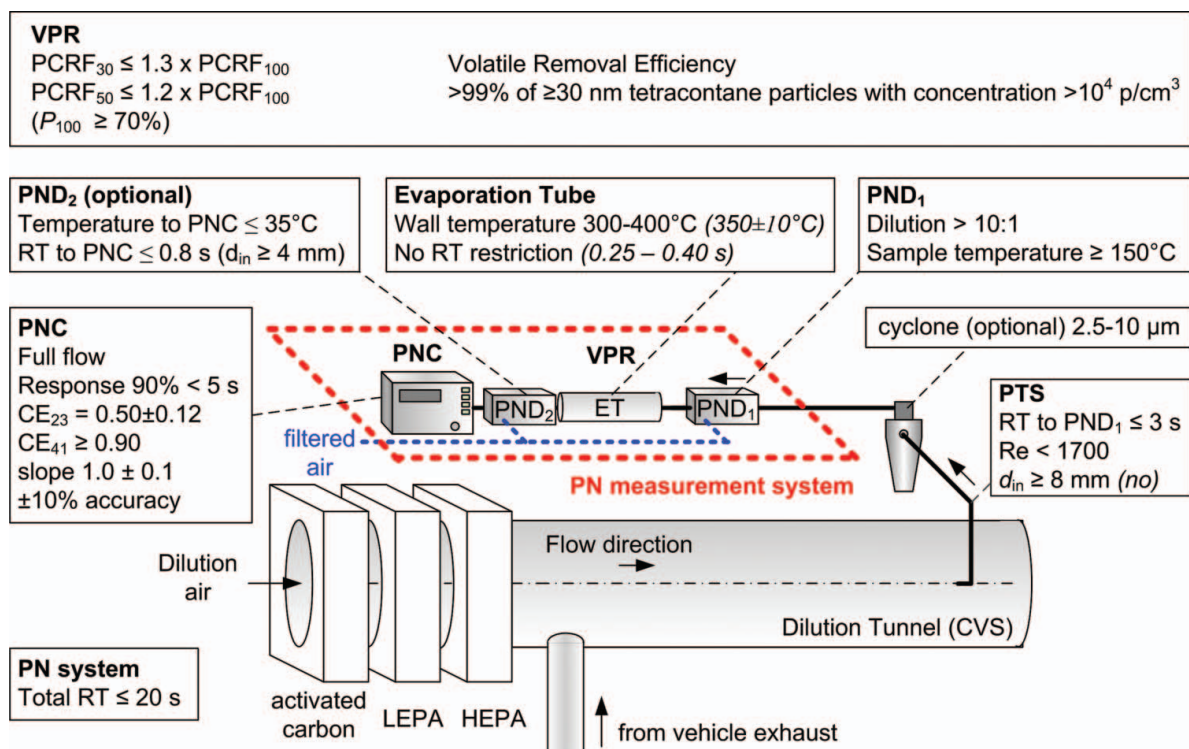


FIG. 2. The particle number (PN) system consists of a volatile particle remover (VPR) and a particle number counter (PNC). The VPR removes volatile particles and dilutes the sample. The PNC measures the number concentration of particles >23 nm. In parentheses, probable requirements in the future World Harmonized procedures. For details, see text. (Color figure available online.)

3.3.2. Calibration of PN systems

The two basic components of the PN systems, namely the VPR and the PNC, are calibrated separately.

The VPR is checked for its volatile organics removal efficiency and is calibrated for each dilution setting. According to the legislation (UNECE Regulation 83) and the document that is mentioned in the legislation (Sandbach and Marshall 2007), the particle (number) concentration reduction factor (PCRF_{*i*} [or *f_r*] for particles with mobility diameters *i* = 30, 50, and 100 nm) has to be determined for each device and dilution setting of the device. The PCRF_{*i*} can be understood as a “particles” dilution that includes the DF of the device (determined with flows) and the particle losses at that size. The PCRF_{*i*} with monodisperse aerosol (for each size *i*) is given by the following equation:

$$\text{PCRF}_i = \frac{N_{\text{in},i}}{N_{\text{out},i}}, \quad [1]$$

where $N_{\text{in},i}$ is the inlet and $N_{\text{out},i}$ is the outlet PN concentration of the monodisperse aerosol with size *i*. The particle concentrations are normalized to 0°C and 1 atm (101.3 kPa). The average PCRF that is used for the calculations of the PN emissions is

$$\text{PCRF} = 1/3 (\text{PCRF}_{30} + \text{PCRF}_{50} + \text{PCRF}_{100}). \quad [2]$$

The PCRF_{*i*} at 30 and 50 nm must be lower than 1.3 and 1.2 times the PCRF_{*i*} at 100 nm, respectively.

The PCRF_{*i*} is related to the DF of the device at the specific setting (theoretical or measured with flow rates or gases for a specific dilution setting) through the particle losses L_i of the instrument, which are size-dependent (Giechaskiel et al. 2009c):

$$L_i = 1 - \frac{\text{DF}}{\text{PCRF}_i} = 1 - P_{\text{VPR},i}, \quad [3]$$

where $P_{\text{VPR},i}$ is penetration at a specific size. It is proposed for the future World Harmonized legislation that the penetration of 100-nm particles is at least 70% (Figure 2).

The volatile organics removal is checked against n-tetracontane ($\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$) particles (a straight-chain alkane with 40 carbon atoms) having a size of at least 30 nm and a concentration at the inlet of the PN system $>10^4$ p/cm³. The PN system should achieve a $>99\%$ reduction of these particles.

The PNC has to be calibrated annually either against an electrometer or a PNC that has been calibrated against an electrometer (Giechaskiel et al. 2009b). Details are given in a document that the legislation refers to (Marshall and Sandbach 2007). In the future, this document will be replaced with the ISO Standard 27891, describing the PNC calibration procedures, which is under preparation at the moment.

The calibration includes the measurement of the counting efficiencies (CE_i) for particles with mobility diameters $i = 23$ and 41 nm, which should be 0.5 ± 0.12 and >0.90 , respectively:

$$CE_i = P_{PNC,i} = \frac{N_{PNC,i}}{N_{Ref,i}}, \quad [4]$$

where $N_{Ref,i}$ is the concentration measured with the reference instrument and $N_{PNC,i}$ is the concentration measured with the PNC under calibration. The CE of a specific size i (CE_i) is practically the penetration of the particles at this size ($P_{PNC,i}$).

In addition, the calibration of the PNC includes the linearity check at different concentrations across the range from 1 p/cm^3 (or 1000 p/cm^3 for the electrometer case) to the upper threshold of the single-particle count mode. The linear regression between the reference instrument and the PNC under calibration should give a slope within 0.9 – 1.1 . The inverse of this value (k factor) must be used as the correction factor of the PNC for the calculation of the vehicle PN emissions. It is also necessary that the particle concentration ratios of the reference instrument and the PNC under evaluation are within 0.9 – 1.1 for the whole tested concentration range. The slope can be greater than 1 because it also compensates for deviations from the nominal PNC flow rate, which is measured and checked separately (but not otherwise taken into account in the calculations for the PN emissions).

4. UNCERTAINTY OF THE PN MEASUREMENTS

One topic of concern regarding PN measurements is the question whether the comparability between different PN systems is guaranteed if the legislation requirements on the CE curve of the PNC and the PCRf of the VPR are fulfilled. Another concern is that no PN standard exists, and this raises concerns regarding the accuracy of the PN measurements. In the following, these two points will be analyzed, beginning with the second one.

4.1. Definitions

4.1.1. Limit of detection

A PN system is required to measure below 0.5 p/cm^3 when a HEPA filter is connected to its inlet. Assuming a VPR with minimum PCRf of 100 , it can be easily calculated that the minimum concentration that can be measured is equivalent to around 10^9 p/km for LD vehicles (CVS $10 \text{ m}^3/\text{min}$) or $5 \times 10^9 \text{ p/kWh}$ for HD engines (CVS $100 \text{ m}^3/\text{min}$). The limit of detection (LOD) is three times these levels, and it is worth noting that the background in the CVS can be much higher than the LOD. Irrespective of this, the LOD is still at least one order of magnitude lower than the current regulatory PN limits.

The maximum concentration that can be measured by a PN system can be estimated on the assumptions that the VPR maximum PCRf is $10,000$ and that the PNC can measure up to $10,000 \text{ p/cm}^3$. The calculations give a value $>10^{15} \text{ p/km}$ or p/kWh .

4.1.2. Traceability

Traceability is defined as “the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty” (VIM 2008). Traceability to a widely accepted higher standard permits comparisons of measurements among users. PNCs, which are used to measure the particle concentration and calibrate the VPR, are calibrated against electrometers, which are considered traceable. Traceability of the aerosol electrometers is (i) through calibration to a low-level current generated by a circuit in which the components are referenced to standards (e.g., National Institute of Standards and Technology [NIST]), which in turn are referenced to the volt (Josephson junction) and the ohm (quantum Hall effect), and (ii) through traceable volumetric quantification (e.g., to the NIST) of the flow rate (Fletcher et al. 2009).

4.1.3. Accuracy

In comparison with a hypothetical PN standard or a PN source with known emissions (*true value*), a measurement with a PN system would report some differences due to systematic and random errors. These errors can be estimated by conducting many measurements. The difference between the mean of these measurements and the true value is the *bias* (systematic error), while the specific proximity of these measurements to their mean gives the *precision* (random error). Note that if only one error estimation measurement is conducted, both bias and precision are included and the difference is the (in)accuracy.

However, the true value in PN measurements cannot be known, because no absolute PN standard or constant PN source exists. Thus, the bias can be estimated from the uncertainty of the calibration and the precision can be estimated from the total uncertainties of the parts of the PN system (see next section). The precision can be compared with the experimentally determined *within-laboratories variability* (*repeatability*), which is the similarity of the measurements in one laboratory. The bias can be compared with the experimentally determined *between-laboratories variability*, which is the scatter, about the mean, of the PN measurements at different laboratories. The combination of the within- and between-laboratories variabilities gives the *reproducibility*, which should be similar to the accuracy of the PN method. Note however that the experimental uncertainty, among others, includes the variability of the particle source as well, while the theoretical estimations do not take this into account. In this text, all uncertainty terms are relative and expressed in percentages.

4.2. Theoretical Estimations

4.2.1. Bias

The bias of a PN system depends on the bias of the PCRf of the VPR and the bias of the concentration measured by the PNC, and can be estimated by the calibration uncertainties (Table 2).

PNCs are originally calibrated against electrometers. Typically, the maximum concentration that PMP PNCs can measure

TABLE 2
Theoretical estimations of accuracy and experimental results of Round Robin tests

Theoretical estimations	PNC CE (p/cm ³)		VPR PCRf (–)		PN system	Experimental (Round Robin)	PN system
	~10,000	~10	~100	~10,000			
Bias	<i>5%</i>	<i>12%</i>	<i>7%</i>	<i>13%</i>	9–18%	Between laboratories	<i>30%</i>
Precision	<i>1%</i>	<i>2%</i>	<i>2%</i>	<i>2%</i>	2–3%	Within laboratories (repeatability)	<i>5%</i>
Accuracy	<i>5%</i>	<i>12%</i>	<i>8%</i>	<i>13%</i>	9–18%	Reproducibility	<i>31%</i>

Values in italics are assumptions (theoretical estimations) or measurements (for the experimental case). The rest are calculated (rounded). For details, see text.

in the single-particle counting mode is 10^4 p/cm³. The accuracy of electrometers in this concentration range is around 5%, especially when the contribution of multiple-charged particles has effectively minimized (Fletcher et al. 2009). Note that in the future, it might be possible to have calibrated linear PNCs with higher concentrations, which will result in reduced bias. The uncertainty (of the calibration) increases as concentrations decrease due to the lower current that is measured by the electrometer. Measurement uncertainty is around 7% at 3000 p/cm³, but at 500 p/cm³, it may exceed 25%.

However, this does not mean that the uncertainty of the PNC measurement is similarly high at low concentrations. The theoretical relative statistical error of the counts e of a PNC is related to the total counts n by the ratio $e = n^{0.5}/n$. The measurement of 10^4 p/cm³, which corresponds to approximately 16×10^4 counts for PMP PNCs, has 0.2% uncertainty (due to errors in counting). The experimental uncertainty using an electrometer is higher (5%) because it includes the uncertainty of the measured current, the flows, the losses, etc. When the PNC measures 10 p/cm³, it has theoretical uncertainty of 8%. Adding the extra uncertainty of the calibration, it should be >10%. Note however that when the measurement is not transient (e.g., every second) and enough time is given (e.g., during a calibration), then by counting in total 10^4 counts, the theoretical counting uncertainty is 1% (5% if the calibration experimental uncertainty is also added). During the VPR calibration, the upstream concentrations⁴ are ~10,000 p/cm³ and for dilution (PCRf) around 100, downstream concentrations are ~100 p/cm³. Assuming that the uncertainty of the PNC is minimized during the low concentration measurement due to prolonged sampling time, then the “ideal” minimum bias of a VPR system is around 7% (5% for the PNC used for the VPR calibration upstream and 5% for the PNC used downstream of the VPR).⁵ Adding the 5% uncertainty of the PNC (assuming it measured close to 10,000 p/cm³), ideally a PN system has uncertainty of 9%.

⁴The legislation requires concentration greater than 5000 p/cm³; at the moment, linearity is proven for PNCs that measure approximately up to 20,000 p/cm³.

⁵The combined uncertainties of all the factors are calculated by adding them in quadrature (i.e., taking the square root of the sum of their squares).

The previous “ideal” values are valid for certification tests (i.e., with the minimum PCRf around 100 and quite high concentrations measured by the PNC). Higher PCRfs and lower PNC concentrations will have higher uncertainties due to the nonlinearity issues, as it will be explained in the next section.

4.2.2. Linearity

The linearity of a PN system (i.e., if it gives the same results regardless of the PCRf and the concentrations measured by the PNC) depends on the linearity of the PNC and the linearity of the VPR. The linearity of the VPR is dependent on the linearity of the PNC that was used for the calibration of the VPR (linearity of PCRfs). Thus, any nonlinear response of a PNC used for calibration can create two problems: firstly, it can affect the final PN results, depending on the dynamic nature of the cycle and depending on the dilution that was used (i.e., if the PNC was measuring at the high- or the low-concentration range); secondly, it can result in nonlinear dilution stages (PCRfs) of the VPR (if a PNC with nonlinear response was used for the calibration of the VPR).

Theoretically, a legislation-compliant PNC could be different by up to 20% when measuring at low or high concentrations, since the differences against the reference instrument are allowed to be within $\pm 10\%$ for the whole calibration range. Thus, a PN system that was calibrated with a nonlinear PNC (20% error) and that contained a nonlinear PNC (another 20% error in the same direction) could present a (maximum) 40% error between low and high concentrations and still remain within legislative specifications.

The linearity of a PNC can be checked by comparing its response to that of the electrometer at different concentration levels. Nonlinear responses of PNCs have been already observed (Fletscher et al. 2009; Giechaskiel and Stilianakis 2009; Takegawa and Sakurai 2011). Note that the comparison with an electrometer is seldom undertaken below 1,000 p/cm³, so information for lower concentrations regarding the linearity is lacking. However, recent studies in this area show that PNCs are linear, or at least there are ways to check their linearity for concentrations <1,000 p/cm³ using a collection of particles on filters and TEM images (Fletcher et al. 2009) or stepwise

dilutions (Owen et al. 2010; Sakurai and Ehara 2010). Checking the linearity of PMP PNCs with a reference PNC has shown that it is typically within 7% above 10 p/cm³ (Giechaskiel and Bergmann 2011), and nonlinear responses >10% are rarely observed. Thus, the uncertainty of a PNC at low concentrations should be <12% (5% calibration uncertainty for the high point, e.g., 10,000 p/cm³, and 7% linearity uncertainty for lower concentrations).

Assuming similar uncertainty in the linearity of a PNC that is used to calibrate the VPR, the nonlinearity uncertainty of the high PCRFS (compared with the low PCRFS) of the VPR system should be within 7%. Relative comparisons (i.e., sampling from the same source and increasing the PCRFS up to 10,000) shows that the calculated emissions remain within 5–10% compared with the emissions with low PCRFS (Giechaskiel et al. 2010c). Similar conclusions are drawn by checks of the PCRFS using traceable gas concentrations. Thus, the uncertainty (bias), even at high PCRFS and by measuring low concentrations with the PNC, should not be >18%. This value is based on a 5% uncertainty of the PNC that was used to measure upstream of the VPR during the calibration of the VPR, 12% for the downstream PNC measurement during the calibration of the VPR, and 12% uncertainty of the PNC measuring low concentrations during the test.

4.2.3. Precision

The precision of the PN measurement depends on the *noise* (scatter of the values when measuring a constant emission level) and the *drift* (change of the measured value in a specific time window, although the true value remains constant) of the parts that comprise the PN system. The noise of PN systems is typically <1%, and it originates from small variations in the flows, pressures, and temperatures that are not taken into account correctly when the instrument reports a value. The drift of PN systems over a short period of time (e.g., one test, 20–30 min) is negligible (<1%) because most PN systems' components (e.g., MFCs, temperature and pressure sensors, etc.) drift more slowly than this time scale. A slightly higher uncertainty is expected at low PNC concentrations due to counting error statistics and at high VPR PCRFS due to the lower flow rates that are being controlled. This value is comparable with, but lower than, the 8% estimation from Vogt et al. (2010) and Kirchner et al. (2010). The main difference derives from these authors' higher uncertainty estimates for the VPR.

4.2.4. Accuracy

Combining the bias and the precision values 9–18% accuracy for a PN system is estimated. This is similar to the proposals of Gilham and Quincey (2007) (15%) but less than the estimations of Vogt et al. (2010) and Kirchner et al. (2010) (28%), who assumed higher uncertainty in the calibration of the VPR. This means that different PN systems measuring the same particle source should give results within 9–18%, depending on

the concentration levels measured by the PNC and the PCRFS setting.

4.3. Experimental Results

Information about the accuracy of the PN systems can be achieved from two kinds of studies: one is by comparing PN systems that sample simultaneously, thus excluding the variability of the source; the other is by conducting Round Robin tests (circulation of a vehicle or engine at different laboratories) and calculating the within- and between-laboratories variabilities, which include the variabilities of the sources.

4.3.1. PN measurements in parallel

The calibration uncertainties for the PN systems can be examined by comparing the results of PN systems measuring in parallel. There are a limited number of studies that compare PMP-compliant PN systems. Figure 3 summarizes the results of these (three in total) studies. The two most comprehensive studies come from the PMP (LD and HD; Andersson et al. 2007, 2010; Giechaskiel et al. 2008b). The PMP LD data come from five laboratories that used 10 PN systems from three manufacturers. The PMP HD data come from four laboratories that used five PN systems from three manufacturers. The LD and HD inter-laboratory exercises showed that most systems had a $\pm 30\%$ difference to the reference “golden” systems (A rotating-disk-based system from Matter Engineering for the LD, and a prototype SPCS from Horiba for the HD exercise). Larger differences were found when the systems were measuring close to their detection limits or the CVS backgrounds (5×10^9 p/kWh). It is important to note that in both LD and HD PMP exercises, no systems were calibrated according to the recently

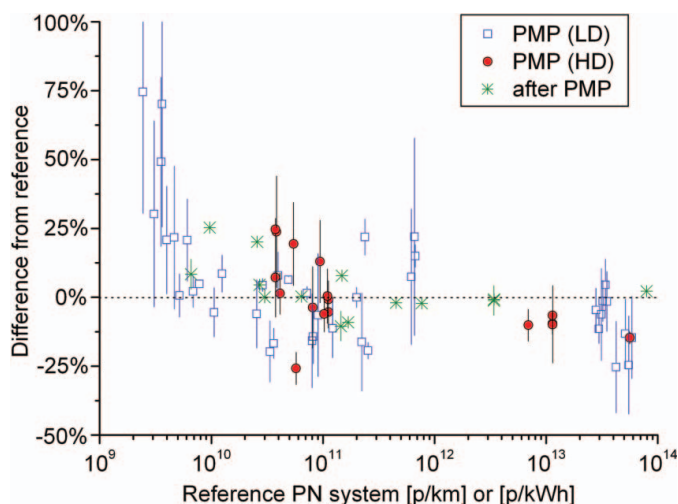


FIG. 3. Comparisons of different PN systems based on three studies: “LD” and “HD” refer to data from the LD and HD inter-laboratory exercises, while “after PMP” refers to data from a calibrated PN system after the LD and HD exercises. Error bars show 1 standard deviation of three or more measurements. (Color figure available online.)

introduced legislation (i.e., with PCRFs): rather, the DF was employed in the calculations. Post-correction of the data to account for the size-dependent particle losses, in accordance to the regulation requirements, improved the agreement to $\pm 15\%$. After the finalization of the PMP protocol, a third smaller study, which included data from four laboratories with four PN systems calibrated with the legislation procedures from four manufacturers, showed differences of the order of $\pm 10\%$ (Figure 3) (Giechaskiel et al. 2010c). The last values are similar to the theoretically estimated accuracy (9–18%).

Good agreement between PN instruments is not always the experience in the field. Various correlation measurements have shown that sometimes the differences are of the order of 30% (AVL unpublished data). Evaluation of the systems has shown that the reasons of the differences can be:

- **Corrections:** pressure and temperature conditions at the inlet of systems not taken (correctly) into account; different normalization temperature (273 or 293 K); the system that is normalized to 273 K measures higher by a factor of 1.08.
- **Calibration material:** if the PNCs have been calibrated with different materials (e.g., emery oil, NaCl, or Combustion Aerosol Standard [CAST]), differences in the final PN result of up to 10% can be observed (Giechaskiel et al. 2009b; Wang et al. 2010). The VPR calibration material can result in some differences, especially if it is not sufficiently thermally pre-treated (Giechaskiel et al. 2009c; Sakurai et al. 2011).
- **Nonlinear response of the PNCs:** it is possible that the PNC is not completely linear. In this case, the PCRf chosen can affect the results (i.e., if the PNC measures low or high concentrations) (Giechaskiel and Stilianakis 2009). If a nonlinear PNC is used for the calibration of a VPR, then the calibration will be incorrect by a factor equal to the nonlinearity of the PNC.
- **Drift:** it has been observed that the PNCs can drift 5–10% every 3–6 months (Giechaskiel and Bergmann 2011). Approximately 30–40% of the PNCs that return for the yearly check (validation) have drifted >20% (AVL internal data based on a database of >40 PNCs). A possible explanation is that the vehicle exhaust gases react with butanol to form esters that deposit on the saturator, affecting the partial pressure of butanol and, subsequently, the supersaturation ratios in the condenser. Contamination of butanol (e.g., from air humidity, or due to low quality) can also be a reason. The VPRs can also drift (e.g., when the orifice starts to block, or when small leaks appear) (Giechaskiel et al. 2004; Andersson et al. 2010). This drift is assumed to be <10% in the dilution range 100–5,000 over 1 year (the time required by legislation between two calibrations). Thus, a 20% drift of a PN system is possible over the period of 1 year.

This drift cannot be identified by the instruments at the moment, and this raises concerns for the measurements conducted in the time between two checks. For this reason, ways to perform easy and frequent on-site checks of the VPR and PNC are important (Giechaskiel et al. 2009c). Since the calibration procedures are time-consuming and complicated, simple checks with polydisperse aerosol or calibration gases are an attractive alternative. For example, measuring with a reference PNC in parallel with the PNC of the PN system can show if the PNC has drifted or not. Using the reference PNC to measure upstream and downstream of the PN system at a specific PCRf can show if the VPR of the PN system has drifted (Giechaskiel and Bergmann 2012).

4.3.2. Round Robin (PN)

Round Robin studies can give information about the repeatability and reproducibility of the PN (and PM) methods, which for engine exhaust includes the variability of the source (vehicle or engine).

Figure 4 summarizes reported within-laboratories variability (repeatability) data for PN from different Round Robin studies. Each point gives the coefficient of variance (CoV) of 3–5 repetitions of the same engine/cycle combination. The HD repeatability data are based on five engines from various HD studies (Andersson et al. 2010; Giechaskiel et al. 2011a; Stein 2001). The LD repeatability data are based on >30 engines (Vouitsis et al. 2003; Mamakos et al. 2004; Zervas et al. 2005, 2006; Andersson et al. 2007; Myung et al. 2009). Figure 4 gives also the between-laboratories variability based on data from the PMP (LD and HD) (Andersson et al. 2007; Giechaskiel et al. 2008a; Andersson et al. 2010), from the Korean PMP exercise that employed a single DPF-equipped vehicle and a “golden”

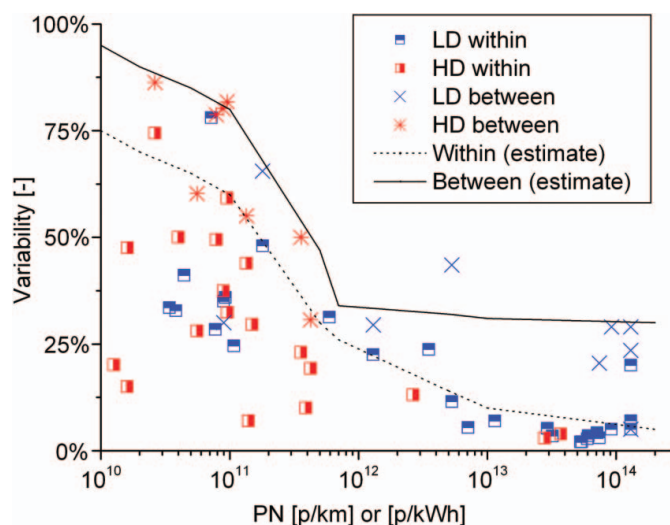


FIG. 4. Within- (squares) and between-laboratories (asterisks) variability for different PN emission levels based on experimental data of different studies. The continuous lines give estimations of the within- and between-laboratories variability. (Color figure available online.)

PN system (Myung et al. 2009), and from a French Round-Robin program (Zervas et al. 2005, 2006). The continuous lines in Figures 4 named “Within” and “Between” are a guide to the eye and give an estimation based on the previous data.

For PN, the repeatability (Figure 4) changes from $\sim 5\%$ at emission levels $>5 \times 10^{12}$ p/km (p/kWh) to 30% for emission levels $>3 \times 10^{11}$ p/km (p/kWh) and $>50\%$ for emission levels at $<3 \times 10^{11}$ p/km (p/kWh). The $\sim 5\%$ variability at high emission levels is slightly higher than the theoretically expected repeatability (2–3%) presented previously because it includes a small variability of the source (vehicle) as well. However, the much higher variability (30%) at lower emission levels $<5 \times 10^{12}$ p/km (p/kWh) is not related to the uncertainty of the PN method, but results from the high sensitivity of the PN method that enables it to easily distinguish between efficient and nonefficient DPFs, loaded or almost soot-free DPFs, and different pre-conditionings or pre-histories of the vehicles. More details about the emissions of vehicles of different technologies can be found in Sections 5 and 6. For DPF-equipped vehicles, details can be found in Sections 5.3 and 6.1.2. Similarly, the $>50\%$ uncertainty at emission levels $<3 \times 10^{11}$ p/km (p/kWh) is a consequence of the PN background of the CVS or PN systems, which is close or sometimes higher than the emissions of the vehicles.

The between-laboratories variability is around 30% for emission levels $>3 \times 10^{11}$ p/km (p/kWh) and $>50\%$ for lower emission levels. For the low emission levels, the different CVS backgrounds can explain the high variability. For emissions in the range of 3×10^{11} – 5×10^{12} p/km (p/kWh), the variability of the vehicles can explain the uncertainty, as discussed previously. However, the high variability at emission levels $>5 \times 10^{12}$ p/km (p/kWh) can only be explained by calibration uncertainties of the PN instruments or drift of the PN systems, as discussed previously (Section 4.3.1).

4.3.3. Round Robin (PM)

For completeness, the within- and between-laboratories variabilities of the PM are given in Figure 5. The data are based on nine HD engines and >30 LD vehicles. The repeatability increases from approximately 10% at 100 mg/km (mg/kWh) to more than 50% at 2 mg/km (mg/kWh), which is the emission level of vehicles and engines equipped with efficient wall-flow DPFs, in agreement with the results from ACEA (1999). The between-laboratories variability of the PM is only slightly higher than the within-laboratories variability, i.e., 25% at 100 mg/km and $>60\%$ for values <2 mg/km. There are two main reasons for the variability increase when using DPFs: firstly, the low mass concentrations emitted are likely to induce uncertainties due to the limited sensitivity of the existing gravimetric procedure; secondly, almost all the collected material comes from anions (sulfate and nitrate) plus volatile organic material (volatile artifacts). Emissions of such species are highly dependent on the sampling conditions and storage/release effects in the DPF, other catalytic and storage elements of the emissions control system,

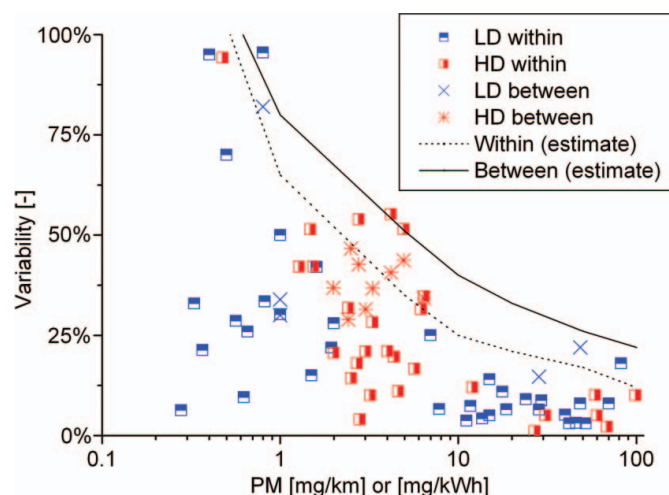


FIG. 5. Within- (squares) and between-laboratories (asterisks) variability for different PM emission levels based on experimental results of different studies. The continuous lines give estimations of the within- and between- laboratories variability. (Color figure available online.)

the transfer line to the CVS (or the PFDS), and the CVS (or PFDS) itself. More details about the FA can be found in Section 7.3.

4.4. Penetrations

The above sections quantified the error due to the unknown accuracy of the PN measurement. There is one more unknown error of the “true” emissions due to the different penetrations of the PN systems and due to the (unknown) inlet size distributions.

The penetration of a PN system (i.e., what percentage of the inlet particle concentration is measured) depends on the penetration of the VPR and the PNC (or CEs). The size-dependent VPR and PNC penetrations can vary from manufacturer to manufacturer, and in the case of the VPR, can depend on the dilution conditions employed. The number concentration measured with each PN measurement system corresponds to the convolution of the size-dependent $PCRFi$ and CEi and the number concentration (size distribution), and therefore, different implementation of the PMP methodology may result in different PN results. In order to improve the comparability of the different PMP systems, the regulations have introduced requirements for the VPR and PNC penetration curves. More specifically, the $PCRFi$ of the VPR at 30 and 50 nm must be lower than 1.3 and 1.2 times that at 100 nm. The PNC must have a CEi of 0.5 ± 0.12 at 23 nm and >0.9 at 41 nm and should also exhibit a 0.9–1.1 slope (i.e., 0.9–1.1 CE at a large size). Still though, systems complying with these requirements can exhibit differences, especially when the count median diameter (CMD) of the measured size distribution is close to 20 nm. However, such a low CMD has not been seen in modern European vehicles or HD engines running on standard reference fuels.

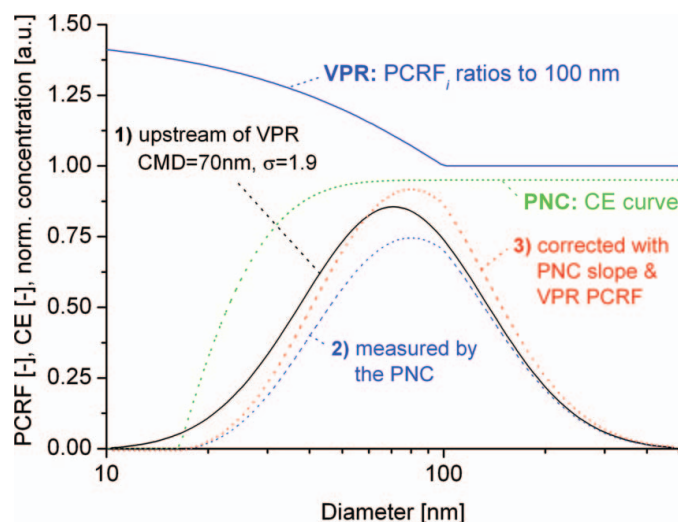


FIG. 6. Example showing size distributions at the inlet of the PN system (1) and the final corrected based on the hypothetical PNC CE (CE_i) curve and the VPR $PCRF_i$ ratios at size i (2). (Color figure available online.)

Figure 6 shows a typical CE curve for a PNC ($CE_{23} = 0.5$, $CE_{41} = 0.9$, slope = 0.95) and a VPR ($PCRF_{30} = 1.3 \times PCRF_{100}$, $PCRF_{50} = 1.2 \times PCRF_{100}$). A typical size distribution upstream of the PN system (VPR) with CMD of 70 nm and standard deviation (σ) of 1.9 is also shown (see size distribution 1, assumed to be the “true” emissions). Due to the penetration of the PN system (VPR and PNC), the measured size distribution by the PNC would be lower and shifted to the right (see size distribution 2). Then, a correction with the average PCRF of the VPR and the inverse of the slope of the PNC would be applied ($\times 1.17/0.95$ in this example). The final size distribution (and the PN concentration) (size distribution 3) would be different from the original size distribution (size distribution 1). For the specific example, the mode has been shifted by 9 nm and the PN concentration is 1% less than the original “true” PN concentration.

Similarly with Figure 6, Table 3 gives the percentage (ratio) of the final PN result (corrected with the PNC slope and the VPR average PCRF) to the inlet “true” concentration for different PNC CE curves and different VPR $PCRF_i$ ratios that are legislation-compliant. The three PNC cases (A, B, and C) cover a very steep CE curve (case C: $CE_{23} = 0.62$, $CE_{41} = 0.9$, slope = 0.9), a smooth one (case B: $CE_{23} = 0.38$, $CE_{41} = 0.9$, slope = 1.1), and an intermediate one (case A: $CE_{23} = 0.5$, $CE_{41} = 0.9$, slope = 1.0). These cases seem extreme, but it should be taken into account that using different calibration materials (i.e., phase, chemical composition, morphology) can result in big differences in the CEs. The differences in CEs between typical PNC calibration materials, emery oil, and soot produced by a diffusion flame generator (mini CAST, Jing 2010) have been found to be ~ 0.15 and ~ 0.06 for 23 and 41 nm, respectively (Giechaskiel and Bergmann 2011). The two $PCRF_i$ ratio cases (I and II) represent the worst case (case I: $PCRF_{30} = 1.3 \times PCRF_{100}$, $PCRF_{50} = 1.2 \times$

$PCRF_{100}$) and an ideal case with no size-dependent particle losses in the VPR (case II: $PCRF_{30} = PCRF_{50} = PCRF_{100}$), respectively.

For typical size distributions with medians between 50 and 90 nm, the PN systems measure 80–106% of the original “true” emissions. The differences due to the different VPR $PCRF_i$ ratios are $< 9\%$ (e.g., compare columns A.I and A.II, B.I and B.II, and C.I and C.II), while those due to the different PNC CEs are $< 11\%$ (e.g., compare columns A.I and B.I and C.I, and A.II and B.II and C.II). The combination of the VPR and PNC can lead to up to a 20% underestimation of the emissions; however, for typical penetrations and size distributions, the underestimation is in the order of 5% (the average of columns A.I and A.II). However, in cases where the size distribution approaches the 50% cut-point of the PNC, 23 nm (e.g., 30 or 40 nm), the measured emissions can be only 60–70% of the inlet PN emissions (see rows with CMD 30 and 40 nm). Furthermore, different PN systems can exhibit up to 10% differences in the PN results, even if they comply with the legislation requirements, due to the different PNC and VPR penetrations (e.g., compare the values in each row).

Table 3 shows also that if there is NM, only a small percentage of it will be measured, which is positive if the NM is volatile, but negative if it is solid. For example, if the median of a volatile NM is 10 nm, then $< 1\%$ of it will be measured, but if the median is 20 nm, then 23–38% of it will be measured. The contribution of these particles to the total PN result depends on the ratio of the NMs and AMs. Typically, the volatile NM is removed efficiently, but not always—especially when high concentration of HCs is present and/or sulfates. It was shown experimentally (Giechaskiel et al. 2010a) that when at the inlet of a VPR, the concentration of the volatiles was 25–50 mg/m^3 (consisting only of organic matter [OM]) or 5 mg/m^3 (consisting of OM and sulfates), then the volatile NM could not be removed completely. The NM with concentration = $7.0 \times 10^8 \text{ p}/\text{cm}^3$, CMD = 19.5 nm, and $\sigma = 1.35$ was reduced to concentration = $9.0 \times 10^7 \text{ p}/\text{cm}^3$, CMD = 7 nm, and $\sigma = 1.35$ in a VPR (Giechaskiel et al. 2010a). The AM of the specific test had concentration = $3.0 \times 10^7 \text{ p}/\text{cm}^3$, CMD = 52 nm, and $\sigma = 1.95$. A PNC with $d_{50} = 23 \text{ nm}$ would measure 0% of the remaining NM. A PNC with $d_{50} = 10 \text{ nm}$ would measure 12% of the remaining NM, which is still a 35% error in the measurement of the nonvolatile particles. Thus, lowering the cutoff size of the PNC would be advisable only when low-enough concentrations of volatile materials at the inlet of the PN system can be ensured.

4.5. Closing Remarks

At this point, the ISO work on the calibration of PNCs should be mentioned (ISO 27891). The publication of the final document is expected in 2012. An inter-laboratory correlation exercise, which was launched under the auspices of the PMP Working Group, aiming at the assessment of the VPR calibration procedures employed at different instrument manufacturers

TABLE 3

Ratio of final PN result compared with the PN concentration at the inlet of the PN system for different inlet size distributions and PNC CE_i and VPR PCRF $_i$ ratios at size i

	Case	A.I	A.II	B.I	B.II	C.I	C.II
PNC	CE ₂₃	0.50	0.50	0.38	0.38	0.62	0.62
	CE ₄₁	0.90	0.90	0.90	0.90	0.90	0.90
	Slope	1.00	1.00	1.10	1.10	0.90	0.90
VPR	PCRF ₃₀	1.3	1.0	1.3	1.0	1.3	1.0
	PCRF ₅₀	1.2	1.0	1.2	1.0	1.2	1.0
CMD	σ	Final PN concentration compared with inlet concentration					
10	1.3	1%	1%	0%	0%	0%	0%
20	1.4	33%	37%	23%	26%	34%	38%
30	1.6	61%	65%	53%	56%	69%	74%
40	1.7	77%	79%	70%	71%	84%	86%
50	1.8	87%	85%	81%	80%	92%	91%
70	1.9	98%	92%	95%	89%	102%	96%
90	2.0	104%	95%	102%	93%	106%	98%

and research institutions (10 in total), is also underway and is expected to conclude in 2012. Finally, a European research project “Emerging requirements for measuring pollutants from automotive exhaust emissions” started in 2011 and one of the targets is to define better and more specific procedures for the calibration of the PN systems. Finalization of these projects is anticipated to result in reduced uncertainties of the PN results. With very careful calibration, the difference can be reduced to 10%, as long as the systems measure above their background levels (detection limits).

5. PN AND AFTERTREATMENT DEVICES

Modern engines and vehicles are equipped with a complex system of aftertreatment devices, which can be roughly divided in two categories: catalytic converters for the reduction of gaseous emissions (CO, HC, and NO_x [(mono)-nitrogen oxides]) and filters for the reduction of particles. The following sections describe the effect of the aftertreatment devices on the nonvolatile PN emissions.

5.1. Oxidation Catalysts

The aftertreatment devices that are installed on diesel engines to control the HC and CO emissions are typically called diesel oxidation catalysts (DOCs). The reduction of HCs results in a decrease in the soluble (or volatile) organic fraction of PM and the number concentration of the volatile NM. An undesirable reaction is the oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃) at high exhaust gas temperatures, which may lead to the formation of H₂SO₄ and an increase in the sulfates, and thus, of the PM and the number concentration of the volatile NM. Storage and release phenomena (to/from the DOC) further complicate things, and for this reason, no clear trend can be found between PM and DOC

or total (volatile and nonvolatile) PN and DOC (Giechaskiel et al. 2007a; Swanson et al. 2009; Herner et al. 2011). DOCs are unable to oxidize the carbonaceous fraction (soot); thus, only a small decrease (if any) is observed in the nonvolatile AM. Promising particle filtration efficiencies and soot oxidation rates in laboratory studies have been achieved with novel “open-filter” catalyst structures (sometimes called partial filters). These catalysts are not designed to achieve soot removal rates as high as seen in wall-flow DPFs. Instead, they target reaching the required PM emission levels by partial removal and later combustion of the soot particles, while strongly reducing the volatile fraction of the particles. Several experiments with diesel vehicles and these types of catalyst called PM-KAT (PM-catalyst-system) and POC (particle oxidation catalyst) have shown PM (and nonvolatile PN) reductions of the order of 20–70% (Rothe et al. 2004; Vakkilainen and Lylykangas 2004; Vaaraslahti et al. 2006; Giechaskiel et al. 2008c).

5.2. SCR, deNO_x, and LNT

These systems are flow-through catalyst types that reduce the NO_x emissions (Majewski and Khair 2006). Catalysts promoting the reduction of NO_x by HCs have been termed lean NO_x catalysts (LNCs) or deNO_x catalysts. Hydrocarbons react with NO_x, rather than with O₂, to form nitrogen, CO₂, and water. Systems that use the HCs of the exhaust gas are called passive deNO_x systems, while those with hydrocarbon enrichment are called active deNO_x systems. NO_x conversion efficiencies can be improved by storing HCs and/or NO_x in the catalyst washcoat (during lean operation) and releasing them under conditions that are more favorable for the catalytic reactions (rich operation). Such storage is realized in HCs and/or NO_x adsorbers (known as lean NO_x traps, LNT). The storage medium is usually barium carbonate, which however preferentially stores sulfur as sulfate

rather than NO_x as nitrate. During high-temperature operation, these sulfates may all be released in a short period, leading to large numbers of NM particles. This can be avoided by using very-low-sulfur fuels and lubricants.

Selective catalytic reduction (SCR) of NO_x by nitrogen compounds uses ammonia (or urea), which reacts with NO and NO_2 to form nitrogen and water. However, at low temperatures, ammonia can react with NO_2 (or SO_3) to form ammonium nitrate (or sulfate). Overdosing of ammonia may result in the release of undesirable ammonia (ammonia slip) and nitrous oxide (N_2O) in the atmosphere.

An increase in the nonvolatile PN emissions due to secondary formation of nanoparticles in the SCR system has been found for both non-DPF (Ntziachristos et al. 2004a) and DPF-equipped HD engines (Czerwinski et al. 2009). Chemical analysis of these particles showed that these are mostly composed of urea that did not decompose or are byproducts from the urea decomposition, mostly ammonium nitrates and sulfates and HNCO (Lee et al. 2007). A study of metal emissions from HD vehicles equipped with DPF and SCR showed the release of constituents of the SCR washcoat ($\text{V}_2\text{O}_5/\text{TiO}_2$) from the catalyst under high-temperature operation (Hu et al. 2009). A dependence of the PN emissions on the urea injection rate and pressure was also found, especially for particles in the micrometer range. High numbers of volatile particles can be observed, but they can be attributed to NM formation due to the existence of a catalyst (Rusch et al. 2003; Biswas et al. 2008a; Herner et al. 2011).

There are also some studies that measured lower nonvolatile PN emissions after SCR (Vaaraslahti et al. 2004b; Hosoya et al. 2007; May et al. 2008). However, the reduction probably originated from the oxidation catalyst or DPF installed simultaneously with the SCR system.

5.3. DPF

The operation principle of wall-flow DPF systems is based on the separation of the airborne particles from the gas stream by deposition on a collecting surface porous to gas but almost impermeable to carbonaceous particles. As soot accumulates in the DPF, there is a need for periodic regeneration (oxidation of the soot) in order to avoid clogging of the DPF or uncontrolled oxidation of the soot, which can potentially damage the DPF. Under some operating conditions of the vehicle or engine, the exhaust gas temperature is high enough to oxidize the soot (passive regeneration). When the increase in the temperature is initiated by the vehicle's engine management system (e.g., post-injection of fuel, electric heaters) it is called active regeneration. These topics will be discussed in more details in the following text. Flow-through filters were discussed in the previous DOC section (5.1).

5.3.1. Filtration efficiency

The performance of DPFs may be expressed as filtration efficiency (E_i) or penetration ($P_i = 1 - E_i$), which is a function of the size of the particles entering the filter. Filtration efficiency

of a size i is the ratio of the particle concentration of that size collected on the filter to the particle concentration entering the filter. Filters may have limited effectiveness, or be totally ineffective, in controlling the volatile fractions of PM (OM and sulfates and nitrates) because they are gaseous in the DPF and form upon cooling and dilution (Andersson et al. 2001). The OM can be reduced if the DPF contains an oxidation catalyst as well, but the sulfates can increase especially at high temperatures (Vaaraslahti et al. 2004a, 2004b).

The DPF filtration efficiency of the nonvolatile particles is typically $>95\%$ (Majewski and Khair 2006, Burtscher 2005). A PN reduction of 2–3 orders of magnitude is common, and parameters that affect the efficiency include the filter microstructure (pore size distribution, porosity) and geometric properties (filter diameter and length, cells per square inch, wall thickness), as well as the exhaust flow and temperature conditions (Konstandopoulos and Papaioannou 2008; Tandon et al. 2010). Furthermore, the DPF filtration efficiency (E) evolves starting from the clean filter with a relatively low value to reach the maximum filtration efficiency when the deposited soot itself acts as the filtering medium (soot cake). Most of the above parameters can affect PN measurement and thus the repeatability of the measurement. As it has been shown in many studies (Andersson et al. 2007; Giechaskiel et al. 2007b), the nonvolatile PN emissions are elevated after a regeneration event (empty DPF), but stabilize at a lower level after a soot cake is formed. The repeatability of the measurement has a $\text{CoV} > 35\%$ immediately after the regeneration, decreasing to $< 15\%$ after soot cake formation (Giechaskiel et al. 2007b).

5.3.2. Cold start

High emissions are observed in DPF-equipped engines at the start of a cold cycle. The elevated number emissions under cold start may be due to particles formed by the nucleation/condensation of volatile material previously stored within the exhaust system, aftertreatment, or particulate layer and released as the exhaust line heats up (when not preconditioned appropriately). They may also be blow-out of loose nonvolatile particle deposits, as the filter is exposed to highly transient operation with respect to thermal and flow conditions (Giechaskiel et al. 2007b). Parameters that have been found to affect the blow-out are gas velocity, soot concentration in the exhaust gas, amount of soot accumulated in the filter, and adhesive and cohesive properties of the particulates (Ciambelli et al. 2005). It has been shown that flow, temperature, and pressure changes and the preconditioning of the measurement (which affects the particles that settle and are trapped in the DPF interstices) contribute to the emission of nonvolatile particles from the DPF (Mohr et al. 2006, Giechaskiel et al. 2007b). In addition, the state of the DPF (empty or loaded) also affects the cold-start emissions (Mohr et al. 2006; Dwyer et al. 2010). Another explanation is that small defects, which affect porosity and, in turn, DPF filtration efficiency, close up as the DPF temperature rises (Braisher et al. 2010).

5.3.3. Active regeneration

During active regeneration, engine measures such as exhaust throttling and late post-injection are employed to raise the exhaust temperature to a level at which the elemental carbon trapped in the DPF burns. During the regeneration period, significant increases in the total PN emissions and gaseous pollutants are observed (Dwyer et al. 2010). Size spectra reveal an NM peaking at approximately 10 nm, at concentrations that can exceed the emission levels under nonregenerating conditions by more than three orders of magnitude (Ntziachristos et al. 2004b; Mathis et al. 2005; Campbell et al. 2006; Giechaskiel et al. 2007b; Bikas and Zervas 2007). These nano-sized particles are found to be mostly volatile in nature, with their concentrations correlating with the sulfate content of the emitted PM (Guo et al. 2003; Bergmann et al. 2009). PN measurements following the PMP methodology are found to be minimally affected by this burst of NM particles, partly because of the large cutoff size of the PNC (23 nm) and partly because a VPR can efficiently vaporize these volatile nano-particles or shrink them to a size that cannot be detected by the PNC (Giechaskiel et al. 2007b). A high concentration of sub-23-nm particles downstream of a VPR system has been observed in some cases: these might be volatile particles that do not evaporate completely in the VPR or even an artifact resulting from pyrolysis of volatile HCs inside the evaporating tube of the VPR (Mathis et al. 2005; Mohr et al. 2006; Dwyer et al. 2010; Mamakos et al. 2011a). Quantitatively, the impact of active regeneration on the production of nonvolatile PN emissions appears to be small compared with the cold-start emissions (Andersson et al. 2007). Active regeneration is triggered when engine load and thus exhaust temperatures are highest, and consequently, these events do not coincide with cold starts and effects can easily be discriminated. For an NEDC (New European Driving Cycle), where the regeneration is occurring at the EUDC (Extra-Urban Driving Cycle) part (high-speed phase), the PN emissions of the EUDC (2×10^{10} p/km) are <5% of the levels seen in the cold-start ECE phase of the NEDC. It has to be noted however that in most cases, the regeneration cannot be finalized during the short high-speed part of the EUDC phase of the NEDC. The percentage of nonvolatile particles during regeneration however can be significantly higher for other more aggressive cycles, including prolonged operation at motorway driving conditions (Mamakos et al. 2011b). The PN emissions (>23 nm) during phases with regeneration can reach 3×10^{12} p/km, which is five times the Euro 5b PN limit.

5.3.4. Passive regeneration

Passive regeneration is possible when the exhaust temperatures and oxygen (and NO₂) levels are sufficiently high to enable the soot to combust without any additional thermal assistance from engine changes, i.e., at high speeds. This is even more likely with HD engines where higher exhaust temperatures are encountered. The PN emissions during passive regeneration are not as high as during active regenerations (Andersson et al. 2007). Passive regeneration results in high emissions

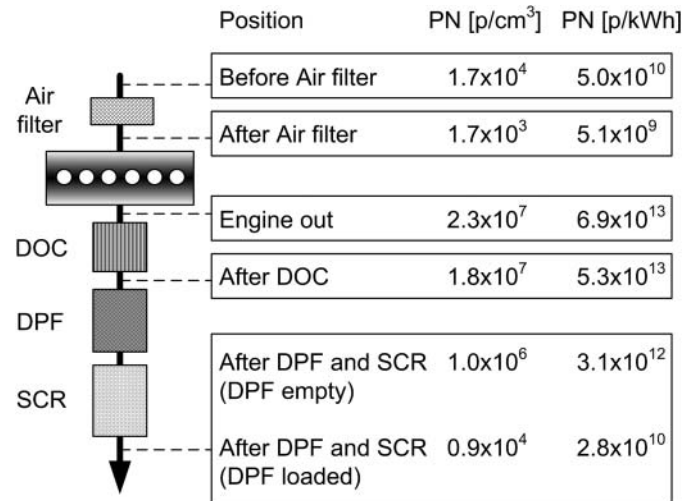


FIG. 7. PN emissions at different locations.

during subsequent accelerations and thus worse repeatability of the tests. For example, during the PMP HD inter-laboratory exercise, the WHSC (World Harmonized Steady Cycle) had worse repeatability compared with the cold WHTC (World Harmonized Transient Cycle) because it was preceded by a warm-up phase at a high exhaust gas temperature mode that passively regenerated the DPF (Giechaskiel et al. 2009a). Whenever possible, a preconditioning that fills the DPF with a soot cake (i.e., an operation mode with low exhaust gas temperature for >30 min) is recommended to improve the repeatability (Andersson et al. 2007).

5.4. PN Emissions along the Tailpipe

Figure 7 shows measurement results (nonvolatiles >23 nm) from a PN system (APC) drawing from different sample points along the intake and exhaust system layout of a 10.5-L engine (tested at the WHTC) (AVL internal data). As Figure 7 shows, the intake air filter reduced the PN concentration by approximately 90%. The PN emissions upstream of the filter were relatively high because they were measured inside the test cell near to the turbocharger of the engine. After combustion, the engine-out emissions are around 7×10^{13} p/kWh. The DOC seems to reduce the PN concentration by ~20%, but this decrease is probably due to coagulation of the particles along the tailpipe. The DPF efficiency depends on the fill state: it ranges from 95% (immediately following regeneration) to 99.9% (filter cake formed). At the tailpipe exit, the PN concentrations are of the same order as the intake air levels. A technically important fact is that all measurements, which cover emission levels of more than three orders of magnitude, were conducted with the same PN system.

6. PN Real-Time Patterns

The following section will give examples of PN (nonvolatiles >23 nm) real-time patterns of LD vehicles and HD engines.

While these are representative of the corresponding vehicle technologies, they can vary considerably between different implementations of similar technologies, depending on each manufacturer's strategy, fuel, driving behavior, etc.

6.1. LD Vehicles

Real-time PN emissions patterns during an NEDC from different LD vehicle technologies are provided in Figure 8a (Diesel) and Figure 8b (Gasoline); all sampled from the CVS with a flow rate normalized to 11 m³/min.

6.1.1. Non-DPF diesel vehicles

The emissions of non-DPF diesel vehicles follow the air-to-fuel ratio changes (and the exhaust flow rate). The emissions increase over accelerations and decrease over decelerations; generally, the higher the load and/or the speed, the higher the emissions (Figure 8a, D1).

6.1.2. DPF diesel vehicles

The real-time patterns of the DPF vehicles are much lower (2–3 orders of magnitude) than the emissions of the non-DPF diesel vehicles for nonregenerating cycles (the emissions during regenerations were discussed in Section 5). The emission pattern strongly depends on the porosity and the fill state of the DPF. Cold-start operation has a profound effect on the PN emissions of vehicles equipped with very efficient DPF systems, with more than 99% of the total produced particles emitted over the first 100 s of the (nonregenerating) cycle (Figure 8a, D1 + DPF). Some increase in PN emissions is also observed over accelerations and the high-speed operation, but with orders of magnitude lower than that seen in the cold-start phase. High-porosity filters exhibiting reduced filtration efficiency over the entire duration of the test cycle have also been reported (Mohr et al. 2006; Mamakos et al. 2011a) (Figure 8a, D2 + DPF).

6.1.3. G-PFI engines

In conventional (multipoint port fuel injection [PFI]) gasoline engines (G-PFI engines; Figure 8b), fuel and air are mixed in the intake system and introduced together in the cylinder. The stoichiometric air-to-fuel ratios, required for an efficient three-way catalyst operation, result in low soot formation. However, brief enrichments may occur due to imperfections in fuel metering, and these can lead to soot formation and increased PN emissions; rich air-to-fuel ratios are intentionally used during cold start to heat up the catalyst and during accelerations to improve drivability and protect catalytic systems from high exhaust temperatures (Mohr et al. 2006; Kayes and Hochgreb 1999; Maricq et al. 1999b) (Figure 8b, G-PFI). There is no evidence that the small rich/lean perturbations around lambda 1 required for a three-way catalyst function lead to measurable changes in PM (Ricardo UK internal research).

6.1.4. G-DI engines

A gasoline direct injection (G-DI) engine delivers fuel directly into the cylinder, after the air has entered. In a manner

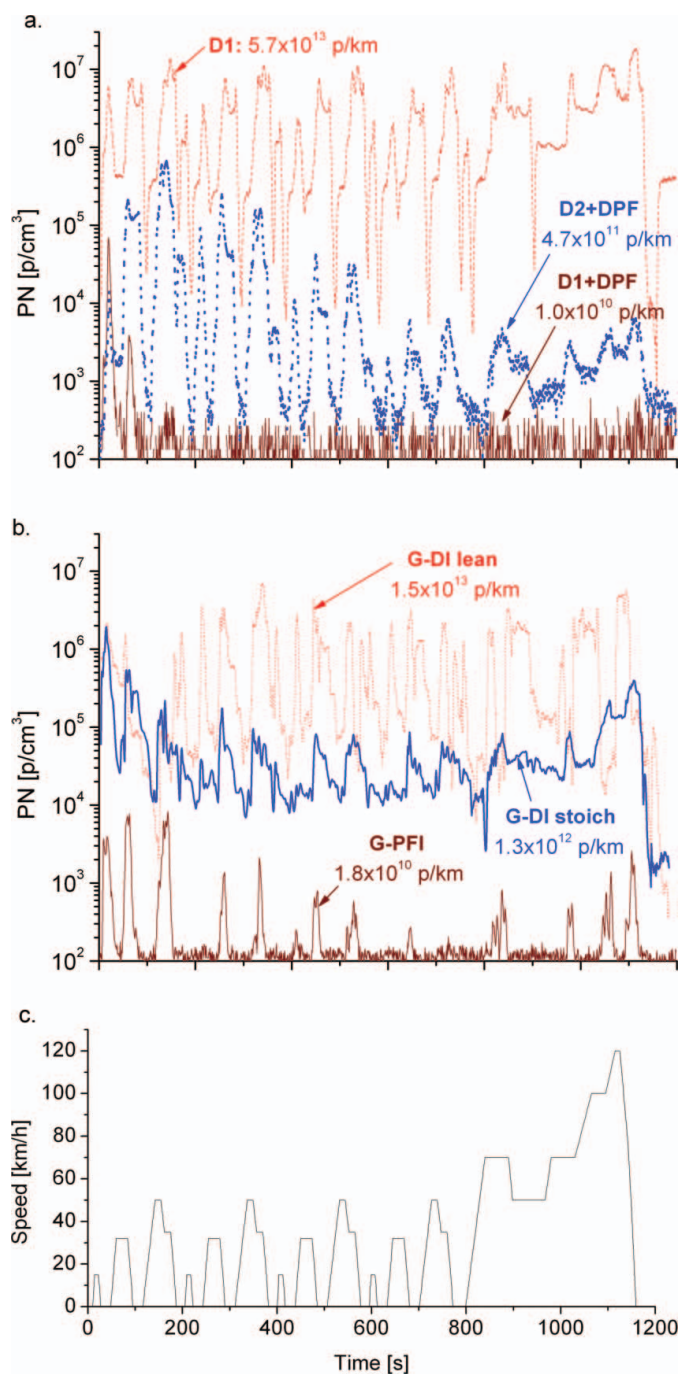


FIG. 8. Real-time examples of various light-duty (LD) vehicles over NEDC cycles (sampled from a CVS): (a) diesel vehicles, (b) gasoline vehicles, (c) NEDC speed pattern. Concentrations refer to the CVS (flow approximately 11 m³/min). (Color figure available online.)

similar to that of a diesel engine, the power output of this engine is controlled by varying the amount of fuel that is injected into the cylinder. Therefore, there is no need for intake air throttling that significantly increases pumping losses and consequently fuel consumption. A spark plug is employed to ignite the air/fuel mixture, thus avoiding many of the requirements of autoignition

quality that are inherent in fuels for the diesel engine (Zhao et al. 1999). The G-DI engines can operate under both lean and stoichiometric mode, even though there is no distinct dividing line between them since the principal difference lies in the fuel injection timing (Maricq et al. 1999). When the fuel is injected late in the compression stroke, a stratified charge develops, which allows operation with overall lean mixtures. Early injection leads to a more homogeneously mixed charge resembling that of conventional G-PFI engines.

There are two main variants of the G-DI technology available in the market. One operates always in the stoichiometric mode, an approach that allows the use of a conventional three-way catalyst for emission control, and the other, in a mixed-mode G-DI (lean G-DI), which under low-load conditions operates on a stratified charge. One shortcoming of the lean G-DI engines is that due to the excess of oxygen in the exhaust, it is not possible to reduce NO_x emissions in conventional three-way catalytic converters. Vehicles equipped with lean G-DI engines utilize an LNT to store the NO_x emissions when the exhaust is oxygen-rich and then convert the stored NO_x to nitrogen (N_2) during intermittent short periods of controlled overfueling.

Figure 8b shows typical PN emission patterns from a lean-burn G-DI vehicle and a stoichiometric G-DI vehicle. The emissions from the lean-burn G-DI vehicle are found to follow the air-to-fuel ratio and are generally higher compared with those of the stoichiometric G-DI vehicle (five times higher in the particular case shown). The cold-start operation has a different effect on PN emissions of these two vehicle categories. Stoichiometric G-DI vehicles operate at slightly high temperatures to heat up the catalyst and improve the drivability, and this results in increased soot formation. For the same reasons, lean-burn G-DI vehicles operate over a prolonged period of time stoichiometrically, and this can actually result in lower PN emissions compared with a hot-start test cycle (Mamakos et al. 2011c; Deutsche Umwelthilfe 2011).

6.2. HD Engines

Figure 9 shows the real-time patterns of different HD engines for hot-start European Transient Cycles (ETCs): a Euro III without any aftertreatment device (D1), the same equipped with an open (partial-flow deep bed or flow-through) filter (D1 + POC) or with a DOC and a DPF (D1 + DPF) (this is the engine used in the PMP HD inter-laboratory exercise), and another diesel engine with DPF (D2 + DPF) certified for the US 2007 regulation. PN emissions follow the cycle and the air-to-fuel ratios irrespective of the technology level. The open filter decreased the emissions by 55%. The DPF showed a reduction of three orders of magnitude on transient cycle—similar to LD applications. The D2 + DPF engine either had a DPF with higher porosity or the engine was calibrated for high engine-out PM/low NO_x , in order to comply with the NO_x limits of the US 2007 regulation. Note that the y-axis scale goes to lower concentrations than for the LD vehicles (Figure 8) due to the lower

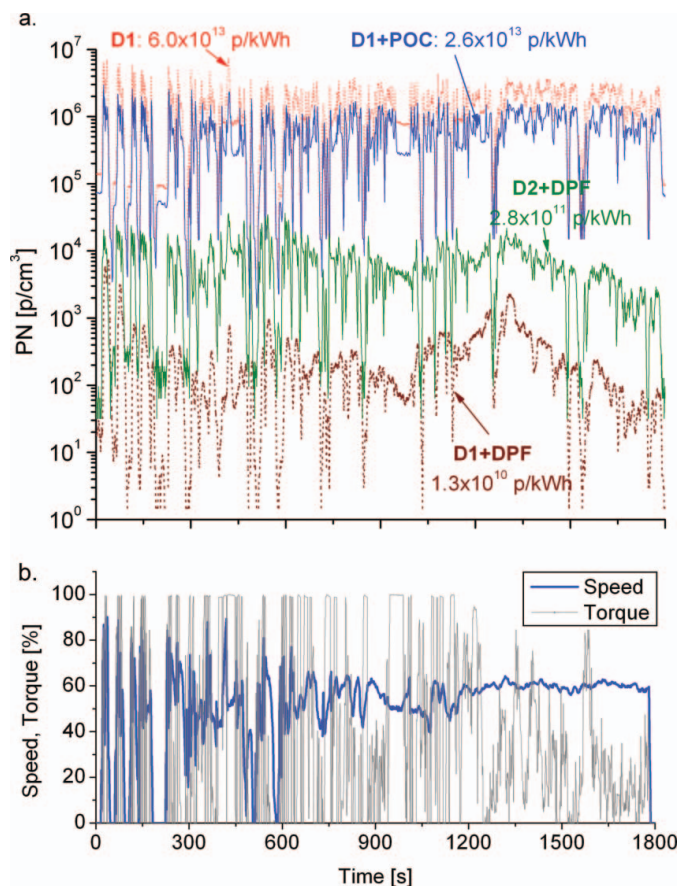


FIG. 9. Real-time examples of an HD Euro III diesel engine (D1) with different aftertreatment devices, and a diesel engine equipped with a DPF (D2 + DPF). POC refers to an aftertreatment device that includes a diesel oxidation catalyst and a partial-flow deep-bed filter (open filter). The engine speed and torque patterns of the tested cycle (hot-start ETC) are also shown in the bottom panel. Measurements from the CVS, with a flow of approximately $100 \text{ m}^3/\text{min}$. Concentrations refer to the CVS. (Color figure available online.)

backgrounds of the CVS and/or PN systems used for the specific engines.

7. PN, PM, AND SOOT

In this section, PN, PM, and soot and the parameters of the size distributions (assuming log-normal distributions) of the different engine technologies are discussed.

7.1. PN and Size Distributions

Table 4 gives typical (nonvolatile $>23 \text{ nm}$) PN emission ranges of various engine technologies. For this analysis, extreme values were not taken into account. The values are based on more than 45 LD diesel vehicles without DPF, 35 with DPF, 40 G-DI vehicles, and 25 G-PFI vehicles (Mohr et al. 2003; Ntziachristos et al. 2004b; Karlsson 2005; Bosteels et al. 2006; Mohr et al. 2006; Vogt et al. 2006, 2010; Andersson et al. 2007; Giechaskiel et al. 2008a; Giechaskiel et al. 2008c; May et al. 2008; Braisher et al. 2010; Giechaskiel et al. 2010b; Zhang et al.

TABLE 4

Typical (nonvolatile >23 nm) particle number emissions (PN), count median diameter (CMD), and standard deviation (σ) of various engine technologies (assuming log-normal size distributions)

Technology		PN (p/km) or (p/kWh)	CMD (nm)	σ (–)	PM (mg/km) or (mg/kWh)	Ash (%)	Soot (%)	OM (%)	Sulfates (%)
HD	D	5×10^{13} – 2×10^{14}	50–100	1.7–2.1	20–80	5–10	40–75	20–50	0–15
HD	D + DPF	5×10^{10} – 2×10^{12}	60–75	1.6–2.0	1–4	0–5	5–20	20–50	5–60
LD	D	2×10^{13} – 2×10^{14}	40–80	1.7–1.9	10–40	0–5	55–90	10–40	5–15
LD	D + DPF	5×10^{10} – 6×10^{11}	45–75	1.7–2.1	0–2	0–5	0–15	40–75	5–35
LD	G-DI lean	2×10^{12} – 2×10^{13}	50–85	1.7–2.1	1–20	0–5	55–80	20–40	0–5
LD	G-DI stoich.	1×10^{12} – 8×10^{12}	40–75	1.7–2.0	1–10	0–5	75–90	10–25	0–5
LD	G-PFI	2×10^{10} – 6×10^{11}	45–75	1.6–2.2	0–2	0–5	10–25	45–80	10–40

Details of typical PM emissions and chemical composition are also given. HD = heavy duty, LD = light duty, D = diesel, G = gasoline, PFI = port fuel injection, DI = direct injection, OM = organic matter, Soot = carbonaceous fraction.

2010; Maricq et al. 2011; Mamakos et al. 2011b; Mamakos et al. 2011c; Mamakos et al. 2011d). The HD results are based on more than 20 engines without DPF and 10 with DPF. Typical diesel (D) emissions are of the order of 5×10^{13} p/km (p/kWh) for both LD and HD and the technology (up to Euro 4 for LD and Euro V for HD) and the fuel has a relatively small effect of <50% (Tzankiozis et al. 2010). A significant decrease in the emissions (2–3 orders of magnitude) is achieved with the introduction of DPFs.

The G-PFI engines emit typically below 1×10^{11} p/km. However, a recent study by the AECC (Association for Emissions Control by Catalyst) found emissions in excess of 10^{12} p/km from a Euro 4 and a Euro 3 G-PFI vehicles having an accumulated mileage of 60,000 and 120,000 km, respectively, raising some concerns on the potential emission degradation for this vehicle category (May 2011).

The G-DI engines emit approximately 5×10^{12} p/km. Prototype G-DI engines with advanced injection systems and engine calibration (Piock et al. 2011; Whitaker et al. 2011) or commercial G-DI engines retrofitted with gasoline particulate filters (GPF) (Saito et al. 2011) have decreased the PN emissions below the diesel LD vehicles PN limit with small fuel consumption penalty. The limit value for G-DI vehicles is under discussion and the European Commission is working on a cost-benefit analysis in order to define the limit value (Steininger 2011). The most recent proposal is that the PN limit should, at this stage, apply to G-DI vehicles only, although a number standard might be applied to all gasoline vehicles at a later date. The limit proposed for G-DI vehicles is 6×10^{11} p/km (the same as the limit for diesel vehicles) but with a footnote allowing a 3-year derogation to 6×10^{12} p/km at the request of the manufacturer.

There are some studies that have examined the (nonvolatile) size distributions of LD vehicles and HD engines. Table 4 summarizes the results of more than 15 LD diesel vehicles without DPF, five with DPF, 10 G-DI vehicles, and 30 G-PFI vehicles (Hall and Dickens 1999; Maricq et al. 1999d, 2002, 2011; Mohr et al. 2000; Harris and Maricq 2001; Mohr et al. 2003a, 2003b;

Ntziachristos et al. 2004b; Ntziachristos et al. 2005; Price et al. 2006; Giechaskiel et al. 2010a; Khalek et al. 2010; Tzankiozis et al. 2010; Mamakos et al. 2011d; Mamakos et al. 2011c; Graskow et al. 1999; Maricq et al. 1999a). The HD results are based on more than 20 engines without DPF and five with DPF (Andersson et al. 2001; Harris and Maricq 2001; Thompson et al. 2004; Virtanen et al. 2004; Giechaskiel et al. 2008c; Giechaskiel et al. 2010a). The standard deviations are derived from approximately one-third of the vehicles for which there was information in the texts. The size distributions have CMDs in the range of 50–75 nm (LD) and 60–85 nm (HD), with standard deviations around 1.8–1.9.

7.2. PM and Chemical Composition of PM

Table 4 gives typical PM emissions and typical percentages of the different fractions of the PM for older and newer HD diesel engines (Kittelson 1998; Schauer 2003; Kittelson et al. 2006a; Khalek 2009; Biswas et al. 2009b; Schauer et al. 1999) and LD vehicles (Andersson et al. 2001; Cheung et al. 2009; Schauer et al. 2008) (see also Ntziachristos and Samaras (2010b) and references within). The values are only indicative since the results are strongly dependent on the driving cycle, the fuel, and the specific engine technology and aftertreatment. The carbonaceous fraction (soot) is significant for diesel engines and vehicles (typically > 50%) but becomes negligible when a DPF is installed. G-DI engines have also a high portion of carbonaceous fraction, while for G-PFI engines, it is much smaller. The OM usually depends on the existence of the oxidation catalyst: it is negligible when one is present, with the exception of cold starts where low temperatures reduce the catalyst function. The sulfate fraction is high at elevated exhaust gas temperatures and/or when fuel with high-sulfur content is used. The ash fraction is small, but might be important when additives are used and when the other fractions are low (Mayer et al. 2010).

7.3. Filter Artifacts

The PM, which is defined as the mass increase in a filter during a cycle, is determined by all particles deposited onto the filter, including the species adsorbed or condensed on the particles. However, some gaseous species are also adsorbed on the filter material, contributing to the filter artifact (FA). For older engines with high PM emissions (>25 mg/km), the contribution of the FA was negligible (Amann et al. 1980). For modern G-PFI and diesel DPF-equipped vehicles, the contribution can be significant.

Figure 10 shows the PM results of a DPF-equipped vehicle (Andersson et al. 2007) for six NEDCs. In parallel, an Engine Exhaust Particle Sizer (description in, e.g., Engine Exhaust Particle SizerTM [EEPS] 2005) was measuring from the CVS. This instrument measures the number-weighted size distributions in real time and can thus provide some information on the mass contribution of the NM and AM. As already mentioned, particles in the NM are considered to be mainly volatiles, while in the AM, they are considered carbonaceous. A density of 1.8 g/cm³ was used for the NM, assuming that it consisted only of H₂SO₄ and ammonium nitrate. Since the NM contains also HCs (density 0.8 g/cm³), the calculated values are expected to overestimate the contribution of the NM. The mass of the AM was calculated as described in Section 7.5 (Equation (5)). The calculated mass of the AM was generally in good agreement with the nonvolatile (soot) mass measured by an LII instrument (description, e.g., in Schraml et al. 2000), confirming that the contribution of volatiles to the AM particles was small.

The calculated EEPS mass for an NEDC without regeneration (#1) (<0.01 mg/km) constitutes $<5\%$ of the corresponding filter mass and almost all of it lies in the AM, with the contribu-

tion of the NM being negligible. The remaining 0.5 – 0.6 mg/km can be attributed to gaseous species adsorbed on the filter (artifacts, i.e., FA). In the following cycle (#2), where regeneration occurred, EEPS mass comprised $\sim 40\%$ of the filter mass. The contribution of both the NM and the AM increased for this test, indicating an increase in both solid and volatile particles. Over the next two regenerating cycles (#3 and #4), the calculated EEPS mass was approximately 7% of the filter mass. The first nonregenerating cycle (#5) showed high emissions of AM particles, which constituted 15% of the filter mass, and subsequently dropped to 5% over the next test repetition (#6), as some soot cake was formed inside the DPF. The contribution of the NM node in these two cycles was negligible. In all cases, even for the first regenerating cycle where the volatile emissions were high, the FA was $>60\%$ of the filter mass, or in absolute levels around 0.5 mg/km. Note that fluorocarbon-coated glass fiber filters (TX40H120-WW) were used, and fluorocarbon membrane filter (Teflo) would probably have shown a smaller volatile artifact (Chase et al. 2004). Similar observations have been made by others as well (Chase et al. 2004; Maricq et al. 2011; Mamakos et al. 2011d), who have identified the importance of the FA for low PM emission vehicles (e.g., DPF-equipped, G-PFI vehicles, etc.) and have it determined to be of the order of 1 mg/km.

7.4. PM and PN

Recently, many discussions were initiated regarding the correlation between PN and PM, especially in the US, where a more “equivalent to PM” PN limit was desired. Figure 11 compares PM and PN for different HD and LD technologies. Each point is a different vehicle (engine) or the same vehicle (engine) with different aftertreatment technology. Tests of more than one repetition or more than one fuel were averaged. Data include those from the PMP inter-laboratory exercise and from various laboratories (see references in Table 4, Section 7.1). In total, data from >20 HD engines and >150 LD vehicles are plotted.

A relatively good correlation is observed between PM and PN for $PM > 5$ mg/km (mg/kWh) (corresponding approximately to $>5 \times 10^{12}$ p/km [p/kWh]). Almost all points are between 1×10^{12} and 4×10^{12} p/mg. As other researchers have noticed (Maricq et al. 2011), the correlation between PN and PM can be expressed with a value of 2×10^{12} p/mg. The correlation disappears at low PM masses. Below 3 mg/km (mg/kWh), the PM method cannot quantify accurately the true emission levels of the vehicles and engines, which can vary by two orders of magnitude in terms of number. Again, this reflects a large number of volatile artifacts on the filter for these low emission levels and the different backgrounds of CVS systems. It seems that the PM HD method has a detection limit of around 2 – 3 mg/kWh, slightly higher than the 1 – 2 mg/km detection limit of the PM LD. One of the reasons is that the typical minimum mass collected on a filter (20 μ g due to the volatile artifacts) translates to different PM emissions for HD and LD due to the different CVS (or exhaust) flow rates and distance or work of a cycle.

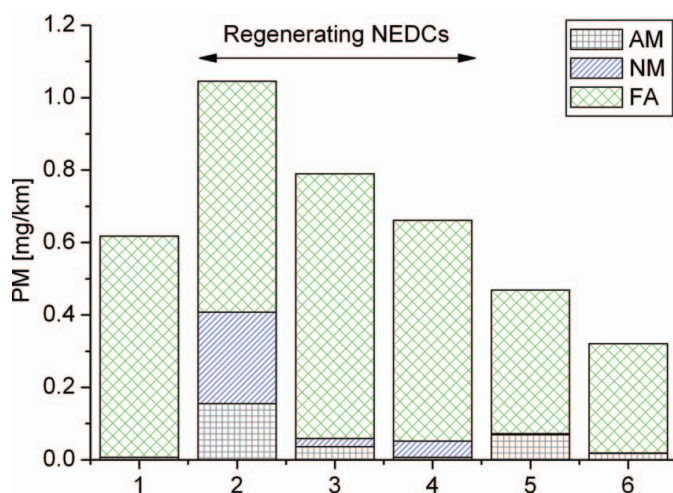


FIG. 10. PM emissions of NEDC cycles (in chronological order). During NEDCs #2–4, partial (incomplete) active regenerations occurred. The nucleation mode (NM) mass and accumulation mode (AM) mass were estimated from the EEPS size distribution. The filter artifact (FA) was estimated as the difference in the filter PM emissions between the AM and the NM. (Color figure available online.)

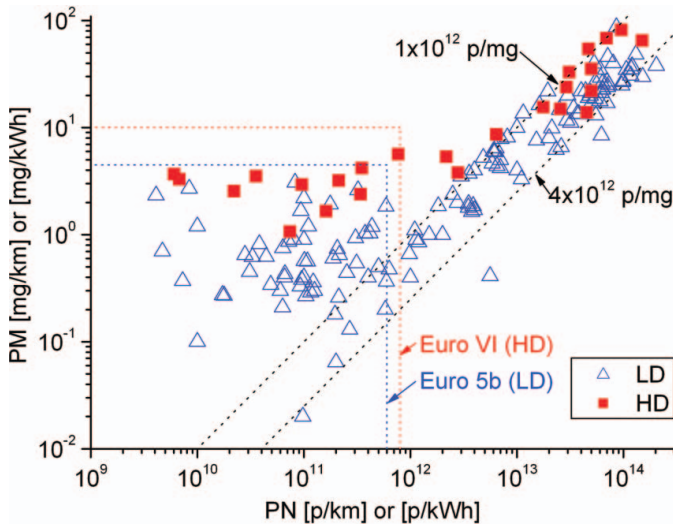


FIG. 11. Comparison of PN and PM emissions for different vehicle technologies. The dotted lines show the legislation limits. (Color figure available online.)

Figure 11 also shows the PM and PN limits for LD and HD vehicles. The graph illustrates that compliance with the PN limit will ensure compliance with the PM limit, but the opposite does not hold. A PN limit that would be equivalent to the established PM threshold of 4.5 mg/km would correspond approximately to 5×10^{12} p/km (one order of magnitude higher than the current PN LD limit). Similarly, the Euro VI HD PM limit of 10 mg/kWh would correspond to 1×10^{13} p/kWh, one order of magnitude higher than the proposed limits of 6×10^{11} p/kWh (WHTC) and 8×10^{11} p/kWh (WHSC). The PN limits were set based on the best-available technology of that time (wall-flow DPFs) and there was no regulatory intent to match the two different metrics.

7.5. PN and Soot

The correlation with PN improves when the nonvolatile mass (soot) is plotted instead of the total PM, as shown in Figure 12. Data came from many studies, which include ~ 50 LD vehicles and ~ 10 HD engines (Mohr et al. 2003a, 2003b; Bosteels et al. 2006; Mohr 2008; May et al. 2008; Braisher et al. 2010; Giechaskiel et al. 2010a; Khalek et al. 2010; Vogt et al. 2010; Mamakos et al. 2011c, 2011d). The soot data are mainly from a photoacoustic sensor (micro soot sensor, MSS, description in, e.g., Schindler et al. 2004). A limited number of tests were conducted with a multiangle absorption photometer (MAAP, description in, e.g., Petzold and Schönlinner 2004), and even fewer with chemical analysis of the PM filters. The above methods use different principles and measure different properties of the carbonaceous fraction and sometimes have big differences. Here, we assumed that all soot measurement methods give similar results.

The three dotted lines in Figure 12 give the estimated non-volatile mass of the carbonaceous fraction (or soot or black

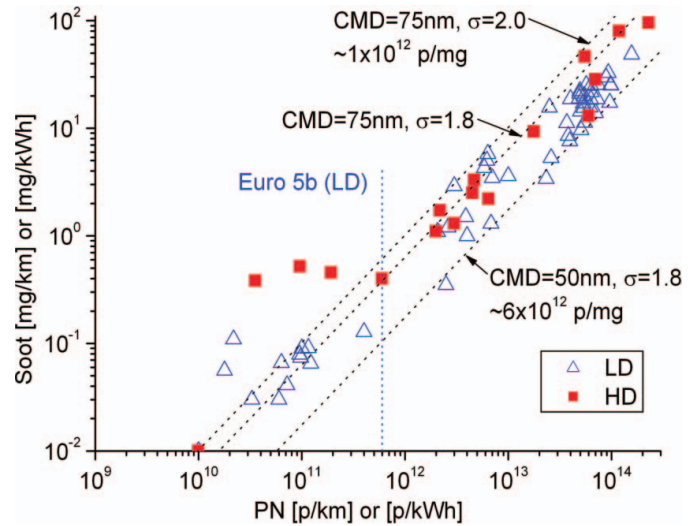


FIG. 12. Comparison of PN and soot emissions for different vehicle technologies. CMD = count median diameter, σ = standard deviation. (Color figure available online.)

carbon or elemental carbon) based on the number concentration, assuming log-normal size distributions with CMD of 50 nm and standard deviation (σ) of 1.8, and CMD of 75 nm and σ of 1.8 or 2. These parameters can be considered representative for most cases (Table 4).

$$\text{Soot} = \frac{\pi}{6} \sum_i^{k_{AM}} d_i^2 \rho_{e,i} N_{i,AM}, \quad [5]$$

where k_{AM} are the size bins, d_i the particle size, $N_{i,AM}$ the PN concentration at bin i , and $\rho_{e,i}$ the effective density of the particle at bin i . Experimentally determined effective densities suggest a power-law dependence on the mobility diameter (Maricq and Xu 2004), characteristic of fractal-like structures, which can be described as:

$$\rho_{e,i} = \min \left(\rho_0, \rho_0 \left(\frac{d_i}{d_0} \right)^{d_f-2} \right), \quad [6]$$

where d_f is the fractal dimension of the particle (2.3) (Maricq and Xu 2004), ρ_0 is the primary particle density (1.8 g/cm^3) (average of values given in Park et al. 2004, Braun et al. 2004, di Stasio 2002), and d_0 is the size of the primary particle (23 nm) (Wentzel et al. 2003).

Most results lie within these lines, which confirm the data presented in Table 4. Note also that the HD results are higher than the LD results, indicating higher mean diameters and geometric standard deviations. Vehicles or engines close to the certification PN limit (6×10^{11} p/km or p/kWh) have soot emissions close to 0.1–0.3 mg/km (or mg/kWh), which seems to be the detection limit of the current soot measurement methods. The LOD of a PN system (at the CVS) is typically $< 10^{10}$ p/km (or p/kWh), which is equivalent to $< 10 \text{ } \mu\text{g/km}$ (or $\mu\text{g/kWh}$), at least one

order of magnitude lower than the detection limit of the soot methods. Using the instruments directly at the tailpipe improves their detection limit at least by a factor of 5.

8. PN AND PM FROM DIFFERENT SAMPLING LOCATIONS

All LD regulations require the measurement of PM and PN from full-flow dilution tunnels (CVS). However, the European HD regulation permits the measurement of PM and PN from PFDS as well. For research and development purposes, PN systems are usually connected directly to the tailpipe due to cost and space considerations. Thus, it is important to understand differences between measurements of PM and PN from the tailpipe, CVS, and PFDS.

Figure 13 shows the differences between PFDS and CVS for PM emissions. These data are based on 15 HD engines of different emission levels (results summarized in Giechaskiel et al. 2011b). Each point is a different engine–aftertreatment combination. Emissions are averages of more than three cycles. Error bars stand for ± 1 standard deviation of the differences between PFDS and CVS for the specific engine–cycle combination. Only one LD result is available (from a G-DI vehicle) because PFDS are seldom used with LD vehicles (AVL internal data).

For PM emissions in the range 20–100 mg/kWh, the partial-flow systems measure approximately from 20% lower up to 10% higher than the CVS. For PM emissions <10 mg/kWh, the differences are of the order of $\pm 40\%$. For emissions at levels below 2 mg/kWh, the differences are $>50\%$. Note that at these low levels (~ 2 mg/kWh), in absolute values, even a 100% difference is <2 mg/kWh. The differences at these low levels, equal or less than the detection limit of the PM method, can be attributed to the different background levels between the PFDS and the CVS. The soot typically comprises $<10\%$ of the filter

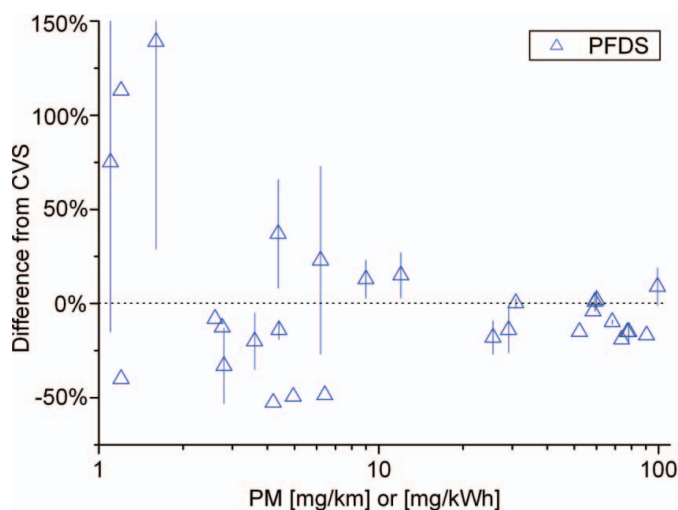


FIG. 13. Comparison of PM emissions from the CVS and partial-flow dilution systems (PFDS). Error bars show 1 standard deviation of three or more measurements. (Color figure available online.)

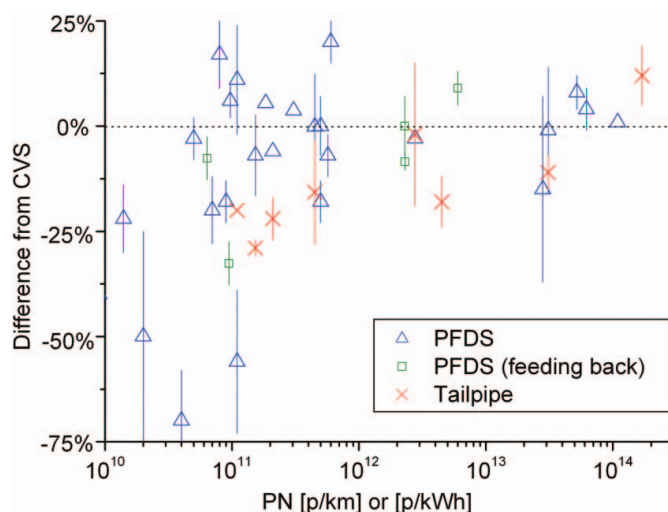


FIG. 14. Comparison of PN emissions from the CVS, partial-flow dilution systems (PFDS), and tailpipe. Error bars show 1 standard deviation of three or more measurements. (Color figure available online.)

mass, the remaining being volatile compounds (Andersson et al. 2010; Mamakos et al. 2011d).

Figure 14 shows the difference between PFDS and CVS for PN emissions. Most data come from the same engines that provided the data for Figure 13 (details in Giechaskiel et al. 2011b). The difference between CVS and PFDS is $\pm 15\%$ for emissions $>1 \times 10^{11}$ p/kWh. However, when the emissions decrease to $<1 \times 10^{11}$ p/kWh, larger differences are observed. At these emission levels, the contribution of the PFDS and the CVS (PN) background becomes important. A limited number of tests in which the flow to the PN measurement system was fed back to the PFDS showed slightly better correlation to the CVS ($\pm 6\%$) than when the flow was simply corrected mathematically.

Figure 14 shows some tests (Giechaskiel et al. 2010c) during which the PN system was connected to the tailpipe with a 50-cm stainless steel tube. In this case, the tailpipe measurements are approximately 20–25% lower than the CVS values (levels 10^{11} – 10^{13} p/kWh) most probably due to thermophoretic losses. Calculations for a 0.5-m insulated stainless steel tube, which was employed in the particular study (Giechaskiel et al. 2010c), suggest 20% thermophoretic losses (Stratmann et al. 1994). The point where CVS and PFDS have no difference (in the figure) corresponds to a G-DI engine. The exhaust gas temperature at the sampling location was $\sim 150^\circ\text{C}$, similar to the temperature of the heated line that was used for the PN system; thus, the thermophoretic losses were negligible. One point shows that the tailpipe PN measurement was 25% higher than the CVS measurement. This point corresponds to a conventional LD diesel vehicle measurement (Ntziachristos et al. 2004a). Probably, due to the high PN emissions and the long tube between the vehicle and the CVS, coagulation decreased the PN concentration. This effect of coagulation-reducing PN emissions has been confirmed elsewhere (Isella et al. 2008).

The key message is that the PN results from CVS and PFDS are similar ($\pm 15\%$), down to the level of dilution system (CVS/PFDS) PN background. The results from the tailpipe are still acceptable ($\pm 25\%$), but improved sampling approaches will further improve the correlation to the CVS. Furthermore, for most cases, the reasons for the differences observed can be easily identified and corrected. In any case, the $\pm 25\%$ value should be considered acceptable, considering the wide range of emission levels that are measured, and proves the robustness of the PMP methodology even in extreme sampling conditions.

9. SUMMARY AND OUTLOOK

Past legislation for limiting particle emissions from diesel vehicles was based on black smoke and later on gravimetric quantification of the mass emissions on a filter. At that time, the adverse health effects were associated with the mass of the particles. However, health effect studies in the 90s showed that the mass might not be the best metric and other properties such as surface area or number concentration might be more relevant. In addition, some studies in the mid-90s showed that newer engine technologies, even though they decreased the mass emissions, sometimes emitted higher PN concentrations than older technologies. It was later determined that the higher emissions observed resulted from the formation of a volatile NM, which depended on the sampling conditions, the pre-history and pre-conditioning of the engine and aftertreatment devices, desorption and adsorption phenomena, etc. The increased interest that was generated in ultrafine particle emissions resulted in many particle investigation projects. However, the lack of standardized protocols did not easily permit comparisons of data from different laboratories.

The introduction of DPFs in the market decreased the particle mass emissions of the vehicles to such low levels that the regulated PM method could hardly distinguish the emissions of the vehicle from the background. In addition, the detection limit was so high that other technologies and/or aftertreatment devices with differences in PN emissions of 1–2 orders of magnitude could fulfill the existing (and future) mass standards. For this reason, the PMP Working Group of the UNECE GRPE developed a new PN measurement method that complemented the existing mass method. This technique was based on the measurement of the nonvolatile PN concentration using a VPR (with hot dilution $> 10:1$ at 150°C and thermal pretreatment at $300\text{--}400^\circ\text{C}$) and a PNC with 50% cutoff efficiency at 23 nm (90% at 41 nm). This measurement procedure, along with calibration requirements for the systems, was introduced in the Euro 5 LD vehicles regulation. HD legislation will also introduce PN limits at the next legislative stage.

The PN method was proven to be sufficiently robust to sampling artifacts. Different engine and aftertreatment technologies could be efficiently evaluated due to the very low LOD ($< 10^{10}$ p/km or p/kWh) of the PN method. The repeatability of the PN method was found to be around 5%. Higher scatter of the

results could easily be explained by effects of the vehicles or the aftertreatment devices on the PN emissions (e.g., DPF fill state, preconditioning, cold start). The reproducibility at the moment is still an issue since it is around 30% or higher. The main reasons are the calibration uncertainties of the PN instruments and the drift of the PN systems (especially PNCs) over time. Thus, stricter calibration procedures have to be defined and simple and fast on-site checks have to be conducted often.

Correlation measurements between the full-flow dilution tunnels (CVS) and the proportional PFDS showed agreement within 15% for the PN method, down to 1×10^{11} p/kWh. At lower concentrations, the PN background of the CVS and/or the PFDS can increase the difference. For PM, the correlation was good ($\pm 20\%$), down to 10 mg/kWh, but this deteriorates for lower PM concentrations due to the large number of volatile artifacts and the different backgrounds of the CVS and the PFDS.

The PM and PN correlated well, down to 2–3 mg/km or mg/kWh ($\sim 20 \mu\text{g}$ on the filter), but adsorption of volatiles on the filters does not permit accurate determination of the true emissions of engines emitting lower levels. The mass-to-number correlation improves when only soot mass is considered. The correlation is relatively good, down to 0.1–0.3 mg/km or mg/kWh, one order of magnitude below the PM. But even at these low limits, the soot mass corresponds to PN emissions close to the certification limits of the engines and vehicles (6×10^{11} p/km or p/kWh).

Although the PN method has been proven robust, there are a few issues that need further consideration. One is that the volatile fraction of the particles is not measured, and this fraction has also been proven to be responsible for some adverse health effects. The measurement of volatiles however needs well-defined conditions (e.g., sampling from the tailpipe with constant-dilution conditions, etc.) and requires more research until systems ready for legislative use will appear. The second point is that at specific engine points and emerging technologies, nonvolatile particles < 23 nm might exist (e.g., coming from additives in the fuel). However, lowering the cutoff size would be advisable only if it is ensured that all volatiles have been removed, and thus, volatile particles will not be (falsely) measured as nonvolatiles. Thus, other approaches might be proven necessary (e.g., catalytic stripper). Finally, it should be taken into account that lowering the cutoff size is challenging, not only due to possible volatile artifacts but also from the perspective of calibration and losses of the PNCs and VPRs.

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