Review

Revisiting Total Particle Number Measurements for Vehicle Exhaust Regulations

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Abstract: Road transport significantly contributes to air pollution in cities. Emission regulations have led to significantly reduced emissions in modern vehicles. Particle emissions are controlled by a particulate matter (PM) mass and a solid particle number (SPN) limit. There are concerns that the SPN limit does not effectively control all relevant particulate species and there are instances of semi-volatile particle emissions that are order of magnitudes higher than the SPN emission levels. This overview discusses whether a new metric (total particles, i.e., solids and volatiles) should be introduced for the effective regulation of vehicle emissions. Initially, it summarizes recent findings on the contribution of road transport to particle number concentration levels in cities. Then, both solid and total particle emission levels from modern vehicles are presented and the adverse health effects of solid and volatile particles are briefly discussed. Finally, the open issues regarding an appropriate methodology (sampling and instrumentation) in order to achieve representative and reproducible results are summarized. The main finding of this overview is that, even though total particle sampling and quantification is feasible, details for its realization in a regulatory context are lacking. It is important to define the methodology details (sampling and dilution, measurement instrumentation, relevant sizes, etc.) and conduct inter-laboratory exercises to determine the reproducibility of a proposed method. It is also necessary to monitor the vehicle emissions according to the new method to understand current and possible future levels. With better understanding of the instances of formation of nucleation mode particles it will be possible to identify its culprits (e.g., fuel, lubricant, combustion, or aftertreatment operation). Then the appropriate solutions can be enforced and the right decisions can be taken on the need for new regulatory initiatives, for example the addition of total particles in the tailpipe, decrease of specific organic precursors, better control of inorganic precursors (e.g., NH3, SOx), or revision of fuel and lubricant specifications.

Keywords: primary aerosol; fresh aerosol; secondary aerosol; nucleation mode; vehicle emissions; road transport; urban pollution; air quality; PMP; PEMS

1. Introduction

The atmospheric aerosol is a complex and dynamic mixture of solid and liquid particles in the air, generated from natural (such as pollen, sea salt, volcanic ash, and soot particles from natural fires) and anthropogenic sources (e.g., combustion, waste incineration, and road abrasion). Anthropogenic emissions of atmospheric aerosol and its precursors have increased over the past century and are known to have significant impacts on human health [1,2] and climate change [3]. Studies have actually shown that the particulate matter (PM) has a greater impact on health than the gaseous components [4,5]. Globally, >50% of the population lives in urban areas with poor PM air quality [6].

Ambient PM concentrations are monitored in many places around the world, together with several gaseous species. Traffic is an important source of PM and the exhaust emissions
of vehicles have been regulated for many years. In the last decade, a solid particle number (SPN) limit has also been imposed in the European Union (EU) legislation [7] and other countries in Asia have followed. There are a few concerns about the representativeness and the usefulness of the SPN limit, as it is today proposed: (i) exhaust and atmospheric particles usually extend to sizes much lower than the cut-point of 23 nm currently included in the regulations; (ii) only solid particles following a thermal treatment are regulated, while atmospheric include additional higher volatility species [8]. Thus, the current standard does not address particles which are representative of real-world exposure to traffic particulate emissions [9,10].

The aim of the current study is therefore to answer the question: is it necessary to change the current SPN approach and include smaller particles and those of higher volatility? To answer this question this review summarizes the current status on various topics: (i) road transport contribution to ambient PM mass and number; (ii) PM mass, number emissions and potential for secondary aerosol formation from vehicles and comparison between solid and total particle number (TPN) (i.e., including higher volatility species) emissions; and (iii) technical feasibility of measuring total particles. In the end the health effects of ultrafine particles will be briefly discussed with emphasis on differences between solid particles and condensable species. This paper builds upon previous reviews on relevant topics [11–16], and focuses on the necessity and feasibility of regulatory changes.

2. Ambient PM
2.1. Primary and Secondary Aerosol

Primary aerosol particles are emitted or injected from individual sources directly into the atmosphere. Secondary aerosol “particles” are the products of atmospheric conversion, primarily oxidation, of inorganic or organic precursor gases, which nucleate to form new particles or condense on pre-existing ones. The secondary aerosol takes hours to days to form, while the primary aerosol has to be characterized within seconds. Both primary and secondary aerosols have either natural or anthropogenic sources, or a combination of both. Depending on the precursor considered, particulate products are referred to as secondary inorganic aerosol (SIA) or secondary organic aerosol (SOA). SIA has been found to contribute from 12–68% to ambient PM mass [17]. The organic aerosol (primary and secondary) is around half (range 20–90%) of the PM [18,19]. Secondary aerosol contributes roughly 60% (urban), and up to 90% (rural), of the organic matter [18,20,21].

The secondary inorganic aerosol (SIA) consists mainly of ammonium nitrate (NH$_4$NO$_3$) and ammonium sulfate ((NH$_4$)$_2$SO$_4$), with some sodium nitrate (NaNO$_3$). These compounds arise from the transformation of precursor nitrogen oxides (NO$_x$) and sulfur oxides (SO$_x$) in the atmosphere to nitric and sulfuric acids, which are then neutralized by atmospheric ammonium (NH$_4^+$), the latter derived by conversion of gaseous ammonia emissions [22].

The secondary organic aerosol (SOA) originates from volatile organic compounds (VOCs) which undergo gas phase oxidation reactions, forming products that have low enough volatility to form aerosol either via nucleation or condensation onto pre-existing particles [23]. Even though VOCs are well known to contribute to SOA formation [24], there are studies that report that the VOCs contribution to SOA is lower than 50% under low NO$_x$ concentrations and even less than 15% under high NO$_x$ concentrations [25].

Table 1 classifies the organic compounds based on their volatility [26–32]. Intermediate volatility organic compounds (IVOCS) partition almost entirely to the gas phase upon dilution to atmospheric conditions [30]. However, they are highly prone to SOA formation during their gradual oxidation in the atmosphere [33,34]. Semi-volatile organic compounds (SVOCs) are partitioned between the gaseous and condensed phases already during primary emission [35]. Their further oxidation practically shifts their partition entirely to the particulate phase.

The primary and secondary organic compounds that comprise organic aerosol are on the lower end of this volatility spectrum, including extremely low volatility organic
compounds (ELVOCs) and low volatility organic compounds (LVOCs), as well as SVOCs, which exist in both phases [27]. Measurements indicate that models poorly predict organic aerosol concentrations and underestimate the contribution made by SOA particularly in polluted regions (e.g., [36,37]), but not for clean biogenic regions [37,38]. For example, IVOCs are not routinely or consistently accounted for in models, due to the lack of reliable emissions data [39]. In other cases, primary organic aerosol (POA) emissions measured in the laboratory, following the dilution tunnel method, are overestimated due to the low constant dilution enabled compared to the atmospheric dilution process [40]. Under ambient conditions, some of the semi-volatile primary PM may evaporate. The vapors produced undergo oxidation, producing previously unrecognized semi-volatile and intermediate volatility compounds (S/IVOC) [26,28,41]. These S/IVOCs may be a substantial additional source of SOA [26,28,42,43]. There are still large uncertainties in the concentrations, reaction rates, and SOA yields of S/IVOC precursors. Measurement of these precursors would need elaborate chemical characterization of the particles. A simplified concept is to use the volatility and oxygen to carbon ratio (O:C) to characterize the thermodynamics and chemical evolution of the compounds (i.e., two-dimensional volatility basis set) [44,45]. Regarding the two-dimensional volatility space, it should be mentioned that accounting for the road transport IVOC seemed not to close the gap [37].

Table 1. Classification of organic compounds based on their saturation concentration and examples of representative alkanes at each class [27,29,30].

<table>
<thead>
<tr>
<th>Definition</th>
<th>Saturation Concentrations</th>
<th>Carbon Number of n-Alkane</th>
</tr>
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<tbody>
<tr>
<td>Volatile organic compounds (VOCs)</td>
<td>&gt;10^7 µg/m^3</td>
<td>≤12</td>
</tr>
<tr>
<td>Intermediate volatility organic compounds (IVOCs)</td>
<td>10^3–10^6 µg/m^3</td>
<td>13-23</td>
</tr>
<tr>
<td>Semi-volatile organic compounds (SVOCs)</td>
<td>1–10^2 µg/m^3</td>
<td>24-33</td>
</tr>
<tr>
<td>Low volatility organic compounds (LVOCs)</td>
<td>10^{-3}-0.1 µg/m^3</td>
<td>34-37</td>
</tr>
<tr>
<td>Extremely low volatility organic compounds (ELVOCs)</td>
<td>&lt;10^{-4} µg/m^3</td>
<td>≥38</td>
</tr>
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1 also called "non-volatile organic compounds (NVOCs)."

2.2. Air Quality Legislation

The EU policy framework has three cornerstones to address air pollution: The Green Deal/Clean air for all (COM(2018) 330) [46] framework strategy, the Ambient Air Quality (AAQ) Directives (2008/50/EC [47] and 2004/107/EC [48]), and the National Emissions reduction Commitments (NEC) Directive (2016/2284/EU) [49]. Emission reduction commitments for NO_x, non-methane volatile organic compounds (NMVOC), SO_2, NH_3, and PM_{2.5} are included in the NEC [5]. The NEC Directive reporting requires information also on emissions of CO, PM_{10}, BC (black carbon) if available, total suspended particulate matter and the heavy metals Cd, Pb, Hg (and if available, As, Cr, Co, Ni, Se, and Zn) and persistent organic pollutants, including selected polycyclic aromatic hydrocarbons (PAHs), dioxins and furans, polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB). International organizations are also evaluating health risk factors for calculating, e.g., the cancer potency of substances. Each Member State publishes annually a report and collectively the data for EU are available by the European Environmental Agency (EEA) [5,50].

As part of the European Green Deal, the EU is revising these standards, to align them more closely with the Air Quality Guidelines of the World Health Organization (WHO). The EU also aims to improve overall EU legislation for clean air, building on the lessons learnt from the 2019 evaluation (fitness check) of the Ambient Air Quality Directives [51]. According to the latest WHO report [1], based on PM adverse health effects, the maximum recommended annual PM_{2.5} level is 5 µg/m^3 (or 15 µg/m^3 as daily average); with proposed limits being three times higher for PM_{10}. Furthermore, it also recommends monitoring ultrafine particles number concentration (i.e., particles of equivalent aerodynamic diameter < 100 nm).

The EU has also introduced legislation addressing pollution at source, for example the industrial emissions Directive [52], the medium combustion plant Directive [53],
the fuel standards (Fuel Quality Directive, 2009/30/EC) [54], and the vehicle emission (Euro) standards.

2.3. Vehicle Emissions Standards

The first emissions Directive was published in 1970, and Euro 1 standards were introduced in 1992 [55,56]. PM mass limits were introduced only for diesel vehicles with Euro 1 and later for gasoline direct injection vehicles with Euro 5 (2009). A solid (i.e., non-volatile) particle number (SPN) limit was introduced in 2011 (Euro 5b) for diesel vehicles and in 2014 (Euro 6) for gasoline direct injection vehicles. SPN limits were also introduced for heavy duty vehicles (2013) and non-road mobile machinery (2019). Gaseous pollutants (CO, total hydrocarbons and NO\textsubscript{x}) have been regulated since 1992 (Euro 1), thus indirectly controlling volatile organic compounds and precursors for inorganic aerosol. The total hydrocarbons (THC), which are typically measured via a heated line at 191 °C (for diesel vehicles), practically cover most of the VOCs (see Table 1), except of those components that do not respond to the flame ionization detection used for THC detection.

The Euro emission limits have decreased significantly over the years. The stringent limits resulted in significant decreases of ambient CO and NMVOC, while trends in PM\textsubscript{2.5}, when also considering non-exhaust emissions, and NO\textsubscript{x} emissions from road transport have been less favorable [5]. For NO\textsubscript{x}, the reason was primarily the (sometimes unlawful) exploitation of the spirit of the regulation, particularly in diesel vehicles (e.g., dieselgate) [57–61]. The situation has been significantly improved with the introduction of the real-driving emissions (RDE) regulation in 2017 (Euro 6d-temp and later) [62,63].

Regarding PM, even though the introduction of Diesel Particulate Filters (DPFs) (around 2009–2011 with Euro 5) significantly decreased black carbon emissions, and the fuel improvements decreased sulfates, other sources such as non-exhaust (brakes and tires) and secondary particles still contribute significantly to transport PM emissions. The pollutants regulated by the Euro standards and the air quality standards are not fully aligned, with some pollutants being regulated by the air quality Directives (e.g., formaldehyde and sulfur dioxide) but not by the Euro standards. It should be noted that there is no particle number limit in the ambient air, but particle number levels are commonly monitored in the atmosphere in recent years.

2.4. PM in Cities

Typically, the urban aerosol is dominated by anthropogenic sources. In 2016, in Europe and North America the population exposed to PM\textsubscript{2.5} levels above the recommended World Health Organization (WHO) level of 10 μg/m\textsuperscript{3} (at that time) was 48.6%, while in Asia this was >99% [64]. The lockdown measures during the COVID period resulted in significant decreases of some pollutants, such as NO\textsubscript{x}, but modest reductions for PM [65]. Nevertheless, the PM mass decreased up to 30% in some cities [5,66].

Older studies found the road transport contribution to PM around 20% or more [67,68], in agreement with studies in the United States [69,70]. For some cities (e.g., Madrid, London, Barcelona, and Milan) the road transport contribution was >40% in 2010 [71]. Recent reviews reported 30% reduction in PM between 2000 and 2015–2017 [72–74]. Yet, in urban-industrial areas, the contribution of automotive exhaust can be higher, for example it was 20–50% in 2016 in Japan [75]. The reduction of the emissions of the road transport has played an important role, resulting in other sources (e.g., off-road engines) increasing relative contribution [76–78]. Residential heating can also be an important source in some countries, contributing up to 60% of PM\textsubscript{2.5} [79]. Since exhaust emissions have decreased a lot in the recent years, non-exhaust contribution (brakes and tires) is almost half of it [80,81].

Road traffic, in addition to primary PM as discussed above, also contributes to secondary aerosol formation. The secondary aerosol from vehicles' exhaust can exceed primary emissions [82,83]. Traffic contributes to secondary aerosol via gaseous emissions (e.g., SIA, mainly ammonium nitrate, and SOA). Studies have shown the importance of NO\textsubscript{x}, NH\textsubscript{3}, and VOC from vehicles in nitrate formation [84,85]. However, the contribution of each com-
pound is complex. For example, PM mass concentration can increase with \( \text{NO}_x \) decrease due to the increased oxidative capacity of the atmosphere, and for this reason combined \( \text{NO}_x, \text{SO}_x, \) and \( \text{NH}_3 \) reductions are recommended [86–89]. Secondary aerosol precursors \( \text{SO}_2 \) and \( \text{NO}_x \) emissions are dominated by combustion; mainly power generation for \( \text{SO}_2 \) and power generation and road transport for \( \text{NO}_x \). \( \text{NH}_3 \) is dominated by agricultural emissions (including animal waste and use of fertilizers), with contributions from waste (e.g., from anaerobic digestion of organic waste) and combustion (e.g., road transport) [90]. In EU, in 2018, road transport was responsible for 47% for \( \text{NO}_x \), but only 3% for \( \text{SO}_x \) mass concentration [5]. The traffic contribution represents around 11% of total organic aerosol all over Europe [21]. However, in urban areas it can reach up to 70% [91]. A study with vehicles fulfilling China 2 to China 5 emission standards found that with the more stringent emission standards the VOCs to total organics mass fraction was reduced from 61% to 46%, while the IVOCs mass fraction increased from 2% to 8%, highlighting that IVOC emissions from light-duty gasoline vehicles need more attention [92]. VOC mass emissions during engine cold start can be >10 times higher than hot start emissions, in particular from gasoline vehicles [30,92,93]. IVOCs were found to contribute 4.5–18% for gasoline vehicles and 51–57% for diesel vehicles of total organics mass emissions [30]. A study found that alkanes contributed >64% to IVOC [94]. A study found that IVOCs were the dominant precursors for the production of SOA from diesel vehicles (75–87%), while aromatic compounds were the dominant precursors of SOA from gasoline vehicles (64–84%) [95]. It should be mentioned that the filter measurements at 47 °C collect some 63% of total SVOC from gasoline vehicles, 48% from non-DPF diesel vehicles, and 11% from DPF equipped vehicles [30]. Thus, there is a need for a better characterization of IVOC and SVOC species not covered with the current PM filter methodology. Such a topic is out of the scope of this paper, but would complicate the regulatory procedures.

2.5. Ultrafine Particles in Cities

In atmospheric studies particles are often grouped into the Aitken mode (up to 100 nm), accumulation mode (100–1000 nm), and coarse particles larger than 1000 nm, though the exact size ranges may vary somewhat depending on the perspective and context. The lower end of the Aitken mode (up to 20 or 30 nm), is sometimes referred to as the nucleation mode [96] and the <10 nm (or <3 nm) range as nano mode or nanoclusters mode [97,98].

Once airborne, particles may change in size and composition by adsorption of gaseous species, condensation or evaporation of semi-volatile species, coagulation with other particles, various chemical reactions, or by activation in the presence of water supersaturation to become fog and cloud droplets [99,100]. The ambient conditions (sunlight, temperature, wind, and relative humidity) are important parameters for these processes. With these processes, individual particles usually grow in size and are eventually removed from the atmosphere by dry deposition on surfaces or wet-deposition as droplets during precipitation [101]. Semi-volatile particles may also be removed by gradual oxidation to lighter species and/or evaporation [102].

Ultrafine particles are particles sized about 100 nm in diameter or less. Particles in this range are often referred to as nanoparticles. The term “ultrafine particles” is mostly used in atmospheric sciences, while “nanoparticles” is used more commonly in material engineering. In the automotive field typically nanoparticles refer to particles <50 nm and those below 100 nm as ultrafine particles [103,104]. As ultrafine particles have little mass, their levels are most commonly measured and expressed in terms of particle number concentration.

Ultrafine particles are directly emitted to the air by various anthropogenic sources, such as residential heating, the heat and power industry, biomass burning, vehicles’ exhaust, and tires and brakes wear [15]. Natural sources include vegetation, forest fires, and wind dust. In addition to direct emissions, nanoparticles can also be formed in the atmosphere from gaseous compounds originated both from natural and anthropogenic sources [105]. (Photo)Nucleation is an important source of ultrafine particles in rural and remote areas.
Nevertheless, some studies found that new particle formation is also responsible for a major fraction of particle number concentrations observed under urban environments [6]. The mechanism involves sulfuric acid, possibly ammonia and stabilizing species such as amines or organic acids [6]. Recently, the importance of aromatic VOCs from vehicles in new particle formation in an urban environment was exhibited [106]. The meteorological conditions have a significant effect on the particle formation (e.g., solar radiation, temperature), while organics concentration is associated with the growth rate [107]. Quantifying the primary/secondary ultrafine particles split is challenging without data on particles composition.

Many studies have found a fresh nucleation mode chasing vehicles or at roadside measurements [108–112]. Particularly in traffic-influenced environments, the nanoparticle concentrations can be high [110,113,114], reaching even concentrations higher than $10^9$#/cm [115–119]. The concentrations decline with distance from the roads. Traffic is the main source in most cases [110,120,121]. A study showed differences of a factor of 7 between highway and rural number concentrations, while the mass concentrations had a difference of a factor of only 1.25 [122]. PM mass and particle number concentrations are different metrics [123]. The sources dominating the particle number emissions are different to those dominating the mass emissions [120]. Particle number is highly affected by traffic, while mass is affected by aged and transported aerosol [123,124]. A study found moderate correlation between PM and accumulation mode particle concentration, but no correlation with Aitken or nucleation mode concentrations [125].

The contribution of road transport to the particle number levels depends on traffic intensity [126], the mix of technologies (e.g., Euro levels) on the road, but also weather conditions [109,113,127,128], and the contribution of other neighboring sources (e.g., residential heating, ships and aviation). High emitters (i.e., vehicles that are in the 90th percentile of emission levels) can also contribute significantly [129,130]. Of concern is the durability of the aftertreatment devices that could result in elevated PM emissions (in case of e.g., cracked DPFs), hydrocarbons or NO\textsubscript{x} (in case of poisoned or aged oxidation catalysts or NO\textsubscript{x} reduction systems) [131,132]. In 2010, road transport contributed over 60% of the total particle number emissions, the contribution varied from 32% in Greece to 97% in Luxembourg [116]. Non-exhaust sources such as brakes and tires probably contribute a relatively small percentage of ultrafine particle numbers in cities, based on the low number emissions reported in tests over the harmonized brakes cycle. Reported emissions over this cycle and generally “normal” braking events at low speeds (<80 km/h) produce two orders of magnitude less particles than the exhaust emissions particle number limit [133–136]. High emissions can be seen in aggressive braking events, typically from very high speeds that lead to high brake pad temperatures. In Kuwait in 2013 the major sources of particles were fresh traffic emissions for particles smaller than 10 nm, and aged traffic emissions for particles 10–30 nm, with contributions to the total particle number concentrations of 46% and 27% respectively [137]. Another study in Barcelona in 2004 made similar findings where vehicle exhaust contributed 52–86% to the ambient particle number concentration [138]. The photo-chemically induced nucleation represented 23% of the total number concentration of particles. Measurements in other cities also gave similar percentages (44–63%) for traffic and new particle formation (14–19%) (in 2009) [96]. All of these studies were performed before the introduction of DPFs on a mass scale (approximately 2010 in EU).

The previous studies and other reviews showed that road vehicles were the major source of particle number emissions until 2010. However, the vehicular particle number emissions are expected to decrease by 25–75% in 2030 due to the full adoption of particulate filters [120]. Comparative measurements in 2002 and 2014 in the USA concluded that particle emissions of gasoline vehicles had not significantly changed over the preceding decade, while these were reduced for diesel vehicles due to widespread implementation of DPFs [139]. Similarly, in Denmark the particle number emissions at urban and rural sites decreased by more than 65% from 1979 to 2018 [102]. In Paris the concentration dropped approximately to half from 2007 to 2017 [140]. In Germany the particle number emissions
decreased by approximately 25% in 2018 compared to 2009 [141]. The decrease in particle number emissions in Los Angeles between 2002 and 2009 confirmed the contribution and importance of the road sector, but also highlighted contribution from other sectors, such as industrial sources [142]. Another study showed that soot (black carbon) emissions measured on California roads decreased by 90% in 2018 compared to 2001 levels [143].

Studies conducted after the DPF was adopted (e.g., after ~2010 for Europe where the share of diesel vehicles is high) can give indications of the situation today. A study in UK with measurements performed in 2014 estimated the road contribution to be 77–81% of ultrafine particles in terms of number [144]. Measurements in the 2014–2016 period in several major cities found a 74–94% contribution from vehicles in particle number concentrations [121]. These studies indicate that even with the introduction of DPFs, vehicles still significantly contribute to urban ultrafine particle concentration levels. Less than one third of them are non-volatiles [145]. It has to be mentioned though that based on the previously mentioned long term studies the absolute particle number concentration levels have decreased 25–50% from 2007–2009 to 2017–2018 [102,140,141]. Nevertheless, based on the still high contribution of road transport, mentioned above, at least monitoring the total emissions from vehicles makes sense. Such measurements would help in understanding the reasons for the high contribution from vehicles.

3. PM Emitted from Vehicles

The previous chapter focused on ambient PM concentrations and contribution from road traffic. This chapter will focus on the physical characterization and chemical composition of the PM emitted by vehicles, along with the potential for secondary aerosol formation.

3.1. Definitions

In the automotive field the term “particulate matter (PM)” is used for the collected matter on a flow-through filter under specific conditions, and the term “particle” for aerosol particles measured while airborne (suspended matter). Particles are divided into “volatile” and “non-volatile” (or solid) at tailpipe conditions (high temperature, high concentration). Species that at tailpipe conditions appear volatile, may partition toward the particulate phase at atmospheric conditions (low temperature), and the term semi-volatile better characterizes them [41]. The term “semi-volatiles” (instead of “volatiles”) will be used loosely in this text to indicate species not counted after dilution and thermal pre-treatment at 300–400 °C.

As mentioned before, the term ultrafine particles (i.e., particles < 100 nm) is not so common in the automotive community. Even though the majority of particles has sizes <100 nm, the tail extends to larger sizes. A recent review argued that a better definition for ultrafine particles (focusing on the automotive field) would be particles <500 nm [16]. The term will not be used in this paper to refer to vehicle exhaust emissions, but only when used by health or ambient studies.

3.2. Primary “Tailpipe” Particles

Figure 1 (left lower corner) plots schematically the exhaust aerosol at the tailpipe and the atmosphere within a few seconds (i.e., primary and delayed primary aerosol) [15,16]. It also shows sampling and measurement (left part), as well as: (i) the resulting PM mass and chemical characterization (lower right part) of a filter [32]; and (ii) particle number size distribution before and after thermal pre-treatment (upper right part) with a solid particle number (SPN) instrument [146].
particles or condense on other particles (e.g., non-volatile core or accumulation mode). Engine and aftertreatment wear particles can also be found at sizes around 20 nm [167,168]. Non-volatile clusters <3 nm have also been reported for compressed natural gas (CNG) engines [117,169]. The modes depend, among others, on the engine, fuel, combustion strategy, and aftertreatment devices [15,170–172]. Recently, in addition to the combustion process related solid particles, nanoparticles during braking (motoring) have been reported, even when no fuel injection and combustion process take place in the cylinder [173–175]. Engine and aftertreatment wear particles can also be found [176]. The introduction of particulate filters has reduced significantly the concentration of primary particles in the exhaust gas of modern vehicles [7,177]. At the vehicles’ tailpipe, only primary non-volatile (solid) particles can be found due to the high exhaust gas temperatures, while the majority of precursors are in the gaseous phase (i.e., “semi-volatiles” in this paper). Typically, a soot or accumulation mode is measured at the tailpipe with a mean size >50 nm [147]. Studies of modern gasoline vehicles have found smaller means, around 30 nm [148,149]. The accumulation mode particles consist of many spherules (sometimes called primary particles, a term that will not be used in this text) of elemental carbon [150] with fuel and lubricating oil components [151]. Particle-bound PAHs are also commonly reported [152–156]. A solid core or nano mode with a mean size of 10 nm has also been found [157,158]. This mode consists of amorphous carbonaceous compounds, PAHs, or metallic ash from fuel or lubricant [159–165]. In one case two separate core modes were found (derived from lubricant and fuel respectively) [166]. Recently, urea non-volatile particles have also been reported at sizes around 20 nm [167,168]. Non-volatile clusters <3 nm have also been reported for compressed natural gas (CNG) engines [117,169]. The modes depend, among others, on the engine, fuel, combustion strategy, and aftertreatment devices [15,170–172]. Recently, in addition to the combustion process related solid particles, nanoparticles during braking (motoring) have been reported, even when no fuel injection and combustion process take place in the cylinder [173–175]. Engine and aftertreatment wear particles can also be found [176]. The introduction of particulate filters has reduced significantly the concentration of primary particles in the exhaust gas of modern vehicles [7,177]. Sometimes, larger coarse mode particles appear originating from the crankcase ventilation, wear, or soot re-entrainment [103,178]. Regarding the precursor gases, oxidation catalysts reduced hydrocarbons, but in many cases increased the SO$_2$ to SO$_3$ conversion and NH$_3$ [179,180]. NO$_x$ reduction aftertreatment decreased NO$_x$ [181].

3.3. Delayed Primary “Fresh” Particles

At the vehicles’ tailpipe outlet the aerosol is diluted and cools down [113,182,183]. The precursors (e.g., sulfuric acid, hydrocarbons) [184,185] that were in gaseous phase at the tailpipe (due to the high exhaust gas temperatures) may nucleate to form new nucleation mode particles or condense on other particles (e.g., non-volatile core or accumulation mode).
Thus, the “fresh” exhaust aerosol comprises the solid particles in the tailpipe (primary PM) and the newly formed particles during the seconds of mixing of the exhaust gas with ambient air [15,108,186] (Figure 1).

The formed nucleation mode (in the absence of a solid core) peaks at approximately 10 nm depending on the availability of the precursors [103,130,187,188]. Sulfuric acid is the key nucleating compound as measurements [189] and models show [190–193]. With low sulfur fuels, lubricants play an important role [189,194] and aftertreatment devices enhance the SO$_2$ to SO$_3$ conversion [179]. Relatively high SO$_2$ concentrations can be measured at diesel vehicles compared to gasoline and gas engines due to the higher oxidative environment in the exhaust [58]. Hydrocarbons are then necessary for the subsequent growth of such sulfate core particles [158,195,196]. A nucleation mode can be typically seen with high sulfur fuel (300 ppm) and/or lubricant [189,197], high speeds (exhaust gas temperatures) [179,198], and during regenerations [199,200] (see also discussion in [14]). Without aftertreatment devices, hydrocarbons (alkanes, PAHs) may also form a separate nucleation mode [187]. Without any aftertreatment devices, this nucleation mode has high particle number concentration and large mean size [201], but with aftertreatment devices the concentration and size is usually low [202]. Both fuel and oil are significant sources of hydrocarbons [155,165,203–208]. Fuel contributes to VOC and IVOC, while oil to SVOC [30]. More on chemical composition of vehicle exhaust can be found elsewhere [170,209–212].

At this primary atmospheric dilution stage no significant chemical transformations take place. When looking the complete particle size distribution, the exhaust aerosol formed by different processes is frequently allocated to separate modes with different concentrations and particle size ranges [103]. The size distribution may consist of a cluster mode, one or two core modes, the soot mode and the coarse mode. The formation and properties of each mode (size, chemical composition) depends on the vehicle (engine, aftertreatment, fuel, lubricant) [130,213–216], driving conditions and the ambient conditions (temperature humidity) [8,217]. Some of the modes may often appear blended and are difficult to distinguish, unless combined with thermal separation techniques, such as treatment with a catalytic stripper or thermodenuder, followed by microscopy.

In terms of mass, under laboratory conditions the soot and ash particles and heavy compounds comprise the solid part (see Figure 1). Organic and inorganic compounds (POA and PIA) condensed on particles or as a separate nucleation mode consist the condensable PM. It should be mentioned that the compounds that are emitted in the gaseous phase under relevant atmospheric conditions are SOA precursors.

Vehicular emissions are eventually diluted by a factor of 1000 or more in the atmosphere [218], but dilution near roads may be lower [219]. A study that summarized measured dilution ratios in function of distance from moving vehicles, reported dilution ratios of 200–500:1 at a distance of 10 m [14,220]. Other researchers provided equations to estimate the dilution ratio [221]. At lower speeds the dilution in the wake of the vehicle can be much higher at the same distance [222,223]. Measurements at different short distances behind moving vehicles (10–50 m) did not find significant evolution of the nucleation mode, after correcting for dilution [220]. In the time scale of a few seconds this nucleation mode seems stable. However, these particles may evaporate after some time in the atmosphere and may subsequently contribute to the formation of secondary aerosol of higher mass [99,128,224]. For example, some studies found that the organic to total carbon ratio is higher for roadside nanoparticles compared to typical exhaust soot particles [225]. On the other hand, other studies found an increase of the particle size from 1.5 m to 15 m from the road [226,227]. Models usually divide the analysis into separate ‘tailpipe to road’ and ‘road to ambient’ parts [6,228]. Most of the changes to particle number concentration and size distribution occur rapidly with the dilution and cooling of the exhaust gas. Later, interaction of fresh particles with relatively aged particles also takes place [229].
3.4. Secondary Particles

In addition to the primary and delayed primary PM, large amounts of secondary particulate matter forms after the exhaust gases are released into the atmosphere [230]. After some hours or days under atmospheric conditions, secondary PM is formed due to oxidation of gaseous precursors. Studies of secondary aerosol formation rate and quantity (yield) are done in smog chambers [231] or oxidation flow reactors [232].

Recent chamber studies have shown that secondary particulate matter from combustion engines consists mainly of organic compounds and ammonium nitrate [233–235] and that the secondary PM formation can be significantly larger than primary PM emission [234,236–239]. Studies that focused on the SOA also found that the contribution of vehicles to SOA can be higher than primary aerosol [234,240,241]. The emissions of secondary PM precursors from internal combustion engines depend on fuel properties [19,175,233,235,242–244]. The advantages of the oxidative exhaust aftertreatment and especially the use of DPF on decreasing aged PM has clearly been shown [82,175,213,243,245–248]. Catalyzed DPFs on road vehicles were also demonstrated to yield very low SOA over transient operation. Gasoline engines have greater secondary aerosol precursor emissions than diesel engines [82,234,242,245,248–250]. However, it was also shown that SOA emissions follow emission standards [238] and recent Euro 6 gasoline vehicles had very low SOA [10]. Gasoline particle filters (GPF) have not shown similar reduction potential against SOA as DPFs [251]. For a natural gas engine, the mass of the aged particles produced by an oxidation flow reactor was hundreds of times higher than the mass of primary particles [215]. Cold start emissions have been shown to have a significant contribution to SOA [10,238,252,253]. These studies highlight the need to better characterize (semi)volatile compounds from vehicles in order to better estimate their contribution to secondary aerosol formation.

4. The Appropriate Metric (Total vs. Solid)

The previous section summarized the dynamics of primary vs. secondary aerosol emissions from vehicles. This section will discuss the appropriateness (suitability) of a new metric, i.e., total particle number (TPN), in comparison to the currently regulated SPN >23 nm limit. The topics that will be addressed are health effects of ultrafine particles, comparison of solid and total particles in vehicle emissions, comparison of total particle limit with a limit on precursors, and available instrumentation and methodological issues.

4.1. Health Effects of Particles

Epidemiological studies have shown that PM mass is associated with adverse health effects, such as short- and long-term cardiovascular morbidity and mortality, diseases of the central nervous system, respiratory morbidity, and lung cancer [1,254] (see also Table 2). Studies establish such findings even for exposure levels to very low levels (<10 μg/m³) [255]. Toxicological studies indicate that ultrafine particles may be more harmful to human health than larger particles, although this is more of a conceptual consideration rather than a robust finding [256]. Ultrafine particles deposit deeper and with higher probability into the lung and stay in the lungs longer (i.e., less efficient removal). This accumulation of particles results in higher inflammation [257]. They rapidly enter the circulatory system and can reach organs such as the liver, spleen, heart, and brain [258–260]. They can provide a vehicle for other substances such as PAHs and other condensed material and play the role of carrier (Trojan horse effect), thus transferring “condensable” material to other organs [177,261]. However, epidemiological studies separately studying the effect of ultrafine particles are limited [262]. The current evidence of adverse health effects of ultrafine particles is summarized in Table 2 [263–266]. The data suggest a link with respiratory, nervous system, and cardiovascular diseases [267–269]. It should be emphasized that it is difficult to draw conclusions about ultrafine particles due to the limited number of long-term studies, the different size ranges involved in the studies, and the variability of concentrations and sizes from the source, and the difficulty to isolate ultrafine particles from other co-pollutants. Furthermore, any assessment of “semi-volatile”
(condensable) ultrafine particles is extremely difficult as they are also affected (e.g., change of size or desorption of condensed material) during inhalation [270,271].

There is also no answer as to which component of ultrafine particles is the most important for health endpoints. An older review claimed that the combustion-derived particles, including condensed material, had adverse health effects [272,273]. Even though many components (and sources) are individually associated with adverse impacts on the human body, there is no clear direction on any one component (or source) that is strongly correlated with health effects, other than PM mass [274]. For example, elemental carbon exhibits a rather strong association with mortality [275,276] but it is not clear if this is due to the specific component or if this stands as a proxy for other components. The presence of transition metals in PM is linked with formation of reactive oxygen species (ROS) and related oxidative damage of macromolecules [277,278]. Organic matter has also been shown to have negative biological effects; the water soluble organic carbon generates reactive oxygen species [279,280], and polycyclic aromatic hydrocarbons (PAHs) [281,282] are highly toxic, mutagenic, and carcinogenic [283,284]. Studies indicate that the toxic effect of adsorbed chemicals is additive to that of solid particles [285]. A recent meta-analysis found that black carbon and organic carbon were most likely to cause adverse health effects [286]. Recently SOA was associated with higher cardiorespiratory death rates than other components considered (sulfate, ammonium and nitrate, sea spray, dust, or soot); it also exhibited a larger association per unit mass than total PM2.5 [287]. A study simplified classified the health effects of lung deposited exhaust particles to [288]: (i) the physical effect of non-volatile (solid) particles due to their contact with the lung-fluid; proportional to their accessible surface area [289,290]; (ii) the chemical effect of the volatile (and semi-volatile) species dissolving in the lung fluid, proportional to the deposited volatile mass (dose) [291]. Therefore, all current evidence suggests that, if anything, volatile and semi-volatile aerosol species aggravate any toxic character of solid particles. In other words, there is no health evidence suggesting that semi-volatile aerosol should be excluded from any control of exhaust aerosol emissions.

Table 2. Health effects from exposure to PM (particulate matter) and ultrafine particles (UFP) [274].

<table>
<thead>
<tr>
<th>Effects</th>
<th>Exposure</th>
<th>PM</th>
<th>UFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Respiratory</td>
<td>Short</td>
<td>Likely to be casual</td>
<td>Suggestive</td>
</tr>
<tr>
<td></td>
<td>Long</td>
<td>Likely to be casual</td>
<td>Inadequate</td>
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<tr>
<td>Cardiovascular</td>
<td>Short</td>
<td>Casual</td>
<td>Suggestive</td>
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<td></td>
<td>Long</td>
<td>Casual</td>
<td>Inadequate</td>
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<tr>
<td>Metabolic</td>
<td>Short</td>
<td>Suggestive</td>
<td>Inadequate</td>
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<tr>
<td></td>
<td>Long</td>
<td>Suggestive</td>
<td>Inadequate</td>
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<tr>
<td>Nervous system</td>
<td>Short</td>
<td>Suggestive</td>
<td>Suggestive</td>
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<tr>
<td></td>
<td>Long</td>
<td>Likely to be casual</td>
<td>Suggestive</td>
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<tr>
<td>Reproductive</td>
<td>-</td>
<td>Suggestive</td>
<td>Inadequate</td>
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<tr>
<td>Cancer</td>
<td>Long</td>
<td>Likely to be casual</td>
<td>Inadequate</td>
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<tr>
<td>Mortality</td>
<td>Short</td>
<td>Casual</td>
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4.2. Emission Levels (Total vs. Solid)

The introduction of a SPN limit clearly resulted to a significant decrease of vehicle emissions. For example, DPF vehicles have by a factor of >10,000 lower SPN emissions than vehicles without DPFs (from >10^{14} #/km to <10^{10} #/km) [7]. Similarly, SPN emission levels of gasoline direct injection vehicles dropped from >10^{12} to <10^{11} #/km [56] with the use of a gasoline particle filter (GPF). In contrast, no SPN emission reductions were observed for vehicle technologies that were not covered by relevant regulations. For example, the SPN emissions of port fuel injection vehicles have remained at the same level (mostly between 10^{11} and 10^{12} #/km) for the last 30 years [56]. Mopeds and motorcycles also exhibit high SPN emissions which, depending on engine tuning, can often reach more than 10^{11} #/km [292]. Any decreases in emission levels of this category were attributed to
technology improvements (two-stroke vs. four-stoke, carburetor vs. electronic injection) which were forced by stricter limits in gaseous pollutants [293]. This is an example that demonstrates that satisfactory control of SPN can be achieved by regulating co-pollutants.

One question is how different formation mechanisms of solid and total particle emissions are; this would have an impact on the emission control technologies in each case. In general, SPN control does not necessarily result in a decrease of total particle number (TPN), because the semi-volatile part is formed by ions and organics while the solid part is mostly elemental carbon and ash. In an exaggerated example of the past, a DPF equipped engine was shown to result to higher particle number emissions than the non-DPF one [294]. Later it was shown that due to the low soot concentration post DPF available volatile species preferentially nucleated and formed new particles in the absence of solid cores on where they could condense [295]. Similar findings have been observed in the atmosphere where high particle number levels can be seen when PM is low [124]. A recent study with 130,000 plume measurements found that the number of semi-volatile particles comprised 85% to 94% of total particles [8]. Even though semi-volatile particles can be dominant in terms of number, their contribution to mass depends on the existence or not of a particulate filter. Detailed studies with heavy-duty engines equipped with aftertreatment devices to fulfill the 2007 and 2010 standards (i.e., oxidation catalyst, DPF and selective catalytic reduction (SCR) for NOx) had elemental carbon <20% of total mass [211,212]. The organic carbon on the other hand was 30–65% and the rest were sulfates and nitrates. A constant nucleation mode over a test cycle ($10^{13}$ #/km, e.g., $10^7$ #/cm$^3$ with mean size 20 nm) would correspond to only 0.1 mg/km (<10 µg on the filter at the end of the cycle). To put these numbers into context, the current SPN limit is $6 \times 10^{11}$ #/km, with the mass limit at 4.5 mg/km. For heavy-duty vehicles, the same number concentration ($10^7$ #/cm$^3$) would translate to >5 times higher emissions due to the higher exhaust flow rate.

There is a significant body of studies that have measured both solid and total number concentrations. For example, large projects funded by the industry [296], and the European Commission, such as the Particulates project which ended in 2004 [11], showed small differences between TPN and SPN at low speeds, but high at high speeds. Other smaller scale studies reported differences of 50–100% between TPN and SPN for Euro1–4 vehicles [200] or recent Euro 5 and Euro 6 [297] or 2009–2012 model years [298] for typical cycles. A review showed that for type approval cycles the trends for solid particles were followed also for total particles (i.e., decreasing for GDIs, no decrease for PFIs) [56]. This decrease is not always so evident in real life [130]. For example, during cold start of gasoline and gas engines nucleation mode particles can be formed [299,300], but not always [301]. Relatively high differences have been reported when fuel specifications change [253,302], and at high speed cycles [298,303,304]. Even for the same vehicle and fuel, different operating points can result to varying TPN/SPN ratios [305,306]. Recent research projects, such as the DownToTen (DTT), which ended in 2020, presented results from many vehicles where the TPN emissions were more than one order of magnitude higher than the SPN [307]. Of particular interest were cases such as gasoline vehicles with GPF, compressed natural gas (CNG) vehicles with and without particulate filter and plug-in hybrids that all under certain conditions exhibited a large range of TPN/SPN values. Another study found more than one order of magnitude higher TPN than SPN for hybrid vehicles even at city driving [308]. All studies mentioned conducted measurements directly from the tailpipe so any volatile particles cannot be attributed to desorption artifacts from the sampling lines.

Similar conclusions have been also drawn for heavy duty engines [309]. A study showed that the total particle number emissions increased from $10^{11}$ #/km to $10^{13}$ #/km when the exhaust gas temperature was >310 °C [310]. In general, due to the high exhaust gas temperatures and consequently high release of desorbed species from the aftertreatment devices and exhaust line, and high SO$_2$ to SO$_3$ conversion, high TPN concentrations are reported [168,179,311]. Tests with L-category vehicles (e.g., mopeds and motorcycles) also resulted in high TPN, especially at high speeds [292,312]. Different combustion technologies
(e.g., temperature reactivity controlled compression ignition (RCCI), hot or low exhaust gas recirculation (EGR) combustion etc.) can also have various TPN to SPN ratios [313].

Specific events, such as DPF regeneration can also produce high concentrations of both solid and semi-volatile particles [310,314–318]. SPN emissions can reach or even exceed the limit of \(6 \times 10^{11} \text{#/km} \) [315,318], while total particle emissions can be one to three orders of magnitude higher (up to \(2 \times 10^{14} \text{#/km} \)) [199,315,318]. Studies with light-duty and heavy-duty vehicles have also shown that even when the emissions during regeneration events are considered, the weighted (over regeneration distance) solid particle number emissions remain below the current SPN limit [168,319,320]. The regeneration frequency is on average around 400–500 km, with a tendency of shorter distance for newer vehicles [62].

Regarding semi-volatiles, many studies have shown that the concentration of sulfates and organics in the exhaust increases during regenerations and this is often linked to the formation of a distinct nucleation mode [199,318,321]. However, one study found that increased particle number emissions during DPF regeneration were still by 83–99% lower than those without DPF [214]. Furthermore, considering the regeneration frequency, the apparent total particulate matter filtration efficiency was reduced by less than 2% over the average driving conditions for medium- and heavy-duty diesel vehicles [245]. Still, the weighted (total) particle number concentrations over the regeneration distance can be up to one order of magnitude higher than the current limit for solid particles.

The collected evidence suggests that there can be technologies, fuels, and operation conditions that lead to SPN and TPN levels and trends exhibiting significant deviations. The same evidence also suggests that the metric chosen for regulatory control may influence which technologies are promoted for future vehicles and what specifications for fuels and lubricants are decided. All of these factors will have an impact, not only on the specific metric, but on other co-pollutants as well. Therefore, deciding on the proper metric for particle number control will be decisive for the wider environmental impacts of road transport.

4.3. Particle vs. Gaseous Measurements

The analysis so far showed that the contribution of exhaust emissions from road transport to ambient primary PM\(_{2.5}\) is low (around 11%), but has high secondary PM formation potential, exceeding in some cases many times the primary PM. Furthermore, the contribution of vehicles in urban areas is still high in terms of number (exceeding 75% in many cases).

A potential new metric for regulatory control (e.g., total particle number (TPN) concentration) should address the pollutants directly or indirectly and present a minimum overlap with other metrics already regulated. For example, total hydrocarbons (THC) control addresses the majority of VOCs; some of them have the potential to form total particles (SOA). The PM control, based on the gravimetric filter method, includes non-volatile, low volatility and, to a certain extent, semi-volatile species. The solid particle number (SPN) method covers only non-volatile particles above a size threshold, and it was only added due to its superior sensitivity to low particle concentrations than the gravimetric PM filter method. However, none of the current regulations particularly targets the S/IVOC component of exhaust aerosol, which have high potential in forming SOA. Other pollutants such as NO\(_x\), NH\(_3\), and SO\(_x\), partly included in the regulations, address the secondary PM (SIA) indirectly.

To address the S/IVOC topic, one approach would be to lower the temperature of the particle number systems from 350 °C to, e.g., 150 °C to include I/SVOC. Such a change would need minor modifications of existing systems, but would exclude other compounds that contribute to secondary aerosol. Another option would be to add gaseous pollutants that are important for the formation of primary or secondary particles (e.g., SO\(_x\)) and/or further reduce the limits of the currently regulated gaseous pollutants (e.g., total hydrocarbons, NO\(_x\), NH\(_3\)). Additional measurement of I/SVOC or PAHs could be another option (methodology e.g., [30,177]). Addressing specific pollutants is not always
possible because it might be that the methodology is not sensitive enough to quantify the specific pollutants. As discussed before, such an example is the mass quantification of the nucleation mode, which is below the detection limit of the gravimetric method. If these options are not sufficient a TPN limit could be the solution. In this case a parallel obligatory measurement of total particle in ambient air would be beneficial for a better understanding and correlation of laboratory and ambient measurements.

4.4. Practical Issues

In this section the practicalities of introducing the TPN methodology will be discussed.

4.4.1. Sampling Conditions

In the laboratory, the engine is connected to a dynamometer or the vehicle is placed on a chassis dynamometer. A prescribed “cycle” is followed where the engine speed and torque vary or, respectively, the vehicle speed profile. The whole exhaust gas is diluted in a dilution tunnel following constant volume sampling (CVS). The instruments sample diluted exhaust gas to determine the pollutants concentrations. For the determination of PM mass emissions, a small portion of the diluted flow is extracted and passes through a filter. The filter mass change over the complete cycle determines the PM mass emissions. The temperature of the filter, depending on the regulatory context is maintained between 20 and 52 °C (EU light-duty) or 47 ± 5 °C (EU heavy-duty, USA). The actual dilution ratio varies over the test cycle since total diluted flow is kept constant: the dilution is high when the exhaust flow is low (idle and low speeds) and, vice versa, low when the exhaust flow is high (high speeds and loads). This is the opposite to what would be experienced with atmospheric dilution. Actually, both mixing and dilution ratio evolution until measurement differs between laboratory and atmospheric conditions. Furthermore, the dilution ratio evolution will be different for different vehicles, different CVS flow rates and different facilities. The influence of the dilution ratio on the PM mass has been discussed in the atmospheric science community [322], but also in the automotive emissions community [323–325]. It has been clearly shown that dilution ratio, temperature, and concentration of semi-volatile species all have significant influence on the partitioning of those species between the gas and particulate phases [326]. For example, decreasing the concentration of organics from 1 mg/m³ to 20 µg/m³ at 25 °C can cause approximately half of the condensed organics to evaporate [41].

PM increases at small dilution ratios (<5:1), as long as diluted exhaust temperature reaches ambient levels, due to the relatively high concentration of semi-volatile species that preferable partition to the particulate phase [322]. Compared to atmospheric dilution, the CVS exposes the exhaust at low dilution ratios for prolonged residence time before measurement, resulting in relatively high PM mass. Increasing the dilution reduces the PM mass as partial pressures of semi-volatile species drop, while diluted exhaust temperature is not significantly affected. This phenomenon is mostly visible with organic species. Inorganics such as sulfuric acid do not evaporate at typical ambient conditions once they have condensed on particles, because of their low volatility [41].

Even though the particulate mass of inorganics is rather insensitive to dilution ratio, this may not be the same for particle number. Actually, several studies have shown that the dilution air temperature, the dilution ratio, the relative humidity, and the residence time at such conditions affect nucleation mode particles [327–331]. The nucleation mode number concentration and mean size depend on the sampling conditions (dilution temperature, dilution ratio, relative humidity etc.) [329]. For the same dilution ratio, the lower the temperature the higher the nucleation mode [327,329,332]. The trend was not so clear for the dilution ratio. Some studies found the maximum nucleation at the minimum dilution ratio they tested, e.g., 4:1 [330,333–335] or 12:1 [187,217,295,327,336,337]. However, another study found higher nucleation at 23:1 [329] than at dilution 9:1. A modeling study found the maximum nucleation at dilution ratio 15:1 due to the interaction of volatile precursors concentration, available soot surface and temperature [338]. Another exception was a study
with humid air that found a higher nucleation mode with higher dilution ratios, probably due to the contribution of the humidity to the sulfuric acid growth [331]. Simplified calculations also estimate maximum nucleation at dilutions between 15–30:1 [16]. The residence (aging) time is also an important parameter because it results in bigger sizes due to particle growth from condensation of organics and agglomeration. Theoretical and experimental studies showed that the nucleation mode number concentration maximized at approximately 0.2 s after initial dilution, whereas particle diameter stabilized approximately 1 s later [190,339,340]. Other parameters might also be equally or even more important for the potential for nucleation mode formation, e.g., turbulence and the relative time constants for mixing and cooling [340–342], cooling of the tailpipe [343], presence of solid particles [295], length of sampling line, and storage/release of volatiles [16,344]. In general, the dilution corrected nucleation mode number concentration and mean size remain constant with dilutions >30:1 [333,337] or 50–60:1 [345]. Very high dilutions (range 200:1 to 1000:1) during chasing experiments did not reveal any changes of the size distributions [14]. Adding a secondary dilution to the primary dilution does not seem to change the characteristics of the nucleation mode [346].

The nucleation mode growth during the first seconds is very rapid (15 nm/s [190,339]). Similar rates are expected in the wake of the vehicle. Note the big difference compared to the growth of the nucleation mode in the atmosphere (diluted) (5 nm/h [144,347]). Such laboratory studies were conducted with high concentrations of sulfur and hydrocarbons, but newer studies with typical concentrations for modern vehicles are needed. Studies found that the organic species condensed onto the soot particles may contribute to 20–40% of the particle volume or mass for accumulation mode particles and up to 80% for nucleation mode particles [195]. Studies with diesel vehicles equipped with oxidation catalysts demonstrated that the condensed material contributed only to a few nm to the diameter of the accumulation mode [348]. The size changes of the accumulation mode due to condensation or agglomeration are typically small.

4.4.2. Laboratory vs. Real-Life Dilution

The agreement between laboratory and plume measurements for the accumulation mode is good in most studies [182,188,197,217]. The agreement in nucleation mode is not always as good [197,222]. Many studies have shown that the presence or absence of the “fresh” nucleation mode can be qualitatively reproduced in the laboratory [14]. However, the exact characteristics (concentration, mean size) depend on the conditions in both the atmosphere or in the laboratory. In most cases, the laboratory number concentrations were lower, probably due to the sampling conditions (relatively high dilution temperature, low relative humidity, lower turbulence in the diluters compared to the wake of the vehicle) [14,223]. However, nucleation mode mass may be higher in the laboratory due to the lower dilution and longer residence time [179]. One study showed that when ambient and laboratory conditions were matched the nucleation mode characteristics also matched [217]. However, to mimic the atmospheric dilution, a partial dilution system should, in principle, produce similar turbulent intensity. Since the ambient conditions are not constant and, even for the same vehicle, these would vary depending on the speed, mimicking any atmospheric process in the lab does not make sense. Instead, establishing sampling and dilution conditions that are preferable for nucleation mode formation would enable measuring the “nucleation formation potential” [12]. As discussed above, it is not clear whether this also could capture the secondary aerosol formation potential.

4.4.3. Desorption/Release

Nucleation mode particles have been observed at roadside measurements [218,226,349], chasing measurements [350], on-board the vehicle [351], and in the laboratory [179]. Thus, they are a “true” vehicle exhaust component, and not a measurement artifact. Nevertheless, storage and release of “condensable” material to/from the sampling lines, as sampling temperature varies may produce nucleation mode particles that are not part of the vehicle
exhaust. Two cases will be discussed to clarify the existence of artifacts: (i) stored material at the lines and aftertreatment devices of the vehicle; and (ii) stored material at the transfer lines after the vehicle tailpipe when measuring these particles in a laboratory. In the second case the stored material might have been desorbed from previously tested vehicles and thus not related to the specific test under evaluation; the term particle “artifact” has also been used.

The storage and release influence on the particle number emissions has been assessed by many researchers measuring directly from the tailpipe or chasing vehicles. One study with a diesel vehicle (no DPF) reported that going from 50 km/h to 120 km/h resulted in a clear nucleation mode that its number concentration and mean size were decreasing over time [352]. Another study with a diesel vehicle (no DPF) showed that the nucleation mode at 100 and 120 km/h was different when ramping from a lower or higher speed [348]. Another older study with diesel engines (no DPF) showed that the nucleation mode depended on the exhaust gas temperature [333]. A few studies with diesel vehicles (no DPF) found that it takes some time (>25 min) to form the nucleation mode (e.g., at 100 km/h) [179,197]. It was suggested that one important parameter is the stored material at the catalyst and the exhaust gas temperature at the catalyst that determines the SO\textsubscript{2} to SO\textsubscript{3} conversion [179,311].

In the laboratory environment, the transfer line that connects the vehicle tailpipe to the dilution tunnel inlet has also been shown to be a source of volatile and semi-volatile species that condense at times of decreasing temperature and are outgassed when the temperature rises [344]. This may lead to spontaneous nucleation in the sampling line, which is not a true vehicle exhaust component (particle “artifact”) [353,354]. In older studies with 0.7–1 m transfer lines and with older diesel engines without any aftertreatment it took >40 min until stabilization of the nucleation mode when the temperature increased from 200 °C to 300 °C [337,341]. In addition, the rate at which outgassing and resuspension take place is a function of the earlier operation history of the transfer line, which compromises the repeatability of the measurement [303]. This can affect PM mass measurements as well.

A study with a Euro 4 motorcycle found a huge nucleation mode particle number concentration during the high speed part of the cycle when measuring from the dilution tunnel. The nucleation mode was not formed (or evident) when some dilution took place at the tailpipe (i.e., open configuration). It was suggested that due to the lower temperatures at the transfer tube no desorption took place in the second case. In the first case, due to the high exhaust gas temperature, the desorbed material formed nucleation mode particles in the dilution tunnel (or pre-existing particles grew at the measurement range of the instrument, i.e., above 5 nm) [355]. Similarly, during DPF regeneration events a clear nucleation mode could be measured at the dilution tunnel, but not at the tailpipe (but with a different sampling system) [315].

The abovementioned phenomena refer to semi-volatile particles. For solid particles the effect is small. For a typical 6 m heated line, the SPN emissions at the tailpipe and the dilution tunnel are similar within 15% [356]. Higher differences (35%) can be found during cold start where the concentrations are higher and agglomeration can result in lower concentrations at the dilution tunnel. However, for levels of non-DPF equipped vehicles (>10\textsuperscript{13} #/km) the effect can be significant: differences of >40% have been reported. The exact difference between tailpipe and dilution tunnel number concentrations depends on the initial levels and the lengths of the tube between the vehicle and the dilution tunnel [357].

To conclude, sampling from the tailpipe is necessary when total particles are being measured. This will not exclude storage and release phenomena, but these will be representative of the actual vehicle emissions and not sampling desorption artifacts.
Tailpipe measurements have some difficulties. One is that the exhaust flow measurement is needed, which introduces one more factor of uncertainty, along with proper time alignment of the different signals [358]. This is not a new issue for heavy-duty engines where this information is already available, but for light-duty vehicles the procedures (instruments, time alignment) need to be defined. One final difficulty is that sampling directly from the tailpipe means that the sampling system and probably the instruments should be in the same room with the vehicle, for sampling lines to be kept as short as possible. This could pose some difficulties when tests at low or high ambient temperatures are conducted. A study showed that such measurements could be conducted with the measurement instruments outside of the room, without influencing the results [359]. Systems for on board applications, e.g., portable emissions measurement systems (PEMS) are designed for such conditions, but the laboratory grade equipment are typically designed for typical laboratory conditions (e.g., 5–30 °C). The same applies to altitude simulation laboratories.

4.4.4. Instrumentation (Particle Counter)

Another point that needs to be addressed is the particle counter. In the European regulation for laboratory systems the counters are full flow condensation particle counters (CPCs). The reason is the high accuracy (i.e., no splitting inside the CPC) and the steep detection efficiency drop at the desired cut-point (low size limit with 50% detection efficiency) size. For 23 nm cut-point CPCs a strong effect of the particle material has been reported [360–362] on particle detectability, and similarly for 10 nm cut-point CPCs [363,364]. In general, smaller material dependency (in absolute numbers) is expected with higher saturator-condenser temperature difference [365]. Full flow CPCs with cut-points down to 4–5 nm are commercially available. A low cut-point size is important to capture the nucleation mode of modern vehicles, which might peak at small sizes. For example, one study with heavy-duty engines and low sulfur fuel and lubricant the nucleation mode was <10 nm, even though the residence time after the primary dilution was 3 s [189], also confirmed by theoretical calculations [192]. This was also found with CNG vehicles [169,366] or regenerating diesel vehicles [318].

Diffusion charging based systems are also used in PEMS as particle number counters. The reason is that diffusion chargers are robust for on-road use, without the need for working fluids [367], and less sensitive to ambient temperature differences. The size dependency is small with the new designs [148,368,369]. Permitting this concept in the regulation for laboratory systems would also allow real time size distribution measurements (which also include charging of particles). For example, the engine exhaust particle sizer (EEPS) [370], differential mobility spectrometer (DMS) [371], and electrical low pressure impactor (ELPI) [372,373] are commonly used in research [146]. It should be taken into account that their uncertainty is much higher than of CPCs, but in most cases it should remain at acceptable levels (30%) [146], in particular when solid particles are measured [374,375]. Measurements of volatile particles with size distribution measurement instruments can, however, have high differences in particle number concentrations (factor of 2) [375–379]. Particularities of each technology then should also be considered for regulatory measurements. For example, CPCs have a saturator temperature typically around 35–40 °C, thus making questionable the need for dilution at much lower temperatures. The ELPI has low pressure at the final stages for small particles, affecting the nucleation mode. ELPI measures based on aerodynamic equivalent diameter, while EEPS and DMS based on electrical mobility equivalent diameter [380]. When the density is not unified, the size classification is different at the two concepts. Such analysis is outside of the scope of this paper, but should be considered when deciding the appropriate instrumentation for regulatory purposes. Instruments measuring sub-10 nm particles have been reviewed elsewhere, and the differences are even higher [381].

Other instruments could also be used for research purposes, depending on the needs of the project. For example, an aerosol gas exchange system (AGES) could be used to
separate volatiles for chemical characterization [382], or a filter holder to collect material on a filter for analysis.

4.4.5. Diluter and Particle Losses

The systems for regulatory purposes are characterized for varying losses according to particle size and these losses are taken into account in the so-called particle number concentration reduction factor (PCRF) in the 30–100 nm range. Penetration curves of various systems can be found in the literature [383]. In general, the agreement of systems corrected for the 30–100 nm losses is good, within 30% or better [384,385]. Such an approach does not cover the sub-30 nm range, where the losses are significant. Thus, size distributions peaking at sizes <30 nm can have big differences [358,386] when measured with different particle counters, even when correcting by the PCRF of each instrument.

Regarding volatile particles, the diluter can have an effect on the nucleation mode formation. For example, a study that compared a porous diluter at the tailpipe with the full dilution tunnel found big differences, even when the conditions were matched [335]. Other studies also found differences between different diluters (including ejector, porous, mini tunnel) [387], partly due to losses in the diluters [388] or heating one of the systems [345,389]. Better agreement was found when the diluters were heated and the nucleation mode was suppressed: ejector vs. rotating disk heated at 80 °C (no nucleation mode) [390]; mini tunnel vs. heated ejector [389]. In general, ejectors have been shown to have low particle losses in the nanometre range [346], but different designs can significantly affect the micrometre concentrations [391].

4.4.6. Recommended System

The recommended system is plotted in Figure 2. It is based on the conclusions of the Particulates project [12] and a review on measuring ultrafine particles [16], taking into account the current SPN methodology [7]. Other approaches (e.g., using separate systems for solid and total particles) are also relevant alternatives. The key characteristics of the system are discussed below.

**Figure 2.** Recommended setup for measurements of solid and total particles. Red temperature > 300 °C Green particle detectors. Dashed lines indicate optional parts. CS = catalytic stripper; PNC = particle number counter; PND = particle number diluter; PSD = particle size distribution instrument; SPN = solid particle number; TPN = total particle number.

The sampling line to the cold particle number diluter (PND0) should be as short as possible (residence time < 0.1 s) and heated at a temperature of >150 °C in order to avoid condensation, especially during cold starts. The dilution ratio should be around 12–25:1, and the dilution air temperature around 20–30 °C. The relative humidity of dilution air at the original setup was minimum (≤5%). However, this should be re-considered as with the low sulphur fuels and lubricants humidity is important to grow the particles in the measurement range of the instruments and a higher value (e.g., around 50%) would be more representative of the ambient air. The diluted sample is then split in two paths.
One path is for the measurements of total particles. After an aging tube with residence time around 1–3 s to grow the nucleation mode within the lowest measurement size of the instruments (typically 5–10 nm), a second diluter follows (PND$_3$), and then a particle number counter (PNC) with appropriate lower cut-point. Optionally, using a splitter, a particle size distribution instrument (PSD) can be used (with an appropriate diluter PND$_4$). The recommended cut-point size of the instruments in this path is around 5 nm, possible with both commercial PSD and full flow PNCs [16]. Using a 10 nm PNC for total particles has the advantage of direct comparability with the solid path. Although sub-10 nm information will be lost, the calibration procedures are the ones already available for existing systems. It is important, however, to ensure that the nucleation mode (if any) has to grow to the 10 nm range.

The other path is the current Particle Measurement Programme (PMP) system for the measurement of solid particles. After a hot dilution (PND$_1$) at 150 °C, a catalytic stripper (CS) removes the volatile particles [210]. A secondary dilution (PND$_2$) is optional, but typically needed to reduce the particle concentration and reduce thermophoretic losses. The important is that the concentration is within the calibrated range of the particle counter (PNC) and the temperature of the sample below the maximum allowed temperature defined by the PNC. The PNC currently has a cut-point size of 23 nm. However, future regulations tend to lower the size to 10 nm.

The recommended system needs evaluation of PND$_0$, but also of the particle losses especially at the 5–10 nm range, which in general is challenging. The expected reproducibility (but based on one system) was 22% [12,352] with non-DFP vehicles at the Particulates project. Higher values are expected for particulate filter equipped vehicles.

A simplified approach is to use PND$_1$ of a PMP system as PND$_0$ (i.e., without heating) and the current transfer lines as aging tube. Then, the path for the measurements of solid particles passes through the catalytic stripper, while the path for the measurement of total through the appropriate diluter and a PNC (5 nm or 10 nm). This approach will probably need higher dilutions at the PND$_2$ than typically used in commercial systems, where the higher dilution is achieved with PND$_1$.

Our suggestion is very similar to other approaches in the literature [12,16]. We consider the harmonization of sampling protocols of high importance for obtaining comparable results and should be discussed at international forums (e.g., PMP group). As mentioned in Section 4.2, controlling these particles will not only have an impact on engines and after-treatments, but also fuels and lubricants.

5. Conclusions

In the European Union (EU) particulate emissions from vehicles have to fulfill a particulate matter (PM) mass limit, and a solid particle number (SPN) limit for particles >23 nm, that may be extended in the future to cover particles >10 nm. There has been criticism that an important fraction of exhaust particles, comprising volatile and semi-volatile, is not addressed by current regulations. The current overview summarized the key aspects that have to be considered before including a new particle metric, including such species, in a potential relevant regulation.

The current SPN regulations have been very effective overall in reducing solid particles, but still conditions with low solid and high total particle number (TPN) concentrations exist. A TPN metric could be a good surrogate for controlling several parameters, including inorganic and organic ones that otherwise would be very difficult to individually regulate. The introduction of a TPN limit is relevant to the atmospheric studies, where total particles are measured. Furthermore, even recent studies demonstrated that road traffic is still an important, if not the most important contributor, of total particles in urban areas. The determination of the contribution of vehicles on secondary aerosol formation is not possible with TPN measurements, and a more detailed chemical characterization would be necessary. It remains to be seen if TPN thoroughly addresses secondary aerosol for all
vehicle technologies. In some cases, the SPN limit already has led to very low secondary aerosol (DPF diesel vehicles).

The TPN measurement cannot cover the wide range of atmospheric conditions, but using fixed sampling parameters it can give the nucleation mode formation potential (i.e., fresh delayed primary particles). The SPN measurement should be kept as continuation to the current regulation. Furthermore, semi-volatile particles can be calculated as difference of total minus solid particles.

At the moment, even though the TPN concept is established, it is not ready for introduction in the regulation. The sampling conditions must be defined and agreed, if possible on a global level, and then instruments need to be compared in order to assess the repeatability and reproducibility of the new method. The knowledge of the past has to be verified and tuned for the latest technologies. Finally, measurements need to be performed to determine the current levels of total particles of already circulating and future vehicles.

In parallel, one major question has to be addressed: which technology is able to control these semi-volatile emissions of modern vehicles (e.g., a better catalyst, or better in-cylinder combustion, or tighter fuel and lubricant specifications). It is also important to understand whether lower limits of particle precursors (e.g., NH$_3$, SO$_x$, hydrocarbons), or even addressing fuels and lubricants, would be more efficient than adding a TPN limit.

Author Contributions: Conceptualization, B.G. and L.N.; writing—original draft preparation, B.G.; writing—review and editing, A.M., G.M., P.D. and L.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The opinions expressed in this manuscript are those of the authors and should in no way be considered to represent an official opinion of the European Commission. Mention of trade names or commercial products does not constitute endorsement or recommendation by the European Commission or the authors.

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