



Investigation of solid particle number measurement: Existence and nature of sub-23 nm particles under PMP methodology

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ABSTRACT

A Particle Measurement Program (PMP) compliant system, an AVL advanced particle counter (APC) and an alternative volatile particle removal system, a catalytic stripper (CS) were evaluated and compared for measuring solid particle number (PN) emissions. The evaluations and comparisons were conducted using sulfuric acid and hydrocarbon particles as model volatile particles in laboratory tests, and diluted exhaust from a diesel particle filter (DPF)-equipped heavy-duty diesel vehicle operated on a heavy-duty chassis dynamometer under steady speed conditions at two different engine loads. For the laboratory test, both the APC and CS removed more than 99% of the volatile particles in terms of PN when using aerosols composed of pure sulfuric acid or hydrocarbons. When using laboratory test aerosols consisting of mixtures of sulfuric acid and hydrocarbons more than 99% of the particles were removed by the APC but the surviving particles were no longer entirely volatile, 12–14% were solid. For the chassis dynamometer test, PN emissions between 3 and 10 nm downstream the APC were ~2 and 7 times higher than the PN emissions of particles above 10 nm at the 74% and 26% engine load, respectively. At the 26% engine load, PN level of the 3–10 nm particles downstream the APC were significantly higher than that in the dilution tunnel, demonstrating that the APC was making 3–10 nm particles. The PN emission of 3–10 nm particles downstream the APC was related to the heating temperature of the APC evaporation tube, suggesting these particles are artifacts formed by renucleation of semivolatiles. Considerably fewer particles between 3 to 10 nm were seen downstream of the CS for both engine loads due mainly to removal of semivolatile material by the catalytic substrates, although some of this difference could be attributed to diffusion and thermophoretic losses. The findings of this study imply that improvement of the current PMP protocol would be necessary if the PMP were to be used in other applications where the PN emissions of particles below 23 nm are important.

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1. Introduction

As regulation of diesel Particulate Matter (PM) mass gets more stringent, the current gravimetric method for the legal determination of emissions will have difficulty accurately quantifying PM mass emissions. Although the United States

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(U.S.) Environmental Protection Agency (EPA) issued an improved protocol for the gravimetric method (EPA, 2008), accuracy will continue to be an issue at the very low emission levels of new diesel vehicles equipped with aftertreatment systems. For the Euro IV heavy-duty engine limit of 0.02 g/kWh, for example, the variabilities of the repeatability and reproducibility of the current gravimetric method are more than 20% and 50%, respectively (Burtscher, 2005).

Progress in regulating diesel particle emissions by non-gravimetric means has been made in Europe. The United Nations Economic Commission for Europe-Group of Experts on Pollution and Energy (UNECE-GRPE) initiated the Particle Measurement Program (PMP) working group to develop new particle measurement techniques to supplement or replace the current gravimetric method. The PMP protocol specifies measuring solid particles larger than 23 nm. Solid particles are operationally defined by the PMP as particles that can survive after passing through an evaporation tube (ET) that has a wall temperature of 300–400 °C (UNECE, 2010). A solid particle number concentration limit of 6×10^{11} particles/km has been included in the Euro 5/6 standards for light-duty diesel vehicles (UNECE, 2008). The Euro VI standard for heavy-duty diesel vehicles includes a solid particle number concentration limit as well, with the proposed limits of 8×10^{11} particles/kWh for stationary cycles and 6×10^{11} particles/kWh for transient cycles (Johnson, 2010).

The PMP only measures solid particles larger than 23 nm to avoid issues with poor repeatability caused by volatile particles present in the nucleation mode of diesel exhaust (Martini et al., 2009). Exclusion of sub-23 nm particles may have some potential issues, since not all sub-23 nm or nucleation mode size range particles are volatile. Some studies have found solid particles in the nucleation mode from heavy-duty diesel vehicles operating at idle or low loads (Filippo & Maricq, 2008; Kittelson et al., 2006). Even at high load operating conditions, solid particles in the nucleation mode have been observed for heavy-duty diesel vehicles (Lähde et al., 2009, 2010; Rönkkö et al., 2007). These references (Filippo & Maricq, 2008; Kittelson et al., 2006; Lähde et al., 2009, 2010; Rönkkö et al., 2007) also define non-volatile or solid particles as particles that can survive after passing through a thermodenuder (Burtscher et al., 2001), but with a slightly larger temperature operating range of 270–400 °C compared with the PMP. By excluding these sub-23 nm solid particles, the full impact of solid particles is not characterized by the PMP standard (Martini et al., 2009). Regulating particle number emissions for other sectors (aviation, off-road) is under discussion (Giechaskiel et al., 2010a). If the current PMP protocol were applied to other sectors, further caution should be taken in excluding sub-23 nm solid particles. For example, solid nucleation mode particles have been found for a gasoline vehicle, when some anti-knock metal additives were used (Gidney et al., 2010). Lead anti-knock additives are also still used in gasoline for general aviation. Czerwinski et al. (2006) even found solid particles below 23 nm emitted from 2-stroke mopeds.

It is also reported that the PMP can remove almost all volatile components of diesel vehicle emissions, and that no nucleation can occur downstream of the PMP (Giechaskiel & Drossinos, 2010). However, during previous California Air Resource Board (CARB)/University of California Riverside (UCR) studies of the PMP, a significant number of appeared-to-be solid sub-23 nm particles were found downstream of the PMP volatile particle remover under conditions that were thought to be unlikely to form sub-23 nm solid particles (Herner et al., 2007; Johnson et al., 2009). In the exploratory work for applying the current PMP protocol to heavy-duty diesel engines, Giechaskiel et al. (2009) also found apparently non-volatile sub-23 nm particles downstream of the PMP system. Thus, it is important to investigate whether these sub-23 nm particles observed downstream of the PMP system are solid or volatile, and if they are solid, whether they come from the exhaust or are artifacts of the measurement system.

An alternative system commonly used by researchers to remove volatile particles is a catalytic stripper (CS) (Abdul-Khalek & Kittelson, 1995; Kittelson et al., 2005; Park et al., 2003; Swanson & Kittelson, 2010a; Swanson & Kittelson, 2010b). In contrast to the PMP system, the CS uses a different approach to remove volatile particles. It removes all volatile hydrocarbon components and sulfur components by catalytic reactions at an elevated temperature. Therefore, renucleation will not occur downstream the CS. A study comparing the volatile removal efficiency of a CS with a thermodenuder, which is another type of volatile particle remover, showed that the CS had a higher efficiency for removing volatile particles (Swanson & Kittelson, 2010a). However, no studies have been conducted to compare the PMP system with a CS in terms of volatile particle removing efficiency.

This study presents laboratory and vehicle experiments of diesel particle penetration/formation using a PMP system and a CS. This study investigated and compared the effectiveness of the European PMP system and CS in removing volatile aerosols (1) using volatile aerosols generated in the laboratory; and (2) using diluted exhaust from a heavy-duty diesel vehicle operating over various cycles on a chassis dynamometer. This study also advances our understanding of the nature of sub-23 nm particles downstream of the PMP system, which were identified in a previous work (Johnson et al., 2009).

2. Experimental

2.1. Solid particle measurement systems

2.1.1. PMP system, AVL particle counter advanced

The PMP system used in the current study was an AVL particle counter advanced (APC), a commercial solid particle measuring system developed by AVL List GmbH. It fulfills the most recent requirements of the PMP protocol (UNECE, 2010). A brief description of the APC is provided here. More detailed schematics and descriptions of the APC can be found in reference (Giechaskiel et al., 2010b) and the manual of the APC. The sample enters the system with a typical flow rate of 5 Lpm (liters per minute) and is diluted by a primary chopper diluter, which has a rotating disk diluter with a dilution ratio

(DR) ranging from 10 to 1000. The diluted sample has a flow rate of 1 Lpm, and is transferred to the ET through a 2 m line. The dilution air, the primary chopper diluter, and the 2 m line are all operating at 150 °C. The ET has a wall temperature of 350 °C. A secondary, perforated, tube diluter that dilutes the sample with ambient temperature air follows the ET. The secondary dilution ratio is usually set at 10. A TSI 3790 Condensation Particle Counter (CPC), with a lower 50% cut off diameter (D50) of 23 nm, then measures the particle number concentration of the sample. The outlet flow rate of the APC was \sim 8.5 Lpm.

2.1.2. Catalytic stripper

The CS used in the current study is similar to others described elsewhere (Abdul-Khalek & Kittelson, 1995; Stenitzer, 2003). Stenitzer (2003) provides a more complete description of the theory, design, and operation of the CS. A brief description of the CS is provided here. The CS uses two different catalysts, provided by Johnson Matthey, to remove sulfur components and hydrocarbon components, respectively, from the diesel exhaust. The catalyst that removes hydrocarbon components by oxidation is called an Oxicat and the catalyst that adsorbs sulfur components is called a S-trap. The sample passes by the Oxicat first and then S-trap. Both the S-trap and Oxicat are heated to 300 °C. Afterwards, a cooling coil cools down the sample to ambient temperature. There are no specific requirements on the flow rate through the CS. In the current study, a flow rate of 10 Lpm was used.

2.2. Laboratory test setup and procedure

For the laboratory tests, aerosols with four different compositions were utilized to evaluate the response of the APC and CS systems under controlled conditions. The aerosol compositions included pure sulfuric acid, pure tetracosane (C_{24} n-alkane), a mixture of sulfuric acid and tetracosane, and a mixture of sulfuric acid and tetracontane (C_{40} n-alkane). These aerosols were chosen as our model aerosols to allow comparisons with the PMP protocol for determining volatile removal efficiency and to mimic real diesel particulate filter (DPF)-out semivolatile diesel particles. The PMP protocol specifies tetracontane particles as the model aerosol to evaluate the volatile removal efficiency of PMP compliant systems (Giechaskiel et al., 2010b). Biswas et al. (2009) reported semivolatile particles downstream of a DPF are mainly composed of sulfate, hydrocarbons, and some ammonium, the source of which could not be identified. It was expected that the particles seen downstream of the after treatment system in the chassis dynamometer testing here would also have a similar composition. Sulfuric acid and hydrocarbons are model aerosols that have been used by other researchers to evaluate the volatile removal efficiencies of PMP-like systems (Giechaskiel & Drossinos, 2010; Swanson & Kittelson, 2010a). Test aerosols were generated using an evaporation and condensation method (Swanson & Kittelson, 2010a), as shown in Fig. 1. Liquid sulfuric acid (73–98%, Fisher Scientific), tetracosane powder (99%, Acros Organics), or tetracontane (90–100%, MP Biomedicals) powder were placed in an alumina crucible, which was then placed in the two parallel stainless steel tubes of a Y shaped apparatus. These compounds were heated to temperatures sufficient to evaporate them, which were 121, 150, and 160 °C for sulfuric acid, tetracosane, and tetracontane, respectively. The temperatures were chosen to provide stable and appropriate mass concentrations. Nitrogen gas with a flow rate of 0.5 Lpm carried vapors of these compounds to a mixing chamber that was heated to 250 °C. The actual mass ratio of mixtures of different compounds was unknown, however. The vapors were cooled and diluted by an ejector pump (TD 110H, Air-Vac Engineering) after the mixing chamber. Compressed air with a gage pressure of 30 psi was supplied to the ejector pump. The compressed air was conditioned by a TSI filtered air supply (model 3074B) to remove oil droplets, moisture, and fine particles. Nanoparticles were formed by nucleation and grew by condensation of the cooled vapors.

These nucleated aerosols were then fed into the APC and CS to evaluate their performances in removing volatile particles. Three setup configurations were employed, the APC alone, the CS alone, and the APC–CS in combination. For the APC–CS configuration, aerosols passed through the APC and CS in series. In the APC–CS configuration, the volatile particle removing efficiency of the APC and the volatility of the particles exiting the APC were evaluated. Particle size distributions were measured by either a nano Scanning Mobility Particle Sizer (nanoSMPS) or a SMPS. The nanoSMPS consists of a TSI 3085 nano Differential Mobility Analyzer (nanoDMA) and a TSI 3776 CPC, and the SMPS consists of a TSI 3081 DMA and a TSI 3776 CPC. A TSI 3790 CPC, which is built into the APC, also measured the particle number concentrations downstream the APC.

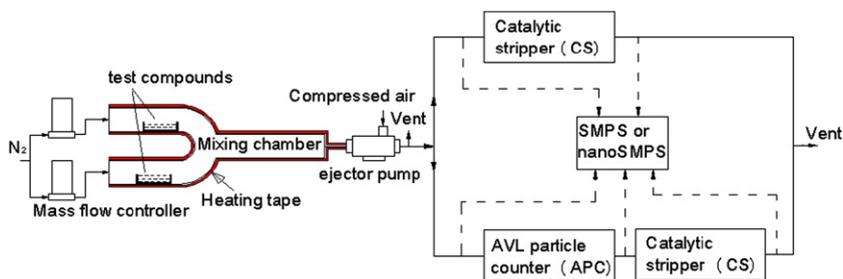


Fig. 1. Schematic diagram of the laboratory test.

2.3. Chassis dynamometer test

2.3.1. Setup

For the chassis dynamometer tests, the APC and CS were tested with exhaust generated by driving a heavy-duty truck on a chassis dynamometer. This provided actual exhaust to test the response of the systems, but under more controlled conditions than would be found under in-use driving. A schematic of the chassis dynamometer test set up is shown in Fig. 2. The setup can be divided into two parallel systems, the CS system and the APC system. Both the CS and APC systems took samples from the same inlet. A cyclone was used on this inlet to remove particles bigger than $2.5 \mu\text{m}$, in accordance with the PMP protocol. After the cyclone, tubes leading to the CS and APC were heated to 150°C , the same temperature used for the primary diluter of the APC. The APC was used following manufacturer's recommendations, as discussed earlier. On the CS side, an ejector pump (TD110H, Air-Vac Engineering) was used to pull exhaust through the CS. A 1 mm critical orifice and compressed air with a gauge pressure of 55 psi produced a flow rate through the CS of 10 Lpm. The exhaust was further diluted by a venturi pump after the ejector pump to avoid saturating the measurement instruments. The flow rate of the compressed air for the venturi pump was controlled by a mass flow controller, which was preinstalled in College of Engineering — Center for Environmental Research and Technology (CE-CERT)'s Mobile Emissions Laboratory (MEL) (Cocker III et al., 2004). The compressed air was produced by compressing ambient air with an Ingersoll Rand (Davidson, NC) OL5D5 oilless compressor. The compressed air was further conditioned by a Speedaire refrigerated compressed air dryer (5UZ85, Grainger), a HANKISON DHW series dryer system, and a HEPA filter. It should be pointed out that there was a difference between the APC and CS dilution systems. For the APC, exhaust in the constant volume sampling (CVS) dilution system was first diluted by the primary diluter, and then went into the ET, which is the key component of the APC, and then was diluted again by the secondary diluter. For the CS, exhaust in the CVS was sampled directly into the CS, without any dilution. All dilution on the CS side was done after the CS.

An Engine Exhaust Particle Sizer (EEPS) spectrometer (TSI, 3090) and a 3022A CPC (labeled as CPC 3022A_CVS) were used to measure particle size distributions and total number concentrations of the diluted exhaust in the CVS tunnel. A 3790 CPC (labeled as CPC 3790_APC) is built into the APC by the manufacturer and it always sampled from the APC side. Similarly, a 3772 CPC (labeled as CPC 3772_CS) and CE-CERT's fast SMPS (labeled as fast SMPS) were fixed to always sample from the CS side. One nanoSMPS and three CPCs with different cut off sizes were switched alternatively between the CS side and the APC side to measure size distributions and number concentrations. For the purpose of this manuscript, this set of instruments is called the "alternating set". The three CPCs were a 3025A CPC, a 3776 CPC, and a 3772 CPC. The specifications of all these instruments are summarized in Table 1, including cut off sizes, maximum concentrations, and sample locations. All of the CPCs used in this study were TSI products.

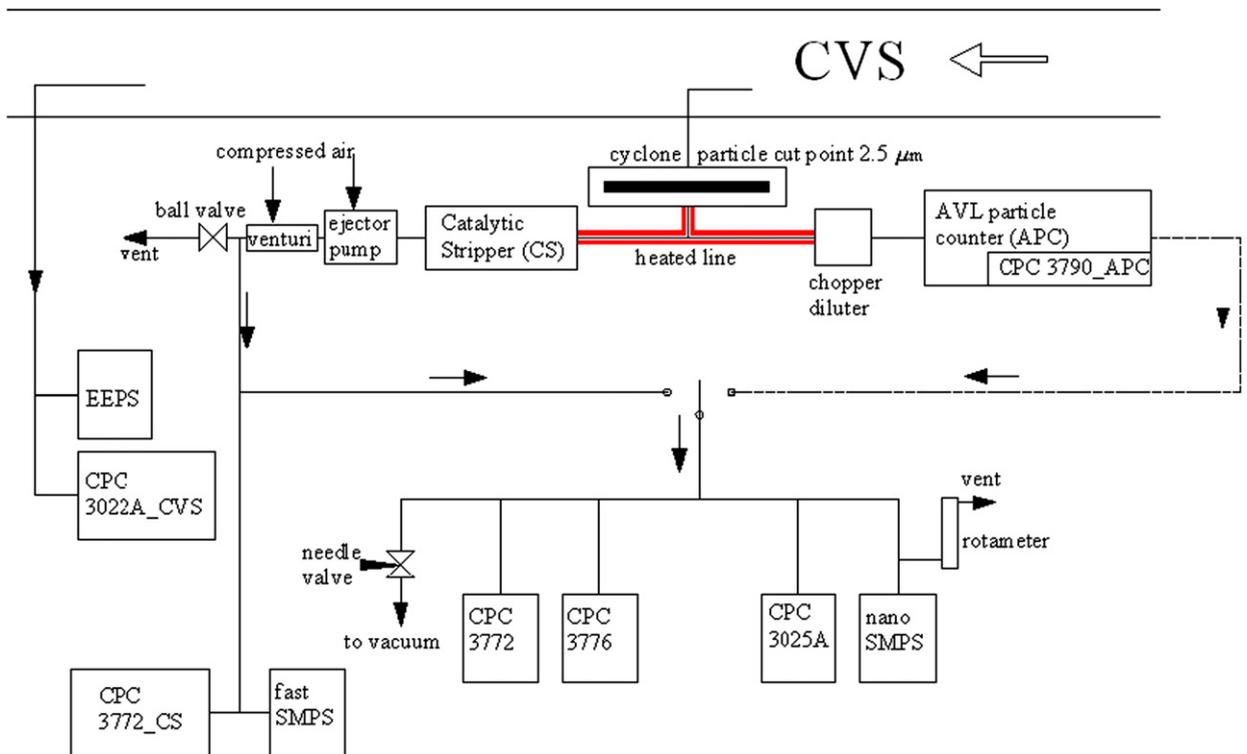


Fig. 2. Schematic diagram of the testing arrangement for the chassis dynamometer test.

Table 1
Specifications of instruments used in this study.

Instrument	Cut off size (nm)	Max. conc. (#/cc)	Sample location
CPC 3022A_CVS	7	9.99×10^6	Always at CVS
EEPS	5.6	–	Always at CVS
CPC 3790_APC	23	1×10^4	Always at APC
CPC 3772_CS	10	1×10^4	Always at CS
fast SMPS	3	–	Always at CS
CPC 3025 A	3	9.99×10^4	Switch either for CS or APC
CPC 3772	10	1×10^4	Switch either for CS or APC
CPC 3776	2.5	3×10^5	Switch either for CS or APC
nanoSMPS	3	–	Switch either for CS or APC

To minimize the effects of diffusion losses on the comparison between systems, efforts were made to equalize the diffusion losses among all the instruments. The EEPS and CPC 3022A_CVS shared one sample line and the split point was connected as close to the instruments' inlets as possible. The same plumbing configuration was applied to the CPC 3772_CS and fast-SMPS. A stainless steel manifold with six equal distance outlets was used in connecting the alternating set of instruments, so that the CPC 3776 and CPC 3025A had the same sample line lengths and flow rates. The flow rate through the manifold was controlled to 8.5 Lpm on both the APC and CS sides, which is the same as the outlet flow rate of the APC.

2.3.2. Test vehicles, fuels, lubricants, and cycles

The vehicle and aftertreatment system used for the chassis dynamometer testing was the same as that used for the on-road test in CARB/UCR's previous study (Johnson et al., 2009). It was a 14.6 liter, 2000 Caterpillar C-15 engine equipped, Freightliner class 8 truck. A Johnson Matthey Continuously Regenerating Trap (CRTTM) was installed on the vehicle. The CRTTM is a passive DPF system that had previously been shown to provide sufficient levels of particles over driving conditions similar to those used in this experiment (Johnson et al., 2009). The MEL trailer and truck combined have a weight of approximately 65,000 lbs, including all emission instruments. The truck had a mileage of 41,442 miles at the beginning of the testing. CARB Ultra Low Sulfur Diesel (ULSD) fuel ($S=8$ ppmw) and standard lubricating oil with sulfur level of 0.29% were used.

Two cruise cycles with extremely different nucleation mode particle number concentrations were tested. The two cycles both used a constant speed of 56 mph, one with a 26% engine load and the other with a 74% engine load. The 74% engine load cycle was performed right after the 26% engine load cycle.

3. Results and discussions

3.1. Laboratory test

The laboratory experiments are an important part of this study, because they allow the formation process of sub-23 nm particle to be investigated using model aerosols under well-controlled conditions. This provides an important link to the vehicle exhaust testing with the chassis dynamometer in this study and the on-road testing in our previous study (Johnson et al., 2009), both of which showed that a significant fraction of the particles downstream of the PMP were in the sub-23 nm size range.

The number concentrations with 95% confidence limits for all the laboratory tests are summarized in Table 2. Total particle number concentrations were obtained by integrating the particle size distributions over all size bins. The size ranges were 3–70 nm and 7–191 nm for nanoSMPS and SMPS, respectively. For all the tests, the upstream aerosol mass concentrations were on the order of $100 \mu\text{g}/\text{m}^3$, assuming a particle density of $1 \text{g}/\text{cm}^3$. The upstream particle size distributions had peaks around 15, 60, and 40 nm, respectively, for aerosols composed of pure sulfuric acid, pure tetracosane, and the mixture of sulfuric acid and tetracosane. Particle size distributions for the APC–CS test using a mixture of sulfuric acid and tetracontane are also shown in Fig. 3. Background concentrations for the laboratory test were checked by turning the heater of the condensation and evaporation apparatus off and measuring the particle size distributions. No particles were seen under this condition for either the CS or APC–CS configurations.

When aerosols composed of pure sulfuric acid were used, both the APC and CS removed more than 99.9% particles by number concentration. When using aerosols composed of pure tetracosane, the APC and CS removed 98.9% and 99.9% particles, respectively. When aerosols composed of a mixture of sulfuric acid and tetracosane were used, the APC and CS removed 99.8% and 99.4% particles, respectively.

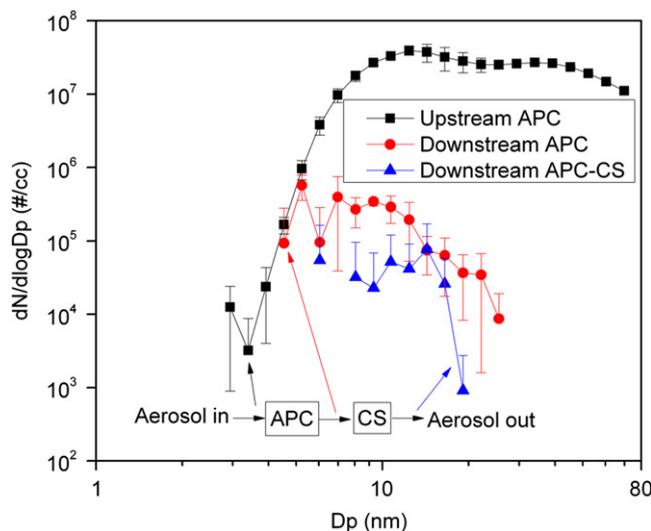
For the APC–CS test, no particles were seen downstream of the APC–CS when aerosols composed of pure sulfuric acid or pure tetracosane were used. When using aerosols composed of a mixture of sulfuric acid and tetracosane for the APC–CS test, a small number of particles were found downstream of both the APC and the APC–CS. As discussed above, these particles represent 0.2% of the input particle number of these particles, 14.2%, on a number concentration basis, were also observed downstream of the APC–CS. This suggested that at least 14.2% of those particles downstream of the APC were non-volatile for the following reasons. First, the concentration of volatile material in the gas phase downstream of the APC was

Table 2

Summary of laboratory tests results.

Note: particle number concentrations are shown with 95% confidence limits.

Aerosol	Config.	Concentration (particles/cm ³)				Dilution ratio		Instrument
		Upstream	Downstream APC	Downstream CS	Downstream APC-CS	Primary	Total	
H ₂ SO ₄	CS	$3.4 \times 10^7 \pm 2.5 \times 10^5$	–	$2.3 \times 10^2 \pm 2.2 \times 10^2$	–	–	1	SMPS
	APC-CS	$2.4 \times 10^7 \pm 2.3 \times 10^6$	$1.9 \times 10^3 \pm 3.7 \times 10^3$	–	$0.0 \times 10^0 \pm 0.0 \times 10^0$	50	500	SMPS
C ₂₄	CS	$5.3 \times 10^6 \pm 3.4 \times 10^6$	–	$4.4 \times 10^3 \pm 3.8 \times 10^3$	–	–	1	SMPS
	APC-CS	$8.9 \times 10^5 \pm 5.4 \times 10^5$	$1.3 \times 10^4 \pm 1.3 \times 10^4$	–	$0.0 \times 10^0 \pm 0.0 \times 10^0$	50	500	SMPS
H ₂ SO ₄ +C ₂₄	CS	$9.3 \times 10^6 \pm 3.1 \times 10^5$	–	$5.7 \times 10^4 \pm 3.0 \times 10^4$	–	–	1	SMPS
	APC-CS	$3.3 \times 10^7 \pm 7.9 \times 10^6$	$2.5 \times 10^4 \pm 2.4 \times 10^4$	–	$9.2 \times 10^3 \pm 3.8 \times 10^3$	20	120	SMPS
	APC-CS	$2.6 \times 10^7 \pm 1.3 \times 10^7$	$5.0 \times 10^4 \pm 1.8 \times 10^4$	–	$7.2 \times 10^3 \pm 3.9 \times 10^3$	20	120	nanoSMPS
H ₂ SO ₄ +C ₄₀	APC-CS	$2.7 \times 10^7 \pm 2.4 \times 10^6$	$1.5 \times 10^5 \pm 4.4 \times 10^4$	–	$1.9 \times 10^4 \pm 5.8 \times 10^3$	20	120	nanoSMPS

**Fig. 3.** Particle size distributions from the laboratory test using mixture of sulfuric acid (H₂SO₄) and tetracontane (C₄₀ n-alkane). Particle size distributions were measured upstream, downstream of the APC, and downstream of the APC-CS.

greatly reduced by dilution. Secondly, volatile particles that survive the APC will be reduced in size and easier to evaporate than the upstream particles. Thirdly, the CS has been shown to remove volatile materials effectively even with high inlet concentrations (Swanson and Kittelson, 2010a). Finally, the penetration of solid particles through the CS is less than 100%, so that if 14.2% of the particles penetrates, the actual solid fraction must be greater than that. The remaining 85.8% of the particles downstream of the APC, were likely predominately volatile, and could be due to renucleation of volatile particles in the APC.

The APC-CS test was also carried out using an aerosol composed of a mixture of sulfuric acid and tetracontane. Like the mixture of sulfuric acid and tetracosane test, the APC removed nearly all of the particles, in this case 99.4%. Particles exiting the APC were then fed into the CS and of these, 12.4% penetrated through the CS, indicating at least 12.4% of those particles exiting the APC were non-volatile. The fact that non-volatile particles were observed downstream of the APC when aerosols composed of mixtures of sulfuric acid and hydrocarbons, which are both volatile, were used suggests that non-volatile particles were formed in the APC from volatile species. This result was similar to what Swanson & Kittelson (2010a) reported in their thermal denuder and CS study, where they found solid particles were formed in the thermal denuder from sulfuric acid and hydrocarbons.

In our previous study (Johnson et al., 2009), the majority of particles downstream of the PMP were in the sub-23 nm size range. Based on the operational definition of solid particles for the PMP method, this means the PMP method is not counting the majority of solid particles, which could be problematic. The laboratory tests show that solid particles are formed with mixtures of sulfuric acid and hydrocarbons that are likely found in real exhaust, but would not be characterized in the tetracontane only volatile removal efficiency tests that are currently in the PMP legislation (Giechaskiel et al., 2010b). The results from the lab experiments also showed that a majority of sub-23 nm particles below the APC are likely re-nucleated semivolatile particles, with some non-volatile solid particles, based on the APC-CS study.

The nature of the solid particles found by using the CS to treat the aerosol downstream the APC is worth more discussion. The mechanism of this type of solid particle formation is not clear yet. It is known that n-alkanes, such as tetracontane and tetracosane, do not react well with sulfuric acid in gas phase (Burwell et al., 1954), but Swanson & Kittelson (2010a) have proposed such reactions to explain this type of solid particle formation. Another hypothesis is that n-alkanes were oxidized on the hot metal tube walls heterogeneously and then reacted with sulfuric acid to produce a non-volatile salt. More studies are needed to thoroughly understand the mechanism of particle formation in the ET of the APC.

3.2. Chassis dynamometer test

3.2.1. Particle measurements from the CVS

As the aerosol in the CVS was the source aerosol being fed into the APC and CS, it is important to characterize the CVS aerosol. A contour plot of particle size distributions in the CVS, as shown in Fig. 4, showed a distinctive bimodal pattern of accumulation mode and nucleation mode particles for the 74% engine load condition. Particle size distributions for the 26% load condition are not shown, as the number concentrations were near the EEPS's detection limit. The number concentrations of both nucleation mode and accumulation mode particles were stable at the 74% engine load and higher than those of the 26% engine load. The observation of higher number concentrations of nucleation mode particles at the higher engine load is consistent with previous studies (Herner et al., 2011), which have shown the formation of nucleation mode particles for vehicles with aftertreatment is a strong function of temperature.

Total particle number concentrations in the CVS measured by the CPC 3022A and the EEPS are shown in Fig. 5a for the 74% engine load. Since the EEPS and CPC 3022A have similar cut off sizes, 5.6 and 7 nm, similar total particle number concentrations were expected. The two instruments tracked closely up to about 4×10^5 particles/cm³, but diverged above that concentration. Above 1×10^4 particles/cm³, the CPC 3022A utilizes a photometric particle counting method that becomes increasingly non-linear as concentration increases. We attribute the discrepancy in particle concentrations above 4×10^5 particles/cm³ to the fact that the CPC 3022A was not calibrated for these high concentrations before the test. Thus, the EEPS should be considered more accurate at higher concentrations in Fig. 5a. Fig. 5b shows particle concentrations at the 26% engine load. EEPS data is not shown, as the concentrations were near the detection limit. Particle concentrations at the 26% engine load were steady and lower by three orders of magnitude compared to 74% load.

Fig. 6 shows number concentrations and estimated mass concentrations determined using the EEPS for the 74% load condition. The mass concentrations were calculated assuming that the nucleation mode consists of spherical hydrated sulfuric acid particles with a density of 1.46 g/cm³, which corresponds to the ambient relative humidity ($25 \pm 3\%$) and temperature (33 ± 1 °C) in the current study, and the accumulation mode particles were assumed to have an effective density of 1.0 g/cm³ following the EEPS manufacturer's recommendations. The number concentrations of nucleation mode and accumulation mode particles were determined by fitting the EEPS size distributions to a bimodal, log normal distribution. The nucleation mode concentrations increase as exhaust temperature increases due to the increase of SO₂ to

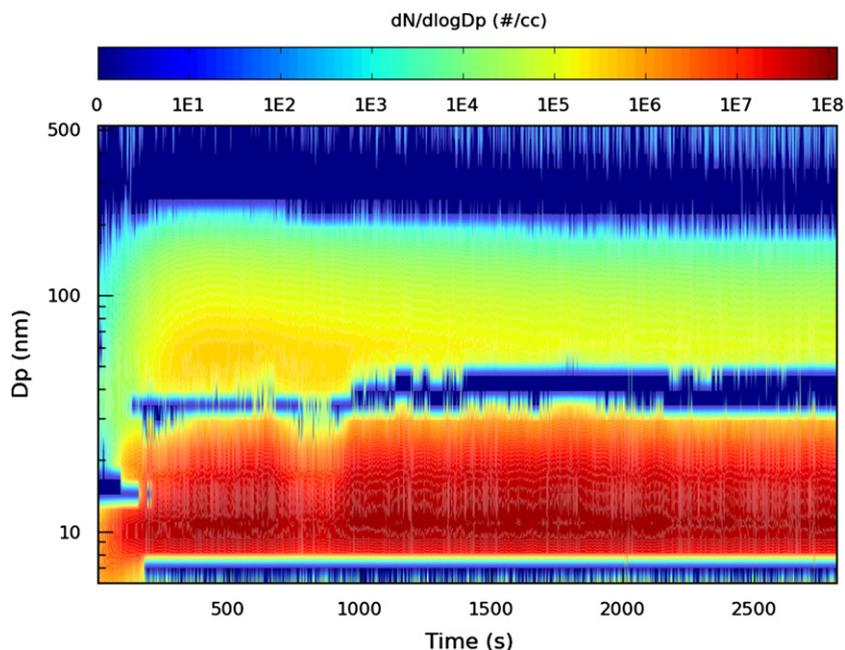


Fig. 4. Contour plot of real-time particle size distributions measured by the EEPS in the CVS at the 74% engine load.

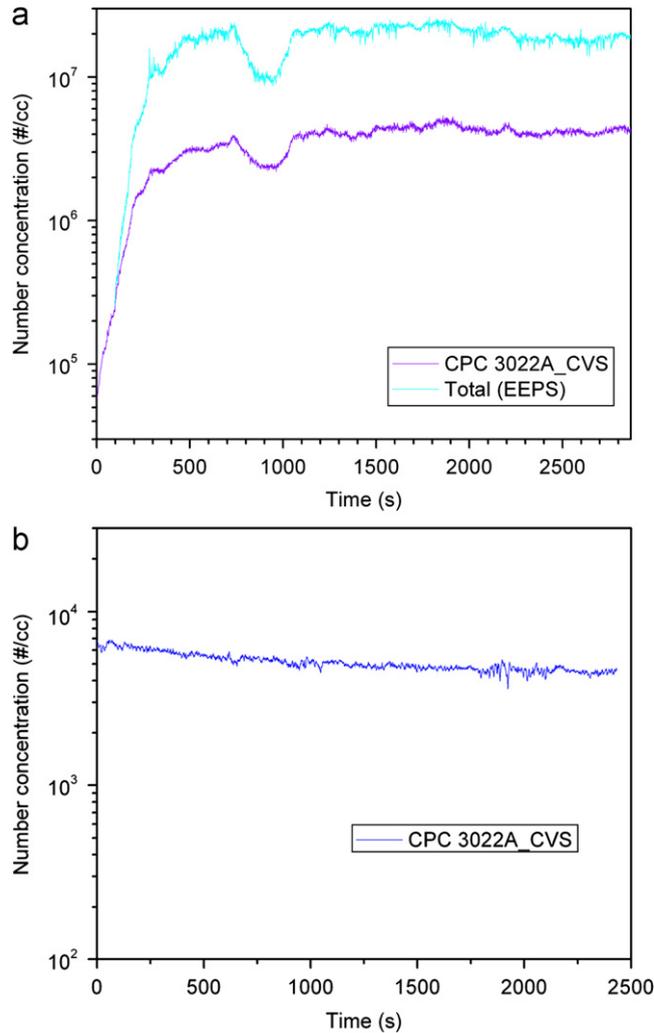


Fig. 5. Total particle number concentrations in the CVS (a) at the 74% engine load and (b) at the 26% engine load.

SO₃ conversion. The dip in number concentration between 700 and 1000 s is associated with a dip in exhaust temperature related to a change in engine coolant temperature, which is utilized as a heat exchanger for engine intake air. This only influences the nucleation mode and does not impact in the accumulation mode concentration. The decrease in accumulation mode particle concentrations as a function of time suggests the CRT is becoming more efficient as it loads with soot, although the exhaust temperatures are high enough for passive regeneration to be occurring simultaneously.

3.2.2. Particle number emissions under the APC and CS

Fig. 7 shows the number concentrations measured by various means plotted against time for the two engine operating conditions. Number concentrations have been corrected for dilution ratio (DR) to reflect the concentrations that would be seen in the CVS. The APC DR used for the concentration correction was the ratio of the total sample plus dilution air mass flow rate to the sample flow rate based on the settings of the APC mass flow controller. The actual DR of the APC varied only about 1% due to flow and pressure variations during the test. The primary and secondary DRs of the APC were 50 and 10 for the total DR of 500, and 10 and 10 for the total DR of 100. Based on our preliminary tests, a DR of ~20 on the CS side was necessary to avoid saturating the particle counting instruments. The actual CS DR was determined by two independent methods, flow rate measurement and CO₂ measurement. These two methods agreed well, and the CS DR was monitored continuously during the test. It had an average value of 21, and the variations over a test were less than 1%. Therefore, the average value of 21 was used for all calculations. For both engine loads, the tests with the “alternating set” of instruments (i.e., the 3025A CPC, the 3776 CPC, the 3772 CPC, and the nanoSMPS) were performed in the following sequence: the APC with a DR of 500, the APC with a DR of 100, and the CS. At the 26% engine load, this test sequence was conducted twice and then the instruments were directly connected to the CVS. At the 74% engine load, this test sequence was conducted three times without directly connecting to the CVS. The direct connection to the CVS was done for the 26%

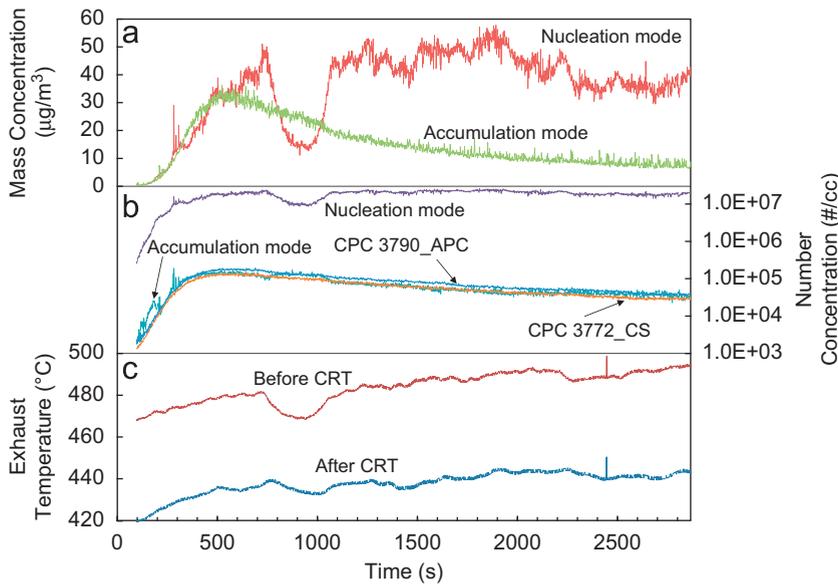


Fig. 6. (a) CVS particle mass concentrations of nucleation mode and accumulation mode particles. (b) CVS particle number concentration of nucleation mode and accumulation mode particles; the mass concentrations were calculated assuming that the nucleation mode consists of spherical hydrated sulfuric acid particles with a density of 1.46 g/cm^3 , which corresponds to the relative humidity and temperature of current study, and the accumulation mode particles were assumed to have an effective density of 1.0 g/cm^3 following the manufacturer's recommendations. The number concentrations of nucleation mode and accumulation mode particles were determined by fitting the EEPS size distributions to a bimodal, log normal distribution. (c) Exhaust temperatures before and after the CRT.

engine load, but not for the 74% engine load, because the particle number concentrations were much lower at the 26% engine load. When the CPCs were switched to the CS side or the CVS, the APC DR was set at 500. As discussed previously, the CPC 3772_CS and the CPC 3790_APC were dedicated to the CS and APC, respectively.

Fig. 7a shows the results for the 74% load condition. The load was increased rapidly to 74% after the vehicle was started. Number concentrations rise rapidly after the load is increased as the engine and CRT adjust to the new operating condition. Several things are happening simultaneously; engine out emissions are adjusting to the new operating condition, and the CRT is simultaneously loading and undergoing passive regeneration. After the operation is stabilized at the 74% engine load, the exhaust temperatures are well over $400 \text{ }^\circ\text{C}$. The catalysts used for passive regeneration not only oxidize NO to NO_2 but also oxidize SO_2 formed from sulfur in the fuel or lubricating oil to SO_3 , especially at temperatures above $350 \text{ }^\circ\text{C}$ (Cooper & Thoss, 1989). The SO_3 emissions are likely associated with the increase in nucleation mode particles seen in Fig. 6. "Solid" particle emissions measured with the CPC 3790_APC and CPC 3772_CS follow a smooth trend of increases and decreases very much like that of accumulation mode particles in Fig. 6b. This consistency suggests that these CPCs are accurately tracking the accumulation mode particles penetrating the CRT. Engine out accumulation mode number concentrations are typically larger than 10^7 particles/ cm^3 , and the concentrations observed here were less than 2×10^5 particles/ cm^3 , suggesting removal efficiencies greater than 98.5%. Peak concentrations are reached at about 500 s. Here, the peak concentration measured with the 3790_APC and the CPC 3772 downstream of the APC agree well, and are about 60% higher than the 3772_CS. The agreement of the CPC 3790_APC and the CPC 3772 downstream of the APC indicates that there were no particles present between 10 and 23 nm, the respective cut sizes of the CPCs, while the disagreement with the 3772_CS is consistent with the expected losses in the CS due mainly to thermophoretic deposition in the cooling section of the CS. On the other hand, downstream of the APC, the 3776 and 3025A CPCs show about 30% higher concentrations than the 3790_APC and 3772, indicating particles between 3 and 10 nm. Moving to the next time window, where most of the instruments are downstream of the CS, agreement is found between the 3772, 3025A and 3776, indicating no particles between 3 and 10 nm. During the next two windows, APC500 and APC100, the low cut size instruments, the 3025A and 3776, essentially agree as do the higher cut size instruments, the 3790 and 3772, but the ratio of low cut to high cut number count grows. The agreement between the 3790 and 3772 suggests that there are few particles between 10 and 23 nm so that the increasing ratio is primarily due to relatively more particles between 3 and 10 nm. During the next window when the instruments are switched downstream of the CS, particles below 10 nm begin to appear, as the 3025A and 3776 show higher concentrations than the 3772. The trend of increasing fractions of particles below 10 nm continues both downstream of the APC and CS in subsequent time windows. The last time windows downstream of the APC and CS show, respectively, 70% and 50% of the observed particles between 3 and 10 nm. It is not likely that the small particles represent penetration through the CRT. The most penetrating particle size for typical filters ranges from 100 to 300 nm, with particles either larger or smaller than that size removed more efficiently. In the case of sub-23 nm particles, although there is some evidence that under some conditions tiny solid nanoparticles are emitted,

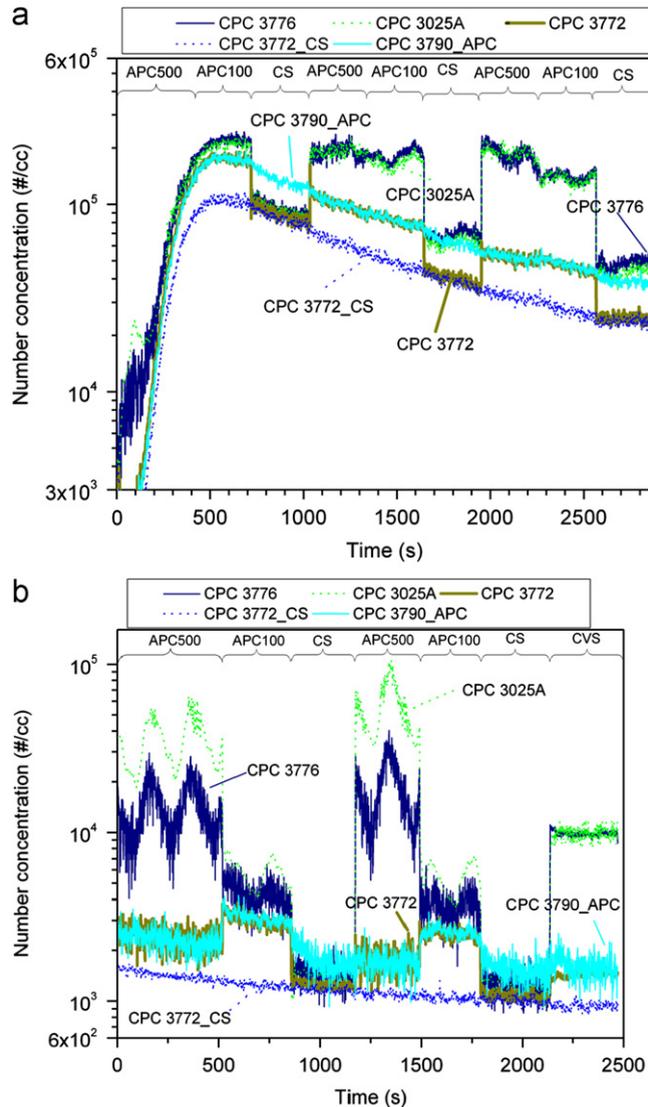


Fig. 7. Real-time particle number concentrations measured by different CPCs (a) at the 74% engine load and (b) at the 26% engine load. Note: The sampling locations and conditions were: APC side with a dilution ratio (DR) of 500 (labeled as APC500), APC side with a DR of 100 (labeled as APC100), CS side (labeled as CS), and CVS directly (labeled as CVS).

there is no evidence in the literature of formation of high enough concentrations of these particles to offset the decreased penetration through the CRT. The only exception to this might be the case when an excess of a metallic fuel additive, like a fuel borne catalyst, is used. Thus, it is extremely unlikely that these particles are due to penetration of solid particles through the CRT. Rather they are likely formed by renucleation downstream of the APC and CS. The question is why the fraction of these particles increases during the run. The accumulation mode particle concentrations and corresponding solid particle concentrations decrease continuously after 500 s, while the fractions below 10 nm increase, although the absolute concentration between 3 and 10 nm changes little. These particles could be formed by nucleation of sulfuric acid. In which case, it would require conversion of only 0.02% of the sulfur in the fuel to account for all the particles observed between 3 and 10 nm below the APC, even making the worst assumption that they are all 10 nm in diameter.

Fig. 7b shows the results of particle number measurements at the 26% load condition. Here, particle number concentrations are much lower than for the higher load condition and the structure is even more complex. As with the high load, measurements are made below the APC at two overall dilution ratios, 100 and 500. The first time window is APC500, i.e., instruments below the APC with a dilution ratio of 500. Here we see the 3772 and 3790_APC in good agreement but the 3025A and 3776 read more than 15 and 6 times higher, respectively, indicating that most of the particles are below 10 nm. All these instruments have been calibrated and agree well for calibration aerosols so the difference between the 3025A and 3776 is likely due to slight differences in the lower cutoff behavior of the two instruments, which are specified to have 50% counting efficiency cut points of 3.0 and 2.5 nm, respectively. Although it

would be expected that the 3776 would read higher than the 3025A, actual instrument cut points may vary from manufacturer's specifications, especially at the extremes of the operating range. In any case, these differences suggest that most of the particles are below the lower counting limits of these instruments, about 3 nm. The large swings in concentrations seen with the 3025A and 3776 are associated with temperature swings in the evaporation tube. This is discussed later in this paper.

The results are even more difficult to understand when the APC dilution ratio is reduced to 100. Here, we see a relatively sharp drop in the CPC 3776 and CPC 3025A counts when normalized to the CVS concentrations. This can probably be attributed to differences in nucleation between the two different dilution ratios. In this regard, it should be noted that the particle concentrations in the evaporation tube are a factor of 5 higher at the lower dilution ratio than the higher dilution ratio. It would be expected that the lower dilution ratio would lead to more particle nucleation and growth downstream of the evaporation tube, but this is only partly true. Actually, there is apparently less nucleation, as indicated by the reduced concentrations for the 3025A and 3776, but more growth, as indicated by agreement between the 3025A and 3776 showing that the particles have grown to well beyond 3 nm, and the increase in the particle concentration indicated by the 3772 and 3790_APC, showing that some particles have even grown above 23 nm. One might argue that the combination of a lower concentration of very small particles and overall growth is due to coagulation, but the low concentration in the evaporation tube, a few hundred particles/cm³, makes this unlikely.

In the first time window, using 3025A, 3776, and 3772 below the CS, the 3025A and 3776 are about 20% higher than the 3772 and 3772_CS, indicating some particle formation between 3 and 10 nm, while the 3772s below the CS are about 40% lower than the 3790_APC. This is the difference expected from thermophoretic losses in the CS. If the 3772s were less than 40% lower than the 3790, it would suggest particles between 10 and 23 nm below the CS, but this is not the case. The same trends continue for the rest of the run until the last condition, where all the instruments, except the 3772_CS and the 3790_APC, are connected directly to the dilution tunnel, so that all particles, both solid and volatile, are being counted. Under these conditions, the 3025A and 3776 are in good agreement, suggesting that most of the particles are above 3 nm. These two instruments also show about 7 times higher concentrations than the 3772, suggesting that most of the particles are between 3 and 10 nm. The average concentration measured by the 3025A during the last APC500 time window case (1200–1500 s) is more than 5 times higher than for the same CPC sampling directly from the CVS. This is further evidence of significant creation of sub 10 nm particles below the APC.

The results for the 26% load condition are quite surprising, and are hard to understand in terms of aerosol physics and chemistry. The concentration of sulfuric acid downstream of the CRT would be expected to be lower because of lower exhaust temperatures, and thus less oxidation of SO₂ to SO₃. Fuel is being burned at a lower rate so the concentration of SO₂ should also be lower. All of this should lead to a lower driving force for the nucleation of sulfuric acid. On the other hand, the total "solid" particle concentrations are also very low, about one and one half orders of magnitude lower than for the high load case, so that there is less surface area available to suppress nucleation by adsorption. Other species may be involved in the nucleation process. Arnold et al. (2006) have shown that nucleation downstream of catalyzed DPFS is sometimes associated with organic acids. Of course questions could be raised about the accuracy of the dilution ratio measurements and the calibration of the CPCs at very low concentrations. In most cases, particle concentrations downstream of the APC and CS were below 100 particles/cm³, and they were often below 10 particles/cm³. However, great care was taken in calibrations of the CPCs and in dilution ratio determinations. Clearly, more work needs to be done to understand PMP type measurements for heavy-duty diesel engines. The results indicate great care should be taken in interpreting the results of so-called solid particle measurements, especially if the measurements are to be extended to sizes below 23 nm.

The CS showed much less of a tendency to form particles downstream than the APC, but still appeared to form particles in the 3–10 nm range under some conditions, but there was no evidence of formation of particles larger than 10 nm. Presumably, the reduced tendency of the CS to form tiny particles is due to removal of semivolatile materials by the catalytic substrates, although diffusion and thermophoretic losses also play a role. During the higher load chassis test the APC did not appear to be making particles between 10 and 23 nm. For these conditions, the number concentrations of particles above 10 nm downstream the CS were about 40% less than number concentrations of particles above 23 nm downstream the APC, which was mainly due to the expected thermophoretic losses in the CS.

Although the tests here were not performed over a standard regulatory cycle, it is of interest to compare with proposed EU number standards. Comparisons to the proposed World Harmonized Stationary Cycle (WHSC) are shown in Fig. 8. At the 74% engine load, the particle number emissions under the APC and CS were both slightly higher than the proposed Euro VI particle number emission limit for heavy-duty (HD) diesel vehicles for the WHSC. At the 26% engine load, particle number emissions under the APC and CS were both below the proposed Euro VI HD limit. This is not surprising since the average load of the WHSC is between a 26% and 74% engine load.

Particle size distributions downstream of the APC and CS from the nanoSMPS for the two engine loads are shown in Fig. 9. As seen in the Figure, the count rates for the size distributions are relatively low, but they still represent important information in understanding the aerosol physics. At the 74% engine load, particles below 10 nm were seen by the nanoSMPS on both the APC and CS sides, which is consistent with the results suggested by the CPC measurements. At the 26% engine load, no particles below 10 nm were observed in the particle size distributions. The differences between the higher number concentrations of sub 10 nm particles seen by the CPC 3776 and CPC 3025A and the number concentrations seen by the nanoSMPS suggest that these particles were extremely small, making them difficult to be seen by the nanoSMPS due to high diffusion losses and a low charging efficiency.

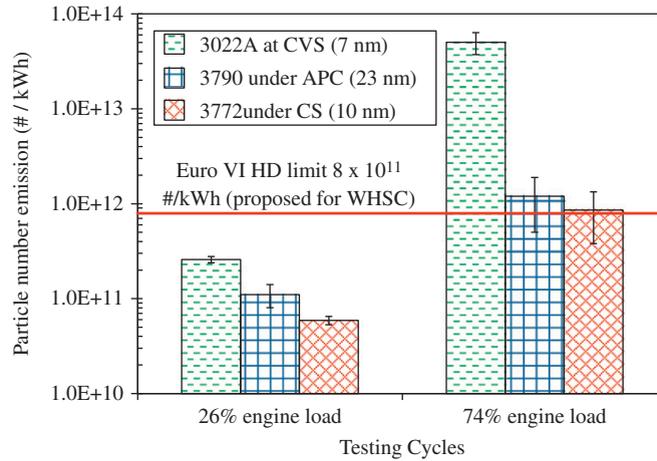


Fig. 8. Integrated particle number emissions for the chassis dynamometer test.

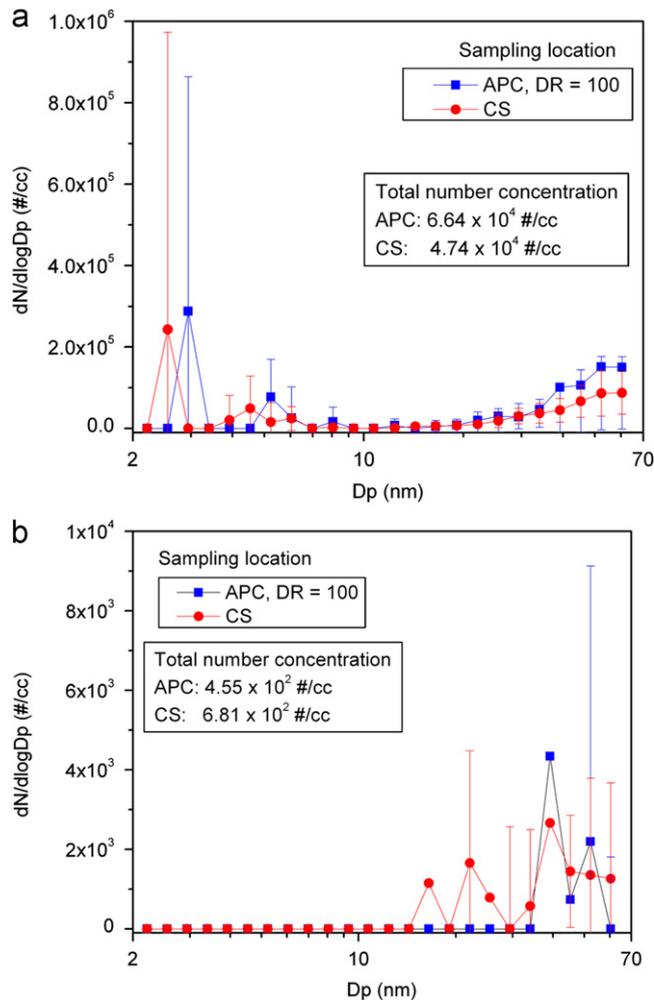


Fig. 9. Particle size distributions measured by the nanoSMPS downstream the APC and CS (a) at the 74% engine load, (b) at the 26% engine load.

Although the ET wall temperature of the APC was set at 350 °C, the actual wall temperature oscillated between approximately 345 and 357 °C. Interestingly, CPC particle number concentrations for both the laboratory test and the chassis dynamometer test also showed oscillations that were related to temperature oscillations of the ET, as shown in

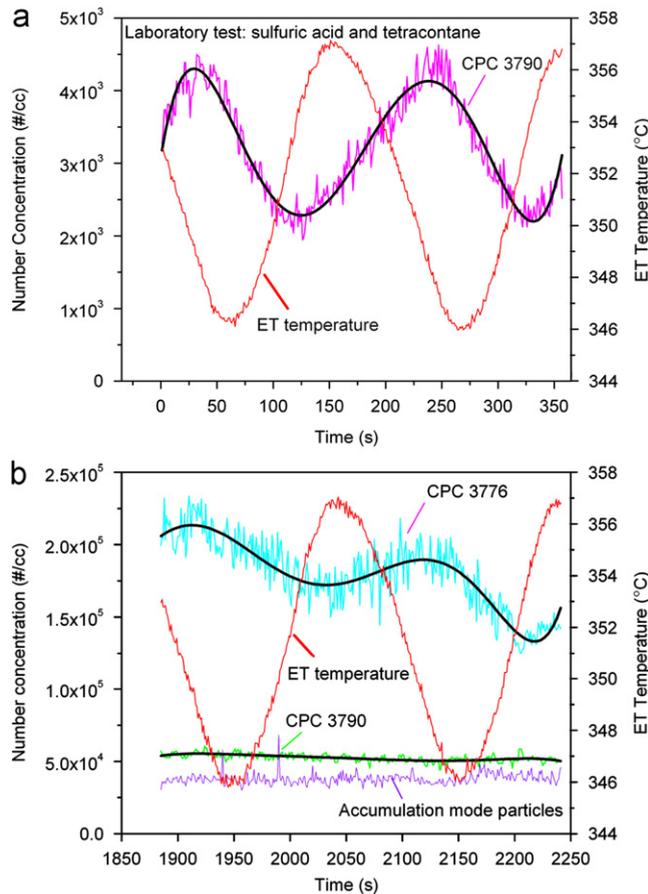


Fig. 10. Real-time ET wall temperature and CPC concentrations: (a) the laboratory test using aerosols composed of mixture of sulfuric acid and tetracontane, and (b) the chassis dynamometer test at the 74% engine load, time scale is the same as Fig. 7a. Wide solid lines are the polynomial fits to the individual curves.

Fig. 10. In the laboratory test, the concentration of the CPC 3790 oscillated with the same frequency as the oscillation of ET wall temperature (Fig. 10a). In the chassis dynamometer test, the CPC 3776 oscillated, as did the 3025A, which is not shown, but the 3790 did not (Fig. 10b). The oscillation curves of the ET wall temperature were identical, and the oscillating patterns of the CPC 3790 in the laboratory test and of the CPC 3776 in the chassis dynamometer test were similar too. These observations suggest that particles found downstream of the APC in the laboratory test and particles below 23 nm found downstream of the APC in the chassis dynamometer test were all formed as a function of ET temperature, through similar, if not the same, mechanisms. The CPC 3790 did not oscillate in the chassis dynamometer test because it only measured solid particles above 23 nm, which were mostly accumulation mode soot particles that had passed through the CRT that were not influenced by the ET temperature. The number concentrations of accumulation mode particles are also shown in Fig. 10b for comparison. The accumulation mode particle concentrations were determined by fitting the EEPS size distributions assuming lognormal bimodal size distribution. Although the aerosol mass concentration upstream the APC of the laboratory test was about 10 times higher than that of the chassis test, the number concentration measured by the CPC 3790 for the laboratory test was about 2 orders of magnitude lower than the number concentration measured by the CPC 3776 in the chassis test. This was because only a small portion of particles were measured by the CPC 3790 due to its large cut off size, i.e., the 3790 was only seeing the upper edge of the size distribution that was moving back and forth with temperature changes. The integrated nanoSMPS number concentration downstream the APC for the same test was about 2 orders of magnitude higher than the CPC 3790 concentration (Table 2 and Fig. 3).

4. Conclusions

A European PMP compliant particle measurement system, the APC, and an alternative system for removing volatile particles, the CS, were evaluated and compared using laboratory-generated model volatile particles and diluted exhaust of a DPF-equipped, heavy-duty diesel vehicle operated on a heavy-duty chassis dynamometer. The goal of this study was to investigate and characterize particles found downstream of the PMP system, with an emphasis on sub-23 nm particles.

The well-controlled laboratory experiments provided an important link to the vehicle exhaust testing by evaluating the formation and volatility of the sub-23 nm particles downstream of the APC. The laboratory tests were conducted with pure sulfuric acid and hydrocarbon aerosols separately, and then with mixed sulfuric acid/hydrocarbon aerosols.

Particles were found below the APC and CS for both the laboratory and the chassis tests. In the laboratory tests, the APC and CS eliminated 98.9–99.9% of the input particles by total particle number. The remaining particles downstream of the APC were almost entirely volatile when aerosols generated from pure sulfuric acid or pure tetracosane were used. However, for tests where particles were generated using a mixture of sulfuric acid and hydrocarbons, 12–14% of the particles downstream of the APC were non-volatile, and appeared-to-be formed in the APC. The temperature of the evaporation tube in the APC fluctuated by ± 5 °C about its 350 °C set point in a roughly sinusoidal manner, and under some conditions in both laboratory and chassis tests, particle concentrations downstream of the APC fluctuated by up to a factor of two or more at the same frequency, suggesting that a highly nonlinear process like nucleation was responsible.

For the two steady state cycles tested on the chassis dynamometer, particle number concentrations between 3 and 10 nm downstream the APC were ~ 2 and 7 times higher than the number concentrations of particles above 10 nm at the 74% and 26% engine load, respectively. At the 26% engine load, number concentration of the 3–10 nm particles downstream the APC was more than half an order of magnitude higher than the total (volatile plus solid) number concentration in the dilution tunnel, demonstrating the APC was making 3–10 nm particles.

The CS showed much less of a tendency to form particles downstream than the APC, but still appeared to form particles in the 3–10 nm range under some conditions. During the higher load chassis test the APC did not appear to be making particles between 10 and 23 nm. For these conditions the number concentrations of particles above 10 nm downstream the CS were about 40% less than number concentrations of particles above 23 nm downstream the APC, which was mainly due to the expected thermophoretic losses in the CS.

The presence of sub-23 nm particles downstream of the PMP poses challenges if the cut off diameter for the PMP protocol were to be reduced to count ash particles or if the PMP were to be applied more broadly to other sectors for measuring solid particles. This study provides evidence that the majority of sub-23 nm particles found in previous studies and the current study are artifact particles formed by renucleation of semivolatiles. Based on the current study, these artifact particles are mainly present below 10 nm, suggesting that artifact formation would not be as great if the cut off diameter of the PMP was only lowered to 10 nm. Overall, more study is needed to find ways to further reduce or eliminate artifact formation under PMP methodology for broader applications.

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Appendix A

Setup

During the chassis dynamometer test, the heating unit of the chopper diluter of the APC was broken. In order to continue the test, a flexible heating tape was wrapped around the chopper diluter to heat it to the desired temperature. A Variac voltage supply controlled the power input to the heating tape, and the built-in thermocouple of the chopper diluter monitored the temperature. The heating temperature stayed at 150 °C with a variation of $\sim \pm 2$ °C.

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