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

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A Particle Measurement Programme (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 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. 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 to 10 nm particles downstream the APC were significantly higher than that in the dilution tunnel, demonstrating that the APC was making 3 to 10 nm particles. The PN emission of 3 to 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.

1. Introduction

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 [1]. 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 [2, 3]. Even at high load operating conditions, solid particles in the nucleation mode have been observed for heavy-duty diesel vehicles [4-6]. By excluding these sub 23 nm solid particles, the full impact of solid particles is not characterized by the PMP standard [1]. Regulating particle number emissions for other sectors (aviation, off-road) is under discussion [7]. 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 [8]. Lead anti-knock additives are also still used in gasoline for general aviation.

An alternative system commonly used by researchers to remove volatile particles is a catalytic stripper (CS) [9-13]. 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 thermal denuder, which is another type of volatile particle remover, showed that the CS had a higher efficiency for removing volatile particles [12]. However, no studies have been conducted to compare the PMP system with a CS in terms of volatile particle removing efficiency.

This study presents 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 using diluted exhaust from a heavy-duty diesel vehicle operating over various cycles on a chassis dynamometer.

2. Experimental

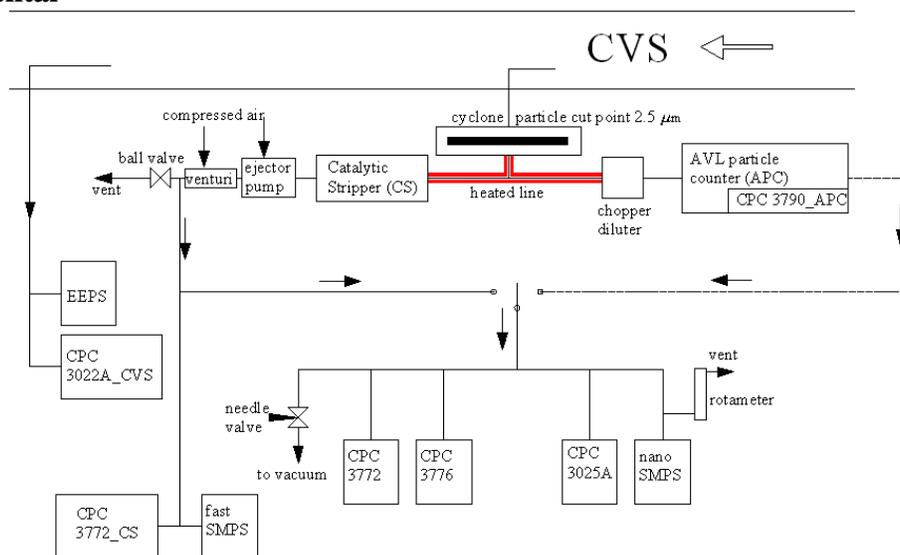


Figure 1 Schematic diagram of the testing arrangement for the chassis dynamometer test.

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 Figure 1. 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 μm , in accordance with the PMP protocol. After the cyclone, tubes leading to the CS and APC were heated to 150 $^{\circ}\text{C}$, the same temperature used for the primary diluter of the APC. 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. 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 condensation particle counters (CPCs) used in this study were TSI products.

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 [14]. 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 [14]. 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.

3. Results and Discussions

Total particle number concentrations in the CVS measured by the CPC 3022A and the EEPS are shown in Figure 2a. 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 Figure 2a.

Figure 2b shows the particle number concentration results for the 74% load condition. 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, there is no evidence in the literature of formation of high enough concentrations of these particles to offset the decreased penetration through the DPF. 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 DPF. 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.

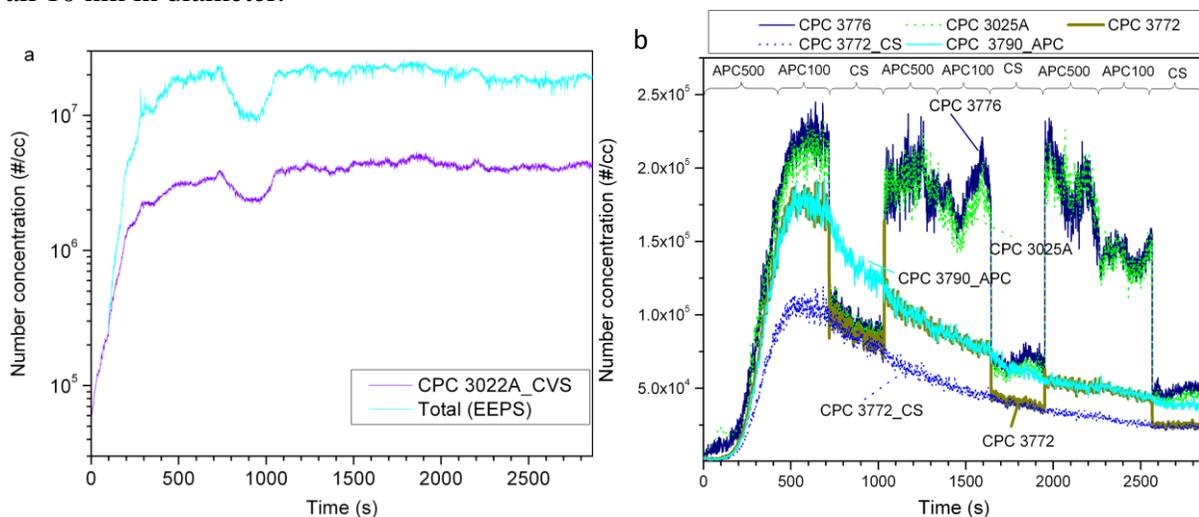


Figure 2 (a) Total particle number concentrations in the CVS; (b) Real-time particle number concentrations measured by different CPCs.

The CS showed much less of a tendency to form particles downstream than the APC, but still appeared to form particles in the 3 to 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.

Figure 3 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/cm^3 , which corresponds to the ambient relative humidity ($25 \pm 3\%$) and temperature ($33 \pm 1 \text{ }^\circ\text{C}$) in the 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. The nucleation mode concentrations increase as exhaust temperature increases due to the increase of SO_2 to SO_3 conversion. The dip in number concentration between 700 and 1000 second 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.

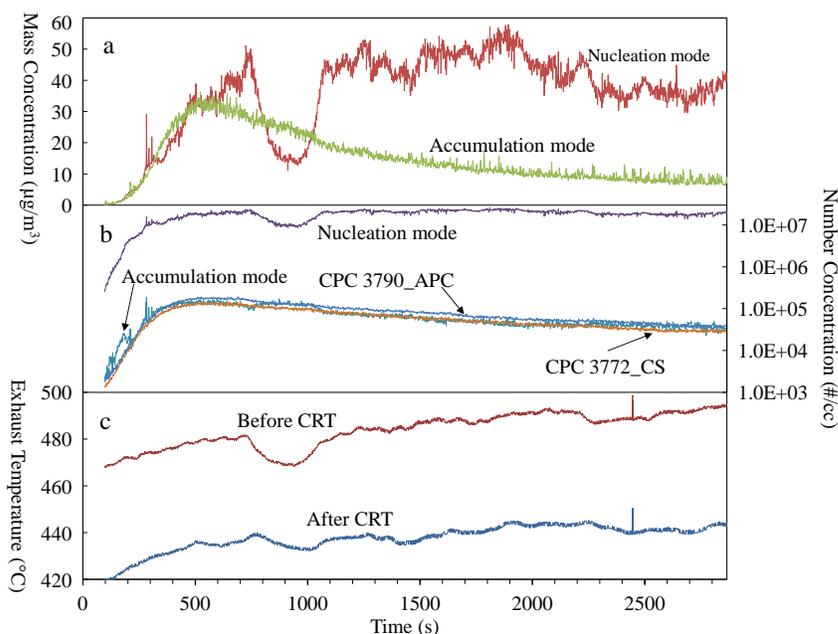


Figure 3 (a) CVS particle mass concentrations of nucleation mode and accumulation mode particles; (b) CVS particle number concentration of nucleation mode and accumulation mode particles; (c) Exhaust temperatures before and after the CRT.

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 diluted exhaust of a DPF-equipped, heavy-duty diesel vehicle operated on a heavy-duty chassis dynamometer.

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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