A source-independent empirical correction procedure for the fast mobility and engine exhaust particle sizers

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7 **A source-independent empirical correction procedure for**
8 **the Fast Mobility and Engine Exhaust Particle Sizers**
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HIGHLIGHTS

- Accuracy of high-time resolution particle sizers is affected by particle morphology.
- These instruments also under-size particles larger than 80 nm.
- We provide a source-independent correction protocol to address this issue.
- The correction protocol ensures agreement within 20% of a reference instrument.

ABSTRACT

The TSI Fast Mobility Particle Sizer (FMPS) and Engine Exhaust Particle Sizer (EEPS) provide size distributions for 6-560 nm particles with a time resolution suitable for characterizing transient particle sources; however, the accuracy of these instruments can be source dependent, due to influences of particle morphology. The aim of this study was to develop a source-independent correction protocol for the FMPS and EEPS. The correction protocol consists of (1) broadening the >80 nm size range of the distribution to account for under-sizing by the FMPS and EEPS; (2) applying an existing correction protocol in the 8 to 93 nm size range; and (3) dividing each size bin by the ratio of total concentration measured by the FMPS or EEPS and a water-based Condensation Particle Counter (CPC) as a surrogate scaling factor to account for particle morphology. Efficacy of the correction protocol was assessed for three sources: urban ambient air, diluted gasoline direct injection engine exhaust, and diluted diesel engine exhaust. Linear regression against a reference instrument, the Scanning Mobility Particle Sizer (SMPS), before and after applying the correction protocol demonstrated that the correction ensured agreement within 20%.

KEYWORDS

EEPS; FMPS; SMPS; Morphology; Vehicle Emissions; Particle Size Distributions

1. Introduction

Shifting trends in particle-phase measurements of traffic-related air pollutants have produced a need for high time resolution (≤ 1 s) particle number and size characterization over a wide concentration range. For example, high time resolution instruments may be required to characterize the performance of emission control technologies, such as diesel particulate filters (Bergmann et al., 2009; Biswas et al., 2008; Kittelson et al., 2006; Zervas and Dorlhène, 2006); the effect of fuel type on particle number concentrations during transient drive cycles (Liu et al.,

2007; Wang et al., 2006); or to characterize particulate matter (PM) in microenvironments near roadways (Baldauf et al., 2008; Choi et al., 2013; Kozawa et al., 2009; Massoli et al., 2012; Reponen et al., 2003; Zhu et al., 2002). Increasingly stringent emissions standards and the need for real-world emission factors necessitate that the employed particle sizing and counting instrumentation be accurate and precise; however, assessing accuracy is difficult due to the lack of traceable measurement standards. These instruments are generally validated against auxiliary, lower time resolution instrumentation, such as the TSI Scanning Mobility Particle Sizer (SMPS). Two commonly applied instruments capable of high-time resolution particle number and size characterization are the TSI Fast Mobility Particle Sizer (FMPS) and the Engine Exhaust Particle Sizer (EEPS). When measuring traffic-related particle sources in parallel, agreement between the SMPS the FMPS and the EEPS has been inconsistent (Asbach et al., 2009; Awasthi et al., 2013; Kaminski et al., 2013; Leskinen et al., 2012).

In Zimmerman et al., (2014) it was established that measuring concentrations and size distributions of different particle sources with an FMPS or an EEPS; including ambient PM, laboratory-generated soot, aerosolized ionic solutions, and diesel PM; all required unique correction procedures based on linear regression with a Scanning Mobility Particle Sizer (SMPS). Differences in the correction procedures were largely attributed to particle morphology; particles with a more agglomerate structure required greater correction than those with a more spherical structure. Reliance on an additional particle sizer to correct for source-specific discrepancies is time consuming, dependent on the user having access to an SMPS, and limits the correction to particle sources that are constant over the SMPS measurement interval. Thus, the objective of this study was to develop an empirical correction protocol independent of PM source that is suitable for high-time resolution applications (i.e. independent of an SMPS). The source-independent correction procedure presented here involves an existing correction protocol developed in Jeong and Evans (2009), broadening the upper fraction of the size distribution, and a scaling factor from parallel measurement by an Ultrafine Water-based Condensation Particle Counter (UWCPC), which has the same time resolution as the FMPS. Application of this correction protocol ensures accuracy between an FMPS or EEPS and an SMPS within 20%. If more accurate agreement is required, linear regression with an SMPS, as described in Zimmerman et al. (2014), is required.

2. Methods

2.1 Particle Sizing Instruments

Particle size distributions and number concentrations were obtained with an SMPS and either an FMPS or an EEPS. The EEPS (TSI model 3090) and FMPS (TSI model 3091) both function according to the same operating principles, measuring particle sizes from 6 to 560 nm using a series of electrometers; particles smaller than 8 nm and larger than 350 nm were excluded from analysis as concentrations were generally below detection. Operation of the EEPS and the FMPS used in this study has been previously described by Zimmerman et al. (2014). The SMPS used in this study consisted of an electrostatic classifier (TSI 3080), differential mobility analyzer (DMA) and ultrafine water-based condensation particle counter (UWCPC, TSI model 3786). Both the long-DMA (TSI 3081) and nano-DMA (TSI 3085) were included in the SMPS configuration. For the urban ambient measurements, an additional SMPS (TSI 3080 classifier) was used configured with the nano water-based ultrafine condensation particle counter (N-WCPC, TSI model 3788) to allow for parallel measurements with the nano-DMA and long-DMA; for the engine exhaust comparisons, the SMPS was equipped with the long-DMA for two replicates and the nano-DMA for the third replicate. The extended time scale (2 minutes, 100 s for scan up time + 20 s for scan retrace) required for a complete size distribution measurement limited the use of this instrument to steady-state testing. The SMPS used in this study has been previously described by Jeong and Evans (2009). For all parallel measurements, carbon filled conductive tubing was used to minimize particle line losses and sample lines to the instruments were identical in length (3 feet). Instrument flow rates were verified at the beginning of each experiment with a mass flow meter (TSI 4045) to ensure accuracy within 10% of the set point. As there is no particle counting measurement standard, auxiliary particle counting and sizing instrumentation (API 651 CPC, additional FMPS 3091) co-located at the Southern Ontario Centre for Atmospheric Aerosol Research (SOCAAR) Field Measurement Facility was used to verify agreement between instruments with the same working principle. A summary of the operating parameters and settings for the SMPS, EEPS and FMPS are provided in Table 1.

2.2 Condensation Particle Counters

In addition to the TSI 3786 UWCPC employed as a component of the SMPS configuration, two additional condensation particle counters (CPCs), a TSI 3788 Nano Water-Based CPC (N-

WCPC) and Teledyne API 651 CPC, were used to measure total particle number concentration. These CPCs use water as their condensing fluid to grow particles for optical counting. A summary of the operating parameters and settings for the CPCs are provided in Table 1.

Table 1: Summary of Instrument Operation Settings and Software

Instrument	TSI SMPS	TSI FMPS	TSI EEPS	TSI N-WCPC	API CPC
Model	Classifier: 3080 DMA: 3081/3085 CPC: 3786	3091	3090	3788	651
Software	Aerosol Instrument Manager (ver. 9.0.0)	FMPS Software (ver. 3.1.0)	EEPS Software (ver. 3.1.1)	Aerosol Instrument Manager (ver. 9.0.0)	Aerosol Instrument Manager (ver. 9.0.0)
Aerosol sample flow rate (LPM)	0.6 (CPC: 0.3)	10.0	10.0	0.3	0.3
Sheath air flow rate (LPM)	6.0 (CPC: 0.3)	40.0	40.0	0.3	0.3
Time Resolution (s)	120	1	0.1	1	1
Size Range	3085 DMA: 3 – 93 nm 3081 DMA: 12 – 340 nm	6 – 560 nm	6 – 560 nm	3 nm – 3 μ m	7 nm – 3 μ m
Notes	TSI diffusion correction; 1 μ m impactor	1 μ m impactor	1 μ m impactor	--	--

2.3 Particle Generation and Sampling

Experiments were conducted with three particle classes: (1) laboratory-generated aerosols, (2) urban ambient air, and (3) diluted heavy-duty diesel and light-duty gasoline direct injection (GDI) engine exhaust (Figure 1).

Figure 1: Process flow diagram of equivalency study experimental setup. Inter-comparisons were completed with three types of aerosol sources: (1) laboratory-generated aerosols, (2) urban ambient air, and (3) diluted heavy-duty diesel and light-duty gasoline direct injection engine exhaust. For the laboratory generated ammonium nitrate and sucrose aerosol, the DMA was used to generate a monodisperse sample.

Aqueous 1% v/v solutions of ammonium nitrate (NH_4NO_3) and sucrose were prepared using deionized water and standard stock chemicals (sucrose: BioShop Canada, Burlington, ON, Canada; NH_4NO_3 : Anachemia, Mississauga, ON, Canada). Two polystyrene latex (PSL) aqueous solutions (147 and 240 nm) were prepared by mixing 3-5 drops of stock solution (NanoSphere™ Size Standards, Thermo Scientific, Fremont, CA, USA) in 100 mL of deionized water and mixed with a vortex mixer. The four aqueous solutions were aerosolized using a constant output atomizer (TSI 3076) connected to a 20 psi filtered air supply (TSI 3074B). The generated aerosol mixture was dried using a silica diffusion drier (TSI 3062) and neutralized in a Kr Aerosol Neutralizer (TSI 3012) to remove any charge from the aerosol particles.

The atomizer aerosol measurements were conducted to evaluate previously observed underestimations in particle size for the upper size range of the FMPS and EEPS (Jeong et al., 2010; Lee et al., 2013). Aerosolized ammonium nitrate (NH_4NO_3) and sucrose was passed through the long-DMA (TSI 3081) to produce monodisperse aerosol in the 80-300 nm size range. The aerosolized PSL solutions were not passed through a DMA since PSL is a monodisperse size calibration standard. The monodisperse aerosol was measured in parallel by the SMPS, the N-WCPC, and either the EEPS or the FMPS. The 1 LPM aerosol flow produced by the atomizer was supplemented with HEPA-filtered air to meet the sample flow requirements of parallel FMPS/EEPS, SMPS and CPC operation. For each monodisperse aerosol, parallel measurements were made for 10 minutes, yielding a total of 600 measurements by the N-WCPC and the EEPS or FMPS, and 5 measurements by the SMPS. Flow constraints prevented parallel operation of the EEPS and FMPS, thus the experiment was repeated for each.

The urban ambient air measurements were conducted at the Southern Ontario Centre for Atmospheric Aerosol Research's Field Measurement Facility located in downtown Toronto, Canada. Ambient air was sampled near the intersection of two high-trafficked roads. The FMPS, two SMPSs, and API 651 CPC were operated in parallel over 5 consecutive days in February 2014, yielding a total of 267,549 measurements by the FMPS and the API 651 and 2860 measurements by the SMPS instruments. These measurements were conducted to validate the correction protocol for a source where the total concentrations measured by the SMPS and the FMPS or EEPS are in agreement.

The engine exhaust comparisons were conducted with a heavy-duty diesel engine (1997 Tier 1 Cummins B3.9-C) and light-duty GDI engine exhaust (2012 Ford Focus) diluted by a TSI Rotating Disk Thermodiluter. Neither engine was fitted with exhaust aftertreatment; all measurements were taken from engine-out exhaust. The diesel engine was operated at steady-state ISO8178 Mode 9 engine operation (1400 rpm, 105 N-m), which is representative of a low-load intermediate speed, urban cruising driving condition. The GDI engine was operated at a steady-state highway cruise condition (2600 rpm, 41.5 ft-lb) representative of highway driving at approximately 100 km/h. Six dilution ratios, ranging from 118 to 202, were tested for 10 minutes each, generating a total of 3600 measurements by the EEPS and N-WCPC and 30 measurements by the SMPS. Experiments conducted were performed in triplicate; two with the long-DMA and one with the nano-DMA equipped on the SMPS. These measurements were conducted to validate the correction protocol for a source where the total concentrations measured by the SMPS and the FMPS or EEPS are in disagreement due to the agglomerate morphology of engine exhaust PM.

3. Results and Discussion

3.1 Laboratory-generated aerosol: broadening the upper size range

For the PSL solutions (147 and 240 nm) and each of the DMA-selected NH_4NO_3 and sucrose aerosols (80, 90, 100, 150, 200, and 300 nm), the number size distribution mode diameter was determined for the SMPS, FMPS, and EEPS. The measured mode diameter was then compared to the predicted mode diameter, which was either the DMA-selected particle size or the specified PSL diameter (Figure 2). The 1% NH_4NO_3 solution was excluded for the EEPS due to concentrations being below instrument detection limits. Assessment of size-segregated particles larger than 300 nm was not possible due to the large gap between size bins in the upper size range and the low concentrations generated by the aerosol atomizer.

Figure 2: Measured SMPS, FMPS, and EEPS number size distribution mode diameter versus the predicted mode diameter from two PSL solutions (147 and 240 nm) and DMA-selected atomized aerosol solutions of NH₄NO₃ and sucrose. A linear least squares regression fit for the SMPS and combined EEPS and FMPS measurements is also shown.

In general, for all particle sources tested, the number size distribution mode diameter measured by the SMPS agreed with the predicted mode diameter (slope = 0.99, $R^2 = 0.99$). In contrast, it was observed that both the FMPS and the EEPS undersized particles larger than 80 nm. A least squares regression fit of the combined FMPS and EEPS measurements provided a relationship between the measured and predicted mode diameters to correct for this discrepancy. In Lee et al. (2013), a similar relationship was observed based on parallel measurement of DMA-selected atomized inorganic aerosols. This relationship was used to adjust the size bins for the FMPS and EEPS (Table 2).

Table 2: Original and adjusted size bins for the FMPS and the EEPS to correct for under-sizing in the >80 nm size fraction based on calibration with laboratory-generated aerosol (see Figure 2). Adjusted Size Bin = (Original Size Bin - 25) / 0.58. Uncertainty is calculated based on the standard deviations on the regression slope and intercept.

Original Size Bin Midpoint (nm)	Adjusted Size Bin Midpoint (nm)
80.6	92 ± 13
93.1	114 ± 14
107.5	139 ± 15
124.1	168 ± 17
143.3	201 ± 18
165.5	239 ± 20
191.1	283 ± 22
220.7	334 ± 25

254.8	393 ± 28
294.3	462 ± 31
339.8	540 ± 35
392.4	631 ± 40
453.2	736 ± 45
523.3	857 ± 51

Adjusting the size bins to the values presented in Table 2 effectively broadens the distribution in the upper size region. This adjustment is particularly important if the number size distribution is converted to a volume or mass size distribution where the particle radius is cubed. The effectiveness of this correction was assessed for three additional particle sources: urban ambient air (Figure 3A), diluted GDI engine exhaust (Figure 3B), and diluted heavy-duty diesel engine exhaust (Figure 3C). In Figure 3, by visual inspection it was observed that adjusting the size bins based on the correction presented in Table 2 improves the agreement of the upper distribution measured by the FMPS or EEPS with that from the SMPS; however, in the cases of diluted GDI engine exhaust (B) and diluted heavy-duty diesel exhaust (C) substantial overestimation in the sub-200 nm size range remains. This suggests that this correction alone is insufficient, and that further correction is needed to compensate for the effect of particle morphology as discussed in Section 3.2.

Figure 3: Particle size distributions of the 80-500 nm size range of urban ambient aerosol (A), diluted GDI engine exhaust (B, dilution ratio = 156), and diluted heavy-duty diesel engine exhaust (C, dilution ratio = 156) comparing an SMPS equipped with a long DMA (3081) to either an FMPS or an EEPS before and after the correction provided in Table 2. Shading represents the standard deviation.

3.2 Development and validation of a source-independent correction protocol

In Jeong and Evans (2009), an equivalence study compared an FMPS and an SMPS operated with a nano-DMA and a UWCPC when measuring urban ambient air in downtown Toronto, Canada. The authors noted size-specific distortions in the number concentrations measured by the FMPS for sub-100 nm particles. These deviations were hypothesized to be the result of limitations within the FMPS's data inversion algorithm in scenarios involving variable charging efficiency and multiple charging of smaller particles. To compensate for these discrepancies, correction factors for the 8 to 93 nm size range were developed using a linear regression analysis that fit the FMPS measurements against size-segregated UWCPC measurements (Table 3). Subsequently, in Zimmerman et al. (2014), it was established that application of this correction factor can be extended to the EEPS when measuring urban ambient air, but that this existing correction factor does not resolve the observed narrower distributions and higher total particle concentrations compared to the SMPS for diluted diesel engine exhaust under ISO8178 Mode 9 operation. Higher total particle concentrations were attributed to the agglomerate morphology of diesel particulate matter produced under load; comparisons of total concentrations measured by a UWCPC and the FMPS for spherical and fractal particles produced by a miniCAST soot generator (model 6200) confirmed this. Further discussion on the influence of particle morphology on FMPS and EEPS accuracy is provided in Section 3.3 of Zimmerman et al. (2014).

Table 3: Linear regression coefficients (b_1) and constants (b_0) developed in Jeong and Evans, (2009) to correct the size-resolved particle numbers measured by the FMPS or EEPS*

Size Bin Midpoint (nm)	b_1	b_0
8.06	1.362	144
9.31	0.820	19
10.8	0.835	44
12.4	1.139	103
14.3	1.294	205
16.5	1.227	443
19.1	1.193	816
22.1	1.215	1324
25.5	1.134	1070
29.4	0.951	624
34.0	0.885	463
39.2	0.935	258
45.3	0.924	266
52.3	0.928	240
60.4	0.904	278
69.8	0.913	126
80.6	0.930	86
93.1	0.936	108

*Corrected = $b_1(\text{Raw}) + b_0$

Accordingly, particle sizing and counting issues observed for the FMPS and the EEPS can be generalized into three components: (1) size-specific distortions in the 8 to 93 nm size region as described in Jeong and Evans (2009); (2) under-sizing of particles in the >80 nm size region, discussed in Section 3.1; and (3) over-counting of particle number if the particle source contains agglomerates. To address the issue of over-counting agglomerate particles, here we propose that the ratio of total number concentration measured by an FMPS or an EEPS to the total number concentration measured by a UWCPC or an N-WCPC be used as scaling factor. This ratio might also serve as a useful surrogate indicator of particle morphology, although this is not covered further here.

It has been previously observed that particle number concentration may be overestimated by the FMPS or EEPS when particles are non-spherical, which affects the electrical charge inversion algorithm; or when agglomerates form, which promotes multiple charging of particles (Kaminski et al., 2013; Shin et al., 2010). These factors do not influence the counting efficiency of CPCs, which use optical counting methods, thus scaling by the ratio of total concentration may reasonably account for these effects. Additionally, butanol-based CPCs meet the Particle Measurement Programme (PMP) requirements for Euro 5 and 6 vehicle exhaust particle number emission legislation, and have been assessed in detail in Giechaskiel et al., 2009. While this study employed water-based CPCs, it has been observed that there is acceptable agreement between water and butanol-based CPCs for diesel combustion, urban ambient air, freeway tunnel, and laboratory-generated particles (Biswas et al., 2005; Franklin et al., 2010; Iida et al., 2008; Kupc et al., 2013).

The application of this single scaling factor across all the particle sizes is an approximation, as the particle morphology likely differs for different particle sizes. The scaling factor is representative of the morphology of the predominant particles, but not necessarily of that of particles in other size ranges. For example, smaller particles are likely single spherules even for soot, and thus close to spherical. Accordingly, this scaling could in theory result in slight underestimation of the number concentration of small particles for sources where the predominant particles are larger agglomerates (e.g. diesel exhaust). However, this potential error

was barely evident in the final corrected data for particles from different sources (Figure 5); it appears that it was negated by the other corrections applied to the small particles.

To assess the impact of the CPC-based scaling factor, this correction was combined with the corrections discussed previously to produce a source-independent correction protocol, summarized in Figure 4. A step-by-step example of applying the empirical correction factor is provided in the Supplemental Information.

Figure 4: Summary of the empirical correction protocol. Dividing by the ratio of total number concentration measured by the FMPS and the CPC should be done at the highest possible time resolution, i.e. 1 second.

To assess the efficacy of the proposed correction protocol, average number concentration size distributions produced by the FMPS or the EEPS before and after correction were compared to the SMPS for three particle sources: (1) urban ambient air, source A (Figure 5-A1); (2) diluted GDI engine exhaust, source B (Figure 5-B1); and (3) diluted heavy-duty diesel engine exhaust, source C (Figure 5-C1). A summary of the total number concentration ranges measured by the FMPS or EEPS, SMPS, and CPC and ratios of total number concentration for the three particle sources used to evaluate the effectiveness of the empirical correction protocol is provided in Table 4.

Raw and corrected number concentrations were then averaged to a two minute time scale and linear regression between the FMPS or EEPS and the SMPS of size bins in the <100 nm size range was conducted (Figure 5-A2, 5-B2, 5-C2). An orthogonal distance regression method was used, as this method is better suited to handle observation errors in both the independent and dependent variables, unlike the ordinary least squares approach (Boggs et al., 1987). The particle source dictated the SMPS-DMA configuration used for linear regression: the nano-DMA for the urban ambient air, and the long-DMA for the diluted engine exhaust. Linear regression was limited to the <100 nm size range since larger size bins in the FMPS/EEPS and SMPS are no longer aligned following the adjustment provided in Section 3.1, Table 2; however, visual inspection (Figure 5) indicated good agreement across this upper size range for all three particle sources and showed improvements in agreement for the diluted GDI and diesel engine exhaust particle sources as compared to Figure 3.

Table 3: Summary of total number concentration ranges and ratios of total number concentration for the three particle sources used to evaluate the effectiveness of the empirical correction protocol.

Particle Source	FMPS _{TOTAL} /CPC _{TOTAL} or EEPS _{TOTAL} /CPC _{TOTAL}	Total Number Concentration Range (#/cm ³)		
		FMPS or EEPS	CPC	SMPS
A: Urban ambient air	1.1 ±0.21	Min: 2.9×10 ³ Max: 2.5×10 ⁵	Min: 3.4×10 ³ Max: 2.5×10 ⁵	Min: 3.9×10 ³ Max: 1.9×10 ⁵
B: Diluted GDI exhaust	1.37 ±0.06	Min: 2.6×10 ⁴ Max: 1.7×10 ⁵	Min: 2.0×10 ⁴ Max: 7.8×10 ⁴	Min: 2.1×10 ⁴ Max: 7.0×10 ⁴
C: Diluted diesel exhaust	1.47 ±0.16	Min: 5.7×10 ⁴ Max: 1.6×10 ⁵	Min: 4.2×10 ⁴ Max: 9.8×10 ⁵	Min: 5.2×10 ⁴ Max: 1.1×10 ⁵

Figure 5: Particle size distributions (A1, B1, C1) and linear regression slopes of the reference instrument (SMPS) vs. either the FMPS or the EEPS (A2, B2, C2) before and after correction with the empirical correction protocol. A1 and A2 are from urban ambient aerosol, B1 and B2 are from diluted GDI exhaust, and C1 and C2 are from diluted diesel exhaust (dilution ratio = 156). Shading in column 1 represents a 95% confidence interval (urban ambient aerosol, A1) or the standard deviation (GDI, B1; diesel, C1), the error bars shown in A2, B2, and C2 represent three times the standard error of the regression slope.

In Figure 5, it was observed that for all three particle sources tested, the empirical correction protocol generally improved agreement between the FMPS, or the EEPS, and the SMPS to within 20%. For the urban ambient air, in Figure 5-A1 it was observed that following correction, the FMPS number concentrations exceeded those measured by the SMPS configured with the nano-DMA; however, in Figure 5-A2 this difference was determined to be within the 20% tolerance limits of the correction protocol. It was also observed that the SMPS configured with the long-DMA measured significantly lower concentrations in the sub-25 nm size region compared to both the FMPS and the SMPS configured with the nano-DMA. This is hypothesized to be a result of large diffusional losses in the longer DMA column, thus potentially indicating that the TSI diffusion correction is not well-suited to the long-DMA, which is an area for future investigation. Comparing the shape of the FMPS size distribution before and after correction, the correction protocol corrects for the tri-modal size distribution and the upper tail shows improved agreement with the long-DMA configured SMPS.

For the diluted GDI (Figure 5-B1 and 5-B2) and heavy-duty diesel (Figure 5-C1 and 5-C2) exhaust, the empirical correction, significantly improved the agreement in the >30 nm size region with the SMPS equipped with either the nano-DMA or long-DMA. In the sub-30 nm size range, the correction protocol made no statistically significant impact except for the 29 nm and 25 nm size bins for the GDI and diesel, respectively, where the correction protocol resulted in regression slopes that diverged farther from unity as compared to the uncorrected distribution. Disagreements between the EEPS and the SMPS in the sub-30 nm size range are likely attributable to the low particle concentrations and higher detection limits for the EEPS in this size range.

The need for the correction protocol presented in this study may be due to limitations in the FMPS and EEPS data inversion algorithms and how these algorithms account for multiple charging of non-spherical particles (Kaminski et al., 2013; Shin et al., 2010). The ideal method to ensure accurate measurements with minimal post-processing would be improvements to the data inversion algorithm; however, the empirical correction protocol presented here represents a viable alternative if instrument agreement within 20% is suitable for the application. If more

precise agreement is needed, source-specific data correction based on linear regression against an SMPS is recommended.

4. Conclusions

In this study, a source-independent empirical correction protocol was developed for the FMPS and EEPS that ensured agreement within 20% against a reference SMPS. This study was undertaken to address the under-sizing and over-counting issues established previously when measuring non-spherical particles. The correction protocol consists of (1) broadening the >80 nm size range of the distribution to account for under-sizing by the FMPS and EEPS; (2) applying an existing correction protocol in the 8 to 93 nm size range; and (3) dividing each size bin by the ratio of total concentration measured by the FMPS or EEPS and a water-based Condensation Particle Counter (CPC). Scaling the size distribution by the total concentration ratio should be done at the highest possible time resolution (i.e. 1 second); however, for steady state systems where this ratio is well-characterized, it is possible to apply one consistent FMPS or EEPS to CPC ratio.

The efficacy of the correction protocol was assessed for three sources: urban ambient air, diluted gasoline direct injection exhaust, and diluted diesel exhaust. Orthogonal distance linear regression against the SMPS of comparable size bins before and after applying the correction protocol demonstrated that the correction ensured agreement within 20%. Improvements to the shape of the particle number size distribution after correction was also observed. If more precise agreement is needed, it is recommended that prior to operation of the FMPS or EEPS when measuring agglomerates, such as those produced in vehicle emission tests or near-road measurement of traffic-related air pollutants, correction factors are established based on parallel SMPS measurements to ensure equivalency.

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TABLES AND TABLE CAPTIONS

Table 1: Summary of Instrument Operation Settings and Software

Instrument	TSI SMPS	TSI FMPS	TSI EEPS	TSI N-WCPC	API CPC
Model	Classifier: 3080 DMA: 3081/3085 CPC: 3786	3091	3090	3788	651
Software	Aerosol Instrument Manager (ver. 9.0.0)	FMPS Software (ver. 3.1.0)	EEPS Software (ver. 3.1.1)	Aerosol Instrument Manager (ver. 9.0.0)	Aerosol Instrument Manager (ver. 9.0.0)
Aerosol sample flow rate (LPM)	0.6 (CPC: 0.3)	10.0	10.0	0.3	0.3
Sheath air flow rate (LPM)	6.0 (CPC: 0.3)	40.0	40.0	0.3	0.3
Time Resolution (s)	120	1	0.1	1	1
Size Range	3085 DMA: 3 – 93 nm 3081 DMA: 12 – 340 nm	6 – 560 nm	6 – 560 nm	3 nm – 3 μ m	7 nm – 3 μ m
Notes	TSI diffusion correction; 1 μ m impactor	1 μ m impactor	1 μ m impactor	--	--

Table 2: Original and adjusted size bins for the FMPS and the EEPS to correct for under-sizing in the >80 nm size fraction based on calibration with laboratory-generated aerosol (see Figure 2). Adjusted Size Bin = (Original Size Bin – 25) / 0.58. Uncertainty is calculated based on the standard deviations on the regression slope and intercept.

Original Size Bin Midpoint (nm)	Adjusted Size Bin Midpoint (nm)
80.6	92 $\pm$ 13
93.1	114 $\pm$ 14
107.5	139 $\pm$ 15
124.1	168 $\pm$ 17
143.3	201 $\pm$ 18
165.5	239 $\pm$ 20
191.1	283 $\pm$ 22
220.7	334 $\pm$ 25
254.8	393 $\pm$ 28
294.3	462 $\pm$ 31
339.8	540 $\pm$ 35
392.4	631 $\pm$ 40
453.2	736 $\pm$ 45
523.3	857 $\pm$ 51

Table 3: Linear regression coefficients* (b_1) and constants (b_0) developed in Jeong and Evans, (2009) to correct the size-resolved particle numbers measured by the FMPS or EEPS

Size Bin Midpoint (nm)	b_1	b_0
8.06	1.362	144
9.31	0.820	19
10.8	0.835	44
12.4	1.139	103
14.3	1.294	205
16.5	1.227	443
19.1	1.193	816
22.1	1.215	1324

25.5	1.134	1070
29.4	0.951	624
34.0	0.885	463
39.2	0.935	258
45.3	0.924	266
52.3	0.928	240
60.4	0.904	278
69.8	0.913	126
80.6	0.930	86
93.1	0.936	108

$$*Corrected = b_1(Raw) + b_0$$

Table 4: Summary of total number concentration ranges and ratios of total number concentration for the three particle sources used to evaluate the effectiveness of the empirical correction protocol.

Particle Source	FMPS _{TOTAL} /CPC _{TOTAL} or EEPS _{TOTAL} /CPC _{TOTAL}	Total Number Concentration Range (#/cm ³)		
		FMPS or EEPS	CPC	SMPS
A: Urban ambient air	1.1 ± 0.21	Min: 2.9×10 ³ Max: 2.5×10 ⁵	Min: 3.4×10 ³ Max: 2.5×10 ⁵	Min: 3.9×10 ³ Max: 1.9×10 ⁵
B: Diluted GDI exhaust	1.37 ± 0.06	Min: 2.6×10 ⁴ Max: 1.7×10 ⁵	Min: 2.0×10 ⁴ Max: 7.8×10 ⁴	Min: 2.1×10 ⁴ Max: 7.0×10 ⁴
C: Diluted diesel exhaust	1.47 ± 0.16	Min: 5.7×10 ⁴ Max: 1.6×10 ⁵	Min: 4.2×10 ⁴ Max: 9.8×10 ⁵	Min: 5.2×10 ⁴ Max: 1.1×10 ⁵

FIGURE CAPTIONS

Figure 2: Process flow diagram of equivalency study experimental setup. Inter-comparisons were completed with three types of aerosol sources: (1) laboratory-generated aerosols, (2) urban ambient air, and (3) diluted heavy-duty diesel and light-duty gasoline direct injection engine exhaust. For the laboratory generated ammonium nitrate and sucrose aerosol, the DMA was used to generate a monodisperse sample.

Figure 2: Measured SMPS, FMPS, and EEPS number size distribution mode diameter versus the predicted mode diameter from two PSL solutions (147 and 240 nm) and DMA-selected atomized aerosol solutions of NH₄NO₃ and sucrose. A linear least squares regression fit for the SMPS and combined EEPS and FMPS measurements is also shown.

Figure 3: Particle size distributions of the 80-500 nm size range of urban ambient aerosol (A), diluted GDI engine exhaust (B, dilution ratio = 156), and diluted heavy-duty diesel engine exhaust (C, dilution ratio = 156) comparing an SMPS equipped with a long DMA (3081) to either an FMPS or an EEPS before and after the correction provided in Table 2. Shading represents the standard deviation.

Figure 4: Summary of the empirical correction protocol. Dividing by the ratio of total number concentration measured by the FMPS and the CPC should be done at the highest possible time resolution, i.e. 1 second.

Figure 5: Particle size distributions (A1, B1, C1) and linear regression slopes of the reference instrument (SMPS) vs. either the FMPS or the EEPS (A2, B2, C2) before and after correction with the empirical correction protocol. A1 and A2 are from urban ambient aerosol, B1 and B2 are from diluted GDI exhaust, and C1 and C2 are from diluted diesel exhaust (dilution ratio = 156). Shading in column 1 represents a 95% confidence interval (urban ambient aerosol, A1) or the standard deviation (GDI, B1; diesel, C1), the error bars shown in A2, B2, and C2 represent three times the standard error of the regression slope.