2016

In-line, Real-time Particulate Matter Sensors for OBD and Exhaust After-treatment System Control Applications

Marc Cyrill Besch

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In-line, Real-time Particulate Matter Sensors for OBD and Exhaust After-treatment System Control Applications

Marc Cyrill Besch

**Dissertation submitted to the
Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy
in
Mechanical Engineering**

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Morgantown, West Virginia

2016

In-line particle sensor, DPF filtration efficiency, OBD, diffusion charging, PN regulation

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Abstract

In-line, Real-time Particulate Matter Sensors for OBD and Exhaust After-treatment System Control Applications

Marc Cyrill Besch

The ability to quantify particle mass and number concentrations in the exhaust stream of combustion engines during in-use operation is of critical importance for continuously monitoring and diagnosing the particulate matter removal efficiency of modern exhaust gas after-treatment systems. Extensive literature survey suggested a sensor operating on the diffusion-charging principle being optimally suited for particle measurements due to their proportional response towards particle surface area. This study was designed to determine and assess the possibility of quantifying particle emissions during on-road measurements using a prototype diffusion-charging type sensor. Such a sensor would not only allow for continuous monitoring capabilities of the exhaust particulate filters integrity, but moreover provide for a simplified tool to assess real-world particle number emissions to verify in-use emissions compliance of engines.

Evaluation of the sensor followed a three tier process, starting with fundamental sensor response analysis using a particle generator in order to develop and parameterize the underlying physical phenomena of the measurement principle. Next, examine the sensor in engine dynamometer experiments under *controlled environment*, and sampling from test vehicles during chassis dynamometer testing aimed at real-world like test conditions. Finally, the sensor was installed on vehicles while operated on the road over diverse driving conditions. This allowed for comparison to laboratory-grade measurement systems and the standard regulatory gravimetric particulate matter measurement method. The diffusion-charging type sensor employed in this study was observed to exhibit a response proportional to particle size $D_p^{1.09}$ and a measurement variability below 2% over consecutive tests. The sensor's sensitivity allowed for distinguishing between Diesel particulate filter efficiencies due to soot cake layer build-up on the substrate walls. In summary, the study concluded that the diffusion-charging type sensor provided a viable method to quantify in-use particle number emissions.

This dissertation is dedicated to my beloved parents Herbert and Beatrice,
and sister Carol.

Acknowledgments

After 8¹/₂ years I finally decided to make a full stop at the end of this document. What merely had been an elusive thought in a dream about a decade ago, has first grown into an idea and then morphed to the research work that led to writing this dissertation. Some may call it *work* what I have done during my time here at West Virginia University, I myself however, would rather describe it as joyous adventure amongst some of the most amazing people and friends.

However, no matter how hard I worked and how much effort I invested into achieving more knowledge, all this wouldn't have been possible without the people that awarded me with possibilities, taught me valuable lessons and skills, motivated me on a daily basis, supported me in whatever I wanted to do, critically assessed my ideas and provided me with the endless love a human being needs to master each and every day on this wonderful planet.

First and foremost I would like to thank my beloved parents Herbert and Beatrice for their endless compassion, and the inspiration and support they provided me with since the day I was born and throughout my long lasting academic career. You guided me through childhood and set the most honorable examples a kid and young adult can strive to achieve. The limitless possibilities you gave me were the foundation of my hunger for knowledge. I bow my head in love, respect and pride towards you!

I'd like to thank my beloved *little* sister Carol for being there and enduring me as the *older* brother over all these years. Much thanks to my mama and daddy for giving me this wonderful sister as a companion. Without you childhood would have been far less exciting. Oh yea and finally, if your friends are asking what your brother does for a living you don't have to answer anymore *he's a student...*

Mridul Gautam, I'd like to thank you from the bottom of my heart for not only serving as my academic advisor during my *grad school* experience, but more importantly being a close friend and offer a family away from home. I'm endlessly thankful for all the possibilities you fostered for me and the research community you introduce me to. You never fell short of your promise to not only provide me with *just a job* at the end of my studies but rather *a career*. I truly appreciate the trust you put in me right from the start of my time with you here at WVU. I was merely 9 months part of your wonderful research group and you already sent me alone around to world to present

our work at the most prestigious conference in the field of combustion derived nanoparticle emissions in Zurich. You taught me that *failure is not an option*... one can make a mistake, but should be honest about it, learn from it, and rectify it such that the expected deliverables are not only met but definitively exceeded by a notable margin. That's how one gains respect in the field. Most important, I'd like to thank Seema for her hospitality whenever I was invited to your house.

I'd like to thank Dan Carder for his friendship and mentoring during my time with CAFEE. You were always there for me and all the other graduate students and relentlessly worked to improve the appearance and recognition of our research group not only at the College and University level but more so with industry partners and governmental agencies nation- and world-wide. Your tireless work culminated in our research group being celebrated for identifying the first indicators of what led to one of the largest emissions scandals in automotive history worldwide. I'm thankful that I could be part of this amazing story together with you and our beloved CAFEE family. You taught us that ingenuity and improvisation can easily make up for a small budget, even to solve the biggest challenges. At the end of the day, that's what differentiates an *Engineer* from someone with an *engineering degree* I believe.

My best friend and *de facto* brother Arvind Thiruvengadam, thank you for your friendship and working with me side-by-side for the past 8¹/₂ years. We went through some of the most amazing adventures together and mastered the most daunting tasks and research projects by working as a team. You would never rest till the job is done, no matter if it meant that we had to pull a 45 hours straight shift to get experimental data for a conference the following day or a non-stop drive from Los Angeles to Seattle and back to collect the necessary data for finishing a project in time. I admire your knowledge of the field of vehicles, engines and emissions, and my greatest ideas most often grew out of discussions with you. Many times we found ourselves with an empty page and a bunch of ideas a day before the deadline for a major proposal submission. However, this did never hinder us from putting some of the most interesting proposal submissions together overnight, and stretch the boundaries of the local traffic laws in order to get the proposal package to FedEx in the last minute (or sometimes even after thanks to the friendly and most welcoming FedEx employees at the Morgantown facility). This I could only achieve with you. *Thank you Sir!*

April Nicole Covington thank you *soooo* much for being an amazing friend.

I'm deeply honored and endlessly grateful to have met you and to got to know you. You're the most wonderful person with the biggest heart and always put helping and looking out for others way ahead of caring for yourself. I affectionately thank you for the support you provided me with my work and finishing this dissertation. It was the motivation you gave me that ultimately allowed me to sit down and finally bring this work to an end. For that I'm truly thankful! I thank you for being there and the only one who would answer when I wanted to chat/message at 3am in the morning. . . and yes, I'm deeply sorry for disrupting your sleep by doing this. Thanks for the kayaking trips and inviting me to your house for dinner or hanging out with the boys, and to let me use your game room if you were out of town. I'm thankful that you introduced me to *wild child* Rylan. . . I still haven't quite figured out if he is dog or beaver or a crossbred between both. But I love him. Thanks for the meals you had cooked and the birthday cakes you had baked for me. You truly are an amazing cook. It was a pleasure to work with you on different projects and most importantly, I'm thankful for everything you taught me, not only in the field of engineering but also in other topics. *To the world you may be one amazing person, but to me you are the world!*

Raffaello and Michelangelo Ardanese, I'd like to thank you for being close friends during all these years here in the US. Thank you very much for teaching me and making me part of the amazing ADECS-team starting with the first day of my arrival in Morgantown. I still remember that one magic night we achieved 0.23g/bhp-hr NO_x with our test setup. I deeply appreciate all the effort you guys were putting forth to offer me the possibility to join GM numerous times. I know for certain that every time I travel to Michigan there is an open door and warm place for me to stay with either one of you. Raffaello, I'd like to thank you very much for serving on my dissertation committee and for guiding me through my PhD adventure. Michelangelo, I still remember all the adventures trips and visits to different places we did together. Walking through Grand Canyon at >40°C in the middle of July was definitively an unforgettable highlight. Thanks for joining me in these adventures. I also would like to thank Fernando for his kindness and being a dear friend. We still gotta have to continue our discussion about the bridges in Chicago. Many thanks to Claudia, Marie and the wonderful kids for their friendship.

Thank you very much to my best friend Hemanth Kumar Kappanna for your friendship throughout all these years at WVU. I looked up to you from the first day you were introduced to me as CAFEE alumni and then *lead* engineer at Cummins, and I continue doing so. I'm thankful that only about

one year after meeting you for the first time, you decided to leave your industry job and join WVU for your PhD. I hope this decision was partly influenced by the fact that you wanted to work with me. I'm grateful to have had you as a companion through the preparation period for the PhD qualifying exam. I will always keep the fond memories of the many long nights of study-sessions in the library, exercising and solidifying our skills in thermodynamics and fluid mechanics...and yes, I can still derive the Reynolds-averaged Navier-Stokes equation. I'd like to thank you for all the adventures we went through. It was always a pleasure to come to your office and discuss or philosophize about any kind of topic, be it technical or anything else that affected the world.

Peter Bonsack thank you very much for your friendship over the past nearly two decades. Whenever I needed help or support with anything I knew I could just call you and things would get done. Thank you very much for teaching me to be detailed, organized and accurate about not only the work I'm doing but more so, everyday life. I would have to write an other dissertation just to describe all the adventures we've been through and all the amazing stuff we've done as friends, starting from apprenticeship to military, college and finally your short stint in Morgantown to get your Master's degree. *Thank you for everything Sir!*

I'd like to thank Manoharan Thiagarajan for being a dear friend at WVU before graduating and leaving to Michigan. I still fondly remember the movie nights and going to *Chili's* for dinner or the many night-shifts during the *ManTech* project with subsequent breakfast at *Eat'n Park*. Thank you very much for all the help you provide me with while you were at WVU and the many interesting discussions we had about all kind of topics. It was never ever boring around you.

Many thanks to Alessandro Cozzolini, Daniele Littera, and Gennaro Campitelli. It was wonderful working with you guys and see how you evolved from *young guys* (living in med-center apartments for the first semester) to excellent top-notch engineers by the time you finished your PhDs. I'd like to thank Ale and Daniele for the many times I got invited for authentic Italian food at their place. It was the most joyful pleasure to work with you guys on many projects and moreover, to learn a lot from your analytical skills. Thanks for building and establishing a nation-, if not worldwide, unique windtunnel facility for CAFEE allowing us to not only study the transformation and faith of vehicle derived pollutants but many other topics as well.

I'd like to express my sincere appreciation and many thanks to Pragalath Thiruvengadam, Saroj Pradhan and Berk Demirgok. Thank you guys for being close friends and part of our wonderful team. I thank you for all the help and support you provided me with during my time at the CAFEE. I'm truly honored to have had the opportunity to work with you and learn from you. *You guys are family!* I also would like to thank Ross Ryskamp for his friendship and support. I always enjoyed to have a technical discussions with you and learn from you, but also hang out with you during an evening or weekend beer.

Derek Johnson thank you very much for your friendship and support. I'd like to thank you for including me in your research and teaching me about the impact of methane emissions and many other things. I'd like to express my appreciation for lending me your personal Diesel vehicle to perform cutting-edge on-road emissions research with it. Also, it was always a pleasure to spend time apart from work with you, go kayaking or hang out for a beer...oh yeah, I still gotta make sure that you finish that pizza oven of yours before I leave town for good. I furthermore would like to thank Nathan Fowler and Robbie Heltzel and express my gratitude for your friendship and support I have received from you guys. It is a pleasure to call you my friends.

Many thanks go to my best buddies Chris Rowe and Jason England. You guys are amazing and I strongly believe that about half of all our projects (if not more) would have failed or come to a screeching halt if not for you guys's tireless effort to get work done and projects moving. I had the unique honor to work closely with both of you on a couple of major projects and for that I'm thankful! Many thanks to Chris for teaching me golfing...I think I still have some bumpy road ahead of me to be able to hit the ball straight of the t-box and not at a 90° angle, but I'm strongly convinced I will eventually reach that point thanks to your teaching.

I'd like to thank all the wonderful members of the CAFEE team (current and former), particularly Brad Ralston, Zac Luzader, Richard Atkinson, Ron Jarrett, Tom Spencer, Petr Sindler, Dave McKain, Byron Rapp, John Revercomb, Chris Beers, and Wyne Hildebrand for all the help they provided me with over these 8½ years at WVU. It was a pleasure to work with you, to learn from you and more importantly, to call you friends. Zac, thanks for enduring me as office mate during the later part of my PhD. Many thanks to current and former CAFEE faculty members Dr. Cosmin Dumitrescu, Dr. Andrew Nix, Dr. Scott Wayne, and Dr. John Nuszowski for their support.

I would also like to recognize and thank my friends from the University of Rome Tor Vergata, Dr. Vincenzo Mulone and Dr. Stefano Cordiner. It was a honor to get to know you and to work with you during your visiting time at WVU. Most important, I'm grateful for the many things I was able to learn while working with Vincenzo and attending Stefano's summer class. I hope we can continue fostering a good relationship and work together with Tor Vergata on future projects as well as have a frequent exchange of students.

Sri Hari Ramakrishna Chalagalla thank you very much for becoming a great friend. Thanks to you I have the luxury of sitting in my office and not having to worry, because I know for sure you're out there running experiments for me with the same meticulous approach as I strive to do. I'd like to thank you and Sadhika for being wonderful neighbors and for providing me with delicious Indian dishes anytime of the day. You guys are amazing cooks.

Many thanks go to Dr. Camille Riley. Thank you very much for taking care of me that first day you found me wandering in Kroger, clueless what I would need to start up a household. You were so kind to take me around town and help me buying the equipment and *stuff* that turns an empty shell of an apartment into a livable and cozy space. I'd like to very much thank you for your continuing friendship and interesting discussions we have during the traditional quarterly or yearly get-togethers. I always enjoy our discussions about history, art and the associated relation to law.

I'd like to thank my undergraduate advisor Dr. Jan Czerwinski. Thank you very much for providing me with a solid theoretical knowledge but also practical experience with engine testing and emissions measurement during my undergraduate studies that gave me great advantage in excelling during my PhD. I'm grateful that you suggested me to join WVU 9 years ago and most importantly, established the connection with Mridul that allowed me to become part of the most wonderful research group I could have only wished for.

I would like to express my deepest appreciation for my dissertation committee members Dr. Nigel Clark, Dr. Gregory Thompson, Dr. Benjamin C. Shade, Dr. Hailin Li, and Dr. Raffaello Ardanese. Thank you very much for taking the time to guide me through my PhD, critically assess my work, and provide me with valuable input that helped improving this document and its underlying study. Thanks also go to Dr. Cosmin Dumitrescu who was substituting on behalf of Dr. Hailin Li during my final dissertation defense.

Finally, I would like to express my thanks to the many students that I had the honor to work with and become friends during my time with the CAFEE.

8¹/₂ years are a *quasi eternity*, thus, I saw many great minds come, do their studies and write the thesis, graduate and then leave of to new adventures. The list below is by far not comprehensive and I greatly apologize for anyone I may have missed.

Nathan Fowler	Adam Sayers	John Revercomb
Robert Heltzel	Yubin Wu	John Smallwood
Bharadwaj Sathiamoorthy	Yu Li	Nathan Music
Mohan Krishnamurthy	Jim Perry	Brock Merritt
Yashwanth Maddineni	Chet-Mun Liew	Clint Bedick
Balakrishnan Ramamoorthy	Greg Yoder	Ganesh Vedula
Donald Sanfillippo	Mario Velardi	Mike Wise
Matthew Robinson	Matthew Shriver	Mrinmoy Dam
Orlando Ugarte	Francisco Posada	Oscar Delgado
Prabash Abeyratne	Sri Satya Ravi	Timothy Gatts
Vishnu Padmanaban		

"Science cannot solve the ultimate mystery of nature. And that is because, in the last analysis, we ourselves are a part of the mystery that we are trying to solve."

Max Planck, 1932

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Chapter 1

Introduction

Epidemiological studies have associated particle matter emissions from diesel combustion with adverse health effects and a possible threat to the environment (*Dockery et al.*, 1993; *Pope III et al.*, 1995; *Englert*, 2004; *Pope III and Dockery*, 2006; *Chow et al.*, 2006; *Pope III*, 2007) which recently culminated in the International Agency for Research on Cancer (IARC), as part of the World Health Organization (WHO), to classify diesel exhaust fumes as *carcinogenic to humans* due to a substantial body of evidence that linked exposure to diesel exhaust with elevated risk for lung cancer (*World Health Organization, International Agency for Research on Cancer*, 2012). As a direct result, regulating agencies within the United States, the European Union (EU) and Japan imposed stringent particle matter emissions limits, defined on a mass basis, on compression ignition (CI) engines that can, at the currently known level of technology, only be met by means of outfitting CI engines with diesel particulate filters (DPFs). Additionally, with nano-sized particles being of special concern, the European Union (EU) implemented particle number (PN) emissions limits, for CI engines powered light-duty vehicles (LDVs) and passenger cars in 2013 (*EU 692/2008*, 2008), and heavy-duty on-road vehicles and busses in 2014 (*EU 582/2011*, 2011)¹. As of 2015, similar type particle number regulations are under intense discussion by agencies in the United States (i.e. U.S. EPA, California ARB), however no specific road-map towards a number based limit has been presented yet.

Streamlined with the introduction of PN limits, the European Union adopted a new methodology aimed at standardizing the measure-

¹LDV Euro 5/6: 6.0×10^{11} [#/km] over NEDC; HD Euro VI: 6.0×10^{11} [#/kWh] over WHTC (transient) and 8.0×10^{11} [#/kWh] over WHSC (steady-state).

ment of total particle number concentrations by only counting non-volatile particles having a diameter between 23nm and 2.5 μ m (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015). The sample conditioning method employs thermal treatment of particles in order to reduce the volatile fraction, thus reducing measurement artifacts and variability. This method has been previously developed under the Particle Measurement Programme (PMP) of the United Nations Economic Commissions for Europe, *group of experts on pollution and energy* (UNECE-GRPE) (*UN ECE/GRPE/WP-1*, 2003; *Andersson et al.*, 2007a,b; *Giechaskiel et al.*, 2008a,b; *Andersson et al.*, 2010).

Diesel particle filters are currently the most effective way to comply with PM mass and number-based emissions regulations. Accurate knowledge of soot loading within the filter is imperative for the implementation of successful regeneration strategies that afford lower fuel consumption, hence, reduced CO₂ emissions (*Rose and Boger*, 2009), while maintaining high particle removal efficiencies. However, due to the absence of reliable in-line particle sensors, engine manufacturers currently apply empirical engine-out emissions models (*Rose and Boger*, 2009) in conjunction with physical filtration and soot oxidation models (*Konstandopoulos and Kostoglou*, 2010; *Mulone et al.*, 2011), that primarily rely on differential pressure measurements across the particulate filter, to estimate soot loading, monitor filtration efficiencies, and detect possible system failures. The semi-empirical nature of such models requires extensive calibration efforts, hence, driving upward the development costs. More importantly, the effective detection limits of currently employed differential pressure methods are expected to be inadequate for detecting DPF malfunctions with high fidelity at levels of upcoming and proposed future on-board diagnostics (OBD) PM regulation threshold values (*Ochs et al.*, 2010)². As a direct consequence, the European Union indefinitely postponed mandatory on-board diagnostic (OBD) threshold limits for particle numbers (*EU 459/2012*, 2012). However, the currently implemented threshold values are subject to a periodic review by the European Commission and if technical feasibility for on-line particle number measurements can be demonstrated, a subsequent introduction of particle number threshold limits is most likely.

The U.S. EPA was the first regulatory entity to introduce in-use emissions compliance requirements for heavy-duty vehicles as a direct consequence of the 1998 consent decree between the U.S. EPA, U.S. Department of Jus-

²U.S. OBD-II, 1.75 x certification limit (*CCR 13/1968*, 2007); EU Euro VI, 2.5 x certification limit by 2016 (*EU 2008/C 182/08*, 2008); both are particulate matter mass based metrics.

tice and seven settling heavy-duty diesel engine manufacturers for violating the clean air act (US Department of Justice, 1998; Environmental Protection Agency, 1999). The European Union will follow in 2017 with a *true*³ in-use emissions compliance program when the *real-driving emissions* (RDE) regulation will take effect for light-duty vehicles. Currently, there exist only four measurement equipment manufacturers that are offering *commercially* available portable emissions measurement systems which are designed to measure particle matter mass emissions following U.S. EPA and EU regulations (i.e. referred to as PM-PEMS). Under the auspices of U.S. EPA's Measurement Allowance Program Khalek (2010) performed a comprehensive assessment of PM-PEMS marketed by AVL Gmbh, Horiba[®] Ltd. and Sensors Inc. with regard to their measurement accuracy and repeatability. A similar test program was conducted in Europe with the European portable emissions measurement system evaluation program (Bonnell *et al.*, 2010; Mamakos *et al.*, 2011a,b), which evaluated all four PM-PEMS and reported that the instruments agreed to within $\pm 30\%$ of each other for particulate matter brake-specific mass emission levels in the range of approximately 5mg/kWh, and exhibited individual differences of up to 120% at lower levels. More recently, an analogous evaluation program has been started by the EU for PEMS systems aimed at measuring particle number concentrations (i.e. PN-PEMS) (Riccobono *et al.*, 2014b).

In summary, there currently exists no on-board diagnostic and only vaguely formulated in-use compliance (EU 595/2009, 2009) (i.e. in-service conformity) requirements for particle number emissions. Moreover, the upcoming European *real-driving emissions* (RDE) regulation, effective by 2017, does not yet specify any portable emissions measurement systems to be used for particle number quantification nor does it include finalized PN limits (EU G3/1515125/PE RDE/Draft, 2015). On the other hand, *commercially* available PM-PEMS systems for in-use PM emissions compliance testing are characterized by their complexity, increased footprint (i.e. size and weight) and cost associated with operation and purchase of the system.

³the EU has an *in-service conformity* requirement which, however, is based on taking selected vehicles out from their regular operation after accumulation of a given amount of driven kilometers, and quantify their emissions during chassis dynamometer testing using laboratory-grade instruments.

1.1 Problem Statement and Hypothesis

The ability to quantify particle mass and number concentrations within the exhaust stream of internal combustion engine equipped vehicles during in-use operation is of critical importance in order to continuously monitor and diagnose the particle matter removal efficiency of modern exhaust gas after-treatment systems. However, as the introduction highlighted there exists a discrepancy between current and upcoming emissions regulations and available technology, and thereby emphasizes the urgent need for reliable in-line exhaust particle sensors, capable of direct measurement of particulate matter emissions with sufficient accuracy and sensitivity, not only for application in the on-board diagnostic and after-treatment control environment, but moreover with regard to low-cost, reduced complexity, in-use compliance testing. Indeed, currently available PM-PEMS are still of considerable size making it cumbersome to install and place on test vehicles, especially with regard to light-duty testing applications.

There exists, therefore, a critical need to identify suitable sensors along with evaluation procedures and to develop an in-use compliance testing methodology that bridges the gap between vehicle certification procedures and real-world operation. This is essential to guarantee adherence to particle number emissions limits set forth by the regulatory agencies and protection of the population from hazardous emissions over the entire duration of the engine and after-treatment assembly's useful life. Moreover, a possible particle sensor should be capable of measuring or inferring particulate matter on both mass and number concentration basis. This would make it versatile enough to be employed concurrently for in-use compliance verification of a test vehicle towards PM mass and number limits.

This study uses a diffusion-charging type in-line particle sensor from Pegasor (Oy) Ltd. (Tampere, Finland) to develop and calibrate specific sensor response models that will link the sensor's raw signal to a reference aerosol mass and number concentration value in real-time. Furthermore, the study demonstrates the application of this particle sensor to particulate matter mass and number emissions quantification during on-road operation of heavy- and light-duty vehicles.

The *central hypothesis* of this study is that a sensor operating on the diffusion-charging principle of particles can be employed within the exhaust gas stream to accurately quantify particle number emissions for real-time DPF filtration efficiency evaluation and in-use compliance applications.

1.2 Objectives

The *global objective* of this study is to demonstrate the applicability of a low-cost diffusion-charging type sensor, specifically the *Pegasor Particle Sensor* (PPS), to establish a particle number and mass reference to an aerosol in real-time, and thus, being capable of quantifying particulate matter emissions during real-world vehicle operation. Diffusion-charging type sensors have shown to exhibit a response signal proportional to particle surface area, which can be directly related to either the zeroth moment (i.e. total particle number concentration) or third moment (i.e. particle mass concentration) of the particle size distribution through a *power law* relationship. This approach is based on the assumption that, i) for a given engine technology there exists a characteristic particle size distribution that does not significantly alter as a function of engine operating conditions, and ii) the size distribution can be described by two parameters, its count mean diameter and geometric standard deviation. Directed at achieving the global objective of this proposal, three *specific aims* have been investigated.

Specific aim 1: Providing a review and discussion of literature regarding currently available particle sensor technologies and their respective operating principles. Different measurement principles are likely to exhibit a variety of response signals towards changing physical and chemical properties of particles, and to offer technology specific strengths and disadvantages. A brief discussion of particle charging theory and various definitions of particle *surface area* will also be presented.

Specific aim 2: Soot generator experiments will be conducted and results analyzed to establish basic sensor response models and calibrate them against particle mass and number concentrations measured with established laboratory-grade instruments. Furthermore, the sensor response will be evaluated and compared to reference methods during engine dynamometer experiments under *controlled environment* conditions. The same experiments will serve for framing of an in-use NTE quantification methodology based on the calibrated sensor response.

Specific aim 3: The calibrated particle sensor will be installed on test vehicles operated on a chassis dynamometer to assess its applicability for particulate matter measurement under *semi-controlled environment* conditions. Chassis dynamometer testing has the advantage of correlating the sensor response to reference instruments while operating the test vehicle over a variety of duty cycles, thus, exposing the sen-

sor to more *real-world like* emissions rates. Specific aim three will also present a discussion of real-time after-treatment filtration efficiency by virtue of measuring PM emission rates simultaneously up- and downstream the after-treatment system with two sensors. Finally, on-road testing results will be discussed to demonstrate sensor performance during real-world vehicle operation, exposing the sensor to harsh environments and vibrations.

Chapter 2

Review of Literature

The review of literature will commence with discussing physical and chemical properties of combustion derived particles in Section 2.1 on the following page before highlighting health effects attributed to these anthropogenic particles in Section 2.2 on page 31. Having established the epidemiological evidence of possible adverse effects of combustion derived particles on the human health and environment, Section 2.3 on page 42 introduces the different regulatory frameworks that have been developed by legislative agencies in the United States and Europe aiming at controlling exposure to particulate matter and particle number emissions from internal combustion engines. Particle sample extraction, conditioning, and measurement methods will be discussed in Section 2.4 on page 57. This section specifically provides a detailed description of commercially available portable emissions measurement systems (*i.e. as of 2015*) for on-road and in-use compliance testing of particulate matter mass and number emissions.

Section 2.5 on page 82 will be the primary focal point of this literature review providing the reader with a comprehensive discussion of currently available particle sensor technologies (*i.e. as of April 2015*) and their respective operating principle. This section will also emphasize on the different particle measurement applications of sensors, including i) regulatory emissions testing; ii) after-treatment system *health* and particle removal efficiency monitoring and regeneration control; and iii) active combustion control. Finally, the underlying principles and theory of diffusion charging of particles and its application to infer particle number and mass concentrations from an aerosol sample stream will be highlighted in Section 2.6 on page 86.

2.1 Particle Characteristics and Composition

Aerosols are defined as a combination of suspended solid particles or liquid droplets in a gaseous media (Hinds, 1999; McMurry, 2000a) such as the ambient air or in relation to combustion engines, the exhaust gas stream. They can be described as a *multiphase system* and are formed through i) condensation of gases into particles; ii) disintegration of liquids and solids; iii) break-up of agglomerated particles; and iv) resuspension of deposited particles (Eastwood, 2008). According to Hinds (1999) a wide collection of phenomena such as cloud, dust, fume, haze, mist and fog, smog, smoke, spray and bio-aerosol are being traditionally included in the umbrella expression *aerosol* that can range from nanometer sized particles (i.e. 0.001 to 0.01 μm) to the continuum region ($>2\mu\text{m}$). The size of particles is of specific importance as it is a key determinant of physical phenomena in conjunction with health aspects (i.e. respiratory-tract deposition) as well as atmospheric processes (i.e. visibility reduction, cloud formation, solar forcing, and atmospheric photochemistry) (McMurry *et al.*, 2004). Furthermore, atmospheric aerosols can be broadly classified into i) natural background aerosols comprising *biological*, *biogenic*, *oceanic*, and *geogenic* aerosols, and ii) *anthropogenic* aerosols which originate from human related activity such as combustion or material disintegration (e.g. road and building construction) (Hinds, 1999; McMurry, 2000a; McMurry *et al.*, 2004). It is estimated that the anthropogenic sources contribute between less than 10% and up to 50% of the global particulate emissions, and are unevenly distributed with highest concentrations in regions with increased population and industrial activity (Hinds, 1999). A large fraction of atmospheric aerosols are formed as *secondary* aerosols from gaseous emissions originating from both natural background as well as anthropogenic sources (Hinds, 1999; McMurry *et al.*, 2004).

Aerosols are highly dynamic matter, thus, their properties strongly depend on the local conditions they are subjected to or in which they are being observed (i.e. measured) (Eastwood, 2008). Sampling conditions including heating, cooling, dilution rate, and residence time, to only name a few, can noticeably alter the aerosols physical and morphological properties which could possibly give rise to increased measurement variability and more importantly, sampling artifacts (Hinds, 1999; Eastwood, 2008).

The discussion presented in this dissertation will be limited to anthropogenic aerosols derived from internal combustion engines and will only emphasize on primary aerosols and their transformation during dilution and sample conditioning processes within the exhaust stream transfer and

extraction lines, sampling systems and measurement instruments. For a more general discussion of aerosols as well as their impact on the environment the reader is referred to *Hinds* (1999) and *McMurry et al.* (2004).

2.1.1 Physical characteristics and particle size distributions

Internal combustion engine derived particulate matter is a complex mixture of solid or *insoluble* fraction, *soluble* organic matter, sulfur compounds, water and other species (*Kittelson*, 1998; *Burtscher*, 2005). Even though particulate matter *mass* has traditionally been the primary parameter to describe PM emissions from combustion engines, and is to date still the main metric upon which PM emissions limits as well as ambient air quality standards are defined worldwide (*CFR 40/86/A*, 2008; *EU 2008/50/EC*, 2008; *CFR 40/50*, 2011; *CARB*, 2012). However, since particulate matter properties such as chemical composition, solvability, toxicity and respiratory-tract-penetrability strongly depend on the size of particles, their size spectrum and respective number concentrations become parameter of utmost importance to properly assign environmental and health impacts to a given portion of PM emissions, and subsequently allowing to frame regulatory requirements and respective abatement strategies. Indeed, based on such considerations and the notion that particulate mass will inevitably be reduced to *near-zero* levels when limiting particle number concentrations, the European Union introduced regulatory limits for solid particle number (SPN) emissions for light- (*EU 692/2008*, 2008) and heavy-duty (*EU 582/2011*, 2011) vehicles and engines, respectively.

Combustion engine derived particles are frequently described based on their *aerodynamic diameter* (d_a) (*Kittelson*, 1998; *Mayer*, 2005; *Majewski and Khair*, 2006) with the particle aerodynamic diameter being defined as the diameter of a perfectly spherical particle with unit density (i.e. 1g/cm^3) having the same settling velocity and same properties with respect to impaction in air as the measured particle (*Hinds*, 1999; *Mayer*, 2005). Aerodynamic diameter has become the key property to characterize and quantify phenomena such as filtration and respiratory-tract particle penetration and deposition (*Hinds*, 1999). A second metric traditionally used to describe the motion of arbitrarily shaped particle's in a gas is the *mobility diameter* or Stokes diameter (d_s) (*Hinds*, 1999; *Mayer*, 2005). The *mobility diameter* is defined as a sphere which exhibits the same mobility as the particle of interest, where mobility (b) is directly related to the diffusion constant (D) by the Stokes-Einstein relationship given by Equation 2.1, with k and T being the Boltzmann's constant and gas temperature, respectively. Therefore, both *mobility* and *aerodynamic*

2.1. Particle Characteristics and Composition

diameter are defined based on aerodynamic properties of the particles rather than their geometric properties. With diffusion being a more dominant phenomena acting on particles in the nanometer size range, *mobility diameter* is a more characterizing metric for particles below $\sim 200\text{nm}$, whereas the *aerodynamic diameter* would be a more adequate metric to describe the motion of larger particles that are affected by phenomena such as interception, impaction and sedimentation (Mayer, 2005).

$$D = b \cdot kT \quad (2.1)$$

Whitby and Cantrell (Whitby and Cantrell, 1976) were reportedly (Kittelson and Kraft, 2014) the first researchers observing typical combustion engine derived particles to fall into three distinct particle size modes that can be well described by fitting multi *log-normal* (i.e. Gaussian) distributions to the data. The fitting function can be mathematically expressed through Equation 2.2 with d_p being the diameter of a given aerosol particle (Hinds, 1999). A series of three parameters characterize the *log-normal* distribution for each mode and are altered in the process of fitting Equation 2.2 to the experimental particle size distribution data. The parameters include the mode number concentration N_i , the geometric standard deviation $\sigma_{g,i}$, and the geometric mean particle diameter $\bar{d}_{g,i}$ with i referring to the respective mode and n being the total number of *log-normal* modes to be fitted. Since the distribution becomes symmetrical on a logarithmic scale, the geometric mean diameter is equal to the median and thus, for *log-normal* particle count distributions, count median diameter (CMD) and geometric mean diameter can be used interchangeably (i.e. $d_{g,i} = \text{CMD}_i$) (Hinds, 1999).

$$f(d_p, \bar{d}_{g,i}, N_i, \sigma_{g,i}) = \sum_{i=1}^n \frac{N_i}{\sqrt{2\pi} \log \sigma_{g,i}} \cdot \exp \left[-\frac{[\log d_p - \log \bar{d}_{g,i}]^2}{2 (\log \sigma_{g,i})^2} \right] \quad (2.2)$$

Figure 2.1 displays a typical engine exhaust particle size distribution as first introduced by Kittelson (1998), comprising the three characteristic particle size modes termed; *nucleation mode*, *accumulation mode*, and *coarse mode*. The various graphs are representative of the different moments of particles, namely the zeroth moment or number weighting (*red*), the first moment or surface weighing assuming perfectly spherical particles, and third moment or mass weighting calculated based on the assumption of spheric particles

2.1. Particle Characteristics and Composition

Figure 2.1: Typical engine exhaust particle size distribution with number surface and mass weighting assuming spherical particles and unit density (i.e. $\rho = 1 \text{ g/cm}^3$) (adapted from Kittelson (1998)) along with lung-deposited surface area (LDSA) assuming the deposition fraction for the alveolar region of the lung (i.e. using ICRP model (James et al., 1991; ICRP, 1994)).

with unit density (i.e. $\rho=1\text{g/cm}^3$). The size range and general particle properties of the three different modes are broadly identified following literature by Whitby and Cantrell (1976); Kittelson (1998); Burtscher (2005). It has to be mentioned that the specified size ranges limiting the three modes can vary depending on source (i.e. literature), however, the hereinafter presented particle size range boundaries are the ones widely accepted (or applied) by researchers and legislators.

Nucleation mode: The nucleation mode was initially defined by Kittelson (1998) to comprise particles of diameters below 50nm ($d_p < 50\text{nm}$). Based on sufficient data collected from internal combustion engines this range was later redefined to include 3-30nm diameter particles only (Kittelson et al., 2002; Burtscher, 2005; Swanson et al., 2010). The lower size boundary of 3nm was primarily driven by the lower detection limits of available particle sizing and counting instruments. Newer instruments with lower detection limits are becoming available as of 2015, including a particle magnifier by Airmodus Oy (particle size magnifier, Airmodus Oy, model A10, Finland) capable of resolving particle sizes down to diameters of $\sim 1\text{nm}$ (Vanhanen et al., 2011). Nucleation mode particles are primarily formed during exhaust di-

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lution and cooling mainly from semi-volatile and volatile organic material (i.e. hydrocarbons) and sulfur compounds (i.e. sulfates, sulfuric acid), but also from traces of ash and elemental carbon (Kittelson, 1998; Kittelson *et al.*, 2006). The nucleation mode usually contains most of the particles in terms of number concentration (>90%), however, only little particle mass (1-20%) (Kittelson, 1998). Nucleation mode particles are short lived (i.e. lifetime on the order of minutes) and are effectively removed by coagulation and diffusion.

The nucleation mode is very sensitive to sampling methods and conditions with strong influencing parameters including, gas temperature, relative humidity and dilution rates and ratios (Kittelson *et al.*, 2002; Giechaskiel *et al.*, 2014). Lower volatility compounds can possibly undergo gas-to-particle conversion during dilution and cooling processes (Swanson *et al.*, 2010). Furthermore, the introduction of particulate filter technologies intensified the probability of nucleation mode particle formation since with the removal of solid accumulation mode particles, available adsorption sites for volatile and semi-volatile material got drastically reduced, whereof, the nucleation of these compounds that become supersaturated during dilution is more likely. This highly dynamic behavior of the nucleation mode and strong dependency on sample conditioning procedures makes it very daunting to introduce a universal definition for this size mode, especially with regard to possible introduction of regulatory limits and sampling procedures. This will become more evident in later discussions in this chapter. Giechaskiel *et al.* (2014) for example defines particles to be *non-volatile* or *solid* if they do not evaporate up to 350°C, (semi-volatile) if they evaporate in the range of 100-350°C, and *volatile* if they completely evaporate already below 100°C. However, the authors acknowledge that this is not necessarily a universal definition even though it laid the foundation for the European particle measurement programme (PMP) protocol (UN ECE/TRANS/505/Rev.7/Add.48, 2015) which became the regulatory requirement for quantifying particle number emissions (EU 582/2011, 2011; EU 692/2008, 2008).

A multitude of studies, however, has found solid particles in the exhaust gas stream that fall into the nucleation mode from both diesel and alternative fuel (i.e. natural gas) powered engines. A study by Thiruvengadarn *et al.* (2014) found a dominant 10nm particle size mode from natural gas fueled engines installed on transit buses. Based on analysis of the elemental composition of particulate matter sampled on filter media it was concluded that these nano-sized particles originate from lubrication oil consumption and primarily comprise oil additive species such as Calcium, Magnesium, Zinc,

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Sulfur and Phosphorus. Studies conducted with diesel oxidation catalyst and catalyzed diesel particulate filter equipped engines observed significant amounts of solid nano-sized particles appearing in the exhaust gas as soon as the after-treatment system reached a certain threshold temperature in the range of 340-380°C (Khalek *et al.*, 1998; Thiruvengadam *et al.*, 2012; Vaaraslahti *et al.*, 2004, 2005; Herner *et al.*, 2013). These temperature levels were obtained during constant high load operation of the engine. Vaaraslahti *et al.* (2004) postulated the origin of these nucleation mode particles to be sulfur (SO_2) oxidation to SO_3 over the DOC and catalyzed DPF, and subsequently forming sulfate particles (SO_4^{2-}) by reaction with water in the exhaust stream. The experiments were conducted with diesel fuel containing only 2ppm sulfur and thus, the authors concluded that due to the significantly enhanced SO_3 formation by the catalyzed after-treatment components, small amounts of fuel sulfur or sulfur originating from lubrication oil that enters the combustion chamber, is sufficient enough to form large amounts of nucleation mode particles during high load (i.e. high exhaust gas temperatures) operating conditions (Vaaraslahti *et al.*, 2004). In a follow up study, Vaaraslahti *et al.* (2005) discussed the possibility of sulfur to be stored in the particulate filter in form of sulfated ash or adsorbed on the catalyst washcoat as sulfur oxides or metal sulfates, which could then be oxidized to SO_3 and released during high load operation events. This assumption was supported by observation of a reduction in nucleation mode particles if the engine was continuously operated at high load conditions after the initial appearance of the nucleation mode peak, indicating that stored sulfur deposits are possibly depleted over time (Vaaraslahti *et al.*, 2005). Similarly, Herner *et al.* (2013) attributes the change in nucleation mode peak concentrations during prolonged high load engine operation to storage and release phenomenon of sulfur in the after-treatment components. In contrast, sulfur oxidation in the atmosphere takes place on a timescale of *weeks* (Herner *et al.*, 2013).

Solid nucleation mode particles that were observed to remain *non-volatile* up to >400°C and exhibited a bipolar charge with a Boltzmann temperature of 580°C were measured at idle and low vehicle speeds (~30mph) by De Filippo and Maricq (2008) using a thermal denuder sampling setup. The authors suggested that these particles must have formed during the high-temperature combustion event based on the bipolar charge they have acquired, and further ruled out sulfates or hydrocarbons as primary constituents due to their non-volatile nature (De Filippo and Maricq, 2008). No final answer to the formation mechanism of these particles was given by the authors, however, it was concluded that these particles will be efficiently removed by the particu-

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late filter analogous to their carbonaceous counterparts. One possible explanation for the existence of these particles is given by *Khalek et al.* (1998) who suggested that solid nucleation mode particles could possibly be formed by volatilization of lubrication oil metals during the high-temperature combustion event and subsequently nucleate during the expansion stroke and associated cooling process. Additionally, nucleation of these particles is favored by low engine-out soot emissions that would otherwise act as adsorption or condensation sites for the volatilized metal particles (*Khalek et al.*, 1998), thus, possibly explaining why *De Filippo and Maricq* (2008) observed solid nucleation mode particles only during idle and low speed (i.e. low engine load) operation.

Interestingly, *Johnson et al.* (2009) observed a significant fraction of sub-23nm particles downstream a particulate filter equipped engine even though measurements were performed using a volatile particle remover as outlined in the PMP protocol (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015). This indicates the presence of solid nucleation mode particles downstream a filter which is in stark contrast to filtration theory. A study by *Konstandopoulos et al.* (2015) also observed $\sim 10\text{nm}$ solid particles downstream a wall-flow particulate filter and postulated the theory of *binary random fragmentation* of accumulation mode particles that fall into the size range of filter deficiency (i.e. referred to as *Greenfield gap*, $\sim 100\text{-}200\text{nm}$, *Liu et al.* (2003)) and thus, escape filtration (i.e. intersection between diffusional and interception/impaction filtration mechanisms).

Accumulation mode: The accumulation mode was initially defined by *Kittelson* (1998) to include particles of size $50\text{-}500\text{nm}$ which was later altered in accordance with the nucleation mode boundaries to comprise particles between $30\text{-}500\text{nm}$ (*Kittelson et al.*, 2002; *Swanson et al.*, 2010). Contrary to the nucleation mode, the accumulation mode contains the majority of the particulate mass, however, only small fraction of the total particle number concentration. This mode comprises predominantly carbonaceous agglomerates and associated adsorbed or condensed materials including hydrocarbons, sulfuric acid vapors, and volatilized lubrication oil and engine wear metals (*Kittelson*, 1998; *Kittelson et al.*, 2002). Due to their solid nature, particles in the accumulation mode are stable and are only marginally affected by sampling and dilution processes besides the possibility of re-volatilization of adsorbed material. Furthermore, particles falling into the size range of the accumulation mode can be efficiently reduced by particulate filters.

Coarse mode: The coarse mode comprises particles larger than 500nm and contains ~5-20% of the total particulate mass (Kittelson, 1998). Particles in this size mode are not directly generated by the combustion event but are formed by re-entrainment of particulate material that was previously deposited on walls of the engine cylinder, exhaust system, exhaust transfer lines, and exhaust sampling systems (i.e. CVS dilution tunnel, partial-flow sampling system, etc.) (Kittelson, 1998; Burtscher, 2005; Majewski and Khair, 2006). An other source of coarse mode particles are crankcase fumes that are re-routed into the exhaust system (Swanson *et al.*, 2010). With re-entrainment phenomena being a stochastic process, the coarse mode is not very reproducible and largely depends on how much material has been deposited earlier (i.e. history effects) and random vibrations that might cause deposited material to break loose. To suppress the variability in measurements, and also due to the fact that coarse mode particles are not truly representative of particulate emissions rates at a given instance in time, regulatory sampling procedures (CFR 40/1066, 2015; EU 582/2011, 2011; EU 692/2008, 2008) prescribe the use of a 2.5 μ m cut-point cyclic separators to largely remove coarse mode particles.

Ultrafine Particle Definition

Figure 2.1 also displays the traditionally defined particle size bins used for ambient air quality assessments and health studies, namely, PM₁₀ comprising particles with a diameter smaller than 10 μ m ($D_p < 10\mu\text{m}$), fine particles or PM_{2.5} ($D_p < 2.5\mu\text{m}$), and ultrafine particles (UFP) or PM_{0.1} ($D_p < 0.1\mu\text{m}$). Indeed, ambient air quality standards are currently (i.e. as of 2015) defined in terms of PM₁₀ and PM_{2.5} with limits given in terms of mass per volume, averaged over a given time (CFR 40/50, 2011; EU 2008/50/EC, 2008). For example, the national ambient air quality standards (NAAQS) set forth by the United States Environmental Protection Agency (U.S. EPA) (CFR 40/50, 2011) limits PM_{2.5} to 35 $\mu\text{g}/\text{m}^3$ averaged over a 24-hr time interval. However, studies have suggested that PM_{2.5} might not be the best indicator for health effects and that defining ambient air quality limits based on an ultrafine particle metric might be more appropriate. In order to address such questions, the U.S. EPA invited researchers and scientists to a publicly open *Ultrafine Particles Workshop* at U.S. EPA's research facility at Research Triangle Park, NC (February 11th-13th, 2015).

Kittelson (2015) suggested that the boundaries for the ultrafine particle definition should be more related to the actual particle size modes (e.g. UFP are $D_p < 500\text{nm}$). Defining ultrafine particles as $D_p < 500\text{nm}$ would include

both nucleation and accumulation mode and more importantly encompass the *lung deposited surface area* (LDSA) or *active surface*. Kittelson (2015) further proposed that UFP defined in such a way would likely be highly correlated with lung deposited surface area, and thus, provide an alternative metric for assessing health impacts of particulate emissions. An example LDSA distribution is shown in Figure 2.1 (green, dashed line) which is calculated as the product of surface weighted particle size distribution and theoretical lung deposition fraction for the alveolar region of the respiratory tract. A more in-depth discussion of the *lung deposited surface area* will be provided in Chapter 2.1. Kleeman and Sioutas (2015) pointed out that ultrafine particle mass, surface area, and number concentration are all viable metrics with individual advantages and weaknesses. However, the authors indicate that UFP number concentration might not be the most adequate metric as ultrafine particle mass, instead of number, appears to correlate better with particle surface area (Toshihiro *et al.*, 2013). This is of special interest as the original health hypothesis by Seaton *et al.* (1995), and various studies that followed, were based on particle surface area as the primary characterizing metric for health effects (Kleeman and Sioutas, 2015).

Particle surface properties

Particle surface area has been discussed in literature as an alternative or complementing particle emissions characterization metric (Swanson *et al.*, 2010; Burtscher *et al.*, 2001; Fissan *et al.*, 2007; Ntziachristos *et al.*, 2007; Kittelson, 2015; Reche *et al.*, 2015), especially, in light of published research that suggests that adverse health effects caused by diesel particulate matter are strongly associated with particle surface area (Seaton *et al.*, 1995; Oberdörster, 2001; Brown *et al.*, 2001; Oberdörster *et al.*, 2005; Stoeger *et al.*, 2006; HEI, 2013). Oberdörster (2001) for example, suggested that surface properties appear to play an important role with regard to ultrafine particle toxicity. Ultrafine particles exhibit a high *surface-to-mass* ratio due to their large concentrations levels and small diameters. As aforementioned, however, particulate matter emitted by internal combustion engines is a complex and heterogeneous mixture of various species that can be volatile, semi-volatile or solid in nature depending on the conditions they are sampled in. Moreover, particles can range from nearly spherical shaped *spherules* (i.e. primary particles) to complicated agglomerates (i.e. agglomeration of primary particles) and thus, making it difficult to measure or even conclusively define particle surface area (Swanson *et al.*, 2010; Ntziachristos *et al.*, 2007). Furthermore, Ntziachristos *et al.* (2007) indicates that the surface area measurement is strongly dependent on

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the instrument chosen as they respond differently to the variable chemical characteristics and morphology of the particles.

Figure 2.2(left) shows a transmission electron microscope (TEM) picture of a soot agglomerate exhibiting a *grape-like* structure composed of a multitude of near-spherical primary particles (i.e. spherules) (Park *et al.*, 2004). The TEM analysis provides projected two-dimensional properties of the agglomerate which subsequently allows to infer the actual structural properties of the agglomerate. One possible way to characterize agglomerate particles is through *fractal analysis* (Park *et al.*, 2004; Lee and Zhu, 2005), with the fractal dimension (D_f) being a characterizing parameter of a given type of particles.

Figure 2.2: (left) TEM picture taken from Park *et al.* (2004) showing an agglomerate particle with parameters measured from the projected image; A_p projected area of primary particle, A_a , L , and W are projected area, maximum projected length, and width of the agglomerate; (right) schematic of an aggregate particle consisting of near-spherical primary particles taken from Lee and Zhu (2005); R_g radius of gyration, d_p diameter of primary particle.

Equation 2.3 (in Park *et al.* (2004), referenced from Mandelbrot (1982)) allows to calculate the number of primary particles (N) in an agglomerate as a function of the radius of gyration (R_g), which refers to the square of the distance from the center of each spherule to the geometric center of the agglomerate (Lee and Zhu, 2005), and the primary particle diameter (d_p); where k_g is a fractal prefactor and D_f the fractal dimension.

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Figure 2.3: Coastline paradox based on the example of Great Britain's coastline and discussed by *Mandelbrot* (1967).

$$N = k_g \left(\frac{2R_g}{d_p} \right)^{D_f} \quad (2.3)$$

It becomes obvious from inspection of Figure 2.2 that the definition of surface area strongly depends on the fractal dimension of an agglomerate and moreover, the resolution that is being selected for the analysis (or the resolution of the instrument being used). The problem of resolution becomes more clear when looking at the *coastline paradox* discussed by *Mandelbrot* (1967) which in a simplistic way shows how the measured circumference of Great Britain changes as a function of the chosen measurement resolution.

Multiple approaches at quantifying particle surface area of combustion derived particles have been investigated, and four of these methods are commonly used by the scientific community (*Burtscher, 2005; Mayer, 2005; Ntziachristos et al., 2007; Swanson et al., 2010*), including i) *Braunauer-Emmett-Teller* (BET) surface area; ii) *active surface* or *Fuchs* surface area; iii) *sphere-equivalent* surface area; and iv) *projected* surface area.

BET surface: The BET method is based on the *Braunauer-Emmett-Teller* adsorption isotherm (*Braunauer et al., 1938*) and determines the mass of non-reactive gas (e.g. N_2 or CO_2) in a monolayer that adsorb to the surface of the particles (*Burtscher, 2005; Mayer, 2005; Eastwood, 2008; Swanson et al., 2010*). The BET surface area is subsequently estimated from the surface area of the

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adsorbed monolayer of gas molecules. However, it has to be noted that the surface area estimated by this method depends on a range of factors, including the mean free path of the adsorbing gas molecules and how that relates to the pore size of the particles, possible kinetic or diffusional limitations to adsorption for the given material (e.g. soot), if the process is only partly reversible and gas molecules become trapped in the pore structure of the particles, and if the microstructure of the particles might experience distortion due to adsorption-induced stresses (*Eastwood, 2008*). *Maynard (2003)* and *Swanson et al. (2010)* point out that porosity might be an important influencing parameter, especially for diesel particulate matter (DPM) agglomerates as they comprise a chain like accumulation of spherules with unknown porosity, and thus making it difficult to determine if the BET surface is measuring sphere-equivalent surface area. However, *Swanson et al. (2010)* hypothesizes that since BET analysis of black carbon (BC) indicates a non-porous structure and thus, compares well with geometric surface area of black carbon, BET measurements of diesel particulate matter agglomerates should give a reasonable well estimate of their geometric surface area, based on the observation that BC and DPM agglomerates appear visibly similar.

The BET surface method is widely used for quantifying surface area in the fields of health and environmental science (*Swanson et al., 2010*). This is due to its advantage of including particle porosity in estimating the surface area which is important for mass transfer and directly governs the amount of material that could possibly condense or adsorb and thereby, influence health impacts. Indeed, *Mayer (2005)* for example, reported of evidence that BET surface correlates best with health effects of particles.

The BET method is not an online analysis and requires a relatively large amount of sample, collected on a filter media (*Maynard, 2003; Mayer, 2005; Burtscher, 2005; Swanson et al., 2010*). This causes the BET method to be costly and time intensive (*Burtscher, 2005*), especially when being used for analysis of particulate matter emitted from particulate filter equipped vehicles which exhibit *very* low (i.e. with regard to sample accumulation on the filter media) particulate matter mass rates and thus, would require extended engine operation to accumulate the required amount of mass for analysis. *Burtscher (2005)* reports that sample material on the order of 1gram is needed for analysis.

Active surface: The total *active surface* area was first termed by (*Siegmann and Siegmann, 2000*) as a fraction of the geometrical surface area of particles. It is a measure for the total collision cross-section of particles and is therefore,

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related to adsorption kinetics. This makes *active surface* especially valuable as a metric for mass transfer which governs phenomena such as adsorption of gas-phase species, gas-to-particle conversion, and catalytic reactions (Siegmann and Siegmann, 2000). Similarly, according to Bukowiecki *et al.* (2002) the *active surface* represents the portion of the total geometric aerosol surface area that is actively involved in the diffusion-charging process, when being measured by a diffusion-charging instrument. Most importantly, with particle surface area observed to strongly correlate with health effects, *active surface* area has become a parameter of great interest as the surface available for mass transfer between particles and human organs (i.e. through the respiratory tract) was found to induce a proportional response in diffusion-charging type instruments (Fissan *et al.*, 2007; Shin *et al.*, 2007; Wilson *et al.*, 2007). Moreover, miniaturized versions of such instruments (Marra *et al.*, 2010; Fierz *et al.*, 2014) can be employed to monitor workplace environments in real-time and calculate lung deposited surface area (see Section 2.2).

Two mechanisms for particle charging are distinguished, namely, *field charging* by unipolar ions in a strong electric field, and *diffusion charging* by random collision of unipolar ions with particles due to Brownian motion (Hinds, 1999). Field charging is the dominant mechanism for particles larger than $1.0\mu\text{m}$, whereas diffusion charging becomes the dominant mechanism for particles below $0.1\mu\text{m}$ (100nm), even in the presence of an electric field (Hinds, 1999). Diffusion charging does not require an external electrical field and the charging process is independent of particle material for a wide particle size range (Hinds, 1999). Furthermore, the charging rate of particles reduces as a function of the charge acquired by a particle as a field builds up that tends to repel additional ions that won't have sufficient velocity to overcome the repulsive force.

Alternatively to ion attachment, radioactive atoms can be used to be attached to particles via diffusion (Burtscher, 2005; Swanson *et al.*, 2011; Gini *et al.*, 2013). In this case, the *active surface* area is termed as *Fuchs surface* area, named after pioneering work done by Fuchs (1963). The two surface areas, however, are slightly different due to electrical forces such as image forces for particles with Knudsen number (Kn) much larger than unity ($Kn \gg 1$) and repulsion forces for particles in the continuum regime ($Kn < \sim 0.2$) (Ntziachristos *et al.*, 2007). Baltensperger *et al.*, (2001) reported that for particles smaller than 10nm, image forces become more dominant and thus, leading to material dependencies of the *active surface* area. Other than that, *active surface* becomes essentially independent of particle material for a wide particle size range as the diffusion-charging process is primarily governed by Brownian

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diffusion. Furthermore, there exists the tendency for ions to form clusters depending on the carrier gas humidity, which may lead to a change in their mean free path (Ntziachristos *et al.*, 2007). However, Ntziachristos *et al.* (2004) have shown that for polydisperse aerosols in the size range of 10-300nm there exist only minute differences between *active* and *Fuchs surface* area.

The *Fuchs surface* area was defined by Pandis *et al.* (1991) as a dimensionless quantity using experimentally obtained coagulation coefficients between lead atoms and aerosols used for the measurements with the epiphaniometer (Gäggeler *et al.*, 1989). Alternatively, Matter Engineering AG (Matter Engineering AG, 2001) defined the *Fuchs surface* area as a function of the free molecular ($A_{fuchs, fm}$), continuum ($A_{fuchs, cont}$), and transition regime ($A_{fuchs, tr}$) as show in Equations 2.4 through 2.6, where, D_p is the mobility equivalent diameter, λ the mean free path of the diffusing species in the carrier gas, and A , b , Q parameters for the Cunningham slip correction coefficient (Allen and Raabe, 1985).

$$A_{fuchs, fm} = \pi D_p^2 \quad (2.4)$$

$$A_{fuchs, cont} = 2\pi\lambda (A + Q) D_p \quad (2.5)$$

$$A_{fuchs, tr} = \frac{\pi (A + Q) D_p^2}{\frac{D_p}{2\lambda} + \left[A + Q \cdot \exp\left(\frac{-b \cdot D_p}{2\lambda}\right) \right]} \quad (2.6)$$

Instruments available to measure total *active* or *Fuchs surface* area include (Mayer, 2005; Burtscher, 2005; Gini *et al.*, 2013), *photoelectric aerosol sensors* (PAS) (Burtscher, 1992; Siegmann and Siegmann, 2000), *diffusion charging sensors* (DC) or *electrometers* (Ntziachristos *et al.*, 2004; Jung and Kittelson, 2005; Ntziachristos *et al.*, 2007; Fissan *et al.*, 2007; Shin *et al.*, 2007; Wilson *et al.*, 2007; Frank *et al.*, 2008; Marra *et al.*, 2010; Fierz *et al.*, 2008, 2009, 2011, 2014), and the *epiphaniometer* (Baltensperger *et al.*, 1988; Gäggeler *et al.*, 1989; Gini *et al.*, 2013).

In a *photoelectric aerosol sensor* (PAS) ultraviolet light is used to irradiate particles which causes photoelectrons to be emitted from the particle's surface, and thereby, positively charging them (Matter *et al.*, 1999; Ntziachristos *et al.*, 2007). The charge is subsequently measured with a sensitive electrometer upon collection of the particles on a filter. (Matter *et al.*, 1999) mentioned that photoelectric charging is strongly dependent on chemical surface properties of the particles. This unique feature has been used in studies to characterize the chemical composition, such as polyaromatic hydrocarbons (PAH), of the adsorbed semi-volatile material on particle surfaces.

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The epiphaniometer (Gäggeler *et al.*, 1989) estimates the *Fuchs surface* area as a function of radioactive decay from ^{211}Pb atoms (i.e. instable lead isotope) attached to the measured particles by diffusion. The surface area is subsequently determined by measuring the α -activity of the attached atoms after collecting the particles on a filter. The epiphaniometer has a low detection limit, capable of measuring particles in the 20-100nm size range. However, the half-life of the decaying isotopes is on the order of 30min, thus making the measurement method significantly too slow for real-time combustion engine particle emissions quantification (Burtscher, 2005). More recently, Gini *et al.* (2013) have demonstrated a *cascade epiphaniometer* allowing to measure the *Fuchs surface* area on a size resolved basis (i.e. surface area size distribution), and in real-time. The instrument was evaluated using artificial mono- and polydisperse aerosols and the direct measurement of the *Fuchs surface* area size distribution compared on average within 12% to the one calculated by the scanning mobility particle sizer (SMPSTM, TSI Inc.) spectrometer (Gini *et al.*, 2013).

A *diffusion charging sensor* uses unipolar (i.e. positively charged) ions that are produced by a corona discharge to be attached to the sample aerosol in a mixing chamber through diffusion (Burtscher, 2005; Swanson *et al.*, 2010). In the most general design, the charged particles are then collected on a filter acting as a Faraday cup. The resulting current flowing from the charged particles to ground is measured with a sensitive electrometer. Swanson *et al.* (2010) point out that the attachment rate of ions is proportional to the surface area in the free molecular range, whereas in the continuum regime the rate becomes proportional to the mobility diameter. The same distinct ranges are also noticeable from inspection of Equations 2.4 and 2.5, provided for the calculation of *Fuchs surface* area. In the transition regime on the other hand, the charging process becomes a function of the number concentration of ions (N_I), and the duration of time over which the charging occurs (Swanson *et al.*, 2010), yielding the characteristic $N_I - t$ -product. Ultimately, the charged fraction of particles depends on the $N_I - t$ -product, particle size, ion-particle combination coefficient, and is instrument specific, thus leading to slightly different primary responses (Pui *et al.*, 1988; Swanson *et al.*, 2010). The latter however, can be addressed by individual calibration of a given instrument. Intra and Tippayawong (2009) provides a comprehensive literature review of the current state and designs of unipolar chargers based on the corona discharge principle.

Albeit the fact that diffusion-chargers were observed to be largely independent of particle size over a wide size range, research by Jung and Kittelson

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(2005) showed that the number of elemental charges acquired by a single particle (using NaCl particles) is a function of particle size and follows a power-law relationship. Therefore, measurements could be effectively corrected if the particle size distribution is known. Ku (2010) compared the diffusion-charging based surface area for spherical particles, as measured with two different DCs, with the actual geometric surface area for particles ranging from 100-900nm and showed that the surface areas measured by the DCs were proportional to the mobility diameter raised to the power of 1.22 and 1.38, depending on the DC used. The authors concluded that the DC-based surface area was in reasonable agreement with the theoretical calculated *active surface* area to within $\sim 30\%$. In summary, diffusion-charging type technologies have previously been successfully used to characterize ambient aerosols (Fissan *et al.*, 2007; Ntziachristos *et al.*, 2007; Marra *et al.*, 2010; Fierz *et al.*, 2014) as well as internal combustion engine derived particulate matter (Ntziachristos *et al.*, 2004; Jung and Kittelson, 2005; Frank *et al.*, 2008).

Sphere-equivalent surface: The *sphere-equivalent surface* area is calculated from measured particle size and number distributions along with the assumption of the particles to be spherical (Burtscher, 2005). If for example an SMPSTM is utilized to determine the mobility diameter of particles, the resulting calculated surface area is called *mobility-sphere-equivalent surface* area. More precisely this would be the surface area of a spherical particle that has the same aerodynamic drag as the measured particles. The *sphere-equivalent surface* area is related to area available for momentum transfer. It has to be mentioned however, that this surface metric does not have a well defined physical meaning such as the BET and active surface areas (Mayer, 2005; Burtscher, 2005).

Projected area: The projected area is directly obtained from high-resolution transmission electron microscopy such as discussed by Lee and Zhu (2005); Park *et al.* (2004). Additional information regarding estimation of projected area and image processing can be found in Ganesh (2011).

Effective particle density

As previously mentioned, combustion derived particles are of complex structures and a mixture of soot and adsorbed volatile and semi-volatile matter. Particles are chain-like agglomerates and thus, the effective density (ρ_{eff}) becomes strongly dependent on morphology (i.e. structure) and fractal dimension of the individual particle. The primary particles comprise primarily

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soot with a density of $\sim 2\text{g/cm}^3$ (Park *et al.*, 2004), whereas the effective density of the agglomerates reduces as a function of increasing particle size (i.e. due to more void space and also adsorbed matter with lower density). Maricq and Xu (2004) report that for particles with diameters below 50nm, the effective density remains constant at $\sim 1.2\text{g/cm}^3$ and only depends weakly on the combustion source. However, between 50-300nm the effective density continuously falls to $\sim 0.3\text{g/cm}^3$, which Maricq and Xu (2004) conclude is well described by fractal theory. Their study assumed a diameter of the primary particles in the range of 10-25nm with a density of 2g/cm^3 , which was reported to be consistent with TEM-derived values.

McMurry *et al.* (2002) for example, described a method to define effective density, shown in Equation 2.7, based on the simultaneous tandem measurement of particle mobility diameter (d_m) and mass (m) using a differential mobility analyzer (DMA) in conjunction with a aerosol particle mass analyzer (APM) (Park *et al.*, 2003; Maricq and Xu, 2004; Barone *et al.*, 2011; Rissler *et al.*, 2013).

$$\rho_{eff}(d_m) = \frac{6m}{\pi d_m^3} \quad (2.7)$$

Previous studies have demonstrated that the particle mobility diameter can be related to the mass of an agglomerate (m_{gg}) by a power law function, with a pre-exponential factor (K) and a mass-mobility exponent (ϵ_m) (Park *et al.*, 2003; Maricq and Xu, 2004; Rissler *et al.*, 2013). Combining the function for agglomerate mass with Equation 2.7 allows to calculate the effective density according to Equation 2.8 (Rissler *et al.*, 2013), which is the particle mass normalized to the volume of an equivalent sphere with the same mobility diameter as the particle under investigation.

$$\rho_{eff}(d_m) = \frac{6K \cdot d_m^{\epsilon_m - 3}}{\pi} \quad (2.8)$$

Rissler *et al.* (2013) identified two parameters that considerably influence the effective density, namely, the primary particle size and the coating mass fraction. Figure 2.4 shows a comparison of effective density functions developed by different researchers for diesel combustion derived particles. Most effective density models assume a constant density of 1.0-1.2g/cm³ for particles in the nucleation mode range, whereas the density reduces with increasing particle diameter in the accumulation mode. It has to be noted

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that by default particle sizing instruments assume a nominal particle density of 1g/cm^3 over the entire measured particle size range. However, from Figure 2.4 it becomes clear that this might introduce an increasing error in mass estimation for particles larger than $\sim 50\text{nm}$. Finally, *Liu et al.* (2009, 2012); *Thiruvengadam* (2013); *Quiros* (2014) discuss particle mass estimation based on real-time measurements of particle size and number distributions in conjunction with effective particle density models as an alternative to the gravimetric, *off-line* approach.

Figure 2.4: (left) Comparison of effective density versus mobility diameter of diesel combustion particles from three different studies; figure taken from *Liu et al.* (2009), referring to *Maricq et al.* (2000); *Park et al.* (2003); *Maricq and Xu* (2004); (right) comparison of three diesel PM effective densities; solid line represents a medium fractal representation for *Park et al.* (2003) and *Maricq and Xu* (2004) datasets, and dashed lines show uncertainty bounds; figure taken from *Maricq and Xu* (2004), referring to *Virtanen et al.* (2002); *Park et al.* (2003).

2.1.2 Chemical composition of particles

The chemical footprint of total particulate matter (TPM) emitted by internal combustion engines is made up of the *solid* (or insoluble) fraction (SOL), the *soluble organic* fraction (SOF), and the sulfate particles including water (SO_4^{2-}) according to Equation 2.9 (*Kittelson*, 1998; *Burtscher*, 2005; *Majewski and Khair*, 2006). The insoluble fraction is primarily composed of solid carbon that is formed during combustion in locally fuel rich regions (*Kittelson*, 1998). During the later stages of the combustion event, however, much of the soot is oxidized with the residuals exiting the combustion chamber in form of soot agglomerates. The solid fraction further comprises small amounts of ash and metals (*Kittelson*, 1998; *Liati et al.*, 2013), derived mostly from com-

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bustion of lubricating oil that enters the combustion chamber, fuel additives (Jung *et al.*, 2005), and engine wear.

$$TPM = SOL + SOF + SO_4^{2-} \quad (2.9)$$

The soluble organic fraction is the chemically most complex and diverse portion of total particulate matter and comprises organic material derived from lubricating oil and fuel compounds that escaped the combustion process (Kittelson, 1998). Strictly speaking, the soluble organic fraction can be divided into SOF and volatile organic fraction (VOF) of which the first is determined by extraction or dissolution in an organic solvent and the latter by heating or volatilizing (Eastwood, 2008). However, in most cases, SOF and VOF are almost identical in their contribution. The soluble organic fraction can be further divided into three major groupings (Majewski and Khair, 2006; Eastwood, 2008), namely, i) *unburned hydrocarbons*, including alkanes, alkenes, and aromatics; ii) *oxygenated hydrocarbons*, comprising ketones, esters, ethers, and organic acids; and finally iii) *polycyclic aromatic hydrocarbons* (PAH), including nitro-PAHs. The fraction of SOF in total particulate matter can vary between 10-90% as a function of engine design, after-treatment system, and operating conditions, and is usually highest during low engine speed and load operation, whereas the opposite is observed for higher load operation (Kittelson, 1998). In the presence of abundant solid carbonaceous agglomerates, as is applicable for legacy engines without particulate matter after-treatment systems, the majority of SOF will condense or adsorb onto their surface. With the introduction of particulate filters, however, solid adsorption sites got effectively removed, leading the volatile fraction to nucleate and form nano-sized liquid particles.

The third major fraction of TPM comprises primarily hydrated sulphuric acid (H_2SO_4) and lower quantities of *water-soluble* sulfates (SO_4^{2-}), both originating from fuel and lubrication oil sulfur (Kittelson, 1998; Majewski and Khair, 2006; Eastwood, 2008). The amount of water contained in TPM is directly dependent on sulfate content as the predominant portion of water is bound in sulfuric acid (Eastwood, 2008). This makes it possible to calculate the amount of water for a given relative humidity knowing the quantity of sulfuric acid (e.g. at 50%RH and 25°C each gram of sulfuric acid is associated with 1.32grams of water). On the other hand, sulfates are formed via reaction of SO_3 with water. The majority of fuel and lubricating oil sulfur is oxidized to SO_2 during the combustion process with only small amounts to SO_3 (Kittelson, 1998). However, with the introduction of catalytically active

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Figure 2.5: Comparison of typical particulate matter composition between legacy, non-filter equipped, MY' 1998 engines, filter-equipped, MY' 2007 engines, and US-EPA 2010 emissions compliant filter-equipped diesel and three-way-catalyst equipped natural gas engines. **a)** data taken from *Kittelson* 1998, transient operation on engine test bench, OC including 25% unburnt oil and 7% unburnt fuel; **b), c)** data taken from *Khalek et al.* 2013, transient operation on engine test bench; **d)** data taken from *Gautam et al.* 2011, transient vehicle testing on chassis dynamometer.

after-treatment systems such as diesel oxidation catalysts and catalyzed particulate filters, the available SO_2 is oxidized to SO_3 over these components, and readily reacts with water contained in the exhaust stream to form solid sulfate particles, primarily in the nucleation mode size range (*Khalek et al.*, 1998; *Thiruvengadam et al.*, 2012; *Vaaraslahti et al.*, 2004, 2005).

Figure 2.5 provides a comprehensive overview of how typical particulate matter emissions composition from diesel engines evolved as a function of advancements in engine and after-treatment technology as well as reduction in regulatory emissions limits between 1998 and 2010 (*Kittelson*, 1998; *Khalek et al.*, 2013). In contrast, Figure 2.5 also includes particulate matter composition from a stoichiometric operating and three-way catalyst (TWC) equipped natural gas fueled engine, representative of model year 2010 technology (*Gautam et al.*, 2011; *Thiruvengadarn et al.*, 2014).

It can be clearly observed that total particulate matter mass emissions significantly reduced with the introduction of particulate filter after-treatment sys-

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tems in order to comply with U.S. EPA 2007 emissions limits (*CFR 40/86/A*, 2008) of 0.01g/bhp-hr. The definition of PM mass as per *CFR 40/1065* (2015) includes all material that is being collected on a 47mm filter media at $47\pm 5^{\circ}\text{C}$ when sampled within a specified range of dilution ratio and sample flow rate ¹.

2.1.3 Combustion derived particle formation mechanisms

There exist two types of particles that are originating from internal combustion engines (*Kittelson and Kraft*, 2014), specifically, *primary* and *secondary* particles. Primary particles are either i) formed in the engine itself (i.e. elemental carbon, lube oil and wear metals); ii) particles that form during exhaust dilution and cooling after release to the atmosphere (i.e. heavy, partially oxidized hydrocarbons from fuel and lubricating oil, sulfates from fuel or lubricating oil sulfur); and iii) mechanically generated particles (i.e. re-suspended soot, crankcase fumes). Formation of particles inside the engine happens on the order of milliseconds to seconds, whereas particles formed by physical phenomenas during release of the exhaust stream into the atmosphere take place on the order of seconds to minutes. Also, the latter is the dominant mechanism for nanoparticle formation.

Secondary particles on the other hand are primarily formed from gaseous emissions via photochemical reactions in the atmosphere. Oxides of nitrogen and volatile organic carbon are the main precursors to form organic aerosols, sulfates, nitrates, haze, $\text{PM}_{2.5}$, and O_3 . The time-scale for secondary particle formation is on the order of hours to days.

Formation of nanoparticles downstream a particulate filter

Konstandopoulos et al. (2015) investigated the origin of solid nanoparticle emissions in the $\sim 10\text{nm}$ size range downstream the DPF during regeneration events and the associated soot deposit burnout. Current DPF filtration theory is not capable of adequately explaining these *nanosized* particles. Using a CAST soot generator the authors experimentally demonstrated that larger aggregates that pass through the filter walls during regeneration are being oxidized by a precolative fragmentation mechanism that is acting on

¹requirements for gravimetric PM mass quantification of pre-2007 model year engines under *CFR 40/86/N* (2011) were slightly different than for model year 2007, and post-2007 engines under *CFR 40/1065* (2015); specifically, the filter face temperature was only bound by an upper limit of 52°C .

2.1. Particle Characteristics and Composition

Figure 2.6: Particle formation history from combustion chamber to near-road atmosphere. (Figure taken from (Kittelson *et al.*, 2006)).

the *necks* connecting the primary particles in the soot agglomerates (Konstandopoulos *et al.*, 2015). Oxidative fragmentation of soot agglomerates was described by Kostoglou and Konstandopoulos (2003) as surface oxidation of the small solid contacts (i.e. *necks*) that hold the primary particles together. Since the contact points are much smaller relative to the size of primary particles, fragmentation can take place before significant reduction in primary particle size occurs, and thus, result in two separate soot agglomerates of smaller size. This so called *binary random fragmentation* process (Kostoglou and Konstandopoulos, 2003) will continue to repeat itself leading to a large amount of nanosized particles. Subsequently, the more reactive components will oxidize, whereas the less reactive parts will be released as a multitude of nanoparticles in the $\sim 10 \text{ nm}$ size range (Konstandopoulos *et al.*, 2015).

2.1.4 Particulate matter emissions from latest technology engines

Figure 2.7 shows non-volatile particle number concentrations (i.e. with lower cut-point of 23 nm) sampled from different locations along the intake and combustion air path through engine and after-treatment system (Giechaskiel *et al.*, 2012b). It can be seen that the intake air filter reduced ambient air particles by about an order of magnitude, whereas particle number con-

2.1. Particle Characteristics and Composition

centrations after the combustion chamber increase by approximately four orders of magnitude to $\sim 7 \times 10^{13} \#/\text{kWh}$. The reduction of particles over the after-treatment system is a function of the particulate filter's state, with reduction efficiencies ranging from 95% immediately following a regeneration event (i.e. soot cake layer has been burned off (*Suresh et al.*, 2000; *Wirojsakunchai et al.*, 2007; *Yamada*, 2013)) to $\sim 99.9\%$ after the soot cake layer has been built up again on the filter walls (*Giechaskiel et al.*, 2012b).

Figure 2.7: Typical non-volatile ($>23\text{nm}$) particle number concentrations at different sampling locations between inlet and exhaust stack of a 10.5l engine; tested over WHTC; measurements with AVL particle counter (APC, AVL List GmbH, model 489). (Figure taken from *Giechaskiel et al.* (2012b)).

At tailpipe exit non-volatile particle number concentrations are shown to have dropped again to levels of the intake air (i.e. ambient air). *Littera* (2014), has demonstrated from exhaust plume dispersion experiments, conducted in a full-scale², non-recirculating environmental wind tunnel, particle number concentrations exiting the exhaust stack of an U.S. EPA 2010 emissions compliant heavy-duty tractor (i.e. equipped with DPF) to be below ambient background levels. Experiments were conducted at a location without industrial installations, and thus, levels of anthropogenic particulate matter in the background air was assumed to be negligible.

²sampling cross section is 16x16ft and has a length of 90ft; the wind tunnel is capable of accommodating a full-scale Class-8 tractor cabin.

2.2 Health Aspects and Impact of PM/PN

Epidemiological and toxicological studies have associated urban air quality and pollution and more specifically, particulate matter, with adverse health effects and a possible threat to the environment (Dockery *et al.*, 1993; Pope III *et al.*, 1995; Englert, 2004; Pope III and Dockery, 2006; Chow *et al.*, 2006; Pope III, 2007). A significant contribution to anthropogenic particulate matter emissions was identified to originate from diesel combustion processes. This recently culminated in the International Agency for Research on Cancer (IARC), as part of the World Health Organization (WHO), to classify diesel exhaust fumes *as carcinogenic to humans* due to a substantial body of evidence that linked exposure to diesel exhaust with elevated risk for lung cancer (World Health Organization, International Agency for Research on Cancer, 2012). A review of recent epidemiological evidence suggests that adverse health effects are dependent on both *exposure concentrations* as well as *length of exposure* (Pope III, 2007). Furthermore, long-term exposures indicate to have larger and more persistent cumulative effects as compared to short-term exposures.

The American Heart Association (AHA) provided in their updated scientific statement regarding particulate matter air pollution (Brook *et al.*, 2010) a comprehensive review (including 426 references) of new evidence that links exposure to PM with cardiovascular disease. The primary conclusions that were drawn from the vast amount of data included, i) that exposure to PM_{2.5} over the duration of few hours to weeks can trigger cardiovascular disease-related mortality and nonfatal events; ii) that longer-term exposure on the order of years increases the risk for cardiovascular mortality to an even greater extent than exposure over few days and reduces life expectancy within more highly exposed parts of the population by several months to a few years; iii) that reductions in PM levels are associated with decreases in cardiovascular mortality within a time frame as short as a few years; and iv) that many credible pathological mechanisms were elucidated that lend biological plausibility to these findings. In conclusion, the AHA expressed the opinion that the overall evidence is consistent with a *casual relationship between PM_{2.5} exposure and cardiovascular morbidity and mortality* (Brook *et al.*, 2010).

EPA's *Integrated Science Assessments* (ISA) (Hassett-Sipple, 2015) conclude that there is suggestive, however, limited evidence for cardiovascular and respiratory effects associated with short-term exposure to ultra fine particulate matter. For other health effects and for long-term exposure the currently

2.2. Health Aspects and Impact of PM/PN

available evidence is inadequate to infer a casual relationship with exposure to UFP. Also, the assessment identifies the need to further expand the understanding of which roles specific subportions of UFP and PM_{2.5} play with regard to health effects, and what type of metric would be best suited to identify and characterize emissions and impacts from UFP exposure. The assessment closes with the suggestion that there might be more than one *correct* metric needed to adequately describe and limit exposure to UFPs (Hassett-Sipple, 2015).

The *Advanced Collaborative Emission Study*³ (ACES) consisted of three phases, where *Phase 1* (Clark *et al.*, 2007; Khalek *et al.*, 2009, 2011) and *Phase 2* (Khalek *et al.*, 2013, 2015) comprised the characterization of emissions from four new HDDEs that met U.S. EPA 2007 PM standards, and three new HDDEs that were compliant with U.S. EPA 2010 NO_x standards (CFR 40/86/A, 2008), respectively (Costantini *et al.*, 2015). The engines were operated over two different test cycles (i.e FTP and 16-hour cycle) and both regulated and unregulated pollutants were measured (i.e. a total of ~700 species). Results from *Phases 1 and 2* indicated that all regulated emissions were lower for both engine types compared to their respective regulatory standards, and unregulated pollutants were found to be substantially lower compared to 2004 emissions levels. An increase in NO₂ emissions was observed from 2004 to 2007 model year engines due to the use of catalyzed particulate filters, however, was overall reduced by 94% for 2010 compliant engines (Khalek *et al.*, 2015; Costantini *et al.*, 2015). Khalek *et al.* (2015) concluded from *Phase 2* of the ACES study that *dramatic* reductions in regulated and unregulated emissions were observed, which have the potential to significantly reduce possible adverse health effects from diesel combustion related emissions.

Phase 3 of the ACES was split in two sub-parts, with *Phase 3A* (HEI, 2012) establishing the conditions and experimental procedures for animal exposure, and *Phase 3B* (HEI, 2015) designed to study the health effects in rats (i.e. Wistar Han strain) exposed to *new technology diesel exhaust*⁴ (NTDE) over the animal's lifetime (i.e. 28 and 30 months for males and females, respectively). In particular, three out of the four U.S. EPA 2007 emissions

³ACES was a multi-institutional research project guided by the Health Effects Institute (HEI) in cooperation with the Coordinating Research Council (CRC). Funding for the ACES study was provided by the U.S. government and the private sector including the major on-highway engine manufacturers.

⁴NTDE refers to exhaust from modern advanced engines and emissions control systems, whereas *traditional-technology diesel exhaust* (TDE) refers to exhaust from pre-2007 engine technology.

compliant heavy-duty engines were selected for the animal exposure studies as part of *Phase 3*. The overall hypothesis to be tested during *Phase 3B* was framed as follows (HEI, 2015; Costantini et al., 2015):

new technology diesel exhaust emissions will not cause an increase in tumor formation or substantial toxic health effects in rats and mice, although some biological effects may occur.

The study concluded based on results from *Phase 3* that lifetime exposure to NTDE did not induce tumors in the lungs or any other organs of the rats as compared to exposure to *traditional* diesel exhaust (HEI, 2015). Particulate matter mass rates from NTDE used in this study were varied from 0.3 $\mu\text{g}/\text{m}^3$ (i.e. low) to 12.3 $\mu\text{g}/\text{m}^3$ (i.e. high), whereas PM mass rates from *traditional* diesel exhaust are typically three orders of magnitude larger (i.e. 1 mg/m^3) (Costantini et al., 2015). Long-term exposure to the latter levels is positively associated with formation of lung tumors. Limited histological changes observed after NTDE exposure were consistent with exposure to oxidizing pollutant gases, in particular NO_2 . The study further concluded that NTDE exposure showed only few biological effects in the animals (HEI, 2015; Costantini et al., 2015).

From a summary of multiple studies Oberdörster (2001) concluded that ultrafine particles appear to have a greater inflammatory response than fine particles do per unit mass, and that surface properties are suggestive of playing an important role in UFP toxicity. It is further reported of studies showing that low doses of inhaled carbonaceous ultrafine particles can cause mild pulmonary inflammation in rodents. Oberdörster (2001) also mention that certain pre-conditions (e.g. age, sensitized lungs, etc.) of the respiratory tract can increase the susceptibility to effects of ultrafine particles. Seaton et al. (1995) explains that soluble particles will increase through adsorption of water while traveling through the airways, and upon making contact with water-repellent surface in the alveoli be removed by the lung's defense system. Similarly, insoluble particles of complex shape and high surface-to-volume, primarily comprising carbon, will be removed by the lung. However, Seaton et al. (1995) reports of evidence that $<100\text{nm}$ particles behave differently from larger ones, specifically, a non-toxic particle in the micrometer range could become toxic in the nanometer range. Based on the reviewed data from available epidemiological studies, the authors propose that acidic ultra-fine particles provoke alveolar inflammation that could ultimately induce attacks of acute respiratory illness in susceptible individuals (Seaton et al., 1995). Most importantly, Seaton et al. (1995) hypothesize

that *particle number concentrations and size rather than mass* accounts for the observed epidemiological relations.

A detailed review by *Schwarze et al.* (2006) focused on identifying the importance of different particle properties for PM-induced health effects and attempted to assess the consistency between epidemiological and experimental studies. The study highlighted on the fact that sufficient data for a comparison of effects from specific portions of PM is limited and moreover, suggested needed improvements in research designs, exposure assessments for epidemiological investigations, and comparability of experimental studies. Despite conflicting data with respect to PM size-fractions between experimental and epidemiological studies, *Schwarze et al.* (2006) suggests that possible effects of the coarse fraction (i.e. $PM_{10-2.5}$) should not be neglected. It was further concluded that experimental data indicate surface area to be an important metric, however, chemical composition might possibly play a greater role in describing the observed effects. Interestingly, there exists convincing consistency between experimental and epidemiological results with regard to metals, which appear to bear importance for development of both pulmonary and cardiovascular disease (*Schwarze et al.*, 2006). In the same direction, *Thiruvengadam* (2012) observed increased toxicity, based on DTT-bio-assay, as a function of metal emissions originating from lubrication oil combustion in a natural gas fueled engine. Finally, *Schwarze et al.* (2006) mentioned that soluble organic compounds appear to be associated with PM-induced allergy and cancer, however, acknowledge that data from epidemiological studies are insufficient for any conclusion.

Proietti et al. (2013) reviewed the evidence linking air pollution exposure during the prenatal phase to adverse health impacts during pregnancy. The authors list different birth outcomes that are associated with exposure to air pollution, including, higher infant mortality, lower birth weight (although it's acknowledged that the evidence is still controversial), impaired lung development, increased later respiratory morbidity, and early alterations in immune development. *Proietti et al.* (2013) reports on a study that investigated ~ 3.5 million births, including 6639 postneonatal deaths in the U.S. and showed evidence of infants exposed to the highest quartile of particulate matter pollution (i.e. $>34\mu g/m^3$ PM_{10} and $>18.7\mu g/m^3$ $PM_{2.5}$) experienced elevated odds especially for respiratory mortality compared with the lowers quartile. Studies have suggested possible mechanisms of how particles inhaled by the mother might impact the fetus (*Proietti et al.*, 2013), including, i) particle translocation across tissue barriers, or ii) particle penetration across cellular membranes. However, *Proietti et al.* (2013) acknowl-

edged that the exact pathways of how particles are transported beyond the lungs in humans and impact the fetus are still largely unclear and need further research. Furthermore, the study concluded that improved knowledge of toxico-dynamics of ultrafine particles may aid in identifying factors that could protect against air pollution in the future.

A large body of published research has suggests that adverse health effects caused by ultrafine particulate matter are strongly associated with particle surface area, with toxic effects observed to scale well with surface area in both *in-vitro* and *in-vivo* studies (Seaton *et al.*, 1995; Oberdörster, 2001; Brown *et al.*, 2001; Oberdörster *et al.*, 2005; Stoeger *et al.*, 2006; Waters *et al.*, 2009; Sager and Castranova, 2009; HEI, 2013). One of the first health hypothesis based on particle surface area was framed by Seaton *et al.* (1995). Brown *et al.* (2001) investigated the pro-inflammatory responses of different size polystyrene particles (i.e. 64, 202, and 535nm) in the animal model. The observations after instillation of the particles in a rat lung suggested that UFP composed of low-toxicity material, such as the selected polystyrene, have pro-inflammatory activity as a consequence of their large surface area. Research presented by Oberdörster (2001) suggested biological impacts of UFPs to best correlate with particle surface area, and that surface properties appear to play an important role with regard to ultrafine particle toxicity.

Using a macrophage cell model Waters *et al.* (2009) demonstrated that macrophage cytotoxicity induced by inflammatory protein secretion, after administering silica particles, scaled closely with the total particle surface area of the added silica over a wide particle diameter range (i.e. 7-500nm). Furthermore, the magnitude of changes in gene expression after addition of 10 and 500nm silica particles, measured via genome microarray analysis, correlated better with surface area than with either particle mass or number concentration (Waters *et al.*, 2009). In a study performed by Sager and Castranova (2009), rats were exposed by intratracheal instillation to various doses of ultrafine and fine carbon black particles, and inflammatory and cytotoxic potential of each particle type was subsequently assessed on both a mass and surface area dosage basis. The study concluded based on the observed results that particle surface area rather than total mass might be a more appropriate dose metric for pulmonary toxicity studies, especially for particle exhibiting low toxicity and solubility. Furthermore, a study (Thiruvengadam, 2012; Thiruvengadarn *et al.*, 2014) of exhaust particles originating from compressed natural gas powered transit busses indicated that toxicity, quantified based on the DTT-bio-assay, correlated best with particle surface area, as calculated from measurements using an engine exhaust particle sizer

spectrometer (EEPSTM, TSI Inc., model 3090). Finally, the Health Effects Institute (HEI, 2013) mentions in their summary report about health effects of UFPs that the high surface area per unit of mass of UFPs, a function of their vast numbers and small diameters, has been hypothesized to be an important characteristic that might predict greater toxicity of particles in that size range.

2.2.1 The ICRP lung deposition model

A comprehensive discussion of the history and development of different modeling approaches of particle deposition in the human respiratory tract (HRT) is provided by Ensor (2011). The study acknowledges that accurate modeling of respiratory deposition is challenging primarily due to the lung structure and aerodynamic characteristics in the lung airways being relatively complicated, but also due to individuality of the lung depending on person, age, and health. However, Ensor (2011) emphasizes that significant progress in deposition modeling has been made since the inception of the first mathematical model by Findeisen in 1935, termed *Findeisen's deposition model* (i.e. cited in Ensor (2011)). The model was a *series-type* model comprising nine parts that represented the individual penetration probability of different lung sections along the airways from trachea to alveolar sacs. The model considered inertial impaction, gravitational settling, Brownian diffusion, and interception as possible aerosol deposition mechanisms (Ensor, 2011). *Findeisen's deposition model* was subsequently modified in several steps to incorporate refinements in lung morphology, aerodynamic characteristics, and updated calculation methods for deposition efficiency. Finally, in 1960 the International Commission on Radiological Protection (ICRP) began publishing their first deposition model (*ICRP publication 2*) to assess penetration and retention of inhaled radioactive particles (ICRP (1959) cited in Ensor (2011)). The model was subsequently refined once in 1979 (*ICRP publication 30*) and the last time in 1994 (*ICRP publication 66*, ICRP (1994)). A series of other respiratory tract deposition models have been developed in the more recent past, including, *multiple-path deposition* and *continuous* models, however, for more detailed discussion of these models the reader is encouraged to consult the literature review by Ensor (2011) or Hinds (1999). The model employed hereafter is the third generation ICRP model (ICRP, 1994), described in more detail in the following.

The updated ICRP lung deposition model (James *et al.*, 1991; ICRP, 1994) has been designed to estimate deposition in each region of the respiratory

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Figure 2.8: **a)** Human respiratory tract (HRT) model; **b)** empirical representation of the inhalability of particles and their deposition in regions of the respiratory tract during inhalation by transport through a series of filters (ICRP, 1994). (Figure taken from *McCreddin et al.* 2013).

tract for which radionuclide retention and dose need to be assessed. The model is designed to be used in conjunction with the clearance and dosimetry models to provide defensible estimates of doses to radiosensitive tissues in the respiratory tract. Empirical and theoretical modeling methods were adopted in order to simulate the experimental data, and make prediction of regional deposition for a wide particle size range, from atomic dimensions (i.e. $\sim 0.0005\mu\text{m}$) to large environmental aerosols with an *activity median aerodynamic diameter* (AMAD) on the order of $100\mu\text{m}$ (*James et al.*, 1991; ICRP, 1994).

The human respiratory tract model represents each region of the respiratory tract as an equivalent particle filter that acts in series, with the deposition in each region being expressed as a function of the efficiency of the equivalent filter (η_f). The different regions of the respiratory tract considered in the model comprise the extrathoracic (η_{ET}), the tracheobronchial including the bronchial (η_{BB}) and bronchiolar (η_{bb}) sub-regions, and the alveolar-interstitial (η_{AI}) regions. Figure 2.8 depicts a schematic of the human respiratory tract on the left along with the respective *filter elements* considered in the HRT model on the right.

The deposition efficiency of each region is evaluated considering both particle deposition due to *aerodynamic* processes (η_{ae}) (i.e. impaction and gravita-

tional settling), and deposition by *thermodynamic* processes (η_{th}) (i.e. particle diffusion by Brownian motion). Both processes act competitively to remove particles, and are therefore modeled as a combined deposition efficiency for each region as given by Equation 2.10. The deposition due to gravitational settling and impaction is represented in terms of the particle aerodynamic diameter (d_a) in μm , whereas the thermodynamic particle motion is represented in terms of the particle diffusion coefficient, (D) in cm^2/s .

$$\eta(R) = \sqrt{\eta_{ae}^2 + \eta_{th}^2} \quad (2.10)$$

The *inhalability* (η_I), or efficiency with which particles in ambient air enter the nose or mouth is represented by Equation 2.11, where d_a is the aerodynamic diameter of the particle and U is the wind speed in m/s . This empirical expression is based on experimental data by Vincent *et al.* (1990) that describe the efficiency of the human head as a *blunt particle sampler* in moving air (Hinds, 1999). The second term in Equation 2.11 accounts for increased *inhalability* of larger size particles at higher wind speeds. In order to evaluate the intake of large particles in an indoor environment (i.e. wind speeds $< 4\text{m/s}$), James *et al.* (1991) proposed to set $U = 0$, which will yield a constant value of 50% for the *inhalability* of particles larger than $\sim 30\mu\text{m}$. Particle *inhalability* does not appear to be influenced by breathing rate or dimensions of the nose or mouth, thus, it is assumed that Equation 2.11 defines *inhalability* of particles for subjects of any age, and under all conditions (James *et al.*, 1991; ICRP, 1994).

$$\eta_I = 1 - 0.5 \cdot \left[1 - \frac{1}{1 + 7.6 \cdot 10^{-4} \cdot d_a^{2.8}} \right] + \left[1.0 \cdot 10^{-5} \cdot U^{2.75} \cdot e^{0.055 \cdot d_a} \right] \quad (2.11)$$

Hinds (1999) fitted a series of empirical functions to the ICRP model in order to predict the regional deposition fractions for mono-disperse spheres of standard density (i.e. $1\text{g}/\text{m}^3$) at standard conditions. The selected data used for fitting the functions included an average of three different exercise levels for both male and female subjects. Equations 2.12 through 2.14 represent the regional deposition fractions for head airways (η_{HA} , i.e. η_{ET} in ICRP model), tracheobronchial (η_{TB} , i.e. including η_{BB} and η_{bb}), and alveolar regions (η_{AL} , i.e. η_{AI} in ICRP model) as a function of particle diameter (d_p) in μm . Hinds (1999) reported the predicted deposition fractions, using the empirical functions, to be within ± 0.03 of the ICRP model for particles ranging between 0.001 and $100\mu\text{m}$.

$$\eta_{HA} = \dots$$

$$\eta_I \left[\frac{1}{1 + \exp(6.84 + 1.183 \ln(d_p))} + \frac{1}{1 + \exp(0.924 - 1.885 \ln(d_p))} \right] \quad (2.12)$$

$$\eta_{TB} = \dots$$

$$\left(\frac{0.00352}{d_p} \right) \left\{ \exp[-0.234(\ln(d_p) + 3.40)^2] + 63.9 \exp[-0.899(\ln(d_p) - 1.61)^2] \right\} \quad (2.13)$$

$$\eta_{AL} = \dots$$

$$\left(\frac{0.0155}{d_p} \right) \left\{ \exp[-0.416(\ln(d_p) + 2.84)^2] + 19.11 \exp[-0.482(\ln(d_p) - 1.362)^2] \right\} \quad (2.14)$$

The total deposition fraction (η_{total}) is the sum of the individual, regional deposition fractions and can be expressed by the empirical Equation 2.15 (Hinds, 1999). The *inhalable fraction* given by Equation 2.16 was derived from Equation 2.11 assuming still air (i.e. $U = 0$ for $U < 4\text{m/s}$) around the subject's head, and thus, dropping out the second term of the equation. Even though η_I does not explicitly appear in Equations 2.13 and 2.14, the data from the ICRP model used to fit the empirical functions to, included the effects of *inhalability* (Hinds, 1999).

$$\eta_{total} = \dots$$

$$\eta_I \left[0.0587 + \frac{0.911}{1 + \exp(4.77 + 1.485 \ln(d_p))} + \frac{0.943}{1 + \exp(0.508 - 2.58 \ln(d_p))} \right] \quad (2.15)$$

$$\eta_I = 1 - 0.5 \cdot \left[1 - \frac{1}{1 + 7.6 \cdot 10^{-4} \cdot d_p^{2.8}} \right] \quad (2.16)$$

Based on experimental data comparing particle size measurements as determined by electrical mobility analysis versus diffusion batteries, Sinclair *et al.* (1976) observed that the mobility diameter governing the particle charging behavior is in close agreement to the geometric diameter. Experiments with methylene blue showed the largest discrepancy of about 20%, however, results for most other types of particles were reported to be *much better* and

Figure 2.9: Theoretical human respiratory deposition model of standard density spheres during nasal breathing (*James et al.*, 1991; *ICRP*, 1994).

discrepancies were observed to lay within the experimental errors (*Sinclair et al.*, 1976). Therefore, *Sinclair et al.* (1976) suggested that mobility diameter (d_m) can be used interchangeably with aerodynamic (d_{ae}) diameter for ultra-fine particles, and thus, based on these findings *Marra et al.* (2010) concluded that d_m can be applied directly to estimate the deposition efficiency of UFPs in the HRT model.

Figure 2.9 depicts the predicted total and regional deposition fractions for particles between 0.001 and 10 μm based on the empirical equations provided by *Hinds* (1999). It can be noticed that the largest particles are being removed by settling and impaction in the head airways (blue line), which contributes the majority of total deposition for particles larger than 1 μm . Additionally, deposition of ultrafine particles with diameters less than 0.01 μm significantly increased in the head airways region, primarily due to their high diffusivity, especially in the nose. This causes the deposition of these small particles to drop off in the tracheobronchial (red line) and alveolar (green line) regions.

The deposition in any lower lying lung region is directly dependent on the size specific deposition of the preceding region. In the tracheobronchial region, impaction and settling are important for particles larger than 0.5 μm although it can be observed from Figure 2.9 that the overall deposition frac-

tion in this size range is quite small. This is primarily due to the fact that the majority of particles has already been removed in the head airways. Furthermore, ultrafine particles are quite effectively removed by deposition in the tracheobronchial region as well due to their fast Brownian motion. Deposition in the alveolar region is reduced by both preceding lung regions. However, any particles entering the alveolar region will have increased deposition efficiency independent of their size. Settling is the dominant phenomena trapping larger particles, whereas smaller particles are getting deposited via diffusion. The head airways and tracheobronchial region of the lung act as effective filters and are of importance in protecting the more susceptible alveolar region from harmful particles.

2.2.2 LDSA and diffusion-charging instruments

Quantification of the lung-deposited surface area (LDSA) requires measurement of the entire size spectrum of particles followed by subsequent summation of particles in each defined size bin and weighting according to the size specific lung-deposition probability given by the ICRP human respiratory tract model (*Marra et al.*, 2010; *Fierz et al.*, 2011, 2014; *Reche et al.*, 2015)). However, diffusion-charging type instruments have shown to exhibit a particle size dependent response, where the relationship between charge transferred to the particle (q) and its diameter can be well described by a power law function shown in Equation 2.17, with (x) being an exponent of ~ 1.1 , and (c) a constant. From Figure 2.9 it can be observed that for the lower lung sections comprising the alveolar region (i.e. green line), deposition fraction is approximately inversely proportional to particle diameter in the range of 20-300nm. Indeed, results by *Reche et al.* (2015) indicated that LDSA concentrations are primarily influenced by particles in the size range of 50-200nm. Thus, following the definition of lung-deposited surface area it becomes possible to estimate LDSA directly from the diffusion-charger instrument signal, as demonstrated in Equation 2.18 (*Kasper*, 2004; *Fierz et al.*, 2011, 2014).

$$q \cong c \cdot d_p^x \quad (2.17)$$

$$LDSA = S_p \cdot DF_{AL} \cong d_p^2 \cdot d_p^{-1} = d_p^1 \approx q \quad (2.18)$$

Using an Electrical Aerosol Detector (EAD, TSI Inc., model 3070A), *Fissan et al.* (2007) and *Wilson et al.* (2007) independently demonstrated good corre-

lations between the EAD signal and model predictions of the penetration of aerosol particles into the respiratory system (in *Frank et al. (2008)*). Likewise, *Shin et al. (2007)* found a linear relationship between the particle surface area of particles deposited in the human lung, in both trachea-bronchial as well as alveolar regions, and the electrometer current as measured by the Nanoparticle Surface Area Monitor (NSAM, TSI Inc., model 3550). The authors concluded that the NSAM is suited for quantifying the particle surface area deposited in the human lung in real-time and further noted that no significant dependency of the NSAM signal towards different particle materials and morphology has been observed (*Shin et al., 2007*). Both EAD and NSAM are diffusion-charging type instruments that comprise a corona charger, a mixing chamber where aerosol particles come in contact with free ions, thus acquiring their charge, and a subsequent measurement using a sensitive electrometer. *Reche et al. (2015)* used a NSAM instrument in conjunction with an SMPSTM (TSI Inc., model 3936) to quantify LDSA concentrations in the alveolar region, sampling from urban background air in Barcelona (Spain). Conclusions indicated that LDSA concentrations measured by the NSAM were comparable to calculations based on particle size and number distributions collected with the SMPSTM. Moreover, average LDSA concentrations in the alveolar region were observed to be within $37 \pm 26 \mu\text{m}^2/\text{cm}^3$ in the urban environment of Barcelona.

Marra et al. (2010) introduced a new miniature diffusion-charging type airborne nanoparticle monitor, termed *Aerasense NP*, capable of measuring particle surface area concentrations in real-time. The salient feature of the monitor is that it can directly output lung-deposited surface area concentrations for selected regions of the respiratory tract. A sensor for personal monitoring using a new particle detection technique, based on pulsed unipolar charging followed by non-contact measurement of the rate of change of the aerosol space charge in a Farady cage, was presented by *Fierz et al. (2014)*.

2.3 Regulatory Framework for Controlling PM/PN

With vehicle exhaust particles constituting a significant percentage of anthropogenically emitted particles, legislations are in place worldwide to enforce a decrease of particle emissions from vehicles. With the introduction of the clean air act (CAA) by the U.S. Congress in 1974, heavy-duty both compression and spark ignition engines are mandated to be certified for emissions compliance on a standard heavy-duty engine dynamometer while being operated over the federal test procedure (FTP) cycle (*CFR 40/1065, 2015*). Simi-

larly, light- and medium-duty vehicles (LDV and MDV) as well as passenger cars (PC) have to comply with mandated regulatory emissions limits while being operated over a transient test cycle (i.e. FTP-75) on a chassis dynamometer (CFR 40/1066, 2015). Engine dynamometer testing was selected for heavy-duty engines as they are traditionally built by an engine manufacturer and subsequently sold to vehicle manufacturers to be integrated in a broad range of applications and vocations, including, goods movement tractors, transit buses, refuse haulers, fire engines, and many more. Testing of such a wide variety of vehicles would not be feasible and thus, it was decided to certify heavy-duty engines and their associated after-treatment packages independently from the vehicle. On the other hand, passenger cars and light-duty vehicles and their propulsion systems are traditionally built by the same manufacturer and sold as a package, thus, these vehicles are certified as one unit. The European Union follows a similar strategy for certification of heavy-duty engines and light-duty vehicles (EU 692/2008, 2008; EU 582/2011, 2011).

Since the introduction of particulate matter mass emissions limits for heavy-duty engines in California in 1985 with the entire U.S. following in 1988 (see Table 2.1) and Europe in 1992 (see Table 2.2), legislations have been based on gravimetric quantification of PM deposited on a filter media after extraction from a diluted exhaust sample (Majewski and Khair, 2006; Giechaskiel *et al.*, 2014; Adachi and Nakamura, 2014). Till today, gravimetric based particulate matter mass quantification is the established technique for evaluating compliance of an engine/after-treatment package with regulatory emissions limits in the U.S. and Europe (CFR 40/1065, 2015; CFR 40/1066, 2015; CFR 40/86/N, 2011; EU 692/2008, 2008; EU 582/2011, 2011). However, with the introduction of the most stringent particulate matter mass emission limits in the U.S. in 2007 (i.e. 0.01g/bhp-hr) and the EU in 2013 (i.e. 0.01g/kWh $\approx$ 0.013g/bhp-hr) for heavy-duty engines, manufacturers equipped their engines with particulate filter after-treatment systems in order to comply with the emissions regulations. The resulting low PM mass concentrations in the exhaust stream significantly increased the signal-to-noise (S/N) ratio of the gravimetric PM mass quantification method using a filter paper. This ultimately led the traditional gravimetric approach to reach its detection limit (Andersson *et al.*, 2007b; Giechaskiel *et al.*, 2008a; Andersson *et al.*, 2010). Maricq *et al.* (2011) compared different measurement methods and encountered significant obstacles with accurately measuring PM mass at the LEV-III/Tier-3 level of 3mg/mi using the gravimetric method.

Aimed at addressing measurement uncertainty and improving the accuracy

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and moreover, repeatability of the gravimetric filter method, the Coordinating Research Council initiated the *E-66* study (Khalek, 2005, 2006, 2007, 2008) which resulted in a series of recommendations that were subsequently implemented to the regulatory prescribed measurement procedure and finalized in 2007 (i.e. CFR 40/1065 (2015)). A follow up study was conducted under the title *E-99* (Jung *et al.*, 2015) to assess the feasibility of the gravimetric method to be used in conjunction with the ultra-low particulate matter emissions limits of 3mg/mi for light-duty vehicles, introduced under the CARB LEV-III and U.S. EPA Tier-3 standards⁵ (CFR 40/86/S, 2014). Both studies investigated the influence of various parameters associated with sampling, conditioning, and filter media handling procedures in order to alleviate effects of sampling artifacts onto the gravimetric measurement method.

Coefficients of variation for the gravimetric method were reported by Khalek (2005) to be on the order of 50% and 6% for PM mass rates at a level equivalent to <10% of the U.S. EPA 2007 standard as well as at the standard, respectively. The study identified the adsorption of gaseous compounds onto the filter media as a dominant positive artifact that imparts additional mass to the filter (Khalek, 2008). In an earlier study, Chase *et al.* (2004) found that vapor artifacts (i.e. primarily due to hydrocarbon adsorption) represent a substantial fraction of the 2007 regulatory Tier-II standard of 10mg/mi for light-duty vehicles, on the order of 10-20% and 30-50% for Teflo and TX40 filter media, respectively. The study concluded that these filters will not be able to provide an equivalent measurement result under the Tier-II standard. Similarly, with regard to LEV-III/Tier-3 standards, Maricq *et al.* (2011) found adsorption of organic material from tunnel background (i.e. without vehicle exhaust) to account for ~1.5mg/mi of mass collected on quartz fiber filters, and ~0.5g/mi on Teflo filters. All these studies (Chase *et al.*, 2004; Khalek, 2008; Maricq *et al.*, 2011) concluded the use of Teflo filter material to be least conducive towards gaseous adsorption and hence, resulting in lesser positive artifacts.

Khalek (2006) observed that longer sampling times led to a reduction in filter mass which could either be due to a reduction in positive artifacts or the occurrence of possible negative artifacts. On the other hand, more recent studies focusing on PM mass measurements at LEV-III/Tier-3 emissions levels suggested the use of a single filter for all three *bags* of the FTP-75 in order to reduce the magnitude of the artifacts while increasing the actual PM mass

⁵phase-in period between 2017-2025 with additional reduction to 1mg/mi phased in between 2025-2028.

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collected (Maricq *et al.*, 2011; Jung *et al.*, 2015). Changes in primary dilution ratio (i.e. CVS dilution tunnel) and residence time of secondary dilution stage were found to be more influential compared to other sampling parameters (Khalek, 2006). Both *E-66* and *E-99* studies stated that changes in filter face velocity (FFV) did not appreciably influence the measurement, however, the *E-99* study reported that the signal-to-noise ratio was improved by increasing FFV. Additionally, the third phase of the *E-66* (Khalek, 2007) compared five different partial-flow sampling (PFS) systems to the reference CVS dilution (i.e. with secondary dilution) method and demonstrated their ability to maintain proportionality with the exhaust flow. At a particulate matter mass rate equivalent to 6% of the U.S. EPA 2007 heavy-duty standard, five PFS systems were comparable to the CVS measurement with two exhibiting errors between -70% and +400%. The observed variability reduced to $\pm 30\%$ for a PM mass level representative of 70% the U.S. EPA 2007 heavy-duty standard.

The accumulation of scientific results linking ultrafine particle emissions to adverse health effects, along with the observation that newer engine technologies, designed for lower particulate matter mass emissions, emitted significantly increased particle number emissions in the nucleation mode range (Kittelson, 1998; Kittelson *et al.*, 2002), shifted the focus towards a PM number-based regulation as possible complement to the existing gravimetric method (Giechaskiel *et al.*, 2012b). One of the early studies was the *verification of emission reduction technology* (VERT[®]) project in Europe (1994-2000) aimed at defining a test protocol to evaluate and verify the particle filtration efficiency of retrofit particulate filters (Mayer *et al.*, 1998, 1999; Mayer, 2005; Mooney, 2007; SNR 277205, 2009; Mayer, A. and Lemaire, J. and Czerwinski, J., 2010; Giechaskiel *et al.*, 2012b). The VERT[®] protocol was designed to measure solid, insoluble ultrafine particles in the 20 to 300nm range, which were considered the most toxic portion of diesel exhaust (Mooney, 2007). Limiting the quantification to solid particles was done since diesel particulate filters can only remove solid particles in a predictable fashion, thus, making it possible to frame a repeatable measurement procedure (Giechaskiel *et al.*, 2012b). Two important conclusions drawn from the VERT[®] project were, according to Giechaskiel *et al.* (2012b), that i) non-volatile *can* be measured repeatably, and ii) that the sensitivity limitations of the gravimetric method make it difficult to quantitatively assess the different particle emissions reduction technologies.

Under the auspices of the United Nations Economic Commission for Europe (UNECE), the *group of experts on pollution and energy* (GRPE) developed dur-

ing a three phase project called Particle Measurement Programme (PMP), a particle number emissions based regulation along with the recommended measurement protocol (*UN ECE/GRPE/WP-1*, 2003; *Andersson et al.*, 2007a,b; *Giechaskiel et al.*, 2008b,a; *Andersson et al.*, 2010). A detailed historical review and description of the PMP project can be found in *Giechaskiel et al.* (2012b, 2014). The PMP strived to implement a robust measurement protocol aimed at providing reproducible measurement results, and was therefore designed to only account for non-volatile (i.e. solid) particles above a certain size threshold (*Giechaskiel et al.*, 2012b). *Kasper* (2004) provides a comprehensive overview of different sample conditioning and treatment methods to phase separate volatile from solid particles, including thermal conditioning (i.e. vaporizing volatile material under high temperature conditions), and thermal desorption (i.e. adsorption of volatile matter onto activated charcoal). The main difference between these two processes is that the former transforms volatile matter into the vapor phase where it however, remains part of the sample, whereas the latter physically removes the volatile matter via adsorption. A possible disadvantage of volatilizing organic material is the chance of re-nucleation under certain sampling conditions and formation of volatile particles again downstream the thermal conditioner (*Zheng et al.*, 2015; *Jung et al.*, 2012). On the other hand, *Kasper* (2004) argues that the lower particle cut-point of 23nm that was introduced for the PMP protocol (*Giechaskiel et al.*, 2012b), ensures minimal contribution of such re-nucleated particles. With the Euro 5 standard for light-duty vehicle (*EU 692/2008*, 2008) and Euro VI standard for heavy-duty engine (*EU 582/2011*, 2011) certification, the European Union introduced as the first regulatory body worldwide, total non-volatile particle number limits for internal combustion engines, with the mandated measurement protocol specified in *UN ECE/TRANS/505/Rev.7/Add.48* (2015).

Giechaskiel et al. (2012b) provides a comprehensive review of regulatory measurement procedures with special regard to operation-dependent particle number emissions from light- and heavy-duty vehicle and engines, respectively. The review finds the *repeatability* of the particle number measurement method (i.e. PMP protocol) to be on the order of 5%, with observed higher scatter results being a function of the after-treatment state (i.e. before or after particle filter regeneration event). On the other hand, *reproducibility* was identified as a possible issue with variabilities seen to exceed 30%. *Giechaskiel et al.* (2012b) concludes these problems to primarily originate from calibration uncertainties of the instruments employed, and improved procedures should alleviate them. The official PMP protocol (*UN ECE/*

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TRANS/505/Rev.7/Add.48, 2015) allows two sampling approaches, namely, CVS and PFS dilution methods, which showed agreement within 15% for total particle numbers down to $1 \times 10^{11} \#/\text{kWh}$. At lower particle concentration levels the contribution of particles in the dilution air, though filtered, can result in larger inconsistencies. The advantage of the PMP method is the ability to provide an in-situ analysis of particle number emissions as compared to the off-line quantification via the gravimetric method.

As discussed thus far, to date (as of 2015) there exist two different regulatory methods for particulate matter quantification with the traditional approach based on gravimetric analysis of PM mass, and the newer approach based on solid particle number counting. PM mass limits are part of the certification process in both the U.S. and EU, whereas the particle number metric is only mandated by the EU. In summary, neither particle mass nor number are defined on precisely measurable physical or chemical properties, but rather in terms of *operational definitions* as detailed below:

Operational definition for particulate matter mass emissions: *all material that is being collected on a 47mm filter media at $47 \pm 5^\circ\text{C}$ when sampled within a specified range of dilution ratio and sample flow rate.*

Operational definition for particle number emissions: *measurement of solid particles having a diameter between 23nm and $2.5 \mu\text{m}$ and are of sufficiently low volatility to survive a residence time of 0.2sec at 300°C (Johnson et al., 2009).*

More recently, a number of studies (Liu et al., 2009, 2012; Thiruvengadam, 2013; Quiros, 2014), have proposed particle mass estimation based on real-time measurements of particle size and number distributions in conjunction with effective particle density models as an alternative to the gravimetric method. The authors argue that the inherently increased measurement accuracy of particle sizing instrumentation could greatly improve the sensitivity of PM mass quantification as compared to the gravimetric method.

Variability in PM and PN measurements

Giechaskiel et al. (2012b) found gravimetric based particulate matter mass and total particle number to correlate well down to levels of 1-2mg/km and 2-3mg/kWh for light-duty vehicles and heavy-duty engines, respectively. If only the carbonaceous fraction of the PM mass is considered, the correlation was observed to improve by an order of magnitude down to levels of 0.1-0.3mg/km or mg/kWh. Similar results were shown by Maricq et al. (2011)

who identified a strong correlation between PM mass and number concentrations on the order of $2 \times 10^{12} \#/\text{mg}$. This specific correlation was found to be universally applicable to both GDI and Diesel fueled engines in the absence of a nucleation mode.

In order to estimate the *precision* of a measurement method multiple experimental results obtained from the same laboratory and measurement setup can be used to calculate the variability (i.e. within-laboratory variability). Similarly, the *bias* of a method is determined based on variability calculation from different laboratories attempting to measure the same quantity (i.e. inter-laboratory variability) and represented by the scatter of results around the mean. The combination of both variabilities yields the *reproducibility* which is used as measure of *accuracy* of a measurement method. As part of the PMP project Andersson *et al.* (2007b, 2010) conducted an inter-laboratory exercise⁶ aimed at understanding the measurement precision and reproducibility of particle number quantification methods from light-duty vehicles and heavy-duty engines.

Figure 2.10 (*left*) and (*right*) shows results from round robin studies for particle number and particulate matter mass measurement methods, respectively (Giechaskiel *et al.*, 2012b). Within-laboratory variability data was based on 3-5 repetitions of the test cycle. It can be seen from Figure 2.10 (*left*) that the repeatability of the PN methods is within 5% for particle emissions levels above $5 \times 10^{12} \#/\text{km}$ (or $\#/\text{kWh}$ for HD), subsequently reduces to $\sim 30\%$ and $>50\%$ for emissions levels $>3 \times 10^{11} \#/\text{km}$ and $<3 \times 10^{11} \#/\text{km}$, respectively. In contrast, the repeatability of particulate matter mass measurements was observed on the order of 10% for emissions levels at $100 \text{mg}/\text{km}$ (or mg/kWh) and rapidly increased to above 50% for levels $<2 \text{mg}/\text{km}$, which is an emissions level representative of the Euro 5 (i.e. $4.5 \text{mg}/\text{km}$ by EU 692/2008 (2008)) and U.S. EPA Tier-3 (i.e. $3 \text{mg}/\text{mi} \approx 3.2 \text{mg}/\text{km}$ by CFR 40/86/S (2014)) standards for light-duty vehicles. As discussed earlier, the increased uncertainties for the gravimetric method (i.e. PM mass) primarily stems from the limited sensitivity at low mass emissions rates, and the high dependency of material deposited on the filter paper on sampling conditions and storage/released phenomena of the after-treatment system (Giechaskiel *et al.*, 2012b).

On the other hand, the increased variability of the PN methods for emissions levels $<5 \times 10^{12} \#/\text{km}$ is described (Giechaskiel *et al.*, 2012b) to be a result of the increased measurement sensitivity of this particular method, allowing

⁶including data from 5 laboratories and 10 different PN measurement systems.

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Figure 2.10: (*left*) Variability for different PM emissions levels, data from nine HD engines and >30 LD vehicles; (*right*) variability for different PN emissions levels, data from five HD engines and >30 LD vehicles; (*squares*) and (*asterisks*) indicate within- and between-laboratory variabilities; continuous lines give estimations of the within- and between-laboratory variability. (Figures taken from *Giechaskiel et al. (2012b)*).

to distinguish between different states of the particulate filter (i.e. loaded, not loaded with soot or possibly damaged) as well as being influenced by pre-conditioning and history effects of the vehicle or engine. Increased CVS or PFS background concentrations on a similar order as the engine exhaust, are a possible source for the relatively large variability observed for below $3 \times 10^{11} \#/\text{km}$ emissions levels. *Giechaskiel et al. (2012b)* provides a detailed discussion about engine after-treatment component effects on particulate matter emissions variability (i.e. both from number and mass perspective), whereas *Isella et al. (2008)* elucidates on the dynamics of non-volatile particles between the vehicle tailpipe and the sampling plane in the dilution tunnel from an experimental and theoretical point of view.

2.3.1 Regulatory limits for PM and PN in the U.S. and EU

Figure 2.11 depicts the historical evolution of PM mass emissions limits in the U.S. and Europe for the example of heavy-duty vehicles and urban buses (*Delphi, 2012*; *CFR 40/86/A, 2008*; *EU 582/2011, 2011*). Major improvements in emissions rates mark the introduction of electronic engine control and electronic unit injectors (EUI) resulting in improved combustion control between 1990-1995. An additional 90% reduction was accomplished by the introduction of particulate filter after-treatment systems for post 2007 model year engines, allowing to achieve the low PM mass emissions rates of 10mg/bhp-hr and 10mg/kWh ($\sim 7\text{mg/bhp-hr}$) as mandated by the U.S. (*CFR 40/86/A, 2008*) and European Union (*EU 582/2011, 2011*) standards.

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Figure 2.11: Overview of historical particulate matter emissions standards in the United States and Europe between 1985 and 2015 (*Delphi*, 2012; *CFR 40/86/A*, 2008; *EU 582/2011*, 2011).

In the U.S. the transition from the 1994 to 2007 emissions standards was disrupted by a landmark settlement between seven heavy-duty diesel engine manufacturers and both the U.S. EPA and U.S. Department of Justice (DOJ) in 1988 for violating the clean air act (CAA) by equipping their on-road engines with so called *defeat devices* (*US Department of Justice*, 1998; *Environmental Protection Agency*, 1999). These *defeat devices* were implemented in the form of control algorithms into the engine control unit with the purpose to reduce the effectiveness of emissions control devices to achieve increased benefits in fuel economy while operating on the road. The algorithms were laid out such that engines would pass the certification procedure due to the transient nature of the test cycle, however, once being operated in near steady-state cruise operation (i.e. typical highway driving conditions), the algorithm would switch to the more fuel efficient mode, and thereby, significantly increase NO_x emissions rates. The U.S. EPA estimated an excess of 1.3 million tons of NO_x to have been released by the affected engines in 1998 alone, which constitutes about 6% of total NO_x emissions from cars, trucks, and industrial sources for this calendar year (*US Department of Justice*, 1998). The settlement resulted in a consent decree with the manufacturers, requiring them, beside paying a fee for their violations, to comply with 2004 NO_x emission standards by already as early as October 1st, 2002 (*US Department of Justice*, 1998). Additionally, a new 13-mode steady-state engine dynamometer test cycle (i.e. supplemental emission test (SET)) was introduced to ensure emissions are being controlled during steady-state opera-

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Table 2.1: Historical overview of emissions standards in [g/bhp-hr] set by the U.S. EPA and CARB for heavy-duty vehicles and buses (GVW>14,000lbs), evaluated over the FTP certification engine-dynamometer cycle; SET for post model year 2002 engines; NTE evaluated during on-road testing (*CFR 40/86/A*, 2008).

Standard	Urban bus	General HD			Regulation
	FTP	FTP	SET	NTE	
1985-1987	-	0.6 ^a	-	-	
1988-1990	-	0.6	-	-	
1991-1992	0.1 ^b	0.25	-	-	
1993	0.1	0.25	-	-	(<i>CFR 40/86/A</i> , 2008)
1994-1995	0.07	0.1	-	-	
1996-2003	0.05 ^c	0.1	-	-	
2004-2007	0.05 ^c	0.1	1.0 x ^d	1.5 x ^d	
2007-2015 ^e	0.01 ^f		1.0 x	1.5 x	(<i>CFR 40/86/A</i> , 2008) (<i>CFR 40/1065</i> , 2015)

^a California only, no federal limit

^b California standard 0.1 g/bhp-hr

^c in-use PM standard 0.07 g/bhp-hr

^d phase-in of SET and NTE requirements; CA required SET and NTE effective for MY' 2005

^e in-use PEMS became enforceable by Nov. 2009

^f for Otto-cycle heavy-duty engines starting in 2008

tion such as line-haul truck driving conditions on a highway. The 13 modes are individually weighted in order to calculate a composite emissions factor in [g/bhp-hr] which has to comply with the same limits introduced for the FTP cycle (*CFR 40/86/A* (2008) §86.007-11 and §86.1360). Furthermore, a *not-to-exceed* (NTE) testing procedure was introduced with the aim to limit emissions rates during real-world operation that are emitted within a pre-defined NTE control area⁷. NTE emissions quantification is used for *in-use compliance* evaluation of the engine and after-treatment package and has to be performed during actual on-road operation of the vehicle using portable emissions measurement systems (PEMS) as outlined in *CFR 40/86/N* (2011) §86.1370, with emissions limits⁸ specified in *CFR 40/86/A* (2008) §86.007-11.

⁷engine operating area under the torque-curve that is limited by minimum speed, lower torque, and engine power bounds, as well as a set of ambient (e.g. altitude, temperature) and engine/after-treatment (e.g. temperatures, state of after-treatment, etc.) conditions.

⁸NO_x, CO, NMHC: 1.25 x applicable emissions standard; PM: 1.5 x applicable emissions standard; to calculate the final NTE limit value an accuracy margin (i.e. accounting for lower accuracy of PEMS vs. lab-grade analyzers) and a compliance margin (i.e. account for engine deterioration as function of miles traveled) are added; for detailed discussion see Kappanna (2015).

Table 2.1 provides an overview of the PM mass emissions standards for heavy-duty engines in the U.S.. Particulate matter is quantified using the gravimetric method (*CFR 40/1065*, 2015) while the engine is operated over the transient FTP and steady-state SET cycles on a engine dynamometer. As mentioned earlier, with the introduction of the in-use compliance requirements, PM mass emissions compliance with the standard (*CFR 40/86/A*, 2008) has to be additionally demonstrated during on road operation using appropriate portable PM mass measurement devices.

Table 2.2 provides an overview of the PM mass emissions standards for heavy-duty engines in the European Union spanning from Euro I (1992) to the latest Euro VI (2014) (*EU 582/2011*, 2011). The Euro VI procedure requires the engines to be certified over the transient *world harmonized transient cycle* (WHTC) and steady-state *world harmonized steady-state cycle* (WHSC). Additionally, and most importantly, with the introduction of Euro VI standards non-volatile particle number emissions limits were introduced at a level of $8 \times 10^{11} \#/\text{kWh}$ and $6 \times 10^{11} \#/\text{kWh}$, evaluated over the WHSC and WHTC, respectively, using the PMP prescribed sampling procedure (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015). As of 2015 there exists no finalized regulation for in-use compliance of heavy-duty engines in the EU. However, multiple methods are being evaluated including portable emissions measurement systems for PM mass and number emissions in conjunction with moving average window (MAW) methods (*Bonnel et al.*, 2010; *Mamakos et al.*, 2011a,b) or real driving emissions (RDE) (*EU G3/1515125/PE RDE/Draft*, 2015). A more detailed description of the European legislation can be found in *Giechaskiel et al.* (2014).

Similarly to the heavy-duty engine standards, particulate matter limits are framed for light-duty vehicles and passenger cars. In the U.S. PM mass emissions limits are on the order of 10mg/mile (i.e. with slight variations depending on bin and specific test e.g. FTP-75, US06, or SC03) according to the U.S. EPA Tier-2 standard and will be further reduced to 3mg/mi between 2017-2015 and finally 1mg/mi between 2025-2028 under the U.S. EPA Tier-3/ CARB LEV-III standards (*CFR 40/86/S*, 2014). In the EU light-duty PM emissions limits are currently (as of 2015) at the level of Euro 5 with Euro 6 being phased in between 2015 to 2019 (*EU 692/2008*, 2008). Both Euro 5 and 6 PM mass emissions limits are 4.5g/km. Similarly to the heavy-duty regulation in Europe, light-duty vehicles also have to comply with a particle number based standard starting with Euro 5 and beyond on the order of $6 \times 10^{11} \#/\text{km}$, evaluated over the *new European driving cycle* (NEDC) using the measurement procedure defined by the PMP project (*UN ECE/-*

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Table 2.2: Historical overview of emissions standards in [g/kWh] set by the European Union for vehicles used for transportation of passengers and goods; depending on standard emissions are evaluated over steady-state cycles: ECE R-49 (13-mode cycle), ESC (European steady-state cycle, 13-modes plus 3 random points), ELR (European load response), WHSC (world harmonized steady-state cycle, 13-modes); and transient cycles: ETC (European transient cycle), WHTC (world harmonized transient cycle) (*EU 88/77/EEC*, 1987).

Standard	Enforced	PM limit		SPN limit [#/kWh]	Regulation
		Steady-state ^a	Trans. ^b		
Euro I	1992 $\leq 85\text{kW}$	0.612	-	-	Dir 91/542/EEC
	1992 $> 85\text{kW}$	0.36	-	-	
Euro II	Oct 1996	0.15 ^c	-	-	Dir 91/542/EEC Dir 96/1/EEC
Euro III	Oct 2000	0.1 ^{d,e}	0.16 ^{d,f,g}	-	Dir 1999/96/EC Dir 2001/27/EC
Euro IV	Oct 2005	0.02	0.03 ^{d,f}	-	Dir 1999/96/EC Dir 2005/55/EC Dir 2005/78/EC Dir 2006/51/EC
Euro V	Oct 2008	0.02	0.03 ^{d,f}	-	Dir 2005/55/EC Dir 2005/78/EC Dir 2006/51/EC Dir 2008/74/EC
Euro VI	Oct 2013	0.01 ^h	0.01 ^h	8.0x10 ¹¹ ⁱ	EC 595/2009
				6.0x10 ¹¹	EC 582/2011

^a Euro I & II: ECE R-49, Euro III-V: ESC/ELR, Euro VI: WHSC

^b Euro I & II: none, Euro III-V: ETC, Euro VI: WHTC

^c 0.25g/kWh for engines with a cylinder swept volume $< 0.7\text{l}$ and rated power speed $> 3000\text{rpm}$ and engine power $< 85\text{kW}$ until Sept. 1998

^d 0.02 g/kWh for enhanced environmentally friendly vehicle (EEV)

^e 0.13 g/kWh for engines with a cylinder swept volume $< 0.75\text{l}$ and rated power speed $> 3000\text{rpm}$

^f not applicable for gas engines

^g 0.21 g/kWh for engines with a cylinder swept volume $< 0.75\text{l}$ and rated power speed $> 3000\text{rpm}$

^h applicable to both compression and positive ignition engines

ⁱ WHSC: 8.0x10¹¹ #/kWh; WHTC: 6.0x10¹¹ #/kWh; not applicable to gas engines

TRANS/505/Rev.7/Add.48, 2015). A historical overview of light-duty emissions regulations worldwide can be found in *Delphi* (2014), whereas a more in-depth discussion of current regulations and their implications for PM mass and number quantification is given by *Giechaskiel et al.* (2014).

2.3.2 Particulate Measurement Programme (PMP)

Streamlined with the introduction of particle number emissions limits, the European Union adopted a new methodology aimed at standardizing the

measurement of total particle number concentrations by only counting solid particles having a diameter between 23nm and 2.5 μ m and that are thermally treated in order to reduce the volatile fraction, thus reducing measurement artifacts and variability (UN ECE/TRANS/505/Rev.7/Add.48, 2015). As described before, this method has been previously developed under the PMP project (UN ECE/GRPE/WP-1, 2003; Andersson *et al.*, 2007a,b, 2010; Giechaskiel *et al.*, 2008a,b, 2012b).

Figures 2.12 and 2.13 provide a schematic overview of the two permissible sampling setups according to UN ECE/TRANS/505/Rev.7/Add.48 (2015), including sample extraction from the CVS dilution tunnel or through a partial-flow sampling system directly from the exhaust stream. The recommended measurement system comprises six different components, namely, i) a sampling probe and transfer tube; ii) an optional particulate pre-classifier (i.e. cyclone to remove 2.5-10 μ m particles); iii) a first stage diluter; iv) an evaporation tube; v) an optional second stage diluter; and vi) an ultrafine particle number concentration counter optimized for a 50% counting efficiency for 23nm size particles. Both the dilution stages and the evaporation tube are considered as a combined system and referred to as the *volatile particle remover* (VPR). The VPR is designed to remove the volatile and semi-volatile fractions in the exhaust sample, thereby aiming at suppressing particle nucleation and the formation of artifacts in the sample stream. A first stage hot dilution at temperatures between 150-400°C and with a dilution ratio of 10 to maximum 200 is used to reduce particle concentration in the sample before being directed into the evaporation tube (i.e. operated at 300-400°C) where the volatile and semi-volatile components are being transferred to a gaseous state. It follows a second cold dilution stage with a dilution ratio between 10 to 15 to i) rapidly lowering the partial pressures of the gaseous components aimed at preventing their re-condensation, and ii) lowering the sample temperature to below 35°C prior to entering the particle counting device. The VPR is designed to remove >99% of ≤ 30 nm tetracontane (CH₃(CH₂)₃₈CH₃) particles, with an inlet concentration of $\leq 10^4$ #/cm³. Particle losses in the VPR are assessed based on the particle concentration reduction factor of solid reference particles with a mobility diameter of 30, 50, and 100nm UN ECE/TRANS/505/Rev.7/Add.48 (2015).

However, the PMP approach for particle number measurements has come under scrutiny as recent studies have on one hand observed significant semi-volatile particles downstream the VPR (Zheng *et al.*, 2015; Jung *et al.*, 2012), and on the other hand measured increased concentrations of particles below the size of 23nm being emitted from DPF equipped vehicles. These ultrafine

Figure 2.12: Schematic diagram of recommended particulate sampling system for *full-flow sampling* according to the European regulation for particulate number emissions measurement (i.e. PMP) (UN ECE/TRANS/505/Rev.7/Add.48, 2015).

particles are believed to comprise sulfuric acid and assumed to be emitted from catalytic oxidation of sulfur from lubrication oil and fuel (Thiruvengadam *et al.*, 2012; Vaarasmahti *et al.*, 2005; Kittelson *et al.*, 2008). Johnson *et al.* (2009) evaluated the PMP methodology during on-road vehicle testing and observed a significant portion of particles in the size range below 20nm even though the sample stream was thermally treated according to PMP requirements, thus questioning the applicability of the 23nm lower cut-point for particle measurements, as mandated by the European PMP regulation. See Giechaskiel *et al.* (2012b) for additional discussion of criticism of the PMP method.

Alternatively, researchers have proposed volatile particle remover systems using catalytic oxidation of volatile and semi-volatile material as opposed to thermal vaporization (Khalek and Bougher, 2011; Swanson *et al.*, 2013; Giechaskiel *et al.*, 2014). This would have the benefit of these compounds being physically removed and thus, eliminating the possibility of re-nucleation phenomena. Khalek and Bougher (2011) presented a solid particle number measurement system (SPNMS) using a catalytic stripper heated to 300°C and reported system performance to within 2% of a commercially available PMP system, using vehicle exhaust for evaluation. However, the study also acknowledged an observed increase in variability which needs to be further addressed and identified. Extension of the PMP method to particles

2.3. Regulatory Framework for Controlling PM/PN

Figure 2.13: Schematic diagram of recommended particulate sampling system for *partial-flow sampling* according to the European regulation for particulate number emissions measurement (i.e. PMP) (UN ECE/TRANS/505/Rev.7/Add.48, 2015); *alternatively, the control software might account for the flow removed by the PN system.

below 23nm is partially limited by the effectiveness of the volatile particle remover to reliably prevent nucleation downstream the sample conditioning unit (Giechaskiel *et al.*, 2012b), and would require catalytic stripper technology to remove possible sources of artifacts (Swanson *et al.*, 2013). For that purpose, a catalytic stripper setup was built by Swanson *et al.* (2013) showing solid particle penetration of 50% for 10.5nm particles, and sulfur storage capacity to chemically remove sulfuric acid vapors and prevent nucleation up to levels of 10mg/m³ of sulfuric acid.

2.3.3 In-use compliance of PM/PN emissions

As discussed before, resulting from the 1998 consent decree in the U.S., heavy-duty engine manufacturers are mandated to demonstrate in-use compliance of their engines with particulate matter emissions limits while being operated inside the pre-defined NTE area (CFR 40/86/N, 2011). Work-specific emissions factors are calculated over a finite amount of operating time referred to as *NTE events*, and then compared to mandated threshold values. The technical definition of *NTE events* differs between regulating bodies, with the U.S. EPA defining it on a *time-basis* where the engine has to operate for at least 30 continuous seconds within the NTE zone. Contrary,

the European Union defines *NTE events*⁹ on a work-basis with an event being the time an engine requires to produce the same amount of work as over a given reference cycle (i.e. certification cycle). Since in-use compliance testing is performed while the test vehicle is operated over the road, following its intended vocation, measurement instruments need to be portable, compact in size and withstand the harsh physical and environmental conditions of on-road driving. For simplicity, instruments meeting these requirements will, hereinafter, be termed *particulate matter - portable emissions measurement systems* (PM-PEMS or just PEMS).

With regard to PM mass- and particle number-based (i.e. Euro VI, and Euro 5/6) emissions regulations, PM-PEMSs should be versatile enough to offer both mass and number concentration based measurement capabilities. In particular, they have to comply with the operational definition for both gravimetric PM as well as particle number measurements.

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The characteristics of particles and particulate matter is *shaped* by the particle sample extraction, conditioning and measurement methods (Eastwood, 2008) as they undergo continuous transformation from the point of exiting the combustion chamber to the location of measurement (Eastwood, 2008; Isella et al., 2008; Giechaskiel et al., 2012b, 2014). Furthermore, under certain conditions, new particles can be formed during the sampling and conditioning process leading to *sample artifacts* which are not representative of the original particle emissions spectrum emitted by the engine (Kittelson, 1998; Eastwood, 2008). Eastwood (2008) rightfully mentions, that particles are *isop facto* defined, which translated means, *purely in terms of the method of measurement*. This problem is further elevated by the fact that there exists no universally defined standard or reference for particles (or particulate matter or soot from combustion sources), as there is for mass or distance for example¹⁰. In fact, the only two currently (as of April 2015) implemented particulate matter emissions standards for combustion sources (i.e. PM mass and number emissions) are defined on an *operational basis* as discussed in Section 2.3.

The primary parameters that have been identified to affect the measurement of aerosol particles emitted by internal combustion sources can be summa-

⁹usually referred to as *work window* for heavy-duty engines and *CO₂ window* for light-duty vehicles.

¹⁰or similar to NIST traceable characteristics for measurement parameters in the United States.

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Table 2.3: Sampling and conditioning requirements for regulated gravimetric filter method as mandated by the U.S. EPA (*CFR 40/1065*, 2015).

Parameter	Setting
Dilution air quality and temperature	HEPA filtered, $25 \pm 5^\circ\text{C}$
Dilution ratio	Primary: minimum 2:1 Overall: minimum 5:1 to 7:1
Residence time [§1065.140(e)(3)]	minimum of 1.0 sec maximum of 5.5 sec
Filter face temperature	$47 \pm 5^\circ\text{C}$
Filter face velocity [§1065.170(c)(vi)]	Approx. 100 cm/s

rized as (*Khalek et al.*, 1999, 1998, 2000; *Kittelson et al.*, 2002; *Majewski and Khair*, 2006; *Eastwood*, 2008; *Isella et al.*, 2008; *Giechaskiel et al.*, 2012a); i) environmental conditions experienced by the exhaust stream during sample extraction and conditioning (i.e. dilution ratio, temperature, etc.); ii) sampling and measurement systems utilized to characterize the emissions; and iii) chemical and physical composition of the engine exhaust and particulate matter to be measured.

Traditionally and for regulatory particulate matter mass quantification (*CFR 40/1065*, 2015; *EU 582/2011*, 2011) exhaust gas is diluted in a constant volume sampling dilution tunnel and then sampled through an extraction probe and subjected to a secondary dilution stage before being collected on filter media at a controlled temperature. Table 2.3 provides an outline of the specific boundary conditions that need to be observed for regulatory PM mass measurements in accordance with *CFR 40/1065* (2015) (i.e. similar conditions apply for PM mass quantification in Europe). Since for heavy-duty engine applications, full-flow CVS tunnels are associated with significant cost for initial installation as well as operation, partial flow dilution systems (PFDS) have been developed that extract a proportional slip stream directly from the raw exhaust and subject the sample to a single stage dilution before being collected on a filter media (*Giechaskiel et al.*, 2014). The filter media can be weighed before and after sample collection to calculate the net particulate matter mass collected. As discussed in Section 2.3, by this method not only solid particles will be retained on the filter media but also volatile and semi-volatile matter that adsorbed onto solid particles or condensed on the filter media.

The advantage of collecting particulate matter on filter media lays in the possibilities for further analysis of PM (*Eastwood*, 2008; *Giechaskiel et al.*, 2014),

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including but not limited to; i) *extraction in a Soxhlet apparatus* for determination of soluble organic and inorganic fraction as well as the non-soluble fraction; ii) *ion chromatography* for detection of sulfate, nitrate, and phosphate; iii) *gas chromatography* to analyze the fuel and lubrication oil fractions of PM; iv) *thermogravimetry* for determination of elemental and organic carbon fractions (i.e. EC/OC); and v) *biologically assaying* to quantify the mutagenic potency (i.e. mutagenicity) of PM via the use of *bioassays*. While these extraction methods had become a standardized way to gain more information about the chemical composition of PM, the introduction of particulate filters drastically reduced the PM mass rates and thereby, significantly increased the sampling time to collect sufficient mass in order to perform any of the extraction analysis.

Similarly to the collection of particulate matter on filter media, particles can be collected on specific substrates (e.g. copper or SiO coated iron-grids) for subsequent microscopic analysis to analyze the particle's morphology or approximate the size distribution. The sample flow is directed onto the substrates such that individual particles impact and *stick* to the surface. Two methods are typically employed to enhance the chance of particles impacting with the substrate, including, *thermophoretic* and *electrostatic* precipitation. The former generates a net particle flux onto the substrate by virtue of a temperature difference between the substrate and the sample stream, whereas the latter induces an unipolar charge onto particles in a first stage and then subjects the substrate to an opposite voltage in order to attract the charged particles. Microscopic analysis of the collected particles is performed by means of *scanning electron microscopy* (SEM) and *transmission electron microscopy* (TEM).

While the sample analysis methods introduced thus far provide *ensemble* information for particulate matter, measurement methodologies listed in Table 2.4 allow either for individual particle analysis or real-time characterization of particle properties, including, mass, number concentration, surface, and size spectrum. A detailed discussion of the different measurement principles and specifics of instrument application can be found in Kittelson *et al.* (1998); Burtscher (2005); Mayer (2005); Eastwood (2008); and Giechaskiel *et al.* (2014). For the interested reader, a history of diffusion batteries is given by Knutson (1999), a detailed discussion of the development of condensation nucleus counters by McMurry (2000b), and finally, a chronological presentation of the history of electrical aerosol measurement by Flagan (1998).

A comprehensive study by Mohr *et al.* (2005) compared 16 different partic-

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Table 2.4: Typical particle characterization methods used to quantify particle mass (m), number (#), surface (S), and size spectrum information; data taken from instrument manuals and Giechaskiel et al. (2014); LOD - limit of detection.

Principle	Instrument	Unit	LOD	Real-time
<i>Optical methods</i>				
Light scattering	Scattering photometer	m (smoke)	$1\mu\text{g}/\text{m}^3$	Yes
	OPC ^a	#	-	Yes
	CPC ^b	#	-	Yes
Absorption	Spotmeter (reflection) ^c	FSN	$25\mu\text{g}/\text{m}^3$	No
	Aethalometer	m (BC)	-	Yes
	PASS ^d	m (BC)	$5\mu\text{g}/\text{m}^3$	Yes
	LII ^e	m (BC)	$5\mu\text{g}/\text{m}^3$	Yes
Extinction	Opacity meter	opacity	0.1% opacity	Yes
<i>Electrical charge based methods</i>				
Electrical corona	Diffusion charger	S (active)	$20\mu\text{m}/\text{cm}^2$	Yes
Ultraviolet light	Photoelectric sensor	S (photoelec.)	-	Yes
<i>Size distribution methods</i>				
Microscopical	SEM, TEM, AFM ^f	#, S		No
Impaction	MOUDI ^g	m	-	No
Diffusion	Diffusion battery	#	-	Yes
Charging	DMA	#	-	No
Charging + classifying + counting	SMPS	#	$100 \#/\text{cm}^3$	No
	CPMA ^h	m	-	No
	DMS, EEPs, FMPS	#	$1000 \#/\text{cm}^3$	Yes
	FIMS ⁱ	#	-	Yes
	ELPI, DMM	#, m	$1000 \#/\text{cm}^3$	Yes
	EDB ^j	#	-	Yes

^a optical particle counter

^b condensation particle counter

^c measures the filter smoke number (FSN)

^d photo-acoustic soot sensors, e.g. AVL MSS

^e laser-induced incandescence

^f AFM - atomic force microscopy

^g micro-orifice uniform deposit impactor

^h centrifugal particle mass analyzer

ⁱ fast integrated mobility spectrometer

^j electrical diffusion batteries

ulate matter quantification systems, including mass and non-mass related methods. The mass-based methods included, *gravimetric filter samples*, *laser-induced incandescence* (LII), *photo-acoustic detection* (PAS), *photo-electric charging* (PAS), *combined inertial and mobility sizing*, and *opacity*, whereas the non-mass-based systems evaluated in this study included, *condensation particle counter*, *diffusion battery*, *diffusion charger*, *electrical low-pressure impactor* (ELPI), and *light-scattering*. Experiments were conducted on a heavy-duty engine with exhaust samples being extracted downstream a diesel particulate filter, thus in a low particle concentration environment representative

of current technology on-road engines. The different measurement methods were compared based on repeatability, detection limits, sensitivity, temporal sampling resolution, and benchmarked against the regulated gravimetric filter method ¹¹ as well as elemental carbon fraction. The authors (*Mohr et al.*, 2005) found opacimeters and light-scattering to reach their detection limits at the low concentrations measured. In general, poor correlation between all the time-resolved and the regulated filter method was observed. On the other hand, the same set of instruments showed good correlation with the elemental carbon fraction of particles. These results highlight the importance of sample conditioning and extraction methods as they can significantly impact the volatile particulate matter fraction (*Mohr et al.*, 2005). The authors further reported a clear improvement in sensitivity of non-mass-based measurement methods such as particle number and surface related methods (*Mohr et al.*, 2005).

2.4.1 Particle sample extraction and transport considerations

Particulate matter quantification is strongly dependent on sample extraction and conditioning as discussed in the previous section. Moreover, particle size plays an important role as operational sampling and transport phenomena in particular, are strongly dependent on particle size (*Hinds*, 1999; *Von der Weiden et al.*, 2009; *Giechaskiel et al.*, 2012a). Small particles with an aerodynamic size below about 100nm and large particles with a size above $\sim 0.5\mu\text{m}$ are particularly affected by physical mechanisms (*Von der Weiden et al.*, 2009). Inaccurate sampling and transport of the aerosol from the sample extraction to the measurement location can possibly lead to significant particle losses (*Giechaskiel et al.*, 2010) and thus, incorrect results (*Giechaskiel et al.*, 2012a). Furthermore, comparison of results from different sampling locations can be challenging due to intrinsic aerosol processes and size dependent loss mechanisms that need to be taken into account (*Giechaskiel et al.*, 2012a), and non-uniform particle losses may alter particle size distributions from *bimodal* to appear *monomodal* (*Von der Weiden et al.*, 2009). For mechanisms that depend on the inertia of particles such as sample extraction and line bends, losses are generally a function of aerodynamic particle diameter (d_a), whereas *diffusion*, *thermophoresis*, and *electrostatic* losses for example, depend on the mobility particle diameter (d_m) (*Giechaskiel et al.*, 2012a). *Von der Weiden et al.* (2009) states that the ideal sampling system should perform its

¹¹method described in *EU 582/2011* (2011) for European Union and in *CFR 40/1065* (2015) for United States.

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function without altering aerosol characteristics, composition, number concentration or size spectrum. The primary objective of a particle sampling system is to minimize the formation of sampling artifacts, while maximizing the sampling efficiency during extraction and transport of aerosols from the sample location to the measurement instrument *Von der Weiden et al.* (2009).

A study by *Isella et al.* (2008) investigated the dynamics of non-volatile particles in the exhaust transfer tube emitted by an Euro 3 compliant light-duty vehicle (i.e. without DPF). The study concluded that agglomeration and particle convection (i.e. transport by the exhaust gas) phenomena were the primary aerosol processes. However, the authors suggest that agglomeration might play a less significant role for exhaust sampled from a particulate filter equipped vehicle. Thermophoretic losses were calculated to be non-negligible and on the order of 5.5% and 6.5% for vehicle speeds of 50 and 120km/h on a mass basis (*Isella et al.*, 2008). These losses are assumed to most likely increase for PM sampling from filter equipped vehicles. Finally, diffusional losses were calculated to be minimal in the sample transfer tube. In conclusion, *Isella et al.* (2008) reported an increase in geometric particle mean diameter of ~ 22 - 23 nm and ~ 16 - 17 nm for a 9 and 6 meter long transfer tube, respectively, for tests with both 60 and 120km/h vehicle speeds. At the same time, particle peak concentrations reduced by 40% and 30% for the 9 and 6 meter long transfer tube, respectively.

This section will provide a brief discussion of sampling and transport related loss mechanisms as a function of particle size. Numerous literature exists, examining particle sampling and deposition mechanisms (*Kittelson et al.*, 1999; *Hinds*, 1999; *Willeke and Baron*, 2011) with various studies presenting simplified particle loss calculator tools (*Willeke and Baron*, 2011; *Von der Weiden et al.*, 2009; *Ahlvik et al.*, 1998; *European Commission*, 2003). Specifically, *Giechaskiel et al.* (2012a) provide a simplified *sampling guide* which summarizes and discusses physical particle sampling and transport phenomena that are applicable to quantification of non-volatile particles from automotive combustion engine sources. On the other hand, a detailed analysis of general aerosol sampling mechanisms ¹² is given by *Von der Weiden et al.* (2009), and *Ayala et al.* (2003) discuss diffusion losses in sampling transfer pipes and lines between the exhaust stack and the measurement instrument.

The overall particle sampling system efficiency (η_{system}), which describes

¹²the discussion by *Von der Weiden et al.* (2009) is largely tailored towards ambient aerosol sampling, however, also provides valuable information for phenomena affecting particles below 100nm, the particle size range generally emitted by combustion engines.

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the fraction of particles that penetrate through the sampling system, can be described as the product of particle sampling ($\eta_{sampling}$) and transport ($\eta_{transport}$) efficiencies, both a function of particle size, as given by Equation 2.19 (Von der Weiden *et al.*, 2009; Giechaskiel *et al.*, 2012a). The overall system efficiency can be alternatively understood as the ratio between particle number concentrations measured at the instrument inlet and in front of the sample extraction probe.

$$\eta_{system}(d_a) = \eta_{sampling}(d_a) \cdot \eta_{transport}(d_a) \quad (2.19)$$

Sampling mechanisms and efficiency

The sampling efficiency can be divided into aspiration efficiency into the sampling probe (η_{asp}), and gravitational ($\eta_{trans,grav}$) and inertial ($\eta_{trans,inert}$) transmission efficiencies within the probe as shown by Equation 2.20. The aspiration or sample extraction efficiency is primarily related to iso/non-iso-kinetic and iso/non-isoaxial sampling (Von der Weiden *et al.*, 2009; Giechaskiel *et al.*, 2012a). The former is determined by differences in the free-stream velocity¹³ and the velocity of the sample flow within the probe. The latter refers to the alignment of the extraction probe with the streamlines of the free-stream (i.e. total exhaust flow in transfer pipe). Furthermore, the extraction efficiency is dependent on i) type of sampling probe used (i.e. tee, straight blind, hat, multi-hole or 45°-cut probe), ii) inhomogeneities in the particle concentration within the sampling environment (i.e. exhaust transfer pipe), and iii) pressure fluctuations in front of the sampling probe (Giechaskiel *et al.*, 2012a).

$$\eta_{sampling}(d_a) = \eta_{asp}(d_a) \cdot \eta_{trans,grav}(d_a) \cdot \eta_{trans,inert}(d_a) \quad (2.20)$$

Transport mechanisms and efficiency

The transport efficiency describes the fraction of particles lost between the sample extraction location and the measurement instrument (Giechaskiel *et al.*, 2012a). The overall transport efficiency is defined as the product of the individual efficiencies of each sample line section or component within the sampling system. Each line section or component experiences a series

¹³this refers to the total exhaust flow velocity in the transfer pipe in case of emissions sampling.

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of different loss mechanisms, including; i) *diffusion loss* (η_{diff}), ii) *sedimentation loss* (η_{grav}), iii) *turbulent inertial deposition* ($\eta_{turb,inert}$), iv) *inertial deposition in bends* ($\eta_{bend,inert}$), v) *inertial deposition in contractions* ($\eta_{cont,inert}$), vi) *inertial deposition in enlargements* ($\eta_{enlarge,inert}$), vii) *electrostatic deposition* ($\eta_{electrostatic}$), iix) *thermophoresis* (η_{thermo}), ix) *diffusiophoresis* ($\eta_{diff-phoresis}$), x) *interception* ($\eta_{intercept}$), and *agglomeration/coagulation* ($\eta_{coagulation}$).

$$\eta_{transport}(d_a) = \prod_{line\ section} \left\{ \prod_{mechanisms} \eta_{line-sec,mechanism}(d_a) \right\} \quad (2.21)$$

2.4.2 General lab-grade particle instruments

The discussion of laboratory-grade particulate matter measurement instruments presented herein will be limited to the systems that are most frequently employed for particulate matter characterization from combustion sources, in particular; i) the differential mobility analyzer and condensation particle counter; ii) the engine exhaust particle sizer for transient particle spectrometry; iii) the photo-acoustic based micro soot sensor for quantification of carbonaceous soot; and iv) a diffusion-charging type aerosol detector. The described instruments were used to conduct experimental testing for this study. A comprehensive description of a wide range of particle instruments and their operating principles can be found in Kittelson *et al.* (1998); Burtscher (2005); Mayer (2005); Eastwood (2008) and Giechaskiel *et al.* (2014).

Differential Mobility Analyzer and Condensation Particle Counter

Particle size spectrum analysis with high sensitivity and resolution is traditionally conducted by means of combining a differential mobility analyzer (DMA, Knutson and Whitby (1975)) and a condensation particle counter (CPC) for particles in the range of ~ 5 to 600nm (Mayer, 2005). One such combined and commercially available instrument is the scanning mobility particle sizer (i.e. short SMPSTM) from TSI Inc. (TSI Inc., 2008).

A differential mobility analyzer classifies a polydisperse aerosol into a series of monodisperse particle size bins by means of a force balance between drag (F_D) and electrostatic (F_E) forces acting on a particle (Knutson and Whitby, 1975; Hinds, 1999; Franklin *et al.*, 2010; TSI Inc., 2008). The electrostatic force (F_E) is defined as the force acting on a particle with n elementary charges e (i.e. $1.6 \times 10^{-19}C$) in an electric field with intensity (E) given by Equation 2.22. On the other hand, the drag force acting on the particle traveling through

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the DMA is given by Equation 2.23 and depends on the sample fluid viscosity (μ), the particle velocity (V), the Cunningham slip correction factor (C_C), and the particle mobility diameter (d_p) (*Hinds, 1999*). Equating these two equations and knowing the DMA properties such as geometry and sample flow rate as well as the sample fluid properties it becomes possible to calculate the terminal particle velocity and thus, predict its trajectory.

$$F_E = neE \quad (2.22)$$

$$F_D = \frac{3\pi\mu V d_p}{C_C} \quad (2.23)$$

The DMA is designed as a tubular shaped device with a center electrode (i.e. collector rod) and an annular flow section (see *TSI Inc. (2008)* for illustrations) where the particle laden aerosol and sheath flow enter at the top and travel down the annular section. Before entering the DMA column however, the polydisperse aerosol stream is passed through a bipolar ionization source ¹⁴ (i.e. neutralizer) in order to establish a bipolar charge equilibrium on the particles (i.e. particles receive either a positive, negative or zero charge). Upon exiting the neutralizer the particles are assumed to have a uniform Boltzmann charge distribution which will subsequently allow to estimate the actual number of particles based on counted singly charged particles (*Franklin et al., 2010*).

A known negative voltage is applied to the center electrode, causing positively charged particles to get attracted towards to it, while negatively charged particles get repelled and deflected towards the outer DMA shell that is electrically grounded. Particles with *zero* charge will continue to flow with the laminar sample flow down the annular section and eventually exit the DMA. For a given negative voltage applied to the collector rod, particles with high electrical mobility are precipitated along the upper portion of the rod while particles with low electrical mobility travel further before impacting with the collector rod (*TSI Inc., 2008*). At the bottom of the center electrode is a small slit allowing particles with one specific electrical mobility to exit through the slit. By changing the negative voltage applied to the collector rod it is now possible to size separate particles according to their electrical mobility which is inversely related to the particle size and

¹⁴this is a neutralizer (or electron emitter); most often radioactive Krypton-85 (⁸⁵Kr) or in newer applications, alternatively a soft X-ray source.

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proportional to number of charges on the particles. An additional transfer function is applied to account for non-uniformity of the particle's point of origin after entering the DMA, and variations in aerosol flow and electric field (*Franklin et al.*, 2010). Also, the instrument software accounts for possible transport losses within the DMA, specifically diffusion losses (*TSI Inc.*, 2008). The measurement range of a DMA is limited at the lower end due to diffusion phenomena for very small particles and at the upper end due to a wide charge distribution on large particles (*Mayer*, 2005).

Condensation particle counters grow nano-sized particles to micrometer-sized droplets by saturation of an aerosol and subsequent cooling through adiabatic expansion or flow through a cold tube to generate a supersaturated environment (*Hinds*, 1999; *Mayer*, 2005; *Eastwood*, 2008; *Franklin et al.*, 2010; *Giechaskiel et al.*, 2014). Two methods of aerosol saturation are typically employed, specifically, either by water or alcohol (i.e. butanol) vapor. A more in depth discussion of different CPC technologies can be found in *Eastwood* (2008), whereas *McMurry* (2000b) provides a detailed historic overview of the evolution of condensation nucleus counters.

Figure 2.14 depicts a schematic diagram of a CPC (i.e. specifically model 3772/3771, TSI Inc.) with the particle growth section in the lower and the optical particle counter in the upper half of the figure. In a butanol-based CPC, liquid butanol is heated in the saturation region to a temperature level significantly above the one in the condensing region. In the adjacent condensing region, temperatures are lowered by thermoelectric cooling, thereby lowering the saturation pressure and thus, bringing the previously saturated butanol vapor in a supersaturated state (*Franklin et al.*, 2010). The rate of thermal diffusion is significantly faster relative to the mass diffusion of butanol in air. After growing the particles to micrometer-range they can readily be counted by optical means. The lower detection limit of the CPC is defined by the saturator and condenser temperatures as well as the properties of the working fluid and is usually in the range of 3-10nm (*Giechaskiel et al.*, 2004). Thus, increasing the temperature difference between saturator and condenser will allow to lower the minimum particle size limit that can be grown (*Franklin et al.*, 2010). The limiting factor for the lower size limit however, is the possible onset of homogeneous nucleation (*Mayer*, 2005).

In contrast, the water-based CPC features a cooling region first, exhibiting temperatures below the growth region. The first stage is surrounded by a saturated water wick that allows the relative humidity to be brought to 100% through diffusive mass transfer from the saturated wick (*Franklin et al.*,

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Figure 2.14: Schematic diagram of condensation particle counter, model 3772/3771, TSI Inc. (TSI Inc. 2007).

2010). It follows the heated growth region which is also surrounded by a saturated water wick, and where the saturation pressure of water increases. The presence of the supersaturated region in the growth tube is explained by *Franklin et al.* (2010) through the increased rate of mass diffusion of water vapor in air as compared to thermal diffusion of air.

Franklin et al. (2010) compared multiple water- and butanol-based CPCs using diesel combustion derived aerosols. The authors found one of the water-based CPCs to perform comparably to the butanol-based instruments for most mobility diameters. Towards the lower cut-off size the water-based CPC however, was observed to undercount for both diesel and biodiesel exhaust particles. *Franklin et al.* (2010) concluded that the instruments shows some degree of sensitivity towards particle composition affecting condensation and growth. This was found to be consistent with literature that re-

ported deviations in performance between water- and butanol-based CPCs especially for highly pure hydrophobic aerosols (*Franklin et al.*, 2010). A second water-based CPC showed significant differences which however, was attributed to the different instrument design and the lack of sheath flow. *Giechaskiel et al.* (2014) on the other hand, states that water-based CPCs are usually not used in conjunction with the volatile particle remover to quantify vehicular exhaust particles due to the hydrophobic nature of soot after passing through the VPR.

Engine Exhaust Particle Sizer - EEPSTM

Differential mobility spectrometers have the similar underlying operating principle as the DMA, making use of particles electrical mobility in an electric field. The primary difference is that the aerosol sample is introduced inside the sheath flow and charged particles are deflected outwards by the center electrode as opposed to the DMA where particles are attracted by the center collector rod. Furthermore, instead of a single monodisperse aerosol exit for subsequent particle counting via a CPC, differential mobility spectrometers comprise a stack of multiple collection electrodes, allowing to resolve the particle spectrum in the size range of 5-1000nm in a single scan. This makes it possible to measure particle size distributions in real-time at a data frequency of up to 10Hz. On the other hand, mobility spectrometers generally have a lower sensitivity and size resolution when compared to an SMPSTM (*Giechaskiel et al.*, 2014). There currently (as of April 2015) exist two commercially available systems that are widely employed for internal combustion engine derived particle research, specifically, the engine exhaust particle sizer (EEPSTM), model 3090 from TSI Inc. (*Johnson et al.*, 2004; *TSI Inc.*, 2011), and the fast particulate spectrometer (DMS), model DMS-500 from Cambustion Ltd. (*Reavell et al.*, 2002; *Cambustion Ltd.*, 2010).

Figure 2.15 shows a schematic cutaway drawing of the EEPSTM's measurement column. Particles enter the instrument through a cyclone separator with a 1 μ m cut-point to remove large particles, at a flow rate of 10lpm. The sample then flows through the charger area where a pair of corona-wire type unipolar diffusion chargers establish an unipolar charge distribution on the particles. The first charger is used to put a negative net charge onto particles in order to i) reduce the number of highly charged particles, and ii) prevent overcharging in the second stage charger where a predictable positive net charge is added onto the particles (*Johnson et al.*, 2004). The aerosol flow is then introduced inside the 40lpm, HEPA-filtered sheath flow into the particle sizing column through an annular gap near the center electrode

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Figure 2.15: Schematic diagram of measurement column of the EEPSTM spectrometer, model 3090, TSI Inc. (TSI Inc. 2011).

as depicted in Figure 2.15. The particle sizing column consists of an outer cylinder with a stack of 22 sensing electrodes that are electrically insulated from each other and are connected to sensitive electrometers, and a center electrode to which a high positive voltage is applied. The positively charged particles entering the sizing column are repelled by the center electrode and attain a trajectory towards the outer cylinder wall while being carried downwards in the sizing column by the sheath flow (TSI Inc., 2011). Similarly to the DMA, particles with high electrical mobility (i.e. small particles) are impacting on sensing electrodes in the upper part of the sizing column, while particles with low electrical mobility (i.e. large particles) are impacting with sensing electrodes further downstream (Johnson *et al.*, 2004).

Upon impaction of a particle with a given sensing electrode, their charge is transferred and the resulting current is measured and amplified by the electrometer (TSI Inc., 2011). An inversion algorithm is subsequently used

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to deconvolve the data and compensate for influencing parameters such as image charge and time delays in the sizing column. The former is caused by charged particles flowing close past a sensing electrode without actually impacting, whereas the latter is due to the time delay till impaction with the sensing electrode. Particles with low electrical mobility have to travel further down the sizing column however, originate from the same finite sample volume as particles with high electrical mobility that impact in the upper portion of the sizing column (*Johnson et al.*, 2004). Furthermore, the 22 electrometer readings are converted to 32 particle size bins that are equally spaced in logarithmic domain between 5.6 and 560nm.

Overcharging of agglomerates has been identified to be a common problem associated with DMS and EEPSTTM instruments (*Giechaskiel et al.*, 2014; *Awasthi et al.*, 2013; *TSI Inc.*, 2015). In particular, unipolar charging was observed to give agglomerates a larger charge than spherical particles of the same mobility diameter on the order of 20-50% depending on particle size (*Awasthi et al.*, 2013). This causes their mobility to increase in the electric field and effectively shifts them to smaller size channels which leads the particle size distribution to be biased towards a smaller count mean diameter and therefore, underestimating particles of larger size. Knowing the morphology of particles to be measured (i.e. spheres or agglomerates), this apparent bias can be addressed via correction algorithms in the instrument software (*TSI Inc.*, 2015).

Finally, *Zervas and Dorlhène* (2006) conducted a comparison between the EEPSTTM, CPC, and electrical low pressure impactor (ELPI, Dekati Ltd.) to measure exhaust particle numbers of a Diesel engine while sampling from both upstream and downstream DPF locations. The authors observed good agreement for all instruments when measuring in the high particle concentration environment upstream the DPF with the CPC performing best. However, for downstream DPF sampling *Zervas and Dorlhène* (2006) reported CPC and ELPI to give similar results while the EEPSTTM was generally measuring below its detection limit.

AVL Micro Soot Sensor - MSSTM

The micro soot sensor (MSS) from AVL List GmbH (*AVL List GmbH*, 2009) belongs to the family of photo-acoustic soot sensors (PASS). It's operating principle is based on the photo-acoustic effect first identified by *Bell* (1880) which describes the phenomenon of pressure waves generated by light-absorbing materials due to periodic heating and cooling. An aerosol stream containing

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particles is drawn into a thermodynamically stable measurement chamber where the particles are irradiated by an amplitude-modulated laser beam at 4000Hz (Schindler *et al.*, 2004; AVL List GmbH, 2009; Silvis, 2012) as depicted in Figure 2.16(left). The absorption of radiation by the particles causes their internal temperature to momentarily increase, whereas during the *off* state of the laser beam the particles internal temperature is again equilibrated via heat transfer with the surrounding gas. This periodic heating and cooling of the gas surrounding the particles generates pressure waves which are detected by sensitive microphones (Schindler *et al.*, 2004; AVL List GmbH, 2009). In order to enhance the acoustic wave, a standing acoustic wave is produced by means of a resonant cell as shown in Figure 2.16(right) and digitally processed using *lock-in* amplifiers to distinguish between actual particles and ambient acoustic noise (Silvis, 2012). The frequency of the measured *sound* wave with the microphone is proportional to the black carbon (BC) concentration of the sample stream.

Figure 2.16: (left) Operating principle of photo-acoustic soot measurement; (right) simplified schemata of a longitudinal resonant photo-acoustic cell; both AVL micro soot sensor™, model 483, AVL List GmbH, Graz Austria. (AVL List GmbH, 2009; Schindler *et al.*, 2004).

Schindler *et al.* (2004) describes that interference with other light-absorbing molecules such as NO₂ or water is minimized by selection of a laser beam wavelength specifically tailored towards the resonant vibration frequency of BC. Experimental results show that for example, 300ppm NO₂ in the sample stream may lead to an interfering response equivalent to $<5\mu\text{g}/\text{m}^3$ black carbon. Furthermore, the sensor response can be influenced by the type and thickness of condensed volatile material on the solid BC core (Giechaskiel *et al.*, 2014). On the other hand, Schindler *et al.* (2004) reports that adsorption of hydrocarbons and other transparent liquids will have a negligible influ-

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ence on the photo-acoustic response for volatile mass fractions below 85% of the total particle mass. Since particle properties may vary for different type of soot (e.g. spark, diffusion flame or diesel combustion generated soot) specific calibration factors for the different soot absorption coefficients will be needed (*Giechaskiel et al.*, 2014).

The AVL MSS has a lower detection limit of $5\mu\text{g}/\text{m}^3$ and a wide dynamic range up to soot concentrations of $50\text{mg}/\text{m}^3$ at a measurement frequency of 10Hz (*AVL List GmbH*, 2009). The instrument features a dilution and sample conditioning unit that is attached to the sample extraction probe allowing to dilute the sample directly at the extraction location and thus, prevent possible condensation issues in the heated sample transfer line to the measurement cell by dropping the partial pressures of the gaseous species. The MSS can be employed to sample from elevated pressure environments such as experienced upstream exhaust particulate filters due to a variable-orifice type pressure reduction valve integrated into the dilution unit. Periodic *zeroing* of the instrument with HEPA filtered air is conducted in order to offset contamination of the optical windows due to soot accumulation that effectively reduce the transmission of laser light into the measurement cell (*AVL List GmbH*, 2009).

A detailed discussion of the instrument design and evaluation is given by *Schindler et al.* (2004), whereas the instrument manual (*AVL List GmbH*, 2009) provides additional information about details of photo-acoustic signal processing and conversion to a soot mass concentration. A description of the historic evolution of photo-acoustic soot sensors can be found in *Eastwood* (2008).

Electrical Aerosol Detector - EAD

The operating principle of the electrical aerosol detector (EAD, TSI Inc., model 3070A) is based on diffusion-charging of particles with subsequent aerosol detection using an electrometer connected to a Faraday cage. The instrument measures an aerosol parameter referred to as *total aerosol length* in $[\text{mm}/\text{cm}^3]$. It reports the d^1 -weighing of particles which falls between number concentration and surface area, and can effectively be regarded as the number concentration multiplied by an average particle diameter (*TSI Inc.*, 2005). The EAD is capable of measuring data at 5Hz and has a wide dynamic range of $0.01\text{mm}/\text{cm}^3$ to $2500\text{mm}/\text{cm}^3$ ¹⁵ which corresponds to 0.002pA to 400pA. Figure 2.17 provides a schematic diagram of the EAD

¹⁵resolution of $0.01\text{mm}/\text{cm}^3$ or 0.001pA.

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and the respective sample flow paths. The particle laden sample flow enters through a cyclone separator with a $1\mu\text{m}$ cut-point and then splits into the charger flow and the remaining sample flow. The charger flow passes through an activated carbon and a HEPA filter in order to remove any solid and volatile particles before subsequently being ionized via a corona charger (i.e. at 2kV). In a counter-flow mixing chamber both streams, the free ions and aerosol sample, are mixed and the particles acquire charge by diffusion of ions onto the particle surface. Downstream the mixing chamber an ion-trap removes excess ions before the sample is directed into a Faraday cage containing a conductive filter connected to a sensitive electrometer to measure the retained charge carried by the particles.

Figure 2.17: Schematic diagram of measurement principle of the electrical aerosol detector, model 3070A, TSI Inc. (TSI Inc. 2005).

The response of the EAD towards particles was extensively studied by Jung and Kittelson (2005); Fissan *et al.* (2007) and Wilson *et al.* (2007), and results indicated a linear relationship between active particle surface area and the instrument signal. Furthermore, a study conducted by Shin *et al.* (2007) using a *sister instrument* of the EAD ¹⁶ reported no significant dependency of the diffusion-charging instrument towards particle materials and morphology.

¹⁶Nanoparticle Surface Area Monitor (NSAM, TSI Inc., model 3550) has the same operating principle and sampling path layout as the EAD, including counter-flow mixing chamber.

If the particle size distribution is known, the particle mean diameter can be computed and the instrument sensitivity can be specifically adjusted for the measured particle size.

2.4.3 Portable emissions measurement systems for PM/PN

PEMS development for PM quantification during on-road operation has been primarily driven by the heavy-duty diesel sector in recent years. Currently, there exist only four measurement equipment manufacturers that are offering commercially available instruments which are designed to measure particle matter mass emissions following U.S. EPA (CFR 40/1065, 2015) and EU regulations (EU 582/2011, 2011), including i) AVL List GmbH (M.O.V.E PM-PEMS); ii) Horiba® Inc. (OBS-TRPM); iii) Sensors Inc. (SemTech PPMD); and iv) Control-Sistem S.r.l. (Micro-PPS). Under the auspices of U.S. EPA's measurement allowance program, *Khalek* (2010) performed a comprehensive assessment of PM-PEMS marketed by AVL List GmbH, Horiba® Inc. and Sensors Inc. with regard to their measurement accuracy and repeatability. A similar test program was conducted in Europe with the European portable emissions measurement system evaluation program (*Bonnel et al.*, 2010; *Mamakos et al.*, 2011a,b; *Rubino et al.*, 2009), which evaluated the four commercially available PM-PEMS and reported that the instruments agreed to within $\pm 30\%$ of each other for particulate matter brake-specific mass emissions levels in the range of approximately 5mg/kWh, and exhibited individual differences of up to 120% at lower levels. It is essential to highlight that all PM-PEMS that are compliant with regulations, incorporate a filter media based particulate matter sampling approach for subsequent gravimetric analysis.

Sensors Inc.'s *proportional particulate mass device* (PPDM) measures PM using quartz-crystal microbalances (QCM), exhibiting a typical mass resolution of $\sim 2\text{ng}$. *Booker et al.* (2007) demonstrated on a 5400 miles long cross-country trip the suitability of the PPMD for in-use compliance PM mass measurements. Horiba®'s *on-board system for transient PM mass measurement* (OBS-TRPM) (*Wei et al.*, 2008; *Wei and Rooney*, 2010) is a combination of a proportional dilute sampling system for gravimetric PM sampling on 47mm filter media and real-time measurements of particle length [mm/cm³] (i.e. including soot, sulfates and volatile particles), which can be defined as the product of total number concentration and average particle diameter, by means of a diffusion-charging type sensor (i.e. electrical aerosol detector (EAD), model 3070A, TSI Inc.). The underlying assumption is that the mass accumulated

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on the filter is proportional to the PM length parameter as measured by the EAD, therefore, making the OBS-TRPM ultimately capable of calculating a quasi *real-time* PM mass concentration rate. The OBS-TRPM has shown to have similar or better repeatability compared to the constant volume sampling dilution tunnel serving as reference method (Wei *et al.*, 2008). AVL's M.O.V.E (model PM-PEMS 494) measurement system combines the AVL micro soot sensor, a photo-acoustic type soot sensor, with gravimetric collection of PM on filter media to account for the organic fraction and sulfates. A research study conducted by Silvis (2012) reported good correlations between the soot sensor augmented with the on-board gravimetric filter mass and the CVS reference method for engine dynamometer tests with a *cracked* DPF, thus higher soot levels. For measurements downstream of a functioning DPF, the author observed increased variability, possibly caused by measurement artifacts absorbed onto the on-board filter media. However, levels of variation were comparable to variability in the CVS reference method (Silvis, 2012).

Khan *et al.* (2012) evaluated three different PM-PEMS on a MY 2009 engine with diesel particulate filter, installed on a Class 8 tractor, in comparison to the regulated reference method for sampling total particulate matter from a CVS system (CFR 40/1065, 2015). In addition, a bypass valve was installed on the DPF allowing to route portions of the exhaust flow around the trap and thereby, simulating a cracked or damaged DPF resulting in a PM mass emissions rates of $\sim 25\text{mg/bhp-hr}$. Results indicated the photo-acoustic based PM-PEMS (i.e. AVL M.O.V.E PM PEMS) to perform best, exhibiting a linear regression slope of 0.9¹⁷ (i.e. with $R^2 = 0.88$) in comparison to the reference method measured during non-DPF regenerative conditions (Khan *et al.*, 2012). When augmented by the filter media sample accounting for the organic fraction and sulfates, the AVL M.O.V.E PM PEMS slightly over-predicted the total PM mass resulting in a regression slope with the reference method of 1.10 (i.e. with $R^2 = 0.87$). On the other hand, the QCM-based system from Sensors Inc. was reported to perform poorest (Khan *et al.*, 2012) resulting in a regression slope of 0.22 and 0.66 for an original and modified (i.e. upgraded by the manufacturer after analysis of initial results) PM-PEMS unit compared to the gravimetric reference method, respectively. Finally, Khan *et al.* (2012) observed that all PM-PEMS underperformed when sampling during DPF regeneration events with the best unit exhibiting a slope of 0.2. This was partly attributed to the shift in particle size distribu-

¹⁷regression results for measurements with the photo-acoustic sensor only; not corrected for organic fraction and sulfates retained on filter media.

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tion from $\sim 64\text{nm}$ to $\sim 13\text{nm}$ during the ongoing DPF regeneration (*Khan et al.*, 2012).

Giechaskiel et al. (2011) performed, as part of the European PEMS evaluation program, a comparison of real-time particle sensors, including Dekati ETaPS, Dekati Mass Monitor (DMM), AVL MSS, and TSI EAD (model 3070A) as well as DustTrak (model DRX8533) with regard to on-board particle number measurements following the particle measurement programme protocol (i.e. non-volatile particles $>23\text{nm}$). All candidate sensors and systems were verified against the standard gravimetric PM sampling method used for engine certification and type-approval. The authors highlight that the number based methods have the advantage of allowing for direct comparison with the certification limits of the number based particle regulations (i.e. Euro VI (EU 582/2011, 2011), and Euro 5/6 (EU 692/2008, 2008)). Finally, *Johnson et al.* (2009) evaluated the PMP methodology during on-road vehicle testing and observed a significant portion of particles in the size range below 20nm even though the sample stream was thermally treated according to PMP requirements, thus questioning the applicability of the 23nm lower cut-point for particle measurements, as discussed in Section 2.3.2.

With the introduction of the European total particle number emissions standard and with special regard towards the implementation of the *real-driving emissions* test procedure (EU G3/1515125/PE RDE/Draft, 2015) by 2017 in Europe, it became important to evaluate particle number based PEMS systems, short PN-PEMS *Riccobono et al.* (2014b,a). A study conducted by the European Joint Research Center *Riccobono et al.* (2014b,a) assessed the applicability and performance of five candidate PN-PEMS instruments¹⁸ that were all operating based on the diffusion-charging principle, for on-road particle number quantification. Controlled experiments were conducted for five different vehicles (i.e. GDI, gasoline port injection, diesel with DPF) over four cycles on a chassis dynamometer to compare the linearity of the PN-PEMS instruments with a reference PMP compliant (UN ECE/TRANS/505/Rev.7/Add.48, 2015) system installed to the CVS system. In addition, four of the PN-PEMS candidate instruments were evaluated during on-road tests while sampling from a GDI vehicle. Results indicated that 95% of all measurement points fall within $+100\%/ -50\%$ of the CVS PMP system. *Riccobono et al.* (2014a) conclude based on the data that diffusion-charging systems provide a promising alternative to CPCs for PEMS measurements.

¹⁸three of the instruments were available on the market, whereas the other two were prototype units under development as of 2014 when the study was conducted.

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Furthermore, the measurement variability of the systems under evaluation was estimated at 2, with the authors foreseeing it to be reduced to an allowance factor of 1.5 upon establishing standardized instrument designs¹⁹ and calibration procedures.

In the following the two most widely employed PM-PEMS instruments will be discussed in more detail, specifically, the AVL M.O.V.E PM-PEMS and the Horiba® OBS-TRPM. Both instruments were accepted by the U.S. EPA to be used for official in-use compliance testing of heavy-duty, on-road vehicles equipped with post-2010 engine and after-treatment technologies. It needs to be highlighted at this point that the primary difference between the two PM-PEMS is the methodology used to define the total particulate matter mass during a test interval or route. The AVL M.O.V.E PM-PEMS utilizes the *micro soot sensor signal as the primary metric* of carbonaceous soot emissions and corrects the sensor output signal with a correction factor obtained from the gravimetric (i.e. off-line weighing) analysis of PM sampled onto filter media which accounts for sulfates, sulfuric acid, ash and metal emissions as well as semi-volatile material that condenses or adsorbs onto the filter media at $47\pm5^{\circ}\text{C}$ (Silvis, 2012). On the contrary, the Horiba® OBS-TRPM uses the *gravimetrically evaluated particulate matter sampled on filter media as the primary measure* of PM mass, and uses the continuous EAD signal to correct it for PM mass emitted during *NTE events* only (Wei et al., 2008). A detailed comparison of the instrument specifications for both AVL M.O.V.E PM-PEMS and the new Horiba® OBS-ONE PM²⁰ can be found in Table A.3 in Appendix A.

Horiba® On-Board Transient Response Particulate Measurement unit

The Horiba® OBS-TRPM instrument has been specifically developed for the primary purpose of in-use certification of on-road heavy-duty diesel vehicles, as mandated by the U.S. EPA²¹ (CFR 40/86/N, 2011) and is designed to be used in conjunction with Horiba®'s OBS-2200 gaseous system (Wei et al., 2008; Wei and Rooney, 2010). The OBS-TRPM is a combination of a proportional diluted sampling system for gravimetric PM mass sampling on 47mm filter media and real-time measurements of particle length [mm/cm³]

¹⁹in terms of thermal treatment and dilution of the extracted exhaust sample.

²⁰the Horiba® OBS-ONE PM is the successor system of the OBS-TRPM that is scheduled to be commercially available by Q2 of 2016 (according to personal correspondence with Horiba®).

²¹the OBS-TRPM complies with requirements outlined in CFR 40/1065 (2015) for PM mass measurements, as well as EURO VI in-service conformity requirements for PM-PEMS.

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(i.e. including soot, sulfates and volatile particles), which can be defined as the product of total number concentration and average particle diameter, by means of a diffusion-charging type sensor (EAD, model 3070A, TSI Inc.). The underlying assumption is that the mass accumulated on the filter is proportional to the particle length parameter as measured by the EAD, therefore, making the OBS-TRPM ultimately capable of calculating a *quasi real-time* PM mass concentration rate. However, the gravimetric sampling component of the OBS-TRPM, requiring physical weighing of the filter media on a microbalance, makes *real-time* PM mass concentration information only available after post-processing of the measured data.

Figure 2.18 provides a schematic overview of the Horiba® OBS-TRPM system comprising four primary components, including a i) dilution tunnel; ii) filter holder box called *HF-47 OB*; iii) particle measurement box called *DCS*; and iv) flow control box referred to as *DLS*. A proportional sample is extracted through a 3/8" stainless steel J-type probe located downstream the OBS-2200 exhaust flow meter (EFM) unit. Proportionality is calculated based on the EFM signal and controlled by a series of fast acting piezo-valves and mass-flow controllers (MFC). Close-coupled to the sampling probe is a dilution unit (i.e. dilution tunnel) that uniformly introduced HEPA filtered dilution air. A 1/2" heated stainless steel line connects the dilution unit to the temperature controlled filter holder compartment (i.e. *HF-47 OB*) where the exhaust sample is first directed through a PM_{2.5} cut-point cyclone separator to remove particles bigger than 2.5µm (with a 50% efficiency at cut-point), and then through the filter media holder where particulate matter is retained on 47mm (i.e. diameter) Pallflex® Emfab™ filter membranes (TX40HI20WW, Pall Life Sciences, Pall Corp., USA) for subsequent gravimetric analysis. All components, including dilution tunnel, transfer line and HF-47 filter box are heated in order to maintain the filter-face temperature at constant 47±5°C. A constant slip stream is extracted from the sample flow before entering the filter media holder and routed to the diffusion-charger (i.e. EAD) for quantification of the particle length parameter. Dilution and sample flows for the entire system are controlled by the flow control unit (i.e. DLS).

The OBS-TRPM's footprint is relatively large as the system includes a total of three sub-devices and a power supply unit, each contained in a separate enclosure. This makes it involved and sometimes complex to install on test vehicles. While there is no problem to find sufficient space on a Class-8 tractor with *sleeper cabin*, installation of the system on trucks with *day cabin* or refuse haulers becomes more daunting. Application of the OBS-TRPM

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Figure 2.18: Schematic diagram of flow paths for OBS-TRPM PM-PEMS, model OBS-2000TRPM, Horiba® Instruments Inc. (Horiba Instruments Inc. 2010).

to light-duty testing might become even more challenging from a space perspective ²².

Horiba® will be introducing a successor system of the OBS-TRPM, called OBS-ONE PM (Horiba Instruments Inc., 2015), during the second quarter of 2016. The new instrument is depicted in Figure 2.19 and will comprise

²²see Thompson et al. (2014) as an example for installation of OBS-TRPM on a light-duty vehicle.

Figure 2.19: Gravimetric filter unit (*top*) and real-time PM measurement unit (*bottom*) OBS-One PM from Horiba® Instruments Inc. (Horiba Instruments Inc. 2015).

of a compact system containing the real-time particle sensor (i.e. EAD) in one and the heated gravimetric filter media holder and sample flow control equipment in a second enclosure. The OBS-ONE PM's operating principle is the same as was introduced for the OBS-TRPM and the instrument will work in concert with the gaseous OBS-ONE system to share exhaust flow meter data for proportional sample flow control. Detailed specifications for the OBS-ONE PM can be found in Table A.3 in Appendix A.

AVL M.O.V.E PM PEMS unit

The AVL M.O.V.E PM PEMS, model 494 (AVL List GmbH, 2012), allows for PM mass characterization by augmenting real-time soot measurements with an *artifact-adjusted on-board gravimetric reference* (Silvis, 2012) thus, making it possible to quantify *NTE event* specific PM mass rates in compliance with U.S. EPA requirements (CFR 40/86/N, 2011; CFR 40/1065, 2015). The PEMS unit comprises two enclosures, one for the photo-acoustic based micro soot sensor (i.e. MSS for M.O.V.E) and the second, housing the gravimetric filter module (GFM) as shown in Figure 2.20. As described in Section 2.4.2 the MSS measures carbonaceous soot on a real-time basis and serves as the primary estimation value of particulate matter mass for the AVL M.O.V.E PM PEMS system. The GFM allows to collect total particle matter samples in par-

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allel to the MSS on a 47mm filter media for subsequent gravimetric analysis and augmentation of the soot sensor measurement by particle contribution from volatile matter and sulfates (AVL List GmbH, 2012; Silvis, 2012).

A heated dilution cell is directly mounted to the sampling probe allowing to dilute the exhaust gas at the point of sample extraction. The dilution system offers the ability to select between proportional dilution as required for the European in-service conformity or constant dilution as needed for heavy-duty vehicle in-use compliance testing in the United States. The exhaust sample is then drawn through a heated sample line, maintained at constant 52°C, to a manifold located in the gravimetric filter module. From there the sample flow is diverted to the micro soot sensor and either the filter media holder (i.e. maintained at $47\pm5^\circ\text{C}$) or bypass filter, depending if the system is set to *measure* or *standby* mode. It has to be emphasized that contrary to the Horiba® OBS-TRPM, which only initiates sample collection onto the filter media upon entering the NTE zone and meeting all necessary NTE conditions, the filter media in the AVL PM-PEMS is continuously collecting PM samples throughout the entire test (i.e. in-use operation or route). Detailed specifications for the AVL M.O.V.E PM PEMS can be found in Table A.3 in Appendix A.

Figure 2.20: (left) AVL M.O.V.E PM PEMS unit, model 494; left top: AVL micro soot sensor, left bottom: gravimetric filter module (GFM) with holder for 47 mm filter media, right: control module and external signal input unit, AVL List GmbH, Graz Austria (AVL List GmbH, 2012); (right) AVL M.O.V.E PM PEMS unit installed in a transit bus (Sacramento Regional Transit) during on-road testing in Sacramento, CA (Summer 2013).

Upon post-weighing the filter media the real-time particulate matter mass emissions are calculated by multiplying the micro soot sensor measurement value by a *scaling factor* (SF). This factor is calculated as the ratio between the net mass collected on the filter media ($m_{PM,filter}$) over the integrated soot mass measured by the MSS as shown in Equation 2.24 (AVL List GmbH, 2012), where $c_{Soot,filter}$ is the real-time soot concentration in $[mg/m^3]$ and $\dot{V}_{filter}$ the sample flow rate through the filter media in $[m^3/sec]$. A study by *Silvis* (2012) presented different approaches to correct the real-time soot measurement for soluble organic matter and sulfates that contribute to the total particulate matter metric as measured according to the gravimetric reference method outlined in *CFR 40/1065* (2015). Proposed methods include hydrocarbon adsorption models based on gaseous hydrocarbon measurements and temperature dependent adsorption isotherms to estimate the soluble organic matter, whereas an SO_2 -to- SO_3 conversion model over catalyst surfaces (i.e. DOC or catalyzed DPF) as a function of exhaust gas temperatures was discussed to predict the sulfate fraction of total PM mass (*Silvis*, 2012).

$$SF = \frac{m_{PM,filter}}{\int c_{Soot,filter}(t) \cdot \dot{V}_{filter} \cdot dt} \quad (2.24)$$

2.5 Particle Sensors

Presently, known in-line PM sensor technologies can be categorized into five general subsets (*Johnson*, 2011), based on their detection principles, namely i) *conductivity* and ii) *capacitance* of collected soot, iii) *charge* measurements of particles carried out of a Faraday type volume or passed by a sensing electrode, iv) *radio frequency* and v) other more exotic principles not described in further details.

A non-collective electrical particle measurement sensor (Electrical Tail Pipe Sensor, ETaPS), making use of a corona discharge to impose an equal charge onto particles with subsequent measurement of the leakage current from the discharge was developed by Dekati Ltd. (Finland) (*Rostedt et al.*, 2009). A model characterizing the charging process was presented in order to correlate the current measured by the sensor to PM mass concentrations. It was shown that the particle charging efficiency is strongly dependent on exhaust flow rate, hence, the time each particle remains within the electrical field (i.e. residence time), and the physical size (i.e. diameter) of the particles under investigation (*Rostedt et al.*, 2009).

Osara et al. (2010) were studying the electrical charge carried by particles within the exhaust stream between two electrically conductive electrodes. While high voltage ($\sim 1\text{kV}$) was applied to one of the electrodes, the other served as sensing element. The method was also applied to investigate the natural charge imposed onto particles during the combustion process, depending on how far downstream the combustion chamber outlet the measurement was performed. A compact PM sensor was developed based on this principle and in-use measurements were performed with the sensor output signal being compared to AVL's micro soot sensor and an opacimeter (*Osara et al.*, 2010). PM concentration readings from the sensor were found to be affected by the exhaust flow rate, however, could be minimized by refining the sensor's housing and installation configuration.

An OBD PM sensor, having comparable dimensions as the widely employed oxygen sensors (Lambda sensor), operating based on the electrical conductivity principle, was introduced by Robert Bosch GmbH in early 2010 (*Ochs et al.*, 2010; *Baars*, 2010). The measurement was based on a drop in resistance due to the formation of electrically conductive soot paths between *two inter-digitated, comb-like* sensing electrodes, printed onto a ceramic surface (*Ochs et al.*, 2010). The sensor however, required periodic regeneration of the sensing element, by elevating the temperature with an internal resistance type heater, in order to burn off the deposited soot. Performance measurements included chassis dynamometer testing over the CARB unified driving cycle (UDC) as well as the U.S. FTP-75 cycle employing a partially deteriorated particulate filter to assess the sensors sensitivity. Additional test bench experiments with artificial soot showed a good reproducibility (*Ochs et al.*, 2010).

A PM sensor operating based on changes in electrostatic capacitance between two sensing electrodes was being development by NGK starting in 2011 (*Kondo et al.*, 2011). The sensor is based on a cyclical three stage process, including soot accumulation on the sensing element and periodic regeneration to burn off the deposited soot. First results were obtained from a sensor equipped vehicle operating over the new European driving cycle.

In order to directly estimate the amount of particulate matter trapped within a DPF substrate, *Sappok et al.* (2010) developed a radio frequency (RF) based method. The measurement principle makes use of the difference in dielectric properties caused by the deposition of soot and ash on the filter walls. The RF sensor was compared to pressure drop measurements over the DPF, engine-out PM measurements by means of a tapered element oscillating

micro-balance as well as gravimetric measurements of the actual DPF weight. Results reported the RF technique to be insensitive to exhaust flow changes. Furthermore, a limited comparison between conventional and PCCI combustion showed a non-appreciable influence of the PM composition (i.e. organic or elemental carbon) onto the RF measurement (*Sappok et al.*, 2010). A similar RF based measurement technique has been under investigation by *Fischerbauer et al.* (2010). This study reported a relationship between the DPF soot loading state and the RF signal, however, emphasizes that influences such as temperature and agglomeration of un-burnt hydrocarbons or water in the filter need to be investigated in further detail. Additional discussion regarding application of radio frequency methods to DPF loading state estimation can be found in *Nanjundaswamy et al.* (2015).

Sappok et al. (2015) discusses single and two-antenna RF measurement systems. The authors performed RF sensor validation over multiple loading and regeneration cycles, while comparing the sensor measurements to AVL MSS, Sierra BG3, and a smoke meter results. The radio frequency based sensor was observed to exhibit a response on the order of <1 second. DPF regenerations were carried out with both the OEM ECU and the RF-controlled approach. Results showed a 15-30% reduction in regeneration duration relative to the stock ECU controller. This is explained due to the fact that the RF controller directly monitors the PM levels inside the DPF during the duration of the ongoing regeneration event and terminates the HC dosing once the soot oxidation is completed as compared to the stock ECU controller that employs a time-based regeneration approach. Based on these results, *Sappok et al.* (2015) emphasize the potential of the RF method for fuel savings as a result of extended regeneration intervals and reduced regeneration duration relative to stock OEM controllers.

Additionally, *Sappok et al.* (2015) shows transient response of a two-antenna system while changing EGR rates in order to induce different engine-out soot levels. The RF signal is observed to qualitatively capture the changes in soot rates and follow closely the response of the AVL MSS and TEOM used as laboratory-grade reference instruments. Furthermore, accumulation of ash levels in the DPF were observed to correlate well with a frequency shift of the resonance frequency, allowing to estimate and track the ash loading of the DPF as a function of time or mileage (*Sappok et al.*, 2015).

Preliminary results for six different particle OBD sensors from program years 1 and 2 of the Particle Sensor Performance and Durability (PSPD) consortium research conducted at the SwRI was presented by *Khalek and*

Premanth (2015). The first year of the program concentrated on sensor performance, whereas the second year focused on sensor performance as a function of their durability. The selected exhaust parameters the sensors were evaluated over included, i) exhaust temperature (range between 200-500°C at sample zone); ii) exhaust velocity (range between 10-90 m/sec); iii) exhaust particle concentration, size distribution and chemical composition (three soot levels: 0.001 g/bhp-hr, 0.01 g/bhp-hr, 0.02 g/bhp-hr); and iv) duration of engine operation (i.e. *short term* operation = few days, *long term* operation = 1400 hours $\approx$ equivalent to 50,000 miles). The 50,000 miles of accelerated soot exposure was described to be equivalent to 520,000 miles of operation assuming a fully functional DPF and average soot levels of 0.001 g/bhp-hr (remember that the applicable OBD threshold is 0.03 g/bhp-hr).

Additionally, the sensors under evaluation were also exposed to increased ammonia concentrations (i.e. $\sim$ 500 ppm) and elevated exhaust gas temperatures (i.e. 700°C) for up to 8 hours. *Khalek and Premanth* (2015) concluded that the real-time sensors response to soot compared *reasonably well* to AVL's MSS, which served as reference instrument, and the change in resistance of accumulation-type sensors correlated with integrated MSS concentrations. The primary issue identified with all sensors was the variability of their response during steady-state engine operating conditions (*Khalek and Premanth*, 2015). Errors in determined soot levels relative to the reference instrument (i.e. AVL MSS) ranged from $\pm 60\%$ down to $\pm 20\%$ at the 1 g/m³ and 20 g/m³ soot concentration levels, respectively.

Table A.1 in Appendix A provides a comprehensive list of particle sensor technologies currently available or being investigated at different institutions. The table i) identifies the respective sensor operating principle; ii) provides contact information within the companies or research institutions; iii) lists published research regarding each sensor; and iv) presents limited results.

2.5.1 Measurement applications for PM/PN sensors

There exist three primary areas of application for particle sensors related to internal combustion engines and after-treatment systems, namely, i) after-treatment efficiency monitoring as integrated part of the vehicle OBD structure; ii) active control of combustion and DPF regeneration strategies; and iii) for in-use emissions compliance monitoring or during particle number emissions certification in the laboratory. A list of specific sensor requirements for each of the three areas is given below.

After-treatment monitoring - OBD application

- measurement downstream DPF
- monitoring of DPF filtration efficiency
- detection of partial or complete DPF failure
- operating in low particle concentration environment during regular operation and experiencing increased concentrations during DPF regeneration events
- sensor requires high sensitivity and low detection limit
- sensor needs to withstand increased exhaust gas temperatures in excess of $\sim 600^{\circ}\text{C}$ during DPF regeneration events
- exhaust stream includes semi-volatile particles

Combustion and DPF regeneration control

- measurement upstream DPF
- high soot concentration environment
- primarily solid carbonaceous particles and metal particles from engine wear and lubrication oil combustion
- sensor requires wide dynamic range of operation

Certification and in-use emissions compliance testing

- sensor requires high accuracy and sensitivity
- operating in low particle concentration environment during regular operation and experiencing increased concentrations during DPF regeneration events
- sensor should offer number and mass based measurement capabilities

2.6 Diffusion Charging Principle and Theory

Unipolar diffusion charging was extensively studied by Liu and Pui, 1975; Pui 1976, Whitby 1976 (*Lehtimäki*, 1983). The average charge per particle depends on the particle size (d_p) and the product $N - t$, where N is the ion concentration in the charging region and t the charging time. Particle losses,

specifically for particles below $0.1\mu\text{m}$ are taken into account by a loss factor g_{d_p} (Lehtimäki, 1983).

The *Knudsen number* is defined as the dimensionless ratio between the mean free path (λ , [m]) of the carrier gas and the particle diameter (d_p , [m]) as shown in Equation 2.25. The mean free path for air is defined by Equation 2.26, with R being the universal gas constant in [J/(mol·K)], N_A the Avogadro's number ($6.0221 \times 10^{23} \text{mol}^{-1}$), d_m the collision diameter for air molecules ($3.6678 \times 10^{-10} \text{m}$), and P_g and T_g the carrier gas pressure in [Pa] and temperature in [K], respectively (Hinds, 1999). With regard to diffusion-chargers it is of interest to calculate the Knudsen number based on the mean free path of ions. For positively charged ions Adachi *et al.* (1985) provides Equation 2.27 to calculate the mean free path, where Z_{ion^+} is the electrical mobility of positive ions ($1.4 \times 10^{-4} \text{m}^2/\text{Vs}$), M_{ion^+} the molecular weight of positive ions (0.109kg/mol , (Vohra, 1969), referenced by Adachi *et al.* (1985)), M_{air} the molecular weight of air (0.02897kg/mol), e the elementary charge ($1.60217657 \times 10^{-19} \text{C}$), and k the Boltzmann constant ($1.38064852 \times 10^{-23} \text{m}^2 \text{kg}/(\text{s}^2 \text{K})$).

$$Kn = \frac{2 \cdot \lambda}{d_p} \quad (2.25)$$

$$\lambda_{air} = \frac{R}{\sqrt{2} \pi N_A d_m^2} \cdot \left(\frac{T_g}{P_g} \right) \quad (2.26)$$

$$\lambda_{ion^+} = 1.329 \cdot \frac{Z_{ion^+}}{e} \sqrt{\frac{k T M_{ion^+} M_{air}}{(M_{ion^+} + M_{air}) N_A}} \quad (2.27)$$

Figure 2.21 depicts the Knudsen number as a function of particle diameter for mean free paths of both air and positively charged ions at ambient temperature of 20°C as well as the operating temperature of the *Pegasor Particle Sensor* of 200°C . The Knudsen number is seen to increase by about 61% and 27% when carrier gas temperatures are increased from 20 to 200°C for air and positive ions, respectively. Marquard (2007) discusses the three different regimes for unipolar diffusion-charging, namely, i) the *continuum regime* for $Kn \ll 1$ or $Kn < \sim 0.2$ as defined by Jung and Kittelson (2005); ii) the *free molecular regime* for $Kn \gg 1$; and iii) the *transition regime* for $Kn \approx 1$. The particle size range between 30 to 150nm is of specific interest as the majority of combustion engine derived particles, in terms of number and surface area,

Figure 2.21: Knudsen number (Kn) as a function of particle diameter (d_p) for mean free path of air and positive charged ions; data plotted for ambient temperature of 20°C and operation temperature of *Pegasor Particle Sensor* (i.e. 200°C); pressure $P = 101.325\text{kPa}$.

fall into this range (Harris and Maricq, 2001; Jung and Kittelson, 2005) which coincides with the *transition regime* according to the Knudsen number.

Figure 2.22 shows the calculated total surface area (S_{tot}) as a function of particle diameter for the different Knudsen regimes. The *Fuchs surface area* (Gäggeler et al., 1989), which is based on particle diffusion, was calculated according to Equations 2.4 through 2.6 for the free molecular, the continuum, and the transition regime (Matter Engineering AG, 2001). The coefficients for the Cunningham correction factor were given by Hinds (1999) as $A = 1.17$, $Q = 0.525$, and $\beta = 0.78$. The surface area expression for the free molecular regime is identical to the geometric surface area (i.e. $\pi \cdot d_p^2$). Figure 2.22 depicts both the continuum regime and the transition regime for a mean free path of air (λ_{air} , solid blue line) and positive ions (λ_{ion+} , dotted blue line). Additionally, the total active surface area (Siegmann and Siegmann, 2000), which depends on ionic diffusion, is shown in Figure 2.22 and was calculated according to Equation 2.28 given by Heitbrink et al. (2008) (i.e. referenced in Ku (2010)) for particles in the entire size range. The Cunningham slip correction (C_c) factor is given by Equation 2.29, whereas the scattering parameter (δ) by Equation 2.30. The latter is a measure of the tendency of a gas molecule to bounce off from the surface of a particle (Ku, 2010) and can

2.6. Diffusion Charging Principle and Theory

Figure 2.22: Fuchs surface area for free molecular, transition and continuum regimes along with active surface area; mean free paths for air and positive ions; pressure $P = 101.325 \text{ kPa}$, and temperature $T = 473.15 \text{ K}$ (i.e. representative of *Pegasor Particle Sensor* operating temperature).

be estimated based on the accommodation coefficient α for air of 0.91, described by *Heitbrink et al.* (2008). In the free molecular regime Equation 2.28 becomes equivalent to the geometric surface area.

$$A_{active} = \frac{3\pi\lambda d_p}{C_c \cdot \delta} \quad (2.28)$$

$$C_c = 1 + \frac{2\lambda}{d_p} \left[1.257 + 0.4 \exp \left(-1.1 \frac{d_p}{2\lambda} \right) \right] \quad (2.29)$$

$$\delta = \frac{2}{3} \left(1 + \frac{\pi}{8} \alpha \right) \quad (2.30)$$

Chapter 3

Particle Sensor - Pegasor Particle Sensor

Through the compilation of research papers that discuss and synthesize ideas concerning current and possible future particle matter measurement philosophies, *Swanson et al.* (2010) concluded that a measurement method based on diffusion-charging techniques is the most promising with consideration in a future regulatory framework. In light of that, and considering the extensive number of published literature (see Chapter 2.5 and 2.6) demonstrating diffusion-charging type sensors exhibit a proportional signal towards particle surface area they could be regarded advantageous with respect to their possibility to infer either particle number (i.e. zeroth moment) or particle mass (i.e. third moment) concentrations directly from the sensor's measurement signal. Such flexibility is particularly of interest with regard to recently introduced emissions regulations (e.g. Euro VI, and Euro 5) that require the simultaneous measurement of both mass and number based emissions factors, since it would allow to use one single instrument for quantifying both components, thus, effectively reducing measurement complexity and associated costs.

The diffusion-charging type particulate matter sensor selected for this study was developed by Pegasor (Oy) Ltd. (Finland) (*Pegasor Ltd.*, 2011) and will be, hereinafter, referred to as the *Pegasor Particle Sensor* (PPS). Initial research and development of this sensor technology was conducted by researchers at Tampere University of Technology (Finland) and Dekati Ltd. (Finland) (*Rostedt et al.*, 2009; *Gautam et al.*, 2010b) who marketed the sensor as *Dekati Exhaust Tailpipe Particle Sensor* (ETaPS) (*Dekati Ltd.*, 2008). In 2008 Pegasor (Oy) Ltd. was founded and further developed and refined the design and

Table 3.1: *Pegasor Particle Sensor* models and respective serial-numbers of units employed during this study (sensor version will serve as unique identifier).

Sensor Model	PPS-M1			PPS-OBd
Sensor Version	V1	V2	V3	V1
Sensor S/N	1000	4288 4289	4667 4668	610241 610242
Evaluation Period	2010-2011	2011-2014	2014-present	2014-present

measurement principle of the particle sensor that became known as the *Pegasor Particle Sensor* from that point onwards. Discussion of the sensor technology and presentation of selected results demonstrating its response to heavy- and light-duty diesel emissions can be found in a series of publications (Ntziachristos *et al.*, 2009; Besch *et al.*, 2010; Ntziachristos *et al.*, 2011; Lanki *et al.*, 2011; Gensdarmes *et al.*, 2011; Besch *et al.*, 2011b,c; Beck *et al.*, 2012; Karim, 2012; Ntziachristos, 2012; Ntziachristos *et al.*, 2012; Wachtmeister, 2012; Ntziachristos *et al.*, 2013a; Tikkanen *et al.*, 2013; Amanatidis *et al.*, 2013; Ntziachristos *et al.*, 2013b; Maricq, 2013; Ahlvik and Rajagopal, 2014; Tikkanen *et al.*, 2014; Amanatidis *et al.*, 2014; Rostedt *et al.*, 2014; Ce-Cert, 2015). More recently, the *Pegasor Particle Sensor* has been adapted for real-time outdoor air quality monitoring as part of the *Pegasor Urban Air Monitoring System* (PUAMS) (Pegasor Ltd., 2015). It has to be emphasized at this point though, that the discussion presented in this document will solely focus on the application of the PPS to measurements of internal combustion engine derived particle emissions.

The individual *Pegasor Particle Sensors* employed during the course of this study are listed in Table 3.1 along with the sensor serial-numbers (S/N) and approximate time period of their evaluation. Version V1 of the PPS was a pre-production prototype, V2 the first commercially available version, and V3 a refined version of V2 featuring primarily upgraded electronics components and electrometers with improved sensitivity. Furthermore, starting with version V2 the sensor included a heater element allowing to control and maintain the temperature of the internal sample paths and components in order to reduce possible thermophoretic losses. Also, maintaining the exhaust sample at an elevated and constant temperature can effectively prevent condensation and nucleation phenomena of soluble matter in the sample stream that could otherwise lead to a change in particle size, concentration, and composition, and introduce possible sample artifacts.

3.1 Particle Sensor Technology Description and Operating Principle

The operating principle of the *Pegasor Particle Sensor* is based on diffusion-charging of particles and subsequent measurement of the current leaving the sensor with the charged particles (Tikkanen and Ntziachristos, 2009; Tikkanen, 2009). This is customarily referred to as the *escaping current* principle. The basic theory of directly measuring the current escaping with charged particles, rather than measuring the charge carried by particles after collection on a screen, was first discussed by Lehtimäki (1983). A detailed technical schematic of the PPS is shown in Figure 3.1 and depicts the main sensor components as well as the sample gas flow paths, comprising: i) a pre-cut cyclone to prevent the sensor from fouling due to large particles; ii) a corona charger as ion source for particle charging; iii) an ejector-type sample pump; iv) an ion trap to remove excess ions or act as a simplified particle mobility analyzer; and v) a wide-dynamic range electrometer. An illustration of the actual sensor is provided in Figure 3.2¹.

Dry, HEPA filtered dilution air is supplied at about 22psig (~ 1.52 bar) to an unipolar corona charger using a $50\mu\text{m}$ Tungsten wire at $\sim 2\text{kV}$ and $5\mu\text{A}$ to produce ions. The pressurized dilution air, carrying the unipolar ions, then draws raw exhaust gas through an ejector-type sampling pump into a mixing chamber, where the ions are turbulently mixed with the exhaust sample and thereby charges the particles by a diffusion-charging process. The fact that the ion-containing pump flow is mixed extremely rapidly prior to the ejector throat enables efficient particle charging in a small volume and thus, resulting in a rapid response time of the sensor. On the other hand, the resulting relatively low residence time for the charging process will affect the charging efficiency of particles (Rostedt et al., 2014). Due to the ejector pump, the sample-flow rate and sensor response is independent of the exhaust flow conditions around the sampling inlet (Ntziachristos et al., 2013b; Wachtmeister, 2012). Furthermore, since the sample gas flow is controlled by means of a critical flow orifice in the ejector pump it becomes therefore, primarily a function of the supplied dilution air pressure (Lanki et al., 2011).

An electrostatic precipitator (i.e. ion trap) installed downstream of the mixing chamber removes excess ions that escaped the charging zone and prevents them from leaving the sensor eventually contributing to the charge

¹the pictures shows version V1 of the PPS-M1 sensor; version V1 is visibly only distinguishable from versions V2 and V3 by the missing connection for the internal heater.

3.1. Particle Sensor Technology Description and Operating Principle

Figure 3.1: Pegasor particle sensor, model PPS-M1, measurement principle with sample gas and dilution air flow paths. Figure taken from *Tikkanen and Ntziachristos (2009)*.

measurement. The ion trap is designed in an annular shape as depicted by Figure 3.1 and the electrical field strength can be altered through the sensor's software interface or through communication via AK protocol. A salient feature of the ion trap is that by changing the electrical field the lower cut-point of trapped ions or particles can be changed allowing for it to be used as a simplified zeroth-order (i.e. number) mobility size analyzer by virtue of modulating the trap voltage (*Rostedt et al., 2009, 2014*). *Ntziachristos et al. (2013a)* showed that the sensitivity to smaller particles decreases as a function of increasing trap voltage, allowing to more precisely measure mass concentrations. This means that increasing the trap voltage decreases the sensitivity of the mass response to the actual particle size distribution. Analysis of results showed that a trap voltage of 400V provided best response for both number and mass calibration coefficients (*Ntziachristos et al., 2013a*). Computational fluid dynamics (CFD) analysis by *Rostedt et al. (2014)* indicated that the flow field around the ion trap is turbulent. Based on that, the authors concluded that the turbulence will lead to a less steep collection efficiency curve, and thereby, limiting the size resolution of the ion trap when being used as mobility analyzer.

Finally, the charge carried away by particles is measured using a built in wide-dynamic range electrometer (*Tikkanen, 2009*). The corona charger, higher-voltage power supply, and the ion trap are located inside a Faraday cage which is isolated from the ground and floats at the input of the electrometer (i.e. virtual ground) (*Lehtimäki, 1983; Rostedt et al., 2014*). An operational amplifier with capacitive feedback circuit (*Rostedt et al., 2014*) is used

3.1. Particle Sensor Technology Description and Operating Principle

Figure 3.2: Pegasor Particle Sensor, model PPS-M1 V2 (Picture: Marc C. Besch, 2012).

as a high sensitivity electrometer to measure the leakage current between the isolated virtual ground and ground potential. According to *Lehtimäki* (1983), by carefully filtering the disturbances caused by the high-voltage power supply, it is possible to reach current measurement sensitivities in the *femto* ampere range (i.e. below 10^{-14} Amps). The measured current signal is amplified and filtered by the internal electronic control unit of the sensor and output either as current or voltage value (i.e. via a $3.33\text{k}\Omega$ shunt resistor).

The sensor was designed as a flow-through device and therefore does not involve collection or contact with particles in the exhaust stream, which is especially advantageous for long-term stability and operation without frequent maintenance; hence, best suited for in-use application. Indeed, soot deposition on electrical insulators might cause leakage currents offsetting the measurement and contamination of the corona wire will negatively affect ion production (*Lanki et al.*, 2011). Furthermore, *Rostedt et al.* (2009) showed that charging efficiency of the particles is strongly dependent on the exhaust flow rate which ultimately influences the $N_I - t$ -product. Thus, changes in exhaust flow rate would translate into alterations in residence time the particles remain inside the charging environment, therefore, affecting the charge they can acquire. The PPS however, was designed in such a way that a constant slip stream of exhaust sample is extracted from the exhaust transfer pipe and thus, flow rates and thereby residence times for the particle charging process remain constant for a given sample flow setting (i.e. dilution air pressure settings and selected orifice plate) (*Tikkanen and*

3.1. Particle Sensor Technology Description and Operating Principle

Ntziachristos, 2009; Rostedt et al., 2014).

In order to reduce particle losses within the sample path of the sensor due to thermophoresis as well as prevent condensation of volatile components within the sensors, the PPS includes temperature controlled heating elements surrounding the internal sensor components and maintaining them at constant 200°C. No internal heating was available for version V1 of the sensor (i.e. pre production prototype) and therefore, the sensor was wrapped in resistive heated tape in conjunction with a PID controller and insulation material. *Ntziachristos et al. (2013a)* showed that the sensor response coefficients for particulate matter mass and number concentrations are affected by exhaust sample gas temperature and are decreasing as a function of increasing temperature. This was attributed to thermal effects onto the charger efficiency and flow dynamics. In order to suppress the temperature dependency of the calibration coefficients, *Ntziachristos et al. (2013a)* suggest to use a short heated sample line between the sample extraction probe and the sensor inlet in order to stabilize and condition the sample to a constant temperature of 200°C.

Depending on the application, the *Pegasor Particle Sensor* is available for two different temperature ranges. All sensors employed during the course of this study were capable of withstanding operational gas temperatures of up to 850°C (high range), hence, well suited for post DPF measurements during active or semi-active regeneration events. The PPS exhibits an upper particle size detection limit of approximately 2.5µm (*Pegasor Ltd., 2011*), whereas the lower limit depends on the actual voltage settings of the ion trap. However, according to the manufacturer (*Pegasor Ltd., 2011*), the sensor should be capable of measuring particles in the below 10nm range if the ion trap is set so that only excess ions are being removed due to their high mobility. Table 3.2 provides an overview of PPS-M1 specifications for sensor version V3.

Figures 3.3(*left*) and 3.3(*right*) show a picture and a schematic drawing, respectively, of the PPS positioned inside the enclosure that provided thermal insulation from the surroundings during chassis dynamometer and on-road testing. Sample inlet and outlet ports are visible in the bottom right corner of Figure 3.3(*left*), whereas the pressure transducer to monitor dilution air supply pressure can be seen in the upper part of the picture. The sensor is insulated using a cellular glass based pipe insulation jacket.

3.1.1 Application of PPS to various particle measurements

Lanki et al. (2011) investigated the applicability of the *Pegasor Particle Sen-*

3.1. Particle Sensor Technology Description and Operating Principle

Table 3.2: Specifications of *Pegasor Particle Sensor*, model PPS-M1, V3 (*Pegasor Ltd.*, 2011).

Parameter	Value/Description
Min. detectable particle size	min. few [nm] up to 23nm ^a
Max. detectable particle size	2.5μm
Particle concentration range (high conc. version)	10μg/m ³ to 500mg/m ³
Particle concentration range (high sensitivity version)	1μg/m ³ to 250mg/m ³
Max. electrometer range	6.82x10 ⁶ fA
Dimensions [dia x L]	51mm x 200mm
Response time	10ms
Sampling rate	up to 100Hz (default 10Hz)
Data communication	RS 485
Environmental conditions	<50°C, IP45

Figure 3.3: (left) Picture of enclosure used for Pegasor Particle Sensor, model PPS-M1, during on-road and chassis dynamometer experiments; (right) schematic diagram of PPS-M1 enclosure.

for particle concentration monitoring in a workplace environment, and observed good agreement of the PPS signal in comparison to both an electrical low pressure impactor (ELPI, DetkaiTM Ltd., Finland) and an electrical aerosol detector (TSI Inc.). It has to be noted that both reference instruments used during this study rely on unipolar diffusion-charging, and thus employ the same measurement principle as the PPS which explains the close agreement observed by *Lanki et al.* (2011). As part of this project, the authors studied the effects of changing trap voltage onto three polydisperse aerosols with count mode diameters of 8-15nm. Results show a reduction of ~76% and ~98% in 15nm and 8nm diameter particles, respectively, at a trap voltage of 400V compared to 0V. The relationship between trap voltage and particle removal efficiency was observed to follow an exponential decay

3.1. Particle Sensor Technology Description and Operating Principle

function. Similar results were obtained by *Ntziachristos et al.* (2013a) showing a 60% and 95% reduction for 10nm particles at 100V and 400V, respectively. This allows, depending on the voltage applied, not only to remove excess ions but also to trap particles of a certain mobility diameter analogous to a cyclone-type particle separator. Thus, increasing the voltage on the center electrode leads to a stronger electrical field causing particles to deflect and impact inside the PPS, and thereby escape from being counted. This particle removal mechanism can be utilized towards inducing a lower particle cut-point similar to the 50% counting efficiency for particles of 23nm in an ultrafine particle counter as required by the PMP method (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015).

The *Pegasor Particle Sensor* has the advantage of not having a very limited range requirement for sample inlet temperatures (i.e. up to $\sim 800^{\circ}\text{C}$), thus allowing for direct measurement of raw exhaust gases and thereby, ultimately reducing the magnitude of size dependent particle losses as occurring in a sampling and dilution system. However, due to the observed temperature dependency of the sensor response *Ntziachristos et al.* (2013b) suggested the use of a $\sim 1\text{m}$ long heated line section, between the sample extraction probe and the PPS inlet, and to maintain temperatures of both the heated line as well as the sensor internal heater at constant 200°C . This allows for the exhaust gas temperature to stabilize before reaching the sensing region of the PPS. Furthermore, maintaining the exhaust sample temperature at elevated levels has the advantage of reducing the probability for volatile and semi-volatile components to condensate and adsorb on solid particles or possibly nucleate and form measurement artifacts. Indeed, *Ahlvik and Rajagopal* (2014) mentioned that the PPS is compatible with the PMP protocol² given the condition that there would be no cold-spots and the sample line and sensor are heated to constant 200°C . However, this is below the recommended temperatures for the first stage dilution (i.e. $150\text{--}400^{\circ}\text{C}$) and evaporation tube (i.e. $300\text{--}400^{\circ}\text{C}$) prescribed for the volatile particle remover according to the PMP protocol. A study by *Giechaskiel and Drossinos* (2010) experimentally investigated the removal efficiency of tetracontane particles³ at different VPR wall temperatures. Results indicated that 50nm volatile tetracontane particles are removed with $>90\%$ efficiency at 200°C , however, removal effi-

²according to correspondence with the Joint Research Center (JRC) of the European Union in Ispra, Italy.

³tetracontane ($\text{CH}_3(\text{CH}_2)_{32}\text{CH}_3$) is used to demonstrate volatile particle removal efficiency according to the PMP protocol (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015); $>99\%$ reduction in concentrations of monodisperse tetracontane particles with a diameter of $\leq 30\text{nm}$ and inlet concentration of $\leq 10^4\text{#/cm}^{-3}$ has to be achieved.

3.1. Particle Sensor Technology Description and Operating Principle

ciency was observed to rapidly drop for particles $>50\text{nm}$ down to $\sim 10\%$ for 100nm particles. Increasing the wall temperature to 250°C resulted in $>95\%$ removal efficiency for particles up to 100nm , and increased further to $>99\%$ at 300°C (Giechaskiel and Drossinos, 2010). On the other hand, it has to be considered that the PMP method is designed to sample from an already diluted, and therefore *cooler*, sample stream from either a CVS dilution tunnel or a partial-flow dilution system (UN ECE/TRANS/505/Rev.7/Add.48, 2015) as opposed to the PPS sampling from the raw exhaust at elevated gas temperatures. It has been shown that particle nucleation phenomena are strongly driven by exhaust gas dilution and cooling (Khalek *et al.*, 1999) which does not occur when the sample is extracted directly from the exhaust stack (or transfer line). As described, the PPS requires a small amount of pressurized dry air (i.e. dilution ratio $\sim 1.4\text{-}2.5$) to drive the sample flow via the internal ejector diluter, however, the dilution process is assumed to be rapid and without the necessary residence time required to form artifacts before particle charging and measurement occurs.

Most importantly though, it needs to be understood that the diffusion-charging based measurement principle will respond to every particle that can carry a charge, including volatile material that has condensed or nucleated as well as liquid droplets. The latter includes water vapor condensates forming inside the PPS measurement cell during *cold* sampling (Amanatidis *et al.*, 2014). This makes the sensor response dependent to the sampling location if heated line and sensor heater temperatures are not selected appropriately. However, if maintained at constant 200°C , studies have shown good agreement⁴ between measurements with the PPS sampling directly from the tailpipe versus sampling from the CVS dilution tunnel with the latter having a higher propensity for adsorption and nucleation phenomena of volatile matter due to the associated dilution process (Amanatidis *et al.*, 2013, 2014). Similarly, Tikkanen *et al.* (2013) found good agreement between a PPS measuring directly from the exhaust stack and a second PPS, equipped with a catalytic stripper (CS) to remove volatile and semi-volatile particles, sampling from the diluted exhaust gas in a CVS dilution system for both light and heavy-duty engines. There is a possibility that a future version of the PPS might be heated to 300°C and equipped with a catalytic stripper (Tikkanen *et al.*, 2013) (e.g. CS was installed prior to PPS during experiments by Tikkanen *et al.* (2013); Amanatidis *et al.* (2014)) to oxidize volatile components.

⁴PPS at tailpipe vs. PPS at CVS: Amanatidis *et al.* (2013) slope = 1.05, $R^2 = 1.00$; Amanatidis *et al.* (2014) slope = 1.06, $R^2 = 0.99$; both from light-duty vehicle testing on chassis dynamometer.

3.1. Particle Sensor Technology Description and Operating Principle

In light of the above observations it can be concluded that, even though the PPS sampling method for particle number concentration measurements does not strictly comply with recommendations outlined in the European regulation for PN measurements (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015), it nonetheless follows the spirit of the PMP protocol of measuring *only non-volatile particles of size larger than 23nm (and smaller than 2.5 μ m)*, given the heated line and sensor temperatures are maintained at 200°C and the trap voltage is selected accordingly. However, it has to be strongly emphasized that the PPS does not directly measure particle number concentrations but rather infers particle number counts from a charge measurement as opposed to the ultrafine particle counters required by the PMP protocol that are based on optical counting of individual particles after they were allowed to grow to a detectable size in a saturated Butanol or water environment.

Results by *Gensdarmes et al.* (2011) indicated that response times only slightly increase from 0.19 to 0.24sec if a 1m (i.e. with diameter of 6mm) long sampling line is added to the inlet of the sensor. *Ntziachristos et al.* (2013a) reports a t_{90} response time of 0.4sec, with the difference to *Gensdarmes et al.* (2011) most likely arising due to differences in actual sample flow rates employed during the experiments, which vary for each sensor as will be discussed in Section 3.2. Additionally, *Gensdarmes et al.* (2011) investigated sensor response and acquisition rate effects as a function of particle size and concluded that particle size distribution and concentration have no effect on the response time of the PPS. Also, the data acquisition frequency (i.e. 10Hz vs. 100Hz) was not observed to influence the response time of the sensor. However, *Gensdarmes et al.* (2011) noticed a significant difference in response time between step increase (~ 0.18 sec) versus decrease (~ 0.23 sec) in particle concentration levels. No possible explanation was provided for the observed discrepancy in step response though.

3.1.2 On-board diagnostic version of the Pegasor Particle Sensor - PPS-OBd

Pegasor (Oy) Ltd. (Finland) developed in parallel to the PPS-M1 version of the *Pegasor Particle Sensor* a miniaturized version of the sensor technology targeted at OBD application, referred to hereinafter as *PPS-OBd* sensor (*Pegasor Ltd.*, 2014). The operating principle remained the same as for the PPS-M1 as well as did all the internal components that solely differ by arrangement/packaging and dimensions. Analogous to the PPS-M1, the PPS-OBd requires pressurized dilution air supply at 14.5psig (~ 1.0 bar) to

extract a constant amount of exhaust sample via a ejector-type pump. Figure 3.4 shows a picture of the PPS-OBD sensor on the left as well as a picture of the sensor installed to the 5" diameter exhaust stack of a Class-8 tractor during on-road testing. It has to be emphasized that the present study will not discuss any results from the PPS-OBD sensor, and for more information the reader is directed to other publications.

Figure 3.4: (*left*) Pegasor Particle Sensor, model PPS-OBD V1; (*right*) PPS-OBD V1 sensor installed in the exhaust transfer pipe of a Cummins ISL-G natural gas engine equipped Class-8 tractor (downstream three-way catalyst); data collection as part of *Cross-California project* sponsored by CARB and South Coast AQMD, Sacramento, CA (December 2014).

3.2 Particle Sensor Flow Calibration

Experiments conducted by *Ntziachristos et al.* (2013b) indicate a non-linear sensor response to changes in sample flow rates, with the sensor calibration coefficients reducing as a function of increasing sample flow rates. It is hypothesized that particle losses in the charging region as well as particle retention in the trap region due to a change in residence time might give rise to the observed non-linear behavior. *Ntziachristos et al.* (2013b) suggest that altering the trap voltage in accordance with the sample flow rate could decrease the sensor's sensitivity to sample flow changes. Similarly, in a comparison between the PPS and the AVL MSS and AVL particle counter (APC), *Beck et al.* (2012) showed a positive linear relationship between dilution air pressure and an increase in sensor response. For example, when pressure was increased from 14.5psig to 29psig, the sensor response was observed to increase by $\sim 37\%$. A computational fluid dynamics simulation of the PPS was conducted by *Rostedt et al.* (2014) in order to understand ejector pump performance, turbulent flow patterns, as well as diffusional losses inside the

sensor by employing a SST- $k-\omega$ turbulence transfer model. The sample inlet and outlet of the PPS is always routed to the same location along the exhaust stack or transfer line and thereby effectively experiencing the same pressure at both ports. This is done in order to reduce the dilution air consumption needed to drive the sample flow in the ejector pump (*Rostedt et al.*, 2014). The CFD analysis further revealed that the flow pattern in the annular section of the ion trap is turbulent. Despite the turbulent flow pattern, *Rostedt et al.* (2014) found that diffusional losses inside the sensor are best modeled by equations governing transport efficiency for laminar flow through a cylindrical tube (i.e. according to *Gormley and Kennedy* (1948)). Furthermore, the particle charging efficiency in a diffusion-charger is a function of the characteristic $N_I - t$ -product (*Lehtimäki*, 1983; *Pui et al.*, 1988; *Swanson et al.*, 2010), thus the duration of time over which the charging occurs which is ultimately a function of the sample flow rate into the PPS.

In summary, the sample flow rate is a primary influencing parameter in the *Pegasor Particle Sensor* as it not only governs the charging efficiency but also effects the behavior of particles in the ion trap (i.e. mobility analyzer) section, as well as particle loss mechanisms (i.e. diffusional and inertial losses, *Rostedt et al.* (2014)) inside the sensor. Alternatively, the ejector pump can be regarded as a dilution stage of the particle-containing exhaust gas sample by the ion-carrying dilution sheath air. Effectively, this results in a dilution ratio between the measured particle concentration inside the sensor and the actual concentration at the sample extraction probe.

Since both the sample flow rate ($\dot{V}_{\text{samp}}$) and effective dilution ratio (DR) are a function of the ejector pump performance, they become dependent on a range of parameters that are known to influence ejector diluter characteristics, of which pressure and temperature of the dilution air are the most dominant (*Giechaskiel et al.*, 2004). *Bergmann et al.* (2008) for example provided a simplified method to calculate dilution ratio as a function of only differential pressure across the diluter and temperature, over both critical and non-critical regimes of the ejector diluter. *Ntziachristos et al.* (2013b) suggested to perform sample flow calibrations of the *Pegasor Particle Sensor* at the typical operating temperature of the sensor of 200°C in order to minimize temperature effects during actual operating conditions. Indeed, experimental work by *Giechaskiel et al.* (2004) and *Bergmann et al.* (2008), using commercially available ejector diluter, indicated a $\sim 20\%$ dilution ratio increase as a result of a 140°C increase in sample temperature.

For the purpose of this study it was decided to model the sample flow

Figure 3.5: Description of PPS-M1 sample flow calibration and fitting of model to experimental data.

rate and dilution ratio solely as a function of dilution air pressure (p_{dil}). Flow bench experiments were performed in order to characterize the sample flow rate and sensor outlet flow rate. Dry dilution air was provided to the sensor at discrete pressure levels ranging from 10 to 42psig, while the sample ($\dot{V}_{smp,i}$) and sensor outlet ($\dot{V}_{outlet,i}$) flow rate were measured with a Gilibrator-2 (Sensidyne LP, St. Petersburg, FL) flow meter⁵. The dilution air flow rate ($\dot{V}_{dil,i}$) was subsequently calculated as the difference of measured outlet and inlet flow rates. Both inlet and outlet ports to the PPS were held at constant, atmospheric pressure and the dilution air was at a temperature of $\sim 25^\circ\text{C}$.

Figure 3.5 depicts the measured sample flow rates (i.e. red dots) as a function of dilution air pressure. The two characteristic flow regimes of the ejector pump (Bergmann *et al.*, 2008), namely non-critical and critical flow are readily noticeable from Figure 3.5. It was observed that the transition area between the two regimes for this specific ejector pump is at a dilution air pressure of $\sim 22\text{psig}$ and thereby, coincides with the manufacturer specified dilution air pressure setpoint for the PPS-M1.

A simple second order polynomial function was used to model the non-linear sample flow behavior of the non-critical flow regime, whereas a linear

⁵average of three consecutive measurements used for each flow rate; corrected to standard conditions, i.e. $T_{std} = 293.15\text{K}$ and $p_{std} = 101325\text{Pa}$.

relationship between dilution air pressure and sample flow rate was found to be adequate for the critical flow regime above 22psig. In order to have a continuous transition between both flow regimes a Gaussian-type transition function, as depicted in the insert in Figure 3.5, with $\mu = 22\text{psig}$ and $\sigma = 1\text{psi}$ was utilized to link the second order polynomial and linear functions. The resulting function to calculate $\dot{V}_{smp}(p_{dil})$ [in slpm] based on dilution air pressure [in psig] is given by Equation 3.1, where constants a_0 through a_4 are sensor specific calibration factors. The calibration factors were obtained for each sensor by fitting Equation 3.1 to the experimental data using a *trust-region reflective Newton* least-squares method as part of the Matlab® Optimization Toolbox™ (Matlab® R2008a, The MathWorks Inc.). Coefficients a_0 through a_4 for each sensor are given in Table 3.3.

$$\dot{V}_{smp} = \underbrace{(a_0 + a_1 p_{dil} + a_2 p_{dil}^2) \left\{ \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{p_{dil} - \mu}{\sigma \sqrt{2}} \right) \right] \right\}}_{\text{non-critical regime}} + \dots \quad (3.1)$$

$$\underbrace{(a_3 + a_4 p_{dil}) \left\{ \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{p_{dil} - \mu}{\sigma \sqrt{2}} \right) \right] \right\}}_{\text{critical regime}}$$

Table 3.3: Calibration coefficients a_0 through a_4 for sample flow rate ($\dot{V}_{smp}$) [in slpm] calculation according to Equation 3.1; numbers for versions V2 and V3 refer to sensor S/N.

C	V1	V2					V3	
		4289		4288			4667	4668
a_0	1.5546	2.6744	2.9634	2.4882	2.5466	3.2685	3.0573	2.6164
a_1	0.2488	0.2570	0.1796	0.2664	0.2312	0.1357	0.2066	0.2557
a_2	-0.0042	-0.0037	-0.0017	-0.0048	-0.0044	-0.0005	-0.0019	-0.0032
a_3	3.7965	4.4249	4.2578	5.0138	4.4079	4.0560	4.6504	4.5621
a_4	0.0634	0.1010	0.0841	0.0468	0.0646	0.0936	0.0970	0.1001
R^2	0.9949	1.0000	1.0000	0.9992	0.9971	0.9993	0.9982	0.9997

Figure 3.6 shows a comparison of the sample flow rates for all three sensor versions at a nominal dilution air pressure of 22psig with the variation bars indicating sample flow rates at $\pm 2\text{psi}$ from the default pressure. Additionally, for PPS version V2 multiple flow calibrations are shown over a time span of ~ 1 year. It can be noticed that sample flow rates are on one hand

dependent on the specific sensor but on the other hand also on the actual condition or state of the sensor. The former is influenced by slight production variabilities in terms of ejector pump and orifice dimensions, whereas the latter can be a function of possible deposits accumulated inside the ejector pump and sample flow paths. Indeed, multiple studies (*Giechaskiel et al.*, 2004; *Bergmann et al.*, 2008; *Swanson et al.*, 2011) have highlighted the fact that soot deposits on the ejector nozzle or orifice could alter the geometric characteristics and surface roughness of the ejector pump and thereby, affecting the sample flow rate and dilution ratio. It was observed that the sample flow rates increased for every newer iteration of the sensor, with version V1 exhibiting a sample flow rate on the order of 5slpm, V2 6slpm, and finally V3 on the order of 6.7slpm⁶. Sample flow rates from multiple calibrations performed with sensor V2 show a change of up to 7.5% (S/N 4289) and 6% (S/N 4288) in flow rate as a function of the sensor state. For example, calibration of S/N 4288 in January 2013 was conducted in uncleaned conditions (i.e. with soot deposits), whereas the subsequent calibration in March 2013 was performed after the sensor was disassembled for maintenance and cleaning, showing only a marginal change of 0.5% in sample flow rate compared to the sensor in unused, *brand new* condition.

Figure 3.7 depicts the changes in sample flow rates due to deviations of the dilution air pressure from the default setpoint of 22psig by ± 2 psi. This analysis is of special interest as dilution air pressures are not completely stable over time and are observed to vary as a function of reservoir pressure and upper/lower air compressor switching point. Furthermore, fluctuations in dilution air pressure are more pronounced during on-road or in-field (i.e. chassis dynamometer) testing, where the volume of the pressurized air vessels is smaller and thus, experiences increased pressure fluctuations as a function of compressor operation. However, from experience it was observed that for most compressor systems used during this study, dilution air pressures variations were bounded by ± 2 psi. It also has to be emphasized that mechanical-type (i.e. spring loaded) pressure regulators were used in conjunction with the PPS dilution air system which are not capable of as accurately maintaining pressure setpoints as would be expected from a fast acting piezo-valve with pressure-feedback⁷. Figure 3.7 indicates that pressure deviations of ± 2 psi resulted on average in a $\sim \pm 3.3\%$ ($\sigma \approx 0.65\%$)

⁶flow calibrations for sensors V1, V3, and first column shown for V2 were performed before the sensors were used for testing, i.e. *brand new* condition without exhaust deposits.

⁷new fast-acting pressure regulators have been purchased to upgrade the PPS dilution air system at the CAFEE, however, will not be part of the discussion in this study.

3.2. Particle Sensor Flow Calibration

Figure 3.6: Variations in sample flow rate as a function of dilution air pressure for the three different sensor versions of the PPS-M1; default dilution air set pressure is 22psig (~ 1.52 bar); variation bars show sample flow change for ± 2 psi pressure fluctuations; multiple flow calibrations shown for *Version 2*.

change in sample flow rate for all sensors evaluated as part of this study. It can be concluded that limited pressure variations in dilution air pressure have a smaller effect on sample flow rates in comparison to the effects of individual sensor conditions (i.e. accumulation of deposits) and sensor model differences (i.e. between different versions).

Calculation of the dilution ratio was performed according to Equation 3.2 by taking the ratio between the outlet and inlet flow rates to the *Pegasor Particle Sensor* as measured with the Gilibrator-2 for a series of discrete dilution air pressure settings. The resulting discrete dilution ratios were best modeled by a linear relationship with dilution air pressure shown in Equation 3.3, with coefficients β_0 and β_1 . The coefficients for each sensor were evaluated by fitting Equation 3.3 to the experimental data using a simple least-squares method within the dilution pressure interval of 10 to 42psig. Coefficients β_0 and β_1 for each sensor are given in Table 3.4.

$$DR_i = \frac{\dot{V}_{outlet,i}}{\dot{V}_{samp,i}} \quad (3.2)$$

$$DR(p_{dil}) = \beta_0 + \beta_1 \cdot p_{dil} \quad (3.3)$$

3.2. Particle Sensor Flow Calibration

Figure 3.7: Changes in sample flow rate [%] due to deviations in dilution air pressure from the selected reference pressure of 22psig (~ 1.52 bar) for the three different sensor versions of the PPS-M1; multiple flow calibrations shown for Version 2.

Table 3.4: Calibration coefficients β_0 through β_1 for dilution ratio calculation according to Equation 3.3; numbers for versions V2 and V3 refer to sensor S/N.

C	V1	V2						V3	
		4289		4288				4667	4668
β_0	1.2760	2.0084	1.3607	2.0273	2.3196	2.2858	2.1385	2.0269	
β_1	0.0065	0.0159	0.0826	0.0470	0.0396	0.0268	0.0168	0.0134	
R^2	0.9942	0.9952	0.9671	0.9941	0.9946	0.9894	0.9914	0.9944	

Figure 3.8 depicts the dilution ratios for all three sensor versions at a nominal dilution air pressure of 22psig with the variation bars indicating dilution ratios at ± 2 psi from the default pressure. Similarly to the sample flow rates, the dilution ratios were observed to vary as a function of sensor version between 1.4 for V1 and ~ 3 for V3 with version V2 being in the range of 2.3-2.5. In parallel, Figure 3.9 depicts the changes in dilution ratios due to deviations of the dilution air pressure from the default setpoint of 22psig by ± 2 psi, and was observed to be on average within $\pm 2\%$ of the default DR for most sensors. A variation of up to $\pm 4\%$ was noticed for PPS version V2, unit 4289 during the March 2013 sensor calibration sequence.

In summary, results underline the need for an individual calibration of each

3.2. Particle Sensor Flow Calibration

Figure 3.8: Variations in dilution ratio as a function of dilution air pressure for the three different sensor versions of the PPS-M1; default dilution air set pressure is 22psig (~ 1.52 bar); variation bars show dilution ratio change for ± 2 psi pressure fluctuations; multiple DR calibrations shown for *Version 2*.

Figure 3.9: Changes in dilution ratio [%] due to deviations in dilution air pressure from the selected reference pressure of 22psig (~ 1.52 bar) for the three different sensor versions of the PPS-M1; multiple DR calibrations shown for *Version 2*.

3.3. Sample Extraction and Particle Loss Considerations

Pegasor Particle Sensor with regard to sample flow rate and dilution ratio as differences could effect the sensor response, especially when sampling particulate matter from low concentration environments such as downstream a particle filter. Variations in dilution air pressures on the order of ± 2 psi from the default pressure of 22psig (i.e. $\pm 9\%$) resulted on average in a $\pm 3.3\%$ and $\pm 2\%$ change in sample flow rates and dilution ratios for all sensors, respectively. It has to be emphasized that the herein presented ejector pump models do not account for changes in dilution air or exhaust sample temperatures and the only independent variable is dilution air pressure. Moreover, effects of the actual composition and physical properties of the exhaust sample are not considered. For example, *Giechaskiel et al.* (2004) have shown that CO_2 concentrations up to 12.1% in the sample gas can lead to a 6% increase in dilution ratios of an ejector diluter compared to the reference condition (i.e. dry air).

3.3 Sample Extraction and Particle Loss Considerations

Figure 3.10 depicts the different sampling configurations employed to extract an exhaust sample into the *Pegasor Particle Sensor* during this study. The PPS-M1 was either connected directly to the exhaust stack or transfer line (i.e. *Config. 1*) or through a 39.4in (~ 1.0 m) long heated line with an internal diameter of $\frac{3}{8}$ in (~ 9.5 mm) (Hillesheim GmbH, H900-series) that was maintained at constant 200°C via a PID controller (i.e. *Config. 2*). The heated line was utilized following suggestions by *Ntziachristos et al.* (2013b) in order to assure a more stable and constant temperature of the exhaust sample gas entering the PPS. This allows to reduce the temperature dependency of the sensor response due to changes in exhaust gas temperature. In case of *Config. 2*, a $\frac{3}{8}$ in (ID) corrugated and insulated stainless steel pipe was used as return line from the PPS to the exhaust stack. As mentioned in Section 3.2 the sensor outlet is always connected close to the sample location (i.e. slightly downstream of the sample probe) so that the sensor is experiencing equivalent pressure levels up- and downstream the ejector pump thereby, making differential pressure effects onto the sample flow characteristics negligible.

Furthermore, Figure 3.10 shows various sample probe configurations, including, i) straight probe with 45° -cut facing towards flow direction, *A*; ii) *T-sampling* or blind sampling port without probe, *B*; iii) straight probe with 45° -cut facing opposite of flow direction, *C*; iv) blind sampling with straight probe, *D*; v) *J-type* probe facing towards flow direction, *E*. A comparison study by *Stein* (2001) between an open 45° probe, a probe not facing the flow,

3.3. Sample Extraction and Particle Loss Considerations

Figure 3.10: Schematic overview of PPS-M1 installation to exhaust stack or transfer pipe; *Config 1:* sensor sample and return ports mounted directly to exhaust pipe; *Config 2:* sensor sample port connected via 39.4in heated line (200°C) and return line via insulated stainless steel tube; sampling probe configurations A through E.

a probe with a hat, and a multihole probe connected to the tailpipe of a heavy-duty engine did not show any statistically significant differences in sampled particulate matter mass using a partial-flow sampling system (at PM mass levels of $\sim 50\text{mg/kWh}$). Results indicated slightly higher values for tests conducted with the open probe. If sampling is conducted immediately upstream or downstream of after-treatment devices spatial inhomogeneity of aerosol concentrations may exist and therefore, *Giechaskiel et al.* (2012a) suggest the use of multi-hole probes for such situations.

However, in this research only two out of the five probe configurations depicted in Figure 3.10 were applied, specifically, the straight probe with a

45°-cut facing towards the flow direction (i.e. config. *A*), and the *T-sampling* probe (i.e. config. *B*). The sample aspiration angle (Θ_s) for both probe configurations is 90°. *Giechaskiel et al.* (2012a) indicate that sampling effects for the 45°-cut probe are negligible for particles with a diameter (d_p) below 10 μ m, however, emphasizes that caution has to be exercised to account for possible spatially non-homogeneously mixed exhaust in the vicinity of the exhaust stack or transfer pipe walls. Particle movement along the walls can additionally be influenced by boundary layer phenomena (*Richard et al.*, 2008). Furthermore, CFD simulations have shown the existence of a re-circulation zone just inside the entrance of the sample tube (*Richard et al.*, 2008) for *T-sampling* probes, which could possibly affect particle sampling efficiencies. The same study found based on simulations that if a probe with a 45°-cut at the end is used, sampling is conducted from the top portion of the 45°-cut and also exhibits a re-circulation zone in the probe entrance area. It has to be pointed out however, that the simulations conducted by *Richard et al.* (2008) were based on water as a working fluid as opposed to exhaust gas with significantly different physical properties than water. Thus, results might be qualitatively similar but are expected to be different from a quantitative aspect.

3.3.1 Particle sampling efficiency for the PPS

Particles within the exhaust gas stream will have to overcome a 90° turn in order to enter the *Pegasor Particle Sensor* inlet port for both probe configurations *A* and *B*, shown in Figure 3.10. However, with particle sample extraction efficiency being strongly dependent on the sampling method and the particle size range, calculations were made to characterize possible sample concentration deficiencies due to the chosen method of installation of the PPS. Anisokinetic sampling and probe misalignment (i.e. anisoaxial sampling $\Rightarrow$ sample velocity direction is different from stream velocity) are two primary factors, influencing representative particle collection and leading to either possible over or under estimation of the measured particle concentrations (*Hinds*, 1999; *Von der Weiden et al.*, 2009; *Giechaskiel et al.*, 2011).

Anisokinetic sampling occurs by virtue of a velocity difference between the gas stream in the exhaust stack or transfer pipe (v_{exh} ⁸) and the sample flow within the sample probe (v_s), whereas misalignment (i.e. anisoaxial sampling) is defined as the angle (θ) between the streamlines of the exhaust gas stream and the streamlines within the sampling probe (*Hinds*, 1999; *Von der*

⁸pipe diameter averaged flow velocity.

3.3. Sample Extraction and Particle Loss Considerations

Weiden *et al.*, 2009). Both phenomena can be described as a function of the Stokes number (Stk), hence, are ultimately a function of particle size described by their aerodynamic diameter. According to a comprehensive review of methods used in the automotive sector for quantifying combustion engine derived particulate matter emissions, sampling for particle number measurements is typically done sub-isokinetically with ratios $v_{exh}/v_s = 1.4$ -4.1, whereas, particulate matter mass is sampled at super-isokinetic conditions (i.e. $v_{exh}/v_s = 0.3$ -0.9) (Giechaskiel *et al.*, 2012a). Table 3.5 lists typical exhaust and PPS sample flow parameters from heavy-duty and light-duty vehicles used as part of this study. It has to be noted that exhaust gas temperatures provided in Table 3.5 were measured at the location of sample extraction for the PPS and are thus, representative for the local gas properties. Temperatures will be higher immediately downstream the after-treatment components.

The Stokes number can be defined as shown by Equation 3.4 (Hinds, 1999) with v_{exh} being the exhaust flow velocity (i.e. free stream velocity) in [m/s], D_s the internal probe diameter and τ the relaxation time in [sec].

$$Stk = \frac{\tau v_{exh}}{D_s} \quad (3.4)$$

The relaxation time characterizes the time required for a particle to adjust or *relax* its velocity to a new condition of external forces and is described as the product of particle mass (m_p) and particle mobility (b_p) (Hinds, 1999). Alternatively, the relaxation time can be defined in terms of the standard particle density⁹ (ρ_0) in [kg/m³], the sample gas viscosity (η_s) in [Pa·s], the aerodynamic particle diameter (d_a) in [m], and the Cunningham slip correction factor (C_c) as shown by Equation 3.5.

$$\tau = \frac{\rho_0 d_a^2 C_c}{18 \eta_s} \quad (3.5)$$

The Cunningham slip correction factor was further defined according to the expression developed by Allen and Raabe (1985) for solid particles as a function of the physical particle diameter (d_p) in [m], and the mean free path (λ) of the sample gas as shown in Equation 3.6.

⁹standard particle density of 1g/cm³.

3.3. Sample Extraction and Particle Loss Considerations

Table 3.5: Typical exhaust and sample flow parameters for heavy-duty (data from *Thiruvengadam et al. (2015)*) and light-duty (data from *Thompson et al. (2014)*) applications; exhaust pipe diameter (D_s) for heavy-duty: 5in, and light-duty: 2in; pressure of exhaust (P_{exh}) and sample (P_s) streams both 101,325Pa; different Q_s for PPS versions V1 through V3.

		Heavy-Duty			Light-Duty		
		Min.	Max.	μ	Min.	Max.	μ
Q_{exh}	[m ³ /min]	2.42	42.48	15.63	0.26	8.50	3.65
v_{exh}	[m/s]	3.19	55.88	20.56	2.13	69.86	30.01
T_{exh}	[C]	85.08	272.45	183.29	94.45	197.18	145.24
ρ_{exh}	[kg/m ³]	0.99	0.65	0.77	0.96	0.75	0.84
η_{exh}	[Pa·s]	2.14E-5	2.90E-5	2.56E-5	2.19E-5	2.61E-5	2.40E-5
Re_{exh}	[-]	18,596	158,629	78,949	4,763	101,959	53,530
T_s	[C]		200			200	
ρ_{exh}	[kg/m ³]		0.75			0.75	
η_{exh}	[Pa·s]		2.62E-5			2.62E-5	
Q_s	[lpm]		5.04			5.04	
v_s	[m/s]		1.18			1.18	
Re_s	[-]		319			319	
v_{exh}/v_s	[-]	2.70	47.41	17.44	1.81	59.26	25.46
Q_s	[lpm]		6.09			6.09	
v_s	[m/s]		1.43			1.43	
Re_s	[-]		386			386	
v_{exh}/v_s	[-]	2.24	39.22	14.43	1.50	49.02	21.06
Q_s	[lpm]		6.71			6.71	
v_s	[m/s]		1.57			1.57	
Re_s	[-]		425			425	
v_{exh}/v_s	[-]	2.03	35.60	13.10	1.36	44.51	19.12

$$C_c = 1 + \frac{\lambda}{d_p} \left[2.34 + 1.05 \exp \left(-0.39 \frac{d_p}{\lambda} \right) \right] \quad (3.6)$$

For simplicity, ideal air rather than real exhaust gas properties have been assumed in order to estimate the mean free path according to Equation 3.7, with R being the universal gas constant in [J/(mol·K)], N_A the Avogadro's number in [1/mol], d_m the collision diameter for air molecules in [m], and P_s and T_s the sample gas pressure in [Pa] and temperature in [K], respectively (*Hinds, 1999*). The sample gas viscosity (η_s) in [Pa·s] was calculated using Sutherland's formula with the coefficients chosen for air (i.e. $T_0 = 291.15$, $\eta_0 = 18.27 \times 10^{-6}$, $C = 120$).

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$$\lambda = \frac{R}{\sqrt{2} \pi N_A d_m^2} \cdot \left(\frac{T_s}{P_s} \right) \quad (3.7)$$

Using the empirical Equations 3.8 and 3.9 provided by *Durham and Lundgren* (1980) the particle concentration ratio ($C/C_{0,isoaxi}$) due to anisoaxial sampling can be calculated as a function of the probe misalignment angle (θ) in [deg]. According to *Hinds* (1999) the empirical Equation 3.8 is valid between $0^\circ \leq \theta \leq 90^\circ$ and for isokinetic sampling flow conditions with Stokes numbers in the range of $0.01 < Stk < 6$. It can be noticed from Table 3.5 that sampling under all considered conditions was performed sub-isokinetically. However, for the purpose of estimating $C/C_{0,isoaxi}$ in this analysis it was assumed that the sample flow rate was of similar magnitude as the exhaust flow rate (i.e. $v_{exh} \equiv v_s$).

$$\frac{C}{C_{0,isoaxi}} = 1 + [\cos \theta - 1] \cdot \left\{ 1 - \frac{1}{1 + 0.55 (Stk') \cdot \exp(0.25 \cdot Stk')} \right\} \quad (3.8)$$

$$Stk' = Stk \cdot \exp^{0.022 \cdot \theta} \quad (3.9)$$

Assuming a properly aligned sampling probe (i.e. $\theta = 0^\circ$), *Belyaev and Levin* (1974) provide an empirical expression to calculate the concentration ratio ($C/C_{0,isokin}$) due to anisokinetic sampling conditions given by Equation 3.10. According to *Von der Weiden et al.* (2009) this formula is valid for Stokes numbers between $0.051 \leq Stk \leq 2.03$ and velocity ratios between $0.17 \leq v_{exh}/v_s \leq 5.6$, however, has also been applied outside this range by *Giechaskiel et al.* (2012a) for estimation of particle sampling efficiencies from CVS dilution tunnel or raw exhaust stack.

$$\frac{C}{C_{0,isokin}} = 1 + \left[\frac{v_{exh}}{v_s} - 1 \right] \cdot \left\{ 1 - \frac{1}{1 + (2 + 0.62 v_s/v_{exh}) \cdot Stk} \right\} \quad (3.10)$$

Figure 3.11 depicts the square root of the Stokes number as a function of particle diameter on the *right y-axes* along with the concentration ratio for anisoaxial flow conditions as a function of Stokes number on the *left y-axes* for a probe misalignment angle of $\theta = 90^\circ$ (i.e. conditions expected for sampling probes A and B). The data shown is representative of average exhaust flow and sampling conditions for a heavy-duty engine application (see Table 3.5) and was plotted for particle diameters ranging from 1nm to 40 μ m

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at standard pressure conditions of 101.325kPa and at an exhaust gas temperature of $\sim 183^\circ\text{C}$. The *dotted line* provides a visual aid to identify the Stokes number representative of a particle with diameter $1\mu\text{m}$ for the given exhaust gas properties.

In parallel, Table 3.6 gives an overview of the concentration ratios for $1\mu\text{m}$ particles due to anisokinetic and anisoaxial sampling conditions for the range of typical parameters provided in Table 3.5 for both heavy- and light-duty applications as well as the three different *Pegasor Particle Sensors* (i.e. their respective sample flow rates). On one hand it can be observed that particle concentrations inside the sampling probe are slightly reduced by a factor of 0.98 and 0.97 for heavy-duty and light-duty vehicles, respectively, due to probe misalignment. On the other hand however, calculations indicate an enrichment of particles in the sampling probe due to sub-isokinetic sampling on the order of 1.15 to 1.33 for heavy- and light-duty applications, respectively. These values are estimated for $1\mu\text{m}$ particles. In a comprehensive analysis of typical exhaust particle size distributions from diesel and gasoline fueled engines, *Harris and Maricq* (2001) showed that count mode mobility diameters are ranging within 80-100nm for both non-filter equipped diesel and direct injected spark-ignition (DISI) engines, and are considerably lower between 20-30nm for port-fuel injected (PFI) gasoline engines. Therefore, when considering 200nm diameter particles, $C/C_{0,isoaxi}$ increases to 0.99 for both heavy- and light-duty, whereas $C/C_{0,isokin}$ is reduced to 1.008 and 1.017 for heavy- and light-duty applications, respectively.

The analysis provided herein was based on the assumption of isokinetic flow conditions when estimating concentration ratios due to probe misalignment and vice-versa, a properly aligned probe to calculate sampling efficiencies due to anisokinetic flow conditions. In the present case of the PPS with a combination of probe misalignment ($\theta = 90^\circ$) and anisokinetic sampling due to the changing exhaust flow rates during engine operation while the sampling flow rate is kept constant, a more general analysis described by *Brockmann* (1993) might be applicable. In case of a combination of anisokinetic and anisoaxial sampling conditions *Hinds* (1999) introduces the limiting concentration ratio where the overestimation due to sub-isokinetic sampling is canceling the underestimation due to probe misalignment.

Furthermore, *Giechaskiel et al.* (2012a) showed in a similar analysis as presented herein, that for Stokes numbers between $\sim 10^{-3}$ and 10^{-4} the over- or underestimation of both particle number or particulate matter mass penetrations is within 2% for all evaluated cases and therefore, negligible even

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Figure 3.11: Effect of anisoxal probe alignment on the concentration ratio ($C/C_{0,isoaxi}$) for $\theta = 90^\circ$; medium values for typical heavy-duty engine with 5in exhaust stack; assuming isokinetic sampling conditions $v_{exh} \equiv v_s$ ($v_{exh} = 20.6\text{m/s}$); dotted line indicating $\sqrt{Stk}$ for $1\mu\text{m}$ particles.

for particles up to $1\mu\text{m}$ diameter. Results indicated that even *extreme* cases of anisokinetic sampling lead to a penetration of only 102% for 100nm particles. Similarly, *Ntziachristos and Samaras (2002)* estimated that deviations from isokinetic sampling are insignificant for number concentrations during chassis dynamometer testing of light-duty vehicles. The study reports $\sim 4\%$ higher number concentrations for a maximum deviation ratio of 1.32.

Based on the results obtained from this analysis, and supported by literature, it was concluded that anisoxal sampling conditions for probe configurations *A* and *B* as well as the expected impact of changing exhaust flow rates on isokinetic conditions will not noticeably affect the ability of the PPS to measure particulate matter directly from the exhaust stack, and can therefore be neglected.

3.3.2 Particle transport efficiency for the PPS

A detailed discussion of general particle loss mechanisms affecting the transport of the sample from the extraction location (i.e. sampling probe) to the point of measurement is provided by *Von der Weiden et al. (2009)*, and with particular emphasis towards PM mass and number sampling from automotive combustion sources by *Giechaskiel et al. (2012a)*. Particle agglomeration and coagulation effects are practically negligible for concentration levels be-

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Table 3.6: Concentration ratios for anisokinetic ($C/C_{0, isokin}$) and anisoaxial ($C/C_{0, isoaxi}$) sampling of $1\mu\text{m}$ particles for typical exhaust and sample flow conditions for heavy-duty and light-duty applications provided in Table 3.5; different Q_s for PPS versions V1 through V3.

		Heavy-Duty			Light-Duty		
		Min.	Max.	μ	Min.	Max.	μ
$Q_s = 5.04\text{lpm}$ (PPS-M1, V1)							
$\sqrt{Stk}$	[-]	0.0301	0.1137	0.0718	0.0245	0.1314	0.0887
$C/C_{0, isoaxi}$	[%]	99.64	94.99	97.97	99.76	93.37	96.92
$C/C_{0, isokin}$	[%]	100.34	217.66	117.08	100.11	295.68	138.32
$Q_s = 6.09\text{lpm}$ (PPS-M1, V2)							
$\sqrt{Stk}$	[-]	0.0301	0.1137	0.0718	0.0245	0.1314	0.0887
$C/C_{0, isoaxi}$	[%]	99.64	94.99	97.97	99.76	93.37	96.92
$C/C_{0, isokin}$	[%]	100.25	197.07	114.01	100.07	261.53	131.52
$Q_s = 6.71\text{lpm}$ (PPS-M1, V3)							
$\sqrt{Stk}$	[-]	0.0301	0.1137	0.0718	0.0245	0.1314	0.0887
$C/C_{0, isoaxi}$	[%]	99.6	95.0	98.0	99.8	93.4	96.9
$C/C_{0, isokin}$	[%]	100.2	187.9	112.6	100.1	246.4	128.5

low $\sim 10^7 \#/\text{cm}^3$, and thus, only become relevant for sampling from locations upstream a particle filter in the high particle concentration environment. Also, gravitational and inertial loss mechanisms are typically negligible for ultrafine particles (Giechaskiel et al., 2012a) and only become more dominant for larger size particles (Von der Weiden et al., 2009), thus are not being considered with regard to particulate matter sampling with the PPS.

Electrostatic deposition can be a factor in case the sampling setup and instrumentation is not properly grounded or non-conductive sample tubing is being used that could lead to a local charge build-up. However, the *Pegasor Particle Sensor* is manufactured from stainless steel as were sampling lines and probes, and it was assured that the sampling system was properly grounded to the exhaust stack of transfer line. Thus, it could be safely assumed that electrostatic deposition in the sample probe and lines leading to the PPS was negligible. Indeed, Von der Weiden et al. (2009) point out that if proper grounding is applied and conductive material being used, even highly charged particles will not be electrostatically deposited, with the exception of unipolar charged particles where mutual repulsion forces might cause a net flux of particles towards sampling line walls. Diffusional losses are dominant for small particles below $\sim 100\text{nm}$ (Ayala et al., 2003; Von der Weiden et al., 2009; Giechaskiel et al., 2012a) and strongly depend on the length of the sample transfer lines as well as the flow regime (i.e. laminar or tur-

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bulent, with turbulent flow leading to increased diffusion losses). However, *Giechaskiel et al.* (2012a) indicated particle losses on the order of 5% and <1% for 10nm and 50nm diameter particles sampled through a 1m long line at a flow rate of 5lpm. In comparison, sampling configuration *Config. 1* for the PPS utilizes a 39.4in (i.e. 1m) long heated line with sample flow rates observed to vary between 5.04 to 6.71lpm for all three sensor versions. In light of this, it was concluded that diffusional losses in the sampling system connecting the PPS to the exhaust stack or transfer line can be neglected.

Finally, *Giechaskiel et al.* (2012a) mentioned that thermophoretic losses are the most dominant particle removal mechanisms during raw exhaust sampling from modern combustion engines. Sampling exhaust gas at a temperature of $\sim 300^{\circ}\text{C}$ through a heated line with wall temperatures maintained at 150°C is estimated to lead to approximately 10% loss in total particles (*Giechaskiel et al.*, 2012a). On the other hand, *Von der Weiden et al.* (2009) indicate that thermophoretic losses become negligible for temperature gradients below 40K. From Table 3.5 it can be seen that typical exhaust gas temperatures were on the order of $\sim 180^{\circ}\text{C}$ and $\sim 145^{\circ}\text{C}$ for heavy- and light-duty vehicles, respectively. As the heated sample line as well as the *Pegasor Particle Sensor* were maintained at constant 200°C it was assumed that thermophoretic losses remained relatively low, but certainly below the 10% level as reported by *Giechaskiel et al.* (2012a) for a 150°C temperature gradient.

3.4 Particle Sensor Response Calibration - Soot Generator Experiments

The *Pegasor Particle Sensor* has been compared to laboratory-grade reference instruments by multiple published studies for the purpose of developing sensor response models and obtaining individual calibration coefficients. The response models are often simplistic linear regression models (*Gensdarmes et al.*, 2011; *Beck et al.*, 2012; *Ntziachristos et al.*, 2013b) that link the sensor signal to either a particulate matter mass or particle number concentration. In contrast, a physical phenomena based response model with a set of specific calibration parameters was developed by *Rostedt et al.* (2014). The aim was to understand the sensor response to particle number concentration as a function of particle mobility diameter and collection efficiency of the mobility analyzer (i.e. ion trap) inside the PPS.

Beck et al. (2012) compared the raw *Pegasor Particle Sensor* signal to both an AVL micro soot sensor and an AVL particle counter while sampling exhaust

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from a heavy-duty engine operated over steady-state and transient (i.e. ETC) test cycles. Two sets of sensor calibration coefficients were obtained by linear regression against the reference instrument during steady-state engine operation for measurements performed up- and downstream a particle filter. Intermediate values of both sets of coefficients were subsequently used to validate the sensor calibration over the transient ETC cycle. Results indicated 0.8% and 8.35% lower particle number concentrations as compared to the AVL APC when measured in the raw exhaust or downstream the particle filter, respectively. On the other hand, using the calibration coefficients obtained for mass correlation with the AVL MSS yielded 23.6% and 6.8% lower PM mass concentrations as compared to the AVL MSS for raw exhaust and downstream particle filter sampling, respectively (*Beck et al.*, 2012). In particular, downstream DPF measurements showed a better correlation with particle number concentration as compared to mass concentration, which is primarily due to the very low particulate matter mass downstream the trap, leading to the reduced signal-to-noise ratio.

Similarly, *Wachtmeister* (2012) found a good correlation between the raw PPS response and a Horiba® *solid particle counting system* (SPCS). However, results indicated a changing correlation during DPF regeneration events which was hypothesized to originate from the sensor's sensitivity to different particle size distributions that might affect the PPS counting efficiency. Indeed, a particle size dependent influence on sensor linearity was reported by *Gensdarmes et al.* (2011) and *Ntziachristos et al.* (2013a) with the latter suggesting the use of multiple calibration factors for different size distributions. As described by *Harris and Maricq* (2001), there exist distinct particle size distributions for a given engine technology and fuel used. Furthermore, it is known that the particle filters efficiently remove particles over a wide size range, and that during, and immediately following, a DPF regeneration event increased particle concentrations in the below 50nm range can be expected due to temporary filter inefficiencies (*Suresh et al.*, 2000; *Yamada*, 2013). In light of that knowledge it would be possible to adjust the sensor's calibration coefficients in anticipation of a change in particle size distribution. Most importantly, however, *Gensdarmes et al.* (2011) showed that if the sensor response was normalized by the active surface area following the approach described by *Jung and Kittelson* (2005), and using an exponent of $x(d_p) = 1.39$, good linearity of the PPS with number concentration was observed. This is characteristic of diffusion-charging based instruments which are known to exhibit a response proportional to surface area (*Lehtimäki*, 1983; *Pui et al.*, 1988; *Ntziachristos et al.*, 2004, 2007; *Ku*, 2010).

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Ntziachristos et al. (2013a) showed that the sensor response (R_{PPS}) is proportional to $d^{\sim 1-1.05}$ for most of the range to monodisperse aerosol and thus, lies between particle number (i.e. d^0) and particle mass (i.e. $d^{\sim 2.5}$). A simple response model was developed to provide linear calibration coefficients for the *Pegasor Particle Sensor* assuming a monodisperse particle distribution with a count mode diameter of 50nm and a geometric standard deviation of 1.7nm. The calibration coefficients by *Ntziachristos et al.* (2013a) are given in Equations 3.11 (L) and 3.12 (N) for calculation of particle mass [mg/m^3] and number [$\#/\text{cm}^3$] concentrations, respectively, as a function of PPS sample flow rate ($L, N = f(V_{\text{sample}})$). To obtain the final particle mass or number concentrations, the calibration coefficients have to be multiplied into the raw sensor signal in [fA].

$$L \left(\frac{\text{mg}}{\text{m}^3 \text{ fA}} \right) = \frac{6.3 \times 10^{-5}}{Q_{\text{in}}[\text{slpm}]} \quad (3.11)$$

$$N \left(\frac{1}{\text{cm}^3 \text{ fA}} \right) = \frac{288}{Q_{\text{in}}[\text{slpm}]} \quad (3.12)$$

A detailed response model was presented by *Rostedt et al.* (2014) including prediction of the diffusion-charger's charging efficiency (E_{ch}) and particle penetration (P_{ma}) through the mobility analyzer (i.e. ion trap). Both are considered primary contributors to the sensor response. The effects of inertial and diffusion losses inside the sensor on the other hand, play a smaller role but nevertheless were also considered in their model. The overall response of the sensor was modeled based on two independent variables, namely, particle size (d_p) and ion trap voltage (V_{ma}) (*Rostedt et al.*, 2014). The raw sensor response or sensitivity was obtained by taking the ratio between the measured current with the PPS and the number concentration as measured by a CPC. Results suggested that the mobility analyzer voltage was affecting the sensor response. *Rostedt et al.* (2014) hypothesized that ion losses in the charging region possibly increase as a function of increasing collection voltage. This was accounted for by introducing a functional form of the pre-exponential parameter used in the power law expression typically employed to describe a diffusion-charger's response to particle size (*Lehtimäki*, 1983). In order to calibrate the response model, nearly monodisperse aerosol particles that contain only one elemental charge each were used.

The experimental setup utilized for basic sensor response analysis as part of this study is shown in Figure 3.12. As particle source an AVL particle

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Figure 3.12: Schematic diagram of experimental setup for particle sensor response evaluation using the AVL particle generator (APG) (AVL List GmbH, 2013) as particle source.

generator (APG-499, AVL List GmbH, AVL List GmbH (2013)) was used to produce monodisperse particle size distributions. The AVL APG is based on a propane diffusion flame and particle size and composition can be adjusted by changing the air-fuel ratio of the flame and the quenching rate of the extracted sample from the flame with nitrogen (N_2). This allows to produce particles containing different amounts of volatile fraction. The particle stream leaving the burner chamber is referred to as *burner-out* particle concentration. A second particle stream is routed through a volatile particle remover with a hot dilution stage and evaporation chamber maintained at 350°C in order to volatilize any adsorbed or condensed matter and produce a stream of non-volatile particles. Particles extracted after the VPR are referred to as *VPR-out* particle concentration hereinafter.

Since the particle flow exiting the AVL APG was not sufficient to provide all instruments with the required amount of sample flow, a Dekati™ Diluter was installed downstream the APG as seen in Figure 3.12. The dilution ratio was on the order of ~ 10 , thus providing a 10 times increased particle stream. Dried and HEPA filtered dilution air was used to prevent the introduction of artifacts. Downstream the diluter a four-way flow splitter (TSI Inc., model 3708) was installed that diverted the sample flow to the different instruments measuring in parallel arrangement. Any excess sample flow was vented from the Dekati™ Diluter. The range of instru-

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Figure 3.13: Picture of the experimental setup for particle sensor response evaluation at California Air Resources Board's Depot Park (Sacramento, CA) facility in December 2014; *from left to right on table:* AVL particle generator [1], Dekati™ Diluter [2], Pegasor PPS-M1 V3 [3], TSI SMPS™ 3080 [4], TSI CPC 3786 [5], TSI EAD 3070A (i.e. below CPC) [6]; *right side:* AVL MSS-494 [7]; *below table* dilution air control box for Dekati™ Diluter and Pegasor PPS-M1 [8].

ments included, i) a AVL MSS-494 for estimation of carbonaceous soot mass concentration in $[\text{mg}/\text{m}^3]$; ii) an electrical aerosol detector (EAD, TSI Inc., model 3070A) which is a diffusion-charging type instrument that measures a particle length parameter in $[\text{mm}/\text{cm}^3]$ and thus, having an identical measurement principle as the PPS; iii) an electrostatic classifier (SMPS™, TSI Inc., model 3080) in conjunction with a water-based condensation particle counter (TSI Inc., model 3786). Additionally to parallel measurements of all instruments, the SMPS™ and EAD were selectively connected downstream the PPS in order to assess particle penetration through the sensor as a function of PPS mobility analyzer (i.e. ion trap) voltage settings (i.e. indicated by numbers 1 through 3 in Figure 3.12). PPS version V3, unit 4667 was used for the soot generator experiments and the sensor underwent maintenance and cleaning before testing commenced. Figure 3.13 shows a picture of the experimental setup located at California Air Resources Board's laboratory facility in Depot Park, Sacramento, CA. All the instruments and the AVL soot generator utilized for the fundamental sensor response experiments were courtesy of CARB staff at the Sacramento, CA, headquarter office.

Figures 3.14 and 3.15 show the different number-weighted particle size dis-

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Figure 3.14: Different *burner-out* particle size distributions generated with the AVL particle generator and measured with SMPSTM; *circles*: experimental data, *solid lines*: fitted log-normal distribution $f(\mu, \sigma, N)$.

tributions and number concentrations generated with the AVL APG and extracted from the *burner-out* and *VPR-out* location, respectively. The experimental data was fitted with a *log-normal* distribution according to Equation 2.2 in order to obtain the count mode diameter (CMD, μ), the geometric standard deviation (GSD, σ_g) as well as the total number concentration (N_{tot}) for each distribution. It can be clearly seen that particle distributions both up- and downstream the VPR are monodisperse and range from 19nm to 65nm and 36nm to 73nm for *burner-out* and *VPR-out* conditions, respectively.

The concentrations for all distributions were observed to reduce by approximately one order of magnitude over the VPR which is on one hand attributed to the dilution process but also due to evaporation of absorbed volatile material. The latter can especially be noticed for the 50 and 65nm distributions that change significantly in magnitude with respect to the 29 and 40nm distributions. The 29 and 40nm distributions remain similar in magnitude difference between each other and only appear to be reduced by the constant dilution ratio in the VPR. Furthermore, there was a tendency to a shift in CMD towards slightly larger particle size downstream the VPR. This could possibly be explained by the smaller particles of a given distribution (i.e. left slope) comprising more volatile particles that vaporize in

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Figure 3.15: Different *VPR-out* particle size distributions generated with the AVL particle generator and measured with SMPSTM; circles: experimental data, solid lines: fitted log-normal distribution $f(\mu, \sigma, N)$.

the VPR, thus leading to a larger reduction of particles on the *left slope* and therefore an apparent shift of the CMD towards larger particles.

The geometric standard deviation remains relatively constant for all distributions with the exception of the 19nm distribution, at around 1.68-1.79¹⁰ both up- and downstream the VPR. The 19nm distribution is significantly narrower with a GSD of 1.23. It has to be noted that the 19nm distribution was not measured from the *VPR-out* location. Table 3.7 lists the specific parameter settings for the AVL particle generator for each particle size mode along with the fitting values for the *log-normal*, number-weighted size distributions. The VPR temperature (T_{VPR}) and dilution air flow ($V_{VPR-air}$) were held at constant 350°C and 2lpm, respectively, for all size distributions. Data for each particle size mode was collected for approximately 7min allowing for three repeated particle size distribution scans with the SMPSTM. The SMPSTM was operated with 15lpm sheath flow, 0.6lpm sample flow (i.e. with long DMA, model 3081, TSI Inc.) and an up scan and retrace time of 120sec and 15sec, respectively. Only the *multiple charge correction* algorithm was enabled, whereas diffusion correction and nanoparticle aggregate mo-

¹⁰this is comparable to Harris and Maricq (2001) who showed that the geometric standard deviation (σ_g) is around 1.7 ± 0.1 for a wide range of engines, fuels, and operating conditions.

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bility analysis were turned off.

Table 3.7: AVL particle generator settings and fitting parameters for *burner-out* and *VPR-out* log-normal particle number weighted distributions.

CMD (nominal)	19nm	30nm	40nm	50nm	65nm
T_{VPR} [°C]	350	350	350	350	350
$V_{fuel-gas}$ [ml/min]	20	18	18	18	16
$V_{mix-gas}$ [ml/min]	15	0	0	0	0
$V_{oxid-air}$ [l/min]	0.35	0.7	0.8	1	0.8
$V_{burner-air}$ [l/min]	5	5	5	2	2
$V_{VPR-air}$ [l/min]	2	2	2	2	2
<i>Burner-out</i> Sampling					
μ [nm]	19.3	29.4	40.1	49.5	64.7
σ_g	1.23	1.77	1.77	1.74	1.68
N [# /cm ³]	8.52×10^5	4.04×10^6	3.97×10^6	4.92×10^6	5.05×10^6
<i>VPR-out</i> Sampling					
μ [nm]	-	35.9	40.6	56.0	73.3
σ_g	-	1.70	1.76	1.79	1.73
N [# /cm ³]	-	6.78×10^5	6.60×10^5	6.67×10^5	5.94×10^5

Figure 3.16 depicts the correlation between the average *Pegasor Particle Sensor* response (R_{PPS}), normalized by sample flow rate (V_{samp}), and carbonaceous soot mass measured through the AVL micro soot sensor. The variation bars indicate one standard variation ($1 \cdot \sigma$) over a sample period of ~ 7 min. Linear regression lines were fitted to the experimental data using a $m_{MSS} = \beta_1 \cdot R_{PPS} + \beta_0$ relationship. It is immediately visible from Figure 3.16 that there exists a different slope for the correlation when sampling from *burner-out* (blue circles) versus *VPR-out* (red triangles) location. This can be explained by the different sensitivities of the two measurement principles towards volatile particles and adsorbed volatile material. The MSS is only measuring the carbonaceous soot fraction, whereas the PPS is sensitive to all type of particles that can be charged via the diffusion-charging process, which encompasses volatile material in a condensed or adsorbed state. Therefore, when measuring from *burner-out* with an increased volatile matter content, the particles will carry more charge per unit carbonaceous soot due to adsorbed matter increasing the *active surface* available for ion attachment (i.e. diffusion charging) or condensed volatile particles. The difference between the slopes for both regression lines is on the order of 58.5%.

Figure 3.16 additionally provides correlation curves from studies by *Beck*

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Figure 3.16: Correlation between PPS-M1 response and AVL MSS for different monodisperse burner-out and VPR-out particle size distributions; dashed black lines: linear regression for PPS vs. MSS; point-dash lines: correlation from literature, 1) pre-DPF, Beck *et al.* (2012), 2) post-DPF, Beck *et al.* (2012), 3) sensor calibration by Ntziachristos *et al.* (2013b); variation bars indicate $1 \cdot \sigma$; $V_{ma} = 400V$.

et al. (2012) (orange lines) and Ntziachristos *et al.* (2013b) (blue line). The latter was developed as the official PPS-M1 particulate matter mass calibration coefficient comprising only a slope (β_1) with the offset forced to zero. The slope for the burner-out correlation function is within $\sim 12\%$ of the slope found by Ntziachristos *et al.* (2013b). The observed offset of about 0.1 mg/m^3 is assumed to be primarily due to a zero-drift offset of the MSS. The natural charge that is induced to particles in the high temperature flame region was estimated, based on measurements with the corona charger turned off, to account for $\sim 4\%$ of the observed offset. Correlation lines 1) and 2) (i.e. orange lines) are for up- and downstream DPF measurements (Beck *et al.*, 2012), respectively, and are observed to be shifted slightly towards a larger MSS mass concentration. This offset could possibly be explained by the fact that the pre-DPF correlation was based on 0 to $\sim 25 \text{ mg/m}^3$ data, thus introducing an increased fitting error at the lower tail shown in Figure 3.16. The post-DPF correlation appeared to be pivoted upwards for the lower concentrations due to increased measurement variability which was also reflected in a lower coefficient of determination (i.e. $R^2 = 0.83$ vs. $R^2 = 0.97$ for pre-DPF).

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Table 3.8 provides a comprehensive list of correlation coefficients between the PPS-M1 and reference particulate matter mass instruments, as published in literature. It can be observed that the slope for correlation with the AVL MSS is on the same order of magnitude and varying between 5.17×10^{-5} and 8.77×10^{-5} for all available literature. Correlation coefficients between a calibrated PPS for mass and reference PM mass measurements, including Dekati DMM, DustTrack, and gravimetric obtained mass from filter media sampling are seen to be ranging from 1.2 (i.e. Dekati DMM) to 1.7 (i.e. DustTrack).

Table 3.8: Calibration and correlation coefficients for PPS-M1 versus reference particulate matter mass measurement instruments from published literature in comparison to calibration coefficients obtained from this study.

Source	Instr.	β_0	β_1	R^2	Trap
R_{PPS} [fA] vs. mass [mg/m ³] $\Rightarrow$ calibration coefficients					
Figure 3.16 (<i>this study</i>) ^a	AVL MSS	-0.1148	5.53×10^{-5}	0.9816	400
	AVL MSS	-0.0680	8.77×10^{-5}	0.9968	400
Beck et al. (2012) ^b	AVL MSS	0.5720	7.17×10^{-5}	0.97	-
	AVL MSS	0.1202	5.17×10^{-5}	0.83	-
Ntziachristos et al. (2013b) ^c	AVL MSS	-	6.30×10^{-5}	-	400
R_{PPS} [mg/m ³] vs. mass [mg/m ³] $\Rightarrow$ correlation coefficients					
Karim (2012) ^d	Dekati DMM	-6.9779	1.5165	0.9944	-
Karim (2012) ^e	Dekati DMM	1.5085	1.2110	0.8575	-
Karim (2012) ^d	DustTrack	-8.5059	1.7106	0.9021	-
R_{PPS} [mg/km] vs. mass [mg/km] $\Rightarrow$ correlation coefficients					
Tikkanen et al. (2014) ^f	Gravi. PM	-	1.4493	0.97	400

^a first line: including volatile particles (burner-out); second line: only non-volatile particles (VPR)

^b first line: pre-DPF; second line: post-DPF measurements

^c official PPS-M1 calibration coefficients (see Equation 3.11)

^d using PPS-M1 calib. coeff., pre-DPF, TRU engine

^e using PPS-M1 calib. coeff., w/o DPF, MDV, on-road driving (6.4l, Navistar, 2009, Power Stroke V8)

^f using PPS-M1 calib. coeff., CVS, w/o DPF, transient test

To highlight the possible differences in soot mass between the *burner-out* and *VPR-out* the measured carbonaceous soot mass with the MSS was compared to the calculated particulate matter mass based on particle size distributions and effective density. Equation 3.13 was provided by Maricq and Xu (2004) and allows to calculate PM mass for a *log-normal* particle size distribution

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given by the total particle concentration (N_{tot}), the geometric mean diameter (μ) and standard deviation (σ). The density (ρ_0) and diameter (d_0) of the primary particles was given by *Maricq and Xu* (2004) as $\sim 2\text{g/cm}^3$ and $\sim 20\text{nm}$ for typical primary combustion-type particles. d_f is the fractal dimension and was described to vary between $d_f = 2.15 \pm 0.1$ for flame-generated soot to $d_f = 2.3 \pm 0.1$ for typical vehicle exhaust particles (*Harris and Maricq*, 2001).

$$M = N_{tot} \frac{\pi}{6} \rho_0 d_0^{(3-d_f)} \mu^{d_f} e^{(d_f^2 (\ln \sigma)^2 / 2)} \quad (3.13)$$

Figure 3.17 depicts the comparison between the MSS mass (*empty symbols*) and the calculated effective density based mass (*filled symbols*) for *burner-out* (*circles*) and *VPR-out* (*triangles*) measurements. A fractal dimension of 2.18 was selected for *burner-out* and 2.25 for *VPR-out* particles leading to close agreement with the micro soot sensor mass measurements. This would be in agreement with *Maricq and Xu* (2004) who mentioned that hydrocarbon condensation onto the solid particle cores might explain the apparent increase in fractal dimension. As reference, Figure 3.17 also contains calculated PM mass values assuming standard particle density of 1g/cm^3 (*empty square symbols*), which is observed to significantly under-predict the measured soot mass over the entire considered particle size range.

Figure 3.18 depicts the correlation between the average *Pegasor Particle Sensor* response, normalized by sample flow rate, and total particle number concentration ($N_{tot\ SMPS}$) calculated from particle size distributions measured by the *SMPSTM*. Only data for *burner-out* particles is used for the linear regression between the sensor response and $N_{tot\ SMPS}$. The total number concentrations for the *VPR-out* distributions appear close together and thus, would cluster up at one point only, thereby not aiding in improving the regression. The relatively low coefficient of determination stems from the fact that total number concentrations, even for the *burner-out* distributions, are within the same order of magnitude of each other allowing to fit data only within a narrow bandwidth of particle concentrations (i.e. 1×10^6 to 5×10^6).

Nevertheless, the slope obtained from the linear regression is $\beta_1 = 214$, which is within $\sim 25\%$ of the slope reported by (*Ntziachristos et al.*, 2013b) as the official PPS-M1 calibration coefficient. Forcing the regression line through the origin yields a slope of $\beta_1 = 333$, which would be around 15% higher than the official PPS-M1 particle number calibration. Table 3.9 provides a comprehensive list of correlation coefficients between the PPS-M1

3.4. Particle Sensor Response Calibration - Soot Generator Experiments

Figure 3.17: Comparison between soot mass measured by the AVL MSS (*filled symbols*) and particulate matter mass calculated from different particle size distributions (SMPS™) and effective density (*empty symbols*) using Equation 3.13; (*triangles*) are VPR-out, and (*circles*) burner-out measurements; *dashed lines* indicate linear regression fits to the data; $V_{ma} = 400V$.

Figure 3.18: Correlation between PPS-M1 response and total particle number concentration as calculated from TSI SMPS™ particle size distributions for different monodisperse burner-out distributions; *dashed black line*: linear regression for PPS vs. $N_{tot SMPS}$; variation bars indicate $1 \cdot \sigma$; $V_{ma} = 400V$.

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and reference particle number concentration instruments. It has to be mentioned that both the AVL APC and Horiba[®] SPCS, listed in Table 3.9, are instruments complying with the PMP protocol to measure total non-volatile particle concentrations, thus, comprising a volatile particle remover.

Table 3.9: Calibration and correlation coefficients for PPS-M1 versus reference particle number measurement instruments from published literature.

Source	Instr.	β_0	β_1	R^2	Trap
R_{PPS} [fA] vs. number [$\#/cm^3$] $\Rightarrow$ calibration coefficients					
Figure 3.18 (<i>this study</i>) ^a	SMPS/CPC	1.63×10^6	2.14×10^2	0.7697	400
<i>Beck et al.</i> (2012) ^b	AVL APC	1.72×10^5	1.12×10^1	0.98	-
	AVL APC	-1.91×10^4	1.74×10^1	0.97	-
<i>Ntziachristos et al.</i> (2013b) ^c	AVL APC	-	2.88×10^2	-	400
<i>Wachtmeister</i> (2012) ^d	Horiba SPCS	-3.60×10^2	5.37×10^6	0.9153	50
	Horiba SPCS	4.91×10^2	4.90×10^6	0.9890	50
R_{PPS} [$\#/cm^3$] vs. number [$\#/cm^3$] $\Rightarrow$ correlation coefficients					
<i>Tikkanen et al.</i> (2014) ^e	AVL APC	-	0.5525	0.95	400

^a including volatile particles (burner-out)

^b first line: pre-DPF; second line: post-DPF measurements

^c official PPS-M1 calibration coefficients (see Equation 3.12)

^d first line: steady-state test; second line: transient test; w/ DPF

^e using PPS-M1 calib. coeff., CVS, w/o DPF, RMC

For a monodisperse aerosol sampled with a unipolar diffusion charger such as the *Pegasor Particle Sensor* the resulting measured current (I_{PPS}) can be related to the sensitivity of the detector (i.e. sensor response, R_{PPS}) by Equation 3.14 (*Lehtimäki*, 1983). The sensor response can be expressed as the sum of the charging efficiency and the particle penetration through the sensor device (η). In the case of the PPS, the penetration depends on diffusional and inertial losses as well as the penetration through the mobility analyzer (i.e. ion trap) (*Rostedt et al.*, 2014). The charging efficiency is a measure of the mean number of elementary charges acquired per particle (n_q) during the charging process, and thus, depending on the $N - t$ product. The product of charging efficiency and penetration is typically lumped together into the overall sensor response (R_{PPS}) and evaluated through individual instrument calibration (*Shin et al.*, 2007; *Ntziachristos et al.*, 2007; *Rostedt et al.*, 2014). In Equation 3.14, I_{PPS} is the current measured by the PPS in [A =

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Coulombs/sec], $\dot{V}_{samp}$ is the sample flow rate in [cm³/sec], N_{tot} the total particle concentration for a given distribution in [# / cm³], and e is the elementary charge in [Coulombs/charge] (i.e. $1.60217657 \times 10^{-19}$).

$$R_{PPS} = \eta n_q = \frac{I_{PPS}}{e \dot{V}_{samp} N_{tot}} \quad (3.14)$$

Figure 3.19 shows the PPS response in [charge/#] as a function of different particle size distributions, including total particle (i.e. with adsorbed volatile matter, *burner-out*, blue circles) and non-volatile particle (i.e. *VPR-out*, red triangles) distributions. Literature has shown that the sensitivity of a unipolar diffusion charger can be approximated by a *power law* function (Lehtimäki, 1983; Ntziachristos et al., 2004) as given by Equation 3.15, with a and b being constants. The exponent b is dependent on the specific instrument technology/design, the particle composition and morphology, and the particle size. For particles with diameter ranging between 12nm to 1μm the exponent b is approximately 1.2, whereas for $d_p < 12$ nm b is observed to increase to 4. . . 6, leading to a significantly reduced sensitivity of the sensor (Lehtimäki, 1983).

$$R_{PPS}(d_p) = \eta(d_p) n_q(d_p) = a \cdot d_p^b \quad (3.15)$$

Equation 3.15 was fitted to the experimental data for both *burner-out* and *VPR-out* sensor response, using a least-squares method, with the resulting curves shown in Figure 3.19. It can be noticed that the exponent for the *burner-out* response is slightly less steep than for the sensor response towards non-volatile particles (i.e. *VPR-out*). The response to the 18nm particle distribution appeared to have pulled the fitted function upwards, thus, lowering the exponent. The combined response ($R_{PPS,comb.}$) to all samples resulted in an exponent of $b = 1.09 \pm 0.11$ which is comparable to $b = 1.05$ obtained through experimental work by Rostedt et al. (2014) using monodisperse and single charged particles to calibrate the PPS-M1. Maricq (2013), using soot particles and PAO oil droplets, found exponents of 1.29 ± 0.04 and 1.14 ± 0.03 , respectively, for the PPS response as a function of particle size. The discrepancy could possibly stem from the fact that Maricq (2013) might have operated the PPS at a lower ion trap voltage¹¹ as compared to voltage setting used for collecting the experimental data presented in Figure 3.19

¹¹the paper did not provide any specific ion trap settings for the presented soot and PAO oil droplet experiments.

3.4. Particle Sensor Response Calibration - Soot Generator Experiments

Figure 3.19: Response of PPS-M1 to burner-out (circles) and VPR-out (triangles) particles of different size; solid blue and red lines indicate power law regression fit to the data; dashed lines are regression lines from literature for PPS (Maricq, 2013; Rostedt et al., 2014) and other DC instruments (Jung and Kittelson, 2005); $V_{ma} = 400V$.

(i.e. $V_{ma} = 400V$). The power law function used by Rostedt et al. (2014) introduced a new expression for the pre-exponential constant a as a function of the ion trap voltage. Using the $V_{ma} = 400V$ setting in their equation might explain the close match with experimental data obtained from this study (see Figure 3.19). Finally, sensor responses from two other diffusion-charging instruments (Jung and Kittelson, 2005) are added to Figure 3.19 to underline the general adherence to an exponent in the range of 1.2 for unipolar diffusion-charging instruments (Lehtimäki, 1983). In addition, Table 3.10 provides a comparison of exponents from different instruments measuring a range of aerosols.

Equation 3.15 is valid for monodisperse aerosols. For the case of polydisperse aerosols, Equation 3.15 can be adapted by integration over the *log-normal* distribution (Maricq, 2013) to yield sensor response as shown in Equation 3.16, where μ and σ_g are the characteristic parameter of the particle size distribution in logarithmic space. However, comparison of both equations for the particle size distributions utilized herein did not reveal any difference in exponential parameter b and only a slight change in pre-exponential parameter a , which altered from 0.0163 to 0.0138 ($\Delta \approx 15\%$) between the

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Table 3.10: Comparison of power law exponents available from literature for different unipolar diffusion-chargers and a variety of aerosols.

Source	Aerosol	Instrument	a	b (exp.)
(Lehtimäki, 1983)	$0.012 \leq d_p \leq 1 \mu\text{m}$	general DC		1.2
(Ku, 2010)		DC2000CE ^a		1.22
		LQ1-DC ^b		1.38
(Jung and Kittelson, 2005)	NaCl aerosol	LQ1-DC	0.0028	1.36
	NaCl aerosol	TSI EAD	0.0181	1.13
(Ntziachristos et al., 2004)	soot	DC		1.41
(Maricq, 2013)	PAO oil, mono	PPS-M1		1.15 ± 0.03
	PAO oil, poly	PPS-M1		1.14 ± 0.03
	soot	PPS-M1	0.007	1.29 ± 0.04
(Rostedt et al., 2014)	SCAR ^c , mono	PPS-M1	0.0514	1.05
	soot & volatiles	PPS-M1	0.0288	0.93 ± 0.12
Figure 3.19	soot	PPS-M1	0.0138	1.14 ± 0.03
	combined	PPS-M1	0.0163	1.09 ± 0.11

^a Ecochem Analytics

^b Matter Engineering AG

^c single charged aerosol reference, nearly monodisperse aerosol containing single charge per particle

monodisperse and polydisperse power law expressions, respectively. Therefore, it can be concluded that the particle size distributions produced by the AVL particle generator were nearly monodisperse with a geometric mean diameter of $\sigma_g \sim 1.7$. Assuming a polydisperse particle size distribution, however, would certainly be more adequate for real engine exhaust emissions.

$$R_{PPS}(d_p) = \eta(d_p) n_q(d_p) = a \cdot \mu^b e^{b^2 (\ln \sigma_g)^2 / 2} \quad (3.16)$$

Figure 3.20 depicts active surface-weighted (*left*) and soot mass-weighted PPS response as a function of particle diameter. The surface and mass weighing was achieved by replacing the total particle number concentration (N_{tot}) in Equation 3.14 with either the total active surface area ($S_{active,tot}$) or the soot mass measured by the AVL MSS (m_{MSS}). A power law expression analogous to Equation 3.15 for monodisperse aerosol distributions was fitted to the experimental data for both *burner-out* and *VPR-out* samples. It can be observed that for both response weighings, data from the two different sampling locations collapse onto one single line, which exhibit a slope of

3.4. Particle Sensor Response Calibration - Soot Generator Experiments

Figure 3.20: (left) Active surface-weighted and (right) soot mass-weighted response of PPS-M1 to burner-out (circles) and VPR-out (triangles) particles of different size; surface based on SMPSTM, soot mass measured with MSS; lines indicate power law regression fits; $V_{ma} = 400V$.

$b_{active-surface} \approx -1.06$ and $b_{soot-mass} \approx -0.66$ for active surface and soot mass weighing, respectively. It has to be mentioned that the 18nm particle diameter was excluded from curve fitting for the soot mass weighted sensor response as the data point appears to be laying far off the *best* fit curve for the remaining points. The large discrepancy for the 18nm diameter could be explained by the very low soot mass measured with the AVL MSS near its detection limit and thus, within the lower signal-to-noise region of the instrument. More data points in the sub-30nm size range would be needed to gain a better understanding of the sensor response towards particle mass in this range. However, it has to be understood that particle mass in the nucleation mode range is often negligibly small and difficult to quantify accurately with a direct measurement method.

Figure 3.21 shows a comparison between the PPS response in [fA/(slpm)] and particle length concentration in [mm/cm³] measured by the TSI EAD. The *blue circles* and *red triangles* indicate burner-out and VPR-out particle median diameters, respectively. From a linear regression analysis between the two instrument responses it becomes evident that both are linearly correlated with a slope of unity for burner-out and ~ 0.96 for VPR-out particles. It has to be mentioned that the actual slopes shown in Figure 3.21 were both multiplied by a constant factor of 100 which is due to unit conver-

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Figure 3.21: Comparison between PPS-M1 response and TSI EAD for both *burner-out* and *VPR-out* particle size distributions; dashed black lines: linear regression for PPS vs. EAD; $V_{ma} = 400V$.

sion between the two instruments. The close agreement in response slope was expected as both instruments quantify particles based on the same diffusion-charging type measurement principle. Possible differences in sensor response arise from differences in sensor design, charger efficiency, and particle penetration through the instrument (i.e. particle losses inside the sampling system and sample flow paths). More interestingly however, is the constant offset of $\Delta \approx +79.2 \text{ mm/cm}^3$ between the *VPR-out* and *burner-out* measurements for the EAD. If shifted by Δ , the *VPR-out* measurements fall onto the same regression line as the *burner-out* particles. No conclusive explanation was found to describe this discrepancy yet. The PPS response appears to be fairly insensitive to the different particle composition due to adsorbed volatile material in case of *burner-out* samples, whereas the EAD shows this distinct but constant offset. It is expected that the EAD would only have a dependency on particle materials and morphology as discussed by Shin *et al.* (2007).

As introduced earlier, the *Pegasor Particle Sensor* includes an electrical trap for the primary purpose of removing any excess ions from leaving the sensor and thereby offsetting the actual measurement. Moreover, as an added feature the ion trap can also serve as a simplified mobility analyzer by trap-

ping particles below a certain size range. The charges these particles are carrying are returned by virtue of impaction with the ion trap which is due to the particles mobility in the electrical field attracting them towards the trap (Maricq, 2013; Rostedt *et al.*, 2014). Successively increasing the voltage applied to the mobility analyzer will cause increasingly larger particles to be deviated towards the trap, impact thereupon, and be removed from the particle stream leaving the sensor and therefore, effectively reduce the sensor response. In light of that, the ion trap can be regarded as a particle remover, introducing a lower particle measurement cut-point such as for example prescribed by the PMP protocol (UN ECE/TRANS/505/Rev.7/Add.48, 2015) with a 23nm cut-point. However, a possible drawback of applying higher voltages to the ion trap is the progressive reduction in sensor sensitivity (Maricq, 2013). Ntziachristos *et al.* (2013b) had suggested to use a trap voltage (V_{ma}) of $\sim 400V$ as this setting had shown the best trade-off between efficient removal of excess ions without significantly affecting the sensitivity.

Figure 3.22 depicts the PPS-M1 response towards 18nm (*circles*) and 40nm (*triangles*) diameter particles as a function of increasing ion trap voltage in the range of 0-600V. It can be observed that the sensor response towards 40nm particles initially drops by $\sim 42\%$ from the $V_{ma} = 0V$ to 50V setting. Thereafter, the rate at which the response reduced, is lowered to $\sim 47\%$ between 50 and 600V. On the other hand, the $V_{ma} = 0V$ setting for 18nm diameter particles indicates a significantly higher sensor response on the order of 11charges/# with a subsequent drop of about 65% to 3.87charges/#. The rate of response reduction was observed to remain larger till approximately the 400V trap setting, where the reduction rate becomes more similar to the rate exhibited by the 40nm particles. Similarly shaped sensor response curves as a function of increasing V_{ma} were observed by Lanki *et al.* (2011) for 8-15nm particles and by Rostedt *et al.* (2014) for 20-920nm particles.

The sensor responses at the $V_{ma} = 0V$ trap setting for both particle sizes appear significantly higher as expected. This can be explained by the fact that at 0V also excess ions will leave the sensor, thus carry charge away and thereby inducing a net current. The probable cause for the 18nm experiments to exhibit a significantly steeper increase in sensor response towards lower ion trap voltages could be due to the saturation of the particles for the given $N - t$ product of the charger, resulting in a larger amount of excess ions. Also, Rostedt *et al.* (2014) mentioned that due to ion leakage it would be impossible to accurately quantify the sensor response at $V_{ma} = 0V$, and therefore, suggested to rather extrapolate the data collected for trap settings above $\sim 50V$ to find the *true* sensor response due to particle concentration

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Figure 3.22: Response of PPS-M1 as a function of varying mobility analyzer (i.e. ion trap) voltages between $V_{ma} = 0$ -600V for two particle diameters $D_p = 18\text{nm}$ (circles) and 40nm (triangles); experimental data fitted by cubic spline method; extrapolation to evaluate corrected sensors response at $V_{ma} = 0\text{V}$ (square symbols).

at $V_{ma} = 0\text{V}$. Following the idea of this approach, cubic interpolation splines were fitted to the experimental data, excluding the 0V data point, as shown in Figure 3.22. The obtained splines were subsequently extrapolated to the 0V intercept in order to find the *true* sensor response at $V_{ma} = 0\text{V}$, of 5.97 and 1.71charges/# for the 18nm and 40nm particle sizes, respectively.

Using the newly obtained zero intercept response values, normalized sensor response (i.e. mobility analyzer penetration) was calculated and plotted in Figure 3.23. It can be noticed that both particle sizes follow a different normalized response trend as a function of mobility analyzer voltage. The sensor response towards 18nm particles still significantly reduces within the 0-200V range (i.e. $\sim 60\%$ reduction for $V_{ma} = 100\text{V}$) and subsequently flattens out. When the charged particles flow through the electric field generated by the ion trap they are acted upon by an electrostatic force that causes the particles to deviate from their straight flow path and drift away from the center electrode, eventually impacting on the outer wall of the annular section inside the trap. The movement of particles inside an electrical field is described by the *electrical mobility* (Z) which depends on the particle velocity and the strength of the electric field (i.e. $Z = V_{TE}/E$) (Hinds, 1999). Based

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Figure 3.23: Normalized response of PPS-M1 based on extrapolated zero-intercept for both 18nm (circles) and 40nm (triangles) particle diameters as a function of varying mobility analyzer voltages between $V_{ma} = 0-600V$; dashed lines are cubic spline method fitting curves to the data.

on that Maricq (2013) suggested to express the normalized sensor response as a function of $V_{ma} \cdot Z(d_p) / \dot{V}_{samp}$ in $[m^{-1}]$, where $Z(d_p)$ is the electrical mobility given by Equation 3.17. A similar approach was also chosen by Rostedt et al. (2014) to describe the mobility analyzer penetration fraction. The *electrical mobility* depends on the number of charges per particle (n), the elementary charger (e), the Cunningham slip correction factor (C_c), the viscosity of the carrier gas (η) as well as the particle diameter, all in SI units. Sutherland's formula was used to calculate the gas viscosity at 293.15K (i.e. 20°C), mean free path of air at 20°C to calculate C_c and the number of charges per particle were assumed to be unity.

$$Z(d_p) = \frac{neC_c}{3\pi\eta d_p} \quad (3.17)$$

Figure 3.24 shows the normalized sensor response plotted against the movement of the charged particles due to their electrical mobility. It becomes evident from this plot that the mobility analyzer penetration for both particle diameters collapses onto one single curve as opposed to the two individual curves shown in Figure 3.23, when plotted solely against the ion trap voltage. Maricq (2013) suggested a power law expression to best describe the

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Figure 3.24: Normalized response of PPS-M1 for 18nm (circles) and 40nm (triangles) particle diameters electrical mobility metric; solid line: fitted mobility analyzer penetration model as a function of V_{ma} .

experimental data. However, in this research it was found that an exponential function better describes the particle penetration through the mobility analyzer¹² (i.e. ion trap). The resulting expression ($P_{V_{ma}}$) is shown in Equation 3.18 as a function of the PPS sample flow, the applied ion trap voltage as well as the particle mobility for a given size particle. Non-linear least-square regression method was used to fit Equation 3.18 to the experimental data, and to obtain constants $a_{V_{ma}} = 0.96$, and $b_{V_{ma}} = -2.23$ ($R^2 = 0.9859$).

$$P_{V_{ma}} = a_{V_{ma}} e^{b_{V_{ma}} \frac{V_{ma} \cdot Z}{V_{samp}}} \quad (3.18)$$

Finally, Equation 3.18 was used to correct the sensor response model given by Equation 3.15¹³ and compared to the two particle diameters 18nm and 40nm for changing V_{ma} settings between 0-600V. It can be noticed that the sensor response model, adjusted for mobility analyzer penetration fraction,

¹²Rostedt et al. (2014) followed a similar approach, describing the mobility analyzer penetration fraction (P_{ma}) using an exponential expression of the ratio between particle electrical mobility and the limiting electrical mobility at which all particles would be collected.

¹³same approach can be used for both Equations 3.15 for monodisperse and 3.16 for polydisperse aerosols.

3.4. Particle Sensor Response Calibration - Soot Generator Experiments

Figure 3.25: Response of PPS-M1 for 18nm and 40nm particle size distributions as function of varying mobility analyzer voltages between $V_{ma} = 0$ -600V; *dashed lines* indicate PPS response model corrected for mobility analyzer penetration as function of V_{ma} .

qualitatively predicts the variation in sensor response of 40nm particles due to mobility analyzer voltage changes. However, for the 18nm size particles only the sensor response for the ion trap settings of 400V and 600V can be qualitatively well described by the corrected response model. The sensor response for the 50-250V settings significantly deviates from the model prediction as was already evident from the sharp increase in sensor response shown in Figure 3.22. As mentioned before this could be due to an increase in excess ions because the available particles are already saturated with charge for the given residence time in the diffusion charger. Additional experimental data would be required in the sub-30nm particle size range to better understand ion trap efficiency for this size range and possibly explain why the 18nm particles did not follow a similar trend as was observed for the 40nm particles.

Studies by *Shin et al. (2007)*; *Marra et al. (2010)*; *Fierz et al. (2011)* (and many others) suggested that diffusion-chargers could be directly used to measure lung-deposited surface area in the different sections of the human respiratory tract (see discussion in Section 2.2.2). Figure 3.26 provides an example of the PPS-M1 response in comparison to the deposited surface area in the alveolar region of the human lung. Following Equation 2.18, the LDSA is cal-

3.4. Particle Sensor Response Calibration - Soot Generator Experiments

Figure 3.26: Comparison of normalized PPS-M1 response with i) normalized geometric and active surface, and ii) respective normalized lung-deposited surface areas for alveolar penetration fraction; data normalized with respect to $D_p=40\text{nm}$; $V_{ma} = 400\text{V}$.

culated as the product of total particle surface area (S_{tot}) and size dependent penetration fraction into the alveolar region of the respiratory tract (η_{AL}) given by Equation 2.14. Two different definitions of surface area were chosen for this comparison, namely the geometric surface area (i.e. $S_{geo} = \pi d_p^2$) and the *active surface* area given by Equation 2.28. All data presented in Figure 3.26 was normalized based on a particle diameter of 40nm and the experiments were conducted with the ion trap set to $V_{ma} = 400\text{V}$. It can be noticed that the experimental data for both *burner-out* and *VPR-out* sampling locations follow the calculated lung-deposited surface area for the alveolar region, with exception of the measured 18nm diameter particles.

In order to infer particle number and particulate matter mass concentrations from the raw *Pegasor Particle Sensor* signal during combustion engine testing, three calculation methods will be employed as listed below.

Method 1: Default calibration coefficients for particle number (Equation 3.12) and particulate matter mass (Equation 3.11) concentrations provided by Pegasor (Oy) Ltd. and described by (Ntziachristos *et al.*, 2013b).

3.4. Particle Sensor Response Calibration - Soot Generator Experiments

Method 2: Calibration coefficients obtained from linear regression during the soot generator experiments between the PPS-M1 response and i) AVL MSS for PM mass, and ii) SMPSTM particle size distributions for total particle number concentrations.

Method 3: Using the calibrated sensor response model and assumed geometric mean diameter (μ_g) and standard deviation (σ_g) of a characteristic particle size distribution (i.e. see *Harris and Maricq* (2001)) to calculate total particle number concentrations using Equation 3.19 and 3.20 for monodisperse and polydisperse particle size distributions, respectively. Using the obtained N_{tot} and the assumed particle size distribution, the particulate matter mass concentration can subsequently be calculated with Equation 3.13.

$$N_{tot_{mono}} = I_{PPS} \cdot \left[\frac{1}{e\dot{V}_{samp}} \left(a \cdot d_p^b \right)^{-1} \right] \quad (3.19)$$

$$N_{tot_{poly}} = I_{PPS} \cdot \left[\frac{1}{e\dot{V}_{samp}} \left(a \cdot \mu^b e^{b^2 (\ln \sigma_g)^2 / 2} \right)^{-1} \right] \quad (3.20)$$

Chapter 4

Experimental Equipment and Procedures

This chapter will provide a general overview of the experimental setups, procedures and instrumentation equipment employed during different stages of this study. Since specific instrument settings and details of the exhaust gas sampling systems changed for the various measurement campaigns discussed in this thesis, description of experimental setups will be limited to solely a generic illustration of the equipment and more details will be provided accompanying the respective discussion of results in Chapter 5. Furthermore, a wide range of laboratory facilities were utilized to evaluate the particulate matter sensor under various operating conditions, and sampling from different technology internal combustion engines (i.e. in terms of fuel, combustion strategy, after-treatment package), spanning from engine and chassis dynamometers to on-road testing setups.

Section 4.1 on the following page of this chapter will discuss the *partial-flow sampling* (PFS) systems employed to extract a representative exhaust sample for subsequent characterization with various particle sizing and counting instruments or for physical collection of particulate matter on filter media for gravimetric mass quantification. This section will further highlight on sample conditioning and treatment considerations and provide an estimation of particle losses associated with the PFS systems utilized. Sections 4.2 on page 158 and 4.3 on page 170 will describe the engine dynamometer facility as well as the chassis dynamometer, respectively, including a presentation of the instruments available for quantification of gaseous and particle phase emissions. Finally, Section 4.4 on page 185 will present the experimental setups employed for real-world, on-road demonstration of the particulate

matter sensor performance on both light- and heavy-duty vehicle platforms.

4.1 Partial-Flow Sampling System for Particle Characterization

Partial-flow sampling systems are employed to extract a representative sample from the exhaust stream to be directed towards various particulate matter characterization instruments or to be sampled on either, i) specific sampling substrates (e.g. copper grids, mica sheets) for microscopic analysis using TEM or SEM instruments or ii) gas-permeable filter media for subsequent gravimetric or chemical analysis of the retained particulate matter. From a physical point of view, exhaust dilution is employed in an attempt to mimic particle transformation and dilution phenomena occurring during real-world dilution of exhaust gas upon exiting the exhaust stack or pipe and mixing with the ambient air (Kittelson *et al.*, 2002, 2006; Swanson *et al.*, 2011). On the other hand, from a measurement point of view, dilution of exhaust gas is required because of (Bergmann *et al.*, 2008; Swanson *et al.*, 2011) i) particle concentrations in the raw exhaust stream need to be reduced to levels suitable for the operating range of particulate measurement instruments, and ii) the gas temperature of the exhaust sample needs to be cooled to acceptable levels for instruments, while preventing possible condensation of water vapor and other gaseous components.

A wide collection of studies (including but by far not limited to Khalek *et al.* (1999, 2000); Kittelson *et al.* (2002, 2006); Swanson *et al.* (2011)) has been dedicated to understand and quantify how different parameters of the partial-flow sampling system influence the physical nature of particles and possibly enhance or suppress nanoparticle formation during the dilution process. Characteristic parameters include the i) mini-dilution tunnel design and operation; ii) diluter geometry; iii) dilution ratio, rate, and temperature; iv) transfer line size and placement; v) residence time in different parts of the sampling system; and vi) possible heat loss across the sampling system. Studies by Khalek *et al.* (1999), Kittelson *et al.* (2002), and Venkatasubramaniam (2007) found that dilution air temperature, relative humidity, residence time in the dilution system and *residence chamber* (i.e. mini-dilution tunnel) as well as the dilution ratio and rate are the primary influencing parameters for nanoparticle formation or suppression and adsorption phenomena of volatile compounds onto solid particles (for more detailed discussion see Sections 2.1 and 2.4). For example, results showed that nanoparticle formation is enhanced by low dilution air and mini-dilution tunnel tempera-

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tures along with high relative humidity (*Khalek et al.*, 1999, 2000; *Kittelson et al.*, 2002). Furthermore, the same studies reported that if the residence time is increased, particles are observed to grow in size via adsorption of gaseous compounds and coagulation. *Kasper* (2004) provides an in-depth discussion of possible pathways to dilute a hot exhaust gas sample to concentration and temperature levels suitable for particle characterization instruments while controlling/understanding the impact of the volatile fraction onto nanoparticle formation and formation of possible sample artifacts. *Lyyrinen et al.* (2004) compared different dilution methods and combinations thereof, including ejector diluters, porous wall diluters, and mass-flow controller based dilution systems and concluded that particle size and concentration strongly depended on the diluter geometry. Thus, a partial-flow sampling system would need to be designed with these parameters in consideration and in accordance with the specific objective of a given study (i.e. suppression of nanoparticle formation to study solely solid particles or enhancement of nanoparticle formation and adsorption phenomena on the other hand).

The partial-flow sampling system employed for this study, allowing to extract and precondition the exhaust gas sample directly from the exhaust stack as depicted in Figure 4.1, was designed based on results and recommendations found from studies by *Khalek et al.* (1999); *Kittelson et al.* (2002); *Venkatasubramaniam* (2007). It comprised at the minimum a double-stage mini-dilution tunnel system with a first *heated* and second *cold* dilution stage, along with the provision to expand it by a third *cold* dilution stage for particle characterization from legacy engines or when sampling upstream a particulate filter if concentration levels exceeded necessary instrument ranges.

Hot dilution with dilution air maintained at temperatures in the range of 130 to 150°C (controlled to $\pm 5^\circ\text{C}$ via a PID controller) was employed for the first stage dilution to reduce the possibility of organic and volatile materials from condensing on carbonaceous particles or from nucleating and forming new nuclei-mode particles. Diluting the sample gas at elevated temperatures leads to a reduction in partial pressures of the volatile species, thus, effectively lowering the temperature where they might start condensing. The mini-dilution tunnel of the first stage was additionally wrapped with heating wire and insulated, allowing for it to be heated and maintained at $150 \pm 5^\circ\text{C}$ or $185 \pm 5^\circ\text{C}$ depending on experimental requirements. This was done analogously to the concept of a heated residence chamber as described and applied by *Khalek et al.* (1999); *Kittelson et al.* (2002). Subsequently, the sample underwent a second stage of dilution at a lower temper-

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Figure 4.1: Schematic diagram of *PMP-like* partial-flow sampling system using a constant flow mini-dilution tunnel with an ejector diluter (Air-Vac, model TD-110-H *Air-Vac Engineering Company, Inc.* (2015)) and heated 1st stage dilution.

ature of about $25 \pm 5^\circ\text{C}$ in order to stabilize the sample gas and to reduce its temperature to the required instrument inlet conditions. Since exhaust particle concentrations from legacy diesel engines and when sampling upstream particulate filters still exceed the upper measurement range for some instruments after the second dilution stage, a third stage was utilized to further reduce concentrations using dilution air at $25 \pm 5^\circ\text{C}$. The combination of a first *hot* and second *cold* dilution of the exhaust sample has proven to be a relatively simple way to suppress adsorption and nucleation phenomena of the volatile compounds without having to actively remove them from the sample stream with a more complex apparatus such as a catalytic stripper (Khalek and Kittelson, 1995) or thermal denuder (Burtscher *et al.*, 2001). Indeed, Venkatasubramaniam (2007) showed that the impact of volatile fraction onto particle formation in the nucleation mode range as well as adsorption onto particles in the accumulation mode range was reduced when employing a hot first dilution stage. The study further concluded that a *hot* dilution approach could be used as an alternative to thermodesorbers in order to minimize the effects of the volatile exhaust fraction onto measurement results. Furthermore, the volatile particle remover specified by the European PMP protocol (UN ECE/TRANS/505/Rev.7/Add.48, 2015) for regulatory particle number quantification similarly comprises a combination of *hot* dilution with an evaporation tube and a second *cold* dilution stage, as was described in more detail in Section 2.3.

A sharp-edged, stainless steel, *J-type* sampling probe with an internal diameter of 0.18" ($\sim 4.6\text{mm}$) was mounted into the exhaust stack or transfer pipe to

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extract an exhaust sample at a constant flow rate and routed to the ejector diluter of the first stage. The sampling line from the probe to the ejector diluter was either i) a short $\frac{1}{4}$ in (with ID 0.18", ~ 4.6 mm) stainless steel tube, insulated with fiber-glass wrap if the dilution system was close-coupled with the exhaust pipe or ii) a $\frac{3}{8}$ in, 39.4in (~ 1.0 m) heated line (Hillesheim GmbH, H900-series, 200°C) if the dilution system was placed some distance away from the exhaust transfer pipe as done during chassis dynamometer experiments. Each mini-dilution tunnel was equipped with the same sharp-edged, stainless steel, *J-type* sampling probe (with ID 0.18", ~ 4.6 mm) to extract a diluted exhaust sample and route through a $\frac{1}{4}$ in (with ID 0.18", ~ 4.6 mm) stainless steel tube to the ejector diluter of the subsequent dilution stage. Finally, flexible, $\frac{1}{4}$ in conductive silicone tubing (TSI Inc.) was utilized to route the diluted exhaust sample from the last dilution stage to the respective particle characterization instruments. Conductive silicone tubing is impregnated with carbon and thus, exhibits very low resistivity (i.e. $\sim 8\Omega/\text{cm}$). This leads to reduced buildup of static charge and ultimately minimizes particle losses to the tubing walls via electrostatic deposition (*Von der Weiden et al.*, 2009). Great care was taken to keep the sample transport distance between last dilution stage and instruments as short as possible to reduce diffusional particle losses. Losses due to thermophoresis were assumed minimal as the sample gas exiting the last dilution stage has attained a similar temperature level as the ambient air surrounding the transfer tubing, thus, exhibiting a negligible temperature gradient (i.e. for $\Delta T < 40^{\circ}\text{C}$ particle loss due to thermophoresis is negligible (*Von der Weiden et al.*, 2009)).

Compressed air from the house-air supply system in the engine laboratory or from the on-board compressor in the transportable emissions measurement system (see Section 4.3.2) during chassis dynamometer and on-road testing was used to supply the ejector diluters with the required dilution air. The dilution air was filtered with a HEPA filter and dried with an in-line desiccant air dryer. When dilution air was supplied on-board, an additional heatless, regenerative desiccant absorbent dryer (Perma-Pure Inc., model HD-2000-6-110) was installed to assure a low dewpoint of the dilution air in order to prevent water condensation and any associated impact onto particles in the dilution system (i.e. increased dilution air relative humidity is known to enhance nucleation of nano-sized particles (*Khalek et al.*, 1999)). The dilution air for the *hot* first stage ejector diluter was routed through a 9ft (~ 2.7 m) heated line to be elevated to temperatures between 130 to 150°C .

Table 4.1 provides an overview of the different dilution settings used for experiments presented in this study. Specifically, two different dilution setups

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Table 4.1: Settings and configuration of the two partial-flow sampling systems employed during this study; comparison to settings required for European PMP system *UN ECE/-TRANS/505/Rev.7/Add.48* (2015); tunnel diameter in [in], residence time in [sec].

	System 1 (ATS out)	System 2 (Engine out) (ATS out)	PMP
	1 st stage	1 st stage	1 st stage ^c
DR	6.7	6.2 - 58.1 6.2	10 - 200
T _{dilution air}	150 ± 5°C	130 ± 5°C 130 ± 5°C	>150°C ≤ 400 ± 10°C
T _{tunnel wall}	150 ± 5°C	130 ± 5°C 130 ± 5°C	300 - 400 ± 10°C ^d
Ø _{tunnel}	3	2 2	-
t _{residence}	1.84	0.43 - 0.53 0.45	-
	2 nd stage	2 nd stage	2 nd stage ^e
DR	8.1-23.8 ^a , 67.8 ^b	11.4 - 58.1 23.8	10 - 15
T _{dilution air}	25 ± 5°C	25 ± 5°C 25 ± 5°C	~35°C ^f
T _{tunnel wall}	25 ± 5°C	25 ± 5°C 25 ± 5°C	-
Ø _{tunnel}	3/4	2 2	-
t _{residence}	< 0.01	0.49 - 0.53 0.52	-
	(no 3 rd stage)	3 rd stage	(no 3 rd stage)
DR	-	8.1 - 11.4 -	-
T _{dilution air}	-	25 ± 5°C -	-
T _{tunnel wall}	-	25 ± 5°C -	-
Ø _{tunnel}	-	1 -	-
t _{residence}	-	< 0.01 -	-
DR _{tot}	55 ^h -159 ^a , 455 ^b	2550 - 5377 148	100 - 3000
t _{residence}	~1.84	0.95 - 1.03 0.97	< 20 ^g

^a for Diesel engines

^b for CNG engines

^c particle number diluter PND₁

^d evaporation tube (wall)

^e particle number diluter PND₂

^f inlet temperature to CPC

^g total residence time of entire system incl. t₉₀ for CPC

^h dilution ratio only selected for one test vehicle

were employed (i.e. labeled *System 1* and *System 2*) with the first comprising a 3in (ID, ~76mm) heated mini-dilution tunnel followed by a short residence time (<0.01sec) second stage dilution. *System 2* on the other hand, comprised two identical 2in (ID, ~51mm) mini-dilution tunnels, with the first stage being heated, and subsequently followed by a short residence time (<0.01sec) third stage dilution for samples extract from *engine-out* location. All mini-dilution tunnels presented herein were made out of smooth wall, grade 316 stainless steel pipe material.

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The two dilution systems are compared to the requirements for sample dilution/conditioning prescribed for regulatory particle number quantification according to the European PMP method (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015) listed in the right most column of Table 4.1. Overall, both *Systems 1* and *2* exhibited a total dilution ratio of ~ 159 and ~ 148 , respectively, for PM after-treatment equipped Diesel engines, and *System 2* a DR of $\sim 2550 - 5377$ for *engine-out* measurements. *System 1* was also utilized in conjunction with particle emissions characterization from stoichiometric operating, CNG fueled engines with a total dilution ratio of ~ 455 . It can be noticed from Table 4.1 that the total dilution ratios are within the range specified by the PMP protocol. Dilution ratios for *engine-out* measurements were, as expected, at the upper limit or exceeding the PMP protocol requirement of maximum 3000, as it should be noted that the PMP dilution system was designed for after-treatment and ultra-low particle emitting engines able of complying with the European PN limits. Dilution ratios for the first stage were selected slightly below, whereas DRs for the second stage to be above the PMP protocol specifications. The other notable difference was the temperature prescribed for the VPR of $300 - 400 \pm 10^\circ\text{C}$ (*UN ECE/TRANS/505/Rev.7/Add.48*, 2015) as compared to $130 - 150 \pm 5^\circ\text{C}$ chosen for the first stage mini-dilution tunnels presented in this study. More specific details about the dilution system and respective settings can be found in Table 4.1.

4.1.1 Ejector diluter

Ejector diluter are widely used for sample dilution in conjunction with particle emissions characterization. The primary advantage is their lack of moving parts and their ability to draw an exhaust sample from a source without the need of an additional pump (*Bergmann et al.*, 2008). During the extraction process a finite amount of raw sample is homogeneously mixed with a finite amount of dilution gas, and by adding multiple ejector diluter in series overall high dilution rates can be achieved, while keeping dilution air consumption low (*Koch et al.*, 1988).

For the partial-flow sampling systems employed during this study commercially available ejector diluter from Air-Vac Engineering Company Inc., in particular model TD-110-H (*Air-Vac Engineering Company, Inc.*, 2015), were utilized. Figure 4.2 shows a picture (*left*) and a schematic of the ejector diluter (*right*) and the respective internal flow paths. The same or similar (i.e. model TD-260) model of ejector diluter have been applied for particle emissions sampling in previous studies with results published in literature

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Figure 4.2: (left) Ejector diluter, Air-Vac, model TD-110-H (single-stage vacuum generator); (right) Schematic of ejector diluter working principle, left side: raw sample inlet, right side: diluted sample outlet (Pictures taken from manufacturer specification document, Air-Vac Engineering Company, Inc. (2015)).

(Khalek *et al.*, 1999; Kittelson *et al.*, 2002; Venkatasubramaniam, 2007; Swanson *et al.*, 2011). An interchangeable critical flow orifice is installed at the inlet of the ejector diluter (i.e. left port in Figure 4.2(left)) in order to maintain a constant raw sample flow. Compressed dilution air supplied to the ejector (i.e. top port in Figure 4.2(left)) flows around the nozzle and expands at high velocity into the open vacuum passage, thereby developing sufficient under-pressure to draw the sample gas through the orifice into the mixing chamber. The residence time of the dilute exhaust mixture was not explicitly calculated for the setup utilized in this study, however, Swanson *et al.* (2011) used a similar, but slightly larger (model TD-260) ejector diluter and reported residence times on the order of ~ 3 milliseconds for a diluted exhaust gas flow rate of 180slpm. With flow rates during this study observed to be in the range of 116slpm to 145slpm for a smaller sized ejector diluter as Swanson *et al.* (2011) were using, the residence time was assumed to be on the same order of magnitude as reported by Swanson *et al.* (2011), and thus, too short for particle transformation phenomena to occur inside the ejector diluter itself.

Two parameters are typically available to change the dilution ratio for a given ejector diluter, specifically, the dimension of the critical flow orifice, and the dilution air pressure. Increasing the dilution air pressure or reducing the flow rate of the orifice will lead to an increase in dilution ratio, whereas a reduction in pressure or an increase in orifice flow rate will result in a reduced dilution ratio. In order to achieve the desired dilution ratios during this study a combination of a series of orifices (i.e. 2, 5, 11, 16, 20,

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22slpm) operated at two different dilution air pressure levels (i.e. 60 and 80psig) was applied.

The dilution ratio of an ejector diluter is affected by a number of parameters (Giechaskiel *et al.*, 2004), including the i) geometry of the raw sample nozzle; ii) lines of the dilution and diluted sample gas; iii) composition of the dilution and sample gas; and iv) operating conditions (i.e. pressure and temperature) of the sample, dilution, and diluted gas. For exhaust sampling from combustion engines, the geometry of the ejector diluter and the dilution gas composition usually remain the same for a given test setup, however, the operating conditions of the diluter and the composition of the exhaust sample gas might change considerably during testing (Giechaskiel *et al.*, 2004).

As ejector diluter usually are calibrated at ambient conditions (i.e. temperature and pressure), real exhaust gas sample conditions might significantly impact the actual dilution ratio of the ejector diluter (Bergmann *et al.*, 2008; Giechaskiel *et al.*, 2004). Giechaskiel *et al.* (2004) investigated the influence of composition, pressure, and temperature of the exhaust gas sample, the dilution air pressure as well as the pressure at the ejector diluter outlet onto the dilution ratio, and provided an iteratively solvable, and fluid-dynamic based model to serve as possible correction algorithm (i.e. experiments performed using a Dekati[®] diluter DI-1000 (Dekati Ltd., 2014)). Results indicated that CO₂ concentrations up to 12.1% in the sample gas, a level common for diesel engines during high load conditions and slightly higher than expected from natural gas fueled engines operating on a stoichiometric combustion strategy, increased the dilution ratio by ~6% over the reference condition (Giechaskiel *et al.*, 2004). Furthermore, the same study (Giechaskiel *et al.*, 2004) as well as Bergmann *et al.* (2008) found that an increase in raw sample gas temperature by 140°C leads to an increase in dilution ratio of about 20% (i.e. both studies used experimental data from a Dekati[®] diluter DI-1000 (Dekati Ltd., 2014)). Bergmann *et al.* (2008) provided a simple method to calculate dilution ratios over a wide range of sample gas pressures and temperatures, for both critical and non-critical flow regimes, as a function of only the pressure difference across the diluter and sample gas temperature. The study concluded that ejector diluter exhibit a relatively high accuracy with errors in the range of ± 4 to $\pm 8\%$ over a differential pressure range of -10mbar to 3200mbar (i.e. diluter inlet vs. outlet pressure), and sample temperature range of 40°C to 200°C (Bergmann *et al.*, 2008). A possible influencing factor is soot deposition onto the ejector nozzle or orifice that can alter the geometric characteristics, and thus, effectively change the dilution ratio as a function of operating time (Bergmann *et al.*, 2008; Giechaskiel *et al.*, 2004; Swanson

Figure 4.3: Dilution air flow rate [scfm] for the ejector diluter (Air-Vac, model TD-110-H) as a function of dilution air supply pressure [psig]; Graph adapted from *Air-Vac Engineering Company, Inc.* (2015) and supplemented with curve fit (i.e. red colored line).

et al., 2011). An increase of $\sim 1\%$ in dilution ratio was observed by *Giechaskiel et al.* (2004) for each *milligram* of sampled diesel particulate matter through the ejector diluter. However, this is a more predominant impediment associated with measurements of diesel PM from non-filter equipped, legacy engines or when sampling upstream the particulate filter. In this case, more frequent cleaning of the ejector nozzle will assure a repeatable dilution ratio for a given ejector diluter setting.

During this study the dilution air flow rate was extracted as a function of dilution air pressure from charts provided by the ejector diluter manufacturer (*Air-Vac Engineering Company, Inc.*, 2015) shown in Figure 4.3. In order to allow for calculation of a continuous dilution air flow rate as a function of pressure, a curve was fitted to the chart (i.e. red line in Figure 4.3) with the resulting function given by Equation 4.1, where P_{dil} is the provided dilution air pressure in [psig], and Q_{dil} the resulting dilution air flow rate in [scfm]. From inspection of Figure 4.3 it's possible to identify the two flow

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regimes, namely, the non-critical flow regime below ~ 20 psig, and the critical flow regime above ~ 40 psig, where the dilution air flow increases roughly proportional with an increase in pressure. Using Equation 4.2 the dilution ratio was calculated based on the estimated dilution air flow rate and the known sample flow rate (Q_{sample} in [slpm]) specific to a given critical flow orifice installed at the ejector diluter inlet. Venkatasubramaniam (2007) compared the method of calculating dilution ratios using the dilution air flow chart (i.e. the study used the same Air-Vac, model TD-110-H ejector diluter) with a second method based on CO₂ concentration measurements in the raw sample and diluted exhaust flow, and observed good agreement in the range of $\pm 5\%$ between the two methods. The study concluded that the flow chart based method is of sufficient accuracy for dilution ratio estimation of an ejector diluter.

$$Q_{dil} = f(P_{dil}) = \frac{1}{1.74} \sqrt{P_{dil}} - 0.42 \quad (4.1)$$

$$DR = \frac{Q_{sample} + Q_{dil}}{Q_{sample}} \quad (4.2)$$

The actual dilution air pressure will slightly vary around the desired set pressure, and thereby affecting the dilution ratio. This will be even more pronounced for mobile applications where the compressed air is supplied from an on-board compressor coupled to a reservoir with the pressure level being affected by the upper/lower threshold governing the on-off cycle of the compressor. Figures 4.4(left) and 4.4(right) show changes in dilution ratios as a function of deviations in dilution air pressure from the selected reference pressure of 60psig and 80psig, respectively. It can be noticed that pressure deviations have a lesser impact on the dilution ratio for the higher pressure setting (i.e. 80psig). Also, the different curves plotted in both figures represent the six critical flow orifices utilized during this study. Increasing the sample flow rate, thus lowering the dilution ratio for a given pressure, was observed to slightly reduce the effect of dilution air pressure variations. From pressure measurements taken with the different experimental setups it was concluded that maximum dilution air pressure deviations are typically within ± 3 psig. This would translate into an approximately $\pm 2.5\%$ and $\pm 1.8\%$ maximum deviation in dilution ratio for the 60 and 80psig pressure settings, respectively.

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Figure 4.4: Changes in dilution ratio [%] due to deviations in dilution air pressure from the selected reference pressure of (left) 60psig, and (right) 80psig, for typical sample gas flow rates (i.e. selected sample flow orifice) with the Air-Vac, model TD-110-H ejector diluter.

4.1.2 Particle loss considerations for partial-flow sampling system

As discussed in Section 2.4.1 sampling trains and systems utilized for the quantification of particle emissions are subject to particle losses as a function of particle size, sample flow rate, sample temperature, and system geometry. Particle loss phenomena associated with the partial-flow sampling system described in this chapter for the 10 - 300nm particle size range include, diffusional losses, turbulent inertial deposition, inertial deposition in bends and contractions/enlargements, thermophoretic losses, and electrostatic deposition (Kittelson *et al.*, 2002; Ayala *et al.*, 2003). In order to minimize electrostatic deposition losses, sampling probes and mini-dilution tunnels were made out of 316 grade stainless steel and transport lines were either stainless steel or conductive silicone tubing. To address thermophoretic losses, the sample extraction probe inserted into the exhaust transfer pipe, and the sample transfer tube to the first stage ejector diluter were heated and insulated to maintain a wall temperature of ~ 130 to $150 \pm 5^\circ\text{C}$. In case of PFS *System 1* the 39.4in heated line used to connect the extraction probe to the ejector diluter was heated and maintained at $200 \pm 5^\circ\text{C}$. For both setups the heated first stage mini-dilution tunnels were heated and insulated minimizing diluted sample-to-wall temperature gradients. Subsequent dilution stages (i.e. 2nd and 3rd stage) were not insulated as diluted sample gas temperatures had attained near ambient air temperatures, thus reducing temperature gradients to a level where thermophoretic losses become negligible (i.e. for $\Delta T < 40^\circ\text{C}$ (Von der Weiden *et al.*, 2009)). With exception of the *J-type* sampling probes all transfer lines were kept straight to reduce possible inertial deposition losses in bends. The dominant particle loss phenomena are diffusional losses, espe-

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cially for particles of size range below $<100\text{nm}$ (Hinds, 1999; Von der Weiden *et al.*, 2009), due to Brownian motion.

In order to quantify particle transport losses associated with the sampling probe, the ejector diluter and the mini-dilution tunnel as part of the partial-flow sampling system presented herein, experiments using an aerosol generator to produce artificial particles were conducted. A schematic drawing of the experimental setup is shown in Figure 4.5 along with a picture thereof in Figure 4.6. An electrospray aerosol generator (EAG, TSI Inc., model 3480) was used as particle source. A sample solution containing particles is stored in a vial that is enclosed in a pressure chamber inside the EAG (TSI Inc., 2003). The solution is being charged via a high-voltage platinum wire that is immersed into the vial and by virtue of an applied differential pressure the solution is pushed through a capillary into the electrospray chamber. There an electrical field pulls the charged solution out of the capillary which is subsequently mixed with HEPA filtered air and CO_2 to form droplets. The charged droplets are neutralized via a radioactive source (Polonium-210) and the liquid is evaporated generating an aerosol of defined size (count mode diameter) that finally leaves the EAG (TSI Inc., 2003). As particle source, nominal 21nm and 50nm polystyrene particles (Duke Scientific Corp., 3000 series nanosphereTM size standards, 21nm: 3020A, 50nm: 3050A, particle density $1.05\text{g}/\text{cm}^3$) were used to quantify particle losses of the partial-flow sampling system.

The sample flow rate selected for these experiments was 5lpm (i.e. via critical flow orifice at ejector diluter inlet) and the dilution air pressure for the ejector diluter 60psig, leading to a dilution ratio of 23.8. A sample was extracted at 1.5slpm from four locations of the PFS system, labeled P_1 through P_4 in Figure 4.5, and routed via $1/4\text{in}$ (ID) conductive silicone tubing to an SMPSTM (TSI Inc., model 3080) operated in manual mode to only select particles of either 20nm or 50nm electrical mobility diameter before being counted by a CPC (TSI Inc., model 3025A). Upstream ($N_{CMD_i,in}$) and downstream ($N_{CMD_i,out}$) particle concentrations were continuously recorded over 120sec for each particle size and location, and this was repeated three times. The study was conducted under ambient temperature conditions allowing to neglect thermophoretic losses.

The particle penetration or the transport efficiencies were subsequently calculated for i) the sample probe, including the conductive silicone tubing (P_1 - P_2); ii) the ejector diluter (P_2 - P_3); and iii) the mini-dilution tunnel (P_3 - P_4) including the *J-type* extraction probe. A smooth-angle *Y-type* flow splitter

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Figure 4.5: Schematic diagram of experimental setup for particle loss quantification in a constant flow mini-dilution sampling system with ejector diluter using the TSI Electro Spray Aerosol Generator (EAG) (TSI Inc., 2003) as particle source.

Figure 4.6: Picture of experimental setup for particle loss quantification in a constant flow mini-dilution sampling [1] system with ejector diluter [2]; *instruments from left to right:* TSI EAG 3480 [3], TSI SMPSTM 3080 with long DMA (model 3081) [4], TSI CPC 3025A [5].

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was used to extract the sample flow to the SMPSTM without significantly affecting the flow through the PFS. Great care was taken to keep the silicone tubing at the same length when switching between the sampling locations in order to maintain similar diffusional losses. Equations 4.3 and 4.4 were used to calculate the losses through probe, line, and mini-dilution tunnel as well as the ejector diluter, respectively, where, $N_{CMD_{i,in}}$ is the total particle number concentration upstream in $[\#/cm^3]$, $N_{CMD_{i,out}}$ the total particle number concentration downstream in $[\#/cm^3]$, and DR the dilution ratio of the ejector diluter.

$$L_{CMD_{i,probe/line/tunnel}} = \left(1 - \frac{N_{CMD_{i,out}}}{N_{CMD_{i,in}}}\right) \cdot 100 \quad (4.3)$$

$$L_{CMD_{i,ED}} = \left(1 - \frac{N_{CMD_{i,out}}}{N_{CMD_{i,in}}} \cdot DF\right) \cdot 100 \quad (4.4)$$

Table 4.2 lists the measured particle number concentrations for all four sampling locations and both particle sizes evaluated, and Table 4.3 provides the calculated particle losses over the three sub-components of the partial-flow sampling system. It can be readily noticed from Table 4.3 that losses over the sampling probe and transfer tube to the ejector diluter are greatest and account for $33 \pm 3.1\%$ and $36 \pm 0.9\%$ of total system losses for 21nm and 50nm (i.e. CMD) particles, respectively. This is comparable to the magnitude of losses through sampling and transport lines reported by *Ayala et al.* (2003).

Table 4.2: Measured particle number concentration at different locations along the partial-flow sampling system with TSI SMPSTM set to manual mode and respective particle CMD (i.e. 20nm or 50nm).

CMD	$N_{probe_{in}}$ (P_1)	$N_{probe_{out}}$ (P_2)	$N_{ED_{out}}$ (w/o dil.) (P_3)	$N_{ED_{out}}$ (w/ dil.) (P_3)	$N_{tunnel_{probe}}$ (P_4)
[nm]	$[\#/cm^3]$	$[\#/cm^3]$	$[\#/cm^3]$	$[\#/cm^3]$	$[\#/cm^3]$
50	21,203	13,605	544	12,868	531
21	30,027	20,145	813	19,240	837

Particle losses over the ejector diluter were observed to be of a similar level for both 21nm and 50nm particles with $4 \pm 6.0\%$ and $4 \pm 6.8\%$, respectively. *Giechaskiel et al.* (2009) investigated the losses of volatile and non-volatile diesel exhaust and as well as solid NaCl particles when sampled through an ejector diluter. Results indicated that particle losses in the size range

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Table 4.3: Calculated losses for nominal CMD 20nm and 50nm particles over components of partial-flow sampling system; 1) sample probe and transfer tube; 2) ejector diluter; 3) mini-dilution tunnel and extraction probe (negative number indicates measured increase in particle concentration).

CMD [nm]	Loss _{probe} (P_1-P_2) [%]	Loss _{ED} (P_2-P_3) [%]	Loss _{tunnel} (P_3-P_4) [%]
50	36±0.9	4±6.8	2±7.8
21	33±3.1	4±6.0	-3±3.1

of 15 - 300nm were below 5% and are thus assumed negligible, which the authors conclude to be consistent with findings from other published literature. The same was observed to hold true for both particles with and without volatile matter absorbed on the solid core. The study further found the impact of ejector diluters on volatile (i.e. liquid) nucleation mode particles of sizes larger than 10nm to be negligible (Giechaskiel *et al.*, 2009). A study by Venkatasubramaniam (2007) reported that dilution ratios of 240 to 504 did not significantly affect the particle size distributions nor concentrations (i.e. study used 15, 30, 70nm sucrose particles with EAG, TSI Inc., model 3480). Based on these findings the study concluded that the effect of dilution ratio onto accumulation mode particles is negligible other than the expected reduction in concentration respective to the dilution factor.

Overall particle losses of 21nm and 50nm particles were measured to be approximately 40% over the combination of sample extraction probe, transfer line ejector diluter, and mini-dilution tunnel with extraction probe for 2nd stage dilution. In comparison, UN ECE/TRANS/505/Rev.7/Add.48 (2015) Annex 4C, Appendix 1, §2.2.1 specifies the allowable particulate concentration reduction factors for the volatile particulate remover of the PMP particle number emissions measurement system. The procedure requires the use of solid particulates of 30, 50, and 100nm electrical mobility diameter at a minimum concentration of 5,000 particulates per cm³ to quantify particle losses across the VPR. The particulate concentration reduction factors (f_r) are calculated as the ratio of the total measured particle concentrations upstream (N_{in}) and downstream (N_{out}) the VPR for each of the three particle diameters. The validation criteria is worded such that *particulates of 30nm and 50nm diameter shall be no more than 30% and 20% higher, respectively, and no more than 5% lower than that for particulates of 100nm diameter* (UN ECE/TRANS/505/Rev.7/Add.48, 2015; Giechaskiel *et al.*, 2012b).

4.2 Engine Dynamometer Test Facility and Setup

Engine dynamometer experiments allow for studying the PM sensor's response in a controlled environment where a desired particle concentration and size distribution can be *produced* from an engine by virtue of modifying its operating parameters, while still exposing the sensor to *real* exhaust comprising the entire range of solid and semi-volatile particles. Exhaust sampling and conditioning systems can be tightly controlled and modified to study the impact of various sampling parameters. Furthermore, an engine dynamometer test cell is equipped with laboratory grade instruments that are operated in a stable and conditioned environment thus, reduce measurement variability and thereby, allowing to develop and train calibration algorithms for the particle sensor.

All engine dynamometer experiments performed for the study presented herein were conducted at the *Engine and Emission Research Laboratory* (EERL) at West Virginia University. The EERL is part of West Virginia University's Center for Alternative Fuels, Engines and Emissions (CAFEE) and the transient engine dynamometer test cell and associated emissions quantification instruments are designed and operated according to recommendations outlined in the Code of Federal Regulations, Title 40, Part 1065 (CFR 40/1065, 2015). Figure 4.7 provides a schematic overview of the exhaust measurement setup and the full-flow constant volume sampling dilution tunnel at the EERL. The CVS dilution and engine intake air are HEPA filtered and conditioned with a high capacity AC (HVAC) unit to a constant air temperature of $25 \pm 5^\circ\text{C}$ and a relative humidity (RH) of $\sim 50\%$. Additional individual steam injection to the dilution and engine intake air allow to raise the relative humidity levels after the AC's chiller unit.

4.2.1 Engine dynamometer

Two different engine dynamometers were used during this study, specifically a 800hp (see Figure 4.8(*right*)) and a 500hp (see Figure 4.8(*left*)) General Electric® (GE) motoring/absorbing dynamometer capable of running both steady-state and transient test cycles up to speeds of 3000rpm.

The intake air flow rate to the test engines was measured using a laminar flow element (LFE, Meriam, model Z50MC2-6, max. flow: 1007.5cfm at 8inH₂O). The exhaust was either routed through an exhaust gas after-treatment system or a butterfly-type exhaust flow restriction was installed to *simulate* similar exhaust backpressure as experienced with an after-treatment

4.2. Engine Dynamometer Test Facility and Setup

system, before being directed into the CVS dilution tunnel. The test engines and associated after-treatment systems were instrumented with K-type thermocouples and pressure transducers (Omega, Inc.) to quantify the thermodynamic states of different engine components and flow streams (i.e. exhaust, EGR flow, intake flow, coolant, etc).

Instantaneous diesel fuel flow measurements were performed using an AVL fuel mass flow meter (AVL, model 7351CST), operating based on the *Coriolis* principle, in conjunction with an AVL temperature control unit (AVL, model 753CH). The fuel flow meter was capable of flow and density measurements with an accuracy of 0.12% (pt.). In addition to the AVL fuel flow measurement, total fuel consumed during a test cycle was inferred from gravimetric measurement of the fuel drum placed on a scale (Ohaus, model CD-11). Furthermore, carbon balance calculations based on recovered carbon fractions in the exhaust stream (i.e. CO₂, CO, THC) were performed to corroborate direct fuel measurements.

Figure 4.8: (left) General Electric® (GE) 800 hp DC dynamometer [1] ([2] engine, [3] exhaust to CVS, [4] air intake); (right) General Electric® 500 hp DC dynamometer [1] ([2] engine, [3] exhaust to CVS); both located at the *Engine and Emissions Research Laboratory* (EERL), West Virginia University, Morgantown, WV.

4.2.2 Constant volume sampling (CVS) dilution tunnel

Gaseous and total particulate matter (TPM) exhaust emissions were measured on a diluted basis using a full-flow constant volume sampling dilution tunnel as recommended by the Code of Federal Regulations, Title 40, Part 1065, §1065.140 (CFR 40/1065, 2015), and shown in Figure 4.9(left). The total exhaust stream is routed through a transfer pipe from the engine or after-treatment system outlet to the CVS tunnel and injected upstream a mixing orifice allowing for homogeneous mixing of dilution air and exhaust gas. From the perspective of gaseous emissions sampling, the dilution tunnel

has the advantage of lowering the water vapor concentration in the exhaust sample and therefore, effectively reducing the probability of water condensation in sample transfer lines and analyzers. This aids in reducing losses of certain water soluble exhaust species including nitrogen dioxide NO₂ and hydrocarbons. Depending on the water content in the exhaust stream, water condensation inside the dilution tunnel may occur which can be either prevented by heating the dilution tunnel to above dewpoint temperatures or adjust dilution air flow (i.e. via adjustment of total dilute & exhaust flow) and humidity such that condensation can be prevented. The CVS dilution tunnel installed at the EERL is not being actively heated, however, water vapor content and dewpoint temperatures inside the tunnel are closely monitored to prevent operation in a flow regime where water condensation could occur. On the other hand, from the viewpoint of TPM sampling, the dilution tunnel's primary purpose is to simulate quasi real-world conditions and transformation of the exhaust particulate matter as it is being released into the atmosphere and mixes with ambient air. The CVS dilution tunnel is made out of 300 series stainless steel material as recommended by CFR 40/1065 (2015), and has an internal diameter (ID) of 0.4m (i.e. 15.7in) and a total length between exhaust injection and sample extraction plane of 6.1m (i.e. 20ft).

During the course of this study two different CVS dilution tunnels were utilized for testing, one as described above compliant with CFR, Title 40, Part 1065 (CFR 40/1065, 2015) (hereinafter referred to as *2007 tunnel*), and a second, *legacy* dilution tunnel compliant with recommendations outlined in CFR, Title 40, Part 86, Subpart N (CFR 40/86/N, 2011) (hereinafter referred to as *legacy tunnel*). The primary difference between the two dilution tunnels was that the flow through the first was controlled via a sub-sonic venturi (SSV) flow meter coupled with a variable speed blower, whereas the flow through the latter was governed by a critical-flow venturi (CFV) and a fixed speed blower. The SSV for the *2007 tunnel* was manufactured out of 300 series stainless steel material with a throat diameter of 0.19m (i.e. 7.5in). In order to ensure accuracy and repeatability of the flow measurement, the SSV was *sandwiched* in between two 3m (i.e. 10ft) long straight pipe sections with the aim to minimize impact of eddies or flow recirculation induced by pipe bends or increased tunnel wall roughness. The variable speed blower was controlled by a commercially available motor drive from Bardac (Bardac, smarty). The sub-sonic venturi flow meter was calibrated against a NIST traceable reference SSV following procedures outlined in CFR 40/1065 (2015) §1065.340, with the molar flow rate being calculated according to equations

provided by *CFR 40/1065* (2015) §1065.640 and §1065.642.

Gaseous and particulate matter emissions samples are extracted from the sample plane shown in Figure 4.9(*right top*), which is located ~ 12 times the dilution tunnel diameter downstream the exhaust injection point into the tunnel. Heated and temperature controlled (PID controller, Omega Inc., i-Series) sample probes, filters, and lines were employed to transport the exhaust gas samples to the respective analytical instruments. Gaseous emissions were extracted through an averaging sample probe spanning the dilution tunnel perpendicular to the flow, whereas sample extraction for particulate matter was performed using a *J-type* probe facing upstream the dilution tunnel and featuring sharp edges at the inlet to minimize particle losses through impaction. Furthermore, the PM sample flow was adjusted such that nearly isokinetic flow conditions could be achieved in the extraction probe. The heated components were maintained at $191 \pm 11^\circ\text{C}$ and $47 \pm 5^\circ\text{C}$ for gaseous and particulate matter emissions extraction, respectively.

In order to correct the emissions concentrations measured in the CVS for the contribution of emissions constituents already present in the dilution air (i.e. most notably CO_2 with a typical concentration of $\sim 400\text{ppm}$ in ambient air), a slip stream was extracted from the dilution air prior to mixing with the exhaust stream (see Figure 4.7) and collected in a sample bag, labeled *background bag*, over the duration of a test cycle. Subsequent analysis of the bag's content allowed for subtraction of the background air contribution from the total emissions masses measured in the CVS to yield the actual exhaust mass rates from the test engine.

4.2.3 Gaseous phase emissions sampling system

Regulated gaseous emissions, including total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogen (NO_x) as well as carbon dioxide (CO_2), nitric oxide (NO) and methane (CH_4) were measured using a Horiba® MEXA-7200D automotive emissions analyzer system shown in Figure 4.10 (*Horiba Instruments Inc.*, 2004). CO and CO_2 were detected by the non-dispersive infrared (NDIR) method (cold dry sample); NO_x (heated dry atmospheric sample) and NO (cold dry atmospheric sample) using the chemiluminescence (CLD) method; THC and CH_4 using heated-flame ionization detectors (HFID) with the latter being routed through a non-methane hydrocarbon cutter (NMC) before entering the HFID. Table 4.4 gives an overview of the individual analyzers installed in the MEXA-7200D system.

4.2. Engine Dynamometer Test Facility and Setup

Figure 4.9: (left) Full-flow constant volume sampling system [1] with sub-sonic venturi (middle [2]) for flow rate measurement; (right top) exhaust sample extraction plane with heated averaging and J-type probes [1] for gaseous and particulate matter, respectively ([2] temperature controller, [3] heated filter); (right bottom) mini-dilution tunnel [1] connected to CVS with particle sizing instruments [2]; located at the *Engine and Emissions Research Laboratory (EERL)*, West Virginia University, Morgantown, WV.

Table 4.4: List of gas analyzers comprising the Horiba® MEXA-7200D automotive emissions analyzer system (*Horiba Instruments Inc.*, 2004).

Constituent (diluted)	Analysis Method	Analyzer (type)
CO	NDIR (cold, dry)	AIA-721
CO ₂	(cold, dry)	AIA-722
THC	HFID (heated, wet)	FIA-725A
CH ₄	HFID (NMC, heated, wet)	FIA-721HA
NO	CLD (cold, dry)	CLA-720
NO _x	CLD (NO ₂ -to-NO, heated, dry)	CLA-720MA

The THC-HFID analyzer was verified for operation as per CFR, Title 40, Part 1065 regulations (*CFR 40/1065*, 2015), including linearity verification (*CFR 40/1065* (2015) §1065.307) and O₂ interference verification (*CFR 40/1065* (2015) §1065.362). For samples requiring a non-methane hydrocarbon calculation the HFID's response factor to methane was determined prior to

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Figure 4.10: Picture of the Horiba® automotive emission analyzer system MEXA-7200D with oven; located at the *Engine and Emissions Research Laboratory (EERL)*, West Virginia University, Morgantown, WV.

testing as per *CFR 40/1065 (2015) §1065.360*. The flame in the HFID analyzer is fueled by a mixture of 40% hydrogen and 60% helium.

The model FIA-721HA analyzer has the ability to function in two modes, namely THC and CH₄. Under *THC mode* its operation is the same as noted above for regular THC sampling. However, when operated in *CH₄ mode*, the exhaust sample is first passed through a non-methane hydrocarbon cutter before being routed to the HFID in order to remove hydrocarbons other than CH₄. The CH₄-HFID analyzer was verified for operation as per *CFR, Title 40, Part 1065 regulations (CFR 40/1065, 2015)*, including linearity verification (*CFR 40/1065 (2015) §1065.307*) and O₂ interference verification (*CFR 40/1065 (2015) §1065.362*). Additionally, the NMHC cutter of the analyzer was subject to the cutter efficiency test as prescribed in *CFR 40/1065 (2015) §1065.365*.

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The NMHC cutter temperature was optimized to achieve a methane penetration factor of over 85% and an ethane penetration factor of less than 2%.

In order to remove moisture content from the exhaust sample, the sample gas was routed through a chiller unit controlled to a maximum dewpoint temperature of 5°C prior to entering the NDIR analyzer cell. Since moisture is a major interference component for both, CO and CO₂ measurements with the NDIR analyzer, a water interference check was performed according to *CFR 40/1065* (2015) §1065.350 and *CFR 40/1065* (2015) §1065.355 for the CO₂ and CO NDIR, respectively.

The total NO_x detector was additionally equipped with a NO₂-to-NO converter prior to entering the CLD. A converter efficiency test was performed to ensure that the NO₂-to-NO converter operates satisfactorily. A conversion efficiency of less than 95% is considered a failure and maintenance would need to be performed to rectify the situation. Linearity verifications (*CFR 40/1065* (2015) §1065.307) and H₂O and HC quench verifications (*CFR 40/1065* (2015) §1065.370) were performed according to CFR, Title 40, Part 1065 regulations (*CFR 40/1065*, 2015). Since a chiller unit was used to remove moisture content upstream the NO₂-to-NO converter in the NO_x sample train, a chiller NO₂ penetration verification was performed according to *CFR 40/1065* (2015) §1065.376.

4.2.4 Particulate matter emissions sampling system

Following the regulatory prescribed methods for particulate matter emissions quantification (*CFR 40/1065*, 2015; *CFR 40/86/N*, 2011) a slip-stream was extracted from the sample plane on the CVS dilution tunnel (see Figure 4.7) and directed through a secondary dilution system onto the filter media. The dilution air was HEPA filtered and chilled to reduce the moisture content before being reheated and controlled to a constant temperature of 25±5°C (*CFR 40/1065* (2015) §1065.140). *CFR 40/1065* (2015) §1065.140 requires the minimum overall dilution ratio of the exhaust stream for PM quantification to be within 5:1 and 7:1 over a given test interval (i.e. FTP cycle for regulatory testing). Immediately after sample extraction from the CVS dilution tunnel and prior to the secondary dilution system a PM_{2.5} cyclone separator was installed in order to remove particles bigger than 2.5µm. After the secondary dilution system the sample flow is directed through a stainless steel filter holder shown in Figure 4.11(right top), containing a cartridge with the selected filter media. The filter media holder itself was placed inside a temperature governed enclosure that is maintained at constant 47±5°C using

4.2. Engine Dynamometer Test Facility and Setup

Figure 4.11: (left) Temperature controlled enclosure with secondary dilution system for PM sampling on filter media for gravimetric or chemical analysis designed according to *CFR 40/1065* (2015) ([1] cyclone separator, [2] filter media holder, [3] sample bypass, [4] temperature controller); (right top) 47mm stainless steel filter media holder shown with filter cartridge (blue); (right bottom) AVL micro soot sensor, model 483; located at the *Engine and Emissions Research Laboratory* (EERL), West Virginia University, Morgantown, WV.

a PID-type controller as seen in Figure 4.11(left). The governing parameter for temperature control as specified by *CFR 40/1065* (2015) §1065.140 is the *filter media face* temperature, measured anywhere within 20cm upstream or downstream the PM sampling media. To that aim, all components including the secondary dilution tunnel were heated and maintained at constant $47 \pm 5^\circ\text{C}$. In order to accurately design and size the particulate matter sampling system installed at the EERL at West Virginia University, an in-depth study of thermal behavior of the secondary dilution tunnel and possible associated particle sampling losses, using Simulink® (The MathWorks™ Inc.) modeling, was performed by Wu (2010).

Depending on the desired subsequent analysis (i.e. gravimetric or chemical analysis) of the collected PM sample the filter media needs to be chosen. Since for the purpose of this study only the total collected PM mass was of interest 47mm (i.e. diameter) Pallflex® Emfab™ filter mem-

4.2. Engine Dynamometer Test Facility and Setup

branes (TX40HI20WW, Pall Life Sciences, Pall Corp., USA) were used, that are woven glass cloth reinforced, pure borosilicate glass microfibers. Figure 4.12(*right top*) shows an example of two filter media after being exposed to emissions sampling from a DPF (left) and non-DPF (right) equipped engine (47mm Teflo membrane (PTFE) filter media).

An environmentally controlled clean room (Class Six as specified by ISO 14644-1 or Class 1000 according to old standard) was utilized for PM filter media handling, storage, conditioning and pre/post-weighting for gravimetric analysis (see Figure 4.12(*left*)). The clean room is maintained at constant environmental conditions prescribed by *CFR 40/1065* (2015) §1065.190, including i) temperature to $22\pm3^{\circ}\text{C}$, ii) dewpoint to $9.5\pm1^{\circ}\text{C}$, and iii) relative humidity to $45\pm8\%$. A dewpoint of 9.5°C was specifically selected as at this level the amount of water associated with sulfuric-acid-type (H_2SO_4) PM will be maintained such that 1.2216g of water will be associated with each gram of H_2SO_4 (*CFR 40/1065* (2015) §1065.190). Filter media were pre/post-weighted using a precision micro-balance, shown in Figure 4.12(*right bottom*) with an accuracy of $0.1\mu\text{g}$ (Sartorius, model SE-2F) following conditioning and weighing procedures as outlined in *CFR 40/1065* (2015) §1065.590 and §1065.595.

4.2.5 Particle characterization and Pegasor Particle Sensor

Additionally to PM sampling on filter media for subsequent gravimetric analysis, following the regulatory requirements, various aspects of particle emissions were being quantified in the engine dynamometer test cell by extraction of samples from the raw exhaust gas stream using a partial-flow sampling system. Specifically, for all experiments conducted at the EERL, partial-flow sampling *System 2*, as described in Section 4.1, was employed for sample extraction and dilution. The *Pegasor Particle Sensor* (PPS-M1, version V1) was mounted directly to the exhaust transfer pipe using sampling probe configuration *B* (i.e. no probe protruding inside pipe; see Section 3.3) as seen in Figure 4.13(*left*). The sample extraction probe for the PFS system was close coupled to the exhaust transfer pipe and installed such that the probe inlet was on the same plane as the PPS sample inlet port.

Total particle number concentrations were measured using a condensation particle counter (CPC, TSI Inc., model 3025A (*TSI Inc.*, 2002)) with a lower particle cut-point size of 3nm. An engine exhaust particle sizer spectrometer (EEPSTM, TSI Inc., model 3090 (*TSI Inc.*, 2011)) was used to sample from the 2nd stage mini-dilution tunnel and characterize particle number and size

4.2. Engine Dynamometer Test Facility and Setup

Figure 4.12: (left) Class six clean room (ISO 14644-1) for filter media conditioning and weighing; (right top) 47mm Teflo membrane (PTFE) filter media (Pall Corp., USA), left: sample from DPF equipped engine, right: engine-out sample; (right bottom) precision scales for filter media weighing, left: Mettler Toledo UMX2 [1], right: Satorius SE-2F [2]; located at the *Engine and Emissions Research Laboratory (EERL)*, West Virginia University, Morgantown, WV.

distributions. Additionally, an aerosol electrometer (TSI Inc., model 3068B (TSI Inc., 2006)) was connected to the *Pegasor Particle Sensor* outlet to quantify particles leaving the sensor and to study the impact of particle charging inside the PPS. Finally, for one test engine the experimental setup included measurements of exhaust soot concentrations by means of an AVL micro soot sensor (model 483, AVL List GmbH) which was sampling directly from the exhaust transfer pipe downstream the PPS as shown in Figure 4.13(right). The micro soot sensor utilized a straight sampling probe with a 45° cut at the sample inlet that was facing the exhaust flow direction and protruded into the center of the exhaust pipe (i.e. similar probe as configuration A described in Section 3.3).

4.2. Engine Dynamometer Test Facility and Setup

Figure 4.13: (left) *Pegasor Particle Sensor* [1] installed to exhaust transfer pipe [2], probe and 1st stage mini-dilution tunnel visible on left side [3]; (right top) *Pegasor Particle Sensor* [1] installed to exhaust transfer pipe [2] of Mack MP-7 engine, probe and 1st stage mini-dilution tunnel visible on the left side [3] and AVL micro soot sensor probe [4] above PPS; located at the *Engine and Emissions Research Laboratory* (EERL), West Virginia University, Morgantown, WV.

4.2.6 Test engines

The *Pegasor Particle Sensor* was evaluated on three different test engines while being exercised over transient and steady-state test cycles. Details of the test engines are provided in Table 4.5.

Table 4.5: Specifications of test engines used for engine dynamometer evaluation of the *Pegasor Particle Sensor*

Engine	1	2	3
Manufacturer	DDC	Cummins	Mack
Model	S60	ISM-370ESP	MP-7 355E
Model Year	1992	1999	2004
Configuration	Inline 6 cyl.	Inline 6 cyl.	Inline 6 cyl.
Displacement [L]	12.7	10.8	10.8
Bore x Stroke [mm]	130 x 160	125 x 147	123 x 152
Aspiration	Turbocharger, Intercooler	Turbocharger, Intercooler, EGR	VGT, Intercooler, EGR
Injection System	EUI	EUI	EUI
Max. Torque [Nm]	1966 @ 1200rpm	1830 @ 1200rpm	1844 @ 1200rpm
Max. Power [kW]	268 @ 1810rpm	276 @ 2100rpm	265 @ 1800rpm
Emissions Standard	NO _x : 5.0	NO _x : 4.0	NO _x : 2.4
[g/bhp-hr]	PM: 0.25	PM: 0.1	PM: 0.1

Experiments on *Engine 1*, the legacy DDC S60 engine, included sampling from engine out location (i.e. no aftertreatment) with the engine being fueled with either commercially available ultra-low sulfur diesel (ULSD) fuel or a ULSD based candidate fuel containing additional additives. *Engine 2*, a Cummins ISM-370ESP, was used to evaluate two different catalyzed DPFs and PPS sampling was performed upstream (i.e. at engine-out location) and downstream the trap to span a wide range of particle number concentrations. Additionally, the *degreening* process of the two filters allowed for assessment of the particulate sensor's sensitivity by measuring a continuously reducing particle concentration as a function of the soot *cake layer* build-up (Suresh *et al.*, 2000; Wirojsakunchai *et al.*, 2007; Yamada, 2013) on the new filter substrate walls, leading to an enhanced PM filtration efficiency of the DPF. Finally, a model year 2004 Mack MP-7 355E (i.e. *Engine 3*) engine, typically installed on refuse haulers and equipped with variable geometry turbocharger (VGT) and exhaust gas recirculation (EGR) was used to perform comparison experiments with the AVL micro soot sensor (model 483, AVL List GmbH) over 13 different engine operating modes (combination of engine speed and torque), evenly covering the area under the engine's torque curve.

4.3 Chassis Dynamometer Test Facility and Setup

4.3.1 Chassis dynamometer

Heavy-duty vehicle chassis dynamometer

The heavy-duty chassis dynamometer utilized for vehicle testing as part of the study presented herein, and shown in Figure 4.14, was designed and built by West Virginia University researchers and personnel (Ferguson, 1993). The dynamometer was integrated into a semi-trailer frame, thus allowing it to be lifted using four permanently mounted, hydraulic columns (i.e. jacks), outfitted with a tandem trailer axle underneath the rear end, and ultimately being pulled behind a tractor as a regular, street-legal trailer. Detailed description of WVU's heavy-duty vehicle chassis dynamometer can be found in a multitude of publications and student thesis/dissertation documents, including Ferguson (1993) and Thiruvengadam (2012), therefore, the discussion provided herein will be limited to a brief overview of the most important aspects of the setup.

The salient feature of this chassis dynamometer design is that the simulated load is directly applied to the vehicles drive axle by means of drive shafts

4.3. Chassis Dynamometer Test Facility and Setup

attached to hub adapters that have been fitted in place of the outer most drive tires. This eliminates possible slippage between the drive-tire and dynamometer roller interface and further reduces the potential for damage to the vehicles tires due to overheating. The test vehicle itself rests on a set of free-spinning rollers that are linked side-to-side to ensure equal wheel speed on both sides of the vehicle axle. The dynamometer was outfitted with two sets of rollers on each side, allowing to test both vehicles with single or tandem drive axles (see Figure 4.14 for an example of the latter).

The heavy-duty chassis dynamometer is capable of simulating a wide range of gross vehicle weight ratings (GVWR) between ~24,000lbs and 66,000lbs depending on the configuration of inertial weights selected. The main components comprising the heavy-duty chassis dynamometer are depicted in Figure 4.15 and include the i) tire rollers; ii) hub adapters; iii) differentials; iv) flywheel assemblies; 300hp eddy-current power absorbers; v) variable-speed 20hp AC electric motors; and vi) in-line torque and speed transducers. As seen from Figures 4.14 and 4.15 both sides of the chassis dynamometer are outfitted with an identical set of the aforementioned components to be connected to each side of the test vehicle.

Tire rollers: Two sets of free-spinning rollers with a diameter of 12.6in (32cm) each, on both sides of the chassis dynamometer to support single and tandem axle vehicles. Each pair of rollers is linked by a flexible coupling to have uniform rotational speed on either side of the vehicle. Furthermore, the coupling was designed to accept ~20% of the wheels torque in case of any imbalance due to an uneven surface at the test location, thus compression of the tire onto the roller (*Ferguson, 1993*).

Hub adapters: Are used to couple the vehicle drive axle with the flywheel assembly and eddy current power absorber via torque and speed transducer. The adapter is made out of a 1/2in (12.7mm) thick aluminum plate with a diameter of 1.8ft (~0.55m).

Road-load simulation system: The primary parts of the road load simulation system installed on each side of the test vehicle include the flywheel assembly, eddy-current power absorber, variable-speed motor, speed and torque transducer, double differential and universal couplings as shown in Figure 4.15. The power from the test vehicle's drive axle is transmitted to the flywheel assembly and power absorbers via the hub adapters that are connected to a 24in (~0.61m) long spline shaft running into a pillow block.

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.14: Picture of the heavy-duty vehicle chassis dynamometer; [1] test vehicle, [2] exhaust transfer line, [3] hub adapter, [4] flywheel assembly, [5] power absorber, [6] variable-speed motor, [7] hydraulic column, [8] tire roller (Picture taken in November 2011, Location: Riverside, CA).

The spline shaft is then connected to the in-line speed and torque transducer by a universal coupling which is rated to withstand torque up to 16,415lb-ft ($\sim 22,255\text{Nm}$) on either side. The output of the in-line torque transducer is connected to a double reduction differential with a ratio of 1:3.65 which drives the flywheel assembly. In parallel, a second differential with a ratio of 1:5.73 drives the eddy-current power absorber which is connected in series to the AC motor.

Flywheel assembly: The flywheel assembly is designed to simulate vehicle gross weights of $\sim 24,000\text{lbs}$ to $66,000\text{lbs}$. The assembly consists of a drive shaft with four drive rotors running into two pillow blocks. Each drive shaft supports eight flywheels of different sizes (i.e. inertias) with bearings resting on the shaft. By selectively engaging the flywheels to the drive rotors, vehicle mass can be simulated in discrete 250lbs (113kg) increments.

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.15: Picture of the various components comprising the heavy-duty vehicle chassis dynamometer; [1] hydraulic column, [2] flywheel assembly, [3] power absorber, [4] differential, [5] torque transducer (Lebow), [6] hub adapter, [7] exhaust transfer line support (Picture taken in April 2011, Location: *Mobile Emissions Research Laboratory (MERL)* in Westover, WV).

Power absorbers: An air-cooled, eddy-current power absorber (Mustang, model CC300) mounted on two bearings is used to simulate load due to rolling friction of the tires as well as the simulated aerodynamic drag resistance of the test vehicle. The eddy-current power absorber has the capability of absorbing 300hp ($\sim 224\text{kW}$) continuously and 1000hp ($\sim 746\text{kW}$) intermittently during peak operation. The absorbed load at any speed is controlled by the current supplied to the coils. A force transducer (i.e. load cell), mounted to an arm perpendicularly exiting the power absorber, is utilized to measure the effective power absorbed.

Variable-speed motor: A 20hp ($\sim 15\text{kW}$) variable-speed AC motor, installed in series to the eddy-current power absorber, is aimed at providing limited motoring effort and helping to overcome frictional losses in the chassis dynamometer's drive train.

A chassis dynamometer is ultimately employed to simulate the different loads acting onto a vehicle while it would be driving on a road under real-world conditions. The sum of these loads is termed *road load* and comprises aerodynamic drag, frictional rolling losses between the vehicle tires and road surface, inertial mass of the vehicle to be accelerated, and road grade (Delgado-Neira, 2012). Traditionally, chassis dynamometer driving schedules are developed assuming level grade, thus, the impact of road grade is neglected in the *road load* equation. The flywheels simulate the vehicle inertia

by loading the drivetrain with inertial masses during acceleration, whereas providing motoring during deceleration portions of the drive cycle. With the road grade being neglected and the vehicle's inertial mass being simulated by the flywheels the parts of the *road load* to be controlled reduce to aerodynamic drag and rolling resistance. The appropriate *road load* to be applied to the vehicle is determined by the *road load power* Equation 4.5 as a function of vehicle speed and the physical dimensions and aerodynamic characteristics of the test vehicle; where, μ represents the coefficient of rolling resistance, m is the test vehicles mass, g is the acceleration due to gravity, ρ is the ambient air density, A is the frontal cross-sectional area of the test vehicle, C_D is the aerodynamic drag coefficient, and V is the instantaneous vehicle velocity.

$$P_r = \mu mgV + \frac{1}{2}\rho AC_D V^3 \quad (4.5)$$

The calculated *road load power* as a function of vehicle speed is used to control the power applied by the eddy-current power absorbers and variable speed motors in closed loop control. Prior to testing, the road load profile is verified by a coast-down procedure as outlined in CFR, Title 40, Part 1066 (CFR 40/1066, 2015).

Medium-duty vehicle chassis dynamometer

West Virginia University's medium-duty chassis dynamometer, shown in Figure 4.16, is capable of simulating gross vehicle weight ratings in the range of 3,000lbs to 24,000lbs, and was entirely designed and built by WVU researchers and personnel. The dynamometer comprises six main components, specifically, i) the inertial flywheels; ii) a 400hp power absorber (i.e. air-cooled eddy-current power absorber, Mustang, model CC300); iii) a two-speed transfer case; iv) a variable-speed 25hp AC electric motor; v) an in-line torque transducer; and iv) a set of two tire rollers to absorb or add load to or from the driven vehicle wheels, respectively.

The two-speed transfer case allows for a larger range of vehicle speeds with a selectable gear ratio of 1:1 and 2.04:1, whereas the eddy-current power absorber makes it possible to simulate road grades by inducing additional load to the tire rollers. Similarly to the heavy-duty chassis dynamometer, the medium-duty chassis dynamometer is controlled by a commercially available motor drive from Bardac (Bardac, smarty) in conjunction with an in-house developed control software (Scimitar, Zac Luzader). The driving cycle input to the control software comprises vehicle speed and road grade

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.16: (*left*) Picture of medium-duty vehicle chassis dynamometer; (*right*) dual-roller assembly to absorb the load from the driven vehicle wheel; located at the *Mobile Emissions Research Laboratory (MERL)* in Westover, West Virginia University, Morgantown, WV.

as a function of time. An interface monitor located inside the test vehicle allows the human driver to follow the prescribed driving cycle. More specific details about the medium-duty chassis dynamometer are discussed by Zia (2009).

4.3.2 Transportable emissions measurement system (TEMS)

The transportable emissions measurement system (TEMS) was designed as a *laboratory-grade* analytical emissions quantification system according to recommendations outlined in *CFR 40/1065* (2015), however, with the advantage of being built inside a reconstructed, 30ft (9.1m) long, cargo container, and thus, allowing to be transported to virtually any test location together with the transportable chassis dynamometers described earlier. Furthermore, the compactness of the TEMS makes it possible to be placed onto rail-cars or cargo ships for possible in-use locomotive or marine engine emissions characterization, respectively. The transportable laboratory was designed and commissioned in 2007-2008 time frame by WVU researchers and personnel, with a detailed account of this process provided by Wu (2010).

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.17: CAD schematic of the transportable emissions measurement system; 1) exhaust inlet to dirty tunnel, 2) exhaust inlet to clean tunnel, 3) clean CVS dilution tunnel, 4) dirty CVS dilution tunnel, 5) air compressor, 6) vacuum pumps, 7) Horiba® MEXA-7200D oven, 8) temperature controlled PM sampling compartment, 9) filter media handling compartment, 10) zero-air generator, 11) MEXA-7200D automotive emission analyzer system, 12) laboratory control table, 13) pressurized air tank, 14) DAQ rack, 15) subsonic venturi, 16) air conditioner deck, 17) outlet to variable-speed blower, 18) ventilation fan, 19) HEPA filters (Picture taken from Wu (2010)).

Figure 4.17 provides a CAD schematic of the interior arrangement of the different measurement setups and instruments housed in the TEMS (Wu, 2010), whereas Figure 4.18 shows an outside view of the transportable laboratory installed on a flatbed trailer (Landoll, model 435). The TEMS was designed to mirror as closely as possible the experimental setup of the full-flow CVS dilution tunnel at the *Engine and Emissions Research Laboratory* at West Virginia University (Morgantown, WV). As can be seen from Figure 4.17 the laboratory was originally outfitted with two CVS dilution tunnels with one specifically designated for sampling exhaust from legacy diesel engines (i.e. non-PM after-treatment equipped engines with increased soot concentrations; referred to as *dirty tunnel*), while the second tunnel was utilized for testing of low particulate matter emitting, *post-2007* model year on-highway engines that are equipped with exhaust gas filtration systems (e.g. DPF; referred to as *clean tunnel*). As of summer 2015 the legacy CVS dilution tunnel (see lower tunnel in Figure 4.19) has been removed as testing of older, non-exhaust-gas-filter equipped engines drastically declined, and also to provide for more space for ancillary instrumentation and setups required for newer studies.

The exhaust stream is routed from the test article (e.g. vehicle, locomotive,

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.18: Picture of the transportable emissions measurement system; [1] exhaust transfer pipe, [2] CVS outlet flow (downstream blower), [3] AC unit for container, [4] control stand window, [5] air compressor and vacuum pump compartment (Picture taken in October 2012, Location: Riverside, CA).

etc.) to the transportable laboratory via an insulated transfer pipe, and is directed through the container roof (see labels 1 & 2 in Figure 4.17, and insulated pipe top left in Figure 4.18) into the CVS dilution tunnel followed by a mixing orifice. The dilution air for the CVS tunnels is filtered by a set of HEPA filters installed in a plenum box upstream the tunnel inlet (see label 19 in Figure 4.17). The primary difference between the CVS dilution systems installed at EERL and inside the TEMS is that the dilution air for the transportable laboratory is not being conditioned for humidity and temperature and will solely depend on the local meteorological conditions at the test site. Analogous to the EERL (see Section 4.2.2) a sub-sonic venturi flow meter coupled with a variable speed blower is utilized to measure and control the total flow through the CVS dilution tunnel. Exhaust samples are extracted from the sampling plane shown in Figure 4.19, and directed to the analytical emissions measurement systems via heated and temperature controlled (i.e. maintained at constant $191 \pm 11^\circ\text{C}$) probes, filters and sampling lines.

Figure 4.19: Picture of the sampling planes with emissions extraction probes [1] on the two CVS dilution tunnels installed inside the transportable emissions measurement system; [2] *clean tunnel*, [3] *dirty tunnel* (Picture taken in April 2011).

The transportable emissions measurement system is equipped with an air compressor and vacuum pump, installed in the roof section of the container (see labels 5 & 6 in Figure 4.17, and top right end of container in Figure 4.18), to be fully independent of shop air supply in order to operate any secondary dilution systems and provide on-board generated *zero air* to the measurement instruments. Additionally, a high volume HVAC system is installed in the front compartment of the container (see label 16 in Figure 4.17, and grayish device left in Figure 4.18) to provide for a stable environment for the instruments inside the TEMS.

Gaseous exhaust emissions are quantified using the same Horiba® automotive emission analyzer system MEXA-7200D as already been discussed in Section 4.2.3 for the EERL. The analyzer rack seen in Figure 4.20(right) is mounted on a *spring-damper* system to absorb any shocks and vibrations while the TEMS is being transported or operated during on-road measurement campaigns. The particulate matter emissions sampling system is an exact replica of the experimental setup discussed in

Figure 4.20: (*left*) Temperature controlled enclosure with secondary dilution system for PM sampling on filter media (*CFR 40/1065*, 2015) [1], and ventilated filter media handling and preparation compartment [2], [3] sample flow controller; (*right*) Horiba® automotive emission analyzer system MEXA-7200D installed on a *spring-damper* system to compensate for shock and vibrations (Pictures taken in April 2011).

Section 4.2.4 for the EERL. It is designed according to recommendations outlined in *CFR 40/1065* (2015) comprising a secondary dilution tunnel, heated transfer lines and a temperature controlled filter media holder compartment both maintained at constant $47 \pm 5^\circ\text{C}$. Figure 4.20(*left*) shows the heated compartment along with the ventilated filter media handling and preparation enclosure below. In-depth analysis and design, including particle loss quantification of the secondary dilution PM sampling system was conducted by Wu (2010) during the commissioning process of the transportable laboratory.

A detailed overview of different exhaust gas sample streams, measurement setups and instrumentation inside the transportable emissions measurement system is provided in Figure 4.21. The depicted setup configuration was used for *semi-controlled environment* studies (i.e. chassis dynamometer studies) and evaluation of the *Pegasor Particle Sensor* discussed in this thesis.

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.21: Schematic diagram of the constant volume sampling system and ancillary measurement instrumentation in the *Transportable Emissions Measurement System*; encircled numbers indicate instruments for particulate matter quantification.

Figure 4.22: (left) *Pegasor Particle Sensor* sampling from upstream after-treatment location, [1] sensor located inside *green* colored compartment, [2] temperature controller, [3] sample inlet, [4] sample return ; (right) PPS [1] sampling from downstream after-treatment location (seen on top of exhaust transfer line [2]); partial-flow sampling *System 2* [3] with heated line (center top) routing sample from exhaust transfer line to 1st stage [4] heated mini-dilution tunnel (center); 2nd stage dilution seen towards bottom left [5]; (Pictures taken in January 2013).

4.3.3 Particle characterization and Pegasor Particle Sensor

Different aspects of particulate matter emissions were characterized and quantified using five specific measurement methods, namely, i) sampling of PM on filter media according to *CFR 40/1065* (2015) for subsequent gravimetric analysis (discussed before); ii) particle number concentration and size distribution measurements directly inside the CVS dilution tunnel using an *EEPSTM* spectrometer (TSI Inc., model 3090); iii) total particle number concentration sampled from the raw exhaust stream using partial-flow sampling *System 2*, described in Section 4.1, in conjunction with a CPC (TSI Inc., model 3025A); iv) *Pegasor Particle Sensor* measurements *upstream*; and v) *downstream* any exhaust gas after-treatment system.

A $\frac{3}{8}$ in (OD) stainless steel, *J-type* probe with a sharp-edged inlet section was inserted into the CVS tunnel at the sampling plane (see Figure 4.19) in order to extract an exhaust sample at ~ 10 slpm, and route it through con-

ductive silicone tubing (TSI Inc.) to the EEPSTM. The partial-flow sampling system is shown in Figure 4.22(right) with the 1st stage mini-dilution tunnel seen vertically in the center of the picture (i.e. silver colored pipe), and the 2nd stage towards the bottom left. A 1/4in conductive silicone tube was used to route the diluted sample to the CPC which had a lower particle cut-point size of 3nm. For all vehicles equipped with PM after-treatment systems, one *Pegasor Particle Sensor* was installed upstream the particulate trap as shown in Figure 4.22(left), whereas a second PPS was sampling from downstream the after-treatment system shown in Figure 4.22(right). For three-way catalyst equipped natural gas engines both PPS's were installed downstream the TWC. For the upstream sampling location, a 39.4in (~1.0m) long heated line (3/8in (ID), Hillesheim GmbH, H900-series, 200°C) was used to transfer the sample from the exhaust pipe to the sensor. The return line was an insulated and corrugated stainless steel tube. The *Pegasor Particle Sensor* sampling from downstream the after-treatment system was directly mounted to the exhaust transfer pipe. Both sensors were equipped with a configuration A type probe for sample extraction (see Section 3.3).

4.3.4 Test vehicles

Chassis dynamometer testing to evaluate the *Pegasor Particle Sensors* (PPS-M1, version V1) response and performance during semi-controlled real-world operation was conducted for one medium-duty vehicle and fourteen heavy-duty vehicles. The medium-duty vehicle selected for testing was a GMC, model C4500 flatbed truck equipped with a model year 2004, 6.6liter V8 diesel fueled engine and diesel oxidation catalyst after-treatment system. Specific details for test vehicle and engine are provided in Table 4.6. The vehicle was operated on the medium-duty chassis dynamometer and exercised over the FTP-75 certification cycle as well as three different *real-world cycles*, representative of typical vehicle operation within the city of Morgantown, WV, and on two arterial interstate highways (i.e. I-79 South, and I-68 East) of which, one comprised route sections with increased road grade. A detailed description of the test routes and experimental matrix for the medium-duty vehicle testing can be found in Merritt (2011).

The heavy-duty vehicle testing was part of an extended research project awarded to the Center for Alternative Fuels, Engines and Emissions at West Virginia University by South Coast Air Quality Management District (SC-AQMD). The test vehicles comprised three different applications, namely, over-the-road (OTR) heavy goods movement trucks, refuse haulers, and

4.3. Chassis Dynamometer Test Facility and Setup

Table 4.6: Specifications of medium-duty vehicle and engine used for chassis dynamometer evaluation of the *Pegasor Particle Sensor*.

Vehicle	Manufacturer	GMC
	Model	C4500
	Model Year	2004
	Chassis test weight [lbs]	12,000
	On-road test weight [lbs]	12,500
Engine	Manufacturer	GM
	Model	Duramax
	Model Year	2004
	Configuration	V8 cyl.
	Displacement [L]	6.6
	Aspiration	Turbocharger / Intercooled
	Max. Power [kW]	220 @ 3100rpm
	After-treatment	DOC

transit buses. A total of six different engine and after-treatment technology packages were evaluated and are listed below (*Thiruvengadam et al.*, 2015), including engines fueled by ULSD, natural gas, as well as a combination of ULSD and natural gas using Westport Innovations Inc.'s Westport™ high pressure direct injection (HPDI) technology. Specific vehicle and engine information are provided in Table A.2 in Appendix A, whereas a detailed description of the technologies, test cycles, and experimental matrix is given by *Thiruvengadam et al.* (2015).

Cat. I natural gas engine with three-way catalyst, cert. $<0.2\text{g/bhp-hr NO}_x$

Cat. II HPDI engine with EGR and DPF, cert. at 0.8g/bhp-hr NO_x

Cat. III HPDI engine with EGR, DPF, and SCR, cert. at 0.2g/bhp-hr NO_x

Cat. IV diesel engine, cert. at 1.2g/bhp-hr NO_x

Cat. V diesel engine with heavy EGR, and DPF, cert. $>0.2\text{g/bhp-hr NO}_x$

Cat. VI diesel engine with EGR, DPF, and SCR, cert. $<0.2\text{g/bhp-hr NO}_x$

Figure 4.23 shows schematic diagrams for five out of the six (Cat. I, natural gas engine with TWC is missing) technology categories evaluated on the heavy-duty chassis dynamometer, outlining their specific after-treatment system packages. The figure further indicates the individual exhaust sampling locations of the two *Pegasor Particle Sensors* (PPS-M1, version V2). This unique configuration allowed to estimate real-time particulate removal efficiencies of the different after-treatment packages.

4.3. Chassis Dynamometer Test Facility and Setup

Figure 4.23: Schematic diagram of heavy-duty engine and after-treatment configurations used for chassis dynamometer testing with sampling location of *Pegasor Particle Sensors*; figures (a) through (e) refer to engine categories; (a) Cat. VI; (b) Cat. IV; (c) Cat. V; (d) Cat. II; (e) Cat. III; not shown Cat. I natural gas engine with TWC and PPS installed downstream TWC.

4.4 Experimental Setup and Instrumentation for On-Road Testing

Final evaluation of the *Pegasor Particle Sensor* was conducted during real-world, on-road operation while sampling exhaust from light-, medium-, and heavy-duty vehicles. This allowed to expose the sensor to the harsh environment of in-use operation and assess its durability and sensitivity under various ambient conditions (i.e. temperature, humidity, vibration, etc.). Data was collected as part of three different research projects, allowing to measure exhaust from a variety of vehicle platforms. In particular, two particulate filter equipped light-duty vehicles, one non-filter equipped medium-duty pickup truck, and one US-EPA 2010 emissions compliant heavy-duty goods movement tractor, all fueled with ultra-low sulfur diesel fuel, were used for on-road testing and operated over various driving conditions. For all vehicles tested, the *Pegasor Particle Sensor* was sampling from a location downstream any available after-treatment system. The following sections will provide a brief description of the individual experimental setups employed for the three measurement campaigns.

4.4.1 Light-duty on-road testing setup

As part of a research project awarded to the CAFEE at West Virginia University by the International Council on Clean Transportation (ICCT) (Thompson *et al.*, 2014) exhaust particle emissions were characterized using the *Pegasor Particle Sensor*, model PPS-M1 version V2.

The vehicles tested in this study comprised two MY 2012 and one MY 2013, diesel-fueled passenger cars, and will hereinafter be referred to as *Vehicle A* through *Vehicle C*. *Vehicle A* and *B* were equipped with the same 2.0L turbocharged, four cylinder base engine. However, they were equipped with two different NO_x reduction technologies. *Vehicle A* featured a lean NO_x trap (LNT) for NO_x abatement, whereas *Vehicle B* was fitted with an aqueous urea-based selective catalytic reduction system. Both vehicles had a DPF installed for controlling particulate matter emissions. The drive-train of both *Vehicles A* and *B* comprised 6-speed automatic transmissions with front wheel drive. Since *Vehicle C* was not equipped with a PPS during testing, results of this vehicle will not be discussed as part of the study presented herein. More detailed specifications of the test vehicles and engines are listed in Table 4.7 or can be found in Thompson *et al.* (2014).

On-road test routes comprised five pre-defined routes within the three pri-

4.4. Experimental Setup and Instrumentation for On-Road Testing

Table 4.7: Specifications of light-duty test vehicles and engines used for on-road evaluation of the *Pegasor Particle Sensor*.

Vehicle	A	B
Vehicle Manufacturer	VW	VW
Vehicle Model	Jetta TDI	Passat TDI SE
Model Year	2013	2012
Certification Family	DVWXV02.0U5N	CVWXV02.0U4S
Mileage at test start [miles]	4,710	15,226
Fuel	ULSD	ULSD
Engine Configuration	In-line, 4 cyl., 16V	In-line, 4 cyl., 16V
Displacement [ccm]	1968	1968
Engine Aspiration	Turbocharged, Intercooled	Turbocharged, Intercooled
Compression Ratio	16.5:1	16.5:1
Max. Power [kW]	104 at 4200rpm	104 at 4200rpm
Max. Torque [Nm]	320 at 1750rpm	320 at 1750rpm
After-treatment System	OC, DPF, LNT	OC, DPF, urea-SCR
Drivetrain	2-wheel drive, front	2-wheel drive, front
Applicable Emissions Limits (US-EPA and CARB)	T2B5 (LDV) ULEV II (PC)	T2B5 (LDV) ULEV II (PC)

mary population centers in California, namely, Los Angeles, San Diego, and San Francisco, aimed at reflecting a rich diversity of topological characteristics, driving patterns, as well as ambient conditions. The routes can be split into four categories, including i) *highway operation*, characterized by high speed driving during regular hours and frequent stop/go patterns during rush-hours; ii) *urban driving*, characterized by low vehicle speeds and frequent stop and go; iii) *rural driving*, medium vehicle speed operation with occasional stops in the suburbs of the selected metropolitan areas; and finally iv) *uphill/downhill driving*, characterized by steeper than usual road grades and medium to higher speed vehicle operation. Additionally, *Vehicle B* was operated over a multi-state route between Los Angeles, CA, and Seattle, WA, comprising predominantly highway driving. Detailed information regarding route characteristics and experimental matrix are given by *Thompson et al.* (2014).

Figure 4.24 provides a schematic diagram of the experimental setup employed during on-road testing of the light-duty vehicles. Gaseous exhaust emissions were quantified using the on-board measurement system, OBS-2200, from Horiba® which included a Pitot-tube type exhaust flow meter (EFM) to quantify real-time volumetric exhaust flow rates for subsequent

4.4. Experimental Setup and Instrumentation for On-Road Testing

Figure 4.24: Schematic diagram of the experimental setup for on-road light-duty vehicle testing; gaseous emissions: Horiba® OBS-2200, PM emissions: PPS-M1 V2 and Horiba® OBS-TRPM (latter for *Vehicle C* only); details see *Thompson et al. (2014)*.

emissions mass calculations. The Horiba® OBS-2200 has been specifically developed with regard to PEMS requirements for on-road vehicle emissions testing according to recommendations outlined in CFR, Title 40, Part 1065 (CFR 40/1065, 2015). The emissions of CO and CO₂ were measured using a non-dispersive infrared (NDIR) spectrometer (heated wet sample), THC using a flame ionization detector (FID) (heated wet sample), and total NO_x using a chemiluminescence detector (CLD) in conjunction with an NO₂-to-NO converter (heated wet sample).

Figure 4.25(*left*) shows a picture of the experimental setup used during light-duty testing. The exhaust stream is routed from the exhaust tip via a flexible high temperature hose to a 2in (OD) stainless steel pipe that mounts to the EFM and exhaust extraction probes. A 3/8in (~9.5mm) configuration A (see Section 3.3) stainless steel sampling probe was utilized to extract an exhaust sample and route it through a heated line to the enclosure housing the *Pegasor Particle Sensor*, shown in Figure 4.25(*right*). Pressurized air supply for the PPS was provided by a small electrical air compressor (Blue Hawk, 0.3hp with 2 gallon reservoir). Prior to the sensor inlet, the pressurized air was dried and HEPA filtered as seen in the top left corner of Figure 4.25(*right*).

4.4. Experimental Setup and Instrumentation for On-Road Testing

Figure 4.25: (left) Picture of experimental setup in *Vehicle A*, from left to right: Horiba® OBS-2200 [3], 2kW generator [4], heated sample lines to PPS-M1, front: exhaust transfer line with EFM and sample extraction probes [2], high temperature flexible hose [1]; (right) picture of enclosure housing for PPS-M1 [1], pressure control for dilution air pressure [2] (Pictures taken in March 2013).

4.4.2 Medium-duty on-road testing setup

The identical medium-duty pickup truck as was used for chassis dynamometer testing and has already been described in detail in Section 4.3.4 was utilized for on-road evaluation of the *Pegasor Particle Sensor* while sampling from a non-particle after-treatment equipped engine. Figure 4.26 provides a schematic outline of the experimental setup employed for this measurement campaign. Gaseous exhaust emissions were measured concurrently with two PEMS units, namely, the Horiba® OBS-2200 and the Semtech-D from Sensors Inc., and are described in more detail by *Merritt* (2011).

The *Pegasor Particle Sensor* PPS-M1, version V1 was used for this study with the sensor being directly mounted to the exhaust stack using probe configuration *B* (see Section 3.3). The sensor body was wrapped in heated tape and insulation material and maintained at a constant temperature of $200 \pm 10^\circ\text{C}$. Pressurized air for dilution was supplied by an on-board compressor and routed through a dryer and HEPA filter prior to being injected to the PPS. The actual mounting location of the sensor can be recognized in Figure 4.27, towards the right side and behind the wire-mesh front wall of the flatbed. Parallel to the PPS, exhaust was sampled through a one stage dilution system and particulate matter collected on 47mm (i.e. diameter) Pallflex® Emfab™ filter membranes (TX40HI20WW, Pall Life Sciences, Pall Corp., USA) for subsequent gravimetric analysis. The heated filter holder enclosure shown in Figure 4.27 (center) is identical with the PM sampling setups used in the Engine and Emissions Research Laboratory (see Section 4.2.4) and the Transportable Emissions Measurement System

4.4. Experimental Setup and Instrumentation for On-Road Testing

Figure 4.26: Schematic diagram of the experimental setup for on-road medium-duty vehicle testing; gaseous emissions: Horiba® OBS-2200 and Sensors Inc. Semtech-D, PM emissions: PPS-M1 V2 and gravimetric filter samples (in-house developed system); details see (Merritt, 2011).

(see Section 4.3.2) and thus, the reader is referred to these sections for more detailed information about the specific setup. Exhaust was extracted using a 3/8in (OD, ~9.5mm) *J-type*, stainless steel sampling probe inserted into the exhaust stack (see top right in Figure 4.27). A porous wall diluter was utilized to dilute the exhaust sample at a constant dilution ratio before it was routed through a 3ft (~0.9m) long, 3/8in heated line, maintained at $47 \pm 5^\circ\text{C}$, into the heated filter holder enclosure.

The test routes selected, originated from the mobile emissions measurement system (MEMS) development study at West Virginia University and included a *city route*, representative of typical urban and suburban vehicle operation within the Morgantown, WV, metropolitan area as well as two arterial *interstate highway routes* of which, one was characterized by route sections with increased road grade. A detailed description of the test routes selected and the experimental matrix can be found in Merritt (2011).

4.4.3 Heavy-duty on-road testing setup

On-road evaluation of the *Pegasor Particle Sensor* on a heavy-duty, Class-8 tractor was performed as part of a research project sponsored by South Coast AQMD and CARB. The tractor was coupled to a flatbed trailer that

4.4. Experimental Setup and Instrumentation for On-Road Testing

Figure 4.27: Picture of experimental setup on medium-duty vehicle, *from left to right*: span gas bottles [1], heated compartment with filter media sample holder [2], heated sample line [3], Sensors Inc. Semtech-D [4], PPS-M1 V1 mounted to the exhaust stack [5] (i.e. seen behind grating), Horiba® OBS-2200 [6] (Picture taken in May 2011).

was loaded with WVU's transportable emissions measurement system, discussed in Section 4.3.2, amounting to a gross vehicular weight of 66,740lbs, and is shown in Figure 4.28(*left*). As seen from the same picture, the truck's exhaust was routed through a combination of 5in (127mm) stainless steel transfer pipes and a high-temperature flexible hose into the CVS dilution tunnel housed inside the TEMS. Figure 4.29 provides a schematic overview of the entire experimental setup.

Additionally to the already discussed gaseous and particle phase measurement setups and instrumentation inside the TEMS, an engine exhaust particle sizer spectrometer (EEPSTM, model 3090, TSI Inc.) was utilized to characterize particle number concentrations and size distributions directly from the CVS dilution tunnel (see Section 4.3.3 for details). The *Pegasor Particle Sensor* PPS-M1, version V1, was mounted directly to the exhaust stack (i.e. downstream the after-treatment system) via sampling probe configuration *B* as depicted in Figure 4.28(*right*). The sensor body was wrapped with

4.4. Experimental Setup and Instrumentation for On-Road Testing

Figure 4.28: (left) Picture of the transportable emissions measurement system on a flatbed trailer, connected to a Class-8 heavy-duty tractor; Loveland Pass, CO, during cross-country project; (right) PPS-M1 V1 [1] mounted directly to the exhaust stack [2], Horiba® OBS-TRPM [3], exhaust flow meter [4] (Pictures taken in October 2011).

heated tape and insulation, and maintained at a constant temperature of $200 \pm 10^\circ\text{C}$. In order to protect it from environmental impacts such as rain or airborne debris, the PPS was enclosed in a custom made sheet metal enclosure (not shown in Figure 4.28(right)). In parallel to the *Pegasor Particle Sensor* Horiba®'s OBS-TRPM system (discussed in Section 2.4.3) was utilized to quantify particulate matter emissions following regulatory requirements for in-use PM measurement (CFR 40/1065, 2015).

The test vehicle selected for this study was a model year 2011, Class-8 Mack® tractor equipped with a 12.8liter, MP8-445C engine. The after-treatment package comprised a diesel oxidation catalyst, a state of the art catalyzed particulate filter, and a liquid-urea based SCR after-treatment system. The same vehicle was also used for chassis dynamometer experiments discussed in Section 4.3.4 and vehicle and engine specific details are listed in Table A.2 in Appendix A (14th vehicle in list). The vehicle was operated predominantly under highway driving conditions over a 2450 miles route between Morgantown, WV and Riverside, CA, during a six days journey. Driving conditions ranged from the smooth hills of the Appalachian Mountains, the flat steppes of the mid-west, the Rocky Mountains all the way to the busy highways of the greater Los Angeles metropolitan area, resulting in a multitude of operating conditions induced to the after-treatment system. Furthermore, the route provided with a range of environmental conditions, including temperature variations from 3 to 36°C , relative humidity variations from 12 to 78% as well as changes in ambient pressure between 65.5

4.4. Experimental Setup and Instrumentation for On-Road Testing

to 100.5kPa. The overall net change in elevation between Morgantown and Riverside was only -57ft (i.e. final destination lower than start in Morgantown), with the highest encountered elevation being 11,990ft during the Loveland Pass, CO crossing. An in-depth description and analysis of the various route sections is given by *Kappanna et al.* (2013).

4.4. Experimental Setup and Instrumentation for On-Road Testing

Figure 4.29: Schematic diagram of the constant volume sampling system and instrumentation in the *Transportable Emissions Measurement System* and the raw exhaust measurement systems during on-road experiments; encircled numbers indicate instruments for particulate matter quantification.

Chapter 5

Results and Discussion

This chapter will discuss the application of the *Pegasor Particle Sensor* to measure actual exhaust emissions from a variety of internal combustion engines. The chapter is divided into two primary sections, namely, i) *controlled environment studies* in Section 5.1, which includes engine dynamometer testing under the controlled umbrella of laboratory conditions allowing to generate individual exhaust particulate matter characteristics by operating the engine at specific speed/load points, and thereby, engine control parameter settings; and ii) *real-world studies* in Section 5.2 which will ultimately apply the *Pegasor Particle Sensor* to emissions quantification in the harsh environmental conditions and vibrations as experienced during real-world, every-day on-road vehicle operation. *Semi-controlled environment studies* which include chassis dynamometer testing and exposes the particle sensor to more realistic engine and vehicle operating conditions and particulate matter rates emitted over specific drive cycles have been conducted as part of this work but will not be presented within the context of this dissertation.

The engine dynamometer studies in Section 5.1 will evaluate the sensor regarding measurement repeatability over consecutive test cycles, and highlight its sensitivity towards minute changes in particulate matter emission rates. The latter is of specific interest with regard to the ability to detect possible DPF inefficiencies or onset of failures for both in-use emissions compliance testing and OBD application. Distinguishing a damaged DPF from a momentarily reduced filtration efficiency due to a preceding regeneration event is indeed challenging as studies (*Honeywell ACS Laboratories*, 2010) have shown, that in case of a real crack in the DPF substrate an increase in particle concentration downstream the filter may only be sensed for a

short duration, until a soot cake layer will build up and act as a *seal* for the damaged area. This will make it especially cumbersome for OBD algorithms to correctly flag such an event as a *real* DPF failure. Furthermore, Section 5.1 will present correlations between laboratory-grade particle instruments and the PPS response model calibrated based on soot generator experiments discussed in Chapter 3. Finally, an NTE methodology is presented based on the *Pegasor Particle Sensors* real-time particulate matter measurement capabilities.

Chassis dynamometer testing was conducted for medium- and heavy-duty vehicle platforms for the purpose of evaluating the *Pegasor Particle Sensor*. During testing of heavy-duty vehicles as part of a South-Coast AQMD funded project (Thiruvengadam et al., 2015), two PPS-M1 V2 sensors were employed to simultaneously measure particulate matter emission rates up and downstream the vehicle specific after-treatment system. This allowed to estimate real-time after-treatment filtration efficiencies. For brevity, no chassis dynamometer results will be discussed in this document and the reader is referred to other publications of this author for a detailed description of results. Finally, Section 5.2 will present results from actual on-road emissions quantification using the PPS-M1, and discuss the sensors applicability to in-use compliance testing.

5.1 Controlled Environment Studies - Engine Dynamometer

This section will discuss the *Pegasor Particle Sensor* evaluation under the controlled environment conditions of a laboratory test cell with the engine being operated on an engine dynamometer over prescribed speed/load conditions. First, sensor repeatability will be discussed based on analysis of consecutive test cycles to assess its short term stability. Furthermore, a multi-day fuels evaluation study will serve as dataset to quantify sensor drift and repeatability over a longer time interval. This study was of special interest as it was conducted with a high-emitting legacy Diesel engine without after-treatment system¹, thus, exposing the PPS to increased soot mass rates which have the potential to foul the sensor or clog its internal sampling pathways. Secondly, the sensitivity of the sensor towards minute changes in particulate matter emission rates will be discussed based on measurements made downstream a *brand new* (i.e. non-degreened) DPF and during its initial aging phase. Due

¹Detroit Diesel Corp., Series 60 engine, see Table 4.5 for detailed engine information.

to the successive build-up of the *soot cake* layer on the filter walls, which is known to increase the particle trapping efficiency of the DPF (Suresh *et al.*, 2000; Wirojsakunchai *et al.*, 2007; Yamada, 2013), it is hypothetically expected to observe a reduction in PPS response signal. A similar phenomena will occur preceding a DPF regeneration event which causes the *soot cake* layer to oxidize and subsequently build up again, leading to momentary reduction in apparent filtration efficiency.

The third part of this section will present correlations between the PPS-M1 response and a range of laboratory-grade instruments, specifically, i) an EEPSTM measuring real-time particle size distributions; ii) a CPC measuring total particle concentrations; iii) an MSS measuring carbonaceous soot rates; iv) an aerosol electrometer measuring particle charge downstream the PPS; v) a tapered-element oscillating microbalance (TEOMTM, Thermo Fisher Scientific Inc.) measuring particulate matter mass rates; and vi) total PM from gravimetric analysis of filter media samples. With the exception of TEOM and gravimetric TPM measurements that were conducted in the dilute exhaust stream (i.e. CVS dilution tunnel), the other instruments sampled raw exhaust through a PFS system. This part of the section aids in verifying the PPS response model which was calibrated using monodisperse aerosols produced by the AVL particle generator.

The fourth and last part of this section will highlight the application of the PPS-M1 for possible NTE PM mass emissions quantification as required by the U.S. EPA heavy-duty in-use compliance program (CFR 40/86/N, 2011). Experiments were conducted over individual engine operating modes to apportion specific PM mass rates, and then compared to a composite test (i.e. all individual modes run as a single combined test cycle) to evaluate a selected NTE PM quantification methodology.

The *Pegasor Particle Sensor* used in conjunction with all controlled environment studies was version *V1*, and the sensor was installed directly to the raw exhaust transfer pipe using *Config. 1* and a *T-sampling* method without probe (i.e. probe *B*) as outlined in Figure 3.10. As PPS version *V1* did not feature an internal heater, the sensor housing was wrapped in resistive heated tape and insulation material.

5.1.1 Repeatability of particle sensor

Repeatability and long-term stability are important attributes for a particle sensor to be used in, i) a laboratory environment alongside lab-grade instruments for engine calibration and development purposes but also emis-

sions certification or compliance verification; and ii) as integrated part of a portable emissions measurement system for on-road emissions compliance evaluation. Moreover, it is one of the key requirements for a physical sensor to be implemented into either the OBD structure or the after-treatment control environment. Therefore, the primary task of this section was to evaluate the particle sensor response over multiple consecutive test runs in order to quantify measurement repeatability and the observed amount of sensor drift. Different engine dynamometer test cycles were utilized allowing to expose the particle sensor to a wide range of particle emissions rates.

Figure 5.1: Raw PPS-M1 signal over three consecutive hot-start FTP cycles; engine-out sampling location; $V_{ma} = 100V$; $\dot{V}_{samp} = 5.08slpm$.

Figure 5.1 shows the PPS output signal in milli-volts [mV] over three consecutive hot-start FTP cycles, sampled at engine-out location without having any after-treatment device installed. Using the native sensor signal for this analysis is justified as the sensor was operated under identical conditions (i.e. dilution air pressure, sensor temperature), and was sampling from the same location for this set of experiments. It can be seen that the sensor signals from the three runs line-up considerably well for the entire duration of the test cycle. Furthermore, no evidence of a possible sensor drift was found when comparing the PPS values between the idle portions at the beginning and end of each FTP cycle, respectively. Additionally, Figure 5.3(a)

depicts the cumulative PM sensor signal over the FTP. The slight difference shown for the third test run during the first idle portion of the *Los Angeles Non-Freeway*² section (i.e. ~ 300 to ~ 380 sec) was attributed to a minute difference in engine control since the same event was also observed in the results reported by the CPC, which was sampling parallel to the PPS. The average of the three PPS signals, integrated over the entire duration of the cycle, was $\sim 1.12 \times 10^6$ mV with a coefficient of variation (COV) of 1.69%, as listed in Table 5.1.

Figure 5.2: Raw PPS-M1 signal over three consecutive hot-start ETC cycles; engine-out sampling location; $V_{ma} = 100V$; $\dot{V}_{samp} = 5.08$ slpm.

Similar results were obtained while operating the engine over three consecutive European transient cycles, as can be seen from Figure 5.2 for the continuous and Figure 5.3(b) for the cumulative PPS signal, respectively. Considering the fact that the ETC is a more transient cycle having also a more extended high speed portion compared to the FTP cycle, the repeatability of the PM sensor shows a slightly lower COV on the order of about 0.14%.

Figure 5.4 depicts the sensor's repeatability over three consecutive steady-

²the FTP cycle comprises four distinct sections, namely i) New York Non-Freeway (NYNF); ii) Los Angeles Non-Freeway (LANF); iii) Los Angeles Freeway (LAFY); and iv) a repeat of the NYNF from the first section. Each section is 300sec in duration amounting to a total cycle duration of 20min. Detailed cycle information is given in (CFR 40/86/N, 2011).

Figure 5.3: Raw PPS-M1 signal over three consecutive hot-start, 4 mode steady-state cycles; engine-out sampling location; $V_{ma} = 100V$; $\dot{V}_{samp} = 5.08slpm$.

state cycles showing similar characteristics as for both transient cycles. It can be noticed that the overall PPS signal level is lower compared to the ETC and FTP cycles as there are no highly transient engine operating mode (i.e. speed/load) changes, which are a primary contributor to increased soot levels. Furthermore, it is interesting to note the sudden drop from ~ 80 to $\sim 50mV$ in the particle sensor signal during mode 1. This is characteristic for *pre-consent-decree* heavy-duty Diesel engines as they were shifting engine control parameters to a more fuel efficient setting during cruise mode. The drop in PPS signal went hand in hand with a sudden increase in gaseous NO_x emissions.

Finally, Table 5.1 summarizes the average, standard deviation and COV of the integrated PPS signal for different transient and steady-state test sets, each consisting of three consecutive test runs. It should be mentioned that the second FTP set, listed in Table 5.1, was measured with the PPS sampling from engine-out location, however, with a catalyzed DPF installed downstream, hence, leading to an increased back-pressure imposed onto the engine, which ultimately resulted in slightly elevated soot production

Figure 5.5 shows a comparison of total particle number concentrations be-

5.1. Controlled Environment Studies - Engine Dynamometer

Figure 5.4: (a) Cumulative PPS-M1 signal over three consecutive hot-start FTP cycles; (b) cumulative PPS-M1 signal over three consecutive hot-start ETC cycles; both measurements at engine-out sampling location; $V_{ma} = 100V$; $\dot{V}_{smp} = 5.08slpm$.

Table 5.1: Average (μ_{PPS}), standard deviation (σ_{PPS}) and coefficient of variation (COV) for integrated PPS signal over different test cycles; each test set consisting of three consecutive repeats; two sets of FTP data collected on two different days; all cycles were run as hot-starts; standard deviation expressed as $1 \cdot \sigma$.

Test Cycle	μ_{PPS} [mV]	σ_{PPS} [mV]	COV [%]
FTP (1 st set)	1.120×10^6	1.905×10^4	1.69
FTP (1 st set)	1.268×10^6	2.489×10^4	1.96
ETC	2.109×10^6	2.991×10^3	0.14
Steady-State ^a Mode 1	1.372×10^5	1.113×10^3	0.81
Steady-State Mode 2	1.948×10^5	5.238×10^2	0.27
Steady-State Mode 3	7.750×10^4	2.686×10^3	3.47
Steady-State Mode 4	1.740×10^5	1.730×10^3	0.99

^a steady-state (speed/load) mode 1) low/100%; 2) med./50%; 3) med./100%; 4) med./25%

tween the CPC (blue circle) and EEPSTTM (green triangle) versus the PPS-M1 response model (R_{PPS}) for total particle numbers (red diamond). Data was collected over a period of four days and from three fuels, specifically, a reference fuel (solid symbols) and two candidate fuels labeled Cand. #1 (empty symbols) and Cand. #2 (gray filled symbols). The details of the different fuels

are not of importance to this analysis and will therefore not be discussed herein. First of all, Figure 5.5 highlights the consistency of the different measurement methods over a period of four days. From a qualitative standpoint, the PPS was observed to track the pattern of both CPC and EEPSTM closely. This can especially be seen from close analysis of Day 1 and Day 4 data, where trends in total particle number concentrations are matched by all three instruments.

Overall, from a quantitative standpoint the PPS compares better to the EEPSTM measurement to within $\sim 1.9\%$ to 18.96% for reference fuel testing on Day 1 and Day 4, respectively. The slightly higher discrepancy between R_{PPS} and EEPSTM for Day 4 could possibly be explained by a fact that the dilution ratios for the first and second stage of the PFS system were changed for *Cand. #2* fuel and Day 4 testing of the reference fuel. As observed from Figure 5.6, depicting the averaged particle number-weighted size distributions for all fuels, an increased nucleation mode (i.e. with $CMD \approx 10\text{nm}$) can be noticed for the reference fuel on Day 4. The first stage dilution ratio of the PFS system was increased from ≈ 11 to ≈ 58 possibly slightly enhancing the formation of nuclei mode particles. Furthermore, with the critical flow orifice for the first stage dilution being only on the order of 2lpm , and thus, relatively small, there is a tendency for soot to build up on the orifice surface leading to a modification of the flow pattern and dilution ratio. This is especially enhanced for high particulate matter emitting engines as the one used for these experiments. On the other hand, the increased soot build up inside the PPS might have led to a reduction in measurement sensitivity due to possible leakage current caused by the deposits. Indeed, average total particle concentration measurements with the PPS dropped by $\sim 10.8\%$ between reference fuel tests on Day 1 and 4, whereas CPC measurements indicated a nearly identical total concentration within 0.7% as seen from Table 5.2. It has to be highlighted that there exists no significant difference in total particle number concentrations between the different test fuels as is emphasized by the *log-log* graph inserted in Figure 5.6.

Figure 5.5 indicates a systematic difference between the CPC and the EEPSTM and PPS-M1 measurements on the order of a multiplication factor ~ 2.5 - 2.7 . On one hand it has to be remembered that both EEPSTM and PPS-M1 measurement principles are based on electrical charging of particles and their *electrical mobility* through an electrical field (i.e. the latter in the case of the EEPSTM), whereas the CPC measurement is based on particle growth and optical counting. Thus, the CPC will count more accurately single particles whereas the other two instruments are dependent on charg-

5.1. Controlled Environment Studies - Engine Dynamometer

Figure 5.5: Comparison of total particle number concentrations measured by the CPC, EEPSTM and PPS-M1 via response model (R_{PPS}), for a reference fuel and two candidate fuels over consecutive FTP cycles; 2-stage PFS system for EEPSTM with 3rd stage for CPC; label 1) indicates corrected sensor response for ion trap penetration ($P_{V_{ma}}$) PPS: $V_{ma} = 100V$ and $V_{samp} = 5.08\text{slpm}$.

Figure 5.6: Comparison of average particle size distributions between a reference fuel and two candidate fuels over the FTP cycle; measured with TSI EEPSTM; insert shows the same data on log-log axis; 2-stage PFS system with two different dilution settings sampling from raw exhaust.

5.1. Controlled Environment Studies - Engine Dynamometer

Table 5.2: Comparison of average total particle number concentrations [$\#/cm^3$] measured by the CPC, EEPSTM and PPS-M1 for a reference fuel and two candidate fuels; over FTP cycle; PPS-M1 data shown for i) response model (R_{PPS}), ii) calibration coefficients by *Ntziachristos et al.* (2013b) ($R_{PPS,Ntz}$), and iii) linear calibration coefficients from soot generator experiments ($R_{PPS,LR}$); corrected CPC concentration (CPC_{corr}) for 2-6nm particles.

Fuel	Ref. (Day 1)	Cand. #1	Ref. (Day 3)	Cand. #2	Ref. (Day 3)
CPC	1.45×10^{11}	1.56×10^{11}	1.44×10^{11}	1.48×10^{11}	1.46×10^{11}
CPC_{corr}	5.62×10^{10}	4.23×10^{10}	5.52×10^{10}	3.85×10^{10}	5.73×10^{10}
EEPS TM	5.29×10^{10}	5.64×10^{10}	-	5.76×10^{10}	5.70×10^{10}
R_{PPS}	5.19×10^{10}	4.83×10^{10}	5.91×10^{10}	4.58×10^{10}	4.62×10^{10}
$R_{PPS,Ntz}$	3.66×10^{10}	3.41×10^{10}	4.17×10^{10}	3.24×10^{10}	3.27×10^{10}
$R_{PPS,LR}$	2.92×10^{10}	2.73×10^{10}	3.29×10^{10}	2.60×10^{10}	2.62×10^{10}

ing efficiency and number of charges that were acquired by particles as a function of their size. On the other hand, the CPC employed for this study exhibited a lower particle detection limit of 2-3nm, whereas the EEPSTM measured particles down to ~ 6 nm only. Also, the PPS-M1 was operated with the ion trap voltage of $V_{ma} = 100V$, which has shown to translate into a mobility analyzer penetration fraction of ~ 0.4 for a particle size distribution with CMD = 18nm according to Figure 3.24. Based on that it can be assumed that particles below 18nm are removed to some extent by the PPS internal mobility analyzer (i.e. ion trap), and are thus not being counted. A simple assumption was made by multiplying the measured concentration of 6nm particles by the EEPSTM into the missing particle sizes between 2-6nm to estimate the possible amount of particles in this size range. Using the obtained particle concentration for the 2-6nm range, the CPC measurement was corrected and observed to fall within the same order of magnitude as both EEPSTM and PPS-M1 measurements.

Finally, Figure 5.5 shows two instances where the corona charger in the PPS-M1 turned off during the test, leading to a loss in sensor response and thus, a significant reduction in calculated total particle number concentration (see measurements with label: *corona partial off*). Furthermore, three tests (i.e. #31-32) were conducted with the ion trap voltage set to $V_{ma} = 500, 1000$, and 1500V. They can be recognized by the successively lower sensor response as more particles are being trapped by the mobility analyzer, leading to a lesser amount of charge leaving the sensor. Increasing the ion trap voltage is also equivalent with reducing the sensor sensitivity (*Maricq*, 2013). Measurement #30 (i.e. indicated by label 1)) was corrected for mobility analyzer penetration ($P_{V_{ma}}$) using the proposed Equation 3.18, and seen to increase the total

particle number concentration estimated by the R_{PPS} model as expected.

Additionally, Table 5.2 shows a comparison between the total particle number concentrations estimated by the PPS response model (R_{PPS}) versus the PPS response using calibration factors provided by *Ntziachristos et al. (2013b)* ($R_{PPS,Ntz}$) and obtained from the soot generator studies discussed in Chapter 3 ($R_{PPS,LR}$). All three methods exhibit a response on the same order of magnitude, however, $R_{PPS,Ntz}$ leads to $\sim 29\%$ and $R_{PPS,LR}$ to $\sim 43\%$ lower total particle number concentrations. The increased difference for the $R_{PPS,LR}$ method can possibly be explained by the fact that only a narrow range of number concentrations within 1×10^6 to 6×10^6 were available for linear regression to obtain the calibration coefficients for this method (see Figure 3.18). The R_{PPS} model was used with an assumed count mode diameter of 40nm and a geometric standard deviation (σ_g) of 1.7.

5.1.2 Sensitivity of particle sensor

While serving as an integral part of an OBD structure or being used for the purpose of in-use emissions compliance verification, a physical PM sensor would need to be capable of detecting DPF malfunctions, such as small cracks in the filter substrate, caused by thermal stresses, hence, leading to slightly increased particle concentration within the exhaust gas downstream of the DPF. It is known that DPF filtration efficiencies are temporarily reduced during, and more importantly immediately following a filter regeneration event as the *soot cake* layer that has built-up on the filter substrate walls during regular operation is being oxidized by the high temperature regeneration (*Suresh et al., 2000; Wirojsakunchai et al., 2007; Yamada, 2013*). The soot particles that enter the pores and eventually deposit on top of the filter substrate, building a membrane like layer during the early stage of an empty filter (i.e. new or regenerated filter), are the primary reason for the high particle retention efficiencies (i.e. especially for nano-sized particles) achieved by wall-flow type particulate filters. In order to assess the PPS-M1 sensitivity towards minute particle concentration changes the test engine was retrofitted with a catalyzed wall-flow type DPF, with the particle sensor sampling plane located downstream the filter.

The DPF employed for this study was *brand new*, meaning it had not undergone any *degreening* procedure prior to installation and therefore no soot cake layer was yet built-up on the substrate walls. The test engine used for these experiments was a model year 1999 Cummins ISM-370ESP which was originally certified at a PM level of 0.1g/bhp-hr (see Table 4.5). Fig-

Figure 5.7(a) depicts the raw PPS-M1 signal in its native milli-volt unit from the first three consecutive FTP cycles, operated with the new DPF installed. A clear reduction of about one order of magnitude can be observed by comparing the sensor signal from engine-out sampling shown in Figure 5.1 to the PPS signal measured during the first FTP cycle downstream the trap seen in Figure 5.7 (dark line). However, more interesting is the clearly distinguishable reduction of the raw PPS signal over subsequent test cycles, indicating the slow build-up of the soot cake layer on the filter substrate walls and therefore, leading to an enhanced particulate filtration efficiency of the DPF (Suresh *et al.*, 2000). The same trend was observed for total particle number concentrations measured by the CPC as shown in Figure 5.7(b). After the three initial FTP cycles, the DPF was *degreened* by operating it for a total of 30 hours over a 2-mode steady-state as well as a multitude of FTP cycles. For comparison, the *green line* (i.e. labeled FTP #60) plotted in Figure 5.7(a) and 5.7(b) for PPS and CPC, respectively, represents the magnitude of particles after the *degreening* process has been completed and the soot cake layer was built-up. It has to be emphasized that the latter represents a DPF filtration efficiency state that falls into the time period between considerably after or any time before a DPF regeneration event, where the *soot cake* layer is sufficiently stable to provide maximum filtration efficiency.

Figure 5.7: (a) Raw PPS-M1 signal and (b) CPC total particle number concentration over consecutive FTP cycles sampled after a *brand new* (i.e. non-degreened) catalyzed DPF; CPC data corrected for dilution ratio, $DR_{CPC} \approx 145$; $V_{ma} = 100V$.

A direct comparison between the PPS signal and the total particle concen-

tration as measured by the CPC, both integrated over the entire duration of the FTP cycle, is shown in Figure 5.8(right) for the three FTPs run prior to DPF *degreening* as well as for one FTP cycle run after 30hours of operation. All values were normalized by the total engine work [bhp-hr] performed over the respective test cycle. A linear least-squares regression fit indicates a fairly good correlation between the two particle measurement instruments exhibiting a coefficient of determination (R^2) of 0.9832. In a similar fashion, Figure 5.8(left) depicts the correlation between the integrated raw PPS signal and gravimetrically sampled total particulate matter according to requirements outlined in CFR 40/1065 (2015), for the same four FTP cycles as mentioned before. Even though the linear least-squares analysis shows a relatively well correlation ($R^2 = 0.9531$) between the two particulate matter measurement methods, it has to be kept in mind that the gravimetric sampled TPM includes semi-volatile and volatile fractions that condensed or nucleated during the course of the dilution process, whereas particles measured by the PPS primarily comprises of solid particles due to the elevated sampling temperature of $\sim 200^\circ\text{C}$. Possible correction algorithms, which take additional factors such as, but not limited to, fuel sulfur content and hydrocarbon emissions into account are discussed in literature and are possible pathway to augment the PPS-M1 measurement to a TPM-like metric. Indeed, Clerc and Johnson (1982) for example presented an early hydrocarbon adsorption model to predict the soluble and solid particulate matter fraction collected from dilution tunnels. Their model was reported to predict SOF and combined SOF & SOL concentrations to within 35% and 25% of experimentally obtained mass values, respectively. Silvis (2012) describes a more simplified approach to estimate SOF as well as sulfates and water content in order to correct the carbonaceous soot signal measured with the AVL micro soot sensor to a quantity which is representative of TPM collected on a filter paper at the prescribed $47 \pm 5^\circ\text{C}$ filter face temperature.

In order to assess the magnitude of particle matter concentration reductions, DPF filtration efficiencies based on the raw PPS signal, the CPC total particle number count as well as the gravimetrically sampled TPM have been calculated according to Equation 5.1. Results are reported in percent removal efficiency with respect to upstream DPF particle concentrations, and are listed for comparison in Table 5.3. Parameter W in Equation 5.1 is a place holder for either the work-specific PPS signal [mV/bhp-hr], the work-specific total particulate number count measured by the CPC [$\#/\text{cm}^3$]/bhp-hr] or the work-specific gravimetric TPM [g/bhp-hr], all integrated over the FTP cycle. As seen from Table 5.3, DPF filtration efficiencies for the three described

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Figure 5.8: Work-specific, integrated raw PPS signal in comparison to (*right*) total particle number concentration measured by the CPC, (*left*) particulate matter mass obtained from gravimetric filter media analysis; samples over three consecutive and one additional FTP cycle; downstream *brand new* (non-degreened) DPF; CPC data corrected for dilution ratio; $V_{ma} = 100V$.

Table 5.3: Comparison of DPF filtration efficiencies as calculated from PPS-M1, CPC and gravimetric PM mass measurements; samples over three consecutive and one additional FTP cycle; downstream *brand new* (non-degreened) DPF.

Test Run	PPS-M1 [mV/bhp-hr]	CPC [(#/cm³)]	TPM ^a [g/bhp-hr]
FTP #1	80.52%	93.84%	80.08%
FTP #2	91.16%	96.67%	91.66%
FTP #2	94.32%	97.82%	97.10%
FTP #2	99.02%	99.87%	98.50%

^a TPM - total particulate matter measured gravimetrically

measurement methods are of similar order and clearly show an increasing trend over consecutive FTP cycles, thus, confirming the continuous build-up of the *soot cake* layer on the DPF substrate walls.

$$\eta_{DPF} = 1 - \frac{(W)_{pre\ DPF}}{(W)_{post\ DPF}} \quad (5.1)$$

A second example provided herein emphasizing the sensitivity of the PPS was observed during three consecutive 4-mode steady-state cycles while

sampling downstream the *degreened* DPF. The solid line, labeled *Steady-State #1*, in Figure 5.9(a) and 5.9(b) for the raw PPS signal and CPC total particle number concentration, respectively, indicates particle emissions at background levels during the initial portion of the first steady-state cycle. At about 160 seconds, during the first engine operating mode (i.e. 1261rpm, 100% load) particle numbers (CPC) and PPS signal suddenly increased by more than an order of magnitude, indicating the onset of a DPF regeneration event initiated by high exhaust gas temperatures ($\sim 510^\circ\text{C}$) and a high soot content within the filter, possibly accumulated over previous FTP cycles.

Figure 5.9: (a) Raw PPS-M1 signal and (b) CPC total particle number concentration over consecutive 4-mode steady-state cycles; sampled downstream a *degreened*, catalyzed DPF; CPC data corrected for dilution ratio, $\text{DR}_{\text{CPC}} \approx 145$; $V_{\text{ma}} = 100\text{V}$.

After switching to operating mode 2 (i.e. 1569rpm, 50% load) at $\sim 390\text{sec}$ the particle concentration (CPC) as well as the PPS signal reduced to lower

levels again as the regeneration is either completed or interrupted by the changing thermodynamic properties of the exhaust gas. However, it can be clearly seen from Figure 5.9 that particle emissions remain at an elevated level, compared to the initial portion of the cycle, and only slowly decreased over consecutive test cycles, hence, indicating the cyclical *soot cake* layer build-up and regeneration process.

In order to highlight the sensitivity of the electrometer towards naturally charged particles, Figure 5.10 provides a comparison between the PPS response in [fA/(slpm)] and the raw aerosol electrometer current (I_{AEM}) in [fA]. To conduct this experiment the corona charger in the PPS was turned *off* and the voltage of the mobility analyzer set to $V_{ma} = 0V$. The AEM is observed to be sensitive enough (*blue line*) to measure the natural charge particles have acquired during the combustion process and carry with them in the exhaust stream. The majority of the charge acquired by particle is usually lost by diffusion to exhaust components such as after-treatment systems and transfer pipe walls while the exhaust gas is traveling from the combustion chamber to the exhaust stack (*Honeywell ACS Laboratories, 2010*). Additionally, the AEM current signal is seen to closely track the engine load pattern of the FTP cycle. From close analysis of the PPS response signal it becomes evident that during each engine acceleration event that causes charged particles to exit the engine, and that are measured by the AEM, an opposite, negative response is detected by the PPS. This can be explained by the accumulation of charge inside the sensor due to particles impacting and transferring their natural charge to the virtually grounded internal sensor components, thus, induced a net negative current.

On one hand this demonstrates the sensitivity of the PPS to bipolar charged particles and to register natural charge of particles if the corona charger is turned *off*. However, on the other hand and more importantly, this could also lead to a possible measurement under- or over-estimation of particles. A study performed by *Maricq (2013)* discussed the influence of negative, neutral and positive charged particles onto the PPS-M1 response³ and found that naturally positive charged particles will induce a negative offset, whereas negatively charged particles entering the sensor will cause a positive offset in sensor response. This is due to the fact that the unipolar corona charger produces positively charged ions, leading to a positive charge acquired by the particles during the diffusion-charging process. If now a given amount of particles enters the sensor containing already some level of pos-

³see Figure 6 on page 569 of *Maricq (2013)*.

Figure 5.10: Comparison between AEM current (I_{AEM}) and PPS-M1 response over FTP cycle while corona charger is turned off and ion trap set to $V_{ma} = 0V$; AEM measuring at outlet of PPS-M1; engine-out sampling location.

itive charge, less charge will attach during the diffusion-charging process and thus, the escaping current will be lower, ultimately causing the sensor response to reduce compared to the response to the same amount of *neutral* particles. Indeed, a negative PPS response offset has been observed in actual testing of after-treatment equipped engines by various groups, however, no definite answer was found to why some after-treatment systems cause more positively charged particles in the exhaust stream compared to others⁴. Pegasor (Oy) Ltd. suggested to install a charge neutralizer upstream the sensor inlet to possibly mitigate this problem.

5.1.3 Correlation of particle sensor to reference instruments

During the particle sensor response experiments conducted with monodisperse aerosols generated with the AVL APG and discussed in Section 3.4 three different sensor calibration methods were presented. They include a basic sensor response model (R_{PPS}) as a function of a selected reference particle size distribution characterized by the CMD and σ_g , the calibration

⁴this is based on personal correspondence with Peter Ahlvik, ExIS AB, Sweden; and Pragalath Thiruvengadam, Cummins Inc.

Figure 5.11: Engine-out sampling correlation between PPS-M1 response and total particle number concentration by the CPC over FTP (blue circle), ETC (red triangle), and 4-mode steady-state cycles (green diamond); dark lines: linear regression for R_{PPS} vs. $N_{tot,CPC}$; CPC corrected for dilution ratio; $V_{ma} = 100V$.

coefficients given by *Ntziachristos et al.* (2013b), and a linear least-squares regression model based on raw PPS-M1 signal and reference instruments⁵. In order to compare and verify the models and calibrations with actual polydisperse engine exhaust particle emissions engine dynamometer testing was conducted. Test engines were operated over different transient and steady-state test cycles, allowing for exposure of the PPS-M1 to a variety of particulate matter concentration rates. The sample flow corrected, raw PPS signal was subsequently correlated to an $EEPS^{TM}$ measuring particle size distributions and a CPC quantifying total particle number concentrations.

Figure 5.11 depicts a comparison between the raw PPS-M1 signal in $[fA/(slpm)]$ versus the total particle number concentration as measured by the CPC over two transient cycles (i.e. FTP and ETC) and a 4-mode steady-state cycle. Similarly, Figure 5.12 shows the correlation between the PPS signal and the total particle number concentration, integrated over each particle size bin, as measured by the $EEPS^{TM}$. The data presented in these two figures is from engine-out sampling on a 1999 Cummins ISM-370 engine. First of all, it can be noticed that both CPC and integrated particle $EEPS^{TM}$

⁵ $SMPS^{TM}$ for particle number and MSS for particulate matter mass concentrations.

Figure 5.12: Engine-out sampling correlation between PPS-M1 response and total particle number concentration as calculated from the EEPSTM over FTP (blue circle), ETC (red triangle), and 4-mode steady-state cycles (green diamond); dark lines: linear regression for R_{PPS} vs. $N_{tot,EEPS}$; EEPSTM corrected for dilution ratio; $V_{ma} = 100V$.

concentrations are closely agreeing in magnitude, exhibiting maximum concentrations up to $\sim 2.5 \times 10^8 \# / \text{cm}^3$ with the bulk being below $\sim 1.0 \times 10^8 \# / \text{cm}^3$. Compared to the raw PPS signal the CPC measurement was observed to be more scattered and there appears to be a distinct difference in correlation between transient and steady-state engine operation. Linear least-squares regression indicates a $\sim 45\%$ steeper slope (β_1) of 481 for the steady-state versus on average 330 for the two transient cycles. Also as expected the steady-state test exhibited lesser scatter and thus, an increased coefficient of determination of $R^2 = 0.9$. Data was aligned using an auto-correlation function, however, it has to be kept in mind that the PPS was sampling directly from the exhaust transfer line while the CPC was sampling from a three stage PFS system, thus, experiencing particle size dependent transfer losses and reduced sensitivity to fast transient particle emission rates. Also noticeable from Figure 5.11 is a significant systematic offset of the CPC especially for the two transient cycles which exhibited lower concentration levels during engine idle operating portions.

Conversely, the correlations between raw PPS-M1 signal and calculated total particle concentrations with the EEPSTM were observed to be very similar

for the two transient and the steady-state cycles as seen from Figure 5.12. The linear least-squares regression slope (β_1) ranges between $\pm 4\%$ of 330. Interestingly, the correlation slope for the steady-state test is highest for the correlation with CPC (i.e. ~ 481) and lowest with the $EEPS^{TM}$ (i.e. ~ 320). A possible explanation for the overall lower correlation slope between the PPS and $EEPS^{TM}$ versus PPS and CPC is, as already mentioned earlier, the fact that the $EEPS^{TM}$ does not count particles below 6nm and the PPS was operated with a mobility analyzer setting of $V_{ma} = 100V$, thus, is less sensitive to particles at the lower end of the size range. In contrast, the CPC's lower detection limit was in the 2-3nm particle diameter range.

Table 5.4 provides an overview of the offsets (β_0) and slopes (β_1) calculated from linear least-squares regression analysis for engine-out and post DPF sampling. The table also lists the slopes of the linear regression lines if forced through the origin ($\beta_{1,origin}$), which was observed to lead to a $\sim 40\%$ and $\sim 4\%$ increase for *PPS vs. CPC* and *PPS vs. $EEPS^{TM}$* slopes, respectively. This additionally highlights the approximately one order of magnitude larger offset of the *PPS vs. CPC* correlation. In comparison to the sensor calibration slope established during soot generator experiments against the SMP^{TM} of 214 and the calibration factor provided by *Ntziachristos et al.* (2013b) of 288, the *PPS vs. CPC* slope is on average 78% and 32% higher (i.e. 381), respectively, whereas the *PPS vs. $EEPS^{TM}$* slope is on average 54% and 15% higher (i.e. 381), respectively. The difference between the soot generator determined slope and above discussed CPC and $EEPS^{TM}$ correlations, closes to 22% and 5%, respectively, if the soot generator slope is forced through the origin (i.e. 313, see Table 3.9).

In a similar fashion as Figures 5.11 and 5.12, Figures 5.13 and 5.14 depict the *PPS vs. CPC* and *PPS vs. $EEPS^{TM}$* correlations for downstream DPF sampling, respectively. First of all, the nearly two orders of magnitude reduction in total particle number concentrations due to the particle removal efficiency of the DPF becomes evident from inspection of these figures. For both instruments, correlations to the PPS become significantly weaker during transient engine operation as compared to upstream DPF correlations, exhibiting R^2 values for linear regression on the order of 0.19 and 0.14 for CPC and $EEPS^{TM}$, respectively. Concurrently, the slope of the regression lines reduced on average to ~ 18.5 and ~ 13 for CPC and $EEPS^{TM}$, respectively. A possible explanation for the higher PPS signal values between 1×10^4 to $4 \times 10^4 fA/(slpm)$ while the reference instruments do not sense any increased particle concentrations could be due to fast transient particle concentration spikes during acceleration events of the engine. With the PPS

Figure 5.13: DPF-out sampling correlation between PPS-M1 response and total particle number concentration by the CPC over FTP (blue circle), ETC (red triangle), and 4-mode steady-state cycles (green diamond); dark lines: linear regression for R_{PPS} vs. $N_{tot,CPC}$; CPC corrected for dilution ratio; $V_{ma} = 100V$.

Figure 5.14: DPF-out sampling correlation between PPS-M1 response and total particle number concentration as calculated from the EEPSTM over FTP (blue circle), ETC (red triangle), and 4-mode steady-state cycles (green diamond); dark lines: linear regression for R_{PPS} vs. $N_{tot,EEPS}$; EEPSTM corrected for dilution ratio; $V_{ma} = 100V$.

sampling directly from the exhaust stack these fast transient events could be measured, whereas are being dampened out due to transfer losses in the PFS system and thus, not registered by the reference instruments. These data points have the effect of dominating the linear regression and significantly pulling the slope to a lower as expected value.

On the other hand, when looking at the steady-state data in Figures 5.13 and 5.14 correlation slopes of 225 and 223 for *PPS vs. CPC* and *PPS vs. EEPSTM* can be observed, which is closer to what is expected based on upstream DPF sensor response. Moreover, both instruments exhibit a similar correlation to the raw PPS signal for downstream DPF measurements. It has to be emphasized that the steady-state data was collected immediately after a DPF regeneration event with the three consecutive steady-state cycles falling into the time period of *soot cake* layer build-up on the filter substrate walls and thus, continuous improvement in filtration efficiencies. This can be easily noticed by the reduction in particle number concentrations starting from about 4×10^6 and reduced to $1 \times 10^6 \text{ \#}/\text{cm}^3$ after the third steady-state cycle. The EEPSTM was only measuring during the third cycle and thus, started at a higher DPF efficiency level, leading to the measurement data only ranging up to $\sim 2.2 \times 10^6 \text{ \#}/\text{cm}^3$.

In summary, the correlation between the raw PPS signal versus CPC and EEPSTM was observed to exhibit a slope $\sim 41\%$ and $\sim 32\%$, respectively, lower for the downstream as compared to upstream DPF measurements. This excludes the transient data for downstream DPF sampling which was seen to be skewed by fast transient response signals of the PPS. A changing correlation as a function of up- or downstream DPF measurements is consistent with findings by other researchers (*Beck et al.*, 2012; *Wachtmeister*, 2012) who associated the difference with varying particle properties depending on sampling location. Indeed, as the soot generator experiments have shown (see Figure 3.19), the PPS response is dependent on particle size and to a much lesser degree on particle composition (*Shin et al.*, 2007) (i.e. *burner-out* vs. *VPR-out* experiments). Taking the average of β_1 all up- and downstream DPF measurements (i.e. excluding downstream transient cycles) listed in Table 5.4, the CPC and EEPSTM are found to exhibit correlation slopes of 342 and 303 with respect to the raw PPS signal. This is 60% and 19% higher for the CPC, and 42% and 5% higher for the EEPSTM correlation slopes as compared to the calibration slopes based on soot generator experiments and provided by *Ntziachristos et al.* (2013b), respectively. In conclusion, the soot generator experiments were found to underestimate the correlation slope for PPS response towards total particle number concentrations somewhat,

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Table 5.4: Linear least-squares regression coefficients between raw PPS-M1 signal [fA/(slpm)] and total particle number concentrations [$\#/cm^3$] measured by CPC and EEPSTM; up- and downstream DPF over transient FTP/ETC and 4-mode steady-state cycle; $\beta_{1,origin}$: slope for regression line forced through origin; $V_{ma} = 100V$.

Instr.	Location	Cycle	β_0	β_1	R^2	$\beta_{1,origin}$
CPC	pre-DPF	FTP	3.02×10^7	314	0.7560	439
		ETC	1.36×10^7	346	0.8819	403
		Steady-State	4.34×10^6	481	0.9033	567
	post-DPF	FTP	6.73×10^4	19	0.2345	26
		ETC	9.87×10^4	18	0.1389	32
		Steady-State	4.28×10^5	225	0.9384	299
EEPS	pre-DPF	FTP	3.56×10^6	347	0.9540	362
		ETC	2.08×10^5	323	0.8957	324
		Steady-State	1.19×10^6	320	0.9394	343
	post-DPF	FTP	2.05×10^5	18	0.2460	37
		ETC	1.42×10^5	8	0.0383	27
		Steady-State	2.49×10^5	223	0.8731	267

which is possibly due to the fact that the utilized range of particle concentrations was limited to within one order of magnitude only.

Figure 5.15 shows a correlation between total particle number concentrations as estimated by three different PPS response models and measured with the CPC and EEPSTM. The three response models include the basic sensor response model (R_{PPS}) with an assumed particle size distribution of $CMD = 70nm$ and $\sigma_g = 1.7$, the calibration coefficients provided by *Ntziachristos et al.* (2013b) (PPS_{Ntz}), and the linear least-squares regression calibration coefficients (PPS_{LR}) obtained from soot generator experiments described in Section 3.4. Data included in this analysis comprises two legacy engines⁶, up- and downstream DPF sampling locations and two transient (i.e. FTP, ETC) and one steady-state cycle.

First of all, a clear distinction between up- and downstream DPF sampling can be observed from Figure 5.15 with post DPF data being clustered towards the lower left corner. Two post DPF tests exhibited increased particle concentrations which were identified as steady-state tests that immediately followed a DPF regeneration event, thus, the oxidized and temporarily missing *soot cake* layer led to a reduction in filtration efficiency. Interestingly, the

⁶1999 Cummins ISM-370 and 1992 DDC S-60.

Figure 5.15: Correlation of total particle number concentrations between three PPS-M1 response models versus CPC and EEPS™; PPS-M1 data shown for i) response model (R_{PPS} , $CMD = 70nm$ and $\sigma_g = 1.7$), ii) calibration coefficients by *Ntziachristos et al. (2013b)* ($R_{PPS,Ntz}$), and iii) linear calibration coefficients from soot generator experiments ($R_{PPS,LR}$); test cycles: FTP, ETC, and 4-mode steady-state; dark solid line: $y = x$ line; dark dashed line: $+100\%/-50\%$ range; $V_{ma} = 100V$.

PPS response was observed to be slightly increased during the regeneration event when compared to the total particle number concentration measured by the CPC. A possible effect of the increased exhaust gas temperature or a change in particle morphology emitted during the regeneration event might be the root cause for this observed discrepancy. No EEPS™ data was available for these two test points that could aid in elucidating on possible effects due to a changes in particle charging efficiency. Furthermore, it might be hypothesized that the increased PPS response could stem from negatively charged particles entering the sensor, leading to a positive measurement offset. However, this would mean particles are getting negatively charged during the regeneration event. No data or measurements are available though to corroborate this hypothesis. Towards the top left of Figure 5.15 a set of measurement points can be seen for which the corona turned *off* partially through the test cycle causing the PPS response to become zero.

In general the total particle number concentration calculated by the PPS can be seen to closely correlate with total number concentrations measured by the CPC and EEPS™ as the data largely falls onto the $y = x$ line or within

+100/ – 50% of it (*dashed lines*). Downstream DPF data is observed to more closely correlate than engine-out data, which in general is shifted towards higher particle number concentrations measured by the reference instruments, thus, being under-predicted by the PPS response models. Furthermore, a clear discrepancy between the sensor response and the reference instruments can be seen for total PPS number concentrations of around 2×10^9 in conjunction with the linear regression calibration based response model (PPS_{LR}). This evidently is due to the constant coefficient $\beta_0 = 1.63 \times 10^6$ used in the linear model causing the constant to become the dominating driving factor for small sensor responses as expected downstream a filter. Table 5.4 additionally emphasizes this problem with coefficients β_0 seen to be up to two orders of magnitude smaller for downstream versus upstream DPF correlations. This highlights the possible shortcoming of using a constant factor in a linear model. On one hand it aids in improving accuracy over a limited range for which the sensor was calibrated, however, extrapolating out of that range might lead to less accurate results. One possibility would be to use a separate calibration for up- and downstream measurements (Wachtmeister, 2012).

Figure 5.16 shows the same dataset as presented in Figure 5.15 on a work-specific basis in units $[\#/cm^3]$ by multiplying the average particle number concentrations over the test cycle into the total exhaust volume and divided by the total engine work performed. With the exception of the PPS_{LR} response model for the lower concentrations the majority of the data falls within the +100/ – 50% bounds around the $y = x$ line. The data points separated towards the top left are representative of the tests that exhibited a partially turned *off* corona charger. The CPC vs. $EEPS^{TM}$ correlation data clustered around $10^{15} \#/\text{bhp-hr}$ (*empty circles*) originated from FTP cycles run with the DDC S-60 engine for different fuels and was already discussed in more detail in Figure 5.5, including a possible explanation for the offset compared to $EEPS^{TM}$ and PPS measurements. Work-specific particle number emission rate is the metric based on which the European total particle number concentration limits for heavy-duty vehicles are defined (see Section 2.3).

A comparison of work-specific particulate matter mass emissions rates, calculated based on different PPS response models and measured by the TEOM in $[\text{mg}/\text{bhp-hr}]$ is given in Figure 5.17. The PPS response models for PM mass estimation included the approach outlined in Equation 3.13, with N_{tot} being derived from the R_{PPS} response model for particle number concentrations for an assumed log-normal size distribution given by $CMD = 70\text{nm}$

Figure 5.16: Correlation of engine work-specific total particle number concentrations between three PPS-M1 response models versus CPC and EEPSTM; dark solid line: $y = x$ line; dark dashed line: $+100\%/-50\%$ range; $V_{ma} = 100V$.

and $\sigma_g = 1.7$, and fractal dimension $d_f = 2.3$. The three other PM mass estimation methods were based on the calibration coefficients provided by *Ntzichristos et al. (2013b)*, and the coefficients derived from soot generator experiments for total particle matter ($PPS_{LR}(TPM)$) (i.e. including volatile matter, sampled from *burner-out*) and non-volatile particles only ($PPS_{LR}(Soot)$) sampled from *VPR-out* location. Data in Figure 5.17 clearly shows a linear correlation between the PPS response models and the TEOM measurement. However, the TEOM data appears to be shifted by 10mg/bhp-hr indicated by the dotted line (i.e. shifted $y = x$ line). This appears to be a systematic offset for which no explanation could be given other than a possible zero-offset of the TEOM instrument. The small insert graph shows a magnification of the downstream DPF data, indicating the successive increase in DPF filtration efficiency as a function of *soot cake* layer build-up. This is described by the labels *FTP #1* through *FTP #3* which refer to consecutive test runs performed on a *brand-new* DPF (see discussion in Section 5.1.2). The R_{PPS} and ($PPS_{LR}(Soot)$) response models show the closest correlation over the entire range of PM mass concentrations. For engine-out data, the linear regression model based on non-volatile particles only (i.e. *VPR-out* calibration) indicates the closest correlation with TEOM results within 8.7%. The R_{PPS} ,

Figure 5.17: Correlation of engine work-specific PM mass emissions between four PPS-M1 response models versus TEOM measurements; FTP cycles; *dark solid line*: $y = x$ line; *dark dashed line*: $+100\%/-50\%$ range; $V_{ma} = 100V$.

PPS_{Ntz} , and $PPS_{LR}(TPM)$ response models exhibit a difference of 26.6%, 33.6%, and 43.7% compared to the TEOM, respectively. Interestingly, the TEOM correlates best with the response model calibrated for non-volatile particles when measuring engine-out PM emissions. The TEOM was sampling from the dilution tunnel thus, it is expected that a given amount of adsorbed volatile matter would be present on the particles, therefore, being theoretically closer to TPM like particulate matter. On the other hand, the exact operating conditions of the sampling cell encapsulating the tapered element were not known and if operated at increased temperature there would theoretically be the chance that volatile matter could re-evaporate.

Figure 5.18 depicts a comparison between the raw PPS-M1 signal in [fA/(slpm)] versus the mass concentration of carbonaceous soot as measured by the AVL MSS over the transient FTP cycle and steady-state ESC. The data presented in this figure was collected from a 2004 Mack MP-7 355E engine while sampling from engine-out location. Firstly, it can be noticed that the transient data (i.e. *red triangles*) exhibits increased scatter when compared to the steady-state data (i.e. *blue circles*) even though both instruments were aligned using an auto-correlation function. The MSS shows a higher response in comparison to the PPS-M1, especially for increased soot con-

Figure 5.18: Correlation between PPS-M1 response and AVL MSS over steady-state (*blue circles*) and transient (*red triangle*) engine operation; sampling from engine-out location; *dashed dark lines*: linear regression for PPS vs. MSS; *point-dash lines*: correlations from soot generator exp. 1) VPR-out, 2) burner-out, and literature, 3) *Ntziachristos et al. (2013b)*, 4) pre-DPF, *Beck et al. (2012)*, 5) post-DPF, *Beck et al. (2012)*; $V_{ma} = 100V$.

centrations during steep engine acceleration events and higher engine load operation. Similarly, the steady-state data indicates a slight change in correlation slope (i.e. increase in slope) for PPS response above $\sim 1 \times 10^5 \text{ fA/(slpm)}$. As will be discussed in more detail in Section 5.1.4 this change might be attributed to boundary-layer phenomenon for the Pegasor Particle Sensor sampling setup utilized for this test campaign. The sample was extracted employing the *T-sampling* method without probe ⁷, whereas the MSS sampling probe was a straight probe with 45°-cut reaching to the center of the exhaust transfer pipe. During conditions of increased exhaust flow rates (i.e. high engine loads and speeds) the boundary layer along the exhaust transfer line might grow and thus, effectively reduce the particle movement across the layer into the *T-sampling* probe. This could lead to a slight under-prediction of particle concentration inside the exhaust transfer pipe by the PPS and therefore, possibly explain the observed discrepancy and increased scatter between MSS and PPS.

Furthermore, Figure 5.18 provides individual linear regression models for

⁷probe B as outlined in Figure 3.10.

both transient and steady-state data in comparison with correlation curves obtained from i) soot generator experiments (i.e. lines 1 and 2), ii) PPS calibration coefficients by *Ntziachristos et al.* (2013b) (i.e. line 3), and iii) experimental work by *Beck et al.* (2012) (i.e. lines 4 and 5). The linear regression slopes calculated from both transient and steady-state data are similar with former being $\sim 12.9\%$ lower. The *VPR-out* calibration curve (i.e. only non-volatile particles, line 1) obtained from soot generator experiments compares within 1.24% with the regression line for the transient data. This highlights the fact that the MSS is only sensitive to carbonaceous soot particles and will not account for any adsorbed matter or volatile particles in the exhaust stream. In contrast, the *burner-out* calibration curve (i.e. line 2), which includes non-volatile particles, exhibits a difference of 37.7% compared to the regression slope (β_{1FTP}) for transient data. This is similar to the difference for slope found by *Beck et al.* (2012) for pre-DPF sampling (i.e. line 4) of $\sim 39.2\%$. The PPS calibration coefficient published by *Ntziachristos et al.* (2013b), which was developed based on AVL MSS data, was observed to be within 29.1% of the slope found for the transient data set shown in Figure 5.18.

5.1.4 Description and evaluation of in-use NTE methodology

The NTE area defines an engine operating range underneath the torque-curve and is bound by minimum engine speed, lower torque and power criteria as prescribed in *CFR 40/86/N* (2011) for in-use certification of heavy-duty vehicles in the United States. As introduced in Section 2.3 and discussed in detail in *Kappanna* (2015), *NTE events* are defined on a *time-basis* where the engine has to operate for a minimum duration of 30 continuous seconds within the NTE zone. Furthermore, a number of criteria regarding ambient and engine/after-treatment conditions have to be met in order to be counted as *valid NTE event* (*CFR 40/86/N*, 2011; *Kappanna*, 2015). For the purpose of gaseous emissions quantification the NTE procedure becomes a *fairly* straightforward process as emissions concentrations are measured on a continuous basis (i.e. in time-domain) and can be readily combined with volumetric exhaust flow rate to calculate mass of gaseous emissions constituents for a given *NTE event*. However, for particulate matter estimation this is a more complex process since the sample has to be diluted and temperature controlled to within $47 \pm 5^\circ\text{C}$ before being collected on filter media for subsequent gravimetric analysis (*CFR 40/1065*, 2015). Two main problems arise in conjunction with PM estimation for *NTE events*. Firstly, since particulate matter is accumulated on filter media during sampling pe-

riods (i.e. valid NTE events) and only weighted once, following completion of a test, it is only possible to obtain a single integrated value of PM for the entire duration of data collection rather than *NTE-event-resolved* PM mass rates. Secondly, it is not known *a priori* if an *NTE event* will be valid or not until the duration of 30 continuous seconds, where the engine is operating within the NTE zone, has passed. Because particulate matter is only collected on the filter media while the engine is operating within the NTE zone and otherwise directed through a bypass line, an incomplete *NTE event* (i.e. if the NTE zone is left before the duration of 30sec, for example during a transmission shifting event where engine torque momentarily falls below the lower torque boundary of the NTE zone) would result in PM mass collection on the filter media and thus, an overestimation of particulate matter during *valid NTE events*.

As described in Section 2.4.3 two approaches to this problem have been developed by Horiba® Instruments Inc. and AVL List GmbH. The former instrument manufacturer utilizes a real-time aerosol instrument to apportion fractions of the PM mass collected on the filter media to *valid NTE events* (Wei *et al.*, 2008; Wei and Rooney, 2010; Horiba Instruments Inc., 2010), whereas the latter makes use of the photo-acoustic based micro soot sensor (i.e. AVL MSS) to obtain a real-time carbonaceous soot measurement and subsequently corrects this value for volatile organic and sulfate particles via the total PM mass retained on the filter media sample (Silvis, 2012; AVL List GmbH, 2012).

In a similar fashion a methodology has been developed to quantify in-use particulate matter mass emissions during *NTE events* using the Pegasor Particle Sensor, referred to as *PPS_{NTE-ratio} method* as part of this dissertation. For the purpose of describing and evaluating the proposed method a heavy-duty engine was operated over a 13-mode steady-state cycle⁸ while PM was collected on filter media for each individual mode using a PM sampling system compliant with CFR, title 40, subpart 1065 (CFR 40/1065, 2015). The steady-state cycle was repeated three times to provide data for statistical analysis. Finally, a fourth cycle was run with particulate matter being collected for the duration of all 13 modes on a single, *integrated* filter media sample. For illustration purposes, Figure 5.19 depicts in the upper graph the raw PPS response (R_{PPS}) in [fA/(slpm)] over 13 modes of two consecutive steady-state cycles, whereas the lower graph indicates a *fictitious NTE*

⁸a MY 2004 Mack MP-7 355E engine was utilized for these experiments and operated over the 13-mode ESC.

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Figure 5.19: Description of NTE-zone particulate matter emissions quantification approach based on PPS-M1 response signal (R_{PPS}).

event occurring during mode 2. Since the Pegasor Particle Sensor provides a real-time signal proportional to active particle surface area it is possible to calculate a ratio ($Ratio_{PPS,NTE-event_i}$) between the integrated PPS signal over a given *NTE event* (i.e. mode 2 for the provided example) and the integrated PPS signal over the entire test duration according to Equation 5.2. Based on the assumption that the particulate matter concentration measured in real-time by the PPS directly in the exhaust stream should be proportional to the mass of PM retained on the filter media, Equation 5.3 allows to calculate PM mass of an individual *NTE event* ($m_{TPM,NTE-event_i}$) as the product of the PPS-ratio for a given event i , and the total PM mass collected on the filter media over the entire test cycle ($m_{TPM,total-cycle}$). Integrating the estimated PM masses for each *NTE event* according to Equation 5.4 will give the total NTE PM mass ($m_{TPM,NTE-total}$) that can subsequently be compared to the in-use certification standard for PM.

$$Ratio_{R_{PPS},NTE-event_i} = \frac{\int_{t_{Start,NTE-event_i}}^{t_{End,NTE-event_i}} R_{PPS}(t) dt}{\int_{t_{Start,Test}}^{t_{End,Test}} R_{PPS}(t) dt} \quad (5.2)$$

$$m_{TPM,NTE-event_i} = m_{TPM,total-cycle} \cdot Ratio_{R_{PPS},NTE-event_i} \quad (5.3)$$

$$m_{TPM,NTE-total} = \sum_{i=1}^{i=N_{NTE-event}} m_{TPM,NTE-event_i} \quad (5.4)$$

At this point it is important to highlight a possible shortcoming of such a simplified method that could result in possible under-/overestimation of the PM mass ($m_{TPM,NTE-event_i}$) for individual *NTE events*. As discussed in Section 2.3, TPM as measured per the regulatory standard sampling procedure (CFR 40/1065, 2015) is defined as the total mass retained on a filter media, conditioned at a given temperature and sampled at a specific flow rate and dilution ratio. In addition to soot and ash emissions a significant part of TPM emitted by engines equipped with post-2010 technologies constitutes volatile organic particles that condense on the filter media as well as sulfate and nitrate particles originating from lubrication oil combustion⁹. Even though the Pegasor Particle Sensor is capable of measuring any particle that can carry a charge, including volatile and semi-volatile particles that pass through the sensor in a condensed or adsorbed state, deviations in sample conditioning compared to the TPM sample stream will lead to differences in local PM mass rate quantification. For example, during an NTE event with increased THC emissions, which acts as a surrogate indicator for increased organic fraction, more mass might be temporarily accumulated on the filter media, whereas the PPS will not be able to detect this contribution to TPM as the emissions pass in a gaseous state through the sensor. One possibility at minimizing this discrepancy could be to measure with the PPS directly from the sample stream that enters the filter media holder such that it measures from the same sample environment¹⁰. In the experiments presented herein, the Pegasor Particle Sensor was sampling directly from the exhaust stack with sample and sensor body temperatures maintained at 200°C thus, not measuring any volatile or semi-volatile particles that might possibly condense on the TPM filter media sample.

Figure 5.20 depicts the average particle number concentration and size distribution for each of the 13 modes of the steady-state cycle (i.e. mode 14 is a repeat of mode 1; engine idle). The exhaust sample was extracted at engine-out location and conditioned using a 2-stage PFS system (i.e. see Table 4.1, System 2) before being measured with a TSI EEPSTM. A distinct difference in size distributions between modes with engine load and idle conditions can be observed, with the latter being characterized by a nucleation mode peak with a count mode diameter of $\sim 10\text{nm}$. Nucleation mode particles during

⁹see Figure 2.5 in Section 2.1.2.

¹⁰this is done in the Horiba[®] OBS-TRPM system where the real-time particle instrument extracts a slip stream directly before the filter media holder. However, an elaborate control system is utilized to account for the removal of the slip stream and add it back to the total sample flow in order to maintain sampling proportionality (Wei *et al.*, 2008).

Figure 5.20: Comparison of average particle size distributions for the thirteen ESC modes; measured with TSI EEPSTM and 2-stage PFS system; sampled at engine-out location; concentrations corrected for dilution ratio.

engine idle operation are predominantly composed of ash particles originating from increased lubrication oil consumption and subsequent combustion. During idle conditions with in-cylinder pressure being relatively low, piston rings will seal with reduced efficiency and thus, allow for increased amounts of oil being pumped into the combustion chamber. For modes with engine load applied, count mode diameters are within the accumulation mode and range from ~ 50 - 70 nm with particle peak concentrations to span an order of magnitude between ~ 0.15 to 1.5×10^6 #/cm³. Highest particle concentrations were observed for mode 2, a full load mode at low engine speed.

Figure 5.21 shows a correlation between the modal PM mass emissions calculated using the $PPS_{NTE-ratio}$ approach versus AVL MSS measurements of carbonaceous soot. In addition, total PM mass for each mode was calculated using the four PPS-M1 response models integrated over the respective mode. The variation bars indicate one standard deviation ($1 \cdot \sigma$) over three consecutive 13-mode steady-state cycles. In general the total particulate matter mass calculated by the four PPS response models and estimated via the $PPS_{NTE-ratio}$ approach correlate well with total soot mass emissions measured by the MSS as the data largely falls onto the $y = x$ line (solid dark line)

Figure 5.21: Correlation of modal PM mass emissions between NTE methods calculated based on four PPS-M1 response models and the $PPS_{NTE-ratio}$ versus AVL MSS measurements; total mass calculated over individual ESC modes; *dark solid line*: $y = x$ line; *dark dashed line*: $+100\%/-50\%$ range; variation bars indicate one standard deviation ($1 \cdot \sigma$); $V_{ma} = 100V$.

or within an area of $+100/-50\%$ of it (*dashed lines*). Based on the average particle size distributions shown in Figure 5.20 a count mode diameter of 60nm and a geometric standard deviation (σ_g) of 1.7 was assumed for the PPS response model R_{PPS} .

It can be observed from Figure 5.21 that both the $PPS_{NTE-ratio}$ method and the PPS response model based on coefficients derived from soot generator experiments for non-volatile particles only ($PPS_{LR}(Soot)$) show closest correlation with the MSS derived mass. The slopes (β_1) estimated by a linear least-squares regression, with the origin forced to zero, are 1.0090 ($\Delta_{vs, MSS} = -0.9\%$) and 0.9293 ($\Delta_{vs, MSS} = 7.1\%$) for the $PPS_{LR}(Soot)$ and $PPS_{NTE-ratio}$ method, respectively. The two methods were found to overestimate the PM mass emissions for modes with lower mass rates and in contrast, slightly underestimate it for modes with larger PM mass rates such as ESC mode 10 for example (i.e 1780rpm and full load).

On the other hand, the modal PM masses calculated based on the PPS response model (R_{PPS}), the calibration coefficients by Ntziachristos *et al.* (2013b),

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Table 5.5: Comparison of modal PM mass emissions in [mg] between NTE methods calculated based on four PPS-M1 response models and the $PPS_{NTE-ratio}$ versus AVL MSS measurements; standard deviations given as $1 \cdot \sigma$ for 3 repeats; numbers in brackets indicate under (*negative*) and overestimation (*positive*) vs. MSS in [%]; bold numbers indicate differences exceeding +100%/−50% range.

AVL MSS [mg]	R_{PPS} [mg]	PPS_{Ntz} [mg]	$PPS_{LR}(TPM)$ [mg]	$PPS_{LR}(Soot)$ [mg]	$PPS_{NTE-ratio}$ [mg]
3.7±0.1	3.5±0.3 (-3.8)	3.8±0.3 (4.8)	2.9±0.3 (-27.0)	5.1±0.5 (27.6)	5.6±0.7 (34.7)
340.3±4.5	230.8±7.5 (-47.4)	251.6±8.2 (-35.3)	217.7±7.2 (-56.3)	348.2±11.4 (2.3)	372.5±40.9 (8.7)
85.2±4.5	80.1±5.4 (-6.4)	87.3±5.9 (2.4)	74.1±5.2 (-15.0)	120.0±8.2 (29.0)	129.5±13.2 (34.2)
97.1±3.3	76.2±5.0 (-27.4)	83.0±5.5 (-16.9)	69.8±4.8 (-39.1)	113.7±7.6 (14.6)	124.2±13.5 (21.8)
93.2±2.3	93.2±4.6 (0.1)	101.6±5.0 (8.3)	87.3±4.4 (-6.7)	140.2±7.0 (33.6)	150.5±16.8 (38.1)
185.3±7.7	140.1±7.3 (-32.2)	152.7±8.0 (-21.3)	131.5±7.0 (-40.9)	211.0±11.1 (12.2)	227.8±22.2 (18.7)
28.8±0.8	40.9±2.9 (29.6)	44.6±3.2 (35.4)	37.9±2.8 (24.0)	61.3±4.5 (53.0)	65.7±8.7 (56.1)
188.8±6.1	130.8±5.0 (-44.4)	142.5±5.5 (-32.5)	121.4±4.8 (-55.5)	196.1±7.6 (3.7)	215.2±19.8 (12.3)
27.9±1.1	44.4±4.4 (37.2)	48.4±4.8 (42.4)	40.8±4.2 (31.7)	66.3±6.6 (58.0)	72.2±10.3 (61.4)
583.4±17.6	317.3±13.2 (-83.9)	345.9±14.3 (-68.7)	299.6±12.6 (-94.7)	478.8±19.9 (-21.8)	525.5±51.7 (-11.0)
64.2±1.0	94.6±5.0 (32.1)	103.1±5.4 (37.7)	88.4±4.8 (27.3)	142.2±7.6 (54.8)	154.0±14.9 (58.3)
359.9±16.0	228.5±11.3 (-57.5)	249.1±12.4 (-44.5)	215.1±10.8 (-67.3)	344.5±17.2 (-4.5)	374.5±34.2 (3.9)
210.7±13.7	169.2±7.7 (-24.5)	184.5±8.4 (-14.2)	159.0±7.4 (-32.5)	254.9±11.7 (17.3)	276.6±14.7 (23.8)

and the coefficients derived from soot generator experiments for total particle matter ($PPS_{LR}(TPM)$) (i.e. including volatile matter) were found to generally underestimate the soot emissions measured by the MSS on average by 51.1%, exhibiting linear regression slopes on the order of 1.52, 1.39, and 1.62, respectively. Since both instruments, PPS and MSS, were measuring from the same location in the exhaust transfer line and the PPS sample probe and sensor body were heated to constant $\sim 200^\circ\text{C}$, thus, measuring in an elevated temperature environment that reduces the possibility of adsorption and condensation phenomena of volatile matter, a close correlation between the PPS response model calibrated for non-volatile particles ($PPS_{LR}(Soot)$)

and the MSS can be expected. Table 5.5 summarizes the results for each of the 13 modes for the different NTE PM mass estimation methods discussed. The numbers in brackets indicate the percent-deviation from the MSS measurement, with negative numbers indicating underestimation and positive numbers overestimation of modal PM mass by the individual PPS methods.

Interestingly, a larger deviation was observed for all PPS response models and the $PPS_{NTE-ratio}$ method for high exhaust flow rate conditions such as experienced in mode 10 (i.e. data with highest PM mass emissions in Figure 5.21). It has to be remembered that for this measurement campaign a *T-sampling* probe mounted flush with the exhaust transfer line (i.e. probe B in Figure 3.10) was utilized to extract an exhaust sample into the Pegasor Particle Sensor. As discussed in the previous section, possible boundary layer phenomenon during high exhaust flow rate conditions might have negatively affected particle movement across the layer into the *T-sampling* probe, thus, leading to an under-prediction of particle concentration inside the exhaust transfer line.

Similarly to the correlation between PPS NTE methods and AVL MSS, Figure 5.22 depicts a correlation between the modal PM mass emissions calculated using the $PPS_{NTE-ratio}$ approach and four PPS response models versus the total particulate matter sampled onto filter media according to CFR, title 40, subpart 1065 (CFR 40/1065, 2015). Compared to Figure 5.21 it can be readily seen that the total PM mass estimated with the gravimetric filter method is higher compared to the PPS methods as well as the AVL MSS measurements for all engine modes evaluated. This difference can be attributed to the fact that the filter media retains not only solid soot and ash particles, but also contains condensed volatile matter as discussed earlier in this section. Furthermore, both PPS and MSS were sampling directly from the exhaust transfer line, whereas TPM was sampled through the CVS and secondary dilution system leading to differences in sample conditioning and treatment. In general the total PM mass calculated by the four PPS response models and estimated via the $PPS_{NTE-ratio}$ were found to largely fall within the $+100\%/ -50\%$ range around the $y = x$ line.

Both the $PPS_{NTE-ratio}$ method and the PPS response model based on coefficients derived from soot generator experiments for non-volatile particles only ($PPS_{LR}(Soot)$) were observed to correlate closest with TPM mass emissions. The slopes (β_1) estimated by a linear least-squares regression, with the origin forced to zero, are 1.2612 ($\Delta_{vs.TPM} = -26.1\%$) and 1.1620 ($\Delta_{vs.TPM} = -16.2\%$) for the $PPS_{LR}(Soot)$ and $PPS_{NTE-ratio}$ method, re-

Figure 5.22: Correlation of modal PM mass emissions between NTE methods calculated based on four PPS-M1 response models and the $PPS_{NTE-ratio}$ versus gravimetric evaluated total particulate matter sampled onto filter media (i.e. CFR 40/1065 (2015)); total mass calculated over individual ESC modes; dark solid line: $y = x$ line; dark dashed line: $+100\%/-50\%$ range; variation bars indicate one standard deviation ($1 \cdot \sigma$); $V_{ma} = 100V$.

spectively. In contrast, the linear regression slopes obtained for the PPS response model (R_{PPS}), the calibration coefficients by Ntziachristos *et al.* (2013b), and the coefficients derived from soot generator experiments for total particle matter ($PPS_{LR}(TPM)$) are 1.90, 1.74, and 2.02, respectively. The $PPS_{LR}(TPM)$ calibration compared worst to TPM, with the calculated modal PM masses lying on or exceeding the $+100\%$ deviation range from an ideal $y = x$ correlation. Table 5.6 summarizes the modal PM masses for the five evaluated NTE methods based on PPS measurements in comparison to gravimetrically quantified total particulate matter collected on filter media following regulatory sampling procedures.

A possible method to improve the correlation between the PPS-based PM mass estimation and TPM as defined by the regulatory standard, is to introduce an estimation of the SOF as well as sulfates and water content adsorbed onto the filter media. Work presented by Clerc and Johnson (1982), and Silvis (2012) provide a discussion of prediction models for adsorption of soluble organic matter as a function of hydrocarbon concentrations in the exhaust

5.1. Controlled Environment Studies - Engine Dynamometer

Table 5.6: Comparison of modal PM mass emissions in [mg] between NTE methods calculated based on four PPS-M1 response models and the $PPS_{NTE-ratio}$ versus gravimetric evaluated total particulate matter (TPM) sampled onto filter media (i.e. *CFR 40/1065* (2015)); standard deviations given as $1 \cdot \sigma$ for 3 repeats; numbers in brackets indicate under (*negative*) and overestimation (*positive*) vs. TPM in [%]; bold numbers indicate differences exceeding +100%/−50% range.

TPM [mg]	R_{PPS} [mg]	PPS_{Ntz} [mg]	$PPS_{LR}(TPM)$ [mg]	$PPS_{LR}(Soot)$ [mg]	$PPS_{NTE-ratio}$ [mg]
13.4±7.9	3.5±0.3 (-280.0)	3.8±0.3 (-248.7)	2.9±0.3 (-365.0)	5.1±0.5 (-165.0)	5.6±0.7 (-139.1)
398.4±10.1	230.8±7.5 (-72.6)	251.6±8.2 (-58.3)	217.7±7.2 (-83.0)	348.2±11.4 (-14.4)	372.5±40.9 (-6.9)
117.0±9.6	80.1±5.4 (-46.1)	87.3±5.9 (-34.0)	74.1±5.2 (-57.8)	120.0±8.2 (2.5)	129.5±13.2 (9.6)
121.3±13.8	76.2±5.0 (-59.1)	83.0±5.5 (-46.0)	69.8±4.8 (-73.7)	113.7±7.6 (-6.6)	124.2±13.5 (2.3)
105.3±28.3	93.2±4.6 (-12.9)	101.6±5.0 (-3.6)	87.3±4.4 (-20.6)	140.2±7.0 (24.9)	150.5±16.8 (30.1)
199.7±12.8	140.1±7.3 (-42.5)	152.7±8.0 (-30.8)	131.5±7.0 (-51.8)	211.0±11.1 (5.3)	227.8±22.2 (12.3)
32.7±6.1	40.9±2.9 (20.1)	44.6±3.2 (26.7)	37.9±2.8 (13.8)	61.3±4.5 (46.7)	65.7±8.7 (50.2)
249.7±3.2	130.8±5.0 (-91.0)	142.5±5.5 (-75.2)	121.4±4.8 (-105.7)	196.1±7.6 (-27.3)	215.2±19.8 (-16.0)
32.7±8.6	44.4±4.4 (26.4)	48.4±4.8 (32.5)	40.8±4.2 (19.9)	66.3±6.6 (50.7)	72.2±10.3 (54.7)
751.0±13.8	317.3±13.2 (-136.7)	345.9±14.3 (-117.2)	299.6±12.6 (-150.7)	478.8±19.9 (-56.8)	525.5±51.7 (-42.9)
87.2±7.9	94.6±5.0 (7.8)	103.1±5.4 (15.4)	88.4±4.8 (1.3)	142.2±7.6 (38.7)	154.0±14.9 (43.4)
448.5±40.3	228.5±11.3 (-96.3)	249.1±12.4 (-80.1)	215.1±10.8 (-108.5)	344.5±17.2 (-30.2)	374.5±34.2 (-19.8)
275.6±3.5	169.2±7.7 (-62.9)	184.5±8.4 (-49.4)	159.0±7.4 (-73.3)	254.9±11.7 (-8.1)	276.6±14.7 (0.4)

stream and respective saturation curves dependent on exhaust gas temperatures. *Silvis* (2012) further describes an estimator for sulfate contribution to TPM using SO_2 to SO_3 conversion efficiencies over oxidation catalysts as a function of exhaust gas temperature. However, introduction of such corrective model parameters to the herein presented PPS-based methods is beyond the scope of this dissertation document, and will be discussed in more detail in subsequent publications by this author.

5.2 Real-World Studies - On-Road Experiments

On-road experiments were conducted in order to expose the *Pegasor Particle Sensor* to exhaust emissions representative of real-world vehicle operation. Furthermore, during on-road operation the sensors durability and possible impact of to the harsh environment and vibrations can be quantified. For the purpose of in-use compliance testing the sensor has to be easily installable and in many applications will have to be positioned outside the protective cover of the vehicle cabin. This will expose the sensor to changes in humidity and temperature. However, one of the primary challenges for on-road application of the PPS is the availability of compressed, dry and HEPA filtered air for dilution and operation of the ejector pump. The daunting part involves drying the compressed air, especially on days with increased ambient air humidity. During compression the water vapor in the dilution air condenses and eventually causes the corona charger to fail as water droplets accumulate inside the charger. During the course of this study a cascade of up to three coalescing filters have been used.

Experiments were conducted as part of two externally and one internally funded studies on light-, medium- and heavy-duty vehicles. Two light-duty vehicles were equipped with the *Pegasor Particle Sensor* and operated over diverse driving routes in California as part of an ICCT funded study aimed at quantifying off-cycle NO_x emissions in early 2013 (*Thompson et al.*, 2014). Both vehicles were equipped with Diesel particulate filters and sampling was performed downstream the filter. Experiments on a medium-duty flatbed truck were performed as part of an internal study (*Merritt*, 2011), while the vehicle was driven over local (Morgantown, WV) interstate and urban/city test routes that were originally defined during the CAFEE's MEMS study (*Shade*, 2006). Finally, the PPS was also installed on a heavy-duty Class-8 tractor as part of a CARB and South Coast AQMD funded study in Fall 2011. The vehicle was predominantly operated on interstate routes over 2450 miles between Morgantown, WV and Riverside, CA (*Kappanna et al.*, 2013).

For the purpose of this document and for brevity, only the light-duty results will be presented and discussed in detail hereinafter. For more information and results regarding the medium- and heavy-duty application of the PPS, the reader is directed to consult companion documents and published papers from those studies (*Merritt*, 2011; *Besch et al.*, 2012; *Kappanna et al.*, 2013).

5.2.1 Application of PPS on light-duty vehicles

This section will present the application of the *Pegasor Particle Sensor* to on-road quantification of particulate matter emissions from two DPF equipped light-duty vehicles, operated over four distinct and one extended driving route. Details regarding the test vehicle, the experimental setup and specifics of the PPS operation, as well as the route characteristics are given in Section 4.4.1. The data will be discussed based on the three PPS response models mentioned previously, namely, R_{PPS} , PPS_{Ntz} , and R_{LR} . A log-normal particle size distribution with $CMD = 40nm$ and $\sigma_g = 1.7$ was assumed for the R_{PPS} response model. All experiments discussed in this section were performed with the mobility analyzer voltage set to constant $V_{ma} = 400V$.

Figure 5.23 depicts a comparison between the calculated average distance-specific total particle number emissions in $[\#/km]$ for the three different response models over the four pre-defined test routes. Each data point represents the average of two individual test repetitions. For reference purposes the European Euro 5/6 particle number emissions limit of $6 \times 10^{11} \#/km$ is indicated by the *green dashed line*. It has to be emphasized again in this context that the PPS sampling method is strictly speaking not equivalent to the PMP protocol which is the prescribed method for regulatory particle number quantification. However, as discussed in more detail in Section 3.1.1 the PPS measurement is comparable to the PMP approach for the case of a heated sensor and mobility analyzer voltage settings such that below 23nm particles are more likely to be trapped inside the sensor and will not add to the sensor response (Tikkanen et al., 2013; Amanatidis et al., 2014; Riccobono et al., 2014b).

First of all it can be noticed from Figure 5.23 that increased variability in particle number emissions, indicated by the *red* variation intervals, was observed for test routes that included DPF regeneration events during one of the route repetitions. The upper and lower end of the variation bar indicate minimum and maximum average emissions for the respective data set. For tests which did not include a DPF regeneration event, particle number emissions remain below $\sim 10^{11} \#/km$, whereas tests with DPF regeneration were observed to exceed the Euro 5/6 limit for the given route. It is important to remember that the PN emissions limit is applicable to vehicles operated over the NEDC chassis dynamometer cycle in contrast to the data collected over diverse driving patterns presented herein. DPF regeneration events lead to a one or two order of magnitude increase in particle number emissions when compared to test runs without DPF regeneration as seen for routes 1, 3, and

Figure 5.23: Comparison of three PPS response models to calculate distance-specific particle number emissions; data shown for two vehicles operated over four routes; *green dashed line*: Euro 5/6 particle number limit for LDV (6.0×10^{11}); repeat test variation intervals are presented as minimum/maximum test value; *R*: test with DPF regeneration event; $V_{ma} = 400V$; R_{PPS} input: $CMD = 40nm$, $\sigma_g = 1.7$.

4 as well as routes 2, and 3 for vehicles A and B, respectively. Route 3 for vehicle B exhibited DPF regeneration events during both repeats thus, leading to the observed low variability between repeated tests.

Comparing the different PPS response models shows a constant discrepancy between the R_{PPS} and PPS_{Ntz} method of 29% with the latter estimating particle numbers systematically lower. As mentioned earlier, the R_{PPS} response model assumed a default particle size distribution with $CMD = 40nm$, whereas *Ntziachristos et al. (2013b)* developed the calibration coefficients for nominal $CMD = 50nm$ particles. With the sensor response being proportional to $D_p^{1.09}$, based on the soot generator experiments, a reduction in assumed CMD would translate into an increase in estimated particle concentration (see Equation 3.20). Regarding the linear regression based response model (PPS_{LR}) with constant offset β_0 the same conclusions as already discussed for engine dynamometer testing downstream a particulate filter can be drawn. For tests with DPF regeneration events and thus, increased particle number emissions the PPS_{LR} method shows agreement with the two

5.2. Real-World Studies - On-Road Experiments

Table 5.7: Distance and time based DPF regeneration frequencies and durations for test vehicle B during extended on-road operation; data calculated based on the PPS-M1 response signal.

		Vehicle A			Vehicle B		
		$\mu_{N_{tot}}$	C_{min} [#/km]	C_{max}	$\mu_{m_{tot}}$	-1σ [mg/km]	$+1\sigma$
Rte 1	R_{PPS}	3.26×10^{11}	6.28×10^{10}	5.90×10^{11}	4.21×10^{10}	3.59×10^{10}	4.82×10^{10}
	PPS_{Ntz}	2.3×10^{11}	4.43×10^{10}	4.17×10^{11}	2.97×10^{10}	2.54×10^{10}	3.41×10^{10}
	PPS_{LR}	2.16×10^{12}	1.78×10^{12}	2.55×10^{12}	2.09×10^{12}	1.94×10^{12}	2.24×10^{12}
Rte 2	R_{PPS}	9.71×10^{10}	4.07×10^{10}	1.53×10^{11}	4.00×10^{12}	1.28×10^{11}	7.88×10^{12}
	PPS_{Ntz}	6.86×10^{10}	2.88×10^{10}	1.08×10^{11}	2.83×10^{12}	9.04×10^{10}	5.57×10^{12}
	PPS_{LR}	3.42×10^{12}	3.36×10^{12}	3.48×10^{12}	5.65×10^{12}	3.69×10^{12}	7.61×10^{12}
Rte 3	R_{PPS}	1.85×10^{13}	8.82×10^{10}	3.69×10^{13}	1.62×10^{12}	1.08×10^{12}	2.15×10^{12}
	PPS_{Ntz}	1.31×10^{13}	6.23×10^{10}	2.61×10^{13}	1.14×10^{12}	7.65×10^{11}	1.52×10^{12}
	PPS_{LR}	1.22×10^{13}	2.40×10^{12}	2.21×10^{13}	3.50×10^{12}	3.18×10^{12}	3.81×10^{12}
Rte 4	R_{PPS}	8.86×10^{11}	1.55×10^{11}	1.62×10^{12}	3.47×10^{10}	3.14×10^{10}	3.81×10^{10}
	PPS_{Ntz}	6.26×10^{11}	1.09×10^{11}	1.14×10^{12}	2.45×10^{10}	2.22×10^{10}	2.69×10^{10}
	PPS_{LR}	3.63×10^{12}	3.39×10^{12}	3.86×10^{12}	3.65×10^{12}	3.63×10^{12}	3.66×10^{12}

other response models (i.e. within $\sim 34\%$ for route 3 and vehicle A), however, for all the other tests it vastly over-estimated the PN emissions. Specifically, the large β_0 makes it impossible for this method to estimate particle number concentrations below a level equivalent to β_0 (i.e. $\beta_0 = 1.63 \times 10^6$). This highlights the need for either a linear regression correlation that is forced through the origin or the use of specific calibrations for up- and downstream DPF measurements. The former has the advantage of providing a meaningful response over the entire measurement range, however, at the cost of reduced local accuracy, whereas the use of specific calibrations would aid in improving accuracy for a given concentration range. Table 5.7 provides a detailed overview of the specific values presented in Figure 5.23.

Figure 5.24 depicts the average distance-specific particulate matter mass emissions for the different test routes and vehicles. In particular, four different sensor response models to estimate particulate matter mass are compared. The R_{PPS} model is based on total particle number estimation as calculated for Figure 5.23 in conjunction with Equation 3.13 and an assumed fractal dimension of $d_f = 2.3$ as suggested by *Harris and Maricq* (2001) for actual engine soot particles. The other three methods were based on calibration coefficients by *Ntziachristos et al.* (2013b) (PPS_{Ntz}) and as established during soot generator experiments for non-volatile particles ($PPS_{LR, Soot}$) and

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Figure 5.24: Comparison of four PPS response models to calculate distance-specific particulate matter mass emissions; data shown for two vehicles operated over four routes; *green dashed line*: U.S. EPA Tier2-Bin5 standard for LDV (10mg/mile); repeat test variation intervals are presented as minimum/maximum test value; *R*: test with DPF regeneration event; $V_{ma} = 400V$; R_{PPS} input: $CMD = 40nm$, $\sigma_g = 1.7$.

total particulate matter ($PPS_{LR,TPM}$), with the latter including volatile matter. As reference, the U.S. EPA Tier2-Bin5 standard of 10mg/mile is plotted in Figure 5.24 (i.e. *green dashed line*). The variation bars indicate ± 1 standard deviations ($\pm 1\sigma$) computed over two consecutive repetitions of a given test route.

Conversely to total particle number emissions, the PPS_{Ntz} method was observed to estimate more particulate matter mass emissions as the R_{PPS} method, by a constant factor of $\sim 70\%$. The linear regression model which was calibrated based on soot generator *burner-out* particles, thus, including adsorbed volatile matter, was seen to best correlate with the R_{PPS} response model within 18% to 50% depending on test route. The non-volatile particle based regression model on the other hand significantly over-predicted PM mass emissions in comparison to the three other response models.

Figure 5.25 through 5.32 show comparisons of particle number concentrations measured in the exhaust stream between two consecutive test runs for each route and test vehicle, plotted against driving distance. It has to be

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noted that for the purpose of this comparison the continuous particle number concentrations were estimated using the PPS_{Ntz} calibration coefficients. The data reflect particle concentrations in the exhaust stream per unit volume (i.e. cm^3) and not total number count of particles released from the engine which would be obtained by multiplying the average particle number concentration into total exhaust flow. Exhaust gas temperatures, as measured at the exhaust sample extraction point (i.e. at outlet of exhaust tip), were plotted along with particle number concentrations to aid in identifying possible DPF regeneration events. An increase in exhaust gas temperature along with an observed increase in PPS response is indicative of an on-going DPF regeneration event.

To the right side of each continuous particle number concentration and exhaust temperature graph is a bar chart providing total particle number emissions in $[\#/ \text{km}]$ for each individual test and the three different PPS response models.

Figure 5.25 and 5.26 depict particle number emissions concentrations during highway driving (i.e. route 1) for vehicles A and B, respectively. Vehicle A can be noticed to have experienced a moderate DPF regeneration event between 15 and 25km into the test route leading to an order of magnitude increase in total particle number emissions for test 2 as compared to test 1. However, the observed regeneration event did not cause particle number emissions to exceed the Euro 5/6 PN standard. No DPF regeneration event was seen for vehicle B during highway operation over route 1.

Figure 5.25: Comparison of particle number concentrations between two tests of Route 1 for Vehicle A, DPF regeneration event during test 2; $V_{ma} = 400\text{V}$.

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Figure 5.26: Comparison of particle number concentrations between two tests of Route 1 for Vehicle B, no DPF regeneration event observed; $V_{ma} = 400V$.

Figure 5.27 and 5.28 show particle number concentrations during route 2 for vehicles A and B, respectively. Contrary to route 1, during route 2 driving vehicle B exhibits a DPF regeneration event during the second half of the first test run as recognizable from either the significantly increased particle number concentrations (>2 orders of magnitude) or the increase in exhaust gas temperature by a factor of 2 when compared to test run 2 which lacks a regeneration event. Furthermore, the DPF regeneration event resulted in total particle number emissions to exceed the applicable PN standard by an

Figure 5.27: Comparison of particle number concentrations between two tests of Route 2 for Vehicle A, no DPF regeneration event observed; $V_{ma} = 400V$.

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Figure 5.28: Comparison of particle number concentrations between two tests of Route 2 for Vehicle B, DPF regeneration event during test 1; $V_{ma} = 400V$.

Figure 5.29: Comparison of particle number concentrations between two tests of Route 3 for Vehicle A, DPF regeneration event during test 1; $V_{ma} = 400V$.

order of magnitude (i.e. $5.51 \times 10^{12} \#/\text{km}$ vs. $6.0 \times 10^{11} \#/\text{km}$).

Figure 5.29 and 5.30 depict particle number concentrations during route 3 for vehicles A and B, respectively, with DPF regenerations noticed for both vehicles. Vehicle A exhibited a regeneration event during the uphill portion of the first test run (at 18 to 27km) with the PN standard being exceeded by two orders of magnitude ($2.61 \times 10^{13} \#/\text{km}$), whereas Vehicle B showed repeatable signs of moderate regeneration events at the same location for both test runs. Also, total particle number emissions for vehicle B are exceeding

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Figure 5.30: Comparison of particle number concentrations between two tests of Route 3 for Vehicle B, DPF regeneration event during both tests; $V_{ma} = 400V$.

Figure 5.31: Comparison of particle number concentrations between two tests of Route 4 for Vehicle A, DPF regeneration event during test 2; $V_{ma} = 400V$.

the Euro 5/6 PN standard during both consecutive test runs of route 3.

Finally, Figure 5.31 and 5.32 show particle number concentrations during route 4 for vehicles A and B, respectively. While vehicle B does not experience any DPF regeneration event with particle number emissions remaining well below the regulatory standard, vehicle A exhibits the onset of a regeneration event towards the end of the second repetition leading to total particle number emissions one order of magnitude greater than observed for the test run without event.

5.2. Real-World Studies - On-Road Experiments

Figure 5.32: Comparison of particle number concentrations between two tests of Route 4 for Vehicle B, no DPF regeneration event observed; $V_{ma} = 400V$.

Additionally, it is interesting to notice that while there was no DPF regeneration event occurring exhaust gas temperatures for both vehicles show a strong similarity. This can be explained by the fact that both vehicles A and B were equipped with an identical engine that most likely was programmed with same or at least nearly similar base calibration parameters. Also, the actual vehicle test weight only differed by 29kg between vehicle A and B leading to similar load conditions for both engines during testing.

Figure 5.33 depicts particle number concentrations (*blue line*) estimated by the PPS_{Ntz} response model during an extended driving route of nearly 4000km in distance. The secondary y-axis shows exhaust gas temperatures as measured at SCR outlet location by an on-board temperature sensor, and acquired via ECU CAN interrogation. Four distinct DPF regeneration events can be identified in Figure 5.33 based on dominant particle number concentration spikes that increase by up to four orders of magnitude to $1.4 \times 10^8 \text{ #/cm}^3$ over the typical concentration level of $2 \times 10^4 \text{ #/cm}^3$. These events of drastic increase in particle number concentrations are accompanied, as expected, by excursions in exhaust gas temperatures as thermal conditions of after-treatment and exhaust stream are increased in order to initiate soot oxidation on the DPF substrate (i.e. initiate regeneration). Exhaust gas temperatures were observed to increase from typical levels throughout the route of $\sim 320^\circ\text{C}$ to $\sim 560^\circ\text{C}$ during the DPF regeneration events.

Even though four distinct exhaust gas temperature excursions can be noticed from Figure 5.33, thus indicating four DPF regeneration events throughout

5.2. Real-World Studies - On-Road Experiments

Figure 5.33: Particle number concentrations estimate with PPS_{Ntz} response model and exhaust gas temperature at SCR outlet location of the test vehicle during extended route driving; spikes in particle number concentrations are indicative of DPF regeneration events; $V_{ma} = 400V$.

the entire route, only three particulate number concentration spikes are observed. This is due to the fact that the *Pegasor Particle Sensor* was not operational after $\sim 2600\text{km}$ as the electrical air compressor providing pressurized air to the sensor had failed. However, even though lacking actual particle measurements, but solely based on the preceding data it can be concluded with the necessary confidence that the temperature excursion around 3023km is indicative of a DPF regeneration event.

It is interesting to notice from Figure 5.33 that the observed DPF regeneration events were nearly equally spaced both on a spatial (i.e. distance traveled) and temporal (i.e. duration between event) basis as can be seen from Table 5.8. On average the vehicle traveled approximately $756 \pm 29\text{km}$ ($\pm 1\sigma$) between individual regeneration events which was observed to correspond to $\sim 7.07 \pm 0.06\text{hours}$ ($\pm 1\sigma$, not including third event) on a temporal basis. Even though the distance traveled between events 2 and 3 is of similar length than for other events, the time required was observed to be $\sim 17\%$ longer (7.07hours vs. 8.3hours). A possible explanation for this difference is that the route between regeneration events 2 and 3 included low vehicle speed urban/suburban driving in and around Seattle, WA, leading to increased travel time to accumulate $\sim 756\text{km}$. Overall, these results ultimately led to conclude that DPF regeneration intervals are predominantly distance based which agrees with descriptions given for after-treatment control strate-

5.2. Real-World Studies - On-Road Experiments

Table 5.8: Distance and time based DPF regeneration frequencies and durations for test vehicle B during extended on-road operation; data calculated based on the PPS-M1 response signal.

Event [#]	Dist. to Event [km]	$f_{regen,dist.}$ [km]	Time to Event [hr]	$f_{regen,time}$ [hr]	t_{event} [min]
1	717	717	7.0	7.0	22.4
2	1,503	786	14.1	7.1	15.2
3	2,269	766	22.3	8.3	7.5
4	3,023	754	29.5	7.1	15.8

gies for vehicle A by *Hadler et al.* (2008)¹¹. This is most likely similar to vehicle B as well as the same engine and DPF configurations are used in both vehicles. Furthermore, the observed average duration of a DPF regeneration event was $15 \pm 6 \text{ min}$ ($\pm 1\sigma$) as seen from Table 5.8, thereby in agreement with system descriptions provided by *Hadler et al.* (2008).

¹¹see from Figure 12 in (*Hadler et al.*, 2008).

Conclusions and Recommendations

6.1 Conclusions

Measuring and accurately quantifying particulate matter emissions from combustion engine equipped vehicles in real-time while being operated on the road is of prime importance, not only to guarantee compliance with emissions regulations but also to monitor after-treatment filtration efficiency as part of the OBD structure. Furthermore, real-time information of soot mass rates entering the particulate filter could aid in more closely predicting the filling status of the filter and thus, in conjunction with physical models be used in a feedback-loop to control particulate filter regeneration strategies.

A literature survey was conducted as initial part of this study to identify currently available particle sensor technologies. Based on that, diffusion-charging type sensors appeared promising as they have been previously utilized to measure combustion derived particles in laboratory settings (*Ntziachristos et al.*, 2004) and have shown to exhibit a response proportional to active particle surface area (*Lehtimäki*, 1983; *Shin et al.*, 2007; *Wilson et al.*, 2007; *Ntziachristos et al.*, 2007). Furthermore, this technology allows for real-time measurements which makes it more attractive from an emissions quantification and after-treatment control standpoint. Sensor technologies based on periodic accumulation and regeneration of collected particles such as resistive and capacitive type sensors provide for an integrated measurement as pass/fail criteria for a particulate filter in an OBD structure. However, research by *Hopka* (2014) emphasized on the long response times and dead bands for these sensors which were reported to exceed the necessary time interval for OBD monitor demonstration over the certification FTP-75 cycle.

In light of that, this study selected a diffusion-charging type sensor to assess the possibility of quantifying particle emissions in real-time during on-road measurements.

A prototype diffusion-charging type sensor from Pegasor (Oy) Ltd. was presented in this study and its operating principle was discussed in detail. A simple ejector pump model was presented based on dilution air pressure as sole input along with a set of calibration coefficients that have to be evaluated for a given sensor during off-line flow calibrations. It was found that a deviation of ± 2 psi from the default dilution air pressure setting of 22psig will result on average in a $\sim 3.3\%$ change in sample flow rate. This study further discussed possible particle size specific sample losses associated with exhaust sample extraction and transport to the sensor. A ~ 1 m long heated sample line maintained at 200°C was utilized to stabilize sample gas temperatures prior to inlet to the sensor as was suggested by *Ntziachristos et al.* (2013b). Maintaining the sample line wall and sensor body at 200°C further helped minimizing possible thermophoretic particle losses by negating temperature gradients. Based on theoretical calculations, over- and underestimation of particle concentrations due to anisokinetic and anisoaxial sampling were found to be below 2% for 200nm diameter particles which is consistent with results reported by *Ntziachristos and Samaras* (2002); *Giechaskiel et al.* (2012a). Possible boundary layer effects when using *T-type* wall sampling (i.e. without probe protruding inside exhaust pipe) was not investigated as part of this study, could however, explain some of the differences observed during this study when sampling during high speed, high load engine operating modes (i.e. high exhaust flow rates.)

Soot generator experiments were conducted with an AVL particle generator to study the particle size specific response of the diffusion-charging type sensor. The *Pegasor Particle Sensor* was observed to exhibit a response proportional to particle size on the order of $D_p^{1.09 \pm 0.11}$, which is consistent with typical values found in published literature as listed in Table 3.10. Two different response models were presented, whereof one was based on linear regression between the sensor response and an AVL MSS and TSI SMPSTM for particle mass and number concentration calibrations, respectively. The second response model was based on the assumption of a given *log-normal* particle size distribution, characterized by the count median diameter (CMD) and geometric standard deviation (σ_g) as shown again in Equation 6.1 to calculate the total particle number concentration. The assumption of a constant particle size distribution for a given engine technology is based on work by *Harris and Maricq* (2001) who suggested the existence of respective *signature*

size distributions. Results from the study presented herein suggest to use the second response model as it provides a means of quantifying particle concentrations across the entire dynamic range of the sensor. Conversely, the linear regression models are only locally valid if used with a constant offset, however, will still provide good results when specifically used within the calibrated sensor response range. The latter shows the need for individual pre- and post-particle filter calibrations when using the linear regression model approach. Throughout the study a value of 1.7 was used for σ_g , whereas the CMD value was adjusted according to the expected size distribution. For example for engine-out and DPF-out measurements values of $CMD = 70nm$ and $CMD = 40nm$ were chosen, respectively.

$$N_{tot_{poly}} = I_{PPS} \cdot \left[\frac{1}{e\dot{V}_{smp}} \left(a \cdot \mu^b e^{b^2(\ln \sigma_g)^2/2} \right)^{-1} \right] \quad (6.1)$$

The sensor response model for particle matter mass emissions was utilizing an expression presented by *Maricq and Xu (2004)* based on effective particle density, assumed particle size distribution, and the total particle number concentration as calculated from Equation 6.1. The resulting Equation 6.2 allows to calculate particle matter mass rates in $[mg/m^3]$. Throughout this study, the density and diameter of primary particles was assumed as $2g/cm^3$ and $20nm$ as was suggested by *Maricq and Xu (2004)* for typical primary combustion type particles. The fractal dimension was chosen as $d_f = 2.3$ based on *Harris and Maricq (2001)* for typical vehicle exhaust. Good correlation of this approach was found with the AVL micro soot sensor for particles within the size range of 18 to 73nm. Finally, an exponential expression based on applied ion trap voltage and electrical mobility of particles was found to best describe the particle size specific penetration through the mobility analyzer (i.e. ion trap) of the diffusion-charging type sensor.

$$M = N_{tot} \frac{\pi}{6} \rho_0 d_0^{(3-d_f)} \mu^{d_f} e^{(d_f^2(\ln \sigma)^2/2)} \quad (6.2)$$

After basic calibration with the soot generator, the sensor was evaluated under *controlled environment* conditions in an engine dynamometer test cell and compared to laboratory-grade reference instruments, including the AVL MSS, TSI EEPSTM and CPC, TEOM, and total particulate matter via collection and gravimetric analysis on filter membranes. Measurements over consecutive transient and steady-state test cycles indicated an average coefficient of variation of the sensor response below 2% (i.e. 1.8% for FTP, 0.14%

for ETC, 1.4% for 4-mode steady-state). Over the course of a multi-day testing campaign with different fuels, the calculated total particle number concentration based on the sensor response compared to within $\sim 1.9\%$ to 18.9% of total particle concentrations obtained by integration over each particle size bin measured by the EEPSTM.

A sensitivity study was conducted by sampling downstream a particulate filter during the initial *degreening* phase as well as during and immediately after filter regeneration. The sensor proved sensitive enough to detect changes in DPF filtration efficiency due to *soot cake* layer build-up on the substrate walls and correlated with trends observed for CPC total particle concentration and gravimetric total particulate matter mass measurements (i.e. TPM: $R^2 = 0.953$, CPC: $R^2 = 0.983$).

Furthermore, the sensor was observed to correlate closer with total particle concentrations calculated from integration of particle size specific EEPSTM data as opposed to the total particle concentration measured with the CPC. Downstream particle filter measurements were observed to exhibit a $\sim 41\%$ and $\sim 32\%$ lower correlation slope for CPC and EEPSTM as compared to upstream measurements.

Finally, the diffusion-charging sensor was applied to on-road emissions testing of two light-duty vehicles operated over diverse driving conditions within major metropolitan areas in California. Additionally, one vehicle was driven between Los Angeles, CA and Seattle, WA exposing the sensor to extended sampling period including four regeneration events. The particle sensor has shown to clearly identify DPF regeneration events which was observed in agreement with an increase in exhaust gas temperatures on the order of $\sim 120^\circ\text{C}$. One of the primary challenges identified with the particle sensor was the ability to provide dry pressurized air for driving the ejector pump and to produce the ion stream over the corona charger. Especially during test days that experienced increased humidity, achieving a low dewpoint without major equipment has proven to be difficult. Increased humidity in the dilution air can lead to a leakage current in the corona charger which causes the sensor to turn the corona off in order to protect the sensitive electronic components. Beside this, the study concluded that the diffusion-charging type sensor provided a viable method to quantify in-use particle number emissions.

6.2 Recommendations

The recommendations provided herein will highlight areas of suggested further investigations to better understand a diffusion-charging type sensor's response towards combustion engine derived particulate emissions with specific emphasis for in-use applications. Furthermore, there exists a wealth of experimental data which has not been analyzed or discussed within the confines of this study, including a recent (i.e. 2015) California ARB and South Coast AQMD sponsored on-road evaluation of seven 2010 U.S. EPA emissions compliant heavy-duty vehicles which were instrumented with two PPS-M1 version V3 and a PPS-OBD sensor.

One key recommendation is to improve the sensor response model based on additional experimental investigation using laboratory generated particles of known size and number concentration. This would further allow to better understand sensor internal and size dependent particle losses. Furthermore, the particle removal effects and penetration efficiency of the mobility analyzer (i.e. ion trap) need to be studied and characterized in more detail as this allows the sensor to be specifically tailored towards a PMP protocol compliant measurement system with a defined lower particle cut-point. Moreover, it is recommended to explore the possibility of the PPS to be employed as particle sizing instrument, analogous to the differential mobility analyzer in the SMPSTM, by successively stepping the ion trap voltage (V_{ma}) up. This of course, would lead to a loss in real-time measurement capability, however, could provide useful information about particle size distribution of the exhaust stream during phases of sustained steady-state engine operation (e.g. highway driving).

This study provided a simple model to calculate sample flow rates based on dilution air pressure and a set of calibration coefficients specific to a given sensor, assuming constant sample gas temperature. The assumption of constant sample temperature is based on the application of a $\sim 1\text{m}$ long heated line section upstream the sensor inlet, allowing the sample gas to attain a constant and defined temperature. However, in case of applications that do not permit the use of an additional heated line between sample extraction point and sensor (e.g. due to space requirements, loss in signal response due to smearing effects in the sample line, etc.) or in particular with regard to the PPS-OBD sensor that is directly mounted into the exhaust pipe, varying temperatures will impact the ejector pump and thus, the sample flow rate and internal dilution ratio. It is therefore recommended to develop a more detailed model of the ejector pump/diluter inside the PPS similar to work

presented by *Giechaskiel et al.* (2004).

Personal correspondence with OEM's and other research groups applying diffusion-charging type instruments for vehicular exhaust measurements downstream of after-treatment devices has indicated natural charge of particles to have the potential to offset the measurement. This is of specific importance when sampling downstream a particulate filter, in the low particle number concentration environment, as the resulting offset could be on the same order of magnitude as the actual signal or even higher. This would prevent the ability to detect minute filtration deficiencies in the after-treatment system. Therefore, it is recommended to attain a better understanding of the extent naturally charged particles can affect the sensor response. A possible preventive measure could include the application of a *charge neutralizer* upstream the sensor.

Studies (*Johnson et al.*, 2009) have shown that nucleation mode particles are being measured downstream PMP protocol compliant particle counting systems which comprise a thermal *removal* process of volatile particles and adsorbed matter. In an analogous fashion, the PPS maintains sample tube and sensor body temperatures at constant 200°C with the aim to reduce the probability of semi-volatile and volatile components from condensing or adsorbing on solid particles or moreover, possibly nucleate and form measurement artifacts. However, as the study by *Johnson et al.* (2009) and research by *Giechaskiel and Drossinos* (2010) showed there exists the chance for re-nucleation or re-condensation of certain volatile exhaust species, which is even more pronounced at evaporator temperatures below 300°C (*Giechaskiel and Drossinos*, 2010). In light of these findings and results from this study that have indicated discrepancies between PPS response towards PM mass and carbonaceous soot measurements by the AVL micro soot sensor, it is recommended to investigate the volatile particle removal efficiency of the PPS sampling stream in a more controlled study. Such a study should include a range of hydrocarbons known to be existing in the exhaust stream. It is recommended to investigate different sample tube and sensor body temperature settings. A possible alternative solution could be the implementation of a catalytic stripper upstream the PPS sample inlet which has already been discussed by *Tikkanen et al.* (2013); *Amanatidis et al.* (2014). Catalytic strippers have shown superiority over thermal-type *volatile particle removers* as they actively remove the volatile components by oxidation rather than solely changing their phase into the gaseous state by heating (*Khalek and Kittelson*, 1995; *Swanson et al.*, 2010, 2013).

Furthermore, it is suggested to study the application of two sensors simultaneously installed up- and downstream the particulate filter to estimate real-time filtration efficiencies. Measurements from the two sensors can then be used as input to physical DPF models (*Mulone et al.*, 2011) in order to calculate the actual filling state of the filter with soot, and allow for feedback-controlled DPF regeneration. This could have the potential to reduce regeneration frequency and thus, possibly improve fuel economy similar to research presented by *Sappok et al.* (2015) based on radio frequency type sensors.

Finally, it is recommended to perform a similarly rigorous evaluation of the OBD version of the diffusion-charger type sensor, as presented in this study for the laboratory version of the sensor.

Appendix A

Appendix

The appendix contains following documents:

- **Table A.1** contains a detailed list of all currently (as of April 2015) know in-line soot and particle sensors, including contact information and brief description of operating principles.
- **Table A.2** contains specifications of the heavy-duty vehicles and engines used for chassis dynamometer testing as part of the South-Coast AQMD funded project (*Thiruvengadam et al.*, 2015).
- **Table A.3** contains specifications of the AVL M.O.V.E PM-PEMS 494 (*AVL List GmbH*, 2012) and Horiba[®] OBS-ONE PM (*Horiba Instruments Inc.*, 2015) instruments.

Table A.1: List of in-line soot and particle sensors.

Company / Org.	Sensor Name	Sensor Technology	Link	Lit.	Status	Comments
Pegasor Oy , Contact: Juha Tikkanen, juha.tikkanen@pegasor.fi, (+35-850-350-90-64)	PPS-M1 (Pegasor Particle Sensor)	Particle charging by corona discharge and subsequent measurement of escaping current via electrometer	http://pegasor.fi	<i>Ntziachristos et al.</i> (2012); <i>Besch et al.</i> (2011c); <i>Ntziachristos et al.</i> (2011); <i>Lanki et al.</i> (2011); <i>Rostedt et al.</i> (2009); <i>Beck et al.</i> (2012); <i>Ntziachristos et al.</i> (2009); <i>Gensdarmes et al.</i> (2011); <i>Ntziachristos</i> (2012); <i>Karim</i> (2012); <i>Gautam et al.</i> (2010a); <i>Besch et al.</i> (2010, 2011a,b, 2012); <i>Wachtmeister</i> (2012); <i>Tikkanen et al.</i> (2013); <i>Ntziachristos et al.</i> (2013a); <i>Ahlvik and Rajagopal</i> (2014); <i>Tikkanen et al.</i> (2014)	In production as of 2012 (2 nd gen.) and 2014 (3 rd gen.), Offer also integrated system PPS-Mi2 (incl. dilution sys.)	Non-collecting, constant sample flow $\Rightarrow$ hence charging efficiency not effected by exhaust flow rate, needs external air supply (basic sensor technology initially developed by Dekati Ltd. as ETaPS Electrical Tail Pipe Sensor)
Pegasor/NGK Spark Plug , Contact: Noriyuki Adachi, N_Adachi@ngkntk.de, (+49-2102-974-501)	OBD-PM sensor (Pegasor-NGK collaboration lead by NGK)	Particle charging by corona discharge and subsequent measurement of escaping current via electrometer	http://pegasor.fi/en/our-technology/engine-emission-monitoring/obd-pm-sensor-technology/		Under development, first sensor was available by late 2014	Non-collecting, constant sample flow $\Rightarrow$ hence charging efficiency not effected by exhaust flow rate, needs external air supply, works fine downstream DPF
Bosch GmbH , Contact: Enno Baars, Enno.Baars@de.bosch.com, (+49 711 811-52189)	PM Sensor	Electrical conductivity - based on a drop in resistance due to the formation of electrically conductive soot paths between two inter-digitated, comb-like sensing electrodes, printed onto a ceramic surface		<i>Baars</i> (2010); <i>Ochs et al.</i> (2010)	Introduced in 2010, current status unknown	Periodic regeneration required to burn collected soot off

Table A.1: List of in-line soot and particle sensors (continued).

Company / Org.	Sensor Name	Sensor Technology	Link	Lit.	Status	Comments
NGK, Contact: Atsuo Kondo, akondo@ngk.co.jp		Electrical capacitance - measurement of changes in electrostatic capacitance between two sensing electrodes due to soot deposition		<i>Kondo et al.</i> (2011); <i>Kondo</i> (2011)	Under development as of 2011, current status unknown	Periodic regeneration required to burn collected soot off, capacitance method shows smaller temperature influence than resistance measurement
Honeywell		Particle charge sensor - measures charge of particles as induced by the combustion process		<i>Honeywell ACS Laboratories</i> (2010); <i>Kittelson et al.</i> (2004)	Test performed at UofM in 2010, current status unknown	Sensor for up- and downstream of DPF, particle charge strongly influenced by exhaust configuration/structure, suggested to use two sensors (up and downstream) in series in order to be able to evaluate the state of the DPF
GE	ACCUSOLVE	Radio frequency - measuring PM mass (carbon and ash) retained within the filter			Currently in production (as of Jan. 2012), used by equipment manufacturer in off-road applications	Information are from a quarterly report of research projects at MTU (Prof. J. Johnson), as of Jan. 2012
Delphi Automotive Systems LLC, Contact: Harry Husted, Harry.L.Husted@Delphi.com, and Scott Nelson, Scott.Nelson@delphi.com		Electrical conductivity - increase in conductivity between two electrodes due to soot deposition	http://delphi.com/manufacturers/au-to/sensors/engine-and-transmission/diesel/prt-mtr-sensor/	<i>Husted et al.</i> (2012)	Production targeted to start in late 2012 early 2013, sensors available as of Fall 2014	Periodic regeneration required to burn collected soot off, sensor position and flow over particle deposition area are major influencing parameters

Table A.1: List of in-line soot and particle sensors (continued).

Company / Org.	Sensor Name	Sensor Technology	Link	Lit.	Status	Comments
Continental Corp. , Contact: Peter Schauer, Peter.Schauer@continental-corporation.com	Smart Particulate Matter Sensor	Electrical conductivity - change in electrical resistance to measure amount of soot deposited on a ceramic surface between electrodes		<i>Weigl et al.</i> (2010); <i>Continental Corporation</i> (2011)	B-sample phase as of June 2012, C-sample phase during Q1/2013, vehicle implementation by Q2/2014 $\Rightarrow$ sensor prototype available as of 2015	Periodic regeneration required to burn collected soot off (850°C), sensor can be used of 12V and 24V applications, Continental offers necessary integration of sensor into engine management system, measurement range: 0-25mg/m ³ , accuracy: ± 1.5 mg/m ³ @ range < 10mg/m ³ , $\pm 15\%$ @ range > 10mg/m ³
Siemens VDO		Electrical conductivity - change in electrical resistance between two electrodes			Current status unknown	Patent filed in Oct. 2011
EmiSense Inc. , Contact: Jim Steppan, jsteppan@emisense.com		Particle charging - measurement of electrical charge carried away by particles in the exhaust stream between a charging and sensing electrode	www.emisense.com	<i>Steppan et al.</i> (2011); <i>Warey et al.</i> (2004); <i>Warey and Hall</i> (2005)	1 st generation has been evaluated by UCR CE-CERT and SwRI, 2 nd released and 3 rd generation in development as of late 2014	Concentration readings affected by exhaust flow rate $\Rightarrow$ charging efficiency $\Rightarrow$ can be optimized by refining sensor housing and installation configuration (basic sensor technology initially developed by Uof Texas at Austin, Prof. R. Matthews et al.)
Watlow		Technology not yet publicized			In develop. as of 2012, current status unknown	
Electricfil Automotive , (France), Contact: innovation@electricfil.com, (+334-72-88-75-75)		Electrical conductivity - measuring change in resistance between two comb-shaped electrodes while soot particles are being deposited	www.electricfil.com	<i>Electricfil Automotive</i> (2011, 2012)	Status as of Jan. 2011 (prototype for pilot tests available in 48hours)	Needs periodic regeneration, sensor is in two versions available: 1) passive sensor with analog output, 2) active sensor with integrated electronics for autonomous regeneration control and CAN output

Table A.1: List of in-line soot and particle sensors (continued).

Company / Org.	Sensor Name	Sensor Technology	Link	Lit.	Status	Comments
Stoneridge Inc., Control Devices Division		Electrical conductivity - thick film sensor measuring changes in electrical resistance between two electrical layers	www.stoneridge.com	<i>Stoneridge Inc.</i> (2012)	Current status unknown	Single layer design, providing fast regeneration at high-flow, includes CAN output (J1939 or OBD 2.0), soot concentration 0-25mg/m ³
U of Wolfenbuettel, Contact: Prof. Hauser		Electrical charge measurement $\Rightarrow$ particles being charged by a charging electrode and subsequently repelled to a sensing electrode where the current is being measured	www.cle.de	<i>Hauser</i> (2006)	Research stage, $\Rightarrow$ see comments	Multiple configurations have been developed $\Rightarrow$ one sensor version has been acquired by Saxon Junkalor and is being marketed as a vehicle inspection/service (garage) PM measurement instrument
Filter Sensing Technologies Inc., Contact: Alex Sappok, asappok@mit.edu	RF-DPF TM	Radio frequency measuring PM mass (soot and ash) retained within the filter, RF signal changes as a function of differences in dielectric properties caused by the deposition of soot and ash on the filter walls	www.dpfsensor.com	<i>Sappok et al.</i> (2010, 2015); <i>Nanjundaswamy et al.</i> (2015)	In development, multiple generations of prototype sensors as of June 2012 (testing activities within a small group of customers), FST was acquired by CTS Corp. in Fall 2015	RF technique reported to be insensitive to exhaust flow changes, shows negligible influence due to PM composition (EC/OC)
Nordic Innovation Center, Contact: Prof. A. Spetz	SootSens	Electrical conductivity - soot deposition via thermophoresis	www.nordic-innovation.net	<i>Spetz and Bjorklund</i> (2009, 2011); <i>Malik et al.</i> (2011); <i>Lutic et al.</i> (2010)	Research, not yet commercial	Two patents have been filed, sensor evaluation together with Volvo
U of Bayreuth, Contact: Gunter Hagen		Radio frequency - RF signal changes as a function of differences in dielectric properties caused by the deposition of soot and ash on the filter walls, Electrical conductivity - conductometric soot sensor	www.bayceer.uni-bayreuth.de	<i>Fischerauer et al.</i> (2010); <i>Hagen et al.</i> (2010, 2011)	Research stage only	Influenced by temperature and agglomeration of un-burnt HC or water in the filter substrate $\Rightarrow$ further investigation needed

Table A.1: List of in-line soot and particle sensors (continued).

Company / Org.	Sensor Name	Sensor Technology	Link	Lit.	Status	Comments
U of Applied Sciences Hamburg , Contact: Prof. Victor Gheorghiu	Spark Discharge Soot and Particle Sensor	Spark discharge - principle based on the influence of particles passing through and electrical field between two electrodes ⇒ breakdown voltage	http://www.haw-hamburg.de/pers/Gheorghiu/index.html	<i>Gheorghiu (2005); Gheorghiu et al. (2006)</i>	Research stage only	
Institut Francais du Petrole (IFP) , Contact: Houssemeddine Abassi	In partnership with EFL, Volvo, CTI, EMSE	Electrical conductivity - accumulation of soot on a ceramic substrate between two conductor rings will change the conductivity	http://fr.linkedin.com/pub/houssemeddine-abassi/13/644/a97/en	<i>Bouchez and Dementhon (2000)</i>	Only research (⇒ Bosch GmbH is believed to have acquired the patents)	Patent by Dementhon, J.B., et al. (IFP) <i>Dispositif destiné à détecter l'encrassement et à chauffer localement un milieu isolant</i> , PN:FR 97/02823
Royal Military College of Canada		Based on spark discharge principle ⇒ particles within the gap between electrodes influence voltage during arc and glow modes of the spark		<i>Allan et al. (2003)</i>	Only research	Absolute sensitivity was found to be not very consistent, strong gas temperature influences

Table A.2: Specifications of heavy-duty test vehicles and engines used for chassis dynamometer evaluation of the *Pegasor Particle Sensor*.

Cat. ^a	Vehicle					Engine			Cert. ^b			
	Vocation	MY ^c	GVWR ^d	Odometer	OEM ^e	Model	MY	Fuel	Disp.	Max. Power	ATS ^f	NO _x
I	[-]	[-]	[lbs]	[miles]	[-]	[-]	[-]	[-]	[L]	[hp]	[-]	[g/bhp-hr]
I	Transit Bus	2008	42,540	116,232	Cummins	ISL-G 280	2008	CNG ^g	8.9	280@2200	TWC ^h	0.2
I	Refuse Truck	2008	58,000	21,465	Cummins	ISL-G 320	2008	LNG ⁱ	8.9	320@2100	TWC	0.2
I	OTR/ ^j	2011	52,000	192	Cummins	ISL-G 320	2011	CNG	8.9	320@2100	TWC	0.2
I	OTR	2008	52,000	45,563	Cummins	ISL-G 320	2008	LNG	8.9	320@2100	TWC	0.2
I	OTR	2010	50,000	63,256	Cummins	ISL-G 320	2009	LNG	8.9	320@2100	TWC	0.2
II	OTR	2008	48,000	196,562	Westport	ISXG 450	2008	LNG\ULSD ^k	14.9	450@1800	DOC-DPF	0.8
II	OTR	2009	48,000	368,080	Westport	ISXG 450	2008	LNG\ULSD	14.9	450@1800	DOC-DPF	0.8
II	OTR	2008	48,000	379,860	Westport	ISXG 450	2008	LNG\ULSD	14.9	450@1800	DOC-DPF	0.8
III	OTR	2011	34,700	12,300	Westport	GX 450	2011	LNG\ULSD	14.9	450@1800	DOC-DPF-SCR	0.2
IV	OTR	2010	52,000	80,412	Navistar	Maxxforce 13	2009	ULSD	12.4	430@1700	DOC-DPF	1.2
V	OTR	2011	52,350	67,373	Navistar	Maxxforce 13	2011	ULSD	12.4	475@1700	DOC-DPF	0.5
V	Refuse Truck	2012	33,000	10,014	Navistar	Maxxforce A260	2011	ULSD	7.6	260@2200	DOC-DPF	0.5
VI	Refuse Truck	2011	60,000	14,269	Cummins	ISC-8.3 300	2011	ULSD	8.3	300@2000	DOC-DPF-SCR	0.2
VI	OTR	2011	52,000	36,982	Mack	MP-8 445C	2011	ULSD	12.8	445@1500	DOC-DPF-SCR	0.2

^aTest vehicle category as defined by

^bRegulatory certification level for given engine (CFR 40/86/A, 2008)

^cModel year

^dGross vehicle weight rating

^eOriginal Engine Manufacturer

^fAfter-treatment system

^gCompressed natural gas

^hThree-way catalyst

ⁱLiquefied natural gas

^jOver-the-road tractor for goods movement operation, Class-8 tractor

^kDual-fuel engine with Westport Innovations *high pressure direct injection* (HPDI) technology

Table A.3: Specifications for AVL M.O.V.E PM-PEMS 494 (AVL List GmbH, 2012) and Horiba® OBS-ONE PM (Horiba Instruments Inc., 2015) instruments.

Parameter	AVL M.O.V.E PM-PEMS 494	Horiba® OBS-TRPM
Measuring principle	Carbonaceous soot measured with MSS (photo-acoustic method, real-time, primary signal), corrected by gravimetric filter media (batch sampling)	Gravimetric filter media sample (batch sampling, primary signal), corrected by real-time particle length measurement with EAD (diffusion-charging method, real-time)
Measuring range (real-time sensor)	up to 1000mg/m ³ (at DR=20)	0 to 2500mm/cm ³ (conc. after dilution)
Detection limit	~5µg/m ³	-
Rise time real-time signal	<1sec	-
Dilution method/ratio	up to DR = 20 (constant), DR = 2 to 100 (proportional)	Partial flow dilution method (proportional sampling mode / fixed dilution ratio mode)
Flow rate of diluted gas	-	10 to 15 L/min (for 20°C and 101.3kPa)
Sample flow rate	6lpm	-
Filter holder	47mm, measurement and backup filter	47mm, effective dia. 26.2mm (w/o backup filter)
Particle pre-classifier (Cyclone)	-	99% penetration of particle size less than 1µm, 50% cut-off point: particle size between 2.5 and 10mm
Exhaust inlet pressure	-80mbar to +60mbar (for higher pressures an optional available high pressure reduction module is required)	-
Data logging frequency	1 Hz standard, 5Hz for selected values	1Hz standard
Interfaces	Analog (0-10V, 2 In/ 4 Out), Digital (4 In/ 4 Out), 1 TCP/IP	TCP/IP
Warm-up time at 20°C amb. temp.	<1/2hr	-
Power demand	~400W (after warm-up)	max. 0.6kVA
Operating voltage	either with 24 VDC or 110/230 VAC (depending on the version)	24VDC from power unit or vehicle
Dimensions [w*h*d]	~19"(482.6mm) x 9.5"(422.3mm) x 20.9"(530mm)	~13.8" (350mm) x 18.1" (460mm) x 18.5" (470mm)
Weight	~99lbs (45 kg)	~99lbs (45 kg)
Operating temperature	5 to 40°C	5 to 40°C
Storage temperature	-40 to +70°C	-
Ambient rel. humidity	corr. max. humidity of 95% at 25°C	<80%
Altitude	-	0 to 2000m a.s.l.

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