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Anderson Robert / TSI USA

A Comparison of Aerosol Instruments to Regulated PM/PN Emissions from GDI and PFI Vehicles

Current regulations world-wide are driving simultaneously lower greenhouse gas and lower criteria pollutant emissions from engines and motor vehicles. These demands have spurred engine and exhaust aftertreatment development that has been unseen since the introduction of the Clean Air Act. In addition to enhanced aftertreatment, such as particulate filters and selective NOx reduction for existing engine technologies, such as diesel, new technologies are being offered, including gasoline direct injection and hybrid electric vehicles.

Engineering vehicles that meet the greenhouse gas and pollutant emissions standards, and at the same time provide customer desired performance is increasingly complex. The ability to do this simply with the regulatory measurement reference methods is hampered by the lack of useful information these methods provide. Gravimetric filters only give PM mass integrated over a prescribed drive cycle making it difficult to attribute emissions to engine / aftertreatment behavior. And solid particle number, while on line and time resolved is subject to distortion by particle coagulation of exhaust species which is different than the prescribed CVS method. This specific difference lacks information on semi volatile PM components which the reference filter captures.

Over the past decade a number of aerosol instruments have been adopted into dynamometer test cell use. Amongst others this includes the TSI Engine Exhaust Particle Sizer (EEPS, Model 3090, TSI Inc.), Dekati Mass Monitor (DMM, Dekati Oy) and Micro Soot Sensor (MSS, Model 483, AVL List GmbH)

The paper compares these three instruments sampling from a CVS dilution tunnel, to the regulatory PM mass and solid particle number emissions for a set of 6 GDI and 2 PFI vehicles. This includes examination of a recently developed "soot inversion" for the EEPS instrument. In general, the PM mass derived from this new matrix using integrated particle size distribution (IPSD) exhibit good correlation to gravimetric PM mass. In addition, the new matrix shows an improved correlation to solid particle number as well as better particle sizing accuracy and reproducibility for particles less than 23nm in anticipation of future regulation in Europe.

The paper will also describe the fundamental development of the improved inversion matrix for combustion aerosols and comparison methodology on how the results were obtained including instrument to regulatory method and instrument to instrument comparisons.



Figure 1. EEPS transient size distributions of GDI exhaust PM (vehicle 1) for the cold start phase of the FTP drive cycle. Left panel: Default (original) inversion. Right panel: Soot optimized inversion.

Curves display bimodal lognormal fits.

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Arnold Frank / MPI-Kernphysik

Modern Diesel-generated nucleation-particles: formation, growth, and lung intrusion

Modern Diesel-Vehicles, fitted with increasingly sophisticated exhaust after-treatment systems (ATS), release only very little soot and other combustion related primary aerosol particles. However, they generate large concentrations of nucleation-particles (NUP), formed in the cooling exhaust just downstream of the vehicles exhaust pipe. NUP have diameters around 10-20 nm, allowing maximum lung intrusion efficiency. Sticky molecules, including certain toxic and carcinogenic molecules, may attach to NUP and thereby may become transported to the deepest region of the human respiratory tract, the alveolar region, which is least protected and most vulnerable. If not attached to NUP, sticky gas molecules would be deposited preferably in the upper regions, the nasal and tracheo-bronchial regions. During recent years concern about NUP induced adverse health effects has increased. However unfortunately, due to their small mass, NUP escape current particle mass oriented legal regulations. The chemical nature, formation and growth of NUP are still poorly understood. Here, we report on a search, in Modern Diesel-Vehicle exhaust, for gases having a potential for NUP formation and growth. The search builds on ION-TRAP-MASS SPECTROMETER trace gas and NUP particle counter measurements, conducted in Modern Diesel-Vehicle exhaust. Emphasis is placed upon acidic gases, including H2SO4 and numerous low-vaporpressure di-carboxylic and tri-carboxylic acids. We find, that H2SO4 is the mayor driver of nucleation, and that organics contribute to NUP growth and perhaps even to nucleation. We also find, that significant carboxylic acid concentrations are still present downstream of the ATS. Obviously, carboxylic acids are not sufficiently removed by the ATS, and some may even be formed by the ATS. Our investigations support the view that NUP deserve increased future attention.

Ayala Alberto / CARB

Evaluation of DPF in HDV Applications

Modern emission standards have required that all new diesel engines sold in California since 2007 achieve greater than 98% reductions in PM emissions. To meet this standard, and with the advent of low-sulfur diesel fuel, engine manufacturers have made wide use of the DPF. In 2008, CARB adopted the Truck and Bus Regulation to meet toxic risk reduction goals, help attain ambient air quality standards, and protect public health. This is a comprehensive, in-use regulation that requires more than one million trucks that operate in California to achieve substantial reductions of PM and NOx emissions. Ultimately, by 2023, this regulation requires 2010 model year engines or newer on every heavy-duty vehicle operating in California. To assess progress toward the 2023 goal, CARB conducted the first extensive field investigation of DPFs in California and considered cost, reliability, safety, and userreported impacts of filters on performance. CARB interviewed fleets, carried out truck inspections, worked with DPF retrofit installers and truck dealers, and surveyed truck drivers. CARB also reviewed relevant vehicle testing and compliance reporting data. The findings from this investigation suggest that DPFs are effective, safe, and are operating as designed. Some fleets are experiencing problems with the use of DPF. However, these problems are due to engine durability issues or inadequate maintenance practices. Fleets are experiencing vehicle downtime due to mechanical failures of engines caused by component failures such as turbochargers or EGR. And these component failures are generally caused by underlying issues that have occurred over time in the past. Warranty claims for some engine components such as turbochargers and EGR systems, which must be reported to CARB by the engine manufacturers, indicated that up to 40 percent of these components require repair or replacement during the warranty period. Some fleets continue to experience component problems throughout the life of the truck. And unfortunately, many of these failures are incorrectly diagnosed as DPF filter issues. These findings bring into sharp focus the overall guality, or lack thereof, of the heavy-duty products on the market. Thus, CARB will work through the regulatory process to hold manufacturers accountable, educate owners and operators, enhance certification, develop stronger inspection and maintenance requirements, and continue to provide wide assistance to fleets.

Barro Christoph / ETHZ

Diesel Engine Operating Strategies: PM, NOx and CO2; A Three Dimensional Trade-Off, as opposed to a single-pollutant minimization

The ETH Conference of Combustion Generated Nanoparticles was convoked for the first time in 1997, with the aim to reduce health impacts from particle emissions generated in diesel engines. At that time, Diesel engines were known to have high efficiency, but also low specific power, and emit high levels of noise and emissions. In the automotive sector, the share of diesel-powered vehicles was only around 15 percent. The introduction of common rail and the applicability of multiple injections increased the power output and reduced noise to a widely accepted level, and as a result their market share increased rapidly. The introduction of a Diesel Particulate Filter (DPF) in the beginning of the 21st century gave the opportunity to reduce PM by orders of magnitude and increased the market acceptance, with the market share reaching a stable 50% in Europe. However, this forced the OEMs (Original Equipment Manufacturers) to apply so-called "low-NOx" strategies, resulting in high amounts of soot in the raw, engine-out exhaust stream, which was to be reduced in the DPF. The goal of this strategy is to reduce engine out NOx already to an acceptable level without further aftertreatment. The consequence of this strategy is short time intervals between the DPF regeneration events, and low filter efficiency immediately after the regeneration event. In the last few years, the legislation limits have been reduced to levels which cannot be achieved without the combination of DPF and NOx aftertreatment. The new limits forced the OEMs to increase the complexity of their engines, now encompassing with a large number of components and numerous degrees of freedom. Nowadays such a propulsion system contains both low and high pressure EGR paths, an externally actuated valve for the introduction of swirl, a piezo injector enabling up to 7 injections per cycle, a variable turbine geometry turbocharger, a DPF, oxidation catalyst, a NOx trap and/or an SCR-catalyst. The proper operation of the entire aftertreatment system requires a minimum exhaust gas temperature level which has an influence on the operating strategy and thus again on the raw emissions of PM and NOx, as well as on the engine efficiency and thus on the CO2 emissions. Since fleet CO2 emissions are also regulated, the engine operating strategy cannot be set independently for PM, NOx and engine efficiency. It is a 3-dimensional trade off which needs to be optimized for the required situation.

Since the diesel engine of the 21st century has numerous degrees of freedom, only a systematic optimization strategy can lead to the required emission levels (CO2 included). This work presents a model based optimization concept allowing weighting factors for soot and NOx and provides set point values for the key actuators (recirculated exhaust gas, swirl level, start of injection, etc.). In combination with an emission feedback loop, the desired emission levels are always achieved at the minimum fuel consumption for all operating conditions.

In 1997, a DPF was a central tool to decrease environmental impacts of a diesel engine. Today, the DPF and its necessity of regeneration influence the optimum operation of such an engine. In the future, the pressure difference across the DPF due to the loading, as well as the required regeneration energy demand depending on soot reactivity during the DPF loading will be included in such an engine optimization an thus will influence the operating strategy for overall CO2 emission minimization.

Bhattu Deepika / PSI Villigen Switzerland

Wood combustion: Emissions and contribution to Secondary organic aerosol budget

Approximately, 3 billion people worldwide use wood, coal and other solid fuels for residential cooking and heating purposes. Among these fuels, wood burning has been found to be a major contributor (17% to 49%) to PM₁ mass at several rural and urban locations in Central Europe. Emission of complex gaseous mixtures and particulate pollutants from this combustion source influences the Earth energy budget and human health. Sufficient information is available for particulate emissions but large uncertainties still persist regarding the secondary aerosol production potential of unspeciated non-methane organic gases (NMOG's). To reduce the large under-prediction of secondary organic aerosol (SOA) concentrations from existing chemical transport models, smog chamber experiments have been performed to identify the precursors and their relative contribution to SOA formation simulating atmospheric aging conditions from residential wood burning.

We found that in addition to traditional SOA precursors such as benzene, toluene, and alpha-pinene (contributing ~3-27% to total SOA mass), the inclusion of 22 non-traditional precursors from beech wood smoke could explain ~84-115% of SOA formed. Routine ambient measurements of these dominant SOA precursors can be included in atmospheric models to reduce the discrepancy between measured and modelled SOA mass yields. Further, extending this work, investigation of the primary and secondary emissions in six different wood combustion devices has been performed under varying combustion conditions using different oxidation setups. First, a 27 m³ smog chamber is used to oxidize the emissions of the stable flaming phase of an old logwood stove, a modern logwood stove, and a pellet stove. The evolution of NMOG's and particulate emissions is studied using a series of instruments such as HR-ToF-AMS, PTR-ToF-MS, SMPS, Aethalometer, as well as gas monitors. The SOA formation from a modern logwood stove is compared to old logwood and pellet stoves.

In the second phase, the same instrumentation is employed with a potential aerosol mass (PAM) chamber to study the SOA formation potential of the emissions from different boilers namely, pellet boiler (optimal and sub-optimal: excess or lack of O_2 conditions simulating the most prevailing conditions in household fireplaces and stoves), industrial wood chip boiler (30% and 100% power consumption), and log wood stove (different loads, and fuel with different carbon and moisture content). The effect of different burning conditions on primary organic aerosol (POA) emissions and SOA concentrations is evaluated. We further tend to investigate the effect of different combustion devices and oxidation regimes on the detailed speciation profile of NMOG's, their oxidation products, and SOA mass closure.

This work is supported by the Swiss National Science Foundation (NRP 70 "Energy Turnaround").

Bonner James / North Carolina State University

Mechanisms of Susceptibility to Carbon Nanotube Lung Disease

Carbon nanotubes (CNTs) are an engineered nanomaterial that have numerous applications as part of the emerging nanotechnology industry. Because of their fiber-like shape and biopersistence in tissues, there is concern that CNTs will pose a risk for human health, particularly lung diseases such as pulmonary fibrosis and mesothelioma, as well as exacerbation of pre-existing respiratory diseases such as asthma. However, to date there is no epidemiological evidence to show that CNTs cause or exacerbate lung diseases in humans. However, evidence from rodent studies demonstrate that CNTs stimulate immune, inflammatory, and fibroproliferative responses in the lung, suggesting a possible risk for lung diseases in humans as a consequence of occupational, environmental, or consumer exposure. We have shown that pre-existing allergic lung inflammation in mice increases the pulmonary fibrotic response to CNTs delivered by inhalation exposure or by bolus dose delivered via oropharyngeal aspiration. The mechanisms mediating the exaggerated pro-fibrotic responses to CNTs during pre-existing lung inflammation involve increased production of soluble cytokines and growth factors (e.g., platelet-derived growth factor and transforming growth factor-beta) as well as enhanced responsiveness of lung connective tissue cells (fibroblasts) through altered expression of cell-surface growth factor receptors or sustained cell signaling patterns initiated by these growth factors. Moreover, we have also identified specific transcription factors that mediate genetic susceptibility to CNT-induced lung disease in mice. In addition to addressing environmental and genetic susceptibility factors in CNT-induced lung disease, we have shown that functionalization of CNTs by thin film coating with metals applied by atomic layer deposition alters the lung inflammatory and fibrotic response in mice. Studies with human lung cells in vitro are currently being used to predict in vivo lung responses in susceptible mouse models or in mice exposed to functionalized CNTs. Collectively, these studies contribute to nanosafety research through identifying mechanisms of susceptibility in vitro and in vivo that predict the potential lung fibrotic hazards to CNTs.

Brem Benjamin / EMPA Switzerland

The first aircraft engine certification measurement of non-volatile particulate matter emissions

Particulate matter (PM) emissions from aircraft gas turbines are a concern for human health, environmental pollution and climate change. Emission regulations require a robust, traceable and standardized method for measuring these emissions. This has been a major focus of an international collaboration in recent years.

This work presents the technical details of the method, results, and challenges for the worldwide first attempted engine certification measurement for non-volatile PM emissions of an in-production turbofan source according to the drafted sampling standard¹. The regulation focuses on the measurement of four engine thrust levels, covered by the so called landing and take-off (LTO) cycle, which are proxies for taxi, approach, climb-out and take-off engine thrust at international standard atmospheric conditions (15 °C, 1013.25 hPa).

The measurements were performed at the engine test cell at SR Technics, Zürich Airport. The standard requires that PM laden exhaust is continuously sampled by a sampling probe which is manufactured for specific engines and provides representative measurement in terms of a combustion carbon balance. The aerosol sampled is then diluted with dry synthetic air by a factor of eight to thirteen and transported via trace heated lines to minimize condensation, particle agglomeration, and gas-to-particle conversion. Non-volatile PM mass is measured by a photoacoustic- or laser induced incandescence- instrument that has been previously calibrated with filter collected elemental carbon mass on a diffusion flame source. In parallel to the mass instrument, a particle number counting system consisting of two dilution steps and a condensation particle counter (CPC) that has a counting efficiency of greater than 50% for particle diameters of 10 nm is utilized. The determination of CO₂ allows the calculation of non-volatile PM mass and number emission indices (mass or number of particles per kg of fuel burnt) which are intended to be used by the regulatory agencies as the future non-volatile PM certification criteria for engines. In this work raw CO₂, oxides of nitrogen (NOx), carbon monoxide (CO), and hydrocarbons (HC) were also monitored for quality check and assurance purposes (The emission levels of these pollutants are known and already regulated²).

Quality check results indicated representative sampling: the expected air to fuel ratio based on engine performance and fuel flow could be met with the monitored emitted gaseous carbon within ± 10%. The emissions of the gaseous pollutants agreed with the certification data for the engine model used. The targeted non-volatile PM mass and number measurements themselves could be performed without any major issues indicating a good performance of the designed sampling methodology. However, several challenges remain concerning the calibration of the mass instrument and various data corrections. An effect which has to be corrected for in the future standard is the dependence of the non-volatile PM number emissions on ambient temperature. Other variables that need to be understood are the effects of fuel composition, exhaust gas temperatures, and mainly particle losses within the sampling system, a key area of current research. These data are important not only for the standard but also for making the results environmentally meaningful.

¹ Procedure for the Continuous Sampling and Measurement of Non-Volatile Particle Emissions from Aircraft Turbine Engines. In SAE International: 2013; Vol. AIR 6241, 2013-11-18

² ICAO, Annex 16 to the Convention on International Civil Aviation: Environmental Protection. In Volume II -Aircraft Engine Emissions, Third Edition - Juillet 2008 ed.; ICAO: Montréal, Quebec, Canada H3C 5H7, 2008.

Bugarski Aleksander / NIOSH USA

Assessment of the effectiveness of disposable filter elements used in permissible underground coal applications

Disposable filter elements (DFEs) are widely used in filtration systems that are designed to remove diesel particulate matter (DPM) from cooled exhaust of permissible diesel-powered underground coal mining equipment. Presence of water-bath exhaust conditioner systems or dry exhaust conditioner systems in the permissible power packages to maintain temperature of exhaust gases below 77°C (170°F) and 150°C (302°F), respectively, allow for use of DFEs made of paper or synthetic materials. Some of the DFEs made of synthetic material can sustain temperatures up to 343°C (650°F) and are used in high-temperature non-permissible applications. The major drawbacks of the permissible filtration systems with DFEs are high initial costs, high operational cost, and large dimensions.

The results of a study conducted to evaluate two types of high-temperature DFEs in the system with dry exhaust conditioner were used to discuss various issues related to assessment of the effectiveness of DFEs. The experimental work was conducted in the NIOSH Diesel Laboratory at the Lake Lynn Experimental Mine, a facility developed to allow evaluation of these and other control technologies directly in an underground environment. DFEs were examined for four repeatable steady-state engine modes using an engine controlled by eddycurrent dynamometer.

For the majority of test cases, the DFEs were found to be effective in reducing contribution of mechanically controlled, naturally aspirated engine to mass and number of aerosols in mine air. After the first hours after the installation, the reductions in mass concentrations were found to be in the 80 percent range, but a substantial increases in their efficiency were observed with accumulation of operating time and buildup of DPM within the pore structure of the filter elements. Tested DFEs were also found to be effective in removing aerosols by number, but their effectiveness in doing so was found to be strongly influenced by engine operating mode. The concentration of nucleation mode aerosols was found to be significantly higher for high-load modes than for low-load modes. In contrast, the concentration of accumulation mode aerosol was found to be relatively higher for low-load modes than for high-load modes. Aerosol emissions during the first several minutes of operation after installation of new element were substantially different from those exhibited later in the DFE life. Those emissions were characterized by visible white smoke and a relatively high concentration of otherwise not present nucleation mode and accumulation mode aerosols. These were attributed primary to off-gassing of filter media binder during heat-up process.

Variability in the effectiveness of currently used DFE during their relatively short life and secondary emissions make difficult to assess actual protection provided by this control technology. In addition, the presentation will discuss need to address few other issues pertinent to use, evaluation, and certification of DFEs and filtration systems for permissible applications, such as availability of engine packages for permissible applications, role of water-bath exhaust conditioner systems in removal of DPM, and effects of evaporated water on performance of DFEs.

Corbin Joel C. / PSI Villigen Switzerland

Dependence of ship-engine aerosol emissions on fuel type: trace metals, black carbon, and light absorption

Shipping emissions represent a rare source of aerosol pollution in the relatively-clean marine atmosphere. The radiation and cloud interactions of these polluting aerosols are influenced by their content of light-absorbing carbon, which includes both black carbon (BC) and light-absorbing organics (Mueller et al., 2015). The production and emission of these species by a ship engine depends on the composition of the fuel, which has traditionally been the sulfurrich residual fuel Heavy Fuel Oil (HFO).

Since 2010, European regulations have required low-sulfur distillate fuels like Marine Gas Oil (MGO) or diesel to be used in and around European ports (Jonson et al., 2015). Relative to HFO, the lower sulfur content as well as the lighter-hydrocarbon composition of distillate fuels like MGO lead to different fractions of BC and organics being produced (Mueller et al., 2015), and potentially to fundamentally different BC properties due to changes in combustion chemistry.

This study focuses on the shift in particulate matter (PM) properties for emissions of the same engine run on HFO, MGO, or diesel fuel. To characterize the trace-metal content of the PM, an Aerodyne High-Resolution Aerosol Mass Spectrometer equipped with a laser vaporizer at 1064 nm (SP-AMS) was employed. To quantify BC mass and mixing state, a Single-Particle Soot Photometer (SP2) was used; optical properties were simultaneously measured by the Aerodyne CAPS PM-ssa (extinction and scattering) and an aethalometer (wavelength dependence of absorption).

The SP-AMS detected such trace metals as V, Fe, Ba, and Ni at significant concentrations in the HFO exhaust. Ratios of these trace metals, often used to identify ship emissions, varied over time. The distillate fuels MGO and DF emissions contained negligible amounts of trace metals; the possibility of using other mass spectral features for source apportionment will be discussed. These discussions will incorporate aerosol light absorption measurements, which for HFO indicated a domination of light absorption by organic carbon ("brown carbon").

Measurements were performed as a function of engine load for all three fuels. The relationship between trace-element emission and aerosol optical properties across these loads for all three fuels will be discussed. These data provide a basis for the understanding of atmospheric shipping emissions, and the prediction of the climate and health-effect response to a switch from HFO to MGO or diesel fuel.

D'Anna Andrea / Università degli Studi di Napoli Federico II

Exposure to sub-10nm particles emitted from combustion sources: in-vitro toxicity and inflammatory potential

The size distribution of combustion-generated particles is generally bimodal. It has a nucleation mode, sub-10nm particles, mostly constituted of organic carbon and an accumulation mode, sizes larger than 10nm, composed of more graphitic soot particles with an elemental carbon structure. Nucleation mode particles are formed in local slightly fuel-rich conditions with a bluish flame luminosity; they are stacks of few aromatic molecules held together by van der Waals interactions. Coagulation of the nucleation mode particles, dehydrogenation reactions and gas-phase mass addition to the sub-10nm particles lead to the formation of soot primary particles with sizes around 20-40nm. These processes occur in hydrocarbon richer conditions. Chain-like aggregates with sizes between 100 nm and 1 micron are formed as typically observed in diffusion controlled combustion conditions.

Modern combustion technologies tend to avoid the emission of particles with sizes larger than 10nm however, a concern remains about the huge emission of sub-10nm particles that have insignificant mass but very high number concentrations. These particularly small particles have a larger surface area to mass ratio compared with larger particles and have very high potential for reaching target organs. Consequently, their health effect can go beyond what may be expected from such low mass concentrations. These nanoparticles are formed in many combustion activities which we encounter every day and which are considered clean or particle-free. Filters and exhaust treatments are typically very effective at removing sub-100 nm particles, but collection efficiency for such sub-10nm particles is not unambiguous and these particles are often overlooked by the difficulty in measuring them at exhausts or in the atmosphere.

In this paper, we present the results of a water-based sampling procedure for small nanoparticles that allows to isolate them from soot and low molecular weight gas-phase organic products for biological and toxicology studies. Nanoparticles are collected from bluish premixed laboratory flames, from cook-top stove burners, and from diesel and gasoline vehicle exhausts. Fossil fuels and biofuels are used; biofuels are well-known to reduce the formation of soot but they produce a large amount of nucleation mode particles.

First results indicate that in comparison to flame-formed nanoparticles - and even if characterized by approximately the same sizes - diesel and gasoline engine emitted nanoparticles bear an elevated mutagenic potential. Since most of the molecules forming the nanostructure in these nanoparticles are actually at the surface, the biological reactivity seems strictly associated with molecular constituents as well as particle size. In this context, nanoparticles emitted from a common-rail diesel engine fueled with a standard diesel oil or diesel fuels doped with additives, including aromatic and oxygenated components, induce cytotoxic and proinflammatory effects on epithelial cells. By contrast to these effects from engines and premixed flames, nanoparticles generated by a partially-premixed diffusion flame, as in a domestic cooktop burner, fed with network natural gas, showed neither after a treatment of up to three days a reduction in epithelial cell viability, no any activation of pro-inflammatory pathways. The latter result highlights the impact of the chemical nature of the molecules forming the nanostructure, in addition to the size of the nanoparticles.

Davies Brian / University of Wollongong NSW Australia

Disposable Diesel Exhaust Filters Used in the Australian Underground Coal Mining Industry

Disposable diesel exhaust filters (DDEFs) were first proposed by the US Bureau of Mines (Ambs and Hillman 1992) as a means of controlling the level of diesel particulate matter (DPM) being dispersed into the atmosphere from the exhaust of diesel engines operating in underground coal mines. The process involves the fitting of a canister to the exhaust system after the water filled conditioning tank (designed to suppress sparks), inserting a DDEF and operating the vehicle until the backpressure from the retained DPM on the filter exceeds predetermined limits or some other parameter (number of hours in service).

The original filters were low cost commercially available cellulose filter elements typically used as air cleaner elements on "over-the-road" diesel transportation vehicles. In Australia the use of flammable cellulose filters was deemed to be too high a fire risk and alternate non-flammable materials were introduced in 1995.

Initial evaluation of these non-flammable exhaust filters involved measuring worker exposures pre and post fitting DDEFs either in operating mines or purpose built controlled ventilation environments. Davies (2004) developed a test procedure using an in-service diesel engine measuring elemental carbon (EC) levels pre and post DDEFs using an R & P Inc Elemental Carbon Analyser. The acceptance criterion was arbitrarily set at 85% retention (measured as mg/m³ EC) and this became the default acceptance value for many years.

The introduction of DDEFs have resulted in worker exposures in coal mines to DPM (measured as mg/m³ EC) decreasing significantly over the past 20 years. As new technology engines slowly enter diesel fleets the characteristics of exhaust DPM entering the workplace atmosphere will change however no formal test method to evaluate current and future DDEFs in terms of particle size and number currently exists in Australia.

In recent years the significant drop in mineral prices has caused mine operators to question the cost of DDEFs to the extent numerous suppliers have now offered products, many of them imported from overseas.

Testing of these alternate products has been limited to proving that they provide the same level of filtration efficiency (as mg/m³ EC) as those currently in service. This has been generally performed by the supplier using an approved test facility and a diesel engine operating in a steady state at peak torque and approximately 75% load. The selection of the test conditions appears to be what would be considered a "worst case" situation and does not take account of the duty cycle of the vehicle in which the DDEF will be used.

A more rigorous approach to the evaluation of DDEFs would seem appropriate and the challenge is to develop a test procedure that evaluates the filtration efficiency not only in terms of mass but also particle size and number so that all filters can be compared on the same basis.

This presentation will discuss the history of DDEFs in Australia, current testing methods and preliminary research by the University of Wollongong in the development of an appropriate test procedure.

Ambs, J.L. and Hillam, T (1992); Disposable and re-usable diesel exhaust filters, US Bureau of Mines, September 1992

Davies, (2004); The control of diesel particulates in underground coal mines, Victoria University February 2004

De Falco Gianluigi / / Università di Napoli "Federico II", Italy

A thermophoretic-thermocouple method for soot measurement in combustion

From a diagnostic point of view, the possibility to follow both qualitatively and quantitatively the entire process of carbonaceous nanoparticle formation in flames is particularly valuable. In this study, quantitative and qualitative measurements of flame-generated soot nanoparticles are presented.

To this aim, an improved version of the thermophoretic particle densitometry (TPD) method, introduced by McEnnaly et al. [Combust. Flame 109 (1997) 701-720] has been developed and used. When the thermocouple is inserted in a particle-containing flame, thermophoretic transport and deposition of particles on the thermocouple junction produces a change of measured temperature in time, which is strongly dependent not only on particle concentration but also on the properties of collected material. Indeed, flame-formed carbonaceous particles are shown to exhibit different size, chemical composition and nanostructure, resulting in a large variety of thermal emissivity values ranging from $\varepsilon \approx 0.4 - 0.5$ for early nucleated particles and increasing to a value of $\varepsilon = 0.95$, i.e. the typical soot particle emissivity.

The improved TPD method is first tested to investigate a premixed flame, whose particle physical/chemical evolution was the object of a recent work [M. Commodo, G. De Falco, A. Bruno, C. Borriello, P. Minutolo, A. D'Anna, Combust. Flame 162 (2015) 3854-3863]. The results constitute the basis for implementing the TPD experiment in a diffusion flame. The obtained data demonstrate that a correct determination of emissivity allows a more accurate evaluation of the particle volume fraction at the early stage of formation process, in a flame region where particle concentration measurement is particularly challenging.

Data also evidence that oxidation has a severe role in affecting both particle emissivity and particle concentration determination. So, an attempt to include carbon nanoparticle oxidation in the TPD volume fraction procedure is also illustrated resulting in a good agreement of the data obtained with other techniques.

Finally, a Raman spectroscopy analysis has been conducted, in order to better understand and to support the variation in the thermal emissivity values of the carbon nanoparticles that were observed, and to correlate it to particle physicochemical properties. Particularly, the thermal emissivity is shown to be related to the particle hydrogen content, and also to the optical bandgap.

Eberwein Burkhard / Berliner Verkehrsbetriebe (BVG)

Bus Fleet of Berlin since 2001

All large cities are challenged with curtailing vehicular emissions. The Berlin public transport authority (BVG) is the largest German fleet operator of urban buses. They decided on an exemplary emission curtailment program, which enabled environmental protection within an economical framework. The most modern technology was deployed, initially with the Mann & Hummel particle filter in 1990 and later MAN Duplex particle filter in 1991. The required soot ignition temperature of 250 °C is not always attained in urban bus operation. That is a disadvantage for the Mann & Hummel system. The MAN Duplex system is technically complex and was too expensive till recently. CNG fueled buses were found to environmentally and economically inappropriate in Berlin. Consequently, BVG decided in 1998 to test the CRT exhaust-gas filter technology, which becomes available.

The CRT filter was field tested under the Berlin deployment conditions of rather slow moving traffic.

The logged data clearly shows that Berlin buses attain the necessary exhaust-gas temperature, on average, during about 30% of the daily deployment to ensure the continuous regeneration of the filter.

Over 1300 CRT fitted city buses now ply daily and proven dependable in dense urban traffic. In the following years the BVG has, in collaboration with the vehicle manufacturers and system supplier HJS, systematically monitored and integrated the technology into the garage procedures.

This includes the launching of low-ash engine oils, the continuous exhaust gas backpressure monitoring and the cleaning of the filter as well as the proof of the effective exhaust gas purification in the general inspection.

The outcomes of this are, in combination with the SCR technology, new technological requirements. The SCR system requires, in contrast to the CRT system, a continuous exhaust gas temperature of above 200 ⁰C to provide the required NOx reduction. Under consideration that this condition won't generally achieved in real driving operation, the NOx conversion rate is too low and furthermore lots of Euro 5 SCRT-systems do show system functionality issues.

Fierz Martin / Naneos particle solutions GmbH Switzerland

Electrical Particle Number Measurement for Automotive Applications

Since the introduction of particle number emission standards, specially designed CPCs with a cutoff diameter of 23nm have been used to measure particle number emissions of vehicles in laboratory settings. Such CPCs may not be ideally suited for the harsh conditions of the upcoming on-road, real driving emissions measurements. We present a novel alternative, the "automotive partector", which is a single-stage electrical detector which has a counting efficiency curve which is very similar to that of the automotive CPC in the relevant size range. This device has the potential to replace the automotive CPC for some applications, particularly when ease of use, small size and low cost are paramount.

The automotive partector follows a decade-old idea by Burtscher&Schmidt-Ott, in which particles are first charged in a unipolar charger, and then partially deposited in a pulsed electrostatic precipitator. The resulting modulation of the particle charge is detected as an induced current in the Femtoamp range in a Faraday cage. This electrical detection is much less sensitive than the single particle counting employed in CPCs, so systems built around the automotive partector operate at much lower dilution ratios than those with CPC to achieve the necessary sensitivity.

In our presentation we will give an overview of the device; we will present counting efficiency curves of the device for different particle types and morphologies; we will show how large the typical variations of these efficiency curves are between instruments; and we will show how and within which limits the counting efficiency curve can be tuned if desired. Finally, we compare it to alternative electrical particle number detection schemes.

Frölich Albert / Umwelt- und Gesundheitsschutz Zürich

DPF-Quality in Swiss Construction Sites FOCUS

Construction sites were found to contribute significantly to the emissions of particulate matter and nitrogen oxides. In Switzerland the focus was placed on these important sources guit later than on the classical pollutants so as industrial factories. Special attempts were made in the Canton and the City of Zurich to reduce the emission loads mainly of diesel particulate matter. The most important measures to emission reduction and the results achieved during the last ten years are presented. In the Canton of Zurich the control of emission reduction regulations on construction sites is delegated to the communities. Depending on the communal resources and priorities a more or less inhomogeneous implementation can be assumed. The results of the communal controls are collected and stored in a cantonal database. Official cantonal controls are executed on construction sites in the competence of the canton itself, road construction sites. The results of the cantonal controls since 2006 show a percentage of correctly equipped construction machines oscillating around 80%, or a failure rate around 20% respectively. Several accompanying measures contribute to this: penalty in the range of 2'000 to 6'000 CHF for each construction machine without DPF and a reinforced communication on the construction sites. Control on the machines of one selected company showed results corresponding the results in the field.

The City of Zurich might be an exception between the communities in the Canton as a clear focus associated with clearly defined resources was put on this category of pollutants. The visual inspections on the construction sites in Zurich show an improved quality of the machines with respect to the equipment with DPF. One reason might be the implementation of the clean air prescriptions into the approval procedure. For the start of the construction work activities an informational meeting with the responsible person and following administrative steps are required. Our experience can be summed up as follows: Remarkable effort during the introduction of the measures for the responsible operators on the side of the construction enterprises as well as for our administration. In the case of CRT-systems the emission of NO2 remains a problem. On the other hand the DPS can be actually be considered as established and state of the art. It is an effective instrument to reduce the particulate matter emissions. The use of alkylate petrol has proved its worth not only for the protection of the environment outside of the construction site but also for better and healthier working conditions on the working site.

Our conclusions are to ensure the use DPF and to promote the use of electric motors especially in our own competence range (city and cantonal administration). Beside of the operational application of our regulations we will attempt to contribute to improved legal bases. In our work on the construction sites we are approaching a new chapter: the particle number measurement.

Geiler Jan Niklas / Power train and Electrical System Robert Bosch GmbH

Investigation of the fuel property influence on number of emitted particles and their size distribution in a gasoline engine with direct injection

With the Euro 6c emission standard, the limit for the number of emitted particles of gasoline engines with direct injection will be lowered to 6×10^{11} particles per kilometer in 2017. To comply with this challenging limit, an improved understanding of particle formation inside of the combustion chamber of a gasoline engine is needed. Earlier endoscopic examinations show that the particle formation is correlated with locally fuel-rich mixture zones [1]. These zones arise from in-homogeneities in the gas phase or from wall fuel films due to spray-wall interaction. In the first part of this work, the influence of the fuel is investigated. Subsequent a brief overview about the ongoing development of laser-induced fluorescence (LIF) techniques for quantitative fuel-film thickness measurements will be given.

In our work, the impact of fuel composition was studied by adding selected additives (5 % by mass) to a reference fuel (CEC). In the diluted (DEKATI fine particle sampler) exhaust gas of a single-cylinder engine, particle size distributions (PSD) down to diameters of 5.6 nm were measured by a TSI engine exhaust particle sizer. The particle number (PN) concentration relative to CEC is plotted in Figure 1. Adding decene caused doubling of the PN with respect to decane, which has a similar boiling point. This is consistent with [2], which found the boiling point and the number of double bonds in a molecule to be the main factors influencing the number of emitted particles. For indene, an aromatic with a high boiling point, the number of emitted particles increased by a factor of 43. Also, the influence of sulfur and oxygen containing fuels was examined. The results confirm the effect of fuel composition on the emitted particles and show additionally an impact on the PSD. A further comparison between directly injected liquid fuel and perfectly premixed gaseous methane indicates that about 70 % of the emitted particles were caused by inadequate fuel-mixture formation.



Figure 1: Measured particle emissions normalized to those from CEC

For a deeper understanding of the cause-and-effect relationship of particle formation, it is necessary to develop a measurement technique that can quantify the fuel mass remaining in the liquid phase at the time of ignition. One possible technique is LIF, which is already established for determining the local air/fuel ratio in the gas phase. An overview of a potential LIF-based measurement strategy and first results will be given.

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Haffner-Staton, Ephraim / The University of Nottingham

Uncertainties in the traditional 2D-TEM characterization of carbon nanoparticles

Soot forms in automotive engines due to incomplete combustion conditions, and takes the form of clustered or chain-like fractal agglomerates, usually 50-500 nm in size, composed of tens to hundreds of monodisperse spherical particles with diameters in the range of 20-50 nm. As exhaust matter, soot is harmful to human health and contributes to environmental degradation and global warming. Design of improved exhaust particulate filters first requires the high-resolution study of individual particles. Due to their size, transmission electron microscopy (TEM) has been the most widely used method to achieve this. TEM produces 2D projections of particles and the lack of depth perception means measured morphological parameters may be underestimated compared with actual values. Some 3D properties such as volume, surface area, and number of primary particles require application of approximations and corrections factors to be inferred from the measurable 2D quantities, and consequently have an inherent associated error.

The present study, however, is concerned with uncertainty associated with the orientation of the particle. 2D-TEM projections provide us with a single view of the particle, and in choosing to characterise the particle only in the orientation it has happened to deposit in, as is the traditional approach, we ignore all the different interpretations of the particles that alternative projections can offer. Considering the fractal and highly irregular nature of soot particles the apparent morphology of a particle can change beyond recognition when seen from another direction, and consequently so will the values of any characterising parameters we measure. Tilting the TEM specimen stage at incremental angles allowed production a so-called 'tilt-series' of images over a $\pm 60^{\circ}$ range, and by characterising particles at each angle we were able to quantify a portion of the orientation uncertainty.

Flame-generated soot and diesel engine particles were studied. Projection area of agglomerate, and directly related parameters (number of primary particles, volume, and surface area) varied significantly over the range of viewing angle, with differences as large as 32% observed between the minimum and maximum in the series. Fractal dimension was calculated via the Minkowski-Bouligand or so-called 'Box Counting' method. This method is also suitable for use with 3D images, where cubes are counted as opposed to boxes. 2D calculations of fractal dimension underestimate the 3D value by 25%. By considering multiple views of particles, we have been able to show that large uncertainties exist in 2D-measured morphological parameters. The findings add further impetus to the development of 3D-reconstruction methods such as electron tomography to soot to eliminate this particular source of uncertainty.

Hartmann Hans / TFZ-Technology and Support Centre, Straubing, Germany User and fuel impact on emissions of wood stoves

Purpose. Wood stoves are widely used and release high fractions of gaseous emis-sion and particulate matter depending on several impacts such as wood log size, fuel mass loaded per batch, moisture content as well as fuel type. Also the number of pellets stoves is increasing and therefore some combustion tests were conducted using EN-plus pellets. From the obtained results recommendations for fuel preparation, fuel load as well as fuel selection for stoves are given.

Approach. Measurements were performed using two different chimney stoves with grate and one tiled stove insert without a grate. All stoves were fired with beech wood without bark which was prepared as cuboid-shaped test fuel as required in the Norwegian test standard NS 3058. The log size as well as the number of logs were varied. Moreover the moisture content of beech and spruce wood was investigated. Different wood briquettes were used. Finally 12 different wood pellet assortments were applied in a pellet stove.

Results. In general it can be summarized that too small and too large logs lead to in-creased emissions. All three stoves show negative combustion behaviour when only single logs are loaded or when the stove is overloaded. The fuel load as recom-mended by the manufacturer should be chosen. Moreover, a moisture content be-tween 8 and 17 w-% proved to be most favourable due to lowest PM emissions. Pure wood briquettes show similar combustion behaviour as log wood, but the different shape of briquettes can influence pollutant emissions. The combustion of 12 wood pellet samples showed large variation for CO- and PM-emission, although there was no correlation to chemical composition or any other physical properties.

Conclusions. Several recommendations for the user of stoves can be given. Hard wood (beech) should preferably be used in a chimney stove rather than soft wood (spruce). Too small and too large wood logs should be avoided and logs with a di-ameter of about 7 cm showed the best performance in this comparison. The moisture content for e.g. beech wood should vary between 8 and 17 w-% for a good combustion performance. Wood briquettes in general show no better emission behaviour compared to log wood. Round briquettes with a cylindrical hole performed better than those without a hole. Cubiformed briquettes as well as pure bark briquettes release remarkably higher pollutant concentration than other wood briquettes used in this investigation. The combustion of certified wood pellets creates largely variable particle and gaseous emissions while no correlations could be identified to any of the also investigated chemical or physical fuel properties. Further investigations for the causes of such variations are necessary.

Heeb Norbert / EMPA Switzerland

$\label{eq:particle-NO_x} \mbox{ trade-off: Two decades of diesel converter technologies have not settled both issues}$

At first glance, the trade-off between particle and NOx emissions offers two ways for pollutant abatement. One option is to minimize NOx emissions of the engine and remove particles down-stream with diesel particle filters (DPFs). The second option is to minimize particle formation in the engine and apply deNOx-technologies down-stream. The former approach has been widely used in Europe for diesel passenger cars, light-duty vehicles and in Switzer-land for construction machinery and buses too. The latter approach has been applied mainly for heavy-duty vehicles.

Today, there is not much of a choice and combined filter-deNOx systems are needed. Particle number emission limits can only be met with efficient filter technologies. But the progress in NOx conversion is poor in real world conditions and discrepancies between NOx emissions in artificial test cycles and on-road measurements are large. The use of NOx defeat devices, as confessed by one car manufacturer, is violating legislation that has been established in 1970 (Clean Air Act). This illegal practice together with persistently high NOx emissions has damaged the reputation of the diesel technology despite substantial progress in particle abatement.

The 20th anniversary of the CGN-conference is a good occasion to look back to two decades of diesel converter technologies and report on those issues that could be settled. But it is as important to highlight those aspects that have not been solved.

The presentation will discuss the impact of state-of-the-art filters on particle emissions and genotoxic compounds. It will address the problem of persistently high NOx emissions, the substantial increase of NO₂ proportions due to the implementation of diesel oxidation catalysts (DOCs) and DPFs with high oxidation potential and the poor deNOx-efficiencies achieved under cold start or low engine load conditions.

Despite more stringent NOx emission limits which were lowered from 0.70 (1995) to 0.08 g/km (2014) for diesel vehicles real world emissions did not follow these limits as will be shown from long-term measurements with an IR-based remote sensing method at the curbside of a road near Zürich. From such on-road data one can conclude that those converters applied on road are not sufficiently deNOx-active.

Meanwhile, millions of people in cities are exposed to NO_2 concentrations above the European air quality standard of 40 µg/m³. What contributed to the high NO_2 burdens is the fact that DOCs, DPFs operated with DOCs and DPFs with high oxidation potential all support a secondary formation of NO_2 . NO_2 is far more toxic than NO, but not regulated under current vehicle legislation.

The appearance of combined deNOx-DPF-systems is an important step in the right direction. Several authorities on federal, state and city level are not willing to accept high NOx emissions any longer and consider measures (fines, bans, restricted access to environmental zones) against diesel vehicles.

In conclusion, despite substantial progress on particle emissions, the reputation of the diesel technology is damaged due to unacceptably high NO and NO_2 emissions and the efficiency of deNOx-technologies will be crucial for future diesel application in urban traffic.

Hess Adrian / PSI Switzerland

Size-Resolved Element Characterization of Aerosol Particles Emitted from Thermal Wood Treatment

Conventional element characterization of particles in the nanometer to sub-micrometer range is either performed offline, or does not include size information of the investigated particles. In the last years, a hyphenated instrumentation was presented, making use of the size separation capability of a Scanning Mobility Particle Sizer (SMPS) and the element detection performance of Inductively Coupled Plasma Mass Spectrometry (ICPMS). A Rotating Disk Diluter (RDD) was implemented as sample introduction interface, which makes the arrangement independent of specific source aerosol flows and carrier gas.^{1,2}

A Thermogravimetric Analyzer (TGA) allows applying a well-defined thermal treatment to a sample and recording the sample weight, while parameters like the temperature or the availability of different gases, including oxygen, to the sample, can be controlled. Such a TGA had earlier been equipped with a gas quench interface, to immediately cool and dilute the aerosol released by the sample, to prevent further condensation and particle agglomeration, and to preserve the aerosol for subsequent analysis.³

This TGA was used to generate reproducible model aerosols released by biomass fuel samples. A number of wood sawdust pellets, impregnated with different salts containing K, Cl, and Cu, were used as model fuels. The same temperature curve was applied to each fuel sample, and the resulting emissions were characterized concerning the size-resolved particle number concentration and the presence of sodium, chlorine, potassium, and copper in the size classes between 13 and 340 nm, recorded with a temporal resolution of 3 min.⁴

The recorded SMPS-ICPMS data were visualized in color maps, representing number concentrations or mass-related ICPMS intensities, depending on particle diameter and experiment run time, or TGA temperature. Besides, particulate emissions can be visually distinguished from gaseous compounds in these diagrams. The aerosol signals were compared to the TGA weight information, and the influence of the sample impregnations onto the emissions during the thermal treatment was discussed.

This measuring series allowed demonstrating the capabilities of the RDD-SMPS-ICPMS to characterize combustion generated aerosols concerning the size-resolved elemental particle composition, with similar temporal resolutions as are usually achieved with SMPS measurements. Further experiments with setups which are closer to real wood and waste incineration situations are planned, and in a long-term perspective, a mobile RDD-SMPS-ICPMS arrangement might allow doing similar measurements outside the laboratory, i.e. on a test bench or an industrial site.

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⁴ Hess, Tarik, Foppiano, Edinger, Ludwig. *Energy Fuels*, accepted work:

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Hofmann Heinrich / EPFL Lausanne, Switzerland

Dosage and metrics: Impact of physico-chemical properties of UFP

The physical and chemical properties of ultrafine particles are well investigated but still the behavior of UFP in a biological environment is under discussion. To investigate the biological impact of UFP well established test methods were used, but we have to take in consideration, that these tests were developed for chemicals and molecules mostly dissolved in gas or a liquid. In the last years, more and more problems in application of the established in vitro method to investigate toxicity of nanoparticles were reported and several EU and national research programs started to investigate in detail the possible false positive/negative results using the existing test methods. One of the key question is dosage and metrics: is it possible to use the dosage as applied for chemicals (mass/volume) or should we use instead of the applied dosage the deposited dosage on the cells (mass/area). Additional question coming up answering this question like: is the particle surface in contact with the cells or the number of deposited particles more relevant?

To predict the deposited mass/area interesting models exists and a calculation is possible if density and hydrodynamic size and size distribution are known. Important is that the hydrodynamic size, which includes coatings and functionalization of the particles and the density of such complex particles has to be determined. It is evident that, in the case the toxicity tests are standardized, the measurement of the mentioned properties have also to be standardized. OECD, ISO and several European programs are working on the development of such protocols. In this presentation the different approaches will be explained and the most interesting methods will be presented.

In a second part, the difference of interpretation of the results of cell viability studies using mass/volume or mass/area as dosage will be shown and discussed. To transfer the deposited ed mass in to deposited surface or number of particles, beside the hydrodynamic diameter the core particle size and size distribution as well as the core density has to be known. Again, the determination of these properties are still under discussion and we will give a short overview of the state of the art based on the activity of the EU-Project NanoReg.

The final aim of the ongoing activity in these field is to determine the important properties of UFP which will allow to predict or measure the deposited mass/area and to transfer this dose in surface/area and number/area so that toxicologists are able to present the results in the most meaningful manner, but based on reproducible and robust measurements of the relevant characteristics of UFP.

Hosseini Vahid / Saidi Mohammad /Sharif-University of Technology, Tehran, Iran Analyses of effects of fuel sulfur content on DPF particle removal efficiency and particle deposition in human lung

Iranian large agglomerations including capital – Tehran – are influenced with high concentration of particles measured according to national ambient air quality standards in PM2.5 and PM10. Approximately 1/3 of the days of a given year are marked as unhealthy due to public exposure to the particulate matters. Further studies including particle counting and source apportionment of PM2.5 indicate a high contribution of UFPs, elemental and organic carbon in PM2.5. It is worth to mention that UFPs are known as the most hazardous group of particles due to their high penetration into the respiratory system. Tehran emission inventory shows a large contribution of mobile source (~70% of total PM) with considerable portion belonging to heavy duty diesel vehicles including pre-Euro, Euro-1, Euro-2, and limited number of Euro-3 certified buses and trucks. According to the successful history of DPFs usage and its high efficiency, this after treatment system could be effective on reducing particulate's adverse public health effects.

Fuel quality and its high sulphur content were seemed to be a challenge of using DPF in the nation. Other than large cities which have below 50 ppm sulphur content diesel fuel, the rest of the country utilizes extremely high sulphur content diesel up to 7500 ppm. In order to introduce closed filters for diesel fleet as a step to cleaner air and considering fuel sulphur content challenge, an experimental investigation was carried out using 10 VERT-certified closed filters of various technologies under various sulphur content diesel up to 7700 ppm on engine dynamometer. A heavy duty, 220 kW, Euro-2 certified diesel engine was used for the purpose of the study. Both active and passive regeneration were examined. All technologies exhibited PN removal efficiency of more than 97% regardless of diesel fuel sulphur content. CRT filters had low even negative PM efficiencies depending on the operating conditions due to sulphate condensate contaminations of the samples for mass measurement. The systems using FBC, showed lower PM efficiency for high sulphur level fuel compared to low and medium due to weakened sulphate condensation effect..

A durability tests were performed with 7 non-catalysed and 2 catalysed (CDPF) filters on Tehran city bus fleet of various routes. More than 75000 km was achieved for the first installed filter under local operating conditions and diesel fuel of <50 ppm.

A numerical model was developed to predict the particles deposition in the respiratory system in order to evaluate the DPF effectiveness. The model results showed that, using DPF not only reduced particles number up to 99% but also it shifted the average diameter of particles to a less risky region.

The result of deposition fraction which was derived from the numerical model, the efficiency of the DPF in reducing health risks was established. Also, it proved that medium sulphur content, high sulphate ash, high idling time, and low exhaust temperatures of the city buses does not pose any considerable negative effect on the operation of closed non-catalysed filters.

Jokiniemi Jorma / University of Eastern Finland

Chemical and physical properties of biomass combustion aerosols

Keywords: biomass combustion, fine particles, characterisation, chemistry, measurement. Fine particle emissions from combustion sources have gained attention recently due to their climate effects and adverse effects on human health. Residential wood combustion (RWC) is widely used for heating in many countries during winter and is increasing due to its $CO_{2^{-}}$ neutrality. At the same time, RWC is an important source of both gaseous and particulate pollutants, such as fine particles, PAHs, and VOCs.

It has been proposed that RWC accounts a large fraction of the stationary combustion based primary fine particles in many countries. On the other hand, it has been estimated that RWC can locally produce as much as 20–90% of the wintertime fine particle emissions (Boman et al., 2003). However, the main source of fine particles in many countries is a long-range transport, while wood combustion contributes to particles with a relatively high content of organic compounds. Thus, local emissions from RWC can be a real problem in densely populated areas where wood combustion is very common.

In this study, we compare the results of PM and gaseous species emissions from various residential wood combustion appliances. With novel sampling and dilution techniques several instruments measuring PM properties (PM, mass size distribution, number size distribution, chemical composition) can be used parallel to get the full spectrum of PM physico-chemical properties (Leskinen et al., 2014).

Batch combustion in various stoves and some logwood boilers typically generates rather high emissions containing a lot of organic matter and soot. Modern air staging combustion can decrease especially organic emissions from these devices, however based on our new results soot emissions are more difficult to decrease as soot oxidation is more challenging as compared to organics (Nuutinen et al., 2014). Also secondary organic aerosols (SOA) emissions are significant from these appliances. The emissions can be decreased using secondary emission reduction measures based typically on electrostatic effects or by hybrid solutions applying also pellet combustion in batch combustion devices. On the other hand modern automatic wood boiler emissions contain almost no organics or soot and ash species are dominating their PM emissions. In these boilers ash emissions can be decreased by optimised air staging combustion (Lamberg et al., 2011).

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Karjalainen Panu / Tampere University Finland

Nanoparticle emissions from an SI engine fueled with gasoline and Methanol reforming Products

Changes in vehicle emission reduction technologies significantly affect traffic-related emissions in urban areas. In many densely populated areas the amount of traffic is increasing, keeping the emission level high or even increasing. To understand the health effects of traffic related emissions, both primary (direct) particulate emission and secondary particle formation (from gaseous precursors in the exhaust emissions) need to be characterized. In this study, we used a comprehensive set of measurements to characterize both primary and secondary particulate emissions of a gasoline vehicle. Our measurements cover the whole process chain in emission formation, from the tailpipe to the atmosphere, and takes into account also differences in driving patterns.

The test vehicle was a modern gasoline passenger car: model year 2011, 1.4 I turbo-charged GDI engine, and emission level Euro 5 with a three-way catalytic converter (Karjalainen et al., 2015). The driving cycle used was the New European Driving Cycle (NEDC). Three different ethanol content fuels were used in the tests; commercial fuels E10 and E85, 10% and 85% ethanol respectively, and also close to pure ethanol (E100).

The sampling system consisted of a porous tube diluter (PTD) (dilution ratio (DR) 12), residence time chamber (2.5 s) and secondary dilution conducted by Dekati Diluter (DR 8). In terms of exhaust nucleation particle formation, the sampling system mimics the real exhaust dilution and nanoparticle formation processes in atmosphere. A potential aerosol mass (PAM) chamber (Kang et al., 2007, Lambe et al., 2011) is a small flow through reactor developed to simulate aerosol ageing in the atmosphere. Several published studies show that the PAM chamber produces particles similar to those produced in the atmosphere, so that the PAM chamber should be an effective tool to evaluate the contribution of various driving conditions and vehicle technologies on secondary particle formation and secondary particle mass potential. The PAM chamber was installed between the residence time chamber and secondary dilution. The particle instrumentation consisted of an ultrafine condensation particle counter (UCPC), a High-resolution low-pressure impactor (HRLPI) and aerosol mass spectrometer (SP-ToF-AMS).

We observed that in mass terms, the amount of secondary particles was 13 times higher than the amount of primary particles for E10, whereas significantly smaller ratios were measured for E85 and E100. The formation, composition, number, and mass of secondary particles was significantly affected by driving patterns and engine conditions (Fig. 1). The highest gaseous and particulate emissions were observed at the beginning of the test cycle when the performance of the engine and the catalyst was below optimal. The key parameter for secondary particle formation was the amount of gaseous hydrocarbons in primary emissions.



Figure 1. (a) Primary particle and (b) formed secondary particle concentrations (number, N, UCPC data) and size distributions measured by the HR-LPI during the NEDC test cycle.

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Lambe, A. T et al. Atmos. Meas. Tech., 4(3), 445–461, doi:10.5194/amt-4-445-2011, 2011.

Keller Alejandro / University of Applied Sciences Northwestern Switzerland High time resolution SOA-formation potential of emissions from GDI engines

In the next decades to come, we will be exposed to exhausts of gasoline direct injection (GDI) vehicles with yet unknown consequences. The GASOMEP (Current Status and New Concepts of Gasoline Vehicle Emission Control for Organic, Metallic and Particulate Non-Legislative Pollutants) project investigates the emission characteristics of various GDI vehicles and evaluate the potential of gasoline particle filters (GPFs) currently developed by our industrial partners. The project is a joint effort of the industry, regulators, and the Swiss research institutions PSI, the Universities of Applied Sciences and arts Northwestern Switzerland and Biel, and Empa.

One of the aspects investigated in GASOMEP is the secondary organic aerosol (SOA) forming potentials from GDIs. This is being investigated with smog chamber experiments, executed by PSI Switzerland, and two independent flow reactor approaches. One of the reactors, the Micro Smog Chamber (MSC), exposes the emissions to high intensity UV light to achieving photochemical aging within 10 seconds. Experiments with the MSC are performed on the gas-phase of the emissions. In absence of seed aerosol, the result is a nucleation mode formed exclusively of secondary aerosol, which is measured by means of SMPS or CPC systems, during steady state conditions and transient operation respectively. Steady state data is used to establish an average size distribution of the secondary particles, which is then used in combination with the fast number concentration information to establish a real time (seconds resolved) emission factor during transient cycles.

We will show data of different GDI vehicles and give an estimation of the emission factor for cold-start and warm-start driving cycles. These experiments cannot be performed from a CVS sample since the dilution air of a CVS already has a high secondary aerosol forming potential. We will discuss the consequences of that and show that a high time-resolution is crucial to quantify the secondary aerosol forming potential of the emissions.

Khalek Imad A. / SWRI US

Effect of Jet Fuel Properties on Solid Particle Number and Mass Emission from Aircraft Gas Turbine Engine: Development of a Jet Fuel Particle Index

Jet engines will be subject to new particle emissions regulations worldwide. The new regulation under consideration focuses on solid particle number and soot mass emissions. Jet fuel properties are expected to play an important role in affecting the particle emissions from aircraft gas turbine engines. While there are some limited body of work on the effects of jet fuel properties on solid particle number and soot mass emissions, there is no concise coherent way of characterizing such effects.

In our work, we characterized solid particle number, size distributions, and soot mass emissions from a gas turbine facility, in our army laboratory, under simulated idle, cruise, and take-off conditions. This combustor facility has been extensively used in the past for various fuel studies. We used five separate and different fuels consisting of Jet A, JP-8, synthetic paraffinic kerosene (SPK), and different 50/50 blends of SPK/Jet A and SPK/JP-8.

To characterize the fuel propensity for soot formation in jet engines, we developed a jet fuel Particle-Emissions Index (JFPI), which is an extension of that used for gasoline fuels as a predictor for particle emissions from automotive combustion sources. The JFPI is a function of double bond equivalent (DBE) values, vapor pressures, and weight fractions of more than 500 compounds measured in jet fuels. To compute JFPI, we needed to perform detailed hydrocarbon analyses of the fuels that included various classes of compounds in the C2-C12 range, PAH analyses, C10-C20 normal alkane and polar compounds analyses.

In this presentation, we will report on solid particle number, size distribution, and soot mass emissions using the five different fuels tested. We will define and discuss the JFPI development in more details. We will also correlate particle emissions with the JFPI, and discuss the implication and usefulness of such parameter in comparing jet fuels in the US and worldwide.

Kittelson David / University of Minnesota

Carbon Nanotubes, Nanorods, and Nanoparticles from Engines

Carbon nanotubes (CNTs) have been studied extensively during the last two decades because of their unique structure, properties and potential applications, while at the same time concerns have been raised about their potential adverse health effects. A recent study (Kolosnjaj-Tabi, et al., 2015) reports that CNTs are much more prevalent in ambient air than previously believed. Furthermore, the study suggests that vehicle exhaust particulate matter (PM) is a major source of CNTs. If PM from vehicles is as rich in CNTs as this study suggests, these structures could be a major contributor to the adverse health effects associated with engine exhaust PM. However, Kolosnjaj-Tabi, et al. report much higher concentration of CNTs in vehicle PM than have been reported in other studies. Reasons for this are unknown but possibilities will be discussed in this presentation.

The presentation will review our previous work on the formation and measurement nanotubes and nanorods as well as ordinary carbonaceous nanoparticles in Diesel engine exhaust and critically discuss more recent work. The synthesis of nanotubes requires three essential elements (Height et al., 2004), namely heat, sources of carbon and a metal catalyst. We found that diesel combustion might inadvertently fulfill the conditions leading to CNT formation under certain engine conditions. Metals are always present in engine combustion and are associated with oil additives, fuel additives, and engine wear. The presentation will also touch on recent work (Swanson, et al. 2016), reported elsewhere, that links a process developed at the University of Cambridge for commercial production CNTs to their formation in engines. When the same precursors used for synthesis of CNTs are added to engine fuel, the engine becomes a CNT synthesis reactor.

Our study and other studies of CNT like structures in engine PM generally report much lower concentrations than Kolosnjaj-Tabi, et al. Possible explanations including differences in sample collection, preparation, and measurement will be discussed.

Konstandopoulos Athanasios / CPERI-CERTH

Effects of Catalyst Particle Structure on Soot Oxidation Kinetics

Catalysts for direct soot oxidation in catalyzed diesel particulate filters (CDPFs) consist typically of various mixed oxide compositions (frequently with CeO₂ as the dominant component) that assist soot oxidation by enhancing the supply of oxygen from the catalyst to the soot. Apart from the composition, the material morphological characteristics may also contribute to the catalytic activity. Different CeO_2 nanoparticle catalysts have been obtained employing aerosol-based synthesis and sol-gel methods. The obtained catalyst particles have been characterized with respect to their physical and morphological properties as well as with respect to their catalytic soot oxidation activity. The results have been analyzed with the aid of a multi-population kinetics model motivated by the presence of distinct families of surface oxygen complexes (SOCs) on the carbon surface, which are involved in gasification reactions, in agreement with accepted mechanisms of soot oxidation in the literature. The detailed kinetic data obtained are shown to correlate very well to a composite morphological parameter, derived here for the first time, combining the catalyst particle size, surface area, crystallite size, and porosity. A similar study was conducted with sub-micron/micron sized, dense catalyst particles obtained by milling for various time intervals a CeO_2 rich powder, resulting in a poly-disperse multimodal distribution. In this case, the kinetic data are shown to correlate well with the total surface-weighted mean particle size (also known as the Sauter mean diameter in spray literature). This study establishes to our knowledge for the first time a guantitative mechanistic link between catalyst particle structure and kinetic parameters. facilitating much the rational estimation of kinetic parameters in simulation studies of catalytic soot oxidation.

Kook Sanghoon / The University of New South Wales, Sydney, Australia In-flame and exhaust soot particles under the influence of jet-jet interactions in a small-bore diesel engine

The variations in soot particle structures due to jet-jet interactions have been investigated in a single-cylinder, optically accessible light-duty diesel engine by conducting thermophoretic particle sampling (Figure 1) and subsequent transmission electron microscope (TEM) imaging of both in-flame and exhaust soot particles. To this end, the soot sampling experiments were conducted for three different jet configurations including two single-jets (Jet A and Jet B) and a double-jet (Jet A&B). Two different sampling techniques were applied: one using a carbon-coated mesh grid for standard TEM imaging of soot particle aggregates and the other using a lacy grid for high-resolution TEM imaging of nano-scale carbon fringes as shown in Figure 2. The results exhibit that the double-jet leads to the increased number of soot particles compared with the single-jet cases, suggesting higher soot formation due to locally rich mixtures formed in the jet-jet interaction region. Both the soot aggregate and primary particle sizes of the double-jet are lower than those of the single-jets, implying that the soot particles in the jet-jet interaction region are in the earlier stage of soot formation. The nanostructure analysis using higher magnification TEM images show that soot primary particles from all the jet configurations are comprised of two distinctively different structures of multiple amorphous cores and concentrically-oriented carbon-layer shells. From about 5000 carbon fringes processed for each jet configuration, the double-jet soot particles display similar tortuosity; however, higher fringe separation distance and the increased proportion of highly reactive short carbon fringes suggest that soot particles formed in the jet-jet interaction region are more pre-mature and reactive than those formed in the single-jet head region, consistent with the results of the standard TEM images. For the exhaust samples, both the soot aggregates and primary particles appear to be smaller for the double jet but the differences are much less due likely to the progression in soot formation/oxidation occurred inside the cylinder of the engine before the particles exit through the exhaust. Compared to measurable variations in the soot particle size, the fractal dimension is largely unchanged due to jet-jet interactions in both in-flame and exhaust soot particles.



Figure 1. Optical diesel engine used for the in-flame and exhaust soot sampling experiments



Figure 2 Soot particles sampled directly from diesel flames inside the cylinder of the engine (left) and exhaust stream (right) for single-jet and double-jet configurations.

Leskinen Ari / University of Eastern Finland

Daytime and nighttime aging of logwood combustion aerosols

Emissions from small-scale wood combustion have a significant global contribution to the atmospheric particulate matter by increasing submicron black carbon and primary organic aerosol concentrations, and by forming secondary organic aerosol. The secondary organic aerosols are formed via atmospheric aging processes, such as oxidation of volatile organic compounds. The aging processes may alter remarkably the physical and chemical properties of the emissions.

In this work, wood logs of birch, beech, and spruce were combusted in a modern heat-storing masonry heater, and the emissions were introduced into a 29 m³ environmental chamber, in order to study their atmospheric aging processes. Different ignition speeds ("fast" and "slow" ignition) were applied by using kindlings of different sizes. The emissions were aged in the smog chamber both in the dark (oxidation by ozone and nitrate radical) and under the influence of ultraviolet radiation (oxidation by hydroxyl radicals). In the latter case, hydroxyl radical concentration of $(1-5)\times10^6$ molecules cm⁻³ were used, corresponding to atmospheric ages of up to 18 hours.

The aging combustion aerosols were analyzed by using a scanning mobility particle sizer for particle size distribution and number concentration, and a soot particle aerosol mass spectrometer in order to determine changes in the mass concentrations and chemical compositions of submicron species. The organic aerosol spectra were analyzed by using positive matrix factorization and categorized into subgroups according to their formation mechanisms.

Substantial secondary organic aerosol formation (1.6–2.6 times the initial primary organic aerosol mass concentration) was observed during both dark and light aging which lasted altogether up to 7 hours. In the light aging the secondary organic aerosol formation rates were faster than in the dark aging. Most (> 75 %) primary organic aerosol was found to be oxidized in processes involving evaporation and homogeneous gas-phase oxidation as well as heterogeneous oxidation of particulate organic matter.

The oxidatively aged wood combustion emissions exhibited Van Krevelen slopes of -0.7 in every experiment, yet slightly steeper in the experiments with fast ignition than in those with slow ignition. These results are in the region of the Van Krevelen space where ambient organic aerosol components are typically measured. Furthermore, aging of the organic aerosol followed a trend similar to ambient observations, suggesting that our chamber experiments are well-suited to simulate polluted boundary-layer conditions.

The results prove that logwood burning emissions are subject to intensive chemical processing in the atmosphere, and that the time scale for these transformations is relatively short. The results also indicate that the observed nitrate for logwood combustion is most likely present as organonitrates. The enhancement of organic aerosol mass during both dark and light aging highlight the importance of dark aging.

Lohmann Ulrike / ETH Zurich Switzerland

Chemical characterization of freshly emitted particulate matter from aircraft exhaust using single particle mass spectrometry

The continuous increase of commercial air traffic has led to rising public awareness and concerns about the associated Particulate Matter (PM) emissions. The annual future growthrate is estimated to be 3.4 % - 6.1 % (ICAO, 2013) in terms of passenger revenue kilometers. Since it is much more complex and expensive to measure the mass and number basedemissions from aircraft engines than from other combustion sources (e.g. road traffic), thelegislation regarding aircraft emission are lagging behind general emission regulations. Non-volatileaircraft engine emissions are an important anthropogenic source of soot particles in the uppertroposphere and in the vicinity of airports. They influence climate and contribute globalwarming. In addition, they impact air quality and thus human health and the environment.

The chemical composition of non-volatile emission from aircraft engines was investigatedusing single particle time-of-flight mass spectrometry. The exhaust from several engines was sampled and analyzed. The soot particulate matter was sampled directly behind thedismounted turbines running in a test cell at Zurich Airport. Single particle analyses focusedon the identification of the particle types with focus of metallic compounds. The particlesanalyzed herein represent a subset of the emissions composing of the largest particles due toinstrumental restrictions. A vast majority of the analyzed particles were shown to containelemental carbon, and depending on the engine and the applied thrust the total carbon toelemental carbon ratio ranged from 83 % to 99 %. The detected metallic compounds wereall internally mixed with the soot particles. The most abundant metals in the exhaust wereCr. Fe, Mo, Na, Ca and Al; V, Ba, Co, Cu, Ni, Pb, Mg, Mn, Si, Ti and Zr were also detected.We further investigated potential sources of the ATOFMS-detected metallic compounds using Inductively Coupled Plasma Mass Spectrometry. The sources to be considered werekerosene, engine lubricant oil and engine debris. An unambiguous source apportionment wasnot possible because most metallic compound were detected in several of the analyzedsources. Cobalt and zirconium were found to originate solely from engine wear.

Lonati Giovanni / Politecnico di Milano

In vitro assessment of proinflammatory and genotoxicological effects of wood combustion-generated ultrafine particles

Background

The TOBICUP (TOxicity of Blomass COmbustion generated Ultrafine Particles) project was designed to gain deeper insight on the possible health effects of ultrafine particles (UFP, dp<100 nm) by assessing the potential toxicological responses of UFP samples collected either directly from the Residential Wood Combustion (RWC) emissions or where biomass burning for residential heating is widely used.

In this work, pro-inflammatory and genotoxicological responses of THP-1 and A549 cell lines, used as surrogates of alveolar macrophages and lung epithelial cells, treated with UFPs generated by the combustion of wood pellets and logs are presented.

Methods

Ultrafine particulate matter generated by wood (beech and fir) combustion in a 11 kW pellet stove and in a 8 kW wood stove was sampled with three parallel multistage impactors; a fourth impactor was used for the measurement of the number concentration and size distribution.

Combustion cycles were intended to simulate the behaviour of a real-world user.

UFP samples were analyzed for metals (ICP-AES), for the main inorganic ions (IC), for anhydrosugars (HPLC coupled to pulsed amperometric detection), for total organic carbon by thermal-optical approach, and for PAH (GC-MS).

Cell viability was assessed by lactate dehydrogenase leakage, and IL-8 was measured to evaluate pro-inflammatory effects; for genotoxicological assessment cells were treated with UFP samples at 50-100 μ g/ml concentrations for 24h. Genotoxicological effects have been evaluated in terms of DNA damage (Single SB and double breaks DSB in alkaline comet assay and DSB evaluation with immunostaining of γ H2AX histone proteins), and of intracellular ROS (oxygen reactive species) and RNS (nitrogen reactive species) formation time course. The UPF intracellular disposition was evaluated by transmission electron microscopy analysis (TEM). Observed pro-inflammatory and genotoxicological effects were compared to those in cells treated with Diesel exhaust particles (DEP, dp 2.5 μ m).

Results

Both A549 and THP-1 cells responded to UFP producing IL-8, with logwoods UFPs more active compared to pellet UFPs. With the exception of the higher effect of beech logwood UFPs only in THP-1 cells, the induced release of IL-8 was not influenced by the kind of wood; in addition, on a weight base, IL-8 release was similar or even lower compared to DEP, arguing against a higher biological activity of UFP compared with larger particles. The release of IL-8 induced by UFP could be significantly reduced by SB203580, indicating a role of p38 MAPK activation in IL-8 production. A qualitatively different protein adsorption profile was observed, with less proteins bound to beech UPFs compared to fir UFPs or DEP, which may provide higher intracellular availability of bioactive components, e.g. levoglucosan and galactosan.

From the genotoxicological standpoint, statistically significant increase of all DNA damage markers was highlighted in all samples, more evident for wood combustion than for pellet samples but without differences between the two types of wood. Cells treated with DEP showed more damage than those treated with UPFs from both logwood and pellet combustion. ROS/ RNS production was evident only after 30-60 minutes of treatment with pellet UPF.

Acknowledgments

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Lutz Thomas / ETHZ Switzerland

DPF Inspection & Maintenance, Methodology and Practice

Engine life and emission stability of diesel engines with exhaust emission after-treatment devices depend mainly on maintenance. It must be a periodic routine and emission control has to be an integrated part of maintenance. Thus emission stability can be achieved and overall running costs be reduced by preventive repair, avoidance of operation interruptions etc.

An important tool for a regular emission check during the vehicle maintenance, for roadside measurements and official periodic checks, are fast, handheld, accurate and certified PN measurement devices. PN measurements at low idle are sufficient accurate even to verify the filter efficiency if necessary by measuring also upstream of the filter, to detect small repairable DPF defects and also engine malfunctions.

Besides an on-road or on-site supervision by the authorities, different organization models for I & M are applied. Periodic checks might be made by test-only-stations, run by the authorities or an authorized private organization. Or private test+repair-stations or even the vehicle user or fleet owner do the check and just in case the necessary repairs/re-adjustments. The most important engine system data and the inspection activities should be documented in an individual inspection document. The elements and the procedures of a chosen I&M concepts have to be defined by the authorities.

PN emissions above a given limit can be caused not only be a failed filter. In the case of a CRT system the reason for an insufficient filter efficiency might also be a DOC, inhibited by thermal or chemical poisoning or contamination. With a CO measurement during a load step up to about 250°C the conversion capability of the DOC can thus determined. Not only the PN measuring instruments but also sensors for measuring CO (and NOx) should correspond to guidelines like the ones of the Swiss Federal Office for Metrology (METAS). A simple and practicable DOC test is actually in discussion.

The filter system must be monitored with regard to overload and filter damage. Today's datalogger measure and store data, produce alerts (e.g. with a red light at the dashboard). In the future filter monitoring systems will collect much more different data and send them by GSM or local WLAN to a central monitoring station. This will allow fleet owners the monitoring of functions, alerts, failure diagnostics and to generate statistics of DPF and vehicle operation, vehicle and filter comparisons and prediction of maintenance needs.

Moussa Fathi / Université Paris-Sud, France

Anthropogenic carbon nanotubes and air pollution

Among air pollutants, fine particulate matters of less than $2.5 \ \mu m$ in diameter (PM2.5) were recently ranked as one of the leading causes of death and disability worldwide. However, to the best of our knowledge, PM had never been accurately characterized inside human lung cells and the most responsible components of the particulate mix are still unknown. For instance, a study reported a dose dependent link between carbon content in alveolar macrophages and the decline in lung function, but carbon was assessed only by optical microscopy.

Based on recent finding obtained by our group as well as on the available data in the literature, we show that: 1- PM that can reach the lungs are mostly composed of anthropogenic carbon nanotubes and other carbon nanoparticles; and 2- that human are routinely exposed to such carbon nanoparticles.

We used high-resolution transmission electron microscopy and energy dispersive Xray spectroscopy to characterize PM present in broncho-alveolar lavage-fluids (n = 64) and inside lung cells (n = 5 patients) of asthmatic children. We selected asthmatic patients rather than healthy subjects for this study because of the availability of broncho-alveolar lavage fluids. Indeed, fiber-optic bronchoscopy with broncho-alveolar lavage is routinely performed in France as a diagnostic tool for other missed diseases with symptoms similar to asthma.

Our results show that inhaled PM mostly consist of carbon nanotubes. These carbon nanotubes are present in all examined samples and they are similar to those we found in dusts and vehicle exhausts collected in Paris. They are also similar to those previously characterized in ambient air in the USA, in spider webs in India, and in ice core, thus indicating that humans are routinely exposed to anthropogenic carbon nanotubes.

Our data clearly indicate that in order to detect carbon nanoparticles in a biological or an environmental sample; first it is necessary to use TEM in order to localize the suspected entities. Then EDX must be used to confirm the elemental composition. To identify MWCNTs among carbon nanoparticles, it is necessary to use HRTEM to measure interlayer distances. Finally, NIRFM is the most appropriate method to identify semiconducting individualized SWCNTs. Thus, previous studies linking the carbon content of airway macrophages and the decline of lung function, should be reconsidered.

Current research suggests that fibrous shape of carbon nanotubes could elicit effects similar to asbestos. Although the toxicity of carbon nanotubes is still a matter of debate, it is well established that under certain conditions they can induce a granulomatous reaction.

The implication of these findings will be discussed.

Notter Benedikt / INFRAS Switzerland

Non-road mobile machinery as a PM/PN source in Switzerland

Introduction

Non-road mobile machinery (NRMM) contributes about a third of the primary PM emissions of mobile sources, and about 5% of the total emissions of all sources in Switzerland. The non-road emissions inventory commissioned by the Federal Office for the Environment (FOEN 2015) quantifies exhaust PM emissions from NRMM in Switzerland for the period 1980-2050.

Methodology

PM emissions are calculated in a bottom-up approach. Activity data (operating hours segmented by machine type, technology, size classes with respective nominal power, and age) are multiplied with load factors, and the resulting energy demand is multiplied with fuel consumption and emission factors in g/kWh. Diesel particle filter (DPF) use is accounted for by applying correction factors for the share of machinery equipped with DPF. The correction factors are differentiated by emission standard and size class and take into account the differences in specific emissions without DPF.

Stock and operating time per machine, as well as DPF use for the ex-post period were sourced from official registers, market studies, experts from the respective sectors, and specific surveys. The data for the ex-post period mostly comprised machinery up to the Euro-IIIA standard. Since the emissions limits of Euro-IIIB and Euro-IV can be met with or without DPF, DPF equipment for these standards was estimated by analyzing the aftertreatment strategies of different manufacturers (Integer 2013) and their respective market shares in Switzerland. An exception are the machines operating on construction sites – their DPF use can be estimated from the entry into force dates of the particle filter requirements of the Swiss Ordinance on Air Pollution Control (OAPC). For the planned Euro-V standard, it is assumed that all machines will have to be equipped with a DPF due to its particle number (PN) limits.

Key results

Exhaust PM10 emissions from NRMM in Switzerland amounted to 360 tons in 2015. This implies a decrease of 68% from the peak value of the year 2000 (Figure 1). The largest emitter in 2015 was agricultural machinery, contributing 63% of the total. Due to the lack of regulations and its age structure, agriculture has surpassed construction, which was the largest emitter in 2005 but has since drastically lowered emissions with the introduction of particle filter requirements through the OAPC. The second-largest emitter groups in 2015 are construction, industry, and ships, which each contribute about 11% of PM emissions. On average, roughly a quarter to a third of smaller Euro-IV diesel machines (up to 56 kW) is estimated to be equipped with DPF ex works, and about half of the larger machines. PM10 exhaust emissions from NRMM in Switzerland are expected to decrease to about 230 t/a in 2020 and to about 35 t/a in 2050.



Figure 1. PM10 emissions in Switzerland from non-road mobile machinery (NRMM) by machine family.

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Nussbaumer Thomas / Verenum Zürich

Keynote

Particulate Matter (PM) from biomass combustion: An overview on particle types and measures to reduce biomass particles

Biomass is used as renewable energy carrier to substitute fossil fuels for heat and power production. Its combustion is, however, a significant source of particulate matter (PM). Considering the combustion process, the following formation mechanisms and particle types are distinguished:

- 1. Particles from incomplete combustion:
 - 1.1 a) Solid particles emitted as soot and as primary organic aerosol.

b) Condensable organic compounds (COC) as liquid droplets or condensed matter on solid particles and counted as primary aerosol.

- 1.2 Volatile organic compounds (VOC) as precursors for secondary organic aerosol (SOA).
- 2. Particles from fuel constituents:
 - 2.1 Ash constituents (K, Na, P, CI, S) lead to primary inorganic particles such as KCI, K₂SO₄, CaCO₃, CaO.
 - 2.2 fuel nitrogen forms nitric oxides (NO_X) contributing to secondary inorganic particles.

For most combustion conditions, the particle number concentration is dominated by nanoparticles < 100 nm. At near-complete combustion, wood with low ash content exhibits an unimodal size distribution with nanoparticles contributing to up to more than 90% of the particle mass. The particle mass and the size distribution are, however, strongly influenced by the fuel properties and the combustion regime:

- A high ash content, as e.g. for bark, can cause a second peak in the micrometre range and resulting in a bimodal size distribution.
- An incomplete combustion in simple combustion devices or due to maloperation leads to an increase of the particle size and the total particle mass due to soot formation.
- Incomplete combustion can also cause COC which may exceed the mass of primary solid particles including soot by up to one order of magnitude. This is most relevant for residential combustion and has been demonstrated by flue gas quenching both in liquid sampling and by dilution with cold air.

Due to the different formation mechanisms, not only the particle mass, but also the apportionment of soot and COC can vary in a wide range. Therefore, to estimate the contribution of biomass to PM in the ambient air, solid particles and COC need to be considered and in addition, potential SOA formation from VOC needs to be accounted for.

From the formation mechanisms, different reduction measures are derived. To reduce particles from incomplete combustion, two stage combustion is widely applied in modern log wood boilers and automated combustion plants. Due to forced draft, significant pressure drops are applicable enabling an aerodynamic optimisation of the process with increased turbulence and accurate control of the stoichiometry. For wood stoves, ideal operation with ignition from the top and slow heat release enables significant PM reduction. For industrial combustion plants, electrostatic precipitation (ESP) and fabric filters are applied as secondary measures enabling an efficient separation of inorganic particles. Due to safety and operational reasons, these systems are not applicable to carbonaceous particles. For residential combustion devices, small scale ESP have also been developed and are applied with positive experiences if correctly implemented but exhibit limited efficiencies in case of unsuitable applications.

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Oberdörster Günter / University of Rochester, USA

Dosimetry, Dosemetrics, Biokinetics and Bioprocessing of Inhaled Nanoparticles: A basis for toxicity testing and dosimetric risk extrapolation

Size and chemistry of airborne particles are important properties and determinants of toxicity not only in the respiratory tract, but also in secondary organs such as the cardiovascular and central nervous systems. Particles up to ~100 nm in diameter, ultrafine particles (UFP), became a major research focus, further bolstered by the introduction and rise of nanotechnology and the related manufacture of diverse engineered nanoparticles (NPs, <100 nm), with inhalation as the major route of human exposure. Exponentially increasing numbers of publications have reported about the seemingly unique toxicological properties of NPs, including their propensity to cross cell membranes, enter cells, causing oxidative stress and significant toxicity, culminating in the suggestion that all NPs are toxic. However, an understanding of appropriate dosemetrics as well as establishing realistic Exposure-Dose-Response relationships, are necessary for a meaningful interpretation of results. In vitro studies may be well suited to obtain information about mechanisms and for hazard identification and hazard ranking; however, dosimetric in vitro/in vivo correlations still have to be developed. In contrast, dosimetric extrapolation of results from well-designed repeat particle inhalation studies in experimental animals to humans is well established to derive limit values for occupational or environmental exposures. Sophisticated dosimetry models have been developed for both in vivo and in vitro toxicity testing, providing predictions of deposited and retained doses of aerosolized particles in vivo for all regions of the respiratory tracts of experimental animals and humans, and in vitro for the dose to cells in a conventional, microfluidic or ALI system. For the purposes of NP risk assessment, detailed information about their physico-chemical properties, airborne characteristics of agglomerated and singlet NPs, animal/human-specific respiratory tract geometry and breathing parameters is required. Results of repeat multi-dose rodent inhalation studies with NPs have been used to derive a human equivalent concentration (HEC) that causes no adverse effect and to establish a "safe" exposure level for human exposure. Such studies in rodents have shown that particle size, size distribution, concentration, composition, diverse particle surface properties (specifically surface reactivity or particle bound ROS), dissolution rate, aggregation/agglomeration, density, sources, aging can all influence toxicity. Some of these (e.g., mass, number, surface-area reactivity) serve as dosemetrics which is useful for comparative hazard ranking of NPs and UFPs from different sources. Two case studies, inhaled nano-TiO₂ and nano-SiO₂, demonstrate: the selection of appropriate dosemetrics associated with induced inflammatory and functional effects; and the impact of significant in vivo dissolution for deriving an HEC. Important mechanisms of NP bioprocessing at subcellular level will be discussed, involving ultra-high resolution spectral imaging which confirmed in vivo dissolution and subsequent formation of 2nd generation NP in contiguous reaction zones, indicating the importance of biopersistence coupled to modifications of NP's reactive surface area for deriving the HEC. Quantifying dissolution utilizing dynamic acellular in vitro dissolution systems and validating it would be useful to evaluate biopersistence of NPs to be combined with *in vivo* results. The long-term goal is to develop and validate cellular in vitro models for quantitative risk characterization.

Paulson Suzanne / University of California at Los Angeles, USA

Effects of the built environment, micrometeorology and traffic on street-level ultrafine particle concentrations at a block scale

This study attempts to explain explicitly the direct and quantitative effects of complicated urban built-environment on near-road dispersion and levels of vehicular emissions at the scale of several city blocks, based on ultrafine particle concentrations ([UFP]). On short timescales, ultrafine particles are an excellent proxy for other roadway emissions. Five measurement sites in the greater Los Angeles with have different built environments but similar mesoscale meteorology were explored. After controlling for traffic, for most sampling days and sites, morning [UFP] were higher than those in the afternoon due to limited dispersion capacity combined with a relatively stable surface layer. [UFP] at the intersection corners were also higher than those over the sampling sites, implying that accelerating vehicles around the intersections contributed to [UFP] elevation. In the calm morning, the areal aspect ratio (Ararea), developed in this study for real urban configurations, showed a strong relationship with block-scale [UFP]. Ararea includes the building area-weighted building height, the amount of open space, and the building footprint. In the afternoon, however, when wind speeds were generally higher and turbulence was stronger, vertical turbulence intensity s_w was the most effective factor controlling [UFP]. The surrounding built environment appears to play an indirect role in observed [UFP], by affecting surface level micrometeorology. The effects are substantial; controlling for traffic, differences in Ararea and building heterogeneity were related to differences in [UFP] of factors of two to three among our five study sites. These results have significant implications for pedestrian exposure as well as transit-oriented urban planning.

Pucher Ernst / TU Wien

Short Test Procedures for Nanoparticles Emission and Gaseous Exhaust Components of Combustion Engines

Real world measurements that we have carried out over more than 15 years showed that motor vehicles of the same emission standards may be subject to enormous fluctuations of their pollutant emissions. This should be detected in the context of periodic exhaust inspections. However, the measuring procedures currently used for so-called short tests no longer match the advanced engine technology as well as the measurement devices.

Currently are in the context of the periodic inspection vehicles fitted with positive-ignition engines in Europe according to Lambda and carbon monoxide measurement (developed by the author of this abstracts, 1988) at elevated idle speed and with regard to carbon monoxide and hydrocarbons at idling speed. In California, an examination of gasoline engines with increased idle speed and idle speed of carbon monoxide and hydrocarbons is done on older vehicles every two years. This test can be carried out also on dynamometer at constant load.

Diesel vehicles are measured in Europe at free engine acceleration with respect to exhaust gas opacity. This is true for both passenger cars and trucks. In California, no exhaust emissions are measured in the periodic inspection for diesel vehicles. There is generally no measurement of pollutant components such as particulate matter and oxides of nitrogen (NOx).

For car either readout of the on-board diagnosis evaluates the emission-relevant data of the vehicle's electronic system. However, no exhaust gas measurement is performed. This method is particularly vulnerable to software manipulation by a third party.

The situation is particularly unsatisfactory for the measurement of particulate emissions. The employed measurement method for exhaust opacity is too insensitive for modern diesel engines with particle filters. Caused by new direct-injection combustion in gasoline engines these now also have significant particulate emissions due to partial non-premixed operation mode, which should be subject to an inspection. It is required a direct tail pipe check that is independent of the vehicle itself.

In this presentation the common measurement methods for in-use testing are faced preliminary. This is followed by the presentation of present research results of different categories of vehicles such as passenger cars, light commercial vehicles and heavy trucks. Then results of powertrain variants and combustion processes are discussed.

Finally, a presentation of possible short test procedures that allow a verification of particle emissions and other pollutants is carried out.

Reinoso Aliosha / Geasur, Chile

Bus fleet of Santiago with DPF since 2008 – experience with respect to maintenance; Study of the Chilean Ministry of Environment.

As a result of partnership between Ministry of Environment of Chile, Clean Air and Climate for Latin American Cities (CALAC) and Swiss Agency for Development and Cooperation (SDA), aiming to implement Best Available Technology to control diesel particle emissions, 3,200 buses are functioning with DPF in the fleet of public transport buses in Santiago of Chile. At moment these are between 150,000 to 750,000 km. aged DPF.

In order to follow up maintenance conditions and evaluate a testing method and instrument to implement a short inspection test to enforce (road side and periodic inspection plants), or maintenance diagnosis, 400 buses were measured in Solid Particle Number (SPN). In this sense a recently CH-METAS certified portable, low cost, highly sensitive SPN number counting instrument was used: NPET of TSI.

Measurements were linked up to routine and randomly road side opacity control done by National Enforcement Program of Chile, measuring SPN at end of pipe, in parallel, with NPET-TSI. Additionally, 22 of these buses were tested in-depot, at exhaust upstream and downstream of DPF, to compare efficiency and end of pipe values with roadside results.

Comparing opacity and SPN values, during road side control, 30% of opacity values were below 0.025 [m⁻¹] of extinction coefficient, but between 10² to 10⁹ [#/cm³], when measured in SPN, which evidences opacimeter is not sensitive enough to detect abnormal maintenance conditions of these DPF equipped buses.



In order to try a SPN limit to detect abnormally high emitters as indicator of engine or DPF maintenance problems, we binned measurements into log-spaced concentration ranges looking for a bimodal structure (normal and abnormal). This separation was clearest for low idle mode. Additionally, low idle was easier to implement in road side control because no driver or RPM electronic control interferences and was sensitive enough to distinguish high emitters. Bimodal structure determines limit of 2.2x10E+5 [#/cm³] as threshold.



In order to compare proposed end of pipe threshold with DPF efficiency, we tested 22 buses selected randomly. They were measured at low idle downstream and upstream of DPF. All buses with efficiency over than 95% passed limit (with average efficiency of 99.5%). All but one bus with efficiency below 90% failed limit (with average efficiency of 50%). However, because of extremely high engine raw emissions could produce high end of pipe emissions, despite of DPF condition, considering an additional efficiency test, in-depot, for rejected vehicles is going to be needs.



We conclude that SPN concentration is more sensitive metric than opacity for determining abnormal maintenance conditions of DPF equipped buses. SPN limit of 2.2x10⁵ #/cm³, at Low Idle speed, could be a good indicator for detecting abnormal emissions, considering an additional efficiency test, in-depot, for rejected vehicles.

Rienks Rafael / HJS Germany

Quality Control during Filter Manufacturing

Nearly everyone knows the citation of Harold F. Dodge: "You cannot inspect quality into a product." Considering this statement doesn't mean, that there is no need for inspection during production. In fact, the earlier one start to inspect during production process, the earlier he has the chance to influence the quality of his production, the less necessity is given for total inspection of finished products.



HJS does the complete filter production in house, starting with raw materials and ending with filter systems, which are ready to mount. Basis of the Sintered Metal Filter (SMF[®]) is a porous sintered metal sheet, which is produced in a continuous process in our production plant in Menden, Germany. Expanded metal is filled with metal powder to create a porous sheet of constant thickness and porosity. To ensure the required quality, each batch is undertaken accurate incoming inspection. During production we continuously inspect several process parameters of the green material before it is treated in the sintering furnace in vacuum atmosphere.

Sintering is an important step in production of the HJS Sintered Metal Filter. To ensure the quality of this process, temperature and pressure during sintering is monitored and each batch undergoes several tests to ensure the quality of our material.

Automatically transmitted light inspection ensures that only fault free material is taken for production of the filters. Folding and welding of filter pockets is a well-established automated process with periodic inspection during production. The finally inspection confirms the quality of all welding's and the completion.

Filter quality is not only a question of customer satisfaction. It's also a legal requirement. Regulations and criteria for approval of filters retrofitting as well as for serial applications set ambitious minimum values for efficiency. In VERT test for example, a filter has to show particle number efficiency above 98 % after 2,000 hours endurance run. Other regulation set emission limits in particulate mass and / or particulate number. To confirm, that HJS filter meet all demands, we use a test bench, which allows reliable efficiency tests in a fast and easy way. Volume of testing is determined according to our or our customers' requirements corresponding to the relevant Concept for Conformity of Production.



Filtration Efficiency - Particle Number HJS Production Control

All tests show that the measures in quality control lead to high quality in serial production. Also field experience confirms the high efficiency and long term durability of HJS $SMF^{\$}$. Tests conducted according to Swiss Norm 277206 on an aged Sintered Metal Filter that ran 2.267 hours on a front end loader in rough daily work demonstrates the durability of our systems. Even during regeneration this system showed particle number efficiency better than 99 %.

Rindlisbacher Theo / BAZL Switzerland

Introduction of the first particulate matter standard for aircraft engines

Since the 1980s, large aircraft engines have been required to meet emission limits that have been gradually tightened over time. Air traffic contributes relatively little to pollution levels, and visible smoke trails in the sky from jet engines are a thing of the past. However, no-one has yet found a solution to the emission of ultra-fine particles from jet engines. These micro-scopically small particles can penetrate deep into the lungs and thus adversely affect health. As a precautionary measure, these emissions from air traffic will now also be measured, regulated and reduced.

From a technical standpoint, robust measurements of ultra-fine combustion particles are extremely complex. As part of a close collaboration between the Swiss Civil Aviation Authority FOCA, SR Technics, the Swiss Empa and partners from Europe and North America, experts have spent years developing a standard test setup and method that can be used to measure fine particulate emissions from aircraft engines. Both the measuring system and the corresponding instruments were tested by way of international campaigns until they were considered ready for deployment. Most of the campaigns were performed at the SR Technics facility in Zurich. The measuring system gives the mass of the particulate matter as well as the number of particles emitted per kg of fuel. It even captures the smallest particles with diameters of less than 10nm. The first standard is focused on tracking the emissions performance in terms of mass and number as the base for new regulatory limits.

The work on this new global standard was led by FOCA in partnership with the US aviation authority. On 2 February 2016 in Montreal, the ICAO's Committee on Aviation Environmental Protection approved the new global standard, which relies heavily on contributions by FOCA, SR Technics and Empa. Final approval of the standard is expected by the ICAO Council in one year.

All engine types for passenger aircraft that are in production as of 1 January 2020 must be certified in accordance with the new standard. Most engine manufacturers have already developed their own measuring systems that comply with the standard and have started remeasuring their engines. Technologies are also emerging that will further reduce the emission of fine particulates.

Rothen-Rutishauser Barbara / University of Fribourg Switzerland

Differentiating the mechanism of lung cell interactions between diesel exhaust particles and carbonaceous fibrous structures

Diesel exhaust is a highly complex mixture, consisting of a gaseous and particulate fraction mainly (upon number) composed of soot nanoparticles, which range in diameter from the smallest (~10 nm primary particles) to between 50-100 nm sized agglomerates. Adsorbed to these nano-sized particles are hundreds of different polyaromatic hydrocarbons as well as metal oxides, wind blown dusts and endotoxins [1]. Due to their size, diesel exhaust particles (DEPs) can penetrate to the bronchiolar and alveolar regions of the lung with up to 33% of the inhaled particles deposited in the respiratory tract [6]. By acting as a Trojan horse, DEPs may transport toxic compounds inside cells [7] but also across the air-blood barrier [8]. Once inside cells, DEPs can initiate the onset several biological responses including the generation of enhanced reactive oxygen species and expression of pro-inflammatory cytokines, as well as DNA damage [2]. Long-term exposure to the exhaust from current diesel engines has been shown to correlate with the onset of cardiovascular diseases [3,4] and based on the proven genotoxicity of diesel exhaust, and its constituents, it is classified as a human type 1A carcinogen by the WHO [5].

In a recent study the particulate matter (PM) fraction in broncho-alveolar lavage fluids and inside lungs cells of asthmatic children in Paris was investigated and revealed that inhaled PM may consist of structures resembling, but not confirmed as, carbon nanotubes (CNTs) [6]. From these findings, the authors of this study suggest that humans are routinely exposed to these CNT-like structures, although no supporting evidence is provided from analyzed healthy patients, due to ethical reasons. This study has further raised increased doubts as to the robustness of the conclusions drawn from the data, with experts from the particle (inhalation) toxicology field stating that these results should be treated with extreme caution, since numerous other, similar studies have not reported observing such nano-sized structures in PM. It has, however, been demonstrated that the diesel combustion process has the potential to generate structures resembling carbonaceous fibres [7], which raises concerns and questions the necessity to study the inhalatory effects of these carbonaceous, fibrous structures.

Since these fibrous structures can be considered to resemble carbon nanotubes (CNTs); defined as either single, or multiple layers of graphene rolled into a tube with one dimension in the nanoscale; it is pertinent to consider the lung cell interaction of the fibrous structures observed in PM in a similar fashion. A lot of research has already been conducted to assess the possible human health hazard associated with CNTs (both single- and multi-walled). Evidence suggests that the biological impact of CNTs is strongly reliant upon their specific physico-chemical characteristics, and CNTs with extreme length (>15µm), and thus a high aspect ratio (\geq 1:3) have been shown to cause granuloma formation in the peritoneal cavity *in vivo* [8], as well as a multitude of other significant adverse biological effects *in vitro* [9]. At the single cell level frustrated phagocytosis was described which occurs when macrophages are unable to successfully internalize fibres longer than 15 µm and with a diameter <5 µm, defining them as biopersistent (the hallmark characteristic for any fibre to cause an adverse biological impact). This enables a constant flux from the immune cell attempting to phagocytose the nanofibre, causing the release of both oxidative and (pro-)inflammatory mediators that are known to be detrimental towards the normal homeostasis of the cell/organ [10].

Thus, due to their geometry, there are distinct differences in the manner of interaction with lung cells between DEPs and CNTs/CNT-like structures which has a significance as to the biochemical effect noted. Further to this, as mentioned above, the surface of DEPs further

contribute. This was recently shown in a study where investigation of DEPs and CNTs interacting with the gram-negative bacterium *Salmonella typhimurium* (which is used to assess the mutagenicity of chemicals, *i.e.* the Ames test). Transmission electron microscopy indicated that CNTs entered the bacterium whereas DEP remained extracellular to the bacteria, however, only DEPs caused a significant mutagenicity[11], an effect attributed to the organic layer (*e.g.* PAHs) coating the carbonaceous fraction of DEPs.

In summary therefore, the observation that carbonaceous fibres are found among PM in air polluted areas requires further attention. This presentation aims to give an overview about the differences in particle and fibre lung-cell interactions, explaining the underlying biological mechanisms observed for these two distinctly different material types which are important towards understanding their (possible) long-term, adverse health effects.

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Rueda Jaime / District Secretariat of Environment, Bogotá

Field evaluations of retrofit DPF in public transport buses using number concentration of solid particle number in Bogotá..

Nowadays in Bogota, the Secretaría Distrital de Ambiente (District Secretariat of Environment) is in the initial state of fleet DPF retrofit program to reduce emissions of Particulate Matter in the city. Policy establish as strategy to control emission in retrofitted buses the measurement of nanoparticles in idle speed upstream and downstream DPF, followed by calculating the removal efficiency with an accepted value above 97%, also establish opacity cycle downstream DPF with a threshold of 0.24 m-1 in k-value.

In this study is evaluated the behavior of field measurements of Solid Particle Number in nanoscale range, Mass of PM2.5 and opacity in three buses with DPF installed (1 Euro II+DPF and 2 Euro III+DPF) and its comparison to other technologies present in the city (Euro II to V), also is evaluated the behavior of CPC nanoparticle emission tester TSI NPET 3795 under six engine speed conditions testing (idle speed, 1200 rpm, 1500 rpm, Stoll test, Opacity cycle and Chilean cycle). A Maha 6.2.1 Opacimeter (Laser Light Scattering Principle), a Capelec Optical Opacimeter and a TSI NPET 3795 have been used in parallel measurements. The measurement campaign was conducted during 4 weeks with a total of 224 validated tests, analyzed with descriptive statistics and normality tests.

The results shows, as it is to be expected, medians concentrations of solid particle number SPN above 10^6 #/cm³ in all vehicles upstream or without DPF for all technologies, and below 30.000 #/cm³ in the buses with DPF, considering only the test in steady state and 0% load. In the other hand, evaluating the removal efficiency, we found that when the bus just arrived from operation during all morning, presented removal efficiency below 97% (96,62%); the measurement was developed once more time after two hours and the efficiency increased up 97% (97.47%), therefore is necessary know about temperatures and pressures upstream DPF during the test of SPN and establish a range to made the tests.

Additionally, the NPET had good behavior in steady state test, although in transient state it presented frequently "Low pulse height error", the second generation Maha Opacimeter presented values of PM2.5 out of range in test downstream DPF for steady tests, and the optical opacimeter has in some cases errors above 0.5 m⁻¹ downstream DPF, It was found a correlation between SPN and PM2.5 of R²=0.7343. Concluding, SPN is a superior metric to opacity for determining DPF conditions, although the Maha opacimeter could detect malfunctions in DPF as from detection of high concentration of PM2.5.

Engine Load	State	Engine Speed	Condition	Time of measuring	Notation
0%	Steady	Idle	upstream DPF	3 minutes	M1-A
			downstream DPF or w/o DPF	3 minutes	M1
		1200 rpm	upstream DPF	1 minute	M2-A
			downstream DPF or w/o DPF	1 minute	M2
		1500 rpm	upstream DPF	1 minute	M3-A
			downstream DPF or w/o DPF	1 minute	M3
	Transient	Opacity Cycle (4 free acc.)	downstream DPF or w/o DPF	2 minutes aprox.	M-Opa
		Chilean Cycle (4 free acc.)	downstream DPF or w/o DPF	2 minutes aprox.	M-Chile
Gearbox in Drive	Shifting D	Idle	upstream DPF	30 seconds	D1-A
			downstream DPF or w/o DPF	30 seconds	D1
	Transient	Stoll Test	upstream DPF	10 seconds aprox.	D-Stoll



Linear correlation between PM2.5 and SPN

Schmatloch Volker / Sparherm Germany

Emission Testing of wood fired stoves or fireplaces – Standards and Test Procedures in Australia/New Zealand, Europe and North America

Wood fire may be the oldest source of heat used by man. Today small wood fired heating appliances such as stoves or fireplaces are used in many countries not only to provide heat but also for decorative purposes. Therefore it is obvious that modern wood fired appliances are available in a large variety of designs and are operated in a large range of operating conditions. On the other hand wood fired appliances contribute significantly to the PM10 concentration in ambient air of many industrialized countries. For this reason emission limits for these appliances exist in many countries. General European emission limit values will be implemented by 2022 and are expected to replace national regulations by then. The current national regulation predominantly rely on the European Standards EN13229 or EN13240 which are expected to be replaced by a new revised and unified standard EN16510. Besides these European Standards there are specific methods in the UK (Clean Air Act 1993 and BS PD 6434) and in Norway (NS 3058 and NS 3059). In northern America the relevant regulation (80 FR 13671) has been revised by the US Environmental Protection Agency (EPA) in 2015. Canadian standards are similar but also offer additional procedures. In Australia and New Zealand test procedures have been described in standards AS/NZS 4012 and 4013. Since any limit values set in a specific country are related to given test procedures, different test methods have been defined in several countries. For this purpose type test standards need to aim at well reproduceable procedures that still do decently reflect behavior of real operating situations. For this purpose some parameters need to be carefully controlled while others may be chosen in a manner that more resembles practical use of the appliances. In this respect the various methods differ by setting different priorities. This is reflected by some methods relying on premanufactured fuel, such as stapled crib wood in northern America. while others use more natural cord wood in Europe or Canada.

Another important difference between methods results from the method of sampling. While methods based on the original northern American sampling method by full flow dilution tunnel that simulates condensing conditions and allows measurement of a sum of solid particles and condensables, in Europe there is the approach to measure solid particles separately and consider condensables by a parallel VOC measurement.

This paper gives an overview of major procedures for testing the particle emissions of appliances such as wood stoves or fireplaces. Practical aspects of the applications of different test procedures are shown. Specific cases of stoves show results from different test procedures. Details of relevant test methods offer important background information for understanding the impact of upcoming regulations on air quality.

Schmidl Christoph / BIONERGY 2020+, Austria

Real-life emission of automatically stoked biomass boilers

Background: Emission reduction is one of the major topics in the development of residential biomass boilers. National and European legislation is the main driver by reducing the thresholds for emission parameters like TSP, CO or OGC. These parameters are measured according to harmonized European Standards (i.e. EN303-5) under steady-state operation modes (full-load and partial-load). As a result state of the art technologies perform very well under these conditions. A side effect, however, is that development usually does not focus on non-steady operation modes like starting, stopping or load-modulation. All operation modes which might be important in real life operation. Therefore it is desirable to obtain information on the performance of biomass boilers under these non-steady operation modes as a basis for advanced development of combustion technology and heating system design to minimize emissions in real life application.

Investigation methods: Four pellet boiler types with a top feed burner, which are designed for operation without buffer storage tank, were investigated in a first test series. Gaseous and particulate emissions as well as energy efficiency were measured in different operation regimes under laboratory and under real life conditions, and compared with standard type testing:

- 8 hours load cycle test simulating real life situation at a test stand
- Full load test under field conditions
- 24 hours variable heat demand in field tests of various heating system configurations (solar panel, different heat distribution systems,...)

A second test series focused on PAH-emissions from pellet boilers. Measurements were conducted for seven different boilers with different types of burner design. Emissions of BaP were determined in different operation phases which were full-load, partial-load, start-up and shut-down. For all tests also gaseous and total particulate matter emissions were determined to enable correlation analysis for BaP emissions with standard emission parameters.

<u>Results:</u> Measurements confirmed that real life operation of pellet boilers including transient phases (start, stop, modulation mode) leads to increased emissions (CO, NOx, VOC and TSP) compared to type testing. Furthermore it could be evidenced that load cycle test results are in good accordance with 24 hours operation performance under real-life conditions, and therefor appear a suitable tool to estimate real life performance of pellet boilers. The BaP-measurements revealed significantly higher emissions in start-up and shut-down compared to steady-state operation phases (full-load and partial-load mode). The factors between start-and full-load-BaP-emissions were between 10 and 1000 indicating huge variations of BaP-emissions among typical operation phases.

Conclusions: A decrease of emissions of CO, NOx, VOC and TSP but also of PAHs under real life operating conditions relies on a reduction of emissions in transient operation phases like start-up, shut-down or modulation mode. Consequently not only the combustion technology is influencing the real-life emission release, much more the sizing and design of the heating system and its control strategy are influencing the occurrence of these operation modes. A load cycle test is capable to assess the performance of automated combustion appliances under variable operation conditions and consequently is suited to be applied for estimating its real-life emissions and efficiency.

Seljeskog Morten / Department of Thermal Energy Norway

Variables affecting particulate emissions from residential wood combustion – simultaneous sampling on hot and ambient filter

Wood heating is an important worldwide source of emissions of particulate matter, comprising black and organic carbon. In Norway, woody biomass combustion is a significant source of particle emissions. In the current work we have performed simultaneous gravimetric filter sampling of particulate matter in flue gas from wood stove combustion, both in-stack and from dilution tunnel, on hot filter (\geq 70 °C) and on ambient filter (\leq 35 °C) respectively, to determine to which extent variables inherent to EN 13240 DIN+ and NS3058-59 affect the amount of measured particulate matter.

For all the tests the collected mass of TSP on the FFDT filters were found to be substantially higher than on the HFs. When compared on a common unit in g/GJ, about 4X and 8X more was measured on the FFDT filter for birch and spruce, respectively. More mass due to condensation of organic gaseous compounds on the FFDT filter was expected. Overall, the amount of particles collected with the FFDT method was about 6.5X higher than the amount of particles collected on the HF, when comparing overall results. Comparing only the nominal series, 7.6X more particles were collected with the FFDT method. At high load the difference were only 2.7X more particles collected.

As DIN+ requires only 30 minutes of sampling after 3 minutes, it was expected that when testing in accordance with NS, over the whole batch period, this would produce significantly more particulate matter on both the HF and the FFDT filter. However, the results were mixed. At DIN+ conditions, with 30 min. of sampling, only a marginal portion of the particles is captured relative to the amount on the FFDT filter. A further increase in the sampling period do not seem to increase the amount of captured particles on the HF.

The current results also indicate that fuel load as an important factor, which actually significantly affects the particle emissions. A fuel load of 1.7 kg, as opposed to 1.1 kg given by the manufacturers specification of nominal load, produces 3x more emissions on the HF and 2x more on the FFDT filter, in spite of only sampling for 30 min. Any new method should therefore take into consideration how the mass of the test fuel is defined, like in NS3058-59, rather than following the manufacturers recommendation.

When comparing the variation between the two methods under investigation, DIN+ and NS3058-59, the results showed less pronounced variation for the FFDT compared to the HF method. The most reasonable explanation for this is that the FFDT collects more particulate mass, and therefore is less vulnerable to deviations due to fuel type and sampling period. In addition, the fuel is more homogeneous in size when applied according to NS3058-59, aiding the improvement of the relative standard deviation.



Collected particle emissions on HF and for FFDT for all experiments in g/GJ

Keywords: Wood stoves, test standards, particulate emissions, EN 13240 DIN+, NS3058-59

Sioutas C. / University of Southern California

Fine and Ultrafine Particulate Organic Carbon in the Los Angeles Basin: Trends in Sources and Composition

In this study, $PM_{2.5}$ and $PM_{0.18}$ (particles with dp < 2.5µm and dp < 0.18µm, respectively) were collected during 2012-2013 in Central Los Angeles (LA) and 2013-2014 in Anaheim, California, USA. Samples were chemically analyzed for carbonaceous species (elemental and organic carbon) and individual organic compounds. Concentrations of organic compounds were reported and compared with many previous studies in Central LA to quantify the impact of emissions control measurements that have been implemented for vehicular emissions over the past decades in this area. Moreover, a novel hybrid approach of molecular marker-based chemical mass balance (MM-CMB) analysis was conducted, in which a combination of source profiles that were previously obtained from a Positive Matrix Factorization (PMF) model in Central LA (Heo et al., 2013), were combined with some traditional source profiles. The model estimated the relative contributions from mobile sources (including gasoline, diesel, and smoking vehicles), wood smoke, primary biogenic sources (including emissions from vegetative detritus, food cooking, and re-suspended soil dust), and anthropogenic secondary organic carbon (SOC). Mobile sources contributed to 0.65±0.25 µg/m3 and 0.32±0.25 µg/m3 of PM₂₅ OC in Central LA and Anaheim, respectively. Primary biogenic and anthropogenic SOC sources were major contributors to OC concentrations in both size fractions and sites. Un-apportioned OC ("other OC") accounted for an average 8.0 and 26 % of PM2.5 OC concentration in Central LA and Anaheim, respectively. Based on the MM-CMB model output, a 57% decrease in contribution of mobile sources to the total OC from 2009 to 2013 was estimated. Comparison to previous studies in Central LA indicated that PAHs concentrations decreased by 40-70% from 2008-2013. Hopanes and steranes, important tracers of vehicular emissions, also decreased by roughly 50-70% over the past decade in Central LA. The reduction trend in vehicular emissions tracers indicates the impact of implemented regulations on vehicular emissions in LA Basin in the past decade. This has likely had a positive impact on public health as recently evidenced in a study showing improvements in pediatric lung-function growth that paralleled improvements air quality from the 1990s compared with the period of 2007 to 2011 in the LA basin (Gauderman et al., 2015).



Figure 1. Monthly average source contributions (µg/m3) to ambient OC for PM2.5 and PM0.18 in a) Central Los Angeles and b) Anaheim. Primary biogenic source accounts for emissions from vegetative detritus, food cooking and re-suspended soil dust.

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Swanson Jacob / Minnesota State University

Fuel sulfur impacts the formation of carbon nanotube-like particles in diesel engines

Previous work has indicated the potential for the production of carbon nanotubes in diesel engines (Jung et al., 2013, Lagally et al., 2012). A recent study indicates the presence of anthropogenic carbon nanotubes in the lungs of children exposed to ambient air in Paris (Kolosnjai-Tabi et al., 2015). While this evidence is suggestive, a full evidence-based explanation has not yet been put forward. Based on a known methodology and recipe for the gas phase synthesis of carbon nanotubes in a tube furnace reactor (Li et al., 2004), we developed the hypothesis that fuel sulfur content and the presence of iron nuclei would significantly affect the generation of carbon nanotubes in diesel engines. Experiments were conducted on a four-stroke overhead valve Yanmar L100V 435 cm³ single cylinder engine that was aircooled and naturally aspirated. The engine was connected to a dynamometer to control speed (1800 rpm and 2400 rpm) and load (75% load) and fueled with diesel fuel containing varying concentrations of sulfur (from 0 - 4500 ppm) and ferrocene (0 - 36 ppm Fe). Particle size distributions were measured with and without a catalytic stripper to determine the fraction of solid particles. TEM samples were collected at every condition. At the 1800 rpm, high load condition, zero sulfur and zero ferrocene condition, spurious carbon nanotube-like structures were identified on 3 out of 100 randomly selected TEM images. At the 1800 rpm, high load condition, high sulfur and high ferrocene condition, carbon nanotube-like particles were clearly identified on 46 out of 100 randomly selected TEM images. As shown in Figure 1, some images contained more than one carbon nanotube-like particle. Further image analysis is being conducted to fully elucidate whether these particles are carbon "rods or carbon "nanotubes." While these levels of sulfur and ferrocene are not present in on-road diesel fuels in the US or many other developed countries, they are relevant concentrations for onroad diesel fuel used in many other countries, marine fuels used internationally, and aviation fuels. Our results provide highly conclusive evidence that supports the continued reduction of sulfur and organometallic additives in fuels everywhere.



Figure 1. Example TEM images showing carbon nanotube-like particles.

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Vojtisek-Lom Michal / Czech Technical University Prague

FTIR-PEMS, Mini-PEMS and Micro-PEMS: Extending portable on-board monitoring systems to non-regulated pollutants and small engines

Damage caused to the human health, and consequently to the society in general, by exhaust emissions from internal combustion engines is increasingly higher than predicted based on decreasing emissions limits, as real-world emissions, in many cases, increasingly exceed type-approval levels. Modern engines increasingly rely on precise controls of combustion and exhaust aftertreatment to achieve low emissions of regulated pollutants, and departures from the optimum, whether intentional or not, lead to excess emissions. Such departures are more frequent in the real world as engines tend to be optimized primarily for test cycles and for regulated pollutants.

The concept of real driving emissions measurement by portable on-board systems (PEMS) has been introduced to assess realistic emissions of vehicles under real-world operation, first for research purposes, and recently for in-service conformity testing. This paper extends the concept of the present measurements of primarily NOx and PM on primarily road vehicles and large non-road mobile machinery to small engines and to non-regulated pollutants.

For measurement of non-regulated gaseous pollutants resolvable in the infra-red spectra, two different commercial Fourier Transform Infra-Red (FTIR) spectrometers with a 0.5 cm-1 optical resolution have been modified for in-vehicle operation. This paper reports on the measurement of real-world exhaust emissions (real driving emissions, RDE) of reactive nitrogen compounds (NO – nitrogen oxide and NO2 – nitrogen dioxide, together labelled as NOx, NH3 – ammonia, N2O – nitrous oxide) from diesel cars, trucks and buses.

NOx contribute to the formation of tropospheric ozone, NO2 is a lung irritant, N2O is a potent greenhouse gas. The combustion process in the engines produces primarily only NO formed from atmospheric nitrogen at high combustion temperatures. Three-way catalysts used on gasoline engines produce NH3 when run with excess fuel, and selective reduction catalysts (SCR) on diesel engine produce NH3 when overdosed with NOx-reducing reagent (urea, sold as AdBlue). N2O is released from some NOx storage catalysts (LNT) during regeneration, and SCR under some conditions. Some types of oxidation catalysts intentionally produce more harmful NO2 from NO to reduce regeneration temperature of diesel particle filters. Efforts to reduce the emissions of CO2, NOx and particulate matter (PM) have therefore created a concern about NO2, NH3 and N2O emissions. NOx and other emissions have been also reported to be higher during real driving than during laboratory tests historically used for both type-approval of new vehicles and for establishment of emissions factors, based on which the total emissions of the general vehicle fleet are estimated. This is due to increasing complexity of advanced combustion and exhaust aftertreatment controls, which are – partly unintentionally, partly deliberately – tuned primarily to achieve low, compliant emissions during the type-approval test.

Data presented here confirms that two "new" pollutants originating from aftertreatment - ammonia, a particle precursor, and N2O, a potent greenhouse gas - can be emitted in non-negligible amounts.

For measurement of small vehicles, a **miniature system (Mini-PEMS)** composed of primarily garage equipment has been used to estimate the emissions of CO, CO2, NOx, and particulate matter on small engines which are subject to lenient or no emissions limits.

The authors expect that the disproportionality of distribution of vehicle emissions (small fraction of operating time being responsible for large share of emissions of a given vehicle, and small fraction of vehicles being responsible for large share of fleet emissions) will increase, and the RDE measurements will need to be expanded, requiring simple, low-cost PEMS, without particular need for high accuracy. It is expected that PEMS will be further miniaturized, with a Micro-PEMS fitted at the end of the tailpipe, featuring on-board diagnostic sensors used on heavy-duty vehicles and a flow measurement element, being already technically feasible. Processing and interpreting RDE data will therefore become the next challenge. The authors recommend considering treating RDE measurements and data in a similar manner as data from Monte-Carlo simulations of complex nonlinear systems.

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Assessment of the effectiveness of the low emission zone Leipzig by measurements of soot and the ultrafine particle number concentration

A low emission zone aims vehicles with high particulate engine emissions in areas. The engine emissions of diesel and gasoline injection vehicles are believed to be toxic and carcinogenic. Diesel vehicles without particle filters emit ultrafine and fine particles, which consist largely of soot and carry other pollutants. The ultrafine diesel particles contribute to PM10 mass concentration only a very little and the control of the effectiveness becomes very uncertain. Therefore a joint scientific monitoring program has been realized by the Saxon State Office for Environment, Agriculture and Geology and the Leibniz Institute for Tropospheric Research to accompany and evaluate the introduction of the low emission zone in Leipzig by measurements.

The low emission zone in Leipzig was directly introduced with the green bagde in 2011. It comprises 62 % of the urban area. The announcement and enforcement of the low emission zone caused an accelerated modernization of the vehicle fleet in the city. The most modern car fleet of Saxony exists Leipzig presently.

Figure 1 shows the weekly variation of the ultrafine particle number concentration, which corresponds to similar traffic volumes. The weekly variation of the soot particle mass concentration is basically identical. The concentration decreased in 2014 to half compared with those of 2010 during daytime. The assessment of the effectiveness of the low emission zone, the increment of the particle concentration of the local traffic was determined by the so called Lenschow approach.

After four years Low Emission Zone, the soot mass concentration and the ultrafine particle number concentration were reduced by 47 and by 56%, respectively. This significant reduction was achieved due to the introduction of diesel particle filters pushed by more stringent European emission standards. However, the most modern fleet of Saxony brought no improvement for the NO₂ concentration in the city. The low emission zone in Leipzig led to an accelerated modernization of the vehicle fleet in Leipzig and to a reduction of highly toxic composition in particulate matter.



Figure 1: Weekly variation of the ultrafine particle number concentration (30 bis 200 nm) at the a roadside in the city of Leipzig before the implementation of low emission zone in 2010 and years later

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A simple sampling method to analyze cell toxicity of nanoparticles and condensable compounds from biomass combustion

Energy wood utilization is expected to significantly increase within the next years in order to replace fossil fuels. However, biomass combustion contributes to air pollution, especially with inhalable particulate matter (PM), which induces adverse health effects. The current air pollution control legislation considers emission limits on filterable solid PM in the hot flue gas only. Condensable organic compounds (COC) and potential secondary organic aerosols are usually not directly measured and rarely investigated. Furthermore, experimental methods to investigate health effects of emissions in the stack applied so far are complex and costly. Hence information available on health issues from flue gases is scarce and limited to a small number of specific applications.

Therefore, the aim of the present investigation is to develop an economic and less complex method for the collection and subsequent in vitro cell analysis of flue gases from biomass combustion containing all relevant particle classes, i.e., salts and soot contained in solid PM, and additionally including COC. For this purpose, sampling methods US-EPA-5H and VDI-2066 are adapted. Hot flue gases are passed through impingers which are cooled to 5°C. The rapid cooling induces the condensation of mainly COC, into the impinger fillings. Subsequently, cells are exposed to these liquids and the cell viability is analyzed. Two parallel sampling trains are applied: one with a filter upstream of the impingers to determine the cytotoxicity of COC only and one without a filter to determine the cytotoxicity of total PM.

To characterize the sampling procedures and subsequent cell analyses, the influence of different parameters (e.g., blanks, reproducibility, different cell types) is investigated. Furthermore, different combustion devices and conditions are compared. In addition to the cell analysis, a detailed characterization of the flue gas (particle size distribution, PM mass, O₂, CO, NO_x, CH₄, total hydrocarbons) is carried out.

First results indicate that the proposed method is capable to distinguish between cytotoxicity of COC only and the one of total PM for some combustion devices and conditions. Furthermore, the method reveals significant differences in cytotoxicity of flue gases from the investigated combustion devices and conditions in the following order (highest to lowest, Figure 1): re-fill of a log wood stove, pellet boiler operated at combustion with high excess of air, flaming combustion in the log wood stove, pellet boiler operated at lack of air and with optimum conditions. The industrial wood chip boiler reveals no detectable cytotoxicity.



Figure 1: Cell viability as function of fuel input causing the organic carbon amount which was detected in the solvent. Solid and dashed lines denote cell viability of COC only and total PM, respectively.

Example A: In the log wood stove at re-fill conditions, a fuel input of 0.06 kWh (0.01 kg wood) leads to organic carbon in the solvent which induces 50% dead cells. Example B: In the pellet boiler at excess of oxygen conditions, a fuel input of 0.5 kWh (0.1 kg wood) leads to organic carbon in the solvent which induces 50% dead cells.