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Bogota DPF retrofitting Program for the BRT System of Bogota operating at high Altitude

As an attempt to improve air quality, Bogota District's Government established that all new buses to be used for public transportation since 2014 must meet EURO IV and V emission levels. Nowadays, in-use diesel vehicles in the District are equipped with EURO II and III engines and will have a 10-year lifespan. The PM₁₀ levels are high for Bogota. 1400 tons per year of PM₁₀ are emitted by mobile sources in Bogota, according to the Bogota Secretary of the Environment. Virtually all these PM emissions come from public buses and cargo trucks. The public transport system has had two components. The first one is formed by small capacity buses running in a rather informal way. The second one is a BRT system that started its operation in 2000 with 900 Euro II articulated buses. In 2005, 1000 Euro II and III diesel buses were added to the system. Nowadays, the BRT system of Bogota is supported by 4000 diesel buses. In 2010, the integrated public transport system initiative started a transformation of the informal transport system, reorganizing bus routes, bus stops and, most importantly, the public transport financial scheme. Most of these buses are equipped with Euro II and Euro III engines.

In 2010, the Mayor of Bogota issued a decree that forces the implementation of Diesel Particulate Filters for all buses of the Public Transport System of the city. As a consequence, Bogota is implementing a DPF retrofit program, in association with the Swiss Agency for the Development and Cooperation, as part of the "Climate and Clean Air Program In Latin-American Cities". Under this program, the city's Secretary of Environment is testing 13 old diesel buses and 2 new buses. 4-weeks datalogging exhaust pressure and temperature have been recorded. The buses have also been tested for performance and exhaust emissions, including particle number, under dynamometer conditions. Maintenance practices were evaluated in order to define the feasibility of implementing DPF devices.

Large vehicles (articulated and 12-meter buses) show high exhaust temperatures and opacity values are low, owing to good maintenance practices. However, particle number concentrations are over 50 million particles/cm³. Small buses, mostly Isuzu and Mercedes Benz for 50 passengers, are in a very poor maintenance state, and opacity values are high. Particle number concentrations are also high, similar to those measured in large and well-maintained vehicles.

Amini H. / Kurdistan University of Medical Science, Iran

Estimating Spatial Variability of Ambient Particulate Matter Using Land-use Regression in Tehran

Background: The Middle Eastern city of Tehran, Iran has poor air quality compared with cities of similar size in Europe and North America. In this study, the authors aimed to develop land use regression models in Tehran to estimate spatial annual and seasonal patterns of ambient particulate matter with an aerodynamic diameter of 10 μm or less (PM_{10}).

Investigation methods: Hourly PM_{10} concentrations for the 2010 calendar year were obtained from 23 air quality monitoring stations. The mean of the PM_{10} data from January 1st, 2010 through January 1st, 2011 for all monitors was used as the response variables. We also divided the year into warmer and cooler seasons, which were defined, respectively, as April through September and October through March based on World Health Organization (WHO) guidelines and on the highest and lowest mean daily temperatures at Mehrabad International Airport. We generated 210 potentially predictive variables in 6 classes and 73 sub-classes within geographic information systems (GIS) to be used as the predictor variables in the LUR model building. The six classes were Traffic Surrogates, Land Use, Distance Variables, Population Density, Product Variables, and Geographic Location. A systematic algorithm for LUR model building was developed to select variables based on (1) consistency with *a priori* assumptions about the assumed directions of the effects, (2) a p-value of < 0.1 for each predictor, (3) improvements to the leave-one-out cross-validation (LOOCV) R^2 , (4) a multicollinearity index called the variance inflation factor, and (5) a grouped (leave-25%-out) cross-validation (GCV) for final model.

Results: The annual, warmer season and cooler season mean concentrations of PM_{10} across the stations were 100.8, 100.4, and 101.2 $\mu\text{g}/\text{m}^3$, respectively. The Pearson's correlation for the whole year, warmer season, and cooler season averages ranged from 0.94 to 0.99. The R^2 values ranged from 0.62 to 0.67. The LOOCV and GCV R^2 values ranged, respectively, from 0.48 to 0.57 and 0.50 to 0.55, respectively. The models were consistent across the seasons. Concentrations increased with increasing street density and proximity to bus terminals, airports or air cargo facilities, major roads, and military areas. The highest partial R^2 values were for proximity to bus terminals and airports or air cargo facilities. The high concentrations of PM_{10} were dispersed throughout the city, and a clear area of low concentrations was evident in the north.

Conclusions: Air pollution is an emerging public health concern in Tehran, and local evidence about its effects—as a vital part of evidence based public health—is needed to drive the changes that will lead to further air quality improvement. We generated LUR models and regression maps of PM_{10} for use in upcoming population-based epidemiologic studies and science based policy making in the city. Although there are limitations inherent to using regulatory network data for LUR modeling, we have developed methodological approaches to reduce the impacts on the quality and utility of our results.

Andres H. / METAS Switzerland

Field Measurement, Measuring Instruments Ordinance: Calibration, Certification, Measurement Cycle

Since January 1st 2013 the ordinance of the FDJP on exhaust gas analyzers (SR 941.242) includes the new measuring instrument category “Nanoparticle measuring instruments for combustion engines”. These instruments shall be used in replacement of today’s insensitive opacimeters for periodic official controls as well as emission tests of owners of construction machinery. The ordinance regulates their metrological requirements; their procedures for bringing into circulation as well as their procedures to maintain the measurement stability.

Instruments must have a minimal measurement range of $5 \times 10^4 \text{ cm}^{-3}$ to $5 \times 10^6 \text{ cm}^{-3}$; indicate results at ambient conditions; operate between -10 °C and $+40 \text{ °C}$; 860 hPa and 1060 hPa; withstand vibrations class M2 and electromagnetic disturbances class E2. The error limits are derived from the UN-ECE R83 requirements. Yet, adapted for the use in the field, the required counting efficiencies at defined particle sizes are less stringent and thus accomplishable with different measurement principles. As only solid particles are regulated the instruments has to efficiently remove volatile particles ($> 95 \%$). The instruments have to be robust, respond within 10 s and be tamper-resistant and portable.

Only conformity assessed and certified “Nanoparticle measuring instruments for combustion engines” can be brought into circulation in Switzerland. After a successful type testing (Module B) the conformity of each instrument is certified by a product testing (Module F). Conformity certified instruments will be marked with the conformity label CH followed by the number of the issuing conformity assessment body, the metrology label M and the last two digits of the year of bringing in circulation. At the moment the only conformity assessment body for “Nanoparticle measuring instruments for combustion engines” is METAS-Cert (number = CH01).

To maintain its measurement stability over time, each instrument has to be maintained at least annually by a qualified person and annually verified by METAS or an authorized verification body. For the moment only METAS will be verifying “Nanoparticle measuring instruments for combustion engines”.

In correspondence to other regulated exhaust gas analyzers “Nanoparticle measurement instruments for combustion engines” have to follow an “official” measurement mode. This mode ensures that measurements are done according to the procedures defined by the Federal Office for the Environments. At the end of an “official” measurement at least the following parameters have to be permanently stored: the term “official” measurement, the date and time of the measurement, the weighted mean of the particle number concentration, and the duration of the measurement.

Arnold F. / Max Planck-Institute Germany

**Combustion Mediated Sulphate Nanoparticle Formation at the Tropopause:
SO₂ lifted from Ground-level Combustion Competes with Air Traffic SO₂**

The tropopause region (TR) offers ideal conditions for photochemical formation and growth of new volatile nanoparticles. In middle latitudes, most air traffic takes place in the TR. In the TR, the relevant major nanoparticle formation mechanisms are homogeneous nucleation (HONU) and heterogeneous ion induced nucleation (INU). The positive and negative ions involved in INU, in the TR, are generated by galactic cosmic rays. The key trace gas, involved in HONU and INU in the TR, is H₂SO₄. It is formed by atmospheric OH-induced conversion of SO₂. A local source of SO₂, present in the TR, are air craft cruising in the TR. In addition, SO₂ from volcanic activity may reach the TR. Still another, but previously not well characterized SO₂ source is upward SO₂-lift from ground-level combustion sources. Here we report on our recent unique air borne measurements, which reveal that cyclone mediated SO₂-lift from East-Asian and North-American ground-level combustion sources is a major source of SO₂ and the resulting volatile aerosol particles present in the extra-tropical TR. A key of our airborne measurements were measurements of the ideal transport tracer Xe-133, accidentally released by the nuclear disaster at Fukushima. Our combined airborne Xe-133, SO₂, and aerosol measurements, identify unambiguously a very efficient transport path connecting the globally strongest SO₂ emission region (North-East-China/Korea/Japan) with the TR. Furthermore, our measurements also indicate cyclone mediated lift to the TR of SO₂ from North-American ground-level combustion sources. These findings and their consequences for aerosol and aerosol effects deserve future attention

Barro Chr. / ETHZ Switzerland

Soot Reduction Mechanisms Using Post-Injections under Varying EGR Conditions

Past research has shown that post injections have the potential to reduce Diesel engine exhaust PM concentration without any significant influence in the NO_x emissions. However, an accurate and general rule of how to parameterize a post injection such that it provides a maximum reduction of PM emissions does not exist. Moreover, the underlying mechanisms are not understood thoroughly. In earlier research it was observed that soot reduction due to a post injection is mainly based on two reasons: increased turbulence from the post injection during soot oxidation and lower soot formation due to lower amount of fuel in the main combustion at similar load conditions. A third effect of heat addition during the soot oxidation is debated in the literature.

The experimental investigation presented in the current work aim to link the in-cylinder and exhaust soot measurements of a passenger car diesel engine with detailed optical analysis of measurements, obtained using a cylindrical constant volume combustion chamber (CVC) with high optical access. The bore of the chamber is 90mm; similar to the bore of the passenger car diesel engine. The engine and the CVC are equipped with fast pressure analysis system and a miniaturized optical light probe (OLP, applicable through the glow plug bore of the engine). The CVC is further equipped with a 2-colour pyrometry setup with 2-D spatial resolution (2D2CP). The measurements acquired using the OLP and the 2D2CP are a representative soot mass evolution over time in 0-D and 2-D respectively. Additional cycle-end data are provided using a fast NO_x analyser and particle spectrometer connected to the exhaust line of the CVC.

The results show many similarities between the real engine and the CVC. The exhaust soot emissions increase with increasing EGR rate. The soot evolution shows deteriorated soot oxidation with increasing EGR rate. In addition, the spatially resolved soot distribution confirms an influence of the soot from the post injection on the soot formed in the main injection for cases with short dwell, compared to no influence for cases with long dwell between main and post injection. The soot oxidation rate improves if interaction occurs. Furthermore, the mean particle diameter is not significantly affected by post injection application.

Bielaczyc P. / BOSMAL Poland

Particulate Emissions from Passenger Cars with DISI Engines Tested at Sub-Zero Temperatures

The abstracts for papers and posters must contain unpublished information on your research subject: background, investigation methods, results and conclusions. Graphs and references are very welcome. Acronyms should be avoided. Abstracts with < 300 words can not be considered. General information on products which are already commercially available can not be accepted as presentations for the conference but are very welcome at the exhibition. Please note, that submission of an abstract includes your agreement to publish your contribution as part of the proceedings of the conference.

The particulates present in vehicular exhaust are coming under ever closer scrutiny and are subject to legislative limits in many cases (in the European Union, the only exception being port fuel injected petrol fuelled vehicles, for the time being). It is widely acknowledged that current legislative laboratory test procedures in many ways represent a best case scenario – more aggressive driving cycles and less favourable ambient conditions can increase particulate emissions substantially.

Ambient temperature is generally the *environmental* parameter of most importance regarding particulate emissions from an engine, particularly for the relatively brief, periods of operation typical for passenger cars operating from a cold start. This paper discusses the phenomena in question for vehicles with DISI engines and identifies and discusses some key findings from the literature, as well as presenting recent results from BOSMAL's research.

In general, cold start is challenging for an internal combustion engine for many reasons, with multiple emissions impacts [1,2]. Sub-zero ambient temperatures exacerbate these problems, leading to significant difficulties in forming combustible mixtures. Furthermore, increased fuel flow rates and a lack of particle elimination via oxidation in the cold three-way catalyst conspire to increase cold start emissions further still [1].

While particulate matter limits are not specified for any vehicle type at low ambient temperature in EU legislation, various studies have examined particulate matter emissions at the "legislative" test temperature of -7°C. Such tests are performed in a laboratory on a chassis dynamometer, measuring diluted exhaust emissions with the aid of filters and a condensation particle counter, over well-known driving cycles. A review of some recent studies, together with further data obtained at BOSMAL, revealed reasonably consistent increases in particulate matter emissions as ambient temperature fell. However, the increase in particle number count is normally significantly greater than the increase in particle mass.

In the latest experimental work, two direct injection petrol vehicles were tested at low ambient temperatures (-7°C/-15°C) on three fuels, with particulate emissions results compared to results from the same fuels when the vehicles were tested at 25°C. Over the whole test cycle, the results implied a linear relationship between ambient temperature and particle mass and a power-type relationship for particle number. Simple corrections were applied to the results to better understand the impact of ambient temperature on the emissions. The results showed that even when the engine is fully warmed up, ambient temperature continues to have an impact on particulate emissions from this engine type.

A brief evaluation of the subcycles of the NEDC driving cycle also elucidated further trends regarding the impact of ambient temperature on particulate matter emissions from shorter 'trips' [4]. In addition to research on particulate emissions themselves, research on test methods for testing under highly demanding conditions (e.g. low ambient temperature, among others) is also an important research direction.

Brem B. / EMPA Switzerland

Variability in non-Volatile Particulate Mass and Number Emissions of Aircraft Turbine Engines

Particulate matter (PM) emissions from aircraft gas turbines are a concern for human health, environmental pollution and climate change. Expected future regulations on emissions require a reliable determination and understanding of PM emission factors under variable engine and environmental conditions.

This work presents results of non-volatile PM mass and number emission indices (mass or number PM/ mass fuel) for aircraft gas turbine sources obtained with “piggy back” measurements at the engine test cell at SR Technics, Zurich Kloten. In total, emissions of 29 engines were measured over a period from January until October, 2013. The engines included eleven Pratt and Whitney (PW) 4000 engines (94” and 100” variants) and 17 CFM 56 engines (-7B, -5B and -5C variants).

The sampling system and system operation corresponded to the recently issued standard¹ and are only briefly outlined here. PM laden exhaust was continuously sampled by a single point retractable Inconel sampling probe at the engine exit plane. The aerosol sampled was then diluted with dry nitrogen or synthetic air by a factor of eight to ten and transported via temperature-controlled lines to minimize condensation, particle agglomeration, and gas-to-particle conversion. Non-volatile PM mass was determined with a micro soot sensor (MSS, Model 483, AVL Inc.) based on the photoacoustic detection principle. In parallel to the MSS, an AVL particle counter (APC) and a CO₂ analyzer (Model 410i, Thermo Inc.) provided PM number and CO₂ concentrations emitted.

At the current stage of the data analysis the following tendencies were identified in the data collected:

PM emissions show a clear dependence on combustor technology; while all single annular combustors have increasing non-volatile PM mass and number emission indices with increasing static engine thrust, the engines equipped with a double annular combustor have unique emission profiles with highest non-volatile PM emissions near 28% static thrust and extremely low emissions at higher to full thrust. In addition, improved newer combustor types designed for lower nitric oxide emissions such as the Talon type combustor of the PW 4000 engine have up to 50% lower PM mass and number emissions than the ones equipped with the traditional combustor types.

While PM relevant fuel parameters such as total aromatics content, naphthalenes and sulfur had little variability over the entire testing period, a clear effect of ambient temperature on PM emissions, in particular on the number emission index, could be identified for the same engine model (CFM56-7B). An increase in ambient temperature of 8°C lowered the PM number emission index by approximately 18% at all thrust levels.

Besides the determination of emission indices for various engine models and ambient conditions, current work further investigates the effect of engine deterioration on emissions, so a robust dataset can be provided in the long run to policy makers and the climate modeling community.

This work is supported by the Swiss Federal Office of Civil Aviation (FOCA)

Cachón L. / Matter Aerosol AG, Switzerland

The Golden PEMS: Technical Aspects and Outlook

The Portable Emission Measurement System (PEMS) methodology has been recognized by many governmental entities, such as the US Environmental Protection Agency and the United Nations Framework Convention on Climate Change. Particle counting on diesel cars is mandatory through Euro 5b since September 2011 and will be also introduced for GDI vehicles through Euro 6 by September 2014. The European Union and other countries throughout the world will continue to integrate particle counting into their emission standards, especially since the World Health Organization identified diesel exhaust as one of the most dangerous pollutants in existence. Moreover, the European Commission is working on the approach for the technical assessment of PEMS for particle number emitted by light-duty vehicles. The oncoming test procedure may include on-road measurements as an extension of the Particle Measurement Program (PMP).

With an eye on real driving measurements proposed in forthcoming European Emission Standards, Matter Aerosol has unveiled a novel portable instrument for solid nanoparticle counting and classification. NanoMet3 measures number concentration in a wide range of $1E3...3E8 \text{ \#}/\text{ccm}$ and average diameter in the size range 10...700 nm under real driving conditions.

To measure only the solid particle fraction, it is necessary to condition the sample thermally to eliminate the volatile fraction. The instrument features a separate sample at the source (tailpipe, CVS tunnel or stack) and conditioning of the exhaust probe according to the Post-Dilution Thermo-Conditioning principle, which is fully PMP compliant. The portable system is completed with a Diffusion Size Classifier sensor. Since its measuring principle uses electrical charging to count particles, it not only enhances the quality of the global measurement under real world conditions, but also the cost of acquisition and costs per test are significantly lower. Hydrocarbon emission measurement will no longer be affected by butanol contamination in the testing room or vehicle, nor will it be influenced by contaminated air.

The latest results, published by JRC during the evaluation of the PEMS-PN measurement technology on behalf of the European Commission, highlighted the optimal operability of the NanoMet3 under real driving conditions and the very good correlation of particle number in comparison with PMP Benchmark systems on the chassis dynamometer.

This paper intends to present the instrument functionality and the calibration procedure followed by some results from comparisons with traditional aerosol instruments in the laboratory and on-road.

Deinlein R. / Dinex, Germany

Dual Layer Coated High Porous SiC for SCR integration into DPF

In the recent years many papers have drawn attention in which the integration of DeNO_x functionality into wall flow filters for the after treatment of diesel engine exhaust gases as a new field of technology is described. The major target for this new area of development is to save space and costs in the whole after treatment system. Yet to integrate a sufficient amount of catalyst wash coat high porous substrates are needed. For this purpose a high porous SiC material was used to provide a new solution based on a dual layer coating. The main drawback of high porosity levels of 60 % and beyond is a significant reduction in the mechanical strength. Therefore the first layer consists of a nanoparticle coating to enhance the mechanical strength of the above mentioned filter substrate. On the other hand it can also be used to improve the catalytic performance and consequently to decrease the wash coat loading of the second layer which is supposed to be the active catalyst for the selective catalytic reduction (SCR) of NO_x by ammonia.

For this second layer three different types of SCR catalysts were investigated as potential candidates: zeolites, ceria/zirconia based mixed metal oxides and a titania/vanadia based composition. The respectively coated SiC filter substrates were analyzed in accordance to the impact on the pore structure and resulting back pressure as well as to their SCR performance. The results clearly demonstrate that the initial inactive nanoparticle layer in combination with the second active layer based on different catalysts lead to high SCR efficiencies at low catalytic wash coat loading.

For verification of the SCR data generated at the lab flow bench, engine bench tests on filters of 9"x10" in size were performed. A diesel oxidation catalyst (DOC) was used to adjust the NO₂/NO_x ratio in order to reach high NO_x reduction values. Moreover high NO₂ amounts are needed to support soot combustion likewise. The results demonstrate that a new type of diesel particle filter (DPF) has been developed, in which various types of SCR catalysts can be integrated. This new filter with integrated SCR functionality can be used in the design of exhaust systems with reduced volume, weight and costs, which still meets the EURO 6/VI requirements in respect to NO_x and PN reduction for petrol and diesel engines.

Di Iorio S. / Istituto Motori – CNR, Italy

Experimental Investigation of Ethanol-Gasoline Dual-Fuel on Particle Emissions of a Small Engine

The concerns on the air pollutants harmful effects on the human health and the environment and the depletion in the supply of fossil fuels have prompted to the necessity of engine efficiency improvements and exhaust emissions reduction. For these reasons great attention was paid to direct injection systems and oxygenated alternative fuels. Despite the higher complexity and cost, in fact, the direct injection system is even more applied also on spark ignition engines as the higher thermal efficiency and power output, as well as the lower fuel consumption and lower CO₂ emissions. On the other hand, direct injection spark ignition (DISI) engines are characterized by large particle emissions since less time is available for fuel evaporation and mixing and because of the fuel impingement. For this reason particle mass and number regulation has been introduced from Euro 6 also for gasoline light duty car. The alternative fuels are gaining even more attention both in Europe and USA as they can reduce both the exhaust emissions and the fossil fuel consumption. Among the liquid alternative fuel ethanol is the most widely used as it can improve engine efficiency by using higher compression thanks to its increased knock - limit due to its higher octane number. Typically, the blending of the conventional and alternative fuels takes place outside of the cylinder. The dual fuel modes, instead, allow an alternative approach to using gasoline–biofuel blends. In this case, in fact, the blend is formed inside the cylinder as the fuels are separately injected through a port fuel injection (PF) and direct injection (DI) systems. This configuration allows the blending of the fuel at different ratios according to the engine operating conditions. Typically, the fossil fuel is injected using the PFI system, while the biofuel is injected using DI. This configuration allows to exploit the charge-cooling effect of ethanol to lower the in-cylinder temperature and then increase knock limit and reduce NO_x emissions, and the beneficial effect of the oxygenated fuel on particle emissions reduction. The aim of the paper is the analysis of the effect of ethanol-gasoline dual fuel on particle emissions. The experimental activity was carried out on a small single-cylinder four stroke engine representative of the most wide spread motorcycles in Europe. The engine can operate both in gasoline direct injection (GDI) and port fuel injection (PFI) configuration. Ethanol was directly injected in the combustion chamber (DI fuel). The measurements were performed under steady state conditions at different engine operating conditions and dual-fuel ratios. The particle concentration was measured by means of a smoke meter. Moreover, the particle size distribution function was measured in the range from 5.6 nm to 560 nm by means of an Engine Exhaust Particle Sizer (EEPS). For dual fuelling was observed a strong decrease of particle emissions in terms of mass concentration. Nevertheless, the analysis of the particle size distribution highlighted for DF engine configuration a larger emission of ultrafine particles, which are the most dangerous for human health

Fierz M. / FHNW Switzerland

Towards Hand-Held DPF Inspection

Legal limit values for particle number emissions of on- and off-road vehicles as well as construction machines have been or are being introduced in many countries. In type-approval testing, the PMP protocol for the measurement of solid particle number has been introduced in the EU, but the PMP setup is far too complex for routine inspection in workshops or in the field. There is therefore a need for instruments that will enable inspection of particle filters in the field. For field use, such instruments should preferably be robust and easy to use.

In Switzerland, a new regulation has been introduced which defines requirements for particle number emission measurements (amendment of VAMV); however, so far no commercial instruments exist that fulfil these requirements. We are working on a simple particle measurement system that can be used to measure particle emissions in the field, and therefore also for field inspection of particle filters. We are placing particular emphasis on the development of a system that can be used easily under the harsh conditions of construction sites, i.e. it is imperative that the system is light-weight, small, and battery powered.

The new instrument is based on a previously developed prototype for a PMP-like field measurement, presented at the 2010 ETH nanoparticle conference. Both the particle detector (a nanecos partector instead of a diffusion size classifier) and the dilution system (circulating dilution, with the instrument in the dilution path) have been changed since then to reduce size, weight and complexity of the system.

We will present data both from the lab (removal of volatile particles, comparison with traditional instruments) as well as from field experiments with the new system.

Geiser M. / University of Bern, Switzerland

Responses of Healthy and Diseased Airway Epithelia to Aged Aerosols from Wood Combustion

Wood combustion for domestic heating and cooking is very common in many parts of the world and well recognized as a major source of atmospheric particles. A variety of organic compounds, including polycyclic aromatic hydrocarbons (PAHs) and particulate matter is emitted, their fraction depending on stove load. Particulate emissions are almost entirely in the inhalable size range and contain a variety of toxicants. Epidemiology identified individuals with pre-existing respiratory diseases as being more susceptible to adverse effects of air pollutants. This study aimed at investigating effects of primary and photo-chemically aged particles from wood combustion on normal and diseased human airway epithelia.

Beech wood was combusted in a logwood stove (Attika Avant, 2009) under low (2-3 kg) and high load (7-8 kg) conditions. The exhaust was diluted and injected through heated lines (200°C) into a 27m³ smog chamber. Particulate and gas phase were closely monitored and precisely measured by a combination of state-of-the-art instruments. After equilibration of particulate and gas phase in the smog chamber, a versatile aerosol concentration enrichment system (VACES) (Wang et al., *Aerosol Sci Technol* 47, 2012) was used to deposit a constant and high particle dose on lung cell cultures during each experiment. The enriched air stream was then guided through a charcoal denuder (removal of harmful gases) and entered an aerosol deposition chamber (Mertes et al., *J Aerosol Med Pulm Drug Deliv*, 26, 2013) for online deposition on cells at the air-liquid interface (ALI) under physiological conditions (37°C, RH 85%). Re-differentiated human bronchial epithelia (HBE) from normal and cystic fibrosis (CF) donors as well as the human bronchial epithelial cell line BEAS-2B were exposed to the aerosol for 2 hours. Additionally, particles were sampled on filters for further off-line analyses. After the exposure to primary emissions, secondary organic aerosols were produced by photochemical aging of the exhaust in the smog chamber under realistic atmospheric conditions. The enrichment and exposure processes were repeated for the secondary aerosols. Cell responses were analyzed within 24 hours after exposure to the aerosol. Cytotoxicity was assessed by measuring lactate dehydrogenase (LDH) release for necrosis and caspase-3 activation for apoptosis. Inflammation was monitored via gene expression and release of interleukin-6 and interleukin-8.

Exposure to all aerosol types resulted in significant changes of cellular responses. The results provide evidence for adverse effects of particles from wood combustion on airway epithelia after a single short-time exposure. Furthermore, HBE and BEAS-2B cells responded differently to aerosols.

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Gerlofs M. / NIPHE, The Netherlands

Health Effects of combustion Sources in Perspective

Exposure to air pollution from traffic is related to adverse respiratory and cardiovascular effects. Both particulates (PM) and gaseous components of engine exhaust contain many mutagens, carcinogens and chemical species known for their toxic effects at low exposure levels. For example, the PM fraction of diesel engine exhaust, a rich source of combustion-derived ultrafine or so-called nanoparticles, is especially relevant to thrombotic and vascular alterations. Vehicular emissions are the predominant source of fine particulate matter in the urban environment. With the reduction of engine exhaust by strict regulation, other emission sources might become more relevant. The relative burden of PM emissions from non-traffic sources (e.g. road/tyre/brake wear emissions or wood smoke) could become of greater concern when PM from tailpipe exhaust is diminished. In this light, it is not only important to elucidate what physicochemical properties play a crucial role in the development of adverse health effects but also which sources are most important.

To investigate independent contributions of PM characteristics, we exposed 31 healthy volunteers to ambient air pollution at five different locations in the Netherlands: an underground train station, two traffic sites, a farm and an urban background site. Each volunteer visited at least three different sites between March and October 2009, and was exposed for 5 h including intermittent exercise. During each 5 h exposure we performed a detailed characterization of air pollution on-site, including PM mass and number concentrations (PNC, highly dominated by the ultrafine particles), PM composition (e.g. elemental and organic carbon (EC/OC)), metals, PAHs, endotoxin, PM10 oxidative potential and gaseous pollutants (NO₂, O₃). We conducted measurements of lung function and exhaled nitric oxide (FeNO) and analysed blood and nasal lavage samples before exposure, 2 h after exposure and the next morning. OC, nitrate and sulfate were most consistently associated with different biomarkers of acute cardiovascular risk. The PM characteristics OC, endotoxin and NO₂ were associated with nasal inflammatory markers. Furthermore, changes in PNC, NO₂, and NO_x were associated with evidence of acute airway inflammation (i.e., FeNO) and impaired lung function. PM mass concentration and PM10 oxidative potential were not predictive of the observed acute responses. These results will be discussed in context of data from experimental and human studies.

Goudeli E. / ETHZ Switzerland

Coagulation of Fractal-like Aerosols in the Transition Regime

Gas-phase processes offer a proven scalable route for the synthesis of nanoparticles for the large scale production of commodities like fumed silica, carbon black and pigmentary titania (Pratsinis, 2010). Such processes allow the production of particles with different structures (e.g. spheres, rods, aggregates and agglomerates). Modeling the particle growth is of utmost importance for the design of aerosol reactors. Their particle dynamics span 10 and 15 orders of magnitude in length and time, respectively, and determine particle structure that affects the electrical conductivity, optical performance, processing and mechanical stability of product films and powders. Agglomeration (i.e. particles consisting of loosely attached primary particles) occurs both in environmental and industrial processes, especially in low temperature regions where sintering or coalescence are rather slow. The dominant coagulation mechanism is cluster-cluster agglomeration leading mainly to the formation of filamentary structures that are attractive in nanocomposites and particle suspensions (paints or polishing slurries).

Here the growth and detailed structure of fractal-like particles undergoing Brownian coagulation is investigated from the free molecular to the continuum regime. Particles in the free molecular limit follow random ballistic trajectories described by an event driven method whereas in the near continuum and continuum regime Langevin Dynamics are used to effectively describe their diffusive motion (random walk). The growth mechanism is controlled by the ratio of the characteristic sintering to collision times. The method is validated for fully coalescing particles by comparing the results from the mesoscale simulations to those from discrete-sectional models (Otto et al., 1994) and applied for aerosol coagulation-agglomeration (e.g. without any coalescence). The evolution of the properties of the resulting fractal-like agglomerates (e.g. geometric standard deviation and structure) is traced in the transition regime. The self-preserving size distributions of agglomerates are validated at the known limits of the free molecular and continuum regime (Vemury & Pratsinis, 1995) under dilute conditions (effective volume fraction, $\phi < 10^{-2}$).

Hagen D. / Missouri University, USA

PM Line Loss Correction without Direct Size Measurement

There is an increasing international concern for the environmental impact of jet engine exhaust emissions in the atmosphere, particularly their effect on the air quality around airports. The growth of commercial air traffic over the last decade has led to an increased contribution to the local inventory of gaseous and particle emissions from the operations associated with airports and aircraft engines. An accurate assessment requires that the number density and size of the aerosols within engine exhaust and aging plumes be understood and well characterized. The near field jet engine exhaust plume is a dynamic environment, initially at high temperature and rich in small soot particles and relatively high concentrations of water vapor and reactive trace gas species, which then cools by mixing with ambient air promoting gas-to-particle conversion processes leading to dramatic changes in the composition and size distribution of the resulting aerosol. The Missouri University of Science and Technology (MST) Center for Excellence for Aerospace Particulate Emissions Reduction Research has led numerous jet engine exhaust sampling campaigns to characterize the number density and size of PM emissions at different locations in the expanding exhaust plume ranging from the engine exit plane to as much as 150m downstream from the engine.

The SAE E-31 committee is currently developing an Aerospace Recommended Practice (ARP) for the measurement of non-volatile particulate matter mass and particle number emissions from the exit plane of aircraft gas turbine engines based on SAE Aerospace Information Report 6241. Particle loss, due to various mechanisms, occurs in the sampling train that transports the exhaust sample from the engine exit plane to the measurement instruments, since PM have a stronger tendency to stick to the wall of the sampling line upon collision as compared to inert gas molecules. For particle sampling from gas turbine engines, the most significant particle losses are due to thermophoresis (particles are forced to the tube wall when the wall is cold and the gas is hot) and diffusion. Thermophoretic losses are nearly independent of particle size, whereas diffusional losses increase with decreasing particle size. To account for the losses, both the size dependent penetration functions and the size distribution of the emitted particles need to be known to quantify corrections to the measured mass and number of the particle emissions. In the proposed ARP particle number and mass are measured, but size is not measured due to difficulties in method standardization and traceability. Here we present a methodology to generate number and mass correction factors for line loss, without using direct size measurement. A lognormal size distribution is used to represent the exhaust aerosol at the engine exit plane and is defined by the measured number and mass at the downstream end of the sample train. The performance of this line loss correction is compared to corrections based on direct size measurements using data taken by MST during the recent engine test campaign, APRIDE 5.

Heeb N. / EMPA Switzerland

Catalysis – a Key Property of Diesel Particle Filters to Lower Emissions of Genotoxic Compounds

In 2012, the world health organization has classified diesel exhaust (DE) as a class 1 carcinogen with sufficient evidence that exposure to DE induces lung cancer in humans. This has considerable consequences for the application of diesel engines at work places such as tunnel construction sites and mines, where best available technology (BAT) has to be applied to minimize exposure to genotoxic compounds.

Catalytic diesel particle filters (DPFs) have evolved to a powerful technology, some claim they are BAT, to remove solid soot and ash particles. DPFs are now widely used on roads and in many off-road applications. Despite high filtration efficiencies, a reduction of particle-number emissions of 98% is required to fulfill the VERT standard, the efficient removal of solid nanoparticles is not necessarily correlated with an as efficient reduction of genotoxic compounds.

Some of the identified genotoxic compounds found in untreated DE are polycyclic aromatic hydrocarbons (PAHs) and their nitrated forms (nitro-PAHs). Obviously, soot can not penetrate DPFs via evaporation to the gas phase, but most genotoxic compounds are volatile enough and will over time escape from DPFs at higher temperatures unless converted.

We have shown for many catalytic DPFs that PAHs including the genotoxic ones are removed [1,2]. But we also reported that DPFs with low catalytic activity can support the formation of certain nitro-PAHs [1,2]. We conclude that the catalytic activity of a DPF is a key property to remove such compounds and with it lower the genotoxicity of diesel exhaust.

In the presented paper, we will discuss the impact of a non-catalyzed DPF, either new or soot loaded, on the emissions of selected PAHs and nitro-PAHs and compare the findings with those of widely used catalytic DPFs with low- and high oxidation potential (lox- and hox-DPFs).

We noticed that filters without catalytic activity accumulate genotoxic compounds in the cold (<180 °C) and release them again at higher engine loads and increased temperatures rather than converting them. Such storage-release phenomena can lead to intervals of increased emissions of genotoxic compounds. Such effects may also occur in catalyzed DPFs if part-time inactive, e.g. at low engine loads and cold start conditions.

The formation of nitro-PAHs in non-catalyzed DPFs can even increase the mutagenicity as will be discussed. We concluded that the efficient filtration of soot and ash particles is not a sufficient condition to lower the genotoxicity as well. Genotoxic PAHs and nitro-PAHs are volatile enough to penetrate DPFs if not converted and the secondary formation of mutagenic nitro-PAHs is a substantial risk of non-catalyzed, inactive or inefficient DPFs. In other words, without catalytic activity, DPFs will just accumulate genotoxic compounds, possibly even form new ones and release them again at higher engine loads. Results from *in-vitro* cell assays on diesel exhausts of non-catalyzed and catalyzed DPFs are in line with these findings and will also be presented at this conference [3].

Hess A. / EMPA Switzerland

On-Line SMPS-ICPMS Coupling for Simultaneous Analysis of Nanoparticles

The characterisation of airborne particles in the nanometre to sub-micrometre size range concerning physical and chemical properties is highly demanded in various work and research fields, e.g. monitoring of combustion processes or risk assessment of products containing engineered nanoparticles.

Sensitive analytical techniques are required to gain knowledge on important aerosol characterisation parameters such as particle size distribution and elemental composition, possibly obtained simultaneously and with high time resolution. However, most of the available techniques are not able to provide physical as well as chemical information at the same time.

Scanning Mobility Particle Sizer (SMPS) is a well-established technique offering information on size distribution and number concentration of airborne particles in the above mentioned size range within scan durations of a few minutes, or information on distinct size fractions within seconds. Nevertheless, chemical information is not directly available.

Inductively Coupled Plasma Mass Spectrometry (ICPMS) allows a determination of elemental composition with excellent detection limits and a wide dynamic measuring range. Some standard applications are e.g. analysis of trace elements in biological or ambient samples or nanoparticles which first have to be collected, then brought into solution, and finally nebulised and introduced to the plasma as a fine spray. Besides, dry aerosols can be introduced to ICPMS, e.g. originating from laser ablated solid materials.

Coupling these two analysis techniques, i.e. SMPS and ICPMS, allows on-line achieving size and chemical information at the same time. Typical SMPS scan durations enable transient particle observation, and SMPS-ICPMS opens the possibility to chemically characterise aerosol particles in their original conditions instead of prior particle sampling and subsequent analysis.

Due to the low oxygen tolerance of the inductively coupled plasma the SMPS has to be operated using argon as particle carrier and sheath gas instead of air. Therefore a new flow concept was developed and a Rotating Disk Diluter (RDD) was implemented to transfer the initially airborne particles to an argon atmosphere.

First model aerosols were generated in the laboratory and successfully characterised using SMPS-ICPMS concerning size resolved elemental composition of the nanoparticles. In the next steps, the instrumentation will be further optimised and real samples are going to be investigated, i.e. aerosols emitted by consumer spray products containing engineered nanoparticles (ENP).

The concept of the SMPS-ICPMS setup as well as first results obtained with the coupling technique will be presented here.

Horn H.-G. / TSI, USA

Field Measurement, Technical Aspects of the First Generation PN Field Instrument

Emissions of particulate matter from diesel engines have been significantly reduced since the introduction of diesel particulate filters (DPF). Due to their inherently low sensitivity, traditional mass or opacity based emissions measurement techniques have become impractical. To overcome this difficulty, the European emission limits complemented particle mass (PM) measurements with particle number (PN) measurements for the certification of light duty vehicles (Euro 5 & 6) and heavy duty engines (Euro VI). Switzerland advanced this further by requiring installation and certification of either OEM or retrofit DPFs on non-road mobile machinery (NRMM) with more than 18 kW. In addition to engine certification, bi annual in-use tests must be made. To better characterize emissions of NRMM with DPF, the Swiss regulation SR 941.242 for in-use tests was recently amended: concentration measurement of solid PN will replace opacimetry.

SR 941.242 defines both the new test procedure and the technical requirements for portable instruments measuring solid PN concentration. A new, portable instrument which fulfills all these technical requirements - the TSI Model 3795 Nanoparticle Emission Tester (NPET) - was developed during the last year by TSI Inc.; its commercial launch will be at this conference. NPET consists of a sample dilution and conditioning system that removes condensate and large particles (greater than 1 μm) from the sample using a water trap and cyclone. Volatile particles are then removed using a built-in catalytic stripper (CS) and the resulting number concentration of solid particles is measured by an isopropanol based condensation particle counter (CPC).

Verification and validation data obtained during the development of the instrument demonstrate its capability of measuring number concentration from less than 1,000 to more than 5,000,000 particles per cubic centimetre. The NPET has a solid particle detection efficiency of < 50 % at 23 nm, > 50 % at 41 nm and > 90 % at 80 nm. The volatile particle removal efficiency of the built-in CS has been determined to be greater than 99% by measuring the number concentration of 30nm geometric mean diameter tetracontane particles upstream of the CS using a TSI 3025A CPC and downstream of the CS using the built in isopropanol CPC of the NPET.

NPET has successfully passed all tests at the Swiss metrology institute METAS; the new instrument is approved for Swiss official, bi-annual in-use measurement of PN emissions of NRMM

Hosseini Vahid / Sharif University, Tehran

Tehran air Pollution with Respect to Particles: Problem and Mitigating Solutions

Tehran with a population of 8.5 million suffers from air pollution on most days of the year. On an average, more than 1/3 of the days of a specific year is unhealthy according to national standards. The annual mean average of concentration of PM_{2.5}, PM₁₀, NO₂, and SO₂ are also above national standards.

The criteria pollutant for air quality index is PM_{2.5}. The particle pollution in the city of Tehran is mostly related to trans boundary-dust, and combustion generated particles. It seems that traffic related particles, specifically particles produced by diesel powered vehicles (heavy and semi-heavy duty vehicles) and spark ignition engine powered vehicles are the most responsible source of small particles in Tehran air. Tehran has still a large fleet of SI-engine powered vehicles and motorcycles with carburetor fuel system.

Several measures have been taken to mitigate combustion generated particle problem in Tehran air. Those include implementation of the first Tehran low emission zone, pilot test of electric bikes, more vigorous inspection and maintenance program, and more importantly, Tehran DPF retrofit project.

A pilot test on the fleet of Tehran City Bus Co. is being conducted between Sharif University of Technology, VERT, Tehran City Bus Co., and Tehran Air Quality Control Co., The purpose of the study is to evaluate VERT-certified filters for the driving conditions, diesel fuel quality and lubricant quality of Iranian market. 9 different technologies from 8 manufacturers have been selected for the pilot runs. The filters are being tested on an engine test bed using Mercedes OM457 LA 6-cylinder in-line turbocharged diesel engine which is typically used in the bus fleet. Filter technologies which are approved after engine tests will be installed on selected buses for the pilot run.

Karjalainen P. / Tampere University, Finland

Exhaust Particles Formed During Engine Braking of GDI Vehicles

Particles in urban air have been observed to be one of the most significant environment-originated risks for human health. On the other hand, in urban areas the vehicle traffic is known to be significant source of those particles, both in Western Europe and in developing countries. In general, vehicles and engines can emit several types of particles, having differences in particle size, particle number and formation mechanisms as well as in physical and chemical characteristics.

In recent studies we have observed that diesel and gasoline vehicles can emit particles also during decelerations and downhill driving conducted under engine braking conditions (Rönkkö et al. 2014; Karjalainen et al. 2014). Thus, our results indicate that the particles are formed without combustion process. These particles seem to be originated from engine oil, their size is typically smaller than 30 nm in diameter, and their emissions occurs as bursts over a short period of time. However, when the emission happens, the particle concentration in the exhaust plume can rise to substantially high concentrations.

In this study we aim to show how much the particles emitted during engine braking contribute to the total exhaust particle emission of the tested gasoline direct injection (GDI) vehicles. In order to do that, we evaluate critically the particle measurement methods and point out the problematic; it seems that the comprehensive analyses requires (1) careful choice of exhaust sampling location, (2) sampling without typical exhaust tracers like CO₂, (3) real-time (~1 Hz) particle instruments capable to detect sub-10 nm particles, (4) possible ways to separate different particles from each other and (5) data related to exhaust flow rate and temporal differences in it.

However, we have solved all these problems. The contribution of engine braking related particles was about 10% in particle number emissions detected by a Condensation particle counter (CPC) (~35% in average concentrations) over the NEDC for one GDI vehicle. Actually, the largest concentration peaks detected by the CPC occurred during decelerations (Figure 1). In the tests under on-road conditions the engine braking related particles added up to 3–18% of total observed particles by instruments in the mobile laboratory. The emissions during engine braking were especially remarkable when the engine braking started with high rpm. Thus it seems that the particles related to engine braking may be substantial contributor to total particle emissions and thus the urban air quality. However, these emissions are strongly affected by the test routine or the real driving conditions.

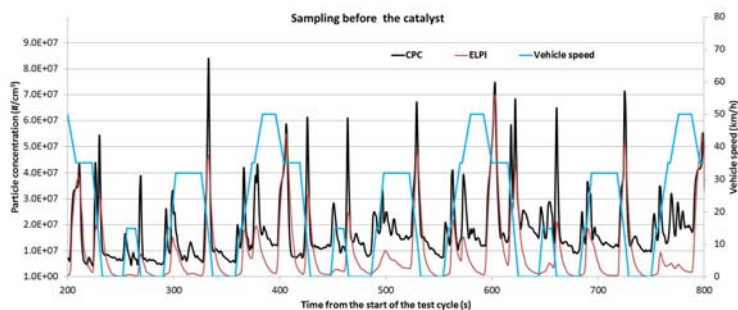


Figure 1. Particle concentrations in the exhaust of a GDI vehicle during the NEDC cycle.

Kato Kyohei / NGK, Germany

Advanced Catalyzed Gasoline Particulate Filter to Fulfill Future Emission Targets

Gasoline Direct Injection (GDI) technology usually combined with charged aspiration is expanding as efficient powertrains to meet 95 gCO₂/km 100% fleet from 2021. One side effect of GDI is the increased particle formation in comparison to PFI engines. The European Commission has agreed to implement a particle number limit of 6E+11 /km from September 2017 for newly certified vehicles. In addition to the particle number in the certification cycle NEDC, certification of Real Driving Emission (RDE) including a particle number limit is considered to be implemented by the European Commission from 2017. This new test procedure would request stable low particle emissions in a wide range of engine operation points. It has come into focus of vehicle manufacturers to meet the limits by emission control devices like a Gasoline Particulate Filter (GPF).

Two main stream gasoline exhaust systems including GPFs are under consideration: An uncoated type GPF placed downstream of an existing Three Way Catalyst (TWC). Another system is the coated type GPF that can be added either downstream of an existing TWC or completely replace an existing TWC.

Considering system compactness, a coated type GPF which replaces the original TWC is preferred. But the design optimization of a coated type GPF is more challenging than of an uncoated type GPF due to the more complex combination of coating and GPF design. Cell structures and pore characteristics have a strong influence on GPF performance like PN filtration and pressure drop of the GPF. Also TWC function of coated type GPF over life time might be affected by soot and ash accumulation inside the GPF. This poster will describe design optimization of a coated type GPF. Additionally the stable emission performance of a vehicle over a distance of 160,000 km will be presented. The detailed results are described below.

1. A material with a porosity of more than 60% contributes to minimize backpressure after coating.
2. The material's Mean Pore Size (MPS) affects the backpressure. The backpressure significantly increases for MPS below 15 µm.
3. Changing the cell density has relatively small impact on the filtration efficiency compared to changing the wall thickness.
4. After installing a catalyzed GPF the particle emissions were well below the limit of 6E+11 /km for several driving cycles.
5. Even after accumulating oil ash (over 160,000 km) the vehicle equipped with a GPF did not show any measureable increase of CO₂ emissions.
6. The power loss from an aged GPF is negligible.

The conclusion is that the catalyzed GPF has the potential to effectively and reliably reduce PN emissions over a wide range of engine operating points. At least it is robust over 160,000km which was proven by an extended field test. The GPF is one solution to reduce harmful particle emissions and help preserve clean air.

Keller A. / FHNW Switzerland

SOA - from Wood burning Appliances in a Simplified Total Carbon Measurement

Current emission control legislation and type-approval testing focuses on direct emission of pollutants. However, it is a well-known fact that these emissions do not remain inert in the atmosphere. Atmospheric aging oxidizes the organic fraction, lowering its volatility and transforming gas-phase pollutants into condensed-phase secondary organic aerosol (SOA). The result is a higher contribution of wood combustion appliances to ambient-air particulate matter than would be expected from emission measurements at the source.

The potential for production of SOA strongly depends upon the gaseous-precursor emissions and thus on the combustion conditions. The highest production of SOA is linked to manually-operated small combustion installations. Predictions of the SOA Production Potential (SOAPP) from the emissions of organic gaseous carbon (OGC), non-methane OGC, or even well-known single SOA precursor yields unsatisfactory results. The SOAPP must therefore be determined throughout experimental method (e.g. using a continuous-flow reactor).

We have previously shown that SOA production can be stimulated in a continuous-flow reactor-tube for emissions from pellet and log wood combustion. Using our setup, SOA production occurs within a few seconds. Measurements with an Aerodyne Aerosol Mass Spectrometer (AMS) run by ETH Zurich show that the mean oxidation state of carbon (<OSC>) is higher than what is typically found in the atmosphere. This suggests a SOA corresponding to a very highly-aged aerosol was formed.

So far, we determined the produced SOA by measuring particle size distributions downstream the reactor by a SMPS or by continuously measuring the particle mass by a TEOM. Both techniques are not usually available at test facilities for type approval tests and not applicable for standardized field measurements. In addition, a size distribution is not an adequate metric to quantify particulate mass and decide if a limit value is exceeded or not.

Therefore we have simplified our measurement setup by replacing SMPS or TEOM by collecting filter samples of emissions before and after conditioning in our reactor-tube. After collection, the filters are analysed for organic carbon (OC) and elemental carbon (EC) by means of thermo-optical methods. The SOA and primary organic aerosol (POA) fractions can be inferred by comparing the total OC on both filters. This setup is very simple and does not require specialized aerosol measurement devices on site. The filter analysis can be done off-line by a commercial laboratory or quasi-online by a carbon analyser. This makes this setup also applicable for field measurements.

However, first results show that the OGC is also absorbed by the filters causing a positive artefact that surpasses the contribution of organic aerosol. Additionally, the high levels of O₃, up to 60ppm, downstream of the flow tube reactor can further oxidize the SOA/POA to a state where it becomes volatile, thus causing a negative artefact. For this reason, we have tested different setups that account for these artefacts and/or eliminate them.

Finally, we will discuss the measurement of the carbonaceous fraction, including SOA, as an alternative to the total PM measurements.

Khalek I.A. / SWRI USA

Solid Particle Number and Size and Ash Emissions from Vehicles during Engine Start-Up

Vehicle particle emissions without an exhaust particle filter continue to be of concern, especially during off-cycle operation. While an engine can be calibrated to emit low particulate matter on a specific laboratory cycle, it is difficult to calibrate an engine for low particle emissions across the entire range of engine operation, regardless of the engine type. One operation of high concern is engine start-up. Engine start-up occurs in home garages, parking lots, city streets, and in hybrid vehicles with stop and go strategy. Thus, it is important to characterize particle emissions from vehicles under engine start-up trying to differentiate different vehicle technologies.

For our work, we plan to present on solid particle number emissions, size distributions, and ash emissions from over 90 vehicles during engine start-up. The vehicles were composed of 4, 6, and 8 cylinder port fuel injected gasoline, 4 and 6 cylinder direct injected gasoline, and diesel with DPFs. The work was done in public at one of SwRI parking lots and at the University of Texas at San Antonio campus. The work will highlight the importance of using exhaust particle filters onboard vehicles as the best means to protect against particle emissions exposure. We will also rank the vehicles from highest to lowest using a particle number index on a scale from 1 to 10.

Kittelson D. / University of Minnesota, USA

Nanoparticle Emissions from a Second Generation Biofuel: DME

Dimethyl ether (DME) is a potential second generation diesel fuel and propane fuel blending agent that is made by the gasification of biomass, natural gas or coal feedstocks. In the U.S. there is limited interest in DME as a liquid fuel because of technical and economic concerns. The objectives of this project include: 1) A business/economic analysis to demonstrate the viability of a Bio-DME as a transportation fuel in areas with substantial biomass resources like Minnesota; 2) A review of life cycle greenhouse gas emissions associated with Bio-DME; 3) Use of a single cylinder Navistar DME research engine to establish baseline performance and emissions of DME with focus on nanoparticle emissions; 4) Design, prototype development and evaluation of new fuel system components suitable for both DME and propane. This presentation will focus on nanoparticle emissions from the DME fueled Navistar engine.

The DME fuel system for the modified Navistar single cylinder research engine consists of the fuel supply, external pressurization, the fuel injector system, along with an engine internal oil system to actuate the fuel injector. The fuel injection system is a modified HEUI (Hydraulically actuated Electronically controlled Unit Injection) system. The system has been designed for easy switching between diesel fuel and DME. For simplicity and safety in a laboratory system the DME is provided from a tank pressurized with nitrogen. Other parts of the fuel system from the fuel supply to the engine were instrumented with sensors to monitor temperature and pressure. DME has no lubricating properties so that it was necessary to add a lubricity additive, supplied by Lubrizol, to the fuel. The original Navistar ECU was not suitable for single cylinder operation so that a new system based on National Instruments hardware and LabView software was developed. An array of instruments were used to measure gaseous and particulate emissions including an AVL FTIR for gaseous measurements, a sampling and dilution system specially designed to facilitate nanoparticle measurement, a TSI nano-SMPS for particle size and concentration measurements, an AVL micro soot sensor to measure black carbon, and a catalytic stripper to differentiate between solid and volatile particles.

Significant concentrations of extremely small, 10 to 20 nm geometric mean diameter, volatile nanoparticles but no detectable black carbon were observed. The concentration and size of the volatile nanoparticles increased with the concentration of lubricity additive. The only solid particles observed, were extremely small, between 3 and 7 nm diameter, and believed to be related to lubricating oil ash.

Konstandopoulos A.G. / CPERI/CERTH Greece

Asymmetric and Variable Cell Geometry Diesel Particulate Filters

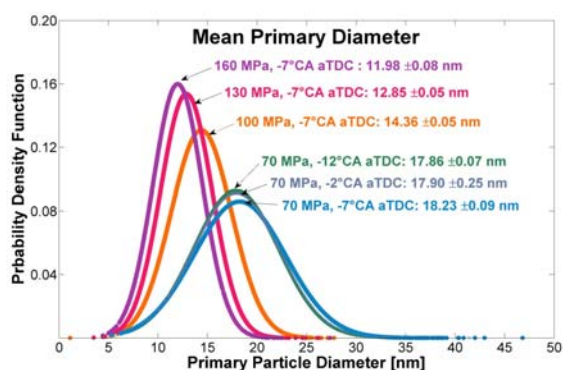
Diesel Particulate Filters (DPFs) have entered their fourth decade of life and they are here to stay as the undisputable most effective technology for the abatement of particle emissions from Diesel engines. Their application field now spans passenger cars, heavy duty vehicles, off-road machinery and in the near future it is expected to extend into marine and locomotive applications. DPFs are in their most prevalent form multichannel monolithic reactors direct descendants of the honeycomb structured catalytic converted substrate. For many years the geometric configuration of these reactors has relied on a multichannel assembly configuration with equal numbers of inlet and outlet channels of identical cross-sectional geometry obtained by the alternate plugging of the basic honeycomb structure. Various channel geometries have been described in the scientific and patent literature but the predominant cell shape is that of a square channel. Only in the last decade this trend has been broken as the introduction of asymmetric cell designs has been pursued to provide additional filtration area and storage space for the ashes that inevitably accumulate in the DPF. Very recently variable cell plugging layout configurations (with unequal number of inlet and exit channels) have also emerged, so we may today refer in general to Asymmetric and Variable Cell (AVC) geometry Diesel Particulate Filters (DPF) designs and configurations.

In the present work we present an approach for designing and optimizing AVC DPFs by providing a quantitative description of the flow and deposition of soot in these structures. Soot deposit growth dynamics in AVC DPFs is studied computationally, primary and secondary flows over the inlet channels cross-sectional perimeters are analyzed and their interactions are elucidated. The result is a rational description of the observed growth of soot deposits, as the flow readjusts to transport the soot particles along the path of least resistance (which is not necessarily the shortest geometric path between the inlet and outlet channel, i.e. the wall thickness). The theoretical description is in excellent agreement with experimental data obtained with two different families of AVC DPFs operated in the exhaust of a diesel engine and can be employed to design new DPF configurations with substantially lower pressure drop than existing designs.

Kook Sanghoon / University of New South Wales, Australia

In-Flame Soot Particles in an Automotive-Size Diesel Engine

The negative impacts of combustion generated soot particles on human health and the environment are serious concerns in diesel engines. Measurements of exhaust soot level and particle size distribution have been widely used to address this issue. In-cylinder soot volume fraction measurement using an optical engine and laser-based diagnostics has been another approach to understand soot formation processes. None of these measurements however provide important details of size, shape and structure of soot particles that are in the formation and oxidation stages within the diesel flame inside the engine cylinder. To bridge this gap, in-flame soot sampling based on the thermophoresis of particles and subsequent transmission electron microscope (TEM) imaging has been conducted in a working diesel engine. Sampled soot particles were imaged by a TEM and post-processed to acquire the number of aggregates, projection area on the sampling grid, and size distribution. Of particular interest is the evolution of soot particles at four different stages of diesel combustion as the diesel flame develops prior to the wall impingement, propagates after the wall impingement, extinguishes during the late-cycle burn-out, and flows out to the exhaust pipe. The results suggest that soot particles aggregates with various sizes and structures form within the diesel flame, which breakdown and become smaller due to oxidation as the flame continues to develop through the jet-wall interaction. Then the large aggregates further breakdown, small aggregates disappear completely, and the primary particles become smaller due to the continued oxidation throughout the late-cycle burn-out. The remaining aggregates are very concentrated, agglomerated, and compact-shaped, which are emitted to the exhaust as final products. Towards its practical application, the effect of fuel injection pressure and timing on the size distribution of soot aggregates and primary particles are also discussed. The results show that the number of soot particles, the soot projection area, and the size of soot aggregates decrease when the injection timing is retarded at a fixed injection pressure. The primary particle size, however, is found to be insensitive to the variations in fuel injection timing. For injection pressure variations, both the size of primary particles and soot aggregates are



found to decrease with increasing injection pressure, demonstrating the benefits of high injection velocity and momentum. Detailed analysis shows that the number of soot aggregates increases with the increasing injection pressure up to a certain point and those are mostly small aggregates. The fractal dimension shows an overall decrease with the increasing injection pressure; however, there is a case that the fractal dimension shows an unexpected increase because the small ag-

gregates with more compact and agglomerated structures outnumber the large aggregates with more stretched chain-like structures.

Krähenbühl S. / Federal Office for the Environment, Switzerland

New Instruments for PN-based Periodic Inspection: Results of a First Measurement Campaign

For the periodic inspections of construction machines, new types of particle counters shall replace the opacimeters. Portable, light and handy instruments will check the quality of diesel particle filters (DPF) during their lifetime. A first measurement campaign from FOEN with prototypes of three companies tests the practicability of the intended procedures and the corresponding reference value.

Switzerland has experience with Diesel Particulate Filter (DPF) on tunnel construction sites since 2000. Since 2009 a particle number limit in the Ordinance on Air Pollution Control (OAPC) requires DPF on almost all construction machines. The majority of construction machines are equipped with DPF.

In Switzerland, all construction machines have to be inspected every second year by the owner with a periodic control. Until now, the measurement of the exhaust gas is done with opacimeter. But this instrument is ineffective for machines with particle filters, as sensitivity of opacimeters is too low.

The metrological requirements for portable PN-measuring instruments are defined in the ordinance VAMV (<http://www.admin.ch/opc/de/classified-compilation/20051389/index.html>) by FOEN and METAS. Measuring procedures are also written down and a reference value is determined. The quality of the particle filter is sufficient, if the measurement passes the reference value. If the measured result is above the reference value, the problem has to be resolved. In the meantime, the construction machine may not be used on construction sites.

A measurement campaign for testing the procedure and the reference value is scheduled for the end of April. Prototypes of three companies take part. The results will be presented at the ETH conference.

Künzli N. / Swiss Tropical and Public Health Institute, Switzerland

New Proposal of Swiss FCAH on how to Regulate Ambient Particulate Matter (PM)

Background and Methods

The Swiss Federal Commission for Air Hygiene (FCAH) advises the Swiss Government on the regulation and air quality standards of ambient air pollution to protect public health. FCAH reviewed the current Swiss standards of particulate matter (PM) in light of the current scientific evidence. The committee took into account international assessments of the health literature and the state of international standardization in PM monitoring.

Results

FCAH confirmed the validity of the current Swiss air quality standards defined for PM₁₀, set in accordance with WHO guideline values, namely the 24-hour mean not to exceed 50 µg/m³ and an annual mean standard of 20 µg/m³. The committee proposes to also regulate the fine fraction of PM – namely the PM_{2.5} – for which Switzerland does not have standards yet. As in the case of PM₁₀, the science based WHO guideline long-term mean value should be adopted: the annual mean should not exceed 10 µg/m³. In light of the evidence of adverse health effects related to diesel soot with its toxic characteristics heavily related to the ultrafine fraction of PM, the committee requests the enforcement of stringent emission control strategies for particles from all sources. Within 10 years, the elemental carbon concentrations – a marker of carcinogenic fine and ultrafine combustion related particles – should be reduced, at all sites, down to 20% of current concentrations.

Discussion

Based on the increasing evidence of partly independent and complementary health effects related to the various size fractions of PM, and given the partly size-specific impact of current (e.g. Euro VI) and possibly future clean air regulations and policies, the commission emphasized the need to separately regulate and control the coarse, fine and also ultrafine fractions of particles. Although the correlation between PM_{2.5} and PM₁₀ is still high in Switzerland, the protection of health cannot be achieved through the sole regulation of PM₁₀. The PM_{2.5} fraction of PM₁₀ is high (70-80%) and varies across seasons and sites. Thus, with a PM₁₀ annual mean standard of 20 µg/m³ the WHO annual mean target for PM_{2.5} (10 µg/m³) will not be achieved through compliance with the PM₁₀ standards. Given the lack of internationally certified monitoring standards for ultrafine particle number concentrations (PNC), and the very strong PNC dependence on proximity to sources with, thus, very high small-scale spatial variation, the committee did not propose ambient standards for PNC but calls for strict control of emissions. The Government should actively support the international development and adoption of monitoring standards and should continue the monitoring of not yet regulated air pollutants such as PNC, elemental carbon, and others. The rigorous reduction of elemental carbon is clearly warranted to protect public health also along busy roads, highways or in street canyons. While a reduction to 20% of current levels may be considered ambitious, the enforcement of using best available technologies on all sources of combustion (including all on- and off-road diesel and gasoline engines, wood stoves, and combined heat and power technologies) still has an untapped potential for a very substantial decline in EC levels, which are still above 1 µg/m³ in most sites in Switzerland.

Kureti S. / University of Freiberg, Germany

Soot Oxidation on Manganese Oxide Catalysts in Diesel and Gasoline Exhaust Gas

In this paper we present novel highly active manganese oxide catalysts for the regeneration of diesel and gasoline particulate filters using the CDPF technique. CDPF implies the combustion of soot deposits by a catalyst coated onto the filter. Cerium and iron oxide based materials are known to be effective in soot oxidation [1, 2]. Due to tightened European emission standards, particulate filters are currently not only discussed for diesel engines, but also for gasoline vehicles with direct fuel injection.

The present work deals with the evaluation of a series of manganese oxide samples towards their soot oxidation activity in synthetic model exhaust mimicking diesel as well as gasoline exhaust conditions. In the screening tests made by temperature programmed oxidation (TPO) powder mixtures of soot and catalyst were taken, while a home-made soot originated from C₃H₆ combustion was employed. As a result of the TPO tests, Mn₃O₄ prepared by flame spray pyrolysis (FSP) was identified to be one of the best catalysts reported so far providing soot combustion already at 300°C under diesel exhaust conditions (Fig. 1). The catalyst also exhibited outstanding soot oxidation performance under gasoline exhaust conditions showing

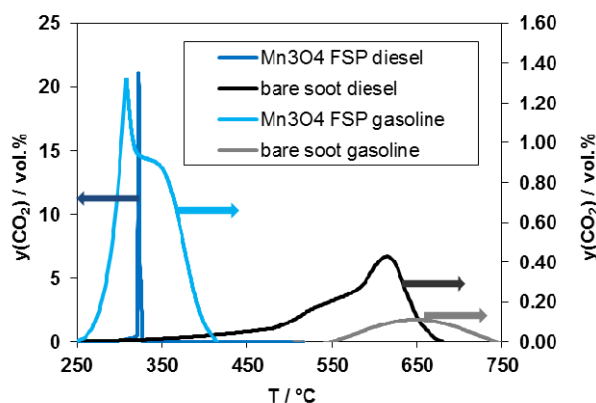


Figure 1: CO₂ evolution upon TPO study with bare soot as well as mixtures of soot with Mn₃O₄ catalyst under diesel and gasoline exhaust conditions. F = 500 ml/min, β = 3.3 K/min, m(soot) = 0.12 g, m(Mn₃O₄) = 0.96 g; gasoline conditions: $y(\text{O}_2) = 1\%$, $y(\text{H}_2\text{O}) = 2\%$, N₂ balance; diesel conditions: $y(\text{O}_2) = 10\%$, N₂ balance.

soot conversion above 250°C. Furthermore, clear benefit of the Mn₃O₄ catalyst was observed as referred to bare soot when performing tests with coated laboratory-scaled particulate filters. Moreover, the Mn₃O₄ catalyst revealed high thermal stability. After hydrothermal exposure at 600°C and thermal treatment at 1050°C its activity did not alter significantly in the TPO tests carried out with the Mn₃O₄/soot powder blends.

Furthermore, all the catalysts were thoroughly characterized by BET, XRD, SEM and NH₃-TPD to derive physical-chemical properties. From these investigations, it was concluded that particle size, surface area and crystallinity determine the soot oxidation efficiency of the manganese oxide catalysts. These results substantiate the high efficiency of the Mn₃O₄ obtained from FSP.

Leskinen A. / Finnish Meteorological Institute

Aging of Diesel Engine Exhaust, Pellet Boiler Exhaust, and their Mixture

Aerosols are known to induce health and climate effects, which depend on their physico-chemical properties. In the atmosphere the aerosol properties change in transformation processes, which can be studied in environmental chambers.

In this work, the exhaust from a diesel engine, a pellet boiler burning softwood pellets, and their mixture, and ozone was injected into a 29 m³ environmental chamber. In some experiments also nitrous acid, a hydroxyl radical (OH) precursor and/or alphapinene was injected. The mixture was aged for 4 hours under the influence of UV irradiation. During the aging the size, number concentration, hygroscopic growth factor (HGF), chemical composition, morphology, optical properties, and mixing state of the particles, as well as oxides of nitrogen, sulfur dioxide, ozone, selected ions, and volatile organic compounds in the gas phase were monitored.

The mobility equivalent, as well as the projected area equivalent diameter of the particles from both sources, both separately and in the mixture, increased from 80–90 to 120–130 nm during aging. At the same time the number concentration decreased, but aerosol volume increased by 10–30 %.

The initial mass concentration in the chamber was 45 (pellet) and 35 µg/m³ (diesel). The concentration of the particulate organics, based on aerosol mass spectroscopy, increased from 4 to 12 µg/m³ (pellet) or remained at 2 µg/m³ (diesel), even in the presence of OH. The increase in organics originates from secondary organic aerosol (SOA) formation, which is known to be more intense at low nitrogen monoxide (NO) concentrations. The initial NO concentrations were 16–46 (pellet) and 81–143 ppb (diesel).

The concentration of particulate nitrate increased from 1 to 8 µg/m³ (pellet) or was very low (diesel). The increase was remarkably faster when OH was present. The HGF for 100 nm particles was initially and remained at 1.55–1.60 (pellet), indicating highly hygroscopic particles, or remained at 1.01–1.03 (diesel), indicating that both the fresh primary and aged particles were hydrophobic. A small decrease in the fractal dimension of pellet burner exhaust particles was seen.

The evolution of the mixed aerosol was between those of the separate emissions. Both more and less hygroscopic fractions were seen, and the particles from each source could be separated from the electron micrographs. The HGF of the less hygroscopic fraction increased to 1.05, while that of the more hygroscopic fraction decreased from 1.60 to 1.45 or as low as 1.35 when alphapinene was present. The increase in particulate organics was less than (the expected) 50 % of that in pellet boiler exhaust, which indicates that the high NO concentration of the diesel exhaust inhibits SOA formation from the pellet boiler exhaust.

In conclusion, the exhaust from a diesel engine is quite passive during aging while that from the pellet boiler produces SOA and particulate nitrate. In mixtures, the characteristic features of the particle phase from individual emissions persisted during aging, indicating an externally mixed aerosol identifiable from each other. However, the gas phases mixed affecting the SOA formation potential of the individual emissions.

Leuenberger Chr. / LEUPRO Switzerland

Legislation Towards Risk based Ambient Air Quality Standards

During the last decades ambient air quality standards have been established for a few lead air pollutants and operational metrics such as particulate matter. The concept for the setting of these standards was based on the effects of these indicators on the health of the population. The prerequisites for setting standards were toxicological and epidemiological evidence, well known emission-immission-relationships, and standardized methods for the measurement.

In Switzerland the Federal Commission for Air Hygiene has performed an analysis and evaluation of ambient particulate matter on the health of the population. The Swiss approach comprises the following elements :

1. Short and long term air quality standard specified for PM10
2. Adding an new annual mean ambient air quality standard for PM 2.5
3. Specyfing a new binding 10-year interim target for the reduction of carcinogenic soot to 20% of the present day-level.

On the other hand, there are noxes which do not show short-term-effects, whereas a delay between exposition and symptoms cannot be excluded, and showing high spatial and temporal variability. With regard to these, a more risk based approach has to be found as a basis for setting ambient air quality standards. Such concepts have to be discussed in order to prevent long-term health risks.

This paper intends to discuss a risk based approach for the setting of ambient air quality standards.

Liati, A. / EMPA, Switzerland

Electron Microscopic Analysis of Metal-bearing Particle Emissions from Diesel Engines

The exhaust of diesel engines is known to contain a minor fraction of metal-bearing compounds (the so-called ash), apart from abundant carbonaceous components (soot). The nature, morphology and variability of the metallic fraction of combustion-generated particulate matter (PM) remain poorly understood. These properties are, however, important for a better understanding of the behavior of the emitted particles in the atmosphere and the human body.

PM from the exhaust of a diesel engine was sampled directly on transmission electron microscope (TEM) grids for scanning electron microscopic (SEM) and TEM studies of their morphology (shape, size, structure), mode of occurrence and chemical composition. Moreover, variations in the relative amount of metallic PM upstream and downstream of the diesel particulate filter (DPF) were investigated.

The results of the SEM and TEM analyses reveal that ash PM escapes into the ambient air both attached onto soot, as well as in form of pure ash aggregates, ~0.2-2 μ m in size. The individual constituents of the aggregates are ~20-400nm large. The ash PM consists chemically of Ca, Zn, P, Mg, S, Na, Al, K (originating from lubricating oil additives), as well as Fe, Cr, Ni, Sn, Al, Sb (deriving from engine wear and corrosion). Noble metal particles (in the present case Pd) escaping from the diesel oxidation catalyst located upstream of the DPF were found among the ash PM.

Upstream of the DPF soot agglomerates are free of ash whereas downstream of the DPF, the very few escaping, usually large soot agglomerates commonly carry metallic compounds taken away from the ash deposited inside the DPF. These ash-bearing soot agglomerates may liberate ash in the atmosphere either mechanically or by chemical means (e.g. soot oxidation). In addition to lubricating oil-related and wear/corrosion-derived ash, very few branch-like agglomerates of iron oxide nanoparticles were found among the metallic particle emissions downstream of the DPF, probably formed by melting of engine wear (steel) in the combustion chamber.

The results of the present study emphasize the need for further study of the metal fraction of PM emissions, especially having in mind that ash occurs in the exhaust of all types of internal combustion engines, thus increasing its total absolute amount in the atmosphere and therefore its contribution to air pollution and human health effects.

Lohmann U. / ETHZ Switzerland

Climate Effects of Black Carbon Aerosols

Aerosols scatter and absorb radiation and influence the radiation budget indirectly by acting as cloud condensation and ice nuclei and thereby modifying cloud microphysical properties. Since pre-industrial times, the amount of black carbon, sulphate, nitrate and organic aerosols has been increasing. In the fifth assessment report (AR5) of IPCC, a new terminology for the climate effects of aerosols was introduced. The anthropogenic radiative forcing due to aerosol-radiation interactions (RF_{ari}) formerly called the direct aerosol effect refers to the scattering and absorption of radiation by atmospheric aerosol particles. Its best estimate is given as -0.35 [-0.85 to $+0.15$] W m^{-2} (high confidence) using evidence from aerosol models and some constraints from observations (Boucher et al., 2013; Stocker et al., 2013). The RF_{ari} is caused by multiple aerosol types. In addition to the radiative forcing, rapid adjustments, like changes in atmospheric stability and cloud adjustments, occur. These are included in the effective radiative forcing (ERF). For RF_{ari}, rapid adjustment leads to a more negative forcing, that is attributable primarily to black carbon and is estimated to be -0.45 [-0.95 to $+0.05$] W m^{-2} . The assessment for RF_{ari} is less negative than reported in AR4 because of a re-evaluation of aerosol absorption. The total anthropogenic RF due to black carbon including emissions from fossil fuel, biofuel, biomass burning and the effect of black carbon on snow amounts to 0.64 [0.25 to 1.09] W m^{-2} with the largest single contribution from fossil fuel and biofuel [0.4 W m^{-2}]. However, black carbon never occurs in isolation but is associated with organic aerosol emissions. The anthropogenic RF due to organic carbon is -0.29 [-0.47 to -0.08] W m^{-2} resulting in an anthropogenic RF due to carbonaceous aerosols of 0.35 W m^{-2} . In this talk I will discuss the climate effects of black carbon highlighting the results from AR5 and from the assessment of Bond et al. (2013).

Mayer A. / TTM

Request for BAT-Level of All In-Use Engines – a New Challenge for the OEM

Although Euro 6/VI Diesel engines using high efficient DPF is available exclusively in Europe, proof to have impressively low particle emissions, in a worldwide perspective emissions of solid, lung penetrating, carcinogenic nanoparticles are increasing and thus the global health impact as well as a very high health cost burden – WHO just informed that new estimates predict a nearly doubling of mortality compared to earlier estimates. Reason is urbanization, these fast growing megacities require mobility and continue to use a large fleet of dirty in-use engines and introduce continuously insufficient technology. Air pollution is reaching and exceeding levels of $PM_{10} > 1000 \mu g/m^3$ and $PN < 800'000 P/cc$.

City councils introduce low emission zones but all they have is in-use technology. They require modern technology but what the OEM is supplying might even be worse with respect to nanoparticles than the existing. Policies, even those which are very strict, introducing DPF in city center LEZ can hardly solve the problems; most measures are cosmetic, superimposed and counteracted by growing dirty fleets – desperate and pointless facing this depressing situation threatening all of us.

Our life style depends on engines, and our life quality on engine emissions and the “polluter pays” principle is not applied. Why not.

Technically, logistically and financially the problem can be solved and can be solved fast and cost effective. In use engines can be upgraded to reach the low emission nanoparticle levels of Euro 6/VI engines. This has been proven by retrofit in many projects, for all engines, all applications and reliability is proven.

But OEM does not support this upgrade of in-use engines by emission retrofit measures – in particular with their own products they refuse every support.

Whether we as a society can tolerate that the responsible industry is refusing her responsibility is an important question. We definitely cannot and we have to ask why we still do.

On the other side of the coin we see the chances for the industry, chances for big money by introducing emission reduction innovation under the umbrella of environmental laws. An incredible chance for new markets. Why does industry not jump on that? Not yet. Simply because it is not required and our engine industry is not proactive with respect to emissions, never was.

So let's require that all engine generations must be at BAT-level – nothing new, just as we require for waste incineration plants, emission turnaround required by law. Let's apply the same law. If an old engine lags behind this requirement the OEM must provide an emission kit. Be sure they can. They are just not asked yet to do so and we don't enforce “polluter pays” principle. The OEMs are technically perfectly able to provide best available solutions. This will create fast growing new large markets. Society has to cover the cost of course but since benefits are 10 times higher than reinvestment costs, this is making money for the society as well.

Meier R. / Swiss Tropical and Public Health Institute, Switzerland

Indoor and Outdoor Concentrations of Ultrafine Particles, PM_{2.5}, PM_{absorbance} and NO₂

Background: Indoor air quality is a growing concern as we spend the majority of our time indoors and as new buildings are increasingly airtight for energy saving purposes. In this study, we aimed to better understand indoor air pollution in Switzerland, with a focus on ultrafine particles in this paper.

Methods: A total of 80 homes in four areas in Switzerland (Basel, Geneva, Lugano and Wald) were selected for indoor and outdoor measurements of ultrafine particles (UFP), particulate matter (PM), and Nitrogen Dioxide (NO₂). Repeated measurements during up to three seasons were conducted at each home. UFP were measured in real-time with miniature diffusion size classifiers (miniDiSC). PM₁₀ and PM_{2.5} were collected on Teflon filters and NO₂ was measured with passive diffusive samplers. Residents of all homes were enrolled in the Swiss Cohort Study on Air Pollution and Lung and Heart Diseases in Adults (SAPALDIA) and provided detailed information about home characteristics by questionnaire.

Results: We collected the following indoor/outdoor data: 95 real-time measurements of ultrafine particle number concentrations (PNC) with a median duration of 7 days (range 6 to 14 days); 176 two-week measurements of PM₁₀, PM_{2.5} and PM_{absorbance}; and 198 two-week measurements of NO₂. Mean indoor / outdoor PNC [particles/cm³] were 9'025 (SD=6'208) / 11'886 (7'926). Mean PM_{2.5} concentrations [µg/m³] were 12.8 (18.8) / 14.2 (9.8) and mean NO₂ concentrations [µg/m³] 12.6 (9.2) / 21.9 (12.0). Comparable indoor PNC with means around 11,000 particles/cm³ were found in Basel, Geneva and Lugano. The highest outdoor PNC were measured in Geneva and Lugano with mean concentrations of 17,926 particles/cm³ (6,875) and 15,192 particles/cm³ (7,702), respectively. The lowest PNC were found in Wald, with mean indoor / outdoor concentrations of 5'812 (SD 4'629) / 5'397 (2'522). Spearman correlations of indoor and outdoor PNC were low within each area (ρ=0.02 to ρ=0.36) but moderate (ρ=0.55) when all four areas were pooled. Diurnal patterns of outdoor UFP levels, characterized by peaks during rush hour, were reflected indoors. In addition, we observed a peak of indoor UFP around noon, indicating emissions from cooking. If indoor smoking was reported, indoor PM₁₀ and PM_{2.5} levels were significantly higher than outdoors. Smoking sites also had higher indoor levels for other pollutants, but the difference was not as large as for PM.

Conclusions: Mean indoor PNC were generally lower than outdoors. However, indoor sources, such as cooking and smoking, influenced indoor UFP levels and the lower regional variation of indoor PNC, compared to outdoors, may be a consequence of comparable regional indoor source influence in all four areas. We will look further into the association of indoor UFP with elemental constituents of PM of outdoor origin to strengthen our understanding of indoor exposures to outdoor pollution.

Müller M.D. / EMPA Switzerland

Modelling Ultrafine Particle Number Concentration in Zurich with High Spatio-Temporal Resolution

Air pollutant concentration monitoring is an important task in the field of health protection to ensure compliance with legislation, to estimate the exposure of the population and to analyze health effects related to air pollutants.

Adverse health effects caused by the exposure to ultrafine particles (UFP) are being investigated, for example in epidemiological studies. These require accurate estimates of the exposure of participating individuals which are difficult to obtain at present, especially in the urban environment where the spatial and temporal variability of the UFP concentration is high. UFP concentrations strongly depend on the proximity to emission sources, the conditions for UFP dispersion and meteorology.

Recent progress in the development of small and inexpensive sensors for measuring concentrations of ambient trace gases and aerosols led to first wireless sensor networks for air pollution monitoring. These deployments consisting of a large number of nodes are so far focusing on technical aspects and important operational aspects require further attention (e.g. quality control and quality assurance or network design). However, first data sets provided by such networks are ready to be analyzed in terms of accuracy and information content. In combination with dedicated modeling approaches sensor networks might have the potential of substantially improve the knowledge of the time-dependent pollutant concentration field and hence the accuracy of exposure estimates.

The Opensense mobile sensor network (www.opensense.ethz.ch) is an example of such a monitoring network. Operation started in 2012. It consists of 10 nodes. The nodes are equipped with sensors measuring UFP, O₃, temperature and humidity as well as the position. They are installed on the rooftop of 10 streetcars. These are operating on a regular schedule in the city of Zurich.

We investigate statistical modeling approaches such as General Additive Models (GAM) to model the UFP concentration in Zurich with high spatio-temporal resolution (10 m, 30 min). The models rely on spatial information such as traffic, heating systems and building density as explanatory variables offered to the model by appropriate representations. Model parameters are fitted by using UFP concentration measurements obtained by the Opensense mobile sensor network. UFP concentration maps for the city of Zurich are computed based on the derived models.

In this presentation we outline the employed statistical modeling approaches and show preliminary results of the modeling of UFP number concentrations in Zurich for the period December 2013 to February 2014. The model performance was evaluated by comparison with measurements obtained at four permanent air pollution monitoring sites in Zurich as well as leave-one-out cross-validation. In addition, estimates based on the computed UFP concentration maps were compared to the exposure of pedestrians. For this purpose we equipped pedestrians for 15 tours of one to three hours duration with a UFP monitor to measure personal exposure in January 2014. The data collected during these tours is used for the evaluation of the accuracy of personal exposure estimates based on the calculated UFP concentration maps.

Nowak A. / PTB
Andres H.P. / METAS Switzerland

**Measuring Soot Particles from Engines:
Recommendations from EMRP-ENV02 Project in WP1**

The pollution of combustion aerosol particles from automotive-emissions is of particular significance as modern engines with high-pressure fuel injection can emit a large amount of fine and ultrafine particles. These emissions have a high variability in particle number concentration and are chemically dominated by black carbon. Due to their morphological structure, they efficiently uptake organic vapors which further increases their toxicity level. In 2012 the World Health Organisation (WHO) classified especially diesel engine exhaust as carcinogenic to humans.[1] In order to ensure that emissions of ultrafine particulate pollutants (PM 0.1 μm and below) can be controlled, the European Commission has in addition to the mass-based limit value introduced a number-based limit value for particle emissions for type approval of Euro 5b and Euro 6 engines.[2] The particle number measurements follow the procedures described in the vehicle emission regulations UN-ECE R49 and R83.[3-4]

Within the EMRP-project *ENV02* "Emerging requirements for measuring pollutants from automotive exhaust emissions" eleven European organisations work together to establish a metrological basis for the measurement of automotive exhausts. The project is part of the European Metrology Research Programme (EMRP), which is jointly funded by the EMRP participating countries, and the European Union.

The scope of the work package 1 (WP1) within *ENV02* is to develop metrological criteria for automotive particle emission metrics like SI traceability, temperature stability and "soot likeness" for a suitable calibration aerosol. Therefore, it is necessary to build up in Europe an infrastructure of primary standards for particle size and number concentration for soot particles between several hundred and ten thousand particles per cubic centimeter as well as particle sizes between 10 nm up to 100 nm at different NMIs like METAS, NPL and PTB. Aerosol electrometers were chosen as reference instrument for particle number (PN) concentration measurements. An international comparison workshop of the PN reference instruments cloud showed a good agreement between different NMIs within $\pm 3\%$ for particle number concentration.

The aim of WP1 is to develop and provide manufacturer independent calibration services for the end users and industry, in particular for the calibration and characterisation of measurement instruments used for the type approval of Euro 5b and Euro 6 vehicles (e.g. light vans and passenger cars) like the particle concentration reduction factor of the volatile particle remover, the counting efficiency of condensation particle counters, electrical and diffusion charging sensors.

Okamura Kazumasa / Toyota, Japan

Chemical Composition of the Size-Classified Nanoparticle Exhausted from Gasoline Vehicle

As for the nanoparticle, there is the concern for the influence of cardiovascular system. In automobile emission, the relationship between chemical composition and the biological effect of nanoparticles are not clear yet.

Therefore, we investigated the chemical composition (metals, polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons) of the size-classified particles to clarify an actual property of the nanoparticles exhausted from gasoline DI engine.

We compared the chemical composition of 10 nm, 56 nm and 100 nm particles, sampled by reiteration of the NEDC mode driving (Cold start : Hot start = 1 : 12).

For metal compositions by ICP-MS analysis, Na, K, Ca, Zn and Fe were detected in 56 nm and 100 nm particles, and they were assumed oil and abrasion derivations. Na, K, Ca and Zn were detected in the 10 nm particles, but no unique metal compositions in this particle size were detected.

We analyzed US EPA's 16 priority pollutant PAHs by GC-MS. In 56 nm and 100 nm particles, Chrysene, Benz(a)anthracene, Benzo(k)fluoranthene, Benzo(a)pyrene and Indeno(1,2,3-cd)pyrene were detected in the common. Furthermore, Naphthalene and Anthracene were detected only in the 56 nm particles, and Benzo(b)fluoranthene and Benzo(g,h,i)perylene were detected only in the 100 nm particles. PAHs of five rings or more in the 100 nm particles had tendency to be higher than that of 56 nm (The PAH concentrations of 56 nm vs. 100 nm were 0.28 ng/m³ to 0.85 ng/m³ at five rings or more, and 1.21 ng/m³ to 0.14 ng/m³ at four rings or less). On the other hand, PAHs in the 10 nm particles were less than lower limit of quantification.

For other hydrocarbons by thermal desorption GC-MS analysis, hydrocarbons of C8-C24, organic acids of C8-C18 and esters of C17-C28 were detected in each particle size. However, we could identify no specific hydrocarbon compositions in the 10 nm particles. In addition, it was confirmed that the surface of each particle size was more likely to be covered with hydrocarbons (especially organic acids) by FT-IR analysis.

In conclusion, it was confirmed that there was not so much difference of chemical compositions between each particle size.

Peters A. / Helmholtz Zentrum München, Germany

Health Effects of Ambient Ultrafine Particles – Do we know enough?

Health effects of ultrafine particles defined as particles with a diameter less than 100 nm are being studied since two decades. Short-term health effects have been studied repeatedly in different settings assessing the link between ultrafine particles and time-series of mortality or hospital admissions. In addition, panel studies have assessed the short-term impact of ultrafine particles on respiratory and cardiovascular function in healthy as well as in patients suffering from for example asthma, coronary artery disease or diabetes. In contrast, studies on long-term health effects of ultrafine particles have not been published. The presentation will summarize the evidence on from epidemiological studies. It will contrast the strength of the evidence for ultrafine particles to the evidence available for fine particulate matter and other particle metrics. Evaluating the health effects of ambient ultrafine particles in epidemiological studies poses several methodological challenges due to their high temporal and spatial variability. For an overall evaluation, the presentation will integrate evidence from epidemiological and toxicological studies and highlight the implications of current gaps in knowledge.

Pieber S.M. / PSI, Switzerland

Catalytic Reduction of VOCs from Wood Burning Emissions

Residential wood combustion with log wood stoves is a significant source of primary particulate matter (PM) and volatile organic compounds (VOCs), particularly in cold seasons in regions with moderate and cold climate. In addition to the primary PM emissions, the formation of secondary organic aerosol particles (SOA) is significant (Grieshop et al., 2009a,b; Heringa et al., 2011).

Secondary organic particulate matter is formed when volatile precursors (VOCs) partition from the gas phase into the particle phase. Partitioning takes place by condensation or nucleation, due to a change in the volatility of VOCs based on dilution, temperature changes or a changed oxidation state due to atmospheric oxidation with OH radicals, O₃ or NO₃. Therefore, removal of VOCs from the exhaust gas stream will decrease the SOA formation potential of the emissions.

Primary emissions from wood combustion (PM and VOCs) can be reduced by changing the burner technology and burning procedure. Where these parameters are limited (e.g. for log wood stoves), exhaust gas after-treatment systems may be effective. While primary PM emissions may be reduced by applying mechanical measures (e.g. electrostatic precipitators), catalytic conversion is required for the reduction of VOCs.

The performance of catalytic material on the conversion of VOCs from real world emissions was tested in our study. Exhaust from a log wood stove fueled with beech wood was sampled from the chimney into a 3 m³ batch chamber (Teflon). This mixed sample of PM and VOCs was used to evaluate the efficiency of catalytic materials at different temperatures (100 – 600°C). The SOA potential of the treated exhaust gas samples was investigated by oxidizing the sample in a Potential Aerosol Mass Chamber (PAM Chamber, Lambe et al., 2011).

The VOC composition of the exhaust gas sample was determined with a HR-proton transfer reaction-TOF-mass spectrometer (Ionicon). The particle phase was characterized using an HR-TOF-aerosol mass spectrometer (Aerodyne), SMPS and CPC. Black carbon was quantified using Aethalometers (Magee Scientific). The initial concentrations were around 10.000 ppmC CO₂, 1.000 ppmC CO, 240 ppmC CH₄, 250 ppmC NMHC, and 8 mg m⁻³ PM₁ and 3 mg m⁻³ BC. The water content of the sample was below 1 vol%.

The temperature dependent conversion of CH₄, CO, and NMHC was determined. A speciation between different VOCs from the NMHC fraction measured by the PTR-TOF-MS showed also temperature dependent conversion and breakthrough of different aromatic hydrocarbons (benzene, toluene, naphthalene, etc.). These temperature dependent conversion curves and their effect on the SOA formation potential of the exhaust gas will be presented and discussed in the conference contribution.

Riccobono F. / JRC, Italy

How to Extend the Real Drive Emission Test Procedure to Particle Number

The European Regulation (EC) 715/2007 as amended by Regulation (EC) 459/2012 requires the application of a complementary test procedure assessing the real-driving Particulate Number (PN) emissions of vehicles at type approval as from 2017. PN emissions should be determined using portable equipment during on-road vehicle tests, according to the general rules for the Real Driving Emissions (RDE) test procedure (Weiss et al., 2011).

In this respect, the European Commission has published a call for "Participation in the development of a test protocol to measure PN emissions on-board of light-duty vehicles for type approval using Portable Emission Measurement Systems (PEMS)". Several major instrument manufacturers expressed their interest to participate and joined the exercise, aimed at evaluating the possibility to extend the RDE procedure to particle number.

The main objective of the PN-PEMS programme is to assess whether the PN-PEMS equipment is suitable for measurements against a regulatory emission limit of $6 \cdot 10^{11} \text{ km}^{-1}$. In this case, the European Commission will proceed to the full integration of PN emission measurements into the general regulatory RDE test procedure.

Five vehicles (DPF equipped diesel vehicle and gasoline direct injection vehicles) were tested on a chassis dynamometer and on-road under RDE test conditions. PN-PEMS results were compared to reference (PMP) laboratory systems and will be used to define the setup of the PN-PEMS Pilot Study. The overall instrumental variability will be absorbed by the conformity factor to be applied to the current PN emission standard. The implications of different calibration procedures (i.e.: versus a primary laboratory aerosol standard or a secondary aerosol standard, PMP) will be discussed. The presentation will cover the current status of the PN-PEMS programme and present the roadmap for future activities of PN-PEMS.

Rodriguez L. / Universidad Nacional de Colombia

Particle Number Measurements of a CNG Euro VI Bus Operating in Bogotá for Public Transport

As an attempt to improve air quality, Bogota District's Government established that all new buses to be used for public transportation since 2014 must meet EURO IV and V emission levels. Nowadays, in-use diesel vehicles in the District are equipped with EURO II and III engines and will have a 10-year lifespan. However, Colombia has natural gas reserves for more than 20 years. Some cities in Colombia uses compressed natural gas buses in the BRE systems. A CNG Scania bus which meets the European standard Euro VI was tested under local conditions. The results will be used to establish the technical viability of the fleet implementation in the mass transport systems of the biggest Colombian cities. In order to carry out the evaluation, some SAE recommended practices were modified to apply to this type of bus. Performance parameters like tanks filling time, acceleration, startability, driveability, fuel consumption, and flexibility were obtained. In addition, portable emission measurement systems were used to determine on-road emission factors (EFs) - expressed as the amount of pollutant emitted per distance driven, as well as energy and fuel consumption. The tests were made in Bogota, Colombia's capital with 10 million inhabitants and located at 2,600 meters above sea level. Bogota is implementing new emissions standards in order to determine the effects of emission control technologies, real-world driving conditions, speed, altitude, load and traffic on Particulate Matter (PM), Particle Number (PN), and Nitric Oxides (NOx) emissions. The CNG Euro VI Scania bus was loaded with an equivalent of 120 passengers, using water barrels plus equipment and staff riding the bus under the test. The bus was evaluated under real-world urban traffic conditions, following previously selected routes and bus stops from those covered by the Integrated Public Transport and BRT systems, as established by transport authorities (Secretaría Distrital de Movilidad, 2012). Representative route and reference route cover 73.9 km and 39 km, respectively. The bus was tested with at least three times over the selected routes. Speed and position data were recorded along the routes using high-resolution Global Position System (GPS) receptors. On-road measurements were carried out by a mobile laboratory instrumented with an Electrical Low-Pressure Impactor (ELPI+, Dekati Ltd., Finland), a two-stage exhaust diluter (Fine Particle Sampler -FPS4000, Dekati Ltd. Finland), a PMS Particle Counting Nanomet 3 (Matter Aerosol – Testo INC, Switzerland), a real-time gas exhaust flowmeter (Semtech EFM-HS High Speed Exhaust Flow Meter, Sensors Inc., Saline, MI), a gas analyzer (Semtech-D, Sensors Inc., Saline, MI), and a Vehicle Activity Monitor – VAM – unit (International Sustainable Systems Research Center, La Habra, CA). An external 5 kW genset was used to power the instruments.

The particle number of the CNG Euro VI Scania bus is extremely low compared to diesel Euro IV and V buses running on local conditions. In general, a 20,000 particles/cm³ are emitted by the CNG bus. Diesel Euro IV and V buses emit 50 millions of particles/cm³. The CNG bus fuel consumption was also low compared to the diesel buses. Fuel consumption of the CNG Euro VI bus, Hybrid diesel Euro V bus, and Diesel Euro V bus are 0.76, 0.62 and 0.87 American gallons/ton, respectively. Euro VI standard fuelled with CNG is feasibility technology for the BRT system in Bogota.

Seipenbusch M. / TU Karlsruhe, Germany

Interdependence of Particle Number Concentration and PM 2.5 in Highly Polluted Urban Atmospheres

The number concentration of urban aerosols is dominated by the fraction of fine and ultrafine particles, mostly from anthropogenic sources such as soot and sulfuric acid, while in the mass concentration the coarse mode of the size distribution prevails, which originates mostly from natural sources such as mineral dust from erosion, sea salt from ocean spray or pollen. Due to size and composition health effects are predominantly attributed to the fine and ultrafine fraction. Observations of the particle number concentration in the highly polluted urban atmospheres of mega cities such as Beijing (Yue et al., 2009) or Mexico City show a clear coincidence between the occurrences of extreme events in the number concentration with minima in the overall mass concentration of the aerosol. In Beijing number concentrations of $1.2E5 \text{ cm}^{-3}$ were measured at a reported particulate mass below $2.5 \mu\text{m}$ (PM_{2.5}) of $300 \mu\text{g}/\text{m}^3$ while in the same location $2-5E5 \text{ cm}^{-3}$ were measured at $50 \mu\text{g}/\text{m}^3$. This example illustrates that regulations which are entirely based on particulate mass are not suitable to target the number concentration and the fine particle fraction appropriately and may not be adequate for the control of emissions and the protection of public health.

One explanation for the mismatch between number concentration and PM 2.5 is binary coagulation between the two size modes which can have a pronounced effect on the concentration of fine particles if the size difference of the two constituents of the aerosol is large enough and the concentration of the coarse mode is high (Seipenbusch, Binder, & Kasper, 2008). The contribution will discuss experimental data available on this issue, the possible mechanisms explaining it as well as ensuing regulatory implications.

Steiner S. / Adolphe Merkle-Institute, Fribourg, Switzerland

***In-vitro* Genotoxicity of Diesel Exhausts: Impact of Filtration and Catalysis**

Diesel exhaust filtration by diesel particle filters (DPFs) is one of the key strategies for the detoxification of diesel engine emissions. It is well documented that exhaust particles strongly contribute to the overall exhaust toxicity (1) and given the excellent filtration efficiency of modern DPFs, it is not surprising that numerous toxicological studies report decreased exhaust toxicity downstream a DPF, at least with respect to pro-inflammation, oxidative stress and systemic (e.g. vascular or prothrombotic) effects (1, 2, 3, 4).

Detailed studies on how DPFs affect the non-particulate exhaust fractions imply however, that exhaust filtration may result in the formation and increased emission of nitrated polyaromatic hydrocarbons (NPAHs)(5, 6). Such secondary emissions are formed by the reaction of organic compounds temporarily stored in the filter with nitrogen dioxide and other reactive nitrogen species that either pass the filter or are directly formed on the filter. Many NPAHs are well known for their ability to chemically attack DNA, the genetic material of cells and thereby potentially act mutagenic and cancerogenic, and an increase in exhaust mutagenicity can be assumed to result from their increased formation.

In light of the potential formation of such carcinogenic secondary emissions, we investigated how exhaust filtration by a non-catalyzed DPF influences diesel exhaust mutagenicity, and what the role of catalysts is in this context. We exposed cultures of the Ames-test bacterium *Salmonella typhimurium* to diesel exhaust that was either *i)* untreated *ii)* filtered by a non-catalyzed DPF *iii)* produced from diesel additized with Satacen®3 (a fuel borne additive for DPF regeneration) or *iv)* produced from diesel additized with Satacen®3 and filtered by the same DPF.

Untreated and filtered exhaust both acted mutagenic, but the effect was about 10-fold higher for the filtered exhaust. Inclusion of Satacen®3 without filtration resulted in the same mutagenicity as untreated exhaust, whereas additional filtration completely eliminated exhaust mutagenicity. At the level of resolution available in this study, the DPF and Satacen®3 only affected the particle concentration in the exhausts, whereas the concentrations of gaseous components (volatile hydrocarbons, carbon monoxide, nitrogen oxides, nitrogen dioxide and nitric oxide were measured) were not substantially changed. Our results imply that filtration is necessary but not sufficient for the elimination of mutagenic exhaust components, and most importantly, that filtration may even increase exhaust mutagenicity by inducing chemical modifications of organic compounds stored in the filter. Properly catalyzed filters may overcome the problem of secondary emissions. They allow efficiently removing the mutagenic activity of particles and particle-adsorbed organic compounds by simultaneously avoiding the formation of secondary mutagenic emissions.

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Stettler M.E.J. /University of Cambridge, UK

Nanoparticle Emissions from Heavy Duty Dual-Fuel Diesel and Natural Gas Engines

This paper presents the first detailed characterization of nanoparticle emissions from heavy duty diesel engines prior and subsequent to an after-market dual-fuel (natural gas-diesel) conversion. Commercially available after-market conversion systems enable existing compression ignition engines to operate in dual-fuel mode with combustion of a pre-mixed air and natural gas charge with a diesel fuel pilot direct injection. The dual-fuel combustion can lead to reduced fuel costs and CO₂ emissions and has previously been shown to reduce emissions of NO_x and soot when compared to diesel combustion (Polk et al. 2013). The objective of this study is to quantify the emissions of the solid and semi-volatile PM (number, mobility and mass), as well as gaseous pollutants (NO_x, N₂O and speciated hydrocarbons). Methane emissions are evaluated to determine whether greenhouse gas emissions savings due to fuel switching are offset by methane slip.

A DAF CF75 tractor (PACCAR Engine PR228, 228 kW, EURO V) was tested on a chassis dynamometer at steady state and transient operating conditions. Engine emissions were sampled both before (engine out) and after (tailpipe) the Selective Catalytic Reduction (SCR) exhaust after treatment. Particle number concentrations were measured using condensation particle counters (TSI, 3776 and 3022) with and without semi-volatile removal (Catalytic Instruments GmbH, CS015). Particle size distributions were measured using a Scanning Mobility Particle Sizer (SMPS, TSI, 3080, 3081 and 3025) and Differential Mobility Spectrometer (DMS 500, Cambustion Ltd).

A time series of the total engine exhaust particle number concentration at several steady-state test points in diesel only mode is shown in Figure 1. The results indicate that particle number emissions are largely dependent on engine operating conditions (i.e. load and RPM) and number concentrations measured pre-SCR were typically greater than those measured post-SCR. In Figure 2, particle size distributions at a single test point (1079 s, 4120 N, 1000 rpm) are shown for the SMPS and DMS500; significantly more nucleation mode particles are observed at the engine out sampling location than the tailpipe.

Further results depict the measured nanoparticle and gaseous engine emissions as a function of engine operating conditions (i.e. load and RPM) when the engine is operating in both dual-fuel and diesel-only mode. We will compare measured emissions to regulatory standards and discuss the effectiveness of and necessity for exhaust after-treatment devices on after-market dual-fuel engine conversions.

Tartakovsky L. / Technion Israel

Analysis of Ultrafine Particle Emissions by In-Use Buses of Different Generation in Tel Aviv

This work presents results of particle mass, number and size measurements inside passenger cars (PCs). Effects of the built-in and the retrofit in-cabin air purifiers on particle concentrations and average size inside a vehicle are studied. The measurements are made with various vehicles of different makers, under different ventilation conditions and different starting particle concentrations in the vehicle cabin. Particle number concentrations (PNC) in the cabin of vehicles without an adequate air filter, with a genuine OEM-made filter of different types and a non-original air filter are studied. Influence of a retrofit high efficiency cabin air filter was investigated too.

Various parameters are known as influencing the ultrafine particles concentration inside a vehicle: ventilation mode, fan speed, cabin air filter, outside particle concentrations, driving speed, vehicle age, etc. The time required to reduce the in-cabin particle levels to the value of 4000 cm^{-3} , typical for a clean office is found to be at least 6 minutes. An old car couldn't reach this PNC value. Genuine filters are proved to be more efficient as compared with the non-genuine ones. The lowest values of particle concentrations inside a PC without air purifier are registered under the recirculation ventilation mode, but the issue of CO_2 accumulation limits the use of this mode to very short driving events. The results of our measurements suggest that in case of using the recirculation ventilation mode, acceptable CO_2 concentrations inside a car are exceeded after approximately 6-7 min of driving. We studied particle concentration values that may be achieved inside a vehicle's cabin after 7 min of driving in the recirculation ventilation mode at different initial particle concentrations. It was found that PNC decreased after 7 min to values $2500 - 22000 \text{ cm}^{-3}$ for the initial in-cabin particle concentrations of $45000 - 428000 \text{ cm}^{-3}$, respectively. Increasing the speed of the ventilation fan reduces the time required to reach the clean-office PNC.

Van Ham J. / EFCA, The Netherlands

A Fraction-by-Fraction Approach for Particulate Matter

In recent years the conviction has become stronger that the present approach of regulating particulate matter through inadequately defined, mass-based metrics has too many deficiencies. A fraction-by-fraction approach, recently advocated by EFCA, may obviate the most important deficiencies of present PM-regulation. In such an approach fractions are defined according to their specific toxicity; this means in practice that chemical identity as well as size fraction are being considered in connection. In this paper the fraction-by-fraction approach will be explained in more detail and its feasibility will be discussed.

Violi A. / University of Michigan, USA

How Chemical Composition of Nanoparticles Affects Interactions with Biological Systems

Combustion-generated particles are present not only in a very large amount, but are produced, at the smallest scale, in the form of clusters with nanometric dimensions. Given that such great quantities of carbonaceous nanoparticles are being introduced into the atmosphere by combustion sources, the question naturally arises as to their environmental fate. Experimental evidences show that particle deposition on the epithelial cells in the lungs trigger a number of responses including cell activation leading to inflammation; production of cytokines (proteins) that stimulate the release of fibrinogens, which bind to platelets, contribute to their aggregation, and enhance their ability to clot.

In this work we present a new model to predict the formation of nanoparticles from different fuels and study their interactions with biological cells. Specifically, we will address the differences between petroleum-based fuels and renewable fuels. 1) How the presence of oxygen in the fuel affects the formation and the characteristics of nanoparticles? How does the presence of oxygen influence the interactions of nanoparticles with biological membranes? Simulations can provide molecular-level insight into the relationship between nanoparticle characteristics and mechanisms of direct physical interaction with biological matter.

Using Molecular Dynamics simulations, we investigate the thermodynamics and mechanism of the permeation of carbon-based nanoparticles through cell membranes.

Preliminary results have demonstrated that the presence of oxygen on the surface of nanoparticles changes dramatically their interactions with cell membranes. In particular the free energy of insertion of hydrophilic particles will show a different permeation as compared with the corresponding hydrophobic material.

The simulations will identify non-canonical uptake mechanisms and their role in subverting cellular functioning. These studies will provide a better understanding of the fundamental biophysical conditions that predicate benign or toxic nano-biointeractions.

Vojtíšek M. / Czech Technical University

Measurement of Particle Emissions from Small Engines During Real World Operation

The focus of this work is the application of portable on-board monitoring systems (PEMS) and real-driving emissions (RDE) concepts to small engines such as in scooters, lawnmowers, and similar equipment.

While particulate matter (PM) emissions from on-road engines are being targeted and in many cases have been successfully reduced with advanced engine and aftertreatment technologies, small inexpensive engines in scooters, garden equipment and various mobile machinery are much less sophisticated, and their PM emissions can match or exceed those of on-road engines. On the other hand, the operators of small engines are in close proximity to their exhaust, and are therefore likely to be at risk.

The aggregate PEMS experience to date suggests that RDE emissions often tend to be higher than during certification tests, notably under conditions not covered by laboratory tests; that large portion of PM is emitted during short high-emission episodes; that large portion of total fleet PM originates from a small fraction of engines; and that the relative magnitude of the mentioned excess emissions increases with the degree of technical sophistication of the engines and with their decreasing emissions. There is no apparent reason to believe that the situation will be different for small engines, which therefore should be subjected to RDE evaluations just as the on-road engines.

Several alternatives for a low-cost small engine PEMS are offered here. In one case, a scooter has been equipped with a 13-kg PEMS consisting of a garage-grade gas analyzer with additional sensors to measure HC, CO, NO, NO₂, CO₂ and O₂, a light scattering instrument to measure PM, and a ionization chamber to measure total PM length. The intake air flow has been computed from measured engine rpm, measured temperature and pressure of the intake manifold charge, and assumed volumetric efficiency. Speed and position has been recorded with GPS. In another case, where on-board installation was not feasible, a hand-held weed-whacker has been fitted with a sampling line from a PEMS installed on an accompanying yard tractor.

In another case, a miniature full-flow dilution tunnel has been fabricated using a turbine from an industrial vacuum cleaner, placed on a baby stroller chassis, and exhaust from a lawnmower has been directed to this tunnel. The tunnel flow has been measured with a thermal mass flow meter, and the concentrations of gaseous and particulate pollutants from the diluted sample were measured using the described PEMS.

Further, a 150-mm filter holder has been installed into the tunnel, and all PM emitted by the engine was captured on a filter, yielding a sufficient amount of material not only for gravimetric measurement of total PM mass, but also for a detailed analysis of carcinogenic polycyclic aromatic hydrocarbons (cPAH) and for simple toxicological assays. A HEPA filter has been installed on the air inlet of the tunnel to reduce artefacts from grass cutting operation. Cold start of a recent production four-cycle lawnmower engine has produced hundreds of micrograms of 7 cPAH per kg of fuel, an order of magnitude more than „stabilized“ operation.

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Von Garnier Chr. / Inselspital Bern, Switzerland

Health Effects of Nanoparticles in Susceptible Persons

Individuals with chronic cardiovascular and pulmonary disorders are at risk for adverse health effects caused by combustion-derived particles. Once inhaled, such particles trigger inflammatory responses in the respiratory tract and entire organism, leading to worsening of underlying chronic disease.

Weise F. / NMI, Reutlingen, Germany

Toxic Effects of Nanoparticles from Biomass Combustion

The employment of energy for heating is currently characterised by two trends, namely the trend towards decentralised, domestic heating plants, and the trend towards CO₂-neutral, i.e. renewable sources of energy. In the light of such global trends, we became interested in assessing the toxic potential of nanoparticles emitted from domestic biomass combustion. To this end, we employed a commercially available log wood stove (Buderus blueLine 4W, 8 kW) and analysed the stress responses of two types of lung cells exposed to particles with diameters of up to 1 µm at the air liquid interface.

As initial experiments had revealed that the particle deposition efficiency on cells exposed to conventional exhaustive aerosol flow is too low to elicit a significant effect, we have developed an exposure system in which the efficiency of deposition is increased by a moderate electrical field (approx. 330 V/mm; see Fig. 1): A549 cells (reflecting human type II pneumocytes) and SK-MES-1 cells (reflecting type I pneumocytes) were seeded onto the semi-permeable membrane of a Transwell cell culture insert, allowing for exposure to the aerosol at the upper side whilst enabling the uptake of liquid and nutrients from the cell culture medium at the bottom. The deposition of nanoparticles from the aerosol entering the chamber via a trumpet-shaped inlet is greatly enhanced by the application of an electrical field without compromising cell viability.

In order to minimise the background noise caused by cellular stress due to prolonged exposure at the air-liquid interface whilst at the same time ensuring a sufficiently long exposure time, cells were cumulatively exposed for 6 h on three consecutive days, in three exposure sessions of 2 h each. The expression of four genes indicative of cellular stress (HMOX1, HSP27, IL-6, and IL-8) was analysed 24 h after the last exposure session: Whereas A549 cells did not show a significant change in the marker gene expression, exposure to nanoparticles induced a significant expression of heme oxygenase 1 (HMOX1) in SK-MES-1 cells. Interestingly, this cellular response was less pronounced when the cells were exposed to the nanoparticles under submerge conditions, stressing the importance of the exposure at the air-liquid interface.

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Yamada Hiroyuki / NTSEL Japan

Measuring Particles less than 23 nm using PMP Methodology

We evaluate the validity of enhancing the measurement size range with PMP methodology to 2.5 nm by replacing PNC from various aspects. D50 evaluation of PNC using electro-spray particle generator indicates that increasing uncertainty in lower particle diameters. This is because the number of particles produced by electro-spray aerosol generator decreased with smaller particles. CoVs are more than 15 % for the particles below 5 nm.

For evaluating PCRF, and volatile particle removal efficiency at VPR, we did not find any difficulties about the procedures of yearly checks with 15 nm particles. However, particle losses at VPR increased with the smaller particles and it was almost 30 % at 15 nm.

In the measurements of exhaust gas from gasoline DI vehicles, the ratio of particles below 23 nm in total emission in cold mode was 13.7 %. In hot mode, the ratio increased to 42.7 %. In this condition, these small particles were emitted mainly during high speed operations. Experimental fluctuations of the measurements with PNC_{2.5} in cold and hot modes were similar to those by PNC₂₃ suggesting the enhancement of the size range to 2.5 nm with PMP methodology did not increase experimental uncertainty. Re-nucleation effects of semi-volatile particles were disappeared by increasing PCRF over 1000 in case of gasoline DI measurements. In the experiments of measuring size distributions of the particles from heavy duty diesel engine with DPF at the exit of VPR, re-nucleated particles were observed below 10 nm, and it did not disappear even in the condition whose PCRF is 3000. It is because diesel fuel contains higher amounts of the larger hydrocarbons than gasoline, and these larger hydrocarbons are also higher in the exhaust gas.

These results indicate the measuring particle size range with the PMP methodology can be enhanced to 10 nm.

Yamamoto Kazuhiro / Nagoya University Japan

Size Distribution and Oxidation Rate of Carbon Nanoparticles

An after-treatment of exhaust gas for cleanup of diesel emissions generally includes devices for reducing both emissions of PM and NO_x by controlling the engine system itself, together with a diesel particulate filter (DPF) to trap PM in the exhaust gas. The major issue with DPFs is that they become clogged with collected PM to cause a pressure rise across the filter, resulting in a subsequent worsening of fuel efficiency and a decrease in engine output. Therefore, a regeneration process is required, which is an incineration step to remove deposited PM. Technically, this involves a regeneration system that use some type of electric heating or burner system, which raises the temperature of the PM to be oxidized. Alternatively, an innovative soot and NO_x conversion system has been proposed. It is possible to continuously oxidize PM trapped by the filter, and therefore is called a continuously regenerating trap (CRT). There are two stages for PM oxidation. As the first stage with an oxidation catalyst (e.g., a platinum catalyst), nitrogen oxide (NO) becomes nitrogen dioxide (NO₂). In the second stage, PM is oxidized by NO₂ as well as oxygen. In our previous studies, we have conducted a numerical simulation of this type of continuously regenerating DPF.

So far, it is difficult to evaluate the oxidation process of diesel soot, because we cannot observe the variation of particle size of trapped soot during the oxidation. Moreover, characteristics of diesel soot depend on fuel properties, exhaust gas component, and engine conditions. Then, we used carbon particles as model soot, and carbon particle size and its number concentration were experimentally measured in the presence of NO₂. To realize the oxidation at uniform temperature, a tubular furnace was used. The particle size was measured by SMPS, together with the measurement of CO and CO₂ concentrations.

Results show that the carbon particle size and the number concentration decrease as the furnace temperature is increased. When only oxygen is an oxidizer, little change is observed in the particle size distribution until the temperature is 345 °C. The carbon particle starts to be oxidized at temperature of 420 °C. The bulk particle size firstly decreases, and then, the particle number becomes smaller. When NO₂ is added, the oxidation temperature is reduced, and the particle size is much smaller with less number concentration. In the Arrhenius plots, a good linearity is confirmed, showing that the reaction rate constant of carbon oxidation becomes larger when more NO₂ is added. Roughly, in the presence of NO₂, the carbon oxidation rate is close to the value of diesel soot with catalyzed DPF.

Zarcone M. / Leiden University Medical Center and TNO, The Netherlands

Development of an Innovative in Vitro Inhalation Model for Studying the Effects of Diesel Exhaust

Exposure to diesel exhaust (DE), a major traffic-related component of air pollution in urban areas, is associated with a wide spectrum of negative health effects, especially in vulnerable populations such as patients with respiratory or cardiovascular disease. The underlying molecular mechanisms that explain these health effects are not fully understood, and mechanistic studies require a realistic in vitro inhalation model to whole DE. Therefore the aim of the present study was to develop a model in which well-differentiated primary bronchial epithelial cells (PBECS) cultured at the air liquid interface (ALI) are exposed to whole diesel exhaust (gas and particles). A diesel generator was used to generate exhaust (4 mg/m³ PM) which was collected in a tank where humidification level, PM size distribution (SMPS) and O₂ /CO₂ concentration were measured. The DE was directed (undiluted and further diluted to 1.2 and 0.4 mg/m³) to 3 dedicated exposure modules (Vitrocell®) in which 3 cell inserts per unit are exposed to the mixture, followed by a filter for PM concentration measurement. A fourth module was exposed to humidified air as control exposure. We first assessed the variability of the exposure in 4 independent exposure sessions of 1hr using cells from the same donor, and measured the activation of the oxidative stress response (HMOX1) at 6hr after the exposure. Next, we developed a time curve of exposure to DE for 01:00, 02:30 and 06:15hr; samples were collected at 6 and 24hr after exposure, and assessed for cytotoxicity (LDH release), epithelial barrier function (TEER measurement), oxidative stress (HMOX1 mRNA) and endoplasmic reticulum (ER) stress response (CHOP, GADD34 and spliced XBP1 mRNA). No cytotoxic effects or effects on barrier function were noted after 1 hour exposure, but prolonged exposures resulted in cytotoxicity at the highest DE dose (4 mg/m³; up to 30% LDH release after 06:15hr exposure and 24hr incubation). Dose-dependent increases in HMOX1 (till 15~f.i.), CHOP (till 2~f.i.) and GADD34 (till 2.5~f.i.) expression were observed at 6hr after exposure, and were no longer observed after 24hr. No increase in XBP1 spl was observed. These results demonstrate the feasibility of an in vitro model of fully differentiated airway epithelial cells to whole DE. Use of this model will enable comparisons of the susceptibility of PBECS from different patient populations, investigations into the effect of exposure dose and exposure duration on the cellular response, and mechanistic studies. This study was supported by the Lung Foundation Netherlands (grant# 3.2.11.009)

Zellner R. / University of Duisburg-Essen, Germany

Strategies for Research and Policies to Reduce Health Effects from Fine Particles in Ambient Air

Despite an extensive body of EU regulatory legislation to control and reduce particulate matter concentrations in Europe, first entered into force in 2005, humans remain to be affected by exposure to pollutants in ambient air. The principles of EU legislation include that Member States should undertake assessments of air pollution levels using measurements, modelling and other empirical techniques. Where levels are elevated, the Member States should prepare an air quality plan or programme to ensure compliance with the limit value. The most notorious programme regarding PM was the introduction of Low Emission Zones (LEZ) with traffic reductions according to the vehicles' emission levels. The expected beneficial effects of these, however, are still discussed controversially.

At DECHEMA/ProcessNet in Frankfurt we have been operating an interdisciplinary working group for several years now with the aim to (1) evaluate and assess scientific findings and to (2) recommend regulatory measures for ambient fine particles. The group is supported by the German Chemical Society (GDCh) and the Commission of Air Pollution Prevention of VDI/DIN. Whilst the status of fine particles and their health effects in Germany has resulted in a 2010 position paper

(http://www.processnet.org/processnet_media/FG+SuPER/Statuspapier+final+klein.pdf), we have now delineated the strategies for further improvements of air quality in Germany regarding PM and fine particles. This strategy is based on a reevaluation of the different sources of human technology that contribute to ambient fine particles including agriculture, domestic heating, traffic and industry. In addition we have focused on biological particles as well as on secondary organic aerosols (SOA) from VOCs and SOCs. We conclude that each of these sources contributes substantially to current levels of PM and fine particle concentrations and their exceedences but are currently inadequately investigated and controlled. In addition we suggest that the current metrics for ambient particles, namely mass/volume, is inadequate to capture the full dimension of health effects. Rather we propose to develop and deploy a chemically (and size) differentiated and biological effect related metric that takes into account the specific effects of fine particles with different chemical composition.

Zotter P. / PSI, Switzerland

14C-based Source Apportionment of Carbonaceous Aerosols in Switzerland for 2008 – 2012

Carbonaceous particles (total carbon, TC) are a major fraction of the fine aerosol and affect climate and human health. TC is classified into the sub-fractions elemental carbon (EC) and organic carbon (OC). EC originates only from fossil fuel combustion and biomass burning. OC can be emitted directly as primary organic aerosol from biogenic emissions, wood burning and fossil fuel combustion or can be formed in-situ in the atmosphere (secondary organic aerosol). Radiocarbon (¹⁴C) analysis is a direct and quantitative tool for distinguishing fossil and non-fossil sources, since ¹⁴C in fossil fuels is completely depleted whereas other sources have a contemporary ¹⁴C level.

This study presents source apportionment results from the winter season over a time period of 5 years (2007/2008–2011/2012) using ¹⁴C measurements on aerosol filters collected simultaneously at 16 air quality monitoring stations across Switzerland. For every year 5 winter-smog-episode days were selected from which filters from all stations were analyzed. The samples are also analysed for EC/OC, major water-soluble ions and levoglucosan content. Black carbon (BC) was measured at 4 stations by Aethalometers and apportioned into a traffic and wood-burning fraction. This is an unprecedented dataset in terms of number of samples analysed and methodologies applied, providing unique insights into wintertime carbonaceous aerosol sources.

OC and EC account respectively for ~80% and ~20% of TC, the second largest component of PM during the measurement period after Nitrate (25%) contributing 23% of total PM. ¹⁴C-results indicate that carbonaceous aerosol is overwhelmingly non-fossil (83% of OC and 46% of EC), suggesting that wood burning is the major source of TC in Switzerland during winter smog episodes. The highest non-fossil values (100% and 87% for OC and EC, respectively) were registered for alpine valley sites and the lowest at highly traffic influenced sites (47% for OC and 15% for EC). The spatial and temporal trends of biomass burning contribution observed during 5 winters and at the different sites will be further discussed and related to the prevailing meteorological and wood combustion conditions.

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