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Chemical Characterization of Particulate Matter Aircraft Turbine Engine Exhaust using Single Particle Mass Spectrometry

Background

Commercial air traffic has steadily increased in the past in terms of passenger revenue kilometers and the trend continues with an estimated annual growth rate of $3.4 - 6.1 \%^{1}$. The emitted particulate matter (PM), mainly soot, is of special interest because it alters the Earth's radiation budget by absorbing and scattering solar radiation. Moreover, these particles could act as Ice Nucleating Particles (INP) and initiate the formation of contrails which, depending on the conditions, could emerge into cirrus clouds. This aerosol-cloud interaction was reported as the most important radiative effect with regard to aviation². However, the microphysical processes and aerosol species involved in ice nucleation are not yet completely understood. A recent study³ shows that a dominant fraction of Ice Residuals (IR) collected in cirrus clouds contain metals (e.g. sodium, potassium, copper, iron), which have also been found in aircraft emissions by sampling the exhaust⁴. Thus, to investigate the link between aircraft emissions and ice formation in the atmosphere, a thorough chemical and physical characterization of fresh aircraft PM emissions is needed.

Herein, we present chemical and statistical analysis of fresh aircraft PM exhaust derived from single-particle mass spectrometry. The PM emissions were analyzed with respect to the occurrence of metal-containing particles and the mixing state. Furthermore, we try to identify particle sources e.g. engine abrasion, fuel or lubricant oil.

Investigation methods

Single particle mass spectrometry on PM from fresh aircraft exhaust was performed using an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS, TSI Model 3800). The measurements were conducted in the framework of the ongoing "Aviation - Particle Regulatory Instrument Demonstration Experiment" (A-PRIDE) campaigns. The aircraft engine studied was a CFM56-7B26/3. The unattached engine was operated in a test cell by SR Technics. The particles were sampled directly behind the engine with a probe and passed to the ATOFMS ~30 m downstream.

The ATOFMS measures the chemical composition of single particles. An ionization laser ablates the particle and ionizes its constituents. The emerged ions are then classified according to their mass-to-charge ratio resulting in a mass spectrum. The mass spectra are used to identify the chemical components, the mixing state of individual particles and to provide semi-quantitative information on the content of specific particle components.

Results and Discussion

Soot from combustion sources typically contain Elemental Carbon (EC) which is reflected in the mass spectra by a C_n (n = 1, 2, 3, etc.) pattern. This EC pattern was found on a vast majority of the particles analyzed.

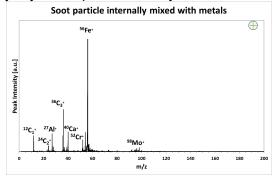


Figure 1 Positive mass spectrum of an internally mixed fresh aircraft exhaust particle showing an EC pattern and multiple metals (Aluminum, Calcium, Chromium, Iron and Molybdenum). A large particle fraction contained additional individual metal species. The most abundant were Cr, Fe, Mo, Na, Ca and Al, but V, Ba, Co, Cu, Ni, Pb, Mg and Si were also present. The metals were internally mixed with the soot particles as exemplarily depicted in *Figure 1* showing a positive mass spectra of a single particle.

The source-identification of the metal compounds found within the exhaust particles is still ongoing. For this, the presented study will include a comparison between our chemical characterization of single particles with data from chemical bulk analysis of the jet fuel and jet engine lubricant oil used in this study. The latter was obtained from inductively coupled MS.

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Anderson M. / Chalmers University Sweden

Nanoparticle Emissions from LNG and other Low Sulphur Marine Fuels

The shipping sector faces new challenges with existing and up-coming regulations of allowed sulphur content in marine fuels. The International Maritime Organisation (IMO) sets the regulation and limit the fuel sulphur content to 0.1 wt% in sulphur emission control areas (SOx ECAs) from 2015 and to 0.5 wt% at global level from 2020 (IMO, 2013). The driving force for the implementation of this regulation was reduced acidification, but has changed to health aspect of particle emissions (Svensson, 2011). This stricter regulation force ship owners to use low-sulphur marine fuels or use other types of fuels, e.g. liquefied natural gas (LNG). Few studies consider emissions of nanoparticles from ships running on low-sulphur marine fuels and, to our knowledge, no other studies have estimated the particle emissions, i.e. particle number and size distribution by number, from a ship running on LNG.

The measurements were done during two different campaigns. A test-bed engine in an engine lab at the department was used for studies of particle emissions from heavy fuel oil (HFO, 0.1 wt% S) and marine diesel oil (MDO, 0.5 wt% S), i.e. comply with regulation. Onboard measurements were done to estimate particle emissions from dual-fuel engines running on LNG. An Engine Exhaust Particle Sizer (Model 3090, TSI Inc.) and a dust monitor (Grimm, Model 1.108) were used for particle measurements.

The measurements showed that combustion of HFO leads to highest particle emissions followed by emissions from MDO and last LNG. The particle emissions were dominated by nanoparticles (diameter < 50 nm), independent of fuel type. Analyses of the size distribution by number showed a pronounced peak around 10 nm for both HFO and MDO and a second peak at 100-110 nm for HFO and at 45-50 nm for MDO. For LNG a peak around 10 nm was found. Solid particles were found in all sizes, while volatile particles were mainly nanoparticles. These measurements emphasize that both sulphur content and quality of the fuel are important to consider in evaluation of the particle emissions, though sulphur content mainly impacts the amount of nanoparticles, while fuel quality mainly affect particles with diameter above 50 nm. In the aspect of LNG, the main part of emitted particles is assumed to originate from the lubrication oil. The measurements indicate that the regulation of sulphur content in marine fuel oils will reduce the particle emissions, if ships begin to use high-quality fuels or other fuels, e.g. LNG and that other compounds in the marine fuel oils are of importance as well when consider particle emissions and eventual future legislation.

Financers: Göteborg Energi AB's Foundation for Research and Development (on-board measurements), *Ångpanneföreningens* Foundation for Research, the Foundation of IVL, Swedish Maritime Organisation and Lighthouse (test-bed engine measurements).

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Anderson R. / TSI USA

Near-Road Monitoring of Ultrafine Particle Number from Heavy Duty Diesel Truck Traffic

New regulations and health studies have increased the importance of assessing the exposure impacts to air pollution on and near congested roadways. Ultrafine particles (UFP, Dp < 100 nm) exposure may cause adverse health effects such as stroke, systemic inflammation, and asthma exacerbation. UFP are measured using condensation particle counters (CPC). Traditional CPC use butanol as a working fluid, are very expensive, not robust enough, and need constant operators' attention. In addition, the use of butanol may interfere with measurements of toxic contaminants when placed in the same air monitoring station along with toxic monitoring instruments.

This study evaluated the durability and precision of a water-based CPC (WCPC) designed to measure UFP concentrations with short time resolution and minimal operator attention for long periods in a routine ambient air monitoring network.

In this study, the WCPCs were placed within 15 meters of the Interstate 710 Freeway in Carson, California at an existing near-road monitoring site operated by the South Coast Air Quality Management District (SCAQMD). Interstate 710 is a busy freeway with approximately 180 to 240 vehicles per minute; heavy-duty diesel trucks account for about 25 percent of the traffic. The data presented here were collected from March 14 - April 17, 2014.

Durability was measured by the continued operation of the instruments using routine monitoring practices. Instrument precision was assessed using data from three collocated instruments for 35 days of operations. Results were analyzed using the criteria set forth to evaluate precision of PM2.5 Federal Equivalent Method candidate instruments as prescribed in 40 CFR Part 58 Appendix A. Percent coefficient of variation (%CV) analysis between the instruments was conducted

For the second part of the study, we expand the data set to include the traffic count and vehicle type by lane correlated to one meteorological instrument to measure wind speed and direction to verify when the CPCs are downwind of the freeway. SCAQMD obtained weigh-in-motion (WIM) data from the California Department of Transportation's on-road sensors located near the study site. WIM data was used to determine the type and number of vehicles passing by the study site during the study period. This data was evaluated to uncover correlations with the PN data to assess the contribution of gasoline powered cars and diesel powered trucks to the ambient air. This work was supported by the California Air Resources Board, Sacramento CA and South Coast Air Quality Monitoring Division (SCAQMD)

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Andersson J. / Ricardo UK

Origins and Development of European Particle Number Legislation

The application of diesel particulate filters (DPF) to heavy-duty engines and light-duty vehicles enables substantial reductions in particulate mass emissions to be realised. However, the European regulatory process does not enable the use of an emissions control technology to be mandated. Instead, a sufficiently challenging emissions limit has to be applied that effectively forces the desired best available emissions control technologies (BAT) to be adopted. In the case of particulate mass emissions, the existing gravimetric procedure was considered both inaccurate and insufficiently sensitive to be able to discriminate well enough between different PM emissions control approaches to force the fitment of closed wall-flow DPFs.

In Europe, from the mid 1990's, there was political desire, especially in the UK, Switzerland and Sweden, to reduce the negative health impacts of particulate matter emissions from vehicles. Research programmes aimed at achieving this culminated in the development of the particle measurement programme (PMP), which had the objective of developing an alternative measurement approach to "complement or replace the (filter-based) mass measurement metric". Research in the PMP led to the development of the non-volatile particle number metric, and eventually legislation to control PN emissions.

This presentation will overview the political drivers for a more sensitive metric, the process undertaken to develop the European PN approach, the development of limit values, the benefits seen, current status and possible future directions for PN measurements in Europe.

Bailey Brett / IVHCO USA

Global Non-Thermal Active SCR/DPF Emissions Reductions Technology

In developed countries, the reduction of emissions from internal combustion engines will become ever more challenging, as more efficient methods of vehicle operation, such as future diesel electric hybrid systems and exhaust energy recovery, place further thermal constraints on the current state-of-the-art Selective Catalytic Reduction, SCR effectiveness and Diesel Particulate Filter, DPF regeneration aftertreatment technologies. The stop/start advantages of a hybrid and anti-idling systems reduce the time available for thermal particulate filter regeneration along with creating multiple low temperature starts during normal operation. Exhaust energy recovery systems will require high differential exhaust temperature in order to attain sufficient conversion efficiency placing further constraints on current thermal management approaches. Before these next generation technologies are available, the cost and reliability improvement for the removal of Exhaust Gas Recirculation, EGR system will require quicker light off of the SCR catalyst and subsequent placement directly downstream of the engine or operation at lower temperatures. In order to additionally reduce packaging size and costs, the combining of the SCR and DPF functionality, by applying the SCR catalyst directly onto the DPF substrate, will provide further challenges for the passive regeneration of the DPF while placing more emphasis on the introduction of a non-thermal active regeneration technology.

The implementation of Cool Particulate Regeneration[™], CPR[™], an innovative non-thermal regeneration strategy, that physically rather than thermally removes the particulate from the combined SCR/DPF substrate, has been demonstrated with advanced low temperature catalysts capable of operating with high sulfur fuels. In vehicle applications, regeneration energy is harnessed from waste braking forces and requires seconds instead of 10-40mins for regeneration. Additionally, the removal of high temperature thermal regeneration eliminates the thermal aging stresses on the SCR catalyst and filter substrate opening up the potential for the aftertreatment system to operate effectively for the life of the engine. Analysis and results of a CPR demonstration project are discussed and detailed.

Although many developing countries have high air pollution, the implementation of internal combustion engine particulate filter aftertreatment has been delayed due to the unavailability of Ultra Low Sulfur Diesel, ULSD fuel. These developing countries require an efficient, low owning and operating cost, and robust Diesel Particulate Filter, DPF regeneration system, such as CPR, that can operate on high sulfur fuel. Instead of replacing legacy vehicles in developed and developing countries, they can be retrofitted in the market allowing the swift attainment of Euro VI particulate mass and number standards.

Barro C. / ETH ZURICH Switzerland

Particulate Matter from "Soot-Free" Fuels in Diesel Engines

Oxygenated fuels produced from methane-based products are currently a hot topic in research. These fuels show significantly reduced soot emissions at the exhaust of internal combustion engines due to their lack of chemical C-C bonds.

In the present study different oxygenated fuels, as well as blends in commercial diesel were investigated in a cylindrical constant volume chamber with large optical access. In order to study the combustion evolution and soot formation and oxidation process, optical techniques (luminosity of OH and Soot, e.g two colour pyrometry) have been applied. In particular the dimethoxymethane (DMM) and a poly(oxymethylene) dimethyl ether (POMDME / OME) with a CH3-O-(CH2-O)2-CH3 molecular structure have been studied for different temperatures at start of combustion. Moreover a fast particle spectrometer and a transmission electron microscope (TEM) grid were used to measure and sample the soot at chamber exhaust and observe the different particles forming from the investigated fuels, respectively.

Results from the two colour pyrometry and the fast particle spectrometer show an increasing soot reduction with increasing percentage of oxygenated fuel in diesel with maximum reduction when neat POMDME is injected. The luminosity indicates that the reduction of exhaust soot is mainly due to suppressed soot formation process. In addition, TEM imaging combined with energy dispersive X-ray (EDX) analysis provided the morphology and chemical composition of the nanoparticles measured with diesel and neat DMM. The particles from neat DMM show typical soot nanostructures commonly decorated with a few nm large iron nanoparticles (coming from the injection system) interpreted to form the core of primary soot particles.

Bisig C. / University of Fribourg, Switzerland

Risk Assessment of Exhaust Aerosols from Ethanol Supplemented and Normal Gasoline on Human Lung Cells in Vitro

Risk assessment of exhaust aerosols from ethanol supplemented and normal gasoline on human lung cells in vitro

Background: Even though ethanol supplemented gasoline (E10 and E85) is not widely sold in Switzerland (only 38 gas stations sell E85) in comparison to gasoline or diesel, its use is increasing e.g. in Germany and France. Most of the risk assessment is performed nowadays for diesel exhaust, however, only few data is present for other fuel sources. The aim of this work was to investigate possible toxic responses of exhaust aerosols from ethanol supplemented gasoline using an air-liquid exposure approach with a 3D lung cell model cultured. Method: A flexfuel gasoline passenger car was driven on a chassis dynamometer with either 10 % (E10) or 85 % (E85) ethanol, or normal gasoline (REF). The steady state cycle (20 min each 95 km/h, 61 km/h, 45 km/h, 26 km/h, and idling) was driven for 6h, followed by a post incubation in an incubator of 6h, this accounts for an acute exposure of gasoline exhaust. The exhaust was directly applied to a 3D human epithelial airway model composed of a tight layer of bronchial cell line (16HBE14o-), supplemented with human monocyte derived dendritic cells at the bottom and monocyte derived macrophages on top, cultured at the air-liquid interface. Biological endpoints included cytotoxicity, pro-inflammation, oxidative stress, and mutagenicity. As a control, filtered air was applied to cells in parallel to gasoline exhaust. **Results:** For E10 we observe a 100 times higher particle number compared to the other two exhausts. For the volatile compounds, we measured for E85 at 95 km/h a significant increase in total hydrocarbon and non-methane hydrocarbon. Apart from these two elevated parameters, no differences in exhaust characteristics could be measured between the three exhaust types.

No cytotoxicity and no morphological changes were observed in the lung cell cultures, in addition, the pro-inflammatory cytokines TNF α and IL-8 were not elevated and no oxidative stress with the glutathione assay was measured. Gene expression analysis also shows no induction of any of the tested genes, including mRNA levels of genes related to oxidative stress, pro-inflammation, and aryl hydrocarbon receptor activation. Finally, no mutagenicity was observed with the OxyDNA assay.

Conclusion: The acute exposure with the steady state cycle for exhaust types from E10, E85, and REF fuels did not induce adverse cell responses for any of the conditions tested.

Biswas P. / Washington University St. Louis, USA

Nanoparticle Measurement, Formation and Capture in Coal Combustion Systems

Several stationary combustion systems such as fossil and biomass fuel power plants produce a large concentration of submicrometer and nanometer sized particles. Results of a series of studies on controlled coal and biomass fuels will be reported. The use of novel instrumentation that has enabled develop a mechanistic understanding of the particle formation process will be described. Pathways of both inorganic and organic constituents of the aerosol will be elucidated. Inorganic constituents are vaporized and undergo a gas to particle conversion by nucleation. Volatile species such as lead and other heavy metals are readily vaporized in the high temperature regions. Refractory and higher boiling point species such as silicon and iron oxide are vaporized by a sub-oxide formation pathway. Following the gas to particle conversion, the nanometer sized particles grow by coagulation and condensation mechanisms. The resultant aerosol therefore has a distribution of sizes of varying concentrations. Organic aerosol formation in coal combustors is not well studied due to the assumption that these species will be completely oxidized. Our studies have indicated that trace organic species are observed in the resultant combustion aerosol. Using a time of flight mass spectrometer, pathways of formation of the organic constituents were established. An association of the organic constituents with the inorganic oxides was established as the mechanism that prevents their complete oxidation.

The size distribution and particle charging information is used to study the capture of submicrometer and nanometer sized combustion aerosols in electrostatic precipitators (ESPs). ESPs are low pressure drop systems that are widely used in industry. Due to the partial charging and difficulty in charging of nanometer sized particles, there is a penetration observed in the ESPs. Only a fraction of the nanometer sized particles are charged in the corona region, and as a result these are not captured with high efficiency. To overcome the problem of effective charging of nanometer sized particles, a novel soft x-ray irradiation methodology has been demonstrated. Methodologies (experimental and theoretical) to improve the charging and capture of nanometer sized aerosols in ESPs will be discussed.

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Costantini M. / HEI USA

Advanced Collaborative Emission Study (ACES): Summary of New-Technology Diesel Engine Emissions Characterization and Chronic Rodent Inhalation Study

Because of health concerns related to exposure to diesel exhaust (DE) emissions, health and environmental agencies in industrialized countries have adopted progressively more stringent standards for heavy-duty diesel (HDD) engine emissions. In the United States, starting with model-year 2007, engines were required to meet a new standard for particulate matter (PM) of 0.01 g/hp-hr. In 2010, they were required to meet a new standard for nitrogen oxides (NOX) of 0.2 g/hp-hr. Industry developed a combination of advanced-technology engines, exhaust control systems, and reformulated fuels to meet these stringent standards, which were expected to result in substantially reduced emissions of other pollutants as well.

ACES was a collaborative, multi-party effort to characterize the emissions (Phase 1 and 2) and assess the possible health impacts (Phase 3) of the exhaust of new-technology HDD engine systems and fuels that were introduced into the market during the 2007–2010 time period.

Both Phase 1 and 2 were conducted at the Southwest Research Institute and overseen by CRC. In Phase 1 four 2007-technology HDD engines were tested. The emissions of NMHC, CO, and PM were more than 89% lower than the 2007 standards. Both regulated and unregulated emissions were substantially reduced relative to 2004 engines. NO2 emissions were higher than in 2004 engines due to the use of DOC and C-DPF technology. Phase 2 demonstrated another large step in emissions reductions with 2010-technology engines. The testing of three 2010-technology engines showed substantially lower emissions of NOX, CO, NMHC, and PM relative to the 2010 standard and also relative the 2007-technology engines' emissions. NOX reductions were achieved using urea-based selective catalytic reduction and ammonia catalyst. A wide spectrum of particle- and gas-phase unregulated emissions species, including NO2, were also reduced relative to 2007- technology engines.

In Phase 3, conducted at the Lovelace Respiratory Research Institute and overseen by HEI. an engine randomly selected from the four tested in Phase 1 was used to generate the exposure atmosphere for a chronic inhalation study in rats. Dilutions of exhaust were maintained at target average concentrations of 4.2, 0.8 and 0.1 ppm NO2. Exposures were conducted 16 hr/day, 5 days/wk. Exposure atmospheres were characterized in detail. Rats were evaluated for respiratory function, hematology, serum chemistry, and histopathologically at interim time points up to final sacrifice at 28 months (males) and 30 months (females). The majority of the biological markers were unchanged with exposure and little inflammation was observed. Histological analyses found that exposure to new-technology diesel exhaust (NTDE) produced no tumors or pre-cancerous effects in lungs and no increase in tumor incidence outside the lung that could be attributed to NTDE exposure. Mild epithelial hyperplasia in the central acinus region of the lung, interstitial fibrosis, and bronchiolization were observed at the high exposure level; these histologic changes were consistent with previous findings in rats after long-term exposure to NO2 — a major component of the exposure atmosphere, which is substantially reduced in 2010-compliant engines. Comparisons with findings from previous studies of long-term exposure to "traditional" diesel exhaust (TDE) will be presented.

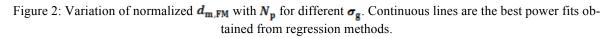
Dastanpour R. / University of British Columbia Canada

The Effect of Primary Particle Polydispersity on the Morphology and Mobility of Agglomerates

Properties of colloidal and aerosol agglomerates depend on the morphology of these particles. Production rate and handling of synthetic clusters, and emission measurement of cluster-like particles, including soot, are influenced by the mobility of these particles. Inevitably accurate estimation of hydrodynamic interaction of these particles with flow fields in different regimes is essential in many industrial processes and advanced measurement techniques. Several methods have been developed for the estimation of the hydrodynamic properties of clusters; however they have only been used for the study of clusters of monodisperse primary particles. Agglomerates formed in real processes, e.g. soot aggregates, are usually formed from polydisperse monomers.

The purpose of the present work is to evaluate the effect of primary particle size variations on aerosol mobility. In particular, we consider the effect of the variation on geometry (i.e, relation between particle mass, area and radius of gyration), as well as on the continuum regime hydrodynamics. Using numerically generated agglomerates of point touching primary particles, it is shown here that the mobility equivalent diameter of agglomerates increases with polydispersity in both free molecular and continuum regimes.

The first effect of primary particle polydispersity on mobility diameter is simply geometric: for a fixed number and mean primary particle diameter, the physical size of the aggregate increases with polydispersity of the monomers. The mobility diameter in this regime is measured from the average projected area of agglomerates. The effect of primary particle polydispersity can be substantial (Fig. 1), i.e. ~26% increase in the mobility diameter for a constant number of the monomers at high polydispersity; this highlights the importance of reporting primary particle size statistics carefully.



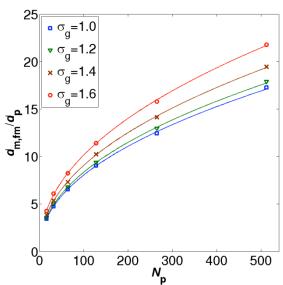


Figure 1: Variation of normalized $d_{m,FM}$ with N_p for different σ_g .

Stokesian dynamics method is used in the limiting case of zero Reynolds number flow. This method is capable of resolving the effect of structure accurately. We have found that the considerable variation of the ratio of the mobility diameter to the gyration diameter in the literature (Fig. 2) cannot all be ascribed to calculation or measurement error: different cluster

aggregation mechanism yield different structures that affect this ratio. Similar to the freemolecular regime, the effect of the primary particle polydispersity is substantial in this regime, i.e. ~23% increase in the mobility diameter for a constant number of the monomers at hi polydispersity levels (Fig. 3).

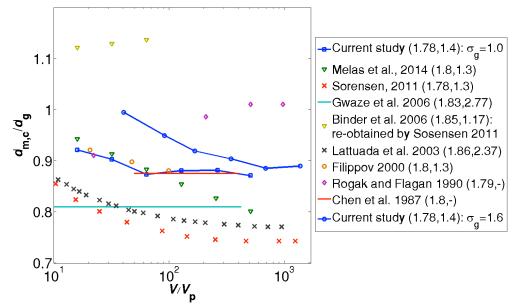


Figure 2: Variation of $R_{m,c}/R_g$ with N_p in fractal agglomerates. All literature data are for monodisperse primary particles. Values in parenthesis are (D_f, k_f) . For some cases k_f was not provided. V_p is the volume of a sphere having diameter equal to the median diameter of the monomers in each agglomerate.

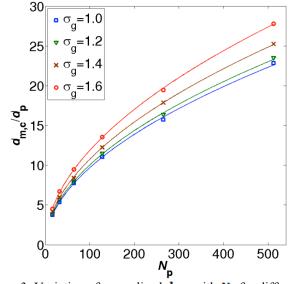


Figure 3: Variation of normalized $\mathbf{d}_{m,c}$ with N_p for different $\boldsymbol{\sigma}_{g}$.

Combining free molecular and continuum regime results, corresponding correlations are developed for the calculation of the mobility diameter as a function of the number, size, and polydispersity of the primary particle.

Durdina L. / EMPA Switzerland

Spatial Variability of PM and Gaseous Emissions at the Exit Plane of an in-Service Commercial Aircraft Turbine Engine

Air traffic has steadily grown over the past decades (5% annually) which has raised attention to airport air quality and global impacts of aviation emissions and fuelled numerous experimental studies over the past two decades.

To minimize environmental impacts, the International Civil Aviation Organization (ICAO) has set strict criteria for gaseous emissions and visible smoke from commercial aircraft engines. Because modern aircraft engines generate no visible smoke, this obsolete criterion is about to be replaced by a non-volatile PM (nvPM) number and mass emissions standard. To representatively sample gas turbine exhaust at the exit plane, engine manufacturers use most often multi-orifice sampling probes unique for each engine type. Researchers rarely have access to these probe types and resort to simplified single-orifice sampling probes. Representative sampling is ever so important if the resulting data are to be used for emission inventories and air quality modeling. Modelers should also know the estimated experimental uncertainties of the single-point measurements. An important question is then if the sample for nvPM measurements is representative, using the same probe as used for gaseous and smoke measurements.

We determined how the PM emissions vary at the exit plane of an in-service turbofan engine source burning conventional Jet A-1 fuel, compared to variations in gaseous emissions. To do so, we deployed a 2D traversing single orifice probe and a standard-ized sampling and measurement system in the engine test cell at SR Technics, Zurich airport. The sample was drawn by the 8 mm I.D. probe within 0.75 m of the engine exit, diluted with synthetic air by a factor of 8-10, and drawn to the instruments through a 25 m long heated sample line. An AVL Particle Counter Advanced (APC) with a catalytic stripper measured the nvPM number whereas an AVL Micro Soot Sensor (MSS) measured the nvPM mass concentration. A Thermo 410i NDIR analyzer reported the diluted CO₂ concentration. We measured at 5 thrust levels close to those of the ICAO landing and take-off cycle: idle (~3%), taxi (7%), approach (30%), climbout (85%), and take-off (100%). We performed two full-day experiments that totalled ~300 position-thrust level combinations.

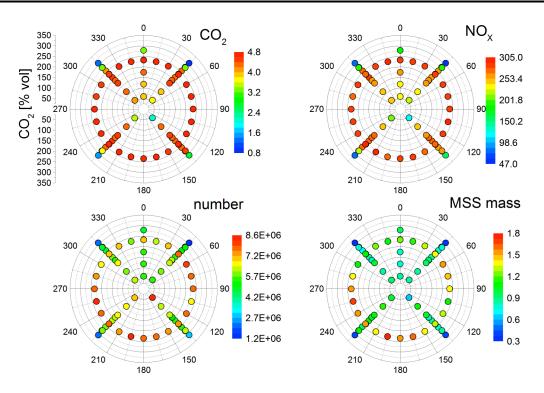


Fig 1. Spatial variability of the PM and gaseous emissions at take-off thrust. Flight direction is into the paper plane.

The nvPM varied more than gaseous emissions across all engine conditions. All emissions varied most at engine idle (factor of 4 for nvPM mass and number and factor of 2 for gaseous emissions measured at the same radius). Because the traversing probe was further downstream of the engine exit than the certification probe, the bypass flow could have entrained the core flow before sampling and caused asymmetric patterns. The variability decreased with increasing thrust level. At take-off thrust, gaseous emissions were axisymmetric, but the nvPM still varied by a factor of 2 at a constant radius and different angles (Figure 1). This study will help to optimize the single point sampling for the given engine, quantify the uncertainty of those measurements, and provide material to assess the appropriateness of the multi-orifice probe used for gaseous certification of the engine.

El Haddad Imad / PSI Switzerland

Emissions from Heavy Fuel Oil Combustion in a Ship Research Engine and Associated Secondary Organic Aerosol Formation Potential

Maritime transport is a globally important source of submicron particulate matter (PM) and gaseous pollutants, from the combustion of low-grade fuels without the application of exhaust gas after-treatment systems. Emission factors (g kg⁻¹_{fuel}) of primary PM from ship engines currently exceed those from modern four-stroke (4S) on-road vehicles by far. The contribution of ship engine emissions to the secondary organic aerosol (SOA) budget remains, however, unknown.

Secondary organic PM is formed when gaseous precursors partition into the particle phase, after transformation by chemical reactions in the atmosphere. Previous studies have pointed to the importance of intermediate- and semi-volatile species (I/SVOCs), and thereby to the volatility distribution of the carbon found in the total organic aerosol, when estimating SOA potentials.

Therefore, we investigate the volatility and photochemical processing of the primary organic aerosol emitted from a 4S single-cylinder diesel engine when operated with heavy fuel oil (HFO) and marine gas oil (MGO), both fuels globally used in maritime transport. The emissions were sampled from the exhaust pipe into a 10 m³ teflon smog chamber. Instrumentation included a HR-ToF-AMS to determine non-refractory PM, SMPS for size-distribution measurements, DMA-APM for measurements of effective densities, Aethalometer, SP2 for black carbon (BC) mass measurements and CAPS to measure optical properties of the particle phase. A flame ionization detector (FID) and HR-ToF-PTR-MS were used to characterize the gas phase hydrocarbons. For estimations of the volatility, (i) stepwise injections into the chamber were conducted to see partitioning based on changes in total aerosol loadings, (ii) a thermodenuder was deployed to investigate changes based on temperature, and (iii) offline samples were collected on quartz fiber filters and Tenax to determine the volatility based on gas-chromatography-mass spectrometry. Finally, photochemistry was initiated in the smog chamber.

Combining the results from these different measurements, we derive volatility distributions and estimate the SOA formation potential of the emissions.

Fleischman R. / TECHNION Israel

Nanoparticle Emissions from an SI Engine Fueled with Gasoline and Methanol Reforming Products

Most of modern transport systems rely on internal combustion engines (ICEs) as a main power plant, which are greatly responsible for fossil fuels consumption, as well as for environmental pollution due to hazardous pollutants and GHG gases emission. The utilization of more fuel-efficient ICEs together with low-carbon-intensity fuels is, therefore, of great importance, as it mitigates the negative impacts of petroleum fuels usage.

One of the ways to improve ICE's overall efficiency is to utilize the thermal energy contained in the exhaust gases, which represents about one third of the fuel energy delivered to the ICE and is usually wasted. This energy can be used to promote endothermic reactions of alcohol reforming, which converts the original liquid fuel into gaseous hydrogen-rich fuel. The reforming products have better combustion properties [1], allow a more efficient combustion and therefore lead to lower pollutants formation.

Nanoparticles are one the most hazardous ICE's emissions and have received increasing attention in the last years due to their adverse health effects. Recent studies indicate an increase in particle's toxicity as its size decreases [2]. Severe pulmonary diseases are caused by the nanometric carbon particles, which have the ability to rapidly enter the systemic circulation after inhaled [3].

The main goal of this study is to compare the nanoparticle emissions of an ICE fuelled with gasoline and methanol reforming products. For this purpose, a gen-set gasoline-fed carbure-tor single-cylinder SI engine was modified to allow the work with both liquid gasoline and gaseous methanol reforming products. The latter were directly-injected into the engine cylinder to prevent the pre-ignition and the backfire problems. For this purpose a dedicated gaseous fuel direct injector was developed. An engine instrumentation system allowed measuring and controlling various performance parameters. Emissions of gaseous pollutants and particles were measured in the gasoline-fed and the reformate-fed operating modes. Particle emissions were measured using TEOM (particle mass), Nanomet-3 and Engine Exhaust Particle Sizer (EEPS-3090) equipment.

The obtained results show a great potential of energy efficiency improvement and emissions reduction by applying thermo-chemical recuperation of the waste heat through methanol steam reforming and direct injection of the reforming products into the engine's cylinder.

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Frederiksen M. / Danish Technological Institute

Particle Emissions From Burning of Waste in Wood-Burning Stoves

Burning of illegal fuel in private wood-burning stoves is a "grey area" that is very hard for the authorities to control. Nonetheless, it is a common known problematic that needs to be considered. The "fuel-types" could for instance be old construction materials, wood with paint coating, pallets, laminate wood, creosot wood (telephone poles and railway sleepers), advertisement paper and gift wrapping paper, plastic containing materials, etc. The burning gives rise to several issues such as poor indoor climate, deteriorate immediate environment, and generally unanswered questions regarding volatiles and organic matter, and particle emissions.

As a consequence, a "sampler" is being developed with the purpose to detect illegal burned materials in private wood-burning stoves. As part of this study, several test burnings for proving the usefulness of the "sampler" have been conducted, and in parallel with these tests particle emissions have been measured.

This study therefore gives a unique insight in particle emissions from "fuel types" that is not often seen. Particle size and number concentration are measured in the size interval 14-710 nm using a SMPS (TSI) with a time resolution of 3 minutes. Furthermore, for instant peak measurements, a P-Trak (TSI) counts the number concentration in the size interval 20-1,000 nm with a time resolution of 1 sec. Parallel with these measurement particle mass is determined using a DustTrak (TSI), also continuously logging PM1, PM2.5, PM4, PM10 and PMtotal. Number and size measurements have been conducted in the dilution tunnel above the wood-burning stove and hereafter using a rotating disc diluter (Matter). Mass measurements is conducted directly in the dilution tunnel.

Preliminary emission data is shown in the graphs below, showing a full day of burning CCAimpregnated wood (cupper, chromium and arsenic).

Particle emissions from painted wood	Ignition phase	Pre- charge	1. charge	2. charge	3. charge	4. charge
SMPS, avg. [#/cm ³]	5.0E7	3.9E7	3.3E7	3.8E7	5.5E7	
SMPS, mean diameter [nm]	118	144	127	113	112	
P-Trak, avg. [#/cm ³]	5.2E7	3.6E7	2.6E7	2.9E7	5.5E7	
DustTrak, avg. PMtotal [mg/m³]	1045	1804	1476	1046	1231	
Particle emissions from (pure) birch	Ignition phase	Pre- charge	1. charge	2. charge	3. charge	4. charge
SMPS, avg. [#/cm ³]	2.8E7	1.9E7	2.1E7	2.5E7	2.9E7	2.5E7
SMPS, mean diameter [nm]	133	106	102	104	94	107
P-Trak, avg. [#/cm ³]	2.5E7	1.7E7	2.4E7	1.8E7	1.7E7	9.4E6
DustTrak, avg. PMtotal [mg/m³]	271	154	142	504	335	649

Table 1: Particle emission data from burning of (pure) birch and painted wood. Painted wood gives rise to an enhanced amount of emitted particles compared to burning of normal wood used for wood-burning stoves.

Friedrich A. / Berlin, Germany

Road Particle Number measurements from GDI vehicles compared to a Euro 6 Diesel vehicle

Modern GDI vehicles have the advantage to have lower fuel consumption than MPI gasoline vehicles. But this concept has also serious negative aspect for the environment, namely much higher particle number and NOX emissions than MPI vehicles. Because vehicle manufacture can optimize the emissions to the test condition of the official New European Driving cycle. Real world emission testing is the only way to detect these behavior. In addition it is much more important to check the emissions in real world. 6 modern GDI cars were measured with a PEMS delivered by Sensor Europe. The PEMS system consist an CO2, CO, NOx/NO2 analyzer and an Pegasor particle number instrument. In addition a GPS sensor and temperature sensor were mounted to the vehicles. Four different driver were used and the test round was repeated up to ten times. In addition to the driver a second person was on board to manage the test equipment and the computer The test round included urban driving, extra urban driving and autobahn driving and again urban driving. The test round was flat with maximum altitude difference of 15 m. The average speed was around 40 km/h. The driver had the instruction to follow the speed limits and the gear change recommendation of the vehicle. On the Autobahn the maximum speed was around 125 km/h. This speed was selected to be above the maximum speed of the NECD, which is 120 km/h. For most of the test driving the on the track the vehicles were undisturbed from other vehicles. One Euro 6 Diesel car equipped with particle filter and SCR was measured for comparison. The results show that the Euro 6 diesel vehicle had very low particle number emissions. The GDI vehicles had between 10 to 100 times higher particle number emissions than the Euro 6 Diesel car.

Gerlofs-Nijland M. / RIVM Netherlands

Hazard Assessment of Source-Specific fine Particulate Matter

Since air pollution, and especially traffic emissions, are linked to adverse health effects many efforts have been taken to diminish these emissions. This has resulted in a considerably reduction of engine emissions in the last decades. However, particulate matter (PM) from traffic emissions is not only derived from engine combustion but consist of wear emission from the road, tyres and brakes as well. With reducing engine emissions, the relative contribution of non-exhaust emissions to particulates is increasing although the implications for health are mainly unknown. In addition, other local PM sources like wood combustion influence the composition and thereby the toxicity of the air pollution mixture. Since not much is known about the relative toxicity of different sources, we examined the hazard of fine particulate matter in a mice inhalation study.

Fine particulate matter (PM2.5) from different sources was collected directly into liquid using the Versatile Aerosol Concentration Enrichment System. Four types of brake pads were used to collect PM2.5 in an experimental setting under realistic combined driving conditions. Tyre/road wear was sampled in an experimental setting using spiked tyres and tarmac road pavement. Diesel engine exhaust PM came from an idle heavy duty engine (mainly Euro III combustion settings) running under typical motorway conditions. The following wood combustion PM samples were collected: 1) modern stove, efficient combustion, 2) modern stove, deliberate-poor combustion, 3) old iron stove, efficient combustion. The last source from which PM2.5 was collected is a poultry farm housing ±70.000 animals. A PM aerosol was prepared using a spray nozzle and mice were exposed for1.5, 3 or 6 hours by nose-only inhalation to different PM sources or 6 hours to clean air (control). This resulted in three exposure doses namely low exposure (expo L; 0.3-0.4 mg/kg bw), medium exposure (expo M; 0.6-0.8 mg/kg bw) and high exposure (expo H; 1.2-1.6 mg/kg bw). One day after exposure changes in biological effect markers related to cytotoxicity, inflammation, and cardiovascular effects were assessed in lungs and blood.

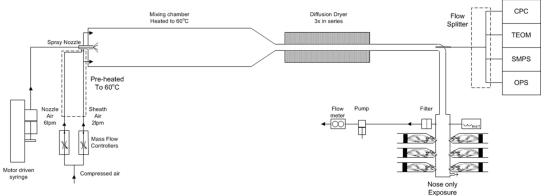


Figure 1: Experimental exposure setup

Preliminary data revealed that the inflammatory response is different for the various PM sources. Exposure to PM2.5 from the poultry farm and deliberate-poor wood combustion modern stove showed the highest increase in inflammation as indicate by the absolute numbers of neutrophils in the lung. The dose needed to reach a 10% or 20% increase for a specific biological effect parameter (e.g. neutrophils) was determined by benchmark modeling¹; the lower the PM dose needed to observe this increase, the more hazardous the PM material is. For the inflammatory marker lung neutrophils, the following PM toxicity ranking order can

be given: deliberate-poor wood combustion modern stove > poultry farm >> brake wear type 3 and 4 = efficient wood combustion modern stove = diesel combustion \geq efficient wood combustion old iron stove \geq tyre/road wear = brake wear type 1 and 2. Combining the out-comes of all biological effect markers will make it possible to rank these PM sources based on their hazard. Preliminary analyses indicate a higher hazard on a per mass basis for wood combustion and brake wear PM compared to the other PM sources examined in this study. However, to elucidate the source-specific-risk for adverse health effects (or health impact assessment), the hazard should be combined with the exposure to that specific source. Only this combination of hazard and exposure to actual risks will support source-specific-policy to improve public health.

¹ Slob W. 2002. Dose-response modeling of continuous endpoints. Toxicol Sci 66:298–312.

Gieré R. / University of Pennsylvania USA

BIOCOMBUST- Biomass, Energy, Health

BIOCOMBUST is an interdisciplinary European research project, which is funded through the INTERREG IV program and involves partners from France, Switzerland and Germany. The energy transition requires a switch from fossil fuels to renewable energy resources. The Upper Rhine region is determined to exploit its considerable energy potential through biomass combustion. However, incomplete combustion in poorly maintained stoves can affect air quality, especially during adverse weather conditions. The project examines both particulate emissions and residual ashes generated during biomass combustion. The focus is on selected types of solid biomass fuels, including wood chips, pellets, wood logs, and miscanthus (a grass grown for energy purposes). The main emphasis of the project is on the impact of biomass combustion on air quality and the associated effects on human health, but also on the potential use of the fly ash as clinker substitute in cement production.

Although great efforts have been made to reduce air pollution, particle emissions still pose a considerable threat to human health in many areas. The recent increase in the use of solid biomass as energy source has increased air pollution in both urban and remote areas, especially during winter months. However, little is known about the health effects of particles emitted by biomass combustion. The BIOCOMBUST project investigates the biological effects of such particles. For this purpose, we expose human lung cells in the laboratory to various types of particles and identify the effects on the genetic material and the viability of the cells. Further indicators include inflammation and defense mechanisms that can be measured by molecular biological methods and indicate possible cell damage. In addition to conventional cell cultures, the cell culture systems of three different types of cells, tissue sections and 3Dcell culture sets are used for the toxicological investigations. First results show that particulates from biomass combustion can cause cytotoxic and genotoxic effects in human lung cells and that these effects depend not only on the size but also on the type of particles. Particulates from combustion of miscanthus, for example, do not impact negatively the cells. The content in polycyclic aromatic hydrocarbons has a considerable effect on the cellular reactions. On the other hand, the studied particulate samples did not stimulate significant inflammatory responses. These results were obtained from short-term exposure experiments, and it remains to be seen what the effects are if the human lung cells are exposed to particulates for a prolonged period of time.

Hasset Sipple Beth / US EPA

US-EPA-Workshop on Ultrafine Particles - Summary and Consideration of Next Steps

The United States Environmental Protection Agency (through the Office of Research and Development's Air, Climate, and Energy and Human Health Risk Assessment Research Programs and the Office of Air and Radiation's National Vehicle and Fuel Emissions Laboratory) organized and hosted a workshop on Ultrafine Particle Metrics and Research in February 2015. Internal and external experts representing multiple disciplines (e.g., source emissions, atmospheric science, ambient air monitoring, air quality analysis, and health assessment) discussed new and emerging research related to ultrafine particles. Specifically, this workshop provided an overview of the state-of-the-science on ultrafine particle emissions and controls, air quality impacts, population exposures, and health effects. The workshop concluded with a discussion of issues related to translating the scientific evidence to inform policy considerations in the US and Switzerland. Workshop participants from the United States, Europe, and Asia included government officials, industry representatives, academics, and the general public.

The presentation offered at the 19th ETC Conference on Combustion Generated Nanoparticles will summarize the objectives and key issues discussed at the February Ultrafine Particle Metrics and Research workshop. In particular, the presentation will discuss the difficulty of integrating information across research studies because methods and metrics for identifying and characterizing emissions, ambient concentrations, and potential impacts of ultrafine particle exposures have not been consistent. Potential opportunities to build on the workshop discussions to improve our understanding of emissions, air quality impacts, exposures, and potential health impacts will be highlighted. Additional actions that could be considered to promote discussions on the strengths of various ultrafine particle metrics in order to foster consistency and collaboration in on-going and future research efforts will be summarized.

Hohl Y. / Liebherr Switzerland

Impact of different fuels on engine out emissions and on the SCR on Filter system

n order to evaluate the aging capability of the LMB SCR on Filter (SCRoF) technology, LIEBHERR Machines Bulle asked to start an INTERREG project which involved Industry and university from Switzerland and France.

R&D Moteur (testbed), the University of Haute Alsace and the "Berner Fachhochschule Biel" were involved in this project.

To perform this investigation, a D944@230kW Tier4F Liebherr engine was installed in the testbed at R&D Moteur. The SCR was replaced with a SCR on Filter System.

1st Part:

Objectives

Evaluation of the impact of three different fuels (EN590, B10R20H, US-Fuel) on the engine out emissions on different cycles (NRTC, NRSC).

Results 8 1

On NRTC the engine behavior with EN-590 and B10R20H was comparable. Slight differences were observed due to measurement tolerances. Significant differences were observed with the US-Fuel. The CO emissions increase of about 40% and the PM of about 16%. On NRSC, tendencially, the PM and CO emissions with the US-Fuel are higher than with the two other fuels

2nd Part:

Objectives

Evaluation of the fuel impact on the soot reactivity on different cycles (NRTC, customer cycles). For that, soot was collected on different cycles and analyzed

Results

Several DPF (wo coating) were used to collect soot produced with the 3 different fuels on 2 different cycles (NRTC and wheel loader cycle). It was observed, that the engine cycle impacts significantly the soot reactivity. The highest soot reactivity was observed with the NRTC cycle. Soot produced with the fuel EN590, B10R20H and US-Fuel during wheel loader (L566) cycle showed comparable reactivity for passive oxidation (with NO2 and O2), while, soot produced with EN590 fuel during wheel loader (L566) cycle showed highest reactivity for active oxidation.

3rd Part:

Objectives

Evaluation of the coating chemical impact during a short endurance of about 1'000 hrs with B10R20H fuel.

Results

No significant NOx conversion efficiency decrease was observed during the 1000 hrs endurance with B10R20H fuel. A reduction of about 1.5% was observed @ 500°C with high space velocity. The alpha dosing as well as the NH3 tailpipe for the max NOx conversion were comparable

Hosseini V. / AOCC Tehran

Tehran Air UFP Study: Mass, Number, and Composition

Tehran air pollution is an eminent thread to its citizen. With a large fleet of LDVs and HDVs, high elevation, bowl-shaped topography between high mountain ranges, and long winter inversion periods, more than one thirds of the typical year in Tehran are reported as unhealthy. The criteria pollutant is always PM2.5 measured and reported by several air quality monitoring stations.

This study is to identify Tehran particle characteristics to be used in mitigating measures. It includes investigation of particle mass at various locations, UPF counting with portable particle counter, chemical composition analyses for EC and OC, and inventory studies using Tehran traffic model.

The result shows that Tehran particles are more of anthropogenic sources and despite of the dry weather and occurrence of dust storms, most of UFP are highly traffic-related and the contribution of EC in total mass is quite significant.

Jurányi Z. / FHNW Switzerland

Determination of the Shape of Combustion Aerosol Particles based on their Angular Light Scattering

Soot particles have a fractal-like shape, are produced during incomplete combustion processes and are a major constituent in the atmosphere. These fractal-like particles have a self-similar structure, are composed of spherical primary particles (monomers) of black carbon. Due to the fractal-like shape the number of primary particles scales as a power law with the characteristic size of the aggregate, where the exponent is called the fractal dimension (D_f). Combustion generated aerosol particles are usually not pure soot particles but rather a complex mixture of black carbon, organic matter, sulfate, ash and other components. Therefore, dependent on the combustion process these particles can also have different shapes varying between highly fractal-like and almost spherical. Measuring the angular light scattering of combustion originating aerosol particles in the power law regime can give us information on the shape of these particles.

At the University of Applied Sciences Northwestern Switzerland an instrument was developed in order to measure the angular scattering of combustion produced aerosols. It is able to measure the scattering signal simultaneously at seven different angles and at two different wavelengths (405 and 852 nm) with a time resolution of some seconds. This setup makes it possible to probe the structure factor with high time resolution and therefore to observe fast structural changes of the aerosol particles that are expected to happen in fires during the different burning phases. Several experiments were done on aerosols with different shapes such as highly fractal-like Cast or Palas soot, spherical paraffin oil particles and different kinds of fire originating particles (e.g. wood burning). We have seen that the fractal-like and spherical particles can be well separated based on their angular light scattering patterns. Smoldering fires produced on average more spherical particles than flaming ones, where lower fractal dimensions were observed. This finding can be also used to identify the different burning phases during combustion processes.

This work was supported by the Swiss Commission for Technology and Innovation (CTI).

Karjalainen P. / Tampere University Finland

Real-Time Exhaust Particle Measurements with High-Resolution Low-Pressure Cascade Impactor

The measurement of particle size distribution is one of the key aspects in nanoparticle research. In emission characterization, the focus often is in the particle size range of below 100 nm, and the changes in particle size distribution are highly transient (e.g. Karjalainen et al., 2014). This drives the need for high-end measurement devices that operate in real-time and in nanoparticle size range.

There are only a few instruments that can measure below 100 nm particle size distribution in real time: an Electrical Low Pressure Impactor (ELPI, Keskinen et al., 1992) and an Engine Exhaust Particle Sizer (EEPS, TSI Inc.) The ELPI with an additional impactor stage (Yli-Ojanperä et al., 2010) measures aerodynamic size distribution using the electrical detection of particles with a cascade impactor, and has 12 channels in the measurement range of 16-10000 nm, and below 100 nm, 4 channels. The EEPS measures electrical mobility size distribution using electrical detection of particles and has 22 current measurement channels in the size range of 5.6-560 nm. The ELPI has coarse resolution under 100 nm compared to the EEPS limiting its applicability in nanoparticle studies.

In this study, we used a new high-resolution low-pressure cascade impactor (HRLPI, Arffman et al., 2014) in several exhaust particle emission studies. The HRLPI has 10 impactor stages in the size range of 7.7-142 nm and a filter stage. The essential features in the HRLPI are slit type, short throat length nozzles in the impactor stages. This type nozzles produce very steep collection efficiency curve shape (Arffman et al., 2012). Sharp cut-curve shape allows doubling the number of measurement channels below 100 nm compared to the ELPI impactor without significant overlap of kernels. The minimal overlap makes the inversion or interpretation of the measurement results simple and robust. All the impactor stages, charger and inlet were fully calibrated with monodisperse dioctylsebacate (DOS) particles produced by the SCAR instrument (Yli-Ojanperä, 2010) and an evaporation-condensation generator.

In the laboratory (Figure 1), the performance of the HRLPI was compared to the ELPI+, the ELPI with improved nanoparticle resolution (EELPI), the EEPS, and two SMPSs (DMA models TSI 3071 and TSI 3085). Results of the test measurements (Figure 1) showed that the HRLPI is a well-suited aerodynamic size measurement instrument. Compared to the other low-pressure impactors, it has a better size resolution and the lowest cut point.

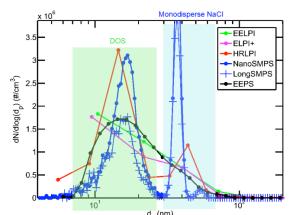


Figure 1. Particle size distribution measured with different instruments for externally mixed DOS and NaCl aerosol.

The instrument was tested in the exhaust studies of several modern vehicles and engines: (1) gasoline passenger cars, (2) diesel passenger car, (3) heavy-duty diesel truck and bus, and (4) heavy-duty nonroad diesel engine. The exhaust particles were characterized with the HRLPI, EELPI (or ELPI+) and EEPS in parallel. Figure 2 shows particle size distributions measured by the EEPS and HRLPI for a gasoline passenger car (direct injection technology) over the NEDC test cycle. Both instruments responded rapidly to the changes in exhaust gas particle concentrations, also the size distribution profiles seem similar. By combining the mobility and aerodynamic particle size distributions, the effective density of the particles down to 7 nm can be determined in real time.

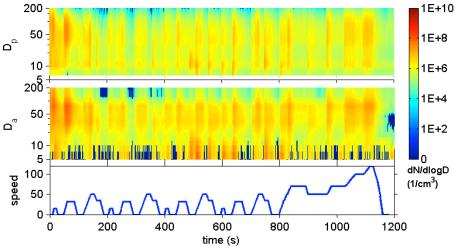


Figure 2. Particle size distribution of a GDI passenger car measured with the EEPS (top) and HRLPI (middle) over the NEDC (speed profile at bottom).

Arffman A. et al. (2012) J. of Aerosol Sci, 53, 76-84 Arffman A. et. al. (2014) J. Aerosol Sci.. 78, 97–109 Karjalainen P. et al. (2014) Environ. Sci. Technol. 48 (4), 2336-2343 Keskinen J. et al. (1992) J. Aerosol Sci. 23, 353-360 Yli-Ojanperä et al. (2010) J. Aerosol Sci. 41, 719-728

Khalek I. / SWRI USA

Particle Sensors for Onboard Diagnostics

Spark-plug sized particle sensors are developing rapidly due to onboard diagnostics (OBD) regulations demand in the United States (California) and eventually throughout the US, Europe and the rest of the world. Particle sensors will be one of the key enablers for exhaust particle filters to continue their success in keeping particle emissions below or equal to the regulatory limits not only in brand new vehicles, but also in vehicle lifetime. Beyond OBD, particle sensors have numerous applications in engine research and development, retrofit technologies, environmental research and modeling, and instrumentations.

Before spreading the use of particle sensors in the market place, it is critical that their performance and durability are well understood. The performance of particle sensors is critical as we need to understand what property of particulate matter (PM) do they measure (mass, number, surface area, size, etc...), the fundamentals of such measurement and the dependent variables, and how it relates to our current measurement method of PM. After performance characterization of particle sensors, it is equally critical to demonstrate that such performance is durable. Without such important information on performance and durability, PM measurement with particle sensors will lose its credibility in being able to protect human health and the environment onboard vehicles in OBD applications.

The focus of this paper is on particle sensor performance and durability. First, we will describe available particle sensor technologies and principle of operation. Second, we will discuss the approach taken to characterize sensor performance and durability in an engine test cell facility. Finally, a limited set of normalized results will be presented for steady-state and transient engine operation. This is part of Year 1 and 2 of SwRI Particle Sensor and Durability Consortium (PSPD-I).

Kittelson D. / University of Minnesota, USA

Ultrafine Particles: How Should They Be Defined and Measured?

Clear epidemiological evidence links exposure to fine particles ($PM_{2.5}$) to adverse health effects, but the association between exposure to ultrafine particles (UFPs) and adverse health effects is much less clear. In fact a recent Health Effects Institute report (HEI Perspectives, Jan. 2013) states that: "The current evidence does not support a conclusion that exposures to UFPs alone can account in substantial ways for the adverse effects that have been associated with other ambient pollutants such as $PM_{2.5}$." The report also suggests that part of the difficulty in finding an association is that is that UFPs are much less commonly measured than $PM_{2.5}$ and show much more temporal and spatial variation. Thus measurements made at a few central monitoring stations may not accurately reflect population exposures. An additional problem is that when UFPs are measured, the methods are not consistent, for example, sometimes measurements are based on total particle number concentration, sometimes particle mass below 100 nm, sometimes mass below 300 nm. If we are to understand association between UFPs and health there is a need for agreement on standard, relatively easy to deploy, and inexpensive means of measuring them.

In this presentation the various metrics that might be used to describe UFPs in ambient air or in vehicle exhaust are discussed. Particles are typically found in the atmosphere in three size modes, each of which is related to a distinct formation process. These modes may shift and overlap depending on details of combustion, dilution, and distance and time from the source. The nucleation mode (~3-30 nm) typically forms as exhaust dilutes and cools in the atmosphere and is usually composed of semi-volatile materials like organic carbon and sulfates but may also contain ash and soot precursors. These particles may also form directly in the atmosphere by homogeneous nucleation. The accumulation mode (~30-300 nm) is comprised of carbonaceous aggregates and adsorbed organic carbon from fuel and lube oil as well as secondary aerosols formed by atmospheric transformation of gaseous emissions. The coarse mode (> ~300 nm) consists mainly of mechanically generated particles, soot blown off in-cylinder and exhaust system surfaces, and oily crankcase fumes. Coarse particles are also formed near roadways by re-entrainment of road dust and brake and tire wear. Both chemical and physical properties of UFPs are likely to impact health effects but the focus will be on physical properties because they are much more easily measured using relatively low cost methods. Metrics that will be discussed include solid and semi-volatile number, surface area, active or lung deposited surface area, ultrafine mass, and accumulation mode mass. Instruments used for their measurement and correlations among the metrics will be discussed.

Konstandopoulos A. / CPERI/CERTH Greece

Soot Deposit Evolution and the Mechanism of Particle Emissions During Regeneration in Diesel Particulate Filters

The structure and properties of soot deposits in Diesel Particulate Filter (DPF) affects significantly the DPF pressure drop, hence the fuel penalty imposed on the vehicle. If one tries to describe the soot laver grown on by a uniform density (or equivalently porosity), surface area and permeability, and try to determine these parameters from experiments he would arrive at widely varying values. We have shown (Konstandopoulos et al. 2002; 2007) that during DPF loading the microstructure of the soot cake is determined by the convective-diffusive transport of the soot aggregates towards the deposit and it was also demonstrated that soot cake packing density and permeability are related to the local value of the dimensionless mass transfer Peclet number. In addition as shown here these parameters can be related to the fractal-like morphology of the aggregates. During regeneration events the soot deposit reacts in a generally inhomogeneous fashion and frequently one observes increased particle emission during these events. While emissions of volatile particles during regeneration events of Diesel Particulate Filters (DPFs) is commonly understood to be caused by the thermal desorption of organic compounds that are condensed on the accumulated solid soot particles, the emissions of very small solid particles during regeneration events is less understood. Filtration theory and testing experience over many years indicates that small soot nanoparticles should and are very efficiently collected by DPFs. What is then the mechanism by which very small solid particles are emitted during some regeneration events? In the present work we provide a fundamental mechanism responsible for the emission of small solid nanoparticles during DPF regeneration and investigate measures that can be employed to prevent such emissions.

Lee Chun Beom / Korea Automotive Techn. Inst.

Morphology and Structure of Engine-like Soot Particles formed by a Soot/SOF Generator

Soot generators which can control particle size distributions and mimic engine particulate emissions have been usefully applied to diesel particulate filters (DPFs), soot sensor development and exhaust gas recirculation (EGR) fouling, as well as the calibration of soot measurements. Many studies show that particulates generated from those devices are similar to diesel particulates in morphological shape and size. Despite similarity in apparent aggregate shape and primary & aggregate sizes, however, detailed information of nanostructure and statistical size results is still rare.

KATECH has developed a soot generator; in principle, aerosol particles generated from diesel fuel pass through a furnace. Particle sizes are controllable by fuel flow rate, dilution flow rate and furnace temperature. In this work, impacts of dilution flow rate were investigated, when the fuel flow rate and furnace temperature were kept constant. Detailed examinations include primary & aggregate size information by transmission electron microscopy (TEM), nanostructures by high-resolution TEM (HR-TEM) and crystalline structures by Raman analysis. The size analysis showed that with increasing dilution flow rate, primary and aggregate particles shift to smaller sizes and average primary particles were observed to be in a range of 25 to 31 nm in diameter, as found in diesel particulates. It was evident from agglomerated shapes and detailed nanostructures that with increasing dilution flow rate, soot changed from well-defined graphite-like carbon, such as typical diesel and GDI gasoline soot, to amorphous carbon, such as GDI E85 soot, resulted from delayed soot formation. Despite big differences in nanostructure, these aggregates from different conditions were all chain-like structures as compact as light-duty diesel soot and GDI soot, according to fractal analysis. Moreover, the poster will contain their Raman results, in comparison to various engine soot samples.

Ma Dong / VECC China

China Air Quality Status and Emission Reduction for Mobile Sources

In recent years, along with the rapid growth of motor vehicle population, vehicle emission has already become the main air pollution resource in large and medium-sized cities in China. In recent years, along with the rapid growth of motor vehicle population, vehicle emission has already become the main air pollution resource in large and medium-sized cities in China. The presentation first shows the air quality status of megacities in China and the monitoring results based on the new ambient standard of China.

While air pollution has long been recognized as a serious problem in China, the recent emergence of haze-filled skies has helped dramatize just how serious it is. The data help tell the story. Since January 2013, smog episodes have affected 25 provinces and 100 large and medium-sized cities. There was the highest average number of days of haze in the last 52 years. In addition, the average numbers of hazy days in 14 provinces were the highest annual figures recorded over the same five decade plus period. China's capital has arguably been hit hardest. According to results released by the Beijing Environment Monitoring Center, Beijing had 184 hazy days between January and November, 2013; in January only 4 days complied with air quality standards, and during the month there were three episodes of at least three consecutive days of haze. The twelve 5 years plan and other action plan of China central government and Beijing local government on the air quality improvement were introduced.

The pollution status of the transport sector in China and its contribution was presented in detail, including emission amount and emission inventory of different vehicle classes. Pollutants emitted from non-road mobile sources were estimated. The measurements and implements on mobile source control, including new vehicle/engine emission standards, in-use vehicle management and fuels were taken by local city governments. Other actions on green transportation taken by cities were summarized. The last part of the presentation concludes the road map of vehicle emission control in the future and the challenges faced, including fleet and fuel cleaner, emission total amount control and air quality improvement, low emission zone and fiscal policy.

Mathies K. / TÜV SÜD Germany

The new Heavy Duty Diesel Environmental Regulation of Iran

The new IRAN Heavy Duty Diesel Environmental Regulation is currently developed to control Ultra-Fine-Particle emissions from new Heavy Duty Vehicles. Motivation for this legislation is the presence of one of the highest pollution conditions in the world in all Iran Mega Cities, namely Tehran. Because of home heating by clean natural gas, the pollution can mainly contributed to vehicle traffic under high altitude conditions. The solution for this problem can only be solved to get all major stakeholders to one negotiating table, to cover the issue of potential high sulphur content diesel fuel of domestic production, of protection of the national motor vehicle production, of importation of European and Japanese engine manufacturers with "CKD" "completely knocked down" vehicle production in Iran, and the interests of environmental Iran organizations like AQCC, the Air Quality Control Company of Tehran and "DOE" the Department of Environment" for Iran, as well as the ministry for Industry, ministry for Oil and the organization for the domestic Industry and representatives of the domestic and foreign engine producers.

The Iran Motor Vehicle type approval process up to now relys on European sytem regulations. For the first time a nation has to decided to go their own ways for legislation heavy duty vehicles, because the most advanced EURO VI legislation does not fit the Iran conditions for traffic, altitude, technology and fuel conditions, and therefore choses an precedented route of EURO III/IV emission level with PN particulate number emission limit to apply for Iran. The Public-Private-Partnership Process is moderated in meetings by an expert on international motor vehicle type approval from TÜV SÜD in Germany to assure that all contributions and issues are recognized at the negotiating table.

The new regulation is covering transport vehicles of N1, N2 and N3 types of motor vehicles as well as M2 and M3 buses with compression ignited engines.

Merkisz J. / Poznan University Poland

Selected Problems of the Measurements of Particulate Matter from Vehicles Performed under Actual Operating Conditions

The paper presents selected results of investigations related to the emission of particulate matter from vehicles, collected for 8 years of research of a variety of modes of transport under actual operating conditions. This type of research has been conducted at Poznan University of Technology and it utilizes the **P**ortable **E**mission **M**easurement **S**ystem (*PEMS*) technology. Investigations conducted with this method identify the relations between the exhaust emissions and the operating parameters of vehicles and their engines. The presented test results of different modes of transport in terms of the emission of particulate matter under actual traffic conditions (RDE - *Real Driving Emissions*) led to a creation of emission correction coefficients, characterized as a multiple of the increase or decrease of the emission under actual operating conditions compared to the homologation test. Emission correction coefficients have been created based on tests performed on a variety of modes of transport under actual conditions of operation for different emission categories of light-duty vehicles, heavy-duty vehicles, city buses (including hybrids) and non-road machinery; all fueled with different types of fuels.

From the performed analysis it results that passenger vehicles fitted with diesel engines equipped with diesel particulate filters meet the PM emission requirements. This is also the case for have-duty vehicles and non-road machinery. Direct injected gasoline engines, however, significantly exceed this admissible PM level. The change in the emission of PN and PM during filter regeneration has been analyzed in heavy-duty vehicles and city buses, thus drawing attention to the problem of size, mass and number of particles emitted from engines fueled with gaseous fuels (natural gas).

The expertise in the measurement of exhaust emissions under actual traffic conditions have pushed the authors to analyze the problem of retrofitting in heavy-duty vehicles fitted with diesel engines. Following the exhaust emission tests performed under actual traffic conditions on city buses and non-road machinery of categories not requiring DPF, a significant increase in the emission of particulate matter has been observed compared to vehicles of low mileage. The application of DPF in such vehicles leads to its considerable reduction (95%- mass, approx. 90% - number). The obtained results have been used to analyze a variety of aftertreatment systems in terms of reduction of exhaust emissions. A review of possible configurations of aftertreatment systems in retrofitting has been performed in terms of their applicability as well as the size and porosity of their catalytic supports. On this basis the authors have proposed a method of DPF filter regeneration suitable for city buses and non-road machinery.

The performed investigations and the ascertained particulate matter emission indexes have led to an assessment of the environmental performance of vehicles of different emission categories at the same time serving the proactive purpose in terms of exhaust emissions.

Müller L. / University Children's Hospital Basel

Effect of Gasoline Exhaust Emission on Bronchial Epithelial Cells and Natural Killer Cells

Air pollution can cause respiratory and cardiovascular diseases. Several studies have shown that diesel exhaust emission can modify natural killer (NK) cells in their cytokine production or ability to kill target cells, whereas there are only few studies on gasoline exhaust emissions. The majority of European cars, however, run on gasoline and emit air pollutants. Therefore we investigate the effect of gasoline exhaust on human bronchial epithelial cells (ECs) alone and co-cultured with NK cells.

We exposed ECs (16HBE14o⁻ cell line) to freshly produced gasoline exhaust from a Volvo V60 (T4F, 3-way catalyst). We used once E85 gasoline mixture (85% ethanol, 15% gasoline) and once normal gasoline. The car was run on a roller dynamometer with multiple steady state cycles (95km/h, 61km/h, 45km/h, 26km/h and idling, each 30min). As a control, cells were exposed to filtered ambient air for the same durations (2hrs and 6hrs). Subsequently NK cells were added to the pre-exposed ECs forming a co-culture. 20hrs later, the samples (n=4) were harvested and analyzed for oxidative stress (by glutathione (GSH) levels), DNA damage (by oxyDNA assay), surface and intracellular markers and NK cells' cytotoxicity potential (by FACS). All data are normalized to EC 2h air (for EC endpoints) or co-culture air 2h (for NK cell endpoints).

For the exposure to E85, we found no effect of exhaust on the cytotoxic potential, NK cell surface (CD16, CD56, CD158b, CD159a, CD183, CD314, CD335), NK cell intracellular (IFN- γ , IL-4, granzyme B) or EC surface (MICA/B, ULBP2/5/6, ULBP3, CD183) markers. GSH was increased significantly in ECs alone after 6hrs exhaust emission exposure (1.42, CI=1.03-1.81), but not after 2h exhaust, 6h air or in co-cultures. DNA damage was reduced in ECs alone after exhaust exposure (2h 0.77 (CI=0.57-0.97), 6h 0.71 (CI=0.44-0.98)), a results which is surprising and needs to be further investigated. Experiments with the exposure to normal gasoline have been performed, but are still being analyzed. Results will be presented at the conference.

E85 gasoline car exhaust reduces DNA damage and increases GSH in human bronchial EC. Further investigations with normal gasoline will clarify if effects depend on gasoline type.

Muñoz M. / EMPA Switzerland

PAH and nitro-PAH Emissions from GDI Vehicles

Background

Gasoline Direct Injection (GDI) vehicles are quickly replacing traditional port fuel injection vehicles. They are expected to account for 1/3 of the EU fleet (53 MIO vehicles) by 2020. It has been shown that large numbers of particles are emitted from GDI vehicles exceeding the current Euro 6 limits (6x10¹¹ particles/km). Filters will be required to reduce particles, as now it is for diesel vehicles. But filters may also support the formation of new pollutants. Thus the new GDI technology will produce changes in exhaust composition that may produce new health risks on humans. Some of these pollutants are PAHs, alkyI-PAH and nitro-PAHs and have been studied in this research. Some of these compounds are genotoxic. Genotoxicity describes the property of chemical agents damaging the genetic information within a cell causing mutations, which may lead to cancer. According to the WHO, some of these PAHs are carcinogenic, like Benzo(a)pyrene which is considered as a group 1.

Methodology

In this study, complete exhaust samples, including solid, condensed and gaseous fractions, have been collected from 3 different GDI vehicles at the chassis dynamometer of the UASB. The vehicles were driven following the WLTC under hot and cold start conditions and with steady state conditions. Diluted exhausts were sampled from a CVS tunnel. In addition, a non-coated filter has also been tested with one vehicle. In the laboratory, samples were processed following extraction and cleanup procedures. The final extracts were analyzed by HRGC-HRMS and concentrations of PAH, alkyl-PAHs and nitro-PAHs were determined.

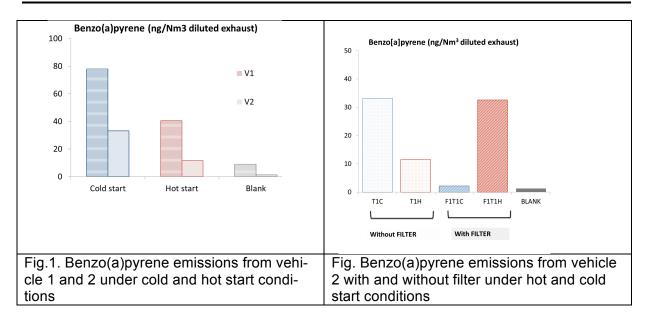
Results and conclusions

Figures 1 and 2 are typically results for one of the many PAHs observed in the study. For the most genotoxic compound, benzo(a)pyrene, emissions under cold start conditions are higher compared to hot start conditions. Nevertheless, concentrations differ for both vehicles (fig. 1). This trend is seen for most of the compounds analyzed.

When a filter is used, the emissions under hot start conditions increase compared to those under cold start conditions or those without filter (Fig. 2.). We concluded that higher boiling point compounds like Benzo(a)pyrene are being adsorbed in the filter under cold start conditions but not under hot conditions. This phenomenon of storage/release has been observed before in other non-catalyzed filters.

The increase emissions could also be interpreted as the result of the result of a PAH formation during soot combustion, which is to our opinion, less likely because the filter has no catalytic coating.

Research on of these new exhausts is urgent in order to assess potential risk on human health which is of importance to all of us, since we will be exposed to these exhausts, to the automotive sector and to the public administration.



Northrop W. / University of Minnesota USA

Semi-Volatile Nanoparticle Emissions From Diesel Low Temperature Combustion Modes

Low temperature combustion (LTC) operation in diesel engines can simultaneously reduce NOx and soot emissions but is known to result in higher CO and hydrocarbon (HC) emissions compared to conventional diesel combustion. LTC in diesels can be achieved with diesel fuel alone by using high levels of exhaust gas recirculation or by using both gasoline and diesel in dual fuel reactivity controlled compression ignition (RCCI). Diesel oxidation catalysts (DOCs) are effective at removing HCs and CO at high temperature but cannot achieve full conversion at low exhaust temperatures common when operating in LTC modes. HC species that slip through aftertreatment have been shown to result in semi-volatile nanoparticles that nucleate and grow once diluted and cooled in the primary exhaust plume. This work focuses on characterizing the volatility of HC emissions from two diesel engines using diesel-only LTC and dual fuel RCCI. This study uses tandem differential mobility analysis (TDMA) to perform detailed experimental characterization of semi-volatile nanoparticle evaporation in real time and a phenomenological evaporation model to better understand underlying physics. Our work shows that RCCI combustion results in fewer low volatility particles than dieselonly LTC but contains a higher solid fraction. Generally, our work finds that nanoparticles from LTC modes are comprised of organics with a range of volatility spanning from alkanes found in unburned fuel to low volatility species like polycyclic aromatics and larger oxygenates. TDMA results show that larger particles have higher volatility than smaller particles reinforcing the hypothesis that semi-volatile particles from LTC modes originate from nucleation of low volatility species and consequently grow heterogeneously after dilution with air. The modeling work shows how the Kelvin effect plays an important role in shifting the particle size distribution to larger particles at higher dilution temperatures due to early evaporation of smaller particles. More generally, our work shows that low concentration of semi-volatile HC species from diesel LTC combustion modes could be a significant source of particle emissions from engines employing these strategies.

Nowak A. / PTB Germany

Optimization of Silver Particle Number Size Distributions from a Nucleation Furnace by Modification of Heat Shields and Injection Nozzles

With the implementation of the EURO 5 and EURO 6 legislation, the European Union (EU) established for the first time a number limit of engine exhaust particles emitted by light vans and passenger cars, which are powered by diesel or even gasoline engines. Therefore, a metrological basis for the measurement of particle number concentration of mostly nano-scaled pollutants is required. Within the work package 1 (WP1; *Automotive particle emission metrics*) of the EMRP project ENV02 (PartEmission¹) metrological criteria like SI traceability, temperature stability and "soot likeness" were investigated and implemented at several national metrological institute in Europe. [1]

One well-suited reference aerosol is silver from a nucleation furnace. PTB, the national metrological institute of Germany, is using this reference aerosol to establish a calibration service for Engine exhaust condensation particle counters (EECPC). For that purpose a tube furnace is used to generate silver aerosol. Compared to Scheibel and Porstendörfer [2] a larger tube furnace is used to provide nucleated particles at larger particle sizes up to 100 nm based on homogenous nucleation.

To influence the shape and the width of the particle number size distributions (PNSD) several process modifications were investigated. The modification consists of heat shields combined with a nozzle at the inlet and a hopper at the outlet of the tube furnace. Additionally, several disks at the heat shields were mounted to adjust the heat in the middle of the tube furnace and to provide a more uniform temperature profile over the entire tube length. Also, a faster temperature drop was achieved with the disk for both heat shields in the furnace.

Using different nozzle sizes (1 mm up to 3 mm) it is possible to adjust the maximum of PNSD towards larger diameters and to generate a higher particle number concentration (Figure 1). Without a heat shield an unwanted bimodal size distribution was observed in the longer tube. Including both heat shields smaller silver particles were generated and the PNSD showed a sharper peak in a lower size range. With only the inlet heat shield at the beginning of the tube a higher particle number concentration was generated and again a bimodal size distribution in the larger size range was observed.

Finally, we investigated with the presented setup a more flexible use of the common tube furnace and managed to adjust the particle size of homogenously nucleated silver particles by up to a factor of 3.

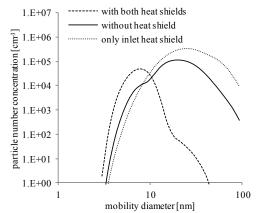


Figure 1: Influence of the heat shields at 1200 °C furnace temperature for PNSD

¹ The project is part of the European Metrology Research Programme (EMRP), which is jointly funded by the EMRP participating countries and the European Union.

In conclusion, the measurements of particle emission from these unusual "fuel types" gives very interesting new knowledge, contributing to the debate whether these "fuel types" is an relevant focus area or not, and possible also to the health researching scientists. For instance, the DustTrak was in saturation during large periods of the burning of all the charges of painted wood except in the ignition phase, which therefore only gives indicative (minimum) values – which still are a factor 2-10 higher than for (pure) birch.

Further test burning campaigns with other illegal "fuel types" such as gift wrapping paper and milk cartons, and PCB-containing window frames (polychlorinated biphenyl) will be performed during spring and summer time, again with the focus of developing a "sampler" but with parallel particle emission measurements, before conclusions will wrap up the project ultimo 2015. Of course, measurements of the various "fuel types" will be compared with results gained from measuring campaigns on normal ("clean") wood for the final conclusions.

This study is part of a 2-year Danish project, co-financed by the Danish Environmental Protection Agency, constituted by Danish Technological Institute, several Danish municipalities and chimney sweepers

Probst-Hensch N. / Swiss Tropical and Public Health Institute Switzerland

Health Consequences of Ultrafine Particles – an Exposome Perspective

Inhaled pollutants, particularly traffic-related fine and ultrafine particles, exert broad effects on different chronic disease outcomes. Research into the molecular mechanisms mediating particle effects on different cells and organs of the body may therefore unravel pathophysiological pathways of relevance to the process of aging and age-related chronic diseases. The exposome approach integrates exposures in the external environment and lifestyle beyond a single factor like air pollution. It applies -omics profiles to understand the endogenous footprints that exogenous exposures leave on molecules assesses the health impact of these molecular alterations. Exposome tools (sensoring technology; systems biology) integrated into well characterized cohorts and biobanks help unravel the "urban exposome" as it may relate to life in a megacity. The contributions of according studies to exposome research including health effects of ultrafine particles will be presented. The SAPALDIA cohort was established in 1991 and randomly recruited close to 10'000 persons from across Switzerland. A biobank has been integrated into the study. Detailed lifestyle and environmental information was collected on the study participants during three interviews with detailed health examinations. With the increased information density on participants the study evolved from an air pollution study to a chronic disease study. The next follow-up in 2015/2016 will start observing how persons age and how this process relates to more than 20 years of exposure to air pollution as well as other environmental pollutants and lifestyle. Early results already suggest an association of ultrafine particles with carotid intima media thickness, a marker of atherosclerosis. In the context of the EU project Exposomics, this association will be put into the broader context of additional aging related biomarkers including blood pressure and lung function.

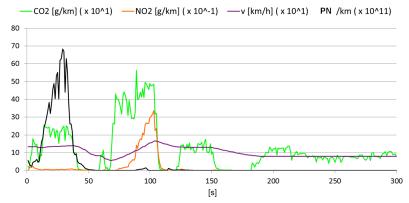
Pucher E. / Vienna University of Technology, Austria

Route Related Real-World Particulate Number and NOx Emissions of Euro 5 and Euro 6 LDV

Euro V and Euro VI passenger cars were analyzed in real-world situations with main emphasis on particulate number and nitrogen oxides emissions. For this purpose, representative test routes in urban and suburban areas have been defined. Furthermore driving tests at different mean speeds on freeways up to 130 km/h were performed. Special attention was given to the measurement of transient operations. As test vehicles cars with direct injection gasoline turbo charged engine and diesel engines with particulate filter were used.

Methodology: The test vehicles were equipped with a new developed, extremely compact wireless all-in-one portable emission measurement system. The device determines the exhaust mass emissions and particulate number and mean size in real time with an output data rate of one second. The method is based on a modal analysis of the concentrations in the tailpipe of the vehicle. The exhaust gas mass flow is calculated in real time from the air mass flow and the gaseous components with a mass flow balance and reaction kinetics model. The emission rates are calculated in mass per distance, time or energy. The fuel consumption is given by the carbon balance method. GPS is integrated to link the geographical information of the test routes with the measured exhaust emission data and to determine the related driving resistances.

Results: The measurement system worked satisfying. Especially the very short setup time of less than 30 minutes per vehicle allowed carrying out all experiments within half a day per vehicle. The results showed the typical trade-of between low diesel fuel consumption and increased nitrogen dioxide emissions for city driving conditions. Special situations like particulate trap regeneration and ramp acceleration indicated significantly increase in NO₂ emissions as well as particulate number per distance for both propulsion systems. The outcomes will be presented in second by second traces and as mean values for typical driving situation with average speed from 30 to 130 km/h.



Euro 6 Diesel transient freeway driving

Due to the specific emission behavior of gasoline and diesel engines NO_2 values were measured in the range of some milligram up to some gram per kilometer. NO_2 emissions are of extraordinary importance due to the particularly high exceeding of this constituent on road-side air quality measurement stations and as precursor of aerosols.

Querol X. / IDAEA-CSIC Spain

Outdoor and Indoor Particle Concentrations in Schools of Barcelona during the BREATHE-ERC-AG study

Intensive online measurements of particle number (PN), black carbon (BC), and PM2.5 concentrations, as well as PM2.5 offline chemical speciation and levels of NO₂, were performed at 39 schools of Barcelona to provide exposure information for the BREATHE-ERC-AG epidemiological study. To this end a whole year of indoor (classroom) and outdoor (playground) PN measurements were performed at pairs of schools (one close and the other far from intensive road traffic hotspots) from Monday to Thursday from 27/01/2012 to 22/06/2012 (campaign 1) and from 14/09/2012 to 22/02/2013 (campaign 2). Simultaneously, similar measurements were recorded along the year at an urban background air quality reference station. Measurements of PN were carried out using DiSCmini portable PN sensors that record data on PN concentration (10-700 nm, accuracy: ± 500 # cm⁻³) and average diameter, based on the electrical charging of the aerosols (Matter Aerosol). BC and PM2.5 were obtained using mini-aethalometers (AE51, AethLabs) and laser photometers (Dusttrack, TSI). Furthermore, weekly-averaged NO₂ concentrations were determined with Gradko Environmental passive dosimeters. With the exception of NO₂, measurements were recorded on a 5 or 10 minute basis. All the online devices employed were compared and corrected to minimise any measuring differences (prior and post each sampling campaign). Finally, 54 children were selected for BC exposure measurements during consecutive 48 h.

40% higher PN levels were recorded on average at schools near heavy traffic, highlighting thus the increased exposure of children due to urban planning decisions. A well-defined spatial pattern of outdoor PN concentrations were observed. In spite of this relevant road traffic influence, in a number of schools, midday PN increases (by 15%-70%) were observed, coinciding with BC daily lows. These PN increases were mainly attributed to nucleation processes and have been recorded both at high and low temperatures. The variation of these increases also followed a characteristic spatial pattern. Indoor PN concentrations were to some extent explained by outdoor PN concentrations during school hours, together with average temperatures (the last being related with opened windows during warmer conditions). Outdoor midday increases were generally mimicked by indoor PN concentrations, especially under warm temperatures. At specific cases, indoor concentrations during midday were 30%-40% higher than outdoor. The time scale of these observations evidenced the possible role of: a) secondary particle formation enhanced by indoor precursors or conditions, maybe related with surface chemistry reactions mediated by O₃, and/or b) PN from cooking activities. Significant indoor PN increases were detected after school hours, probably associated with cleaning activities, resulting in indoor PN concentrations up to 3 times higher than outdoor. The BC personal exposure measurements are also presented and the home, school and commuting contributions to daily exposure are discussed.

Results evidenced that urban and school PN exposure in high insolation regions are highly influenced by secondary new particle formation. The potential health outcomes of this type of UFP shall be evaluated.

Robertson W.H. / CARB USA

Toward Widespread e-Mobility and the Ultimate Solution for Combustion-generated Nanoparticles

California is meeting the challenges of reducing exposure to air toxics, conventional pollution like NOx and PM, and greenhouse gases (GHGs) while remaining economically vibrant. Over the last several decades, major strides have been made for clean air in the interest of public health. Ozone levels in Southern California have decreased 80% even as population doubled, the number of vehicles increased by 4 times, the miles traveled by those vehicles increased by 5 times, and the State's economy grew by a factor of 5. Similarly, there has been remarkable progress on ambient particles and black carbon and we are on the path to reach the State's 2020 GHG reduction goal. However, the downward trend in emissions must continue because further substantial improvements are still needed to meet both Federal and State ambient air quality requirements, some of which are progressively becoming more stringent. In addition, to meet California's long-term climate goal of 80% GHG reductions will require transformative, disruptive change in transportation, vehicles, and simply the way we move people, goods, and services. Incremental reduction of tailpipe emissions, while an initially game-changing strategy, tends to see the airshed inventory benefits overshadowed in time by increased fleet population and economic activity. The rising unit cost of subsequent emission reductions combined with the unrelenting pressure from population growth drives interest in true zero emission technologies capable of decoupling pollution emissions from VMT and population growth. But most importantly, meeting our clean air and climate goals in 2032 and 2050, respectively, will only be possible with zero or near-zero emissions.

The transformation of transportation will take time. In the meanwhile, internal combustion of fossil fuels will continue to dominate the transportation sector. Thus, on-going efforts are needed to promote the emission performance and efficiency of fuels, engines, and vehicles. California has adopted the most stringent PM mass emission regulation for passenger cars and light-duty vehicles in the world. The 1 mg/mi LEVIII standard has important implications for nanoparticles. In the heavy-duty sector, the PM mass limit for engines has forced the wide deployment of diesel particulate filters across all on-road applications. These two regulatory actions have been informed by extensive investigation and study of a broad range of topics related to PM and particles including nanoparticle formation, emissions and plume processing, measurements, sources, technology, fuel effects, and technological options for control. We will discuss highlights and some of the lessons learned from these activities as a framing for a policy articulation for widespread e-mobility in California and beyond.

The same zero-emission technologies identified for reducing transportation dependence on GHG producing petroleum fuels are often equally effective at reducing combustionrelated emissions including PM. e-mobility technologies show promise across a range of transport applications in effecting an enabling separation of energy generation from the point of energy usage thus allowing for increased application of clean and renewable energy sources—sources that might be prohibitively cumbersome to utilize directly on-board individual vehicles (solar, wind, geothermal, hydro, as well as powerplant scale Best Available Technology (BAT) emissions aftertreatment systems and efficiencies).

Through a combination of legislation, executive orders, Governor mandated goals, voluntary agreements and incentives (monetary and non-monetary), California is actively preparing for electrification of goods and passenger transportation to facilitate parallel reductions of GHG and combustion emissions including PM. Programs include technology assessments, new vehicle standards, electrified vehicle infrastructure development, land useplanning, goods movement planning, and demonstration funding to support early market penetration of e-mobility technologies.

Sappok A. / Filter Sensing Technology Inc., USA

Real-Time Particulate Filter Soot and Ash Measurements via Radio Frequency Sensing

Radio frequency (RF) techniques provide a direct, non-contact means for monitoring the loading state of particulate filters. The technique is equally applicable to both diesel particulate filters (DPF) and gasoline particulate filters (GPF). Using the metallic filter housing as an RF resonant cavity allows for highly sensitive measurements with fast response times to directly monitor both soot and ash levels in the particulate filter. In addition, the use of a broadband signal allows for information related to the spatial distribution of the material within the filter to be determined.

This presentation covers the fundamentals of RF-based sensing applied to particulate filter systems, as well as the development and evaluation of on-board instrumentation systems and sensors. The work includes a comparison of the RF measurement accuracy relative to gravimetric measurements of new and aged particulate filters for both soot and ash. In addition, results cover transient RF system performance relative to measurements of engine-out particulate matter (PM) emissions using AVL Micro Soot sensors and tapered element oscillating microbalance (TEOM) systems. The results indicate a high degree of RF sensor measurement accuracy to measure PM levels over a wide range of operating conditions, including during low-speed and idle engine operation, as well as during high temperature regeneration events. In particular, in situ measurements of the DPF PM oxidation rate over the course of both active and passive regeneration events are described, and suggest additional opportunities for further system optimization.

This work also compares conventional pressure- and model-based measurement and control systems, which provide only indirect estimates of the filter loading state, with direct measurements of filter loading base on radio frequency resonance techniques. Examples from a two-year on-vehicle fleet evaluation, engine dynamometer testing with both light-duty and heavy-duty engines, the use of different filter materials (cordierite and aluminum titanate), and system benchmarking of an RF-based aftertreatment control system relative to the stock controls on a heavy-duty MY 2013 engine platform are presented. Results demonstrate the direct measurement of soot and ash levels in the particulate filter over the full-useful life (simulating over 250,000 miles or 400,000 km of operation), with both new and aged components, as well as potential for additional system optimization and advanced diagnostics enabled through RF sensing and control.

Sheng Su / VECT, Xiamen, China

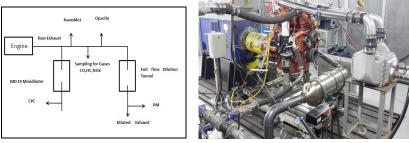
Diesel Particle Filter Testing for in-use Vehicle Retrofit

1. Background Information

The Chinese Ministry of Environmental Protection Vehicle Emissions Control Centre (MEP-VECC) wishes to explore the possibilities for lowering particulate emissions by retro-fitting Diesel Particulate Filters (DPFs) onto commercial vehicles. It is planned that a pilot trial will be run with a number of Xiamen city buses retro-fitted with DPFs. The first phase of the project involves the selection of a suitable DPF for the trial. The selection will be made based primarily on the results from engine tests to be undertaken on the test bench utilizing a typical Xiamen city bus engine. The testing is to be accomplished by making use of the experience, assistance and test methods from the Swiss organization "Verification of Emission Reduction Technologies" (VERT). Xiamen Environment Protection Vehicle Emission Control Technology Center (VETC) undertakes the engine tests with different DPFs manufactured by three different manufacturers.

2. Testing

A 4-cylinder engine was selected for testing which fulfill the China emission legislation and represents typical bus usage in China. The engine was installed on a test bed that was equipped to measure gaseous and particulate emissions. The emissions were measured at four steady-state conditions. These test points were chosen according to standard ISO 8178/4 based on data from a full load power curve conducted at the start of the test program. To evaluate the DPF's filtration, the emission test was conducted with no DPF fitted, with the de-greened DPF and with DPF after regeneration. The pollutants of Particulate Mass (PM), Particle Number (PN), Nitrogen Oxide (NOx), Nitrogen Dioxide (NO2), Carbon Monoxide (CO), Carbon Dioxide(CO2) and Hydrocarbon (HC) were measured by high accuracy test equipment. The sulfur content of the diesel test fuel was 164ppm, which meets China stage level. The fuel bone catalyst (FBC) was mixed in fuel with required proportion. The regeneration test was performed after at least 10 hours soot loading and the emission test was performed following.



3. Results

All sample DPFs have high efficiency in reducing Carbon Monoxide and Hydrocarbon emissions, especially the Particle Number. The DPFs can be well regenerated at certain condition. The efficiency of Particulate Mass reduction following regeneration was slightly higher than the brand new one in most states due to the formation of soot cake.

The Particle Mass was found increased at coated DPF testing. Filter baking tests were performed to preliminary investigate particulate components. Results indicated that the hydrated sulfates oxidized by the coated DPF might the primary cause of increasing of PM.

Compare to the coated DPFs, the soot loading rate was higher than un-coated ones. Nitrogen Dioxide was also found increased on coated DPF due to the oxidation of the precious metal.

The use of FBC (fuel bone catalyst) made a clear effect on reducing the soot ignition temperature. It helps the active regenerate at lower temperature.

Sioutas C. / University Southern California USA

New technique for online measurements of trace metals in ambient particulate matter (PM)

A novel monitor for online, in-situ measurement of several important toxic metal species (i.e. Fe, Cu, Mn and Cr) in ambient fine and ultrafine particulate matter (PM) is developed based on a recent published high flow rate Aerosol-Into-Liquid Collector (Wang et al., 2013). This Aerosol-Into-Liquid Collector operates under a flow rate of 200 L/min, and collects particles directly as highly concentrated slurry samples. The concentrations of target metals in slurry samples are subsequently determined in a Micro Volume Flow Cell coupled with absorbance spectrophotometry to detect colored complexes produced from the reaction between target metals and specific reagents. The system configuration is presented in Figure 1.

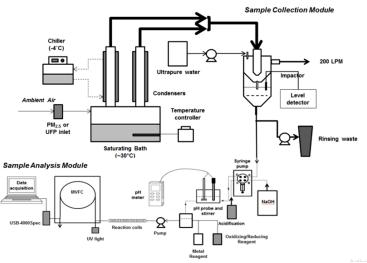


Figure 1. System configuration.

The absorbance spectrophotometry approach has been widely used for the direct determination of metals in liquid samples, and has very high sensitivities (Majestic et al., 2006). The specific reagent and absorptivity for each species are summarized in Table 1.

Table 1. Spectrophotometric methods for selected me	tals
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Species	Ligand	Absorptivity LM ⁻¹ cm ⁻¹	LOD (µM)
Chromium VI	Diphenylcarbazide	40,000 @ 540 nm	0.001
Iron II (III)	Ferrozine	25,300 @ 562 nm	0.002
Manganese II	Formaldoxine	~30,000 @ 450 nm	0.01

Laboratory tests are conducted to evaluate the performance of the Micro Volume Flow Cellabsorbance system. The calibration curves of the system are determined using standard solutions prepared by serial dilution. As part of the evaluation, the effects of reaction time, reagent amount and interferences on the system are also evaluated.

Field evaluations of the online monitor were carried out to validate the performance of this new online sampler by comparing its online metal data to results obtained by offline samples analysed by inductively coupled plasma mass spectrometry (ICP-MS). Overall, very

good agreements between online monitor data and ICPMS results for all metal species are observed, as shown in Figure 2(a-c) below, indicating a robust measurement accuracy of the new online metal monitor. Both laboratory and field evaluations of the novel monitor indicate that it is an effective and valuable technology for PM collection and characterization of important metal species in ambient aerosols.

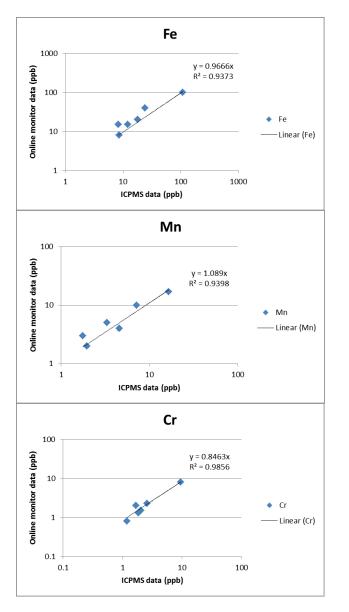


Figure 2(a-c): Comparison of total metal concentration obtained by online monitor and offline ICP-MS results: a. total Fe; b. total Mn and c. total Cr.

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Soppa V.J. / University of Düsseldorf, Germany

Controlled Human Exposures to Fine and Ultrafine Particles from Indoor Sources – Changes in Lung Function and Blood Pressure

<u>ackground:</u> Elevated levels of ambient air pollution are linked to cardiovascular diseases and impaired respiratory health. A few studies investigated the effects of indoor exposures to fine and ultrafine particles (UFP).

<u>Aim:</u> We investigated whether exposure to fine and ultrafine particles from candles burning, frying sausages and toasting bread as common indoor activities leads to changes in lung function and blood pressure (BP) in healthy volunteers.

Investigation methods: In a cross-over sham-controlled exposure study, 55 healthy volunteers (20 to 79 years of age) were exposed to emissions from candles burning, toasting bread, frying sausages and to room air as controlled exposure for 2 h. Lung function (FEV₁, FVC and MEF_{25%-75%}) and BP were examined before, during (only BP), immediately after (only BP), 2 h (only BP), 4 h and 24 h after exposure. Emitted particles were characterized concerning their size-specific particle mass and number concentration (PMC & PNC) and their lung deposited surface area concentration (PSC). To estimate exposure related effects we used mixed linear regression models with a random participant intercept, adjusting for personal characteristics, temperature, humidity, travel time and means of transportation to the study center. Health effects were estimated for each exposure separately. Results: PNC was dominated by UFP (<100 nm) (maximal calculated mean value at candles burning: 2.699,700 ± 205,900 particles/cm³), PSC by particles between 100-1000 nm in diameter (maximal calculated mean value at candles burning: $3839.6 \pm 248.6 \,\mu m^2/cm^3$) and PMC by super-micron particles (maximal calculated mean value at frying sausages: 296.9 ± 133.9 μ g/m³ (PM10)). While no effect was seen comparing the exposure scenarios in the unadjusted model, inverse associations were found for PMC. After 4 h in the adjusted model an increase of 10 µg/m³ PM_{2.5} from candles burning and frying sausages was associated with a change in FEV₁ of -19 mL (95%-confidence interval:-43; 5) and -6 mL (95%-confidence interval: -12; 0) respectively. PMC from toasting bread and PNC were not associated with lung function changes, but PSC from candles burning was. Preliminary analyses for BP show a positive association with PMC from candles burning, most pronounced for PM_{2.5} and at 2 h and 4 h after exposure in the adjusted model. An increase of 10 µg/m³ PM_{2.5} from candles burning was associated with a change in systolic BP of 1.3 mmHg (95%-confidence interval: 0.45: 2.01) and 1.4 mmHg (95%-confidence interval: 0.58: 2.17) respectively. Conclusion: Exposures to elevated concentrations of fine particles from common indoor sources are associated with small and transient decreases in lung function and increases in arterial blood pressure in healthy adults.

Thiruvengadam A. / West Virginia University USA

Real-World On-Road Particulate Matter Emissions from Latest Technology Heavy-Duty Vehicles using a Mobile CVS Laboratory

Since the promulgation of the United States Environmental Protection Agency's 2010 emissions regulation, the use of diesel particulate filter (DPF) and selective catalytic reduction (SCR) systems has become the norm. With continuous advancements in exhaust aftertreatment technology the mass emissions of particulate matter have decreased to levels that are close to detection limits of the gravimetric system. However, studies have shown that particle number emissions are elevated under certain real-world operating conditions. The objective of this study was to investigate PM number concentration and size distribution characteristics from modern heavy-duty diesel and natural gas goods movement trucks. Towards this goal particle size distributions and number concentrations were measured using different sample dilution and conditioning methods (i.e. raw exhaust dilution using ejector. constant volume sampler and European PMP compliant setup) to study the real-world particulate matter emissions. West Virginia University's transportable emissions measurement system was utilized to conduct on-road emissions measurement over a total distance of 1500 miles per test vehicle in the State of California. The study is unique in characterizing exhaust particle emissions during real-world operation of heavy-duty trucks as opposed to traditional chassis dynamometer or engine dynamometer studies. The study tested vehicles equipped with engines from all major US heavy-duty manufacturers. Hence, the results provide an insight into the DPF management strategies employed by the different engine manufactures and the resulting impact on PM emissions characteristics. Particle size distributions were measured using TSI's EEPS, while solid particle concentrations were measured using a Horiba SPCS 2000 and a TSI-Dekati thermodilutor in conjunction with a CPC. The routes where characterized by varying road grades and traffic conditions that are unique to California. The results of the study provide continuous measurements of DPF efficiency and emissions of solid particles as measured using a European PMP compliant measurement system. The results further illustrate the storage and release of sulfate based particles during high temperature operation of the SCR. Furthermore, results allow for comparison of solid particle emissions from current technology heavy-duty trucks to the European number count regulation.

Topinka J. / Czech. Academy of Sciences

Genotoxicity of Diesel Emissions in real World Driving: Effects of Cold Starts, Congestion, and DPF

Genotoxicity of organic extracts of particulate matter collected during real driving of two diesel trucks was evaluated in this study. A Euro 3 lveco Trakker with no aftertreatment and a Euro 5 Iveco Daily truck with DOC+DPF were driven around Prague each for two days. Exhaust emissions were measured by portable on-board emissions monitoring system. Particulate matter was sampled on Pall TX40HI20-WW filters by a miniature on-board proportional sampling system. The filters were extracted by the mixture of dichlormethane/hexane (20:1 v/v). The aliquot of the extracts was used for chemical analysis of priority polycyclic aromatic hydrocarbons (PAHs), including 7 carcinogenic PAHs (cPAHs)The analysis of PAHs in exhaust of lveco Trakker indicates significant concentrations of several cPAHs benzo[a]pyrene, benz[a]anthracene and chrysene during cold idle, cold takeoff and cold city drive, while no PAHs were detected for any driving conditions in Iveco Daily Truck equipped with DOC+DPF. We further study genotoxicity (DNA adducts) and oxidative damage (8-oxodeoxyguanosine, 8-oxo-dG) induced by organic compounds bound to exhaust particles. In agreement with cPAH content, the results show that on the engine without aftertreatment, genotoxicity of emissions was significantly elevated during cold start and cold operation of the engine. Over the warmed-up phase, exposure to an equivalent of 10 dm³ of undiluted exhaust collected during congestion and during operation following the congestion has lead to more DNA adducts than "ordinary" urban and freeway operation (Fig.1). Exhaust from the truck equipped with DOC+DPF had less DNA adducts, by approximately two orders of magnitude, compared to the truck without aftertreatment. In contrast to non-detectable PAHs in Iveco Daily truck emissions, we observed detectable DNA adducts induced by exhaust from this truck. This observation suggests high sensitivity of DNA adducts as a marker of genotoxic effects of engine emissions. The levels of 8-oxo-dG suggest weak effect of particle bound organic compounds on the extent of oxidative damage of DNA.

The results confirm that the benefits of DPF, observed in the reductions of particle mass and particle number emissions, also extend to the reduction of genotoxicity. The results suggest that cold start, cold operation and congestion increase the genotoxicity of exhaust emissions.

Funded by EU LIFE+ project MEDETOX, Innovative methods for monitoring diesel exhaust toxicity under realistic urban operating conditions, LIFE10 ENV/CZ/651.

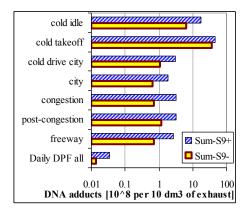


Fig.1: Induction of DNA adduct levels in DNA treated with extractable organic matter (EOM) mass corresponding to 10 dm³ of undiluted engine exhaust for 24 h. Results for various engine regimens are shown for samples with metabolic activation of PAHs by rat liver microsomal fraction S9 (+S9) and without metabolic activation (-S9). The values represent the mean from two replicates varying by <±15%.

Date

Trentini A. / ARPA Italy

Comparison nucleation event in rural and urban sites in Po Valley, Italy

Under the framework of the Supersito project, particle number concentration and size distribution were investigated with continuous measurements and intensive field observation at an urban background site (Bologna, about 400.000 residents) and a rural site (San Pietro Capofiume, about 1.500 residents) for three years. The distance between two sites is about 30 Km. The Po Valley (northern Italy) is characterized by a high density of anthropogenic emissions: mainly traffic, domestic heating, industry emissions and agriculture. In this study we collected 2013 data in order to analyze new particle formation events when they were recorded at the same time in both site or only in one site, in order to identify meteorological or physical conditions that allowed these differences. Data have been collected by a Scanning Mobility Particle Sizer with 5 minutes of time resolution (Model 3936, Nano 3085 and Long 3081, TSI Inc., 148 channels) and a twin Differential Mobility Particle Sizer with 10 minutes of time resolution (119 channels) respectively in urban and rural area. The measured particle size ranges were 3-600 nm for both instruments. Others parameters analyzed were meteorological and physical data and gaseous species concentration.

The nucleation events were classified in Bad Data, Non Event, Undefined event (class 0) and Event class 1, 2 and 3 (A.Hamed et al., 2007). The percentage of events during 2013 (class 1, 2, 3), excluded No Data and Bad Data days, was about 17% in urban site and 40% in rural area with the maximum in May and June for both sites. The event frequency in the same days was about 13%.

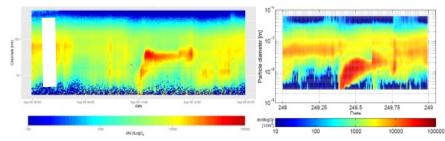


Figure. 1: Example of new particle formation at both sites in the same day (September 2013)

The annual average of total number concentration (Fig. 2), as expected, was higher in the urban site, however the differences considerably decrease for particles with a diameter > 100nm. Furthermore, the maximum value during the 2013 was $5.8*10^4$ in rural site and $6.6*10^4$ in urban site.

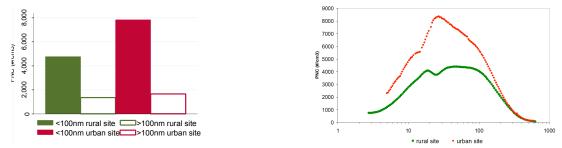


Figure 2 and 3. 2013 annual average PNC (d<100nm and d>100) and mean aerosol size distribution.

This research was conducted as part of the Supersito Project, which was supported and financed by Emilia-Romagna Region and Regional Agency or Prevention and Environment (ARPA) under Deliberation Regional Government n. 1971/13.

Tsai Ming-Yi / Swiss Tropical and Public Health Institute, Switzerland Insights into the Spatial and Temporal Distribution of UFP from Swiss Health Studies

Background: In the world of air pollution epidemiology, ultrafine particles (UFP) are of increasing research interest. We have conducted extensive measurements of UFP as part of two air pollution exposure health studies: SAPALDIA (Swiss cohort study on air pollution and lung & heart disease in adults) and an EU FP7 EXPOsOMICs (Enhanced exposure assessment and omic profiling for high priority environmental exposures in Europe) study. The latter study is being conducted with cohorts from five European areas and explores the 'exposome' concept describing human exposure via omics analyses on human biological samples.

Methods: In the 3rd examination of the SAPALDIA study (S3), in addition to extensive questionnaire assessments and health examinations, indoor and outdoor measurements for UFP, NO2, PM2.5, PM10, black smoke (BS) were made in four Swiss areas (Basel, Geneva, Lugano, Wald). UFP monitoring was conducted over 1-week periods at 20 residences per area per season in 2011/2012. In the EXPOSOMICs study, 24-hour personal and home-outdoor UFP & PM2.5 seasonal measurements were conducted with 50 cohort subjects per study area in 2013/2014. For the latter study, we only present results from SAPALDIA subjects in Basel.

Results: In S3, ambient seasonal average UFP spatial contrasts were low (90th/10th percentile), but spatial contrasts during rush-hour periods increased significantly demonstrating high temporal variability. Overall median indoor/outdoor ratios of pollutants indicated lower levels indoors versus outdoors with ratios ranging between 0.55(NO2) to 0.74(BS). Pearson correlations of indoor versus outdoor levels differed by pollutant (UFP: 0.38, NO2: 0.63, BS: 0.79). Simultaneous 24-hour EXPOSOMICs personal and home-outdoor measurements clearly document the importance of time-activity patterns on a subject's exposure on top of their home-outdoor levels

Conclusion: For epidemiological studies, this raises the concern about misclassification of UFP exposure, likely more so than for other pollutants, resulting from use of long-term estimates which do not consider subject-specific time-activity patterns. EXPOSOMICs measurements clearly demonstrated that subjects at homes with high-traffic can have low personal exposures while homes with low-traffic can have high personal exposures.

Van Ham J. / EFCA The Netherlands

Policies on Particulate Matter Miss Adequate Tools

Clean air policies for particulate matter in Europe and elsewhere are primarily based on the epidemiological database on its long-term health effects. Estimates of premature death which are derived from it have proven to be effective in the communication with politicians and have resulted in legislation for better air quality. The metrics used, PM₁₀ and PM_{2.5}, are unhelpful for implementing such legislation: they ignore that fractions of particulate matter, both in size and chemical composition, are having different toxicities and do not connect to sources in sufficient detail. As a result the overall effectiveness and cost-effectiveness of PM-policies cannot be optimised.

Only a fraction-by-fraction approach, pleaded for by EFCA in recent years, which considers, in addition to PM-fractions presently in use, the ultrafine fraction and its chemical composition could improve this situation. Such an approach – which could include particle numbers concentration – should consider the aerosol fractions of black carbon, organic carbon and (heavy) metals. Of these, the database on organic aerosols is least developed, while evidence on their health impacts accumulated in recent years.

The presentation will summarise two recent panel discussions organised by EFCA (7th International Symposium on Non-CO2 Greenhouse Gases (NCGG7), November 5-7, 2014, Amsterdam, and 5th International Symposium on Ultrafine Particles (UFP-5) on May 4-5 2015 in Brussels) on organic aerosols, also considering the present parallel interest for their role in climate forcing (brown carbon)

Vojtisek-Lom M. / Technical University Prague, Czech Republic

Lowering Laboratory and Real Driving Particle Emissions of direct Injection Spark Ignition Engines with n-Butanol and Isobutanol Blends.

The emissions of a typical automobile direct injection spark ignition engine were evaluated both in the laboratory and during real driving. In the laboratory, particle mass and number emissions, particle size distributions and regulated and unregulated gaseous emissions were evaluated online, and particles were sampled by high-volume samplers for chemical analyses and toxicity assays. Due to the known deficiencies of the NEDC cycle, WLTP, US06 and Artemis driving cycles were used. During real driving, particle size distribution were measured using a portable on-board emissions monitoring systems. To evaluate the effects of candidate renewable oxygenated fuels, the vehicle was tested using non-oxygenated gasoline and its blends with a) 15% ethanol, b) 25% n-butanol, and c) 25% isobutanol, with all oxygenated blends having similar content of oxygen by mass.

Comparison of size distributions of all particles with total count of non-volatile particles > 23 nm suggest that about half particles are smaller than 23 nm, and about half of the particles larger than 23 nm are volatile. Thermogravimetric analysis (EC/OC) shows, however, that elemental carbon accounts for most of the weight found during gravimetric analysis, suggesting that most of the larger particles are solid.

While ethanol had only moderate effects during real driving and negligible effect during laboratory tests, blends of both butanol isomers have resulted in consistent and significant reduction in particle number emissions, both in the laboratory and during real driving. The fuel did not have a consistent and significant effect on size distribution normalized to the total particle concentrations.

Tens of mg of particulate matter were collected per fuel for subsequent chemical analyses and toxicity assays. The contents of US EPA priority PAH in the particulate matter, expressed as mass of PAH per mg of PM, were not significantly different among the fuels, suggesting both butanol isomers have reduced PAH.

Supported by Czech Science Foundation project 13-0148S, BIOTOX – Mechanisms of toxicity of solid particles from biofuels.

Wolff T. / Dinex Germany

Using SCR on Filter Technology for Downsizing Future HDD On-Road and Off-Road Systems for Euro VI and Stage V

The Euro VI is now established for on-road heavy duty Diesel (HDD) vehicles. In these applications the combination of Diesel particle filters (DPF) with catalysts for the selective catalytic reduction (SCR) of NOx with ammonia can be found, in which Cu- and Fe-zeolites as well as Vanadia based catalysts are used. Most of these systems are using active regeneration^{1,2}. The ongoing fuel efficiency improvements lead to lower exhaust gas temperatures and this makes improvements of the low temperature SCR performance necessary. Potential solutions are 4-ways-systems with a DPF with integrated SCR functionality. In the off-road sector the Stage IV was introduced and the main solution here are SCR-only systems. With the new Stage V the integration of the particle filtration is needed. As this leads to challenges regarding packaging and total system costs the integration of SCR functionality in the DPF is also a potential solution.

The aim of this paper is to present a concept for downsizing after treatment systems for HDD engines by a single box solution which contains DOC (Diesel oxidation catalyst), AdBlue dosing, SCR coated DPF (F-SCR) and subsequent SCR. The main focus in the development of this concept was on the design of the SCR coating on the filter and the combination with the subsequent SCR unit. Different type of catalyst combinations have been tested - zeolite based versions as well as zeolite free solutions based on mixed metal oxides and vanadia or vanadates. The main criteria for testing and selection of the SCR catalyst for the DPF have been: low temperature SCR efficiency in respect to the cold HDD test cycles, the temperature stability in respect to the active regeneration of the filter and Sulfur resistance. With the selected catalysts tests of different F-SCR setups and their combination with subsequent SCR units have been performed in stationary mode with a 4.9 liter Stage IV engine. We found NOx reduction efficiencies up to 85%/230°C and 95%/300°C for the F-SCR and up to 95%/230°C and 99%/300°C for the F-SCR+SCR combination. The performance in transient mode was tested for one selected setup in full size using a 10.5 liter Stage IV engine. The test data has been used to perform simulation on flow distribution and back pressure of the single box design. Finally the box was build up and tested. NOx reduction efficiencies of 97% in an ETC (European Transition Cycle) and 91% in a WHTC (World Harmonized Transition Cycle) have been found. The particle filtration efficiency was >99%.

¹ A. Dittler, Abgasnachbehandlung mit Partikelfiltersystem in Nutzfahrzeugen, Shaker Verlag Aachen, 2014 ² Volvo, <u>http://www.volvotrucks.com/trucks/global/en-gb/trucks/environment/Pages/Euro6.aspx</u>

Yamada H. / Traffic Safety and Environment Lab. Japan

Emissions from HD Truck with Damaged DPF and its Detection at PTI

Particulate matter (PM), particulate number (PN) and other emissions were measured from a truck with damaged diesel particulate filter (DPF). The tested truck meets with the most recent Japanese exhaust gas regulation which is almost equal to Euro VI and aftertreatments of the truck were a diesel oxidation catalyst (DOC) and the DPF. Damaged DPF was produced by removing bottom side seals of the DPFs from 0 to 100 % in surface area. Using the damaged DPF, changes of emissions in JE05 mode were evaluated. In addition, detection methods of the emissions at a periodic technical inspection (PTI) were also evaluated. In addition to an opacity measurement which is adopted in present PTI protocol, some devices which based on laser light scattering photometry (LLSP) were tested. The tests were conducted in free acceleration in no load conditions by considering use at PTI. As the results, PM emissions exceeded the regulation limit (10 mg /kWh) when the damaged surface ratio exceeded 9.3 %. On the other hand, increase of PN emissions by increasing damaged surface ratio was quite high and only 2.7 % damage resulted exceeding the regulation limit (6x10¹¹ g/kWh). LLSP devices with free acceleration tests had enough sensitivity to detect the emissions within the regulation limits, however the K values varied almost twice as much among the different devices. The free acceleration test condition is not a steady state condition and emissions changed dramatically second by second. Thus, the varied K values seem to come from the difference of response time among the devices. To adopt the LLSP systems to PTI, setting the standard of response time is required.

During the whole tests, on board diagnostics (OBD) did not detect any failure even when DPF with 100 % damaged surface area was tested. The PM and PN emissions were 8 times and 200 times higher than the regulation limits, respectively.

This study was financially supported by National Agency of Vehicle Inspection, Japan.

Zinola S. / IFP Energies nouvelles, France

Comprehensive Analysis of Phenomena during Catalyzed DPF Active Regeneration.

Since the European regulation has limited the maximum particle number at 6.10+11 part/km for Diesel passenger cars in 2009, the Diesel Particulate Filter (DPF) is generalized in Europe. Even if DPF is a very efficient device, it still needs to be periodically regenerated to avoid its clogging. This regeneration phase corresponds to around 1% of the total time of vehicle using, and during this phase, released particles could appear downstream of the DPF. The purpose of this study is to better understand the key parameters that drive the particulate emissions during this phase, and to promote strategies to reduce them.

This study focuses on the detailed characterization of the particulate emissions during the regeneration phase of the DPF. Experimental tests were carried out at the engine test bench with a commercial Euro 5 1.6 liter Diesel engine and a catalyzed DPF. These tests were based on a specific protocol to emphasis the phenomena occurring during regeneration. This protocol is not that implemented by car manufacturer for their regeneration strategy. The increase of the temperature upstream of the DPF was obtained by using late in-cylinder post-injection over a much longer duration. The particulate number (PN) was measured downstream of a catalyzed DPF during the regeneration phase with several dedicated devices (DMS500, SMPS,...) The composition of the particles was also analyzed in two different ways: the first one uses an Aerodyne Aerosol Mass Spectrometer (AMS) for helping to determine the nature of the volatile fraction of the particles in real-time. The second one allows to visualize the presence of carbonaceous and non-carbonaceous particles in the sample on TEM grids at the laboratory and to determine their compositions.

From this experimental phase, it appears that the nature, the size, the composition of the emitted particles strongly vary during the regeneration duration.

In these regeneration specific conditions for a new catalyzed DPF, during the early stage, the addition of the post-injection leads to an increase in unburned hydrocarbons downstream of the filter, but no particles peak is detected. When the internal catalyst temperature becomes sufficient, sulfates are detected by AMS. These sulfates are formed from the sulfur contained in the fuel and the lube oil and stored onto the catalyst material during normal operation stages. Desorbed sulfates form nucleation seeds on which organic compounds coming from post-injection may adsorb.

As the regeneration moves forward, the nucleation peak starts to decrease and a second peak of particles appears, in the accumulation mode. These particles are related to the approaching end of the filter regeneration. Since the filtering efficiency decreases due to the progressive decrease of the soot bed filtration, a part of particles emitted by the engine can start to pass through the particulate filter.

By analyzing the different phases of the regeneration step, it appears that the two key parameters that control the particulate emissions are the regeneration temperature and the regeneration duration. These conclusions strengthen the strategy of a self regenerating DPF at low temperature that limits these particulate emissions.