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Netkueakul Woranan / EMPA, ETHZ

Development of Soot Sensor for Candle Emission Measurement

Candle combustion generates carbon soot nanoparticles, which can cause adverse health effect especially when candles are used indoor. In recent years, the awareness of particulate matter (PM) emissions from candles has been raised by consumer protection and regulatory agencies. This has led to the development of some basic emission standards, which are based on visibility criteria. However, these basic standard methods[1,2], which involve the measurement of light transmission through a soot loaded glass plate, are labor intensive and excessively time-consuming. Approximately one and a half days are needed to evaluate one candle. Therefore, cheaper, less time consuming, and more meaningful methods are needed for candle evaluation and for quality check purposes in the candle production process.

This research project had two objectives: first, to measure physical properties of candle emissions with state of the art instrumentation and second, to develop a low cost candle soot sensor. The emission properties evaluated included particle size distribution measured by scanning mobility particle sizer (SMPS) and aerodynamic particle sizer (APS), number concentration measured by condensation particle counter (CPC), mass concentration measured by cavity attenuated phase shift single scattering albedo monitor (CAPS), and emission factors (number and mass of emitted particles per mass of burned wax). Three types of candles were tested including a hand-made paraffin outdoor candle, a paint-coated paraffin candle, and a standard machine-made paraffin indoor candle. Regarding the sensor development, a low cost light scattering sensor (Sharp GP2Y1010AU0F) was placed in an airtight box, connected to a multifunction data acquisition device (NI USB-6341, National Instruments), and wired to a microcontroller. The sensor provided analog output signals, which could be correlated to particle mass concentration. The results from the developed sensor were compared to those from CAPS.

Size distributions of the hand-made outdoor candles and paint-coated candles are similar and had a peak at 250 nm based on the number or 500 nm based on the mass distribution. The standard machine-made indoor candles had relatively smaller particle sizes with a mode at 10-14 nm based on number or 135 nm based on mass distribution. Number emission factors of the standard candles were in the range of $10^7 - 10^9$ particles/g wax, while those of the hand-made outdoor and paint-coated candles were in the range of $10^8 - 10^9$ particles/g wax. Mass emission factors ranged from 0.30 to 14 µg/g wax for the hand-made outdoor candles, from 0.10 to 15 µg/g wax for the paint-coated candles, and from 0.04 to 0.12 µg/g wax for the standard machine-made indoor candles. These results indicated that number emission factors of the three candles were not significantly different with 95% confidence interval. On the other hand, mass emission factors of the hand-made outdoor candles and paint-coated candles were significantly different than those of the standard machine-made indoor candles with 95% confidence interval. Regarding the performance of the developed sensor, the preliminary results showed that the sensor could differentiate between PM emissions from the hand-made outdoor and the paint-coated candles, and those from the standard machine-made indoor ones.

[1] DIN EN 15426:2008-01; Kerzen-Spezification für das Russ verhalten; Deutsche Fassung EN 15426:2007
[2] ASTM F2326 - 04(2015); Standard Test Method for Collection and Analysis of Visible Emissions from Candles as They Burn

Olzem Katharina / Volkswagen AG Wolfsburg

Counting particles with the principles of Condensation vs. Diffusion

The real driving emission (RDE) legislation for passenger cars in Europe requires the use of portable emission measurement systems (PEMS) for the measurement of gaseous and solid particle number (SPN) emissions. For measuring SPN two different counting principle sensor-types are available. One type is the condensation particle counter (CPC) and the other is the diffusion charger (DC). The measurement principle of a CPC is based on optical single particle counting, whereas a DC measures charges. The advantages and disadvantages of each sensor type are still being under determination.

In the following lab-experiments the behavior of the two sensor-types will be compared. Each sensor was studied in consideration of its linearity and counting efficiency for different particle sizes.

The laboratory-setup is shown in **Fehler! Verweisquelle konnte nicht gefunden werden.**.. The aerosol is generated by a propane-diffusion-flame burner (CAST). It passes through a thermodenuder to remove volatile components. It is then transferred into a scanning mobility particle sizer (SMPS) to select the required particle size. The monodisperse aerosol is diluted, split and fed to the reference-CPC, which is an ultrafine CPC (D_{50} = 3 nm). In parallel the aerosol is also directed to the two different sensors (CPC or DC). Before it enters the sensor under test it is diluted and led through a catalytic stripper (CS).

For measurements with the test-sensor the aerosol must first be diluted by a rotating disc thermodiluter. If a CPC is used as a test-sensor it is directly connected to the CS (case a in fig. For the application of the DC a cyclone is additionally used to avoid unwanted influences of multiple charged particles. The cyclone is located between the rotating disc thermodiluter and the DC (case b in fig.1).

The linearity is checked with a monodisperse aerosol, particle size of 70 nm and concentration between 500 - 50000 #/cm³.

The efficiency is also tested with a monodisperse aerosol with the particle sizes of 20, 30, 40, 50, 70, 100, 150, 200 nm and a concentration of approximately 50000 #/cm³.
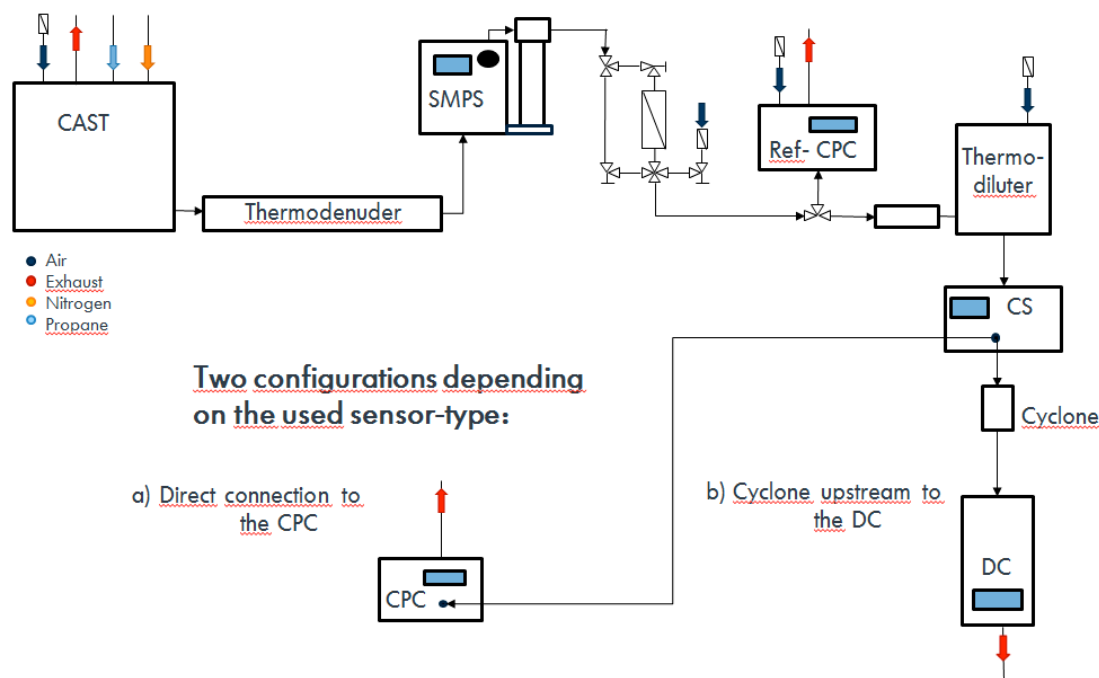

Figure 1: laboratory-setup

Padhi Annada / Indian Institute of Technology, Delhi

Laboratory based assessment of a portable multi-arm smoke collector system developed for *in-situ* aerosol emission measurement from residential biomass burning sources in the Northern part of India

In developing nations including India poor combustion of solid biomass fuel (i.e. fuelwood, dried cattle manure and agricultural residue) for energy requirement in the residential sector is one of the wide spread and less understood source of aerosol emission. Emissions from biomass combustion source as residential cooking need better characterization since it is an important input to the climate models. Emissions from biomass fuel also recognized for adverse health including respiratory and cardiac illness. Emissions from biomass fuel combustion in low efficiency, small scale cooking devices have been reported as significant source of particulate matter (PM) and light absorbing elemental carbon (EC) for Indian subcontinent and other South Asian region. However, a substantial underestimation of emissions from this source is stated as one of the reasons for factor of 2-4 discrepancy between climate model simulated and satellite retrieved absorbing aerosol optical depth. Over the last few decades, numerous studies have measured gaseous and particulate emissions from biomass fuel burning cook stoves in standardized or laboratory tests, however variations have been reported in literature between laboratories based studies and on-field measurements. Hence, more field-based emission studies are needed to better characterize the emissions from biomass fuel combustion in residential cook stoves. Our goal in this work was to account for the limitations in field based measurements and overcome the challenges that exist in performing and accessing emissions from on-field cooking fires in rural kitchens in India. Hence, this study will present the laboratory based assessment of a portable multi-arm smoke collector system developed based on literature to carry out comprehensive on-field measurements in the rural region of northern India. The emission factors will be estimated using the carbon balance approach. Climate relevant chemical characteristics of the aerosol including organic and elemental carbon, water soluble organic carbon, and water soluble inorganic species will be discussed.
Keywords: Emission factor, cook-stove, WSOC, PM2.5

Pagels Joakim / Lund University Sweden

Probing the evolution of soot characteristics during soot formation, soot oxidation and in the exhaust of a modern CI engine equipped with EGR

An effective method to reduce NOx pollutants from Compression Ignition (CI) engines is exhaust gas recirculation (EGR). When EGR is applied, exhaust gases are recirculated to the engine inlet air. This technique lowers NOx formation by decreasing the O2 availability and temperature during combustion. However, EGR increases soot emissions and the soot characteristics change. It is therefore important to understand: 1) the impact of EGR on soot emissions for different fuels and 2) the evolution of soot concentrations and characteristics in the cylinder during soot formation, soot oxidation and soot emission levels.

This study was carried out using a modern CI engine operated at different levels of EGR, corresponding to inlet oxygen concentrations from 9% to 21%. In the first part of the study, soot mass concentrations (Micro Soot Sensor, AVL) and size distribution (DMS500; Cambustion) measurements were performed in the exhaust for three different fuels: ethanol, gasoline and diesel. When adding EGR with gasoline and diesel fuels, engine out soot emissions first increase as more EGR is introduced and then decreases upon further increased EGR in the low temperature combustion (LTC) region. Ethanol emitted almost zero soot for all EGR levels. Soot emissions were about a magnitude lower for gasoline than for diesel. In a second part of the experiment the evolution of soot characteristics (maturity) as a function of the combustion cycle was investigated at EGR corresponding to 13-21% O2. A fast gas sampling valve (FSV; Shen et al. 2015) was mounted in one of the exhaust ports to extract in-cylinder soot particles at well-defined parts of the combustion cycle (a given crank angle). The extracted aerosol was diluted and the chemical composition of the particles was characterized on-line with a soot-particle aerosol mass spectrometer (SP-AMS, Onasch et al., 2012). With the SP-AMS, the composition of the refractory soot core (refractory Black Carbon) and non-refractory organic coating can be separated.

The results show that the altered combustion conditions induced by applying EGR strongly influence both soot formation and oxidation. The highest in-cylinder concentration of rBC occur at no EGR, about an order of magnitude higher than the maximum in-cylinder concentration at EGR corresponding to 13% O2. On the other hand, soot oxidations rates are significantly reduced when EGR is applied and exhaust soot emissions increase by about a factor of 30 when introducing EGR corresponding to 13% O2. The in-cylinder measurements reveal differences in the chemical properties of both soot core and coating over the combustion cycle and as EGR increases. Mid-carbon (C6-C31) and fullerene-carbon fragments (C32-C58) from the soot core are markers of immature amorphous soot (Onasch et al. 2012). These measurements showed presence of immature soot in the soot formation phase and a slower soot maturation process when adding EGR. Additionally, similar trends were found for the fraction of PAHs, other condensable aromatic species and oxygenated species. The MW distribution of PAHs was shifted towards larger molecules during the soot formation phase compared to the soot oxidation phase and in the exhaust. The altered soot properties and concentrations obtained from different fuels and EGR has implications for the efficiency of soot after-treatment systems and toxicological effects as the soot maturity may be related to the soot reactivity.

Onasch, T. B., et al. Aerosol Sci. and Techn. 46.7 (2012): 804-817.
Shen, M., et al. No. 2015-24-2448. SAE Technical Paper, 2015.

Pagels Joakim / Lund University Sweden

Characteristics of Major Particle Types in Emissions from Biomass Combustion - Implications for Health and Climate Effects

By converting energy-production from fossil fuels to biomass net greenhouse gas emissions can be mitigated. At the same time small-scale biomass combustion is responsible for an increasing fraction of ambient air pollution and is estimated to contribute with at least 40.000 pre-mature deaths each year in Europe (Sigsgaard et al. 2015). Additionally, Black Carbon (BC) and Brown Carbon (BrC) emissions lead to short-lived climate forcing at a poorly constrained magnitude. Particle emissions from biomass combustion are heterogeneous and there is a need to provide information of major particles types and the mixing of different chemical components within these particle types. The aim of this work was to identify relationships between combustion conditions and health and climate relevant particle characteristics of fresh and photo-chemically processed biomass combustion emissions.

Emissions were studied from a conventional log wood stove operated at different burn rates and from two wood pellet combustion systems. Highly time-resolved measurements, where the dynamics of emissions in individual combustion cycles could be followed, were carried out in diluted flue gas. Additionally, emissions from select burn phases were diluted down to ambient mass loadings and investigated under steady state conditions in a 15 m^3 steel chamber (Martinsson et al. 2015). We used a suit of techniques including a Soot Particle Aerosol Mass Spectrometer (Onasch et al. 2012), Differential Mobility Analyzer – Aerosol Particle Mass Analyzer and Transmission Electron Microscopy to investigate the physical and chemical properties of soot particle cores and their organic coatings and the occurrence of different particle types in the emissions. The optical properties were investigated with an Aethalometer. Intense atmospheric processing was simulated with an Oxidation Flow Reactor (PAM; OHexp. ~$3*10^8$ cm^{-3}h).

The particle emissions could be grouped into three main classes. Wood stove emissions from flaming combustion were dominated by BC dominated soot aggregates, which were internally mixed with a thin coating of oxidised organic aerosol (OA) and alkali salts. Soot aggregates from biomass combustion are larger than those in diesel exhaust and slightly more dense at a given size. During flaming combustion, the BC, OA and PAH emission factors as well as the OA enhancement (processed OA / fresh OA) increased during elevated burn-rates with partly air-staved combustion conditions.

Low-temperature pyrolysis following fuel-addition resulted in a second class of particles: tar-ball type particles dominated by organic aerosol with clear fragments in the aerosol mass spectra representing mono-sacharides and methoxy-phenols. Light absorption was primarily in the UV-region (Brown Carbon dominated) For this particle type the organic aerosol (OA) enhancement upon processing and particle density increased and the volatility decreased with increasing organic aerosol O:C ratio. PM_1 mass emission factors were substantially higher for low temp. pyrolysis compared to flaming combustion. However, absorption emission factors at 520 nm (in m^2/MJ) were of similar magnitude.

A third particle type was nucleation mode particles (30-60 nm) which were the dominant particle type in pellet combustion under more efficient combustion conditions. These emissions were dominated by water-soluble potassium salts (ash). Nucleation mode particles also dominated the wood stove burnout emissions, in this case consistent with dense ash-dominated cores onto which varying proportions of less dense organic aerosol had condensed.

Emissions from integrated whole combustion batches in the wood stove were externally mixed and contained all three particle types.

Onasch, T. B., et al. Aerosol Science and Technology 46 (2012): 804-817
Martinsson, J. et al. Environmental science & technology, 49 (2015): 14663-14671.

Sigsgaard, T. et al. European Respiratory Journal, 46 (2015): 1577-1588.

Paur Hanns-Rudolf / Karlsruhe Institut für Technologie

Field performance of Carola®- Precipitators for Small Wood-fired Boilers

Wood combustion provides an important share of renewable energy at competitive cost in Europe. The increasing use of woody fuels however impacts air quality due to emission of gaseous and particulate products of incomplete combustion, which have been associated with environmental health problems. Recent legislation in Europe sets stringent emission limits for particles and of CO from small wood combustion boilers and stoves.

The Carola®-precipitator, is suitable for wood-fired boilers in the range of 25 up to 200 kW: The particles are charged by a compact Corona electrode and the particles deposit on a metal brush downstream. The agglomerated particles are removed by periodical rotation of the brush and fall into the ash box, from where the dust is disposed. The precipitator is constructed from stainless steel and durable materials to prevent thermal and corrosive damage. Long-term performance of the Corona charger is ensured by automatic cleaning devices. The precipitator and the high-voltage system are regulated by electronic control systems, which assure optimal performance even under difficult combustion conditions.

Recently the Carola®-precipitators received their certification by DIBt and VKF after rigorous testing by TÜV with respect to thermal and electrical safety. Small commercial series are being produced and a quality management system is established. The Carola®-precipitators have meanwhile been installed at many industrial test facilities and private customers. In the focus of these tests are long term performance and availability at various fuel and operational conditions. The field performance is monitored with respect to removal efficiencies and stability of corona discharge during the heating season 2015/16. A total of more than 10.000 h of operation has been achieved, without major defects of the precipitators. Preliminary conclusions regarding the field performance of Carola®-precipitators are drawn:
• Removal efficiencies range between 70 – 90 % during long term operation
• The German emission limits are met reliably for various fuels and boilers.
• Stable operational performance is achieved by automatic cleaning of the electrodes and electronic systems.
• Besides cleaning of the ash box every 500 hours; other maintenance or exchange of spare parts is not required.

A study concerning the influence of precipitator costs on specific heat costs (€/kWh) shows, that the installation of a precipitator has only minor influence. More important are the fuel costs. Thus the installation of a precipitator may even improve the competitiveness of biomass combustion as variable, low cost biofuels can be incinerated without exceeding the emission limits.

Pechout Martin / Technical University of Liberec

Experimental investigation of particles produced by combusting blends of "high-quality" and "cost-competitive" biofuels in a tractor engine

Diesel engines powering the agricultural machinery throughout the world will probably be, especially in rural areas, among the last ones to be retrofitted with particle filters or replaced by electric drives. Also, while road traffic can be reduced by shift to rail and non-motorized traffic, and by promoting, for example, local economy and walkable communities, considerably less alternatives are offered for agricultural machinery. Therefore, suitable replacements for diesel fuel are sought, for sustainability, self-reliance, climate change, and other reasons. While such engines typically operate in less populated areas, particle emissions remain of concern and should be considered, or at least not neglected, when assessing candidate alternative fuels.
Of particular interest in this study were combinations of alcohol fuels with vegetable oils and their derivatives, biodiesel and hydrotreated (hydrogenated, hydrodeoxygenated) vegetable oils (HVO). Alcohols can be produced inexpensively and with low embedded fossil energy from different agricultural residues, and their oxygen content offers a reduction in particulate matter. A drawback is their low cetane number and the resulting deterioration in combustion. The common problem with vegetable oil derivatives is potential conflict with food production. HVO and synthetic fuels offer a wider variety of feedstocks, but their present downside is their high cost. The potential of extending "traditional" biofuels with alcohols was investigated. Due to ethanol having low cetane number and other undesirable properties, focus was on two isomers of butanol, n-butanol and isobutanol, which are expected to be produced from biomass at a cost comparable to ethanol [Tao et al., Biofuels Bioprod. Biorefin. 8(1): 30-48, 2014].
In this study, various blends containing petroleum diesel, fuel-grade rapeseed oil, biodiesel (methylesters of rapeseed oil), hydrogenated vegetable oil, ethanol, n-butanol and isobutanol were tested in a Zetor EU Stage III tractor engine operated in a series of 12 steady-state operating points including the 8 points in the Non-road Engine Stationary Test Cycle (NRSC). In addition to monitoring in-cylinder pressures for combustion analysis purposes, gaseous pollutants were measured by a Fourier Transform Infra Red spectrometer, particulate matter was sampled on filters for gravimetric analysis, and particle size distributions (including volatile particles) were measured by an electric mobility classifier.
Addition of butanol into diesel fuel reduced (all comparisons here are relative to diesel baseline) accumulation mode particles. Rapeseed oil and its blends with alcohol featured high nanoparticle peak around 10 nm and relatively high accumulation mode at low loads. HVO has increased particle number emissions, however, a blend of HVO with 50% biodiesel has resulted in a considerable decrease in primarily the accumulation mode. Alcohol fuels are believed to have caused a gradual decline in the baseline diesel fuel emissions of the engine.

Pedersen Peter Bøgh / Danish Technological Institute

Particle emissions from various candle types

All sorts of candles are being used in widely different situations and locations all over the world. New types of candles see the light of day every year, such as candles made of beeswax, mixes of traditional candle waxes and paraffin, vegetable waxes, animal fat based waxes, and so on and so forth.

The growing awareness regarding particle emissions from various sources is increasing, demanding additional information and knowledge. In a study, particle emissions in 56 Danish homes were measured, and it was found, that in the homes where candles were used, candles were responsible for approx. 60% of the residential integrated exposure (Bekö). This has resulted in an increasing demand for measurements on particle emissions from various candle types, such as square candles, tealight candles, candlestick candles and oil lamps.

In the present work, particle emission from 16 different types of candles and oil lamps have been measured upon to quantify and compare the emissions from different wax types and lamp/candle types.

Danish Technological Institute has developed a standardized method for measuring particle emissions from candlelight. The method has been approved by the Danish Environmental Protection Agency, and set a precedent for *Svanemærket* who is responsible for the official ecolabels in Denmark: The Nordic Ecolabel and the European Ecolabel.

Instrumentation
Particle emissions have been measured using a SMPS (Scanning Mobility Particle Sizer), model 3080 from TSI, nanoDMA (Differential Mobility Analyzer), model 3085, and CPC (Condensation Particle Counter), model 3776. The particles have been counted and size distributed in the size interval from 4.3 nm to 167 nm.
Older equipment for particle sizing in the nano-range has often been limited down to 10-20 nm, giving an enormous bias in the results, as the main part of the particles emitted from candles are in the 5 nm to 25 nm range in size (see Fig. 1).

Sooting behavior has been measured on half of the samples according to the well-established standard EN15426 Candles – Specification for sooting behavior.
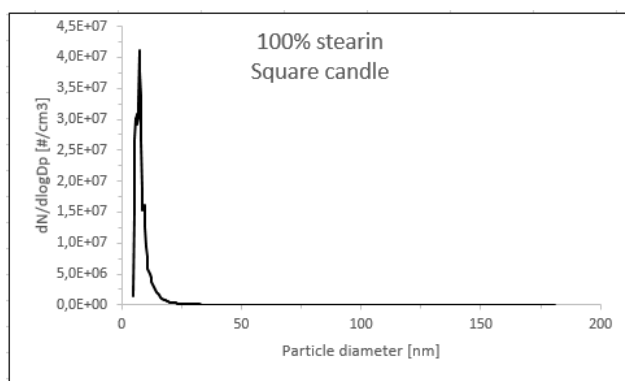

Fig. 1. Particle concentration as function of the particle mobility diameter measured on a square candle of 100% candle wax.

Table 1. Selected examples of correlation between candle type, wax type and particle emission concentrations. Uncertainty is calculated as std.dev.

Candle type	Wax type	Particle concentration [#/cm^3]
Tealight candle	Soya	1.6E4 ± 3.3E3
Tealight candle	Vegetable	3.2E5 ± 2.2E4
Tealight candle	Paraffin	1.0E6 ± 2.3E5
Tealight candle	Candle wax	3.0E6 ± 3.6E5
Square candle	Paraffin	1.0E6 ± 2.2E5
Square candle	Candle wax	8.4E6 ± 5.3E6
Oil lamp	Paraffin	1.1E4 ± 5.0E3
Oil lamp	Vegetable	6.8E3 ± 4.0E2
Oil lamp	Palm kernel oil	8.4E4 ± 2.7E4

Conclusion
As seen in Table 1, the measurements indicate that candles made of traditional candle wax emit more particles than the other candles. On the other hand, it seems that the oil lamps emit by far the lowest amounts of particles together with the soya candle.

This work is based on commercial tasks.

Bekö et al. (2013), Ultrafine Particles: Exposure and Source Apportionment in 56 Danish Homes, Environ, Sci. Technol. 47, 10240-10248.

Pedersen Peter Bøgh / Danish Technological Institute
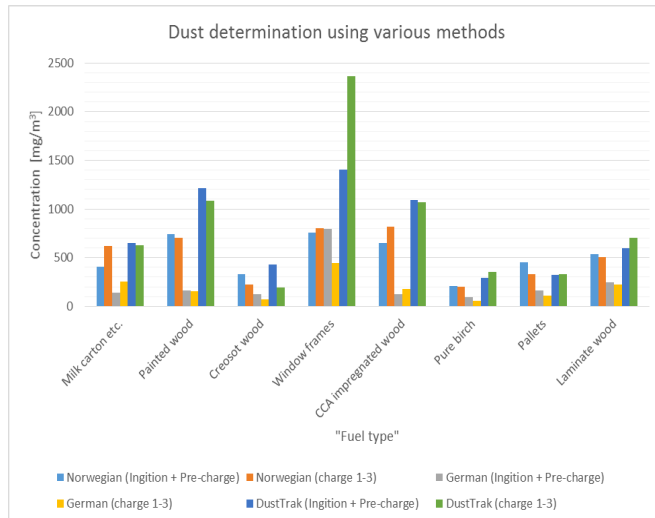
Illegal "fuel" in Private Wood-Burning Stoves

Burning of illegal "fuel" in private wood-burning stoves is an area that the Danish authorities in recent years have been giving increased focus. Danish Technological Institute has, together with several municipalities and chimneysweepers attempted to develop a "sampler" with the purpose to detect illegal burned materials in private wood-burning stoves. The purpose of the "sampler" was to adsorbing unique chemical components from various illegal "fuels". These "fuel types" comprise CCA-wood (copper, chrome and arsenic impregnated wood), creosote wood (old railroad sleepers and telephone poles), painted wood, wood with remains of PCB containing joint filler (polychlorinated biphenyl), paint and lacquer, a combination of milk cartons, gift wrapping paper and catalogues, pallet wood, laminate wood, and pure birch wood. Several test burning campaigns for proving the usefulness of the "sampler" have been conducted, and in parallel with these tests particle emissions have been measured.

The project did not succeed in developing a useful adsorption-"sampler". What went wrong? What could have been done instead? One of the surprises was the monitored high peak temperatures in the chimney, totally toasting the adsorption materials in the sampler. A lot of experience has been gained in the project and new ideas and angles have come to mind. Instead of a chemical angle to prove the presence of illegal "fuels", a physical angle is beginning to take shape for a future project…

The project did also show some positive results, though. It can be clearly detected and proved, that CCA wood has been burned in the wood stove by performing an ash analysis. Indications of appearance of some of the other mentioned illegal "fuel types" have also been found in either ash or soot samples, but has been harder to prove unambiguous when taking high variations in fuel type, burning style, etc. and uncertainties into account.

In parallel with the development work, particle emission measurements have been conducted, giving unique insight in particle emissions from "fuel types" that is not often seen. Particle size and number concentration were 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) counted the number concentration in the size interval 20-1,000 nm with a time resolution of 1 sec. Parallel with these measurement particle mass was determined using a DustTrak (TSI), also continuously logging PM1, PM2.5, PM4, PM10 and PMtotal. Number and size measurements were conducted in the dilution tunnel above the wood-burning stove and hereafter using a rotating disc diluter (Matter). Mass measurements was conducted directly in the dilution tunnel.

One interesting outcome was the large variation in results when performing measurement of dust content using the 'German' method (warm collection, in the chimney), 'Norwegian method' (cold collection, in the dilution tunnel), and by using online equipment (DustTrak, cold collection in the dilution tunnel).

This study is part of a recent completed Danish project, co-financed by the Danish Environmental Protection Agency, constituted by Danish Technological Institute, several Danish municipalities and chimneysweepers, e.g. the president and vice-president of their professional network.

Pielecha Jacek, Poznan University of Technology, Poland

Evaluation of Exhaust Emissions of Vehicles with Emission Euro 6 Class According to RDE Tests Proposed by the European Union

New test procedures for determining exhaust emission from passenger vehicles will be introduced in 2017. For several years, the European Commission is developing new procedures, which aim is to perform tests under road conditions. The purpose is to determine the real value of emissions, which do not always reflect the level of emissions in the laboratory. Proper and accurate procedures for determining emissions in real traffic conditions (RDE – Real Drive Emission) have not yet been approved (as opposed to Heavy-Duty Vehicles for which such conditions already exist), but there are proposals that are currently analyzed by major research centers in Europe. There are many differences between those proposals such as determining road emission or research methodology related to emission measurement of hydrocarbons.

The work compares the results of emissions measured in road tests using the latest legislative proposals related to passenger cars. The results are shown in relation to the used measurement method:

– classic method of determining exhaust emission; uses all measurement data determining the mass of harmful compounds and distance traveled during the test,
– method of averaging the measuring windows (MAV – moving average windows), also in the literature called EMROAD method, which determines the measurement windows (on the basis of carbon dioxide emissions from the WLTP test) and on its basis determines the road emission in RDE test,
– generalized method of instantaneous power (Power Mining), known in the literature as CLEAR – Classification of Emissions from Automobiles in Real driving, determines road emissions on the basis of generalized instantaneous power during the RDE test.

The research objects were vehicles with emission class Euro 6c (MY 2015) with spark ignition engines and Diesel engines. Spark ignition engines were equipped with multi-point fuel injection (MPI) and direct injection (DI SI), while passenger cars with Diesel engines were equipped with a particulate filter and selective catalytic reduction (SCR) to reduce emissions of oxides of nitrogen.

In road tests conformity factors (CF) – depending on the applied technical solutions – for gasoline engines with multi-point fuel injection for emissions class Euro 6 are less than 1. Values of the conformity factors for vehicles with Diesel engines look otherwise: a road tests have shown that the values of the conformity factors of carbon monoxide are less than 1 (meet the standard), whereas the emission of oxides of nitrogen were obtained between $CF_{NOx} = 1.7–4.8$ (according to the classical method: $CF_{NOx} = 2.5–4.8$, according to the MAV method – $CF_{NOx} = 2–4.8$; and the CLEAR method – $CF_{NOx} = 1.7–3.2$). Also, same situation applies to the determination of particulate emissions. In terms of mass, conformity factors reached $CF_{PM} = 0.2–1.3$ (all methods), and in terms of number $CF_{PN} = 0.3–0.9$.

Conducted research and determined values of emissions allowed to carry an ecological assessment of vehicles with various classes of emission standard, and at the same time served to activities leading to reduction of emission from passenger vehicles.

Poluzzi Vanes / Agency for Prevention Bologna

Particle number concentrations and size distributions in Po Valley (Northern Italy) during PoAIR experiment

The densely populated and heavily industrialized area of the Po Valley is a well known hot-spot for PM pollution, especially in the cold season, due to the frequent thermal inversion and stagnant meteorological conditions. Nevertheless, knowledge on particle number concentration (PNC) and related size distribution (PNSD) in this area are still rather scarce.

Within the PoAIR experimental project, an intensive multi-site field campaign was conducted during February 2014, aiming to investigate the temporal and spatial variations of PNC levels and PNSD. Measurements with different instruments were taken at five sites: two urban background sites, Milano (MI-UB), Bologna (BO-UB), two rural site, Molinella (SPC-R) and Ispra (ISPRA-R) and one mixed site Padova (PD-MX).
Compared with the typical winter conditions in this area, February 2014 was warmer, more unstable and rainy during the first and last decade and very warm in the middle because of a southern anticyclonic configuration thus, particulate matter mass concentration levels were quite low.

At UB sites PNC showed similar daily time patterns, with two typical peaks in correspondence with the traffic rush hours; conversely, the SPC-R rural site showed a pattern mainly driven by the boundary layer evolution and much less affected by emission activity.

The contribution of ultrafine particles (UFP, 20-100nm) to PNC levels were between 74-76% at urban sites, in agreement with data reported for other similar urban areas (1); a lower UFP contribution (mean 63%) was observed at the rural site SPC-R and ISPRA-R.
Data comparison highlighted a much larger variability for UFP concentrations at the urban sites than at the rural site, likely as a consequence of primary emissions from urban sources, namely traffic (2). Conversely, with the exception of PD-MX site, NoUFP (>100nm) displayed a less relevant spatial variability, apparently deriving from a diffused regional background.
This behaviour was partially confirmed by the time series analysis: site correlations for NoUFP number concentrations were comparable to those observed for PM2.5, not so evident for ISPRA-R, whereas correlations for UFP, mainly influenced by local emission, were noticeably lower.
This study was conducted as a part of the Supersito project which was supported and financed by Emilia-Romagna Region and by the Agency of Prevention, Environment and Energy of Emilia-Romagna region (I) under the Deliberation of Regional Government n.. 428/2010 and 1971/13.

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Press-Kristensen Kaare / Ecological Council, Denmark

Residential wood burning: Particle pollution and solutions

Residential wood burning is a dominating and increasing source to emissions of fine particles and black carbon in most European countries and in the EU as a whole. However, the emission and ambient air concentration (indoor and outdoor) of ultrafine particles from residential wood burning have not been investigated in details. Even though much new research suggests that these particles probably cause significant health effects and should be regulated by specific air quality limits.

Particles from residential wood burning were measured with an ultrafine particle counter from TSI (model 8525 Ultrafine Particle Counter). The particle size interval was 20-1,000 nm and measured in particles per cm^3. Thereby the interval includes particles larger than 100 nm not considered as ultrafine. However, since far the majority of the measured particles are believed to be in the ultrafine size interval (< 100 nm), we refer to the particles measured in this study as ultrafine. One particle measurement was taken per second but minute averages were used in data treatment. Wind speed, humidity and temperature were measured with a WindMate-300.

Three types of measurements from residential wood burning were conducted:
1) Emissions directly from the chimney using different types of wood.
2) Outdoor air quality in areas with and without smell of wood smoke.
3) Indoor air quality in houses with and without wood stoves in operation.

The emission measurements show that chimneys without any visible smoke connected to a new eco-labelled stove emit high levels of ultrafine particles even during optimal stove operation. The outdoor measurements show that the level of ultrafine particles from wood burning can be up to 50 times higher in residential areas with smell of wood smoke compared to spots in the same areas without smell of wood smoke. The indoor measurements show that wood stoves can cause high indoor air pollution with ultrafine particles. Furthermore, indoor air in houses without stoves can be polluted with ultrafine particles from wood burning in outdoor air when opening windows.

In conclusion, wood stoves are significant sources to pollution of outdoor and indoor air with ultrafine particles in many residential areas during the heating season. Pollution from wood burning should be reduced by taxation, bans, filters, better stoves and general public information about optimal stove management, insulation and cleaner heat sources.

Quinn Cian / University College Dublin

Analysis of particulate matter emissions from combustion of peat briquettes in a domestic-scale stove

This study presents the size distribution data for particulate matter (PM) emissions from a conventional household stove burning peat briquettes, a common biomass fuel used in Ireland. Emissions from the residential sector are of a growing concern; combustion of renewable biomass is increasing [1] and is viewed as attractive due to its near CO_2 neutrality [2]. However, there is concern over the PM emissions generated. Several authors have identified it as having an adverse effect on human health, as discussed in the review by Kim et al. [3]; in particular it is viewed as harmful to the cardiovascular and respiratory systems. Particle size has been identified as an important parameter [3] as it determines the depth of penetration of PM into these systems. Despite this, there is a paucity of information regarding PM emissions from residential stoves, both in terms of size distributions and chemical composition of the emissions. Thus, this work examines PM size distributions for peat briquettes, along with scanning electron microscope (SEM) micrographs and energy-dispersive X-ray spectroscopy (EDX) analysis.

Particle size measurements are obtained using a Palas Welas/Promo 2000 H aerosol spectrometer, which operates on a principal of white light dispersion (Mie Theory). These particle size measurements are taken every 10 seconds for the duration of a burn. SEM micrographs and EDX analyses are performed on PM samples that are collected on high-efficiency quartz fibre filters. All PM measurements are obtained directly from the flue gas without dilution. An important aspect of this work is that it attempts to reflect real-world usage in order to obtain a more representative picture of household stove emissions. Thus, a test begins from a cold start, and includes the ignition, full-burn and smouldering phases.

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Rossi Michel J. / PSI Villigen, Switzerland

**Surface Composition and Reactive Oxygen Species (ROS) Generation:
Evaluation of Health Risks of Soot Nanoparticles**

The conditions of hydrocarbon combustion determine to a large extent the bulk and interfacial properties of the resulting combustion aerosol (soot). Our **goal is to understand the human health effects of emitted combustion aerosol nanoparticles (NP) in relation to the surface composition of the particle-air interface** which we understand as the gateway to chemical reactivity. In order to establish this relationship we need (a) molecular information on the surface functional groups responsible for chemical reactivity of soot, and (b) the reaction rate of a diagnostic chemical reaction (proxy) in aqueous solution such as the oxidation of DTT (DiThioThreitol) that mimicks the deleterious ROS generation in the presence of soot and air oxygen. We are limiting our scope to NP's from a Diesel engine (powered by standard Diesel and Hydrotreated Vegetable Oil (HVO) fuels) and a few soot reference samples (GTS (Graphitic Thermal Soot)-6, GTS-80 and Printex XE-2B amorphous carbon). Regarding (a) we have used a titration technique using four reactive probe gases interacting with the solid samples in a Knudsen flow reactor. We are focusing on NO_2, O_3, HCl and CF_3COOH as reactive probe gases: NO_2 reveals the surface composition of **strongly** reducing surface functional groups because NO_2 is a weak oxidizer whereas O_3 retrieves the **total number** of reducing groups owing to its strong oxidizing capacity. CF_3COOH is a stronger acid than HCl in the gas phase so that CF_3COOH neutralizes all bases, weak and strong, whereas HCl only neutralizes the strong bases.

Regarding (b) we have obtained the result that the rate of DTT oxidation by dissolved O_2 in aqueous solution correlates unexpectedly well with the number of **strongly** reducing sites. This indicates the importance of the oxidation of reduced surface sites which have been identified as hydroquinones.

When measuring both the consumption of DTT and dissolved O_2 we conclude that quinones and hydroquinones derived from polycyclic aromatic hydrocarbons are not consumed but are involved in efficient redox cycling with turnover numbers of 30-600 depending on the type of soot NP's. Therefore, the functional groups on NP's act as **catalysts** in the air oxidation of DTT and are not consumed. This oxidation will lead to ROS and affect the lifetime, hence the abundance of antioxidants *in vivo*, and may lead to deleterious health effects. In addition, the rate law for O_2 consumption has been verified for two soot NP's and is given by $-d[O_2]/dt = k[O_2]_2[DTT][NP]$. Hydroquinone oxidation is the rate-limiting step in the overall catalytic surface oxidation of DTT by dissolved oxygen. We are now able to claim that both Diesel and HVO fuels and GTS-80 represent an accrued risk for ROS production compared to the other characterized NP's of this study owing to the large abundance of strongly reducing surface functionalities. The simultaneous presence of weakly basic groups (pyrones) and quinones, the presence of which have been independently verified using FTIR absorption spectroscopy, leads to free radicals on the surface of soot NP's that are stable under environmental conditions (Environmentally Persistent Free Radicals (EPFR)).

Rossner Jr. Pavel / Academy of Sciences Prague

Emissions from standard and alternative diesel and gasoline fuels: chemical characterization and genotoxicity

Emissions from internal combustion engines powered by diesel and gasoline represent a major source of air pollution in metropolitan areas. Recently, biofuels and their blends with standard fuels became a popular alternative to diesel and gasoline. However, possible negative health impacts of emissions from new fuels are not well characterized. In our study, we compared chemical composition and genotoxicity of organic extracts from extractable organic matter (EOM) obtained from emissions from various blends of biofuels with diesel and gasoline. We tested one type of diesel and two types of gasoline engines. The diesel engine was powered by: 1. standard diesel fuel (B0), diesel fuel with 30% biodiesel (B30), biodiesel only (B100) and a new generation biodiesel (NEXBTL100). The Direct Injection Spark Ignition gasoline engine (DISI) was operated using standard gasoline, gasoline with 15% ethanol (E15), 25% n-butanol and 25% iso-butanol. The Multi-Point Injection gasoline engine (MPI) was powered by standard gasoline and E15. For the diesel fuels, the highest content of polycyclic aromatic hydrocarbons (PAHs), their oxy-, nitro- and dinitro- derivatives/mg EOM was found for B30 and B100 fuels; the lowest PAHs concentrations were observed for NEXBTL100. For gasoline-operated engines, the lowest PAH content was detected in EOMs from MPI/standard gasoline, while MPI/E15 produced highest levels of both PAHs and oxy-PAHs. EOMs from DISI/standard gasoline were characterized by low PAH-derivatives content. Genotoxicity was tested in calf thymus DNA (CT-DNA) acellular system in the presence of rat liver microsomal S9 fraction. Levels of bulky DNA adducts and 8-oxo-7,8-dihydro-2'-deoxyguanosine (8-oxodG) in CT-DNA after 24-h treatment with EOMs (50, 100, 250 µg/mL) were analyzed. All diesel emission EOMs induced similar DNA adduct levels; EOMs from emissions from all DISI fuels had 2-3-fold higher genotoxicity then EOMs from MPI emissions. Oxidative DNA damage was comparable in samples from diesel and biodiesel, with the exception of B100 where no induction of 8-oxodG was observed. EOMs from most emissions from the DISI engines induced low levels of oxidative DNA damage, while the MPI engines generated EOMs with slightly higher oxidative potential. All results were evaluated per mg of extract and do not take into the account changes in the total mass of the emitted particulate matter as a function of the fuel used. In summary, EOMs from the biofuels contained comparable or higher PAHs levels than standard fuel. The highest genotoxicity was observed for EOMs generated by the DISI engines regardless the fuel used.

Rossnerova Andrea / Institute of Experimental Medicine, Czech Republic

Frequency of micronuclei in human bronchial epithelium cells induced by major diesel exhaust components and organic extracts from diesel emissions

Despite substantial technological advance resulting in decreased fuel consumption and lower emissions, road traffic remains a significant source of air pollution, particularly in metropolitan areas. From a complex mixture of chemicals and particles produced by incomplete combustion of organic material, polycyclic aromatic hydrocarbons (PAHs) are the most important as they may bind to nucleic acids and proteins, cause their damage and/or loss of function and induce mutations. Nitro-derivatives of PAHs, characteristic for diesel exhaust, are persistent in the environment and highly mutagenic and carcinogenic in model systems. Recently, alternative fuels based on blend of standard diesel with biodiesel compound became popular. However, little is known about genotoxicity of emissions of the alternative fuels. In our study, we compared DNA damage, measured as the frequency of micronuclei (MN) in human bronchial epithelium cells (BEAS-2B), induced by major diesel exhaust components [benzo[a]pyrene (B[a]P), 1-nitropyrene (1-NP), 3-nitrobenzanthrone (3-NBA)] and organic extracts from extractable organic matter (EOM) obtained from emissions from various blends of biodiesel with diesel fuels. The cells were treated for 28 h and 48 h with three non-cytotoxic concentrations of individual compounds and extracts. The frequency of MN was assessed in cytochalasin B-blocked cells using manual scoring. The samples were analyzed in triplicates; 1500 cells/sample were scored. All the tested compounds and diesel emission extracts increased MN frequency above the control level (2% cells with MN) in both time intervals; the MN frequency was generally higher after the longer treatment period. Among the individual compounds, 3-NBA was the most potent (the MN frequency reached almost 8%), followed by 1-NP and B[a]P. The extracts from emissions from diesel and bio-diesel fuel blends did not differ in their ability to increase the MN frequency; for all these samples, the frequency of cells with MN reached up to 4% after the 28 h treatment. After the 48 h treatment period, higher doses of individual compounds, as well as diesel fuel emission extracts tended to decrease the MN frequency probably reflecting negative impacts of tested compounds on cell viability. In summary, our data demonstrate greater genotoxic potency of nitro-PAHs when compared with the parent compound. Moreover, genotoxicity of extracts from diesel and biodiesel emissions seems to be comparable regardless the content of alternative fuel. Support: Ministry of Education Youth and Sports CR (#LO1508), EU LIFE+ (LIFE10 ENV/CZ/651).

Rubinetti Donato / University of Applied Sciences Northwestern Switzerland

Electrostatic Precipitator – Numerical Modeling and Verification Concept

Electrostatic precipitators (ESP) are a reliable technology to control emissions of airborne particles. Their ability to capture substantial concentrations of particles of nearly every size without pressure loss and low power intake has made them first choice for combustion-based industrial processes.

Numerical calculations allow further straightforward development of these devices. Within an ESP the flow and electric field interact simultaneously both on particle charging processes as well as on particle motion. The presented model to simulate an ESP includes all main physical phenomena in a coupled way.

For the setup a wire-tube ESP is chosen. The numerical model is based on the Navier-Stokes equations for the fluid flow analysis and Maxwell's equations for the electrostatic part. The ionization processes of the Corona discharge are respected by adding the charge conservation condition. The delicate part of representing the distortion of the electric field by Corona discharge is implemented with a user-operated algorithm which performs both numerically stable and accurate. By means of a simplified test-case the results for the electric field and the space charge density have been analytically verified.

Ruzal-Mendelevich Michal / Ben-Gurion University Israel

Grouping Manipulation of Nanoparticles Emitted from ICEs

Exposure to emissions from internal combustion engines, especially to particulate matter (PM) is well known as harmful for the health and has raised a considerable public concern over the last two decades. Human epidemiological and clinical studies have pointed out a clear connection between asthma, lung cancer and mortality, and particulate matter exposure [1].

The advent of particle sizing instrumentation has opened the possibility of measuring the number of nano-size particles in motor vehicle exhaust. Due to their small size, their residence time in the air is longer and so is the human exposure to these harmful particles.

Over the last years a number of attempts have been made to suppress the formation rate of particles inside the cylinder as a results of combustion and that by increasing fuel injection pressure, optimizing injection timing and duration, and improving the miscibility of the charge. Today, emission reduction is achieved with after-treatment devices. The Diesel Particulate Filters (DPF) is one of the most efficient after-treatment devices for micron scale particulate matter. Using finer filters to capture the smaller particles, in particular in the nano-size, may lead to higher engine back pressure even with more complex and expensive DPFs. For this reason, there is a strong desire for new means and technologies to reduce the number of nanoparticles emitted from vehicles.

Grouping, a new method recently developed by Katoshevski and co-workers [2-4], induces clustering and coagulation of particles leading to a significant reduction in particle number and increasing particle size thus allowing effective capturing of those particles by relatively simple DPFs. This approach is presented in our current study with focus on nano-size ones. The clustering is governed mainly by manipulating the characteristics of the flow.

The grouping, followed by coagulation ends up with a dramatic decrease in particle number [3,4] which is also a stringent requirement of the new Euro-6 regulations. For each engine we have designed a specific grouping exhaust-pipe according to its parameters and operating conditions [4]. These include exhaust gas mass flow-rate, range of engine speed, valves' timing, and other relevant data. The parameters were introduced into the mathematical model to optimize pipe geometry and dimensions.

Our current research, presents measurement results from different tests, different engines and combined systems such as DOC (Diesel Oxidation Catalyst) +POC (Particulate Oxidation Catalyst) to emphasis the influence of the "grouping pipe" on the reduction of particle number and particle surface area (Fig 1).
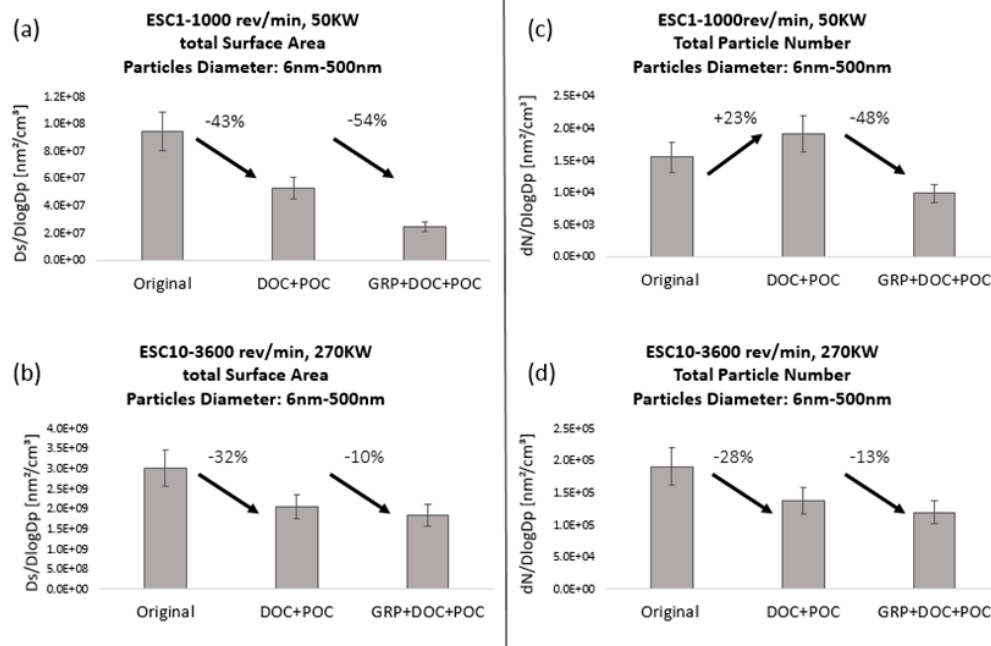
Figure 1- Particle total surface area for three systems: Original pipe, DOC+POC and GRP+DOC+POC for 2 different engine conditions 3a ESC1 and 3b ESC10 and Particle number density for the same three systems for 2 different engine conditions 3c ESC1 and 3d ESC10.

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Saidi Mohammad Said / Sharif University Tehran

Modeling lobar nano and micro aerosol particles deposition in the respiratory system during successive respiratory cycles

Particulates are a group of air pollutants. Due to development of industries and increment of motor-vehicles, the concentration of particulates, specifically nano-particles (ultrafine particles) generated by combustion have increased in the industrial regions all over the world. Air-borne particles entrance into the respiratory system by breathing can cause adverse effects on the lung performance. Prediction of particle deposition in the lungs can provide useful information to study these effects. Many researchers have investigated particle deposition in the lung, but to our knowledge, they all have studied a single respiratory cycle. Taking successive respiratory cycles into account, can result in more accurate model than considering a single respiratory cycle. This model can be used to enhance the accuracy of calculating the particle deposition to the respiratory system due to particulate pollution, or medical equipment such as nebulizers and other inhaled drug delivery systems.

In this study, using a 5-lobe symmetric model, particle deposition in the lungs during several successive respiratory cycles is investigated. Due to small size of nano-particles, it was anticipated that axial diffusion would take part in the results, so this phenomena is modeled. But, because of inherent high deposition of nano-particles compared to micro-particles (fine particles), the mentioned effect has been found negligible. It has also been found that for particle size range of 0.05 to 2 micrometers and respiratory tidal volumes greater than 1000 milliliters, considering the effect of successive respiratory cycles predicted more aerosol deposition fraction per cycle compared to considering a single cycle.

Sakellarakis Vasileios David / ETH Zurich

Large Eddy Simulations for detailed Soot Formation Investigations

The detailed understanding of the soot particle formation and oxidation processes is of high importance in the field of combustion system development. The chemical and physical properties of soot particles are "assigned" during the formation process. Large Eddy Simulations (LES) offer an advanced framework for turbulence modelling, which resolves the larger, energy-containing turbulent motions in a flow and only models the small scales. With this tool, the soot formation processes can be modelled under more realistic flow conditions.

In the present work formation of soot in an auto-igniting *n*-dodecane spray under diesel engine relevant conditions has been investigated by means of LES simulations using the Direct Integration combustion model. The gas and liquid phases have been modeled using the standard Eulerian-Lagrangian approach. A reduced *n*-heptane chemical mechanism has been employed and artificially accelerated, in order to predict the ignition for *n*-dodecane accurately. Soot processes have been modelled with an extended version of the semi-empirical, two-equation model of Leung that treats C_2H_2 as the soot precursor and accounts for particle inception, surface growth by C_2H_2 addition, oxidation by O_2, oxidation by OH and particle coagulation. The results are also compared with simulations based on the traditional concept for turbulence modelling (RANS, Reynods Averaged Navier Stokes), which solves for the mean flow and models the influence of all turbulent scales.

Predicted global soot mass is found to be roughly one order of magnitude lower than the experimentally measured, which is attributed to a possible underestimation of the pre-exponential factor in the surface growth step and presumably to the absence of additional important soot precursors in the soot model. Nevertheless, both turbulence modelling frameworks are shown to successfully predict the time-averaged distribution of soot volume fraction in physical space (Figure 1). LES is clearly superior to RANS in this respect, because it additionally succeeds at capturing the intermittency of soot formation and oxidation and reproducing the mechanisms that drive it. Furthermore, the chemical source term is linked to the flow-field both on the side of soot formation and soot oxidation via the concentration of soot precursor and oxidizers. Both oxidation pathways are found to be important, although oxidation by OH is more dominant overall.
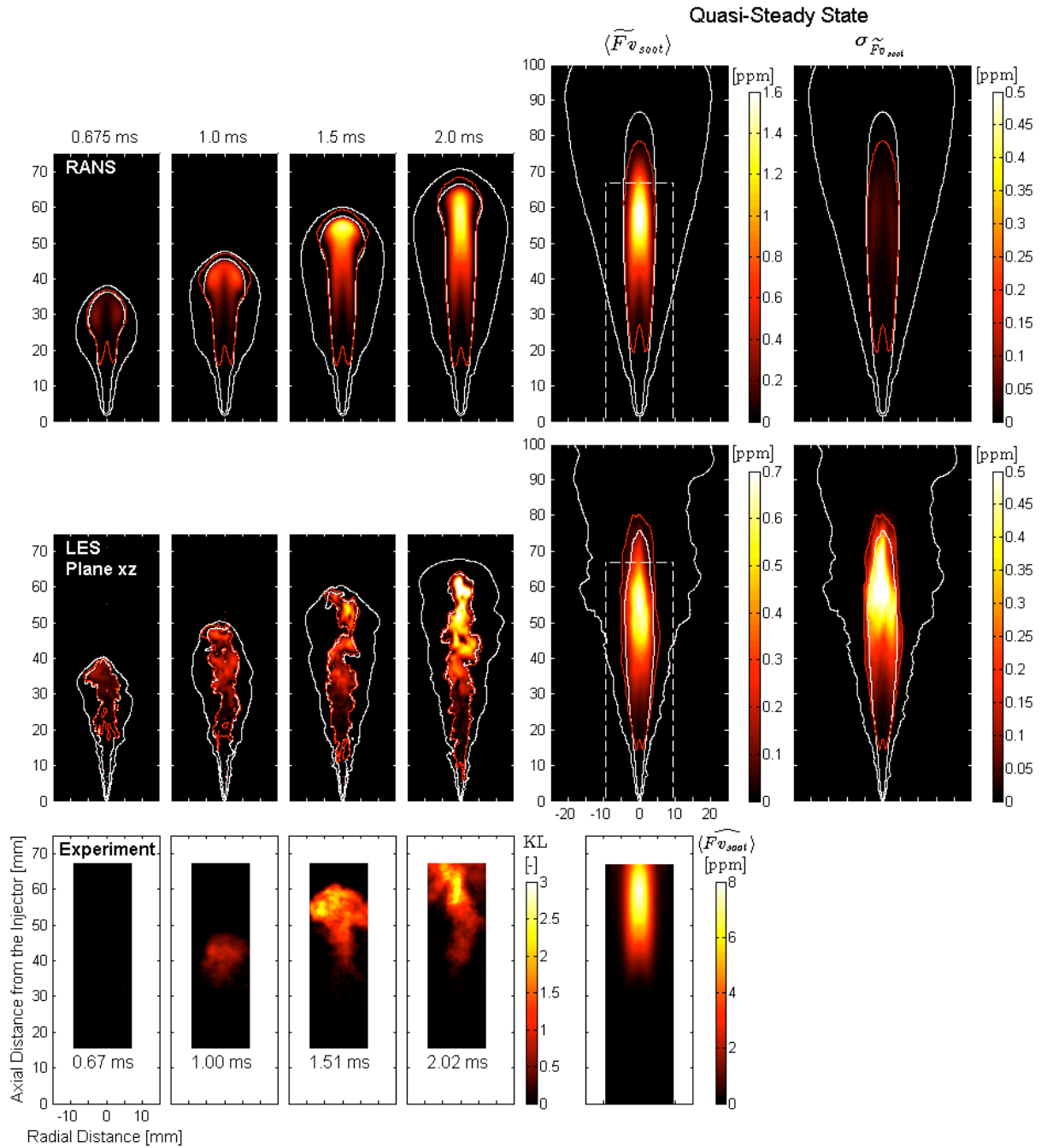
Figure 1: Instantaneous contours of soot volume fraction at four selected time instants during soot onset and time-averaged contours of soot volume fraction during the quasi-steady state for RANS (top) and LES (middle). The outer white isoline denotes the spray boundary, the inner white isoline denotes the stoichiometry and the red isoline denotes the soot cloud. Bottom: instantaneous images of soot optical thickness during soot onset and contours of soot volume fraction time-averaged over the quasi-steady state, ensemble-averaged for multiple realizations of the spray event, as measured by Sandia National Laboratories.

Sanui Ryoko / Tokyo Institute of Technology

Electron Microscopic Visualization of Soot Bridge Formation and Configuration Analysis of Diesel Particulate Filter

The initiation of the soot accumulation process inside a diesel particulate filter (DPF) is an important study topic, not only for lower filter pressure drop and high filtration efficiency during the soot trapping process but also for achieving a perfect soot oxidation strongly affected by the geometry of the soot inside the filter.

In the first part of this study, time-lapse images of soot deposition on a surface of SiC grains composing the DPF at the soot particle scale were captured using a field-emission scanning electron microscope (FE-SEM). This FE-SEM time-lapse visualization of the cross-sectional and surface views of the DPF wall showed that the dendrite structures grew perpendicularly to the SiC surface obstructing the porous flow channel as shown in Figure 1, and then finally bridged the porous channel at a certain depth. Once the bridge, acting as a filter made of soot, was obstructing the porous channel, all the soot introduced into the pore was trapped on the bridge, thereby filling the upstream pore (referred to as a surface pore). While soot accumulated in the surface pores, the pressure drop increased drastically before uniform cake filtration started on the DPF wall top surface.

Therefore, in the second part of this study, we investigate the factors governing the site of bridge formation, which determines the soot penetration depth. Porosity distribution and tortuosity of two different DPFs were investigated by using X-ray CT scan data, and pore size distribution was measured using a mercury porosity meter. The visualization indicates that the soot bridge formation tends to occur at the contracted flow area between the SiC grains. The configuration analysis shows that the abundance ratio of such a contracted flow area strongly depends on the grain size of SiC composing the DPF and the porosity distribution near the wall surface from 100 % on the top surface to the mean porosity inside the bulk.

In the final part of this study, we investigated the effect of porosity distribution through microscopic observation and pressure drop measurements during the soot accumulation inside the DPF. We accumulated soot on both the DPF sample having uniform porosity in the depth direction and the usual DPF sample having the porosity distribution near the wall surface. For the uniform porosity DPF, the soot penetration depth was shallower and the pressure drop increase was smaller for the soot accumulation in the surface pores. This is because fewer bridge formation sites exist in the area where the porosity is larger than the bulk porosity.
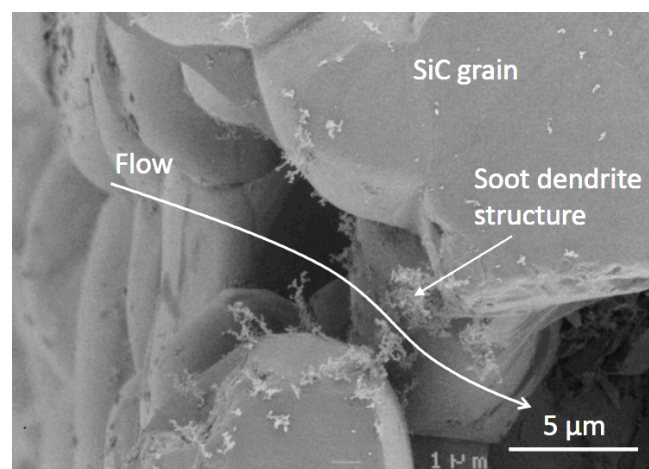

Figure 1. Bridge structure obstructing the porous channel of the DPF

Sattler Michael / Ökozentrum Langenbruck Switzerland

Determination of particulate matter emissions from solid biomass fuel burning appliances and boilers – Proposal for a common European test method

The 20/20/20 target for Europe, i.e. to decrease the emissions of greenhouse gases by 20 % and to increase the use of renewable energy to 20% by the year 2020, will lead to an increased use of biomass combustion, e.g. using wood logs and wood pellets. On the other hand, the Air Quality Directive (2008/50/EC) lies down stringent requirements on maximum levels of particulate matter (PM) in the ambient air. Solid fuel burning appliances and boilers produce particulate matter emissions (PME) which are of concern to authorities and the public. The soot and organic components of these emissions are of most concern because they include compounds known for their potential impact on human health and the environment. Some organic gaseous carbons (OGC) in the flue gas are precursors for secondary organic aerosols (SOA) formed in the atmosphere due to photo-oxidation under the influence of UV-radiation.

Many different methods have historically been used to measure PME from the flue gas of solid fuelled residential appliances and boilers. Confusion has arisen in the market as different and conflicting results have been quoted in manufacturers' literature. It became important to agree on a method applicable for all types of residential appliances and boilers burning solid fuels. This method shall give repeatable results that are of a guaranteed traceable accuracy, and by this means give the consumer reliable information on the suitability of a particular appliance or boiler.

In January 2012 the joint European Co-normative Research Project Common European method for the determination of particulate matter emissions of solid fuel burning appliances and boilers (EN-PME-TEST) started. Its aim was to develop and validate a common European test method to determine particle matter emissions from residential heating appliances and boilers burning solid fuels. The project group is a well balanced consortium of research and test establishments comprising some 18 partners from 10 European countries, coordinated by INERIS, France.

Following the work performed during the project, within the different methods tested, one was selected by the consortium to be proposed, as candidate for standardisation. It is based on well-known measurement techniques. It consists of the collection of the solid PME fraction using a heated filter and probe and the measurement of OGC using a FID analyzer. PME and OGC sampling gas trains are kept at the identical temperature of 180°. For the definition of the method, the parameters that have influence on the measurement result, such as temperature control have particularly been tested. The uncertainty of the method has been determined thanks to two inter-comparisons on real sources (pellet boiler and wood log stove) performed during the project. The paper proposed here will present:
- the different steps of the project that lead to the selection of the candidate method;
- a detailed description of the candidate method;
- the characteristics of the methods in terms repeatability, reproducibility;
- the perspectives and coming steps concerning dissemination of the method and standardisation.

Saukko Erkka / Pegasor Oy, Finland

Dynamic cutpoint switching of nanoparticle detector for improved aerosol characterization

The output signal of aerosol nanoparticle detectors based on diffusion charging is typically the active surface area of the aerosol sample, or with limited accuracy, the lung deposited surface area (Rostedt et al., 2014, Järvinen et al. 2015) The more recognized parameters, particle number concentration and mass concentration, require some knowledge of the particle size distribution. This can be achieved with size selective particle trapping at different cutpoints with electrical or diffusive means, for example (Amanatidis et al. 2015, Fierz et al. 2011).

The particle charging probability –weighed median size is derived based on calibration from the signal level ratio at different stages of the trap. This size estimate can then be used to increase the accuracy of the converted number or mass concentrations. However, for wide size range instruments predefined cutpoints may be prone to noise and error. Especially, unknown shape of the size distribution may yield significant errors, when the median size deviates considerably from the predetermined cutpoint.

We present a method to sustain optimal or near-optimal signal ratio between the signals while having a wide particle size range available for the size correction calculation.

The method relies on a diffusion charger and a zeroth order electrostatic classifier, with dynamically adjustable trap voltage, providing variable cutpoint for the classifier. The total signal is read using a low cutpoint at low voltage (reference), and subsequent signal measurement with higher, adjustable trap voltage. The adjustable trap voltage is continuously controlled so that the current signal is 50% of the reference signal. This cutpoint voltage then corresponds to the charging –weighted median particle size. As the particle size distribution typically changes more slowly than the concentration, the method works while the cycle is faster than the timescale changes of the measured aerosol.

As a result the cutpoint is kept in in optimal value in varied particle-size range, while obtaining estimate of the median particle size and thus improve particle number and mass measurement accuracy.

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Schindler Wolfgang / AVL List Graz

Black Carbon: Shades of Gray

"Soot" particles in the atmosphere have been recognized as a substantial factor contributing to global warming. "Soot" is a weakly defined expression for particles mainly generated in combustion processes. Its main constituents are organic carbon (OC) and elemental carbon (EC). The latter has a high absorption coefficient for visible and Infrared "light", while OC contributes to the scattering of light ant therefore to the albedo. The highly variable structure of EC, often expressed as the grade of "graphitization", results in a varying optical absorption coefficient, which influences the specific warming effect.

We have investigated the relation between the specific optical absorption and the thermal properties of the EC fraction of "soot" particles. The specific optical absorption was determined from the eBC / EC ratio, where eBC mass [1] was measured by a calibrated photoacoustic analyzer. The EC (and OC) mass was measured with the widely used Sunset Labs OC/EC analyzer. This instrument analyzes the thermal properties of carbonaceous materials, i.e. the evolved CO_2 as a function of temperature in an inert (for OC) and an oxidizing (for EC) atmosphere according to e.g. the NIOSH 5040 protocol. The particles were generated in a CAST propane burner. The fuel and oxidation air were varied such that the generated particles always consisted of more than 50% EC, but showed a substantial variation in the optical and thermal properties of their EC fraction.

The eBC / EC ratio of the analyzed particles was found to range from 0.5 to 1. Low absorption coefficients, corresponding to a low eBC / EC ratio, were associated with lower temperatures of the peak concentration and broader peaks for the evolved CO_2 in the oxidizing atmosphere. Thus, a qualitative relation between the optical and thermal properties of EC has been found as expected, but a robust determination of optical properties from the thermal profile of the evolved CO_2 could not be established. Further investigations are encouraged.

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         Atmos. Chem. Phys. Discuss. **13** (2013), 9485

Schmatloch Volker / DBFZ Deutsches Biomasseforschungszentrum Germany

Small Wood fired Appliances - Emission Reduction by combined Methods

Today small wood fired heating appliances such as stoves or fireplaces are known to con-tribute significantly to the PM10 concentration in ambient air of many industrialized countries. Besides PM10 also emissions of CO and unburnt hydrocarbons may be an issue.
Since these appliances are manually fed by batches of wood and rely on natural chimney draught the operating conditions in the field may vary significantly between different installa-tions. The user handles the fueling and refueling, selects the quality of wood and usually op-erates the controls for ignition and refueling. Therefore the user has a big influence on the proper operation.
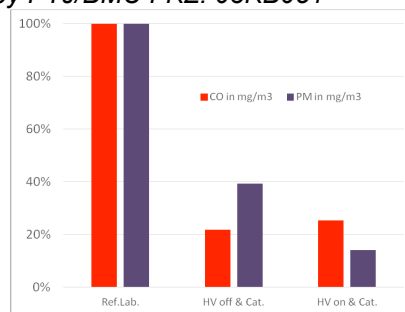This paper reports of a study that aimed at addressing the problems mentioned above by combining several approaches to improve the operation of wood fired fireplaces. For this purpose a standard fireplace insert was equipped with an automatic combustion air control, an electrostatic precipitator and a catalyst. The latter two components remove pollutants from the flue gas while the automatic combustion air control reduces the possibilities of errors by the user and at the same time helps to avoid operating conditions that might be harmful to the other two components.
In order to evaluate the efficiency of the methods reference measurements with the unmodi-fied fireplace insert were performed at the laboratory. These results were taken as reference for measurements that were carried out with two inserts installed in the living room of houses under realistic conditions. The inserts were of the same standard type but equipped with dif-ferent components that also were optimized during the study.
Gravimetric particle measurements were done based on the VDI 2066 method. In the field additionally a portable gravimetric measurement system SM96 was used. Specific measure-ments were performed by particle counting (CPC) or a scanning mobility particle sizer (SMPS).
Measurements were repeatedly performed over the course of three years. This way some information on long term behavior of the insert is provided. The final configuration during the study the insert was close to a setup that was ready for practical use and commercialization. In this configuration reduction of CO emissions compared to the reference value of the labor-atory of more than 70% could be achieved while the particle emission could be reduced by more than 80%. The results show that the approach of combining several technical methods can be integrated in commercially available wood fired appliances and can achieve signifi-cant reduction of emissions.

Measurements with the final configuration of automatic combustion air control, electrostatic precipitator and built-in catalyst; reference measured at laboratory with unmodified fireplace insert.

Setyan Ari / EMPA Switzerland

Emission measurement of airborne pollutants in two municipal solid waste incineration plants in Switzerland

A field campaign has been performed in two municipal solid waste incineration plants in Switzerland. The aim was to measure particles at different locations of the abatement system and those released from the stacks into the atmosphere, in order to assess the efficiency of the abatement system and the environmental impact of these plants.

During this study, we measured the particle number concentration with a condensation particle counter (CPC), and the size distribution with a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer (APS). We also sampled particles on filters for subsequent analyses of the morphology, size and elemental composition with a scanning electron microscope coupled to an energy dispersive X-ray spectroscope (SEM/EDX), and of water soluble anions by ion chromatography (IC). Finally, volatile organic compounds (VOCs) were sampled on adsorbing cartridges and analyzed by gas chromatography/mass spectrometry (GC/MS), and a portable gas analyzer was used to monitor NO_x, SO_2, CO, CO_2, and O_2.

Both incineration plants were equipped with an electrostatic precipitator, a DeNOx system based on the selective catalytic reduction (SCR) technology, and a bag-house filter. Measurements after the electrostatic precipitator were performed in two conditions, with the precipitator running and stopped. 90% of particles larger than 1 μm and 80% of submicron particles were removed when the electrostatic precipitator was running. In addition to that, one of the incineration plants had a wet scrubber for the abatement of particles, but this system removed only 25% of the particles. Then, the DeNOx system removed up to 97% of the nitrogen oxides, but the use of a catalyst increased the particle concentration by a factor of 3 during this step (from 5'000 to 15'000 #/cm^3). Finally, the two incineration plants had bag-house filters at the end of their abatement system. The filters had a significant effect in the abatement of particles, given that the particle concentration dropped from 15'000 #/cm^3 before the filter down to 50-300 #/cm^3 in the stack. However, the total volume of air released by the stacks into the atmosphere was very large (> 150'000 m^3/hour), suggesting that the impact of these incineration plants on the environment is not negligible.

Sharma Pooja / Indian Institute of Science, India

Heteroatomic Nanostructures of Jet Fuel Soluble Macromolecular Oxidatively Reactive Species (SMORS)

Introduction:
Aviation fuel, Jet A is a middle distillate fuel prone to thermal oxidative instabilities that results in the formation of deposits undesirable for gas turbine engine operation. Thermal stressing of Jet A produces heteroatomic deposits primarily as a result of fuel free radicals (FFRs) such as $R^•$, $H^•$, $ROO^•$, $OH^•$ oxidation reactions. Soluble macromolecular oxidatively reactive species (SMORS) are deposit precursors with molecular weight more than 350 Da and contain polar heteroatomic fuel components N, O and S. SMORS are generated primarily as a result of peroxy radical chain reactions in the autoxidation and transition regime (150 to 400 ^{0}C). Objective of this study is to investigate the composition, morphology and possible alternative reaction mechanisms of SMORS and fuel deposits formation. It is imperative to understand the fuel thermal oxidative properties of alternative aviation fuels such as blends of biomass derived and kerosene type fuels with more additives and relatively higher heteroatomic content.

Methods:
Jet A was thermally stressed during static tests at 190 ^{0}C for 6 hours without oxygen sparge. Analysis of thermally stressed Jet A deposits revealed their unit nanostructures and heteroatomic components. Spectroscopic methods used to analyze Jet A were mass spectrometry with electrospray ionization source (ESI-MS), Fourier transform infrared attenuated total reflection (FTIR-ATR) and 13C nuclear magnetic resonance (NMR). Microscopic analysis was conducted with transmission electron microscope (TEM) and scanning electron microscope (SEM) with energy dispersive x-ray spectroscopy (EDS).

Results:
 • ESI-MS has recorded jet fuel SMORS in the molecular weight range 350 to 1000 Da. FTIR and 13 C NMR spectra revealed additional alkoxy species in the thermally stressed fuel.
TEM and SEM-EDS show deposits composed of heteroatomic nanospheres of 10 to 30 nm and their micron size agglomerates.

 • Noticeably, amount of deposits formed are a function of fuel sample volume. Fuel solids generated in higher volume fuel sample i.e., 125 ml are less than 50 ml for same experimental conditions suggesting more deposition in the compact combustion systems and heat exchanger.

• Jet fuel deposit's nanoparticles and their spherical agglomerates show morphological similarities with soot which suggest investigating similar reaction pathways for deposition without oxygen in longer static tests. Although SMORS are generated in liquid phase and low temperature in contrast with soot produced in gas phase primarily by hydrogen abstraction carbon addition (HACA) and oxidative pyrolysis at higher temperatures, both are made of similar fuel components. Fuel composition contributes in the SMORS and soot formation. SMORS contain heteroatoms substituted cyclic and aromatic compounds such as quinones, pyrroles, quinolines and polynuclear aromatic hydrocarbons (PAH). Aromatics and cyclic compounds are prone to dehydrogenation during pyrolysis. Increased residence time even in the autoxidation regime during longer static tests is similar to indirect fuel heating while storage and routing. It is important to emphasize that heteroatomic fuel components are present in trace levels in kerosene type fuels such as Jet A and their contribution as deposit precursors both qualitatively and on the quantity of deposition should be further investigated and are next steps in this study.

Shaygani Afshin / Sharif University of Technology Tehran

Electrode Interface Design for High-accuracy Size Distribution Measurement of Aerosol Nanoparticles using Electrical Mobility Spectrometer Integrated with Triplet Charger

Application of nanoparticles classification and measurement is ubiquitous in scientific and industrial fields such as combustion and environmental studies, emission control, and nanotechnology. Accurate size distribution measurement of a wide spectrum of polydisperse nanoparticles up to one micrometer is quite challenging by a single apparatus. On the left side of the size spectrum, Brownian motions of ions and ultrafine particles (as background noise and diffusion broadening effect), and on the right side, multiple charging phenomena or non-uniformity of charge distributions (as uncertainties) account for this difficulty. The present study employs Computational Fluid Dynamics (CFD) simulations of Electrical Mobility Spectrometer (EMS) integrated with a corona charger, and particle tracking method in the entire spectrum, to map regions in the classifying section of the instrument targeted by particles with the highest probabilities. This gives the signals (charges) which can be potentially transferred to electrometers by particles, through landing on the detectors connected to the electrometers. In a traditional EMS, detectors are identical electrode rings placed sequentially in the classifying section. Configuration of the detectors has direct impact on the transfer matrix of the instrument and therefore accuracy of the measurements. The transfer matrix contains a vector signal for every monodisperse diameter in the spectrum, given by the set of electrodes. Any size distribution can be reconstructed by a linear combination of these vectors. This work bridges the gap between data interpretations (signal processing part) and uncertainties dictated by physics through Brownian motions and non-uniformity of charge distributions; Feeding CFD results into Genetic Algorithm (GA), optimal configuration of electrodes (called interface) is found, corresponding to the transfer matrix with the highest rank and entropy. According to Shannon's information theory, this matrix transfers maximum information possible, about size distributions of injected particles. It is shown that utilizing a triplet charger (with three different charging conditions) can add more information to the system, and lead to more accurate measurements if well-chosen electrode interface is embodied. Incorporating the electrode interface, not only helps for gaining more accurate measurements, but reduces computational costs of data interpretations, as well.

Shaygani Afshin / Sharif University of Technology Tehran

Outfitted Electrical Mobility Spectrometer with Spatial Coded Aperture Mask for Accurate Size Distribution Measurement of Aerosol Nanoparticles

Coded-aperture masks are spatial or temporal patterns, incorporated in detection of high-energy radiations, molecular spectroscopy and regular photography. Role of the masks is to improve throughput and signal to noise ratio, by means of encoding the extra information made by patterns, into the injected stream of particles or photons. This study introduces another application of the coded masks in Electrical Mobility Spectrometers (EMSs), to improve accuracy of size distribution measurements of aerosol nanoparticles. In a typical EMS, charged particles are classified according to their electrical mobilities in the classifying section of the instrument. This section contains two concentric cylinders with high electric potential difference. Charged particles travel in-between, and due to mass to charge ratio, land on the detectors and transfer their charges. Detectors are identical electrode rings placed sequentially along the axial direction on the outer cylinder. In this study, instead of one cylinder, two eccentric cylinders with different sizes were used inside the outer cylinder to add another component to the electric force influencing the charged particles. Instead of electrode rings, different configuration of detectors was used on the outer cylinder to report angular variations of data, as well. Since aerosol inlet is a narrow ring with relatively large radios, resolution of angular data reported by detectors is much lower than axial data, because angular variation of starting points of injected particles makes the landing points deviated with a great extent. The problem was solved by implementing a one-dimensional coded aperture mask in the aerosol inlet and encoding the starting points in angular direction. To study the effect of coded aperture mask on the accuracy of size distribution measurements, the proposed EMS integrated with a corona charger was simulated using Computational Fluid Dynamics (CFD). Tracking particles inside the classifier, gave the signals (charges) transferred by particles, upon which an appropriate configuration of detectors was obtained. The setup with coded mask led to a transfer matrix with higher entropy and rank, by which more information about the size distribution of injected particles can be transferred. The transfer matrix contains a vector signal for every monodisperse diameter in the size spectrum, given by the set of detectors. Any size distribution can be reconstructed by a linear combination of these vectors. A matrix with higher rank and entropy has more linearly independent rows and columns and leads to more accurate measurements. Furthermore, encoding also helped for eliminating background noise, caused by propagation and diffusion of unwanted ions (generated in the charger) through the classifier.

Singh Gaurav / Indian Institute of Technology

Health Risk Assessment for Carcinogenic and non Carcinogenic Trace Elements in Ambient Fine Aerosol over New Nelhi, India

Background: Fine aerosol ($PM_{2.5}$, particles less than or equal to 2.5µm) remain in the air for days or weeks, traveling up to hundreds of kilometres are important for sever health effect including respiratory illness (asthma), cardiovascular problem and lung cancer. Fine aerosol range from nm to µm in size and is complex mixture of toxic compounds such as heavy metals, ionic species and combustion generated elemental carbon and organic carbon. The trace metal such as Ni, Cr, As, Pb and Cd can be potential carcinogenic or non-carcinogenic and can cause chronic effect to the receptor. These fine particles after inhalation can travel deep into the respiratory system up to the aleveor region of lungs causing serious health hazards.

Investigation Methods:

Ambient Aerosol Sampling: The present study characterizes the $PM_{2.5}$ (March 2013 to August 2014) samples collected over IIT Delhi campus, an area of residential and commercial settlement in India. The $PM_{2.5}$ concentration in winter, summer and monsoon season are 198 ± 106 µg/m^3, 91 ± 74 µg/m^3 and 95± 10 µg/m^3 respectively.

Chemical Characterization: A detailed chemical constitutes in terms of carbonaceous aerosol like elemental carbon (EC), organic carbon (OC) using TOT analyzer, Ionic species (i.e. Cl-, NO^{3-}, SO_4^{2-}, NH^{4+}, Na^+, K^+, Mg^{2+}, Ca^{2+}) with ion chromatography and elements (Mg, Al, Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Mo, Cd, In, Sn, Sb, Ba and Pb) by X-ray fluorescence (XRF) will be analysed.

Health Risk Analysis: The carcinogenic and non-carcinogenic risk due to exposure of trace elements i.e. Ni, Cr, As, Pb and Cd, and $PM_{2.5}$ will be determine using unit risks reported in literature with the help of 4 step risk assessment process.

Results and conclusions: This study will provide the life time carcinogenic and non-carcinogenic risk of specific trace metal to the healthy individuals. In adition to this, cumulative cancer risk will also be estimate. The exceedance factor is also be presented as daily risk frequency distribution plot.

Sippula Olli / University of Eastern Finland

Primary and secondary organic aerosol emissions from a gasoline engine and small-scale wood combustion: First results with the new photochemical emissions aging reactor

Combustion processes are the major anthropogenic sources of particulate and gaseous pollutants, causing significant environmental and health effects. One of the main challenges for the assessment of the effects of combustion emissions is their constant transformation in the atmosphere, due to photochemical aging reactions. Traditionally atmospheric reactions of various biogenic and anthropogenic emissions have been studied in laboratory chamber setups. More recently different flow tube reactors have been developed to achieve a wider degree of oxidant exposure times and a continuous aging process. In this work, a recently developed photochemical emission aging flow tube reactor (PEAR) was applied to simulate the atmospheric aging of a gasoline engine and different wood-log fired stoves as a continuous process.

The reactor is constructed from stainless steel tube (Ø 34 cm) which has four 254 nm UV lamps assembled at the inner walls. The lamps are surrounded by quartz glass tubes, which are flushed with cooling air. Ozone and water vapour are added into the reactor to produce OH radicals via photolytic decomposition of O_3 similar to Kang et al (2007). The OH exposure times were estimated by measuring D9-butanol gas decay with proton transfer reaction mass spectrometry (PTR) during the experiments. Ozone concentration and lamp intensities were varied to achieve the desired OH exposure times. The engine applied for the experiments was AUDI 1.8 TSI which was operated with two different gasoline-ethanol fuel mixes (E5 and E85). Both the New European Driving Cycle (NEDC) and selected steady state conditions were used. The wood stoves were representing modern technology of both heat storing and non-heat storing appliances. The stoves were operated with spruce and beech logs.

The combustion emissions were first diluted and then introduced to the tube reactor. Downstream the tube reactor the aerosols were sampled to the aerosol measurement in-struments, including AMS (Aerodyne), SMPS (TSI) and Aethalometer (Magee Scientific).

With all processes the photochemical aging clearly increased organic aerosol emissi-ons. In gasoline engine experiments (Figure 1), it was observed that the carbon oxidation state of the aerosols, estimated according to Kroll et al. (2011), increased with OH-exposure in E5 fuel case, while there was no clear effect for the E85 fuel case. Wood combustion primary emissions exhibited relatively high oxidation states which were further increased during the aging process up to a value of 1.5.
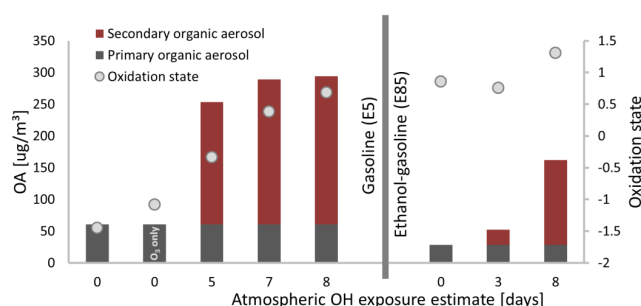

Figure 1. Primary and secondary organic aerosol emissions and the carbon oxidation state of the organic aerosols in gasoline engine emissions of two different fuel blends.

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Sjöblom Jonas / Chalmers University, Gothenburg

Particulate emissions from aromatic containing fuels

Background:
PM emissions are increasingly important, especially for marine applications. Aromatic fuel is known to increase PM emissions, but preliminary tests of drop-in aromatics in a marine diesel engine resulted in lower PM emissions. The objective was to investigate the interplay between fuel properties and the engine operations in order to try to explain the lowered PM emissions

Investigation Methods:
A single cylinder diesel engine was used with different fuel mixtures. Standard low Sulphur diesel and an aromatic fuel mixture (Caromax-28) at two levels (20% and 30%) was used in combination with ignition improver to adjust the cetane number. In total five different fuels were prepared. The engine was run at load points selected from a stationary driving cycle. In order to further investigate the effect of combustion and fuels on PM emissions, variations in rail pressure and EGR was made.
The PM emissions were sampled from the exhaust pipe using a dilution system (Fine particle sampler 4000, Dekati) and supplementary NOx measurements to derive dilution factors. The extracted flow was also passed through a thermodenuder to reduce the volatile components of the PM emissions. A DMS500 (from Cambustion) was used to record the particle size distributions.

Results:
When comparing the different fuels without ignition improver, the lowered emissions could be explained by the increased degree of pre-mixed combustion (lower cetane number) as expected.
When comparing the rate of heat release (RoHR) for the fuels with same cetane number, the RoHR curves were very similar. This means that the cylinder-global phenomena were very similar between the different fuels. However, the PM emissions for aromatic containing fuels were constantly lower and the reason was assigned to the local phenomena of soot formation not visible on the RoHR (measuring cylinder-global phenomena, including soot oxidation).
The PM emissions were very sensitive to EGR levels and the experiments without EGR were more informative for the comparison of the different fuels. When decreasing the rail pressure (keeping CA50 constant), the RoHR shifted as expected and also the PM emissions. Higher rail pressure gave lower PM emissions in accumulation mode. At high rail pressures, the accumulation mode particles became sufficiently low that small (10nm) nucleation mode particles became dominant in the particle size distribution. The aromatic containing fuels gave lower PM emissions at all investigated operating conditions. The reasons are at this point still not conclusive, since a number of different factors co-vary in the present investigation (fuel density related to spray breakup, local equivalence ratio related to the carbon-oxygen balance at the flame front), and future investigations are needed to completely understand the findings.

Conclusions
By using ignition improver, the RoHR analysis showed very similar combustion (cylinder global phenomena) for the different fuels containing varying amounts of aromatics. This indicates that differences are due to local phenomena in the flame front. By changing the operating conditions outside the certification conditions (here: no EGR) the comparison was improved and aided the direction for future work

Sjögren Staffan / University of Applied Sciences Northwestern Switzerland

Development of a photothermal interferometer for aerosol absorption measurements

Introduction

Aerosol in the atmosphere has health, visibility and climate effects. The aerosol absorption is mainly influenced by the black carbon part of the aerosol. Background air often has an absorption coefficient lower than 1 Mm^{-1}. Current commercial monitoring instrumentation uses predominantly filter substrates for collecting aerosol during measurements (e.g. Aethalometer), which require corrections. We aim to develop a robust field-deployable instrument using photothermal interferometry (PTI), which measures aerosol absorption in situ, in the air, directly (Moosmüller et al., 2009). This allows for a measurement with better accuracy.

Methods

Our PTI prototype consists of a folded Michelson interferometer. The aerosol absorption is measured in one interferometer arm due to the heating of the particles as they are exposed to pulses of light with a certain wavelength (currently green light at 532 nm, diode laser, cw 0.5 W, duty cycle 50%). The heat is transferred to the surrounding air, changing its refractive index. This change is measured with the interferometer (HeNe laser, 5 mW), i.e. as the phase shift ($\Delta\Phi$) between the reference arm and the arm with the aerosol and pulsed light in a measurement chamber. The resolution (determined by the noise) of the interferometer is about $\Delta\Phi$ = 1 μrad (at 1-minute time resolution).

Results

The prototype was tested with NO_2 (1 ppm, 3% accuracy, in synthetic air 5.0, Messer gases, Switzerland) and a typical result is shown in Figure 1. NO_2 has a well-known molecular absorption cross section of $1.42x10^{-19}$ cm^2 $molecule^{-1}$ which corresponds to an absorption coefficient of 345 Mm^{-1} at 25°C, 1000 mbar and 1 ppm). Soot from a Palas soot generator (model GFG 1000) was similarly detected. Further the prototype was tested with ammonium sulphate (scattering only) and no signal was detected, confirming that non-absorbing aerosol do not generate a signal in PTI instruments. Our current prototype has a detection limit of about 35 Mm^{-1}.
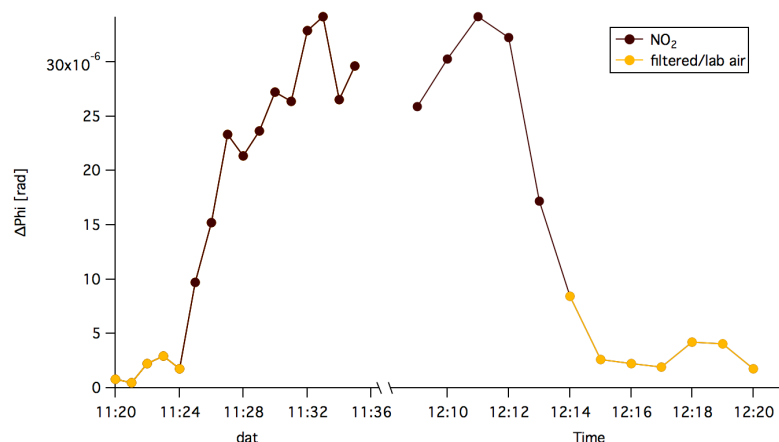

Figure 1. Typical measurement of 1 ppm NO_2 with the photothermal interferometer prototype.

Conclusions

A photothermal interferometer has been tested. Advantages of the setup are its stability (quadrature point and easy interferometer adjustment during setup) and that the instrument is based on OEM components, readily available. Work is currently underway to develop the prototype to become less prone to external vibrations using shock-absorbing materials. The sensitivity will be further improved by using other pump light sources.

The interferometer absorption measurement allows comparison and validation with aethalometer-type instruments. This results in a better accuracy of aerosol absorption measurements.

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Soroudi Bazzaz Amir / Combustion Chamber Group, Tehran

LES of Soot Evolution during Biofuel Spray Combustion and Gasification

Biomass-derived fuels are gaining worldwide attention due to dwindling of conventional fossil fuel sources and environmental concerns such as greenhouse gases and air pollutant emissions. Several studies have proved that liquid fuels are (and will be) the fuel of choice in the transportation sector. Biofuels could technically substitute oil in all transport modes, with existing power train technologies and existing re-fuelling infrastructures. On the other hand, gasification of slurry fuels in entrained flow gasifiers is widely used for industrial purposes and is proposed as a vital step in the development of forthcoming Biomass-to-Liquid (BtL) Plants. Soot formation is a major problem to face with in both of these processes, i.e. biofueled combustion engines of transportation sector and bioslurry-fueled gasification reactors of BtL Plants. Soot is formed in almost every hydrocarbon-fueled combustion and gasification system as a pollutant emission. Although soot chemistry has been studied extensively over decades, some of the primary mechanisms in soot formation, growth, and oxidation are uncertain. Controlling soot emissions will require focused efforts to understand soot formation and oxidation under a variety of combustion and gasification conditions. The main purpose of this work is to provide new insights into the soot evolution during combustion and gasification of bio(slurry)-fuel spray in a generic injector using large eddy simulation (LES) tool. LES is a mathematical model for turbulence used in computational fluid dynamics (CFD) that is growing and is currently applied for many engineering applications. LES applies a low-pass filter on the Navier-Stokes equations to reduce the range of length scales to solve and thus the computational cost. The large scales of the flow field are resolved, allowing better fidelity than traditional approaches such as Reynolds-averaged Navier-Stokes (RANS), whereas the smallest scales are modeled rather than solved as direct numerical simulation (DNS) does, which makes the computational cost for practical engineering applications attainable using supercomputers. Simulation of multiphase flow field of sooting spray flame in gasification/combustion mode has been performed using an Eulerian-Lagrangian Approach. For each type of fuel, an appropriate chemical/physical surrogate has been proposed and a semi-detailed chemistry is used in the gas phase. Soot production is described by a single reaction based on C_2H_2 species concentration and heterogeneous soot oxidation reactions. A detailed investigation have been performed to study the effects of fuel type and operating conditions on the soot evolution in biofuel spray gasification and combustion processes.

Spielvogel Jürgen / TSI Germany

CEN/TS 16976 – Harmonizing number concentration measurements of ultrafine particles in atmospheric aerosol

Drastically lower particle emissions from the tailpipe due to modern engine technologies and efficient aftertreatment (e.g. DPFs) have led to monitoring particle number (PN) in addition to monitoring the mass of particles collected on a filter (PM). The Particulate Measurement Programme (PMP) introduced PN measurements with a condensation particle counter (CPC) that resulted in amendments to UNECE Regulation No. 83. Since September 2011, the Euro 5B standard requires a PN limit of 6×10^{11} particles /km for type approval of all new light-duty diesel vehicles, the first PN legislation implemented by the European Union [1]. With the continued input of the VERT association, Switzerland recently pioneered using portable PN instruments for periodic control of off-road construction machinery [2].

On the other hand ambient air quality monitoring following the Directive 2008/50/EC focused on PM_{10} and $PM_{2.5}$ measurements. Standards such as DIN EN 12341 and stringent equivalence criteria ensure high data quality with reduced uncertainties so that data can be compared and limit values be observed.

Lately, it's been realized that ultrafine particles (UFPs) can impact human health and our climate, yet contribute very little to the mass of atmospheric particles. In order to assess their impact and provide guidance in future air quality regulations it is therefore necessary to supplement gravimetric air quality measurements with a time resolved measurement of PN concentration.

In order to harmonize continuous measurements of UFPs in the atmosphere, the European Committee for Standardization (CEN) drafted Technical Specification CEN/TS 16976 [3] which defines a set of requirements for the condensation particle counter (CPC), its sampling system, the measurement procedure and the reporting of measurement results. This Technical Specification is currently under review and expected to be released in summer of 2016.

TSI Incorporated just released a new CPC (model 3772-CEN) and dedicated sampling system, both of which are fully compliant with the proposed CEN/TS 16976. This CPC brings the same technology that the engine exhaust CPCs use around the world to atmospheric monitoring. It measures UFPs from 7 nm (d_{50}, see figure 1) up to concentrations of 50,000 particles/cm^3 and features a pulse height analyzer that monitors wick health, supersaturation state, and instrument status.

We will present detailed information on the proposed CEN/TS 16976 and show data from the characterization and calibration of the first compliant CPCs by the World Calibration Centre for Aerosol Physics, Leibniz Institute for Tropospheric Research (TROPOS).
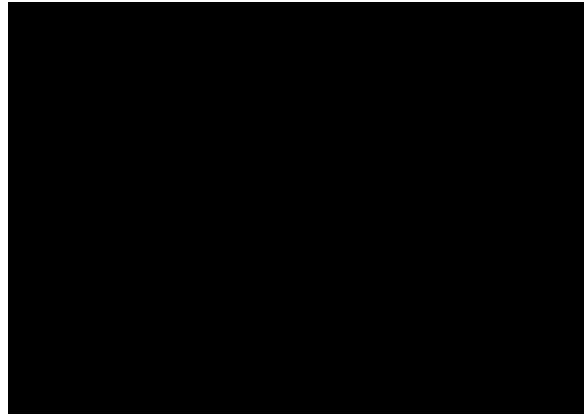
Figure 1: Counting efficiency of the 3772-CEN CPC for silver particles generated by the evaporation/condensation method (courtesy of TROPOS, Leipzig)

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[3] CEN/TS 16976. Ambient air - Determination of the particle number concentration of atmospheric aerosol

Tanda Stefan / University of Graz, Austria

Size-resolved element distribution in airborne (nano)particles

In urban areas, outdoor air pollution is one of the major concerns, possessing the single largest environmental health risk in Europe today [1]. One of the main air pollutants affecting air quality in cities is particulate matter (PM). It is a complex mixture of very small particles and liquid droplets originating from various natural and anthropogenic sources. On a global scale the main sources of $PM_{2.5}$ in urban environments are traffic (25 %), industrial activities (15 %), domestic fuel burning (20 %), various other anthropogenic sources (22 %) and natural dust and salt (18 %) [2].

The size of particles is directly linked to their potential for causing health problems, since ultrafine particles (< 100 nm) can deposit in all regions of the respiratory tract, while larger particles are retained in the upper parts of our respiratory tract. Numerous studies have linked the exposure to PM to a variety of adverse health effects, such as increased respiratory symptoms, decreased lung function, asthma and even premature deaths in people with heart and lung disease. Since toxicity is related to particle size and source, it seems obvious to determine the chemical composition of airborne particles broken down by size classes.

Therefore, we started to collect particulate matter in different urban environments using the electrical low pressure impactor ELPI®+. After microwave-assisted acid digestion and determination of element content using inductively coupled plasma mass spectrometry, we are able to determine distribution patterns for different elements in the particle size range from 6 nm to 10 µm. ELPI®+ provides us additionally with real-time particle size distribution and concentration in this particle size range.

First results already show different distribution patterns for analyzed elements indicating different particle sources (e.g. Figure 1). These findings are in good accordance with the few publications available, dealing with this type of measurements [3,4].

Future investigations should clarify if distribution patterns are source dependent, which would provide us with an excellent tool for source assignment of anthropogenic and geogenic mobilized elements.
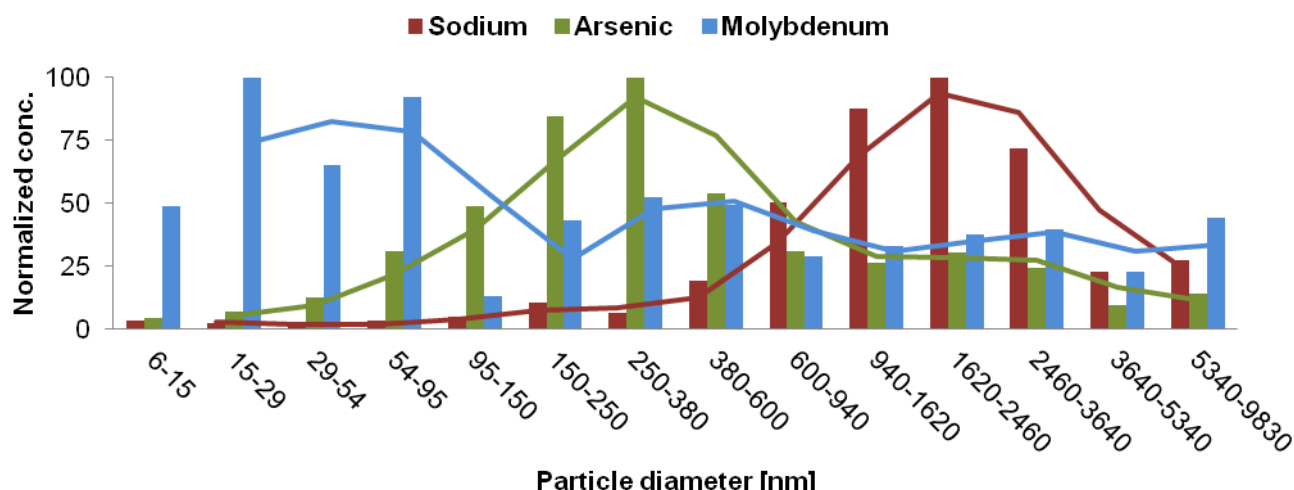

Figure 1 Element distribution (Na, As, Mo) in airborne particulate matter from intersection Kotlářská street and Kounicova street, Brno

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Thiruvengadam Pragalath / West Virginia University USA

Determination of a Preconditioning Protocol to Stabilize NOx and PN emissions for Euro 6 Engine Certification

The purpose of this study is to understand and determine the preconditioning protocol for Euro 6 engine certification in order to obtain repeatable NOx and particle number emissions results, specifically for engines equipped with DPF and SCR after-treatment systems. With Euro-VI (Euro 6) emissions limits being phased in by 2016, more and more engines are being certified under these standards. The emissions limits defined in Euro 6 regulations are comparable to US-EPA 2010 emissions standards with the additional introduction of particle number (PN) emissions limits to the regulations. This adds complexity to the engine testing and certification process. Although current model year diesel engines are equipped with catalyzed diesel particulate filters (DPF) that have a filtration efficiency of 95% to 99% by mass on an average over an entire particle size distribution, the particle number-based filtration efficiency of a catalyzed DPF can be as low as 50% after regeneration and up to 80% efficient in filtering with significant soot loading. In addition to this, engine parameters such as exhaust temperatures, DPF soot load, as well as exhaust flow rates adds an extra dimension to the problem of obtaining repeatable PN results.

The study was conducted on an MY2016 ISX 15 Liter engine equipped with a de-greened DOC-DPF-SCR after-treatment system in a CVS test cell at Cummins Technical Center, Columbus, Indiana. Although UN ECE's R49 document regulates the use of a newly manufactured engine with a run-in time of up to 125 hours, this study made use of an engine and after-treatment system that had over 125 hours of operation on it prior to the study. Moreover, three distinct engine calibrations were developed with varying levels of engine-out NOx (EO-NOx) emissions in order to simulate the effect of different engine technology packages and calibration strategies on the after-treatment system. The engine was exercised over 10 repeats of the World Harmonized Transient Cycles (WHTC) followed by 3 repeats of World Harmonized Steady-state Cycles (WHSC) with a 20 min soak in between tests for the three different EO-NOx engine calibrations where the Moderate EO-NOx calibration met 2010 EPA emissions standards. The scope of this study is to obtain a generic engine preconditioning cycle or procedure specifically for engines tested for emissions compliance in the CVS test cells under Euro 6 regulations to obtain repeatable NOx and PN results. Also, a MY2008, 6.4L Power Stroke diesel V-8 equipped with a DOC-DPF aftertreatment system was tested WVU-CAFEE's EERL engine test cell with an in-use DPF as well as a new de-greened DPF with less than 140hrs of operation. The engine was exercised over a custom designed soot loading cycle. The work done at WVU aims to understand the effects of aftertreatment age on stability of PN emissions from catalyzed DPFs.

Results obtained from this study show that the moving average and standard deviations from consecutive tests show that 3 preconditioning cycles are required to stabilize brake-specific NOx and PN emissions for the three different EO-NOx levels. The effect of the type of duty cycle used for preconditioning and the age of after treatment was not found to be significant.

Toro Huertas Eliana / District Secretariat of environment – Bogotá

Study of Personal exposure to nanoparticles considering meteorological variables in 4 roads with different types of vehicles in Bogotá

One of the strategies to improve the air quality in Bogotá, Colombia, is led by Secretaría Distrital de Ambiente (District Secretariat of Environment) with the DPF retrofit program to Euro II and Euro III buses in the integrated system of transport, which is in their implementation stage. As a first step, it was done a study of personal exposure to Nano-particles to serve as a baseline of the DPF retrofit program focused on the Bus Rapid Transit BRT system of Bogota, Transmilenio. The study considered the personal exposure inside the Buses in a length of 5.48 km in the principal road of the system, this road has two flow directions with an exclusive lane for BRT, and a mixed lane where principally passenger cars drive away it. For the measurements, a diffusion counter device DISCmini has been used to determine the concentration and the modal diameter of the particles, analyzed using descriptive statistical analysis as well as hypotheses test to made comparison between the flow directions on the road, locations of the engine in the bus and emission standards of the buses. The measurement campaign was conducted between September 28 and November 6, 2015, from 11:00 to 13:00 for the two directions of the traffic considering a sample of 83 buses. The results shows the level of concentration is different according to the direction of the road, a median value near to 230.000 pt / cm3 for the North-South direction, in contrast, 172.000 pt / cm3 for the South-North direction. Furthermore, the standard emission and the position of the engines in the chassis of buses were evaluated, finding the average concentration and the dispersion of data decrease when the technology engine emission increases. Therefore, there are nano-particle concentrations 30% lower inside Euro V buses compared to Euro II buses, although there are in the same magnitude order. Also, the interquartile ranges of concentrations for buses with this technology were 50% lower. In the same way, higher concentrations were found when the engine is at the front of the bus, about 20% bigger than those vehicles with engines in the rear of the chassis, the dispersion of the data in those cases were similar (detailed graphs are shown below). In comparison between international researches, local concentrations are 4 times above European cities [Knibbs, et al., 2011; Kumar et al., 2014; Klompmaker et al., 2015; Weichenthal et al., 2014; Ragettli et al., 2013; Hasegawa et al., 2004].
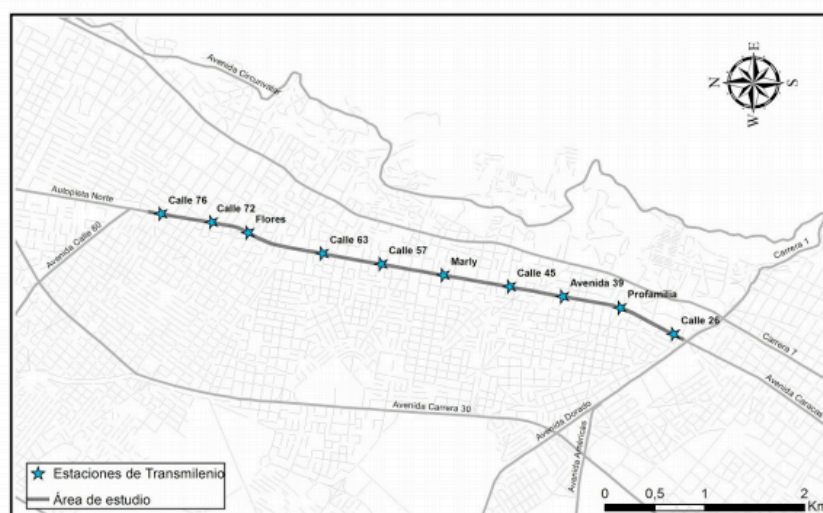

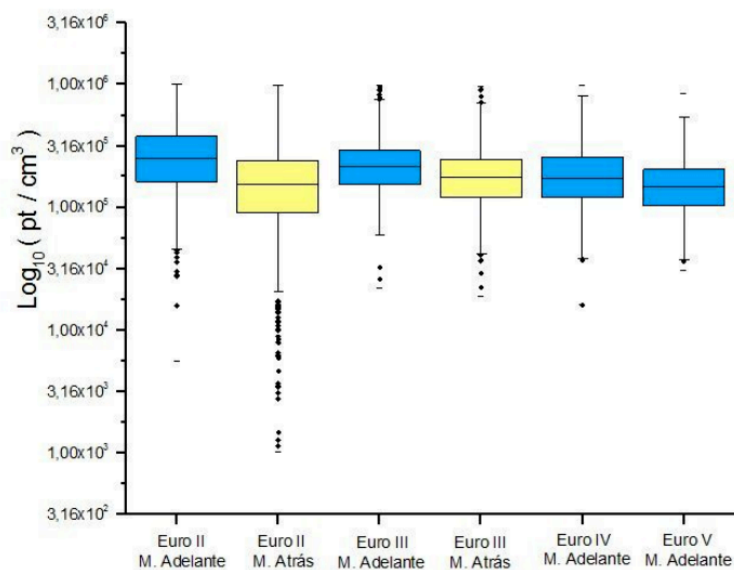**Figura 1.** Mapa del área de estudio.

Figura 7. Diagramas de cajas y bigotes de los datos logarítmicos de la Avenida Caracas, junto con las respectivas tecnologías de los vehículos que transitan por esa área en relación con la posición del motor.
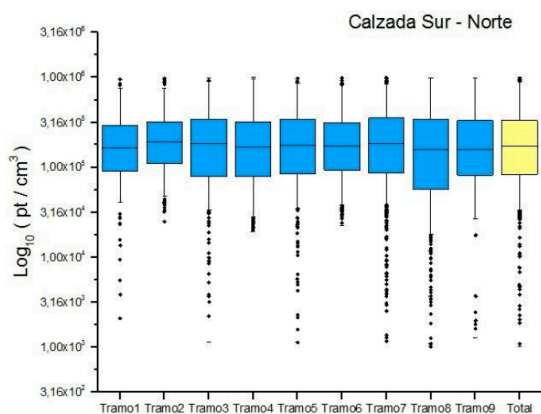

Figura 3. Diagramas de cajas y bigotes de los datos logarítmicos de la calzada sur - norte, junto con los respectivos tramos del trayecto.
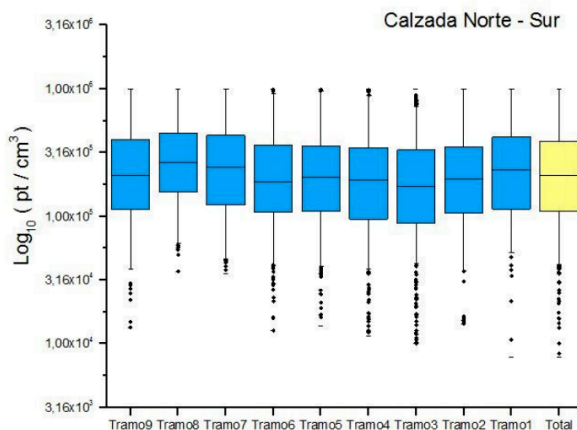

Figura 4. Diagramas de cajas y bigotes de los datos logarítmicos de la calzada norte - sur, junto con los respectivos tramos del trayecto.

Vanhanen Joonas / Airmodus Finland

Spark discharge as a calibration source for particle detectors in the sub 5 nm size range

Growing concern over nanoparticle emissions of combustion engines emphasizes the need for accurate, repeatable and comparable aerosol particle measurements over a wide size range. Emission regulations (UN-ECE Regulation 83) do not cover the smallest particles emitted by e.g. direct injection gasoline (P. Karjalainen, et al. 2014) and natural gas engines (J. Alanen et al. 2015). Both new measurement technology and calibration methods are needed. In this work aerosol particle detector capable of measuring particles down to molecular sizes (the Airmodus A11 nano Condensation Nucleus Counter nCNC) was calibrated using an aerosol generator based on electrode atomization by spark ablation (Meuller et al 2012), developed by VSParticle. The main benefits of spark ablation are a high production rate of particles of almost any desired size range and the possibility to easily change the electrode material and thus the composition of the generated particles. Both copper and silver electrodes were used to produce particles in the 1-5 nm size range. Nitrogen (grade 5.0) was used as a carrier gas to avoid contaminants. Particles were size selected with a high resolution differential mobility analyzer (Half mini by SEADM; de la Mora et al. 2013) and detected with an aerosol electrometer and A11 nCNC. The DMA was calibrated using tetra-heptyl ammonium bromide (Ude and de la Mora, 2005) and the resolving power for mobility diameter of the DMA was measured to be 37.

Figure 1 presents the aerosol size distribution of negatively charged particles from just below 1 nm up to 5 nm for copper electrodes, and figure 2 for positively charged particles for silver electrodes. There is a distinct mode of particles at around 1.0 to 1.5 nm detected with both electrometer and nCNC for both copper and silver particles. From both figures the detection efficiency of the A11 nCNC can be calculated. For both cases the nCNC was used with the same settings and 50% cut-off diameter of 1.68 and 1.66 nm for positive silver and negative copper particles was estimated.

The spark discharge generator had a stable concentration output throughout the whole measurement period for the studied particle sizes and thus was proven very suitable for calibration of an nCNC.
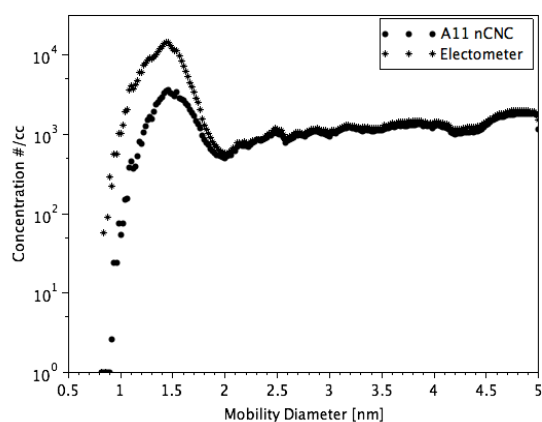

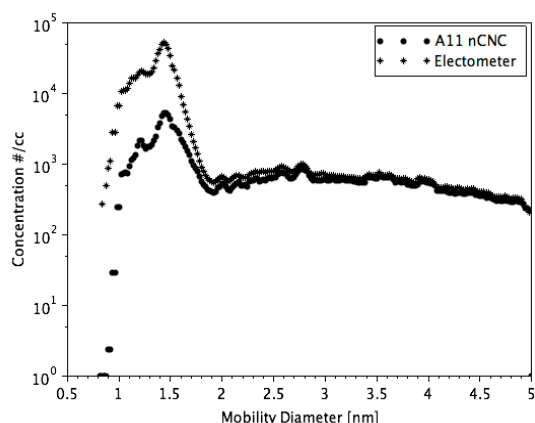Figure 1. The particle size distribution of negatively charged copper particles.

Figure 2. The particle size distribution of positively charged silver particles.

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Volz Florian / Kutzner + Weber, Maisach, Germany

Deposition of particulate matter on the surface of foam bubbles

As part of a project funded by ZIM (Central Innovation Programme for SMEs), Kutzner + Weber conducted tests for separating particulate matter from wood firing on the surfaces of foam bubbles. The Clausthal University of Technology supported us and through tests was able to confirm some theoretical approaches for the fundamental mechanisms.

At Kutzner + Weber tests were conducted using the real flue gasses from a wood chip furnace and the filtration efficiency was measured using raw gas and clean gas measurements according to VDI 2066. While it was not yet possible to reach the desired filtration efficiency in the test facility, the results of the basic principles from Clausthal University revealed the reasons for this and at the same time show the great potential of foam columns for the filtration of fine dust.

The tests with a foam column prototype with different kinds of surfactants showed that the main filtration mechanism for the particles is diffusion and therefore sufficiently long dwell times are required for medium sized bubbles. While the size of the bubbles can be reduced to about 1-2 mm by using fine nozzles, the desired size of about 0.2 mm cannot be achieved. In order to create extremely small foam bubbles further tests were conducted in a cylindrical foam column prototype, reducing the bubble size using an agitator. These tests have been promising.

This method is interesting because, as shown above, the primary bubbles can be created with large nozzles, and therefore little pressure loss, and are only broken down afterwards through agitation with virtually no pressure loss. However, this means that it is necessary to create foam that is stable for a sufficiently long period of time and yet breaks down. The ideal solution would be foam with a adjustable "durability" which can only be achieved by optimizing the surfactant properties and the stress on the foam within the device. Another special challenge is the agitator shaft, because in the case of fine foams there can be a bubble breach (bypassing of the actual foam layer) which leads to correspondingly bad particle separation.

Experiments with a rectangular prototype have shown good filtration efficiency even with large bubbles. However, the dwell times have to be relatively long for this and therefore large flue gas volumes require correspondingly large designs for the separator.

Reducing the size of the bubbles with smaller nozzles would cause a pressure loss that is no longer manageable. This means that a reduction of the bubbles' size using the above mentioned stirring technology (e.g. a combination of needle and slotted blade agitator) seems most useful. In the simple foam columns described above, a filtration efficiency of up to 90% could be achieved. Using the results from these tests for a specific design of the device can lead to even higher filtration efficiency.

The test devices and the results are demonstrated with corresponding graphics and would be illustrated on a poster with explanations.

Wahl Claus / German Aerospace Center

Comparing Particle Emissions of a EURO 6 Plug-In Hybrid Passenger Car and a EU-RO6 Diesel Car

This poster presents some results of a measurement project of vehicles with different power-train technologies fulfilling EURO 6 norm. The focus of the study is the analysis of exhaust emissions from vehicles under different conditions. The measurements have been taken on a four-engine all-wheel roller dynamometer with climate control. Several driving cycles have been analyzed to detect the influence of traffic situations (urban, suburban and motorway) on the vehicle emissions. The influence of temperature is studied by performing the measurements at 23 °C and 0 °C and by comparing the emissions of both hot and cold starts. Apart from exhaust emissions, the data of the onboard diagnostics (OBD) has been logged in order to monitor various vehicle parameters like revolutions per minute, catalyst temperature etc.

Two of the tested vehicles are a EURO 6 plug-in hybrid vehicle with a direct injection gasoline engine (1.4 l engine, 150 kW system performance) and a conventional EURO 6 diesel car (2.0 l, 110 kW).

The particle measurements setup was a heated stainless steel sampling line, followed by Dekati diluters and an EEPS system. All the relevant gaseous species like CO2, CO, NO, NO2, UHC's are measured by an FT-IR.
The driving cycles used for both cars are the WLTC (World Harmonized Light Vehicles Test Cycle) and ERMES (European Research on Mobile Emission Sources).
The gasoline and the diesel was certified test fuel with known C/H value and known heat of combustion.

Due to the random engine on-off in the plug-in hybrid vehicle, we decided to calculate emission indices (EI in mg/kg burned fuel) instead of mg/km. (In aviation, all emissions of aircraft engines are given as EI in mg/kg burned fuel.)

As result we plot EI's [mass, #, NOx....] vs driving-cycle-time for the two cars. Finally we compare the EI's of the two cars and the EI's of flight gas turbines.

Wang Fenjuan / Politecnico di Milano

Black carbon and aerosol optical property measurement at a midsize city in Po valley, Italy

Background

Particles in atmosphere effect human health and climate change, and black carbon (BC) is recognized to responsible for global warming (IPCC, 2013). Piacenza is one of those midsize cities exposure in the European air pollution hot-spot Po Valley with density particle pollution sources.

Methods

During the UPUPA measurement campaign in Piacenza in September 2011, black carbon was measured by A Multi Angle Absorption Photometer (MAAP 5012), an Aethalometer AE31 and a Micro Aethalometer AE51 and the inter-comparisons were conducted. Optical columnar properties of aerosols were also measured by Ocean Optics S2000 radiometer. Aerosol Optical Depth (AOD), Angstrom extinction parameter (alpha) and size distributions were analyzed to investigate particles optical and microphysical properties and their origin, supported by back trajectories calculation.

Results and conclusions

The BC levels and trends measured by three instruments are correlated with each other. During the measurement period BC records pronounce morning and evening peaks at rush hours. The average concentrations are 3686 ± 136 ng/m^3 by Maap, 4404 ± 166 ng/m^3 by AE31 and 4185 ± 144 ng/m^3 by AE51 during the simultaneous measurement period. For the entire analysis period (6 days) a mean value of AOD(780) nm of 0.21 ± 0.17 has been recorded with a maximum value of 0.53 ± 0.04 on 28 September and a minimum of 0.06 ± 0.02 on 20 September. Alfa recorded between a minimum of 0.70 ± 0.12 on 21 September and a maximum of 1.77 ± 0.48 on 20 September with a mean value of 1.24 ± 0.38. The mean AOD and alpha values are comparable to other studies (Calvello et al., 2010).
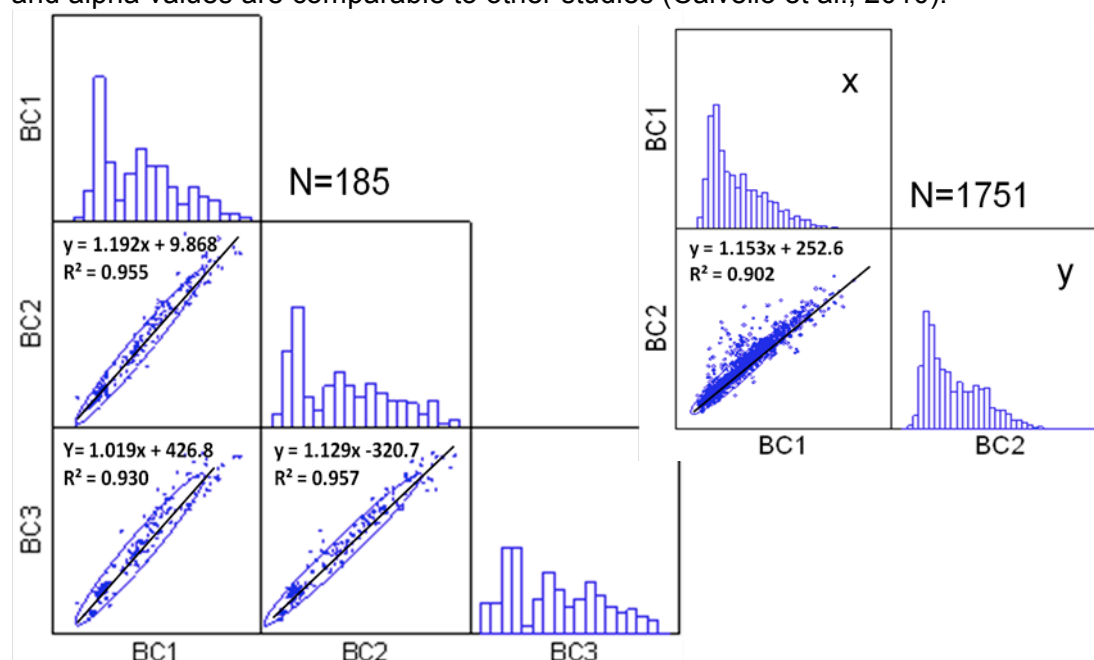

Figure 1 Relationship of BC levels by Maap (BC1), AE31(BC2), AE51(BC3)

Figure 1 presents the BC concentration distribution and a line regression for the two simutanious dataset respectively. The results show coeffecence of black carbon concentrations obtaind by three instruments are higher than 0.9. The regeration indicates that AE31 over estimated BC concentration about 10-15% compared to Maap and AE51. When the BC

concentration is lower than 1st quartile or higher than 3st quartile more difference are record-ed by Maap and AE31.
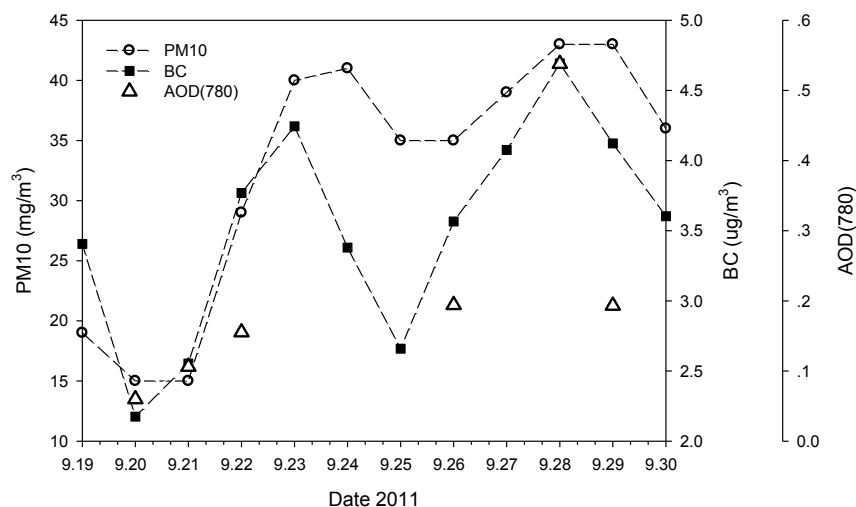

Figure 2 Temporal variations of PM10 (daily averaged surface mass concentration) columnar fine fraction particle of BC (daily averaged surface black carbon by AE31, 880nm), AOD(daily averaged columnar data) for measurements days.

In Figure 2, PM10 and BC averages are calculated over 24h, whereas for radiometer only measurements from 8:00 to 15:00 are available. During September 20, 21, lower levels of PM10, BC and AOD are observed, when the air mass was from North-West sea with high loading of water soluble ions. Maximum values correspond to air mass from East Europe with more particle loading of aged urban emissioins on September 28. This distinguish of aerosol origins has also been reflected by the relationship between AOD and alfa. Apart from local emissions, air mass origins also have detectable effect on the black carbon and particle optical properties in Piacenza.

References

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Yamada Hiroyuki / National Traffic Safety and Environment Lab., Tokyo

Correlations of Particle Mass and Particle Number with PMP Method

Particles from Diesel and gasoline direct injection (DI) engines have been evaluated by filter weighing method (PM) and PMP number counting method (PN) simultaneously. PM from diesel vehicles with diesel particulate filter (DPF) were well below European regulation limit of 6×10^{11} /km. And the results exhibited almost no correlation against PM. It is because high impact of tunnel blank PM. On the other hand, PN from gasoline DI are slightly higher than 6×10^{11} /km exhibiting good correlation against PM. According to the correlation of gasoline DI vehicles, PN of 6×10^{11} /km can be regarded as PM of 0.3 mg/km. Considering that PM regulation limit in Europe is 4.5 mg/km, particles from passenger cars in Europe already have been regulated by PN and the limit is 0.3 mg/km of PM. This limit is stricter than future limit in US of 1 mg/mi.

Zauli Sajani Stefano / ARPAE Italy

Indoor/Outdoor Seasonal Variability of Different Particle Metrics

Background
A number of studies in the Mediterranean area1,2 showed much higher short term health effects of airborne particles during the warm season compared to the cold season. We analysed whether the seasonal variability of the different metrics of airborne particles may produce different toxicological properties.

Methods
Two 15-days monitoring campaigns were conducted in winter and summer during 2014. Measurements were performed simultaneously indoor and outdoor in an uninhabited apartment in the city of Modena (Italy). The city is located in one of the most urbanized, industrialized and polluted areas of Europe. Measurements included size distribution, mass and chemical composition of PM2.5 (metals, ions, organic and elemental carbon). Air Exchange Rate were measured in both seasons in open windows conditions as well with closed windows. We simulated the typical behaviour of elderly people in regulating natural ventilation based on the data collected on an hourly basis in a previous survey.

Results
We found much higher daily mean Air Exchange Rates during the warm compared to cold season (2.7 vs 0.8 h-1, ratio 3.4). I/O ratios were higher in summer for both PM2.5 (0.92 vs 0,51 ratio1.8) and UFP (1 vs 0.59 ratio 1.7). Relevant differences in the shape of the size distributions were found between warm and cold season with a higher relative contribution of nanoparticles (diameter <50 nm) to total number of particles during the warm season. A relevant reduction of particle concentration during the winter season was found for all particle sizes. The relative weight of the chemical components showed also relevant seasonal differences. Indoor concentrations of nitrates during the cold season were much lower than outdoor (I/O ratio 0.26 compared to 0.73 during the summer season). During the cold season indoor particles show a higher contribution of total carbon and nitrates and a lower contribution of sulfates, ammonium and metals. The highest ratio between season specific (cold/warm) average concentrations was found for nitrates (7.17 for the indoor data and 20.45 for the outdoor data).

Conclusions
We found relevant differences between seasons in the I/O relationships of various physical and chemical characteristics of particulate matter. Air Exchange Rates seasonal differences are not capable to entirely explain the seasonal variability of the health effects.

References
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2)   Biggeri A, Bellini P, Terracini B. Meta-analysis of the Italian Studies on Short-term Effects of Air Pollution – MISA 1996-2002. Epidemiol Prev 2004; 28(4-5): S1-100.

Zauli Sajani Stefano / ARPAE Italy

3D Variability of Different Particle Metrics in Urban Areas: Findings from the "Supersito" Project in Bologna (Italy)

Background
The study aims at assessing the 3D spatial variability of various particle metrics within urban areas and the potential for misclassification in epidemiological studies.

Methods
Several monitoring campaigns were conducted in different sites and seasons during the period 2012-2015. Measurements included size distribution, mass and chemical composition of PM2.5. Chemical speciation was carried out in terms of a number of metals and ions, and organic and elemental carbon. The measurement activities were conducted in the city of Bologna (Italy), located in one of the most urbanized, industrialized and polluted areas of Europe. Gravimetric and optical monitors were used for PM2.5 mass. Size distributions were provided by spectrometers (FMPS-TSI). Monitoring sites included high and low traffic areas, front and back of buildings placed near busy streets, and high rise building with measurements at different floors. Some measurements were also performed in terms of NO2 and BTEX.

Results
A comparison between high and low traffic sites showed a very little variability of PM2.5 concentrations (< 15%). On the contrary very strong variability was found in the finer fractions of the size distribution and Ultrafine Particle Concentrations (3.5 times higher concentrations at the traffic site). Measurements at the front and rear of a building which fronted onto a major urban road showed differences very similar to those found comparing high and low traffic areas. A sharp peak at 20-30 nm was found in the particle size distribution at the front site. Marked differences in relations to traffic proximity was found for some chemical species such as Elemental Carbon, Iron, Manganese and Tin. Little vertical variation was found for PM2.5 while no linear trend was found for UFP. Large vertical gradients resulted for NO2 and BTEX. During the winter season NO2 concentrations at the 16th floor were 74% lower than at ground floor. Lower vertical gradient was found during the summer season.

Conclusions
The results of the study provided the basis for a ranking of potential for exposure misclassification in epidemiological studies in relation to different particle metrics. Ultrafine and nanoparticle concentrations were especially affected by traffic proximity.

Zhou Jun / PSI Villigen Switzerland

Toxicity assessment of wood combustion emissions from different burning and aged conditions by using a reactive oxygen species (ROS) instrument

Air pollution, particularly due to particulate matter, has adverse effects on human health. An important
pathway underlying these effects is externally induced oxidative stress. Wood as a renewable and domestic source of energy does not contribute to net CO_2 emissions and is thus widely considered nowadays to decrease the dependency from fossil fuels. However, wood combustion emits a wide range of pollutants (e.g., NO_x, volatile organic compounds and particulate matter (PM)), which may, either directly or after oxidation in the atmosphere, induce oxidative stress in the lung caused by reactive oxygen species (ROS).

A modified ROS online analyzer was developed to quantify particle phase ROS in real time, using an aerosol collector coupled to a 2',7'-dichlorofluorescin (DCFH) based assay. Wood burning particles emitted under different combustion regimes and aged using different photochemical reactors (including flow tubes and smog chambers) were measured. Concomitantly, the aerosol chemical composition was quantified using an aerosol mass spectrometer in order to investigate the ROS formation mechanism.

The ROS content of these primary and aged particles was compared to primary and aged particles from other combustion sources, secondary organic aerosol (SOA) from α-pinene ozonolysis, and to ambient particles from two urban locations in Beijing (China) and Bern (Switzerland).

Results from flow tubes and smog chambers show, that aging substantially increases the ROS content of the SOA. Different aging processes didn't give significant differences when comparing smog chamber aging and flow tube aging. By comparing different combustion regimes in a pellet boiler, we found that ROS containing particles under bad burning combustion conditions (high excess of O_2) are ~ 5 times higher than under optimum burning conditions. The ROS content in SOA from wood burning emissions is slightly higher than from all other investigated sources. The results obtained from laboratory experiments will be compared and put into perspective with the ambient measurements.

Zöllner Christian / University of Bayreuth

Influence of engine operating conditions on soot loading and regeneration behavior of diesel particulate filters

The removal of particulate matter (PM) from diesel exhaust is necessary due to environmental protection and human health. To meet the strict emission standards for diesel engines of passenger cars an additional exhaust aftertreatment system is essential. Diesel particulate filters (DPF) are established devices to remove emitted PM from diesel exhaust. But the deposition and the accumulation of soot in the DPF influences the filter back pressure and therefore engine performance and fuel consumption which is why a periodical regeneration through PM oxidation is necessary. This regeneration mode can be achieved by post injection to increase the exhaust temperature and promote soot oxidation. The oxidation behavior should result in an effective regeneration mode that minimizes the fuel penalty and limits the temperature rise while maintaining a high regeneration efficiency. But the process of DPF regeneration depends on the soot characteristics which are influenced by a variety of parameters such as engine operating conditions.

The present study was carried out at the engine test-bench with a 2.1 l light-duty diesel engine. Standard DPF were soot loaded under different transient engine operating conditions until a certain specific soot mass was reached. The subsequent active regenerations of the filters were performed in an identical engine mode with 1500 rpm and 65 Nm via post injection to demonstrate and compare the implications of the different loading conditions. During soot loading and regeneration, filter pressure drop, temperature distributions inside the DPF and conditions in the exhaust pipe were recorded. Particle size distribution before and after the DPF was recorded with a Scanning Mobility Particle Sizer.

The results show the different pressure drop behaviors and temperature levels during the DPF loading with different engine modes. Consequently the temperatures inside the particulate filter show distinct differences. During the regeneration mode the decrease of the filter back pressure shows differences due to the different oxidation rates of the soot originating from varying engine modes. The temperature distribution inside the filter during soot oxidation is non-uniform with a faster temperature rise in the rear of the DPF. Figure 1 shows that different engine modes during DPF loading affect the regeneration mode regarding the pressure drop behavior and length of the oxidation as well as the peak temperature in the rear of the DPF.

To sum up, the thermal and temporal control during the DPF regeneration is difficult to handle. Thus, the development of an effective regeneration mode is important for a uniform and complete soot oxidation. But the DPF loading conditions have a crucial impact on the process of regeneration. Some of these loading conditions are pointed out in this study.
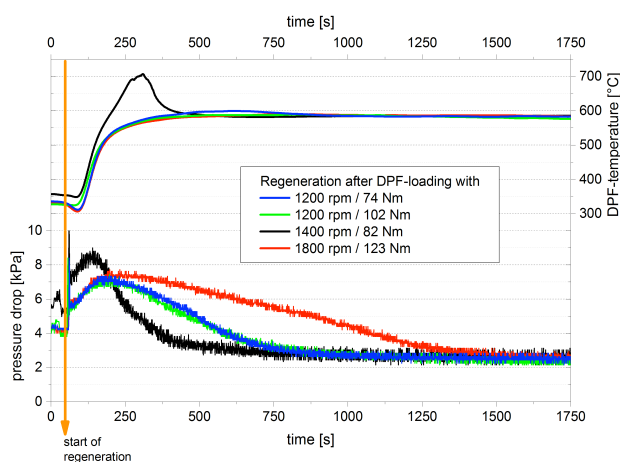

Figure 1: Pressure drop and DPF-internal temperature behavior during active regeneration with 1500 rpm and 64 Nm after loading with different engine modes

Zotter Peter / University of Lucerne, Switzerland

Wood combustion for energy in buildings

Wood is an important renewable energy source and its use is expected to increase as a substitute for non-renewable energies. However, wood combustion significantly contributes to ambient air pollution, especially with particulate matter (PM) thereby, negatively impacting human health. Consequently, there is a target conflict between air pollution and wood as a renewable energy source. Furthermore, PM in ambient air not only results from primary particles emitted at the source and accounted for by emission limit values, but is also caused by secondary organic aerosol (SOA) formed from oxidation of volatile organic compounds (VOC).

Therefore, the aim of this project is to quantify primary emissions and SOA formation from different combustion devices of both, simple technology as well as of newest technology. The experimental setup enables an on-line characterization of the flue gas (O_2, CO, CO_2, NO_x, VOC (CH_4 and NMVOC), black carbon, organic PM, particle number concentration and size distribution). SOA formation potential is investigated by the means of a potential aerosol mass (PAM) chamber wherein the photochemical ageing in the atmosphere can be simulated. In addition, reactive oxygen species (ROS) are measured to determine the oxidative potential of primary and secondary PM as a measure for PM-induced oxidative stress within the lung. To identify the influence of the combustion type and fuel characteristics tests are performed with different log and pellet stoves, log and pellet boilers as well as industrial wood chip boilers. In addition, influences of operation type, combustion phase, and particle precipitation are investigated. Consequently, this data base can be used to improve the design of combustion technologies and serves as a basis for governmental authorities to develop target-oriented air pollution strategies.

First experiments with a pellet boiler, a log wood stove with one stage combustion and a 150 kW industrial with moving grate wood chip boiler, show clearly different gas phase and primary PM emissions as well as different SOA yields. The log wood stove, especially during re-fill and operation with humid wood and the pellet boiler in bad operation (high excess or lack of combustion air) exhibits high emissions. The optimum combustion condition in the pellet boiler and the industrial wood chip boiler reveal low emissions. SOA yields are low for devices and conditions with low VOC emissions with an average SOA to primary organic aerosol ratio of 1.6 for the pellet boiler during optimum combustion conditions, while ratios of around 5 are observed for the operation with high air excess in the pellet boiler.