Abstracts Contributed Talks

24th ETH-Conference on Combustion Generated Nanoparticles

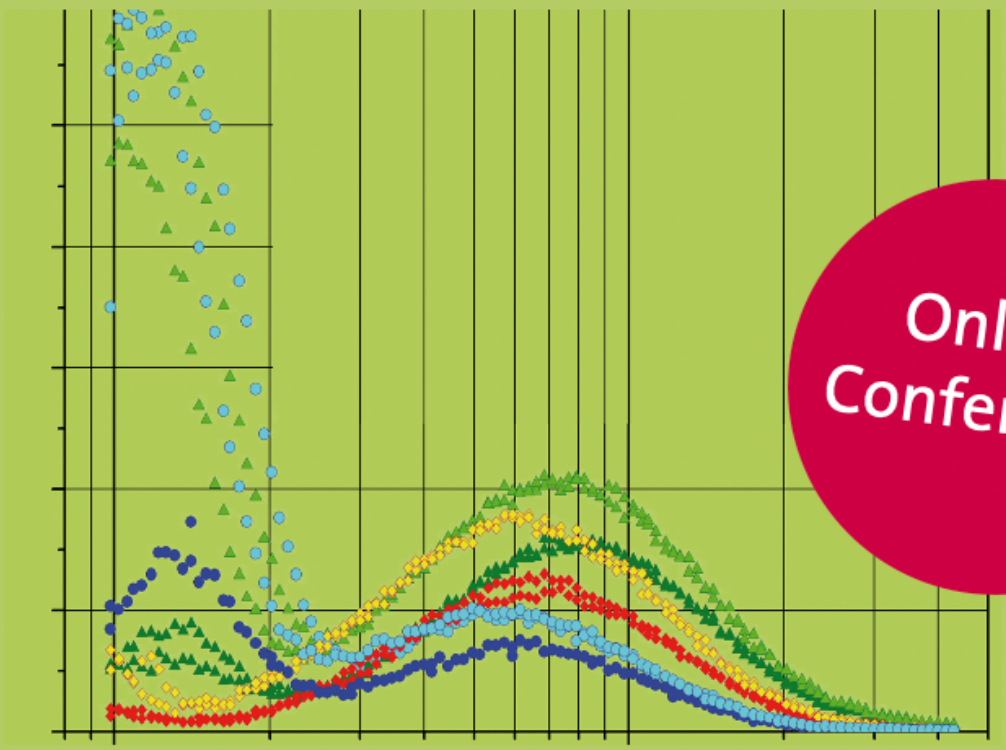
June 22 - 24, 2021, online conference

Focus Event: Combustion and Climate Change

Scope

The conference served as an interdisciplinary platform for expert discussions on all aspects of nanoparticles, freshly emitted from various sources, aged in ambient air, the impact of particles on health, environment and climate, technical mitigation and legislation. The conference briought together representatives from research, industry and legislation.

ETH zürich



Online Conference

SCS
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The Impact of Ultrafine Particles on Mental Health

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While there is robust evidence of the critical role of $PM_{2.5}$ in mental health and psychiatric disorders, much less is known about the specific role of ultrafine particle exposure. Lack of assessment of ultrafine particles (UFP) makes it difficult to attribute adverse effects specifically to this size range of particulate matter. This is despite a wealth of predominantly short term epidemiological studies indicating that some of the adverse effects of particulate matter on health are strongly mediated by UFP. The objective of this review is to summarize evidence of the role of UFP in cognitive and mental health from studies of humans and related animal models. Strategies to enhance both human and animal studies through increased collaborative interaction are also discussed. Human studies of UFP clearly indicate the potential for adverse effects on mental health. In areas where $PM_{2.5}$ concentration exceeds government standards, there are increased risks of impaired cognitive development, autism, Alzheimer's/dementia, depression, and ADHD.

Air pollution and UFP specifically may cause cognitive deficits in both early and late life. Compared to other research areas where there are often differences between the findings of clinical and animal studies, work in animal models of the effects of UFP on mental health have been consistent with, and supportive of, the epidemiological and clinical findings. The further optimization of lab related experimental studies through the expansion of naturalistic paradigms and increased direct collaboration between basic researchers and clinicians will enhance the collection of translationally relevant data. Taken together, these human and animal studies indicate that elevated concentrations of UFP air pollution have a considerable adverse impact on the brain and mental health, both in early and late life.

Secondary nanoparticles formation and composition from open and residential wood burning

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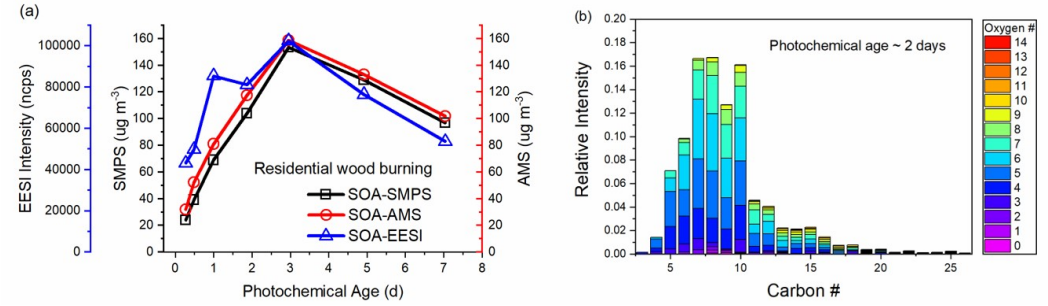
Biomass burning is one of the largest combustion-related sources of volatile organic compounds (VOCs) and nanoparticles to the atmosphere. However, the contribution of biomass burning to the regional and global secondary organic aerosol (SOA) burden is quite uncertain, limiting our understanding of its impacts on air quality, climate, and human health. One important issue related to the contribution estimating is the large uncertainty and variation of SOA yield and emission rate, especially the scarce data over long-timescale oxidation. Another issue is the lack of molecular composition and markers which can be used as references for ambient source apportionment. In this work, we studied the long-timescale oxidation of emissions from open and stove wood burning, representing wildfires and residential wood combustion, respectively. By deploying an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) [1], we also provided the molecular-level chemical composition of the formed SOA. The results of this work can largely improve our understanding of the contribution of biomass burning to the SOA burden. **Methods.** Pine and spruce wood were burned open or in a residential stove, and the burning emissions were injected into a holding chamber. Photooxidation experiments were conducted using a custom-made oxidation flow reactor (OFR) [2]. The burning emissions were introduced into the OFR from the holding chamber with a small flow. Particle size distribution was measured with a scanning mobility particle sizer (SMPS, TSI), and was used to determine the SOA mass concentration. Bulk composition and oxidation state of particles were determined using a long time-of-flight aerosol mass spectrometer (LTOF-AMS, Aerodyne). The molecular composition of particles was measured with an EESI-TOF-MS [1]. **Results.** SOA mass concentration measured by SMPS and AMS matches very well. Although EESI data has some variations, the general trend in the SOA concentration is very similar: it firstly increases and then decreases with increasing photochemical age. This indicates that fragmentation reactions might play an important role, which can be proved by the decreasing average carbon number (from 10 to 8) measured by EESI with increasing photochemical age (from 0.3 to 7 days). In addition, it is found that there is no significant difference in SOA production from open or stove burning emissions. The carbon and oxygen distributions of the formed SOA show that the majority of SOA are species with carbon number ≤12 and oxygen number ≤7. The time evolution of these species provides insights into the chemistry in the oxidation of biomass burning emissions.



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Study of soot production in ethylene pyrolysis using a sectional model

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The interest in studying nanoparticle formation from hydrocarbons oxidation and pyrolysis is twofold. On one hand, it is crucial for suppressing undesirable soot emissions that might impact the environment and human health. On the other hand, it is of interest for the developing of more efficient processes for nanoparticle synthesis. Within this context, this work aims at modeling soot production in ethylene pyrolysis using a sectional approach. To that end, the main focus is placed on the assessment of results sensitivity to the gas-phase mechanism, soot precursors and surface growth mechanism.

The consecution of the objective relies on the validation of polycyclic aromatic hydrocarbons (PAH) and major species concentration along with soot predictions. For this validation, two experimental datasets are targeted. The first dataset comprises measurements from experiments conducted in a plug flow reactor (PFR) at atmospheric pressure and low temperature (1223-1423 K) [1]. The second dataset includes time-resolved profiles from the pyrolysis of ethylene in a shock tube (ST) at high pressure (around 0.38 MPa) and high temperature (1961-2179 K) [2]. Cantera is used to solve the chemical kinetics from several gas-phase mechanisms describing ethylene pyrolysis. Implemented within the framework of Cantera, a soot sectional model (SSM) [3] is used to account for soot production. The SSM considers soot particles to be a solid and distinct dispersed phase interacting with the gas-phase through a two-way coupling.

Modeling results evidence large differences in the prediction of PAH mole fraction for the different gas-phase mechanisms evaluated for the PFR cases. These differences, in addition to the choice of soot precursors, are shown to heavily influence soot predictions. Time-resolved soot volume fraction profiles, from the ST cases, allow assessing how the soot onset time is influenced by the soot precursors choice. In relation to the sensitivity of results to the soot surface growth mechanism, both PFR and ST results point out to the importance of the carbon balance between the soot and the gas-phase to the accurate prediction of soot production. In that sense, PFR cases show a clear over-prediction of acetylene mole fraction if soot production is not accounted for.

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Surface growth, coagulation and oxidation of soot by a monodisperse population balance model

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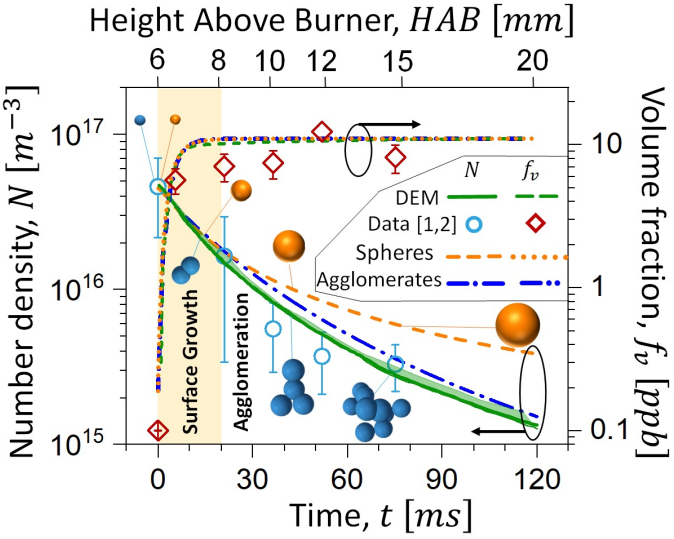
A monodisperse population balance model (MPBM) is developed here that capitalizes on the rapid attainment of the self-preserving size distribution and asymptotic fractal-like structure of agglomerates by coagulation to simulate their evolution with only three equations. Total agglomerate carbon molar, C, number (N) and area (A) concentrations are tracked. The model accounts for the polydispersity of agglomerates by enhancing their collision frequency by that of their self-preserving size distribution based on the radius of gyration in the free molecular regime. Scaling laws from detailed discrete element modeling (DEM) simulations are used to describe the fractal-like morphology of the agglomerates. The MPBM predicts the evolution of soot f_v, N and average mobility and primary particle diameters during surface growth and agglomeration in laminar premixed ethylene flames as well as soot oxidation in a tube reactor within 30% of detailed DEM, sectional population balance simulations and measurements. Thus, when self-preserving size distribution and asymptotic structure of agglomerates are attained, this simple MPBM has unprecedented accuracy and can be readily interfaced with computational fluid dynamic (CFD) to model soot formation in combustion devices or process design and optimization for the synthesis of carbonaceous agglomerate nanoparticles.



Evolution of soot volume fraction, f_v (dashed green line) and number density, N (solid green line) during agglomeration and surface growth.

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The UNREAL (Unveiling nucleation mechanism in aircraft engine exhaust and its link with fuel composition) project: Results from simulation chamber and reactor experiments

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Aviation emissions are not limited to greenhouse gases like CO_2 but include other gases as well, such as nitrogen oxides (NO_x) or sulfur oxides (SO_x) and volatile and non-volatile particulate matter (vPM and nvPM respectively). Sulfuric acid formed in the engine exhaust seems to be linked to the formation of vPM. However, the amount of sulfur present in the fuel converted to sulfuric acid in the exhaust is too small to explain the amount of vPM observed and organic species seem to play a key role in their formation [1]. The UNREAL project aims at studying at the molecular level the different mechanisms of new particle formation from the exhausts of aircraft engines fed by different fuels (Figure 1). We used a Combustion Aerosol STandard (CAST) generator especially designed to work with liquid fuel to generate the emissions from different fuels (from the standard Jet A-1 to 100% Sustainable Aviation Fuel (SAF). Total, or only gas-phase, emissions were injected in both, an atmospheric simulation chamber (CESAM) and a Potential Aerosol Mass Oxidation Flow Reactor (PAM-OFR) for aging. Both systems used in parallel provide a point of comparison between in near-real time and hours-long time chamber aging approaches. The chemical and physical evolution of primary and secondary CAST emissions, were monitored by different instruments to measure particle number, mass concentrations as well their size distribution, and the chemical composition of both, the particulate and gas phases. In addition to online techniques, samples were collected to study off line, the gas and aerosol chemical composition at molecular level by mass spectrometry.

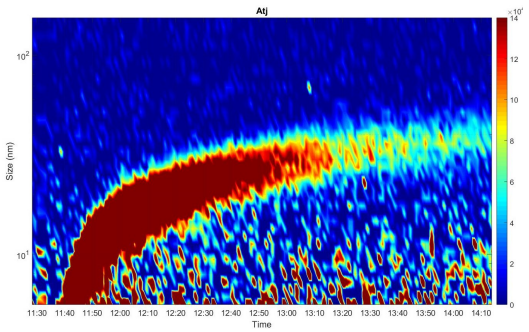

Figure 1. Nucleation event from emissions of 100 % AtJ fuel in reaction with OH radical when only gases were introduced into the atmospheric chamber.

This work benefited from the support of the project UNREAL ANR-18-CE22-0019 of the French National Research Agency (ANR).

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Health effects from combustion ultrafine particles: consistent observations from controlled human exposure studies

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The human health effects from exposure to ultrafine particles are challenging to assess. The exposure has complex spatial, temporal, multi-source and co-pollutant variables and the health indicators have multiple etiologies, besides the inter-individual variation in susceptibility. Controlled human exposure studies are a particular study design that allows investigating short-term effects from combustion particles, consisting of experiments where human volunteers agree to be intentionally exposed to pollutants, in a controlled short-term scenario, to provide information on biological changes caused by the exposure. These studies are usually performed in an exposure chamber with controlled air composition, ventilation, temperature, and humidity conditions. Particles are generated by combustion and/or concentration processes or resuspension, and forced into the chamber also allowing the control of mixtures and co-exposures. We revisited the strengths and limitations of this study design and reviewed and compared 64 controlled exposure studies following exposure of a total of 1338 healthy, non-smoking subjects to combustion-generated particles, including 12 chamber studies on wood smoke, 33 on diesel exhaust, 15 on concentrated ambient particles and 4 on indoor carbonaceous sources (candle burning, cooking and printing). Besides different combustion source and generation conditions for the same source, the studies differ by design (crossover or sequential), protocol definitions (with or without moderate physical activity), administrated doses and duration of exposure, as well as the assessed biomarkers and functional markers and methods used in the assessment. The most common markers assessed were inflammation, vascular function and lung function, with less studies focusing on neurotoxicity, arrhythmia and genotoxicity. Consistency of effects (observed in ≥75% of the studies from the same source and involving more than 50 study subjects) were observed after exposure to concentrated ambient particles (vascular function, heart rate variability, arrhythmia and oxidative stress) and diesel exhaust (airway inflammation and vascular function).

Maria Helena Guerra Andersen, Steffen Loft, Jakob Bønløkke, Anne Saber, Ulla Vogel. In *Ambient Combustion Ultrafine Particles,* **2021**, Nova Science Publishers, 205-253.

Ultra-Low PN_{10} Emissions of a Close-Coupled Emission Control System on a Heavy-duty Truck Application

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Heavy-duty vehicles represent a significant portion of road transport and they need to operate in a clean and efficient manner. Their exhaust emission control systems need to be enhanced to sustain the high conversion efficiencies seen during motorway conditions to other operating conditions.

The European Commission is developing legislative proposals for Euro 7 and Euro VII emissions regulations for light- and heavy-duty vehicles. The new Euro VII regulation will likely focus on ensuring the emissions from heavy-duty vehicles are minimized over extensive on-road operating conditions and in particular on operating conditions such as urban driving and cold start. These challenges are increased by the need to ensure low secondary emissions like PN_{10}, NH_3 and N_2O as well as low impact on CO_2 emissions.

The low pollutant emissions achieved by an AECC heavy-duty Diesel demonstrator vehicle will be presented. The vehicle is equipped with an innovative layout of state-of-the-art emission control technologies, combined with an advanced engine strategy implemented to an existing Euro VI-C long-haul truck. The new emissions control system integrates a close-coupled Diesel Oxidation Catalyst (DOC), a first Selective Catalytic system Reduction (SCR) in close-coupled position, a 2^{nd} DOC followed by a catalyzed Diesel Particulate Filter (DPF), and the 2^{nd} SCR from the dual-SCR system with twin AdBlue® dosing controlled by FEV developed software. Both SCR systems contain an Ammonia Slip Catalyst (ASC).

The presentation will focus on the sub-23 particles emissions PN_{10} measured over a broad range of operating conditions, including cold start and urban driving as well as for different payloads and ambient temperatures.

To show the potential CO_2 reduction on life cycle assessment basis, the vehicle has also been tested with a 100% renewable fuel. This, in combination with engine efficiency improvements, should enable the next generation heavy-duty vehicles to operate with ultra-low pollutant emissions, whilst maintaining their path towards the required CO_2 targets.

Impact of fuel composition on primary and secondary aeronautic emissions: gaseous and particulate chemical characterization at molecular level

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One of the actual concerns of aviation industry is to reduce its impact on climate and air quality using for example Sustainable Aviation Fuels (SAF, [1]). As part of the UNREAL Project [2], the objective of this work was to study and compare chemically, at a molecular level, gaseous and particulate phases of primary and secondary emissions from various aircraft fuels, from the standard Jet A-1 to 100 % SAF (Alcohol to Jet). Related emissions from a liquid CAST burner [3] were injected into an atmospheric chamber (CESAM), and in parallel, into a Potential Aerosol Mass Oxidation Flow Reactor (PAM-OFR) to age the emissions (OH reactivity in both cases). To collect these fresh and aged particles, a system with two quartz fiber filters was used: the Front Filter (FF) traps the particulate phase while the Back Filter (BF) is coated with activated carbon to retain the gas phase [4]. Samples were analyzed with a Two-Step Laser Mass Spectrometry (L2MS) technique to study the chemical composition of emissions, in particular Polycyclic Aromatic Compounds (PAC) and sulfur such as SO2, SO3 or H2SO4. The chemical composition of the filter-deposited samples is compared to on-line measurements performed by an Aerosol Mass Spectrometer and an Aerosol Chemical Speciation Monitor for particles, and a Proton Transfer Reaction Mass Spectrometer (PTRMS) for gaseous species. A comparison of the primary and aged emission molecular chemical fingerprints obtained, as well as between both atmospheric reactors (CESAM vs PAM-OFR), will be proposed.

This work benefited from the support of the project UNREAL ANR-18-CE22-0019 of the French National Research Agency (ANR).

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Dual particle counter for measuring simultaneously automotive exhaust solid particle number emissions larger than 10 nm and 23 nm

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>Introduction and Background

The Solid Particle Number (SPN) emissions of Light Duly (LD) vehicles are regulated in Europe since 2014. The tests are conducted by sampling diluted exhaust from a Constant Volume Sampling (CVS) system. Current legislation (UNECE R83) requires a Volatile Particle Remover (VPR) which consists of an Evaporation Tube (ET) and a Condensation Particle Counter (CPC) with a cut-off of 23 nm. The latest Amendment of the Global Technical Regulation for certifying LD vehicles specifies a catalytic stripper (CS) instead of the ET and a CPC with a cut-off of 10 nm instead of 23 nm.

Methodology

A dual line SPN system (APC xApp) was developed to allow for parallel measurements with an AVL 10 nm and an AVL 23 nm CPC. The APC xApp was employed in parallel to a system fully compliant with the UNECE R83 regulation (APC^{plus} [1]) in measurements of Gasoline Direct Injection (G-DI) LD vehicles from a CVS. The APC^{plus} employs an ET and a 23 nm AVL CPC. The vehicles were tested under the Worldwide harmonized Light vehicles Test Procedure (WLTP) and other driving protocols. The study investigates the influence of the CS on the > 23 nm, as well as the ratio of the SPN 23 to SPN 10 emissions.

Results and Conclusions

The ratio SPN 10 to SPN 23 ranged from 1.1 to 1.5, in line with already reported literature figures [2, 3]. The SPN >23 nm differences between APC^{plus} (ET) and APC xApp (CS) were found to be confined within ± 10%. The observed differences were within the measurement uncertainty (e.g. originating from calibration [1]), and showed no dependence on the ratio of 10 to 23 nm concentrations (and therefore size of emitted particles). The results verify that the use of a CS has no effect on SPN > 23 nm, in good agreement with what anticipated from the efficiency curves of the CPCs and APCs.

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Assessment of global particle number emissions from shipping and effect of scrubbers

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Globally, ship exhausts are the main source of particles over large areas in open seas and coastlined, and the particles emitted both contribute to impaired air-quality and have climatic effects. Combustion aerosols indirectly affect climate by influencing the formation of clouds and their light scattering properties. In order to accurately estimate the climate-forcing impacts of ship emissions, particle number (PN) and size distribution (PSD) of the emitted aerosols are important, further to total particle mass (PM). From 2020 onwards, ships are forbidden to burn fuel with sulphur content over 0.5%, unless they apply scrubbers for SO_2 abatement.

Particle measurements were conducted in laboratory on 1.6MW marine engine and 6 different fuels with varying properties and sulfur contents were tested ath low and high load points. In addition, measurements were conducted on-board a cruise ship, before and after scrubber, from the exhaust lines of two main engines (ME1 and ME2, applying SCR). Identical sampling setup was applied in all campaigns, consisting of a porous tube diluter together with residence time chamber and ejector diluter, which simulates atmospheric dilution conditions [1]. PN and PSDs were studied by scanning mobility particle sizer and condensation particle counters (CPC). To study the effect of scrubber on non-volatile particles, a catalytic stripper was applied. The obtained PN emission factors were compared to ship plume observations conducted on the Finnish coastline, by chasing ship plumes by aircraft. STEAM ship emission model was applied to assess the globally distributed PN emissions from international shipping and estimate the influence of the sulfur regulation.

The PN emission factors for different fuels varied between $1.38\text{-}5.83\times10^{16}$ 1/kgfuel [2]. The scrubber efficiently removed volatile particles in nucleation mode size range and reduction was larger with engine applying SCR [3]. The global PN emissions from shipping are localized close to coastal lines and busy port areas, but significant emissions exist also on open seas and oceans. The global annual PN produced by marine shipping was 1.2×10^{28} ($\pm0.34\times10^{28}$) particles in 2016, which is of same magnitude with total anthropogenic PN emissions in continental areas [4]. The potential to reduce global PN emissions from shipping depends strongly on the adopteed technology mix, and is possible with wide adoption of natural gas and scrubbers, but no significant decrease is expected if heavy fuel oil is mainly replaced by low sulfur residual fuels.

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Solid and volatile brake-wear nanoparticles under real-world operating conditions

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Recent studies have identified brake-wear as the major contributor to road transport Particulate Matter (PM) emissions, as a result of an efficient implementation of exhaust PM regulation worldwide. Accordingly, there has been a growing interest in the characterization of brake-wear emissions over the last years. In an attempt to establish a standardized test procedure that would facilitate comparison of results from different studies, the United Nations Particle Measurement Programme Informal Working Group (PMP IWG) has been actively working on the development of a harmonized brake-dynamometer methodology, including a novel test cycle (WLTP-Brake).

In this study we have applied the proposed PMP IWG methodology for the characterization of particulate emissions of the same brake system on two different dilution tunnels. The two tunnels were designed to operate at different flowrates (170 to 270 m^3/h compared to 300 to 1800 m^3/h). The brake system was tested under the WLTP-Brake cycle but also under another real-world brake cycle derived within the Lowbrasys European research project from analysis of the Los Angeles City Traffic (3h-LACT). The effect of bending procedure on particle emissions was also evaluated through dedicated tests in which the last and more demanding section of the WLTP-Brake was employed for the conditioning of the brake.

Particulate measurements included $PM_{2.5}$, PM_{10} as well as particle number (PN) following the recently introduced exhaust PN methodology that extended the detector cut-off size to 10 nm. Measurements also included real time size distributions and number concentrations of thermally untreated samples. Disc temperature profiles were investigated with a thermographic camera and an array of thermocouples embedded on the brake disc.

Both PM_{10} and $PM_{2.5}$ emissions were found to agree within 20% at the two facilities, despite the vastly different operating flows of the tunnels. Similarly, no statistically significant effect of the cycle could be identified on the PM emissions despite the nearly two times higher average disc temperatures over the LACT cycle (~110°C compared to 60°C over the WLTP). Most of the airborne PM was larger than 2.5 µm, with the ratio of PM10 to PM2.5 raging between 3.5 and 4.

Elevated concentrations of nanosized particles, thermally stable at a catalyst operating at 350°C, were released over the WLTP-Brake, under specific burnishing procedure. Their nature and formation pathways are currently unclear. Volatile nanoparticles were observed over the 3h-LACT cycle but only at the high tunnel flow. Their relative concentration decreased with increasing tunnel flow. This behavior is in accordance to nucleation theory since increased tunnel flows imply increased dilution of vapor precursors and potentially reduced release of vapors through more efficient cooling of the brake disc.

Evaluating the performance of a particle counting sensor based on continuous-wave laser-induced incandescence

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Introduction & Background:

We investigate the influencing factors for the performance of an optical particle sensor based on the principle of continuous-wave laser-induced incandescence (cw LII). The sensor's main target is the determination of the number concentrations for soot particles with a detection limit regarding the particles' diameter of below 100 nm. In our previous work, we presented a functional compact sensor demonstrator using the focused light of a laser diode for the heating of soot nanoparticles and a silicon photomultiplier for the detection of LII events [1]. With a comparable laboratory setup, the use of such a sensor to reliably determine the soot particle number concentration was shown [2]. For the introduction of the size-dependent count rates, a SMPS was used to measure the mean diameters of the investigated size distributions. In future, this information can be directly deduced from the registered LII signal shapes.

Methodology:

The choice of suitable optical components such as laser source, lenses and mirrors was supported by a systematic study of the associated laser light distribution in the focus and the filter efficiencies regarding the LII transmission and stray laser light suppression. Based on these results, functional demonstrators were built. One critical value to assess the sensor's performance is the determination of the minimum detectable particle size. By using an indirect method that compares the created particle size distribution to the events registered with the LII sensor, an indication about this figure-of-merit can be derived. We compare the influence of different parameters like the laser power densities, particle velocities, and signal detection methods on the detection limit.

Results & Conclusions:

Through experiments with a variation of the particle distribution generated by a miniCAST soot generator, the indirect method to determine the detection limit helps to understand the cause-effect relationships influencing the sensor performance. The obtained results support further improvements of the sensor setup. The use of near-monodisperse particle distributions allows to improve the accuracy of the determination of the sensor's detection limit. For the most promising setup, this approach led to a detection limit well below 100 nm. Measurements with various particle sources showed a broad range of derived size distributions. This includes the use of a miniCAST, a kerosene soot point lamp, and a diesel engine. The evaluation of the registered signal peaks reveals a dependency between particle size and signal shape, which opens the possibility to directly correct the monitored count rates.

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High Dimensional Fast-Response Particle Number (PN) Surrogate Model Building Methodology for Heavy Duty (HD) Diesel Engine Applications

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India's existing BS-VI emissions standards on sub-23 nm particle number (PN) emission limit applies to the engine testbed level. As heavy-duty (HD) diesel engines are always fitted with Diesel Particulate Filter (DPF), meeting PN emissions legislative limits at the tailpipe level is not difficult. However, future legislation requirements may be similar to European on-road In-service Conformity (ISC), by using Portable Emission Measurement System (PEMS) for vehicle level PN measurements. Therefore, it is an important aspect to understand the physics involved in the generation and evolution of particles, the corresponding sensitive parameters, and therefore to develop a capability to robustly estimate engine-out PN for HD diesel engines. This technical work is focused on estimating the engine-out PN for HD diesel engine by using the MoDS-SRM Engine Suite digital workflow. The purpose is to build detailed physico-chemical engine models and a high dimensional, fast-response surrogate model that is capable of accurately capturing combustion characteristics and engine-out emissions at steady-state operating points. The PN measurement data is collected with AVL APC 489 device, covering various operating conditions with distinct engine speed and load across the entire operating window of a HD compression ignition diesel engine. The physico-chemical models are calibrated (parameter estimation) as part of the MoDS-SRM Engine Suite workflow with 40% of the measured operating points. Subsequently, the calibrated detailed models undergo validation (blind-testing) against the remaining 60% of the measured operating points. The calibrated models are able to simulate the validation points with satisfactory accuracy, capturing the general trend across various operating conditions for gas-phase and particulate emissions. For particulate emissions, 80% and 62% of the validation points are within 50% error in relation to the measurement data for soot mass and PN. Had it been a purely statistical or data-driven model, approximately 85%-95% of the measured operating points would be required for model calibration to reach the level of accuracy that is achieved in this work. In order to reduce computational expense further, a fast-response model is developed to simulate steady-state and transient operating conditions. The surrogate model generated from the MoDS-SRM Engine Suite digital workflow is applied to perform transient cycle simulations in MATLAB. The future scope of the work includes the addition of more measurement data with respect to variations in EGR, injection pressures, high and low ambient temperatures, high altitude, and cold zones to demonstrate the cost-reduction potential of the digital workflow in some of the aforementioned measurements-intensive scenarios.

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Calibration of Black Carbon Instruments with the CPMA-Electrometer Reference Mass Standard (CERMS)

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A wide range of instruments employing a number of different measurement principles report the mass concentration of black carbon (soot). The reported values depend both on the characteristics of the source particles used in the calibration and the reference method applied, neither of which are unique or traceable. The limitations associated with the reference method are avoided by using the centrifugal particle mass analyser (CPMA)–electrometer reference mass standard (CERMS) technique. All aspects of the CERMS technique are traceable to the SI, resulting in a traceable mass standard similar in principle to the calibration for CPCs. The CERMS is capable of classifying and measuring *in-situ* reference mass concentrations down to levels below 1 μg/m^3 and in real-time (~1 Hz). Additional advantages of the CERMS are its low uncertainty (~3 %) and its measurement of a well-defined quantity: total post-CPMA suspended PM mass. The classification of the particles is not affected by particle morphology or composition. When presented with a nonvolatile black carbon (BC) aerosol for calibration, CERMS may be used to calibrate instruments for the measurement of BC mass concentration.

Results for calibration of a number of instruments, including those based on photoacoustic (PAX and MSS), attenuation (CAPS PMssa), and laser-induced incandescence (LII 300) principles are presented. A number of sources for BC are evaluated, including laboratory soot generators (MISG and miniCAST) and engine emissions (gas turbine and diesel). The results show that the BC instrument responses for different sources do vary, as a result of differences in the particle morphology, internal structure, or composition. As thermal-optical analysis (TOA) to determine elemental carbon (EC) mass is the reference method for the mass concentration measurement of aircraft gas turbine engine nonvolatile particulate matter (nvPM) emissions, a comparison between EC mass from TOA and nvPM mass from CERMS is also discussed and closure for mass is demonstrated under carefully-controlled conditions [1]. The sensitivity of the CERMS is shown by characterizing the limits of detection of the LII 300 and PAX instruments. The results support the use of CERMS with well-characterized BC sources to provide reference mass concentrations for the calibration of instruments measuring BC mass concentrations.

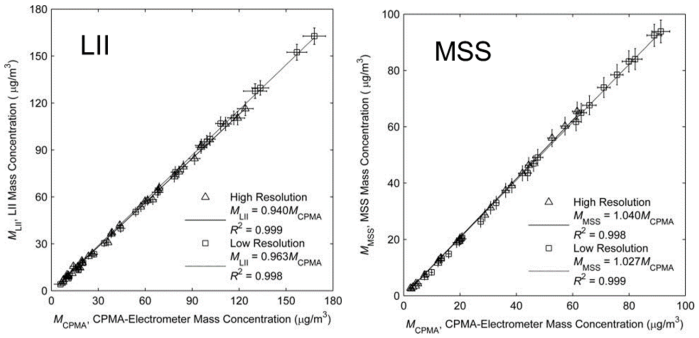

Figure 1. Demonstration of using the CERMS technique to determine calibration factors for the LII 300 (left) and MSS (right) instruments with a black carbon aerosol.

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Differential impact of biogenic and anthropogenic secondary organic aerosol compounds adsorbed on soot particles in lung cell models at the air-liquid interface

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BACKGROUND & MOTIVATION: Secondary organic aerosols (SOA) formed from anthropogenic or natural gaseous precursors are substantially contributing to the ambient $PM_{2.5}$ burden, which is known to correlate with adverse human health effects [1]. However, our knowledge is mostly limited to the effects of collected airborne particles under submerged exposure conditions rather than the direct deposition and interaction of aerosols with cell cultures [2]. Moreover, a direct link between single aerosol compounds and their health hazards remains largely unknown [3, 4]. Therefore, we were interested in differentiating the toxicological effects of combustion-derived soot particles (SP) from the effects induced by the soot photochemically aged together with a biogenic (β-pinene) or an anthropogenic (naphthalene) volatile organic compound in two different lung cell models exposed at the air-liquid interface (ALI).

METHODS: Monoculture of lung epithelial cells (A549) and a co-culture model with A549 and endothelial cells (EA.hy926) were exposed at the ALI for 4 h to different aerosol concentrations of pure SP or a photochemically-aged mixture of primary combustion SP and β-pinene ($SOA_{\beta PIN}$-SP) or naphthalene (SOA_{NAP}-SP). The internally mixed soot/SOA particles were comprehensively characterized in terms of their physical and chemical properties. We conducted toxicity tests to determine cytotoxicity, intracellular oxidative stress, primary- and secondary-genotoxicity as well as inflammatory and angiogenic effects.

RESULTS & DISCUSSION: Both investigated SOA types caused significant toxicological effects, while the nano-sized soot cores alone showed only minor toxic effects under the current experimental settings. The toxicological assays furthermore indicated greater adverse effects of SOA_{NAP}-SP compared with $SOA_{\beta PIN}$-SP in both cell models. At the functional level, we showed that SOA_{NAP}-SP augments the secretion of e.g. malondialdehyde and interleukin-8, and may induce the activation of endothelial cells in the co-culture system. This activation was confirmed by comet assay suggesting secondary genotoxicity and an increased angiogenic potential. Chemical characterization of PM revealed distinct qualitative differences in the composition of the two secondary aerosol types. It is shown that SOA-compounds can increase the toxicity of primary SP, which are ubiquitous in inhabited and wildfire influenced areas. Aromatic precursors, such as naphthalene caused the formation more oxidized, more aromatic SOA of higher oxidation potential with higher toxicity compared to an aliphatic precursors, such as β-pinene. The influence of atmospheric chemistry on the chemical PM composition thus can play a crucial role for the adverse health outcome of emissions.

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Particle emission from direct injection internal combustion engine fed with various gaseous fuels

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Introduction & Background: Gaseous fuels as hydrogen and methane are considered most frequently as possible alternatives to conventional liquid fuels. Besides, on-board production of a hydrogen-rich reformate using Thermo-Chemical Recuperation improves thermal efficiency and reduces emissions of gaseous pollutants. Commonly, gaseous fuels are introduced into the ICE intake manifold through a port fuel injection (PFI). The latter results in improved combustion and concomitantly reduced exhaust emissions, as compared to liquid fuels. However, PFI may lead to abnormal combustion phenomena, as well as maximal power loss. Direct injection (DI) of gaseous fuel eliminates these problems, and contrary to the PFI method it reduces the compression work caused by the additional volume of gaseous fuel in the intake manifold. Most of previous studies dealt with particle emissions of IC engines fed with gaseous fuels, considered fuel supply to the engine intake manifold. These works reported on the reduction of particle emission as compared to gasoline. There is a limited number of studies investigating particle formation in DI engines fed with gaseous fuels, and no comparative information is available on the effect of fuel type. The main goal of this work is to investigate particle formation in a direct injection SI engine fed with different gaseous fuels like hydrogen, methane, and hydrogen-rich reformate (containing 75% mol. hydrogen and 25% mol. CO_2). The effect of the end of injection timing (EOI) and fuel type was investigated, and a comparison to PFI with the same fuels was performed.

Methodology: The experimental setup was based on a single-cylinder Lister-Petter AD1 4-stroke engine with a high compression ratio (r=15.5) modified for spark-ignition operation. Particle number concentration and size distribution measurements were performed with TSI model 3090 Engine Exhaust Particle Sizer (EEPS) Spectrometer. A direct experimental comparison was performed between the PFI and DI fuel supply methods and different gaseous fuels: hydrogen, methane, and the reformate.

Results & Conclusions: The results showed that the total particle number emitted from the engine fed by DI of the hydrogen-rich reformate was the highest among the studied fuels. Besides, hydrogen fuel, with no carbon content, resulted in a higher total particle number compared to methane. The increase in particle emissions was noticed especially at high engine loads, while for the lower engine loads, which can be achieved using both PFI and DI methods, no significant difference was noticed between the various fuels. The direct experimental comparison of particle emission between the reformate port and direct injection on the same engine elucidates that the increase in particle formation is a result of the applied direct injection method. Notably, the reformate fuel requiring the longest injection duration due to the lowest fuel heating value resulted in the highest particle emission. Studying the effect of EOI with the DI method for the various fuels revealed the same trend of excessive particle formation at high engine loads. The retarded EOI timing (-70 CA BTDC) with longer injection duration resulted in a higher particle emission compared to the earlier EOI timing (-100 CA BTDC). The observed higher particle formation with direct reformate injection is attributed to the lubricant involvement in the combustion process. The fuel jet developed during the injection causes lubricant vapor entrainment into the jet, while the jet impingement on cylinder walls causes oil removal from the walls. This lubricant is mixed in the cylinder bulk which led to incomplete combustion with resulting excessive particle formation.

Primary organic aerosol emissions and chemical composition from biomass and cow dung burning characterized using extractive electrospray ionization mass spectrometry

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Primary organic aerosol (POA) emitted from combustion processes (including biomass, waste and cow dung, etc...) may contribute a large fraction of organic aerosol (OA; including brown carbon (BrC)) on regional and global scale. POA from various sources has been closely linked to adverse health effects. However, comprehensive chemical characterization of POA emission is rarely reported due to its complexity and limitations of current instrumentation. The recently developed extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) achieves real-time and near-molecular (i.e., molecular formula) measurement of water soluble constituents of POA[1], which improves our understanding of the composition of POA. In this work, a series of experiments were conducted to investigate the emission factors (EFs), chemical composition, and marker ions of the POA from different combustion sources including wood, straw, and cow dung. The EFs of CO, CO_2, non-methane hydrocarbon, and POA are 63.5±6.8, 1668.9±26.7, 10.4±2.7, and 3.7±1.1 g kg^{-1} for wood open burning and 73.2±15.4, 1661.7±30.3, 11.7±2.9, and 1.7±0.4 g kg^{-1} for wood stove burning, generally equivalent to straw burning (except for POA EF which is only 0.86 g kg^{-1}) and lower than cow dung emissions. The carbon and oxygen distributions of POA vary between different burns and fuel types. Levoglucosan is the main marker for wood combustion, while its contribution to straw and cow dung burning is lower. In contrast, the total abundance of compounds with carbon number > 10 in the emission of straw and cow dung is higher than wood combustion. The proportion of nitrogen-containing compounds for cow dung burning is around 7%, which is higher than the proportion for wood and straw combustion with an average around 4%. The evaporation of main components of POA with temperature was analysed, providing insights into the volatility of POA and the effects of gas-particle partitioning on POA chemical composition.

We acknowledge the support of the SNF grant MOLORG (200020_188624).

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Impact of organic carbon on soot light absorption

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Carbonaceous nanoparticles (e.g., soot, carbon black and quantum dots), nanotubes and graphene are produced by fuel-rich combustion in aerosol and biomass reactors. The light absorption of these nanoparticles is essential for their characterization by laser induced incandescence and light extinction [1]. For example, carbon black and graphene absorb strongly light due to their similar composition of sp^2-bonded aromatics. In contrast, the optical properties of soot may differ significantly from those of carbon black and graphene [10]. This is due to the fact that light absorption of soot depends on its C/H, maturity [2], morphology [3] and organic carbon (OC) content [4]. Here, the impact of OC on the light absorption of soot is determined by discrete element modeling coupled with the discrete dipole approximation for computing the scattering of radiation by soot particles. The mass absorption cross-section (*MAC*) of soot is used widely to determine its light absorption. Typically *MAC* is obtained from the mass average refractive index of OC and elemental carbon (EC) with large C/H that make up mature soot. As such, *MAC* can be overestimated by a factor of 3 in fuel-rich flames where newly-formed young soot contains EC with small C/H and OC that predominantly scatters light reducing its absorption by soot. Here a relation for the soot refractive index is derived accounting for soot morphology, maturity and OC content through its band gap at wavelength, λ = 266 - 1064 nm. Using this relation, the *MAC* of soot containing OC (up to 50 wt%) is in excellent agreement with carbon black, graphene and soot data at λ = 300 - 840 nm. This confirms that soot morphology, maturity and OC content greatly influence light absorption during characterization of in-flame and freshly-emitted soot by laser induced incandescence and light extinction, especially in fuel-rich flames, and need to be properly accounted for in the soot refractive index.

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Applying lessons learned from diesel exhaust to brake wear nanoparticle measurements and regulation

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Automobile friction brakes generate, in addition to coarse particles generated by mechanical processes, highly variable amount of nanoparticles from high temperature processes. In this work, four sets of front brake pads for a typical mid-size passenger car were subjected to selected parts of standardized brake performance tests believed to be reasonably realistic for common driving, and one set of pads also to the newly developed WLTP brake wear testing procedure. Tests were done on a brake dynamometer with an enclosed chamber and particles were measured in the duct serving at the outlet of the cooling air. A fast electric mobility particle sizer, checked to provide a reasonable response to different types of non-carbonaceous nanoparticles, was used to measure particle size distributions. The particle production was found to vary over about 5 orders of magnitude on both per-stop and per-kWh basis, with higher intensity, higher total energy dissipated, and higher temperature all correlated with a non-linear increase in emissions. While the emissions over the WLTP cycle were relatively low, the very high contribution of more aggressive, yet still realistic braking events, even though relatively infrequent, should not be overlooked. Just like with driving a non-DPF vehicle, aggressive, high-speed driving produces substantially more particles than defensive, gentle, do-not-spill-your-coffee driving.

Behavior of particles and gases in vehicle cabin

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The impact of air pollution on human health is a major concern and various anthropogenic sources of particulate exposure are under investigation to better understand their contributions to adverse health effects. Travel in vehicles represents a primary source of human exposure to particulate matter. A recent report estimated that for Los Angeles residents, 33-45% of exposure to ultrafine particles occurs while traveling in vehicles. Commuters on highways may be at particular risk, since particulate levels are demonstrably higher on highways. People living in urban areas are keen to reduce their exposure to particulate matter while riding a vehicle but there is a lack of information to make intelligent choices.

This study will show characteristic behavior of carbon monoxide, nitrogen oxides, ozone and particles in vehicle cabin in the presence of a passenger under various ventilation condition. This will give insight on how to control these pollutants in vehicle cabin.

The study will also definition a Cabin Air Quality Index (CAQI) to assess vehicle’s ability to maintain clean cabin air quality similar to MPG for fuel economy. The study developed both static and dynamic test methods, which characterize and quantify vehicle cabin air quality from consumer’s perspective.

The presentation will include details of the test method, results, and their implications. Standardization effort on CAQI via CEN workshop and VIAQ (Vehicle Interior Air Quality) IWG (Informal Working Group) under UNECE will be briefly explained at the end of the presentation.

Development of a new photothermal interferometer for the in-situ measurement of carbonaceous aerosols

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Filter-based instruments are commonly used for the determination of ambient aerosol light absorption. With the assumption of a specific light absorption efficiency, the mass concentration of the light-absorbing carbonaceous particles, particularly black carbon (BC) can be determined. These methods have the advantage of being simple and robust, but the properties of the aerosol change upon deposition in the filter. These methods are prone to measurement artefacts, such as filter loading effects, increased transparency of the filter due to wetting in elevated humidity conditions, and cross-sensitivity to aerosol light scattering.
In-situ methods such as photoacoustics and photothermal interferometry (Moosmüller and Arnott, 1996; Sedlacek, 2006) measure light absorption of aerosols directly in their natural suspended state. They provide an alternative to traditional filter-based instruments. Measurements performed with these techniques are independent of aerosol light scattering and loading effects. Resonant photoacoustic measurements, however, are susceptible to changes in the resonant frequency caused by environmental influences, and suffer from measurement artefacts when absorbing gases are present. In a photothermal interferometer, the aerosols are drawn through a set of measurement chambers where a pump laser illuminates the sample. A small part of the laser light is absorbed by the sample and heat is transferred to the air, locally increasing the temperature, reducing the density and the refractive index. This perturbation is measured with a sensitive interferometer: the change of the refractive index in one arm of the interferometer relative to the unperturbed arm is measured as a change in phase. The pump laser is modulated and the signal at this modulation frequency increases the measured signal.

We present our latest development of a new photothermal interferometry setup (Visser et al., 2020). The use of only one single laser beam allows for a compact optical set-up and significantly easier alignment compared to standard dual-beam photothermal interferometers, making it ideal for field measurements. Due to a unique configuration of the reference interferometer arm, light absorption by aerosols can be determined directly – even in the presence of light-absorbing gases. The instrument can be calibrated directly with light-absorbing gases, such as NO_2, and can be used to calibrate other light absorption instruments. Our current detection limit (1 σ, 120s averaging time) is ~40 ng/m^3 BC.
In new projects, we are investigating the possibility of further significant miniaturization of our existing setup. A unique kind of photothermal interferometer is currently realized using optical fibers and waveguides. Such a miniaturized sensor has many key advantages: It will be smaller, lighter and cheaper than existing BC instruments, which are expensive and rather immobile. The miniaturization into a fully integrated optical circuit board will make it also less susceptible to external vibrations and misalignment. Our goal is to develop a novel miniaturized PTI instrument that can be used airborne to detect the local distribution of BC particles with high temporal resolution.

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Super Polluter IDentifiER (SPIDER) – a tool for on-road detection of vehicles that contribute disproportionally to the vehicle fleet emissions

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Traffic is a diverse and disperse source of air pollution. The amount of pollutants emitted depends on vehicle parameters; the engine type and displacement, the exhaust after-treatment system, maintenance status, as well as traffic conditions, topography, driver behavior and the weather conditions. Different statistical analyses and measurement approaches have been employed to evaluate traffic emissions; these vary in complexity in terms of describing traffic activity and emission factor (EF) determination. The EF determination methods performed on-road in real driving conditions have been described as less precise than the dynamometer studies because the tests are not as repeatable due to the absence of standard cycles and additional uncontrolled parameters, such as environmental or traffic conditions, driver behavior or highly transient operations [1]. Their advantage over dynamometer/laboratory measurements is that, over a short period of time, emissions of many different in-use vehicles can be measured and EF distributions for different vehicle categories can be obtained. There have been several studies measuring EF of individual vehicles using different approaches [1-2] and references therein.

We have repeated the on-road measurement campaign using the chasing method as descried in Ježek et al. [2] and determined EF of BC and nitrogen oxides (NO_x) from 435 individual vehicles of different types and particle number (PN) EF of 145 different type vehicles. We have acquired technical data from the national registry information about the measured vehicles and analyzed the data according to vehicle type, age and fuel used. The data-processing method was re-evaluated and optimized, especially from the point of view of background concentration determination, which can represent an important source of uncertainty.

The vehicles were firstly grouped to three categories - diesel cars, gasoline cars and goods vehicles, and then according to age and introduction of new European emission standards. Significant reductions in BC EF with introduction of EURO5 and EURO6 emission standards in diesel cars and goods vehicles groups were observed. The reduction in NO_x EF for diesel cars was small and found only in the EURO6 group. We observed the reduction in NO_x EF in goods vehicles and gasoline cars categories. PN EF were also significantly reduced in all three vehicle categories. We will compare measurement results to the results of Ježek et al. [2] and the contribution of super emitters in the main three vehicle groups. We will demonstrate that the optimized SPIDER method can be used in real-world to determine supper emitters, and the associated reduction of fleet emissions, if these supper emitters were eliminated from the fleet.

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Ultrafine particle concentrations in Kloten near the Zurich Airport (Switzerland)

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Ultrafine particles (UFP) comprise the smallest particle fraction of atmospheric particulate matter with particle diameters of less than 100 nm. In recent years, studies in the surroundings of international airports have shown that air traffic can be an important source of UFP. We report on UFP measurements performed since February 2019 in a residential area in Kloten (urban background), a site located 1 km east of Zurich Airport and about 500 m east of highway A51 (approximate traffic activity of 100'000 vehicles per day). Both the airport and the highway are located to the west of the measurement site, making it challenging to distinguish the contributions from both potential major sources of UFP at this location. UFP at the site in Kloten are measured as number size distribution of particles with diameters between 10 and 100 nm. Reported UFP number concentrations ($PN_{[10\text{-}100nm]}$) cover this size range.

Between February 2019 and February 2020, the mean concentration of UFP was about 20'000 particles per cm^3, a value that corresponds to typical UFP concentrations in Switzerland at roadside locations directly adjacent to busy roads. However, in Kloten the UFP concentration depends strongly on wind direction, wind speed and time of day. For example, the average UFP concentration at wind directions from west to northwest was for the February 2019 to February 2020 period about 40'000 particles per cm^3 and therefore three times higher than for winds prevailing from southeast (about 14'000 particles per cm^3). Beside total UFP concentration, the mean particle diameter in Kloten also shows a strong dependence on wind direction with the smallest particle diameters for winds from western and northwestern directions, i.e. from the directions in which both the airport and the highway A51 are located. The strongly enhanced UFP concentrations at winds from west to northwest, as well as the fact that the measured average UFP concentration is clearly higher than at typical Swiss roadside sites indicates significant contributions from air traffic at the site in Kloten. However, the quantitative determination of the air traffic contribution to total UFP concentration requires more elaborated analysis of the measured particle size distributions and consideration of information from the scientific literature. For the measurement site in Kloten, we determined the contribution of air traffic at Zurich Airport (landing and takeoff) to the total UFP concentration in 2019 to be 40%, based on the distribution of concentration peaks combined with wind conditions. While air traffic is a dominating source of UFP at this site, it is of minor importance for the concentration of the regulated air pollutants NO_2, PM2.5 and PM10.

The intervention measures to reduce transmission of the SARS-CoV-2 virus implemented in March 2020 resulted in a marked decline of road traffic on highway A51 and had a dramatic effect on the air traffic activity at Zurich Airport. Consequently, the UFP concentrations at the site in Kloten strongly declined. The change in UFP concentrations was much stronger linked to the change in air traffic activities compared to road traffic, confirming the influence of air traffic on the level of UFP in the studied residential area in Kloten.

Clean air test-zone – reduction of emissions from wood stoves

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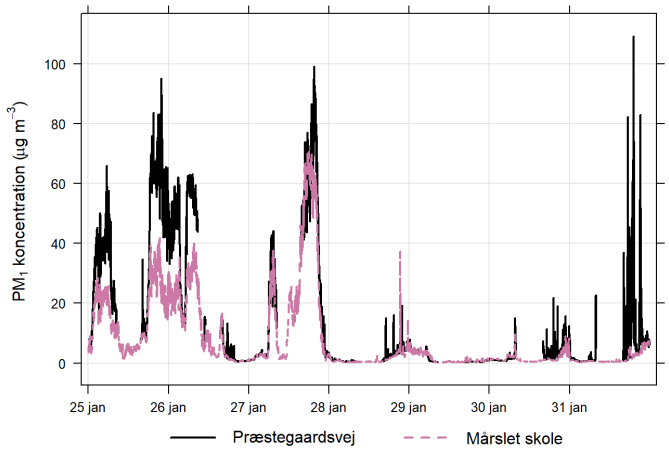
Today, wood stoves and boilers are estimated to account for 65-70% of particle and black carbon emissions in Denmark. At the same time, the legislation relates exclusively to type approval of stoves in the laboratory, which rarely reflects real-life emissions when used in private homes. A new Danish lighthouse project (2020-2023) demonstrates modern stoves and emission-reducing technology under real-life conditions in a dedicated residential neighborhood (test zone) in the municipality of Aarhus, Denmark. The objective is, from a cost-benefit perspective, to identify measures that provide most impact on real-life emission reduction from wood stoves, including automatic control stoves, low-emission stoves, new types of chimneys, draft boosters, ESP filters and catalysts. Additionally, digital apps can help the consumer firing more correctly. In order to evaluate effect of the various approaches, distributed low-cost sensors continuously quantify local air pollution levels (PM, CO, NOx, temperature, wind direction and speed). Through developed data algorithms, we expect to identify which point sources are actually problematic and which are acceptable. The distributed sensors are supported by dedicated point source emission measurements (PM, PN, NOx, CO, CO2, OGC).

The dedicated test-zone, with around 25 actively participating households, was established in the city of Mårslet in autumn 2020. Several outdoor and indoor sensors (Leapcraft) are mounted and continuously logging PM and gases in the 20/21 heating season. Present measurements in the 20/21 heating season will serve as a reference background for technical interventions targeting wood stove emission reductions during the coming two heating seasons. One of the main challenges in the data analysis is separating the wood stove signal from other sources. Present efforts involves pattern recognition and comparing with parameters such as background level, wind direction, relative humidity and chimney temperature. As an example, below is shown the PM1 concentration measured in a lamppost in the test zone (Præstegårdsvej) and background (Mårslet school) for a week by the end of January. In general, the concentration measured at Præstegårdsvej is significantly higher than at Mårslet school, very likely due to local sources of particles, of which wood-burning stoves are expected to make up a significant part. This is supported by the fact that the high concentrations occur in the evening and at night, where an increased use of wood-burning stoves can be expected. At ETH 2021 a more detailed analyses will be given on the above, expected to include a preliminary quantification of the signal from wood stoves - as well as results from reference measurements on individual chimneys in the test zone.



The development and convergence of co-pathologies associated with Tau, Aβ, α-synuclein and TDP-43 proteinopathies in Metropolitan Mexico City children and young adults: a health crisis is in progress. Nanoparticles a common denominator?

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Complex interacting pathways play key roles in Alzheimer's disease and other fatal neurodegenerative diseases, wherein we have multiple misfolded proteins causing a range of neuropathological changes and contributing strongly to clinical symptoms, including cognition deficits as well as brain MRI, gait and equilibrium, olfaction and brainstem auditory evoked potentials (BAEPs) alterations.

Quadruple misfolded proteins (tau pre-tangles and neurofibrillary tangles, amyloid-β [Aβ], α-synuclein, and transactive response DNA-binding protein 43 [TDP-43]) in the same brain are common in children and young residents in Metropolitan Mexico City (MMC) exposed to high concentrations of fine particulate matter $PM_{2.5}$ and nanoparticles. Indeed, 99.5% of 203 consecutive forensic autopsies in subjects younger than 40y, exhibit AD hallmarks, 20% Parkinson's disease and 18.7% TDP-43 pathology. Cortical tau pre-tangles, neurofibrillary tangles (NFT) Stages I-II, and amyloid phases 1-2 are documented by the 2sd decade. Of critical importance is the documentation of NFT stages III-V in 24.8% in 30-40 y old subjects.

Cognitive changes in subjects age 21.6±5.8 years are likely an indication of the neuropathology seen in forensic young cases. The Montreal Cognitive Assessment (MoCA) administered to 517 urbanites, showed an overall MoCA score of 23.92±2.82 (normal 26-30), with 24.7% and 30.3% individuals scoring ≤24 and ≤22, respectively (Mild Cognitive Impairment MCI≤24, Dementia scores D≤22). Cognitive deficits progressively targeted Visuospatial, Executive, Language, and Memory domains.

Alzheimer Continuum subjects have higher numbers of brain NPs versus clean air controls with normal brains. Iron rich NPs and transitional metals and non-metals are identified in neural cells and endothelium's mitochondria, Golgi, and endoplasmic reticulum and are associated with significant structural organelle damage.

We strongly support combustion and industrial NPs are key players in early ROS generation, neurovascular unit, mitochondria, endoplasmic reticulum and endolysosomal dysfunction, and catalysts for protein misfolding, aggregation and fibrillation. Fe-rich NPs respond to external magnetic fields and thus might be involved in cellular damage by agglomeration/clustering, magnetic rotation and/or hyperthermia.

Nanoparticle exposure regardless of sources carries a high risk for the developing brain homeostasis and ought to be included in the AD, PD and TDP-43 research framework. The ultimate neural damage and neuropathology could depend on NP characteristics and the differential access and targets achieved via their portals of entry. Control of NP sources becomes critical.

Neurodegenerative fatal diseases are likely the result of complex interactions between environmental and genetic factors. A more complete understanding of NPs as plausible and modifiable environmental risk factors for the development of diseases such as Alzheimer and Parkinson's, Frontal-Temporal Dementia and Amyotrophic Lateral Sclerosis evolving from childhood will help guide their early detection and prevention. We are in the midst of a devastating crisis too big to ignore, with profound health, social and economic consequences.

Performance of the new continuous carbonaceous aerosol measurement system FATCAT during long term unattended measurement campaigns

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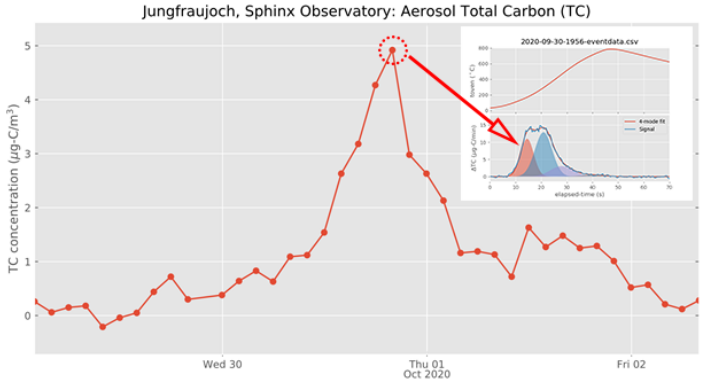
Total aerosol carbonaceous mass (TC) is a major constituent of atmospheric fine aerosol particle mass. However, this fraction is generally not continuously monitored with an adequate time resolution. Adding a TC measurement is crucial to complement the existing measurement programs for a comprehensive interpretation impact of aerosols on our climate. To fill this gap, we developed the “fast thermal carbon totalizator” (FATCAT), a carbonaceous aerosol measurement system for long-term monitoring of TC. FATCAT has been deployed since 2019 at different measurement sites, including Zurich (urban roadside), Windisch (urban background), Payerne (suburban background), and the Sphinx observatory at the Jungfraujoch global GAW station (JFJ; above the planetary boundary layer) for unsupervised long-term measurement campaigns. FATCAT collects a sample on a sinter metallic filter, and subsequently heats it to 800°C under an oxidizing atmosphere. The fast-heating cycle of 50 seconds allows a low limit of detection (LoD) of 0.2 µg of carbon (µg-C).

We will discuss our experience during the first two year of continuous TC measurements and the possibility of using our instrument to distinguish carbonaceous aerosol from different source using its fast thermograms. This unique feature allows us to identify source specific fingerprints. For instance, several high TC episodes during September 2020 at the JFJ station show the typical pattern for biomass combustion. With the identified fingerprint and back trajectories, these episodes were attributed to long-range transported emissions from Californian wildfires (see figure). In general, refractory, crystalline carbon from, e.g., fossil fuel combustion evolves at high temperatures, whereas aerosol particles from, e.g., biomass burning sources containing more amorphous organic carbon decompose and evolve at lower temperatures. The dataset generated by our instrument and post-analysis data products represent an improvement to the available measurement inventory. It can also serve as quality control for other measurement systems. Prominently, measurements of eBC via MAAP or Aethalometer and organic mass using ToF-ACSM require calibration and are susceptible to systematic errors. TC measurement data can be used in parallel for these devices as a quality check but also to warrant total carbon mass closure and reduce systematic biases.



This work has been supported by global atmosphere watch (GAW) and by MeteoSwiss through the GAW-CH Science Projects 2018-2021 The authors acknowledge the support from MeteoSwiss, the city of Zurich, EMPA, University of Bern, and the Paul Scherrer Institute (PSI Switzerland) for their assistance during the measurement campaigns.

Differentiating Translocated Exogenous vs Bio-generated Endogenous Nanoparticle Types in Olfactory Bulb of Humans with Neurodegeneration

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An increased risk for Alzheimer's and related dementia has been hypothesized to be causally associated with ambient PM air pollution. Aerosol constituents in polluted air contain redox-active metal- and other nanoparticles (NPs), and mounting evidence supports their role via neuronal nose to brain transport for neurodegeneration at and beyond the rostral (olfactory bulb (OB)) and caudal (brain stem) point of CNS entry. We examined autopsied OBs to determine whether inhaled pollution-derived NPs reach the brain via the olfactory nerve. To understand the accumulation of ambient nanoparticles in the OB requires to differentiate between the sources that are coming either from exogenous (aerosol pollution) or endogenous origins (biomineralization). An example are iron NPs for quantifying the various iron components which is crucial to link exogenous iron to neurodegeneration. Our approach uses analytical high-resolution transmission TEM of OB thin-sections coupled with electron energy loss spectroscopy (EELS) to assess compositions, relative quantities, and redox-activities of distinct NPs and to identify the physiochemical fingerprints of individual iron NPs that either translocated to OB regions (exogenous) or precipitated in vivo (endogenous). We also analyzed particles in OBs that seem to have originated from specific occupational aerosol exposures, for example tungsten particles that were present predominantly in sub-nano scale (0.3-1.5 nm) inside glomeruli and axons. Analyses were performed using a cryo-stage to stabilize the biological sections. We grouped NPs with identical characteristics and used digital imaging and spatial statistics to assess their frequency in the OB. Information on exogenous NPs locations and interactions with axons, mitochondria, amyloid plaques and or Lewy bodies were systematically correlated with Subjects that have well-documented impaired olfaction and dementia. Exogenous silica NPs are typically associated with heavy metal inclusions (Fe, Mn, Zn, Co, Ti, Zr, Cr, As, Se, Pb, among others) which typically occur as ultrafine dispersions and co-translocated (Trojan Horse Mechanism) to OB of select subjects. Exogenous iron NPs included iron oxides and phosphates. The location and frequency of endogenous iron NPs in OB (iron oxyhydroxide; ferritin) are related to the occurrence of amorphous silica, alumina, and carbon NPs as well as heavy metal NPs and may be a marker for inflammation and oxidative stress.

Macro tracer model as a technique for source apportionment of particulate matter in Krakow agglomeration – an optimization approach

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Introduction:

Receptor models are mathematical procedures used to identify the sources of pollutant emissions and to estimate their contribution in the overall balance of atmospheric aerosol emissions based on measurements of the concentrations of aerosol components, without the need to carry out an inventory of emission sources or data describing meteorological conditions. The concept of a *macro tracer* model consists in determining a chemical compound - an indicator - specific to a given source. The basis of the model is the work of P. Lenschow et al. who took the first steps to match a given indicator compound with a given particulate matter emitter[1]. The *macro tracer* model was then developed in Austria by scientists from Vienna University of Technology[2,3]. The assumptions of the model had to be optimized in order to implement this model to the region where coal is the main source of energy. New factors have been calculated on the basis of source profiles obtained in preliminary studies presented by Katarzyna Szramowiat-Sala et al[4]. Afterwards, the optimized *macro tracer* model was used for the identification of emission sources of atmospheric aerosols from Krakow agglomeration.

Results & Conclusions:

The *macro tracer* model enabled to obtain reliable results on the contributions of individual sources of atmospheric aerosols in the Krakow agglomeration in winter. The optimized model allowed to reconstruct the PM mass with the higher R^2 linear coefficient than using the F coefficients estimated by Gonçalves et al and Kistler et al. However, to obtain more appropriate results, it is necessary to broaden the research studies on chemical composition of particulate matter from individual sources and to identify the more specific tracer for them.

Acknowledgement:

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Exposure-response functions relating intensity and duration of ambient traffic-related air pollution to systolic blood pressure

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Exposure to traffic-related air pollution (TRAP) is associated with adverse health outcomes, including elevated blood pressure and hypertension. However, the nature of the exposure-response functions for these associations is not well established. We recently published a three-exposure, three-period crossover trial where we showed that using portable high-efficiency particulate air (HEPA) filters to reduce indoor infiltration of TRAP was effective at preventing short-term increases in systolic blood pressure (SBP). We measured particle number concentrations (PNC) and black carbon (BC) concentrations continuously during the trial, and we measured participant blood pressures every 10 minutes. In the present study, we derive exposure-response functions that incorporate both intensity and duration of PNC and BC.

A total of 1514 SBP measures arising from 77 participants were analyzed. The average age of the participants was 60 years, 79% were female, 77% were Asian, and 17% were White. None had serious health conditions. The average SBP was 120 mmHg, the average PNC was 13,000 particles/cm^3 (range 860 to 99,000 particles/cm^3), and the average BC concentration was 450 ng/m^3 (range 16 to 2700 ng/m^3). Linear mixed models were used to fit logarithmic relationships between PNC and SBP and between BC and SBP. The models included the variable ‘time from study entry’ as a measure of exposure duration and a random intercept to account for the interdependence of multiple SBPs recorded from each participant. The resulting models, yielding statistically significant regression coefficients ($p < 0.001$), can be written (and displayed in Figures 1 and 2) as: $SBP = 101.22 + 0.98 \log_e PNC + 2.38 \log_e TIME$ and $SBP = 104.97 + 0.93 \log_e BC + 2.32 \log_e TIME$. The similarity in coefficients between the PNC and BC models can be explained by the relatively high correlation between these two measures of exposure (Pearson correlation = 0.80). Although both models describe a progressive dampening of the increase in SBP for increasing intensities and durations of exposure, duration of exposure has a greater effect on SBP than does intensity; a 1 mmHg increase in SBP is related to an approximate 53% increase in duration but a 185% increase in intensity.

In summary, the results of the present study suggest exposure-response functions for PNC and SBP, and for BC and SBP, that are logarithmically dependent on two dimensions of exposure, intensity and duration.

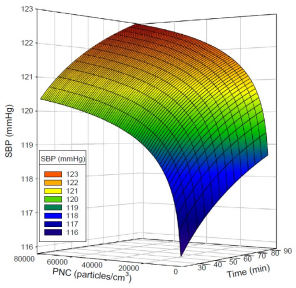

Figure 1. Exposure-response relationship between intensity and duration of PNC and SBP.

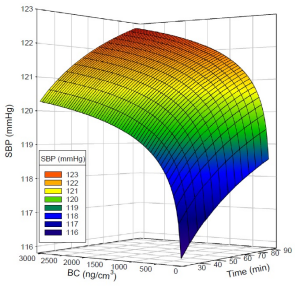

Figure 2. Exposure-response relationship between intensity and duration of BC and SBP.

Occurrence and Radiative Properties of Long-range Transported Wildfire Aerosol Measured at the Jungfraujoch

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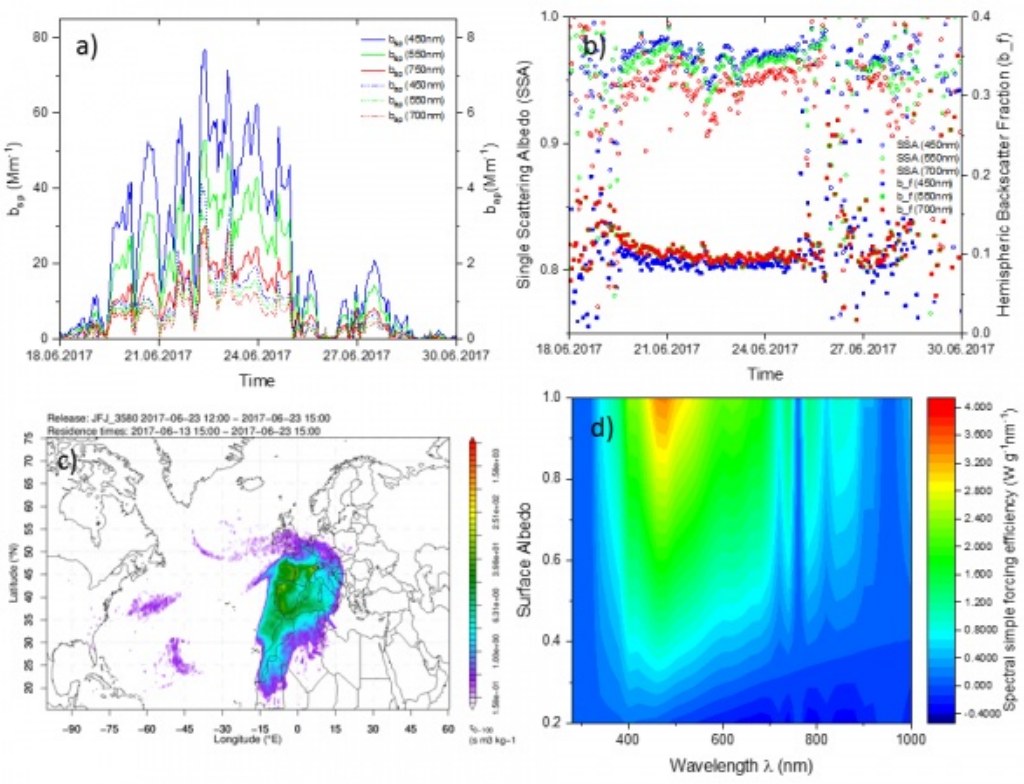
Our history has been a story of how we and fire have co-evolved. The same holds for our future. Wildfires are often not “wild” and can be linked to human activity. Hence, some claim that we are living in the “Pyrocene” [1]. Large-scale biomass burning events emit substantial amounts of primary particulate matter (PM) and gaseous secondary PM precursors. Fractions of these emissions can be injected into the free troposphere where they can be transported over long distances and exhibit a stronger radiative forcing efficiency than at ground level [2]. Large light absorbing carbon concentrations in the free troposphere can also alter the vertical temperature profile, leading to a stratification of the atmosphere below with consequences for clouds and precipitation [3]. This work characterizes the optical and microphysical properties of wildfire plumes transported to the Jungfraujoch (JFJ) Station (3571m a.s.l.). Forty-eight wildfire plumes were identified from hourly averaged data for the period between January 2015 and December 2020 using a data filter based on gaseous data and aerosol optical properties. The Figure below shows the scattering and absorption coefficients (a), the SSA and backscatter fraction (b), the source sensitivities (c) and the Mie theory derived simple forcing efficiency (d) of the most significant plume event in the period analysed, that originated from the Pedrógão Grande wildfire in Portugal in June 2017. Ongoing work validates the optical data filter with particle size distribution-, gaseous- and source sensitivities- data. In addition, plume occurrence frequency and plume microphysical properties will be presented at the conference.



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Analysis of the influence of marine fuels on particle emissions from ships

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In contrast to the extensive requirements for land-based particulate and fine dust emissions, the maritime sector is still in its infancy and has not yet been able to provide any global limit value regulations. It can be assumed that this topic will become more and more important in the future. With the last tightening of the IMO regulations on January 1st, 2020 (sulfur content in fuel ≤ 0.5% or use of an exhaust gas cleaning system outside of the ECAs), a change in the composition of the fleet emissions is to be expected. In this context, the joint project SAARUS was launched at the University of Rostock, with the aim to investigate ship-based emissions and to reduce them through optimized and expanded exhaust gas cleaning. In addition to reducing SOx emissions, the focus is on separating fine particles that measure smaller than 2.5 µm (PM2.5). In particular, the health-endangering fine dust fractions (aerosols) with particle diameters below 1 µm are only slightly reduced by conventional wet scrubbers. The approach to further decrease the particle load is therefore to use the scrubber as an optimized particle prefilter in order to create the boundary conditions for downstream filter technologies to be tested.

In this context, an extensive measurement campaign with six different fuels available on the market took place on a medium-speed single-cylinder research engine, which is representative of the maritime sector and located at the Chair for Piston Engines and Internal Combustion Engines. As part of the investigations, the fuel-based changes in emissions and the combustion behavior of a hydrogenated vegetable oil (HVO), a MGO, a limit-compliant HFO (sulfur content ≤ 0.5%), a standard HFO (sulfur content 2.4%) and two highly aromatic heavy fuel oils (sulfur content 0.06% and 1.3%) are analyzed. The following measurement methods were used to characterize the particle emissions: gravimetric filter analyzes, tapered element oscillating microbalance (TEOM), scanning mobility particle sizer (SMPS), Pegasor particle sensor, online single particle mass spectrometry (SPMS), filter sampling and two-dimensional gas chromatography / mass spectrometry (GCxGC-TOFMS), high-resolution mass spectrometry (HRMS for organic matter) and inductively coupled plasma / mass spectrometry (ICP-MS for elements).

The focus of the article is on the presentation of the most important findings of this measurement campaign. In addition to a comparison of the properties of the fuels examined, their effects on the particle load in terms of concentration, size distribution and chemical composition are discussed. In addition, the simulation approach for particle separation in the scrubber and the approaches for separating fine particles measuring smaller than 2.5 µm (PM2.5) as well as the harmful fine dust fractions (aerosols) with particle diameters below 1 µm are presented in an outlook.

Network analysis for the formation of aromatics in a co-flow flame

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An important step in predicting the growth of soot nanoparticles is understanding how gas phase variations affect the formation of their aromatic precursors. Once formed, these aromatic structures begin to assemble into nanoparticles and, regardless of the clustering process, the molecular properties of the aromatic precursors play an important role.

In this work, we report on a detailed study of the spatial evolution of molecular structures of polycyclic aromatic compounds (PACs) and their corresponding formation pathways. To this end, we employed the SNapS2 kinetic Monte Carlo software to simulate the chemical evolution of PACs along multiple streamlines. The results show that growth only occurs along streamlines that traverse regions of high acetylene concentrations in the center of the flame. The PACs predicted in various conditions show diverse chemical properties, including aliphatic chains, five-membered, and heteroaromatic rings. PACs in streamlines close to the flame wings begin growing immediately due to the high temperature and large amounts of radical species, while PACs originating along inner streamlines do not appreciably grow until they pass through an area characterized by high radical concentrations. Using graph theory and network analysis, we investigated the complex reaction network generated by SNapS2 and determined that the growth pathways of many PACs center around a few stable structures that also promote oxygen addition reactions due to their morphology and long lifetimes.

These pathways play a significant role along streamlines near the centerline, compared to the flame wings, which show more variety due to the highly reactive environment encountered during early growth. The results of this study provide insights on the reaction pathways that determine the properties of PACs at different flame locations as well as information on the chemical characteristics of the formed PACs, with emphasis on oxygenated structures.

Particle Emissions from Aircraft Gas Turbines: A Coarse Size Mode from Low Emission Engines

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This presentation is about coarse particle emissions from a commercial aircraft gas turbine engine. These particles were found in a series of test campaigns focused on understanding and improving methodology for measuring non-volatile particles from these engines. Measuring or even finding coarse particles was unexpected. Before describing these measurements, some background is useful.

Motor vehicle engine exhaust particle size distributions typically show three distinct modes: a nucleation mode between about 3 and 30 nm diameter consisting mainly of semi-volatile material, an accumulation mode between about 30 and 300 nm diameter consisting mainly of carbonaceous aggregates, and a coarse mode consisting of larger mechanically generated particles – from oil atomization and re-entrainment from in-cylinder and exhaust surfaces.

Measurement of particles from commercial aircraft gas turbine engines is much more challenging than from ground-based vehicles with exhaust temperatures as high as 900 C or more and exhaust velocities approaching Mach 1. This necessitates the use of very long sampling lines that complicate particle measurements. These lines tend to adsorb much of the semi-volatile material and suppress the formation of a nucleation mode. The carbonaceous aggregates in the accumulation mode are much smaller than from typical piston engines with geometric mean diameters in the 15 to 50 nm range. Coarse mode particles are also smaller and here we define them as particles larger than 150 nm.

The results reported here were observed during a series of measurement campaigns conducted by the U. S. Environmental Protection Agency in collaboration with the U. S. Air Force's Arnold Engineering Development Complex. The main purpose of these campaigns was to refine methodology for measurement of non-volatile particles from aircraft engines. A General Electric J-85 turbojet running with a range of test conditions and fuels was used as the particle source. Particle size and concentration measurements were made using a range of instruments. The focus of these studies was measurement of accumulation mode soot aggregates. Compared to piston engines there is less opportunity for the exhaust to interact with surfaces and there are no piston rings to atomize oil so coarse particles were not expected to be an issue.

Coarse particle size measurements were made using a range of instruments. Four measurement campaigns were conducted. In the first, a pair of TSI SMPSs operating in the sizing range of 8 to 300 nm were used. In the second, SMPSs in the 6 to 225 nm range were used. In the third, SMPSs were still operated in the 6 to 225 nm range but a TSI EEPS that operated in the 6 to 500 nm range was added. In the fourth and final study, three SMPSs were operated in the 6 to 225 nm range, and a fourth in the 15 to 690 nm range. The TSI EEPS was again used in the 6 to 500 nm range and a Cambustion DMS500 operating in the 5 to 1000 nm range was added.

The significance of the course mode was not noticed until the fourth campaign when volume fractions, (V above 150 nm)/Vtotal, V150/V) of nearly 50% were observed in some tests. After that, all test campaigns were reexamined. In most case, V150/V varied inversely with engine load and total volume (mass) emissions. Biofuels, hydrotreated camelina oil blends with Jet-A generally produced higher V150/V.

Test results will be presented, and possible sources and formation mechanisms will be discussed.

Combustion-generated carbonaceous urban atmospheric UFPs: Efficiencies of face mask control of urban atmospheric particulate pollution: A pointer to control of future pandemics

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Each day an adult human inhales on average 13.6kg [1] or 10,000 litres of air that potentially contains 0.1-10 trillion particles [2]. Some of these may be ultrafine carbonaceous combustion- and traffic-generated particles (UFPs) smaller than 100nm [3]. Others may be microbiological and bioaerosols (e.g. bacteria, fungi, viruses [4], excreta of insects and spores) and larger particulate (PM2.5 or PM10) pollutants [3]. The corona COVID-19 virus is about 60-140nm [5,6]. Since we 'cannot cease breathing for more than a few minutes' [7] the atmosphere that bathes each of us is critical; locally this air is part of our personal ecosphere [8]. It has been suggested that pollution of urban air in London contributed to the death of Ella Kissi-Debrah in 2013. It is therefore worthy of assessing how filtration of critical atmospheric pollutants by face masks can be most beneficial. The ultrafine particles prevailing in the urban air in a covered carpark at UK postcode UB7 7GN were used to test the filtration efficiency of these masks using the P-Trak 8525.

Fine (100mmx100mm) and coarse (500mmx500mm) stainless steel filters had UFP filtration efficiencies of 50.87% and 7.29%. As one would expect, the bandana UFP filtration efficiency increased progressively from 45% to 90% as the number of bandana layers used to cover the face increased from 1 to 4. This is an important finding for control of current particulate air pollution and future pandemics. The UFP filtration efficiency of cycle and DIY masks was no better than a single layer bandana. The diodic valve KN95 mask was more than twice as efficient at filtering UFPs in an inhalation mode than in an exhalation mode, presumably protecting the wearer more than those around them.

Here the authors report which type of urban carbonaceous UFPs are filtered out and how this can be made selective with filter surface modification. The authors were also intrigued that passage through water stripped out carbonaceous UFPs from the atmosphere and this may affect the impact of the particles on our health and the modification of masks to protect us from these (and other) airborne hazards. Control of airborne infection and particulate pollutants is important as we protect personal ecospheres. Here we explore the varying respiration and retention of airborne carbonaceous UFPs by those of different gender, age group, fitness level and ethnic background so that they may be better protected in the future. For the moment, face masks show varying efficiencies for protecting us from inhaling combustion-generated airborne ultrafine particles (UFPs). Real-time technology to spot ineffective facemasks at their end-of-useful-life may need deploying. In addition, our understanding of the design of facemask filtering out carbonaceous UFPs will enable us to design even better masks for future pandemics.

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Particle number emissions from a Euro 6d-temp GDI under extreme European temperature and driving conditions

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With the introduction of gasoline particulate filters (GPFs) the particle number (PN) emissions of gasoline direct injection (GDI) vehicles are below the European regulatory limit of 6×1011 p/km under certification conditions. Nevertheless, when considering more robust legislation for light-duty vehicles at Euro 7, concerns have been raised regarding the emission levels at the boundaries of ambient and driving conditions of the real-driving emissions (RDE) regulation. A Euro 6d-Temp GDI vehicle with GPF was tested on the road and in the laboratory with cycles simulating urban congested traffic, dynamic driving, and uphill driving towing a trailer at 85% of the maximum payload. The ambient temperatures covered a range from -30°C up to +50°C. The solid PN emissions were ten times lower than the current PN limit under most conditions and temperatures. Only dynamic driving that passively regenerated the filter, and the cycle after, resulted in relatively high emissions, but still below the limit. The results of this study confirm the effectiveness of GPFs in controlling PN emissions under a wide range of conditions. Related analysis of late Euro 6 diesel vehicles indicates continued effectiveness of DPFs irrespective of boundary conditions. Potential limit values, proposed by the CLOVE Consortium, for PN emissions of light-duty vehicles at Euro 7 will be presented.