Aircraft, marine and other non-road sources, Contributed Lecture

Jet aircraft lubrication oil droplets as contrail ice-forming particles

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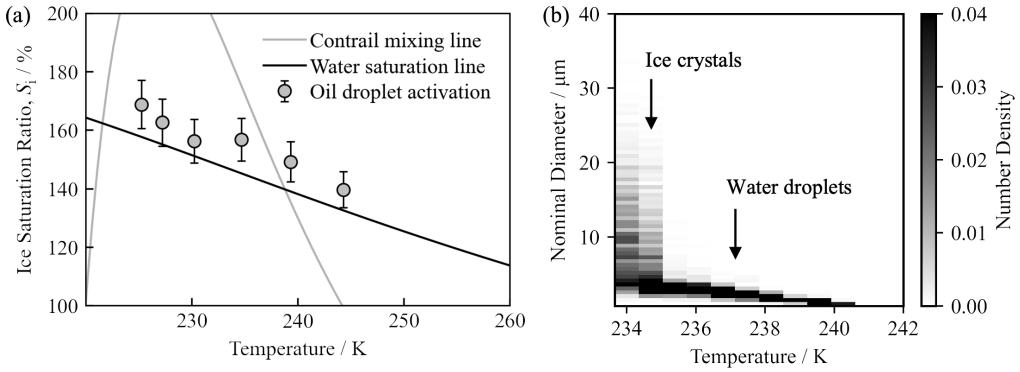
The radiative effects of condensation trails (contrails) account for the majority of present-day warming attributable to aviation [1]. The radiative characteristics and lifetime of contrails are dependent on the number concentration of ice-forming particles in the engine exhaust plume [2]. Aircraft gas turbine engines produce a variety of particles, yet it has been understood from in-situ measurements that non-volatile black carbon aggregates are the dominant source of ice-forming particles. However, with cleaner combustion technologies and the adoption of alternative fuels, non-volatile black carbon particle emissions are expected to decrease or even be eliminated [3]. Under these conditions, contrail properties will depend upon the concentration and characteristics of particles other than black carbon.



Ultrafine (<100 nm) jet lubrication oil droplets constitute a significant fraction of the total organic particulate matter released by aircraft [4], however their ability to form contrail ice crystals is hitherto unexplored. In this work, we experimentally investigate the activation and freezing behaviour of lubrication oil droplets using an expansion chamber [5], assessing their significance as ice-forming particles. We generate lubrication oil droplets with a geometric mean mobility diameter of (100.9 ± 0.6) nm and show that these activate to form water droplets, despite their hydrophobicity (see Fig. 1a). These droplets subsequently freeze homogeneously at ~235 K, as shown in Fig. 1b. This study demonstrates that ultrafine lubrication oil droplets have the potential to form contrail ice crystals under typical mixing conditions behind an aircraft. While further work is needed, these results will support the understanding of contrail properties and the impacts associated with new combustion technologies, sustainable aviation fuels and hydrogen gas turbine engines.

[1] David Simon Lee et al., *Atmospheric Environment*, **2021**, 244, 117834

[2] Ulrich Schumann et al., *Journal of Applied Meteorology and Climatology*, **2012**, 51 (7), 1391 - 1406

[3] Christiane Voigt et al., *Communications Earth & Environment*, **2021**, 2 (114)

[4] Florian Ungeheuer et al., *Communications Earth & Environment*, **2022**, 3 (319)

[5] Ottmar Möhler et al., *Atmospheric Measurement Techniques*, **2021**, 14, 1143 - 1166

Aircraft, marine and other non-road sources, Contributed Lecture

Connecting size-resolved aerosol composition and gas-phase volatile emissions from aircraft engines at the Zürich airport

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Aircraft at airports emit ultra-fine particles (UFPs) into the surrounding community. Aircraft oil includes metals and phosphates linked to neurotoxicity [1]. It was only recently suggested that gas-phase oil molecules nucleate UFPs [2].

As part of the Aviation Plume PROPeRtIes AT point of Exposure (APPROPRIATE) research campaign, we carried out laboratory, engine test site, and airport ambient field measurements. Measurements included VOCUS Proton Transfer Reaction Time of Flight Mass Spectrometry (VOCUS PTR-ToF-MS), Extractive Electrospray Ionization ToF-MS (EESI-ToF-MS) coupled to an Aerodynamic Aerosol Classifier (AAC) for size-selection, Aerosol MS (AMS), cavity ring-down detection of 10 trace gasses, multi-orifice uniform deposition impactor (MOUDI), PM size distribution (1-560 nm), and total PM number (>2.5 nm and > 7.5 nm).

In the laboratory, we tested the gas and chemical composition of aerosolized fresh and used aircraft engine oils to determine several unique tracers. At the engine test site (SR Technics, Switzerland) we sampled the emissions of newly overhauled engines in several operating states. Finally, we conducted six weeks of ambient measurements near a runway at the Zürich airport (Fig. 1A).

Aerosol chemical markers of used oil and commonly known oil components (e.g. tricresyl phosphate) were detected at both the test site and field site. We will present their emission size distribution with the engine state (Fig. 1B) and connect these observations with volatile gas-phase measurements.

Finally, we show that ambient field measurements detected several individual aircraft UFP plumes (e.g. Fig. 1C) and many oil markers. We will discuss efforts to connect the observed gas-phase and aerosol phase markers to relate these components to UFP nucleation mechanisms and thus identify key factors affecting local air quality.

This work was supported by the Swiss Federal Office of Civil Aviation (SFLV 2020-080). We would like to acknowledge the support from SR Technics, Frithjof Siegerist, and the Zürich Env. Protection Office AWEL.

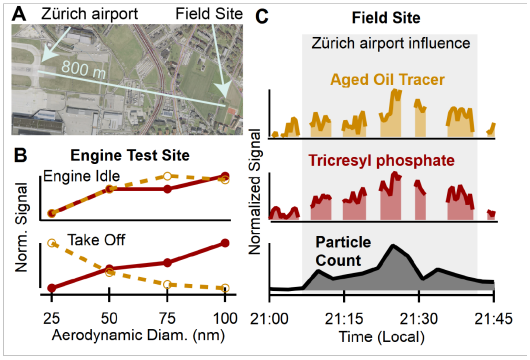

Figure 1: (**A**) Map of the airport field site. (**B**) Unique tracers (labeled in C) detected at the engine test site differ in size distribution depending on the engine operating state. (**C**) Unique aircraft oil tracers detected in particles downwind of the Zürich airport. Results in (B) and (C) are from the AAC + EESI-ToF-MS.

[1] Rahim, M. F., Pal, D. and Ariya, P. A. *Environ. Pollut.* **2019,** 246, 734-744.
[2] Ungeheuer F., et al. *Commun. Earth Environ.* **2022**, 3, 1-8.

Aircraft, marine and other non-road sources, Contributed Lecture

Field Study on the Impact of Sustainable Aviation Fuels on Helicopter Engine Emissions

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In contrast to aircraft jet engine emissions, the number of studies reporting emission factors of helicopters are limited due to different certification procedures. Nevertheless, the emissions from helicopter engines may contribute to the impact of airports on local air quality. With regard to the emission of non-volatile particles, the application of sustainable aviation fuels (SAF) has proven to be beneficial in jet engines when comparing to fossil Jet A-1 with lower fuel hydrogen content. Therefore, it is of interest if similar observations are true for helicopter engines as has been indicated by test rig studies using SAF or alternative fuel components [1]. The present study describes in-field measurements on an Airbus H145 helicopter that is operated by the German ADAC air rescue service. The helicopter is operated on a 30% SAF blend for several months. The comparison on emission properties bases on a regular fossil Jet A-1.

Figure 1: Sampling probe behind the engine during the test runs

Sampling on the helicopter has been performed with a probe behind the starboard engine at a distance of approx. 1 m to the engine exit plane. The aerosol is transported via a 30 m heated sampling line to a nearby van equipped with instruments for aerosol and gas characterization. The particle number concentration and particle size distribution were monitored via a DMS500 (Cambustion) and a Scanning Mobility Particle Sizer (TSI). Within a stable power setting of the engine, the instruments were switched between regular sampling and catalytic strippers (CS10, CS015, Catalytic Instruments) to remove the volatile fraction (nvPM). Further the concentrations of CO2 and NOx were continuously monitored. The engine was operated at three different power settings that roughly correspond to “idle”, “cruise” and “take-off” conditions. The experiment was performed with two different fuels, a 30% SAF blend and a fossil Jet A-1. During the different fuel runs, a shift in the particle size distribution was observed which hinders a direct comparison based on nvPM_number. This shift might be caused by agglomeration in the sampling system. The comparison based on the nvPM_volume, however, reveals a significant reduction in particle emission when changing from fossil Jet A-1 to the SAF blend. Further details on the experiment will be presented in the conference contribution.

[1] Alexander Rabl, Christopher Mull, Martin Härtl, Christian Helcig, Volker Gümmer, Experimental Investigation of Performance and Soot Emissions of Oxygenated Fuel Blends in a Small Aero Engine, 2023, submitted for publication.

Aircraft, marine and other non-road sources, Contributed Lecture

Swiss research of particle emissions reduction with sustainable aviation fuels

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It is the year 2035. Mr. and Mrs. Swiss are flying for a long trip far away. Their aircraft is fueled with a blend of fossil and sustainable aviation fuel (SAF) from a biogenic feedstock, for which they paid a premium. How much lower are the non-volatile PM (nvPM) emissions on the ground and at cruise with different SAF blends compared to a fossil jet fuel today?

To answer this question, we first look at fuel parameters used for correlating fuel composition effects for nvPM and results of emission test campaigns with SAF using the Swiss Mobile Aircraft Emissions Measurement System (SMARTEMIS). The emission tests with different fuels were done in an engine test cell at SR Technics, Zurich airport, and in a ground test of an engine installed on aircraft. The exhaust sample was extracted < 1 m downstream of the engine exhaust nozzle, either with a single-hole traversable probe or a multi-hole cruciform fixed probe. SMARTEMIS sampling and measurement downstream of the probes was done in compliance with the nvPM and gaseous emissions certification standards [1].

The seminal work of Brem et al. 2015 [2] investigated the effects of different types of fuel aromatics and confirmed the power-dependent effect of the fuel composition on nvPM mass and number for a common large turbofan engine. The same engine type was used for the first-ever test with a SAF blend in a commercial engine done in Switzerland [3]. The SAF made using hydrotreated esters and fatty acids (HEFA) was tested at volumetric blending ratios of 5%, 10%, and 32%. Both these campaigns provided data for the development of a standardized fuel composition correction now utilized in the nvPM emissions certification procedure [1]. While this correction is based on numerous datasets, more work is needed to confirm its applicability for various engine types and higher SAF blending ratios. Most recently, we performed emission tests of a small turbofan engine of a business jet fueled with regular Jet A-1 and a HEFA-SAF blend close to the currently highest permitted blending ratio of 50%.

These findings will help us further develop the nvPM measurement methodology, emissions predictions, and health effect assessment. Moreover, we intend to popularize the SAF benefits beyond lifecycle CO2 to foster production scaling and inform the future travelers in our story.

[1] Annex 16 to the Convention on International Civil Aviation: Environmental Protection, Vol. II – Aircraft Engine Emissions, 4th ed., ICAO: Montreal, CA, **2017**.

[2] Benjamin Brem et al., *Environmental Science & Technology*, **2015**, 49, 22, 13149–13157.

[3] Lukas Durdina et al., *Environmental Science & Technology*, **2021**, 55, 21, 14576–14585.

Ambient air particles, secondary pollutants, Contributed Lecture

Development and Evaluation of a High-Flow-Rate Cascade Impactor for the Collection of Coarse, Fine, and Ultrafine Particulate Matter on Gelatin Filters

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This study presented the development of a high-flow-rate cascade impactor that uses water-soluble gelatin filters for the collection of multi-sized ambient PM. The gelatin cascade impactor (GCI) was designed with an operating flow rate of 100 lpm and two impaction stages with cut-points of 2.5 µm and 0.2 µm. Laboratory tests with artificially-produced aerosols were conducted to obtain the particle collection efficiency curves of the GCI's impaction stages. In addition, field tests were carried out using the GCI with a personal cascade impactor sampler (PCIS) simultaneously to collect ambient $PM_{2.5}$ for further toxicity tests, including dithiothreitol consumption (DTT) and macrophage-based reactive oxygen species (ROS). The findings showed that the experimentally determined cut points of the two impaction stages matched the theoretical calculations, even with the use of alternative substrates (e.g., quartz filters) instead of gelatin substrates. Additionally, the GCI was demonstrated to more effectively collect toxic PM constituents compared to the PCIS, as evidenced by its higher (i.e., 2-4 times) ROS and DTT activities (i.e., 8813 µg Zymosan Units/mg PM and 26.4 nmol/min/mg PM, respectively). The GCI's ability to collect large amounts of toxic PM constituents, as well as its use of water-soluble filters for 100% particle extraction efficiency, has made it a valuable technology for aerosol sampling and inhalation/toxicity studies.

Biomass-, biofuel- and synfuel combustion, Contributed Lecture

Particulate matter and CO_2eq. emissions from three Euro 6d bi-fuel LPG passenger cars, fed by an innovative LPG/DME 80/20 (V/V) blend

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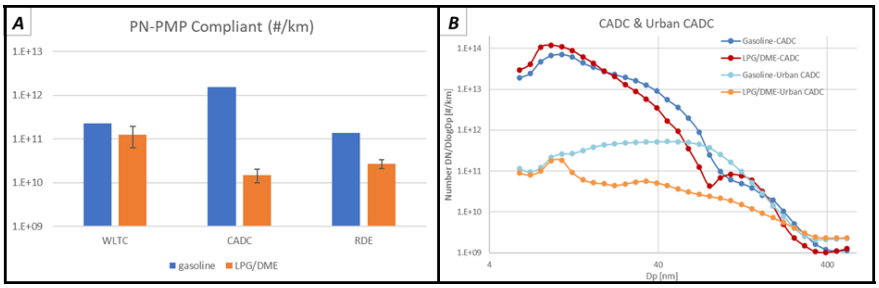
Exhaust emissions of particulate matter and gaseous species, both regulated and unregulated, also evaluated as CO_2equivalent, were measured during laboratory and on-road tests on bi-fuel LPG/gasoline passenger cars fed by both gasoline and an innovative LPG/DME blend, which represents a potential renewable fuel since LPG and DME can both be produced from biomass and renewable sources. For this reason, DME (Dimethyl ether) has been considered by the EU as a part of its biofuel energy mix of 2030 and it is then mentioned in the Renewable Energy Directive (RED) II [1]. Its use has been investigated as a blend component in diesel engines, but not many studies have been conducted on its use for spark ignition engines. The tested blend 80% LPG and 20% DME, which was determined through CFR engine tests, was compliant with the EN 589 EU Standard. Three Euro 6d bi-fuel vehicles (two small and one medium segment) were tested in laboratory, following the homologation WLTC and the hot-start CADC driving cycles. The solid Particle Number emission (PN-PMP compliant) was measured and the total particle size distribution was determined using an Engine Exhaust Particle Sizer (EEPS). The particulate matter mass (PM) was measured as well. Additionally, the CO_2equivalent was determined from CO_2, N_2O and CH_4 detections, useful for an LCA that is under development. During the on-road tests, carried out in the city of Milan in compliance with real driving emission (RDE) regulation, the CO_2equivalent and PN measurements were determined using a Portable Emissions Measurement System (PEMS). Emission factors for gasoline and for LPG/DME fueling were calculated and compared. The use of LPG/DME fuel led to a decrease of solid particles emissions (within 23nm-2.5µm range), as shown in the Figure (A) below. Similar solid and volatile particles emissions within 5.6-560nm range were detected by EEPS-measurements using either gasoline or the LPG/DME blend. Analyzing the particle size distributions, a higher production of some ultrafine particles (< 10nm) was noted by testing cars at high speeds, while lower speeds impacted the production of slightly bigger particles (> 30 nm). During the hot-start cycle, a noticeable decrease was found during the Urban phase of the cycle when the cars were fed by LPG/DME, as shown in the Figure (B) below. It is important to underline how urban routes have the greatest impact on human health since the exposure to the particulate matter is greater. RDE tests confirmed a lower production of solid particles using the innovative fuel blend. When the cars were fed by LPG/DME, lower emissions of CO_2 equivalent were measured both in laboratory and on road. In conclusion, the results of the work show that the innovative and potentially renewable LPG/DME 80/20 (V/V) blend can be helpful in terms of lower PN emissions and especially lower GHG emissions, besides being fully compliant with EN589 and with Euro 6 exhaust emission standards, with interesting perspectives towards the Euro 7 ones.



[1] Directive (EU) 2018/2001, pag.63.

Biomass-, biofuel- and synfuel combustion, Contributed Lecture

An updated mechanism of particle formation in non-premixed hydrogen combustion in internal combustion engines

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[1]Technion - Israel Institute of Technology

Introduction & Background: Gaseous jet dynamics is a major factor affecting formation of particulate matter and gaseous pollutants in combustion of hydrogen or hydrogen-rich reformates. Mitigation of particulate matter formation is essential to ensure penetration of a novel high-efficiency propulsion cycle with High-Pressure Thermochemical Recuperation which has been developed in the Technion. The latter is based on the utilization of the waste heat to produce a hydrogen-rich reformate through endothermic reactions of a primary fuel reforming. The recent experimental studies found elevated particle emissions in a non-premixed hydrogen and hydrogen-rich reformate combustion compared to various hydrocarbon fuels in a wide range of direct-injection (DI) spark-ignition (SI) engine operation regimes. This discovery contradicts all previously published data on particle formation in hydrogen combustion. The main goal of the reported study was is to provide a conceptual description of particle formation mechanism in non-premixed hydrogen combustion in internal combustion engines (ICE) that enabled us to match the previously published and newly gained data.

Methodology: We have accomplished the interlinked series of fundamental and engine-based experiments which allowed us understanding and describing the physics behind the observed peculiarities in particle formation. Optical imaging techniques, as high-speed Schlieren and Particle Image Velocimetry, were employed to characterize the flow field of an underexpanded impinging transient gaseous jet in a confined (engine-like) environment, and a laboratory research engine was used for detailed combustion and particle emission analysis. The engine was based on a single-cylinder Lister-Petter AD1 4-stroke engine with a high compression ratio (r=15.5) modified for SI operation. Particle number concentration and size distribution measurements were performed with TSI model 3090 Engine Exhaust Particle Sizer Spectrometer. Exhaust particles were characterized using the Inductively Coupled Plasma Spectroscopy. Different fuel supply methods (PFI and DI) and gaseous fuels (hydrogen, methane, and the reformate) were experimentally compared.

Results & Conclusions: The gained results showed that non-premixed hydrogen combustion in ICE may enhance particle formation, which is substantially more intensive compared to hydrocarbon fuel combustion. This phenomenon is a result of a combined influence of the hydrogen’s low flame quenching distance that intensifies lubricant evaporation, and the interaction between the lubricant vapor formed near the cylinder surface, and the gaseous jet. The obtained experimental data showed that gaseous fuel vortex evolved after jet impingement with the cylinder wall subsequently climbs over the liner wall, thereby sweeping away the lubricant vapor into the combustion chamber bulk. This entrainment mechanism was found to be stronger compared with the lubricant entrainment in the free-jet region. The excessive entrainment of lubricant vapor into the chamber bulk with its subsequent involvement in the combustion process, results in the elevated particle formation. The lower specific LHV of the reformate fuel compared to hydrogen, requires longer injection duration and/or higher injection pressure. These contribute to longer and more intensive vortex flow along the cylinder wall, thus explaining the previously observed higher particle formation arising from reformate combustion, compared to hydrogen.

Biomass-, biofuel- and synfuel combustion, Contributed Lecture

The optical properties of combustion generated particles from 1-D hydrogen doped ethylene flames

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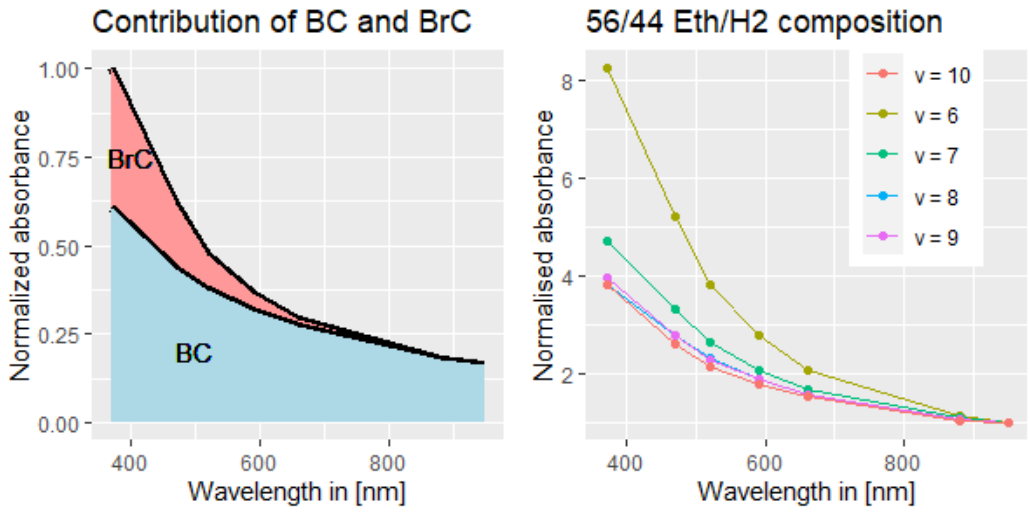
[1]University of Groningen, ESRIG, Centre for Isotope Research, [2]University of Groningen, ESRIG, Energy Conversion

It is well known that black carbon (BC) has a large warming effect on the climate due to the absorption in a wide range of wavelengths [1]. The effects of coloured organic carbon (also known as brown carbon (BrC)) are also significant, as in some studies they account for 10% to 20% of the near atmospheric UV absorption [2]. Due to the complex nature of brown carbon, it is not very known yet which combustion conditions lead to the formation of brown carbon. A study is done to examine the optical properties of combustion generated carbonaceous aerosols. Various premixed burner-stabilized 1-D flat flames of mixtures of ethylene (C2H4) and hydrogen (H2) are analysed by varying H2/C2H4 ratio and exit velocity. The equivalence ratio is kept constant at 2.3. The exit velocities range from 6 cm/s to 10 cm/s, while the hydrogen fraction in fuel ranges from 0% to 50%. An AE43 aethalometer is used to measure the extinction coefficient at different wavelengths. Using an extrapolation of the measured extinction coefficient by the Absorption Angstrom Exponent a qualitative distinction can be made between the absorption contribution by BC and BrC. A representation of such a distinction is shown in the left figure, where one arbitrary sample is used to display the contribution of BC and BrC to the total wavelength depending absorption.

Additionally, the flame temperature as a function of height above the burner (HAB) is modelled using the San Diego mechanism. The in-situ soot volume fraction is also measured using Laser Light Extinction (LLE) at different HABs. The preliminary experimental results show that a lower temperature and a higher hydrogen content in the fuel result in higher BrC values. The soot volume fraction in flame is found to be the lowest for a higher hydrogen content and a higher exit velocity. A preview of some results is seen in the right figure, where the wavelength depending absorbance for a fixed fuel composition (56% ethylene, 44% H2) is shown for exit velocities ranging from v = 6 to 10 cm/s.



[1] Bond et al, *J. Geophys. Res. Atmos.,* **2013,** 118:5380-5552

[2] Kumar et al, *Atmos. Chem. Phys.,* **2018**, 18, 17843-17861

Biomass-, biofuel- and synfuel combustion, Contributed Lecture

Catalytic solutions for the cleansing of wood stove emissions: a physico chemical characterization of effluents generated by wood combustion and their maturation in the atmosphere

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In this time of energy crisis with supply instability, biomass combustion has been seen by numerous citizens as an alternative way for heating their home. This paradigm shift was reflected in the increase in sales of wood stoves. At the same time, it was estimated by Clean Air For Europe (CAFE) in 2000 that domestic wood stoves emit 38% of $PM_{2.5}$. In this context, international and national regulation commissions are working on new norms such as Ecodesign or Blauer Engel to prompt a decrease in emission of new products. To comply with these emission limits, new abatement technologies have been developed. One of the most promising technologies is the catalytic oxidation.

The Bao-Lian Su's group has experience with the catalytic oxidation of volatile organic compounds (VOC) and recently they have developed a catalytic solution for wood stoves. This patented technology has been used to create a spin-off company that specialises in the development of catalytic systems. A first approach to evaluate the catalyst's performance was done according to the norm EN16510. It was measured respectively a decrease in 87%, 25% and 66% of CO, total hydrocarbons (THC) and total suspended particles (TSP). However, the reduction in THC does not take into consideration the generated products and the formation of secondary organic aerosol (SOA).

Further testings were done on to achieve a better understanding of the impact of the catalyst on fumes. One of them was a study showing that polycyclic aromatic hydrocarbons (PAHs), known for their toxicity, were reduced by 90% when our catalyst was in place. Correspondingly, there was also a 80% reduction in cell moratility, when cells were exposed to emissions that were passed through the catalyst. Thus, the catalyst we developed was effective at removing primary emissions and reducing the toxicity of the primary emissions.

However these studies did not probe the effect of aging of VOCs nor the production of SOA, which Weitekamp *et al.* (2019) has shown that increases their toxicity. The photochemical transformation of VOCs with OH radicals creates SOA. To have a holistic view of the effect of the catalyst we have developed, it is necessary to simulate and analyze the formation of SOA in state-of-the-art facilities. In this context, the atmospheric chemistry laboratory of the Paul Scherrer Institute internationally recognized for its expertise on SOA, have been contacted.

In conclusion, this multidisciplinary study will detail the impact of a novel catalyst on the composition of SVOC from a wood stove and investigate their SOA potential. From an industrial point of view, this work will provide unprecedented insight into the efficacy of our catalyst and its use with a wood stove under real conditions and assist our spin-off company to better understand this technology and highlight the real impact of the implementation of this catalyst.

Biomass-, biofuel- and synfuel combustion, Contributed Lecture

Reduction of Particulate Emissions from Logwood Stoves by an Electrostatic Precipitator and the Influence of Their Position in the Flue Gas Duct and Stove Operation Conditions

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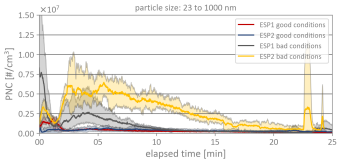
The Flue gas aerosol from logwood stoves consists of a wide range of particulate and gaseous pollutants. According to projections of the German Environmental Protection Agency (Umweltbundesamt (UBA)) those stoves* are responsible for about 25 % of PM2,5, most of which are ultrafine particles (UFP), emitted in Germany [1]. This work addresses the potential of electrostatic precipitators (ESPs) to reduce the emitted fine and ultrafine particles of logwood stoves. The focus is on the influence of the position of the ESP in the flue gas duct and stove operation conditions. An ESP shows deposition rates of > 90% regarding particle number concentration of fine and ultrafine particles. However, the reduction efficiency can decrease significantly due to negative impact of the above-mentioned influences.

The reduction effect towards particle number concentration (PNC) of the ESPs at different positions in the flue gas duct was investigated. ESP 1 was positioned at the outlet of the stove (average temperature: 300 °C) and ESP2 8 m downstream the furnace (average temperature: 120-150 °C). Additionally the reduction efficiency for good and bad stove operation conditions was compared. The results show a similar reduction-potential for both ESP-positions under good stove operation conditions with reduction rates of about 96 % for both ESPs. With deterioration of the operation conditions the reduction-rate for ESP2 decreases down to 80 % under bad conditions. For ESP2 the changes are much less pronounced, with a decrease of the reduction rate down to 92 %. Figure1 shows the particle number concentration regarding fine and ultrafine particles for ESP1 and ESP2 over the duration of one batch for the best and the worst operation-condition-categories. The curves for each point of investigation reflect the different performance of the ESPs under changing conditions. It is well known that temperatures between 100-200 °C negatively affect dust resistance, attenuating the reduction efficiency [2]. Which likely contributes to the higher decrease of the performance of ESP2. Due to the lower temperature at Position 2, there is also an expectedly higher concentration of condensed and adsorbed organic compounds (e.g., polycyclic aromatic hydrocarbons (PAHs)) bound to the particles than at Position 1.This likely leads to changes in dust resistance, and thus, also effects the reduction efficiency. To investigate the two assumptions, we measured the current of the ESPs at the two positions and the particle size distribution of the emitted particles. We discuss connections between the observations made and present an approach to improve precipitation at Position 2.

**the data refers to emissions due to residential wood combustion and small furnaces, the majority of the emissions (PM2,5) in this group is attributable to logwood fired stoves.*



[1] Umweltbundesamt, *Emissionen ausgewählter Luftschadstoffe nach Quellkategorien*. *Nationale Trendtabellen für die deutsche Berichterstattung atmosphärischer Emissionen seit 1990, Emissionsentwicklung 1990 bis 2020*, **2022.**

[2] Stackelberg, J. von and Schmoch, *Handbuch Elektrofilter*, Springer Fachmedien Wiesbaden, Wiesbaden, **2018.**

Biomass-, biofuel- and synfuel combustion, Contributed Lecture

Realization of Efficient and Environmentally Sustainable Combustion of Sargassum and Waste Biomass

B. M. Bailey[1]

[1]Global Clean Diesel

Abstract for 2023 ETH

The realization of economical bio-oil utilization via heat engine combustion (less fuel processing) is accomplished through efficient direct combustion. This effectively removes the costly upgrading and subsequent transportation requirements. Limited fuel processing and direct energy utilization, near the biomass location, are hence realized. Global attention has recently been shed on the ecological challenges of the >10 million metric tons of Sargassum located in the Atlantic Ocean. Global Clean Diesel, GCD has had their long-term goal focused on meeting such challenges with an economic bound technology enabling real world global warming reduction opportunities.

GCD's presentation will focus on how biocrude can achieve negative emissions of Particulate Matter (PM) while achieving efficient operation. Unburned hydrocarbons and PM are efficiently captured and recycled back into the HTL biofuel production cycle. Hydrothermal Liquefaction, HTL of the biomass in combination with their globally patented ultra efficient exhaust aftertreatment Cool Particulate Regeneration (CPR) technology, next generation production Gasoline Particulate Filters (GPFs), and sophisticated catalysts applied directly to the Diesel Particulate Filter (DPF) are the technology enablers to be highlighted. Laboratory testing results will be presented for discussion.

Will provide references.

Brake and tyre wear, on-combustion emissions, Contributed Lecture

Developing real-world emission factors for individual vehicles using low-cost sensors

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Vehicular exhaust emissions are known to be one of the primary contributors to the poor air quality in urban areas. However, quantification of real-world vehicular emissions is quite limited in low- and middle-income countries such as India. Developing real-world vehicle emission factors (EFs) using reference-grade instruments requires a significant amount of resources. This study aims to develop the individual and fleet vehicle EFs and the fraction of high-emitting vehicles using high-time resolution, low-cost sensors from near-road measurements – a first-of-its-kind study in India. Traffic and air pollutant measurements were conducted at the kerbside of a street canyon in Mumbai, India. The individual vehicle fuel-based EF_{CO} and EF_{NOx} were estimated using the plume-identification technique coupled with the information obtained from the vehicle registration number plates. The fleet mean (±SD) EF_{CO}, EF_{NO}, and EF_{NO2} were 6.69 (±3.36), 1.47 (±1.24), and 0.45 (±0.33) g/kg, respectively, while for EF_{PM1}, $EF_{PM2.5}$ and EF_{PM10} were 0.75 (±0.36), 1.27 (±0.60) and 2.22 (±1.12) g/kg, respectively. The developed individual vehicle EF_{CO} and EF_{NOx} were greatly varied within each vehicle type due to differences in emission control technology, engine size, and the prevalence of “super-emitters”. Approximately 14% of vehicles in the fleet were identified as super-emitters, responsible for 37-54% of total emissions, primarily from private passenger vehicles such as cars and two-wheelers. The EF_{CO} and EF_{NOx} from these super-emitters were 3 to 30 times greater than the laboratory-reported emissions. Our study highlights the importance of stringent vehicle inspection and maintenance programs in addition to improving emission standards to control tailpipe emissions from vehicles.

Brake and tyre wear, on-combustion emissions, Contributed Lecture

Particle Emissions from Brake and Tyre Wear – Results from the Phase 1 study for the UK DfT

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Ricardo was contracted by the UK Department for Transport (DfT), to develop a “proof-of-concept” system for measuring mass and number of non-exhaust emissions (NEE) particles, under real-world driving conditions. The project is planned to comprise three phases. The initial, recently completed phase, saw the development of on-board approaches to sample and measure brake and tyre wear particles from light-duty vehicles.

Tyre wear particles were sampled from a VW Caddy van, using an open duct situated immediately behind the contact patch between tyre and road, while brake wear particles were sampled from an enclosed fixed volume created by enclosing the pad and disc. In both cases, particles were transported near-isokinetically from the point of release to a sample tunnel, where measurements of number-weighted particle size distributions were determined by two Dekati ELPI+ systems. One ELPI+ was heated, with the other at ambient temperature, allowing discrimination between particle volatilities. A Dekati eFilter was used to provide a real-time mass signals and cumulative PM mass samples, the latter were photographed and subjected to basic chemical analyses.

To avoid particle losses from the brake enclosure, and to manage temperatures, a constant stream of HEPA filtered air was supplied to move particles to a sample tunnel, this also providing brake system cooling, positive pressure within the enclosure and preventing particle ingress from ambient air.

Measurements were made on the chassis dynamometer from a bespoke drive cycle constructed to produce high particle emissions, from road tests in the urban area and from repeated moderate and aggressive braking events on a test track.

Results showed strong signals of particle release from brakes and tyres in response to braking events, with both solid and volatile particles produced. Particle number emissions from brakes were of a similar order to published values from brake dynamometer testing, while mass emissions sampling appeared to be consistent with collecting PM2.5. Tyre emissions sampling proved more challenging than brake sampling, with background contributions often dominating overall collected masses.

Brake and tyre wear, on-combustion emissions, Contributed Lecture

Evaluation of Tailpipe Solid Particle Number Measurement Methodologies

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The measurement of solid particles down to 10 nm is being incorporated into the global technical regulations (GTR) and also being proposed for Euro 7 regulations. Currently, these measurements can only be made either from constant volume sampler (CVS) tunnel or from partial flow dilution system (PFDS). However, there has been interest in understanding if tailpipe measurements of SPN should be allowed and subsequently recommended to European Commission. Thus, this study is the major contributor would be critical in deciding the tailpipe SPN measurements for certification testing. This extensive study evaluates two different tailpipe measurement methodologies. One methodology adds the 0.5 m heated line typically at 150°C upstream of PN system. The other system adds a heated diluter close to the sampling point maintained at 190°C followed by a 4 to 6 m heated transfer tube. Overall, measurements from two PN systems with different tailpipe methodology and with capability to measure down to 10 nm were compared against each other and against reference measurement at CVS or PFDS, if available. So far, measurements have been taken from three natural gas (NG) and three diesel engines. In case of NG 1, cold dilution PN system was at tailpipe and reference was at PFDS. Later, 0.5 heated line was added to the reference and sampled from the similar location as cold dilution PN system. It was found that the heated line temperature may need to be reduced to ensure that the sample inlet temperature remains less than 150°C due to NG engine exhaust temperature up to 800°C which resulted in significant thermophoretic losses. Accordingly, measurements were made with 120°C and results were compared against cold dilution PN system. For NG 2 & 3, both PN systems with cold dilution and heated line at tailpipe were compared against the reference PN system with 23 nm condensation particle counter (CPC) and additional 2.5 nm CPC. Reference PN system with 2.5 nm CPC gave insight on which tailpipe methodology could be more accurate for a given brake-specific PN level. In case of diesel 1 & 2, all tailpipe PN systems (without heated line and cold dilution) and reference PN system with 23 nm and 2.5 nm CPCs were installed at the CVS tunnel. This was done to ensure that systems are in within measurement variation of each other and differences observed at the tailpipe are only due to the additional losses of tailpipe kit and due to complexity of tailpipe measurements. Data from diesel 3 was collected from the tailpipe location and reference system with two different CPCs was situated at PFDS. More data has been collected which will help in answering following questions. What causes the difference between two tailpipe methodologies and impact of sampling location? Does increase in sub-23 nm fraction impacts the tailpipe measurement? Does tailpipe SPN concentration impact the tailpipe measurement? Are tailpipe methodologies independent of engine technologies? And finally, are differences observed through tailpipe within acceptable measurement variation?

Brake and tyre wear, on-combustion emissions, Contributed Lecture

Evaluation of a miniaturized exhaust emission measuring system using an optoacoustic BC sensor and low-cost gas sensors

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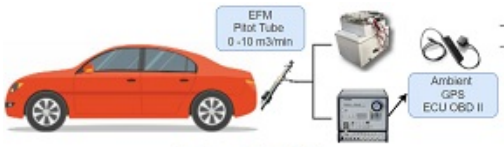
Introduction

The Portable Emissions Measurement Systems (PEMS) is used to measure vehicle emissions while operating in real-driving conditions. The high cost of purchasing, as well as the elaborate testing using PEMS, indicate the need to develop simple systems that could be used as screening tools. The current study aims to assess whether a simple sensor-based emission measurement system (SEMS), which uses a novel optoacoustic black carbon (BC) sensor combined with low-cost gas sensors, can offer complementarity to commercial PEMS. This study focuses on the sensitivity and robustness of the implementation, using on-road tests as reference.

Methodology

The SEMS system has been first evaluated in the lab showing very good correlation with reference instruments. Within the framework of this study, a sampling system has been designed, consisting of a custom-made heated line and a dilution system to enable testing under on-road measurement conditions. Fig. presents the experimental setup for the on-road measurements and the sensors specifications of the SEMS. A Pitot tube-based exhaust flow meter (EFM) has been installed at the vehicle's tailpipe where both the PEMS and the SEMS sampling probes are directly mounted.



Experimental description

Detection Species	Technology Used	Measurement Range
BC	Optoacoustic	Detection Limit: 2 μg/m³
CO_2	Non-Dispersive Infrared	0-20 %
CO	Electrochemical	0-10000 ppm
NO	Electrochemical	0-500 ppm

SEMS Sensor Specifications

Results & Conclusions

The results aim to compare the measurements from the two devices for each pollutant in terms of average deviation, response time and overall ability to capture fluctuations and trends. The measurements performed included representative routes and driving behaviors, according to and beyond the RDE profile. Since the PEMS system measures PN and there is no other device that can measure tailpipe BC on road, an estimation can be made about the percentage of total particles that are BC under on-road testing. Overall, for the first time a SEMS system that can also measure BC concentration was demonstrated during real-driving conditions and showed satisfactory operation for screening high emitting vehicles. This first campaign indicated the need for further miniaturization and optimization of the sampling system.

Acknowledgments

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Brake and tyre wear, on-combustion emissions, Contributed Lecture

Elemental content of brake and tire wear PM2.5 and PM10 at Near-Road Environments.

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Brake and tire wear particulate matter (PM) have become the dominating source of traffic-related emissions in California, USA. The EMission FACtor (EMFAC) model from California Air Resources Board predicts these non-tailpipe emissions to remain dominant contributors of on-road PM. Brake and tire wear contain traces of heavy metals, therefore may dominate metal emissions near major roadways and highways. This creates concern as these particulate sources can increase toxicity and impact the health of exposed populations and nearby communities.

The objective of this study is to assess the level of exposure to non-tailpipe emissions in near-road environments. The study investigates metal contents and size distributions found in PM2.5 and PM10 measurements next to two major highways in California, USA.

Real-time and gravimetric measurements occurred over a two-week period in the winter of 2020 prior to the COVID-19 pandemic. PM measurements were collected at the proximity of both sides of the highways to subtract urban background at the measurement location. This study is part of a Real-World Tire and Brake Wear Emissions Project funded by the California Air Resources Board. The results of this analysis are in conjunction to chemical analysis, source apportionment, and health effects of the particles in the near road environment studies by project collaborators [1-4]. The presentation includes the signature brake mode in particle size distributions measured at near road, size speciated elemental analysis to identify markers for brake, tire, and road dust.

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Brake and tyre wear, on-combustion emissions, Contributed Lecture

CARB updates to EMFAC brake emissions factors using dynamometer tests for light-duty vehicles

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The projection of the environmental effects of particulate matter emitted by light vehicles' brakes must rely on current and representative methods. To accomplish this objective, the California Air Resources Board embarked on a project to use a dedicated driving cycle as part of the laboratory measurements to update the EMissions FACtor model (EMFAC) 2021. After an overview of the test campaign, this presentation focused on three aspects of the project:

1. Detailed comparison of the California Brake Dynamometer Cycle (CBDC) to the Worldwide Harmonised Light Vehicle Test Procedure (WLTP) Brake Cycle developed by the European Commission as part of the GRPE-87-40e, including differences in emissions factors during laboratory testing

2. Overview and examples of the updates to the EMFAC model for Light-Duty Vehicles incorporating the results from current vehicles, friction formulations, and using a laboratory setup aligned with the PMP setup for particle mass and particle number measurements

3. Overview of the trace metals and chemical composition analysis on brake wear particulate matter emissions

The presentation relies on vehicle measurements, inertia dynamometer testing, and chemical analysis at the CARB laboratories.

Brake and tyre wear, on-combustion emissions, Contributed Lecture

Integrating a particulate filter system in the frontend: a step towards achieving emission-neutral vehicles

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The European Environmental Agency (EEA) has identified fine dust as a major environmental threat to human health [1]. While current regulations focus primarily on vehicle exhaust emissions, up to 85% of fine dust emissions come from unregulated sources such as brakes, tires, and road abrasion [2].

To address this issue, a comprehensive approach has been developed that involves an integrated fine dust particle filter. This filter can be installed in unused spaces in the front end of vehicles and is an effective and sustainable way to improve the emission balance of vehicles and promote better air quality, regardless of the drive system used.

However, the implementation of this filter requires the development of specific, high-efficiency filter elements that have a low-pressure loss level to ensure proper thermal management. Additionally, the filter must have a high dust holding capacity to ensure customer-friendly service intervals, and must be reinforced to withstand harsh operating conditions.

The integrated fine dust particle filter system makes it possible for all types of vehicles to become PM10 emission-neutral in a central Europe representative use case.

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Emission control of combustion engines, Contributed Lecture

Evolution of nano-scale particle structures within a pilot-main injected jet fuel flame in a small-bore optical diesel engine

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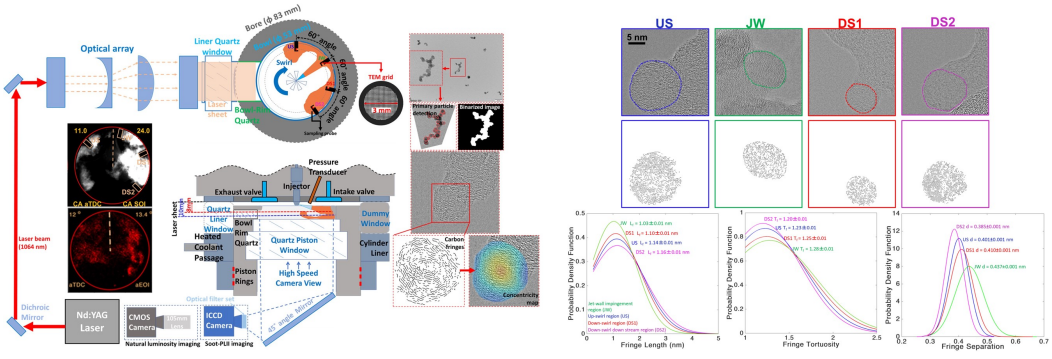
For a surrogate jet fuel specifically formulated for nanoparticle studies in an optically accessible small-bore diesel engine, combustion generated soot particles are sampled from multiple in-flame points and their structural evolution is analysed. The fuel contains 24% aromatics, similar with a conventional diesel fuel; however, its cetane number is only 40, posing a significant challenge for ignition and combustion control [1]. It is a type of low-reactivity jet fuel used in unmanned aerial vehicles for various tactical reasons, which requires pilot injection prior to the main injection and thus produces more soot particles during combustion. The sooting flame trajectory is first identified by performing planar laser-induced incandescence imaging and high-speed soot luminosity movie recording. Along this trajectory, four soot sampling probes are installed on the piston-bowl wall with 60° spacing angles for simultaneous sampling from the same firing cycles [1]. The first sampling point represents a jet-wall impingement region (JW) from which a jet flame starts to travel along the bowl wall while interacting with the swirl flow to both up-swirl and down-swirl directions. Three more sampling points therefore are selected for an up-swirl point (US), a down-swirl point 1 (DS1) and a down-swirl point 2 (DS2). The soot particles deposited on transmission electron microscope (TEM) grids via thermophoresis are image post-processed to extract various morphology parameters such as the size of soot aggregates, primary particles and fractal dimension as well as concentricity [2], length, tortuosity and gap of the carbon-layer fringes. The results indicate a large amount of small soot aggregates form at JW point due to fuel-rich mixtures. These aggregates grow in size while the number counts decline, suggesting the aggregate-to-aggregate agglomeration and soot oxidation occur at the same time. This process is accelerated on the up-swirl side due to the counter-flow condition, showing similar parameter values between US and DS2 points. Interestingly, the primary particles show minimal changes on both up-swirl and down-swirl points; however, the significant soot particle oxidation is evident in the subnano-scale carbon layer fringes with increased length and decreased tortuosity/gap. The concentricity also indicates the soot particles become a clearer core-shell structure as they flow along the bowl wall. This trend is also more evident on the up-swirl side, indicating a significant effect of increased flow/turbulence on soot evolution.



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Emission control of combustion engines, Contributed Lecture

Physical and chemical characterization of the particles emitted by a hydrogen fueled DI SI engine: the role of lube oil

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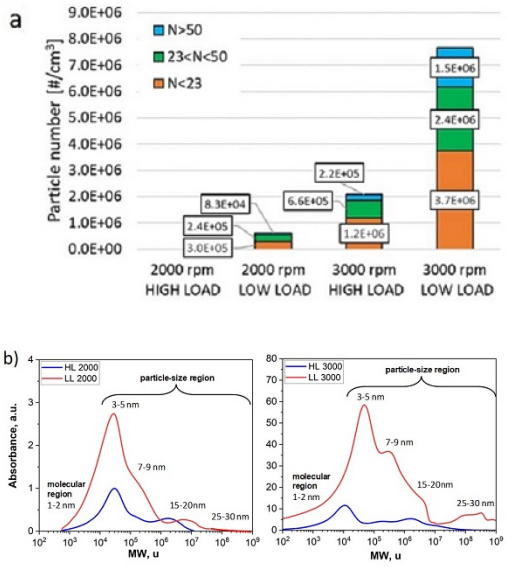
The use of low/zero carbon fuels such as hydrogen has great potential in reducing particle emissions. Since the carbon is not present in the structure of hydrogen, the lube oil plays a strategic role on particle formation. A thorough examination of the impact of lubricating oil on particle emissions and high levels of hazardous pollutants was made possible in the present study by the combination of two distinct analytical approaches, on-line and off-line, on gas and condensed exhaust, respectively. Experiments were carried out on a single cylinder, 250 cm^3 direct injection spark ignition engine fueled with hydrogen. Particles were characterized on-line in terms of number and size through an Engine Exhaust Particle Sizer coupled to a single diluter. Off-line chemical characterization by several analytical techniques was carried out on the condensed exhaust and particles, collected through a condensation sampling line connected to the tailpipe. Particles were detected at exhaust except for the condition at 2000 rpm high load where the size distribution is within the limit values of the spectrometer, Figure 1a. The extent of the particles varies according to the engine speed and load evidencing the different role of the oil because of the environmental conditions. The molecular weight (MW) distribution evaluated off-line on condensed exhaust with Size Exclusion Chromatography (SEC), reported in Figure 1b, offers complementary information with respect to the on-line particle number and size detection. A good agreement was observed between MW and the PSD in the common size region, evidencing higher concentration of particles in LL condition and at 3000rpm. Moreover, at 3000 rpm the MW distribution is shifted toward bigger sizes with both the techniques. Further, the SEC analysis is more sensible as it allows detecting the presence also of the particles at 2000 HL, which because of the low concentration are not resolvable with the EEPS. This study highlighted that the use of hydrogen as fuel for ICEs can result in the contamination not only of the atmosphere but also of water and soil thus reveling the necessity of optimizing the lubrication characteristics of hydrogen fueled engines.

Figure 1. a) Particle number and size b) MW distribution profiles of condensed exhaust from SEC acquired with UV-Visible detector at 370 nm



Emission control of combustion engines, Contributed Lecture

Off-Cycle Emissions of Particle Number from Gasoline and DPF diesel passenger cars in extremely low temperature and high-load conditions

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To evaluate regulated gases and solid particle number (SPN) emissions in high-load off-cycle conditions, two diesel vehicles with a diesel particulate filter (DPF) and a urea selective catalytic reduction (SCR) system, respectively, and four gasoline port fuel injection (PFI) vehicles were tested with the worldwide light-duty test cycle, including an Ex-hi phase. All the tested vehicles were developed for the Japanese market and did not comply with the Ex-hi phase. All vehicles exhibited higher CO_2 emissions in the Ex-hi phase than in low, mid and high phases. Increased NOx and SPN10-23 emissions were observed with the DPF vehicle. These increased emissions were due to the occurrence of passive regeneration of the DPF, and the urea SCR system was stopped as a result. The small gasoline PFI cars showed increased CO and SPN emissions in the Ex-hi phase. These emissions were due to enrichment control which occurred in a quite high load operation condition. The feature of emissions with enrichment control differed from that observed in a warming up process of cold start mode. SPN23 were mainly increased in the warming up process, although SPN10-23 increased in the Ex-hi phase with enrichment control. Hybrid vehicles seems to have less opportunities to show the enrichment control due to a motor assist.

Emission control of combustion engines, Contributed Lecture

HORIZON AeroSolfd project: Retrofit Filtration Devices for Cleaner Urban Mobility - Focus on highly efficient filter systems for large scale petrol engine retrofit

L. Rubino[1], A. Mayer[2], J. Czerwinski1[2], T. Lutz[2], L. Larsen[2]

[1]VERT Association, [2]VERT Association

HORIZON AeroSolfd is an EU co-funded project that will deliver affordable, adaptable, and environmentally friendly retrofit solutions to reduce tailpipe emissions, brake emissions and pollution in semi-closed environments. VERT, according to the long experience on retrofit and nanoparticle emissions reduction strategies, will focus on reducing emissions at tailpipe of gasoline vehicles by using best available retrofit technology. VERT will use demo retrofit systems using latest available GPF technology in three high mileage fleets, in Germany, Switzerland and Israel. The project will also serve as a platform to continue research on PN emissions and secondary emissions from GDI as well as PFI Petrol engines. In addition, the “high emitter phenomena” will be further analyzed with a NPTI testing campaign of 1000 gasoline vehicles, including GDI, PFI and GPF equipped vehicles.

Emission control of combustion engines, Contributed Lecture

The Influence of a Diesel Particulate Filter with Low-Temperature Regenerability on Diesel Engine Emissions

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Introduction

The diesel particulate filter (DPF) effectively suppresses the emission of particulate matter from diesel engines mostly through regeneration. There are main 2 types, active regeneration which uses fuel burners or electric heating devices to produce a high temperature such that particulate deposits will be oxidized and burned off, and passive regeneration which utilizes the innate high temperature of the exhaust generated by a constant run of the engine. It is aided by catalysts to lower the temperature requirement as certain external conditions (i.e. short distance travel) prevent the scenario to enable regeneration. And for diesel engines, ineffective regeneration means high soot accumulation leading to severe backpressure ultimately reducing the power generated by the engine which could have detrimental consequences.

Regrettably, the operation of DPF triggers the formation of dioxins due to incomplete combustion, soot accumulation, and temperature windows (200°C to 450°C de novo synthesis; 500°C to 800°C homogenous pathways). A DPF regenerating with a high PM content in the filter saw an approximately 2.5-fold increase in the PCDD/F concentrations (Chen et al., 2017). Hence, a DPF capable of regenerating at 200°C is developed to bypass this problem. The aftertreatments are assessed on the following conditions: (i) new DPF, (ii) during regeneration, and (iii) post-regeneration. Afterward, the investigation for PM, gaseous pollutants, PAHs, and POPs commenced.

2. Methodology

The engine, Cummins ISC 315, is attached with a dynamometer and is assessed under US FTP Transient Cycle Procedure. Alongside it, DOC + DPF are installed, and the engine is then left idle for 30 hours to accumulate the soot and force the regeneration. Lastly, RDE was guided by Euro VI-C which suggests proper velocities for different test terrains, while the RDD test ran the engine for 15,000km which allows the measurement of the difference in power generated by the engine over a significant period of time.

3. Results

The result shows the use of DOC+DPF reduced the amount of PM by at least 95.0% while its maximum effectiveness reached 97.9% which means that it met the Euro Stage 5 standards. For gaseous pollutants, CO has seen a minimum reduction of 88.0%, while 98.1% for THC. The high conversion of both CO and THC suggests that the DOC used performed well which is also reflected in the PM removal efficiency as the capability of DOC to purify NO to become NO_2 helped in reducing the temperature requirement of POC for its regeneration. The PCDD/Fs managed a removal efficiency of 74.3% - 88.0% indicating that passive regeneration can be started at 180°C. Lastly, the RDE has shown that after 216km. (about 3 hours) of driving, a 99.7%, 91.7%, and 56.3% reduction occurred for PM, THC, and CO, respectively. For RDD tests, 15,000km (about 3 months) worth of driving revealed that the smoke opacity of the exhaust is still 0 m^{-1} after the DOC + DPF was installed.

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Emission control of combustion engines, Contributed Lecture

PM Mass-Based Standard for Achieving PM Emissions Commensurate with Model Year 2022 GPF Technology for Light-Duty and Medium-Duty Vehicles

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The presentation begins with an overview of criteria emissions standards proposed by EPA in April 2023 for light-duty and medium-duty vehicles in 2027-2032. The talk then focuses on the tailpipe PM standard and test procedures, whose aim is to require PM emissions below or commensurate with model year 2022 series production GPF technology. The proposed PM standard is 0.5 mg/mi, which must be met across three test cycles: 25°C FTP, US06, and -7°C FTP.

European, Chinese, and Indian regulations have used solid particle number (PN) standards to drive the use of gasoline particulate filters (GPF) on light-duty vehicles since 2017, 2020, and 2023, respectively, and the Particle Measurement Programme (PMP) affords very good sensitivity for this purpose. In contrast, light-duty and medium-duty vehicle PM standards in the U.S., including the proposed EPA rule for 2027-2032, are based on mass emissions. EPA chose mass-based emissions standards in the proposed rule because health benefits can be more directly quantified using epidemiological studies that use ambient air mass PM2.5, and because PM mass includes semi-volatile PM. The solid number PN standard gives substantially more consideration to small particles, which pass through the alveolar-capillary barrier, while the PM mass standard includes semivolatile PM, which can have high toxicity and is emitted even from GPF-equipped vehicles.

PM mass measurements were conducted according to existing EPA test procedures (40 CFR Part 86, 1065, and 1066) using five vehicles (2011 F150, 2019 F150, 2021 Corolla, 2021 F150 HEV, 2022 F250) tested across three organizations (EPA, ECCC, and FEV) without GPF, with MY2019 GPF technology, and with MY2022 GPF technology. Key elements of the EPA test procedures are described, including the purpose of each of the three test cycles. Results show that existing EPA test procedures, which use PTFE membrane filters and alpha emitter charge neutralizers such as Po_{210}, can resolve PM mass emissions to well below 0.5 mg/mi. It is demonstrated that light-duty and medium-duty vehicles employing MY 2022 GPF technology can meet the 0.5 mg/mi standard across all three test cycles (25°C FTP, US06, and -7°C FTP) with a large compliance margin.

Emission control of combustion engines, Contributed Lecture

HORIZON AeroSolfd project: Retrofit Filtration Devices for Cleaner Urban Mobility - Focus on highly efficient filter systems for large scale petrol engine retrofit

L. Rubino[1], A. Mayer[1], J. Czerwinski[1], T. Lutz[2], L. Larsen[2], V. Hensel[3], D. Engelmann[4], M. Lehmann[5]

[1]VERT Association, [2]VERT Association, [3]Aurigna, [4]University of Applied Science Biel, [5]Mann + Hummel

HORIZON AeroSolfd is an EU co-funded project that will deliver affordable, adaptable, and environmentally friendly retrofit solutions to reduce tailpipe emissions, brake emissions and pollution in semi-closed environments. VERT, according to the long experience on retrofit and nanoparticle emissions reduction strategies and filtration, will focus on reducing emissions at tailpipe of gasoline vehicles by using the best available retrofit technology. VERT will use demo retrofit systems using the latest available GPF technology in three high mileage vehicle fleets, in Germany, Switzerland and Israel. The project will also serve as a platform to continue research on PN emissions and secondary emissions from GDI as well as PFI Petrol engines. In addition, the “high emitter phenomena” will be further analyzed with a NPTI testing campaign of 1000 gasoline vehicles, including GDI, PFI and GPF equipped vehicles.

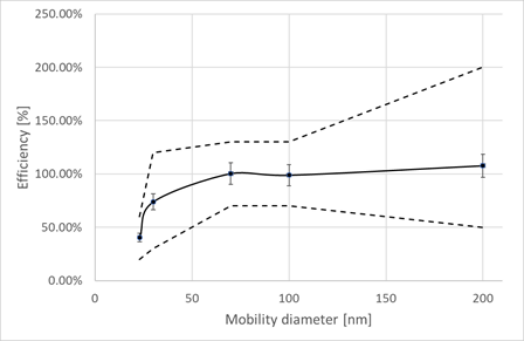
Emission control of combustion engines, Contributed Lecture

Improving counting efficiency and linearity beyond the on-road emission measurement regulations for Portable Emissions Measurement Systems (PEMS)

A. Nowak[1], M. Kazemimanesh[2], T. Hammer[3], A. Bescond[4], K. Vasilatou[3], J. Saturno[1]

[1]Physikalisch-Technische Bundesanstalt (PTB), [2]Air Quality and Aerosol Metrology Group, National Physical Laboratory (NPL), [3]Particles and Aerosols Laboratory, Federal Institute of Metrology (METAS), [4]Laboratoire National de Métrologie et des Essais (LNE)

Particle diameter and particle number concentration are the key physical parameters of interest targeted by several regulations on vehicular emissions, including the current European real driving emissions (RDE) regulation [1]. However, metrological validation of PEMS is currently lacking. Compared to lab-grade instruments like reference particle number counters, PEMS are likely to have larger measurement uncertainty or bias due to their small size and simpler design. Thus, it is critical to understand this measurement uncertainty to support the accuracy and comparability of conformity factors. The MetroPEMS project on vehicle exhaust quantification by portable emission measurement systems started in 2020 and has developed calibration methods for the required linearity and counting efficiency. In this study, we used PN reference instruments available at different National Metrology Institutes (NMIs) for an inter-comparison exercise with a *golden PEMS*, a PEMS device aimed to be calibrated with the primary standards at national authorities, to determine the best possible linearity and counting efficiency of the target unit (golden PEMS). The aerosol source was a propane combustion flame generator (miniCAST, Jing Ltd.) and particles were polydisperse (50 nm) for linearity measurements and size-selected with a DMA (monodisperse) for counting efficiency (CE) measurements. Linearity was measured from 15,000 up to 800,000 cm^{-3} and CE was measured for particles of 23, 30, 50, 70, 100 and 200 nm (mobility diameter). Diffusion losses, flow correction factors and multiple charge correction factors were applied to the PN concentration results, and an uncertainty budget was calculated. As shown in Fig. 1, counting efficiencies determined by the golden calibration method were within the regulation thresholds and plateau were reached at about 100 % for particles larger than 50 nm. The expanded uncertainties (k = 2) were on the order of ± 7.5 to 11 % for the counting efficiency. Linearity check was done up to 800,000 cm^{-3} with a resulting expanded uncertainty (k = 2) of 15 % for high concentration levels.



This study sets the current state-of-the-art of PN measurements at NMI level and proposes a series of recommendations to improve current PEMS calibrations and to address future regulatory challenges.

This project has received funding from the EMPIR 19ENV09 MetroPEMS project (MetroPEMS). EMPIR is co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

[1] Giechaskiel, B.; Melas, A.; Martini, G.; Dilara, P.; Ntziachristos, L. (2022) *Atmosphere* **13**, 155.

Emission control of combustion engines, Contributed Lecture

Monitoring vehicle emissions with the on-road chasing method over a decade

I. Ježek Brecelj[1], L. Zgonik[2], M. Ivančič[1], B. Alföldy[1], T. Rutar[2], G. Močnik[2], A. Gregorič[1,2]*, M. Rigler[1]*

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All new vehicles sold into the EU market must comply with certain regulations with the aim of reducing emissions from traffic all. Among regulated pollutants are nitrogen oxides, particle matter, and particle number concentration (PN). Over the years new and stricter standards were introduced. In 2015 the “Dieselgate” scandal prompted extensive emissions testing of Euro 5 and Euro 6 diesel passenger cars, which showed excess NO_x emissions across nearly all manufacturers. Vehicles showing compliant levels of NO_x during official laboratory testing had much higher emissions when operating on the road. Follow-up action by authorities was very limited, and many of these vehicles continue to operate today. ICCT reported a summary of 1,400 total tests conducted under controlled settings by government authorities, where 85% of tests on Euro 5 vehicles and 77% of tests on pre-Real Driving Emissions (RDE) Euro 6 vehicles exceeded the suspicious emissions threshold [1].

The EF determined with the chasing method can provide useful insight into individual vehicle emissions during on-road operations when vehicles cannot detect that testing is occurring.

We show how the results of three on-road measurement campaigns conducted in 2011 (published [2]), 2017, and 2023 compare. In all three we used the chasing method to measure the emission factors (EF) of random individual vehicles by chasing them on the road. We installed instruments with high-time measurement resolution in our measurement platform. We measured CO_2, NO_x, PN, and BC.

We show how the emission factors for different vehicle groups (gasoline cars, diesel cars, and goods vehicles) changed over the decade. We show how some of the new technologies improved the emissions i.e., BC and PN emission factors were reduced in all vehicle groups with the introduction of particle filters in EURO 5 standard while reducing NO_x was not as efficient. We also show how the introduction of new test standards in 2017 with RDE has affected vehicle emissions as determined by the on-road chasing method.

[1] ICCT (2023), Reassessment of excess NOx from European diesel cars

[2] Ježek, I., et al. (2015). Atmos. Meas. Tech., 8, 43–55.

Emission control of combustion engines, Contributed Lecture

New Proposed Light-Duty PM Mass Regulations in the USA: Can it be Controlled and Measured

I. Khalek[1]

[1]Southwest Research Institute

Current Tier 3 EPA regulation compliance requires light-duty vehicles to meet particulate matter (PM) emissions of 3 mg/mi. CARB LEV III regulations mandate PM emissions reduction from 3 mg/mi to 1 mg/mi by 2025. A new US EPA proposed regulations for light and medium duty vehicles includes PM mass emissions of 0.5 mg/mi starting in 2027. Since 2017, EU light-duty vehicles are meeting a PM emission level of less than 1 mg/mi indirectly through the enforcement of GPFs to meet EU solid particle number stringent regulations. In the USA, however, using solid particle number emissions as a regulatory metric might not be feasible for now (although accepted for aircraft), without an epidemiological study showing a link between solid particle number and health effects. Thus, it is of high interest to regulators and stakeholders to study the feasibility of measuring and controlling low PM MASS emissions below 0.5 mg/mi. PM mass will need to be collected on a PM filter that is maintained at 47 oC, and pre- and post-weighed using a high sensitivity microbalance with 0.1 microgram sensitivity.

In this presentation, the new regulations will be discussed in more details and in context with the current and future regulations in the US, California, and the EU. Furthermore, measurement variability and examples of PM emissions control via gasoline particle filters (GPF) and E-Fuel with ultra-low PM index will be shown.

Effects of GPF substrate structure on pressure drop and filtration efficiency

K. Yamamoto[1]

[1]Nagoya University

Although gasoline direct injection (GDI) engines are more fuel efficient, they emit a large amount of particulate matter (PM) including soot. Thus, a gasoline particulate filter (GPF) is needed. Since the use of the GPF would increase the filter back pressure and decrease the fuel efficiency, the filter with lower pressure drop is desirable. So far, we have conducted numerical simulations of GPFs using a lattice Boltzmann method (LBM). In this study, we investigated the effect of the substrate structure on pressure drop and filtration efficiency. Figure 1 shows the distributions of porosity adopted in the simulation. The inner structure of the bare (original) filter was obtained by an X-ray CT. Then, we creased three more filters by increasing or decreasing the original porosity. Uniquely, the filter of the front thick rear thin was the sample for improving the filtration efficiency by decreasing the porosity in the upstream region of the filter, while the porosity was increased in the downstream region for reducing the pressure drop. Figure 2 shows the flow field of the original filter. The inlet velocity across the filter was set to be 2 cm/s. When the exhaust gas passes through the filter wall, the flow changes significantly and the maximum velocity is approximately 25 times. Figure 3 shows the distributions of the maximum velocity of four filters. When the porosity is decreased, the maximum velocity is roughly twice that of the original velocity. The maximum velocity becomes smaller as the porosity is increased. Expectedly, the pressure drop would be simultaneously affected through the change in the flow field. Figure 4 shows the initial pressure drop and the filtration efficiency. The initial pressure drop can be reduced by decreasing the porosity, but the initial filtration efficiency is also smaller. It is interesting to note that both the pressure drop and the filtration efficiency of the front thick rear thin are almost the same as those of the original filter, even though the porosity distribution is different. In the presentation, more results of soot filtration simulations will be given for further discussion on the GPF substrate structure.

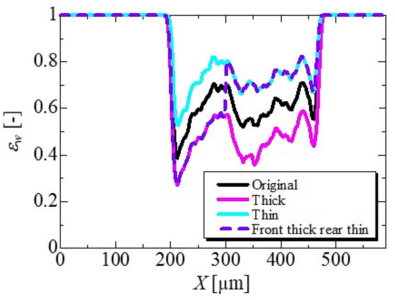

Fig.1 Porosity distributions of 4 filters.

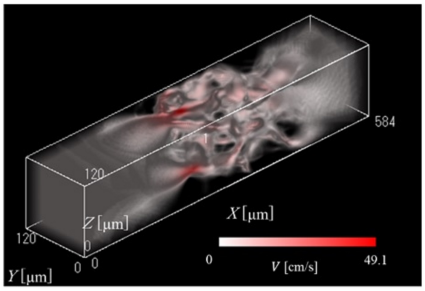

Fig.2 Flow field across the filter wall of original.

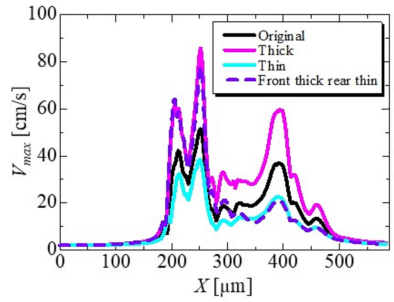

Fig.3 Maximum velocity distributions.

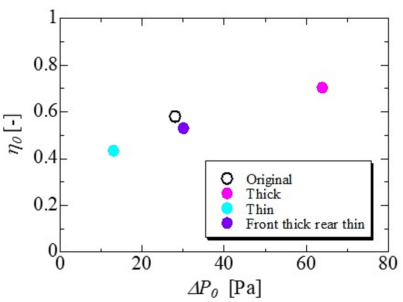

Fig.4 Initial pressure drop and filtration efficiency.

Health effects, Contributed Lecture

Nano- and microparticles in babies' brain in SIDS cases

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The study proposes a novel autopsy approach which consists of neuropathological analysis procedures combined with EDS-FEG-ESEM (Energy Dispersive Spectroscopy- Field Emission Gun Environmental Scanning Electron Microscopy) investigations implemented on 10 SIDS/SIUDS cases (Sudden Infant Death Syndrome /Sudden Intrauterine Death Syndrome) [1,2]. As control samples, 10 cases of fetal (or infant) deaths were considered. The study was aimed to verify the presence of inorganic micro- and nano-sized entities in the brain tissue. The presence of inorganic debris, never investigated, could be a potential co-factor that compromises the brain tissue functionality and its proper functions. Their chemical composition, sometimes, induced the authors to hypothesize a possible external source. Physical abnormalities of the brain were associated with foreign bodies' presence. Although nanoparticles were present as well in control samples, they were not associated with histological deformities, as was the case in SIDS/SIUDS. The presence of inorganic particles in the brain tissue demonstrated their ability to cross the haemato-encephalic barrier and to interact with tissues and cells in an unknown, yet pathologic, fashion. This gives a rationale to consider them as co-factors of lethality.

[1] Antonietta M. Gatti, et al. Novel chemical-physical autopsy investigation in sudden infant death and sudden intrauterine unexplained death syndromes Nanomedicine (Lond) **2022** ,eb;17(5):275-288.

[2] Antonietta M. Gatti, et al.Silver nanoparticles in the fetal brain: new perspectives in understanding the pathogenesis of unexplained stillbirths Nanomedicine (Lond) **2021** Feb;16(4):265-274

Health effects, Contributed Lecture

Nano- and microparticles in human blood: An analysis of the eluate from double filtration plasmapheresis

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The study of the presence and characteristics of micro- and nanoparticles in blood is an important area of research. We investigated which particles can be found in the blood plasma, i.e. the residue of filtered blood plasma (eluate) obtained by blood using double-filtration plasmapheresis (DFPP). In our case study, we used field emission scanning electron microscopy/energy-dispersive X-ray analysis (FE-SEM-EDX) to examine if the eluate obtained by a specific type of DFPP (INUSpheresis with a TKM58 filter) contains nano- and microparticles and what chemical composition these particles have. Micro- and nanoparticles of various sizes and chemical composition were found, including particles high in the concentration of calcium, iron, silicon, aluminium and titanium. In addition, thread-like objects were identified. We discuss the possible origin of the particles and objects, their potential pathophysiological relevance as well as the potential of FE-SEM-EDX analysis of the eluate with regard to diagnostics and therapy for environmental medicine applications on patients. A detailed description of our investigation has been published [1].

[1] Felix Scholkmann, Antonietta M. Gatti, *Compounds*, **2022**, 2(4), 367-377.

Health effects, Contributed Lecture

Early life health impact of diesel exhaust particles: Unravelling placental accumulation, fetal transfer and interference with maternal-fetal communication

T. Buerki-Thurnherr[1], B. Dugershaw-Kurzer[1,6], J. Bossart[1,6], P. Nowak-Sliwinska[2,7], J. R. van Beijnum[3], A. W. Griffioen[3], S. Majosthusmann[4], E. Zühr[4], E. Fritsche[4], R. Hornung[5,5]

[1]Laboratory for Particles-Biology Interactions, Swiss Federal Laboratories for Materials Science and Technology (Empa), St. Gallen, Switzerland, [2] Institute of Pharmaceutical Sciences of Western Switzerland, Geneva, Switzerland, [3]Angiogenesis Laboratory, Department of Medical Oncology, Amsterdam UMC loacation Vrije Universi-teit Amsterdam, Amsterdam, The Netherlands, [4] IUF - Leibniz Research Institute for Environmental Medicine, Duesseldorf, Germany, [5]Department of Gynaecology and Obstetrics, Kantonsspital St.Gallen, St. Gallen, Switzerland, [6]Department of Health Sciences and Technology, ETH Zurich, Zurich, Switzerland, [7]School of Pharmaceutical Sciences, University of Geneva, Geneva, Switzerland

Prenatal air pollution exposure, in particular to traffic-related combustion particles, is associates with adverse pregnancy and fetal outcomes but the mechanisms underlying the observed developmental toxicity remain elusive. In particular, the impact of combustion particles on the placenta, as central mediator of maternal-fetal crosstalk, is largely unexplored.

We therefore investigated the accumulation and translocation of diesel exhaust particles (DEPs) in human perfused placenta using label-free detection by femtosecond-pulsed laser illumination [1]. In addition, we studied the effects of DEPs on maternal-fetal communication in placental explant cultures from early and late stage pregnancy including targeted and global secretome profiling and compared them to other exposure-relevant nanoparticles (TiO_2, SiO_2 NPs). To understand potential downstream impacts on angiogenesis and neurodevelopment, conditioned media (CM) were depleted of NPs and applied in HUVEC spheroid sprouting assays, to chicken chorioallantoic membrane model and to human neural progenitor cell (NPCs)-based neurospheres.

The results showed an accumulation of DEPs in placental cells, especially in the syncytiotrophoblast layer mediating most essential placental functions, and low fetal translocation. DEPs induced extensive pregnancy-stage dependent alterations in the secretion of placental signaling factors, which were different from those induced by TiO_2, SiO_2 NPs. Moreover, NP-induced alterations in the placental secretome elicited anti-angiogenic effects *in vitro* and *in vivo* but had only limited impact on neurodevelopmental processes.

In conclusion, our work suggests a key role of placental signaling to mediate indirect developmental toxicity of DEPs in addition to direct fetotoxic effects from translocated particles, and provides a rich source of lead candidates for further studies.

[1] Eva Bongaerts, et al., *Journal of Nanobiotechnology*, **2021**, 19, 144.

Health effects, Contributed Lecture

Tire wear and ambient temperature - Their accelerating effect on neurodegenerative diseases and aging in the animal model *Caenorhabditis elegans*

I. Scharpf[1], A. Limke[1], F. Blesing[1], A. von Mikecz[1]*

[1]IUF - Leibniz Research Institute for Environmental Medicine

Recent studies link air pollution to neurodegenerative diseases like Alzheimer's (AD) and Parkinson's disease (PD). Large cohort studies were conducted that showed positive associations between living close to heavy traffic roads, air pollution and the prevalence of dementia and PD. Another emerging angle of air pollution and its adverse health effects is the contribution of rising temperatures in heavily built up residential areas due to climate change. However, the underlying molecular mechanisms are still unknown. Transmission electron microscopy and fractal analysis identified fractal-like aggregates composed of solid nanoparticles in urban aerosols. Similar aggregates of nanoparticles were found in non-exhaust emissions like tire and brake wear.

Here, we utilize models of neurodegenerative diseases in the nematode *C. elegans* to elucidate bio-interactions of different silica nanoparticles (silica NPs) including genuine tire wear components. We include the non-chemical factor ambient temperature to investigate interactions between adverse health effects of silica NPs and climate. The worm possesses a neural system that comprises only 302 neurons, but with known patterns of synaptic connectivity. *C. elegans* is particularly suited to analyze NP-effects in an age-resolved manner, since its life span as an adult hermaphrodite worm lasts for 3-4 weeks. We determine nanoparticle-organism interactions that manifest later in adult life, e.g. in young, middle-aged and old worms.

Silica NP exposition in wild-type, AD and PD worm models significantly reduced locomotory fitness, but the AD disease model was more susceptible to the pollutant than wild-type nematodes. In addition, we found that different silica NPs, including genuine tire wear components, induced neurodegeneration in dopaminergic neurons, which is a hallmark of PD. Here the phenotype dendritic beading was observed in the single posterior deirid neuron (PDE). With increasing temperature silica NP-induced neurodegeneration and reduced locomotory fitness was aggravated. Particularly middle-aged cohorts were determined as most vulnerable. Overall our study indicates that the exposome factor temperature critically impacts the susceptibility against pollutants in AD and PD.

This study represents a starting point for investigation of the neural decline pathways by non-exhaust pollutants in *C. elegans* AD and PD models. The idea is to comparatively interrogate defined chemical constituents of non-exhaust air pollution, urban aerosol samples and non-chemical exposome factors such as temperature. We recently showed that silica NPs and other neurotoxicants corrupt the resilience pathways of aging. It will be important to learn if these resilience pathways are likewise targeted by nanoparticulate tire wear and ambient temperature in *C. elegans* models of AD and PD as well as human cohorts.

Limke A, Scharpf I, Blesing F, von Mikecz A. Tire components, age and temperature accelerate neurodegeneration in *C. elegans* models of Alzheimer's and Parkinson's disease. *Environ Pollut*. 2023. doi:10.1016/j.envpol.2023.121660.

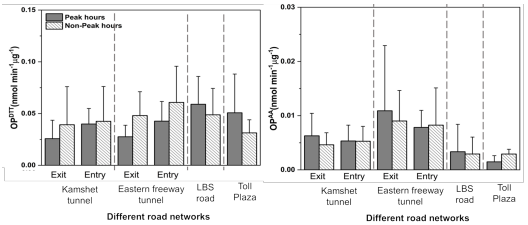
Health effects, Contributed Lecture

Toxicity of Respirable Particulate Matter of Traffic Origin: Effect of Different Driving Conditions and Fleet Characteristics

S. Dubey[1], S. Debbarma[1], N. Raparthi[1], H. C. Phuleria[1]*

[1]Indian Institute of Technology Bombay

Urban air pollution caused by vehicular emissions is a significant health hazard, especially in India, where elevated levels of PM10 are observed. To better understand the adverse effects of these pollutants, oxidative potential (OP) analysis can be helpful, as it quantifies the reactive oxygen species (ROS) induced by PM, leading to inflammation and oxidative stress. In this study, PM10 was measured at four different traffic sites in and near Mumbai, India, including two roadway tunnels, and two kerbside locations, to examine the toxicity of PM10 and its relationship with driving conditions and fleet characteristics. Kamshet-I tunnel (KT) on the Mumbai-Pune expressway has 20% heavy-duty vehicles (HDVs) with 80 km/hr average speed while the Eastern freeway tunnel (EFT) is dominated by Light-duty vehicles (LDVs) running at 60 km/hr. The kerbside location at Lal Bahadur Shashtri (LBS) road is dominated by motorized two-wheelers and automobiles at 20-30 km/hr while the other location at the Mulund Toll Plaza (MTP) has creeping traffic with a speed DTT (Dithiothreitol), and OP^{AA} (ascorbic acid) for examining toxicity, followed by elemental analysis through Inductively coupled plasma-Mass spectrometry (ICP-MS). The traffic volume and characteristics were analysed through video surveillance and random vehicle registration plates at all four locations.OP^{DTT} at the entry of the KT (Mean± S.D: 0.04±0.02 nmol min^{-1} μg^{-1}) and EFT (0.05±0.03 nmol min^{-1} μg^{-1}) are 12 and 15% higher than the exit, respectively. The tunnel exit is representative of uncontaminated traffic emissions, while the tunnel entry has emissions from mixed sources (both primary and secondary) likely responsible for the higher OP^{DTT}. Further, the enhanced resuspended road dust due to higher speeds during non-peak hours contributed to the increased OP^{DTT} in tunnels, while the high traffic volume along with lower driving speeds during the rush hours resulted in more OP^{DTT} at the kerbside as depicted in Figure 1. In contrast, KT and LBS show comparable OP^{AA} during peak and non-peak hours, suggesting the generation of homogeneous ROS in both time periods. EFT shows a higher OP^{AA} at exit peak hours which is greatly contributed by primary aerosol emissions due to significant traffic volume ($r=0.89$, $p<0.01$). Higher OP^{AA} was observed at MTP during non-peak hours due to the idling condition by > 50%HDDV (Heavy duty diesel vehicles) fractions. Our findings suggest that vehicular fleet, volume, and driving speed are the significant drivers of PM-induced ROS activity. Currently, elemental characterization is underway to gain further insight into these results.



Impact on climate, Contributed Lecture

Heterogeneous ice nucleation of soot particles: measurements, predictions and implications

C. Marcolli[1], F. Mahrt[2], B. Kärcher[3]

[1]Institute for Atmospheric and Climate Science, ETH Zurich, Switzerland, [2]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Switzerland, [3]Institut für Physik der Atmosphäre, DLR Oberpfaffenhofen, Germany

Copious amounts of soot particles are emitted into the atmosphere due to incomplete combustion. Soot particles play a critical role for air quality, human health and climate. They affect climate directly by absorption and scattering of radiation and indirectly by acting as seeds for clouds. Despite extensive previous work, our understanding of the climate effects of soot remains incomplete. A key example are the aerosol-cloud interactions of soot particles from aviation emission: During flights, aircraft soot particles are directly emitted into the upper troposphere, where cirrus cloud conditions prevail. At these altitudes, soot particles can nucleate ice and thereby modify formation of cirrus clouds. Estimates of the total climate impact associated with these aerosol-cloud interactions, usually expressed in terms of radiative forcing (RF), range from a net positive (warming) to a net negative (cooling) RF. These uncertainties reflect the poorly constrained ability of soot particles to nucleate ice.

Here, we integrate laboratory measurements of ice nucleation on soot particles, theory and cloud modelling to address the ice nucleation mechanism and ability of soot particles. Starting from ice nucleation laboratory measurements that evidenced a pore condensation and freezing (PCF) process [1], we developed a novel framework that incorporates key soot particle physicochemical properties, such as aggregate and primary particle size, in the description of their ice nucleation abilities by PCF [2]. This framework can easily be adjusted to soot particles with other characteristics, e.g. those from aviation emissions. Implementing the soot-PCF framework into a novel cirrus parameterization scheme, we studied how aircraft-emitted soot particles can nucleate ice in the presence of liquid solution droplets and mineral dust particles [3]. In our simulations aircraft soot, liquid solution droplets, mineral dust particles and updraft velocity were represented by characteristic distributions based on atmospheric measurement data. To represent atmospheric variability in our modelling, we analysed 2500 different combinations of soot particle, liquid solution droplet and mineral dust number concentrations and updraft velocities, by randomly sampling from their respective distributions.

Our results demonstrate that when both soot and mineral dust particles coexists with liquid solution droplets in the same air mass, dust particles most often prevent ice nucleation by aircraft soot. We further find that aviation soot particles only affect cirrus properties if updrafts are weak, soot particles are large and if their number concentrations are considerably higher than those typically observed in emission studies.

Overall, our results elucidate the role of soot in cirrus cloud formation and have important implications for the climate impact of aviation. In particular, our combined experimental and modelling results show that when assessed under increasingly realistic conditions, soot ice nucleation is often outcompeted by mineral dust. This suggests that aviation soot only plays a minor role in aerosol-cirrus interactions, challenging results from previous studies that reported large RF values associated with aviation soot-cirrus interactions.

[1] Fabian Mahrt, Claudia Marcolli, Robert O. David, Philippe Grönquist, Eszter J. Barthazy Meier, Ulrike Lohmann, and Zamin A. Kanji, *Atmospheric Chemistry and Physics*, **2018**, 18, 13363-13392.

[2] Claudia Marcolli, Fabian Mahrt, Bernd Kärcher, *Atmospheric Chemistry and Physics*, **2021**, 21, 7791-7843.

[3] Bernd Kärcher, Claudia Marcolli, Fabian Mahrt, *Journal of Geophysical Research: Atmospheres*, **2023**, 128, e2022JD037881.

Impact on climate, Contributed Lecture

Millions of Soot Filters mitigating Climate Change

A. C. Mayer,[1]

[1]VERT

Millions of Soot Filters mitigating

Climate Change Due to their black colour, soot particles finely dispersed in the atmosphere absorb radiant energy from the sun, heat up, and then immediately release the heat into the surrounding air. This effect occurs immediately after emission, and ceases immediately after these particles have been washed out of the atmosphere or lose their absorption activity. Mark Jacobson of Stanford University has calculated these effects in a comprehensive atmospheric model including the albedo reduction effects on polar ice and glaciers and has numerically determined the global warming equivalence of BC/CO2 to be 360'000-840'000 by mass. He has presented this at the ETH Nanoparticle Conference in 2002. At this time we still hat many Diesels heavily smoking and hardly any particle filters in place. This has changed dramatically : Switzerland implemented DPF offroad and onroad for public transport from 2000. EU followed for diesel cars in 2011, later for HDV, in 2017 for gasoline direct injection (GDI) cars. Trucks were using exhaust filters in the US since 2007, China implemented laws 2016 (now 60% DPF) and India 2019, so the size of the filtered vehicle fleet became quite large, market reseach results in around 300 Mio. DPF and GPF sold until today and and about 150 Mio might be in operation during last 10 years in Europe. Given these numbers we estimate the mass of soot not emitted due to the legal use of particle filters implemented in Europe over the last decade for Diesel LDV and HDV, also for NRMM and GDI assuming a filter efficiency near 100% to be about 0.70 Mio ton of BC during the last decade and 0,16 Mio tons for each following year. We can however, not apply Jacobson’s episode equivalence factors BC/CO2 of 500'000 :1 because we must respect the different residence time of soot in the atmosphere, which might be one week to one month depending on precipitation while CO2 might remain 20 years or longer active in the atmosphere. We are finding the following proposals for an effective equivalence ration BC:CO2:

ICCT, M Walsh: 1600:1 (6/2009)

Atlantic consult.: 2200:1 (2009)

VERT: 1449:1 (2012)

STRE M.Jacobson (2400-7200):1 (2009)

With 2500 :1 the yearly 0.16 Mio ton of BC not emitted in Europe are equivalent to the effect of 400 Million CO2 per year. For comparison: this is equal to the target of Germany for 2030, EU member states today emit yearly approx. 4 billion tons CO2, the world 37 billion tons)

Retrofitting more combustion engines with DPF and GPF might be the fastet and cheapest way to mitigate global warming while at the same time avoiding millions of premature death by cancer, stroke or hart attack. One tool to be recommended is CO2 credits to engine soot avoided by filtration, which comes for a HDV-life to 250 ton CO2 equivalent, with 60 $/ton this pays for the filter and keeps the truck perfectly emission free. 16.4.2023 /A.Mayer /VERT

Impact on climate, Contributed Lecture

Aerosol optical properties measured from two heterogenous mix of Indian vehicular fleets

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On-road vehicular emissions are significant and growing contributor to carbonaceous aerosols, especially in large urban conglomerates. These aerosols directly affect the atmospheric-radiation balance leading to visibility degradation and alteration of cloud lifetime [1]. While organic carbon (OC) is light scattering and causes atmospheric cooling, black carbon (BC) and some of the light absorbing OC, also known as brown carbon (BrC) cause warming of the atmosphere [2]. The optical properties of aerosols from vehicular emissions are not fully understood, specifically in Indian context. This study analyses the absorption and scattering properties of aerosols measured from on-road vehicles and how they are impacted by varying fleet composition and driving conditions. Low to intermediate speed, including idling, of vehicles play significant part of Indian Driving Cycle (IDC) in urban areas due to the traffic far lesser observed in developed countries. Aerosol measurements were carried out at the kerbside of two major arterial roads with distinct traffic characteristics and an urban background location in India's biggest metropolitan city, Mumbai. Measurements covered morning peak and afternoon non-peak traffic hours for a week each at 1). LBS road (Dec 2021): with an hourly average traffic volume of 2878±541 vehicles comprising 95% light-duty vehicles (LDV) and 5% heavy-duty diesel vehicles (HDDV) at an average speed of 15-32 km.hr^{-1}, and 2). Mulund toll plaza (MTP) (Mar 2023): with higher traffic volume (4633±710 veh.hr^{-1}) comprising twice the HDDV fraction at a lower speed (idling to 15 km.hr^{-1}). Real-time aerosol light absorption coefficient ($bab_{s,\lambda}$) and light scattering coefficient (s_{sp}) were measured using Aethalometer (AE-33) and Nephelometer, respectively. Gravimetric $PM_{2.5}$ was collected using a low-volume air sampler (5 L.min^{-1}) and the light absorption properties were analyzed using the Optical Transmissometer (OT-21) for total $PM_{2.5}$ and UV-vis spectrophotometer by extracting $PM_{2.5}$ in water and methanol to examine the light absorption of BrC. Kerbside aerosols at both the roads had significantly higher b_{abs} at 370 and 880nm as compared to the corresponding background aerosols ($p<0.05$) (Fig.1). However, light absorbing coefficient of the aerosols at MTP was 1.3 to 2 times more, than at LBS road, likely due to the presence of higher diesel, HDDV, and super-emitter (high-emitting vehicles) fraction at MTP leading to the release of higher soot emissions. The $b_{abs,880}$ at MTP was 1.4 times higher during the afternoon period when the HDDV fraction was 62% higher due to the restricted entry of such vehicles during morning peak hours. In case of light absorption of BrC, $b_{abs\text{-}BrC,370}$ was greater in methanol extracts than in water extracts, indicating that water-insoluble BrC was likely an important contributor to light absorption by organic aerosols. The $b_{abs\text{-}BrC,370}$ at LBS was 1.6 times higher than at MTP which could be due to the higher gasoline vehicle fraction at LBS which is known to emit more OC than diesel vehicles. The average mass absorption cross-section (MAC) of water soluble-BrC and methanol-soluble-BrC was in the range of 0.4 to 1.7, which is comparable to the previously reported values for vehicle emissions and is less than biomass emissions. Average absorption Ångström exponents (AAE) was higher at background (1.7 to 2.4) than at roadsides (0.8 to 1.3) which indicates the dominance of the other sources like residential emissions at the background location. Single scattering albedo (SSA) ≤0.7 indicated that the aerosols from on-road vehicles are atmospheric warming aerosols. The association of optical properties with chemical characteristics is being further investigated. This work will add to the pool of literature to allow informed policy interventions in mitigating vehicular emissions and their impacts on climate.

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Indoor particles, Contributed Lecture

Health risk assessment of Sub-Micron Particles and Heavy Metals on Children in North Indian Indoor Air - An Interim Analysis

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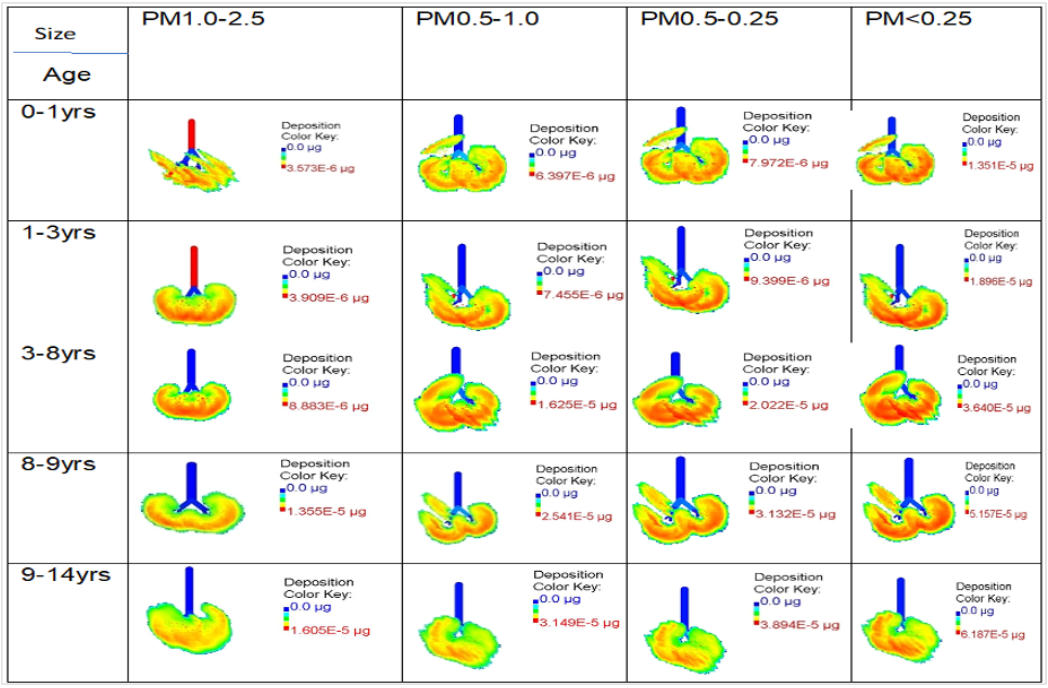
The present study depicts a relationship between particulate-bound heavy metals and children's health. The indoor air quality of the urban city households in northern India was monitored for four PM sizes namely $PM_{1.0-2.5}$, $PM_{0.50-1.0}$, $PM_{0.25-0.50}$, and $PM_{<0.25}$ in major seasons observed in the city; summer and winter. Further 7 heavy metals viz. Cr, Cu, Fe, Mn, Ni, Pb, and Zn were analyzed in $PM_{1-2.5}$ samples. Moreover, statistical tools such as PCA and wilks' test were applied. In PCA the first factor was found to be largely dominant as it expresses itself in 86.68%, 77.19%, and 84.52% in the three microenvironments selected during the study. These axes present an amount of inertia greater than those obtained by the 0.95-quantile of random distributions. Further health risk assessment was performed using mathematical models for assessing dermal adsorbed dose (DAD), chronic daily intake (CDI), exposure concentration (EC) and MPPD model V-3.0 for dose estimation. According to the results (Fig.1), for the largest particle size i.e., $PM_{1.0-2.5}$ the highest deposition was in the head region (49.1%) followed by pulmonary (43.6%) and TB region (7.21%) whereas, for other particle sizes deposition varied. The study is the first of its kind as it addresses the gap between indoor air quality and children's health accordingly with age. Also, the microenvironment selected in the study is the archetype depicting the effect of the zonal nature of the outdoor environment on the concentration of indoor pollutants thereby, providing possible policy recommendations for cultivating children's well-being.



Indoor particles, Contributed Lecture

The airborne transmission of respiratory pathogens: the importance of ventilation and air distribution in the infection risk

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[1]University of Cassino and Southern Lazio, [2]Queensland University of Technology, Australia

The COVID-19 pandemic has affected our society and the economy on an unprecedented global scale. While much has been done to understand the transmission of respiratory infections, little of this knowledge has been applied to buildings systems to combat it and to create spaces filled with clean indoor air. The rapid growth in our understanding of the mechanisms behind respiratory infection transmission should drive a paradigm shift in how we view and address the transmission of respiratory infections to protect against unnecessary suffering and economic losses. One focus of this presentation concerns the modelling of airborne risk assessment of SARS-CoV-2. Modelling can i) demonstrate building-specific and activity-specific factors to be understood, and potentially modified to reduce risk, ii) be made accessible to non-technical persons and accommodate more sophisticated users as well, iii) permit sensitivity analyses to be simply calculated and iv) provide valuable public health guidance for decision-makers. The importance of these factors will be discussed illustrating the Airborne Infectious Risk Calculator (AIRC) and its validation. The developments of risk assessment for short (“conversational”) or longer distances after emission from an infected person together with advanced ventilation and the management of air distribution for reduction of airborne transmission indoors will be discussed.

Indoor particles, Contributed Lecture

Comparison of outdoor and indoor emissions of ultrafine particles (UFPs) generated by combustion

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[1]Brunel University

Comparison of outdoor and indoor emissions of ultrafine particles (UFPs) generated by combustion

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Air pollution and UFPs have contributed to human deaths. Ella Kissi-Debrah, who lived near the South Circular Road in Lewisham, south east London, died at the age of 9 in 2013 after having seizures for three years. The High Court has indicated that air pollution was a contributory factor. Jocelyn Cockburn, a partner at the law firm Hodge Jones & Allen, who represents Rosamund Kissi-Debrah, said in May 2019 that ‘air pollution is costing people’s lives and those most vulnerable are children.’

Here we compare the nature, concentration (UFPs/mm3) and effect of UFPs emitted from E10-fuelled vehicles and lawnmowers and garden bonfires and within rooms with a night candle, gas cooker hob or wood burners and show how nanoengineered solutions could minimise their production and impact.

Nanoparticle chemistry and toxicology, Contributed Lecture

Biomonitoring of airborne- and waterborne- ultrafine particles (UFP) emitted from combustion

P. A. Sermon[1]

[1]Brunel University

Biomonitoring of airborne- and water-borne- ultrafine particles (UFP emitted from combustion

U.K.Onwukwe, P.A.Sermon, and I.A.Jaaffer AL-Timimi

Holdgate [1] suggested many years ago that pollutants have targets that include people, animal, ecological systems, and human artefacts to which they diffuse and where they may cause damage to receptors that can be acute or chronic or synergistic. He suggested that living targets integrate the influence of the pollutants

We report the impact on and the effect of combustion-generated ultrafine particles and their fractal aggregates on blood, lung efficiency, mosses, spores and plant leaves and we suggest how these can be technically minimised temporally and spatially by nanoengineered solutions.

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Nanoparticle chemistry and toxicology, Contributed Lecture

Interactions of PAHs and nanoparticles with biological systems

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[1]University of Michigan

Understanding the permeation time of pollutants into cellular membranes as well as their propensity to interact with biological systems can help us assess the potential environmental impact of these pollutants. While several models have been developed to predict the interaction of specific biological components, they use system-specific information that hinders their application to more general materials. Here, we present NeCLAS, a general and efficient machine learning pipeline that predicts the location of nanoscale interactions, providing human-intelligible predictions.

NeCLAS is used to predict the interactions of carbon-based nanoparticles with proteins. NeCLAS outperforms current nanoscale prediction models for generic nanoparticles up to 10-20 nm, reproducing interactions for biological and non-biological systems. Two aspects contribute to these results: a low-dimensional representations of
nanoparticles and molecules (to reduce the effect of data uncertainty), and environmental features (to encode the physico-chemical neighborhood at multiple scales). We report on the interactions of PAH and nanoparticles with cellular membranes as well as carbon-based nanoparticles with various proteins. This framework has several applications, from basic research to rapid prototyping and design in nanobiotechnology.

Nanoparticle metrology and chemical characterization, Contributed Lecture

Determining the Impact of Sulfur Exposure on Catalytic Stripper Performance Using Propane Oxidation Efficiency Measurements

V. Berger[1], H. Schulz[1], A. Boies[1,2], U. Sonkamble[1], J. Swanson[1,3]*

[1]Catalytic Instruments GmbH & Co. KG, Germany, [2]University of Cambridge, United Kingdom, [3] Minnesota State University, United States

Catalytic Strippers (CS) are commonly used to remove semi-volatile compounds from aerosols, when only non-volatile particles are to be measured. Offering more safety against measurement artifacts, the use of a CS will be mandatory in future EU vehicle regulations [1]. It has been pointed out that the sulfur storage capacity of a CS should not be exceeded, as it might impair its oxidation efficiency [2] or produce particles [3]. Observations of sulfur poisoning in automotive emission testing are limited, as exhaust sulfur levels are low (calculated to be in the range of 100 ppb to 700 ppb for diesel and gasoline engines using fuel with 10 ppm sulfur content, dependent on engine air-fuel-ratio), and exhaust is usually diluted at least 10:1 before entering the CS. It is not known if long term usage of CS in these conditions is impacted due to sulfur storage. Concerns have been expressed when measuring in marine applications using heavy fuel oil (HFO) with fuel sulfur contents (FSC) of up to 5000 ppm [4], where CS service life seems to be limited [3]. It is the motivation of this work to investigate CS performance under sulfur exposure in more detail.

Propane oxidation efficiency (POE) was measured for different CS models with the goal of establishing a quick and reliable method for the detection of deteriorated catalysts. A flame ionisation detector (FID) was used to measure propane concentration upstream and downstream of the CS. Propane in air is available in calibration gas bottles and therefore the propane concentration is constant, improving measurement accuracy and repeatability. An upstream concentration of 20 ppm of propane in air was chosen in order to obtain high POEs for fresh catalysts, and therefore achieve the best sensitivity for lowered POEs. Repeatability of the method and similar performance of different units of the same CS model are demonstrated. To study the impact of sulfur exposure on CS performance, catalysts were exposed to 50 ppm SO2 gas in air at nominal flow rate of each CS. The SO2 concentration was chosen to approximately match the calculated exhaust SO2 concentration of a marine diesel engine running on HFO with the maximum allowed FSC of 5000 ppm. To investigate whether POE measurements cause a partial regeneration of the CS, two different exposure strategies were carried out: the first strategy measures POE after every hour of SO2 exposure, the second only once after five hours. Each strategy was performed on a fresh CS of the same type. To correlate POE testing with Particle Measurement Programme (PMP) standards, tetracontane removal tests were performed with fresh and sulfur-exposed CS. The renewed PMP tetracontane test requires 99.9% removal of tetracontane particles with a count median diameter larger than 50 nm and mass above 1 mg/m³ for a complete volatile particle remover (VPR) setup, i. e. including a minimum dilution of 10:1 before the CS. For more sensitivity, this test is performed with the CS only, without dilution.
The effect of regenerating sulfur-poisoned CS at elevated temperatures under propane atmosphere was investigated by subsequent POE measurements.

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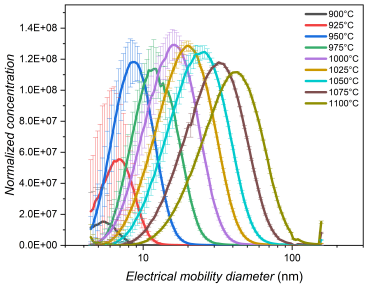
Nanoparticle metrology and chemical characterization, Contributed Lecture

Impact of Operating Conditions on the Performance of a Silver Particle Generator

H. Schulz[1], V. Berger[1], T. Hammer[2], A. Boies[1,3], U. Sonkamble[1], J. Swanson[1,4], K. Vasilatou[2]

[1]Catalytic Instruments GmbH & Co. KG, Germany, [2]Federal Institute of Metrology METAS, Switzerland, [3]University of Cambridge, United Kingdom, [4]Minnesota State University, United States

Silver ultrafine particles have been used in a broad variety of applications for years [1,2,5] and demand in industry and academia is increasing; particularly for better control and more reproducible silver particle sources [3]. Finding materials for calibration purposes, that show a similar detection and counting probability as the material being investigated, maintains a major challenge. Environmental aerosols, consisting of a wide range of organic, non-organic, soot-like, metal, ion, and semi-volatile materials, are best to be detected when a CPC is calibrated with a source of silver particles (ISO 27891:2015). Similarly silver particles have been accepted for calibration of CPCs for brake wear emission measurements (ECE/TRANS/WP.29/GRPE/2023/4). Currently the calibration of CPCs for soot measurements of ultrafine particles from combustion processes, such as combustion engines, turbine engines, stoves and open fireplaces is still not uniquely regulated. Many CPCs are calibrated with emery oil [4], which demonstrated differences in the detection probability, or soot, generated in a soot generator with optional post treatment to remove organic compounds. Silver is highly suitable due to its inert property as well as the shape of non-spherical agglomerates at larger sizes, similar to soot particles [3].



We present a silver particle generator, that serves as a highly stable particle source of silver nanoparticles, that allow a size range between 2 to 200 nm to cover all needs for calibration of CPCs, allows calibration with spherical silver nanoparticles, and can guarantee a distinct calibration with only one element - silver - when using nitrogen as a carrier gas. Our results show that agglomerated particles can be made spherical by sintering. The generated particle size distribution is stable within ± 1 % in GMD, and ± 1,25 % in total concentration (± 1σ, respectively) over 15 hours of operation. The day-to-day variation is less than ± 20 % for GMD and total concentration.

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Nanoparticle metrology and chemical characterization, Contributed Lecture

The M2AS - Mass and Mobility Aerosol Spectrometer

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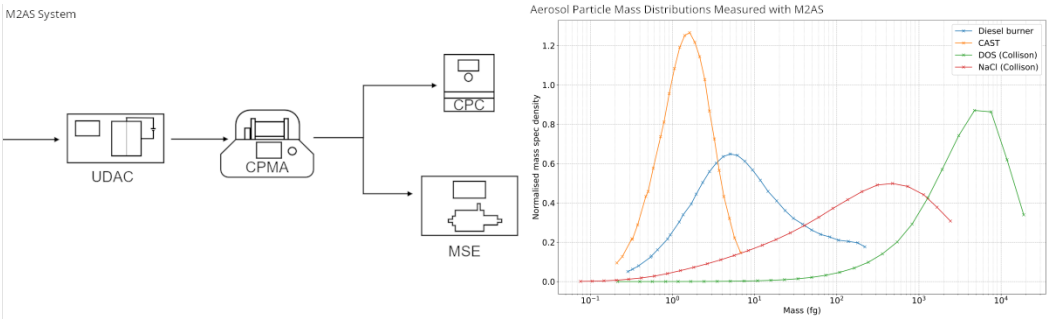
In this presentation we describe the M2AS, a new system for the measuring aerosol particle masses. Measurement of the mass of aerosol particles has significant advantages over conventional particle diameter metrics:

- For non-spherical particles, diameter measurements are dependent on both the particle size and its shape whereas the mass is always well-defined.
- Different diameter metrics (e.g. mobility diameter, aerodynamic diameter) measured by different instruments are differently dependent on density, which is often not well known for real-world aerosols.
- In many areas such as health effects and pharmaceuticals, the mass of material in the particle is of primary importance on its effects on the human body.

With instruments such as the CPMA Centrifugal Particle Mass Analyser or APM used alongside a DMA, or by comparison of different equivalent diameter metrics, it is possible to determine particle masses but this requires a long experiment with multiple scans and correction for multiple electrical charge peaks [1].

The M2AS consists of a unipolar charger feeding a CPMA with the selected aerosol measured by a CPC and a new instrument, the MSE Mobility Separator - Electrometer. The aerosol mass distribution is measured in a single scan of the CPMA. The high concentration unipolar ion charging produces a charge distribution which is effectively continuous and this allows the charge state to be calculated from the ratio of electrometer and CPC counts rather than requiring a prior assumption. Thus the particle mass at any point in the scan can be unambiguously calculated from the CPMA selected mass : charge ratio.



The Mobility Separator is a classifier which divides the aerosol output from the CPMA into two streams according to their electrical mobility: each stream is fed to a separate electrometer detector. The classification voltage required to maintain a given ratio of these two electrometer signals is directly proportional to the median electrical mobility of the aerosol. From this and the charge state the mechanical mobility is thus obtained. This allows the CPMA transfer function width to be calculated, which is required to accurately determine the input aerosol concentration from the CPC measurement. The mobility diameter is also calculated from the mobility, and thus the particle density is also calculated.

Data is presented showing the measurement of the mass and mobility diameter distributions of a range of aerosols from liquid, combustion, and powder sources, and comparison with other measurement methods.

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Nanoparticle metrology and chemical characterization, Contributed Lecture

A New Working Fluid for Condensation Particle Counters with Proprietary Benefits

P. Weber[1,3], O. F. Bischof[1,4], M. Berg[1], J. Schmitt[1], G. Steiner[2], L. Keck[2], B. Fischer[1], A. Petzold[1,3], U. Bundke[1]*

[1]Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research 8 – Troposphere (IEK-8), Jülich, Germany, [2]GRIMM Aerosol Technik Ainring GmbH & Co. KG, Dorfstraße 9, 83404 Ainring, Germany, [3]Institute of Atmospheric and Environmental Research, University of Wuppertal, 42119 Wuppertal, Germany , [4]TSI GmbH, Particle Instruments, Aachen, Germany

We made the discovery of a new working fluid when faced with pending restrictions of passenger aircraft operators that will prohibit the use of butanol as the working fluid in condensation particle counters (CPC) as part of the IAGOS research infrastructure. The working fluid is essential for a condensation particle counter to operate as specified. Butanol is commonly used in alcohol-based CPCs, although it has several disadvantages. These include its pungent, unpleasant odour, negative effects when inhaled over prolonged periods, and flammability. Even so, it has proven its performance over the past almost five decades.

Our research led to the discovery of Dimethyl sulfoxide (DMSO) as a substitute working fluid that meets the restrictions of strict safety regulations. DMSO is an odourless, non-flammable, non-toxic substance that is easily accessible and inexpensive. In our experiments, we could show that the new working fluid behaves equivalent to butanol when used to operate a CPC in terms of the instrument`s counting efficiency, D50 cut-off diameter and concentration linearity. We tested the new substance with four different types of test aerosols and ambient air as shown in Fig. 1. Another focus of our presentation will be the chemical characteristics of the substance and its compatibility with the environment and instrument.

We used the same experimental set-up as Bundke et al. 2015 and Bischof et al. 2019. The particle size was selected using a differential mobility analyser (Model M-DMA 55-U, Grimm Aerosol Technik, Ainring, Germany). At the same time, an electrometer (Model 5.705, Grimm Aerosol Technik, Ainring, Germany) was operated as a reference instrument for the particle number concentration. Our new working fluid was operated on three CPC units representing two different models. Those units include two Sky-CPCs (Model 5411 Sky-CPC; Grimm Aerosol Technik, Ainring, Germany) and a CPC 3772-CEN (TSI Inc., Shoreview, MN, USA).

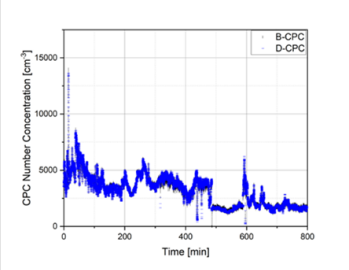

Figure 1. Comparison of the particle concentration measured by two Sky-CPCs operated with two different working fluids (D: DMSO; B: Butanol) during field operation.

Parts of this work were supported by IAGOS-D (Grant Agreement No. 01LK1301A), and HITEC Graduate School for Energy and Climate.

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Nanoparticle metrology and chemical characterization, Contributed Lecture

Electrochemical Synthesis of Ammonia by Zinc Oxide Electrocatalysts

K. Kunene[1,2], A. Braun[1]

[1]Empa: Swiss Federal Laboratories for Materials Science and Technology, [2]ETH Zürich, Department of Academic Services

Ammonia is an important precursor of fertilizers and nitrogen compounds, and it is also a potential energy storage medium and alternative fuel for vehicles [1]. The main ammonia production process is the Haber–Bosch process, which is energy- and capital-intensive [2]. Therefore, it is crucial to find an alternative method for the synthesis of ammonia. In this work, we reported a zinc oxide electrocatalyst (ZnO) for the electrochemical synthesis of ammonia. ZnO was synthesized via an electrochemical method and characterized by X-ray diffraction (XRD) and UV-Visible spectroscopy (UV-Vis). Ammonia will be synthesized from hydrogen and nitrogen under atmospheric pressure using ZnO as catalyst at the cathode and 0.1 M potassium hydroxide (KOH) as the electrolyte. We believe that this work will provide a new opportunity to design a new catalyst for the nitrogen reduction reaction (NRR) and also open a new route to solve the global energy and ecological crisis. The authors acknowledge support from Durban University of Technology, and from the Swiss SERI as Swiss Government Excellence Scholarship, EDA/SBFI no° 2022.0299 / Südafrika / OP. This project originates from the Swiss South African Joint Research Programme (SSAJRP).

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Nanoparticle formation and transformation, Contributed Lecture

High-throughput generation of aircraft-like soot: Dynamics of soot surface growth and agglomeration by enclosed spray combustion of jet fuel

U. Trivanovic[1], G. A. Kelesidis[2], S. E. Pratsinis[1]*

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[2]Nanoscience and Advanced Materials Research Center, School of Public Health, Rutgers University

Aircrafts constitute an important source of ultrafine soot. High costs and limited access, however, make it difficult to perform routine characterization of soot generated from aircraft engines. So, high-throughput, laboratory units for generation of aircraft-like soot are needed to understand the impact of such emissions on public health and climate change. Here, enclosed spray combustion (ESC) of jet fuel is used to generate high concentrations of soot with characterstics similar to soot from aircraft engines [1]. The characteristics of such soot are controlled by the ESC Effective eQuivalence Ratio (EQR). At low EQR, soot had similar mobility, primary particle diameter, organic carbon to total carbon ratio and Raman spectra to that measured from real aircrafts. To this end, soot formation during ESC of jet fuel along the centerline of the flame [2] is investigated at heights above the burner (HAB) 5 – 63 cm and EQR 1.46 – 1.88. At residence times, t < 12 ms and HAB < 5 cm, soot grows largely by surface growth. Then, agglomeration dominates and increases the median mobility diameter, d_m, up to 88 nm at HAB = 63 cm, while the median primary particle (PP) diameter, d_p, remains constant. While d_p is constant at EQR ≤ 1.59, increasing the EQR up to 1.88 increases the d_p to 23 nm. Simultaneously, the Raman D/G decreased from 0.9 at EQR = 1.46 to 0.8 at EQR = 1.88 suggesting that larger PPs have more graphitic nanostructure than smaller ones, as shown previously [3]. To confirm this, X-ray diffraction was used to obtain the soot crystallite length, L_c (Fig. 1, triangles) and interlayer distance, d_{002} (Fig. 1, circles). Fig. 1 shows a clear correlation between both d_{002} and L_c of soot as a function of d_p. So, the ordered nanostructure attained by large soot nanoparticles results in small oxidation rates [4] and large light absorption [4] affecting both its cytotoxicity [5] and radiative forcing [6].

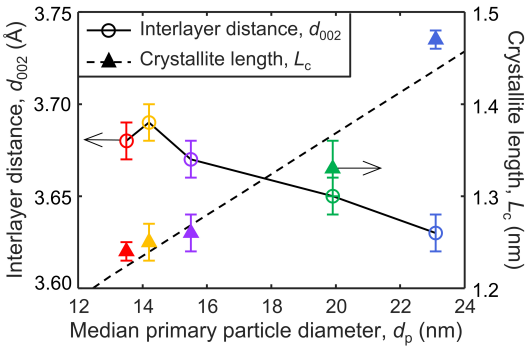

Fig. 1: Crystallite length, L_c and mean interlayer distance, d_{002} of soot from enclosed spray combustion (ESC) of jet fuel that matches the characteristics of aircraft soot as a function of d_p.

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Nanoparticle formation and transformation, Contributed Lecture

Formation, Growth, and Photochemical Aging of Laboratory-Generated Nanoparticles

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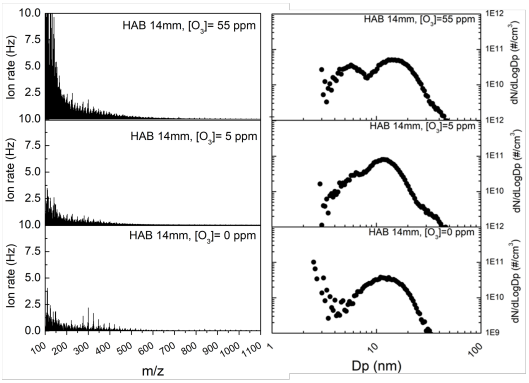
Atmospheric aerosol nanoparticles have important implications for global warming, climate change and human health [1]. The characterization of the dynamics contributing to the formation of atmospheric aerosol nanoparticles is crucial to reduce the anthropogenic footprint on the Earth. In this sense, a central role is occupied by the identification of the precursors of these compounds to further investigate nanoparticles formation, growth, and oxidation processes.
In this work, through an experimental system simulating secondary aerosol (SOA) formation, i.e., those particles that are formed in the environment after the interaction of solar radiation with primary emitted pollutants [2], the chemical and physical precursors of nanoparticles are investigated. The formation and growth processes are studied through the analysis of exhaust gases of an ethylene-rich premixed laminar flame. The products of the pre-mentioned system, collected at different heights above the burner, are conveyed into an oxidation flow reactor (DOFR^{TM}), simulating various atmospheric conditions. Different aging times in the atmosphere are reproduced. To investigate the nucleation growth of new-born particles and to follow the evolution of particle size distribution, a Scanning Mobility Particle sizer (SMPS) system and a High Resolution- Time of Flight- Aerosol Mass Spectrometer (HR-ToF-AMS) are used. The products of the analysed system are extracted by a tubular dilution probe positioned at different residence times in the flame, representing particle nucleation zone and mature soot particles. In the plot, the effects of different ozone concentrations are shown for the condition in which mature soot is withdrawn from the flame (Heigh Above Burner of 14mm). As oxidation proceeds in the ageing reactor, the size distribution of the particles changes and a new particle mode appears at low sizes; these newly particles are formed in the oxidation flow reactor; mass spectra show an increase of low m/z signals, probably due to an oxygen-induced fragmentation of the primary larger particles. Measurements performed on biofuel-based flames are under investigation to understand if the same mechanism is exhibited also by sustainable fuels.



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Nanoparticle formation and transformation, Contributed Lecture

Chemically resolved volatility of biomass burning emission

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Primary organic aerosol (POA) emitted from biomass burning contributes a large fraction of carbonaceous aerosol and trace gases on regional and global scale. These emissions play an important role in air quality, climate, and human health. Volatility dictates the partitioning of compounds between the gas and particle phase. Recently, many methods are available for estimating the volatility of compounds on the basis of molecular formula[1]. However, there are large uncertainties when applying parameterizations to estimate the volatility of the same compounds from different sources of OA. Further, the volatility can be dependent upon the mixture of molecules that are present due to deviations from Raoult's Law. Therefore, the volatility of biomass burning OA, as a large contributor to global OA, should be further clarified. Here, the thermodeunder (TD) is applied to investigate the evaporation behavior of beech logs burning combined with the extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF)[2] which achieves real-time and molecular formula measurement of water soluble constituents of OA. An evaporation-kinetics model was used to retrieve the effective saturation concentration (C*) which was constrained by the empirical relationship between C* and H_{vap}. Almost all the POA evaporated in the TD at 100 ℃ with the effective residence time at 6 s. The larger compounds evaporated generally slower than compounds having smaller molecular weight. The $\log_{10}$C* of compounds from beech logs burning varied from -4 to 1 ug/m^3 combined with H_{vap} in the range of ~110 to ~170 kJ mol^{-1}. As shown in Figure 1, more than half of the biomass burning POA is composed of low-volatility organic compounds (saturation concentration of <0.3 μgm^{-3}). The modelled volatility is compared with other estimations in the literature, and the new parametrization for BBOA is proposed based on molecular formula.

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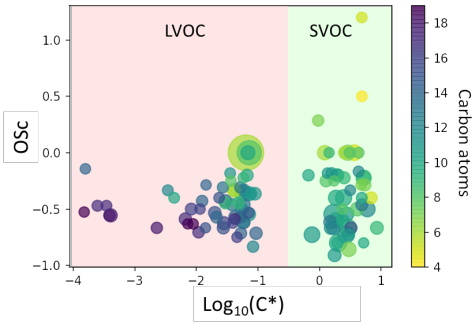

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Nanoparticle formation and transformation, Contributed Lecture

Investigating the transition from gas-phase species to nanoparticle formation in high temperature regimes

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Understanding the formation of polycyclic aromatic compounds (PACs) in combustion not only bridges the knowledge gap between the small gas-phase species and incipient soot particles, but may also help address the global emission issues of both PACs and soot. In this work, we present a stochastic modeling code, named SNapS2, to study the chemical processes that link gas-phase species to nanoparticle formation. SNapS2 utilizes kinetic Monte Carlo scheme and a kinetic mechanism of 430 generic reactions.

In addition to the chemical growth, the physical clustering of polycyclic aromatic compounds (PACs) is a central step in the transition of gas-phase molecules to mature soot particles. Properly accounting for these phenomena requires a comprehensive understanding of the energy barriers which control the PAC dimerization process.

In this work, we demonstrate how machine learning can use basic molecular features to accurately predict the dimer dissociation energy barrier, which can be directly related to the dimerization rate and reversibility of the soot inception process.

For a diverse set of PACs at multiple temperatures, we perform molecular dynamics simulations to obtain the free energy surfaces of the dimerization process. Using this data, we then show that at multiple temperatures, machine learning can predict free energy barriers significantly more accurately than commonly used mass correlations.

In making its predictions, the machine learning algorithm automatically identifies a set of specific molecular descriptors which can both quantitatively be related to the energy barrier and qualitatively related to interpretable properties important to the dimerization process such as size, surface area, presence of functional groups, and oxygenation.

The machine learning of energy barriers in this work offers soot inception models a means of taking into account complex PAC chemical features to derive accurate physical aggregation rates at minimal computational cost.

Periodical technical inspection for in-use vehicles, Contributed Lecture

Roadside detection of excess particle emitters: practical limits & potential for "garage-grade" instruments

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In this work, the practical limits of remotely detecting defunct particle filters by roadside instrument are reviewed, and the potential for the use of “garage-grade” particle instruments intended for new periodic technical inspection (NPTI) is examined.

With nearly all combustion engines equipped with particle filters, an increasing portion of exhaust emissions of compounds hazardous to human health is attributable to a relatively small portion of vehicles with emissions malfunctions. Remote sensing of vehicle emissions by open-path spectrometers, useful in capturing high emitters of gaseous pollutants, has a practical limit on particle measurement, as it is insensitive to particles smaller than several hundreds of nanometers. As an alternative, instruments sampling from the side of the road [1], from bridges [2], manholes, or a drive-through enclosure [3] were proposed to detect vehicles with defective or absent particle filters but little or no visible smoke. Typically, particle concentrations measured by counters, diffusion chargers, classifiers, photoacoustic or laser induced incandescence detectors were divided by CO_2 concentrations measured by infrared analyzers, producing a fuel-specific emissions factor (particle number or mass / kg fuel).

Overall, the finite speed and the variability of plume dispersion pose a practical limit on minimum vehicle spacing of several (mid units of) seconds, higher than both the range of typical light-duty vehicle spacing and the safe distance of approximately 2 seconds, effectively restricting the method to heavy vehicles (as in [2]) or to metered access areas such as a drive-through tent [3]. The limit of quantification of the emission factor is affected both by the exhaust dilution ratio (CO_2 concentration) and by the particle concentration detection limit, which is inherently limited by background particle concentrations, including temporary spikes from very high emitters.

It is the opinion of the authors that the particle background levels and other factors pose much higher inherent limitations than the technical capabilities of low-cost portable diffusion chargers, and that with careful selection of the measurement location and placement of the sampling inlet, remote drive-by filter integrity tests can be done, for example, at gated entrances to university campuses and similar areas with NPTI-style particle counters and other relatively simple and low-cost instruments.

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