Conference report:

22nd ETH Conference on Combustion Generated Nanoparticles

The 22nd ETH Conference on Combustion Generated Nanoparticles was held on June 18-21, 2018 in Zürich, Switzerland. The Conference program included a number of presentations and posters on a range of topics, including particle fundamentals, ambient air pollution and health effects, emission control from diesel and gasoline engines, particles from other combustion sources, and emission measurement. The conference also included an exhibition with the participation of suppliers of emission measurement instruments, emission control systems and related products and services.

PTI. A significant portion of the conference was devoted to recent developments around in-use emissions compliance at periodic technical inspections (PTI) in Europe. Currently, emissions compliance at the PTI is determined through the OBD system. If no OBD trouble codes indicating an emissions problem are indicated, the vehicle is assumed to meet emission requirements. If a trouble code is indicated, the vehicle may be required to undergo an emissions test. For diesels, this means a measurement of exhaust opacity and for gasoline vehicles, an idle CO measurement. This approach has proved to be unreliable because emission control systems can be tampered with or failures such as damaged DPFs may not be reliably detected with an opacity measurement. Recent studies conducted in The Netherlands, Switzerland and Belgium have shown that ~10% of DPF-equipped passenger cars have high PN emissions that could indicate a damaged or removed DPF [Suarez-Bertoa][Gloor].

As a result, a number of countries are moving to a mandatory emissions test at the PTI. For example, in September of 2017, Germany modified its PTI emission requirements to require a mandatory emissions test at the PTI regardless of the ODB status. Starting 01/2018, vehicles will require an emissions test at the PTI. While diesel vehicles will only require an opacity measurement for the next few years, a new PTI test procedure for PN is anticipated starting 2021. Other nations including The Netherlands, Belgium and Switzerland are following similar paths.

With regards to the anticipated PTI PN test procedure, an informal working group was set-up in 2016 through an initiative of the VERT-Association and chaired by Dr. Andreas Mayer to develop such a procedure. Participants in this group include researchers, instrument manufacturers, governments, type approval authorities and the European Commission's Joint Research Centre (JRC).

The JRC has evaluated a number of CPC and DC charge-based instruments for their suitability for evaluating PN from both gasoline and diesel vehicles during PTI [Suarez-Bertoa]. They have found that a low idle measurement is suitable to detect DPF failures and that the instruments should avoid measuring volatile particles. As far as extending a PN-PTI test to GDI vehicles, further

study is required as there is significant variation in PN over time even with some GPF equipped vehicles.

A preliminary proposal for a minimum PTI PN instrument specification has been put forward by TNO: a 70 nm size cut-off and a range from $0\text{-}5\times10^6$ #/cm^3 [Kadijk]. Smoke meters currently cost around about €3,000 and a similar price point is desirable.

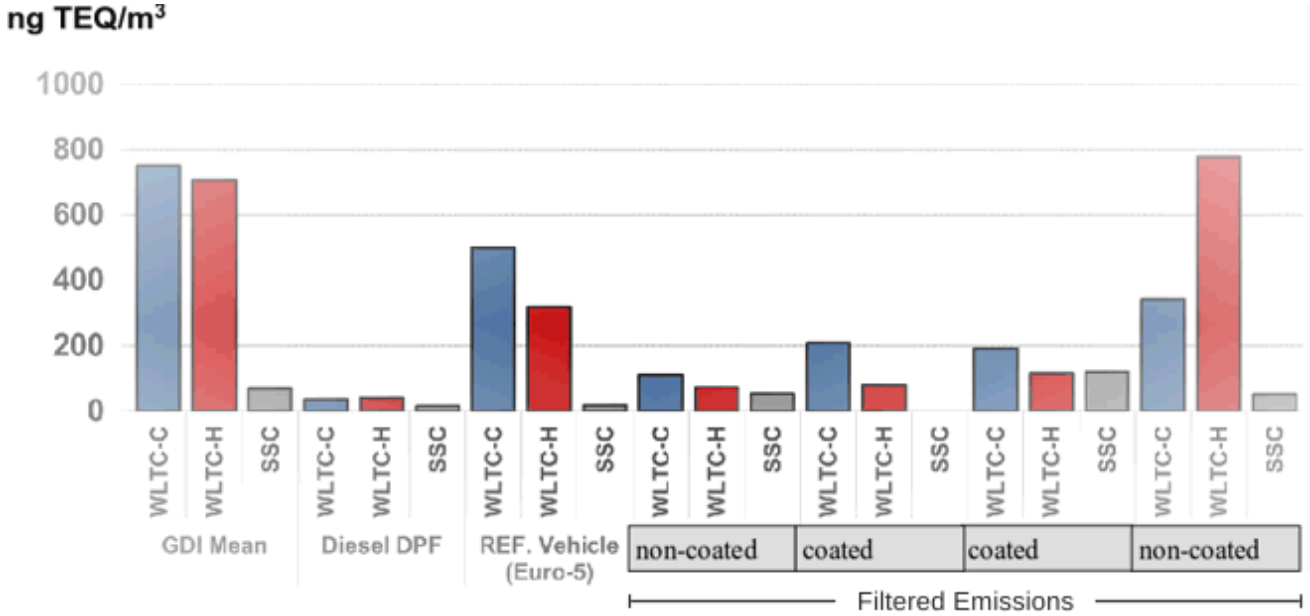
Several manufacturers have been developing instrumentation for PTI PN. Sensors, Inc. have developed a microprocessor controlled module, the Automotive Particle Bench (APB), that incorporates an iso-propanol condensation particle counter (CPC) and an ejector diluter; additional dilution and a VPR are required to be added for a complete instrument [Bokker]. TSI is developing a simplified version of is iso-propanol CPC based instrument approved for Swiss construction machinery, the TSI 3795. This uses a single stage of dilution and will likely use a catalytic stripper VPR [Spielvogel]. Naneos, makers of the Partector instrument that is based on pulsed high voltage particle charging followed by detection and used in the AVL PEMS system, is developing a version for PTI. The Partector provides a signal related to the lung deposited surface area. External dilution may not be required [Fierz].

Some participants of the VERT working group would also like to see an emissions test for NOx incorporated into PTI [Müller][Czerwinski]. However, this is much more complicated than for PN. To be useful, NOx emissions would need to be measured under engine load; requiring chassis dynamometers or on-road testing. Also, NOx control uses a number of strategies such as aftertreatment, EGR and engine calibration that can be active only under some engine operating conditions and that vary from one manufacturer to another. Relating NOx emissions from a simple PTI test to type-approval limits will undoubtedly be challenging.

GDI. Work at Toyota is attempting to identify the contribution of vehicle exhaust to ambient secondary organic aerosol (SOA) formation [Okamura]. The majority of $PM_{2.5}$ in Japan consists of SOA and the contribution from vehicle exhaust to this SOA is unknown. Toyota has built a flow reactor to attempt quantification of SOA formation potential of vehicle exhaust. With vehicle exhaust from a single vehicle, SOA formation was sensitive to dilution ratio and NMHC concentration with maximum rates of 1.5 mg/km reported for a MY 2016 1.2 L DISI Japanese vehicle. Rates were highest over the cold start WLTC. If sufficient seed particle surface area is available in the chamber, very little SOA is formed; seed surface area below 1×10^9 (nm^2/cm^3)/ppm NMHC was required to form SOA.

EMPA presented more results from their work looking at genotoxic PAH emissions from GDI vehicles [Muñoz]. In the past, they have discussed emission rates of these compounds from several GDI vehicles. This year, they presented results from a Euro 5 GDI vehicle to which they installed a GPF at the tailpipe. Four prototype GPFs were tested; two catalyzed and two uncatalyzed. The Euro 5 GDI vehicle without a GDF had emission rates of the genotoxic PAHs a little lower that the average rate of several Euro 3-6 GDI vehicles, see Figure below. Adding a GPF at the tailpipe lowered the emission rates with 3 of the 4 GPFs. However, one uncoated GPF increased genotoxic PAHs during a hot start WLTC. Genotoxic PAH emissions with the GDI vehicles with the GPF were higher than for the diesel vehicle. Interestingly, the other uncoated GPF had the lowest emission rates of genotoxic PAHs of all the GDI vehicles. It should be noted that the engine and vehicle were not optimized for any of the GPFs and it is unclear whether the behavior of the genotoxic compounds with the GPFs is reflective of GPF characteristics or the

impact of their increased backpressure on engine operation. Additional details of this project are available elsewhere.



Emission rates of 8 genotoxic PAH compounds from a Euro 5 GDI vehicle fitted with 4 different GPFs on the tailpipe. In units of toxic equivalency concentration (TEQ).

Measurements. Work on reducing the minimum particle size of the PMP method from the current 23 nm to 10 nm or less to make it more sensitive to the smaller particles expected from GDI vehicles has picked up momentum. Three programs that are partially funded by the EU and meant to address this problem were discussed. These programs focus not only on the development of a PN measurement procedure for particles down to 10 nm or less, but also on characterization of particles below 23 nm.

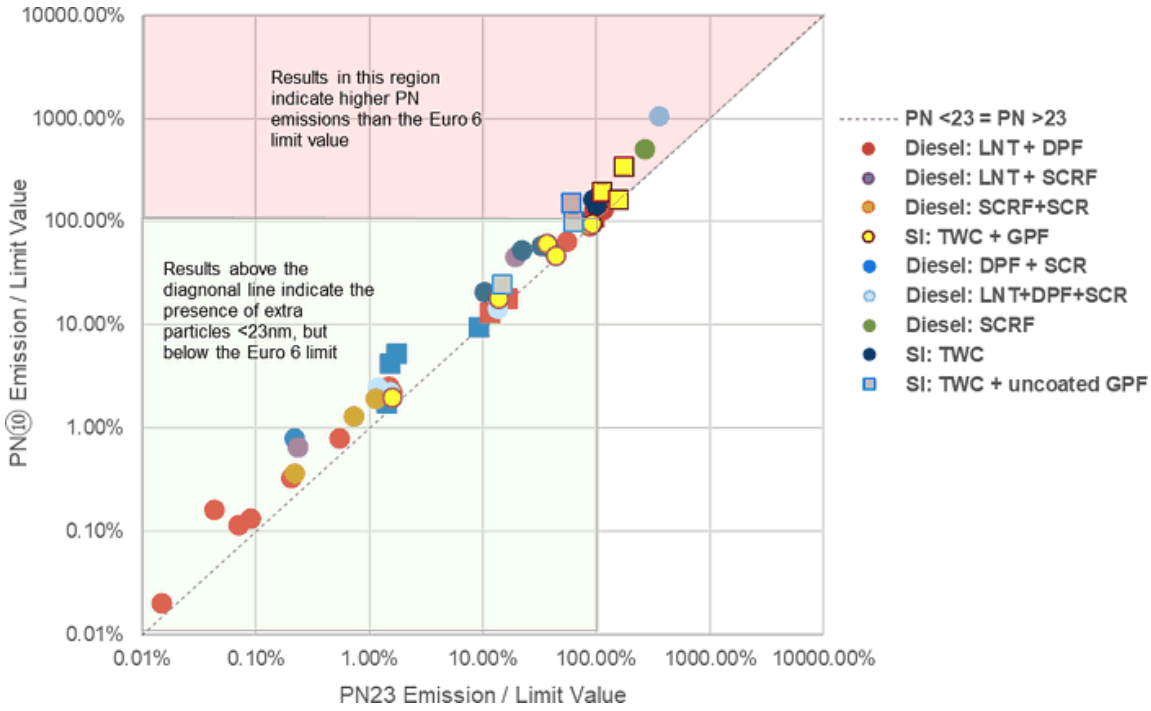
The SUREAL-23 project is coordinated by the Aerosol and Particle Technology Laboratory (APTL) at the Centre for Research and Technology-Hellas (CERTH) [Vlachos]. To extend the two-stage dilution sampling system of the PMP method to smaller particles, they are developing a mixed oxide catalytic stripper VPR as an alternative to the evaporation tube VPR currently used in the PMP. A catalytic stripper will not only oxidize heavy-hydrocarbons that could potentially form volatile particles upon cooling, it can also adsorb SO_2.

Another path being considered in the SUREAL-23 project is the use of a single stage of dilution combined with an instrument capable of accepting a high temperature sample; up to 200°C. In addition to a simpler dilution strategy, this approach could also avoid the need for a VPR. A half mini DMA capable of 200°C operation by SEADM and a variation of the diffusion charging Partector by Fachhochschule Nordwestschweiz (FHNW) [Rüggeberg] capable of 150°C operation are potential instruments for this approach.

The DownTo10 program coordinated by Aristotle University of Thessaloniki includes project partners Ricardo and AVL. A prototype system has been built that consists of two porous tube diluters and a third, optional ejector diluter stage for sampling high particle number concentrations [Andersson]. An evaporation tube or catalytic stripper can be placed between the two porous diluter stages. The catalytic stripper is preferred because of its ability to eliminate

potential artifacts from volatile particles. A CPC is used for particle detection and a 50% counting efficiency at about 10 nm has been demonstrated.

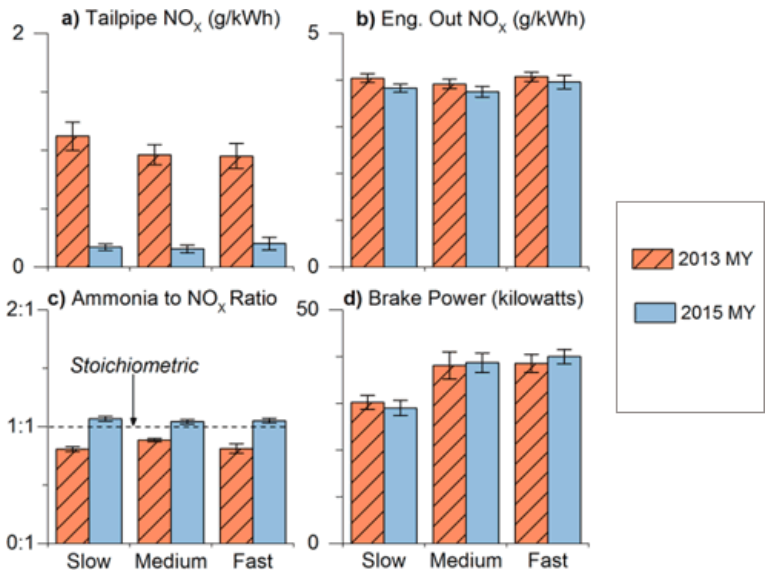
Preliminary test results from a number of vehicles have been collected and compared to the current PMP method, see Figure below. The results that exceed the Euro 6 limit in this Figure include diesels undergoing a regeneration, a GDI with a GPF over a "hot RDE", a GDI without a GPF and a diesel with LNT/DPF over the WLTC. On average, PN10 is about 40% higher than PN23.



PN measurements with a 50% counting efficiency at 7 or 10 nm (PN10) compared to the current PMP method (PN23) collected on a chassis dynamometer. Results include US cycles, Japan cycles, NEDC, WLTC, moderate RDE and some cruises cycles.

The PEMS4Nano project is coordinated by Horiba and includes Bosch and TSI. Efforts in this project include the development of a catalytic stripper and a CPC [Focsa].

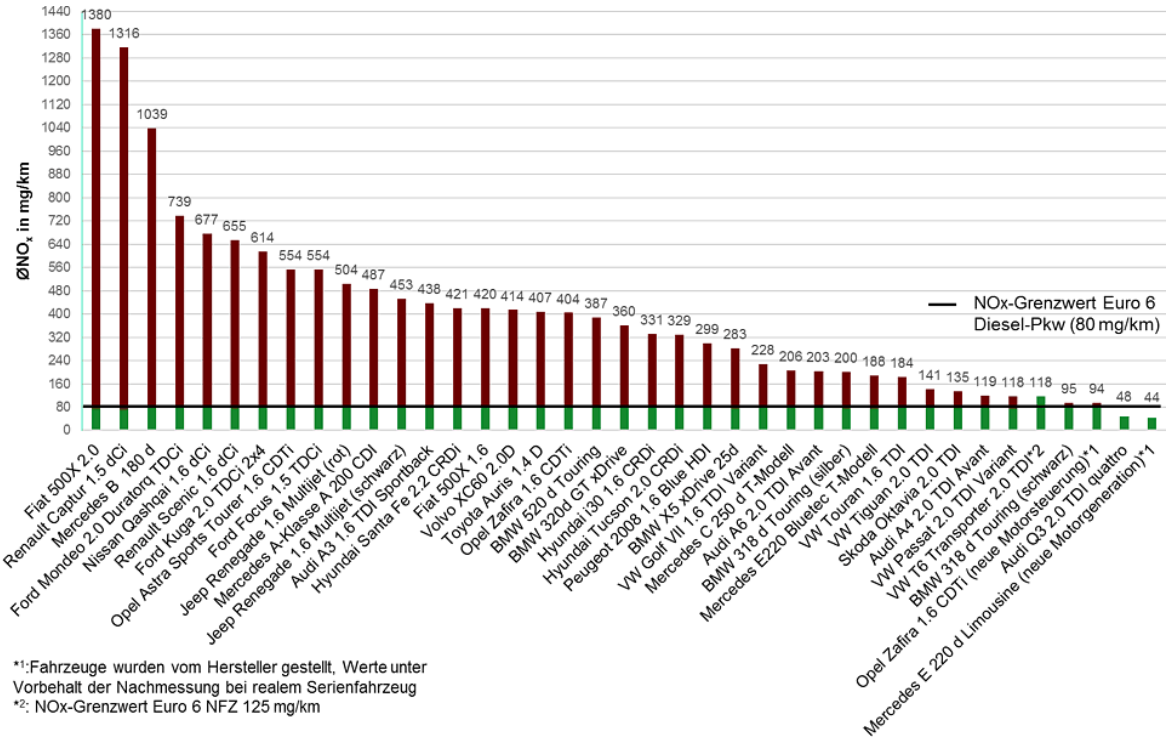
Diesel. Particle emission results from in-use emissions measurements from two transit buses, a MY 2013 and MY 2015 each with a Cummins ISL 8.9 L engine carried out by the University of Minnesota were presented [Kittelson]. NOx and urea dosing control from these buses has been discussed elsewhere and is summarized in the Figure below. The PN emissions for these buses were analyzed in an attempt to determine if there was any contribution to PN from urea as has been reported in the literature. While the PN emissions from the MY 2015 bus were higher (MY 2015 1.27×10^{11} #/kWh, MY 2013 1.34×10^{10} #/kWh), a significant portion, but not all, of this increase could be explained by an active regeneration that occurred during testing. The regeneration caused a spike in PN emissions and the filtration efficiency of the DPF post-regeneration would have been lower until a significant soot cake formed. Further characterization of the PN emissions is required to determine if the remaining difference is indeed due to the higher urea dosing rates in the 2015 bus.



Average tailpipe and engine-out NOx emissions, ammonia/NOx ratio (ANR) and brake power from two transit buses with Cummins ISL 8.9 L engines.

It should be noted that the MY 2013 engine used a urea dosing strategy that incorporated an NH_3 sensor in the mid-brick position of the SCR catalyst while the 2015 MY engine used a model based dosing strategy.

Deutsche Umwelthilfe (DUH) tested a number of Euro 6 diesel passenger vehicles over a combined urban/motorway route in Berlin [Friedrich]. The route chosen was shorter than the RDE with the rationale that few Europeans drive the distance represented by the RDE test in one trip. The results are shown in the Figure below; the three highest emitters were MY 2016 vehicles.



In-use NOx emissions from a number of Euro 6 passenger vehicles

EMPA tested disposable cellulose based DPFs to characterize the emissions of genotoxic PAHs and nitro-PAHs [Heeb]. Cellulose based filters must be maintained at temperatures below 200°C

so these materials will accumulate and potentially be released as the filter is loaded. It is also possible that NO_2 can react with PAHs accumulated on these filters to form nitro-PAHs. They tested a new cellulose filter and one that had accumulated >2000 h and was heavily loaded (n.b., 2000 h is a very long time of operation for a cellulose filter—some manufacturers recommend replacement intervals of no more than 30 h). For the clean filter, volatile PAHs such naphthalene were not retained but semi-volatile PAHs with 3 or more rings had retention efficiencies >75%. With the loaded filter, PAHs with 4 or more rings were released at rates 3-6 times higher than that at the filter's inlet. With regard to nitro-PAHs, they tend to be reduced with the clean filter; the exception being lighter nitro-PAHs such a n-naphthalene which pass through the filter. With the loaded filter, emission rates of all nitro-PAHs were from 2-50 times higher than that at the filter's inlet suggesting either release of these compounds well after accumulation on the filter or that they are formed by a reaction of PAHs and NO_2.

Health Effects. Recent media coverage of "dirty diesel" and the resulting fallout from a health perspective was discussed by the Swiss Tropical and Public Health Institute Basel (Swiss TPH) [Künzli]. The primary health effect of the cycle-focused strategies that have been used by some vehicle manufacturers to certify many diesel passenger cars is related to an increase in traffic related NO_2. While there are increased adverse health outcomes and even deaths that can be associated with increased NO_2 from diesel cars, the numbers pale in comparison to the 7 million annual deaths that can be attributable to air pollution. The "diesel scandals" have served to shift focus away from more important global air pollutants such as $PM_{2.5}$ and SO_2 and lead to irrational policy decisions such as the diesel bans appearing in some European cities. For example, the recent diesel ban in Hamburg bans older diesel vehicles from 2 streets and may actually have the effect of increasing air pollution as drivers of these vehicles must find longer alternative routes. Interestingly, the location of the selected streets coincides with the location of at least two air monitoring stations for NO_2. Another example of an irrational policy choice is the EU's refusal to lower ambient air quality standards for $PM_{2.5}$ from the current 25 $\mu g/m^3$ to the WHO science-based guideline of 10 $\mu g/m^3$ (annual average). The US annual average ambient air quality standard for $PM_{2.5}$ is 12 $\mu g/m^3$.

One important issue regarding ultrafine particles (UFPs) is the demonstration of adverse health effects associated with their exposure. While the evidence for adverse health effects for exposure to $PM_{2.5}$ and PM_{10} is clear, that for UFPs has been elusive. While it is believed by many that there are adverse health effects due to exposure to UFPs beyond those attributed to PM_{10} and $PM_{2.5}$, there have been an insufficient number of epidemiological studies that clearly demonstrate this. In order to clarify the current state of the epidemiological evidence, a survey of studies published between 2011-2017 was carried out by the University of Düsseldorf and the Swiss TPH [Hoffmann]. This survey builds on a prior study carried out by the HEI in 2013. A total of 85 studies were identified that met the inclusion criteria. One significant challenge was that few studies used a consistent criteria for exposure assessment; the size range of particles considered in the studies varied considerably from one study to the next and in some case extended well beyond what is considered UFP (i.e., < 100 nm). Another challenge was that few studies adjusted for co-pollutant exposure. Those that did, found that morbidity results were attenuated after adjusting for PM_{10}, $PM_{2.5}$ and NO_2; the adjustment for NO_2 being the most significant. The most significant adverse effects of UFP, even after adjusting for co-pollutants, were found to be for subclinical outcomes such as lung function and cardiovascular effects.

Climate Effects. An issue that seems to be gaining increased attention with regard to climate forcing is that of brown carbon. Until very recently, it was widely believed that the black carbon

portion of atmospheric PM was the primary component responsible for absorption and thus a contributor to global warming while the organic fraction was thought to be reflective and thus had a cooling effect. However, this appears to be an oversimplification. Between these two cases lies a class of organic compounds that are light-absorbing and also could contribute to warming. These compounds are broadly categorized as brown carbon. They absorb primarily at shorter wavelengths - this gives them a brown color. An important source of brown carbon is biomass burning. It can also be produced by marine engines burning HFO.

Brown carbon deposited on snow can have a very significant regional impact on direct radiative forcing (DRF); much larger than that implied by its global importance. Up to 18% of the DRF (~10 W/m^2) of HFO PM deposited on snow can be attributed to brown carbon. This can have important implications for ships traveling through arctic waters for example [Corbin].

Conference website: nanoparticles.ch