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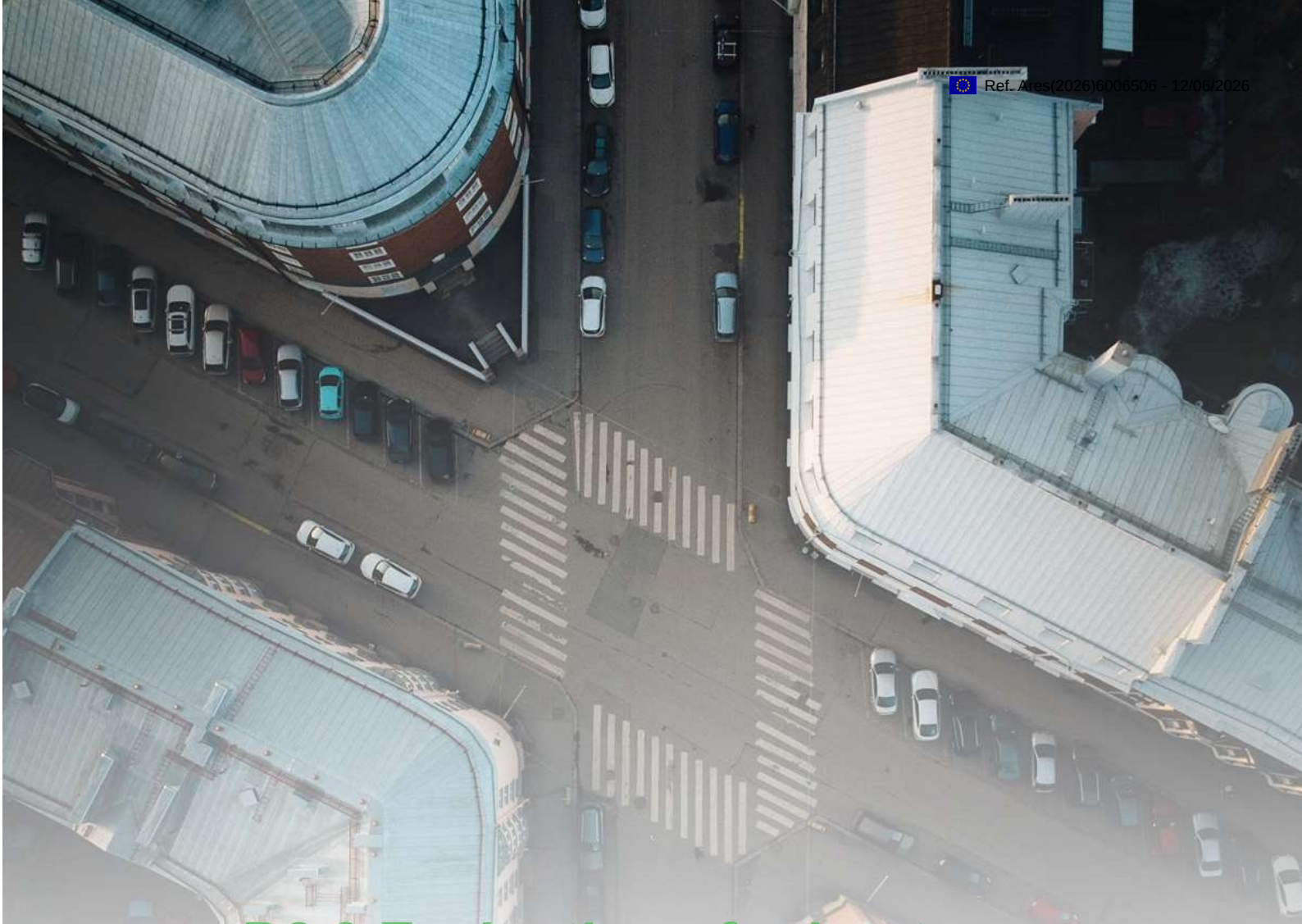

D2.3 Evaluation of robust measurement methods for estimating secondary aerosol mass

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PAREMPI
Particle emission prevention and impact: from real-world emissions of traffic to secondary PM of urban air

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PAREMPI Particle emission prevention and impact: from real-world emissions of traffic to secondary PM of urban air

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Appendix 1. Characteristics of the selected FTIR instruments.

Appendix 2. Principles of exhaust and fuel flow based calculations

List of abbreviations

BC	Black carbon
CAN	Controller Area Network, a communication system of vehicles
CLD	Chemiluminescent
CVS	Constant volume sampler
CO	Carbon monoxide
CO_2	Carbon dioxide
EF	Emission factor
EFM	Exhaust flow meter
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy
NDIR	Nondispersive infrared
nv	Non-volatile
OFR	Oxidation flow reactor
OH	Hydroxide
PAM	Potential aerosol mass chamber
PM	Particulate matter (mass)
PN	Particle number
ePMI	Equivalent total particles emissions index module
PM_{aged}	Particulate matter (mass), aged particles including SecA
PM_{fresh}	Particulate matter (mass), fresh particles before ageing
PTR-MS	Proton Transfer Reaction Mass Spectrometer
QCL	Quantum cascade laser
RH	Relative humidity
SecA	Secondary aerosols
SNR	Signal-to-noise ratio
STP	Standard temperature and pressure, 273.15 K, 100 kPa
UV	Ultraviolet
VOC	Volatile organic compounds

1. Executive summary

This report details robust measurement methods for estimating the contribution of PM2.5 from transport sectors, formed through secondary aerosol (SecA) reactions, and methods to estimate harmfulness of PM2.5. The term “robust measurement system” refers to its applicability in real-life field conditions without the need for dedicated specialists, although expertise in emission measurements is still required. The robust measurement methods were evaluated alongside a complex measurement system within the PAREMPI project.

The system comprises of a portable Oxidation Flow Reactor (OFR), a dilution system, a particle number size distribution (PSD) device, from which the results are converted to PM mass, and instruments for measuring precursor gases (NO_x, NH_3, SO_x, aromatics) as well as other necessary gases (NO_x, CO, CO_2) and toxicity. The recommended emission metric for aged PM (per megajoule) is defined based on the CO_2 concentrations and fuel properties, eliminating the need for exhaust or fuel flow measurements and therefore simplifying the setup. Although not detailed in this report, regulated PM is also an important parameter, enabling the presentation of the ratio of aged to fresh PM.

For the first time, the robust measurement system was defined to estimate transport sectors’ PM2.5 through SecA formation, suitable for real-life conditions, which enables increased number of studies to fill in gaps in knowledge. A significant milestone in PAREMPI was the integration of an Air-Liquid Interface (ALI) exposure chamber into a moving vehicle, enabling on-road sampling of heavy-duty truck emissions, and in situ toxicity testing.

The outlook beyond PAREMPI encompasses the precise definition of conditions and the target settings for the OFR, as well as the detailed requirements for instruments. These elements are critical to ensure comparability of results across different studies.

2. Introduction

Exhaust emission measurements have been carried out since the 1950s (Keenan 2017). Emission standards define so called regulated emissions, including nitrogen oxides (NO_x), carbon monoxide (CO), total hydrocarbons (THC), particulate matter (PM) mass, the number of non-volatile particles exceeding 23 nm (nvPN23) and black carbon (BC). The forthcoming Euro 7 emission standards will extend to nvPN above 10 nm and potentially introduce new emissions species (EU 2024, Samaras et al. 2022). These standards define the measurement methods to be employed both in laboratory and in the field, such as on-road measurements.

In this study, we evaluate the robust measurement system to investigate the potential particle mass formed through atmospheric reactions involving primary particles and gaseous precursors, which is an approach that extends the scope of tailpipe emissions (Figure 1). Currently regulated PM mass emissions (hereinafter PM_{fresh}) increase through atmospheric reactions as precursor gases convert into additional mass on PM_{fresh}. This additional PM mass, the difference between PM_{aged} and PM_{fresh}, is known as SecA mass. Thus, SecA is not directly measured.

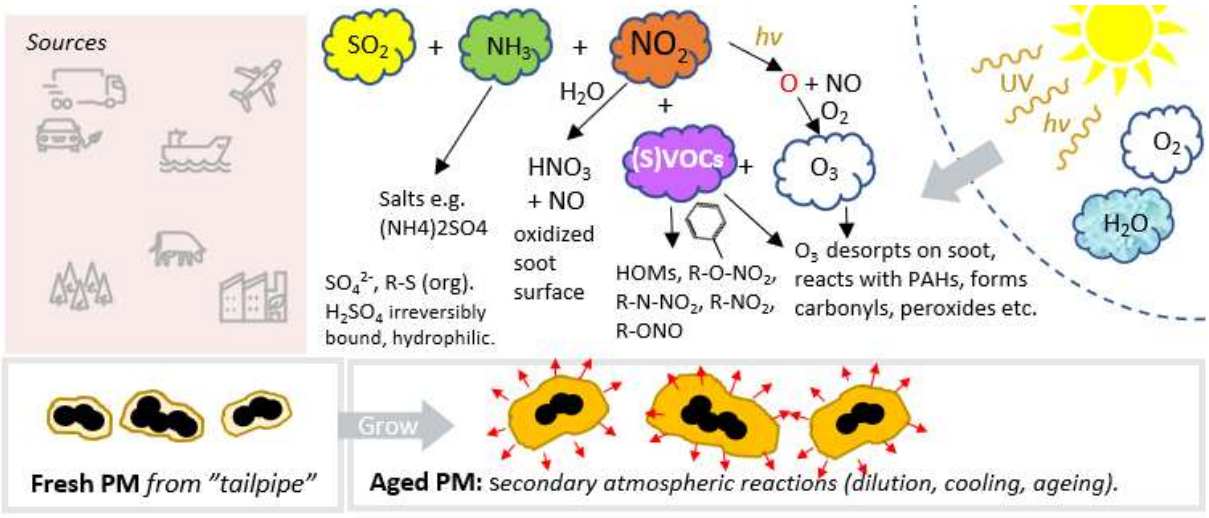

Figure 1. Schematic figure of the transformation and growth of fresh "tailpipe" PM to aged ambient PM through atmospheric reactions during dilution, cooling and ageing.

The measurement of potential PM_{aged} mass formed through secondary reactions of precursor gases in atmosphere is challenging with the current methods used by the scientific community. These methods are typically unsuitable for on-road or on-board measurements due to their relatively large size, complexity and sensitivity to challenging conditions. However, smaller instruments are being developed, such as PEMS-type FTIRs, oxidative flow reactors (OFR) and toxicity incubators, some of which are already available in portable sizes. The SecA mass could also be estimated from the measured gaseous precursors; however, current knowledge on the relationship between precursor gases and SecA formation is limited, encompassing only a few exhaust compositions and surrounding conditions.

In this report, we evaluate the robust methods for determining the potential PM_{aged} mass formed from precursor gases and methods to estimate the harmfulness of aged PM. The term "robust measurement system" refers to a system designed for measurements in real-life field conditions, such as on-road and on-board environments. These measurement methods should not require dedicated specialists, although expertise in basic emission measurements of transport applications is necessary. Important

aspects of the robust measurement system include its complexity, weight, dimensions, operation, validation possibilities, and general pros and cons. Some of these features, particularly the protocol for operational details and target settings for the OFR, are not within the scope of this report. However, these are necessary actions that should be addressed beyond the duration of PAREMPI. Although not emphasized in this report, it is recommended to measure regulated emissions, especially the regulated PM (PM_{fresh}) emission, in parallel with the potential PM_{aged} emission. Additionally, measurements of the other exhaust characteristics, such as semi-volatiles, polycyclic aromatic hydrocarbons (PAHs), anions, BC, organics and metals, would enhance understanding of the phenomenon studied.

Robust measurement methods facilitate the generation of a comprehensive knowledge base on aged particulate matter derived from transport applications. This information is necessary for supporting policies aimed at limiting and preventing ambient PM levels originating from transport sources. Reliable and robust measurement systems enable the extension of studies to a wide range of transport technologies. In PAREMPI, these results are also essential for the modelling activities and health impact assessments. Molecular-level experiments and the modelling of reactions and processes leading to the formation of SecA due to atmospheric aerosol chemistry provides insights into the contributions of precursor gases. All these findings are necessary for the development of the equivalent total particle emissions index (ePMI) module in PAREMPI.

3. Robust measurement system

This section presents an overview of the robust measurement system proposed for quantifying aged PM emissions and gaseous precursors forming secondary aerosols. The system configuration comprises a portable oxidation flow reactor, dilution system, and measurement of aged PM mass, as well as the measurement of gases and a toxicological assessment.

Robust measurement methods were evaluated to quantify PM_{aged} and gaseous precursors potentially forming SecA. The pathway from sampling to the measurement of precursor gases and PM_{aged} is presented in Table 1. In addition to the key elements presented (sampling, dilution, OFR, PM_{aged}, priority gases, and toxicity), the regulated PM (PM_{fresh}) is also an important parameter to be measured, although it is not emphasized in this report.

Table 1. Key elements of robust measurement system to be considered.

Sampling	Gases	Dilution	OFR	Aged PM
•Sampling guidelines, i.a. need for heated raw exhaust transfer lines.	•Precursor gases. •Gases needed to define e.g. OFR settings.	•Dilution ratio. •Requirements for dilution system.	•Requirements for the OFR. •Settings for the OFR.	•Methods to determine PM. •Emission factors •Toxicity.

The schematic layout of the robust measurement system identified in PAREMPI to determine exhaust-derived potential PM_{aged} emissions (including SecA) is presented in Figure 2. The system comprises a portable OFR, dilution before the OFR, and measurement of the potential PM_{aged} mass using the particle number size distribution (PSD) device (PN results converted to PM mass). It is necessary to measure precursor gases (NO_x, NH_3, SO_x, aromatics) that potentially form SecA, as well as gases (NO_x, CO) required to define settings for the OFR and CO_2 for calculation of emission factors. In the following sections, each component of the suggested robust measurement system is discussed in detail, along with the robust toxicity setup. In PAREMPI, these methods were employed in parallel with the complex system, and the experiences gained are presented where appropriate.

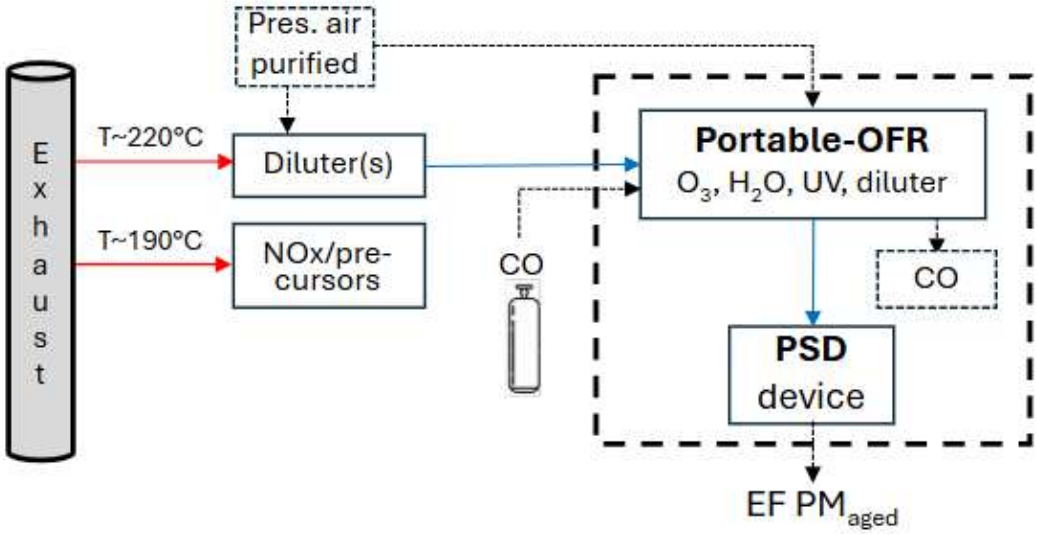

Figure 2. Schematic layout of the robust setup suggested for measuring PM_{aged}.

The elemental component for measuring PM_{aged} is the OFR (section 5). Portable OFRs are already available on the market and are easier to handle than traditional OFRs due to their advanced control software. Although the operation and adjustment of the portable OFRs are straightforward with the control software, a protocol for designing the settings for each measurement is still necessary to achieve comparable results across different measurements. These guidelines should include at least the dilution requirements, the targeted ageing period, and its verification.

In PAREMPI, a maximum aging of 2–3 days in the OFR was selected based on photochemical considerations and a comprehensive assessment of previous studies to support the chosen timeframe where the maximum potential aerosol mass is achieved. Specifically, Xu et al. (2022) reported that secondary organic aerosol (SOA) formation at urban roadsides occurs over 1–2 days of photochemical aging, which is shorter than the approx. 3 days observed in forests dominated by biogenic volatile organic compounds (VOCs) (Slowik et al., 2012) and within the 0.8–6 day range found in urban Los Angeles (Ortega et al., 2016). According to Monod et al. (2001) the atmospheric lifetime of most significant anthropogenic aromatic compounds from engine emissions ranges between 11.8 hours and 2.9 days, with the exception of benzene, which persists up to 9.4 days (assuming an OH concentration of 10^6 rad cm^{-3}), supporting the SOA formation period reported by Slowik et al. (2012). Therefore, the majority of the most relevant VOCs from engine emissions would be nearly fully oxidized within three days. Additionally, oxidation products can partition into the particle phase quickly, as shown in a study by Monge et al. (2012) that has reported typical atmospheric particle growth rates between 1 and 20 nm h^{-1} using data from over 100 field studies, with consistent daytime values. After most VOCs have undergone oxidation and equilibrium between gas and particle phases has been reached, further SOA formation from precursor VOCs emitted by a specific engine becomes minimal, while particle losses due to decomposition and deposition become more relevant. As a result, a 2–3 day maximum aging period is a reasonable upper limit for engine emission experiments using OFR, beyond which particle sizes may also become less relevant from a toxicological perspective due to further growth e.g. through condensation or coagulation.

The control of ageing period for forming the potential aerosol mass in the OFR is defined by several factors, including humidity, ozone level temperature, the intensity of UV lamps, and the residence time in the OFR. A tracer gas is required to verify the ageing period in the OFR, as OH concentrations cannot be directly measured. It is necessary to monitor the depletion of OH due to NO_x or VOC concentrations in the sample. **Dilution prior to OFR** is necessary to adjust suitable concentrations of NO_x, CO and reactive VOCs, which can deplete the oxidants and thus prevent secondary aerosol formation (section 4). However, the dilution ratio should not be too high, as this may prevent the detection of signals after the OFR. A diluter after the OFR increases the flow for the PSD device and provides continuous air flow through the OFR when the instruments are not measuring. This ensures the cleaning of the OFR, which is necessary to reduce the particle background in the OFR. Cleaning is faster with a smaller size of the OFR.

The determination of PM_{aged} mass emissions after the OFR is discussed in section 6. The AMS has been widely utilized for measuring the PM_{aged} mass and composition; however, this instrument is expensive, large, has a limited particle size range, and requires specialized expertise. In the robust setup, it is recommended to measure the size-distributed particle number concentration using a “PSD device” and convert the size-distributed particle number concentrations to PM_{aged} mass.

Toxicological assessment of transport-derived exhaust with the robust measurement system suitable for real-life conditions is described in section 8. A significant milestone in PAREMPI was the integration of an Air-Liquid Interface (ALI) exposure chamber into a moving vehicle, enabling on-road sampling of heavy-duty truck emissions, and in situ toxicity testing.

Summary of the basic parameters of the robust measurement system discussed in this report, instruments and comments from PAREMPI, and recommendations are summarized in Table 2. Please refer to the respective sections for more details. Different instruments could be employed for emission measurements of vehicles, marine engines and aircrafts; however, the same robust setup could be used regardless of the transport sector studied.

Table 2. Summary of the evaluation of the robust measurement methods for SecA.

Parameter/ devices	**Instruments in PAREMPI**	**Recommendations**
Sampling of raw exhaust Flows of fuel and exhaust Emission factors (EF)	Sampling principles in the emission standards. In PAREMPI, in-house sampling system for trucks. Exhaust flow meter (EFM) and CAN data corresponded well in PAREMPI. Calculated exhaust flows (CO_2, lambda) biased in transient tests.	• Examples of sampling systems recommended to be collected in a database. • Emission factors in unit of mass per MJ (section 6) do not require exhaust flow determination.
Priority gases	PEMS-FTIR • Many gases can be measured simultaneously • Aromatics missing from the recipe of the PEMS-FTIR used • Interferences observed • Detection limits and measurement ranges need consideration	• Requirements for the PEMS-FTIRs to be defined. • Aromatics recommended in the recipes of PEMS-FTIRs. • Capability of fuel aromatic content to indicate these precursors to be evaluated.
Diluters	PTD, ED, eDiluter • Ejector type diluters and eDiluter, for example, are relatively robust, e.g. maintaining dilution ratio. • Dilution air needs to be efficiently purified before the OFR. • Adjustable dilution ratio.	• Requirements for the diluter characteristics to be defined. • Portability of diluters with accessories. • Cleanliness of compressed air to be defined.
Portable OFR	DOFR • Robust to adjust and control	• Settings (photo-chemical age) to be defined. • Interfering gases to be defined, e.g. NOx at ppm level.
PSD device	ELPI+ • ELPI+ provides PM mass and PN data directly in data output file. • ELPI+ PN data was also converted to PM.	• Specifications of the PSD devices. • Procedure to convert PN to PM. • Particle density should not affect significantly conversion with instrument chosen.
Toxicological assessment	See section 8	See section 8

4. Sampling, dilution and electricity

This section addresses issues related to the sampling of raw exhaust, dilution systems, purity of dilution air as well as electricity needs.

4.1 Sampling of raw exhaust

Sampling of the raw exhaust is decisive for the reliability of the results. A critical step is the transfer of the raw exhaust to the first diluter without any cold spots, which could cause condensation of substances such as water, sulphuric acid and organic compounds. Transfer lines for raw exhaust are designed as "exhaust duct extension" to ensure that the raw exhaust remains unaltered before dilution. Emission standards for regulated emissions define representative sampling, and the same principles apply here. However, sampling in real-life conditions outside the laboratory environment is challenging, even for regulated, standardized PEMS measurements. Guidelines for sampling include probe design, suitable dimensions, heated transfer lines and temperatures needed to keep the sample above the dew point. These principles are consistent regardless of the exhaust source or transport sector. However, the placement of the probe and the length of the transfer lines may vary depending on the application being measured, as illustrated in Table 3, which exemplifies the variation of exhaust parameters across different transport sectors.

Table 3. Examples of sampling conditions across different transport sectors.

	Fuel cons. (kg/h)	Exh. temp. (°C)	Exh. duct id. (cm)	Exh. flow (m3/h)	Raw exh (m/s)
Car example[1]	4	240-600	5	23	3.3
Bus/truck example[1]	19	240-400	15	226	3.6
Marine engine, 1.6 MW[2]	250	240-400	45	6700	11.9
Ship engine, 10 MW[3]	2034	240-400	180	56700	6.2

[1] PAREMPI measurements. [2] Aakko-Saksa et al. 2016 [3] Timonen et al. 2016

In PAREMPI, sampling from trucks was particularly challenging due to the complex setup located in a semi-trailer. However, such challenges may be mitigated with a robust measurement setup. Based on experiences in PAREMPI, several remarks can be made: **Good practices for sampling setup** could be collected. For instance, the procedures followed can be adjusted when the measurement devices are located inside a bus or truck cabin, or in a trailer. The procedures for **inspecting leakages** in the system, as described in emission standards, should be adhered to. **Monitoring the temperatures of heated lines** is recommended to detect potential damages that may occur due to the vibrations in on-road or on-board conditions. Installations for sampling require **modifications in transport applications**, such as drilling holes for probes, which needs to be negotiated with the owners of the applications being measured. **The electricity requirements for heated transfer lines** are substantial, depending on the length of the heated lines and the temperature settings. The location of the measurement system may be far from the probe location, depending on whether sampling in conducted in moving vehicles, marine engines or aircrafts. **Personnel measuring** emissions should possess skills in PEMS exhaust emission measurements to follow good practises in constructing raw exhaust sampling probes and lines.

4.2 Dilution needs and proposed systems

4.2.1 Dilution methods

Dilution of the raw exhaust is necessary to achieve appropriate NO_x concentration for the OFR. The dilution requirements depend on the NO_x concentration range of the raw exhaust and the target NO_x concentration prior to the OFR. Examples of NO_x concentrations in the raw exhaust from different transport sector applications are presented in Table 4. Typically, the target NO_x concentration prior the OFR is at ppm levels. Consequently, the desired dilution ratio varies depending on the NO_x levels of applications measured and the different conditions of measurements. For instance, decisions are needed on whether to target suitable NO_x concentrations on average over the test or also in conditions where the highest NO_x concentrations in raw exhaust appear, such as during cold starts. In transient testing, where emissions vary depending on driving conditions, the calculated ageing period of aerosol varies accordingly.

Table 4. Examples of the NO_x concentrations in the raw exhaust from different transport sector applications and examples of possible dilution ratios.

	NO_x (mg/m^3 STP)	NO_x (ppmv)	PM (mg/ m^3 STP)	BC (mg/ m^3 STP)	DR needed (NO_x based)
Cars, buses, trucks[1]	10-200-1000-higher	5-100-500-higher	<2	<1	e.g. 10-100-higher
Marine engine[2]	~2000	~1000	<30	<3	e.g. 200-1000
Diesel generator[1]	<700	<350	20	<5	e.g. 100-350-higher
CAST[1]	<100	<50	50	<5 or <15	e.g. 50-higher

[1] PAREMPI measurements (low, typical and high concentrations) [2] 1.6 MW, 10 MW (Aakko-Saksa et al. 2016, Timonen et al. 2017).

As mentioned, a dilution system is necessary to achieve appropriate NO_x concentrations prior to the OFR, and to ensure suitable sample temperature. During dilution, it is important to maintain the representativeness of the sample and avoid particle losses, thus preferring short lines for the diluted sample. Different dilution ratios are needed depending on the exhaust source; therefore, diluters with adjustable dilution ratios that do not require verification by gas analysers would maintain system robustness. The dilution system used in standardised PEMS emission measurements involves the removal of volatiles, making it unsuitable for this system designed for PM_{aged} measurements. Heating of the diluters should be avoided to mimic atmospheric dilution. However, when using high-sulphur fuels in marine and aviation sectors, the first diluter typically requires heating to prevent clogging by sulphuric acid.

Various types of diluters are available. **The porous-tube diluter** (PTD) operates based on porous tube where the sample flows axially in the middle and is diluted with clean gas flowing through the porous material from the outside to the inside. The PTD resists contamination exceptionally well; however, the sample suction flow and consequently the dilution ratio depend on balance of dilution and sample flows, which must be precisely controlled. Therefore, the system performs optimally at low dilution ratios, preferably close to 10 or lower, for the most accurate measurements. Similar dilution systems can be constructed without using the porous tube, only by simply mixing the sample and dilution flows.

The ejector diluter utilizes a small nozzle where dilution air is accelerated to high speeds, creating momentum that provides suction for the sample flow. The principle is simple and does not involve any

moving parts. The inside diameter of the sample nozzle defines the dilution ratio, which typically ranges from 4 to 50. One significant advantage is that variations in the outlet flow do not affect the dilution ratio, and sequential installation of multiple ejector diluters can provide a very high dilution ratio. However, high particle or condensing vapor concentrations may clog the device, usually increasing the dilution ratio. Clogging effects can be mitigated by heating the dilution air, although this method is not preferred as it may evaporate semivolatile compounds from particles. Additionally, variations in sample pressure can affect the dilution ratio. Active stabilization of the ejector diluter dilution in cases of variable inlet pressure is possible. Commercially available devices, such as eDiluter and eDiluterPro with adjustable dilution ratios (Dekati Oy), are insensitive to inlet pressure variations but require dilution air up to 200 L/min (273.15 K) at relatively high pressure (5-7 bar absolute). Consequently, the energy consumption of this option is high.

The rotating disc diluter relies on a rotating disc that contains holes through which the sample enters. As the disc rotates, these holes containing the sample move to the outlet side of the device where dilution gas is introduced. The dilution ratio is adjusted by the rotation speed and the flow of dilution gas. This configuration is relatively insensitive to variations in sample pressure variations and can be designed to require only low-pressure dilution gas. However, the construction is relatively complex and includes rotating parts. These devices are commercially available from manufacturers such as AVL List GmbH and Cambustion Ltd.

4.2.2 Proposed dilution systems

In PAREMPI, complex dilution system based on the PTD and ejector diluters was used, along with robust system consisting of several ejector diluters or eDiluter. For a robust dilution system, we recommend a two-stage ejector diluter system equipped with inlet pressure compensation, capable of operating at low dilution air flow rates and pressures. When robustness of dilution is not the priority, PTD and ejector diluters, or other type of diluters, are also viable options. If necessary, some heating (e.g. 50 °C) can be applied to the first ejector stage to prevent nozzle clogging. Dilution is less demanding when sampling relatively clean exhaust, such as from modern vehicles with diesel or gasoline particulate filters. Heating of the first diluter stage (>200 °C) is recommended for challenging applications, such as exhaust from marine engines using high-sulphur fuels. Another reason to maintain the transfer line of raw exhaust at approx. ~200 °C is to keep the raw exhaust unaltered before dilution. To minimize energy needs, dilution can be located near the sampling point. After dilution, the temperature of the transfer line can be lower than in the case of raw exhaust due to the lower partial pressure of condensing compounds. Thus, installing the diluter near the sampling point reduces the need for sampling lines heated to high temperatures and decreases energy consumption. Generally, sampling lines should be as short and straight as possible to prevent particle losses.

4.2.3 Dilution air generation and purification

Dilution systems require pressurized air, which needs to be generated either internally within the dilution system or externally using a compressor, blower or pump, as listed in Table 5. The required pressure depends on the dilution system and can reach several bars. The required flow rate, under standard conditions (273.15 K, 100 kPa, STP), ranges from a few L/min up to 200 L/min. The power requirement is linearly proportional to the required pressure and flow.

The power required to compress 10 L/min (STP) of air to 1 bar gauge pressure is 17 W isothermally and 42 W adiabatically, while compressing 100 L/min (STP) to 5 bar gauge pressure requires 830 W

isothermally and 2100 W adiabatically. Compressor efficiency from 65% to 90%, depending on the device type, needs to be considered when calculating the required intake power. In PEMS applications, compressed air can be a significant energy consumer.

Other factors to consider when selecting the air supply include noise, which can be substantial requiring ear protection. If compressor uses oil, additional filtration is necessary (see the filtration section below).

Table 5. Potential pressurized air generation methods. If numerical values are presented, they are only approximate for typical models.

Pump/compressor	Flow	Pressure	Noise	Oil
Centrifugal blower	High	Low, 0-100 mbar	Low	No
Rotary-vane pump	Medium	Low, 0-400 mbar	Low	No
Piston/ Diaphragm pump	Low	Medium/High, 0-8 bar	Medium	No
Piston compressor	Medium	High, 0-8/0-12 bar	High	Yes/No
Screw compressor	High	High, 0-8/0-12 bar	High	Yes

In PAREMPI, compressed air was supplied by the laboratory air network during measurement campaigns for the light-duty, marine and aviation sectors. In the heavy-duty campaign, a high-power screw compressor was utilized. Due to the extensive setup in PAREMPI, a significant quantity of air was needed, far exceeding the needs of the proposed robust measurement setup.

Filtration of the dilution air

The measurement of secondary aerosols necessitates high-quality, clean dilution air. Both particulate matter and interacting gaseous compounds, particularly organic vapors, must be filtered with extremely high efficiency.

Proposed filtration setup stages:

0. **Optional water/oil separator.** Compression of humid air often leads to water condensation, necessitating a drainage method. Oil-free compressors are recommended. If compressors use oil, some may be present in the outlet air.
1. **Prefilter.** This filter should remove large solid and liquid particles and be capable of collecting condensed liquid, which may be present after the compressor.
2. **HEPA filter or equivalent**. With at least 99.95 % filtration efficiency, this filter should remove all remaining particles before the activated carbon filter.
3. **Activated carbon filter**. This filter should remove organic vapors that may produce liquid or solid material during the oxidation process.
4. **HEPA filter or equivalent.** With at least 99.95 % filtration efficiency, this filter ensures that carbon or other particles potentially released from the activated carbon are not entering the dilution system. Often, a combined gas and particle filter can be used, which integrates stages 3 and 4 above.

The dilution air should have a relative humidity low enough to avoid condensing conditions after mixing with the exhaust. The required humidity depends on the applied dilution ratio and temperature. It should be noted that OFR-chemistry requires humidity. Thus, extensive drying of dilution air is neither necessary nor optimal. Generally, compressing normal pressure indoor or outdoor air into high

pressures results in water condensation due to increased partial pressure. A removal system for the liquid water should be installed in the dilution air filtration system. This system may include a separate water separator or a filter with water separation capability or/and an additional compressed air dryer, such as semipermeable membrane. If only relatively low pressure, less than approx. 2 bar absolute, is used, additional drying of dilution air may be necessary, for instance, with the aid of desiccant.

The lifetime of the filters should be evaluated with background measurements to determine if the dilution air is not clean enough and/or if the filters have reached their capacity.

4.2.4 Materials of dilution system

Special attention needs to be paid to sampling line materials prior to OFR in order to prevent VOC and particle losses, as well as artifacts due to VOCs produced by the sampling lines that would be converted to SecA in the OFR. Recommended materials prior to OFR cause minimal losses of VOCs and particles, such as stainless steel. Plastics are not recommended materials due to their potential VOC release. However, for applications requiring flexible lines, certain antistatic polymer materials, such as antistatic polytetrafluoroethylene, may be considered viable options.

4.3 Electricity needs

The portability of the measurement system imposes stringent requirements on electrical energy consumption. During the PAREMPI heavy-duty measurements, energy consumption was managed by employing a large diesel generator, which produced approx. 20 kW during the experimental work. For a robust setup, significantly lower power consumption is essential.

The following steps should be considered to minimize electricity consumption:

- **Minimize the length of high-temperature heated sample lines.** For instance, in PAREMPI HD measurements, the sample line's maximum power was 300 W/m and the length of the sample line was approx. 9 m, resulting in a maximum power consumption of 2.7 kW for the sample line.
- **Minimize compressed air pressure.** Without considering compressor efficiency, the power required to adiabatically compress 10 L/min (STP) from atmospheric to 10 bar gauge pressure is 420 W, with a linear dependency on pressure. For example, 1 bar gauge pressure consumes only 42 W.
- **Minimize flow of compressed air.** Similarly to pressure, the power required has a linear dependency of the flow rate.
- **Select instruments with low energy consumption.** Choose devices that utilize low flow rates, small pressure drops if compressed air or vacuum is needed, and low operating temperatures.
- **Utilize grid power during preparative actions.** If the system is battery-powered, use grid power during preparative actions, especially when instruments and sample lines are warming up.

Unfortunately, only a limited number of dilution systems with robust operation principles and instruments measuring real-time mass concentration exist. These are principally designed for laboratory environment, and energy consumption has not been major design factor, necessitating compromises in planning of the robust setup.

5. Oxidation flow reactors, OFRs

In this section, the oxidation flow reactors are discussed, along with the challenges in defining and verifying suitable target settings and dilution needs prior to the OFR. Additionally, experiences with a portable OFR utilized in the PAREMPI project are evaluated.

5.1 OFR principle and devices

In laboratory conditions, Aged PM is typically formed using oxidation flow reactors. In the OFRs, irradiation with UV light is used to form high concentrations of oxidants (O_3, OH, HO_2) which ensure fast oxidation of compounds and initiation of SecA formation (Figure 3). The settings of UV light (wavelenghts, intensity) are selected to represent atmospheric aging of emissions from minutes to weeks as the sample flows through chamber, and consequently, these settings affect substantially the quantity of SecA formed in the OFR.

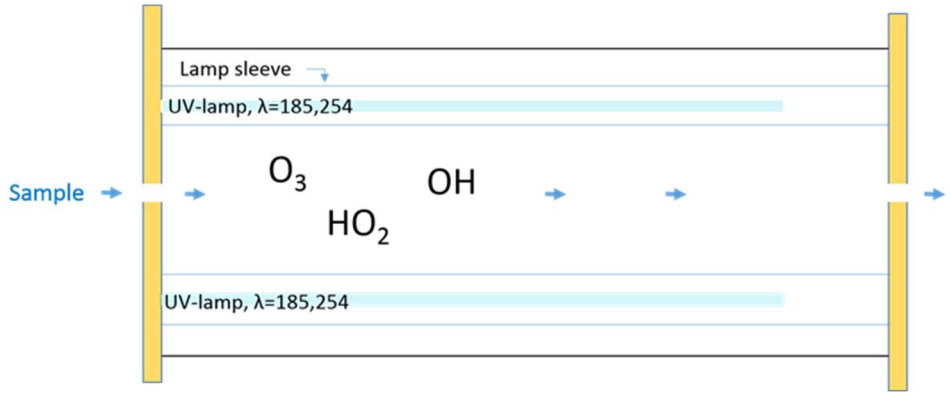

Figure 3. A schematic presentation of a PAM OFR.

The key challenge in the measurement of PM_{aged} is to find the optimal settings of the OFR. While portable OFRs already available on the market are easier to handle than traditional OFRs in respect of control software, a protocol to design the settings for each measurement is still required to achieve commensurable results from different measurements. As already mentioned in section 3, guidelines should include, amongst others, how to define the dilution ratio needed before the OFR, which is the targeted ageing period for forming the potential aerosol mass that may be produced and how to achieve that and many practical issues, such as cleaning recommendations of the OFR to reduce background.

Typically, target NO_x concentrations before the OFR are at ppm level (Kang 2011), since NO_x emissions can deplete the oxidants and therefore prevent secondary aerosol formation. Hence dilution of the raw exhaust is needed, and appropriate dilution ratio is estimated based on the NO_x concentrations measured from the raw exhaust. NOx emissions from different transport sectors and applications vary leading to a wide range of dilution needs depending of the exhaust source. In section 4, examples of the NO_x concentrations and dilution ratios needed are presented.

The targeted ageing period for forming the potential aerosol mass that may be produced is a critical parameter for using the OFR or designing the experiment and also for interpreting/comparing the results. Ageing period is controlled by the humidity, ozone level and temperature of OFR, intensity of UV lamps and the residence time in the OFR (adjusted by the sample flow). In PAREMPI, a maximum

aging of 2–3 days was selected based on photochemical considerations (see Introduction for justification of this choice).

A gas, called “tracer”, to verify the ageing period in the OFR is needed, since the OH concentrations cannot be directly measured. OH will get depleted or age might change in the presence of high NO_x or volatile organic compound (VOC) concentrations, especially with a short residence time. With a tracer gas, depletion of the oxidants can be monitored. Tracer gas should be a compound that is measurable, reacts with OH radical with a suitable reaction rate and does not produce secondary aerosol mass (Simonen 2024). Potential tracer gases are for example CO, SO_2 or d9-butanol, from which CO is the most practical when considering its availability and analysis capabilities. Simultaneously, work safety aspect should be emphasized especially when using CO tracer, and the potential impurities of tracer gases should be taken into account due to their potential effects on OFR operation and results for aged aerosol measurement. The tracer gas concentrations need to be measured before and after OFR, or in replicate test without UV lights. The use of tracer gas and the measurement of its concentration increase complexity of the system, yet there are limited alternative methods available. Modeling the sample age based on CO, VOC and NO_x concentrations, along with OFR settings (temperature, ozone and humidity), could serve as substitute for tracer gas. This methodology should be considered for the robust measurement system, although the ability to monitor and verify ageing over measurements is compromised.

OFR devices

Several types of OFRs have been adapted into use by the research community. The size of chambers varies from very small, 0.15l chamber with residence time of seconds (Keller and Burtscher, 2012) to very large chambers with volume up to 155l (Ihalainen et al., 2019). In general, the residence time depends on the flow through chamber and the volume of the chamber. For atmospheric studies or laboratory studies with stable measurement points, the chambers like the Potential Aerosol Mass (PAM, Aerodyne Research Inc.) chamber with larger volume and longer residence time are shown to give representative results (Lambe et al., 2011). PAM chamber, made from aluminum, has volume of 13.3L and two Hg-lamps to produce oxidants (OH, O_3, HO_2). The amount of oxidants is high in order to simulate the atmospheric aging in minutes the sample goes through the chamber. For emission studies with transient emission sources, chambers with shorter residence times are needed. For this end, TSAR, Go:PAM, and MSC have been developed (Simonen et al., 2017, Watne et al 2018, Keller et al., 2012). Article by Zhang et al., (2024) contains a summary of the most commonly used OFRs.

Portable OFRs are already available on the market. These instruments are easier to handle than traditional OFRs in respect of control software.

5.2 Experiences in PAREMPI

In PAREMPI, the portable OFR was a DOFR (Dekati Oxidation flow reactor, Dekati Ltd., Finland). The DOFR is developed for emission studies. The DOFR has smaller reactor dimensions and higher oxidant concentrations enabling the same oxidation in less time and higher time resolution than the PAM chamber. Due to the shorter residence time and laminar flow, sample changes faster and more efficiently in DOFR chamber than in PAM.

The DOFR is equipped with built-in flow controllers, an ejector diluter, a bubbler to increase relative humidity (RH), ozone generation and sensors for RH, temperature and ozone. In the DOFR UVC radiation together with OH and O_3 in the sample create highly oxidative conditions inside the reactor

and the time- scale of secondary aerosol formation is reduced from days to less than one minute, being suitable for transient conditions. The flow through the oxidation chamber is kept constant and laminar to minimize particle losses. The device used in the PAREMPI measurements had also its own diluter in addition to other parts mentioned. From a user experience point-of-view, DOFR has more built-in settings and possibilities for customizing the aging than PAM. While the DOFR control software has a clear overview of the instrument, finding the optimal settings for each measurement can be difficult. This might cause a human error source to the measurement results.

One of the aims was to study, whether more robust OFR could be better suited for transportation exhaust studies than PAM that is widely used in the research studies. In the light-duty campaign, these two oxidation flow reactors were used in parallel to simulate the atmospheric aging of the exhaust. Figure 4 presents a comparison of PM_{aged} total mass measured after the DOFR and the PAM with identical ELPI+ instruments measuring in parallel. From the Figure it can be seen that 1) The higher time resolution in the DOFR allows to better investigate the temporal variation of secondary emissions during accelerations and decelerations, which seem to be an important contributor for the CNG car studied. 2) The overall concentrations are smaller in DOFR than in PAM, which might be partially explained by PAM background. Wall losses in PAM are greater than in DOFR because of the longer residence time, and the particles/LVOCs/SVOCs deposited to the walls might resuspend later, causing uncertainty in the results. This resuspension might play a role in the difference between PAM and DOFR at the start of the cycle in this Figure.

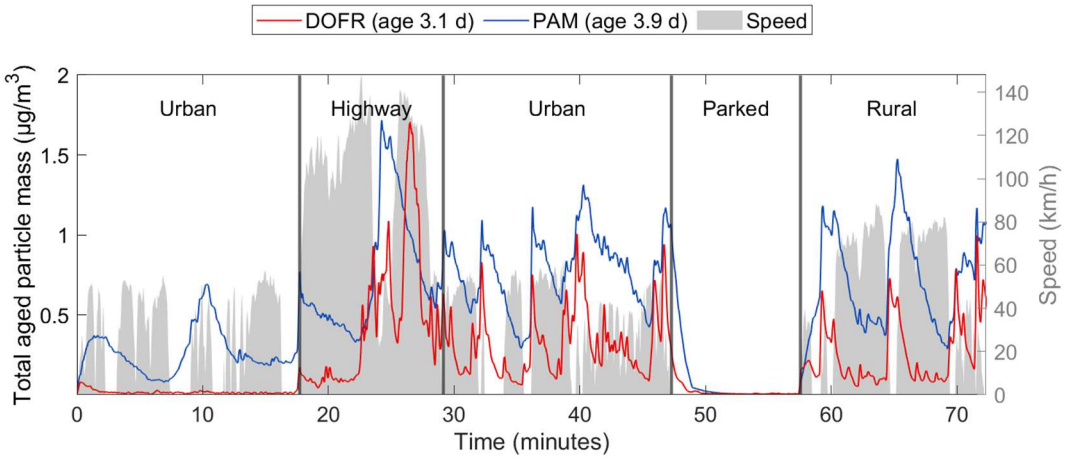

Figure 4. An example time series of total PM_{aged} particle mass for the CNG car. Dilution corrected to raw exhaust. Legend shows atmospheric equivalent age in the chambers. PM_{Aged} contains primary and secondary particles. The results are from the same test with instruments measuring in parallel.

The pros of the DOFR compared to the PAM are as follows: 1) The higher time resolution in the DOFR allows to better investigate the secondary emissions during accelerations and decelerations. 2) The background is lower for the DOFR than for the PAM in some conditions. 3) Wall losses are smaller in DOFR than in PAM having a longer residence time. The particles/LVOCs/SVOCs deposited to the walls might resuspend later, causing uncertainty in the results. This resuspension might play a role in the difference between PAM and DOFR at the start of the cycle in this Figure.

6. Aged PM mass emissions

After ageing in the OFR, the aged PM mass emission needs to be determined. This section discusses common methods for PM measurements and evaluates their suitability for a robust setup. Then, a proposal for the methodology to determine the PM_{aged} emission is given, along with the metrics and calculations fpr PM_{aged} emission factors.

6.1 Aged PM measurement

6.1.1 Methods for PM measurements

One of the methods employed in various studies for measuring aerosol before and after the OFR has been the Aerosol Mass Spectrometer (AMS). This instrument measures the submicron non-refractive PM composition, hence, excluding black carbon (Saarikoski et al., 2024, Simon et al., 2025). Since AMS does not measure the black carbon fraction of PM, the results are supplemented with BC obtained from other instruments such as aethalometers, MAAP, photoacoustic technique (PAS) or laser-induced incandescence (LII) for PM mass determination. The AMS is notably large and requires spesialized expertise for both operation and interpretation of the results, hence, it is not suitable for the robust measurement system.

The filter method[1] can be used only when PM emissions are sufficiently high to allow for accurate weighing, which is not the case after the OFR. Hence, filter-based methods designed for PM_{fresh} measurements are not applicable for measuring PM_{aged}. It is worth noting that for PM (PM_{fresh}), the filter method is a regulated procedure for on-ground transport applications. In the aviation sector, PM mass emission is not included in the emission standards, resulting in limited PM data availability. Conversely, in the marine sector, substantial studies have employed the filter method (ISO 8178 standard), although PM emissions are not regulated, and in some studies, in-stack sampling have been employed with the filter holder positioned inside the exhaust duct to sample raw exhaust (Aakko-Saksa et al. 2018).

In the automotive sector, one of the PEMS options measures black carbon using the photoacoustic technique and employs a factor to estimate the corresponding PM mass as defined in the US regulation. However, when assessing aged PM emissions, the black carbon mass is typically low compared to the total PM mass, and the BC to PM ratio tends to vary substantially across different exhaust sources. Consequently, BC measurement alone is insufficient for quantifying PM_{aged} emissions.

Aged PM mass emissions can be determined is by using size-resolved particle number concentrations (PSD) and converting these to mass emissions (following section). Additionally, other types of instruments could be considered, such as Tapered Element Microbalance (TEOM) or charger-based devices (eFilter, PPS-M etc.). However, the use of these charger-based devices without size-distributed measurement would require validation due to different characteristics of the PM.

[1] In filter method, sample gas is drawn through a filter under defined conditions (for example temperature, dilution and exhaust flow) to achieve repeatable results of total PM consisting of volatile and non-volatile species.

6.1.2 Recommended method for aged PM

For the robust setup, we recommend determining aged PM by using size-resolved particle number concentrations (PSD) and converting these concentrations to mass emissions. Principle for conversion of size-distributed particle number concentrations to mass concentrations is presented in Equation 1, in which the mass of one particle with measured mean particle diameter (Dp) is typically calculated by assuming spherical particles having a unit density (ρ) of 1.0 g·cm^{-3}. For each measured Dp, the mass of one particle is multiplied by total PN (in #).

$$PM = PN * \frac{4\pi}{3} * \left(\frac{Dp}{2}\right)^3 * \rho \qquad (1)$$

Many considerations and theories have been published regarding the conversion of ELPI currents to number concentrations and subsequent conversions to mass concentrations as regards PM_{fresh}, for example by Charvet et al. (2015). For the PM_{aged}, conversion may be more straightforward than for the PM_{fresh}, since the particle size distribution may vary to a lesser extent. An example of the roadside measurements is reported by Virtanen et al. (2006). A protocol is necessary to define the measurement principles suitable for this approach, including the evaluation of using a unit density of 1.0 g·cm^3 in particle number to mass conversion for PM_{aged}, considering the aerodynamic diameter or mobility diameter measured and the applicable particle size range. For determination of the PSD, for example, ELPI+, EEPS, and DMS500 could be used.

6.1.3 Experiences in PAREMPI

In PAREMPI, the PSD devices used in parallel to SP-AMS were electrical low-pressure impactors (ELPI+, HT-ELPI+, Dekati) measuring fresh, non-volatile and aged aerosol. In the ELPI, the exhaust particles are charged, classified into 14 size bins from 6 nm to 10 µm by a cascade impactor and detected with electrometers. In PAREMPI, particle number results measured by ELPI+ were converted to PM_{aged} mass emissions by using selected stages with size range from 6 to 941 nm (Simon et al. 2025).

6.2 Aged PM emission factors

6.2.1 Recommended metrics for aged PM

For defining the emission factors, a reasonable metric for the aged PM is needed. Currently, emission factors have different units in road transport and marine sector (per distance or per work)[2] and aviation sector (per kilogram of fuel burned). Our recommended emission factor metric for aged PM is mass per megajoule (MJ), which eliminates the need for exhaust or fuel flow measurements and therefore simplifies the setup. This principle also serves harmonisation of PM_{aged} emission factors across transport sectors.

Emission factors per megajoule of fuel consumed is calculated by diving the other exhaust species by CO_{2e} concentrations (including equivalent CO and organic gases) and converting CO_{2e} to fuel and

[2] Additional information of calculation methods based on exhaust or fuel flow are presented in Appendix 2.

energy consumed based on the fuel properties (carbon and energy contents). The robustness of measurement system increases when exhaust and fuel flow measurements are not required. Notably, exhaust flow measurements are particularly challenging in aviation and marine sectors.

The PM_{aged} results obtained are rather semi-quantitative regardless of the complexity or robustness of measurement system due to the sensitivity of the ageing on the OFR settings and other uncertainties in the measurements. However, when SecA precursors are substantially present in the exhaust, the PM_{aged} typically increases to many-fold levels when compared to PM_{fresh} emissions. Although not included in the robust measurement system here, measuring the PM_{fresh} emissions is strongly recommended besides the PM_{aged} emissions. This would enable, besides using the recommended metric of mass per MJ, to present a ratio of PM_{aged} to PM_{fresh}. This ratio is illustrative of the differences between applications and fuels, since these ratios may be high, reportedly in one case 13.4 for gasoline (Timonen et al. 2017) and three for high ethanol concentration gasoline (Suarez-Bertoa et al. 2015).

The calculation principle recommended for the emission factor determination is valid only for carbonaceous fuels, while future engines using carbon-free fuels would need another marker than carbon.

6.2.2 Synchronization of response time in calculation

For the calculation of PM_{aged} emission factors, whether using exhaust flow or CO_2 data, the rapid changes measured from the tailpipe are smoothed in the OFR due its long residence time and mixing distortion. Simonen et al. (2024) presented alternative methods to account for this, including the mathematical convolution method to reflect the OFR response on the (Q_{exh}).

In the robust measurement system evaluated here, the accessible method by using moving average is recommended to resolve the mixing of the exhaust sample in the OFR and the consequent mismatch of data response times upstream and downstream the OFR. For the calculation of the moving averages, the residence time of the OFR is used, for example, 94.4 seconds for the PAM in PAREMPI car measurements, based on volume and sample flow of the PAM. Comparison of the Q_{exh} calculated by the moving average and convolution methods correlated quite well in the PAREMPI car measured shown in Figure 5. It is worth noting, that time alignment of data from different instruments, being a routine procedure in exhaust emission measurements, is a distinct topic from the synchronisation issue discussed here.

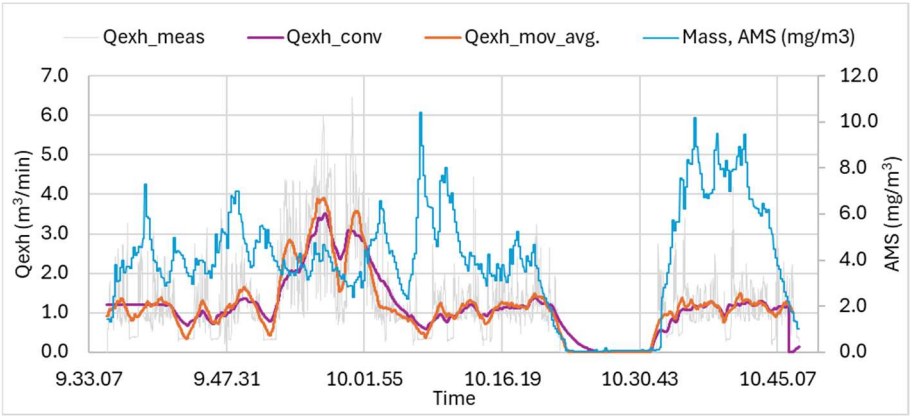

Figure 5. Exhaust flow rate measured upstream the OFR (Q_{exh_meas}) and calculated by convolution (Q_{exh_conv}) and moving average ($Q_{exh_mov_avg}$) methods to simulate exhaust flow downstream the OFR. Aerosol mass measured by AMS (Mass, AMS) excludes black carbon. PAREMPI car measurement no 0711.

7. Gaseous emissions

In this section, the features of some measurement techniques capable of measuring exhaust gases are presented. For the PEMS-FTIRs, a more detailed description of the principle and features are presented, along with experiences in PAREMPI. Additionally, the measurement ranges of the PEMS-FTIRs utilized and the concentrations observed from different transport sectors are shown.

7.1 Priority gases and their measurement

Studies encompassing potential SecA precursor gases (NO, NO_2, NH_3, SO_2 and VOCs, particularly aromatics) are essential to generate sufficient knowledge for constructing models to estimate SecA formation based on precursor gases in exhaust. NO_x and CO concentrations are required to determine the OFR settings (sections 3, 5), while CO_2 is necessary for calculating PM_{aged} emission factors with a principle described in section 6.

Notably, some gases, such as SO_2 and VOCs, originate from fuel and lubricating oil, whereas nitrogen oxides are formed from nitrogen in the air at high combustion temperatures. NH_3 and N_2O are formed in the exhaust aftertreatment systems (Suarez-Bertoa and Astorga 2016, Selleri et al. 2021).

For measuring relevant priority gases, many principles are available, though many instruments are only feasible for use in the laboratory. Various measurement technologies have been evaluated (Mendoza-Villafuerte et al. 2017, Suarez-Bertoa et al. 2017, 2020) and the CLOVE Consortium evaluated those in view for the upcoming Euro 7 standards (EU 2022). Since then, new instruments with broader capabilities and portability have emerged on the market. An overview of measurement techniques for exhaust gases is shown in Table 6.

Table 6. On-line measurement techniques.

	Technique	PEMS availability	Consumables needed	Exhaust sample
NO, NO_2	NDUV	Yes	Cal. gases, Diluent	Diluted
	QCL-IR	Yes	Diluent	Diluted or raw
	FTIR	Yes	LN2 [a], N2 or air	Raw
	CLD	No	Cal. gases, ozone	Diluted
NH_3	LDS	Yes	Diluent	Diluted
	QCL	Yes	Diluent	Diluted
	FTIR	Yes	LN2[a], N2 or air	Raw
Aromatics	FTIR	Limited[b]	LN2[a], N2 or air	Raw
	Micro-GC	Limited[c]	Cal. gases, Diluent	Diluted
	GC-FID, PTR-MS[d]	No	Cal. gases, Diluent	Diluted exhaust
SO_2	NDUV	Possible	Cal. gases, Diluent	Diluted
	FTIR	Yes	LN2[a], N2 or air	Raw
CO_2, CO	NDIR	Yes	Diluent	Diluted
	FTIR	Yes	LN2[a], N2 or air	Raw

[a] Most FTIRs designed for transient tests use LN2, but not all FTIRs. FTIRs designed for steady state tests typically do not need LN2.

[b] Some PEMS-FTIR manufacturers include aromatics in their recipes/methods, but not all manufacturers.

[c] Due to limited time resolution, micro-GC is not regarded feasible for transient tests.

[d] FID = flame ionization detector, PTR-MS = Proton Transfer Reaction

PEMS type measurements of gaseous emissions have been applied using quantum cascade lasers (QCL) operating in the infra-red spectrum for analysing such as NO_x and NH_3. A laser source of specific wavelength and solid-state IR detectors targeting a selected wavenumber range enable precise sample selectivity. Another option adapted to PEMS size is the Fourier Transform Infra-Red (FTIR) technique, which is capable to measure simultaneously many emission species, both organic and inorganic gases.

Nitrogen oxides (NO_x), comprising of NO and NO_2 (calculated as NO_2), are analysed using Non-Dispersive Ultra-Violet Resonance Absorption (NDUV), chemiluminescent (CLD) or QCL-IR techniques in on-road PEMS measurements. Ammonia (NH_3) can be measured using QCL and FTIR techniques. However, NH_3 results may be biased in the presence of interfering compounds or by reactions with e.g. NO_x forming ammonium nitrate.

Sulphur dioxide (SO_2) emissions can be measured using the NDUV principle from diluted exhaust, or by FTIR directly from raw exhaust. CO and CO_2 emissions are commonly analysed using NDIR principle from diluted exhaust, and by FTIR from raw exhaust.

Individual VOCs, including aromatics, particularly benzene, toluene, xylenes, ethyl benzene, and trimethyl benzene, can be analysed using gas chromatographs (GC) and PTR-MS instruments at low concentrations. These instruments are traditionally heavy, large, feasible only for laboratory use, require specialized expertise for operation, and necessitate substantial analysis times, often tens of minutes. Micro-GC instruments are smaller and can be used in field conditions. However, calibration gases are required for micro-GC instruments, and their time resolution is typically several minutes. PEMS-FTIRs can detect many VOCs and even aromatics, however, aromatics are not included in the recipes of all FTIR instruments and the detection limits tend to be high. One option to evaluate roughly potential presence of aromatics in the exhaust could be based on their concentrations in fuel, and amount of unburned organic gases detected.

7.2 FTIR principle

With FTIR spectroscopy, a variety compounds absorbing in the mid-infrared range, approx. 400–4000 cm^{-1}, can be detected, while gases whose vibration does not cause dipole moment cannot be detected, such as noble or diatomic gases (e.g. O_2, N_2 and H_2). Some molecules absorb only slightly leading to high detection limits (e.g. H_2S) (Giechaskiel and Clairotte 2021). Typically, light from a thermal source is divided in an interferometer into two beams. By using a moving mirror, the difference between the optical path lengths of the two beams varies with time. These two beams are then passed through a sample cell into a detector. The resulting signal, an interferogram, represents the beam intensity as a function of the optical path difference. Fourier Transform, a mathematical operation used to transform a function from a time domain to a frequency domain, is then used to convert the interferogram (beam intensity as a function of optical path difference) to a single-beam spectrum (beam intensity as a function of wavelength), which is then converted, by division by a background spectrum, into an absorption spectrum.

Balance between spectrometer resolution, measurement time and signal-to-noise ratio (SNR) depends on instrumental choices. Longer optical path length improves the detection limits, however, the practical upper limit is 5-6 m. Higher number of scans improves SNR, but requires a longer measurement time (lower time resolution). Higher optical resolution improves the ability to discriminate a compound of interest from other interfering compounds, but typically at the expense of longer scan times and lower SNR. For automotive applications, optical resolution of 0.5 cm^{-1} is the

compromise typically used (needed to detect the NH_3 accurately) and a time resolution of around one second. For aviation and marine sectors, lower optical resolution, higher number of scans and lower time resolution are typical. For the FTIRs having the sample cells of 0.2-0.4 L and flow of 10 lpm, corresponding sample exchange time is over one second (Appendix 1). The prototype PEMS-FTIR used in PAREMPI had a sample cell with a smaller volume. In aviation and maritime sectors, time resolution can be longer, e.g. 20 seconds, allowing a high number of scans and a good signal-to-noise ratio (SNR). To meet contradicting requirements of sample cell volume and high optical path length (to increase the sensitivity and decrease the detection limit), multi-pass cells, with tens of reflections of the beam on spherical gold-plated mirrors, are utilized. This, however, places rather high demands on the precision and stability of the geometry of the beam when the instrument is subjected to minor vibrations in the test lab and more pronounced vibrations and jolts in a moving vehicle. Detector performance can be improved by lowering its temperature, and for this reason, higher optical and time resolution instruments use liquid nitrogen (or sophisticated mechanical cooling devices) to cool the detector.

Shortcomings of the FTIRs include **interferences of different compounds** making separate recipes necessary for different exhaust gases. The primary outcome of FTIR measurement is the absorption spectrum, which is the sum of the absorption spectra of all individual compounds present in the measured gas. The measured absorption spectrum therefore needs to be interpreted by attempting its partial or full deconvolution based on the known absorption spectra (obtained by calibration gases or from spectral libraries) of compounds of interest. The detection limit, range, and uncertainty at which a particular compound can be resolved is therefore dependent not only on the parameters of the spectrometer and the quality of the spectra obtained, but also on the presence of various (and in many cases unknown) interfering compounds. Since FTIR technique is sensitive to interferences of the other exhaust compounds, device manufacturers have prepared methods (called also recipes) for different applications to take into account concentrations of compounds present in the exhaust. These manufacturers' methods are typically limited only to some exhaust compositions, e.g. diesel, and hence some manufacturers allow users to modify methods to new exhaust compositions.

Validation of an FTIR instrument requires comparative measurements against a known reference in the laboratory for a variety of exhaust compositions, supplemented by comparative measurements on the road of those compounds for which a reliable reference can be found (i.e., comparing NO, CO and CO_2 with a PEMS) (Vojtíšek-Lom et al. 2018). However, FTIR spectroscopy has an inherent advantage in **resilience of the spectra**. Optical anomalies are reflected in the entire spectrum, hence, periodic calibration of the FTIR with one well-selected single compound is sufficient to assess the instrument's health. The linearity of FTIRs may need periodic calibrations by the laboratory.

FTIR instruments designed for exhaust measurements sample raw exhaust. Similarly to all transfers of raw exhaust, heating is needed to prevent condensation of water and other compounds. Removal of water by cooling would also remove water-soluble compounds, such as formaldehyde or ammonia.

7.3 PEMS-FTIRs: experiences in PAREMPI

Several PEMS-FTIR instruments are available and used for on-road exhaust measurements, such as A&D BOB-1000, IAG OFS, AVL M.O.V.E. FT and for steady-state measurements of marine engines, such as Gasmet DX4000. In PAREMPI, the A&D BOB-1000 was utilized, and for light-duty cars, a prototype PEMS-FTIR was used in parallel. Characteristics of the selected FTIR instruments are presented in Appendix 1.

These PEMS-FTIR instruments did not analyse aromatics, although one-ring aromatics can be detected using the FTIR principle. Determination of the exact quantity of individual aromatic compounds is challenging with FTIR. The first FTIR developed for vehicle emission measurements used toluene for calibration of the sum of aromatics (Aakko 1994). Today, many FTIRs include benzene and toluene in their recipes/methods, although detection limits may be high.

Correlations between PEMS-FTIRs and other methods for NO_x, NH_3, CO, CO_2 and SO_2

In PAREMPI, NO_x emissions obtained by FTIR spectroscopy correlated well with regulated "Bag" results (Figure 6a). For NO_x emissions, humidity correction factors were applied, while the necessity of this correction can be considered in the PM_{aged} measurements. NH_3 results obtained by QCL and two FTIRs correlated well (Figures 6b, 7), as did in Selleri et al. (2022). In principle, NH_3 results could be biased in the presence of interfering compounds or by reactions with e.g. NO_x. CO is suggested to be used as a tracer gas for determining the ageing period (section 5). Hence, determining the relative changes over the OFR are more important than the absolute values obtained.

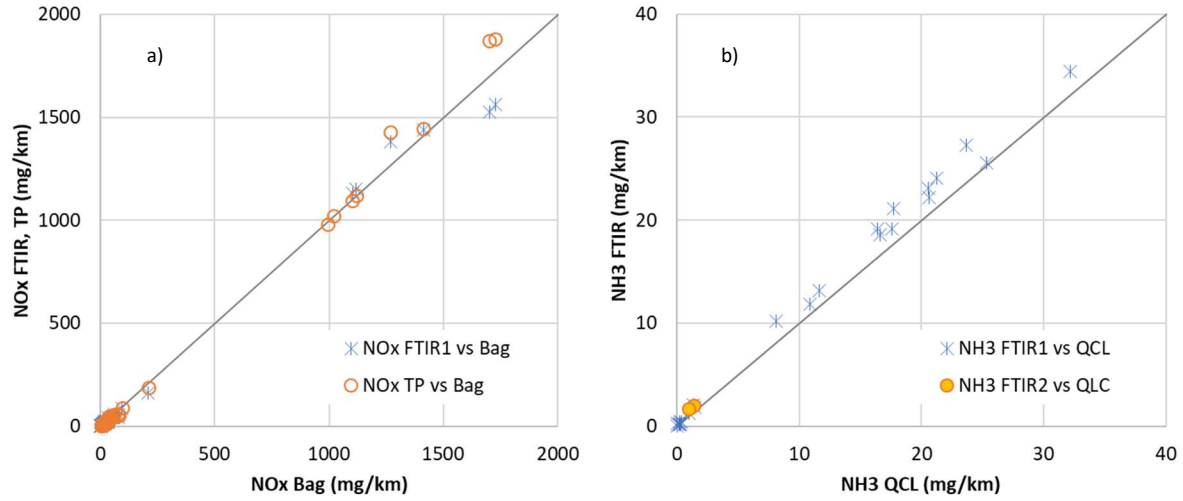

*Figure 6. Results obtained by FTIRs were compared with **a)** NO_x from regulated "Bag" and **b)** NH_3 from QCL-IR (continuous) measurements with cars.*

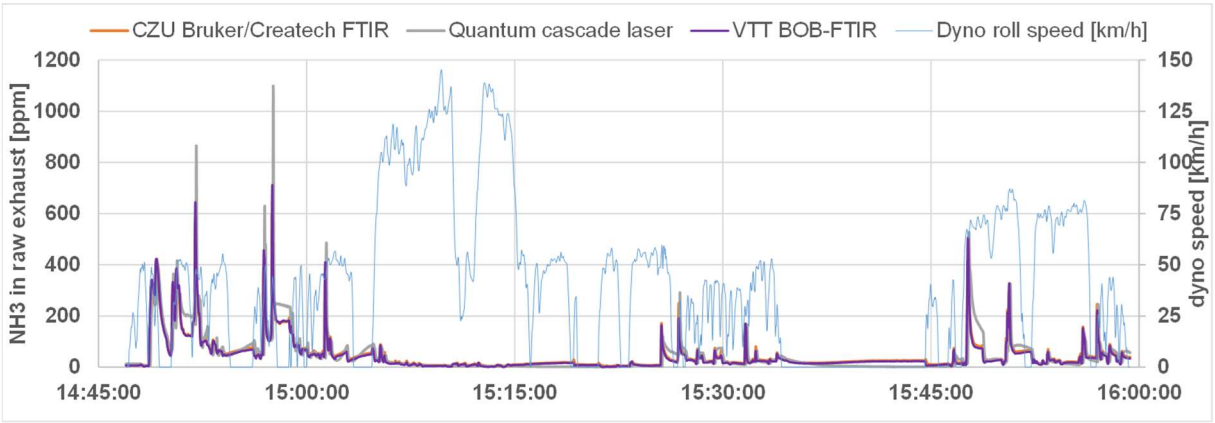

Figure 7. Concentrations of ammonia in raw exhaust (gasoline car, real driving simulation).

SO_2 in exhaust originates from fuel and lubricating oil. Since fuel sulphur content varies substantially across different transport sectors, exhaust SO_2 concentrations also vary. The theoretical SO_2/CO_2 ratio can be calculated based on fuel sulphur and carbon contents (Figure 8). However, this does not account for sulphur originating from lubricating oil, which can also contribute to the secondary aerosol

formation. Comparison of measured SO_2 concentrations with calculated fuel-originated SO_2 concentrations may actually reveal the possible contribution of lubricating oil.

In PAREMPI, for cars and trucks, fuel sulphur contents were below 10 ppm, leading to SO_2 concentrations close to the FTIR's detection limit of approx. 2 ppm. In some driving conditions, SO_2 concentrations were higher, for cars up to 10 ppm and for trucks up to 25 ppm, indicating a possible contribution of lubricating oil on SO_2 emissions. With marine fuels containing substantially sulphur (DMB grade up to 1000 ppm, and another fuel up to 4000 ppm), measurable exhaust SO_2 concentrations were detected. In high load conditions, measured and calculated SO_2 concentrations fitted well, while at low engine load, higher than expected SO_2 concentrations (expected 3.6 ppm, measured 17 ppm) indicated the possible contribution of lubricating oil. In the aviation campaign, dilution was applied prior to FTIR to provide sufficient sample flow for all instruments in the complex measurement system, leading to low SO_2 concentrations. Without dilution, SO_2 concentrations would have been within the measurable range of FTIR, as sulphur contents of jet fuels can be substantial (for Jet A, standard ASTM D1655 defines total sulphur limit of max. 3000 ppm).

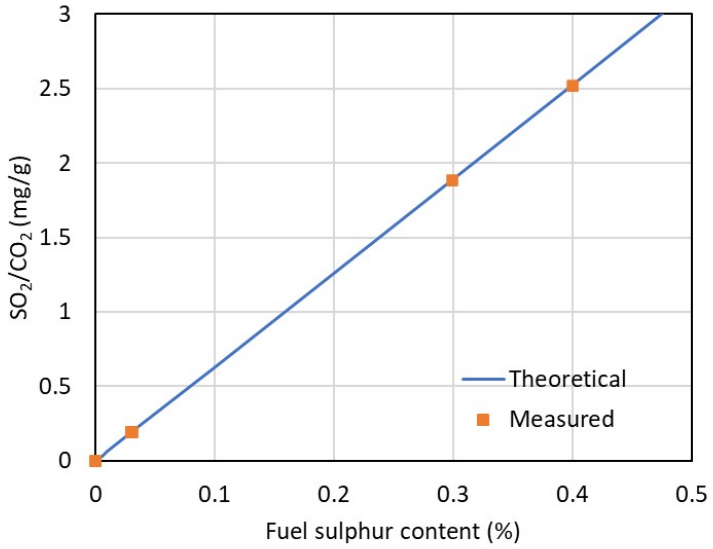

Figure 8. Relationship of fuel sulphur content and SO_2/CO_2 ratio in the exhaust with marine fuels.

In PAREMPI, CO_2 emissions measured by FTIR were consistent with NDIR bag results. The discrepancy previously reported in earlier versions of Deliverable D2.3 for spark-ignited (SI) cars was traced to incorrect dry-to-wet ($k_{d\text{-}w}$) correction factors applied to regulated raw CO_2 concentrations measured by NDIR and processed by the automation system (Horiba). NDIR-based CO_2 measurements are performed on a dry basis following water vapour removal via sample cooling. Therefore, second-by-second $k_{d\text{-}w}$ correction factors are required to derive wet concentrations, as well as to calculate dilution ratios in the CVS system and raw exhaust mass flows. Incorrect correction factors lead to biased CO_2 concentrations in raw (wet, without water removed) exhaust. This causes a bias in the calculated exhaust flows, and, consequently, tailpipe emission results calculated from raw exhaust measurements. The accuracy of $k_{d\text{-}w}$ factors could be improved through more explicit guidance in emission standards for manufacturers and emission laboratories, including defined procedures, default fuel-specific parameters and validated example calculations. Alternative approaches, such as direct water measurements (e.g. via FTIR) or independent exhaust flow measurement (EFM), could be applied. This issue is particularly critical when considering CVS-based validation of tailpipe emissions, where accurate second-by-second exhaust flow determination is essential. Importantly, this issue affects all real-time and tailpipe gaseous and particle emission measurements in laboratory CVS setups,

where exhaust flow is calculated from CO_2 measured in diluted wet exhaust in the CVS and CO_2 measured in dried raw exhaust sample from the tailpipe.[3] In this study, FTIR measurements enabled identification of incorrect $k_{d\text{-}w}$ correction factors. Notably, when using correct $k_{d\text{-}w}$ factors for calculation of raw exhaust flows in the CVS measurement related automation system, CO_2 emissions measured by FTIR and NDIR (bag) were consistent in PAREMPI, and also N_2O measured by FTIR and QCL-IR (Figure 9).

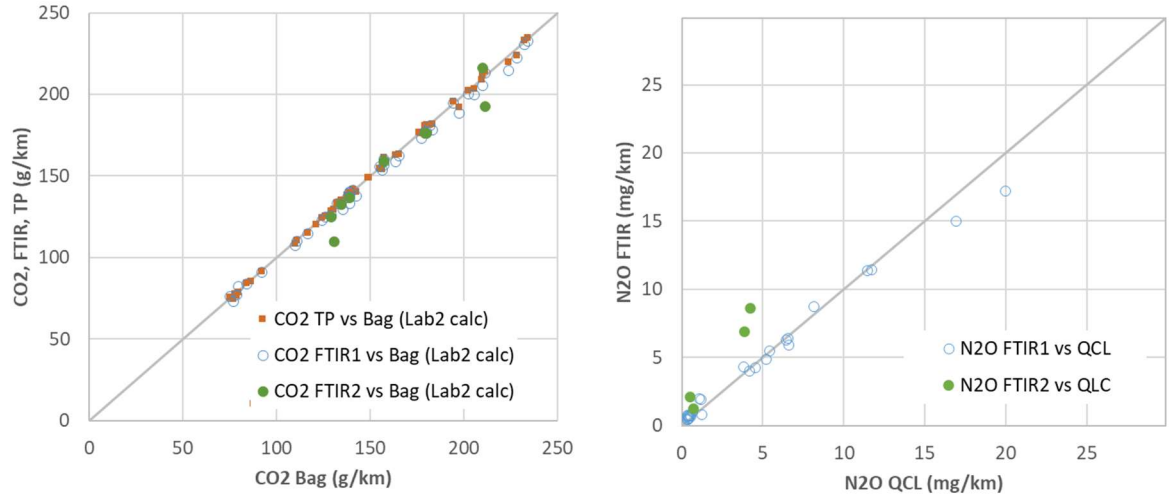

Figure 9. Results obtained by FTIRs were compared with a) CO_2 from regulated "Bag" and b) N_2O from QCL-IR (continuous) measurements with cars.

PEMS-FTIR measurement ranges and exhaust concentrations

Regardless of the measurement technique, instruments need to be calibrated over the entire range of exhaust species present in the exhaust gas measured. Actual concentrations of gases in the exhaust vary substantially depending on the type, age and technology of transport applications. This variability is evident from the concentrations detected in PAREMPI, as shown in Table 7 and Figure 10, which also presents the ranges calibrated in the PEMS-FTIRs used. The range of concentrations observed varied from zero to extremely high concentrations, depending on applications and operating conditions. Calibrations of the BOB-1000 covered the exhaust concentrations observed for the other priority gases than NH_3 and N_2O. Careful consideration is needed when selecting the multi-point calibrations.

Table 7. Original equipment manufacturers' calibrations of the PEMS-FTIRs used and concentrations detected in PAREMPI. Priority precursor gases for SecA formation in boldface.

Compound	BOB-1000 Calibrations (ppm)	CZU/Createch prototype Calibrations (ppm)[1]	Trucks, Euro VI max (ppm)	Aviation Jet A-1, SAF max (mean) (ppm)	Marine max (mean) (ppm)
CO	5 000; 50 000	<80 000	<2500	<1000 (~300)	<4000 (<200)
CO_2	40 000; 200 000	<150 000	<110 000	~9300	~40 000
H_2O			<120 000		~40 000
NO	5000	<4000	<1200	<2	<300
NO_2	1000	<1000	<600	<100 (~24)	<100 (~15)
N_2O	200	<200	<900, range[2]	<10 (2-3)	<1

[3] The mechanism described here is different from cold-start effects involving water condensation reported by Giechaskiel et al. (2019).

NH_3	500	<1000	<900, range[2]	<5 (<1)	<100 (<10)
CH_4	2000	<4000	<60	<200 (~35)	<1000 (0-3)
C2-C4/N-C8	1000	Library	<100	<300 (<30)	<500 (<10)
HCHO, CH_3CHO	1000	Library	<30	<50 (<10)	<110 (<10)
HNCO, HCN,HCO_2H	1000		<40	bd	bd
SO_2	1000		<50	<10	<100 (~12)
Aromatics	–		–	–	–

[1] Upper ranges of multi-point calibrations with calibration gases; calibration based on library spectra verified for formaldehyde and ethylene [2] Exhaust concentrations exceed measurement range of the FTIR instrument.

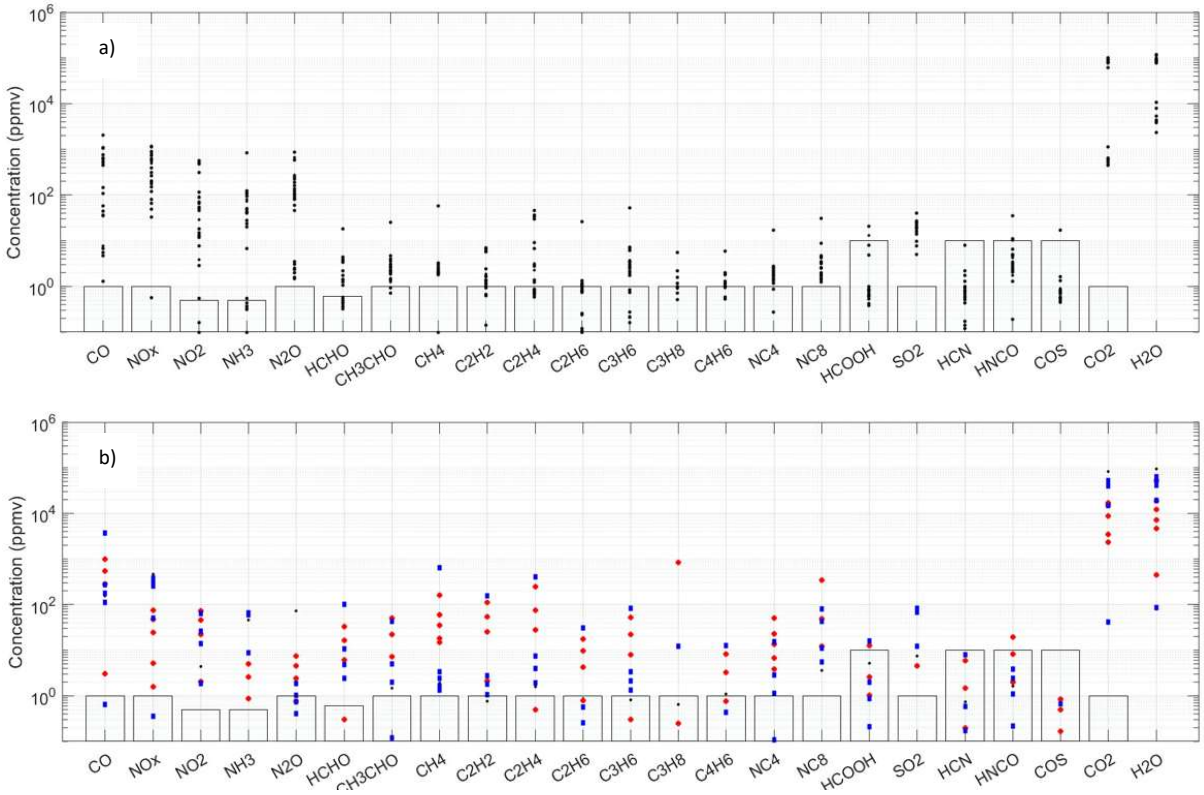

Figure 10. PAREMPI measurements: ***a)*** *HD, two Euro VI trucks* ***b)*** *Simulated measurements for aviation, Jet A1 and SAF fuels (in red) and for marine fuels (up to 0.4% sulphur, in blue). Concentrations present max, mean and 2-98 percentiles of data (negative values excluded). Bars show estimated detection limits, which are not empirically determined (particularly indicative for HCN, HNCO, HCOOH and COS).*

Operational experiences

The BOB-1000 instrument performed smoothly in PAREMPI campaigns, including on-road truck measurements. The nominal sample flow of the BOB-1000 is relatively high at 10 lpm; however, the sample flow is adjustable, and lower sample flows were used when necessary. FTIR instruments require a sampling unit and a pre-filter, which increases the size and weight of the system. PEMS-FTIRs used for transient measurements needed liquid nitrogen, which was manageable in on-road measurements with trucks. It is worth noting that LN2 is not needed for all FTIRs, such as the AVL M.O.V.E. FT and FTIRs designed for steady-state tests. The connection to the computer was loosened during driving a couple of times, which could be avoided by using a computer rack.

A prototype FTIR instrument package developed by the Czech University of Life Sciences and by CreaTech was used during laboratory tests of cars in the PAREMPI project, in parallel with the portable FTIR BOB-1000. This package, optimized for robustness and low power consumption (~200 W including a heated sampling system), was developed specifically for on-road emissions measurements of scooters, motorcycles and other vehicles difficult to test with traditional instruments. More than 20

mopeds, scooters and motorcycles were tested with the instrument within the Horizon Europe LENS project.

8. Toxicological assessment

This section describes toxicological assessment of transport-derived exhaust, and for the first time, the robust measurement system suitable for real-life conditions. Traditionally toxicity has been assessed on off-line filter samples, with some studies incorporating air-liquid interface (ALI) systems designed to laboratory experiments. A significant milestone in PAREMPI was the integration of an Air-Liquid Interface (ALI) exposure chamber into a moving vehicle, enabling on-road sampling of heavy-duty truck emissions, and in situ toxicity testing.

8.1 Methods for Toxicity Assessment

8.1.1 Selection of Cell Models

Toxicity assessments utilize well-established human lung models cultivated at the air-liquid interface (ALI) to mimic real-world exposure conditions. When selecting a cell model for testing engine exhaust toxicity in the lungs, it is essential to balance physiological relevance, ease of use, and experimental feasibility.

Traditional 2D cell models, such as bronchial epithelial cells (BEAS-2B, 16HBE) and alveolar epithelial cells (A549, H441), are widely used due to their ease of culture, reproducibility, and high availability. However, these models lack the structural complexity of the lung, and monolayer cultures do not fully replicate real-world exposure scenarios, such as air-liquid interface (ALI) interactions with pollutants. Similarly, macrophage models (THP-1, RAW264.7) are valuable for studying immune responses but, when used alone, fail to capture epithelial-macrophage interactions that occur in vivo.

To address these limitations, advanced 3D ALI models such as MucilAir® (Epithelix) and EpiAirway™ (MatTek) provide more physiologically relevant conditions, allowing long-term exposure studies under realistic inhalation conditions. These models consist of fully differentiated, human-derived airway epithelium that can be maintained for extended periods, making them superior for studying chronic exposure effects, barrier integrity, and inflammatory responses. Their primary drawbacks are their higher cost, longer culture time, and increased technical complexity compared to 2D models. Additionally, lung-on-a-chip systems offer dynamic fluid flow and mechanical stretch, further mimicking realistic in vivo conditions, but they require specialized equipment and expertise.

Ultimately, while 2D models are cost-effective and suitable for initial screenings, advanced ALI systems (e.g., MucilAir®, EpiAirway™) provide a more accurate representation of lung physiology and exposure dynamics, making them the gold standard for high-fidelity in vitro toxicity testing of engine exhaust.

By providing a physiologically relevant environment, these models enable comprehensive evaluations of secondary aerosol toxicity to humans.

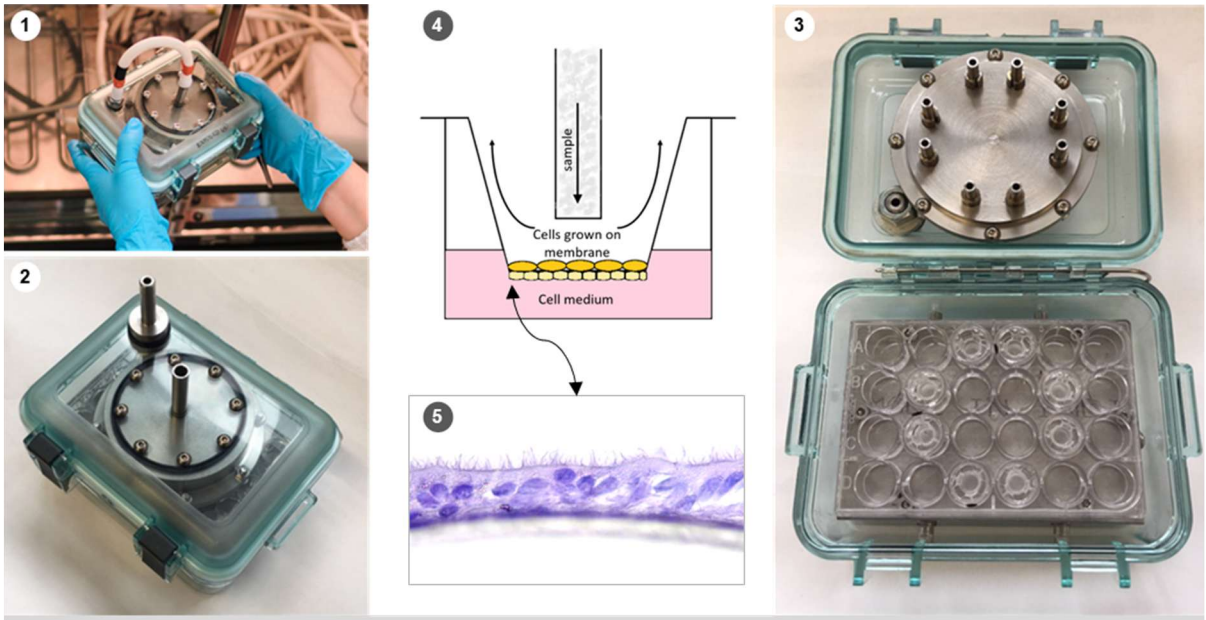

Figure 11. Air-liquid interface system for cell exposure as used in Vojtisek-Lom et al. 2025

8.1.2 Exposure Conditions

Controlled experimental setups are designed to expose cells to both fresh emissions and secondary aerosols collected using oxidation flow reactors (OFRs) and real-world transport emissions. In laboratory settings, chassis dynamometers allow for controlled and repeatable emission sampling under standardized conditions, ensuring reproducibility and precision. On the other hand, real-world emissions are assessed through on-road and on-board sampling, capturing actual driving conditions as seen in the heavy-duty campaign within PAREMPI.

Each approach offers distinct advantages. Laboratory-based testing provides consistency and controlled experimental conditions, making it easier to compare results across studies. Meanwhile, real-world sampling delivers insights into emissions under dynamic driving environments, which are more representative of real-world exposure scenarios. By combining both methodologies, toxicity assessments become more robust, covering a comprehensive range of exposure conditions.

Exposure is facilitated through commercially available air-liquid interface (ALI) exposure systems or custom in-house setups, depending on research needs. These systems ensure that aerosols are deposited directly onto cell cultures in a controlled and reproducible manner, effectively simulating real-world inhalation exposure. Several critical factors are considered when designing these setups, including particle size distribution, deposition efficiency, exposure duration, portability, and ease of use. Additionally, technical requirements such as electricity supply, temperature control, and the need for special gases are accounted for to maintain optimal exposure conditions.

By integrating laboratory-controlled experiments with real-world emissions assessments, researchers can enhance the reliability and applicability of toxicity studies, ensuring that findings are both scientifically rigorous and relevant to real-world exposure scenarios.

8.1.3 Toxicological Assays

Toxicological assays provide critical insights into the biological impact of secondary aerosols on human health. By assessing various endpoints, these evaluations determine the potential cytotoxic, oxidative, inflammatory, genotoxic, and metabolic effects of exposure. Each assay serves a specific function in toxicity assessment, ensuring a comprehensive understanding of emissions-related health risks.

Viability Assessment: Determining cell viability is a fundamental step in toxicity assessment, as it indicates the extent to which aerosol exposure compromises cell function and survival. Viability assays, such as MTT or LDH release tests, help identify acute cytotoxic effects, providing early indicators of harmful exposure levels.

Oxidative Stress Measurement: Oxidative stress is a key mechanism of toxicity in secondary aerosols, often leading to cellular damage and inflammation. Measuring reactive oxygen species (ROS) formation and glutathione (GSH) depletion helps assess the oxidative burden placed on cells, which is closely linked to respiratory and systemic health effects.

Inflammatory Response: Inhalation of toxic aerosols can trigger an immune response, leading to inflammation in the respiratory system. Measuring cytokines such as IL-6 and TNF-α provides insight into the degree of immune activation, which is associated with conditions such as airway irritation, chronic inflammation, and increased susceptibility to respiratory diseases. Additionally, evaluating a broader panel of inflammatory mediators provides a more detailed understanding of immune activation pathways.

Genotoxicity Assessment: Evaluating potential DNA damage caused by secondary aerosols is crucial in understanding long-term health effects. Standard assays, such as the comet assay, help assess whether emissions contribute to genetic instability and carcinogenic risk.

Metabolic Disruptions: Exposure to aerosols may alter cellular metabolism, impacting energy production and lipid metabolism. Monitoring metabolic shifts through targeted biomolecular assays provides insight into systemic effects beyond localized respiratory toxicity.

8.2 Experiences in PAREMPI

As part of the PAREMPI project, a systematic toxicological assessment was conducted on emissions from various transport sources, incorporating both fresh and secondary aerosol (SecA) emissions. The study utilised an array of measurement techniques and experimental setups to evaluate the toxicity of these emissions, employing a dedicated toxicological incubator (Vojtisek-Lom et al., 2025). Several novel approaches were implemented, including a portable exposure chamber, an auxiliary toxicological laboratory, and direct exposure to photochemically aged exhaust.

The experimental setup involved exposing BEAS-2B and MucilAir™ cell models to primary and secondary aerosol emissions collected via controlled oxidation flow reactors (OFRs). Cells cultured on standard 6 mm inserts were placed in airtight exposure boxes, which were subsequently housed within a modified incubator (Figure 12). This incubator was strategically located near key testing environments: next to the vehicle dynamometer test cell at Bosmal for car measurements, within the engine test cell at VTT for marine and aviation measurements, and in a measurement container towed by heavy trucks in Tampere. The exposure chamber functioned analogously to conventional sampling instruments, drawing in diluted engine exhaust for direct cell exposure.

In this setup, conditioned exhaust (37 °C, ~85% relative humidity) was introduced to the culture surface, allowing for natural aerosol deposition via diffusion, closely replicating conditions in the human lungs. To maintain methodological consistency, no artificial enhancements such as aerosol charging (Aufderheide et al., 2003) or thermophoretic processes (Ihalainen et al., 2018) were applied to modify deposition rates. The mobile exposure system's parameters have been detailed in a forthcoming publication (Vojtisek-Lom et al., 2025).

Exposure durations ranged between one to two hours, striking a balance between achieving detectable cellular responses, minimising culture degradation, and maintaining a practical experimental timeline. In select tests, the exposure chamber was positioned downstream of a photochemical oxidation reactor, enabling the assessment of aged exhaust emissions. To mitigate artefacts, an ozone trap was installed upstream of the reactor to capture residual ozone from the accelerated photochemical aging process, ensuring the delivery of uncontaminated aged exhaust to cell cultures.

A significant milestone of the PAREMPI project was the successful integration of an ALI exposure chamber into a moving vehicle for the first time. This innovative approach enabled on-board sampling of heavy-duty truck emissions during real-world driving conditions in Tampere, marking a breakthrough in in situ toxicity testing.

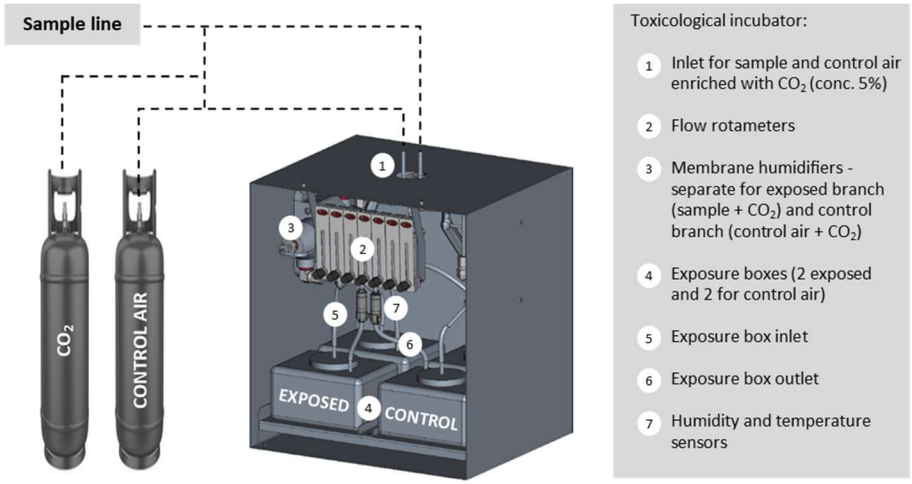

Figure 12. Toxicological incubator used during PAREMPI campaigns. Detailed information is described in Vojtisek-Lom, 2025.

8.3 Reliability and Robustness

Reliable and robust toxicity assessments are essential for obtaining consistent and comparable results across different studies. Several key factors define their effectiveness, including reproducibility, standardization, exposure relevance, and regulatory compliance. Ensuring methodological reproducibility requires the standardization of toxicity assays across laboratories, including cell culture conditions, exposure parameters, and data analysis methodologies. Adhering to Good Laboratory Practice (GLP) and following internationally recognized guidelines (OECD, ISO, EPA, ICCVAM, REACH) enhances the reliability of results and ensures regulatory acceptance.

The robustness of measurement techniques is crucial, ensuring that instruments and assays remain resilient to variations in environmental conditions, sample compositions, and operational factors. Proper validation of exposure methods includes precise control of particle size distribution (PM2.5, ultrafine particles), exposure duration, and chamber conditions (humidity, temperature, and airflow velocity) to replicate real-world inhalation scenarios. Inter-laboratory comparisons and referencing established toxicity endpoints further strengthen data reliability. Additionally, long-term sample stability is necessary to maintain sample integrity over time, enabling retrospective analyses and regulatory evaluations.

Maintaining cells in optimal, stress-free conditions before, during, and after exposure is critical for minimizing variability in experimental outcomes. Proper temperature control, nutrient supply, and careful handling reduce cellular stress, ensuring accurate and reproducible results. The selection of appropriate cell models plays a pivotal role, as different lung cell types exhibit varying sensitivities to toxicants. Choosing relevant human airway models, such as bronchial epithelial cells or advanced 3D air-liquid interface (ALI) models (e.g., MucilAir®, EpiAirway™), provides physiologically relevant evaluations.

A reliable toxicity assessment strategy should incorporate biological replicates, proper use of controls, blinded study designs to minimize bias, and standardized statistical analyses. Furthermore, integrating toxicity assessments with real-world applications, such as field studies and on-road exposure scenarios, enhances their relevance for emission control strategies and public health policies. Finally, prioritizing non-animal alternatives in toxicity testing, following the 3R principles (Replacement, Reduction, Refinement), aligns with modern ethical standards while ensuring scientific rigor. By considering these factors, researchers can improve the reliability, reproducibility, and applicability of toxicity evaluations, ensuring their effectiveness in guiding policy decisions and emission control strategies.

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Appendix 1. Characteristics of the selected FTIR instruments.

Characteristics of the selected FTIR instruments.

	PEMS BOB-1000FT A&D	**PEMS CZU/Createch prototype**	**Gasmet Cr-2000**	**Gasmet DX4000**	**Rowaco MKS MiniMega 2030**
Suitability for transport sectors	PEMS, transient cycles, on-road, off-road	PEMS, transient cycles, on-road, off-road	Transient (lab, also on-road)	Steady-state, on-board. Designed for wet, corrosive gases.	Lab, transient (here as a reference)
Operation temperature (°C)	down to -20	-10 to +30	20±20, non-condensing	5-30, non-condensing	
Spectrometer					
Resolution (cm^{-1})	0.5	0.5	8	8 or 4	0.5
Scan frequency (Hz)	5 (1 Hz avg)	5	10	10	1 or 5 Hz
Spectrum (cm^{-1})	500-6000	700-4200	600-4200	900-4200	400-4000
Detector, cooling	MCT, LN2 (50mL/h)	MCT, LN2	MCT, LN2	MCT, Peltier cooled	MCT (HgCdTe), LN2 (1 L for 12 h)
Interferometer	MKS	Bruker	Temet Carousel	Temet Carousel	MKS
Cell and sample					
Path length (m)	5.1	5	2.0	Multi-pass, fixed 5.0, 2.5 or 9.8.	5.11
Cell temp. (°C)	191	121 nominal (50-180)	180	180	191
Sample cell (L)	0.2	Not disclosed; T90: 1.8 s @ 10 lpm	0.22 (change in ~ 3 s)	0.4 (changed ~6 s at 4 L/min)	0.2
Sample	Raw exhaust + sample unit + heated filter	Raw exhaust; self-contained heated line controls, filter, pump	Raw exhaust, filtered (2 µm, 0.1µm)+Sampling unit	Raw exhaust, filtered (2 µm, 0.1µm) +Sampling unit	Raw exhaust, particles filtered 2 µm, in sampling unit 0.1 µm
Sample flow (L/min)	10	1-20 adjustable, 10 nominal	2-10	2-10	12 (or 0–18)
Purging gas		None	Nitrogen	Nitrogen	N2 or air. 9L per measurement. Pressurised air for ventils and back-flush
Size	40 kg + sampling unit 40 kg + filter 15 kg	65x35x30 cm, <40 kg including filter+pump	26 kg	13.9 kg 390x445x164 mm	200 kg + sampling unit
Detection limits for emission species of interest (ppm)	OEM	Estimated practical detection limits.	Determined by VTT (in N2, 1 s)	Determined by VTT (in N2/est** 20 s)	OEM 1 Hz (Higher DLs for 5 Hz)
CO2		Not evaluated	600	100/600	600
CO	1	<1	7	1/3	0.75
NO	1	<1	13	2/10	1
NO2	0.5	2-3	2	0.1/3	0.6
NH3	0.5	<1	2	1/3	0.4

SO2	1	Not evaluated	2	0.5/3	2.5
Aromatics	not included	not included	Benzene 5, toluene 4	Toluene 2/5	Benzene 10, toluene 7
Others	HCHO 0.6 CH4 1	HCHO <1 CH4 <1 N2O <3	HCHO 5, various HCs, alcohols, carbonyls ethers at DL of ~1-4	HCHO 1 CH_4 0.5/3 N_2O 0.1/4	HCHO 0.75, various HCs, alcohols, carbonyls ethers at DL of ~1-2
Zero	N2 before measurement	Not required, air or N2 recommended	N2 before measurement.	N2, 24 hours	
Calibration*	Only OEM calibrations possible.		Water calibration twice a year (essential for e.g. NOx accuracy).	Water calibration.	User calibrations possible.

*Calibration with single-component gases. ** Estimated in exhaust gas

Appendix 2. Principles of exhaust and fuel flow based calculations

The current calculation procedures of emission factors may appear to vary in different transport sectors; however, they adhere to fundamental chemistry principles. These include conversions of volume concentrations (V/V) to mass per volume concentrations (m/V) under standard conditions (273.15 K, 100 kPa), which are then multiplied by exhaust flow to achieve emission mass, which is subsequently divided by sector-dependent parameters. Weighing and correction factors are used depending on sector and applications. For instance, in aviation, emission factors are corrected to the reference atmospheric condition (ISA at sea level) based on engine compressor inlet pressure, air-to-fuel ratio, fuel split and humidity.

Exhaust flow in road transport and marine sectors is an important parameter, as illustrated in Eq. 2 for the distance-based emission factors in road-transport sector.

$$EF_{p(i-j)} = \frac{\sum_{n-i}^{j}(DR * c_p * Q_{exh})}{d_{i-j}} \quad (2)$$

Where EF_p corresponds to emission factor for pollutant p over time period from i to j seconds [mg/km], C_p to concentration of pollutant, background corrected depending on instrument, [mg/m^3 STP], DR to dilution ratio, d to distance accumulated from i to j seconds [km], Q_{exh} to raw exhaust flow [m^3/s STP].

Emission standards define methods for determining exhaust flow. In on-road PEMS measurements of cars and vehicles, exhaust flow is measured by the EFM. Exhaust flow can also be determined as a sum of fuel consumption and intake air flow of CAN data. However, CAN data is not always accessible, and its reliability depends on the procedures of the engine manufacturer.

Exhaust flow can be calculated based on the theoretical CO_2 formed in stoichiometric combustion, where a sufficient amount of air oxidizes hydrocarbon fuel completely (Eq. 3, Heywood 1988), and measured CO_2. For calculation of the stoichiometric CO_2 concentration, the fuel consumption and the carbon content of the fuel are needed.

$$C_aH_b + \left(a + \frac{b}{4}\right) \cdot (O_2 + 3.773 \cdot N_2) = a \cdot CO_2 + \frac{b}{2} \cdot H_2O + 3.773 \cdot (a + \frac{b}{4}) \cdot N_2 \quad (3)$$

Where C_aH_b corresponds to fuel composition, a is molar ratio carbon and b is that of hydrogen.

The combustion of hydrocarbon fuels is not complete, resulting in the formation of products from incomplete combustion, such as CO and THC. These products need to be considered alongside measured CO_2 in calculation. In Eq. 4, the CO_{2e} concentration includes equivalent CO and THC concentrations. This procedure reveals the excess air used in combustion and lambda can be used for the same purpose.

$$Q_{ex} = \frac{Q_{CO_st} * 100}{c_{CO2e}} \qquad Q_{CO_st} = FC * \frac{C_{fuel} * MW_{CO}}{100 * MW_C * d_{CO}} \quad (4)$$

Where Q_{exh} corresponds to exhaust flow (m^3/h STP), Q_{CO2_st} is stoichiometric CO_2 flow (m^3/h STP), c_{CO2e} is equivalent concentration of CO_2 (%V/V), FC is fuel consumption (kg/h), MW_i is molecular weight of compound i (g/mol), C_{fuel} is fraction of carbon in fuel.

This calculation principle is more challenging to apply in transient driving conditions of cars and vehicles than in constant loads of marine engines. The uncertainty of the calculated exhaust flow increases at low CO_2 concentrations. For cars and vehicles, exhaust flow measurements can be validated in laboratory using a CVS system.

In PAREMPI, exhaust flow was measured for cars (CVS based) and one truck (A) by EFM. For truck (B), EFM was not available, and inlet air CAN data was not accessible. The calculation methodology in Eq. 3 was tested for truck A based on FTIR and CAN data, and the results were validated against EFM measurements and the sum of fuel and air consumption data (CAN). The CO_2-based calculation principle overestimated the exhaust flow rate, which may be due to the increased uncertainty when air-to-fuel ratio is high, although data was filtered to avoid exhaust flow turning infinite in these conditions. The results with adjusted CO_2 concentrations correlated quite well with the EFM results (Figure 14). However, due to the high uncertainty related to this calculation method, it cannot be recommended for determining the exhaust flow in transient tests.

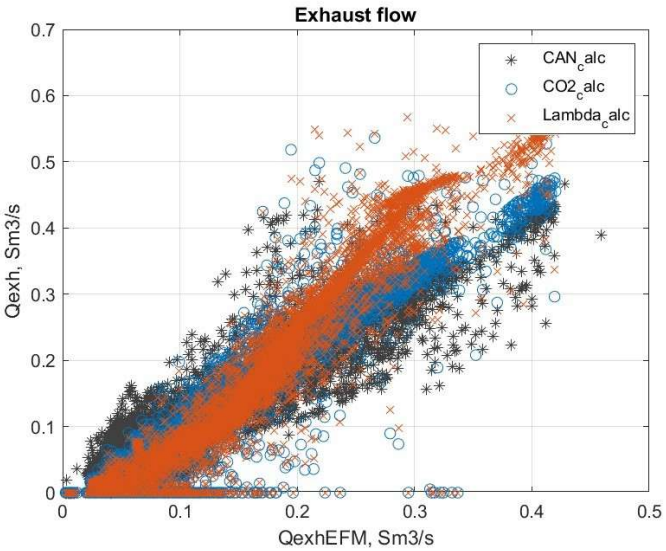

Figure 13. Comparison of measured and calculated exhaust flows (route TJT, 180324).

Features of aviation

In aviation, emissions are expressed using the amount of fuel burned as reference. By measuring concentrations of CO, CO_2 and THC in the exhaust, and knowing the fuel composition, the concentration of fuel burned can be estimated in unit of mg/m3 (STP, 273 °C). The balance between fuel combusted and air needed for combustion is applicable for aviation (ICAO 2020). Emission factors are calculated by dividing the concentrations of the emission species by the concentration of fuel burned.