PAULI SIMONEN

Development and Application of Oxidation Flow Reactors in Engine Exhaust Studies
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ACADEMIC DISSERTATION
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and Turku University of Applied Sciences. Thank you Prof. Leonidas Ntziachristos, Dr. Hilkka Timonen, Dr. Sanna Saarikoski, Ms. Päivi Aakko-Saksa, and Mr. Pekka Matilainen.

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Tampere, April 2024
Pauli Simonen
Combustion engines emit pollutants, including aerosol particles that affect air quality and climate. Some of the gaseous pollutants create secondary aerosol mass, that is, they react with oxidants in the atmosphere and form new particle mass in a time frame of hours to days after the initial emission. To decrease the atmospheric impacts of vehicle emissions, one should address the secondary aerosol formation potential because the primary particle emissions of modern vehicles are already low. However, the measurement of secondary aerosol formation potential is not as straightforward as that of the primary emissions.

This thesis focuses on oxidation flow reactors (OFR) that can be used to measure the secondary aerosol formation potential from combustion engines. The first part of the thesis concerns the OFR development, characterization and methodology of OFR measurements and data analysis in engine exhaust studies. The second part utilizes the established methodology to study the effect of driving conditions, exhaust after-treatment and fuel type on the secondary aerosol formation potential.

Characterization of an OFR is an essential step in OFR usage since the OFR characteristics affect both experimental planning and post-experimental data analysis. Characterization of the OFR response to changing gas concentrations is important especially in transient driving cycles, where the measured secondary aerosol must be aligned with changes in exhaust conditions.

The experiments in this thesis showed that it is possible to decrease the secondary organic aerosol (SOA) formation with a fuel change or by increasing exhaust after-treatment. The most notable effect of driving condition on SOA formation was related to engine and after-treatment temperature, but also differences in secondary aerosol formation between e.g. accelerations and steady speed driving were observed.
TIIVISTELMÄ


Hapetusreaktorin karakterisointi on tarpeellista koska reaktorin ominaisuudet vaikuttavat sekä mittausten suunnitteluun että mittausten jälkeiseen datanalyticselleyn. Reaktorin vasteen karakterisointi muuttuu kaasupitoisuuksiin on erityisen tärkeää muuttuvissa ajo-olosuhteissa, joissa mitattu sekundääriaerosoli täytyy kohdistaa pakokaasun muutoksien.

Tämän väitöskirjan kokeet osoittivat, että organisen sekundääriaerosolin (SOAn) muodostumista voi vähentää vaihtamalla polttoainetta tai lisäämällä pakokaasun jälkkäsittelyä. Merkittävin ajo-olosuhteiden vaikutus SOAn muodostumiseen liittyi moottorin ja jälkkäsittelyn lämpötilaan, mutta myös muutoksia SOAn muodostumisessa esimerkiksi kiidhtysten ja vakiohpeuden välillä havaittiin.
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<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>$D_m$</td>
<td>particle mobility diameter</td>
</tr>
<tr>
<td>$\rho_{\text{eff}}$</td>
<td>effective density</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerosol mass spectrometer</td>
</tr>
<tr>
<td>APM</td>
<td>Aerosol particle mass analyzer</td>
</tr>
<tr>
<td>CE</td>
<td>collection efficiency</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation particle counter</td>
</tr>
<tr>
<td>CPOT</td>
<td>Caltech photooxidation flow tube reactor</td>
</tr>
<tr>
<td>CVS</td>
<td>constant volume sampler</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
</tr>
<tr>
<td>DOC</td>
<td>diesel oxidation catalyst</td>
</tr>
<tr>
<td>DOFR</td>
<td>Dekati oxidation flow reactor</td>
</tr>
<tr>
<td>DPF</td>
<td>diesel particulate filter</td>
</tr>
<tr>
<td>DR</td>
<td>dilution ratio</td>
</tr>
<tr>
<td>EAT</td>
<td>exhaust after-treatment</td>
</tr>
<tr>
<td>EEPS</td>
<td>Engine exhaust particle sizer</td>
</tr>
<tr>
<td>EF</td>
<td>emission factor</td>
</tr>
<tr>
<td>EGR</td>
<td>exhaust gas recirculating</td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
</tr>
<tr>
<td>ELPI</td>
<td>Electrical low-pressure impactor</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionization detector</td>
</tr>
<tr>
<td>GDI</td>
<td>gasoline direct injection</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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| HC           | hydrocarbon |}
<p>| HRLPI        | High-resolution low-pressure impactor |
| IE           | ionization efficiency |
| IVOC         | intermediate-volatility compound |
| LVOC         | low-volatility organic compound |
| MCP          | micro-channel plate |
| MSC          | Micro-smog chamber |
| NEDC         | New European Driving Cycle |
| OA           | organic aerosol |
| OBD          | on-board diagnostics |
| OFR          | oxidation flow reactor |
| OHR          | OH reactivity |
| PAH          | polycyclic aromatic hydrocarbons |
| PAM          | potential aerosol mass |
| PEAR         | Photochemical emission aging flow tube reactor |
| PF           | production factor |
| PFI          | port fuel injection |
| POA          | primary organic aerosol |
| PTD          | porous tube diluter |
| PTR-MS       | proton-transfer-reaction mass spectrometer |
| RIE          | relative ionization efficiency |
| RTD          | residence time distribution |
| SCR          | selective catalytic reduction |
| SMPS         | Scanning mobility particle sizer |
| SOA          | secondary organic aerosol |
| SP-AMS       | Soot-particle aerosol mass spectrometer |
| TSAR         | Tampere secondary aerosol reactor |</p>
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>TWC</td>
<td>three-way catalyst</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compound</td>
</tr>
<tr>
<td>WLTC</td>
<td>Worldwide harmonized light duty test cycle</td>
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Publication I  

Publication II  

Publication III  

Publication IV  
Publication V


Author’s contribution

Publication I The author calculated the theoretical losses of LVOCs formed in the PAM reactor. The photochemical model free parameters were fitted by the author and the model was then used to determine the time resolved OH exposure in the experiments. The author calculated the theoretical SOA production based on the measured VOCs, and prepared the text, figures and tables corresponding to the aforementioned calculations.

Publication II The author did the characterization experiments and the associated modeling. The author participated in the engine exhaust experiments, did most of the data analysis and wrote most of the manuscript.

Publication III The author participated in the planning and execution of the experiments, and in the data analysis. The author calculated the theoretical LVOC losses and used a photochemical model to determine the OH exposure. Together with Dr. Paxton Juuti, the author developed an algorithm to determine the particle mass concentration based on EEPS and ELPI data. The author prepared the text and figures corresponding to the aforementioned contributions, and participated in other parts of manuscript writing in a minor role, and in a major role in the review process.

Publication IV The author participated in the planning and execution of the experiments and in the data analysis in a major role. The author wrote most of the manuscript. Mr. Joni Kalliokoski participated in the planning and execution of the experiments and in the data analysis.

Publication V The subject of the research was based on the author’s idea. The author guided the experimental work and did most of the data analysis. The author did the computational analysis and wrote the manuscript.
Pollutants that originate from human activity and are emitted to the atmosphere affect climate, worsen the ambient visibility, and have an adverse effect on human health. The atmospheric pollutants include both gaseous compounds and aerosol particles, i.e., solid or liquid particles suspended in air. (Baklanov et al., 2016; Pope III and Dockery, 2006; Pöschl, 2005)

The potential health issues related to smoke originating from combustion were recognized already at least approximately 2000 years ago, although without sound scientific evidence due to lack of quantification methods (Fowler et al., 2020). Later, the issue was apparent for example in 18th century London, where the pollution from coal burning was reported to cause poor visibility, various health issues, discoloring, unpleasant odours and crop damage (Evelyn, 1772). In 1952, stagnant air and local pollution sources led to an event called 'Great London smog' (derived from words smoke and fog), where the London city was covered in yellow-black smoke that limited the visibility to less than 10 m. The health effects were immediate, since 4000 excess deaths and numerous excess hospitalizations were reported during the smog episode. (Laskin, 2006; Polivka, 2018) While the London smog is attributed to combustion of high-sulfur coal, the source of smog that was frequently observed in Los Angeles during the same decade was different. Haagen-Smit (1952) studied the composition and formation of smog in Los Angeles, and found that the atmospheric photochemistry played an important role in the formation process: gaseous compounds emitted from gasoline evaporation and gasoline vehicle exhaust were oxidized in the atmosphere, producing ozone, other harmful gaseous compounds and aerosol particles. The particle mass formed from photo-oxidation of gases was later called secondary aerosol (Wilson Jr et al., 1973).

Although significant improvements since 1950s have been made to mitigate anthropogenic pollution (Fowler et al., 2020; Valavanidis et al., 2008), smog episodes still occur around the world (e.g., An et al., 2019; Angyal et al., 2021; Barboza, 2018;
Czerwińska et al., 2019). However, long-term exposure to aerosol particles affects health even when the concentrations are lower and the air is seemingly clean (i.e., the visibility is good), since even a relatively small increase in particle mass concentration correlates with increased mortality (Pope III and Dockery, 2006; Valavanidis et al., 2008).

Aerosol particles affect human health because they are deposited in airways and lungs during breathing. Depending on particle size, morphology, composition and solubility, the particles may directly influence the lungs or airways, or the particles or particle-phase compounds may enter blood circulation and affect other organs. (Hinds, 2012; Riediker et al., 2019; Valavanidis et al., 2008) Adverse health effects that are correlated with exposure to aerosol particles include mortality, cardiovascular disease and pulmonary issues. Potential mechanisms through which the particles affect health include oxidative stress, inflammatory damage and genotoxicity of particle-phase compounds. (Pope III and Dockery, 2006; Valavanidis et al., 2008).

In addition to visibility and health effects, aerosol particles affect the global climate. The net effect of anthropogenic aerosol particle emissions on climate is estimated to be cooling, although the uncertainty in the magnitude of the cooling effect is high due to the complexity of direct and indirect phenomena. (Bellouin et al., 2020) The direct effects include scattering, reflection or absorption of radiation. (Pöschl, 2005) For example, emissions of black carbon particles lead to climate warming because the particles absorb solar radiation (Bond et al., 2013). On the other hand, e.g. sulphate particles in the stratosphere backscatter the incoming solar radiation and thus cool the climate (Robock, 2000).

The indirect effects of aerosol particles on climate are related to cloud formation. Particles can act as cloud condensation nuclei or ice nuclei, promoting cloud formation and affecting the cloud properties. The effect of clouds on climate can be either cooling or warming, because they can reflect solar radiation but also absorb terrestrial radiation. (Pöschl, 2005)

Combustion engine vehicles have been a significant source for aerosol particles. In a time span of last 50 years, increasingly strict regulations have led to the development of engine technology and advanced after-treatment systems, so that the direct particle emissions of the vehicle fleet have decreased even though the number of vehicles has increased. (Frey, 2018) Despite the reductions in primary pollutants, combustion vehicles are still an important source of secondary aerosol mass and therefore their
contribution to mortality is significant (Nault et al., 2021).

Secondary aerosol is defined as particle-phase material that is formed in the atmosphere from gaseous compounds through atmospheric chemical reactions (Akimoto and Hirokawa, 2020; Hallquist et al., 2009). For example, combustion engine vehicles emit both gases and particles from the tailpipe. After the emission, some of the gases react with atmospheric oxidants and form new particle mass in a time frame of hours to several days (Gentner et al., 2017; Hallquist et al., 2009; Ortega et al., 2016). This newly formed particle mass is called secondary aerosol, and it is not included in the regulatory particle emission limits that consider only the primary particles measured directly from the tailpipe (Giechaskiel et al., 2019).

In order to mitigate the secondary aerosol formed from vehicular exhaust, it is necessary to find means to estimate the secondary aerosol formation potential by a direct measurement from the tailpipe. This would allow regulatory measurements and research on how different improvements (e.g. better after-treatment) affect the secondary aerosol formation. Since the formation takes place in the atmosphere, it is possible to simulate the atmospheric oxidation by exposing the exhaust to the same oxidants that are present in the atmosphere. This can be done by injecting the exhaust from the tailpipe to a large chamber (called smog chamber) and generating the atmospheric oxidants inside the chamber. Measuring the aerosol mass concentration inside the smog chamber as a function of time shows how much secondary aerosol is formed after certain exposure to the oxidants. The oxidant concentrations in smog chambers are typically of the same order of magnitude as in the atmosphere and the duration of the experiment is several hours. Thus, the total exposure to oxidants (concentration \times time) is typically limited to approximately one day of equivalent atmospheric oxidation. Because of the long experiment duration, the chambers need to be large (several cubic meters) in order to decrease the non-atmospheric effects of the chamber walls. (Chu et al., 2022; Peng and Jimenez, 2020)

By increasing the concentrations of oxidants significantly above atmospheric levels, the oxidation process is accelerated and several days of atmospheric oxidation can be simulated in few minutes. Since the experiment duration is short, the wall interactions decrease and the chamber size can be smaller. Following these principles, it is possible to continuously inject exhaust to a relatively small flow reactor, where the sample is oxidized during the residence time of seconds to minutes and the formed secondary aerosol mass is continuously measured at the flow reactor outlet. Such
devices are called oxidation flow reactors (OFRs). (Peng and Jimenez, 2020)

The advantages of the OFRs compared to smog chambers are their portability due to their small size, and the short experiment time that allows more experiments conducted per time unit. Another advantage is the continuous operation that allows time-resolved studies of secondary aerosol formation e.g. during a driving cycle. (Keller and Burtscher, 2012; Peng and Jimenez, 2020) In typical smog chamber experiments, the exhaust emitted during the driving cycle is first injected to the chamber and the oxidation process is actuated only after the driving cycle is finished. Thus, only the total secondary aerosol formation potential of the entire driving cycle is obtained, while OFRs can resolve between different events within the driving cycle and pinpoint the driving conditions that are responsible for the highest secondary aerosol formation potential. (Pieber et al., 2018)

The use of OFRs in engine exhaust measurements requires careful planning of the experiments, since the operation of the OFR is sensitive to concentrations of reactive gases in the sample. If the exhaust is not diluted enough, the reactive gases will suppress the oxidant formation and lead to non-atmospheric chemistry in the OFR. (Peng and Jimenez, 2020) Post-processing the results obtained with an OFR is necessary because the delay caused by the OFR needs to be accounted for to align the measured secondary aerosol mass with the transient events in the driving cycle. Thorough characterization of the OFR is needed both for planning the experiments and post-processing the data.

1.1 Aim and scope

The aim of this work is to resolve how to use an OFR in engine exhaust measurements and to determine the requirements for an OFR that is to be used in transient driving cycles. Another aim is to utilize the OFR to gain information on secondary aerosol formation from combustion engine emissions. Thus, the research questions are divided into methodology-related and application-related questions.

The first aim is reached through the following research questions:

- What are the **desirable characteristics of an OFR** intended to measure vehicular SOA formation potential?
- How should one **design the OFR experiments** to measure the secondary
aerosol formation potential of combustion engines, especially in transient driving cycles?

- How to **interpret the results** and determine secondary aerosol production factors in **data-analysis**?

Once the necessary characterizations and the experimental procedures are established, the OFR can be used to study the secondary aerosol from combustion engines and in transient driving cycles. By applying the established methodology, the following research questions are answered:

- What are the **secondary aerosol formation potentials of modern light-duty vehicles**?
- What is the **effect of varying driving conditions** on secondary aerosol formation potential?
- What are the possible **methods to mitigate secondary aerosol formation** from combustion engines?

Despite the order of the research questions, the methodology-related and application-related objectives were resolved in parallel: the observations in the first papers motivated developing the measurement and data-analysis methods in later papers.
2 SECONDARY AEROSOL FROM COMBUSTION ENGINES

2.1 Secondary aerosol formation

Secondary aerosol formation is initiated by the reaction between the precursor gas and atmospheric oxidants, such as OH radicals, ozone (O₃) and nitrate radicals (NO₃). The anthropogenic precursor gases are mainly oxidized by OH radicals, but for certain anthropogenic precursor gases the NO₃ radical is a significant oxidizer as well during nighttime. The oxidation products that are less volatile than the precursor gas can transform to the particle phase and form secondary aerosol, whereas the oxidation products remaining in the gas phase can oxidize further to generate secondary aerosol. However, the oxidation of organic compounds can also lead to generation of higher-volatility compounds. That is, usually only a fraction of the oxidation products will end up in the particle phase. This fraction is called the secondary aerosol yield. (Akimoto and Hirokawa, 2020; Kroll and Seinfeld, 2008; Seinfeld and Pandis, 2006)

The inorganic precursor gases for secondary aerosol formation are sulphur dioxide (SO₂) and nitrogen oxides (NOₓ; NO and NO₂). Also ammonia (NH₃) participates to secondary inorganic aerosol formation.

Sulphur dioxide is oxidized by OH radicals to form sulphuric acid (H₂SO₄) that condenses to the particle phase due to its low vapor pressure. Nitric oxide (NO) oxidation by O₃ forms nitric dioxide (NO₂), which, when oxidized by an OH radical, produces nitric acid (HNO₃). Nitric acid alone does not condense to the particle phase, but it reacts with particle-phase sodium chloride (NaCl) to form particle phase sodium nitrate (NaNO₃). Another pathway for nitric acid is to combine with ammonia to form semi-volatile ammonium nitrate (NH₄NO₃) that partitions between gas and particle phases depending on the atmospheric conditions. Ammonia can also
combine with sulphuric acid and form particle phase ammonium sulphates. Thus, while ammonia itself is not oxidized in the atmosphere, it will form secondary aerosol when other inorganic gases are oxidized. (Akimoto and Hirokawa, 2020)

Compared to the small number of inorganic precursors, the diversity of organic precursor gases is much higher and their chemistry is more complicated. For example, Marques et al. (2022) identified 147 different volatile organic compounds (VOCs) or intermediate-volatility compounds (IVOCs) from gasoline and diesel vehicle exhaust, and each compound has its own oxidation scheme. Toluene, one of the detected VOCs, is one of the most common anthropogenic organic VOCs. The OH-initiated oxidation of toluene results in several different oxidation products that further branch into different reaction pathways, yielding a large number of possible products (Dong et al., 2023). The same complexity in the oxidation process applies for other VOCs as well (Rissanen, 2021; Srivastava et al., 2022).

There are both natural and anthropogenic sources of secondary aerosol precursor gases (Calvert, 2002; Seinfeld and Pandis, 2006). Hallquist et al. (2009) estimated that globally the SOA formation from biogenic sources exceed that from anthropogenic sources. However, Nault et al. (2021) showed that in urban areas the anthropogenic sources are significant, and when trying to mitigate the harmful effects of secondary aerosol particles, it is easier to influence the anthropogenic emissions. Anthropogenic organic secondary aerosol precursor gases are emitted from fuel combustion in e.g. power generation, traffic and industry, from industrial processes and usage or processing of volatile chemical products (Calvert, 2002; Shah et al., 2020). The anthropogenic sources for inorganic precursors are likewise fuel combustion and industrial processes (SO\(_2\), NO; Chin et al. 2000; Huang et al. 2015), agriculture (NH\(_3\); Streets et al. 2003) and after-treatment devices in vehicles (NH\(_3\); Mejía-Centeno et al. 2007; Suarez-Bertoa et al. 2017).

The origins of secondary aerosol precursors in the vehicular context and their chemistry in the atmosphere are summarized in Fig. 2.1. The precursor formation and emission mechanisms are described in more detail in the following section.
2.2 Origins of secondary aerosol precursors from combustion engine vehicles

The main sources of secondary aerosol precursors from combustion engines are unburnt or partially combusted fuel and lubricant oil, combustion products, and ammonia from after-treatment devices. The unburnt fuel is also emitted from vehicles due to evaporation from the fuel system as illustrated in Fig. 2.2. (Gentner et al., 2017; Mejía-Centeno et al., 2007; Pundir, 2017)

2.2.1 Organic precursors

Unburnt or partially combusted fuel and lubricant oil are emitted from engines because of incomplete combustion in the cylinder. The reasons for incomplete combustion are illustrated in Fig. 2.2 and listed below, based on research by Pundir (2017), Dorsch et al. (2016), Kaiser et al. (1997) and Cheng et al. (1993). The numbering in the list refers to Fig. 2.2.
The crevices inside the cylinder create small pockets where the flame front does not reach the fuel vapor (1, 2, 3).

The fuel vapor can absorb in the oil film on the cylinder wall (7) or on deposits (4) inside the cylinder before ignition and then desorb to exhaust during the exhaust cycle.

Dissolved fuel and oil-related hydrocarbons in the oil film (7) may evaporate to the exhaust.

Liquid fuel droplets deposited on cylinder surfaces can evaporate during the exhaust cycle (5).
• Fuel vapor can survive unburnt through the combustion cycle because of wall-quenching, where the flame does not reach a thin layer close to cold walls (8).

• Flame quenching may happen elsewhere as well, especially during transient operation when the mixture is momentarily lean.

• During the compression cycle, fuel vapor can escape the cylinder by leaking past the exhaust valve before ignition (9).

• The fuel may leak due to blow-by from the cylinder to crankcase (6). Even though the vapors from crankcase are vented back to engine intake, a fraction of blow-by fuel vapor can dissolve in the engine oil and evaporate from the oil film during the exhaust cycle.

The emission of unburnt fuel is highest during cold starts due to low temperatures in the engine and in the catalytic converter. In normal operation, the unburnt fuel is efficiently converted to CO$_2$ in the hot exhaust and in the catalytic converter before emission to the atmosphere (Cheng et al., 1993; Pundir, 2017). However, it is possible that the gaseous organic compounds are modified in the catalyst but not oxidized all the way to CO$_2$ (Heeb et al., 2010; Heeb et al., 2008; Inomata et al., 2015; Liu et al., 2015), and that a fraction of the organic compounds flow through the catalyst unaffected. Typical hydrocarbon conversion efficiencies in normal operation conditions are higher than 80% for both three-way catalysts (TWCs) and diesel oxidation catalysts (DOCs) (Herreros et al., 2014; Pundir, 2017).

Gasoline fuel consists of alkanes, ~30% aromatic compounds, and a small fraction of cycloalkanes. In addition, various amounts of ethanol are added to gasoline to decrease the use of fossil fuels (Iodice et al., 2018). The number of carbon atoms for the majority of the compounds in gasoline is less than 10. The composition of diesel fuel is more diverse, both regarding the carbon number, and the distribution of different compounds. The majority of the compounds in diesel fuel contains more than 10 carbon atoms. The aromatic content of diesel fuel is ~20% and the majority of the remaining fraction is relatively evenly distributed between alkanes, cycloalkanes, and bicycloalkanes. A small fraction of diesel fuel consists of tricycloalkanes and polycyclic aromatic hydrocarbons (PAHs). (Gentner et al., 2012)

Aromatic hydrocarbons are well-known SOA precursors, and according to the estimation by Gentner et al. (2012), aromatics dominate the SOA formation potential of unburnt gasoline fuel. For diesel fuel, aromatics are an important source of SOA as
well, but the SOA formation potential from different aliphatic compounds exceeds that of aromatic compounds. Most of the SOA formation potential of diesel fuel originates from intermediate-volatility organic compounds (IVOCs), whereas most of the gasoline precursors are smaller and fall into the VOC (volatile organic compound) range. (Gentner et al., 2012)

2.2.2 Inorganic precursors

The inorganic combustion products that are able to form secondary aerosol are NO\textsubscript{X} and SO\textsubscript{2}, whereas NH\textsubscript{3} emissions originate from the catalyst.

SO\textsubscript{2} is formed from sulphur compounds in the fuel and lubricant oil during combustion (Durbin et al., 2004; Pundir, 2017). SO\textsubscript{2} emissions of vehicles have decreased significantly due to strict regulation of fuel sulphur content: currently, the sulphur content of diesel fuel must be less than 15 parts per million (ppm) while the content was almost three orders of magnitude higher in 1980s (1%) (Pundir, 2017). The sulphur content in marine fuels can be higher - the upper limit for sulphur content was reduced from 3.5% to 0.5% in 2020 (IMO, 2016). Despite the low sulfur content in land vehicle fuel, the storage-release phenomena of SO\textsubscript{2} in catalyst may still lead to high momentary emissions (Maricq et al., 2002).

Because of the high temperature during combustion, the diatomic oxygen in the combustion air dissociates and reacts with N\textsubscript{2} to form NO and N. The atomic nitrogen will oxidize to NO when it reacts with diatomic oxygen or an OH radical. NO can further oxidize into NO\textsubscript{2} in the hot exhaust and in the catalyst. The engine-out emissions of NO\textsubscript{X} are higher for diesel engines than for gasoline engines because of the higher combustion temperature in diesel engines. In gasoline engines, NO is efficiently converted to N\textsubscript{2} and CO\textsubscript{2} in TWC by the reaction between NO and CO. Modern diesel vehicles use an after-treatment device utilizing selective catalytic reduction (SCR) to reduce NO\textsubscript{X} to N\textsubscript{2}. The SCR operates by mixing urea (CO\textsubscript{(NH\textsubscript{2})\textsubscript{2}}) with the exhaust gas. The urea decomposes to NH\textsubscript{3}, which reacts with NO\textsubscript{X} in the catalyst producing N\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2}. In addition, the combustion temperature, and therefore also NO\textsubscript{X} formation, is controlled with an exhaust gas recirculating (EGR) valve, both in gasoline and diesel engines. (Pundir, 2017)

The TWCs in gasoline vehicles generate NH\textsubscript{3} as a by-product of NO reduction. The ammonia formation is highest during fuel-rich combustion. The SO\textsubscript{2} present
in the exhaust inhibits ammonia formation, and thus, the reduction in fuel sulphur content has increased the ammonia emissions from gasoline vehicles. (Mejía-Centeno et al., 2007) Modern diesel vehicles can emit ammonia as well because potential excess urea injection in the SCR leads to so called ammonia slip, i.e., not all ammonia is consumed for the NO\textsubscript{X} reduction (Suarez-Bertoa et al., 2017).

2.3 Estimating secondary aerosol formation potential

In order to mitigate the pollution caused by secondary aerosol formation from combustion engine exhaust, it is necessary to be able to estimate its secondary aerosol formation potential. While the primary particle emissions can be directly measured from the tailpipe, the estimation of secondary aerosol formation potential requires indirect methods because the formation takes place in the atmosphere during several days after the emission. The indirect methods discussed here include measurement of the precursor gases or controlled oxidation of the exhaust sample in a way that resembles the atmospheric oxidation process.

As discussed earlier, the secondary aerosol formation pathway for inorganic gases is relatively straightforward. First, there is a limited number of inorganic precursor gases relevant to secondary aerosol formation, so it is possible to measure all of them from the exhaust. Second, the end products of oxidation of these gases are reached after only a few oxidation steps. Third, it is possible to model the partitioning of the oxidation products between particle and gas phase, depending on the environmental conditions (e.g., Renner and Wolke, 2010).

Compared to the inorganic gases, the secondary aerosol formation from organic precursor gases is more complex. Diesel and gasoline engines emit a large variety of organic gases, and not all of them produce secondary organic aerosol in the atmosphere. It is challenging to speciate all the organic compounds and to estimate their contribution to total SOA formation potential. The first issue is the measurement of each compound, which requires different mass spectrometers, extensive data analysis and calibration of instrument response for each compound (e.g., Zhao et al., 2015). Another issue is the estimation of SOA formation from all the detected compounds because of their large number. For organic gases the final oxidation product is CO\textsubscript{2}, but the intermediate products may have low enough volatility to partition to the particle phase. In addition, the oxidation pathways are complex because there can be
multiple oxidation steps before the SOA-forming oxidation product is reached, and the pathways may have several different branches, of which only a few lead to SOA-forming products. The distribution of oxidation products depends on environmental conditions and concentrations of other gases, such as NO$_X$. The oxidation products also have different volatilities, so that their partitioning between the gas and particle phase depends on the total organic particle mass and the ambient conditions. (Srivastava et al., 2022) As a summary, accurate determination of the total SOA formation potential based on exhaust gas measurements would require identification of each relevant organic precursor gas, knowledge of their complex oxidation chemistry and volatility measurements of each oxidation product.

A simpler approach for SOA formation potential estimation is to measure only the most important precursor gases from the exhaust and determine the SOA formed from each of them by applying known SOA yields, i.e., how much organic aerosol mass is formed per loss of precursor mass due to oxidation. The yield is determined experimentally by injecting single precursor gas into a large chamber with atmospherically relevant oxidant concentrations, and then measuring the formed SOA mass. The yield can be measured at different NO$_X$ regimes to account for some of the oxidation pathway dependency on other gas concentrations, and measuring the yield as a function of total organic particle mass reveals some volatility properties of the oxidation products. (Odum et al., 1996) The main issue with this approach is that it requires a priori knowledge of what the most important precursors are that should be measured, which is not trivial. For example, in 1997, Odum et al. showed that they could estimate the SOA formation from evaporated gasoline based on the aromatics present in the fuel with good accuracy, except for one fuel. This fuel contained the highest non-speciated mass, i.e., the most non-measured compounds. It was later shown that the SOA formation from engine exhaust is more complex than that of the evaporated fuel: In 2006, Volkamer et al. discovered that the observed SOA formation in an urban environment was almost ten times higher than the modeled SOA formation when the model included 51 known SOA precursors and their yields, including the aromatics observed by Odum et al. (1997).

Instead of measuring precursors and applying the yield for each of them to estimate the SOA formation, another approach is to measure SOA formation directly from different emission sources. Already in 1973, Wilson Jr et al. sampled exhaust from a gasoline vehicle to a smog chamber where the exhaust was exposed to atmo-
spheric oxidants, simulating atmospheric oxidation. However, they did not measure the formed aerosol mass but instead the change in aerosol light scattering upon oxidation, and the resulting secondary aerosol was not speciated between organic and inorganic aerosol. With more modern instrumentation, Weitkamp et al. (2007) did similar smog chamber experiments for diesel exhaust. They observed SOA formation that was an order of magnitude higher than the one modeled based on 58 known precursor gases, which highlights the need for direct measurements of SOA formation potential instead of measuring the known precursors. Similar experiments with gasoline vehicle exhaust were performed by Nordin et al. (2013) and Platt et al. (2013). The observed SOA formation in the idling experiment by Nordin et al. was 1.7 times higher than expected from the measured precursors. The discrepancy between the expected SOA and the observed SOA was higher, a factor of 5, for the driving cycle experiments by Platt et al.

Advancements in measurement techniques allow extending the speciation of organic gas-phase compounds well beyond only aromatics. For example, Pieber et al. (2018) utilized a proton-transfer-reaction mass spectrometer (PTR-MS) to measure the composition of organic gases emitted from gasoline vehicles, and were able to identify the molecular structure of approximately 65% of gas-phase non-methane organic carbon mass. The dominant identified organic gases were aromatics. Pieber et al. measured the SOA formation as well and observed that the apparent SOA yields of the gasoline exhaust were up to factor of 2 higher than the calculated SOA yields of corresponding aromatic mixtures. The authors suspected that the reasons for the discrepancy could be the non-identified gaseous compounds (e.g. IVOCs) that could not be measured with PTR-MS, or that the yields of the aromatic compounds were different in the complex mixture of gasoline exhaust compared to the laboratory yields that were determined based on single precursor or simple mixture experiments.

Deng et al. (2020) performed similar experiments as Pieber et al. (2018), but for a diesel vehicle. The aromatics, oxidized VOCs and PAHs measured with a PTR-MS could explain only 15-30% of the observed SOA, and the aromatics only ∼5%. Zhao et al. (2015) extended the measurement range of organic gases to IVOCs by sampling diesel exhaust to quartz filters and adsorbent tubes and analyzing them off-line with a combination of a gas chromatograph and a mass spectrometer. They estimated that single-ring aromatics contributed only ∼1% to the SOA formation potential and that the IVOCs were responsible for the majority of the SOA. Drozd et
al. (2019) measured the IVOC emissions from gasoline vehicles in a similar manner, and deduced that IVOCs contribute $\sim$45% to total SOA formation from gasoline exhaust, although they did not verify the result with a smog chamber experiment.

As a summary from the studies by Pieber et al. (2018), Deng et al. (2020), Zhao et al. (2015) and Drozd et al. (2019), it can be said that determining the SOA formation potential of vehicles, especially diesel vehicles, based on on-line PTR-MS measurements of VOCs is not sufficient, whereas smog chamber experiments or laborious IVOC sampling and off-line analysis result in more accurate estimation.

There are some limitations to smog chamber experiments. Smog chambers are typically large, several cubic meters in volume, which limits their mobility and applicability to experimental environments where space is limited. Another issue is that because of the wall losses, the oxidation time is limited to approximately one day, which is also approximately the maximum atmospheric photochemical age that the chambers can simulate since the OH concentration in the chambers is usually close to ambient levels. (Peng and Jimenez, 2020)

Smog chambers are usually operated in batch mode, which means that the sample is first injected to the chamber, then the instruments start sampling from the chamber and the oxidation in the chamber is actuated (e.g., Nordin et al., 2013; Platt et al., 2013; Weitkamp et al., 2007). Because of this, there is no temporal information on the SOA formation potential, but only the total SOA formation of the sampling period is acquired. In the context of vehicle emissions, the precursor concentrations in the sample can vary significantly because of different driving conditions. To address vehicular SOA production, it is necessary to identify which driving conditions are responsible for most secondary aerosol formed, but such analysis is not possible with a smog chamber sampling a full driving cycle. Another limitation is the long measurement time and flushing procedures, which limits the number of experiments that can be conducted in one day (e.g., Platt et al., 2013). For example, to test the difference in vehicular SOA formation between two different fuels would require approximately two measurement days.

To address the limitations in smog chambers, Kang et al. (2007) presented an oxidation flow reactor (OFR) that allowed continuous measurement of SOA formation potential from the precursors present in the ambient air with time resolution of few minutes. Figure 2.3 illustrates the emissions of organic species from a combustion engine and how the gas-phase VOCs and IVOCs evolve both in atmosphere and in
an OFR. Measuring the aged organic aerosol (OA) from atmosphere or from a smog chamber (Fig. 2.3c) does not reveal the temporal variation of SOA formation potential in the exhaust (Fig. 2.3a). The temporal behaviour can be measured with an OFR (Fig. 2.3d), although the signal will be distorted because the aerosol constituents will disperse inside the OFR and have different residence times due to the OFR flow velocity distribution.

Figure 2.3 Organic aerosol emissions, and the organic gas-phase chemistry in atmosphere and in an oxidation flow reactor. The SOA formation potential in the tailpipe depends on the gas-phase VOCs and IVOCs (a). The actual SOA formation occurs in the atmosphere, smog chamber or OFR, where a fraction of the gas-phase precursors are oxidized to low-volatility organic compounds (LVOCs) that can condense to the particle phase. Only the first steps of oxidation are shown, but the gas-phase oxidation products may further oxidize into LVOCs. The time scale of SOA formation in the atmosphere or a smog chamber (c) is hours to days, while the SOA measured from an OFR (d) preserves some of the temporal variation of the tailpipe emissions. The aged OA measured after the oxidation consists of primary organic aerosol (POA) emitted from the tailpipe and SOA formed from the gas-phase emissions.
2.4 Oxidation flow reactors

The operating principle of the OFR called Potential Aerosol Mass (PAM) reactor, designed by Kang et al. (2007), was to expose the sample to high concentrations of ozone and OH and HO$_2$ radicals (up to thousands of times the ambient concentration). When the oxidant concentrations are high, the exposure of the sample to the oxidants can reach atmospheric exposures of several days only in few minutes. Instead of the batch process used in smog chambers, the PAM reactor operated in a flow-through mode with a residence time of a few minutes. The compact size (15 l) and design of the updated PAM reactor (Lambe et al., 2011) enables mobile measurements, and the short residence time enables good temporal resolution and possibility to test the sensitivity of SOA formation to different parameters time efficiently. Later development of the PAM reactor allows also simulation of the atmospheric nighttime NO$_3$ chemistry illustrated in Fig. 2.3 (Palm et al., 2017).

Chemical reactors existed already before the PAM reactor, but in aerosol research they were used to study e.g. ozonolysis of VOCs (Jonsson et al., 2006) and heterogeneous oxidation of particle phase organics (Hearn and Smith, 2006). After Kang et al. presented their concept to use an OFR to estimate the secondary aerosol formation potential, several OFRs for this purpose with differences in design and residence time have been developed. Comprehensive lists of different OFRs have been reported by Peng and Jimenez (2020) and Zhang et al. (2024), and three examples are described here. The Micro-smog chamber (MSC) is smaller than the PAM reactor and operates with residence time $< 10$ s (Bruns et al., 2015; Keller and Burtscher, 2012), whereas the Photochemical Emission Aging flow tube Reactor (PEAR) is larger and operates at higher flow rate than the PAM reactor to provide enough sample for toxicological studies (Ihalainen et al., 2019). The Caltech photooxidation flow tube reactor (CPOT) differs from the previous OFRs by its isothermal conditions: the reactor is surrounded by a cooling jacket that can control the reactor temperature between 20 and 38 °C (Huang et al., 2017).

The oxidant concentrations that are thousands of times higher than the ambient concentrations have evoked questions of the atmospheric relevance of the oxidation chemistry in the OFRs. The underlying question is whether all the processes that VOCs and their oxidation products undergo in the reactor scale with OH concentration, i.e., whether they are accelerated with the same rate as the oxidation by OH
is accelerated. For example, when the oxidation of precursors depends only on OH concentration, the distribution of oxidation products does not depend on the OH concentration itself, but only on OH exposure ([OH] x residence time), so this process scales with OH concentration. An example of a process that does not scale with OH concentration is condensation of low volatile oxidation products to the particle phase, because the rate of condensation depends on particle surface area, which is not linearly dependent on OH exposure. (Peng and Jimenez, 2020) As illustrated in Fig. 2.3, in the atmosphere the condensation of low-volatility organic compounds (LVOCs) is the major pathway, whereas in the OFR the LVOCs may further oxidize because of higher OH concentration.

Peng and Jimenez presented also other processes that do not scale with OH concentration in their review of OFR chemistry. These include reactions of organic gases with non-OH reactants, photolysis of gases and particle phase organics, peroxy radical (RO$_2$) chemistry, heterogeneous oxidation, and particle phase oligomerization. Another non-atmospheric effect of OFRs is gas and particle interactions with the reactor walls (Fig. 2.3) (Palm et al., 2016). Despite all of these potential differences between the processes in an OFR and the ambient oxidation, it has been shown that the OFRs produce SOA from precursor gases with yields and compositions that are close to those of smog chambers, which in turn resemble the atmospheric oxidation better, because their OH concentrations are close to ambient levels (Bruns et al., 2015; Lambe et al., 2015). Peng and Jimenez also showed that it is possible to minimize non-atmospheric processes by adjusting the experimental conditions carefully.

As shown in Fig. 2.3, the aged OA measured from an OFR does not perfectly replicate the SOA formation potential in the tailpipe, but is distorted and includes the primary organic aerosol (POA) in addition to SOA. The extent of distortion depends on the OFR transfer function. The original PAM OFR presented by Kang et al. (2007) was developed for ambient measurements and is not ideal for measuring engine exhaust in transient driving cycles because of its broad transfer function - rapid changes in the driving conditions cannot be distinguished from each other. In the next chapter, an OFR that was designed for engine exhaust measurements is characterized in terms of its transfer function and other properties. Chapter 4 discusses the application of OFRs to study secondary aerosol formation from engine exhaust.
3 KEY CHARACTERISTICS OF AN OXIDATION FLOW REACTOR DEVELOPED FOR ENGINE EXHAUST STUDIES

An OFR that is used to determine secondary aerosol formation from exhaust emissions in laboratory testing should have as narrow a transfer function as possible to respond to rapid changes in emissions during driving cycles. It was observed in Paper II that the PAM reactor could not differentiate between two consecutive SOA precursor pulses that were 10 s apart. The broad transfer function of the PAM reactor is also problematic when determining the exposure to OH radicals. Even though it is possible to determine the average OH exposure, the output of the reactor will have a broad distribution of residence times and consequently a broad distribution of OH exposures. Two experiments with identical average OH exposure but different OH exposure distribution may lead to drastic differences in e.g. the cloud condensation nuclei activity of the oxidized aerosol (Friebel and Mensah, 2019). Thus, a narrow transfer function is desirable to achieve uniform OH exposure.

A prototype OFR (Tampere secondary aerosol reactor; TSAR) suitable for exhaust emission studies was designed by Dr. Erkka Saukko and built in Tampere University of Technology, and it was characterized in Paper II. The reactor was designed to operate close to laminar conditions by using conical inlets, and to have a short residence time and a narrow transfer function by using a smaller volume than the PAM reactor. The total volume of TSAR in the first prototype was 5.5 L, and 4.6 L after reducing the length of the mixing tube (Kuittinen et al., 2021), whereas the PAM reactor volume is ~13 L.

The original TSAR layout is presented in Fig. 3.1. The sample, humidified air and ozone are injected to the mixing tube (1) (previously called ‘residence time chamber’ in Paper II) where they are allowed to mix before entering the oxidation reactor.
Figure 3.1 The layout of Tampere secondary aerosol reactor (TSAR) (Paper II).

(3) which has a volume of 3.3 L. The expansion tube (2) between the mixing tube and the oxidation reactor has a half-cone angle of 6° to keep the flow laminar. The axial position of the outlet tube (4) can be changed so that it is possible to adjust the residence time while keeping the flow rate constant. Two additional suction flows are possible: one between the mixing tube and the expansion tube to reduce the residence time in the mixing tube, and another one at the end of the oxidation reactor to reduce the effects of the dead space between the outlet tube and the end of the oxidation reactor.

A commercial OFR based on TSAR design was released in 2022 by Dekati Ltd and is called Dekati oxidation flow reactor (DOFR) (Zhang et al., 2024). The DOFR was used in Paper V. The dimensions of the DOFR are very similar to the TSAR, but some differences exist: i) there are no additional suction flows in the mixing tube or at the outlet, ii) the outlet is conical, iii) there is a laminarizing grid element at the inlet, and iv) the UV lamps are different and are air-cooled with a fan.

The TSAR oxidation reactor is made of quartz glass with a thickness of 5 mm and is surrounded by two low-pressure mercury lamps that emit 254 nm UV light.
The UV radiation photolyses the injected ozone and generates excited oxygen atoms ($O(^1D)$):

$$O_3 + hv \rightarrow O_2 + O(^1D) \quad (3.1)$$

The excited oxygen atoms react with the water vapor to produce hydroxyl radicals (OH):

$$O(^1D) + H_2O \rightarrow 2\text{OH} \quad (3.2)$$

It is possible to operate the PAM reactor in a similar way to the TSAR by injecting ozone and using UV lamps that emit only 254 nm radiation. However, the PAM reactor is typically operated in OFR185 mode, where the lamps emit also 185 nm radiation. In that case, the external ozone generator is not necessary as reaction 3.1 occurs inside the chamber and OH is produced also from water photolysis. Another difference between the PAM reactor and the TSAR is the shorter residence time in the TSAR. Because of this, the OH concentration in the TSAR needs to be higher than in the PAM to obtain similar OH exposure. Thus, a comparison measurement to the PAM reactor operating in OFR185 mode was needed to determine whether the TSAR can be used as an alternative to the PAM reactor.

### 3.1 Residence time

The residence time distribution (RTD) is related to the transfer function of a reactor. The concentration of gases and particles measured downstream the reactor ($C_{\text{out}}$) is the result of convolution between the concentration entering the reactor ($C_{\text{in}}$) and the transfer function ($E$), which is the distribution of residence times at the reactor outlet following an ideal Dirac delta input impulse (Conesa, 2020):

$$C_{\text{out}}(t) = E(t) * C_{\text{in}}(t) = \int_0^t C_{\text{in}}(\tau) E(t - \tau) d\tau \quad (3.3)$$

If the transfer function itself was a Dirac delta function, the changes in the input concentration would be perfectly repeated in the outlet concentration. The broader the transfer function, the less details of the dynamic input concentration will be observed in the outlet concentration. This is demonstrated in Fig. 3.2a, where a
pulse of CO$_2$ measured downstream of the TSAR is flatter and broader than the one measured upstream.

![Figure 3.2](image)

**Figure 3.2** CO$_2$ pulse measured upstream and downstream of the TSAR oxidation reactor and modeled downstream a laminar reactor (a), and the residence time distribution of a 10 s CO$_2$ pulse in TSAR oxidation reactor and in a laminar reactor (b). The PAM RTD is based on the measurements by Lambe et al. (2011). Modified from Paper II.

The RTD of TSAR oxidation reactor was determined in Paper II by injecting pulses of CO$_2$ into the TSAR and measuring the CO$_2$ concentration up- and downstream of the oxidation reactor part. Figure 3.2b shows that the RTD is very close to laminar RTD when the UV lamps are off. When the lamps are on, the RTD is broader as the UV lamps heat the reactor walls and cause convection inside the reactor. Even though the RTD is not perfectly laminar, the assumption of laminar flow can be used to simulate the signal distortion and delay in the TSAR. The simulation is necessary when comparing data measured upstream of the TSAR to data that is measured downstream. For example, in Paper IV, the fresh aerosol mass concentration was measured upstream of the TSAR while the aged aerosol mass concentration was measured downstream. To determine the momentary secondary aerosol mass concentration, i.e. the difference between aged and fresh, the original fresh mass concentration was first convolved with the laminar transfer function, as illustrated in Fig. 2.3.

The laminar transfer function was used in Paper IV because the measured RTD in Fig. 3.2 corresponds to a 10 s pulse, whereas the transfer function $E$ in Eq. 3.3 must correspond to a Dirac delta input impulse, which was available for ideal laminar flow (Conesa, 2020). Later, in Paper V, a method was developed to determine the
unit response transfer function for an OFR by measuring the RTD of a 10 s pulse, so that the actual transfer function could be used in the simulations instead of an ideal laminar reactor transfer function.

The short residence time and relatively narrow transfer function of the TSAR allow higher time resolution of SOA formation measurement than the PAM reactor. This was demonstrated in Paper II (Fig. 3.3), where three 5-10 s square pulses of toluene were injected into the two OFRs at 10-15 s intervals. With the TSAR, it was possible to distinguish the three pulses of SOA originating from toluene oxidation, while the PAM reactor produced only one broad peak of SOA. In a similar manner, such short phenomena in driving cycles would be indistinguishable with the PAM reactor.

![Figure 3.3](image.png)

**Figure 3.3** SOA formed in TSAR and in PAM from three consecutive square pulse injections of toluene. Modified from Paper II.

In driving cycles, the driving conditions may change fast, which may induce rapid changes in the exhaust composition and consequently, rapid changes in the SOA formation potential. The fast response of the OFR is not only needed to distinguish such events and to link them to specific driving conditions, but also to accurately determine the SOA production factor. The effect of the RTD narrowness on the accuracy of SOA production factor measurement was further studied in Paper V, and the results are discussed in Chapter 4.
3.2 OH exposure

OH exposure is a key parameter affecting the amount and properties of the secondary aerosol. As the OH radical is the most important daytime oxidant for anthropogenic VOCs, its concentration determines the extent of SOA precursor gas oxidation and the following SOA formation (Srivastava et al., 2022). The OH exposure serves as a link between the laboratory-generated secondary aerosol and atmospheric secondary aerosol: a known OH exposure in the laboratory experiment corresponds to the age of atmospheric aerosol when the average atmospheric OH concentration is known. However, the OH exposure at the OFR outlet is not a single value but a distribution of different OH exposures of which the average value is typically reported. Hereafter, the term ‘OH exposure’ refers to the average OH exposure.

OH exposure can be determined by injecting a known amount of OH-reactive tracer gas into the sample and measuring its decay in the OFR. The concentration of the tracer decreases due to its reaction with OH, as defined in the following differential equation:

$$\frac{d[C]}{dt} = -k_{OH}[C][OH], \quad (3.4)$$

where $[C]$ is the concentration of the tracer gas, $[OH]$ is the concentration of OH radicals, and $k_{OH}$ is the reaction rate constant between the tracer gas and the OH radicals. Assuming that the OH radical concentration is constant, we get the OH exposure (OH$_{exp} = [OH] \times t$):

$$OH_{exp} = \frac{1}{k_{OH}} \ln \frac{[C]_o}{[C]_f}, \quad (3.5)$$

where $[C]_o$ is the tracer concentration upstream of the OFR and $[C]_f$ is the downstream concentration.

Ideally, the tracer gas would not create any secondary aerosol and it would be distinguishable from the compounds in the exhaust gas. There are several organic gases fulfilling these requirements, for example deuterated butanol, but a mass spectrometer would be needed to measure them (e.g., Platt et al., 2013). Other potential tracers are
carbon monoxide (CO) and sulfur dioxide (SO₂), which both can be measured with relatively simple gas analyzers. However, variable amounts of CO may be present in engine exhaust, so that the CO concentration upstream of OFR is not constant even though the injection would be constant. Thus, two analyzers measuring the CO up- and downstream of the OFR would be needed. In addition, some compounds, such as formaldehyde (which is an oxidation product of many hydrocarbons) and acetaldehyde produce CO upon oxidation with OH, so that the CO concentration does not depend only on the OH exposure but also on the aldehyde concentrations (Seinfeld and Pandis, 2006).

Sulfur dioxide as an OH tracer is not ideal because its oxidation with OH produces sulfuric acid particles. The injected SO₂ would generate artificial secondary aerosol, which could be difficult to distinguish from the secondary aerosol originating from the exhaust. Thus, there was no continuous injection of SO₂ in any of the exhaust experiments in this thesis. Instead, the oxidant generation in the used OFRs was characterized in separate SO₂ experiments. The results of the off-line SO₂ experiments were then adapted to the exhaust measurements by utilizing a photochemical model.

The photochemical model used in this thesis is based on the PAM_chem model by William Brune (PAM_chem Model 2017) and it calculates the concentrations of gas-phase chemical compounds downstream of the OFR by solving the differential equations describing the chemical reactions of the gases with Euler’s method. A model similar to the one used here is described by Li et al. (2015), although their solver did not use Euler’s method. Once the model free parameters (UV lamp photon flux, wall losses of OH radicals and O₃, OFR transfer function) have been fixed, the OH exposure can be modeled by using the OFR inlet gas concentrations as the model input.

The TSAR OH exposure was measured in an off-line SO₂ experiment in Paper II by injecting SO₂ into the reactor, first with UV lamps turned off to determine C₀ in Eq. 3.5, and then turning the lamps on to obtain C_f and varying the inlet ozone concentration. The model parameters were varied until a good agreement between the measured O₃ concentration at TSAR outlet and the measured OH exposure agreed well with the model predictions. The comparison between the measured and modeled values with final model parameters is shown in Fig. 3.4.

The OH exposure in other experiments (e.g. exhaust gas measurements) is not equal to the exposure determined in the off-line SO₂ measurements because gas-phase
species in the sample consume OH radicals in the OFR (Peng and Jimenez, 2017). However, the model parameters are constant, and thus the OH exposure in other experiments can be obtained by changing the model inputs accordingly. For example, the OH exposures in Paper II toluene measurements (Fig. 3.6) were obtained by utilizing the model. Application of the model to exhaust experiments is described in Sect. 4.1.

3.3 Fate of oxidation products

The TSAR transfer function and the time resolution could be further improved by either increasing the flow rate or decreasing the volume of the oxidation reactor. Both operations would also shorten the average residence time and thus the OH concentration should be higher to obtain similar OH exposure. Increasing the OH concentration has a drawback: the time scale of OH oxidation would decrease while the time scale of condensation would not (necessarily) change. This can lead to increased fragmentation of the low-volatility oxidation products (Low-volatility organic compounds; LVOC) before they have time to condense to the particle phase, and as the fragmented molecules are more volatile, they never end up in the particle phase. In the atmosphere, the time scale of condensation is typically much shorter than the time scale of the OH oxidation because of lower OH concentration, and thus the
increased fragmentation of LVOCs is non-tropospheric and considered as loss. (Palm et al., 2016; Peng and Jimenez, 2020)

The fate of LVOCs can be modeled with a set of differential equations describing their possible pathways. Palm et al. (2016) designed a model where the SOA is formed from LVOCs that are oxidation products of the precursor gases. The LVOCs can either produce SOA by condensing to the particle phase, condense on the reactor walls, react with OH, or exit the reactor before condensing to the particle phase. The LVOC molecule is considered fragmented if it reacts with OH five times before condensing to the particle phase, and thus will not produce SOA.

The rate of condensation to the particle phase depends on the particle size distribution, the LVOC diffusion coefficient and the accommodation coefficient. As a simplification, the higher the total surface area of the particle population, the higher the condensation rate. The rate of condensation on walls depends on the LVOC diffusion coefficient, the reactor wall surface area to volume ratio, and the reactor volume. The higher the surface area to volume ratio, the higher is the wall condensation rate. The effect of reactor volume itself is minor. The rate of OH oxidation is directly proportional to the OH concentration. The model does not consider nucleation of the particles, which can lead to an overestimation of the LVOC loss. (Palm et al., 2016)

The effect of increasing the OH concentration (i.e. shortening the residence time) on the non-tropospheric LVOC losses can be studied by solving the differential equations at different residence times while keeping the OH exposure constant. This was done in Paper II and the results are shown in Fig. 3.5. The effect of the residence time is modeled for two cases: ambient air and vehicle exhaust. The only difference between the two is the particle size distribution, which causes a higher particle surface area concentration in the vehicle exhaust case. For both cases, the loss is modeled for accommodation coefficients of 0.1 and 1.0 since the actual value of accommodation coefficient is unknown. The LVOC loss in the figure corresponds to the fraction of LVOCs that did not condense to the particle phase. This is considered as loss because in the atmosphere, condensation to the particle phase is the dominating LVOC fate.

Figure 3.5 shows that decreasing the residence time leads to higher losses of LVOCs, and this is mainly due to increased fragmentation. In the case of vehicle exhaust, the TSAR losses are moderate (~25%) at the typical residence time (~40 s at 5 lpm flow rate) if the accommodation coefficient is close to unity. Decreasing the residence time
Figure 3.5 TSAR LVOC losses at constant OH exposure as a function of residence time using mass accommodation coefficients ($\alpha$) of 0.1 and 1.0. The losses for other OFRs are shown at their typical flow rates (Paper II). The other OFRs are Micro-smog chamber (MSC), Potential aerosol mass reactor (PAM), and Caltech photooxidation flow tube reactor (CPOT).

in the TSAR is risky because of the steep increase in the LVOC losses.

Another problem with shortening the residence time is the increased nucleation, which leads to smaller average particle size. This was demonstrated in Paper II, where the geometric mean diameter of particle mass size distribution of toluene SOA was 47 nm with the TSAR, and 110 nm with the PAM that had longer mean residence time. Despite the different particle size, the total mass concentration was almost equal between the reactors. In a similar manner, Bruns et al. (2015) observed that the Micro smog chamber (MSC) with 8 s residence time produced a particle mass size distribution with a smaller geometric mean diameter than the PAM reactor with 98 s residence time. The smaller particle size may be problematic for the analysis of the particles, as e.g. the chemical speciation of particles with an Aerosol Mass Spectrometer (AMS) is limited to particles larger than ~50 nm vacuum aerodynamic diameter (Peck et al., 2016).

It is possible to decrease the losses of LVOCs by increasing the condensation sink, as seen from the difference between the ambient and the vehicle exhaust case. The condensation sink can be increased by injecting seed aerosol to the reactor (Ahlberg et al., 2019; Lambe et al., 2015). The increased condensation sink from the seed aerosol also inhibits nucleation, which would improve the detection of the particles with
instruments that have low transmission efficiencies for small particles. The use of seed particles, however, complicates the experimental setup and data-analysis.

Even though the LVOC losses are minimized when the residence time is maximized according to the model results in Fig. 3.5, this is not the case for total losses in the OFRs, because the model considers only the fate of LVOCs. In reality, when the residence time is increased, both particle and precursor gas wall losses are increased, as well as the losses of possible intermediate products. Finding an optimal residence time would require a model that combines all the possible losses.

### 3.4 SOA production

The comparison of SOA formed with the TSAR and the PAM reactor was performed in Paper II by injecting an equal concentration of toluene into the reactors and operating the reactors with different OH exposures. The SOA yield as a function of OH exposure for both reactors is shown in Fig. 3.6.

![Figure 3.6](image)

**Figure 3.6** The SOA yield of toluene as a function of OH exposure for the TSAR and the PAM reactor (Paper II).

At OH exposures higher than $3 \cdot 10^{11}$ molec. s cm$^{-3}$, the toluene SOA yield from both reactors agreed well except for the outlier of the TSAR at $6.5 \cdot 10^{11}$ molec. s cm$^{-3}$. At lower OH exposures, the PAM SOA yield was higher than that of the TSAR, but the uncertainty at the low OH exposures was very high. The yields at low OH exposures may differ also because even when the TSAR and the PAM had equal average OH exposure, the distribution of OH exposures was broader in the PAM.
The composition of the produced SOA was studied by comparing the mass spectra of the aerosol particles generated by both reactors. The aerosol was divided into three categories based on its average oxidation state, which was dependent on the OH exposure. The dot product of aerosol mass spectra from the two reactors was above 0.99 when comparing aerosols with similar oxidation state, indicating that the composition was similar since a dot product of unity implies identical spectra.

Based on the similar yields and compositions between the SOA produced in the two reactors, the SOA production in the TSAR is similar to that of the PAM reactor even though their operation principles, residence times and geometry differ. Thus, it is possible to use the TSAR as an alternative for the PAM for experiments where high time resolution is needed.

### 3.5 Further development

In **Paper II** and **Paper IV**, the OH exposure in the TSAR was adjusted by changing the input ozone concentration. After these experiments, the TSAR was upgraded with dimmable UV lamps that allow adjusting the intensity of the UV light remotely, which can be used to adjust the OH exposure as well. The light intensity is monitored with photodiodes (OPT101, Texas Instruments) placed next to each lamp. (Kuittinen et al., 2021) Even though these photodiodes do not detect UV radiation, the signal from visible light correlates well with the UV intensity setting. In addition, the response was improved by shortening the TSAR mixing tube from 50 cm to 15.5 cm, resulting in total 4.6 L volume of the TSAR (originally 5.5 L). This does not affect the LVOC losses because the oxidation reactor dimensions were not changed.
Secondary aerosol research with OFRs started with ambient measurements (Kang et al., 2007). Utilizing an OFR in engine laboratory measurements requires consideration of different aspects compared to ambient measurements because of two distinctive differences: i) the OH-reactive gas concentrations are much higher in exhaust than in ambient air, ii) the amplitude and frequency of changes in gas concentrations are higher. The high concentrations can be addressed with the experimental setup, and the fast variations require high time-resolution from the OFR and the instruments measuring the produced secondary aerosol mass.

The frequent temporal variation is related to changing driving conditions. Figure 4.1 shows the speed profile of the New European Driving Cycle (NEDC) that was used in chassis dynamometer experiments in Papers I, II and IV. The cycle starts with starting the engine, which itself is a transient phenomenon as the engine and after-treatment temperatures are not stable. Soon after the engine start, the vehicle is accelerated to a target speed. The cycle then proceeds with different accelerations, steady speed driving and decelerations, resulting in a changing engine load. Each engine load requires different engine parameters that affect the exhaust composition.

Even more aggressive driving cycles have been introduced to better represent real-world driving, for example the worldwide harmonized light duty test cycle (WLTC) that was used in Paper IV. The maximum acceleration in WLTC is higher than in NEDC, and the speed changes are more frequent. (Marotta et al., 2015)

An ideal experimental set-up for OFR measurement that addresses the specialities in engine exhaust experiments is shown in Fig. 4.2. The essential parts of the set-up include:
1. logging the on-board diagnostics (OBD) to calculate the time-resolved exhaust flow rate,
2. dilution upstream of the OFR to bring the sample to room temperature and to decrease the concentration of OH reactive species,
3. a humidifier to enable OH production in the OFR,
4. measurement of $\text{H}_2\text{O}$ concentration to be used in the photochemical model,
5. measurements of the particle size distribution with high time resolution before and after the OFR to determine the secondary aerosol mass formed in the OFR,
6. an ejector diluter downstream of the OFR to maintain a constant flow rate irrespective of the instrumentation downstream,
7. raw exhaust measurement of OH-reactive gas-phase species to estimate the OH exposure and theoretical SOA, and to estimate the dilution needed,
8. injection and measurement of an OH tracer to determine the OH exposure,
9. an aerosol mass spectrometer to determine the chemical composition of the aerosol, and
10. a measurement of $\text{CO}_2$ to determine the total dilution ratios up- and downstream of the OFR.

Some of the aspects listed above are self-explanatory, but others will be discussed in the following sections mainly by analyzing the results achieved in Paper I. In this paper, the effect of the ethanol content of fuel on primary emissions and secondary aerosol formation potential was studied by using three fuels with different ethanol content, and measuring the diluted exhaust with and without oxidation in
the PAM reactor when driving NEDC on a chassis dynamometer with a flex-fuel gasoline vehicle. The effect of fuel ethanol content on secondary aerosol formation will be discussed in Chapter 5, whereas this chapter concentrates on the general OFR operation in engine exhaust experiments.

### 4.1 Gas measurements and OH exposure

In contrast to Fig. 4.2, there was no on-line OH tracer injection in any of the exhaust experiments in this thesis. Instead, the OH exposures in Papers I-IV were determined with the photochemical model presented in the previous chapter. The model inputs include OFR inlet concentrations of NO\textsubscript{X}, CO, H\textsubscript{2}O and O\textsubscript{3}, and the OH reactivity of VOCs. Concentrations of CO and NO\textsubscript{X} were calculated based on raw exhaust measurements, and O\textsubscript{3} and H\textsubscript{2}O were measured after their injection. The measured inlet O\textsubscript{3} and H\textsubscript{2}O concentrations served also as diagnostics to adjust and monitor the humidifier and ozone generator. Compared to ambient measurements, there can be substantial amounts of NO present in the exhaust that needs to be addressed. The NO reacts fast with O\textsubscript{3} to produce NO\textsubscript{2}. Thus, e.g. 5 ppm of NO in the sample will consume 5 ppm of ozone before the sample enters the reactor, and thus the required ozone injection is higher in exhaust studies than in ambient sampling (Paper II). When the O\textsubscript{3} was measured downstream of the OFR as shown in Fig. 4.2, the outlet O\textsubscript{3} data could be used in model validation, and the inlet O\textsubscript{3} was measured by switching off the UV lamps.
The chemistry between OH and VOCs is not explicitly included in the photochemical model, but the effect of VOCs on the OH exposure is addressed by a single model input, OH reactivity (OHR):

\[
\text{OHR} = \sum_i [\text{VOC}_i] \cdot k_i, \tag{4.1}
\]

where [VOC] is the concentration of a VOC, and \( k \) is its reaction rate constant with the OH radical. The model input of OHR is the OHR at the reactor inlet. Inside the reactor, the OHR will change, because the VOC concentrations decrease due to oxidation, which is incorporated in the model.

In Paper I, the total VOC concentration was measured with a flame ionization detector (FID) in high time resolution. However, the total concentration of VOCs was not sufficient to determine the OH reactivity of the VOCs because of different reaction rate constants between different VOCs and OH radical. Thus, also the VOC composition was measured in Paper I by collecting the exhaust gas into three bags which were analyzed off-line, resulting in average VOC compositions of the three phases of the test cycle.

Figure 4.3, showing the concentrations and OH reactivities of VOCs in the cold start phase of Paper I, demonstrates the importance of measuring the VOC composition. The contribution of methane to the total VOC concentration was highest, but its contribution to the total OH reactivity was negligible. The concentrations of iso-butene and o-xylene were almost equal, but the contribution of iso-butene to the total OH reactivity was more than three times higher than that of o-xylene because of the higher reaction rate constant of iso-butene. Thus, it is necessary to determine the composition of VOCs in addition to total VOC concentration in order to accurately determine the total OH reactivity of the VOCs.

While FID provided the total VOC concentration at high time resolution, the time resolution of the off-line VOC composition measurement was lower. However, it was possible to estimate the OH reactivity in high time resolution by combining the two measurements. For example, the time-dependent toluene concentration (\([\text{toluene}]\)) in Paper I was obtained by

\[
[\text{toluene}](t) = f_{\text{toluene}} [\text{VOC}_{\text{FID}}](t), \tag{4.2}
\]

where \( f_{\text{toluene}} \) is the proportion of toluene based on the off-line measurements and
Figure 4.3 Concentrations and OH reactivities of the measured VOCs during the cold start phase of NEDC in Paper I (E10 fuel).

\[ [\text{VOC}_{\text{FID}}](t) \] is the time-dependent total VOC concentration measured by the FID.

In vehicle exhaust regulations, the emissions of total hydrocarbons must be measured with a FID (e.g., European Union, 2017), so that FID data is typically available in engine exhaust laboratories, whereas the exact VOC composition measurement is not as common. For example, in Paper IV, the OH reactivity was estimated by combining the FID measurement of Paper IV and assuming that the VOC distribution was similar to that measured in Paper I. Similarly, in Paper III, the FID measurement was combined with the VOC distribution reported by Jathar et al. (2017).

In addition to VOCs, the other significant OH reactive gases in engine exhaust are carbon monoxide (CO) and NO\textsubscript{X}, which are also model inputs. For example, in Paper I, the OH reactivity of CO was approximately 590 s\(^{-1}\) in the cold-start phase, which was almost equal to the OHR due to the VOCs. Expressing the NO\textsubscript{X} simply as OHR is not possible because the cyclic reactions of NO\textsubscript{X} in the OFR differ from the VOC oxidation chemistry.

The driving cycle run in Paper I with nominal fuel ethanol content of 10% serves as an example of the OH exposure modeling, and shows how the OH-reactive gases in the exhaust affect the OH exposure. The time series of the OH-reactive gases and the modeled OH exposure during the driving cycle are shown in Fig. 4.4. The model parameters for the PAM reactor used in this experiment were determined in a similar manner as for the TSAR in Paper II (Sect. 3.2).
In Fig. 4.4, the lowest OH exposures were observed in the beginning of the cycle, where the concentrations of OH-reactive gases were highest. However, the OH exposure in the OFR did not recover immediately after the gas concentrations decreased. This was because of the broad residence time distribution of the PAM reactor: some of the gases injected in the OFR in the beginning of the cycle were still present in the reactor after 200s, and this was accounted for in the model.

According to the model results, there was large temporal variation in the OH exposure. In the beginning, the SOA corresponded to atmospheric SOA at a photochemical age of less than 10 hours, whereas in the mid-cycle, the photochemical age was approximately 40 atmospheric hours. Because the SOA yield and e.g. the oxidation state of SOA depend on the OH exposure (Paper II), the SOA formed in the beginning of the cycle was not directly comparable to the mid-cycle SOA.

Based on the high concentration of VOCs in the beginning of the cycle, there was presumably most potential for SOA formation in that section of the driving cycle. However, it is possible that the maximum potential SOA was not observed because the photochemical age in the beginning of the cycle was too low, as the SOA yield of precursor gases is typically lower at low OH exposures (Paper II). Thus, it would be advantageous to improve the experimental set-up so that the variations in OH exposure would be minimized and that the OH exposure would be high enough to observe the maximum potential SOA. This can be achieved by increasing the oxidant concentrations inside the OFR, by using a longer residence time, or by decreasing
the concentrations of OH reactive gases by dilution.

4.2 Dilution

As described in Sect. 4.1, all OH reactive compounds introduced to an OFR will suppress the OH radical concentration in the OFR, and too high a suppression will lead to low OH exposure, and also increased non-tropospheric chemistry (Peng and Jimenez, 2017). The engine exhaust must be diluted, since the concentrations of NO\textsubscript{X}, CO and OH reactive VOCs can be very high in the raw exhaust. In all papers in this thesis, a porous tube diluter (PTD) was used as a primary diluter when measuring engine exhaust in laboratory. This diluter operates with 30°C dilution air, which simultaneously cools down and dilutes the exhaust. This process mimics the atmospheric dilution, where some gas phase compounds present in the hot exhaust will condense or nucleate into the particle phase. (Keskinen and Rönkkö, 2010)

The dilution air should be free of contaminants, so that no secondary aerosol is formed from the dilution air alone. However, it is impossible to reach absolute purity, and thus even with dilution air alone there is typically particle formation in the OFR due to the contamination from sampling lines, OFR walls and the dilution air. This OFR background should be measured and subtracted from the actual secondary mass measurement. In order to frequently measure the OFR background, the diluter should easily allow a flushing mode even when connected to the exhaust source, and the PTD fulfills this requirement.

In Paper I, pure nitrogen from gas cylinders was used as a dilution gas instead of compressed air to ensure purity. However, the oxidation chemistry in the OFR requires oxygen present in the sample, so pure oxygen from a gas cylinder was mixed with the sample upstream of the OFR. Activated carbon filters were used to purify the dilution air in Paper II and Paper IV on-road experiments. In Paper IV laboratory measurements and in Paper V, the zero air was generated with a pressure swing adsorption device.

The PTD dilution ratio (DR) in Paper I was 12, and the dilution ratio caused by mixing of oxygen to the sample was 1.25, so that the total dilution ratio upstream of the OFR was 15. Apparently, this low dilution ratio led to high OH suppression in the beginning of the driving cycle as shown in Fig. 4.4. Increasing the OH concentration inside the OFR e.g. by increasing the UV light intensity would lead to a higher
OH exposure, but there would still be large variation in the OH exposure between different parts of the driving cycle because of high absolute variation in OH-reactive gas concentrations in the exhaust.

By increasing the dilution, the OH exposure increases because of decreased OH reactivity of the sample. When the maximum OH reactivity is limited enough by dilution, the OH exposure will not be very sensitive to the variations in OH reactivity below the maximum level, and thus the differences in OH exposure between different parts of the driving cycle will be smaller despite the high relative variation in OH-reactive gas concentrations. Thus, the extent of dilution was increased in the experiments conducted after Paper I. The choice of the dilution ratio was based on the expected exhaust gas concentrations, the guidelines presented by Peng and Jimenez (2017), and practical considerations. A simplified criterion that the NO\textsubscript{X} concentration should be less than 8 ppm at the OFR inlet for the majority of the time was considered based on the model results of Peng and Jimenez (2017).

In Paper IV, a dilution ratio of approximately 54 was used when measuring a cold-start cycle, but a lower dilution ratio of 18 for hot-start cycles due to lower gas concentrations. Figure 4.5 shows that a high OH exposure was achieved even in the beginning of the cold-start cycle, as opposed to the cold-start cycle in Paper I, although one must note that the OFR in Paper IV was different to that of Paper I. In a similar manner, the dilution ratio in Paper III was adjusted according to the NO\textsubscript{X} concentration in the exhaust: with the most extensive after-treatment setup, the NO\textsubscript{X} concentration was an order of magnitude lower than in the case without after-treatment, and thus the DR was decreased in attempt to keep the OH exposure constant.

While a high dilution ratio is advantageous in terms of close-to-constant OH exposure, it may also be problematic. First, as discussed in Chapter 3, the oxidation products with low vapor pressures may condense either on the OFR walls or on the pre-existing aerosol particles. With a higher dilution ratio, the primary particle surface area decreases, leading to a lower condensation rate onto particles, and thus a higher dilution ratio will lead to higher losses of the low-volatility oxidation products. Another problem with a high dilution ratio is the low signal. With a high dilution ratio, the absolute concentration of secondary aerosol will be low and possibly close to the instrument noise or the OFR background mass. The actual background-subtracted measurement result would be multiplied with a high dilution ratio, am-

40
Figure 4.5  OFR OH exposure during cold-start and hot-start driving cycle with different dilution ratios. Based on Paper I and IV data.

plifying the noise. As a consequence, the dilution ratio needs to be chosen so that the OH exposure will be high and constant enough, while the condensation to particle phase is still the major pathway for the low-volatility oxidation products and the secondary aerosol mass signal is above the instrument detection limit. Often the choice of dilution ratio requires a priori measurement of the raw exhaust gas concentrations with the gas analyzers shown in Fig. 4.2 and modeling the OFR chemistry with different dilution ratios.

4.3 Mass measurement in transient conditions

The OFR experiments are used to estimate the potential secondary aerosol mass, and thus the accurate measurement of particle mass concentration is crucial. The challenge in engine exhaust experiments is the transient operation – the mass should be measured with high time-resolution and with sensitive instruments.

In steady state conditions, the mass measurement can be switched between up- and downstream of the OFR to determine the amount of secondary mass formed in the OFR. In transient conditions, such as driving cycles, the mass measurement should be performed both up- and downstream of the OFR simultaneously or by repeating the driving cycle and changing the sampling point or switching the OFR UV lamps off in between. The mass concentration measured at OFR outlet is the aged mass, i.e., the sum of fresh and secondary mass. To determine the secondary
aerosol mass, one needs to simulate the temporal behaviour of primary mass at OFR outlet by convolving the mass concentration measured at OFR inlet with the OFR transfer function, as illustrated in Fig. 2.3.

In this work, both an aerosol mass spectrometer and particle size distribution measurements were used to estimate the particle mass concentration and composition. When calculating the mass concentration based on the number mobility size distribution, the effective density \( \rho_{\text{eff}} \) as a function of particle size must be known. For each mobility diameter \( D_m \) bin in the distribution, the total mass concentration \( m \) is:

\[
m(D_m) = N(D_m) \frac{\pi}{6} \rho_{\text{eff}}(D_m) D_m^3,
\]

where \( N(D_m) \) is the particle concentration in the size bin with geometric mean mobility diameter of \( D_m \) (Kulkarni et al., 2011).

The mobility number size distribution can be measured accurately with a scanning mobility particle sizer (SMPS), which is a combination of differential mobility analyzer (DMA) and condensation particle counter (CPC) (Wiedensohler et al., 2012). The size-dependent effective density could be measured with a combination of a DMA and an aerosol particle mass analyzer (APM) (Rissler et al., 2013). The SMPS measurement requires approximately two minutes (Wiedensohler et al., 2012) and the DMA-APM measurement tens of minutes (Weingartner et al., 2011). Thus, this method for determining the mass concentration is suitable only for situations where the particle source is stable, but not for transient driving cycles. Instruments measuring the size distribution at high time-resolution are not as accurate as the SMPS because the associated inversion problems involve more uncertainty.

To estimate the effective density with high time resolution, one would need two instruments: one measuring the mobility size distribution and another measuring the aerodynamic size distribution (Ristimäki et al., 2002). Still, combining the two measurements to obtain the effective density, and finally the particle mass concentration, is not straightforward, which will be discussed in Sect. 4.3.4.

The instruments used to determine the composition (SP-AMS), mobility size distribution (EEPS) and aerodynamic size distribution (ELPI) of aerosol in the exhaust measurements will be presented in the three following sections, and the methods to combine the data from different instruments to obtain the mass concentration are discussed in Sect 4.3.4.
4.3.1 Aerosol mass spectrometer

The aerosol mass spectrometer used in this work was a soot-particle aerosol mass spectrometer (SP-AMS; Aerodyne), which measures the particle mass by first evaporating the particles with a laser and a tungsten oven. The evaporated compounds are ionized with electron impact (EI) ionization, and the ions are classified with a time-of-flight chamber and detected with a micro-channel plate (MCP). Thus, the SP-AMS provides chemical classification and ion rate measurement, from which the particle mass concentration can be derived. However, the detection of the particles is limited to approximately 50 nm – 2.5 μm range because of losses in the aerodynamic lens that is used to collimate the particle beam. (Drewnick et al., 2005; Onasch et al., 2012; Peck et al., 2016) While sub-50 nm particles in ambient environment typically contribute little to the total particle mass, in OFR measurements this is not always the case, because of new particle formation inside the OFR (Paper II).

Other sources of uncertainty in determining the particle mass concentration with an SP-AMS are related to collection efficiency (CE) and ionization efficiency. The particles impacted on the tungsten vaporizer may bounce off instead of evaporating, thus decreasing the collection efficiency. The degree of bouncing depends on the particle phase, so that liquid particles are less likely to bounce off than solid particles. The CE can be estimated based on the inorganic content of the particles, which largely defines the particle phase of atmospheric particles. (Middlebrook et al., 2012) On the other hand, laboratory experiments have shown that liquid organic coating can increase the CE of solid inorganic particles (Matthew et al., 2008). Thus, the parametrization for CE by Middlebrook et al. based on atmospheric aerosol measurements cannot be directly applied to laboratory measurements. The phase of organic aerosol originating from combustion may depend on the degree of oxidation or the chemical composition. As a consequence, the CE of fresh exhaust aerosol can be different to that of the exhaust aerosol oxidized in an OFR.

The ionization efficiency includes the efficiency of the ionization process, the degree of vaporization and thermal decomposition in the vaporizer, the adsorption and desorption of the molecules on the ionizer surfaces, the ion transmission efficiency and the detection efficiency of the MCP. Typically, the ionization efficiency (IE) of SP-AMS is calibrated for NO₃⁻ by sampling a known mass concentration of ammonium nitrate (NH₄NO₃) particles. Then, the IEs for NH₄⁺ and SO₄²⁻ are calculated by
assuming that the IEs of these ions are directly proportional to the IE of NO$_3^-$, i.e., their relative ionization efficiencies (RIE) are constant. (Xu et al., 2018) The RIEs of many oxygenated and hydrocarbon-like organic compounds have been shown to be close to a constant value of 1.4 (Jimenez et al., 2016). However, Nault et al. (2023) show that while the value of 1.4 is applicable for aerosol that is not affected by very fresh emissions, for some organic species the RIE can be as high as 11. The species with RIE higher than 1.4 are associated with fresh organic emissions. Thus, the mass concentration of an organic compound could be overestimated in the worst case by a factor higher than 7 if the universal RIE of 1.4 was used instead of the correct one. Based on the observations by Nault et al. (2023), the expected RIE for organic aerosol aged in an OFR would be close to 1.4, while the RIE of the organic aerosol measured directly from tailpipe could be significantly higher.

As a summary, the SP-AMS is useful for estimating the composition of the secondary aerosol formed in the OFR, but since the CE and IE of particles are not necessarily the same for particles up- and downstream of the OFR, and because particles smaller than ~50 nm are not detected, the SP-AMS alone is not sufficient to determine the amount of secondary aerosol mass.

4.3.2 Electrical low-pressure impactor

The electrical low-pressure impactor (ELPI) measures the aerodynamic size distribution of the particles at 1 Hz time resolution. ELPI first charges the particles and then measures the electric current caused by the particles deposited on impactor plates. The impactor plates are placed in series as shown in Fig. 4.6 so that the largest particles are deposited on the uppermost impactor plate, and the average aerodynamic diameter of the particles deposited on each following impactor plate depends on the cut-off diameters of the stage in question and the previous stage. (Keskinen et al., 1992)

The primary result from ELPI measurement is a current distribution as a function of particle aerodynamic diameter. This can be further converted to a particle number distribution when the aerosol charger is characterized and the instrument flow rate is known. (Keskinen et al., 1992) The aerodynamic number distribution can be further converted to mobility number distribution and then to mass distribution with Eq. 4.3 if the effective density of the particles is known.
Figure 4.6  Simplified schematic of the electrical impactor operation principle (a), the current distribution resulting from impaction and secondary collection (b), and the mass distribution based on the current distribution that is not corrected for secondary collection (c). Majority of the current observed in 1 µm collection plate originates from 20 nm particles, which leads to a large error in the mass concentration if the secondary collection is not corrected for.

A proportion of the small particles travelling towards the lowest collection plates will deposit on the upper collection plates due to diffusion and other secondary collection mechanisms, as illustrated in Fig. 4.6 (Virtanen et al., 2001). This creates an artificial current signal to the upper collection plates that correspond to the largest diameters. While the error in the total number concentration due to secondary collection is typically small, it results in a large error when the number distribution is converted to particle mass distribution, since even a low concentration of very large particles contributes significantly to the total mass concentration. Because of this, the ELPI current distribution is typically corrected in the data analysis by an algorithm that shifts the current from the upper stages to the lower stages. The extent of this current transfer can be deduced based on the current detected in the lower stages. (Moisio, 1999)

According to Charvet et al. (2015), even though the effective density is a coefficient...
in Eq. 4.3, the mass concentration calculated from the ELPI current distribution is only weakly dependent on the effective density because it affects also the conversion from aerodynamic diameter to mobility diameter in an opposite way. However, the conclusion by Charvet et al. was based on one experiment and simulations of only four perfectly log-normal particle size distributions with different median diameters, which does not represent the particle population in engine exhaust measurements, especially downstream of an OFR. In addition, they presumably used the original version of ELPI, which uses a trap voltage of 400 V to remove the ions and smallest particles upstream of the impactor. This trap prevents the measurement of particles smaller than approximately 20 nm (Marjamäki et al., 2002), but simultaneously mitigates the high secondary collection related error in mass calculation that could be caused by such small particles. In this work, a trap voltage of 9 V was used because in some cases particles < 20 nm formed in the OFR may contribute significantly to total mass.

Contrary to the result of Charvet et al. (2015), the experiments in this work showed that using a wrong value for particle effective density for ELPI inversion may lead to a large error in particle mass, usually because the OFR generated high number concentration of small (< 20 nm) particles that readily diffused onto upper collection plates and because the low trap voltage did not remove these particles. The secondary collection efficiency depends on the particle mobility diameter, and the effective density is needed when converting the aerodynamic diameter measured by ELPI to the mobility diameter that is used in the secondary collection correction. Thus, using a wrong effective density will either under- or overestimate the current that should be transformed from the upper stages to the lower ones. The underestimation will lead to residual current on the upper stages that results in a serious overestimation of the mass concentration.

Figure 4.7 shows an example of ELPI current distribution without correcting for the secondary collection and with the correction using different effective densities. The current distribution originates from an OFR background measurement during the experiments in Paper IV. It is not expected that the OFR produces particles larger than 1 µm. Thus, the current observed in the collection plates with aerodynamic cut-off that is larger than 1 µm originates from secondary collection of smaller particles. Using the typical unit density for the secondary current correction in Fig. 4.7 did not transfer all current from the upper stages, while using effective density of
1.36 g cm$^{-3}$ resulted in smaller residual current in the three uppermost stages. The mass concentration calculated with unit density was approximately 5 times the mass concentration calculated with the higher effective density when the signal from the three uppermost stages were neglected in both cases. The approach to obtain the correct effective density, and the validity of the result will be discussed further in Sect. 4.3.4.

4.3.3 Engine exhaust particle sizer

The engine exhaust particle sizer (EEPS) measures the mobility size distribution of particles at 0.1 Hz time resolution. EEPS first charges the particles and then collects the particles to different electrometers according to their electrical mobility. (Johnson et al., 2004) Because all particles with diameter larger than $\sim$200 nm have close to constant mobility after they are charged in the EEPS charger, it is not possible to accurately measure particle size distributions with geometric mean diameter larger than 200 nm, even though the reported particle size range for EEPS is 5.6...560 nm (Levin et al., 2015) However, Wang et al. (2016a) and Wang et al. (2016b) showed that when measuring log-normal particle size distributions and using correct inver-
sion matrix, the EEPS reported correct geometric mean diameters (GMD) even for distributions with GMD higher than 200 nm.

The relation between electrical mobility and particle size depends also on the particle morphology, which cannot be determined based on the EEPS measurement alone. For example, fractal-like soot agglomerates originating from combustion require a different inversion matrix than spherical particles. (Wang et al., 2016b) This is an issue in engine exhaust OFR measurements, where the particle population may be a mixture of soot agglomerates, agglomerates coated with secondary mass, and newly formed spherical particles.

Like ELPI, the particle size distribution reported by EEPS is a result of solving an inversion problem where the observed current distribution from a finite number of electrometers is used to estimate the practically continuous particle size distribution. Thus, the mobility size distribution reported by EEPS does not always agree with the size distribution measured with an SMPS (e.g., Arffman et al., 2014).

4.3.4 Synthesis of aerosol mass measurements

In this work, a combination of several instruments was used to determine the particle mass concentration and composition, and comparisons between different instruments were performed to evaluate the validity of the results. In a typical experiment, two identical ELPIs measured the aerodynamic size distribution up- and downstream of the OFR simultaneously, representing fresh and aged aerosol, respectively. An EEPS and a SP-AMS were connected to a three-way valve to enable measurement either up- or downstream of the OFR. In transient driving cycle measurements, two repetitions of the driving cycle were measured to obtain both fresh and aged data for EEPS and SP-AMS.

In Paper I, a high-resolution low-pressure impactor (HRLPI) was placed downstream of the OFR instead of regular ELPI. The measurement principle of HRLPI is similar to ELPI, but the resolution is better while the size range is limited to particles smaller than $\sim 200$ nm (Arffman et al., 2014). The average size distribution measured with HRLPI showed that the majority of particle mass was located in particles within the SP-AMS detection range, so the SP-AMS was used to determine both particle composition and total particle mass concentration.

When comparing the TSAR and PAM reactor in Paper II, it was observed that a
significant fraction of the particle mass formed in the TSAR was located in particles below the SP-AMS cut-off size. Thus, the SP-AMS was only used to determine the particle composition and elemental ratios. The SMPS was used to determine the total mass concentration for experiments with stable precursor gas source, and the EEPS was used for transient measurements. A literature value of SOA effective density was used to convert the number distributions to total particle mass concentration.

The calculation of particle mass concentration in Paper III was more sophisticated: the mass was calculated with Eq. 4.3 after determining the effective density as a function of particle size with an algorithm that resembles the one used by Virtanen et al. (2004). However, Virtanen et al. used unimodal particle size distributions with uniform composition, whereas in Paper III the aerosol comprised of two modes: one originating from nucleation or secondary aerosol formation for which a constant effective density was assumed, and the other mode consisting of soot particles with size-dependent effective density. Thus, the algorithm developed by Virtanen et al. could not be directly used.

The algorithm developed in Paper III proceeds as follows. For size distributions that were observed to be close to unimodal according to EEPS, we fitted a log-normal distribution to the EEPS data. The constant effective density of this distribution was obtained by simulating ELPI currents for the fitted distribution and varying the effective density until the simulated currents agreed well with the measured ELPI current distribution. This was feasible for the aged aerosol measurements (downstream of the OFR). In most fresh aerosol measurements (upstream of the OFR), the number distribution was not dominated by a single mode, so it was not possible to estimate the effective density as described above. Instead, we assumed that the effective density of two unimodal fresh measurement cases represented the effective density for the mode of smaller particle size for all fresh measurements.

After assigning the effective density of the mode of smaller particle size for all cases, the particles that were not part of the fitted mode were assumed to be soot particles that had similar size-dependent effective density than the coated soot particles measured by Pagels et al. (2009). The final size-dependent effective density for the full size distribution was calculated based on the fractions of nucleation mode and soot mode particles for each size bin.

In addition to applying the particle size dependent effective density for the ELPI inversion, the signal from ELPI stages where current was below 2.35% of total current
was neglected, similar to Salo et al. (2019), and the stages representing cut-off sizes of 1.6 µm and 4 µm were ignored. After these actions and applying the particle size dependent effective density to EEPS data as well, the mass concentration determined from the ELPI agreed typically within ±30% with the mass concentration determined from EEPS data, as shown in Fig. 4.8.

![Figure 4.8](image_url)  
**Figure 4.8** The correlation between the mass concentrations measured with EEPS and ELPI when assuming unit density (a) and particle size dependent effective density (b). The results are not multiplied with dilution ratios, and therefore the highest concentrations are observed in the fresh sample. The total dilution ratio of the aged sample was approximately ten times the dilution ratio of the fresh sample. Modified from Paper III.

In some of the cases in Paper III, the majority of the secondary mass was located in small particles below the SP-AMS transmission limit. Thus, the SP-AMS was only used to determine the composition of particles. This was the case in Paper IV as well.

In Paper IV, the absolute mass concentration of particles was inferred from two ELPIs: one measuring upstream of the OFR and one downstream. The issue of uncertainty related to secondary collection of small particles in the upper stages of ELPI was solved by neglecting all signal from stages with cut-point larger than ~600 nm and assuming constant effective density of 1.0 g cm$^{-3}$. This resulted in rather good agreement in mass concentration result between EEPS and ELPI when measuring fresh aerosol (regression slope of 0.9) but higher discrepancy when measuring the aged aerosol downstream of the OFR (regression slope of 3.4).
4.4 Linking SOA formation to driving cycle events

When measuring the secondary aerosol formation of a vehicle during a transient driving cycle, it is necessary to synchronize the mass concentration data with the speed profile and the exhaust volumetric flow rate of the driving cycle for two reasons. First, to recognize which driving conditions are responsible for the highest SOA formation potential, and second, to calculate the SOA production factor (PF) as accurately as possible.

The data analysis of the transient driving cycles measured in Paper I and IV motivated studying the methods to determine the time-resolved SOA formation, as it was observed that the OFR transfer function affects the calculation of SOA PF. The fast response of an OFR has been utilized by Zhang et al. (2023) to determine the dependency of SOA PFs on different driving parameters during a transient cycle, but they did not address the potential error caused by the transfer function.

The SOA PF is defined as

$$\text{SOA PF} = \frac{\text{SOA mass produced}}{\text{fuel consumed}}, \quad (4.4)$$

where the produced SOA mass is measured from a smog chamber or an OFR (Nordin et al., 2013; Zhao et al., 2018). The emission factor (EF) determined for primary emissions is analogous, but the numerator is replaced with the emitted mass. In such case, the emitted mass can be determined by multiplying the time-dependent mass concentration in the tailpipe with time-dependent exhaust flow rate, and integrating the result over the driving cycle or the period of interest. Likewise, the produced SOA between $t_0$ and $t_f$ could be determined by multiplying the SOA mass concentration ([SOA]) measured at OFR outlet with the exhaust flow rate:

$$\text{SOA mass produced} = \int_{t_0}^{t_f} [\text{SOA}] (t) \cdot Q_{exh}(t) \cdot \text{DR} \, dt, \quad (4.5)$$

where $Q_{exh}$ is the exhaust flow rate and DR is the dilution ratio between the OFR and the tailpipe. The consumed fuel in Eq. 4.4 can be calculated based on the measured CO$_2$ emission.

As shown in Eq. 4.5, the SOA PF depends both on the secondary aerosol mass concentration and the exhaust flow rate of the vehicle. If the transfer function of the
OFR is much broader than the timescale of the changes in the exhaust flow rate, it is challenging to link the mass concentration data to a certain exhaust flow rate. For example, in Paper I, the VOC concentration time series differs significantly from the SOA concentration time series shown in Fig. 4.9. The approximately 50s peak of VOCs in the beginning of the cycle resulted in a wide peak of approximately 400s in the OA mass concentration downstream of the OFR. If the elevated mass concentration at e.g. 400s originates from the VOCs emitted in the beginning of the cycle, it would be incorrect to determine the emitted mass at 400s by simply multiplying the mass concentration at 400s with the exhaust flow rate at 400s. In a similar manner, it would be incorrect to assume that the driving condition at 400s is responsible for the secondary mass observed at that time. The extent of signal broadening depends on the OFR transfer function: the narrower the transfer function, the faster the OFR responds to changing concentrations in the tailpipe.

![Graph](image)

**Figure 4.9** Organic aerosol (OA) mass concentration measured downstream of the PAM reactor in Paper I using E10 fuel, and the corresponding VOC concentration upstream of the PAM reactor. The OA concentration shown here is essentially SOA, since the OA concentration measured without the PAM reactor in a separate experiment was negligible. Modified from Paper I.

The effect of the OFR transfer function on the accuracy of the SOA production factor was studied in Paper V by assuming that the momentary SOA formation potential is directly proportional to the gaseous hydrocarbon concentration in the tailpipe, and by evaluating the error in the hydrocarbon emission factor when measured downstream of an OFR. In this analysis, the term ’true SOA PF’ corresponds to the measured hydrocarbon gas emission factor multiplied with a proportionality
constant. The tailpipe hydrocarbon concentration was available for one gasoline vehicle and two NEDCs: one starting with cold engine and after-treatment and the other starting with pre-heated vehicle. Two OFRs with distinct residence time characteristics were used in the analysis: the Dekati oxidation flow reactor (DOFR), similar to the TSAR, represented a narrow transfer function, and a PAM reactor represented a broader transfer function.

Different calculation methods in data analysis were developed in Paper V to account for the OFR delay and signal broadening. The delay caused by the OFR can be corrected by simply shifting the data with a time constant, but it does not help for the signal broadening. To address the broadening, it is possible to normalize the measured SOA emission to the tailpipe CO$_2$ emission (standard method) or the CO$_2$ emission measured downstream of an OFR (OFR CO$_2$ method). In these methods, the SOA emission is calculated by multiplying the delay-corrected SOA concentration with the exhaust flow rate. In the convolution method, the SOA emission is calculated by multiplying with the exhaust flow rate convolved with the OFR transfer function instead, and then normalizing to the CO$_2$ emission determined from CO$_2$ measurement downstream of the OFR. An alternative approach is a deconvolution method, where the high-time resolution SOA formation potential is retrieved by inverse calculation from the SOA concentration measured downstream of an OFR. The suitability of the aforementioned data analysis methods were also studied in Paper V. Two other methods used in the literature were studied as well: the averaging method that is based on average ratio of SOA to CO$_2$, and the CVS method, where the exhaust is sampled from a constant volume sampler (CVS) (Zhang et al., 2023; Zhao et al., 2018).

The study in Paper V showed that it was possible to determine the SOA PF for the two full driving cycles relatively accurately with both reactors when using the OFR CO$_2$ calculation method (within 90% of the true PF with the PAM and within 95% with the DOFR). However, since the advantage of OFRs is the time-resolved SOA measurement, it is of interest to study the error in the OFR-derived SOA PF for shorter segments within the driving cycle.

When dividing the driving cycles into shorter time bins to determine the SOA PFs of different driving conditions, the narrower transfer function of DOFR was advantageous. The driving cycle was divided into 14 s segments and both true SOA PF and OFR PFs were calculated for each segment. The segment duration of 14 s
was chosen because it was the median duration of different driving conditions in the NEDC (accelerations, decelerations, idle periods and constant speed periods). The use of the PAM for these short-duration events resulted in overestimation of the SOA PF and broader variation in the error compared to the DOFR, as shown in Fig. 4.10.

![Figure 4.10](image)

Figure 4.10  Ratios of OFR SOA PFs to true PFs for 14 s bins in hot-start (a) and cold-start (b) NEDC. The x-axis shows alternative calculation methods that convert the OFR measurement into SOA production factors. (Paper V)

Figure 4.10 shows that the deconvolution method resulted in the least error for both reactors. The result was based on the assumption that the SOA mass is measured perfectly without noise and that the OFR residence time is constant. In reality, there is noise present in the mass measurement and slight variation in the residence time due to pressure changes in the sampling line. Thus, the applicability of deconvolution in real measurements should be further studied.

The analysis above was based on only two driving cycles, so the result could not be generalized to all possible situations. When extending the analysis from the two real driving cycles to 10,000 synthetic driving cycles, the error distribution broadened for both OFRs, so that the ratio of the OFR PF to the true PF was between 0.71 and 4.28 for 50% of 14 s segments for the PAM reactor and between 0.81 2.10 for the DOFR (Fig. 4.11d). The OFR CO₂ or convolution method should be used when calculating the full cycle SOA PFs, especially with the PAM reactor (Fig. 4.11b). While the narrow transfer function of the DOFR led to better results than with the PAM reactor, the error in 14 s segments was still very high in the worst cases. If longer time segments are considered, e.g. 400 s (Fig. 4.11c), the DOFR is reliable with range
of true-to-OFR ratios of 0.81...1.40 for 98% of cases while the use of the PAM reactor can lead to more than factor of 2 error (range of 0.54...2.50 for 98% of cases).

Figure 4.11  Ratios of OFR SOA PFs to true PF with different bin widths and calculation methods for synthetic driving cycles. (Paper V)

The inaccuracy due to a broad residence time distribution when determining the PF could be partly avoided by sampling the exhaust downstream of a CVS. In a CVS, the dilution ratio is inversely proportional to the exhaust flow rate, so that there is no need to multiply the measured mass concentration with time-dependent exhaust flow rate in order to obtain the secondary aerosol PF. However, as shown in Paper V, this works only when determining the PF for the full cycle; for the shorter time segments, the use of a CVS did not offer clear advantages.
5 NEW FINDINGS ON VEHICULAR SOA FORMATION

By applying an OFR to engine exhaust studies as described in Chapter 4, it was possible to determine the secondary aerosol formation potential for several gasoline vehicles (Papers I and IV), one diesel vehicle (Paper IV) and one off-road diesel engine (Paper III). In addition, the use of an OFR allowed studying the effect of fuel (Paper I) and exhaust after-treatment (Paper III) on the secondary aerosol formation. The light-duty vehicle experiments were conducted on a chassis dynamometer running transient driving cycles, which enabled studying the effect of driving conditions on the secondary aerosol formation potential.

The experimental setups were all close to the one presented in Chapter 4 (Fig. 4.2), and the instrumentation to measure the mass concentrations and the composition of particles is described in Sect. 4.3. The TSAR was used in Paper IV, and the PAM reactor in Papers I and III.

5.1 Light-duty vehicles

Figure 5.1 gives an overview of the SOA PFs of light-duty vehicles. In addition to the data shown for gasoline direct injection (GDI) and gasoline port fuel injection (PFI) vehicles in the figure, we also tested a Euro 6 diesel vehicle equipped with a DOC and a diesel particulate filter (DPF), and observed that the aged aerosol mass was typically below detection limit (Paper IV), consistent with previous research (Gordon et al., 2014; Platt et al., 2017).

There are four different driving cycles shown in Fig. 5.1: cold NEDC, hot NEDC, hot WLTC and steady driving at 80 km h\(^{-1}\). The NEDC consists of different stable operation points, whereas the WLTC is more transient with frequent accelerations and decelerations and only short segments of constant speed. The speed profiles of
different cycles are shown in Fig. 5.2. The cold-start experiments were preceded by soaking the vehicle overnight, so that the engine and after-treatment systems were at room temperature when starting the cycle, whereas the hot-start driving cycle was preceded by driving at 80 km h\(^{-1}\) so that the engine and after-treatment system were at normal running temperature.

![Figure 5.1](image1)

**Figure 5.1** Production factors of secondary organic aerosol for different light duty vehicles. For Euro 5 GDI, only cold-start NEDC was run, and for the Euro 6 PFI the cold-start cycle is missing. Combined from Paper I and IV results. The Euro 5 secondary aerosol production was determined with the PAM reactor and the Euro 6 production factors were determined with the TSAR.

Figure 5.1 shows that the highest driving condition-dependent effect is seen between cold- and hot-start cycles. The cold surfaces in the cylinder and the cold three-way catalyst lead to a SOA PF that was \(~5\) times higher than that of the hot-start cycles for the Euro 6 GDI. In hot engine operation, the Euro 6 PFI was more sensitive to driving conditions than the Euro 6 GDI, since there was little difference between the NEDC and the WLTC in the GDI SOA PF, whereas the more aggressive WLTC resulted in a higher SOA PF for the PFI than the NEDC. Similarly, the steady driving at 80 km h\(^{-1}\) resulted in the smallest SOA PF for the PFI. There was some dependence on the driving condition for the Euro 6 GDI as well, since the SOA PF at steady driving was higher than that of the hot-start driving cycles.

The time series of aged organic aerosol and fresh aerosol mass for each Euro 6 driving cycle are shown in Fig. 5.2 to further analyze the effect of driving conditions on SOA formation potential.

Figure 5.2a shows that the first 200 s were responsible for the majority of the SOA
formed in the cold-start cycle. This was similar to what was observed for Euro 5 vehicle (Paper I; Fig. 4.9), although the SOA peak in the beginning of the cold-start cycle was delayed and lasted longer for Euro 5, probably because of the broader residence time distribution in the PAM reactor that was used in the Euro 5 experiment.

In the hot-start cycles (Fig. 5.2), different dependencies on the driving conditions could be observed for Euro 6 GDI and PFI: in both driving cycles, the GDI exhaust SOA formation potential was close to constant throughout the cycles, whereas the PFI presented more variability. In the PFI, the peaks in SOA formation potential aligned with the accelerations in the beginning of the cycles and at the end of the driving cycles. In the middle of the NEDC, the PFI SOA formation potential did not show transient behaviour, unlike the WLTC, where the SOA formation potential was changing during the whole cycle. It was not possible to allocate each observed SOA peak to a certain driving condition in the WLTC because the time scale of driving condition changes were faster than the TSAR transfer function standard deviation. However, some of the peaks aligned well with accelerations, and a clear decrease in SOA formation potential was observed at rather steady high-speed driving at $\sim 1200...1300$ s. During that period, the SOA formation potential decreased to a similar level that was observed for most part of the NEDC; otherwise the average SOA formation potential was higher during the WLTC than during the NEDC.

The average compositions of aged aerosol in Fig. 5.2 show that in addition to SOA,
significant secondary inorganic aerosol formation was observed as well. Typically, the highest secondary inorganic aerosol formation occurred in the last part of driving cycles, but for the WLTC with PFI, continuous ammonium nitrate formation was observed.

5.2 Effect of fuel and after-treatment

The effect of fuel on SOA formation potential was studied in Paper I and Paper III. In Paper I, a Euro 5 light-duty GDI flex-fuel vehicle was tested by driving cold-start NEDCs and varying the fuel ethanol content. In Paper III, an off-road diesel engine was fuelled either with fossil diesel or with renewable diesel. In Paper III, also the effect of different after-treatment devices on the SOA formation potential was studied by switching the sampling point in the exhaust line.

5.2.1 Light-duty GDI fuel ethanol content

Figure 5.3 shows the effect of the fuel ethanol content on the Euro 5 light-duty vehicle SOA formation potential. Three fuels were tested: gasoline that contained maximum 10% ethanol (E10), gasoline that contained 70-85% ethanol (E85) and pure ethanol that contained 4.4% water (E100). Increasing the ethanol content decreased the SOA formation potential, so that the SOA PF with E85 fuel was approximately 30% of the SOA PF measured with the E10 fuel. When running the vehicle with E100 fuel, the SOA PF was negative but very close to zero. The negative PF means that the aged OA emission factor was lower than the fresh OA emission factor, which can occur for three reasons. First, the aged and fresh measurements were conducted separately, and although the driving cycles were reproducible, slight variation in the emissions between two driving cycles are possible. Second, the oxidation and increased temperature inside the PAM reactor may lead to evaporation of fresh OA and fragmentation of the evaporated or particle phase organics, and thus to decreased fresh OA. Third, the HRLPI measurements showed that there was new particle formation in the OFR even with the E100 fuel, but the size of most newly formed particles was too small to be detected with the SP-AMS that was used to determine the OA mass concentration.

The gaseous VOCs were also measured in Paper I. Based on the comparison between FID and other analysis methods, it was observed that only 73 m-% of the
Figure 5.3  The measured and predicted Euro 5 GDI SOA PFs over cold-start NEDC as a function of fuel nominal ethanol content. The prediction is based on VOC measurements and laboratory SOA yields in low-NOx and high-NOx conditions. Modified from Paper I by assuming fuel consumption of 7.9 l/100 km and fuel density of 0.75 kg/l.

total hydrocarbons (HCs) were identified. If the missing 27 m-% of HCs contributed to SOA formation significantly, the HC analysis alone would not be sufficient for predicting the SOA PFs, justifying the need for an OFR. In this case, the predictions were sufficient for the E10 fuel because the SOA PF calculated from the VOC results and literature low-NO\textsubscript{X} SOA yields was close to the value determined with the OFR measurement. For the E85 fuel, the observed SOA PF was approximately half of the predicted low-NO\textsubscript{X} case. For the E100 fuel the predicted SOA PF was higher than that of E85 fuel, while the OFR measurement showed no SOA formation. The discrepancy between the measured and predicted PFs for the E100 fuel may result e.g. from CVS artifacts, since the OFR was sampling directly from the tailpipe while the gas samples were drawn from the CVS. Another reason can be that the size of secondary particles from E100 combustion was below the SP-AMS detection range as mentioned earlier.

5.2.2  Effect of fuel and after-treatment for a Diesel engine

The effect of fuel type and different after-treatment options on secondary aerosol formation for a diesel engine are shown in Fig. 5.4. The diesel engine was run in two different load conditions that are labeled as Mode 1 (2100 rpm, 100% load) and Mode 7 (1500 rpm, 50% load) in Fig. 5.4. The main difference between the two fuels
used was their aromatic content, which was 28.6% for the fossil fuel and 3.5% for the renewable fuel. The secondary aerosol formation was measured without any after-treatment (no EAT), with a diesel oxidation catalyst (DOC) only, with a combination of DOC and SCR (DOC+SCR), and with a combination of DOC, DPF and SCR (DOC+DPF+SCR).

![Graph](image)

**Figure 5.4** The effect of fuel and after-treatment on diesel exhaust secondary aerosol formation. Panels (a) and (b) show the total aerosol mass emission factors of fresh and aged aerosol. Panel (c) shows the composition of fresh and aged aerosol measured with SP-AMS for two cases. The secondary aerosol mass PF is the difference between fresh and aged EFs. * indicates a missing data point. Modified from Paper III. The EFs were converted to mg kg\(^{-1}\) fuel by assuming a literature value of 260 g kW\(^{-1}\) h\(^{-1}\) for the fuel consumption (Wang et al., 2011).

Figure 5.4 shows both total aerosol mass EFs, determined from EEPS and ELPI measurements as described in Sect. 4.3, and the composition of the aerosol in two cases determined from SP-AMS measurements. In general, both fresh and aged aerosol emission factors decreased when more after-treatment devices were added. The ef-
fect of fuel was not as clear or consistent, but on average the aged aerosol EFs were lower with the renewable fuel than with the fossil fuel. The reduction in secondary aerosol formation due to renewable fuel was most apparent in Mode 7 when no after-treatment was used.

The compositions measured with the SP-AMS show that the majority of fresh particles consisted of black carbon. The secondary aerosol consisted mostly of SOA, since the fraction of black carbon decreased and the fraction of organics increased. The same was observed for other cases as well that are not shown here. In the case of DOC+SCR shown in Fig. 5.4, also a small fraction of inorganic secondary aerosol was formed.
Secondary aerosol originating from gaseous exhaust emissions worsens the air quality especially in urban areas. The secondary organic aerosol (SOA) formation potential from vehicle exhaust is difficult to estimate because of the diversity of organic species and the complexity of the associated organic chemistry in the atmosphere. Reducing vehicular impact on SOA formation requires reliable measurement methods. This thesis studied the use of an oxidation flow reactor (OFR) from a methodological viewpoint, and the application of the methodology to determine the SOA formation potential in engine exhaust measurements.

Regarding one of the original research questions, the desired characteristics of an OFR used in engine exhaust studies, it was recognized that the OFR transfer function is a key parameter affecting the usability of the OFR. The narrower the transfer function, the more accurately one can link the observed SOA formation to certain driving conditions (Paper II). In addition, the studies in Paper V showed that it is necessary to characterize the transfer function of the OFR in order to determine the time-resolved SOA production factors in a driving cycle. The method developed in Paper V allows calculation of the transfer function based on experimental data.

Another necessary characterization of an OFR is its oxidant generation. Once the rate of oxidant production is experimentally determined, it is possible to model the oxidant exposure of the sample in the OFR in different experimental conditions. The exposure to OH radicals links the OFR result to an atmospheric context. In this work, an OFR developed at Tampere University (TSAR) was characterized in terms of its transfer function and OH exposure (Paper II), and the results were utilized in the data analysis of SOA formation in transient driving cycles (Paper IV).

The characterization is necessary when considering the other research question regarding the design of OFR experiments. It was observed that the extent of exhaust sample dilution is one of the most important parameters to decide in the exhaust experiments, as the concentration of OH-reactive compounds present in the exhaust
affects the OH exposure (Papers I-IV). By utilizing the previously characterized oxidant generation, and prior knowledge of expected concentrations in the raw exhaust, it is possible to pre-determine the required dilution ratio to be used in the experiments through modeling.

Measurement of mass concentration is crucial to determine the SOA formed in an OFR, but the requirement of high time-resolution limits the choice of instruments. It is favorable to include instruments with different operating principles in the measurement set-up because combination of two different instruments was shown to enhance the accuracy of mass concentration measurement (Paper III). Both fresh aerosol (upstream of the OFR) and aged aerosol (downstream of the OFR) may contain other compounds than organics. Thus, the experimental design should include an aerosol mass spectrometer and allow measurement of both fresh and aged aerosol.

The research question on interpreting the OFR measurement results is relevant because the aged aerosol mass concentration measured at the OFR outlet does not directly reflect the temporal behaviour of SOA formation potential in tailpipe. The measured aged organic aerosol (OA) is the sum of primary OA (POA) and SOA. In this work, the SOA concentration was separated by measuring the POA at the OFR inlet and modeling the time-resolved contribution of POA in the aged OA with the help of a previously characterized OFR transfer function (Paper IV).

The SOA concentration measured at the OFR outlet is not enough to determine the amount of SOA formation potential in the atmosphere, because the emission of SOA forming gases depends not only on concentration but also on the exhaust flow rate. Due to the OFR transfer function, the temporal behaviour of SOA concentration at the OFR outlet is different to the behaviour of SOA formation potential in the tailpipe. In this work, it was shown that the transfer function leads to a misalignment between the SOA concentration and the exhaust flow rate, and therefore to error in the calculated time-resolved SOA production factors (Paper V). Different data-analysis methods were developed in Paper V to address the misalignment and minimize the error.

Applying the OFR in engine exhaust studies, the secondary aerosol formation potentials of light-duty vehicles were measured in transient driving cycles. The SOA formation potential was smaller for a gasoline vehicle following a newer emission standard (Euro 6) compared to a Euro 5 gasoline vehicle (Papers I and IV). For a Euro
6 diesel vehicle, the SOA formation potential was negligible compared to gasoline vehicles (Paper IV).

The most notable effect of driving conditions on the SOA formation potential was the engine and exhaust after-treatment temperature, so that the SOA production factor of a cold-started driving cycle was five times that of a hot-started driving cycle (Paper IV). However, even during the hot operation, the SOA formation potential varied between different driving conditions, and the magnitude of changes depended on the engine type (Paper IV). The differences between different driving conditions could be analyzed more quantitatively by using the data processing methods presented in Paper V.

In this work, two different methods to mitigate SOA formation were experimented on: the effect of fuel and the effect of different after-treatment setups. It was observed that increasing the gasoline fuel ethanol content resulted in a decreased SOA formation potential for a gasoline vehicle, and no SOA formation was observed when a 100% ethanol fuel was used (Paper I). Increased after-treatment systems reduced the SOA formation potential of a Diesel engine: without after-treatment, the SOA PF was higher than that of a cold-start cycle of a gasoline vehicle, but by using a combination of all after-treatment systems, the SOA formation potential was below detection limit (Paper III).

As an outlook for future development, one of the main methodological issues observed in this work is the mass concentration measurement downstream of an OFR. The high time-resolution instruments used in this work do not measure the mass concentration directly. The inverse calculation and conversion from particle number concentration to particle mass concentration involve uncertainties. Thus, developing the mass concentration measurement would be beneficial. Another issue is the chemical speciation of the smallest particles, which was not possible with the instrumentation used in this work.

The possibility to use the OFR transfer function to deconvolve the OFR outlet concentration to diminish the effect of OFR residence time distribution was touched upon in Paper V. This method would significantly enhance the time-resolution of SOA formation potential and thus the OFR results could be better linked to different driving conditions. Since the applicability of the deconvolution method in real-world scenarios was not tested in Paper V, this development would be a natural next step.
in OFR methodology in exhaust emission studies.
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Influence of fuel ethanol content on primary emissions and secondary aerosol formation potential for a modern flex-fuel gasoline vehicle

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Abstract. The effect of fuel ethanol content (10, 85 and 100 %) on primary emissions and on subsequent secondary aerosol formation was investigated for a Euro 5 flex-fuel gasoline vehicle. Emissions were characterized during a New European Driving Cycle (NEDC) using a comprehensive set-up of high time-resolution instruments. A detailed chemical composition of the exhaust particulate matter (PM) was studied using a soot particle aerosol mass spectrometer (SP-AMS), and secondary aerosol formation was studied using a potential aerosol mass (PAM) chamber. For the primary gaseous compounds, an increase in total hydrocarbon emissions and a decrease in aromatic BTEX (benzene, toluene, ethylbenzene and xylenes) compounds was observed when the amount of ethanol in the fuel increased. In regard to particles, the largest primary particulate matter concentrations and potential for secondary particle formation was measured for the E10 fuel (10 % ethanol). As the ethanol content of the fuel increased, a significant decrease in the average primary particulate matter concentrations over the NEDC was found. The PM emissions were 0.45, 0.25 and 0.15 mg m⁻³ for E10, E85 and E100, respectively. Similarly, a clear decrease in secondary aerosol formation potential was observed with a larger contribution of ethanol in the fuel. The secondary-to-primary PM ratios were 13.4 and 1.5 for E10 and E85, respectively. For E100, a slight decrease in PM mass was observed after the PAM chamber, indicating that the PM produced by secondary aerosol formation was less than the PM lost through wall losses or the degradation of the primary organic aerosol (POA) in the chamber. For all fuel blends, the formed secondary aerosol consisted mostly of organic compounds. For E10, the contribution of organic compounds containing oxygen increased from 35 %, measured for primary organics, to 62 % after the PAM chamber, whereas for E85, the contribution of organic compounds containing oxygen increased from 42 % (primary) to 57 % (after the PAM chamber), whereas for E100 the amount of oxidized organics remained the same (approximately 62 %) with the PAM chamber when compared to the primary emissions.

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1 Introduction

Vehicular engine emissions are known to degrade air quality in urban areas. Besides gaseous compounds (e.g. CO, NOx, hydrocarbons and volatile organic compounds), vehicle exhaust contains significant amounts of primary particulate matter (PM) (e.g. Mariqu, 2007; Keuken et al., 2013; Gordon et al., 2014a). Primary particulate matter refers to particles directly emitted from the engine, the fuel combustion process or the brakes that have not yet experienced any significant chemical transformation in the atmosphere. Depending on the engine and fuel type, primary exhaust PM emissions from vehicles consist mainly of soot and different fuel and lubricating oil components (Mariqu, 2007; Canagaratna et al., 2010; Karjalainen et al., 2014). In addition to primary PM, burning processes in engine cylinders produce so-called delayed primary aerosol. Delayed primary aerosol includes species such as sulfuric acid which occur in tailpipe conditions in a gaseous phase but will condense or nucleate immediately when the exhaust is cooled and diluted without any significant chemical transformation in the atmosphere (Arnold et al., 2012; Rönnkö et al., 2013; Pirjola et al., 2015). In particle number size distribution, the exhaust PM formed by these different processes is frequently seen in separate modes with different concentrations and particle size ranges (Kittelson, 1998; Rönnkö et al., 2013). In addition to primary emissions, large amounts of secondary particulate matter form after the exhaust gases are released into the atmosphere (Chirico et al., 2010). Secondary particulate matter forms in the atmosphere via gas-to-particle conversion as oxidation processes typically lower the volatility (vapour pressure) of gaseous compounds. The difference between delayed primary and secondary emissions is that secondary emissions form through different transformation processes in the atmosphere, whereas delayed primary emissions form in the cooling process without any significant chemical transformation due to external conditions such as ultraviolet light (UV) or atmospheric oxidants. While a large number of studies have focused on vehicular primary particulate emissions (Giechaskiel et al., 2005; Mariqu, 2007; Lähde et al., 2010; Karjalainen et al., 2014), a relatively limited number of studies have focused on secondary emissions.

Both batch chambers (such as smog chambers) and flow-through chambers combined with modern online composition analysis (e.g. AMS) have been used to study vehicular secondary aerosol emissions in both laboratory and ambient conditions. Smog chambers have been used to study the composition of the primary and secondary PM in the exhaust emissions of gasoline and diesel vehicles, the influence of after-treatment on secondary aerosol formation for diesel vehicles, the fraction of the emissions that forms secondary organic aerosol (SOA) and the relative importance of primary PM emissions versus SOA formation (e.g. Nordin et al., 2013; Platt et al., 2013; Chirico et al., 2014; Gordon et al., 2014a; Presto et al., 2014). A batch chamber is good for detailed oxidation process studies (e.g. Chirico et al., 2014; Suarez-Bertoa et al., 2015), but cannot be used to differentiate the rapidly changing driving conditions during the test driving cycle. Flow-through chambers, such as the potential aerosol mass (PAM) chamber, are designed to simulate secondary aerosol mass formation potential on a nearly real-time basis (Kang et al., 2011; Lambe et al., 2011). Several studies have been recently published for which the PAM chamber was used to study the vehicular emissions from gasoline, diesel and flex-fuel vehicles (e.g. Kroll et al., 2012; Suarez-Bertoa et al., 2015; Karjalainen et al., 2016; Jathar et al., 2017). These studies have shown that secondary particulate emissions from combustion engines mainly consist of organic compounds and ammonium nitrate (Karjalainen et al., 2016; Suarez-Bertoa et al., 2015) and that the secondary PM emissions can be significantly larger than the primary emissions if the conditions favour secondary aerosol formation (Giechaskiel et al., 2005; Chirico et al., 2010; Karjalainen et al., 2016). In gasoline vehicles, the exhaust emissions of secondary aerosol precursors have been shown to depend on driving conditions, fuels and the operation of catalytic converters (Durbin et al., 2007; Mariqu et al., 2012; Gordon et al., 2014b; Karjalainen et al., 2016). Also, previous studies indicate that gasoline vehicles have an impact on secondary aerosol concentrations in urban areas (Nordin et al., 2013; Tkacik et al., 2014; Karjalainen et al., 2016; Suarez-Bertoa et al., 2015). However, the secondary aerosol formation potential and the composition as a function of the driving situation for fuels with different ethanol contents (E10–E100) remain poorly characterized in the literature.

The hydrocarbons of gasoline typically include 4–12 carbon atoms with a boiling range between 30 and 210°C (Owen and Coley, 1995). These may be present in the exhaust gases as unburned hydrocarbons. In addition, exhaust gases contain compounds formed in combustion and originating from engine oil. Lipari (1990) analyzed 137 individual hydrocarbons in C12 in a study with flex-fuel vehicles (FFVs) using the gasoline- and methanol-containing fuels M85 and M100 (85 and 100 % methanol). Toluene, ethylene, propylene, isobutylene, isopentane, pentane, benzene and iso-octane represented 55 % of the total hydrocarbons for gasoline. These gaseous compounds are emitted into the atmosphere directly, or they are evaporated from primary exhaust particles when the exhaust is diluted (Robinson et al., 2007). The oxidation products of organic compounds may contain one or more functional groups, such as alcohol (-OH), aldehyde (-CHO), carboxylic acid (-COOH), nitro (-NO2) and nitrate (-NO3) or organic sulfate (-OSO3). Ambient photochemical reactions take place in the presence of NOx, volatile organic compounds (VOCs), heat and sunlight. Hundreds of different VOC species can participate in thousands of photochemical reactions (Drechsler et al., 2004). The different possible photo-oxidation pathways are also dependent on the conditions. Atmospheric BTEX (BTEX; benzene, toluene, ethylbenzene and xylene; the VOCs typically
found in petroleum derivates) compounds have been suggested to depend on, for example, the prevailing NOx concentrations during the aging process (Andino et al., 1996; Hurley et al., 2001; Sato et al., 2007, 2012).

The European Union has set an obligation that the share of renewable energy should be at least 10 % in the transportation sector by 2020 (Directive 2009/28/EC). Ethanol is the dominant bio-component in transport fuels worldwide. However, in Europe its share in gasoline is limited to 10 % vol, which is equivalent to approximately 6 % energy content (Directive 2009/30/EC). Higher ethanol concentrations up to 85 % vol (E85) can be used in special flex-fuel vehicles. Previous studies have shown that primary PM, CO, HC, NOx and aromatic hydrocarbon emissions are typically lower for the E85 fuel than for gasoline, whereas ethanol, acetaldehyde, formaldehyde and methane emissions increase with the increasing ethanol content of gasoline (Yanowitz et al., 2013; Aakko and Nylund, 2003; Karlsson et al., 2008; Westerholm et al., 2008; Clairiotte et al., 2013). In order to reduce the detrimental effects of pollution caused by vehicles, the emission standards for vehicle PM emissions are tightening globally. However, it must be noted that in the emission standard laboratory tests, the PM mass is measured directly after the tailpipe from a filter sample at an elevated temperature and thus represents mainly primary non-volatile PM emissions. As previous studies have demonstrated (e.g. Chirico et al., 2010; Nordin et al., 2013; Platt et al., 2013; Suarez-Bertoa et al., 2015), the secondary PM emissions formed from gaseous precursors can be significantly larger than primary PM emissions, meaning that the emission limits do not necessarily regulate secondary PM emissions.

In order to properly quantify vehicular engine emissions, the whole transformation chain, from freshly emitted primary PM and gaseous compounds to aged secondary PM measured in urban air quality stations, has to be better understood. The main objective of this study was to investigate primary particulate emissions and simulate the secondary aerosol formation potential of vehicular emissions with an oxidation flow chamber when the ethanol content in the fuel increases. The measurements were carried out with a modern FFV using fuels with three different ethanol contents (10, 85 and 100 %). A comprehensive set of instruments was used for measuring gaseous emissions together with the chemical composition and size distributions of the primary and secondary particles. All measurements were done with high time-resolution instruments and with the PAM flow-through oxidation chamber. The measurement set-up enabled the characterization of the concentration and composition changes during different parts of the driving cycle.

2 Experimental design

2.1 Measurement set-up and sampling

The measurement set-up of this study is described in detail by Karjalainen et al. (2016). The article by Karjalainen et al. (2016) is focused on the primary and secondary emissions of a flex-fuel vehicle using E10 fuel, whereas this article is focused on the influences of the fuel alcohol content on particulate and gaseous emissions and their composition. In this study, the emissions from a flex-fuel passenger car (model year 2011; 1.4 L turbocharged direct-injection spark-ignition (DISI) engine; Euro 5) were measured on a chassis dynamometer at 23 °C using three different fuels (E10, E85 and E100; gasoline with 10, 85 and 100 % alcohol). A schematic figure of the measurement set-up is shown in Fig. S1 in the Supplement. The FFV vehicle was conditioned according to the manufacturer’s instructions, and the adaptation of the car to the new fuel was monitored. Preparation needs and stability issues related to the FFV cars were based on an earlier project (Aakko-Sakska et al., 2014). The driving cycle was the New European Driving Cycle (NEDC; cycle profile shown in Fig. S2). NEDC totals 11.0 km divided into three test phases to study emissions at a cold start and with a warmed-up engine. The first part of the NEDC, the urban driving cycle (UDC), is repeated twice. The first phase, CSUDC, represents urban driving with a cold start (0–391 s; cold start UDC). The second phase, HUDC, represents typical urban driving (392–787 s; hot start UDC). The last phase, EUDC, represents highway driving (788–1180 s; extra-urban driving cycle). NEDCs were run on separate days in order to enable cold start conditions for each fuel. The test fuels were regular commercial E10 (max 10 % ethanol), E85 (85 % ethanol), and E100 (100 % ethanol). To avoid engine problems related to lean ethanol, deionized water was added to E100 to adjust the water content to 4.4 % (m/m). A more detailed description of the car preparation and the driving cycle is given in the Supplement. Particle sampling was conducted with a partial exhaust sampling system (Niziachristos et al., 2004) at the exhaust transfer line. The sampling system consisted of a porous tube diluter (a PTD with a dilution ratio, or DR, of 12), a residence time chamber (2.5 s) and a secondary dilution conducted with a Dekati Diluter (DR = 8; Dekati Ltd., Kangasala, Finland). Regarding particle formation by nucleation, the sampling system mimics the exhaust dilution and nanoparticle formation processes in the atmosphere (Rönkkö et al., 2006; Keskinen and Rönkkö, 2010). Two NEDC tests were conducted for each fuel. While some parameters were monitored similarly during both NEDC cycles (gaseous emissions, particle size distribution of primary exhaust particles; results shown in Table S1), the extensive study for the differences between primary and secondary particle emissions could only be conducted once per fuel.

The PAM chamber was used to evaluate the secondary aerosol formation potential during the NEDC. The PAM
chamber is a small flow-through chamber that is irradiated with ultraviolet light (wavelengths of 185 and 254 nm) to form high concentrations of oxidants (O$_3$, OH and HO$_2$) that can initiate the production of secondary aerosol particles (Kang et al., 2007, 2011; Lambe et al., 2011). High oxidant concentrations (up to 1000-fold to atmosphere, with the same oxidant ratios as in the atmosphere) and high UV lights ensure the fast oxidation of compounds (Kang et al., 2007). The aging as the sample flows through the chamber is shown to represent up to several weeks of aging in the atmosphere (Kang et al., 2011; Ortega et al., 2013). The PAM chamber has been thoroughly characterized in previous studies. These studies include a loss characterization, a comparison to other chamber studies and a comparison on how the SOA formed in a chamber compares to the SOA observed in the ambient atmosphere and the SOA produced in large environmental chambers (e.g. Kang et al., 2007, 2011; Lambe et al., 2011, 2015; Tkacik et al., 2014; Peng et al., 2016). The PAM chamber used in this study is described in detail by Karjalainen et al. (2016). The PAM chamber was installed between the residence time chamber and the secondary dilution unit of the sampling system (Fig. S1). The particle instrumentation was located downstream of the secondary diluter. The sample flow through the PAM chamber was set to 9.75 L min$^{-1}$, resulting in an average residence time of 84 s. The voltage of the two UV lamps was at the maximum value of 190 V. The sample conditions during the test were fairly stable; typically, the relative humidity was 60%, the temperature was 22 °C and the ozone concentration was 6 ppm. All cycles were first run without the PAM chamber to measure the primary emissions and then with the PAM chamber in order to study the formation of secondary particles. The secondary aerosol in the PAM chamber is formed when low volatility vapours condense on aerosols or form new particles. In the PAM chamber, these vapours may also condense onto walls, exit the chamber, or react with OH, which leads to fragmentation and an increase in the saturation vapour pressure. Thus, the potential aerosol mass is underestimated if these chamber-related losses of low volatile vapours are not taken into account. We used the LVOC (low volatility organic compound) fate model presented by Palm et al. (2016) to estimate the losses of the condensing organic vapours in the PAM chamber (model available at https://sites.google.com/site/pamusersmanual/7-pam-photochemistry-model). The free parameters in the model are photon fluxes at 254 and 185 nm of wavelength. Based on the offline calibration, the best-fit values for the photon fluxes are $7.3 \times 10^{14}$ and $1.3 \times 10^{13}$ photons cm$^{-2}$ s$^{-1}$ for the 254 nm wavelength and the 185 nm wavelength, respectively. The inputs for the model are OHR due to VOCs, CO concentration, NO concentration and NO$_2$ concentration. In the model, SO$_2$ is used as a proxy for VOCs; i.e. in the model, the OHR of SO$_2$ equals the input OHR due to VOCs. This method is reasoned to be a realistic approximation by Peng et al. (2015) in terms of estimating the OH exposure.

The input values for the model are obtained from 1 s time resolution measurements of CO, NO, and total hydrocarbons (THC) corrected with the residence time distribution caused by the PAM chamber. The residence time distribution is obtained from the CO$_2$ pulse experiment presented by Lambe et al. (2011). The concentrations of the individual VOCs are estimated using the high time-resolution THC concentration and the distribution of VOCs in different phases of the driving cycle (see Tables S2–S4). The OHR due to VOCs is obtained from these concentrations and the respective reaction constants. The OH exposure in the PAM was modelled at a 20 s time interval for each driving cycle, and the average OH exposures for the cycles are presented in Table 1.

### 2.2 Particle measurements

The Soot Particle Aerosol Mass Spectrometer (SP-AMS; Aerodyne Research Inc., Billerica, MA, USA) was used to measure the chemical composition of the emitted PM. The SP-AMS is a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) with an added laser (intracavity Nd:YAG, 1064 nm) vaporizer. The dual vaporizer system...
enables the real-time measurements of PM mass and the size-resolved chemical composition of submicron non-refractory particulate matter, refractory black carbon and some metals and elements (e.g., Na, Al, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Ba; Carbone et al., 2015). The HR-ToF-AMS is described in detail by Jayne et al. (2000) and DeCarlo et al. (2006), and the design of the SP-AMS is described by Onasch et al. (2012). In the SP-AMS, an aerodynamic lens is used to form a narrow beam of particles that is transmitted into the detection chamber. The particles are vaporized either by a tungsten vaporizer (600 °C) to analyze the non-refractory inorganic species and organics and/or with the laser in order to analyze the refractory black carbon (rBC) and the metals in addition to the inorganics and organics attached to these particles. The vaporized compounds are ionized using an electron impact ionization (70 eV), and the formed ions are guided to the time-of-flight chamber and to the multi-channel plate (MCP) detector. A 5 s averaging time and a dual vaporization system, with both laser and tungsten oven operating, was used in the measurements. Only the V-mode data are used in this study. For the SP-AMS, the 1 s and 1 min 3σ detection limits for submicrometer aerosol are <0.31 µg m⁻³ and <0.03 µg m⁻³, respectively, for all species in the V-mode (DeCarlo et al., 2006; Onasch et al., 2012). The CO₂ concentrations during the measurements were significantly higher (up to 1450 ppm) than the atmospheric values, and thus the CO₂ time series was used to correct the artefact caused by gaseous CO₂.

The collection efficiency (CE) value, representing the fraction of the sampled particle mass that is detected by the MCP detector, is required for the calculation of the aerosol mass concentration measured by the AMS. Previous studies have shown that the collection efficiency of an aerosol mass spectrometer is affected by particle losses (i) during transit through the inlet and the lens, (ii) by particle beam divergence for both tungsten and laser vaporizers and by (iii) the bounce effects from the tungsten vaporizer (Matthew et al., 2008; Huffman et al., 2009; Onasch et al., 2012). Willis et al. (2014) demonstrated that particle morphology also affects the SP-AMS particle beam width, which in turn affects the collection efficiency through the overlap of the particle beam and the laser beam. Similar to Karjalainen et al. (2015), a CE of 1 was used in this study for all SP-AMS data. We acknowledge that it is likely that the collection efficiency might be underestimated for thinly coated primary emissions, whereas the used CE of 1 is likely closer to the correct value for heavily coated spherical secondary aerosol. Also, we note that gasoline soot, consisting of agglomerates with an average diameter below 90 nm, will likely have a low transmission efficiency in the aerodynamic lens and thus might have a lower collection efficiency than regal black, which is typically used for calibration.

The particle number size distributions were measured using a time resolution of 1 Hz with a high-resolution low-pressure cascade impactor (HR-LPI, Dekati Ltd., Finland; Arffman et al., 2014) and an engine exhaust particle sizer (EEPS; TSI Inc., Shoreview, MN, USA; Mirme, 1994; Johnson et al., 2004). The particle number concentration was also measured with an ultrafine condensation particle counter (UCPC; TSI Inc.; model 3025). The UCPC was located downstream of an additional diluter (the operation principle based on the partial filtration of the sample; DR = 42) to ensure that the concentrations to be measured were within its measurement range. All the data shown below have been corrected by a total dilution ratio for each instrument; thus, the presented values represent the tailpipe concentrations.

The particle number size distributions measured by the HR-LPI can be used to estimate how the particle losses in the PAM affect the measured total particle mass. If the measured HR-LPI number size distributions are corrected with the particle loss curve (Fig. S3 in the Supplement), the total mass calculated from the number size distribution increases by 9−16 % depending on the phase of the cycle and the fuel (see Table S5 for details). The masses measured by the SP-AMS cannot be corrected in a similar way, since the SP-AMS did not measure the particle size distributions; different chemical species might also be located in differently sized particles. Thus, the SP-AMS results presented in the following sections are not corrected for the particle losses in the PAM, but we expect that the loss of organic mass due to PAM wall losses to be of a similar order as the loss of total HR-LPI mass.

### 2.3 Gaseous phase composition measurements

The total hydrocarbon (THC) concentrations were measured with a flame ionization detector (FID) developed for the standardized exhaust emission test procedures of cars. The FID detects all carbon-containing compounds, for example carbonyl compounds, in addition to hydrocarbons (HC; Sandström-Dahl et al., 2010; Aakko-Saksa et al., 2014). In addition, samples were collected using Tedlar bags (Sigma-Aldrich, St. Louis, MO, USA) for subsequent analysis by a gas chromatograph (HP 5890 Series II, Al203 KCl PLOT column; Agilent Technologies, Santa Clara, CA, USA; an external standard method). The analyzed hydrocarbons (from C₁ to C₈) included methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p- and o-xylenes.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Average OH exposure (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CSUDC</td>
</tr>
<tr>
<td>E10</td>
<td>6.2</td>
</tr>
<tr>
<td>E85</td>
<td>5.0</td>
</tr>
<tr>
<td>E100</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Table 2. A summary of the measured gaseous compounds, the instruments used and their detection limits.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Sampling</th>
<th>Measured compound</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame ionization detector (FID)</td>
<td>Online</td>
<td>Total hydrocarbon concentration (THC)</td>
<td>3 ppm</td>
</tr>
<tr>
<td>GC (HP 5890 Series II)</td>
<td>Offline collection with Tedlar bag</td>
<td>C_1−C_8 hydrocarbons including methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and n-, p- and o-xylene</td>
<td>0.02 mol m(^{-3}), corresponding to approximately 0.1 mg km(^{-1}) for methane, 0.5 mg km(^{-1}) for 1,3-butadiene and 0.7 mg km(^{-1}) for benzene</td>
</tr>
<tr>
<td>HPLC (Agilent 1260 UV detector; Nova-Pak C18 column)</td>
<td>Offline collection with 2,4-dinitrophenylhydrazone (DNPH) cartridges</td>
<td>Aldehydes; formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal</td>
<td>0.01 mg km(^{-1})</td>
</tr>
<tr>
<td>Fourier transformation infrared (FTIR; Gasmet CR2000)</td>
<td>Online</td>
<td>CO, NO, NO(_x), N(_2O), ammonia, methanol, ethanol, isobutanol, n-butanol, ETBE, formaldehyde and acetaldehyde</td>
<td>2–13 ppm at 1 s measurement interval corresponding to mass concentration of 1–15 mg km(^{-1}) over the European test cycle (Table S6)</td>
</tr>
</tbody>
</table>

Besides HC\(_x\), the selected aldehydes were analyzed by collecting diluted exhaust gas samples from a constant volume sampler (CVS) using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives were extracted with an acetonitrile and water mixture and analyzed using HPLC (high performance liquid chromatography) technology (Agilent Technologies, 1260 UV detector; Nova-Pak C18 column, Waters Corporation, Milford, MA, USA). The aldehydes analyzed include formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal. Ethanol and a number of other compounds were measured online using a Fourier transformation infrared (FTIR) analyzer (Gasmet Technologies, Helsinki, Finland; CR2000). A summary of the measured gaseous compounds, the instruments used and their detection limits is shown in Table 2.

In these measurements, the sum of the hydrocarbons (HC\(_x\)) analyzed by GC, FTIR and HPLC (the sum of HC from the GC + HC portions of ethanol and acetaldehyde) resulted in an HC sum of 15 mg km\(^{-1}\) for E10, 30 mg km\(^{-1}\) for E85 and 216 mg km\(^{-1}\) for E100. The respective THC (FID) results were 22, 30 and 193 mg km\(^{-1}\). This indicated that, on average, 73 % of THCs (FID) were analyzed for E10, and 100 % were analyzed for E85 and E100 by the GC, FTIR and HPLC.

### 3 Results

#### 3.1 Gas phase emissions

The composition of the gas phase emissions was observed to change when the ethanol content of the fuel changed (Fig. 1). As the ethanol content increased, a clearly detectable decrease was observed in both the average NO\(_x\) and ammonia concentrations during the measurement cycle. A decrease in NO\(_x\) with increasing ethanol content is likely caused by decreased flame temperature (Turner et al., 2011). For instance, Turner et al. (2011) reported a decrease of about 20 to 40 % in the NO\(_x\) concentration of a DISI engine when the ethanol content of the fuel changed from 0 to 100 %. Simultaneously, they reported that the NO\(_x\) emissions decreased from 8 to 0.5 g kWh\(^{-1}\), with both values also slightly depending on the ignition timing and strategies. Decreasing trends in the NO\(_x\) emissions have also been observed by Maricq et al. (2012), who reported decreases of 20 % in the NO\(_x\) emissions when the ethanol content increased to values of more than 17 %.

Ammonia is formed in the reactions of the three-way catalyst (TWC; Mejia-Centeno et al., 2007). In theory, ammonia formation is enhanced in slightly rich air-to-fuel ratios at high temperatures (aggressive accelerations) when sufficient HC and NO\(_x\) concentrations are present (Heeb et al., 2006; Mejia-Centeno et al., 2007; Li et al., 2010). Engine-out emissions were not measured here, but it is assumed that the HC and NO\(_x\) concentrations were not a limiting condition for ammonia formation. A decrease in the ammonia emissions for the E85 fuel indicates an enrichment of the conditions in the TWC catalyst when compared with those for the...
E10 fuel. Clairotte et al. (2013) also reported lower ammonia emissions for the E85 fuel than for the E5 fuel. The decreases in both ammonia and NO\textsubscript{x} lead to a decreased contribution to the secondary aerosol formation of ammonium nitrate in the atmosphere when the ethanol content is increased.

The amount of hydrocarbon emissions typically depends on the combustion conditions and exhaust after-treatment by catalytic devices. In this study, the test vehicle was equipped with a three-way catalytic converter with an effectivity which depends on the exhaust temperature and also on the hydrocarbon properties. In this study, the composition of the hydrocarbon emissions was observed to be strongly dependent on the ethanol content; as the ethanol content increased in the fuel, short-chain non-aromatic hydrocarbons and aldehydes increased in the exhaust, while a decreasing trend was observed for all measured aromatic hydrocarbon compounds. Also, as the ethanol content of the fuel increased, the exhaust concentrations of formaldehyde, acetaldehyde, ethanol, methanol, ethene and acetylene increased, whereas the exhaust concentrations of NO\textsubscript{x}, ammonia, PM and BTEX decreased (Fig. 1).

### 3.2 Composition of primary particulate matter emissions

The chemical composition of the primary particulate emissions was observed to vary for different fuels (Fig. 2). The concentration for each chemical component in units of mg km\textsuperscript{-1} for both the primary and secondary emissions is shown in the Supplement (Fig. S4). For E10, approximately half of the primary PM emissions was composed of rBC, and the other half was composed of organics. The contribution of inorganic species (sulfate, nitrate, ammonium and chloride) to PM mass was small (1.2 %). From inorganic ions, sulfate had the highest contribution (47–67 % of the mass of the inorganic ions) for all fuels. A clear decrease in the rBC concentration and its contribution to the total emitted primary PM was observed as the ethanol content of the fuel increased (E10, rBC 53 %; E85, rBC 31 %; E100, rBC 25 %). The contribution of organic matter increased from 46 % (E10) to 65 % for E85 and 75 % for E100. The organics-to-rBC ratios for the E10, E85 and E100 were 0.9, 2.1 and 3.1, respectively.

**Figure 1.** The mean concentrations of the gaseous compounds for different fuels measured during the NEDC.

**Figure 2.** The chemical composition of the primary particulate emissions for E10, E85 and E100 (a). The concentrations of the inorganic ions (b).
Figure 3a shows the elemental ratios (oxygen-to-carbon ratio, O : C; hydrogen-to-carbon ratio, H : C) for the primary organic PM. All values are average values over the NEDC. The average elemental composition and elemental ratios (O : C and H : C) are calculated using a method developed by Aiken et al. (2007) in which the elemental composition is calculated using all measured fragment ions observed in high-resolution mass spectra and H : C and O : C calibration factors derived from laboratory measurements of standard organic molecules. Canagaratna et al. (2015) further developed the elemental analysis to contain a wider range of organic species that are more representative of ambient organic aerosol (OA) species. The improved ambient ratios (IA) calculated according to the method published by Canagaratna et al. (2015) are also shown in Fig. 3. Rather similar O : C values (0.35–0.4) were observed for the primary organic fraction for all fuels. The observed H : C for the primary emissions of E10 and E85 (∼1.5) was slightly lower than for E100 (1.7). The observed elemental ratios are comparable to the elemental ratios typically observed for hydrocarbon-like organic aerosol (HOA), representing traffic emissions in the ambient atmosphere and the elemental ratios observed in chamber studies (Tkacik et al., 2012; Timonen et al., 2013; Carbone et al., 2014; Canagaratna et al., 2015). We note that these O : C ratios measured with an SP-AMS can be slightly higher than the ratios typically measured with an AMS for the primary emissions from gasoline vehicles due to the fact that the SP-AMS also detects the refractory organic species (rCO) incorporated on the structures of black carbon particles (Corbin et al., 2014).

3.3 Composition of secondary aerosol simulated with a PAM chamber

The secondary aerosol formation in the PAM chamber increased the contribution of both organic and inorganic compounds (Fig. 4). For all fuels, most of the particulate matter observed after the PAM chamber (E10, 89%; E85, 79%; E100, 61%) consisted of organic compounds. The organic-to-rBC ratios for the secondary emissions of E10, E85 and E100 were 12, 8.3 and 3.1, respectively. The main inorganic ions observed after the PAM chamber were nitrate, sulfate and ammonium. When the ethanol content of the fuel increased, the relative contribution of the inorganic ions (E10, 4%; E85, 12%; E100, 19%) in the exhaust PM increased after the PAM chamber.

3.3.1 Organic aerosol

Figure 3b shows the average elemental ratios over the NEDC calculated for the organics from the SP-AMS data. For E10, an increase in O : C (from 0.4 to 0.6) and a decrease in H : C (from 1.55 to 1.45) was observed when the PAM chamber was used. In contrast, no change in O : C or H : C was observed for E85 when using the PAM chamber. For E100, a slight decrease in O : C and H : C values was observed when using the PAM chamber. Similar elemental ratios (O : C 0.4–0.7) (Nordin et al., 2013; Suarez-Bertoa et al., 2015) have been observed for the secondary PM emissions in previous batch chamber studies. As shown for the gaseous exhaust compounds (Sect. 3.1), the composition and concentrations of the gaseous precursors change when the ethanol content of the fuel increases, also causing a clear change in the observed secondary aerosol composition and the oxidation state.

Figure 5 shows the contribution of the different organic fragments \( C_n H_m \) (hydrocarbons with \( C_n H_m \)), \( C_n H_O \) (fragments with one oxygen atom \( C_n H_m O^+ \), e.g. CO+ and CHO+) and \( C_n H_m O_2 \) (hydrocarbon compounds containing several oxygen atoms \( C_n H_m O_2 \), e.g. \( CO_2 \)) for all the fuels with and without the PAM. The contribution of \( C_n H_m O^+ \) to organics increased after the oxidation of the exhaust sample in the PAM chamber for all the fuels, whereas the contributions of \( C_n H_m O_2 \) and \( C_n H_m \) decreased. For E10, the contribution of the sum of the oxidized compounds...
(C_{x}H_{y}O and C_{x}H_{y}O_{z}) on exhaust PM increased from 35 to 62 %. For E85, the contribution of the oxidized organic compounds increased from 42 to 57 %, whereas for E100 the contribution of the oxidized organic compounds (approximately 62 %) remained the same with the PAM chamber when compared to the primary emissions. For all fuels, the total contribution of the oxidized compounds (C_{x}H_{y}O. C_{x}H_{y}O_{z}) increased in the PAM chamber when compared to the contribution of hydrocarbons. For E10 and E85, the absolute concentration organic fraction and the total mass concentration of each organic hydrocarbon group increases in the PAM chamber, although the contribution of C_{x}H_{y}O slightly decreases, as shown in Fig. 5. Also, the mass spectra (Figs. S5–S16) show that in the hydrocarbon composition, clear differences can be observed. For E100, both the contributions and concentrations of the different organic families are similar with and without the PAM chamber; however, a change in the composition of these hydrocarbon groups is observed once again.

3.3.2 Refractive black carbon

Refractive black carbon (rBC) is formed during incomplete combustion and is always considered a primary emission; therefore, the rBC concentrations with and without the PAM chamber should be the same. Also, the measurements of the regulated emissions (Table S1) show that the cycles were repeatable and that the rBC concentrations for both cycles should be on the same level. However, some differences in the rBC concentrations were observed when the primary rBC concentrations were compared to the rBC results measured after the PAM chamber. For E85 and E100, a slight decrease in rBC after the PAM chamber was observed (20–30 %). This decrease is likely explained by losses of the primary PM in the chamber. Karjalainen et al. (2016) showed that the particle losses in the PAM chamber were on a similar level as the rBC losses seen here (approximately 8–30 % for particle sizes of 50–400 nm). However, in contrast for E10, a clear increase in rBC (from 240 to 480 µg m^{-3}) was observed when the emissions during the driving cycle were measured with the PAM chamber. In the SP-AMS, rBC is calculated as a sum of the carbon fragments C_{x}^{\bullet}. To explore the observed increase in rBC for E10 after the PAM chamber, the C_{x} frag-
ments before and after the PAM chamber were studied. The increase after the PAM chamber for E10 was seen in all C₃ fragments (Fig. S17; the ratios w PAM and w/o PAM from 1.6 to 2.8 for the C₂–C₅ fragments). The main fragments, C_{2+} and C_{3+}, of the rBC (contributions of 59 and 27 %, respectively) did not have any major interference from isobaric ions (ions observed in the same nominal mass). Larger fragments (e.g., C_{2+}–C_{3+}) had interfering isobaric organic compounds, but their contribution to the total mass was less than 10 %, and the influence of the interference was therefore considered to be insignificant.

There can be several reasons why the SP-AMS detected more rBC in the measurements conducted after the PAM chamber. Firstly, it must be noted that this increase in rBC was only observed for E10, which had the highest secondary aerosol formation potential and thus the largest increase in particle size in the PAM chamber. Previous studies have shown that the soot particles emitted by DISI vehicles are small, typically in the size range of 10–100 nm (Karjalainen et al., 2014). Due to restrictions from the aerodynamic lens, particles smaller than 50 nm are not effectively detected by the SP-AMS. The difference in the rBC results for E10 between the primary emissions and the emissions after the PAM is likely partly explained by the increased mean particle size due to the SOA formation increasing the efficiency through which the particles are detected by the SP-AMS (low volatility compounds formed in the PAM chamber condense on the surfaces of soot particles, increasing their aerodynamic size and thus the detection efficiency of soot and rBC). Also, Willis et al. (2014) demonstrated that the thick coating increases the collection efficiency by changing the particle morphology, thus decreasing the beam divergence and increasing the particle and laser beam overlap. Based on the increased mean particle size and the secondary-to-primary PM ratios, it can be assumed (see also Sect. 3.4 and the size distributions with and without the PAM chamber in Figs. S18 and S19) that for E10 the soot particles are heavily coated with SOA after the PAM chamber, and thus they are more effectively detected by the SP-AMS. In contrast, it has been shown that the dispersion of small and nonspherical particles in the aerodynamic lens inlet of the SP-AMS may cause particles to miss the laser vaporizer (Onasch et al., 2012). Also, based on previous studies, it is known that the black carbon particles emitted by engines are typically agglomerates with irregular shapes and diameters of 10–90 nm (Happonen et al., 2010; Lähde et al., 2010; Karjalainen et al., 2014; Liati et al., 2016), which also might have decreased the detection efficiency of the primary black carbon (soot) particles in this study. We also note that the losses for PM in the PAM chamber are dependent on particle size. Karjalainen et al. (2016) (Fig. S3 in the Supplement) found that the smallest particles incurred the largest losses in PM. However, based on this study, it is not possible to estimate which of the above-mentioned processes is the main reason for the observed rBC increase for E10.

### 3.3.3 Inorganic ions

In comparison to organics, the observed inorganic ion concentrations after the PAM chamber were moderate to low (ion contribution to PM mass for E10, 3.8 %; E85, 12 %; E100, 19 %). The main ions observed after the PAM chamber were sulfate, nitrate and ammonium for all fuels. In this study, the sulfur contents of the E10, E85 and E100 fuels were lower than 10 ppm according to the specifications EN 228, EN 15293 and EN 15376, respectively. These facts strongly suggest that most of the observed sulfate emissions originate from lubricant oil, especially for E100.

### 3.4 Primary-to-secondary particulate matter ratios

Table 3 and Fig. 6 show the submicron PM concentrations for both the primary emissions and for the potential secondary aerosol emissions measured after the PAM chamber averaged over the driving cycle. PM was calculated as a sum of all SP-AMS species in the size range of the SP-AMS (30–800 nm). The PM concentration measured after the PAM chamber is a sum of both the primary particulate emissions and the formed secondary aerosol. The secondary aerosol concentrations were calculated by subtracting the concentrations of the primary particles from the PM concentrations observed after the PAM chamber. It is likely that the wall losses in the chamber will somewhat decrease the primary aerosol concentrations and thus might increase the observed secondary-to-primary PM ratio when the particles go through the PAM chamber. However, based on laboratory PM loss measurements and modelled vapour losses, the influence of these on the results is estimated to be small. Also, one has to note that it is likely that in the PAM chamber new material originating from the gaseous phase will condense on the existing particles, which can change the particle morphology, increase the particle size and change their detection efficiency in the SP-AMS (Onasch et al., 2012; Willis et al., 2014). The observed secondary-to-primary PM ratios are thus also slightly affected.

Large differences in the concentrations between primary and secondary emissions were observed for the different ethanol content fuels. The largest primary and secondary PM concentrations were observed for E10 (0.45 mg m⁻³ for primary PM and 6.7 mg m⁻³ after the PAM chamber). A clear decrease in the primary PM emissions (E85, 0.24 mg m⁻³; E100, 0.15 mg m⁻³) was seen as the ethanol content in the fuel increased. Similar to our results, Maricq et al. (2012) observed a decrease in the primary PM concentrations when the ethanol content of the fuel increased; however, they did not measure the secondary aerosol formation potential. The ethanol content of the fuel also had a large influence on the secondary aerosol formation potential. For E10, the PM measured after the PAM chamber was on average 14.7 times larger than the primary PM. For E85, the secondary PM emissions after the PAM chamber were on average approx-
Figure 5. The contribution of the different organic fragments with and without the PAM chamber. CH refers to hydrocarbons (C\textsubscript{x}H\textsubscript{y}), CHO to fragments with one oxygen atom (C\textsubscript{x}H\textsubscript{y}O\textsuperscript{z}) and CH\textsubscript{O} to compounds containing several oxygen atoms (C\textsubscript{x}H\textsubscript{y}O\textsuperscript{z}, z > 1).

Table 3. The average concentrations of the main chemical compounds of PM (in µg m\textsuperscript{-3} and µg km\textsuperscript{-1} for individual species or mg km\textsuperscript{-1} for total mass) during the NEDC for the primary (w/o PAM) and secondary (PAM) emissions.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Org</th>
<th>NO\textsubscript{3}</th>
<th>SO\textsubscript{4}</th>
<th>NH\textsubscript{4}</th>
<th>CHL</th>
<th>RBC</th>
<th>Total mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µg m\textsuperscript{-3})/ (µg km\textsuperscript{-1})</td>
<td>(µg m\textsuperscript{-3})/ (µg km\textsuperscript{-1})</td>
<td>(µg m\textsuperscript{-3})/ (µg km\textsuperscript{-1})</td>
<td>(µg m\textsuperscript{-3})/ (µg km\textsuperscript{-1})</td>
<td>(µg m\textsuperscript{-3})/ (µg km\textsuperscript{-1})</td>
<td>(µg m\textsuperscript{-3})/ (µg km\textsuperscript{-1})</td>
<td>(mg km\textsuperscript{-1})</td>
</tr>
<tr>
<td>E10 w/o PAM</td>
<td>207.0/158.5</td>
<td>0.8/0.6</td>
<td>3.1/2.4</td>
<td>0.4/0.3</td>
<td>1.3/1.0</td>
<td>239.9/183.7</td>
<td>452.6/0.346</td>
</tr>
<tr>
<td>E10 PAM</td>
<td>5928.3/4538.9</td>
<td>101.1/77.4</td>
<td>119.4/91.4</td>
<td>30.6/23.4</td>
<td>0.9/0.7</td>
<td>481.3/368.5</td>
<td>6661.7/5.10</td>
</tr>
<tr>
<td>E85 w/o PAM</td>
<td>157.3/122.1</td>
<td>0.9/0.7</td>
<td>7.4/5.8</td>
<td>1.3/1.0</td>
<td>1.8/1.4</td>
<td>76.7/59.5</td>
<td>245.4/0.190</td>
</tr>
<tr>
<td>E85 PAM</td>
<td>487.1/378.0</td>
<td>27.2/21.1</td>
<td>5.9/4.6</td>
<td>40.4/31.4</td>
<td>0.6/0.5</td>
<td>58.0/45.0</td>
<td>619.3/0.48</td>
</tr>
<tr>
<td>E100 w/o PAM</td>
<td>112.7/89.7</td>
<td>0.7/0.6</td>
<td>3.6/2.9</td>
<td>0.6/0.5</td>
<td>0.4/0.3</td>
<td>36.3/28.9</td>
<td>154.0/0.123</td>
</tr>
<tr>
<td>E100 w PAM</td>
<td>75.8/60.3</td>
<td>10.8/8.6</td>
<td>7.2/5.7</td>
<td>4.7/3.7</td>
<td>0.9/0.7</td>
<td>24.0/19.1</td>
<td>123.5/0.10</td>
</tr>
</tbody>
</table>

approximately 2 times larger (0.62 mg m\textsuperscript{-3}) than the primary PM emissions. For E100, a slight decrease in PM mass (E100, 0.12 mg m\textsuperscript{-3}) was seen after the PAM chamber, indicating that either the secondary aerosol formation was insignificant (Fig. 2; Table 3) or extensive fragmentation decreased the observed PM mass. Previous studies (e.g. Tkacik et al., 2014) have shown that high OH exposures cause a reduction in the observed mass because of fragmentation, which forms light organic compounds that are more volatile and will evaporate from the particulate phase. In the case of E100, the fragmentation probably did not occur at the beginning of the cycle because of the low OH exposure. The corresponding secondary-to-primary PM ratios were 13.4 and 1.5 for E10 and E85, respectively.

The influence of the fuel composition on secondary aerosol formation has been studied in only a few articles. Suarez-Bertoa et al. (2015) studied the secondary aerosol formation potential of exhaust for vehicles using high ethanol content fuels (E75 and E85). They used a batch chamber in their study and found that the secondary aerosol, mostly secondary organic aerosol (SOA), was on average 3 times higher than the primary emissions for high ethanol content fuels; however, they did not measure the secondary aerosol for a standard low ethanol content fuel or for ethanol fuel (E100). This study shows that the SOA formation from high ethanol content is moderate to low when compared to low ethanol content fuel (E10). Suarez-Bertoa et al. (2015) also concluded that short-chain hydrocarbons could have a role in SOA formation, but not only the aromatic BTEX compounds. We observed an increase in ethanol and total hydrocarbon emissions as the ethanol content of the fuel increased; however, the secondary aerosol formation was observed to be lower for these high ethanol content fuels when compared to low ethanol content fuel (E10). In this study, the concentrations of BTEX and the secondary aerosol formation potential both decreased as the ethanol content of the fuel increased, indicating that the BTEX compounds had a large influence on secondary aerosol formation. This conclusion is in line with the results of Nordin et al. (2013), who found that light aro-
motic precursors (C₆–C₉) were responsible for 60% of the formed SOA in a batch-type smog chamber.

Tkacik et al. (2014) studied the secondary aerosol formation from in-use vehicle emissions using a PAM chamber in a highway tunnel in Pittsburgh. Similar to our study, they observed secondary-to-primary PM ratios of up to 10 inside the tunnel. They also found that the peak in the secondary aerosol production occurred under conditions equivalent to 2–3 days of atmospheric oxidation. With higher OH oxidation values, they saw a decrease in secondary aerosol formation due to continued oxidation fragmenting the carbon compounds. In our experiments, the equivalent atmospheric age was approximately 3.9–6.2 h during the CSUDC, when the most SOA formation took place. Thus, our results are likely on the lower end compared to the maximum secondary aerosol formation potential, but similar OH exposures are reached when compared to SOA formation studies conducted with batch chambers (e.g. Platt et al., 2013; Gordon et al., 2014a; Nordin et al., 2013).

3.5 Predicted SOA formation

The SOA yield is defined as (Odum et al., 1996)

\[ Y = \frac{\Delta M_{SOA}}{\Delta HC} \]

where \( \Delta M_{SOA} \) is the formed secondary organic mass and \( \Delta HC \) is the reacted precursor mass. Using Eq. (1), the measured VOCs and the previously measured yields for these VOCs, we can analyze why the SOA formation potential decreases as the ethanol content in the fuel increases. We assumed that \( \Delta HC \) equals the measured VOC concentration before the PAM. Similarly to Platt et al. (2013), we use low NO\(_x\) yields to get an upper limit for SOA formation. The yields are listed in Table 4. For ethylbenzene, the SOA yield of m-xylene (0.38) was used (Ng et al., 2007; Platt et al., 2013).

According to Volkamer et al., (2009), the acetylene (C₂H₂) SOA yield strongly depends on the liquid water content of the aerosol. Here, a value of 0.1 was assumed. The yields are corrected with corresponding wall-loss correction factors (Table 4) presented by Zhang et al. (2014).

The contribution of each measured VOC to the predicted SOA is shown in the Supplement (Tables S2–S4; Figs. S20–S22). According to the predictions, the decrease in the SOA formation is caused by the decrease in aromatic compounds in the exhaust when the ethanol content in the fuel is increased. The comparison between the predictions and the measurements is shown in Fig. S23. The trends in the predictions generally agree with the measurements except for E100, where the predicted SOA is higher than for E85. The predicted SOA for E100 mostly comes from acetylene (Fig. S22). Thus, the measured SOA formation potential seems to depend rather on the aromatic concentrations than on the acetylene.

3.6 Temporal variation in chemical composition during the driving cycle for primary and secondary emissions

Figure 7 and Figs. S5–S16 in the Supplement show the time series of the organic, inorganic ion and refractory black carbon (rBC) compounds for the primary emissions (panel a) and the emissions after the PAM chamber (panel b). The measurement set-up used and the primary and secondary particulate emissions for E10 have been published previously by Karjalainen et al. (2016). For E10, the largest PM, organic, rBC and nitrate emissions were observed at the beginning of the cycle during the first acceleration (Karjalainen et al., 2015). Occasional increases were also observed during deceleration and engine braking conditions (Rönkkö et al., 2014; Karjalainen et al., 2014). At the end of the cycle, when the speed was above 70 km h\(^{-1}\), the largest inorganic
Table 4. The SOA yields for the different VOCs. The vapour wall-loss correction factors are obtained from Zhang et al. (2014).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (low NOx)</th>
<th>Yield (high NOx)</th>
<th>Correction (low NOx)</th>
<th>Correction (high NOx)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.3</td>
<td>0.13</td>
<td>1.9</td>
<td>1.13</td>
<td>Ng et al. (2007)</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.37</td>
<td>0.28</td>
<td>1.8</td>
<td>1.25</td>
<td>Ng et al. (2007)</td>
</tr>
<tr>
<td>m- and p-Xylene</td>
<td>0.38</td>
<td>0.08</td>
<td>1.8</td>
<td>1.2</td>
<td>Ng et al. (2007)</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>–</td>
<td>0.18</td>
<td>–</td>
<td>–</td>
<td>Sato et al. (2011)</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.1</td>
<td>0.05</td>
<td>–</td>
<td>–</td>
<td>Song et al. (2007)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Volkamer et al. (2009)</td>
</tr>
</tbody>
</table>

Figure 7. The time series of the organic compounds for the primary emissions (a) and for the emissions measured after the PAM chamber (b). The speed profile of the NEDC is also shown. The speed profile and the mass concentration in (b) do not correspond to each other directly due to the broad residence time distribution of the PAM chamber.
Figure 8. The number size distributions for the primary particle emissions. The measurements were made during the driving cycle for all tested fuels, E10 (b), E85 (c) and E100 (d). The driving cycle (NEDC) is shown in (a).

Figure 9. The number size distributions for the secondary particle emissions measured after the exhaust treatment by the PAM. The measurements were made during the driving cycle for all tested fuels, E10 (b), E85 (c) and E100 (d). The driving cycle (NEDC) is shown in (a).

lar increase at the beginning of the cycle was not observed for E100. During the second part of the driving cycle (390–780 s), the secondary organic concentrations stayed at a constant level until the end of the cycle for all fuels. In contrast for E100, the organic PM concentrations measured after the PAM chamber were stable through the cycle with no clear maxima. We note that the speed profile and the mass concentration in Fig. 7b do not correspond to each other directly due to the broad residence time distribution of the PAM chamber (Lambe et al., 2011). Still, the figure shows that the most SOA formation is caused by the cold engine and a cold after-treatment at the beginning of the cycle for both E10 and E85.

The temporal behaviour of the ions during the driving cycle was very different when compared to the organics. After the PAM chamber, elevated nitrate concentrations were observed at the beginning of the cycle after the cold start and at the end of the cycle during the highway driving part. For E85 and E100, the nitrate concentrations measured after the PAM chamber were very low (Figs. S5–S16). Elevated ammonium concentrations were observed at the end of the cycle during the highway driving part for all fuels. The temporal behaviour of the ammonium concentration was observed to be correlated with nitrate, suggesting ammonium nitrate formation. Tkacik et al. (2014) measured high ammonium nitrate concentrations (forming from NO oxidation to HNO$_3$ with subsequent neutralization with NH$_3$) that exceeded the SOA concentrations by a factor of 2 in measurements conducted in a highway tunnel. In this study, the average contribution of inorganic ions to the submicron PM mass was always below 20% and the contribution of ammonium nitrate was always significantly lower when compared to SOA.

3.7 Temporal variation in size distributions of primary and secondary PM

The number size distributions of the emitted particles were measured in order to understand the changes in the particulate phase when the driving conditions, such as speed and
engine load, rapidly change. Figure 8 shows the number size distributions of the primary particles for each fuel as a function of time during the driving cycle. It can be seen that for the E10 fuel, the emissions of particles in the size range of 25–100 nm ($D_p$) were far higher than for E85 and E100. The emissions of the particles in the size range of 25–100 nm depended on the driving condition, so they existed mostly during the acceleration parts of the NEDC. These particles were most likely soot-mode particles consisting of black carbon. This is in line with the chemical composition results, which show that as the ethanol content of the fuel increased, the rBC emissions decreased.

Figure 8 also shows that from the viewpoint of particle number, the role of a cold start remained important with the fuels of high ethanol content. In fact, most of the particulate emissions for E100 are related to the cold start situation. For E10, 37% of the particle number was emitted during the first part of the cycle (CSUDC; 0–391 s; see Karjalainen et al., 2016). For E85 and E100, 43 and 77% of the particle number was emitted during the CSUDC. Although it seems that the mean particle diameter slightly decreased when the ethanol content of the fuel increased, the larger soot-mode particles existed in the exhaust with all fuels. However, the concentration of the soot-mode particles over the NEDC decreased significantly when the amount of ethanol in the fuel was increased. Fuel changes also clearly affected the nanoparticle emissions; the emissions of nanoparticles decreased as the ethanol content of the fuel increased. Still, there were systematic and identifiable sub-10 nm particle emission bursts with all the fuels tested, possibly linking the emissions of the smallest particles to lubricant oil consumption. Overall, we note that the effect of the fuel was larger for soot-mode particles than for nanoparticles. At the end of the cycle (800–1000 s), two distinct peaks were seen for E100. The same peaks were identified in the rBC time series (see Fig. S16 in the Supplement).

The aerosol formation after the engine cold start was also clearly seen in the secondary aerosol concentrations (Fig. 9). The largest particles downstream of the PAM chamber were measured about 100 s after the cycle start when enough diluted exhaust gas was accumulated in the PAM chamber. Under high pollutant concentrations, practically no sub-20 nm particles were measured downstream of the PAM chamber. After around 200 s of the cycle, the vehicle engine and the exhaust system had seemingly warmed up, and the particle size distributions for the rest of the cycle had similar patterns. As the fuel ethanol content increases, the size of the particles during the cold start as well as during the whole cycle decreases. As the ethanol content of the fuel increased, a clear increase in the smallest nanoparticles after the PAM chamber was observed, indicating smaller amounts of condensable vapours to grow particles inside the PAM chamber. Because the nanoparticle emissions were observed to decrease as the ethanol content of the fuel in primary emissions increased, this observation indicates that small particles can also form in the PAM chamber via condensation on particles smaller than the lower size limit of the instruments used or via nucleation. Figure 9 indicates that the average particle size in the exhaust emissions decreased as the ethanol content increased (also shown for the average values in Fig. S18). This will likely affect the efficiency of how these particles are detected with the SP-AMS since the collection efficiency of the aerodynamic lens used in the SP-AMS sharply decreases in particle sizes below 30 nm. It should be taken into account that the size distributions shown here are number size distributions, not mass size distributions.

4 Conclusions
Ethanol is used in fuels to decrease the CO$_2$ emissions of transportation and thus to reduce the adverse climate effects of traffic. This study shows that the use of these fuels produces benefits by decreasing exhaust PM concentrations, thus having a positive influence on air quality. A decrease in PM was seen in both primary emissions and the secondary aerosol formation potential of the exhaust emitted by a modern flex-fuel DISI vehicle.

The composition of the primary emissions was observed to change as the ethanol content of the fuel increased. The relative contribution of rBC to the particulate matter decreased, whereas the contribution of organic particulate matter and inorganic ions increased. The organics-to-rBC ratios for the primary emissions of E10, E85 and E100 were 0.9, 2.1 and 3.1, respectively. For all fuels, most of the particulate matter observed after the PAM chamber consisted of organic compounds (E10, 89%; E85, 79%; E100, 61%). The organics-to-rBC ratios measured after the PAM chamber for E10, E85 and E100 were 12, 8.3 and 3.1, respectively. The role of the cold start was observed to dominate in the secondary aerosol formation for E10 and E85. For E100, no significant increase in the secondary aerosol concentrations due to the cold start was observed. As the ethanol content of the fuel increased, secondary aerosol formation was observed to decrease significantly. For E10, the secondary aerosol formation was significantly larger than the primary PM emissions, with a secondary-to-primary PM ratio of 13.4, whereas for E100 a similar increase in the PM mass after the PAM chamber was not observed.

The large difference in the exhaust secondary aerosol formation between E10 and fuels with a higher ethanol content can be explained by considering the emissions of potential aerosol precursors. The exhaust emissions for low-ethanol fuels contained fewer short-chained organic species (ethanol, formaldehyde, acetaldehyde, methane and ethene) than the exhaust for E85 and E100, but significantly more aromatic compounds (benzene, toluene, ethyl benzene and xylenes). The compounds with a low number of carbon atoms are unlikely to form secondary aerosol due to their high vapour pressure; conversely, aromatic compounds are considered the
most important SOA precursors among the anthropogenic hydrocarbons. Their major atmospheric sink is the reaction with the hydroxyl radical (Andino et al., 1996). It is also known that the SOA yields tend to decrease at high NO\textsubscript{x} concentrations (Henzé et al., 2008). In our case, both the NO\textsubscript{x} concentration and the aromatics concentration decreased when the fuel was changed from E10 to high-ethanol fuels, but the NO\textsubscript{x} decrease was comparatively minor. At the same time, the concentration of OH-reactive, short-chained organic species increased. These factors together cause a strong decrease in the production of aromatic hydrocarbon oxidation products, which in turn decreases the production of secondary organic aerosol. The decrease in aromatic emissions may by itself be enough to explain the SOA reduction, but one should not omit the effect of the added reactivity presented by increased ethanol emissions, for example, which may have an inhibiting effect by taking up a larger fraction of OH (similar to the inhibition caused by isoprene in the case of biogenic SOA formation; see Kiendler-Scharr et al., 2009). The reduction in NO\textsubscript{x} should in principle increase the SOA formation, but the effect is minor compared to the inhibiting causes.

This study shows that the SP-AMS combined with the PAM chamber is an efficient tool to investigate the differences in the secondary aerosol formation potential between vehicle technologies (fuels) with a high time resolution taking the driving conditions into account. However, the study strongly recommends including a high time-resolution particle size distribution measurement parallel with the SP-AMS. In general, the information gathered in this study is important for legislative purposes as well as for modellers and city authorities establishing emission estimates.

**Data availability.** The data used in this publication are available to the community and can be accessed by request to the corresponding author.

**The Supplement related to this article is available online at doi:10.5194/acp-17-5311-2017-supplement.**

**Competing interests.** The authors declare that they have no conflict of interest.

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A new oxidation flow reactor for measuring secondary aerosol formation of rapidly changing emission sources


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A new oxidation flow reactor for measuring secondary aerosol formation of rapidly changing emission sources

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Abstract. Oxidation flow reactors (OFRs) or environmental chambers can be used to estimate secondary aerosol formation potential of different emission sources. Emissions from anthropogenic sources, such as vehicles, often vary on short timescales. For example, to identify the vehicle driving conditions that lead to high potential secondary aerosol emissions, rapid oxidation of exhaust is needed. However, the residence times in environmental chambers and in most oxidation flow reactors are too long to study these transient effects (∼100 s in flow reactors and several hours in environmental chambers). Here, we present a new oxidation flow reactor, TSAR (TUT Secondary Aerosol Reactor), which has a short residence time (∼40 s) and near-laminar flow conditions. These improvements are achieved by reducing the reactor radius and volume. This allows studying, for example, the effect of vehicle driving conditions on the secondary aerosol formation potential of the exhaust. We show that the flow pattern in TSAR is nearly laminar and particle losses are negligible. The secondary organic aerosol (SOA) produced in TSAR has a similar mass spectrum to the SOA produced in the state-of-the-art reactor, PAM (potential aerosol mass). Both reactors produce the same amount of mass, but TSAR has a higher time resolution. We also show that TSAR is capable of measuring the secondary aerosol formation potential of a vehicle during a transient driving cycle and that the fast response of TSAR reveals how different driving conditions affect the amount of formed secondary aerosol. Thus, TSAR can be used to study rapidly changing emission sources, especially the vehicular emissions during transient driving.

1 Introduction

Aerosol particles in the atmosphere affect climate, health and visibility. To reduce these impacts, the sources of aerosol particles have to be resolved. One large but uncertain source of atmospheric aerosol particles is secondary organic aerosol (SOA) formation, which takes place in the atmosphere when particle mass forms as a result of atmospheric oxidation of organic precursor gases. Because the emission of precursor gases and the formation of secondary aerosol mass occur separately, the estimation of SOA sources and their magnitudes is difficult.

The total amount of atmospheric SOA is typically estimated using laboratory data of SOA yields (Y) for known precursors combined with their emission factors and emission profiles (Kanakidou et al., 2005). However, the uncertainty of this method is high. For example, Kanakidou et al. (2005) estimate that approximately 10 % of global SOA is of anthropogenic origin, but measurements by Volkamer et al. (2006) show that the proportion can be as high as 33 %. Thus, more accurate estimations are needed to identify the most important SOA sources in order to identify the most efficient methods to decrease the human impact on aerosol loading in the atmosphere.

An alternative and more direct method for characterizing SOA sources was introduced by Kang et al. (2007). Instead of measuring precursor gases and estimating the amount of potential SOA based on their yields, the SOA formation potential of a single emission source can be measured by oxidiz-
ing the emitted sample and measuring the secondary aerosol mass produced. This method reduces the uncertainty of the SOA emission magnitude, since unknown precursors as well as those whose measurement is difficult are taken into account.

Using this in situ method, the emission oxidation and SOA formation process can be characterized using large environmental chambers, such as the one Platt et al. (2013) used when they measured the SOA potential of a gasoline vehicle. Another alternative is to use an oxidation flow reactor (OFR), in which the sample is oxidized in a similar manner but with higher oxidant concentrations than in large environmental chambers. Such a setup was first introduced by Kang et al. (2007), who also introduced their own oxidation flow reactor, the potential aerosol mass (PAM) chamber, hereafter referred to as PAM. The setup has been used, for example, to estimate the SOA formation potential of in-use vehicle emissions by sampling air from a highway tunnel (Tkacik et al., 2014), to measure the SOA formation from urban ambient air (Ortega et al., 2016) and to measure the SOA formation from ambient pine-forest air (Palm et al., 2016). All these applications show the value of the direct measurement of SOA potential, since the model results either over- or underestimated the SOA formation.

The use of an oxidation flow reactor instead of a large environmental chamber provides multiple advantages: short residence time, higher degree of oxidation and portability (Bruns et al., 2015). The short residence time allows for high-time-resolution measurements of constantly changing situations; for example, the effect of different test parameters on SOA formation can be studied in a shorter time than with environmental chambers. It is also possible to measure SOA formation of a changing emission source in real time because of the short residence time. For example, Karjalainen et al. (2016) measured the time-resolved SOA formation potential of a gasoline vehicle during a transient driving cycle using a PAM reactor. They observed that the secondary aerosol formation potential is highly dependent on the driving conditions. However, the PAM reactor is not ideal for rapidly changing emission sources such as vehicular emissions, since the residence time (~100 s) is still relatively long and the reactor outputs a distribution of different-aged aerosol (Lambe et al., 2011). This limitation is seen, for example, in Karjalainen et al. (2016), where the cold start of a gasoline engine results in an exponentially decaying wide peak of SOA formed in PAM, whereas the concentration of total hydrocarbons measured from the exhaust shows a much more transient behavior. Thus, the SOA formed in PAM cannot be linked directly to the emissions. To address this limitation, the residence time must be shortened. An ultimate example of a short-residence-time flow reactor is the micro-smog chamber (MSC) with a residence time < 10 s (Keller and Burtscher, 2012). However, Bruns et al. (2015) show that the composition and amount of the SOA produced in MSC usually differs from those of the SOA produced in PAM or in an environmental chamber, possibly because of insufficient time for the condensation of oxidant products. Thus, a compromise between PAM and MSC is needed for studying rapidly changing emissions: shorter residence time than in PAM but still long enough to allow the condensation into the aerosol phase.

In this work, we introduce and present a characterization of a new oxidation flow reactor, the TUT Secondary Aerosol Reactor (TSAR). TSAR is better suited to measuring the real-time secondary aerosol formation potential of rapidly changing emission sources than the state-of-the-art oxidation flow reactors, due to its improved flow conditions and shorter residence time. In the following sections, we characterize TSAR by describing its particle losses, oxidant exposure, residence time distribution and laboratory studies on sulfuric acid yield as well as toluene SOA yield and properties, including a comparison between PAM and TSAR. In addition, we present measurements of the secondary aerosol formation of gasoline vehicle emissions during a transient driving cycle. We show that the fast response of TSAR gives valuable information on the effect of the driving condition on secondary aerosol formation potential.

Because of the high oxidant concentrations, high UV light intensity at non-tropospheric wavelengths and limited time for condensation, atmospheric implications cannot be directly drawn from flow reactor measurements. However, there are no methods to measure the absolute secondary aerosol formation potential, because the environmental chambers also have their drawbacks (e.g., limited oxidant exposure and inability to measure time-resolved secondary aerosol potential; Bruns et al., 2015). Despite these artifacts, there is a need for the estimation of secondary aerosol formation from different emission sources. Thus, the flow reactor results also provide useful information, as long as a proper error analysis is made. In this work, we address the flow re-

Figure 1. TSAR layout. The residence time chamber (1), the expansion tube (2), the oxidation reactor (3) and the adjustable outlet (4).
actor related artifacts of TSAR by modeling the vapor losses caused by photolysis and the short residence time.

2 Experimental

2.1 Oxidation flow reactor

TSAR is an OFR254-type oxidation flow reactor, according to terminology proposed by Li et al. (2015), which means that OH radicals are produced from the photolysis of the ozone at 254 nm UV radiation. Its layout is presented in Fig. 1 (see Fig. S3 in the Supplement for a photograph). TSAR consists of a residence time chamber (1 in Fig. 1), an oxidation reactor (3), an ozone generator, three mass flow controllers and an expansion tube (2) that connects the residence time chamber and oxidation reactor. The residence time chamber is a 50 cm × 5 cm ID stainless steel cylinder that ensures the mixing of the sample and makes the sample flow laminar before entering the oxidation reactor. The half-cone angle of the expansion tube is 6°. Two of the mass flow controllers are connected to a vacuum line and are used to control the flow rates inside the residence time chamber and the oxidation reactor. The excess flow from the oxidation reactor is hereafter called “secondary excess flow”. The third mass flow controller adjusts the air flow through the ozone generator. All the components except the residence time chamber and the expansion tube are located inside a single housing, which makes TSAR easy to transfer to different measuring environments.

The TSAR oxidation reactor is a 3.3 L (52 cm × 9 cm inner diameter) quartz glass cylinder surrounded by two constant-power ozone-free low-pressure mercury lamps which emit 254 nm UV light. The lamps are placed outside the reactor to ensure laminar flow and to decrease the surface-to-volume ratio. The UV radiation generates excited oxygen atoms O(1D) from the photolysis of O3. These atoms react with water molecules, producing OH radicals. The O3 needed for this reaction chain is mixed with the sample prior to the residence time chamber. In some cases, the humidity of the sample is too low for sufficient OH generation and additional humidification is required; in these cases, humidified air is also mixed into the sample at this point. If the lamps also emitted 185 nm UV light, no external ozone generator would be needed and TSAR would operate in OFR185 mode. However, we chose the OFR254 mode because of the poor transmission efficiency of the quartz glass for 185 nm light. In addition, the 185 nm light would generate ozone in the room air, which would require special ventilation for the TSAR casing to avoid health issues.

The ozone is generated by an external ozone generator (either model 600 or model 1000, Jelight Company Inc.), which produces ozone from oxygen photolysis by 185 nm UV radiation. The ozone concentration can be adjusted by partially covering the UV lamp (model 600) or by adjusting the flow rate through the generator.

The TSAR outlet is a 10 mm OD stainless steel probe, and its axial position can be adjusted so that the oxidized sample can be measured from any distance from the inlet. From the probe, the sample is led to the measurement devices or to an ejector diluter, which allows the use of multiple instruments while maintaining a constant flow through the oxidation reactor.

2.2 Residence time distribution experiments

The flow conditions inside the TSAR oxidation reactor affect the dynamic transfer function, \( E(t) \), of the reactor for non-reacting compounds. For this case, the measured temporal output concentration, \( C_{\text{out}}(t) \), of TSAR for a measured dynamic input concentration, \( C_{\text{in}}(t) \), is the convolution of the measured input concentration and the transfer function (Fogler, 2006):

\[
C_{\text{out}}(t) = E(t) * C_{\text{in}}(t).
\]  
(1)

The transfer function, \( E(t) \), is also the unit impulse response of the reactor or the residence time distribution following an ideal Dirac delta input impulse. To test the response function, 10 s square pulses of \( \text{CO}_2 \) were injected into TSAR mixed with pressurized air. To keep the shape of the \( \text{CO}_2 \) pulse as sharp as possible, the volumetric flow rate in the residence time chamber was kept at 50 slpm. In the oxidation reactor the flow rate was 5 slpm. \( \text{CO}_2 \) concentration was measured with a \( \text{CO}_2 \) analyzer (Sidor, Sick Maihak). As the same instrument is used for the measurement of both input and output concentrations, its response function is imbedded both in \( C_{\text{in}}(t) \) and \( C_{\text{out}}(t) \).

First, three separate \( \text{CO}_2 \) pulses were measured with sampling at the end of the residence time chamber. The outlet probe was then adjusted to sample at the end of the oxidation reactor, and three separate pulses were again measured. The residence time distributions were determined for different situations: UV lamps and the secondary excess flow were either on or off.

2.3 Particle loss quantification

Particle losses in the oxidation reactor were measured using dioctyl sebacate (DOS) particles with a mobility diameter from 20 to 100 nm and silver particles from 5 to 30 nm. The DOS particles were generated by atomizing a DOS–isopropanol solution. The silver particles were generated with an evaporation–condensation technique (Harra et al., 2012). In these experiments, the volumetric flow in both the residence time chamber and oxidation reactor was 5 slpm. A narrow monodisperse particle size distribution, size-selected using a nanometer differential mobility analyzer (nano-DMA; model 3085, TSI Inc.), was injected into TSAR. The particle number concentration was measured with an ul-
2.4 OH exposure experiments

The length of the duration of atmospheric oxidation that the oxidation flow reactor simulates is determined by exposure of the sample to OH radicals. OH exposure ($OH_{exp}$) is defined as $[OH] \times t$, where $[OH]$ is the mean OH radical concentration in the oxidation reactor and $t$ is the mean residence time of the sample in the reactor. $OH_{exp}$ could be measured indirectly by monitoring the loss of SO$_2$ in the reactor (Lambe et al., 2011). Since the only significant loss of SO$_2$ is due to the reaction with OH radicals (and possible wall loss), the change in SO$_2$ concentration is defined by the following differential equation:

$$\frac{d[SO_2]}{dr} = -k_{OH+SO_2}[OH][SO_2] - k_{wall}[SO_2],$$

(2)

where $[SO_2]$ is the SO$_2$ concentration, $k_{OH+SO_2}$ is the reaction rate constant and $k_{wall}$ is the first-order wall loss for SO$_2$. From this, we get the OH exposure,

$$OH_{exp} = \frac{1}{k_{OH+SO_2}} \ln \frac{[SO_2]_0}{[SO_2]_f},$$

(3)

where $[SO_2]_0$ and $[SO_2]_f$ are the SO$_2$ concentrations of the sample before and after oxidation, respectively. Because both $[SO_2]_0$ and $[SO_2]_f$ are measured after TSAR, the first without UV lights and the latter with UV lights, the wall loss term cancels out from the equation.

Because the OH radicals are produced in a reaction between water molecules and O($^1$D) atoms produced by ozone photolysis, both humidity and ozone concentration affect the amount of OH radicals (Seinfeld and Pandis, 1998). $OH_{exp}$ was measured using three different relative humidities (15, 30 and 45 %) and several different ozone concentrations (0.6–49 ppm). Humidified air, ozone and SO$_2$ diluted with pressurized air were injected into TSAR to determine the OH exposure. First, humidity, ozone concentration and $[SO_2]_0$ were measured after TSAR. Then the UV lamps were turned on, and the concentration rapidly decreased and stabilized to the value of $[SO_2]_f$. SO$_2$ concentration was measured with an AF22M analyzer (Environnement S.A) and ozone with a model 205 analyzer (2B Technologies).

Based on the $OH_{exp}$ measurements, it is possible to deduce the UV actinic flux in TSAR by reproducing the results in a photochemical model and using the photon flux as a fitting parameter. We used the model available in the PAM users manual (PAM_chem_v8 by William Brune, https://sites.google.com/site/pamusersmanual/7-pam-chemistry-model/a-introduction), which is similar to the model described by Li et al. (2015). In this model, the differential equations describing the chemical reactions are solved using Euler’s method (instead of the Runge–Kutta method used in the model by Li et al., 2015).

2.5 Estimating vapor losses and photolysis

In an ideal oxidation flow reactor, all the condensable vapors condense onto particle phase and will be measured as potential secondary aerosol mass. However, there are also other pathways than condensation for the vapors in the flow reactor, and some of them are non-tropospheric. First, the intensity of the UV radiation is higher and the wavelength is smaller than those of the UV radiation in the troposphere. This can cause unrealistic photolysis of the precursor vapors and the secondary aerosol formed (Peng et al., 2016).

Second, the residence time in the flow reactor is small, and thus the condensable vapors may exit the reactor before condensing onto particle phase. Third, because of high oxidant concentrations, the timescale of condensation can be much higher than the timescale of oxidation, leading to fragmentation of oxidized vapor molecules before they have condensed. This is of concern especially in TSAR, where the short residence time requires higher oxidant concentrations than, for example, the PAM chamber. Fourth, the surface-area-to-volume ratio is high in the flow reactor, and thus the vapor wall losses may be significant (Palm et al., 2016).

2.5.1 Photolysis

Peng et al. (2016) have studied the losses of precursor gases and SOA due to photolysis in flow reactors. In their study, they show that the photolysis rate of SOA in oxidation flow reactors is uncertain because of the lack of knowledge on quantum yields. In any case, the loss of SOA due to photolysis is much smaller in oxidation flow reactors than in the troposphere at equivalent OH exposure. However, the photolytic losses of precursor gases in oxidation flow reactors can be higher than in the troposphere.

The photolytic loss is significant if the photolysis rate is high relative to reaction rate with OH radicals. We define relative photolytic loss as follows:

$$\text{relative photolytic loss} = \frac{\text{photolysis rate at 254 nm}}{\text{photolysis rate at 254 nm} + \text{reaction rate with OH}}.$$  

(4)

A relative photolytic loss of zero means that all the loss of the precursor gas is due to reaction with OH, and the relative photolytic loss of unity means that the photolysis is the only pathway of loss for the precursor gas. As Peng et al. (2016) show, the relative photolytic loss depends on the ratio of photon exposure to OH exposure ($F(254)/OH_{exp}$), the reaction rate constant between the precursor molecule and OH radicals, the absorption cross section of the molecule and the quantum yield of the photolysis reaction. The OH exposure in TSAR depends on water vapor concentration ($H_2O$), ozone concentration and external OH reactivity of the sample...
(OHR\textsubscript{ext} = \[X\] \cdot k_{\text{OH} + X}, where \([X]\) is the precursor gas concentration and \(k_{\text{OH} + X}\) is the reaction rate constant between this gas molecule and OH radicals). The photon flux in TSAR is constant.

According to the modeling results by Peng et al. (2016), the relative photolytic loss of studied precursor gases is less than 60 % in most cases in OFR254, even at “riskier” conditions ([H\textsubscript{2}O] < 0.1 % or OHR\textsubscript{ext} > 200 s\textsuperscript{-1}). For most of the studied precursor gases, the relative photolytic loss is less than 20 % in most cases. In all the studied “safer” conditions ([H\textsubscript{2}O] > 0.5 % and OHR\textsubscript{ext} < 50 s\textsuperscript{-1}), the relative photolytic loss is less than 30 % for all the precursor gases. However, these are only the upper limits for the relative photolytic losses because of the assumption of a unity quantum yield. The relative photolytic losses in TSAR are discussed in Sect. 3.4.1.

2.5.2 Vapor losses

We study the fate of condensable vapors (other than photolysis) in TSAR using a similar approach to Palm et al. (2016). We start with a low-volatility organic compound (LVOC, saturation vapor concentration \(\sim 0\)) which can condense on particle phase, condense on the reactor walls, form new particles via nucleation, react with OH radicals or exit the reactor before condensing. Thus, the concentration of the LVOC is described with the following differential equation:

\[
\frac{dC_0}{dr} = -4\pi \cdot D \cdot CS \cdot C_0 - k_w \cdot C_0 - k_{\text{OH}} \cdot C_0 \cdot [OH] - n \cdot J(C_0),
\]

where \(C_0\) is the concentration of the initial LVOC, \(D\) is the diffusion coefficient of the LVOC, CS is the condensational sink, \(k_w\) is the first-order rate coefficient for wall loss, \(k_{\text{OH}}\) is the reaction rate constant between OH radicals and the LVOC, \([OH]\) is the mean concentration of OH radicals in the reactor, \(n\) is the number of molecules in a nucleated particle and \(J\) is the nucleation rate, which depends on the vapor concentration. We assume that the reaction with OH radicals produces another LVOC (\(C_1\)) which has the same loss terms as \(C_0\). Thus,

\[
\frac{dC_1}{dr} = k_{\text{OH}} \cdot C_0 \cdot [OH] - 4\pi \cdot D \cdot CS \cdot C_1 - k_w \cdot C_1 - k_{\text{OH}} \cdot C_1 \cdot [OH] - n \cdot J(C_1),
\]

and, more generally,

\[
\frac{dC_n}{dr} = k_{\text{OH}} \cdot C_{n-1} \cdot [OH] - 4\pi \cdot D \cdot CS \cdot C_n - k_w \cdot C_n - k_{\text{OH}} \cdot C_n \cdot [OH] - n \cdot J(C_n),
\]

assuming that \(k_{\text{OH}}, D, CS, k_w, n\) and \(J\) are equal for all oxidation products.

At some point, the reaction between LVOCs and OH radicals leads to fragmentation and produces high-volatility compounds which cannot condense onto particle phase. Palm et al. (2016) assumed that the fifth oxidation reaction produces fragmented compounds. In addition, the heterogeneous OH reaction on the particle surface may result in fragmentation (Kroll et al., 2009). Thus, assuming that the molecule fragments into two parts, we get

\[
\frac{dC_5}{dr} = 2 \cdot k_{\text{OH}} \cdot C_4 \cdot [OH] + 2 \cdot R_{\text{heterogeneous}},
\]

where \(C_5\) is the mass concentration of fragmented, high-volatility compounds and \(R_{\text{heterogeneous}}\) is the rate of heterogeneous fragmentation. Based on these equations, the molecule flux to the aerosol phase is

\[
\frac{dC_{\text{aer}}}{dr} = 4\pi \cdot D \cdot CS \cdot (C_0 + C_1 + C_2 + C_3 + C_4) - R_{\text{heterogeneous}},
\]

and the mass flux to the reactor walls is

\[
\frac{dC_w}{dr} = k_w \cdot (C_0 + C_1 + C_2 + C_3 + C_4).
\]

The fate of LVOCs is obtained by solving the differential equations using the MATLAB (Release 2016a, The MathWorks, Inc., United States) ode45 numerical solver. The fraction of LVOCs lost to walls is then

\[
F_{\text{wall}} = \frac{C_{w}(t_{\text{res}})}{C_0(0)},
\]

where \(t_{\text{res}}\) is the residence time of the reactor and \(C_0(0)\) is the initial LVOC concentration. Similarly, the fraction of LVOCs condensed onto aerosol is

\[
F_{\text{aer}} = \frac{C_{\text{aer}}(t_{\text{res}})}{C_0(0)},
\]

the fragmented fraction is

\[
F_{\text{frag}} = \frac{1}{2} \cdot \frac{C_5(t_{\text{res}})}{C_0(0)}.
\]

and, finally, the fraction of LVOCs that exits the reactor before condensing is

\[
F_{\text{exit}} = \frac{C_0(t_{\text{res}}) + C_1(t_{\text{res}}) + C_2(t_{\text{res}}) + C_3(t_{\text{res}}) + C_4(t_{\text{res}})}{C_0(0)}. \tag{14}
\]

Looking at Eqs. (5)–(8), the OH radical concentration affects the relative amount of LVOCs that is fragmented. The shorter the residence time, the higher the \([OH]\) must be to attain a certain OH exposure. Thus, shortening the residence time results in an increase in fragmented LVOCs. However, the fragmented fraction depends on the timescales of the other loss terms, namely condensation on reactor walls and on aerosol that in turn depends on the condensational sink. Using this approach, the dependence of LVOC fate on residence time and the condensational sink is studied in Sect. 3.4.2.
We tested the model validity by oxidizing SO₂ in TSAR. SO₂ oxidation is a simple example of secondary aerosol formation. SO₂ reacts with OH radicals to produce sulfuric acid (H₂SO₄) vapor which rapidly enters the particle phase by nucleation and condensation (Sihto et al., 2006). The mass formed by oxidation of SO₂ can be theoretically calculated from the SO₂ loss, and thus comparing the measured mass formation to the theoretical prediction can be used to estimate the capability of TSAR to simulate full atmospheric oxidation. Should the measured mass be substantially smaller than the theoretical, we would assume that there were significant losses of sulfuric acid vapor inside TSAR. The observed losses can then be compared to the losses predicted by Eqs. (11)–(14).

The sulfuric acid yield was measured by injecting humidified air, ozone and SO₂ diluted with pressurized air into TSAR. The relative humidity and SO₂ was measured straight after TSAR, whereas ozone concentration and the particle size distribution were measured after an ejector diluter (Dekati Ltd.). The dilution ratio was determined by measuring the sample flow rate and the dilution air flow rate. The particle size distribution was measured with a nanometer scanning mobility particle sizer (nano-SMPS), which is a combination of a nano-DMA (model 3085, TSI Inc.) and a UCPC (model 3025, TSI Inc.).

In addition to sulfuric acid, the measured particles also contain water. The sulfuric acid mass was calculated from Eq. (15) (Lambe et al., 2011):

\[
m_{\text{H}_2\text{SO}_4} = x_{\text{H}_2\text{SO}_4} \times V \times \rho.
\] (15)

where \(x_{\text{H}_2\text{SO}_4}\) is the mass fraction of sulfuric acid in the particle phase, \(V\) is the volume calculated from the nano-SMPS particle size distribution and \(\rho\) is the density of the particle phase. Both the mass fraction and the density were calculated as a function of relative humidity based on Seinfeld and Pandis (1998). In the calculations, relative humidity after the dilution is used, assuming fast equilibration of the sulfuric acid particles.

The theoretical (maximum) sulfuric acid mass was calculated by multiplying the loss of SO₂ by the molar mass of a sulfuric acid molecule. Thus, the loss of 1 ppb of SO₂ produces 4.03 µg m⁻³ of sulfuric acid aerosol, assuming also that all the sulfuric acid condenses into the particle phase.

### 2.6 Organic precursor experiments

A key application of TSAR is to estimate the amount of secondary aerosol mass formed from engine exhaust emissions, which in turn contains a complex mixture of organic and inorganic gases. Therefore, the SO₂ oxidation experiment alone is not a representative example of engine exhaust oxidation, because the oxidation pathways of organic compounds are far more complex. The ability of TSAR to form SOA was verified by measuring the toluene SOA obtained by TSAR and PAM simultaneously. Previous studies have shown that the amount and properties of the SOA produced in PAM are similar to those of the SOA formed in smog chambers (Bruns et al., 2015; Lambe et al., 2015).

The organic precursor gas in this experiment was toluene, because it is present in engine exhaust gas (Peng et al., 2012; Wang et al., 2013). In addition, toluene is globally one of the most emitted anthropogenic SOA precursors (Kanakidou et al., 2005). Gas-phase toluene was produced using a permeation oven with a toluene permeation tube (KIN-TEK Analytical, Inc.), and its output rate \(\left( M_{\text{toluene}} \right)\) was measured by weighing the change in its mass. The concentration of toluene in the reactors is

\[
C_{\text{toluene}} = \frac{M_{\text{toluene}}}{Q_{\text{tot}}},
\] (16)

where \(Q_{\text{tot}}\) is the total sample flow through the reactors (10 slpm).

The gas-phase toluene was mixed with ozone and humidified air before it was fed to the TSAR residence time chamber. After the residence time chamber, 5 slpm of the sample was introduced into the TSAR oxidation reactor and 5 slpm to PAM. A four-way valve was installed after the reactors, so that the instruments were sampling from one reactor while the sample from the other reactor was drawn to the vacuum line through a mass flow controller.

PAM was used in OFR185 mode (Li et al., 2015), and thus the external ozone generator was switched off when the instruments were sampling from PAM. PAM was operated in OFR185 mode instead of OFR254 mode because the OFR185 mode is used in previous engine exhaust studies (Karjalainen et al., 2016; Timonen et al., 2016; Tkacik et al., 2014). Similar results from the two reactors would then indicate that TSAR operating in OFR254 mode could be used in similar applications as PAM in OFR185 mode. The OH exp of the reactors was varied by varying the light intensity in PAM and the amount of injected ozone in TSAR. The PAM OH exp as a function of output ozone concentration was measured offline in a similar way as for TSAR (Sect. 2.4) at 28 % relative humidity. The PAM reactor OH exp as a function of output ozone concentration is shown in Fig. S1.

The particle size distribution downstream of TSAR and PAM was measured with an SMPS (model 3081 DMA and

<table>
<thead>
<tr>
<th>Cycle 1</th>
<th>Cycle 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (s)</td>
<td>Injection</td>
</tr>
<tr>
<td>0</td>
<td>on</td>
</tr>
<tr>
<td>10</td>
<td>off</td>
</tr>
<tr>
<td>20</td>
<td>on</td>
</tr>
<tr>
<td>25</td>
<td>off</td>
</tr>
<tr>
<td>40</td>
<td>on</td>
</tr>
<tr>
<td>50</td>
<td>off</td>
</tr>
</tbody>
</table>
model 3775 CPC, TSI Inc.) and also with an engine exhaust particle sizer (EEPS; TSI Inc.; Johnson et al., 2004) in some experiments. The EEPS sample had to be diluted with a mass flow controller to keep the total flow rate through the chambers at 5 slpm. Aerosol chemical composition and size distribution were measured with an SP-AMS (soot particle-aerosol mass spectrometer; Onasch et al., 2012). In addition, the ozone concentration (model 205, 2B Technologies) and relative humidity (Hygroclip SC05, Rotronic AG) were measured.

Two different toluene experiments were run: steady-state and pulse experiments. In the steady-state experiments, a constant concentration of toluene was continuously injected into the reactors. Based on these experiments, the toluene SOA yield was determined for both reactors.

The pulse experiments were performed to study the reactors’ behavior during rapid changes of toluene concentration. In these experiments, toluene was injected through a three-way solenoid valve to either the reactors or to the excess line. Three different pulse experiments were performed: a single 10 s pulse and two different cycles with several pulses (cycle 1 and cycle 2). In cycle 1, three toluene pulses were injected with intervals of 10 and 15 s, whereas cycle 2 had intervals of 40 and 50 s. The cycles are described in detail in Table 1.

In both cycles, the total toluene injection time was 25 s, therefore, the total amount of injected toluene was equal. EEPS was used to measure the particle number distribution of produced SOA at a time resolution of 1 s. For the pulse experiments, the flow rate through each reactor was 5 slpm. Since PAM is approximately 4 times bigger than TSAR in volume, a 10 slpm flow rate was also used for PAM to compare the reactors at more similar mean-plug-flow residence times. In this case, TSAR was bypassed to keep the total flow at 10 slpm.

The SOA yield \(Y\) is defined as the produced organic aerosol mass \(\Delta M\) per reacted precursor mass \(\Delta \text{HC}\) (Odum et al., 1996):

\[
Y = \frac{\Delta M}{\Delta \text{HC}}.
\]

The amount of reacted toluene mass depends on the OH\(_{\text{exp}}\); the change in toluene concentration is defined by a similar differential equation as the change in SO\(_2\) concentration (Eq. 2). Thus, the amount of reacted toluene is

\[
\Delta \text{[toluene]} = \text{[toluene]}_0(1 - \exp(-k_{\text{OH+toluene}} \times \text{OH}_{\text{exp}})).
\]

where \([\text{toluene}]_0\) is the initial toluene concentration and \(k_{\text{OH+toluene}}\) is the reaction rate constant between toluene and OH radicals. A rate constant of \(6.18 \times 10^{-12} \text{cm}^3 \text{s}^{-1}\) was used based on the parameters presented by Atkinson (1985).

### 2.7 Vehicle exhaust experiments

The ability of TSAR to produce secondary aerosol mass from engine exhaust emissions was evaluated by sampling the exhaust of a Euro 5 GDI light-duty vehicle during a transient driving cycle (New European Driving Cycle, NEDC) run on a chassis dynamometer. The official cycle begins with a cold engine start but, in this study, the NEDC was run with a warm engine, and this is hereafter called a warm NEDC. Prior to the warm NEDC, the vehicle was run at 80 km h\(^{-1}\) for at least 3 min, and the cycle began with an idling engine.

The sampling setup of vehicle exhaust experiments is shown in Fig. S2. The engine exhaust was sampled from the tailpipe using a porous tube diluter (PTD) followed by a short cylindrical residence time chamber with a residence time of 2.9 s. The dilution air temperature was 30°C, and the dilution ratio was approximately 12. This dilution setup has been shown to mimic the atmospheric cooling and dilution processes of primary aerosol reasonably well (Keskinen and Rönkkö, 2010; Rönkkö et al., 2006). The exact dilution ratio of the PTD was determined by CO\(_2\) measurements from the tailpipe and after the PTD. After the residence time chamber, 3 slpm of humidified air and 3 slpm of ozone were mixed with the sample. At this stage, the dilution ratio was 2.5. Thus, the total dilution ratio before TSAR was approximately 30. The sample from TSAR was drawn through an active carbon ozone scrubber to an ejector diluter (Dekati Ltd.) at 5 slpm flow rate. The total dilution ratio between the tailpipe and instruments was determined by CO\(_2\) measurements which were performed during 80 km h\(^{-1}\) steady-state driving, when the CO\(_2\) concentration in the tailpipe was stable.

The particle size distributions were measured with EEPS, an electrical low-pressure impactor (ELPI+, Dekati Ltd.) and a high-resolution low-pressure cascade impactor (HRLI; Affman et al., 2014). CO\(_2\) concentration after the tailpipe was measured with the Sick Mabihak CO\(_2\) analyzer, using a sample drier prior to the analyzer. Relative humidity and sample temperature were measured after TSAR using an RH sensor (HygroClip SC05, Rotronic AG).

The amount of secondary aerosol mass produced in TSAR was determined by subtracting the primary mass from the mass measured when using TSAR. Primary aerosol was measured with the same setup by operating TSAR with UV lamps and the ozone generator turned off. The primary emission was measured during two warm NEDCs.

In this setup, the sample flow from the tailpipe is constant regardless of the exhaust mass flow. To determine the emission factors, the measured concentrations are multiplied with the corresponding exhaust mass flow.

www.atmos-meas-tech.net/10/1519/2017/ Atmos. Meas. Tech., 10, 1519–1537, 2017
3 Results and discussion

3.1 Residence time distribution

The evolution of a CO$_2$ pulse in TSAR is shown in Fig. 2. A narrow pulse enters the oxidation reactor and exits the reactor as a broader pulse. The theoretical transfer function of the oxidation reactor is calculated based on the residence time distribution of ideal laminar flow:

\[
E(t) = \begin{cases} 
0, & t < \frac{\tau}{2} \\
\frac{\tau^2}{2t^3}, & t \geq \frac{\tau}{2}
\end{cases},
\]  

(19)

where the constant \( \tau \) is defined as

\[
\tau = \frac{\pi R^2 L}{Q},
\]  

(20)

and \( R \) is the inner radius of the reactor, \( L \) is the length of the reactor and \( Q \) is the flow rate (Fogler, 2006).

Figure 2 shows both the measured pulse after the reactor and the modeled pulse calculated according to Eq. (1) using the theoretical transfer function and the measured input concentration.

As seen in Fig. 2, the measured pulse is somewhat broader than the modeled one. There are some possible reasons for this discrepancy: first, the flow inside the reactor is probably not totally laminar because of the expansion in diameter between the residence time chamber and the oxidation reactor and because of the abrupt diameter change at the end of the reactor; second, the pulse becomes broader in the sampling lines, which is not taken into account here.

In Fig. 2, UV lamps are turned off and the secondary excess flow is on. Because both of these affect the flow, the residence time distribution was measured for different combinations of these parameters, and the results are shown in Fig. 3. In all cases, the total flow rate through the oxidation reactor was 5 slpm. Because the incoming pulse is not an ideal Dirac delta function, the residence time distribution cannot be calculated with Eq. (8). Instead, the residence time distribution is the measured concentration, \( C_{\text{out}}(t) \), divided by the total area of the pulse (Fogler, 2006):

\[
\text{RTD}(t) = \frac{C_{\text{out}}(t)}{\int_0^\infty C_{\text{out}}(t) \, dt}.
\]  

(21)

Turning off the secondary excess flow broadens the distribution slightly, probably because there is more dead volume at the end of the reactor. Turning the UV lamps on has a similar effect. The UV lamps heat the reactor walls and cause convection inside the reactor. This effect could be reduced by circulating air through the TSAR housing; however, small heating of the reactor walls may decrease the vapor wall losses. Another method to reduce the convection is to place the reactor vertically.

The residence time distributions show that the flow in the TSAR oxidation reactor is near-laminar. Thus, the mean residence time of the sample in the reactor can be calculated with Eq. (22) (Fogler, 2006):

\[
t_{\text{mean}} = \frac{\tau}{2} = \frac{\pi R^2 L}{2Q},
\]  

(22)

which yields 37 s at 5 slpm flow rate. Turning off the secondary excess flow reduces the laminarity, but this is often necessary to keep the flow rate at 5 slpm since, for example, an ejector diluter alone draws approximately 5 slpm of sample. In any case, the residence time distribution is clearly narrower, and the mean residence time is shorter than those
of PAM (Lambe et al., 2011), allowing the measurement of rapidly changing emission sources.

3.2 Particle losses

The particle transmission efficiency as a function of particle mobility diameter is presented in Fig. 4, as well as the theoretical diffusive losses of particles in a tube with laminar flow (Brockmann, 2011). The markers indicate the particle material, and the error bars denote the standard deviation between separate experiments.

Figure 4 shows that the measured transmission efficiency agrees well with the theoretical efficiency, as expected, and thus the losses are less than 10% when the particle mobility diameter is larger than 5 nm. Therefore, the results in the next sections are not corrected with this efficiency curve because the particle losses are negligible.

According to Lambe et al. (2011), the transmission efficiency of particles is significantly lower in PAM: less than 70% for particles smaller than 100 nm. Since the flow in TSAR is near-laminar, it is not surprising that the measurements agree with the theory. In PAM, the residence time distribution is broad, allowing more time for the particles to diffuse onto walls (and possibly to coagulate or evaporate), resulting in a non-ideal transmission efficiency.

3.3 OH exposure

Figure 5 shows that the OH exposure in the TSAR oxidation reactor is sensitive to ozone concentration at low concentrations but levels off to a near-constant value when the concentration is higher than 25 ppm. The $\text{OH}_{\text{exp}}$ also depends on the relative humidity. The maximum $\text{OH}_{\text{exp}}$ at 30% RH is approximately $1.2 \times 10^{12}$ molec s cm$^{-3}$, equivalent to 9 days of atmospheric OH exposure, whereas in PAM, up to 17 days of equivalent exposure are reached (Lambe et al., 2015; See also Fig. S1). In the calculation of the equivalent atmospheric exposure, an average OH concentration of $1.5 \times 10^9$ molec cm$^{-3}$ in the atmosphere is assumed (Mao et al., 2009). The TSAR OH exposure could be further increased by increasing the RH or by increasing the UV lamp wattage.

The measurement results could be reproduced in the photochemical model using the photon flux, first-order OH radical wall loss and first-order ozone wall loss as free parameters. The best fit values are $1.92 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$ (254 nm photon flux), 8.3 s$^{-1}$ (OH wall loss) and $7.5 \times 10^{-4}$ s$^{-1}$ (ozone wall loss). Using these parameters, the model predicts the measurement results within ±20% uncertainty when the relative humidity, temperature, initial ozone concentration and initial SO$_2$ concentration are used as the input parameters (Fig. S4).

3.4 Vapor losses and photolysis in TSAR

3.4.1 Photolysis

Based on the modeling results in Sect. 3.3, the flux of 254 nm photons in TSAR is $1.92 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$ and does not depend on OH exposure, since OH exposure is adjusted by O$_3$ and H$_2$O concentration. Assuming a residence time of 37 s (Sect. 3.1), the ratio $F_{254, \text{exp}} / \text{OH}_{\text{exp}}$ is shown in Fig. 6a. When the $\text{OH}_{\text{exp}} > 10^{11}$ molec cm$^{-3}$ s$^{-1}$ (≈ 0.8 day equivalent atmospheric exposure), the ratio is less than $10^6$ cm$^{-1}$. According to Peng et al. (2016), the relative photolytic loss for most VOCs (volatile organic compounds) is below 20% at this ratio. The only exceptions are acetylacetone, (E,E)-2,4-hexadienedial, peroxyacetyl nitrate and species with multiple hydroxyls and carbonyls, whose relative photolytic losses are 30–60% when $F_{254, \text{exp}} / \text{OH}_{\text{exp}}$ is $10^6$. At higher OH$_{\text{exp}}$.
the relative photolytic losses decrease. Thus, to avoid non-tropospheric photolysis of precursor gases, the OH exposure must be maintained high enough. However, we note that these relative photolytic losses are upper limits, since a unit quantum yield is assumed in the calculations.

As shown by Peng et al. (2015), the \( \text{OH}_{\text{exp}} \) in OFR254 depends on water vapor concentration, \( \text{OHR}_{\text{ext}} \), photon flux and ozone concentration. Using the photochemical model described in Sect. 2.4, we evaluate the effect of \( \text{OHR}_{\text{ext}} \) on \( \frac{F_{254 \text{exp}}}{\text{OH}_{\text{exp}}} \) while keeping the temperature, relative humidity and initial ozone concentration constants (20°C, 30% and 45 ppm, respectively). According to the model results (Fig. 6b), \( \frac{F_{254 \text{exp}}}{\text{OH}_{\text{exp}}} < 10^5 \text{ cm s}^{-1} \) as long as \( \text{OHR}_{\text{ext}} < 2500 \text{ s}^{-1} \). On the other hand, the \( \text{OH}_{\text{exp}} \) decreases as a function of \( \text{OHR}_{\text{ext}} \). A worst-case scenario regarding the \( \text{OHR}_{\text{ext}} \) in exhaust measurements is a cold engine start, where the \( \text{OHR}_{\text{ext}} \) can be as high as 1000–3400 s\(^{-1}\) (excluding the effect of \( \text{NO}_x \)).

To study the dependence of LVOC fate on residence time and the condensational sink, we define two cases: the oxidation of ambient air (low condensational sink) and diluted vehicle exhaust (high condensational sink). The condensational sink depends on particle number concentration and size and also on the accommodation coefficient (\( \alpha \)), diffusion coefficient and molecular mass of the condensing vapor. The first-order rate coefficient for wall loss (\( k_w \)) is calculated as in Palm et al. (2016; see Supplement for details on the calculation of the CS and \( k_w \)). Following the example in Palm et al. (2016), we assume the following properties for the LVOC: molar mass of 200 g mol\(^{-1}\), diffusion coefficient (\( D \)) of \( 7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \) and \( k_{\text{OH}} = 1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \). For simplicity, we assume that the nucleation rate in Eqs. (5)–(7) is zero. Nucleation is still implicitly taken into account because the condensational sink is calculated from the average size distribution before and after TSAR. In addition, we do not consider the heterogeneous fragmentation.

In the case of oxidation of ambient air, the timescale for condensation on aerosol \( \tau_{\text{acq}} = (4\pi \cdot D \cdot \text{CS})^{-1} \approx 65 \text{ s} \) (when \( \alpha = 1 \)). According to Palm et al. (2016), this is a typical value for ambient pine-forest air oxidized in the PAM chamber when sufficient amounts of precursors are available for SOA formation. This CS is equivalent to that of a log-normal particle size distribution with a total number concentration of \( 1.5 \times 10^5 \text{ cm}^{-3} \), median diameter (\( \mu \)) of 25 nm and geometric standard deviation (\( \sigma \)) of 1.4. The use of a particle size distribution instead of a constant CS allows us to vary \( \alpha \) (since the CS depends on \( \alpha \)). Different values for LVOC mass accommodation coefficients have been proposed. For example, Saleh et al. (2013) measured a value of \( \alpha \approx 0.1 \) for \( \alpha \)-Pinene SOA, whereas Palm et al. (2016) argue that \( \alpha \approx 1.0 \) for ambient pine-forest SOA.

The vapor losses in TSAR for the ambient case as a function of residence time were modeled using the method described in Sect. 2.5.2. Two values of the mass accommodation coefficients were used (\( \alpha = 0.1 \) and \( \alpha = 1.0 \)). The equivalent \( \text{OH}_{\text{exp}} \) is 5 days regardless of the residence time. The results are presented in Fig. 7a. At a typical TSAR residence time (37 s), the LVOC losses in this case are 69–96%, depending on the value of \( \alpha \). Most losses are caused by fragmentation, and a longer residence time results in fewer losses (Fig. S5). This is because the shorter the residence time is, the higher the OH concentration must be to reach the same equivalent OH exposure. When the OH concentration is high enough, the timescale of fragmentation is lower than that of condensation.

The vehicle exhaust case is based on the measurements in Sect. 3.6. The mass concentration and \( \tau_{\text{acq}} \) of diluted primary aerosol are approximately \( 4.8 \mu \text{g m}^{-3} \) and \( 81 \text{ s}^{-1} \), respectively (when \( \alpha = 1 \)). This is approximated as a log-normal size distribution with \( \mu = 31 \text{ nm} \), \( \sigma = 1.9 \) and a number concentration of \( 5.4 \times 10^9 \text{ cm}^{-3} \). According to the measurements in Sect. 3.6, the mass concentration after TSAR is approximately \( 156 \mu \text{g m}^{-3} \) (when background is subtracted). For simplicity, we assume that the increase in mass is caused only by condensation, so the number concentration and \( \sigma \) are constant. Thus, the size distribution after TSAR is otherwise similar to the primary size distribution, but \( \mu = 103 \text{ nm} \). The average CS in TSAR is calculated from the average of these two size distributions.
Figure 7. Modeled losses of low-volatility organic compounds as a function of residence time in TSAR in the case of ambient air (a) and vehicle exhaust measurement (b) using two values for the accommodation coefficient (\(\alpha\)). The model results for other flow reactors are also shown using typical residence times.

The results for the car exhaust case are presented in Fig. 7b. Now, the LVOC losses in TSAR at typical residence time are 25–80 %, depending on the value of \(\alpha\). The losses are lower than in the ambient case because of the shorter timescale of condensation caused by the higher CS. Again, the highest loss is caused by fragmentation (Fig. S5).

In addition to TSAR, we present the estimates for LVOC losses in several other flow reactors, namely MSC, the PAM reactor, and the Caltech Photooxidation Flow Tube reactor (CPOT; Huang et al., 2017) at their typical residence times in Fig. 7. The results differ a little from the TSAR curve because of the different surface-area-to-volume ratios. One must note that the applications of the flow reactors are different; for example, MSC is usually used with a much higher CS than what is modeled here (e.g., Corbin et al., 2015) and, consequently, the losses are smaller than in Fig. 7. Similarly, the main application of TSAR is the engine exhaust measurement, where the CS is usually higher than in ambient air.

The model is tested by comparing the measured and modeled sulfuric acid losses, and the results are shown in Fig. 8. In the model, the following values are assumed for the sulfuric acid molecules: molar mass of 98 g mol\(^{-1}\), \(\alpha = 0.65\) (Pöschl et al., 1998) and \(D = 1 \times 10^{-5}\) m\(^2\) s\(^{-1}\) (Hanson and Eisele, 2000; Palm et al., 2016). We assume there is no fragmentation for sulfuric acid molecules. The CS is again calculated from the average of size distributions after and before TSAR (in this case, the average size distribution is the size distribution measured after TSAR divided by two, since no particles were injected into TSAR). For the three measurements with the smallest error bars, the measured sulfuric acid loss is on average 4 %. The modeled loss, in contrast, is 18 % on average. The reason for this discrepancy may be the underestimated CS, since dividing the measured size distribution by two does not necessarily represent the average size distribution in TSAR. If instead the measured size distribution is used for the CS calculation (the upper limit for the average CS), the model results in an average loss of 6 %, which is much closer to the measured one and indicates that the nucleated particles already generate a high CS during the first steps of oxidation. Thus, the modeled losses for the ambient and vehicle exhaust case are probably slightly overestimated.

The sulfuric acid experiment shows that the model predicts the losses of a non-fragmenting low-volatility compound reasonably well. However, in Fig. S5 we see that it is the fragmentation that causes the highest losses for LVOCs when the residence time is short (< 50 s). The assumption that the five oxidation steps result in fragmentation is artificial but, if we as a sensitivity test assume that the fragmentation does not occur at all, the change in overall loss is small because a
higher proportion of the LVOCs will exit the reactor before condensing (Fig. S6). Still, the losses are a little lower in the case of no fragmentation, and thus more studies on fragmentation are needed to verify the assumptions in the model.

The modeled cases inarguably show that there is a trade-off between residence time and LVOC losses: the smaller the residence time is, the more losses there are. Thus, the residence time must be chosen according to the application. If a short residence time is used and the CS is low, the injection of seed particles in the sample will reduce the LVOC losses. In the car exhaust case, the CS is high enough for TSAR if the mass accommodation coefficient of the condensing vapor is close to unity. For steady-state experiments, we recommend using a long residence time when there is no need for a fast response. However, even though the LVOC losses are smallest for long-residence-time reactors according to the model results, the particle losses are higher (e.g., ~20 % for PAM and CPOT for 100 nm particles and ~0% in TSAR; Huang et al., 2017; Lambe et al., 2011).

3.5 Toluene SOA yield and properties

The SOA formation studies were conducted as described in Sect. 2.6. Toluene concentration in the sample entering the reactors was 320 ppb (±34 ppb). During the experiments, the average temperature of the sample was 23.6 ± 0.2 °C and the average relative humidity was 31.3 ± 2.9 %, where the uncertainty is the standard deviation of the values.

3.5.1 Steady-state experiments

The SOA mass formed in the reactors is calculated from the number size distribution measured by the SMPS, assuming spherical particles with a density of 1.45 g cm⁻³ (Ng et al., 2007). The SMPS was used for PM concentration measurements instead of the AMS because, especially for TSAR, not all particles fall in the AMS detection range (40–800 nm). The background mass, i.e., the mass formed in the reactors in the absence of toluene, was subtracted from the toluene SOA mass. The background mass consists of oxidation products of the dilution air and depends on the purity of the pressurized air. The purity of the air must always be checked by measuring the mass formed in the flow reactor in the absence of any exhaust or precursors. In this experiment, the background mass concentration was on average 1.2 µg m⁻³ for TSAR and 1.1 µg m⁻³ for PAM. For comparison, the average mass concentration in toluene measurements was 137 µg m⁻³.

Figure 9 shows the SMPS mass distributions of toluene SOA for PAM and TSAR at OH exp of 3.6 × 10¹¹ and 6.0 × 10¹¹ molec s cm⁻³, respectively. PAM produces a wide mass distribution where particles above 100 nm contribute to approximately half of the total mass. TSAR produces a narrower mass distribution where approximately half of the total mass is located in particles smaller than 40 nm. This phenomenon was also reported by Bruns et al. (2015): the micro-smog chamber, which is smaller, has a shorter residence time and generates smaller particles than PAM. As discussed in Sects. 2.5.2 and 3.4.2, the shorter residence time limits the condensational growth of particles and may favor nucleation instead of condensation. Implementing nucleation in the LVOC fate model remains a future task, but an estimation of the losses of toluene oxidation products was conducted in a similar way as in Sect. 3.4.2. If the accommodation coefficient of the oxidation products is one, the LVOC losses for the toluene SOA cases are less than 2 %, except for the TSAR measurement at OH exp of 3 × 10¹⁰ molec s cm⁻³, where the losses are approximately 8 %. If the accommodation coefficient is 0.1, the losses are less than 35 %, except for the TSAR low-OH exp measurement, where the losses are approximately 73 %. Since the exact value of the accommo-
Figure 11. The van Krevelen diagram of toluene SOA for both chambers. The color indicates the OH exposure.

Table 2. Dot product between the organic spectra of PAM- and TSAR-generated SOA.

<table>
<thead>
<tr>
<th></th>
<th>Low oxidation</th>
<th>Medium oxidation</th>
<th>High oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSAR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low oxidation</td>
<td>0.999</td>
<td>0.904</td>
<td>0.779</td>
</tr>
<tr>
<td>Medium oxidation</td>
<td>0.904</td>
<td>0.999</td>
<td>0.978</td>
</tr>
<tr>
<td>High oxidation</td>
<td>0.773</td>
<td>0.962</td>
<td>0.999</td>
</tr>
</tbody>
</table>

particles are formed via nucleation inside PAM; thus, it is unknown how long they have spent in the reactor and what the particle size as a function of residence time is. As an estimate, the particle size distribution measured after PAM was corrected with the losses measured for this particular chamber (Karjalainen et al., 2016). With this correction, the PAM yield would increase by 19 % on average.

In addition to yield, the chemical composition of produced SOA was studied. In Fig. 11, a van Krevelen diagram shows the oxidation state of SOA for both reactors. In this diagram, the H/C ratio is shown as a function of the O/C ratio. Elemental ratios are calculated using the method developed by Aiken et al. (2008) and improved by Canagaratna et al. (2015). Oxidation of aerosol usually increases the O/C ratio and decreases the H/C ratio (Heald et al., 2010). This phenomenon is observed in both reactors; based on these ratios, the oxidation state of SOA is similar in PAM and TSAR at comparable OH exposures.

To further compare the SOA oxidation state in the reactors, the average carbon oxidation state (\( \overline{\text{OS}}_C \)) of SOA is shown in Fig. 12. The average carbon oxidation state is a metric which is invariant to hydration or dehydration and is defined as \( \overline{\text{OS}}_C \approx 2 \times \text{O/C–H/C} \) (Canagaratna et al., 2015; Kroll et al., 2011). As well as the O/C ratios and H/C ratios, the \( \overline{\text{OS}}_C \) of the SOA in the reactors also agree at comparable \( \text{OH}_{\text{exp}} \). The trend of TSAR and PAM \( \overline{\text{OS}}_C \) as a function of \( \text{OH}_{\text{exp}} \) seems to differ at higher \( \text{OH}_{\text{exp}} \), but this can be caused by the uncertainty in the \( \text{OH}_{\text{exp}} \) estimation, which is visualized with error bars in Fig. 12.

We also compare the chemical composition of SOA by studying the organic mass spectra. According to Marcoll et al. (2006) and Lambe et al. (2015), a dot product between two normalized mass spectra can be used to determine whether the spectra are similar. The spectra are normalized by dividing each signal by the square root of the sum of the squares of all signals. A dot product of one implies that the spectra are identical and of zero that they are orthogonal.

Toluene SOA here is divided into three categories: low oxidation (\(-0.18 < \overline{\text{OS}}_C < -0.16\)), medium oxidation (\(0.50 < \overline{\text{OS}}_C < 0.69\)) and high oxidation (\( \overline{\text{OS}}_C > 1.10\)). The dot products between the organic spectra of different reactors are shown in Table 2. The dot products of normalized mass spectra of SOA produced in reactors at comparable \( \overline{\text{OS}}_C \) are
The average carbon oxidation state (OSC) as a function of OH exposure for PAM- and TSAR-generated toluene SOA.

Figure 12. The average carbon oxidation state (OSC) as a function of OH exposure for PAM- and TSAR-generated toluene SOA.

above 0.99, indicating that the reactors produce similar SOA matter in regard to chemical composition.

The TSAR and PAM reactors differ in volume, geometry, flow conditions and residence time. The most significant difference is in the oxidation process: TSAR operates in OFR254 mode and PAM in OFR185 mode. However, the agreement between yields and organic mass spectra of SOA produced in both the TSAR and PAM reactors show that the oxidation products are similar in both reactors, at least in the case of toluene. In OFR254, the sample is first exposed to ozone (before the oxidation reactor) and then to both ozone and OH radicals. If the VOCs in the sample react fast with ozone, the resulting SOA mass might differ between OFR254 and OFR185. This was not the case for toluene, as dark experiments (only ozone and no UV light) did not produce any secondary mass. In other applications, for example when oxidizing biogenic precursors which are highly reactive towards ozone, the results between OFR254 and OFR185 presumably differ, with OFR185 being more realistic as the sample is exposed to ozone and OH simultaneously. However, the main application of TSAR is to measure vehicle emissions, which are more reactive towards OH than ozone (Gentner et al., 2012; Tkacik et al., 2014). The potential of ozone to produce SOA from the emission can be measured by injecting ozone into TSAR with UV lights turned off.

3.5.2 Pulse experiments

The SOA mass concentrations as a function of time are shown in Fig. 13 for all pulse experiments. The 10 s pulse of toluene results in a sharp peak in mass in TSAR, whereas the PAM reactor produces significantly broader peaks at both used flow rates. Interestingly, the TSAR mass peak is divided into two distinct peaks. We do not know the reason for this phenomenon since the residence time distributions in Sect. 3.1 do not support this kind of behavior. However, the flow conditions in this experiment are not exactly the same as in Sect. 3.1; here, the flow rate in the residence time chamber is only 10 slpm, whereas in Sect. 3.1 it was 50 slpm.

Cycle 1 with three rapid toluene pulses shows the importance of laminar flow and short residence time in TSAR: PAM produces only one broad peak whereas all three pulses can be distinguished in the SOA mass produced by TSAR. In cycle 2, when toluene pulses are injected between longer intervals, the pulses are also separated in the mass produced by PAM.

As the total amount of toluene injected into the reactors is known and the yield is determined in Sect. 3.5.1, the total mass produced in the reactors can be predicted with Eq. (23).

\[ M_{\text{predicted}} = M_{\text{tol}} \times Y, \]

where \( M_{\text{tol}} \) is the total mass of the toluene injected and \( Y \) is the yield. In these experiments, the OH exposure was approximately \( 6.1 \times 10^{11} \) in TSAR and \( 8.3 \times 10^{11} \) mole \( \text{cm}^{-3} \) in PAM, so a yield of 0.2 is used for both reactors to calculate the expected mass. The mass produced in the reactors is the area of the peaks in Fig. 13 multiplied by the flow rate through the reactors. The comparison between the expected mass and the formed mass is shown in Fig. 14.

In all the experiments, the mass produced in the reactors agrees well with the expected mass. For the 10 s pulse, PAM mass is lower than the expected mass and the TSAR mass; for cycle 1, TSAR produces more mass than expected; and for cycle 2, both reactors produce less mass than predicted. Considering the uncertainties in this experiment, namely the dilution ratio, EEPS inversion and toluene concentration, we conclude there are no significant differences in the total mass the reactors produce, even though the pulse shapes are clearly different. In all the cases, the mass produced in PAM is slightly lower than in TSAR, probably because the particle losses in PAM are higher.

The agreement between the predicted mass and the produced mass suggests that the approach to measure the secondary aerosol formation potential in real time is valid: the narrow residence time distribution of TSAR gives time-resolved information of SOA formation from fast changing precursor concentrations but still produces approximately the same amount of mass as the PAM reactor, where the oxidation process is slower. Based on these results and the LVOC loss estimation in Sect. 3.4.2, this holds when the condensational sink is high enough. When the CS is smaller (e.g., in ambient air measurements), we expect TSAR to produce less mass than PAM due to the higher losses.

3.6 Engine exhaust oxidation

When measuring time-resolved secondary aerosol formation during a transient driving cycle, it is crucial to synchronize real-time aerosol measurements with vehicle speed data. This
Figure 13. The mass produced from SOA formation of toluene pulses in TSAR at 5 slpm flow rate and in PAM at 5 and 10 slpm flow rates. The shaded area shows the standard deviation. The figures show the mass formation of a single pulse (a) as well as cycle 1 (b) and cycle 2 (c), which are both comprised of three adjacent pulses.

Figure 14. The expected and measured masses produced in pulse experiments. The expected mass is calculated from the mass of injected toluene and its SOA yield.

is performed by comparing the CO₂ measurements in the tailpipe and after the dilution steps.

3.6.1 TSAR oxidation

In Sect. 3.3 we showed that the OH_{exp} in TSAR depends on relative humidity and ozone concentration. In engine exhaust experiments, RH was 33–36 % and temperature was 22 °C. Ozone concentration was not measured but, based on later laboratory experiments, the ozone concentration was approximately 11 ppm in the sample flow. According to the results presented in Sect. 3.3, the OH_{exp} with this ozone concentration is approximately 8 × 10^{11} molec s cm⁻³ (equivalent photochemical age of 6.3 days). However, this should only be considered as an upper limit for the OH_{exp}. There is always NO present in the exhaust sample, and the ozone reacts fast with NO, titrating practically all NO to NO₂ before the sample enters TSAR. Therefore, NO emissions cause a loss in ozone concentration, suppressing the OH_{exp}. In addition, NO₂ and other OH reactive compounds in the exhaust further decrease the OH_{exp}. As the concentrations of NOx and other gaseous compounds vary during the driving cycle, so does the OH_{exp}. The time-resolved OH_{exp} during the driving cycle should be determined by monitoring an OH reactive tracer, such as CO. In this work, the OH_{exp} was not measured in real time.

3.6.2 Time-resolved secondary aerosol formation

The secondary aerosol mass concentration formed from the GDI exhaust during a warm NEDC is shown in Fig. 15c. Mass concentration is calculated from the particle number size distribution measured by EEPS assuming spherical particles with a density of 1.0 g cm⁻³ and multiplying the result by the total dilution ratio. The shown mass concentration is an average value of two identical warm NEDCs, and the standard deviation between these two measurements is shown as the shaded area. A constant value of background mass formed from dilution air has been subtracted from the calculated mass. Because of the background mass, the vapor losses here are lower than those modeled in Sect. 3.4.2, at least than 2 % if the accommodation coefficient is 1.0.

Figure 15c shows significant differences in secondary aerosol formation during different driving conditions. The small standard deviation suggests that the operation of TSAR and the phenomena causing secondary aerosol formation are highly reproducible. The least secondary aerosol formation occurs during long steady-state driving, such as at 70 km h⁻¹ at the end of the cycle. When the car is accelerated to 100 and 120 km h⁻¹ at the end of the cycle, the secondary aerosol mass formation increases. During most of the cycle, the secondary mass concentration in TSAR is 10–100 times the primary mass concentration (Fig. 15b). However, the difference
between primary and secondary emission factors is not that high.

The time-resolved emission factor of secondary aerosol mass in Fig. 15c is achieved by multiplying the secondary mass concentration by the exhaust mass flow. Low exhaust mass flow during engine braking cancels out the high mass concentration peaks. Instead, the peak at the end of the cycle dominates the emissions of secondary aerosol precursors. The total emission factor over the cycle is the integral of the time-resolved emission factor over the cycle length divided by the total distance. For the primary emissions, the emission factor is 0.1 mg km\(^{-1}\), and for the secondary aerosol potential it is 25 times higher at 2.7 mg km\(^{-1}\).

The secondary aerosol emission factors for a similar vehicle and driving cycle reported by Karjalainen et al. (2016) and Platt et al. (2013) are 4.3 and 12.7 mg km\(^{-1}\) (SOA only), respectively. The values are higher than in this study, possibly because the OH exposures are different; using a PAM reactor, Tkacik et al. (2014) have shown that the SOA formation from vehicle exhaust depends strongly on the OH exposure. Another reason for the higher values is probably that both Karjalainen et al. (2016) and Platt et al. (2013) used a cold-start cycle. In Karjalainen et al. (2016), most of the secondary mass is indeed formed at the beginning of the cycle, when the engine and the after-treatment system are cold. Interestingly, Karjalainen et al. (2016) do not observe a similar peak in the secondary mass formation at the end of the cycle as we see in Fig. 15c. However, the gas measurements by Karjalainen et al. (2016) and Platt et al. (2013) show that during the last acceleration in the cycle, there were elevated concentrations of total hydrocarbons and ammonia, which could be potential sources of SOA and ammonium nitrate formation in an oxidation flow reactor.

We also observe a new phenomenon, where engine braking results in high concentrations of secondary aerosol forming precursors. Every deceleration (i.e., engine braking) during the warm NEDC produces a peak in secondary mass concentration. The tail at the beginning of the cycle is also a re-
sult of engine braking, as steady-state driving at 80 km h−1 was always performed before the warm NEDC. This phenomenon is not evident in the results of Karjalainen et al. (2016), since the mass concentration does not seem to correlate with vehicle speed in their study. However, they observe repeated events of nanoparticle growth in PAM during the cycle, which could be related to engine braking. Because of the mixing of the sample inside PAM, it is impossible to link these growth events to certain phases in the driving cycle.

Since no aerosol chemical composition measurements were performed, we cannot specify the amount of organic mass in the formed secondary aerosol; therefore, we do not present the emission factor for the SOA potential of the engine exhaust. In addition, the high background mass (i.e., unclean dilution air) and the lack of real-time OH measurements make these data qualitative rather than quantitative. However, this experiment shows the feasibility of TSAR for measuring the time-resolved secondary aerosol formation potential of rapidly changing vehicle emissions. This way, we can identify the driving conditions in which most secondary aerosol forming precursors are emitted. If the sample were injected to a smog chamber with a constant dilution ratio and then oxidized, like Platt et al. (2013) did, the precursor pulses emitted during engine braking events would cause an overestimation of total secondary aerosol formation potential.

4 Conclusions

In this work, we introduced TSAR, a new short-residence-time oxidation flow reactor for secondary aerosol formation measurements. We studied the performance of the reactor by measuring the sulfuric acid yield, toluene SOA yield and the composition and the secondary aerosol formation potential of light-duty gasoline vehicle exhaust during a transient driving cycle. In addition, we characterized the particle transmission efficiency and the residence time distribution of the reactor and did a modeling study on vapor losses in TSAR.

According to the model results, the vapor losses in TSAR are higher than in the reactors with longer residence times. The losses depend strongly on the condensational sink of the sample, which is usually high in exhaust measurements (resulting in lower losses). For applications with the low condensational sink, we recommend a longer residence time than in TSAR or the injection of seed aerosol. When there is no possibility for seed aerosol injection, a tradeoff must be made between fast response and low vapor losses.

The toluene experiments show that both the SOA yield and composition are similar in TSAR SOA and PAM SOA, even though PAM operates in OFR185 mode and TSAR in OFR254 mode. The similarity indicates that TSAR can be used instead of the OFR185 PAM reactor when high time resolution is needed.

The particle losses in TSAR are negligible, and the flow is near-laminar. These properties, together with the short residence time, make TSAR better suited for monitoring the secondary aerosol formation potential of rapidly changing emission sources than the PAM chamber. We demonstrate the importance of this feature by measuring the secondary aerosol formation of car exhaust during a driving cycle. This experiment shows that TSAR is able to differentiate which driving conditions are most significant regarding the secondary aerosol formation potential.

Data availability. The data of this study are available from the authors upon request.

The Supplement related to this article is available online at doi:10.5194/amt-10-1519-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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References


Strategies To Diminish the Emissions of Particles and Secondary Aerosol Formation from Diesel Engines

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Strategies To Diminish the Emissions of Particles and Secondary Aerosol Formation from Diesel Engines

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Supporting Information

ABSTRACT: Particle emissions and secondary aerosol formation from internal combustion engines deteriorate air quality and significantly affect human wellbeing and health. Both the direct particle emissions and the emissions of compounds contributing to secondary aerosol formation depend on choices made in selecting fuels, engine technologies, and exhaust aftertreatment (EAT). Here we study how catalytic EATs, particle filtration, and fuel choices affect these emissions concerning heavy-duty diesel engine. We observed that the most advanced EAT decreased the emissions of fresh exhaust particle mass as much as 98% (from 44.7 to 0.73 mg/kWh) and the formation of aged exhaust particle mass ~100% (from 106.2 to ~0 mg/kWh). The composition of emitted particles depended significantly on the EAT and oxidative aging. While black carbon typically dominated the composition of fresh exhaust particles, aged particles contained more sulfates and organics. The fuel choices had minor effects on the secondary aerosol formation, implicating that, in diesel engines, either the lubricant is a significant source of secondary aerosol precursors or the precursors are formed in the combustion process. Results indicate that the utilization of EAT in diesel engines would produce benefits with respect to exhaust burden on air quality, and thus their utilization should be promoted especially in geographical areas suffering from poor air quality.

INTRODUCTION

Health studies have revealed the association of untreated diesel exhaust with short-term and long-term adverse health effects in humans.1 Due to that, the collective efforts of scientists together with the solutions achieved in technology development and policies to diminish the emissions have brought significant improvements to exhaust emission control. The breakthrough in the control of diesel exhaust particle emissions has been achieved with the enforcement of the usage of diesel particle filters (DPFs) in many diesel applications starting from diesel passenger cars and later extending to trucks and buses. The DPF effectively filters the exhaust gas before it is emitted to the atmosphere and have been shown to lead to very efficient real-world reductions in the emissions of PM mass and in total particle number (PN),7,8 compared to typical pre-DPF levels. Heavy-duty engines equipped with DPFs and complying with the US2010 standards were reported to emit 2 orders of magnitude less mass and number of total particles compared to the pre-DPF ones in a comprehensive laboratory study.7 DPFs have also been shown to result very low nonvolatile particle (mostly soot and metallic ash) emissions.

Vehicles contribute to atmospheric PM concentrations not just through their direct (primary) PM emissions, measured at the tailpipe but, even more significantly, through photo-oxygenation and gas-to-particle processes of initially gaseous exhaust components (secondary PM).9 Primary particulate matter refers to particles directly emitted, e.g., from engine, fuel combustion process or brakes, and not yet experienced any
significant chemical transformation in the atmosphere. Depending on engine and fuel type, primary exhaust PM emissions from vehicles consist mainly of soot and different fuel and lubricating oil components. In addition to primary PM, the combustion process in the engine cylinder produces so-called delayed primary aerosol species (see Rönkkö et al. 6) like sulfuric acid which are in gaseous phase under tailpipe conditions but will condense or nucleate immediately when the exhaust is cooled and diluted, without any significant chemical transformation in the atmosphere. 10-12 In particle number size distribution, the exhaust PM formed by different processes are frequently seen as separate modes with different concentrations and particle size ranges. 11,13 In addition to the primary and delayed primary PM, large amounts of secondary particulate matter forms after the exhaust gases are released into the atmosphere. 14-17

Both batch chambers (such as smog chambers) and flow through chambers have been applied to study vehicular secondary aerosol emissions under both laboratory and ambient conditions. In general, a batch chamber is good for detailed oxidation process studies but cannot be used, e.g., to differentiate the influence of rapidly changing driving conditions to emissions during a test cycle. To overcome this challenge, oxidation flow reactors (OFRs) are designed to simulate secondary aerosol mass formation potential on a close to real-time basis. 18-20 Recent chamber studies have shown that secondary particulate matter from combustion engines consists mainly of organic compounds and ammonium nitrate but that the secondary PM formation can be significantly larger than primary PM emissions. 21,22 The emissions of secondary PM precursors from internal combustion engines have been observed to depend on fuel properties; e.g. Timonen et al. 23 reported significant decrease of these emissions when the fuel of a gasoline direct injection (GDI) passenger car was changed from the mixture of gasoline (90%) and ethanol (10%) to 100% ethanol. However, also the advantages of the oxidative exhaust aftertreatment (EAT) and especially the use DPF 22,23 in terms of secondary aerosol formation from diesel exhaust have been reported. A common way of making the conclusions is based on carrying out smog chamber or OFR experiments for different individual vehicles equipped with their specific EAT systems. It should be noted that in these cases, also the engine-out emission of SOA precursors may differ from an engine to another and thus the conclusions regarding the effects of EAT on secondary PM precursors and also on PM in fresh exhaust are not straightforward.

In this study, we used a comprehensive set of controlled measurements to characterize both primary, delayed primary, and secondary particulate emissions of a modern heavy-duty diesel engine. The measurements were conducted under laboratory conditions with a nonroad diesel engine by varying the EAT and fuel; the effects of a diesel oxidation catalyst (DOC), a selective catalytic reduction (SCR) system, and a diesel particulate filter (DPF) and the fuel change from a conventional fossil diesel fuel to a renewable paraffinic fuel were studied. All measurements were performed with the same engine in order to consistently evaluate the effects of each EAT-fuel combination. This is in contrast with the study by Gordon et al. 25 where the effect of EAT was studied by measuring vehicles with different EATs. In addition, we cover all relevant exhaust catalyst types in a stepwise manner, as opposed to the study by Jathar et al. 26 where one EAT combination was tested. According to our knowledge, this is the first time when secondary aerosol formation from paraffinic diesel fuel is compared to a common fossil fuel.

The engine and the EAT systems used in the study represent modern technologies; hence the results of the study can be seen to describe the diesel engine applications in general. Current emission limits in several regions still do not require the use of DPFs in diesel engine applications, and even in countries with the most advanced emission standards, DPF equipped vehicles only correspond to a fraction of the fleet. However, the engine and EAT systems used in this study also describe the emission situation of nonroad mobile machinery and forthcoming changes in their particle emissions. The new Stage V for nonroad mobile machinery (NRMM) was introduced with Regulation (EU) 2016/1628. Stage V calls for the introduction of diesel particle filters (DPFs) on most diesel engine categories as a result of the decision to regulate particle number on top of particle mass and thus goes forward from Stage IV, for which NO_x specific EAT like selective catalytic reduction (SCR), seemed adequate to reach demanded emission levels.

### EXPERIMENTAL SECTION

The test engine was a prototype high-speed 4.4 L turbocharged intercooled nonroad diesel engine producing at maximum 100 kW. This is a prototype of an engine designed to fulfill Stage IV emission levels, when combined with a DOC and an SCR system with proper calibration. For detailed characterization two load points of ISO 8178 C1 (Non-Road Steady Cycle, NRSC) were selected; “Mode 1” (2100 rpm, 100% load) and “Mode 7” (1500 rpm, 50% load). These points represent two different operation conditions for the engine and especially for the EAT systems. To compare different vehicle technologies, particle emissions were studied for four different EAT combinations and two fuels under laboratory conditions. The studied EAT combinations were: no exhaust aftertreatment (No EAT), a diesel oxidation catalyst (DOC), a combination of diesel oxidation catalyst and an SCR system (DOC+SCR), and a combination of a diesel oxidation catalyst, a diesel particulate filter and an SCR system (DOC+DPF+SCR). Details of the EAT components used are provided in Table 1. The DPF was

<table>
<thead>
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<th>Table 1. Properties of Exhaust Aftertreatment (EAT) Components Used in the Study</th>
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<tr>
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<tr>
<td>cells/in²</td>
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<td>coatings</td>
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a platinum catalyzed wall-flow filter that operates with passive regeneration. SCR dosing rate was selected based on test runs prior to the actual experiments to have constant AdBlue (diesel exhaust fluid) injection rates enabling maximum NO_x conversion below 10 ppm of NH₃ slip. Thus, NO_x stoichiometric ratios (i.e. ammonium to NO_x ratios) were selected to be 0.95 and 1.1, in Modes 1 and 7, respectively, in order to reach typical NO_x reductions.

The engine operated sequentially on two fuels, one being a typical pump-grade fossil diesel fuel and the other a renewable...
paraffinic diesel fuel (Table 2). This paraffinic 100% renewable fuel is made primarily from waste and residues in a hydro
treatment process. The major difference in chemical composition between the two fuels relates to their aromatic content. Fossil fuel aromatics content was 28.6 wt %, of which 3.5 wt % was polyaromatics. The paraffinic fuel only contained 0.3 wt % aromatics, which practically contained species with one aromatic ring. Combining density and mass-specific heat enthalpy, the volumetric flow of paraffinic fuel was somewhat higher than the fossil one for the same load conditions.

The exhaust particle sampling and measurement was designed to produce information on tailpipe exhaust aerosol, fresh exhaust aerosol and aged exhaust aerosol.24 Tailpipe exhaust aerosol includes the primary nonvolatile particles that are found in the particle phase in the hot exhaust gas, and which are counted in the PMP protocol. Fresh exhaust aerosol contains not only the tailpipe aerosol but also the delayed primary PM or PN that are formed in the dilution process with cool air or right after it; in other words, this is the particle population after seconds or minutes from the time of emission. Aged exhaust aerosol is the sum of fresh PM and secondary PM formed due to oxidation processes of gaseous precursors. Secondary aerosol formation typically takes hours or days under atmospheric conditions.

Fresh exhaust aerosol particles were measured downstream of a partial flow dilution system enabling nucleation and condensation processes to take place. In terms of nucleation particle formation, the sampling system mimics atmospheric dilution and the resulting particle size distribution.25–27 As shown in Figure S1, particle sampling was conducted downstream of each EAT configuration under test. The sampling system consisted of a porous tube diluter (PTD) (primary dilution ratio (DR) 12, dilution air temperature 30 °C), a residence time chamber (2.5 s) to let nanoparticles and grow in size and stabilize their concentration,28 and a Dekati ejector diluter (DR 5) for secondary dilution. Primary particles

<table>
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<th>property</th>
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<th>paraffinic diesel</th>
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Figure 1. Measured particle size distributions of tailpipe, fresh and aged diesel exhaust aerosol with different EAT combinations at the Mode 7 test point with fossil fuel. “Tailpipe” dataseries in panel “No EAT” is not available.
(nonvolatile particle fraction) were measured downstream of a thermodenuder connected to the dilution system. Secondary aerosol formation was studied with a potential aerosol mass (PAM) oxidation flow reactor (OFR). The PAM reactor used here was a 13 L aluminum cylinder equipped with two low-pressure Hg lamps. The reactor was operated in OFR185 mode, which means that the sample is exposed both to 185 and 254 nm UV radiation. The estimated photochemical ages achieved with the PAM reactor were between 2.8 and 4.6 equiv days in the atmosphere (assuming average ambient OH concentration of $1.5 \times 10^6$ cm$^{-3}$) with a few exceptions: for the “no EAT” case at Mode 1, the estimated photochemical age was only 1.2 equiv days, whereas for the cases with all of the EATs (DOC+DPF+SCR), the age was 7.5–13.3 days (see SI for more information). The dilution air for the primary and secondary dilution steps was synthetic air (99.999% purity in gas bottles) to minimize any secondary aerosol formation interference from any impurities in the dilution air.

After sampling and dilution, exhaust particle size distribution (PSD) was characterized by an engine exhaust particle sizer (EEPS; TSI Inc.) with soot inversion matrix in data post processing and two identical electrical low pressure impactors (ELPIs; Dekati Inc.) with improved nanoparticle resolution in the state-of-the-art ELPI+ (Dekati Inc.) impactor. A soot particle aerosol mass spectrometer (SP-AMS; Aerodyne Research Inc.) provided the chemical composition of exhaust particles. One ELPI measured downstream of the secondary dilution, whereas the other measured downstream of the PAM (and ejection), thus enabling simultaneous measurement of the fresh and aged exhaust aerosol. Additional details of the measurement setup and associated data analysis are provided in the Supporting Information (SI).

RESULTS

Particle Size Distributions (PSDs). Exhaust number PSDs were measured downstream of all EAT configurations, separately in three sampling branches regarding tailpipe, fresh, and aged aerosol (Figure 1). Without EAT (Figure 1a), the fresh and aged particle size distributions were fairly similar in shape and dominated by nucleation mode particles, showing also particle growth in the PAM reactor. The tailpipe aerosol particle size distribution was not measured for the case "No EAT". Downstream of the DOC (Figure 1b), the tailpipe aerosol mainly comprised a soot (accumulation) mode, peaking at sizes of 40–50 nm. There were also some particles around ~10 nm but the EEPS sensitivity and resolution are fairly weak in that size range. In contrast, nucleation mode particles were clearly detected in fresh exhaust that further grew in size and volume as the aerosol aged in the PAM.

When the SCR was fitted downstream of the DOC (Figure 1c), the clearly distinctive nucleation mode disappeared and fresh and tailpipe PSDs were similar. When exhaust aged in the PAM reactor, PSD hardly changed but particle concentration increased. This would indicate either new particle formation in the PAM reactor or particle growth from a size range earlier found below the EEPS measurement range. Fitting the DPF between the DOC and the SCR (Figure 1d) removed most of the soot mode of tailpipe and fresh aerosol but left traces of particles in the nucleation mode size range. This nucleation mode substantially grew in both concentration and size in the PAM reactor, again a possible result of new particle formation or growth from sizes not detected by EEPS.

PM Emissions Factors. Emission factors (EFs) for both fresh and aged exhaust particulate matter (PM) are shown in Figure 2. These have been calculated on the basis of size distributions measured by ELPIs applying effective particle density obtained from simultaneous ELPI and EEPS measurement. The detailed procedure for determining the effective density is described in the SI. We note that in Mode 1 with no EAT, the aged mass may be underestimated due to significantly lower OH exposure compared to other cases. Likewise, in Mode 7, the aged mass in the case with DOC+DPF+SCR is not directly comparable to other cases because of very high OH exposure (see the SI for details and sensitivity analysis). Emission factors are presented for both the high (Mode 1) and medium load (Mode 7) modes. In general, both the fresh and aged exhaust PM decreased with the use EATs; e.g., during Mode 1, the fresh and aged exhaust PM decreased...
from 5.2 mg/kWh and 24.4–26.6 mg/kWh, respectively, to about 1 mg/kWh when the most advanced EAT (DOC+DPF +SCR) was implemented. At medium load, PM levels without EAT were in the range of 35–106 mg/kWh, depending on aerosol condition (fresh, aged) and the fuel used (fossil, renewable). Although this is much higher level than at high engine load, implementation of advanced EAT again decreased these levels down to 1 mg/kWh or less.

Use of DOC with fossil diesel seemed to increase fresh PM over no EAT levels in Mode 1 but not in Mode 7. The increase in Mode 1 was associated with high nucleation mode concentration in fresh exhaust and is likely caused by continuous SO₂ oxidation in DOC and/or sulfuric acid release from DOC. The storage and release of sulfur compounds in exhaust PM aerosol condition (fresh, aged) have been observed to significantly affect the exhaust aerosol PSD and concentration.²⁹

Despite the inconsistency in the DOC effect on fresh aerosol, overall the use of the DOC decreased the aged PM mass by a factor of 3–16. The addition of the SCR downstream of the DOC seemed to have an inconsistent impact on aged PM mass, whereas the use of the DPF substantially decreased both fresh and aged PM mass. The decrease of fresh PM emissions by the DPF has been well established before. However, our results show that the positive impacts of the DPF are even larger when aged PM is considered. Aged-to-fresh PM ratios in Mode 1 were at maximum 5.1 without EAT (Figure 2) but close to unity with the DOC+DPF+SCR system. With the same EAT configuration, aged PM levels dropped below detection limit in Mode 7. In few cases, the aged-to-fresh PM ratios dropped below one, possibly due to particle losses in the PAM reactor, uncertainties in defining the PAM background aerosol formation and the reduced sensitivity of ELPI due to the additional dilution steps when measuring the aged mass.

Less impact of fuel specifications on PM could be seen, compared to the corresponding impact of EAT. The fresh exhaust PM EFs were at the same level in Mode 1 for both fuels, but the fresh PM EF was about 20% lower with the renewable paraffinic fuel in Mode 7. For all the EAT systems, the use of paraffinic fuel always resulted in lower aged PM EF.

Chemical Composition, Fresh Aerosol. The chemical composition of fresh exhaust aerosol is shown in Figure 3, grouped in the main chemical groups provided by the SP-AMS, including organics (Org), refractory black carbon (rBC), sulfate (SO₄), nitrate (NO₃), and ammonium (NH₄). The higher fresh PM concentration at medium than at high engine load operation observed earlier was also associated with differences in PM composition. Fresh PM was dominated by rBC at high load (Mode 1), but the addition of organic material significantly increased the total mass in Mode 7 especially when no EAT was used. The high PM reduction in the DOC (see Figure 2, Mode 7) seems to relate to the efficient removal of organics in Mode 7 (Figure 3). Instead, in Mode 1, the level of organics was low, and the relative reduction (change in composition) was not directly observed in the SP-AMS data. The choice of fuel was seen in the amount of rBC in Mode 7, where lower levels were detected with the renewable paraffinic fuel. In general, the concentrations of sulfates, nitrates and ammonium were low in fresh exhaust PM, so that the levels that the SP-AMS actually measured were close to the limit of detection.

Regarding the above-mentioned, relatively high fresh exhaust PM in Mode 1 downstream the DOC was observed. The composition measurement support the hypothesis on the role of sulfate release and its effects on PM, since this was the only measurement situation where the sulfates had elevated concentrations in fresh exhaust PM. Simultaneously also the ammonium had higher contribution to the PM, indicating that the PM partly comprised of ammonium sulfate. One difference in composition was also detected in Mode 7 with DOC+SCR and fossil fuel, where almost 20% of PM was composed of ammonium nitrate.

Chemical Composition, Aged Aerosol. The chemical composition of aged exhaust PM is also shown in Figure 3 (bottom panel). Except the measurements during Mode 7 without exhaust aftertreatment (No EAT), the photochemical aging simulated in the PAM chamber increased the fraction of organic compounds in PM. Connecting with results in Figure 2, a clear observation is that the EAT systems reduced the concentrations of SOA precursors (and thus observed SOA), so that organics reduced gradually. The combination DOC +SCR+DPF was extremely efficient with respect to the reduction of SOA formation; even though the DPF filtered majority (~90%) of the soot particles, the average particle
composition was not entirely changed compared to the DOC + SCR situation, indicating that the DPF was almost as effective in removing soot and SOA precursors. It should be noted that the DPF in this study had catalytic coating (see Table 1). The photochemical aging of exhaust sample in the PAM chamber increased also the fractions of sulfates, nitrates, and ammonium in the aged PM so that they reached clearly elevated and detectable concentrations (Figure 3). This was observed with both low sulfur fuels, indicating that also the lubricant oil may contribute to secondary sulfate. In addition, the sulfate concentrations were so high that it should be taken into account when the total secondary aerosol mass from diesel engine is evaluated. In contrast, it can be seen that the ammonium concentration was not remarkable, even when measured downstream the SCR, indicating low levels of ammonia slip in the SCR.

**DISCUSSION**

The study of Timonen et al., made with GDI passenger car, indicates that the aromatic content of fuel may even determine the emissions of SOA precursors from gasoline-fueled internal combustion engines. According to Gentner et al., approximately 53% of SOA from diesel engines originate from the aromatics in the fuel. In this study, the experiments were made with two significantly different diesel fuels in composition, one containing 28.6% of aromatics and the other being nearly aromatic-free. As a result, we did not observe as high exhaust SOA formation reduction as expected. We think that this can indicate a higher role of lubricant oil in SOA precursor formation for diesel engine when compared to GDI passenger cars. This is supported by the result that elevated concentrations of sulfates were observed in the aged PM with both of the low-sulfur tested fuels. However, since fuel compounds can chemically transform during combustion, it is possible that SOA precursors originate from fuel.

Relatively the role of EAT systems was greater than the role of fuel. The installed additional exhaust aftertreatment systems reduced aged PM concentrations step-by-step, finally downstream the DPF the aged PM levels were roughly the same whether the PAM chamber measurement was performed from the diluted exhaust gas or just from the dilution air.

As a strategy to achieve lower fresh or aged PM formation from diesel engines as well as other climate and air quality benefits one can consider to change the fuel (from fossil to renewable (paraffinic)) or add more EAT components (DOC, SCR, and DPF). The fuel can be regulated from the supplier level being quite easy to monitor but the catalyst are owned by users and their functioning is more difficult to quantify for the entire vehicle fleet. Based on our data, the stepwise reduction in emissions by the implementation of advanced technology is shown in Figure 4 where either fuel or aftertreatment is changed as a first step and later additional EATs are applied according to the description in the figure. Apart from Mode 1, fresh, where additional sulfate formation was detected, introduction of theDOC reduced the PM concentrations effectively. The addition of the SCR was also effective but finally the PM was practically removed by adding the DPF. Overall, the fuel change as a first step had only decreasing fresh/aged PM effects.

Based on this study and the literature, gasoline engines have greater secondary aerosol precursor emissions than diesel engines. In addition, gasoline particle filter (GPF) has not shown similar reduction potential against SOA as DPF. This might be due to several reasons, e.g., that gasoline engines...
do not need as high filtration efficiencies or precious metal loading in the filter.

The DPFs have already been used for years in all road diesels in Europe. In the emission regulations of NRMM, the next step in 2019 will be the introduction of nonvolatile particle number limit, which will enforce the DPFs systematically in Europe. Based on the findings of this study and the others, the introduction of DPFs will not only create benefit in terms of primary (or fresh) particle emission but also secondary organic aerosol formation in the atmosphere. Actually, the DPF appears to offer additional benefits in decreasing secondary aerosol formation, over the DOC and DOC+SCR systems. The SOA precursor removal mechanisms in the DPF may include adsorption of precursors on the DPF washcoat or the accumulated soot cake and subsequent oxidation. The contribution of oxidation should be dominant, since we observed no outbursts of SOA emissions during high-load high-exhaust temperature events that are known to lead to desorption of semivolatile compounds. Therefore, the DPF seems to eliminate and not just filter out most of these species. Catalyzed DPFs on road vehicles were also demonstrated to yield very low SOA over transient operation and even some SOA formed during regeneration was attributed to the surplus of fuel used to initiate regeneration rather than the desorption of species from the DPF. So far, the effects of these special occasions like the DPF regeneration events or potential ammonia slip events are beyond the scope of this study, and also the real-world events like highly transient driving conditions and engine cold starts may cause higher primary and secondary PM emission levels.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b04073. Elaborated description of the exhaust sampling system, measurement protocol, and steps in data analysis (PDF)

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The research was conducted and the manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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Characterization of laboratory and real driving emissions of individual Euro 6 light-duty vehicles – Fresh particles and secondary aerosol formation


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Characterization of laboratory and real driving emissions of individual Euro 6 light-duty vehicles — Fresh particles and secondary aerosol formation

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Abstract

Emissions from passenger cars are one of major sources that deteriorate urban air quality. This study presents characterization of real-drive emissions from three Euro 6 emission level passenger cars (two gasoline and one diesel) in terms of fresh particles and secondary aerosol formation. The gasoline vehicles were also characterized by chassis dynamometer studies. In the real-drive study, the particle number emissions during regular driving were 1.1-12.7 times greater than observed in the laboratory tests (4.8 times greater on average), which may be caused by more effective nucleation process when diluted by real polluted and humid ambient air. However, the emission factors measured in laboratory were still much higher than the regulatory value of 6 × 1011 particles km−1. The higher emission factors measured here result probably from the fact that the regulatory limit considers only non-volatile particles larger than 23 nm, whereas here, all particles (also volatile) larger than 3 nm were measured. Secondary aerosol formation potential was the highest after a vehicle cold start when most of the secondary mass was organics. After the cold start, the relative contributions of ammonium, sulfate and nitrate increased. Using a novel approach to study secondary aerosol formation under real-drive conditions with the chase method resulted mostly in fewer emission factors below detection limit, which was not in disagreement with the laboratory findings.

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1. Introduction

Traffic is an important source of both gaseous and particle pollutants (Hasheminassab et al., 2014; Pant and Harrison, 2013; Perez et al., 2010; Rakowska et al., 2014). While the emissions of some of these pollutants are effectively regulated, the formation potential of secondary aerosol or emissions of small (<23 nm) and volatile particles are not directly controlled. European Regulations on vehicle exhaust particle emissions address the number of non-volatile particles with the size of a minimum 50% cutpoint at 23 nm (Commission Regulation (EU) 2017/1151). For light-duty vehicles, the particle number (PN) limit is set to 6 × 1011 particles km−1 and this is applicable to diesel vehicles and gasoline vehicles equipped with direct injection engines. This limit is now well
established and a thorough methodology exists on how to measure and quantify non-volatile particle emissions. However, it is not clear why we should only limit the emissions of this specific fraction of all exhaust particles. The vehicle exhaust plume in the atmosphere contains particle fractions of different volatility, including volatile, semi-volatile and non-volatile ones (Biswas et al., 2007; Momenimovahed et al., 2015; Wang et al., 2017), which have been formed either in the engine (Malmberg et al., 2017), during the dilution process (Ronkko et al., 2006), or in the atmosphere by oxidation (Gentner et al., 2017). Second, it is long known that vehicular exhaust contains particles extending much below 23 nm (Kittelson, 1998). Third, the limit value of $6 \times 10^{11}$ particles km$^{-1}$ seems arbitrarily set, as it is not directly associated with any atmospheric, air quality or health specific targets (Giechaskiel et al., 2012). Thus, the current regulation, limited to only one fraction of particles, does not reflect the actual real-world exposure to aerosol emissions from traffic.

What seems to be a questionable regulation in its scientific underpinning, has actually been very effective in introducing advanced particle emission controls on actual vehicles. It has been effectively mandatory since 2009 that all new on-road diesel light-duty vehicles (and off-road engines since 2019) need to be equipped with diesel particle filters (DPFs). Moreover, the EU will be the first region in the world where the large majority of gasoline vehicles sold – those equipped with direct injection engines – will be equipped with gasoline particle filters (GPFs) to comply with PN limits.

The introduction of advanced emission control systems guarantees that the certified vehicles comply with exhaust PN limits. But the use of advanced emission control per se says little about the actual environmental performance of vehicles, as bitter experience from the diesel NOx scandal has recently revealed (Jonson et al., 2006; Saha et al., 2018; Tkacik et al., 2014). In assessing the actual impact, at least in terms of particle emissions, one will need to study both primary emissions but also the propensity of vehicle exhaust to form delayed primary particulate matter (PM) upon dilution (Ronkko et al., 2017) and secondary PM after oxidation in the atmosphere (e.g. Chirico et al., 2010).

Real-world environmental impacts can be assessed by studying vehicles under actual operation and intervening as little as possible with the actual processes that take place between particle emission and atmospheric transformation. Chase experiments (e.g., Giechaskiel et al., 2005; Ronkko et al., 2006) allow the vehicle to be studied under actual operation while its plume is diluted and dispersed in the atmosphere. However, this provides little time (~second) between emission and sampling for any oxidation reactions to occur. The use of an oxidation flow reactor (OFR; Simonen et al., 2017) in sampling plumes while chasing actual vehicles on the road can be a very powerful tool to study the exhaust’s potential to form secondary PM under actual driving conditions. OFRs are needed to determine the organic proportion of the potential secondary aerosol (SOA; secondary organic aerosol) because it is difficult to estimate the SOA formation potential by measuring the gaseous organic precursor emissions (Gentner et al., 2017). For engine exhaust studies, OFRs have mainly been used under laboratory conditions (Friedman et al., 2017; Ilalainen et al., 2018; Jathar et al., 2017; Karjalainen et al., 2016; Link et al., 2017; Pieber et al., 2018; Timonen et al., 2017; Zhao et al., 2018), and to a smaller extent in roadside environments to study pass-by plumes from individual city buses running on different fuels (Watne et al., 2018) or emissions from a vehicle fleet (Liu et al., 2019; Ortega et al., 2016; Saha et al., 2018; Tkacik et al., 2014).

In this study, we present emission factors (EFs) of primary and secondary particle emissions from latest technology light-duty vehicles fueled by diesel and gasoline. The measurements were performed for all the vehicles on a racing track by chasing the vehicles with a mobile laboratory, and for the gasoline vehicles also in the laboratory on a chassis dynamometer. Overall, the study objective is to assess particle emissions under realistic operation environments in comparison to regulated driving cycles while, at the same time, allowing a comprehensive evaluation of all particle matter emission dimensions relevant to urban air quality.

2. Materials and methods

Three Euro 6 light-duty vehicles were tested: a gasoline vehicle equipped with port fuel injection (PF), a gasoline vehicle equipped with direct injection (GDI), and a diesel vehicle. The gasoline vehicles were equipped with three-way catalysts (TWc) and the diesel vehicle with a diesel oxidation catalyst (DOC), a diesel particulate filter (DPF) and a selective catalytic reduction device (SCR). The emissions of all three vehicles were measured in real-drive conditions by chasing, and the emissions of the two gasoline vehicles were additionally characterized by chassis dynamometer testing. The vehicle specifications are shown in detail in Table S1. Standard market fuel was used in all experiments, but the fuel used in the laboratory experiments was not necessarily from the same batch as the fuel used under real-drive tests.

2.1. Laboratory experiments

Chassis dynamometer testing was conducted in an emissions laboratory. The sampling setup for the laboratory measurements is shown in Fig. S1 and is described in detail in the Supporting Information (SI). Shortly, the engine exhaust was sampled from the tailpipe with a setup that has been shown to produce particle size distributions resembling those after a few seconds following atmospheric dilution (Keskinen and Ronkkö, 2010; Ronkko et al., 2006), where the aerosol contains both nonvolatile primary particles and particle matter formed by condensation and nucleation. Regulated gas species (NOx, CO, THC) were determined following vehicle certification regulations, utilizing a constant volume sampling (CVS) system.

Secondary aerosol formation potential was determined by a Tampere Secondary Aerosol Reactor (TSAR), by comparing the particulate mass downstream of the reactor to that of the untreated aerosol, measured in parallel. TSAR is an oxidation flow reactor (OFR) designed for measuring secondary aerosol formation of rapidly changing emission sources, such as vehicles during transient operation (Simonen et al., 2017). In this, the diluted exhaust is mixed with ozone and humidified air, and is then exposed to 254 nm UV radiation, where ozone photolysis produces OH radicals in the presence of H2O. The oxidation reactions between precursor gases present in the exhaust and OH or O3 lead to the formation of secondary aerosol.

Aerosol mass was measured with electrical low pressure impactors (Keskinen et al., 1992) (ELPI; Dekati Ltd.) with improved nanoparticle resolution (Yli-Ojanperä et al., 2010) by integrating the size distribution determined in impactor stages 1–7, corresponding to particles sized up to ~380 nm in aerodynamic diameter. One ELPI sampled the untreated aerosol, herein referred to as ‘fresh’ aerosol, and a second one was used downstream of TSAR to measure the ‘aged’ aerosol. The aged aerosol thus includes both fresh aerosol and secondary aerosol. Aerosol instrumentation was placed downstream of three-way valves, to selectively measure either aged or fresh sample. This included an engine exhaust particle sizer (Johnson et al., 2004) (EEPS; TSI Inc.), an ultrafine condensation particle counter (CPC; CPC 3776, TSI Inc.), a scanning mobility particle sizer (SMPS), and a soot-particle aerosol mass spectrometer (Onasch et al., 2012) (SP-AMS; Aerodyne Research Inc.). Moreover, a CO2 analyzer (Sick Malhak, Sidor) was used to
determine the dilution ratio (DR) at different stages of dilution during steady state driving at 80 km h\(^{-1}\), by comparing upstream and downstream CO\(_2\) concentrations. A SP-AMS (described in detail in the SI) was used to measure the aerosol mass content in total organic aerosol (OA), ions (sulfate, nitrate, ammonium) and refractive black carbon (rBC). Due to the limited time resolution and the dropping detection efficiency of the SP-AMS for small particles, this was only used here to determine particle composition, while mass concentration was determined from ELPI size distributions. For example, the organic mass concentration \(M_{\text{org}}\) is defined by

\[M_{\text{org}} = \frac{O_{\text{AMS}}}{T_{\text{AMS}}} \times M_{\text{ELPI}},\]

where \(O_{\text{AMS}}\) is the organic aerosol mass and \(T_{\text{AMS}}\) is the total mass, respectively, measured by the SP-AMS, and \(M_{\text{ELPI}}\) is the ELPI-determined mass concentration. This approach implicitly assumes that the composition of small particles not detected by the SP-AMS is the same as the particles actually being measured. This assumption is a source of uncertainty for the composition-specific emission factors. However, the effect of the particles below SP-AMS detection limit on the total mass is generally small, as demonstrated in the average mass size distributions in Figs. S4b–c.

While ELPI is advantageous because of its high time resolution, it does not measure the mass directly and thus introduces uncertainty in the particle mass EFs. This uncertainty is evaluated in the SI (Fig. S9) by comparing the mass determined from ELPI size distributions to gravimetrically determined mass EFs, and by inter-comparison between ELPI and EEPS. Shortly, there is a good agreement between ELPI and EEPS for the fresh aerosol mass, but the gravimetric mass is always higher. For the aged aerosol, the mass determined from ELPI is approximately three times higher than that from EEPS. This may partly depend on the assumption of unit density, but it is also possible that the aged mass determined from ELPI is slightly overestimated.

In the laboratory experiments, the driving cycles were the cold-start New European Driving Cycle (NEDC), the warm-start NEDC, and the warm-start Worldwide Harmonized Light Vehicles Test Cycle (WLTC). In addition, steady state driving at 80 km h\(^{-1}\) was measured for each vehicle. The laboratory schedule is presented in Table S2. Only one cold-start NEDC and warm-start WLTC were measured for each vehicle, and the SP-AMS measured the aged sample during these cycles. Thus, the concentration of fresh OA is unknown in these cases and the amount of potential SOA is approximated by assuming that all fresh aerosol is organic, which may underestimate the SOA formation potential. For the warm-start NEDC and 80 km h\(^{-1}\) steady cycles, the composition of fresh aerosol was measured (although during a separate driving cycle for the warm-start NEDC), so the SOA production factor (PF) is calculated by subtracting the fresh OA EF from the aged OA EF. The sampling setup was not functioning during the cold-start NEDC for the PFI, and thus no particle emission data is available for this driving cycle.

The PF was determined for the total driving cycles but also for specific sections in the cycles, which are hereafter called ‘slow acceleration’ and ‘fast acceleration’. The EFs for slow accelerations are calculated from four identical acceleration phases of warm-start NEDCs, where the vehicle accelerates from 0 to 50 km h\(^{-1}\). The fast acceleration EF is calculated from the warm-start WLTC at 958 s after start, where the vehicle accelerates from 25 to 50 km h\(^{-1}\).

2.2. Real-driving experiments

The real-driving emissions were determined by chase measurements. The chase experiments were conducted at the Säntis racing track, Greece (41°04′20.9″N 23°31′01.4″E; track length 3.2 km). The track is located 3 km southwest of Säntis city center and is surrounded by fields. The measurements lasted for three days, and the schedule with associated ambient conditions is presented in Tables S2–3. All vehicles were equipped with a Portable Emissions Measurement System (PEMS; AVL M.O.V.E Gas PEMS IS) to measure second by second concentrations of CO, CO\(_2\), NO and NO\(_2\) in the tailpipe. In addition, the on-board diagnostics (OBD) data and vehicle coordinates from a GPS device were logged.

The vehicles were chased by the Tampere University Mobile Laboratory, which is a large van equipped with stainless steel sampling lines and instruments to measure exhaust emissions (Rönkkö et al., 2017). The sample was drawn from the lower-mid sampling line at the front of the vehicle, which is located approximately 50 cm above ground. A weather station (Weather Station 200WX; Airmar Technology Corporation) on the roof of the van recorded the ambient temperature, humidity and the coordinates from GPS. The sampling setup is shown in Fig. S10. The sample was drawn directly to a CO\(_2\) analyzer, ELPI, CPC and TSAR. Similar to the lab measurements, the first ELPI was used to determine fresh aerosol mass and a second ELPI downstream of TSAR determined aged aerosol concentrations. A low dilution of 1.9:1 preceding the second ELPI was necessary to keep the total flow rate through the upstream TSAR at 5 lpm. The SP-AMS was installed in the mobile laboratory, but it was not possible to distinguish the composition of exhaust aerosol from the dominating background mass.

All the vehicles drove similar driving patterns at the track: regular driving with varying speed and stops, steady state driving at 80 km h\(^{-1}\), slow accelerations from 0 to 50 km h\(^{-1}\) (identical to the accelerations in the NEDC), and fast accelerations from 20 km h\(^{-1}\) to 50 km h\(^{-1}\) (resembling a fast acceleration in the WLTC). The steady state driving at 80 km h\(^{-1}\) performed on-road is not directly comparable to the laboratory steady driving. In the laboratory, the vehicle was allowed to stabilize after reaching the speed of 80 km h\(^{-1}\), whereas on the track, the measurement started directly after the acceleration, so that some of the particles measured may actually have originated from the acceleration rather than from the steady speed driving, which lasted for approximately 10 s. In addition, the chassis dynamometer NEDC slow acceleration was not representative of the real-drive slow acceleration despite the similar speed profiles, because the type-approval dynamometer load setting in the NEDC was not the same as the actual road load (Mock et al., 2012). The engine was warmed up by driving at least 5 min before the actual measurements.

2.3. Data analysis

Emission factors (EF) of any compound were determined by eq. (2):

\[EF = \frac{\left[\frac{C(t)}{\text{bg}}\right] - \left[\frac{C_{\text{fg}}}{\text{bg}}\right] \times DR(t) \times Q_{\text{exh}}(t) \text{d}t}{N}.\]

where \([C]/[\text{bg}]\) is the time-dependent concentration, \([C_{\text{fg}}]/[\text{bg}]\) is the background concentration, DR is the total dilution ratio, \(Q_{\text{exh}}\) is the volumetric exhaust flow and \(N\) is the quantity to which emissions are normalized (e.g., fuel consumed or distance travelled). In laboratory experiments, the volumetric exhaust flow was calculated from the flow rate and the DR of the CVS. In chase experiments, the exhaust flow was calculated from the engine intake air pressure or intake airflow data combined with the PEMS gas concentration data (SI). The secondary mass PFs were calculated by subtracting the fresh aerosol mass EFs from the aged mass EFs.
In the laboratory measurements, DR was constant and [Cbg] was zero except for the aged mass. The aged mass background was determined by oxidizing pure humidified dilution air with TSAR. In the chase measurements, DR depends on the chase distance and the plume behavior, and was calculated by eq. (3):

$$DR(t) = \frac{[CO_2,\text{raw}](t) - [CO_2,\text{bg}](t)}{[CO_2,\text{dil}](t) - [CO_2,\text{bg}](t)},$$

where $[CO_2,\text{raw}]$ is the raw exhaust CO$_2$ concentration measured by PEMS, $[CO_2,\text{bg}]$ is the background CO$_2$ concentration, and $[CO_2,\text{dil}]$ is the CO$_2$ concentration measured by the mobile laboratory. When defining the EF for the aged aerosol (downstream of TSAR), $[CO_2,\text{raw}]$ and $Q_{\text{exh}}$ are convolved with the residence time distribution of TSAR to take the TSAR delay into account (SI). When calculating the real-drive EFs, we neglect the data where DR was negative or higher than 6000:1.

To determine the background concentrations in real-drive measurements, we assumed that due to the required distance between the mobile laboratory and the vehicle chased, the in-van instruments occasionally unintentionally sampled background air instead of the exhaust plume even when chasing the vehicle. Thus, for a CO$_2$ value measured at time $t$ ([CO$_2$]$_{\text{dil}}(t)$), we define the background concentration ([CO$_2$]$_{\text{bg}}(t)$) as the third CO$_2$ concentrations percentile between t-2 min and t+2 min. The background number and mass concentrations measured by CPC and ELPIs were defined similarly, but the 15th percentile was used because of the higher deviation in the particle measurements. A comparison between the calculated background levels and the actual background concentrations measured while not chasing a vehicle is shown in Fig. S11.

While this approach is suitable to estimate the regional background, it cannot distinguish short peaks of background pollutants from the vehicle exhaust. As a result, the potential noise in background concentration causes a bias in the EF calculated by eq. (2). To estimate the effect of varying background emissions on the calculated EFs, we performed reference measurements by driving around the track without chasing any vehicle. Based on these measurements, we determined the background noise level for the emission factor (EF$_{\text{bg}}$) for each chase measurement by means of eq. (4):

$$EF_{\text{bg}} = \frac{\left[C_{\text{ref}}\right] \times DR(t) \times Q_{\text{exh}}(t)dt}{N},$$

where $C_{\text{ref}}$ is the average background-corrected concentration of the pollutant during the closest reference measurement, whereas DR, $Q_{\text{exh}}$ and N are the values from the actual chase measurement. Effectively, EF$_{\text{bg}}$ defines the EF that would be calculated for a vehicle with no pollutant emissions, and this EF will be nonzero due to the noise in the background concentrations. A similar approach to define EFs below threshold has been used by Wang et al. (2015).

### 3. Results and discussion

Particle emissions and secondary aerosol formation potential are discussed in the following sections. The EFs are normalized to the distance travelled, with emissions normalized to fuel consumed available in the SI. The regulated emissions measured both in laboratory and under real-drive conditions are presented in Table S4.

#### 3.1. Emission factors of particle number

Fig. 1a shows the fresh background-corrected average particle number concentrations measured by a CPC during fast accelerations in chase experiments. The corresponding vehicle speeds and background-corrected CO$_2$ levels are shown in Fig. 1b. The highest particle number concentrations were measured when chasing the PFI, while only a small peak in concentration is observed in the wake of the diesel vehicle. However, due to different dilution ratios, it is necessary to compare the EFs instead of the absolute particle concentrations. Emission factors for fresh particle number for the laboratory measurements are shown in Fig. 2a–b. Values in Fig. 2a correspond to particles above 3 nm measured by a CPC, whereas Fig. 2b shows values corresponding to particles larger than 7 nm, as measured by an ELPI. The error bars for laboratory measurements in Fig. 2 show the standard deviation of two or more repetitions, and EFs without error bars are calculated from a single measurement. Fresh particle emissions of both gasoline vehicles exceeded the limit defined in the Euro 6 regulation. This is only to put levels into perspective, as fresh particles include volatile and semi-volatile ones and range down to 3 nm, while the limit only addresses non-volatile particles larger than 23 nm from diesel and GDI vehicles. The results obtained in the lab indicate that PFI vehicles that are not controlled by regulations emit significant numbers of fresh particles.

The average real-drive EFs for particles larger than 3 nm and 7 nm are shown in Fig. 2c–d along with the average background noise levels. The error bars for the real-drive EFs indicate the minimum and maximum values of the calculated EFs. For the cases where EFs are close to or below the background noise, the actual EF can be anything between zero and the measured EF.

The diesel vehicle EFs were below or very close to the background noise level, indicating low particle emissions. This shows that the DPF was effective at controlling total fresh particle emissions.
emissions, even during real-world driving. Only during slow accelerations did diesel emissions occasionally appear higher than the average background. These cases had higher uncertainties, since the DR and \( Q_{\text{exh}} \) were approximated based on the fast acceleration data, as the PEMS was not functioning during the slow acceleration cases driven with the diesel vehicle. The DR was approximated by assuming an inverse correlation between DR and the measured CO2, and acquiring the fitting parameter from the fast acceleration cases. Similarly, we assumed that \( Q_{\text{exh}} \) depends on vehicle speed and acceleration, and fitted a polynomial function to these parameters for the fast acceleration cases and used the same fits for the slow accelerations. The high variation in the slow acceleration EFs and the difference in the absolute level of the EFs (compared to regular driving and fast acceleration cases) suggest that the high EFs may also be an artefact from a background source or that the vehicle occasionally emits high amounts of particles during this acceleration due to factors such as DPF regeneration or a storage-release phenomena of semivolatile particle precursors in the aftertreatment system (Karjalainen et al., 2014a).

On the contrary, a clear signal for particles larger than 3 nm was produced by the petrol vehicles, with the PFI being higher than the GDI, similar to the laboratory results. In addition, there was more absolute variation in the EFs for the PFI than the other vehicles, which may indicate unstable operation of the PFI under real-driving conditions. The difference between the PFI and GDI was largest during accelerations, where the PFI emitted 3–4 times more particles than the GDI. The PFI particle emissions were more sensitive to the driving condition than the GDI, since the EF of fast acceleration for the PFI was 4.6 times higher than that of steady state driving at 80 km h\(^{-1}\), whereas for the GDI, this ratio was 2.2.

Both gasoline vehicles emitted more particles under real-drive conditions than in laboratory driving based on the EFs determined by CPC. However, the difference between the real-drive and laboratory EFs was much higher for the PFI than the GDI. For example, in slow acceleration the PFI real-driving EF was 5.7 times the laboratory EF, whereas the GDI real-driving EF was 3.4 times the laboratory EF.

More small particles (approximately in range 3–7 nm) were emitted or nucleated under real-drive conditions than in the laboratory based on the EFs determined from the CPC with 3 nm cutpoint and ELPI with 7 nm cutpoint. In the laboratory experiments, the EFs calculated based on the number concentration measured by ELPI and CPC were almost equal, whereas in real-drive measurements the CPC-originated EFs were significantly higher during regular driving and slow acceleration while the ELPI-originated EFs were often close to or below the detection limit. There are several possible reasons for the higher amount of the small particles under real-drive conditions. First, the vehicle operation during the real-drive test may differ from the laboratory operation because of factors such as different engine loads. For example, the average real-driving CO2 EFs for regular driving were 1.4–1.5 times higher than the laboratory cycle EFs (Table S4). Second, the driving history can be different, leading to a difference in storage-release phenomena of particle precursors in the catalyst, which affect the nucleation mode particle emissions (Karjalainen et al., 2014b, 2014a). Third, nucleation mode particle formation is sensitive to the relative humidity and temperature of the dilution air (Ronkko et al., 2006). Even though the laboratory sampling setup simulates the atmospheric delayed primary particle formation, the used 30 °C dry dilution air may not be able to simulate the actual particle formation in the real-driving conditions in this study, where the average ambient temperatures were 11.8–17.7 °C and relative humidity was higher than 50%. It has been shown earlier that the EFs of volatile particles are higher at lower temperatures (Wang et al., 2017), and the relative humidity affects at least the nucleation dynamics of sulfuric acid and water (Brus et al., 2010).

Previous studies have shown that the particle EFs for GDI vehicles usually exceed those for the PFI vehicles (Chen et al., 2017;
Mamakos et al., 2012; Zhu et al., 2016). The results obtained in this study both in laboratory and under real-drive conditions seem to disagree with the previous studies, since we found higher particle number EFs for the PFI vehicle. However, this is not necessarily a disagreement, since the measurement technique in this study differs from the aforementioned studies. We measured all particles larger than 3 nm, whereas the previous studies report the EFs for solid particles only. Thus, it is possible that the higher EFs for the PFI observed here result from higher emissions of volatile particles.

The hypothesis is supported by the particle number size distributions in Fig. S4a. The accumulation mode, which often contains non-volatile soot particles, is higher for the GDI, whereas the nucleation mode is higher for the PFI. A similar phenomenon was observed by Saliba et al. (2017). We note that we cannot make strong conclusions regarding the two engine technologies because only two vehicles were tested, and we cannot distinguish the solid and volatile fractions based on our measurements.

3.2. Emission factors of particle mass

Because of the low signal-to-noise ratio, the actual real-driving EFs for the fresh and aged aerosol mass could not be determined in most cases. Thus, we only shortly discuss the results here, and show the emission factors in Fig. S12.

In the laboratory, the EFs for both gasoline vehicles were less than 0.2 mg km$^{-1}$, except for the fast acceleration case, where the PFI emitted 0.85 mg km$^{-1}$ and the GDI 0.25 mg km$^{-1}$. In real-drive conditions, the average EFs were below the average background noise levels except for the slow acceleration of the diesel vehicle. This is similar to what was observed for the particle number emissions of the diesel vehicle.

The particulate mass of the aged exhaust in laboratory experiments was always higher than the fresh aerosol mass, and is discussed in Sect 3.3. In real-drive measurements, it was challenging to determine the secondary aerosol formation by the chase method due to the high background noise in the aged mass, similar to the fresh aerosol mass measurements. The only case where the average aged aerosol EF was higher than the background noise was the fast acceleration with the PFI, which also produced the highest EF in the laboratory measurements. However, the real-drive EF in this case was lower than the laboratory EF, and also in the other cases the real-drive EFs of the aged mass were close to the laboratory EFs despite the background influence (Fig. S12). Thus, even though the background noise prevented the determination of exact PFs for the secondary mass, we can deduce that the secondary aerosol formation potential under real-drive conditions was not significantly higher than in laboratory measurements.

3.3. Aged exhaust aerosol in laboratory

The time series of aged organic aerosol mass (average 7–13 days equivalent atmospheric aging; see Fig. 4 and Fig. S2) and fresh aerosol mass measured for the laboratory driving cycles and one real-drive cold start are shown in Fig. 3. To make the fresh aerosol mass and aged mass comparable, the fresh aerosol mass data in the figure is convolved with the TSAR residence time distribution. An average mass particle size distribution of the aged aerosol during an acceleration is shown in Fig. S4c, and the time-resolved particle number size distributions of the aged aerosol during the NEDCs and the WLTCs are shown in Figs. S6 and S8, respectively.

We do not have a direct measurement of SOA formation from the exhaust because the fresh OA was not measured simultaneously with the aged OA. However, when the aged OA is higher than the total fresh aerosol mass, there is obviously SOA formation in TSAR. The most apparent transient SOA formation phenomenon is observed during the GDI cold-start driving cycle (Fig. 3a). The SOA formation begins immediately after the engine start and exceeds the SOA observed during the hot-start cycle by approximately a factor of 25 at maximum. This is reflected in the SOA production factor so that the GDI cold-start NEDC produces 5 times more SOA than the hot NEDC (Fig. 4). Approximately 200 s after the cold start, the aged OA levels off, and its profile for the rest of the cycle is close to that of the hot-start cycle. A similar secondary aerosol formation event was observed for the PFI cold-start at track conditions, measured with the chase measurement set-up (Fig. 3d). This is the only case where a clear signal above the detection limit could be obtained for the aged mass under real-drive conditions, as discussed in the previous section. Thus, in this section, we analyze only the aged mass determined in the laboratory studies.

The high SOA formation in the beginning of the cold-start cycles has been reported in several earlier publications (Karjalainen et al., 2016; Pieber et al., 2018; Timonen et al., 2017), and is most probably related to the catalyst temperature. Specifically, the catalyst temperature during cold start is too low to oxidize the emitted hydrocarbons and thus they are available for oxidation in the OFR. By using the TSAR designed for high time resolution, it allows us to analyze driving condition dependent SOA formation, in contrast to other publications using the potential aerosol mass (PAM) reactor (Kang et al., 2007; Lambre et al., 2011) (see SI).

The SOA formation from the PFI exhaust in the TSAR seems to depend strongly on driving condition, as it was the case for both number and mass EFs. For the PFI hot NEDC (Fig. 3b), there was a peak in SOA formation both in the beginning of the cycle during the first acceleration from 0 to 30 km h$^{-1}$ and at the end of the cycle during high speed driving and acceleration from 100 to 120 km h$^{-1}$. For the PFI cold NEDC (Fig. 3e), there were several peaks in the aged OA, the highest ones again in the beginning of the cycle and for the acceleration at the end of the cycle. On the other hand, the SOA formation decreased when driving at a relatively constant speed of 90 km h$^{-1}$ starting from 1200 s after the start of the WLTC.

The SOA formation from the GDI exhaust showed much less transient behavior than the PFI. For the NEDC (Fig. 3c), the aged OA was relatively constant throughout the cycle with a slight increase for the high-speed part of the cycle. The absolute levels of aged OA were almost equal in the WLTC and in the NEDC, except for a few peaks during high-speed driving at the end of the WLTC.

The differences between the two gasoline vehicles regarding the SOA formation in the TSAR are evident in Fig. 4, where the total SOA production factors are presented. The steady driving at 80 km h$^{-1}$ and hot WLTC with PFI had the lowest and highest PFs of SOA at hot engine operation, respectively, with 3.5 times difference between the two. In contrast, the production of SOA with GDI was almost independent of driving conditions, since the steady state driving at 80 km h$^{-1}$ produced almost equal amount of SOA as the other warm-start driving cycles. The differences in SOA production demonstrate vehicle-to-vehicle variation and cannot be addressed to the different gasoline injection technologies since only two vehicles were tested. A larger set of vehicles was tested by Zhao et al. (2018) in an engine laboratory. Using a PAM reactor, they found no difference between GDI and PFI vehicles in total SOA production integrated over the phases of a driving cycle. However, it is not possible to analyze the dependence of SOA formation on specific driving conditions by using a PAM reactor because of its long residence time. Thus, the two engine technologies may behave differently in terms of SOA production under transient driving conditions even when the integrated SOA production over a certain test cycle is equal.

Most previous studies on gasoline vehicle SOA formation potential report SOA PFs only for cold-start driving cycles (Karjalainen et al., 2016; Pieber et al., 2018; Timonen et al., 2017; Zhao et al.,
2018). The GDI cold-start NEDC SOA formation potential observed here is on the same order of magnitude as PFs of previous publications. Also, the warm-start SOA PFs agree with previously reported SOA PFs of warm-start cycles (Gordon et al., 2014a) (0–20 mg kg\textsubscript{fuel}\textsuperscript{−1}) and warmed-up phases of cold-start cycles (Karjalainen et al., 2016; Pieber et al., 2018) (0.5–1.5 mg km\textsuperscript{−1} and 5–15 mg kg\textsubscript{fuel}\textsuperscript{−1}).

To give a perspective on vehicle SOA formation potential, we compare the warm-start cycle SOA PFs measured in laboratory to SOA PFs from large vehicle fleets determined by roadside and tunnel measurements. The SOA PFs reported for vehicle fleets are 200–400 mg kg\textsubscript{fuel}\textsuperscript{−1} (at 1–8 days eq. photo-oxidation) (Liu et al., 2019; Tkacik et al., 2014) or 40–190 μg m\textsuperscript{−3} ppm\textsuperscript{−1} (at 2–9 days eq. photo-oxidation; normalized to CO concentration) (Saha et al., 2018). These values are much higher than the 8–21 mg kg\textsubscript{fuel}\textsuperscript{−1} or 2–15 μg m\textsuperscript{−3} ppm\textsuperscript{−1} (Figs. S15–16) measured here for the hot-engine operation, which indicates that the SOA formation potential from Euro 6 gasoline vehicles is significantly lower than that of the average fleet in these studies. Even though the Euro 6 values here were measured in the laboratory, the real-drive SOA formation potential of these vehicles is not expected to be significantly higher, because the real-drive measurements were below the detection limit as discussed in Section 3.2 and close to the values measured in the laboratory (Fig. S12). However, a significant difference between this study and the results from larger vehicle fleets is that the latter are measurements of a complex mixture of vehicle exhaust and urban air, whereas we sampled the exhaust of only one vehicle at time.

Even though the SOA formation from Euro 6 gasoline vehicles in this study is lower than that of the vehicle fleets spanning a wide range of model years, it is not guaranteed that the modernization of the vehicle fleet results in lower ambient SOA formation. The oxidation pathways of SOA precursors depend on the ambient NO\textsubscript{X} concentrations, and decreasing NO\textsubscript{X} concentrations may lead to increased SOA formation, despite the low-emitting vehicles (Zhao et al., 2017).

The diesel vehicle emissions were not measured in laboratory conditions. However, we note that previous research showed negligible SOA formation from diesel vehicles equipped with DPFs (Gordon et al., 2014b; Platt et al., 2017). We also measured the aged aerosol mass of another Euro 6 diesel vehicle in the emission laboratory (SI), and found that the aged OA mass was usually below the detection limit. Occasionally, we observed peaks of mass in the aged exhaust of the diesel vehicle at the end of the cycles, but this consisted mainly of ammonium nitrate and the highest peak was related to a regeneration of the DPF (Fig. S3).

The average aerosol compositions presented in Fig. 3 show that the dominant part of aged mass for both gasoline vehicles is inorganic. Mostly the aged inorganic mass is ammonium nitrate, but also a significant contribution of sulfate is observed for the PFI during the NEDC. Some of the sulfur is in the gas phase prior to TSAR because the SO\textsubscript{4}:rBC ratio is higher in the aged aerosol than in the fresh aerosol. The precursor for the secondary sulfate aerosol is presumably SO\textsubscript{2}, which oxidizes in TSAR to form SO\textsubscript{4}, which further produces sulfuric acid. Maricq et al. (2002) have shown that during the beginning of a driving cycle, the sulfur from the gasoline vehicle exhaust is stored in the three-way catalyst, from where it is released as SO\textsubscript{2} during fast accelerations at the end of the cycle. The behavior of sulfur in PFI exhaust in the NEDC here seems to be
consistent with the observations by Maricq et al. as the sulfate is formed in TSAR at the end of the cycle (Fig. S17).

The secondary ammonium nitrate is formed when the ammonia in the exhaust reacts with nitric acid. Nitric acid (HNO₃) in TSAR is formed when the NO in the exhaust reacts with O₂ to form NO₂, and NO₂ further reacts with OH to form HNO₃. Thus, whenever there is ammonia and NO or NO₂ present in the exhaust, there will be ammonium nitrate formation in TSAR. The ammonia in gasoline vehicle exhaust is formed in the three-way catalyst (Heeb et al., 2006) and both ammonia emissions (Suarez-Bertoa et al., 2014; Suarez-Bertoa and Astorga, 2016) and formation of secondary ammonium nitrate from gasoline vehicle exhaust are frequently observed (Link et al., 2017; Nordin et al., 2013; Pieber et al., 2018).

4. Conclusions

The number emissions of fresh particles larger than 7 nm for three Euro 6 vehicles measured in this study in real-drive use were generally below background noise. However, by extending the measured particle size range down to 3 nm, we observed that the real-drive particle emissions for the gasoline vehicles were significantly higher than the corresponding emissions measured in laboratory, whereas the diesel vehicle emissions also in this size range were below background noise levels. The results cannot be generalized to different engine or aftertreatment technologies, but the high vehicle-to-vehicle variation highlights the need for real-drive tests to gain knowledge on exposure-relevant particle emissions and implications on air quality. Clearly, the current regulated particle emissions, considering only solid particles larger than 23 nm, do not reflect the actual emissions for all of the three vehicles measured here, despite all of them belonging to the same Euro 6 class.

In addition, the real-drive secondary aerosol formation potential was below the detection limit, and thus we expect that the laboratory-derived SOA production factors are representative of real driving SOA formation potential. The SOA PFs determined in the laboratory for warmed-up Euro 6 gasoline vehicles are approximately a tenth of the SOA PFs measured for vehicle fleets, and even lower for DPF-equipped diesel vehicles according to this study and two others (Gordon et al., 2014b; Platt et al., 2017). Thus, increasing the proportion of Euro 6 light-duty vehicles in the vehicle fleet will likely diminish the atmospheric traffic-related SOA formation. However, Zhao et al. (2017) showed that transformation to modern gasoline vehicles does not necessarily reduce the SOA concentrations if the ambient NOₓ levels decrease simultaneously. In addition to SOA, a comparable amount of inorganic secondary aerosol was formed from gasoline vehicle exhaust, mainly consisting of ammonium nitrate. Regulation of ammonia emissions should be considered to mitigate the effect of gasoline vehicles on urban air quality (Link et al., 2017).

Due to relatively low emissions of the studied Euro 6 vehicles, it was usually difficult to distinguish the vehicle emissions from the background when chasing a single vehicle. Thus, sampling the exhaust directly from the tailpipe as in PEMS applications may be better suitable for real-drive emission measurements than the chase method. However, this would require a specific dilution system for the fresh PN and the aged aerosol measurement. It is not clear whether the differences in EFs for particle number between laboratory and chase measurement were a function of the atmospheric dilution process or different vehicle operation. If the higher EFs were caused by nucleation during the atmospheric dilution (as discussed by Keskinen and Ronkko, 2010), a PEMS dilution system may not be able to replicate the atmospheric particle formation and would not report exposure-relevant EFs for particle number. In addition, fitting all the equipment needed for the fresh PN and aged aerosol measurement on-board of a light-duty vehicle would be challenging. Another option to determine EFs for low-emitting vehicles is to conduct the chase experiments in a cleaner environment.

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Appendix A. Supplementary data

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References


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Estimating errors in vehicle secondary aerosol production factors due to oxidation flow reactor response time

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Estimating errors in vehicle secondary aerosol production factors due to oxidation flow reactor response time

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Abstract. Oxidation flow reactors used in secondary aerosol research do not immediately respond to changes in the inlet concentration of precursor gases because of their broad transfer functions. This is an issue when measuring the vehicular secondary aerosol formation in transient driving cycles because the secondary aerosol measured at the oxidation flow reactor outlet does not correspond to the rapid changes in the exhaust flow rate. Since the secondary aerosol production factor is determined by multiplying the secondary aerosol mass with the exhaust flow rate, the misalignment between the two leads to incorrect production factors. This study evaluates the extent of the error in production factors due to oxidation flow reactor transfer functions by using synthetic and semi-synthetic exhaust emission data. It was found that the transfer function-related error could be eliminated when only the total production factor of full cycle was measured using constant volume sampling. For shorter segments within a driving cycle, a narrower transfer function led to smaller error. Even with a narrow transfer function, the oxidation flow reactor could report production factors that were more than 10 times higher than the true production factors if the segment duration was too short.

1 Introduction

Aerosol particles affect human health, climate and visibility (Pöschl, 2005; Seinfeld and Pandis, 2006). Organic compounds comprise approximately 20-90% of fine aerosol mass (Kanakidou et al., 2005), and a substantial fraction of organic aerosol originates from secondary aerosol formation (Zhang et al., 2007; Hallquist et al., 2009). The secondary organic aerosol (SOA) is formed in the atmosphere via oxidation of precursor gases. Resolving the total atmospheric SOA budget and the contributions from biogenic and anthropogenic sources is challenging, but it is estimated that the majority of SOA origins from biogenic sources. (Hallquist et al., 2009)

While SOA production from biogenic sources is globally higher than that of anthropogenic sources, the organic aerosol concentrations in large cities are dominated by anthropogenic SOA. High population density combined with local precursor emission sources results in significant contribution to air pollution mortality from anthropogenic SOA. (Nault et al., 2021) Nault et al. (2021) studied the health effects of anthropogenic SOA and used a set of aromatic precursor gases as a proxy for...
total anthropogenic organic precursor emissions in selected cities. 20-62 m-% of these emissions originated from gasoline and diesel exhaust and fuel evaporation, which implies that vehicles are an important source of SOA in urban environments.

Vehicular SOA production is not currently directly regulated. Since SOA originates from gaseous organic compounds, limitations for hydrocarbon (HC) emissions indirectly limit SOA production but there is no universal constant to convert the measured HC emissions to potential SOA formation in the atmosphere. Thus, reduction of HC emission does not linearly translate to reduced SOA formation. Regulating the SOA production specifically would require measuring the SOA production factors (i.e., amount of potential SOA from emissions per fuel consumed) with smog chambers or oxidation flow reactors (OFRs).

SOA production factors (PFs) from vehicles have been measured with smog chambers by driving a driving cycle and injecting the exhaust to the smog chamber during the cycle (e.g., Gordon et al. (2014a); Platt et al. (2013)). The chambers are typically operated in batch mode, so that the oxidation in the chamber is actuated after the driving cycle is finished. The advantage of smog chambers compared to oxidation flow reactors is that the photochemistry and aerosol processes resemble tropospheric conditions better. In contrast, the oxidant concentrations in OFRs are orders of magnitudes higher, which can introduce non-tropospheric effects (Peng and Jimenez, 2020). The OFRs are operated in continuous flow mode, which enables measurement of SOA production factors with good temporal resolution. Smog chamber experiments provide only the total SOA production factor of the driving cycle, while OFR measurements can resolve how the SOA production differs between different driving conditions within the driving cycle. However, the delay caused by the residence time of the sample in the OFR complicates the calculation of SOA production factors. In this work, we address these complications.

While it is possible to measure HC and other pollutants directly from the tailpipe with only a small delay originating from the instrument response, the response time associated with a continuous SOA measurement using an OFR is significantly longer. Considering that potential SOA is always dependent on emitted HC to some extent, a natural first approach to address this issue can be formulated as: How accurately could we estimate the HC emission by measuring HC at (non-oxidizing) flow reactor outlet instead of measuring directly from tailpipe?

When calculating the emission rates (g s\(^{-1}\)) or the total emission (g) of the exhaust gases, the gas concentrations in the tailpipe need to be multiplied with the exhaust flow rate. The total emission of gas \(C\) (in g) is calculated by

\[
C_{\text{emitted}} = \int_{t_0}^{t_f} [C]_{\text{true}}(t)Q_{\text{exh}}(t)\,dt, \tag{1}
\]

where \(t_0\) and \(t_f\) are the start and end times of a driving cycle or event of interest, respectively, \([C]_{\text{true}}\) is the gas concentration (g m\(^{-3}\)) in tailpipe, \(Q_{\text{exh}}\) is the volumetric exhaust flow rate (m\(^3\) s\(^{-1}\)) and the product of \([C]_{\text{true}}\) and \(Q_{\text{exh}}\) is the emission rate (g s\(^{-1}\)).

If the gas concentration (e.g. \([HC]\)) is measured at the OFR outlet instead of the tailpipe, the emission rate and subsequently the total emission will be affected as illustrated in Fig. 1 (assuming that the OFR UV lamps are off so that none of the HC will be oxidized). This is because the gas concentration is modified by the OFR residence time distribution (RTD): the gas
Figure 1. Determining HC emission by measuring HC concentration directly from tailpipe ([HC]_{true}) or downstream of an OFR ([HC]_{OFR}) and multiplying the concentrations with the engine exhaust flow rate (Q_{exh}). In this example, the OFR UV lamps are off so that none of the HC is oxidized. Even though the HC concentration at OFR outlet is lower because of OFR residence time distribution (RTD), the total integral is equal to that of the tailpipe HC concentration. However, the HC measured at OFR outlet will lead to underestimated HC emission because the area under OFR emission rate curve is smaller than the true area.

Concentration at OFR outlet is result of convolution of the original gas concentration and the OFR transfer function, $E$. The transfer function is the RTD of a Dirac delta input impulse. (Fogler, 2006) Thus,

$$[C]_{OFR}(t) = ([C]_{true} * E)(t) = \int_{0}^{t} [C]_{true}(\tau) E(t-\tau) \, d\tau,$$

(2)

where $[C]_{OFR}$ is the gas concentration at OFR outlet (assuming no dilution) and $[C]_{true}$ is the concentration in tailpipe. As shown in Fig. 1, multiplication of $[C]_{OFR}$ with the exhaust flow rate does not lead to the correct emission when the exhaust flow rate is not constant. Determining the correct emission would require solving for $[C]_{true}$ from the OFR measurements. Even though the transfer function $E$ can be determined, it is usually impossible to unambiguously solve for $[C]_{true}$ in Eq. 2 because this is an ill-posed inverse problem. Thus, it is not trivial to determine the SOA production factors from driving cycles with variable driving conditions where the exhaust flow rate is not constant.
Despite the difficulties in calculating SOA PFs with OFRs, this issue is not addressed in earlier publications (Karjalainen et al., 2016; Timonen et al., 2017; Simonen et al., 2019; Pieber et al., 2018; Zhang et al., 2023). Zhao et al. (2018) recognized the problem, but there is no analysis on the magnitude of error caused by the OFR transfer function. It is necessary to estimate how large an error is caused by OFRs with different transfer functions and to determine how to best account for the transfer function when analyzing the data.

Similar issues have been studied for situations where the exhaust system, sampling lines and non-ideal instrument response cause delay and distortion to exhaust gas or particle measurements (Ganesan and Clark, 2001; Ajtay and Weilenmann, 2004; Hawley et al., 2003; Weilenmann et al., 2003; Madireddy and Clark, 2006; Geivanidis and Samaras, 2007; Franco, 2014; Giechaskiel et al., 2021). Mahadevan et al. (2016) studied the error in gaseous emission factors in test cycles due to the phenomena mentioned above. They found that the error could be as high as 51% when using non-corrected data, and 25% after applying a constant time shift to correct for the delay. The effect of delay and distortion is significantly higher for OFRs because their dynamic response is much slower than that of gas analyzers or transportation lines.

In this study, we first present the theoretical background for calculating the SOA PF of vehicles running a transient driving cycle. Second, we study the OFR response in two real driving cycles and compare different measurement and data analysis methods. Third, we use synthetic data to further evaluate the performance of different OFRs and data analysis methods. Finally, we suggest best practices when measuring SOA PF with OFRs and provide computational tools to test the performance of any OFR for which the transfer function is known.

2 Theoretical background

The SOA PF defines the amount of SOA that would be formed in the atmosphere from the emitted SOA precursor gases, normalized to e.g. fuel consumed or distance travelled. Thus, the fuel-specific SOA PF \((\text{mg kg}^{-1}_\text{fuel})\) can be defined as:

\[
\text{SOA PF} = \frac{\text{SOA}}{\text{fuel consumed}} = \frac{\text{SOA}}{\text{emitted carbon}} \cdot k' = \frac{\text{SOA}}{C_{\text{CO}_2} + C_{\text{CO}} + C_{\text{HC}} + C_{\text{PM}}} \cdot k',
\]

(3)

where \(\text{SOA}\) is the SOA formation potential \((\text{mg})\), i.e., the SOA that could be formed in the atmosphere from the emitted precursor gases. The emitted carbon is the mass of carbon emitted \((g)\), which is the sum of emitted carbon mass originating from different exhaust compounds \((\text{CO}_2, \text{CO, HC and particle phase carbon, } C_{\text{PM}})\) (Platt et al., 2013). The fuel consumed can be obtained from vehicle OBD data or by dividing the emitted carbon mass with the fuel carbon content denoted by \(k'\) \((\text{g kg}^{-1}_\text{fuel})\). Since the emitted carbon is dominated by \(\text{CO}_2\), it is a good approximation to neglect the other forms of carbon. For simplicity, the SOA PF in this study is defined as:

\[
\text{SOA PF} \cong \frac{\text{SOA}}{\text{CO}_2} \cdot k,
\]

(4)

where \(\text{CO}_2\) is the emitted carbon dioxide mass and \(k = k' \cdot 44/12\), i.e., the emitted \(\text{CO}_2\) mass is multiplied with the ratio of carbon mass to total molecular mass in a \(\text{CO}_2\) molecule.
To study the ability of OFRs to determine the SOA PFs, we use a simple model for SOA formation in which we assume that the potential SOA is directly proportional to emitted hydrocarbon mass ($HC$), i.e.

$$SOA = Y \cdot HC,$$  

(5)

where $Y$ is the proportionality factor. We assume that the factor $Y$ for the OFRs and for the environmental chamber equals the value of $Y$ in the atmosphere, and that $Y$ is constant (independent of driving conditions). Thus, the total SOA formation potential for time interval $[t_0, t_f]$ in a driving cycle is:

$$SOA_{true} = \int_{t_0}^{t_f} [HC]_{true}(t) \cdot Y \cdot Q_{exh}(t) dt,$$  

(6)

where $[HC]_{true}$ is the mass concentration of gaseous hydrocarbons (mg m$^{-3}$) in the tailpipe and $Q_{exh}$ is the exhaust gas volumetric flow rate (m$^3$ s$^{-1}$).

To simplify the analysis, we treat the product of momentary HC concentration and the proportionality factor $Y$ as a theoretical SOA concentration ($[SOA]$) in the tailpipe, which reflects the potential of exhaust to form SOA in the atmosphere. Hereafter, the term 'true SOA concentration' refers to HC concentration in the tailpipe multiplied with $Y$, and 'SOA emission' refers to SOA formation potential from emitted HC as defined in Eq. 5. In the OFR results, the SOA concentration is the simulated concentration of SOA measured at OFR outlet (HC concentration at OFR outlet multiplied with $Y$).

### 2.1 Determining SOA PF with an OFR

As shown in Fig. 1, the HC emission determined from HC concentration measurement at OFR outlet differs from the true HC emission. If the potential SOA formation is dependent on HC emission as shown in Eq. 5, a similar error is present when measuring the SOA emission with an OFR. The HC signal at the OFR outlet is delayed because of the residence time in the OFR but also distorted because of the residence time distribution as shown in Eq. 2. Ideally, the true HC (or SOA) emission could be resolved from OFR measurements by deconvolution, but the noise present in the measurement prevents a perfect deconvolution of Eq. 2. Even without the noise, it is possible that no unique solution to the inversion problem exists. Thus, it is necessary to evaluate alternative methods to estimate SOA production factor based on the distorted OFR signal.

The delay caused by the OFR can be addressed by shifting the OFR signal with a characteristic time constant of the OFR:

$$[C]_{OFR}'(t) = [C]_{OFR}(t + \tau),$$  

(7)

where $[C]_{OFR}$ is the concentration measured downstream of the OFR and $[C]_{OFR}'$ is the delay corrected concentration. The constant $\tau$ is a characteristic delay of the OFR, which will be discussed in Sect. 5.1. The HC concentration at OFR outlet shown in Fig. 1 is already delay corrected, so that the peak concentration at OFR outlet is approximately aligned with the tailpipe peak concentration. Note that this delay correction requires that the OFR start sampling zero air immediately after the cycle ends, and that the measurement downstream of OFR be continued for at least duration of $\tau$ for the delay corrected OFR measurement to cover the full driving cycle.
By applying the delay correction to OFR data, the SOA emission in OFR measurement is

\[ SOAOFR = \int_{t_0}^{t_f} [SOA]_{OFR}'(t) \cdot Q_{exh}(t) \, dt \]  

(8)

\[ = \int_{t_0}^{t_f} [HC]_{OFR}'(t) \cdot Y \cdot Q_{exh}(t) \, dt, \]  

(9)

where \([HC]_{OFR}'\) is the delay-corrected HC concentration measured at OFR outlet that is affected by the OFR transfer function as shown in Eq. 2. Note that \([SOA]_{OFR}\) is the quantity that is measured in OFR experiments, and the \([HC]_{OFR}\) is the HC concentration that would be measured at OFR outlet only if there was no oxidation in the OFR. In normal experiments where the OFR UV lamps are switched on, Eq. 9 does not hold since part of HC is transformed to particle phase. Here the non-oxidised HC concentration is only used to simulate the theoretical SOA concentration at OFR outlet. Additionally, the exhaust sample is normally diluted before introducing it to the OFR but in this study we assume no dilution. Applying a constant dilution factor does not change the results of the analysis.

Comparison of Eqs. 8 and 6 shows that \(SOAOFR\) is inequal to true SOA emission because the delay correction does not correct for the distortion inside the OFR (Eq. 2), which leads to misalignment between exhaust flow rate and \([HC]_{OFR}\). The only case where \(SOAOFR\) universally equals true emitted SOA is when the OFR transfer function is a Dirac delta function, i.e., when the OFR is an ideal plug-flow reactor.

For a full driving cycle, it is possible to avoid the mismatch between \(Q_{exh}\) and the SOA measured with an OFR by using a constant volume sampler (CVS), like e.g. Zhao et al. (2018), Kuitinnen et al. (2021a, b) and Park et al. (2021) did. In a CVS, the exhaust is diluted with dilution ratio (DR) that is inversely proportional to the exhaust flow rate:

\[ DR_{CVS}(t) = \frac{Q_{CVS}}{Q_{exh}(t)}, \]  

(10)

where \(Q_{CVS}\) is the constant volumetric flow rate of the CVS. CVS should also be used in smog chamber experiments (e.g., Gordon et al. (2014a, b); Roth et al. (2020)); otherwise the injection of the exhaust into the smog chamber will not be proportional to the exhaust flow rate, i.e., the actual emission to the atmosphere.
When an OFR is sampling downstream of CVS, the true SOA emission is obtained with an OFR despite its transfer function by multiplying the SOA concentration at OFR outlet with the CVS flow rate and integrating over the full cycle:

\[
\int_{t_0}^{t_f} [SOA]_{OFR}(t) \cdot Q_{CVS} \, dt = \int_{t_0}^{t_f} [HC]_{OFR}(t) \cdot Y \cdot Q_{CVS} dt = Q_{CVS} \int_{t_0}^{t_f} \left( \frac{[HC]_{true} \cdot Y \cdot E}{DR_{CVS}} \right) (t) \, dt
\] (11)

\[
= Q_{CVS} \int_{t_0}^{t_f} \left( \frac{[HC]_{true} \cdot Y \cdot Q_{exh} \cdot E}{Q_{CVS}} \right) (t) \, dt = \int_{t_0}^{t_f} ([HC]_{true} \cdot Y \cdot Q_{exh} \cdot E) (t) \, dt
\] (12)

\[
= \int_{t_0}^{t_f} [HC]_{true}(t) \cdot Y \cdot Q_{exh}(t) \, dt \cdot \int_{t_0}^{t_f} E(t) \, dt, \quad t_0 = 0, \, t_f \to \infty
\] (13)

\[
= \int_{t_0}^{t_f} [HC]_{true}(t) \cdot Y \cdot Q_{exh}(t) \, dt = SOA_{true}, \quad t_0 = 0, \, t_f \to \infty.
\] (14)

The separation of the convolution in Eq. 13 requires that the limits of integration be for the full defined range, i.e., \( t_0 = 0 \) and \( t_f \to \infty \), as this is the full range of \( E \) (Weisstein, 2023). In this case also the integral of \( E \) is cancelled since it is unity by definition (and when dividing with emitted CO\(_2\) to obtain the SOA PF, also \( Q_{CVS} \) in Eq. 11 is cancelled). Thus, by using CVS it is possible to obtain the true SOA PF for the full cycle but not for parts of it. This issue was noticed also by Zhao et al. (2018) when determining the PFs for different phases of a driving cycle. In practice, \( t_f \) does not need to be infinite, but it should extend beyond the end of the driving cycle to account for the residence time in the reactor, and for this reason also the measurement of \([SOA]_{OFR}\) should be continued after the end of the driving cycle and zero air should be injected to the reactor during that time. For the driving cycles and OFRs studied here, the error in full cycle PF is less than 5% when using CVS sampling where the post-sampling duration is equal to OFR mean residence time, and the error approaches zero with longer post-sampling time (Fig. S13).

The advantage of OFRs is the continuous measurement to study the effect of different driving conditions on SOA formation. Thus, even though the CVS is a good solution for measuring the full cycle SOA PF, the applicability of OFRs for time resolved vehicular SOA studies remain unclear. The extent of the error in measured SOA emission caused by the distortion will be studied for different scenarios in the following sections by simulating direct sampling from the tailpipe and using Eq. 8, and by simulating CVS sampling and using Eq. 11 where the integration range is significantly shorter than the full cycle length.

3 Results and discussion

To study the effect of OFR RTD on the accuracy of SOA production factor, we simulate the SOA concentration at OFR outlet for two OFRs that have distinct residence time characteristics. The Potential aerosol mass (PAM) reactor (Lambe et al., 2011) represents an OFR with a broad transfer function, with mean residence time of 142 s and transfer function standard deviation of 113 s. A prototype version of Dekati oxidation flow reactor (DOFR; Dekati Ltd) has a faster response with mean residence
time of 41 s and transfer function standard deviation of 21 s. All OFR data shown hereafter is delay corrected according to Eq. 7 with the peak residence time of the OFR (see Sect. 5.1).

3.1 Real driving cycles

We measured the HC and CO\textsubscript{2} concentrations in the exhaust of a Euro 6 gasoline vehicle running two driving cycles to obtain reference data. In this analysis, we assume that the measured HC and CO\textsubscript{2} values represent the true concentrations in the exhaust. The driving cycles were cold-start (CS) New European driving cycle (NEDC) which was preceded by soaking time of 15 h and started with an engine start, and hot-start (HS) NEDC which was preceded by driving at 80 km h\textsuperscript{-1} speed for 5 min and started with an idling engine.

Figure 2. Time series of exhaust flow rate (\(Q_{exh}\)), tailpipe and OFR outlet concentrations of CO\textsubscript{2} (a) and SOA (b) in hot-start NEDC, and the cumulative emissions of CO\textsubscript{2} (c) and SOA (d). The OFR data is simulated based on tailpipe concentrations and OFR transfer functions, and the SOA concentration refers to HC concentration multiplied with \(Y\). All OFR data is delay corrected.

It is currently not possible to determine a true reference for the SOA formation potential so we generated semi-synthetic data based on the measured HC concentration and the assumption that SOA formation potential is directly proportional to the HC emission (Eq. 5). The proportionality factor of 0.15 was used, resulting in realistic SOA PFs of approximately 100 and 20 mg kg\textsuperscript{-1} fuel for cold-start and hot-start cycles, respectively. The gas concentrations (and SOA concentration) at OFR outlets were simulated by convolving the tailpipe concentrations with the OFR transfer functions (Eq. 2). We assumed that the reactors
were sampling zero air until the cycle starts; otherwise, the exhaust from preceding driving would be present in the OFRs and affect the cycle-specific SOA PF.

Figure 2 shows the CO$_2$ concentrations and SOA concentrations, and their cumulative emissions in the hot-start NEDC. Similar graphs for the cold-start NEDC are shown in Fig. S2. The SOA concentration at the DOFR outlet follows the true SOA concentration better than PAM, which results in better agreement on the total emitted SOA at the end of the driving cycle (Fig. 2d). However, the DOFR-based total SOA emission is still 7% lower than the true SOA emission, mainly because the response is not fast enough to follow the true SOA concentration during accelerations where the exhaust flow rate is highest. PAM has the same effect, but in addition the PAM-derived SOA emission starts to deviate from the true SOA emission already in the beginning of the cycle because the response is too slow to catch the SOA peak in the cycle start. These two effects result in total SOA emission that is 18% lower than the true SOA emission.

Because the SOA PF is directly proportional to ratio of emitted SOA and emitted CO$_2$, the relative error in PF equals the relative error in the SOA emission. However, for the OFRs both SOA emission and CO$_2$ emission (calculated from the delay corrected CO$_2$ measured at OFR outlet) are underestimated in the driving cycles studied here, so the error in PF could be decreased by normalizing the SOA emission to CO$_2$ emission measured at OFR outlet instead of true CO$_2$ emission. Even though this calculation method leads to better estimation of SOA PF in the two cases studied here, it is not guaranteed that the error in CO$_2$ measurement will always compensate for the error in SOA measurement. It is possible that in some cases the SOA emission determined from OFR measurements is higher than the true emission, and in such case normalizing to OFR CO$_2$ would amplify the error. Therefore, when presenting the integrated SOA PFs (e.g. Fig. 3a), the SOA emission is normalized to true CO$_2$ emission.

Figure 3. Total SOA PFs of subcycles and full driving cycle (a), and time series of true SOA PF and SOA PFs determined from OFR outlet concentrations (b) in hot-start NEDC. The integrated SOA PF in panel (a) is calculated by normalizing the SOA emission to true CO$_2$ emission, whereas for the momentary SOA PF in panel (b), the SOA concentration is normalized to OFR CO$_2$ concentration. The PFs in both panels are calculated from semi-synthetic SOA data that is linearly proportional to the measured HC concentration in the tailpipe or the simulated HC at OFR outlet. CSUDC, HUDC and EUDC represent approximately 400 s subcycles within the full cycle.
The error in full cycle SOA PFs is relatively small for both cold- and hot-start driving cycles despite the distorting effect of OFR transfer functions. In hot-start NEDC, the error in total SOA PF is 7% for DOFR and 18% for PAM (Fig. 3), and in cold-start NEDC the corresponding errors are 4% and 7% (Fig. S3). To study the accuracy of SOA PF in smaller subcycles, we divided the NEDC into three parts according to Karjalainen et al. (2016): cold start urban driving cycle (CSUDC; 0...391 s), hot urban driving cycle (HUDC; 392...787 s) and extra-urban driving cycle (EUDC; 788...1180 s). The division is used here also for the hot-start cycle although the term CSUDC does not represent a cold start in that case. The maximum error in the subcycles was 10% for DOFR (hot-start HUDC) and 23% for PAM (hot-start CSUDC). Note that the SOA PFs for the subcycles (Fig. 3a) are not the average values of momentary PFs shown in Fig. 3b. Instead, the subcycle SOA PF is calculated by normalizing the SOA emitted during the subcycle to the emitted \( CO_2 \).

The continuous operation of the OFRs allows studying SOA production factors at higher time resolution than the \( \sim 400 \) s subcycles. Zhang et al. (2023) investigated SOA PF as a function of driving condition by using a fast-response OFR (Veh-OFR). Such analysis requires time resolution in order of seconds, and the effect of OFR transfer function on the accuracy of momentary SOA PF at such time resolution needs to be determined.

The time-resolved true and OFR SOA PFs are shown in Fig. 3b for hot-start driving cycle and in Fig. S3b for cold-start driving cycle. The time-resolved OFR SOA PFs were calculated by normalizing the SOA concentration to \( CO_2 \) measured at OFR outlet to compensate for the slow response in SOA measurement. This is important especially in the beginning of the cycle, where the \( CO_2 \) levels in the OFRs deviate significantly from the tailpipe concentration.

Figure 3b shows that although the DOFR PF time series resembles better the true PF time series than PAM, neither of the OFRs can follow the rapid changes of the true SOA PF. For example, the maximum OFR PFs during the acceleration starting at \( 313 \) s are approximately 40% of the true maximum PF. However, when integrating the SOA and \( CO_2 \) emissions for a longer time interval, the agreement between the true PF and OFR PFs improves. For the full duration of the acceleration (\( 313...343 \) s), the DOFR PF is 74% and PAM PF is 82% of true PF. In general, the longer the integration time interval, the better the agreement (Fig. S11). Thus, when studying the effect of driving conditions on SOA production, it is better to divide the driving cycle in bins that represent different driving conditions instead of determining the relations based on second-by-second data.

To study the accuracy of different OFRs, we divide the driving cycle in short events according to different driving conditions: accelerations, constant speed driving, idling and decelerations. The time periods are shown in Fig. S14, and the deviations from the true SOA PF for each driving condition are shown in Fig. 4. The corresponding correlation graphs are shown in Fig. S15.

Figure 4 shows that DOFR with narrower RTD is generally better suited for studying SOA PFs of short events than PAM. In the cold-start cycle, PAM typically overestimates the PF because the HC originating from the engine start remain in PAM for a long time. In both cycles, the acceleration PFs are usually underestimated by both OFRs because there is typically simultaneous increase in exhaust flow rate and HC concentration, but the OFR HC does not reach the level of true HC as illustrated in Fig. 1. In constant-speed driving, both OFRs overestimate SOA PF because this driving condition is usually preceded by accelerations, and HC originating from the acceleration is still present in the OFRs. For the same reason, the OFRs overestimate also the deceleration PFs.
As discussed earlier, normalizing the emitted SOA to CO$_2$ emission determined from CO$_2$ concentration measured at OFR outlet may reduce the error in SOA PF. The applicability of this method and other methods to reconcile the distortion in SOA concentration caused by the OFR transfer functions are studied in the next section.

3.1.1 Alternative data analysis and measurement methods

Figure 5 shows the SOA PF deviations for both reactors when using different data analysis and measurement methods. Overall, the different methods (except for the averaging method) result in relatively small error, maximum 37 %. In all methods, the OFR data is delay corrected.

The standard method is the one used in previous sections, i.e., the SOA emission is normalized to true CO$_2$ emission. This method underestimates the SOA PF in most cases (Fig. 5). Note that normalization to true CO$_2$ emission is equivalent to normalizing to true fuel consumed or true distance travelled. When using the other data analysis methods described below and calculating the distance based production factors, one first needs to determine the fuel-specific production factor and only then convert it to distance based by multiplying with the ratio of fuel consumed per distance travelled that is available in the on-board diagnostics data.
Figure 5. OFR SOA PF deviation from the true PF for full driving cycles and ~400 s subcycles when using different data analysis and measurement methods. The PFs are calculated from semi-synthetic SOA data that is linearly proportional to the measured HC concentration in the tailpipe or the simulated HC at OFR outlet.

In the OFR CO\textsubscript{2} method the CO\textsubscript{2} concentration is measured from OFR outlet and the CO\textsubscript{2} emission is determined by multiplying the delay-corrected CO\textsubscript{2} concentration with the exhaust flow rate. In most cases, the OFR CO\textsubscript{2} method results in better agreement with the true SOA PF compared to standard method (Fig. 5), which is in agreement with the observation that both SOA and CO\textsubscript{2} emissions are underestimated with the OFR in Fig. 2.

The convolution method applies the same OFR response to the exhaust flow rate that affects the SOA and CO\textsubscript{2} concentrations that are measured at OFR outlet. The SOA and CO\textsubscript{2} emission rates are calculated by multiplying the concentrations at OFR outlet with exhaust flow rate that is convolved with OFR transfer function. This method was used by Simonen et al. (2019) for determining SOA emission rate, but it was not normalized to CO\textsubscript{2} emission measured at the OFR outlet but to the
true fuel consumption or distance travelled, which is equal to normalizing to true CO₂ emission. The deviation in convolution method is of similar magnitude to the standard method and the OFR CO₂ method (Fig. 5).

In the CVS method, the OFRs are sampling exhaust that is diluted with CVS, i.e., the dilution ratio is inversely proportional to the exhaust flow rate. The emitted SOA is calculated with Eq. 11. The emitted CO₂ is calculated with a similar equation, where the CO₂ is measured at the OFR outlet. The CVS method always leads to correct SOA PF for the full cycle as discussed in Sect. 2.1. For DOFR, the CVS method results in least deviation in subcycles as well compared to the methods presented above. For PAM, the deviation in subcycles with this method is on average larger than the previous methods in cold-start cycle, but performs better in the hot-start cycle.

Although the CVS sampling is favorable especially for DOFR, it has some disadvantages. CVS requires a high flow rate of dilution air compared to partial flow diluters, and purifying such amounts of dilution air is challenging. This may lead to high background SOA formation from dilution air impurities (Zhao et al., 2018). In addition, the heat from vehicle exhaust may cause desorption of previously adsorbed HC from CVS walls (Gordon et al., 2014a). However, the SOA PFs have been measured with CVS sampling with acceptable background SOA formation (Zhao et al., 2018; Kuittinen et al., 2021a; Gordon et al., 2014a).

An inherent feature of the CVS is that the dilution ratio is inversely proportional to exhaust flow rate. As shown in Fig. 2, the HC peaks usually occur during accelerations, where the exhaust flow rate is also elevated. The same is observed for NOₓ, so the use of CVS dilution amplifies the variations in HC and NOₓ concentrations compared to direct sampling from tailpipe with constant dilution ratio. Since the OH exposure and photochemistry in OFRs is sensitive to concentrations of NOₓ and OH reactive gases (Peng and Jimenez, 2017), using CVS may cause too high gas concentrations during e.g. accelerations where exhaust flow rate and gas concentrations are high, and too low signal during e.g. idling where concentrations and exhaust flow rate are low.

The averaging method does not consider the exhaust flow rate. In the study by Zhang et al. (2023), the full cycle SOA PFs were apparently determined by calculating the average of the momentary PFs instead of calculating the ratio of emitted SOA to emitted CO₂, although their description of the PF calculation for full cycle is not unambiguous. Figure 5 shows that in the cold-start cycle, this averaging method leads to an overestimation by a factor of ∼ 2 for DOFR and ∼ 2.5 for PAM. Note that the PFs calculated with the averaging method are not compared to the average values of true momentary PFs, but instead to the true PF which is the emitted SOA normalized to emitted CO₂.

In the deconvolution method, the SOA signal simulated at OFR outlet is first deconvolved (as described by Conesa (2020); see Sect. S2) to obtain the true SOA concentration in tailpipe, and then multiplied with true exhaust flow rate to obtain the SOA emission rate. The emitted SOA is normalized to true emitted CO₂. For PAM, the deconvolution method leads to smallest errors, whereas for DOFR the CVS method is as good as the deconvolution method. The time series of deconvolved SOA concentrations are shown in Fig. S16.

The deconvolution here represents the best possible outcome because there is no noise present in the simulated SOA concentration at OFR outlet. In real-life scenarios, there is noise originating from the instrument measuring the SOA concentration and also some variability in the OFR transfer functions due to small fluctuations in flow rate and temperature. The performance of
Figure 6. The deviation of OFR PFs for 14-s bins in the driving cycles when using different data analysis and measurement methods. Boxes represent 25th and 75th percentiles, and the line inside the box represents the median value. The points are considered outliers if they are greater than 99th percentile or lower than 1st percentile. The whiskers extend to most extreme data points that are not outliers. The PFs are calculated from semi-synthetic SOA data that is linearly proportional to the measured HC concentration in the tailpipe or the simulated HC at OFR outlet.

The deconvolution method in such cases is beyond the scope of this study, but our tests for 10-s square pulses of SOA precursor showed that the deconvolution was able to reproduce the square pulses based on the measured SOA concentration at DOFR outlet, but not perfectly (Fig. S9).

While all calculation methods except the averaging method are able to report the SOA PF for full cycles and ~400-s subcycles with relatively good accuracy, Fig. 4 shows that in some cases, the deviation in short driving events can be very high when using the standard method. Some of the deviations in Fig. 4 could be avoided by normalizing the SOA emission to the CO₂ measured at OFR outlet instead of tailpipe. For example, the most severe underestimations in PAM and DOFR are observed in the beginning of the driving cycles where the response to HC is much slower than the change in the tailpipe CO₂
concentration, and in other occasions where there is drastic change in tailpipe CO$_2$ concentration. Likewise, the changes in tailpipe CO$_2$ concentration during decelerations are much faster than the characteristic residence times of the OFRs. For this reason, we investigate whether the normalization to OFR CO$_2$ or any of the other methods perform better for short events in the driving cycles. For this analysis, we divide the cycle in 14 s bins and calculate the deviation from true PF for each bin using different methods. The 14 s bin duration was chosen because it is the median duration of different events in Fig. 4.

Figure 6 shows that different calculation methods, including the **averaging** method (but excluding the **deconvolution** method), report similar distributions for the deviations in short driving events. However, the **standard** method usually has more deviation at low values due to the CO$_2$ issue mentioned before. The **deconvolution** method is superior for both OFRs: 98% of all OFR data is within factors of 0.81 and 1.39 of true PF. Because of this high accuracy, the applicability of **deconvolution** method in real-world scenarios should be studied in a future publication.

Both reactors tend to overestimate the SOA PFs of short events. For example, in OFR CO$_2$ method the median ratios between OFR PFs and true PFs are 1.08 and 1.13 for DOFR in hot- and cold-start cycles, respectively. For PAM, the median ratios are 1.24 and 1.87 in hot- and cold-start cycles, respectively, and in cold-start NEDC 75% of PAM PFs exceed the true PFs.

### 3.2 Special cases

Although the DOFR usually reports PFs closer to true values than PAM, this is not always the case. Figure 7 shows two synthetic examples: one where the HC concentration increases simultaneously with exhaust flow rate (typical acceleration observed in the driving cycles presented), and another where the peak in exhaust flow rate is not aligned with the HC concentration peak (e.g., a HC peak originating from engine start followed by elevated exhaust flow rate due to acceleration after the engine start).

In the case where exhaust flow rate and HC concentration peaks are well aligned (Fig. 7a-b), both OFRs report too low SOA emission, which was also the case in Fig. 1, but DOFR result is closer to the true one. However, when the two signals are misaligned (Fig. 7c-d), DOFR results in higher overestimation of the emitted SOA because the HC concentration is still elevated when the exhaust flow rate starts to increase. This is the case with PAM as well, but since the HC peak is distributed over a longer time period, the concentration is not as high as in DOFR and the resulting SOA emission agrees better with the true emission.

In Sect. 3.1, the performance of the OFRs was investigated only for one gasoline vehicle running two cycles, and DOFR typically resulted in better agreement with true SOA PF than PAM. However, as shown in Fig. 7, DOFR does not result in better agreement in all cases. Different vehicle types and more aggressive driving cycles may exhibit different behaviour in tailpipe gas concentrations and exhaust flow rate compared to the gasoline vehicle driving the NEDC, and also the alignment between the concentration peaks and the changes in exhaust flow rate may be different. For example, in Diesel vehicles the CO$_2$ concentration is load-dependent whereas in the gasoline vehicle studied here the tailpipe CO$_2$ concentration was almost constant. Hybrid vehicles may repeatedly switch the combustion engine off and on during the driving cycle.

Thus, to investigate the performance of the OFRs and data analysis methods in a broader range of instances, we performed a Monte Carlo analysis on synthetic driving cycles that include various different combinations of exhaust flow rate, CO$_2$ concentrations and HC concentrations.
Figure 7. Two distinct example time series of exhaust gas concentrations and exhaust flow rate. In the typical acceleration case (a)-(b), the DOFR SOA emission is closer to true, whereas in the case where HC peak and exhaust flow rate peak are not aligned (c)-(d), the PAM outcome agrees better with true emission. It is assumed that the SOA formation is directly proportional to HC concentration.

3.3 Synthetic driving cycles

Driving cycles have three variables that affect the SOA PF: CO₂ concentration, HC concentration and exhaust flow rate. The synthetic driving cycles were generated by dividing the cycle in periods of random duration for each variable, where the value of the variable was random (but constant for the period duration). The periods for each variable were generated independently of each other, so that the changes in the values of each variable do not necessarily coincide with changes in the other two variables. The generation algorithm is described in more detail in Sect. S3 and examples of generated cycles are shown in Fig. S17. In total, 10000 synthetic driving cycles were generated.

Figures 8a-b show that the distribution of full cycle SOA PFs was skewed towards underestimation for both reactors, but more severely for PAM, when using the standard method for the synthetic driving cycles. The two other methods shown, the OFR CO₂ and convolution methods, agreed well with the true PF. Only three methods are shown here because it was already observed in Sect. 3.1.1 that the averaging method is not suitable for calculating the full cycle PFs, and that the CVS method always leads to correct full cycle PF. The deconvolution method was too time consuming to apply for all 10000 driving cycles.
Figure 8. The probability distributions for full cycle SOA PFs for 10000 synthetic driving cycles using DOFR (a) and PAM (b), and the deviation in OFR PFs for 400 s (c) and 14 s bins (d) in the synthetic driving cycles. Boxes represent 25th and 75th percentiles, and the line inside the box represents the median value. The points are considered outliers if they are greater than 99th percentile or lower than 1st percentile. The whiskers extend to most extreme data points that are not outliers.

Similar to full cycle PFs, the standard method typically underestimated the PF for PAM when calculating the PFs for 400 s subcycles (Fig. 8c). Among the other calculation methods, the averaging method led to broadest distribution of deviations and the CVS method performed best for both OFRs.

Because of the other disadvantages of the CVS sampling discussed in Sect. 3.1.1, the OFR $CO_2$ and convolution methods seem most feasible for exhaust measurements based on the distributions in Fig. 8c. Using the OFR $CO_2$ method for 400 s subcycles in the synthetic cycles, the median OFR-to-True ratio was 1.00 for DOFR and 1.01 for PAM. 50% of DOFR PF ratios ranged between 0.96 and 1.05 and PAM ratios between 0.89 and 1.16. 98% of DOFR PF ratios ranged between 0.81 and 1.40 and PAM ratios between 0.54 and 2.50.

Figure 8d shows that the different calculation methods resulted in very similar distributions when calculating the SOA PFs for short events. The CVS method led to most negative outliers for both OFRs, and the standard method least. The PAM median was closest to true value when using the standard method, but on the other hand the 25th percentile was more negative than with the other methods. In OFR $CO_2$ method, 50% of DOFR PF ratios ranged between 0.82 and 2.09 and PAM ratios between 0.71 and 4.38. 98% of DOFR PF ratios ranged between 0.41 and 31.00 and PAM ratios between 0.19 and 77.26. A summary of deviations of OFR-derived PFs from the true values in both real cycles and synthetic cycles is shown in Table 1.
Table 1. Ratios of reactor PF to true PF when using OFR CO₂ method. For each case, the median ratio and 25th, 75th, 1st and 99th percentiles of ratios are shown (notation of $P_{25}$ for 25th percentile etc. is used).

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<td>Median $P_{25}$</td>
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<tr>
<td>PAM</td>
<td>1.04</td>
<td>0.88</td>
</tr>
<tr>
<td>DOFR</td>
<td>0.95</td>
<td>0.92</td>
</tr>
<tr>
<td>Synthetic cycles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAM</td>
<td>1.01</td>
<td>0.89</td>
</tr>
<tr>
<td>DOFR</td>
<td>1.00</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Since a significant fraction of OFR-derived PFs were more than 10-fold compared to true PFs for short, 14 s segments, and the agreement was better for longer (400 s) segments, it is of interest to determine what is the minimum segment durations for which the OFR results are accurate enough. If we choose that the OFR result is acceptable when 99% of the PFs are less than three times the true PF, the minimum duration was 110 s for DOFR and 350 s for PAM. The deviations as a function of bin duration are shown in Fig. S12.

4 Conclusions

In this study, the effect of OFR transfer function on the accuracy of SOA PFs in transient driving cycles was investigated by using semi-synthetic and synthetic exhaust gas data. The analysis was done for two OFRs: a PAM reactor with a broad transfer function and DOFR with a narrower transfer function.

Even though the wide residence time distributions of OFRs resulted in momentary PFs that differed from the true PFs, it was possible to determine the integrated PFs relatively accurately for longer periods within the driving cycles. However, a wrong data analysis method could lead to PFs that were more than double of true PF.

When determining SOA PFs of short-duration events in a driving cycle, such as accelerations, the errors were larger for both OFRs compared to PFs of longer periods. The narrower transfer function of DOFR was advantageous, since the 1st and 99th percentiles of OFR-to-true PF ratios in the short-duration events (14 s periods) in real driving cycles were 0.55 and 2.41, respectively, for DOFR and 0.36 and 4.99 for PAM (using OFR CO₂ method).

When extending the study to synthetic driving cycles, the OFRs still reported the full cycle PFs with relatively small error. For 14 s bins in the synthetic driving cycles, it was observed that the OFRs may overestimate the SOA PFs by more than factor of ten. It is questionable whether any of the studied OFRs can be used to determine SOA PFs for that short driving events since the potential error is so high. At least, the uncertainty should be addressed when reporting the PFs. On the other hand, the synthetic driving cycles are random and do not necessarily represent typical driving cycles, so the results represent maximum possible error rather than typical error observed in real driving cycles. More real cycles should be studied in order to evaluate the potential error.
By lengthening the bin duration to 110 s, the 99th percentile of DOFR PF ratios was below 3 in the synthetic driving cycles. The 99th percentile of PAM PF ratios was below 3 when the bin duration was longer than 350 s.

Deconvolution of SOA concentration measured at OFR outlet seemed promising method because it enhanced the accuracy of SOA PFs significantly. However, the result was obtained by assuming noise-free measurement of mass concentration, and thus its applicability to real-world scenarios should be further studied.

There are also other reasons than the transfer function alone for OFRs to report incorrect SOA production factors, such as non-tropospheric gas chemistry or non-tropospheric losses (Peng and Jimenez, 2020, 2017; Peng et al., 2019; Palm et al., 2016). In this paper, we only studied the error that is caused by the OFR transfer function. Other sources of error were isolated by assuming that the oxidation in OFRs perfectly reproduces atmospheric oxidation and that there are no non-atmospheric losses in the OFRs. The analysis is limited to conditions where SOA formation potential is directly proportional to HC concentration and where the proportionality is constant throughout the driving cycle.

Even though the assumption of SOA concentration being directly proportional to HC concentration does not generally hold, the HC measurement from tailpipe accompanied with the methods presented in this study is a good sensitivity test for transfer function -related uncertainties when determining the SOA PFs with an oxidation flow reactor. Similar analysis apply when using any other slow-response instrument to determine emission factors.

Arising from our analysis, we present the following best practise recommendations for OFR emission measurements:

- Before the start of the cycle, the reactor must be sampling zero air to avoid previous driving affecting the cycle SOA PF. The exhaust sampling must start at the same time as driving cycle starts. This concerns the engine-off periods of hybrid vehicles as well: zero air sampling should be started immediately when the combustion engine is switched off, and the tailpipe sampling started when the engine turns back on. When sampling from CVS, this is done automatically.

- When the cycle ends, the reactor must immediately start sampling zero air. The measurement must be continued at least for duration of the OFR $T_{\text{peak}}$ to make the delay correction in data after-treatment possible. When sampling from CVS (or when using the convolution method), the sampling of zero air must be continued at least for duration of OFR mean residence time, but longer sampling time will result in more accurate PF (Fig. S13).

- In order to use the OFR CO$_2$ method or convolution method, CO$_2$ should be measured downstream of the OFR, or the OFR outlet CO$_2$ concentration should be simulated by convolving the tailpipe concentration with the OFR transfer function and dividing with the dilution ratio.

- When using other than standard or deconvolution method, the distance-based production factors should be calculated by first calculating the fuel-based production factor with one of the presented methods, and then using OBD data to convert the fuel-based PF to distance-based.

The Matlab code used in this study is available as a Supplement file to reproduce the analysis for any OFR with a known transfer function and for any driving cycle for which the CO$_2$ and HC concentrations and exhaust flow rate are available.
5 Methods

5.1 OFR characterization

Dekati oxidation flow reactor (DOFR) is a commercial oxidation flow reactor, which dimensions are very close to those of Tampere secondary aerosol reactor (TSAR; Simonen et al. (2017)). The main geometrical additions compared to TSAR are a conical outlet, a laminating grid element in the inlet and unlike TSAR, all sample is evacuated through a single outlet. The oxidation reactor is surrounded by 12 UV lamps of which two can be switched on individually and the rest of the lamps in pairs, whereas TSAR has two intensity-controlled UV lamps (Kuittinen et al., 2021a). The housing of the oxidation reactor is cooled with air. The air cooling in the commercial version is enhanced compared to the prototype version used here. Similar to TSAR, DOFR is an OFR254 type reactor, which means that OH radicals inside the reactor are generated by 254 nm UV light from externally mixed ozone and water vapor.

The transfer function of DOFR was determined for CO$_2$ and toluene by injecting 10 s square pulses of gases into the reactor and measuring them downstream of the reactor. The CO$_2$ was measured with LI-840 analyzer (LI-COR Inc.) and toluene with Vocus proton transfer reaction mass spectrometer (Aerodyne Research Inc.). The gases were injected at the enclosure inlet and CO$_2$ was measured directly downstream of the reactor while the toluene was measured downstream of ejector diluter, which is an integral part of DOFR. Thus, the toluene RTD describes the response of the full unit, although we assume that this is the case for CO$_2$ RTD as well because the residence time in the diluter and its sampling lines is minor. The mean flow rate through DOFR was 6.8 lpm during the CO$_2$ experiments and 6.0 lpm during the toluene experiments.

The square pulses were generated by continuously injecting constant mass flow rate of CO$_2$ or N$_2$ mixed with toluene into a fast pneumatic 3-way valve (MS-151-DA actuator with SS-42GXS6MM-51D 3-way valve; Swagelok Company), one outlet connected to the DOFR inlet and the other to the excess line. The toluene vapor was generated with a permeation oven (V-OVG; Owlstone Inc.). The measurement setup is shown in Fig. S1.

The DOFR RTDs of 10 s pulses were measured for 3 different UV lamp configurations: ‘off’, ‘low’ (two central UV lamps on), and ‘high’ (all UV lamps on). The O$_3$ generation was switched off to prevent toluene reacting with OH radicals when measuring the toluene RTD. The measured RTDs correspond to 10 s input pulses, so they do not represent the actual transfer function which is the response to a Dirac delta input. Thus, the OFR transfer functions were determined by finding the transfer function that resulted in best agreement with the measured concentration when convolving with 10 s square pulse. The candidate function was a linear combination of Taylor distributions (Lambe et al., 2011; Huang and Seinfeld, 2019), and the best fit was found with Matlab function ’fit’. The gas analyzer response was not determined separately, so it is included in the reported transfer functions. In this study, the transfer function corresponding to ‘low’ UV lamp configuration was used to simulate the DOFR output. This lamp configuration resulted in OH exposure of $7.9 \cdot 10^{11}$ cm$^{-3}$s$^{-1}$ according to toluene measurements. The DOFR transfer functions for CO$_2$ and toluene are shown in Fig. S4, and the comparisons between the convolved square pulses and the measured DOFR output concentrations are shown in Figs. S5 and S6.

By switching the O$_3$ reactor on, we also measured the mass concentration that was produced from 10 s toluene pulse for the ‘low’ UV lamp configuration. The mass concentration was measured with an electrical low-pressure impactor (ELPI,
Dekati Ltd.; Keskinen et al. (1992)) with improved nanoparticle resolution (Yli-Ojanperä et al., 2010). It would be possible to determine a transfer function for SOA formation based on these measurements, but since such data was not available for PAM chamber, we simulated the SOA formation in both OFRs by assuming that the SOA formation response is equal to CO$_2$ response. Simonen et al. (2017) did measure the PAM SOA formation for a toluene pulse, but in those measurements the PAM ring flow was not used. Since the usage of ring flow is a standard method in PAM measurements and affects the transfer function, we used the CO$_2$ pulse data measured by Lambe et al. (2011) to determine the PAM transfer function by the same fitting procedure as for the DOFR (Fig. S7). In the measurements by Lambe et al. (2011), PAM ring flow was used and the UV lamps were on. Using the CO$_2$ transfer function to simulate the SOA formation in DOFR resulted in a satisfactory agreement with the experimental data (Fig. S8), so the usage of CO$_2$ transfer function in this study is justified.

For the OFR delay correction (Eq. 7) we used the peak residence time as the correction constant. The peak residence time ($\tau_{\text{peak}}$) is the residence time for maximum value in the transfer function (i.e., $E(\tau_{\text{peak}}) = \max(E(t))$). Figure S10 shows that the error in SOA PF was smallest when the delay correction constant was close to $\tau_{\text{peak}}$.

### 5.2 Vehicle exhaust measurements

The vehicle in real driving cycle measurements was a Euro 6 gasoline vehicle equipped with 1.4 l turbocharged direct injection engine (110 kW). The vehicle was soaked for 15 h before the cold-start cycle and pre-conditioned by driving at 80 kmh$^{-1}$ for 5 min before the hot-start cycle. The hot start cycle started with idling engine. In the simulations, it was assumed that the OFRs are flushed with zero air until the cycle starts and immediately after the cycle ends. So even though engine is running before the start of hot-start NEDC, the OFRs are filled with zero air at $t = 0$ s.

The total hydrocarbon concentration (methane equivalent ppm) was measured with a flame ionization detector and the CO$_2$ concentration with a non-dispersive infrared analyzer. Both gases were sampled directly from tailpipe. The exhaust mass flow rate was calculated based on the intake air flow rate and fuel consumption obtained from the on-board diagnostics data. The fuel carbon content ($k'$) of 860 g kg$^{-1}$ was used in the calculations.

**Code and data availability.** The engine exhaust data for the real driving cycles is available in the Supplement. The Matlab code to reproduce the analysis is available in the Supplement.

### Author contributions.

P.S.: Original idea, data processing, writing the manuscript, planning and execution of experiments. M.D.M.: Manuscript conceptualisation and preparation. P.P.: DOFR experiments, Vocus data processing, commenting the manuscript. A.H., A.K.: DOFR experiments, commenting the manuscript. P.M.: Planning of chassis dynamometer experiments and commenting manuscript. P.K.: Project management, planning and execution of chassis dynamometer experiments and commenting manuscript. J.K.: Funding, project management, manuscript conceptualization and preparation.
Competing interests. J.K. is a member of the board of Dekati Ltd.

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