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Literature review of Particulate Matter (PM) from transport with a special focus on organic aerosols

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Literature review of Particulate Matter (PM) from transport with a special focus on organic aerosols

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SUMMARY

Several recent scientific studies on urban air quality have suggested that air quality modelling based on current emission inventories for mobile sources systematically underestimates the contribution of these sources to ambient particulate matter (PM) levels, and organic aerosol levels in particular.

This document discusses a number of factors that may explain the reasons for this apparent systematic underestimation. An obvious cause is that current road transport emission factors do not fully account for the contribution of primary organic particulate. Secondly the emissions, and the chemical activity of precursor gases (in the atmospheric formation of secondary organic aerosol (SOA)) are not yet fully accounted for in the inventories nor in all air quality models.

Organic aerosol (OA) can be classified based on the volatility of the compounds it consists of. Organic particulate and condensable particulate matter (CPM) may consist of non-volatile compounds (NVOCs), organic compounds with low volatility (LVOCs), semi-volatile organic compounds (SVOCs) and to some degree organic compounds with intermediate volatility (IVOCs). In addition, gaseous SVOCs, IVOCs and certain NMVOCs are very important classes of secondary organic aerosol (SOA) precursors. S/IVOCs in road transport emissions are therefore central to this document.

SOA precursors, such as S/IVOCs, are not distinguished separately in official emission inventories. They may or may not be included in the emissions of PM or hydrocarbons and more specific in those of non-methane volatile organic compounds (NMVOCs). Due to the lack of specified emission data on SOA precursors, air quality models are adapted to estimate SOA precursor emissions and include modules to simulate the transformation of these precursors to SOA. This document starts with a general description on how these models estimate the emission/concentration of SOA precursor gases and how the resulting SOA formation is estimated.

A descriptive analysis is given on the following subjects in order to provide a better understanding on how road transport emission rates for PM are currently assessed and which factors are of influence in this respect:

- Relevant emission legislation for road vehicles
- Currently used emission control technologies
- Testing procedures for characterizing PM emissions
- How PM emissions under testing conditions compare to real-driving cycles
- The contribution by non-exhaust emission of PM
- Fleet composition and renewal rate
- Current PM and hydrocarbons (HC) emissions from road transport

The current assessment of PM emission factors for road vehicles does not however specifically address emission of S/IVOCs. A method is described on how S/IVOCs have been measured in the exhaust of US gasoline and diesel-fuelled road vehicles. The ratio between S/IVOCs and other organic compounds was found to be fairly consistent among different vehicle technologies, suggesting that with the decrease of primary PM and HC emissions, SOA precursors are reduced at about the same pace.

Due to this reduction in primary PM exhaust emission, the emission from wear process will become the main remaining primary PM emission source from road transport. A second study focused specifically on the SOA yield of non-methane organic gases (NMOGs) emitted by road vehicles, based on smog chamber measurements. Total SOA production was determined to be around 0.06 g/kg fuel for pre-LEV, 0.04 for LEV (California legislation CARB Low Emission Vehicles), 0.015 for ULEV (Ultra Low Emission Vehicles), and around 0.002 g/kg fuel for SULEV (Super Ultra Low Emission Vehicles) vehicles.

Based on the above referenced studies, we have furthermore concluded that current measurement methods for vehicular PM emissions may underestimate direct primary CPM emission to some degree, as additional CPM may form when exhaust gases are further cooled from the filter temperature (52°C) in the outside air temperature. At this stage, it is not yet clear how much CPM this involves. However, it is certain that towards 2030, emissions from direct CPM will decrease fairly rapidly, with a few percent per year, due to the natural phase out of older vehicles and the planned introduction of new stringent vehicle emission limit values for PM, particulate number (PN) and HC. The emission of SOA precursors such as S/IVOCs by road transport has also decreased significantly and just as primary CPM, will continue to decrease towards the year 2030, due to the abovementioned reasons.

First order estimates made in this study suggest that in the Netherlands in 2019, the PM burden on ambient air by SOA formation from gaseous S/IVOCs and NMVOCs emitted by road transport, may have been of the same order as the burden caused by primary PM emissions by road transport in 2019. Since the Dutch vehicle fleet is not that different from the European average, albeit the share of diesel vehicles is lower than the European average, as can be deduced from the EEA vehicle registration database but their mileage is higher (Geilenkirchen et al., 2020), this is likely true for other European countries as well.

SOA formation is found to be highly dependent on NOx concentrations. When NOx concentrations decrease, this may increase the SOA yields of SOA precursors emitted by road transport and by other precursor sources such as stationary fuel combustion and food preparation. Both NOx and SOA precursor emissions (such as aromatics and S/IVOCs) from road vehicles is projected to decrease as a result of emission control measures and the phase out of older vehicles. What the overall effect on SOA production from vehicle exhaust will be, needs to be further investigated. It should be remarked that precursor emission by other sources besides road transport (e.g. wood combustion, product use) is expected to decrease to a much lesser extent, up to a point that these other sources dominate SOA precursor emission.

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CONTENTS

1. INTRODUCTION

Emissions from road traffic are responsible for elevated human exposure to different air pollutants because vehicles tend to move in places where people are present. In addition, emissions are highest at the times of day when people are also in the vicinity of traffic-intensive places. The air quality monitoring stations show clear correlations between elevated readings and traffic intensity, and roadside stations usually measure the highest outdoor air concentrations. Particulate matter (PM) measurements also show a decrease in the traffic contribution to particulate matter in ambient air. The amount and characterisation of traffic-generated particulate matter is changing, which is linked to changes in vehicle technology and vehicle legislation. The success of more recent legislation imposing filters on the most polluting vehicles indicates a shift in sources. In particular, a shift between primary and secondary aerosols. This report will focus on the state of knowledge on the emissions of organic aerosols from road transport as these are not yet well understood and the treatment of these aerosols in air quality models is still under development.

Organic aerosols (OA) are an important component of ambient particulate matter (PM). Measurements in the early 2000's showed that at European rural background sites, total carbonaceous material accounted for 30±9% of PM_{10} (Yttri, et al., 2007). A compilation of measurement campaigns in Europe confirmed that the main constituents of both PM_{10} and $PM_{2.5}$ all over Europe are generally organic matter (OM), SO_4^{2-} and NO_3^- (Putaud et al., 2010). More recently, Cavalli et al. (2016) reported that carbonaceous material, measured as total carbon (TC), forms a significant fraction of the aerosol mass, ranging from 21% to 56% at urban and background sites, in different European regions. Despite the importance of OA for ambient PM the origin and formation of OA is not well understood and deserves more attention (e.g., Fuzzi et al., 2015).

Condensable, or semi- and intermediate-volatile organic compounds (denoted as S/IVOC hereafter), are a class of compounds of low volatility that may exist in equilibrium between the gas (S/IVOC(g)) and particle (condensed, S/IVOC(pm)) phase. Such compounds may or may not be included in current emission inventories for fine particulate matter ($PM_{2.5}$ and PM_{10}) with their treatment varying from country to country and from one emissions source to another. The reasons for this inconsistent treatment of S/IVOC in inventories are multiple, including a lack of legislation, varying national definitions or measurement protocols and non-uniform methods for different sources (including transport).

The degree to which these compounds are included in emission inventories may have significant implications for the understanding, formation and modelling of organic aerosol. This was first highlighted by Robinson et al. (2007), and for the European situation evaluated and discussed in Denier van der Gon et al. (2015). Simpson et al. (2020) recommended the systematic inclusion of condensable particulate matter (CPM) in future emission inventories with a priority for the residential wood combustion (as major source). Emissions from other sources need further investigation. Road transport is considered as the second main source besides the residential wood combustion, and thus needs further attention. In this literature review the state of play related to PM (and OA) from road transport is elaborated.

Since organic aerosol is such an important component of total particulate matter, understanding the direct contribution (through condensation) and indirect contribution (as SOA precursor) of S/IVOC is crucial to be able to assess the origin of PM levels in the ambient atmosphere.

At the root of the problem is:

1) the definition of different compounds like NMVOC and PM,
2) the complexity of measuring substances that can be both in the gas and particle phase at ambient temperature, and
3) the variation across Europe in official reporting of NMVOC and PM constituents.

In short, these substances (S/IVOC or condensables) are not volatile enough to be included in the NMVOC class of substances and (often) too volatile to be included in the definition of primary PM. Moreover, the measurement protocols used to derive PM emission factors in Europe differ substantially between source sectors.

Air quality modelling using various assumptions, (e.g. Shrivastava et al. (2008)) has shown that PM formed from S/IVOC emissions, either direct through dilution and cooling leading to condensation (hence the term “condensable particulate matter”) or indirect through ageing, can be a significant contributor to total PM. The fact that PM emission inventory protocols by source category deal with this fraction in a different way is generally overlooked and hardly ever mentioned. Emissions often are reported as PM_{10} or $PM_{2.5}$ without further comment on whether or not they include S/IVOC in their inventories, the method/emission factor used to report them, etc.

As a result, there is ongoing uncertainty about how important these substances really are by different source sectors, and how much they may contribute to organic aerosol concentrations. The latter can only be quantified using atmospheric chemistry and transport models since some of these S/IVOC will only become condensable at ambient temperature after ageing and reaction in the atmosphere.

This study will clarify the various definitions for organic aerosol components and its precursors and assess possible emission of S/IVOC from road transport in Europe. The most important literature has been reviewed, addressing the importance of S/IVOC for organic aerosol formation and providing insight into how important S/IVOC emissions from road transport may be in comparison to the dominant source.

In section 2 of this report relevant definitions related to the different species of PM are elaborated including how PM formation is implemented in air quality models.

Section 3 elaborates the current status of road transport PM emissions covering the topics:

- effect of emission control technology (including legislation)
- testing procedures
- reported emissions inventories characterization of road transport related PM species
- estimate of SOA formation and their relevance to air quality

Future implications and challenges are described in section 4 of the report and in section 5 the conclusions and recommendation from this study are given.

2. DEFINITIONS

There is a large variety of organic compounds in the earth's atmosphere (millions of unique species; Goldstein and Galbally, 2007), each of which can reside in the gas-phase, in the particle phase or can partition between these phases. Because of this chemical complexity, clear definitions are required for a systematic discussion on the origin and fate of these compounds in the atmosphere.

2.1. PM (PRIMARY AND SECONDARY) AND ITS COMPONENTS (ORGANIC, INORGANIC).

As discussed in Robinson et al. (2007) primary particulate matter (PPM) is comprised of directly emitted particle mass plus any material that condenses into the particle phase without undergoing chemical reactions However, estimation of emission factors (EFs) for such emissions are also impacted by evaporation of some of the compounds. The organic component of PPM emissions is usually referred to as primary organic aerosol (POA), which in turn consists of non-volatile (filterable) organic matter (FPOA), and the particle phase of 'condensable' organic aerosol (CPOA): POA = FPOA + CPOA

The CPOA are a class of compounds of low volatility that are in vapour phase inside the exhaust gases, but which may partition between the gas and particle (condensed) phase upon cooling and dilution. Such compounds may or may not be included in current emission inventories for fine particulate matter ($PM_{2.5}$) and PM_{10}, as measured emissions and derived emission factors (EFs) depend strongly on the sampling and analytical approaches followed. Emission measurements protocols may be prescribed in emission legislation, in which CPOA is sometimes deliberately excluded.

PPM can also be divided into so-called filterable (solid) PM, denoted FPM, and condensable compounds, denoted CPM. The FPM fraction includes soot/black carbon (BC), ash, FPOA, and mineral or metallic compounds. The CPM fraction includes inorganic compounds (mostly sulphates from sulphur present in fuels) and CPOA.

2.2. SVOC / IVOC

The most commonly used definitions of classes of organic compounds are based on their volatility. For the definition of non-methane volatile organic compounds (NMVOC), semi-volatile organic compounds (SVOC) and intermediate volatility organic compounds (IVOC), we refer to the naming convention for atmospheric organic aerosol as suggested by Murphy et al. (2014). These definitions are based on the saturation vapour concentrations of the organic compounds. It is possible to derive the saturation vapour concentration for individual compounds, but since in the atmosphere, there will always be a mixture of many different compounds, the saturation vapour concentration is best regarded as the empirical property of a combination of organic compounds with similar volatilities (Donahue et al., 2006). A typical schematic of the emission and chemical evaluation of organic compounds defined below is given in **Figure 2-1**.

NMVOC
Non-methane volatile organic compound, with a saturation vapour concentration[1] at 298 K (C*) >$3.2\mathrm{x}10^6$ µg m^{-3}.

This includes many primary VOCs that are emitted from incomplete fossil fuel combustion and evaporation (e.g. single-ring aromatics like benzene and toluene) or from vegetation (e.g. isoprene, monoterpenes).

IVOC
Intermediate volatility organic compound, with a saturation vapour concentration 320 µg m^{-3} < C* < $3.2\mathrm{x}10^6$ µg m^{-3}.

IVOCS can be primary (directly emitted) and secondary (formed from a NMVOC). Ambient IVOCs are therefore a complex mixture of organics contributed by both primary emissions and photochemical oxidation of gas-phase organics. At atmospheric conditions, they will mostly reside in the gas phase.

SVOC
Semi-volatile organic compound, with a saturation vapour concentration (at 298 K) of 0.32 µg m^{-3} < C* < 320 µg m^{-3}.

These compounds partition significantly between the gas and the aerosol phase at atmospheric conditions. They can be formed by oxidation of a NMVOC or from evaporation of primary OA emissions.

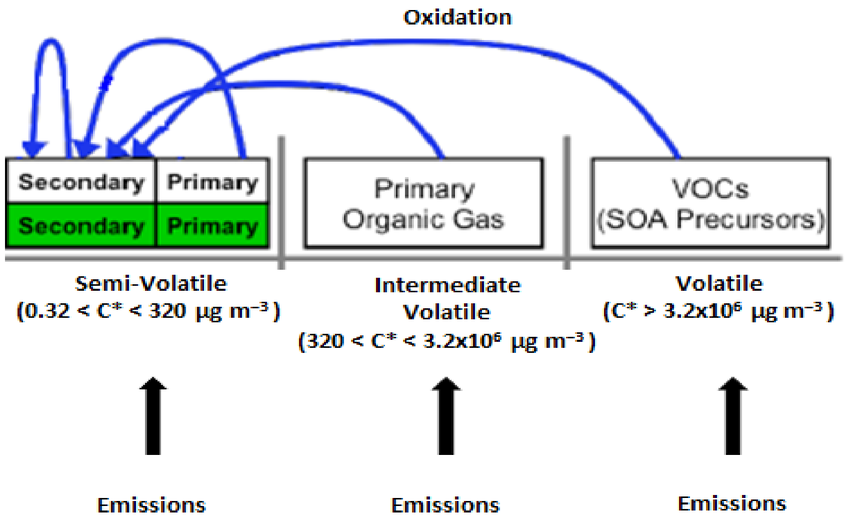

Figure 2-1 Schematic of the emission and chemical evaluation of organic compounds in the atmosphere. Compounds in the particulate phase are denoted with green shading (Fuzzi et al., 2015)

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[1] The saturation vapour concentration is defined as the pressure of a vapour which is in equilibrium with its liquid. For organic vapours, various methods with different degrees of complexity exist for its estimation, usually based on molecular structure.

2.3. OA (PRIMARY OA AND SECONDARY OA)

Organic aerosol (OA) comprises all particulate matter (either in the liquid or the solid phase) in the atmosphere that consists of organic molecules.

Traditionally, OA has been described by just two classes: primary organic aerosol (POA) and secondary organic aerosol (SOA). In this classification, POA consisted of non-volatile organic compounds that were emitted in the particle phase, and which would not experience atmospheric processing other than dilution and deposition. Respectively, SOA included all OA that was formed in the atmosphere by oxidation and subsequent condensation of gaseous precursors (VOCs).

However, the discovery of the semi-volatile nature of emitted POA (Robinson et al., 2007; Grieshop et al., 2009) and the inability of models to explain observed ratios of more and less oxidised organic aerosol components (Shrivastava et al., 2008), which are a proxy for the ratio between secondary and primary OA, showed that this POA/SOA classification is too simple.

Currently, POA is defined as organic material that is emitted as aerosol under atmospheric conditions and either stays in the particle phase, or condenses back to the particle phase immediately after evaporation before any chemical transformations have taken place. Note that soot is not POA, since it is pure (elemental) carbon. Only material containing chemically-bound carbon in particulate form, is considered POA. To put a quantitative constraint on the POA definition, Murphy et al. (2014) define it as material emitted in the particle phase at an OA concentration equal to or below 320 µg m^{-3} and T=298 K, although they acknowledge that this limit is somewhat arbitrary. Note that by this definition, the amount of POA formed from a certain amount of emission depends on atmospheric conditions, and will be lower, for instance, in summer than in winter conditions. So POA is semi-volatile, but how much of it will evaporate depends on the atmospheric conditions.

SOA, in contrast, is the organic aerosol that is formed in the atmosphere from a VOC after one or more generations of oxidation. This VOC can be either a NMVOC, an IVOC or an SVOC. The definitions of the VOC classification is given below.

2.4. SVOCS / IVOCS AND CONDENSABLE PM (CPM)

In EPA Method 202 (Fed. Regist., 2010), CPM is referred to as “material that is [in the] vapor phase at stack conditions but which condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack”. All CPM is assumed to be in the $PM_{2.5}$ size fraction[2]. Since temperature is an important factor in determining the volatility of a substance, it is critical in the definition of CPM. US EPA test methods therefore specify that the temperature of the filter upon which the CPM is collected is maintained at 30°C or less. Together with filterable particulate matter (FPM) it forms total particulate matter (TPM) that is emitted from fossil fuel combustion.

Sample dilution may result in some of the more volatile components of CPM to evaporate again and is therefore of influence to CPM mass. Different measurement methodologies lead to different CPM concentrations, due to differences in dilution that is applied. In EPA Method 202—Determination of Condensable Particulate

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[2] Semi-volatile material condenses primarily onto existing aerosol and shows little tendency to nucleate. Because of its much greater specific surface there is a strong preference to condense on the finest fraction of existing aerosol. CPM remains almost always of small size (well below 2.5 µm).

Emissions from Stationary Sources, sample gases are cooled and CPM is collected on the CPM filter, which is maintained at a temperature between 20 and 30 ºC. Material that is particulate mass at 30ºC without dilution is considered CPM. However, EPA method OTM-37 uses a system that dilutes and cools the sample gas prior to collection of the PM passing through the size separation stage, including condensable PM, on a membrane filter. In addition, more methods to measure CPM exist that may use different rates of dilution and/or filter temperature.

Because these methods lead to different CPM concentrations, derived emission factors from these methods are incomparable. This complicates the compilation of an overall emission inventory for CPM.

The EPA definition for CPM refers to all condensable species and as such is not specific to organic compounds only; SO_3, for instance, can be part of CPM (Feng et al., 2018).

Fossil fuel emissions contain many organic compounds, such as alkanes and esters, which enter the particulate phase immediately after discharge and thus are part of CPM and of primary S/IVOC (Feng et al., 2018). In other words, the definitions of CPM and S/IVOC partly overlap, since both are defined by volatility at a certain temperature. Also note that the organic fraction of CPM contributes to POA, since it forms aerosol without any chemical reaction.

2.5. THE DIFFERENT FORMATION PATHWAYS, ROLE OF IVOC/ SVOC AND CPM

Before discussing the various formation pathways of secondary organic aerosol (SOA), it is instructive to first discuss how POA is formed. As defined in section 2.2, POA is the organic material that stays in the particulate phase after emission or condenses immediately upon emission (so it includes both filterable and condensable PM). Therefore, CPM, by definition, only contributes to POA and not to SOA.

It should be noted however, that the amount of POA formed from a given amount of emitted organic material depends on ambient conditions, such as temperature, dilution and the available mass of pre-existing organic aerosol in the atmosphere, since these factors determine the partitioning of the SVOC between the gas and the particulate phase. Concerning the latter: partitioning of semi-volatile organics is an absorptive process, which means that when a larger pre-existing mass of organic aerosol is present, more mass is available for the SVOCs to absorb into.

SOA is formed from two main categories of organic compounds that are separate species in emission inventories:

- the part of the POA emissions (which themselves are a fraction of $PM_{2.5}$ emissions) that enters the gas phase after emission as primary S/IVOC,
- NMVOC, which are completely in the gas phase after emission.

Both are subject to oxidation in the atmosphere and subsequently form products with lower volatilities. These secondary S/IVOC species will then partition between the gas and the particulate phase, depending on atmospheric conditions, as described above for POA.

2.6. HOW ARE THE FORMATION PROCESSES TREATED IN THE AIR QUALITY MODELS?

In this section the current state of play related to the formation processes as used in air quality models in generic terms will be addressed, ending with specific remarks on how the air quality modelling could be improved to better represent the contribution from road transport to the total OA concentrations.

Traditional OA models treated POA as non-volatile and SOA formation as resulting from first-generation oxidation products of NMVOCs, either by applying a fixed SOA yield for each NMVOC species or by accounting for absorptive partitioning of these oxidation products (Kanakidou et al., 2005; Odum et al., 1996). The discovery of the semi-volatile nature of POA emissions and the notion that several generations of atmospheric ageing may affect SOA yields, called for a different modelling approach.

All models that treat part of the POA emissions as semi-volatile need to include ageing, since it is a fundamental process in the evolution of organic compounds in the atmosphere (Jimenez et al., 2009): ageing affects the volatility of organic compounds, so it is key in determining the partitioning of those compounds between the gas and the particle phase. Therefore, in modelling of the evolution of organic compounds in the atmosphere, dilution, ageing and partitioning need to be addressed simultaneously (Donahue et al., 2006).

The Volatility Basis Set (VBS) framework (Donahue et al., 2006) is currently the most widely applied approach to describe the evolution of organic aerosol in the atmosphere. In its simplest (1 dimensional) form, it groups organic compounds by their volatility in bins that are separated by one order of magnitude in saturation concentration (expressed as C* in µg m^{-3} at 298K), and calculates gas-particle partitioning for each volatility bin. Once S/IVOC, that are formed from evaporation of POA or from oxidation of a NMVOC, enter these volatility bins, they are subject to atmospheric ageing (oxidation) by the OH radical. How this ageing affects the volatility of the S/IVOC, and therefore its shift to a different bin in the VBS depends on the parent organic compound. For a given organic compound, the effect of ageing on its volatility depends on the balance between functionalisation (the addition of functional groups to the carbon backbone of the organic molecule) and fragmentation (the break-up of the carbon backbone into two or more smaller carbon chains). In general, functionalisation leads to compounds with lower volatility than the parent molecule, while fragmentation leads to the formation of smaller and therefore more volatile compounds. Most chemical transport models (CTMs) apply different ageing rates for SVOC that are derived from anthropogenic NMVOCs (e.g. aromatics), biogenic NMVOCs (e.g. monoterpenes) and from primary organic compounds (primary S/IVOC), respectively (Bergström et al., 2012; Fountoukis et al., 2014), to account for the net effects of ageing on volatility for each precursor class.

While OA mass is an important quantity for air quality applications, studies have shown that mass alone is a poor metric for the evolution of OA in the atmosphere (Dzepina et al., 2009; Donahue et al., 2011); there is limited information available from experimental studies that can be used to constrain the parameters of processes such as S/IVOC emissions and S/IVOC ageing. Therefore, including these processes in a model may lead to simulations that get OA concentration right for the wrong reasons (Dzepina et al., 2009), because there is ample room for tuning emissions or aging rates to obtain model results close to observations while staying within experimentally determined constraints. Therefore, approaches have been developed that account for properties other than volatility.

The 2D VBS accounts for both volatility and oxidation state of the OA (Jimenez et al., 2009; Donahue et al., 2011). It has been developed to constrain properties of the OA mixture upon ageing along 2 dimensions that are related to measurable bulk properties of the OA mixture: volatility and oxidation state. However, due to the large number of bins (in both volatility and oxidation state space) the 2D VBS is computationally expensive, which hinders its implementation in 3D models. Intermediate approaches have been developed to alleviate the computational burden of such a model, such as the 1.5D VBS (Koo et al., 2014), which couples volatility and oxidation state through atomic ratios in the organic molecules.

The VBS framework has been applied in global models (GEOS-Chem (Jo et al., 2013), EMAC (Tsimpidi et al., 2014)), regional models (LOTOS-EUROS (Manders et al., 2017), EMEP (Bergström et al., 2012), PMCAMx (Shrivastava et al., 2008), WRF-Chem (Hodzic et al., 2014)) and local models (Dzepina et al., 2009; Hayes et al., 2015; Janssen et al., 2017). Most CTMs apply the 1D VBS, but many variations are available in terms of the assumptions that are made on included SOA precursors, number of volatility bins and volatility distribution of emissions from different sources, ageing parameters etc. In general, the VBS had led to a more realistic representation of OA formation in CTMs. By including the VBS, CTMs are better able to reproduce POA/SOA ratios (Shrivastava et al., 2008), to model contributions of various sectors to OA levels (Denier van der Gon et al., 2015; Fountoukis et al. 2016), and to account for SOA formation from S/IVOCs (Bergström et al., 2012; Woody et al., 2016; Murphy et al., 2017).

The information presented above shows that key elements in modelling ambient OA levels are the volatility distribution of the emitted organic molecules and their oxidation in the atmosphere. Most models use generic basis sets which do not use specific source sector differentiation.

To improve the representation of the road transport sector (or any other) in OA modelling more research is needed to identify the specific speciation of the NMVOC and the amount of S/IVOC emissions from road transport. Such information can be used to improve the total amount of emissions, their speciation and volatility distribution as used in the models.

An example of such an advanced approach for modelling the contribution of road transport to OA is given by Jathar et al. (2017). They included an updated speciation of NMVOC and emissions of unspeciated IVOC from gasoline- and diesel-fuelled mobile sources, based on Jathar et al. (2014). Further, they included separate volatility distributions for diesel, gasoline and biomass burning emissions. Their model calculations predicted that in 2010 30-40% of OA in southern California originated from these mobile sources. The remainder of the organic aerosol was attributed to non-mobile anthropogenic sources (e.g. cooking, biomass burning).

Ots et al. (2016) applied a different approach to estimate the contribution of diesel-related IVOC emissions to OA formation over London. They scaled IVOC emissions with VOC emissions, based on observations. They attributed about 30% of annual average SOA concentrations to diesel-related IVOCs. However, the general applicability of this approach in CTMs seems limited as it depends on the availability of local observations. In a study over the Greater Paris area, Sartelet et al (2018) estimated S/IVOC emissions from VOC emissions based on chamber experiments. They found that the contribution of these sources to OA depends strongly on the assumptions that are made on the volatility of the emissions.

Finally, Jiang et al. (2019) quantified source contributions of various sectors to OA over Europe for a whole year. In their VBS implementation, they distinguished between diesel vehicles with and without a diesel particle filter. They found that average contributions of diesel and gasoline vehicles to OA concentrations were small (around 5%), with exception of urban areas where contributions up to 31% were reached.

How does VBS and SOA modelling relate to substances in the (official) emissions inventories?

Since the realisation that POA emissions are partially semi-volatile (SVOC) and that traditional filter measurements miss a substantial fraction of the organic vapours that are of intermediate volatility (IVOC) (Robinson et al., 2007), many modelling studies have aimed at simulating the contribution of S/IVOC to ambient SOA formation. However, there are major uncertainties regarding the emission and ageing of S/IVOCs that affect all of these studies. The implementation of formation mechanisms of SOA from S/IVOC (S/ISOA) in these models differs mainly in the way that the amount and volatility distribution of the emissions is treated and in the assumptions that are made on gas-phase ageing. We describe here the most common assumptions on these three aspects.

In most studies, the total SVOC emissions (summed over all volatilities) have been set equal to the POA emissions as reported in emission inventories[3] (e.g. Robinson et al., 2007; Bergström et al., 2012; Murphy et al., 2017). However, some modelling studies have applied scaling factors of up to 3 to the POA emissions to derive SVOC emissions (Tsimpidi et al., 2010; Woody et al., 2016), reflecting the fact that calculations using emissions without scaling led to large underestimations compared to measured OA concentrations. Considering IVOC emissions, all models until 2015 applied an IVOC emission of 1.5 times the POA emission in inventories, based on the experiments on diesel exhaust by Robinson et al. (2007). Afterwards, other approaches have been adopted, like scaling the IVOC emissions with ambient observations (Ots et al., 2016), applying VOC speciation profiles for gasoline and diesel sources from measured tailpipe emissions (Jathar et al., 2017), or including one surrogate SOA species to represent several uncertain processes like emission and ageing of organic components from combustion sources (Murphy et al., 2017).

The volatility distribution of SVOC and IVOC upon emission determines the split between modelled POA and SOA formation to a large extent. Initially, it was assumed that this volatility distribution was the same for each fuel type, based on the experiments on diesel exhaust by Robinson et al. (2007). Following the experiments of May et al. (2013c, 2013a, 2013b), separate volatility distributions of S/IVOC emissions from gasoline, diesel and biomass burning, respectively, have been implemented in some models (Koo et al., 2014; Woody et al., 2016).

Incorporating the entire volatility spectrum of primary organic emissions from different sources in emission inventories seems the best way forward to reducing the uncertainties in modelled OA concentrations, associated with these S/IVOC emissions (Murphy et al., 2017).

In addition to emission uncertainties, the uncertainties related to ageing of gas-phase organic compounds need to be highlighted. Since the composition of the mixture of S/IVOC is generally unknown and strongly varies with source and location, parameterising the ageing of this mixture is prone to large uncertainties. Robinson et al. (2007) derived an S/IVOC reaction rate with the hydroxyl radical of

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[3] In emission inventories POA is often not clearly distinguished from other PM. In certain cases it is not even included in PM. Additional analysis and processing of PM emission inventories is often needed to estimate POA emission

$4 \cdot 10^{-11}$ molecules cm^{-3} s^{-1} from their experiments, and this value has been applied in many modelling studies afterwards.

Moreover, several studies have applied variations of this number as a way of evaluating the effect of this uncertainty on simulated SOA concentrations. To account for differences between groups of organic compounds (e.g. those derived from primary, anthropogenic and biogenic VOCs), several modelling studies apply different ageing rates to species from each of these groups (Bergström et al., 2012; Woody et al., 2016). However, it needs to be stressed that these reaction rates are not well constrained by experiments, and thus merely serve as an approximation of the ageing of mixtures of compounds from different categories in the real atmosphere.

What are resulting OA concentrations, how important is SOA in terms of total ambient PM?

Contribution OA to PM

Observations at various locations in the Northern Hemisphere have shown that OA contributes a substantial fraction (20-90%) to PM_1 (Jimenez et al., 2009). Modelled contributions are mostly on the lower end of that spectrum, since models underestimate SOA formation in most cases, even if semi-volatile emissions and ageing are accounted for (Ciarelli et al., 2016; Mircea et al., 2019). In the following sections, we describe what is known about the contribution of organic aerosol (both primary and secondary) to modelled PM concentrations. The focus is on North-America and Europe, since most studies to date have been performed for these regions.

Organic aerosol simulations that only include 'traditional' SOA precursors (short-chain aromatics, terpenes, isoprene) and non-volatile POA are biased low compared to observations (Kanakidou et al., 2005; Volkamer et al., 2006; Heald et al., 2011). Therefore, the inclusion of semi-volatile POA emissions and chemical ageing of S/IVOCs was expected to help close the model-measurement gap (Robinson et al., 2007; Shrivastava et al., 2008). Improvements in model-measurement agreement have indeed been shown under specific conditions (Shrivastava et al., 2008; Murphy et al., 2017), but the complex nature of semi-volatile emissions and ageing of unspeciated S/IVOC mixtures has also introduced large uncertainties in models. Simulations of the global OA budget are actually diverging between models, due to the rising complexity and associated uncertainty in OA parameterisations (Tsigaridis et al., 2014).

An evaluation of modelled OA contributions to total PM should therefore always include a discussion of the uncertainties associated to the result. These uncertainties are mainly related to emissions and process parameterisations. However, uncertainties imposed to observations can also be significant.

The uncertainties related to primary SVOC and IVOC emissions and ageing have been discussed above. Additionally, emissions from some sources, like cooking, are not usually included at all in inventories, but can be an important source of OA in population centres (Fountoukis et al., 2016).

Recent developments have pointed at other gaps in our understanding of the formation and life cycle of organic aerosols. These include the impact of dry deposition of SVOC and IVOC which leads to lower modelled SOA concentrations (by ~50% over the US; Knote et al., 2015), the photolytic breakdown of SOA (Hodzic et al., 2016), the role of aqueous-phase SOA formation (McNeill, 2015) and the inhibition of SOA formation by gas-phase chemical pathways (McFiggans et al., 2019). All of these topics are subject to ongoing fundamental research, which will eventually lead to a better understanding of the fate of organic species in the atmosphere.

Another major factor contributing to uncertainty is the lack of observations that are available for model evaluation over Europe. While multi-annual time series of total organic carbon (OC) observations are available for various locations, and have been used for model evaluation (Bergström et al., 2012; Prank et al., 2016), they miss essential information that is needed to evaluate whether a model captures the types and sources of OA well. It is, for instance, not possible to tell whether a model captures the split between POA and SOA well, even if it simulates the correct amount of total OC. To do so, observations by aerosol mass spectrometers (AMS) or aerosol chemical speciation monitors (ACSM) are useful, which give more information about the origin, volatility and oxidation state of the OA. Over Europe, these have mostly been employed in measurement campaigns for short periods (up to a few months), and these observations have been used intensively in model evaluations (Fountoukis et al., 2011; Zhang et al., 2013; Ciarelli et al., 2016; Janssen et al., 2017; Jiang et al., 2019; Mircea et al., 2019; Yttri et al., 2019;). However, long-term speciated observations would be essential to evaluate the ability of models to reproduce seasonal cycles of OA concentrations and sources.

For Europe, Fountoukis et al. (2011) were the first to simulate OA formation using the VBS approach. They predicted a 32% contribution of OA to total PM_1 during May 2008, with SOA dominating over POA. Compared to AMS observations at 4 stations, this meant an underestimation of 9% of total OA (3.0 versus 3.3 µg m^{-3}).

A more detailed evaluation of the VBS was carried out by Ciarelli et al. (2016), who simulated $PM_{2.5}$ concentrations over Europe for different periods. In general, they found a good model-measurement agreement for $PM_{2.5}$, but noted that this was partly due to compensating errors of overestimated secondary inorganic and underestimated OA concentrations. For the period February-March 2009, they performed various experiments in which different assumptions on POA emissions and ageing were evaluated. A simulation with semi-volatile POA emissions as in (Robinson et al., 2007) actually led to lower OA concentrations than in the control simulation which treated POA as non-volatile. When POA emissions were increased by a factor 3 and IVOC emissions included (amounting to 1.5 x the POA emissions) as in (Tsimpidi et al., 2010), the mean simulated OA increased by 42% (from 1.2 to 1.7 µg m^{-3}), compared to the non-volatile POA case. However, this was still an underestimation, as the mean observed OA concentration over 11 sites was 3.0 µg m^{-3}. When biomass burning emissions were increased by a factor 2 to account for missing residential wood combustion emissions (along with the 3x POA increase), the bias compared to observations was reduced further (simulated mean concentrations of 2.8 µg m^{-3}). In each scenario, the model overpredicted the SOA/POA ratio compared to the observations at one site, both during summer and winter, which suggests that there are remaining issues with the volatility of the emissions and ageing of S/IVOC.

Further, a number of model intercomparison studies have been performed that aimed at evaluating different CTMs against PM observations. The performance of four CTMs in predicting European aerosol chemical composition was evaluated by Prank et al. (2016). Among these models, only the EMEP model included the VBS parameterisation. This model simulated the highest contribution of OC to $PM_{2.5}$ and PM_{10} of all models in the comparison, but still underestimated the contribution of OC compared to observations. Also the seasonal variations were not captured well by the model. Over all models, underestimations in simulated OC in $PM_{2.5}$ ranged from 40-80%.

Recently, Mircea et al. (2019) compared 6 models for OA, of which only two used the VBS approach. Nevertheless, most CTMs predicted similar levels of total OA, irrespective of which SOA formation approach was used. They suggest that processes other than the SOA formation mechanism, such as missing IVOC emissions and heterogeneous chemistry, are the reason for this. Highest concentrations (over 6 µg m^{-3}) were simulated during cold periods with intense anthropogenic emissions. Simulated POA concentrations were highest during cold seasons. All models, except CAMx, simulated anthropogenic SOA concentrations less than 0.5 µg m^{-3}, with maxima close to sources like the Po Valley (Italy). The EMEP and CAMx models simulated higher contributions of anthropogenic SOA than the other models, due to the inclusion of IVOC emissions. Biogenic SOA contribution were highest during summer and autumn for all models, although large differences in absolute values exist due to different biogenic VOC emission models and land-use maps.

A comparison against AMS observations at 14 locations during two periods showed that all models underestimate SOA concentrations (measurements ranging from 2.0-2.6 µg m^{-3} between periods), while most overestimate POA concentrations (0.6-0.8 µg m^{-3}), leading to a net underestimation of total OA levels.

3. CURRENT STATUS OF ROAD TRANSPORT EMISSIONS

3.1. EFFECT OF CURRENT EMISSION CONTROL TECHNOLOGY, FUELS AND FLEET COMPOSITION ON THE EMISSIONS OF PM IN ROAD TRANSPORT.

In this chapter we discuss current and upcoming European legislation on particulate matter and gaseous exhaust emissions, widely implemented exhaust gas after-treatment technologies and their effect on PM emissions, the effect of fuel mixture and quality on PM emissions, how PM emissions under realistic operation testing environments compare to real-driving cycles, and the contribution of different road transport categories as well as of exhaust and non-exhaust emissions. At the moment Europe is leading in the reduction of PM emissions of transport through the wide application of the PN (particle number) limit from 2009 onwards. China and India introduced similar standards from 2016 and 2020 respectively. Even though more stringent PM limits are being introduced such as 4.5 mg/km in China compared to 5 mg/km in Europe, the current PN limit already results in average PM emissions to be well below 4.5 mg/km.

3.1.1. European legislation on primary pm emissions

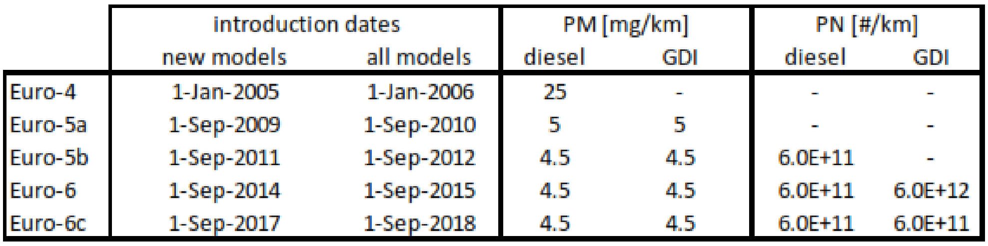
With Euro-5 legislation for light-duty diesel vehicles the PN limit at 6 x 10^{11} #/km, from 1-9-2009 for new type approvals, and 1-1-2011 for all new registrations, the particulate mass emissions have shown a downward trend (Dutch Pollutant Release and Transfer Register 2021). The Euro-5 PN limit is far stricter on particulate emissions than the Euro-5 PM limit of 5 mg/km, as the PN limit of 6 x 10^{11} #/km would already result in less than 1 mg/km for an average particle size of 100 nm. For larger vans, Class II and III, PN limits followed one year later in 1-1-2012, and for heavy-duty vehicles in 1-1-2014 with Euro-VI (8 x 10^{11} #/kWh for the steady state test, and 6 x 10^{11} #/kWh for the transient test), and again particulate mass emissions decimated with the newer vehicles. For heavy-duty vehicles an on-road PEMS test, with cold start incorporated, should meet the 9.8 x 10^{11} #/kWh limit from 1 September 2020, as a safeguard against backsliding technologies and limited durability.

From 2015 particulate mass emission from road transport reduced almost by 5% every year, from the replacement of the pre-DPF vehicles by vehicles with a Diesel Particulate Filter (DPF), both for heavy duty and light duty diesel vehicles. Given the fact that modern light-duty vehicles last 15 to 20 years, and heavy-duty vehicles, 10 to 15 years, it is expected that the tailpipe particulate mass emission of diesel vehicles will not contribute the major part of the overall particulate matter emissions, PM_{10} or $PM_{2.5}$, of transport from 2025 onwards in Europe.

3.1.1.1. Particulate filter implementation

Only a small group of diesel vehicles originally without filter exists at the moment. From 2009 particulate filter is required, therefore these are twelve years or older. The removal of filters, to save on maintenance cost, is becoming illegal and is checked during periodic inspection in several countries across the EU. In European legislation it is currently only illegal to tamper emission control technology of heavy-duty vehicles. For light-duty vehicles such a provision does not exist in European legislation and DPF removal services were advertised, leading to national regulations in a number of countries (Staps and Ligterink, 2018). Many studies show that the PN limit is effective in enforcing a DPF, and a DPF is highly effective in reducing particulate emissions. Therefore, the attention of the legislative body has shifted to petrol vehicles. Gasoline direct injection (GDI) vehicles have a particulate mass (filter) emission limit since Euro-5 in 2011, but no limit for particle numbers, unlike diesel vehicles. With Euro-5 it was announced that petrol vehicles should meet the strict PN limits set for diesel. In **Figure 3-1** an overview is shown of the emission limits in the EU related to particulate matter. However, it still came as a surprise for many engine manufacturers that Real Driving Emissions (RDE) legislation, from 1 September 2019, for all vehicles in independent on-road In-Service Conformity tests required a PN emission limit of 9 x 10^{11} #/km. In a very short time in 2018 the manufacturers switched to the use of Gasoline Particulate Filter (GPF) on almost all new GDI vehicles. Also in this case, especially since particles from petrol engine are smaller, it is expected that the particulate matter emissions of GDI, only introduced less than a decade ago, is decimated as well.

The last remaining sources of particles from light-duty and heavy-duty vehicles are the port fuel injection petrol engines and the natural gas engines. L-category vehicles also have to adhere to an older, less strict euro norm than passenger vehicles and trucks, leading to higher (allowed) emissions. The number and mileages driven of L-category vehicles are smaller, but the emission levels of, in particular, hydrocarbons, are substantial (Ntziachristos et al. 2017). Basically, particulate matter emissions have decreased in the period from 2010 to 2020 from double digits emissions, to levels close to 1 mg/km and 1 mg/kWh for both heavy duty and light duty vehicles (Joshi 2020). Expected with Euro-7, possibly from 2026-2027, no exception is to be made, and all these technologies need to satisfy strict particle number emission limits in on-road tests. The European Commission intended Euro 7 to be technology neutral in the discussions in the Advisory Group on Vehicle Emission Standards. This may ensure the use of filters for particle emissions to be ubiquitous (unlike USA and Japan, which do not have a PN limit). The particle size limit, initially introduced for reproducibility, at 23 nm lower limit, is also expected to be lowered to 10 nm. This may lead to some further development of the GPF and filters for natural gas vehicles.



	introduction dates		PM [mg/km]		PN [#/km]	
	new models	all models	diesel	GDI	diesel	GDI
Euro-4	1-Jan-2005	1-Jan-2006	25	-	-	-
Euro-5a	1-Sep-2009	1-Sep-2010	5	5	-	-
Euro-5b	1-Sep-2011	1-Sep-2012	4.5	4.5	6.0E+11	-
Euro-6	1-Sep-2014	1-Sep-2015	4.5	4.5	6.0E+11	6.0E+12
Euro-6c	1-Sep-2017	1-Sep-2018	4.5	4.5	6.0E+11	6.0E+11

Figure 3-1 European legislated PM limits overview (Ligterink et al. 2020a)

3.1.1.2. Future legislation and after-treatment

For Euro-7 the particle filter is expected to be typically integrated with the catalyst, either Three-Way Catalyst (TWC) for petrol, or the Selective Catalytic Reduction (SCR) (combined with Ammonia Slip Catalyst) for diesel. A heated TWC could be needed, see **Figure 3-3**, depending on the stringency of Euro 7 legislation regarding cold start emissions. However, such technology does not exist yet as the TWC heats up in under 20 seconds after engine start. In diesel vehicles, an oxidation catalyst is likely to remove a part of the hydrocarbons and enhance the oxidation reaction of heavier hydrocarbons and soot, captured in the filter. Thermal management, from placing part of the catalyst close to the engine, or installing heaters (EHC), will ensure that the SCR catalysts function is optimal in most operation conditions. This heater technology has been applied in certain underfloor SCR retrofit solutions, but the question remains if this technology has much added value in an Original Equipment Manufacturer (OEM) solution. The warm oxidation catalyst removes more easily the lower fraction of hydrocarbons, with the exception of methane, and it may change the profile of the hydrocarbon emissions (Hopwood et al. 2020).

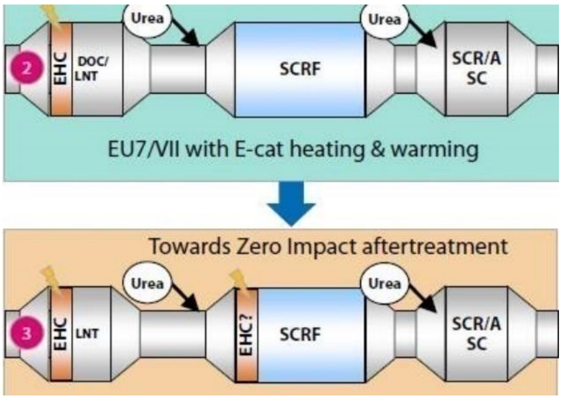


Figure 3-2 Future forms of Diesel engine exhaust gas after-treatment

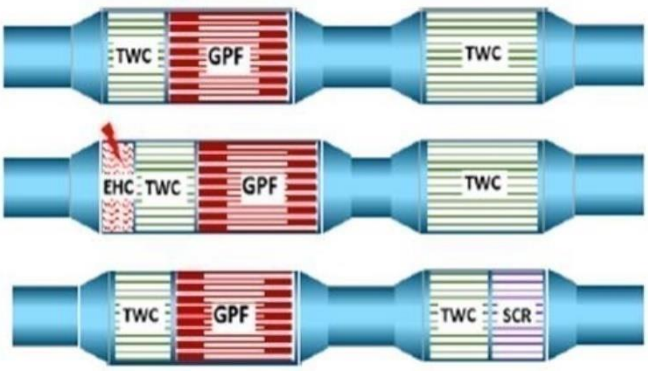


Figure 3-3 Future forms of petrol engine exhaust after-treatment

3.1.2. The effect of engine and after-treatment technology on primary PM emissions, including important SOA precursors

This section describes common and currently available engine configurations and exhaust gas after-treatment systems and their effect on PM emissions. All modern vehicles, both diesel and petrol, are equipped with an oxidation catalytic converter, e.g. the Diesel Oxidation Catalyst and the Three Way Catalyst, responsible for oxidizing partially burned products of combustion and unburned fuel. Specifically, when looking at the partially unburned products of combustion, often labelled as HC and CO, the oxidation process both in the combustion chamber and in the catalytic converter generally favours short carbon chains over longer ones, resulting in an over-representation in long carbon chains, or IVOC, downstream of the catalytic converter. It is important to note that the balance between long and short carbon chains originating from the fuel is shifted towards long carbon chains in the exhaust gas downstream of the combustion and catalytic conversion.

3.1.2.1. Particle filter technology for Diesel

The most distinct technology affecting PM emissions is the Particulate Filter. As highlighted in the previous section there is a Diesel Particulate Filter (DPF) and a Gasoline Particulate Filter (GPF) for direct Injection petrol vehicles.

DPF technology is very effective in decreasing engine particle emissions. A study in 2000 on retrofitting heavy duty vehicles with this technology found it has a filtration efficiency of >95%, both on particle mass and number emissions (Mayer et al. 2000). However, this does not paint the full picture. The filtration efficiency is dependent on multiple factors. It is for instance dependent on the particle size and the loading of the filter. Only after several minutes of loading will the DPF reach its full filtering potential (Yang et al. 2009). In vehicle testing, a minimum mileage of 3000 to 5000 km is set, mainly to ensure appropriate soot loading of the DPF. At the same time, since an uncatalyzed DPF relies heavily on physical filtration of PM emissions, it is most effective on solid PM and to a lesser degree on liquid forms such as organic aerosols. Additionally, high temperatures, typically around 250 degrees Celsius under normal use, cause organic compounds and sulphates to be in gaseous form when reaching the DPF, remaining unaffected by the physical filtering. Downstream of the DPF, these gases will nucleate and condensate under decreasing temperatures forming liquid particles, or aerosols, thereby decreasing the perceived filtering efficiency of the DPF. Even worse, since the amount of solid particles is drastically decreased by the DPF the organic compounds will have no solid forms to use as a sponge and will form small nanoparticles through nucleation (Burtscher et al. 2001). It is important to note here that the amount of gases that nucleate and condensate is highly dependent on factors such as temperature and concentrations. The particle size distribution in **Figure 3-4** shows a clear example of an increase in small nanoparticles. The magnitude of peak is to be noted. More importantly, there have been studies on the effect of catalysed DPFs on exhaust emissions showing significant reduction (>90%) of polynuclear aromatic hydrocarbons (which are SVOC) and hydrocarbons within the C_3-C_{11} size range (Ratcliff et al. 2010). These results suggest a decrease in SVOC emissions from diesel engines equipped with a catalysed DPF. Another study on catalysed DPFs involving smog chambers also shows their effectiveness in reducing both primary and secondary PM emissions of diesel vehicles (Gordon et al. 2014).

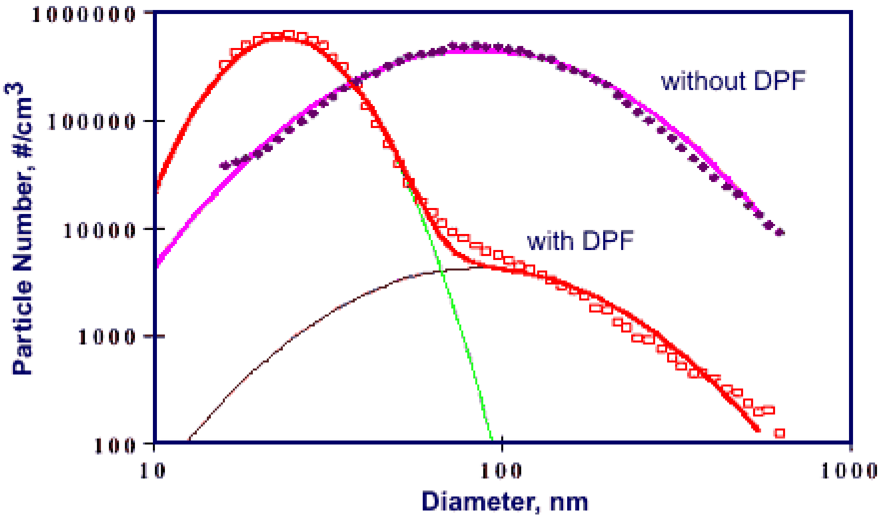


Figure 3-4 Particle size distribution with and without DPF

3.1.2.2. Particle filter technology for petrol

New GDI vehicles come equipped with their own version of the particulate filter: the GPF. GPF technology is very similar to its diesel equivalent, both utilizing wall-flow filtering. The GPF starts off with a lower filtering efficiency when new, around 60% and above, due to the lack of a soot layer. Over time ash, originating from burned lubricants, depending of the lubricant composition and quality, is collected in the GPF and improves the filtering efficiency significantly (Cuelenaere et al.

2019). After several thousand kilometres it can even approach a higher filtering efficiency (>95%). This depends on the porosity of the filter material. GPF do not need a 95% filter efficiency to meet the same PN limits as diesel due to lower engine-out emission levels, and lower filter efficiencies are expected to have higher durability for problems with the deposit of ash. Additionally, some GPFs are being loaded with artificial ash, improving filtering efficiency in new condition, making sure that regulated PN limits can be adhered to under the most cold and high load conditions. A recent study on the effectiveness of GPFs showed that solid PN emissions were below the WLTC and RDE limits, even under the harshest conditions. This study also showed that driving under very low ambient temperatures had a favourable effect on GPF filtering efficiency since it increased engine out soot loading (Giechaskiel et al. 2021). Similar to the DPF, the GPF relies on physical filtration of particles and therefore is best at filtering solid particles and to a lesser degree organic compounds occurring in both particle and gas phase. A study has shown that adding a (catalytic) GPF to a GDI engine can reduce polycyclic aromatic hydrocarbon (PAH) emissions significantly, which fall under the category of the SVOCs, most successfully in particle phase and to lesser extent in gas phase (Yang et al. 2018). The GPF is not expected to reach the filtration efficiency of a DPF at about 99.5%.

Even though new diesel and GDI petrol vehicles are equipped with a particulate filter, Port Fuel Injection (PFI) petrol vehicles get away without one since they remain unrestricted in their PN emissions in Euro-6. Most likely this is going to change for Euro-7, when emission legislation is expected to be similar for DDI and PFI technologies. For GDI and diesel the PN limits are already identical in the Euro-6 standard. Studies with older petrol vehicles show that without a GPF these PFI petrol vehicles emit slightly less PN than DI versions without a GPF. However, the average PN emissions of these PFI vehicles remain above the upper limit of Euro-6d GDI vehicles. This means PFI models have an increasing significant contribution on Particulate Matter emissions; in particular cold start emissions are significant, especially in colder conditions (Kadijk et al. 2018, Ligterink 2016).

3.1.2.3. Catalytic converters

On modern diesel vehicles, both Light Duty and Heavy Duty, besides a DPF there is also an SCR present within the exhaust gas after-treatment system to reduce NOx emissions. Aside from reducing NOx emissions, the SCR could however also affect the PM emissions of a diesel vehicle. The disturbance in exhaust gas flow created by the SCR can promote coagulation of particles, forming larger aggregates of solid matter, while at the same acting as a partial buffer on the PM emissions. A study shows that Euro V trucks, equipped with an SCR (and without a DPF) have a lower fraction of elemental carbon during filter measurements over a driving cycle than their predecessors without an SCR (Ligterink 2018). This means an SCR can even influence the composition of the PM emissions with respect to volatile and non-volatile components.

3.1.3. The effect of different fuel mixture and quality on primary PM emissions

Fuel composition may influence the formation of particulate matter and the particle emissions of vehicles. In particular, gasoline direct injection vehicles are affected by varying fuel compositions. The vehicle manufacturers raised this point several times during the introduction of a PN limit for GDI in independent on-road RDE In-Service Conformity (ISC) testing. Moreover, a wide range of biofuels from different sources may sometimes create a new problem for ensuring proper fuel quality at the fuel stations.

Within the fuel quality specification, fuel composition may vary. With the wide application of biogenetic components, the fuel composition has a wider range of composition that the fossil-based fuels. The effects of the varying composition within specification is not fully known. Fuel quality specifications and requirements, like FQD, EN228, and EN590, ensure that European refinery products are appropriate for modern engine and emission control technology. However, fuel specifications originally based on fossil fuel may leave some room for substandard modern and engineered fuels, according to these specifications.

In 2016, the petrol fuel quality was heavily debated in the development of RDE legislation. It is suspected that the presence of heavier hydrocarbon fractions in petrol fuel led to significant increases in the particle emissions of GDI vehicles, while still complying with the current fuel specification (EN 228). In many cases the fuel specification allows this kind of variations in composition. Moreover, with the introduction of biofuels, MTBE, Ethanol, as well as paraffinic components from hydrotreated bio-stock fuels, the fuel composition shifted further away from the typical products of the standard distillation and cracking products of crude oil. Hence, fuel composition is varying in new ways of which the effects on particle formation are not fully known. Possibly, adding paraffins from different sources may allow the addition of heavy fractions. In the past there were high sulphate emissions, but with the current limit on sulphur of 10 mg per kg fuel this is no longer an issue.

Separate from the varying fuel composition within the national requirements, based on EN228, EN590, and the FQD, there are some concerns with substandard market fuels. There are signals, e.g., from stakeholders, inspection authorities and police, that sometimes the market fuels have varying compositions. An issue reported by inspection and enforcement authorities are incidents of unexpected admixtures in the chain from the refinery, via the biofuels admixture, and bunkers, down to the fuel stations. For example, in the market fuels, substances, like solvents, have been added to fuels to dispose of them. However reprehensible, whether this is illegal is an open question to which the answer may differ from country to country. These are new tasks for authorities. In some cases, especially in off-road use, engine problems like blocked filters, are reported related to fuel issues, which are likely proceeded by substandard engine operation and elevated emissions. Possibly, bio-fuel additives could be contaminated or of poor quality. The parts of the fuel specifications monitored for the Fuel Quality Directive, do not cover the full spectrum of the EN228 and EN590 of petrol and diesel. For example, the presence of ethanol in petrol, makes it possible to contain more water in the fuel (Ligterink 2020b). The effect on emissions was never investigated, although examples of off-specification fuels leading to engine damage have occurred. Engine damage is often damage to the fuel injectors that might possibly act as a precursor in high particle emissions, as faulty injectors typically lead to incomplete combustion and formation of particles. In fossil-based petrol, the presence of water would produce a haze and eventually separation, but in E5 or E10, the amount of water in clear and bright fuel, as prescribed in EN228, can be larger. Possibly, there are other examples, where components can be added to the fuel, which are not covered since the specification is based on fossil-only composition. In the case of RDE legislation, it did not lead to the re-evaluation of fuel specification. The automotive manufacturers shall make engines operate clean within the full spectrum of EN228 for petrol and EN590 for diesel. The uncertainty that the petrol fuel composition posed for particle emissions might probably have been an important factor in the wide introduction of GPFs. Samples of market fuels are to be retained by the test laboratory after a failed vehicle an In-Service Conformity test for the eventuality of off-spec fuels that may cause or aggravate an RDE test result above the emission limit (Ligterink et al. 2020a).

3.1.4. How PM emissions under realistic operation testing environments are compared to real-driving cycles?

Testing environments are designed to replicate real driving, however there is always a difference in emission results compared to real driving. One of the measures to decrease the gap between testing and real driving, is the Real Driving Emissions test (RDE) during type approval. This takes place on the road in real traffic conditions. During the test, different parameters need to be met, e.g. acceleration rates, urban-rural-highway distance and time distribution. The emission limits for an RDE test are higher than for a chassis dyno test because of the decreased accuracy of the portable emissions measurement system (PEMS) equipment used in an RDE test compared to the laboratory equipment used for the chassis dyno test (Cuelenaere 2016). The following sub-sections give further information on how several key parameters differ between testing environments and real driving conditions and what is the associated effect on PM emissions.

3.1.4.1. Cold start emissions

Cold starts and hard accelerations are associated with increased PM emissions (Giechaskiel et al. 2021). In type approval testing environments these have a fixed time and distance portion, are restricted by several factors e.g. (ambient) temperature and maximum vehicle velocity, and are followed by a prescribed amount of driving. In real driving these boundary conditions are much wider. In general, engine out PM during cold starts are higher than during warm operation and can significantly impact the total PM emissions for a certain driving cycle. A petrol vehicle typically already emits around 30 mg of PM just during a cold start. In real driving the portion between cold and warm operation varies significantly, short drives in urban environments is a common yet undesired situation. Both diesel and petrol vehicles, especially those without a particulate filter, will suffer from high PM emissions during cold start.

3.1.4.2. Particulate filters and regeneration

As discussed modern diesel vehicles come equipped with a DPF, reducing both solid and volatile PM emissions significantly. Over time a DPF will saturate and needs to be regenerated by hot exhaust gases. Regeneration can happen on its own under normal driving but regularly this is done in a forced manner. Regeneration creates a peak of PM emissions, as it is burning off the soot in the filter. The size and distribution of these particles is potentially very different than regular exhaust emissions. Recent studies show that during regeneration the composition of the PM emission changes and for a brief period of 2-3 minutes the solid particles with a size of 7-23nm are up to 10-100 times higher than the solid particles with a size of >23nm. Although even with a regeneration, it is not enough to influence a pass or a fail on the non-volatile PM emissions of the entire cycle (Giechaskiel 2020). The forced regeneration is mostly performed with secondary fuel injection, thereby increasing the HC emissions and possibly also the volatile particulates (Andersson et al. 2018, Andersson 2019). Interestingly though, regeneration tends to generate less solid PM emissions during type approval settings such as Worldwide harmonized Light vehicles Test Procedure (WLTP) on the chassis dyno. In the discussions on Euro-7 legislation this issue arose and is the basis to replace the WLTP based Ki factor[4], by the weighing of two on-road tests, with and without regeneration, in the Euro-7 proposal for new legislation.

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[4] Ki factors represent the maximum allowable ratio of emissions from test cycles with a DPF regeneration to emissions from all cycles.

For petrol vehicles equipped with a particulate filter, regeneration is different than for diesel vehicles. Typically, a GPF does not require regeneration in a forced manner, as the exhaust gas temperature is higher than from a diesel and less soot is emitted from the engine. The accumulated PM in the GPF is burned off under high temperature and oxygen rich conditions, since a petrol engine runs (nearly) stoichiometric this is achieved under no-throttle decelerations, as the exhaust line of petrol cars are typically hot, compared to diesel cars. Since regeneration is performed mostly in a passive manner, the associated PM emissions are already measured during a driving cycle. An interesting effect is the increased PM emissions after a dynamic driving cycle, as the GPF is regenerated during dynamic driving and the filtering efficiency decreases with a decreasing soot load in the GPF (Giechaskiel et al. 2021). Although a forced regeneration is not required under normal use, vehicles will be able to force regeneration when operating temperatures have not been sufficiently high, e.g. due to prolonged short distance driving or low speed driving.

3.1.4.3. Vehicle tampering

Brand new vehicles are very effective in reducing engine out emissions, but as vehicles age and accumulate mileage they are prone to defects and vulnerable to tampering with the exhaust treatment. Especially the large engine out emissions of diesel engines are of serious concern with regards to tampering. A survey in 2018 found that at least 1.5% of the DPF’s in the entire fleet of the Netherlands were intentionally removed. Even a small percentage of vehicles without a proper functioning particulate filter can significantly increase the total PM emissions (Staps et al. 2018). Assuming a PM reduction efficiency of 95%, having 1.5% of the fleet without a DPF results in an increase of 28.5% in total PM emissions of the fleet of diesel vehicles originally equipped with a DPF. This is not even considering the possibility of (partially) defective DPFs, e.g. with a small crack in the filter, which remain undetected by On-Board Diagnostics and Periodic Technical Inspection (PTI) testing methods. A small crack can already have a drastic influence on the filtering efficiency of the DPF. Including a particle counter in the periodical inspection, could easily detect improper functioning or removed particulate filters. This includes DPF problems like small cracks, which now go undetected. There are already plans that in the coming future the particle counter be included in the periodical inspection in Belgium and the Netherlands. Although this is currently not being initiated on a European level, countries such as Belgium, Germany and the UK are looking into adding this to their PTI standards as well.

3.1.4.4. Vehicle aging and lubricant consumption

Older diesel vehicles are not the only concern affecting PM emissions. Petrol vehicles tend to have an increasing consumption of lubricants with increasing mileage and age. Lubricants are often consumed via the combustion chamber and ignited together with the fuel, increasing the (volatile) PM emissions and producing ash which is permanently stored in the GPF when present. A study on the effect of burning lubricants in the combustion chamber shows an increase of PN emissions by a factor of 2, where the addition of a GPF significantly reduces PN emissions >99% compared to both non-GPF burning lubricant and the non-GPF non-lubricant burning baseline (Czerwinski et al. 2017). The results also show the highest HC emissions for the GPF + lubricant burning version, which may negatively affect the SOA production later on. Unfortunately, there was no GPF + non-lubricant burning baseline in this paper to compare results to. However, the TNO study on older petrol cars show no correlation between high lubricant consumption and increased particle emissions (Kadijk et al 2018).

In addition, in the characterisation of particulate matter lubricant is often referred to as a relevant source. It remains to be seen if for modern synthetic lubricants the formation of ash and particles are so easily linked to partial lubricant combustion. Lu et al. (2018) give a comprehensive overview of chemical analyses of the hydrocarbon emissions of common petrol, diesel, and kerosene turbine engines. Standard test cycles are used, and cold start is incorporated for petrol engines. Per engine and operation mode the profiles of the molecular composition, and their volatility is fairly consistent and deviating from currently used profiles. The central and largest fraction of the profile is directly related to the molecular composition of the fuel, including larger fractions of aromatics in petrol emissions than diesel, corresponding to the larger fractions of aromatics in the fuel, given the specification. The engines in this study are not the latest generation and complex after-treatment, like Lean NO_x Traps (LNT), which are considered as a source of hydrocarbon emissions in light-duty diesel vehicles, are not included. Moreover, it is important to realize that in USA, the CARB emission legislation for off-road petrol engines is much more stringent than European legislation for the same use. In Europe the amount of unburned fuel is likely larger. It is yet unknown if that would affect the organic profile, but it is likely as in this case the unburned fuel will dominate the profile.

The characterization of Lu et al. (2018) of the organic emissions into “by-product” (i.e., small molecules produced in the combustion), “fuel”, and “lubricant oil” (large molecules) suggests something of a cause allocation. However, the excessive lubricant oil consumption of older petrol cars was raised in the Netherlands as a source of particulate mass emissions, based on studies like by Czerwinski et al. (2017), even if only a small fraction would be emitted unburned or partially burned. It turned out that lubricant oil consumption, up to 1 litre per 1000 to 3000 kilometres, did not lead to higher PM emissions. There was little reason for concern of increasing PM emissions with deterioration of the engine and increase of lubricant oil burning given these studies (Kadijk et al 2018).

It would have been interesting to see if the ratio of automotive PM filter and gaseous hydrocarbons measurements follow the same trend and ratios as observed in the organic profiles. In different automotive measurement programs, this has not been the case (Ligterink 2018, Spreen et al. 2016). There are a number of engine operation regions where the emission profiles, as in the ratio of hydrocarbons and particle emissions are distinctly different. To name a few: a) Cold start emissions, related to cylinder wall wetting and slow burn of fuel, b) Low load operation, with incomplete combustion of fuel, c) Rich operation in petrol cars with excess fuel, d) Regeneration of the DPF filter sometimes forced by late injection with less efficient combustion, etc. Regenerations are likely ignored in the Lu et al. (2018) study, as is common in emission testing. In a test and a test cycle, an attempt is made to have representative vehicle or engine use. This may ensure the collected profiles include a mixture of profiles related to different types of engine operation, and the results of Lu et al (2018) are, in part, the result of the underlying test program.

In later sections we will return in detail to the research by Lu et al. (2018).

3.1.5. Contribution of different road transport categories (i.e., different vehicles, fuels used, Euro norms) as well as of exhaust and non-exhaust emissions.

The contribution of each road transport category is strongly dependent on the fuel and the equipped exhaust gas after-treatment technology. The most important technologies in reducing the PM emissions are the DPF on diesel vehicles, both passenger vehicles (LD) and heavy duty (HD) ones, and the GPF on DI petrol vehicles.

A study on the Dutch fleet in 2017 shows a vehicle renewal rate of around 6.5% for passenger vehicles, both diesel and petrol, and around 8% for HD vehicles, representing the share of the fleet replaced by new vehicles on a yearly basis (Elstgeest et al. 2018).

3.1.5.1. Fleet composition and renewal rate

Looking at the fleet composition in the Netherlands for LD vehicles, around 80% was equipped with petrol engines, of which around 9% DI, and around 15% with diesel engines, the remainder was dominated by petrol hybrids, petrol plug-in hybrids and dual fuel (LPG) versions. The share of GDI vehicles increased to over 50% in recent years, partly to meet low CO_2 values.

Across Europe diesel vehicles gained a share close to 50% around 2015, but declined to about 30% in recent years, partly because of the diesel gate scandal. The HD fleet consisted almost exclusively of diesel vehicles (>95%).

As the Dutch fleet use is close to the European average, it can be used as an indicator for the European fleet and the impact of legislative changes on European PM emissions (see also 3.3.2). The share of diesel vehicles in the Netherlands, with about 15%-20% is low compared to other European countries, but their mileages are among the highest in Europe with more than 35,000 kilometres per year on average for new diesel cars. Moreover, the share of vans, almost exclusively on diesel, in light duty vehicles is with 15% high in the Netherlands, compared to Europe. The Dutch vehicle fleet is older than, e.g., Germany and France, but younger than east European countries. The average CO_2 emission of new registrations is, however, 10 to 15 g/km lower than the European average, partly compensated by the import of older and heavier vehicles. See for example the EEA vehicle registration database and Statistics Netherlands (Geilenkirchen et al., 2020).

For LD diesel vehicles, widespread use of DPFs was introduced between 2009 and 2011 with the Euro-5 norm containing a solid PN limit per driven kilometre. Considering a passenger vehicle renewal rate of around 6.5% per year (see Section 3.1.5), this means around 70% of the LD diesel fleet has a DPF in 2021 and higher than 90% is reached by 2025 with the typical life span of vehicles in the Netherlands. Many old diesel vehicles, without DPF are exported to eastern Europe.

For LD GDI vehicles, widespread use of GPFs was introduced between 2017 and 2019 with the Euro-6c containing a solid PN limit per kilometre driven. Considering again a vehicle renewal rate of around 6.5% per year (see section 3.1.5), this means around 20% of the LD GDI fleet has a GPF in 2021 and higher than 90% is reached by 2033.

For HD vehicles, widespread use of DPFs was introduced in 2014 with the Euro-VI containing a solid PN limit. Considering a vehicle renewal rate of around 8% per year, this means around 56% of the HD diesel fleet has a DPF in 2021 and higher than 90% is reached by 2027.

3.1.5.2. Non-exhaust emissions

With the overall reduction of exhaust emissions both by improved exhaust gas after-treatment systems on new vehicles and large-scale electrification of the fleet, the role of non-exhaust emissions becomes increasingly important. An important part of non-exhaust emissions are wear emissions, predominantly originating from tyres and brakes. The increased weight and torque of electric vehicles increases tyre wear and possibly PM emissions of the fraction of smaller particles into the air, while the majority of wear emissions are large particles, bigger than 10 micron, to ground and water. With a growing share of electric vehicles in the fleet, this is an increasing contribution. At the same time, electric vehicles have the capability of performing regenerative braking, which utilizes the electric motor to decelerate the vehicle instead of using the (disc) brakes, thereby significantly decreasing the wear of brakes and decreasing the corresponding wear emissions (Ligterink et al. 2014).

Tyre wear is expected to be mostly organic and in the size range of around 10 micron. Brake wear however is expected to contain metals and be in the size range of around 2-3 microns, therefore being more harmful for human and environment than tyre PM. A study in 2014 on emission factors found average values of around 6.7 mg/km/vehicle PM_{10} and 6.3 mg/km/vehicle PM_{10} for brake and tyre wear emissions respectively (Grigoratos et al. 2014). Similarly, a study on various emission models shows comparable values (Boulter et al. 2006). In the Netherlands values of 10 and 7 mg/km are used, respectively, of which about a quarter is $PM_{2.5}$ (Geilenkirchen et al, 2020). Comparing these levels to the legislated Euro-6 norm for exhaust emissions of 4.5 mg/km shows the relative importance of these wear emissions for the future. Although one must keep in mind that the wear emissions are dependent on material and use conditions and could be different at this point in time. Depending on the size of non-exhaust particles included, the fraction of non-exhaust is large and increasing. For PM_{10} (particles below 10 micron) already around 2007 the non-exhaust is estimated higher than the exhaust emissions. For $PM_{2.5}$ around 2020 the exhaust and non-exhaust emissions are similar. For PM_1 and especially ultrafine ($PM_{0.1}$) the exhaust emissions are still dominant (Geilenkirchen et al, 2020).

3.1.5.3. International emission standards

The difference between European and USA and Japanese legislation is the PN emission limit and the effective enforcement of particle filters through it. Although European PM limits are higher than CARB, the real world PM emissions are expected to be lower, due to the PN limit indirectly restricting PM emissions. In many cases the PM emissions are close to or below the detection limit. Filters used in experiments of diesel vehicles with a DPF are completely white, almost undiscernible from fresh filters. They cannot be used for chemical analyses, because the loading is too low. Consequently in practice, PM emissions of Diesel passenger cars are below 1 mg/km. This is well below the most stringent USA standards, EPA and CARB, which remain close to the PM measurement uncertainty. The effect of filter regeneration is still an open issue. Based on the industry’s own evaluation it is around 10% of the total emissions, which is a typical Ki factor. These numbers can be requested as part of the transparency act by independent laboratories. In practice, on road, it may be somewhat higher, but still having no significant effect on the average PM emissions. From 2012 onwards, in the Netherlands PM emission factors for diesel vehicles with a DPF are 0.5 mg/km on urban roads, because regenerations occur only on rural roads and motorways. On rural roads and motorways the regeneration emissions are added and these emission factors are 1.5 mg/km. These numbers are based on the Dutch In-Use Compliance testing program, sponsored by the Dutch government, and the result of collecting all filter measurements, with and without regenerations, of vehicles which are extensively testing on the chassis dynamometer. The effects of regeneration are slightly higher than reported by Ricardo in their study for Transport and Environment.

3.2. WHICH ARE THE AVAILABLE TESTING PROCEDURES FOR CHARACTERISING PM EMISSIONS FROM ROAD TRANSPORT?

Measuring and characterising primary PM emissions from road transport can be performed in various manners. The most elaborate and controlled environment way of testing is in a laboratory setting, e.g. chassis dyno testing. Then, there is the less controlled option of on-road testing, e.g. PEMS testing. Furthermore, there is the option of mobile measurement equipment, e.g. stationary idle testing with a particle counter. In general automotive measurement systems are aimed at high resolution and reproducibility. These methods are intended for technology assessment and emission standards compliance testing and not, in principle, to assess air quality indicators.

3.2.1.1. Particulate mass measurements

Particle mass is typically measured using a filter and performing gravimetric analysis. On the chassis dyno the exhaust gas is diluted twice, before depositing the particles on a filter. Dilution is important to minimalize saturation, condensation, nucleation and coagulation. The filter is efficient at catching both solid and volatile particles, however the exhaust gas temperature has a significant influence on the fraction of SVOC in liquid state and over time the semi-volatile particles (SVOC) on the filter will evaporate reducing the total mass on the filter. Filter measurements can also be utilized to determine the composition of the PM with respect to Elemental Carbon (EC). Various methods are available for EC fraction analysis, e.g. Multi Angle Absorption Photometry (MAAP) and European Supersites for Atmospheric Aerosol Research protocol (EUSAAR) (Ligterink 2018). An old and cheap alternative for measuring particle mass is opacity measurement, which is currently still used in periodic inspection. With particulate filters reducing PM significantly and the focus shifting towards smaller particles, this measurement method has an insufficient lower detection limit in current times.

3.2.1.2. Particulate number measurements

The Particle Measurement Program (PMP) method, for determining compliance with European PN limit, utilizes a series of equipment that filter out large particles, dilute the exhaust gas and evaporate all volatile particulates, before the sample enters the condensation particle counter (CPC). The reproducibility of the measurement led to the restriction to particle sizes above 23 nm initially. Moreover, the denuding of the particles at 300 °C to remove all volatile and semi-volatile fractions, retains mainly the carbon fraction, i.e., solid fraction. With the maturity of the DPF technology, and the wide application of GPF technology, more advanced measurement techniques were required to enable the measurement of solid particles down to 10 nm. The particles between 10-23 nm are expected to add about 30%-40% in solid particle numbers, given the size distribution centred around 70 nm (Andersson et al. 2018, Giechaskiel et al. 2021). More and smaller particles may carry a limited amount of mass, but can act as nucleation sites in the ambient air. However, semi-volatile particles without a solid core will still be missed in this measurement technology due to the conditioning of the exhaust gas. Interestingly the PMP method prescribes a volatile particle remover which does not remove gas phase HC, whereas alternatives such as the catalytic strippers and thermo-denuders do.

A key factor that must be controlled is the water vapour that may condensate in the measurement equipment. Since water vapour may be up to 13% of the emission exhaust gas, the temperature at which the measurements, prior to dilution, are performed is kept above 52°C. This will likely “freeze” the phases of the exhaust gas to a relatively low fraction solid and more gaseous hydrocarbons. There is no reason to assume that components are missing, as the sampling for both the PM filter measurements and the hydrocarbon measurements are sampled from the same diluted exhaust gas, in similar conditions. Translating this to on-road conditions and ambient air is, however, not straightforward. The conditions are somewhat different in both temperature as in dilution rate. These measurements are aimed at quantifying volatile hydrocarbon emissions. The commonly used flame ionisation detector (FID) measurement principle does have different responses for the different species. In particular, oxygenated hydrocarbons may be underestimated in these measurements, for example, compared to Fourier Transform Infrared Spectroscopy (FTIR). FID measures roughly proportional to the carbon fraction of hydrocarbons but does not give any data on which hydrocarbon species are responsible for the signal.

3.2.1.3. Automotive measurements and ambient air quality

For PN measurements, with heating and stripped up to 300°C, there is hardly any relation between the solid particle number in exhaust gas (from this automotive standard measurement) and particles in ambient air. There are both mechanisms in place that increase and lower the count differences between the two conditions, in particular evaporation and accumulation. But generally, it is assumed that the automotive PN measurements gives a lower number (*EPAct/V2/E-89, Appendix P)*.

Production of SOAs can be estimated with the use of smog chambers. As they need to form over time and under various conditions, they cannot simply be measured directly from the exhaust gas. Smog chambers are filled with a sample of exhaust gas of a vehicle on the dynamometer together with a gas mixture representing urban environments, subjected to UV light to replicate sunlight and promoting photochemical reactions. Literature shows exhaust gases of different situations, e.g. cold start, high acceleration, highway driving, being combined and put into a smog chamber. Although this provides a nice mixture of the different sections of a driving cycle, the SOA production results are debatable since under real driving conditions these exhaust gases are separated by both location and time. Highway driving exhaust gases are not often in close proximity to stop and go urban traffic (Gordon et al. 2014).

Current automotive emission testing is intended to cover all relevant polluting components, but not necessarily in a manner that translates easily to air quality. Standards for measurements are intended to be reproducible and repeatable, and provide results with high confidence across many laboratories. This makes the link with air-quality observations and measurement principles tenable. However current testing procedures do not include speciation of hydrocarbon emissions; only total HC is determined. To improve future modelling of OA such information will be pivotal.

3.3. INVENTORIES OF PM AND NMVOC EMISSION BY ROAD TRANSPORT IN EU 27.

3.3.1. Official country-reported data

Road transport emissions for non-methane volatile organic compounds (NMVOC) and primary particulate matter (PM, including CPM at 52°C) are part of international emission reporting obligations and the country-reported data are recorded in the CAMS5.1 inventory (Kuenen et al. 2021). There is no targeted SVOC or IVOC emission reporting in Europe for transport, nor for other source sectors. The substances that are sometimes used to estimate or derive SVOC/IVOC emissions specifically are NMVOC or PM. The measurement protocols used to measure PM emissions from transport do include primary condensable particulate matter that is solid at 52°C (PM_{solid} and CPM, including condensed S/IVOCs) but no gaseous IVOCs or SVOCs. All gaseous organic compounds (including S/IVOCs) are in measurement protocols for organic compounds detected by FID as NMOGs. In most reporting however, the term "NMVOC" is used instead of NMOGs, while strictly speaking S/IVOCs are not volatile enough to be considered NMVOC in the 'classic' sense. Note that non-vehicular evaporative NMVOC emissions (e.g. by gasoline distribution and storage) are not included here.

The tables (**Table 1** and **Table 2**) and figures (**Figure 3.5**) below compare road transport $PM_{2.5}$ and "NMVOC" emission sources with $PM_{2.5}$ and NMVOC emitted by other (anthropogenic non-road transport[5]) sources in the EU27 plus UK, Norway and Switzerland (EU27+). Emission data were retrieved from the CAMS5.1 inventories (Kuenen et al. 2021), which are based on country-submitted emission data.

$PM_{2.5}$ emissions in general and diesel exhaust emissions in particular, show a steady decline over the period 2000 to 2018. Note that the relative share of wear emission in road transport increased from 18% of all road transport emission in 2000, to 49% of the road transport emission in 2018. NMVOC emission by road transport decreased from about 3 Mton in 2000 to 0.6 Mt in 2018, with the contribution to the total NMVOC emission decreasing from 25% to 8%. Both the $PM_{2.5}$ and the NMVOC emissions from road transport are expected to continue to decrease from 2018 onwards.

Table 1 Road transport emission of $PM_{2.5}$ (kton) vs. $PM_{2.5}$ emission by other anthropogenic sources, for the period 2000 - 2018

	Road transport sources				
Year	Gasoline, exhaust	Diesel, exhaust	Gaseous fuels, exhaust	Wear emissions	Sources other than road transport
2000	13	242	0.25	55	1531
2005	11	199	0.26	61	1387
2010	6.7	142	0.28	62	1329
2015	5.2	84	0.26	63	1147
2018	4.6	64	0.35	67	1096

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[5] Industry, households, non-road transport, waste, agriculture

Table 2 Road transport NMVOC emission (kton) vs. NMVOC emission by other anthropogenic sources, for the period 2000 - 2018

	Road transport sources				
Year	Gasoline, exhaust	Diesel, exhaust	Gaseous fuels, exhaust	Evaporative emission	Sources other than road transport
2000	2045	336	84	607	9698
2005	1260	232	49	308	8717
2010	630	152	46	193	7784
2015	360	111	32	174	6976
2018	288	100	31	170	6937

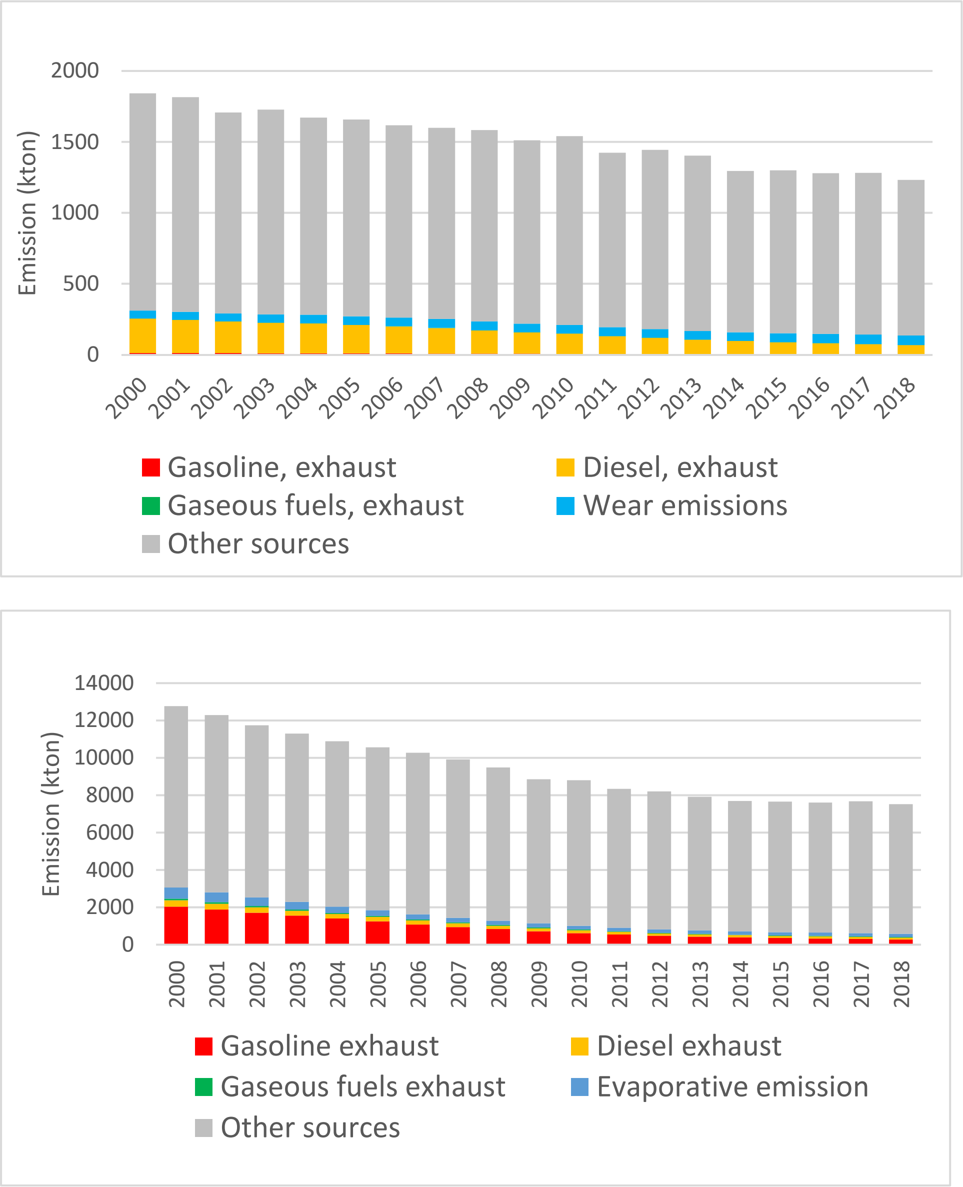
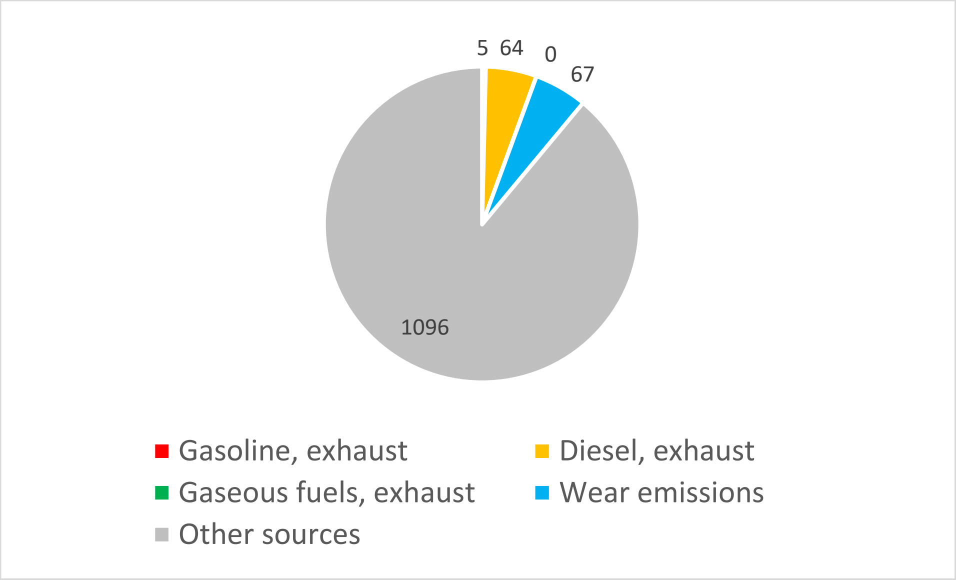


Figure 3.5 $PM_{2.5}$ (top) and NMVOC (bottom) emissions from transport versus other anthropogenic sources for the EU27 plus UK, Norway and Switzerland (EU27+) for the years 2000-2018

The pie charts below (**Figure 3.6**) reiterate data for 2018. Note that diesel exhaust PM emissions (64 kton) were almost equal to PM emissions from wear (sum of tyre, brake and road wear, 67 kton) and that gasoline exhaust primary PM emissions (including primary condensable PM, 5 kton) are only a fraction (7%) of the diesel exhaust emissions. For NMVOC the largest contribution in 2018 is made by exhaust emissions from gasoline vehicles (288 kton), followed by evaporative emissions from gasoline vehicles (170 kton) and diesel exhaust emissions (100 kton). A relatively minor road transport-related contribution is made by vehicles fuelled by gaseous fuels (31 kton).



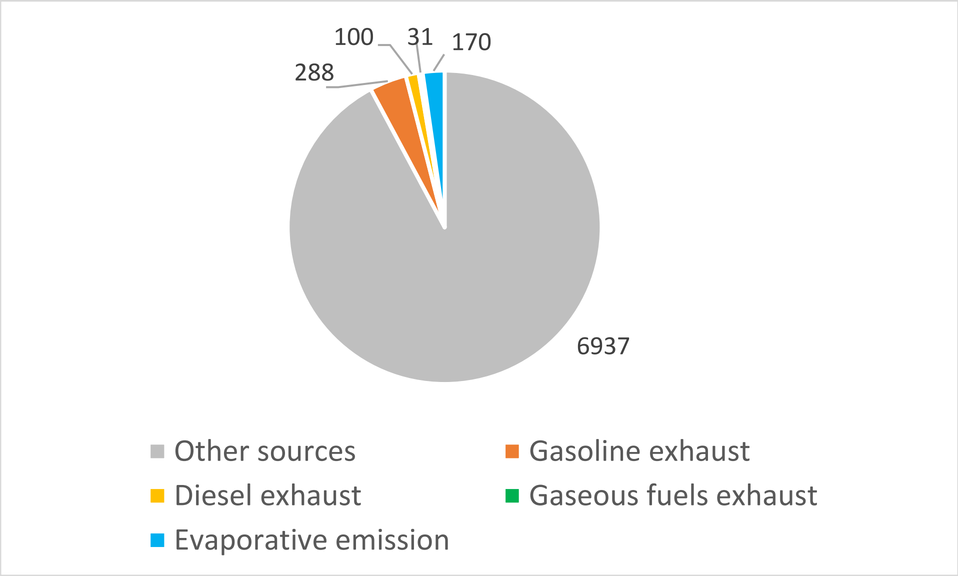


Figure 3.6 Share of $PM_{2.5}$ (top) and NMVOC (bottom) emissions from transport versus other sources for the EU27 plus UK, Norway and Switzerland for 2018

Note that in absolute amounts NMVOC emission from road transport (589 kton, including gaseous IVOC/SVOC) is over four times the mass of the $PM_{2.5}$ emission. Depending on the total SOA yield of the various NMVOC sources, a part of this NMVOC mass may be later converted to PM after emission (forming SOA) and thus add to ambient $PM_{2.5}$ levels. At this stage SOA is not considered or included as (indirect) PM emission in any emission inventory for any source.

3.3.2. Alternative detailed bottom-up emission estimates

The official country-reported emission data shown in **Table 1** and **Table 2** in the previous section do not provide sufficient detail to discern the contributions made by vehicles with different Euro emission standards. To provide insight into which class of vehicles contributes most to the total emission by road transport, TNO has made a parallel bottom-up estimate of $PM_{2.5}$ and NMVOC (NMOG) emission for the EU(27), using detailed vehicle kilometre (vkm) statistics for 2019 and literature emission factors from the EEA Guidebook (EMEP/EEA, 2019). The EEA Guidebook does not give technology stratified emission factors for vehicular evaporation emissions, so this emission source has not been included in the bottom-up results. The total emissions from both inventories are compared in **Table 3**. **Table 3** shows that in general the bottom-up estimate shows slightly lower emissions than the CAMS (country-reported) inventory, which may be partly explained by the different base years (2019 vs. 2018). Overall a reasonable agreement is found, which is encouraging for the robustness of the detailed results of the bottom-up inventory.

Table 3 Comparison of the total road transport emission of $PM_{2.5}$ and NMVOC in the EU(27), according to CAMS5.1 (2018) and the alternative bottom-up estimate (2019)

	$PM_{2.5}$ (kton)		NMVOC (kton)	
Year	2018, CAMS5.1	2019, Bottom-up	2018, CAMS5.1	2019, Bottom-up
Diesel, exhaust	64	66	100	83
Gasoline, exhaust	4.6	2.8	288	267
Gaseous fuels, exhaust	0.35	0.08	31	14
Non-exhaust	67	68	170	N/A

Table 4, **5** and **Table 6** all show detailed emission data per Euro class from the bottom-up estimate, for diesel, gasoline and CNG/LPG-fueled vehicles respectively. Also included are the vehicle kilometers by each Euro class (last column).

Table 4 Detailed overview of $PM_{2.5}$ and NMVOC emission (kton) and vehicle kilometers (10^9 vkm) by diesel-fueled vehicles in the EU(27) in 2019, according to the TNO bottom-up estimate

Vehicle category	**Emission (kton)**			**Vehicle kilometres (10^9 Vkm)**
	Exhaust		**Non-exhaust**	
	NMVOC	**$PM_{2.5}$**	**$PM_{2.5}$**	
Total diesel-fuelled	**83**	**66**	**51**	**2680**
HDV total	**31**	**17**	**21**	**363**
Pre-Euro	6.7	3.7	0.4	8.5
Euro I	2.3	1.5	0.3	5.6

Euro II	5.3	2.8	1.0	19
Euro III	11	5.5	2.3	43
Euro IV	0.6	1.2	2.8	49
Euro V	0.9	1.9	4.4	77
Euro VI	3.6	0.2	9.4	161
LDV total	**52**	**49**	**30**	**2317**
Pre-Euro	2.6	5.4	0.3	18
Euro 1	3.1	3.7	0.5	39
Euro 2	7.4	6.8	1.2	93
Euro 3	11	14	3.8	286
Euro 4	9.3	17	6.6	507
Euro 5	8.8	1.2	8.4	649
Euro 6	9.8	1.0	9.4	725

Table 5 Detailed overview of $PM_{2.5}$ and NMVOC emission (kton) and vehicle kilometers (10^9 vkm) by gasoline-fueled vehicles in the EU(27) in 2019, according to the TNO bottom-up estimate

Vehicle category	**Emission (kton)**			**Vehicle kilometers (10^9 Vkm)**
	Exhaust		**Non-exhaust**	
	NMVOC	**$PM_{2.5}$**	**$PM_{2.5}$**	
Total gasoline fuelled	**267**	**2.8**	**16**	**1384**
HDV total	**4.8**	**0.0**	**0.0**	**0.9**
Pre-Euro	4.8	0	0.04	0.9
LDV total	**262**	**2.8**	**16**	**1383**
Pre-Euro	69	0.5	0.3	30
Euro 1	43	0.4	0.6	56
Euro 2	44	0.3	1.1	100

Vehicle category	**Emission (kton)**			**Vehicle kilometers (10^9 Vkm)**
	Exhaust		**Non-exhaust**	
	NMVOC	**$PM_{2.5}$**	**$PM_{2.5}$**	
Euro 3	45	0.3	2.2	208
Euro 4	24	0.3	3.1	265
Euro 5	14	0.4	3.1	259
Euro 6	22	0.7	5.6	466

Table 6 Detailed overview of $PM_{2.5}$ and NMVOC emission (kton) and vehicle kilometers (10^9 vkm) by CNG/LPG-fueled vehicles in the EU(27) in 2019, according to the TNO bottom-up estimate

Vehicle category	**Emission (kton)**			**Vehicle kilometers (10^9 Vkm)**
	Exhaust		**Non-exhaust**	
	NMVOC	**$PM_{2.5}$**	**$PM_{2.5}$**	
Total Gaseous fuels	**14**	**0.1**	**0.9**	**73**
HDV total	**0.0**	**0.0**	**0.0**	**0.9**
Pre-Euro	0.04	0.004	0.04	0.8
Euro I	0.001	0	0	0.004
Euro II	0.007	0	0.001	0.023
Euro III	0.004	0.001	0.004	0.1
LDV total	**14**	**0.1**	**0.9**	**73**
Pre-Euro	0.9	0.002	0.01	0.9
Euro 1	5.0	0.02	0.08	6.9
Euro 2	3.5	0.02	0.1	10
Euro 3	1.4	0.01	0.1	12
Euro 4	1.3	0.02	0.2	16
Euro 5	1.2	0.004	0.2	14

Vehicle category	Emission (kton)			Vehicle kilometers (10^9 Vkm)
	Exhaust		Non-exhaust	
	NMVOC	$PM_{2.5}$	$PM_{2.5}$	
Euro 6	1.0	0.004	0.1	12

3.4. CHARACTERIZATION OF PRIMARY ORGANIC AEROSOL, IVOCS, SVOCS AND SECONDARY ORGANIC AEROSOL FROM DIESEL AND GASOLINE-FUELLED ROAD VEHICLES, AS REPORTED IN INTERNATIONAL LITERATURE

This section describes and attempts to quantify primary and secondary organic aerosol emissions from diesel and gasoline fuelled vehicles. This subject and related chemical transport modelling discussed earlier in this report (see Section 2) was pioneered in the 2010s by a research group around Professor Allen L. Robinson of Carnegie Mellon University (CMU) in the US. Later attempts by other research groups to perform similar studies, tended to use the work by Robinson's group as a blueprint for their methodology and relied heavily on data originally published by Robinson. We have selected two key publications that investigate SOA formation potential of on-road vehicle exhaust, based on characterisation of chemical composition of gaseous organics emitted by current diesel and gasoline road vehicles. To our knowledge there are no other later studies available that present a comparable emission characterization and involve an equal amount of supporting experimental work as these two. It is important to note that on this subject there is a clear lead in the United States over other regions such as Europe

The first key study is described by Lu et al. (2018), in which emission profiles for organic carbon emissions have been derived, which span the entire volatility range, including VOCs, IVOCs, SVOCs, LVOCs and non-volatile organic compounds (NVOCs). Also discussed by Lu et al. is the potential formation of secondary organic aerosol from these emissions.

A second highly relevant study was performed by Zhao et al. (2017) who investigated SOA formation from a fleet of on-road gasoline vehicles, based on smog chamber measurements, in which diluted ambient level exhaust concentrations were oxidised under a UV light source.

These two studies are discussed in detail in the next sections, with Lu et al. focussing more on the chemical characterisation of the different volatility ranges, while Zhao et al. highlight the measured SOA formation potentials of these compound groups under various NOx regimes. The approaches followed in these studies may be used to make a first order estimate of S/IVOC and secondary organic aerosol formation from on-road vehicles.

3.4.1. Volatility-based organic emission profiles for road vehicles - Lu et al. (2018)

Lu et al. (2018) give a comprehensive overview of chemical analyses of the hydrocarbon emissions of common petrol, diesel, and kerosine turbine engines. Special attention is given to S/IVOCs that may comprise only a small fraction of the released organic gases but are highly relevant for SOA formation. Standard test cycles are used, and cold starts are incorporated for petrol engines. Per engine and operation mode the profiles of the molecular composition, and their volatility is found to be fairly consistent and deviating from currently used profiles. The central and largest fraction of the profile is directly related to the molecular composition of the fuel, including larger fractions of aromatics in petrol emissions compared to diesel, corresponding to the larger fractions of aromatics in the fuel, given the specification. The central volatility mode is found to be enriched in IVOC for modern gasoline engines. The engines measured by Lu et al. are not the latest generation and complex after-treatment, like Lean NOx Traps (LNT), a source of hydrocarbon emissions in light-duty diesel vehicles, are not included. Moreover, it is important to realize that USA, and in particular CARB emission legislation for off-road engines is much more stringent than European legislation for the same use. In Europe the amount of unburned fuel is likely larger for this class of vehicles.

It is important to note that in spite of vehicle technologies being roughly similar, information and findings for the US situation may have limited applicability to the European situation. Another shortcoming of the information given here is that this information could be out of date in certain respects, as at least five years have passed since publication and even longer since the supporting measurements took place. Both these aspects may result in that the applicability to the current European situation may be highly uncertain.

Methodology used

By combining different sampling techniques Lu et al. attempted to capture the complete range of emitted gaseous organic carbon. They then classified organic carbon emission over logarithmically distributed volatility bins. The work was based on experiments conducted during summertime in California in the early 2010s, at typical California summertime temperatures and using California commercial summertime fuels (Lu et al. 2018). Of the 29 gasoline-fuelled road vehicles tested, 10 were pre-Low Emission Vehicle standard (pre-LEV), 9 had the LEV standard and 10 were of the Ultra-Low Emission Vehicle (ULEV) standard. Super Ultra Low Emission Vehicles (SULEV) were not included. Of the five diesel-fuelled medium and heavy duty vehicles, two were equipped with a DPF. With each vehicle between one and 12 tests were performed.

Measured vehicular OC, IVOC and SVOC emissions

Lu et al. used a combination of Tedlar bags, Tenax tubes and quartz filters to capture all emitted organic carbon, irrespective of volatility. The volatility of the organic matter captured by the Tenax partly overlapped with that captured by the quartz filters and care was taken to avoid double counting of organic material.

The total amount of emitted organics (measured with an FID) varied for gasoline vehicles from about 2.5 to 8 g/kg fuel for pre-ULEV vehicles, to about 0.7 – 2 g/kg for LEVs, to about 0.4 – 0.8 g/l for ULEVs. About 4 – 6% consisted of IVOC and 1 to 2% of SVOC.

For diesel vehicles organic matter emissions from non-DPF road vehicles ranged from about 1 g/kg fuel for an EPA Urban Dynamometer Driving Schedule (UDDS) driving cycle to 8 g/kg fuel for idle operation. For DPF-equipped vehicles organic matter emission ranged from about 0.01 g/kg fuel for UDDS to 0.1 – 2 g/kg fuel at idle. Roughly 40% to 60% consisted of IVOC and 4% - 14% of SVOC.

Combining the above suggests IVOC and SVOC emission factors ranging from about 0.03 – 0.3 g IVOC/kg fuel and 0.01 – 0.08 g SVOC/kg fuel for gasoline vehicles, to 0.5 g IVOC/kg fuel and 0.1 g SVOC/kg fuel for non-DPF vehicles, and 0.005 g IVOC/kg fuel and 0.001 g SVOC/kg fuel for DPF equipped vehicles. Comparing ULEVs with DPF equipped vehicles suggests ULEVs to have much higher IVOC and SVOC emission factors than DPF-equipped diesel vehicles, while for older vehicles this is the other way around.

Modes in the volatility distribution of vehicular organic carbon emissions

Lu et al. found many similarities between vehicles, often irrespective of emission standard and engine load, which allowed the aggregation of the results into five distinct general emission profiles:

- Light duty gasoline vehicles, cold start
- Light duty gasoline vehicles, hot operation
- Off-road diesel-fuelled heavy duty vehicles without DPF
- Heavy duty diesel-fuelled vehicles with DPF
- (Jet turbine engines)

All five profiles feature a trimodal volatility distribution, distinguishing in order of increasing volatility, a lubrication oil mode, an unburnt fuel mode, and a combustion by-product mode. The test data are based on real-world tests, which typically combine different engine operation conditions, like low load and high load operations. Cold start is often incorporated, but with the length of the tests, these emissions in the first 20 seconds are smeared over 10 or more kilometers.

Figure 3.7 is taken from Lu et al. and shows the volatility distributions for a gasoline vehicle (top) and diesel vehicle (bottom). Note the logarithmic left Y-axis.

The red dashed red line (corresponding to the right Y-axis) indicates the particle fraction at an organic aerosol (OA) concentration of 10 µg/m^3 (a typical urban OA level) and a temperature of 298 °K. Note that gas-particle partitioning (and hence CPM formation) is highly dependent on temperature.

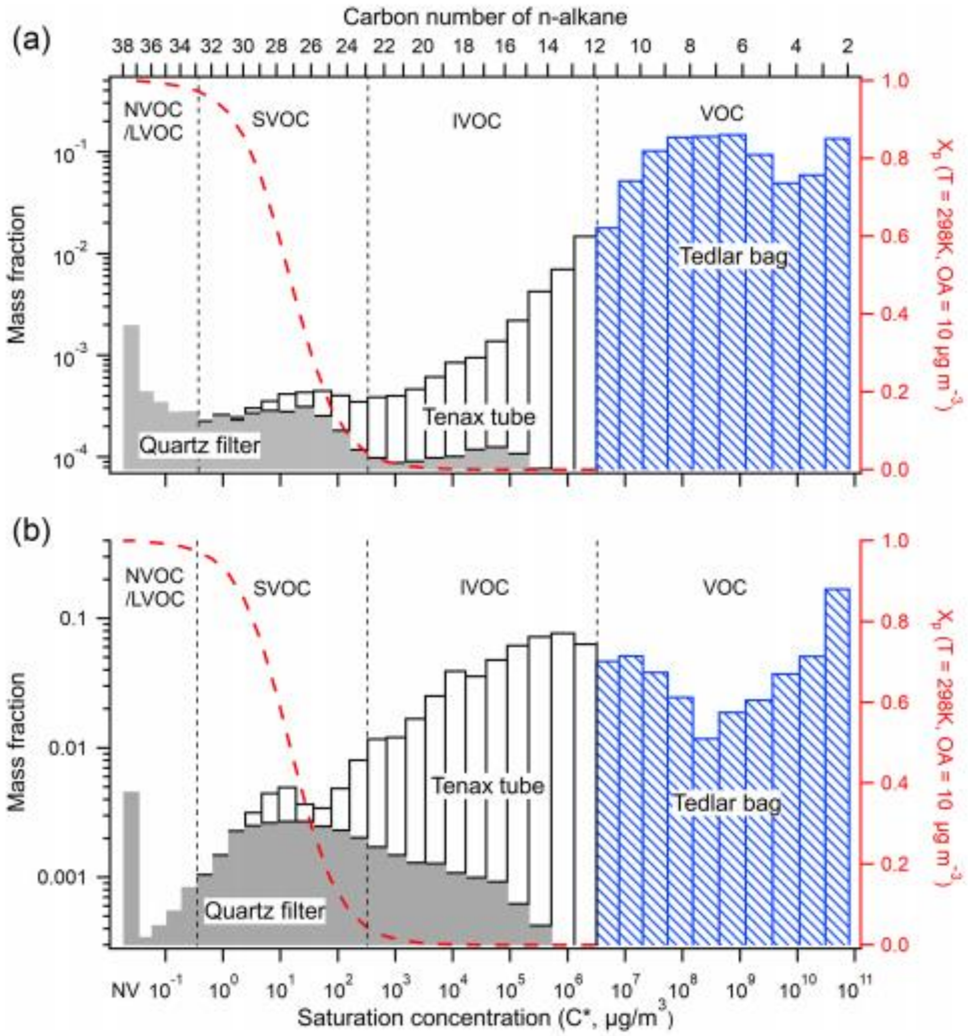


Figure 3-7 Volatility distribution of organic emissions for a typical (a) gasoline (b) diesel vehicle. The emissions are classified by sampling media. As taken from Lu et al., 2018.

The oil mode is in the middle of the SVOC range and comprises 1.4% (0.6 – 4.2%) of the total organic carbon from gasoline vehicles and increases with emission standard. For diesel-fueled vehicles the oil mode is found to make up 5.9% (3.1% – 17.7%) of the total organic carbon and strongly increases with engine load.

The fuel mode is for a small part in the IVOC range for gasoline vehicles and for the largest part in the IVOC range for diesel vehicles. The fuel mode in its entirety is usually the most dominant in all profiles and is the primary source of IVOC emission. For gasoline vehicles, IVOCs are in the lowest volatility tail of this mode and contribute 4.5% (2.4 – 9.6%), for the cold start unified cycle, irrespective of emission standard. For hot operation the IVOC contribution may increase to 18% (5.8% - 31%), suggesting a lower effectivity of catalytic converters for IVOCs (that comprise only 1% in unburned gasoline) compared to VOCs. For diesel fueled vehicles the contribution by IVOCs is much higher (because of the lower volatility fuel), 57% (46.3% - 66%) for non-DPF and 40.1% (17.2% - 55.5%) for DPF equipped vehicles. For diesel vehicles the IVOC volatility distribution resembles that of the unburned fuel, while for gasoline fuelled vehicles IVOCs appear to be enriched compared to the fuel composition.

The combustion products mode is the most volatile and largely consists of C_2-C_5 alkanes, alkenes and carbonyls. It was found to contribute 25.9% (21.1% – 31.0%) to the total organics in gasoline emissions and 26.9% (9.4% - 40.6%) in diesel emissions.

When comparing the profiles shown in **Figure 3.7** with the corresponding profiles in the EPA Speciate database, it seems that the EPA profiles categorize almost the entire SVOC and a significant part of the IVOC content as non-volatile PM (and in that sense not able to form SOA). There are no standard NMOG profiles in use in atmospheric modelling in Europe and profiles assumed for this purpose differ between models.

SOA formation potential of emitted VOCs, IVOCs and SVOC

Per unit of mass, gaseous S/IVOCs are much more potent SOA precursors than VOCs (including aromatics), for both gasoline and diesel vehicles. S/IVOC emissions are however not separately available in current emission inventories. To account for S/IVOCs in SOA modelling, emissions are usually estimated in the model, for instance based on emission of primary organic aerosol or indicator substances. These approaches often give widely varying results however. In the new emission profiles by Lu et al. (2018), S/IVOCs are fully accounted for, and do not have to be estimated based on other compounds.

Lu et al. (2018) estimated the SOA formation potential of each group of compounds in their derived emission profiles for gasoline and diesel road vehicles. Ultimate SOA mass yields for each VOCs were based on State-wide Air Pollution Research Center (SAPRC) chemical mechanism groups and were taken from EPA's CMAQ5.1 tool. For gasoline vehicles a total effective SOA yield of about 4% of the mass of Non-Methane Organic Gases (NMOGs) was estimated, of which more than half is originating from S/IVOCs (in about equal shares). For diesel vehicles an ultimate effective SOA yield of around 18% of the emitted NMOG mass was estimated, of which about 1% is from VOC, 14.5% is from IVOC and 2.5% is from SVOC. Note that the NMOGs emission from DPF equipped diesel vehicles was found to be much lower than that of ULEV gasoline vehicles.

3.4.2. Secondary organic aerosol formation gasoline vehicle exhaust - Zhao et al., (2017)

Zhao et al. (2017) investigated SOA formation by oxidizing dilute, ambient-level exhaust concentrations from a fleet of on-road gasoline vehicles under UV light in a smog chamber. They measured 59 light duty gasoline vehicles (no diesel vehicles) in four classes: pre-LEV, LEV, ULEV and SULEV (model years ranged from 1988 – 2014). They measured total NMOG with an FID and found pre-LEV vehicles to emit about 9, LEV about 0.8, ULEV about 0.4 and SULEV about 0.15 g/kg fuel. Zhao et al. have used partly the same set of measurements as Lu et al. (2018) did but included more vehicles among which seven with SULEV standard.

Total SOA production was measured at around 0.06 g/kg fuel for pre-LEV, 0.04 for LEV, 0.015 for ULEV, and around 0.002 g/kg fuel for SULEV. Zhao concluded that tightening tailpipe emission standards indeed reduces SOA formation from gasoline vehicle exhaust. But they also found that the reductions in SOA production are significantly less than the decrease in NMOG emissions. This was caused by much higher effective SOA yield measured for the LEV, ULEV and SULEV vehicles (around 30%) compared to pre-LEV vehicles (about 4%). Zhao then demonstrates that this is primarily caused by a different NOx regime rather than a different chemical composition of the NMOGs, which remained more or less consistent over the four vehicle classes. NOx likely acts as a hydroxyl radical 'scavenger' and therefore influences the reaction of hydroxyl radicals with NMOG. Zhao et al. found a six times higher effective SOA yield for the LEV, ULEV and SULEV class vehicles compared to the pre-LEV class. This was primarily attributed to the much lower NOx concentrations for the LEV, ULEV and SULEV vehicles. Characteristic for the NOx regime is the NMOG to NOx ratio. This ratio was around 4 for the pre-LEV ("high NOx") and more than 8 for the other classes ("low NOx").

Regarding chemical composition of the exhaust it was found that S/IVOCs made up only 5% of the NMOGs emitted by gasoline vehicles (the other 95% are VOCs) but contributed 45 – 76% of the predicted SOA. Of the VOCs only the single ring aromatics and longer alkanes were found to be SOA precursors. These findings are consistent with those made by Lu et al., (2018). On top of this Zhao concluded that because of the much lower NOx concentrations in the exhaust of modern and future vehicles, the positive effects of the reduced NMOG emission on SOA formation will likely be partly offset by the lower NOx concentrations and higher NMOG/NOx ratios. Future reduction of NOx concentrations may affect not only SOA formation from vehicular exhaust but likely also from SOA precursors released by other (non-vehicular) sources that may not be subject to equally strong emission reduction as vehicular sources.

Comparison between US vehicle standards with European EURO standards

Although the basic technologies to reduce the emissions of organic compounds are comparable for the US and Europe, the emission standards differ. We have made an approximate link between the CARB (California Air Resources Board) emission standards and the European Euro standards. For gasoline fuelled vehicles the following link was established (no diesel vehicles were included in the Zhao et al. (2017) study):

CARB	Euro standards
Pre-LEV	pre-Euro
LEV	Passenger and LDV Euro1 and 2
ULEV	Passenger and LDV Euro3 and 4
SULEV	Passenger and LDV Euro5 and 6

Lu et al. (2018) also measured (heavy duty) diesel road vehicles besides gasoline, which they classified as either with or without DPF, without considering the legislative environmental standard. For passenger and light duty vehicles the Euro4 (partly), Euro5 and 6 standards include a DPF while for heavy duty vehicles Euro5 (partly) and 6 include a DPF.

3.5. PM EMISSIONS FROM ROAD TRANSPORT, AND SOA FORMATION FROM EMITTED PRECURSORS

Based on Lu et al., (2018)

Based on the reported median emission factors for total organics and the effective SOA yields as measured by Lu et al. for the gasoline road vehicle standards (pre-LEV, LEV and ULEV), and diesel road vehicles with and without DPF, two first order estimates of SOA formation have been made for the Netherlands in 2019. In this respect the Netherlands was chosen because of the detailed and up-to-date insight that the project team had in the Dutch vehicle fleet composition and NMOG emission contributions. These indicative calculations are intended to serve as a first order estimate of the relative contribution that SOA formed from vehicle exhaust may make in a European country for a more recent year.

The first estimate used NMOG emissions from the Dutch Emission Registration (measured by FID) and SOA yields from Lu et al., while the second estimate used both median NMOG emission factors and SOA yields from Lu et al. (2018). The estimates amounted to:

- 205 ton SOA for diesel and 565 ton SOA for gasoline (total 769 tonnes), based on the Dutch NMOG estimates
- 338 ton SOA for diesel and 95 ton SOA for gasoline (total 433 tonnes), based on the NMOG emission factors by Lu et al.

For comparison, the total primary PM emission (tailpipe only) in the Dutch Emission Registration was 869 tonnes in 2019. SOA formation was thus estimated to be lower but of the same order as the primary PM emission. As can be noted there is a relatively large difference between the SOA estimate based on the Dutch NMOG emission estimate and the NMOG estimate obtained using the median emission factors by Lu et al. applied to the Dutch vehicle fleet. This difference can be traced back to a five times higher Dutch NMOG estimate for Euro1 to 6 passenger vehicles. One of the reasons for this difference is an increase included in the Dutch emission data to account for the effect of vehicle aging, resulting in higher emission factors than what was measured by Lu and Zhao. Lu et al. furthermore report an approximate lognormal distribution for the NMOG emission factors, for which the median (which is used here) may be significantly lower than the mean.

Similarly to SOA, gaseous IVOC and SVOC emissions (which are the most potent class of SOA precursors) have been estimated for the Netherlands as well. Starting from the Dutch NMOG emission estimates and combining these with the S/IVOC fraction by Lu et al., 1133 ton IVOC and 257 ton SVOC is estimated, while based on both the NMOG emission factors and S/IVOC fractions by Lu et al., 1034 ton IVOC and 111 ton SVOC is estimated. Note that the partition between the particle and gaseous phase of SVOC in particular is very dependent on ambient temperature. S/IVOC fractions in NMOG by Lu et al. were determined at 298°K and may be different at other temperatures.

Based on Zhao et al. (2017)

Zhao et al. reported NMOG and SOA emission factors, and effective SOA yields for gasoline-fuelled road vehicles, with four different CARB emission standards (pre-LEV, LEV, ULEV and SULEV). Zhao et al. base their results on their own smog chamber measurements, while Lu et al. assume SOA yields from literature. A second difference with the study by Lu et al. comes in the fact that Zhao reported effective SOA yields for different NOx regimes, whereas Lu et al. did not.

For a high-NOx regime (ambient NMOG over NOx concentrations in the order of 3 ppb C/ppb NOx), Zhao et al. report comparable effective SOA yields as Lu et al. did. When combined with the Dutch NMOG estimate for gasoline vehicles, 593 ton SOA is estimated, which is similar to what was estimated based on Lu et al. (565 ton, see above). When both SOA yields and NMOG emission factors by Zhao are used, around 100 tonnes SOA is estimated.

However, Zhao projected a change in NMOG/NOx ratio in the Southern California air basin from 3.6 in 2015 to 5.25 in 2025, as a result of foreseen emission reduction policy. This resulted in a drastically higher effective SOA yield. For gasoline vehicles the effective SOA yield rose from 0.042 (as used in our estimate above) to around 0.3, a 7-fold increase. This may be similar for diesel vehicles although these were not considered by Zhao et al.

The NMOG/NOx ratio in the Dutch urban air in 2019 is currently not known but may have been higher than 3.6 in case a similar increase occurred as is projected for Southern California by Zhao et al. This would increase the estimated SOA significantly.

3.6. HOW IMPORTANT IS SECONDARY PM (AND SOA IN PARTICULAR) FROM ROAD TRANSPORT IN TERMS OF TOTAL AMBIENT PM?

In the previous section several first order estimates of SOA formation have been made. Total estimated SOA formation resulting from NMOGs released by road vehicles may be of the same order as the primary PM tailpipe emissions (but is likely less). Note that these estimates have a very large uncertainty. An illustrative example to highlight these uncertainties is for instance the highly different estimates for NMOG emissions in 2019 in the Dutch Emission Inventory and NMOG emission factors as measured for the early 2010s Californian road vehicle fleet. But there are many more factors contributing to this uncertainty, such as the current and future NOx regime in the urban air in Europe.

Exhaust emissions of primary PM, SOA precursors and NOx from road transport will decrease significantly in the coming years as older vehicles are phased out. Zhao et al. warned however that in case NOx would be reduced “too quickly” the suppressing effect that NOx has on SOA formation due to hydroxyl radical scavenging may be greatly reduced, even up to a point that a (temporary) increase in SOA might be observed, in spite of decreasing NMOG emission.

The possibility that a future reduced NOx concentration could lead to a severe increase of SOA formation potential may have far reaching implications, moreover considering the fact that there are other S/IVOC sources besides road transport. The effect of a significantly different NOx regime in the future would have to be investigated by further research.

4. FUTURE IMPLICATIONS AND CHALLENGES

4.1. LEGISLATION FOR MOBILE SOURCES

The largest activity and associated fuel consumption in areas where people live is from passenger cars, light-commercial vehicles, trucks, and busses. Hence, these have been the main sources of relevant particle emissions. However, with the general application of particle filters on all of these vehicles, other mobile sources come into view as contributing to particle emissions. Among the new, or next, sources, there are two main groups. First, diesel engines without particle filters: inland ships below 300 kW, seafaring ships, mobile machinery below 19 kW and above 560 kW, and diesel locomotives (Vermeulen et al. 2021). All of these have traditional diesel particulate emission with a large fraction of elemental carbon and limited organic and volatile matter. Second, the L-category vehicles, two-wheelers, tricycles, and quads, and petrol-fuelled handheld machinery. These have typically high hydrocarbon emissions, partly as aerosols with a small fraction of elemental carbon. For both groups, Stage-V mobile machinery, and Euro-5 L-cat vehicles, one would expect a new round of legislation; Stage-VI and Euro-6 needed to make the legislation more robust and the application of emission reduction technology wider across the categories. With the future relevance of these sources, which are generally more localized and specific the specific exposure is also relevant. The use of mobile machinery in part has been an issue of health and safety regulations for the exposure of workers. The powered two-wheelers, on the other hand share the road side with cyclists and pedestrians. Even if the total emissions of these sources remain limited, the specific, temporal and local exposure should not be forgotten.

Another aspect that will be more important, with the on-road diesel vehicles being no longer the main source of particle emissions, is the wide variety of other sources of particle emissions. Not only exhaust emissions, but also wear emissions of tyre, road, and brakes are signalled as sources of small particles. The wide range of sources raise the question of relevance for health and toxicity, on top of the specific issues of particle formation. Some decades ago PM_{10}, and in particular $PM_{2.5}$, was predominantly defined by the amount of solid particles from diesel combustion. The epidemiological relation was rather straightforwardly linked to these concentrations and sources. This situation is rapidly disappearing. An improved differentiation of particulate matter is needed both for source attribution, and source-related policies, and for the differentiation of impact on health and the environment of the different sources.

4.2. ROAD TRANSPORT AS A SOURCE OF EMISSIONS, INCLUDING S/IVOCS AND SOA

In addition to the emission of primary particles, the emission and activity of SOA precursors from mobile sources may receive more attention in the future. SOA formed from traffic emissions might be regarded equally important to human health as traffic-emitted primary particulate. S/IVOCs, which may make up 3-30% of traffic emission of NMOG, are found to be powerful SOA precursors. In addition, aromatic and other high molecular NMVOCs may also form SOA. The emission of SOA precursors is however expected to remain on par with the reduction of the emission of NMVOC and primary PM, as a result of tighter emission standards and the phase out of older vehicles. Compared to 20 years ago, both the absolute and relative contribution by road transport tailpipe emissions (including SOA precursors) have decreased considerably and with the further phase out of older vehicles, this trend is expected to continue in the years to come. It is however essential that installed emission control technologies are sufficiently robust and continue to function sufficiently as a vehicle ages. It is also important that illegal removal of emission control technologies is actively prevented, wherever this would technically be possible.

4.3. DISTINGUISHING OTHER SOURCES OF URBAN ORGANIC AEROSOL, INCLUDING S/IVOCS AND SOA

Although outside the scope of this study, it should be mentioned that there are many more sources of (urban) organic aerosol that may be even of higher significance than vehicle emissions. These sources include stationary combustion of fuels, especially the residential combustion of solid fuels, and the commercial and domestic preparation of food (cooking). These two sources often have a large primary contribution, but likely also a significant secondary contribution as strong S/IVOC sources. Other potentially strong sources of SOA precursors may be farm animals and the use of volatile chemical products. Compared to road transport, these other sources have been controlled to a much lesser extent or have not been reduced at all, during the past decades. When performing measurements to determine the most important current contributors to urban organic aerosol, it is essential to be able to identify specific and robust tracer components, based on which both primary and secondary contribution by these sources can be assessed independently and reliably.

5. CONCLUSIONS AND RECOMMENDATIONS

Legislation on particle number (PN) limit in the type approval tests on diesel vehicles has caused widespread implementation of the diesel particulate filter (DPF). The subsequent introduction PN limit in on-road testing led to the wide application of gasoline particulate filter (GPF) on Gasoline Direct Injection (GDI) technology. Research shows this filtration technology to be highly effective and to significantly (>99% for Diesel and >95% for GDI) reduce exhaust PM emissions. Under current legislation, by 2030 almost all light- and heavy-duty diesel vehicles and direct injection gasoline vehicles in the European vehicle fleet will be equipped with a particulate filter. Among the remaining exhaust gas PM sources are port fuel injected gasoline and natural gas vehicles, which are expected to be targeted under upcoming legislation, e.g. Euro-7. Others such as L-category vehicles and non-road mobile machinery still require some attention on PM emissions and legislated PN limits.

As vehicles age the engine and exhaust gas after-treatment system are prone to defects and become vulnerable to tampering. Particulate filter technology works excellently as long as there are no cracks in the filter or the filter has not been maliciously removed. Current Periodic Technical Inspection (PTI) standards involve measurement techniques which are not suited to detect an increase in PM emissions. In the near future Belgium and the Netherlands are extending their PTI with particle counter devices, which can easily detect elevated PM emissions. Possibly, a similar PTI extension will be implemented on a European level.

With a large reduction in exhaust emissions due to increasingly stringent regulations, the continuing phase out of older vehicles and electrification, the impact of non-exhaust emissions becomes increasingly important. PM emissions from brakes, tyres and road wear are currently already estimated to be higher per vehicle kilometre than the upper limit of type approval exhaust PM emissions. With electrification it is expected there will be a decrease in brake use (and emissions) due to regenerative braking but an increase in tyre and road wear due to increased vehicle weight and torque. Although brake wear will likely not produce organic aerosols, metals and other materials from brake pads are considered toxic for humans.

With the on-road diesel vehicles being no longer the main source of particle emissions, the wide variety of other sources of particle emissions are becoming more relevant. Not only the remaining exhaust emissions, but also wear emissions, of tyre, road, and brakes, are signalled as sources of small particles. The wide range of sources raise the question of relevance for health and toxicity, on top of the specific issues of particle formation. Furthermore (although outside the scope of this study) it should be mentioned that there are many more non-transport related sources of (urban) organic aerosol that may be of comparable or even higher significance as vehicular emissions.

Even though solid exhaust PM emissions are largely removed with a particulate filter, organic aerosols tend to be only partially affected. In hot exhaust gas these substances are for a large part gaseous and may therefore escape physical filtration. These organic compounds are reduced by catalytic reactions such as in catalytic converters or catalytic particulate filters. In general, these technologies favour the conversion of the small chain organic compounds over the larger chain (with the exception of substances like methane). This effect leads to an altered composition in the exhaust gas compared to that of the fuel. Especially the large chain organic compounds that are of interest for SOA production are, in a relative sense, enriched in the exhaust gas by these technologies.

The way PM emissions by road vehicles are measured may result in an underestimation of condensable particulate matter (CPM) emission. Prior to filter loading, exhaust gases are cooled down to 52°C and passed through a dilution tunnel to simulate low ambient aerosol concentrations. A large part of the emitted CPM will be in the particulate phase under those conditions and will hence be captured by the filter. In real world conditions there may however be additional semi-volatile matter that is gaseous at 52°C but which may condense to PM at ambient temperature. The PM production from semi-volatiles is very dependent on temperature and so can be significantly different in summer and winter and between Northern and Southern Europe.

Current emission measurement techniques also do not specifically address gaseous precursors for the atmospheric formation of secondary organic aerosol (SOA). Although these compounds are principally detected as hydrocarbons (HC) by FID, no distinction is made between NMVOCs, IVOCs and SVOC although each have a very different SOA formation potential. Several studies suggest however that the ratio between these three classes of compounds is found to be more or less independent of the vehicle emission standard. This may justify that, in constructing emission inventories, S/IVOCs may be estimated based on total detected non-methane organic gases (NMOGs) and assuming a constant speciation.

SOA yields of specific organic substances (or mixtures thereof) can empirically be determined by injecting these substances into a smog chamber, in which atmospheric conditions are simulated (including a UV light source). Any solid organic material that may have formed after a certain time interval is then measured and considered SOA. SOA yields are not the same in all circumstances and appear for instance extremely dependent on NOx concentrations. For instance, when transitioning from high-NOx to low-NOx conditions, SOA yields may increase significantly.

Based on accurate measurement of real-world emission NMOGs, irrespective of volatility and subsequent chemical speciation of these gases, specific SOA yields can be used to estimate how much particulate may be formed from these precursor gases. SOA formed from vehicular exhaust emission may then be considered as indirect PM emissions.

A first order attempt to estimate the SOA formation from organic gases released by the Dutch road vehicle fleet has been made, based on two US studies published in the late 2010s and Dutch 2019 road vehicle emission data. This indicative estimate for the Netherlands suggested that SOA formation resulting from NMOGs released by road vehicles may be of the same order of magnitude as the primary PM tailpipe emissions. Starting point was a high-NOx regime, which is expected to represent conditions in the Netherland in 2019.

As a result of further phase out of older vehicles, new and more stringent emission standards for new vehicles, and other emission control policy aimed at NOx emission reduction, the NOx regime may change in the Netherlands in the future. This may result in generally much higher specific SOA yields. However, it is expected that by that time the biggest part of SOA precursor gases will not be originating from road transport anymore, but from other sources.

6. GLOSSARY

ACSM	Aerosol Chemical Speciation Monitors
AMS	Aerosol Mass Spectrometer
API	American Petroleum Institute
CAMS5.1	Copernicus Atmosphere Monitoring Service
CAMx	Comprehensive Air Quality Model with Extensions (A multi-scale photochemical modelling system for gas and particulate air pollution)
CARB	California Air Resources Board
CARB method 429	Method 429 for Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions From Stationary Sources
CPC	Condensation Particle Counter
CPM	Condensable Particulate Matter
CTM	Chemistry and Transport Model
DPF	Diesel Particulate Filter
EC	European Community, and Elemental Carbon
EMAC	ECHAM/MESSy Atmospheric Chemistry (numerical global atmosphere-chemistry model)
EMEP	the Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe
EPA	Environmental Protection Agency (US)
EGR	Exhaust Gas Recirculation
EU27	27 European countries (excl. of UK)
EU27+	EU27 countries plus UK, Norway and Switzerland
EU28	28 European countries
EUSAAR	European Supersites for Atmospheric Aerosol Research
DI	Direct Injection
FAC	Fractional Aerosol Coefficients
FID	Flame Ionization Detection
FPM	Filterable Particulate Matter

FTIR	Fourier Transform Infrared spectroscopy
GDI	Gasoline Direct Injection
GPF	Gasoline Particulate Filter
IARC	International Agency for Research on Cancer
ISOA	Isoprene-derived secondary organic aerosol
IVOC	Intermediate Volatility Organic Compound
Kt	kton, 1000 ton, 1000000 kg
LEV	Low Emission Vehicle
LNT	Lean NOx Trap
LOTOS-EUROS	Long Term Ozone Simulation - EURopean Operational Smog model (open-source chemical transport model)
LVOC	Low Volatile Organic Compound
MESSy	Modular Earth Submodel System
MLV	Most Likely Value
ND	Not Detected
MAAP	Multi Angle Absorption Photometry
NMVOC	Non-Methane Volatile Organic Compound
NMOG	Non-Methane Organic Gases
OA	Organic aerosols
OC	Organic Carbon
OEM	Original Equipment Manufacturer
OLE	Anthropogenic NMVOC species OLE (alkenes),
OM	Organic Matter
PAC	Powdered Activated Carbon
PAH	Polycyclic aromatic hydrocarbon
PAR	Anthropogenic NMVOC species PAR (alkanes)
PEMS	Portable Emission Measurement System
PFI	Port Fuel Injection

PM	Particulate matter, or Particulate Mass (mg/km and mg/kWh)
PM0.1	particles with a diameter of less than 100 nm, ultrafine particles
PM1	particles with a diameter of less than 1 µm
PM10	particles with a diameter of less than 10 µm
PM2.5	particles with a diameter of less than 2.5 µm
PMP	Particle Measurement Program
PN	Particle Number (#/km and #/kWh)
POA	Primary Organic Aerosol
POM	Polycyclic Organic Matter
PRTR	Pollutant Release and Transfer Register
PTI	Periodic Technical Inspection
RDE	Real Driving Emissions legislation
RWC	Residential Wood Combustion
SAPRC	State-wide Air Pollution Research Center (https://intra.engr.ucr.edu/~carter/SAPRC/)
S/ISOA	Secondary and Isoprene-derived secondary organic aerosol
S/IVOC	Semi volatile and Intermediate Volatility Organic Compound
SULEV	Super Ultra Low Emission Vehicle
SO3	Sulphur Trioxide
SOA	Secondary Organic Aerosol
SOAP	Secondary Organic Aerosol Potential
SCR	Selective Catalyst Reaction
SVOC	Semi Volatile Organic Compound
SW-846	Test method for evaluating solid wastes
TC	Total Carbon
TNO	the Netherlands Organisation for applied scientific research

TOL	Anthropogenic NMVOC species TOL (toluene and toluene-like aromatics)
TPM	Total Particulate Matter
ULEV	Ultra Low Emission Vehicle
UNECE	United Nations Economic Commission for Europe
VBS	Volatility basis set
VCP	Volatile Chemical Products
VOC	Volatile Organic Compound
XYL	Anthropogenic NMVOC species XYL (xylene and xylene-like aromatics)

7. REFERENCES

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