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Literature review on emissions of semi- and intermediate volatile organic compounds and formation of organic aerosols with focus on the refinery sector

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Literature review on emissions of semi- and intermediate volatile organic compounds and formation of organic aerosols with focus on the refinery sector

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ABSTRACT

Organic aerosols (OA) are an important component of ambient particulate matter (PM) but their origin and formation is not well understood. Traditionally, OA have been described by two classes: a) primary organic aerosol (POA) and b) secondary organic aerosol (SOA). POA refers to non-volatile organic compounds (VOC) that are emitted directly from the source in the particle phase and do not undergo any atmospheric process other than dilution and deposition, while SOA include all OA formed by oxidation and subsequent condensation of gaseous precursors. Recent studies have shown that this classification of OA is too simple because the semi-volatile nature of emitted POA is not taken into account and that other organic compounds such as condensable particulate matter (CPM) and semi- and intermediate-volatile organic compounds (S/IVOC)[1] are also precursors of OA. The organic fraction of CPM contributes to POA (since it forms aerosol without any chemical reaction) but not to SOA. S/IVOC, on the other hand, can play a significant role in the formation of SOA in the atmosphere. The definitions of CPM and S/IVOC partly overlap, since both are defined by their volatility at a certain temperature.

This report reviews the main literature, and provides insights regarding the sources and emissions of S/IVOCs and CPM and the impact of the former on SOA concentrations. It also provides high-level estimations of S/IVOC emissions from the European refinery sector and reviews their importance in comparison to those from other sectors.

The literature review has shown that there are no published S/IVOC emissions measurements from refineries in Europe. However, S/IVOC emissions can be estimated using indicator substances, such as polycyclic aromatic hydrocarbons (PAHs). An indicative estimate of total S/IVOC emissions from all refineries in the EU27+ is 100 t S/IVOC per year, with a range of 10 to 1000 t/year. This is, by comparison, three orders of magnitude lower than the estimates for wood burning in Europe.

In addition, the results from modelling simulations using atmospheric chemical and transport models (CTMs) have shown that S/IVOC emissions from refineries contribute only a minor fraction to secondary OA concentrations over Europe. Any uncertainties of modelling OA concentrations could be reduced through undertaking refinery S/IVOC measurements that can help to develop representative sectoral emission inventories and determine the refining contribution to OA more accurately.

KEYWORDS

Semi volatile organic compounds (SVOC), Intermediate volatile compounds (IVOC), Condensable Particulate Matter (CPM), Organic Aerosols (OA), Primary/Secondary OA (POA/SOA), emissions

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.eu).

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[1] S/IVOC are defined in Section 2.1

GLOSSARY

ACSM	Aerosol Chemical Speciation Monitors
AMS	Aerosol Mass Spectrometers
API	American Petroleum Institute
BAT	Best Available Techniques
CAMx	Comprehensive Air Quality Model with Extensions
CAMS	Copernicus Atmospheric Monitoring Service
CMAQ	Community Multiscale Air Quality Modelling System
CPM	Condensable Particulate Matter
CTM	Chemical Transport Model
DPF	Diesel Particulate Filter
EC	Elemental Carbon
EDGAR	Emission Database for Global Atmospheric Research
EEA	European Environment Agency
ELVOC	Extremely Low Volatility Organic Compounds
EMAC	ECHAM/MESSy Atmospheric Chemistry
EMEP-CEIP	European Monitoring and Evaluation Programme Centre on Emission Inventories and Projections
EPA	United States Environmental Protection Agency
E-PRTR	European Pollutant Release Transfer Register
ERIC	Louisiana Emission Reporting and Inventory Center
ESP	Electrostatic Precipitator
EUCAARI	European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions
FAC	Fractional Aerosol Coefficients
FCCU	Fluid Catalytic Cracking Unit
FPM	Filterable Particulate Matter
GC-MS	Gas Chromatography – Mass Spectrometry
GEOS-Chem	Goddard Earth Observing System atmospheric chemistry model
GJ	Gigajoule
GNFR	Gridded Nomenclature For Reporting
HAP	Hazardous Air Pollutants
IARC	International Agency for Research on Cancer
IVOC	intermediate Volatility Organic Compounds
LOTOS-EUROS	Long Term Ozone Simulation (LOTOS) European Operational Smog (EUROS) CTM model
LRTAP	Convention on Long-range Transboundary Air Pollution
LS	Low Sulphur
LVOC	Low Volatility Organic Compounds
MEGAPOLI	Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and integrated s for assessment and mitigation
MJ	Megajoule
MLV	Most Likely Values
MW	Megawatt
NAICS	North American Industry Classification System
ND	Not Detectable
NMVOC	Non-Methane Volatile Organic Compounds

OA	Organic Aerosol
OC	Organic Carbon
OGJ	Oil & Gas Journal
OLE	Olefins
OM	Organic Matter
ORACLE	Module for the description of OA composition and evolution in the atmosphere
OTM	EPA Other Test Methods
PAH	Polycyclic Aromatic Hydrocarbon
PAR	Paraffin
PM	Particulate Matter
PM10	Particulate Matter smaller than 10 µm
PM2.5	Particulate Matter smaller than 2.5 µm
PM1	Particulate Matter smaller than 1 µm
PMCAMx	Particulate Matter Comprehensive Air Quality Model with Extensions
POA	Primary Organic Aerosol
POM	Polycyclic Organic Matter
RWC	Residential Wood Combustion
S/ISOA	Semi and Intermediate Volatility Secondary Organic Aerosol
SOA	Secondary Organic Aerosol
SOAP	Secondary Organic Aerosol Potential
SVOC	Semi-Volatile Organic Compound
SW	Hazardous waste test method
TC	Total Carbon
TJ	Terajoule
TNO	Dutch Organisation for Applied Scientific Research
TOL	Toluene
TPM	Total Particulate Matter
TRI	Toxics Release Inventory
UNECE	United Nations Economic Commission for Europe
UVCB	Chemical Substances of Unknown or Variable Composition, Complex Reaction Products and Biological Materials
VBS	Volatility Basis Set
VCP	Volatile Chemical Products
VOC	Volatile Organic Compound
VTT	Technical Research Centre of Finland Ltd
WEC	World Engineers Convention
WRF	Weather Research and Forecasting Model
XYL	Xylene

SUMMARY

Particulate Matter (PM) is a widespread air pollutant, consisting of a mixture of solid and liquid particles suspended in the air. Health studies have shown a significant association between exposure to particle pollution and health risks, including premature death. Organic aerosols (OA) are an important component of ambient PM. Despite the importance of OA for ambient PM, and thus human health, the origin and formation of OA is not well understood and deserves more attention. Research in the last decade has shown that under atmospheric conditions semi- and intermediate-volatile organic compounds (S/IVOC), play an important role in the formation of secondary OA in the atmosphere. The organic fraction of condensable particulate matter (CPM) contributes to primary organic aerosol (POA) (since it forms aerosol without any chemical reaction) but not to secondary organic aerosol (SOA). The definitions of S/IVOC and CPM partly overlap, since both are defined by their volatility at a certain temperature. To get an understanding of the importance of S/IVOC emissions from the refinery sector in Europe, Concawe contracted TNO to do a literature review that addresses air quality issues related to emissions of S/IVOCs and condensable particulate matter and their impact on OA concentrations. The study also includes a high-level estimation of S/IVOCs emissions from the European refinery sector and its comparison to other sectors.

The literature review has shown that there are no published S/IVOC emissions measurements from refineries in Europe. In the absence of (representative) measurements, S/IVOC emissions can be estimated using indicator substances, such as PAHs. Using a ratio of S/IVOC over PAH, which largely varies (Section 3.3.3.1), this yields indicative estimates of total S/IVOC emissions from all refineries in the EU27+ between 10 to 1000 t S/IVOC per year. This is a somewhat low figure compared to the total PM_{10} emissions of 3 kt/yr reported by refineries to the European Pollutant Release and Transfer Register (E-PRTR), and can be explained by the fact that refinery PM emissions are mostly inorganic. In general, S/IVOC emissions are associated with non-methane volatile organic compounds (NMVOC) and primary organic aerosol emissions. A relatively low contribution by refineries is in line with the low contribution of refinery emissions to total NMVOC (~2%) and PM_{10} (~0.15%) emissions in Europe.

To quantify the contribution of S/IVOC emissions to OA concentrations, atmospheric chemical and transport models (CTMs) are used to simulate the formation of particles from gaseous components through aging and condensation. In this study, the formation of OA from S/IVOC was studied using the CTM LOTOS-EUROS model equipped with the volatility basis-set (VBS) framework. The VBS classifies organics using volatility, and takes into account enhanced gas-to-particle conversions in the course of chemical aging that produces less volatile species. Model simulations suggest that emissions from refineries contribute only a minor fraction to secondary OA concentrations over Europe. While this gives indications of the potential importance of the refinery emissions, the large uncertainties in S/IVOC emissions and ageing cause the modelled OA concentrations over Europe to be highly uncertain as well.

The overall conclusions of the literature review, the high-level S/IVOC emission estimation from the refinery sector, and the model simulations are that:

- Refineries emit a small part of the total organic carbon from anthropogenic sources over Europe
- S/IVOC emissions can currently only be estimated indirectly from indicator species or using generic fractions applied to reported primary PM emissions.

- Based on currently available data, the refinery contribution to SOA formation is estimated to be very low.
- The accuracy of the estimates could be increased by conducting representative measurements in the refineries.

CONTENTS

1. INTRODUCTION

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) [85]. 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) [72]. More recently, Cavalli et al. (2016) [6] 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 (Fuzzi et al., 2015) [25].

Semi-volatile and intermediate-volatile organic compounds (denoted 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.

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) [74], and for the European situation evaluated and discussed in Denier van der Gon et al. (2015) [11] and Simpson and Denier van der Gon (2015) [76]. Since organic aerosol is such an important component of total particulate matter, understanding the contribution of S/IVOC is crucial to understand 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 non-methane volatile organic compounds (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)) [75] 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 insight and knowledge 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 and the method/emission factor used to report it. As a result, there is growing confusion about how important these substances really are for different source sectors, including refineries, and how much they may contribute to organic aerosol concentrations. The latter can only be quantified using atmospheric chemical and transport models since some of these S/IVOC will only become condensable at ambient temperature after ageing and reaction in the atmosphere.

2. DEFINITIONS

There is a large variety of organic compounds in the earth's atmosphere (millions of unique species; Goldstein and Galbally, 2007) [29], 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. 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)[1] [67].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) [13]. A typical schematic of the emission and chemical evaluation of organic compounds defined below is given in **Figure 1**.

NMVOC: non-methane volatile organic compound, with a saturation vapour concentration[2] at 298 K (C*) $>3.2\text{x}10^6$ µg m^{-3}. This includes many primary VOCs that are emitted from 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* < $3.2\text{x}10^6$ 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.

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[1] It should be noted, that the saturation vapour concentration ranges used to classify these compounds might be slightly different in other studies (Majdi et al., 2019) [55]. The proposed naming system by Murphy et al. (2014) [67] is considered although more comprehensive and consistent with general classifications used in many field and laboratory studies and therefore is used in this report.

[2] 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

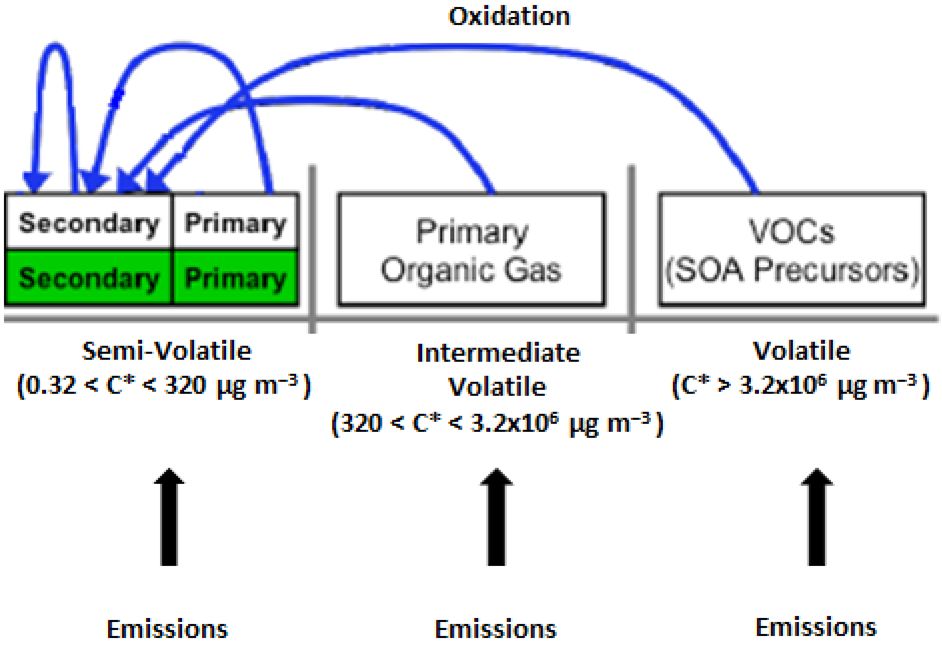

Figure 1 Schematic of the emission and chemical evaluation of organic compounds in the atmosphere. Compounds in the particulate phase are denoted with green shading (Fuzzi et al., 2015) [25]

2.2. OA (POA AND SOA)

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 [74]; Grieshop et al., 2009 [30]) and the inability of models to explain observed ratios of more and less oxidised organic aerosol components (Shrivastava et al., 2008) [75], 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) [67] 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, for summer than for 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 a SVOC.

2.3. CONDENSABLE PM (CPM) (FOCUS MAINLY ON ORGANIC FRACTION)

The US EPA defines CPM as the material that is in vapour phase at stack conditions but condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack (Federal Register, 2010 [20]; Murphy et al., 2014 [67]). All CPM is assumed to be in the $PM_{2.5}$ size fraction[3]. Together with filterable particulate matter (FPM) it forms total particulate matter (TPM) that is emitted from fossil fuel combustion. Sample dilution may cause some of the more volatile components of CPM to evaporate again and is therefore of influence to CPM mass. Since temperature is an important factor in determining the volatility of a substance, it is critical in the definition of CPM. In this respect US EPA test methods specify that the temperature of the filter upon which the CPM is collected is maintained at 30°C or less.

There are two techniques used to measure CPM. The sample gas has to be cooled to form the condensable PM fraction and this is achieved either in a condenser or by diluting with ambient air. The CPM is then collected on a filter. EPA Method 202 – Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources - uses the former technique. The sample gas, after the removal of FPM, is cooled and the CPM formed is collected on a filter which is maintained at a temperature between 20°C and 30°C. Alternatively, dilution is used in EPA Method OTM-37 – Measurement of Direct $PM_{2.5}$ and PM_{10} Emissions at Low Concentrations by Dilution Sampling. In this method the sample gas, after removal of FPM, is diluted to cool it to less than 30°C prior to collection of the CPM on a membrane filter. Comparative testing of these two methods for refinery fuel gas firing have shown that the impinger method gives much higher CPM values (see **Section 3.3.3.1**). Other standard test methods exist that use different rates of dilution and/or have different specifications for the temperature at which the CPM is collected. Because these methods lead to different CPM concentrations, emission factors derived from different methods are incomparable. This complicates the compilation of an overall emission inventory for CPM.

The EPA definition refers to all condensable species and as such is not specific to organic compounds; SO_3, for instance, can also be part of CPM (Feng et al., 2018) [21]. 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) [21]. In other words, the definitions of CPM and S/IVOC partly overlap, since both are defined by their volatility at a certain temperature. Also note that the organic fraction of CPM contributes to POA, since it forms aerosol without any chemical reaction.

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[3] 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).

3. CURRENT EMISSION INVENTORIES (INCLUDING THE PETROLEUM REFINING SECTOR)

3.1. (REPORTED) INVENTORIES OF NMVOC AND PM IN EU28

There is no targeted S/IVOC emission reporting in Europe for refineries nor other source sectors. The substances that are sometimes used to estimate or derive S/IVOC emissions (precursor or direct) are non-methane volatile organic compounds (NMVOC) and particulate matter (PM). Total NMVOC and PM$_{10}$ emission estimates in the EU27 plus UK, Norway and Switzerland (EU27+) have steadily decreased since 2000 (**Figure 2**). For refineries both stack and diffuse emissions are grouped under source sector B (Industry) in **Figure 2**. The emission data shown are officially reported by countries to EMEP-CEIP (https://www.ceip.at/) and gap-filled following the procedure described in Kuenen et al. (2014) [49]. The figure illustrates that over the latest reporting years (2014-2017) the NMVOC and PM$_{10}$ emission levels have been stable at ~6200 kt/year and ~2000 kt/year, respectively (CEIP, 2019) [7].

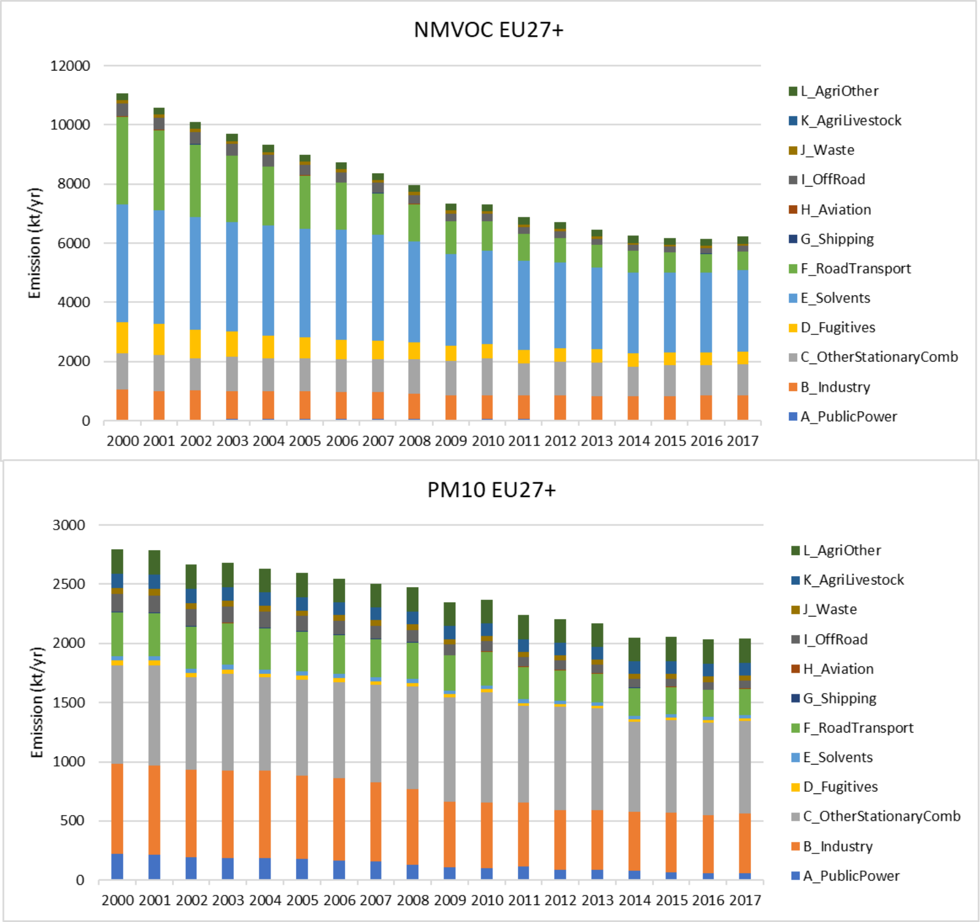

Figure 2 NMVOC and PM$_{10}$ emissions for the EU27 including UK, Norway and Switzerland (EU27+) for the years 2000-2017, by source sector

Emissions vary by both source sector contribution and country as is illustrated for the NMVOC emissions for the year 2017 (**Figure 3**). This is as expected due to differences in the size of countries as well as differences in importance of certain activities and industries between countries. Overall, the most important sector for NMVOC emissions is still the use of solvents.

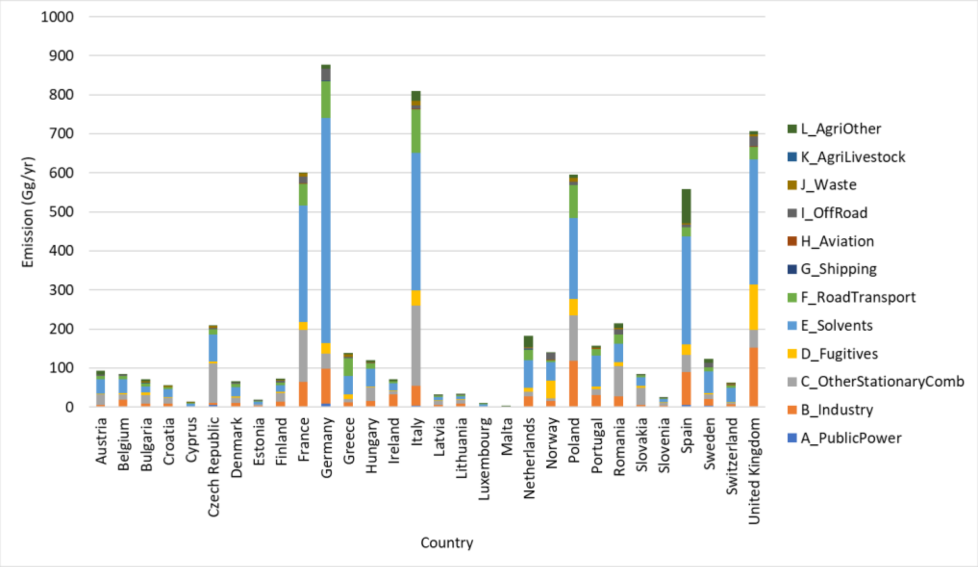

Figure 3 NMVOC emissions for the EU27 including UK, Norway and Switzerland for 2017, by country, by source sector

Table 1 Source sectors codes used for grouping emissions and their description

TNO GNFR sectors	GNFR_Category_Name	Description
A	A_PublicPower	Public power and heat plants
B	B_Industry	All stationary industrial emissions, including process and emissions
C	C_OtherStationaryComb	Residential, commercial, institutional and other stationary combustion
D	D_Fugitives	Fugitive emissions from fossil fuel production and distribution
E	E_Solvents	Domestic and industrial solvent and product use
F	F_RoadTransport	Road transport
G	G_Shipping	Sea and inland shipping
H	H_Aviation	International and domestic aviation
I	I_OffRoad	Other off-road mobile sources
J	J_Waste	Waste treatment and disposal
K	K_AgriLivestock	Agriculture livestock emission
L	L_AgriOther	Other emission from agriculture

3.1.1. European Pollutant Release and Transfer Register (E-PRTR)

The European Pollutant Release and Transfer Register (E-PRTR) is the Europe-wide register that provides accessible key environmental data from industrial facilities in European Union Member States and in the UK, Iceland, Liechtenstein, Norway, Serbia and Switzerland. Reported refinery emissions to E-PRTR[4] contribute only a small amount to the total EU27+ emissions with ~123 kt/year NMVOC (2%) and ~3 kt/year PM_{10} (0.15%). The emissions vary by country, and depend upon the number and size of the refineries (**Figure 4**). The emissions for the refinery sector show a bit more variation over the last 3 reporting years compared to total NMVOC emissions **(Figure 2)** but no large variations exist in the aggregated country data for 2015-2017 (**Figure 4**). Note that E-PRTR reporting is only for emissions in excess of E-PRTR thresholds therefore most, but not all, refineries report NMVOC emissions. E-PRTR and its usage for estimation of CPM is discussed in more detail in Section 3.3.1.1. In **Appendix B** some additional refinery emissions data, and their possible relation to refinery capacity, are shown, mostly to illustrate that generalisation or defining an "average refinery" emission is not straightforward.

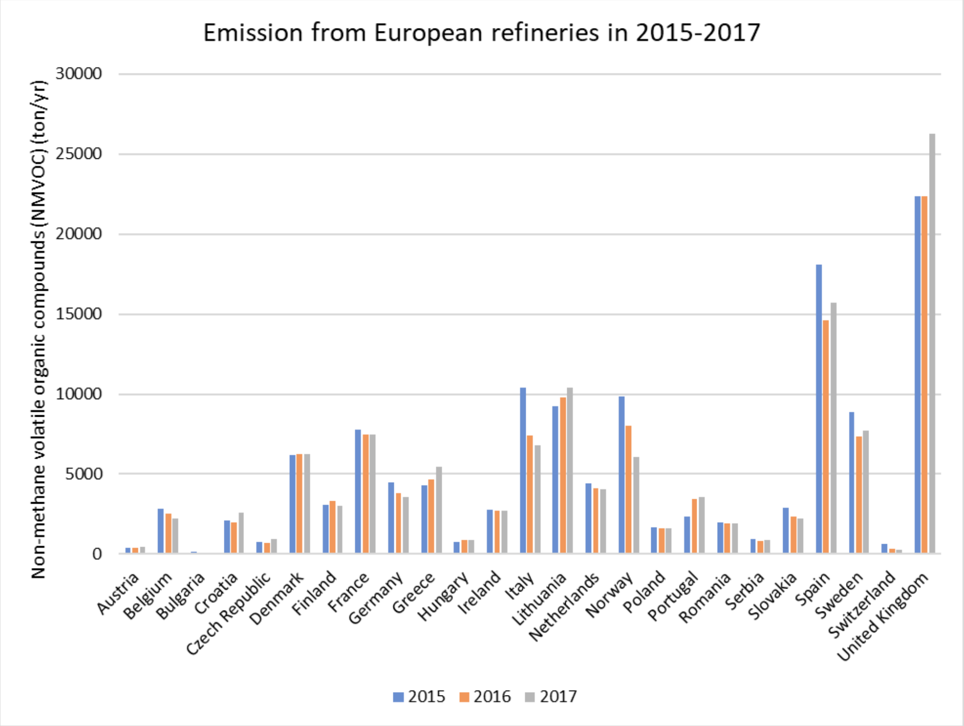

Figure 4 NMVOC emissions from refineries for 2015-2017 by country (source: E-PRTR)

3.2. IDENTIFIED RELEVANT SOURCES OF IVOC, SVOC AND CPM EMISSION

In this section we will list some identified sources of organic CPM. This will be restricted to directly emitted S/IVOCs and will not include SOA precursors such as (specific) NMVOCs. Inorganic CPM is also excluded from this section.

As a group of pollutants, S/IVOCs are not regulated explicitly. Other regulations (addressing for example PM or Polycyclic Aromatic Hydrocarbons emissions) may indirectly include some emissions, but there is no environmental legislation that directly addresses S/IVOC. Partly as a result of this, consistent emission inventories for S/IVOC (or CPM only) have not yet been compiled. However, in recent years the

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[4] In E-PRTR refinery emissions are reported under sector 1 Energy, activity code 1.(a) (https://prtr.eea.europa.eu/#/industrialactivity); As not all facilities under 1.(a) are oil refineries, the refinery emissions shown here are based on a manual selection of operational oil refineries from 1.(a) facilities (see **Section 4.5.2**).

importance of consistent and complete reporting CPM is becoming more recognised in Europe, and there are currently several countries improving their national emission inventories to cover CPM emission in a more complete and consistent manner. Furthermore many emission factors in the EEA Emission Inventory Guidebook have been updated to include CPM for major sources.

Regarding sources, emission of primary S/IVOC usually occurs as a result of organic matter being volatilised and only partly combusted, or not combusted at all. An example of the first would be a wood or coal stove, in which volatile material is released from the fuel and subsequently not completely combusted. Volatilisation is often the result of high heat, but also delayed evaporation of S/IVOC contained in materials and products at ambient temperature may also contribute.

S/IVOCs include many thousands of chemical species that are very challenging to identify on a substance by substance basis. When S/IVOCs are included in PM emission factors, they may comprise up to 100% of the total PM organic mass, depending on the source. Unfiltered diesel soot may contain 10 to 50% organic matter, while wood smoke may contain 50 – 95% organic matter. Biogenic particles and particles released by cooking activities may consist of 100% organic matter. For particulate matter (PM) emissions from refineries, this percentage is much lower as the majority is said to comprise inorganic catalyst material (see **Section 3.3.7**). Considering that wood smoke is such a dominating source of PM emissions in Europe, S/IVOC emissions may prove to be of the same order or even larger than the total emission of filterable PM (PM without CPM). Some sources release high quantities of S/IVOCs per unit of activity while other sources may emit less but are equally relevant because they occur at a vast scale.

Until complete and consistent inventories become available that include all CPM, there are only partial inventories and source-specific studies available that focus on the suspected stronger sources for the more relevant activities. These studies typically address one of the following sources/activities:

- Household combustion of solid fuels like wood or other herbaceous matter, and coal; Denier van der Gon et al. (2015) [11] estimated that for UNECE-Europe in 2005, total emission of condensable PM from residential wood combustion may be close to 1 Mt.
- Fossil fuel-based transportation activities (e.g. diesel or gasoline-fuelled vehicles); see e.g. Lu et al., 2018.
- Open burning of agricultural or household waste; see e.g. Estrellan et al., (2010) [18] or Lemieux et al., (2004) [50].
- Tobacco smoking, as PM released from this source is almost exclusively CPM, with only little ash or elemental carbon contained.
- Cooking (e.g. heating of cooking oils and fats, charcoal grilling of meat); see e.g. Liu et al., (2018) [52].
- Evaporation of IVOC from products/materials like flame retardants and plasticisers (see e.g. Liu et al., (2012)) or volatile chemical products (VCPs) see e.g. McDonald et al., (2018) [60] or Xu et al., (2011) [84].
- (Re-)Volatilisation of organo-chlorine pesticides (see e.g. Bidleman et al. 2006).
- Oil sand production and mining, when occurring at a large scale; see Liggio et al., (2016) [51].

Finally, S/IVOCs released by volatile chemical products VCPs (McDonald et al., (2018) [60] are considered as one of the most important sources of indoor air pollution, and have been receiving a considerable amount of attention as such (Xu et al., 2011) [84]. According to McDonald et al., (2018) [60] these products may include coatings, printing inks, adhesives and personal care products.

Stationary combustion of refinery fuels such as refinery gas is not among the suspected strongest sources of CPM. England et al. (2007) [16] have nevertheless attempted to measure CPM from refinery fuels, which will be discussed in **Section 3.3.3.1.**

3.3. ESTIMATED S/IVOC RELEASE FROM OIL REFINERIES

To our knowledge, there have been no direct S/IVOC measurements taken at specific refinery sources or at refineries as a whole. An exception may be the work by England et al. (2007) [16], which is discussed later in **Section 3.3.3.1**. England et al. measured CPM emission from refinery fuel combustion but did not make any refinery emission estimates. We also did not find any attempts at estimating direct refinery S/IVOC emissions based on a parallel to other sources, or engineering considerations. In the absence of direct measured data we may approximate the potential S/IVOC emissions by using specific indicator substances. S/IVOC indicator substances in this respect are selected substances or substance groups that either comprise a relevant part of S/IVOC or have a similar formation mechanism. In case there is information on the ratio of S/IVOC mass over the mass of the indicator substance, the latter may be used to estimate S/IVOC emission.

One indicator for which data are readily available are polycyclic aromatic hydrocarbon (PAHs) emissions. Most, if not all PAHs are S/IVOCs themselves (Wu et al., 2019) [83] and they are indicative for volatilisation and/or incomplete combustion of high molecular hydrocarbons. Usually only a selection of PAH compounds is reported, as either required by regulation, limited by measurement technique, or based on toxicity or mass contribution. In this study various PAH compound selections are used from different sources: the US EPA TRI list (see **Section 3.3.1.2**), US EPA-16 (EPA's selection of High Priority Pollutants), E-PRTR4 (see **Section 3.3.1.1**) and custom selections. Another indicator, particularly for IVOCs may be naphthalene that is a more volatile PAH and present in considerable quantities in crude oil (e.g. 0.5 – 10% wt, IARC (1989) [37]). Naphthalene can be considered a borderline IVOC, as it has a volatility just above the IVOC range.

To obtain information of S/IVOC indicator emission rates the following information sources are considered:

- S/IVOC indicators in industrial emission registers:
    - E-PRTR (**Section 3.3.1.1**)
    - US EPA TRI (**Section 3.3.1.2**)
    - The State of Louisiana ERIC database (**Section 3.3.1.3**)
- Literature emission factors for indicator compounds in refineries (**Section 3.3.2**)
- Literature on measured S/IVOC and indicator compounds for selected sources relevant for refineries (**Section 3.3.3** and **Section 3.3.4**)
- Information on chemical speciation of a broad range of refinery process streams by API (**Section 3.3.5**)

- Literature on the IVOC and SVOC content of gasoline and diesel fuels (**Section 3.3.6**)

Based on the estimated emission of S/IVOC indicators, the ratio of total S/IVOC over indicators and process stream and product composition, one might "guesstimate" what the order of magnitude of S/IVOC release by oil refineries could be.

3.3.1. S/IVOC indicators in industrial emission registers

3.3.1.1. E-PRTR

The E-PRTR is the Europe-wide register that provides environmental data from industrial facilities in European Union. Under Main Activity "Mineral Oil and Gas Refineries" emissions to air from oil refineries are stored. From "Mineral Oil and Gas Refineries" a selection of around 100 petroleum refineries in the EU28 was selected manually.

For naphthalene emission to air a reporting threshold of 100 kg/year exists and for PAH, the reporting threshold is 50 kg/year (Regulation (EC) No 166/2006 on the establishment of a European Pollutant Release and Transfer Register). PAH in E-PRTR is the sum of four individual indicator substances ("E-PRTR4"):

- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Indeno(1,2,3-cd)pyrene

It is important to mention that these four substances are seen as indicator PAHs and total PAHs emissions may be substantially higher.

For the reporting years 2016 and 2017 only two refineries (out of about a hundred) reported naphthalene emissions and two reported PAH emissions (one refinery reported both). Based on the emission data reported by these refineries and an assumed crude throughput of 70% of the refineries capacities a specific naphthalene emission rate of 670 kg/Mt crude processed and a specific PAH emission rate of 49 kg PAH(E-PRTR4)/Mt crude processed are derived. For all other refineries, emissions are apparently below the threshold, as no emissions are reported to E-PRTR.

3.3.1.2. EPA TRI database

The US EPA Toxics Release Inventory (TRI) Program records information on toxic chemical releases and pollution prevention activities as reported by industrial and federal facilities. It may be seen as the American equivalent of the E-PRTR. In TRI, petroleum refineries are grouped under North American Industry Classification System (NAICS) 324 – Petroleum, together with several other industries, such as asphalt plants, carbon plants, and oil terminals. Data can be retrieved on a plant by plant basis, so petroleum refineries can be identified by the recorded facility name.

Among the chemical substances and substance groups for which there are emissions recorded for NAICS 324, there are two that are I- or SVOCs: Naphthalene (which is considered borderline IVOC) and the sum of 22 high molecular PAH compounds, which may cover a significant part of the refineries SVOC emissions, as the list of included PAHs is relatively large compared to other PAH compound selections. The individual PAH compounds for which the sum of the emission is recorded in TRI are specified in **Table 2**.

Table 2 PAH compounds in US EPA Toxics Release Inventory (TRI) ("TRI-22")

Chemical name	CAS nr
1-Nitropyrene	5522-43-0
3-Methylcholanthrene	56-49-5
5-Methylchrysene	3697-24-3
7,12-Dimethylbenz(a)anthracene	57-97-6
7H-Dibenzo(c,g)carbazole	194-59-2
Benzo(a)anthracene	56-55-3
Benzo(a)phenanthrene	218-01-9
Benzo(a)pyrene	50-32-8
Benzo(b)fluoranthene	205-99-2
Benzo(g,h,i)perylene	191-24-2
Benzo(j)fluoranthene	205-82-3
Benzo(j,k)fluorine	206-44-0
Benzo(k)fluoranthene	207-08-9
Benzo(r,s,t)pentaphene	189-55-9
Dibenz(a,h)acridine	226-36-8
Dibenz(a,j)acridine	224-42-0
Dibenzo(a,e)fluoranthene	5385-75-1
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,h)anthracene	53-70-3
Dibenzo(a,h)pyrene	189-64-0
Dibenzo(a,l)pyrene	191-30-0
Indeno(1,2,3-cd)pyrene	193-39-5

TRI records diffuse releases and point source releases to air separately. For PAHs as a whole there is a reporting threshold of 100 pounds annually (about 45 kg) but many facilities include PAH emissions in their reports even if the amounts are below the reporting threshold.

For this study, naphthalene and PAH emission data for the petroleum sector have been retrieved from TRI. Emission data for over 700 companies were available, from which a sample of 122 petroleum refineries has been selected manually. From these 122 oil refineries, 87 reported PAH emissions above the TRI threshold, for both diffuse and point sources. Likewise, 116 refineries reported naphthalene emissions above the TRI threshold.

Reported emissions in TRI vary widely between refineries, much more than is typical for reported NMVOC or PM emissions. The total emission of the 22 PAH compounds included in TRI ranged from 0.6 to 3289 kg/year (average 118 kg, standard deviation σ = 395). This variation is however not necessarily representative of differences in actual emissions, as emissions estimating methodologies may differ significantly from facility to facility. The refinery configuration may also have an impact on reported PAH emissions.

In TRI, point source emission is about twice as high as diffuse emission. Six refineries reported annual PAH emissions above 1000 pounds (454 kg). Assuming 70% of their capacity as actual crude throughput, an average emission factor of around 87 kg PAH(TRI-22)/Mt crude processed can be derived for the six refineries.

For naphthalene an average emission of 860 kg annually is found for refineries reporting both diffuse and point sources above the threshold (range 1.3 – 10555 kg/year, σ = 1563). For the six refineries discussed above, the average naphthalene emission factor would be 201 kg/Mt crude processed.

3.3.1.3. Louisiana ERIC database

The Louisiana Emission Reporting and Inventory Center (ERIC) contains detailed data on estimated industrial emissions in the State of Louisiana and may cover substances that TRI does not. Unfortunately, access to ERIC was not possible during the time this research took place. Information from ERIC could therefore not be taken into account.

3.3.2. Literature emission factors for S/IVOC indicator components

For S/IVOC indicator components such as PAHs, naphthalene and anthracene, emission factors for refinery processes are available from literature. One of the most relevant documents in this respect is Concawe report 4/19 [Concawe 2019] [9]. Concawe report 4/19 [9] holds a collection of emission factors for refinery processes using a number of sources of emission estimation methodologies and is meant to assist refineries preparing their environmental data submission to E-PRTR.

The report presents PAH emission factors for the combustion of fuels, the destruction of gaseous streams in incinerators, and fluidised catalytic cracking unit (FCCU) catalyst regenerators. Below, a simple calculation is made to investigate what order of magnitude the emission of indicator components would be, using these emission factors.

First the emission from fuel combustion is estimated. Based on the Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas (European Commissions, 2015) [19] we assume a specific energy consumption of 2.75 GJ/t crude processed, supplied by roughly 65% gaseous fuels and 25% residual fuel oil (plus 10% other fuels), resulting in an annual energy consumption in the order of 18 TJ gaseous fuel and 7 TJ residual fuel oil for a 10Mt crude/year refinery. Using the reported PAH emission factors for boilers/furnaces, total PAH (E-PRTR4) from fuel combustion would be, below 1 kg/year. Reported emission factors for gas turbines and gas engines are higher but there are only a very limited number of gas turbines in use in refineries.

For the FCCU regenerators the emission factor is related to the mass of coke burned and is specified at 3.38E-06 kg/t coke burned. If we assume a coke energy content of 31 MJ/kg, this emission factor would be lower than the reported emission factors for fuel combustion used above. Moreover, energy generated from FCCU coke burning is much less than the energy generated from total refinery fuel consumption. The estimated PAH (E-PRTR4) emission would thus also be below 1 kg/year.

Note that in the literature underlying the Concawe report 4/19 [9] there is an emission factor for total PAH given, which is a more substantial part of total S/IVOC and may therefore be a better indicator. This literature source and emission factor will be discussed in **Section 3.3.4.1**.

Besides PAH, emission factors are also given for naphthalene (a borderline IVOC) and anthracene (a true IVOC), as both components may be emitted by refineries. In the Concawe 4/19 report [9], an example emission calculation for a very large refinery is made for these two components, taking both fuel combustion and FCCU catalyst regeneration into account. Similarly to what was demonstrated above, an annual emission below 1 kg/year is estimated for both naphthalene and anthracene.

Based upon the above indicative calculations, estimated PAH emissions are likely below the E-PRTR reporting threshold for many facilities; this may explain why only two refineries reported PAH emissions in E-PRTR.

3.3.3. Literature on measured S/IVOC and indicator compounds for selected sources

3.3.3.1. S/IVOC emission from combustion of typical refinery fuels

Fuel oils

Miller et al. (1996) [63] measured PAH from a 0.7 MWth firetube boiler, firing #2, #5, low sulphur #6 and medium sulphur #6 fuel oil (See **Table 3**). Both the total of semi-volatile organic compound emissions (comparable to the sum of SVOC and IVOC) and PAH (EPA-16 individually, including naphthalene **and** anthracene) were measured. For sampling and analysis of semi-volatile **organic** compounds method SW-846 – 0100/8270 was used and for PAH method CARB 4296. The calculated emission factors resulting from this study are given in **Table 3**. Oils #6 and perhaps #5 may be considered representative for certain refinery fuels, as both are residual fuel oil types. “Other PAH” are the EPA-16 minus naphthalene and anthracene, and are all high molecular PAHs (3 aromatic rings or more).

Table 3 S/IVOC indicator emissions vs. total S/IVOC emission as measured by Miller et al. (1996) [63]

Oil type	Emission factor (mg/GJ)			
	S/IVOC	Naphthalene	Anthracene	Other PAH (“EPA14”)
#2	6.0	0.18	ND	2.4
#5	9.5	0.28	0.02	0.16
#6 LS	3.2	0.09	0.01	0.18
#6 MS	1.3	1.0	ND	0.23

ND = Not Detected

From **Table 3** an apparent ratio between S/IVOC indicators (such as PAHs, naphthalene) and total S/IVOC can be derived. The average ratio S/IVOC over high molecular PAH (“Other PAH” in **Table 3**) for #6 oils is 11. The ratio S/IVOC over naphthalene is about 4. For #2 and #5 oils (distillate and mixed distillate/residual) these ratios are 2.5 and 33 (#2), and 60 and 34 (#5).

Hays et al. (2009) [32] measured condensed particle-bound and vaporous semi-volatile organic compounds from a 250MWth residual oil-fired (high sulphur #6 oil) power plant. They used a dilution tunnel-based method. The plant had a high combustion efficiency and was equipped with a 5-field electrostatic precipitator (ESP), which results in particulate and particle-bound emissions being relatively low. There were some difficulties during S/IVOC sampling and analysis which resulted in no PAH measurement data. In total 24 other S/IVOCs were identified by GC-MS. Total identified speciated S/IVOC emission factor was around 11 mg/GJ fuel used. Main contributors were organic acids, particularly dodecanoic and tetradecanoic acid. NMVOC emission (in total 410 mg/GJ) was much higher than S/IVOC. Fine aerosol was stated to be dominated by metal sulphates rather than carbonaceous matter. ESPs generally run well above atmospheric temperature (>200 °C), so should not remove organic aerosols that are not particulate at those conditions. Therefore, the effect of the ESP on S/IVOCs is expected to be minor.

Bond et al. (2006) [5] measured PAH (EPA-16 plus some other high molecular aromatic compounds) and C18 to C31 alkanes, from a modern industrial size heat plant firing low sulphur residual oil (#6). PAH emission was found to be relatively low in comparison to literature, probably because of its modern design. There was no further emission control. Bond et al [5], calculated a ratio of linear C18 - C31 alkanes (mostly C20 – C26) over EPA-16 PAH (mostly pyrene, phenanthrene and fluoranthene) of 5.5. C18 – C31 alkanes were thought to result from unburned fuel or thermocracking (fuel pyrolysis), and these substances are all SVOCs. There were some high molecular aromatic compounds, oxygenated PAHs, and alkanones measured as well (sum of the same order as the EPA-16 PAHs) but no organic acids.

England et al. (2007) [16] measured total PM emission from an 18 MWth institutional boiler firing residual fuel oil (#6), using a dilution tunnel-based method. A total average $PM_{2.5}$ emission rate of around 7 g/GJ was measured with 60% consisting of sulphate and around 8% of organic matter (OM). This would suggest an S/IVOC emission factor below 1 g/GJ.

Refinery gas

Literature emission factors for PAH or $PM_{2.5}$ from gas-fired equipment are almost always very low. England et al. (2007) [16] measured filterable and condensable PM from several industrial size natural gas and refinery gas-fired boilers and furnaces. Using a dilution tunnel-based method an average $PM_{2.5}$ emission factor (sum of filterable and condensable PM) of around 0.04 g/GJ was measured, with an average OM content of around 60%. He concluded that although SVOCs made up more than 90% of the $PM_{2.5}$ emission, the total $PM_{2.5}$ emission was over a factor of 100 lower than that of an oil-fired combustor. Also in gas turbines, SVOC emissions are very low compared to combustors using other fuels.

England et al. (2007) [16] also compared their dilution tunnel results with PM emission factors based on traditional impinger-based methods, such as the promulgated EPA Method 202. They found that the impinger-based method gave much higher results, especially when residual amounts of sulphur are present in the fuel (which may be the case in refinery gas). The impinger-based method suggested an average CPM emission factor of 1.8 g/GJ, which is almost 50 times higher than the dilution tunnel result. CPM emissions were thus found to be strongly method dependent.

Bond et al (2006) [5] also found very low SVOC emissions from gas-fired combustors, as did Miller et al. (1994) [64].

3.3.4. Literature emission factors for refinery processes

3.3.4.1. FCCU catalyst regeneration

Fluidised catalytic cracking units (FCCUs) are a potential emissions source of S/IVOC. Bertrand et al. (2002) [4] studied the results of a large collection of measurement data of emissions by FCCU catalyst regenerators (more than 1,400 field test data points). In their analysis, both average and median emission factors for 18 PAH individual components, as well as total PAHs were derived. Emission factors are expressed as pounds emissions per 1000 pounds coke burned. Although the emission factor for “total PAH” was based on a very limited amount of data (as almost all other measurements referred to individual compounds or selections of compounds) it is interesting to note that this emission factor is ten times the sum of the emission factors for the 18 individual PAHs.

In Concawe Report 4/19 [9] [Concawe, 2019] it is estimated that for a very large refinery the amount of coke burned off from FCCU catalyst in the regenerator could be around 140,000 t/year. With the emission factor for “total PAH” mentioned above, total PAH emission would be around 200 kg. Using the emission factor for all 18 individual PAHs summed, emission would be around 20 kg. The ratio of S/IVOC over PAH might be lower for FCCU coke combustion than for residual oil fuel combustion (both will contain oxygenated SVOCs but coke burning may result in more PAH and less alkanes that were present in the fuel, compared to residual oil combustion).

PAH emission from oil refinery processes is also discussed in EPA report 454/R-98-014. In this report PAH is called POM (Polycyclic Organic Matter) [EPA 1998] [17]. Compared to Concawe report 4/19 [9], the EPA emission factors are much older (1967) and may no longer represent the current situation. The report gives some background information about possible formation mechanisms of PAH in FCCU catalyst regeneration.

3.3.4.2. Delayed coking

In delayed coking volatiles and semi-volatiles (which may be S/IVOCs) still present in residue are removed. Based on engineering judgement one might reason that emissions from the delayed coking unit steam vent may include S/IVOC. Quantitative data on emissions are however not available.

3.3.5. Chemical composition of refinery process streams (API Report 4723-A)

In API Report 4723-A [2] (“Refinery Stream Composition Data”) a compilation of refinery process stream speciation data has been published. Speciation data are presented for 68 major refinery process streams, for 89 selected chemical species in total. The chemical species have been selected because they are categorised by the US EPA as hazardous air pollutant (HAP) or identified as persistent bio-accumulative toxic or appear on EPA Toxic Release Inventory lists. Summarising the most likely values (MLVs) of the mass percentages per stream, the report suggests that, on average, the selected substances may make up 25% of the mass. However, the composition of the process streams is highly variable, as the selected substances may make up between 1 and 100% of the mass.

It must be noted that the API Report 4723-A [2] is not about air emissions (streams released to air, like flue gases, are not addressed by the report) but in case there would be leakage from a certain process stream, the data in the report could be used to calculate speciated diffuse emissions. In case there is no selective volatilisation possible, a chemical composition identical to the process stream composition may be assumed. In the list of substances covered by the report, 21 S/IVOC indicators have been identified, which are presented in **Table 4.**

Table 4 I- and SVOCs included in API Report 4723-A [2]

Substance	CASNR	Type
Acenaphthene	83329	IVOC
Acenaphthylene	208968	IVOC
Biphenyl	92524	IVOC
Fluorene	86737	IVOC
Naphthalene	91203	IVOC
Phenanthrene	85018	IVOC
PAH Total	-	I- and SVOC
Benzo(a)anthracene	56553	SVOC
Benzo(a)pyrene	50328	SVOC
Benzo(b)fluoranthene	205992	SVOC
Benzo(b/j)fluoranthene	205823	SVOC
Benzo(e)pyrene	192972	SVOC
Benzo(g,h,i)perylene	191242	SVOC
Benzo(k)fluoranthene	207089	SVOC
Chrysene	218019	SVOC
Dibenz(a,j)acridine	224420	SVOC
Dibenzo(a,h)anthracene	53703	SVOC
Fluoranthene	206440	SVOC
Indeno(1,2,3-c,d)pyrene	193395	SVOC
Perylene	198550	SVOC
Pyrene	129000	SVOC

Chemical species in **Table 4** are selected based on their saturation vapour mass concentration, which is in turn estimated based on saturation pressure, molecular weight and the Ideal Gas Law (1 mole of the substance in the vapour phase equals a partial pressure of 0.0248×10^5 Pa). Naphthalene is considered borderline IVOC with a saturation concentration around the limit value, and is included as an IVOC. Phenol and cresols are by a small margin too volatile to be considered IVOC and are not included.

Based on the component classification in **Table 4**, an indicator S/IVOC content in the refinery process streams included in the API report can be calculated. **Table 5** lists this indicator S/IVOC content per stream, sorted in descending order. The primary contributing substance is also listed.

Table 5 Total identified I- and SVOC content for refinery process streams in API Report 4723-A [2]

Table nr in API report			Total indicator (%wt)		Principal component	
Nr	Feed	UVCB$^{*)}$	IVOC	SVOC	IVOC	SVOC
27	ATM DISTILLATION	Straight Run Kerosene	2.54		Naphthalene	
63	KEROSENE TREATING	Commercial Jet Fuel	1.89		Naphthalene	
73	VARIOUS UNITS	Slop Oil	1.66	0.011	Biphenyl	Fluoranthene
38	CATALYTIC REFORMER	Reformate	1.64	0.0015	Biphenyl	Pyrene
59	HYDRODESULFURIZATION	Diesel	1.56	0.0043	Biphenyl	Fluoranthene
55	FLUID CATALYTIC CRACKER	Light Cat Gas Oil	1.44	0.014	Naphthalene	Pyrene
23	ATMOSPHERIC DISTILLATION	Heavy Naphtha	0.76		Biphenyl	
54	FLUID CATALYTIC CRACKER	Heavy Cat Gas Oil	0.41	0.30	Phenanthrene	Pyrene
58	GASOLINE BLENDING	Reformulated Gasoline	0.19		Naphthalene	
42	COKER	Coker Gas Oil	0.17	0.010	Naphthalene	Pyrene
24	ATMOSPHERIC DISTILLATION	Light Atmospheric Gas Oil	0.18		Biphenyl	
51	DISTILLATE BLENDING	Diesel Fuel	0.17		Naphthalene	
57	GASOLINE BLENDING	Conventional Gasoline	0.16	6e-5	Naphthalene	Chrysene
22	ATMOSPHERIC DISTILLATION	Heavy Atmospheric Gas Oil	0.14	0.011	Biphenyl	Pyrene
43	COKER	Coker Heavy Naphtha	0.15		Naphthalene	
53	FLUID CATALYTIC CRACKER	Cracked Gasoline	0.13		Naphthalene	
69	VACUUM DISTILLATION	Heavy Vacuum Gas Oil	0.094	0.013	Biphenyl	Benzo(b/j)fluoranthene
44	COKER	Coker Light Naphtha	0.088		Naphthalene	
35	CATALYTIC ISOMERIZATION	Isobutane	0.076		Biphenyl	
Table nr in API report			**Total indicator (%wt)**		**Principal component**	

Nr	Feed	UVCB[*)]	IVOC	SVOC	IVOC	SVOC
36	CATALYTIC ISOMERIZATION	Isom Naphtha/Isomerate	0.076		Biphenyl	
68	SUPPLY SYSTEM	Crude Oil	0.061	0.014	Biphenyl	Benzo(b)fluor-anthene
34	CATALYTIC HYDROCRACKER	Cat Cracker Feed	0.019	0.054	Phenanthrene	Pyrene
61	HYDRODESULFURIZATION	Jet/Kerosene	0.061		Naphthalene	
8	ALKYLATION	Alkylate/NOT C4 Olefin Feed	0.061		Naphthalene	
29	CATALYTIC HYDROCRACKER	Heavy H/C Distillate	0.019	0.032	Naphthalene	Pyrene
70	VACUUM DISTILLATION	Light Vacuum Gas Oil	0.021	0.023	Phenanthrene	Pyrene
65	NAPHTHA PRETREAT	Desulfurized Naphtha	0.040		Naphthalene	
7	ALKYLATION	Alkylate/C4 Olefin Feed	0.036		Naphthalene	
9	ALKYLATION	Butane	0.029		Acenaphthylene	
56	GASOLINE BLENDING	Aviation Gasoline	0.028		Biphenyl	
39	CATALYTIC REFORMER	Reformate Gas	0.025		Naphthalene	
18	ASPHALT PLANT	(Feed) Pitch	0.018	0.0056	Naphthalene	Benzo(g,h,i)-perylene
45	COKER	Coker Total Naphtha	0.023		Naphthalene	
28	ATM DISTILLATION	Straight Run Naphtha	0.021		Biphenyl	
62	HYDRODESULFURIZATION	Naphtha	0.015		Naphthalene	
72	VACUUM DISTILLATION	Vacuum Residue	0.015		Phenanthrene	

Table nr in API report			Total indicator (%wt)		Principal component	
Nr	Feed	UVCB*)	IVOC	SVOC	IVOC	SVOC
40	CAUSTIC TREATING	Spent Caustic	0.0061	4e-6	Acenaphthylene	Benzo(a)pyrene
32	CATALYTIC HYDROCRACKER	Light H/C Naphtha	0.0033		Naphthalene	
19	ASPHALT PLANT	Asphalt		0.0028		Benzo(g,h,i)-perylene

*) UVCB stands for Chemical Substances of Unknown or Variable Composition, Complex Reaction Products and Biological Materials

Among the 89 selected chemical species the most occurring S/IVOC indicators in refinery process streams appear to be naphthalene, biphenyl, phenanthrene and acenaphthylene (all IVOCs). Indicator SVOCs in refinery streams are all high-molecular PAHs with pyrene, benzo(b/j)fluoranthene, fluoranthene, benzo(g,h,i)perylene, chrysene and benzo(a)pyrene appearing to be the principal components. In general, the IVOC indicator content is much higher than the SVOC indicator content in process streams. The highest recorded indicator SVOC content would be 0.3% in the heavy gas oil stream in fluid catalytic cracking, primarily consisting of pyrene. If we presume that this stream mostly comprises S/IVOCs (see **Section 3.3.6**), a ratio of total amount of S/IVOCs present in this stream over the sum of SVOC indicators (0.3%) of (100% over 0.3% =) ~300 could be derived. Whether or not this ratio is representative for heavy fuels (like residual fuel oil) in general, is highly debatable. Nevertheless, this ratio has been assumed for residual fuel oil in some indicative calculations in the concluding section of this chapter (**Section 3.3.7**).

3.3.6. Literature on the IVOC and SVOC content of fuels in storage

Besides combustion and other thermal sources, S/IVOCs may also be released by fugitive emissions and/or leakage from process streams or refinery product storage and handling.

Lu et al. (2018) [53] report a total PAH content in diesel fuel of 3%. If we assume that S/IVOCs must have at least 14 carbon atoms (Aakko-Saksa, 2019) [1] half to three quarters of diesel fuel consists of S/IVOC (Zeraati Rezaei et al., 2016) [87]. Naphthalene content is reported in levels up to 0.2% in diesel fuel and 0.3% in gasoline and jet fuel (Marr et al., 1999) [56].

S/IVOCs will not detectably evaporate from stored refinery products due to the relatively low storage temperature and exceedance of the saturation concentration under storage conditions. In case liquid products (like diesel) are somehow leaked in the open air, they will eventually at least partly evaporate, including contained I- and perhaps even SVOCs. Only low volatility organic compounds[6] (LVOCs) would not evaporate under ambient temperature. It is considered unlikely though that this occurs at a relevant scale at refineries.

Assuming IVOC n-alkanes to be in the range of C12 to C22 (e.g. Aakko-Saksa, 2019) [1] heavier fuel oils consist for the greater part of IVOC. Assuming SVOC to be in the C23 to C32 range, residual oil may also contain significant quantities of SVOC as well (e.g. Garaniya et al., 2011) [26].

3.3.7. Conclusions

There is not sufficient literature information that can help to make a reliable and representative estimate of S/IVOCs emissions from oil refineries (disregarding SOA precursors). For such S/IVOCs inventories, representative S/IVOC measurements from known activities are needed in order to increase the accuracy of the S/IVOCs emission estimates which currently rely on indirect assessments.

There are limited emission data available to develop S/IVOCs emission estimates using indicators such as PAHs, which in combination with some rough estimates of the ratio of indicators could be used to estimate total S/IVOC.

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[6] LVOCs are organic compounds with a saturation vapour concentration (at 298 K) below 0.32 µg m^{-3}

Also chemical composition data of refinery process streams are available that includes significant number of indicators for S/IVOCs. Chemical speciation of refinery process streams and products may be useful to estimate fugitive emission if, for instance, leakage rates from these process streams would be known. In this study no such attempts have been made however.

We have attempted to make an indicative estimate of what S/IVOC emission for a typical (~10 Mt/year) refinery could be. This estimate is based on our findings reported in the previous sections of Chapter 3. We have considered the total reported refinery release of S/IVOC indicators, as well as the release of S/IVOCs and its indicators for the presumably highest contributing sources in a refinery, i.e. the combustion of residual oil and the regeneration of FCCU catalyst. Finally we consider potential diffuse releases of S/IVOC.

Total S/IVOC release based emission indicator

If we take the absolute highest implied PAH emission factors for oil refining as a whole in both E-PRTR and EPA TRI, we get 49 kg PAH(E-PRTR4)/Mt crude and 87 kg PAH (TRI-22)/Mt crude. If we assume then a ratio of S/IVOC over PAH (TRI-22) of 10, we would estimate a total S/IVOC release of about 1 t/year. If we would assume a ratio of S/IVOC over PAH (TRI-22) of 100 (which is above ratio found for flue gases), we would estimate around 10 t/year S/IVOC.

S/IVOC release from residual oil combustion

If we consider residual oil combustion only and assume a specific use of 1100 TJ/Mt crude processed (based on a refinery fuel use as given in **Appendix 3** of Concawe report 4/19 [9] and a specific energy consumption of 2.75 GJ/t crude processed), as well as an S/IVOC emission factor of 1 to 500 g/TJ (**Section 3.3.3.1**, Miller et al., 1996 [63]; Hays et al., 2009 [32]; England et al., 2007) [16] then for a 10 Mt crude/year refinery we would estimate S/IVOC release from residual oil combustion to be in the range of 0.01 to 5.5 t. This is an extremely wide range but the data to disregard the low or high end of the published emission factors for residual oil combustion are not available.

S/IVOC release from FCCU catalyst regeneration

If we consider FCCU catalyst regeneration then based on Bertrand et al. 2002 [4] we estimated earlier (**Section 3.3.4.1**) that for what Concawe Report 4/19 [9] calls a “very large refinery”, PAH(Bertrand-18) and ‘total PAH’ would be 20 and 200 kg. An S/IVOC over PAH(18) ratio of 10 could be assumed (PAH content of FCCU flue gases may be higher than for residual oil combustion) then S/IVOC emission for this very large refinery may be 0.2 or 2 t/year.

Diffuse S/IVOC releases

Diffuse emissions of S/IVOCs from refineries have never been measured to our knowledge. It is in our view not likely that refinery diffuse S/IVOCs emissions would be higher or more significant than S/IVOC emission from refinery stacks. At ambient temperatures S/IVOCs evaporate only very slowly and substantial volatilisation rates would require a high temperature. High temperatures are more associated with stack conditions than situations where leakage may occur, for instance in product storage. In the EPA TRI, reported diffuse PAH(TRI-22) emission was about one-half of the value reported for stacks. If we would assume that all diffuse PAH emission recorded in TRI would be the result of product evaporation/volatilisation of a heavy type of product, and we would assume an S/IVOC over PAH(TRI-22) ratio as high as 300 (see **Section 3.3.5**), diffuse S/IVOC release based on the highest PAH emission rate recorded in EPA TRI (0.087 t PAH(TRI-22)/Mt crude processed, see **Section 3.3.1.2**) would be 0.087 * $^1/_3$ * 300 = 8.6 t. The S/IVOC over PAH(TRI-22) ratio of

300 could be representative for a product with a very high S/IVOC content (e.g. C_{15+}), like the stream 54 in **Table 5** discussed earlier. For a lighter type of product like diesel fuel (see Section 3.3.6) this ratio would likely be considerably lower than 300. 8.6 t would represent an extreme upper case in which all upper limits of the ranges previously derived are combined.

In the absence of actual S/IVOC measurement data for refineries we estimate that for an average refinery, total S/IVOC (and total organic CPM) could be in the order of 1 (0.1 - 10) t annually, by combining the indicative estimates made above for stack (combustion and process) and diffuse emissions.

For comparison, annual reported refinery emissions of filterable, primary PM (as recorded in E-PRTR) may be in the order of 10 to 100 t for an average sized refinery. Thus, an S/IVOC emission of 1 t/year would comprise only 1-10% of PM emissions. Note that the main refinery FPM emissions are from fuel oil combustion (sulphate particles from sulphur containing fuel) and catalyst particles emitted by the FCCU. The latter is generally the biggest single emitter of particulates at a refinery (European Commission, 2015) [19].

4. FORMATION AND IMPORTANCE OF SECONDARY ORGANIC AEROSOL

4.1. THE DIFFERENT FORMATION PATHWAYS, ROLE OF S/IVOC 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, organic CPM, by definition, only contributes to POA and not to SOA.

Note, 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: 1) 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 SVOC, 2) 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. The following figure taken from Tsimpidi et al. (2010) [80] presents an illustrative example of a typical organic aerosol formation framework.

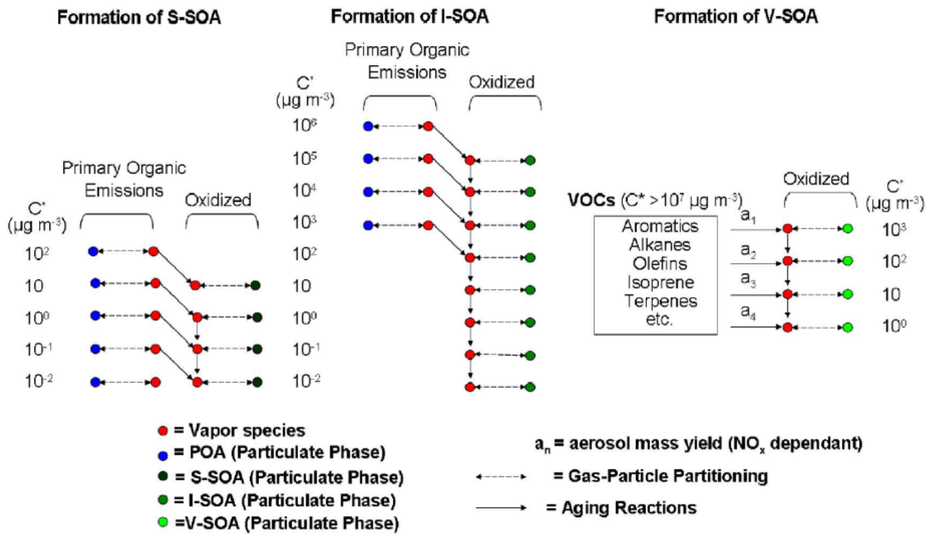

Figure 5 Schematic of a typical organic aerosol framework (Tsimpidi et al.[7], 2010) [80]

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[7] S-SOA: SOA formed from SVOC, I-SOA: SOA formed from IVOC, V-SOA: SOA formed from VOCs

4.2. INTRODUCTION TO THE VOLATILITY BASIS SET (VBS)

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 [44]; Odum et al., 1996) [69]. 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) [42]: 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 models of the evolution of organic compounds in the atmosphere, dilution, ageing and partitioning need to be addressed simultaneously (Donahue et al., 2006) [13].

The Volatility Basis Set (VBS) framework (Donahue et al., 2006) [13] 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 smaller carbon chains). 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 [3]; Fountoukis et al., 2014 [22]), 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 [15]; Bergström et al., 2012 [3]; Murphy et al., 2012 [66]); 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) [15]. 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 [42]; Donahue et al., 2011 [12]). 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) [47], 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) [43], EMAC (Tsimpidi et al., 2014) [79], regional models (LOTOS-EUROS (Manders et al., 2017) [54], EMEP (Bergström et al., 2012) [3], PMCAMx (Shrivastava et al., 2008) [75], WRF-Chem (Hodzic et al., 2014)) [34] and local models (Dzepina et al., 2009 [15]; Hayes et al., 2015 [31]; Janssen et al., 2017) [38]. 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) [75], to model contributions of various sectors to OA levels (Denier van der Gon et al., 2015 [11]; Fountoukis et al. 2016) [23], and to account for SOA formation from S/IVOCs (Bergström et al., 2012 [3]; Woody et al., 2016 [82]; Murphy et al., 2017 [68]).

4.3. 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) [74], 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 in which the amount and volatility distribution of the emissions is treated and in the assumptions that are made on gas-phase ageing. We here describe 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[8] (e.g. Robinson et al., 2007 [74]; Bergström et al., 2012 [3]; Murphy et al., 2017 [68]). However, some modelling studies have applied scaling factors of up to 3 to the POA emissions to derive SVOC emissions (Tsimpidi et al., 2010 [80]; Woody et al., 2016) [82], 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) [74]. Afterwards, other approaches have been adopted, like scaling the IVOC emissions with ambient observations (Ots et al., 2016) [70], applying VOC speciation profiles for gasoline and diesel sources from measured tailpipe emissions (Jathar et al., 2017) [39], 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) [68].

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. Following the experiments of May et al. (2013c [57], 2013a [58], 2013b [59]), separate volatility distributions of S/IVOC emissions from gasoline, diesel and biomass burning, respectively, have been implemented in some models (Koo et al., 2014 [47]; Woody et al., 2016 [82]).

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[8] 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 which can add significantly to the uncertainty.

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) [68].

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 unknown and strongly varies with source and location, parameterising the ageing of this mixture is prone to large uncertainties. (Robinson et al., 2007) [74] derived an S/IVOC reaction rate with the hydroxyl radical of 4×10^{-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 categories (Bergström et al., 2012 [3]; Woody et al., 2016 [82]). 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.

4.4. WHAT ARE RESULTING OA CONCENTRATIONS IN AMBIENT AIR, HOW IMPORTANT IS SOA IN TERMS OF TOTAL 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[9] (Jimenez et al., 2009) [42]. 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 [8]; Mircea et al., 2019 [65]). 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 [44]; Volkamer et al., 2006 [81]; Heald et al., 2011) [33]. 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 [74]; Shrivastava et al., 2008 [75]). Improvements in model-measurement agreement have indeed been shown under specific conditions (Shrivastava et al., 2008 [75]; Murphy et al., 2017 [68]), but the complex nature of semi-volatile emissions and ageing of non speciated 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) [78].

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

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[9] The $PM_1/PM_{2.5}$ ratio may spatially and temporally varies. A value of 0.75 could be considered as an average $PM_1/PM_{2.5}$ ratio (Tronville and Rivers, 2017) [77].

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) [23].

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) [46], the photolytic breakdown of SOA (Hodzic et al., 2016) [35], the role of aqueous-phase SOA formation (McNeill, 2015) [62] and the inhibition of SOA formation by gas-phase chemical pathways (McFiggans et al., 2015) [61]. 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 [3]; Prank et al., 2016 [71]), 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 [24]; Zhang et al., 2013 [88]; Ciarelli et al., 2016 [8]; Janssen et al., 2017 [38]; Jiang et al., 2019 [40] [41]; Mircea et al., 2019 [65]; Yttri et al., 2019 [86];). 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) [24] were the first who simulated 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) [8], 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) [74] 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) [80], 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 3 x POA increase), the bias compared to observations was reduced further (simulated mean concentrations of 2.8 µg m^{-3}). In each scenario, the model over-predicted 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) [71]. 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) [65] 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.

4.5. CONTRIBUTION OF THE REFINING SECTOR TO SOA CONCENTRATIONS OVER EUROPE

4.5.1. Introduction

Studies into the contribution of refinery emissions to organic aerosol levels are scarce. To our knowledge, there have been a few studies published concerning refineries in France (Kim et al., 2014 [45]; Raffort et al., 2015 [73]; Duclaux et al., 2019) [14], as well as one study for a refinery in China (Zhang et al., 2017) [89]. Therefore, we include here the results of a modelling study using LOTOS-EUROS, a 3-D CTM developed by TNO, including the VBS parameterisation to estimate the contribution of refinery emissions to SOA concentrations over Europe. We have limited the impact of refineries to SOA formed from NMVOC emissions, because no detailed information on refinery semi-volatile (S/IVOC) emissions was available yet. In addition, to illustrate the formation of POA and SOA from semi-volatile emissions, we included a simulation with enhanced residential wood combustion (RWC) emissions.

4.5.2. Methodology

To obtain an estimate for the contribution of refineries to organic aerosol concentrations over Europe, we employed the LOTOS-EUROS model over the European domain (0.50x0.25° resolution) for the year 2015, with emissions as described below. Gas-phase chemistry in LOTOS-EUROS is represented by the Carbon Bond Mechanism IV (Gery et al., 1989) [28], which includes reactions for 4 anthropogenic (alkenes, alkanes, toluene and xylene) and 2 biogenic (isoprene and terpenes) NMVOC that are SOA precursors.

The reaction products of these NMVOC enter the VBS bins with yields as in Tsimpidi et al., 2010 [80]. The centres of these four bins have saturation vapour concentrations of 1, 10, 100 and 1000 µg m^{-3}, respectively. Secondary S/IVOC derived from anthropogenic NMVOC are assigned a reaction rate with the OH radical of $1x10^{-11}$ molecules cm^{-3} s^{-1} with a mass increase of 7.5% per oxidation step to account for additional oxygen mass, while S/IVOC from biogenic VOC are assumed to not further decrease in volatility upon ageing.

For the SOA modelling with LOTOS-EUROS we used specific refinery NMVOC emissions, and for non-refinery sources, the emission of SOA tracers (like PM or NMVOC). For the Control / No Refineries run, emission of SOA precursors is taken from CAMS81 European Emissions Dataset (2015) (Kuenen et al., 2018) [48] with the refinery NMVOC removed (see **Table 6** for an overview of the simulations).

Direct emissions of NMVOC from refineries for the New Refineries run are based on overviews of existing/operational petroleum refineries in the EU28 in 2015 (from for instance the OGJ Worldwide Refining Survey, or online directories such as the Wiki site "A barrel full", http://abarrelfull.wikidot.com/european-refineries, accessed February 2020). We have linked our compiled complete list of oil refineries to E-PRTR, from which the total NMVOC emissions per refinery is retrieved. Our list for the EU28 includes about 80 operational refineries with 2015 NMVOC emission ranging from 120 to 9,300 t per refinery.

Table 6 Properties of OA precursor emissions for the three LOTOS-EUROS simulations: the control run without refinery emissions, the New Refineries run and the RWC simulation with enhanced residential wood combustion emissions. Default properties applied unless indicated otherwise

Scenario	Control run / No Refineries	New Refineries	RWC
Base emission	CAMS 1.1 w/ refineries removed	CAMS 1.1 w/ NMVOC refinery emissions. as separate category	CAMS 1.1 w/ additional OC from RWC
Height distribution		Same as 'Industry'	
Time profiles		Same as 'Industry'	
VOC profiles		Default CAMS81 refinery profile	
Temperature variation emissions		Same as 'Industry'	
Composition		Default	
Total POA emissions	1*POA (SVOC)+ 1.5 * POA (IVOC)	1*POA (SVOC)+ 1.5 * POA (IVOC)	1*POA (SVOC)+ 1.5 * POA (IVOC)

For NMVOC speciation of refinery emissions, as well as of other sources, the default CAMS81 NMVOC speciation profiles have been used in the modelling currently. For refineries, the speciation is based on analysis and averaging literature data (by e.g. US EPA, Canadian Fuels Association, formerly known as Canadian Petroleum Products Institute) and is listed in **Table 7** in its aggregated form (90% alkanes, 7.5% aromatics, 2.5% olefins).

Table 7 CAMS81 NMVOC speciation for refineries

EDGAR Code	Substance	Fraction (-)
v02	Ethane	0.05
v03	Propane	0.2
v04	Butanes	0.2
v05	Pentanes	0.25
v06	hexanes & higher alkanes	0.2
v07	Ethane	0.01
v08	Propene	0.01
v12	other alk(adi)enes & alkynes	0.005
v13	Benzene	0.02
v14	Toluene	0.03
v15	Xylene	0.02
v17	other aromatics	0.005

The CAMS81 NMVOC speciation profiles are tailored to the needs of the LOTOS-EUROS CTM and are only used for the SOA modelling. The CAMS81 speciation profile is also used in the EDGAR inventories [Huang et al., 2017] [36].

Finally, a simulation with enhanced residential wood combustion (RWC) emissions is performed to illustrate the difference between formation and spatial distribution of POA versus SOA. In this simulation, we employed harmonised semi-volatile POA emissions from RWC for all European countries as in (Denier van der Gon et al., 2015) [11]. Note that the base emission dataset also includes RWC emissions based on nationally reported PM emissions, while the new RWC emission dataset was based on bottom-up estimates of fuel wood sources per country. This means that by comparing the Control and the RWC run, we do not evaluate the total contribution of RWC to POA and SOA levels, but rather the effect of the harmonised emissions. However, the differences in emitted OA (precursors) is large (the RWC emissions are higher by a factor 2-3), so the results nicely illustrate the impact of increased primary S/IVOC emissions.

4.5.3. Results

4.5.3.1. Refineries

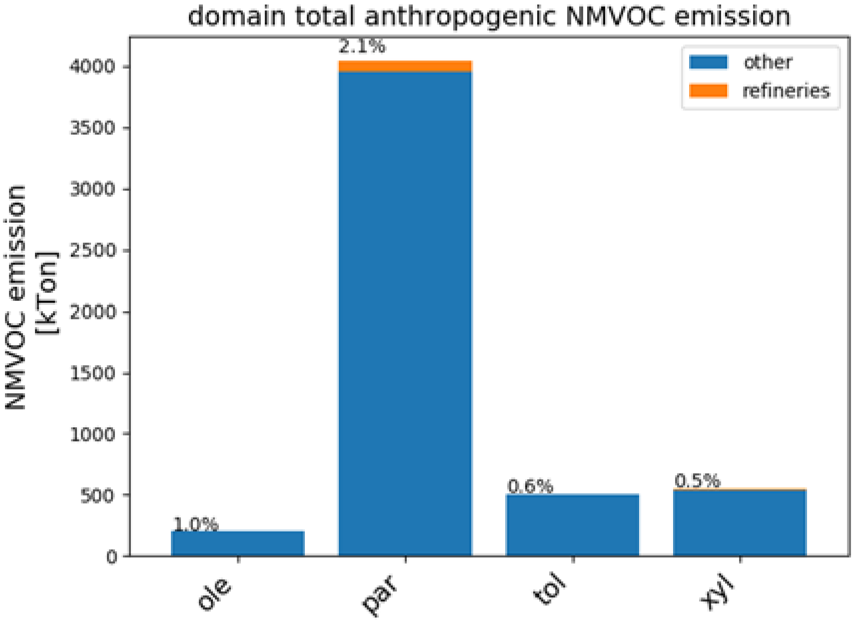

Figure 6 Annual total speciated anthropogenic NMVOC emissions for the European domain from the refinery and other sectors. The contribution of the refineries is indicated as a percentage of the total over all sectors

To get a first impression of how important the refinery NMVOC emissions may be for SOA formation over Europe, it is instructive to have a look at the refinery emissions as a fraction of the total emission according to the CAMS81 inventories **(Figure 6)**. This shows that for the anthropogenic NMVOC species OLE (alkenes), PAR (alkanes), TOL (toluene and toluene-like aromatics) and XYL (xylene and xylene-like aromatics), refinery emissions contribute only a minor fraction (1% or less, except for PAR) to the total.

If we then have a look at the spatial distribution of these emissions **(Figure 7)**, it clearly shows that although the point emissions of PAR from refineries can be substantial, its magnitude over the whole domain is low compared to other sources.

The other NMVOC species show similar distributions for the refineries and other sources. Consequently, the simulated contribution of refineries to SOA concentrations in LOTOS-EUROS is low as well (annual average of 0.02%; **(Figure 8)**.

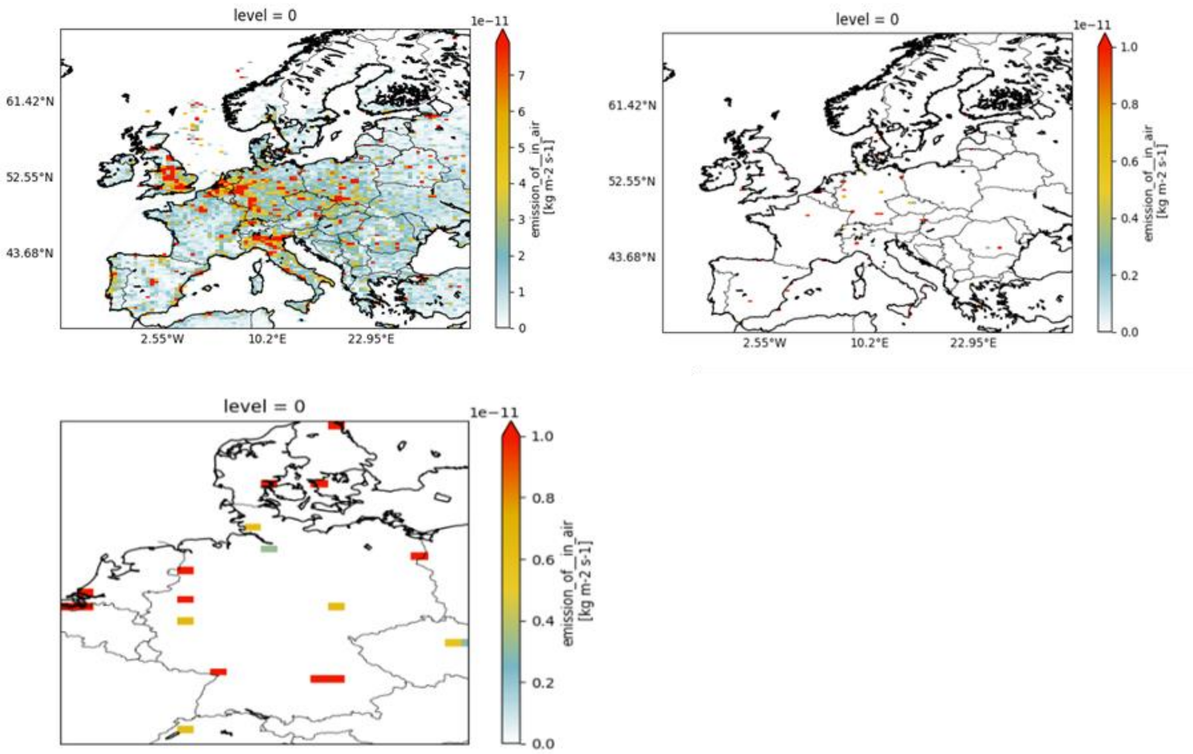

Figure 7 2015 annual average alkene (PAR) emission at LOTOS-EUROS grid cell level: all sectors (top left), refineries (top right) and refineries in Germany and Benelux (bottom)

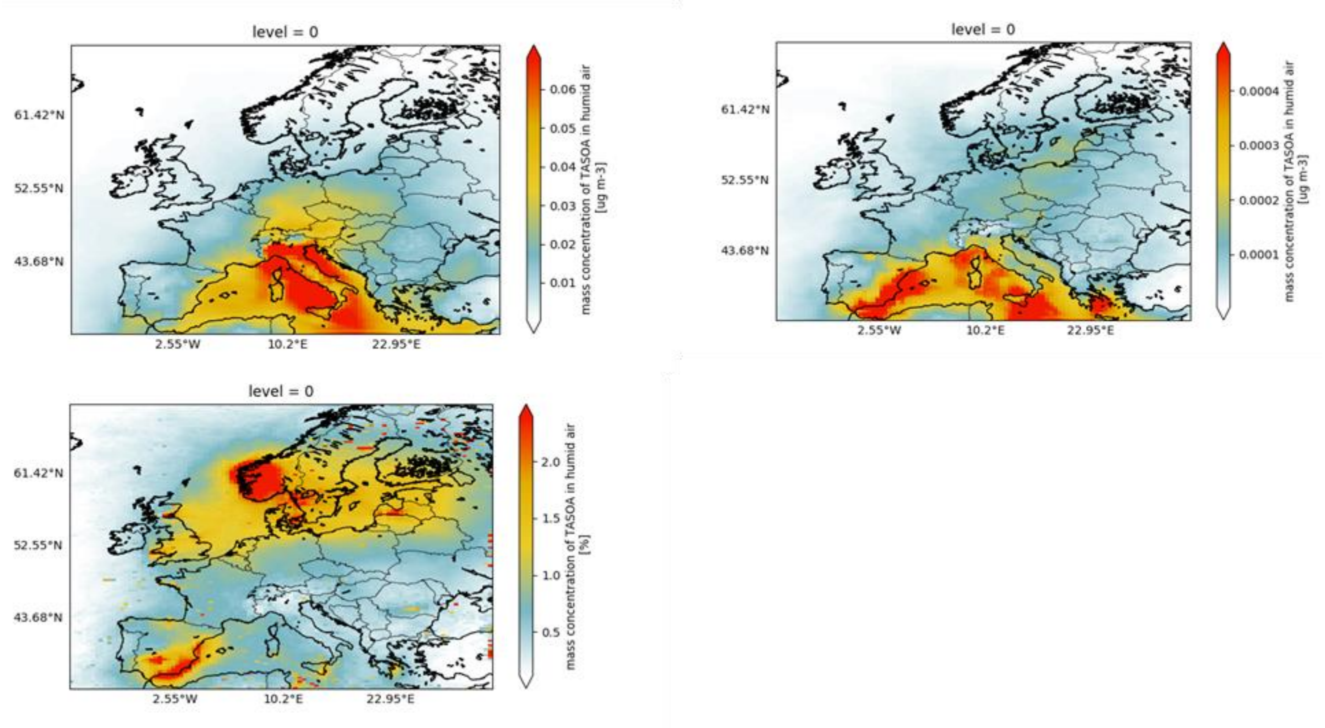

Figure 8 Anthropogenic SOA concentration at the surface for the 'New Refineries' simulation (top left), absolute difference between the 'New Refineries' and the 'Control Run' (top right), and relative concentration difference between these simulations (bottom)

For total SOA, the modelled contribution of the refineries to SOA is even slightly negative in some regions, probably because the enhanced NMVOC emissions compete for oxidants with biogenic emissions in forested areas, leading to lower biogenic SOA formation. Therefore, we show in **Figure 8** the contribution to the anthropogenic component of SOA (aSOA) only.

In the ‘New Refineries’ simulation, aSOA is itself a minor component of total SOA (on average 0.014 of 0.42 µg m^{-3} or 3%). To that aSOA, refineries contribute on average 1.0×10^{-4} µg m^{-3} (0.7%). This means that modelled SOA concentrations from refinery NMVOC emissions are in the sub-nanogram per cubic meter range, which falls close to, or below, the measurement detection limit of ~10^{-2} µg m^{-3} (DeCarlo et al., 2006) [10].

4.5.3.2. Residential wood combustion

To illustrate the potential of a single source sector to contribute to organic aerosol levels, we evaluate the influence of improved residential wood combustion (RWC) emission estimates on both POA and SOA concentrations. We do so by comparing two simulations: the 'Control' run and the 'RWC' run. Note that in contrast to the refineries, which only added to the NMVOC emissions in our simulations, the extra RWC emissions are added to the POA emissions, and thus affect POA and SOA formation through the S/IVOC pathways. **Figure 9** shows the annual average POA concentrations for the Control and RWC runs and the difference between them. Domain average POA concentrations increase by 302% (from 0.10 to 0.40 µg m^{-3}), with some regions like eastern France, southern Poland and the Balkans standing out. Major concentration differences are also visible near cities like Paris and Madrid, which shows that POA formation takes place near sources. The fact that RWC emissions mostly occur in winter, when temperatures are low and mixing is weak, is an important cause for this behaviour.

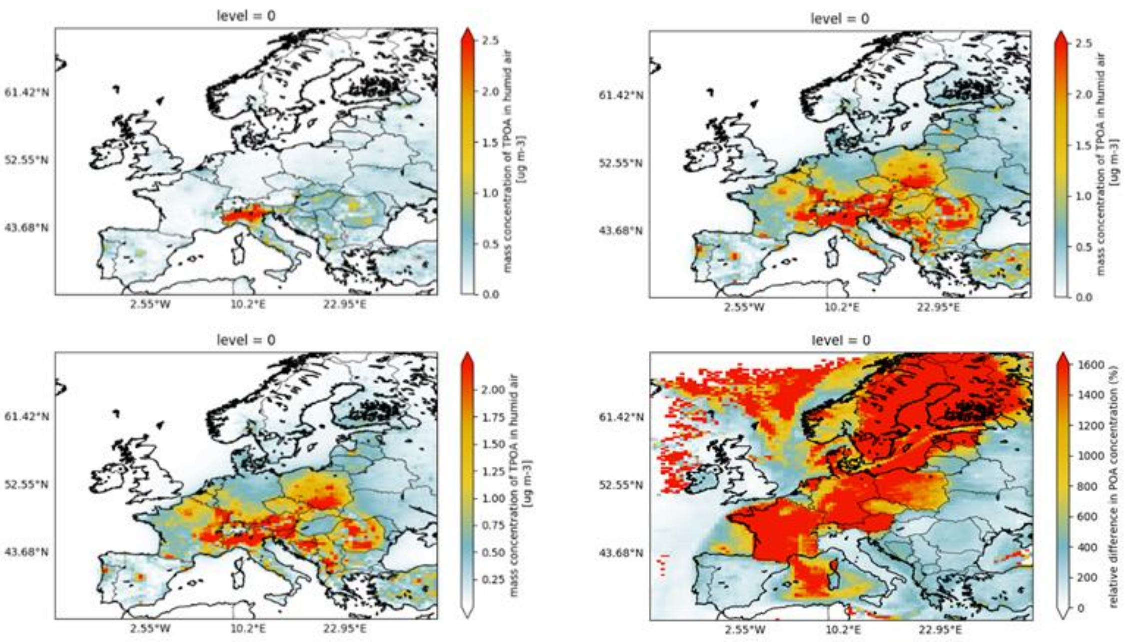

Figure 9 Modelled POA concentrations from the control run (top left), the RWC run (top right) and the absolute difference between these runs (bottom left) and the relative difference between these runs (bottom right)

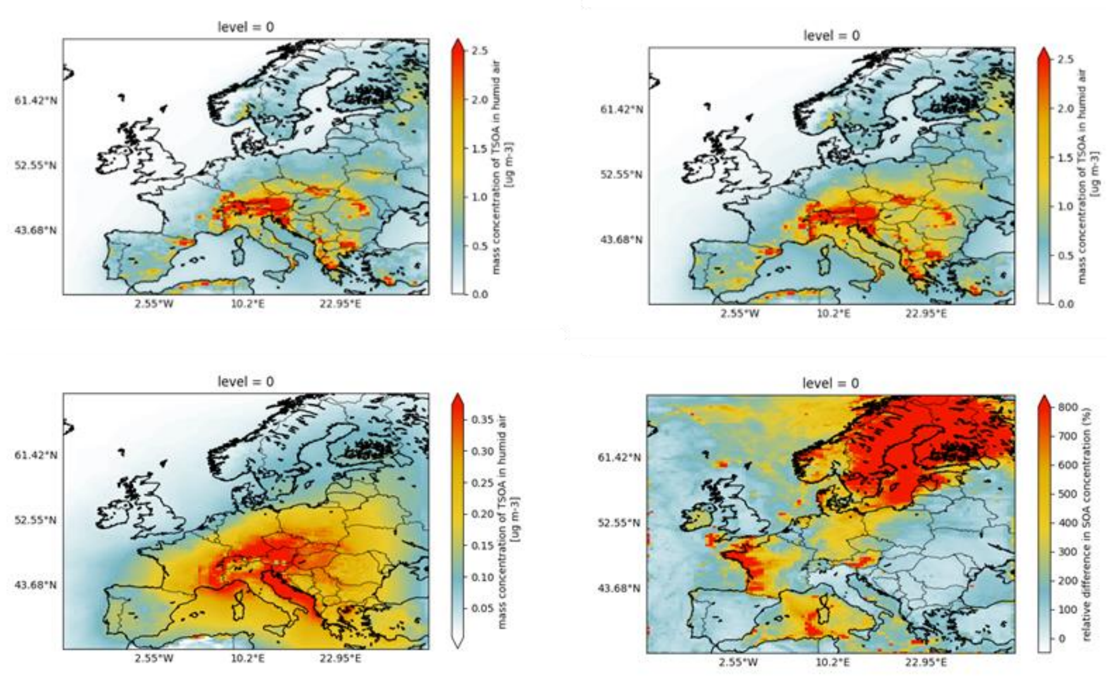

Figure 10 Modelled SOA concentrations from the control run (top left), the RWC run (top right) and the absolute difference between these runs (bottom left) and the relative difference between these runs (bottom right)

For SOA, the enhancement is somewhat less spectacular, with an annual average increase **(Figure 10)**. This shows a different aspect of the RWC emissions in winter: photochemical activity is low, which hinders the formation of secondary species.

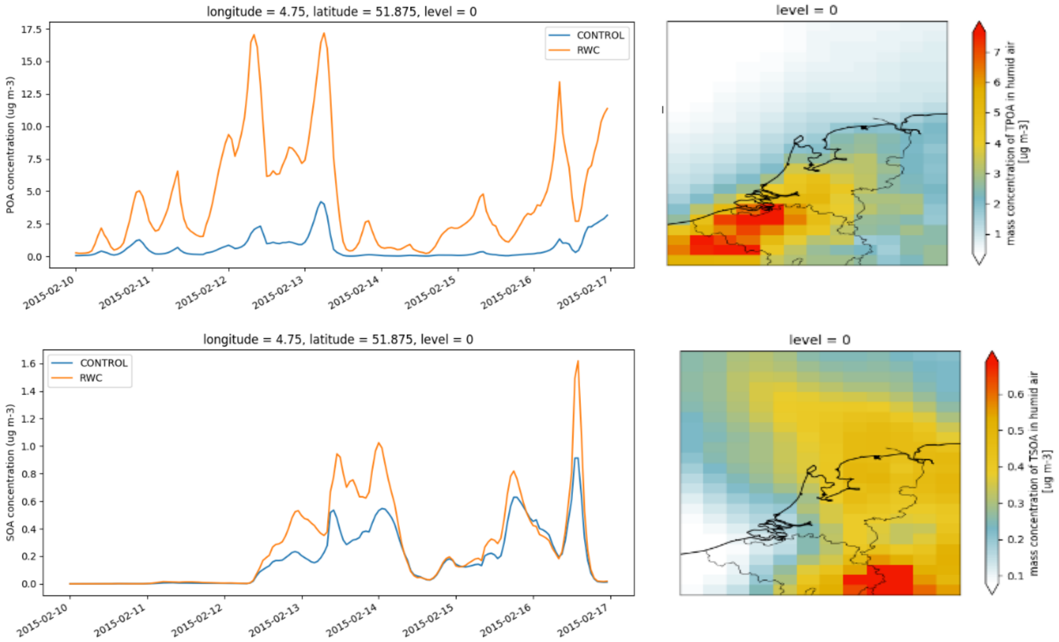

Figure 11 POA and SOA concentration time series at Cabauw, the Netherlands, for the 'Control' and the 'RWC' simulation (left) and average concentrations for the 'RWC' simulation (right) from 10 to 16 February 2015

To show the difference between POA and SOA formation in a bit more detail, we analyse a period with very high additional RWC emissions.

Figure 11 shows modelled POA and SOA concentrations time series for the period from 10-16 February 2015 at a rural measuring site in the Netherlands and as time-averaged concentration maps. This period was characterised by clearly enhanced concentrations (up to 7 times for POA) due to enhanced RWC emissions, as the comparison of the Control and RWC time series of POA show. Especially on the 12th and the 13th of February, two peaks are visible in the POA concentrations, while the map shows high POA concentrations in the south of the Netherlands, western Belgium and northern France. This indicates that POA peaks shortly after emission and in the regions where the RWC takes place. The SOA concentrations, in contrast, show delayed peaks on the 13th and the 14th of February, and high concentrations away from sources with a clear plume extending northwards over the Netherlands and Germany towards the North Sea. The delay and the plume are the consequence of the fact that SOA formation takes some time, especially under these winter conditions when photochemistry is slow. Also note that the absolute concentrations of POA and SOA differ by about an order of magnitude.

4.5.4. Conclusions

We have evaluated the contribution of NMVOC emissions from refineries to SOA formation over Europe. A comparison of two model runs with and without refinery emissions, respectively, suggests that this contribution is very small (0.02% on an annual average basis). This is due to the low contribution of refineries to total NMVOC emissions, and the low simulated contribution of anthropogenic NMVOCs to SOA formation in general. However, refineries may also be a source of semi-volatile organic compounds (SVOC) and intermediate volatile organic compounds (IVOC), with emissions comparable to the refinery NMVOC emissions. These species are currently missing from emission inventories, but have the potential to contribute to atmospheric primary and secondary organic aerosol levels. Including these emissions from all sectors, including refineries, would likely increase the simulated OA formation from refineries somewhat. However, the expected OA formation increase from refineries emissions will still remain minor compared to the respective OA formation increase from other sectors.

As an illustration of how SVOC and IVOC may contribute to organic aerosol levels over Europe, we included a simulation with enhanced organic carbon emissions from residential wood combustion (RWC). These enhanced RWC emissions lead to an increase of annual average simulated SOA and POA concentrations by 29% (from 0.42 to 0.54 µg m^{-3}) and 302% (from 0.10 to 0.40 µg m^{-3}), respectively.

For a selected period in February 2015, the model results demonstrate that enhanced S/IVOC emission from RWC lead to enhanced POA concentrations near the source, while SOA formation takes place over longer time scales and distances, resulting in a plume that spreads over a large area away from sources.

5. COMPARISON OF INDICATIVE S/IVOC EMISSION ESTIMATES USING VARIOUS METHODS

In chapters 3 and 4, it is explained that there is an important knowledge gap in terms of direct emission measurements for S/IVOC from refineries. In those chapters we discuss potential approaches to overcome this lack of data and develop recommendations on calculating primary emissions of S/IVOC (chapter 3) and its associated secondary aerosol formation (chapter 4). There are, however, other methodologies in the literature that can be used to make such estimates. Here we present these briefly and in the final section of this chapter, we put our estimates from chapter 3 and 4 in perspective. Note that these methodologies do not overcome the knowledge gap due to a lack of direct emission measurements for S/IVOC from refineries but it helps in putting various approaches and emission ranges in perspective.

5.1. THE PRIMARY ORGANIC AEROSOL DERIVATION METHOD

One way to estimate the SVOC and IVOC emissions from the reported total $PM_{2.5}$ emissions is to use the ratios first derived by Robinson et al. (2007) [74] for diesel exhaust. They assigned 1x the POA fraction of the emitted total PM mass from emission inventories to SVOC in their model, and added 1.5x the emitted POA as IVOC, resulting in a combined S/IVOC emission of 2.5 times the reported POA emission. These numbers have been applied in many modelling studies (e.g. Bergström et al., 2012 [3]; Fountoukis et al., 2011 [24]; Shrivastava et al., 2008) [75] to derive generic S/IVOC emissions, regardless of the source that they originate from. These number are rough approximations, and consequently alternative factors have been applied in modelling studies, with the aim of closing the model-measurement gap for organic aerosol. For instance, Tsimpidi et al. (2010) [80] applied 3x the reported POA emissions as SVOC, while Robinson et al. (2007) [74] defined a range of IVOC emissions between 1 and 3 times the POA emission.

To investigate what this approach would suggest for European refineries we make an indicative calculation while noting it may only provide order-of-magnitude accuracy due to large inherent uncertainties. Refineries reported a total of 3.2 kt PM_{10} emissions in 2015 to E-PRTR but a number of refineries are below the E-PRTR reporting threshold. If we take the 2015 values from the country reports to EMEP-CEIP the total PM_{10} for the refinery sector is about 4.3 kt PM_{10} /year. For our indicative calculation we use ~4 kt PM_{10}/year. As can be seen in **Section 3.1**, PM_{10} did not vary much in the years 2014-2017. Since there is no reported overall PM speciation for refineries available to us at this stage, we assume an organic PM fraction of 5%, as most of the refinery PM_{10} emission consists of other solid PM compounds, including catalyst material, sulphate, ash and elemental carbon. In this manner we estimate the POA emissions to be 200 t/year and hence SVOC and IVOC emissions of 200 t/year and 300 t/year respectively (using the relationship above) or a total S/IVOC emission of 500 t/year. it should be stressed that this number is highly uncertain, in the first place due to the extrapolation of a relationship assumed primarily for diesel combustion, to oil refineries. In addition, the organic fraction of PM emission is not known accurately and the calculation is highly sensitive to this organic fraction. There is the potential, therefore, for a large error in the S/IVOC estimates due to the uncertainty associated with the split between organic/inorganic composition of refinery PM emissions. It does, however, define an expected order of magnitude.

5.2. THE SOA-YIELD METHOD

Zhang et al. (2017) [89] estimated SOA formation from released NMVOC, for an integrated petroleum refinery – petrochemical complex in the Chinese Pearl River Delta. They tested three simple box model approaches to estimate SOA formation, the fractional aerosol coefficients (FAC) approach, secondary organic aerosol potential (SOAP) approach, and SOA yield approach. The authors concluded that the latter was the most suited for this particular case. This method assumes a specific SOA yield for different chemical species groups. These factors are given in **Table 8**. For example, 1,000 kg C9 straight chain alkane (nonane) released as NMVOC results in a calculated release of 1.2 kg SOA, whereas 1,000 kg C7 aromatics (toluene) results in 99 kg SOA.

Table 8 SOA yields (fraction) as derived from Gentner et al. (2012) [27] and used by Zhang et al. (2017) [89] in their “SOA yield method”

Carbon number	Straight-chain alkanes	Branched alkanes	Cycloalkanes	Aromatics
6	-	-	0.0004	0.17
7	-	-	0.0007	0.099
8	0.0006	0.0001		0.057
9	0.0012			0.092±0.068
10	0.0026			0.14±0.095
11	0.0053			
12	0.01			

NMVOC emissions from the refining area of the complex under consideration consisted mainly of C4 – C7 branched and linear alkanes and a little under 10% total aromatics. The measured NMVOCs and resulting SOA potential are shown in **Figure 12**, with on the x-axis of (a) the carbon number and on the y-axis the measured weight percentage per chemical group indicated. **Figure 12** (b) shows the resulting SOA formation (fraction of measured or emitted NMVOC mass), which is for the refinery in question around 1% of emitted NMVOC. Aromatics in the emitted NMVOC made by far the largest contribution to SOA formation. Note that due to a different chemical composition of the emitted NMVOC, the SOA formation potential of the petrochemical area of the complex was almost 5% of NMVOC. Also, the total estimated SOA contribution of the whole complex was primarily caused by the petrochemical (and not the refining) area.

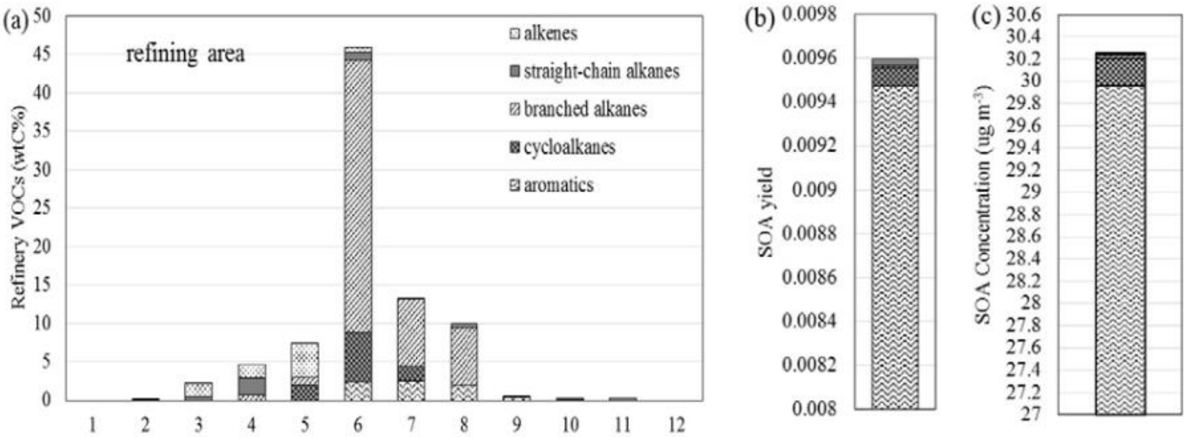

Figure 12 (a) Distributions of mass by chemical class in carbon number of different VOCs emissions; (b) calculated SOA yields based on C2-C12 VOCs measured in this study; (c) calculated SOA concentrations based on C2-C12 VOCs measured in this study (taken from Zhang et al. 2017) [89]

Based on the E-PRTR 2017 the average refinery in Europe may emit 1070 t/year NMVOC, which would result in a SOA mass of ~10 t/year. For all European refineries this would amount to ~ 1000 t/year. Again, as in the previous paragraph this number is highly uncertain but indicates an order of magnitude.

5.3. COMPARISON OF ESTIMATES BASED ON DIFFERENT METHODOLOGIES

The methods discussed in **Section 5.1** and **5.2** suggested an S/IVOC emission of 500 – 1000 t/year for all refineries in the EU(27)+. Given the high uncertainty in these calculated values, they provide only an order of magnitude estimate of actual S/IVOC emissions. These can be compared with the calculations in Chapter 3, where for an average refinery, an estimation of 1 (0.1 – 10) t/year has been made. Taking into account that there are about 100 refineries, that would imply an estimated emission of 100 (10-1000) t S/IVOC per year. This figure is considered our best estimate but the fact that estimates based on the crude methods used in the literature (**Section 5.1** and **5.2**) fall within the range builds confidence. While the range at first sight may seem unacceptably large it is important to realize that a) without representative measurements there is little possibility to be conclusive and, more important, b) this number can be used to put the S/IVOC emission of the refineries in perspective to other sources. For example the SVOC or condensable PM emission from wood burning in Europe is in the order of 500-1000 kt/year (Denier van der Gon et al., 2015) [11]. This is a factor of 1000 higher than the range in estimates shown here for refining in Europe.

6. CONCLUSIONS AND RECOMMENDATIONS

A large variety of organic compounds are emitted by anthropogenic and natural processes into the atmosphere, where they can form organic aerosols. Due to the complexity of this organic mixture, clear definitions are needed to describe the evolution of organic compounds in the atmosphere. The most common definitions use volatility as the main characteristic for grouping organic compounds, resulting in semi-volatile, intermediate volatile, and non-methane volatile organic compound classes.

Organic compounds are included in NMVOC and in PM emissions but the S/IVOC compounds may partly (or even largely) not belong in the NMVOC and/or PM category. The total reported NMVOC and PM_{10} emissions for the EU28 are fairly stable for the reported years 2015-2017. The contribution from refineries to these emissions is small: ~2% for NMVOC, ~0.15% for PM_{10}. There may be substantial uncertainty surrounding these estimates but the numbers clearly illustrate that even if they are uncertain, the contribution would probably remain small in the light of total European NMVOC or PM_{10} emissions. Refinery emissions are reported as part of the sector “Industry”. The main contribution to NMVOC emissions in Europe comes from the sector “Domestic and industrial solvent and product use”, whereas PM_{10} emissions are dominated by the sector “Residential, commercial, institutional and other stationary combustion”. Current emission inventories do not usually account for the semi-volatile nature of primary organic emissions nor provide emission estimates of IVOC. This holds also for refineries. PM_{10} emissions from refineries, and industry in general, include only the filterable fraction of PM_{10} and do not give an estimate for the S/IVOC emissions.

S/IVOC emissions from refineries have not been measured, but may be estimated using indicator substances. Substances such as PAHs can be used as indicators, and be combined with the ratio of indicator to total S/IVOC to obtain S/IVOC emissions. This yields indicative estimates of total S/IVOC emissions from EU refineries between 10 and 1000 t S/IVOC per year (compared to the E-PRTR reported 123 kt/year NMVOC and 3 kt/year PM_{10}). This is a relatively low figure compared to the total PM emissions and is explained by the fact that refinery PM emissions are mostly inorganic (which will have no associated S/IVOC emission).

Organic aerosol can be either formed directly from organic compounds that are emitted, in which case it is called primary organic aerosol, or after one or more generations of oxidation (secondary organic aerosol). The volatility basis-set (VBS) is the most widely used framework to account for the coupled dilution, ageing and gas/particle partitioning of organic compounds. The VBS scheme classifies organics using volatility, and takes into account enhanced gas-to-particle conversions in the course of chemical aging, i.e., the multiple steps of gas-phase oxidation by OH radicals that produce less volatile species. However, the VBS needs emissions over the complete range of volatilities. Such speciated emissions are generally not available from emission inventories and hence are based on assumptions that contain large uncertainties, related to volatility distributions of SVOC and IVOC, and to the amount of IVOC emissions. Additionally, the impact of ageing on S/IVOCs in the atmosphere is uncertain.

As a consequence of the large uncertainties in S/IVOC emissions and ageing, the modelled OA concentrations over Europe are uncertain as well. Despite recent improvements in source and process descriptions, most models underestimate OA levels compared to observations, and overestimate the observed SOA/POA ratio. Unfortunately, a thorough investigation of the causes for these model-measurement discrepancies is hindered by a lack of observational data in environments affected by different sources.

Model simulations with the atmospheric chemical and transport model LOTOS-EUROS suggest that emissions from refineries contribute only a minor fraction to SOA concentrations over Europe, which is in line with the low contribution of NMVOC emissions from refineries to the total NMVOC emissions over all sectors.

To show the potential of semi-volatile emissions to influence POA and SOA concentrations, we evaluated the contribution of residential wood combustion (RWC), a known strong source of SVOC emissions using the same set-up. This analysis showed that these emissions contribute strongly to POA concentrations close to source, while they had a lesser impact on SOA concentrations away from source regions, at least in winter.

The overall conclusions are:

- Refineries emit a small part of total organic carbon from anthropogenic sources over Europe;
- S/IVOC emissions can currently only be estimated indirectly, from indicator species or using crude, generic fractions applied to reported primary PM emissions. It should be noted that there are important reasons why this information is lacking which include:
    - ➢ Lack of good measurement techniques
    - ➢ No separate or uniform reporting guidelines for S/IVOC
    - ➢ Inability to apportion measured S/IVOC formed through atmospheric reactions to specific sources such as refineries.
- Based on currently available data the refinery contribution to SOA formation is very low.

Provided that the pertinent measurement techniques will be significantly improved in the near future, measurements S/IVOC concentrations, for example:

- at refinery fence lines;
- in stacks from combustion units and FCCU regenerators using a dilution-tunnel based method;
- of vaporous releases from hot, high molecular compound streams,

would fill some of the knowledge gaps and help reduce the uncertainties in estimating S/IVOC emissions from oil refineries.

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APPENDIX A - LAYMEN'S QUESTIONS AND ANSWERS

SVOC/OA/CPM Project – List of Layman's Questions

General

1) *What is the definition of particulate matter?*

Particulate Matter (PM) (also known as atmospheric aerosol) is a complex mixture of solid particles and liquid droplets suspended in the air. PM is made up of a number of components, including inorganic compounds (e.g., nitrates, sulphates), organic compounds, metals, as well as dust particles.

2) *What are the definitions of organic carbon, elemental carbon and black carbon, and are the last two essentially the same?*

Organic carbon is the fraction of PM that consists of chemically bound carbon, whereas elemental carbon is the fraction of PM consisting of elemental (non-bound) carbon. Black carbon is an optically defined parameter denoting the amount of light absorbing carbon. Elemental and black carbon are hence related but not the same.

CPM

1) *What's the difference between condensable PM and filterable PM?*

Put simply, filterable PM is what remains on a hot filter with filtering directly after sampling from inside a stack. When after sampling, the flue gas is diluted and cooled to ambient temperature, volatile material (vapours) in the flue gas may condense and form PM. Hence PM mass on a cold filter after dilution and cooling will be higher compared to what would remain on a hot filter. The difference is condensable PM.

2) *What are the main constituents of CPM? Are there inorganics as well as organics present?*

Depending on the source, mostly semi-volatile organic compounds and organic compounds with intermediate volatility (S/IVOCs), for instance with carbon numbers above 15 or when oxygenated above 8. CPM may contain many thousands of individual organic chemical species. In case the flue gas also has a high sulphur content, part of this sulphur may form sulphuric acid mist and solid particles consisting of metal sulphates. Results of impinger-based measurement methods are especially sensitive to sulphur, in some cases measuring pseudo (false) particulate instead of CPM.

3) *If there are both organics and inorganics in CPM, does the combustion source affect the ratio? Is there any other important factor that determines the CPM composition?*

Yes, the ratio will be determined by the fuel type and characteristics, oxygen supply, and combustion temperature.

4) *What's the difference between organic CPM and organic aerosol PM (in different size diameters, such as PM_1, $PM_{2.5}$, and PM_{10})?*

The main difference is that organic aerosol may also contain low- or non-volatile organic matter and CPM does not. Compare for instance a pollen particle and paraffin wax particle. Another difference is the fact that organic CPM is a primary species (i.e. it has not been subject to oxidation in the atmosphere), whereas organic aerosol PM can be both primary and secondary (i.e. formed after oxidation of high-volatility organic compounds). Both CPM and organic aerosol have particle sizes mostly below 1 µm. Biological organic particles are mostly larger than 1 µm.

5) *How do modellers derive organic CPM inventories?*

Deriving organic CPM emissions is a challenge for modellers, since organic CPM is not routinely included in emission inventories. Therefore, modellers need to make assumptions on the amount and volatility distribution of the emitted primary organic aerosol.

6) *What is the fate of inorganic CPM? Is it lost or transformed in the atmosphere?*

It will eventually be removed from the atmosphere by wet and dry deposition. If present inorganic compounds in CPM such as sulphates will, because of its acidity, make the CPM more hydrophilic and more susceptible to wet deposition.

7) *Do all CPM test methods give comparable results?*

Different methods exist to measure CPM on filters that differ in the dilution rate that is applied. This leads to differences in concentrations of CPM that are determined by the different methods, which complicates the compilation of an overall emission inventory for CPM.

POA

1) *What comprises POA?*

POA comprises all airborne organic matter in particulate (solid, liquid or semi-solid) form at atmospheric conditions. Important sources include diesel vehicles without diesel particulate filters (DPFs) and biomass burning. Also, emissions of biological particles like pollen, fungal spores and bacteria contribute to the atmospheric POA concentration. Soot consists of elemental carbon, and therefore is not part of POA.

2) *What's the difference between POA and non-volatile organic compounds? Can POA be volatile?*

POA is defined as the organic aerosol that has not been subject to chemical transformations. In the classic definition, it was assumed that all emitted primary organic carbon was non-volatile and inert. However, research since 2007 has shown that a part of this organic material actually evaporates after emission, and is therefore classified as semi-volatile. These evaporated organic vapours will then be subject to oxidation and contribute to SOA formation. Atmospheric conditions can vary, but under most temperatures and dilutions, compounds with a saturation vapour pressure of 0.1 µg m^{-3} or less are completely in the particle phase, and can thus be considered non-volatile. Non-volatile organic compounds can also be formed by oxidation of volatile organic compounds, but in that case they are part of SOA.

3) What is the fate of POA in the atmosphere?

Just like all PM species, POA is subject to transport and deposition. It is relatively inert, although particle-phase reactions can take place.

4) Does POA form part of SOA without transformation?

By definition, SOA consists of organic compounds that have been subject to atmospheric oxidation, as a result of which their volatility decreases, so POA does not form SOA without any transformation.

5) How are organic CPM distinguished from POA in the emissions inventories?

In the US, the EPA distinguishes the filterable and condensable fraction of particulate matter when emissions are estimated. In Europe this distinction was until recently not common and whether CPM was included or not depended on the measurement protocol and was not always well documented. Industrial emissions have long been reported without CPM included. Recently attempts have been made to ascertain that CPM is always included in PM emission estimates (for instance in updating the EEA emission inventory guidebook). Currently EMEP has agreed that industry PM emissions should continue to be reported solely as the filterable fraction.

In modelling studies that account for the semi-volatile nature of POA, a volatility distribution is applied to the POA emissions to yield SVOCs with different volatilities. Organic CPM are usually not included as a separate category in inventories.

IVOC/SVOC

1) *In what form are IVOCs and SVOCs emitted?*

This depends on the emission temperature. Under cold conditions the saturation pressure of both SVOCs and IVOCs is easily exceeded in the concentrated plume, so both will be primarily in particulate (liquid) form. Upon dilution and ageing IVOCs and part of SVOCs will evaporate again. After time, IVOC are almost completely in the gas-phase under atmospheric conditions but will rapidly form condensable species after one or more generations of oxidation. In hot stacks or plumes IVOCs and SVOCs will be both in gaseous form.

2) *What is the process by which organic compounds in vapour form become an aerosol and over what time period? How does volatility affect the transformation process?*

Organic compounds in vapour form will form aerosol by condensation (absorptive partitioning) onto existing organic aerosol. This process of gas-particle partitioning occurs almost instantaneously (a few seconds) for liquid particles, while for semi-solid or solid particles it can take longer because partitioning is limited by diffusion processes. It is thus the phase of the existing organic aerosol that determines the time scales of gas-particle equilibration.

3) *How are IVOC and SVOC inventories derived?*

Consistent and cross-sectoral emission inventories based on statistical data and emission factors like there are for SO_2 or NH_3, do not exist (yet) for S/IVOCs. There are only some emission estimates for specific sources or regions. In modelling, S/IVOC emissions are derived from estimated POA emissions by distributing the emitted POA over a range of volatilities, usually with a saturation concentration between 0.1 and 100 µg m^{-3}. This means that at the lower end of this volatility range, a large part of the POA will stay in the particle phase, while a significant part of the POA at the high end of the volatility range will evaporate. Since IVOCs are usually not included in the estimated POA emissions, some rather crude assumptions need to be made on their emission. Most regional and global modelling studies assume that the amount of emitted IVOC is between 1 and 3 times the amount of emitted POA, which shows that the uncertainties are large. The factor 1 to 3 is derived from laboratory studies on diesel exhaust but is liberally applied by modellers to other sources as well. This adds further to the uncertainties, as CPM over POA ratios may be very different for specific refinery sources. The saturation concentrations over which the IVOC emissions are distributed range between 10^3-10^6 µg m^{-3}.

4) *If derived from reported VOC inventories, are there different factors used for different sources and/or sectors?*

S/IVOCs are never part of reported VOC emissions as they are not volatile enough to be considered VOC. In S/IVOC modelling, over the years, different factors for the volatility distribution of SVOC and IVOC emissions have been derived from laboratory experiments. These include distributions for gasoline, diesel and biomass burning emissions. Note that these emissions are based on the estimated primary organic part of the PM inventory, not on the NMVOC inventory (with few exceptions).

5) *How much of the IVOC and SVOC inventories will eventually become SOA?*

How much of the SVOC and IVOC eventually forms SOA is strongly dependent on atmospheric processing. Model studies suggest that only a minor part (10-20%) of the emitted SVOC and IVOC forms SOA after a couple of hours of atmospheric processing, with the major part staying in the vapour phase. Multiple days of atmospheric ageing may lead to more SOA formation from a given quantity of emitted S/IVOC.

6) *Are there any other volatility-based VOCs which are important in terms of emissions, SOA formation, etc.?*

In addition to the classes VOC, IVOC and SVOC that are used to classify groups of compounds within a defined range of volatility (in descending order of volatility), classes of compounds with even lower saturation concentrations are found in atmospheric organics. Two classes that contain compounds of low volatility organic compounds (LVOC; saturation concentration between $1x10^{-3}$ and 0.1 µg m^{-3}) and extremely low volatility organic compound (ELVOC; saturation concentration below $1x10^{-4}$ µg m^{-3}) can be added to the lower end of this volatility range. LVOCs are in the particle phase under all but the most extreme atmospheric conditions, while all ELVOC are in the particle phase. LVOC and ELVOC are directly emitted from fossil fuel combustion, and are formed from oxidation of biogenic and anthropogenic VOCs. They can contribute significantly to the atmospheric SOA burden and play an important role in the formation of new particles through nucleation.

7) *What are the contributions to POA and SOA of biogenic OC relative to man-made OC?*

The contribution of biogenic versus anthropogenic SOA has been an ongoing subject of debate in the organic aerosol community. For instance, isoprene, which is the globally most abundant biogenic VOC, was not considered to significantly form SOA for a long time. However, research over the past 15 years has revealed previously unknown formation pathways of isoprene SOA. For POA the situation is clearer: apart from the contribution of primary biological particles (pollen, fungal spores, etc.) to the coarse POA burden, the contribution of biogenic sources to POA is limited. Wildfires and biomass burning do contribute significantly to POA concentrations, but a distinction between purely natural and man-made fires is hard to make.

8) *Are biogenic and man-made OCs transformed into SOA to the same extent?*

There are many biogenic and anthropogenic SOA precursors, and the variety in SOA formation potential between precursors is large. Moreover, the SOA yield of a particular precursor VOC depends on concentrations of other species as well, such as NOx and sulphate. As for the influence of NOx-concentrations, anthropogenic VOCs will often be associated with high-NOx conditions, while biogenic VOCs are usually emitted in low-NOx environments. For most VOCs, low-NOx yields are higher than high-NOx-yields, which means that biogenic VOCs will often have yields at the higher end of the spectrum for that particular VOC, while for anthropogenic VOCs yields will usually be at the lower end of the spectrum.

SOA

1) *What are the relative contributions of i) POA and ii) aerosols formed by OCs emitted in vapour form to SOA?*

A comparison of global organic aerosol models suggested that the median POA production (56 Mt/year) is about equal to the median SOA production (51 Mt/year) for models that account for the semi-volatile nature of primary emissions. However, there are strong regional differences: in regions that are dominated by anthropogenic emissions and/or biomass burning (e.g. cities), the POA contribution will be much higher than in biogenically-dominated regions (e.g. forests).

2) *What is the effect of temperature/time on SOA formation?*

The volatility of the organic vapours which form SOA is temperature-dependent: at higher temperatures, they will be more volatile. This means for instance that higher in the atmosphere where it is colder, a larger fraction of the SVOC will partition to the particle phase than near the land surface. Also, in winter, the POA fraction is generally larger than in summer, because a smaller portion of the SVOC will evaporate after emission. Further, emissions are also temperature-dependent, which affects SOA formation as well: for instance, residential heating emissions are higher at cold temperatures, while biogenic emissions are higher at warm temperatures.

Time-scales in SOA formation are an active topic of research. As already mentioned in response to S/IVOC question 2, the phase of the existing particles onto which the organic vapours partition, determines the time it takes to reach gas-particle equilibrium. The particle phase depends, among others, on the ambient temperature and humidity. As a rule of thumb, it can be said that particles are predominantly liquid in the tropics and in humid polar air, semi-solid in mid-latitudes and solid in dry regions.

APPENDIX B - BACKGROUND DATA REFINERY EMISSIONS

The current study investigates the emissions of S/IVOC but due to a lack of data on these substances we are interested in the NMVOC and PM emissions as these have been used in the literature to derive approximated S/IVOC emissions. Moreover the (reported) emission data may give an indication on existing differences between refineries and the challenges for generalisation.

Emissions of NMVOC from refineries vary between 50 and 10,400 t/year with an average 1070 t/year. The emissions are lognormal distributed **(Figure B.1)**.

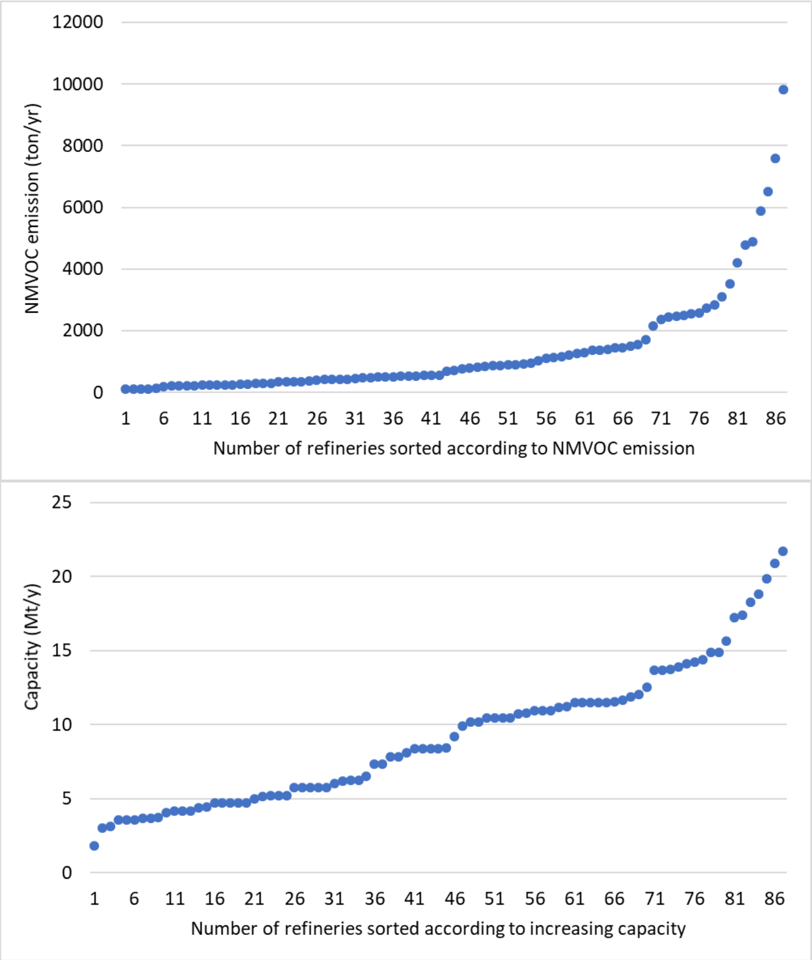

Figure B.1 NMVOC emissions of refineries sorted by increasing emission (top) and by increasing capacity (bottom) (x-axis numbers do not correspond; refinery capacities have been taken from OGJ data)

This variation is not surprising as the capacity of the refineries is also highly variable (**Figure B.1**) and the type of refinery may be quite different. Nevertheless, these data give some insight in variation that is most likely also indicative for the variation in S/IVOC emissions. Note that most refineries have PM emissions below the reporting threshold, so the above figure could not be made for PM.

When we plot the NMVOC emissions as a function of capacity **(Figure B.2)** it can be seen that there is a poor relationship and predictability of NMVOC emissions based on capacity. For PM_{10} it looks slightly better but still a poor predictability.

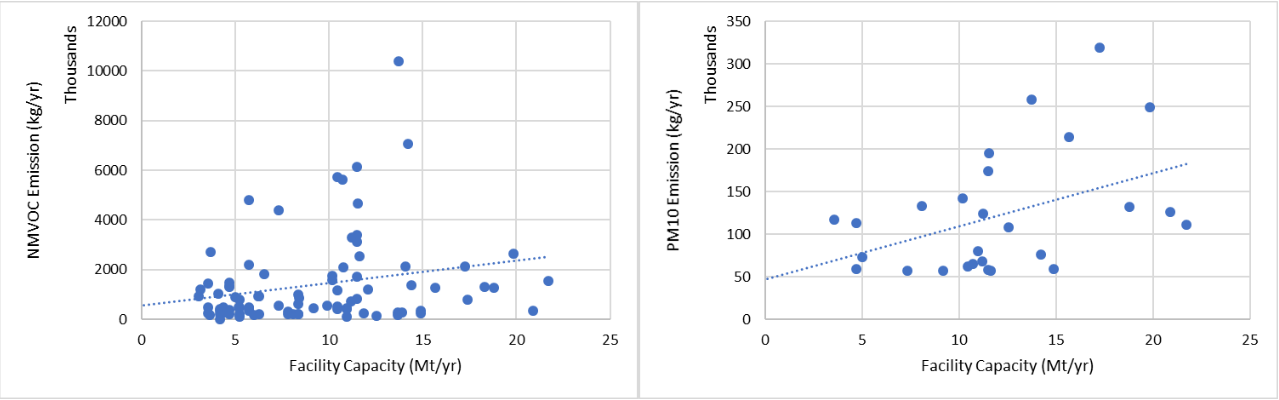

Figure B.2 NMVOC (left) and PM_{10} (right) as a function of capacity

These data are only shown here to illustrate that generalisation of S/IVOC emissions for European refineries is, like NMVOC emission, not expected to be easy (if feasible at all) based on publicly available data.

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