# Cross-cutting WG TFMM-TFEIP on SVOC emissions

**Working document for the workshop on Condensables & Semi-Volatile Organic Compounds**

LRTAP
Long-range Transboundary Air Pollution

# Organic matter in the atmosphere

➢ Organic matter (OM) represents 20 to 30% of the particulate matter in Europe, this fraction is dominated by the secondary organic fraction produced by chemical reactions of organic precursors (Freutel et al., 2013, Crippa et al., 2013)

➢ For primary species, in 2013, 50.5% of the primary PM2.5 emissions were attributed to the residential sector in the EEA-33 regions, road transport represents the second emitting macro sector with 16.1%.

➢ Wood burning combustion represents the main source of the residential sector

➢ Road traffic emissions is an important contributor of organic matter in urban areas

➢ Actually, all activity sectors with combustion processes emit particulate organic matter

# Why this working group?

➢ Official primary PM emissions decrease (e. g. use of filtering techniques for the case of diesel vehicles, improvement of efficiency of wood stoves, etc…)

➢ Air quality models usually underestimate PM, and the lack of some emissions is considered as one of the explanations (particularly in winter due to wood burning)

➢ The secondary fraction and/or the organic fraction are underestimated by models

➢ In smog chambers, the aging of diesel *vs* gasoline exhausts show the importance of SOA formation. In some experiments, gasoline vehicles produce more aerosols than diesel vehicles after several hours in the chambers → role of VOC and SVOC

➢ **Semi volatile Organic Compounds (SVOC) (also called condensables) are partly included in emission inventories**

  ▪ How to complement these emissions inventories?

# SVOC in emission inventories

➢ So far, only VOC is reported in emission inventories, a fraction of SVOC is certainly included in the PM emissions:

- Modellers do their own emission to feed their model with SVOC with very poor data

➢ A bit of history:

- NOx was reported because of its role on acidification and **Ozone** formation (Sofia Protocol & Gothenburg Protocol)

  then

- SVOCs should be known, isolated in the future as they are precursors of **PM**

➤ Models are used in the frame of the Convention to:

- provide an integrated view of the pollution patterns, complement the monitoring & assessment strategy based on measurements and emissions inventories

- evaluate the impact of an emission reduction (source matrix receptor) that is a fundamental basis for the integrated assessment (IA)

| **Emissions** EMEP & Other sources | → | CTMs SR matrix **EMEP** | → | IA **GAINS** |
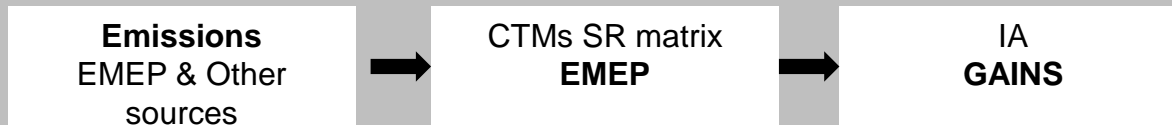
# Concept of SVOC - I

➢ All organic species are more or less volatile and can be considered as semi-volatile, their vapour pressure is the key parameter to define the volatility.

➢ The temperature and the organic aerosol loading (the total mass of organic species into which semi-volatile species can condense) influence the partitioning between the gas and particle phases.

➢ VOCs represent the most volatile fraction of organic species.

➢ The heaviest organic molecules (in term of molecular weight) can be considered to be entirely in the particulate phase, they constitute what is commonly called organic matter.

➢ In between, there is a large spectrum of molecules that are partitioned between the gas and particle phases, they are called in a broad sense SVOC (semi-volatile organic compounds).

# Concept of SVOC - II

- ➢ Organic species can be split in:
  - • ELVOC (Extremely low Volatile Organic Compounds)
  - • LVOC (Low Volatile Organic Compounds)
  - • SVOC (Semi Volatile Organic Compounds)
  - • IVOC (Intermediate Volatility Organic Compounds)
  - • VOC (Volatile Organic Compounds)

  SVOC in a broad sense
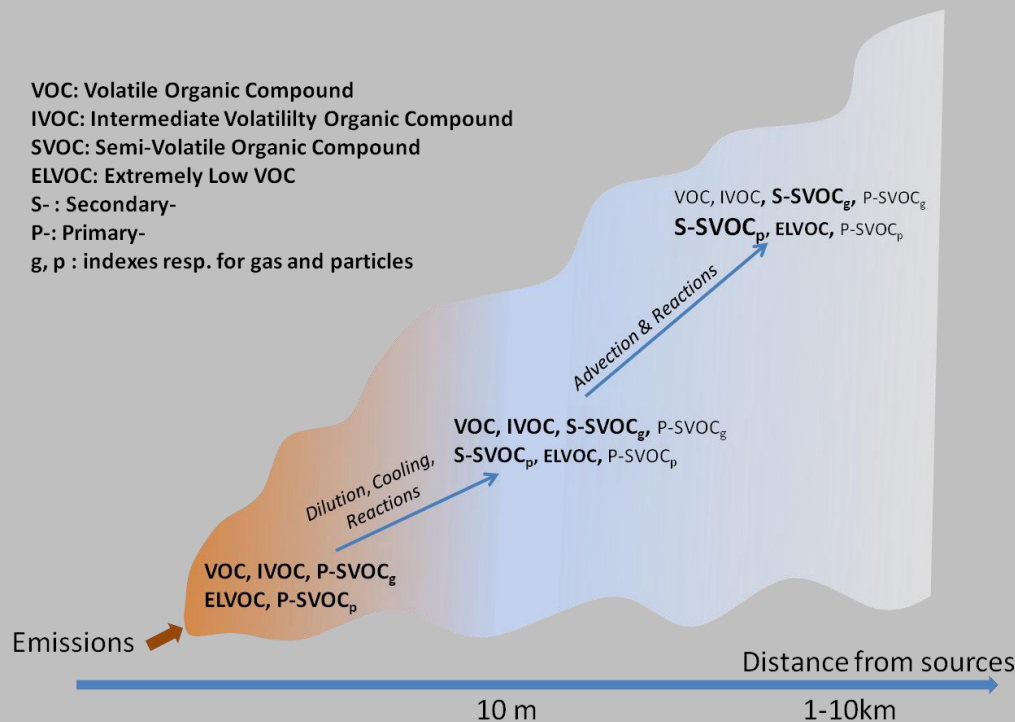
  POA (Primary Organic Aerosol) in gas and particle phases

- ➢ These categories can be delimited by vapour pressure thresholds

- ➢ This delimitation is arbitrary, the Gas/Particle partitioning can change with the temperature and the level of concentrations

- ➢ Chemistry transport models host secondary organic aerosol modules able to produce secondary organic aerosol from gas phase organic species

➢ Air quality models have chemistry modules to account for the VOC and SVOC chemistry

➢ Some simple considerations:

- Dilution of SVOC leads to evaporation
- Decrease of T° leads to condensation/absorption of SVOC
- Oxidation reactions lead to the formation of bigger molecules

VOC: Volatile Organic Compound
IVOC: Intermediate Volatililty Organic Compound
SVOC: Semi-Volatile Organic Compound
ELVOC: Extremely Low VOC
S- : Secondary-
P-: Primary-
g, p : indexes resp. for gas and particles

VOC, IVOC, **S-SVOC$_g$**, P-SVOC$_g$
**S-SVOC$_p$, ELVOC,** P-SVOC$_p$

*Advection & Reactions*

**VOC, IVOC, S-SVOC$_g$,** P-SVOC$_g$
**S-SVOC$_p$, ELVOC,** P-SVOC$_p$

*Dilution, Cooling, Reactions*

**VOC, IVOC, P-SVOC$_g$**
**ELVOC, P-SVOC$_p$**

Emissions

Distance from sources

10 m          1-10km

*NB: A sub category LVOC can be added between ELVOC and SVOC for low volatile organic compounds*

# Evolution of SVOCs in the atmosphere

**In the dilution sampler**
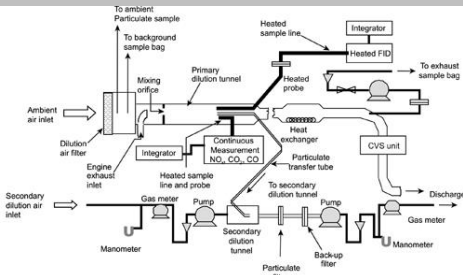
**In the atmosphere**
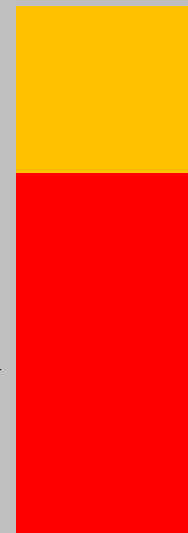


INERIS dilution system for
Wood stove / Fireplaces

Gas

Particle

Fast dilution and
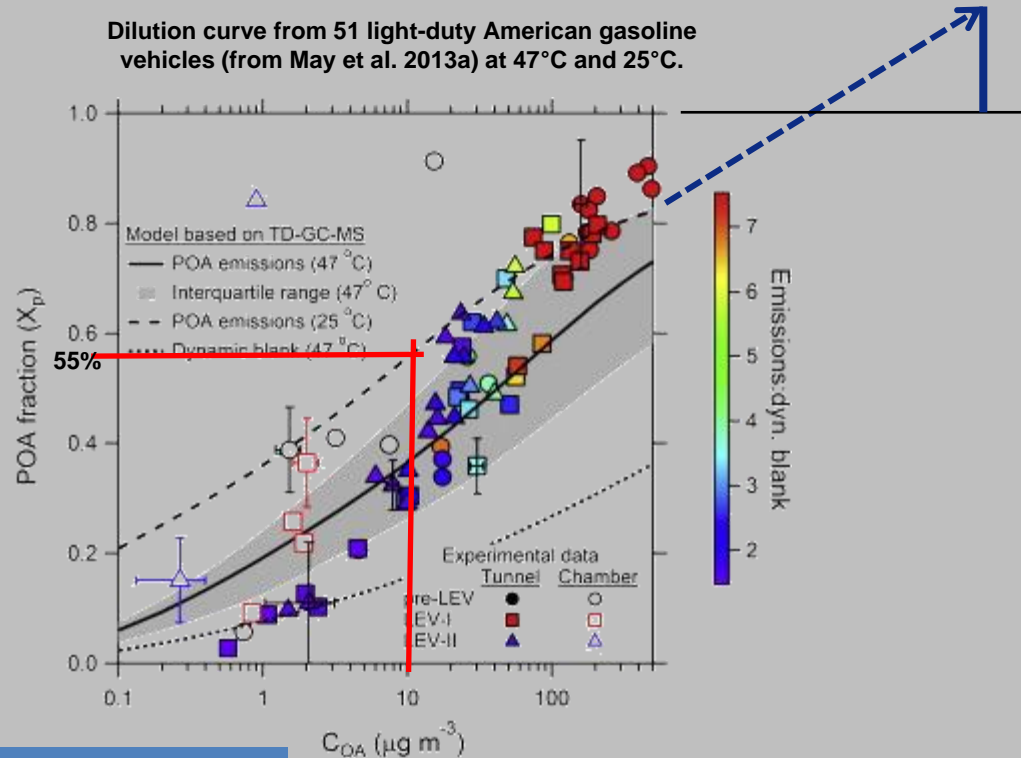cooling in the
atmosphere

Atmospheric
reactions –SOA
formation

# Until now, how do modellers manage SVOC emissions?

➢ So far, emission inventories are targeted on VOC, NOx, SOx, NH3, CO and PM broken down into PM2.5 and PM10

➢ A speciation is often proposed to identify the organic matter in each PM fraction
  • EC / OM / Other
  • OM is organic matter supposed as particulate matter at the emission
  • "other" means non carbonaceous species (dust, inorganics, etc…)

➢ Modellers do their own calculation of **total primary organic aerosol (gas + particles)** emitted by a given sector with coefficients based on dilution curves reported in the literature.
  • TPOA= 2 * OM  (as an example)
  • IVOC can be considered as not included in TPOA then IVOC is estimated from TPOA or VOC emission factors (Ots et al., 2016)

Not consistent !!
Certainly different operating conditions

- At $C_{oa}$=10 µg/m³ and 25°C, about 55% is in the particle phase
  - If you measure solid POA, you have to multiply 1/0.55~2 to get the total organic fraction (Gas+Particles)

- If we could measure higher $C_{oa}$ we could take into account missing SVOC (the so called IVOC)

Dilution curve from 51 light-duty American gasoline vehicles (from May et al. 2013a) at 47°C and 25°C.

➤ **What are the level of PM concentrations and temperatures in the CVS sampling system:**

- Diesel vehicle (without Particulate filter) : $1.10^2$ - $6.10^3$ µg/m³
- Petrol or Diesel vehicle (with Particulate filter) : $4.10^1$ - $1.5.10^3$ µg/m³
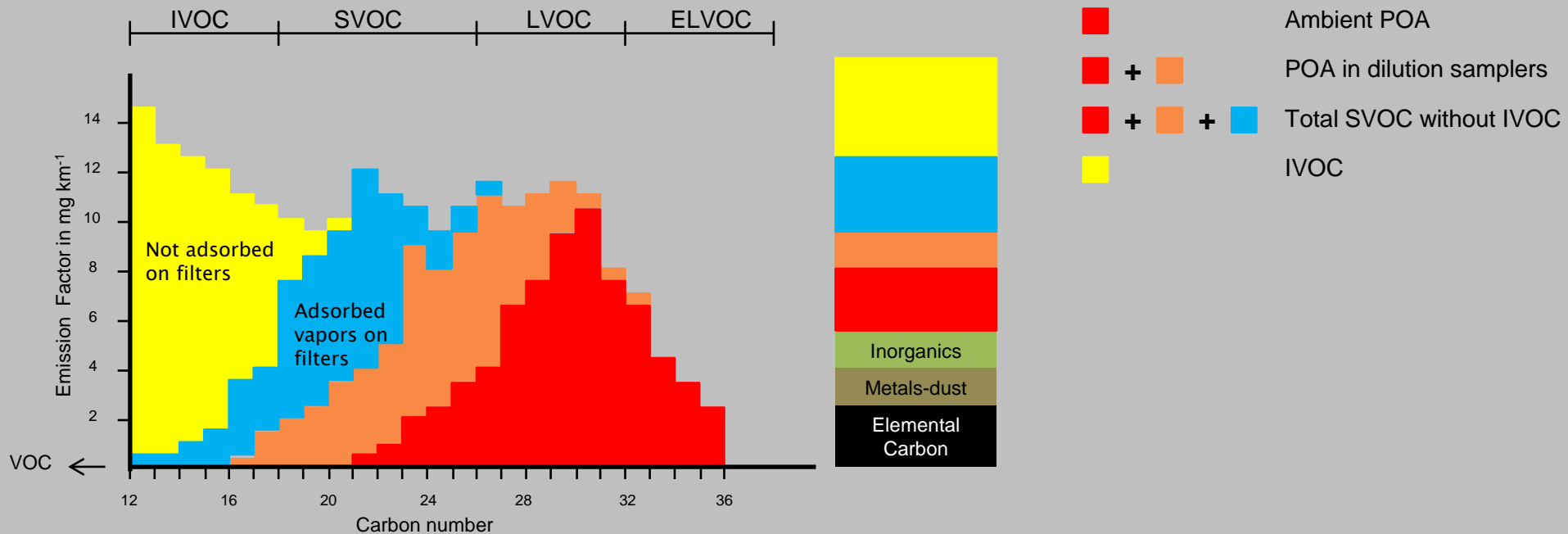- Temperature : 36°C

➤ **Determination of Xp:**
- Diesel vehicle (without Particulate filter) : **70-95%**
- Petrol or Diesel vehicle (with Particulate filter)  : **50-90%**

**Total POA (including all SVOC) could be 2 times that is measured**



May et al, 2013
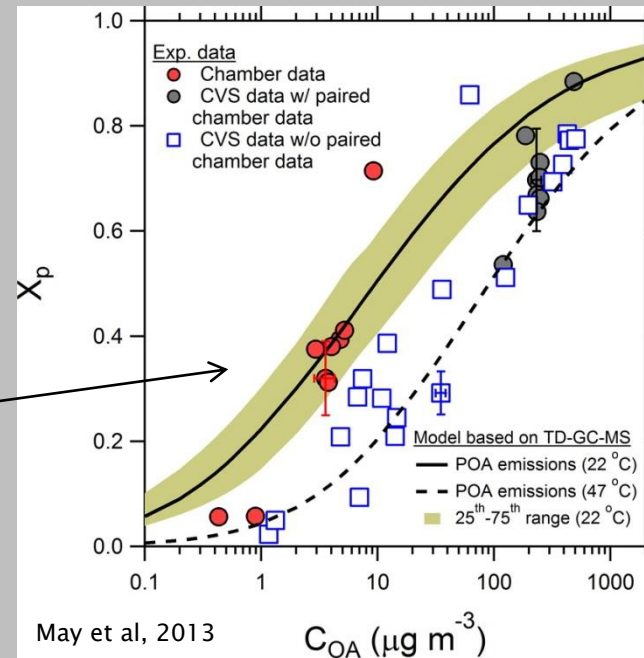
# PM measurements – focus on the organic fraction



*Adapted from Robinson et al. (2010)*

➢ **For a good assessment we need to identify** ■ + ■ + ■ + ■

In the dilution sampler

➢ The coefficients used for this estimation are based on very few publications (dilution curves) and sometimes old coefficients

➢ We don't have any clues about the operating conditions (T° and PM load) of the EF measurements

➢ The two previous informations are certainly not consistent!

?

SVOC

PM

Inorganics

Dust

Elemental Carbon
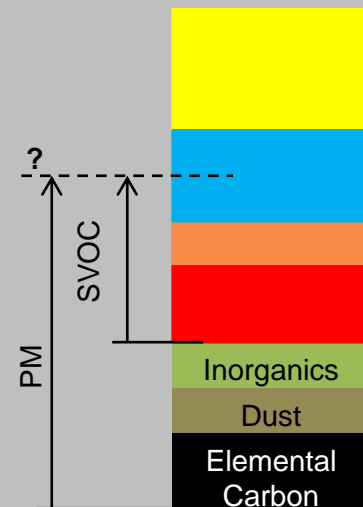
# How to proceed now to identify SVOC for a better air pollution assessment ?

**OPTION I**

➢ PM including SVOC will be determined with (by activity sector):

- A split by components : OM, EC, other (minimum requirement)
- A split by volatility for OM (including SVOC), for each of volatility classes a split by species will be provided

➢ VOC

- Improvement of the VOC split including IVOC

**Impact**:
Automatically, increase the total emissions by country

# Two options for the future (10 years)

**OPTION II**

➢ PM without OM should be known

➢ OM including SVOC will be determined separately
  - A split by volatility for OM (including SVOC), for each of volatility class a split by species will be provided

➢ VOC
  - Improvement of the VOC split

➢ IVOC will be determined separately with a split by species

# Short term actions (2 years)

➤ A "a minima" method would consist in reconstructing the total organic matter emissions in the gas and particle phases. This can be done in several steps:

1. Speciation of PM emissions by SNAPs (level 1 to 3) to separate POA emissions from other compounds, POA being the extremely low volatile compounds (ELVOC) called PCOA here and primary semi volatile organic compounds in the particle phase (primary SVOCp).

2. Estimate the total (gas+particles) primary semi volatile organic compounds emissions from POA emissions and IVOC from VOC

3. Split of total primary semi volatile organic compounds in the gas and aerosol phases on volatility bins by SNAPs (from literature or new experiments) to provide information on how SVOC partition as a function of Temperature and Organic mass load. This split would allow determining ELVOC, LVOC, SVOC according to the convention define by Donahue et al. (2012).

4. Information on how organic compound emissions can evolve with the evolution of the vehicle fleet to manage future emission inventories in order to address emission projections

# Short term actions (2 years) - concretely

➢ The modeling community needs a common "OM/EC/Other" split for emitted PM by activity sector and subsector and by country. **For a good assessment , we need to know what represent OM in this split, what were the experimental conditions: Temperature and PM load in the sampler.**

➢ For the two main PM emitters (traffic and wood burning) we need to know at least by country the **method** used to estimate the PM emission factors and :

- **temperature in the device (dilution tunnel)**
- **PM load (in μg/m3 ) in the device**
- **These two parameters have to be determined by sub SNAP and fuel (diesel, gasoline, Euro1-6 for vehicles)**

➢ We also have to know the composition of the car fleet by country for the vehicle emissions (diesel, gasoline, Euro1-6)

# Long term actions (10 years)

➤ The "idealistic" method would consist in an inventory providing **directly OM emissions including SVOC by volatility bins** at a reference temperature (with recommended values of enthalpies of vaporization by SNAP to take into account the dependency to temperature) from non-volatile compounds to compounds with a volatility close to dodecane.

➤ These emissions by volatility bins could come from an analytic system providing directly emissions for each volatility bins or an analytic system providing total OM emissions and the corresponding dilution curves.

➤ All activity sectors should be addressed

➤ **Certainly research actions are required to define new experimental protocols**