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TREATMENT OF SEMIVOLATILE PROPERTIES OF PRIMARY ORGANIC AEROSOLS AND IMPACT ON SOA FORMATION

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Volatility distribution of SVOC

Primary organic aerosols (POA) are often assumed to be nonvolatile by the regional models but organic compounds are semivolatile and part of POA should volatilize and go the gas-phase.

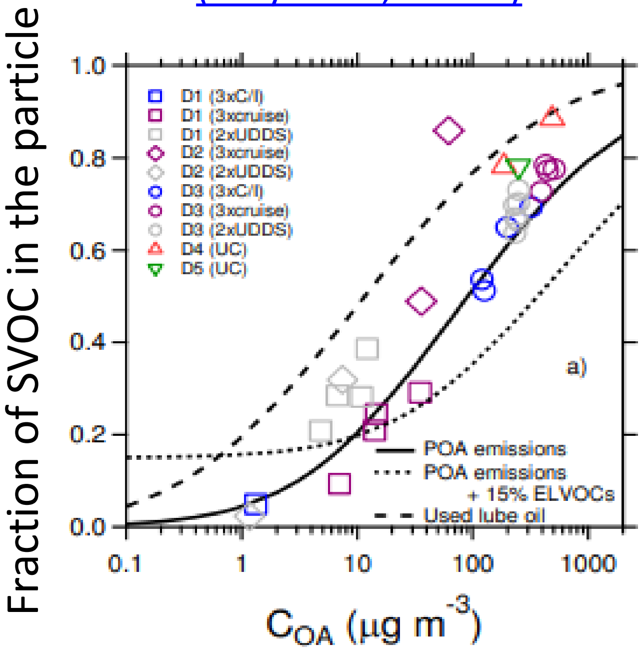
POA can be split by volatility according to a Volatility Basis Set (VBS) approach using dilution curves

POA from different sources can have different volatility profile:

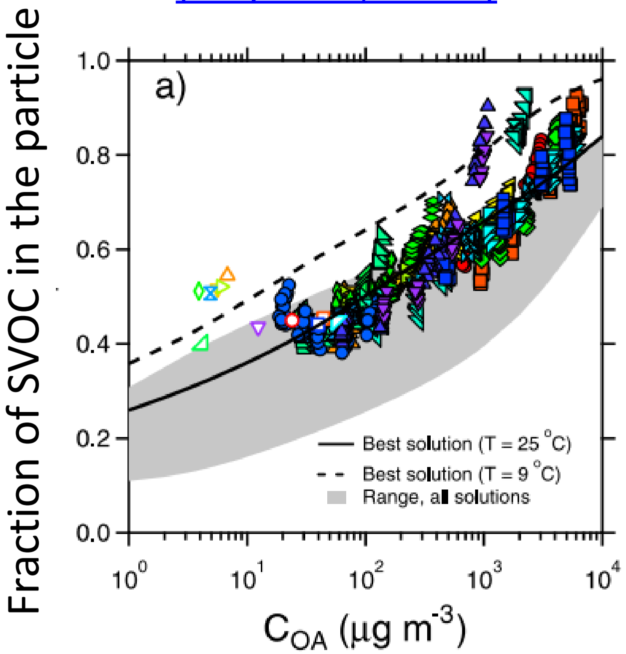
- For diesel vehicles, at 298 K, only a few percents of SVOC in the particle at 1 μg/m³
- For residential wood, around 25% of SVOC in the particle under the same conditions

Example of dilution curves reported in the literature

[Diesel vehicles (May et al., 2013b)]



[Residential Wood Burning (May et al., 2013c)]



Aging mechanisms

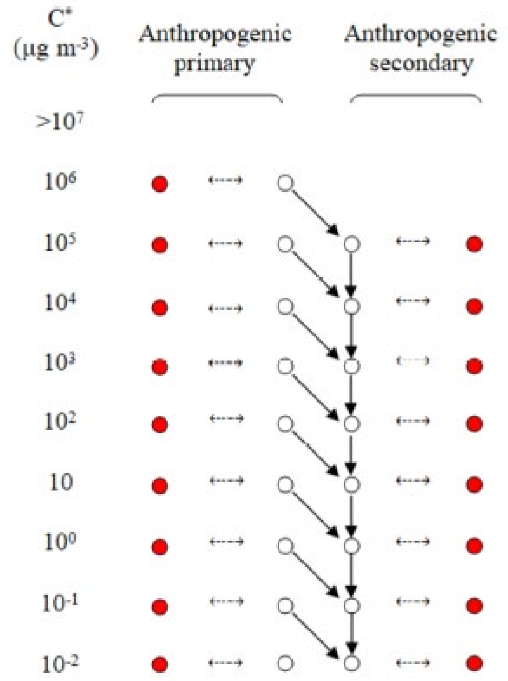
An aging mechanism need to be implemented to represent the oxydation of gas-phase SVOC and the formation of SOA

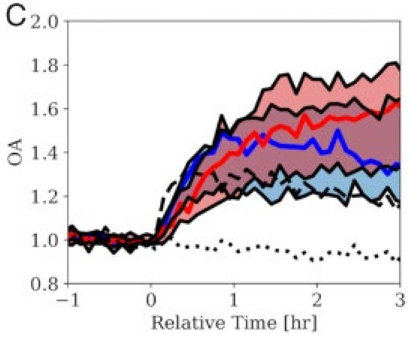
Two commonly used VBS approach:

- **AGING A : Stantard VBS.** Decrease of volatility by **a factor 10**, increase of mass of 7.5% (correspond to the formation of a ketone) with a kinetic of aging of **4×10^{-11} cm^3 $molecules^{-1}$ s^{-1}**
- **AGING B :** Decrease of volatility by a factor 100, increase of mass of 40% (Grieshop et al., 2009) kinetic of aging: **2×10^{-11} cm^3 $molecules^{-1}$ s^{-1}**

Additionnaly, Kodros et al. (2020) propose to consider the nightime oxidation of gas-phase SVOC from RWB

Illustration of AGING A





Chamber experiment. Evolution of OA from wood burning in presence of NO_2, O_3 (and therefore NO_3)

« Simulations that include this understanding of dark chemical processing show that over 70% of organic aerosol from biomass burning is substantially influenced by dark oxidation.”

Use of the kinetic of cresol with NO_3: $k=1.4 \times 10^{-11}$ cm^3 $molecules^{-1}$ s^{-1}

Objectives of the task

Objectives :

- Determine the importance of SVOC treatment on model results with an intercomparison of 4 models: **CHIMERE, DEHM, EMEP and MATCH**
- Propose a common methodology to represent SVOC in the CAMS models

<table>
<tr><td></td><td></td><td colspan="5">Used volatility profile</td></tr>
<tr><td rowspan="4">Volatility distribution</td><td>Wood</td><td rowspan="4">non volatile</td><td rowspan="4">Robinson et al. (2007)</td><td rowspan="4">Robinson et al. (2007)</td><td>May et al. (2013c)</td><td>May et al. (2013c)</td></tr>
<tr><td>Diesel</td><td>May et al. (2013b)</td><td>May et al. (2013b)</td></tr>
<tr><td>Gasoline</td><td>May et al. (2013a)</td><td>May et al. (2013a)</td></tr>
<tr><td>Shipping</td><td>Huang et al. (2018)</td><td>Huang et al. (2018)</td></tr>
<tr><td colspan="2">Aging mechanism</td><td>No aging</td><td>AGING A</td><td>AGING B</td><td>AGING A</td><td>AGING A + oxidation by NO_3</td></tr>
</table>

- Simulation of year 2019, ideally with CAMS-REG-TEMPO and CAMS-REG REF2v6.1

EVALUATION

Comparison to the ACSM data over Europe (around 30 stations)

CHIMERE delivered PM1

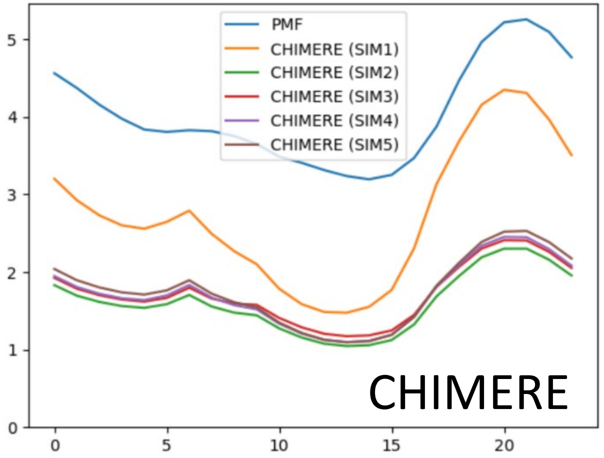
Other models delivered PM2.5

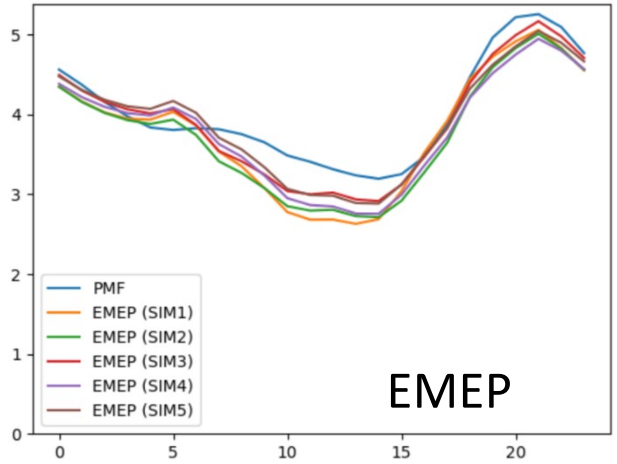
Comparison to PMF results (harmonized database from RI-URBANS):

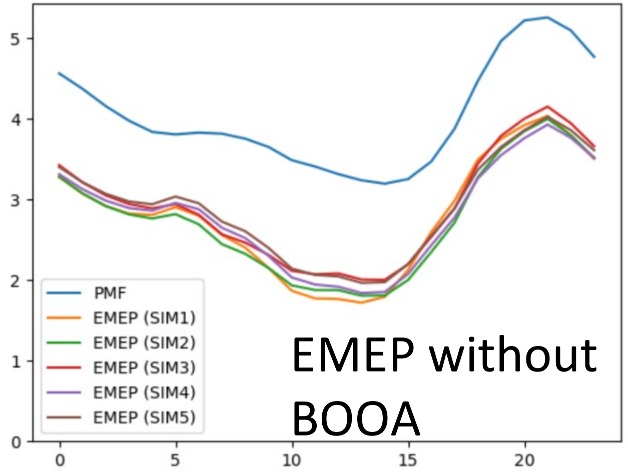
- BBOA: Biomass Burning Organic Aerosol (assumed to correspond to POA from RWB)
- HOA: hydrocarbon-like organic aerosol (assume to correspond other POA)
- OOA: oxidized organic aerosol (assumed to correspond to secondary organic aerosol)

Station Name	Station ID	Country	Latitude	Longitude	Station Type
Athens-Demokritos	DEM	Greece	37.995	23.816	Urban Background
Athens-Thissio	NOA	Greece	37.98	23.7	Urban Background
Barcelona	BCN-PR	Spain	41.3875	2.118	Urban Background
Birkenes	BIR	Norway	58.383	8.25	Regional Background
Magurele-Bucharest	INO	Romania	44.348	26.029	Suburban
Carnsore Point	CRP	Ireland	52.19	-6.34	Regional Background
Dublin	DUB	Ireland	53.3083611	-6.2235555	Urban Background
Helsinki	HEL	Finland	60.1964389	24.9519805	Traffic
Hohenpeißenberg	HPB	Germany	47.8013889	11.009722	Regional Background
Hyytiala	SMR	Finland	61.85	24.28333	Rural
Kosetice	KOS	Czech Republic	49.6	15.12	Regional Background
Krakow	KRK	Poland	50.0666667	19.91666	Suburban
ATOLL-Lille	ATOLL	France	50.611	3.1403	Suburban
London-Marylebone	LON-MR	United Kingdom	51.52	-0.15	Traffic
London-North Kensington	LON-NK	United Kingdom	51.5	-0.2	Urban Background
Marseille Longchamps	MAR-LCP	France	43.3052333	5.39469	Urban Background
Melpitz	MEL	Germany	51.9	13.55	Rural
Nicosia	CAO-NIC	Cyprus	35.1407755	33.3805388	Urban Background
SIRTA-Paris	SIRTA	France	48.71	2.15	Suburban
Tartu	TAR	Estonia	58.3705556	26.7347222	Urban Background
Zurich	ZUR	Switzerland	47.3775556	8.5305	Urban Background
Gennevilliers	GEN	France	48.9298083	2.2946194	Urban Background
Paris Les Halles	HALL	France	48.8627083	2.3446972	Urban Background
Paris BPEst	BPEst	France	48.8385167	2.4126242	Trafic
Rennes	REN	France	48.08965	-1.65911	Urban Background
Metz	MET	France	49.1102806	6.2233361	Urban Background
Strasbourg	STR	France	48.5062222	7.7511806	Urban Background
Creil	CRL	France	49.2597222	2.4744444	Urban Background
Lyon	LYN	France	45.75779	4.85422	Urban Background
Poitiers	POI	France	46.5839885	0.3455967	Urban Background
Talence	TAL	France	44.800442	-0.5893941	Urban Background

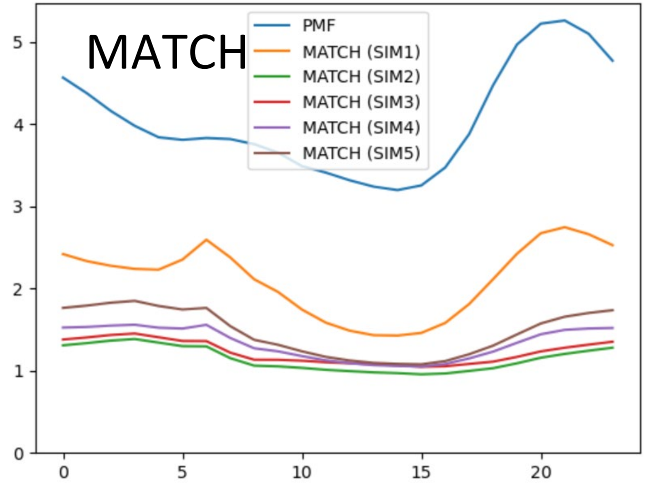
Comparison of annual average diurnal cycles

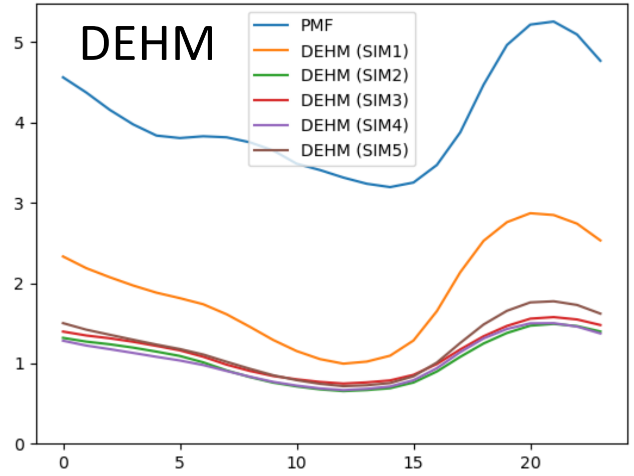






SIM1 similar between EMEP and CHIMERE especially when BOOA (Organic aerosol coming from boundary conditions) is not taken into account

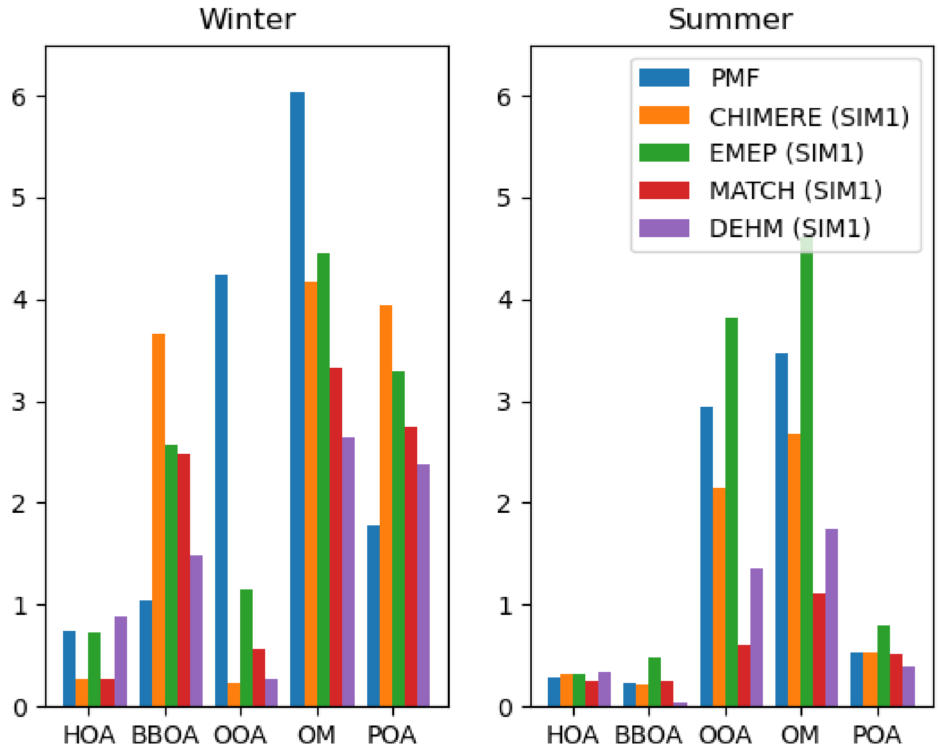




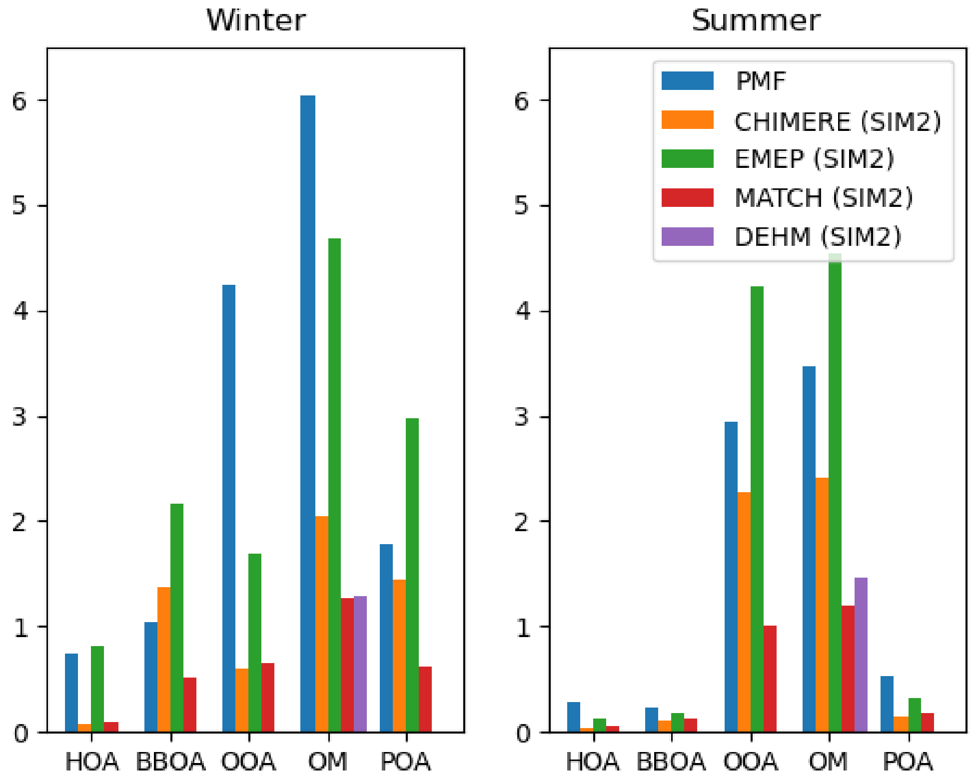
High differences between SIM2 and SIM1 simulated with CHIMERE, MATCH and DEHM but not with EMEP

Comparison to PMF

Nonvolalite POA



Semivolalite POA

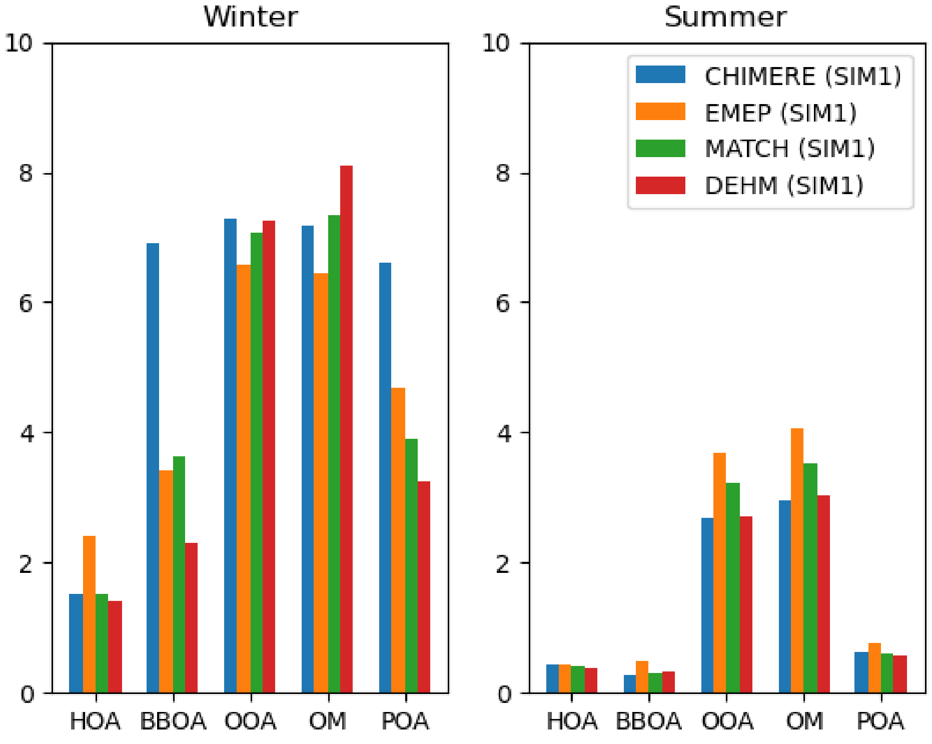


Similar HOA between EMEP and MATCH but higher with EMEP and DEHM

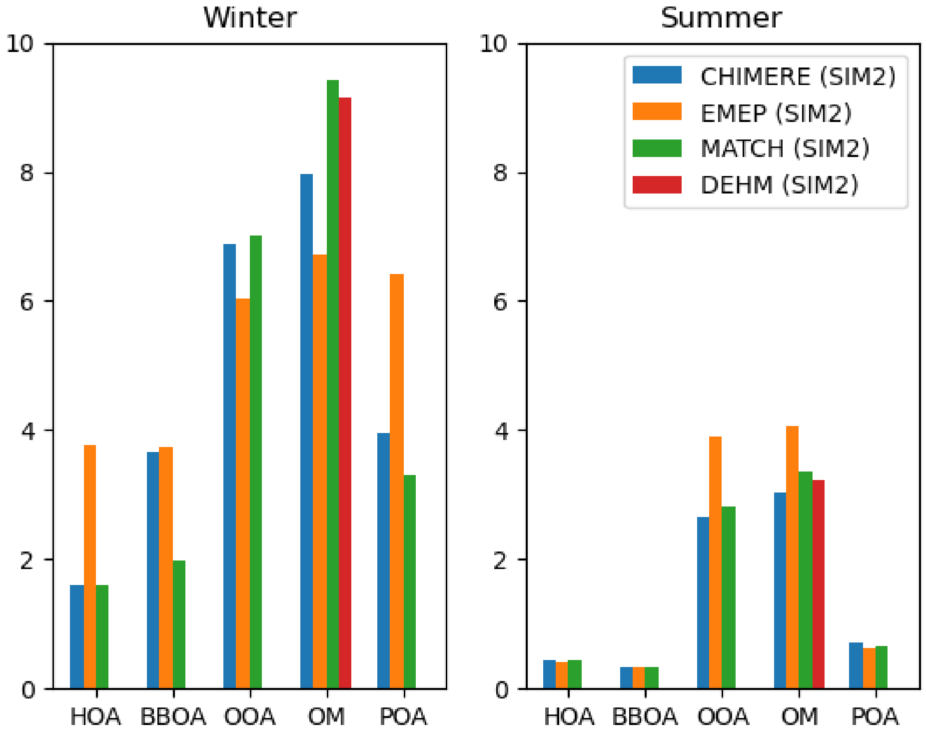
POA (HOA+BBOA) would be better with CHIMERE when accounting for the semivolatile properties of POA. Not that clear for other models.

RMSE

Nonvolalite POA



Semivolalite POA



Decrease of RMSE for POA in winter for CHIMERE and MATCH but increase for EMEP.

RMSE fairly similar in summer.

Conclusions of the evaluation

Conclusions of the intercomparison:

- Taking into account the semivolatile properties of POA do not seem to improve the modeling of organic aerosols
- However, models could overestimate POA if assumed nonvolatile
- An apparent lack of SOA during winter in all models

$\Rightarrow$ Work will continue to investigate the importance of IVOC emissions during WP8. A lot of IVOC emissions (probably higher than the emissions of NMVOC) from RWB would not be added in the model to compensate the lack of SOA

Comparison to PMF results is not that straightforward, HOA tends to be underestimated and BBOA overestimated but HOA in the PMF probably include some lowly oxidized OA from RWB. Some BBOA could be OOA.

How to perform better comparisons?

$\Rightarrow$ Use of a semi-explicit SOA mechanism with around 90 SOA species (constructed by automatic reduction of explicit mechanisms like MCM)

$\Rightarrow$ Development of an aging mechanism that can simulate the evolution of main OA categories

Parameterization for Semi-volatile POAs from fossil fuel burning

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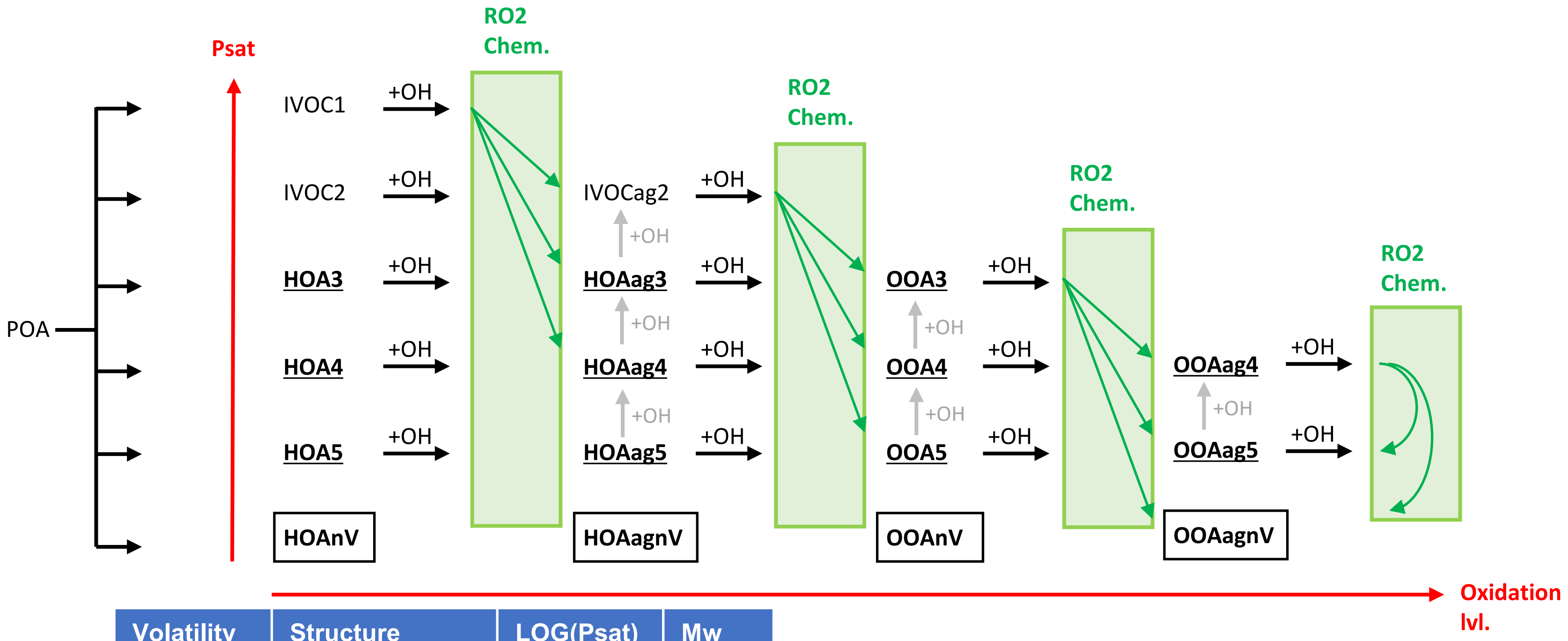
Objective : Better comparisons of PMF products and modeled concentrations



Volatility nb.	Structure (linear alkane)	LOG(Psat) (atm)	Mw
1	C10	-3	142
2	C15	-5	212
3	C20	-7	282
4	C25	-9	352
5	C30	-11	422
nV	C35	-13	492

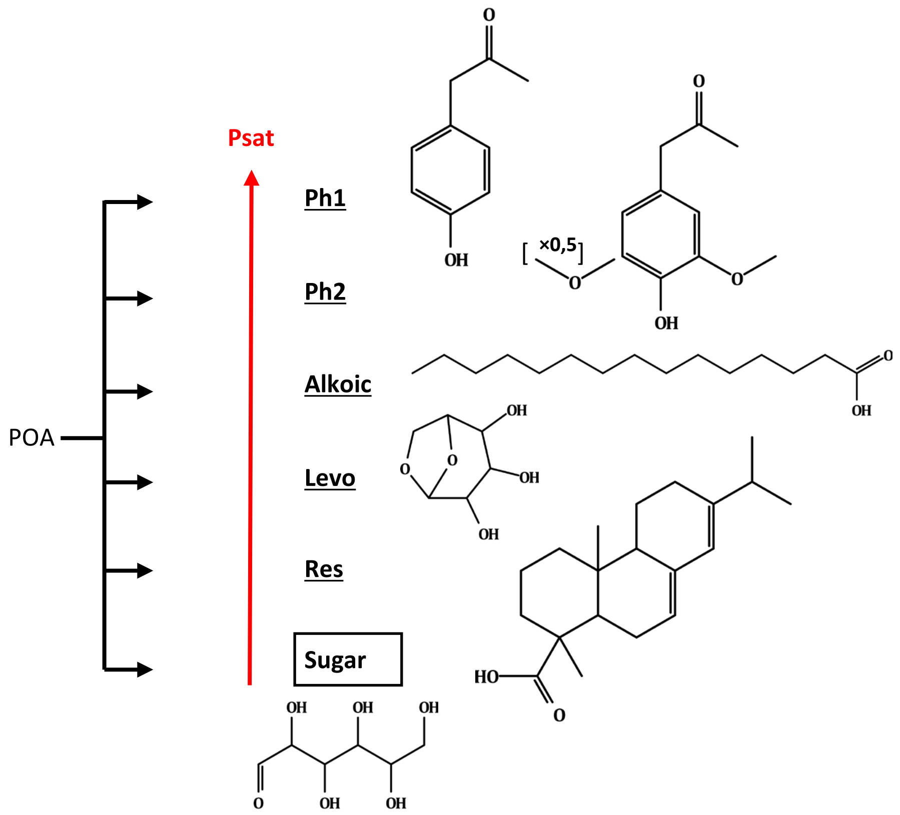
(-5 /ox. Step) (-20 /ox. Step)

Added functions per ox. Step:

+ 47% nitrate
+ 48% alcohol
+ 71% ketone
+ 3% hydroper.

- Emission distribution following May et al. (2013) Work
- Species with real chemical structures for non-ideality and solubility calculation
- Chemistry based on SAR from GECKO-A and MCM mechanisms
- OH chemistry representing functionalization, fragmentation or function modification
- RO2 chemistry representing effect of NOx regime or autoxidation on added functions and loss of volatility
- Possibility to represent IVOCs
- HOA and OOA adjustable separation

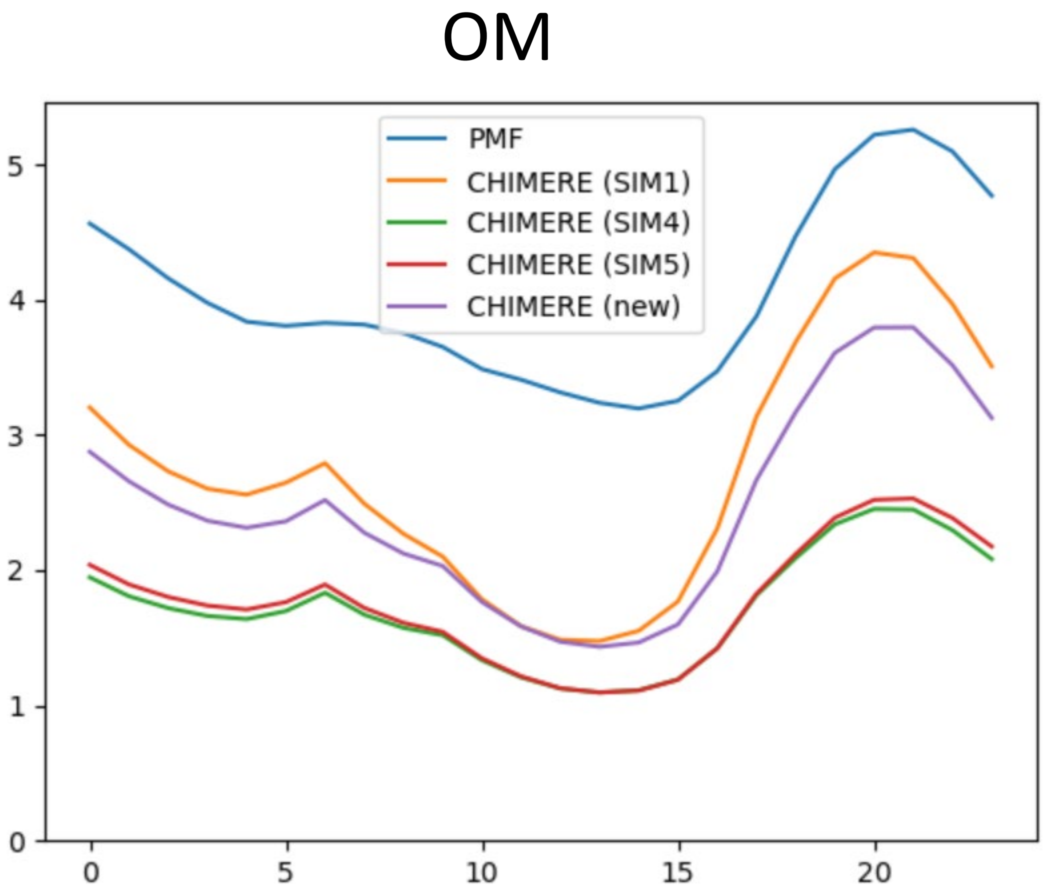
Parameterization for Semi-volatile POAs from Biomass burning

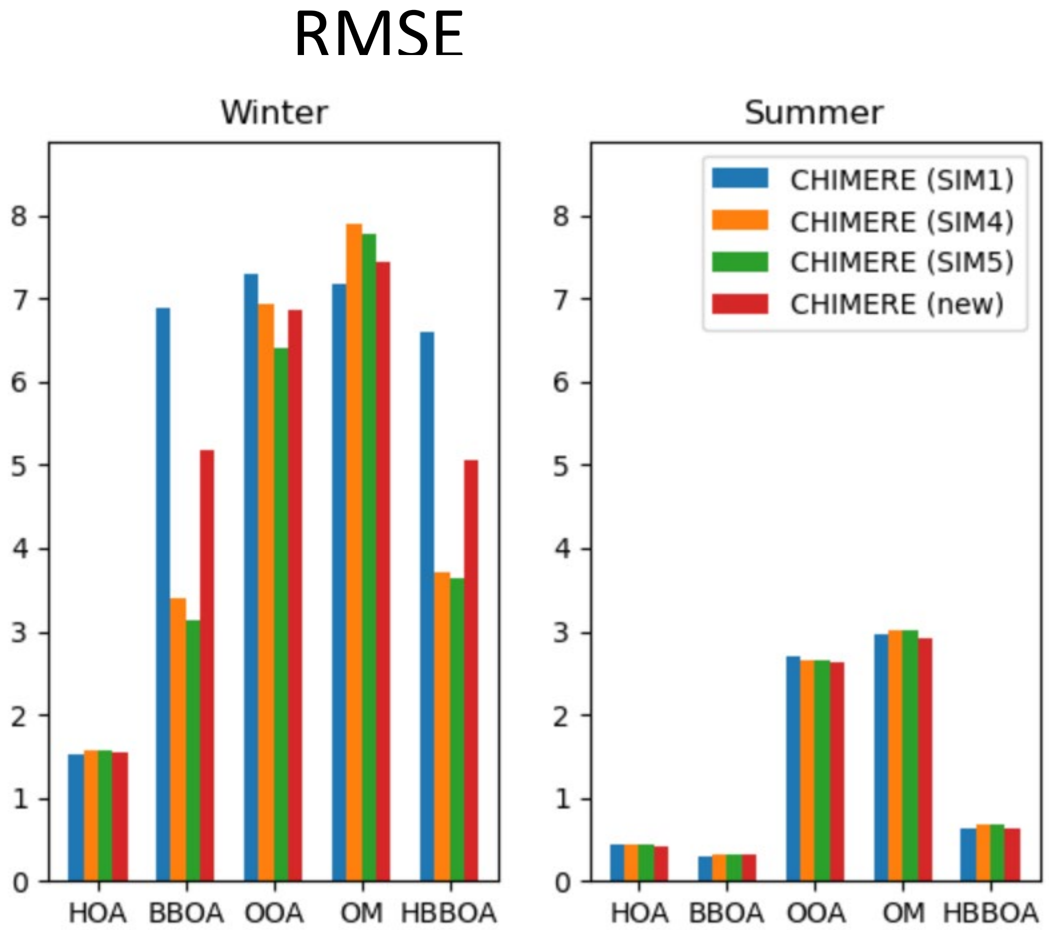


Species	Psat (atm)	EF
Ph1	$3,2 \times 10^{-6}$	0,15
Ph2	$3,2 \times 10^{-8}$	0,15
Alkoic	10^{-8}	0,075
Levo	$2,5 \times 10^{-9}$	0,33
Res	10^{-11}	0,075
Sugar	10^{-13}	0,23

- Complex mixture of very different compounds :Molecular approach
- **Speciation :** Schauer et al. 2001 et Hatch et al. 2018
- **Distribution :** May et al. 2013c et Hatch et al. 2018
- Oxidation according SAR from GECKO-A, simplified (RO2 chemistry, etc.)
- BBOA and OOA adjustable separation (BBOA only linked to levoglucosan?)

Evaluation of the new mechanism





ACSM and PMF calculation

ACSMs measure a mass spectra with a signal for different m/z

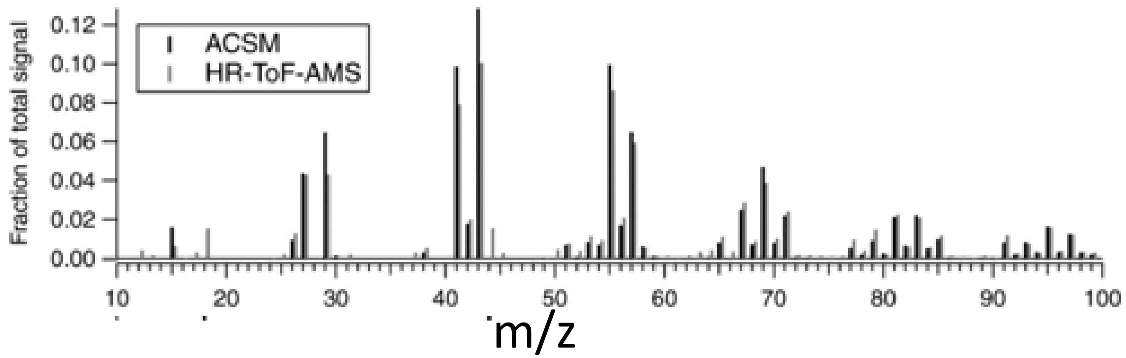
WORK IN PROGRESS (Gherras M. thesis, collaboration with RI-URBANS)

<u>link each measured signals (m/z) and modeled CHIMERE species concentrations with multilinear correlation:</u>

Each m/z signal is written as a linear combination of the concentrations C of the species n :

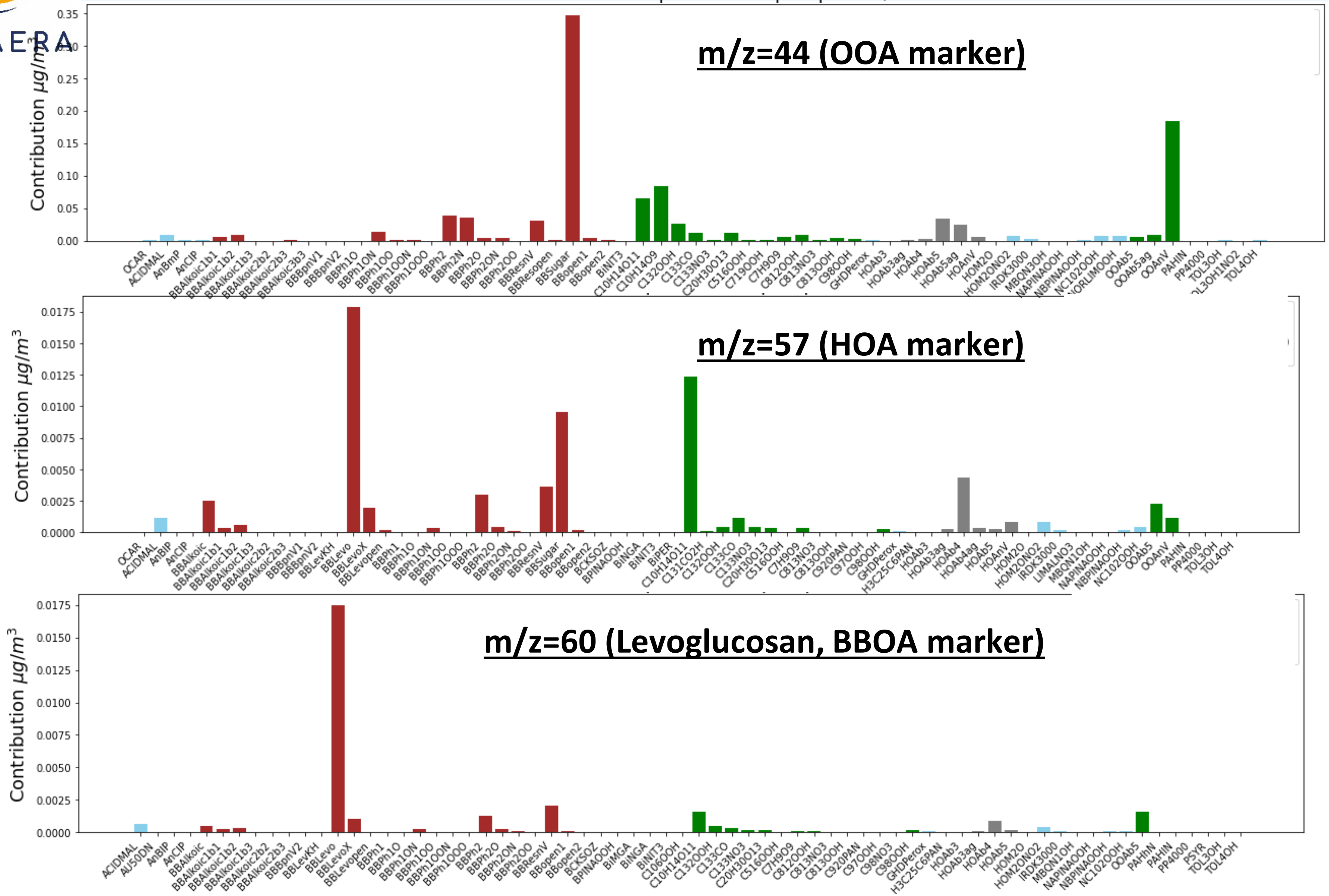
$$(\boldsymbol{m/z}) = \sum(\boldsymbol{A_n} \times \boldsymbol{C_n})$$

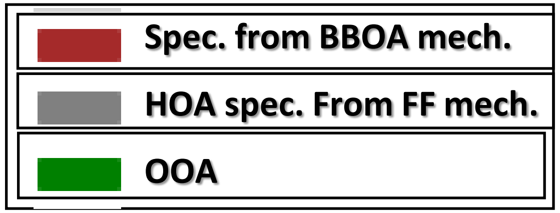
Example of mass spectra from ACSM (Herndon et al., 2011)



- HOA, BBOA and OOA can then be recalculated from the m/z signal concentrations calculated from CHIMERE by a CMB approach in a more consistent way with PMF
- HOA, BBOA and OOA can also be recalculated using the ACSM signals and the multilinear correlations in a more consistent way with CHIMERE

Post treatment of modeled data for PMF comparisons



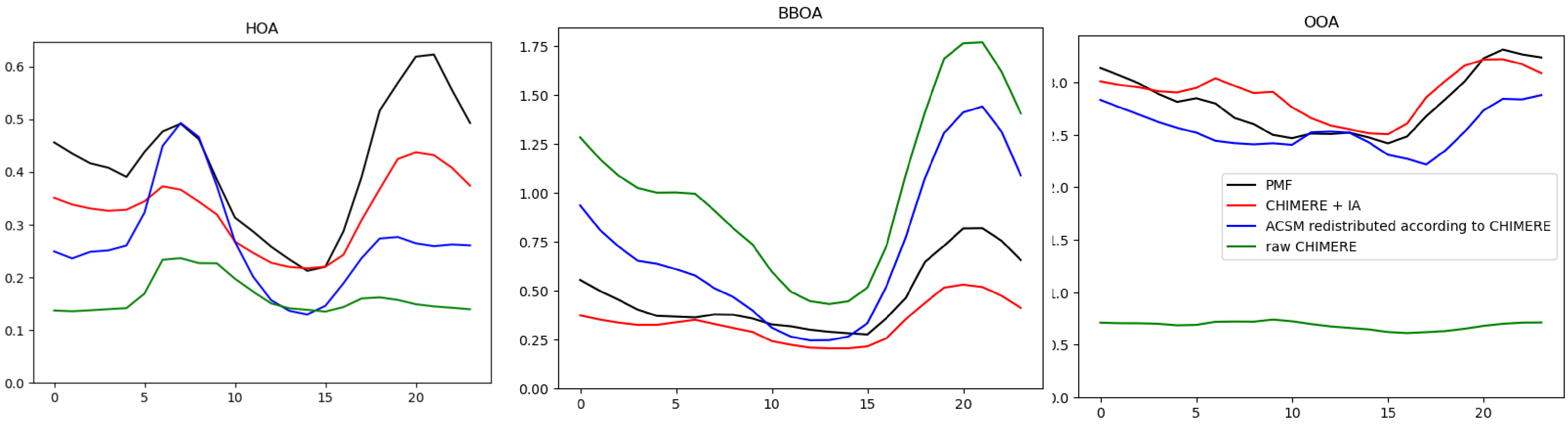


Results seems to chemically coherent
m/z=60 is only link to levoglucosan and not the other wood burning SOA

Application to Lille annual profiles (preliminary results)

Recalculation of HOA, BBOA and OOA according to two new method:

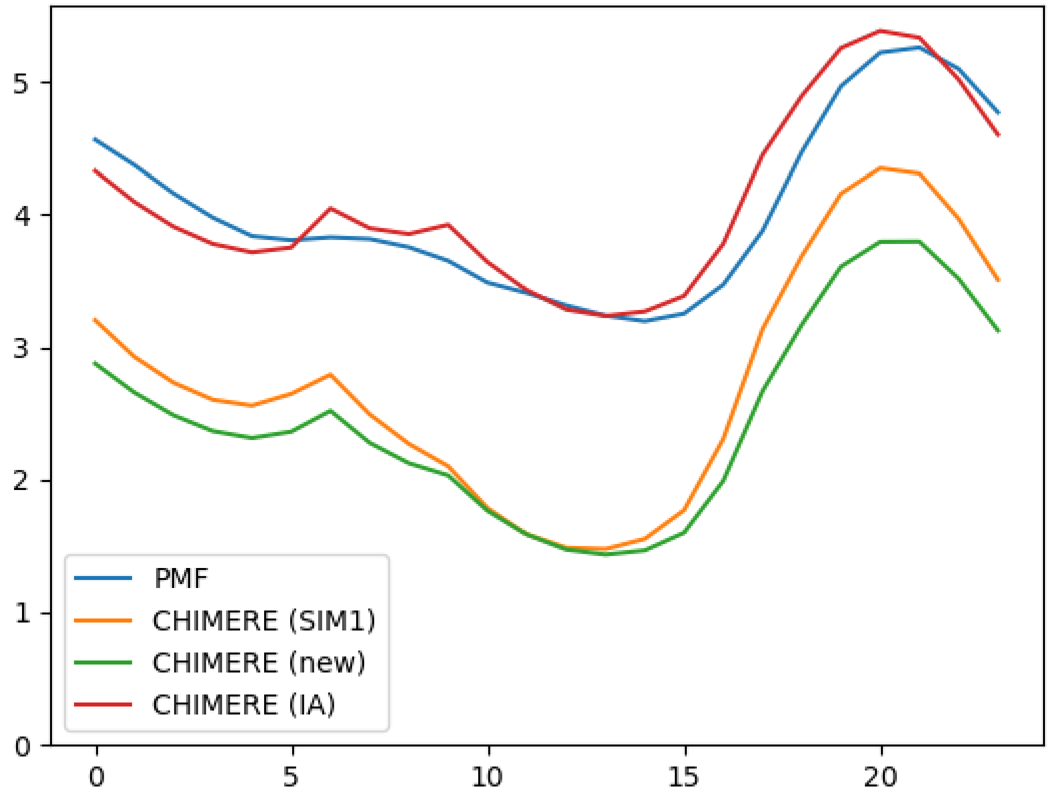
- Application of CMB on CHIMERE m/z concentrations estimated by IA
- Redistribution of each m/z ACSM concentrations according to the contribution estimated from CHIMERE and IA



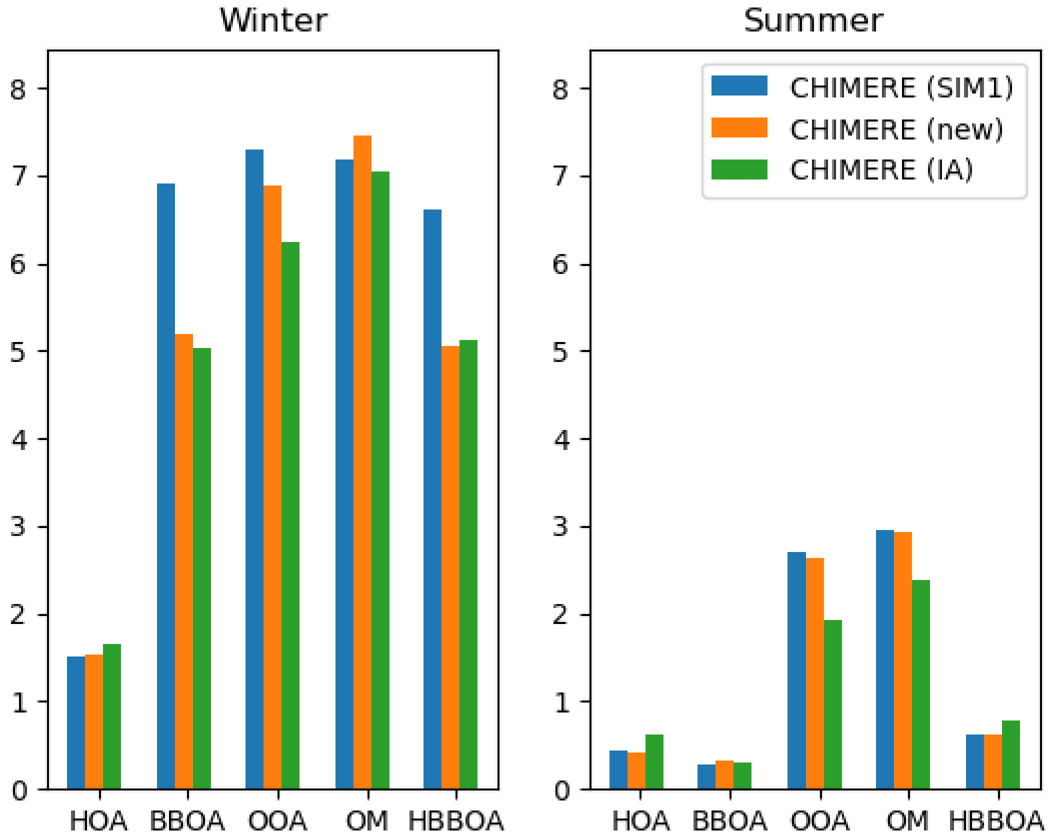
Correction of CHIMERE results (preliminary results)

Application of the IA method (constructed on Lille) on all stations => correct the bias for OM and improve the results during Winter and Summer

Average annual cycle



RMSE



Conclusions

Multilinear regression models between ACSM m/z ratio and SOA model species can:

- help to understand PMF results and the difference with simulation results
- Provide a method to correct simulation results

Inconvenient: the SOA mechanisms need probably to be quite complex for this method to work. The used CHIMERE mechanism has more than 100 particle species.

What is the necessary level of complexity?