EMEP TFMM

26th Meeting 5-7 May 2025

THEMATIC SESSION: PMs CHEMICAL COMPOSITION INCLUDING CEC

(measurements and modeling)

Field observation and modeling of
PM organic chemical speciation and Oxidative Potential

Presented by Jean-Luc Jaffrezo (IGE, France)

Monday May 05th, 16h15 – 16h30

IGE
Institut des géosciences de l'environnement
Université Grenoble Alpes
cnrs INSU Observer & comprendre

Chemical speciation on a single daily HiVol filter

154 cm2

Global mass balance			
	EC / OC	Thermo optical (Sunset EUSAAR2)	
	Trace elements	ICP-MS/MS	
	Ionic species	IC-MS	
Organic Speciation			
	Organic acids	IC-MS	
	Sugars / sugar alcohols	HPLC-PAD or LC-MSMS	
	PAH	HPLC-UV	
	Alkanes, hopanes, etc	GC-MS	
	HULIS	HPLC-UV+ DOC	
	DOC	NDIR	
	Cellulose	HPLC-PAD + enzymes	
CEC	Tyre wear tracers	LC-MSMS	
	PFAS	LC-MSMS	
Others	Oxydative Potential	plate reader	
	Microbiology	DNA sequencing	

IGE (and partners) analytical capabilities

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IGE (and partners) analytical capabilities

IGE central analytical lab for EMEP summer 2022 campaign

Results discussed in

EMEP report 2023
and
Aas et al., *in progress* 2025

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Today :

Connection with modeling

and

“CEC”

IGE (and partners) analytical capabilities

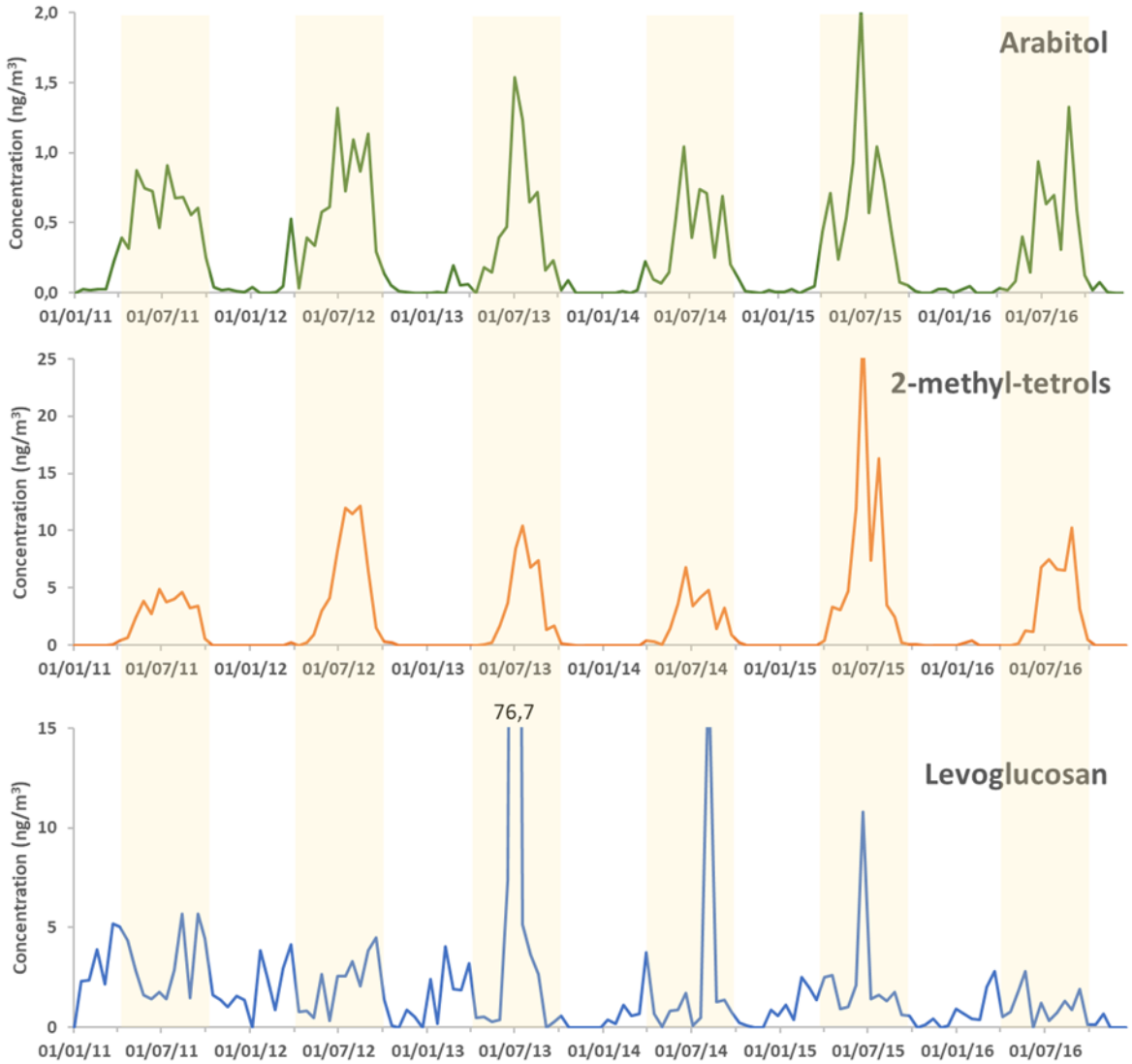
Potential PM sources and their tracers / indicators

	Identified factors	Specific markers and indicators
Anthropogenic	Nitrate rich	NO_3^-, NH_4^+
	Sulfate rich	SO_4^{2-}, NH_4^+, Se, OC
	Biomass burning	Levoglucosan, mannosan, K^+, OC, EC
	Primary traffic	EC, OC, Ba, Cr, Co, Cu, Fe, Mo, Pb, Sb, Sn, Zn
	Tyre wear	Benzothiazoles
	Industries	As, Cd, Cr, Cs, Co, Ni, Pb, Rb, Se, V, Zn
	Heavy fuel oil (HFO)	V, Ni, SO_4^{2-}, EC
	Secondary anthropic organics	Derivative PAH's
Natural	Dust	Ca^{2+}, Al, Ba, Co, Cu, Fe, Mn, Pb, Sr, Ti, Zn
	Sea-salt	Na^+, Mg^{2+}, Ca^{2+}, Cl^-
	Aged sea-salt	Na^+, Mg^{2+}, NO_3^-, SO_4^{2-}
	Primary biogenic (fungi)	Polyols
	Plant debris	Cellulose
	Secondary biogenic (Alpha pinene)	3-MBTCA
	Secondary biogenic (isoprene)	Methylthetrols
	Marine SOA	MSA

Other organic species are good indicators of some processes :

- PAH's are related to numerous combustions sources
- Organic acids and HuLIS are mostly linked to ageing of organic matter
- etc

One exemple among many applications of tracer analyses



Bros et al, in review in AMT

Measurements on 10 years of PM10 samples from the JungFrauJoch site (Switzerland)

Low level sugars in the free troposphere
3580 masl

with LC-MSMS analysis

Collaboration with EMPA and PSI

Weng J, Winiger P, Hueglin C et al., in progress

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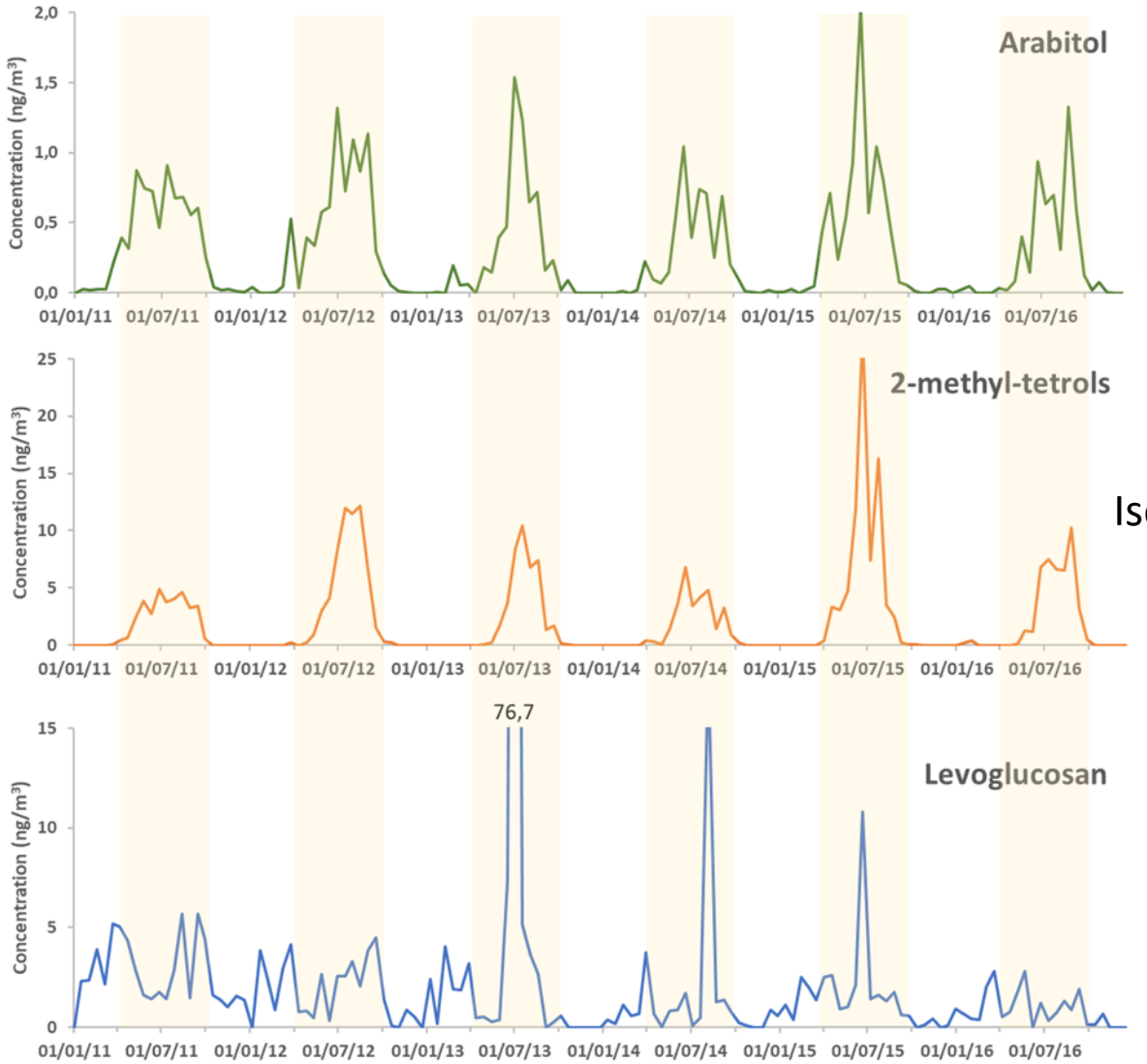

Bros et al, in review in AMT

PBOA
Fungal spore tracer

BSOA
Isoprene oxidation products

BBOA
Biomass burning tracer

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Can we reconstruct the Organic matter with these tracers ?

One exemple among several

Campaign in Kanal (Alpine Valley in Slovenia)

Collaboration with Univ Nova Gorica (G Mocnik)

Comparison of OM = 2.0 * OC
vs
Sum of organic species measured

Glojek et al., *Environ. Interna.*, 10.1016/j.envint.2024.108787

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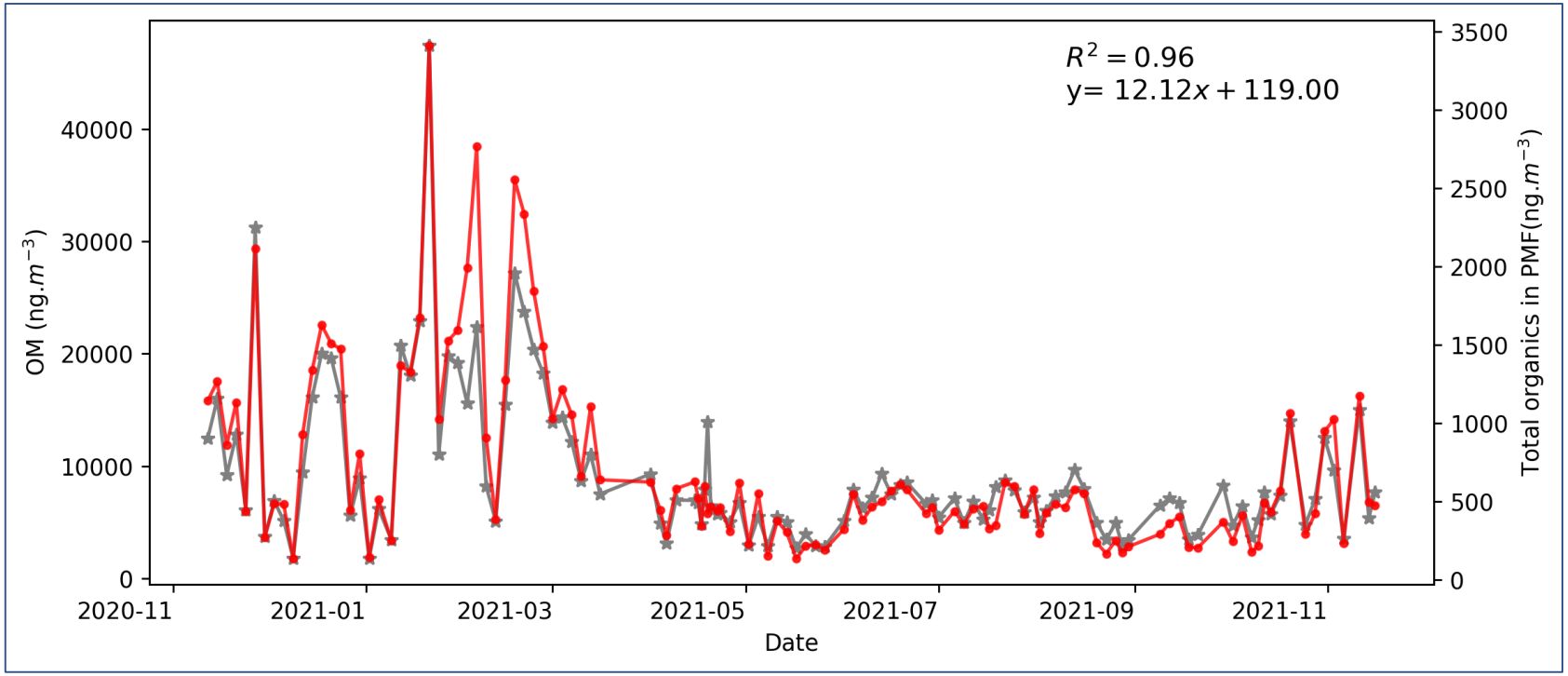

Comparison of OM = 2.0 * OC
vs
Sum of organic species measured

About 12 % of the OM mass
(no HuLIS nor cellulose)

Same temporality, same peaks, same amplitude

The measurements “include the information”

OK in EU

Not OK In Brazil or Vietmam

Strong interest for PM source apportionment (with extended PMF)

Same Campaign

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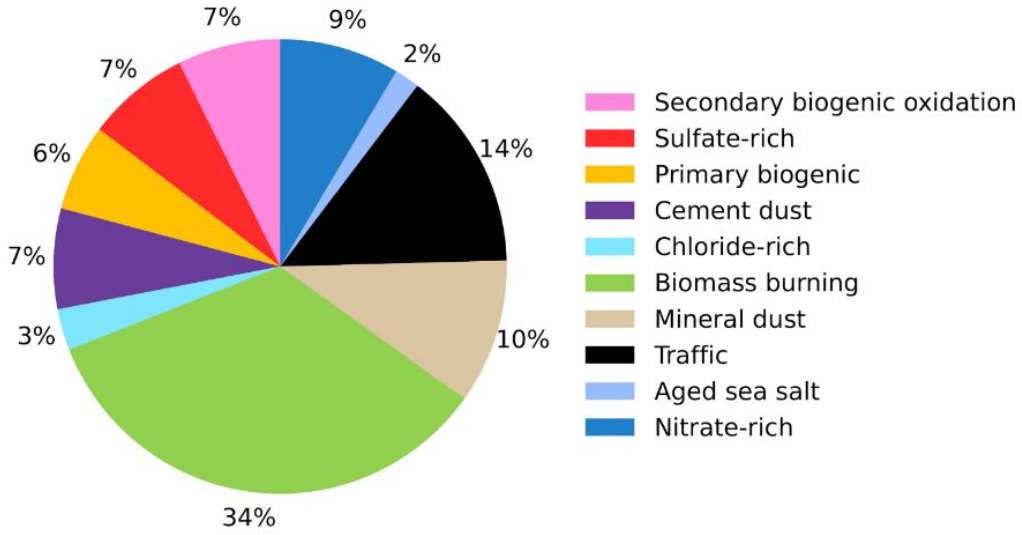
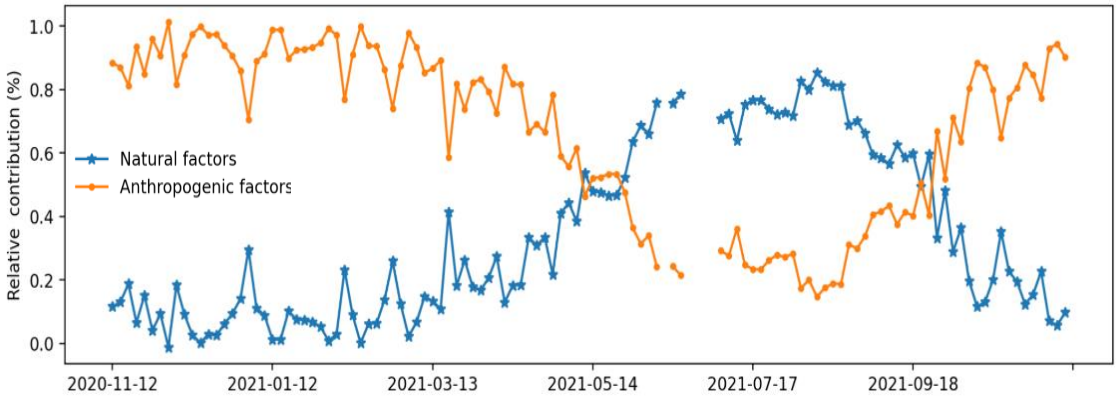


10 sources delineated
(including cement dust from local plant)



Evaluation of natural vs anthropogenic fractions

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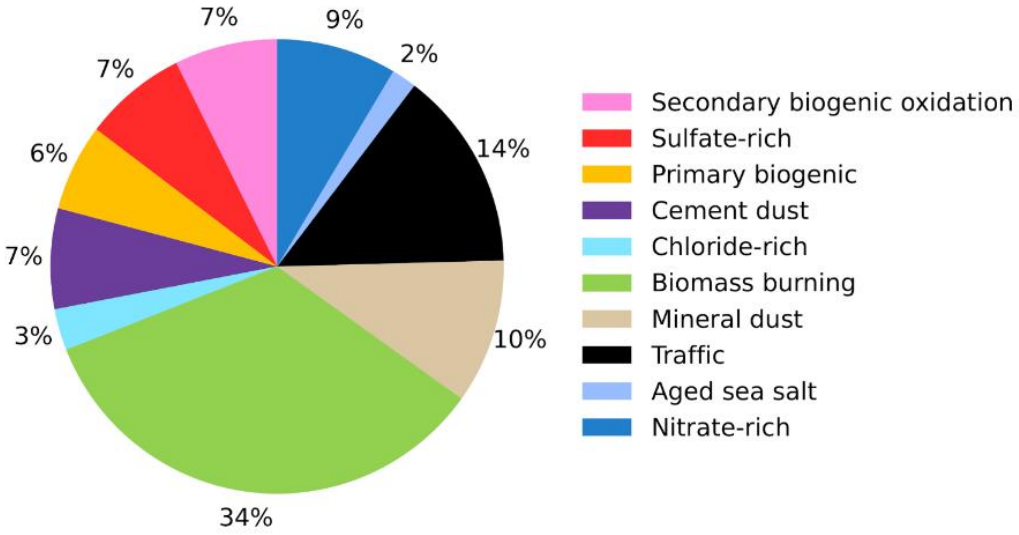

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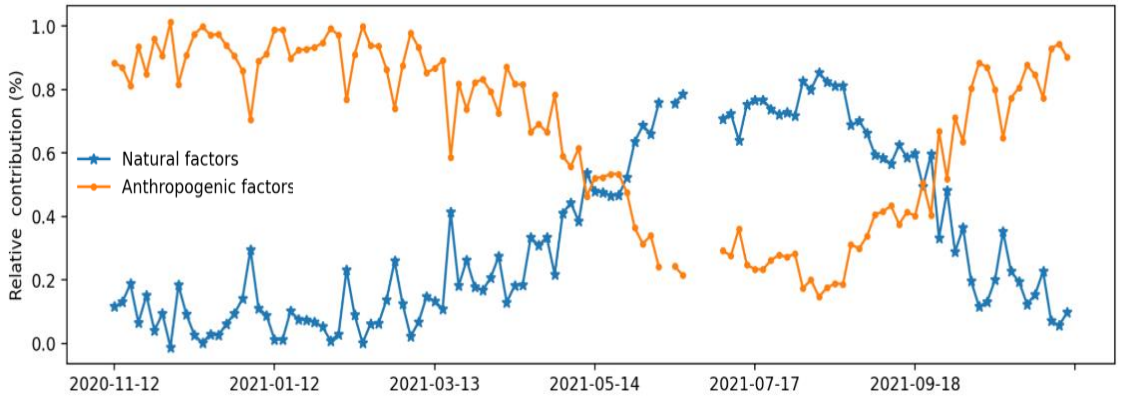

Evaluation of natural vs anthropogenic fractions

Dinh et al., Submitted to Atmos Meas Tech

Toolbox for accurate estimation and validation of PMF solutions in PM source apportionment

Tool kit at : https://github.com/DinhNgocThuyVy/PMF_toolkits

Data base and the collaborative works we do with it

Large data base compiled at IGE since 2012

- About 18 000 samples for (some) chemistry
- About 15 000 samples for OP

Works in several directions, including
aspects within many collaborations for :

Collaborations with

LISA, PSI, IDAEA-CSIC
Met Norway, TNO, HYGEOS

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  - ECOC (Putaud et al., in review)
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  - Trace metals EU (Liu et al., 2024)
  - Oxidative Potential (Tassel et al, in review in *Nature*)
  - PMF over 25 sites in France (Dinh et al., in progress)
  - PMF over 24 sites in Europe (Liu et al., 2025a,b)

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- **Use in mixed model** (obs + land use + inventory + CTM + AI)
  - OP (Dallenbach et al., Nature 2020)
  - Dust (Vasilakos et al., submitted to *Nature*)
  - OA (Several papers in progress)

- **Use in CTM developments**

Collaborations for CTM developments

Trace metals

- Cu and Mn in France with CHIMERE — Vida et al., ACP (2024) 10.5194/acp-24-10601-2024
- Brake wear over EU with CAMx + mixed model — Jiang et al., submitted to Envir Inter.

Primary Biogenic Organic Aerosol

- PBOA with fungal spores in CHIMERE — Vida et al. ACP (2024) 10.5194/acp-24-10601-2024
- PBOA with fungal spores in EMEP MSC-W — Felix Lange et al., in progress
- PBOA with fungal spores in IFS - COMPO — Remy et al., in progress

Biomass Burning Organic Aerosol

- BBOA in CHIMERE — Lanzafame et al., STOTEN (2022) 10.1016/j.scitotenv.2022.155360
- BBOA in EMEP MSC-W — Simpson et al., in the pipe

Oxidative Potential

- OP with CAMx — Dallenbach et al., Nature (2020)
- OP with CHIMERE — Vida et al., STOTEN (2025) 10.1016/j.scitotenv.2025.178813
- OP with CAMx + mixed model — Jiang et al., submitted to One Earth
- OP with LOTOS EUROS — Pekel et al., submitted to Atmos Env X

CEC measurements : UPLC-MSMS analysis of tire wear potential tracers

DECOMPOSE project

Funded by Ademe and ANSES (France)
In collaboration with Atmo Grand Est and SNCF

- In the city of Reims (France)
- 2 field campaigns (summer / winter)
- 50 days each
- 3 sites
  - urban background
  - traffic
  - railway station
- HiVol daily samples
- PM10 and PM2,5

Large chemical speciation

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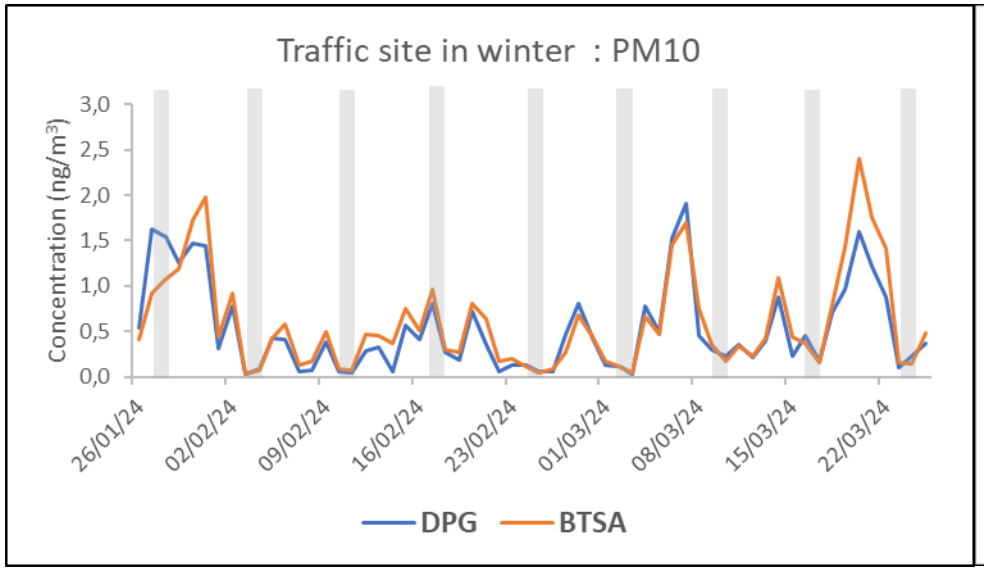
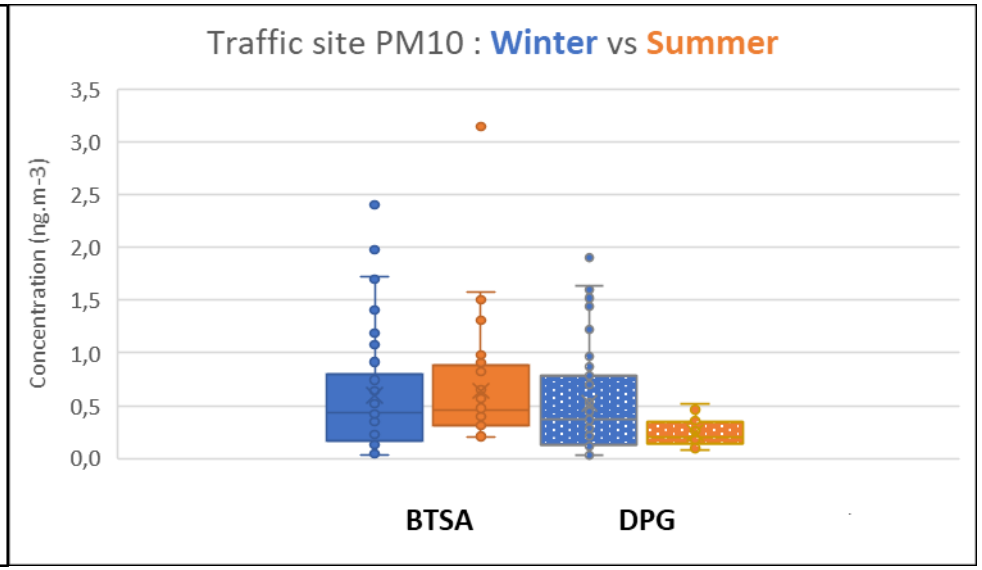
Monitored "tire additives" and some TPs

- 2-NH2-BTH
- 2-OH BTH
- 2-Me-S BTH
- 2-SH-BTH
- 2-Me-BTH
- 2-butyl-1,3-BTH
- 1-H BTR
- 5-Me-BTR
- 4-Me-BTR
- 5,6-diMe BTR
- 5-Cl BTR
- 1H-BTR-5CA
- 4-OH-1H-BTR
- 6PPD-quinone
- HMMM
- DPG Diphenyl guanidine
- DCH
- PH
- DCU
- D-DPU
- CPU
- NCBA
- BTSA Benzothiazol Sulfonic acid

Characteristic evolutions of two of the most prominent tire wear tracers





Nice simultaneous evolutions

Concentrations lower during WE

BTSA : transformation product

DPG : probably photochemical degradation

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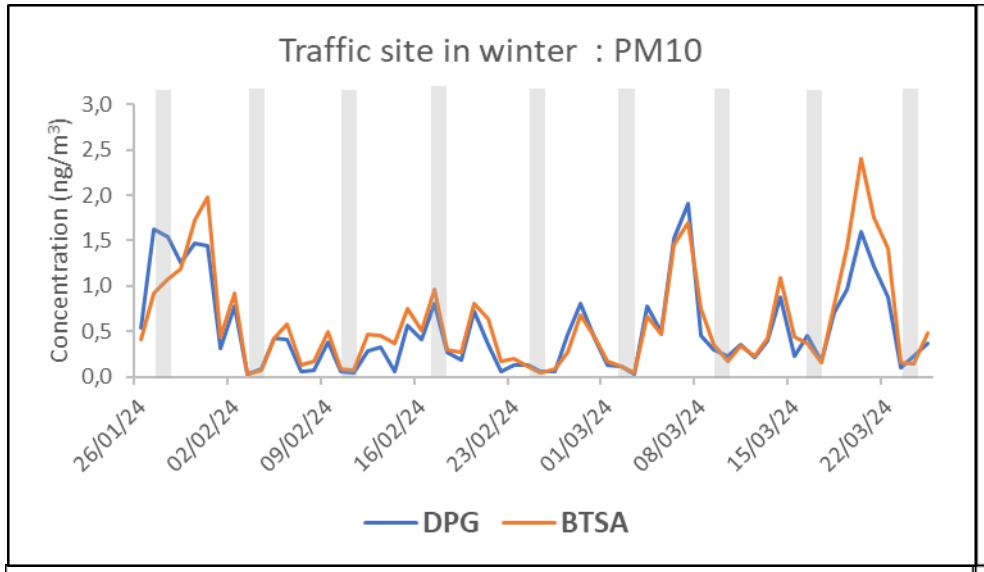
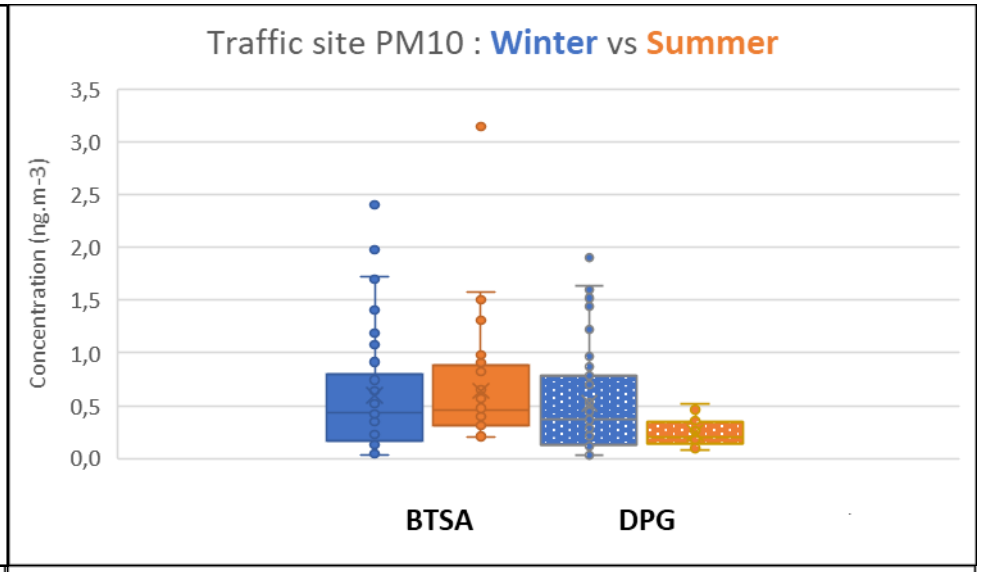
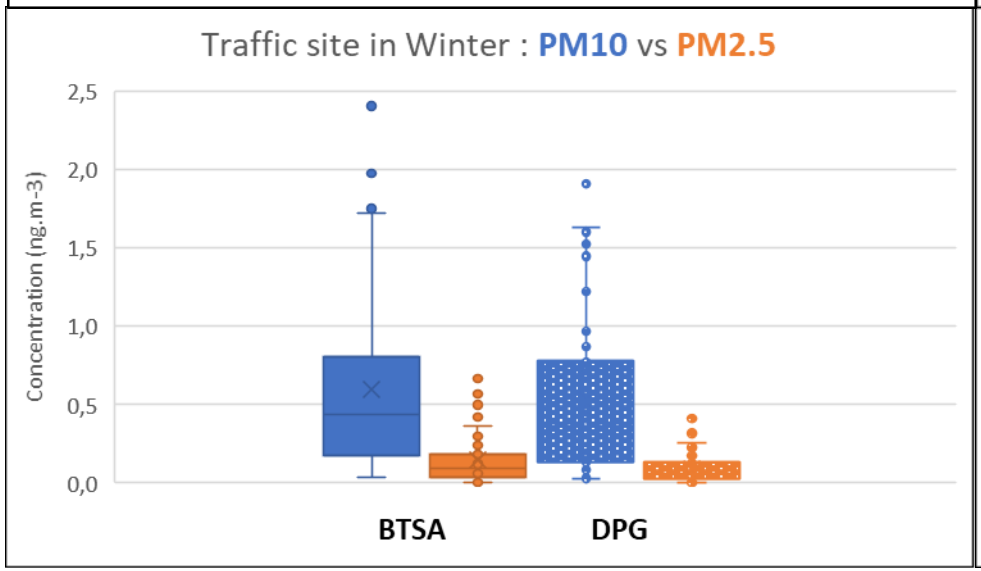
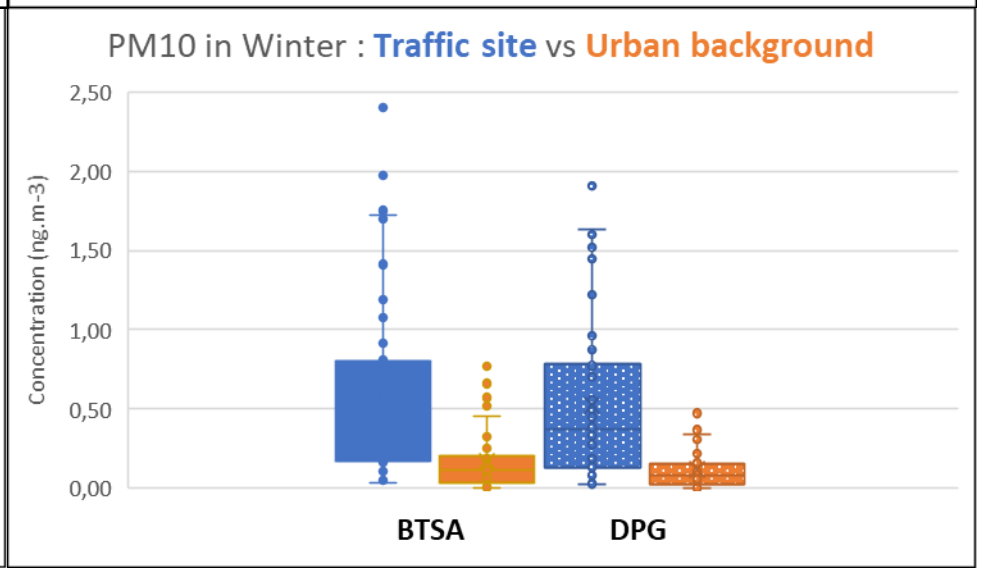


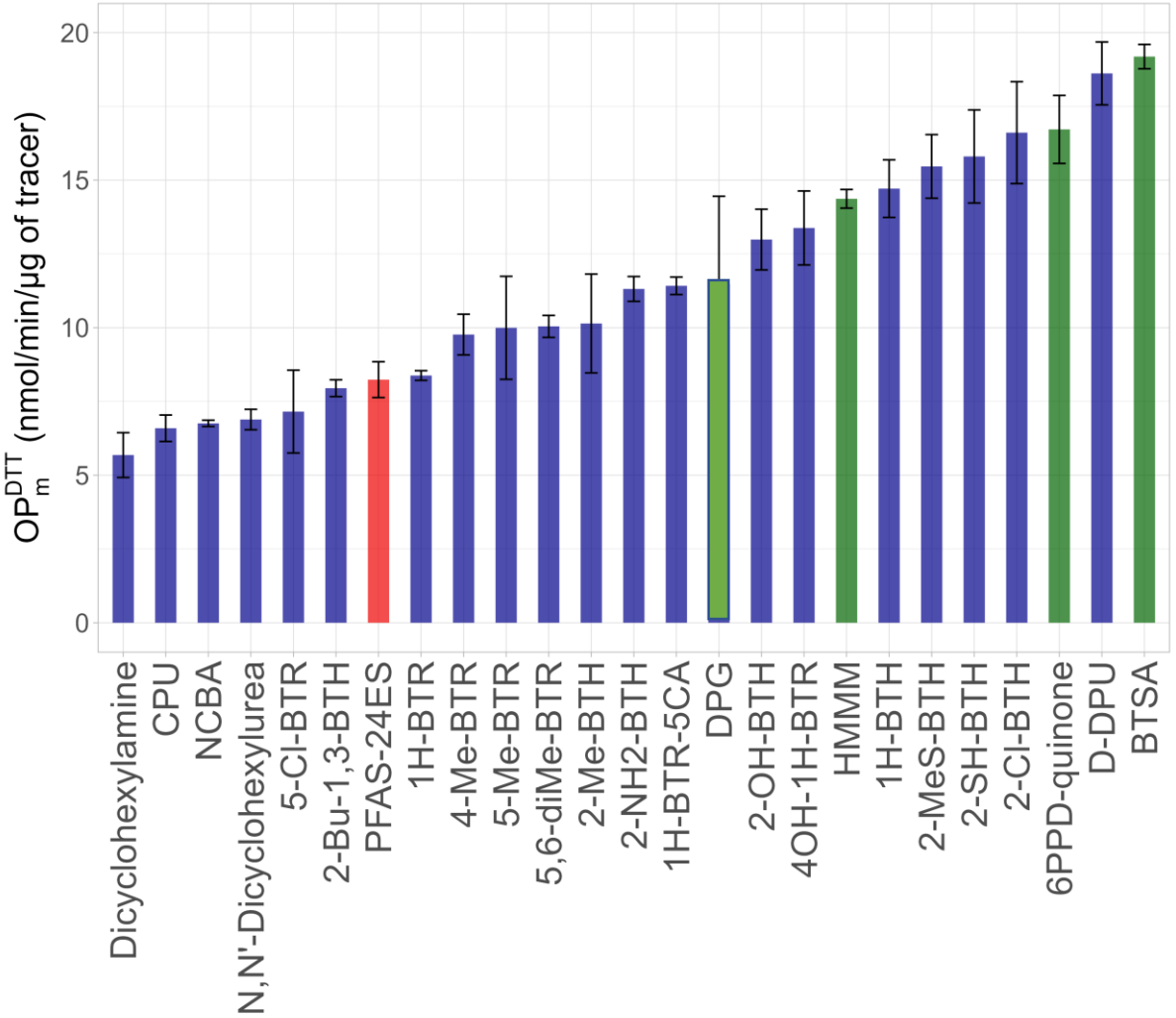






Only a question in traffic areas ...?

Intrisinc OP of tire wear tracers (and PFAS)



Intrinsic OP DTT traffic total primary

0.24 ± 0.07 nmol DTT/min/µg

(10 year average Grenoble)

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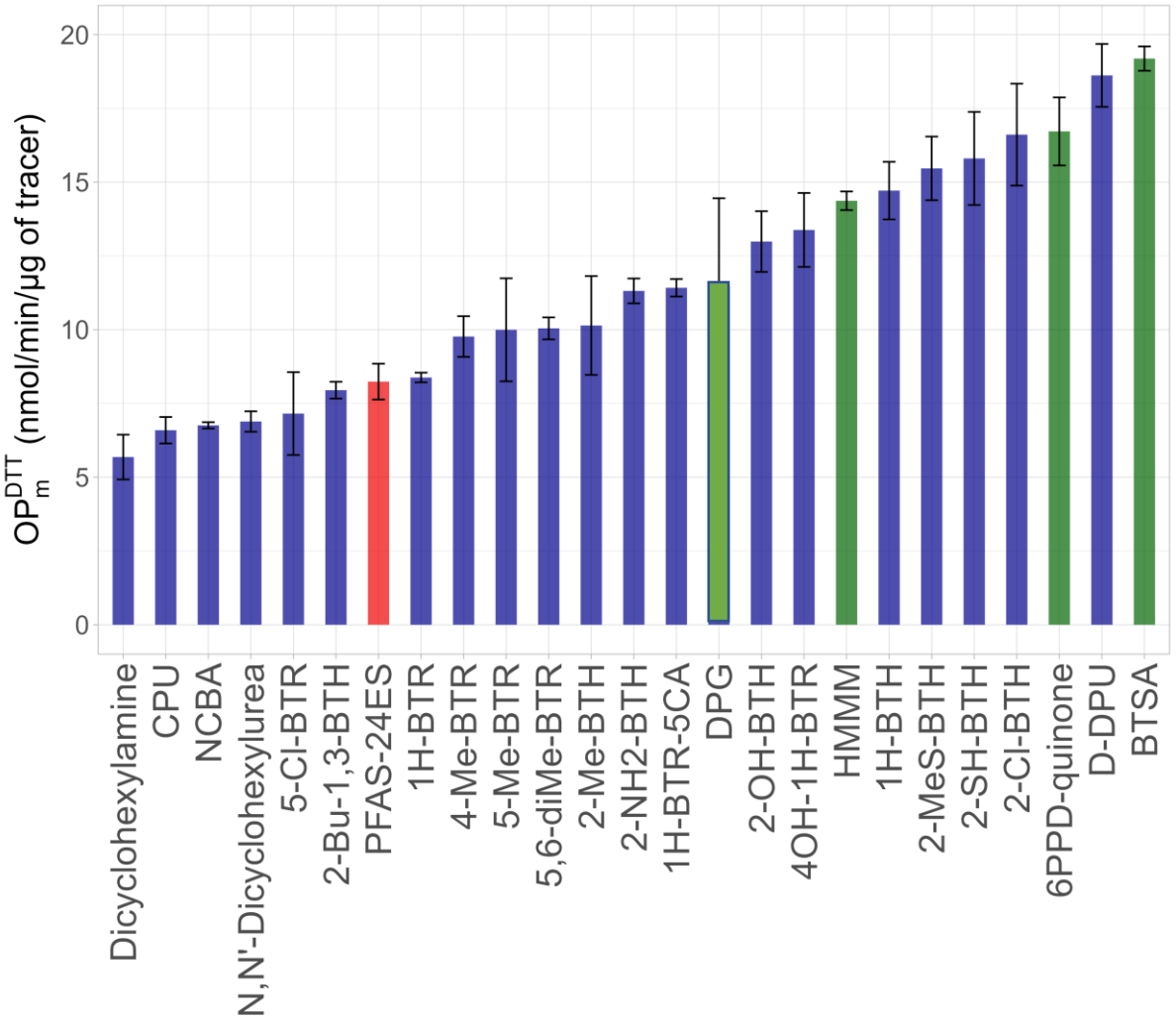

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Back of the envelop calculation :

Mass of the main 3 – 4 tire wear tracers :
0.1 to 0.2 % of the PM_{10} primary traffic factor mass

Their OP :
5 to 7 % of the OP of primary traffic factor
(if OP is additive)

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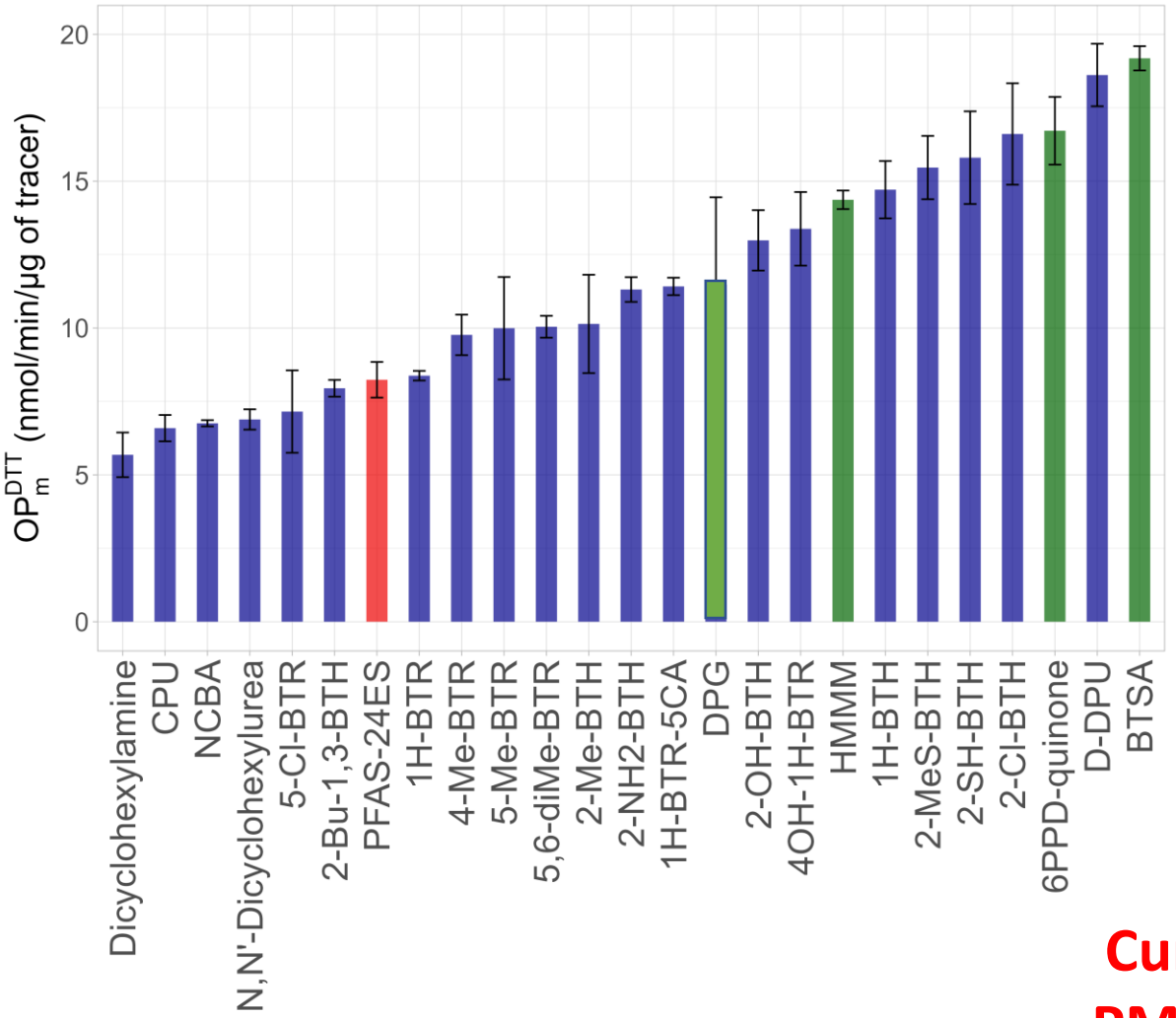

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Current work : introduction of tire wear tracers in PMF source apportionment and OP apportionment to tackle impacts of non tail pipe emissions

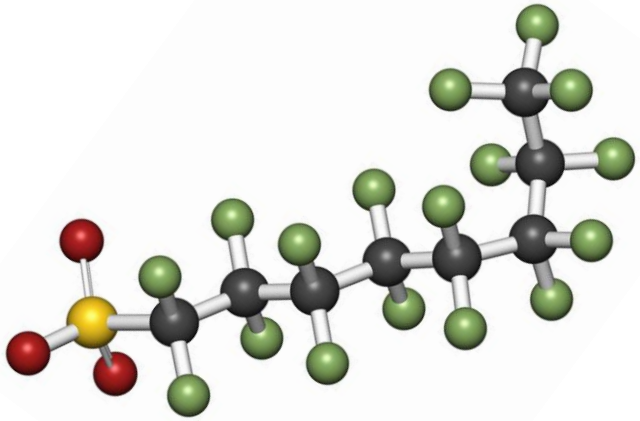
CEC measurements : UPLC-MSMS analysis of PFAS

26 PFASs targeted with UPLC-MS/MS in the PM phase

Including 8 different family groups

→ Legacy PFAS : PFCAs, PFSAs, FTSs, FOSA, FOSAA

→ Emergent PFASs : ADONA, GENX, Cl-PF3ONS



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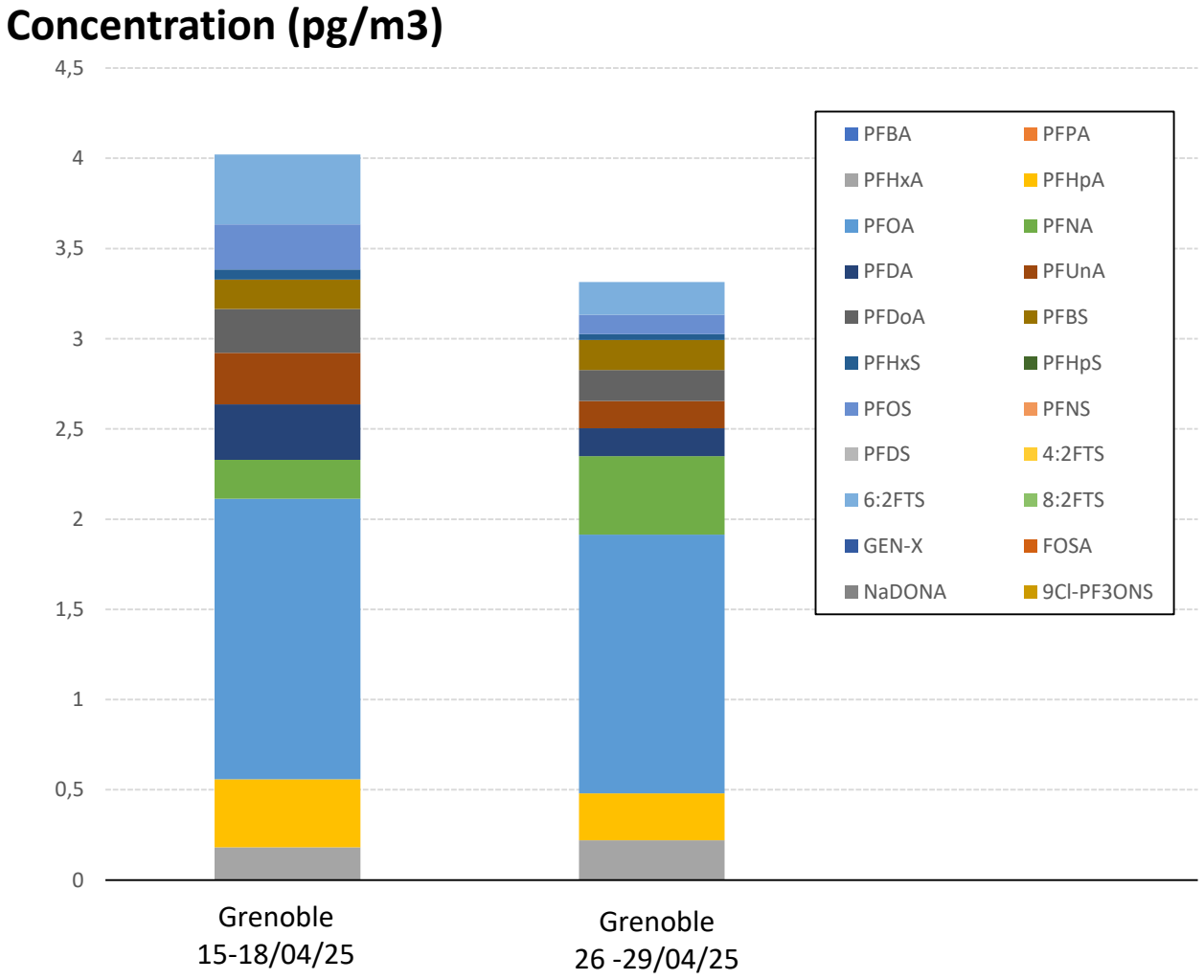


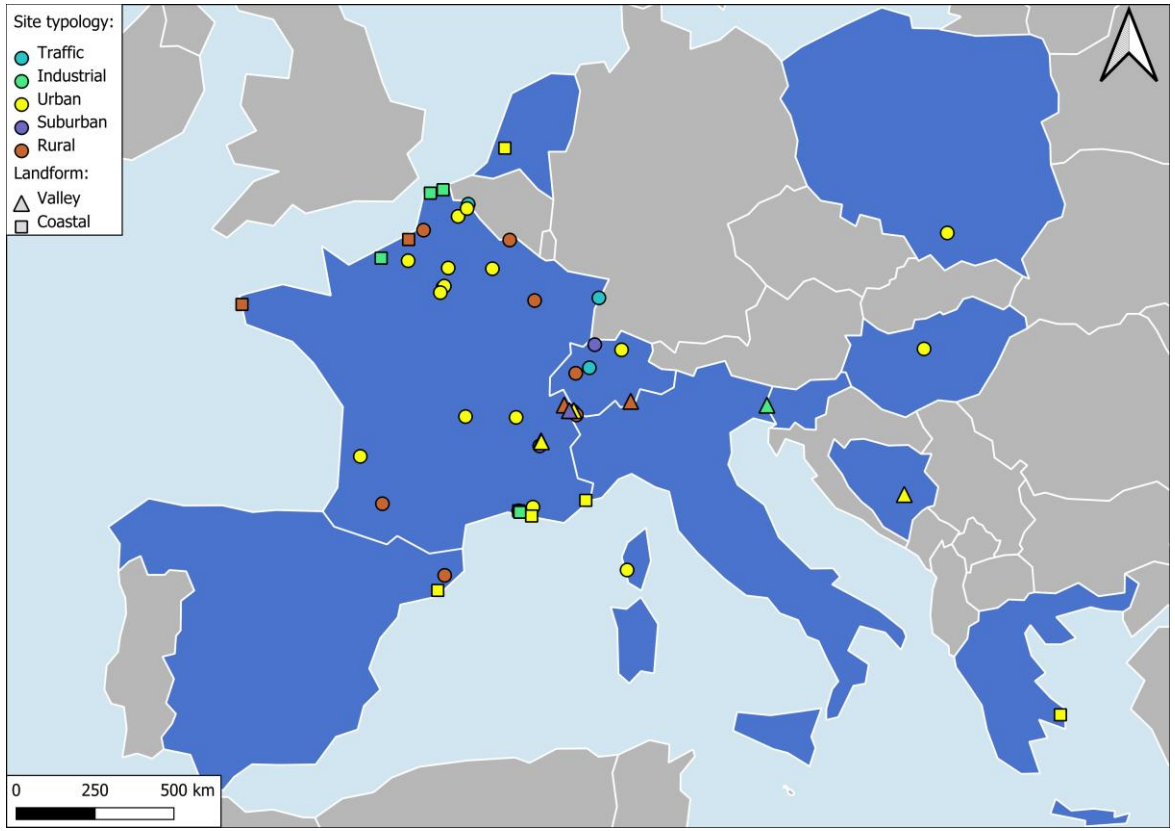
11 PFASs quantified + 1 detected in Grenoble including replacement PFASs

Extremely low concentrations (PM phase)

On-going work :

- One-year monitoring of PFAS is currently underway on archived samples → temporal trend
- Gas / particle phases + TOP Assay measurements
- Comprehensive chemical exploration will be conducted using UPLC-Orbitrap

“New measurements in the EU Directive ” : oxidative potential

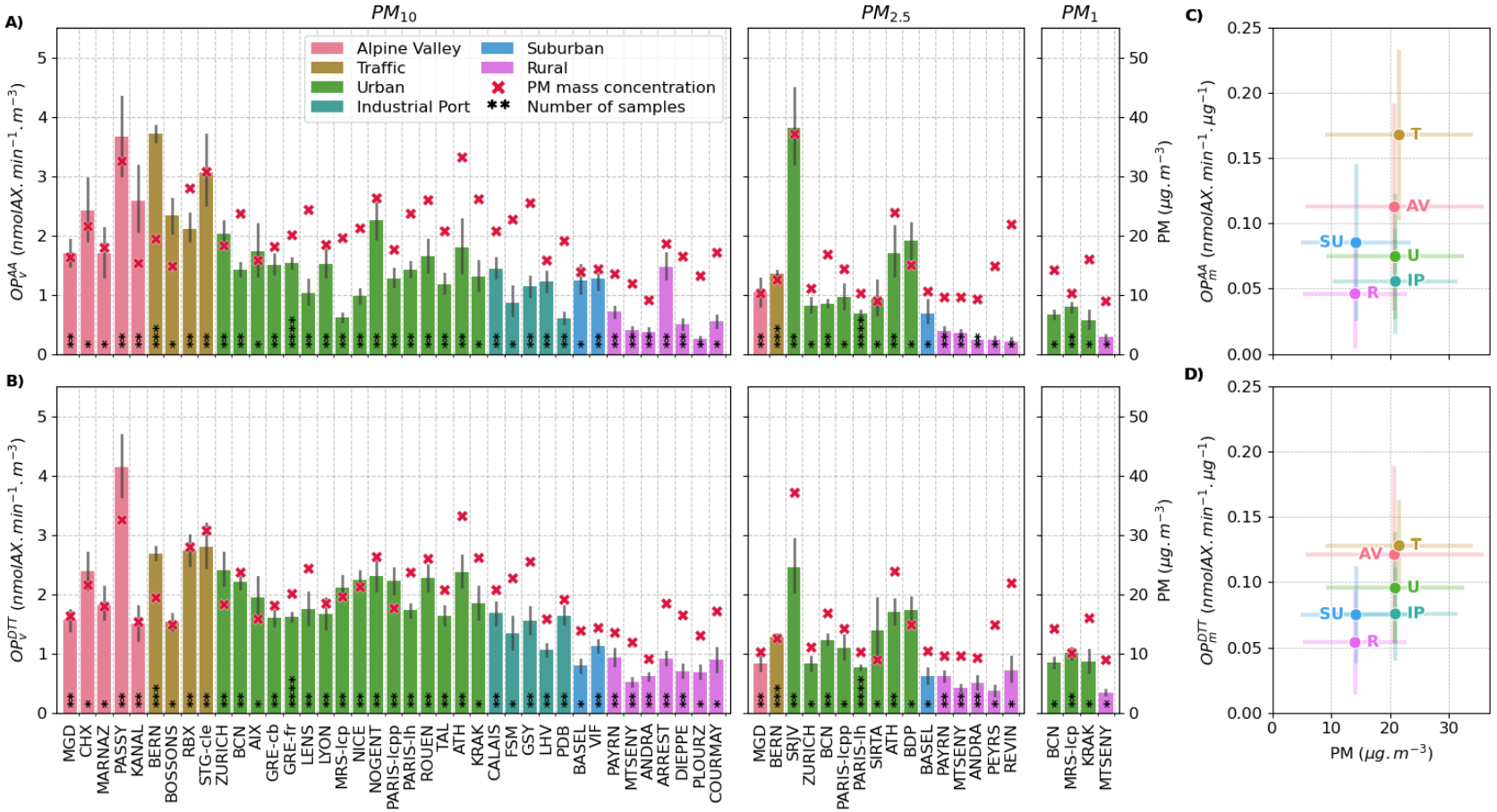


- As of April 25, about 15 000 samples analyzed for OP AA and OP DTT at IGE
- A large fraction of them in Europe, various typologies
- Several sites should be EU super sites
- As said, part of the data base used for CTM developments

- All measurements with the same protocols
- In 2024, first international ILC for OP DTT measurement (20 participants) *(Dominutti et al., AMT, 2025)*
- As of now, second international ILC ongoing for OP AA (28 participants)

ILC’s within RI Urbans and some support from ACTRIS

“New measurements” : oxidative potential



Synthesis of 11 000 measurements in EU

(Tassel et al., in review for *Nature)*

Several types of sites

OP can discriminate the site typologies when mass cannot

Tentative for prefiguration of EU guidelines values

Co-authors from
23 institutions
Very collaborative work over EU

Take home messages

It is possible to analyze

- a wide range of chemical tracers on a single daily Hivol filter
- that are representative of the main sources of PM in Europe,
- and probably describe the Organic Matter rather correctly

Includes also additional properties like Oxidative Potential and “CEC contaminants”

We developed a large data base with these measurements within many collaborations and programs

And worked to reconciliate SNAPs and PMF sources

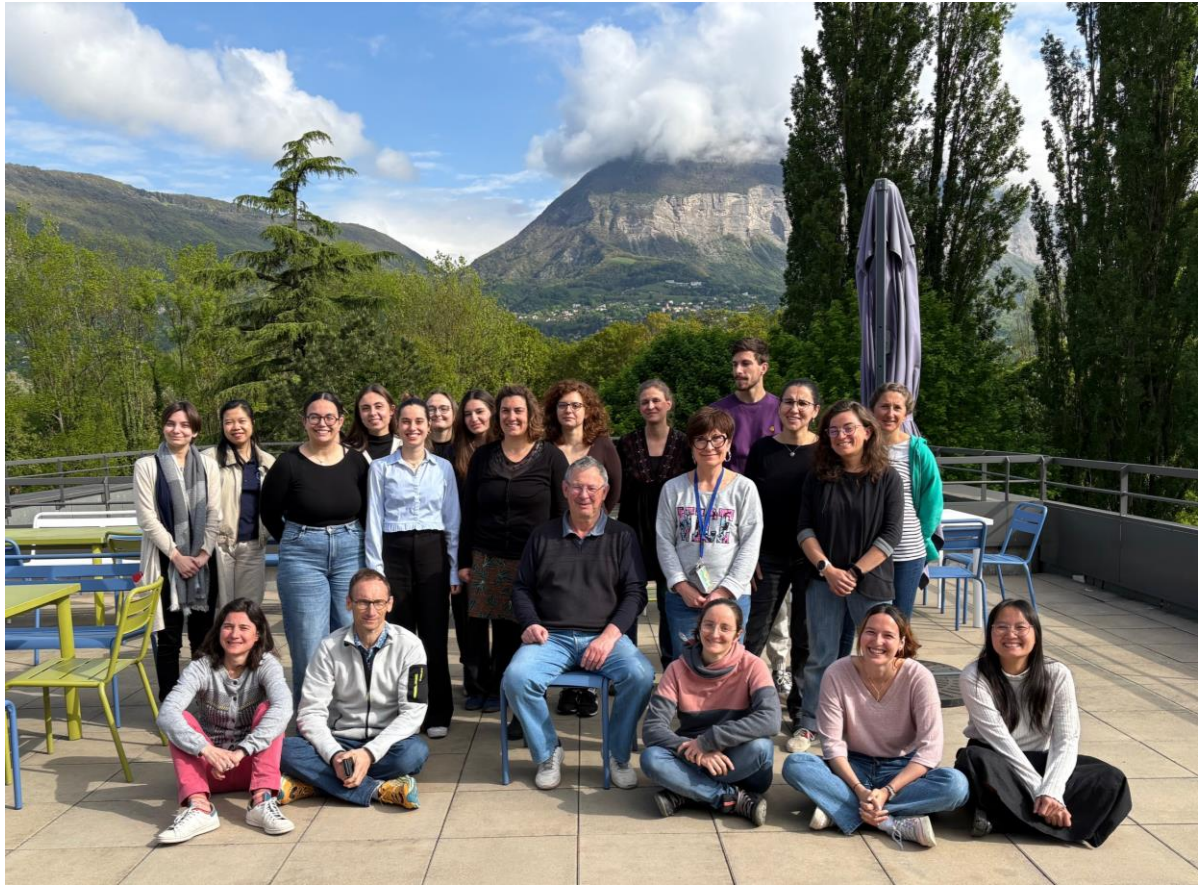
Many works for comparison with and development of various sorts of models

Over the last 2 – 3 years, introduction of PBOA and OP in CTM

Acknowledgements

At IGE

- Many people of the Air Quality group
  (G Uzu, P Dominutti, S Sauvage, …….)
- Many people of the Air O Sol analytical plateau
  (S Darfeuil, A Marsal, C Voiron, R Elazzouzi, P Bros,….)
- Christine Baduel *(IGE, tire wear and PFAS collab)*



And, of course

- Many people in French AASQA for samples collection and opportunities of programs
- Several people at **INERIS / LCSQA** for long term, strong, and interesting scientific collaborations

- Many collaborations with a ton of groups in EU and internationnaly, too numerous to name all

  (PSI, IDAEA-CSIC, EMPA, LISA, TNO, LaMP, LCE, LCME, VNU, ….)

Thank you !