# Sources contribution to the oxidative potential of $PM_{10}$ at 15 French sites

**EAC 2019**

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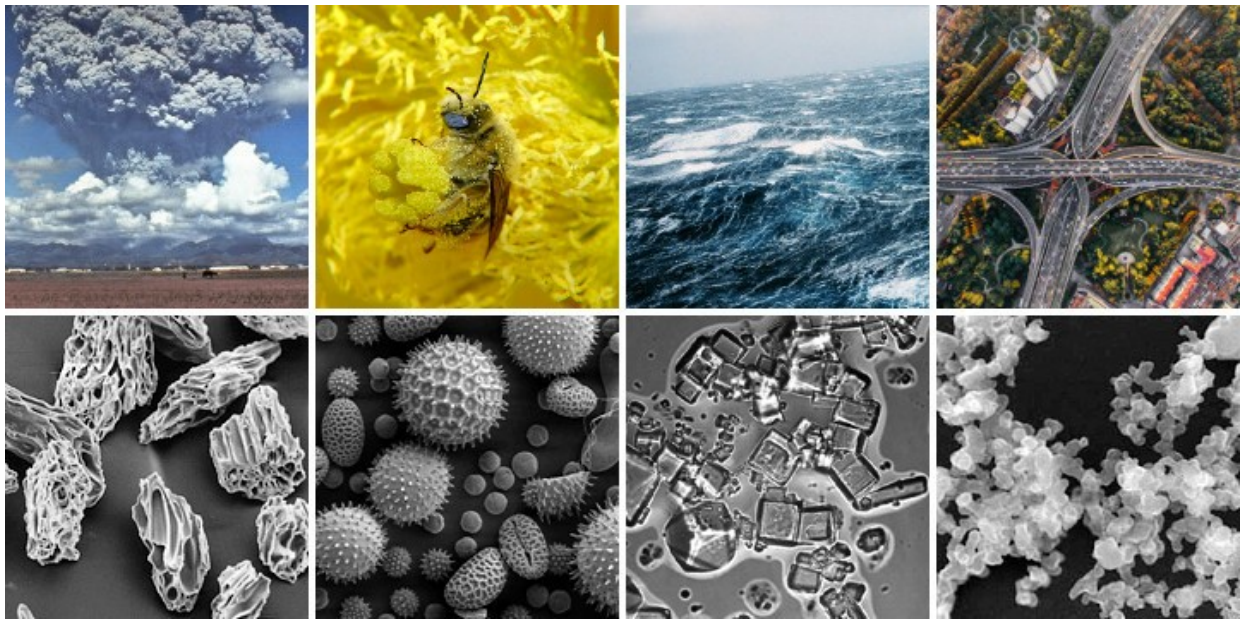
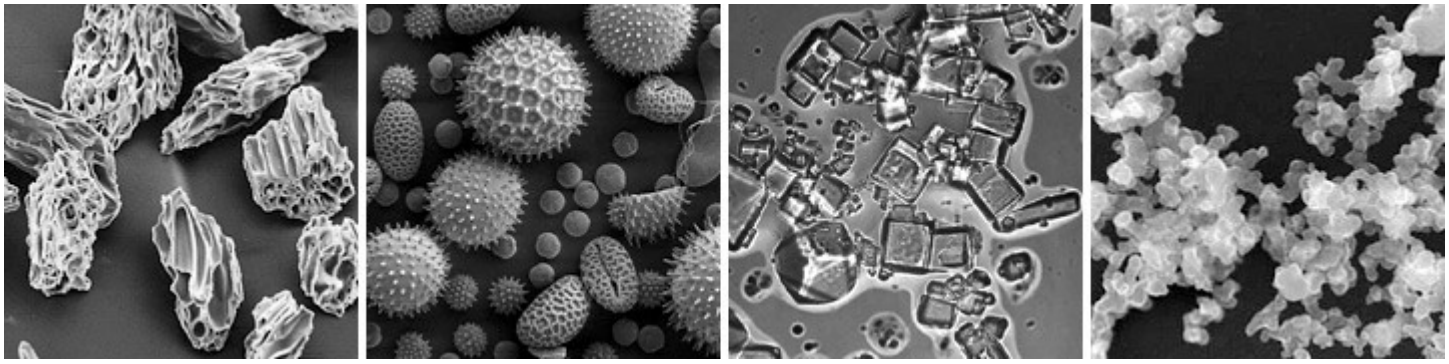


# Introduction – air quality and OP

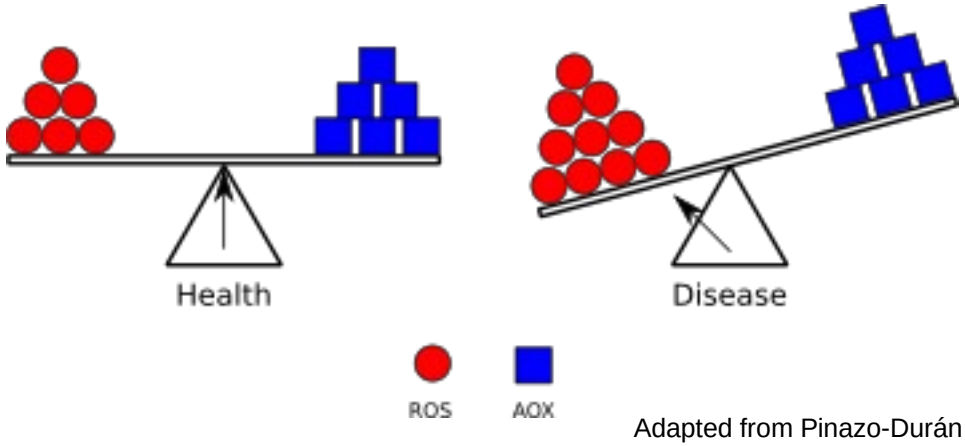
## Aerosols are highly diverse



Micrographies from USGS, UMBC (Chere Petty) & Arizona State University (Peter Buseck).
Credit: NASA earthobservatory https://earthobservatory.nasa.gov/Features/Aerosols/

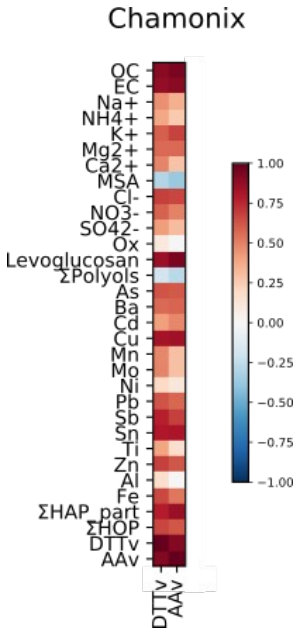
- What proxy(ies) for air quality?
  - Mass,
  - Number,
  - Size,
  - Shape,
  - Chemistry,
  - ...?

**Integrative one:**
The **oxidative potential (OP)** of PM
~ability of PM to generate ROS




Adapted from Pinazo-Durán *et al.* (2013)

## Motivation & objectives




### Univariate correlation OP vs chemistry is not causality

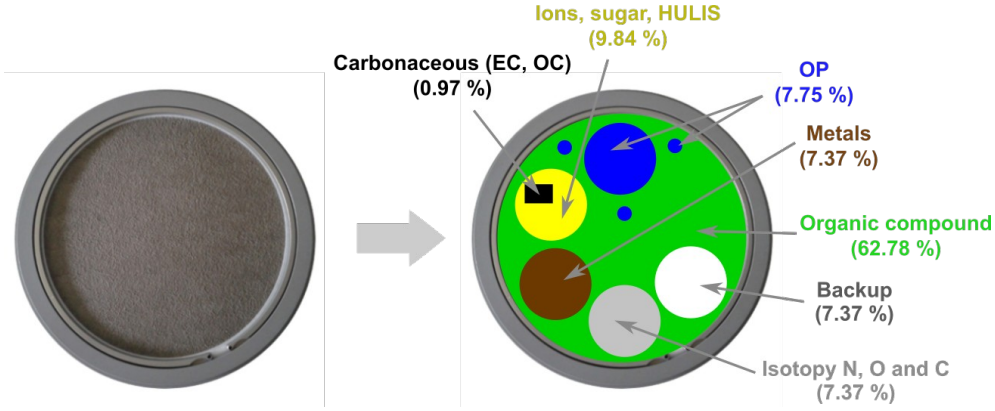
### Inversion by sources (road traffic, BB, …)

→ explanatory variables: concentration in µg $m^{-3}$ of source per day.

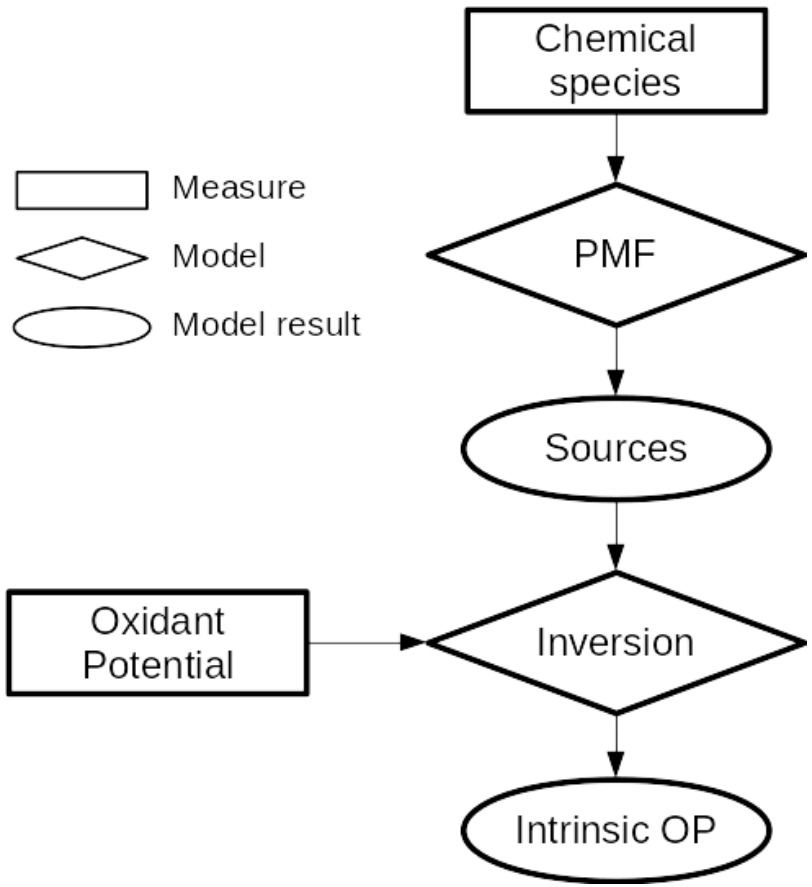
- « Aggregate » chemistry informations (~species covariation).
  Few proxies allow identifying main PM sources
- More relevant for **regulation** and **epidemiological studies**.
- Need **pre-treatment** (e.g. PMF), so adding uncertaintities.
- Need an **inter-comparaison of a "similar" source** at different sites

# Simultaneous measurement of OP and chemistry


- Numerous research programs
  through (inter-)national collaborations
- Unique database
  - 16000 filters samples
  - 82 stations
  - Between 2011 and 2019
  - Up to >130 species
- OP measurements
  - DTT, AA, DCFH
  - SLF: Gamble + DPPC
  - Isomass
  - >5800 samples.



## How to proceed?




### STEP 1: PM SOURCES (PMF)

- Aggregate chemistry (quinone, etc)
- ~10 explanatory variables
- Regulation purposes

### STEP2: OP SOURCES

- Linear mixing model (adapted WLS)

$$OP_{obs} = \sum_i OP_i \times PM_i$$

- Bootstraping → uncertainties
- Intrinsic OP of a source
  (=OP per µg/m³ of PM source)

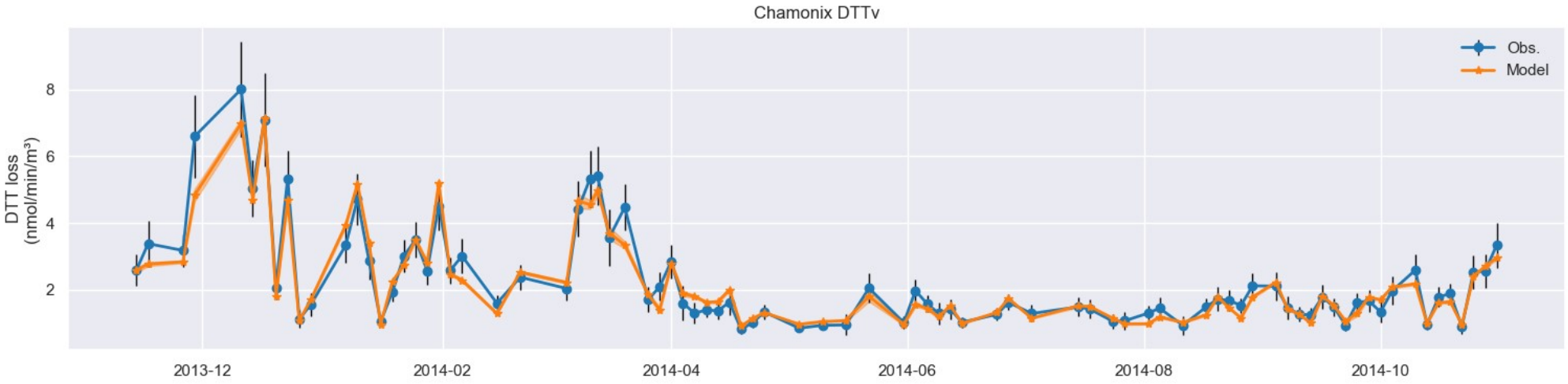
**Let applicate it in Chamonix**

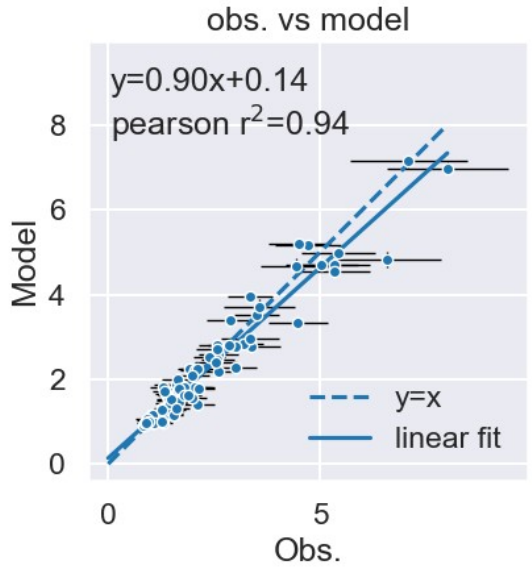
PMF: 8 sources
Year: 2013-2014 (~120 samples)
OP: DTT & AA

**Method & application in Chamonix:** Weber et al 2018, ACP
https://doi.org/10.5194/acp-18-9617-2018

# Example in Chamonix, France – model validation

Model close to observations



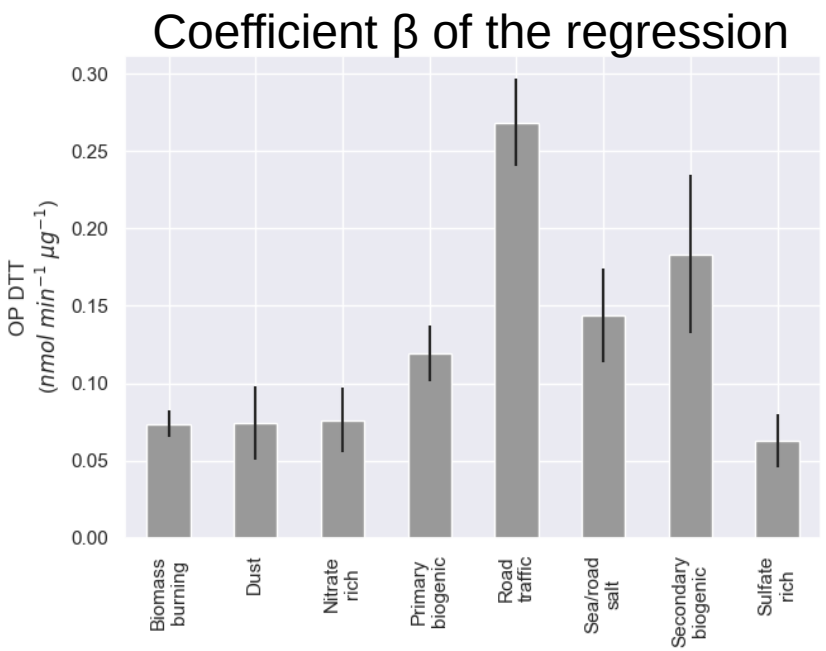

8 sources explain 94% of the OP variance

**Model statistically OK.**
**And geochemically?**

**Method & application in Chamonix:** Weber et al 2018, ACP
https://doi.org/10.5194/acp-18-9617-2018

## Example in Chamonix, France – model results

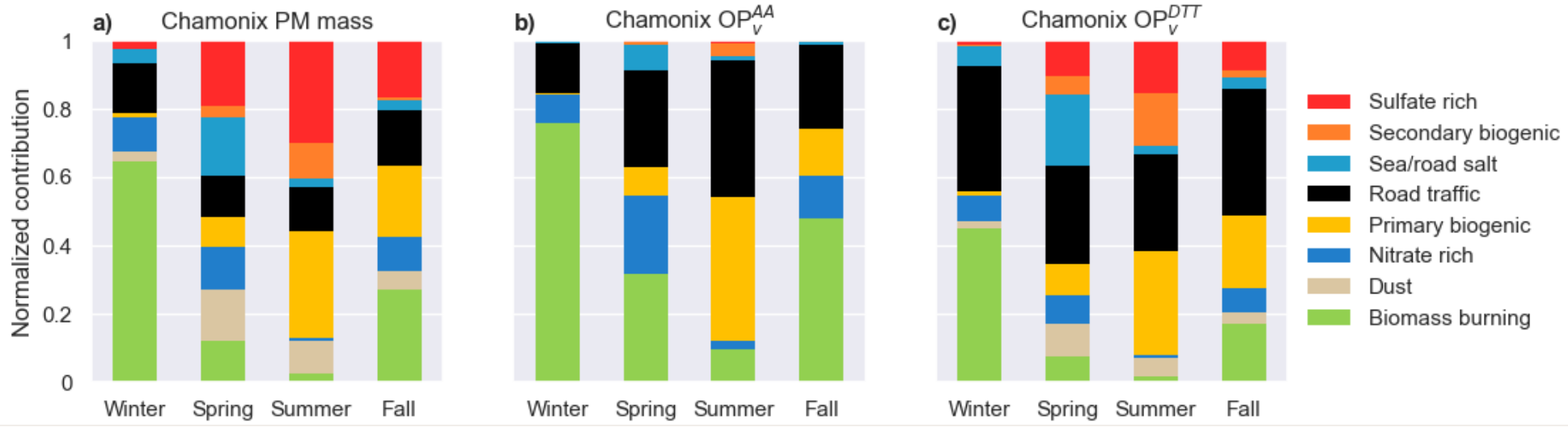
Err. bars: std 1000 bootstraps




Different coefficients
→ different "intrinsics" OP

β × [source]

Redistribution of the sources weight
→ novel view of the aerosol




**Method & application in Chamonix:** Weber et al 2018, ACP
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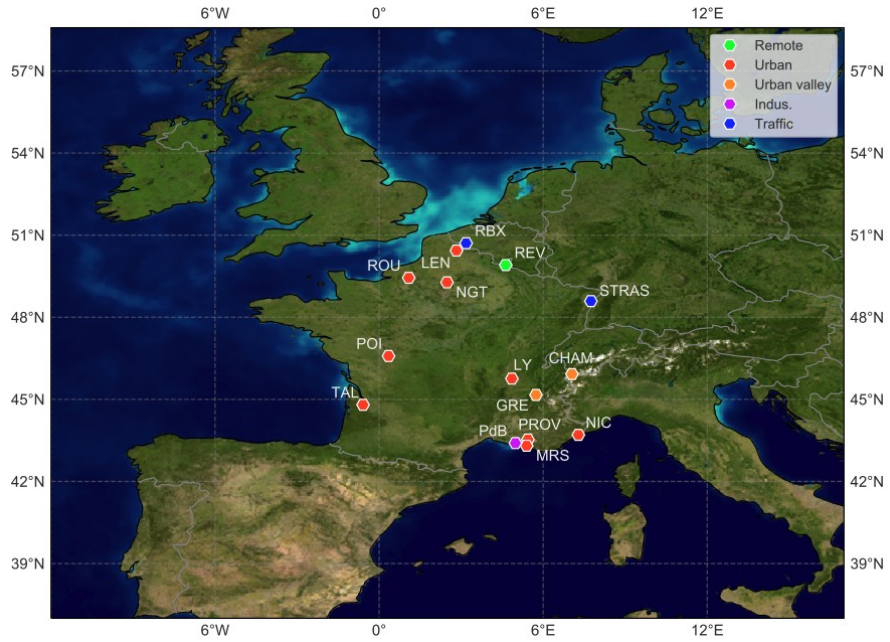
# Generalization – the SOURCES program




- SOURCES project
  - PMF at 15 sites
  - Between 2013 to 2016
  - Min 1 year, 1 every 3rd day
  - 2148 samples
  - Advance chemical speciation
  - Similarity assessment (deltaTool)
- + other programs

*Pernigotti & Belis, 2018*

*Results →* *http://pmsources.u-ga.fr/*

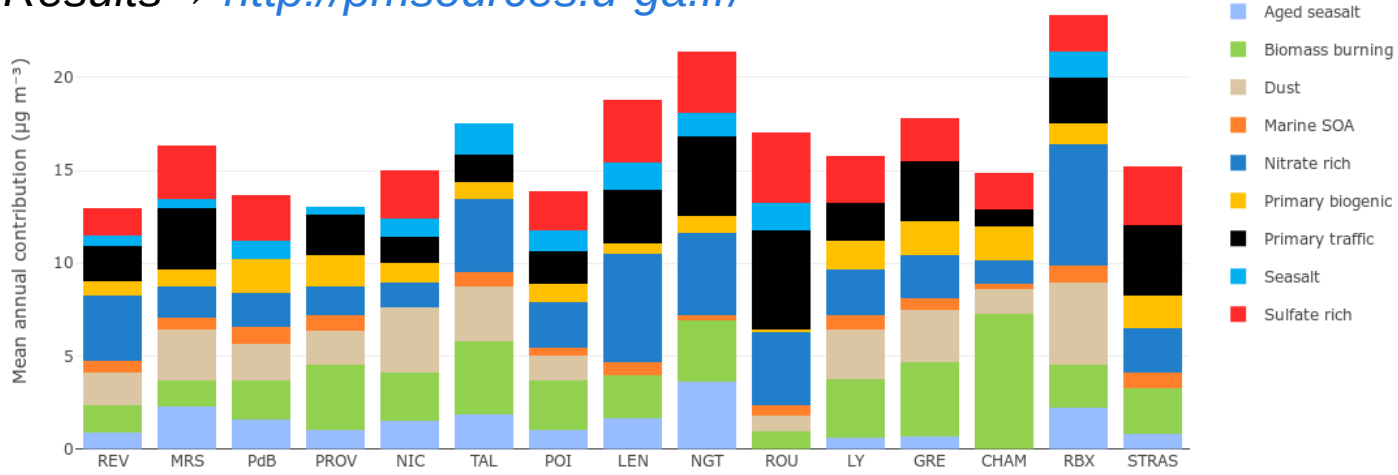



**Fig. 1:** Annual mean contribution of the differents main PM factors in µg m⁻³.

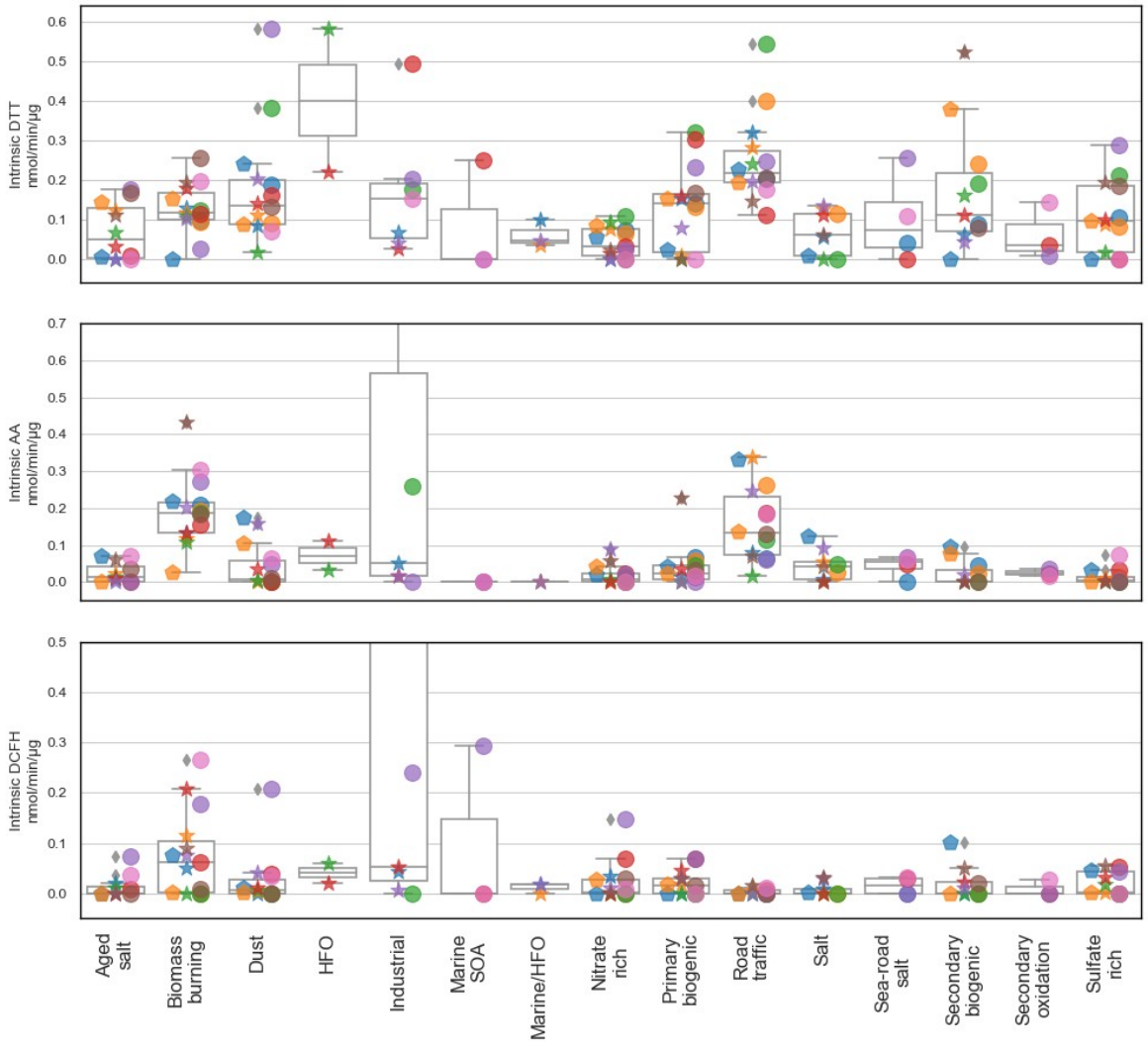
**Are sources' intrinsic OPs stable at regional scale?**

**What are the sources' contributions to OPs?**

**15 PMF, comparison, uncertainties, similarity assessment:** Weber et al 2019, Atmosphere https://doi.org/10.3390/atmos10060310

# Generalization – synthesis of intrinsic OP (OPi)

**Intrinsic OP** (= OP/µg of PM) → "toxicity" of the source



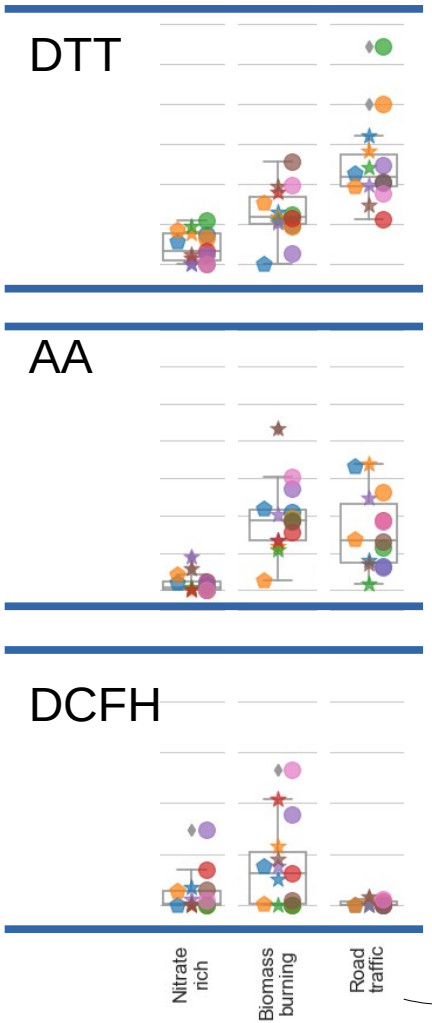

- 3 tests with different reactivities
  - OP DTTv: more homogeneous.
  - OP AAv: BB & traffic.
  - OP DCFHv ???
- Low dispersion within a given source (most of the time).
  - **Geochemical sens**
  - ≠ to investigate (chemistry?)

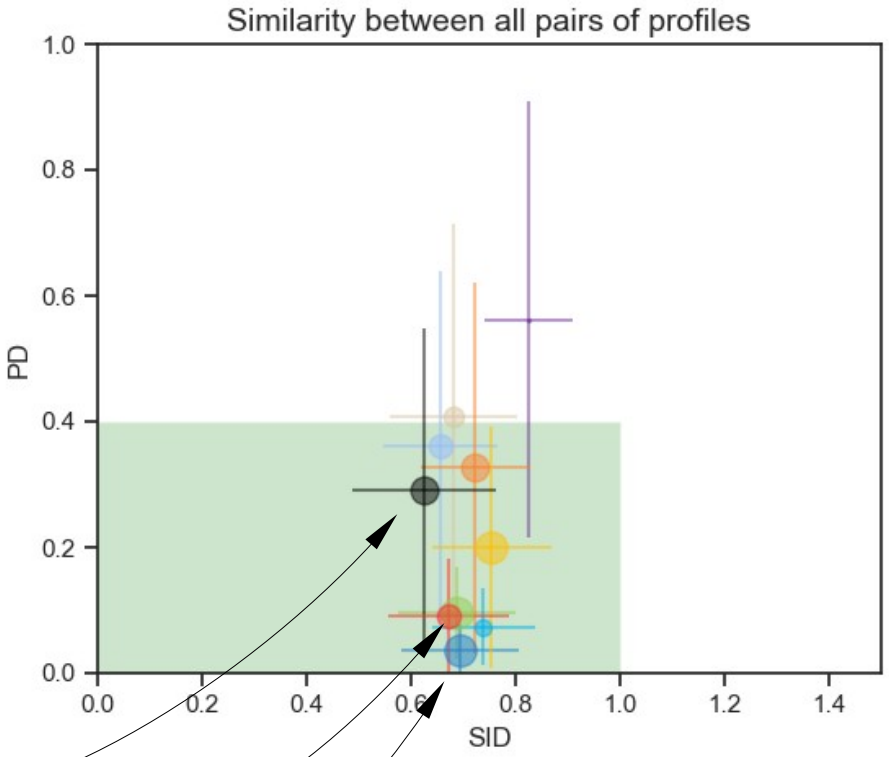
At a national scale, aerosols sources present different reactivities.

*Weber et al, 2019. in prep...*

# Generalization – sources OPi vs. sources chemical variability

High variability of intrinsic OP for the road traffic. Why?




Hypothesis :

Traffic = wide chemistry…

→ direct/indirect emissions

→ strong & fast reactivity: f(d, hν, …)

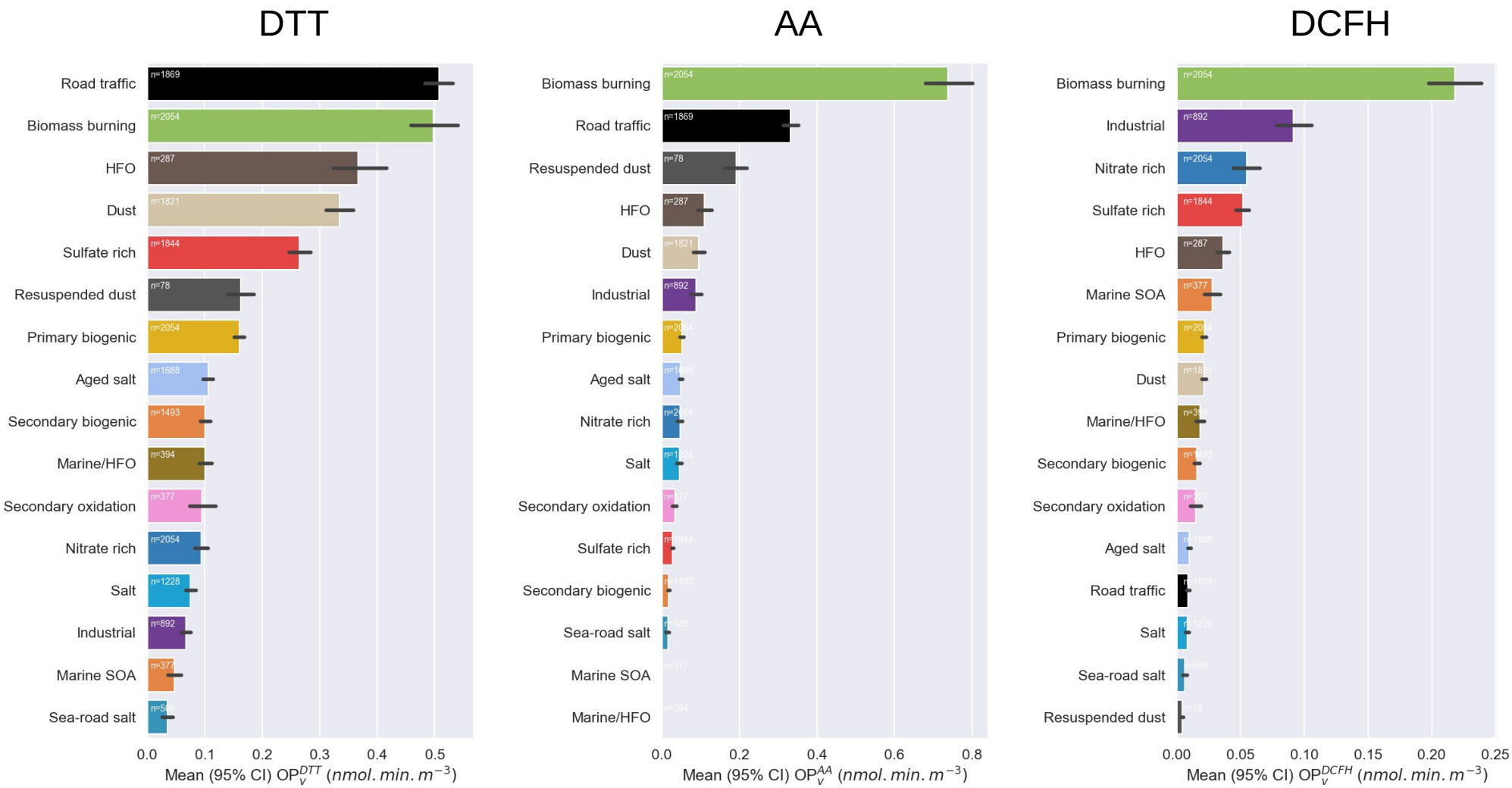
→ fine & coarse

→ …

- **Road traffic**
  ≠ chemistry ↔ ≠ OP
  Ok
- **Nitrate rich**
  = chemistry ↔ = OP
  Ok
- **Biomass burning**
  = chemistry ↔ ~≠ OP
  ?

## Generalization – mean contribution of sources to OP

Err. Bars: 95 % CI mean 15 sites




- **3 tests – 3 results**: DTT ~homogeneous, AA BB++ (& traffic), DCFH BB (& industrial / ø traffic)
- Some local sources contribute significantly to OP (HFO, Industrial)
- $OP^{DTT}$: Importance of PBOA & SOA / Nitrate rich barely contribute
- Important differences. Which one is “the best”???

## Conclusion & perspectives

- Unique database of **coupled** advanced **chemistry and OP** measurements
  - >130 species (carbonaceous, ions, metals, organics…)
  - 3 OP assays (DTT, AA, DCFH), isomass, using simulated lung fluid

*Calas, 2017*

*Calas et al, 2019, submitted*

- Detailed **source-apportionment study** (15 sites, still ongoing)
  - SOURCES program: *http://pmsources.u-ga.fr*

*Weber et al, 2019, atmosphere*

- Development of **OP source-apportionment** based on PMF results

*Weber et al, 2018, ACP*

- Application at the national scale
  - Novel view of aerosols
  - **Redistribution of the sources contribution**

*Weber et al, 2019, in prep*

## What's next?

- Need to understand intrinsic OP variability for some sources
- What OP assays is "the best"? → Epidemiology & toxicology
- Toward OP in CTM

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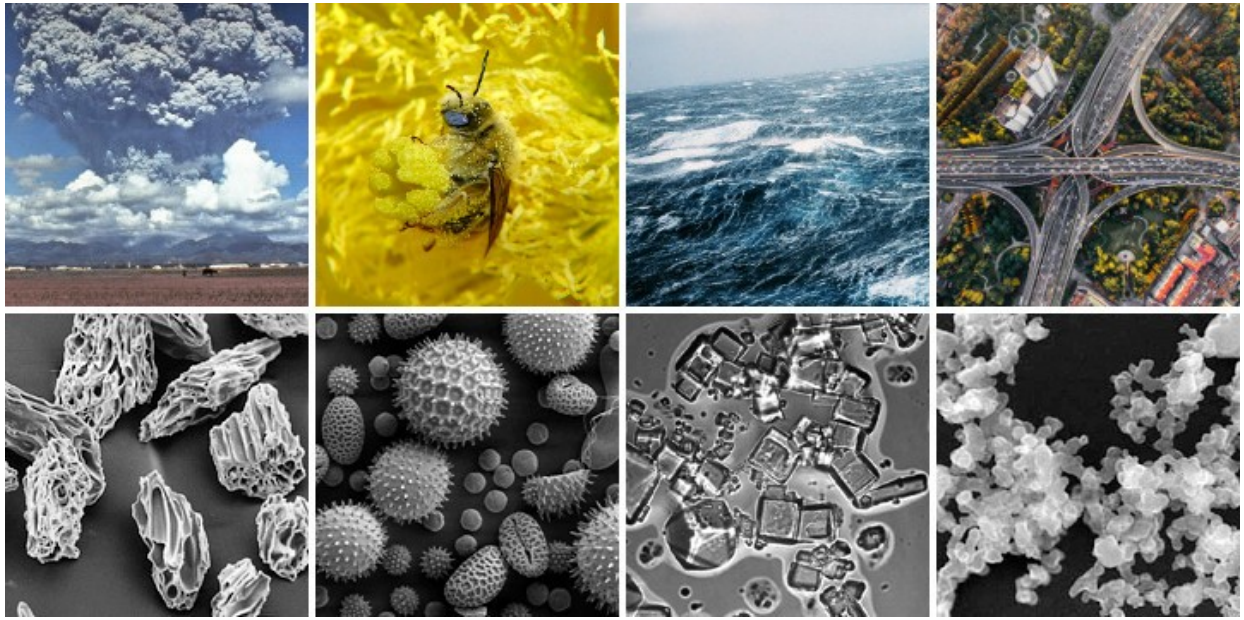
# Thank you for your attention!

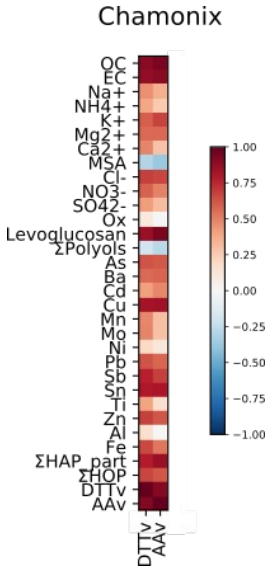
*...and to all the people who made it possible.*



## State of the art

- Different a-cellular OP measurements (mostly DTT, AA, DCFH)
- Univariate statistic (correlation)
  - DTT: balanced between metals & organics
  - AA sensible to metals & OC

**But correlation is not causality (levo, $NO_3^-$…).**
We need multivariate approaches.




- Multivariate statistic (ACP, k-means, MLR…)
  - Few studies with source-apportionment (*see review Bates et al, 2019*)
  - Rapid increase in past few years (Verma et al, 2014 ; Bates et al, 2015 ; Fang et al, 2016 ; Ma et al, 2017…)
  - Mostly focused on BB and traffic: chamber measurement & field sampling

**However:**

There is a **need** of **long time monitoring** together with assessment of the **diversity of sources** and investigation the **spatial variability**.

## Toward spatio-temporal model and prediction

- WIP: Use of source-tracking CTM (LOTOS-EUROS)
- Confrontation CTM / PMF