Harmonized methodology for the source apportionment of PM in France using EPA-PMF5.0 with constraints

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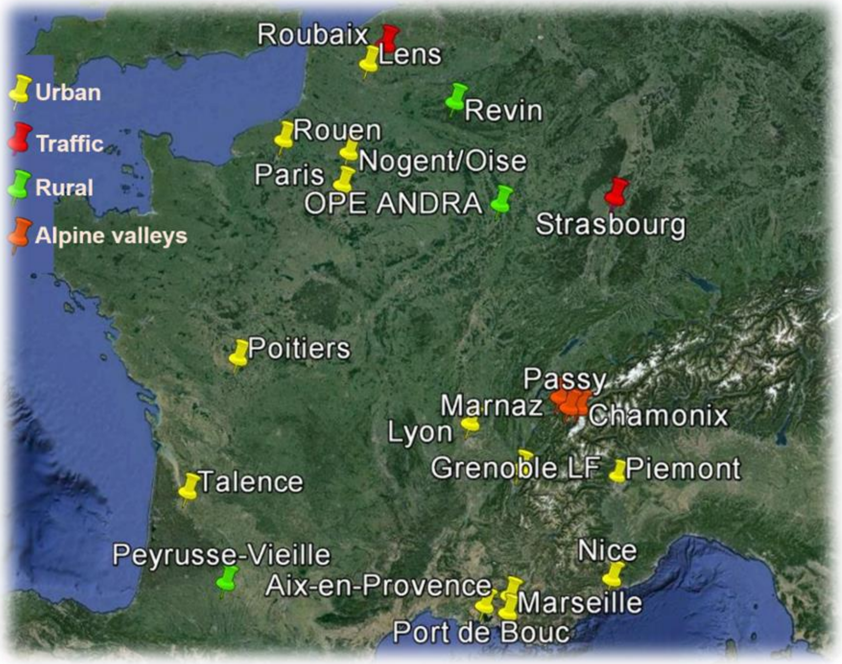
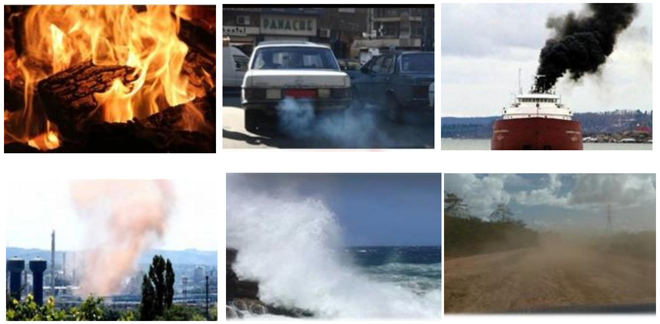
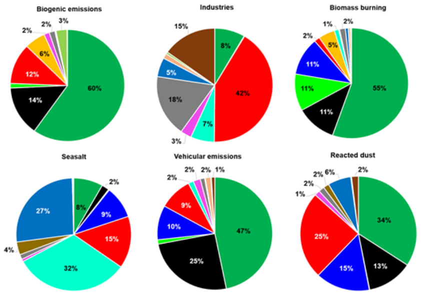
INERIS
maîtriser le risque pour un développement durable

LCME

MINES Douai







FAIRMODE technical meeting, 27-29 June 2016

Outlines

❑ Presentation of the SOURCES project

- ✓ Context, objectives
- ✓ Spatial distribution and characteristics of the sampling sites
- ✓ PM source apportionment methodology
    - ➢ **Selection of input variables**
    - ➢ **Uncertainty estimation** of the variables
    - ➢ PMF5.0 with **constraints**: target species in factor profiles

❑ Ongoing works (innovative methods)

- ✓ Analysis of **new tracers** (e.g. nitrocatechols, cellulose, BSOA,…)
- ✓ **Coupled methodologies (with PMF):** N isotopes; ^{14}C; online AE-33; back trajectories; oxidative potential (OP) of PM

SOURCES project

❑ Objectives of SOURCES project (2015-2018)

Determination of a standard and harmonized methodology for quantifying PM sources at different French urban environments using EPA-PMF5.0 with constraints

✓ **PM sampling sites (n=20):**
- 12 urban (yellow mark)
- 2 traffic: Roubaix, Strasbourg
- 3 rural: Revin, Peyrusse, OPE ANDRA
- 3 alpine valleys: Passy, Marnaz, Chamonix

✓ Generally, 24h PM samples were collected every third day (at least 120 filters/year)

✓ **Detailed PM chemical speciation:**
- OC and EC
- Ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+})
- Metals/trace elements (Al, Ca, Fe, K, As, Ba, Cd, Co, Cu, La, Mn, Mo, Ni, Pb, Rb, Sb, Sr, V)
- Common organic markers: levoglucosan, mannosan, galactosan, arabitol, mannitol, sorbitol, MSA, oxalate

SOURCES project

❑ Objectives of SOURCES project (2015-2018)

Determination of a standard and harmonized methodology for quantifying PM sources at different French urban environments using EPA-PMF5.0 with constraints

1. Homogeneous and harmonized PMF pre-treatment of PM comprehensive chemical dataset (OC, EC, ions, metals, and organic markers) established at various urban environments in France:

- Selection of input variables
- Estimation of the uncertainties

2. Integration of an homogeneous and minimal set of specific chemical constraints to the factor profiles based on external knowledge:

- Improve separation of correlating sources
- “Cleaner” source profiles and better estimation of their contributions

3. Geographical origin of main PM sources (PSCF approach: associating PMF temporal contributions with air mass back trajectories)

4. Integration of the resolved source profiles with constrained PMF approach at the different studied sites into SPECIEUROPE database

PMF methodology

1. Selection of input variables

- Classic PMF inputs: OC, EC, and inorganic components, i.e. metals (Al, Ca, Fe, Ti, V, Ni, Cu, Zn, As, Rb, Pb, Cd, Sn, Sb), and major ions (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Mg^{2+})

- Very few studies involving organic markers

- **Extensive PMF input data matrix**: Classic PMF inputs + additional **organic markers**:
  - **Levoglucosan** (biomass burning)
  - **Polyols** (sum of arabitol, mannitol, sorbitol; primary soil biogenic)
  - **MSA** (marine biogenic, phytoplankton?)
  - **Oxalate** (secondary organic indicator)
  - **PAH** (combustion processes)
  - **Hopanes** (fossil fuel combustion, e.g. vehicular emissions)
  - **Lignin pyrolysis products** (vanillin, coniferaldehyde, vanillic acid…)

- Input variables were selected based on the percentage of values above the detection limit (DL) and the signal-to-noise (S/N) ratios (focus on common species)

PMF methodology

2. Estimation of the uncertainties (literature)

- No standardized methodology is supplied for the treatment of uncertainties

- Commonly used methods (JRC report, 2013):

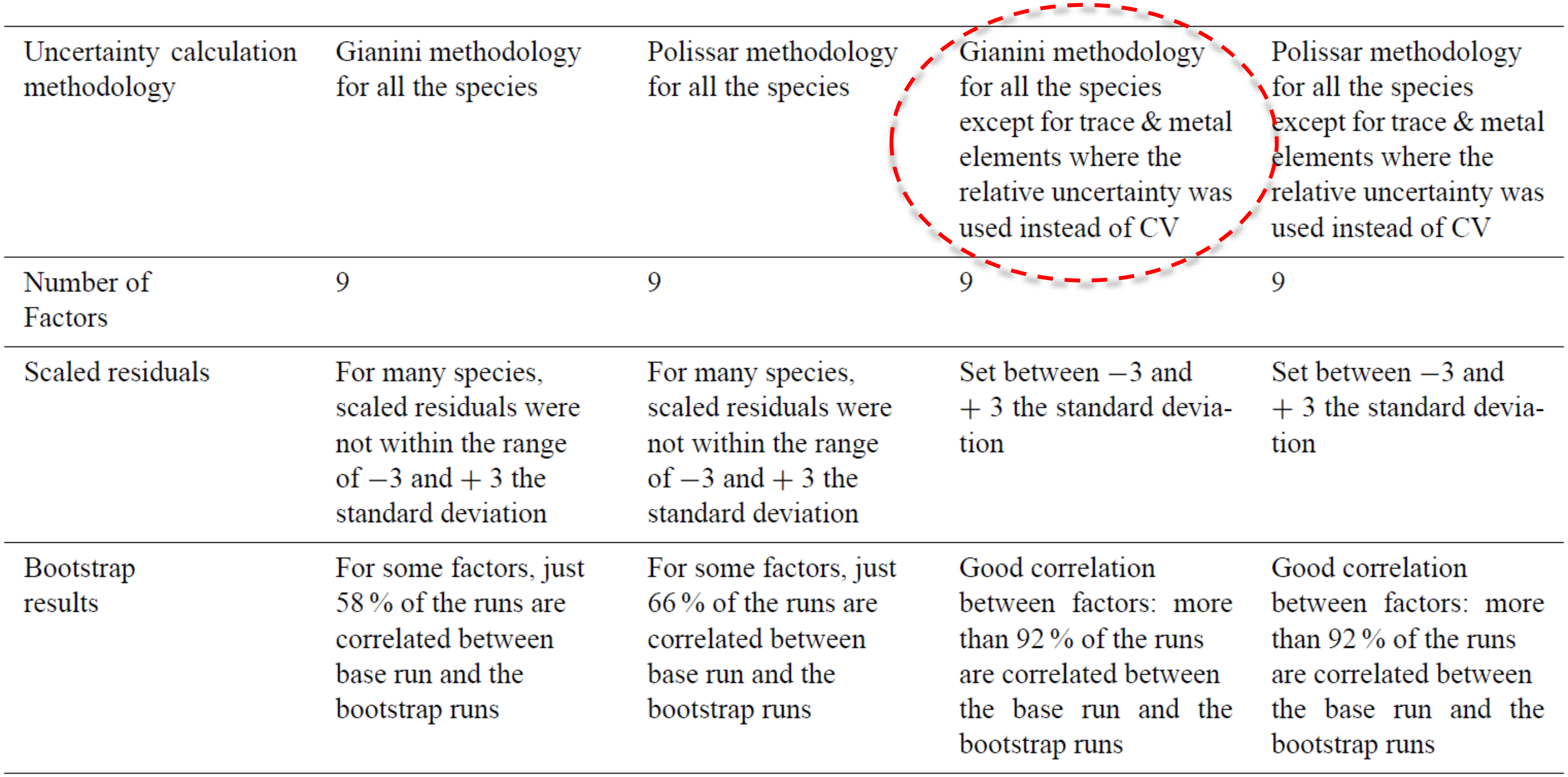
  - **Polissar et al. (1998)** set the uncertainty of values below the detection limit to 5/6 of the detection limit, while the uncertainty of missing values is set at four times the geometric mean

  - **Gianini et al. (2012)** and adapted from Anttila et al. (1995). It uses the detection limit (DL, twice of the standard deviation of the field blanks) and the coefficient of variation (CV, standard deviation of repeated analysis divided by the mean value of the repeated analysis).

PMF methodology

2. Estimation of the uncertainties (LGGE, Waked et al., 2014)

- Previous tests for the uncertainties assessments were performed at LGGE by Waked et al. (2014) (Lens dataset 2011-2012)



Uncertainty calculation methodology	Gianini methodology for all the species	Polissar methodology for all the species	Gianini methodology for all the species except for trace & metal elements where the relative uncertainty was used instead of CV	Polissar methodology for all the species except for trace & metal elements where the relative uncertainty was used instead of CV
Number of Factors	9	9	9	9
Scaled residuals	For many species, scaled residuals were not within the range of −3 and + 3 the standard deviation	For many species, scaled residuals were not within the range of −3 and + 3 the standard deviation	Set between −3 and + 3 the standard deviation	Set between −3 and + 3 the standard deviation
Bootstrap results	For some factors, just 58 % of the runs are correlated between base run and the bootstrap runs	For some factors, just 66 % of the runs are correlated between base run and the bootstrap runs	Good correlation between factors: more than 92 % of the runs are correlated between the base run and the bootstrap runs	Good correlation between factors: more than 92 % of the runs are correlated between the base run and the bootstrap runs

►►Simulation with the Gianini methodology and the relative uncertainty for trace elements was selected

PMF methodology

2. Estimation of the uncertainties (SOURCES project)

- **Trial and error tests** to define a common methodology for the estimation of data uncertainty of all the species (OC, EC, ions, metals/trace elements and organic markers)

- **Current tests** for the optimization of uncertainty estimation using Gianini methodology, 3 sites were chosen: urban, traffic and rural

$$\sqrt{(DL)^2 + (x_{ij} \times CV)^2 + (x_{ij} \times \boldsymbol{a})^2}$$

- Objective: Define a variation range for the **a** coefficient depending on the type of analysis (a=0.03 by default)

- Evaluation of different **statistical parameters** (best model fit):
  - ✓ Signal-to-Noise (S/N) ratios
  - ✓ Variation of Q_{true}-to-Q_{robust} ratios
  - ✓ Coefficients of determination (R^2)
  - ✓ Bootstrap and DISP results
  - ✓ Interpretability of the obtained factor profiles
  - ✓ Distribution of scaled residuals

PMF methodology

3. EPA-PMF5.0 with constraints

- PMF results are generally affected by co-linearity induced by processes other than co-emissions (e.g. seasonality, meteorological parameters), providing mixed factors

- To minimize the influence of mixing between factors, additional environmentally and meaningful chemical constraints can be imposed in the factor profiles

Objective:

- Define and apply a set of **minimal constraints** that are able to provide optimal results across the different studied sites

- Generally, the use of constraints allows obtaining:
  - Better separation of the factors with more “cleaner” source profiles
  - Better estimation of the source contributions
  - Better bootstrap results

PMF methodology

3. EPA-PMF5.0 with constraints

Minimum set of specific and plausible chemical constraints imposed to elements in factor profiles mostly identified in recent PMF studies in France

(e.g. CAMERA, Part'Aera, Decombio, etc.,)

PMF factors	Levo /Manno	Lignin products	PAH	Hopanes	Polyols	MSA	EC	Cl/Na, K/Na, Ca/Na, Mg/Na (0.119)
Biomass burning	Pull up maximally	Pull up maximally						
Vehicular exhaust	= 0	= 0		Pull up maximally				
Biogenic emissions	= 0	= 0	= 0	= 0	Pull up maximally		Pull down maximally	
Marine biogenic	= 0	= 0	= 0	= 0	Pull down maximally	Pull up maximally	Pull down maximally	
HFO combustion	= 0	= 0			= 0	= 0		
Industries								
Coal burning					= 0	= 0		
Seasalt								Ratios sea salt
Aged seasalt								
Mineral dust								
Road dust								
Nitrate rich								
Ammonium rich								
Secondary organics/ Secondary processes								

PMF methodology

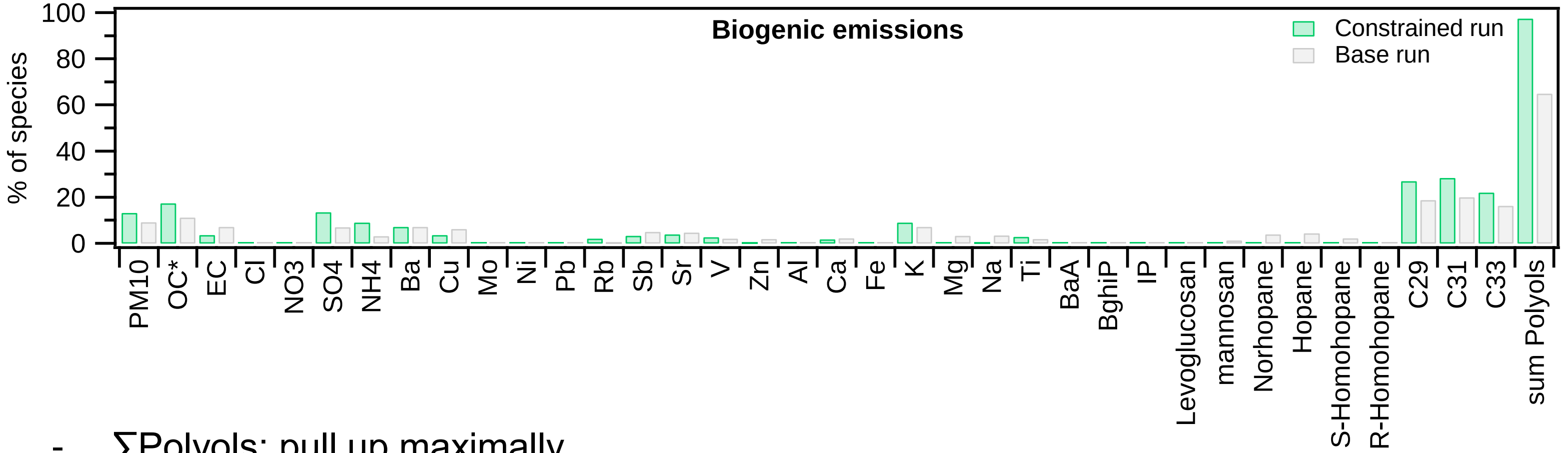
3. EPA-PMF5.0 with constraints

Minimum set of specific and plausible chemical constraints imposed to elements in factor profiles mostly identified in recent PMF studies in France

(e.g. CAMERA, Part'Aera, Decombio, etc.,)

Sampling site: Lens (2011-2012), IE

Biogenic emissions factor: Constrained vs. base run



- ∑Polyols: pull up maximally
- EC: pull down maximally
- Bootstrap from 95 to 100%
- Contribution of this factor increased from 13 to 16%

Innovative approaches

❑ Measurements of new tracers

➢ Cellulose $(C_6H_{10}O_5)_n$ (LGGE, Picot P)

- Following the procedure of *Kunit and Puxbaum (1996):*
  - Double enzymatic hydrolysis
  - Analysis of glucose (=analyte) by HPLC-PAD

- Grenoble, University campus (May-July 2015)
  - OC: 4.9 µgC/m^3 (2.42-8.08 µgC/m^3)
  - Cellulose: 108 ngC/m^3 (25-447 ngC/m^3)

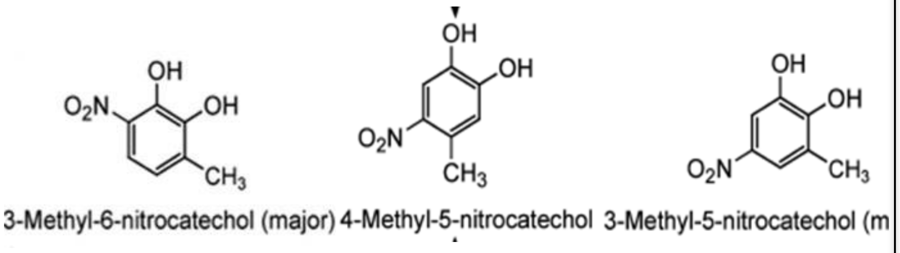
    →→ 2% of OC on avg.

- Analysis of samples from Estonia (collaboration with PSI)

➢ Nitrocatechols (LCME, Besombes J-L)

- Biomass burning SOA tracer (*m-cresol*)
- GC/MS after derivatization

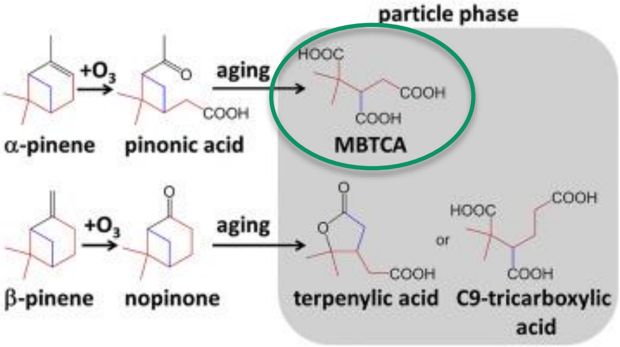
<u>ΣMNC = methyl-nitrocatechol isomers</u>



<u>Alpine valleys:</u>

- Lanslebourg (winter): 26 ng/m^3 (0-85 ng/m^3)
- Passy (winter): 20 ng/m^3 (0-76 ng/m^3)

➢ Biogenic SOA tracer : 3-MBTCA (intercomparison proposed in ACTRIS-2)



(Sato et al., 2016, AE)

MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid

- Formed from the oxidation of α-pinene
- More highly functionalized than traditional SOA markers such as pinonic and pinic acid

- Muller et al. (2012): MBTCA explains about 10% of the newly formed SOA mass (experimental yield about 0.6 %)

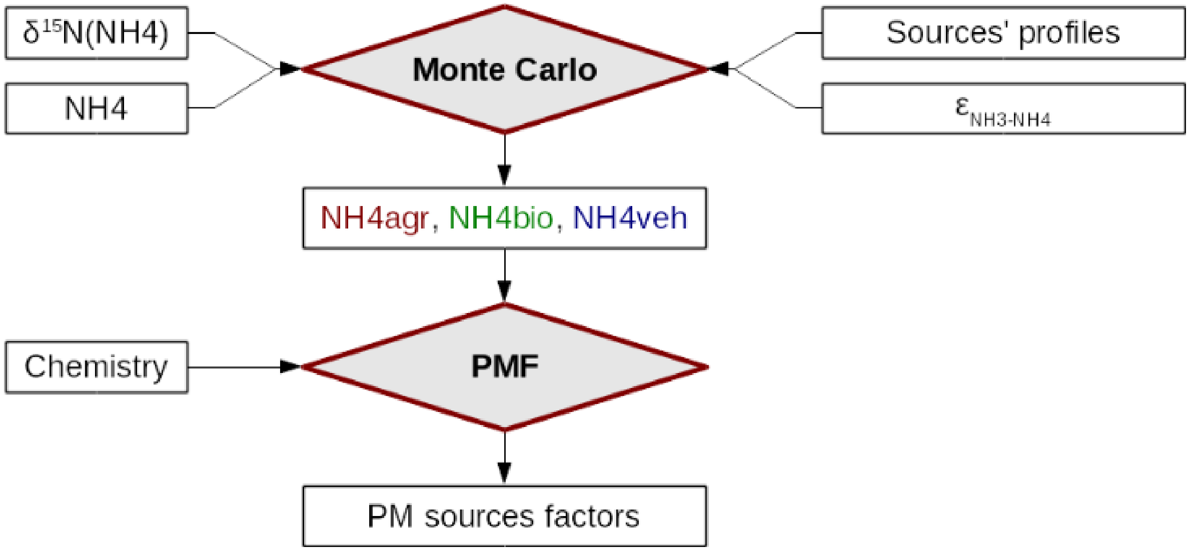
Innovative approaches

❑ Coupled methodologies in development

- **N isotopes with PMF (LGGE, S Weber et J Savarino)**

- Use of Nitrogen isotope ratios to elucidate the primary sources of ammoniac

1. **Monte Carlo simulation (stochastic model)**
   - Determination of $NH4_{bio}$; $NH4_{agr}$; and $NH4_{veh}$
2. **PMF analysis**
   - Input data matrix combining **PM chemical** measurements (e.g. OC; EC; ions; metals) and **isotopy** ($NH4_{bio}$; $NH4_{agr}$; and $NH4_{veh}$)



$\delta^{15}N(NH4)$

NH4

Monte Carlo

Sources' profiles

$\varepsilon_{NH3\text{-}NH4}$

NH4agr, NH4bio, NH4veh

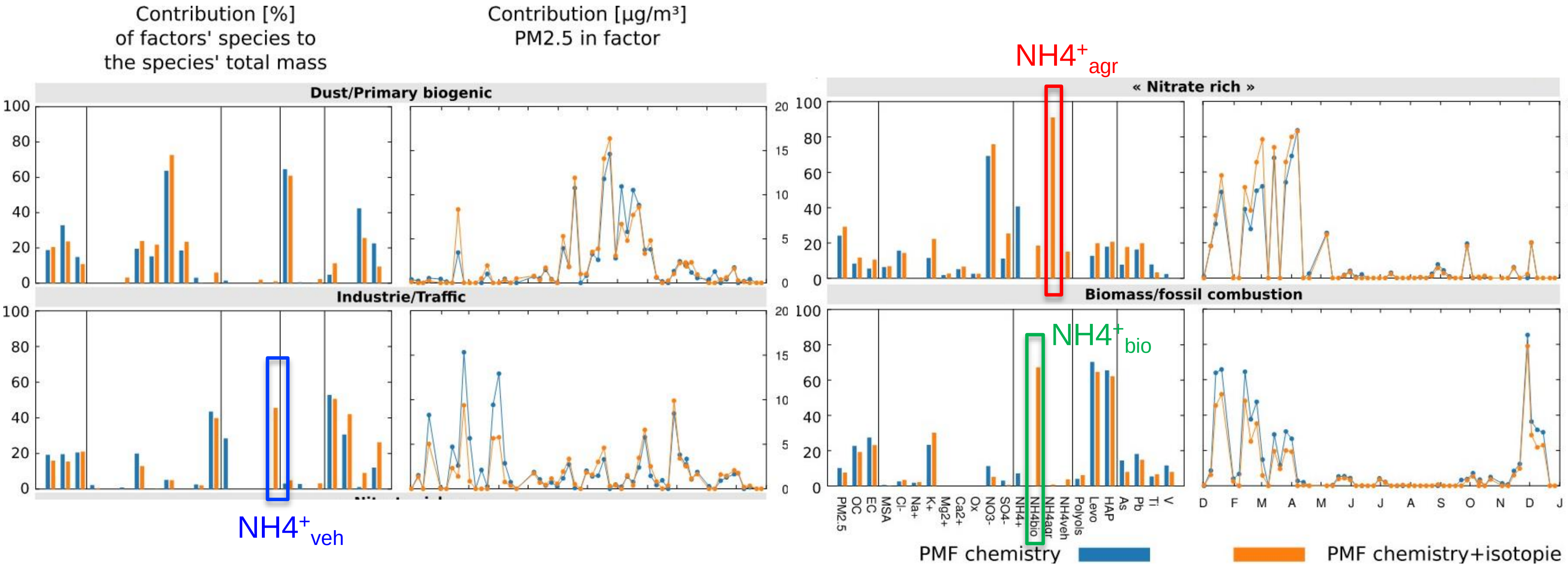
Chemistry

PMF

PM sources factors

Innovative approaches

Sampling site : OPE ANDRA, rural site, 2013 PM and N isotopes data



- Ammonium fractions were relevantly apportioned to their corresponding sources, i.e. nitrate rich (90% of $NH4^{+}_{agr}$); biomass (70% of $NH4^{+}_{bio}$); and Industry/traffic (50% of $NH4^{+}_{veh}$ mass)
- Total ammonium concentrations were well reconstructed by the model

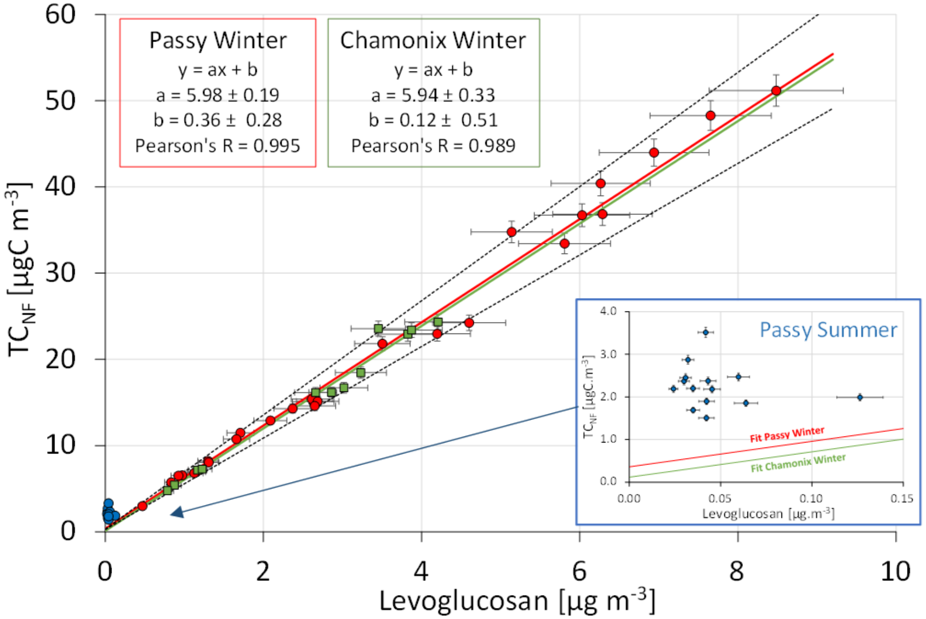
Innovative approaches

❑ Other coupled methodologies in development

➢ Radiocarbon ^{14}C (E Bard, CEREGE)

Passy and Chamonix, Alpine sites, winter

TC_{NF} values against levoglucosan



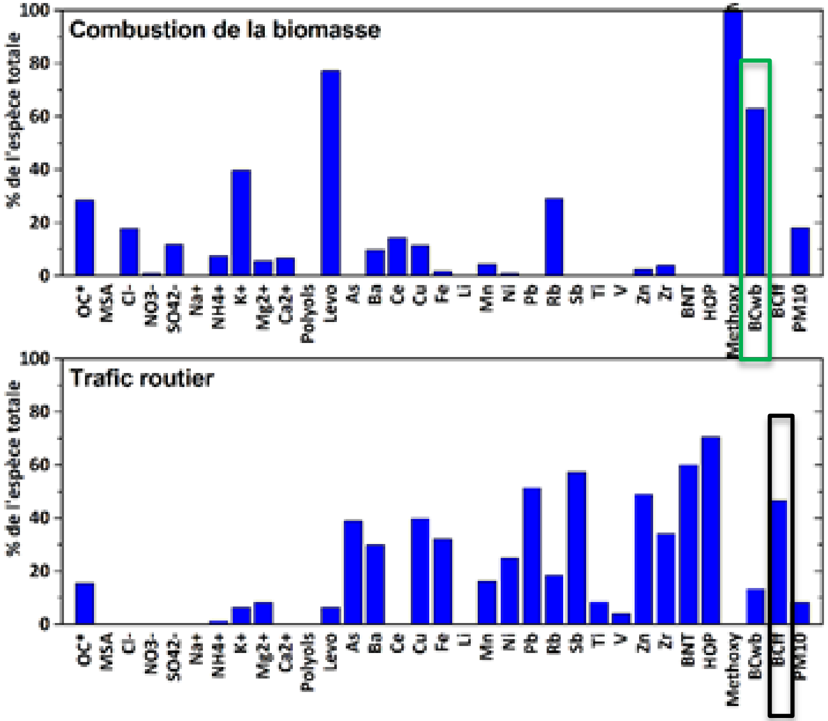
Bonvalot et al. (2016), ACPD

- ✓ High correlation coefficients for Passy (0.995) and Chamonix (0.989)
- ✓ Non fossil fraction represents between 80-90% of total carbon for winter samples ↔↔ dominance of biomass burning
- ✓ Coupling ^{14}C with ME-2 (*PhD A Sylvestre, LCE Marseille*)

➢ Online AE-33 measurements and PMF

Chamonix, Alpine site, 2013-2014

Use of BCff and BCwb variables instead of EC



PhD F Chevrier (LCME, LGGE)

- ✓ Relevant geochemical distribution of BCwb and **BCff**

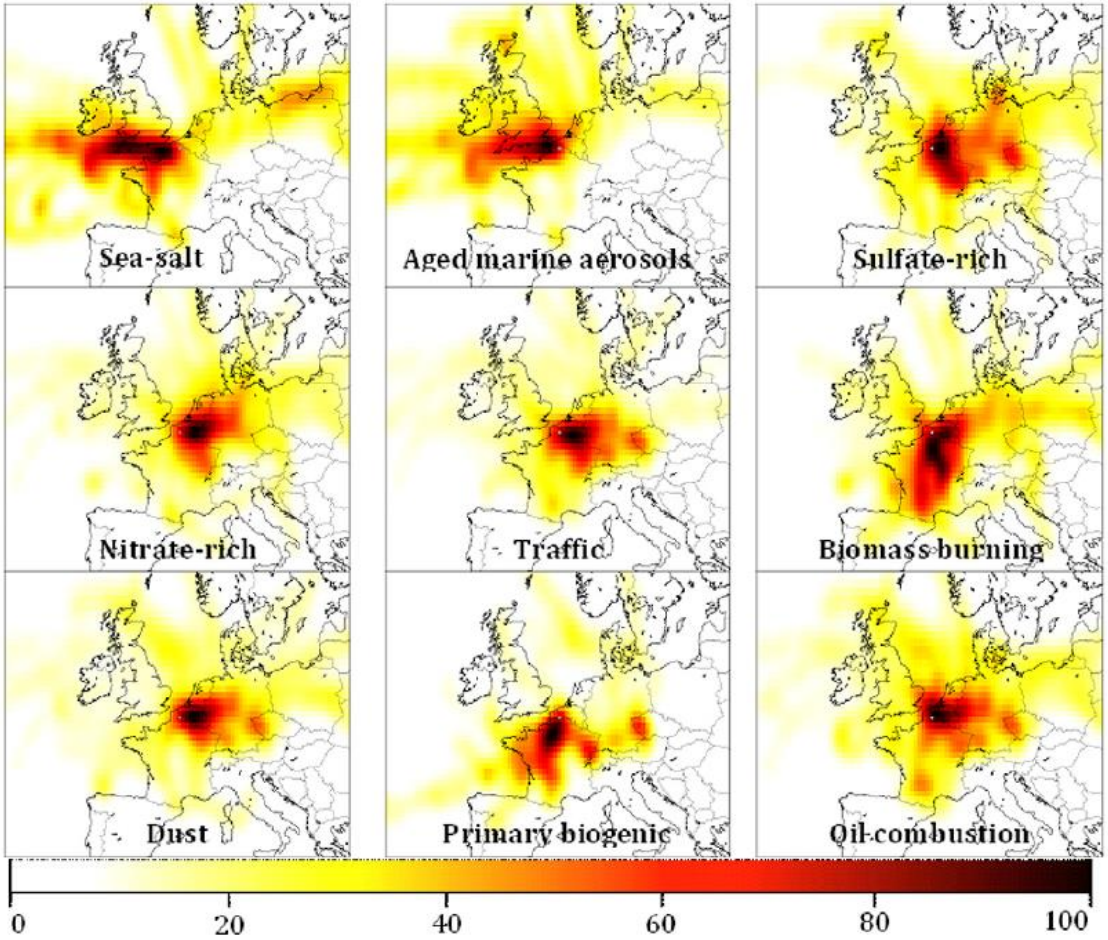
Innovative approaches

❑ Other coupled methodologies in development

➢ PSCF (Potential Source Contribution Function) approach

- PSCF represents the probability that an air parcel may be responsible for high concentrations measured at the receptor site

- Allows geographical identification of potential emission areas by associating temporal contributions of PMF factors with back trajectories (Ashbaugh et al., 1985)



Waked et al. (2014), ACP

Innovative approaches

❑ Other coupled methodologies in development

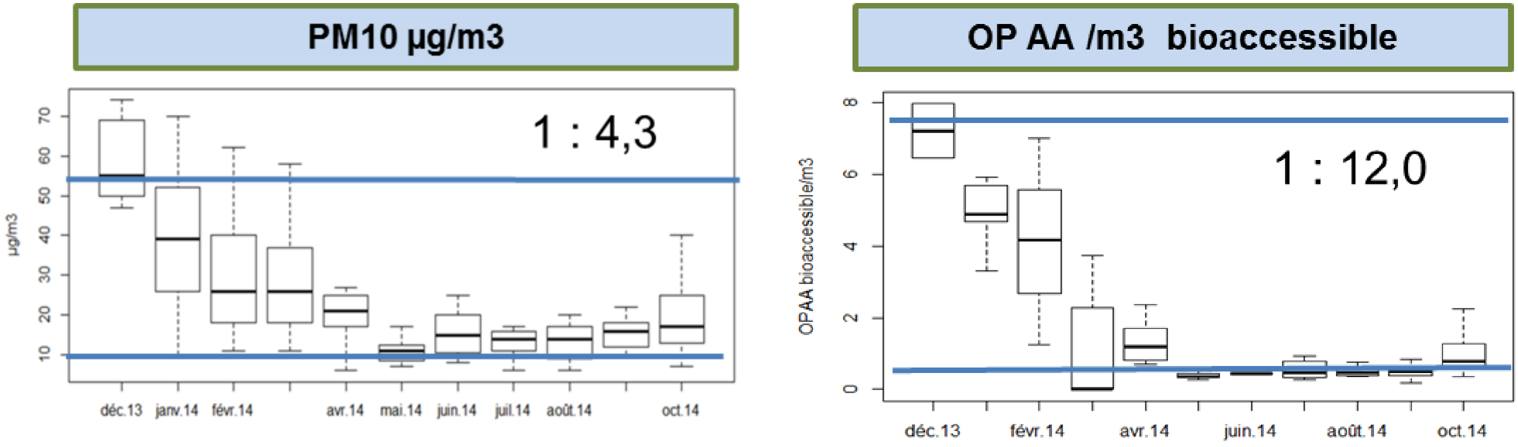
➢ Measurements of the oxidative potential (OP) of PM (LGGE, Uzu G)

OP: capacity of Particulate Matter (PM) to oxidize target molecules

- Different assays exist for measuring OP

- Trying to relate the variability of OP to chemistry and emission sources
- OP already measured on 5 yearly series of SOURCES *(PhD A Calas, LGGE)*

Results from Passy (A-cellular assays; ascorbate acid depletion (AA))



PM10 µg/m3

OP AA /m3 bioaccessible

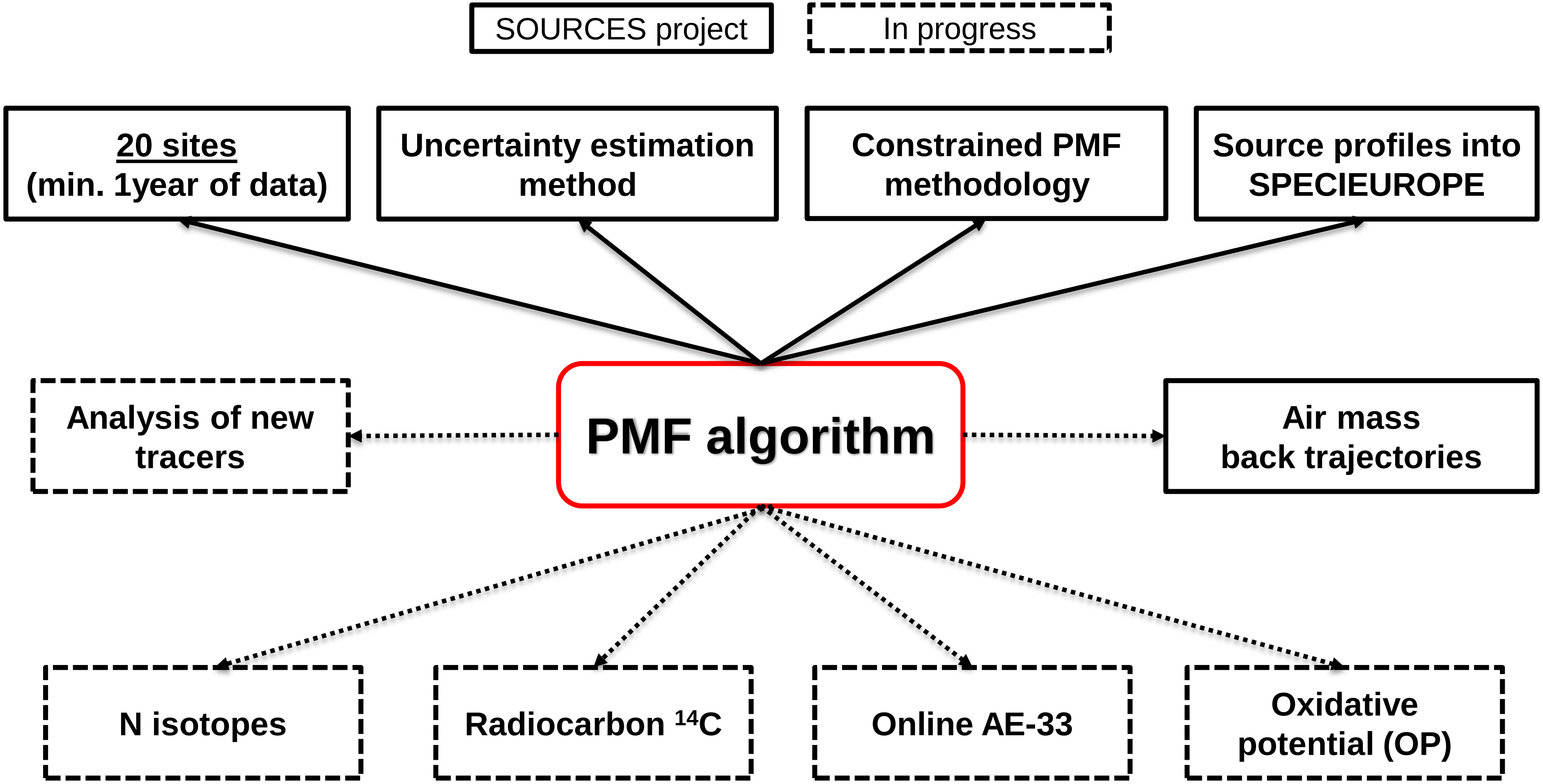
Calas et al., 2016 (in prep)

- PM10 concentrations vary by a factor of 4 (annual avg.)
- OP AA vary by a factor of 12 (annual avg.)

Conclusions, Open questions

Objective:

Determination of a standard and harmonized methodology for quantifying PM sources at different urban French environments using EPA-PMF5.0 with constraints



SOURCES project

In progress

20 sites
(min. 1year of data)

Uncertainty estimation method

Constrained PMF methodology

Source profiles into SPECIEUROPE

Analysis of new tracers

PMF algorithm

Air mass back trajectories

N isotopes

Radiocarbon ^{14}C

Online AE-33

Oxidative potential (OP)

Acknowledgment

SOURCES

- Funding : ADEME (postdoctoral grant for Dalia Salameh)
- O Favez (INERIS, Coord)
- JL Jaffrezo (LGGE)

INACS (N isotopes)

- Funding : ADEME
- JL Jaffrezo (Coord)
- J Savarino (LGGE)
- S Weber (LGGE)
- O Favez (INERIS)

New tracers

- Nitrocatechols :
  - JL Besombes (LCME)
- Cellulose and MBTCA :
  - V Jacob (LGGE)
  - B Golly (LGGE)

DECOMBIO (AE33)

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- JL Jaffrezo (Coord)
- G Mocnik (Aerosol d.o.o)
- F Chevrier (PhD LGGE / LCME)
- JL Besombes (LCME)

Oxidative potential of PM

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- G Uzu (LTHE / LGGE)
- A Calas (PhD LTHE / LGGE)
- JL Jaffrezo (LGGE)

Thank you for your attention

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