Developments of PMF studies using various tracers on off-line measurements

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(LGGE, Grenoble)

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(INERIS / LCSQA, Verneuil)

Meeting FAIRMODE OSLO, 28–29 April, 2014

Some points in this talk

- Biomass burning (levoglucosan)
- Marine biogenic emission (MSA)
- Biogenic (soil ?) emissions (polyols)
- Industrial / coal emissions ? (PASH)
- Tracers of SOA fraction ? (LMW Organic Acids)
- Ammonium Nitrate (Nitrogen isotopes)
- *Vehicular emissions* *(PAH, alcanes, hopanes / steranes)*

Analytical issue

A “complete” speciation on the same filter
(daily HiVol quartz filter)

Organic speciation

HPLC-PAD
GC-MS
HPLC-fluo
LC-MS
HPLC-UV-TOC

Isotopes

N, O, C

OC / EC
thermo-optical method

Anions / cations
Ionic chromatography

Trace metals
ICP-MS

- HPLC-PAD : sugars and polyols
- GC-MS (w/o derivatization) many organic families
- HPLC-fluo : HAP
- LC-MS : Low molecular weight organic acids
- HPLC-UV-TOC : HULIS
- *GC-IrMS ; AMS* *N,O, and C isotopes*

Studies in 5 rural sites

Yearly measurements during 2011-2013 (HiVol 1d /6)

Studies in urban sites

Studies coordinated by INERIS / LCSQA

LCSQA

Bordeaux

AIRAQ
Atmo Aquitaine

Lens

Atmo Nord - Pas de Calais
Surveillance de la qualité de l'air

Lyon

Air Rhône-Alpes

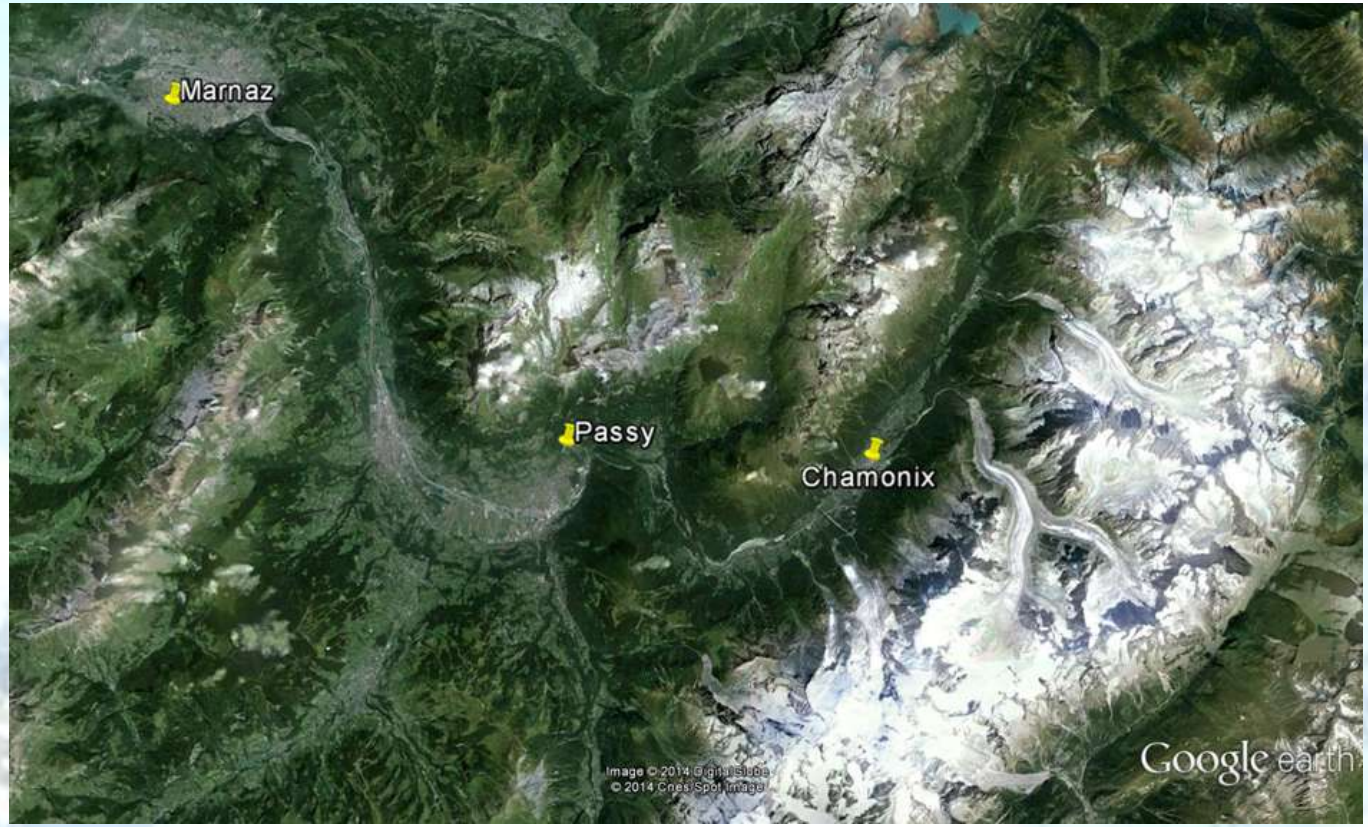
Yearly measurements in 2011-13 (HiVol 1d/3)

Other programs in Rouen, Paris, Nice, Fos-s-Mer, Aix en Provence, Turin

The programs in the Arve Vallée and Lanslebourg are funded by ADEME

Studies in the Arve Valley

Yearly measurements in 2013-14 (HiVol 1d/3) + AE33



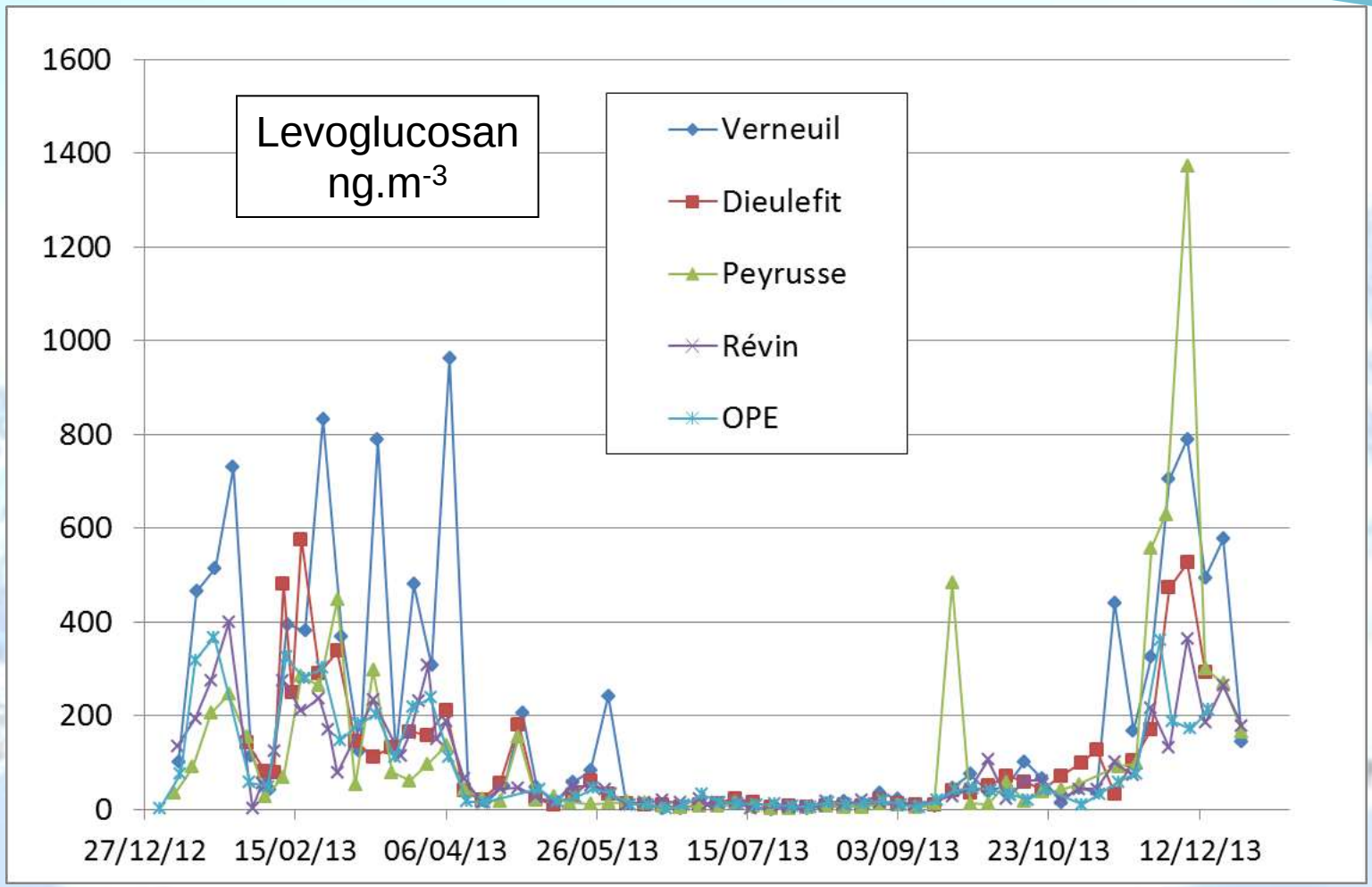
Program DECOMBIO (ADEME Primequal Predit)

Collab : LGGE, LCME, Air Rhône Alpes, Aerosol d.o.o,

In parallel with a large (eg 3 200 / 13 000) wood stove exchange program

Biomass burning tracer

Rural sites (2013)



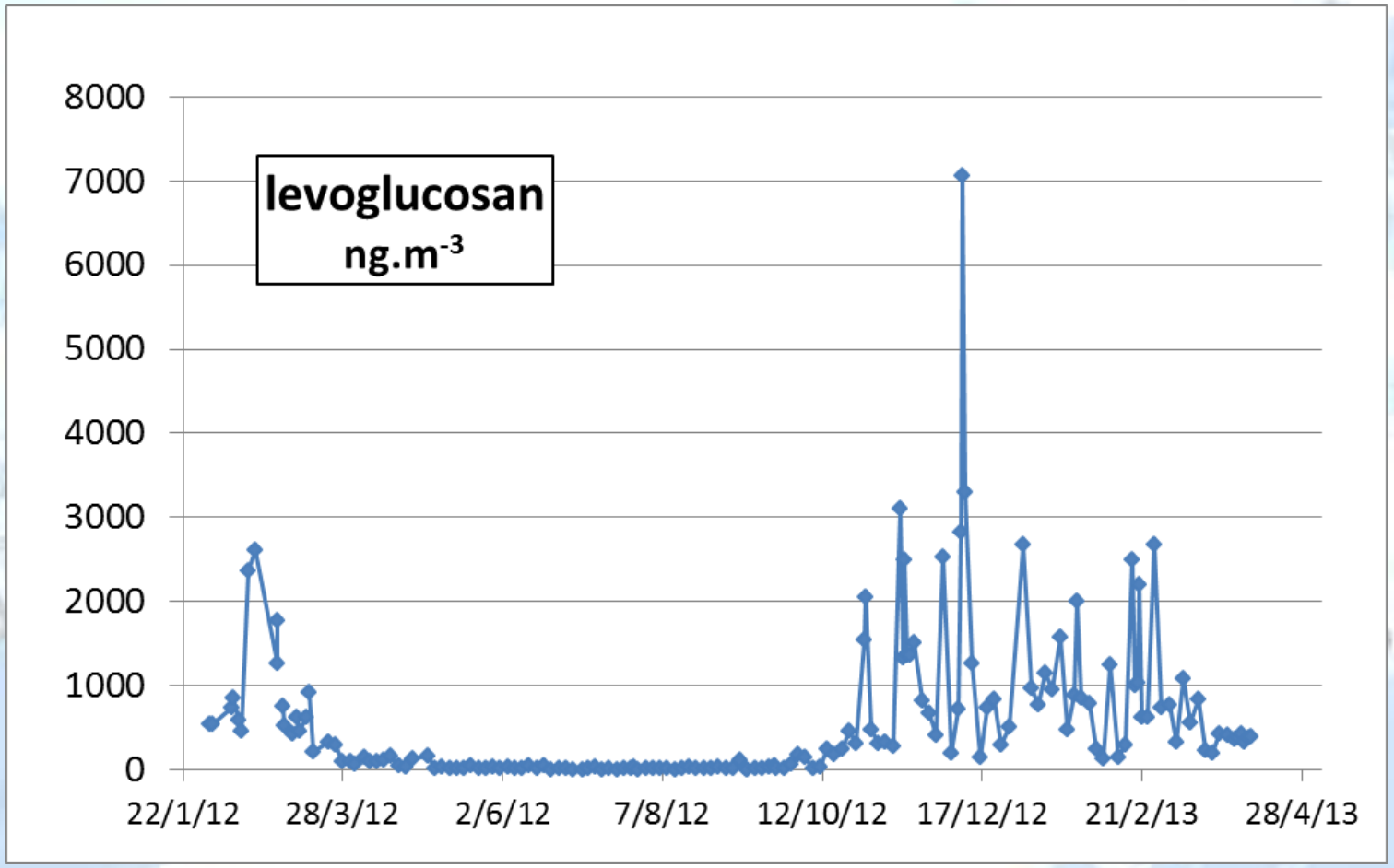
About 60 spls (1d/6)

- Concentrations of levoglucosan increase in winter
- Simultaneous episodes at all sites

Biomass burning tracer

1+ year study in Bordeaux

PMF study : 156 samples (1 d/3)



Biomass burning tracer

Species	Factors	Configurations
OC*, EC, SO_4, NO_3, NH_4, K, Mg, Cl, Na, Ca, MSA, Levoglucosan, As, Ba, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, Zn, ∑Polyols and PM_{10}	From 9 to 12 factors were tested. An optimized solution with 11 factors is obtained **(still in progress)**	PM_{10} taken as total variable, uncertainty method calculation as described in (Gianini et al., 2012)

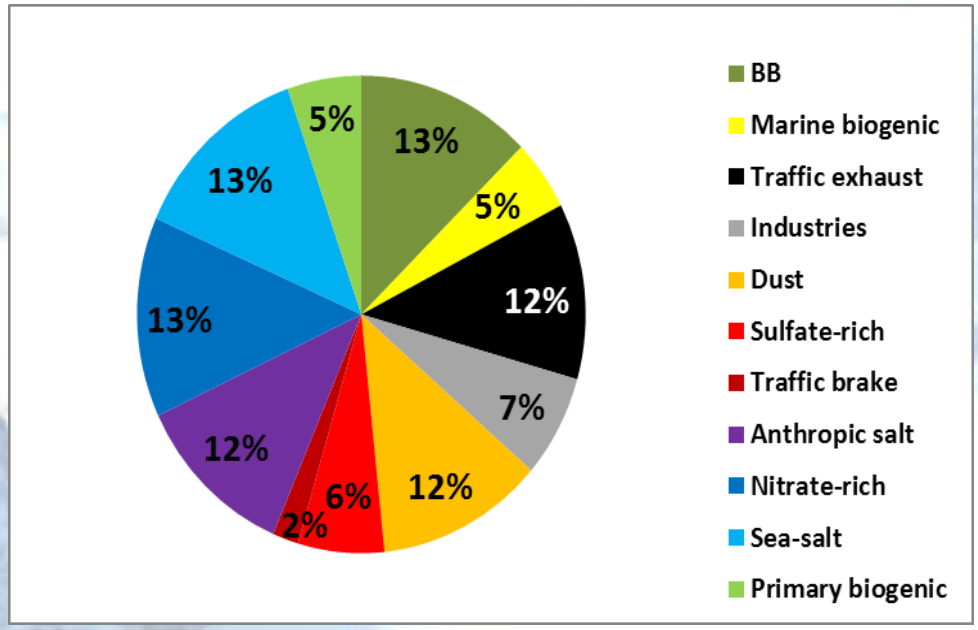
PMF 11 Facteurs			
Species	r^2	Species	r^2
OC	0.9	Cd	0.78
EC	0.9	Co	0.48
MSA	0.98	Cu	0.87
Cl	1	Fe	0.83
NO3	1	Mn	0.9
SO4	0.92	Mo	0.69
Na	0.77	Ni	0.61
NH4	0.99	Pb	0.9
K	0.88	Sb	1
Mg	0.98	Se	0.8
Ca	0.75	Sn	0.89
∑Polyols	0.95	Sr	0.74
levoglucosan	0.88	Ti	0.72
As	0.85	V	0.77
Ba	0.84	Zn	0.23
		PM10	0.94

Bootstrap
(98, 87, 94, 94, 87, 82, 93, 95, 98, 98, 93)

Q true / Q robust = 1,20

Biomass burning tracer

Species	Factors	Configurations
OC*, EC, SO_4, NO_3, NH_4, K, Mg, Cl, Na, Ca, MSA, Levoglucosan, As, Ba, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, Zn, ∑Polyols and PM_{10}	From 9 to 12 factors were tested. An optimized solution with 11 factors is obtained **(still in progress)**	PM_{10} taken as total variable, uncertainty method calculation as described in (Gianini et al., 2012)



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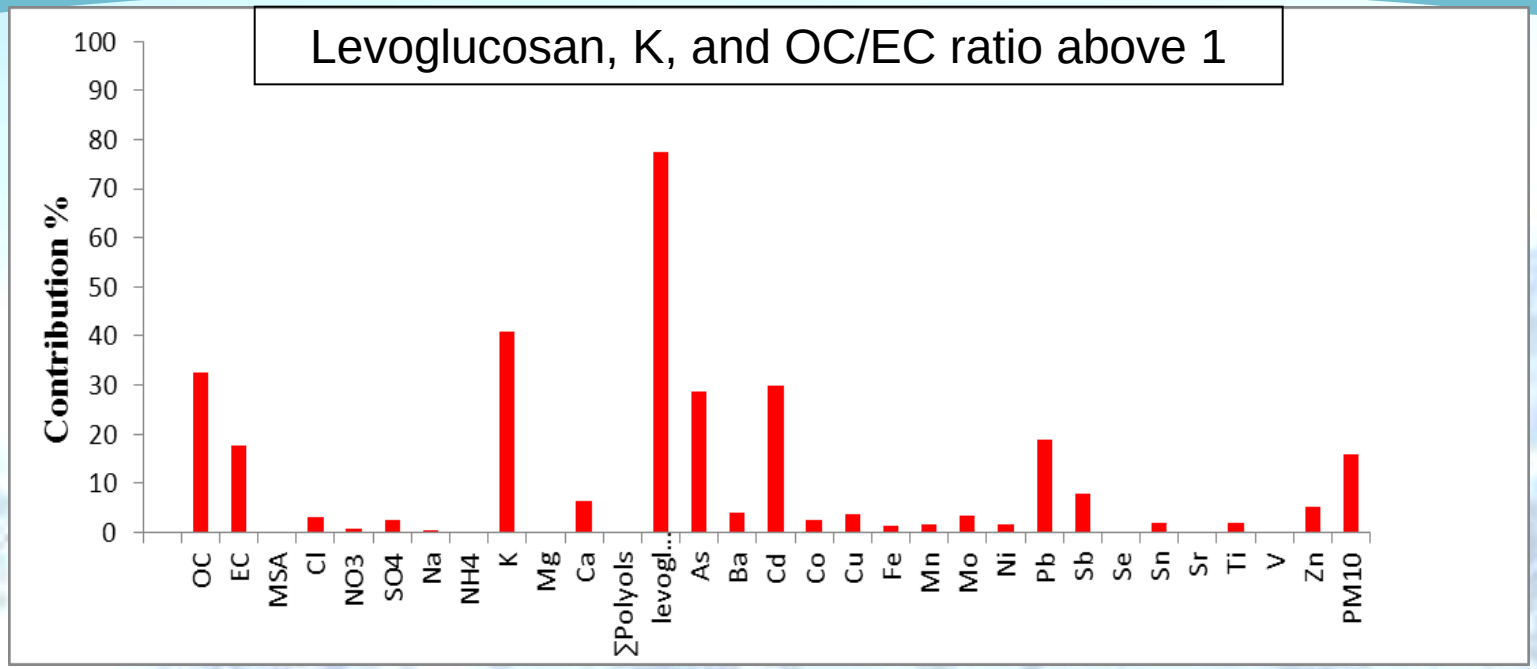
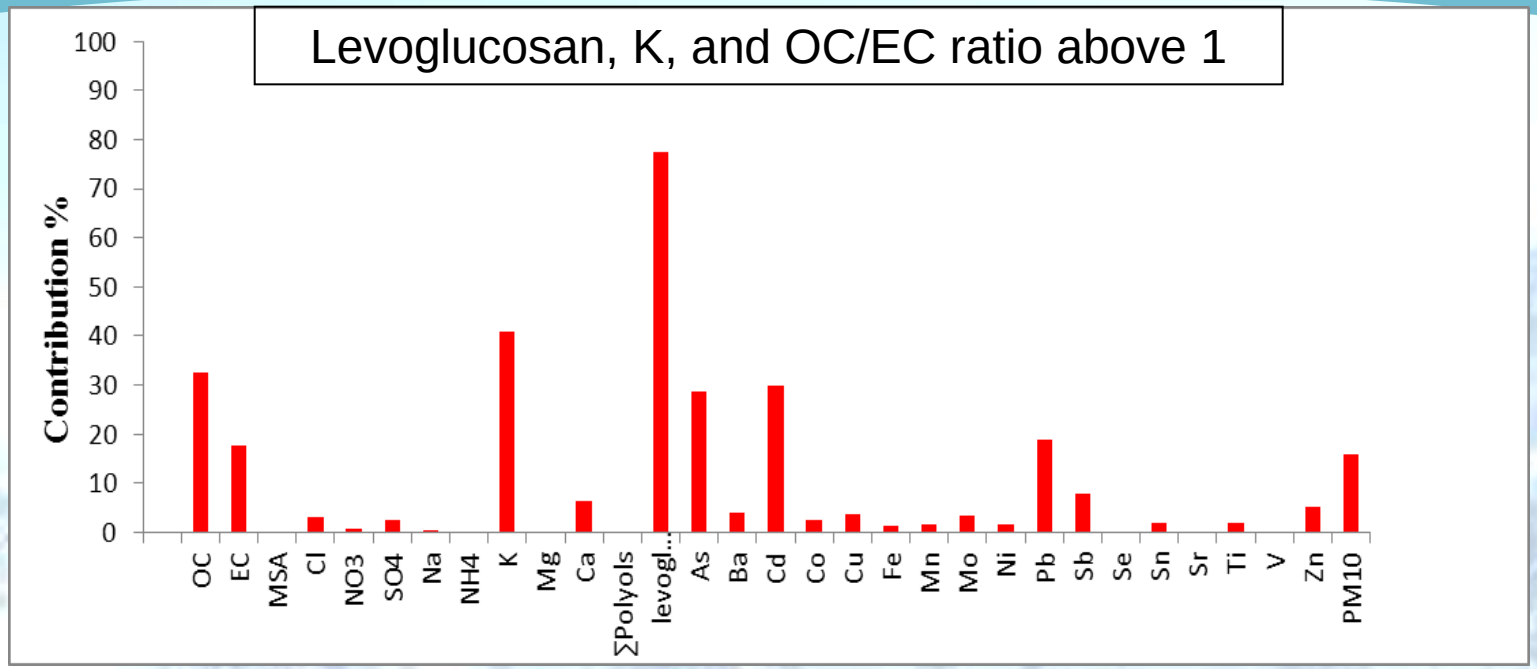
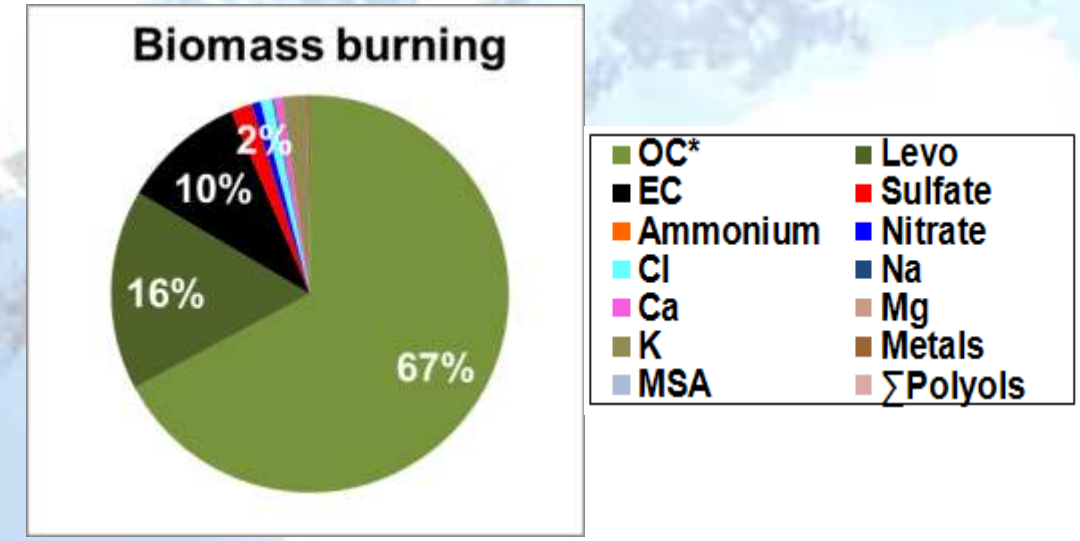
Biomass burning fraction



Work in progress
LGGE / INERIS / Air AQ

Biomass burning fraction





Contributions of the biomass burning source to total modeled PM_{10} mass :

13 % yearly average
29 % in winter

Work in progress
LGGE / INERIS / Air AQ

Biogenic marine tracer

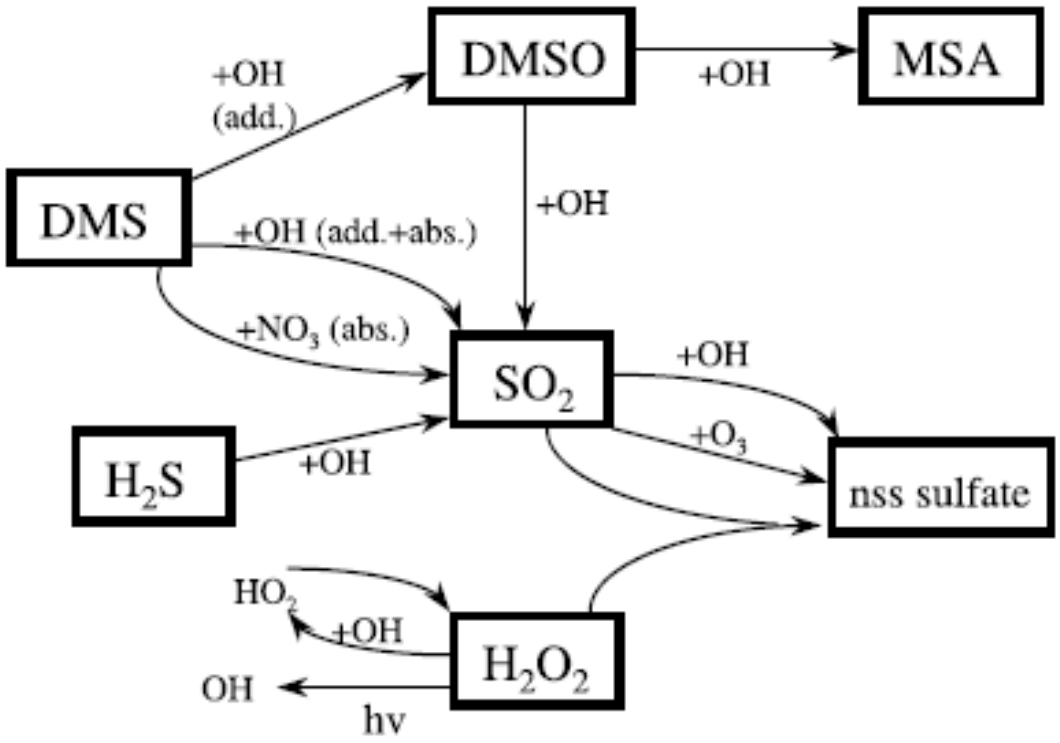


Figure 2. Chemistry scheme used in LMD-ZT. Details of the kinetics are presented by *Cosme et al.* [2002]. Here, "add." and "abs." refer to the addition and abstraction channels of DMS oxidation, respectively. SO_2 oxidation by O_3 and H_2O_2 occurs in the aqueous phase.

Cosme et al., JGR 2005

MSA
(CH_3SO_3H)

Measured by
Ionic Chromatography

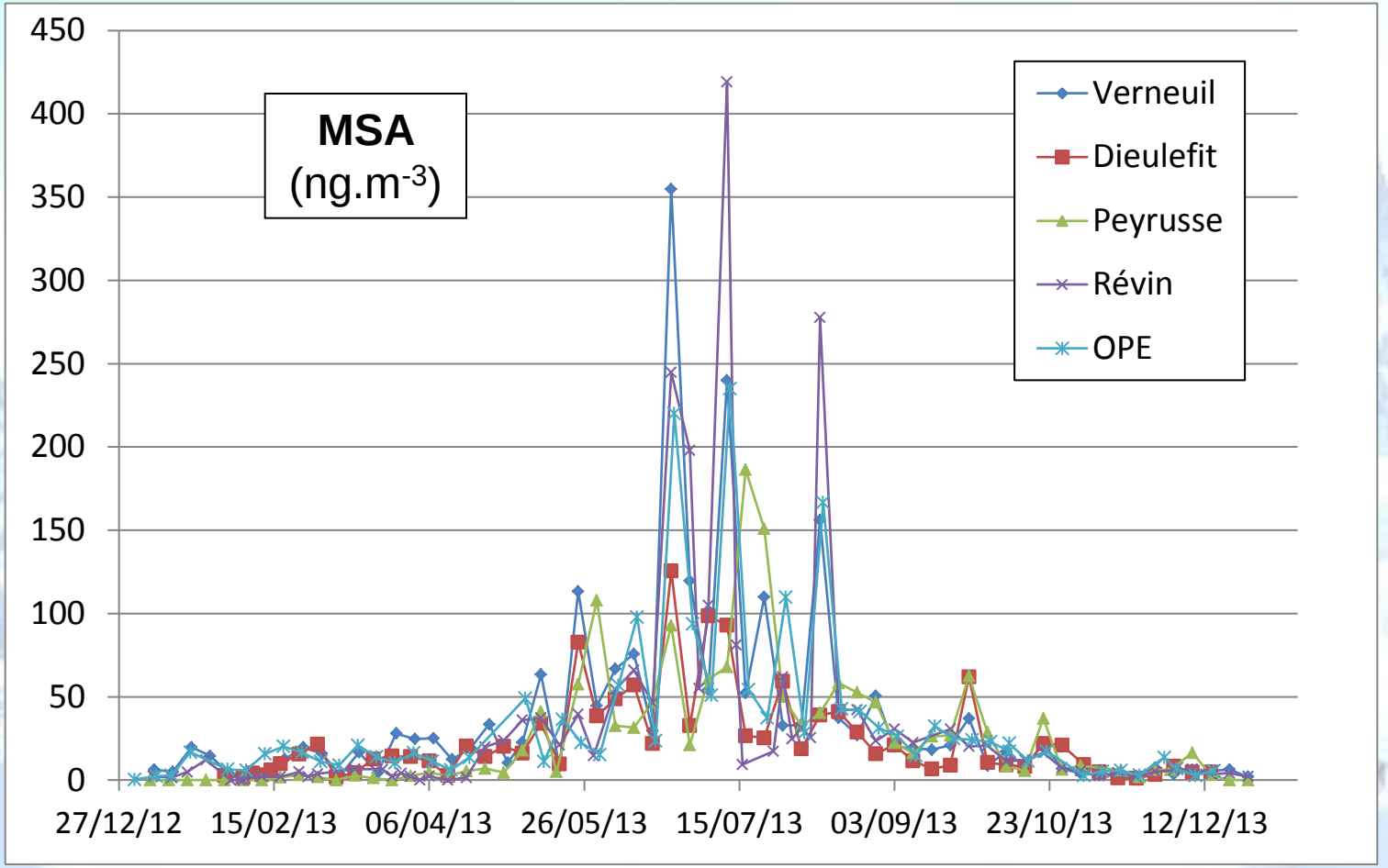
Pio et al, JGR 2007 :

$_{nss}$Sulfate ≈ 6.7 * MSA
(Summer in Azores)

X µg.m^3 from the biogenic marine contribution ??

Biogenic marine tracer

Rural sites (2013)



About 60 spls (1d/6)

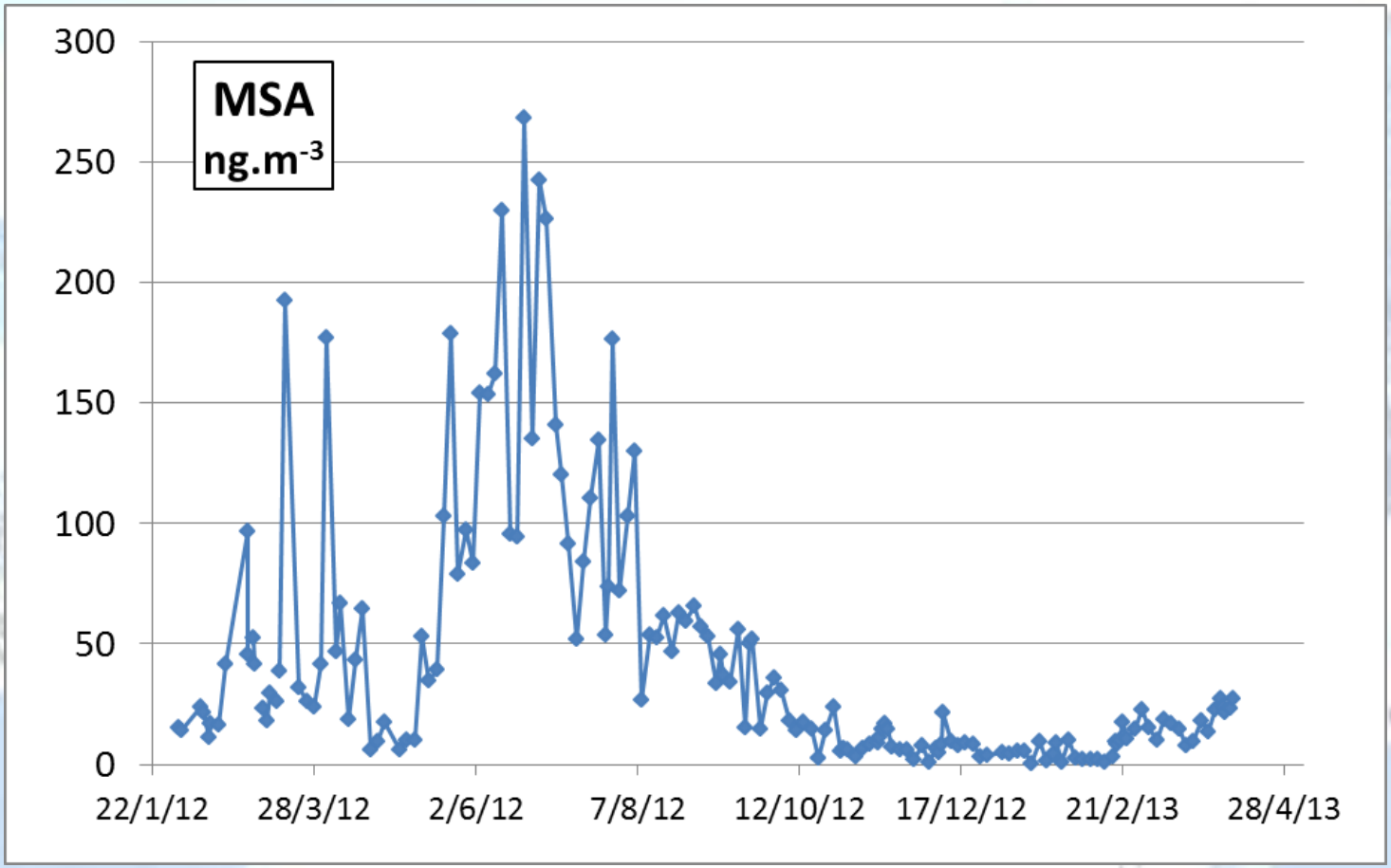
nssSulfate ≈ 6.7 * MSA
(Summer in Azores)

≈ 1.5 µg.m^3 nssSulfate … Really true ?

Biogenic marine tracer

1+ year study in Bordeaux

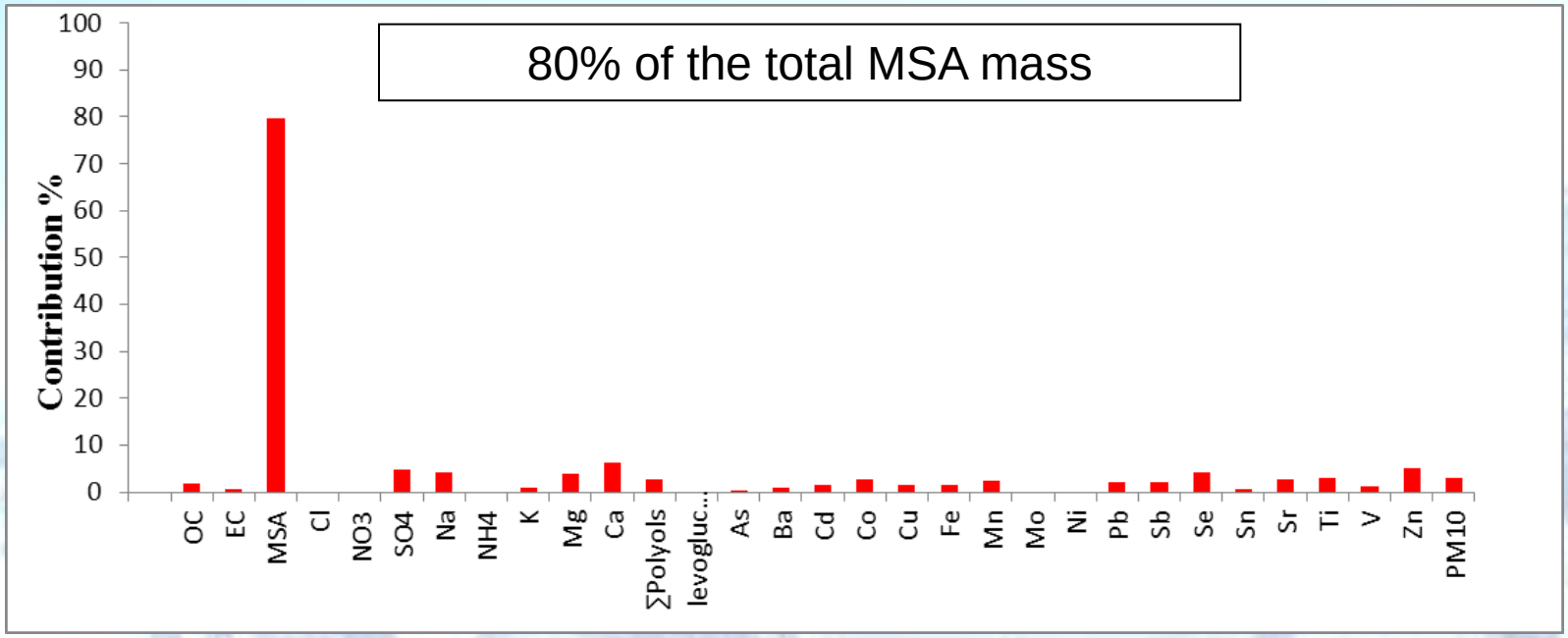
PMF study : 156 samples (1 d/3)



LCSQA

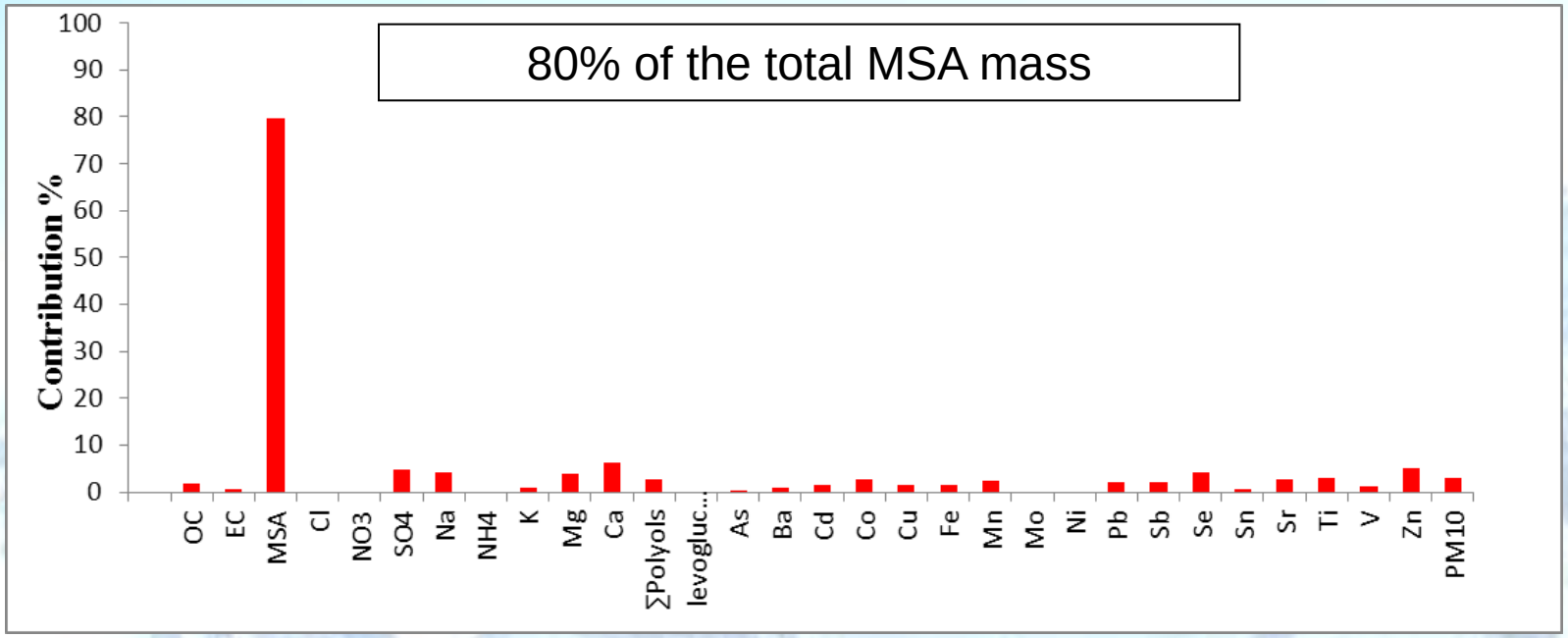
AIRAQ
Atmo Aquitaine

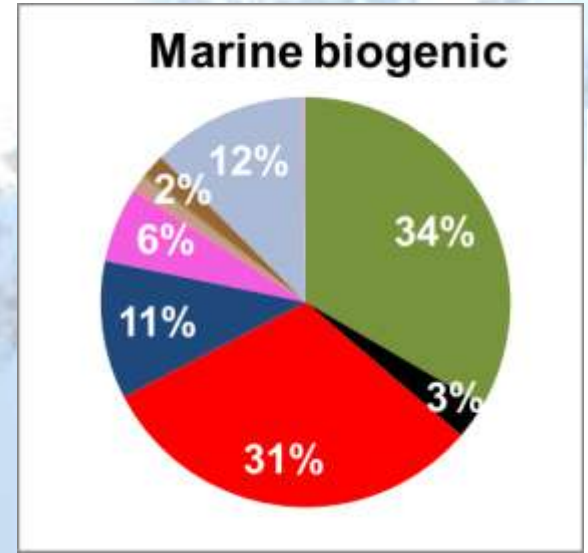
Biogenic marine fraction

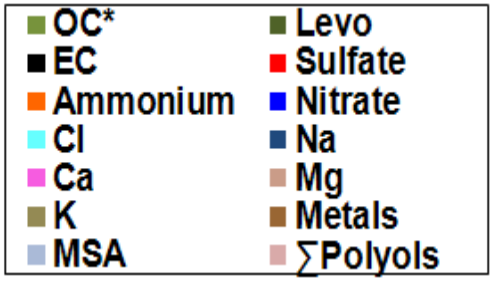


Work in progress
LGGE / INERIS / Air AQ

Biogenic marine fraction







Contributions of the biogenic marine source to total modeled PM_{10} mass :

5 % yearly average
16 % in summer

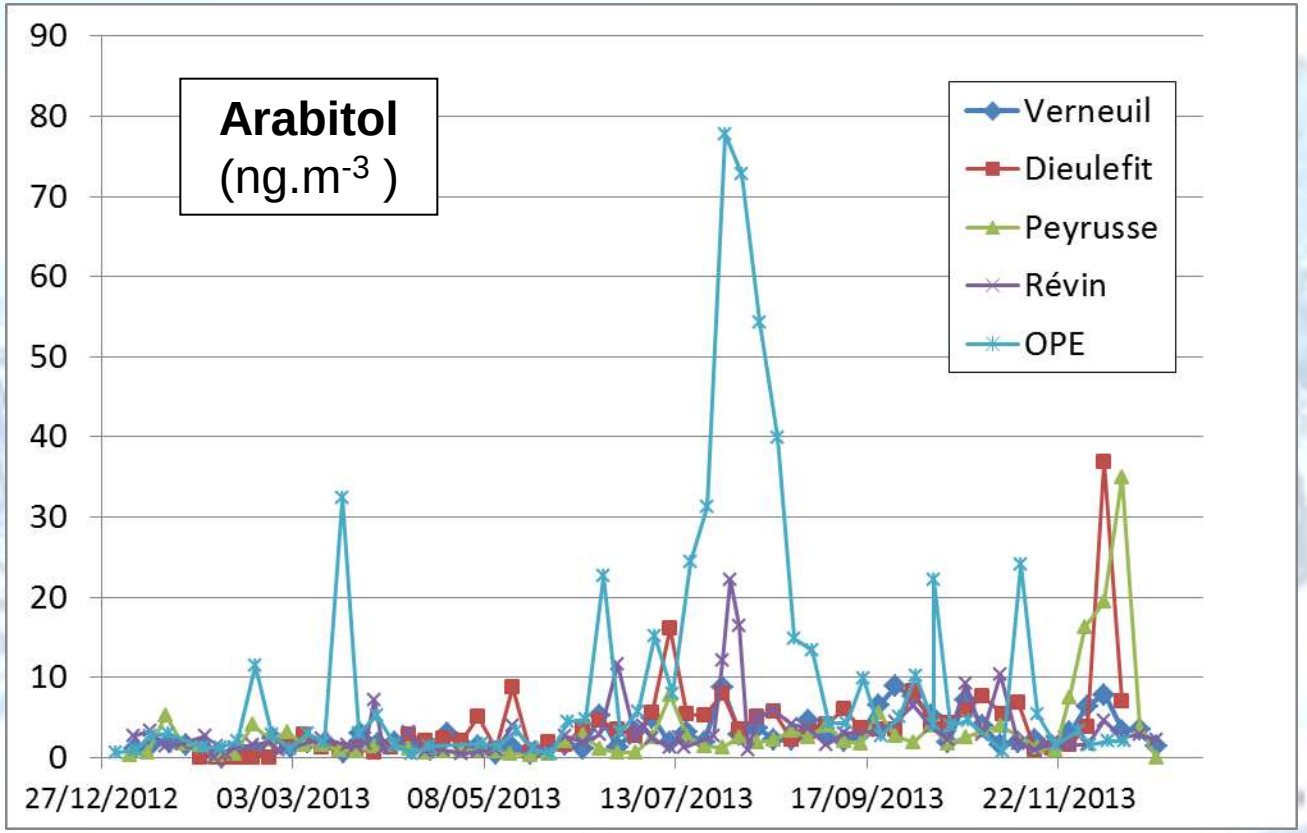
Sulfate / MSA = 2,3

Work in progress
LGGE / INERIS / Air AQ

Biogenic (soil ?) tracers

Rural sites (2013)

It has been suggested that polyols (arabitol, sorbitol, mannitol etc …) are biogenic tracers of soil emissions



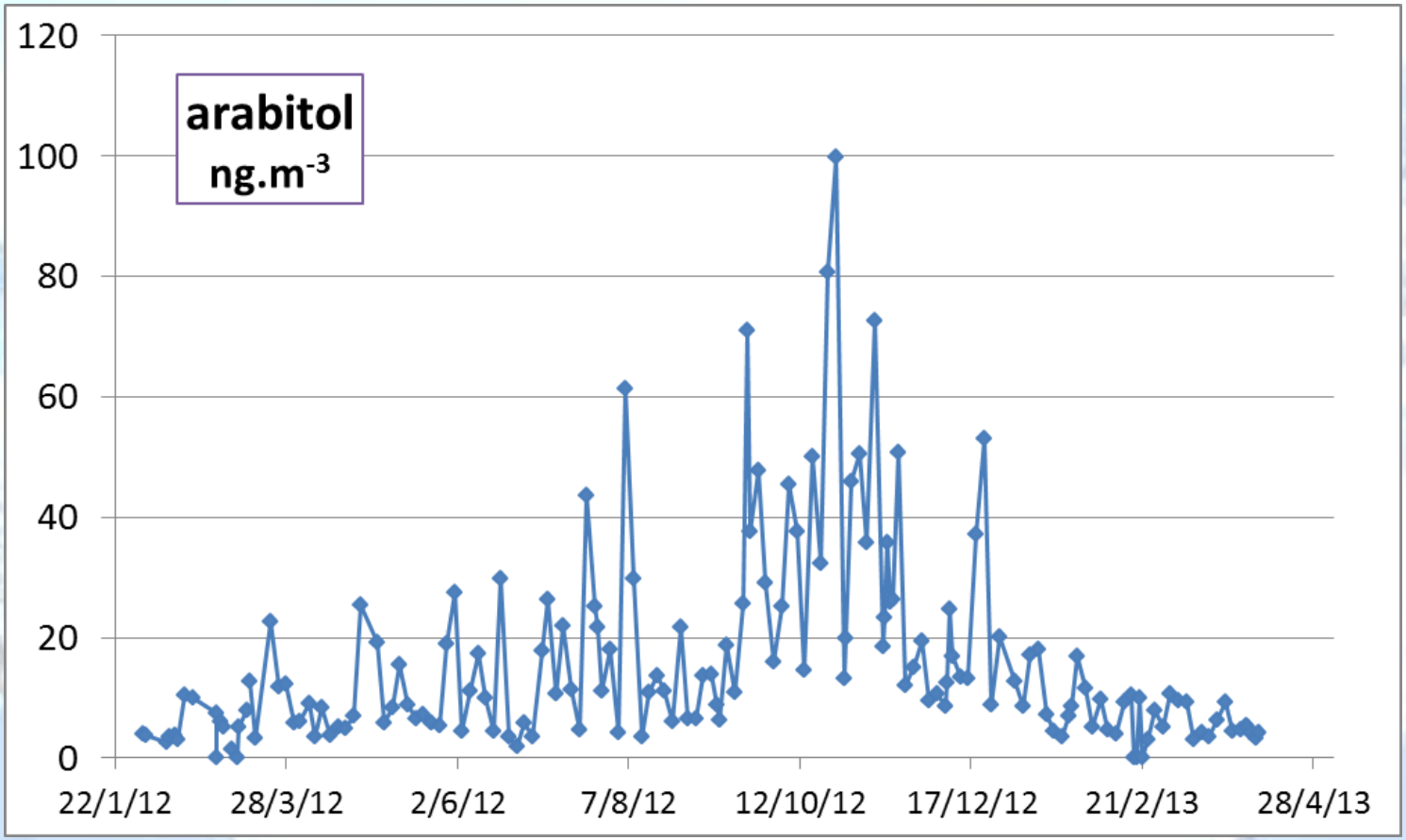
About 60 spls (1d/6)

Measurements indicates large differencies according to the sites .. But rather low concentrations in these rural sites (some exceptions)

Biomass (soil ?) tracer

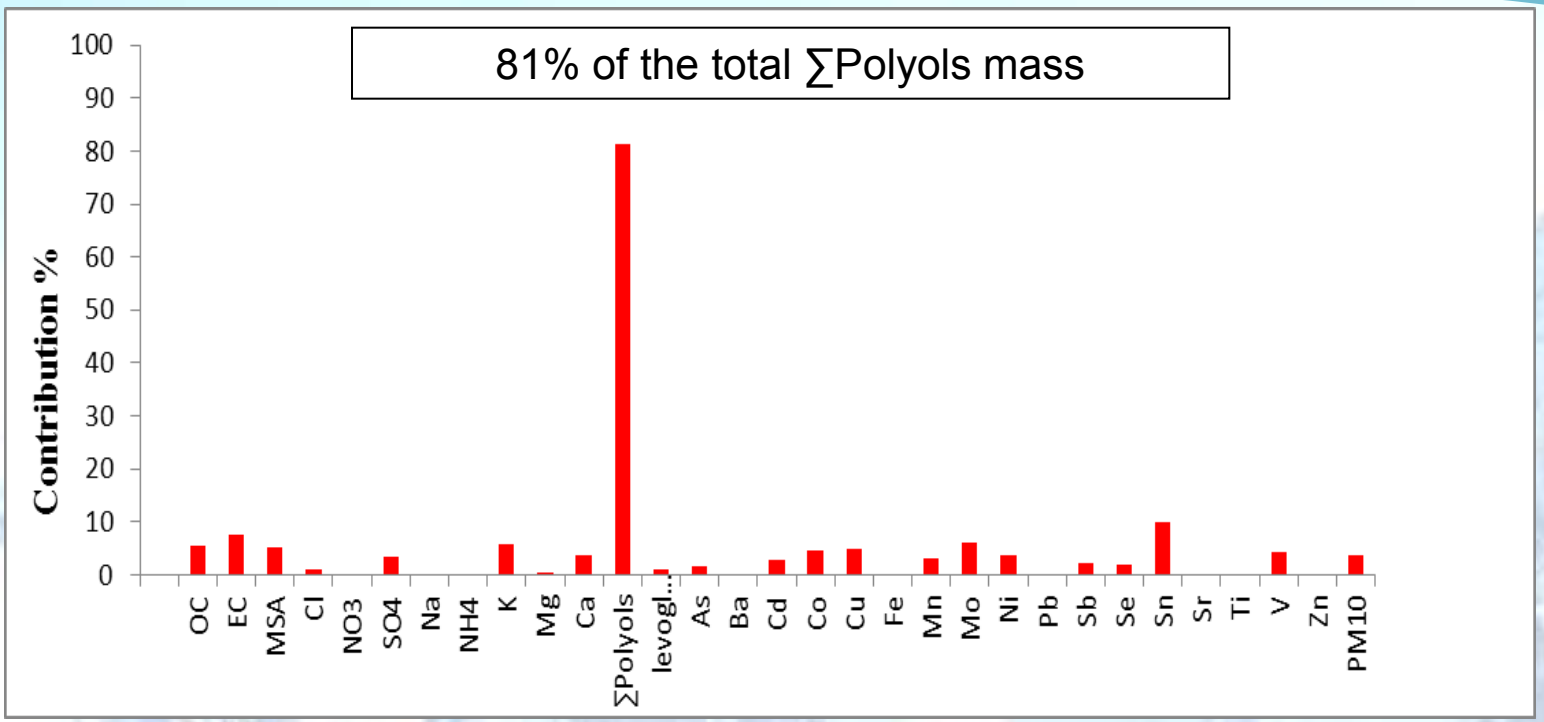
1+ year study in Bordeaux

PMF study : 156 samples (1 d/3)



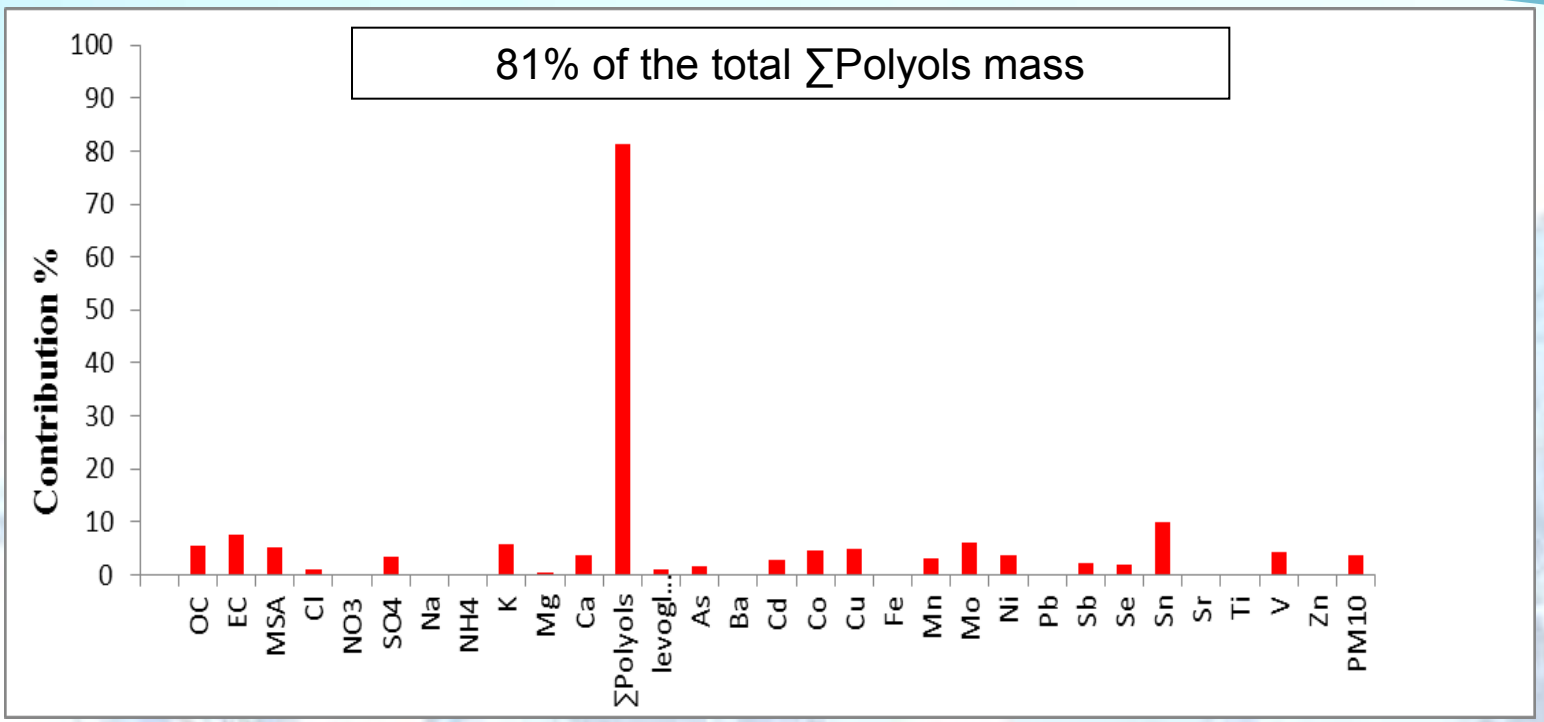
Summ of polyols : Arabitol + Sorbitol

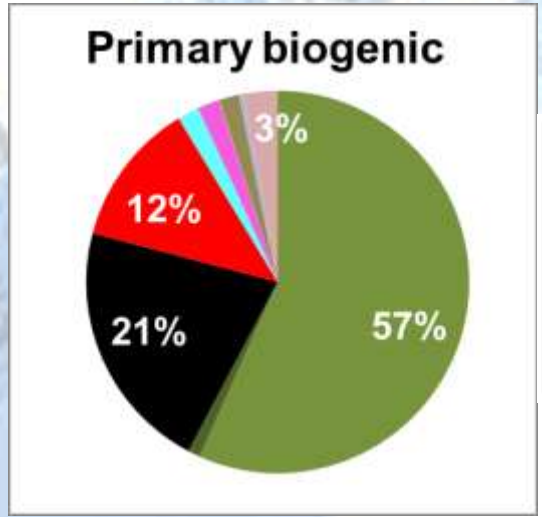
Biogenic (soil ?) fraction

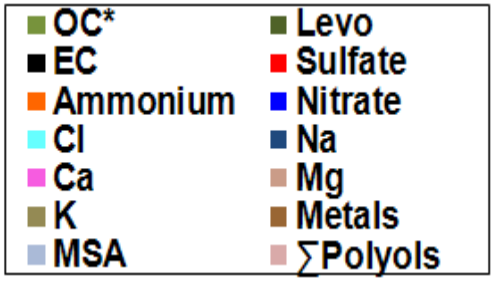


Work in progress
LGGE / INERIS / Air AQ

Biogenic (soil ?) fraction







Contributions of the biogenic soil (?) source to total modeled PM_{10} mass :

5 % yearly average
11 % in fall

Work in progress
LGGE / INERIS / Air AQ

Industrial / coal tracer ?

Measurement of Sulfured PAH (by GC-MS)

Detection of PASHs on several sampling sites

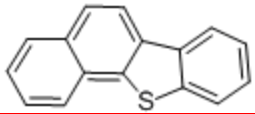
Series in Lens :

7 PASHs series quantified:

- Dibenzothiophene
- Phenanthro[4,5-*bcd*]thiophene
- Benzo[b]naphtho(2,1 –d)thiophene
- Benzo[b]naphtho(1,2 –d)thiophene
- Benzo[b]naphtho(2,3 –d)thiophene
- Dinaphtho[2,1-b; 1´,2´-d]thiophene
- Benzo[*b*]phenanthro[2,1-*d*]thiophene

(Σ BNT)

Major compound is benzo(b)naphtho(2,1-d)thiophène (BNT(2,1))



PhD of B Golly, LCME

MINES Douai

Atmo Nord - Pas de Calais

LCSQA

Industrial / coal tracer ?

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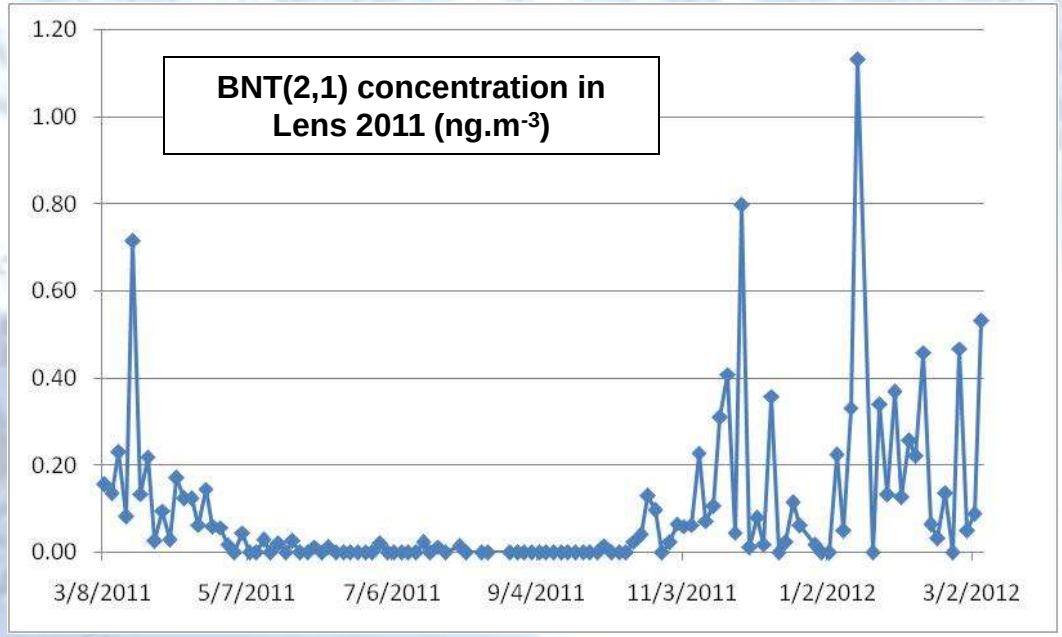

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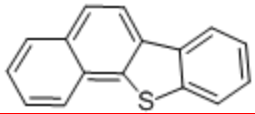

PhD of B Golly, LCME

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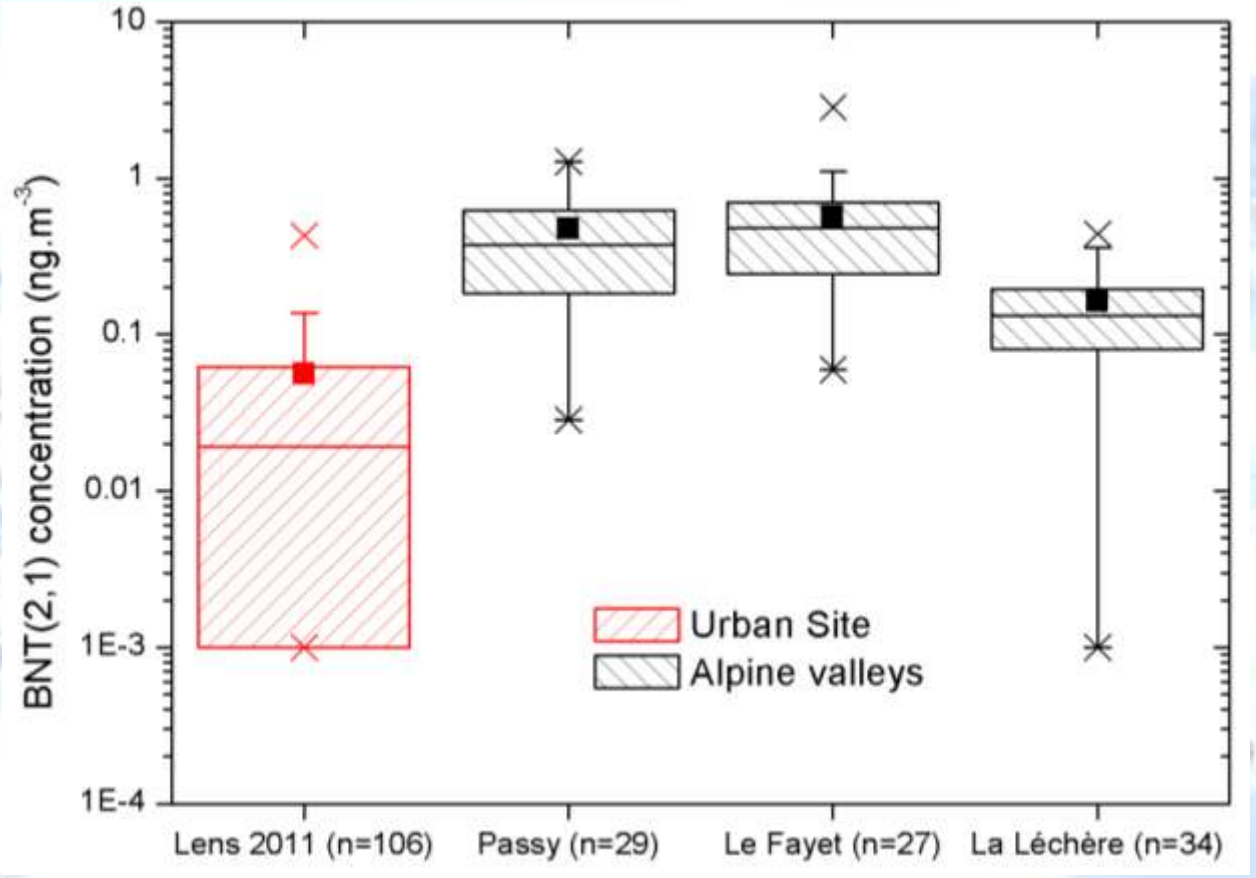
Industrial / coal tracer ?

Measurements of Sulfured PAH in various sites

PhD of B Golly, LCME

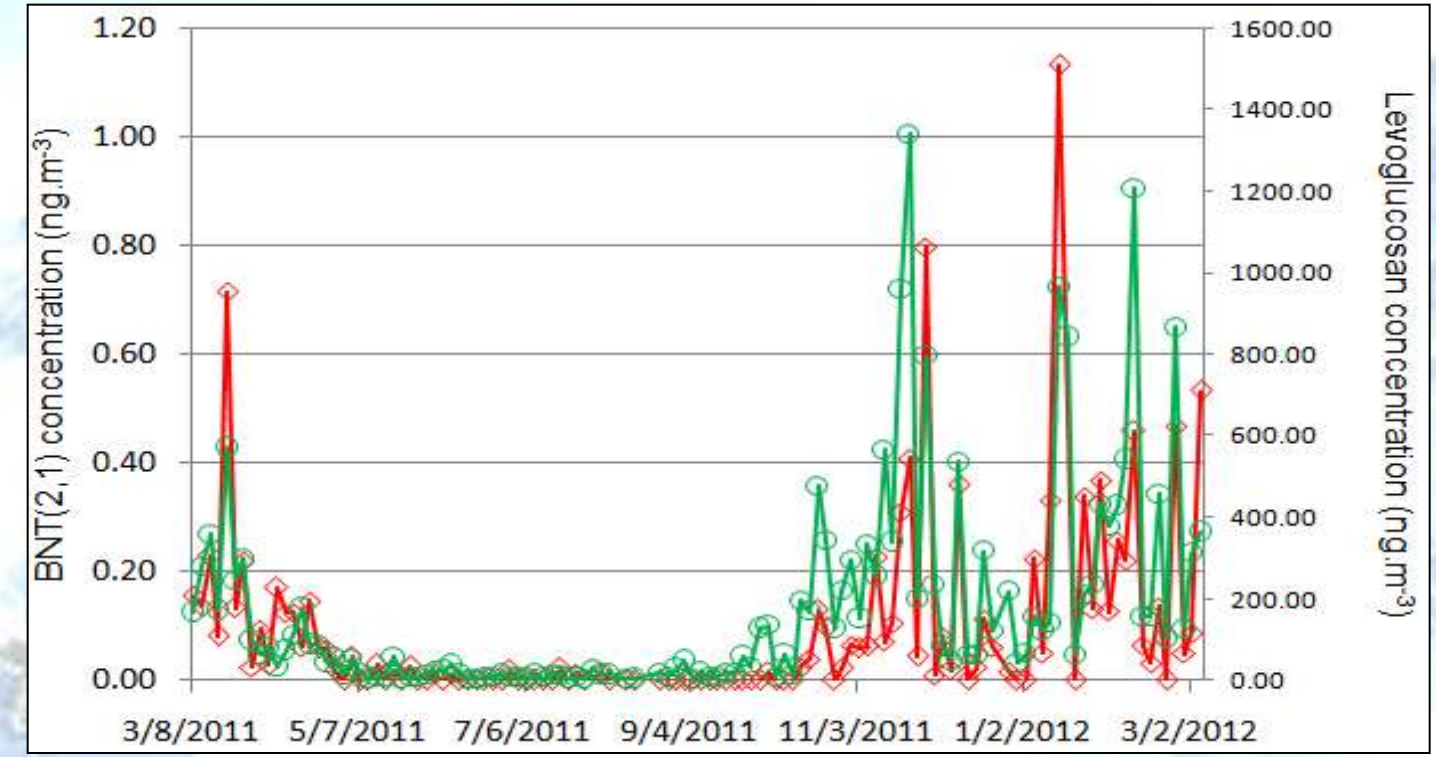
funded by



High concentrations of PASHs in Alpine valleys
= near important industrial areas
(carbon material production)

Industrial / coal tracer ?

Concentrations of BNT(2,1) vs levoglucosan in Lens : close but not the same



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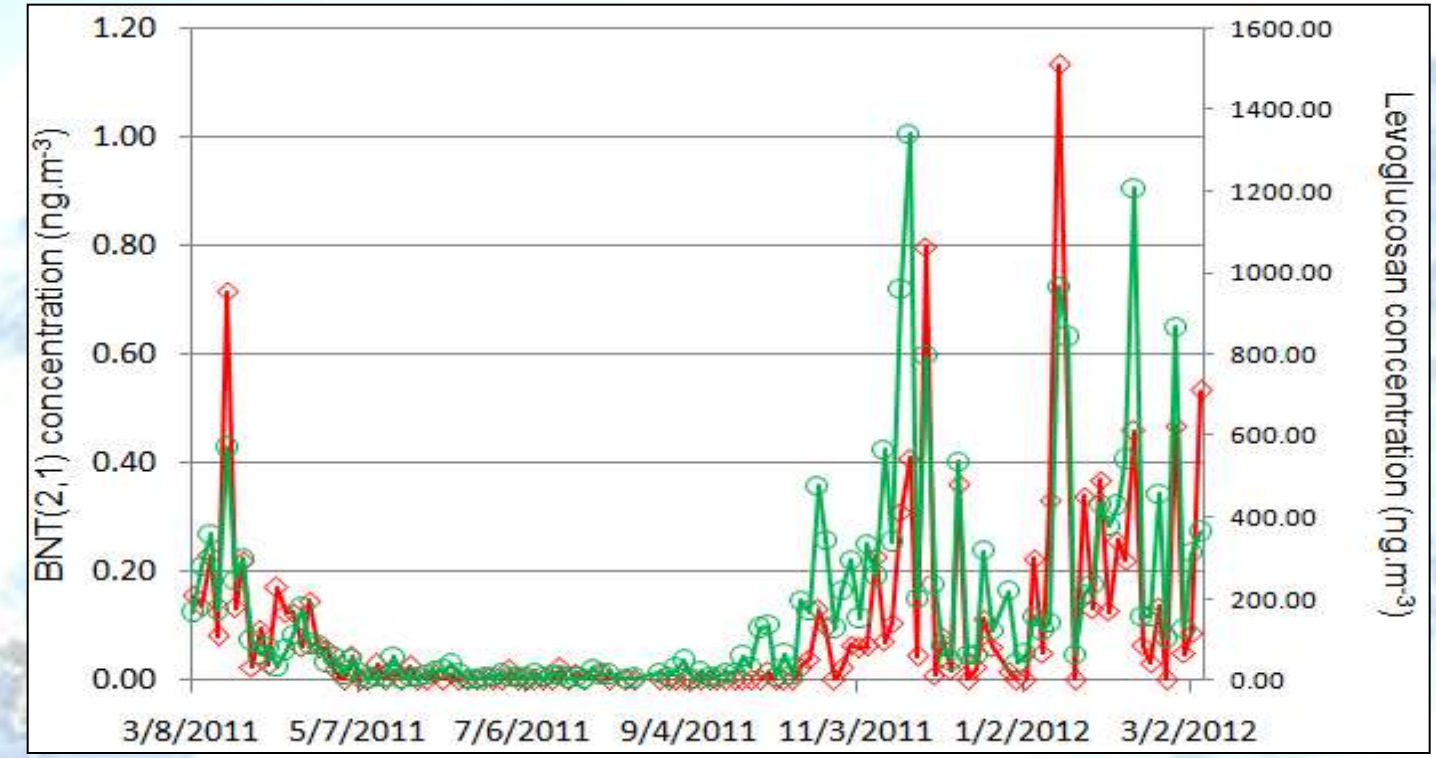


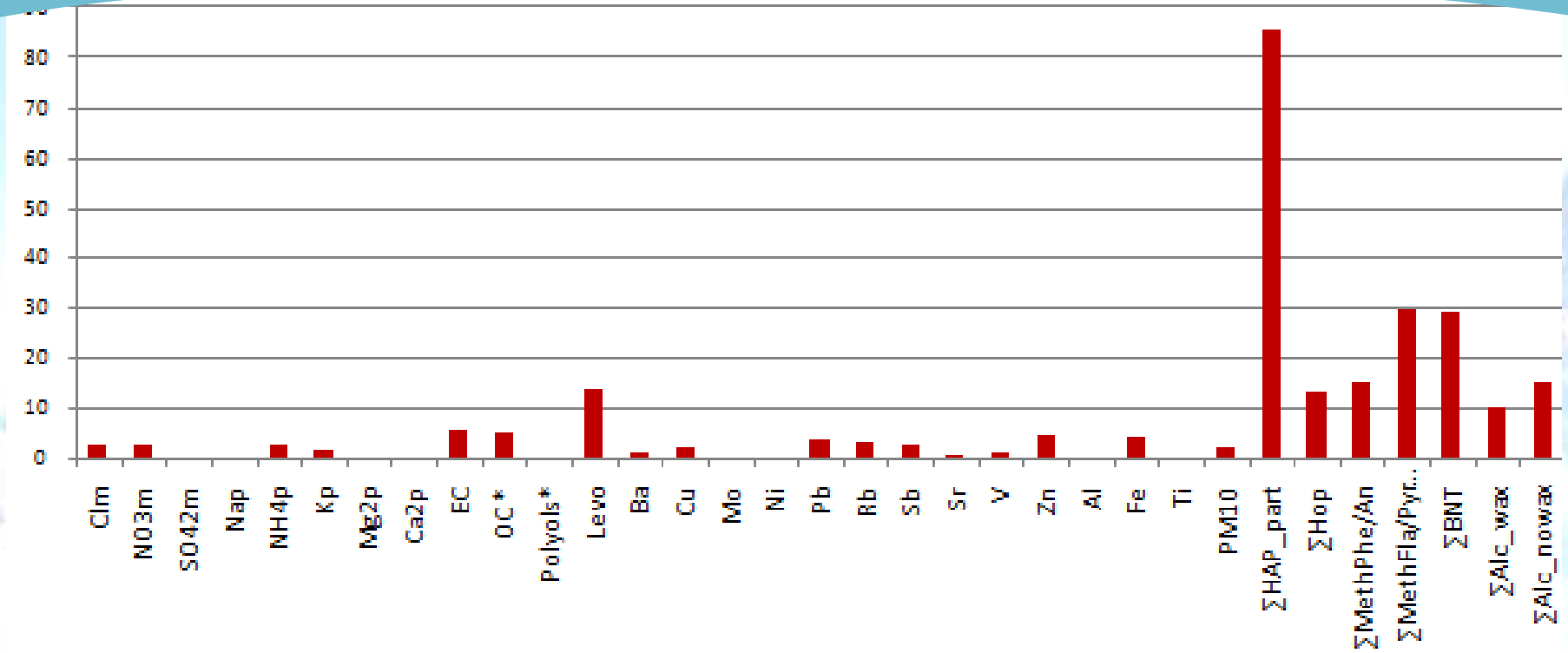
PMF study
(same as in Waked et al., 2014)

+

- PAH particulate bounded
- Hopanes
- Methyl-PAH (LMW and HMW)
- BNT
- n-alkanes (wax series)

PhD of B Golly, LCME

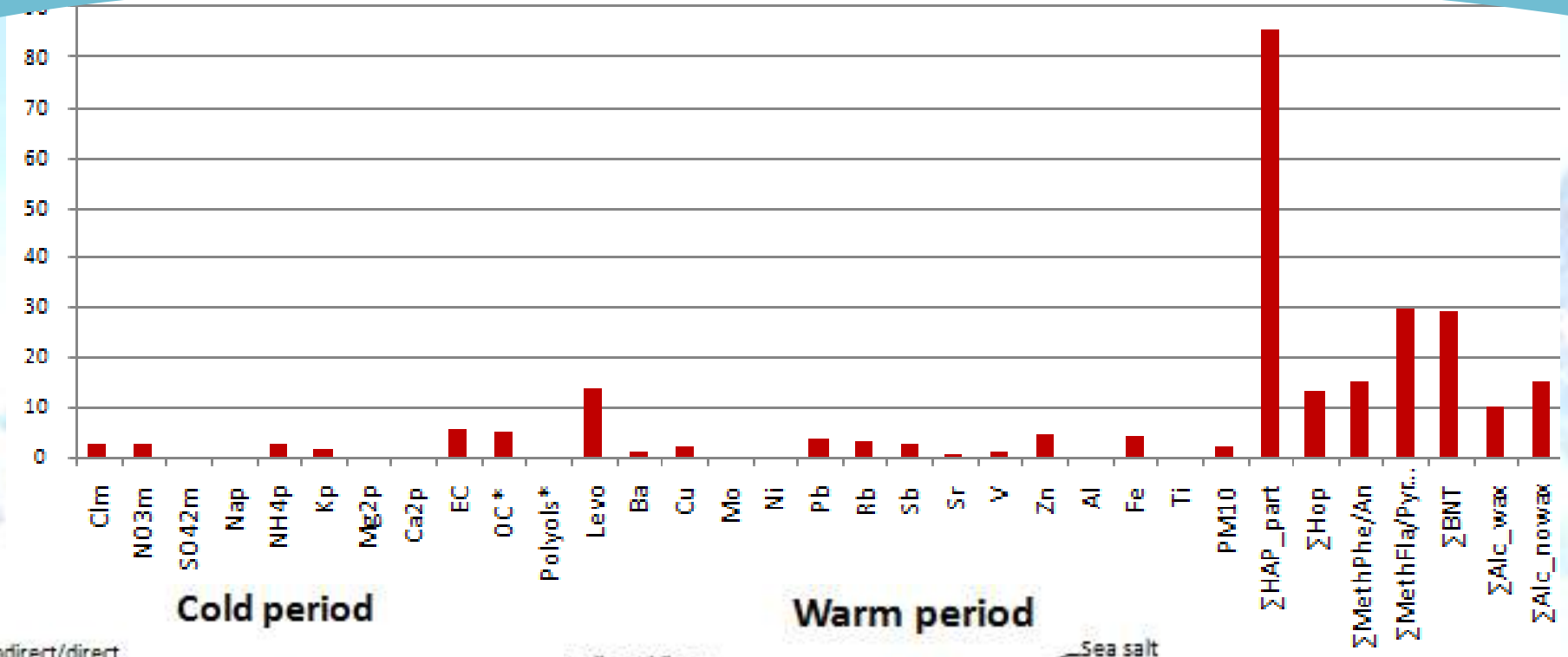
Industrial / coal fraction ?

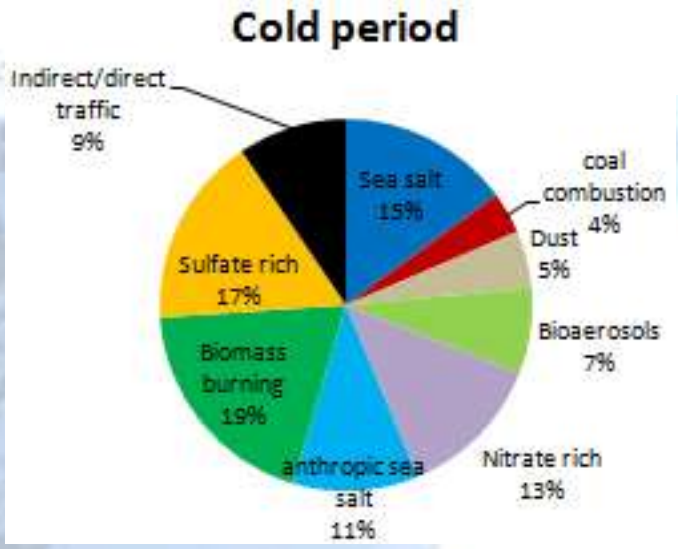


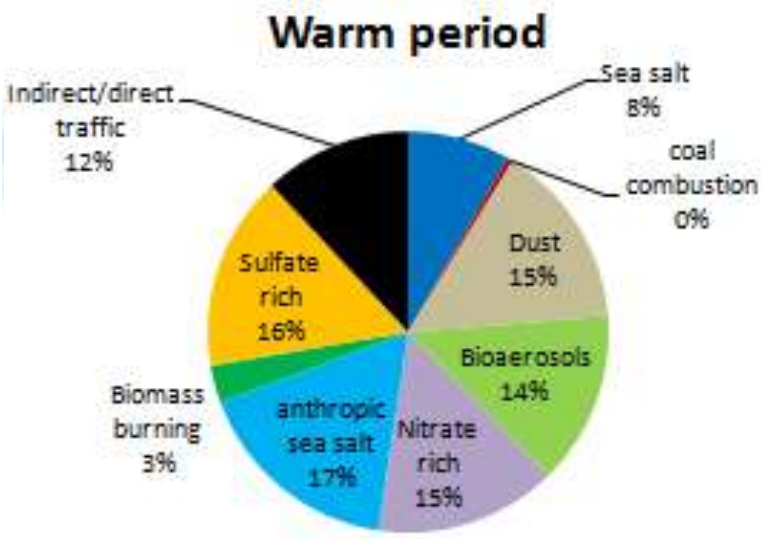
Separation of a new factor containing these organics
Not traffic
Not biomass burning

Proposed « coal combustion » (due to PASHs)

Industrial / coal fraction ?

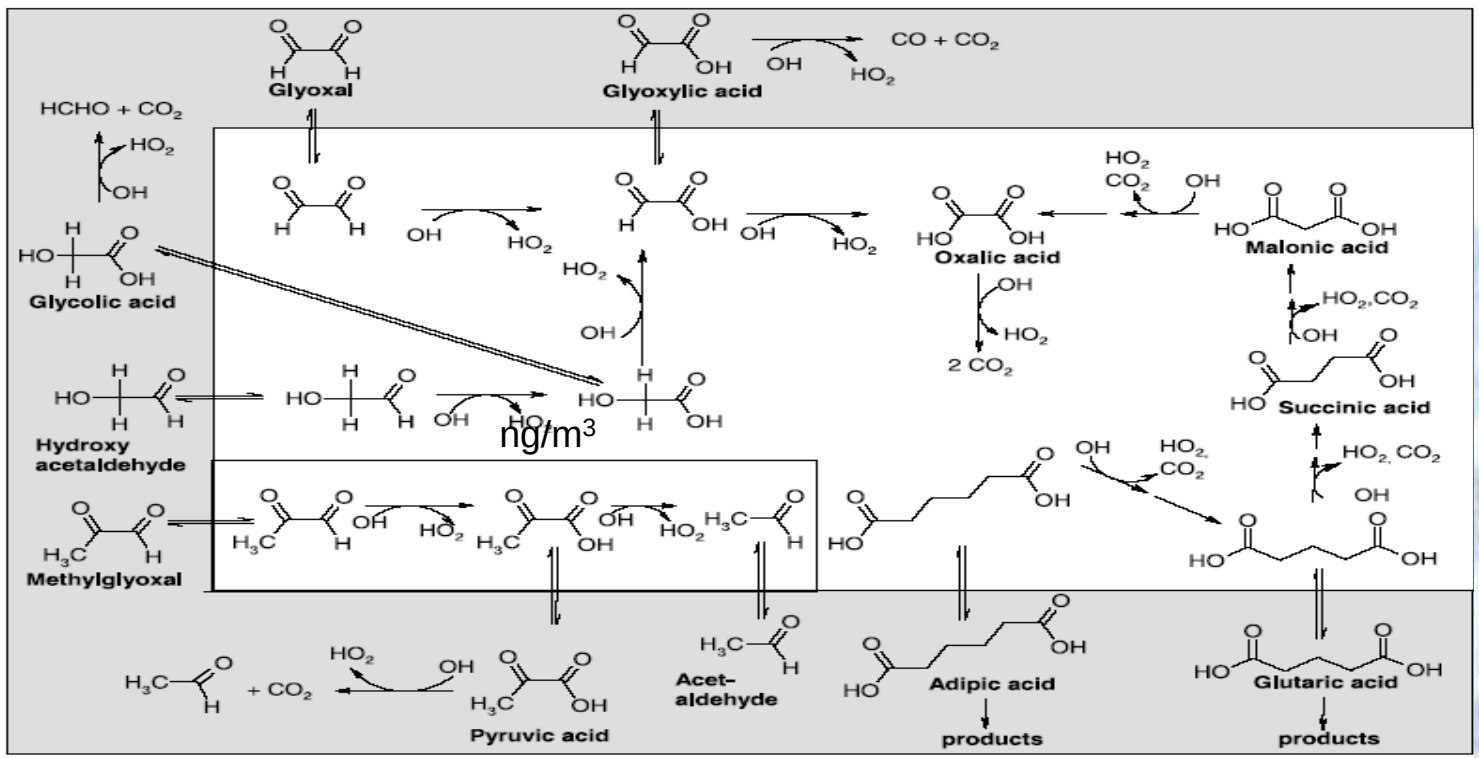






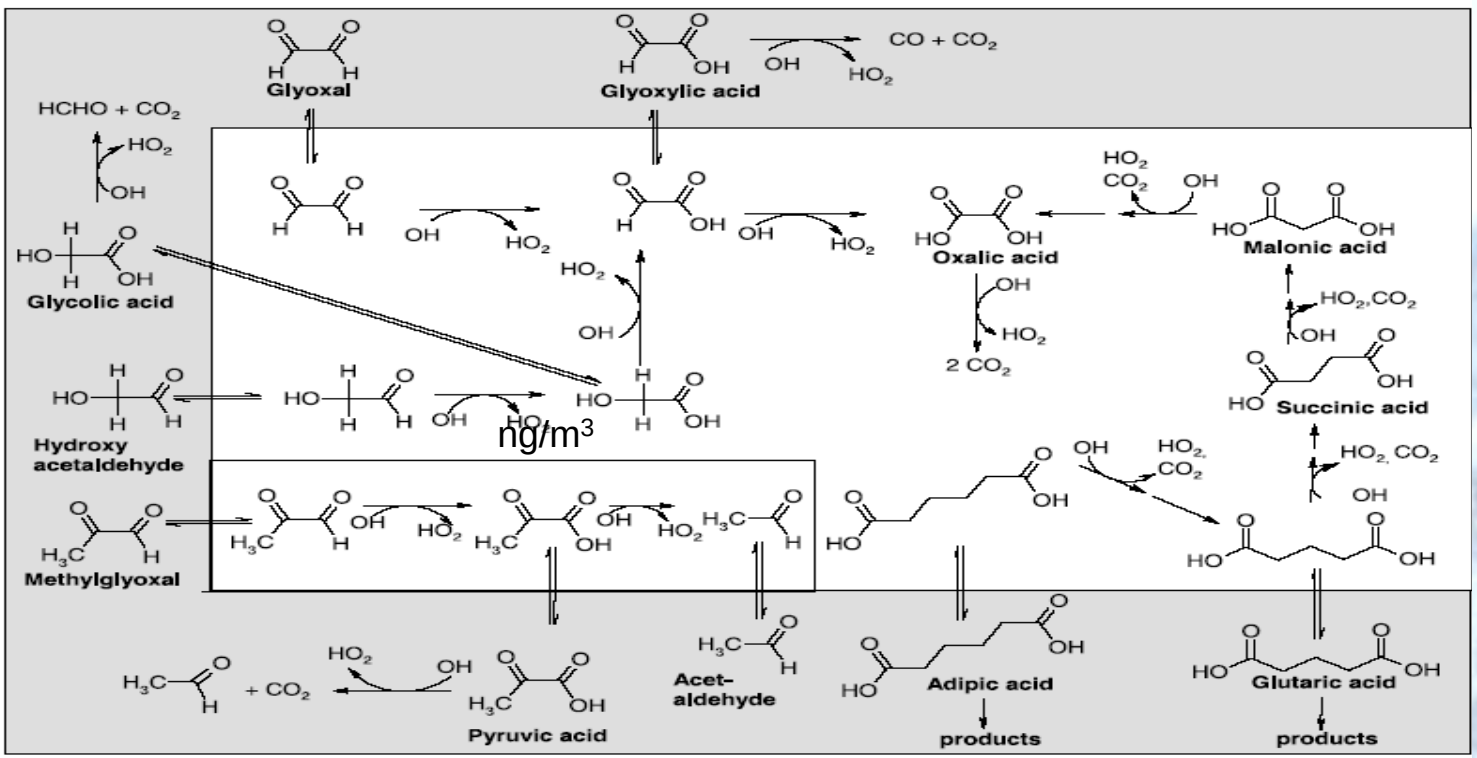
In Eastern European countries or in China ??

Tracers of the SOA fraction ??



Ervens et al., JGR 2004

Tracers of the SOA fraction ??



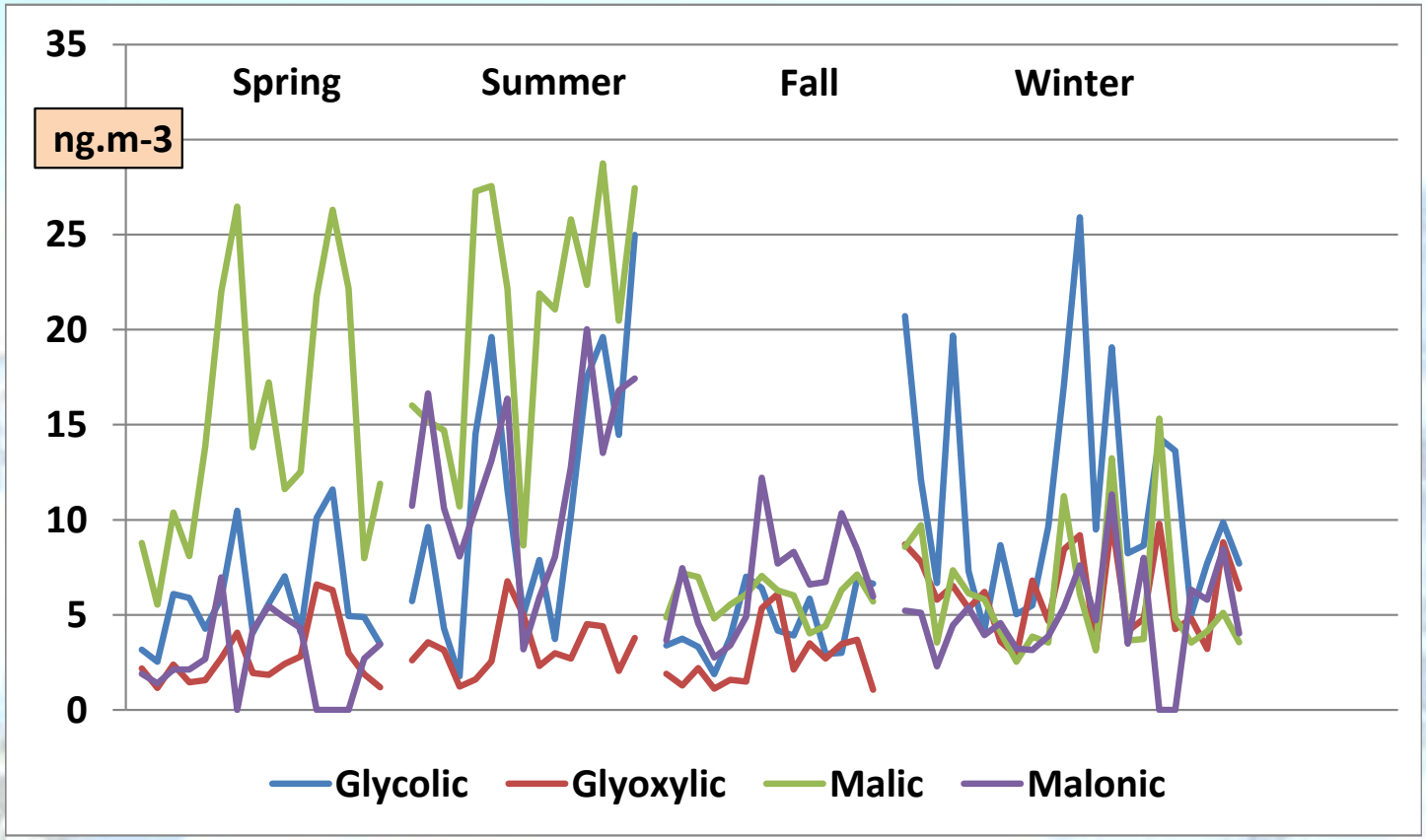
Ervens et al., JGR 2004

Analytical development for analysis of a large series (about 20) low molecular weight organic acids (C2- C9) by LC-MS

Analysis of samples from **Lanslebourg (Maurienne Valley)** for 4 seasonal 15-day campaigns

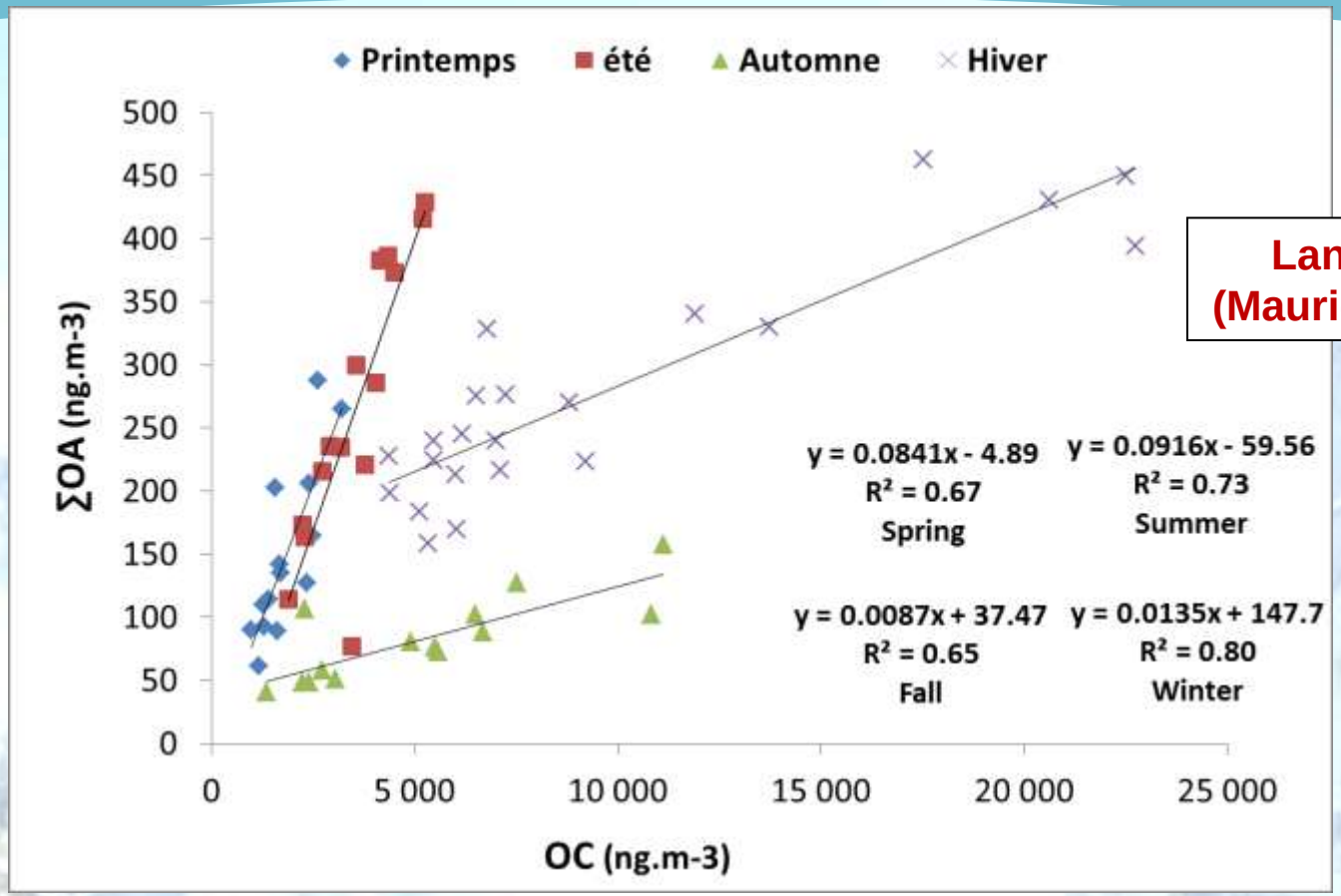
Tracers of the SOA fraction ??

Lanslebourg (Maurienne Valley)



	Spring	Summer	Falll	Winter
OC (ngC.m-3)	1830	3565	5184	9543
∑LMWOA (ng.m-3)	139	267	83	277
∑OA / OC (%)	7,6	7,5	1,6	2,9

Tracers of the SOA fraction ??



Lanslebourg (Maurienne Valley)

Good correlations OC vs Sum Organic Acids

(despite variable tendency of each AO)

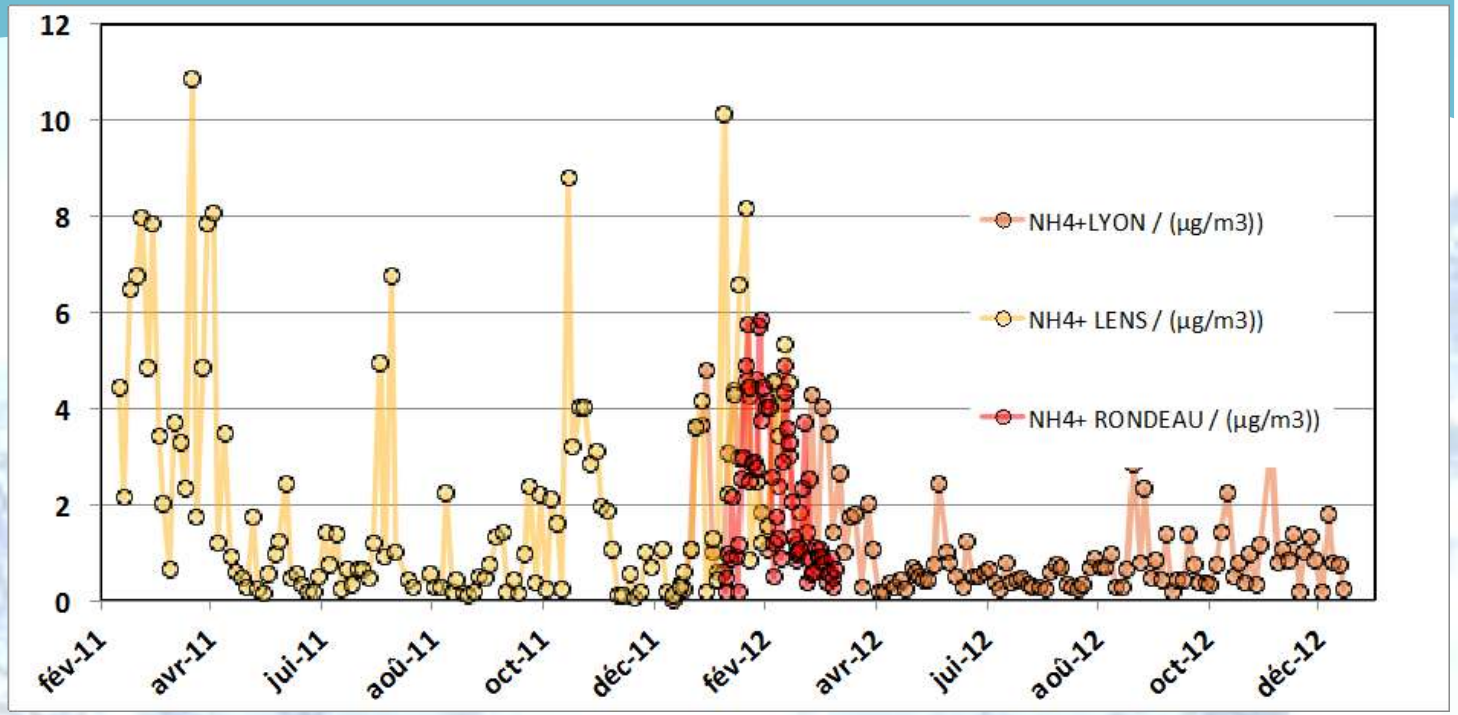
Not the same slopes in all seasons …

Not included in PMF still ……. pbs with conservation during post sampling

How to tackle the sources of Ammonium Nitrate ?

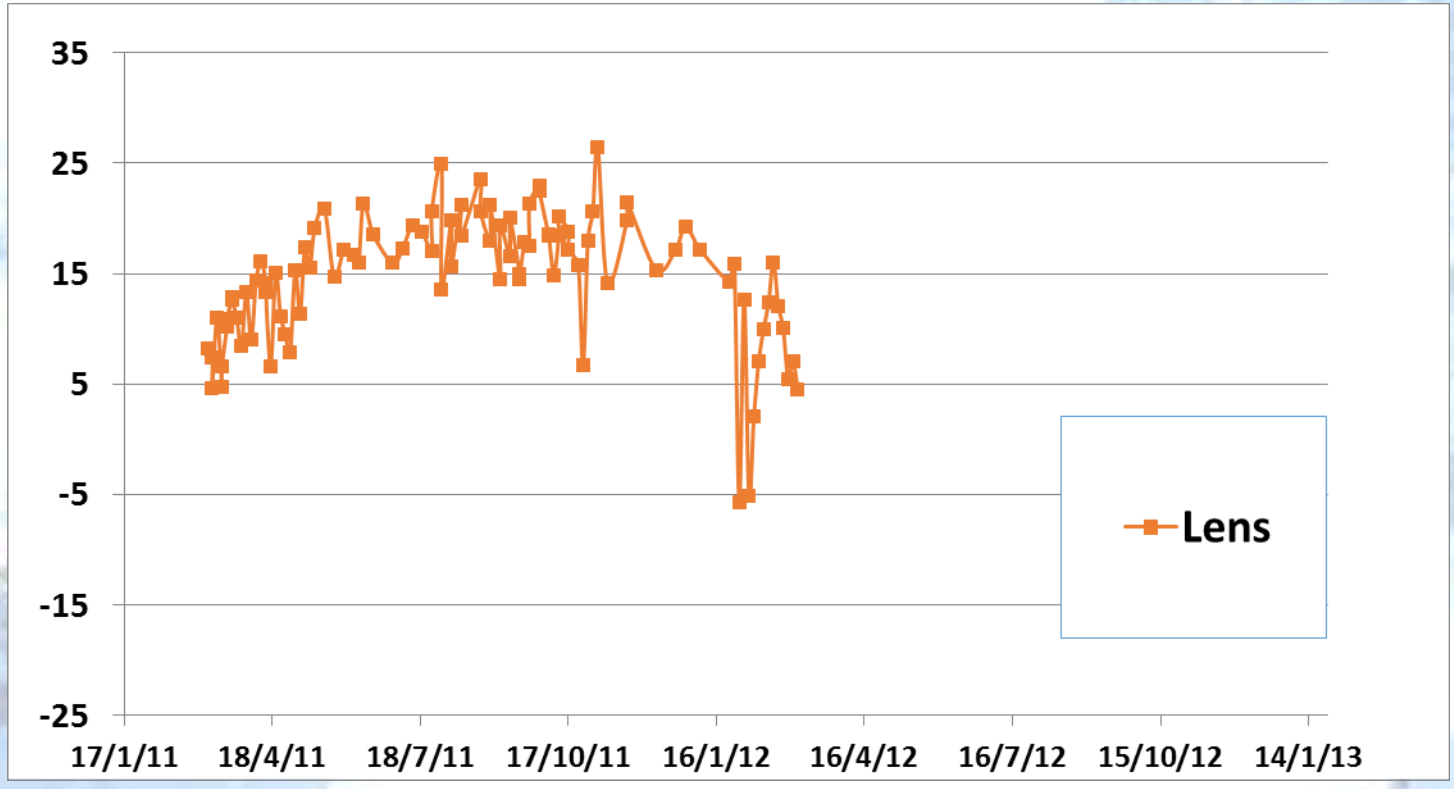
Ongoing **INACS** program funded by ADEME

Collaborations



How to tackle the sources of Ammonium Nitrate ?

Evolution of $\delta^{15}N$ of ammonium



How to tackle the sources of Ammonium Nitrate ?

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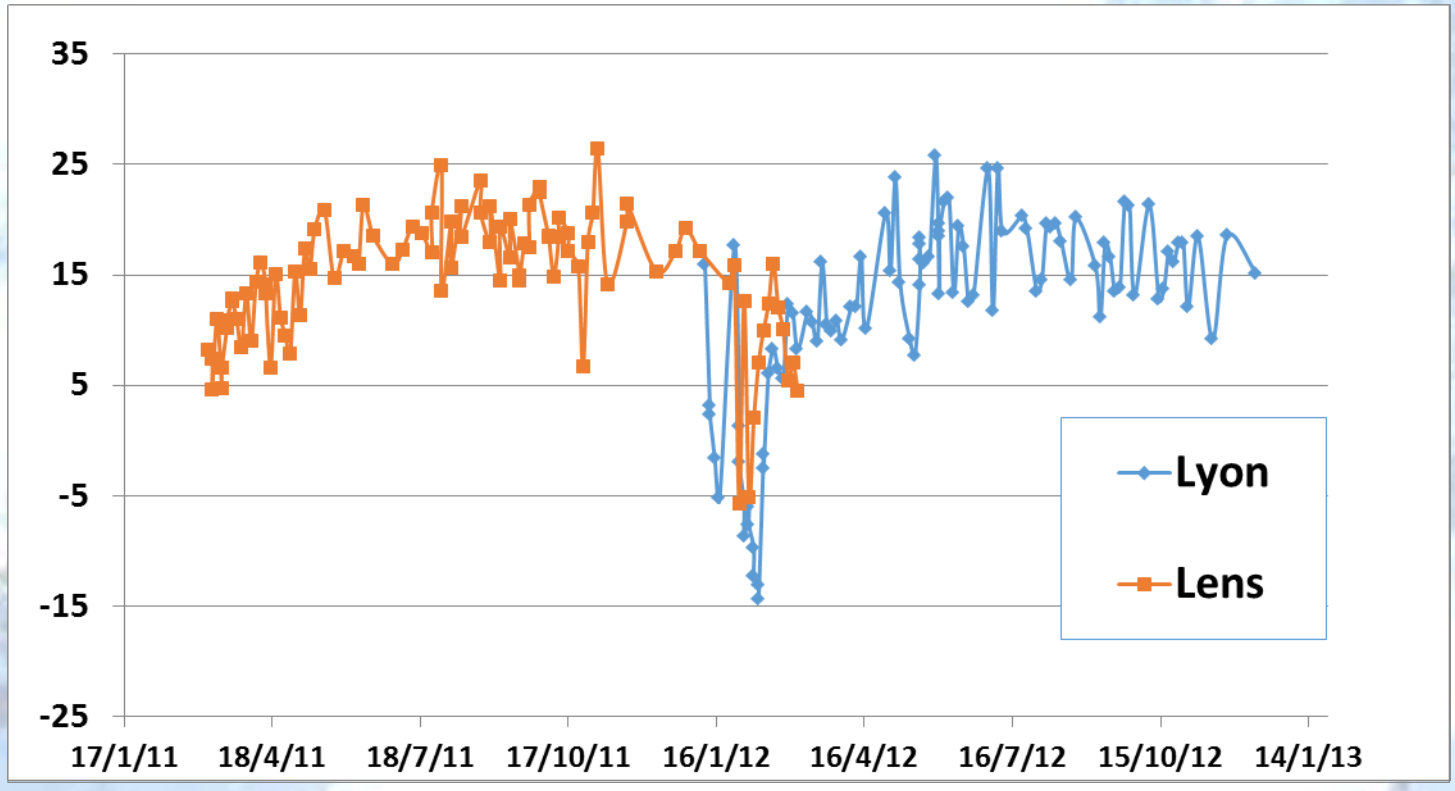

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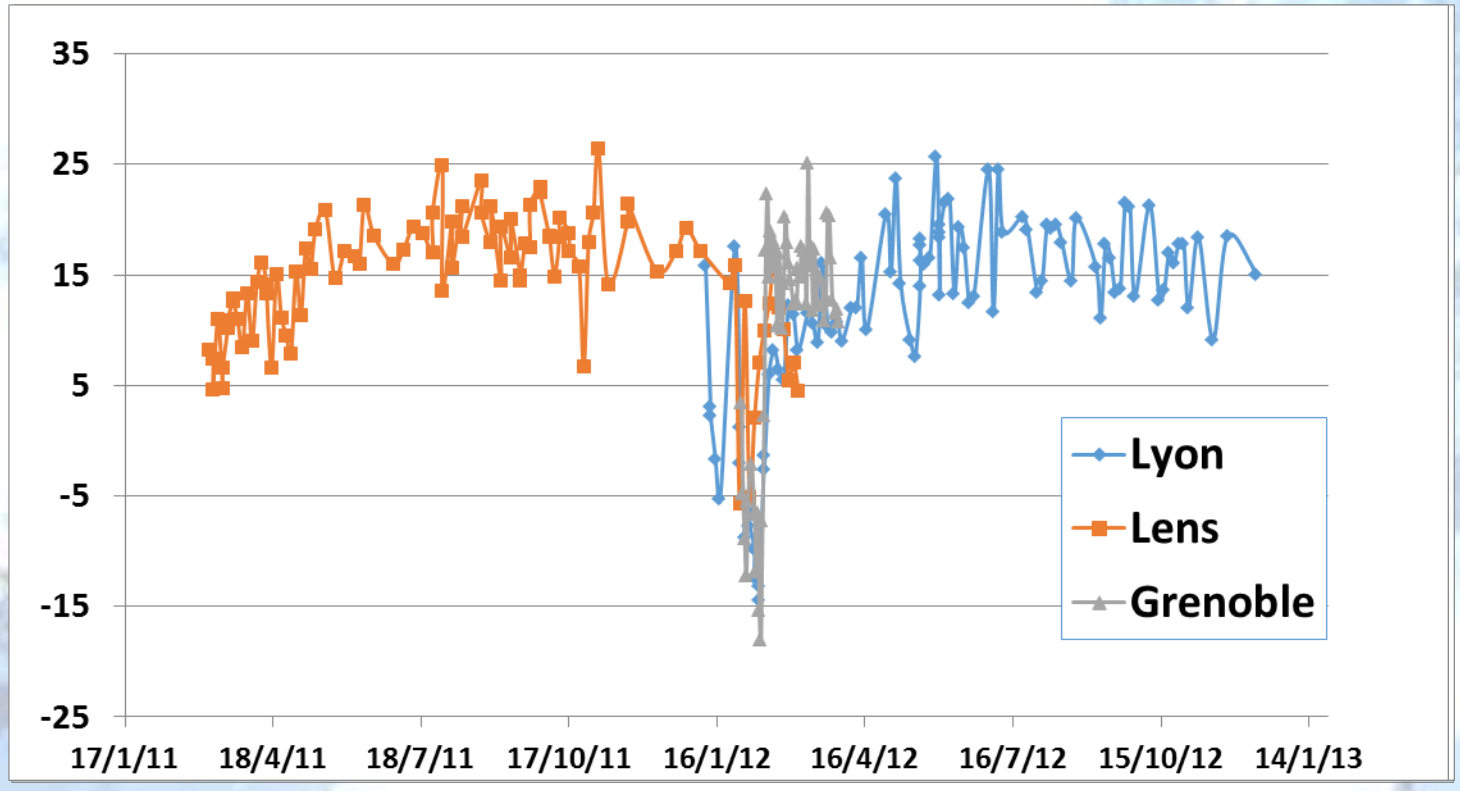

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Well, sorry, no results in PMF study so far !!

However, isotopic ratios and concentrations cannot be mixed in PMF……. Currently looking into other ways for quantification …

And ongoing programs looking into isotopic ratio for N – Nitrate and N- ammonium

- at the sources (NH_3 and NO_x)
- for a large series of episodes in France

We will be back soon with some results ….

Concluding remarks

- Still many ways to improve chemical characterization of off-line measurements for PMF analysis
- Particularly using organic species
  - Biomass combustion
  - Biogenic emissions
  - Industrial sources and coal combustion
  - Secondary organic fraction

- Large improvements also using isotopes (C, O, N)
- Using mixed methods

- Links to ACTRIS / ACTRIS 2

Thanks for your attention !

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