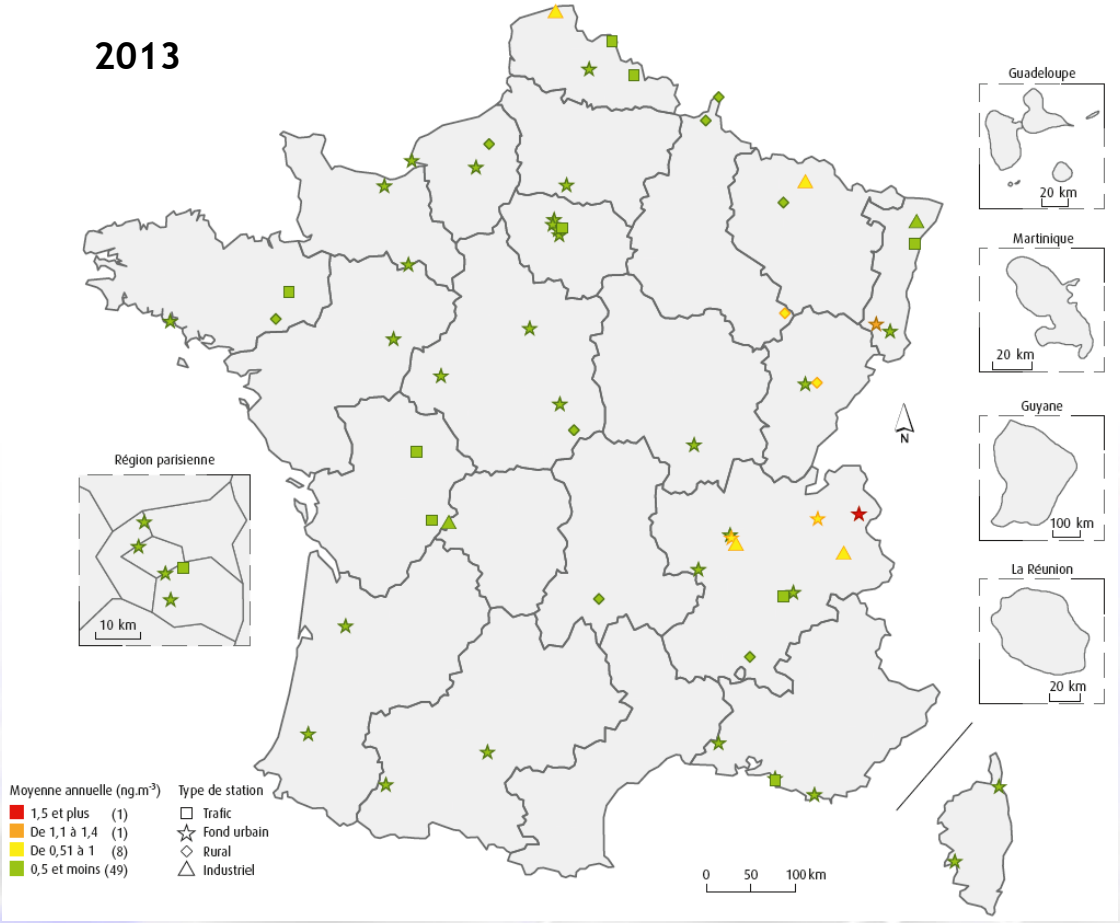
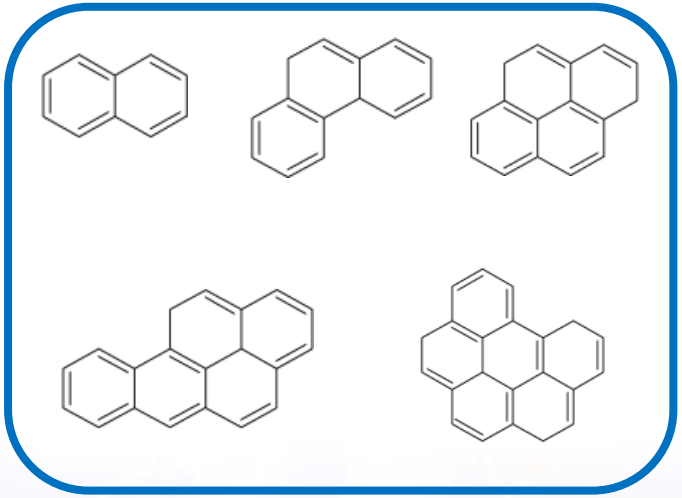
Study of the chemical processes involving nitro- and oxy-PAH in ambient air and evaluation of SOA PAH contribution on PM via annual and intensive field campaigns

A. ALBINET, S. TOMAZ, D. SRIVASTAVA, G.M. LANZAFAME, O. FAVEZ, J.-L. JAFFREZO, J.-L. BESOMBES, N. BONNAIRE, V. GROS, L. Y. ALLEMAN, F. LUCARELLI, E. PERRAUDIN, E. VILLENAVE

Polycyclic aromatic hydrocarbons (PAH)





Regulation

European Directive
2004/107/CE

Target value B[a]P in PM_{10} (annual mean) = 1 ng m^{-3}

Air quality in France (2014)

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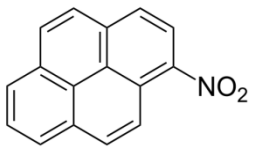
PAH reactivity⇒ oxygenated and nitrated derivatives (nitro- and oxy-PAH)

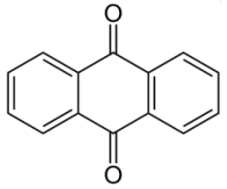
Sources

Primary (combustion processes)

Secondary (parent PAH + photooxidation)
⇒ hν, OH, O_3, NO_2, N_2O_5, NO_3…)



1-Nitropyrene (1-NP)



9,10-Anthraquinone

Interest

Toxicity +++ ? (group 2A and 2B : *IARC, 2012*)

Sources « markers » [1-NP ⇒ diesel (group 1 : *IARC, 2012*)] *Keyte et al., STOTEN, 2016*

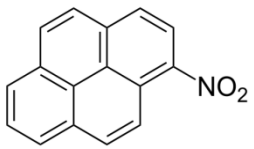
Distribution, sources, processes ⇒ unknowns

PAH reactivity⇒ oxygenated and nitrated derivatives (nitro- and oxy-PAH)

Sources

Primary (combustion processes)

Secondary (parent PAH + photooxidation)
⇒ hν, OH, O_3, NO_2, N_2O_5, NO_3…)



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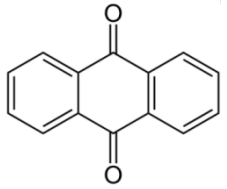

9,10-Anthraquinone

Interest

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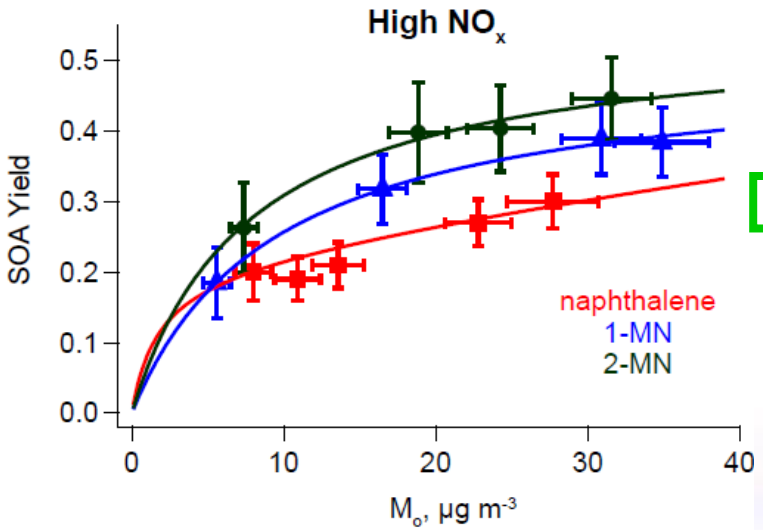
Formation of secondary organic aerosol (SOA)

PAH reactivity ⇒ Source of SOA



Chan et al., ACP, 2009

PAH SOA formation yields > 3 × SOA traditional mono-aromatic compounds

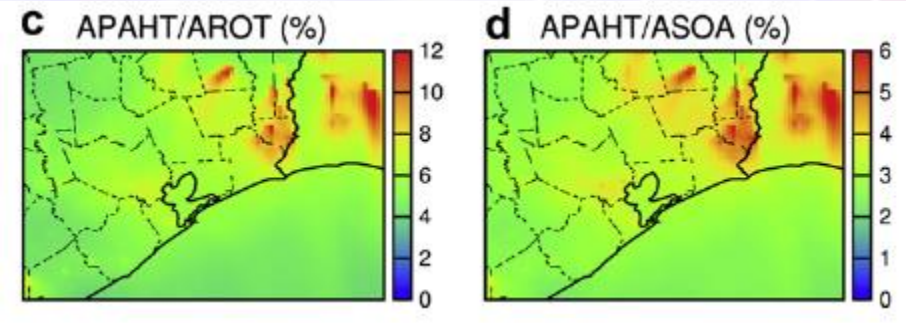
PAH ⇒ about 50% of diesel and wood combustion SOA

PAH ⇒ 10% of urban SOA

Shakya and Griffin, EST, 2010

PAH SOA / Mono-aromatic SOA

PAH SOA / Total anthropogenic SOA



Zhang and Ying, AE, 2012

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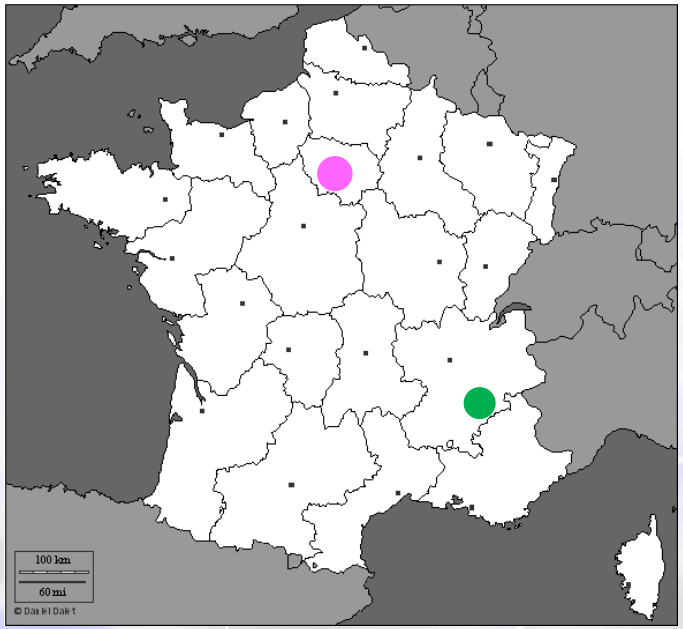
Objectives

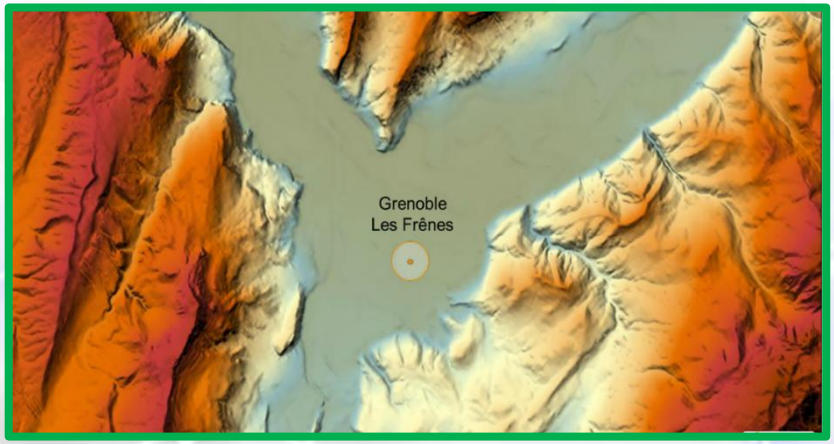
- PAH and PAH derivatives: study of occurrence, seasonal and diurnal variations and risk assessment
- Identification of molecular markers of PAH oxidation and of SOA formation based on field study combined with literature knowledge

PM_{10} source apportionment with evaluation of the contribution of PAH SOA

Sampling sites

Samples collected at an urban station “Les Frênes” in Grenoble (France) and at SIRTA surburban station (25 km SW from Paris city centre)





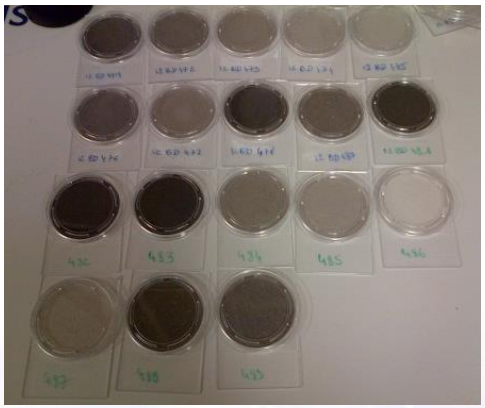
Closely surrounded by three mountainous massifs, and also known for massive wood burning during winters (50% of OM)

Samplings

Gaseous phase

PUF

Particulate phase (PM_{10})



Quartz fiber filter

Annual campaign
2013, Grenoble
2015, SIRTA

24 h, Every third day

Intensive campaign
March 6-22, 2015, SIRTA

Every 4 hour (filter only)

Analyses

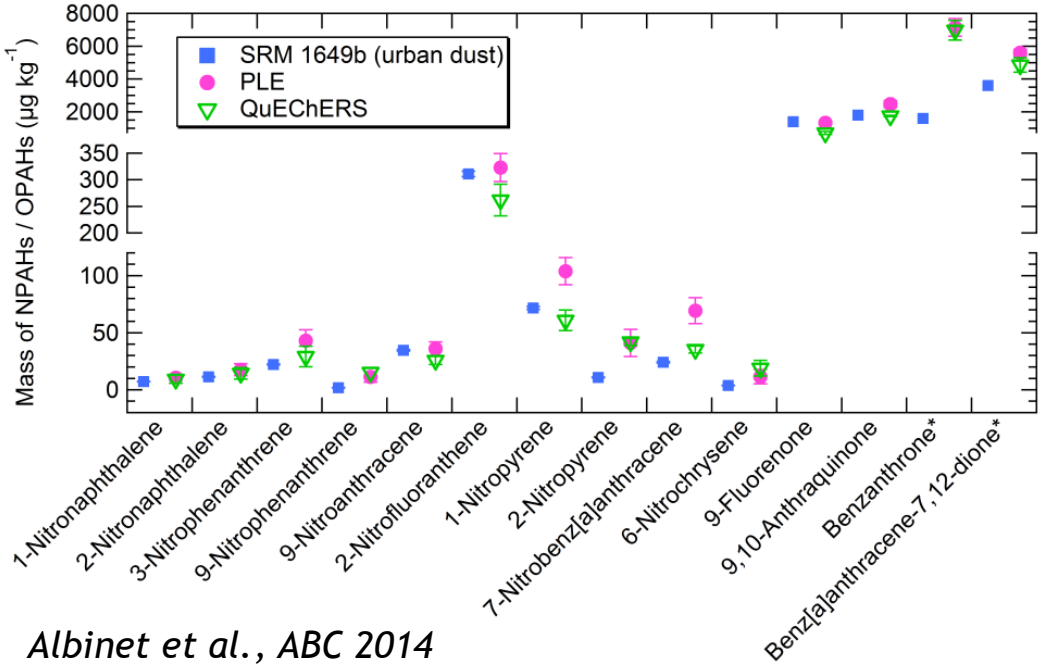
22 PAH ⇒ PLE extraction + UPLC/Fluorescence-UV *EN NF 15549 + TS 16645*

29 Oxy-PAH + 32 Nitro-PAH

- Filters: QuEChERS extraction

(Quick Easy Rugged Effective and Safe)

- PUF: PLE extraction
- Analysis GC/NICI-MS
- QA/QC ⇒ NIST SRM 1649b (urban dust)



Albinet et al., ABC 2014

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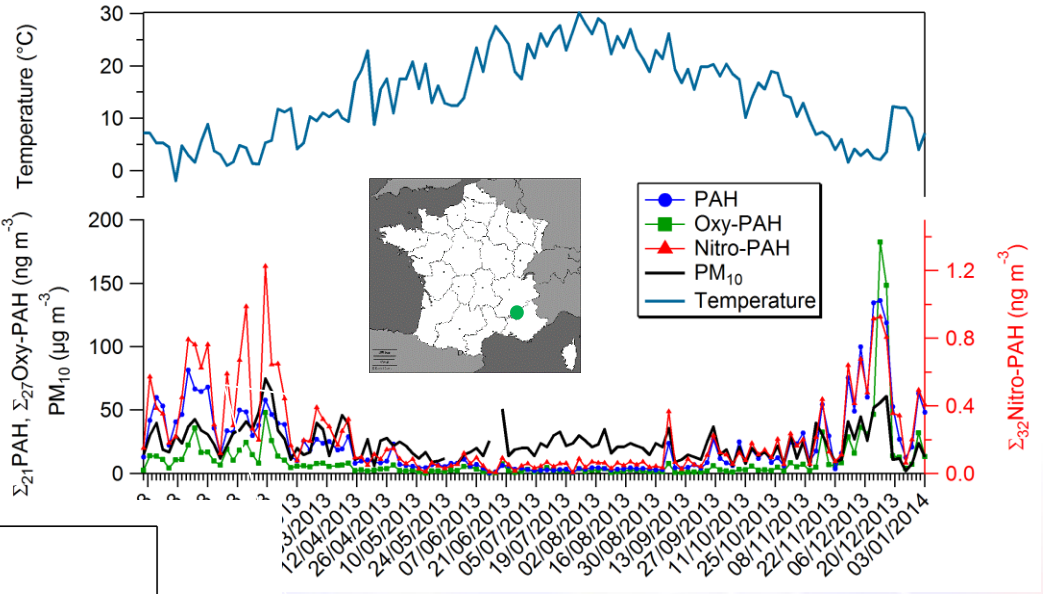
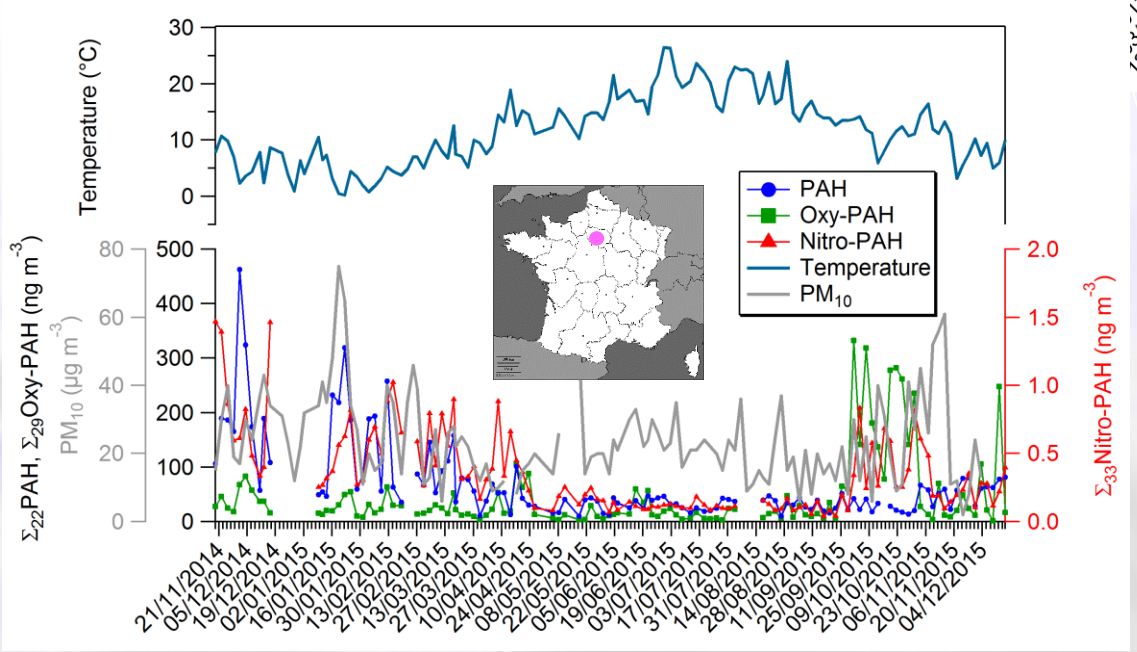
Seasonal variations

Gaseous + particulate phases

Summer season

Degradation by photochemical processes





Winter season

Emission of residential sector (heating)

Thermal inversions

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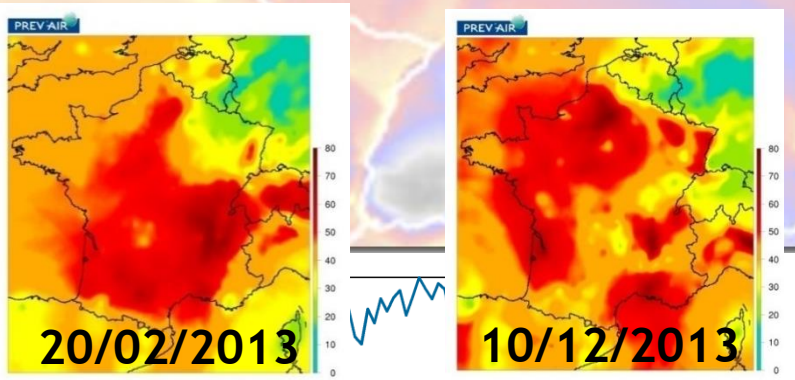
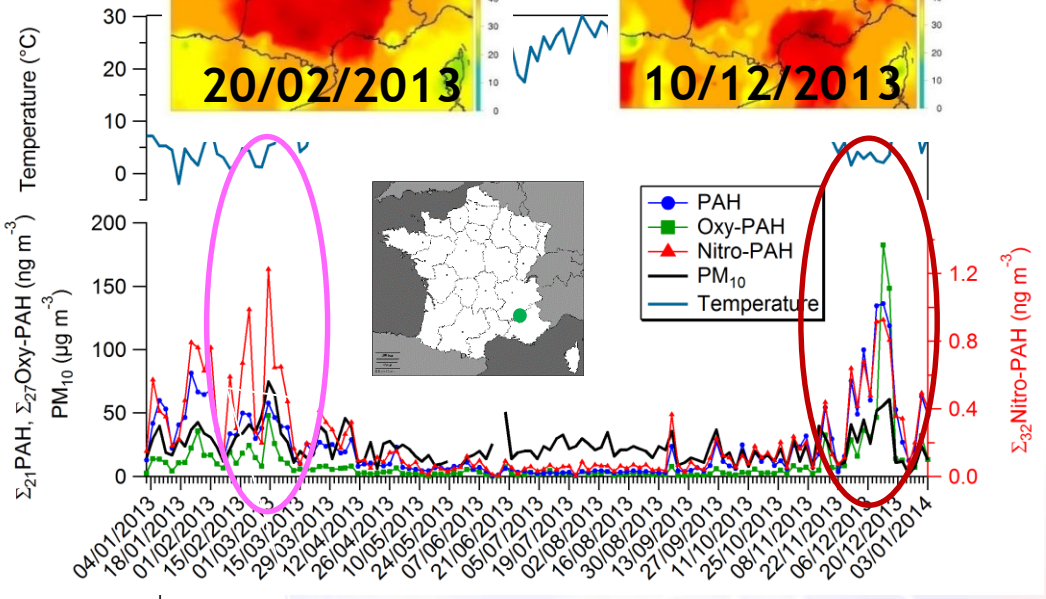
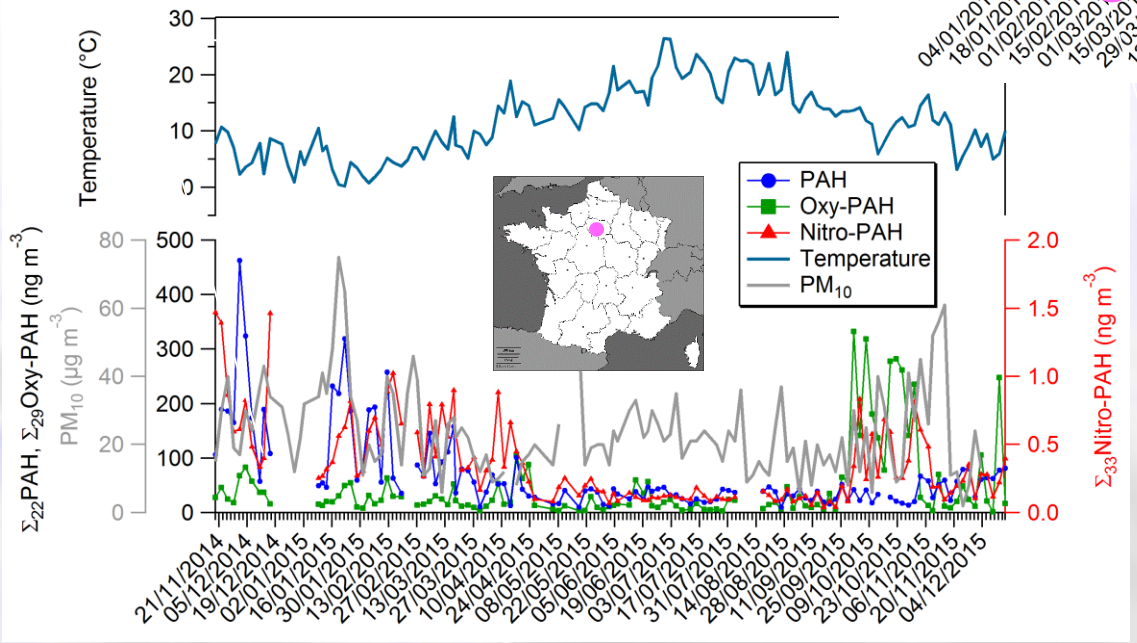
PM pollution events

Gaseous + particulate phases







Winter PM events

⇒ [PAH] and [Oxy-PAH] max

Σ Oxy-PAH>ΣHAP

End winter – Beginning spring PM events

⇒ [Nitro-PAH] max

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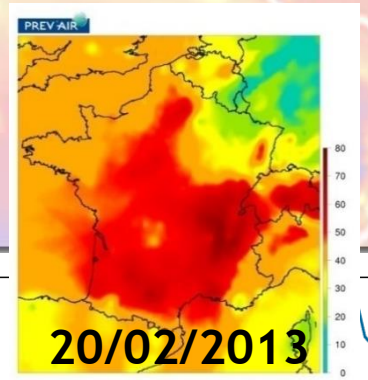
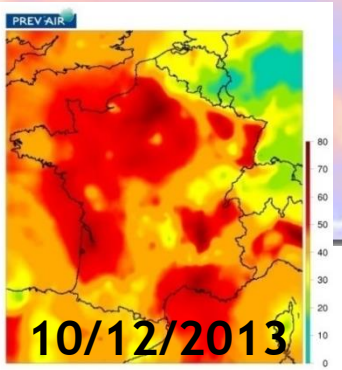
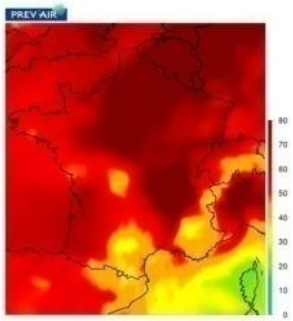
PM pollution events

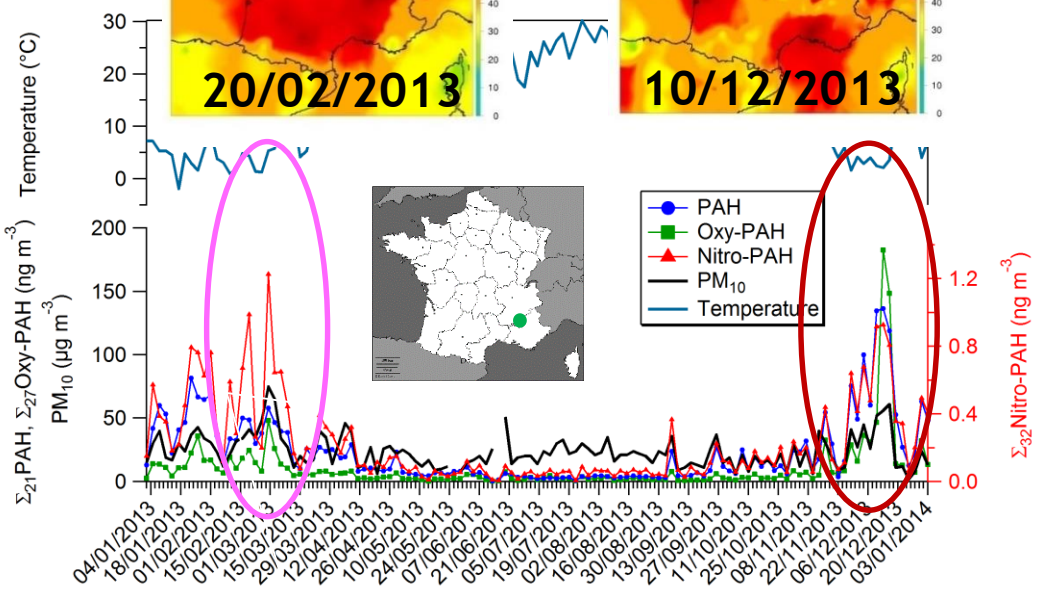


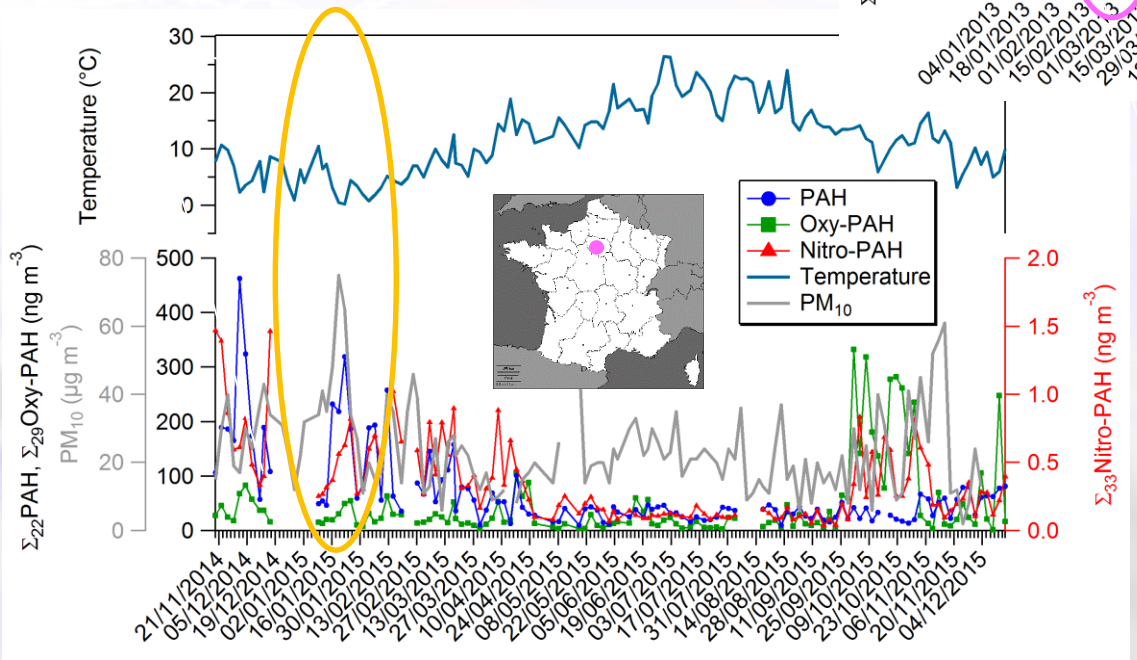


Gaseous + particulate phases



March 2015





Winter PM events

⇒ [PAH] and [Oxy-PAH] max

Σ Oxy-PAH>ΣHAP

End winter – Beginning spring PM events

⇒ [Nitro-PAH] max

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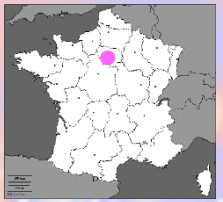
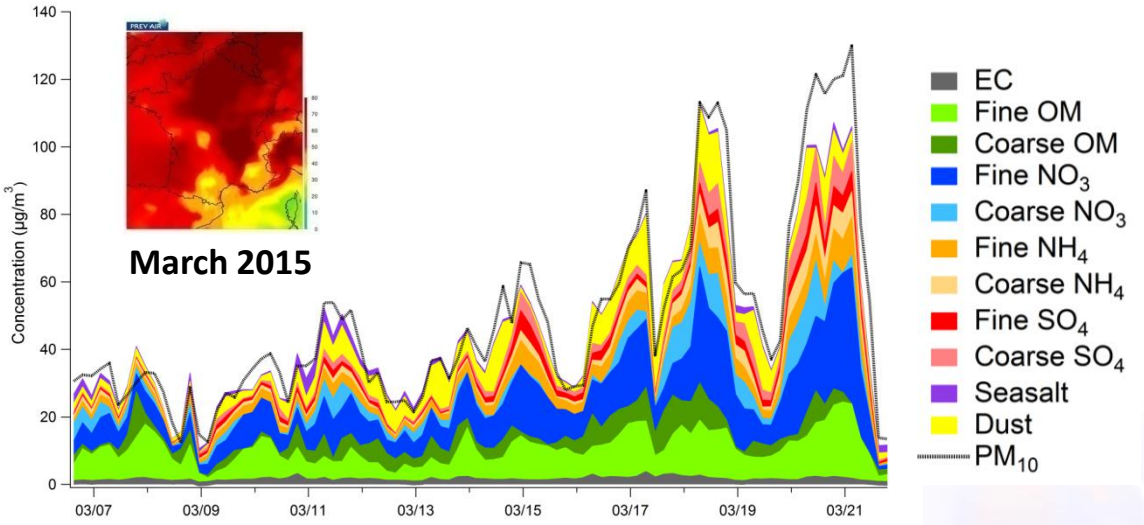
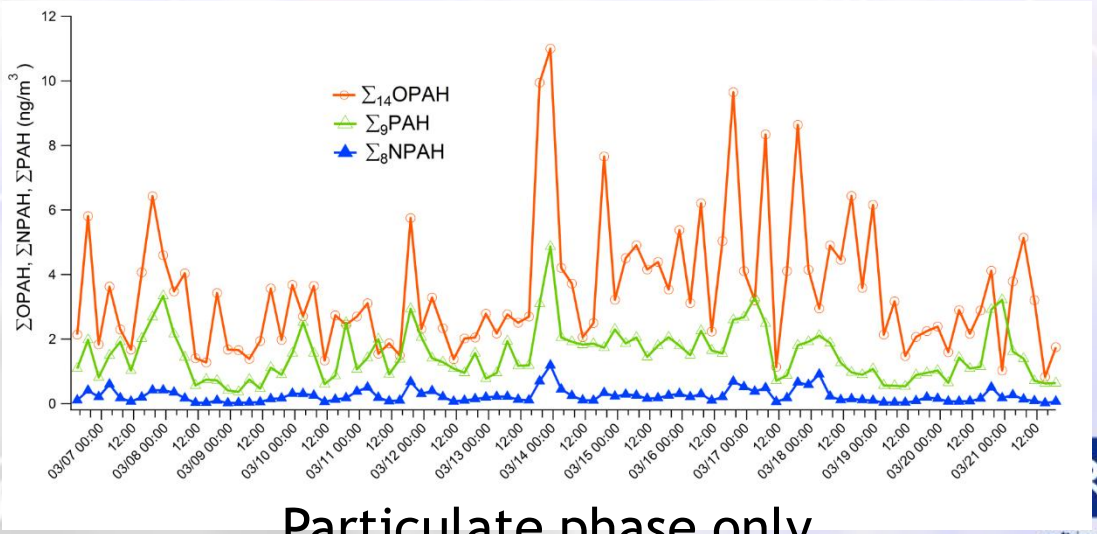
PM pollution event (March 2015), SIRTA





- ✓ In the beginning : low secondary inorganic species
- ✓ At the end, dominated by secondary inorganic aerosols, particularly with ammonium nitrate

- ✓ Very high concentration of oxy-and nitro-PAHs
- ✓ Oxy-PAHs > PAHs

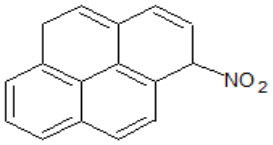


Particulate phase only

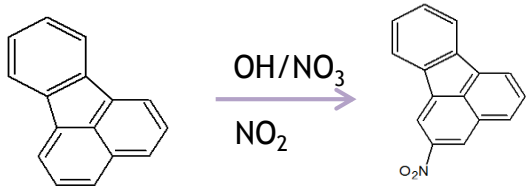
Nitro-PAH: Formation processes (March 2015, SIRTA)

1-Nitropyrene
(1-NP)

Primary emission



Secondary formation

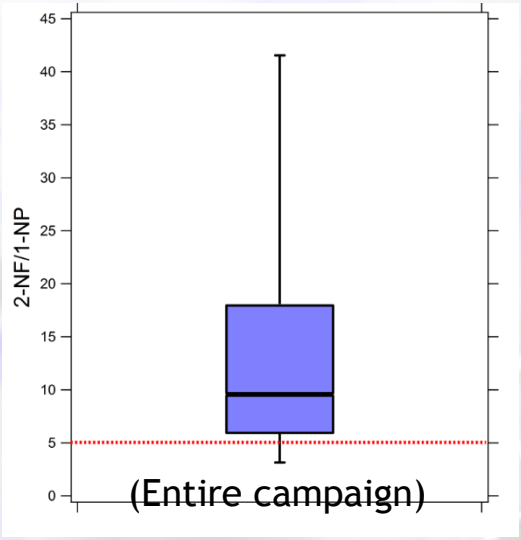


2-Nitrofluoranthene
(2-NF)

2-NF/1-NP < 5 influence of primary emission sources of nitro-PAH

> 5 influence of the secondary formation of nitro-PAH

(Albinet et al., STOTEN 2007, AE 2008; Ciccioli et al., JGR 1996)



Ratio > 5 → **Secondary formation of nitro-PAHs**

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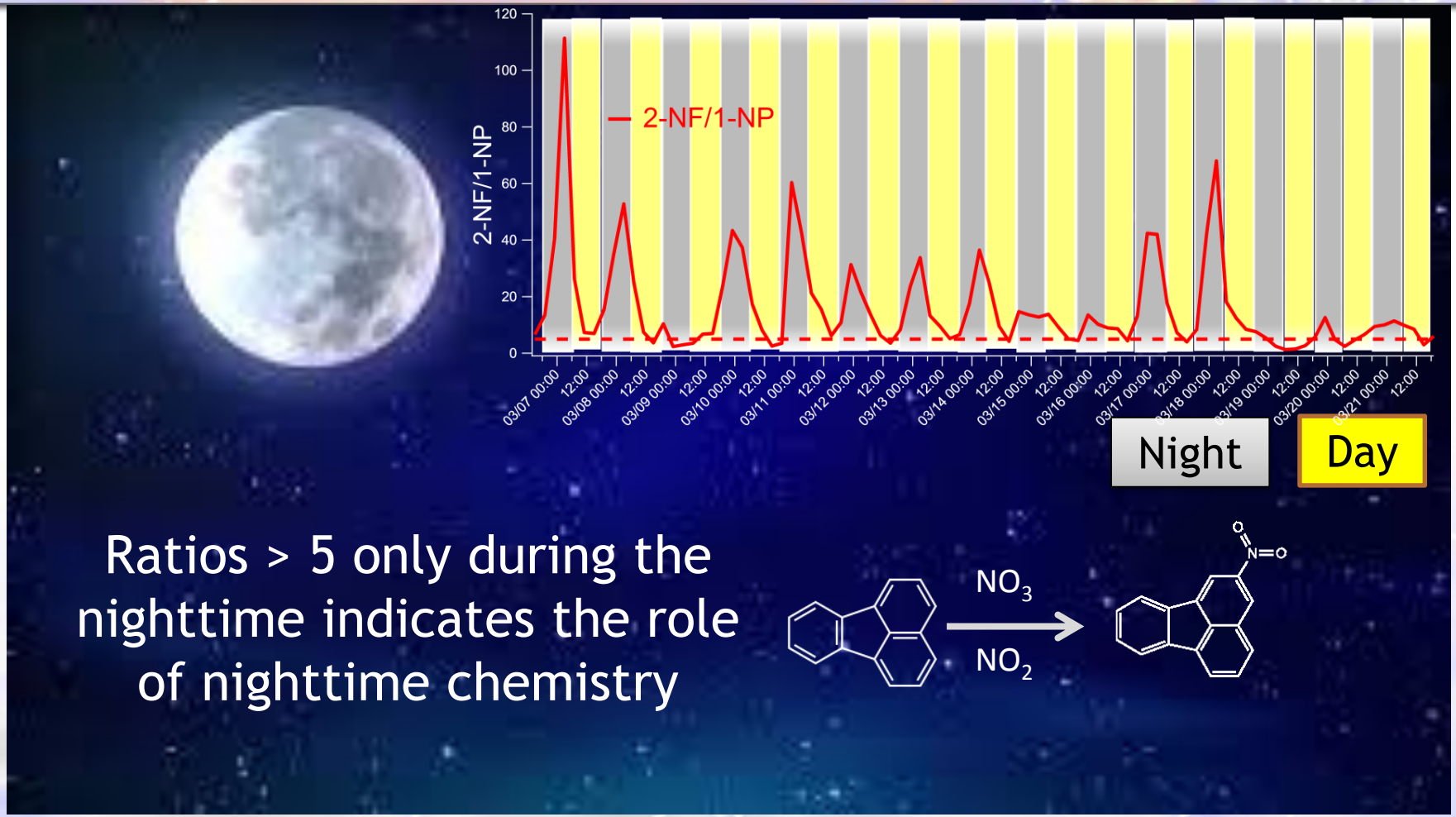
Nitro-PAH: Formation processes (March 2015, SIRTA)



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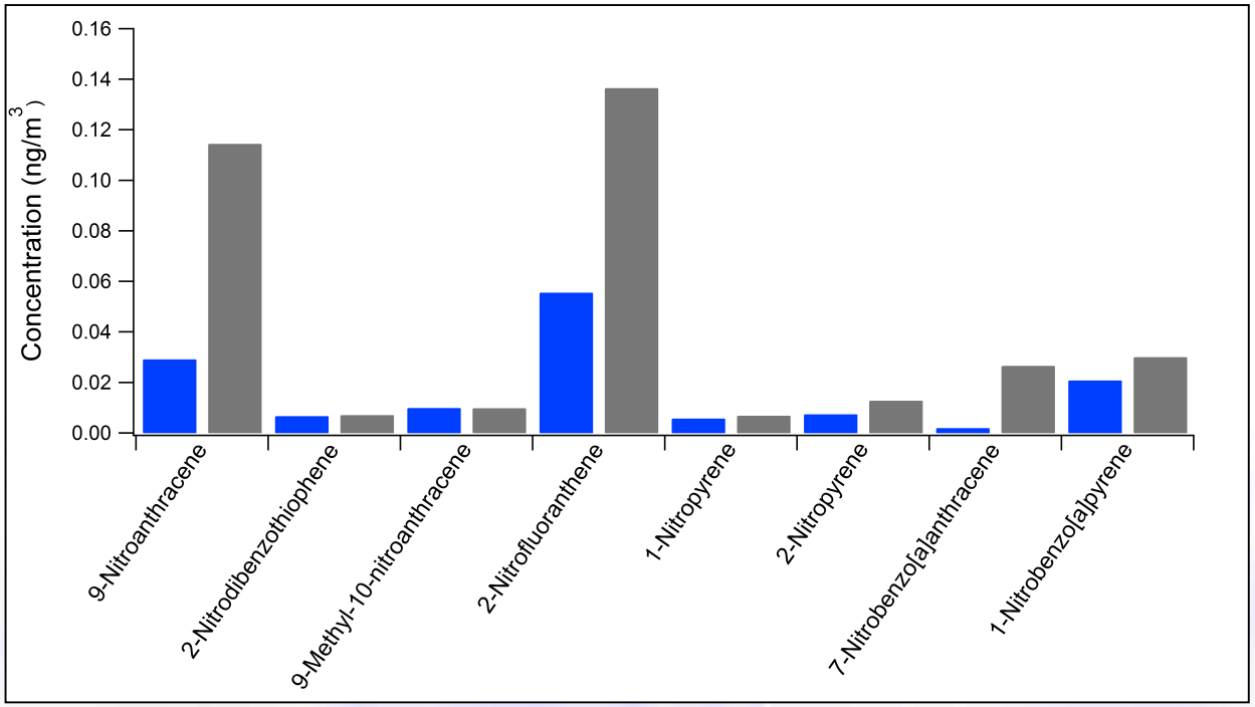
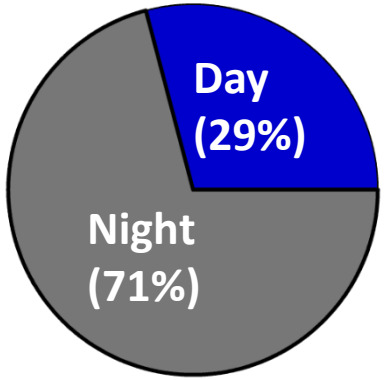
Nitro-PAH: Formation processes (March 2015, SIRTA)





Nighttime ?

Daytime ?

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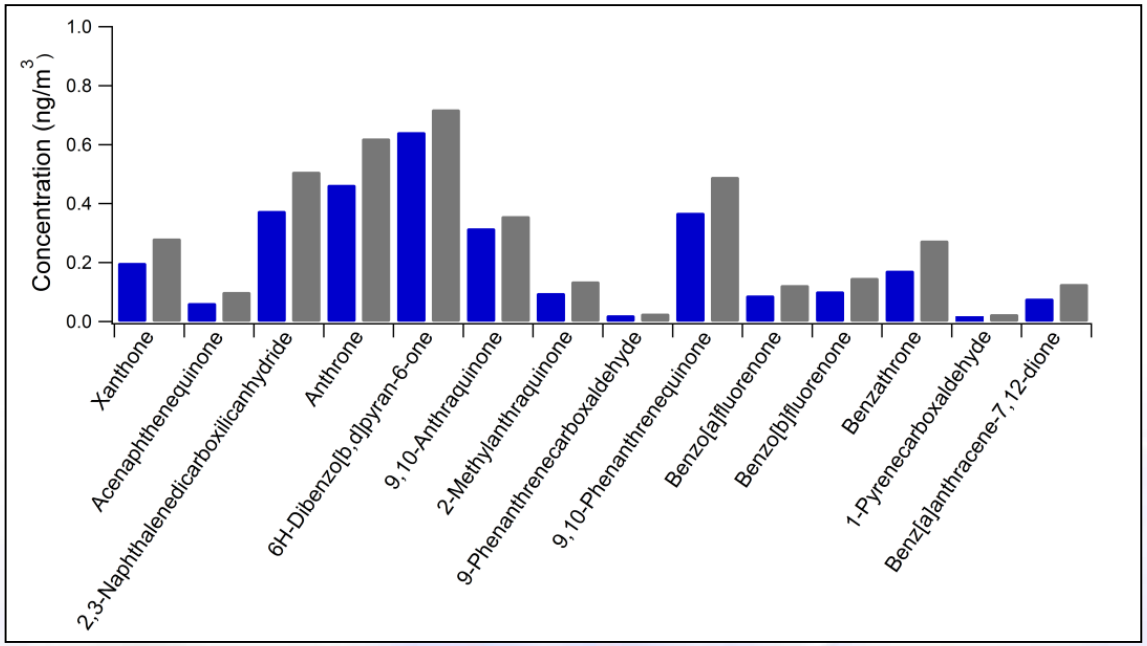
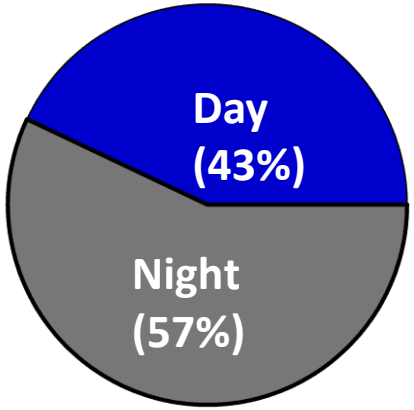
Oxy-PAH: Formation processes (March 2015, SIRTA)





No significant difference observed

Nighttime ?

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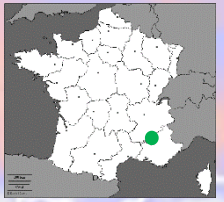
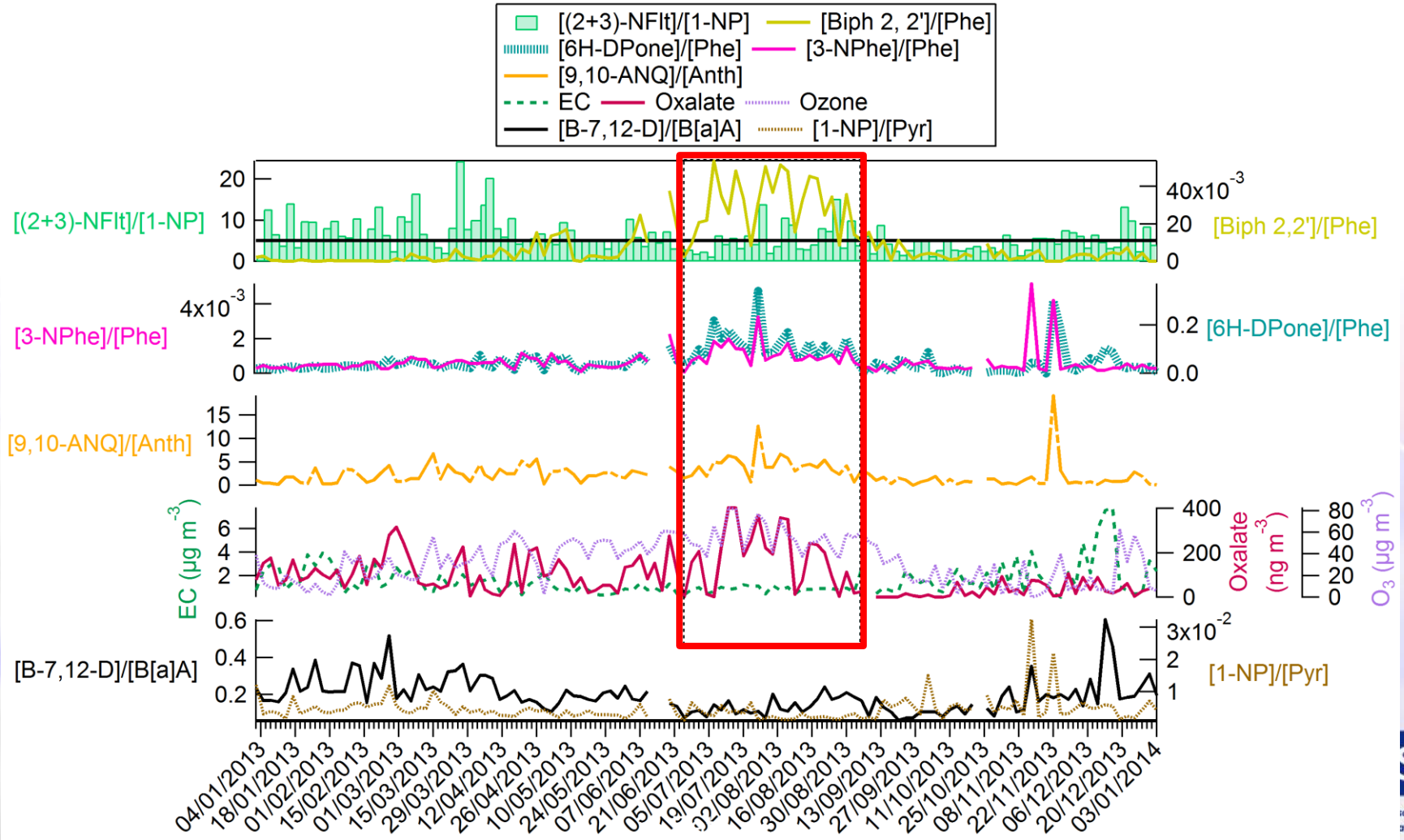
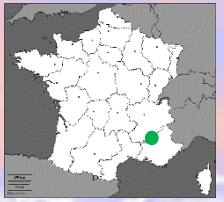
Identification of secondary markers



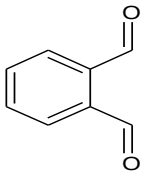
Study of PAC/parent PAH ratios



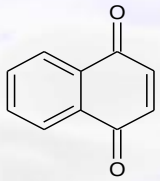
Identification of other secondary markers



Naphthalene



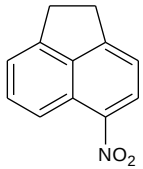
Phtaldialdehyde



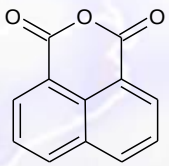
1,4-Naphtoquinone

Lee and Lane, AE, 2009

Acenaphthylene Acenaphthene



5-Nitroacenaphthene

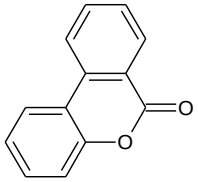


Anhydride-1,8-naphtalique

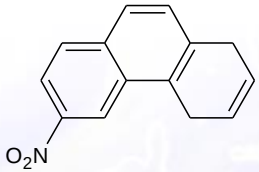
Zhou and Wenger, AE, 2013

Reisen and Arey, EST, 2002

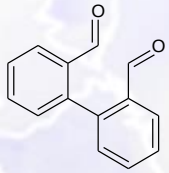
Phenanthrene



6H-Dibenzo[b,d]pyran-6-one



3-Nitrophenanthrene



Biphenyl-2,2'-dicarboxaldehyde

Lee and Lane, AE, 2010

Perraudin et al, AE, 2007

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PM source apportionment

PM chemical composition

Extended chemical characterization was performed

Organics (n=174): Oxalate, PAC (PAH, SPAH (BNT), Nitro-PAH, Oxy-PAH), MSA, HuLiS, Hopanes, Levoglucosan, Higher alkanes (HA), Polyols (arabitol, sorbitol, mannitol and glucose), SOA markers (DHOPA, HGA, MBTCA, …)

Ionic species (n=8): NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+} , K^+, Ca^{2+} , NH_4^+

Metals (n=34): As, Ba, Cu, Al, Ti, Bi, Ni, V, Ce, Co, Sr, Sn, Zn, Cr, Mo…

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et Environnement

UNIVERSITÀ
DEGLI STUDI
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Positive matrix factorization (PMF)

$$X = F*G + E$$

X= input data

F= factor profile

G= temporal contribution

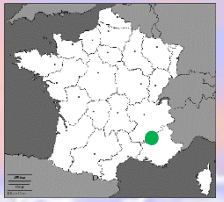
E=residual

EPA PMF software v5.0

No priori knowledge of G, F and no of factors

Extensively used for the source apportionment from off-line measurements

Input for PMF (Grenoble)



Diesel marker

SOA PAH

OC	Benzo[a]pyrene	Sb	HP5
EC	Benzo[g,h,i]perylene	Ti	HP6
HULIS	Ind[1,2,3-cd]pyrene	Zn	HP7
Na^+	Coronene	Cr	HP8
NH_4^+	Acenaphthenequinone	V	Coniferylaldehyde
Mg^{2+}	6H-Dibenzo[b,d]pyran-6-one	Al	Vanillic acid
Cl-	1,8-Naphthalic anhydride	Ca	Alpha-methyl glyceric acid
NO_3^-	1-Nitropyrene	Fe	DHOPA
SO_4^{2-}	PM_{10}	C27	3-Hydroxyglutaric Acid
Levoglucosan	Ba	C29	Phthalic Acid
Arabitol	Cu	C31	2-Methyl erythritol
Sorbitol	Pb	C33	

Fossil fuel

Primary biomass burning

Isoprene

Toluene

α-pinene

Naphthalene

Isoprene

Sea salt

Primary biomass burning

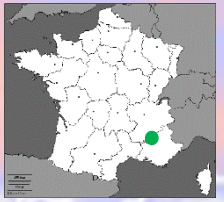
Primary biogenic (fungi)

Plant debris

Primary organic marker

Secondary organic marker

Results for PMF run (Grenoble)

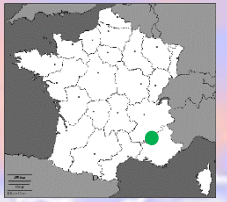


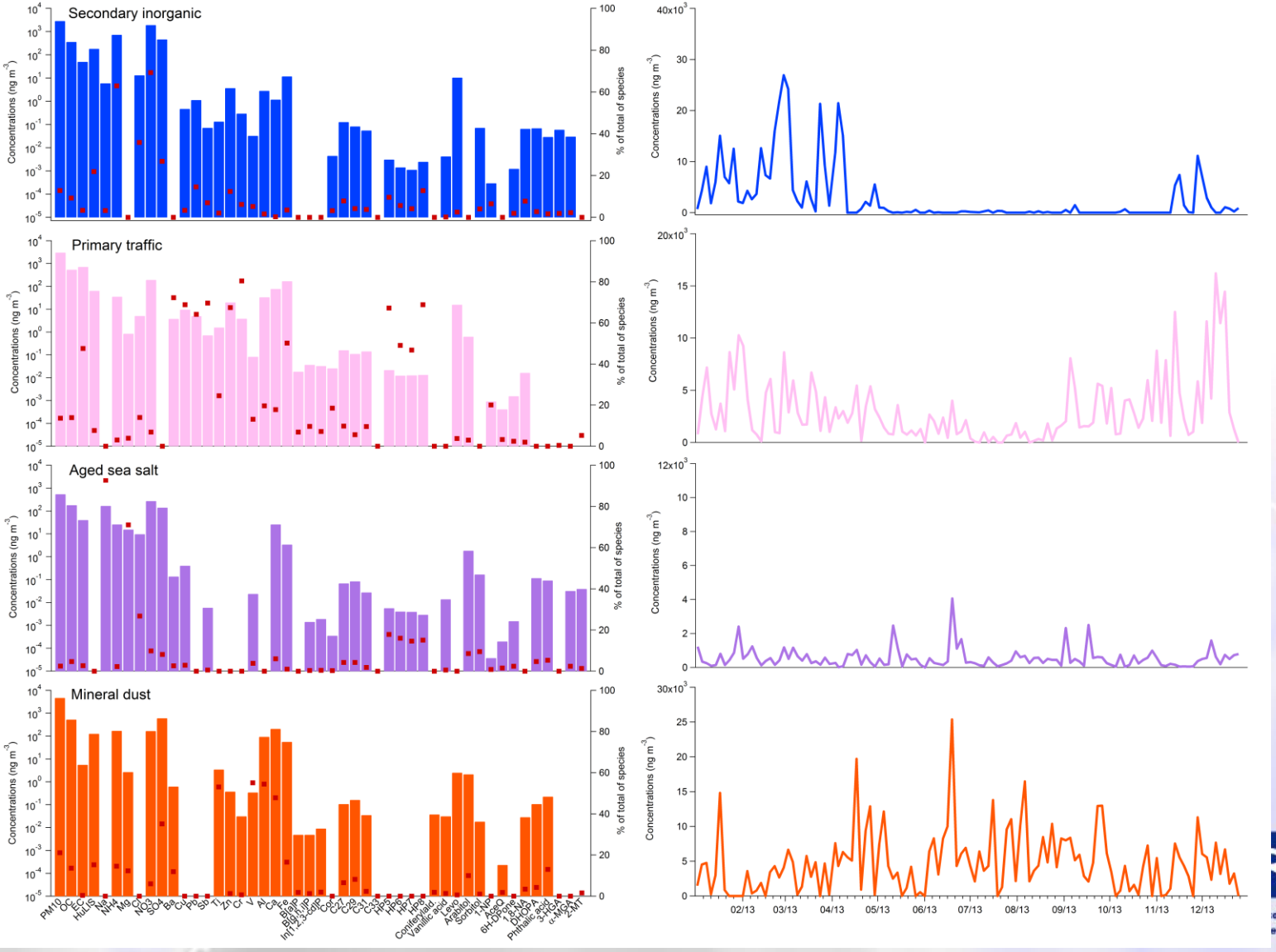
9 factors solution

1. Mineral dust
2. Primary traffic
3. Biomass burning
4. Anthropogenic SOA
5. Biogenic SOA
6. Plant debris
7. Secondary inorganic
8. Primary biogenic (Fungi)
9. Aged sea salt

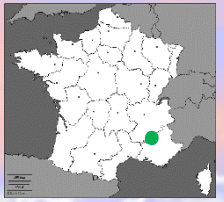
100 PMF runs were performed for each case, and more than 95% of runs were converged in each scenario

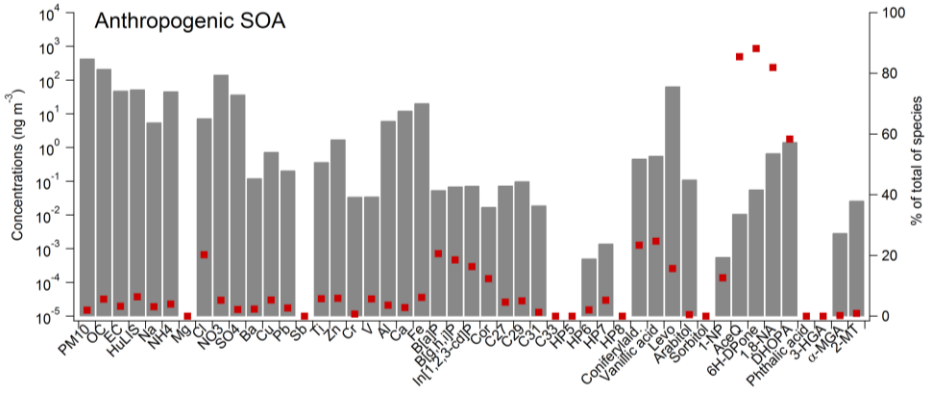
Results for PMF run: few examples

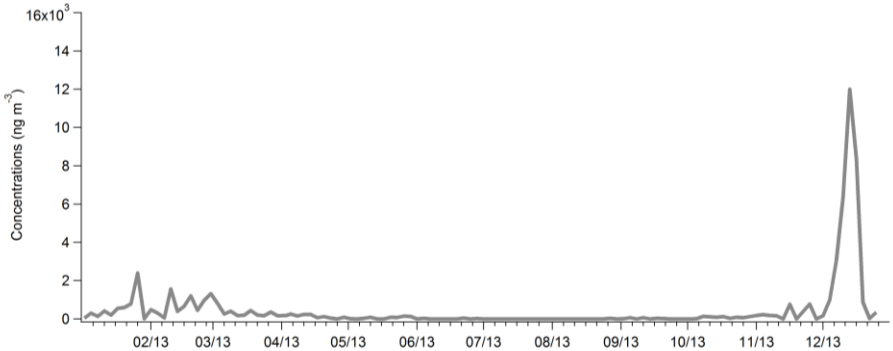




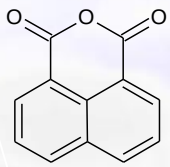
Anthropogenic SOA factor



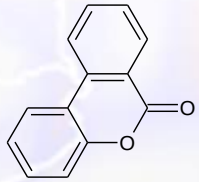




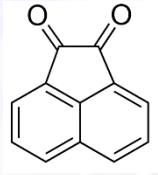
- Oxy-PAH (SOA PAH)



Anhydride-1,8-naphtalique

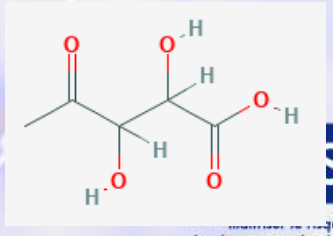


6H-Dibenzo[b,d]pyran-6-one



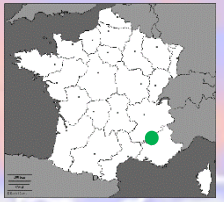
Acenaphthoquinone

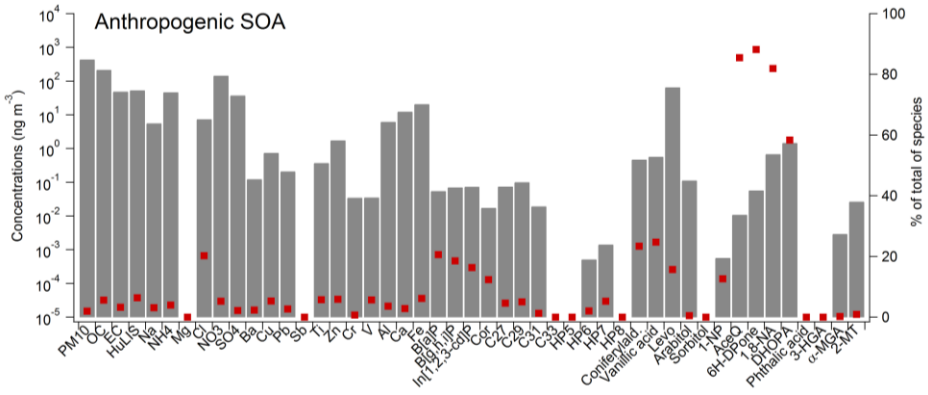
- DHOPA (2,3-Dihydroxy-4-oxopentanoic acid) ⇒ Toluene SOA

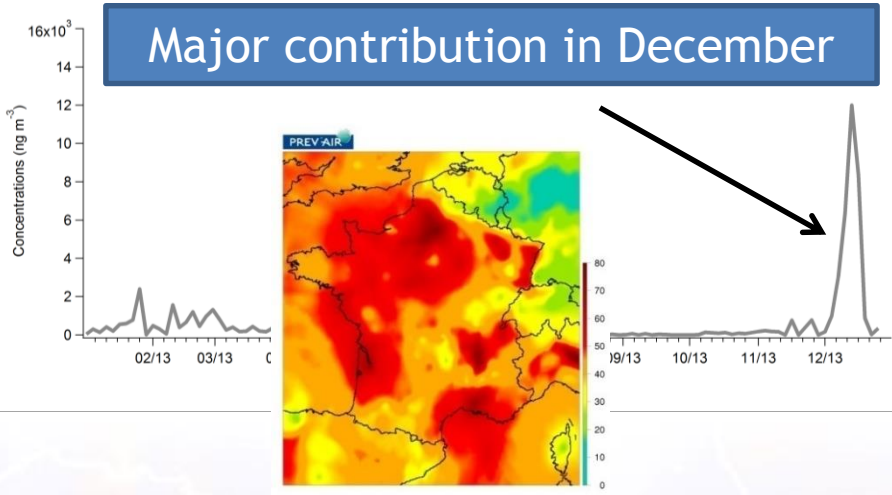


Kleindienst et al., AE 2007

Anthropogenic SOA factor

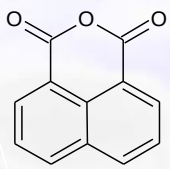




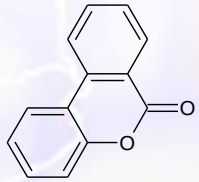


Major contribution in December

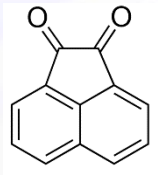
- Oxy-PAH (SOA PAH)



Anhydride-1,8-naphtalique

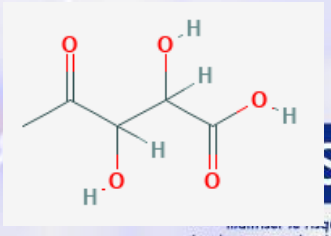


6H-Dibenzo[b,d]pyran-6-one



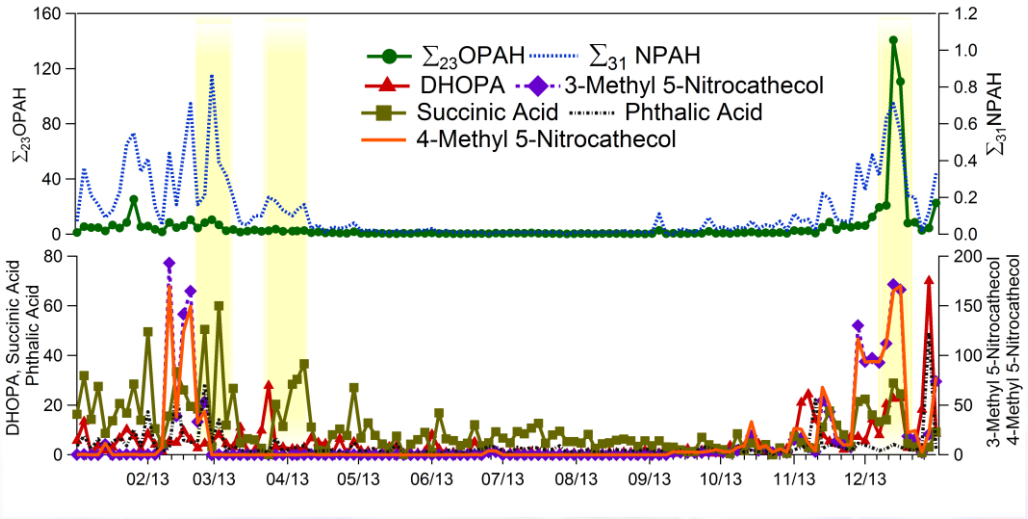
Acenaphthoquinone

- DHOPA (2,3-Dihydroxy-4-oxopentanoic acid) ⇒ Toluene SOA



Kleindienst et al., AE 2007

Secondary PAC during PM pollution event: processes ?



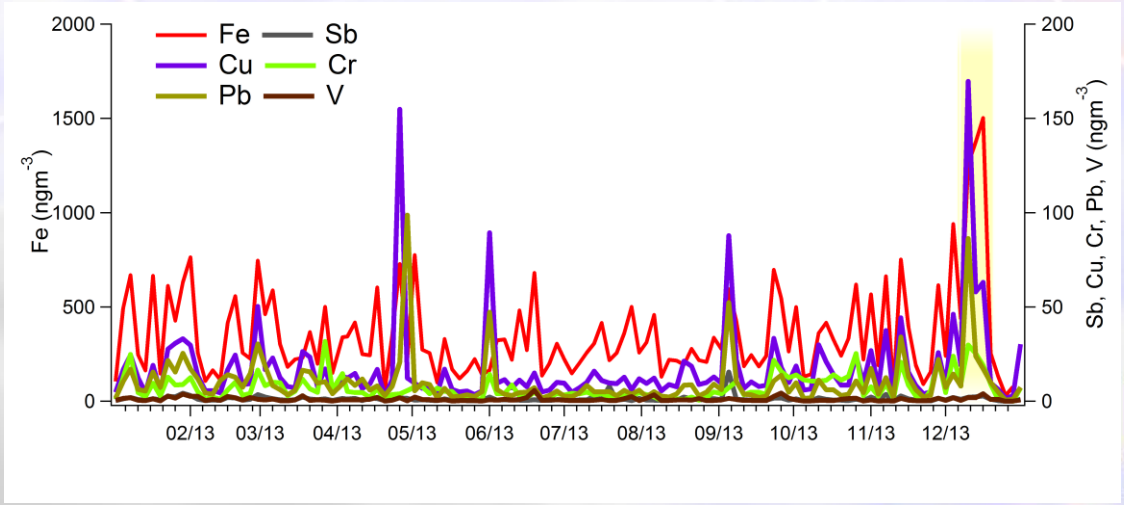
Low inversion layer (over 20 days) ⇒

Accumulation of pollutants + enough reaction time and presence of OH radical

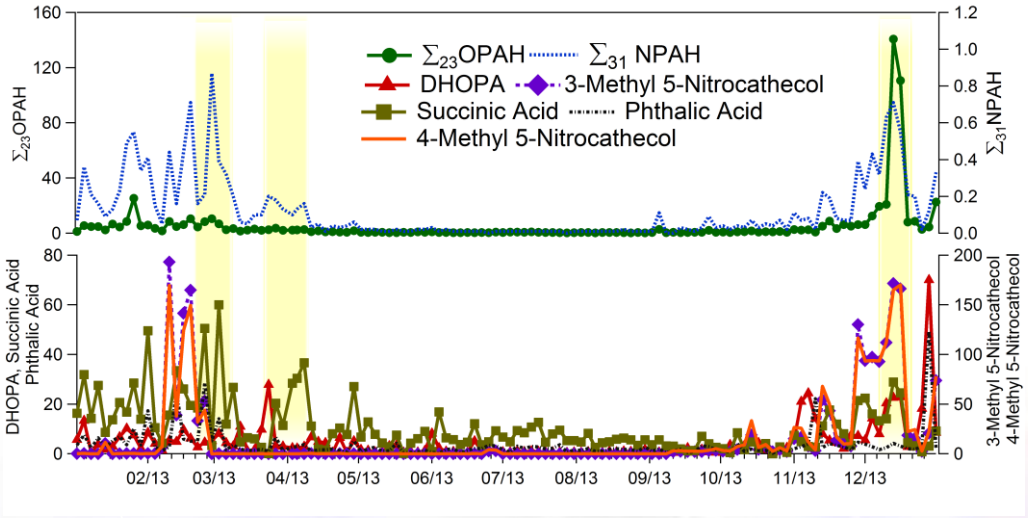
⇒ **Secondary formation**

Presence of Fe ⇒

Fenton like reactions
(OH radical generation)



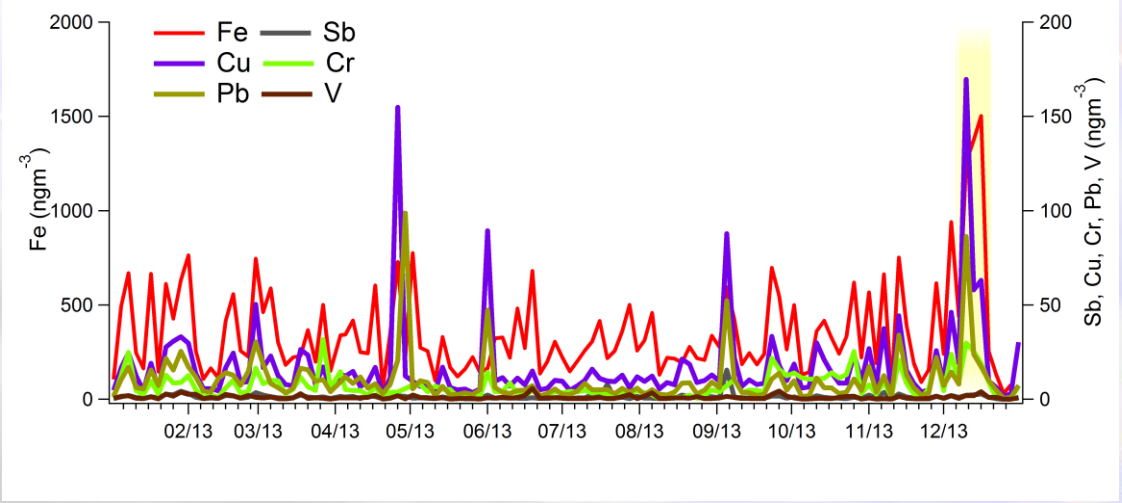
Secondary PAC during PM pollution event: processes ?



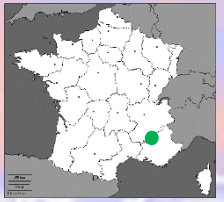
OH radical formed from SOA decomposition ⇒

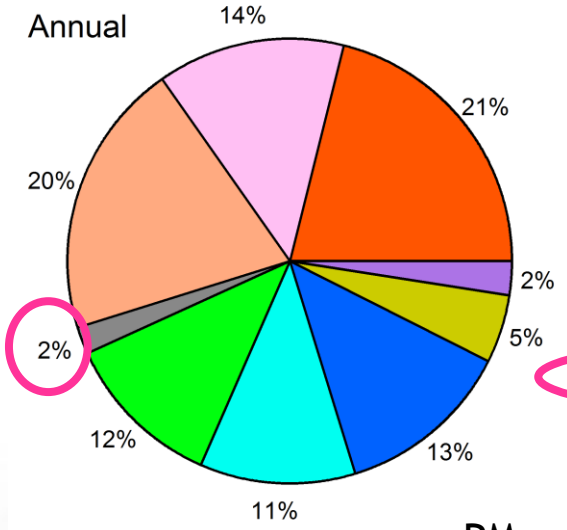
Self amplification cycle of SOA formation

Tong et al., ACP, 2016



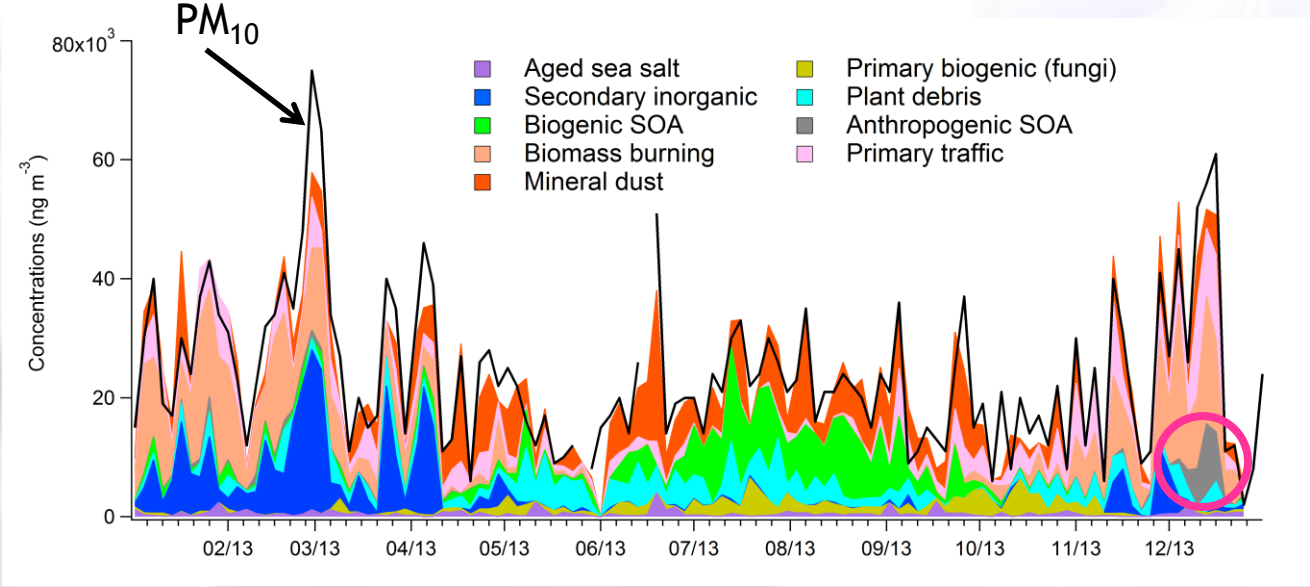
PM source apportionment (Grenoble 2013)





- Mineral dust
- Aged sea salt
- Primary biogenic (fungi)
- Secondary inorganic
- Plant debris
- Biogenic SOA
- Anthropogenic SOA
- Biomass burning
- Primary traffic

= 6% of OC



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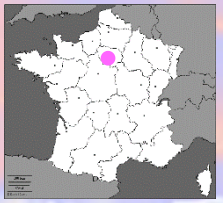
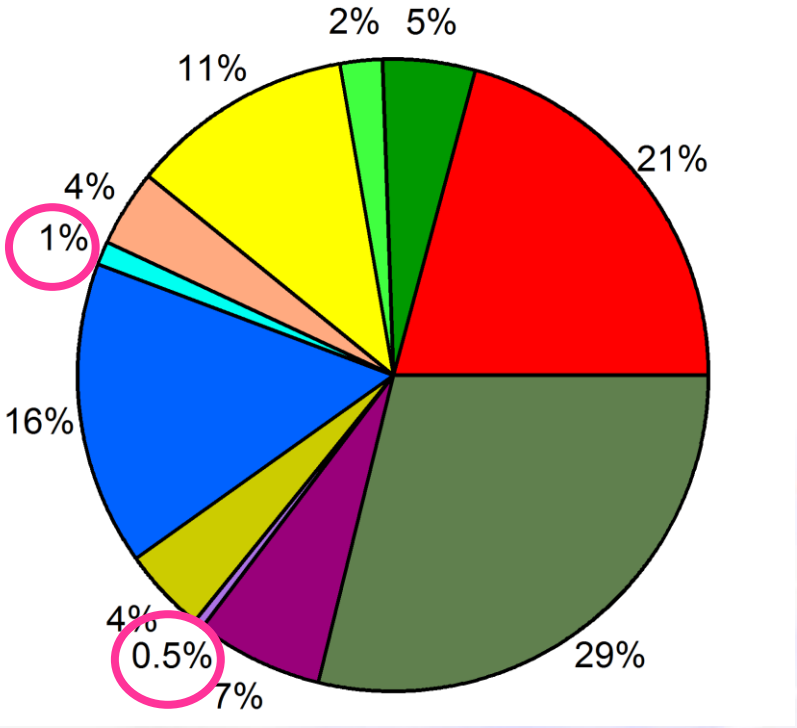
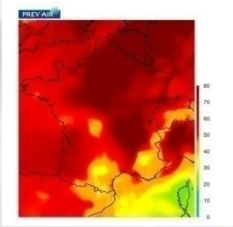
PM source apportionment (March 2015, SIRTA)





- Secondary sulfate
- Secondary nitrate
- Primary traffic
- Anthropogenic SOA1 (nitro-PAHs processes)
- Marine biogenic
- Mineral dust
- Anthropogenic SOA2 (oxy-PAHs processes)
- Sea salt
- Biomass burning
- Isoprene SOA
- α-Pinene SOA



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Papers

Tomaz et al., One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation, STOTEN, 565, 1071–1083, 2016.

Shahpoury et al., Evaluation of a Conceptual Model for Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons Using Polyparameter Linear Free Energy Relationships, ES&T, 50, 12312–12319, 2016.

Tomaz et al., Sources and atmospheric chemistry of oxy- and nitro-PAHs in the ambient air of Grenoble (France), Atm. Env., 161, 144–154, 2017.

Srivastava et al., Demonstrating that speciation of organic fraction does matter for source apportionment: Use of specific primary and secondary organic markers, STOTEN, submitted, 2017.

Financial support

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RÉPUBLIQUE FRANÇAISE
Ministère de la Transition écologique et solidaire

LCSQA
Laboratoire Central de Surveillance de la Qualité de l'Air

Thank you for your attention!

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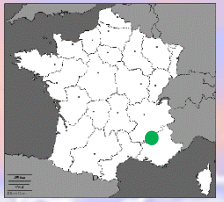
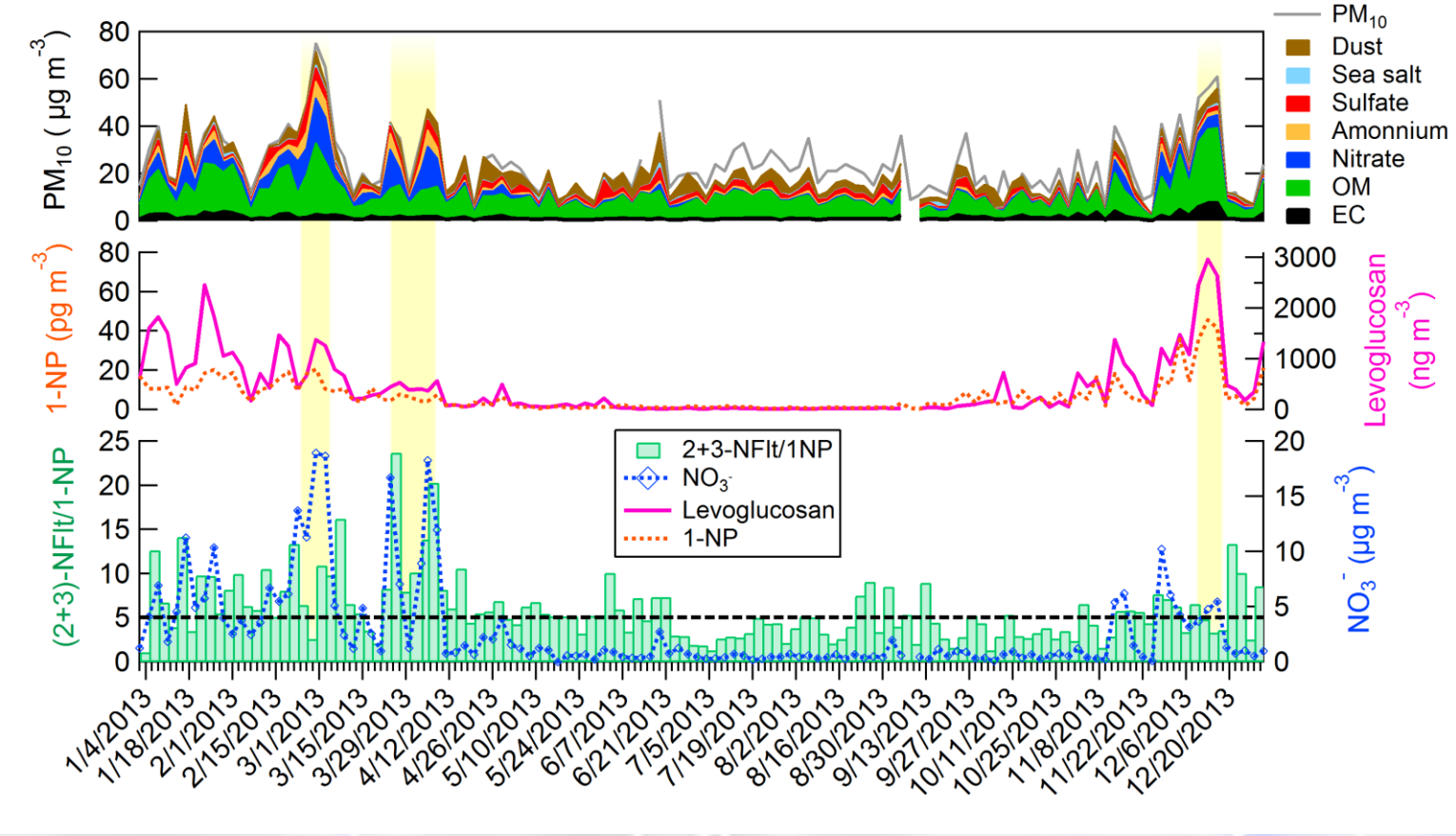
Nitro-PAH: Formation processes (Grenoble)





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