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

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)
PAH reactivity \( \Rightarrow \) oxygenated and nitrated derivatives (nitro- and oxy-PAH)

**Sources**

**Primary** (combustion processes)

**Secondary** (parent PAH + photooxidation) 
\( \Rightarrow h_v, OH, O_3, NO_2, N_2O_5, NO_3... \)

**Interest**

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

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

Distribution, sources, processes \( \Rightarrow \) unknowns
PAH reactivity ⇒ oxygenated and nitrated derivatives (nitro- and oxy-PAH)

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⇒ $h\nu$, OH, O$_3$, NO$_2$, N$_2$O$_5$, NO$_3$...

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Keyte et al., STOTEN, 2016

Formation of secondary organic aerosol (SOA)
PAH reactivity ⇒ Source of SOA

PAH SOA formation yields $> 3 \times$ SOA traditional mono-aromatic compounds
PAH ⇒ about 50% of diesel and wood combustion SOA

PAH SOA / Mono-aromatic SOA
PAH SOA / Total anthropogenic SOA

PAH ⇒ 10% of urban SOA

Shakya and Griffin, EST, 2010

Zhang and Ying, AE, 2012
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 suburban 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).
Gaseous phase

Particulate phase (PM$_{10}$)

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 $\Rightarrow$ 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 $\Rightarrow$ NIST SRM 1649b (urban dust)

Albinet et al., ABC 2014
Seasonal variations

Gaseous + particulate phases

Summer season
Degradation by photochemical processes

Emission of residential sector (heating)
Thermal inversions
PM pollution events

Gaseous + particulate phases

Winter PM events
\[ [\text{PAH}] \text{ and } [\text{Oxy-PAH}] \text{ max} \]
\[ \Sigma \text{Oxy-PAH} > \Sigma \text{HAP} \]

End winter - Beginning spring PM events
\[ [\text{Nitro-PAH}] \text{ max} \]
PM pollution events

Gaseous + particulate phases

March 2015

Winter PM events

$\Rightarrow [\text{PAH}]$ and $[\text{Oxy-PAH}]$ max

$\Sigma \text{ Oxy-PAH} > \Sigma \text{HAP}$

End winter - Beginning spring PM events

$\Rightarrow [\text{Nitro-PAH}]$ max
PM pollution event (March 2015), SIRTA

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

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

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

1-Nitropyrene (1-NP)

Primary emission

Secondary formation

2-Nitrofluoranthen (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
Ratios > 5 only during the nighttime indicates the role of nighttime chemistry.

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

No significant difference observed
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*
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...
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)

<table>
<thead>
<tr>
<th>Input for Primary Biomass Burning</th>
<th>SOA PAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>Benzo[a]pyrene</td>
</tr>
<tr>
<td>EC</td>
<td>Benzo[g,h,i]perylene</td>
</tr>
<tr>
<td>HULIS</td>
<td>Ind[1,2,3-cd]pyrene</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Coronene</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Acenaphthenequinone</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>6H-Dibenzo[b,d]pyran-6-one</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1,8-Naphthalic anhydride</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1-Nitropyrene</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>PM₁₀</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>Ba</td>
</tr>
<tr>
<td>Arabitol</td>
<td>Cu</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>Pb</td>
</tr>
</tbody>
</table>

### Sources
- **Diesel marker**
- **Sea salt**
- **Fossil fuel**
- **Primary biomass burning**
- **Primary biogenic (fungi)**
- **Secondary organic marker**
Results for PMF run (Grenoble)

9 factors solution

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Mineral dust</td>
</tr>
<tr>
<td>2.</td>
<td>Primary traffic</td>
</tr>
<tr>
<td>3.</td>
<td>Biomass burning</td>
</tr>
<tr>
<td>4.</td>
<td>Anthropogenic SOA</td>
</tr>
<tr>
<td>5.</td>
<td>Biogenic SOA</td>
</tr>
<tr>
<td>6.</td>
<td>Plant debris</td>
</tr>
<tr>
<td>7.</td>
<td>Secondary inorganic</td>
</tr>
<tr>
<td>8.</td>
<td>Primary biogenic (Fungi)</td>
</tr>
<tr>
<td>9.</td>
<td>Aged sea salt</td>
</tr>
</tbody>
</table>

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) \(\Rightarrow\) Toluene SOA

*Kleindienst et al., AE 2007*
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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: 21%
- Aged sea salt: 14%
- Primary biogenic (fungi): 13%
- Secondary inorganic: 12%
- Plant debris: 5%
- Biogenic SOA: 2%
- Anthropogenic SOA: 2%
- Biomass burning: 11%
- Primary traffic: 10%

Anthropogenic SOA = 6% of OC

PM$_{10}$ concentrations (ng m$^{-3}$)
PM source apportionment (March 2015, SIRTA)

- Secondary sulfate: 21%
- Secondary nitrate: 16%
- Primary traffic: 16%
- Anthropogenic SOA1 (nitro-PAHs processes): 11%
- Marine biogenic: 7%
- Mineral dust: 5%
- Anthropogenic SOA2 (oxy-PAHs processes): 4%
- Sea salt: 4%
- Biomass burning: 4%
- Isoprene SOA: 1%
- α-Pinene SOA: 0.5%
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.


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.


Financial support

Thank you for your attention!
Nitro-PAH: Formation processes (Grenoble)