Laboratoire CHIMIE Provence

Equipe
Instrumentation **R**éactivité **A**tmosphérique

SMPS (Scanning Mobilty Particle Sizer) : Applications et intégration à la plateforme MASSALYA

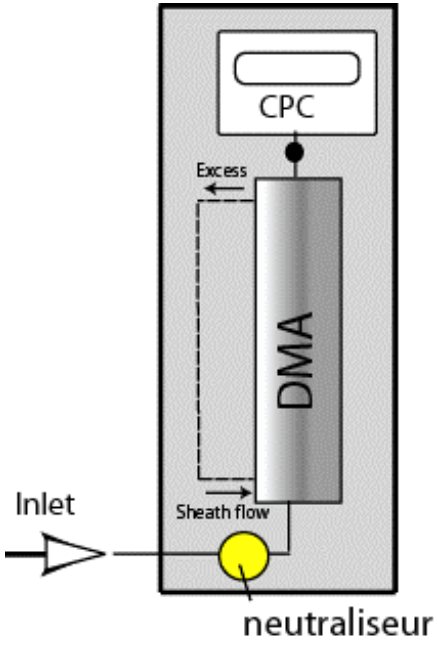
N. Marchand, I. El Haddad, Y. Liu, S. Net, A. Vesin, A. Manoukian, E. Abidi, S. Tlili, Gligorovski S., R. Strekowski, A. Monod, B. Temime-Roussel, E. Quivet, H. Wortham

AEI, Brest, 24 Juin 2010

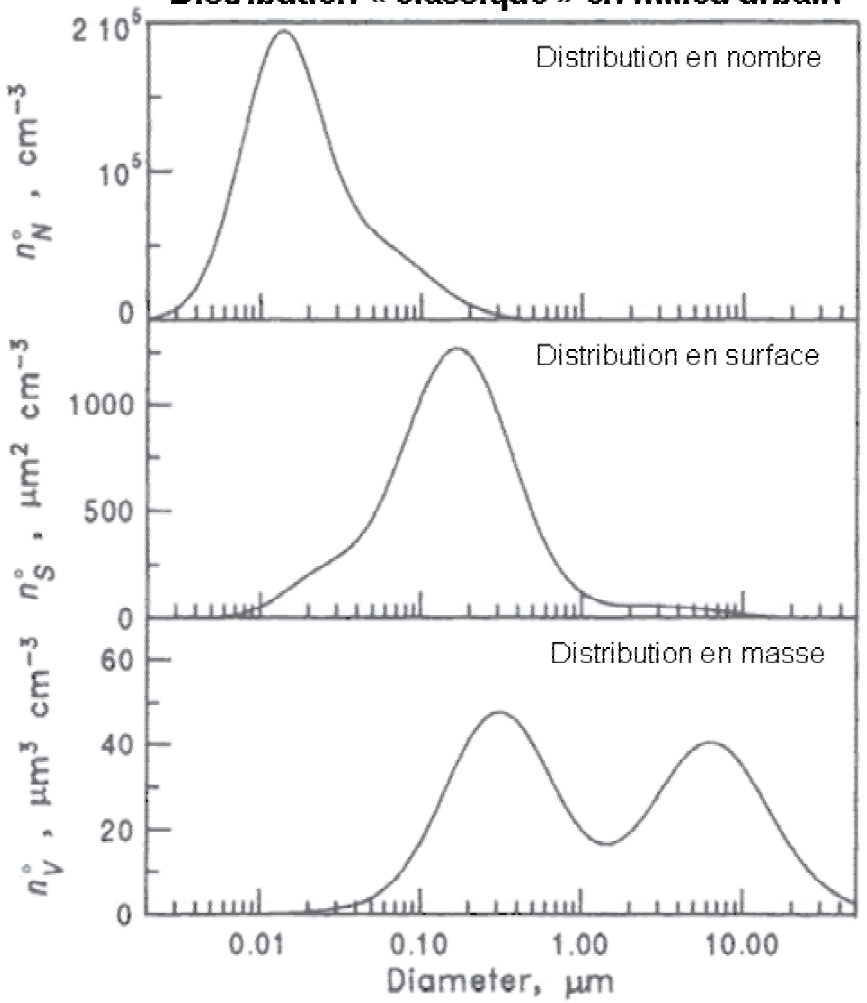
SMPS (Scanning Mobilty Particle Sizer)

Instrument de « base » pour l'étude des propriétés physiques de l'aérosol

Distribution en nombre, en surface et en volume de l'aérosol submicronique



Distribution « classique » en milieu urbain



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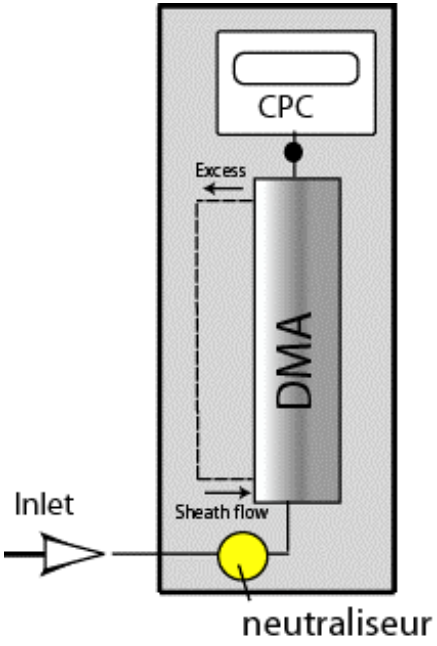

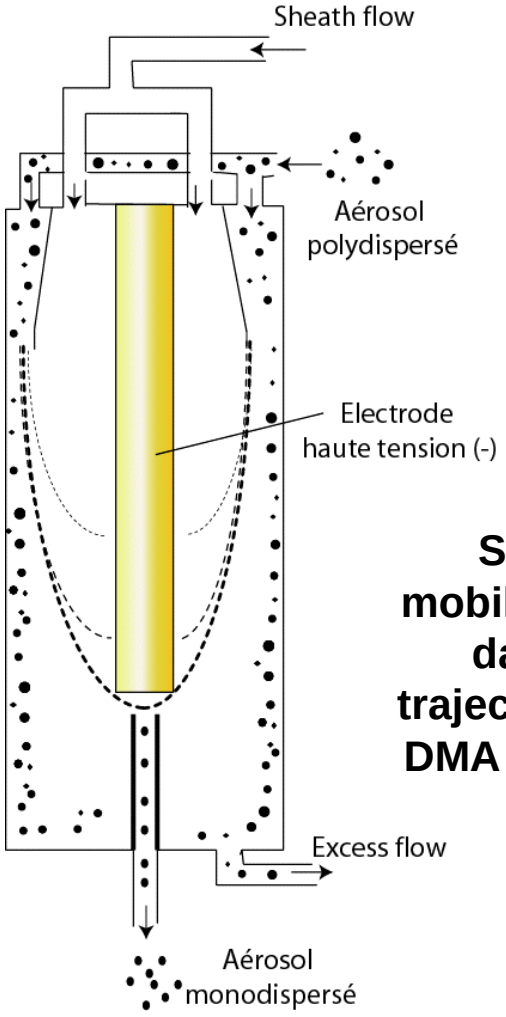

Colonne DMA

Les particules sont séparées en fonction de leur mobilité électrique

Seules les particules dont les mobilités électriques sont comprises dans une étroite fenêtre ont la trajectoire correcte pour s'extraire du DMA et être comptées en aval par un CPC.

15 nm <Dp< 1.2µm

4 nm <Dp< 50 nm (nano DMA)

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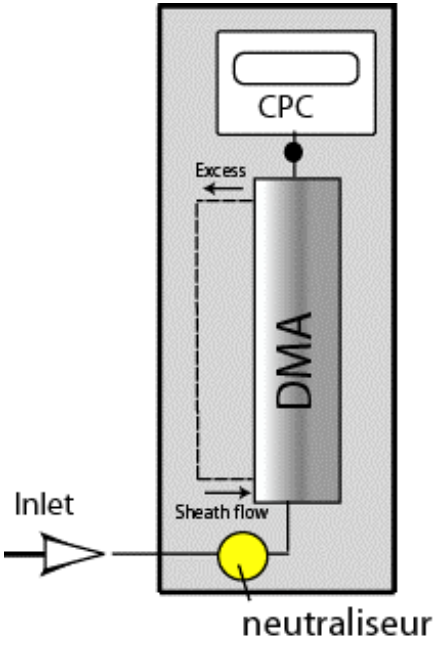
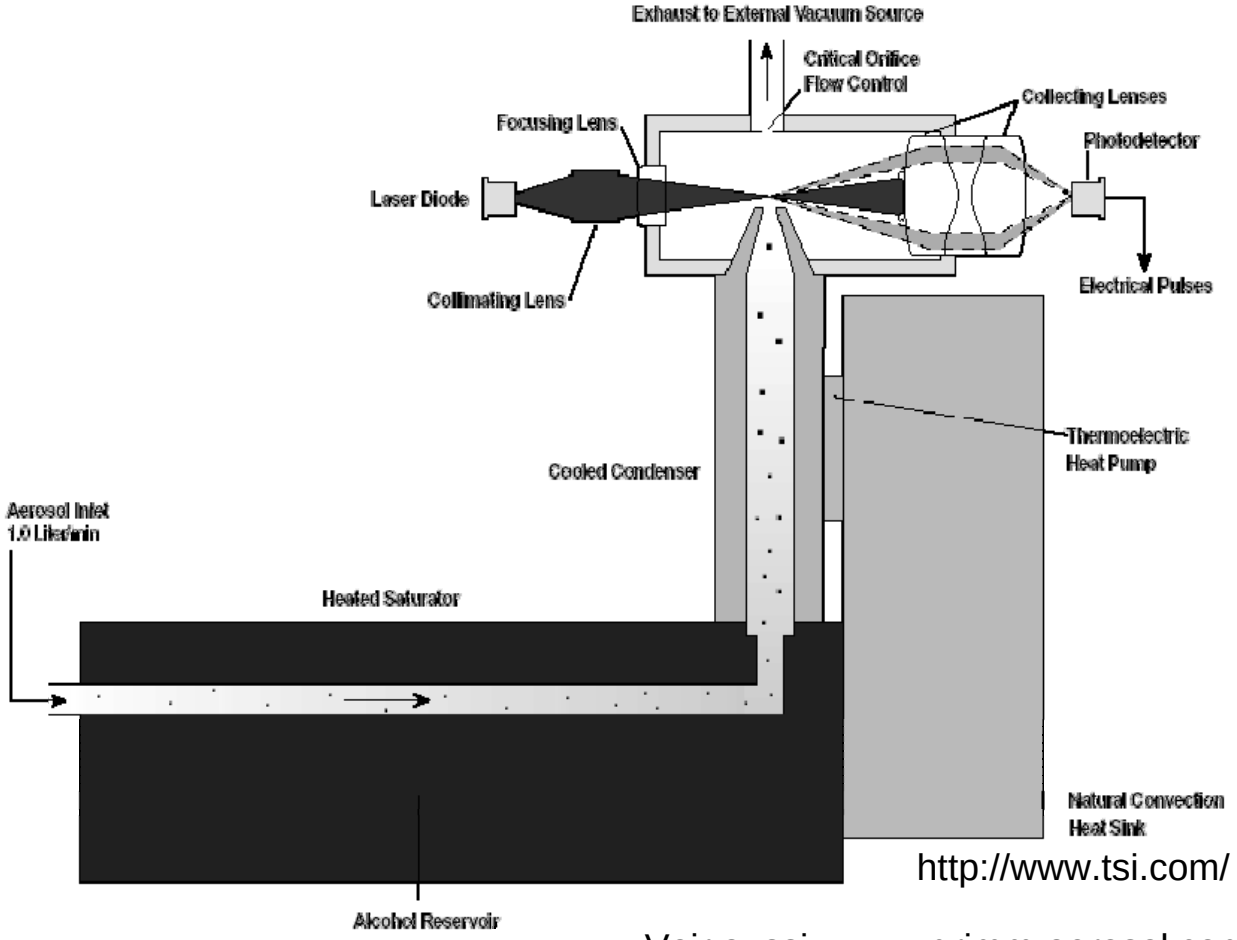


CPC : Condensation Particle counter

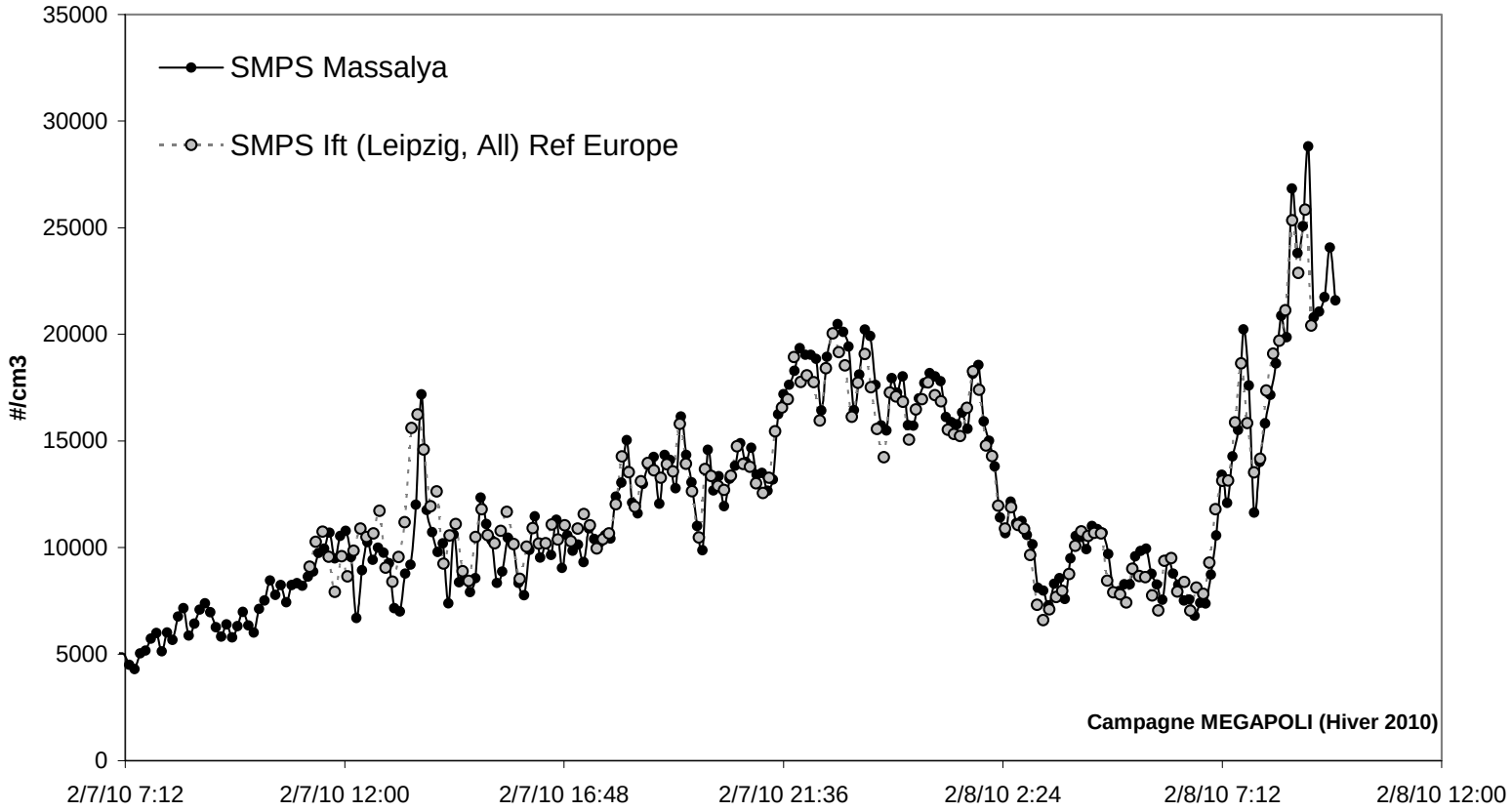
Comptage des particules Dp>~4 nm



http://www.tsi.com/

Voir aussi : www.grimm-aerosol.com

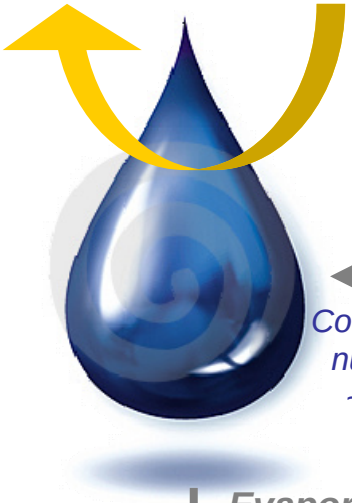
Intercomparaison /SMPS Ref EUSAAR (Ift, Leipzig) Megapoli, Paris, Hiver 2010



Application 1

Formation d'AOS via la chimie en phase aqueuse

Oxydation au sein de la gouttelette (OH,hν)



Solubilisation

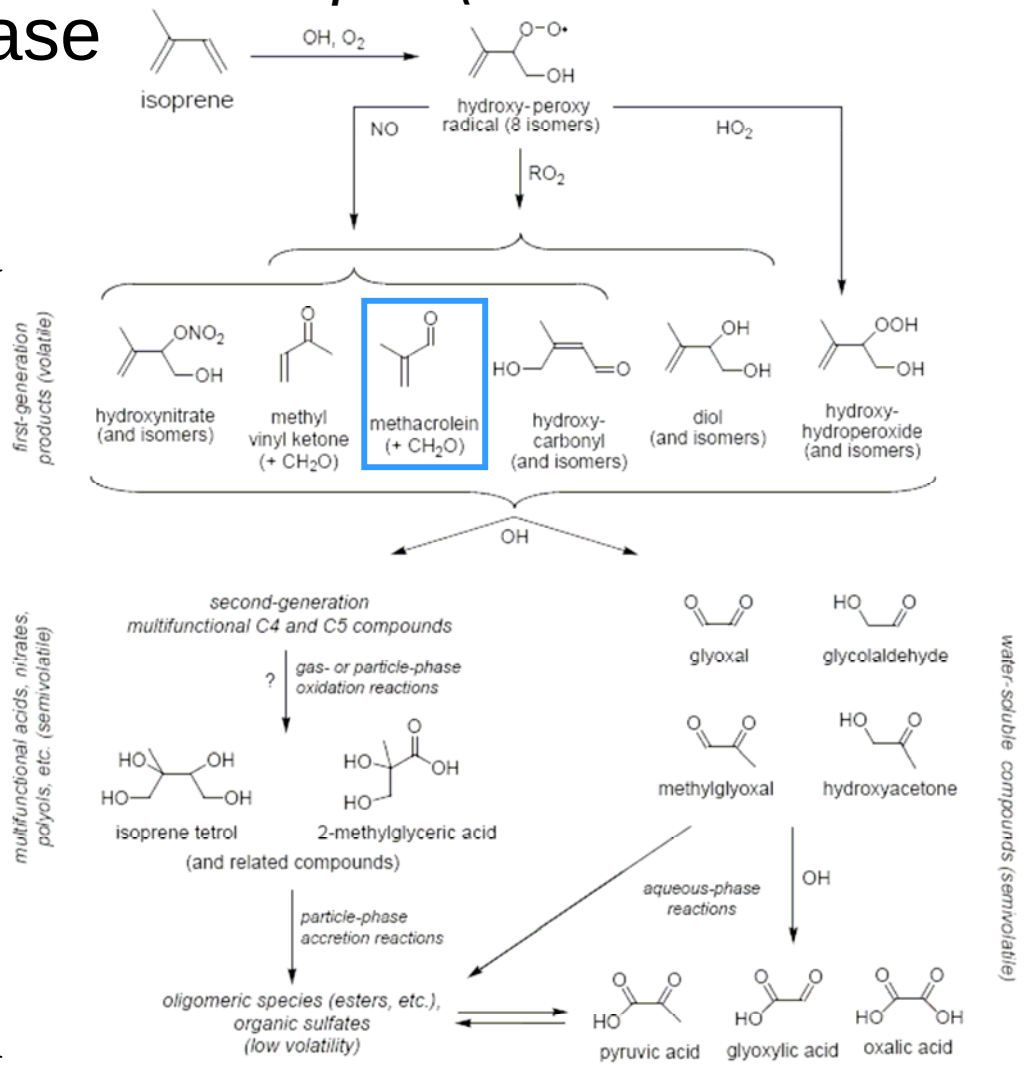
Composés hydrosolubles + nuages ~60% surface et ~15% du volume de la troposphère

Evaporation

~9 cycles evapo/cond avant précipitation

Nature de l'aérosol résultant?

Cas de l'isoprène (~50% de la masse totale en COVs)



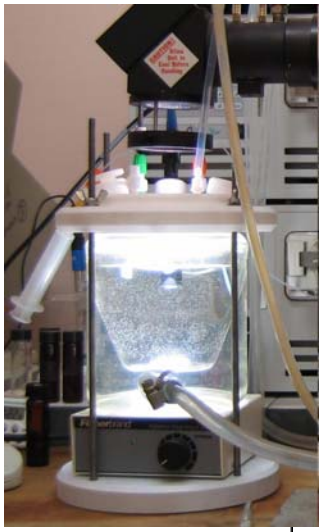
Carlton et al, 2009

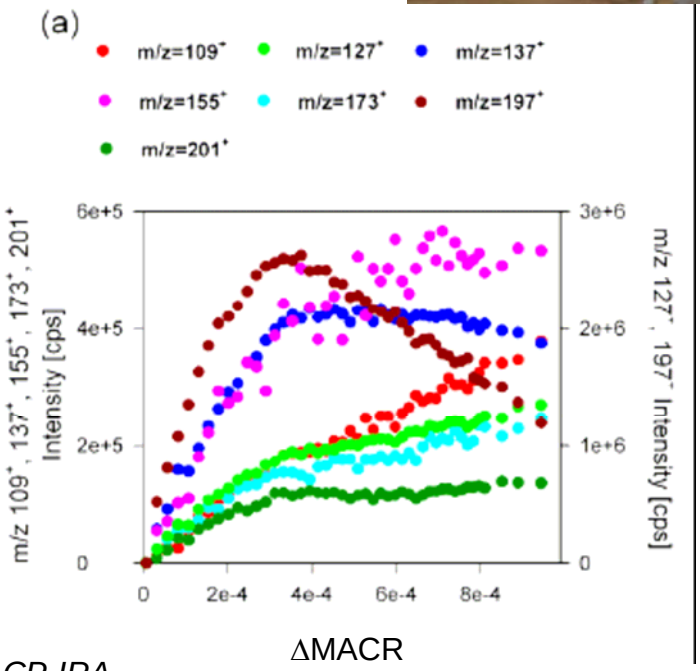
Application 1

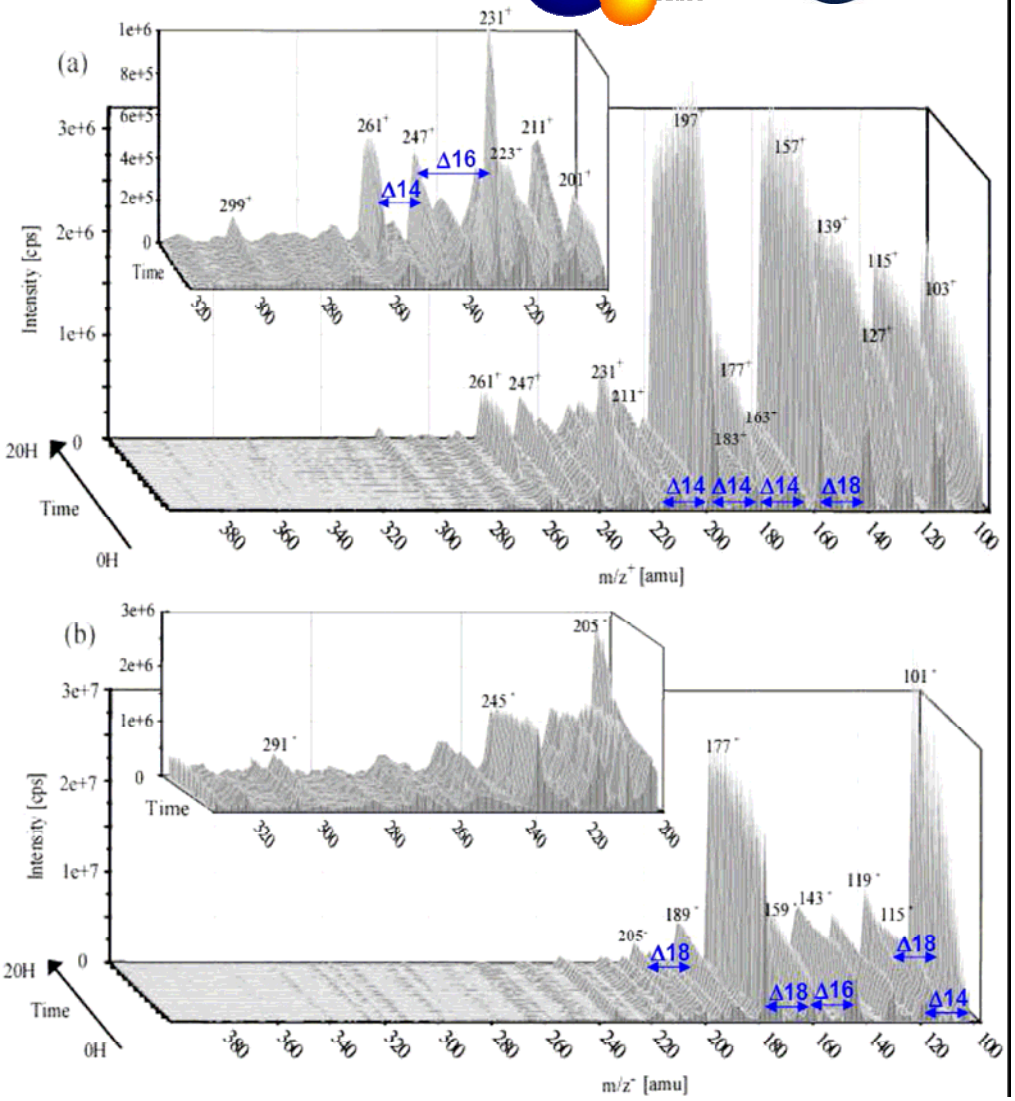
+ H_2O_2 + hν

methacrolein

M=70 g.mol^{-1}



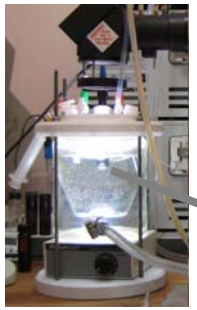




El Hadad et al, 2009
Liu et al., 2009
Michaud et al., 2009)

Source LCP-IRA

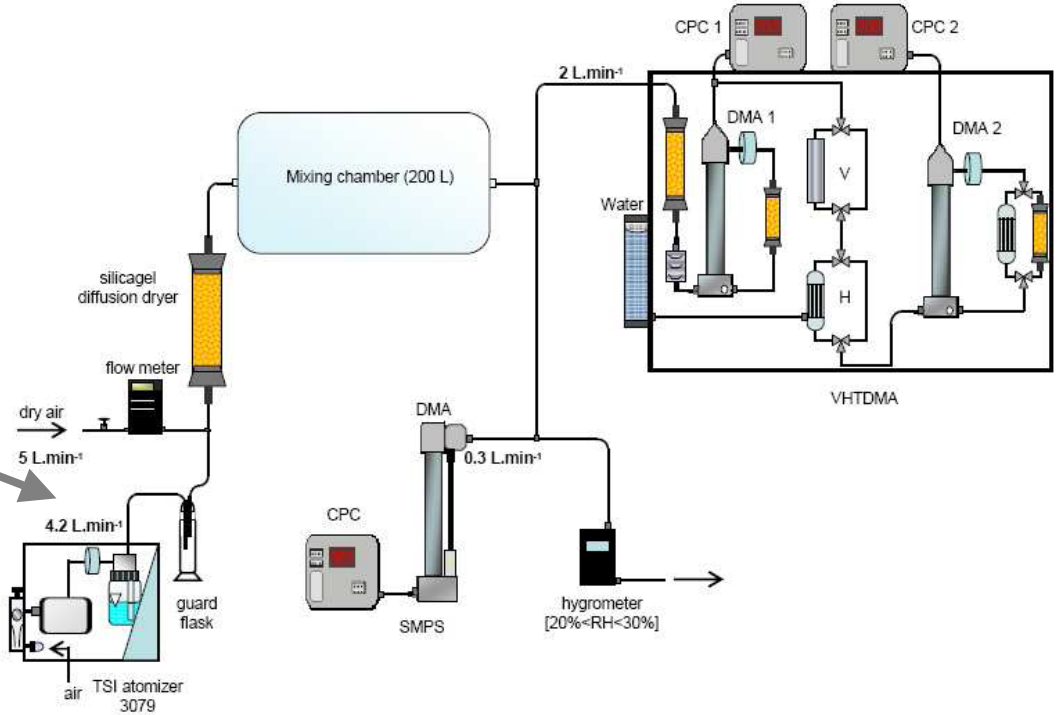
Application 1

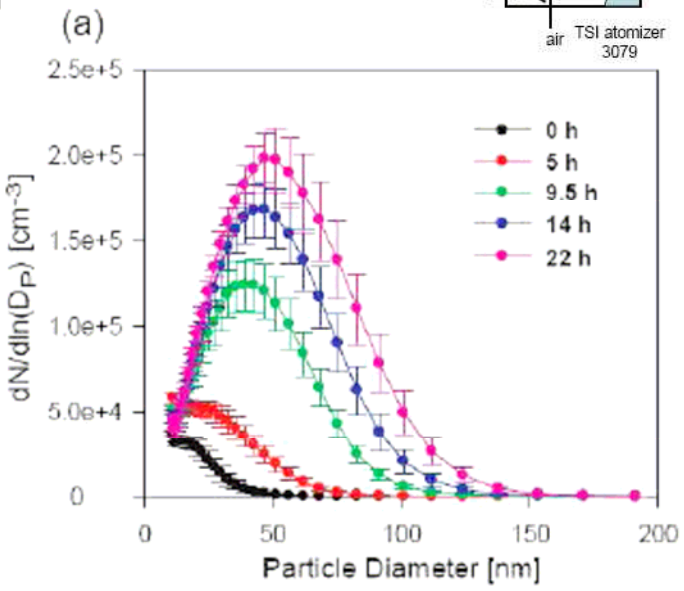


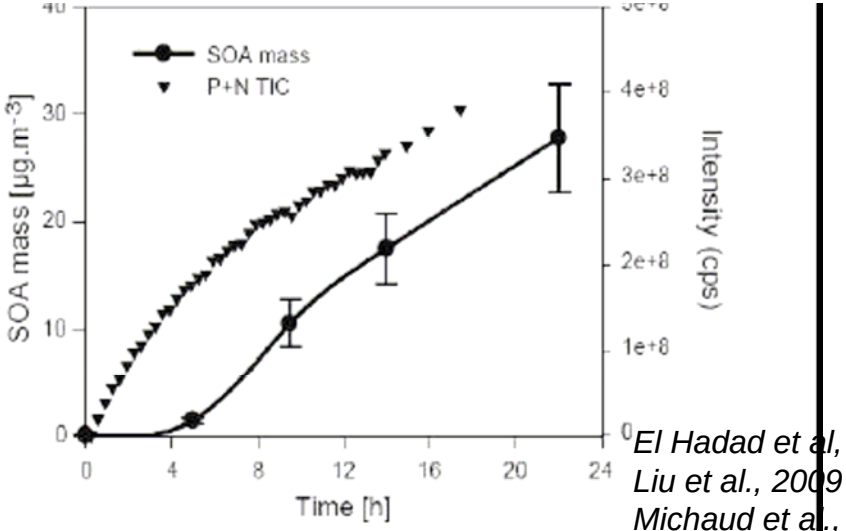
Que se passe t il quand la gouttelette s'évapore?

methacrolein

+ H_2O_2 + hν







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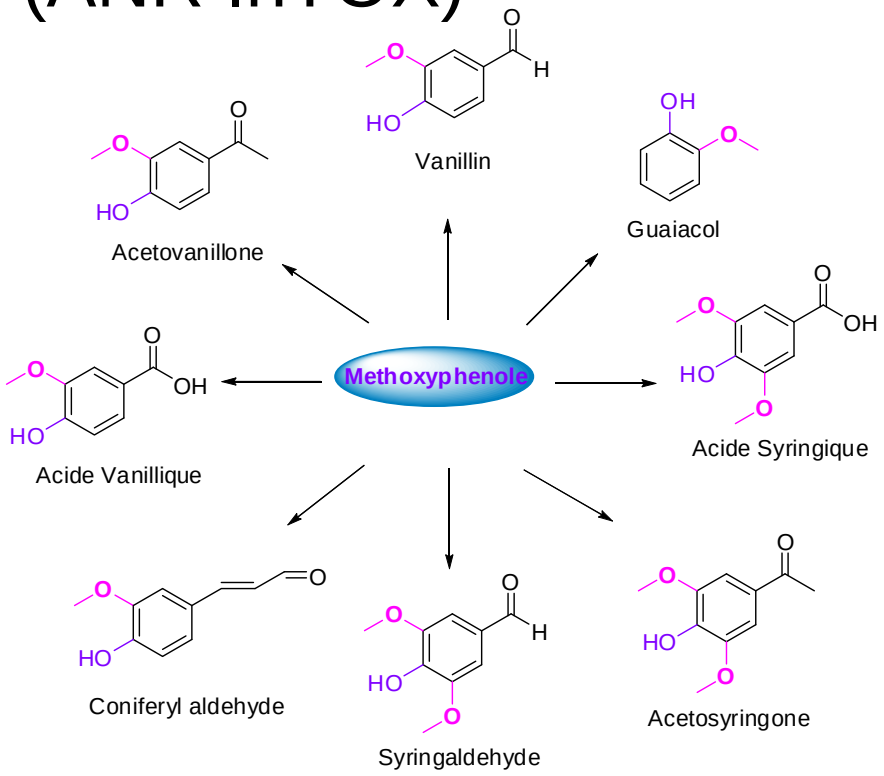
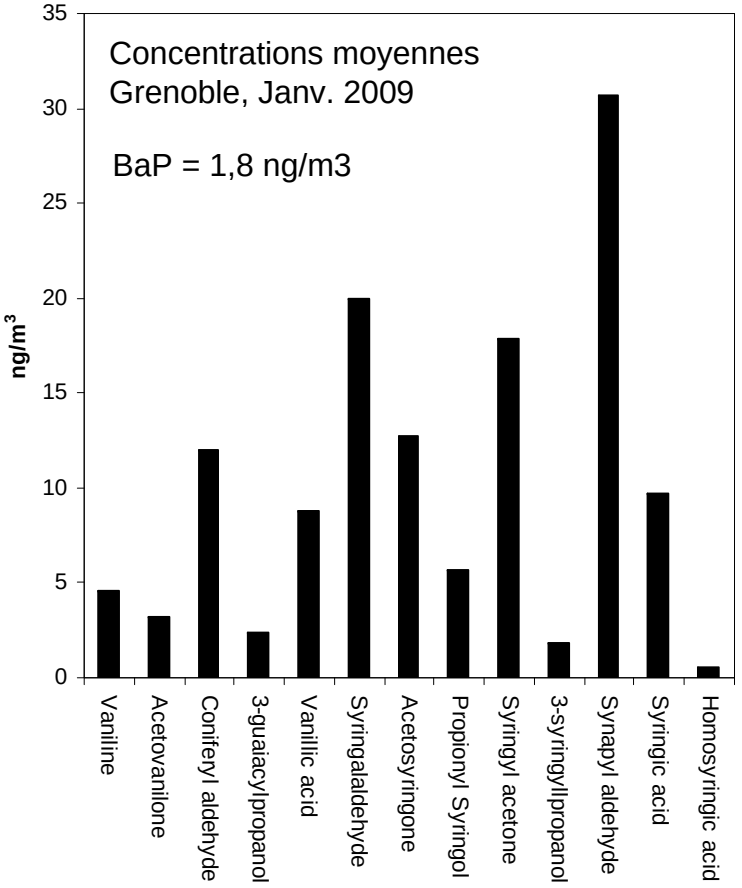
Application 2

Exposition animale à des particules de méthoxyphénols (ANR InTOX)



Produits de dégradation thermique de la **lignine**



Grenoble Janvier 2009 (FORMES)

Application 2

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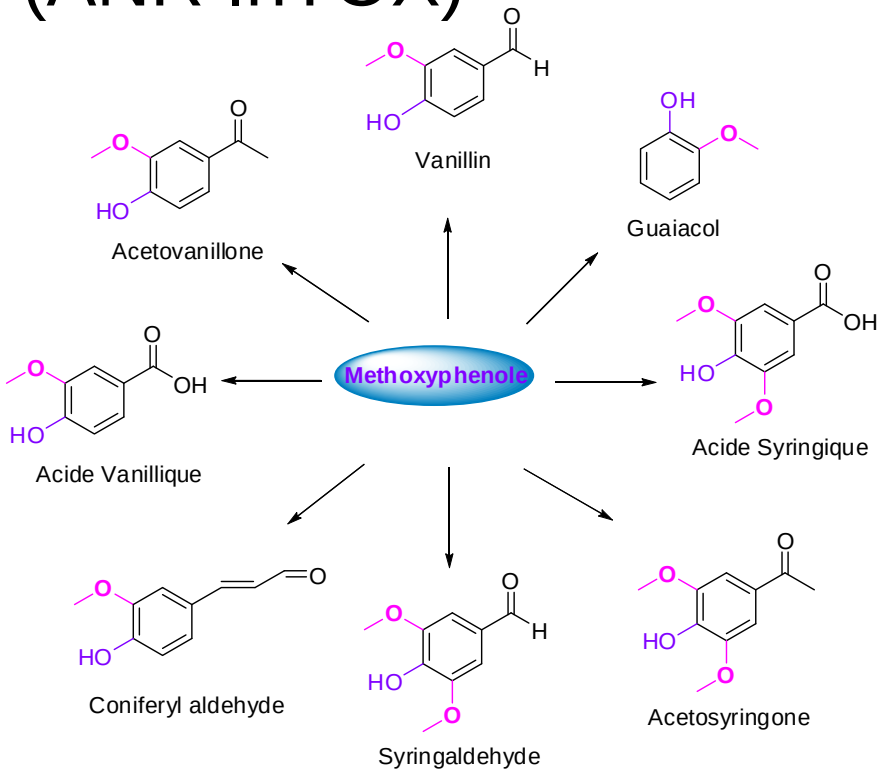
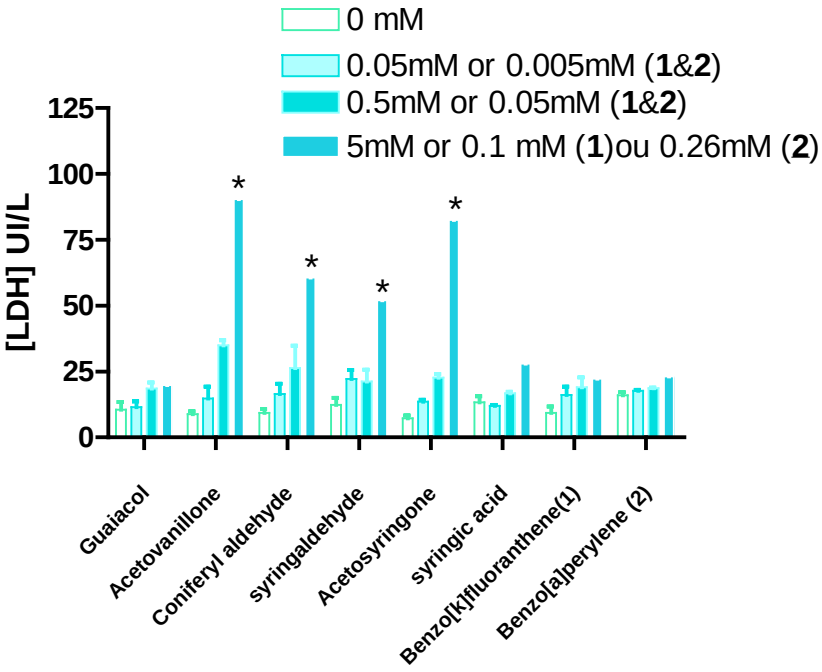


Produits de dégradation thermique de la **lignine**

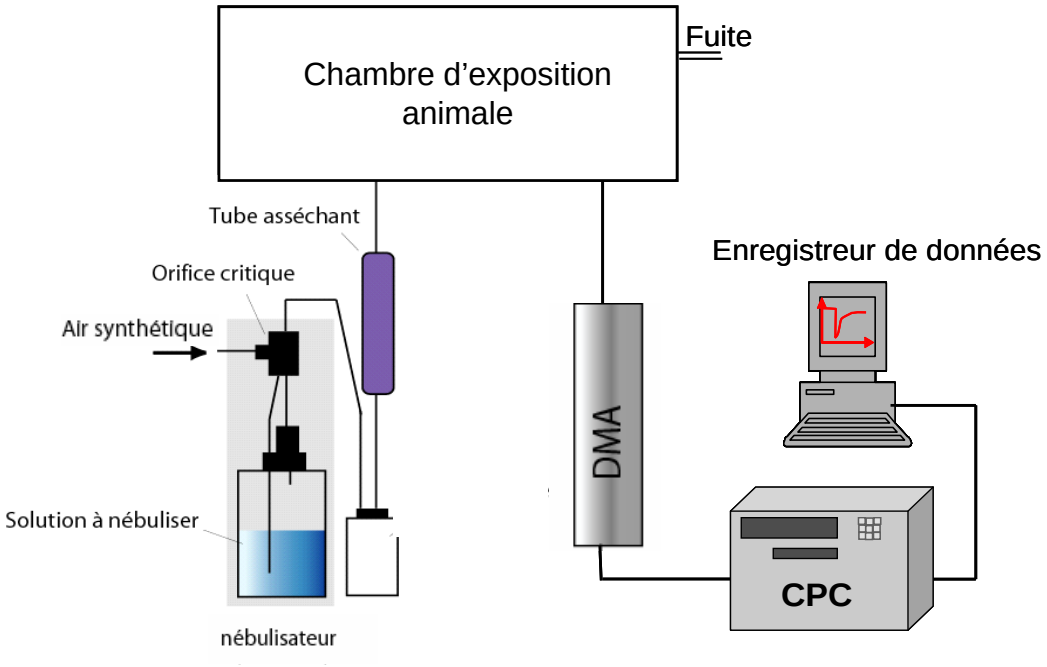
Toxicité des MP's



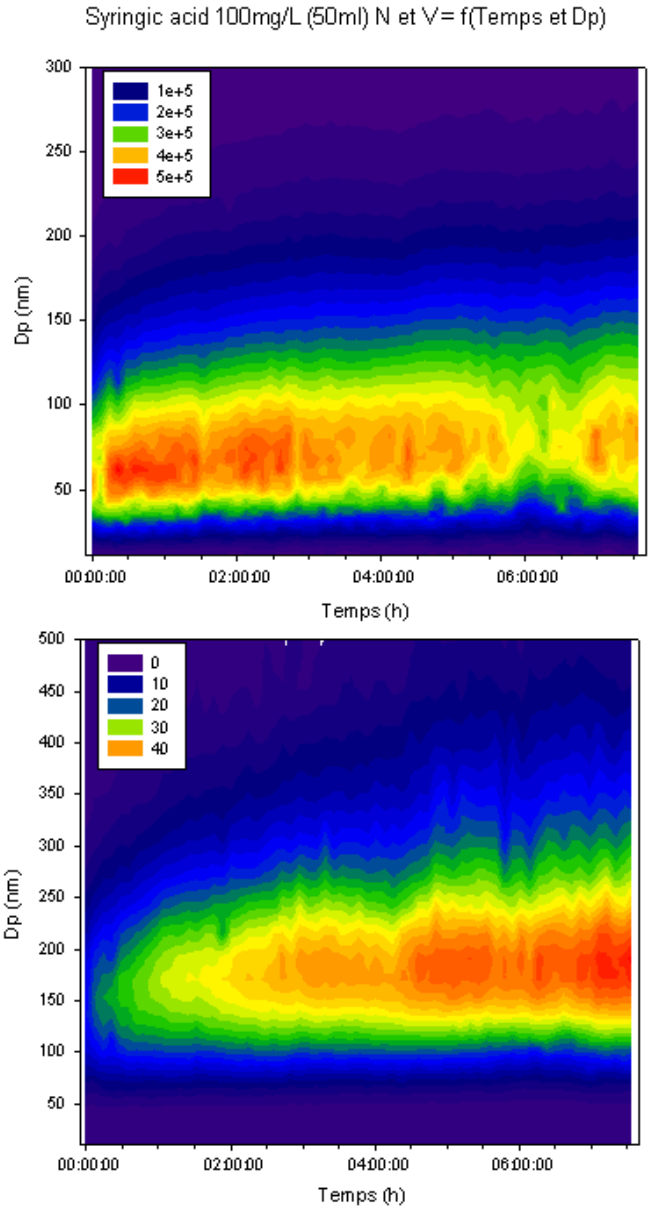
- Cytotoxicité, effet lipopéroxydant , significatif pour certains MPs
- Effets de synergie entre le MPs

Application 2

Exposition animale à des particules de méthoxyphénols (ANR InTOX)



Montage exp. d'exposition animale

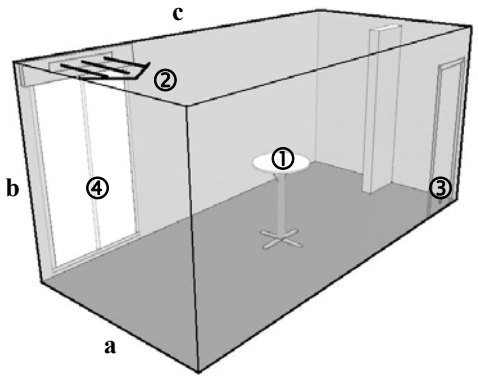


Application 3

Caractérisation des émissions par les bougies et encens

LA MAISON EXPÉRIMENTALE MARIA :
Maison Automatisée pour des Recherches Innovantes sur l'Air

- Maison de 5 pièces principales sur 2 niveaux
- Superficie totale : 140 m^2



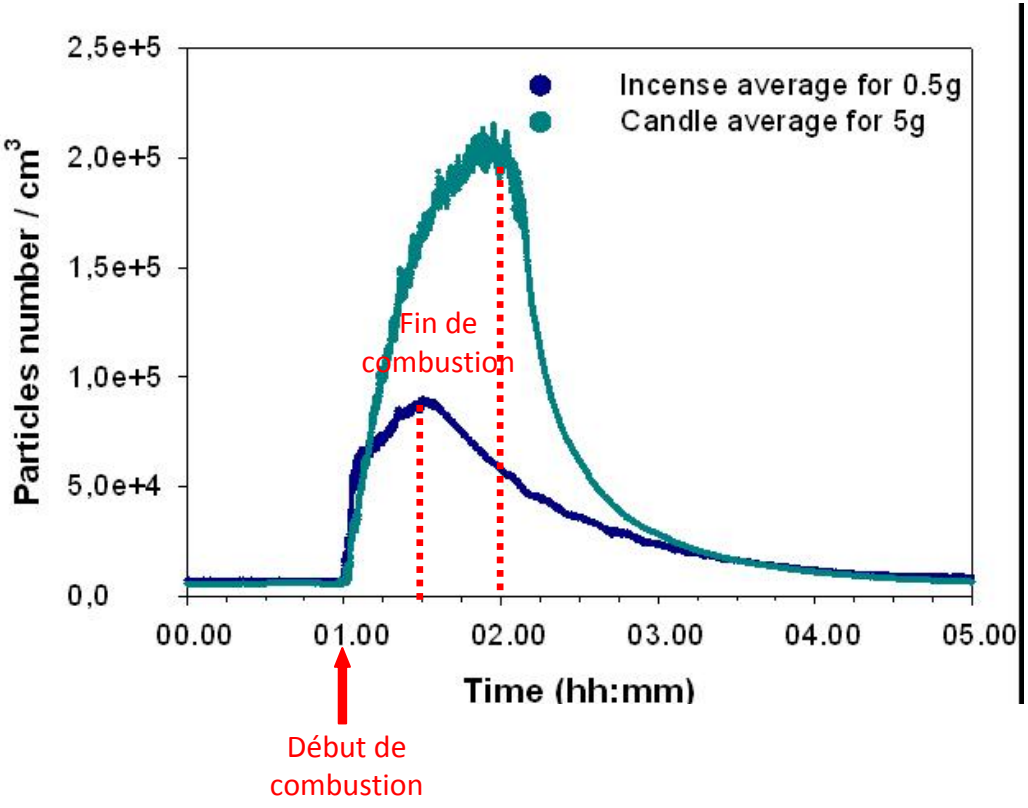
VOLUME PIÈCE ≈ 32 m^3
a: 2.53 m ; b: 2.50 m ; c: 5.15 m
①: place de l'échantillon
②: Air frais entrant
③: système d'extraction mécanique de l'air
④: fenêtre close

Application 3

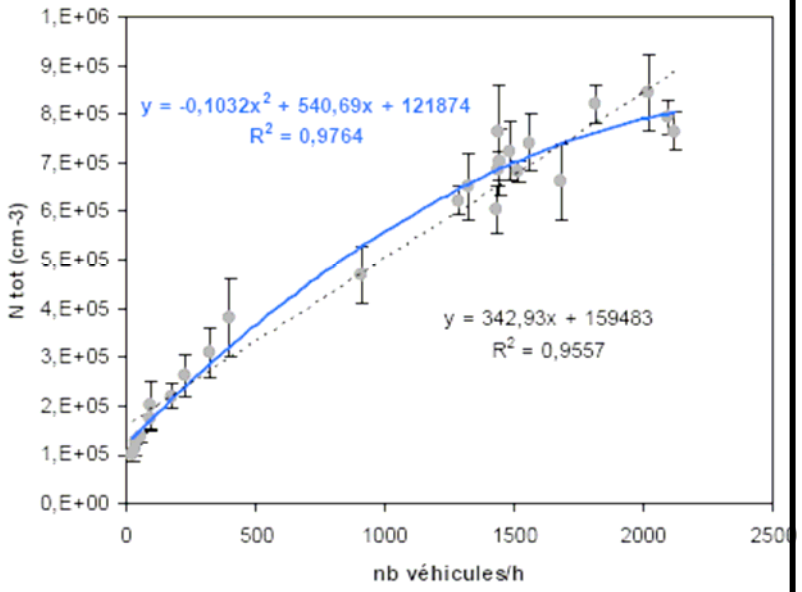
Caractérisation des émissions par les bougies et encens

Moyenne effectuée sur l'ensemble des encens et des bougies testées

Coefficient de variation allant de 5 à 20 %



Tunnel Prado-Carénage Marseille (2008)



Application 4

FORMES
Fraction ORganique de l'aérosol urbain: Méthodologie d'Estimation des Sources

Marseille field campaign

From 29/06 to 15/07/2008
Urban background site

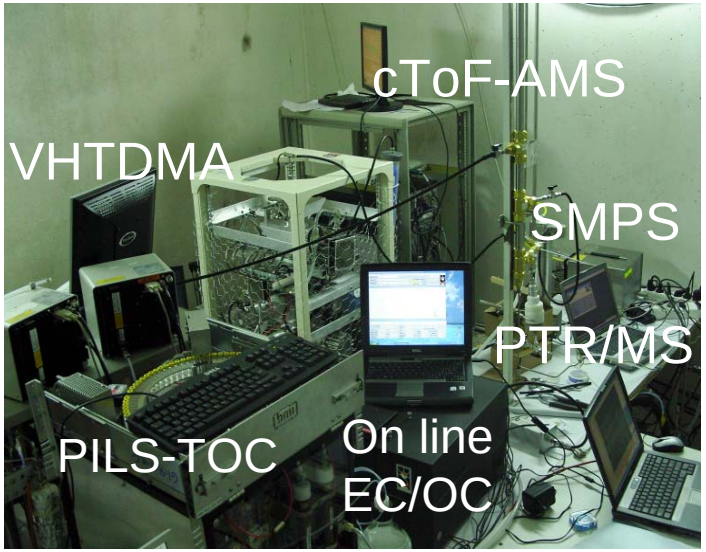
Offline samplers

-PM2.5 high volume samplers (EC/OC, major ions, organic speciation, HULIS, functional groups, metals, ^{13}C)
-Dekati impactor(EC/OC)

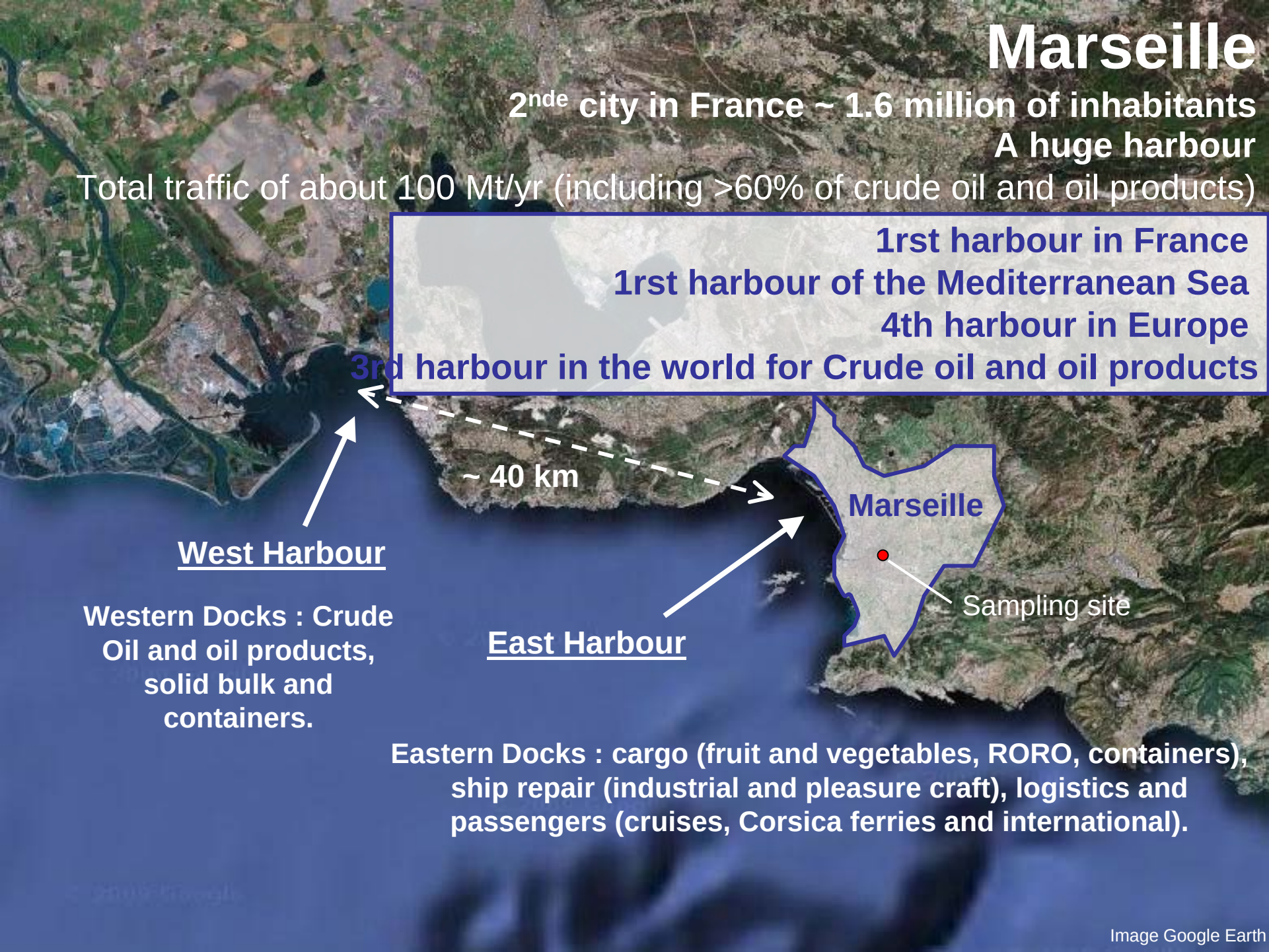
Online analysers

-**SMPS (10nm-1µm)**
- cToF-AMS
- HS-PTR-MS
- VHTDMA
- Online EC/OC (PM1)
- PILS-TOC
- Air quality network analysers (O_3, NOx, SO_2, PM2.5, PM10)

Offline PM samplers



Online analyzers


Marseille
2nde city in France ~ 1.6 million of inhabitants
A huge harbour
Total traffic of about 100 Mt/yr (including >60% of crude oil and oil products)
1rst harbour in France
1rst harbour of the Mediterranean Sea
4th harbour in Europe
3rd harbour in the world for Crude oil and oil products
~ 40 km
Marseille
Sampling site
West Harbour
Western Docks : Crude Oil and oil products, solid bulk and containers.
East Harbour
Eastern Docks : cargo (fruit and vegetables, RORO, containers), ship repair (industrial and pleasure craft), logistics and passengers (cruises, Corsica ferries and international).
Image Google Earth

Marseille

A huge industrial area

Refinery and petro chemical industry of Berre

Refinery of Fos

Refinery of «la Mede»

Refinery and petro chemical industry of Lavera

West Harbour

East Harbour

Marseille

Sampling site

4 Refineries : ~30 Mt/year

~30% of the french refining capacity

Image Google Earth

Marseille

A huge industrial area

Refinery and petro chemical industry

Sollac (Steel Industry)

Refinery of Fos

Industrial area (various activities)
Airport

Refinery of «la Mede»

Refinery and petro chemical industry of Lavera

Marseille

Industrial area (various activities)

Sampling site

West Harbour

East Harbour

Image Google Earth

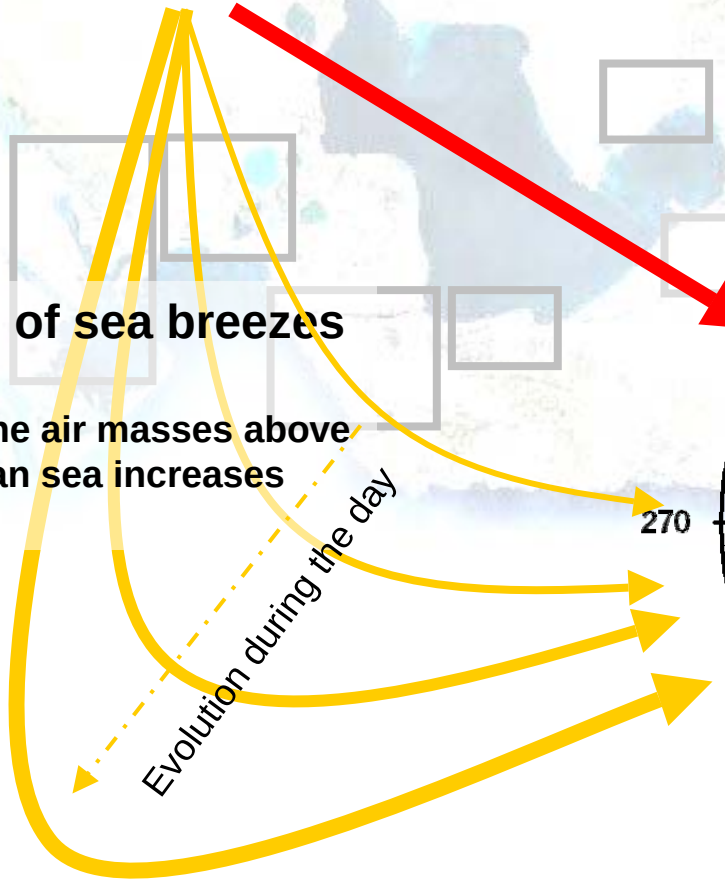
Marseille : 3 characteristic meteorological conditions

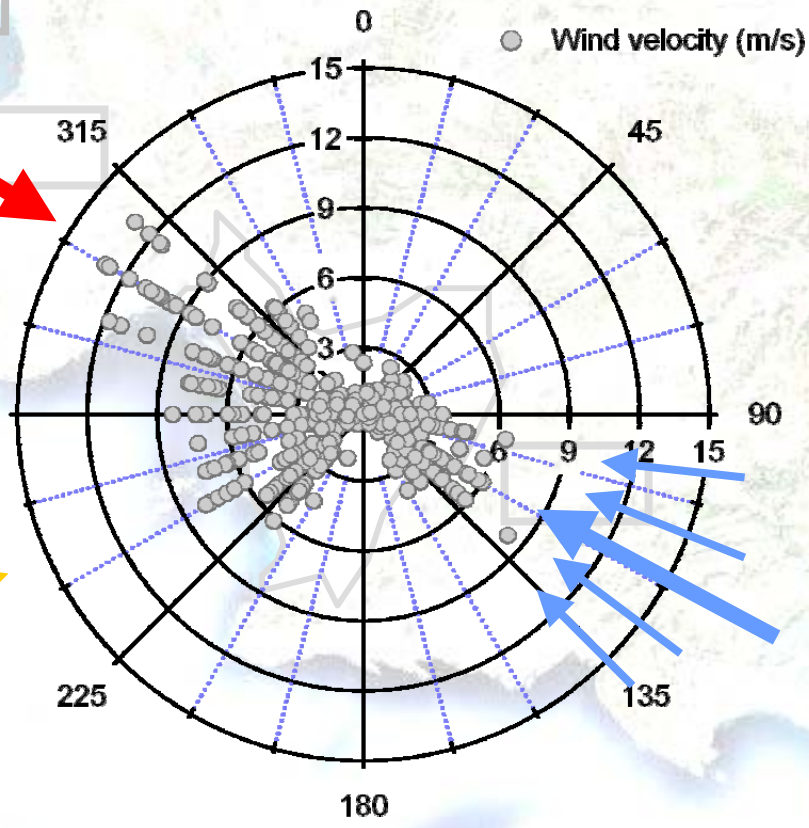
FORMES
Fraction ORganique de l'aérosol urbain: Méthodologie d'Estimation des Sources

Mistral
« Land » and sea breezes
Nocturnal Urban breeze

Composition of sea breezes and mistral

Transit time of the air masses above the mediterranean sea increases during the day

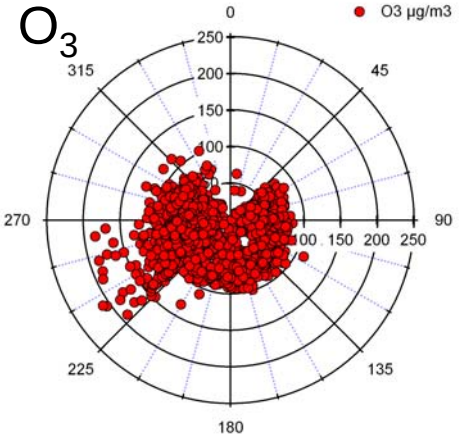




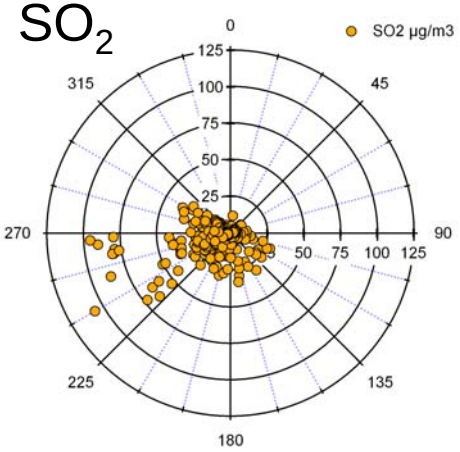
Urban breeze occuring most of the nights (hot spot of Marseille)

Marseille is most of the time downwind industrial areas and harbours

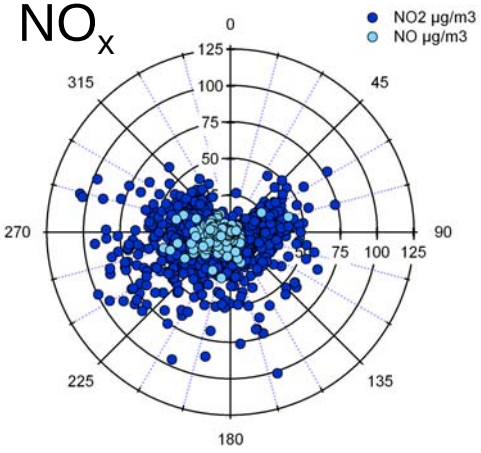
O_3



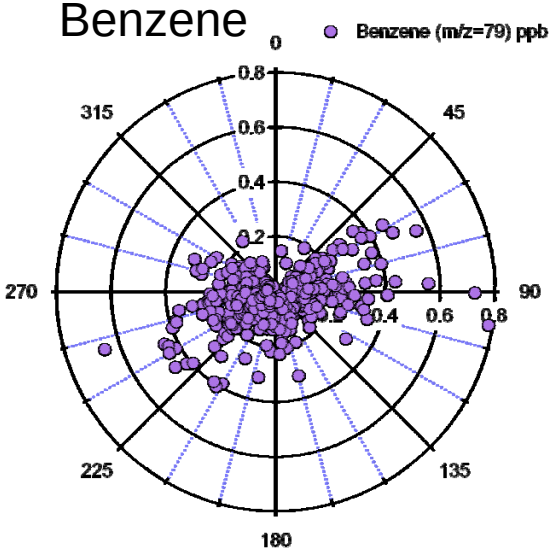
SO_2



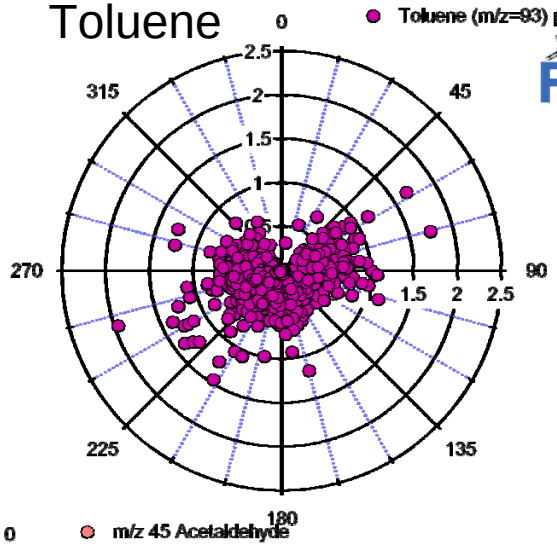
NO_x



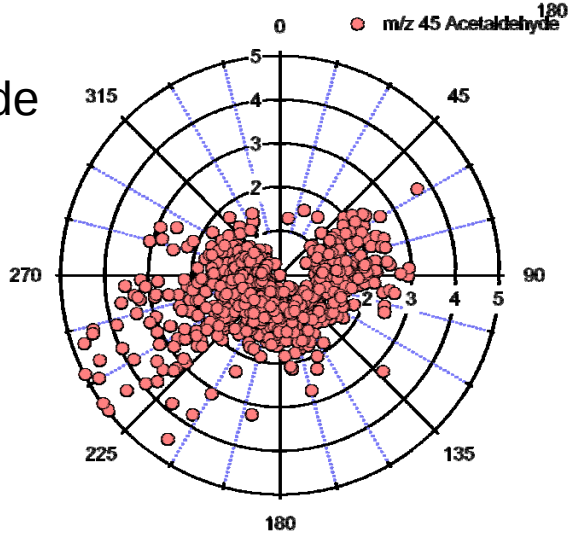
Benzene



Toluene

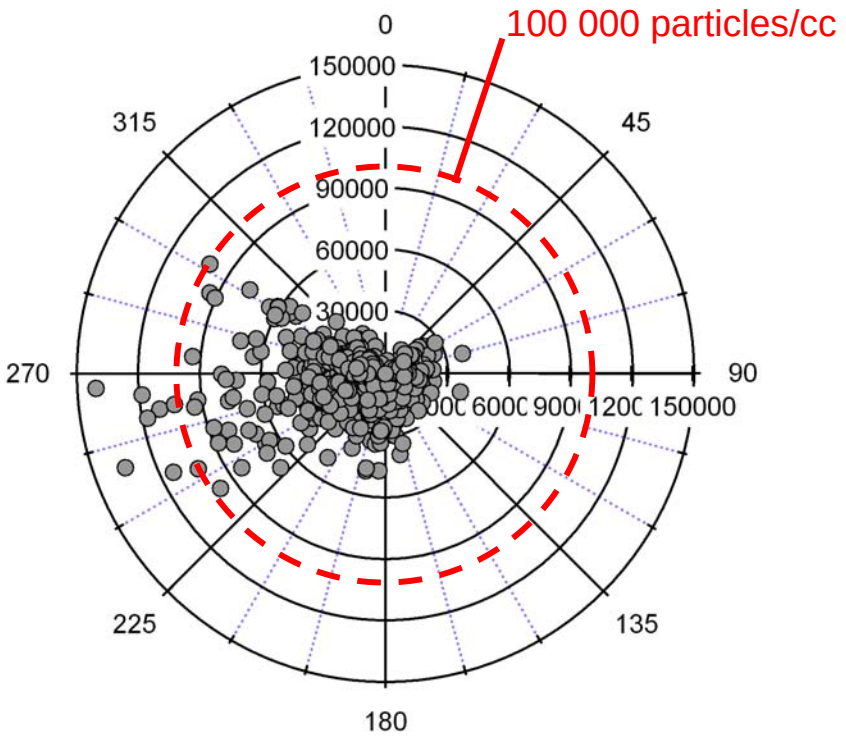


Acetaldehyde

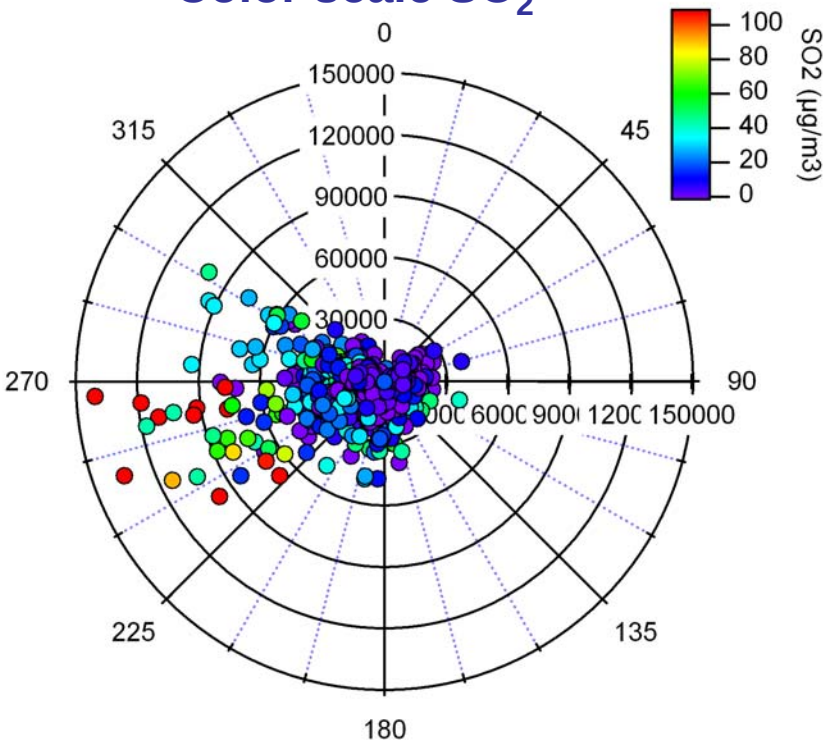


- **Sea breeze conditions** characterized by high concentrations of O_3, SO_2, benzene, toluene, isoprene, Acetaldehyde, *NOx* ;
- **Urban breeze** conditions characterized by high concentrations of benzene, *toluene, acetaldehyde and NOx*
- **Moderate mistral conditions** characterized by high concentrations of NOx, *Benzene, Toluene and acetaldehyde*

Total number of particles (cm^{-3})
(10-1000 nm)

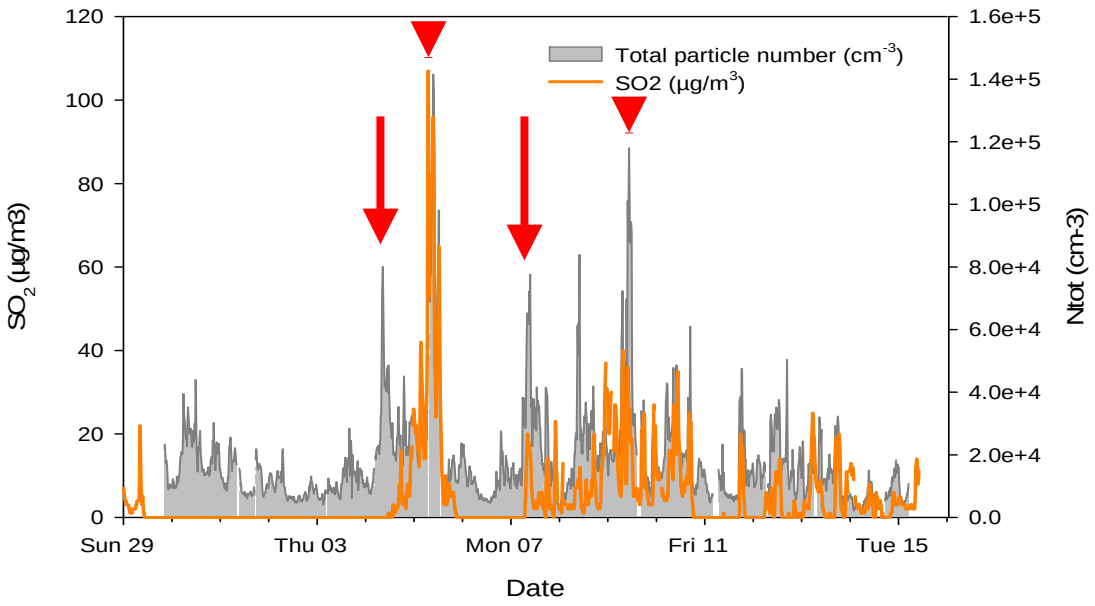


Total number of particles (cm^{-3})
(10-1000 nm)
Color scale SO_2



- In sea breeze and moderate mistral conditions very intense particles events are observed (**total number concentrations higher than 100 000 #/cm³**)
- These particle events are highly correlated with SO_2 and thus most probably linked to petrochemical/steel industrial activities (or maybe shipping emissions)

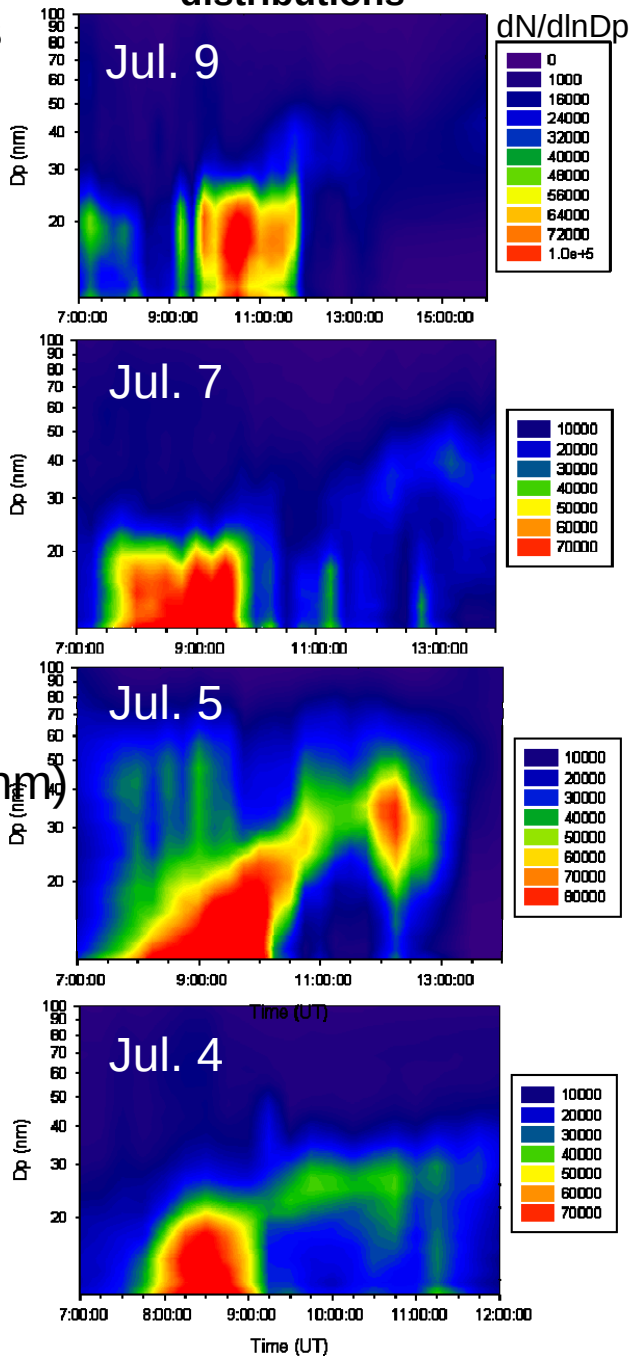
Some examples of fine particle events



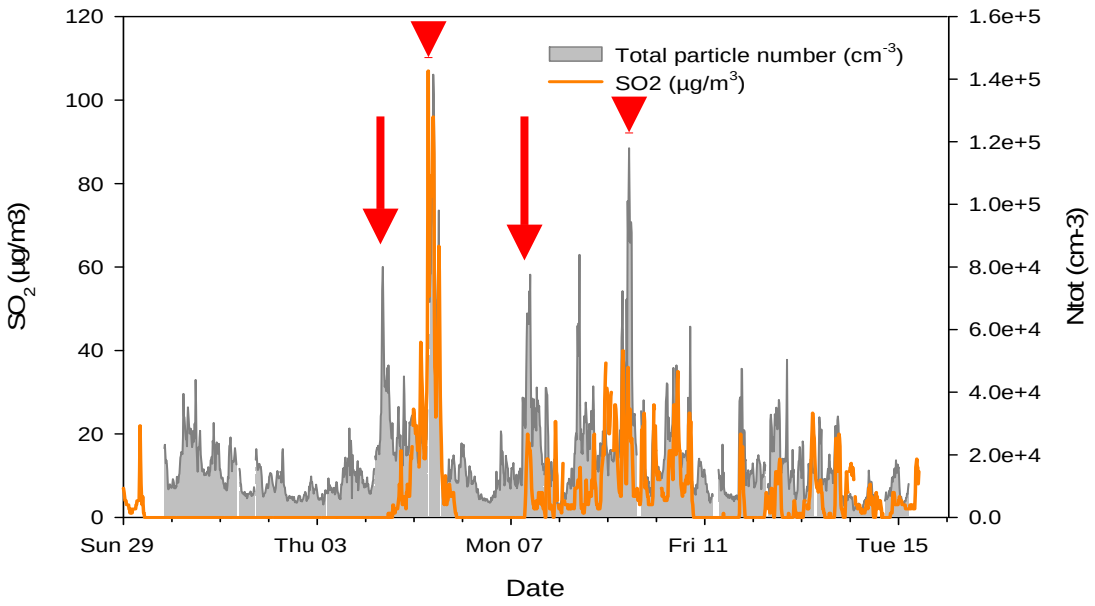
Particle events characterized by very fine particles (<20 nm)

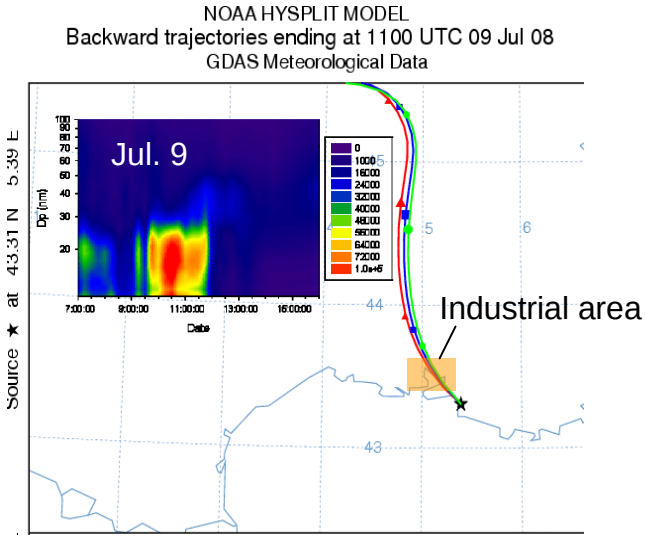
The different shapes reflect the history of the air masses

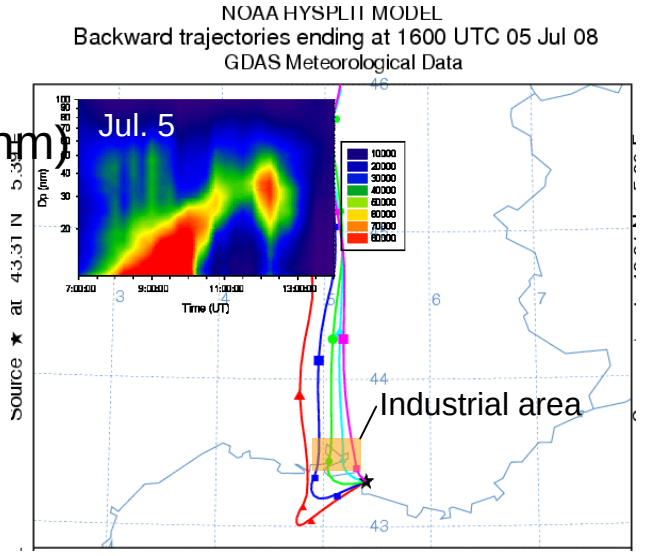
Evolution of the particle size distributions



Some examples of fine particle events







Particle events characterized by very fine particles (<20 nm)

The different shapes reflect the history of the air masses

Jul 9, 7 : Moderate mistral conditions ;

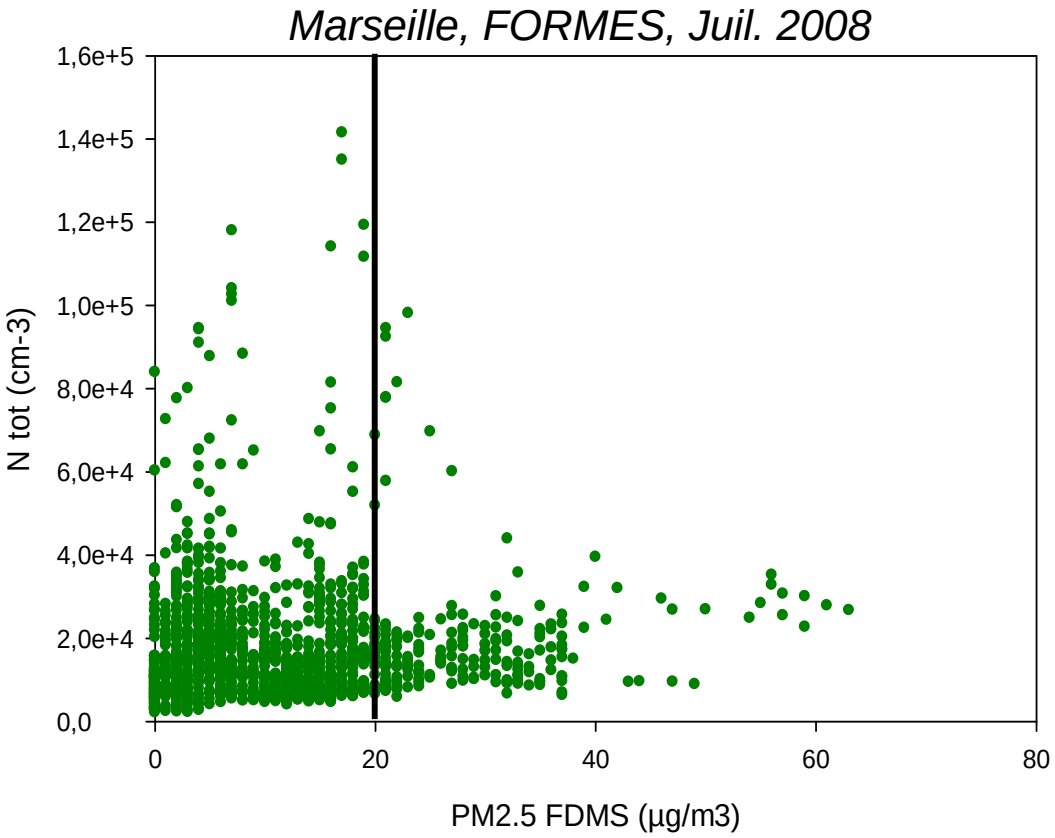
⟶ Receptor site directly downwind the industrial area;

Jul. 4, 5 : Sea breeze conditions :

Atmospheric transit time between sources and receptor site increases during the day

Composition : mainly sulfates and secondary organics

Nombre vs Masse des particules



Si on fixe une limite à **$PM_{2.5}$=20µg/m³**

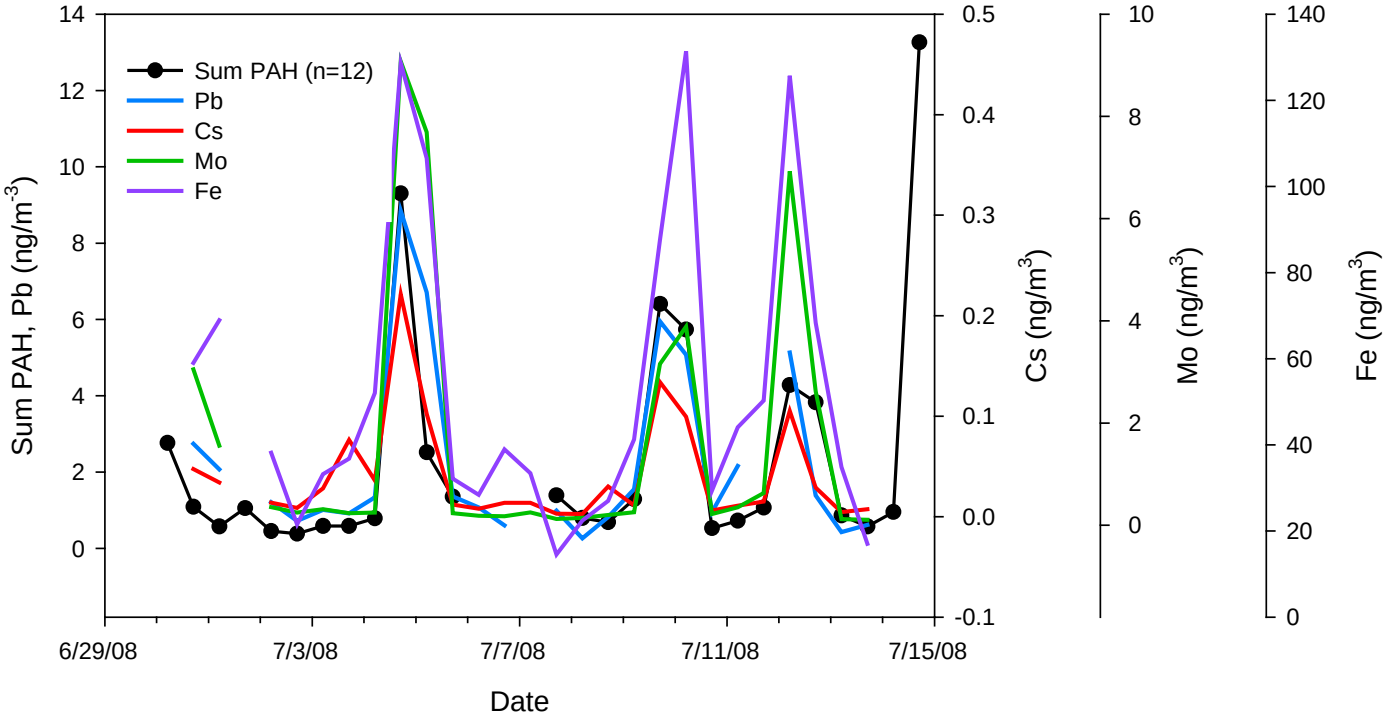
Les pics en masse correspondent à un nombre moyen en particules < 40 000 cm^{-3}

Les pics en nombre >40 000 cm^{-3} sont très majoritairement pour des masses < 20 µg/m³

Le nombre de particules est lié au nombre des particules fines qui ne participent que faiblement à la masse totale

Ce sont pourtant ces dernières qui pénètrent le plus profondément dans le système respiratoire

PAHs and Metals



Temporal trend of total PAHs concentration shows intense pics

… and is very well correlated with those of Pb, Cs, Mo, Fe and also La, V, Zn, Ni, Co

For all these samples the receptor site was downwind from the western industrial area

Université de Provence

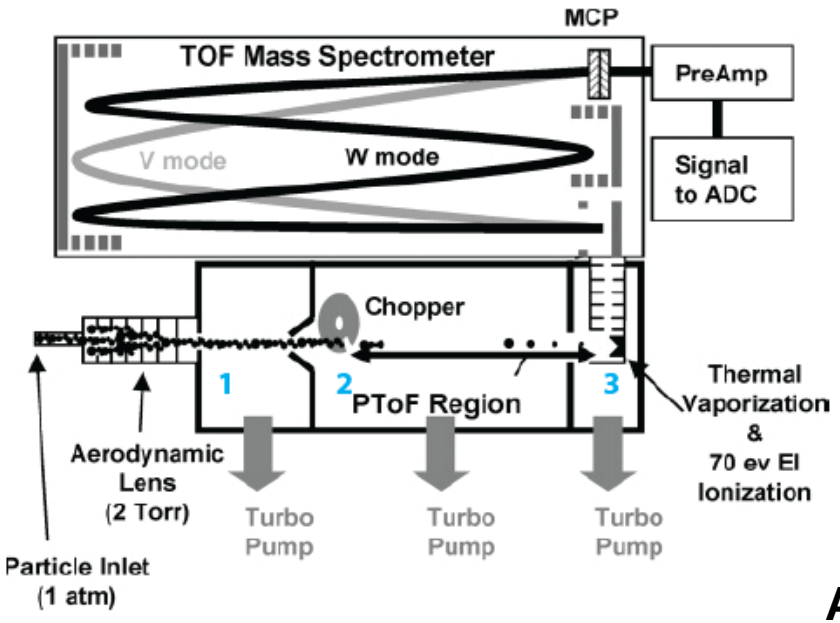
MASSALYA

Laboratoire mobile d'analyse de l'air

Plateforme instrumentale mobile de l'Université de Provence

Analyse de l'aérosol submicronique et COV précurseurs

- **HR-ToF-AMS**
- **PTR-ToF-MS** (Jan. 2011)
  (possibility to use an HS-PTR-MS before 2011)
- **BC analyser (MAAP5012)**
- **SMPS**
- ***PM1 or PM2.5 HVS sampler***
- ***Wind speed and direction (+T, HR)***



HR-ToF-AMS

Analyse en ligne de l'aérosol submicronique

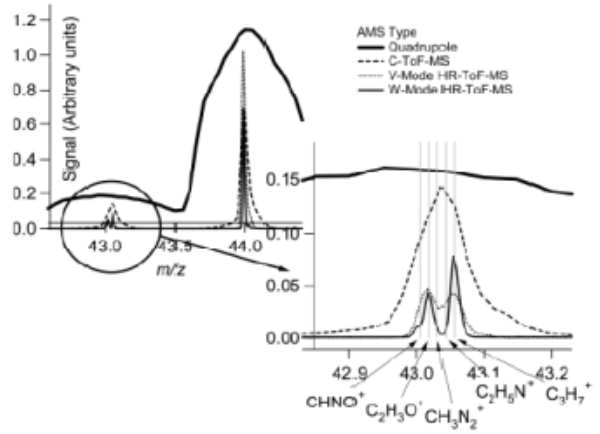
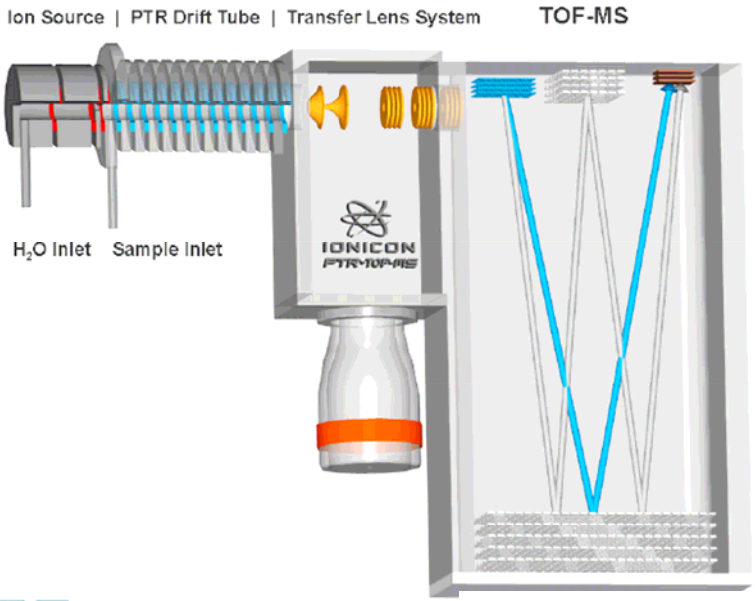


Figure 3. Peak comparisons for the four versions of the AMS. Resolution improvements are obvious in the progression from Q-AMS to C-ToF-AMS to V-mode to W-mode of the HR-ToF-AMS.

From De Carlo et al., 2006, Anal Chem, 78, 8281-8289

- Sulfates, Nitrates, Ammonium, Org.
- Distribution granulométrique mass. de ces fractions
- Fraction HOA, OOAs etc..
- O/C, N/C

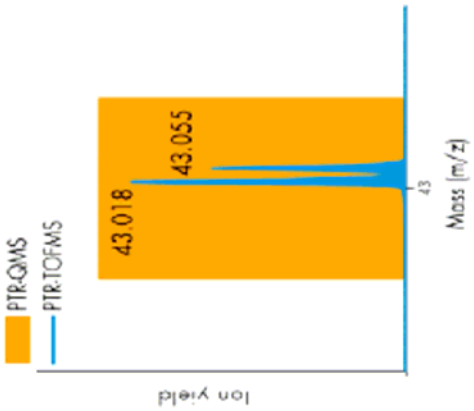
Complété par un analyseur de BC multi-angle (MAAP5012) (PM1)

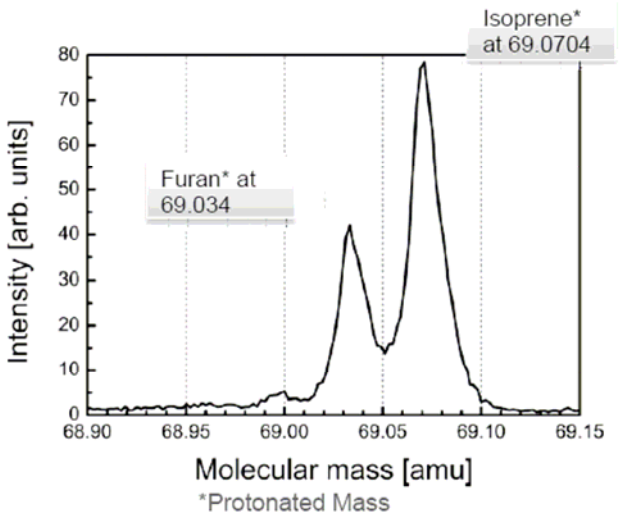


PTR-ToF-MS

Analyse en ligne des COV par transferts de protons et analyse par MS ToF

m/Δm > 6000
DL ~ 10 pptv (1min)





Merci à l’INSU
Merci de votre attention