

Atelier Particules

AirPACA, 25/09/2014

Caractérisation chimique des particules atmosphériques : Quelles approches pour quelles informations?

N. Marchand

Off line

- **Prélèvement sur filtres**
- **Analyses au laboratoire**

Avantages :

- Très large spectre d'analyse possible (OC/EC, ions majeurs, métaux, marqueurs organiques, HULIS, WSOC, 14C, microscopie électronique ..)
- Facilité de mise en œuvre sur le terrain
- Bénéficie directement des progrès instrumentaux (Spectrométrie de masse, particulièrement)

Inconvénients :

- Faible résolution temporelle (Qté de matière/temps machine/manpower)
- Représentativité de l'échantillon collecté ? (modification des équilibres thermodynamiques, réactivité hétérogène)

Online

Analyse *in situ*

Avantages :

- Résolution temporelle (1-30 min)
- Artefact « free »
- Pas de traitements différés
- Très grand nombre d'observations (analyses statistiques plus robustes)

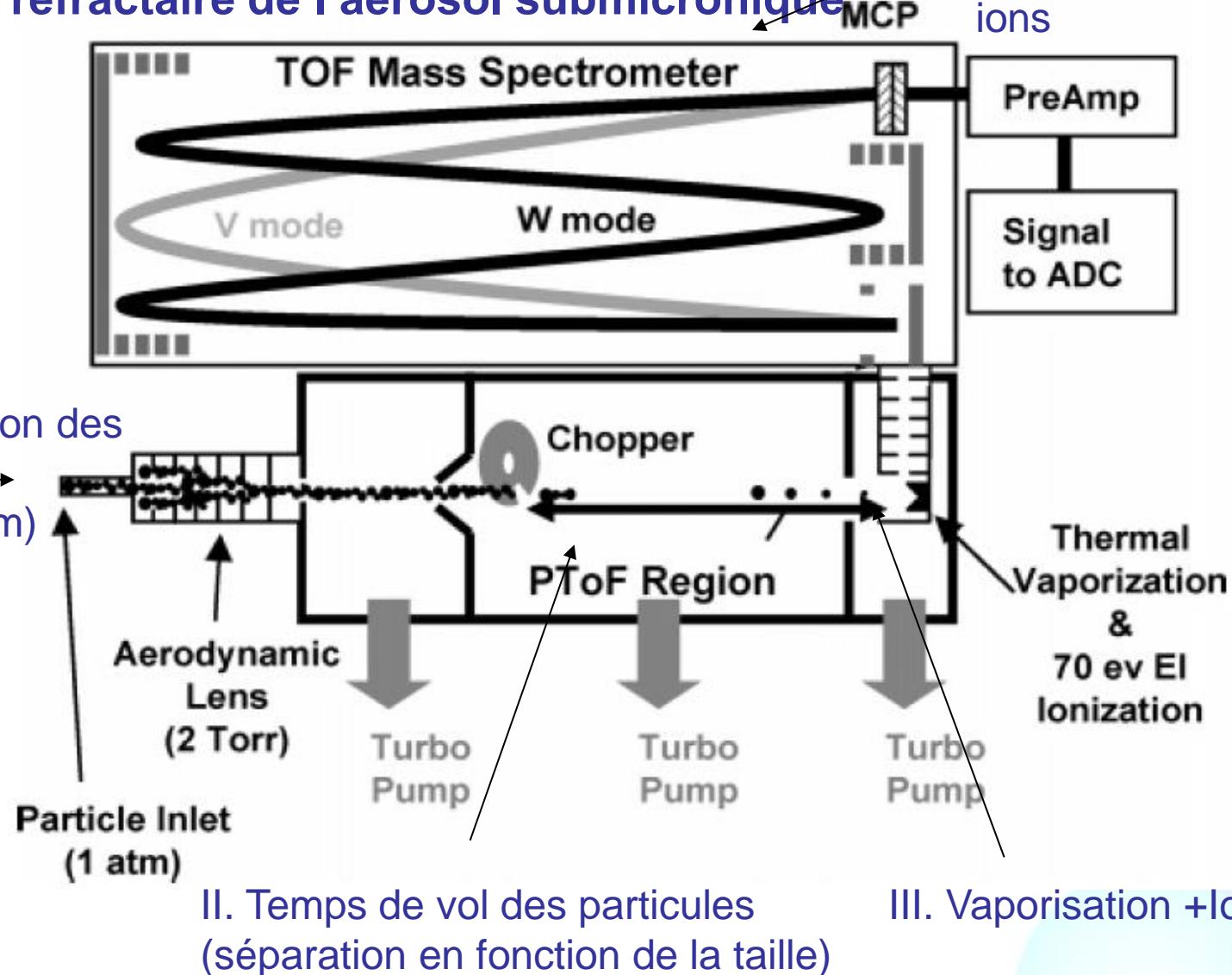
Inconvénients :

- Informations plus limitées/off line (caractérisation globale mais quelques classes seulement)
- Plus difficile à mettre en œuvre sur le terrain
- Peu d'instruments commerciaux (AMSS, PILS, Aethalomètre, Single Particle analyzers)

Aerosol Mass Spectrometer : AMS

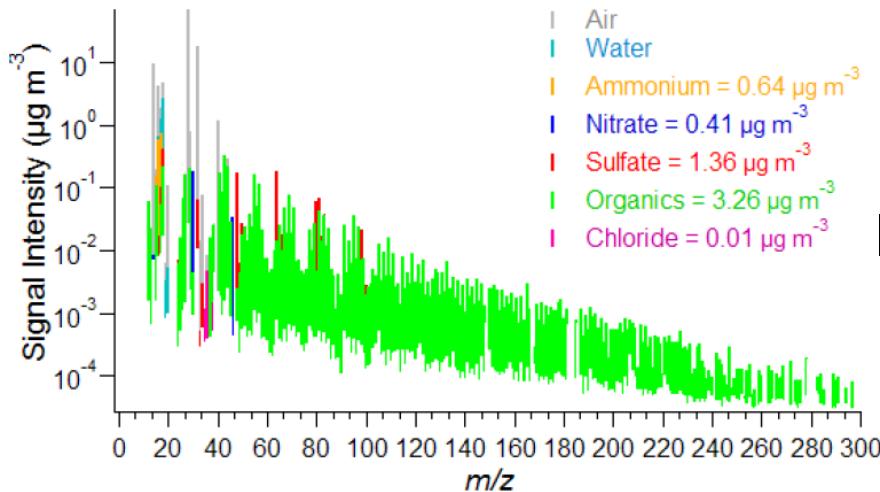
HR-ToF-AMS : analyse de la fraction non
refractaire de l'aérosol submicronique

IV. Séparation des
ions



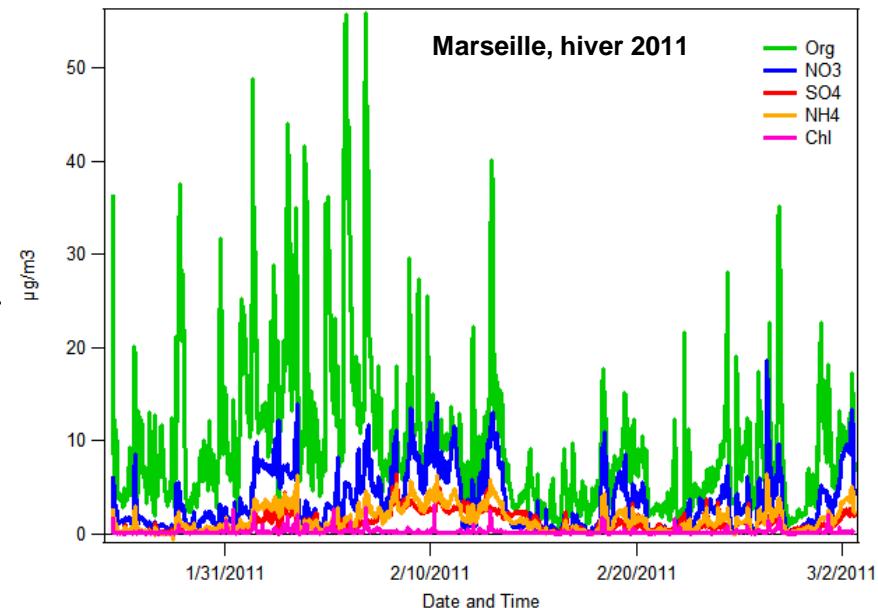
Aerosol Mass Spectrometer : AMS

AMS Ambient Mass Spectrum



Why does this work? See:

- Jimenez et al. J. Geophys. Res., 108(D7), 8425, 2003.
- Allan et al., Journal of Aerosol Science, 35: 909, 2004.



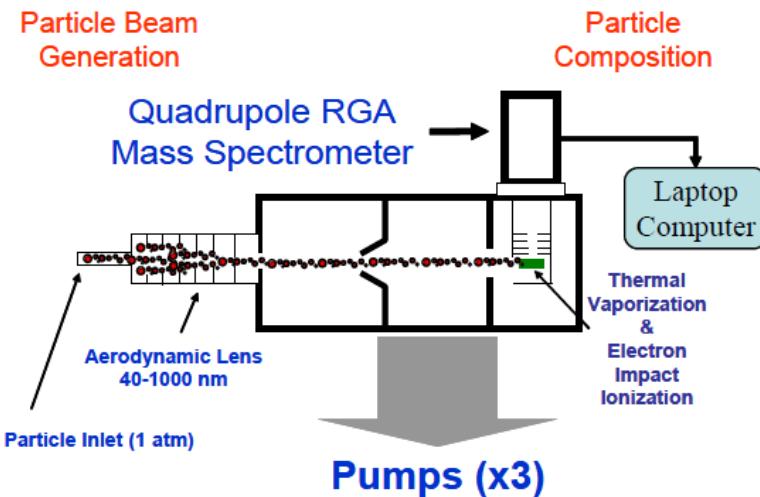
- Déconvolution du signal (Table de fragmentation) permet de quantifier la fraction organique, les sulfates, les nitrates, l'ammonium (+ nss Chloride, HAP)
- L'analyse HR donne également accès aux ratio **OM/OC**, **O/C**, **H/C**, **N/C** etc..

Le traitement des données brutes nécessite un certain degré d'expertise

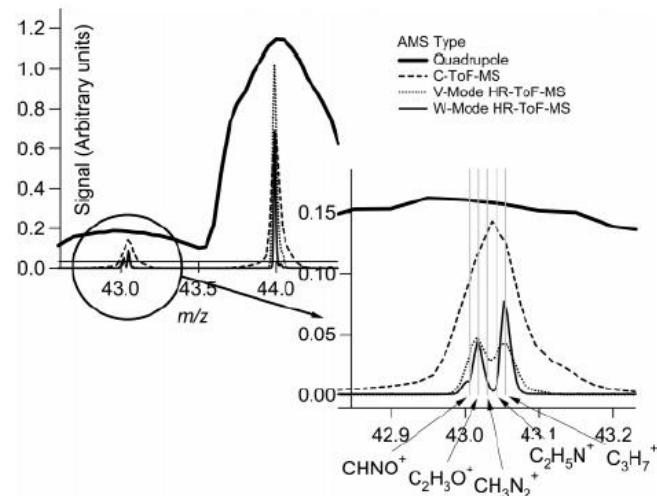
Aerosol Chemical Speciation Monitor (ACSM)

Aix Marseille
université

cnrs



Résolution : Quad vs HR-ToF



Version miniature et « user friendly » de l'AMS

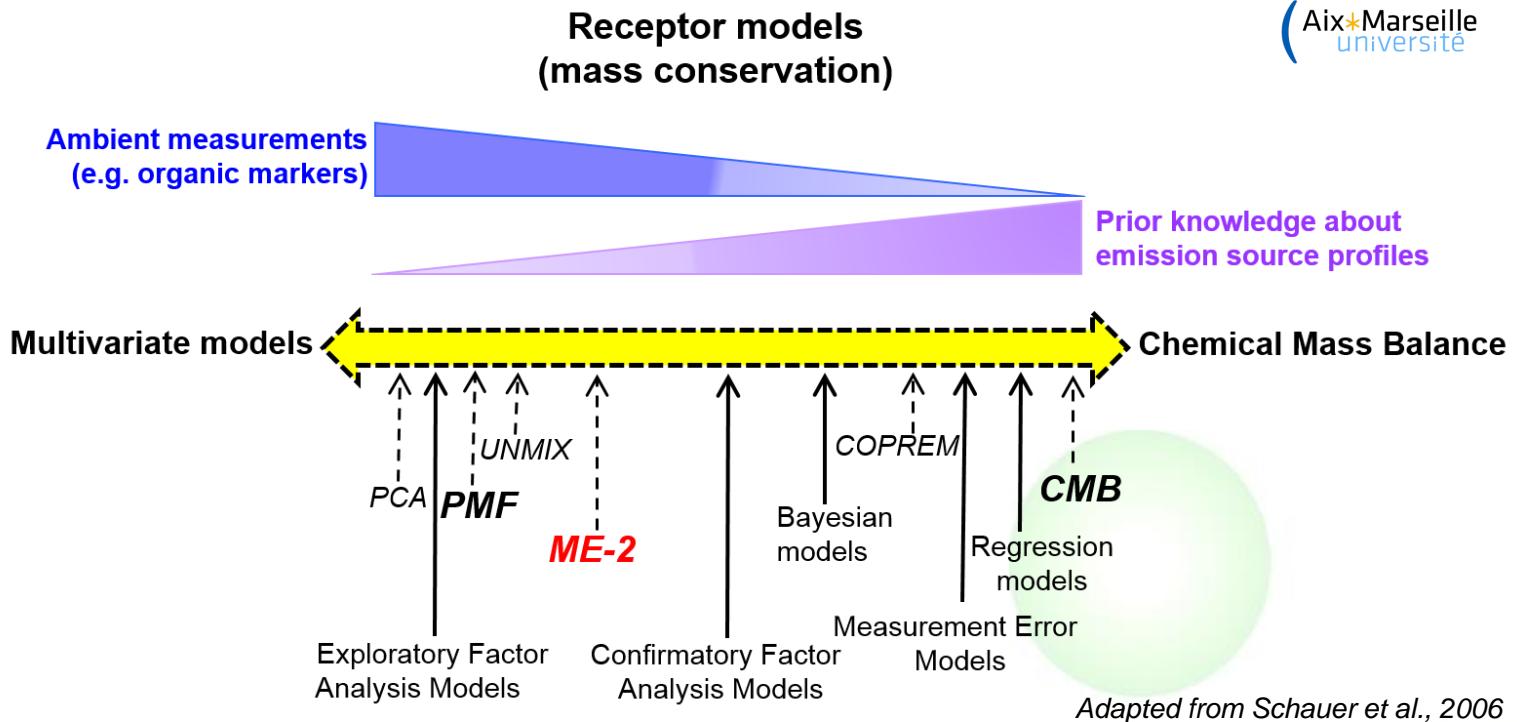
Avantages :

- Peu de maintenance (tourne en routine sans pb majeur)
- Traitement des données « quasi automatique »
- Possibilité de jouer avec les SM

Inconvénients

- Pas de haute résolution (pas accès aux ratio atomiques)
- Pas d'information en taille
- Résolution temporelle 30 min

Déjà 5 en France (LSCE, INERIS, EMD, AirRA et Air Lorraine)



PMF model

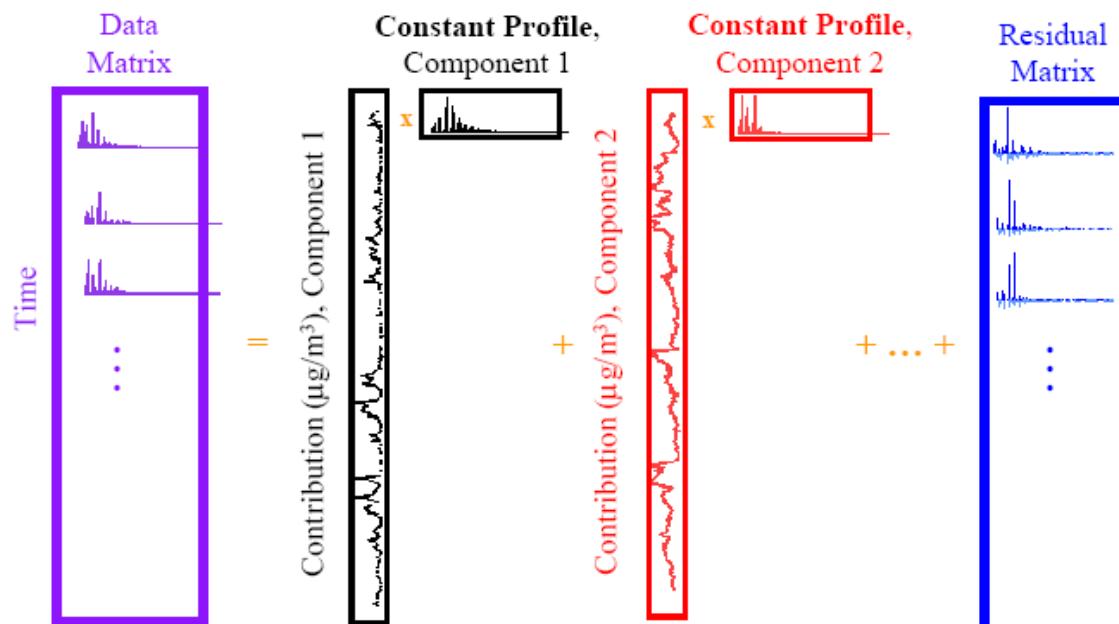
Basé sur les corrélations internes du jeu de données

INPUTS

- Matrice de données
- Matrice d'erreurs

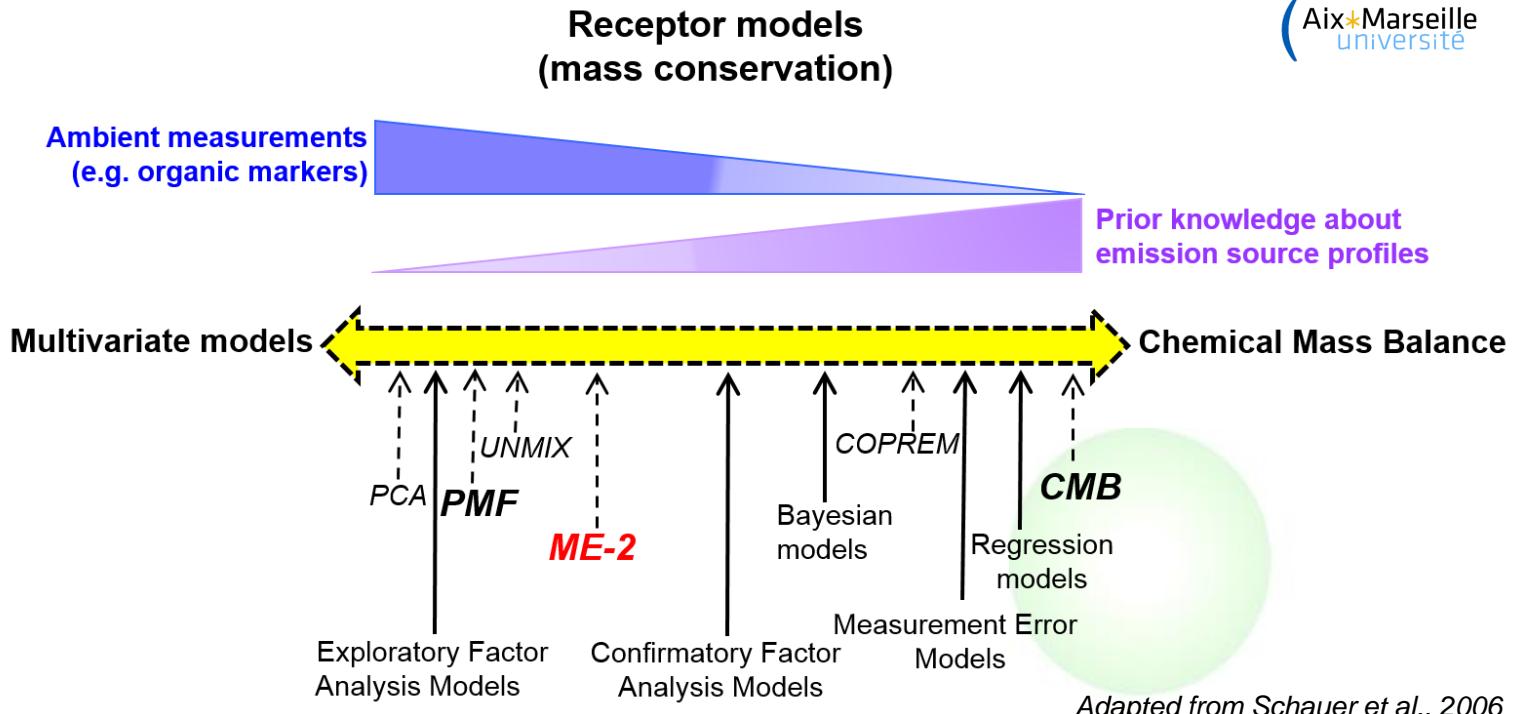
✓ Génère des facteurs constants et leurs évolutions temporelles

Generic Receptor Model Schematic



A data matrix is decomposed into an **arbitrary number** of factors, each of which is represented by a **constant mass spectrum** and a contribution **time series**. There is usually some *residual* of fit.

- Le modèle cherche à minimiser la matrice d'erreur (degrés de liberté internes aux facteurs)
- Les facteurs représentent des typologies d'aérosol, au mieux des sources



PMF model

Basé sur les corrélations internes du jeu de données

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- Matrice d'erreurs

Génère des facteurs constants et leurs évolutions temporelles

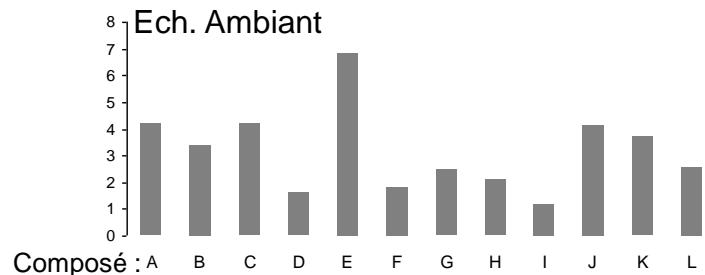
CMB model

De convolution de profils de sources connus

INPUTS

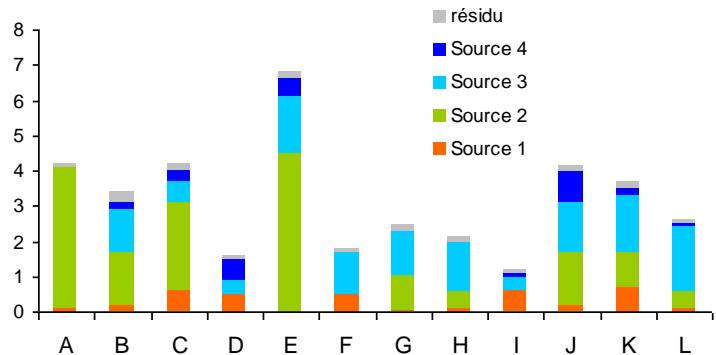
- Sélection de traceurs organiques et métaux
- Sélection de profils de sources (primaires)

Détermine les contributions relatives des sources incluses dans la modélisation

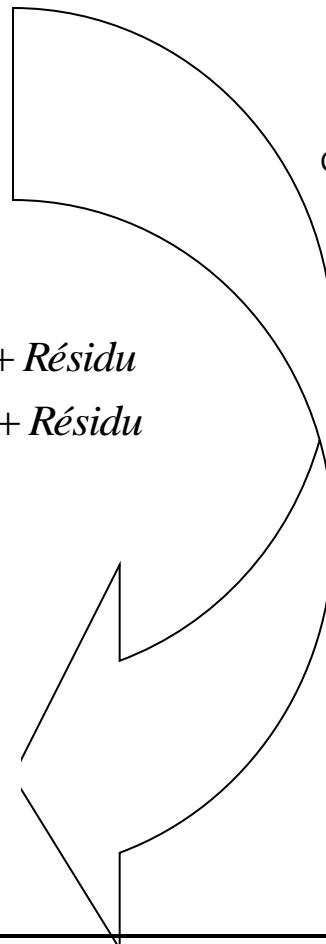


$$C_A = k_{A1}[\text{Source1}] + k_{A2}[\text{Source2}] + k_{A3}[\text{Source3}] + \dots + \text{Résidu}$$

$$C_B = k_{B1}[\text{Source1}] + k_{B2}[\text{Source2}] + k_{B3}[\text{Source3}] + \dots + \text{Résidu}$$



Détermination de la meilleure combinaison linéaire des profils sources pour expliquer la signature chimique de l'aérosol ambiant



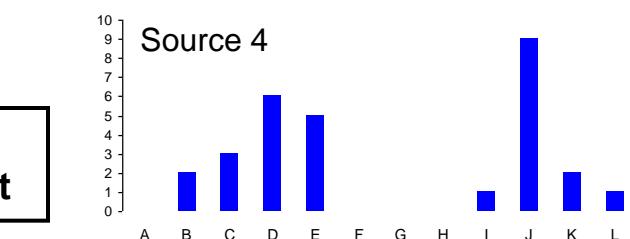
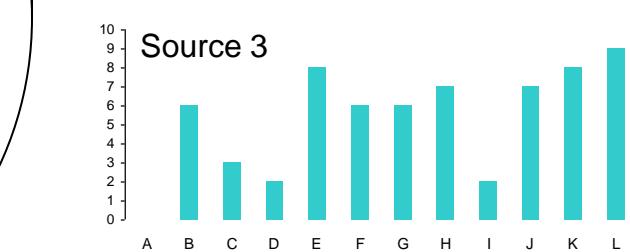
Source 1

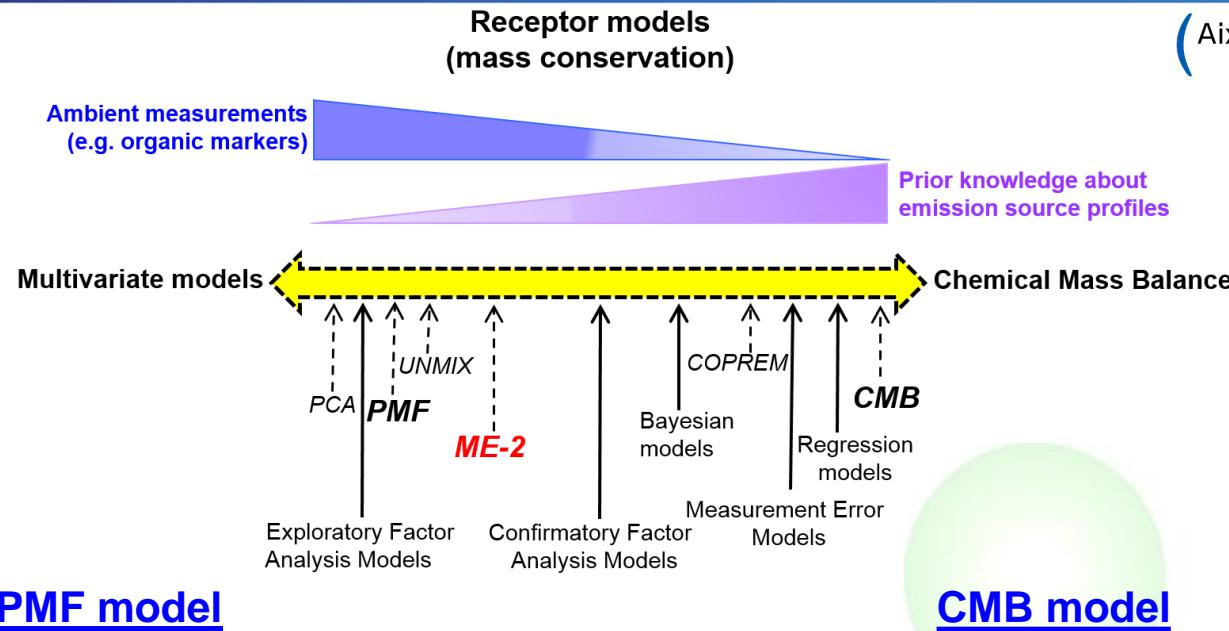
Source 2

Source 3

Source 4

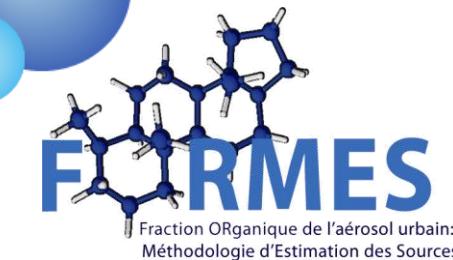
Profils de sources



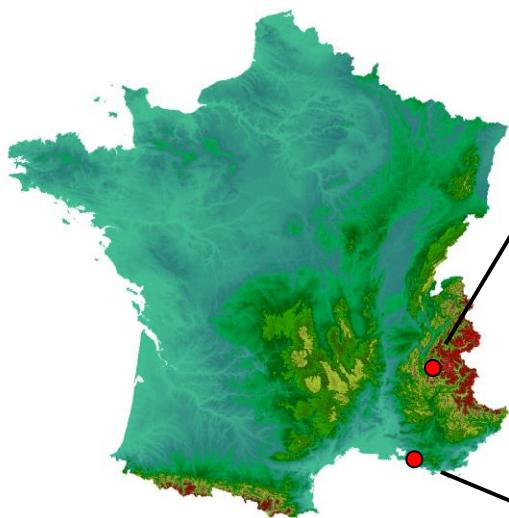


- Pas d'informations a priori sur les sources
- Longue série de données (ie. Nb d'obs>Nb de variables)
- Pas de solutions uniques (subjectivité: l'utilisateur doit choisir le nb de facteurs pour expliquer au mieux la série de données)
- Impact potentiellement fort de la dynamique atmosphérique (mélange de source)
- Quand appliqué à des données AMS, les facteurs traduisent autant l'état d'oxydation de l'OA que ses sources (HOA, BBOA, OOAs)

- Connaissance a priori des principales sources (analyse préliminaire de type PCA souhaitable)
- Choix des marqueurs crucial
- Peut être appliqué sur 1 seul échantillon (dans l'absolu)
- L'approche CMB est aveugle au vieillissement chimique de l'OA (contrairement à PMF-AMS)
- La fraction secondaire (SOA) est traitée comme un apport de Carbone



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



Optimisation et intercomparaison des approches de source *apportionnement*

Grenoble (Jan. 2009)



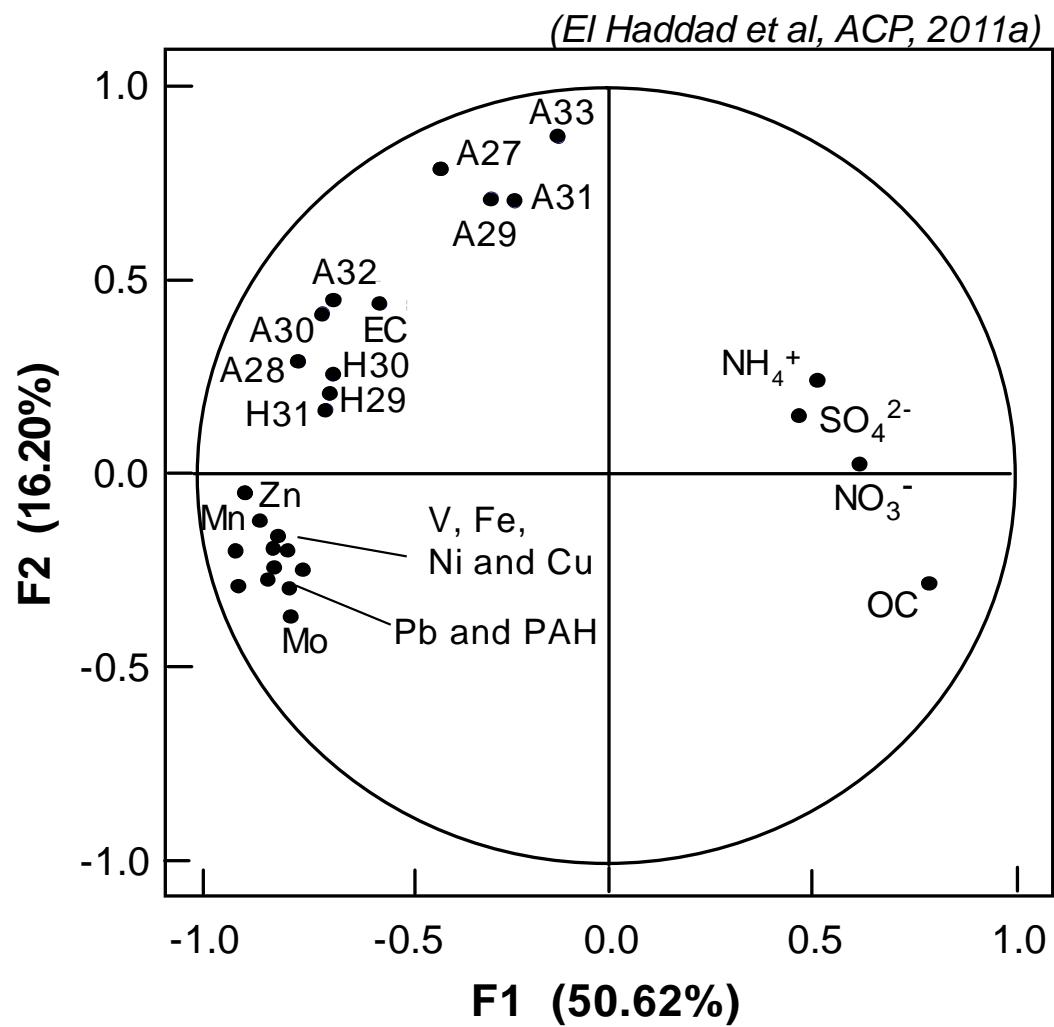
Favez et al., ACP, 2010

Marseille (Jul. 2008)



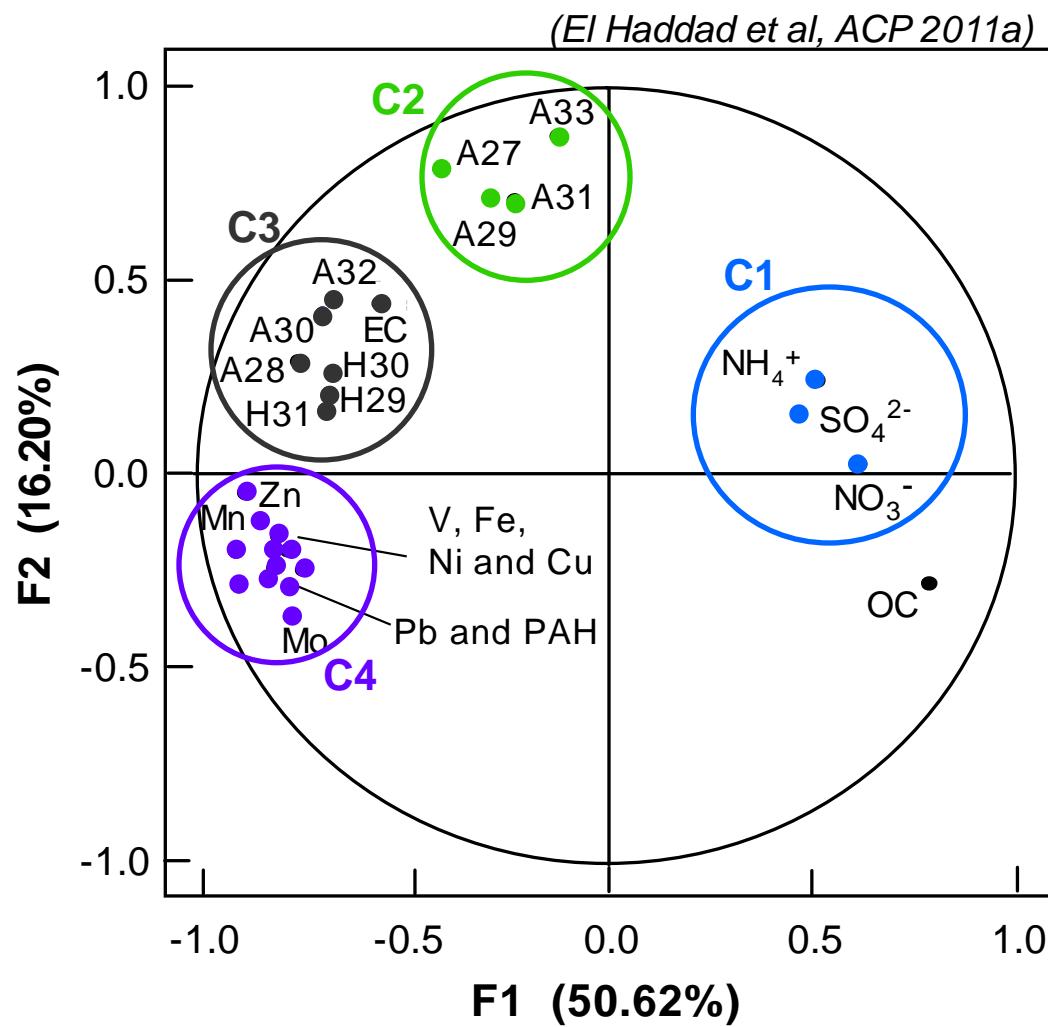
El Haddad et al., ACP 2011a, b et 2013

Choice of markers and source profiles



Preliminary PCA

Choice of markers and source profiles



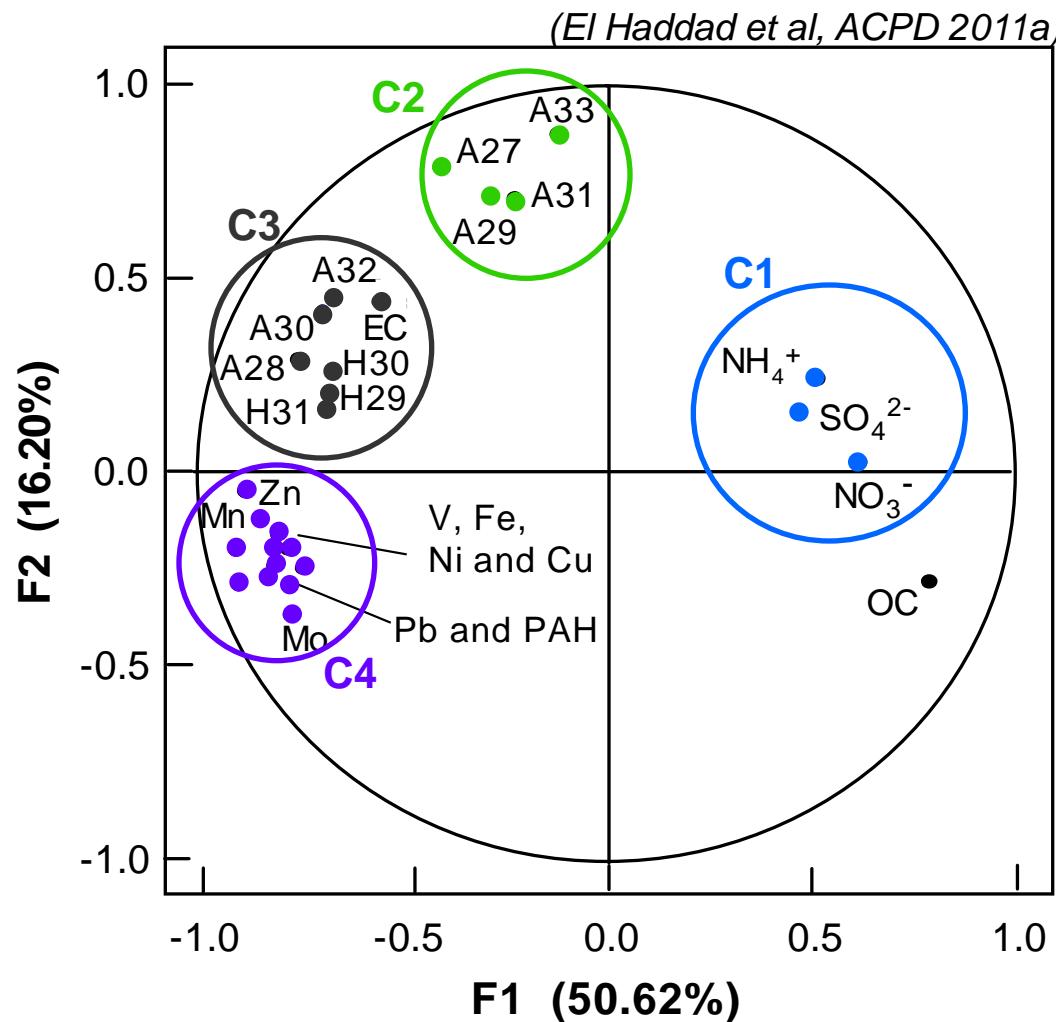
Preliminary PCA

Identified clusters/sources

- C1: secondary origins
- C2: vegetative detritus
- C3: vehicular emissions
- C4: industrial emissions

3 Primary sources

Choice of markers and source profiles



Preliminary PCA

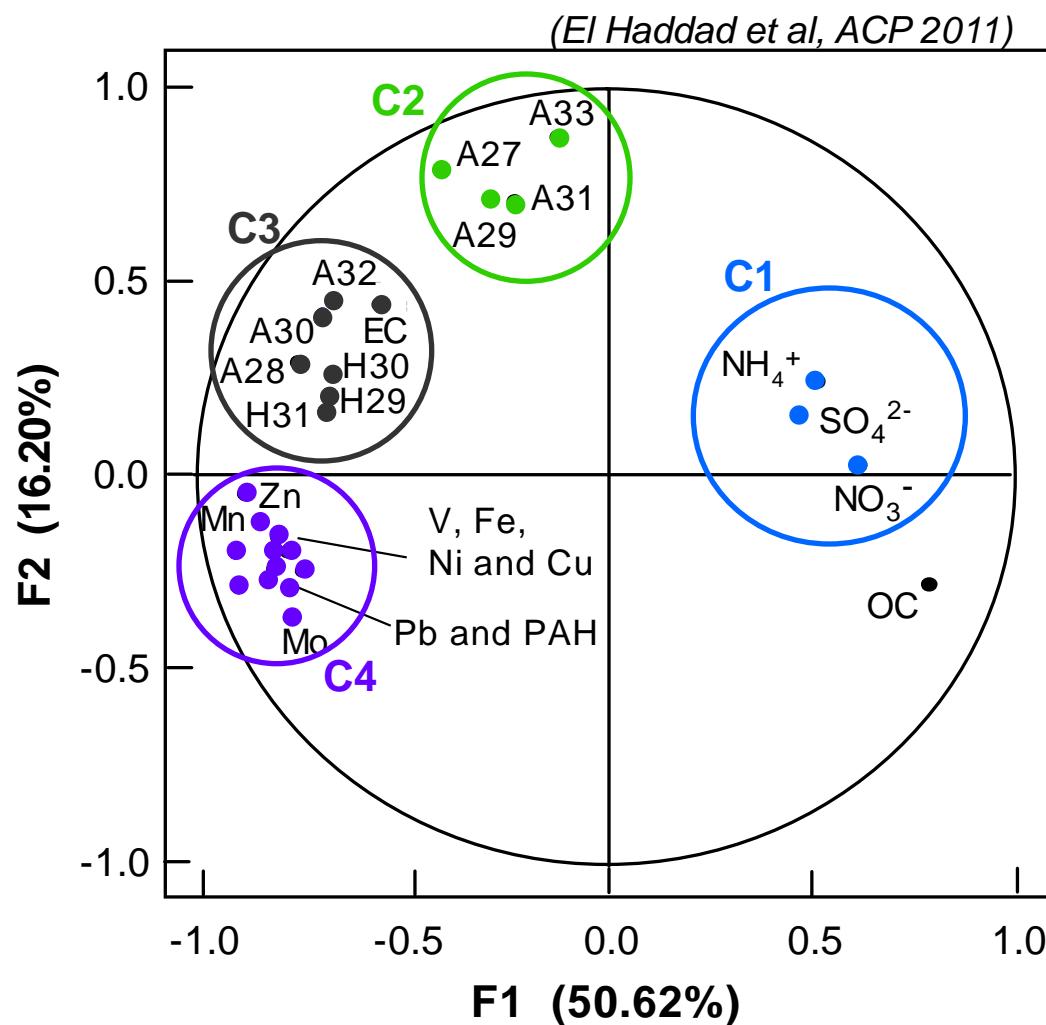
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3 Primary sources

These sources have to be considered in CMB

Choice of markers and source profiles



Preliminary PCA

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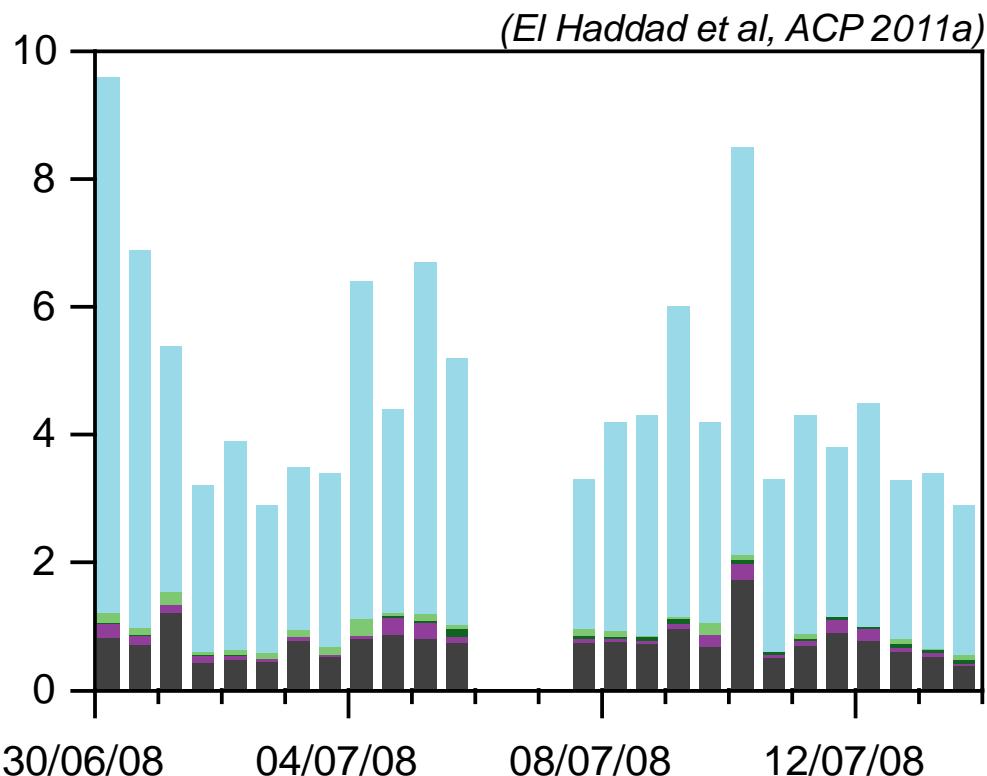
3 Primary sources

These sources have to be considered in CMB

CMB setup

| Source profiles : | |
|--|---|
| Industrial sources : | Non Industrial profiles : |
| <ul style="list-style-type: none"> - Coke production Weitkamp <i>et al.</i>, 2005 - Steel facilities, mean of overall processes Tsai <i>et al.</i>, 2007 - Shipping main engines Agrawal <i>et al.</i>, 2008 | <ul style="list-style-type: none"> - Vehicular emissions ElHaddad <i>et al.</i>, 2009 - Diesel heavy duty trucks Rogge <i>et al.</i>, 1993 - Biomass burning Fine <i>et al.</i>, 2002 - Natural gas combustion Rogge <i>et al.</i>, 1993 - Vegetative detritus Rogge <i>et al.</i>, 1993 |
| Additional Sources : | |
| Sea salt $[\text{sea salt}] = [\text{Cl}^-] + [\text{Na}^+] * 1.47$ | |
| <i>Putaud et al., 2004</i> | |
| Crustal Dust $[\text{Crustal Dust}] = 2.20[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}]$ | |
| <i>Malm et al., 1994</i> | |
| Selected markers : | |
| Specific markers : <ul style="list-style-type: none"> - Vehicular emissions : Elemental carbon + 3 hopanes (i.e. $17\alpha(\text{H}),21\beta(\text{H})$-norhopane, $17\alpha(\text{H}),21\beta(\text{H})$-hopane, and $22\text{S},17\alpha(\text{H}),21\beta(\text{H})$-homohopane) - Biomass burning : levoglucosan | |
| Additional markers : <ul style="list-style-type: none"> - Four PAH (i.e. benzo[b,k]fluoranthene, benzo[e]pyrene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene) markers, for several kind of industrial processes - C27, C32 n-alkanes - Three metals (i.e. V, Ni and Pb) | |

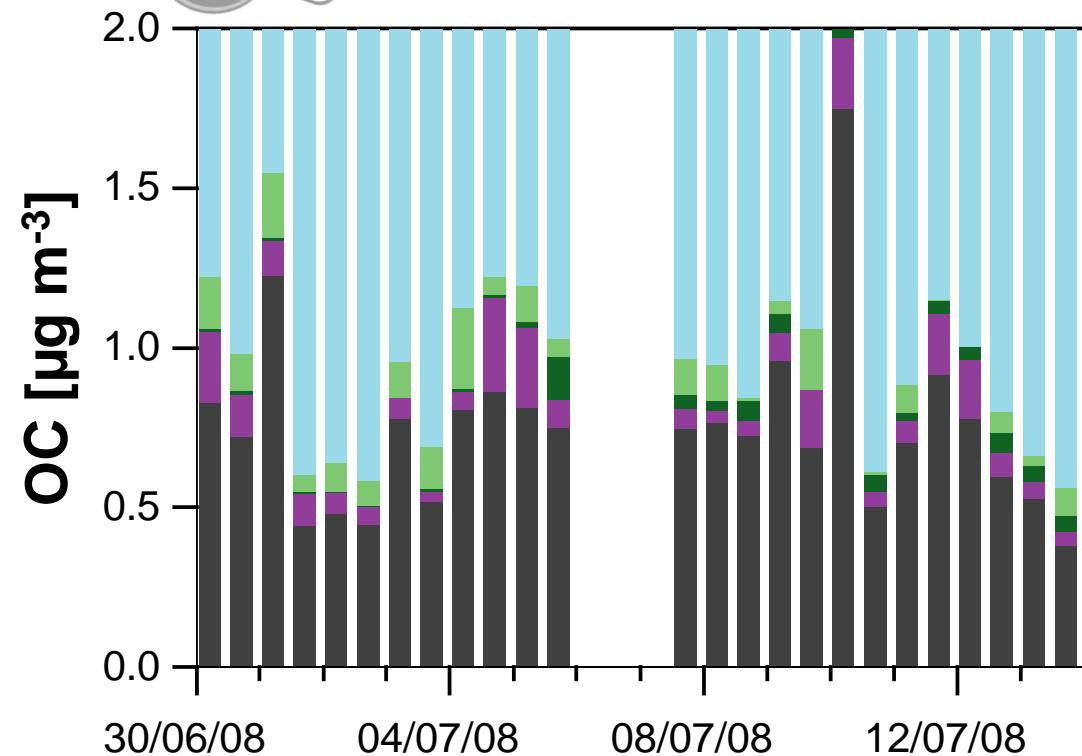
Contributions of primary sources



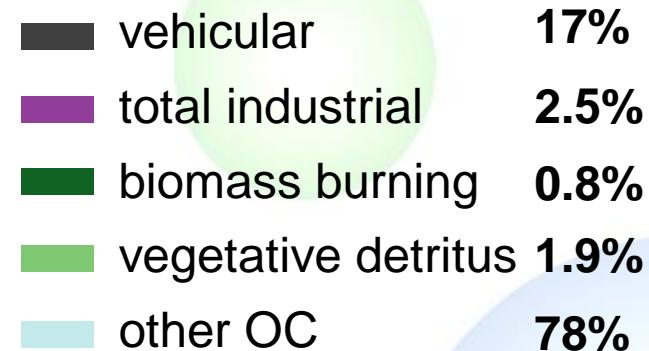
Contributions of primary sources



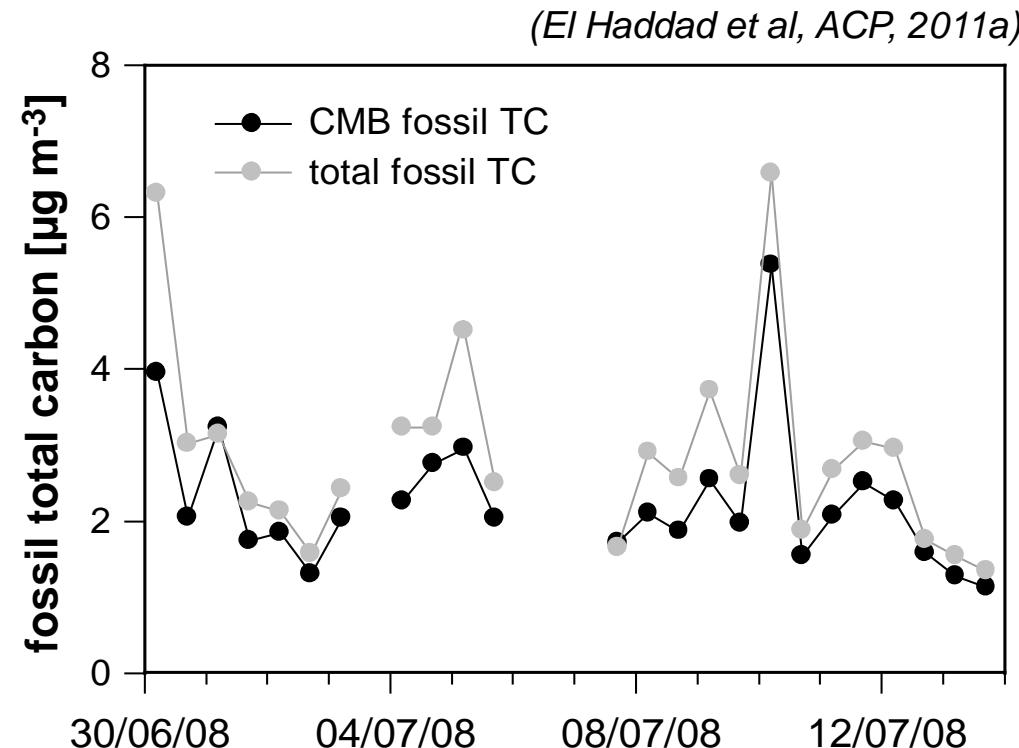
Zoom on primary fraction



CMB modeling



Comparison with ^{14}C data



CMB fossil TC vs. total fossil TC

^{14}C measurements can distinguish between **fossil** and **non-fossil** total carbon (TC=EC+OC)

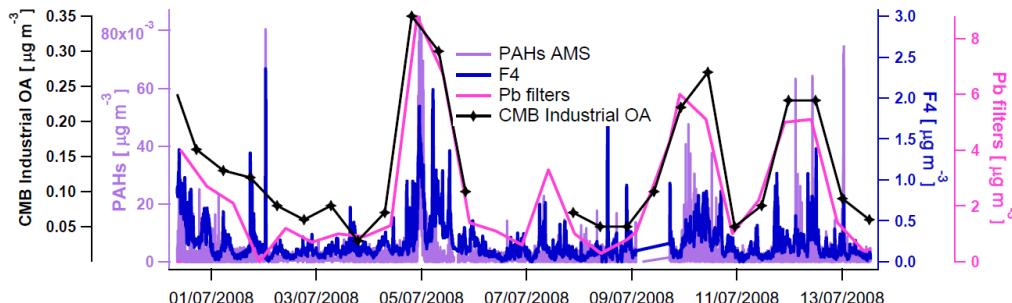
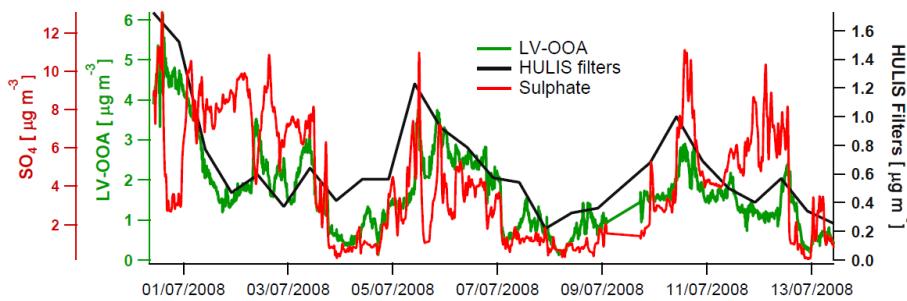
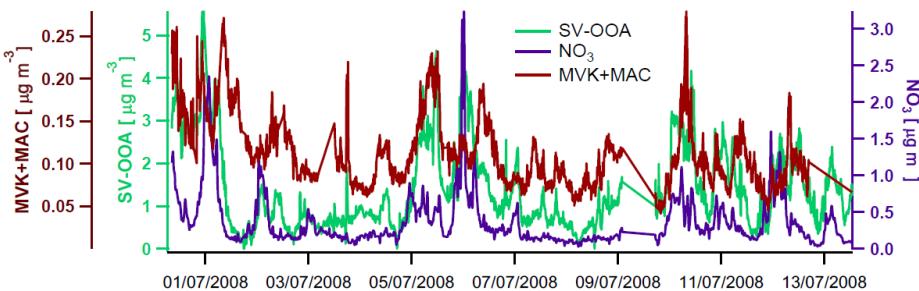
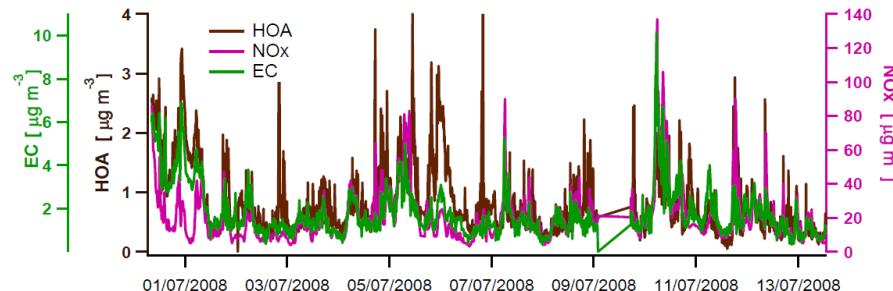
**CMB fossil TC = Vehicular emissions
Industrial emissions +**

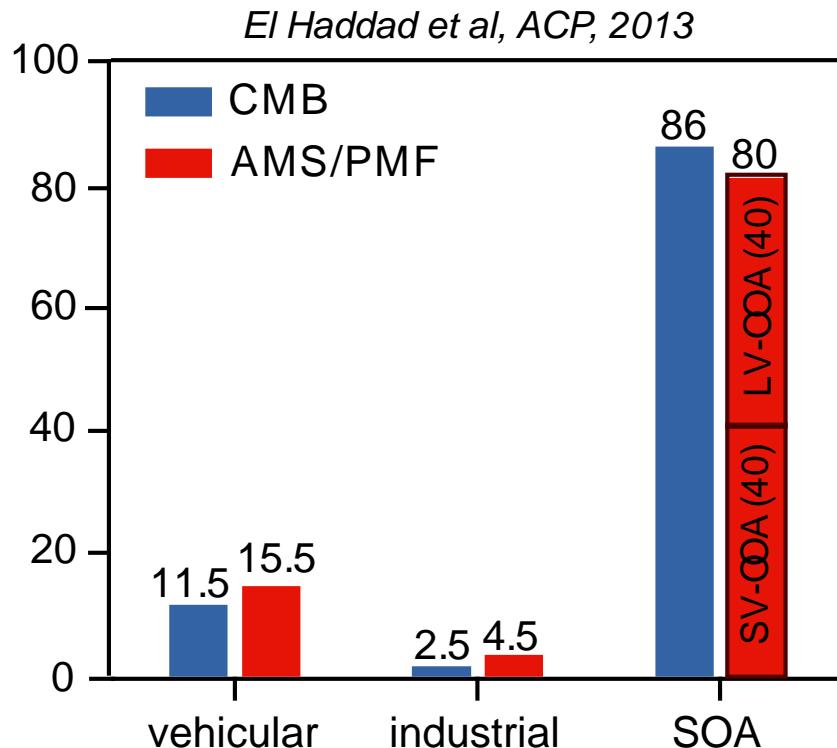
**Good correlation between the CMB and ^{14}C estimates,
validating the CMB estimations of primary fraction**

PMF-AMS analysis

4 Factors :

- HOA (hydrocarbons like OA)
Trafic related sources
- SVOOA (Semi volatile Oxygenated OA)
First generation oxydation products
- LVOOA (Low volatile OOA)
Highly oxygenated organic compounds
Oligomers
- F4 (Industrial factor)
- no cooking factor as been extractted
from the chemical/mathematical « soup »





CMB vs. AMS/PMF

- Good agreement between CMB and AMS/PMF for primary sources.
- LV-OOA + SV-OOA = CMB unapportioned fraction

1/ La majorité de l'OA est secondaire

2/ Impact faible des sources industrielles?

Origines de la fraction secondaire : quelques éléments de réflexion et nouvelle approche



Viellissement émissions véhiculaires

PAUL SCHERRER INSTITUT

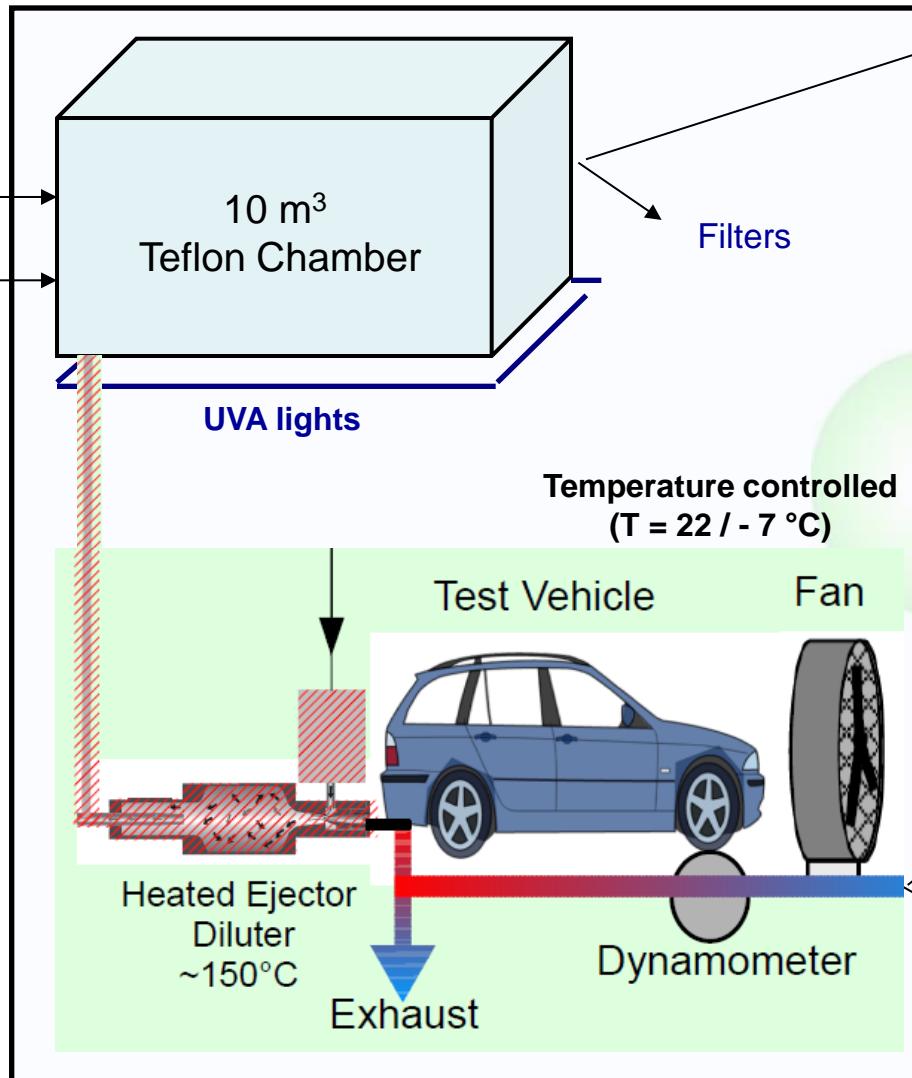


Aix-Marseille
université
Particle- and gasphase
measurements



Continuous HNO₂ injection
 $\text{HNO}_2 \rightarrow \text{OH} + \text{NO}$ (400nm)

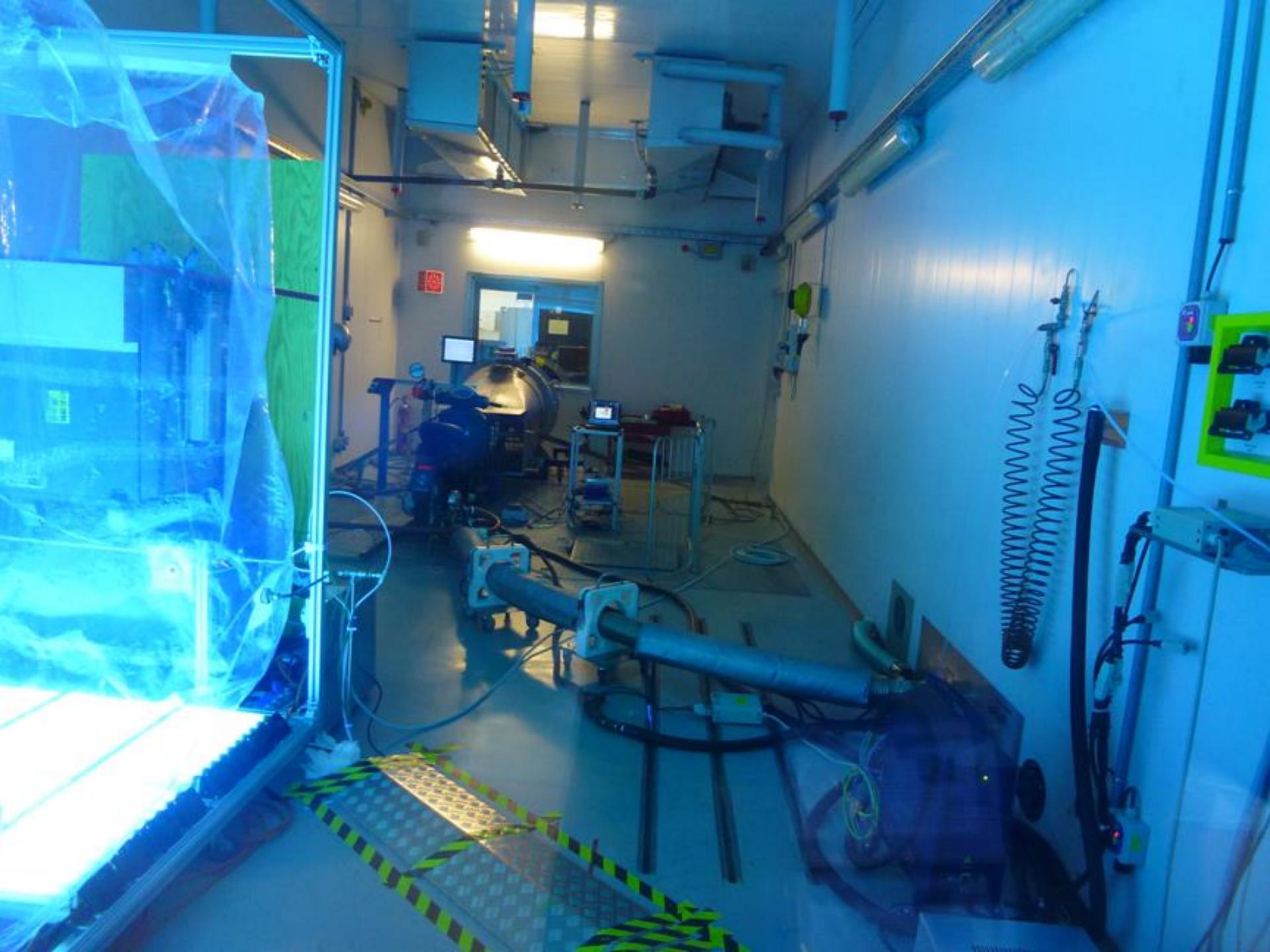
d9-butanol, „OH clock“
Barmet et al., AMT, 2012



- HR-ToF-AMS
- Aethalometer
- PTR-ToF-MS
- SMPS
- Gasphase monitors

VELA Particle- and
gasphase measurements
(incl. GC-FID)

Filters



Experiments

57 expériences

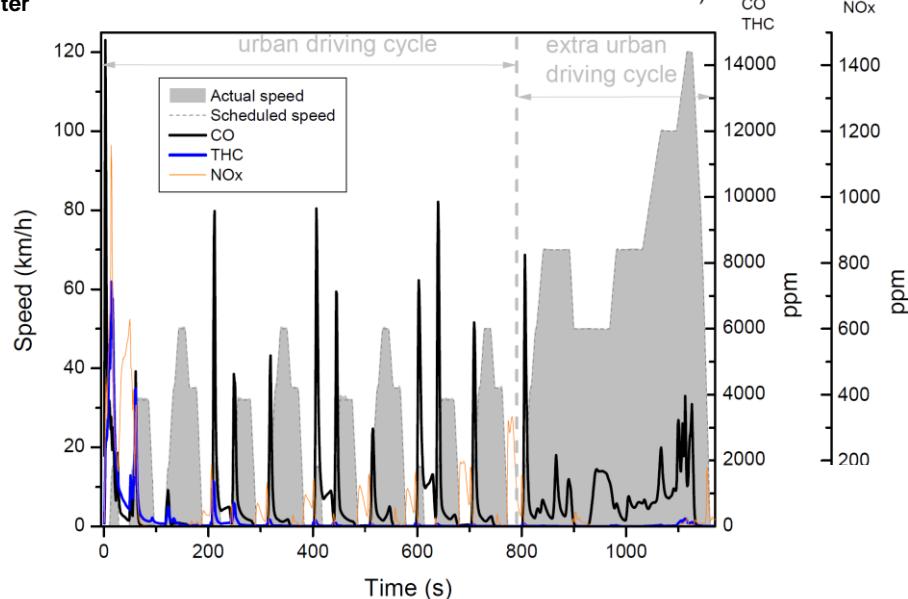
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| Vehicle | Fuel | Technology | Temp. | RH |
|---------|--------------------|--------------------|----------|------------|
| 2S S1 | Scooter, Euro 1 | Gasoline | OC | 22°C |
| 2S S2 | Scooter, Euro 2 | Gasoline | OC | 22°C |
| 2S S3 | Scooter, Euro 2 | Gasoline, Alkylate | OC | 22°C |
| 4S S1 | Scooter, Euro 2 | Gasoline | OC MPI | 22°C |
| 4S S2 | Scooter, Euro 2 | Gasoline, Alkylate | OC | 22°C |
| GC1 | Light Duty, Euro 5 | Gasoline | TWC, DI | 22°C, -7°C |
| GC2 | Light Duty, Euro 5 | Gasoline | TWC, DI | 22°C, -7°C |
| GC3 | Light Duty, Euro 5 | Gasoline | TWC, DI | 22°C |
| DC1 | Light Duty, Euro 5 | Diesel | DPF, DI | 22°C, -7°C |
| DC2 | Light Duty, Euro 5 | Diesel | DPF, DI | 22°C, -7°C |
| DT1 | Heavy Duty, Euro V | Diesel / LPG | SCR | 22°C, -7°C |
| DT2 | Heavy Duty, Euro V | Diesel | DPF, SCR | 22°C |

OC = oxidation catalyst, TWC = three way catalyst, SCR = selective catalytic reduction,
 MPI = Multi-point injection, DI = Direct injection, DPF = Diesel particle filter

Standard Driving Cycle (NEDC)



Data Treatment

AMS organic particle mass

→ „partitioning correction“ to 10 ug m^{-3}

→ carbon mass balance (emission factors)

$$\text{EF}_{\text{MASS}} = \left(\frac{\Delta P}{\Delta C_{\text{CO}_2} + \Delta C_{\text{CO}} + \Delta C_{\text{HC}} + \Delta C_{\text{OC}} + \Delta C_{\text{BC}}} \right) \cdot W_c$$

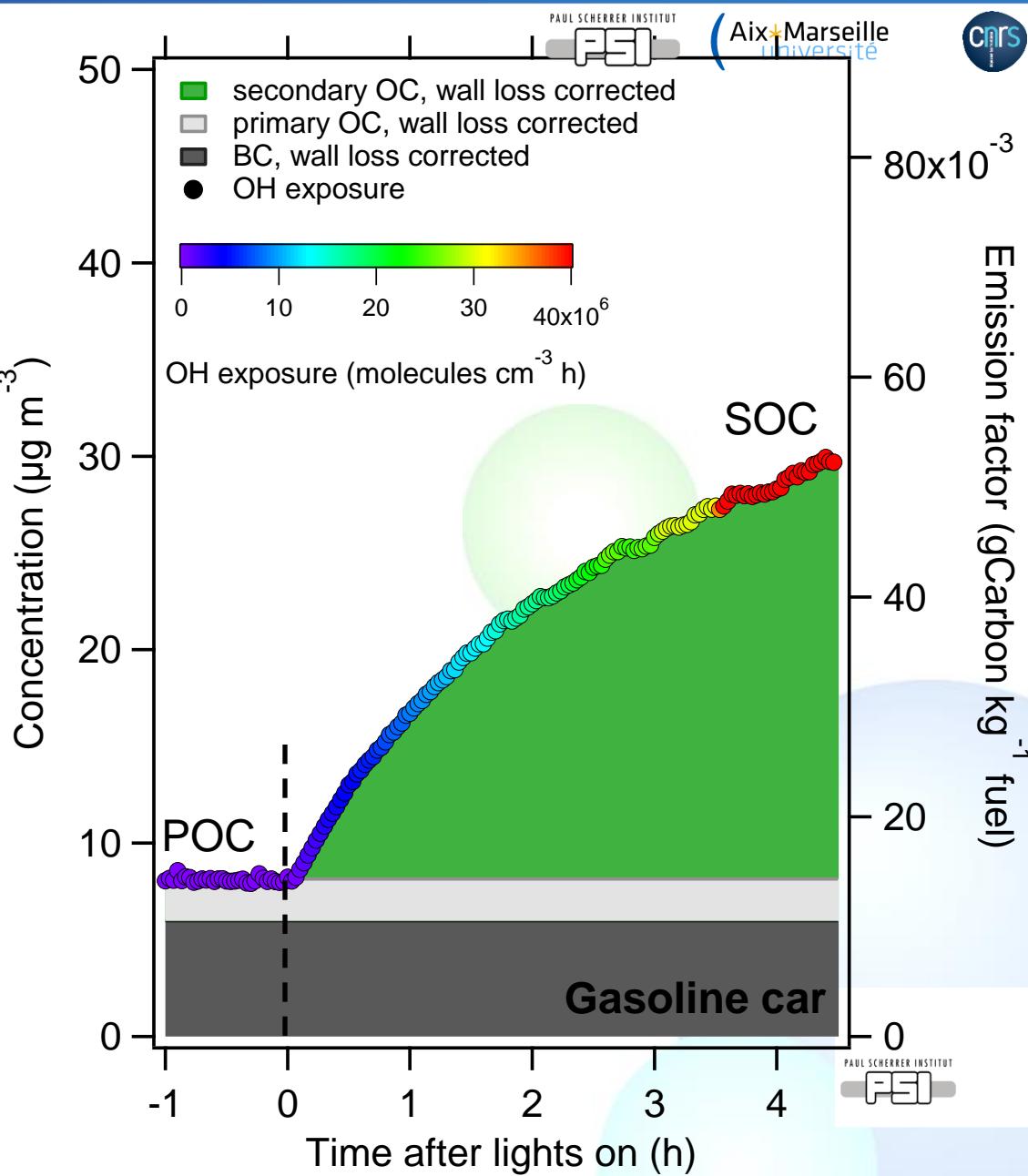
→ wall loss correction

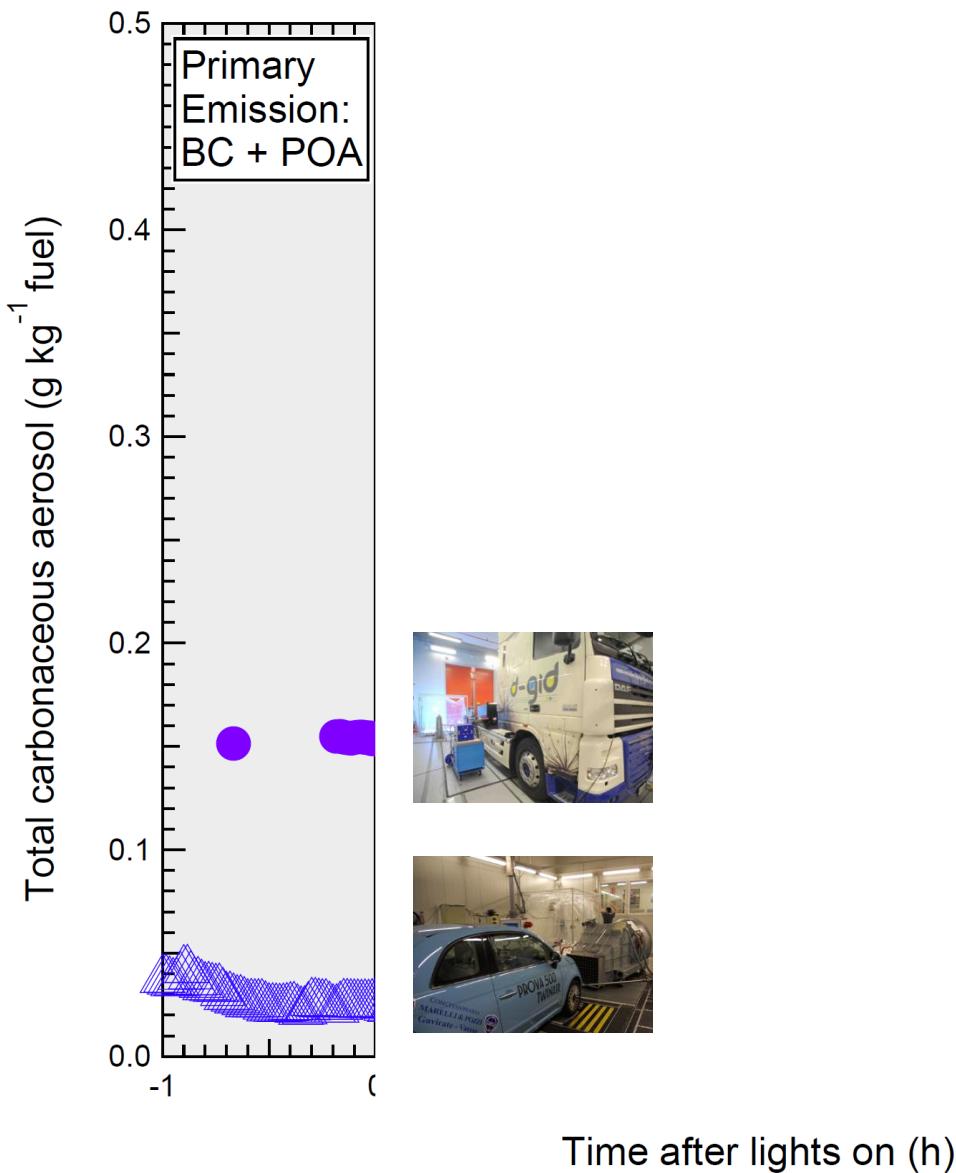
→ conversion to g Carbon

→ BC, POC, SOC

→ determine SOC age
(OH exposure)

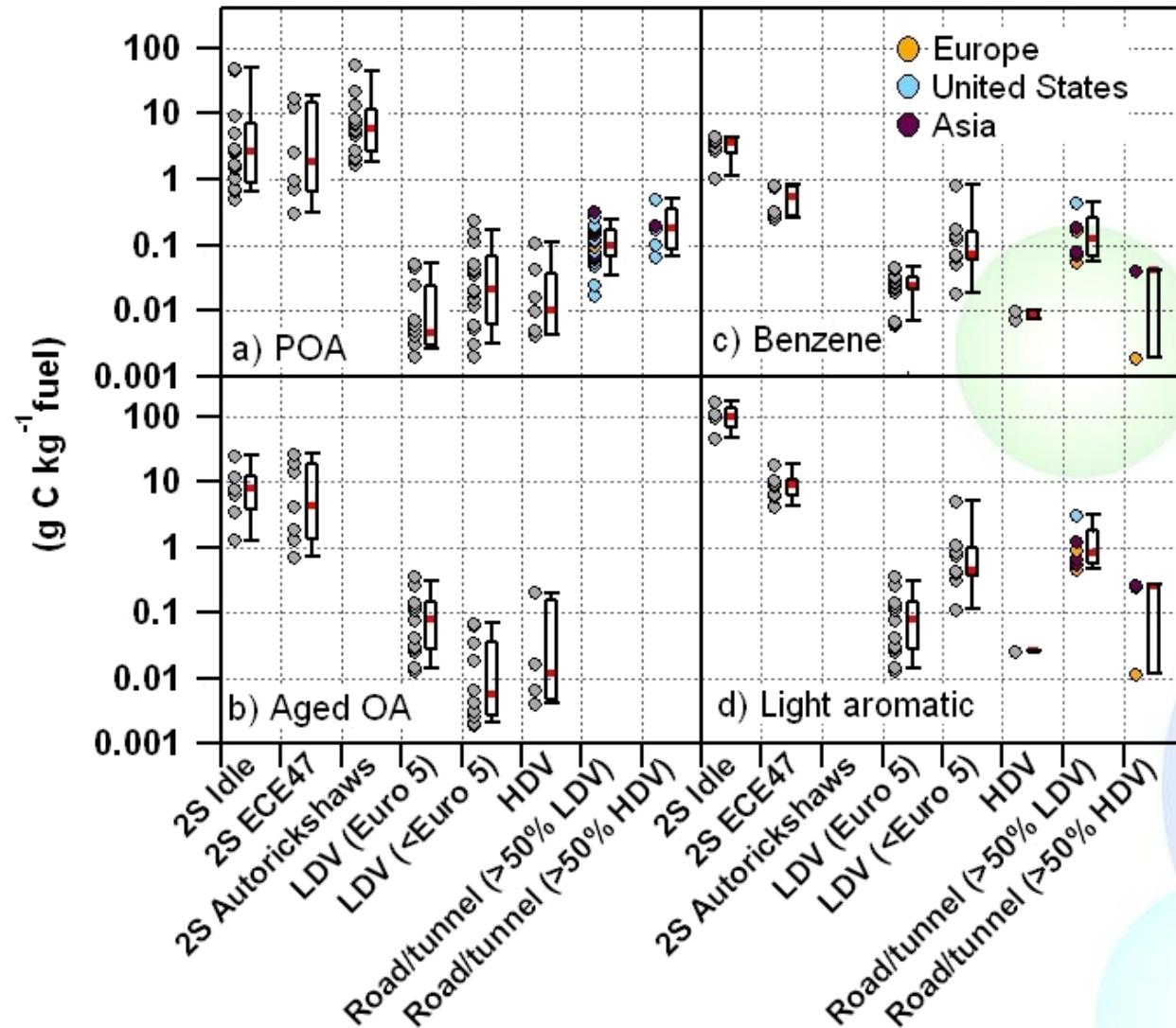
RESULTS



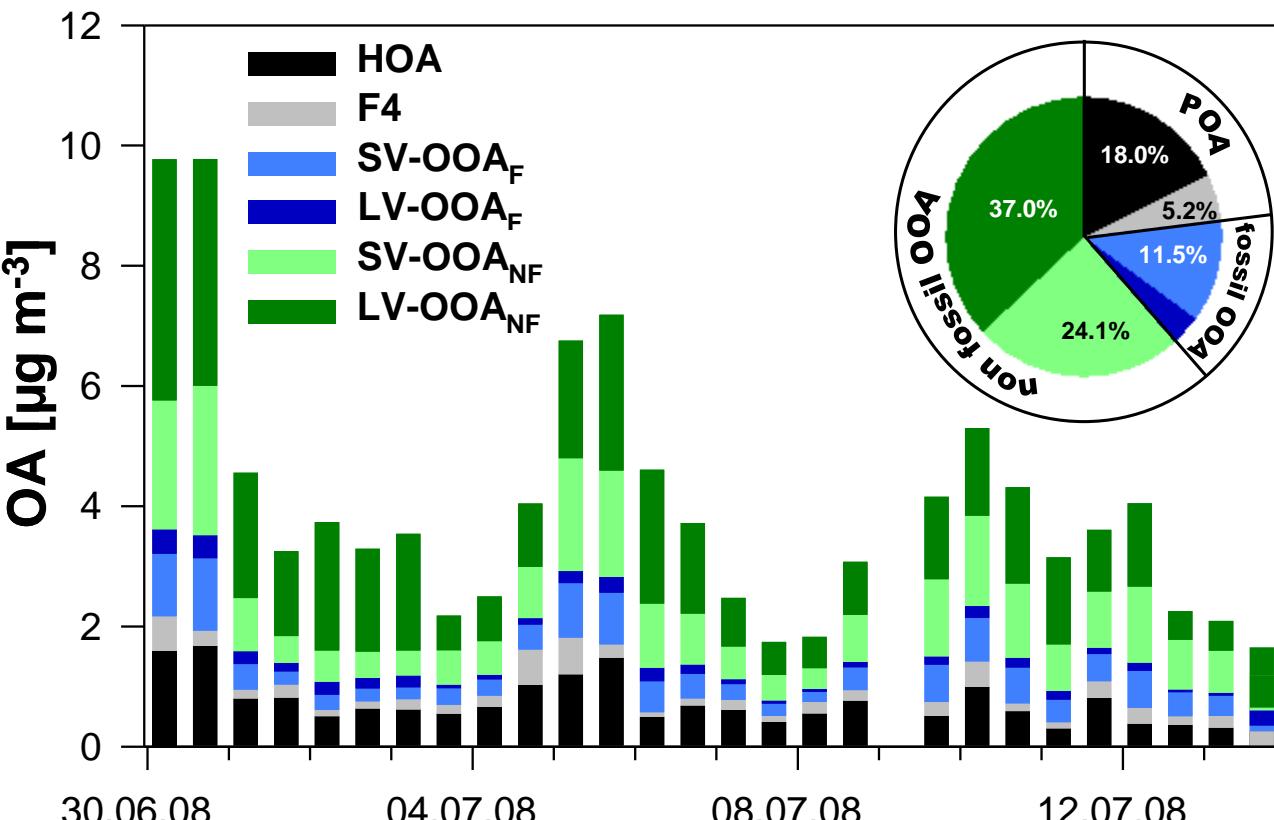


Two-stroke scooters are a dominant source of air pollution in many cities

Platt et al, 2014, Nature Com.



Combination of AMS-PMF and ^{14}C data (multi regression mode)



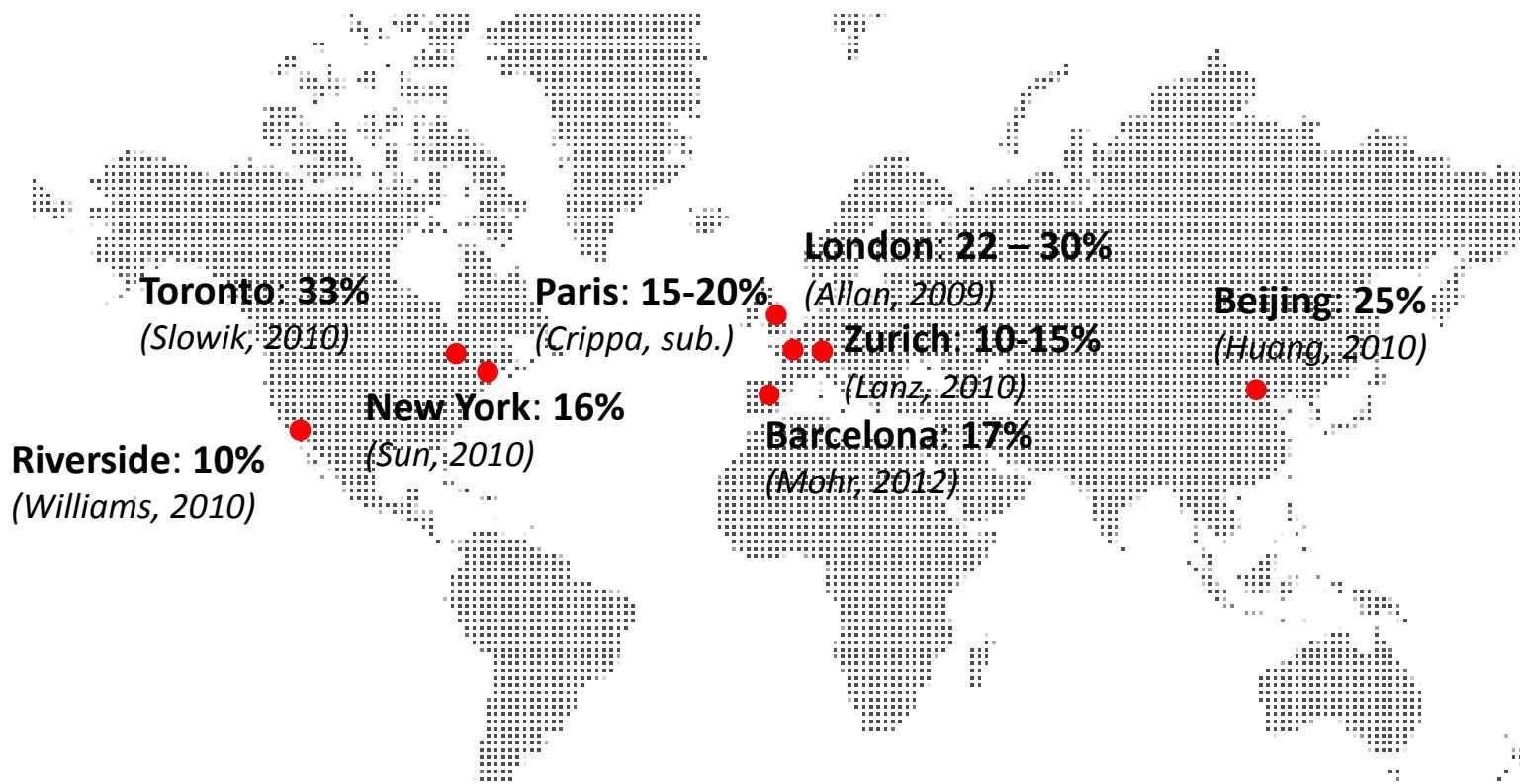
~60 % de l'OA est secondaire et d'origine non fossile !

Idem à Barcelone et même en bordure de périphérique urbain..

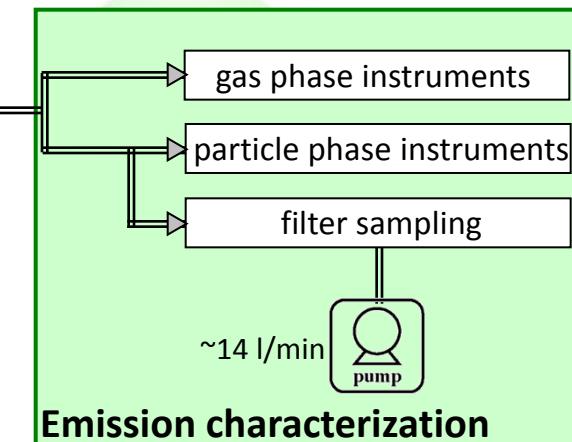
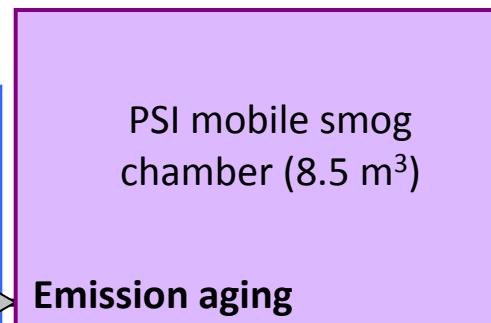
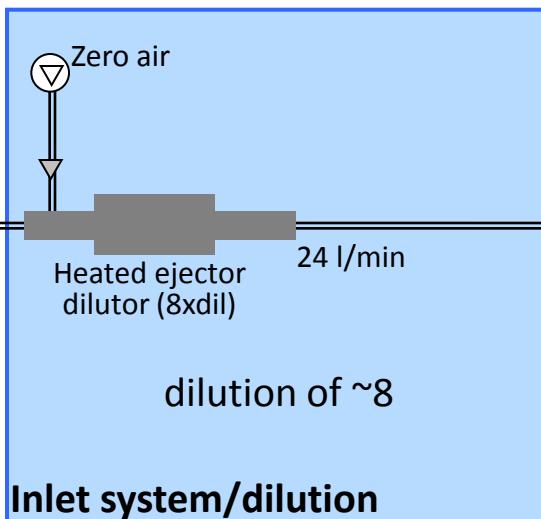
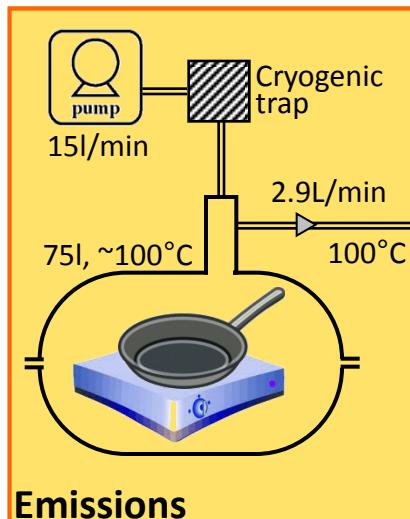
Biogenic SOA?
Cooking SOA?

EI Haddad et al, ACP, 2013

Cooking organic aerosol (COA) in major cities: Aerosol Mass Spectrometer (AMS)– Positive Matrix Factorization (PMF) results



Experimental setup (2/2): Aging experiments



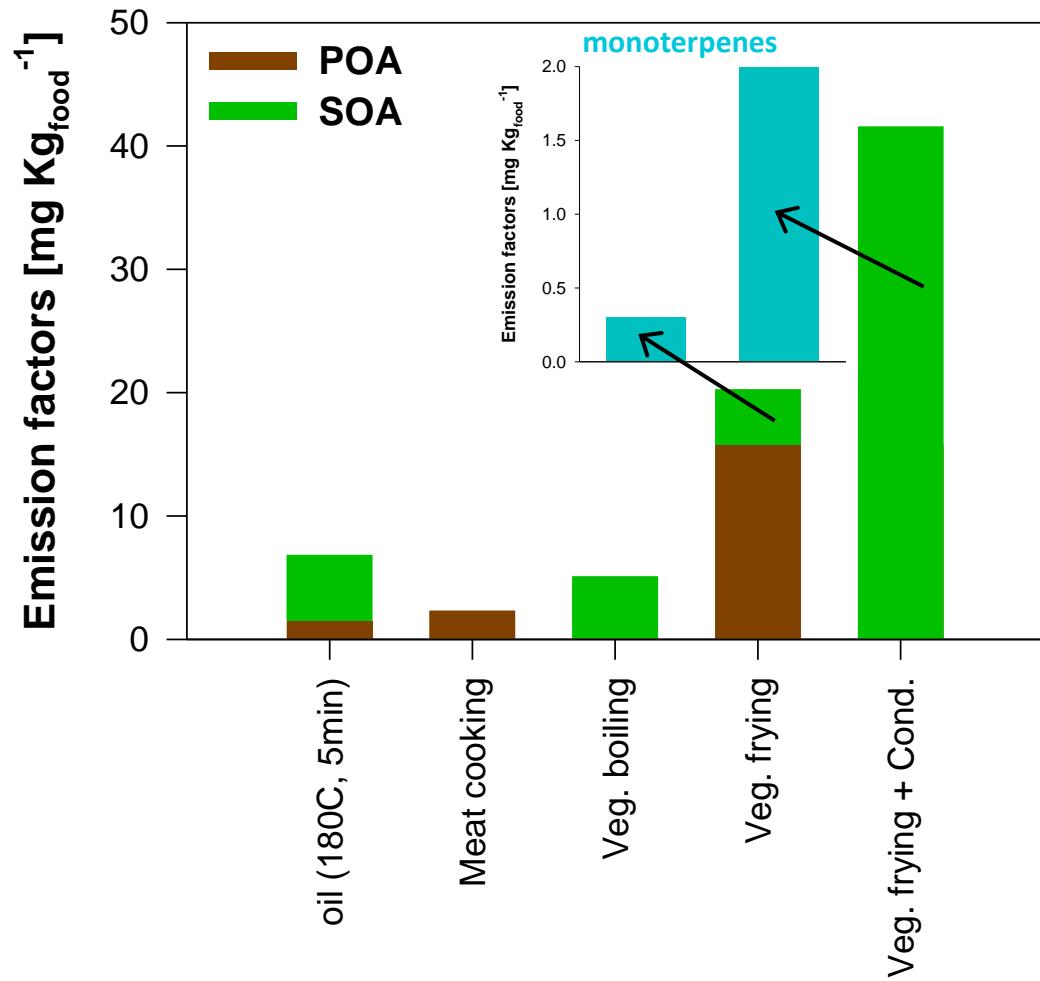
Measurements of SOA potential

Conditions inside the chamber:

- POA concentrations: $[0.5-30]\mu\text{g m}^{-3}$
- NO_x concentrations: 10-25 ppb
- OH concentrations: $2-5\times10^6$ molecules cm^{-3}
- RH: 50-65%
- Temperature: 21-23°C

Can cooking emissions produce non-fossil SOA?

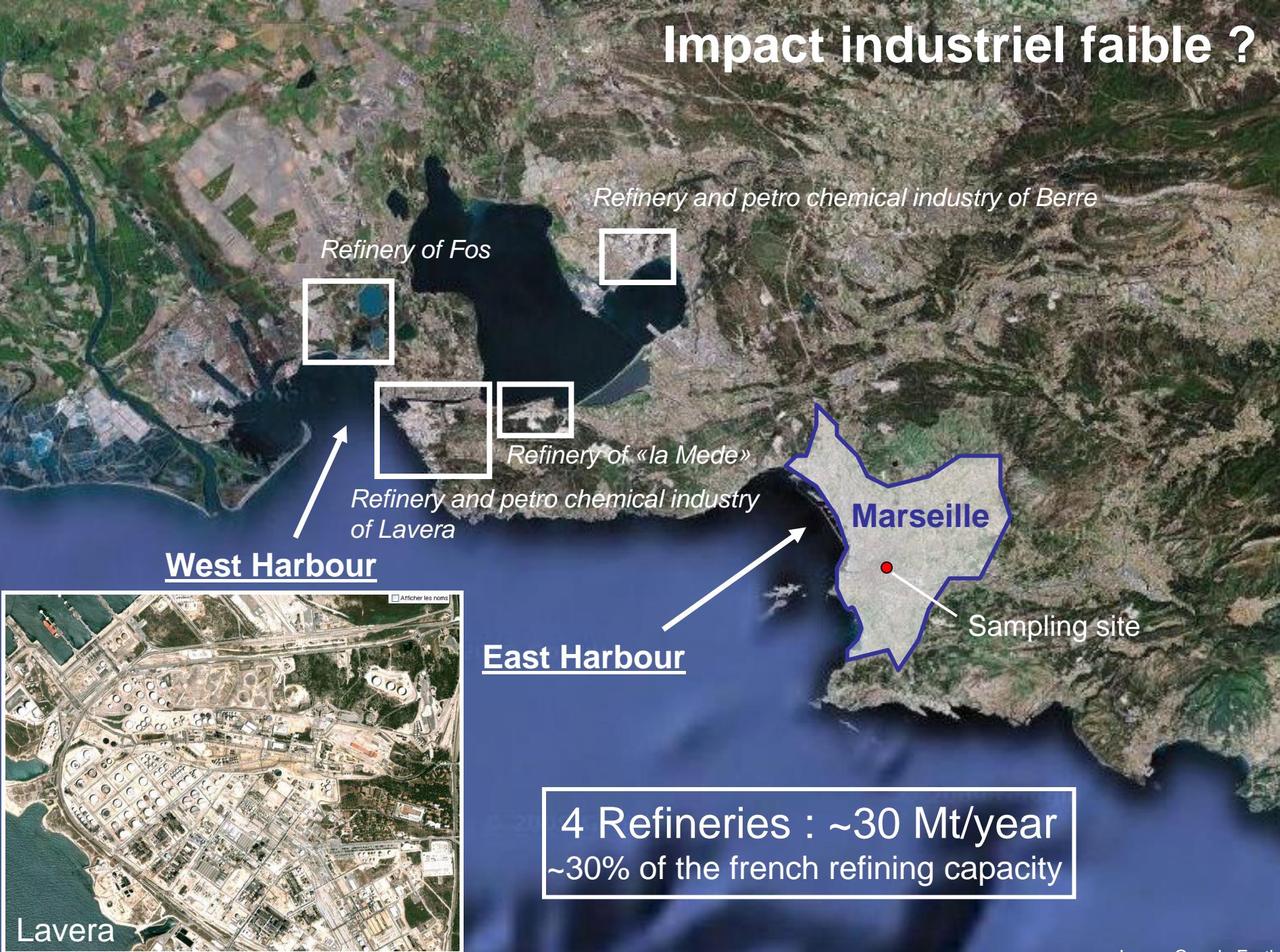
Yes!!



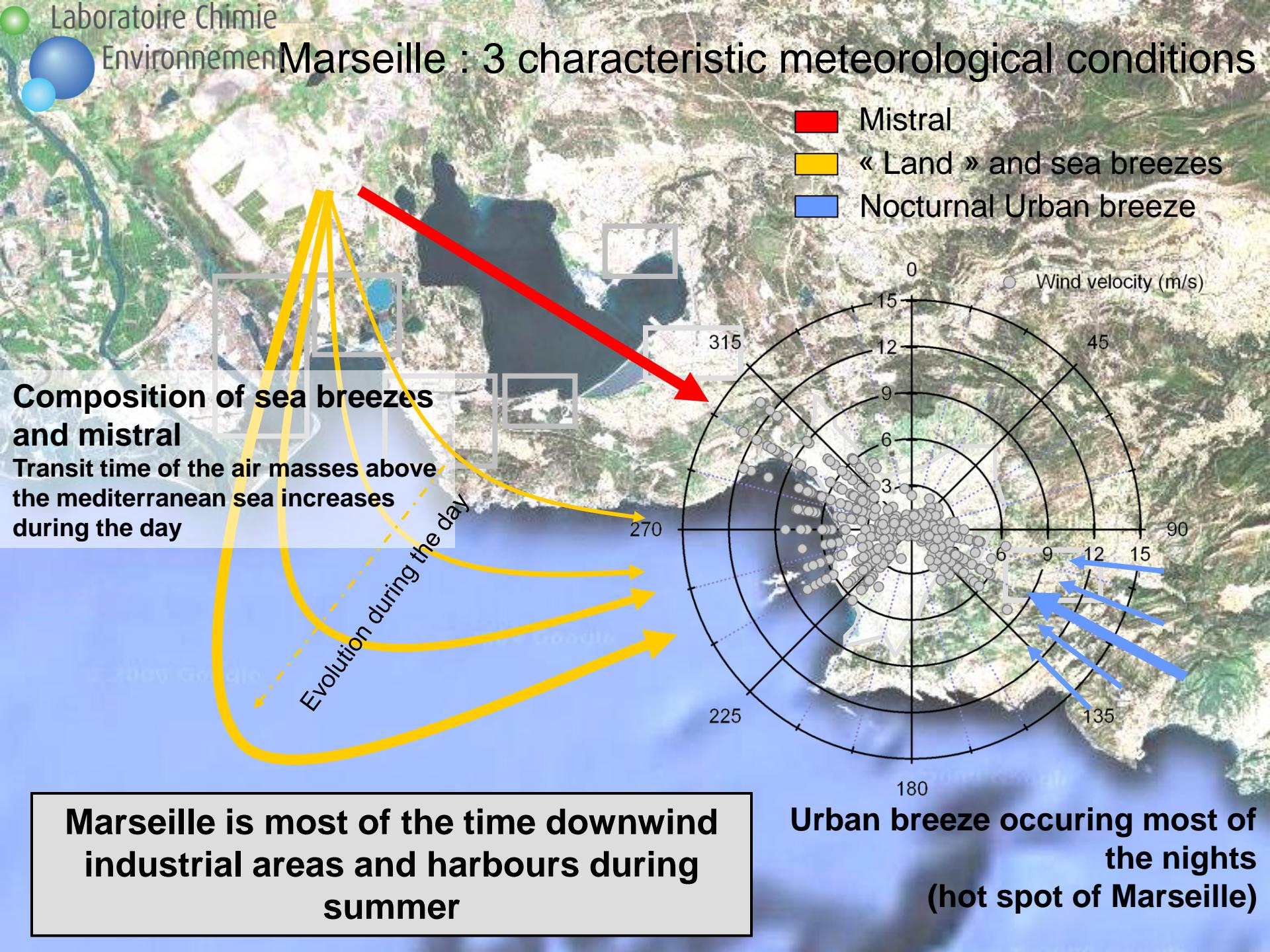
If cooking with oils dominates primary emissions, deep frying and vegetable cooking (terpene emissions) have a high SOA potential

How much??

Impact industriel faible ?

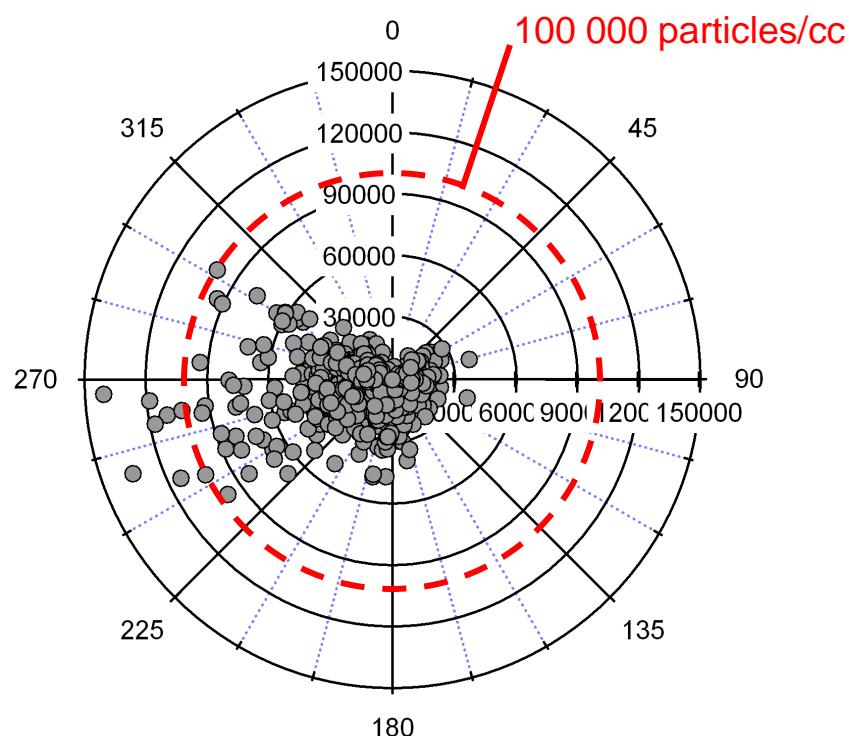


Marseille : 3 characteristic meteorological conditions

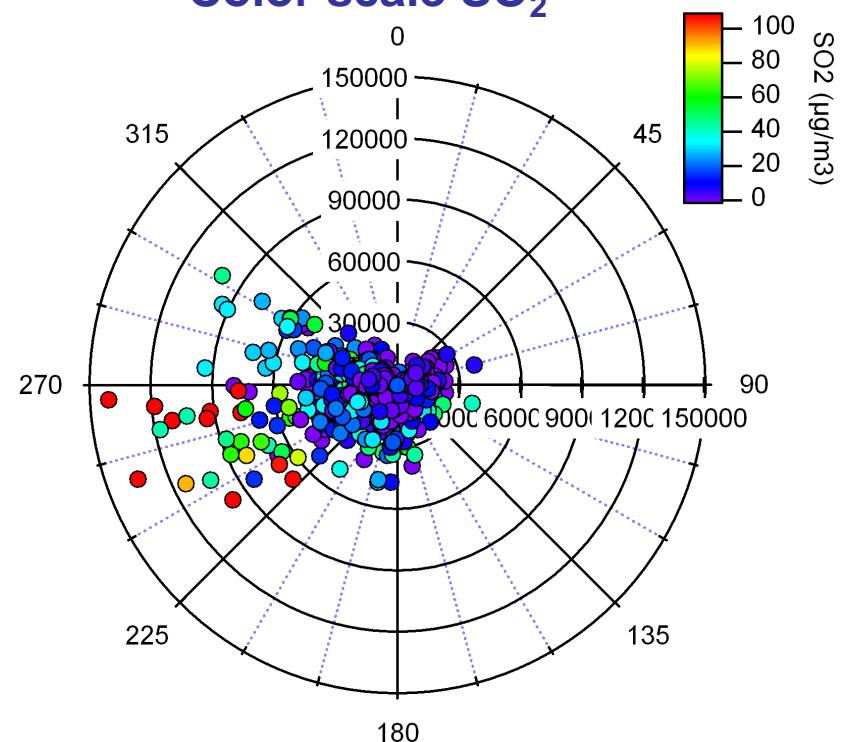


Impact industriel faible ?

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

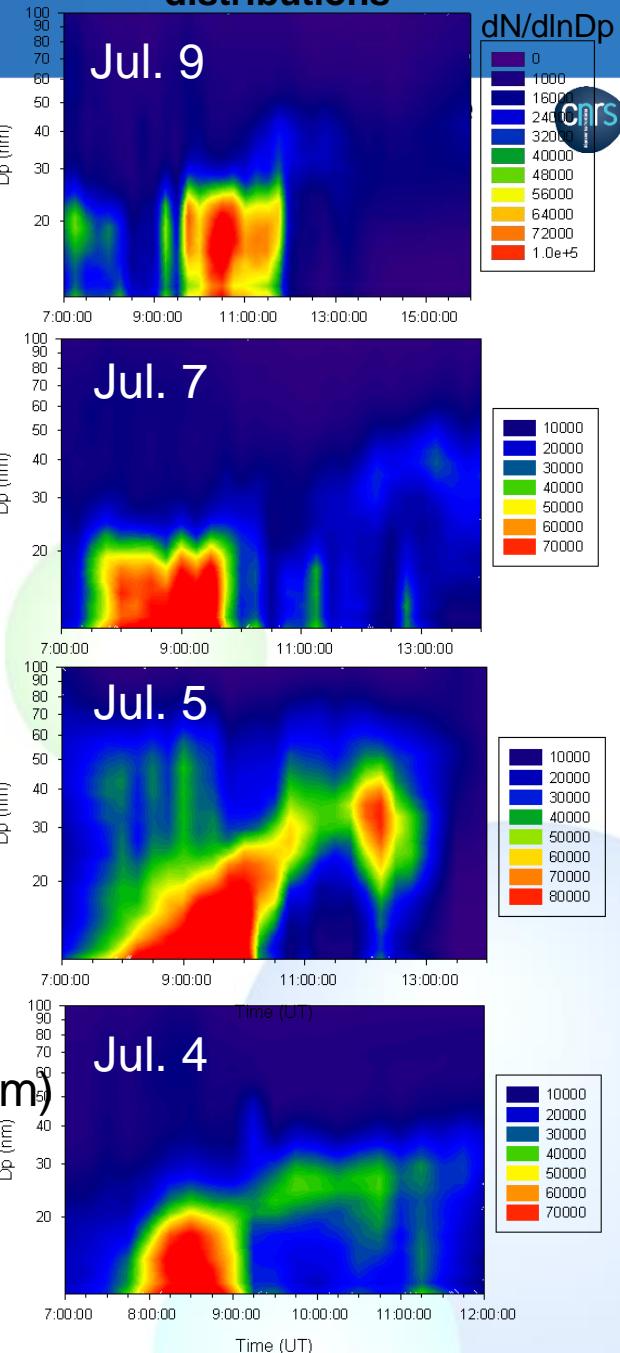


Total number of particles (cm^{-3})
(10-1000 nm)
Color scale SO_2

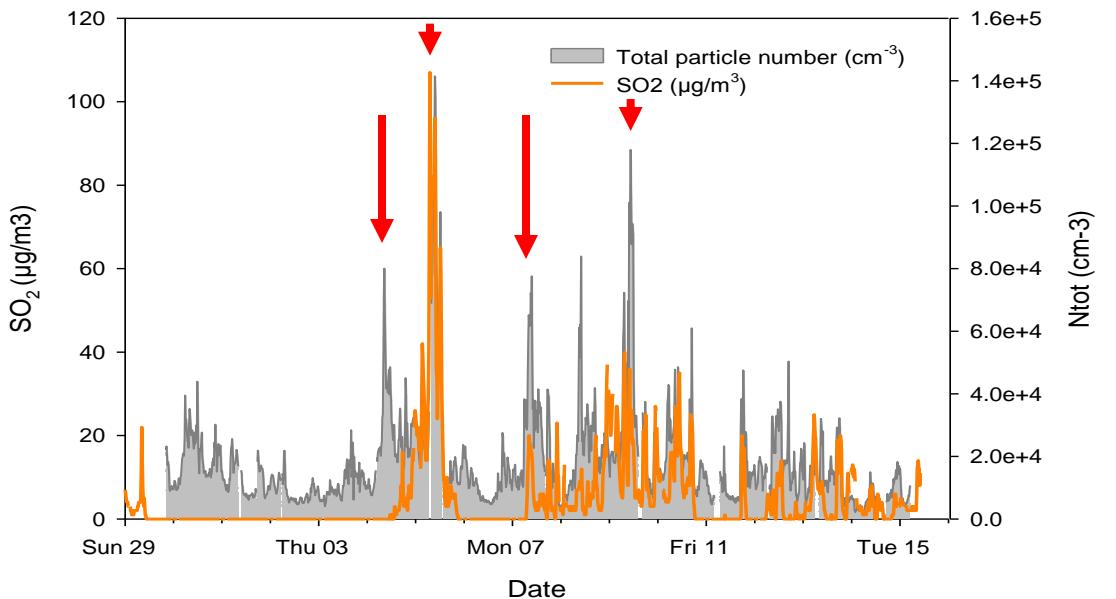


- In sea breeze and moderate mistral conditions very intense particles events are observed (**total number concentrations higher than 100 000 #/cm³**)
- These particle events are highly correlated with SO₂ and thus most probably linked to petrochemical/steel industrial activities (or maybe shipping emissions)

Evolution of the particle size distributions



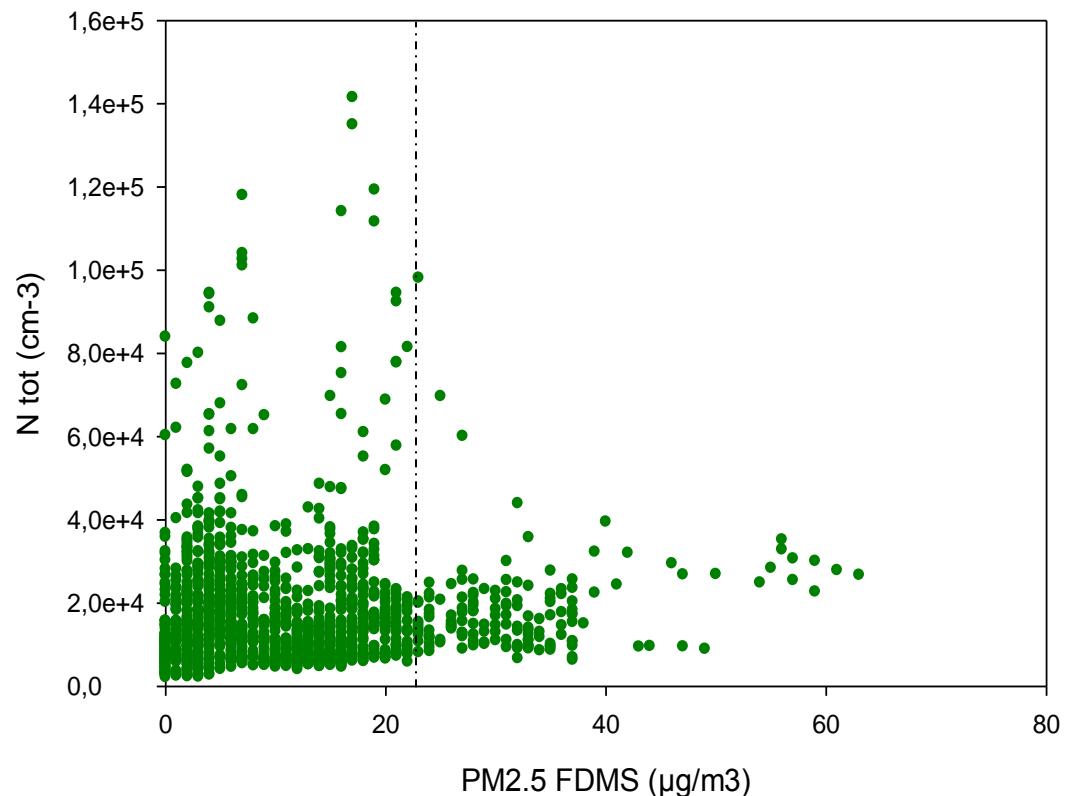
Some examples of fine particle events



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

The different shapes reflect the history of the air masses

Impact industriel faible ?



Si on fixe un limite à **PM_{2.5}=25µg/m³**

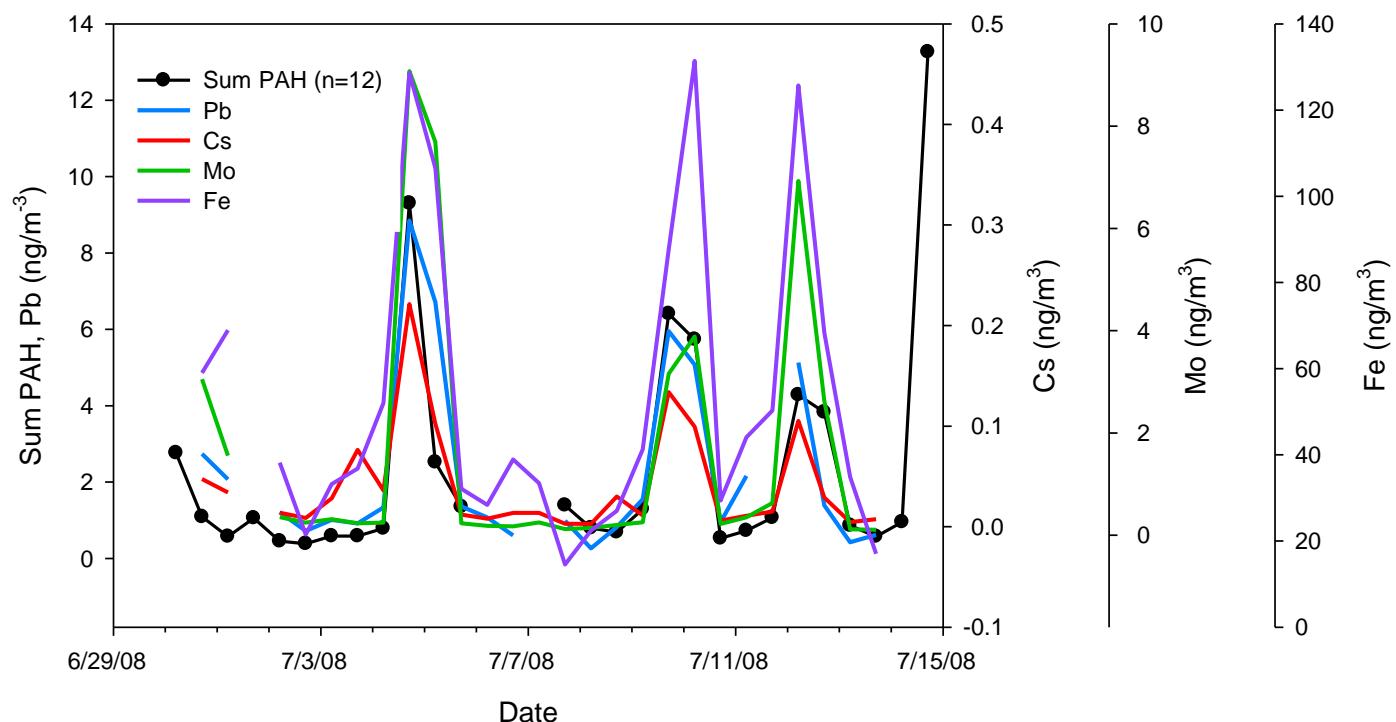
Les pics en masse correspondent à un nombre moyen en particules < 40 000 cm⁻³

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

Impact industriel faible ?



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

→ Steel plant of Sollac and/or heavy fuel combustion

Source apportionment Intercomparaison

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Marseille, Hiver 2011, 6 semaines

- **Principle of the exercise :**
 - Measure of different kind of pollutants, according to different protocols
 - Constitution of different data bases
 - Use of different source apportionment protocols
 - Determine the asset and defaults of every method
 - Improve the apportionment quality for the second part of the APICE project
- **Two apportionment methods selected :**
 - Chemical Mass Balance (Aix-Marseille univ.)
 - Positive Matrix Factorisation (IDAEA-CSIC, ARPA Veneto, UOWM, Genoa univ.)



Projet cofinancé par le Fonds Européen
de Développement Régional

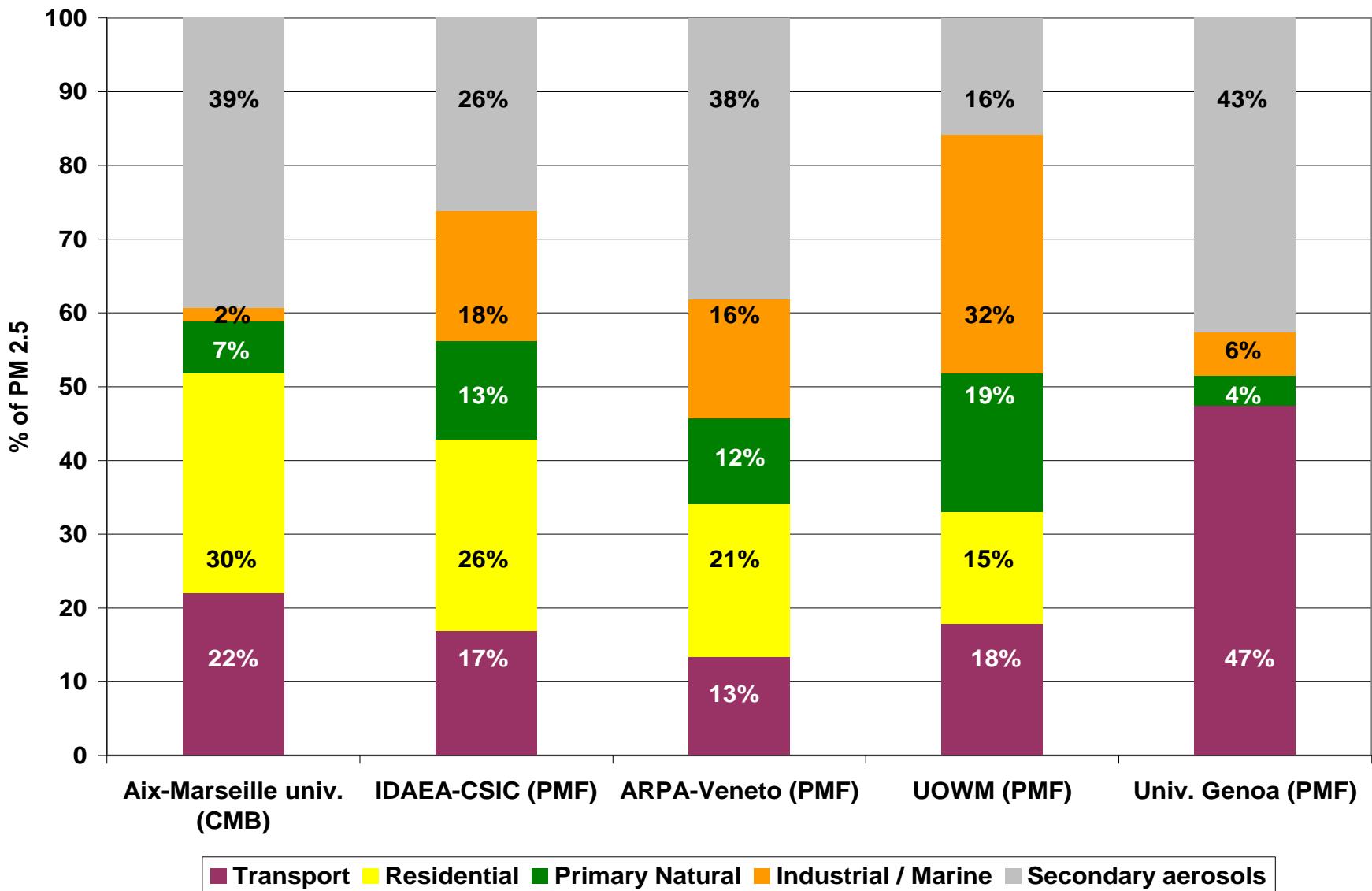
Project cofinanced by the European
Regional Development Fund

| Partners involved | IDAEA-CSIC (Barcelona) | Univ Genoa and IDAEA-CSIC on behalf of ARPA veneto (Venezia) | UOWM (Thassaloniki) | Univ Genoa (Genova) |
|----------------------------|---|--|--|--|
| Species included | 22 Variables | 21 variables | 37 variables | 15 Variables |
| | Ca, K, Na, Mg, Fe, Mn, V, Ni, Cu, Zn, Sn, Sb, Pb, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , EC and Five Oc fractions (OC1, OC2, OC3, OC4 and Pyrolytic C) | Ca, Na, Mg, Fe, V, Ni, Cu, Zn, Sn, Sb, Pb, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , EC, OC, E-Alk, O-Alk, PAH, HOPA, DHAA | 8PAH, SO ₄ ²⁻ , NH ₄ ⁺ , NO ₃ ⁻ , Al, Ca, K, Na, Mg, Fe, Mn, Ti, P, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Sb, Cd, Sn, Pb, Li, Sb, La, OC and EC | Al, Si, P, K, Ca, V, Fe, Ni, Cu, Zn, SO ₄ ²⁻ , NH ₄ ⁺ , NO ₃ ⁻ , OC and EC |
| | => Metals, ions, EC and OC fractions | => Organic compounds, métals, ions, EC and OC | => Organic compounds, métals, ions, EC and OC | => Metals, ions, EC and OC |
| Number of factor / sources | 7 | 7 | 6 | 5 |

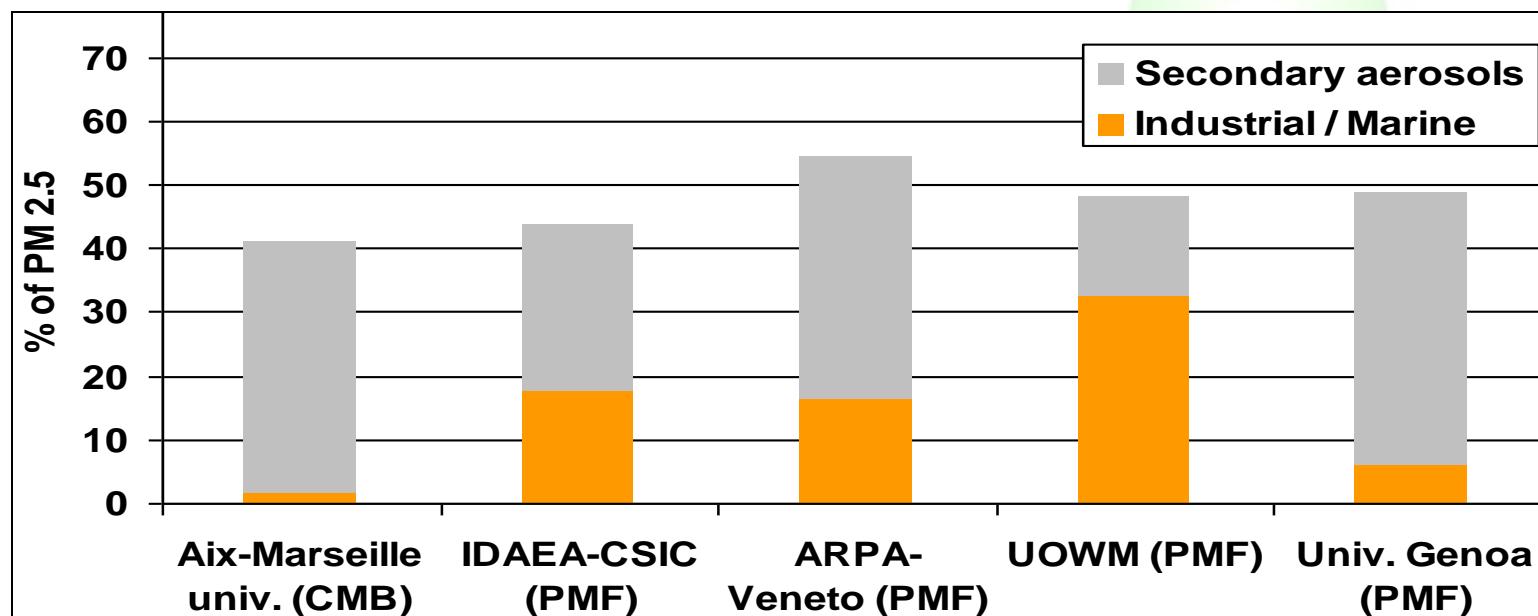
Impact industriel faible ?

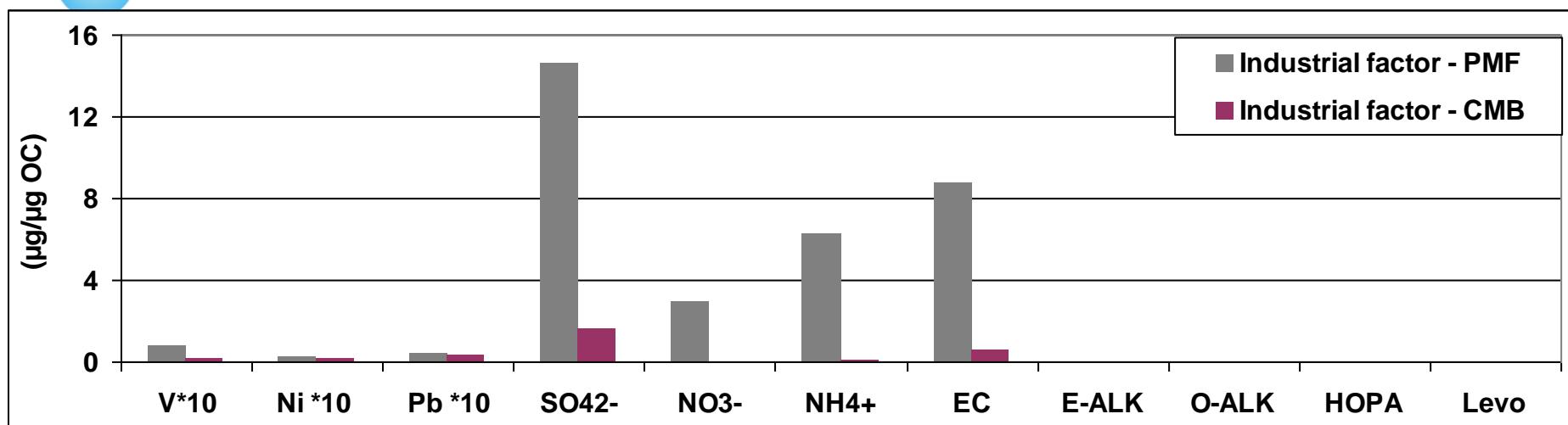
| Source group | Source and Source types derived from each source apportionment analysis | | | | |
|-------------------------|--|--|--|--------------------------------------|------------------------------|
| | Aix Marseille Univ | IDAEA-CSIC | Univ Genoa and IDAEA-CSIC on behalf of ARPA veneto | UOWM | Univ Genoa |
| Road | Vehicular | Vehicular exhaust ; Road dust | Vehicular exhaust + sea spray ; Road dust | Road dust | Road |
| Residential | Biomass burning ; Vegetative detritus (incomplete combustion of wax alkanes) ; Natural gas combustion | Biomass burning | Residential | Residential combustion | - |
| Primary natural | Sea salt ; Crustal dust | Aged sea spray ; Mineral/industrial | Dust | Natural sea salt | Dust |
| Industrial and Shipping | Coke production ; HFO combustion/Shipping ; Steel manufacturing | Fuel Oil Combustion | Industrial / marine | Marine-Shipping emissions / Industry | Industrial / Marine |
| Secondary | Secondary ammonium, nitrate and sulfate ; Unexplained OM | Secondary aerosols | Secondary 1 ; Secondary 2 | Secondary aerosols | Secondary 1 ; Secondary 2 |

Impact industriel faible ?



- Important discrepancies observed about industrial factor
- Comparable results for these two factor sum
 - Difficulty to distinguish those two sources



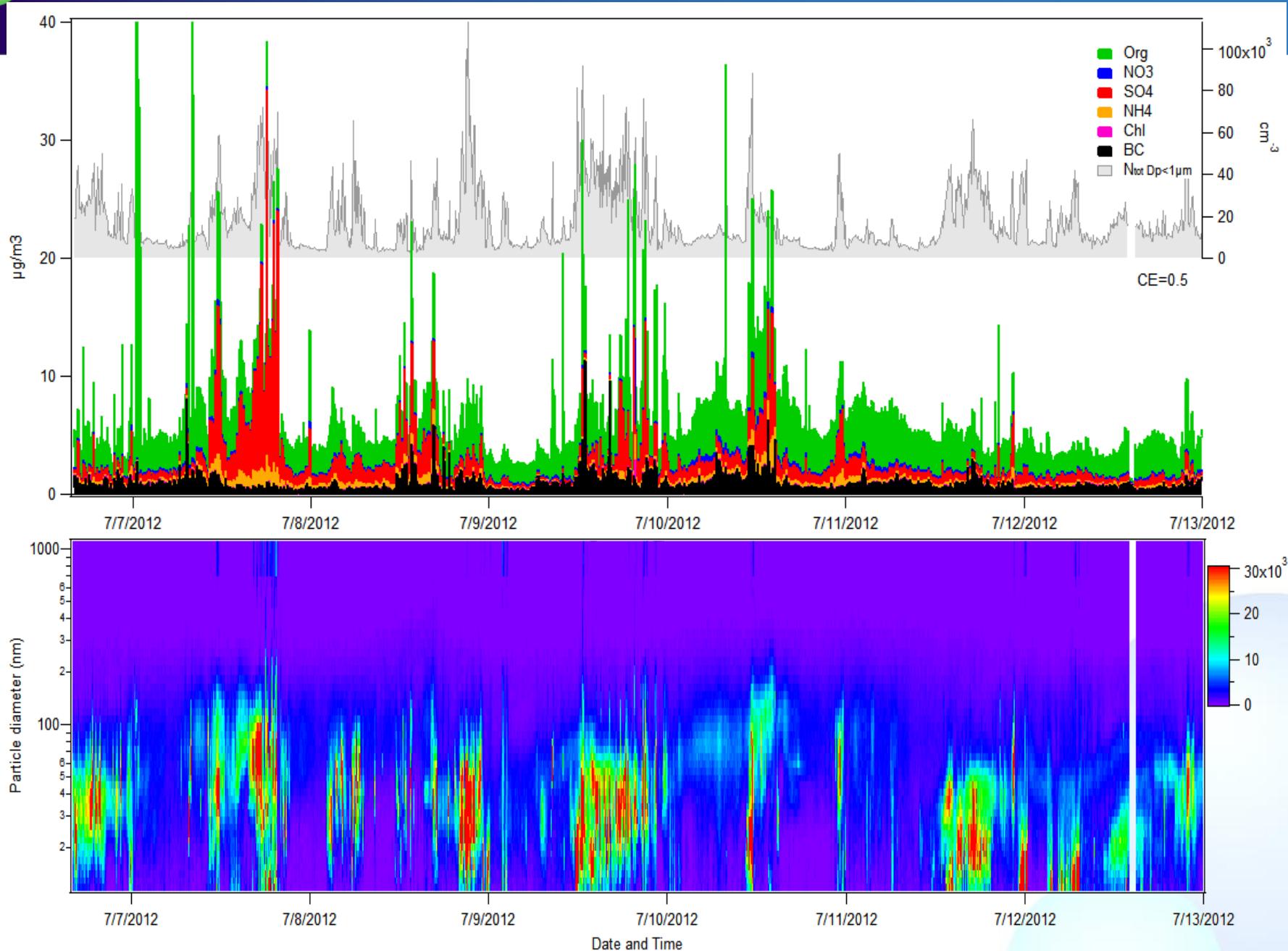


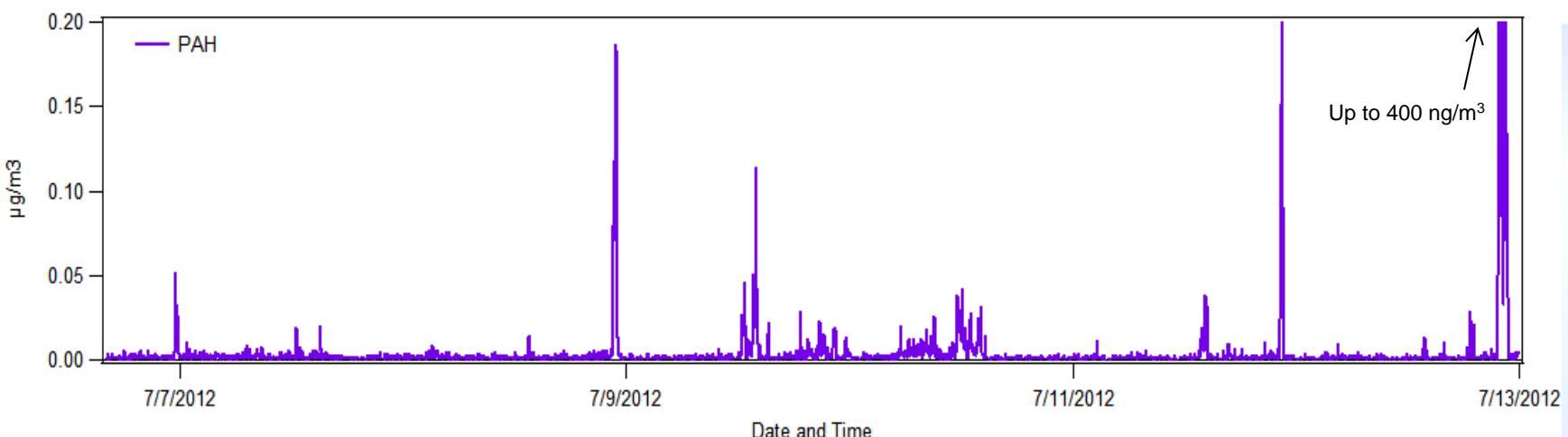
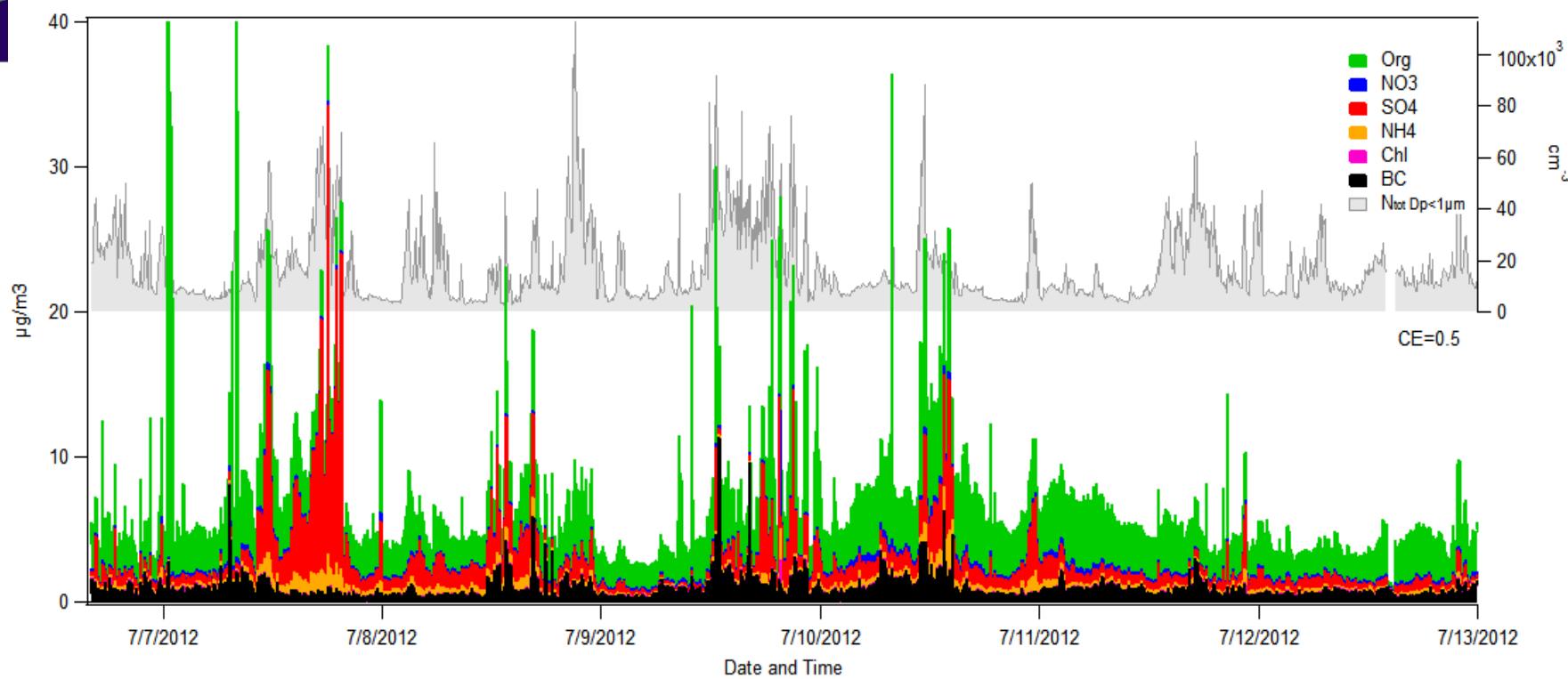
- **What source for these ions ?**
 - Real primary industrial emission ?
 - Accuracy of the CMB source profiles
 - Secondary Industrial emission ?
 - Shall we consider this sulfate as industrial or secondary?
 - Advection of aged air masses ?
 - Internal correlation within the data-base

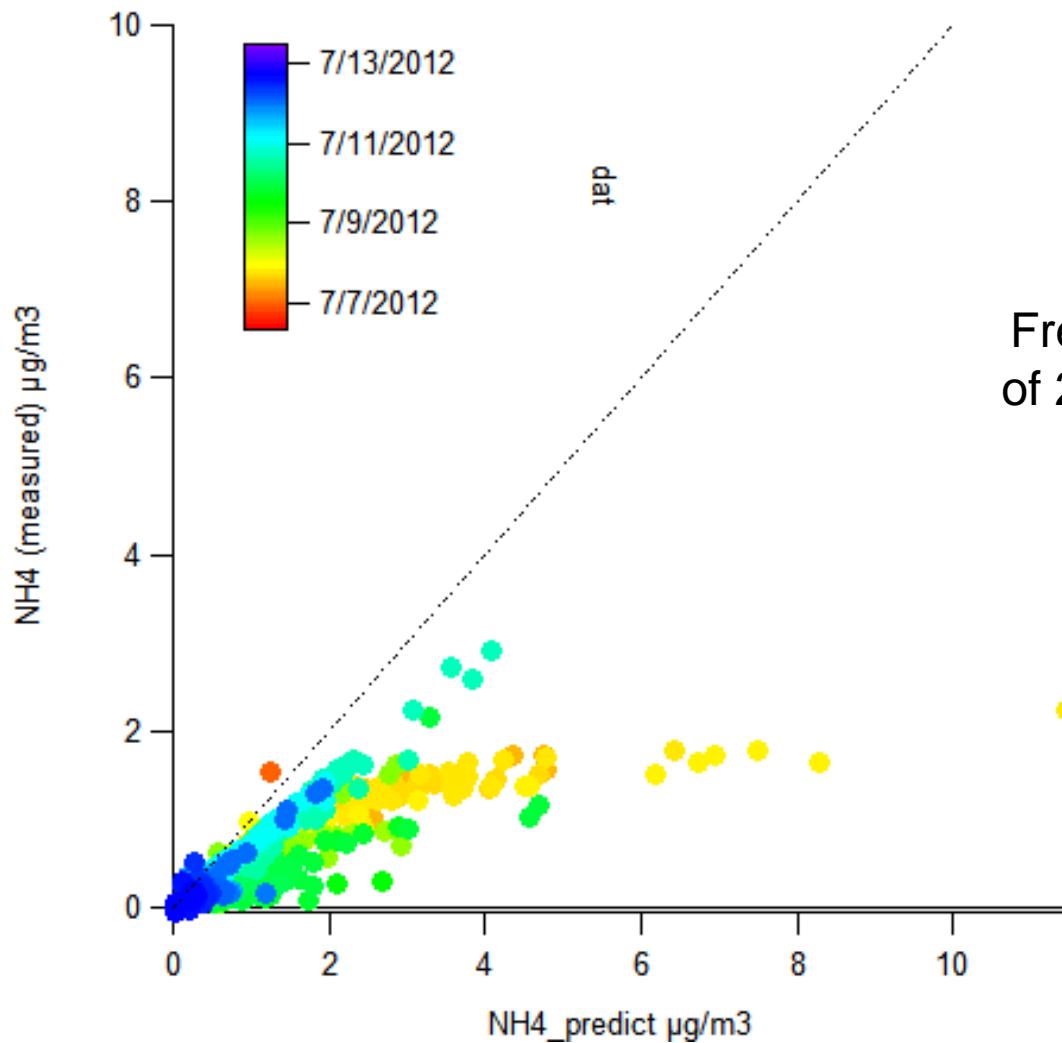
Marseille

A huge industrial area (Fos-Berre)









Fresh industrial emissions = plumes of 20-100nm of sulfuric acid particles

Considering that sulfates and nitrates are fully neutralized by ammonium

- La caractérisation chimique (et physique) de l'aérosol est un élément essentiel à notre compréhension des sources et processus gouvernant les concentrations atmosphériques
- Les mesures rapides (online) sont indispensables pour comprendre la dynamique des populations de particules
- Les mesures off line offrent une information plus complète (utile dans un cadre recherche) mais sont limitées par leur faible résolution temporelle
- Les méthodes de « source apportionment » sont maintenant globalement bien maîtrisées et apportent des informations de premier ordre dans un cadre réglementaire (European Guideline maintenant disponible)
Attention toutefois :
 - Caractère trop souple du PMF (mélange de sources/influence de la dynamique atmos. particulièrement quand la résolution temporelle est faible)
 - Caractère trop contraint du CMB (choix des profils de source est crucial)
- Modèle ME2 est probablement l'option une option d'avenir (Thèse. Dalia Salameh et Alexandre Sylvestre)
- Nécessité de travailler sur les sources industrielles et combustions de biomasse (déchets verts etc..)
- Nous sommes encore aveugle sur les origines de la fraction secondaire

Ce que nous avons appris sur l'aérosol marseillais :

- L'aérosol est majoritairement **organique**
- **Forte influence des combustions de biomasse en hiver et l'automne** (advecté notamment via la vallée de l'Huveaune l'hiver à Marseille) Source probablement responsable d'un grand nombre de dépassements des seuils
- Les « **sources industrielles** » sont caractérisées par des panaches de **particules ultrafines** (<70 nm) auxquelles sont associés des qtés significatives **d'acide sulfurique**, de **métaux lourds** et de **HAP**.
- **L'été la fraction secondaire est prédominante** avec probablement une origine majoritairement biogénique.

Marseille (et ses alentours) constitue un environnement unique (diversité des sources/photochimie intense/large basin de population)

Marseille

From 25th January-2nd March 2011

Sollac (Steel Industry) Refinery of Fos



Refinery and petro chemical industry
of Lavera



West Harbour

Refinery and petro chemical industry



Refinery of «la M



Industrial area (various activities)
Airport



270

East Harbour

225

180

135

Industrial area (various activities)
Airport

45

Industrial area
(various activities)

90

Industrial area (various activities)
Sampling site

0.25

Industrial area (various activities)
Sampling site

0.25

Industrial area (various activities)
Sampling site

0.2

Industrial area (various activities)
Sampling site

0.15

Industrial area (various activities)
Sampling site

0.1

Industrial area (various activities)
Sampling site

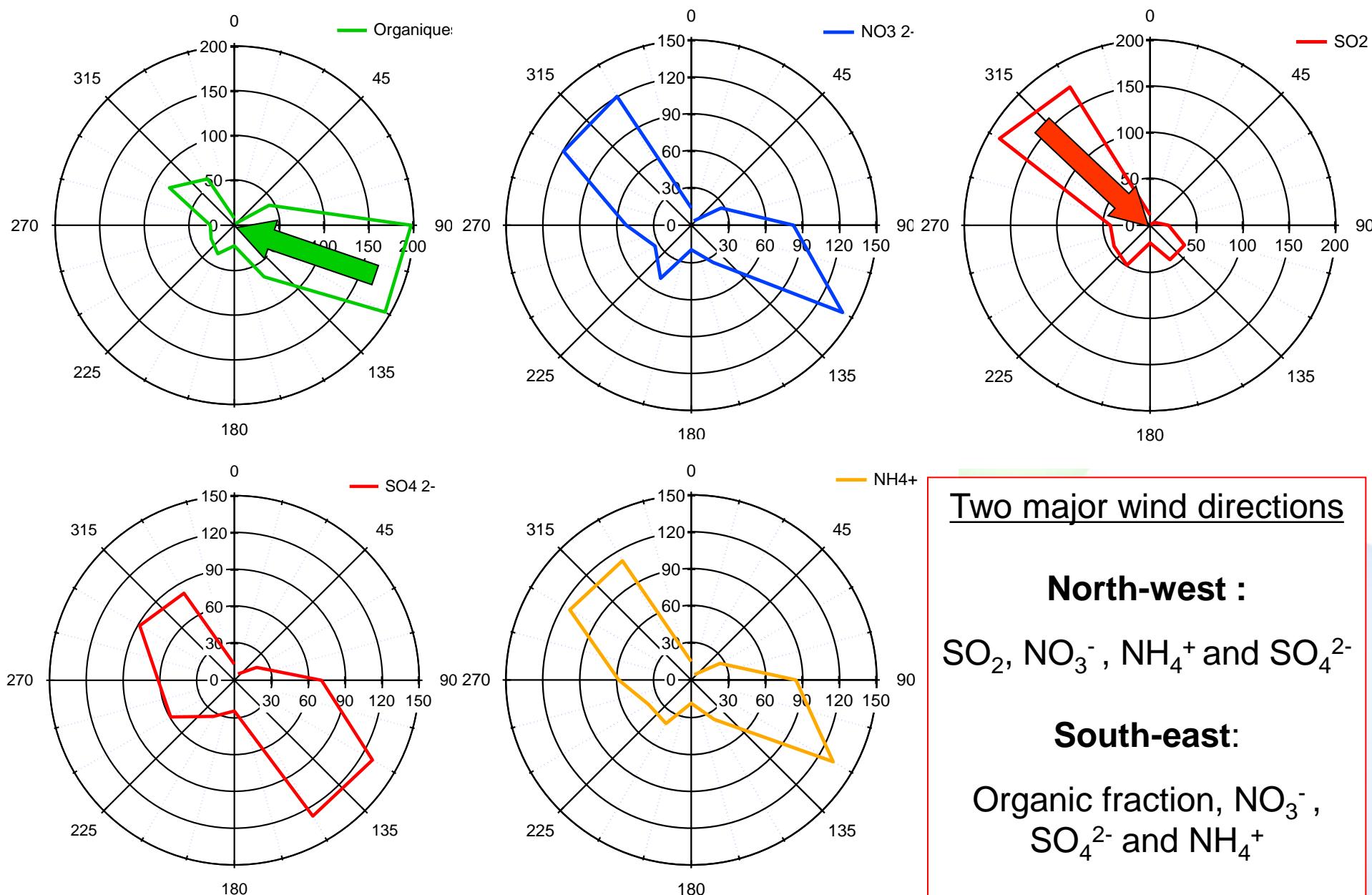
0.05

Industrial area (various activities)
Sampling site

0



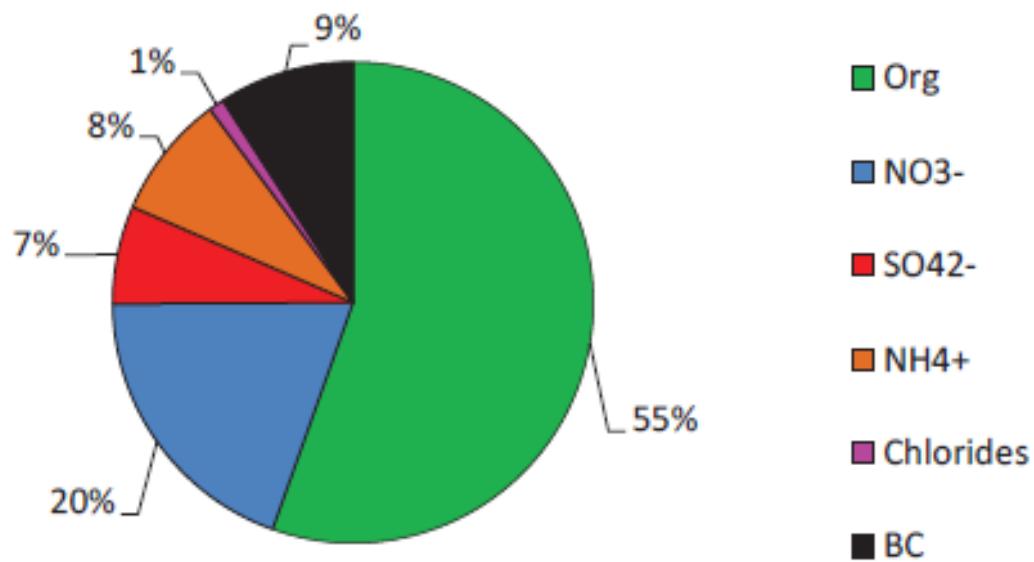
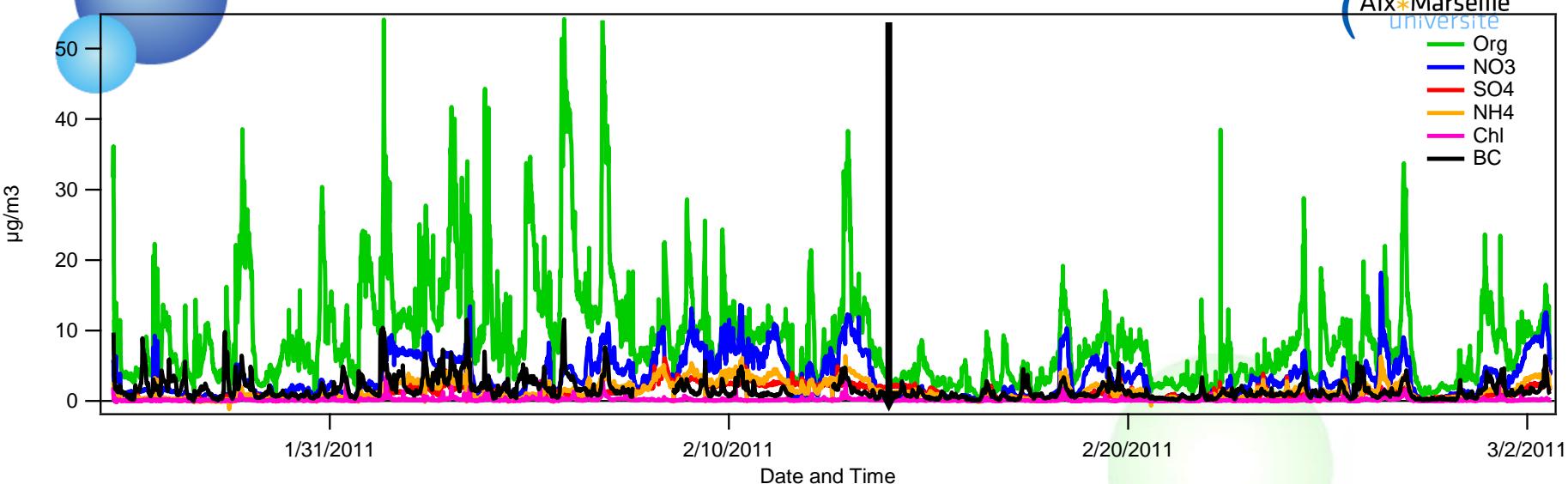
Major emission areas : Conditional Probability Function



AMS data : PM₁ composition

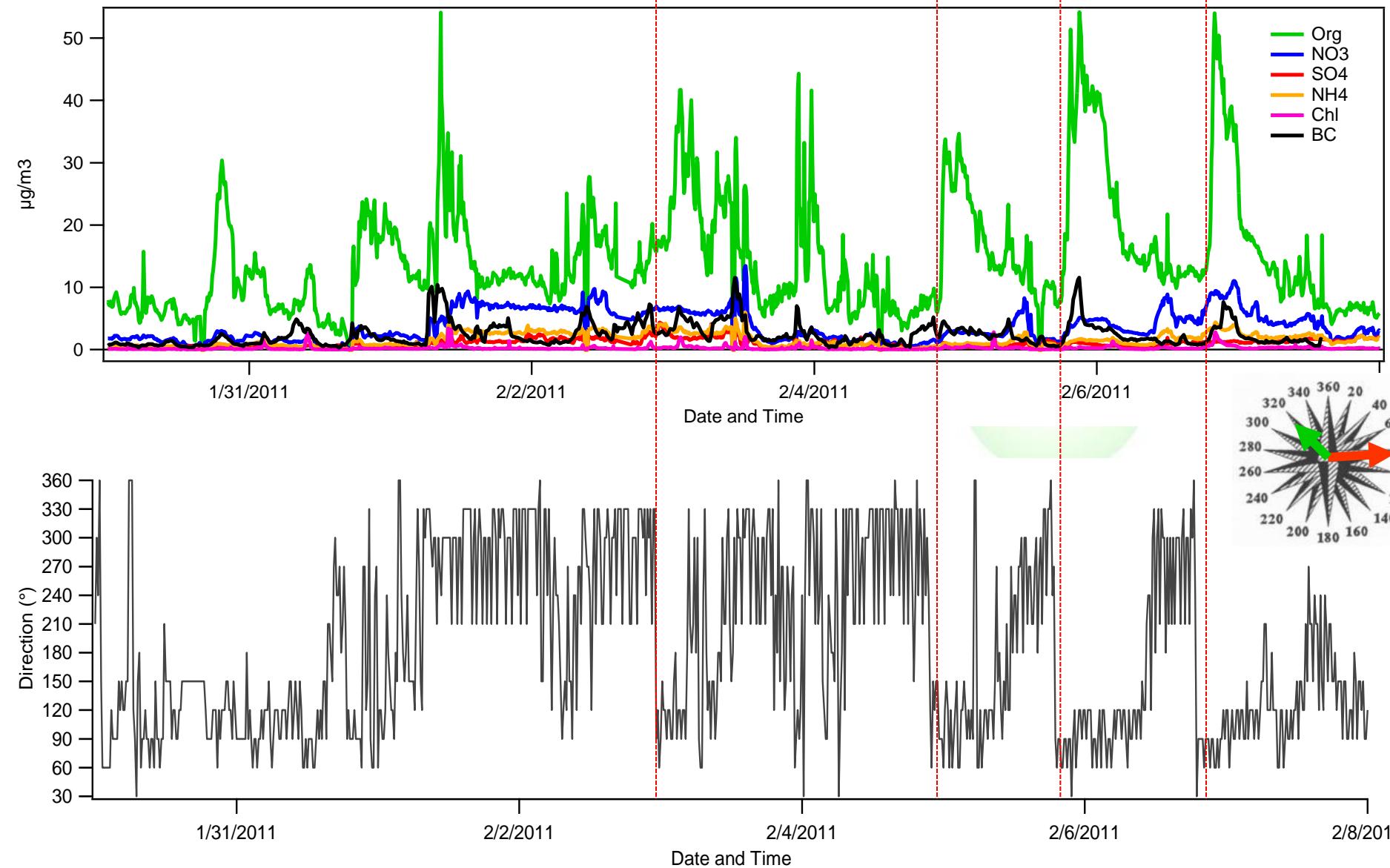
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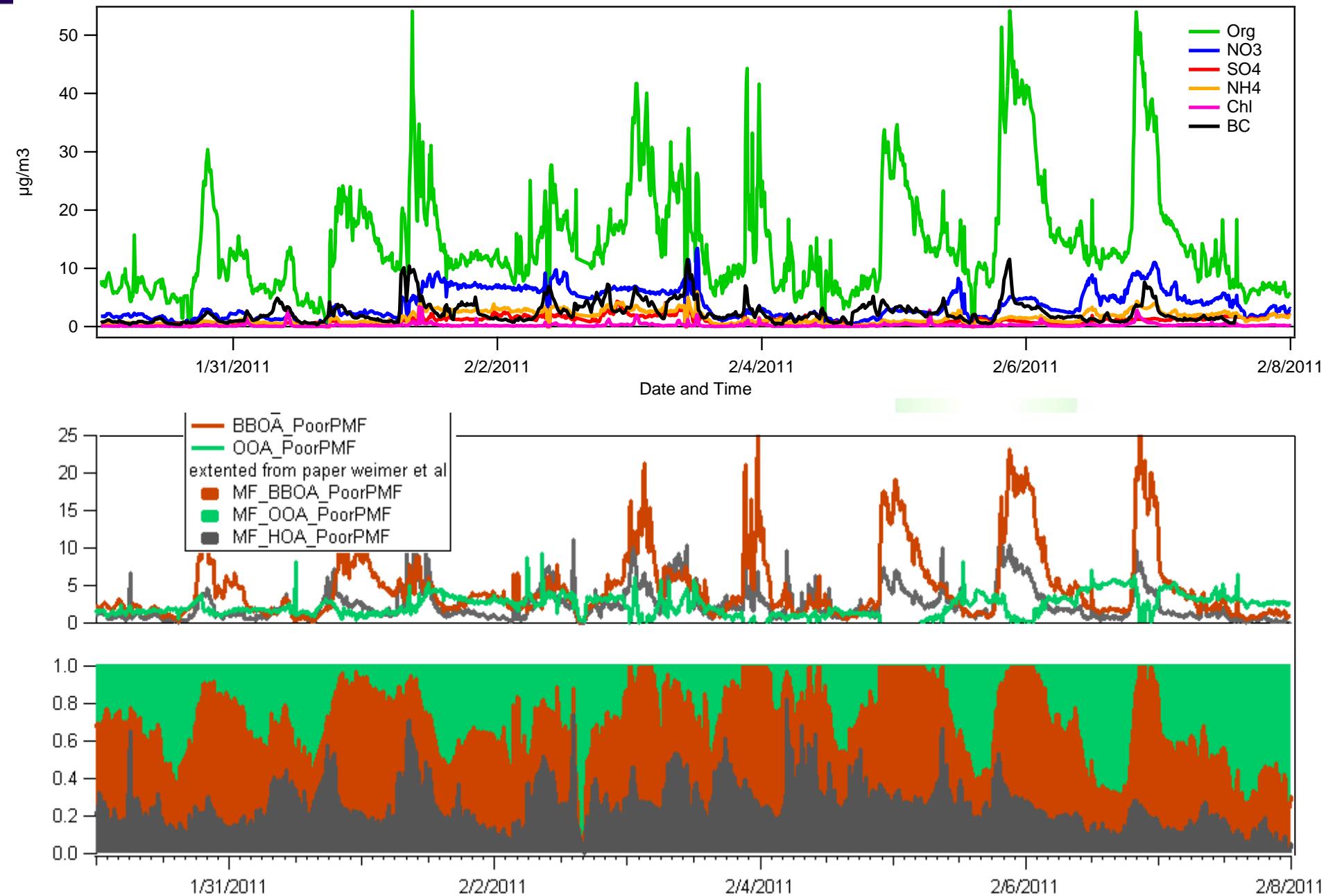


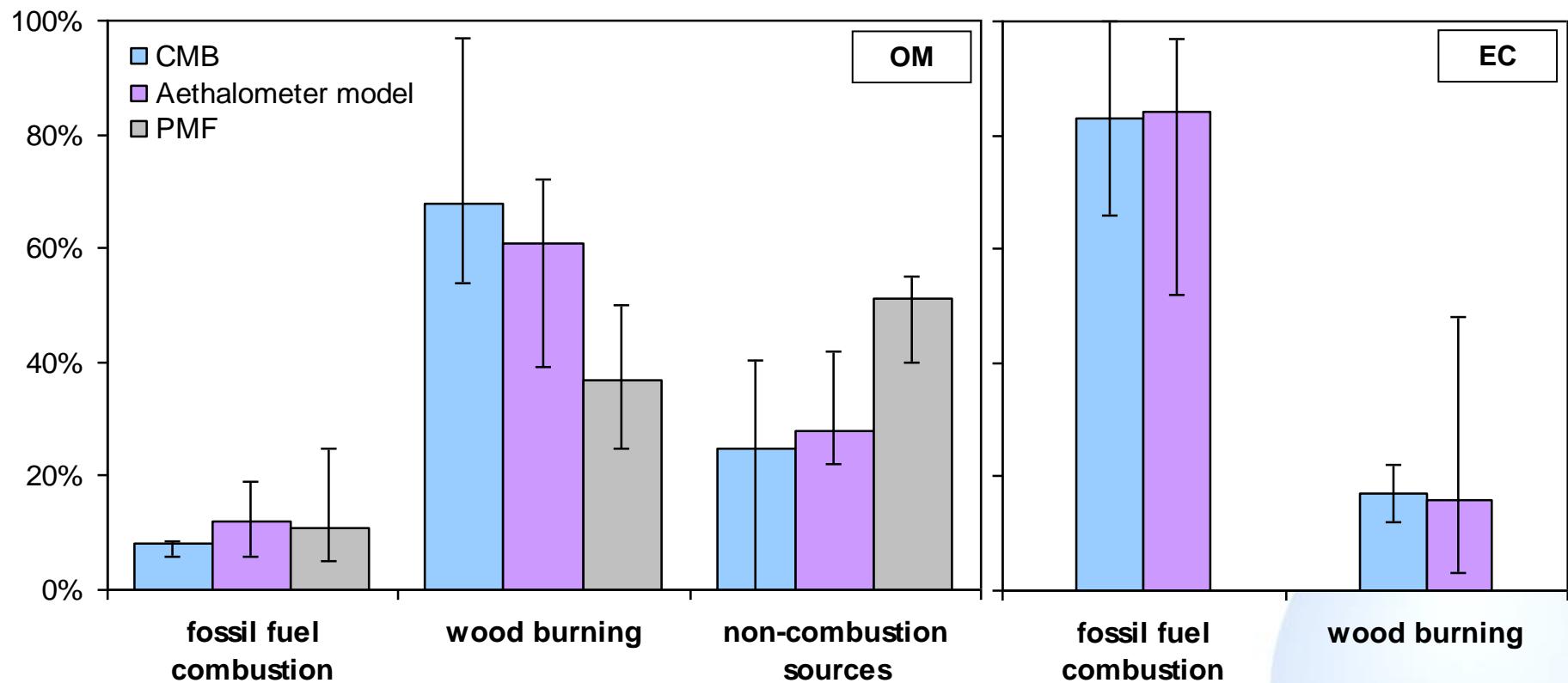
Correspondance with wind-direction changes





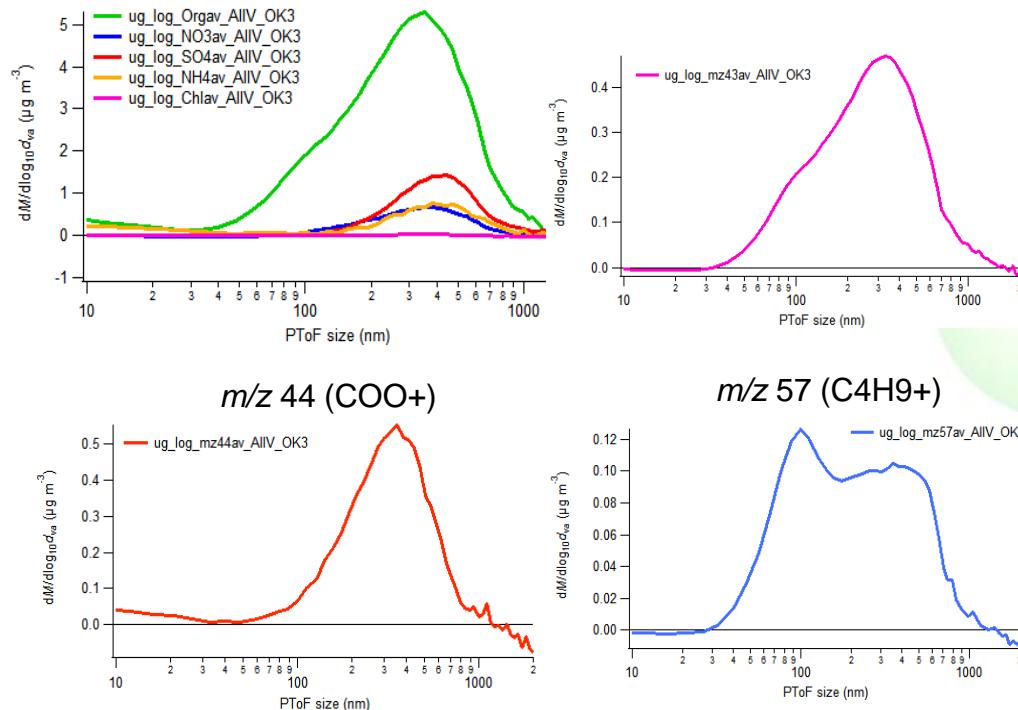
Source of organic fraction peak : PMF analysis





Aerosol Mass Spectrometer : AMS

- Distributions granulométriques pour les fractions majeures ou m/z d'intérêts



Ex. Bord de périphérique,
Grenoble

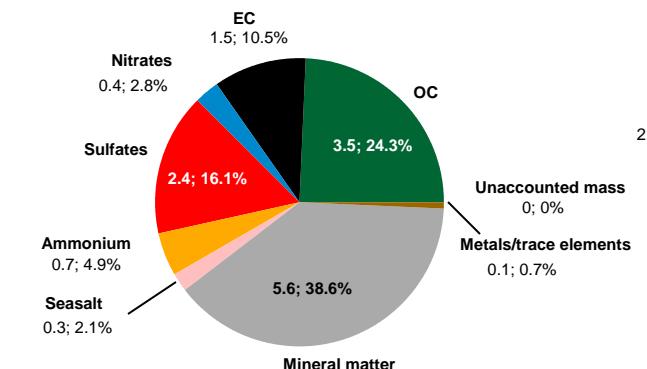
- L'analyse HR donne également accès aux ratio **OM/OC**, **O/C**, **H/C**, **N/C** etc..

Le traitement des données brutes nécessite un certain degré d'expertise

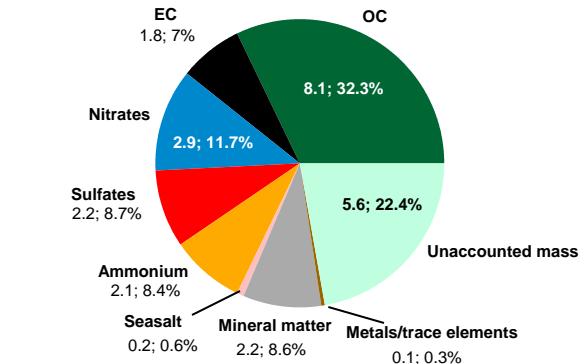
Chemical composition of PM_{2.5}

Seasonal Variations

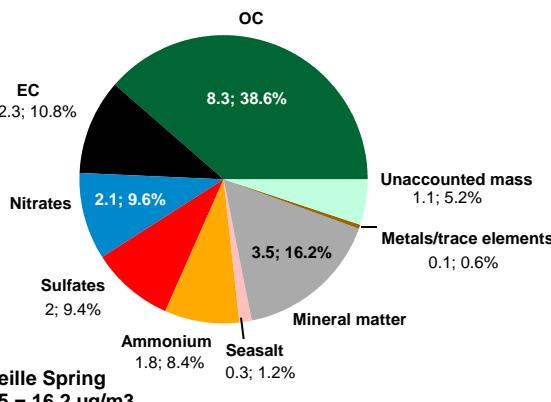
Marseille Summer
PM2.5 = 14.5 µg/m³



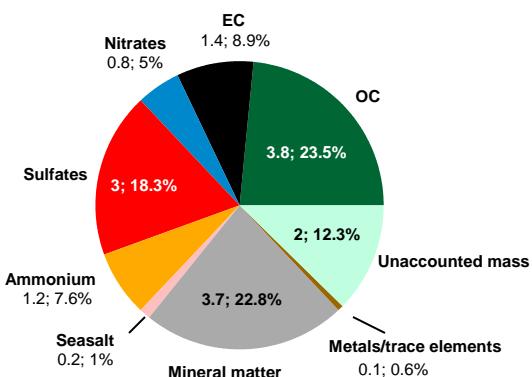
Marseille Winter
PM2.5 = 25.2 µg/m³



Marseille Fall
PM2.5 = 21.5 µg/m³



Marseille Spring
PM2.5 = 16.2 µg/m³



- OC dominant fraction: winter (32%) and in fall (39%)
- OC lower values in summer (24%) and in spring (23%)

- Mineral matter: important fraction in summer (39%)

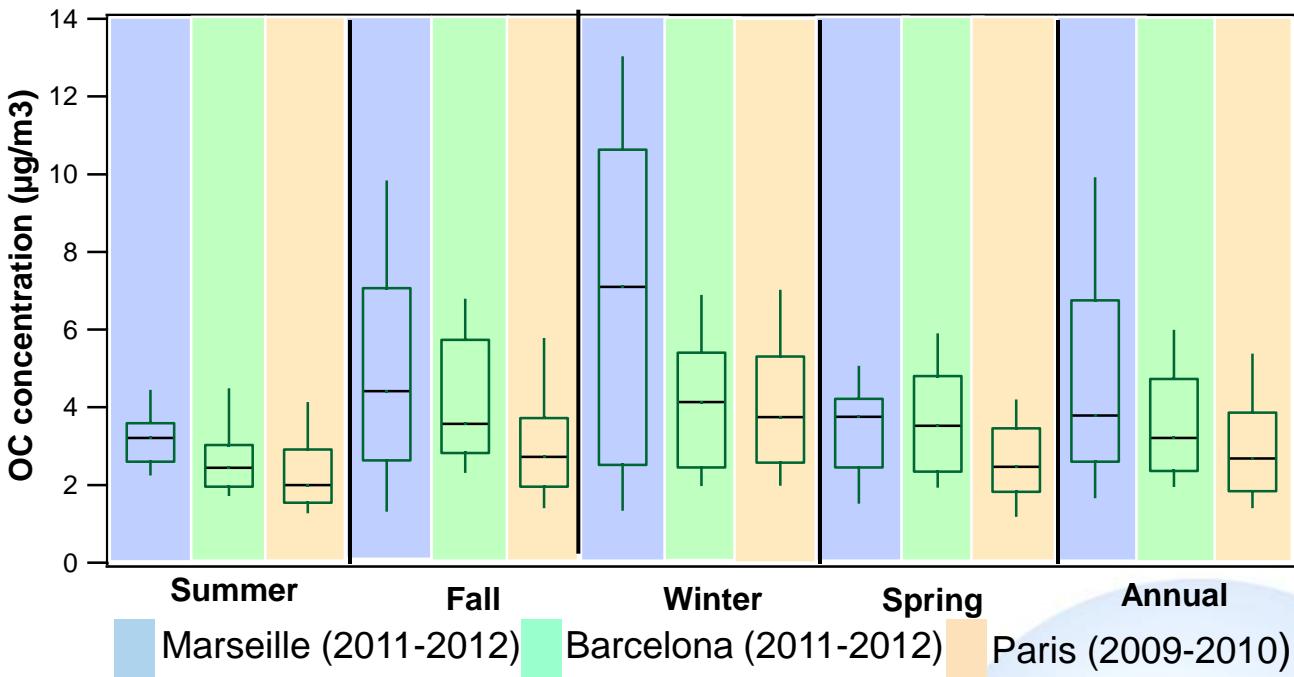
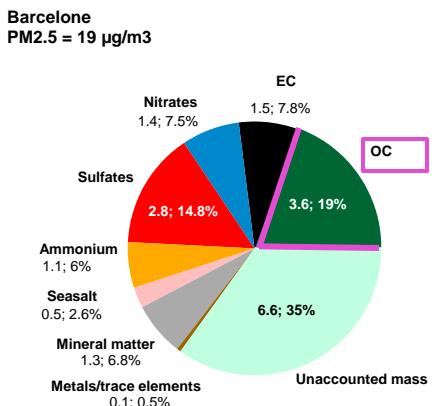
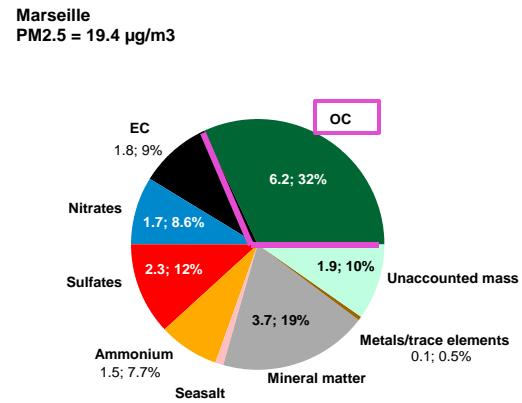
Problematic is limited to Marseille or can we extend it to another Mediterranean city as Barcelona or to an European reference megapole as Paris?

OC seasonal and annual concentrations Marseille/Barcelona/Paris

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Data of Barcelona is a courtesy of Querol., X. II Data of Paris is a courtesy of Sciare., J.



- Annual mean concentrations are similar in the three cities
- Highest concentrations observed in Marseille during winter ($OC_M \sim 2 OC_B$) and fall with high variability
- Lowest concentrations of OC observed in Paris
- Unexpected situation in Marseille (winter-fall) for OC

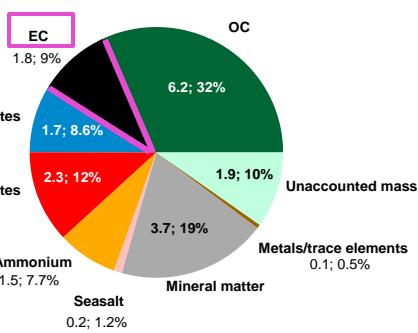
EC saisonnal and annual concentrations Marseille/Barcelona/Paris

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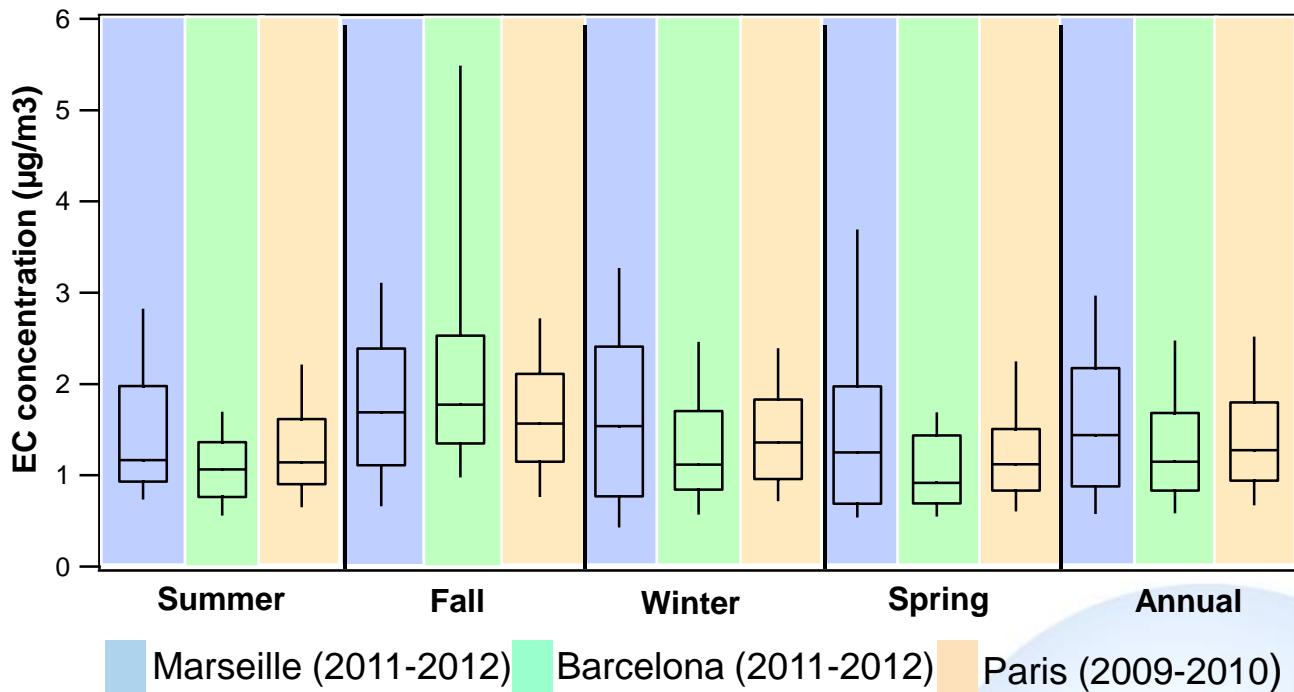
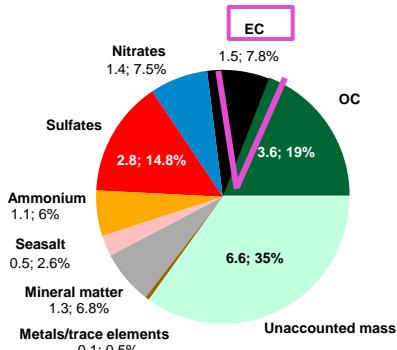
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Data of Barcelona is a courtesy of Querol., X. II Data of Paris is a courtesy of Sciare., J.

Marseille
PM2.5 = 19.4 µg/m³



Barcelone
PM2.5 = 19 µg/m³



- EC concentration in Marseille slightly higher compared to the other cities (same composition of the vehicular fleet)
- Marseille: EC homogeneous concentration is observed over the year (EC is mostly related to traffic)

Annual concentrations of some trace elements: Marseille vs. Barcelona

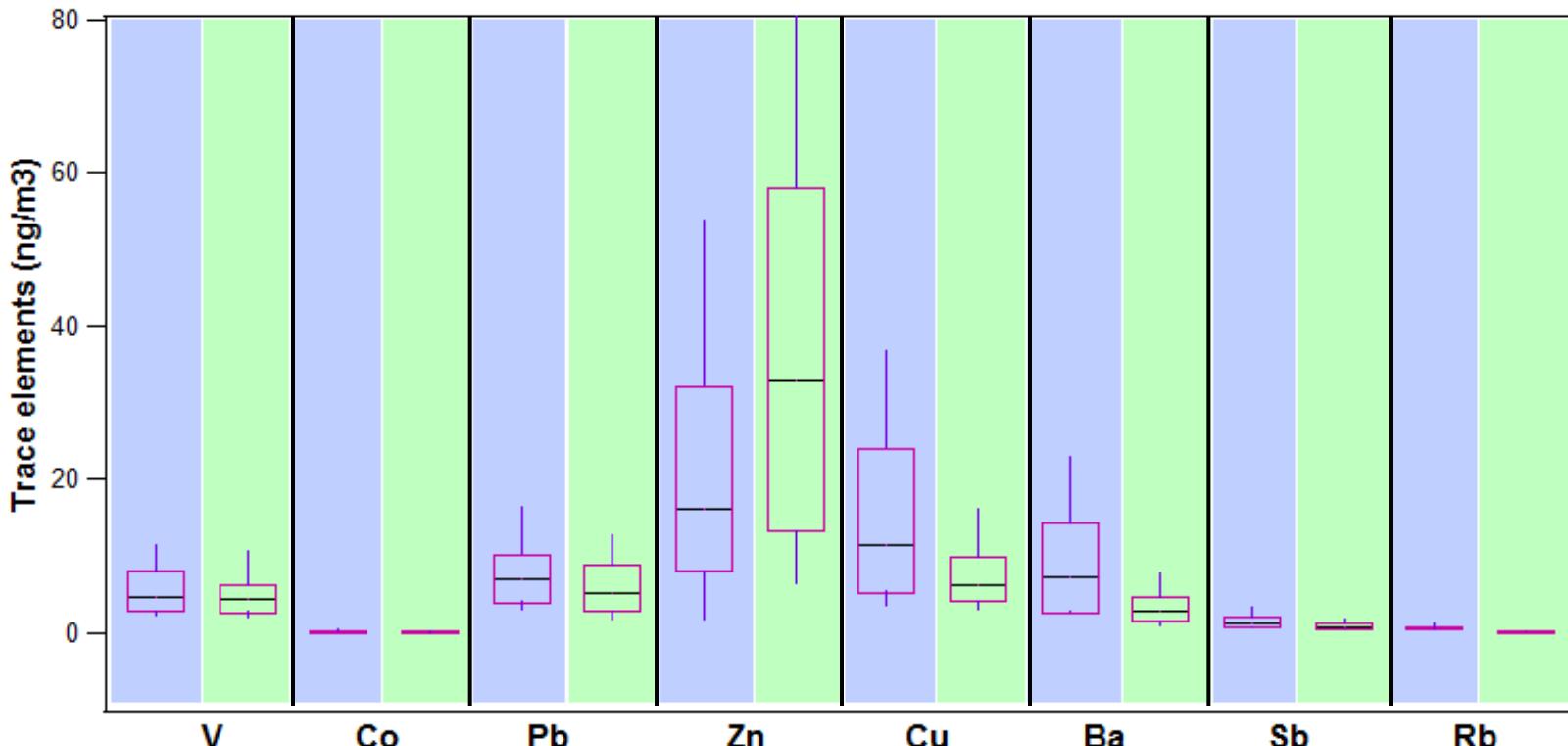
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Marseille (2011-2012)

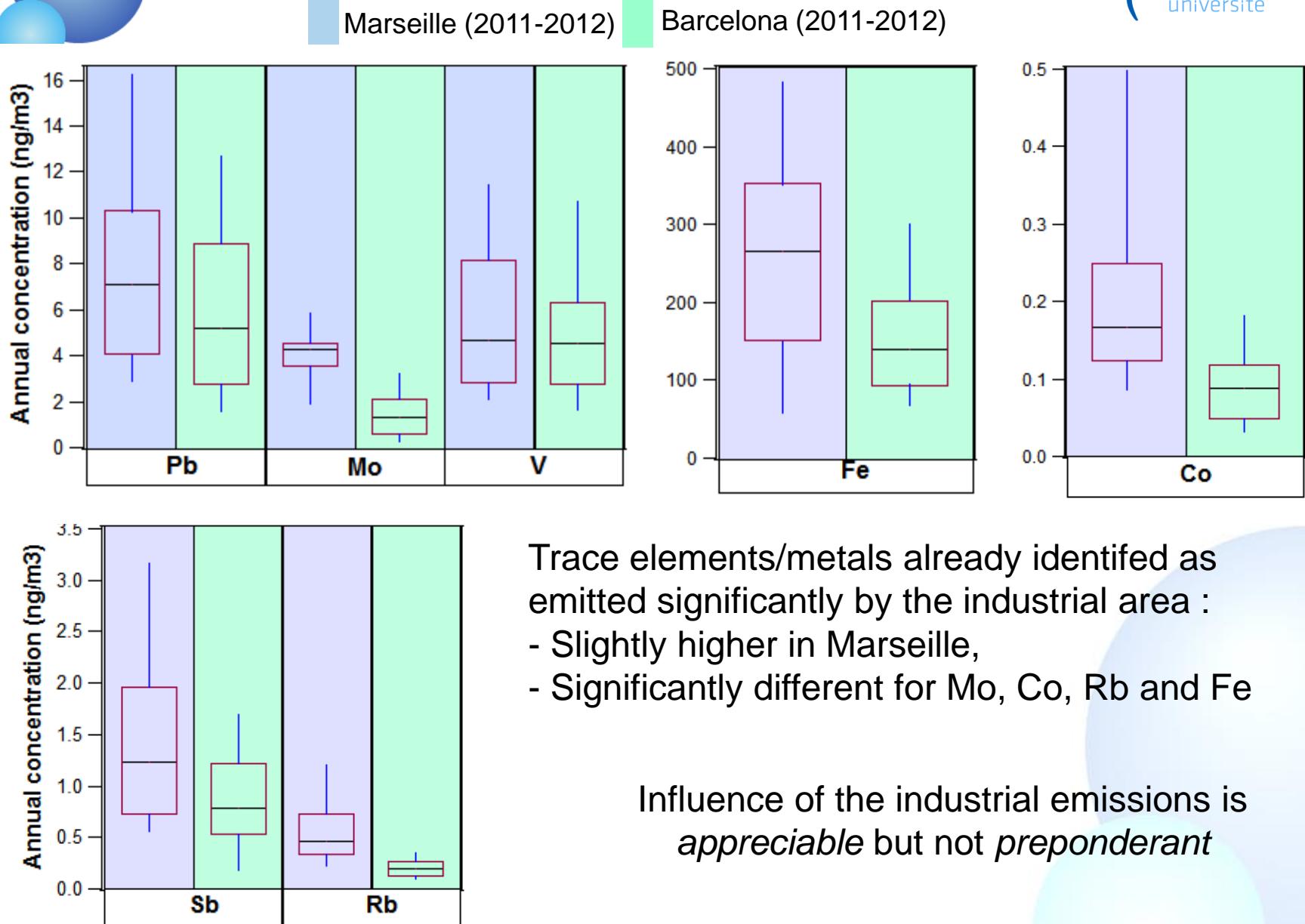
Barcelona (2011-2012)

Data of Barcelona is a courtesy of Querol., X.



- Discrepancies for Zn, Cu, Ba:
- **Zn_B = 2 Zn_M (specific industrial process in Barcelona)**
- **Cu, Ba** (vehicular emissions: brakes, tires), higher concentrations in Marseille which is consistent with EC concentration

Annual concentrations of some trace elements: Marseille vs. Barcelona



Source apportionment Chemical Mass Balance (CMB)

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Methodology (El Haddad et al., 2011a,b)

Selected markers :

Specific markers :

- Vehicular emissions : Elemental carbon + 3 hopanes (i.e. $17\alpha(H),21\beta(H)$ -norhopane, $17\alpha(H),21\beta(H)$ -hopane, and $22S,17\alpha(H),21\beta H$ -homohopane)
- Biomass burning : levoglucosan

Additional markers :

- Four PAH (i.e. benzo[b,k]fluoranthene, benzo[e]pyrene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene) markers, for several kind of industrial processes
- C27, C32 n-alkanes
- Three metals (i.e. V, Ni and Pb)

Source profiles :

Industrial sources :

- Coke production Weitkamp et al., 2005
- Steel facilities, mean of overall processes Tsai et al., 2007
- Shipping main engines Agrawal et al., 2008

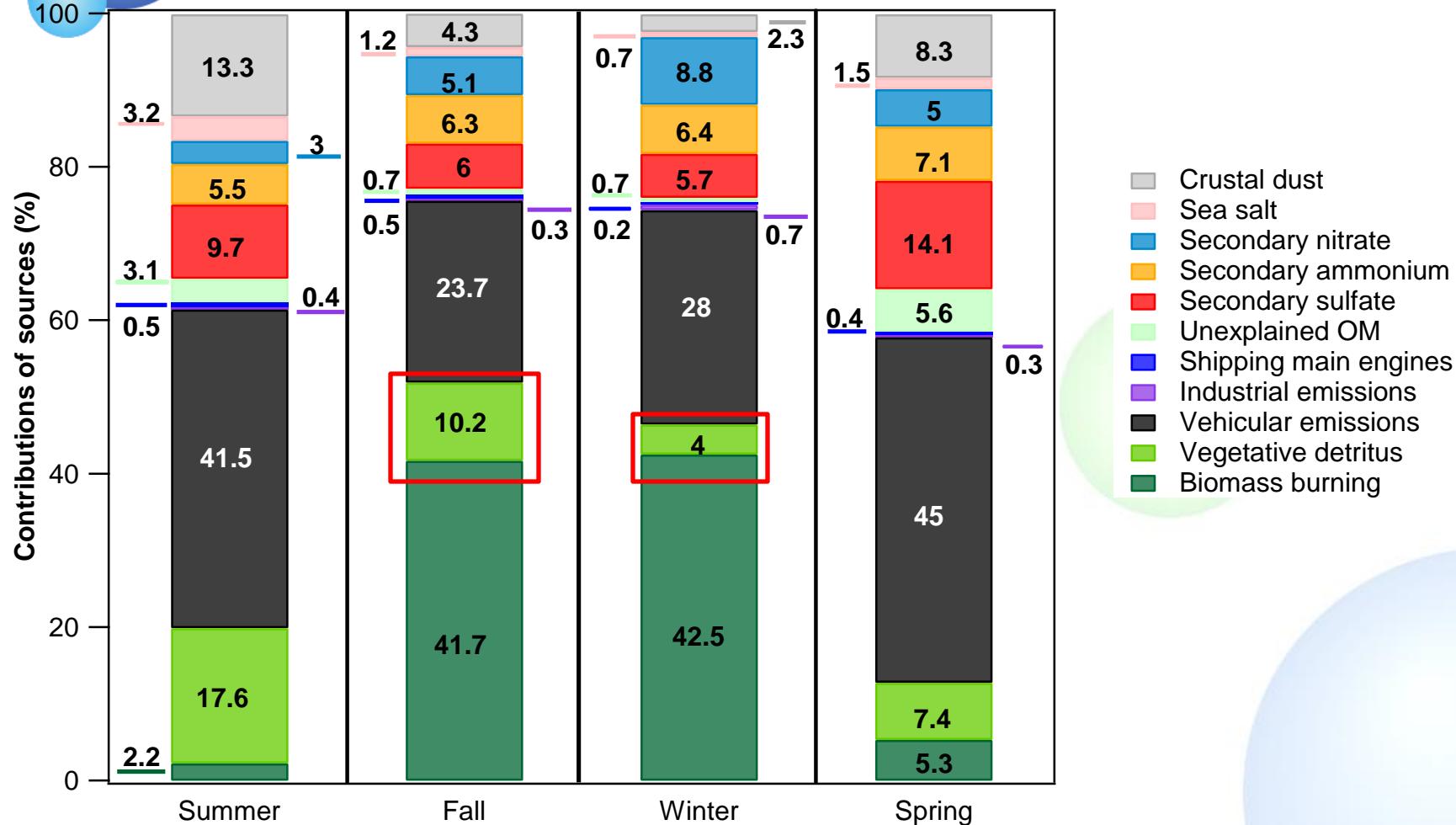
Non Industrial profiles :

- Vehicular emissions El Haddad et al., 2009
- Diesel heavy duty trucks Rogge et al., 1993
- Biomass burning Fine et al., 2002
- Natural gas combustion Rogge et al., 1993
- Vegetative detritus Rogge et al., 1993

Source apportionment Chemical Mass Balance (CMB)

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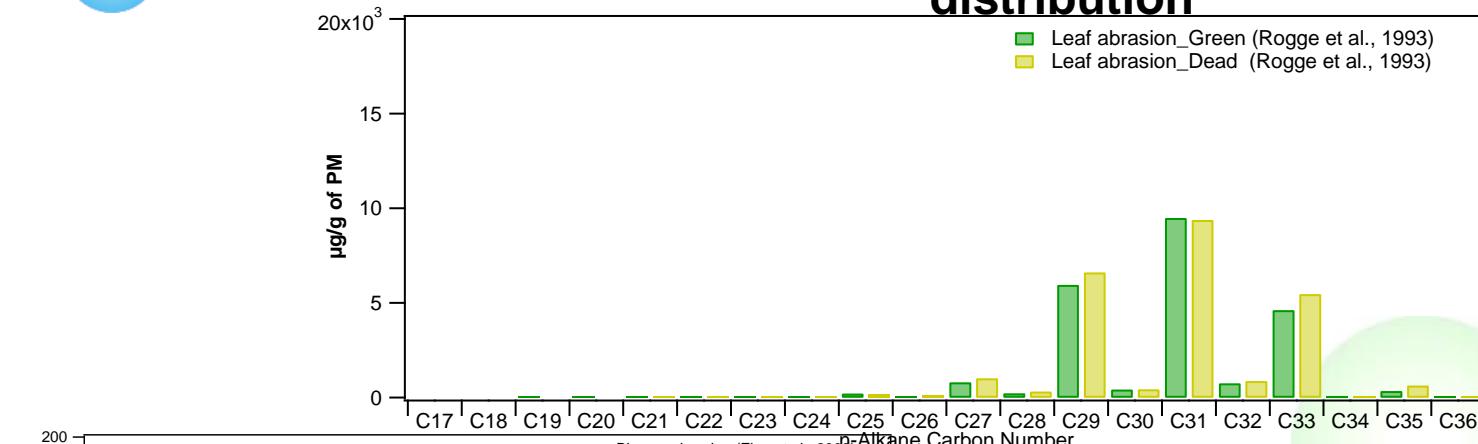
- Important contribution of biomass burning in fall and winter ~ 40% of $\text{PM}_{2.5}$ mass
- 2nd major source is vehicular emissions
- Low contribution of industrial and shipping emissions
- Unexpected contribution of vegetative detritus in fall (10%) and winter (4%)

Source apportionment Chemical Mass Balance (CMB)

vegetative detritus are characterized by their alkanes distribution

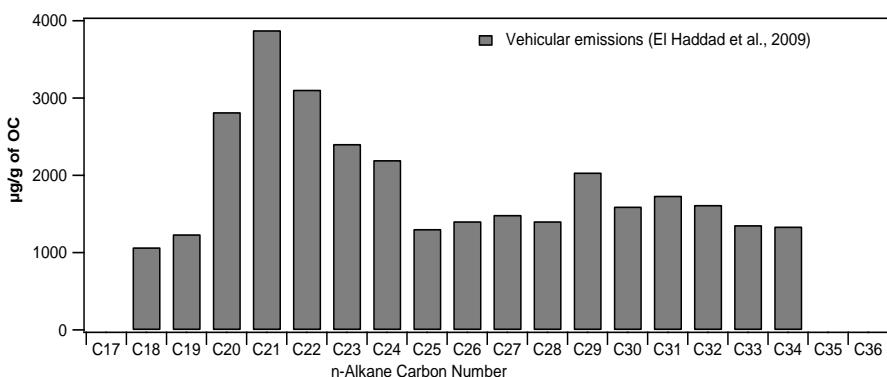
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- Leaf wax n-alkanes exhibit a strong odd carbon number predominance with the dominant wax n-alkanes being C₂₉, C₃₁ and C₃₃.

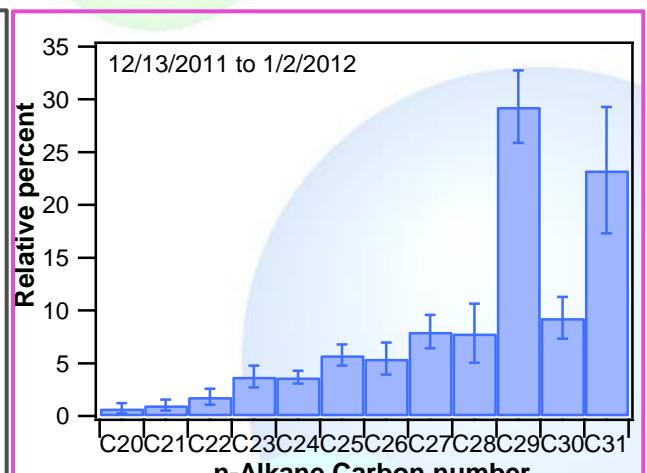
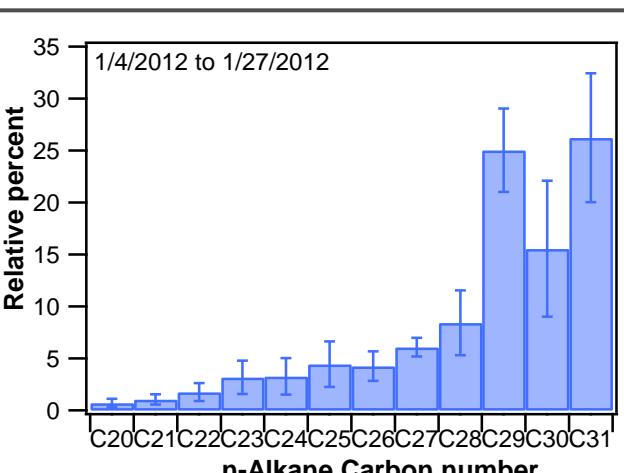
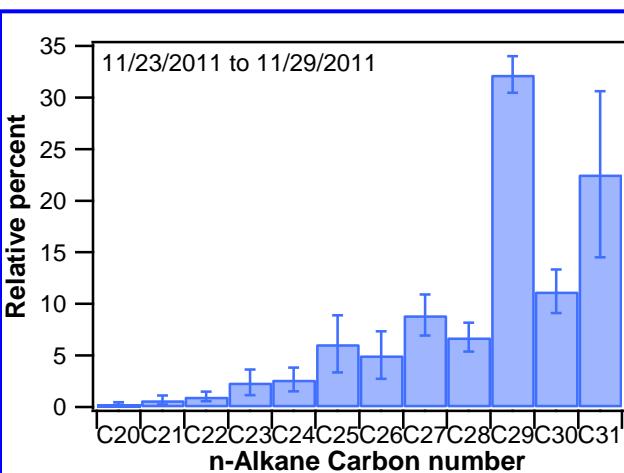
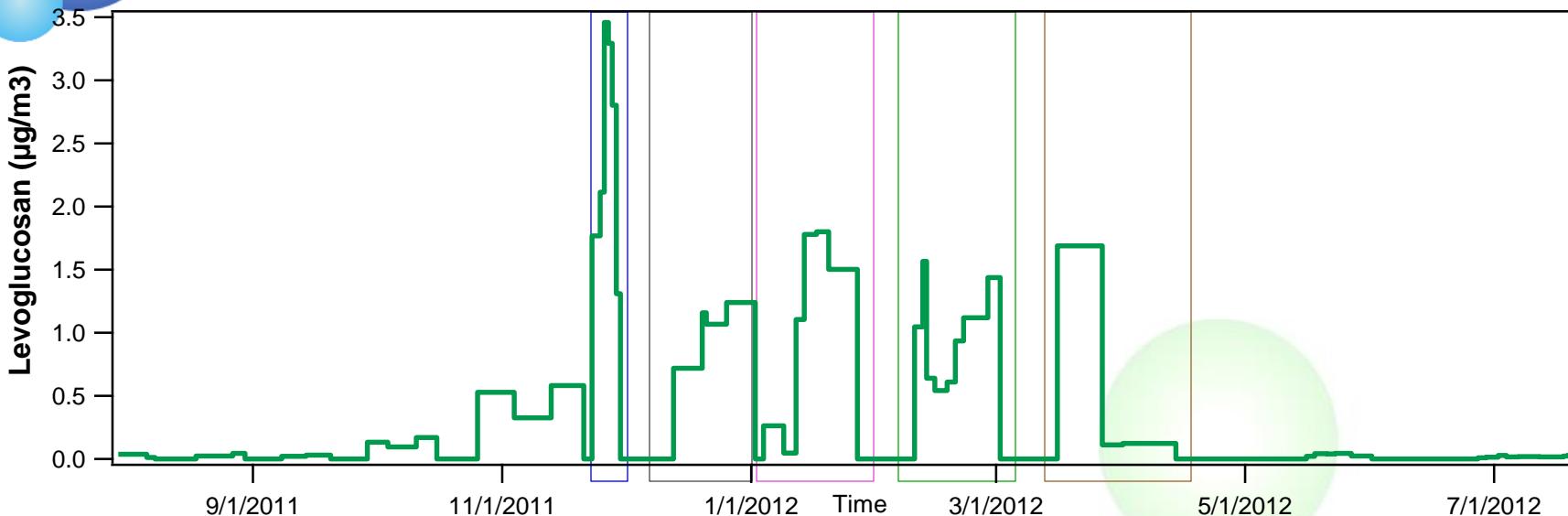
This alkanes profile is very specific of leaf wax



Source apportionment Chemical Mass Balance (CMB)

Distributions of n-alkanes

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Predominance of odd n-alkane carbon number (C₂₉, C₃₁)