

POVA

(Pollution des Vallées Alpines)

General presentation

and some results on PM_{10} characteristics

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(coordinator)

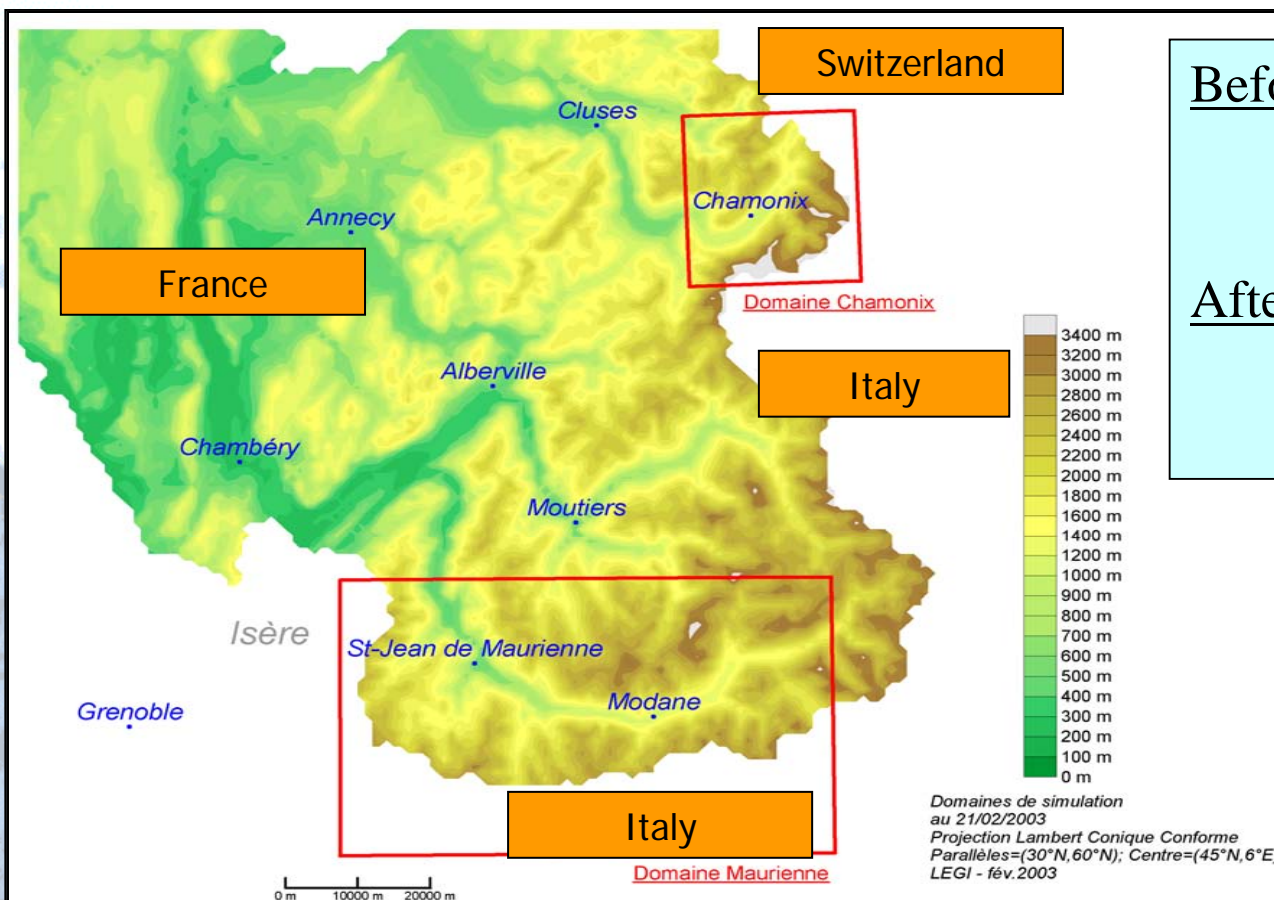
Workshop Kloster Andechs, 11-12 October 2005

I will talk about

- **Context, objectives, and strategy of POVA**
- **The modeling part of the program**
- **The PM₁₀**
 - **Chemistry**
 - **Sources**
 - **Characteristics**

Context

- **Accident under the Mont-Blanc Tunnel (03/99)**
 - International traffic stopped in Chamonix
 - Transit through the Maurienne Valley



Before accident :

2200 HD trucks / day
in each valley

After accident :

- 750 trucks /d Chamonix
- 4250 Trucks / d Maurienne

**Re opening of
the MBT in
March 2003**

Context

■ Specificities of alpine valleys

- Atmospheric dynamics and meteorology
- Emission sources concentrated in the valley floor

- Preservation
- Sustainable
- Environmental

■ Existing studies :

- Large atmospheric concentrations (primary species)
- Contributions from traffic, industries, other sources
- Very few data for winter periods
- Very few data for particles
- No modeling at small scale

■ Possible changes in the legislation

- Lowering of the thresholds for PM_{10}
- $PM_{2.5}$

Objectives of POVA

➤ **Operational objectives :**

- ❑ **Comparison of air quality in the 2 valleys (Chamonix et Maurienne), during and after the closing of the MBT**
- ❑ **Study of sources and processes that impact air quality**
- ❑ **Modeling atmospheric chemistry**
- ❑ **Study of scenarios of emission**

➤ **Behind, there is also a whole series of scientific objectives**

The program started in May 2000 and will be finished by the winter 05

General strategy of POVA

Field studies + 3D modeling

Field studies

- ❑ **Four 1-week intensive sampling campaign in each valley**
 - Winter / summer ; before / after the reopening of the TMB
 - Investigation on the atmospheric dynamics
 - Measurement of a large array of (gaseous and particulates) species
 - Large spatial covering (3D) and fine temporal resolution
 - **Small scale processes, validation of 3D model**

- ❑ **Long term campaign (Feb 01 – July 03)**
 - Daily monitoring at the urban sites of AIR APS (Chamonix et St Jean de Maurienne)
 - Smaller number of chemical species (**chemistry of PM10**)
 - **Seasonal variations ; long term changes**

General strategy for POVA

Field studies + 3D modeling

Modeling

- Specific emission inventories** (small scale)
- Model for atmospheric dynamic** (sub meso scale)
- Coupling with chemistry model** (gas) *not performed for aerosols*
- Validation with field data**
- Definition of the scenarios** (meteo, emission,...)
- Evaluation of the scenarios**

emission
inventory



EMEP inventory
50 km

CITEPA inventory
6 km

POVA inventory
100 m

CHIMERE
27 km

CHIMERE
6 km

TAPOM
300 m

concentrations

Meteo ECMWF
80/40 km, $\Delta t = 3$ hours

MM5
27 km

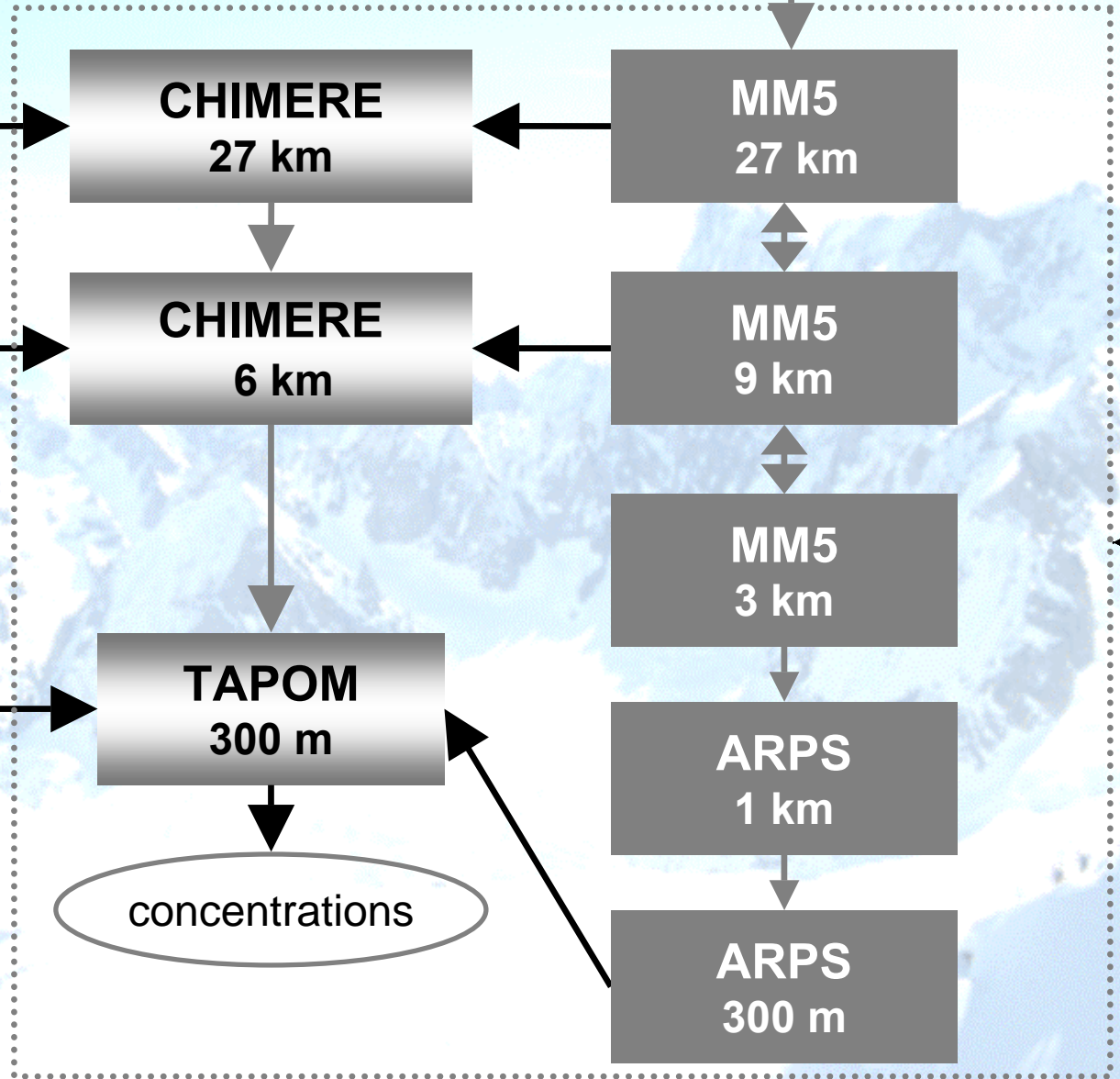
MM5
9 km

MM5
3 km

ARPS
1 km

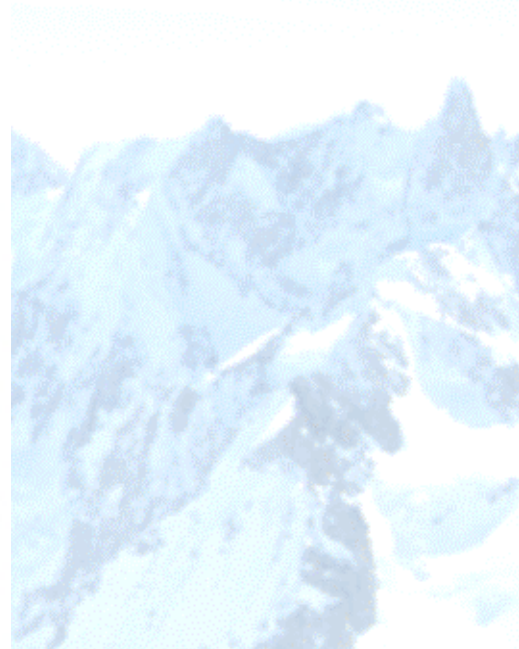
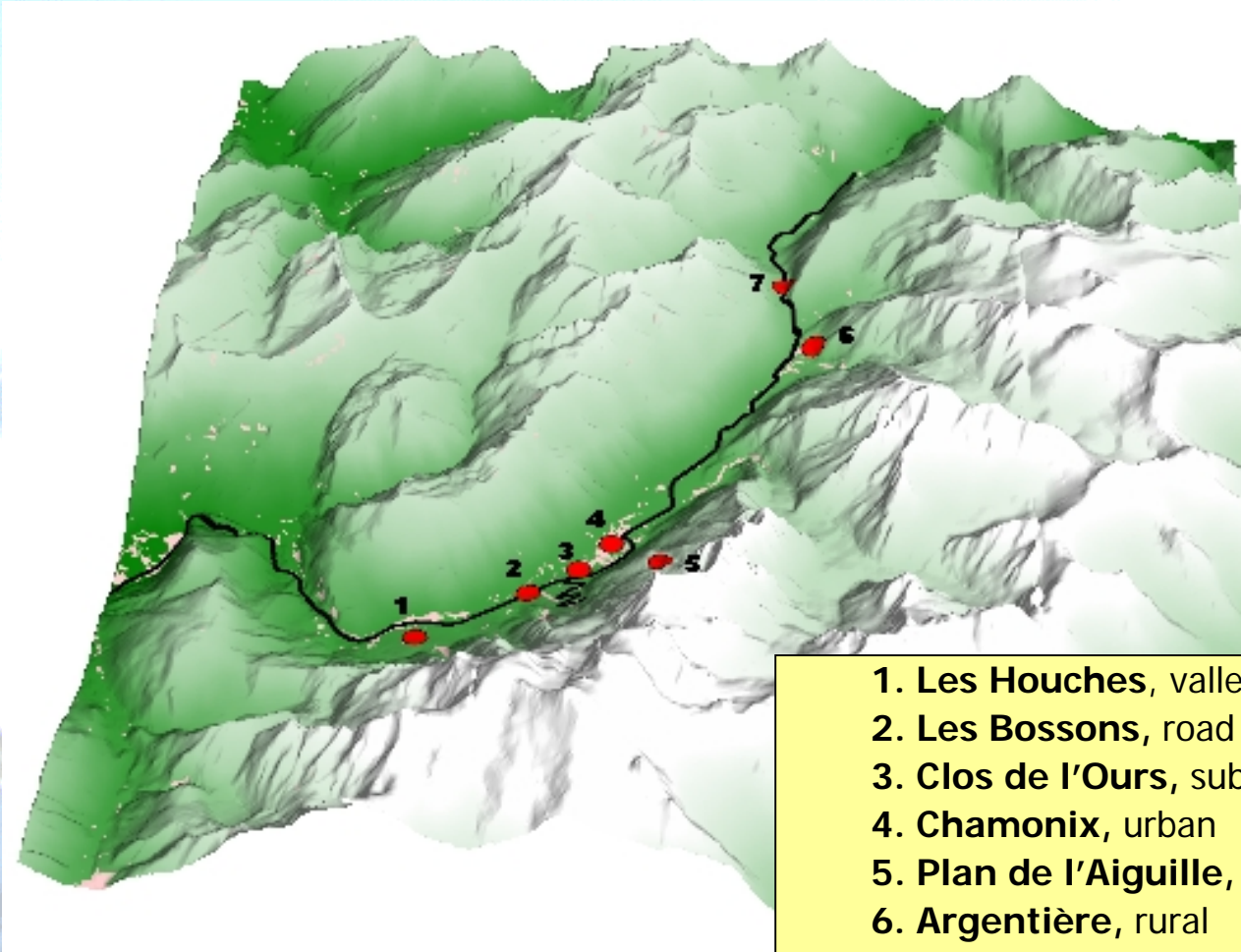
ARPS
300 m

- ➔ Inputs/outputs
- ➔ One-way nesting
- ↔ Two-way nesting



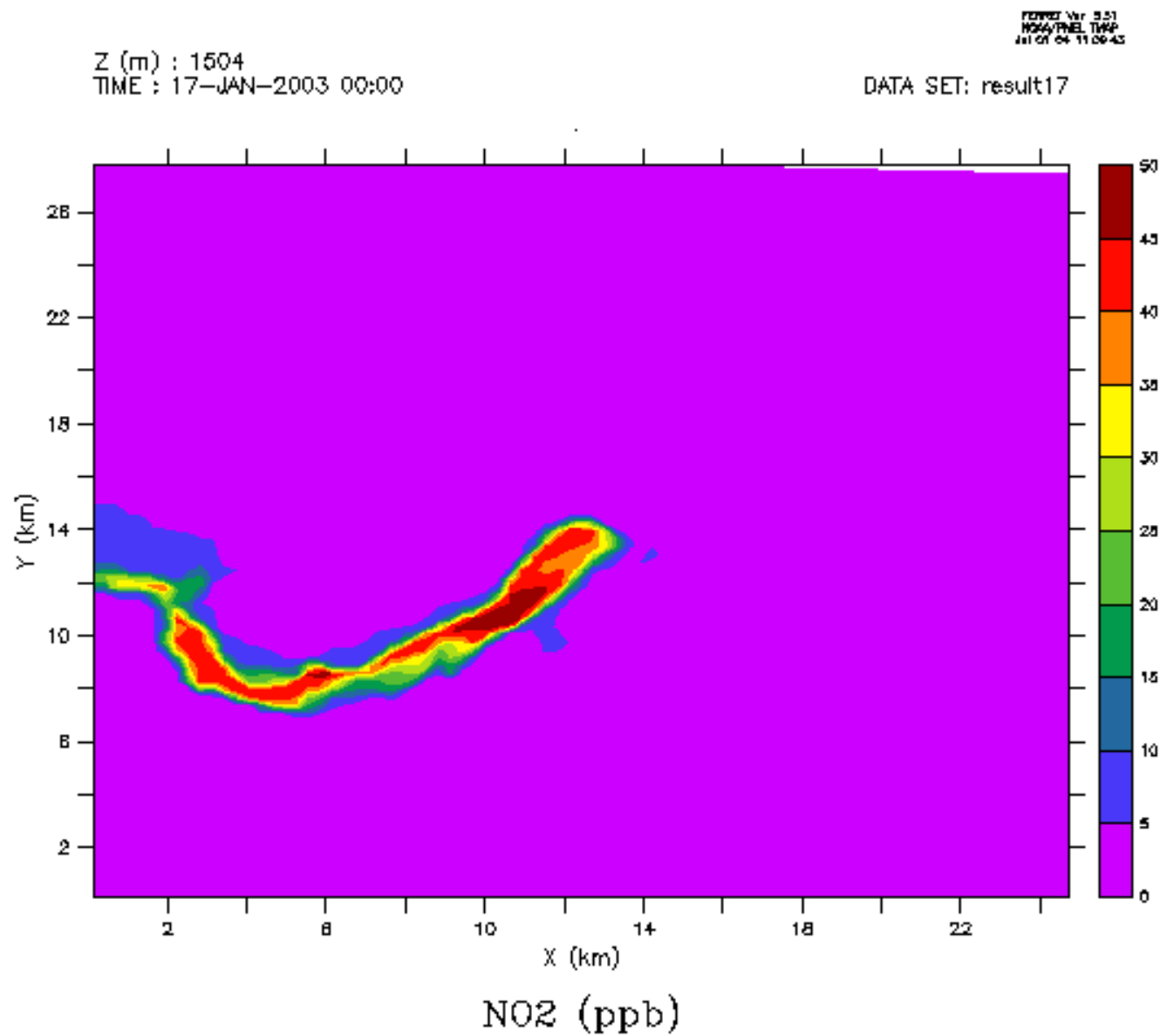
Modeling

Chamonix valley : 23 km



1. Les Houches, valley entrance
2. Les Bossons, road side
3. Clos de l'Ours, sub urban
4. Chamonix, urban
5. Plan de l'Aiguille, altitude
6. Argentière, rural
7. Col des Montets, end of valley

Modeling



Modeling : some results

The model correctly reproduces :

- Wind shifts (day / night) due to thermal heating (strong in summer)
- The depth of the layer concerned by this process
- The lifting of the inversion layer during winter
- The temperature cycles in the valleys
- Atmospheric concentrations of many primary and secondary species

It has been used for :

- Testing the influence of traffic in several configurations
- Looking at respective importance of local production vs regional transport
- The evaluation of scenarios (emissions + meteorology)

Need to further develop the applications for PM

Data base of the long term sampling

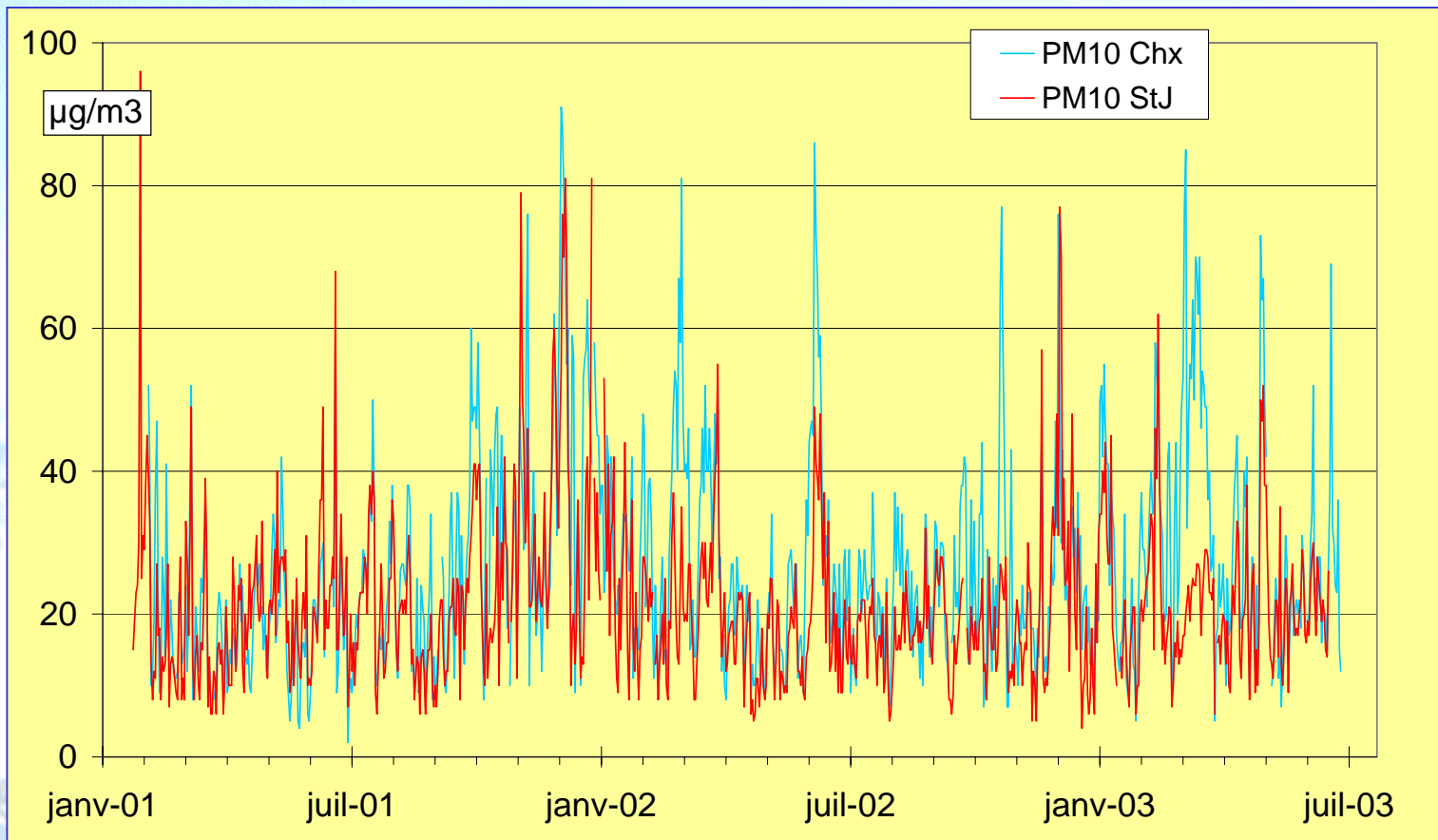
Sampling at the 2 urban sites of the Air Quality Network

- Chamonix (kerbside) and St Jean de Maurienne (background urban)
- 860 days (Feb 01 to June 03)
- O₃, NO_x, PM₁₀, SO₂ (15 min → 24 hrs)
- VOC, aldehydes/ketones (24 hrs)
- **Chemistry of PM₁₀** (24 hrs) (770 samples and 110 blks)
 - Ionic components
 - EC / OC
 - WSOC
- Meteorological data (1 hr → 24hrs)
- Traffic data (24 hrs)

Data base for the intensive campaigns

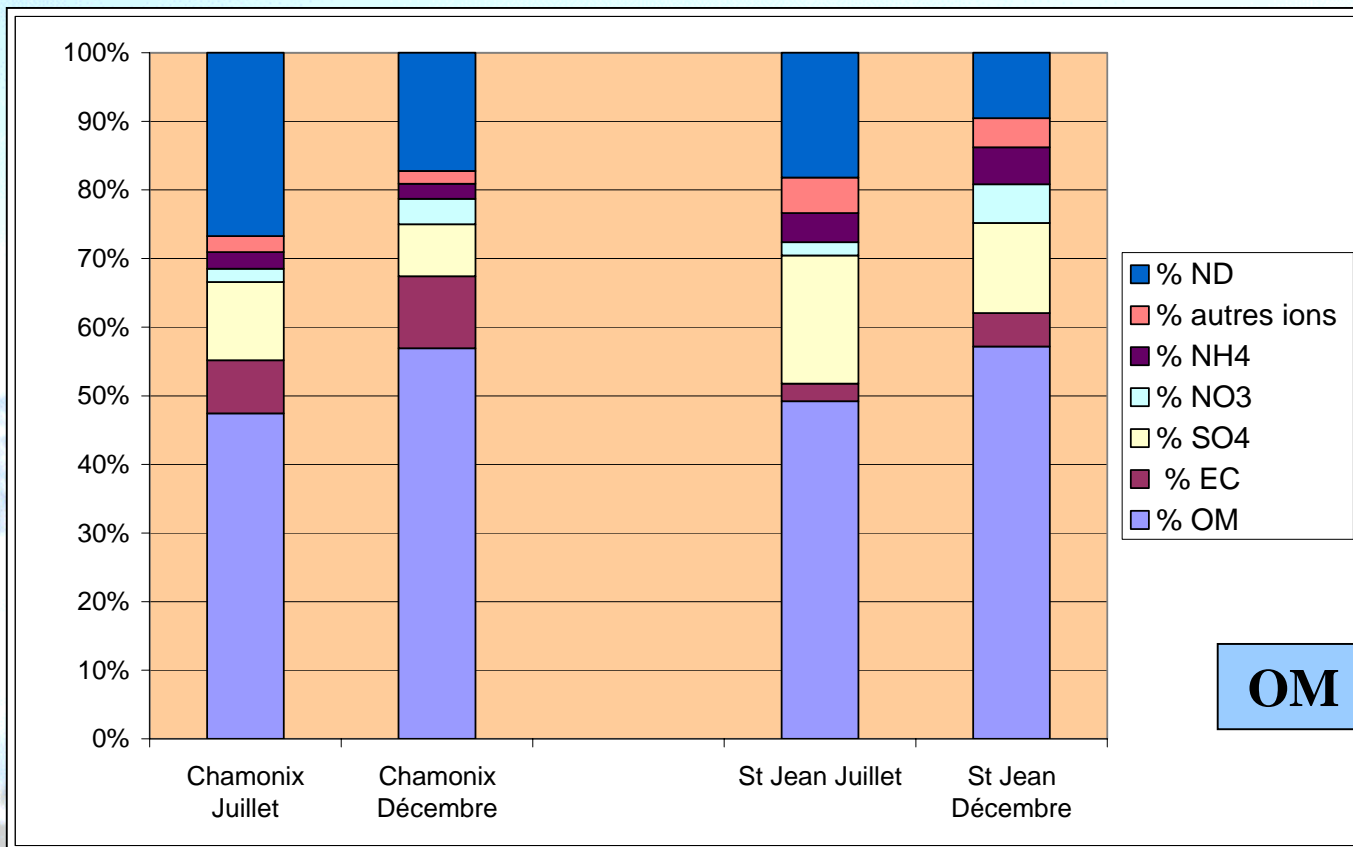
- 4 intensive field campaigns in each valley (winter / summer ; 2000 and 2003)
- 5 – 7 sites in each campaign
- 1 week long
- Sampling with short time resolution (4h for aerosol chemistry)
 - Gas phase : NO, NO₂, NO_y, O₃, SO₂, CO, VOC's, ...
 - Particulate phase : PM₁₀ mass, number size distribution, sampling with total filters, impactors, denuder, sampling for chemistry
 - Ionic species,
 - Elemental composition,
 - EC / OC,
 - Molecular markers
- Ground met station, wind profiler, LIDARs, equipped Ultra Light Plane, cable cars, ...

Daily evolution of PM₁₀ concentrations



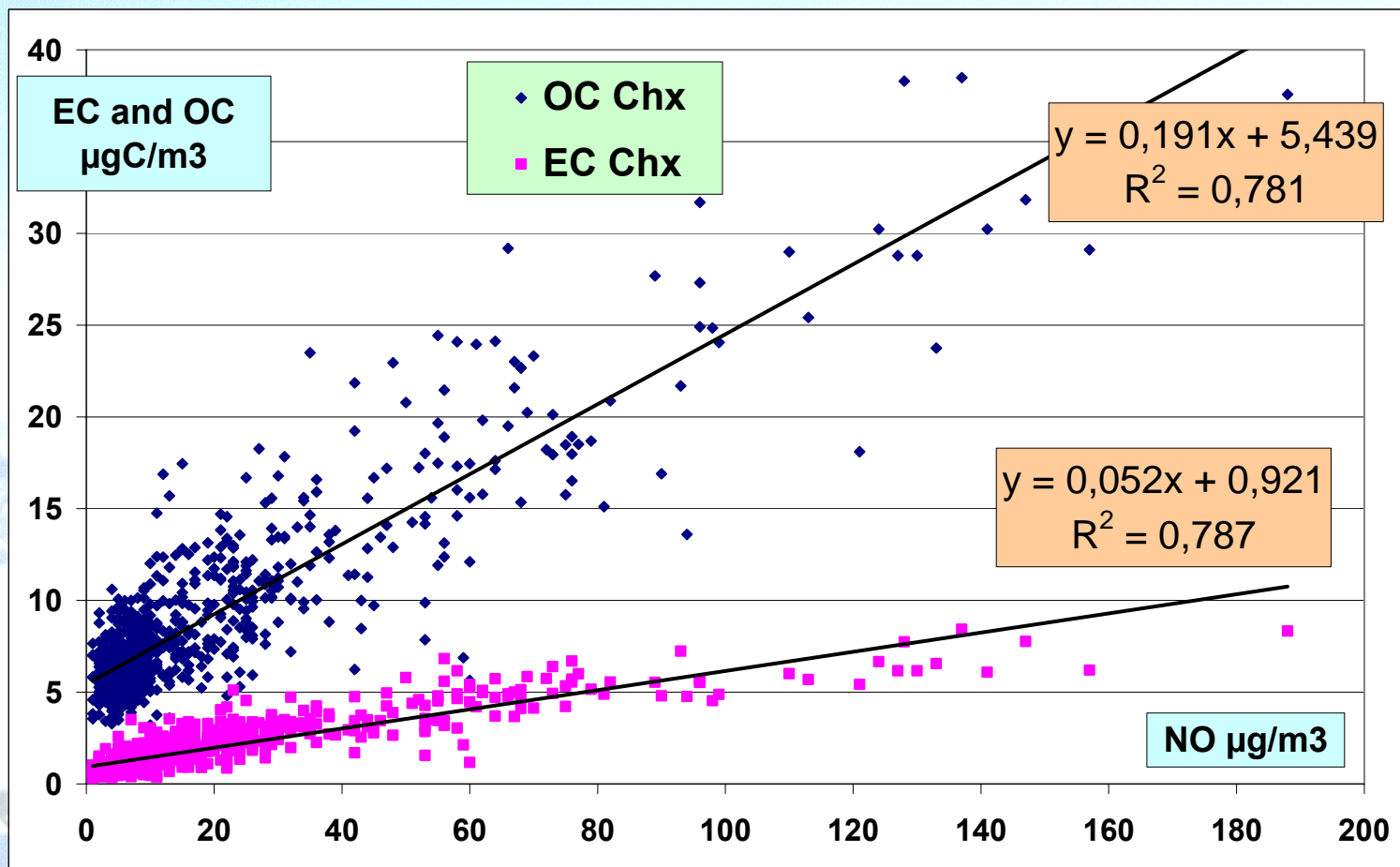
- **Maxima during winter**
- **Large number of episodes > 50 µg/m³**

General chemistry of PM₁₀



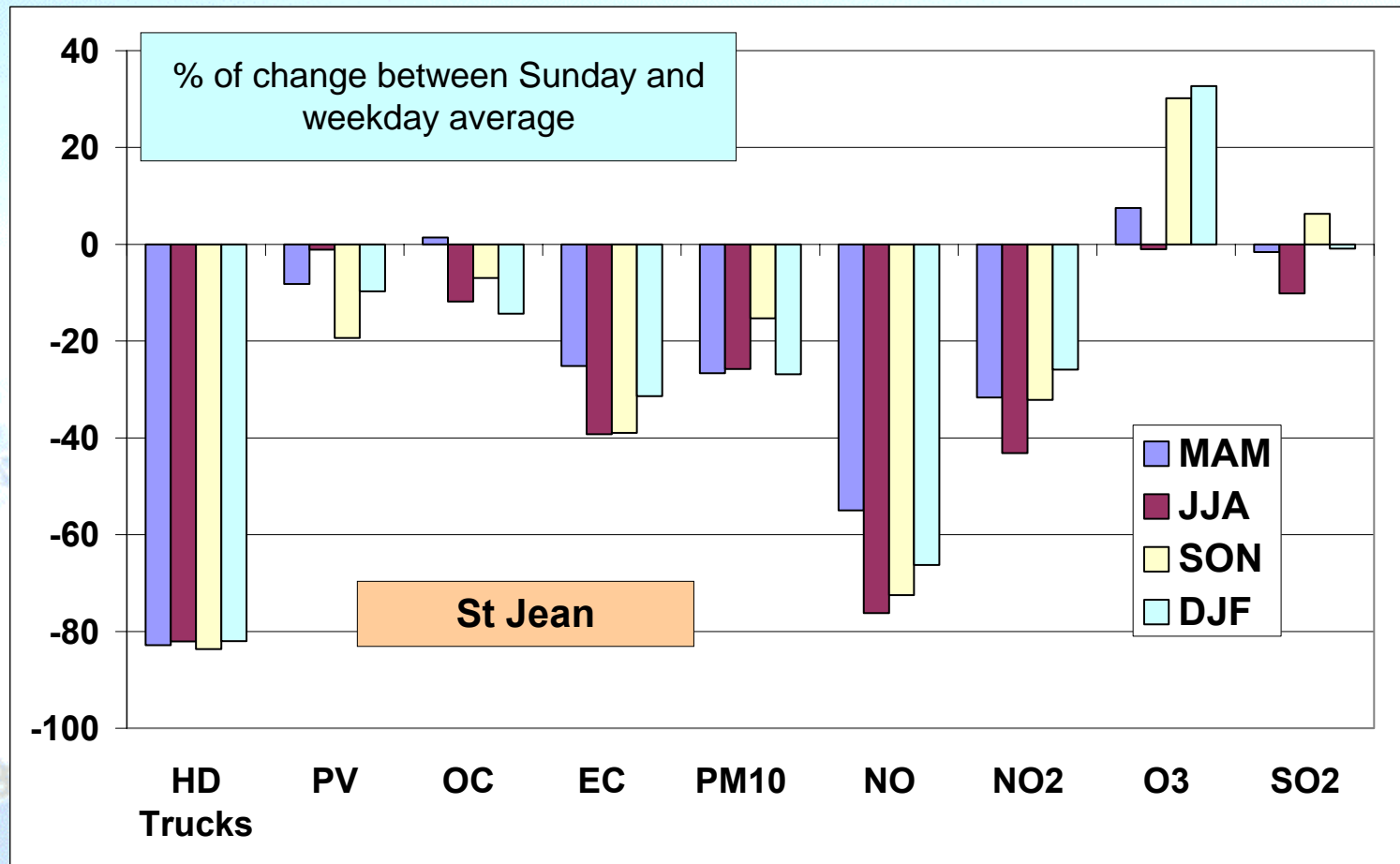
- **Dominated by EC + OM (50 to 75 % of PM₁₀ mass)**
- **Increased fraction of OM in winter**
- **Conversely, increased fraction of sulfate in summer**

Impact of combustion sources



- Very large impact of local combustion sources
- Both on EC and OC

Impact of HD trucks traffic



- HD traffic : 20 % of PM_{10} and 30 % of EC
- Smaller fraction for OC

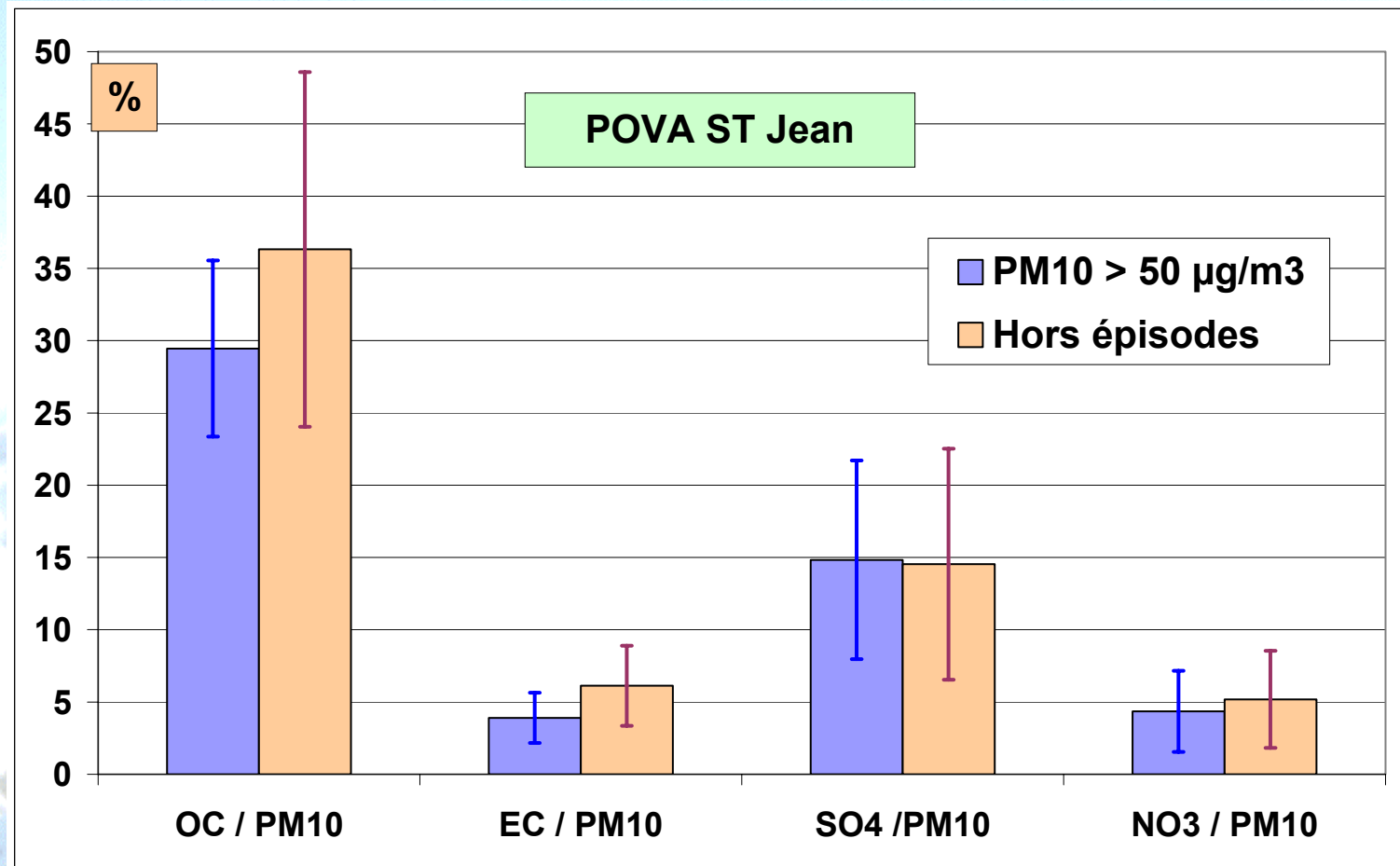
Another source : wood combustion

All in ng/m ³ Winter 02 -03	Vallée de Chamonix		Vallée de la Maurienne	
	Le Clos n = 19	Les Houches n = 14	Modane n = 13	Orelle n = 14
Mostly in the gas phase				
Guaiacol	< dl	< dl	< dl	< dl
Syringol	5.9	< dl	3.7	< dl
Vanillin	40.6	26.2	15.3	13.8
Mostly in the particle phase				
Syringaldehyde	123	70	21.8	14.4
Acetosyringone	71	34.8	20.1	10.1
Coniferyl aldehyde	25.7	27.4	17.6	8.7
Levoglucosan	492	360	224	144
OC (μgC/m³)	11.9	7.6	6.6	2.8

Another source : wood combustion

	Syringaldehyde	Acetosyringone	Coniferyl aldehyde	Levogluconan
(all in ng/ μ g OC)				
Fine et al., 2001				
Red maple	27	7.2	13.7	108.5
Red oak	22	9.9	17.3	168.3
White pine	2.4	0.58	7.4	52.3
Schauer et al., 2001				
Pine	/	/	43.2	258.5
Oak	8.4	9.3	5.0	234.6
Ratio used	12	8	12	200

Chemistry of PM₁₀ during episodes



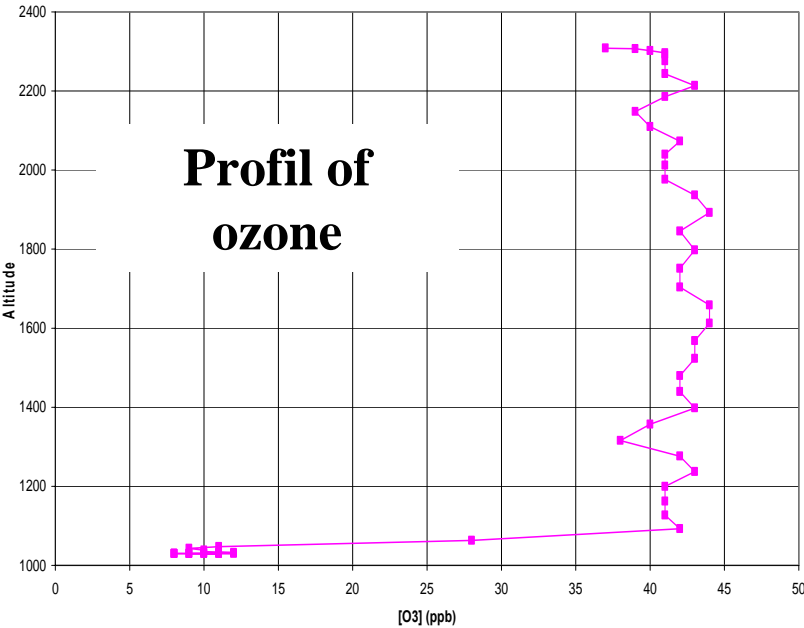
Average of 17 (out of 21) episodes above threshold in NDJF

No strong changes in the chemistry

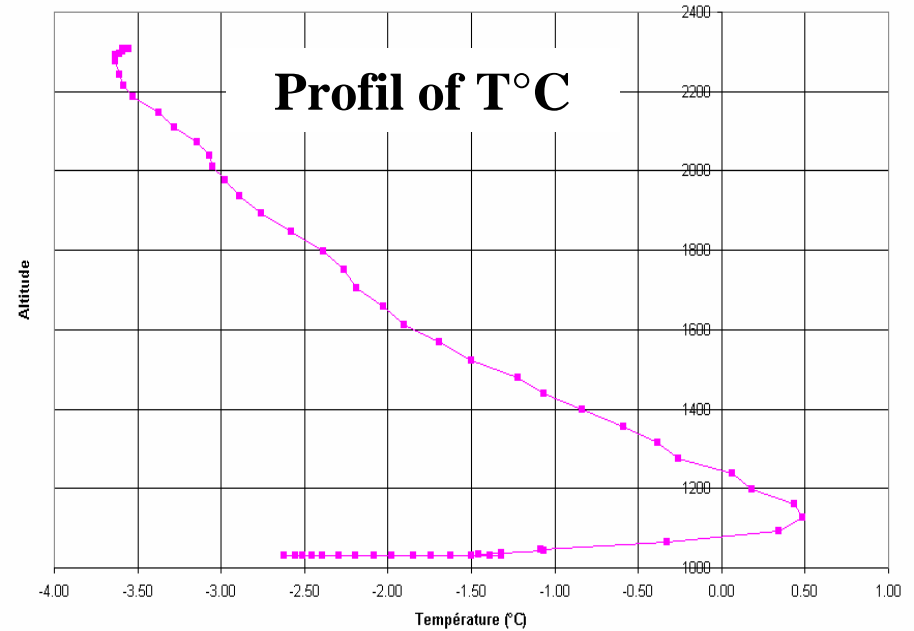
Impact of meteorological factors

Inversion layers

Profil d'Ozone 8h30 TU



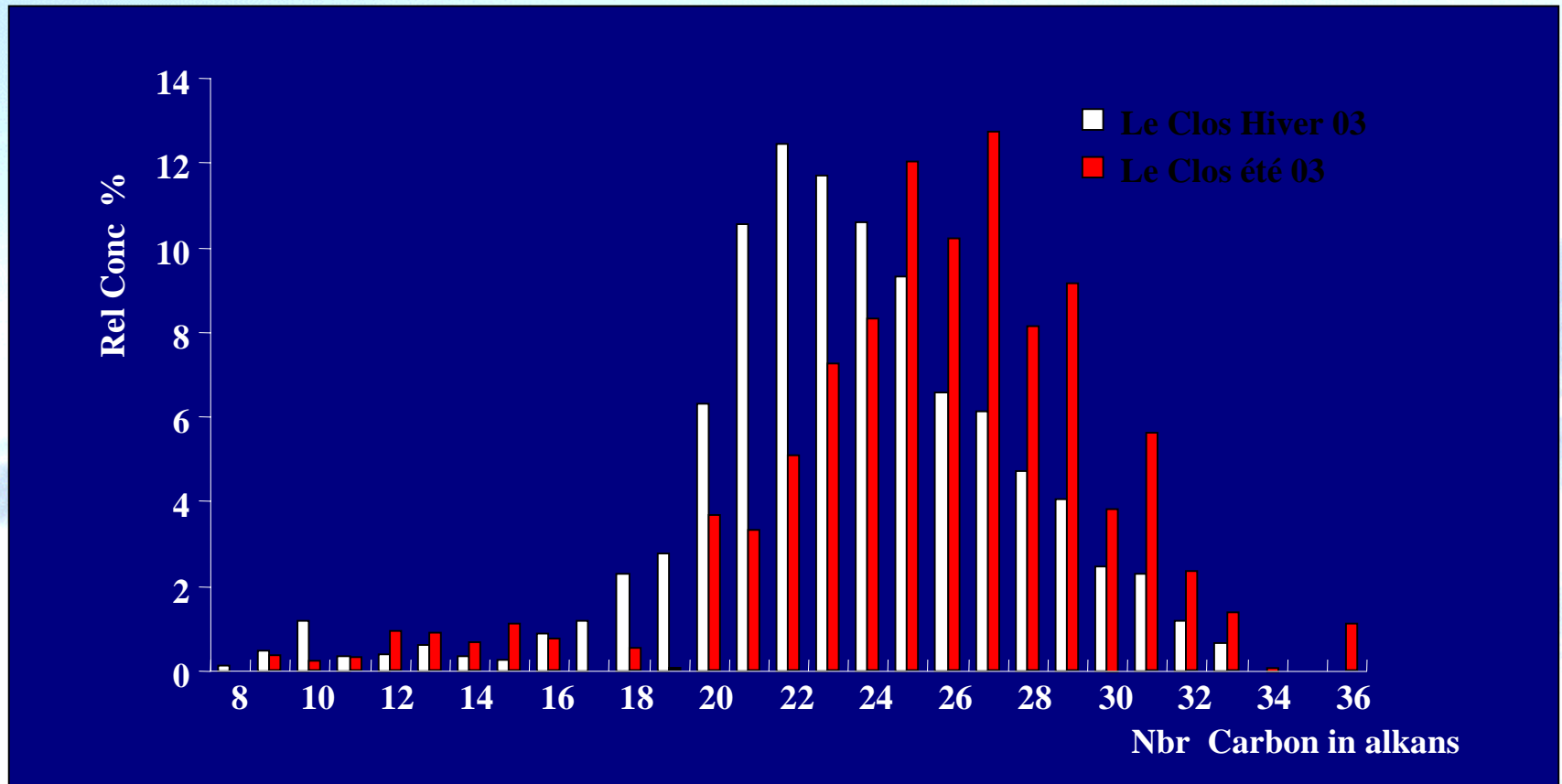
Profil de Température 8h30 TU



17/01/03 in Chamonix

Data : P Perros, LISA

Biogenic sources in summer

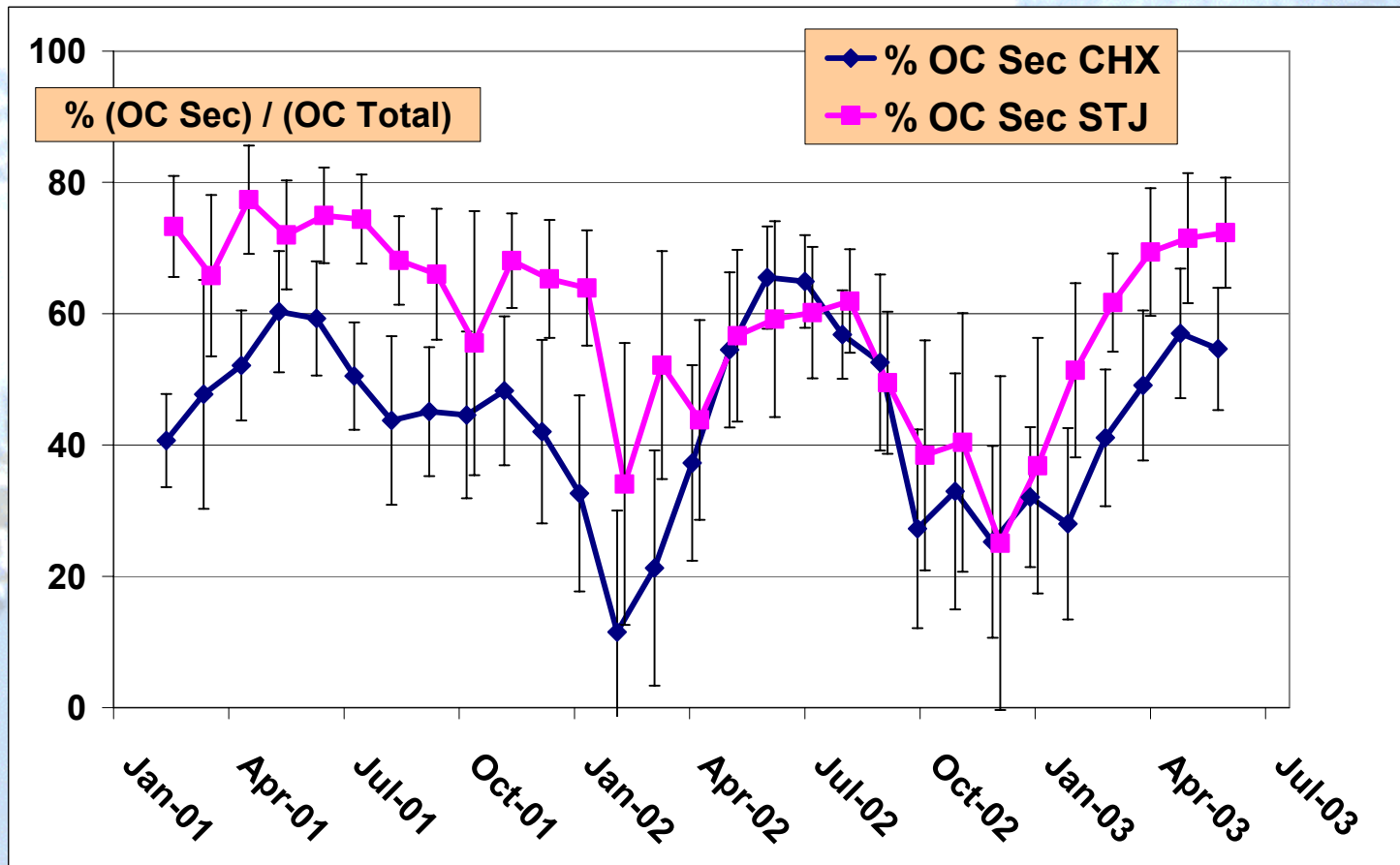


Conc (ng/m ³)	200 (106 – 309)	50 (26 – 93)
Imprint	C ₂₀ -C ₂₄	C ₂₅ , C ₂₇ , C ₂₉
CPI	1,01 (0,92 - 1,08)	1,23 (0,43 - 1,67)

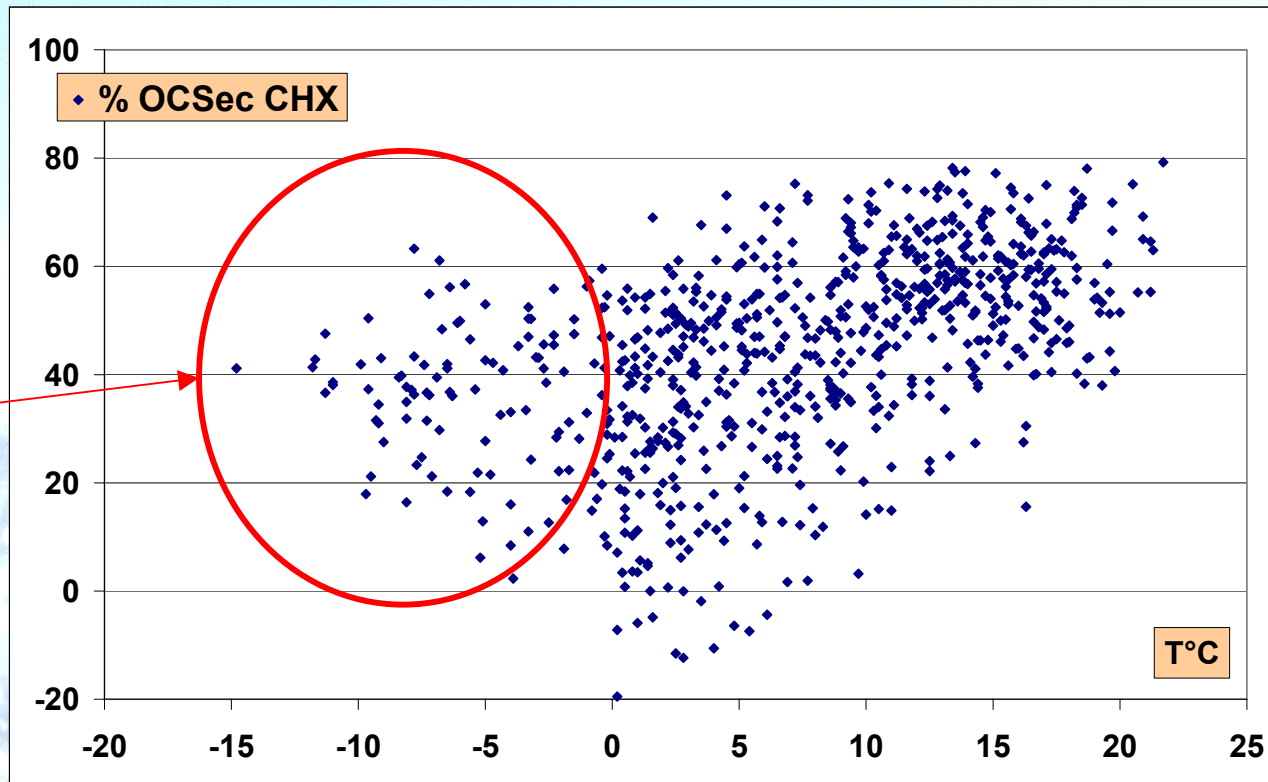
Secondary OC

$$OC_{\text{sec}} = OC - \left(\frac{OC}{EC} \right)_{\text{pri}} \times EC$$

With $\left(\frac{OC}{EC} \right)_{\text{pri}} = 2.83$ (average of lower 5% in Chamonix ; n = 38)



% OC_{sec} and temperature



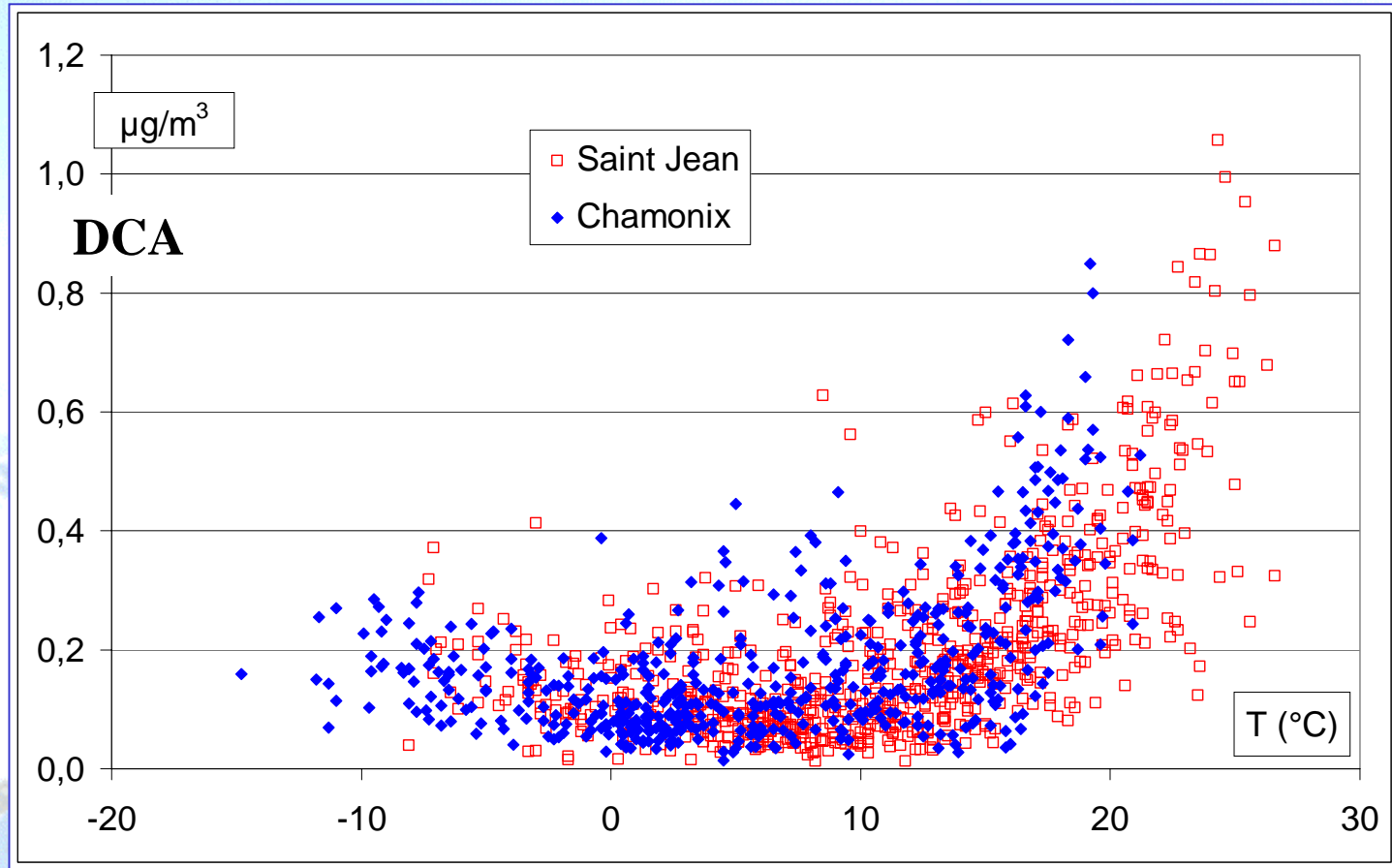
« Secondary »
??

Decrease with temperature. But :

- Minimum around 0 - 5 °C
- Values up to 40-50 % at low temperature
- Wide dispersion for a given temperature

■ Need to better assess this method

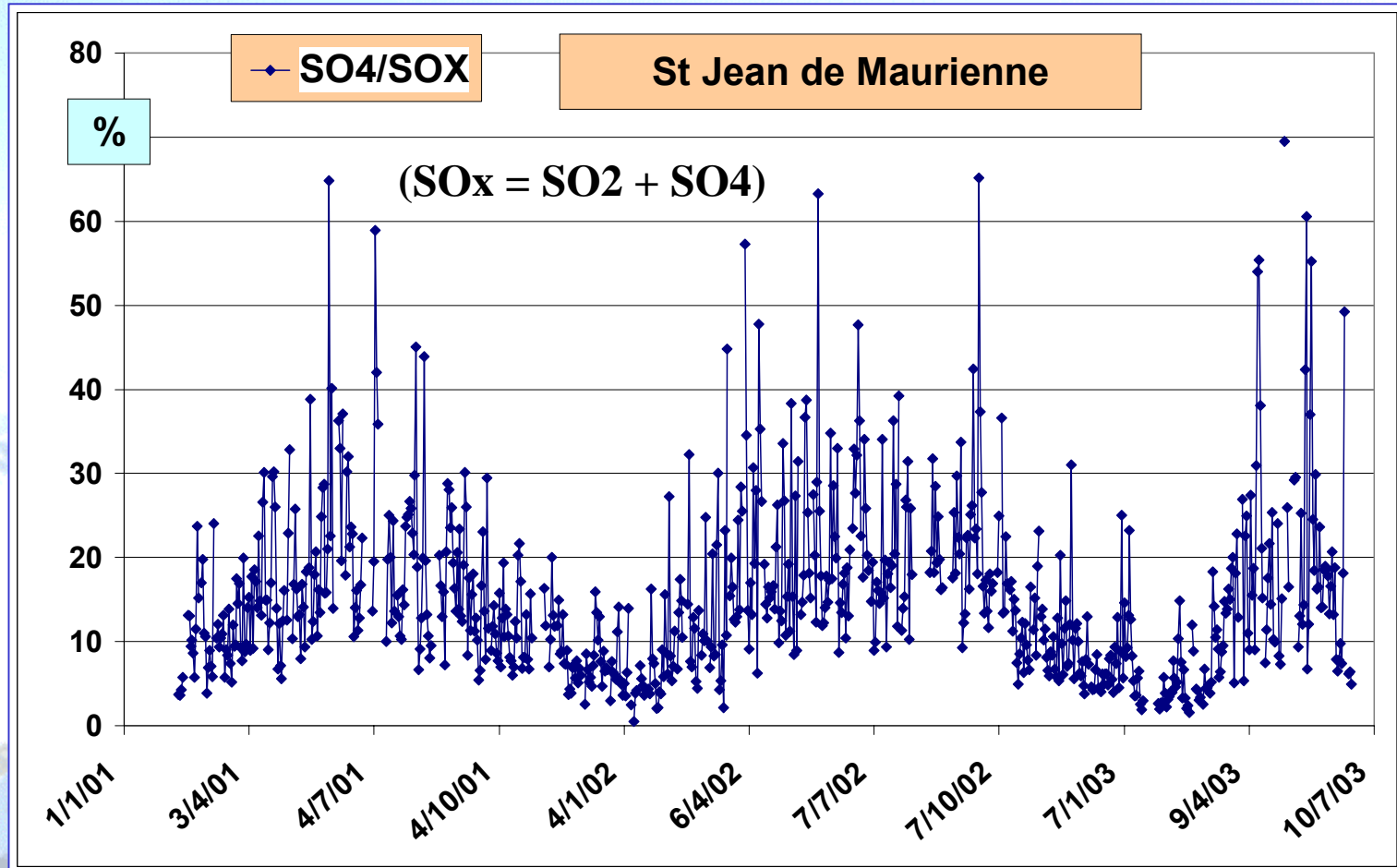
Secondary species : organic diacids



DCA : dicarboxylic acids : oxalic, malonic, glutaric, succinic, tartaric, malic

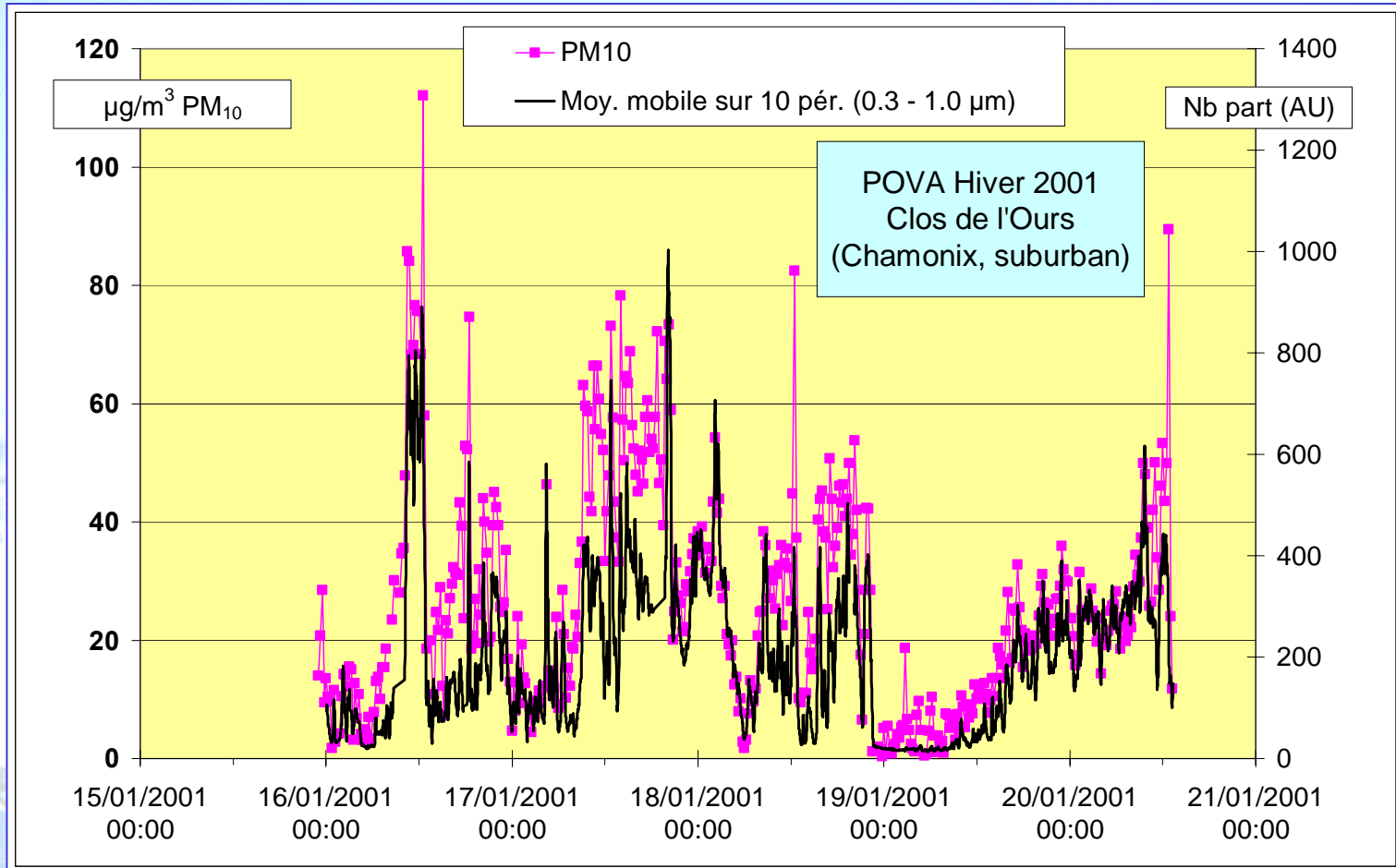
Large increase of concentrations and mass fraction to OC as temperature increases

Secondary species : sulfate



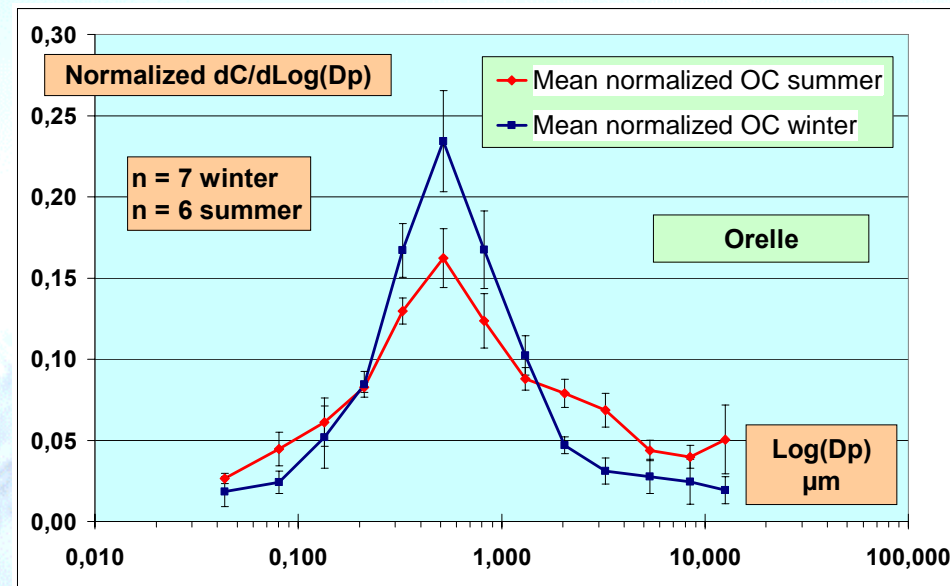
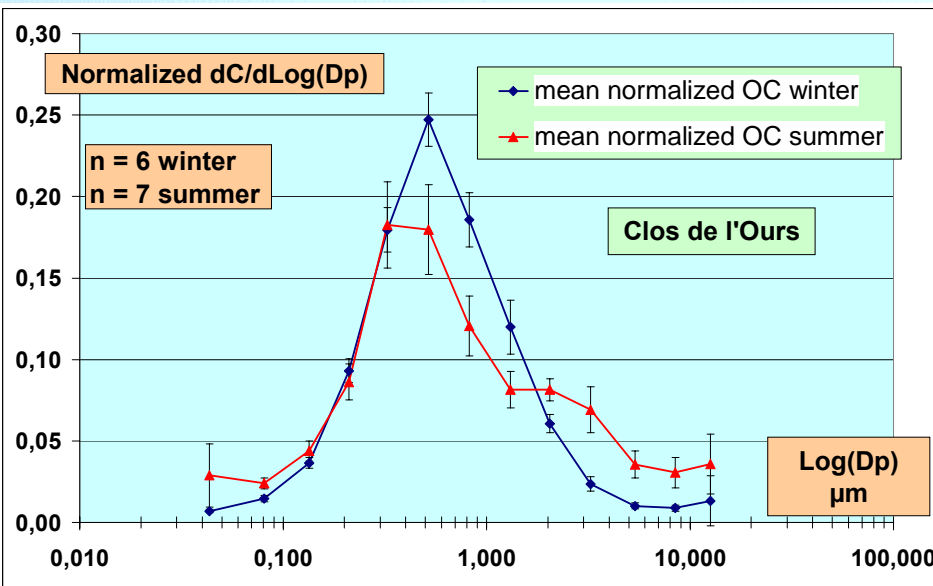
- Increase of the oxidized fraction in summer
- Winter lows are really low

Some characteristics of PM₁₀



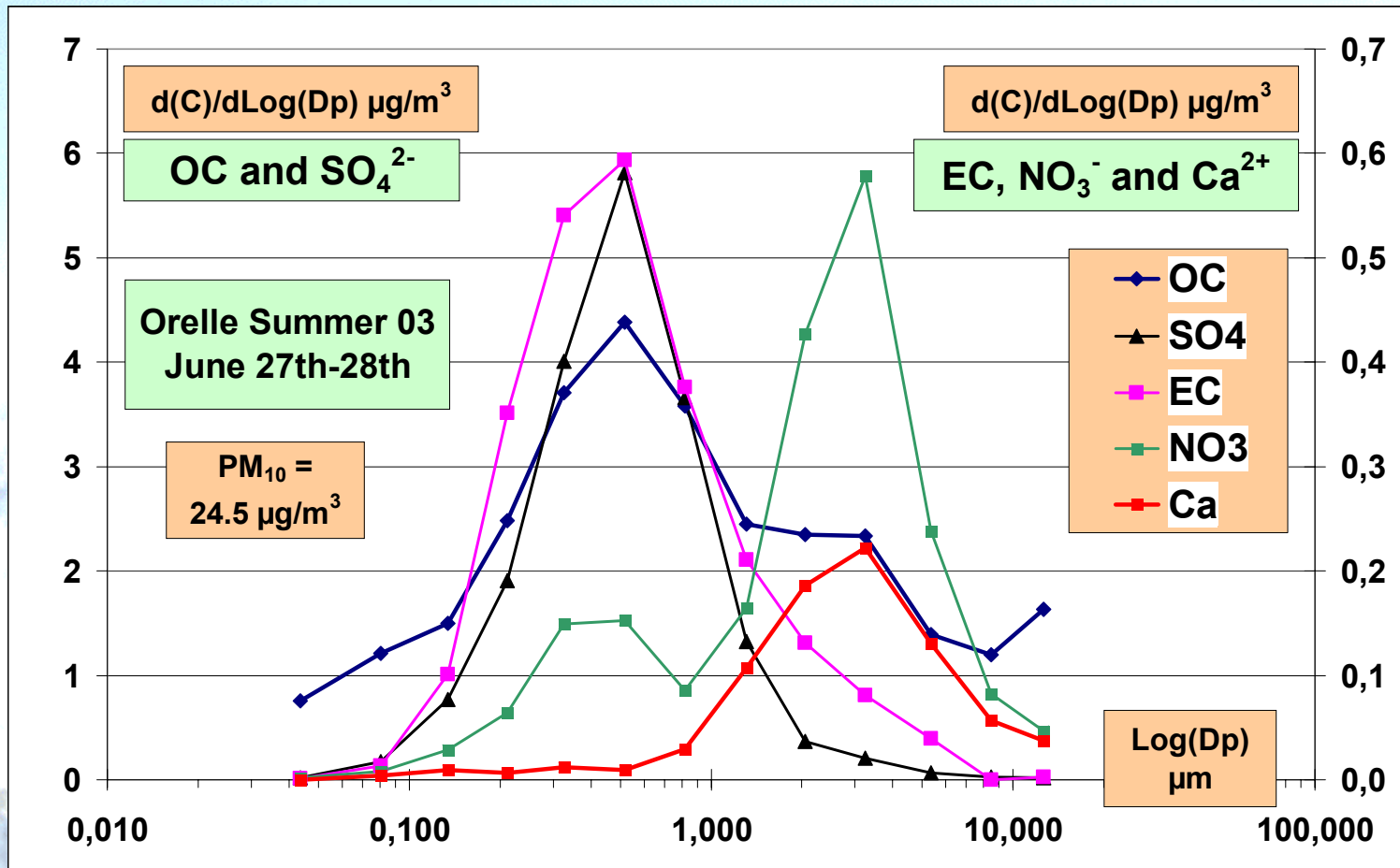
- The fraction 0.3 – 1.0 μm is making up most of the PM₁₀ mass (in a suburban site in winter)

Size distribution of OC



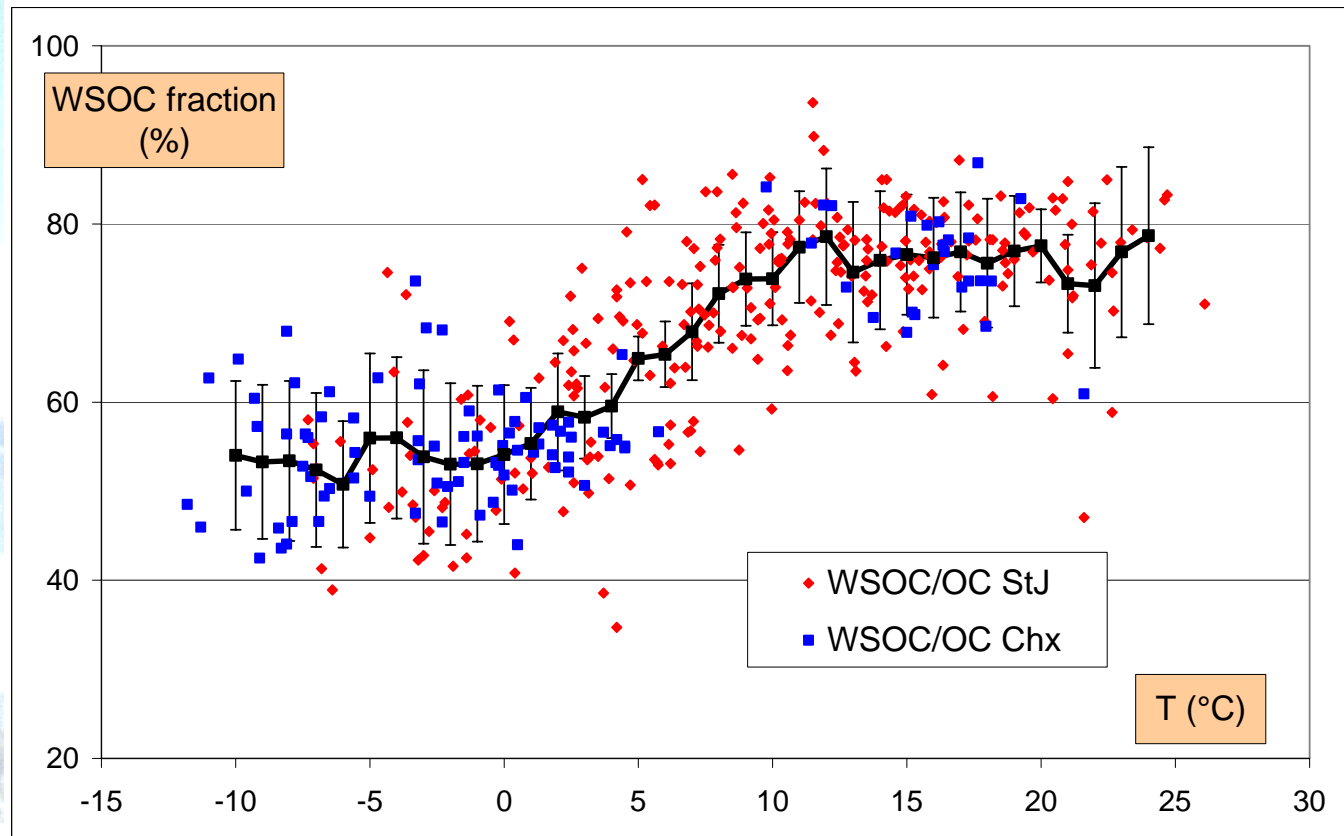
- Size distributions are very stable
- Centered at 0.5 - 0.6 μm in suburban and rural areas
- Formation of a mode below 100 nm in summer
- Also, formation of a mode in the super micron range

Associations between species



- OC in the range below 100 nm not associated with sulfate
- OC in the supermicron range associated with crustal particles

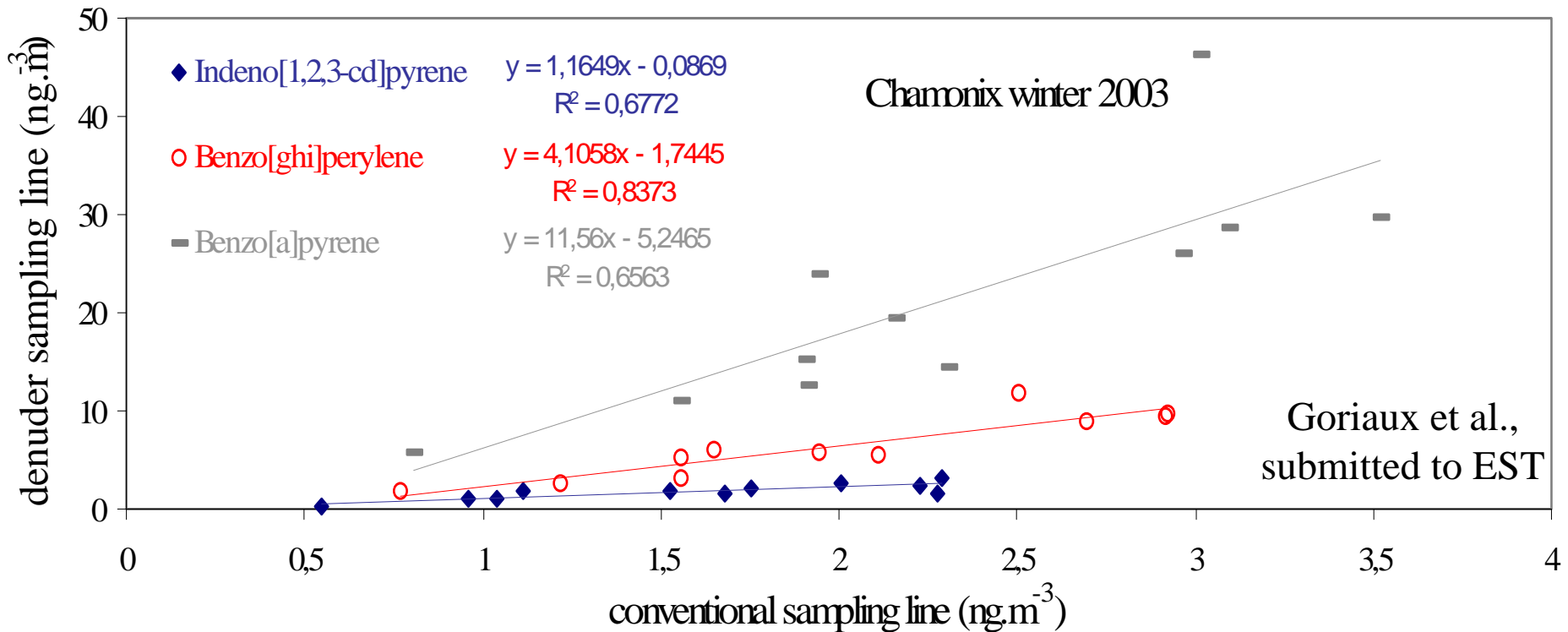
Solubility of OC



- **Seasonal cycles linked with changes in temperature**
- **Limiting processes for high and low values**
- **Range not so large between maxima and minima**

Sampling artifact :

comparison of denuded and un-denuded sampling of PAH



- Huge differences in the concentrations for some species
- Depends on the reactivity
- Attributed to oxidation on the filter of non denuded sampler

Take home message

- **In the valleys, high concentrations of primary species in winter are more problematic than secondary species in summer**
- **Atmospheric conditions are responsible for concentrations above threshold for PM_{10} (probably not linked with specific sources)**

Take home message

- In the valleys, high concentrations of primary species in winter are more problematic than secondary species in summer
- Atmospheric conditions are responsible for concentrations above threshold for PM_{10} (probably not linked with specific sources)
- Very large contribution of EC + OM to the PM_{10} mass
- Contributions from HD traffic and residential wood burning
- Secondary species in summer (but estimation of OC_{sec} problematic)

Take home message

- In the valleys, high concentrations of primary species in winter are more problematic than secondary species in summer
- Atmospheric conditions are responsible for concentrations above threshold for PM_{10} (probably not linked with specific sources)
- Very large contribution of EC + OM to the PM_{10} mass
- Contributions from HD traffic and residential wood burning
- Secondary species in summer (but estimation of OC_{sec} problematic)
- A disproportionate fraction of the mass is submicronic
- Size distribution gives good indication on processes and associations of species
- A large share of OC is soluble even in winter

Teams involved

POVA PI's :

- | | |
|---|--|
| • Jaffrezo JL (LGGE, Grenoble) (coordinateur) | Chimie des aérosols |
| • Chapuis D (AIR APS, Chambéry) (co coordinateur) | Espèces réglementées ; cadastres ; scénario, communication |
| • Jacob V (GRECA, Grenoble) | VOC |
| • Masclet P and Besombes JL (LCME, Chambéry) | HAP et Spéciation de la MOP |
| • Chazette P and Sanak J (LSCE, Gif / Yvette) | ULM instrumenté ; LIDAR |
| • Léoz E (INERIS, Verneuil) | HAP |
| • Fréjafon E (INERIS, Verneuil) | LIDAR |
| • Perros P (LISA, Créteil) | NO _y |
| • Chollet JP (LEGI, Grenoble) | Modélisation |
| • Dumolard P (SEIGAD, Grenoble) | Modèle de trafic |
| • George C (LACE, Lyon) | Code chimique |

Invités :

- | | |
|---|----------------------------------|
| • Wortham H (LCE, Marseille) | HAP |
| • Bergin M (Georgia Tech, Atlanta, GA, USA) | Taille des particules insolubles |

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Particles

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Modeling

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- Programme Primequal 2

- Self financing from laboratories
- CNRS, INERIS, CEA, AIR APS, ...
- Universities (UJF, Paris 12, UCB, etc)

Thank you for your attention !