

# VOC Measurements in France: results and outlook from long term monitoring and intensive campaigns

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and all co-workers*

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# Outline



## **Aim of the presentation**

What is the VOC monitoring strategy about?

## **VOC Monitoring**

Measurement methods

Levels & Trends

Source apportionment

## **Intensive campaigns**

additional data (New species...)

## **Conclusion and outlook**

# VOC Monitoring strategy

## Objectives

*From (EMEP/CCC, 1990)*

- Current ambient concentrations
- Efficiency of the emission control programme
- Support to the transboundary oxidant modelling

## EMEP monitoring strategy (2010-2019) for VOCs

<u>Level 2</u>			
Light hydrocarbons	C <sub>2</sub> -C <sub>7</sub>	Hourly	2002/3/EC and benzene in 2008/50/EC, WMO GAW
Carbonyls,	Aldehydes and ketones	8 hourly twice a week	2002/3/EC,
<u>Level 3</u>			
Hydrocarbons	C <sub>6</sub> -C <sub>12</sub>	Hourly/Daily	WMO GAW report No 172
Dry deposition flux of VOCs	OVOCs and terpenes	Hourly	

# EMEP Monitoring sites for VOC

2000



# EMEP Monitoring sites for VOC

2010



# VOC monitoring : Species

EMEP List (EMEP/CCC, 1990)	Required	Desirable	Interest	Measurement methods for French sites
Alkanes	<u>Ethane</u> <u>Propane</u> <u>i-butane</u> <u>n-butane</u> <u>i-pentane</u> <u>n-pentane</u>	<u>hexane</u> <u>branched hexanes</u> <u>heptane</u> <u>branched heptanes</u> <u>Octane</u>	<i>Primary anthropogenic compounds</i>	<b>Canisters + GC/FID/FID</b>
Alkenes	<u>Ethene</u> <u>Propene</u>  <u>Isoprene</u>	<u>butenes</u> <u>pentenes</u>	<i>Primary anthropogenic compounds (combustion) the most abundant biogenic compound</i>	
Alkynes	<u>Ethyne</u>		<i>main tracer of car exhaust</i>	
Aromatics	<u>Benzene</u> <u>Toluene</u> <u>o-xylene</u> <u>m,p-xylene</u> <u>Ethybenzene</u> <u>Trimethylbenzenes</u>	Styrene Propylbenzenes Ethyltoluenes	<i>anthropogenic precursor of SOA</i>	
Aldehydes	<u>Formaldehyde</u> <u>Acetaldehyde</u>	<u>propionaldehyde</u>	<i>Atmospheric photo-oxydation secondary product</i>	<b>DNPH + HPLC</b>
Ketones	<u>Acetone</u>	<u>methylethylketone</u> <u>methylvinylketone</u>	<i>Primary and secondary compounds, anthropogenic</i>	

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<b>Missing species</b>	<b>Methanol</b>  <b>Ethanol</b> <b>Acetonitrile</b> <b>Terpenes</b>  <b>DMS</b>		<i>oxidation products, biogenic emissions</i>  <i>Biomass burning tracer aerosol precursors Aerosol precursor, tracer for marine emissions/productivity</i>	<b>Other methods (e.g. : GC on-line system, PTRMS)</b>

# VOC monitoring : French sites



**FR15 Tardière**  
(>2003)



**FR08 Donon**  
closed (1997-2007)

**Cap Corse**  
>2012



**FR13 Peyrusse Vieille**  
>2001





# VOC monitoring : Method

## NMHCs C<sub>2</sub>-C<sub>9</sub>

Automatic sampler AVOCs

(Andersen co.)



**Canisters**  
**2 samples/week**  
**Mo. & Tu. 12-16HTU**  
**(6L. , 1 bar)**

Mines Douai Labs &  
Tera Envi co. (>2010)  
Analysis: TD-GC-2FID  
(within 3weeks)

DL: 10-20 ppt  
Accuracy: 5-9%  
Precision: 2-9%

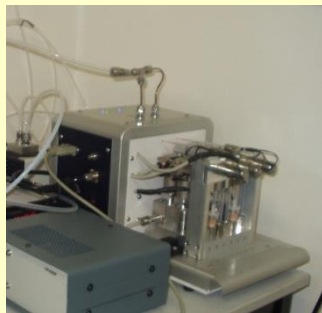
QA/QC following **EMEP** recommendations  
+NPL standard +... towards **ACTRIS (WP4)** « VOC Quality label »

## OVOCs C<sub>1</sub>-C<sub>7</sub>

(Carbonyls)

Automatic sampler SYPAC

(Tera env. co.)



**DNPH cartridges**  
**2 samples/week**  
**Mo. & Tu. 12-16HTU**  
**1,5 LPM**

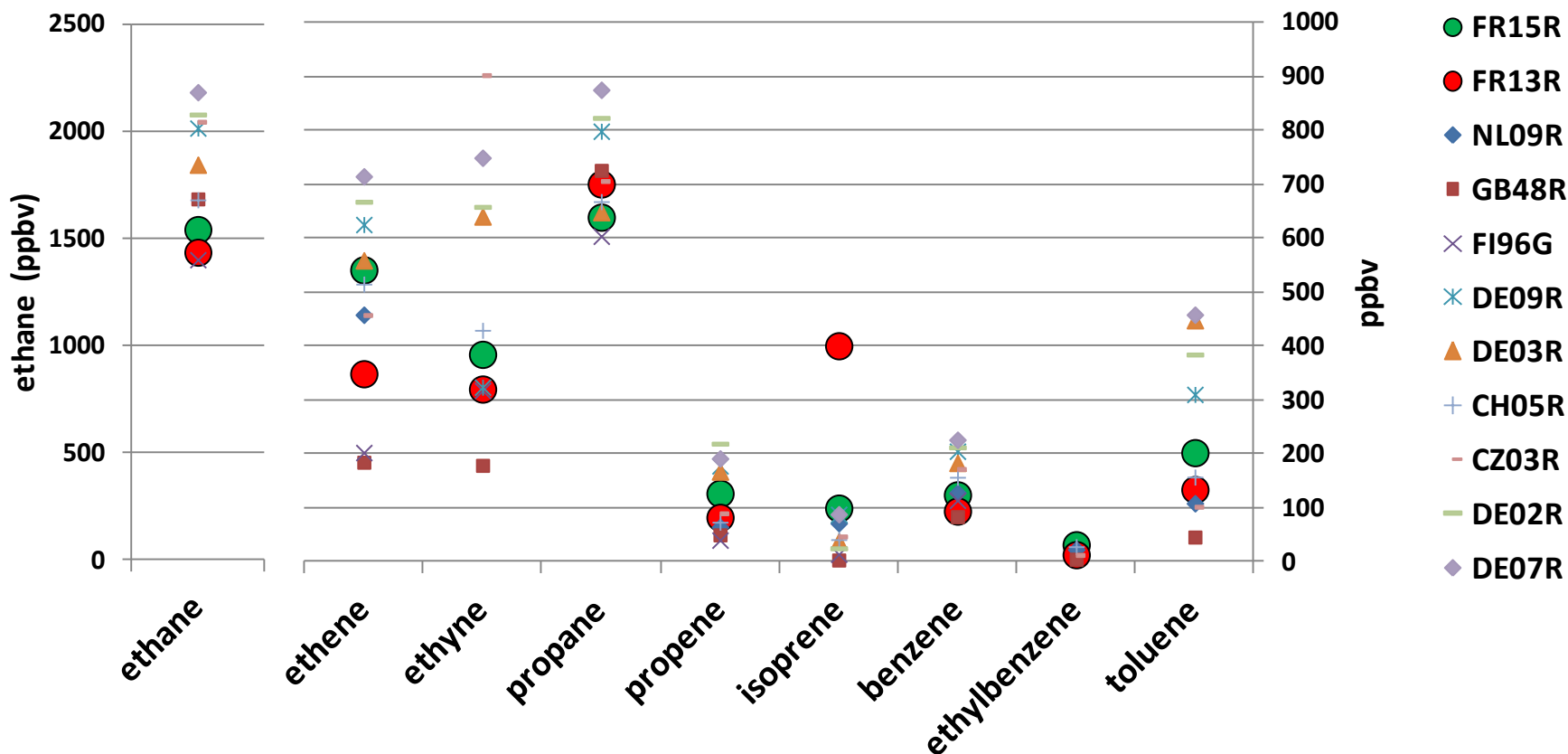
Mines Douai Labs &  
Tera Envi co. (>2010)  
Analysis: HPLC/UV  
(within 3weeks)

DL: 25 ng/m<sup>3</sup>  
Uncertainty: 11-25%

QA/QC following **EMEP** recommendations  
**ACTRIS (WP4)** still in progress for OVOCs

# VOC monitoring : Levels

## EMEP Sites : Annual mean in 2010

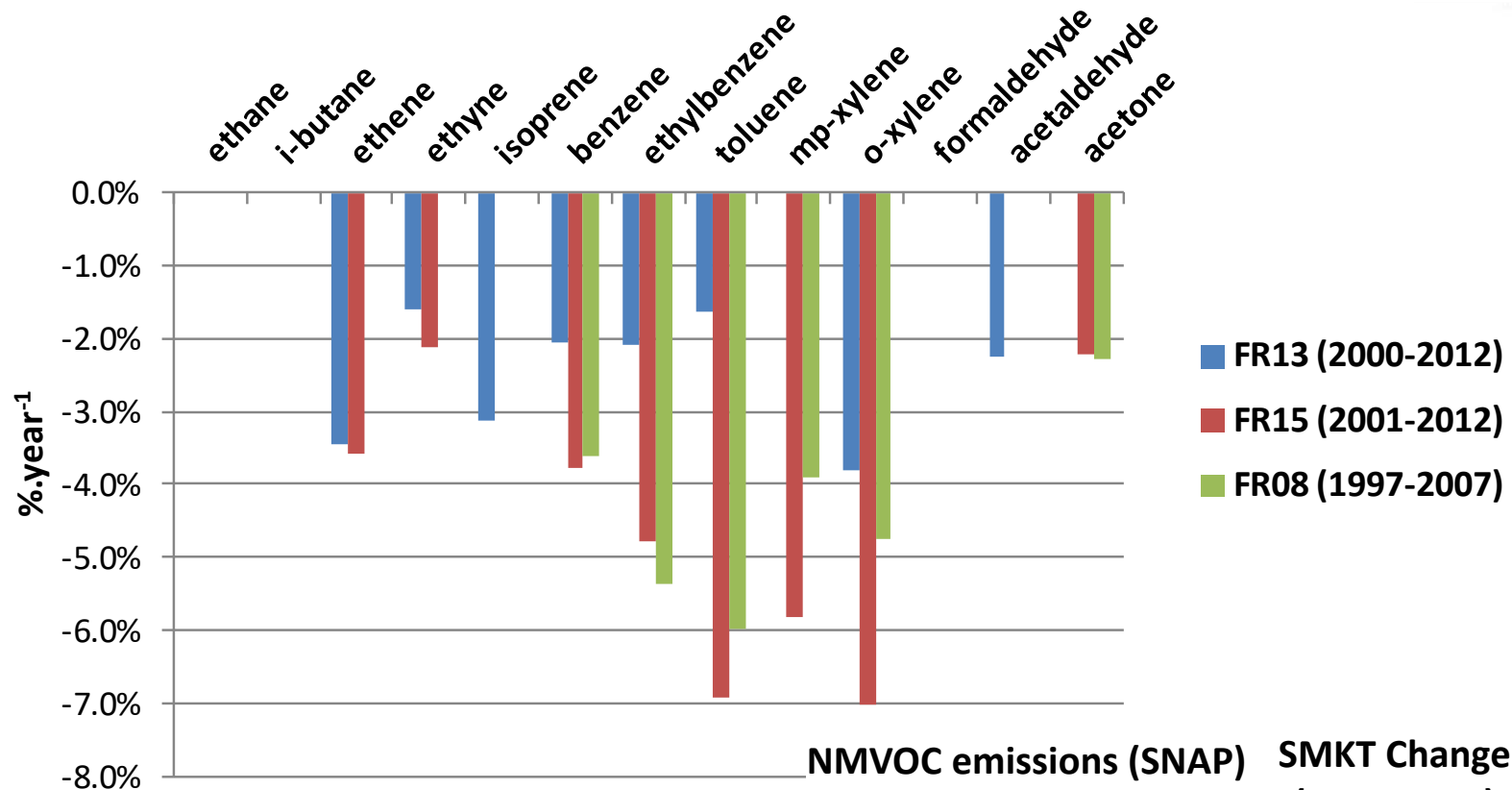


- Background levels for anthropogenic compounds
- Similar with other EMEP sites
- Sites more or less influenced by anthropogenic/biogenic sources

# VOC monitoring : Trends

Sen Man Kendall Test

significant change rate ( $p < 0,1$ ) of the **annual mean**

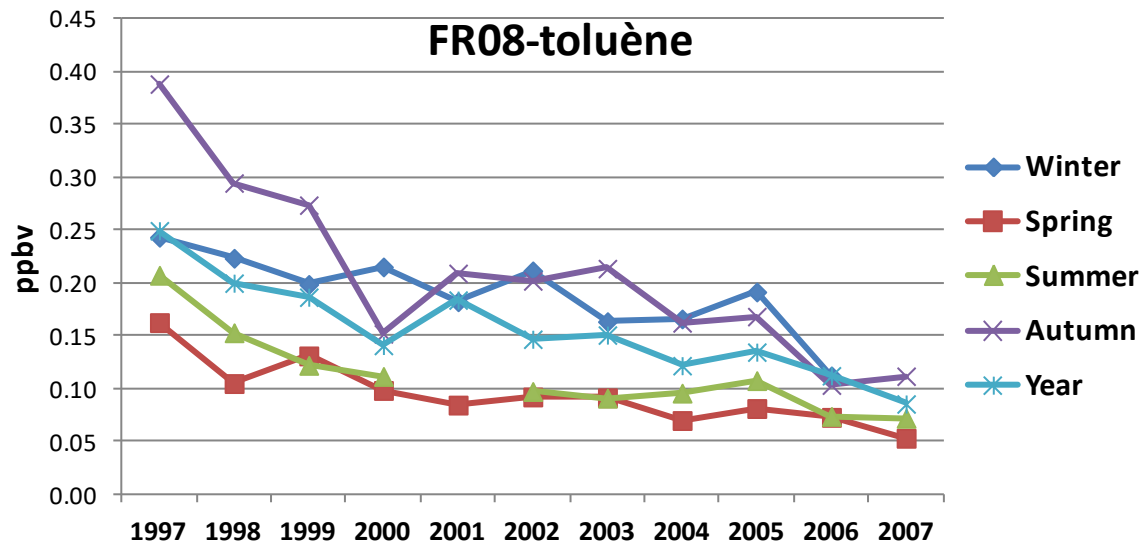


**1998/70/EC Car fuel regulations**

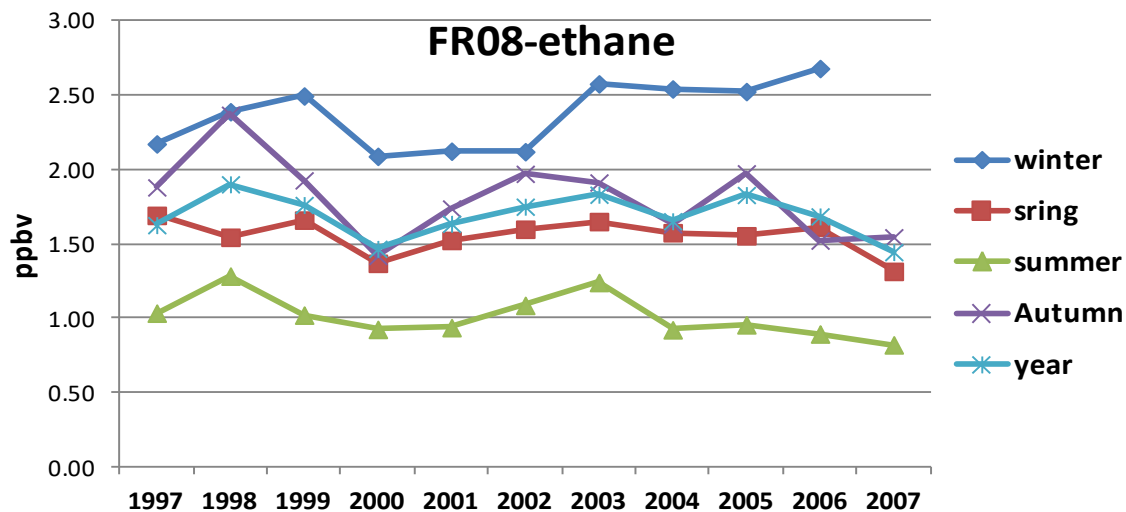
**1999/13/EC VOC emission targets and rules**

NMVOC emissions (SNAP) (data from CEIP)	SMKT Change (2002-2007)
Non industrial combustion	+0,4 %·yr <sup>-1</sup>
Road transport	-7.7 %·yr <sup>-1</sup>
Solvent use	-2,7 %·yr <sup>-1</sup>
<b>total sectors</b>	<b>-3,8 %·yr<sup>-1</sup></b>

# VOC monitoring : Seasonal Trends



Toluene → significant trends for all the seasons:  $-4$  to  $-7$   $\%.\text{yr}^{-1}$  ( $p < 0.01$ )

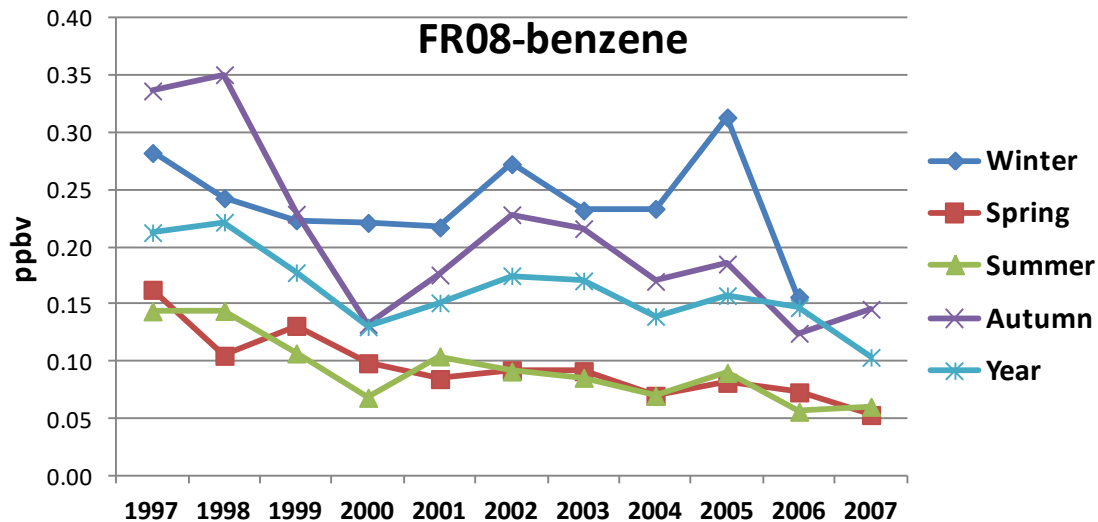


Ethane → from  $-2$   $\%.\text{yr}^{-1}$  in autumn to  $+1$   $\%.\text{yr}^{-1}$  in winter, no trend for the whole year !

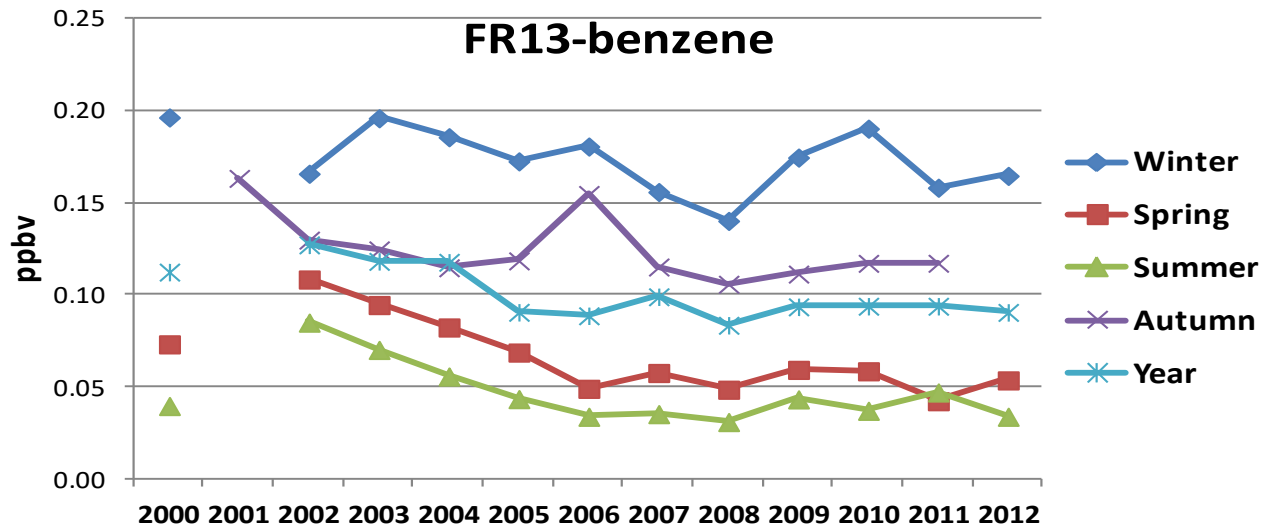
( $p < 0.05$ )

( $p < 0.1$ )

# VOC monitoring : Seasonal Trends



Benzene: significant trends for both sites but  
 - not significant in winter  
 - stable after 2006

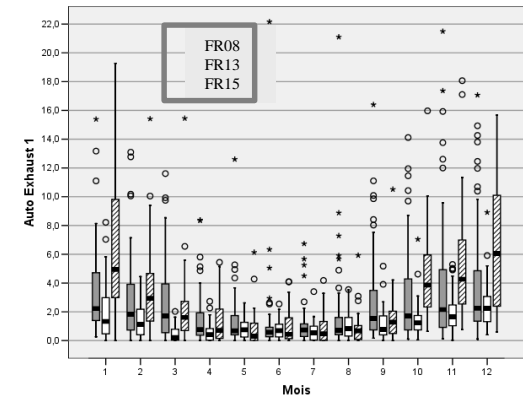
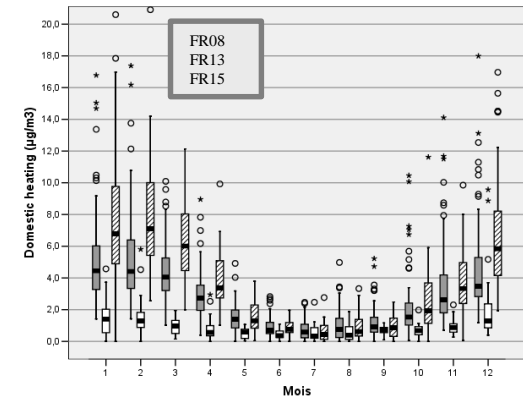
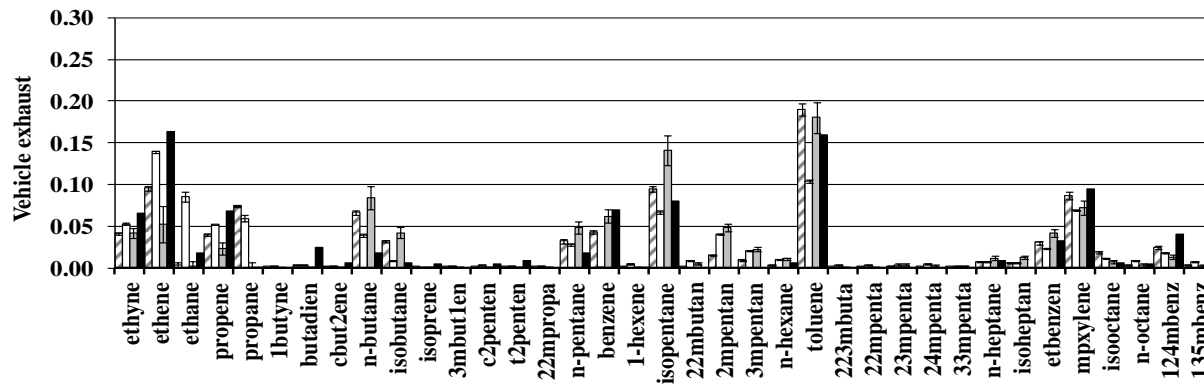
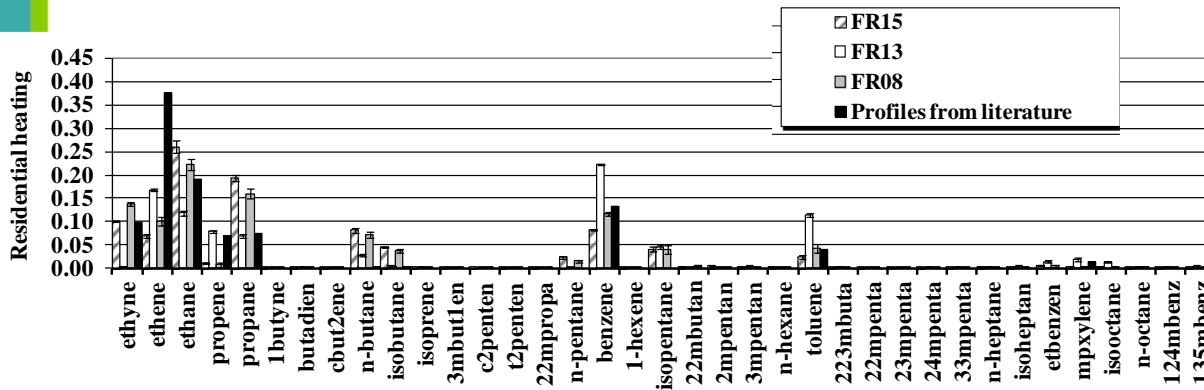


wood burning for residential heating → Main source in France since 2006 :(CITEPA)

# VOC monitoring : Source apportionment

## PMF to get aged profiles and their contributions

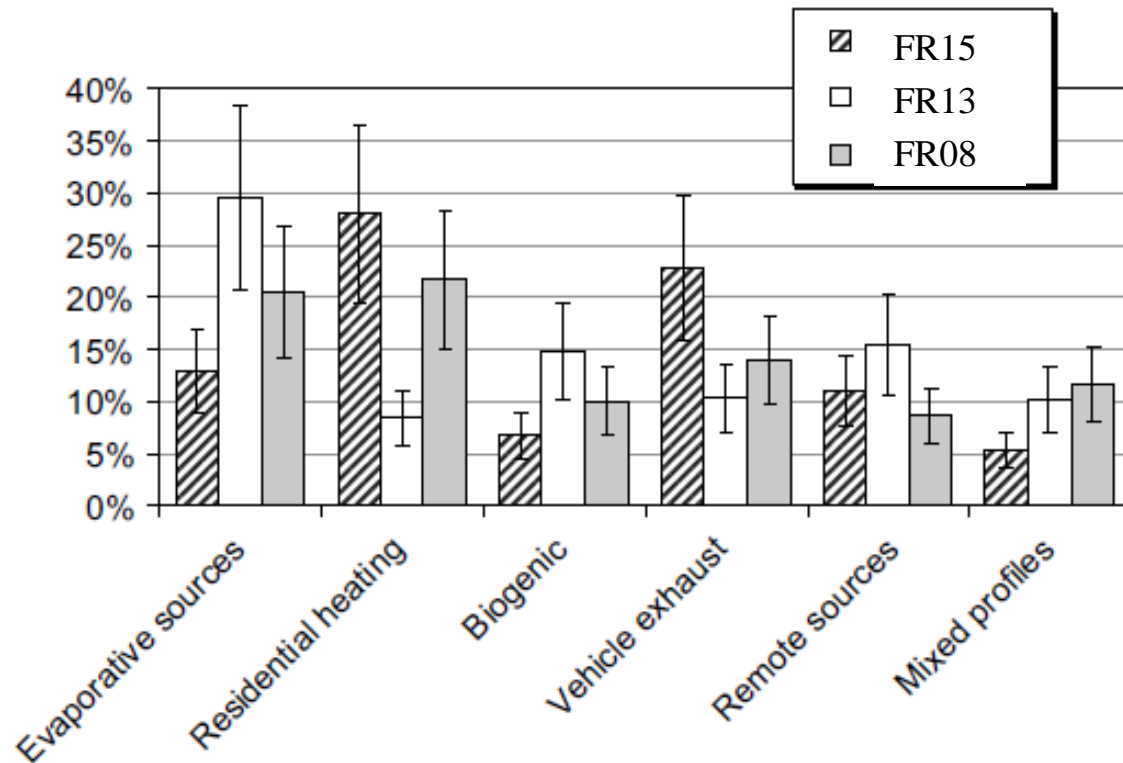
input data 46 NMHCs, FR08 (n=977), FR13 (n=505), FR15 (n=484)  
 measurement uncertainty + potential depletion/species/observations



# VOC monitoring : Source apportionment

## PMF to get aged profiles and their average contribution

Relative contribution and uncertainty over the 2002–2006 period



- Southern Site more under biogenic influence
- Residential heating higher in the North
- Further analysis of these contributions with air mass trajectories in order to locate potential source areas...

# Intensive campaign: Additional species

+ monitoring since 2012 in Cap Corse



Automatic sampler ACROSS

Carbo-pack C/B  
3 h, 100 mL/min

TD/GC/FID/MS

DL <10ppt

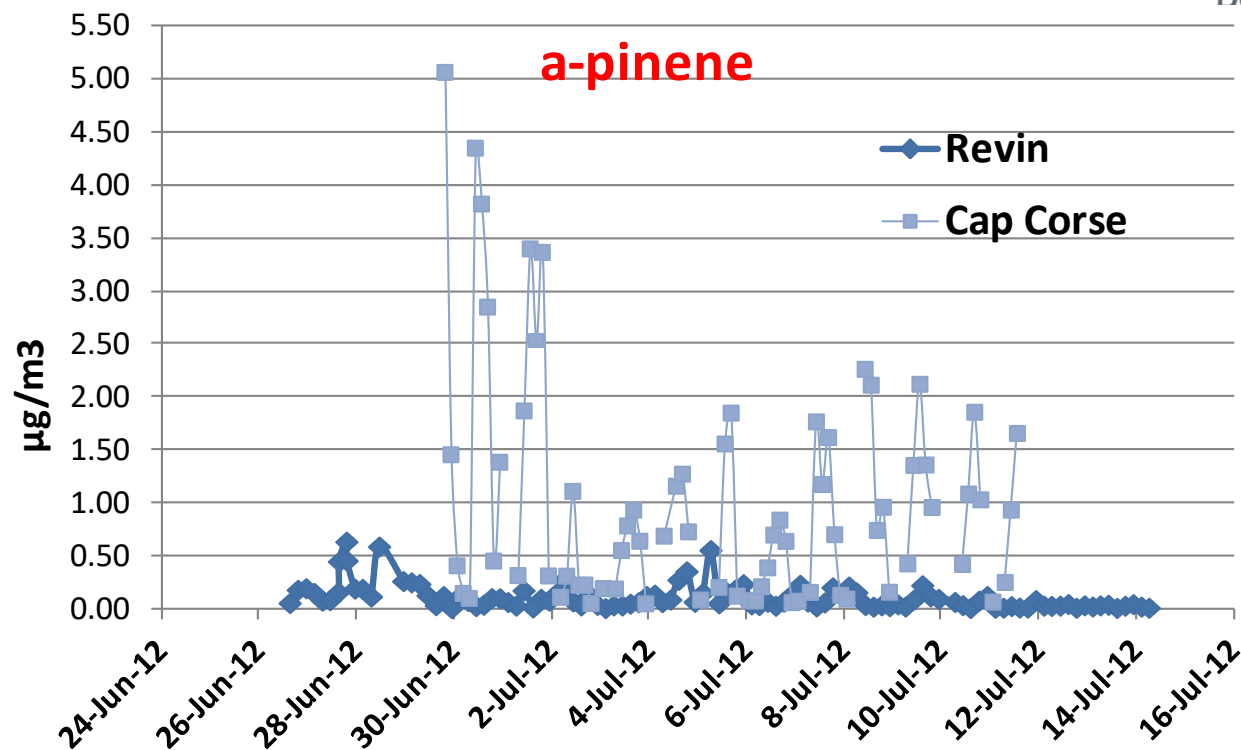


(see Detournay et al., 2011)

n-alkanes	C <sub>10</sub> -C <sub>16</sub>	Primary anthropogenic compound IVOC, important SOA precursor
n-aldehydes	C <sub>7</sub> -C <sub>12</sub>	Secondary products of atmospheric photo-oxidation
6 Terpenes	a,b-pinene limonene,...	Biogenic precursor of SOA

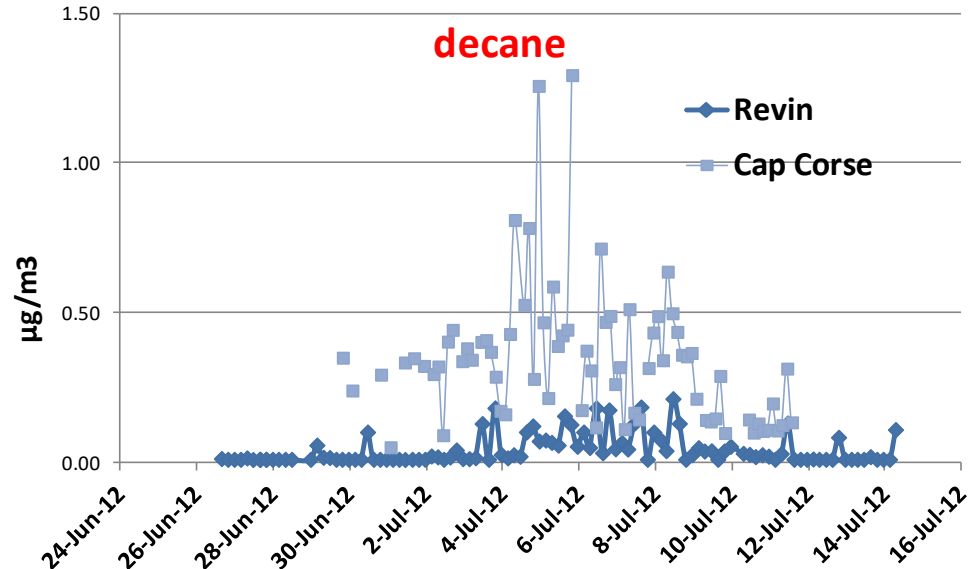


# Intensive campaign (summer):



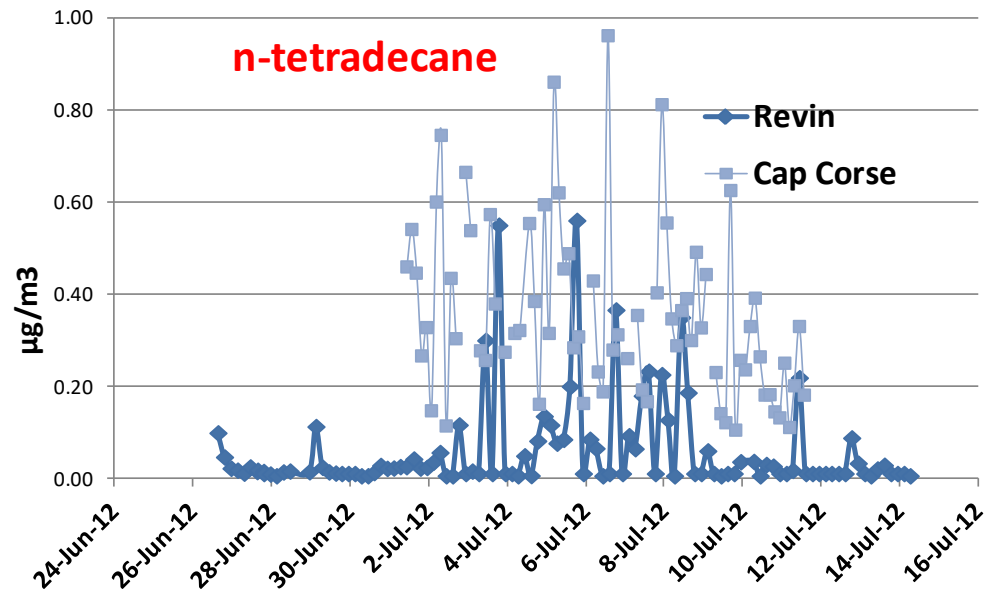
High level of biogenics in Cap Corse (a,b-pinene, isoprene, limonene) also derived products

# Intensive campaign (summer):



Low levels in heavy alkanes,  
lowest in the most anthropogenic  
influenced site (Revin)

Intermediate volatility (IVOCs)  
: linked to temperature



# Conclusion

- More than 10 years of VOC monitoring in France  
(same method, EMEP/ACTRIS)
  - VOCs = relevant tracers to characterize the site typology, air masses (aging, mixing, source typology, SOA precursors...)  
*French works: Borbon et al 2004 ; Sauvage et al 2009 ; Detournay et al 2013*
  - large database required to determine trends (study the efficiency of emission reduction policy)
  
- Intensive campaigns are the opportunity to perform new methods for new species and study the link with aerosols
  - the TOOC concept (C Hörger and S Reimann)
  
- Modelling support
  - French Work in progress (Primequal Project CARBOSOR)  
«Estimation of volatile organic compound emissions for Europe using data assimilation» *Koohkan et al, ACPD 2012*
  - What are the needs ?

Thank you !