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# NEW APPROACH TO REAL-TIME ANALYSIS OF MULTI-SITE VOLATILE ORGANIC COMPOUND (VOC) OBSERVATION DATA FROM AN INDUSTRIAL ZONE IN THE SOUTH OF FRANCE

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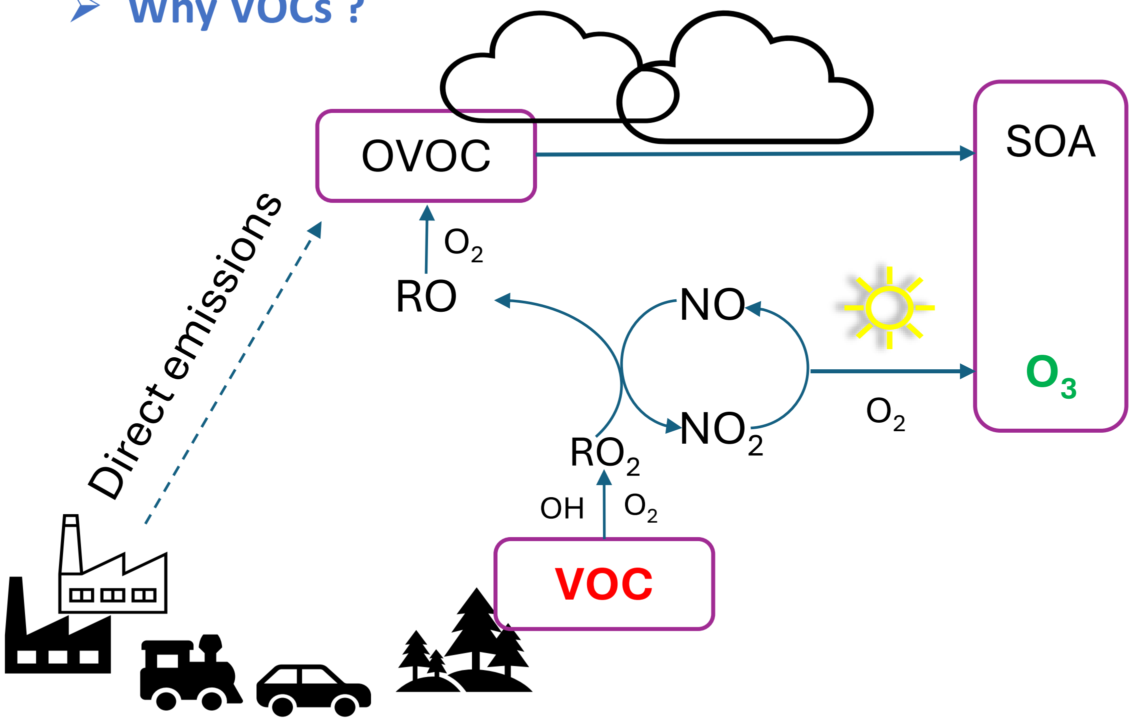
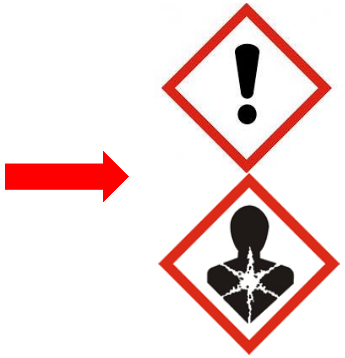
# CONTEXT

## ➢ Why VOCs ?



**Industrial activities :**
**25% of French chlorine production**
**40% of French VCM production**


- $O_3$ and PM threshold values exceeded in 2018- Benjamin Chazeau et al., 2021, Atmospheric chemistry and physics
- 1400 premature deaths and more than 1800 hospitalizations between 2010 and 2018 (Fine particles) - Khaniabadi et Sicard, 2021, Chemosphere

# STUDY AREA

★ Sites equipped with VOC analyzers


## Weather conditions

- ✓ Strong sunlight
- ✓ Specific air mass circulation

## Multiple sources

- ✓ Road transport
- ✓ Maritime transport
- ✓ Industrial

## Large population basin

- ✓ **1 903 173 inhabitants** (in 2020)

➔ More problematic

# Objective & methodology

## *Goal of study :*

**Identify sources using Positive Matrix Factorisation (PMF) and predict pollution events and the factors responsible for these episodes with Machine Learning using observed VOCs data**

## *Methodology :*

**Step 1 :**

- GC-FID analyser
- Online hourly observations
- 3 measurement stations
- Auxiliary parameters ($SO_2$, $NO_x$, PM, $O_3$…)

**Step 2 :**

- Data validation & QA/QC protocol
- Continuous control
- Uncertainty calculation

**Step 3 :**

- Identify main VOCs sources
- Descriptive analysis
- PMF & emission inventories

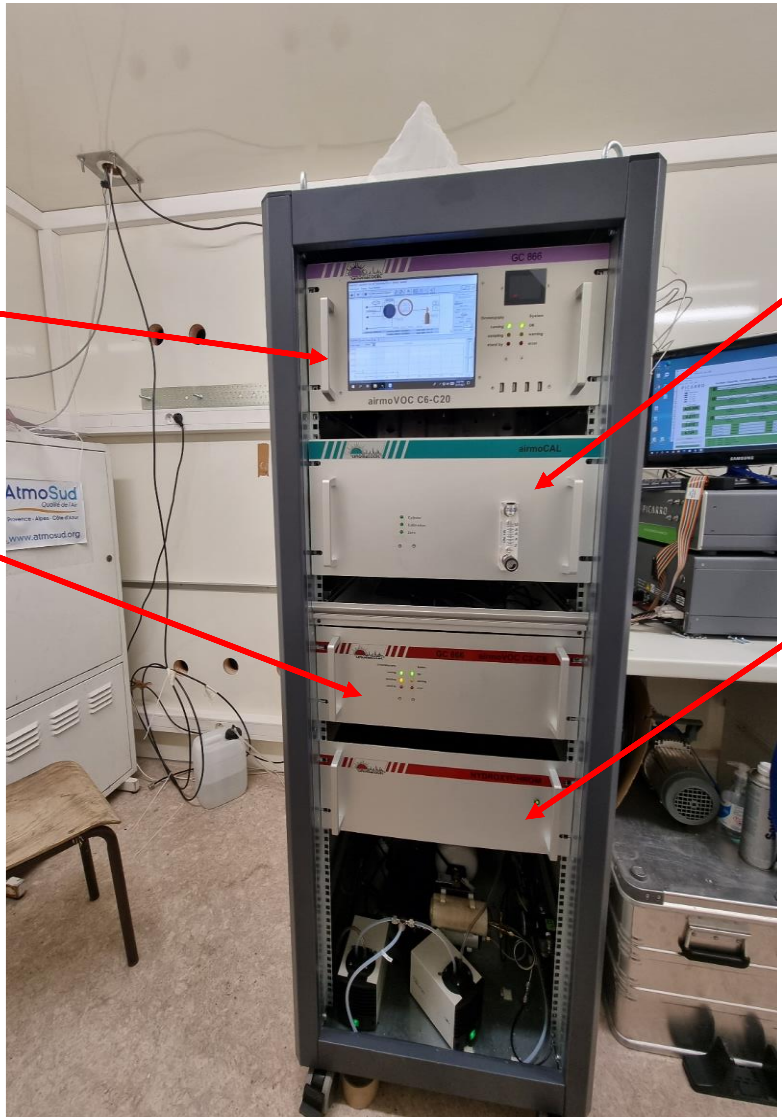
# ON-LINE VOC ANALYZERS

**airmoVOC :**

- GC-FID*
- 2 analytical chains for heavy (C6C20) and light (C2C6) compounds
- Preconcentrator
- Pneumatic injection valve

**airmoPURE :**

- Air generator, membrane dryer and catalyst
- Dry and zero air production




**airmoCAL :**

- 2 ovens + 2 heated valves
- Sampling and calibration system
- Permeation tubes

**hydroxychrom :**

- Hydrogen production (FID + carrier gas)

- 1m long PFA heated sampling line



*Gas chromatographs coupled to a flame ionization detector

# List of measured compounds

| 21 compounds C2-C6 | 23 compounds C6-C20 |
|---|---|
| N-butane | Benzene |
| N-hexane | Toluene |
| 1,3-Butadiene | Ethylbenzene |
| **Vinyl chloride monomer (VCM)** | M+P-xylene |
| Ethylene | O-xylene |
| Ethane | **1,2-Dichloroethane** |
| Propene | Cyclohexane |
| Propane | Trichloroethylene |
| Acetylene | Tetrachloroethylene |
| Trans-2-butene | Styrene |
| 1-Butene | Naphtalene |
| Cis-2-butene | 2,2-Dimethylbutane |
| Cyclopentane | 2-Methylpentane |
| Trans-2-pentene | 1-Hexene |
| Isopentane | 1,4-Dichlorobenzene |
| N-pentane | 123-Trimethylbenzene |
| Isoprene | 124-Trimethylbenzene |
| Methylcyclopentane | 135-Trimethylbenzene |
| 1-Pentene | Methylcyclohexane |
| Isobutane | N-nonane |
| Cis-2-pentene | N-octane |
| | N-heptane |
| | 3-Methylheptane |

**44 VOCs measured at the 3 stations**

**European Directive :** list of 31 ozone precursor compounds

**ANSES** : French Agency for Food, Environmental and Occupational Health and Safety)

(Saisine ANSES n° « 2015-SA-0218 »)

# Uncertainty evaluation

$$uX^2_{inc} = uX^2_{gp} + uX^2_{st} + uX^2_{v} + uX^2_{H2O} + uX^2_{m} + uX^2_{lp} + uX^2_{fp}\, uX^2_{blanc} + uX^2_{prec} + uX^2_{cal} + uX^2_{int} + uX^2_{l}$$

- Parameters related to :

***Environmental conditions of the site :***

- Gas pressure $uX^2_{gp}$ (µg.m$^{-3}$);
- Surrounding temerature $uX^2_{st}$ (µg.m$^{-3}$);
- Voltage variation $uX^2_{v}$ (µg.m$^{-3}$);
- Water vapor interference $uX^2_{H2O}$ (µg.m$^{-3}$);

***Equipment and sampling :***

- sampling line $uX^2_{lp}$ (µg.m$^{-3}$);
- particle filter $uX^2_{fp}$ (µg.m$^{-3}$);
- memory effect $uX^2_{m}$ (µg.m$^{-3}$);
- Uncertainty of blank $uX^2_{blanc}$ (µg.m$^{-3}$);

***Calibration and performance of the instrument :***

- Uncertainty of precision $uX^2_{prec}$ (µg.m$^{-3}$);
- Calibration uncertainty $uX^2_{cal}$ (µg.m$^{-3}$);
- Uncertainty of integration $uX^2_{int}$ (µg.m$^{-3}$);
- real linearity deviation $uX^2_{l}$ (µg.m$^{-3}$);

**Combined uncertainty calculation :**

- Benzene standard (**NF EN 14662-3 12-2015**) **:** Directive 2008/50/CE imposes a limit value of 25% for a concentration of 5 µg.m$^{-3}$.
- ACTRIS approach (**SOP-ACTRIS**)

# Uncertainty summary

- **The uncertainties** calculated for a **concentration of 5 µg/m³** at the three stations ranged from **9% to 20%**, depending on the compound;
- The uncertainty for **benzene**, the only regulated VOC, was around **9%**, well below the European directive limit of 25%;
- A detailed report on the calculation of uncertainties will be available to all AASQAs;
- **Every day**, the 3 stations generate **216 chromatograms**, i.e. a total of **9,504 peaks** to be analyzed daily;
- **Real-time storage** of hourly concentrations, with **specific uncertainties** linked to each concentration and each compound X (**Incert'R**),

# INCERT'R

## General information

### Developed by :

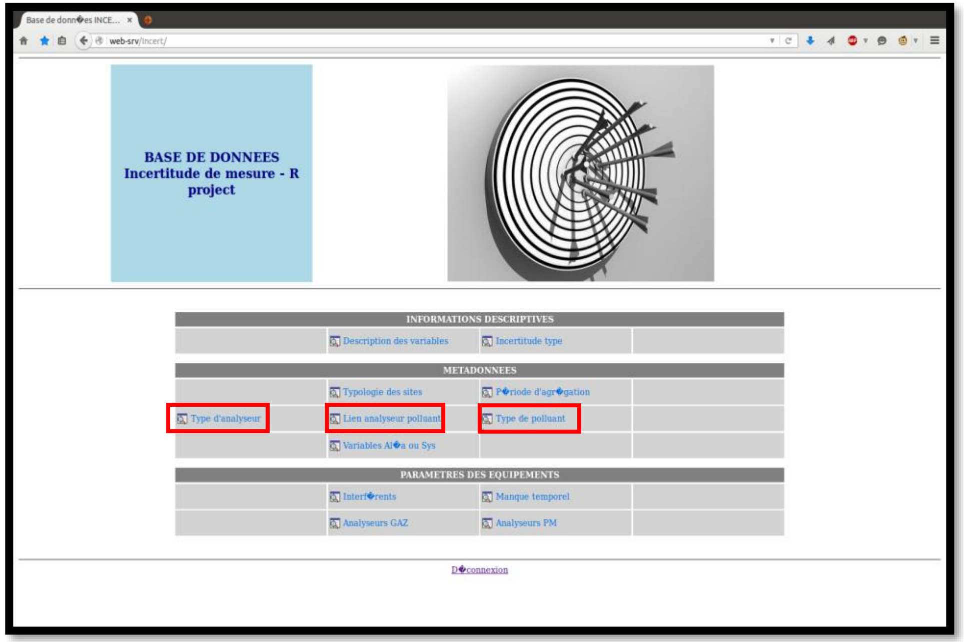
- Air Pays de la Loire;
- Airparif;
- Atmo Nouvelle-Aquitaine;

### Functionalities :

- Calculation of measurement uncertainties at various possible aggregation steps (15 min, hour, day, month, etc.) for regulated automatic measurements (gases and particulates) ;
- From 2023, a new module dedicated to VOCs was added with a help of Vladislav Navel, as part of my thesis;

### Basis of calculation :

- **Data :** Air quality measurements;
- **Complementary database :** Input of calculation parameters;
- **Algorithms :** A set of algorithms grouped together in an R software package;



# Positive Matrix Factorisation (PMF)

## ➢ PMF approach :

Multifactor analysis based on :

- Covariation of input variables;
- Conservation of mass

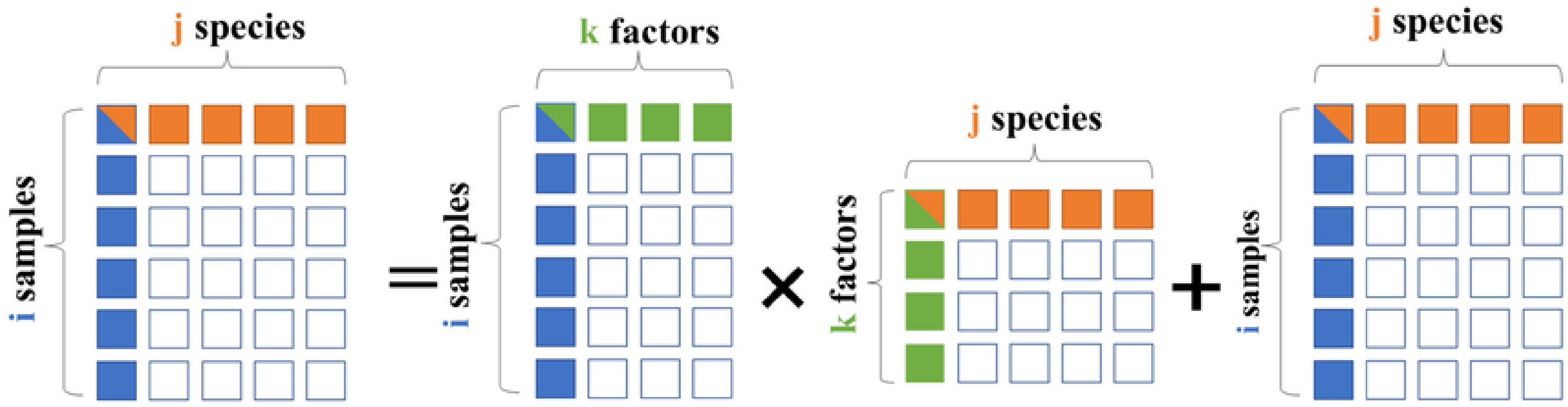
$$X_{i,j} = \sum_{p=1}^{p} \left( F_{i,k} \times G_{k,j} + E_{i,j} \right)$$

VOC measured matrix

Factor profiles (chemical composition)

Factor contribution (time series)

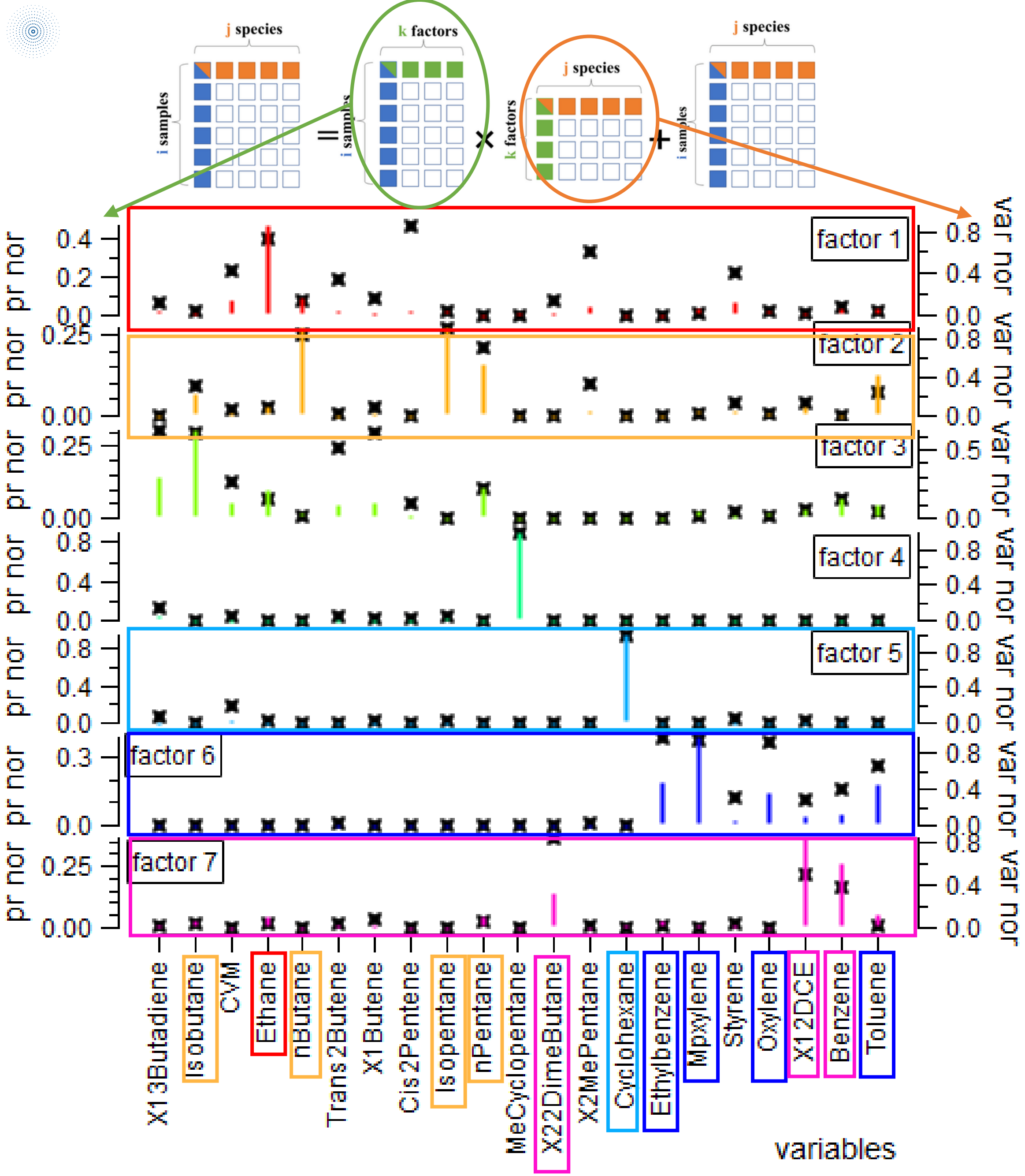
Residual matrix



# Preliminary result

➢ *Example of preliminary results obtained from the initial tests conducted using PMF :*

- Berre l'Etang station;
- Three months of hourly data (**March, April, and May 2022**);
- **5781** light and heavy column chromatograms, i.e. **121 401** processed peaks;
- **21 VOCs** analyzed;
- Factor analysis ranging from 3 to 12 factors across 20 runs;
- Final presentation of results using **7 factors;**
- **80%** of data are explained by the model.



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# Conclusion

- **Online VOCs measurement :** Continuous VOC monitoring using GC-FID at 3 stations since 2022;
- **Chromatogram Monitoring :** Daily oversight to prevent identification errors;
- **QA/QC Protocol Updates :** Ongoing improvements to the quality assurance and control procedures;
- **Uncertainty Calculation :** Uncertainty was calculated by combining the benzene standard with the ACTRIS approach;
- **Automation :** The uncertainty calculation process has been successfully automated (Incert'R).

# Perspectives

- **Expand PMF Analyses**: Conduct additional PMF studies across other seasons or extend the current analysis by another month, and perform the analysis for the years 2022 and 2023;
- **Source Identification**: Identify various VOC sources by integrating auxiliary parameters ($NO_x$, $SO_2$, Ozone, etc.);
- **Key Determinants**: Identify the main factors influencing the observed VOC concentrations;
- **PMF on all Measurement Sites :** Apply PMF on the 3 sites, then combine the result obtained from these stations to study the impact of one site on the others;
- **Automated Approach**: Implement PMF Rolling for automated source identification;
- **Pollution event prediction:** predict pollution events related to the formation of ozone and fine particles;
- **Emission Inventory Improvement**: Improve emission inventories, particularly for industrial emissions.

# THANK YOU FOR YOUR ATTENTION