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AtmoSud

Inspirer un air meilleur



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

Zahra Benmouhoub^{1,2}, Gregory Gille², Liselotte Tinel¹, Céline Cancedda², Vladislav Navel³, Stéphane Sauvage¹, Nadine Locoge¹

¹ IMT Nord Europe, Institut Mines-Télécom, University of Lille, Center for Energy and Environnement, 59500 Douai, France

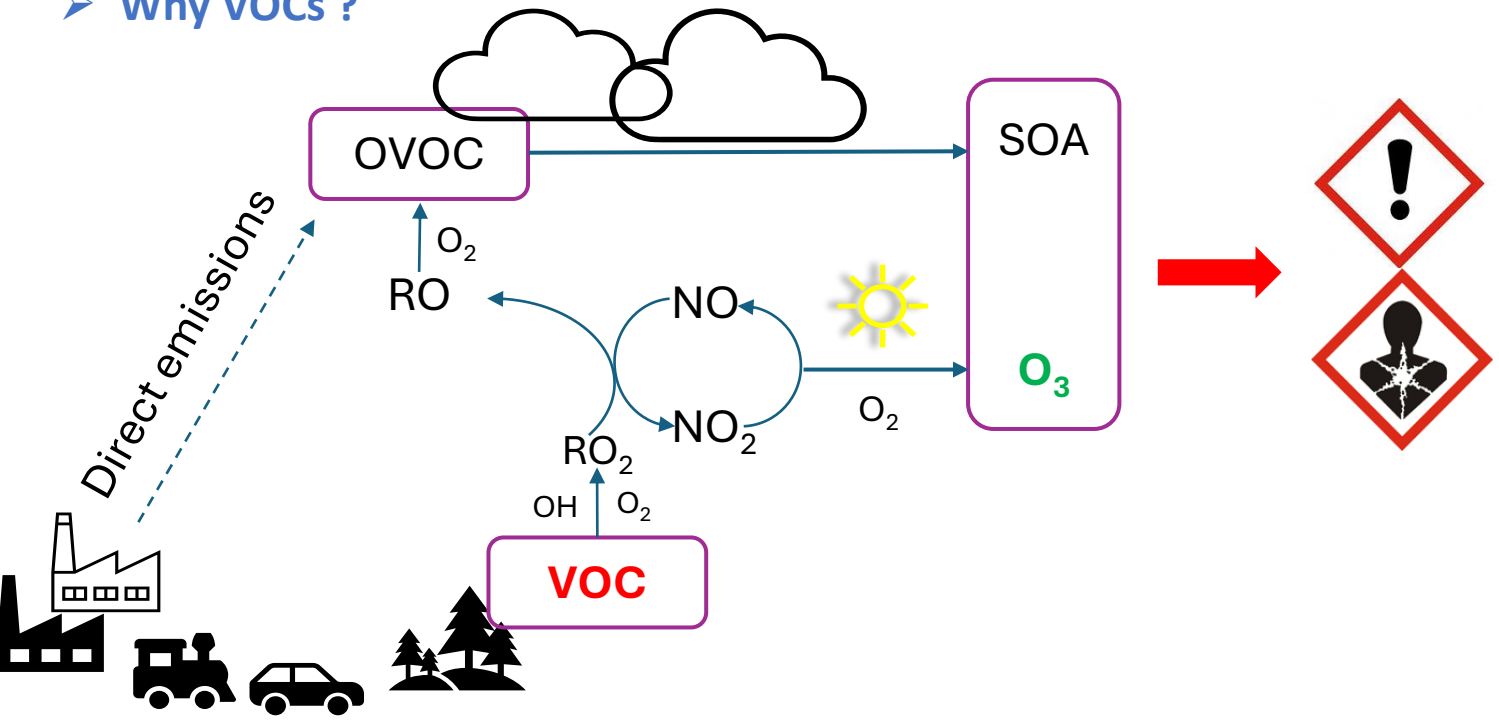
² AtmoSud, Le Noilly Paradis, 146 rue Paradis, 13006 Marseille, France

³ Atmo Nouvelle-Aquitaine, 13 All. James Watt Za, 33700 Mérignac, France



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 (SO₂, NO_x, PM, O₃...)

Step 2 :

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

Step 3 :

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

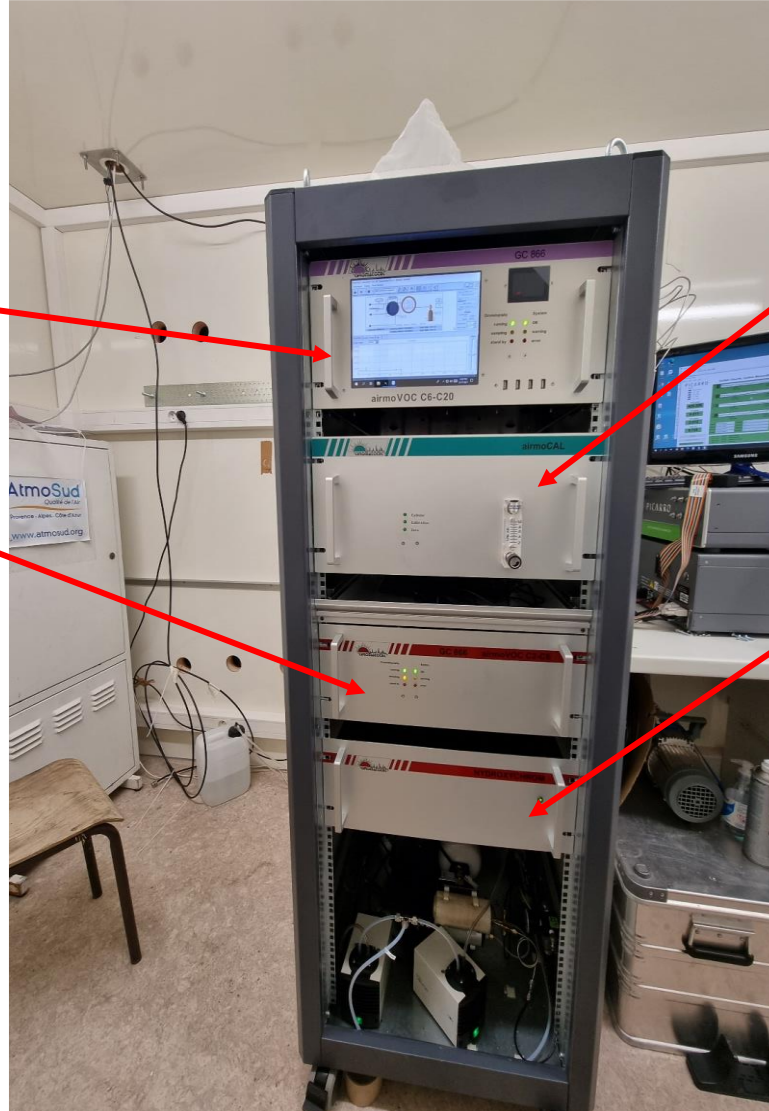
ON-LINE VOC ANALYZERS

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

LIST OF MEASURED COMPOUNDS

216 chromatograms in total,
9504 peaks per day for the 3 sites

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

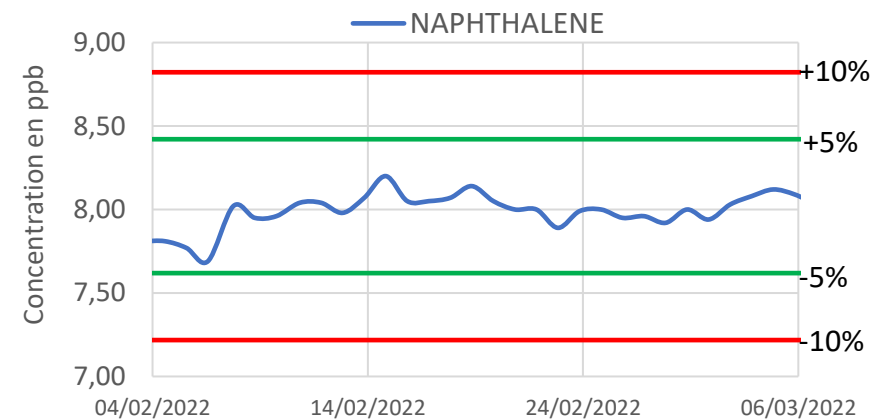
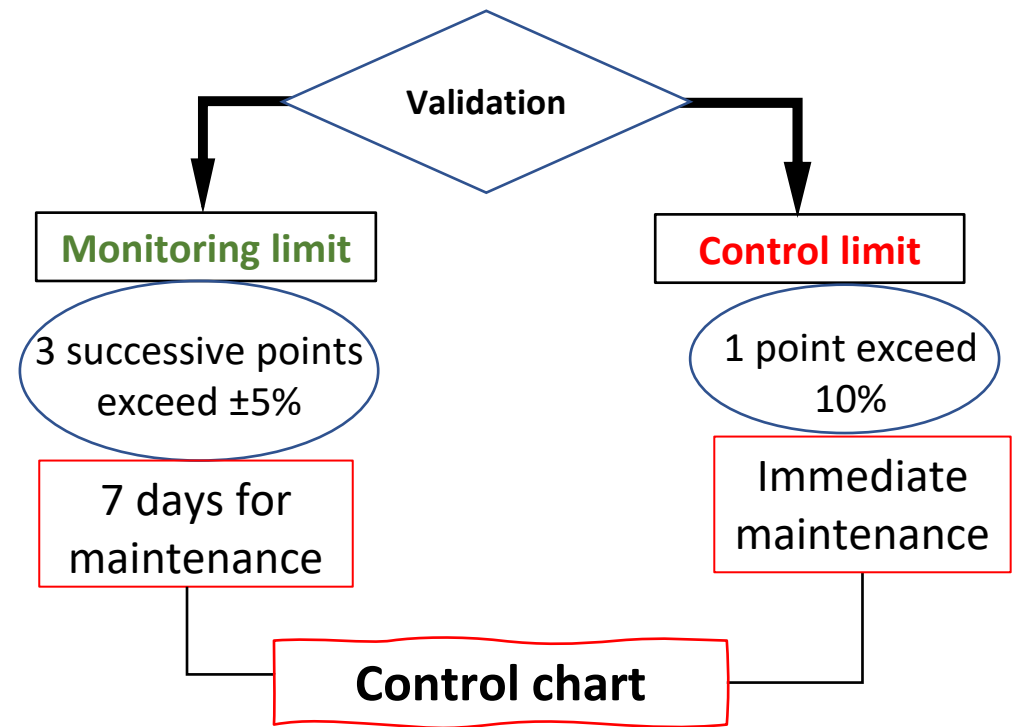
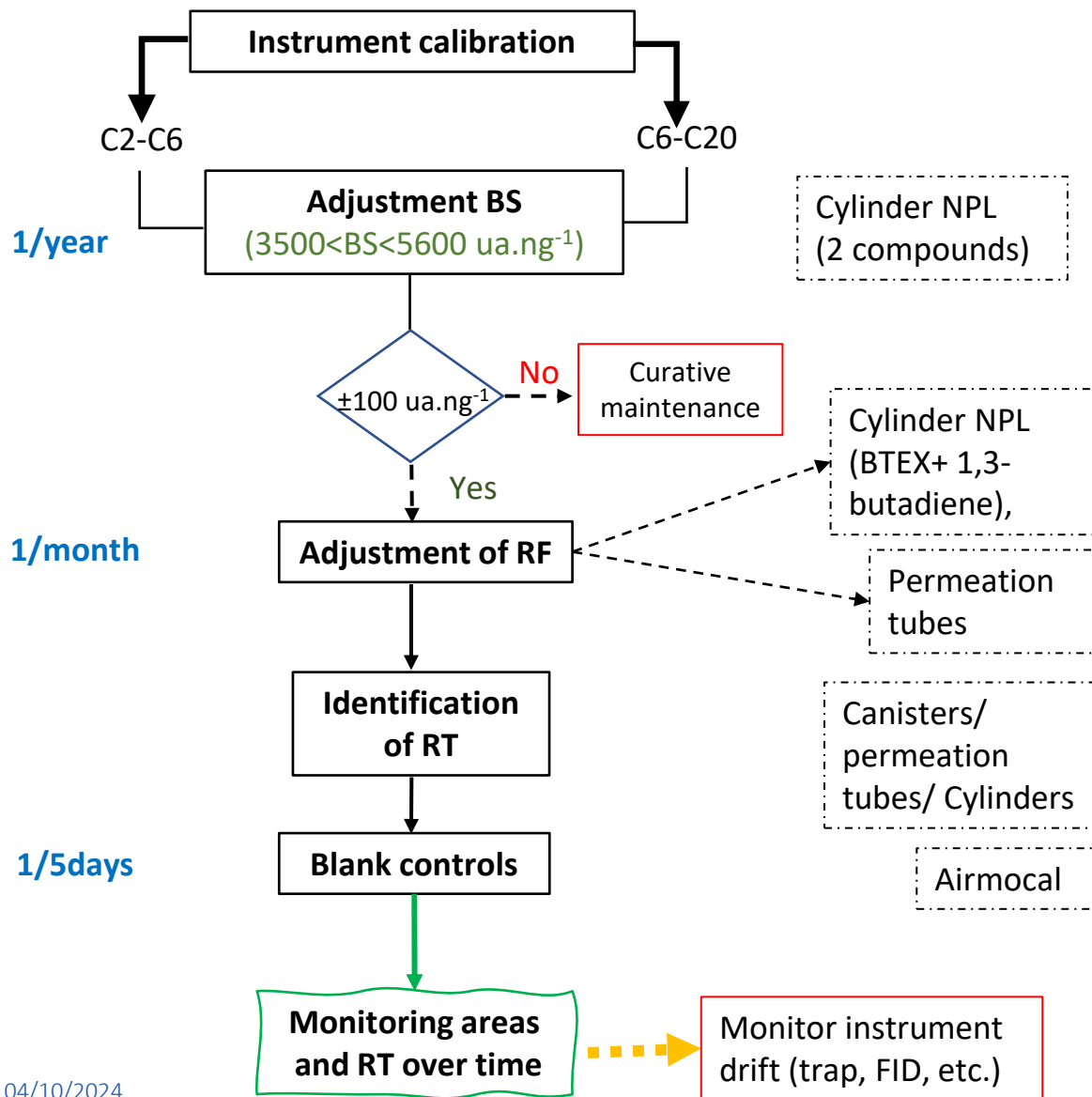
44 VOCs measured
at the 3 stations

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 »)

QA/QC



Variation of naphthalene concentrations over time

UNCERTAINTY EVALUATION

$$uX_{inc}^2 = uX_{gp}^2 + uX_{st}^2 + uX_v^2 + uX_{H2O}^2 + uX_m^2 + uX_{lp}^2 + uX_{fp}^2 + uX_{blanc}^2 + uX_{prec}^2 + uX_{cal}^2 + uX_{int}^2 + uX_l^2$$

➤ Parameters related to :

Environmental conditions of the site :

- Gas pressure uX_{gp}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- Surrounding temperature uX_{st}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- Voltage variation uX_v^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- Water vapor interference uX_{H2O}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);

Equipment and sampling :

- sampling line uX_{lp}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- particle filter uX_{fp}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- memory effect uX_m^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- Uncertainty of blank uX_{blanc}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);

Calibration and performance of the instrument :

- Uncertainty of precision uX_{prec}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- Calibration uncertainty uX_{cal}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- Uncertainty of integration uX_{int}^2 ($\mu\text{g}\cdot\text{m}^{-3}$);
- real linearity deviation uX_l^2 ($\mu\text{g}\cdot\text{m}^{-3}$);

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 $5 \mu\text{g}\cdot\text{m}^{-3}$.
- ACTRIS approach (**SOP-ACTRIS**)

UNCERTAINTY EVALUATION

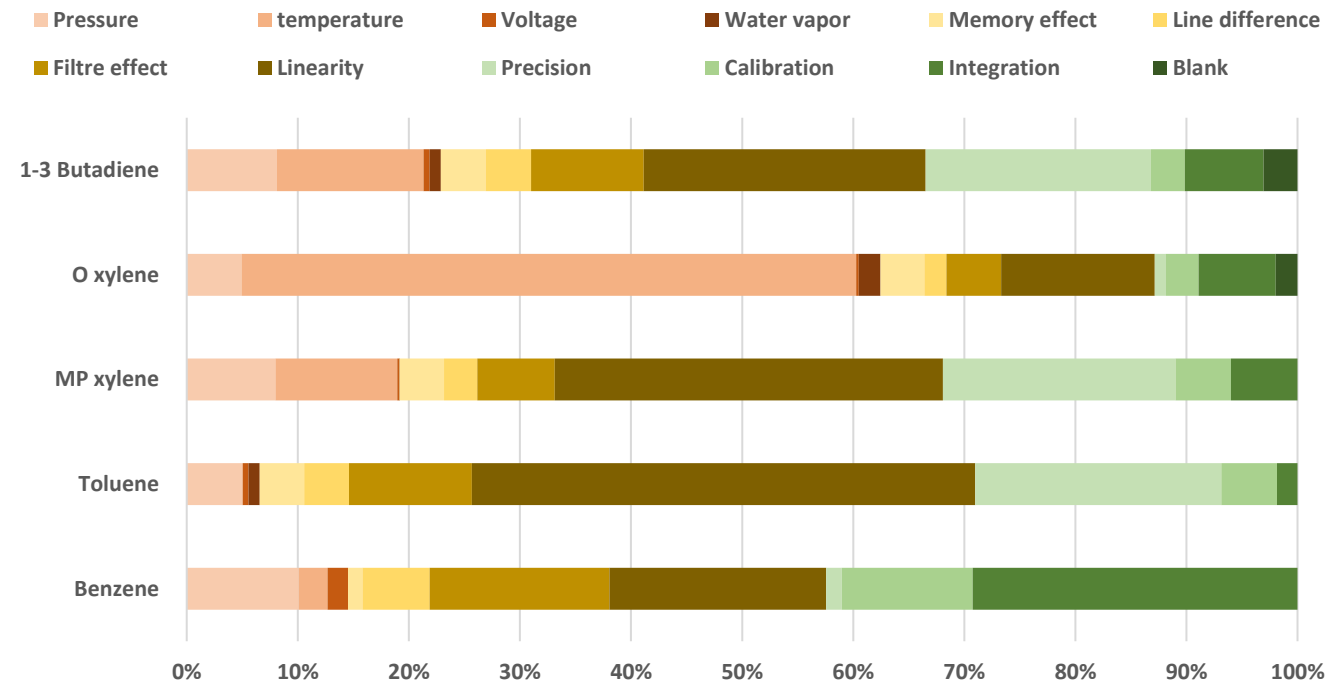
- Uncertainty calculation performed on the analyzer at the Berre station for a concentration of **5 $\mu\text{g m}^{-3}$**

$$\text{Expanded uncertainty} = 2 \times u_{X_{\text{inc}}} \times 100 / C_{\text{SAMPLE}}$$

	Expanded uncertainty
Unit	%
N-butane	11
CVM	15
1,3-butadiene	11
Benzene	9
Toluene	11
Ethylbenzene	11
M-P xylene	13
O-xylene	16

Benzene standard :
25 %

- The relative contribution of the uncertainties of 5 light and heavy VOCs



✓ Detailed uncertainties report

✓ Uncertainty automation with software (Incert'R)

INCERT'R

General information

Developed by :

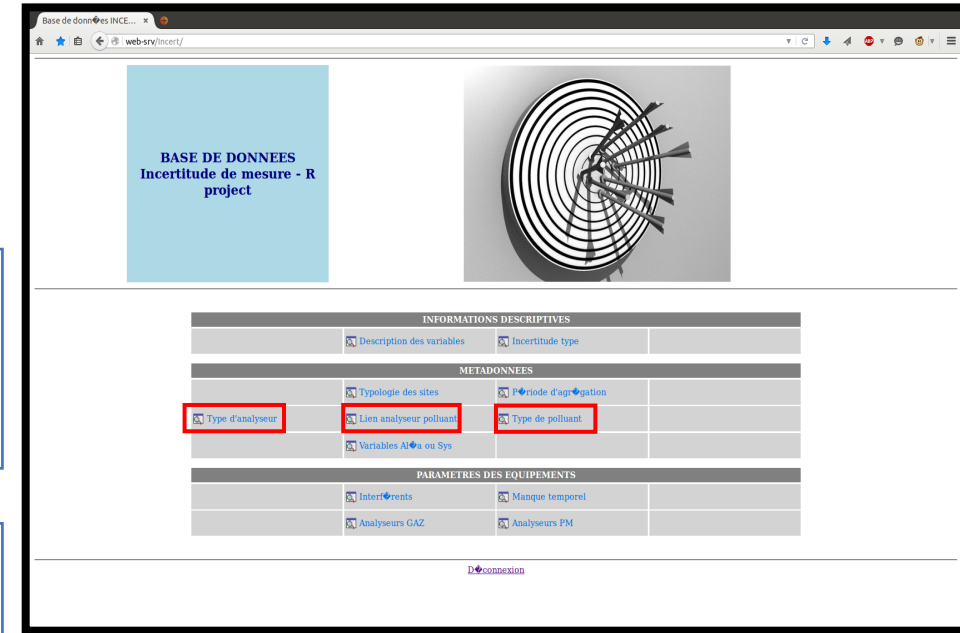
- Air Pays de la Loire;
- Airparif;
- Atmo Nouvelle-Aquitaine;

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;

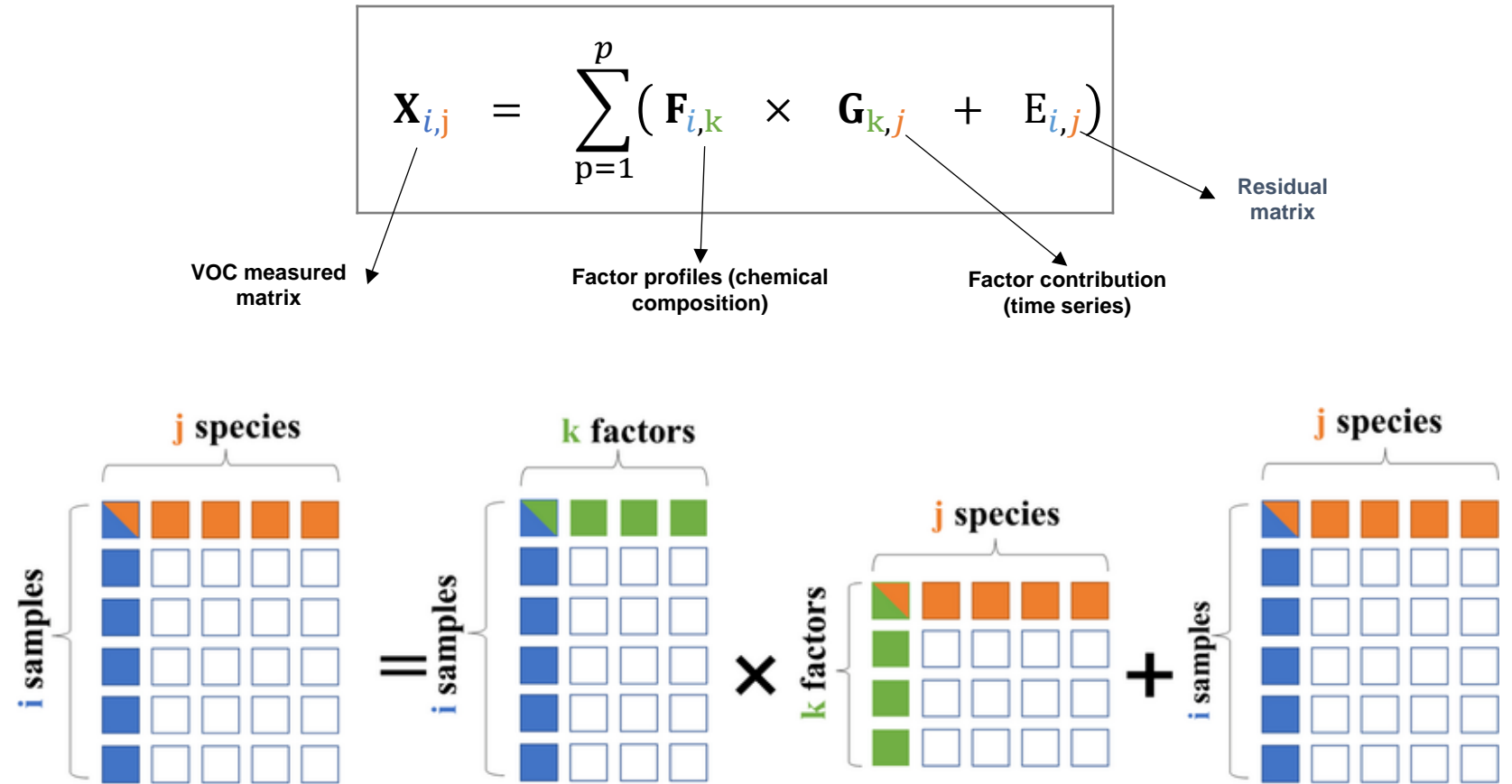


POSITIVE MATRIX FACTORISATION (PMF)

➤ PMF approach :

Multifactor analysis based on :

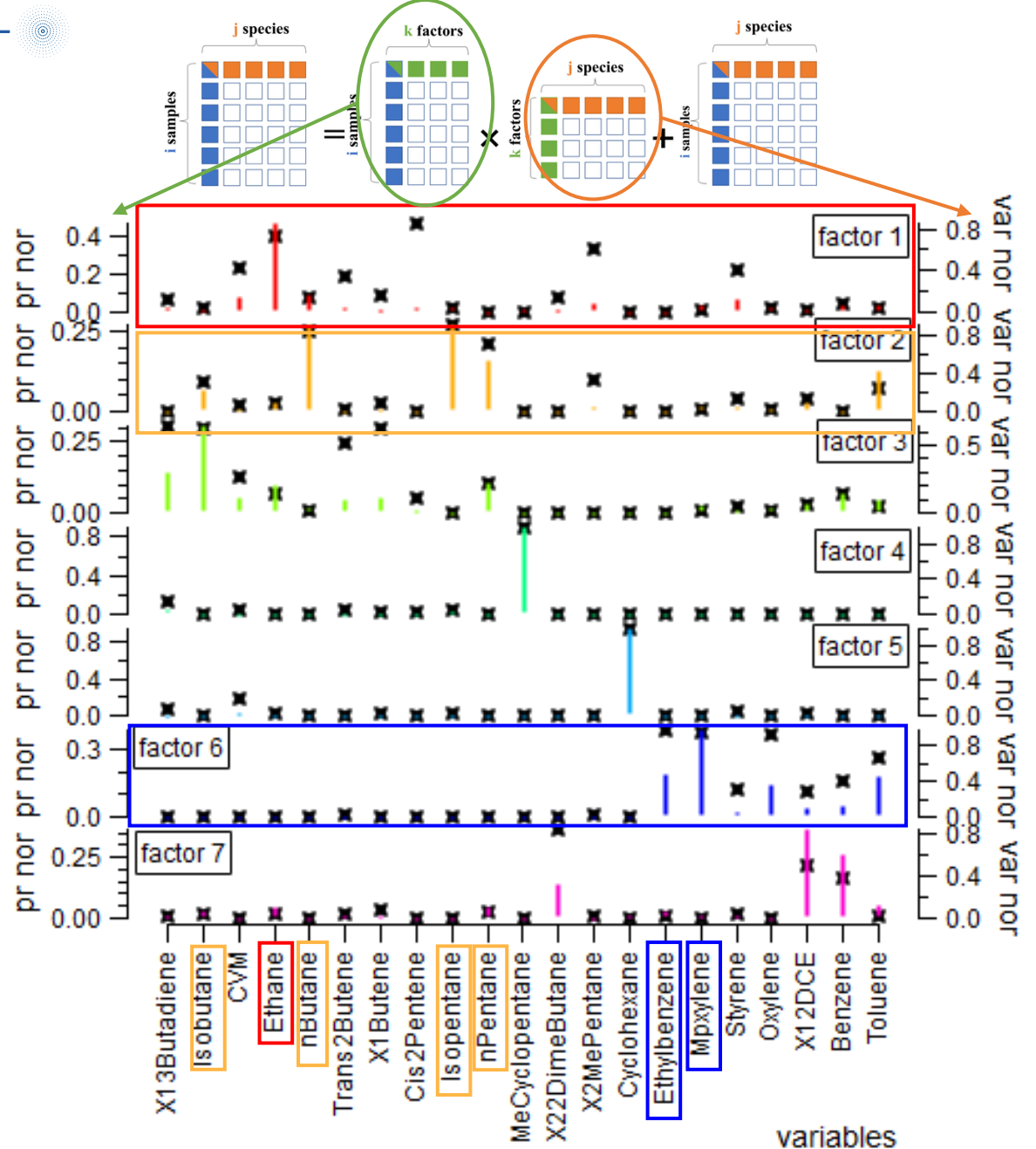
- Covariation of input variables;
- Conservation of mass



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.



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, SO₂, 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**

Calcul de base sensitivity :

$$BS(\text{u.a ng-1}) = RF \times A / C \times V$$

RF : facteur de réponse de n-butane (C2C6) et du benzène (C6C20) qui est égal à 1.

A : aire de pic de n-butane (C2C6) et du benzène (C6C20) (u.a).

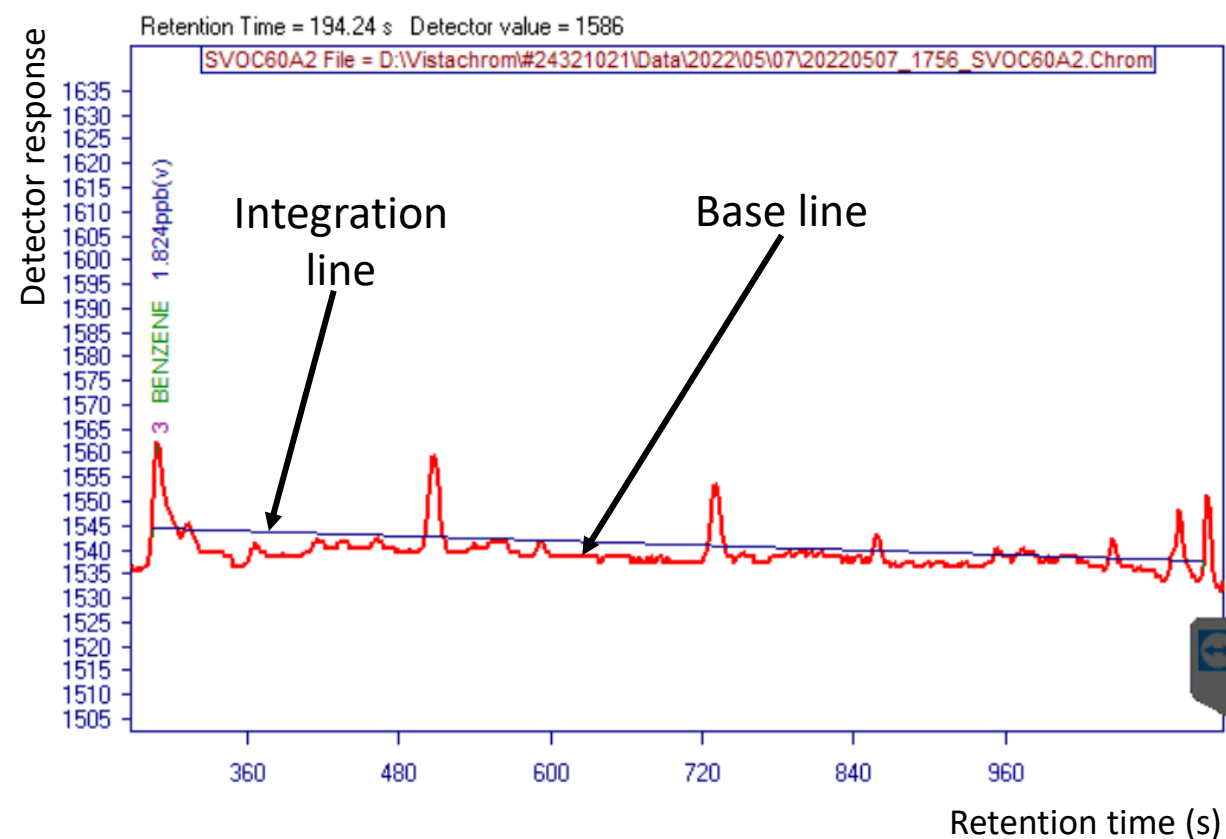
C : concentration en n-butane ou en benzène dans la bouteille de référence NPL (mg/m³).

V : volume d'air prélevé durant le cycle d'échantillonnage (ml).

DATA VALIDATION

Data reprocessing on 3 stations :

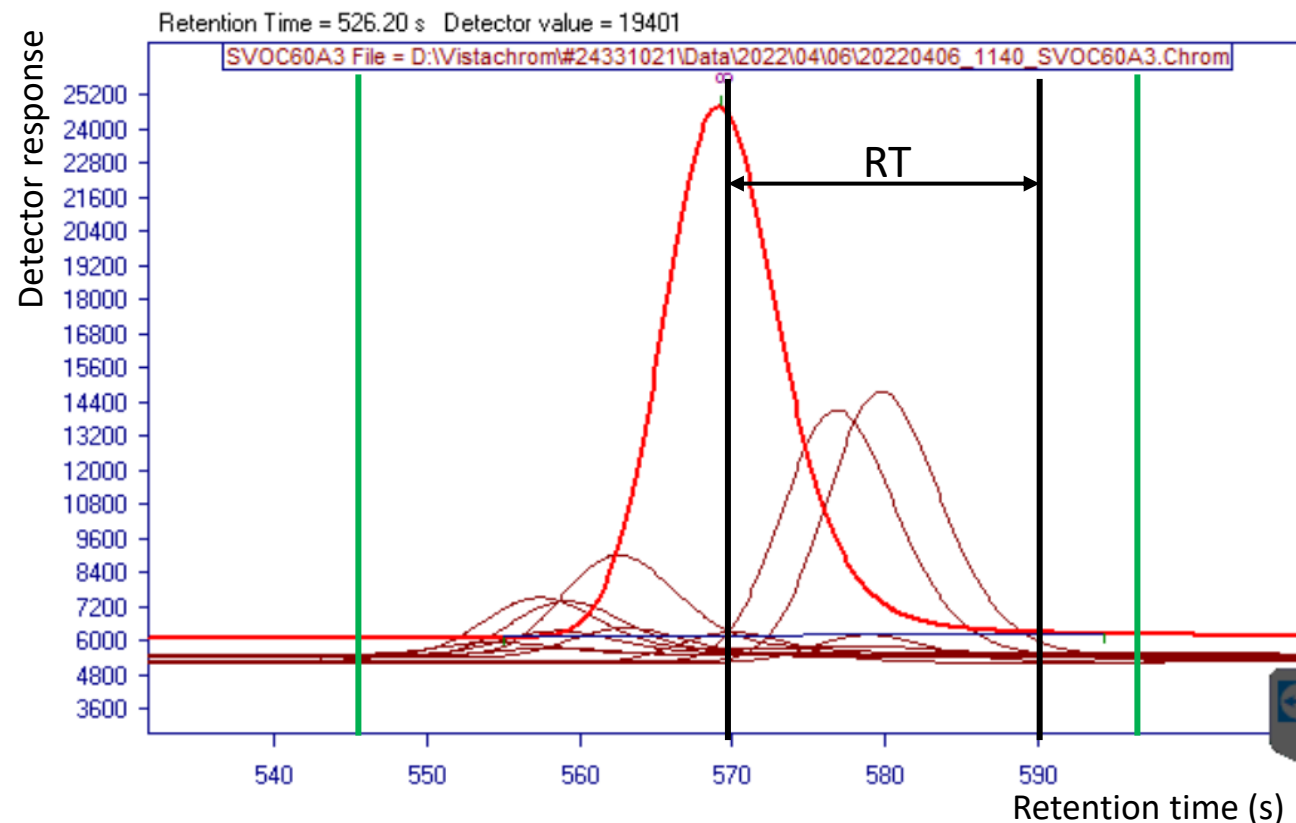
1) Identifying integration errors



Chromatogram showing benzene peak integration

216 chromatograms of light and heavy columns, totaling 7128 peaks to reprocess per day

2) Identifying identification errors



Chromatograms showing toluene peaks over one day

UNCERTAINTY EVALUATION

$$[O\text{-xylene}] = 60,26 \mu\text{g m}^{-3}$$

$$[M,P\text{-xylene}] = 121,82 \mu\text{g m}^{-3}$$

Temperature test for Chromatotec GC 866 FID airmoVOC (Model A21022, serial number 20730509), carried out at the span concentration for benzene (and the corresponding concentration values agreed by the certification body for determinands other than benzene) at 18°C and 24°C.

	ug m-3	ETHYLBENZENE	M&P-XYLENES	O-XYLENE	135-TMB	124-TMB	123-TMB
18°C	13/05/2011 13:39	56.72	109.16	50.49	54.70	Not Recognised	Not Recognised
	13/05/2011 14:09	59.69	116.19	54.07	61.41	Not Recognised	Not Recognised
	13/05/2011 14:39	60.42	117.80	54.94	63.50	Not Recognised	Not Recognised
	13/05/2011 15:09	60.93	121.47	60.22	64.21	64.19	Not Recognised
	13/05/2011 15:39	60.95	121.60	60.19	64.62	Not Recognised	Not Recognised
	13/05/2011 16:09	61.06	121.82	60.26	65.00	65.20	63.53
	MEAN / ug m-3	60.84	120.67	58.90	64.33	64.69	63.53
24°C	16/05/2011 14:09	58.98	111.75	52.37	57.39	55.66	53.13
	16/05/2011 14:39	61.56	117.65	55.32	63.18	62.92	60.40
	16/05/2011 15:09	62.11	119.01	56.11	64.70	64.77	62.86
	16/05/2011 15:39	62.21	119.34	56.27	65.38	65.61	63.89
	16/05/2011 16:09	62.33	119.50	56.31	65.61	66.06	64.49
	16/05/2011 16:39	62.15	119.37	56.21	65.60	66.27	64.43
	MEAN / ug m-3	62.20	119.30	56.23	65.32	65.68	63.92
K (% / K)	0.12	0.06	0.24	0.08	0.08	0.03	

Temperature test for Chromatotec GC 866 FID airmoVOC (Model A21022, serial number 20190309), carried out at the span concentration for benzene (and the corresponding concentration values agreed by the certification body for determinands other than benzene) at 18°C and 24°C.

	ug m-3	ETHYLBENZENE	M&P-XYLENES	O-XYLENE	135-TMB	124-TMB	123-TMB
18°C	13/05/2011 13:39	57.95	114.02	55.89	55.75	53.19	50.30
	13/05/2011 14:09	60.53	120.20	59.26	62.31	61.44	59.07
	13/05/2011 14:39	61.06	121.42	60.02	63.97	63.66	61.65
	13/05/2011 15:09	61.16	121.85	60.29	64.58	64.54	62.72
	13/05/2011 15:39	61.13	121.86	60.30	64.90	65.00	63.30
	13/05/2011 16:09	61.06	121.82	60.26	65.00	65.20	63.53
	MEAN / ug m-3	61.10	121.74	60.21	64.61	64.60	62.80
24°C	16/05/2011 14:09	59.03	111.08	52.11	57.06	55.33	52.78
	16/05/2011 14:39	61.30	116.21	54.75	62.63	62.13	60.25
	16/05/2011 15:09	61.77	117.30	55.34	64.00	63.96	62.39
	16/05/2011 15:39	61.85	117.54	55.47	64.53	64.73	63.25
	16/05/2011 16:09	61.87	117.69	55.54	64.77	65.08	Not Recognised
	16/05/2011 16:39	61.73	117.53	55.47	64.83	65.24	63.89
	MEAN / ug m-3	61.81	117.51	55.45	64.53	64.75	63.18
K (% / K)	0.06	0.18	0.42	0.01	0.01	0.03	

The sensitivity coefficient b_{ts} ($(\mu\text{g m}^{-3})/\text{K}$) is given by :

$$b_{Ts} = \frac{|C_{Ts,max} - C_{Ts,min}|}{|\Delta Ts|}$$

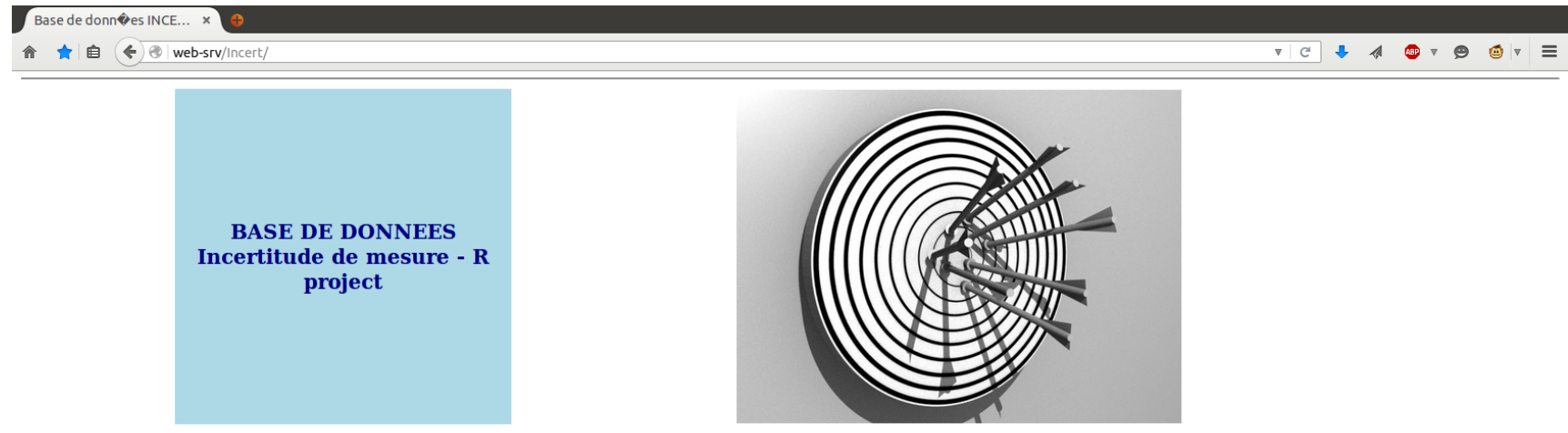
$$b_{Ts} (O\text{-xylene}) = 0,62$$

$$b_{Ts} (MP\text{-xylene}) = 0,47$$

Tool presentation :

Fill in the various tables:

- Analyzer type
- Pollutant type
- Pollutant analyzer link



Fill in the table :

- Analyzer parameters pollutant station → which can be found in SQL

INFORMATIONS DESCRIPTIVES			
	Description des variables	Incertitude type	
METADONNEES			
	Typologie des sites	Période d'agrégation	
Type d'analyseur	Lien analyseur polluant	Type de polluant	
	Variables Aléa ou Sys		
PARAMETRES DES EQUIPEMENTS			
	Interférents	Manque temporel	
	Analyseurs GAZ	Analyseurs PM	

[Déconnexion](#)

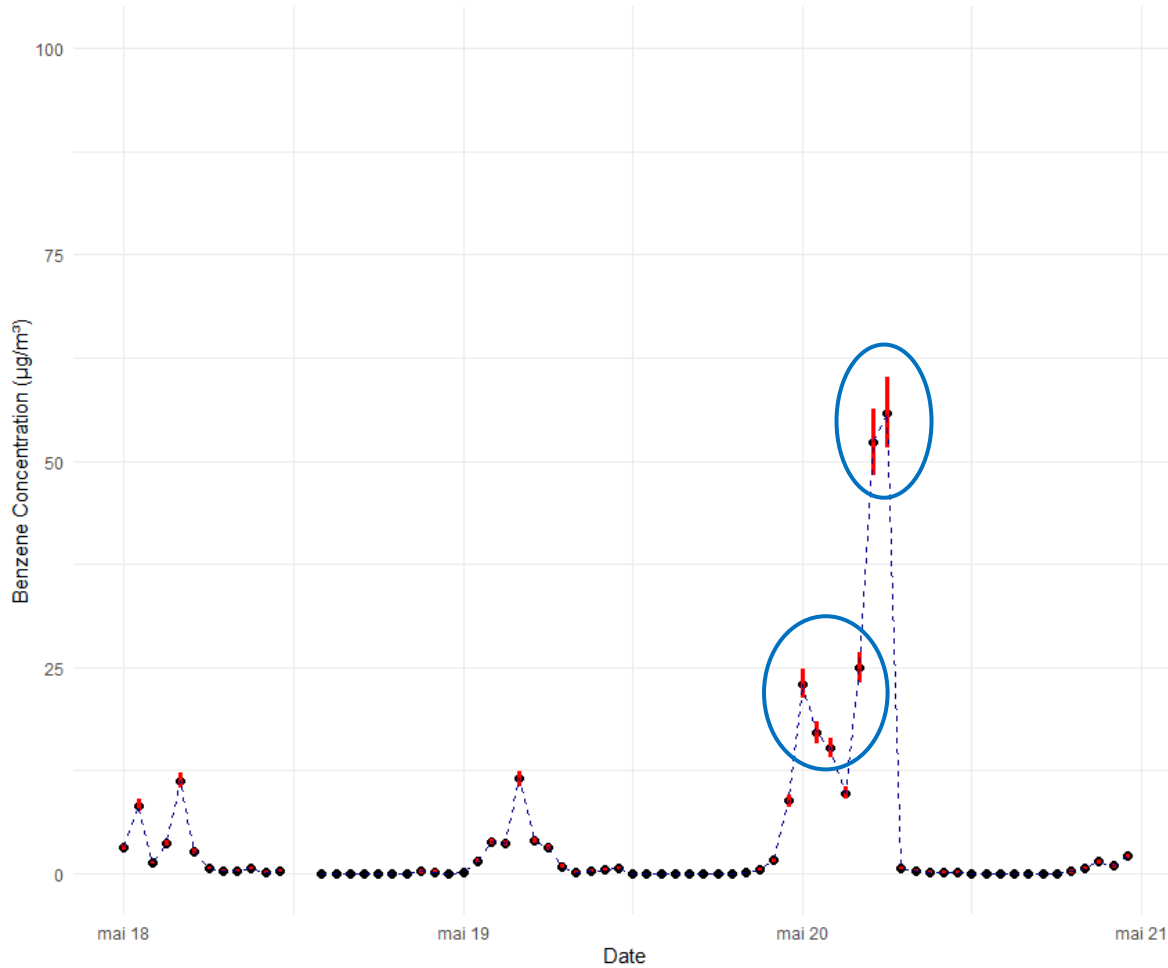
INTRODUCTION :

Overview :

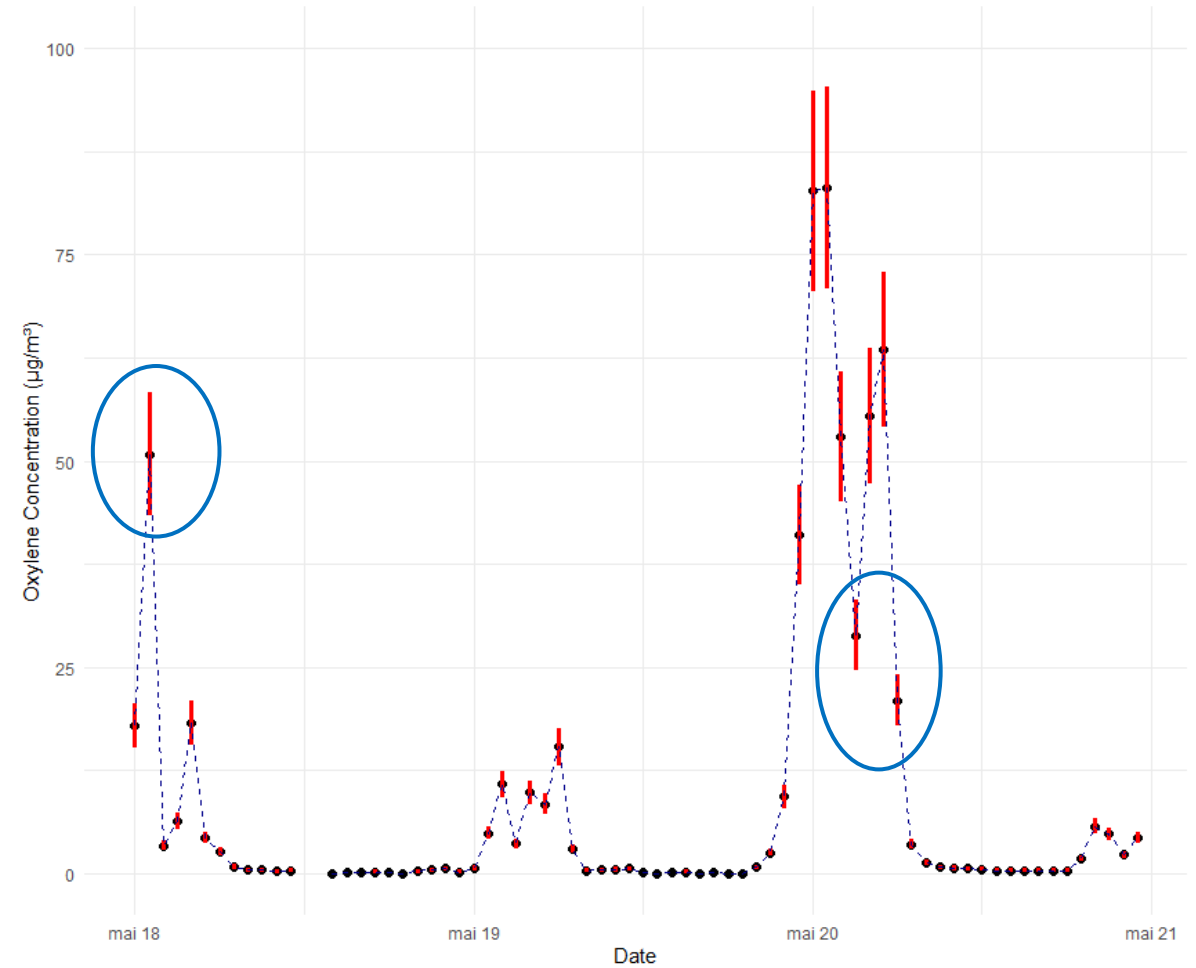
- Air quality;
- WHO: 7 million premature deaths/year;
- Pollutant: nitrogen oxides (NO_x) and particulate matter (PM), volatile organic compounds (VOC);
- Several VOC families: alkanes, alkenes, aromatics, etc;
- Sources: anthropogenic and biogenic.

- The two graphs show the variation in concentrations along with their associated uncertainties for May 18 and 20, 2022

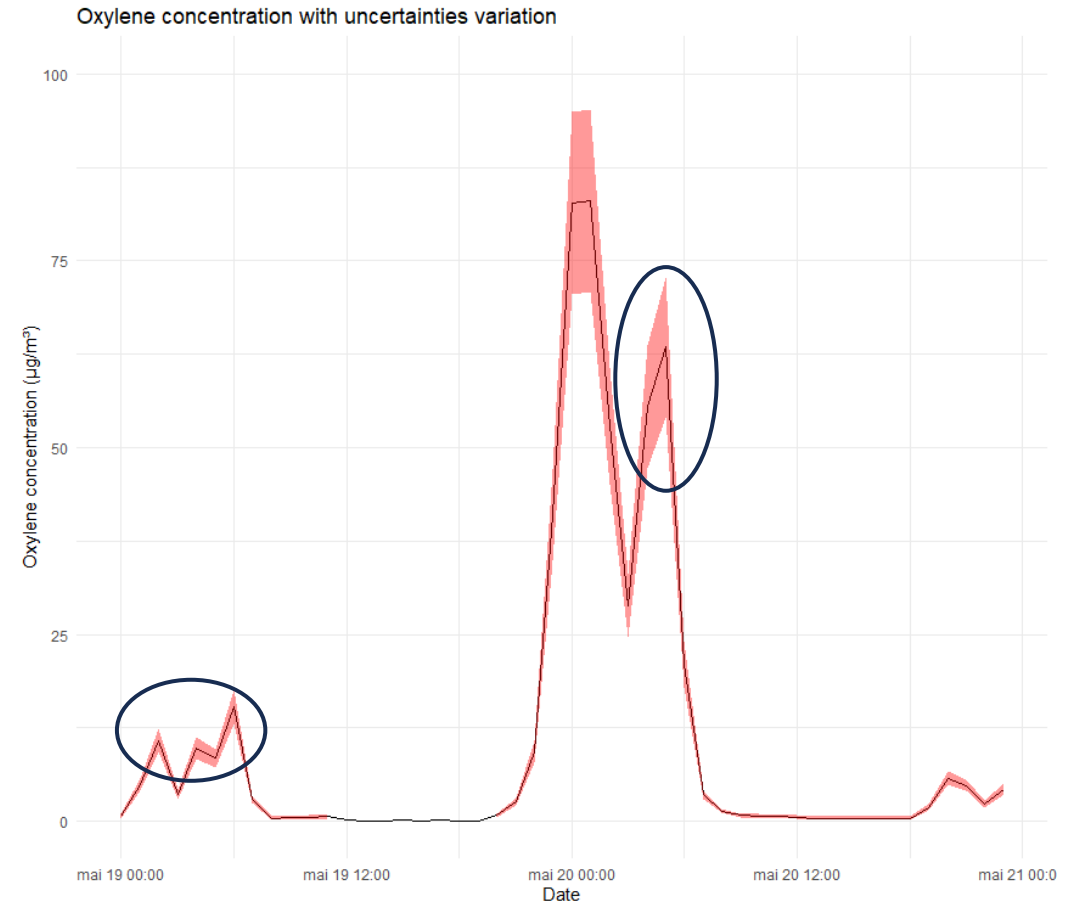
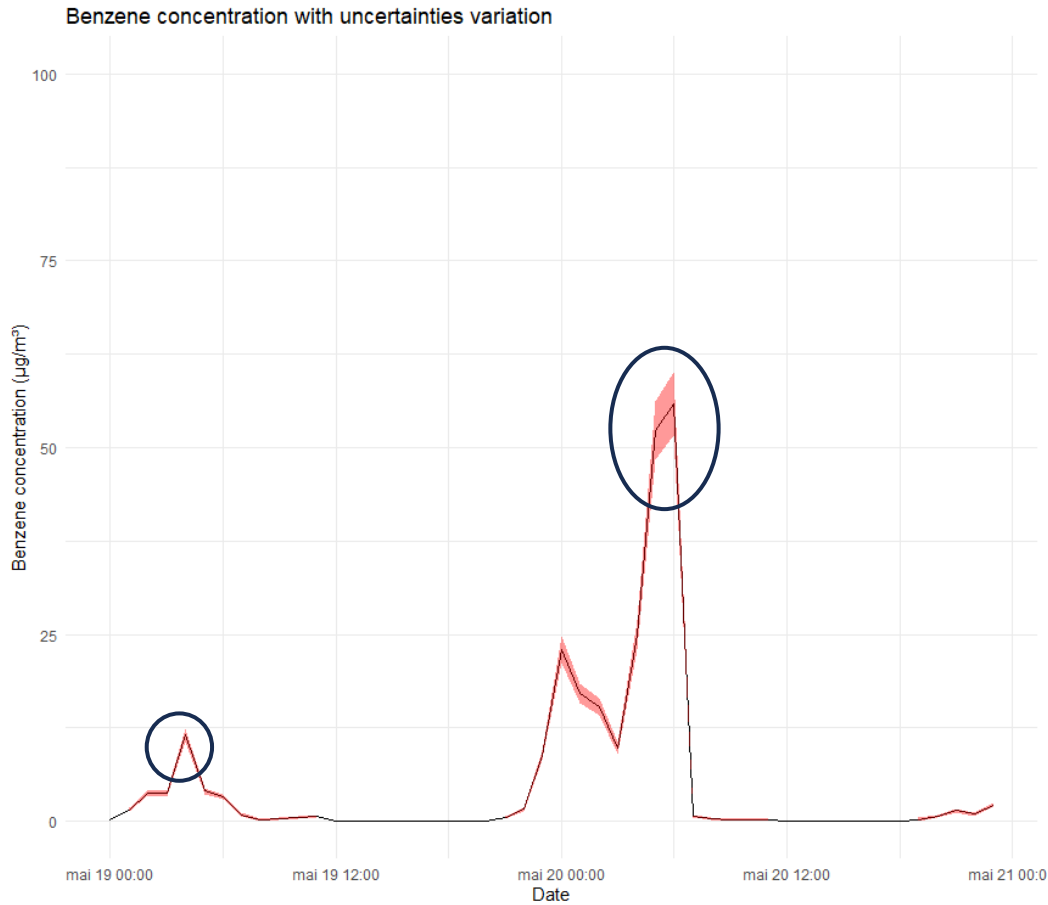
Benzene concentration with uncertainties variation over the time



Oxylene concentration with uncertainties variation over the time



➤ The two graphs show the variation in concentrations along with their associated uncertainties for May 19 and 20, 2022



❑ The difference in uncertainty between the two species are essentially driven by the temperature component for o-xylene.

