



HAL
open science

Development and validation of on-line auto-GC for the analysis of trace level biogenic VOCs for a field measurement campaign

Fanny Bachelier, Damien Bazin, Benoit Grosselin, Véronique Daële

► To cite this version:

Fanny Bachelier, Damien Bazin, Benoit Grosselin, Véronique Daële. Development and validation of on-line auto-GC for the analysis of trace level biogenic VOCs for a field measurement campaign. Analytics 2022, Sep 2022, Nantes, France. hal-03862158

HAL Id: hal-03862158

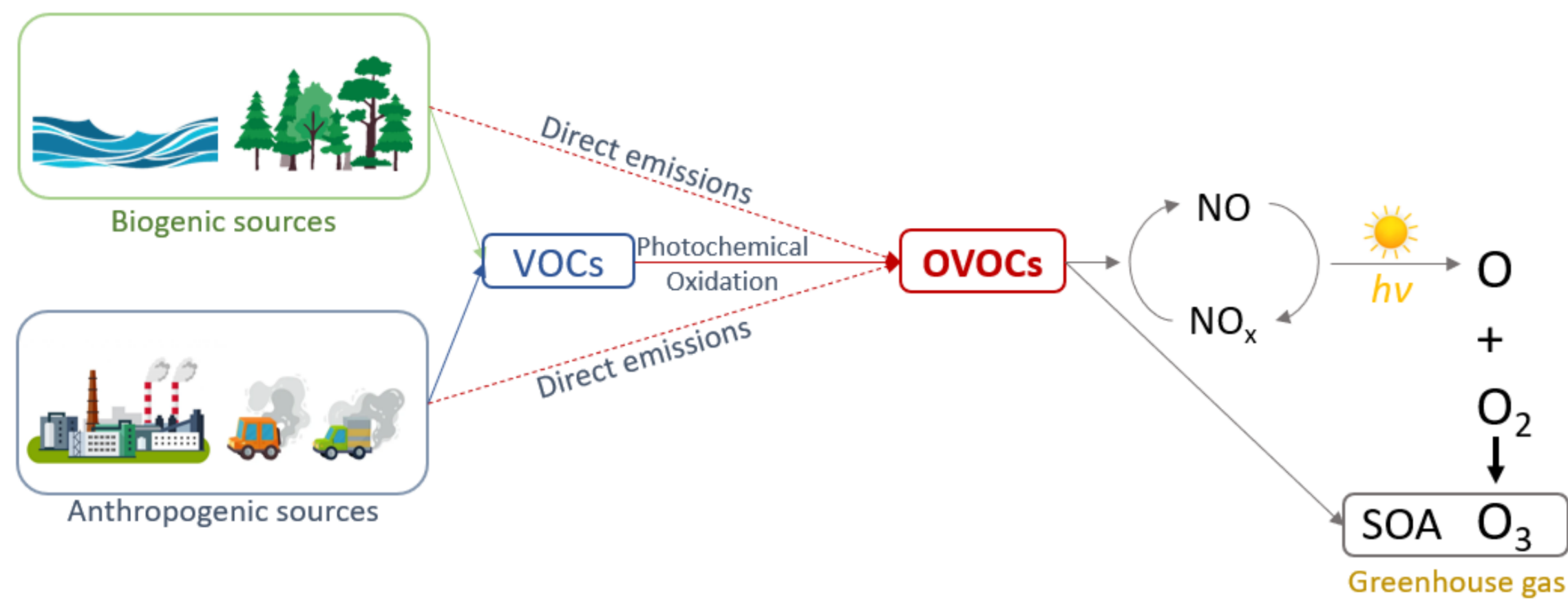
<https://hal.science/hal-03862158>

Submitted on 20 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Introduction



Context:

- Volatile Organic compounds (VOCs) play a major role on atmospheric pollution
- VOCs emitted in the atmosphere from natural or anthropological sources⁽¹⁾
- Biogenic VOCs (BVOCs) = hydrocarbons, isoprene, terpenes & oxygenated compounds (OVOcs)⁽²⁾
- These molecules are found in ambient air from ppt to ppb levels that require sensitive analytical systems

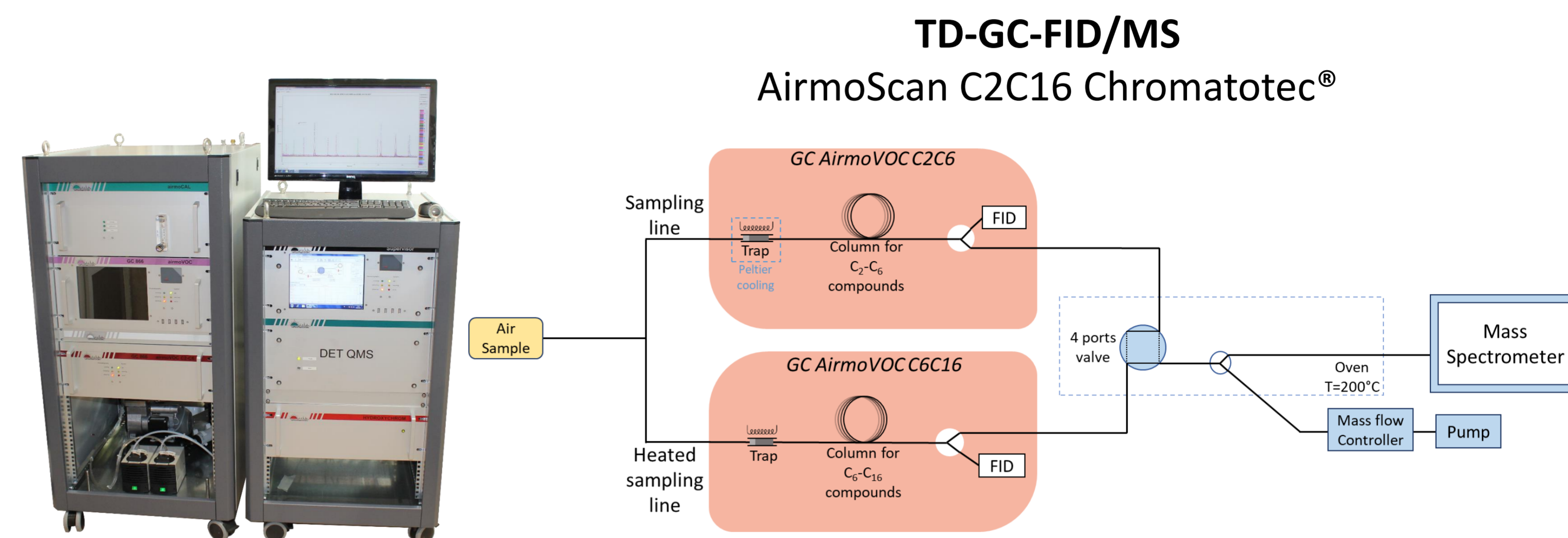
Problem:

- Usually laboratory instruments involving one off-sampling and analysis
- Need for continuous on-site monitoring systems and allowing automatic data reprocessing

Goal:

- Evaluate suitability of continuous and automatic thermodesorption Gas chromatograph with Flame ionization Detector (FID) and Mass Spectrometer (MS) in parallel for BVOCs measurement in ambient air

Material & Method

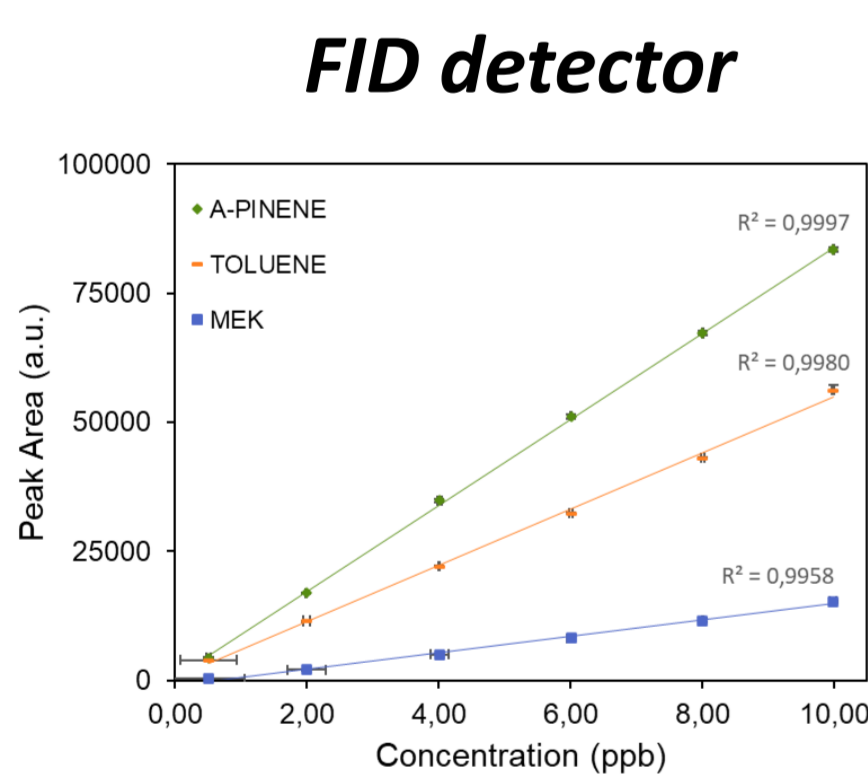


GC AirmoVOC C2C6	GC AirmoVOC C6C16	Mass spectrometer
Carrier gas: H ₂	Carrier gas: H ₂	Single Quadrupole
Flow rate: 3 mL/min	Flow rate: 3 mL/min	EI: 70eV
Sampling flow: 12 mL/min	Sampling flow: 20 mL/min	Transfer line: 200°C
Column: Capillary PLOT column (25m x 0,53mm x 10µm)	Column: Capillary MXT30CE column (30m x 0,28mm x 1µm)	Inlet: 250°C
Trap: Carboxen & Carbopack mixture (-10°C)	Trap: Carbopack mixture	Detection: SCAN mode (0 – 300 amu)
Thermodesorption: 220°C	Thermodesorption: 380°C	SEM voltage = 1200V
Oven: 36 – 202°C	Oven: 36 – 202°C	
Detector: FID at 170°C	Detector: FID at 190°C	
Sampling time: 30 min – Cycle time: 45 min		

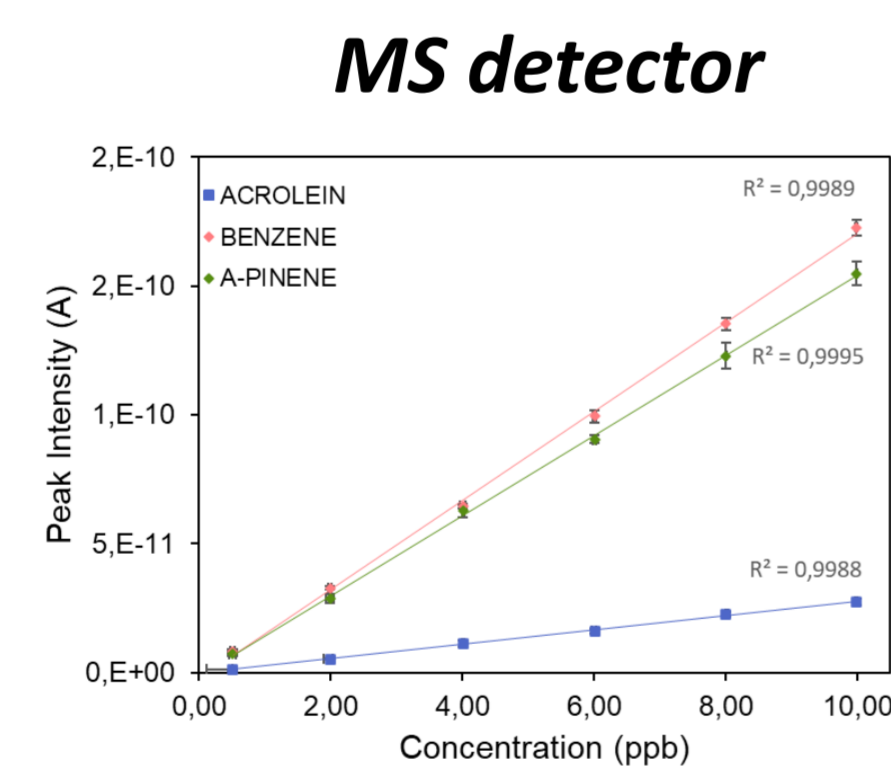
Results

Method validation

- To validate the system, certified gas mixtures PAMS 58 and TO15 (Takachiho, Japan) at 100 ppb(V) were used
- Linearity, limit of detection, precision and accuracy calculated according to the Chinese Norm for ambient air measurements⁽³⁾ for **4 aromatic hydrocarbons, 11OVOCs** and **1 terpene**
- 4 OVOcs not quantified by FID → coelutions



Calibration curves of Methyl Ethyl Ketone (MEK), Toluene and α -pinene



Calibration curves of Methyl Ethyl Ketone (MEK), Toluene and α -pinene

- **R²:** 0,9829 – 0,9992
- **Limits of detection:** 0,035 – 0,325 ppb
- **Precisions at 4 ppb (RSD%):** 0,65% - 5,79%
- **Accuracies at 4 ppb (RSD%):** 0,62% - 18,2%

- **R²:** 0,9871 – 0,9995
- **Limits of detection:** 0,048 – 2,110 ppb
- **Precisions at 4 ppb (RSD%):** 0,66% - 10,6%
- **Accuracies at 4 ppb (RSD%):** 0,33% - 21,4%

Development of automatic reprocessing

Interest of dual detection FID and MS in continuous and on-site measurements:

FID	MS
Good reliability	Sensitive
+ (Stable, linear, sensitive)	Selective
	Allows identification (NIST database)
- Non selective	Time drift

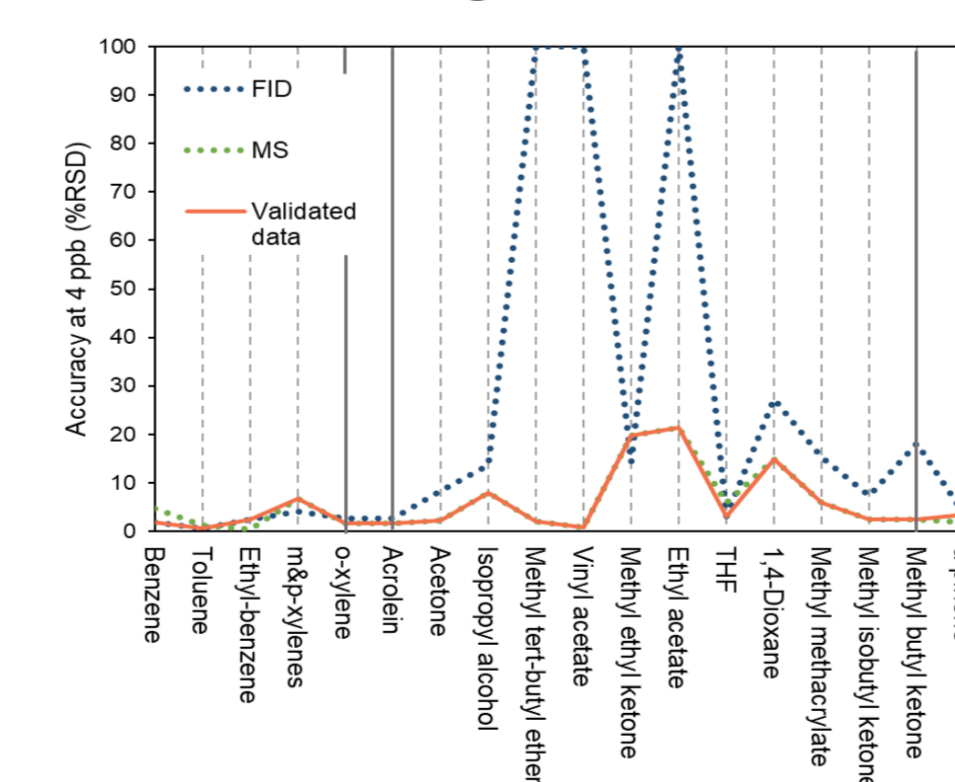
Twice as many results
Need to simplify data reprocessing

Algorithm and validation parameters implemented in data reprocessing software :

If [FID] - [MS] < CST_C_GAP
Or
If $\frac{[FID]-[MS]}{[MS]}$ < PCENT_C_GAP
Then FID value selected
Otherwise MS value

With CST_GAP and PCENT_C_GAP =
Validation parameters optimized for each VOC

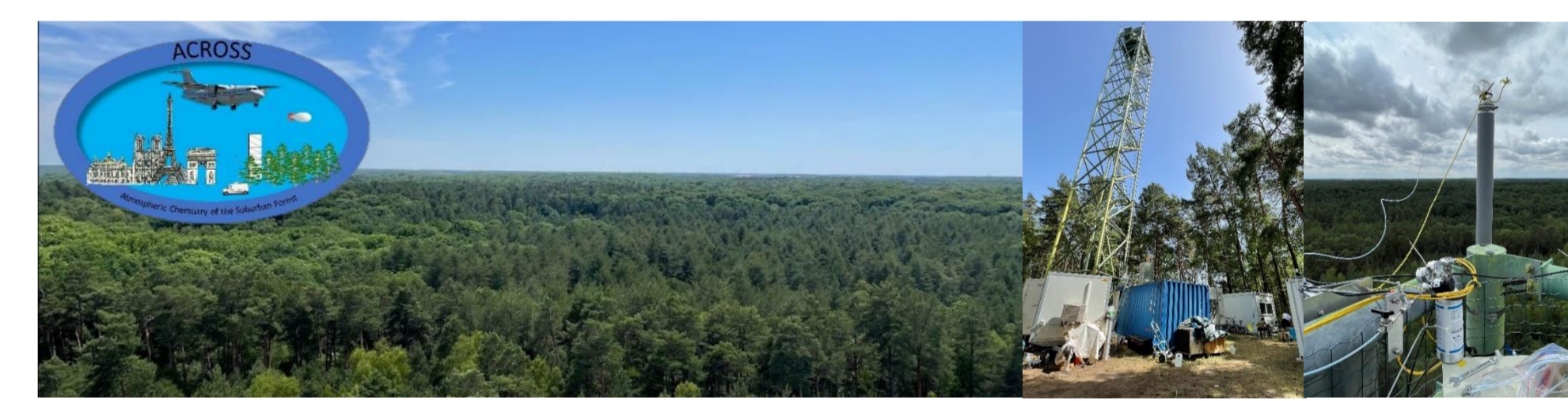
Algorithm efficiency evaluation



FID, MS and validated data accuracies at 4 ppb of aromatic hydrocarbons, OVOcs and terpene

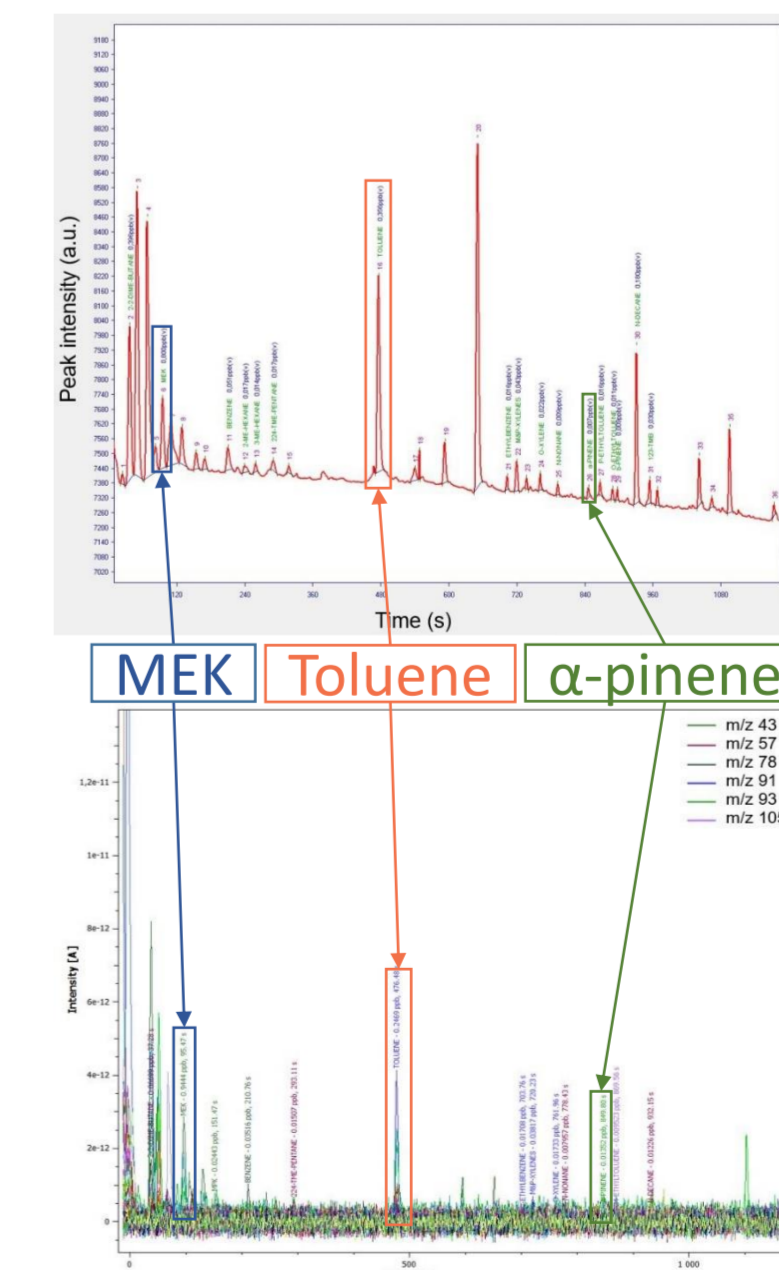
- RSD% of validated data ranged from 0,07% to 21,4%
- Implementation of validation parameters leads to very good overall accuracies

In field measurement campaign



<https://across.cnrs.fr/>

- **ACROSS campaign:** Atmospheric ChemistRy Of the Suburban ForeSt (15 June – 25 July)
- **Location:** 3 sites in Paris including Rambouillet Forest (80 km from Paris)
- **Aim:** Understand physico-chemical interactions of urban and biogenically air masses
- **TD-GC-FID/MS objective:** Measurement of Biogenic compounds above the trees



FID and MS chromatograms of 3 potential BVOCs identified and quantified in Rambouillet field

VOC	[Validated data] (ppb)
MEK	0,944
Toluene	0,357
A-pinene	0,007

Conclusion

- Performance studies of TD-GC-FID/MS were evaluated to quantify 16 VOCs: 4 aromatic hydrocarbons, 11 OVOcs and 1 terpene in ambient air
- Algorithm optimized to simplify data reprocessing and select accurate result between FID and MS
- 3 potential BVOCs identified and quantified with the system during the ACROSS campaign in Rambouillet site

Perspectives:

- Performance studies with an internal standard
- Data analysis and comparison with other instruments deployed during the Rambouillet campaign

Acknowledgements

Acknowledgements to the Mass Spectrometry French Society (SFSM) for providing me the opportunity to participate to the Analytics 2022 congress
This work was carried out as part of a thesis with a CIFRE #2020/1563 agreement from the National Association for Technical Research (ANRT)

References

- (1): Gu et al., (2019) China, Ecotoxicology and Environmental Safety 169, 797 – 806
- (2): Dörter et al., (2020), Science of the total Environment 731, 139 – 201
- (3): HJ 1010-2018 (2019), Specifications and Test procedures for Ambient Air Quality Continuous Monitoring System with Gas Chromatography for Volatile Organic Compounds