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

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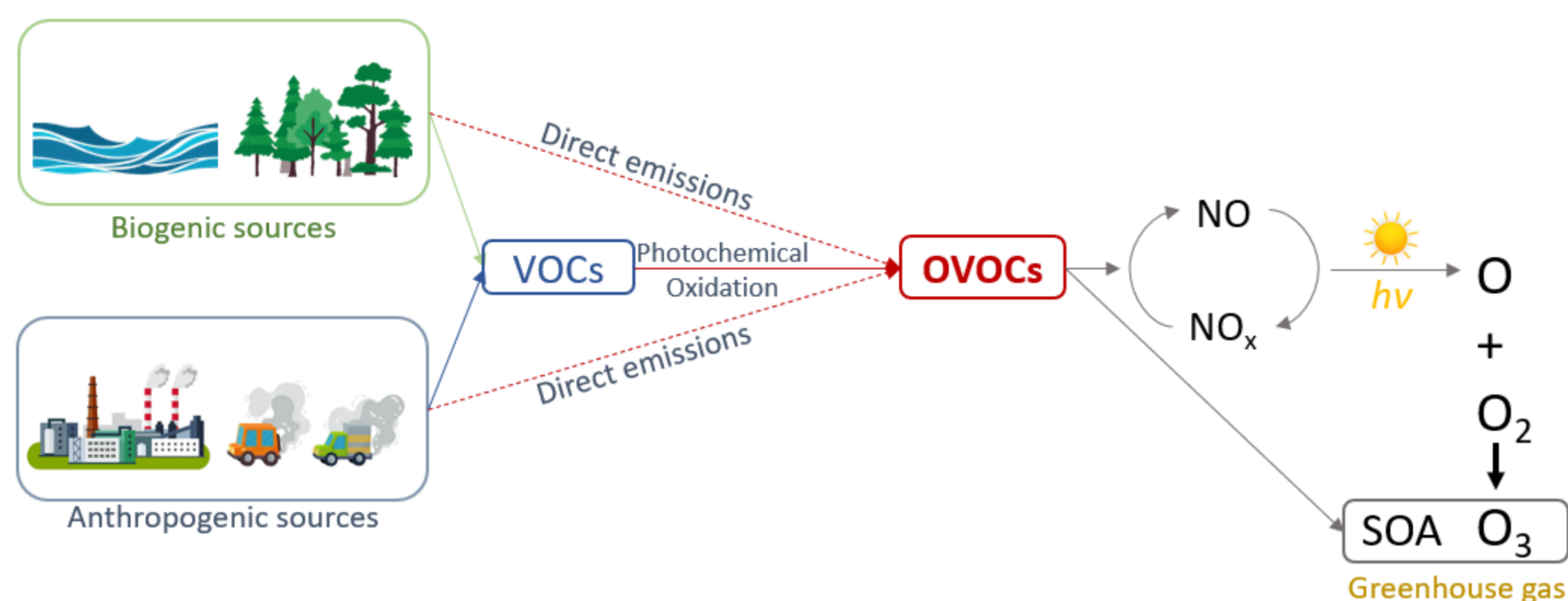
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## Introduction



### Context:

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

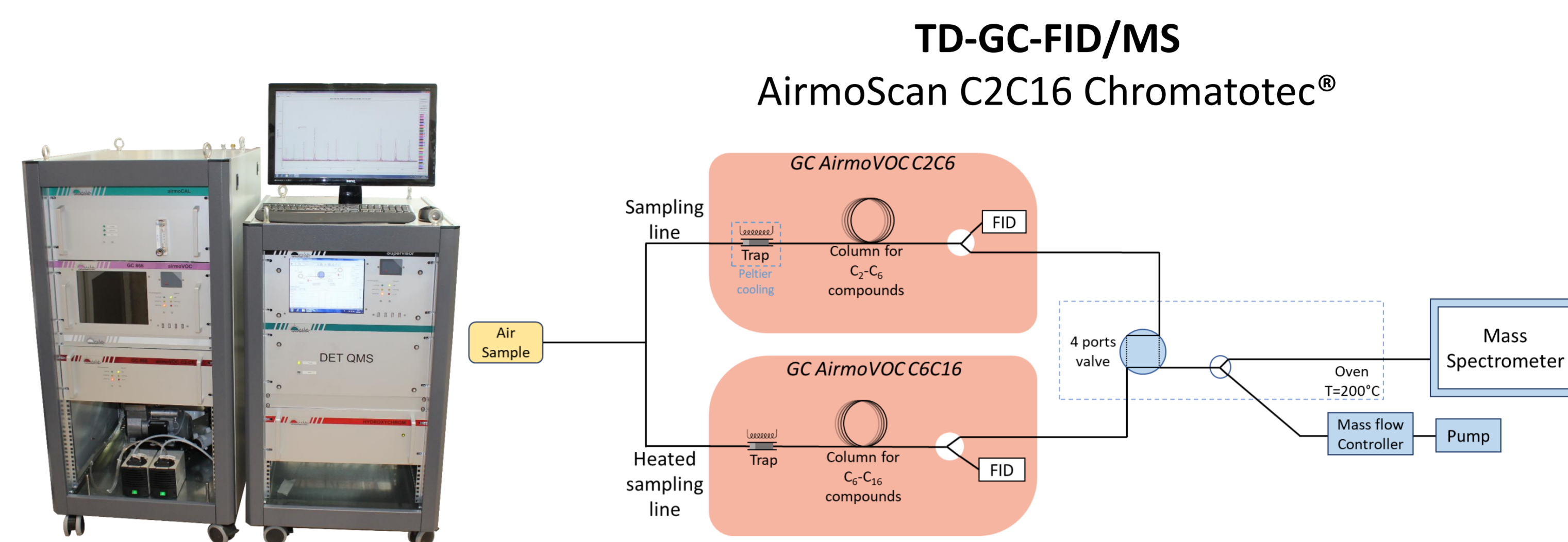
### Problem:

- 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



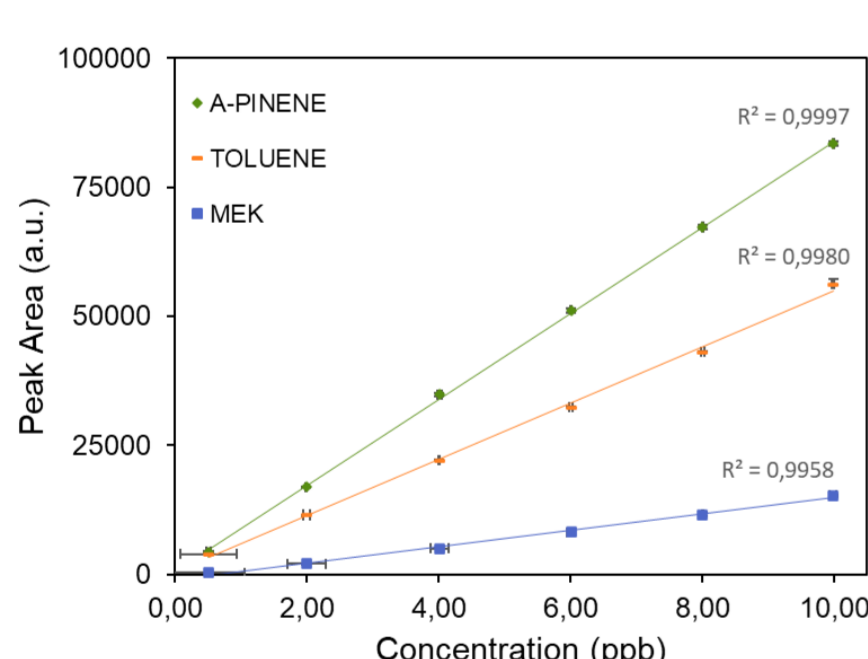
GC AirmoVOC C2C6	GC AirmoVOC C6C16	Mass spectrometer
<b>Carrier gas:</b> H <sub>2</sub> <b>Flow rate:</b> 3 mL/min <b>Sampling flow:</b> 12 mL/min <b>Column:</b> Capillary PLOT column (25m x 0,53mm x 10µm) <b>Trap:</b> Carboxen & Carbopack mixture (-10°C) <b>Thermodesorption:</b> 220°C <b>Oven:</b> 36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

## Results

### Method validation

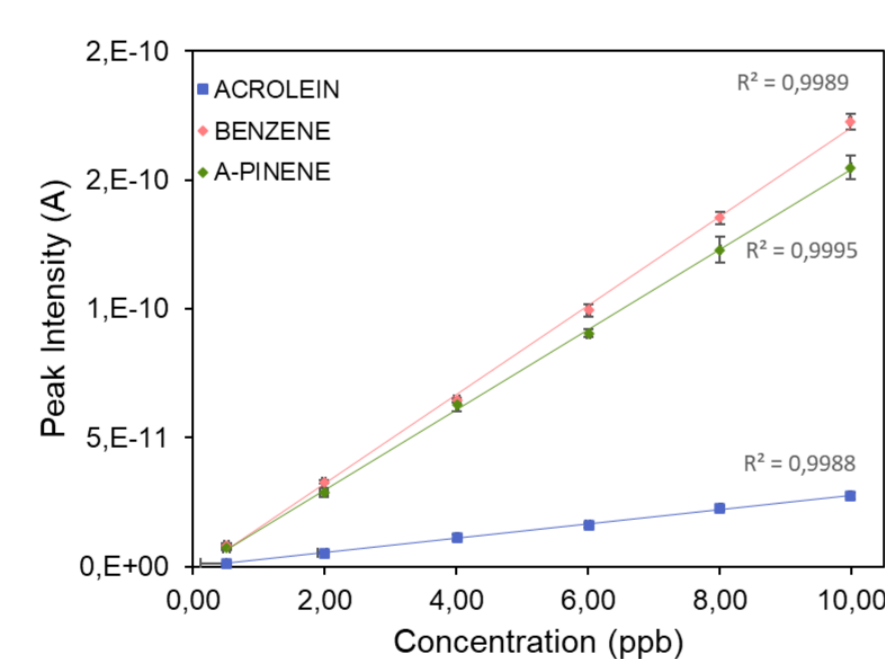
- To validate the system, certified gas mixtures PAMS 58 and TO15 (Takachiho, Japan) at 100 ppb(V) were used
- Linearity, limit of detection, precision and accuracy calculated according to the Chinese Norm for ambient air measurements<sup>(3)</sup> for **4 aromatic hydrocarbons, 11OVOCs** and **1 terpene**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

#### FID detector



Calibration curves of Methyl Ethyl Ketone (MEK), Toluene and  $\alpha$ -pinene

#### MS detector



Calibration curves of Methyl Ethyl Ketone (MEK), Toluene and  $\alpha$ -pinene

- **R<sup>2</sup>:** 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%

- **R<sup>2</sup>:** 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

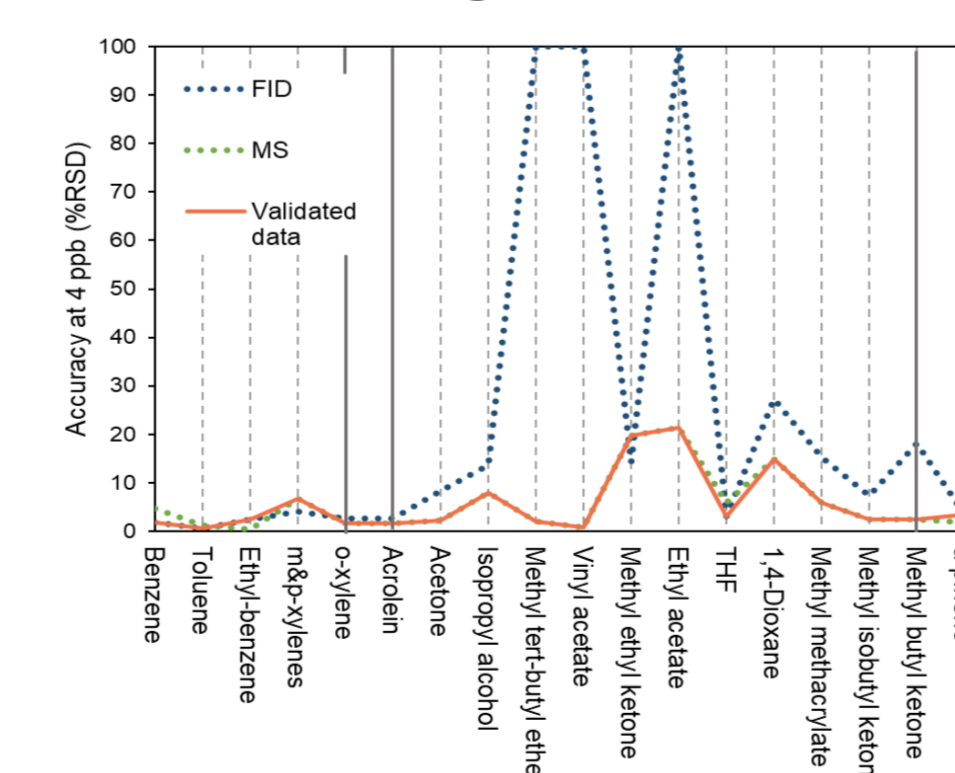
Twice as many results  
Need to simplify data reprocessing

#### 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\_C\_GAP** and **PCENT\_C\_GAP** = Validation parameters optimized for each VOC

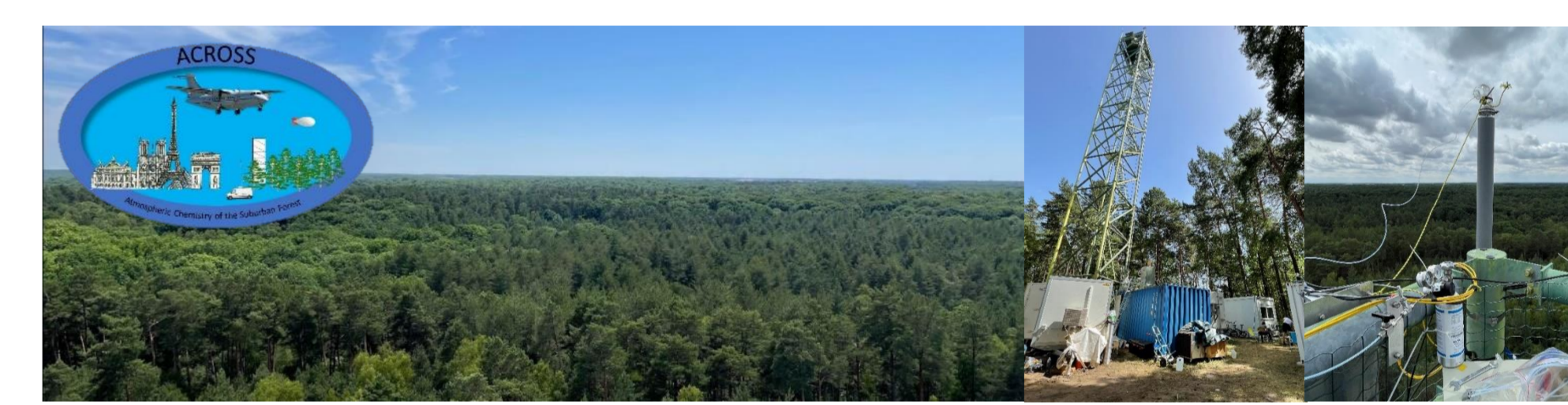
#### Algorithm efficiency evaluation



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

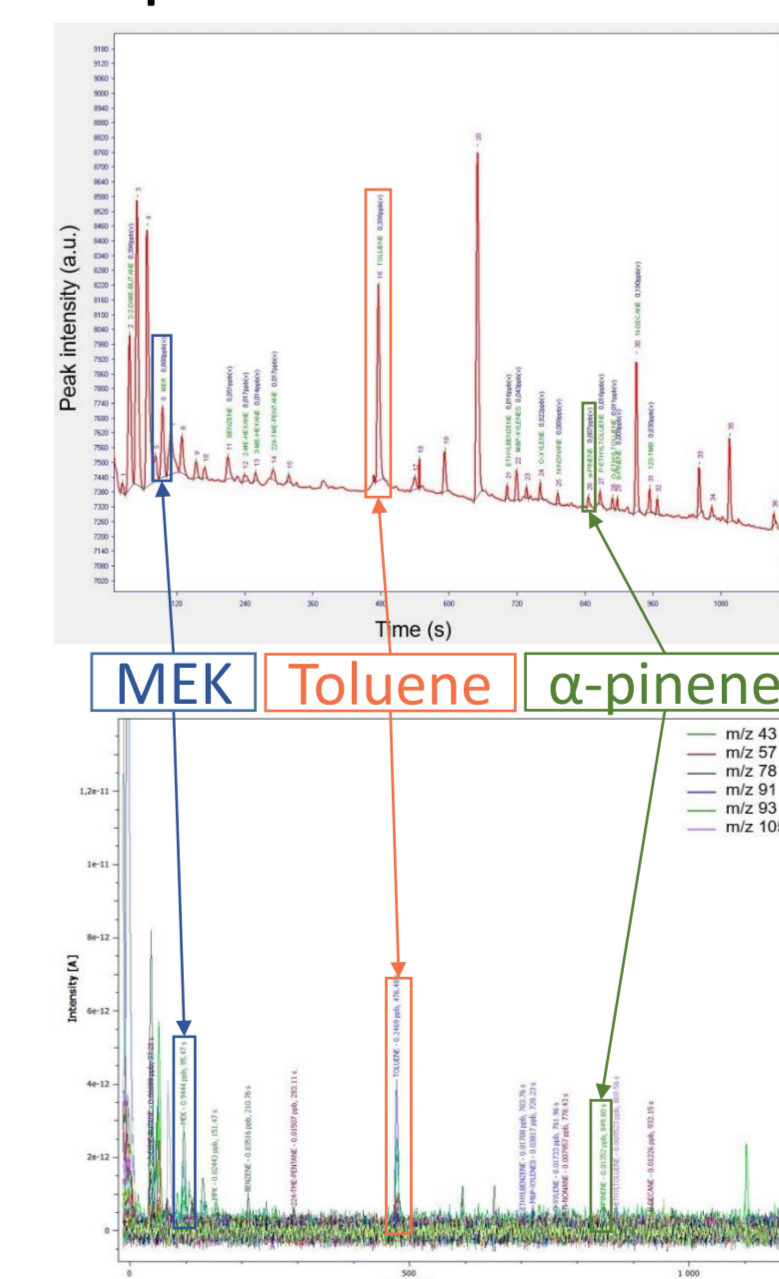
- RSD% of validated data ranged from 0,07% to 21,4%
- Implementation of validation parameters leads to very good overall accuracies

### 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

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## 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