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# Development of on-line and field dual TD-GC-FID/MS for automatic and continuous odorous VOCs monitoring in ambient air

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2022/09/13

# Introduction

Biogenic sources

Direct emissions

VOCs

Photochemical Oxidation

OVOCs

$NO$

$NO_x$

$h\nu$

$O$ + $O_2$

Anthropogenic sources

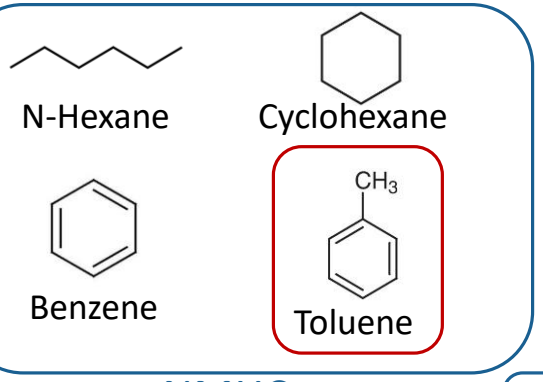
Direct emissions

SOA $O_3$

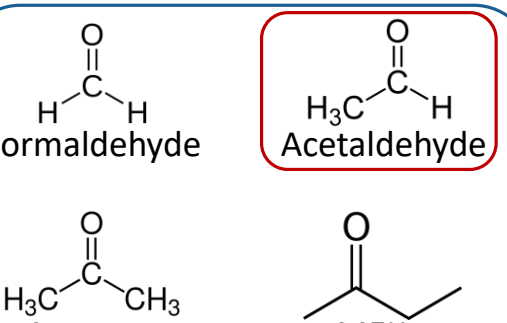
Greenhouse gas

Ehsanul K., et al., **2010,** Atmospheric environment, 44, 3492 - 3502

# Introduction
## VOCs families



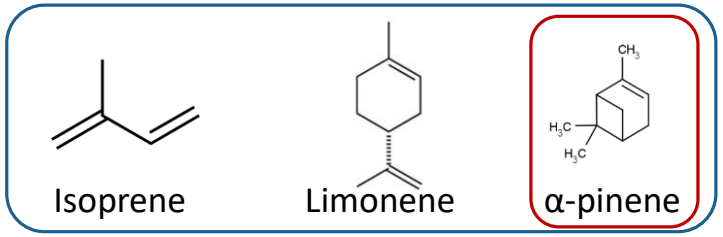

NMHCs



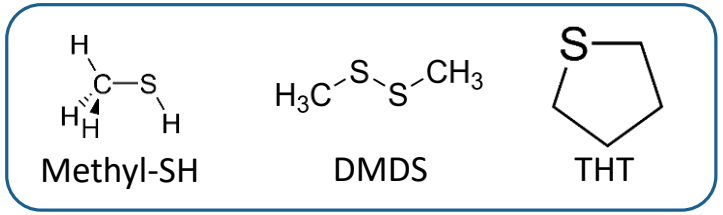

OVOCs

**Some VOCs responsible of odor pollution**:

- Environmental nuisances
- Unpleasantness
- Potential health risks



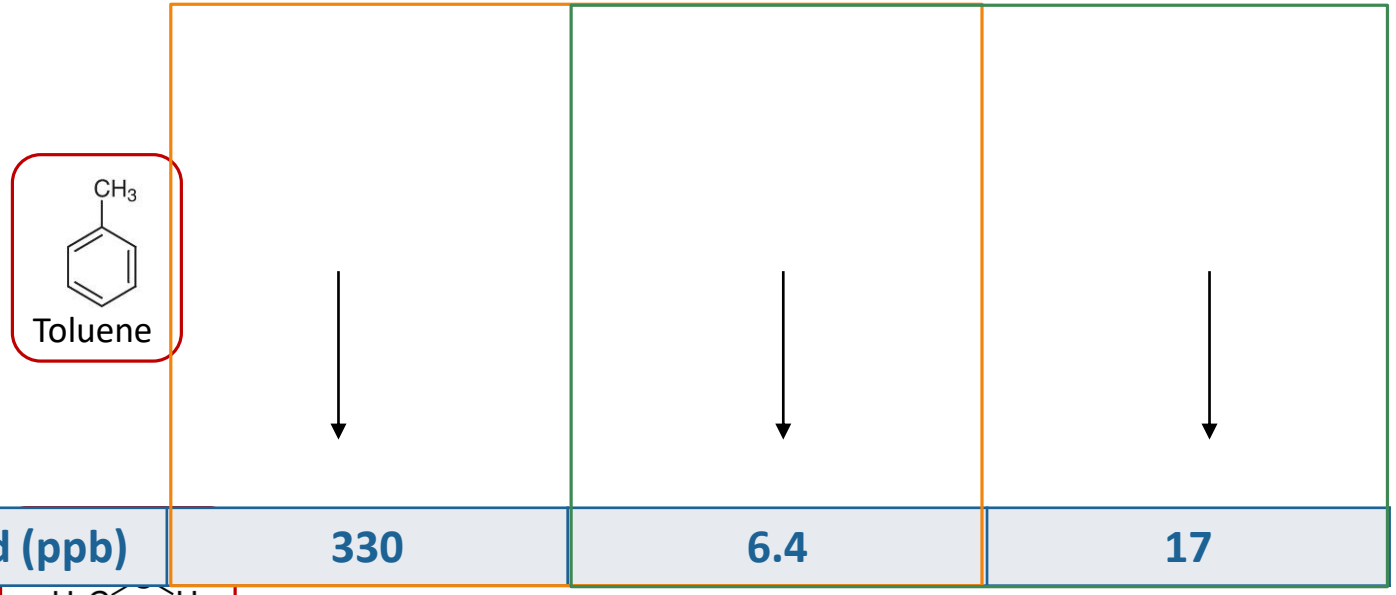

BVOCs

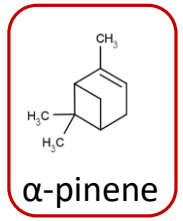



VSCs

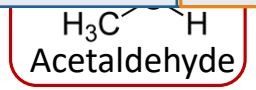
Ehsanul K., et al., **2010,** Atmospheric environment, 44, 3492 - 3502

# Introduction
## VOCs families




| | | | |
|---|---|---|---|
| **Odor Threshold (ppb)** | **330** | **6.4** | **17** |




Urban and industrial areas

Suburban and natural areas

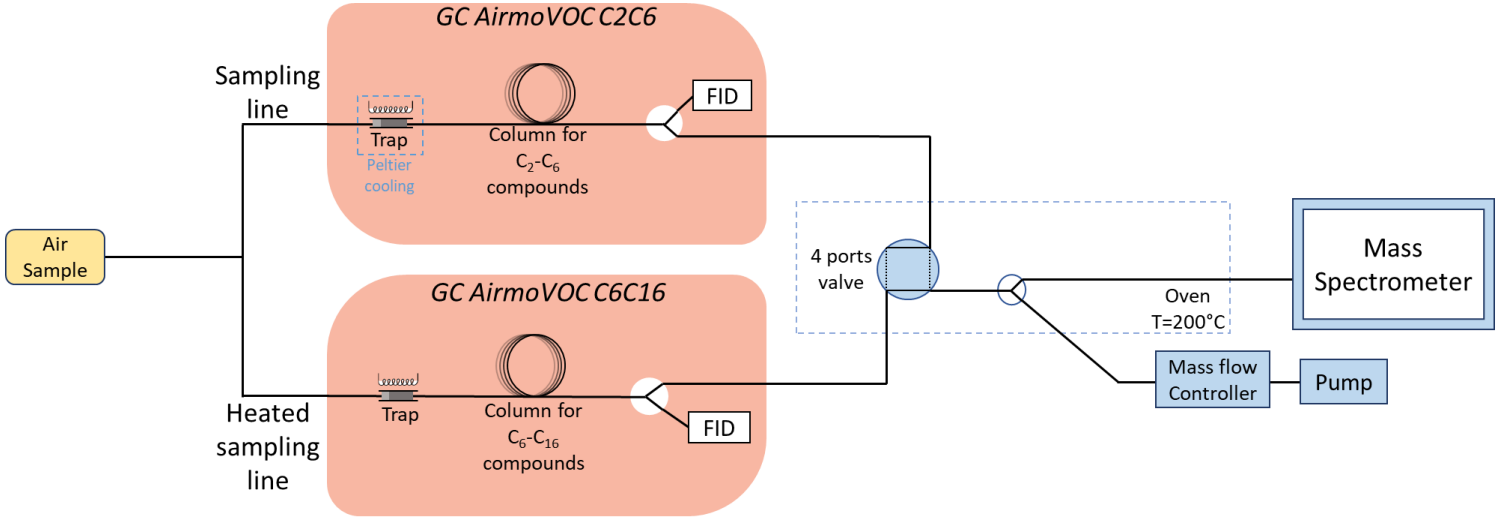
Both areas
an

→ **Objective:** Study the performance and limitations of **on-line auto-TD-GC-FID/MS** to identify and quantify these odorant VOCs

Hiroyuki U., **2021**, Asian Journal of Atmospheric Environment, 15, 1, 2020085

# Material & Method
# auto-TDGC-FID/MS: AirmOzone with process MS

- System configuration:

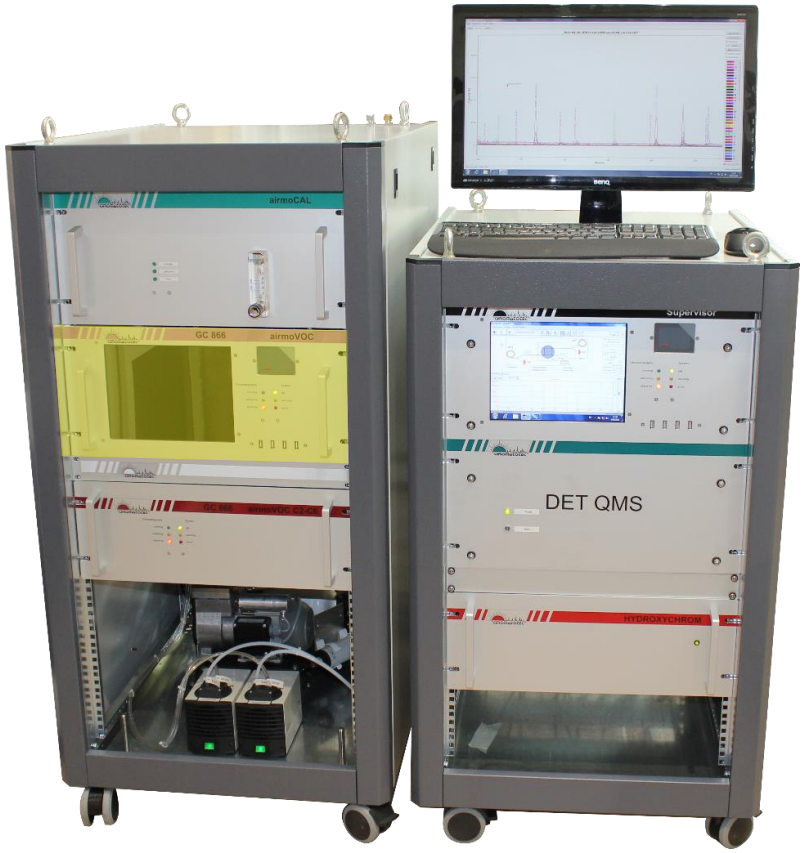


# Material & Method
# auto-TDGC-FID/MS for C2C6 monitoring

- Carrier gas: $H_2$
- Sampling flow: 12 mL/min
- Column: Capillary PLOT column (25 m x 0,53 mm x 10 µm)
- Trap: Carboxen and Carbopack mixture (-10°C)
- Thermodesorption: 220°C
- Oven: 36 – 202 °C
- Detector: FID at 170°C
- Sampling time: 30 min
- Cycle time: 45 min

GC designed for light non polar VOCs containing 2 to 6 carbons

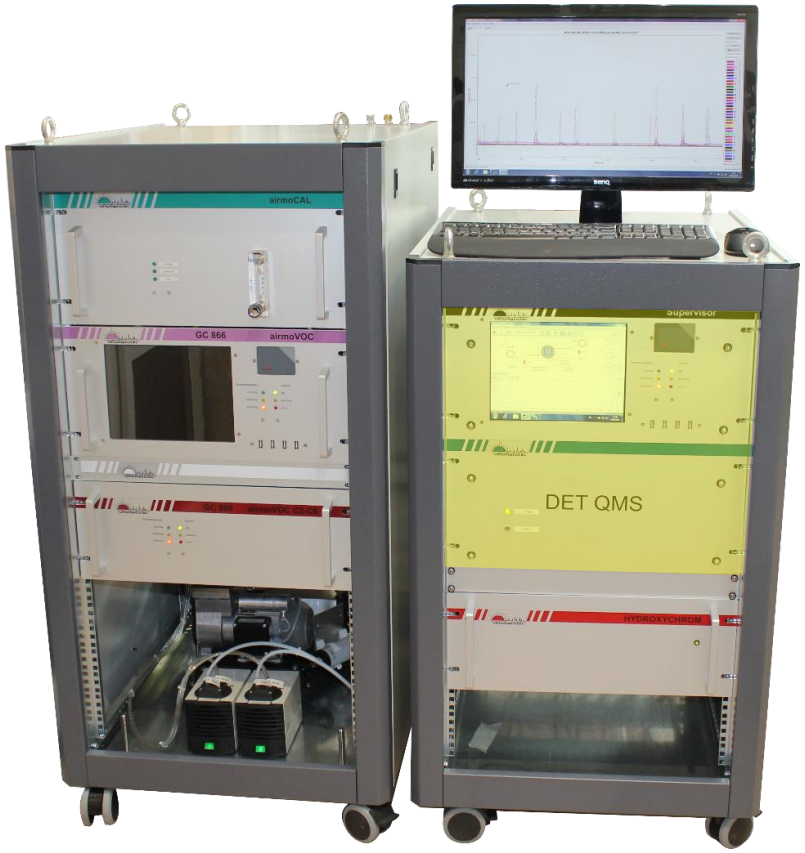
# Material & Method
# auto-TDGC-FID/MS for C6C16 monitoring




- Carrier gas: $H_2$
- Flow rate: 20 mL/min
- Column: Capillary MXT30CE column (60 m x 0,23 mm x 1,0 µm)
- Trap: Carbopack mixture (Room temperature)
- Thermodesorption: 380 °C
- Oven: 36 – 202 °C
- Detector: FID at 190°C
- Sampling time: 30 min
- Cycle time: 45 min

GC designed for VOCs containing 6 to 16 carbons

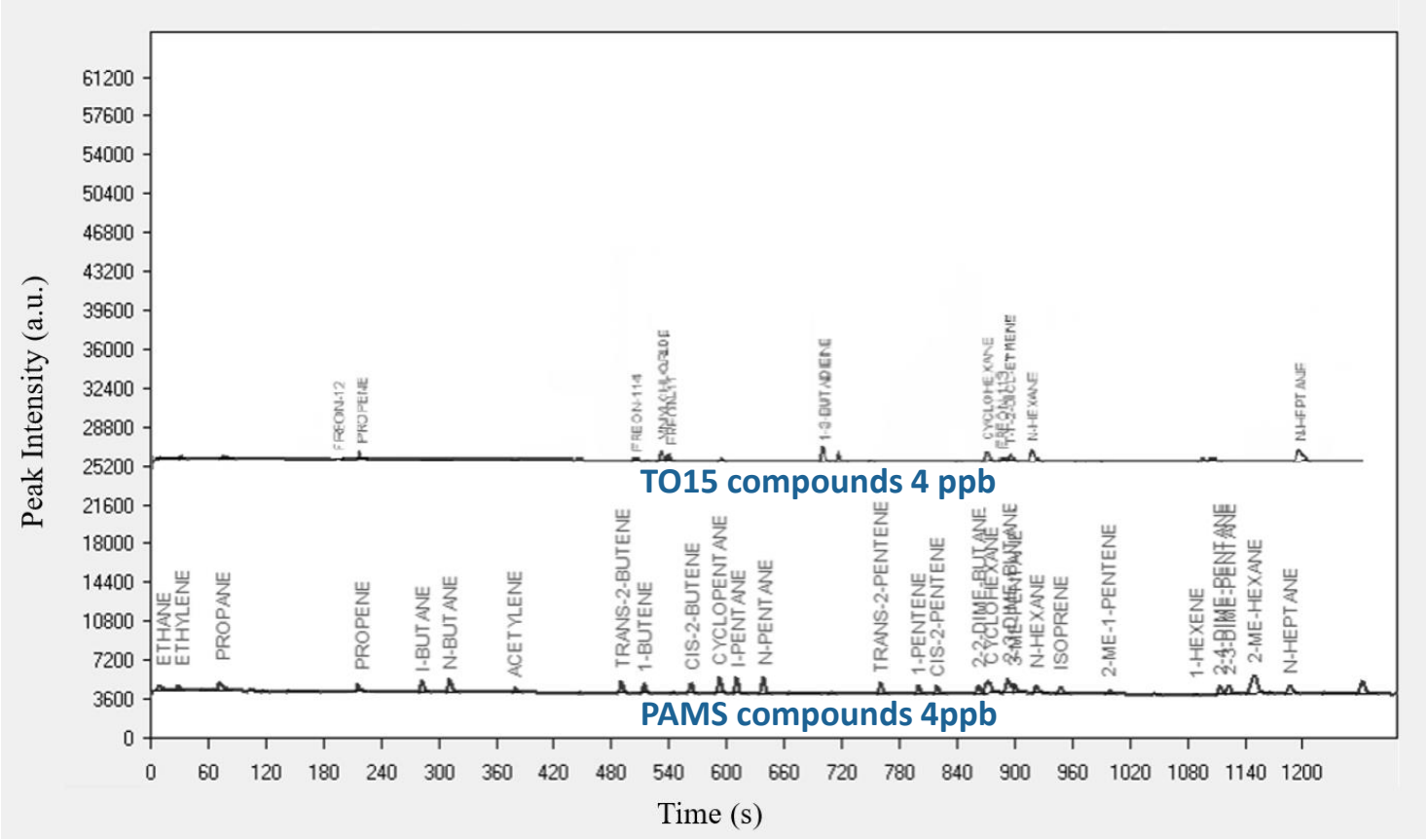
# Material & Method
# Mass spectrometer for C2-C16 monitoring




- Single Quadrupole with Electron Impact Ionization (70 eV)
- Inlet:
  - Deactivated Silica Tube ID 50 µm
  - Temperature = 170 °C
- Transfer line:
  - Deactivated metallic capillary tube
  - Temperature = 200 °C
- Detection: SCAN mode (0 – 300 amu)
- SEM voltage = 1200V

MS connected to TD-GC(C6-C16)-FID-MS for identification and quantification of coeluted VOCs

# Results
# C2 to C6 measurement




✓ C2C6 system suitable to analyze:

- All light Hydrocarbons (from PAMS cylinder)

- Freons, light chlorinated compounds (from TO15 cylinder)

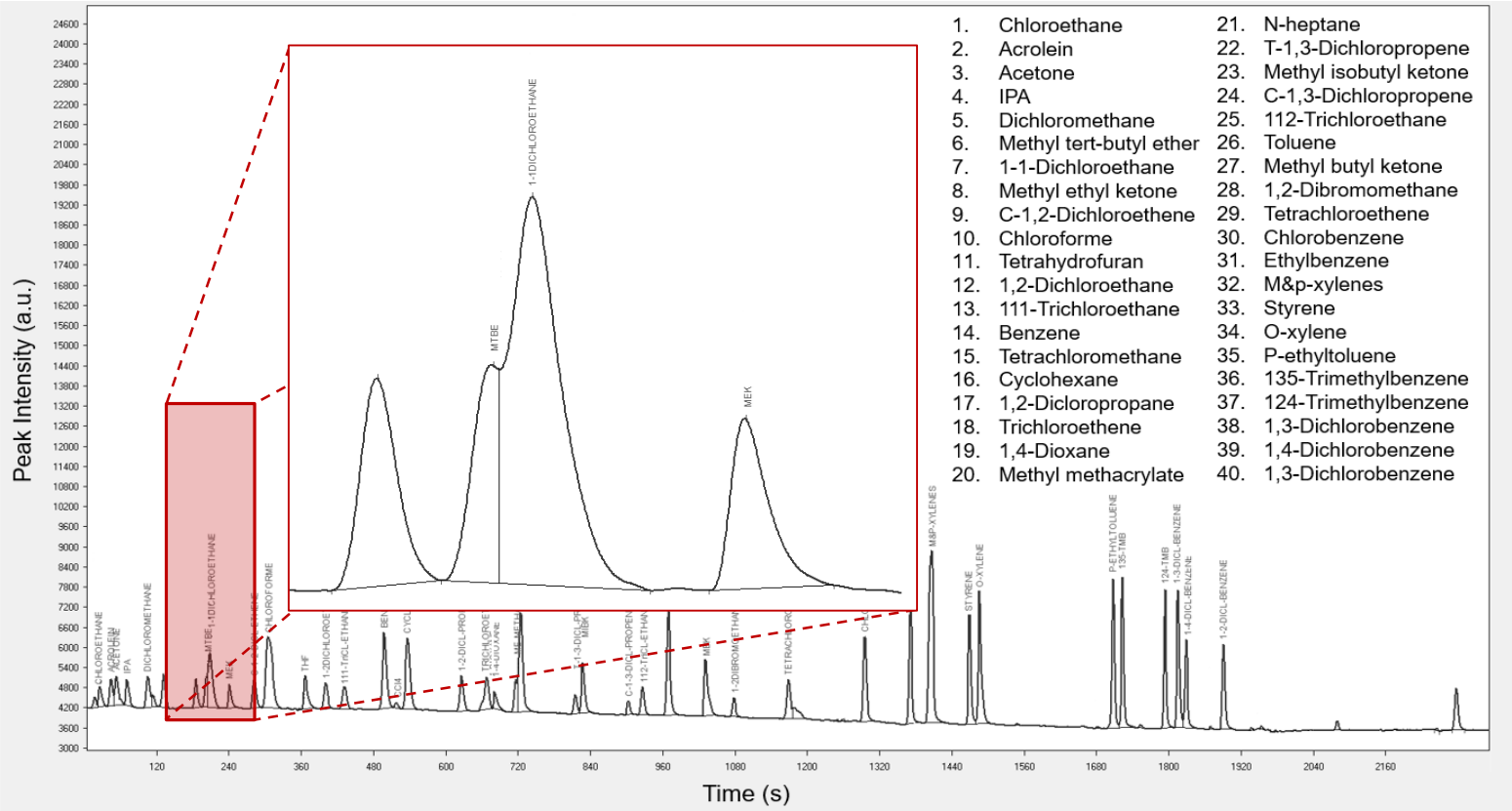
✕ C2C6 system cannot analyze:

- Light OVOCs: Methanol, Ethanol, Formaldehyde and Acetaldehyde

→ Column too polar to elute these compounds

# Results
# C6 to C16 FID measurement

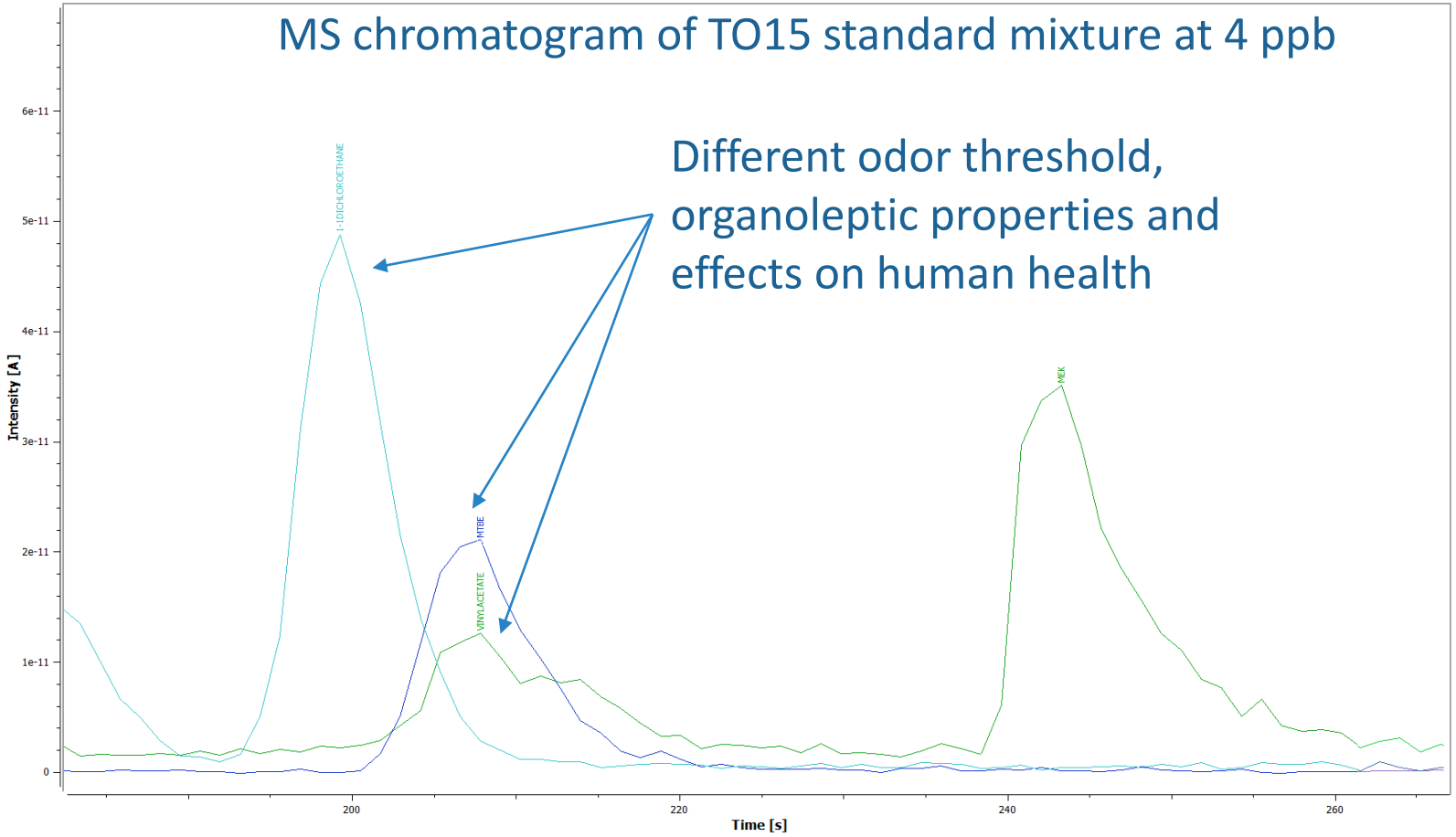
FID chromatogram of TO15 standard mixture at 4 ppb




Identification performed with known retention time of the compounds

→ **Coelutions occur between some VOCs**

# Results
# C6 to C16 MS measurement




| Compound | Specific m/z | Odor Threshold (ppm) |
|---|---|---|
| 1,1-Dichloroethane | 63 | 120 |
| Vinyl Acetate | 43 | 0.4 |
| MTBE | 73 | 0.03 |

**→ MS detection allows the quantification of coeluted VOCs thanks to specific m/z of the compounds**


Deese D. E. et al., **1969**, AIHA Journal, 30, 449 – 457
Smith S. L. et al., **1995**, Chem Health Saf, 2, 3, 32 – 38
Verschueren, K. et al., **2001** Handbook of Environmental Data on Organic Chemicals. Volumes 1-2. 4th ed. John Wiley & Sons.

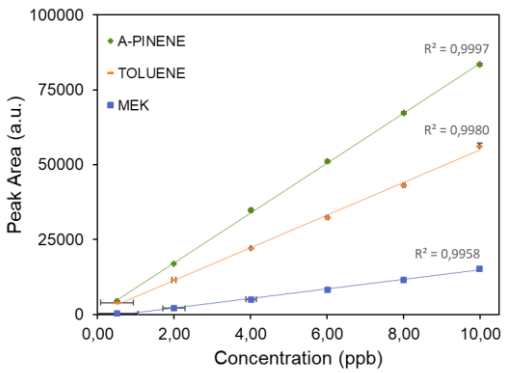
# Results
# Method validation

- Performance studies:

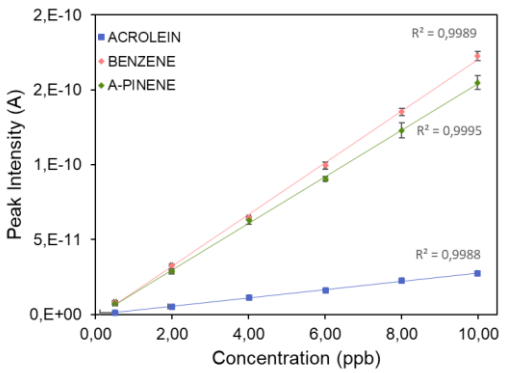
  - 100 ppb certified cylinder:
    - PAMS compounds: containing a mix of 58 hydrocarbons
    - TO15 compounds: containing a mix of 64 oxygenated and halogenated compounds)
  - Linearity tests:
    - Range 0.5 – 10 ppb(v): dilution with zero air performed with 2 MFC
    - Calibration curves with 6 different concentrations
    - 10 replicates for the first point and 6 for the others
  - Precision and accuracy tests:
    - 6 repetitions at 4 ppb

- Example of 3 calibration curves of Methyl Ethyl Ketone (MEK), Toluene and : α-pinene

FID




MS



# Results
# Method Validation

| OVOCs | FID Detection | | | | MS Detection | | | |
|---|---|---|---|---|---|---|---|---|
| | Determination coefficient ($R^2$) | LOD ($ppb_v$) | Precision at 4 $ppb_v$ (%RSD) | Accuracy at 4 $ppb_v$ (%) | Determination coefficient ($R^2$) | LOD ($ppb_v$) | Precision at 4 $ppb_v$ (%RSD) | Accuracy at 4 $ppb_v$ (%) |
| Acrolein | **0.9992** | 0.093 | 2.04 | **2.62** | 0.9990 | 0.277 | **10.6** | 1.67 |
| Acetone | 0,9960 | **0.065** | **5.79** | 8.27 | **0.9995** | 0.253 | 5.45 | 2.22 |
| Isopropyl alcohol | **0.9829** | 0.130 | **1.12** | 13.6 | **0.9871** | 0.404 | 7.76 | 7.87 |
| Methyl *tert*-butyl ether | *Coeluted* | - | - | - | 0.9995 | 0.216 | **2.78** | 2.09 |
| Vinyl acetate | *Coeluted* | - | - | - | 0.9992 | 0.431 | 7.49 | **0.73** |
| Methyl ethyl ketone | 0.9960 | 0.124 | 2.52 | 14.2 | 0.9899 | **0.068** | 4.37 | **19.8** |
| Ethyl acetate | *Coeluted* | - | - | - | 0.9928 | **2.092** | 6.79 | 19.3 |
| 1,4-Dioxane | 0.9894 | 0.150 | 2.44 | **29.2** | 0.9978 | 0.285 | 7.29 | 14.9 |
| Methyl methacrylate | *Coeluted* | - | - | - | 0.9984 | 0.273 | 3.43 | 5.92 |
| Methyl isobutyl ketone | 0.9986 | **0.325** | 1.46 | 7.36 | 0.9979 | 0.760 | 8.12 | 2.34 |
| Methyl butyl ketone | 0.9970 | 0.270 | 2.77 | 7.68 | 0.9988 | 0.159 | 7.79 | 2.47 |

- Linearity: $R^2$ showed linear calibration curves for FID and MS
- Limit of detection (LOD): Overall higher with MS detection

- Precision (RSD%):
  - < 11 % for FID and MS
  - FID is more repeatable than MS
- Accuracy:
  - < 30 % for FID and < 20 % for MS
  - Overall better accuracy for MS detection

# Results
# Development of automatic reprocessing

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

| | FID | MS |
|---|---|---|
| + | Good reliability (Stable, linear, sensitive) | Sensitive<br>Selective<br>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

| Validation parameter | FID | FID |
|---|---|---|
| CST_C_GAP | 0.5 ppb | 0.01 ppb |
| PCENT_C_GAP | 20 % | 1 % |

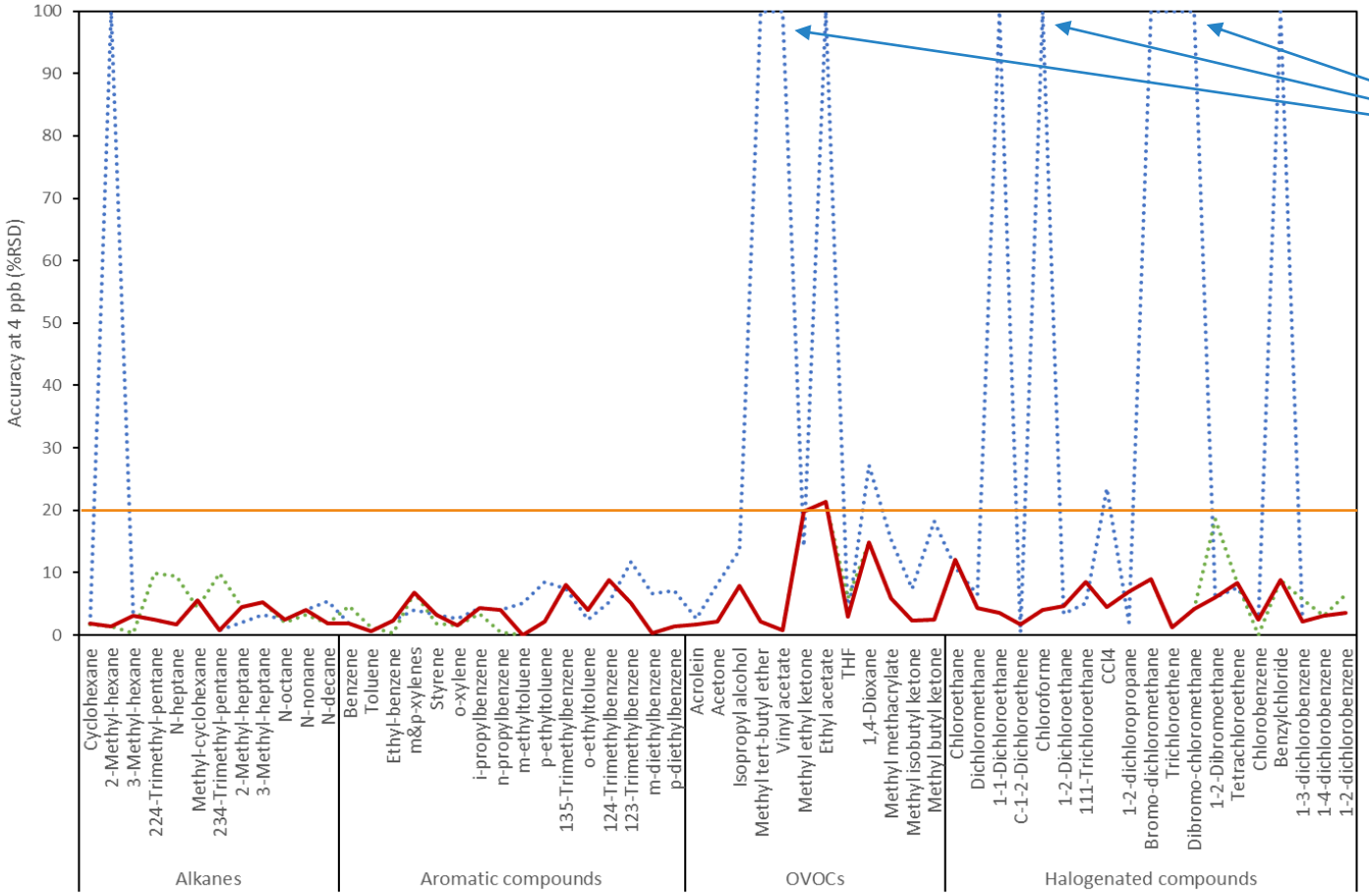
Coelution / bad response

# Results
# Algorithm efficiency evaluation with standard at 4 ppb

FID

MS

Validated data

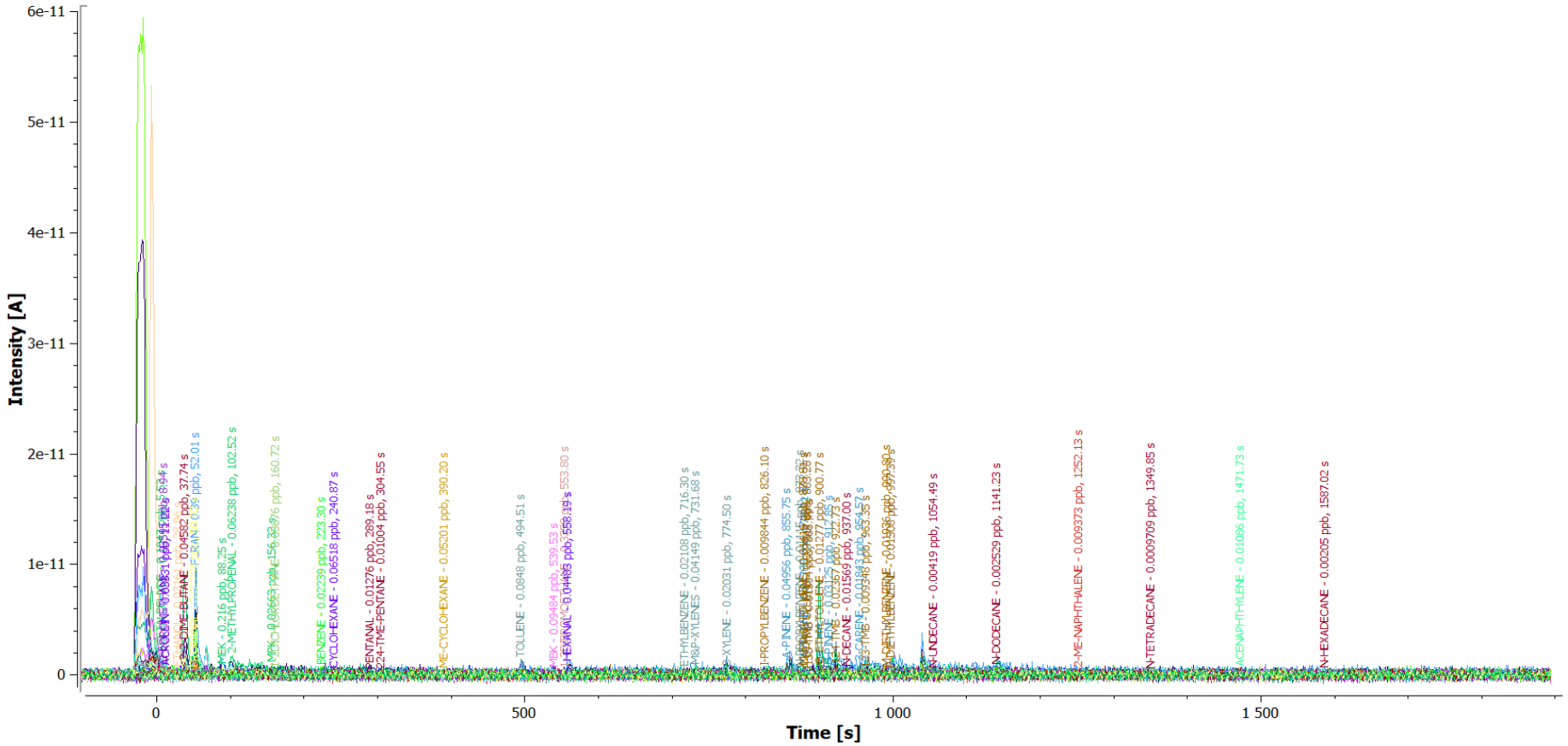



RSD = 100% with FID: coelutions

0.07% ≤ RSD ≤ 21.4%

# Results
# Algorithm efficiency evaluation in field measurement chromatogram

MS **corresponding** chromatogram of ambient air in a field measurement campaign (forest)



# Results
# Algorithm efficiency evaluation in field measurement chromatogram

Algorithm: If [FID] – [MS] < **CST_C_GAP**

Or

If $\frac{[FID]-[MS]}{[MS]}$ < **PCENT_C_GAP**

Then FID value selected

Otherwise MS value

Example of results obtained after algorithm implementation:

| Compound identified | **FID** result (ppb) | **MS** result (ppb) | **Valid** result (ppb) | Detector selected |
|---|---|---|---|---|
| BENZENE | 0,015 | 0,022 | 0,015 | FID |
| 1-2DICHLOROETHANE | - | 0,037 | 0,037 | MS |
| C-1-2-DICL-ETHENE | 0,051 | 0,000 | Unknown | Unknown |
| A-PINENE | 0,053 | 0,050 | 0,053 | FID |
| O-ETHYLTOLUENE | 0,385 | 0,013 | 0,013 | MS |
| CAMPHENE | - | 0,018 | 0,018 | MS |

Automatic RP before algorithm: 49 compounds

- FID id: 29
- MS id: 43

Automatic RP after algorithm: 43 compounds

- Result given with FID detection: 14 (33%)
- Result given with MS detection: 29 (67%)

→ Correction of 6 misidentifications by the algorithm

→ 2 mistakes not detected by the algorithm

Identification of the noise

# Conclusion and perspectives

Performance and limitations of **on-line auto-TD-GC-FID/MS** to identify and quantify odorant VOCs in ambient air studied:

- C2C6:
  - Analysis of light Hydrocarbon, Halogenated compounds and Freons
  - Light OVOCs not detected
- C6C16:
  - Analysis of hydrocarbons, halogenated compounds and OVOCs
  - Method validated to quantify these compounds (Linear, accurate and precise)

→ System suitable to analyze odorant VOCs

Implementation of an algorithm to select the best result between FID and MS detector:

- Algorithm evaluated on standard at 4 ppb
  - Accuracy after algorithm: 0,07% ≤ RSD ≤ 21,4%
- Algorithm evaluated in field measurement chromatogram:
  - Efficient at 95%

Perspectives:

- Adjust the algorithm to improve efficiency
- Extend the study for more than 1 chromatogram: 1 day, 1 month or the entire measurement campaign

# Acknowledgements

**ICARE CNRS Orléans:**

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- Benoit GROSSELIN
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- Max McGILLEN

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- Damien BAZIN
- Analytical team

**Thank you for your attention**

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