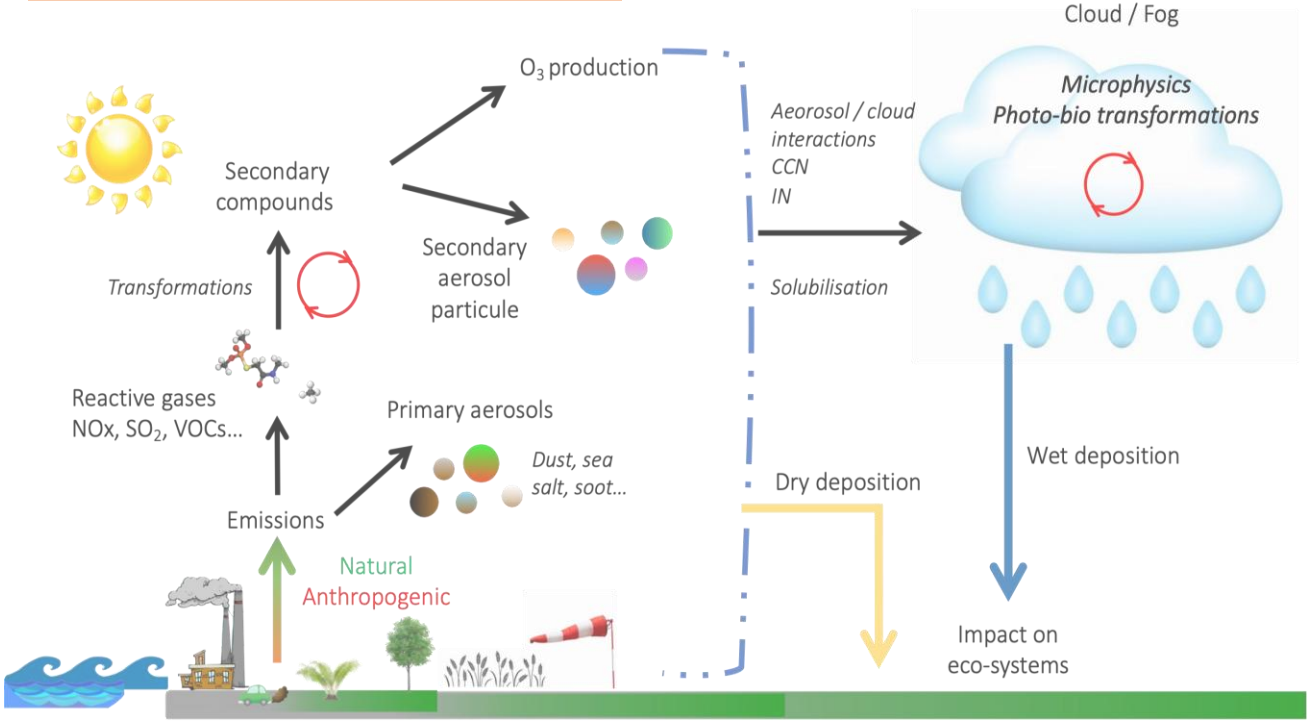
Recent insights on ambient oxygenated VOCs at the puy de Dôme atmospheric station during the TNA RACLET campaign

Fabrice Mollard, Agnès Borbon, Thérèse Salameh, Audrey Grandjean, Sibylle Janoux, Damien Bourgain, Damien Bazin, Alexandre Dembiki, Magdalena Hofman, Maxime Dumont, and the PUY team

Context

Atmospheric transport of gas/aerosol/water vapor air masses

Gas/aerosol transformations



Aerosol cloud interactions (CCN/IN) and gases (mass transfer)

Aqueous phase processes Chemical and biological transformations

Natural/Anthroprogenic emissions

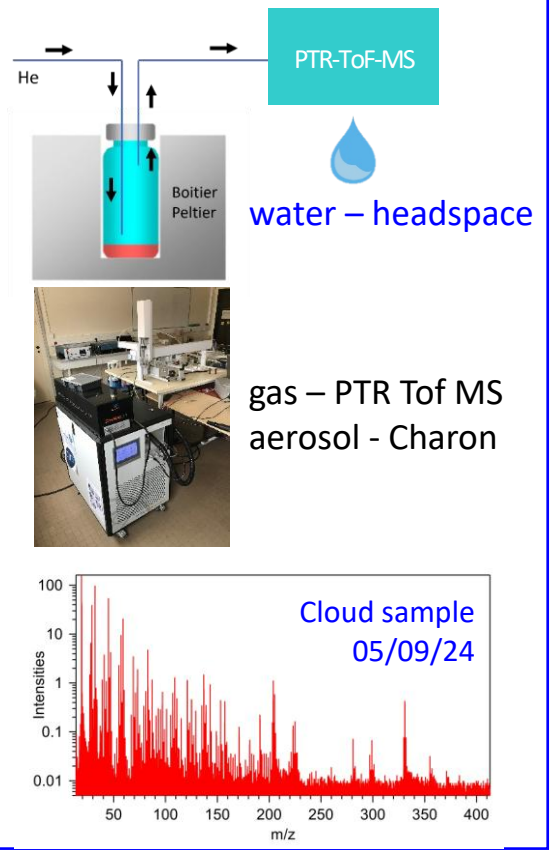
Target : fate of organics in all phases

OVOC within this context

Technical evaluation and development

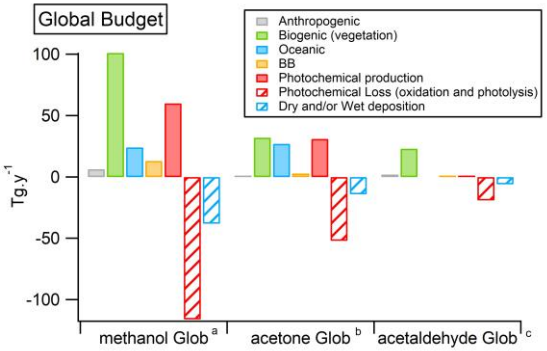
- Few measurements & no traceable standard
- MOCCA mass spectrometry ensemble →
- Commercial instrumentation

MOCCA



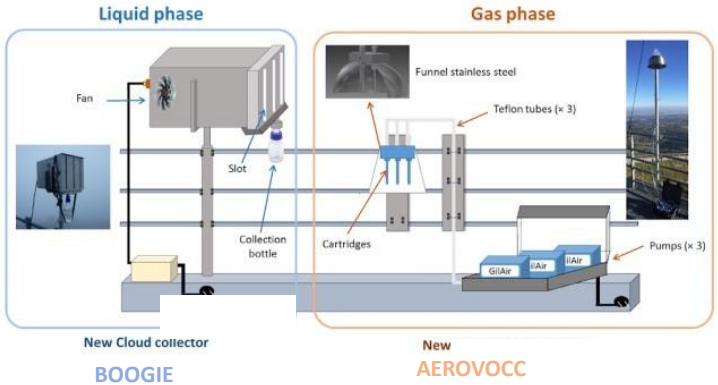
E. Brugere, PhD, 2024

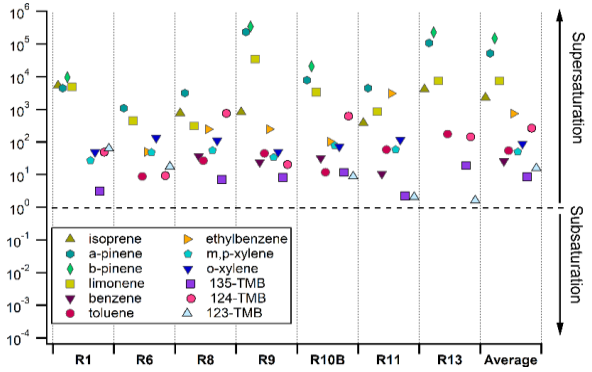
Elucidating their budget and drivers



Borbon et al., 2024

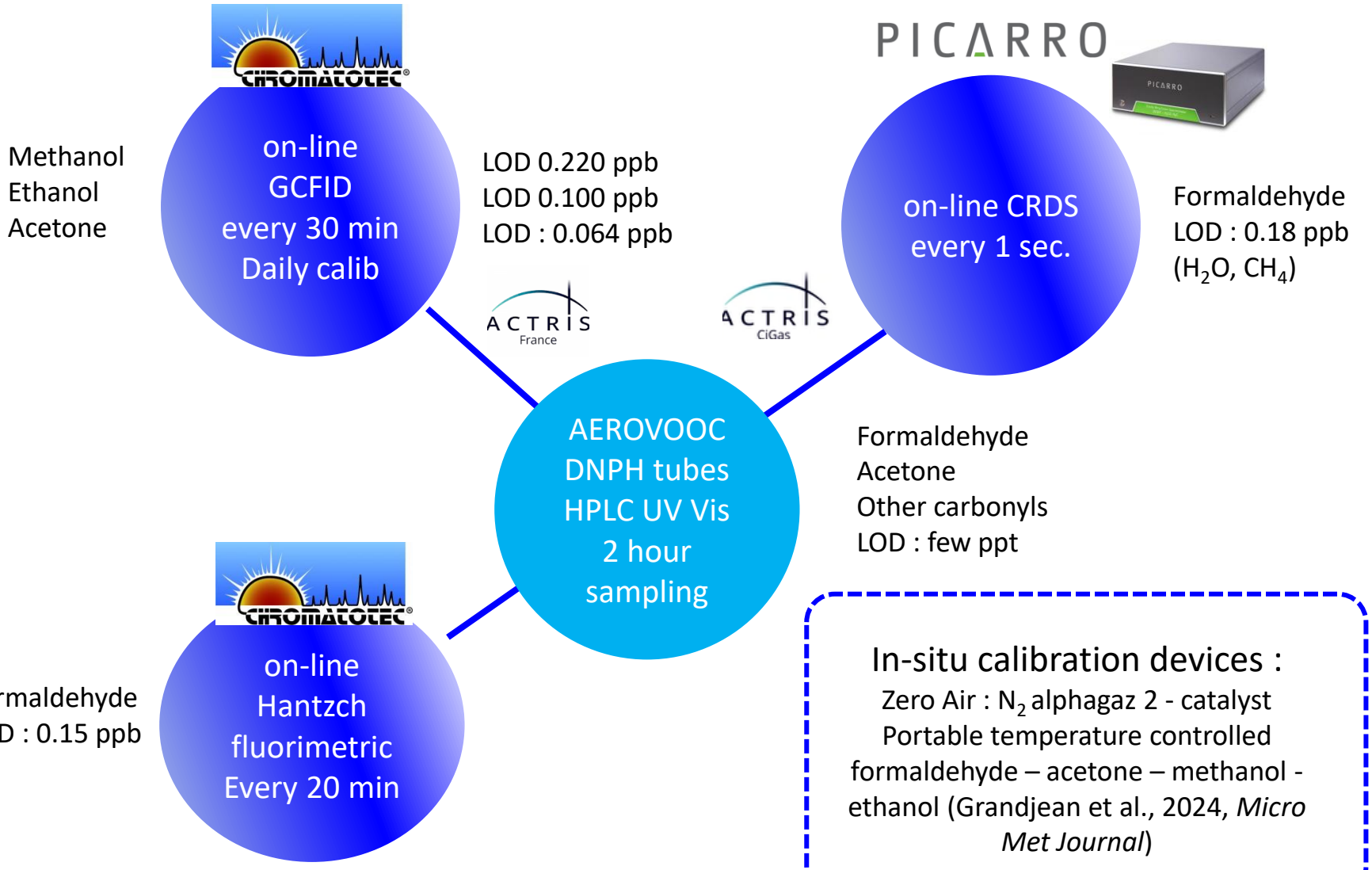
How do VOC partition between cloud phases ?





Instrumentation « *on shelf* »

OVOC = **formaldehyde** – methanol – acetone - ethanol



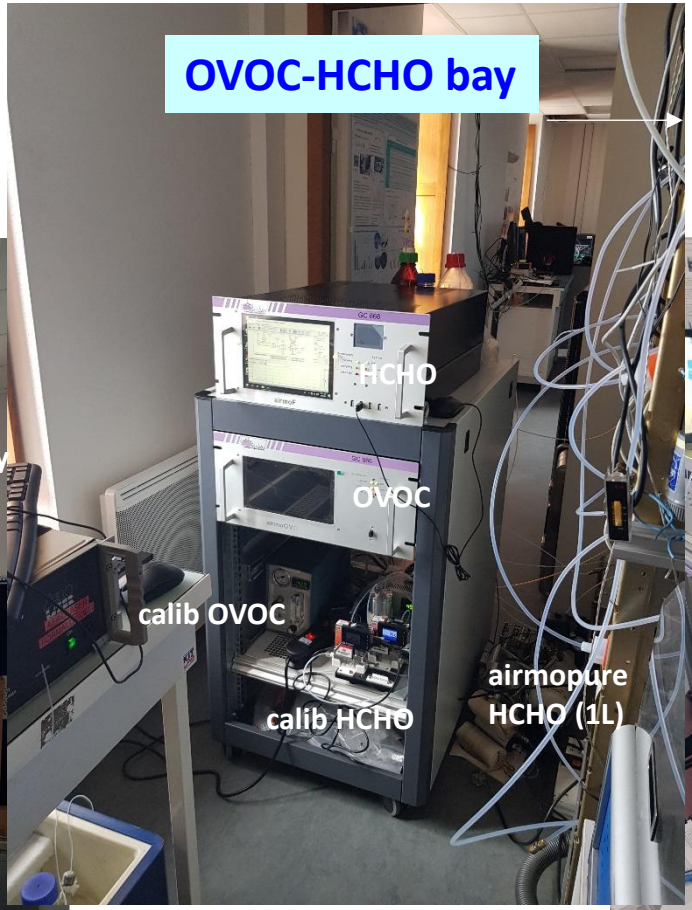
patent under process

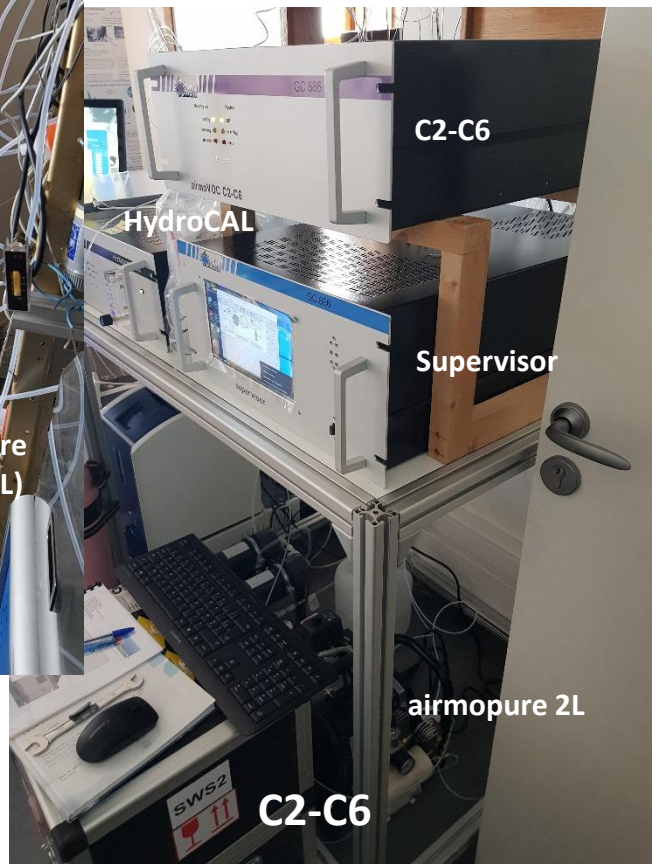
In-situ calibration devices :

Zero Air : N_2 alphagaz 2 - catalyst

Portable temperature controlled formaldehyde – acetone – methanol - ethanol (Grandjean et al., 2024, *Micro Met Journal*)

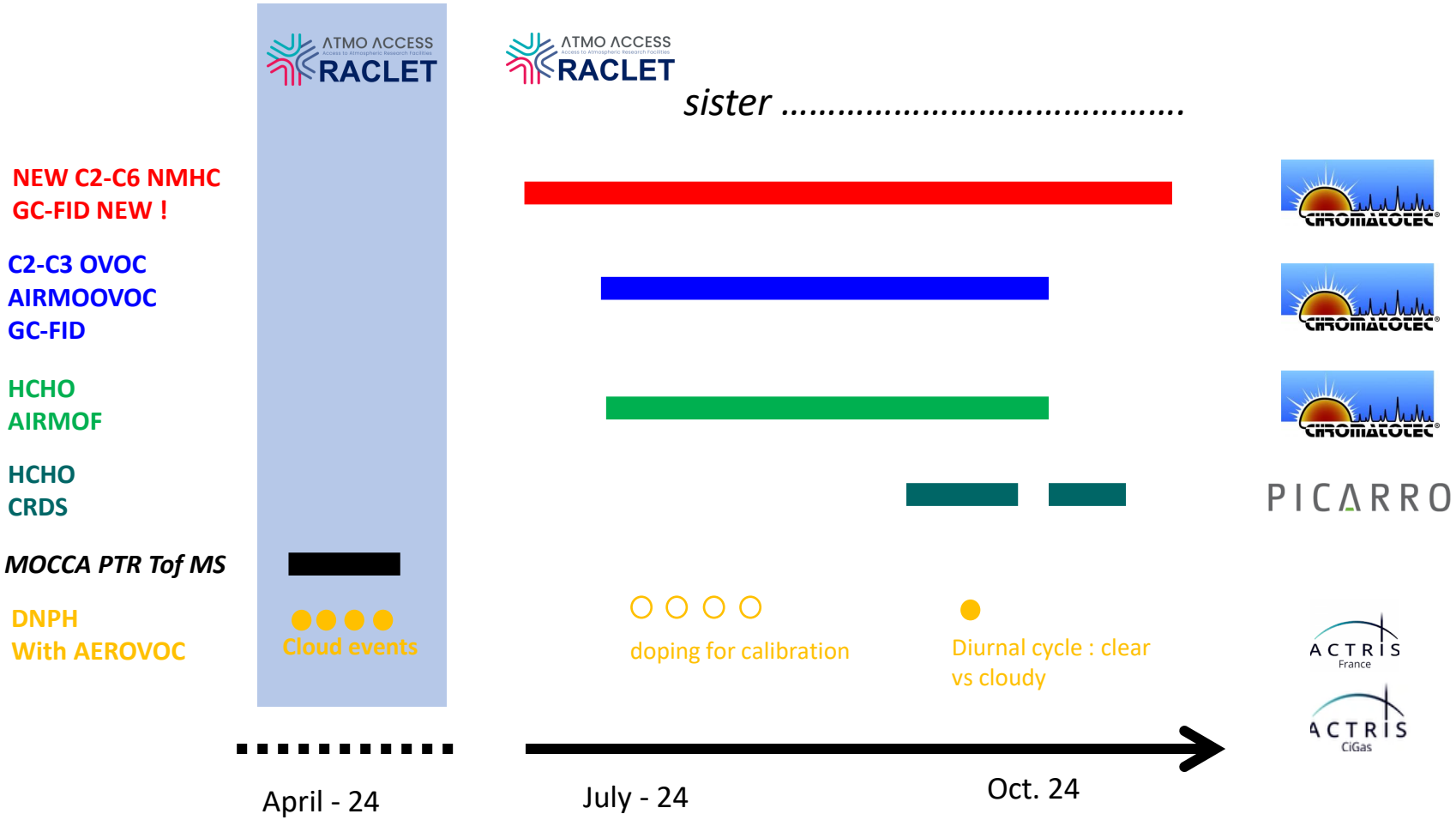

OVOC-HCHO bay
C2-C6
GC
Trace gas lab


OVOC-HCHO bay
HCHO
OVOC
calib OVOC
calib HCHO
airmopure
HCHO (1L)


C2-C6
HydroCAL
Supervisor
airmopure 2L
C2-C6

Strategy for OVOC measurements

Continuous ambient measurement and regular cross checked calibrations



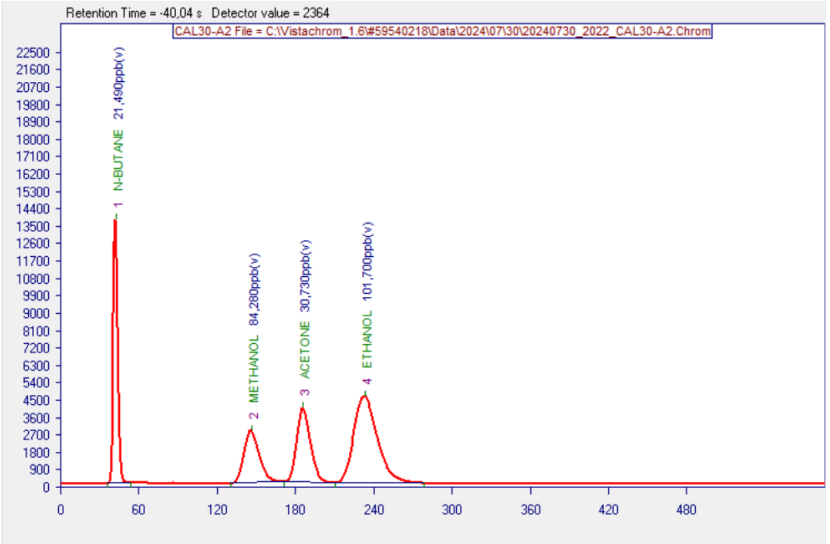
Operating rate during 5 months : more than 80%

Problems: no daily calibration on August on AIRMOVOC – offset of the Picarro

Evaluation of the calibration standards

- Retention time

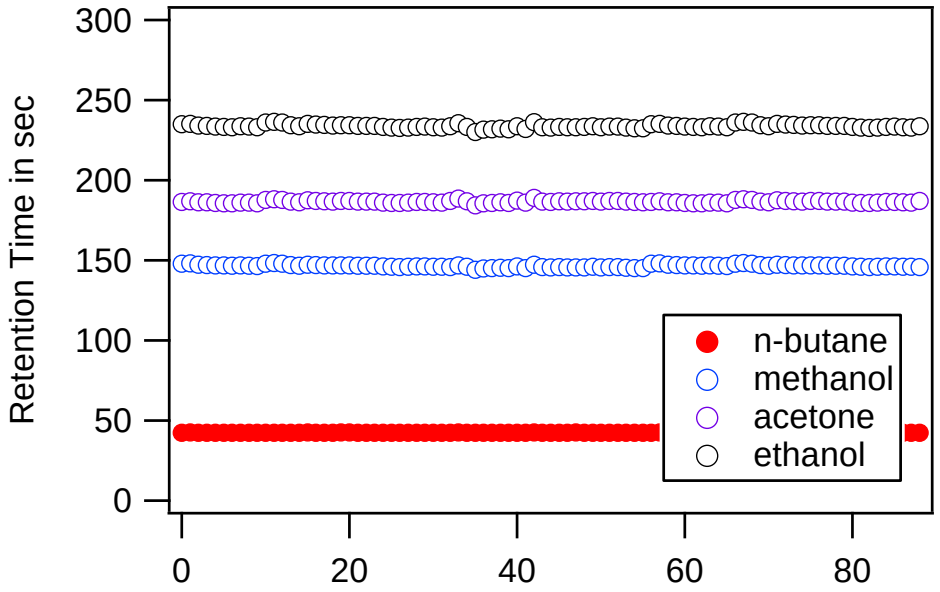
AIRMOOVOC



Less than 1 sec. Shift over the period

Calculation of a base sensitivity relative to butane :

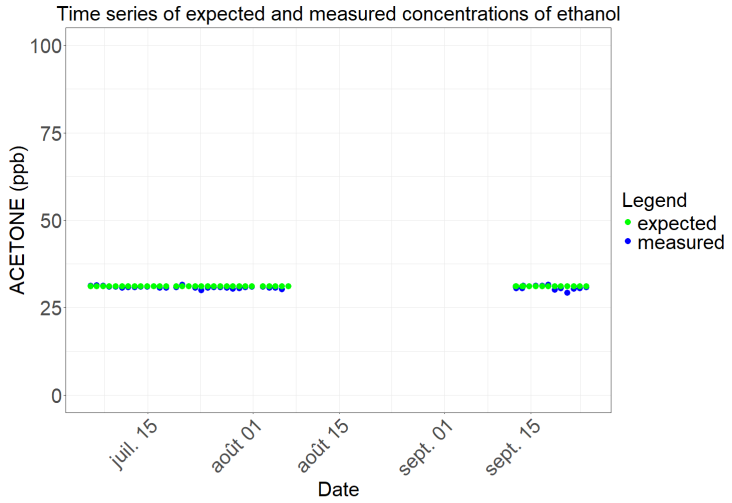
$$BS = \frac{RF.Area}{C.V}$$

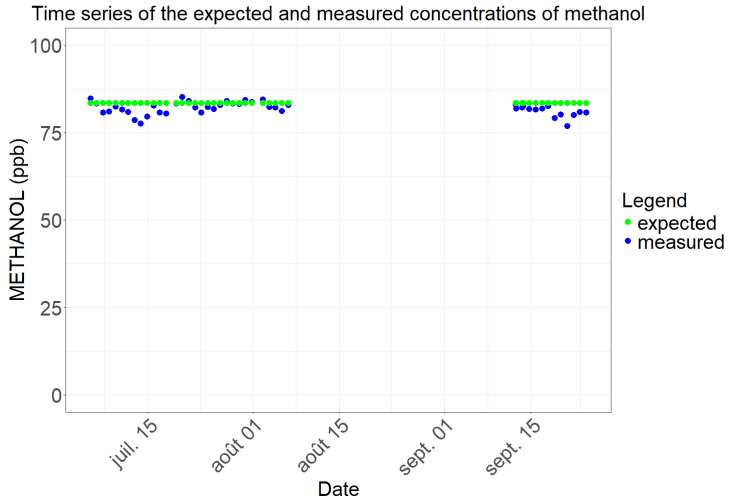


Evaluation of the calibration standards

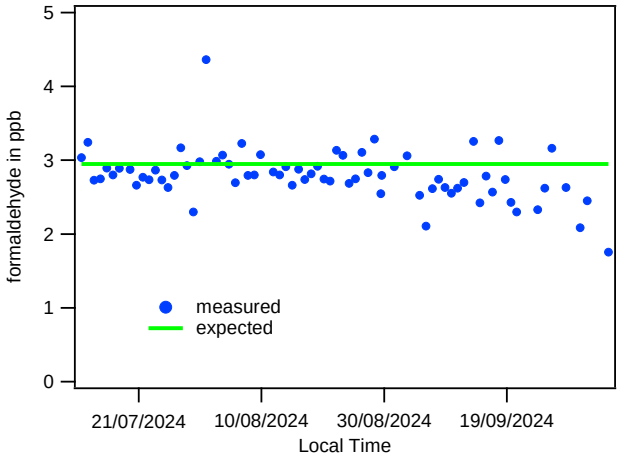
- Stability in time of the gaseous standard generation by the permeation tube

AIRMOOVOC





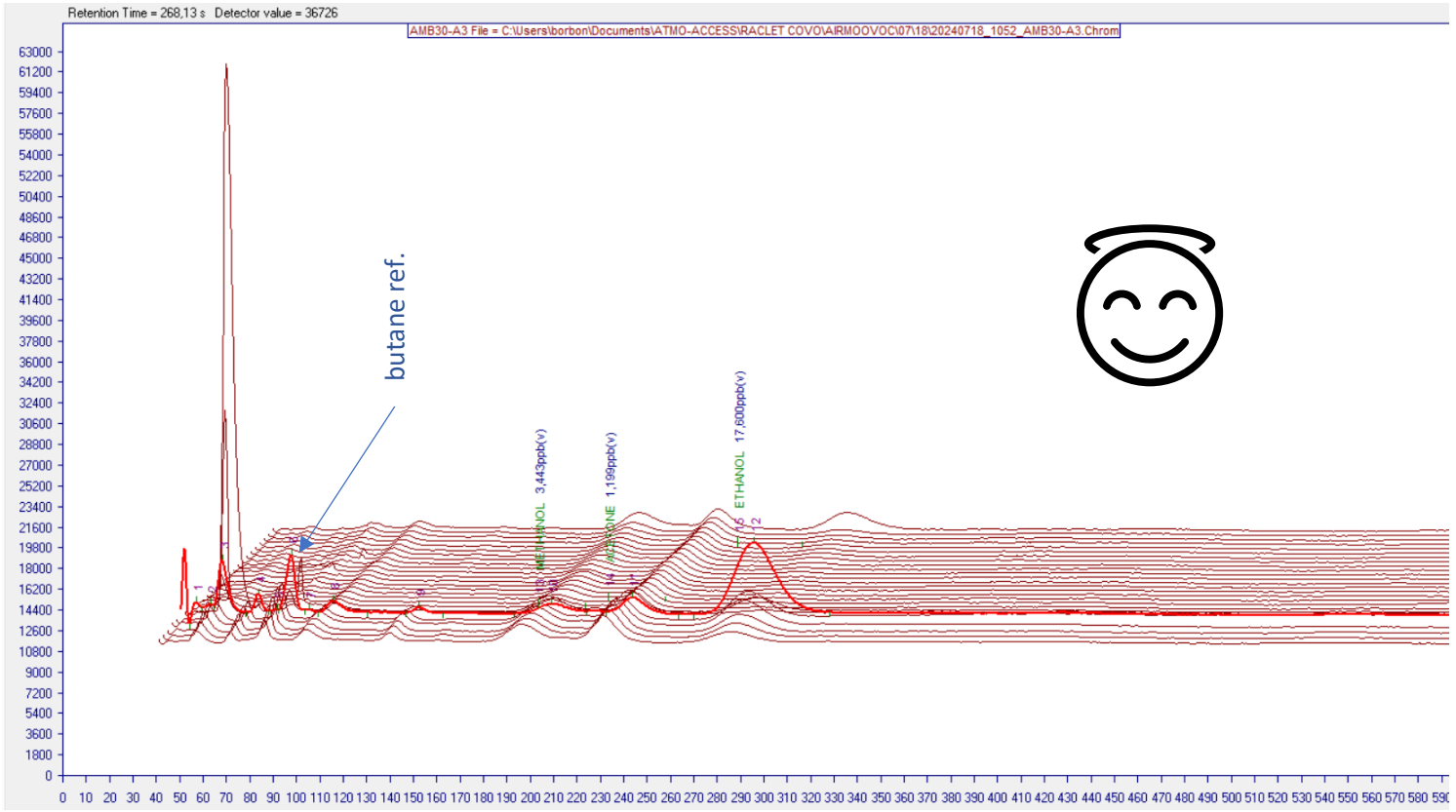
AIRMOF



OVOC	Control chart (RSD)	Absolute RD from expected
Acetone	13%	12%
Methanol	22%	19%
Ethanol	17%	25%
Formaldehyde	11%	8%

Example of ambient chromatogram (July 18th)

AIRMOOVOC



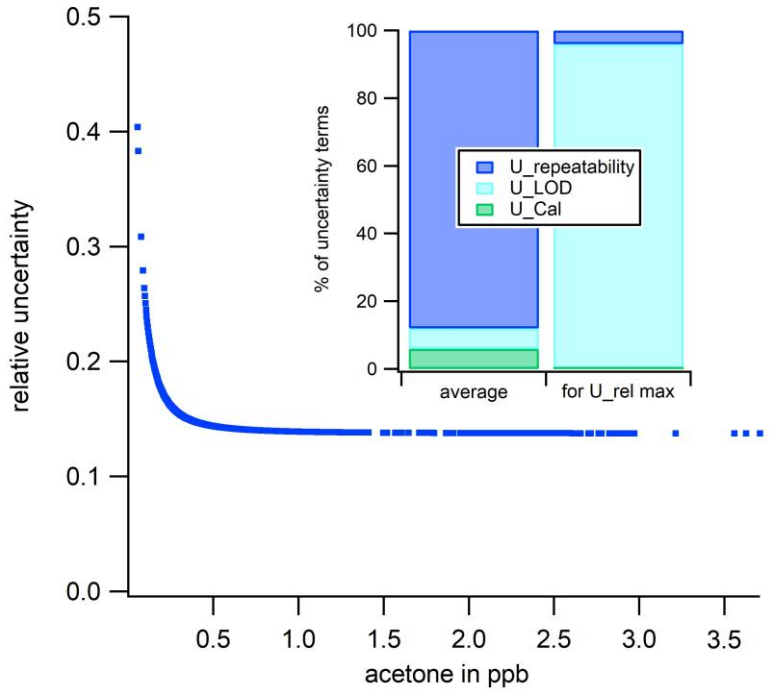
Evaluation of the uncertainty of ambient OVOC

- Evaluation of uncertainty (U) following *GAW Guidelines for NMHC measurements in the troposphere, Report N°281, 2023*
- Combination of the reproducibility and detection limits (precision) and accuracy of the calibration gas

$$u\chi^2_{prec} = \left(\chi_{sample} * \sigma^{rel}_{series}\right)^2 + \left(\frac{LOD}{3}\right)^2$$

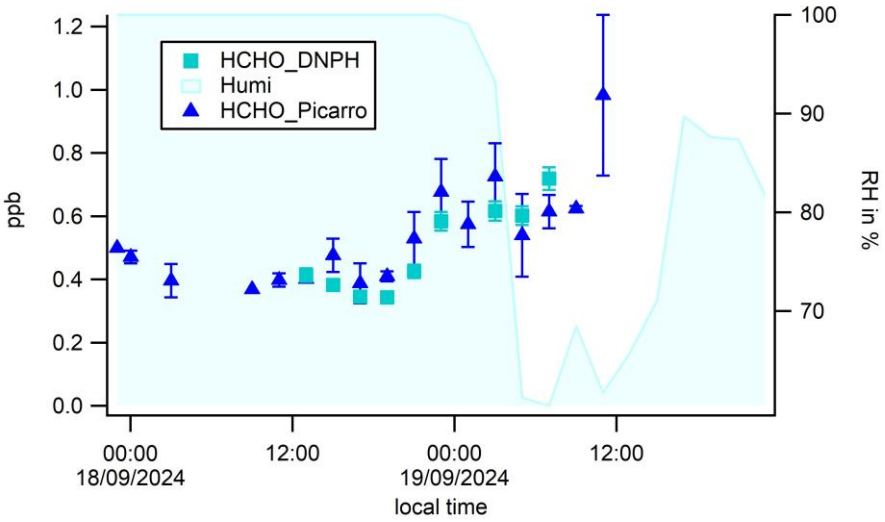
$$u^2_{\chi cal} = \left(\chi_{sample} * u_{cal,rel}\right)^2$$

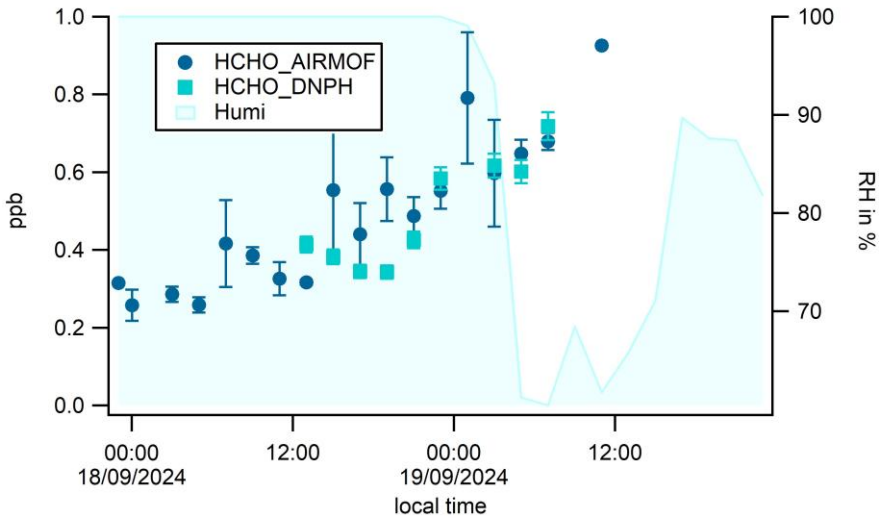
OVOC	U relative
Acetone	17%
Ethanol	60%
Methanol	47%
Formaldehyde	18%

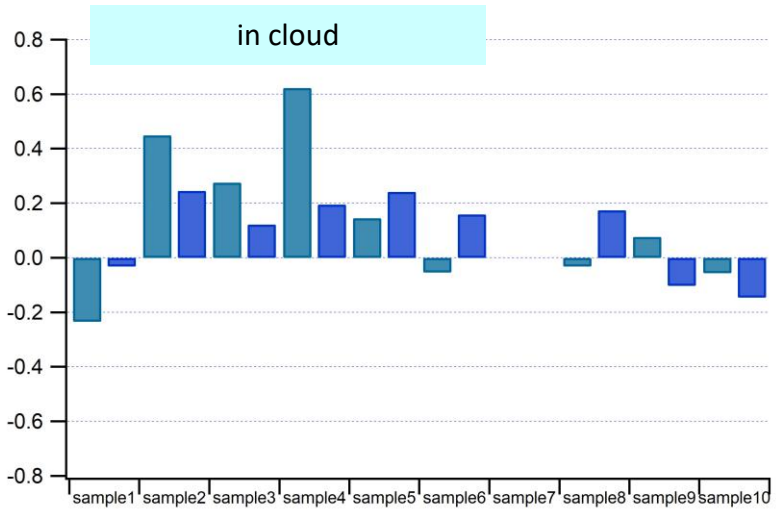


September 18th to 19th : DNPH vs all

- Formaldehyde : 200 – 900 ppt : low HCHO

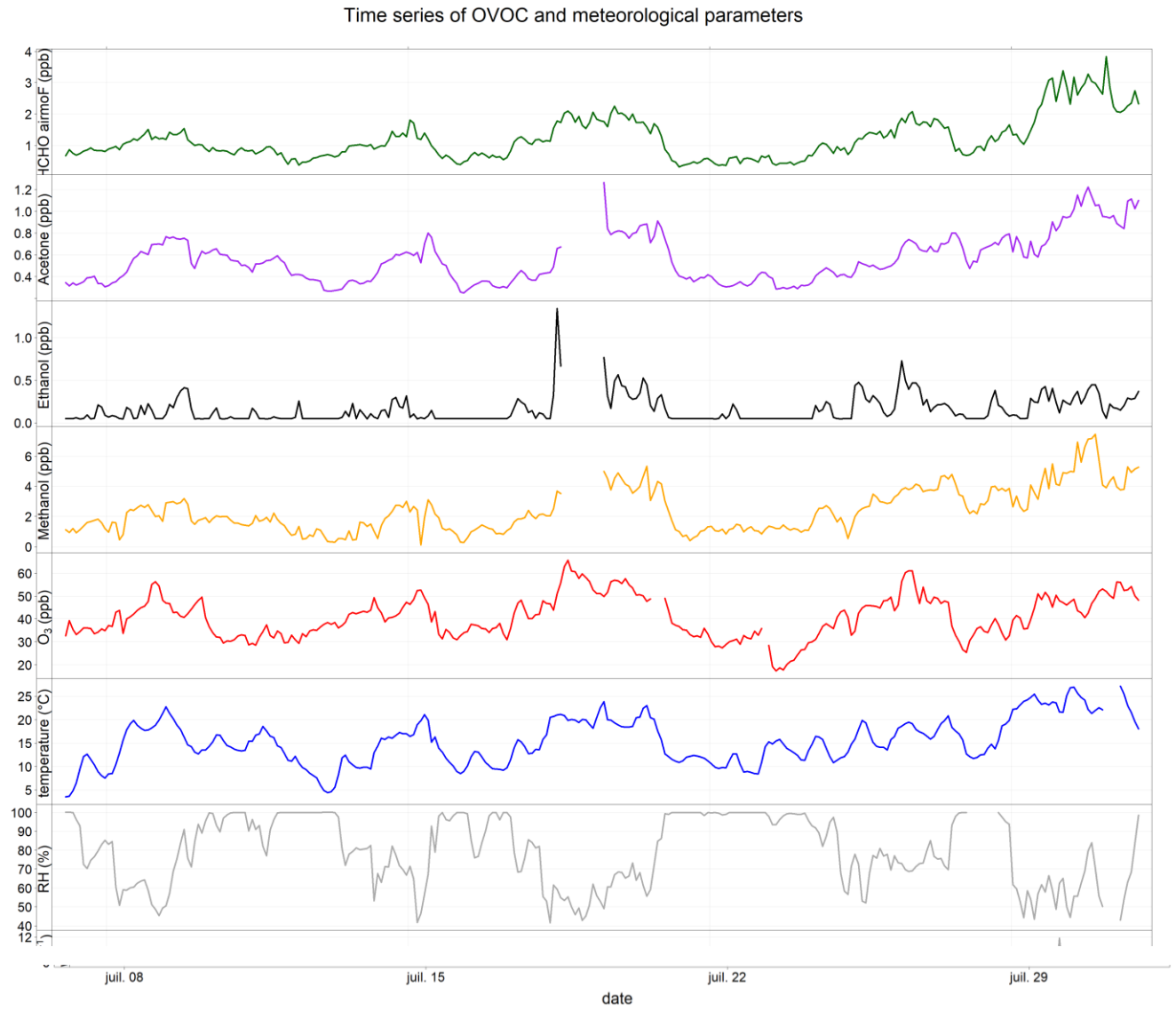






- Variability is consistent
- DNPH values within the SD
- Relative deviation from DNPH : 10% for Picarro and 13% for AIRMOF on average
- Higher in cloud : effect of humidity (no change in air mass direction) ?

Time series : July 2024



formaldehyde

acetone

ethanol

methanol

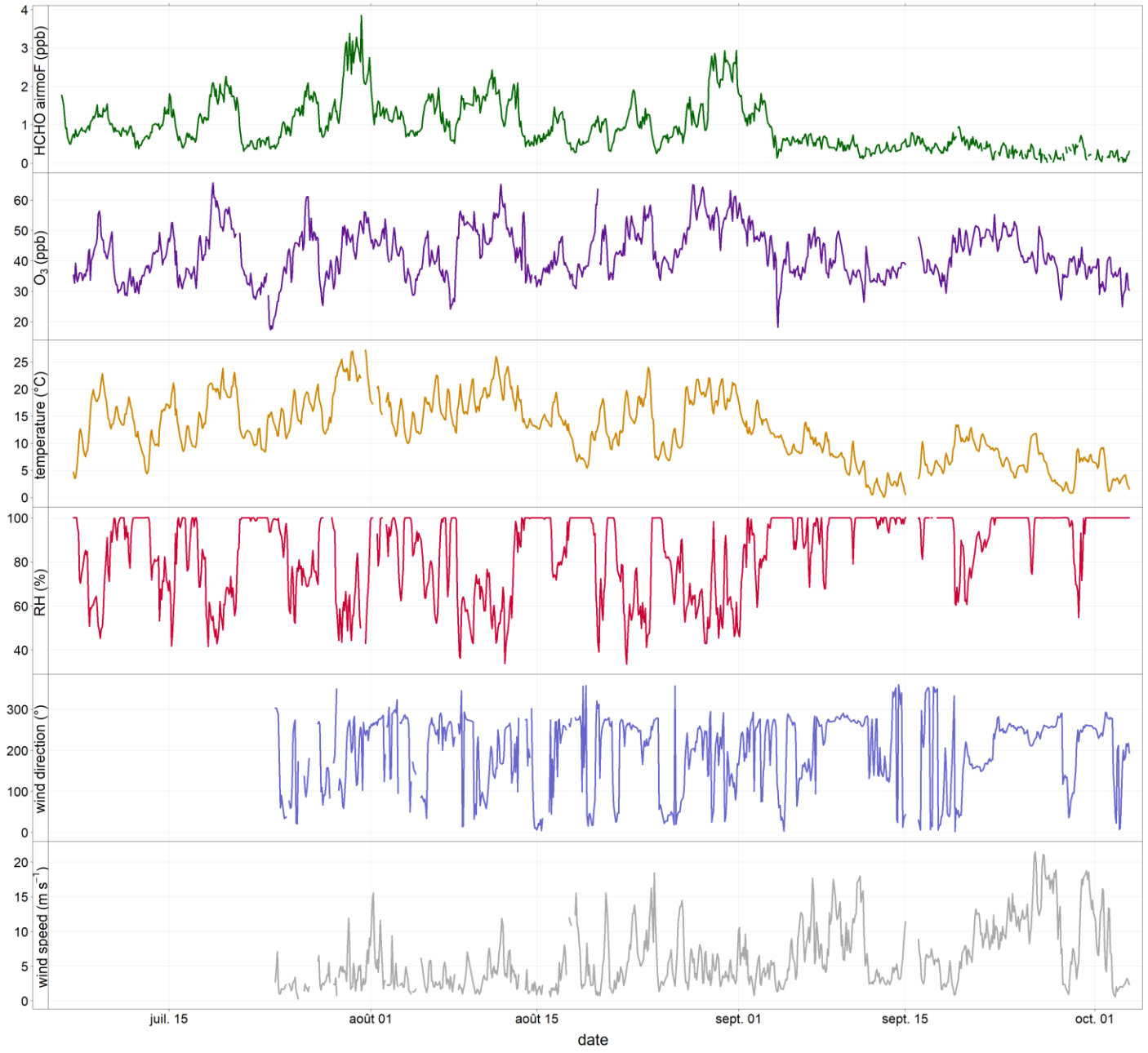
ozone

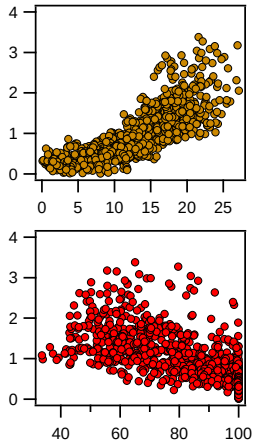
temperature

RH

LaMP

Time series of OVOC and meteorological parameters





UNIVERSITÉ Clermont Auvergne

cnrs

OPGC Observatoire de Physique du Globe de Clermont-Ferrand

Preliminary conclusions and moving forward

- Deployment looks robust but few OVOCs
- Chromatogram integration and peak integration : semi automatic …
- Cross-check calibrations to be analyzed in details
- Analyze the variability of OVOC and their drivers
- To be put in perspective with other initiatives (METCLIMVOC)
- Data to be reported in 2025 ?

LaMP

Thank you

UNIVERSITÉ Clermont Auvergne

cnrs

OPGC Observatoire de Physique du Globe de Clermont-Ferrand