Metrology for climate relevant volatile organic compounds

MetClimVOC

M18 Meeting - Stakeholder workshop

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Project MetClimVOC

https://www.metclimvoc.eu

EURAMET* – EMPIR** project

June 2020 – May 2023

Consortium: 13 partners

Coordination: METAS

EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

* European Association of National Metrology Institutes

** Eur. Metrology Programme for Innovation and Research

Consortium

Consortium made of NMIs and direct end-users (e.g. appointed calibration centres)

DWD Anja Claude

Empa Stefan Reimann, Martin Vollmer, Matthias Hill, Paul Schlauri

FMI/IL Heidi Hellén, Simon Schallhart, Toni Tykkä

IMTelecom Stéphane Sauvage, Thérèse Salameh, Evdokia Stratigou, Sebastien Dusante, Thierry Leonardis

KIT Rainer Steinbrecher

LNE Christophe Sutour, Tatiana Macé

METAS Céline Pascale, Maitane Iturrate-Garcia, Tobias Bühlmann, Andreas Ackermann

POLITO Maricarmen Lecuna, Guido Sassi

PTB Volker Ebert, Gang Li, Mi Eon Kim

TUBITAK Mine Bilsel

UoL Jeremy J. Harrison

UU Rupert Holzinger, Dusan Materic

VSL Annarita Baldan, Stefan Persijn, Jianrong Li

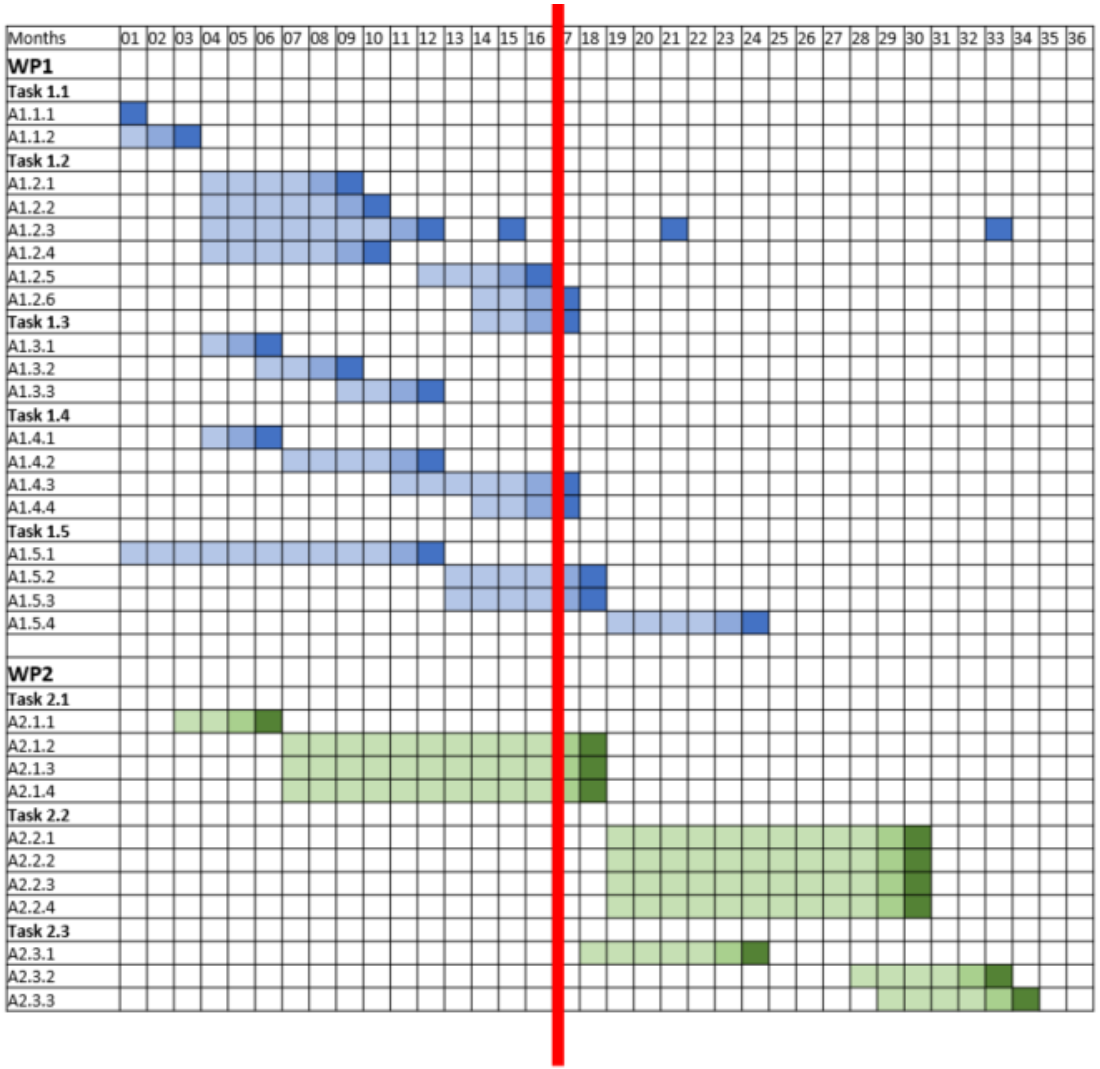
Stakeholder committee and collaborators

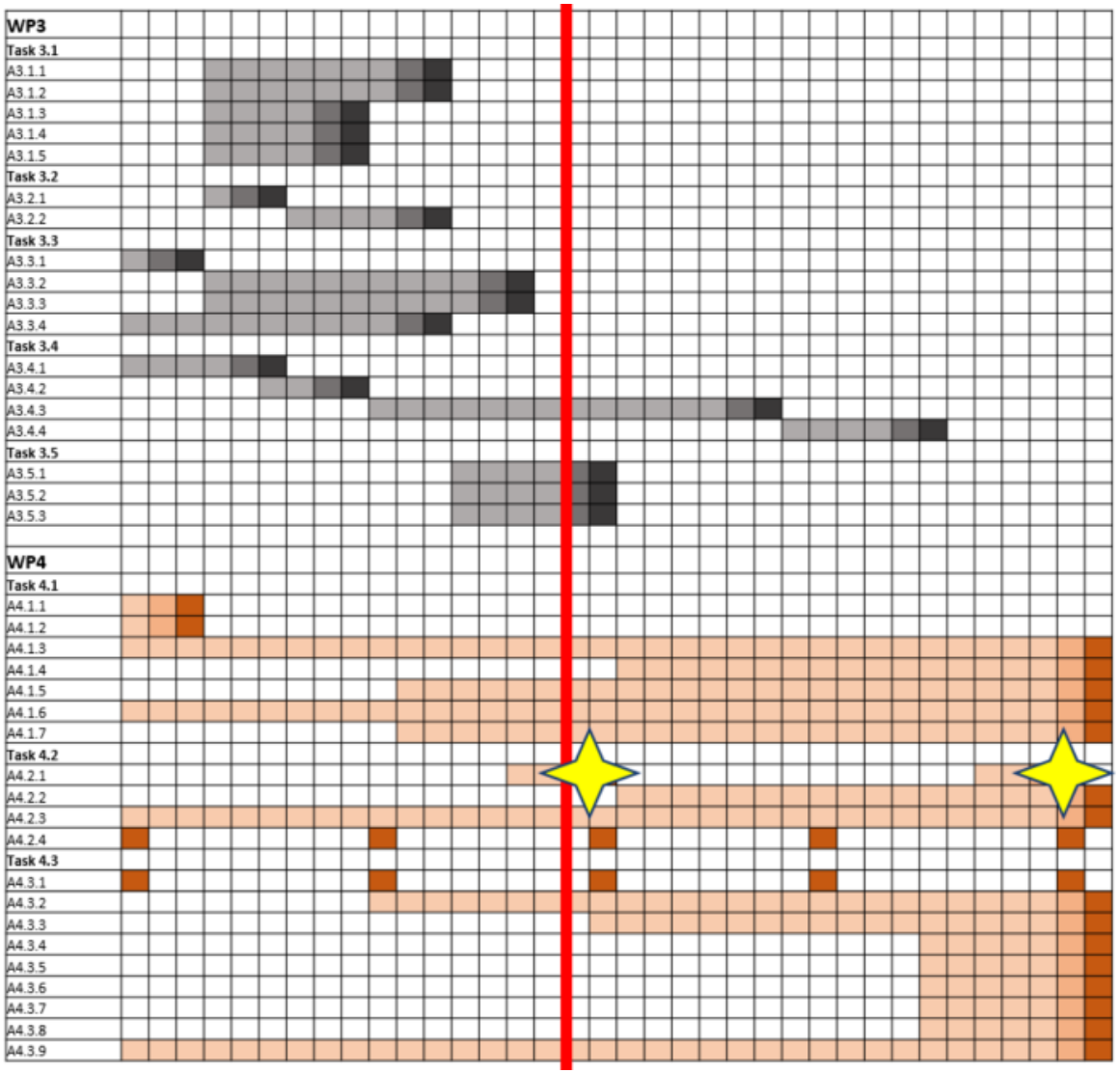
Collaborators

Stakeholders

Gantt chart

Stakeholders workshop





Volatile Organic Compounds (VOCs)

- Definitions
  - boiling point ≤ 250°C at 101.3 kPa *
  - vapour pressure ≥ 0.01 kPa at 293.15 K **
- Reactive, short lifetimes, thermal instability
- Atmospheric low amount fractions (pmol/mol → nmol/mol)

* Directive 2004/42/CE
** Directive 2010/75/EU

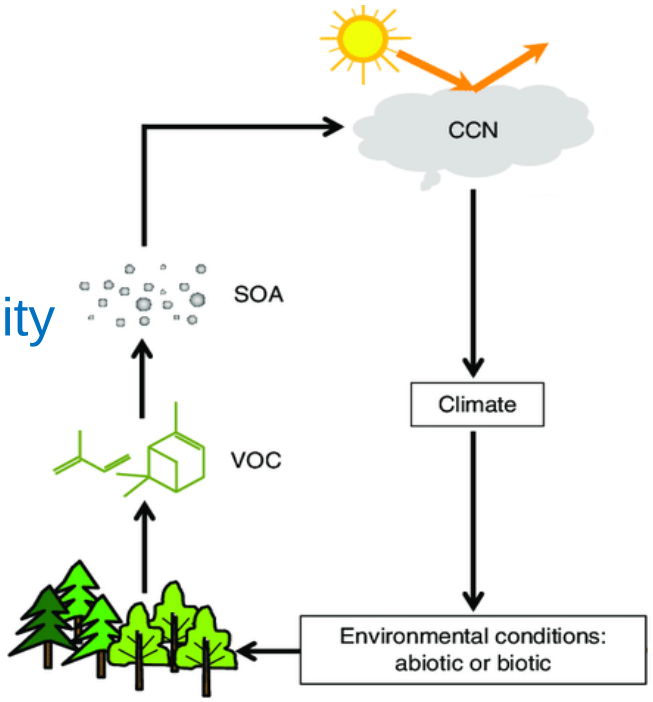
- In the **MetClimVOC** projet:

VOCs and climate

Increase formation of:

- tropospheric O_3
- SOA
- RO_x + OH radicals (OH, HO_2, RO_2)
- PAN

Effects on oxidising capacity of the atmosphere, on climate and on air quality



(Modified from Zhao et al. (2016), Nat. Commun.)

Halogenated VOCs = GHG with high global warming potential

Designated as Essential Climate Variables (WMO-GCOS)

Atmospheric Composition
Aerosols properties
Carbon Dioxide, Methane **other Greenhouse gases**
Ozone
Precursors (supporting the Aerosol and Ozone ECVs)

GCOS GLOBAL CLIMATE OBSERVING SYSTEM

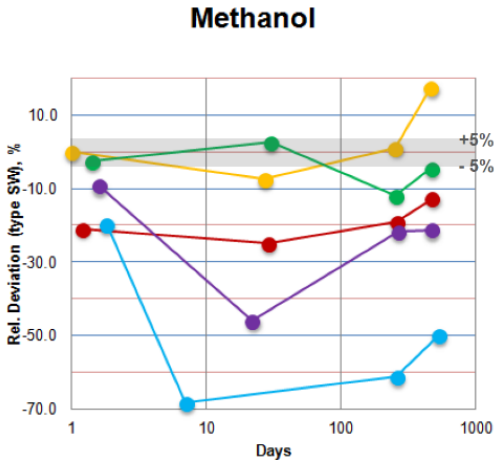
Challenges in monitoring VOCs

For many VOCs, **lack** of **reference gas mixtures (RGMs)** that are:

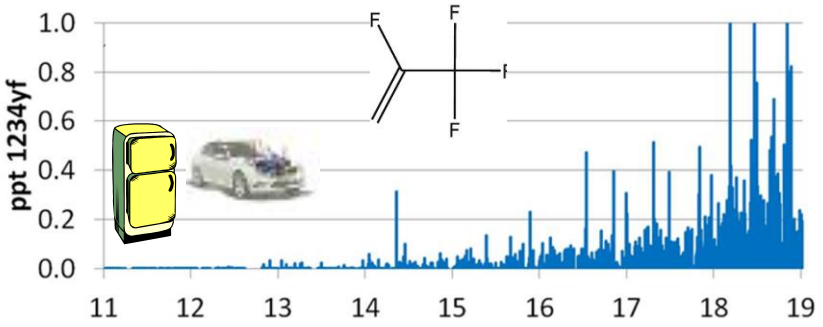
- **stable**
- **traceable** to the international system of units SI
- at **atmospheric level** (pmol/mol to nmol/mol)

At air monitoring sites, **measurements** of VOCs are **extremely challenging** due to:

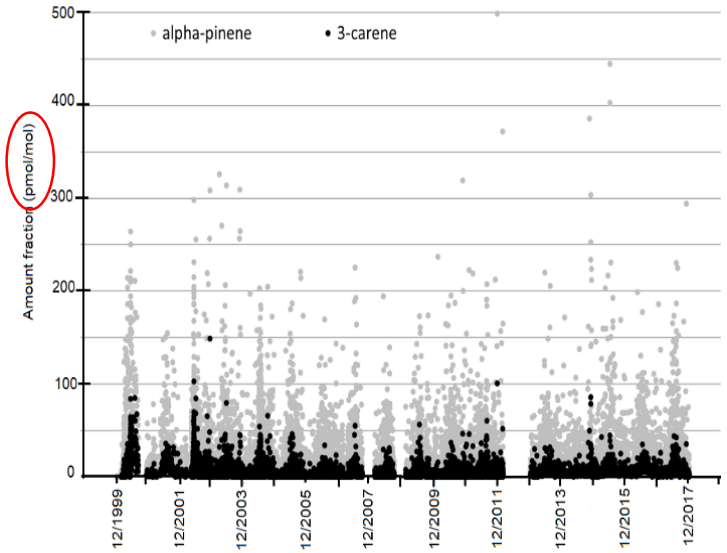
- **Humidity and ozone** interferences (artefacts, memory effects)
- **reactivity** with surfaces
- **low** amount fractions



(Persjin, GAS2017)



(Courtesy of Stefan Reimann, Empa)



(Courtesy of Anja Claude, DWD)

Aims of MetClimVOC

To realize **accurate**, **stable** and **traceable RGMs** of VOCs at atmospheric levels

WP1

To **optimize sampling** and **analytical methods** used in monitoring stations

WP3

To develop **fit-for-purpose working standards** & **disseminate** appropriately to the field, including full **uncertainty** estimations on real air measurements

WP2

WP1: VOCs Reference Gas Standards for the chemistry of atmosphere

- Prioritizing VOCs compounds according to stakeholder needs
- Developing novel RGMs for oxy-VOCs, terpenes and halogenated compounds (static and dynamic) at atmospheric levels
- Reducing uncertainty and improving stability of RGMs
  - oxy-VOCs, terpenes: 1 – 1000 nmol/mol, expanded uncertainty < 5 %
  - halogenated VOCs: < 1 nmol/mol, expanded uncertainty < 3 %

(Source: VSL)

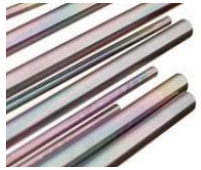
WP3: Development and improvement of measurement methods

- Improving sampling techniques (incl. ozone and water effects)
- Improving analytical techniques (PTR-MS, GC-ToFMS, HPLC)
- Determining uncertainty contribution of sampling and analytical artefacts
- Metrologically validating spectral parameters for remote-sensing techniques

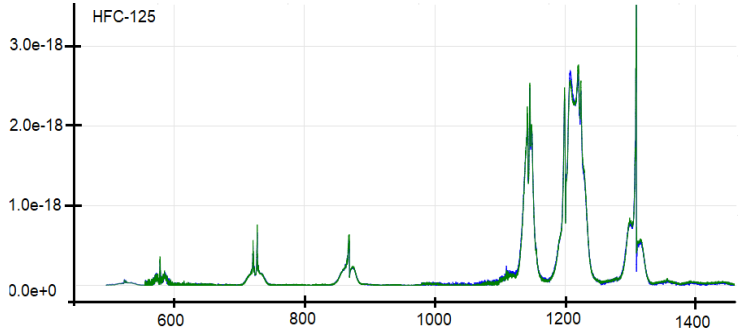
Sorbent tubes

(Source: SKC)

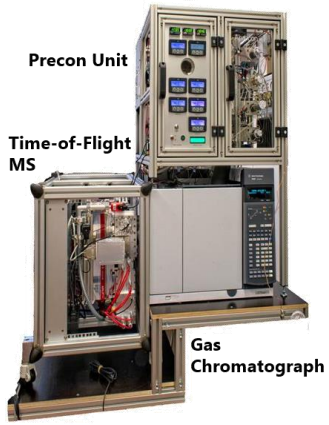
Tubing coating



(Source: Coclema)



(Source: HITRAN (modified))



PTR-TOF-MS

(Source: IONICON)

FID-GC-MS

WP2:Working standards: Traceability, dissemination and comparisons

- Developing fit-for-purpose working standards and (protocoles)
- Ensuring traceability from primary reference to calibration on-site
- Determining uncertainty of working standards and combine with calibration and measurement uncertainty
- Comparison of new working standards and current scales/methods (non-SI standards)
- Developing user-friendly software for measurement uncertainty calculation

First outputs – VOC priority list (Deliverable 1)

Selection of in-situ priority VOCs in collaboration with the project Stakeholder Committee

- criteria: relevance for climate, lack of stable standards at low amount fractions…

Oxygenated VOCs	Terpenes	Halogenated VOCs
Acetaldehyde	β-caryophyllene	1,2-dichloroethane
Acetone	Myrcene	Desflurane
Ethanol	α-pinene	HCFC-124
Methacrolein	β-pinene	HFC-134
Methanol	Terpinolene	HFO-1336mzz-Z
Methyl vinyl ketone (MVK)	--	--

https://www.metclimvoc.eu/blog2.html

First outputs – VOC priority list (Deliverable 1)

Selection of remote priority VOCs in collaboration with the “remote sensing group”

- criteria: relevance for climate, lack of traceable spectral data, easy to handle in experimental setup

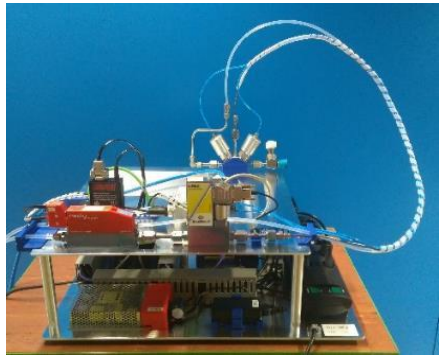
Halogenated VOCs
Carbon tetrafluoride (CFC-14, CF_4)
Dichloro(difluoro)methane (CFC-12, CCl_2F_2)
Trifluoromethane (HFC-23, CHF_3)

https://www.metclimvoc.eu/blog2.html

First outputs – Reference Gas Mixtures for halogenated

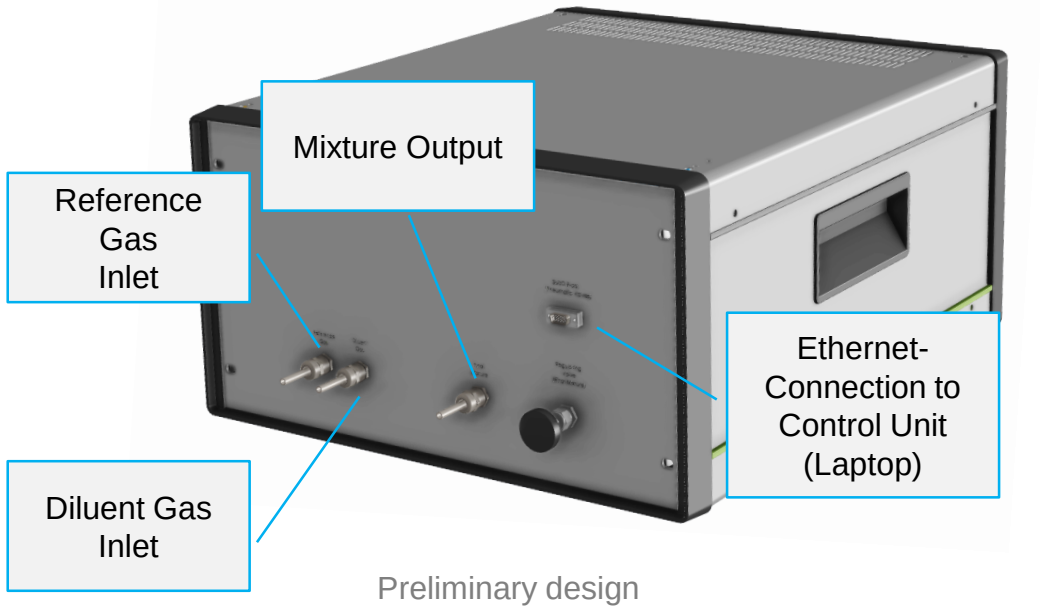
METAS 2021 scale: set of 8 cylinders containing 3 halogenated VOCs from priority list (+ 4 others) at near-ambient amount fractions (0 – 10 pmol/mol)

- 1,2-dichloroethane
- HFC-134
- HFO-1366mzzZ
- HFC-32
- HFC-365mfc
- CH_2Cl_2
- CCl_4



First outputs – Dilution system up to pmol/mol

Development of a novel two-step dilution system to dilute higher-concentrated gas mixture to atmospheric levels



Preliminary design

VeRDi
Versatile Reactive Gas Diluter

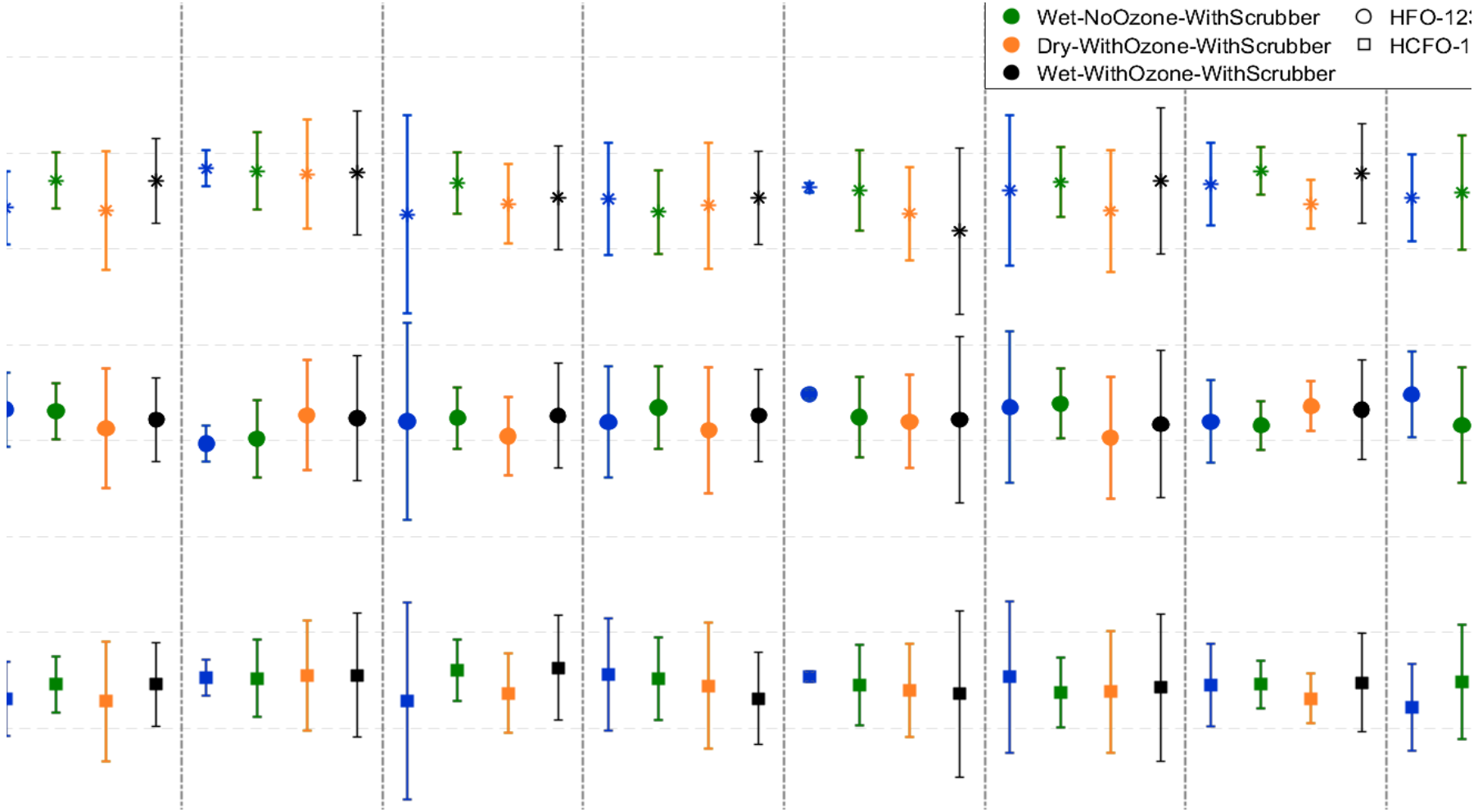
in collaboration with Swagelok SWITZERLAND

First outputs – Whole air standards

Establishment of novel whole air standards → filling and ongoing certification

First outputs – Measurement artefacts

Identification of artefacts for measurement of halogenated VOCs with and without humidity/ozone



First outputs – Sampling lines/devices

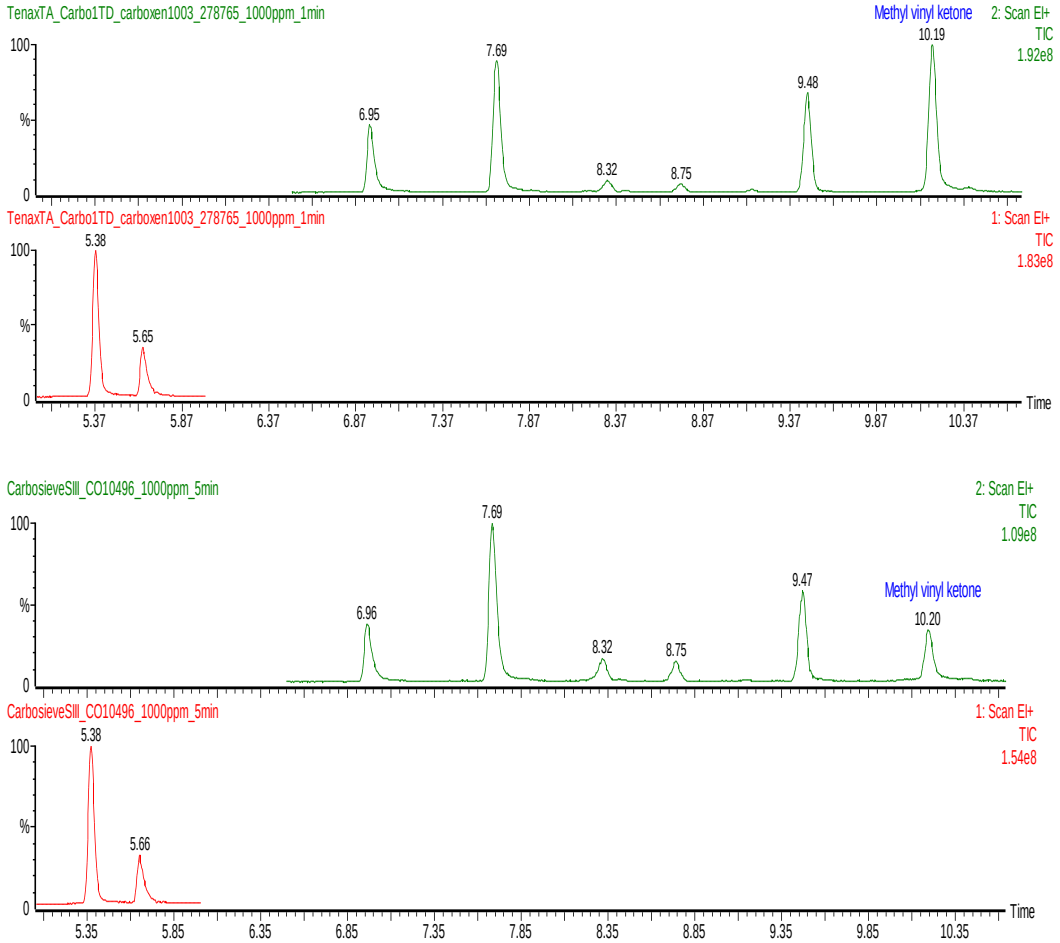
« Pressure reducers » test with methanol gas mixture @ 100 nmol/mol → Shorter stabilisation time with valve or restrictor

→ Long stabilisation time with usual pressure reducer including Silconert pressure regulators (leak problems due to Silconert VCR connectors)

First outputs – off-line methods

Intercomparison for sorbent tubes → data processing on going…

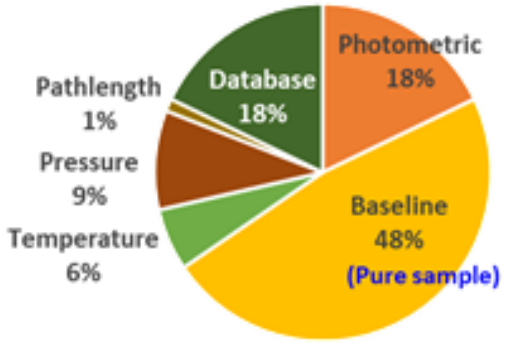
Sorbent Types
Tenax TA (20)
Tenax-Carbograph 5TD (20)
Tenax-Carbograph 1TD (30)
Carbopack C-Carbopack B-Carbosieve SIII (10)
Carbosieve SIII (25)
Carbopack B (10)
Tenax-Carbograph 1TD-Carboxen 1003 (10)
Tenax- Carbopack B (10)
Carbograph 5TD(Carbopack X) (5)

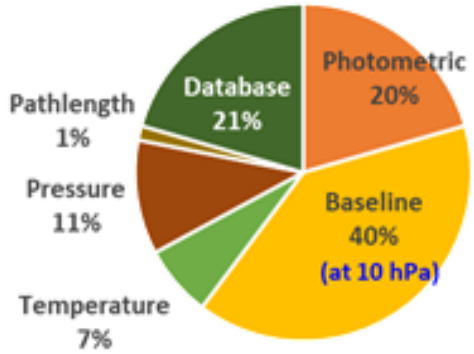


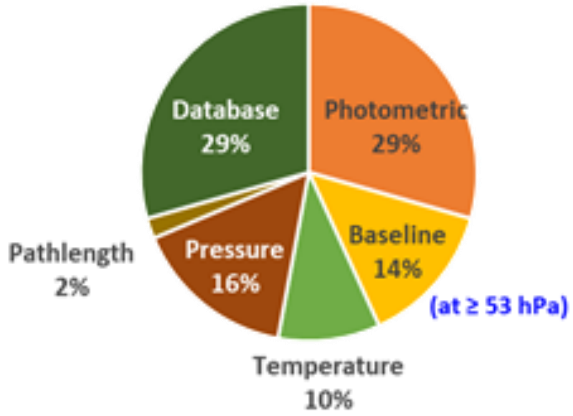
First outputs – spectral parameters

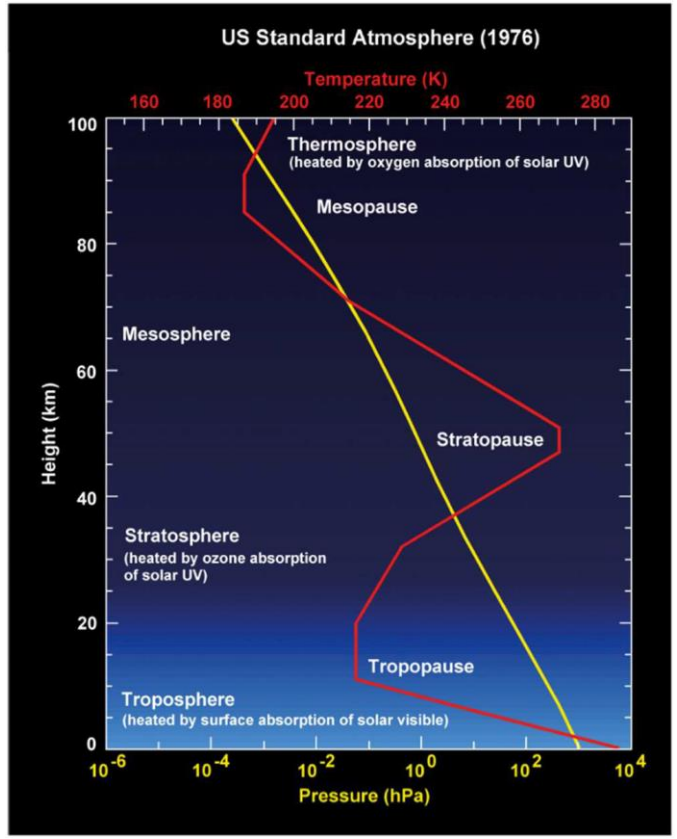
Main uncertainty contributions identified & T/P matrix for remote sensing measurements defined

	P (Torr)	Range 1						Range 2		
T (K)		300	285	270	255	240	225	210	195	180
Air	760	x	x	x						
	600				x					
	400	x	x	x	x	x	x			
	300							x	x	
	200		x	x	x	x	x	x	x	x
	100					x	x	x	x	x
	50			x	x	x	x	x	x	x
	7.5	x	x	x	x	x	x	x	x	x
Self	pure	x	x	x	x	x	x	x	x	x



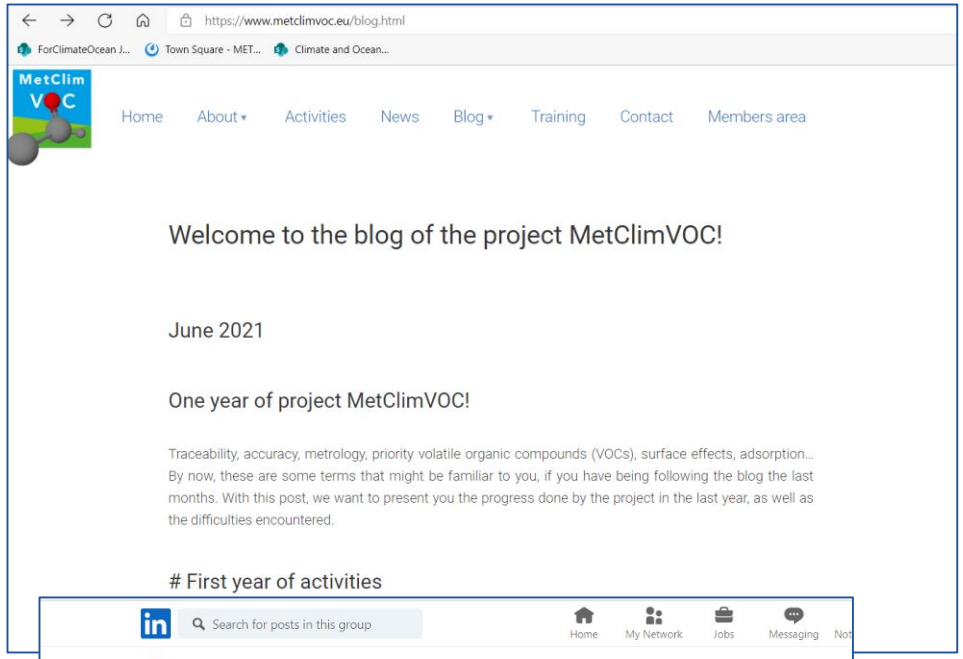


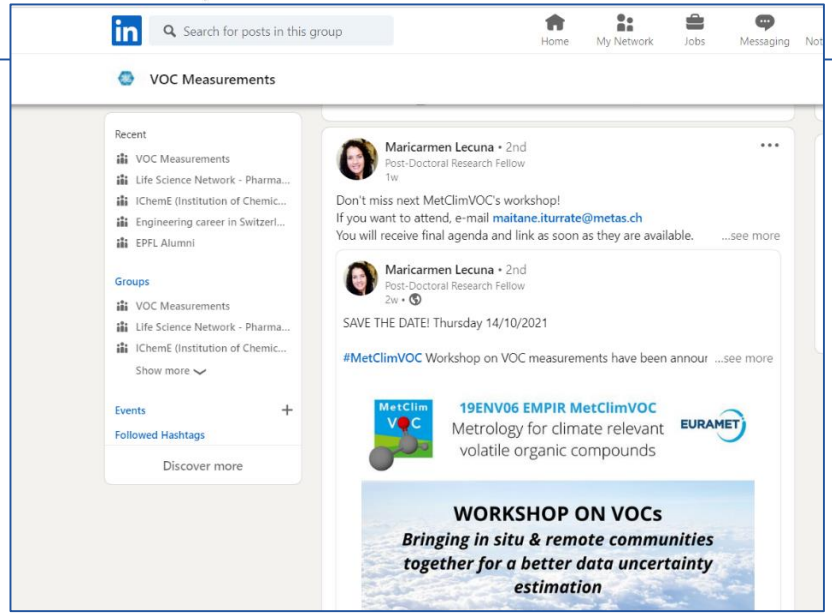




First outputs – Knowledge transfer

- Website (https://www.metclimvoc.eu)
- Training M10 with > 100 participants (available on the website)
- Blog article every 2 months
- > 10 presentations at conferences/workshops/technical committees
- 1 publication (https://doi.org/10.3390/atmos12020280)
- LinkedIn VOC group + ResearchGate project
- Wikipedia page (Volatile organic compound)
- Zenodo Community (MetClimVOC)
- …





Next steps…

Lab-comparison of Reference Gas Mixtures (WP1) = NMIs

Certification of whole air (WP1) = NMIs

Lab-comparison for formaldehyde (WP3) = end users (+NMIs)

Field-comparison of all «working standards» (WP2) = NMIs and end-users

Metrology for Climate Relevant VOCs

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For more information, visit

https://www.metclimvoc.eu

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