Metrology for Climate Relevant Volatile Organic Compounds

New and classical techniques to measure formaldehyde – a laboratory intercomparison

Thérèse Salameh[1], E. Stratigou[1], E. Tison[1], S. Dusanter[1], V. Gaudion[1], M. Jamar[1], R. Tillmann[2] , F. Rohrer[2], B. Winter[2], T. Vera[3], A Muñoz[3], Audrey Grandjean[4,5], F. Bachelier[6], V. Daele[6]

[1]IMT Nord Europe, France; [2]Forschungszentrum Jülich GmbH, Germany; [3]EUPHORE Lab, Fundación CEAM, Spain; [4]ICPEES, France; [5]Chromatotec, France; [6]CNRS – ICARE, France

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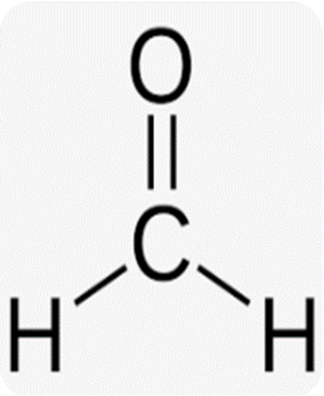
Introduction: Formaldehyde



Direct emissions: anthropogenic (Building materials, industry), biogenic (decay of plants, biological processes) **Secondary emissions:** CxHy oxidation; **Significant source of radicals** in the atmosphere resulting in ozone and secondary organic aerosols formation

Skin/eyes irritant, Cancerogenic

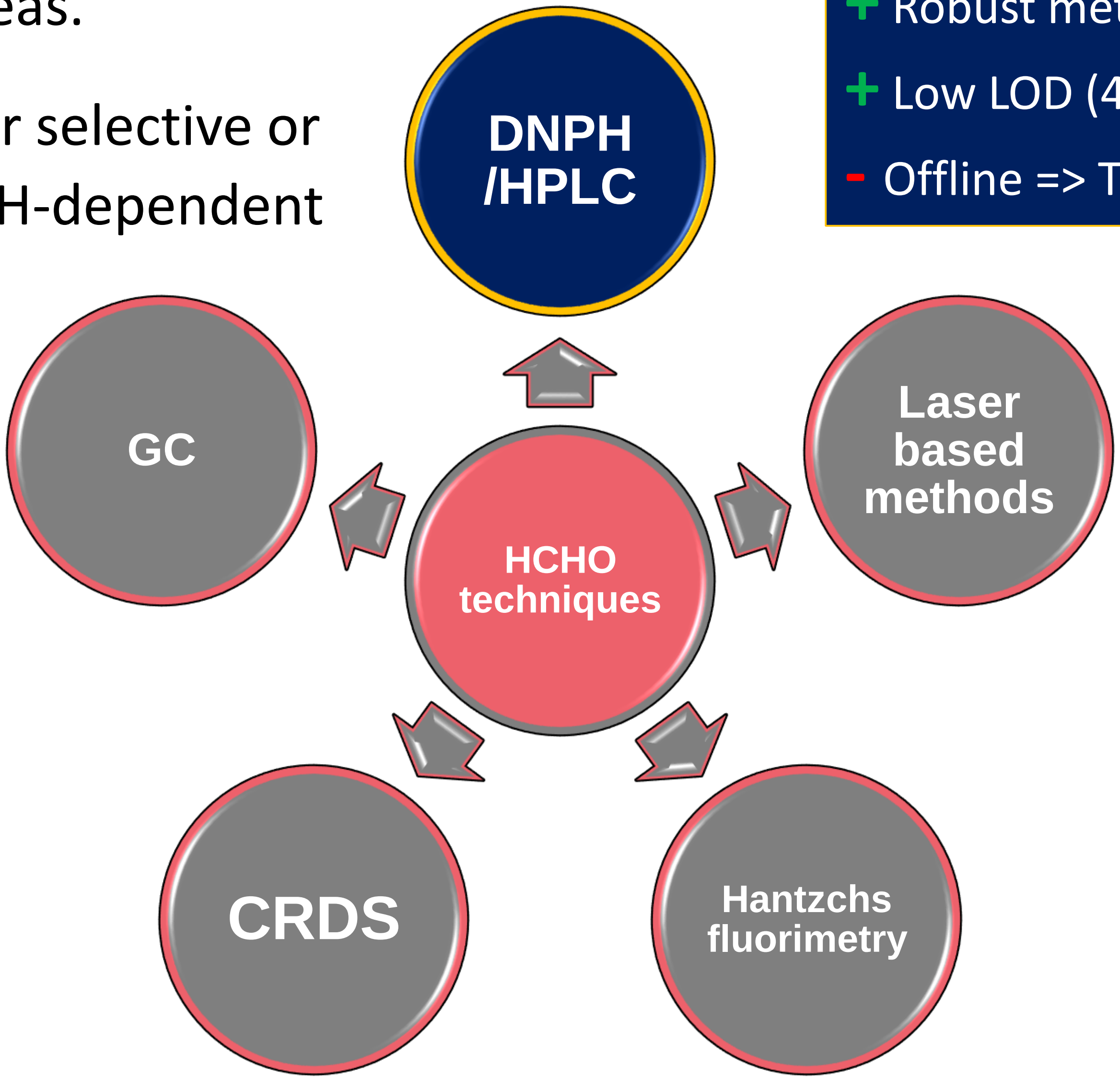
Complexity stickiness

Precise measurement => Challenge

Routine measurements of formaldehyde in regulatory networks within Europe (EMEP) and USA (EPA Compendium Method TO 11A) rely on sampling with DNPH (2,4-Dinitrophenylhydrazine)-impregnated silica cartridges, followed by analysis with HPLC (High-performance liquid chromatography)

Introduction

+ Continuous meas.
+ Low LOD
- Complex, either selective or sensitive, cost, RH-dependent



+ Robust method
+ Low LOD (40 pmol/mol)
- Offline => Time resolution ~hours

Objectives of the intercomparison:
at CiGas IMT NE Douai site – 30/05 -> 08/06 2022

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- Evaluation of the metrological performance of measurement techniques: repeatability, limit of detection, linearity, potential drift, etc.
- Determine advantages/drawbacks of the techniques
- Develop recommendations about best practices

ACTRIS
CiGas

ACTRIS Topical Centre for Reactive Trace Gases in Situ Measurements

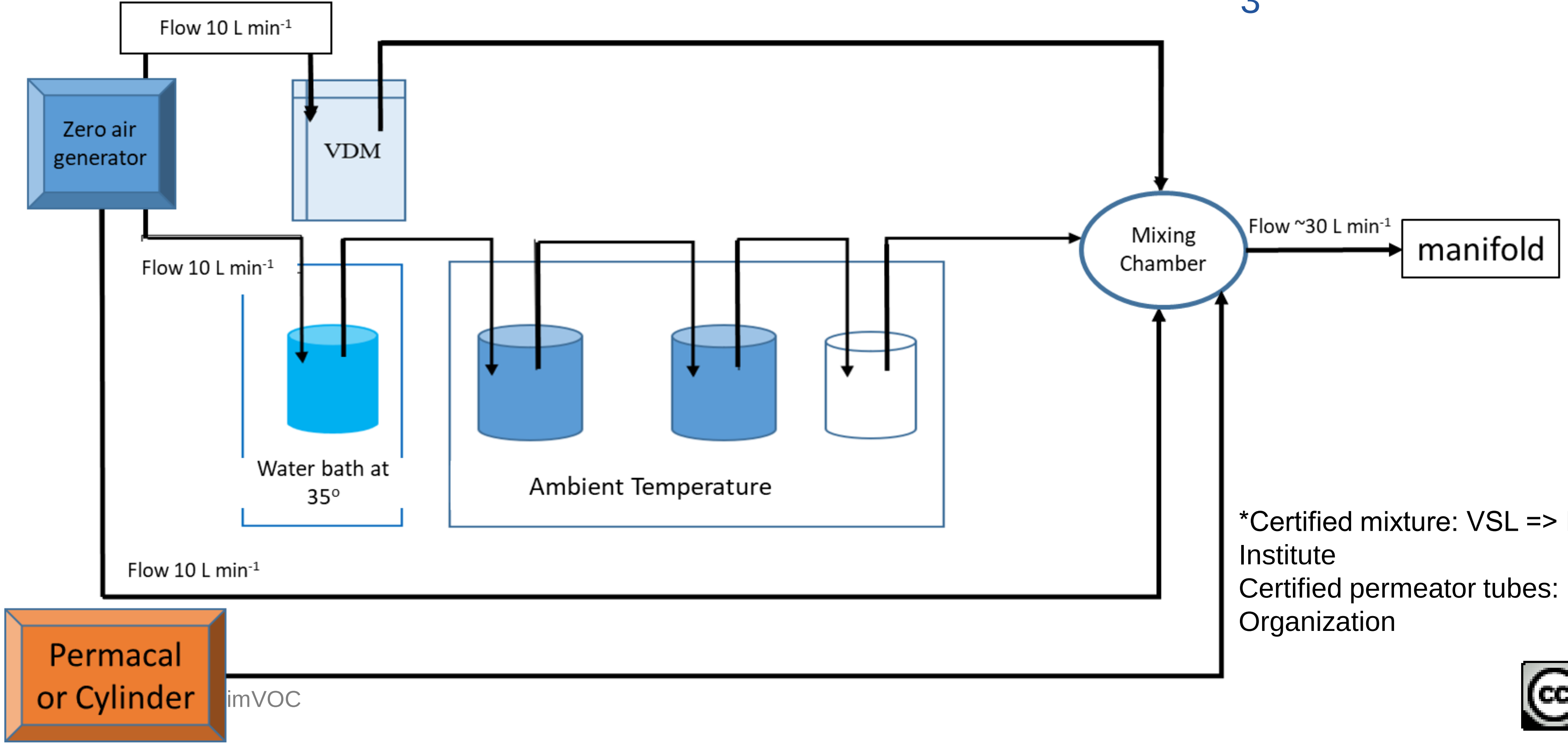
What is ACTRIS?
https://actris.eu/

The Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) is the pan-European research infrastructure (RI) producing high-quality data and information on short-lived atmospheric constituents and on the processes leading to the variability of these constituents in natural and controlled atmospheres.

Set-up of the intercomparison: 10 instruments => 7 techniques

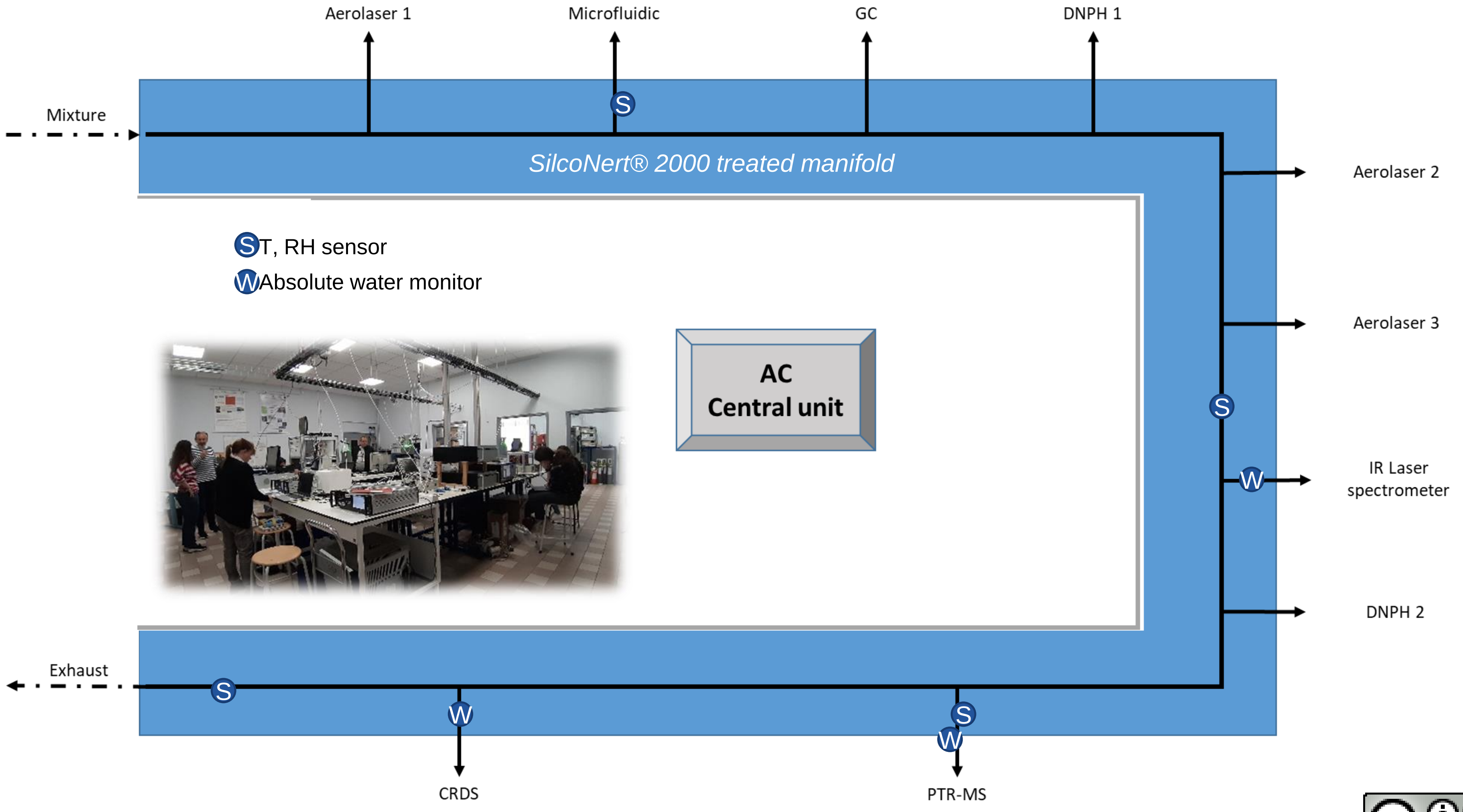
Generation:
from a **cylinder** (5.2 ± 0.26 µmol/mol) or from a **permeation** system

- Different levels: 2-17nmol/mol
- 1 level: RH=60%
- WE: Ambient
- w/ & w/o O_3



*Certified mixture: VSL => Netherland's National Metrology Institute
Certified permeator tubes: METAS => Swiss National Metrology Organization

Set-up of the intercomparison
10 instruments => 7 techniques



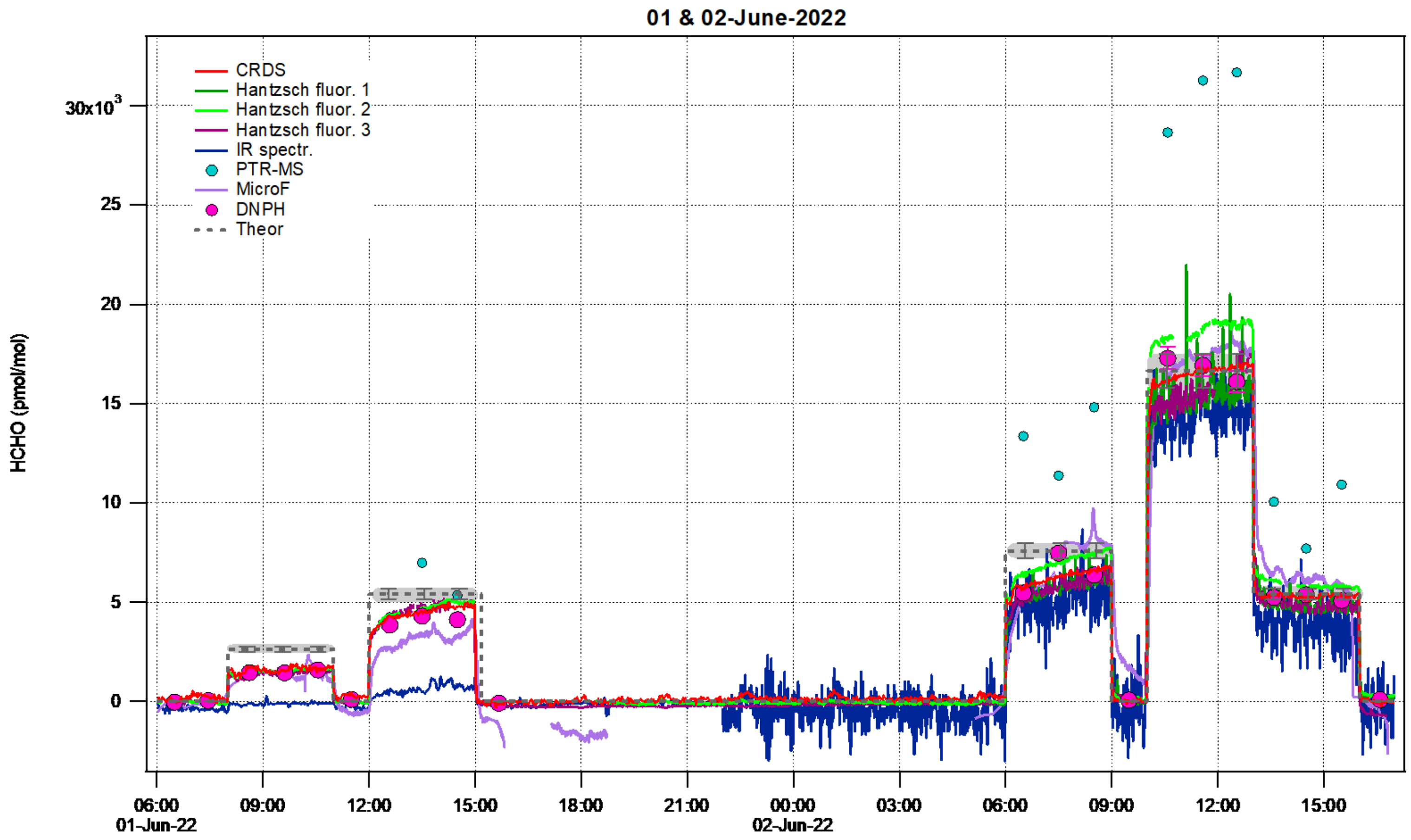
Intercomparison: overview of the instruments & sampling information

Table 1: Sampling information						
Technique	**Calibration standard and method**	**Sampling line from the manifold info**	**Additional materials/info**	**Total flow arriving to the instrument (L min^{-1})**	**LOD (pmol/mol)**	**Time resolution (sec)**
Hantzsch fluorimetry 1	Liquid calibration (external)	Teflon tube, L=1.5 m , ID=1/4''	-	1.00	50	90
Microfluidic Hantzsch fluorimetry (microF)	Permeation tube (external)	Teflon, L=1.5 m, ID=1.5 mm (1/8") + L=0.8 m, ID=3.8 mm (1/4"), inox connectors	particle filter (internal)	0.02	1000	10
DNPH 1	Liquid calibration	PTFE, L=1.5 m, OD=1/4", ID=4 mm	-	1.00	-	3600
Hantzsch fluorimetry 2	Liquid calibration (external)	PFA, L=3 m, ID=4 mm	-	1.00	33	5
Hantzsch fluorimetry 3	Liquid calibration (external)	PTFE, L=1.5 m, OD=1/4", ID=4 mm	-	0.90	-	60
IR Spectroscopy	Cylinder, dilution multipoint	Sulfinert, L=1.5 m, ID=2.159 mm	stainless steel 2µm filter	0.15	300-3500	60
DNPH 2	Liquid calibration	Sulfinert, L=~1.5 m, ID=4.575 mm	-	1.00	43	3600
PTR-MS	Cylinder, dilution & RH multipoint	Silcosteel, L=~1.5 m, ID=4.575 mm	Heated lines: ~40oC	0.2+3.0	1000-1700	3600
CRDS	Calibration standard and method factory default	PFA, L=2 m, ID=4 mm	particle filter	0.30	500 (5min)	120

Schedule of the intercomparison: 01/06 -> 07/06/2022

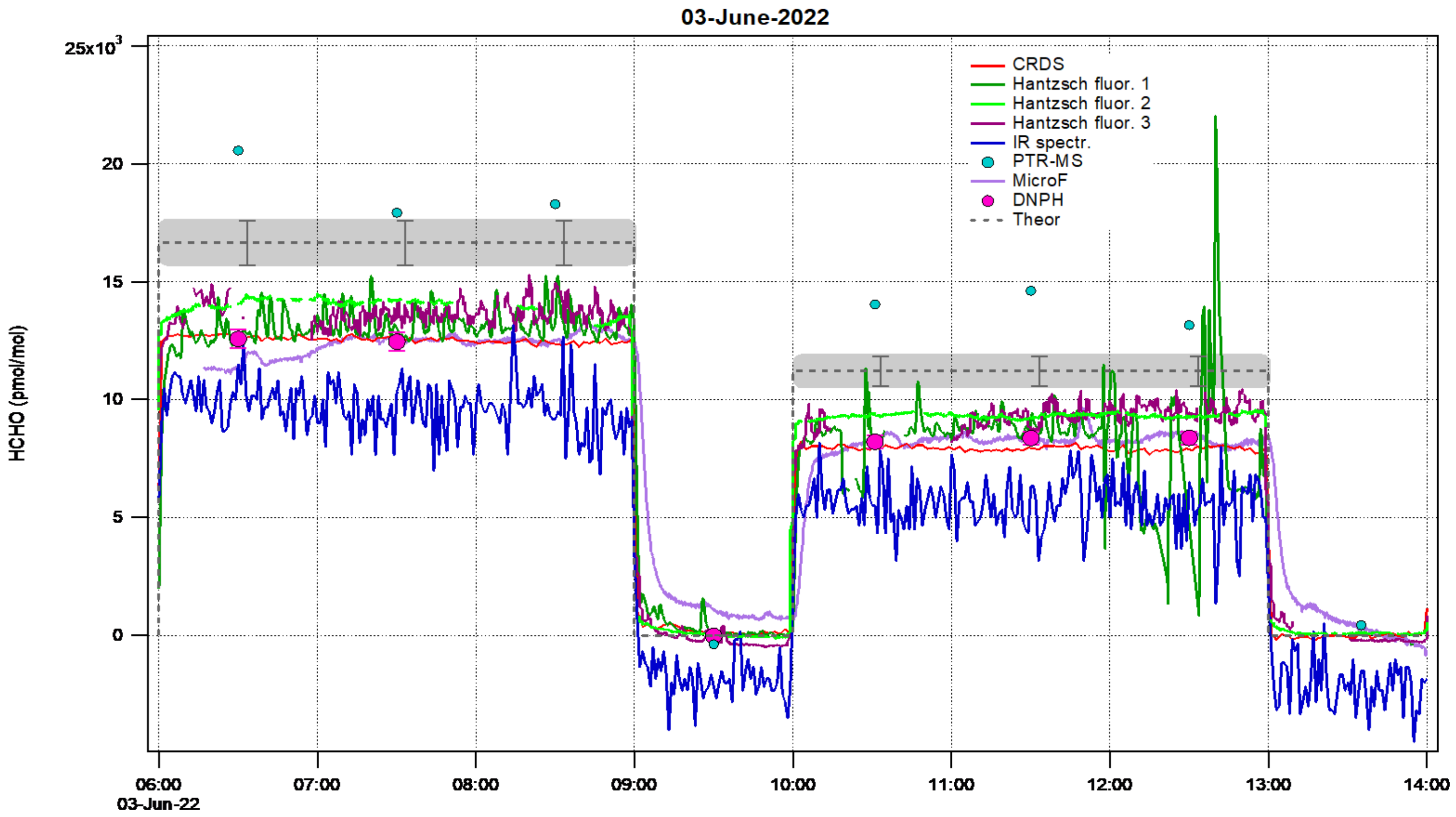
Date	Time start (LT)	Duration	Time end (LT)	Synthetic zero air cylinder	Zero generator	Cylinder HCHO	Permacal	Ambient air	OZONE (nmol/mol)	Theoretical amount fraction (nmol/mol)
01-Jun-22	8:00	1 hour	9:00	x						0.00
	9:00	1 hour	10:00		x					0.00
	10:00	3 hours	13:00			x				**2.65**
	13:00	1 hour	14:00		x					0.00
	14:00	3 hours	17:00			x				**5.41**
	17:00		08:00 of 02/06		x					0.00
02-Jun-22	8:00	3 hours	11:00			x				**7.59**
	11:00	1 hour	12:00		x					0.00
	12:00	3 hours	15:00			x				**16.64**
	15:00	3 hours	18:00			x				**5.41**
	18:00		08:00 of 03/06		x					0.00
03-Jun-22	8:00	3 hours	11:00				x			**16.66**
	11:00	1 hour	12:00		x					0.00
	12:00	3 hours	15:00				x			**11.21**
	15:00	1 hour	16:00		x					0.00
04-05-06 juin 22	8:00							x		0.00
07-Jun-22	8:00	2 hours	10:00		x					0.00
	10:00	3 hours	13:00			x			45	**7.31**
	13:00	1 hour	14h30		x					0.00
	14:30	3 hours	17:30			x				**7.59**
	17:30		End		x					0.00

Intercomparison results : Original time resolution - generation with HCHO cylinder at 60% RH



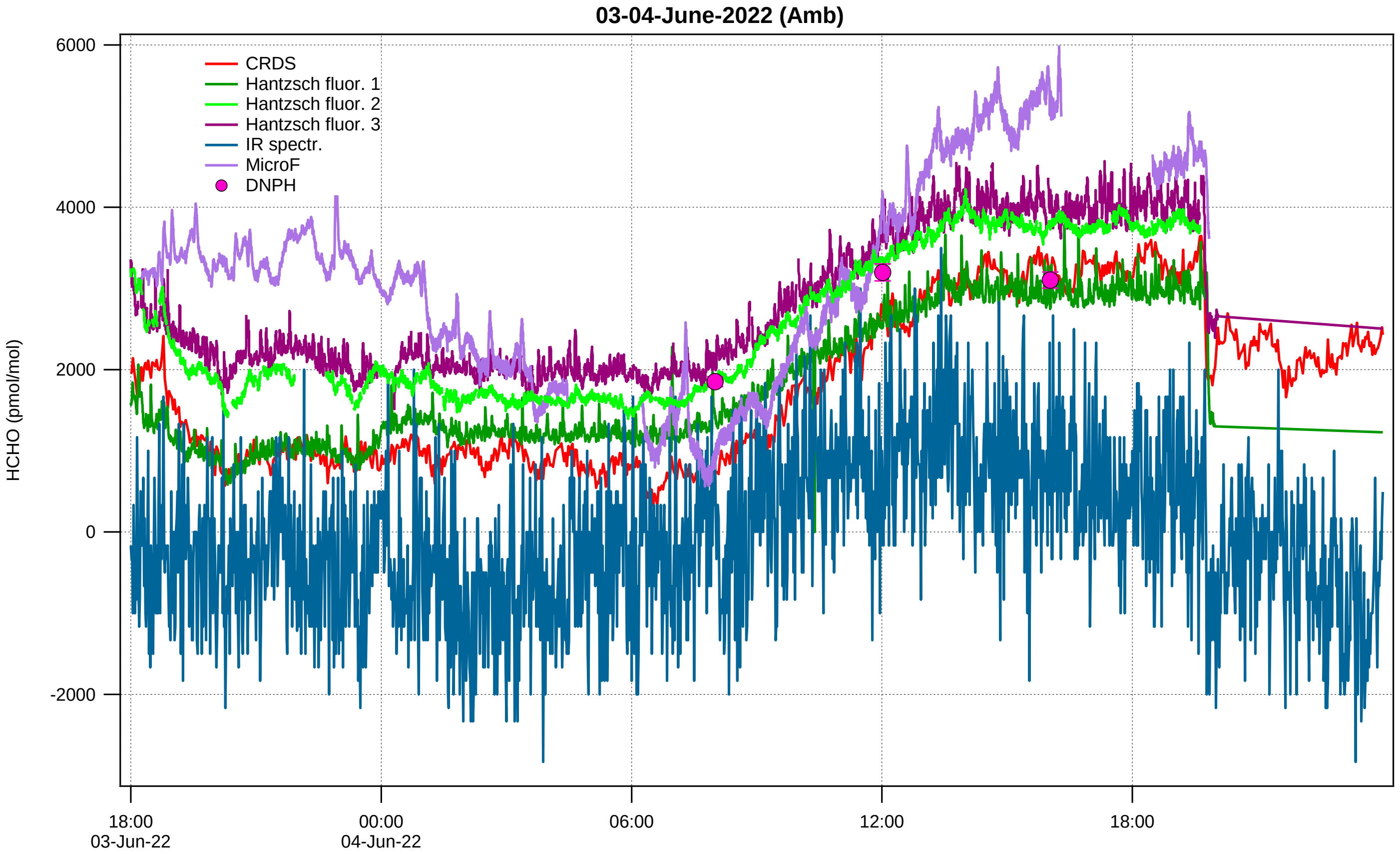
Timeseries of original time resolution during the different days of experiments in manifold. Error bars and shaded areas represent 1σ. microF data corrected with DNPH data

Intercomparison results : Original time resolution – generation with Permacal at 60% RH



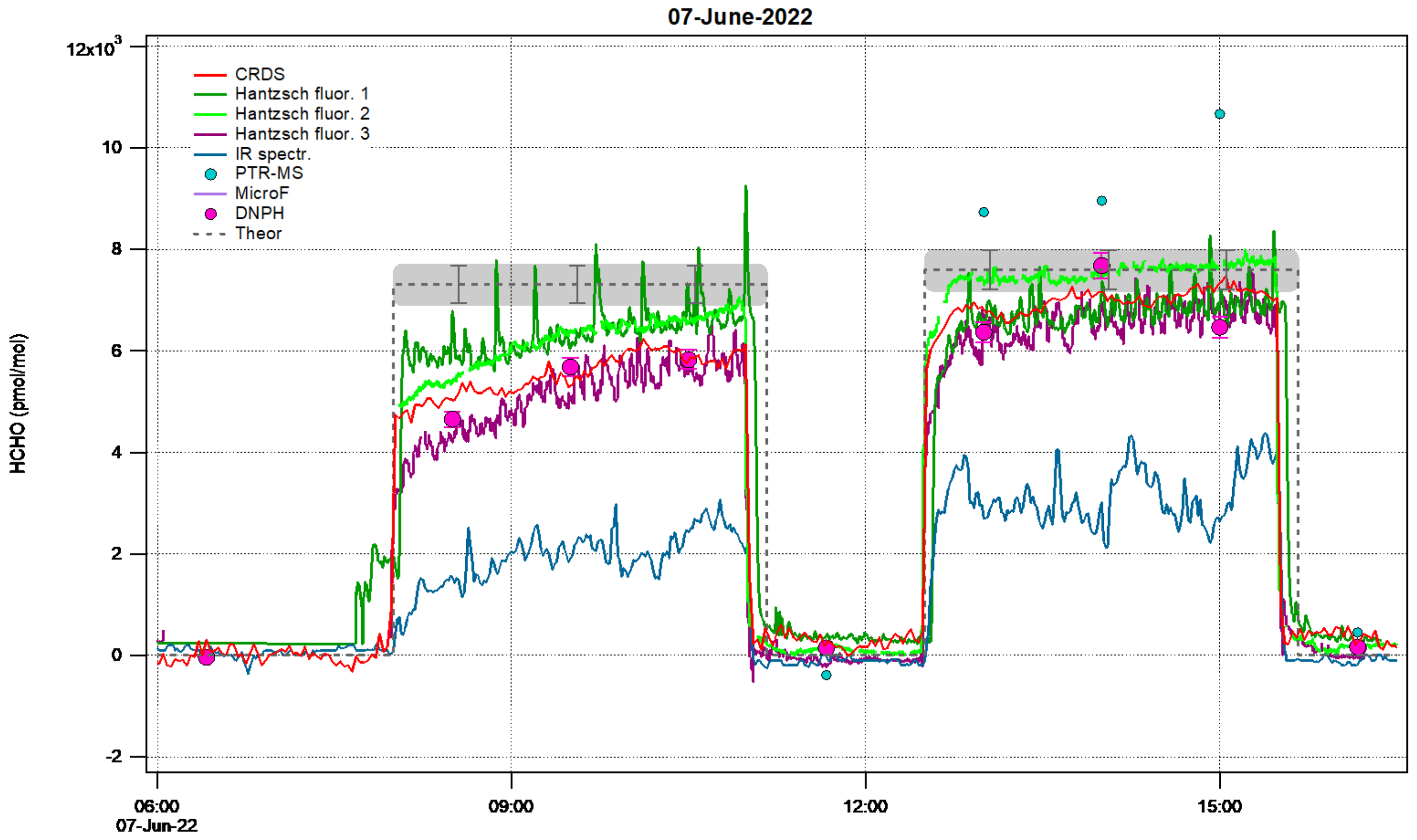
Timeseries of original time resolution during the different days of experiments in manifold. Error bars and shaded areas represent 1σ. microF data corrected with DNPH data

Intercomparison results: Original time resolution – Ambient air



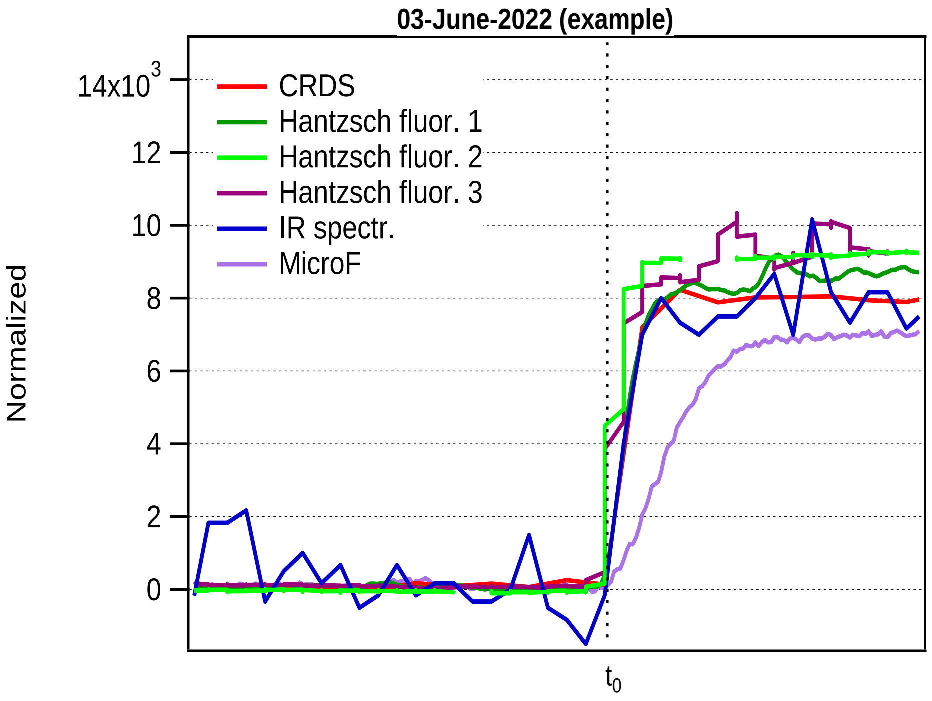
Timeseries of original time resolution during the different days of experiments in manifold. microF data corrected with DNPH data

Intercomparison results: Original time resolution – w & w/o O_3 at 60% RH

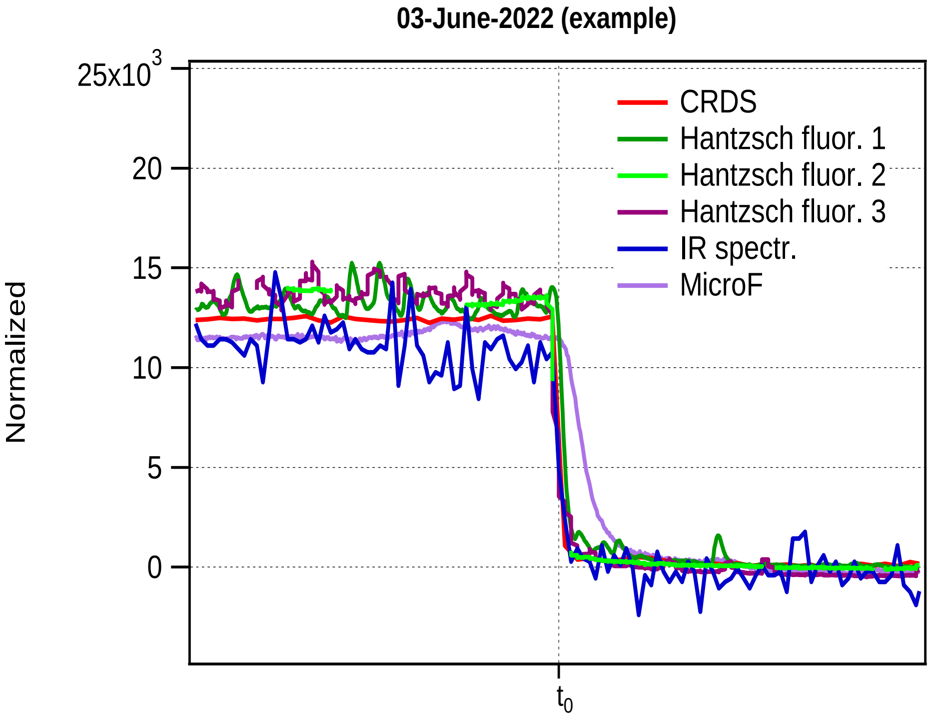


Timeseries of original time resolution during the different days of experiments in manifold. Error bars and shaded areas represent 1σ. microF data corrected with DNPH data

Intercomparison results : Original time resolution: response time & memory effect

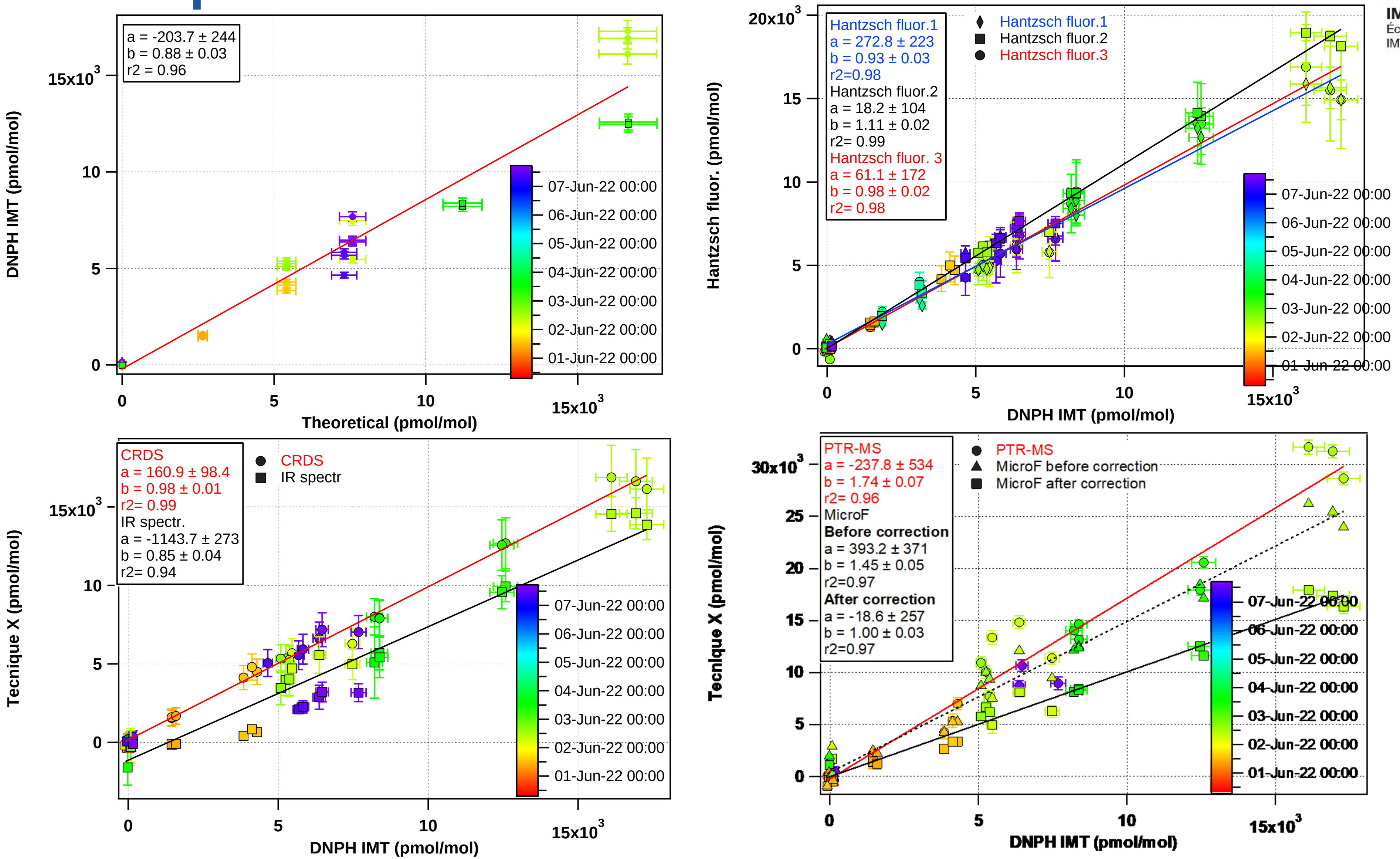


Response time



Memory effect

Intercomparison results



Correlations of DNPH (ref. technique) with theoretical values, and correlations of techniques with ref. technique. Symbols correspond to the respective technique, color coding of symbols corresponds to the date, color coding of the regression lines correspond to each technique. Error bars represent 1σ. microF data corrected with DNPH data

Conclusions & perspectives

- Evaluation of many online and off-line techniques for formaldehyde measurements at nmol/mol levels
- Stable generation of formaldehyde from 2 to 17 nmol/mol at 60% RH regardless the generation way (cylinder; Permacal)
- DNPH, Hantzsch-fluorimetry-based instruments and CRDS -based instrument: more robust for measuring formaldehyde. Good results with microF after correction
- IR-spectrometry-based instrument not suitable for measuring low amount fractions; PTR-MS: overestimation of the HCHO amount fractions.
- Possible losses of < 4-7% of HCHO under typical ozone conditions which is inside uncertainties
- Discrepancies between instruments to be addressed (impact of water vapor levels, internal calibrations especially for Hantzchs techniques, **lack of a SI traceable calibration standard**, etc.)

=> QA/QC measures are crucial to provide high quality formaldehyde measurements for outdoor and indoor ambient measurements

MetClim VOC

Metrology for Climate Relevant Volatile Organic Compounds

ACTRIS CiGas

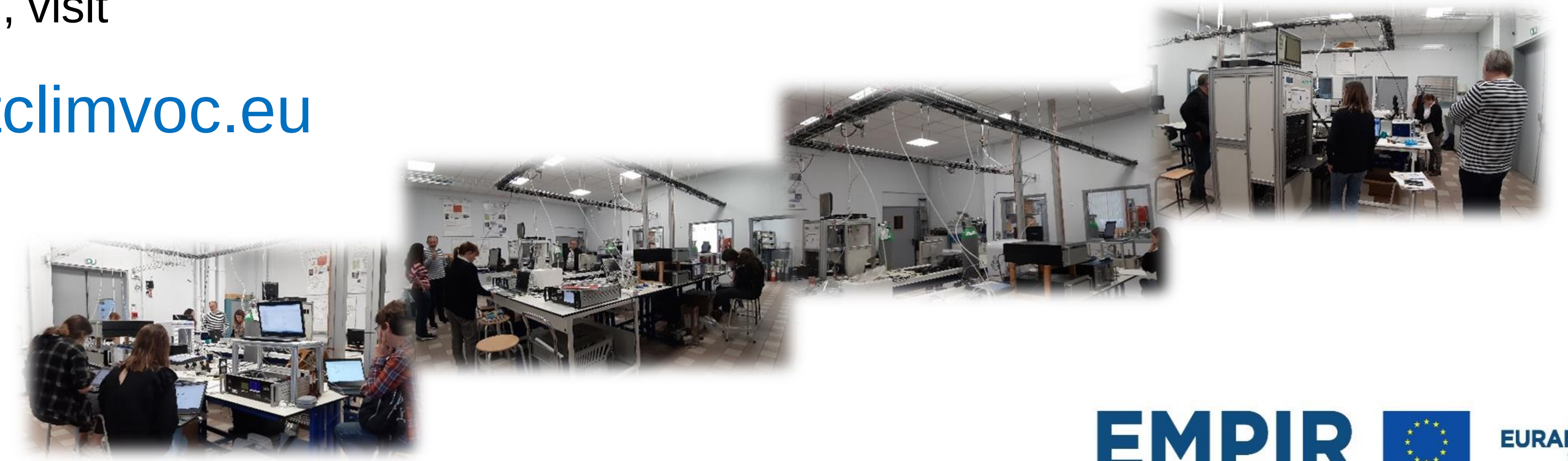
IMT Nord Europe
École Mines-Télécom
IMT-Université de Lille

Thérèse Salameh (therese.salameh@imt-nord-europe.fr)

Thank you for your attention

For more information, visit

www.metclimvoc.eu



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