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DNPH VOC Sampling and Analysis in the EMEP Intensive Measurement Period 2022

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ACTRIS CiGas

OUTLINE

- Background and motivation
- Intercomparison with other measurement techniques
- Method evaluation
- Measurement during EIMP

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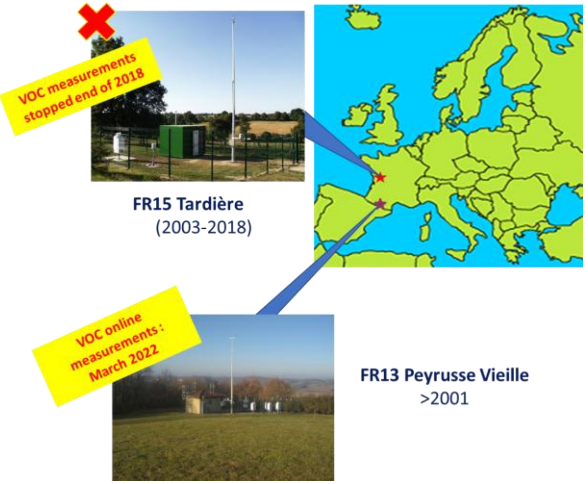
Oxygenated Volatile Organic Compounds (oxy-VOCs)

- **Most abundant** VOCs in ambient air
- **Key compounds** as tracers of primary sources as well as chemical processes (secondary formation)
- **Adverse health effect** (formaldehyde, acrolein…)
- Tracers of solvent use significantly growing source



- **Have the key sources of emission of NMVOCs changed over the past two decades?**

Quick answer: Yes. There has been a substantial reduction in emissions of short-chain hydrocarbons related to fossil fuels and combustion and an increase in the relative contributions of VOCs emitted from solvent and product use. Solvents and the use of chemicals in industry and domestic products, and other non-combustion sources, are estimated to account for ~70% of UK emissions in 2017 according to the NAEI. Over the last decade there has been a growth in the estimated national emissions of oxygenated VOCs, including ethanol, methanol, butanone and acetone.

NMVOC in the UK, 2020: http://uk-air.defra.gov.uk

DNPH, d

Low capital cos
many sites

Very low time resolution

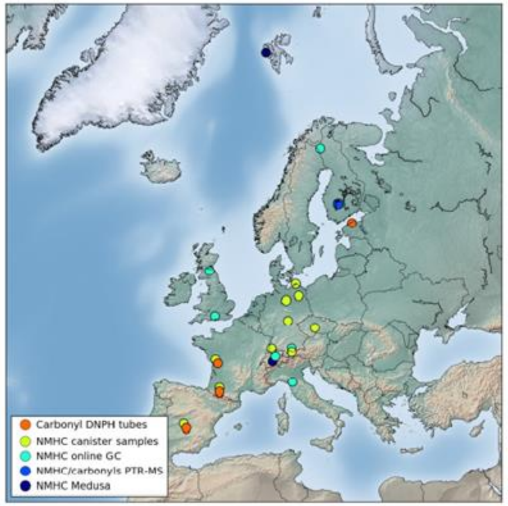
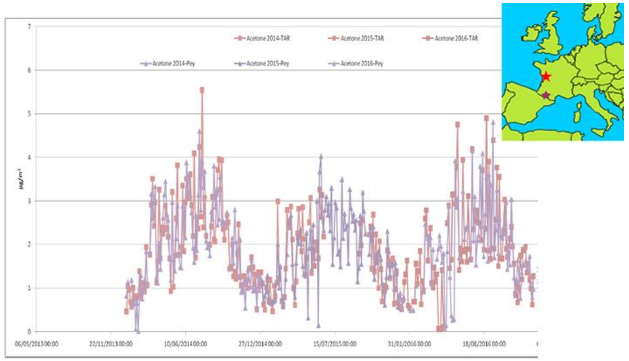


Figure 1: Monitoring sites for VOC in 2018.



Acetone:
High seasonal variability&
Consistency between sites

BACKGROUND AND MOTIVATION - VOC MONITORING : FRENCH EMEP SITES

IMPLEMENTATION DURING EIMP

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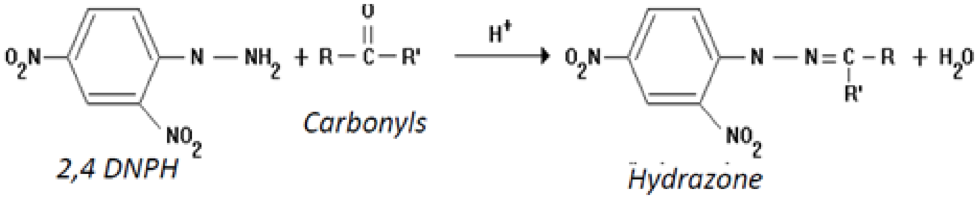
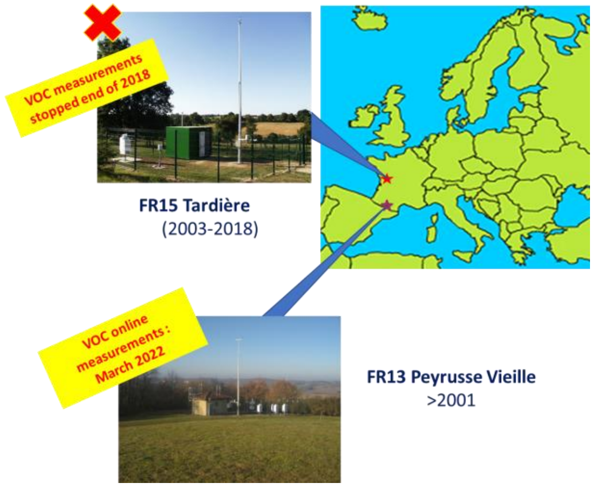


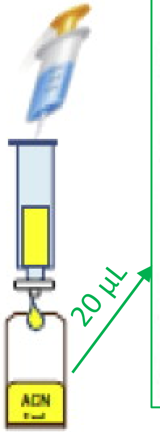


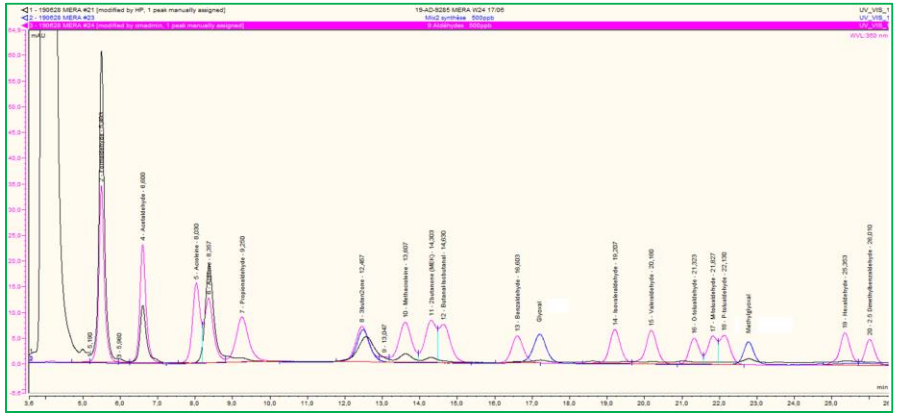
Frequency: 2 DNPH cartridges on Monday & Thursday, 4 hours, at 12-16h UTC
Flow rate: 1.5 L/min
Precautions: leak tests; inox filter of 2 µm; ozone scrubber (KI)

Automatic sampler SYPAC
(Tera env. co.)

DNPH cartridges stored at -21°C, analysis within 3 weeks

3 mL acetonitrile





HPLC-UV (365nm)

Standard: Apel Riemer; SUPELCO for verification
DL: ~10-30 ppt
Uncertainty: 10-20%

11 OVOCs C_1-C_7

formadehyde
acetaldehyde
acetone
acrolein
propanal
methylvinylketone
ethylmethylketone
methacrolein
butanal +isobutanal
glyoxal
methylglyoxal

INTERCOMPARISON WITH OTHER MEASUREMENT TECHNIQUES

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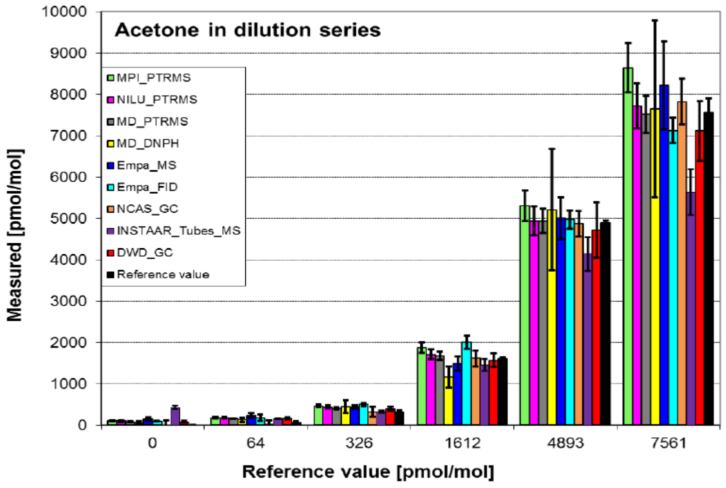
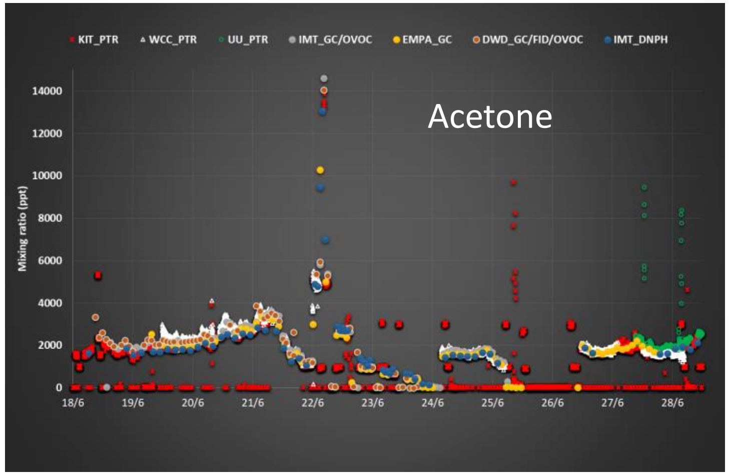
s-b-s OVOCs, ACTRIS (2013-2018):
on-line GC-FID/MS; PTR-ToFMS; off-line DNPH/HPLC-UV

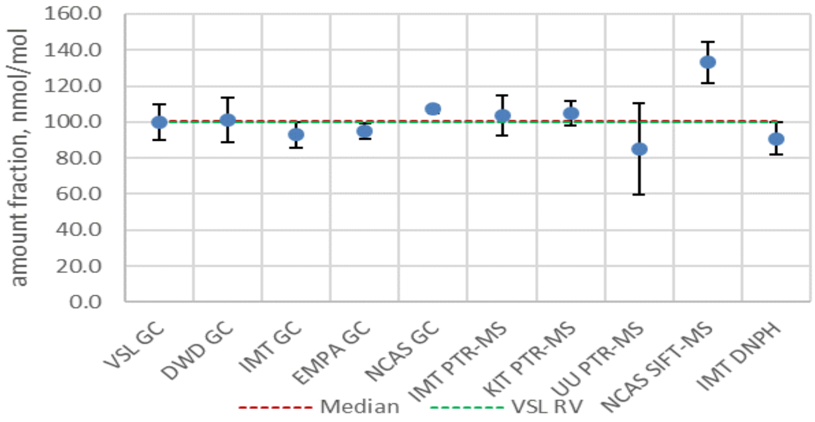
Acetone





Interlaboratory comparison using a novel Oxygenated VOC reference Standard from VSL *(courtesy A-R. Baldan)*

Acetaldehyde



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METHOD EVALUATION

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- Interference with water, ozone (O_3), and nitrogen dioxide (NO_2)
- Impact of the use of scrubbers
- Potentially poor or unknown collection efficiencies
- Poor knowledge on the processes affecting the measurement by DNPH and the associated uncertainty

Need to

- ✓ Evaluate the effect of water, ozone, and nitrogen dioxide
- ✓ Recovery between liquid standard and of gaseous standard
- ✓ Evaluate the uncertainty associated to this method
- ✓ Improve guidelines for the implementation of the method

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DNPH METHOD OPTIMIZATION/EVALUATION

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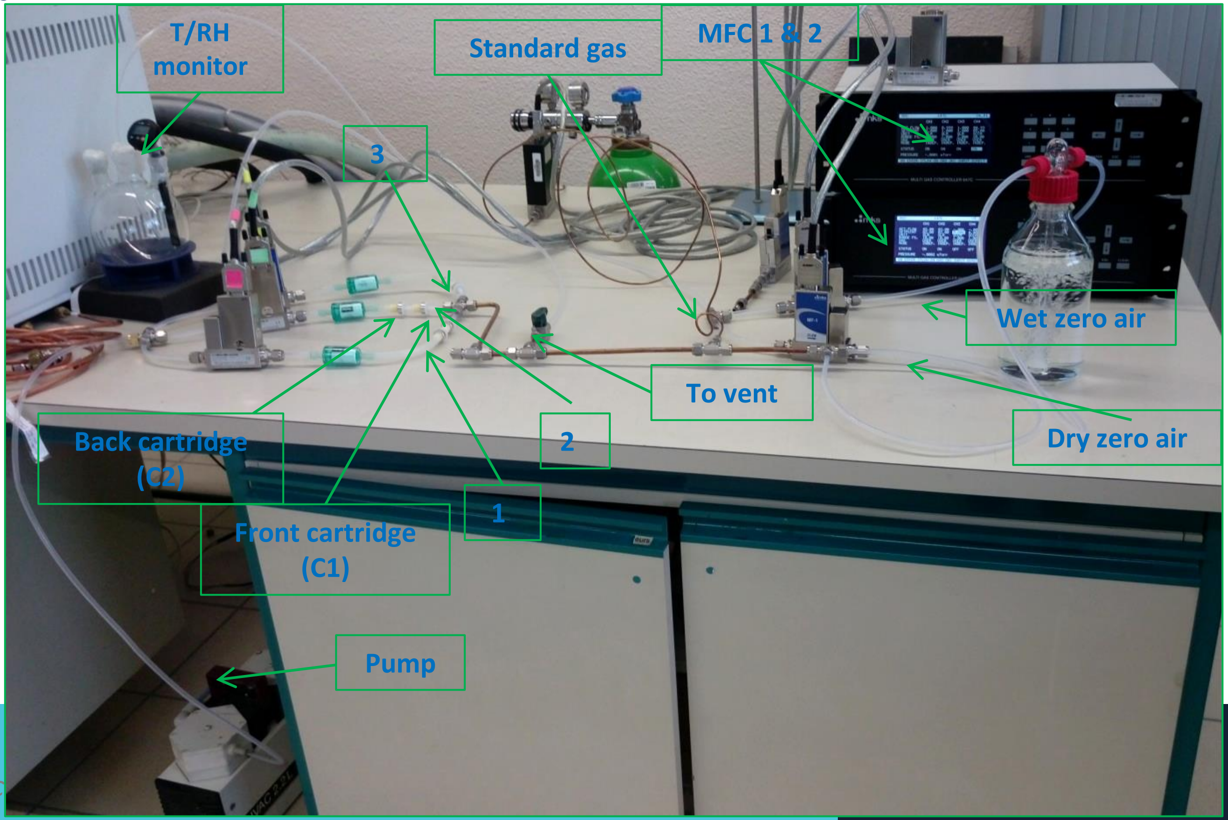
- 3 // sampling (1, 2, 3 in the figure below); 2 cartridges/sampling (in series)
- Flow / sampling: 1L/min ; 4 hours sampling
- Zero air under different RH => blank
- **4 Gaseous standards:**
  - Apel Riemer mixture under # RH (dry, 20%, 50%, and 80%) at different concentrations
  - VSL, PRAXAIR mixture and NPL standard tested as well
- **2 Liquid standards:** Supelco and ACSD
- Influence of NO_2 and O_3



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DNPH METHOD OPTIMIZATION/EVALUATION:
COLLECTION EFFICIENCIES VS. RH UNDER # LEVELS

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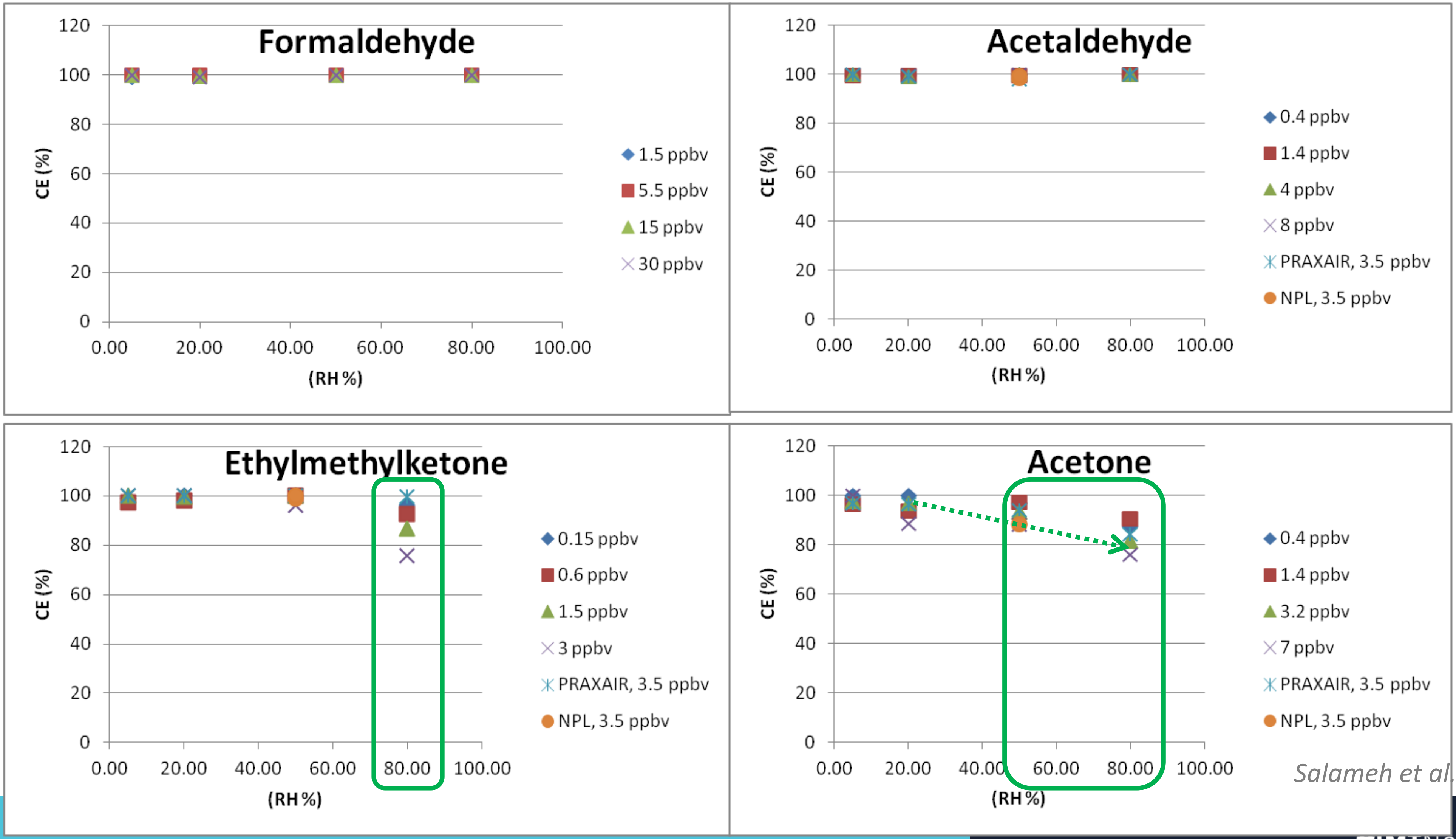
Collection efficiencies vs. RH under # levels

$$CE = (C1/(C1 + C2)) * 100$$



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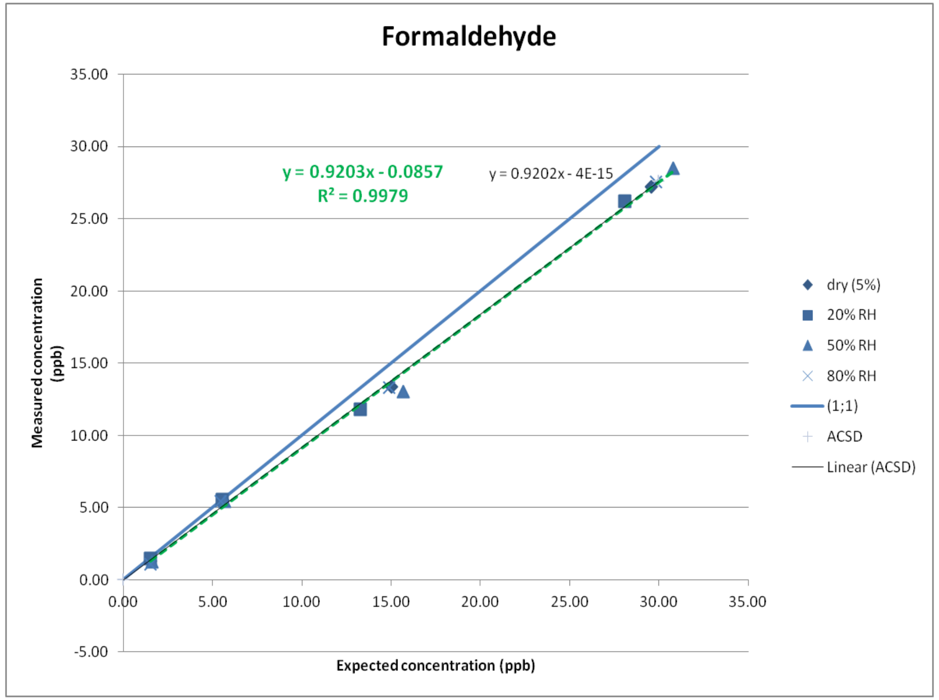
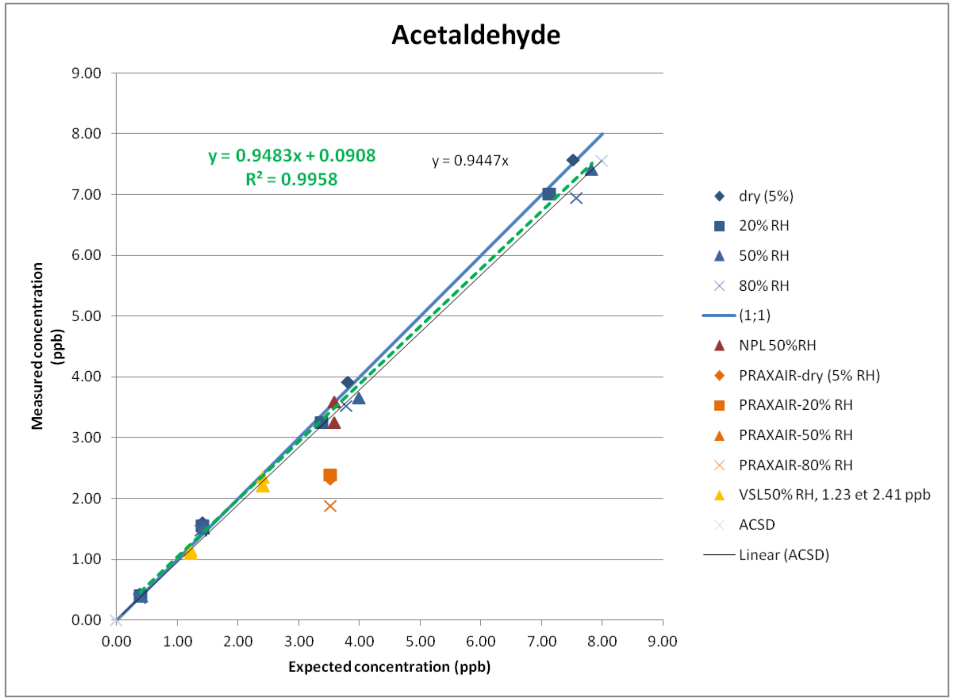
DNPH METHOD OPTIMIZATION/EVALUATION:
MEASURED CONCENTRATION VS. EXPECTED CONCENTRATION UNDER #RH

Aldehydes

✓ Low discrepancies between liquid standard and gas standard, when considering the uncertainties
✓ Very good correlation under # levels and RH





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DNPH METHOD OPTIMIZATION/EVALUATION:
MEASURED CONCENTRATION VS. EXPECTED CONCENTRATION UNDER #RH

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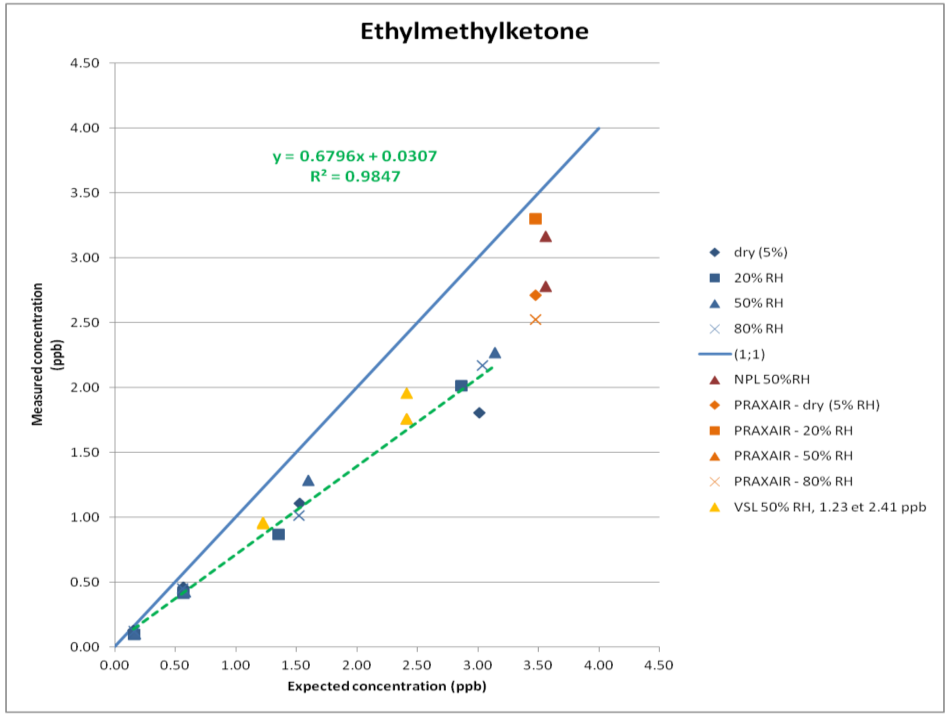
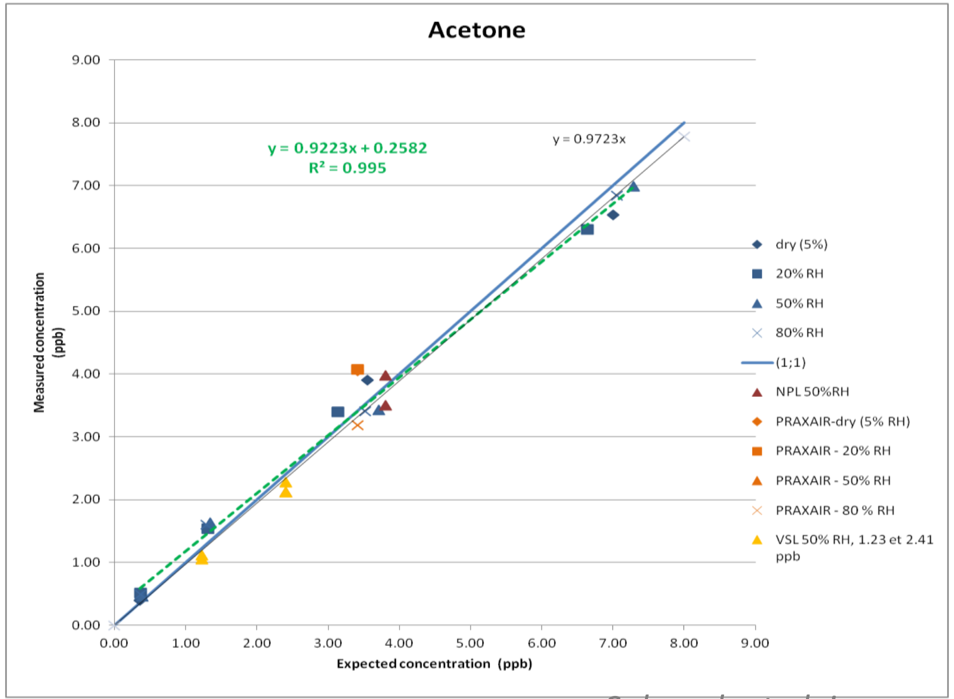
Ketones

- ✓ **Acetone**: Low discrepancies of 8% between gas and liquid phase standards and 3% between the liquid ones => no # when considering the measurement uncertainty
- ✓ **MEK**: High # estimated at 32% between gas and liquid phase standards but also high uncertainty because of integration errors (co-elution)
- ✓ Very good correlation under # levels and RH





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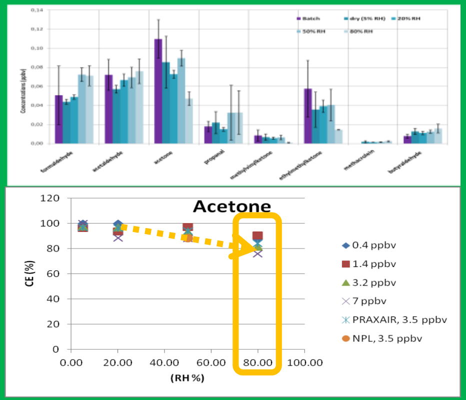
DNPH CARTRIDGES : CHALLENGES



Issues to be considered :

- Blanks
- MVK dimerization,
- MEK selectivity
- Collection efficiency depending on RH especially for ketones
- NO_2: no impact on the identification of OVOC at 365 nm
- O_3: The use of KI scrubber

- Standard comparability with NPL, Apel Riemer, VSL, and Praxair
- Response discrepancy among the liquid standards Supelco and ACSD

☺ Formaldehyde, acetaldehyde, acetone, MACR,

☹ Propanal, butanal, MEK

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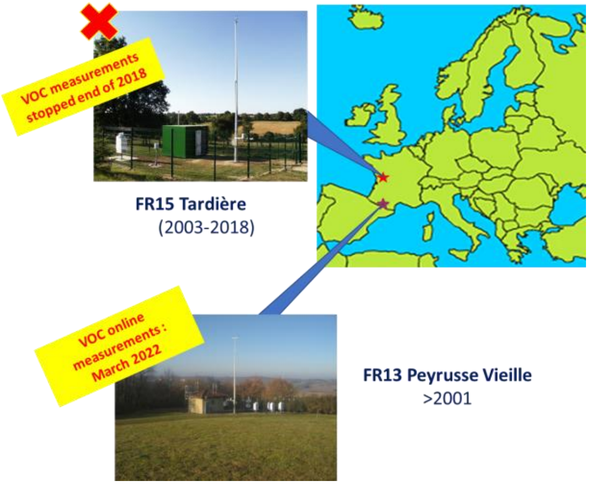
- **IMT contribution:** sending 17 DNPH cartridges (1 as a transport blank) + 2 cartridges to be used in series/sampling; and a KI/Cu ozone scrubber; & performing analysis
- **Frequency**: 8 days (1 day outside ozone episode) of continuous measurement with DNPH cartridges for 4 hours, at 12-16h UTC
- **Flow rate:** 1.5 L/min, if not possible 1L/min
- **Precautions:** leak tests; inox filter of 2 µm; ozone scrubber (KI)



Participation to EIMP, Peyrusse Vieille &:
-Donon (VOC 1993-2007) or Revin
-Coulonche

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