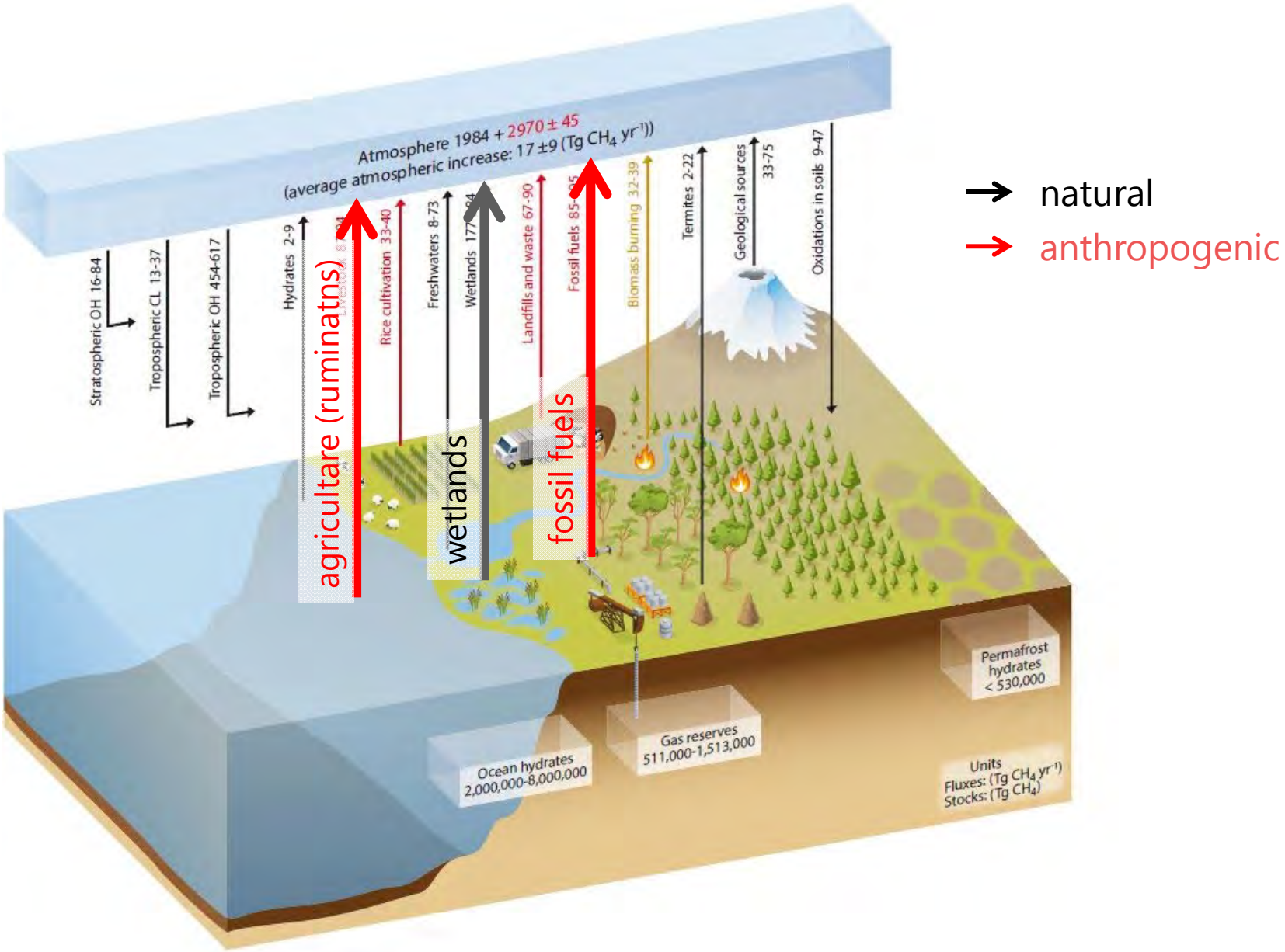
Real-time analysis of $\delta^{13}C$- and δD-CH_4 in ambient air with laser spectroscopy: Method development and first Intercomparison results

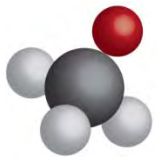
Simon Eyer, Béla Tuzson, Eliza Harris, Lukas Emmenegger and Joachim Mohn, Empa
Elena Popa, Carina van der Veen, Thomas Röckmann, Utrecht University
Rebecca Fisher, David Lowry, Euan G. Nisbet, RHUL
Willi A. Brand, MPI for Biogeochemistry
Matthias S. Brennwald, Eawag
Hubertus Fischer, University of Bern

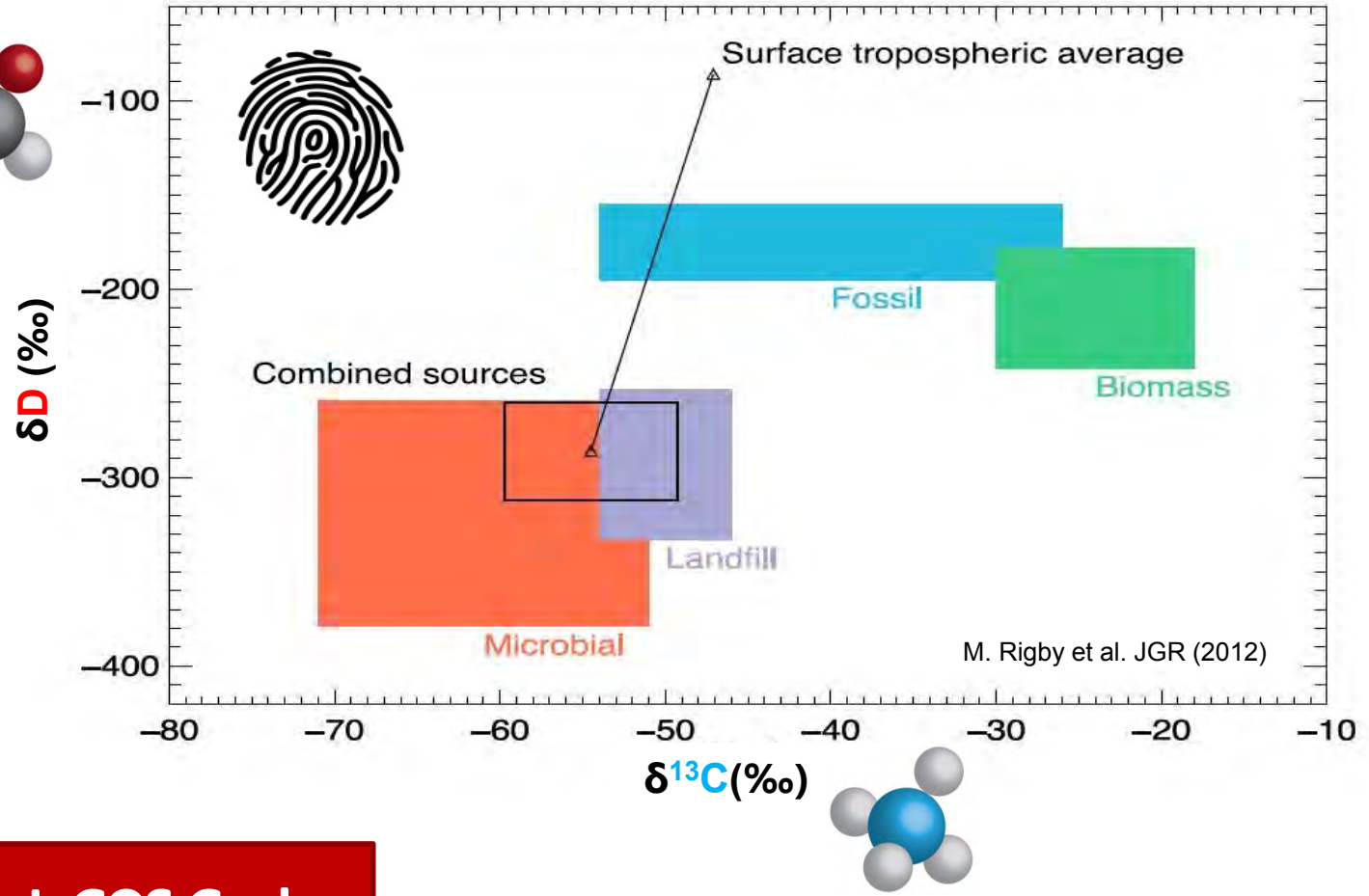
The global CH_4 cycle



IPCC, WG1 The physical science basis (2013)

CH_4 Isotopes

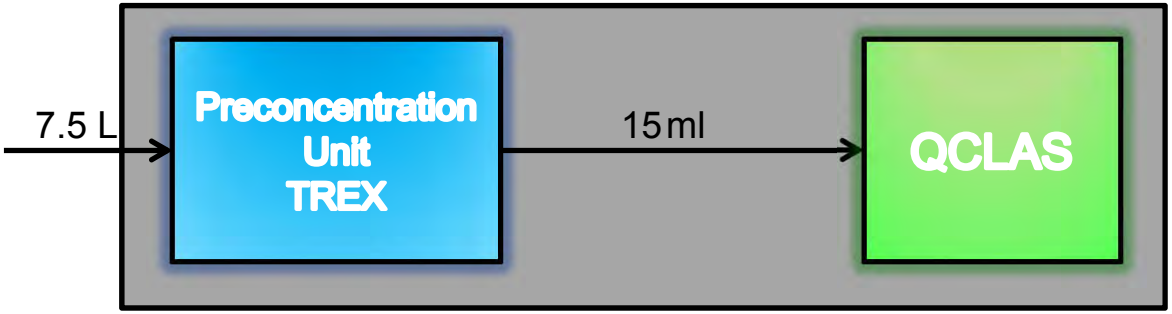


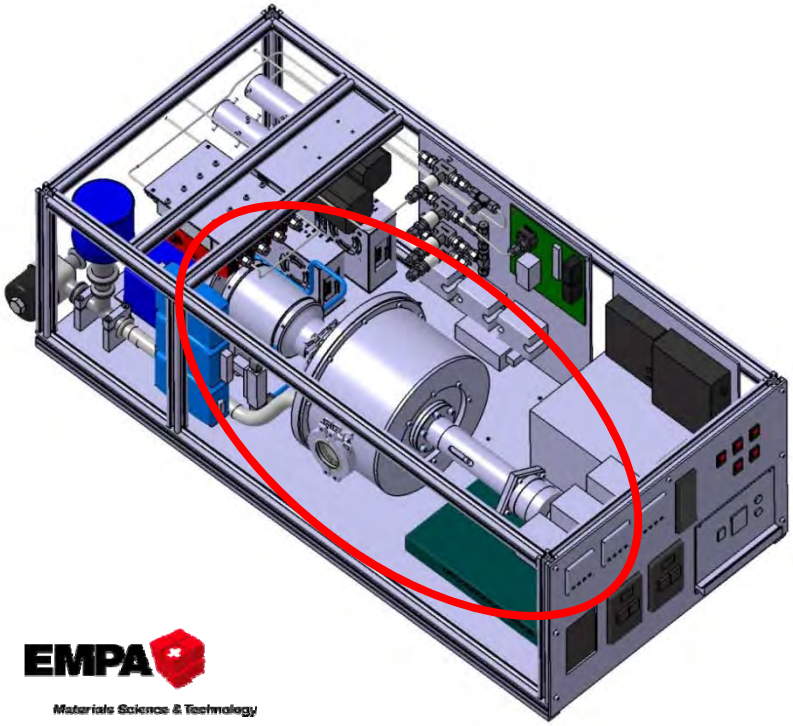


InGOS Goals:
0.1 ‰ for $\delta^{13}C$-CH_4
1 ‰ for δD-CH_4

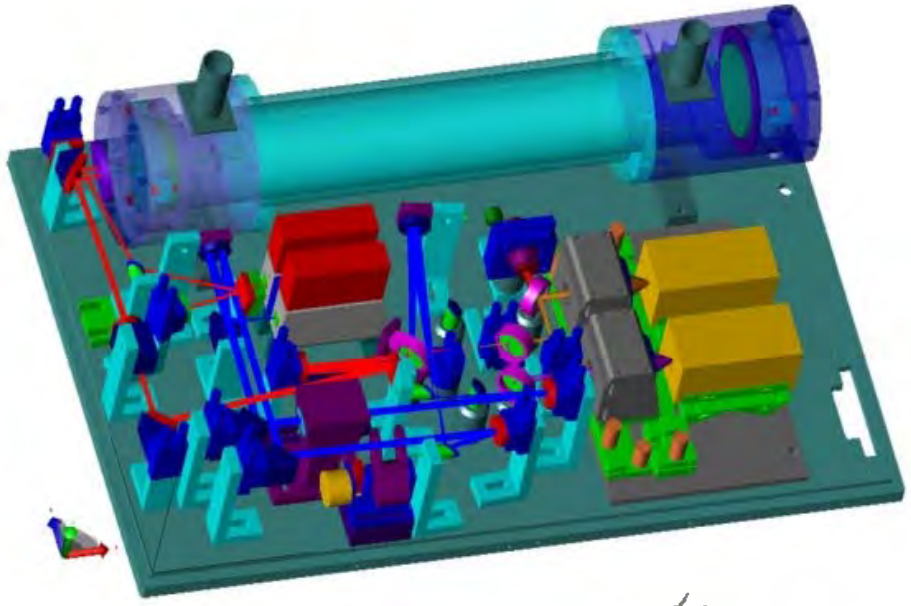
Precision ≈ ppt (10^{-12})

Analytical Technique

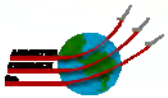




EMPA
Materials Science & Technology

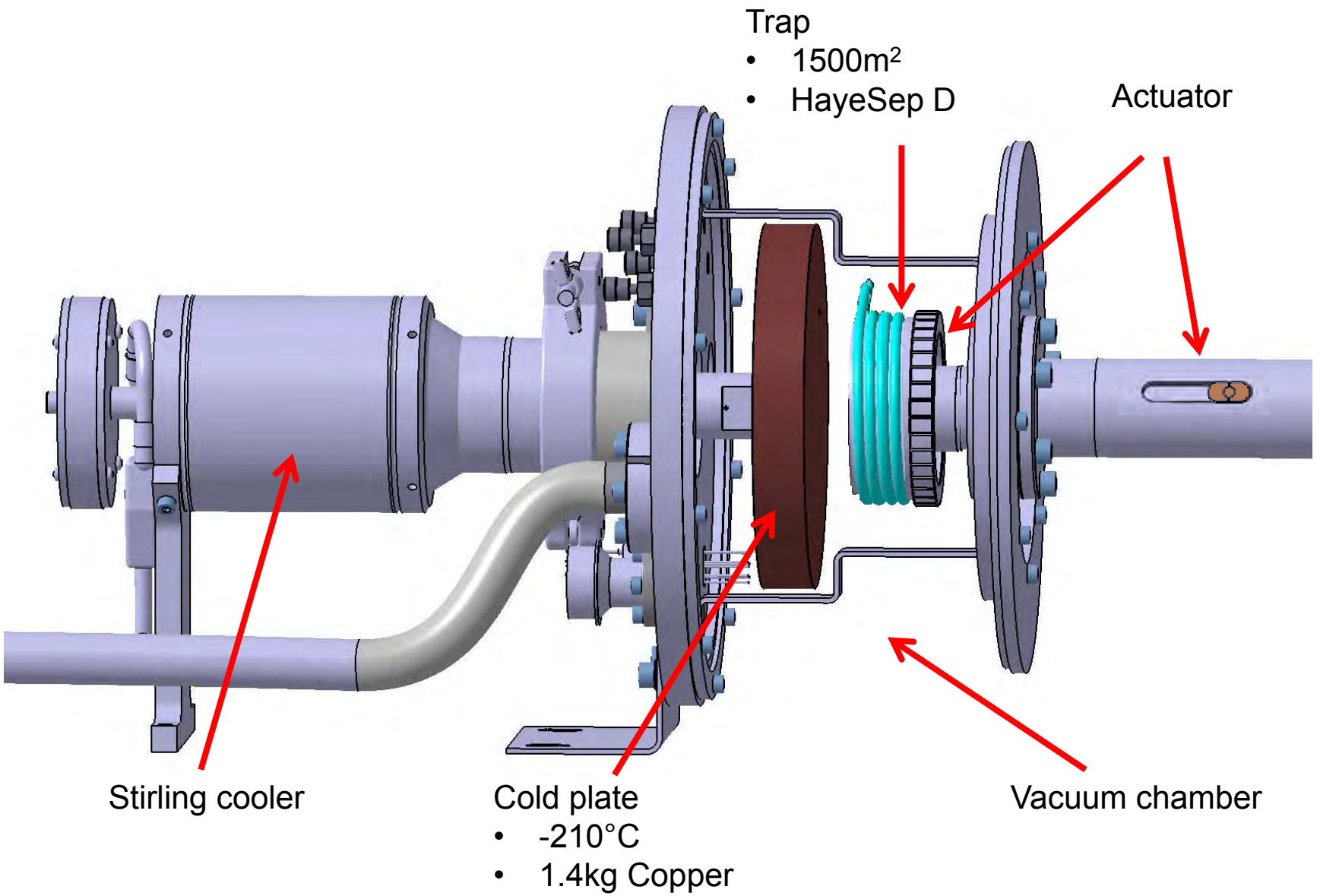


EMPA
Materials Science & Technology

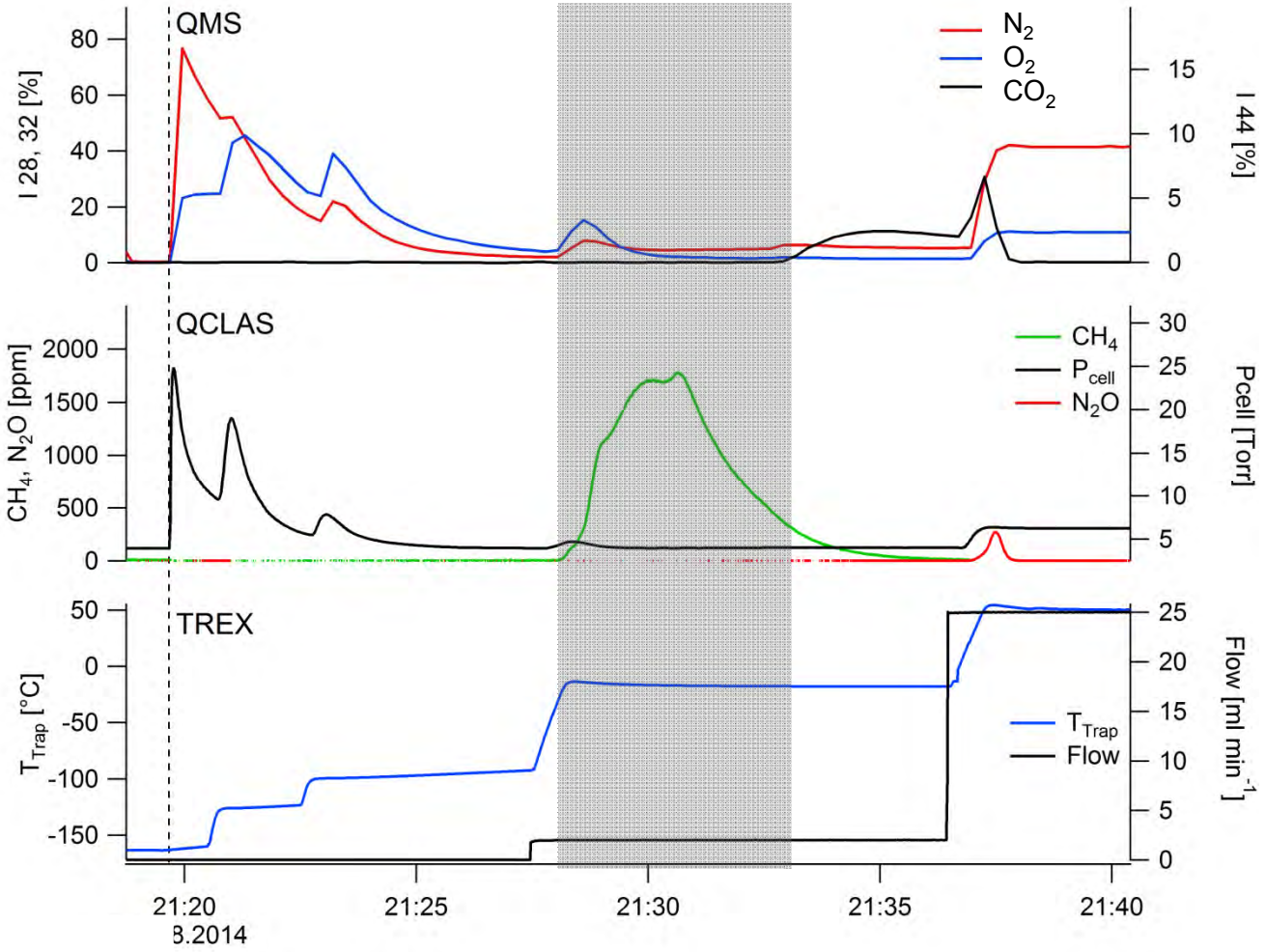


ALPES LASERS

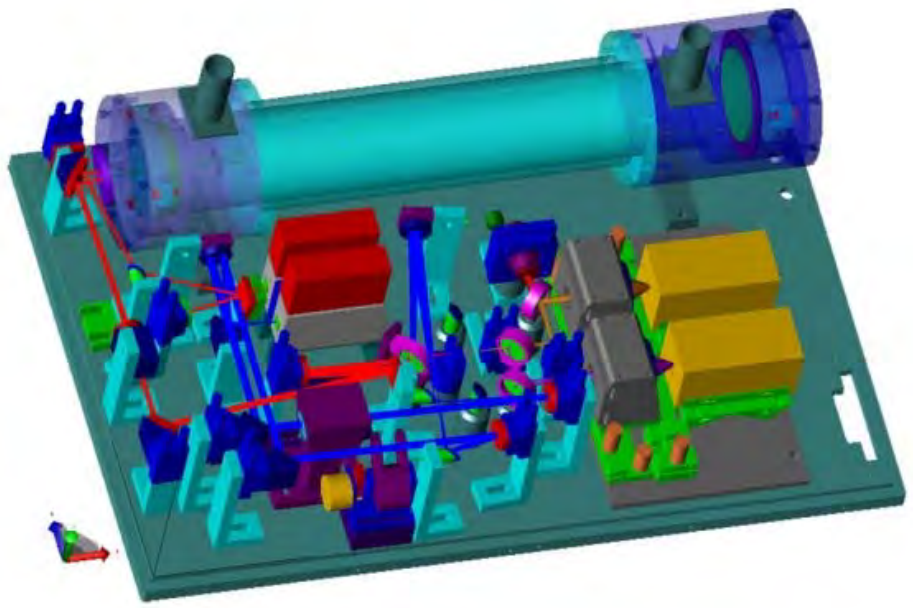
CH_4-Preconcentration



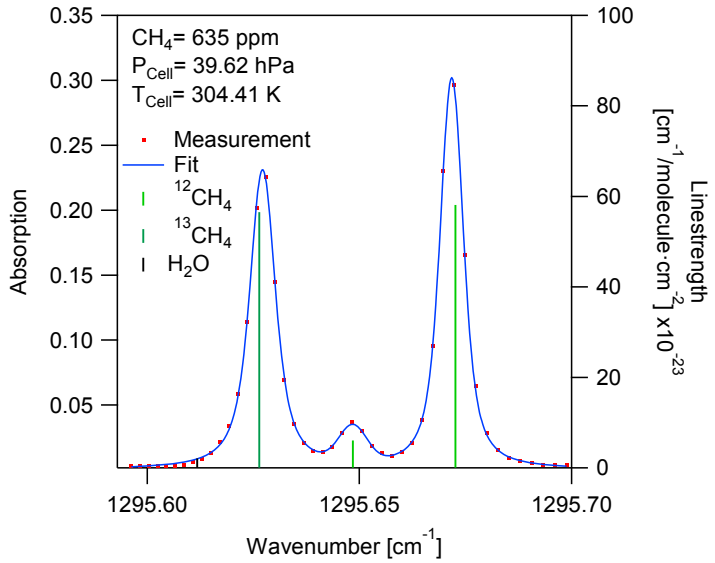
CH_4-Separation

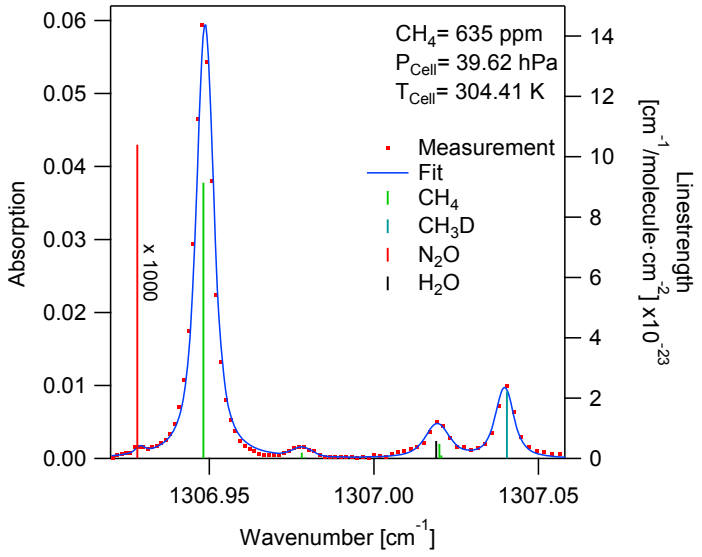


Laser spectroscopy

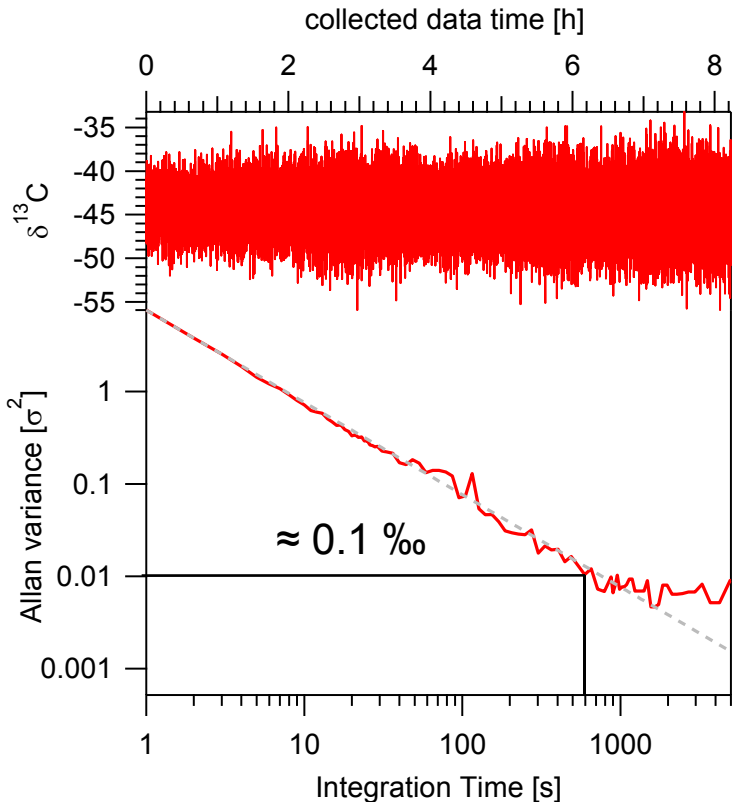


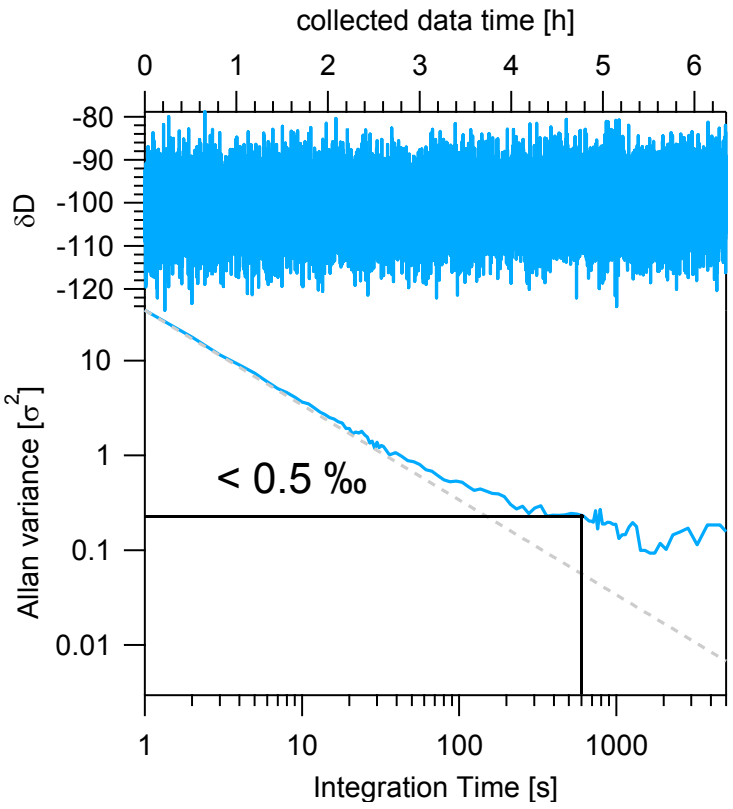
- two cw-DFB-QCLs @ 7.7 µm
- MPC of 76 m optical path
- TEC MCT IR-detector





Laser spectroscopy – Allan precision





Compact & automated measurement system

QCLAS

Electronics (QCLAS)

TREX

Coolers/Pumps

- CH_4, $\delta^{13}C$ & δD
- Compact
- Automated (LabView)
- ~1 hour time resolution

Field Campaign in Dübendorf

Field Campaign in Dübendorf

- TREX-QCLAS (Empa)
- Sampling + IRMS (UU, RHUL, MPI)
- CRDS, OA-ICOS

Universiteit Utrecht

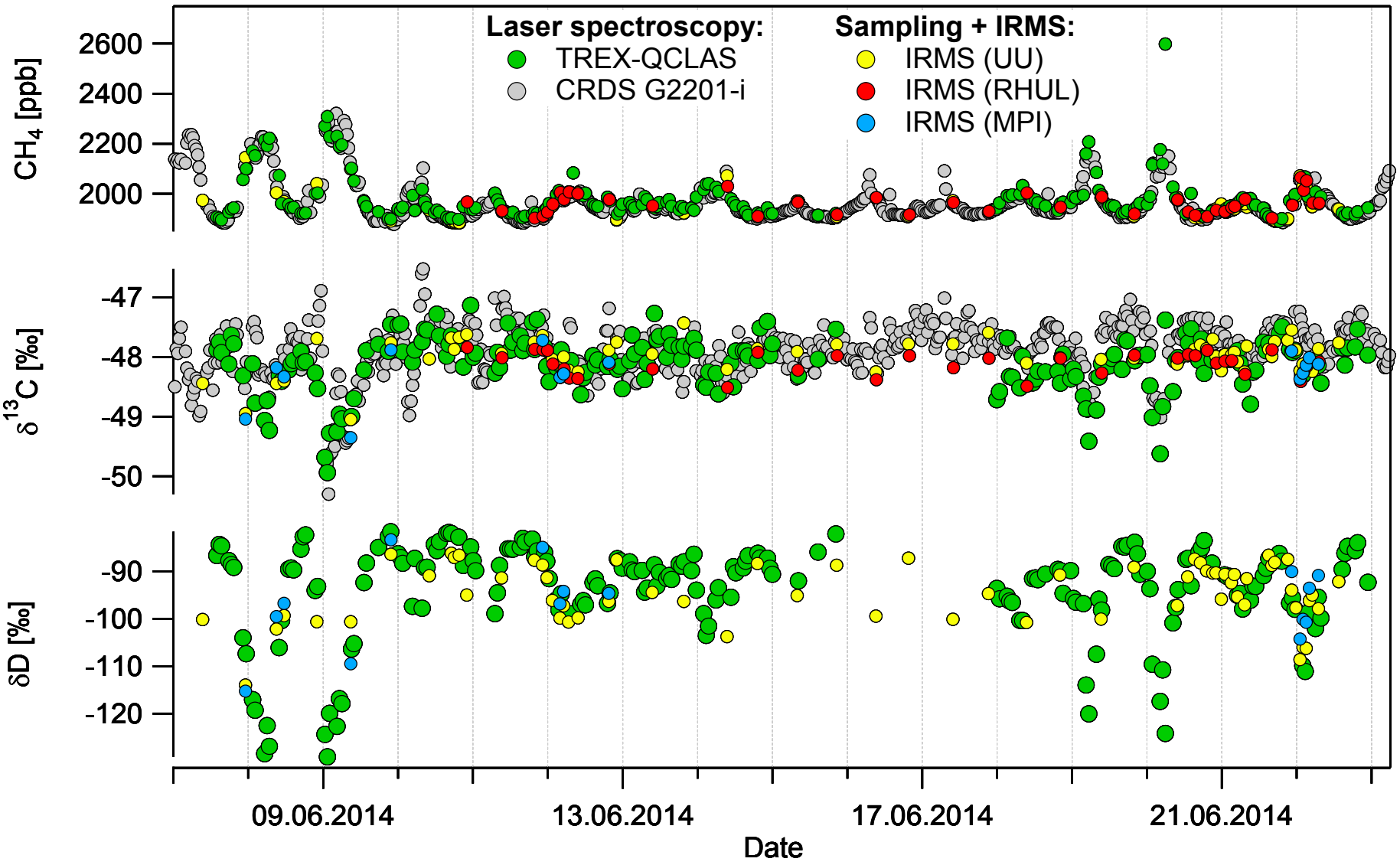
eawag aquatic research

MPI-BGC Jena

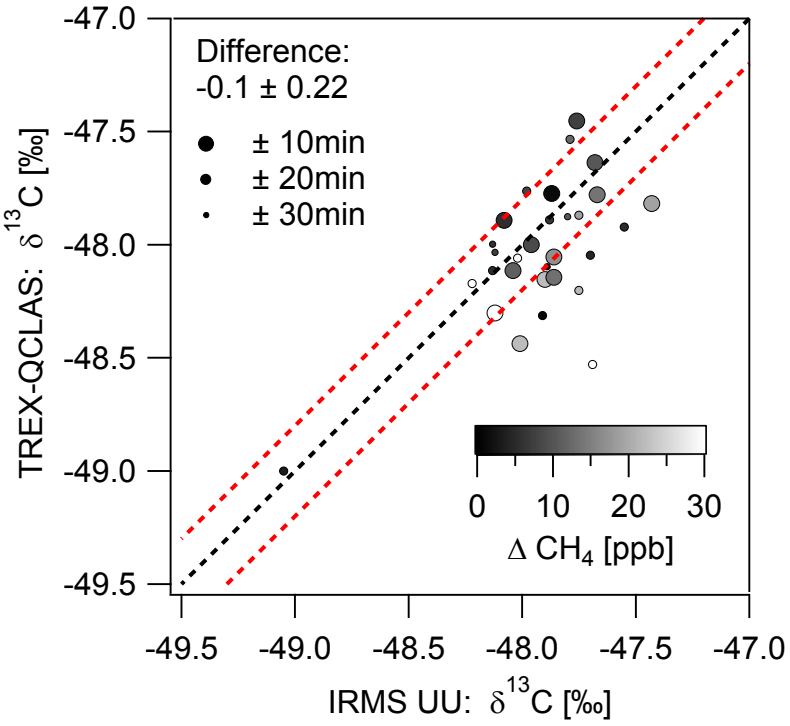
ROYAL HOLLOWAY UNIVERSITY OF LONDON

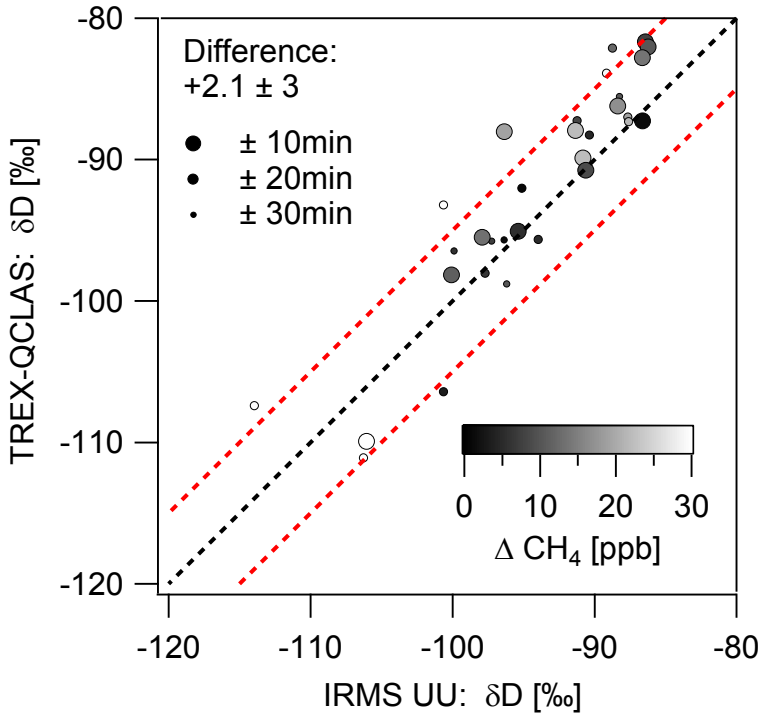
Repeatability

Temporal trends



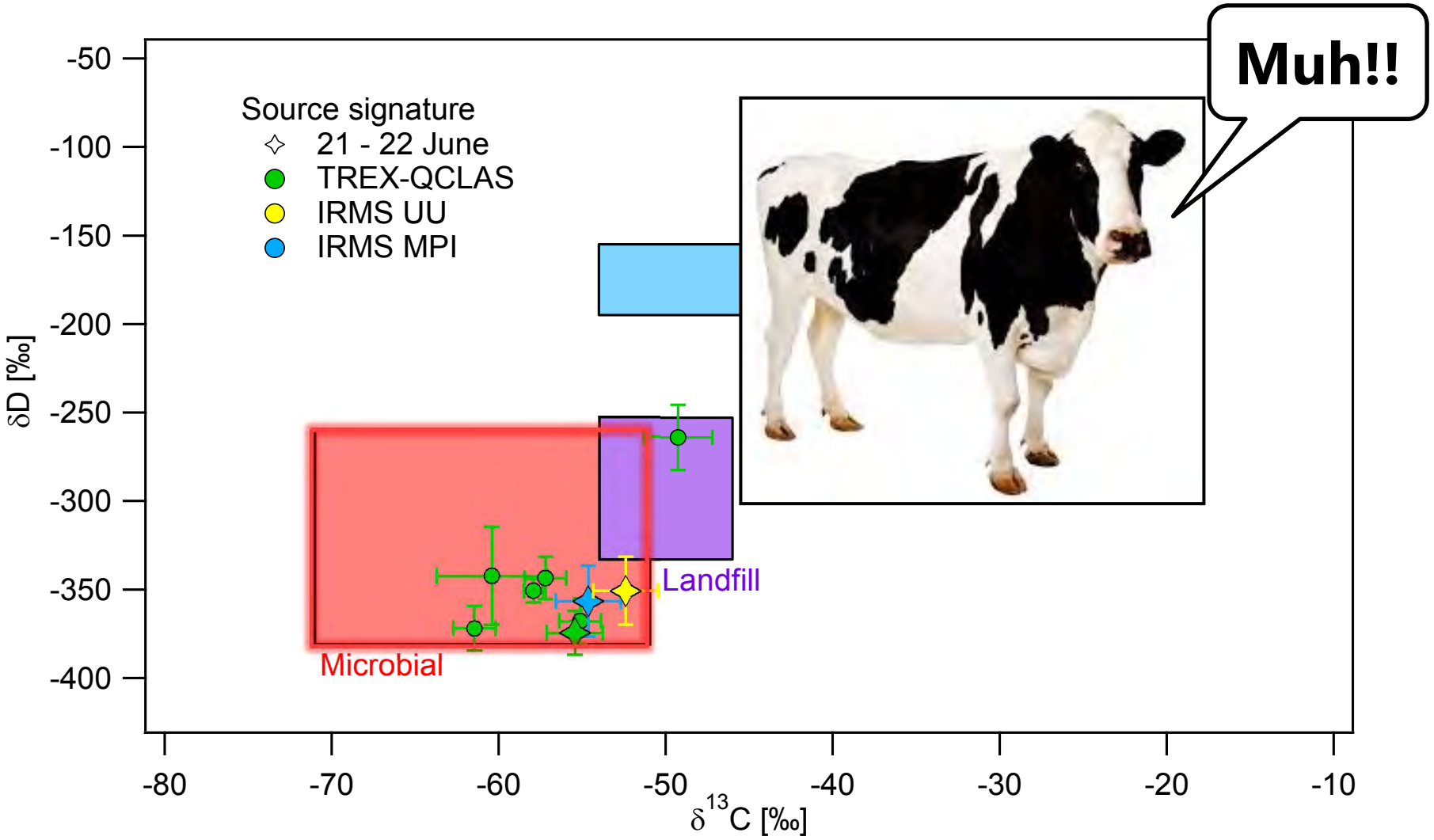
Compatibility





– – – Extended WMO compatibility goals

Source processes



S. Eyer et al., AMTD (2015)

Conclusion & Outlook

- ✓ Successful CH_4 preconcentration by TREX
- ✓ High precision CH_4 isotopic analysis by QCLAS
  ≈0.1 ‰ for $\delta^{13}C$ and <0.5 ‰ for δD-CH_4
- ✓ Repeatability of TREX + QCLAS
  0.19 ‰ for $\delta^{13}C$ and 1.9 ‰ for δD-CH_4
- ✓ Good compatibility of TREX+QCLAS with IRMS for $\delta^{13}C$-CH_4 and δD
- ✓ Successful determination of source processes
- ✓ 6 months field campaign at Cabauw, NL

Special thanks to…

- Empa
  - J. Mohn, B. Tuzson und L. Emmenegger
  - S. Reimann, M. Vollmer, M. Hill
  - C. Zellweger and M. Steinbacher, GAW
  - D. Brunner, Eliza Harris
  - Hydrogen Group, Workshop
- University of Utrecht
  - Thomas Röckmann, Carina van der Veen, Elena Popa
- MPI Jena
  - Willi A. Brand
- RHUL
  - Rebecca Fisher, David Lowry, Euan G. Nisbet
- University Bern
  - H. Fischer
- INGOS & SNF

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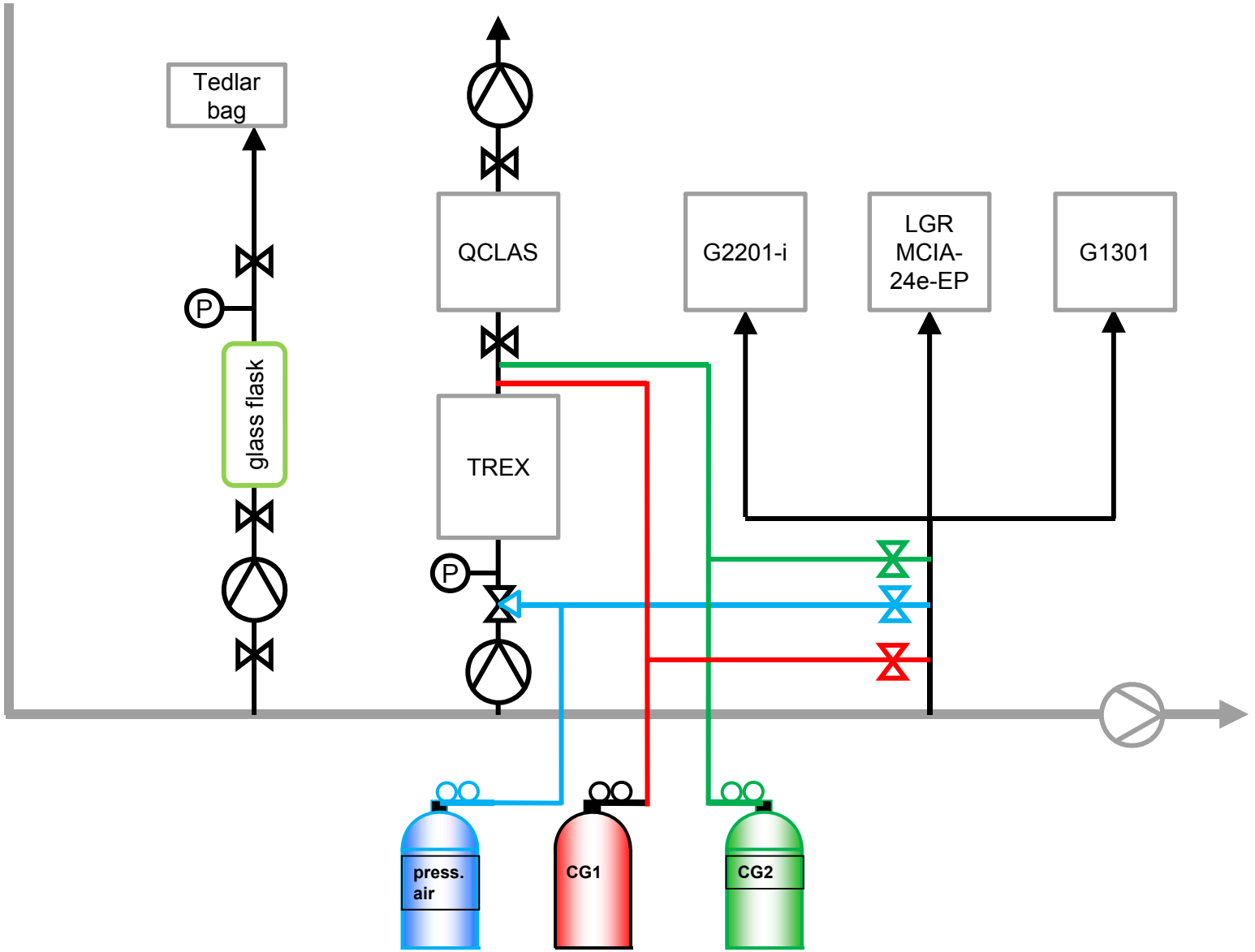
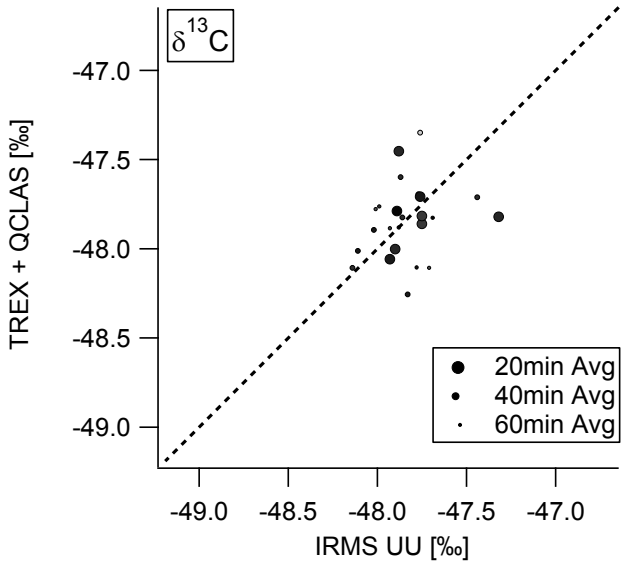
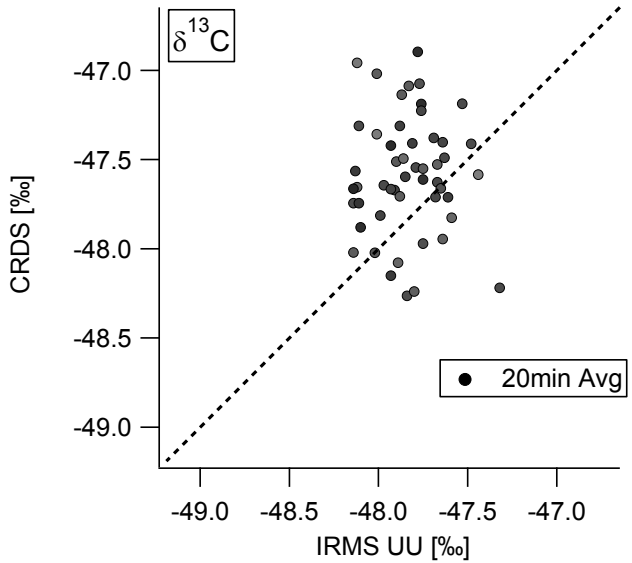
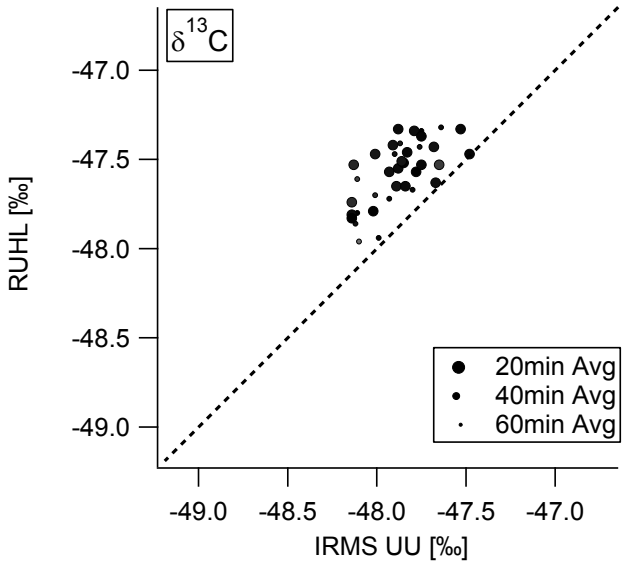
Setup


Tedlar bag
P
glass flask
QCLAS
TREX
P
G2201-i
LGR MCIA-24e-EP
G1301
press. air
CG1
CG2

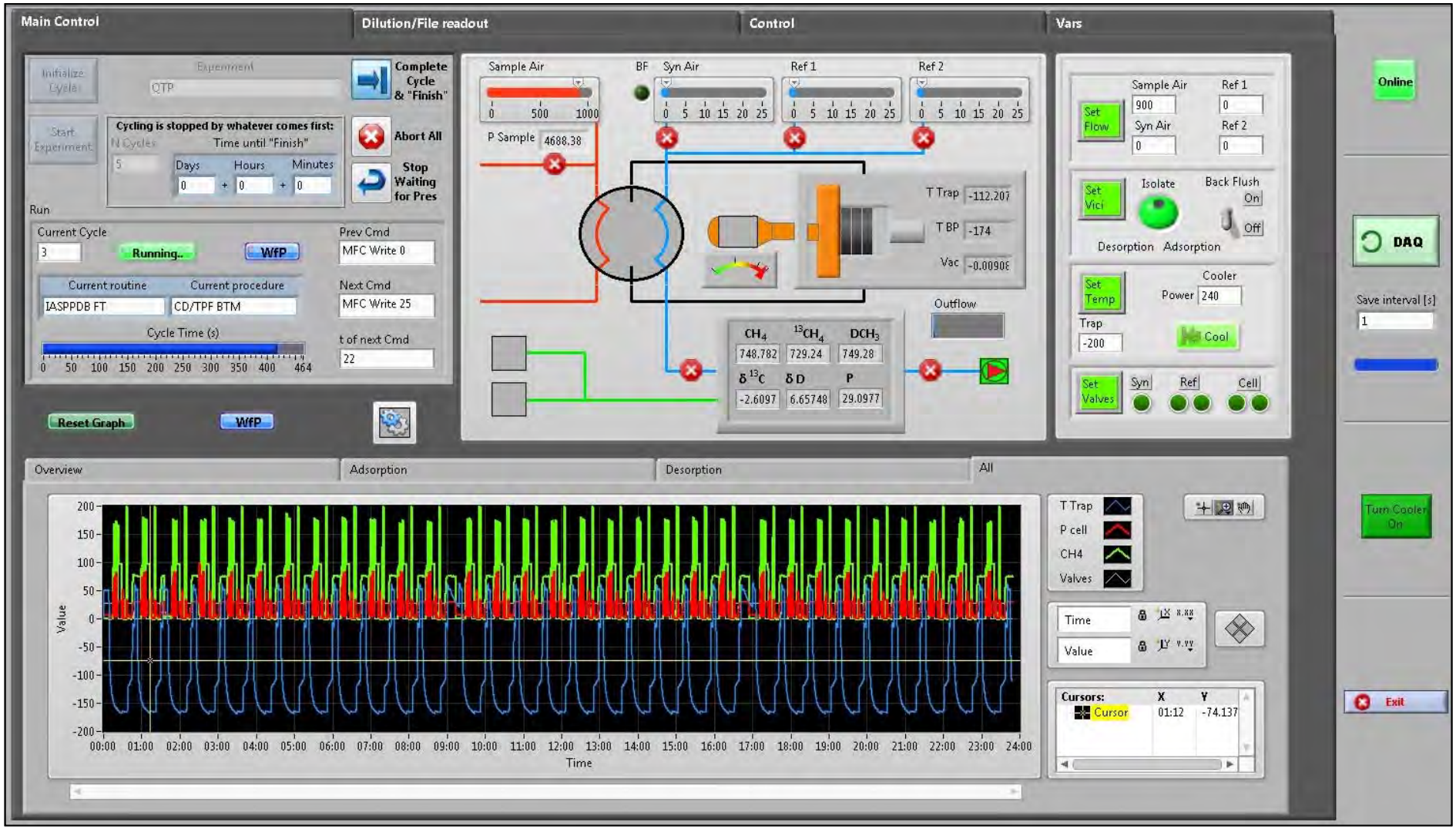
Compatibility – preliminary results







Compact & automated measurement system



Participants campaign Dübendorf

- $\delta^{13}C$ and δD and CH_4 by QCLAS
  CH_4 by CRDS (Picarro)

EMPA
Materials Science & Technology

- $\delta^{13}C$ and CH_4 by OA-ICOS (LGR)
  $\delta^{13}C$ and δD and CH_4 by flask sampling + IRMS

Universiteit Utrecht

- $\delta^{13}C$ and δD and CH_4 by flask sampling + IRMS

MPI-BGC Jena

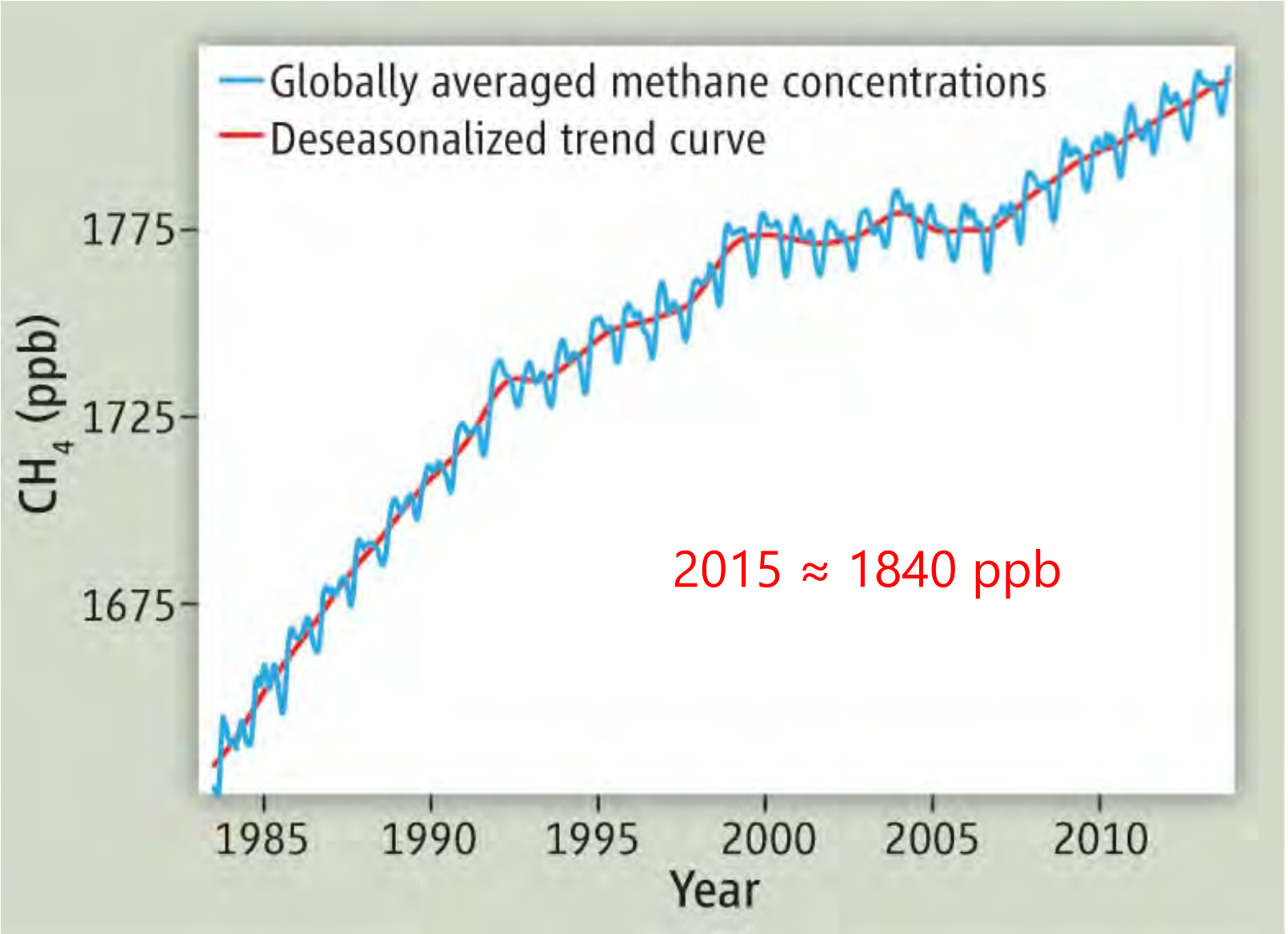
- $\delta^{13}C$ and CH_4 by bag sampling + IRMS

ROYAL HOLLOWAY UNIVERSITY OF LONDON

- $\delta^{13}C$ and CH_4 by CRDS (Picarro)

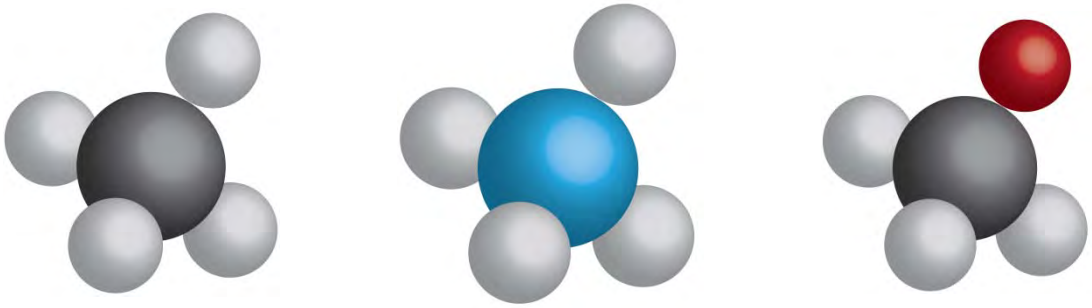
eawag aquatic research

The global CH_4 cycle

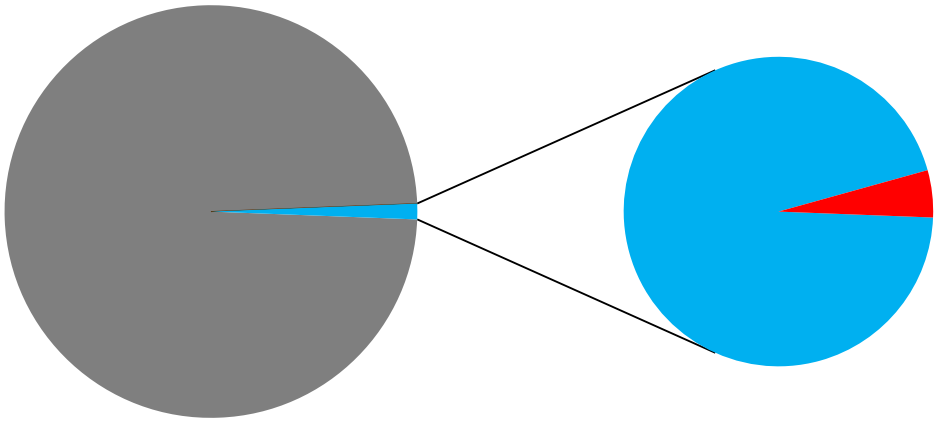


CH_4 Isotopes

$^{12}CH_4$ $^{13}CH_4$ $^{12}CH_3D$



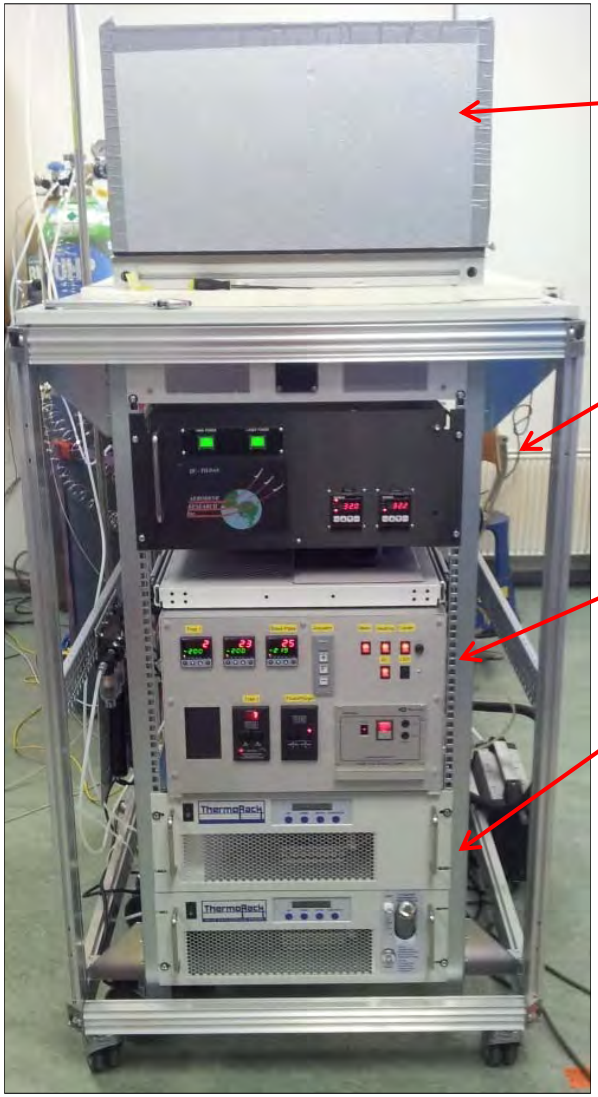
98.9% 1.1% 0.06%



Cabauw - Messkampagne

- Oct. 2014 – March 2015
- 20 m height

Compact & automated measurement system



Optics

Electronics (QCLAS)

TREX

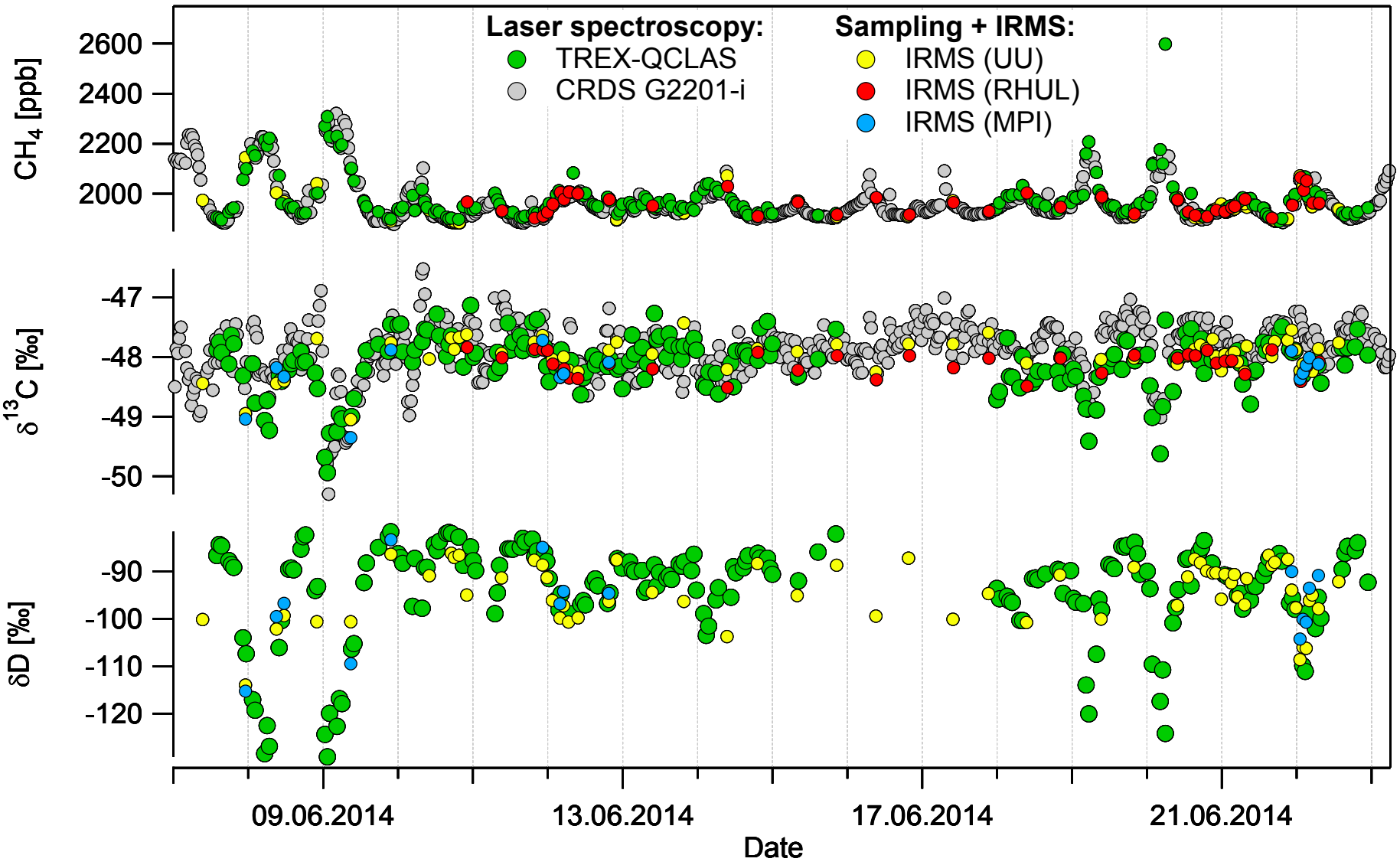
Coolers/Pumps

- $\delta^{13}C$ & δD
- Kompakt
- Vollautomatisch (LabView)
- <2.4kW
- ≈350 kChf

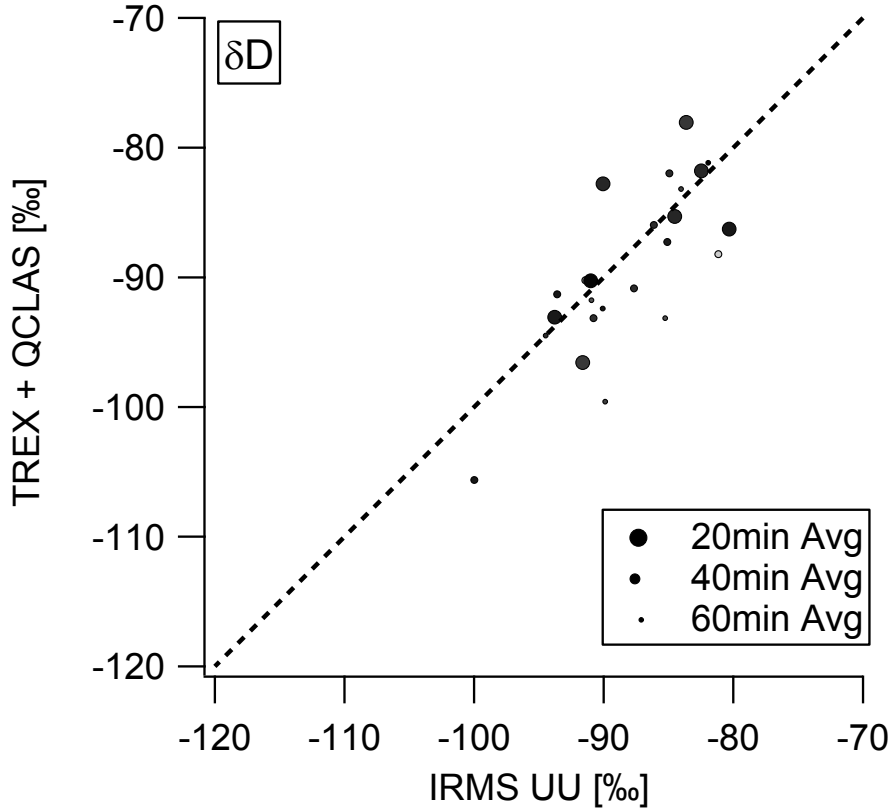
Summary and Outlook

- ✓ Successful CH_4 preconcentration by TREX
- ✓ High precision CH_4 isotopic analysis by QCLAS
  ≈0.1 ‰ for $\delta^{13}C$ and <0.5 ‰ for δD-CH_4
- ✓ Repeatability of TREX + QCLAS
  0.19 ‰ for $\delta^{13}C$ and 1.9 ‰ for δD-CH_4
- ✓ 4 months field campaign at Cabauw, NL
- ✓ Good compatibility of TREX+QCLAS with
  IRMS for $\delta^{13}C$-CH_4 and δD
- ✓ Mainly ruminant sources

Temporal trends



Compatibility – preliminary results



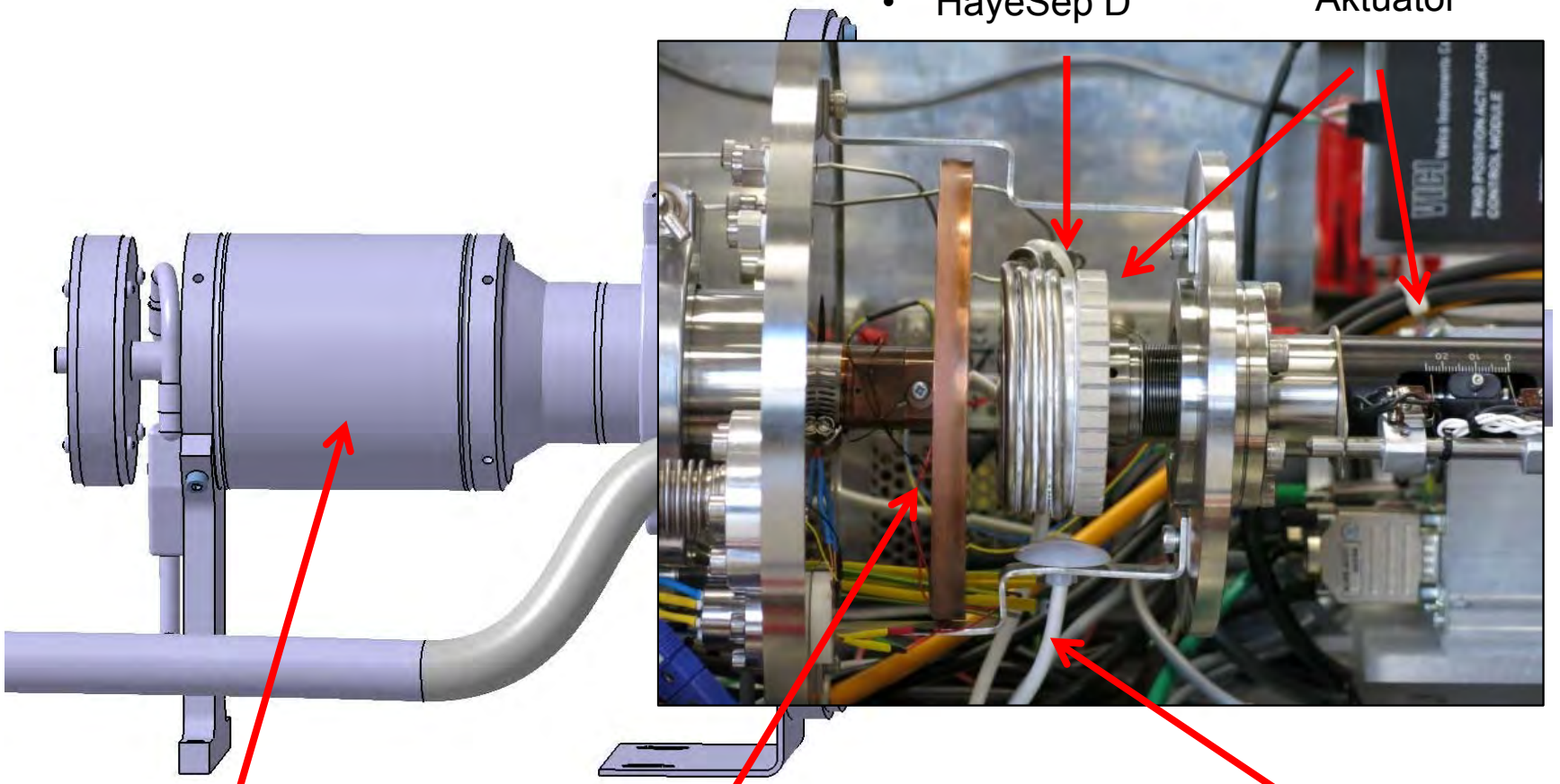
Overview

- Introduction
- Analytical Technique
- Campaign in Dübendorf
- Conclusion and Outlook

CH_4-Extraktion

Trap
- 1500m²
- HayeSep D

Aktuator



Stirling cooler

Cold plate
- -210°C
- 1.4kg Kupfer

Vacuum chamber