Feasibility study of using a “travelling” CO$_2$ and CH$_4$ instrument to validate continuous in-situ measurement stations

S. Hammer$^1$, G. Konrad$^1$, A. Vermeulen$^2$, M. Delmotte$^3$, A. Jordan$^4$, L. Hazan$^3$, D. Griffith$^5$ and I. Levin$^1$

$^1$ Institut für Umweltphysik (IUP), University of Heidelberg, Germany
$^2$ Netherlands Energy Research Foundation (ECN), Petten, The Netherlands
$^3$ Laboratoire des Sciences du Climat et de l’Environnement (LSCE), Gif-sur-Yvette, France
$^4$ Max Planck Institute for Biogeochemistry, Jena, Germany
$^5$ School of Chemistry, University of Wollongong, Australia
ICOS
Atmospheric Demonstration Experiment

- Four atmospheric stations
- Network calibration via the CAL
- Centralized data evaluation in the ATC
- Independent and comprehensive QC by Univ. Heidelberg
Atmospheric Inspection Team

Equipment:

- In-situ FTIR spectrometer for CO$_2$, CH$_4$, CO and N$_2$O analysis
- Independent pumping and drying system
- Standard gases calibrated by the CAL (MPI-BGC)
- Spare intake lines were provided by the stations
CO$_2$ comparison FTIR & GC in Heidelberg

FTIR
GC

23.Apr 12:00
24.Apr 00:00
24.Apr 12:00
25.Apr 00:00
25.Apr 12:00

2011

CO$_2$ [µmol/mol]
CO$_2$ comparison FTIR & GC in Heidelberg

23. Apr 12:00

24. Apr 00:00

24. Apr 12:00

25. Apr 00:00

25. Apr 12:00

FTIR

GC

CO$_2$ [µmol/mol]

2011
Exponentially smoothed FTIR measurements

![Graph showing CO$_2$ concentration over time with exponential smoothing.](image)
CO$_2$ comparison in Heidelberg
April to May 2011

$\Delta$CO$_2$ [µmol/mol] vs. GC-FTIR

10.04.2011 17.04.2011 24.04.2011 01.05.2011 08.05.2011 15.05.2011 22.05.2011
$\Delta$CO$_2$ frequency distribution
Heidelberg, April to May 2011
∆CO$_2$ frequency distribution
Heidelberg, April to May 2011

Gauss fit: mean = 0.02 µmol/mol
1σ = 0.07 µmol/mol
\[ \Delta \text{CO}_2 \] frequency distribution
Heidelberg, April to May 2011

Gauss fit:
mean = 0.02 \, \mu\text{mol/mol}
1\sigma = 0.07 \, \mu\text{mol/mol}
\( \triangle \text{CO}_2 \) frequency distribution
Heidelberg, April to May 2011

Gauss fit:
- mean = 0.02 µmol/mol
- 1σ = 0.07 µmol/mol
- IQR = 0.27 µmol/mol

GC - FTIR
Summary of the initial test phase in Heidelberg

- Buffer systems are indispensable when comparing “sniff”-like GC measurements to a nearly continuous measurement system.
- The buffer inherent smoothing needs to be taken into account for data evaluation.
- Initial CO$_2$ and CH$_4$ comparison between GC and FTIR in Heidelberg show that we are able to reach the WMO compatibility targets.
Cabauw station visit: May/June 2011
Intake line test at Cabauw and Heidelberg
Station STDs measured with the FTIR

\( \Delta \text{CH}_4 \) [nmol/mol] assigned - FTIR

\( \text{CO}_2 \) assigned [µmol/mol]

\( \Delta \text{CO}_2 \) [µmol/mol] assigned - FTIR

\( \text{CH}_4 \) assigned [nmol/mol]

off scale

15
Station STDs measured with the FTIR

FTIR Target

\[ \Delta CH_4 \text{ [nmol/mol]} \]

\[ \Delta CO_2 \text{ [µmol/mol]} \]

assigned - FTIR

assigned - FTIR

[Image of gas cylinders and data plots]

[Table of FTIR data with dates and values]

16
Overview of the entire comparison record for CBW
Time series of the CO$_2$ difference

FTIR - CRDS

ΔCO$_2$ [µmol/mol]

FTIR-CRDS

27 Mai    29 Mai    31 Mai    2 Jun    4 Jun    6 Jun    8 Jun    10 Jun

2011
CO₂ difference and hourly CO₂ change rate

FTIR-CRDS

ΔCO₂ [µmol/mol]

dCO₂ /dt [µmol/mol/h]

27 Mai 29 Mai 31 Mai 2 Jun 4 Jun 6 Jun 8 Jun 10 Jun

2011

-600 -400 -200 0 200 400 600

-600 -400 -200 0 200 400 600
Selection criteria:
hourly CO$_2$ change $< |15|$ [µmol/mol/h]
Frequency distribution
CO₂ differences FTIR-CRDS

Gauss fit:
mean = 0.19 μmol/mol
1σ = 0.08 μmol/mol
IQR = 0.14 μmol/mol

FTIR-CRDS

ΔCO₂ [μmol/mol]

frequency count
CO₂ difference

Lorentz
Gauss
OPE station visit: July/August 2011
OPE station standards

\[ \Delta \text{CO}_2 \text{ assigned - FTIR} \]

\[ \Delta \text{CH}_4 \text{ assigned - FTIR} \]

FTIR Target

HD

OPE

HD


2022

2023

2024

2025

2026

Cabauw STD

FTIR Target

\[ \text{CH}_4 \text{ assigned [nmol/mol]} \]

\[ \text{CO}_2 \text{ assigned [µmol/mol]} \]
Overview of the entire comparison record for OPE

- **CO₂ CRDS**
- **CO₂ FTIR**
- **Smoothed CO₂ CRDS**

![Graph showing CO₂ concentration over time from 21 Jul to 11 Aug 2011. The graph compares measurements from CO₂ CRDS and CO₂ FTIR methods, with a smoothed line for CO₂ CRDS.](image)
Frequency distribution
\( \text{CO}_2 \) differences FTIR-CRDS

Gauss fit:
mean = -0.06 \( \mu \text{mol/mol} \)
1\( \sigma \) = 0.12 \( \mu \text{mol/mol} \)
IQR = 0.19 \( \mu \text{mol/mol} \)
Comparison to travelling instrument reveals periodic features

\[ \text{CO}_2 \text{ CRDS} \quad \text{CO}_2 \text{ FTIR} \quad \text{Smoothed CO}_2 \text{ CRDS} \]
$\Delta \text{CO}_2$ – summary
means and standard deviations

$\Delta \text{CO}_2$ [\(\mu\text{mol/mol}\)]
station - traveling FTIR

- HD
- CBW
- OPE

2011
$\Delta \text{CH}_4$ – summary
means and standard deviations

$\Delta \text{CH}_4$ [$\text{nmol/mol}$]
station - traveling FTIR

2011
Summary

• Two continuous stations have been successfully validated by the travelling FTIR.
• Additional tests are needed to identify the origin for observed differences.
• Comprehensive intake system tests have to be developed and should be routinely implemented.
• Quantitative measure for non-Gaussian distributions need to be defined.
• High temporal resolution of the comparison data reveals very valuable information on system performance.
• Comprehensive quality control using a travelling instrument is possible and strongly recommended.
Planed ICOS network

• 30 atmospheric stations
• 2 month per validation
• => 5 years for one entire check

Acknowledgment: Funding was provided from ICOS PP (European union)
Sensitivity of the $1\sigma$ scattering against hourly CO$_2$ change rate

Theoretical limit due to noise of both instruments
CBW cucumber

Euro-5: Cabauw relative to MPI-BGC reference.

--- WMO intercompatibility goal (± 0.1 ppm)

Aug 08  Nov 08  Mar 09  Jun 09  Sep 09

D88480
D88484
D88478
$\Delta$CH$_4$ frequency distribution

Heidelberg, April to May 2011

Gauss fit:
mean $= 0.3$ nmol/mol
$1\sigma = 2.3$ nmol/mol
IQR $= 3.6$ nmol/mol
Frequency distribution

CH₄ difference FTIR-CRDS

Gauss fit:
mean = 1.01 nmol/mol
1σ = 0.72 nmol/mol
IQR = 1.02 nmol/mol
Frequency distribution
$\text{CH}_4$ difference FTIR-CRDS

Gauss fit:
mean $= 1.01 \text{ nmol/mol}$
$1\sigma = 0.72 \text{ nmol/mol}$
IQR $= 1.02 \text{ nmol/mol}$
Comparing measurements with different turn-over constants

Buffered GC

- \( \tau_{GC} = 30 \text{ min} \)
- \( V=10 \text{L buffer} \)
- \( \Phi=0.33 \text{L/min} \)

FTIR

- \( \tau_{FTIR} = 3.5 \text{ min} \)
- \( V=3.5 \text{L cell} \)
- \( \Phi=1 \text{L/min} \)

CRDS

- \( \tau_{CDRS} = 0.1 \text{min} \)
- \( 0.035 \text{L cavity} \)
- \( \Phi=0.25 \text{L/min} \)

\[
C(t_m) = \frac{1}{\tau} \int_0^\infty C(t_m-t) \cdot e^{-\frac{t}{\tau}} dt
\]
Frequency distribution

$\text{CH}_4$ difference FTIR-CRDS

Gauss fit:
- mean = 0.31 nmol/mol
- $1\sigma = 0.81$ nmol/mol
- IQR = 1.47 nmol/mol
Response of the buffered GC system to a concentration step change

\[ \text{CO}_2 \, [\mu\text{mol/mol}] \]

Elapsed time since step change [h]

GC measurement
Exponentially smoothed input function

CO$_2$ [µmol/mol]

elapsed time since step change [h]

- GC measurement
- Exponential smoothing

Exponential smoothing function
End-to-end Quality Control using „travelling“ Instrumentation

• Within the ICOS Demo Experiment an inspection team was formed equipped with “mobile” instrumentation to perform independent measurements over a few weeks, in parallel to routine observations.

• Two atmospheric stations have been visited:
  – Cabauw, NL, May 24th to June 9th 2011
  – OPE, France, July 25th to August 9th 2011
Intake line test