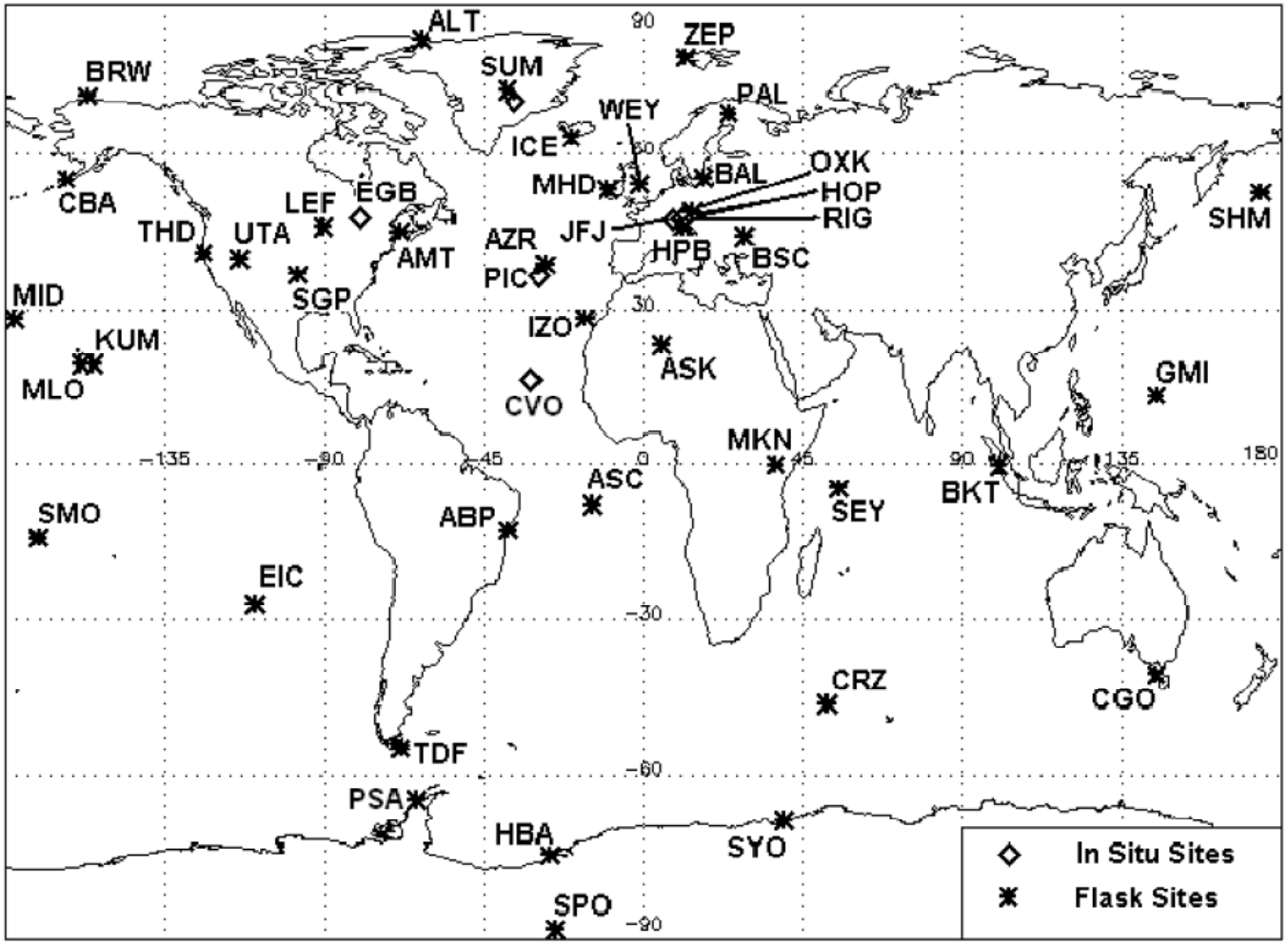
Quality and comparability of VOC-measurements in the GAW-VOC network

Rainer Steinbrecher
Stephan Thiel
Elisabeth Weiß

The WMO GAW-VOC Network in 2010



Helmig, D., *Bottenheim J., Galbally I.E., Lewis A., Milton M., Penkett S., Plass-Duelmer C., Read K. Reimann S., Steinbrecher R., Tans P., Thiel* S. (2009): The WMO-GAW Volatile Organic Compound Program***Eos Trans. AGU, 90*(52), 513–514.**

http://imk-ifu.fzk.de/wcc-voc/

KIT – Karlsruher Institut für Technologie
Universität des Landes Baden-Württemberg
und nationales Forschungszentrum
in der Helmholtz-Gemeinschaftd

GAW Network for VOC

Current status:

- Global coverage only achieved for NMHC based on the NOAA-GMD Glass Flask Sampling Program

Principle Set-Up for NMHC-Analysis in Air Samples

Cryogenically:
- L = 300 mm, i.d. = 1.5 mm
- Silcosteel-tube; no filling
- at -30°C

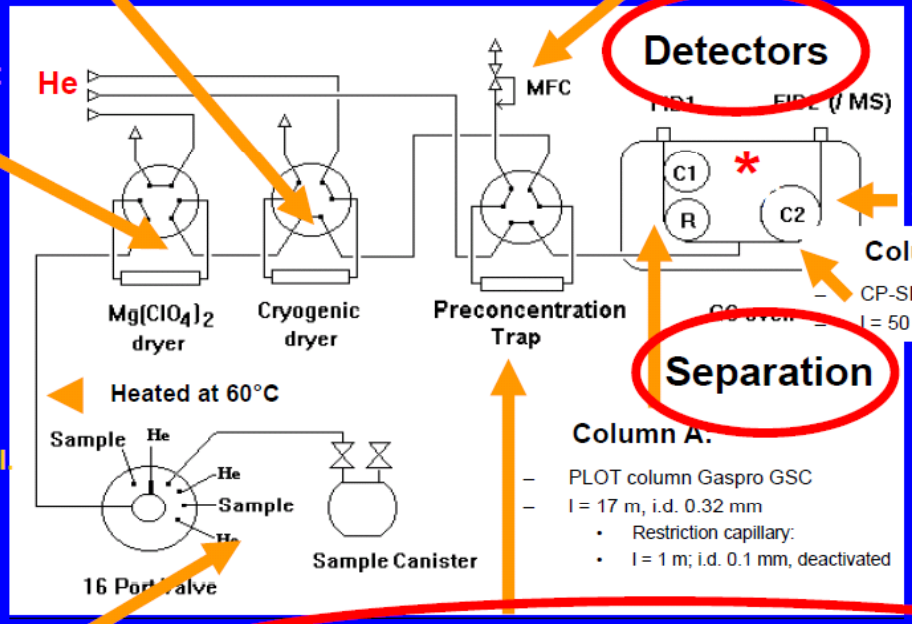
Sample Vol.: 400 ml
Sample Flow: 100 ml/min

Dryers:

Alternatively (mainly for checks): $Mg(CLO_4)_2$

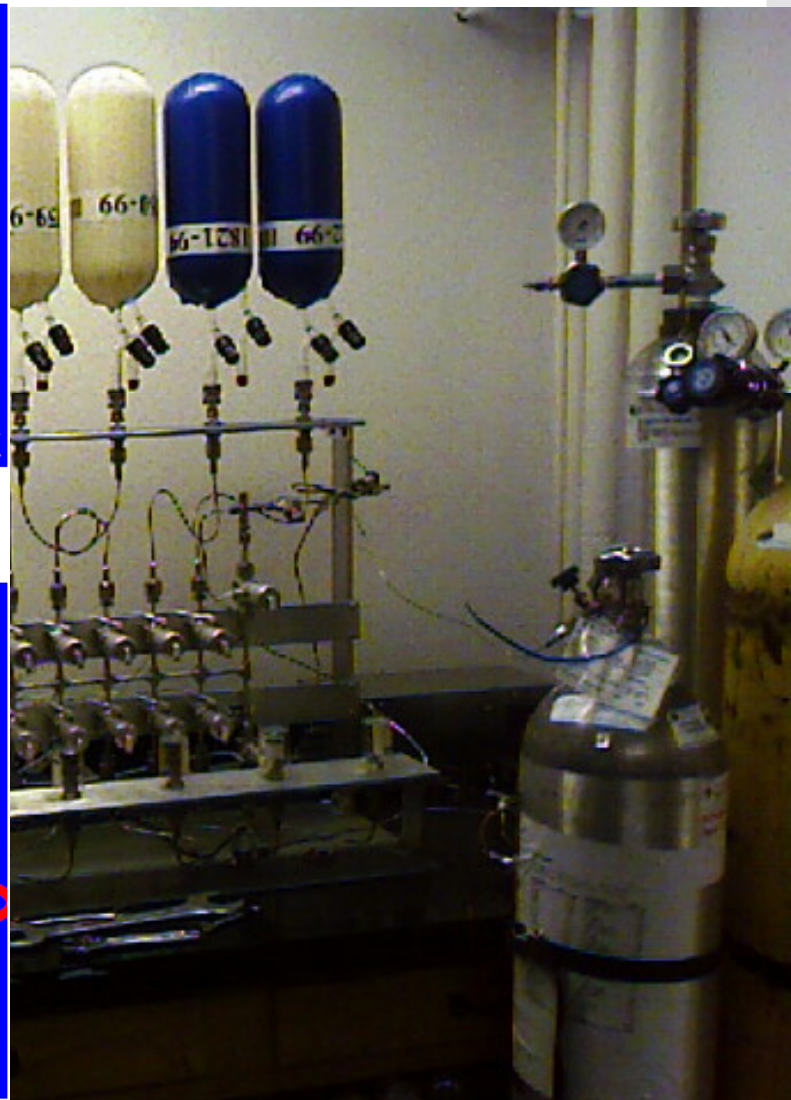
Temp. Progr.(*):
- 30°C
- 2.5 min isothermal
- 3.5 K/min to –13°C
- 20 K/min to 8°C
- 5 K/min to 70°C
- 10 K/min to 240°C
- 12.2 min isothermal

50 min



Up to 8 canisters:
- 6 samples,
- 1 NCAR-canister,
- 1 calibration canister
  - (n-butane/benzene)

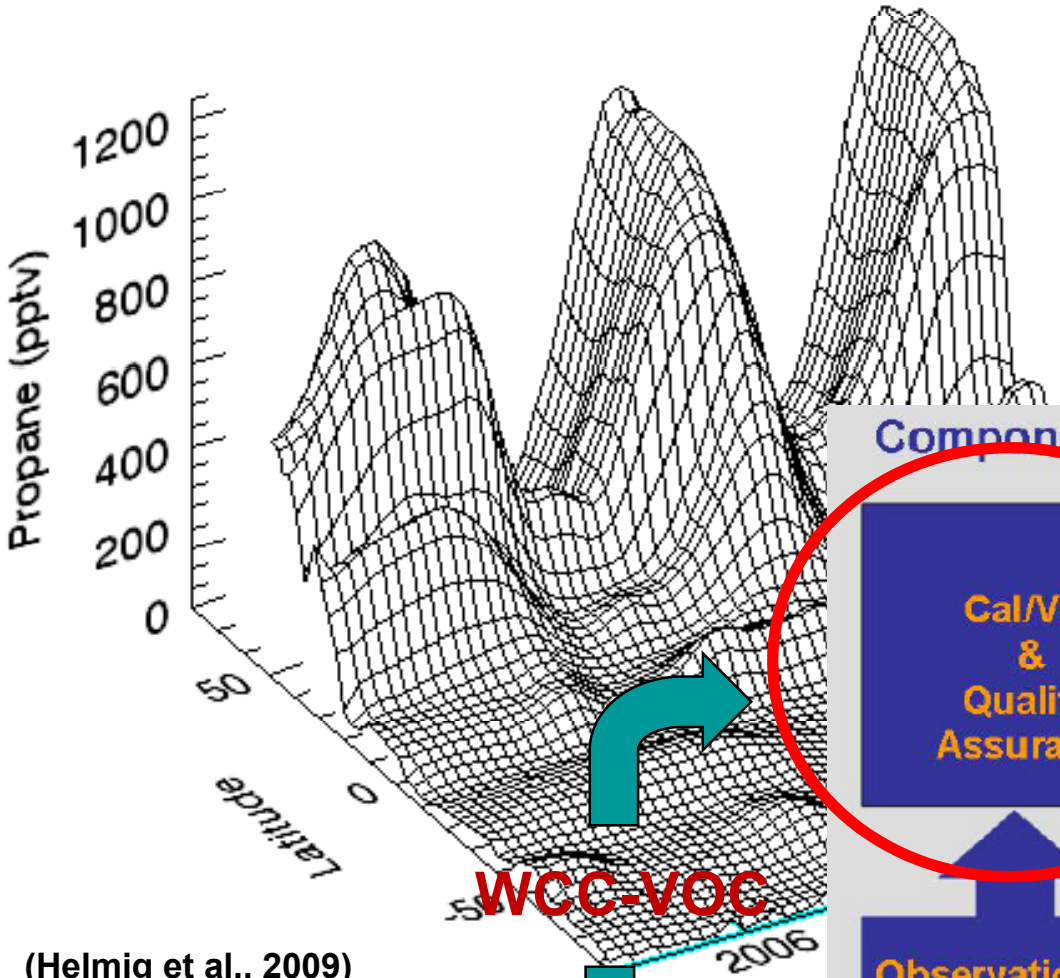
Sample pre-concentration trap (SPT; Varian)
- L = 8 cm, i.d. = 2.1 cm
- Carbopack® BHT)
- at –120°C (liquid N_2)
- Desorption at 200 °C
- sample is back-flushed
- sample transferred split-less to columns.



GAW Network for VOC

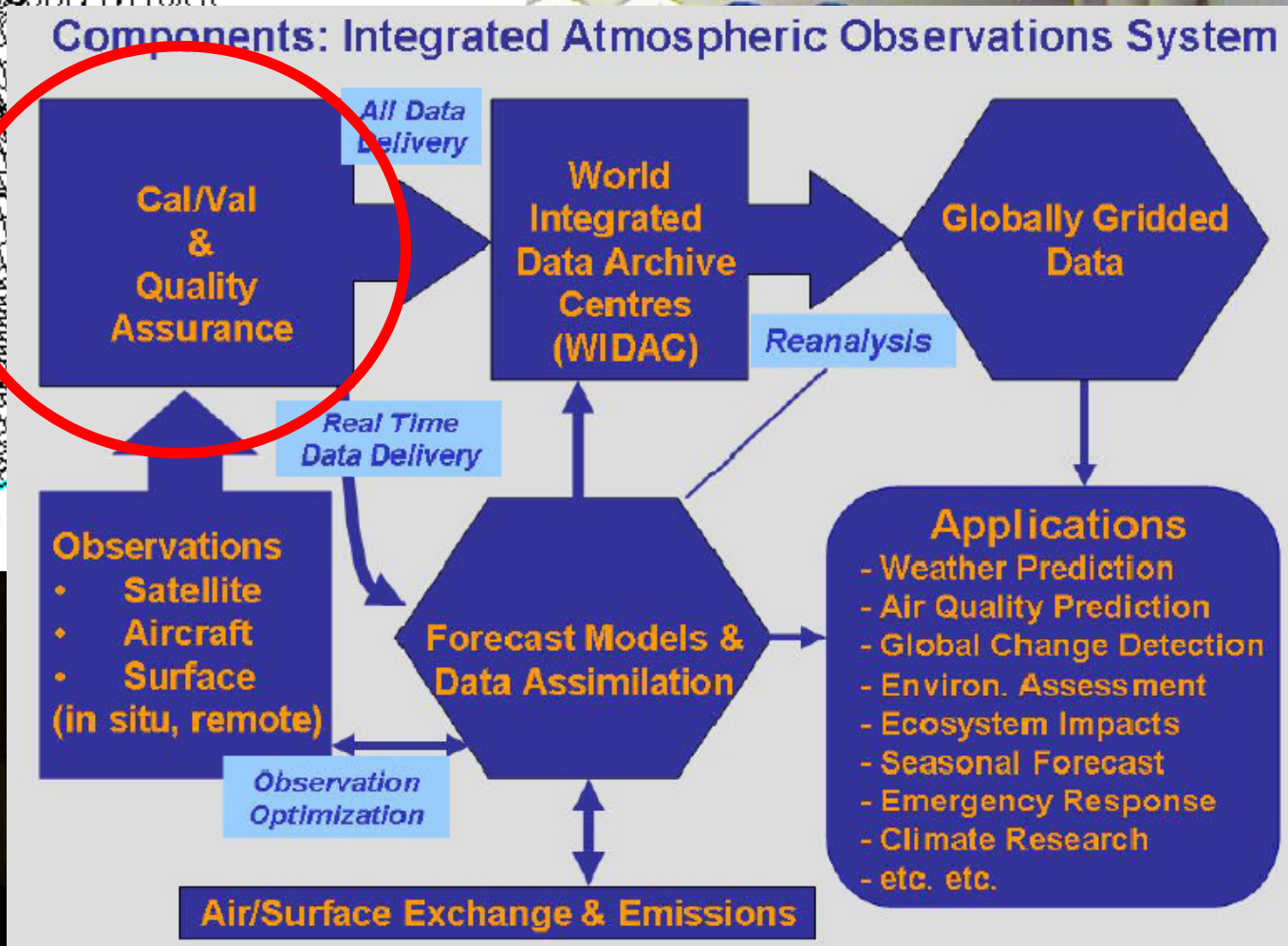
Current status:

- Global coverage only achieved for NMHC based on the NOAA-GMD Glass Flask Sampling Program



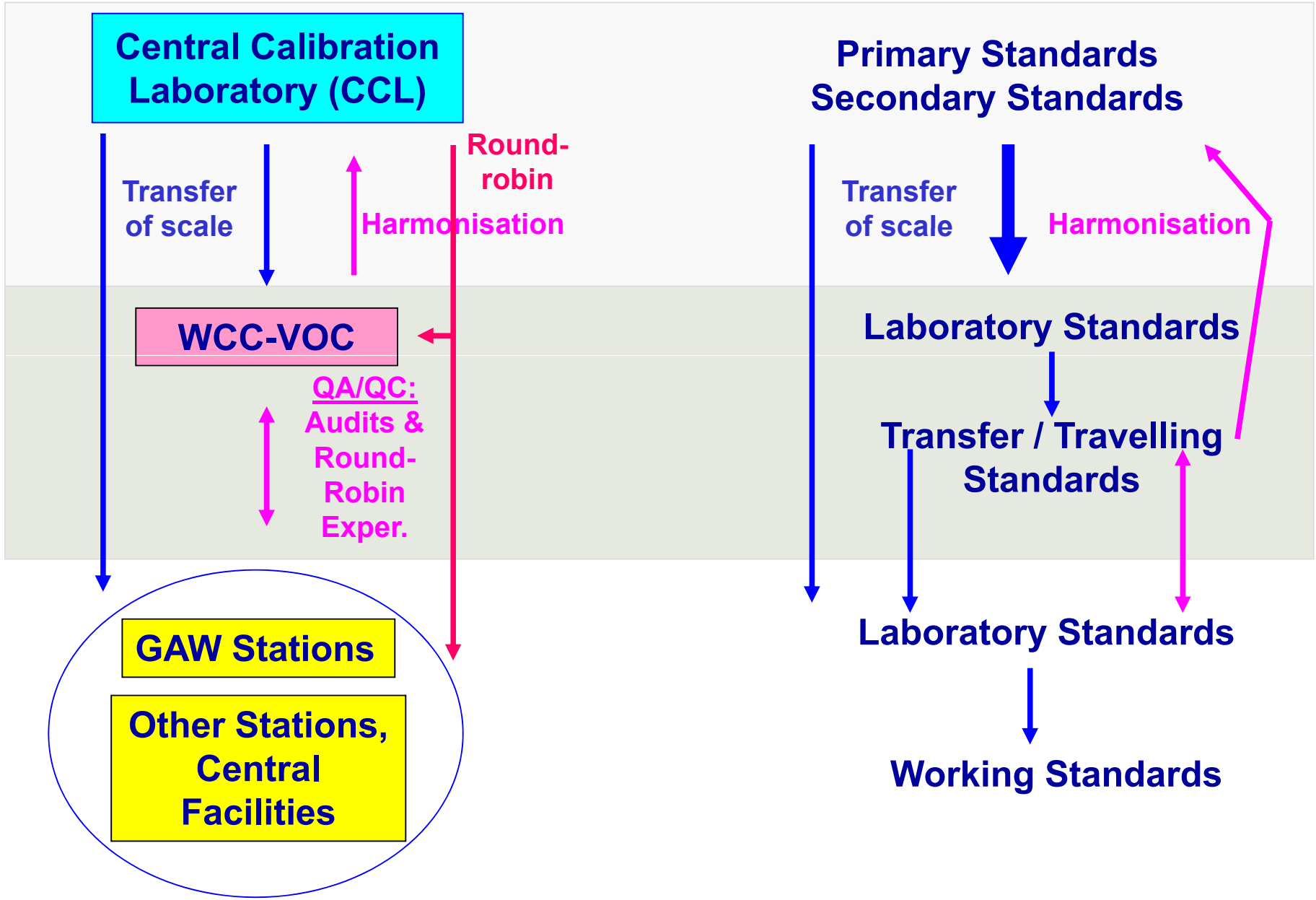
(Helmig et al., 2009)

WCC-VOC



GAW Network for VOC

Traceability of Calibrations and Audits



The GAW-VOC QA/QC: Control of Success

Round Robin Exercises

- Evaluate Results on the basis of data quality objectives
- Report findings to the participants
- Enquire reasons for deviations in bilateral meetings
- Suggest joint measures to improve quality
- Check progress by repeating QA/QC experiments

Audits

- Report discovered discrepancies to station staff
- Take possibilities to solve detected problems on-site
- Define an action list in the final audit meeting with station staff to timely solve encountered problems.
- Check progress by repeating audit

GAW-VOC Targets

Ethane	Acetone
Propane	DMS
Acetylene	Benzene
Isoprene	Toluene
Formaldehyde	Iso-Butane
Monoterpenes	n-Butane
Acetonitrile	Iso-Pentane
Methanol	n-Pentane
Ethanol	

a large number of individual species should be measured:

- **nonmethane hydrocarbons (NMHC),**
- **monoterpenes (MTs) e.g. α-pinene, limonene**
- **oxyVOCs**
- **dimethylsulfid (DMS)**
- **acetonitril (ACT)**

GAW-Scale of standards

WMO Report 171; 2007

GAW-VOC Targets and CCL

Task

Establishment of a Central Calibration Laboratory (CCL) for VOCs for the WMO Global Atmosphere Watch (GAW) network.

Problem

Due to the large number of compounds involved, the task exceeds the capacities of a single laboratory (institution).

Solution

The responsibilities for the individual compound are shared among several laboratories (institutions) and four National Metrology Institutes (NMIs) are working together to form the CCL.

In cooperation with BIPM and the CCQM Gas Analysis Working Group (GAWG) a concept for the future CCL for VOCs has been set up and is being implemented.

VOC Central Calibration Laboratory (CCL)

Ethane	Acetone
Propane	DMS
Acetylene	Benzene
Isoprene	Toluene
Formaldehyde	Iso-Butane
Monoterpenes	n-Butane
Acetonitrile	Iso-Pentane
Methanol	n-Pentane
Ethanol	

Responsibilities (Status 2010)

NMHC

NPL (National Physical Laboratory, GB)

MTs

NIST (National Institute of Standard and Technology, USA)

DMS, ACT

KRISS (Korea Research Institute of Standards and Science, South Korea)

oxyVOC

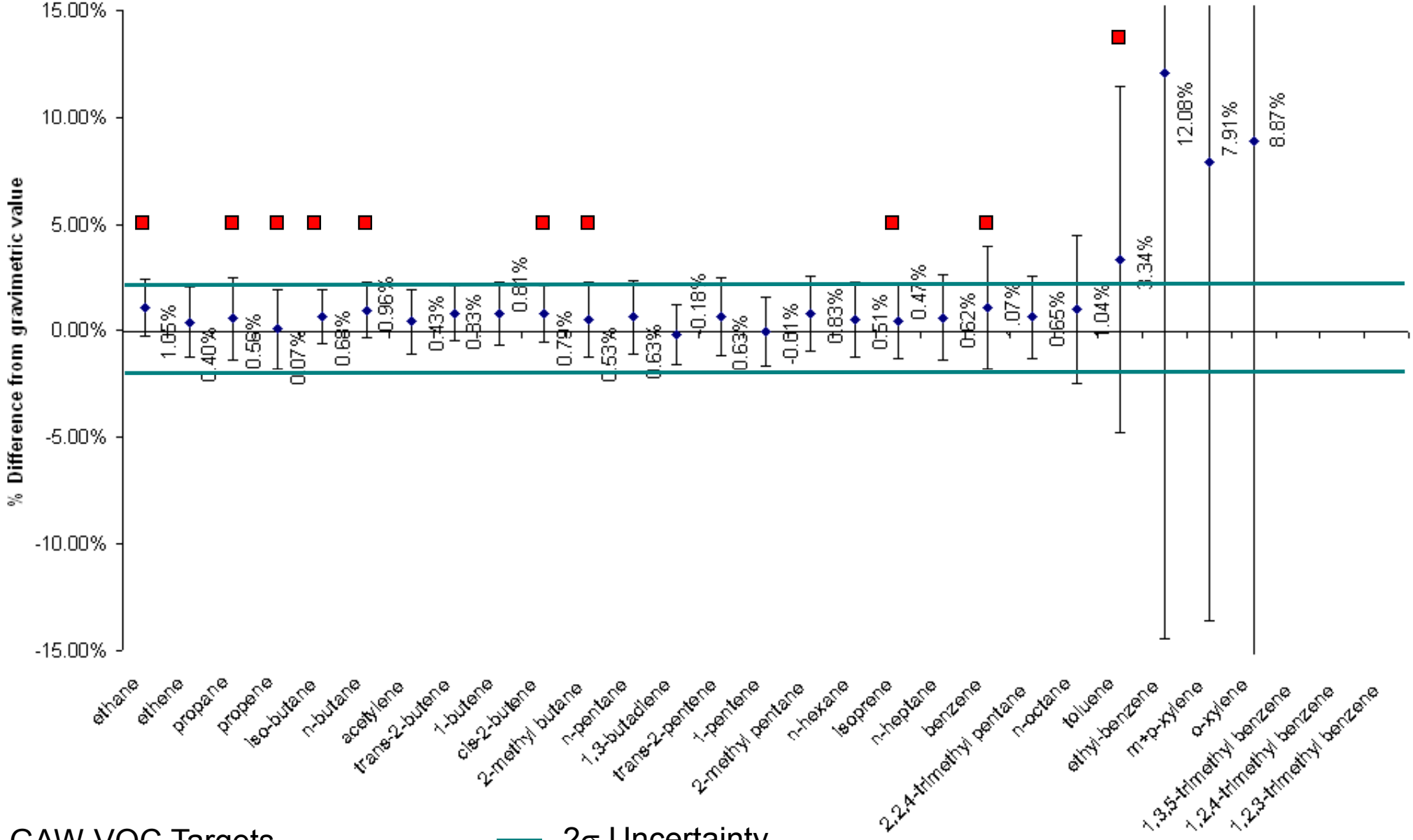
VSL (Dutch Metrological Institute, NL)

Tasks of the WCC-VOC

- Develop quality control procedures.
- Ensure traceability of standards used in the WCC-VOC.
- Conduct performance and system audits at stations.
- Perform round-robin experiments (inter-comparisons).
- Support a network-wide quality review.
- Provide training and long-term technical consulting to station scientists and technicians (e.g. through the GAW Training and Education Centre GAWTEC).

Tracability of the WCC-VOC

Participating in EUROMET-886 VOC inter-comparison of the CIPM-CCQM Gas Analysis Working Group



NMHC Standards in WCC QA/QC Measures

WCC-NMHC Secondary and Laboratory/Working/Travelling Standards (Status 2010)

Compound	GAW/ppb	uncertainty 2σ/ppb	Apel/Riemer /ppb	uncertainty 2σ/ppb	Ambient air/ppb	uncertainty 2σ/ppb
Ethane	2.7	0.05	13.51	0.58	1.25	0.05
Ethine	2.66	0.05	7.55	0.33	1.02	0.05
Propane	2.67	0.05	12.13	0.53	0.53	0.04
i-Butane	2.68	0.05	5.97	0.47	0.49	0.09
n-Butane	2.6	0.05	11.11	0.98	1.17	0.12
i-Pentane	2.59	0.05	7.79	0.32	1.72	0.08
n-Pentane	2.63	0.05	9.35	0.39	0.47	0.05
Isoprene	2.6	0.05	5.34	0.23	n.r.	n.r.
Benzene	2.62	0.05	2.26	0.16	0.36	0.03
Toluene	2.59	0.05	3.52	0.41	0.74	0.08

Round-Robin Exercises and Audits

GAW Stations and VOC Central Facilities (Status 2003)

- Representing GAW, EMEP, CAPMoN and LBA environment monitoring programs
- 7 countries (Brazil, Canada (2 labs), Czech Republic, Finland, Germany (2 labs; 3 instruments), Ireland, and Slovakia)
- 9 different stations/laboratories
- 10 different instruments (off-line and on-line)

Round-Robin Exercises and Audits

Results (Status 2003)

green: NIST-traceable VOC

VOC	Participants									
	A	B	C	D	E	F	G	H	I	J
ethane	3.8	-64.2	-3.4	-1.2			-2.1	-4.4	-1.1	
ethylene	5.2	-73.5	5.2	7.3			-16.5	-7.5	-2.3	
acetylene	-13.8	-54.7		4.0				-22.4	-25.1	
propane	9.6	1.0	-0.1	2.1	-27.6	-3.0	-2.7	-9.1	-1.0	
propylene	8.0	-1.9	5.4	11.5	-66.0	2.3	-15.7	-2.3	1.1	
i-butane	9.4	81.5	8.4	11.0	-33.7	-10.1	1.8	-4.3	2.5	8.1
n-butane	6.7	78.8	-0.2	5.7	-30.6	-9.0	-2.6	-3.5	-0.7	
1-butene	4.2	137.3	6.4	11.2					3.2	
t-2-butene	3.4	47.0	7.5	9.2		-18.1			-2.8	12.7
i-butene	6.9		2.7	10.3				2.3	-3.8	
c-2-butene	-2.4		1.8	4.3		-7.6		-12.7	-7.4	3.2
i-pentane	-14.3		-2.3	5.2	-42.9		-5.8	-12.1		-2.5
n-pentane	-26.3		-1.5	3.7		-0.2	-0.6			
isoprene	5.5	-98.0	-6.2	-17.0	-78.8	-16.7	-2.5	5.2	1.4	-1.2
t-2-pentene	-52.2	-22.9	92.3	6.6		-6.8	-4.0	-29.3	-11.6	23.8
c-2-pentene	-20.8	19.8	3.6	-0.6		-6.4	-1.7	-12.2	-5.4	1.0
2-me pentane			5.9			-17.2	1.2			
3-me-pentane			0.7	13.3		-7.9	-4.6			2.3
n-hexane	-27.3	236.6	-3.0	4.3	-40.8	-11.5	0.2	-30.7	-12.8	-0.6
benzene	6.3	208.2	-5.5	2.9		0.5	-0.4	-14.7	-5.2	
cyclohexane	51.4					-22.7				
n-heptane	5.1		-6.5	4.3	-45.0	6.7	3.5		-1.4	-0.5
toluene	27.2	-79.8	-5.1	10.1	-22.2	16.6		-6.5		10.1
et-benzene			1.1	-3.0	75.5	1.1		-21.1	3.0	5.3
m,p-xylene			4.1	-2.4	34.0	-14.3		-16.3	7.4	0.4
o-xylene		1529.6	5.1		228.2	-22.9		-28.5		
1,3,5 trime-benzene			-29.0			-90.8				-16.6
1,2,4 trime-benzene			30.0			-82.4				0.8

- **Approx. only 50% of the labs perform reasonably well.**

Deviation in % from the WCC-VOC reference values (Standard CC154935)

Results that did not meet the DQOs are shown in red

Rappengluck B., Apel E., Bauerfeind M, Bottenheim J., Brickell P., Cavolka P., CechJ., Gatti L., Hakola H., Honzak J., Junek R., Martin D., Noone C., Plass-Dulmer Ch., Travers D., Wang D. (2006): The first VOC intercomparison exercise within the Global Atmosphere Watch (GAW), Atmospheric Environment, 40, 7508-7527,

Round-Robin Exercises and Audits

Results (Status 2003)

Sometimes large differences (up to a factor of two) from the target mole fractions became obvious.

Strong efforts are needed to harmonise VOC measurements in environmental monitoring networks.

Key topic identified:

Harmonise the calibration standards.

Round-Robin Exercises and Audits

GAW Stations and VOC Central Facilities: (Status 2010)

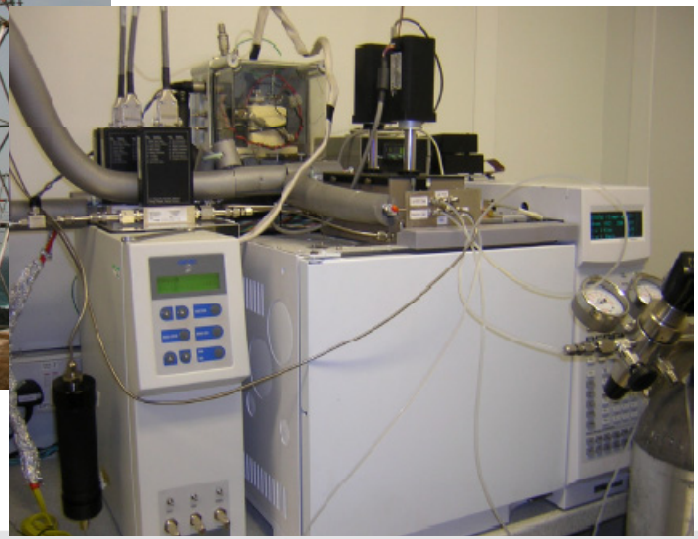
- Global (*in situ*): Jungfraujoch, Hohenpeißenberg, Cap Verde
- Regional: (*in situ*): Rigi, Egbert
- Central Facilities (flasks): Analysis, sampling and transport/storage of air samples
  - Institute of Alpine and Arctic Research (INSTAAR) (Global Monitoring Division (GMD) network, National Oceanic and Atmospheric Administration (NOAA), Boulder CO, USA)
  - Environmental Science and Technology Centre, Environment Canada, Ottawa, Canada (global station Alert)
  - Max Plank Institute for Chemistry, Mainz, (CARIBIC Aircraft Atmospheric Monitoring Program)
  - University of York, Department of Chemistry, (FAAM Research Aircraft BAe146)

Round-Robin Exercises and Audits

Results (selected examples):

- GAW Global Station (*in situ*): Cape Verde

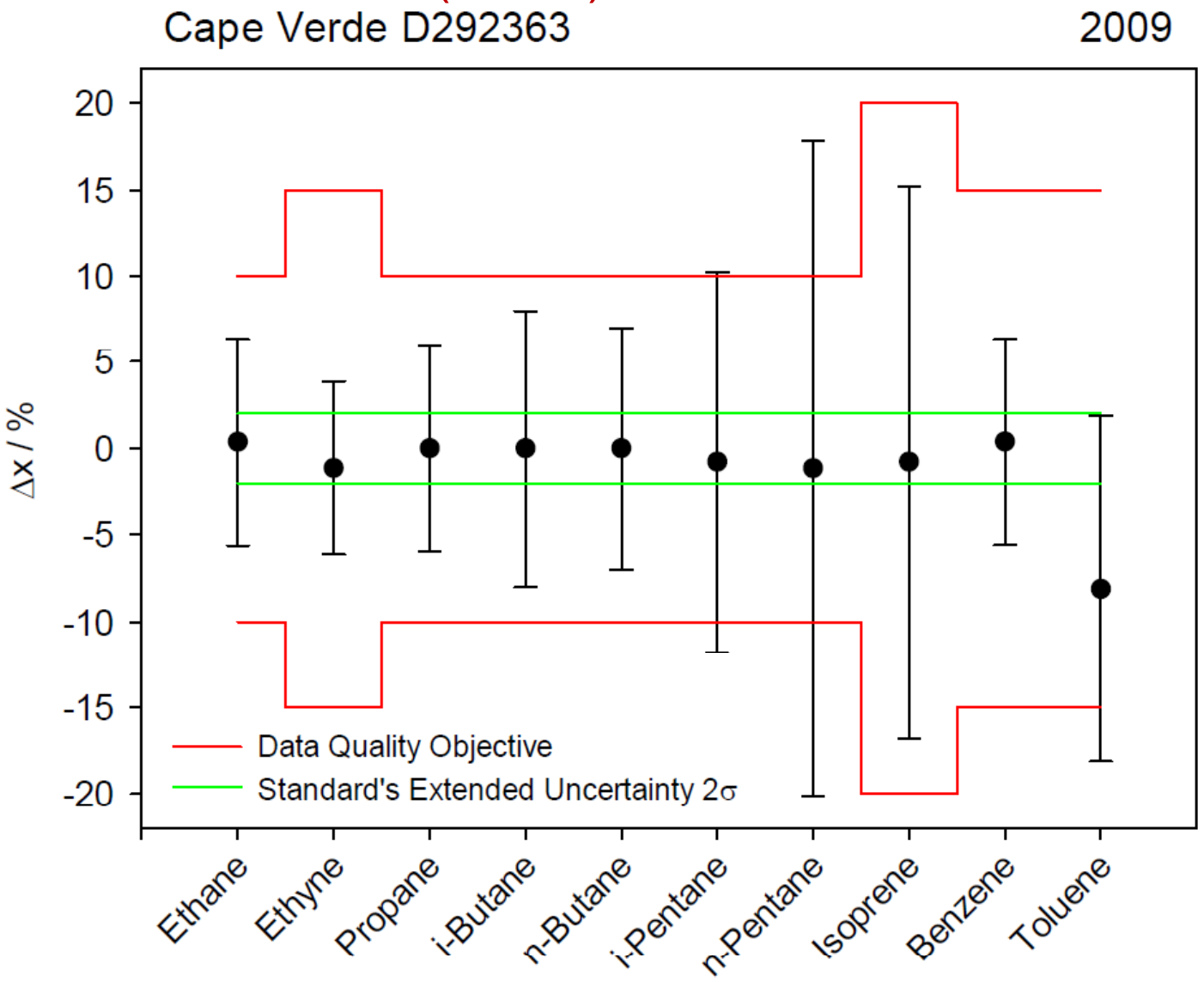
Position: 16.848° N; 4.871° W;
Altitude : 10 m a.s.l.



Round-Robin Exercises and Audits

Results (selected examples):

- GAW Global Station (*in situ*)



Round-Robin Exercises and Audits

Results (selected examples):

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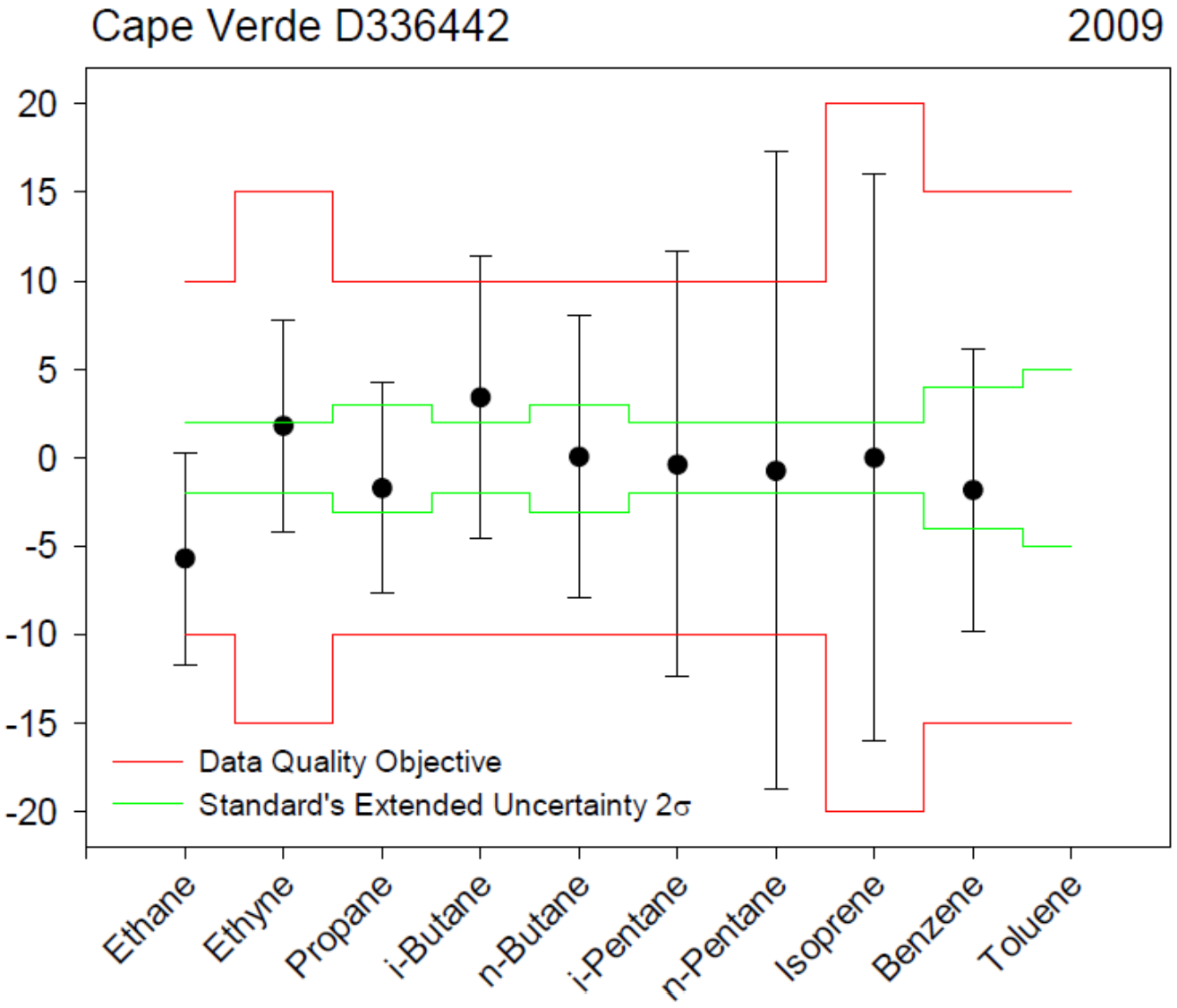

Round-Robin Exercises and Audits

Results (selected examples):

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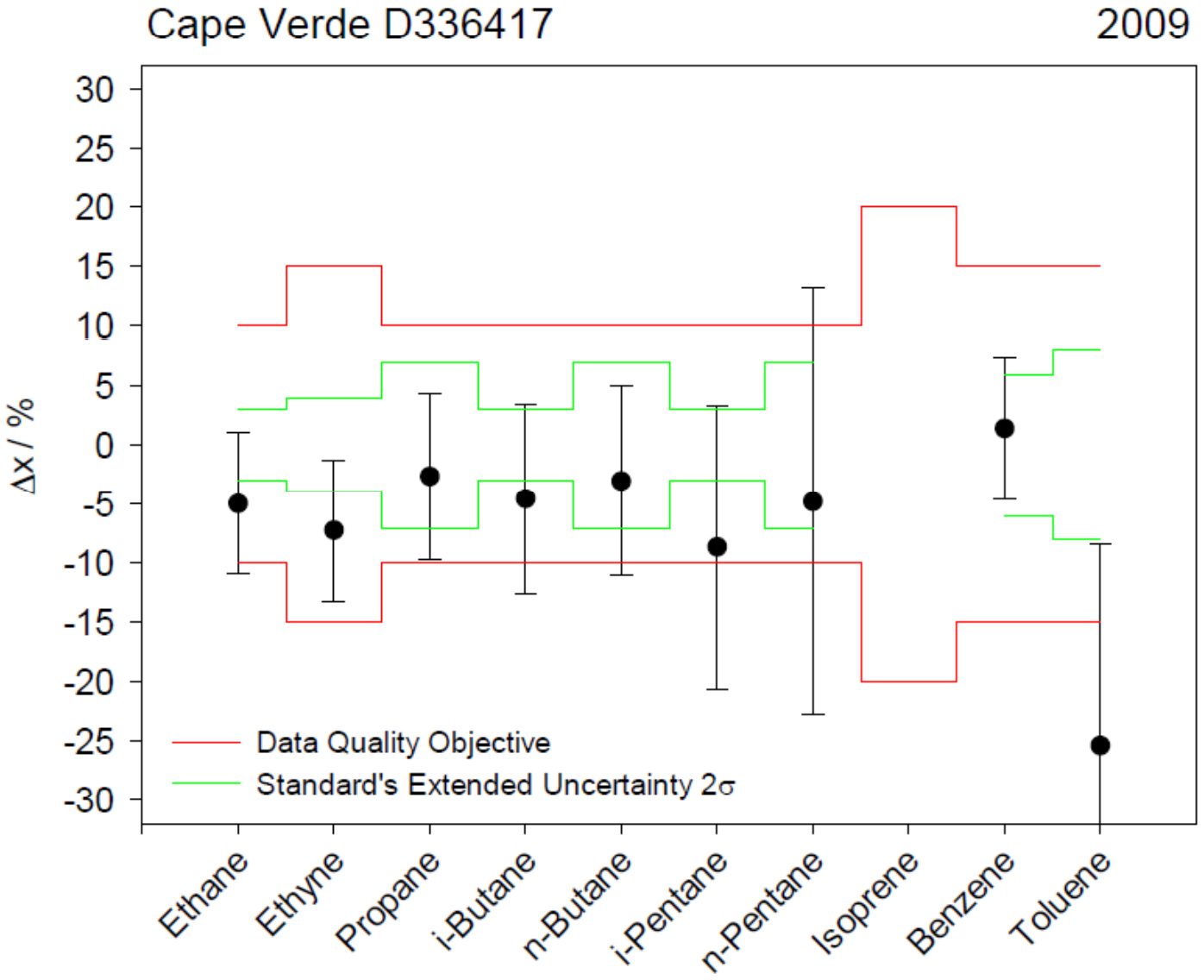
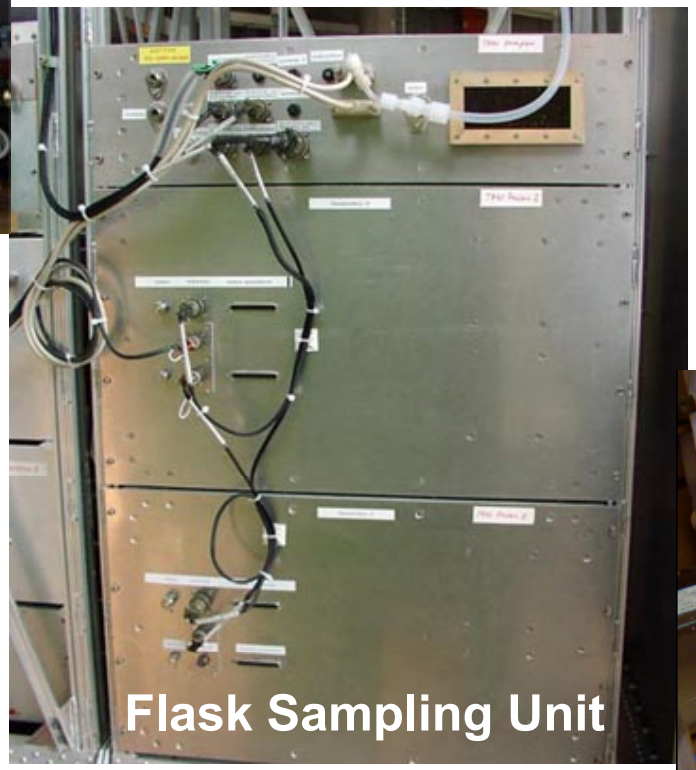
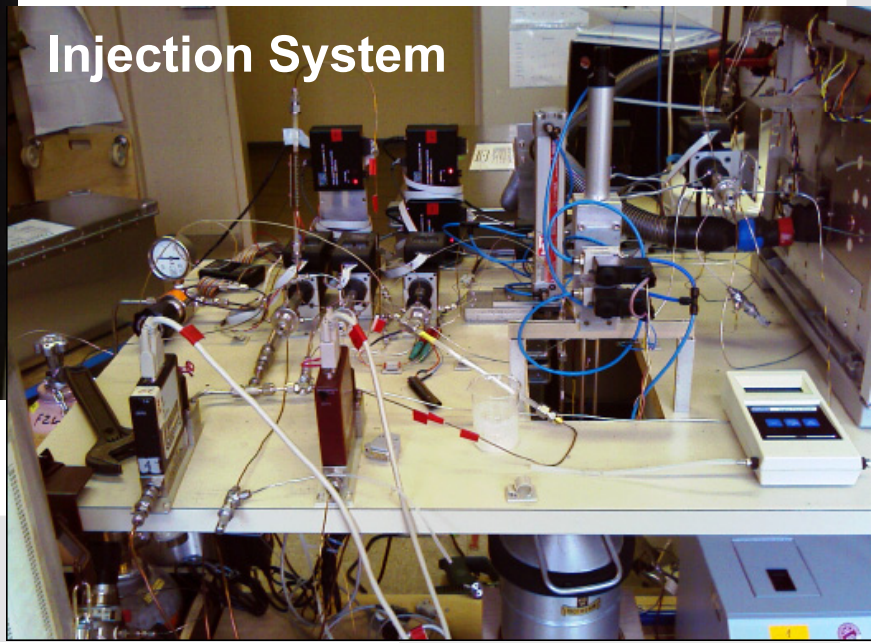


Round-Robin Exercises and Audits

Results (selected examples):

- Central Laboratory CARIBIC (flask)





Round-Robin Exercises and Audits

Results (selected examples):

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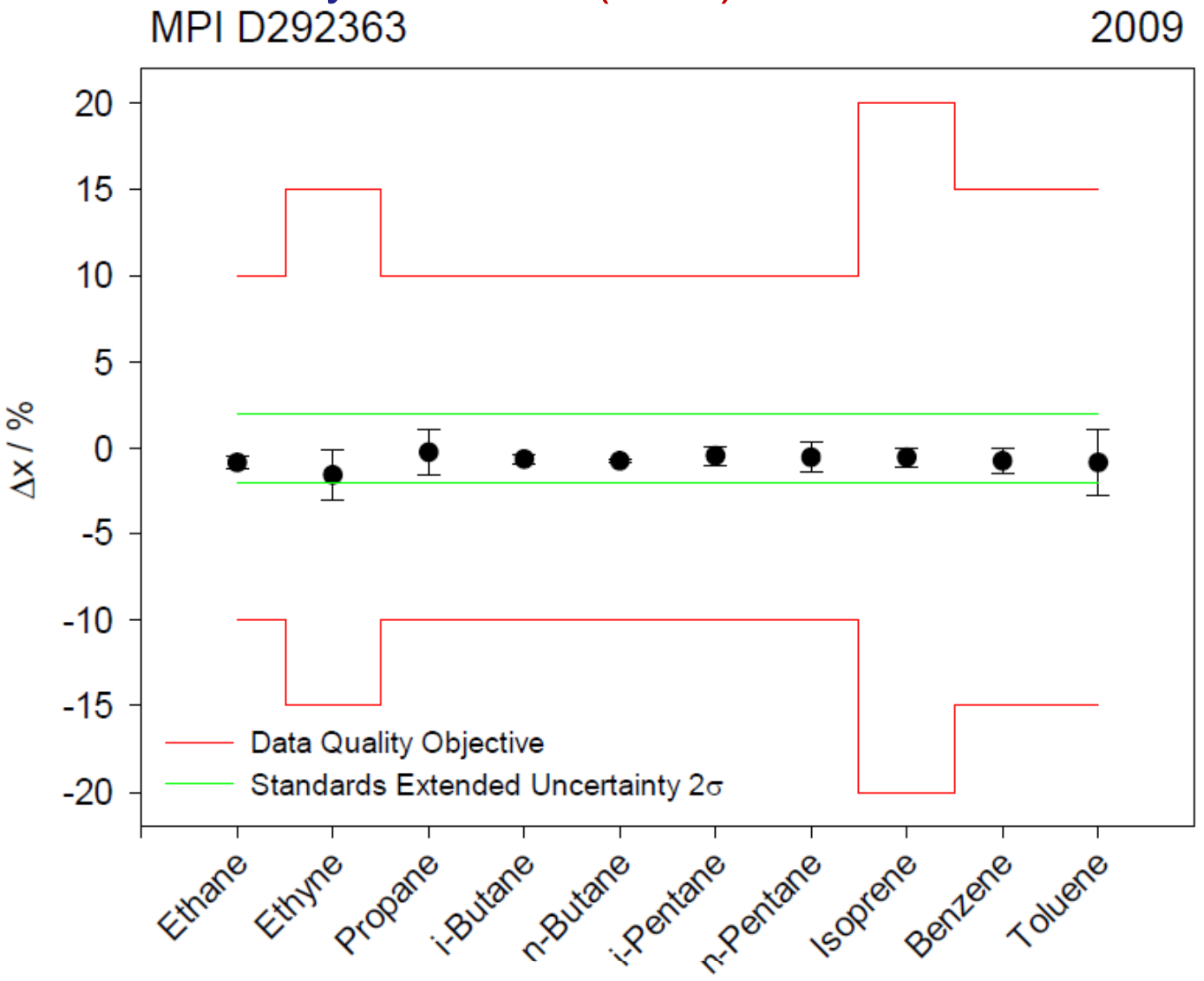

Round-Robin Exercises and Audits

Results (selected examples):

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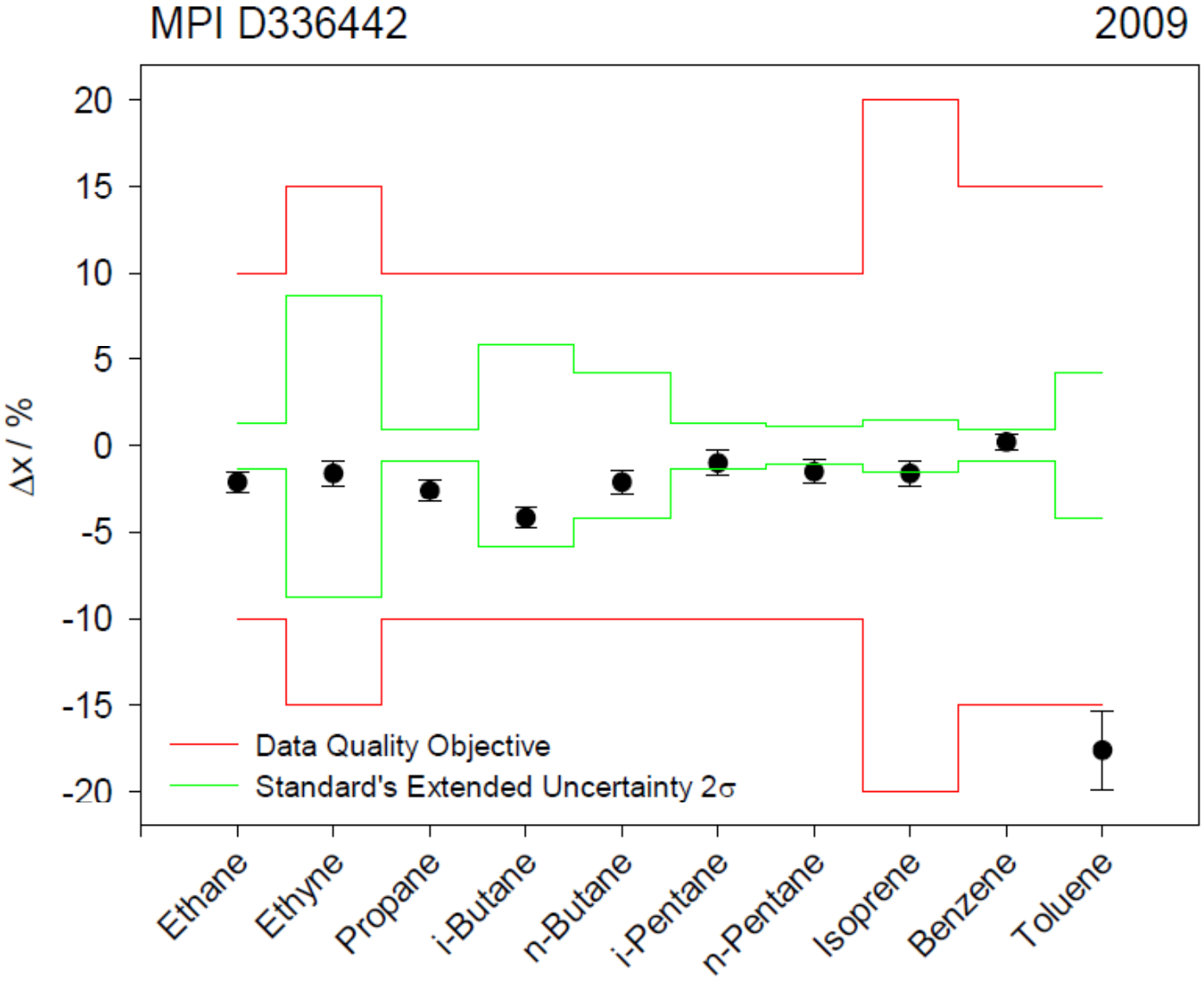
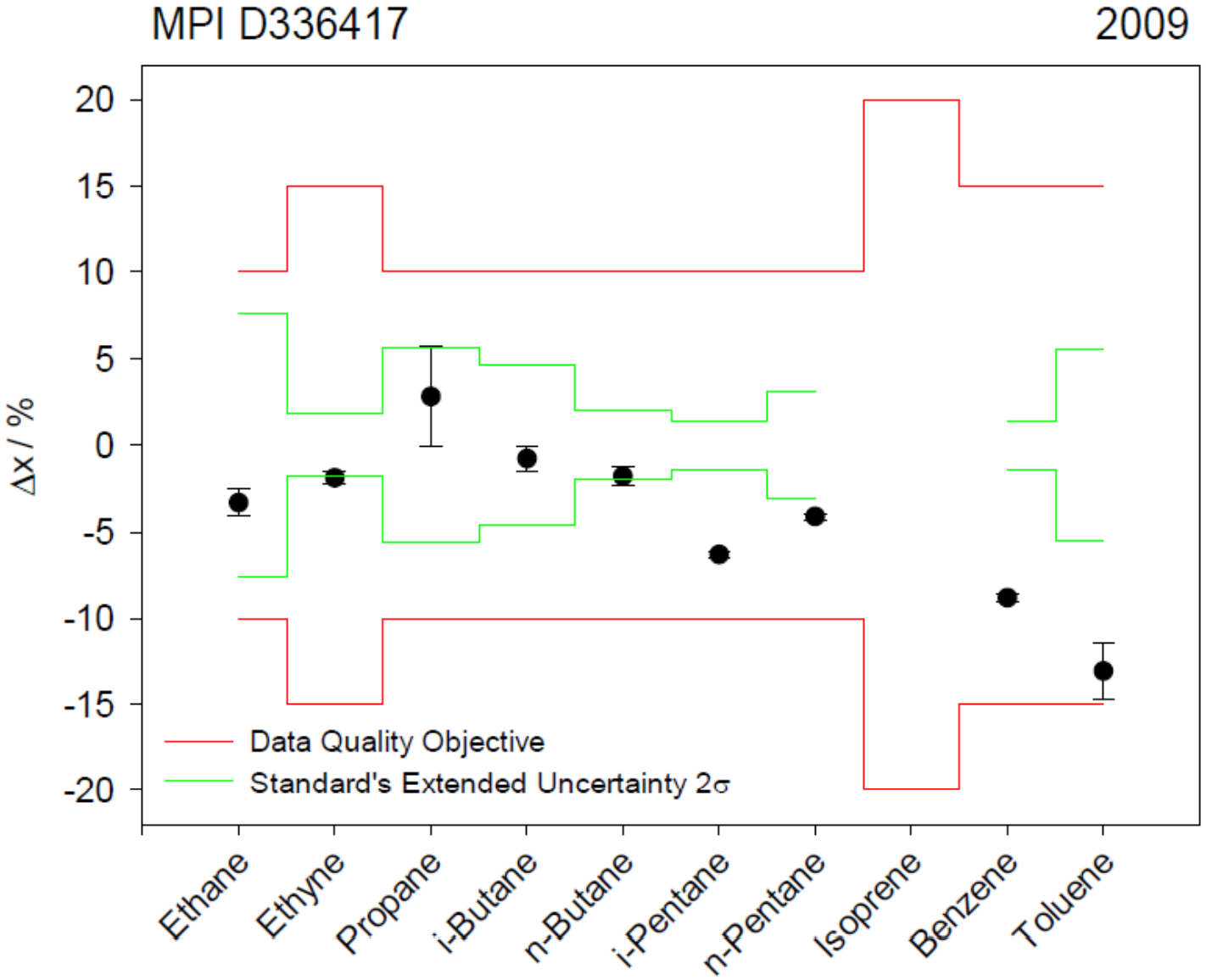


Round-Robin Exercises and Audits

Results (selected examples):

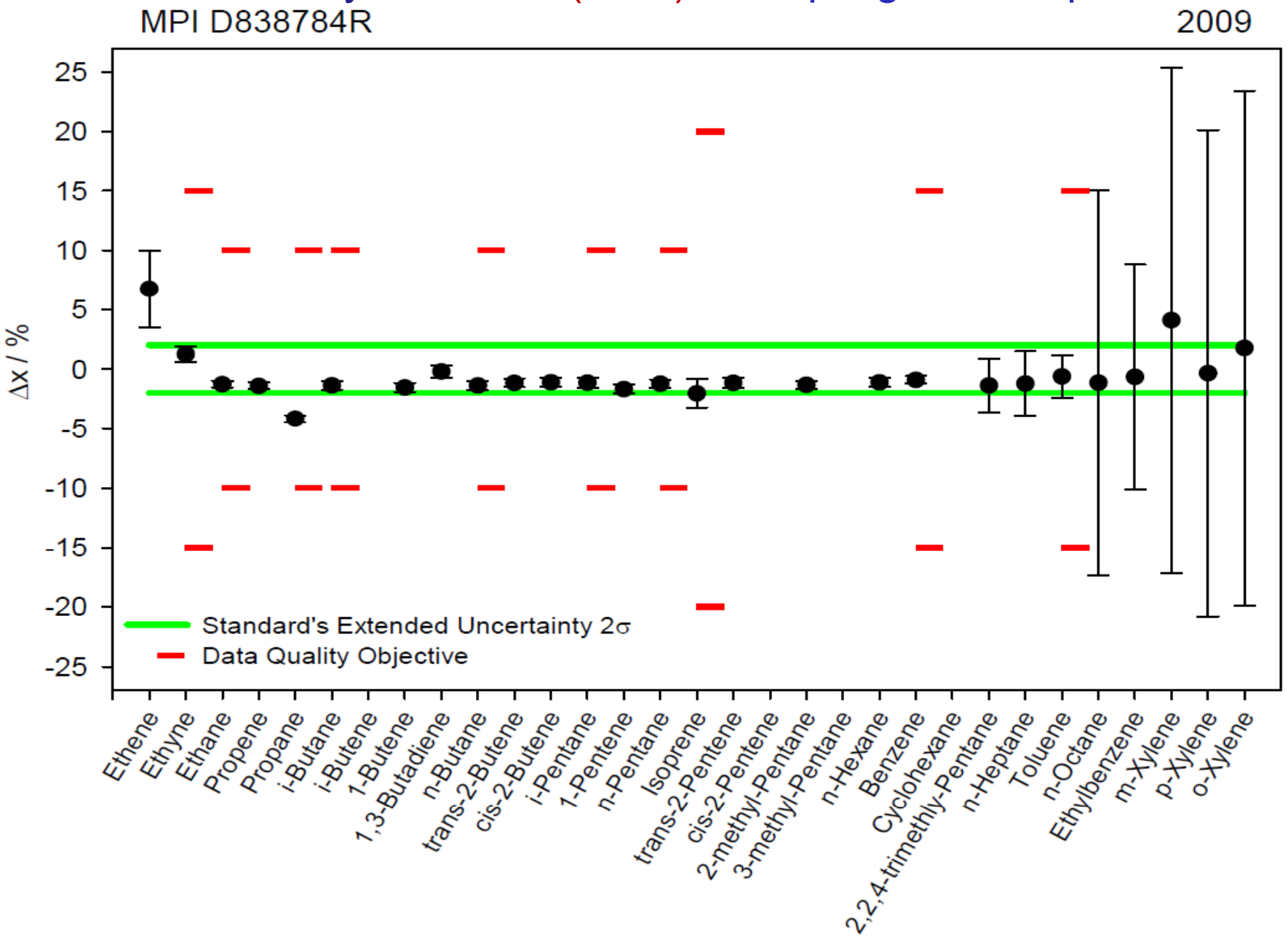
- Central Laboratory CARIBIC (flask)



Round-Robin Exercises and Audits

Results (selected examples):

- Central Laboratory CARIBIC (flask): sampling → transport → analysis



echnologie
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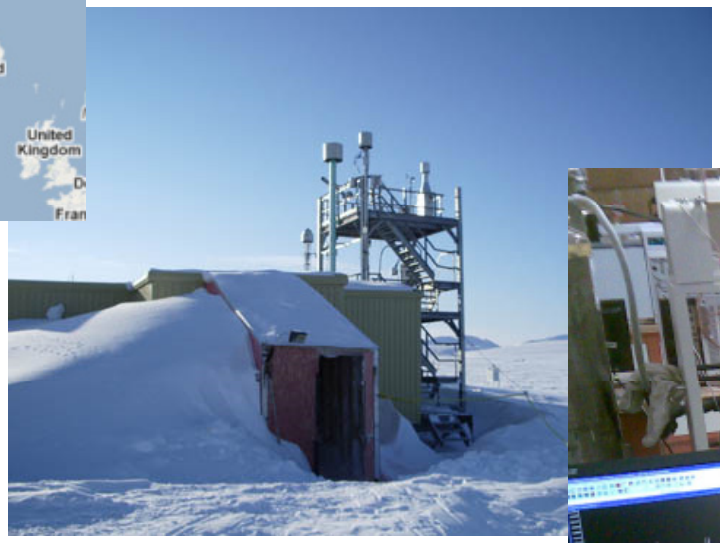
Round-Robin Exercises and Audits

Results (selected examples):

- GAW Global Station (flask): Alert

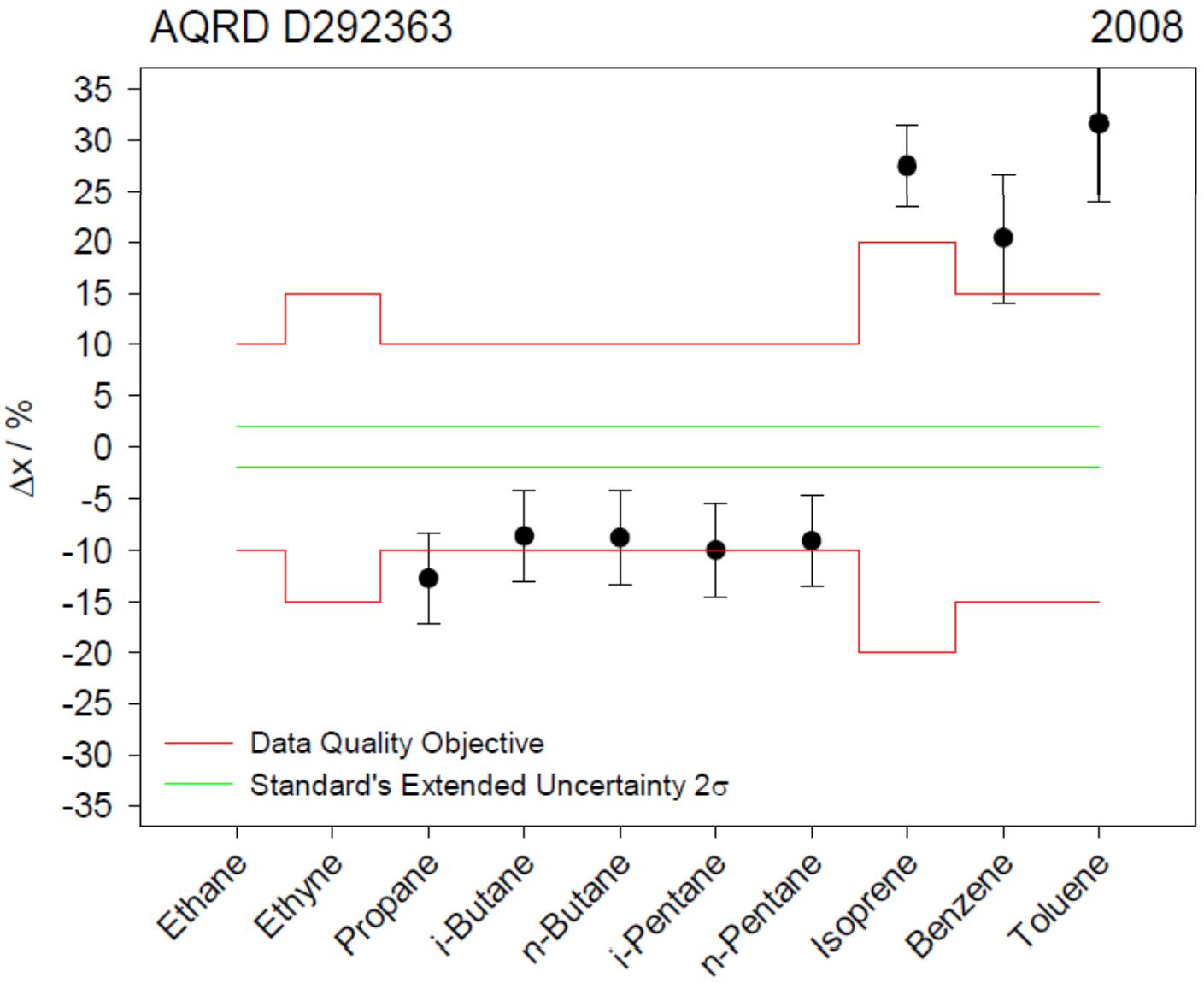
Position: 82.45000° N; 62.51667° W;
Altitude : 210 m a.s.l.



Round-Robin Exercises and Audits

Results (selected examples):

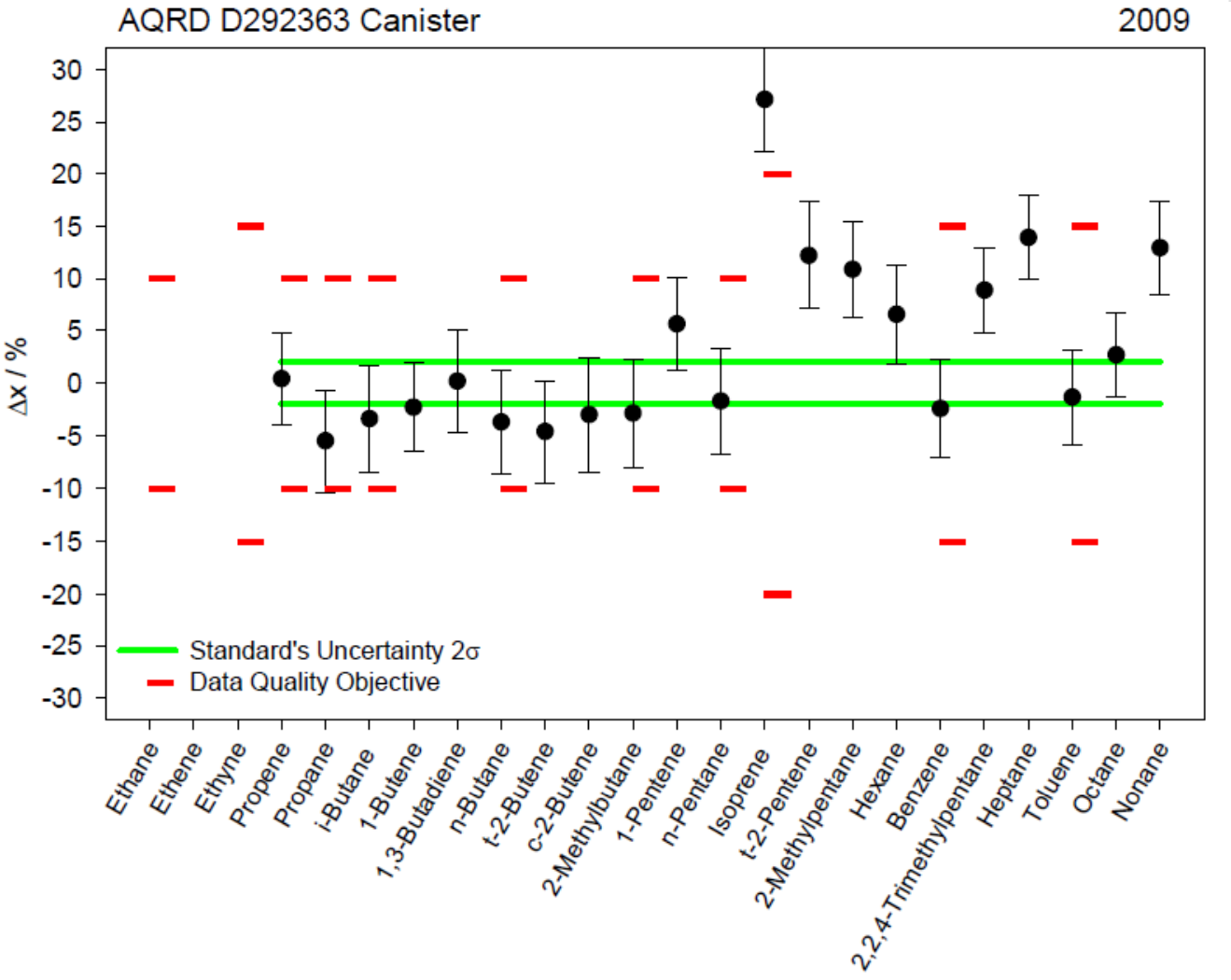
- GAW Global Station (flask): Alert



Round-Robin Exercises and Audits

Results (selected examples):

- GAW Global Station Alert (flask): sampling → storage → analysis



Round-Robin Exercises and Audits

Summary Results (Status 2010)

Compound	A	B	B*	C	C*	D	E	E*	F	G	H	I
Ethane	0.37	-0.78	1.25	-	-	-2.21	0.37	-1.2	-1.36	-	6.57	0.10
Ethine	-1.13	-1.47	1.27	-	-	-14.98	-	-	-	-	6.07	-0.63
Propane	0.00	-0.20	-4.17	-12.72	-5-50	-7.38	-0.37	-1.5	-0.48	-	5.71	-0.45
i-Butane	0.00	-0.61	-1.36	-8.61	-3,39	-2.32	0.00	-1.6	-0.86	-12.65	5.64	-0.47
n-Butane	0.00	-0.68	-1.38	-8.77	-3.70	-4.28	3.47	1.1	-	-6.81	5.37	-2.50
i-Pentane	-0.77	-0.38	-1.15	-9.98	-2.86	-11.62	3.09	1.0	-0.54	-3.44	4.58	-0.42
n-Pentane	-1.14	-0.54	-1.23	-9.08	-1,71	-2.70	0.57	-1.9	-0.64	-11.56	4.52	-0.30
Isoprene	-0.77	-0.51	-2.03	27.45	27,15	-3.29	-6.73	-1.5	0.10	-	-1.93	-0.67
Benzene	0.38	-0.72	-0.91	20.38	-2,42	-0.85	-0.94	-3.9	0.32	-8.97	1.67	-1.71
Toluene	-8.11	-0.81	-0.62	31.61	-1,33	-2.84	-1.74	1.6	-1.28	-3.59	-0.32	-4.43

- Not reported

Within Data Quality Objective

Outside Data Quality Objective

near Data Quality Objective

***Deviation in % from the WCC-VOC reference values (Standard* D296263)**

Coming in 2010

- Finalise the setup of the CCL for VOC.
- Organise and conduct QA/QC missions to the GAW global stations Pallas Finland (PAL) and Cape Grim, Australia (CGO).
- Intra-laboratory QA/QC procedures for NMHC and monoterpene analysis of the WCC-VOC.
- Setup and test of an analysis system for oxyVOC.
- Proceed to phase two of QA/QC measures within GAW-VOC (monoterpenes).

Summary

- **Recent inter-comparisons and audits in the GAW-VOC network on NMHC show good results but there is space for improvements.**
- **Establishing of the CCL for VOC in co-operation with international NMIs, BIPM and GAW-VOC is on an excellent way and will further be promoted.**
- **Further information about WCC-VOC activities are available on the web.**
- **The next step of QA/QC measures in the GAW-VOC network is in focus (other VOC).**

Thank you for your attention and the

Umwelt Bundes Amt
Für Mensch und Umwelt

for funding and

BIPM

thanks to all GAW stations people
for their excellent co-operation