Atmospheric Measurements of VOCs at Monitoring Stations: Network data compatibility is essential

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Atmospheric Measurements of VOCs at Monitoring Stations: History in WMO-GAW

- **History**
- Problem
- Solution
- Lessons Learned

World Metreological Organisation Global Atmosphere Watch Program (**WMO-GAW**) initiative in the 90th of the last century with **VOC as a target component**

Atmospheric Measurements of VOCs at Monitoring Stations: History

Karlsruhe Institute of Technology

- **History**
- **Problem**
- **Solution**
- **Lessons Learned**

Key objective: high quality data with known uncertainty

First assessment of VOC data quality in the GAW-VOC network published in 2006

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The first VOC intercomparison exercise within the Global Atmosphere Watch (GAW)

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First assessment of VOC data quality in the GAW-VOC network published in 2006

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

Results that did not meet the DQOs are shown in red

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

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

Atmospheric Measurements of VOCs at Monitoring Stations: History

First assessment of VOC data quality in the GAW-VOC network published in 2006 by Rappenglück et al.

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

Achieving high quality VOC data with known uncertainty requires:

- an efficient quality assurance and quality control framework with
- calibrations traceable back to a reference amount fraction

WCC-VOC and traceability

Traceability in the GAW-Volatile Organic Compounds (VOC) network

Currently, focus on 21 VOC target compounds

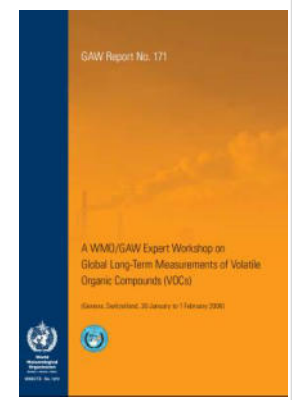
(see GAW-Report 171, 2006)

Central Calibration Laboratories (CCL)

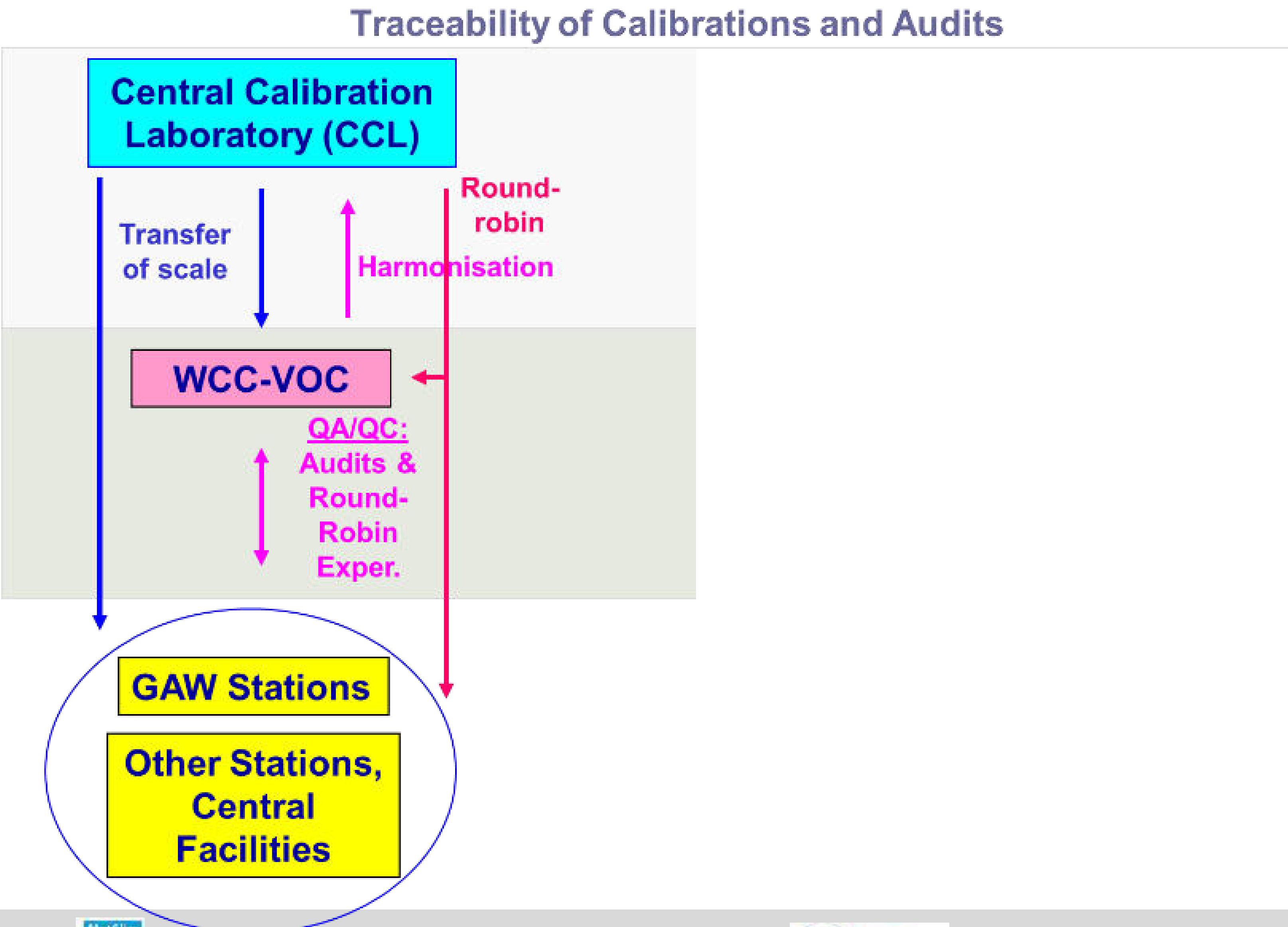
- nonmethane hydrocarbons (NMHC),	National Physical Laboratory (NPL, UK)
- monoterpenes (MTs) e.g. a-pinene, limonene	National Institute of Standards (NIST, USA)
- dimethylsulfid (DMS)	Korea Research Institute of Standards and Science (KRISS, South Korea)

In preparation:

- oxyVOCs	Van Swinden Laboratory (VSL, The Netherlands)
- acetonitril (ACT)	KRISS



WCC-VOC and traceability



VOC Network audits and intercomparisons with a set of traceable VOC mixtures in nitrogen and whole air standards

(single compound amount fraction range: (0.1 to 100 nmol/mol)

- History
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Shipping

Guidance

VOC Network audits and intercomparisons

Example: GAW Global Station Cape Verde

- History
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VOC Network audits and intercomparisons

GAW Global Station Cape Verde: Air sampling and VOC analysis

- History
- Problem
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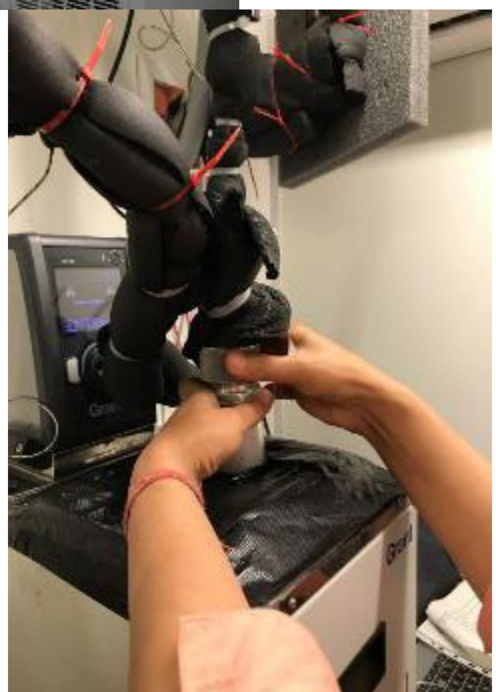
VOC Network audits and intercomparisons

GAW-VOC analysis: Water removal

Two stage
water removal
with cold traps
(-30 °C; -40°C)



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VOC Network audits and intercomparisons

GAW-VOC analysis: Calibration with gas standards

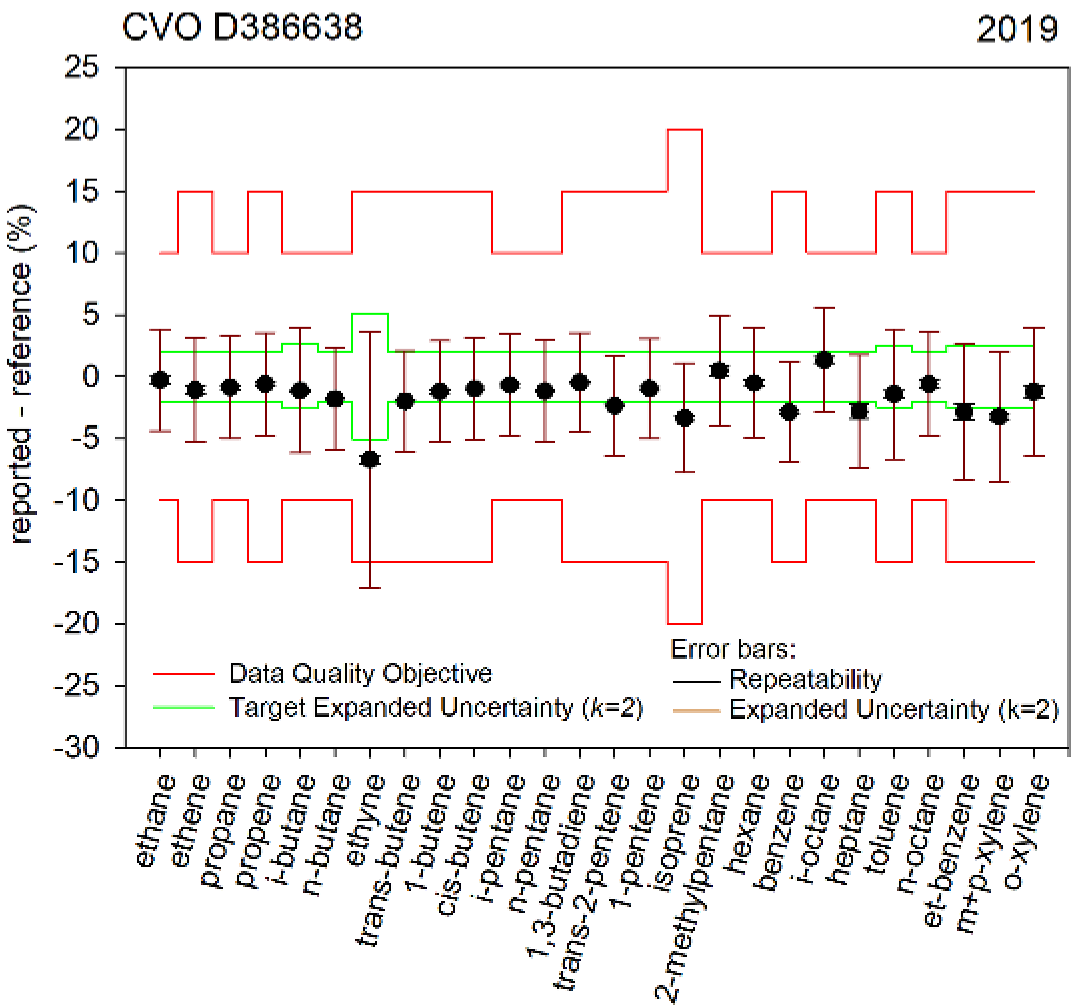
- History
- Problem
- Solution
- Lessons Learned

Pressurised traceable NMHCs gas mixtures

Permeation system for oxy-VOC mixture

VOC Network audits and intercomparisons

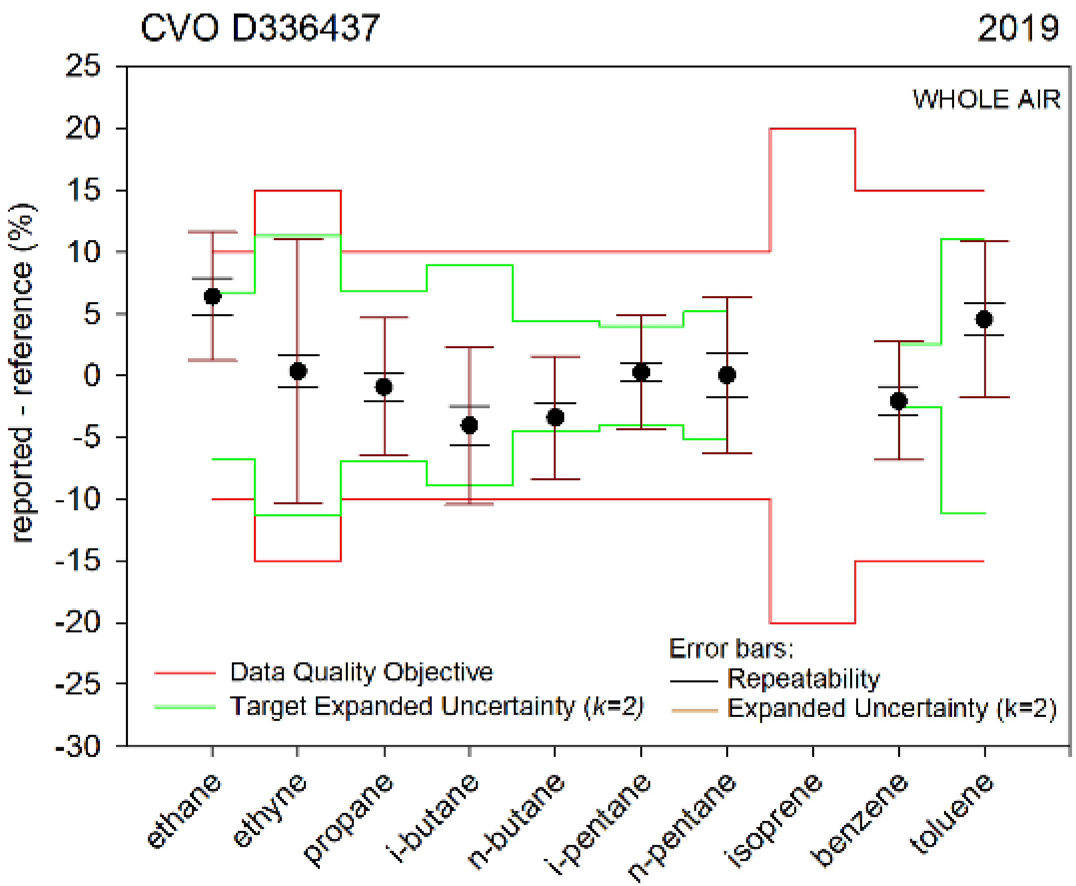
Results: GAW Global Station Cape Verde (NMHCs in nitrogen)



The system is excellently suitable for NMNHCs measurements and reported amount fractions are traceable with no bias to the GAW-VOC scale

VOC Network audits and intercomparisons

Results: GAW Global Station Cape Verde (Whole Air)



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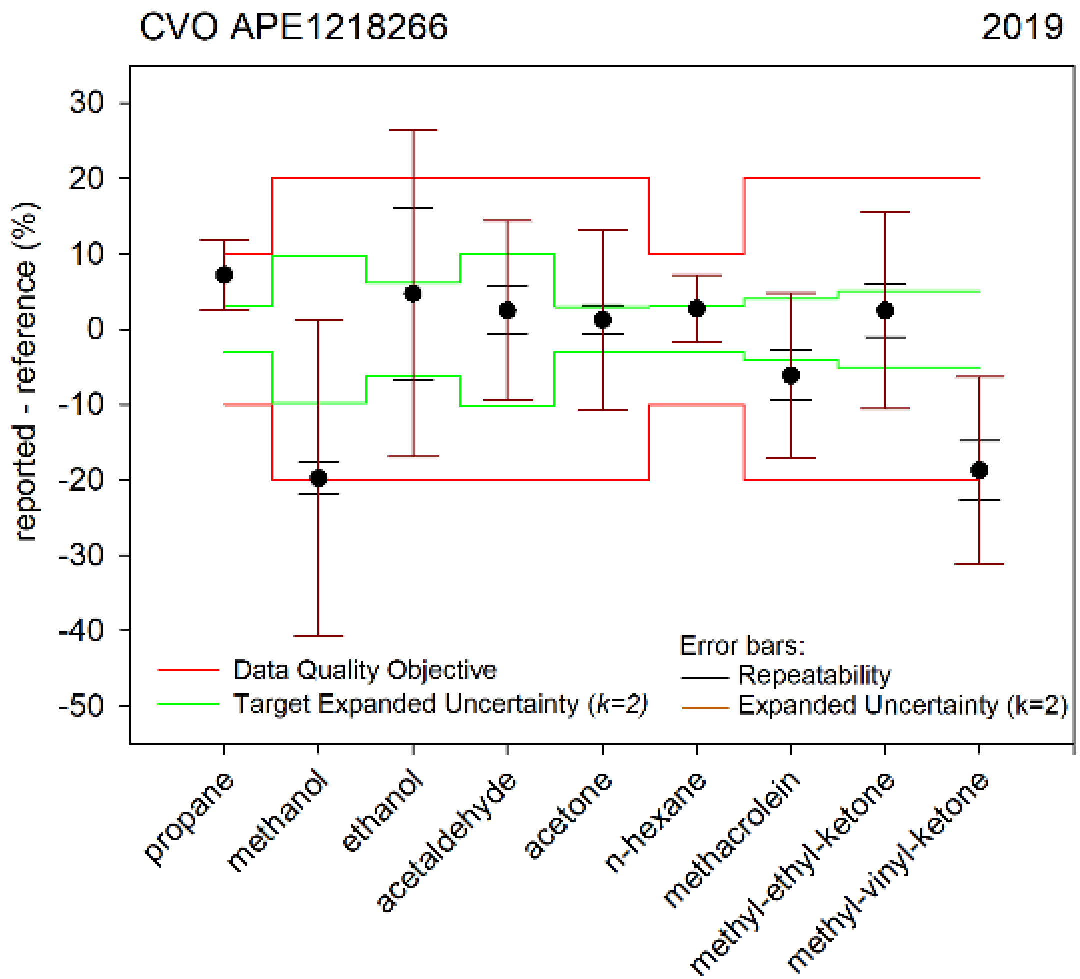
Reported values for the whole air standard are also well within the DQOs demonstrating that GAW-VOC targets in whole air samples are also analysed with excellent quality

VOC Network audits and intercomparisons

Results: GAW Global Station Cape Verde (oxy-VOC)



Determined amount fractions for oxy-VOC meet the DQOs with methanol and methyl-vinyl ketone at the edge of the limit.

VOC Network audits and intercomparisons

Audit summary: GAW Global Station Cape Verde (oxy-VOC)

Audit Aspect	Adequacy (0 = inadequate (□□□□□□) through 5 = adequate (■■■■■■))	Recommendations
Access	■■■■■■	Keep high standard
Facilities	■■■■■■	Keep high standard
Laboratory and office space	■■■■■■	Keep high standard
Air conditioning	■■■■■■	Keep high standard
Power supply	■■■■■■	Keep high standard
General management and operation	■■■■■■	Keep high standard
Organisation	■■■■■■	Keep high standard
Competence staff	■■■■■	GAWTEC training encouraged
Air inlet system	■■■■■■	Keep high standard
Instrumentation	■■■■■	Same tubing/connector material after the manifold; encouraged OH/NO3 reactivity and formaldehyde measurements
Trace gases	■■■■■■	Keep high standard
Instrumental performance VOC	■■■■■■	Keep high standard
Standards	■■■■■■	Keep high standard
Data management	■■■■■■	Keep high standard
Data acquisition	■■■■■■	Keep high standard
Data processing	■■■■■■	Keep high standard
Data submission	■■■■■	oxyVOCs, DMS encouraged
Documentation	■■■■■■	Keep high standard
Log books and internal instructions	■■■■■■	Keep high standard
Web site	■■■■■■	Keep high standard
GAWSIS	■■■■	Data availability and location update

GAW-VOC targets are reported within the current limits of the DQOs demonstrating an excellent analytical performance of the implemented system including calibration procedures.

WMO GLOBAL ATMOSPHERE WATCH KIT

WCC-VOC REPORT 2020/1

Report to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT FOR NON METHANE VOLATILE ORGANIC COMPOUNDS

Global GAW Station – Cape Verde Atmospheric Observatory
Calhau, Cape Verde

December 2019
by
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CVO Team

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WMO Global Atmosphere Watch — World Calibration Centre for VOCs

https://www.imk-ifu.kit.edu/wcc-voc/activities.html

VOC Network comaptibility

89 Stations with data

Station Cape Verde

- History
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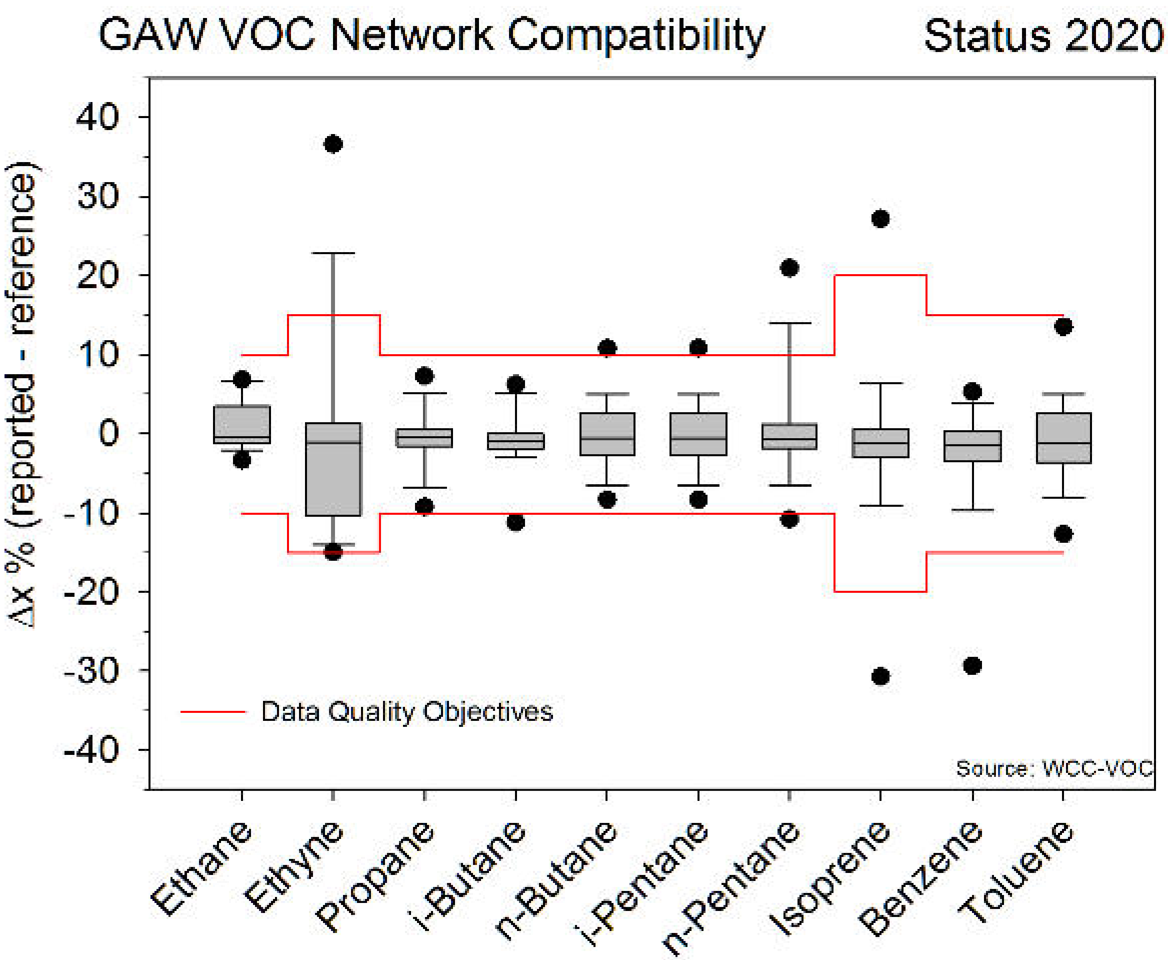
VOC Network compatibility

Results of 23 intercomparisons and audits at 16 facilities (2007 to 2020)

NMHCs traceable standards in nitrogen (single compound range: 1 - 4 nmol/mol)



- ❖ The boxplot ($25^{th}/75^{th}/95^{th}$ percentiles) highlights the good analytical performance in the GAW-VOC network for NMHC targets.
- ❖ Improvements possible for ethyne analysis.

Essentials for good network data compatibility

- A state-of-the-art quality assurance and quality control framework (QA/QC) with:
- Traceable network standards
- Suitable measurement guidelines
- Trained personnel
- Regular audits and intercomparisons
- Closed issue loops
- QA/QC workshops

Key elements of good practice in the upcoming European Research Infrastructure Aerosol, Clouds and Trace Gases (ACTRIS; https://www.actris.eu) with its Topical Centres e.g. Center for Reactive Trace Gases in Situ Measurements (CiGas)

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Happy to take questions