Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 05/4 – Part A

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

AT JMA GAW FACILITIES

PART A

REGIONAL GAW STATION RYORI

JAPAN, NOVEMBER 2005

Submitted by

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WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane

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Empa is accredited as a calibration laboratory for ozone measuring instruments in accordance with ISO/IEC 17025

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ASSESSMENT AND RECOMMENDATIONS

The first system and performance audit at the Regional GAW station Ryori (RYO) run by the Japan Meteorological Agency (JMA) was conducted by WCC-Empa[1] from 22 thru 25 November 2005 in agreement with the WMO/GAW quality assurance system [*WMO*, 2001].

People present during the audit included

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Mr. Kazuhiro Tsuboi	JMA, Head of Greenhouse Gas Observations Section
Mr. Kan Kimura	JMA, Station Manager
Mr. Noriyasu Kudo	JMA, Scientific Officer
Mr. Kiyoshi Tsuchya	JMA, Scientific Officer
Mr. Osamu Yamamoto	JMA, Station Operator
Mr. Takashi Mochizuki	JMA, Station Operator

Our assessment of the station Ryori in general, as well as the surface ozone, carbon monoxide and methane measurements in particular is summarized below. The assessment criteria for the ozone inter-comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003].

This report is distributed to JMA, the station manager and the World Meteorological Organization in Geneva. The executive summaries will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

Ryori Station (39.033 N, 141.833 E, 260 m a.s.l.) is located on a hilly cape on the Pacific coast in the northern part of the Japanese main island, Honshu. The surrounding area is sparsely populated, about 120 km apart from Sendai, the largest city of the region with a population of approximately one million people. The location is adequate for the intended purpose, but the site is subject to frequent pollution episodes from Honshu. Access to the site consists of forest roads which are suitable for normal cars and smaller trucks. The road to the site is closed for public traffic.

Recommendation 1 (, on-going)**
Data analysis and interpretation is an important part of the contribution of the RYO station to GAW. Data analysis should continue to involve adequate flagging of data that are influenced by local pollution sources.

Station Facilities

The Ryori GAW station comprises extensive laboratory and office facilities. It is an ideal platform for atmospheric research.

[1] WMO/GAW GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

Station Management and Operation
The station is permanently staffed during working days with scientific officers and operators. This guarantees the high level quality of the Ryori data. The staff has sufficient technical expertise to operate and maintain the equipment and to work with the data. Positions are usually changed within JMA after two years.

> **Recommendation 2 (**, on-going)**
> *The current station management system with responsibilities of both technical and scientific staff is regarded as optimal and should be continued. However, it must be assured that the technical expertise is transferred after changes of the personnel.*

Air Inlet System
The design of the air inlet system for surface ozone, carbon monoxide and methane is adequate for its intended purpose, although the residence time in the inlet system is relatively long for the greenhouse gas observations.

> **Recommendation 3 (*, 2007)**
> *The residence time in the inlet system (CO and CH_4) is approximately 90 seconds. It should be considered to reduce the residence time with a higher flow rate. Meanwhile the time difference between sampling and analysis should be compensated.*

Surface Ozone Measurements
Instrumentation. Surface ozone measurements are made with an Ebara Jitsugyo EG-2001 FTP ozone analyser. The instrumentation is adequate for its intended purpose.

Standards. The station is not equipped with an ozone standard. The station analyser is exchanged every six months with an identical instrument which has been calibrated against an NIST traceable transfer standard at JMA. An overlap of one month with two instruments running in parallel is done at every exchange. This guarantees the traceability of the RYO measurements to an SRP.

Intercomparison (Performance Audit). The inter-comparisons of the station analyser extended over a period of nearly 14 hours. The results of the assessment are summarised below and are presented in Figure 1.

EG-2001 FTP #3453069: 0 – 90 ppb good agreement

Unbiased O3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.52 ppb) / 0.997 (1)

Here, [OA] represents surface ozone readings obtained from the station data acquisition.

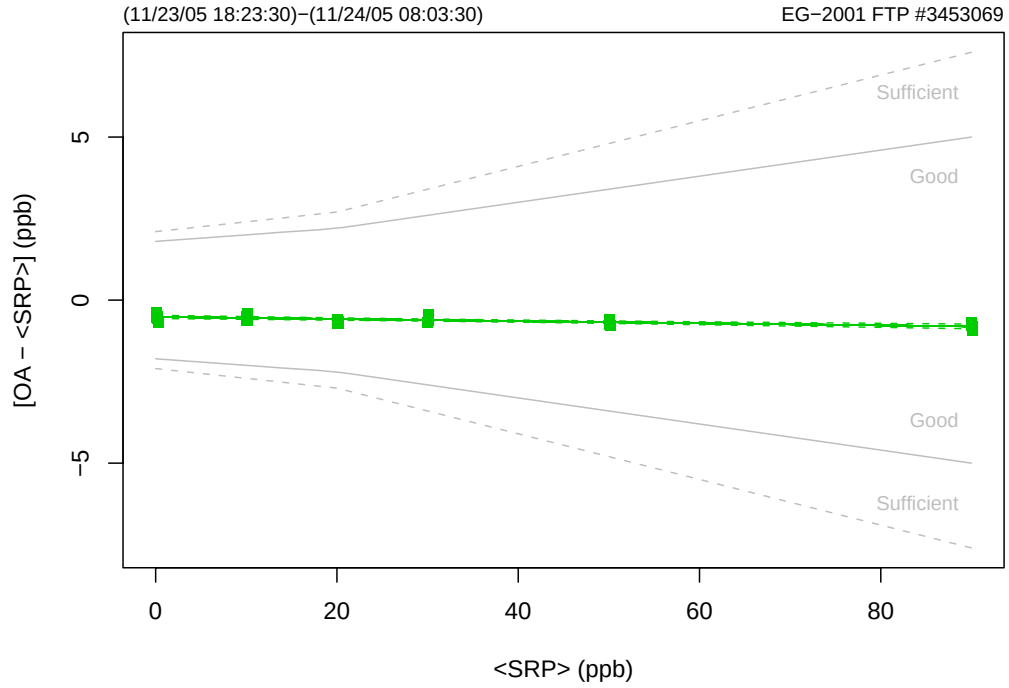

Figure 1. Bias of the Ryori ozone analyser with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen, et al., 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Carbon Monoxide Measurements

Instrumentation. Ryori is currently equipped with one NDIR carbon monoxide analyser. The instrumentation is adequate for the intended purpose, but replacement should be planned considering the age of the analyser (15 years).

Recommendation 4 (, 2006-2008)**
It is recommended to replace the current CO analyser by a new system within the next few years.

Standards. The standard carbon monoxide scale, to which the Ryori CO measurements are referenced, is based on cylinders obtained from Taiyonissan Co. Ltd. These standards in nitrogen are in 48 l aluminium cylinders. The assigned concentration is checked by the Chemical Evaluation and Research Institute (CERI). Usually one station standard is available at the site. In addition working standards are in use at the station. The concentrations of the working standards are assigned by comparison with the station standard. All standards have CO concentrations of approximately 1 ppm. With this equipment, adequate calibration of the carbon monoxide measurements is possible; however the possibility of direct link to the NOAA/GMD WMO-2000 carbon monoxide scale would be preferable. Daily span checks are carried out automatically.

Recommendation 5 (, 2006-2007)**
It is recommended to additionally purchase carbon monoxide standards directly from NOAA/GMD to establish a direct link of the RYO CO measurements to the GAW reference (WMO-2000 carbon monoxide scale)

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instrument with randomised carbon monoxide concentrations from a dilution system.

Currently no formal data quality objectives have been established. The following equation characterises the instrument bias (cf. Figure 2):

Horiba GA-360S S/N 16827903L:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = (CO – 6.5 ppb)/ 0.992 (2)

The results of Ryori deviate significantly from the reference. An offset of approximately 5-6 pbb was found at zero, and was approximately half at the 500 ppb level.

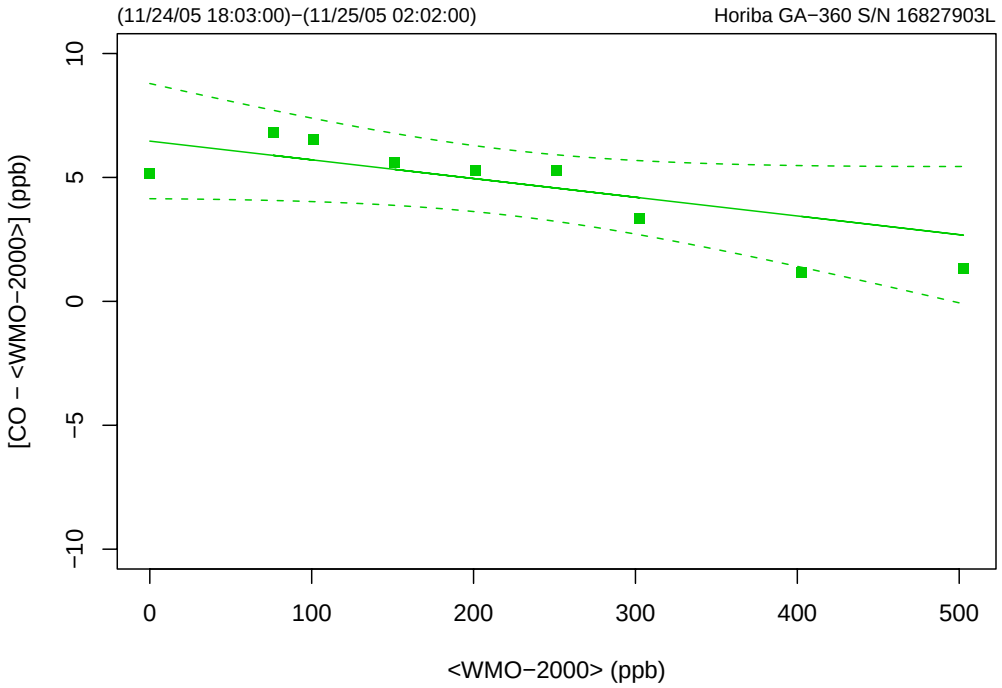

Figure 2. Bias of the Ryori carbon monoxide analyser (Horiba GA-360) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Recommendation 6 (*, 2006)**
WCC-Empa recommends that the instrument calibration always includes a zero calibration using carbon monoxide free zero air before the span calibration. Furthermore automatic zero checks should be performed at regular intervals using carbon monoxide free zero air, e.g. with a Sofnocat scrubber. A zero offset must be corrected in the final data evaluation.

Methane Measurements

Instrumentation. Ryori is currently equipped with one methane analyser. The instrumentation is adequate for the intended purpose, but replacement should be planned considering the age of the instrument (15 years).

> **Recommendation 7 (**, 2006-2008)**
> *It is recommended to replace the current methane analyser with a new system within the next few years.*

Standards. The standard methane scale, to which the Ryori CH_4 measurements are referenced, is based on standards obtained from Taiyonissan Co. Ltd. These are standards containing natural purified air in 48 l aluminium cylinders. Calibration of the station standards is done at JMA against the JMA gravimetric scale purchased from Taiyonissan. Usually two station standards are available at the site. These standards have methane concentrations between 1700 and 2000 ppb. With this equipment, adequate calibration of the methane measurements is possible; however the possibility of a direct link to the NOAA04 methane scale would be preferable. Daily span checks are carried out automatically.

> **Recommendation 8 (*, 2006-07)**
> *It is recommended to purchase methane standards directly from NOAA/GMD in addition to the station standards to establish a direct link of the RYO methane measurements to the GAW reference (NOAA04 CH_4scale)*

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instrument with randomised methane concentrations from travelling standards. No formal data quality objectives have been established for methane. The following equations characterise the instrument bias (cf. Figure 3):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 0.99997 (3)

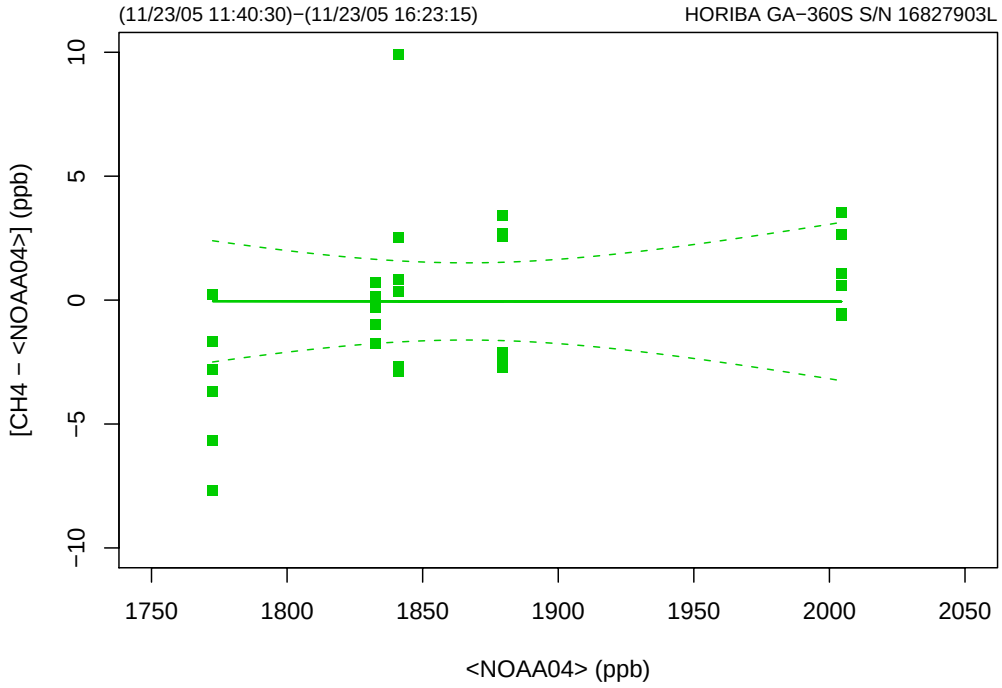

Figure 3. Bias of the Ryori methane analyser (Horiba GA-360) with respect to the NOAA04 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Data Acquisition and Management

Surface Ozone: The data acquisition consists of an Ebara Jitsugyo DQA system, and 15 second values are acquired via RS-232. In addition to the ozone data the system acquires also all relevant instrument information.

Carbon monoxide and Methane: The analogue signal is acquired by a 12 bit A/D board with software from Horiba. Only the CO and CH_4 concentrations are recorded; no additional instrument information is collected. A chart recorder is also connected and is used for quick checks of general instrument operation. The time base of the collected data is local standard time (UTC + 9). One minute data is stored for further analysis, and the data is backed up in regular intervals.

Recommendation 9 (*, 2006)**
The current data acquisition for carbon monoxide (12 bit A/D board) leads to discrete values. The resolution is not sufficient and a replacement is recommended.

Data Submission

Data of all parameters in the scope of WCC-Empa were submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA. The records are complete and data is usually submitted within a maximum of three months after completion of the measurements.

Conclusions

The Ryori GAW station comprises a large suite of ongoing measurements. All assessed measurements were of high quality. Careful evaluation of the data is needed due to the presence of local and regional pollution sources.

Summary Ranking of Ryori Station

System Audit	Adequacy[#]	Comment
Access	(5)	
Facilities		
Laboratory and office space	(5)	
Air Conditioning	(5)	
Power supply	(5)	
General Management and Operation		
Organisation	(5)	
Competence of staff	(4)	
Air Inlet System	(4)	Long residence time (CO and CH_4)
Instrumentation		
Surface ozone	(5)	
Carbon monoxide	(4)	
Methane	(4)	
Carbon dioxide	(4)	
Nitrous oxide	(4)	
Chlorofluorocarbons (CFC_S)	(4)	
Methyl chloroform and CCl_4	(4)	
Aerosol optical depth	(4)	
Aerosol lidar	(5)	Vertical aerosol profiles Nd:YAG laser based lidar
Meteo	(5)	
Standards		
Ozone	(4)	At JMA
Carbon monoxide	(4)	No direct link to NOAA/GMD
Methane	(4)	No direct link to NOAA/GMD
Data Management		
Data acquisition	(3)	Resolution insufficient (CO)
Data processing	(5)	
Data submission	(5)	

[#]0: inadequate thru 5: adequate

Dübendorf, July 2007

Dr. C. Zellweger	Dr. J. Klausen	Dr. B. Buchmann
WCC-Empa	QA/SAC Switzerland	Head of laboratory

APPENDIX

Regional GAW Station Ryori

Site description

Ryori Station (39.033 N, 141.833 E, 260 m a.s.l.) is located on a hilly cape on the Pacific coast in the northern part of the Japanese main island, Honshu. The surrounding area is sparsely populated, about 120 km from Sendai, the largest city of the region with a population of one million. The area has a temperate climate with four distinct seasons. The annual temperature is about 10 °C and annual precipitation is about 1,300 mm. Further information about the site and the measurement programme is available on the internet (JMA homepage, http://gaw.kishou.go.jp/japan/ryo.html), and the station is also registered in GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Programme

The observatory Ryori has a long history of meteorological measurements of the stratosphere with rockets dating back to 1970's. Since the early 1990's Ryori comprises also an extensive suite of observations of the troposphere, but the rocket programme was stopped. The status of the programme as of November 2005 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the RYO Station

Parameter	Current Instrument	Data Coverage (%)		
		<12 m	<3 y	Overall
Aerosol				
Multiwavelength optical depth	Precision Filter Radiometer			
Multiwavelength optical depth	Sun Photometer EKO MS110			
Vertical distribution of properties	Light detection and ranging (LIDAR)			
Ozone				
Surface ozone	Ebara Jitsugyo EG-2001 FTP	98.2	98.3	92.0
Greenhouse Gas				
CFCs, CH_3Cl, CCl_4	GC KANSO/SHIMAZU GC-14B			
Carbon dioxide	Horiba VIA-500R NDIR			
Methane	Horiba GA-360S NDIR	93.6	93.3	72.7
Nitrous oxide	GC KANSO/SHIMAZU GC-14B			
Reactive Gas				
Carbon monoxide	Horiba GA-360S	92.6	91.5	88.9
Radio Nuclide				
Beryllium [Be-7]	Filter sampling + gamma spectrometry EG&E 7500B			
Ancillary Measurements				
Meteo (PTU, wind speed and direction)				

Missing data availability: no data coverage information was available at the time of the audit.

Ozone, Carbon Monoxide and Methane Distribution at Ryori

The monthly and yearly distributions of one hourly mean values for surface ozone and carbon monoxide for the year 2005 are shown in Figure 4.

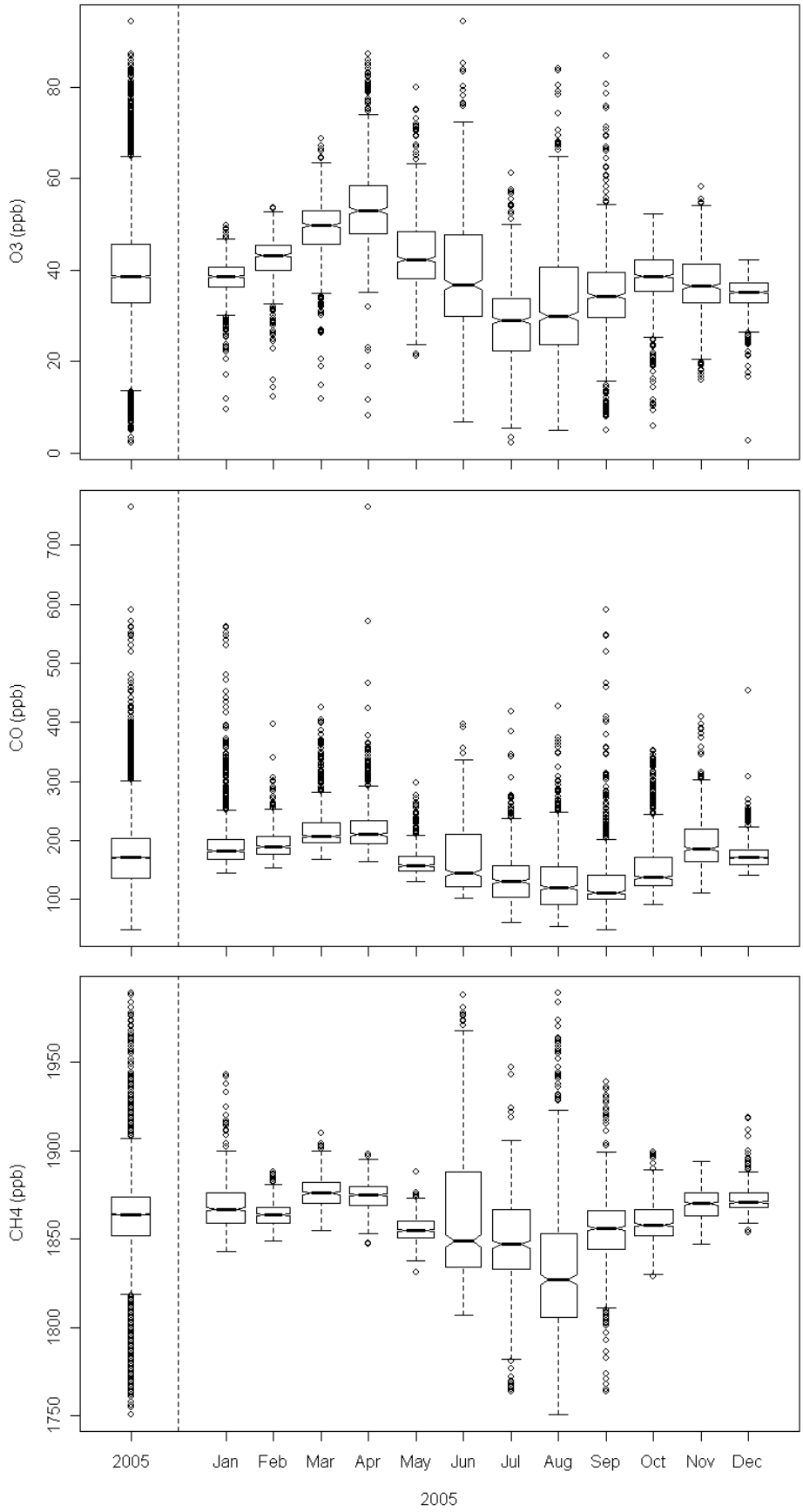

Figure 4. Yearly and Monthly Box Plots of 1-hourly aggregates for the year 2005 for Surface Ozone, Carbon Monoxide and Methane at Ryori. The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organization and Contact Persons

The Ryori GAW station is part of the Global Environment and Marine Department's Atmospheric Environment Division (AED) of JMA. The structure of AED is illustrated in Figure 5.

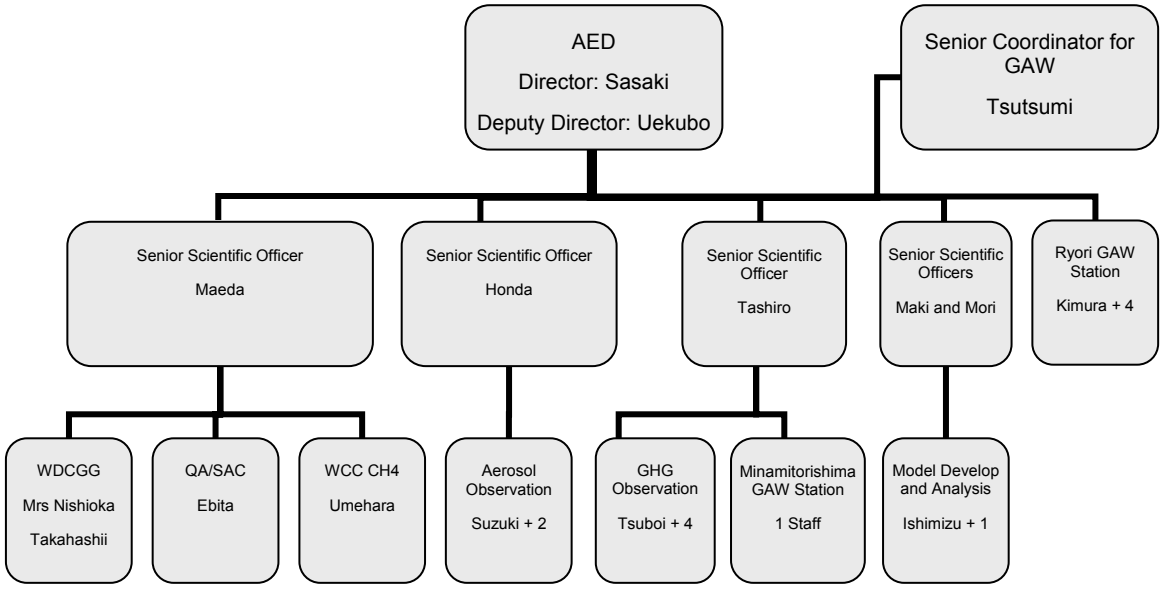

Figure 5. Organization of GAW Activities at JMA as of November 2005.

Surface Ozone Measurements

Surface ozone measurements commenced in 1990 at the Ryori station, and continuous ozone data is available since then.

Monitoring Set-up and Procedures

Air Conditioning

The laboratories of the Ryori station are air conditioned (23°C) and the instruments are protected from direct sunlight.

Air Inlet System

The air intake is mounted on top of the station building approx. 10 m above ground. The inlet is made of PTFE tubing (5 m with 8 mm inner diameter, flow rate with external pump approx. 10 l min^{-1}). A Komatsu dehumidifier is used to dry the air. After the dehumidifier, a glass manifold with a volume of 200 ml allows to connect more than on ozone instrument. From there, ca. 2 m PTFE tubing with an inner diameter of 6 mm is used to connect the instrument. The flow rate is 1 l min^{-1}, and the instrument is protected by a Teflon filter. All materials used are adequate, and the residence time is estimated to be approximately 12 s.

Instrumentation

Surface ozone measurements are made with an Ebara Jitsugyo EG-2001 FTP ozone analyser. Instrumental details can be found in Table 4. The instrument is installed on the first floor of the air-conditioned station building.

Standards

No ozone calibrator is available at the site. However, the ozone analyser is exchanged every six months by an identical instrument which has been calibrated against an NIST traceable transfer standard at JMA. An overlap of one month with two instruments running in parallel is allowed at every exchange. The comparison of the JMA ozone calibrator with WCC-Empa is shown in a separate report [*Zellweger, et al.*, 2005].

Operation and Maintenance

Daily (working days, Mo – Fr):

- Check of instrument operation (flow rate, errors, lamp signal, general operation).

Weekly:

- Time adjustment (DAQ).

Biweekly:

- Inlet filter exchange.

Other intervals:

- Zero / span check at irregular intervals in case of instrument problems.
- Instrument replacement every six months by a calibrated analyser of the same type with one month of overlapping measurements.

Data Acquisition and Data Transfer

The data acquisition consists of an Ebara Jitsugyo DGA system, and 15 second values are acquired via the RS-232 port. The system acquires in addition to the ozone data also all relevant instrument information.

Data Treatment

All raw data is collected in an Access data base; 30 second averages are available. The information of the check list is also added to the data base. The data is visualized and invalid data is flagged at the station. The final data evaluation is done at JMA.

Data Fagging

The following flags are applied to the data (the flagging system is also used at Minamitorishima and Yonagunijima):

Flags are numbers from 0 – 9; positive and negative numbers are possible; negative flag numbers indicate that the values have not been corrected for working standard drift.

The flags and the flagging procedures are described in Table 2 and Table 3.

Table 2.: Flags for CO_2, CH_4, CO and O_3

Flag number	Insufficient number of data points (< 50%)	High standard deviation (exceeding value A*)	Large discrepancy with an adjacent measurement (exceeding value B*)	Selection result o: used for daily / monthly data. ×: not used for daily / monthly data.			
				CO_2	CH_4	CO	O_3
flag 0	yes	yes	yes	×	×	×	×
flag 1	no	yes	yes	×	×	×	o
flag 2	yes	no	yes	×	×	×	×
flag 3	no	no	yes	×	×	×	o
flag 4	yes	yes	no	×	×	×	×
flag 5	no	yes	no	×	×	×	o
flag 6	yes	no	no	×	×	×	×
flag 7	no	no	no	o	o	o	o
flag 9	Missing data						

*: see Table 3

Table 3. Limit values for flags (see Table 2 above)

Station	value A (CO_2)	value B (CO_2)	value A (CH_4)	value B (CH_4)	value A (CO)	value B (CO)	value A (O_3)	value B (O_3)
Ryori	0.6ppm	0.6ppm	7ppb	6ppb	8ppb	4ppb	2.5ppb	2.0ppb
Minamitorishima	0.3ppm	0.3ppm	6ppb	6ppb	4ppb	4ppb	1.5ppb	2.0ppb
Yonagunijima	0.6ppm	0.3ppm	7ppb	6ppb	8ppb	4ppb	2.5ppb	2.0ppb

Data Submission

Data is submitted to the data centre for surface ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG) shortly after validation. Submissions delays are short (a few months maximum).

Documentation

Hand-written instrument specific check lists and instrument manuals are available at the site. All information was sufficiently comprehensive and up-to-date.

Inter-Comparison of Ozone Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2006] and included inter-comparisons of the transfer standard with the Standard Reference Photometer at Empa before and after the inter-comparison of the analyser.

Setup and Connections

Table 4 details the experimental setup during the inter-comparison of the station analyser. The data used for the evaluation was recorded by both WCC-Empa and Ryori data acquisition systems as indicated. No further corrections were applied to the data of the Ryori instrument.

Table 4. Experimental details of the ozone inter-comparison.

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.012
Ozone analyzer (OA)	Model, S/N	Ebara Jitsugyo EG-2001 FTP #3453069
	Principle	UV absorption
	Range	0-100 ppb
	Settings	Offset -1.5, Span 0.948
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm (WCC-Empa)
Connection between instruments		Ca. 2.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS	One minute aggregates from digital output (custom designed LabView programme)
	OA	One minute aggregates from station data acquisition
Pressure readings at beginning of inter-comparison (hPa)	Ambient	986.6 hPa (Station reference)
	TS	984.0 hPa, adjusted to 986.6 hPa
	OA	Not adjusted. The instrument was initially calibrated without adjustment of the pressure sensor.
Levels (ppb)		0, 10, 20, 30, 50, 90
Duration per level (min)		20
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		7 runs (23 thru 24 November, 2005)

Results

Each ozone level was applied for 20 minutes, and the last 10 one-minute averages were aggregated. The results are shown in Table 5. These aggregates were used in the assessment of the inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results refer to the calibration factors as given in Table 4 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analysers (OA) values.

Table 5. Ten-minute aggregates computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the RYO ozone analyzer (OA) EG-2001 FTP #3453069 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2005-11-23 18:28	1	0	0.07	-0.25	0	0.07	0.04
2005-11-23 18:48	1	10	10.07	9.74	0	0.08	0.08
2005-11-23 19:08	1	50	50.06	49.41	0	0.07	0.04
2005-11-23 19:28	1	30	30.05	29.70	0	0.07	0.05
2005-11-23 19:48	1	20	20.08	19.46	0	0.08	0.06
2005-11-23 20:08	1	90	90.02	89.36	0	0.04	0.05
2005-11-23 20:28	2	0	0.24	-0.36	0	0.43	0.05
2005-11-23 20:48	2	50	49.99	49.51	0	0.10	0.03
2005-11-23 21:08	2	10	10.05	9.49	0	0.09	0.06
2005-11-23 21:28	2	90	89.93	89.14	0	0.06	0.07
2005-11-23 21:48	2	20	20.04	19.46	0	0.07	0.02
2005-11-23 22:08	2	30	29.98	29.47	0	0.10	0.03
2005-11-23 22:28	3	0	0.10	-0.41	0	0.10	0.07
2005-11-23 22:48	3	90	89.94	89.26	0	0.05	0.06
2005-11-23 23:08	3	20	19.99	19.43	0	0.08	0.06
2005-11-23 23:28	3	50	49.95	49.46	0	0.07	0.06
2005-11-23 23:48	3	10	10.03	9.58	0	0.08	0.04
2005-11-24 00:08	3	30	29.97	29.45	0	0.07	0.05
2005-11-24 00:28	4	0	0.02	-0.35	0	0.08	0.05
2005-11-24 00:48	4	10	9.97	9.53	0	0.08	0.03
2005-11-24 01:08	4	50	49.97	49.44	0	0.06	0.05
2005-11-24 01:28	4	30	29.95	29.36	0	0.06	0.06
2005-11-24 01:48	4	20	20.04	19.48	0	0.12	0.08
2005-11-24 02:08	4	90	89.89	89.26	0	0.05	0.08
2005-11-24 02:28	5	0	0.03	-0.43	0	0.09	0.05
2005-11-24 02:48	5	50	49.94	49.35	0	0.09	0.06
2005-11-24 03:08	5	10	9.99	9.45	0	0.10	0.07
2005-11-24 03:28	5	90	89.90	89.35	0	0.06	0.06
2005-11-24 03:48	5	20	20.00	19.40	0	0.08	0.04
2005-11-24 04:08	5	30	29.96	29.45	0	0.05	0.06
2005-11-24 04:28	6	0	0.09	-0.35	0	0.07	0.08
2005-11-24 04:48	6	90	89.92	89.24	0	0.05	0.06
2005-11-24 05:08	6	20	19.97	19.47	0	0.11	0.05
2005-11-24 05:28	6	50	49.96	49.32	0	0.10	0.05
2005-11-24 05:48	6	10	10.00	9.66	0	0.11	0.06
2005-11-24 06:08	6	30	29.97	29.43	0	0.09	0.05
2005-11-24 06:28	7	0	0.05	-0.37	0	0.06	0.05
2005-11-24 06:48	7	10	9.94	9.39	0	0.08	0.06
2005-11-24 07:08	7	50	49.93	49.38	0	0.09	0.04
2005-11-24 07:28	7	30	29.95	29.58	0	0.08	0.05
2005-11-24 07:48	7	20	19.95	19.32	0	0.08	0.05
2005-11-24 08:08	7	90	89.88	89.26	0	0.07	0.04

[#]0: valid data

Figure 6 shows the regression residuals of the ozone analyser with respect to the SRP as a function of ozone concentration and time for the range 0 – 90 ppb.

Based on this inter-comparison result, unbiased ozone volume mixing ratios X_{O3} and an estimate for the remaining combined standard uncertainty u_{O3} can be computed from the one-minute data [OA] using equation (1) [*Klausen, et al.*, 2003].

EG-2001 FTP #3453069:

$$X_{O3}\ (ppb) = ([OA] + 0.52\ ppb) / 0.997$$

$$u_{O3}\ (ppb) = sqrt(0.27\ ppb^2 + 2.62e\text{-}05 * X_{O3}^2) \quad (1)$$

Changes Made to Instrument
No changes were made to the instruments, all settings remained.

Conclusions
The findings of the audit demonstrate good agreement between RYO ozone measurements and WCC-Empa. Therefore no further recommendations are made by WCC-Empa.

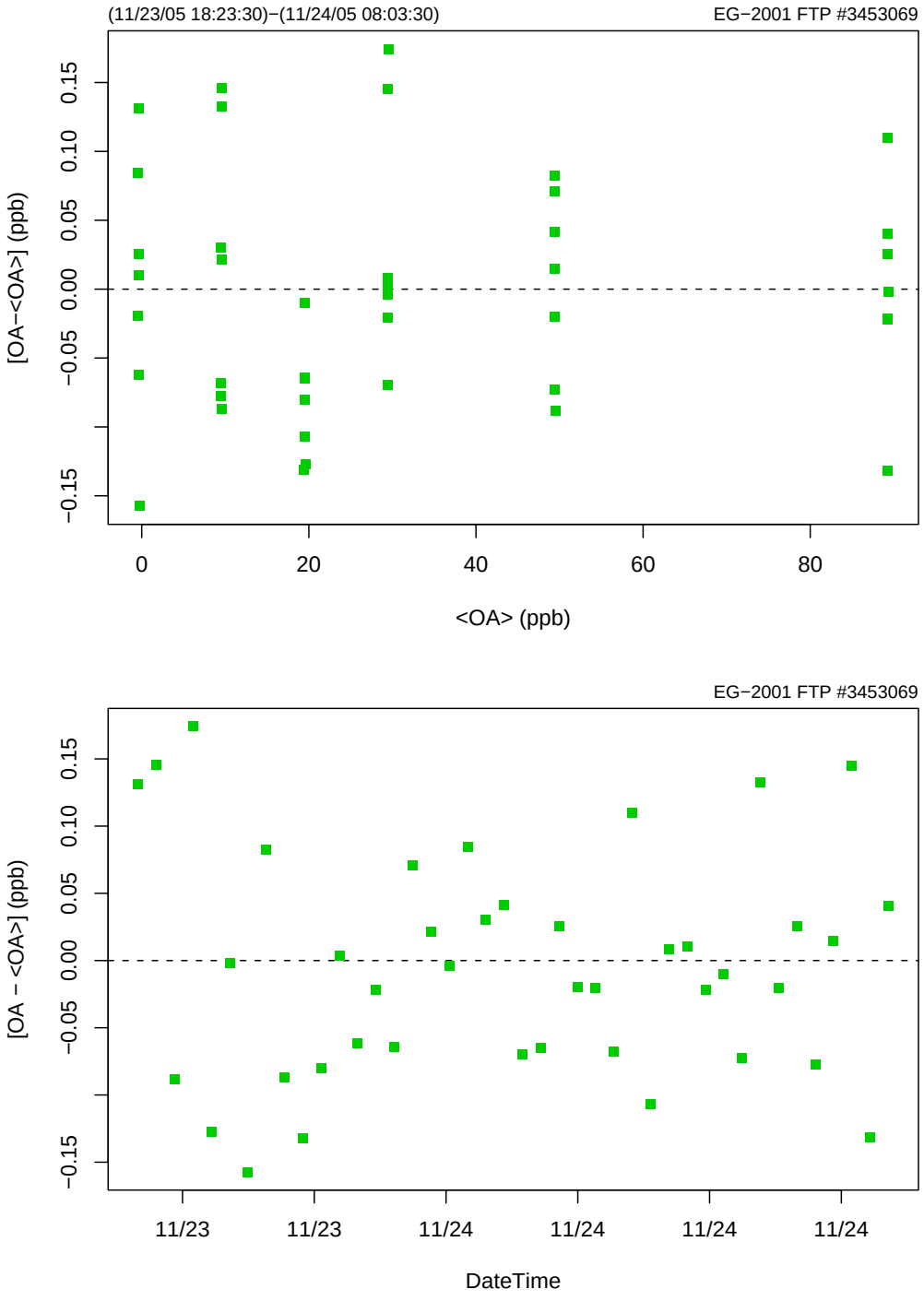

Figure 6. Regression residuals of the RYO ozone analyser as a function of concentration (upper panel) and time (lower panel).

Carbon Monoxide Measurements

On-going measurement of carbon monoxide at Ryori commenced in 1991, and continuous data series are available since then. Carbon monoxide measurements at Ryori are made using NDIR technique. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning

The air-conditioning is identical to the one for surface ozone as described above.

Air Inlet System

Sampling-location is on the top of the 20 m tower next to the laboratory building. The inlet is made of ca. 110 m stainless steel tubing (1/2'' inner diameter). This tubing is flushed by a pump with a flow rate of approx. 15 l/min. The CO (and CH_4) instrument is connected to this tubing with 6 m stainless steel tubing, inner diameter 6 mm. The instrument is protected with two stainless steel filters (40 µm and 5 µm) with a volume of 500 ml. The residence time in the sampling line is estimated to be approx. 90 s. The inlet systems, including all parts and materials are adequate for the analysis of CO (and CH_4).

Instrumentation

The analytical system for carbon monoxide at Ryori consists of an NDIR monitor. The whole system was purchased from Horiba in 1990, and is integrated in a rack together with the methane monitor. The system is fully automated. Instrumental details are listed in Table 7 below.

Standards and Calibration

The standard CO scale, to which the Ryori CO measurements are referenced, is based on standards obtained from Taiyonissan Co. Ltd. These standards in nitrogen are in 48 l aluminium cylinders. The assigned concentration is checked by the Chemical Evaluation and Research Institute (CERI). Usually one station standard is available at the site. Furthermore working standards are in use at the station. The concentrations of the working standards are assigned by comparison with the station standard. Table 6 gives details of the cylinders currently available at the station.

The instrument is currently calibrated using two daily span checks with the following sequence: 0945 (time in UTC+9) CH_4 low, 0952 CH_4 high, 0959 CO zero*, 1006 CO span, 1013 purge, 1018 ambient measurements. The calibration sequence is repeated starting at 2145. (* flow stopped; this is not a real zero check).

Table 6. Carbon monoxide standards available at RYO station

Manufacturer, S/N, Use	**CO Content (ppb) and matrix**	Scale
Taiyonissan CQB 01540 Station standard; CERI certified	1154±24 ppb in nitrogen	Laboratory standard (national scale, CERI)
Taiyonissan CQB 00683 Working standard	1015 in nitrogen	Working standard; no uncertainty assigned
Taiyonissan CQB 01541 Working standard	1029 in nitrogen	Working standard, no uncertainty assigned
Taiyonissan CQB 06942 Working standard	1064 in nitrogen	Working standard, no uncertainty assigned

Operation and Maintenance
The instruments are checked for general operation whenever the station is visited (usually every weekday). The inlet tubing is cleaned once per month with ethanol and pure water. The inlet filter is replaced every 6 months. No other maintenance is done by the Ryori staff. Horiba is contacted in case of instrument problems, and all service and repair works are done by Horiba staff.

Data Acquisition and Data Transfer
The analogue signal is acquired by a 12 bit A/D board and software from Horiba. Only the CO concentration is recorded; no additional instrument information is collected. A chart recorder is also connected and is used for quick checks of general instrument operation. The time base of the collected data is local standard time (UTC + 9).

Data Treatment
All raw data is collected in an Access data base; 30 second averages are available. The information of the check list is also added to the data base. The data is visualized and invalid data is flagged at the station (cf. Table 2). The final data evaluation is done at JMA.

Data Submission
Data is submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA shortly after validation. Submission delays are short (a few months maximum).

Documentation
Hand-written instrument specific check lists and instrument manuals are available at the site. The check lists are sufficiently comprehensive and up-to-date.

Inter-Comparison of Carbon Monoxide Analysers
All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standard to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 14 further below.

Setup and Connections
Table 7 shows details of the experimental setup during the inter-comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the Ryori data acquisition system, and no further corrections were applied.

Table 7. Experimental details of the carbon monoxide inter-comparison.

Travelling standard (TS)		One cylinder (040818_0646B, 50182±176 ppb in synthetic air) and a zero-air generator (silica gel - inlet filter 5 μm - metal bellow pump – Purafil- Sofnocat - outlet filter 5 μm) custom-built by WCC-Empa, in combination with a dilution system (Breitfuss, MGM)
Field instrument	Model, S/N	Horiba GA-360S S/N 16827903L
	Principle	NDIR, Cross Flow Modulation Technique
	Modification	None
	Range	0 - 3 ppm
Connection of TS to field instrument		Sample inlet
Data Acquisition		5-minute aggregates from RYO data acquisition
Levels (ppb)		Level / Reference / St.Uncertainty 1 / 0.00 / 0.06 2 / 101.31 / 0.36 3 / 76.27 / 0.28 4 / 251.32 / 0.90 5 / 302.57 / 1.08 6 / 151.33 / 0.54 7 / 201.34 / 0.72 8 / 502.62 / 1.79 9 / 402.64 / 1.44
Duration per level (min)		60
Sequence of levels		Randomised fixed sequence
Runs		1 run (24 thru 25 November, 2005)

Results

Each carbon monoxide level was applied for 60 minutes, which resulted in a maximum of 12 useable 5' averages per level and run for the Horiba 360-GA instrument. These were further aggregated by level before use in the assessment (cf. Table 8).

Table 8. CO aggregates computed from 5' averages (mean and standard uncertainty of mean) for each level during the inter-comparison of the RYO carbon monoxide analyzer with the WCC-Empa transfer standard (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	CO (ppb)	sdCO (ppb)	No. 5' av.
(11/24/05 18:03:00)	0.00	0.06	5.16	0.54	11
(11/24/05 19:03:00)	101.31	0.36	107.78	0.64	11
(11/24/05 20:03:00)	76.27	0.28	83.06	0.49	11
(11/24/05 21:03:00)	251.32	0.90	256.45	0.42	11
(11/24/05 22:03:00)	302.57	1.08	305.87	0.65	11
(11/24/05 23:03:00)	151.33	0.54	156.82	0.55	11
(11/24/05 00:02:00)	201.34	0.72	206.72	0.42	11
(11/25/05 01:02:00)	502.62	1.79	503.72	0.62	11
(11/25/05 02:02:00)	402.64	1.44	403.82	0.55	11

Figure 7 shows the regression residuals of the Horiba GA-360 plotted against time and concentration. The absence of a temporal trend (upper panel) indicates stable instrument conditions. The concentration dependence (lower panel) shows a slightly higher deviation at higher concentrations. A small remaining non-linearity of the Horiba GA-360 instrument can not be excluded.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the Horiba GA-360 analyser X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the 5' inter-comparison data using equation (2).

$$X_{CO}\ (\text{ppb}) = (CO - 6.5\ \text{ppb})/\ 0.992$$

$$u_{CO}\ (\text{ppb}) = \text{sqrt}(1.6\ \text{ppb}^2 + 2.94\text{e-}05 * X_{CO}^2) \quad (2)$$

Conclusions

The results of Ryori deviate significantly from the reference. An offset of approximately 5 pbb was found at zero. This offset was approximately half at the 500 ppb level. Calibrations are performed at the 1 ppm level. An offset of 5 ppb using a 1 ppm calibration gas leads exactly to the observed result. Zero checks with carbon monoxide free zero air are not performed at Ryori. The only check that is done is a "zero check" with the flow stopped. However, this check results in a zero reading independent of the carbon monoxide concentration (cf. Recommendation 6).

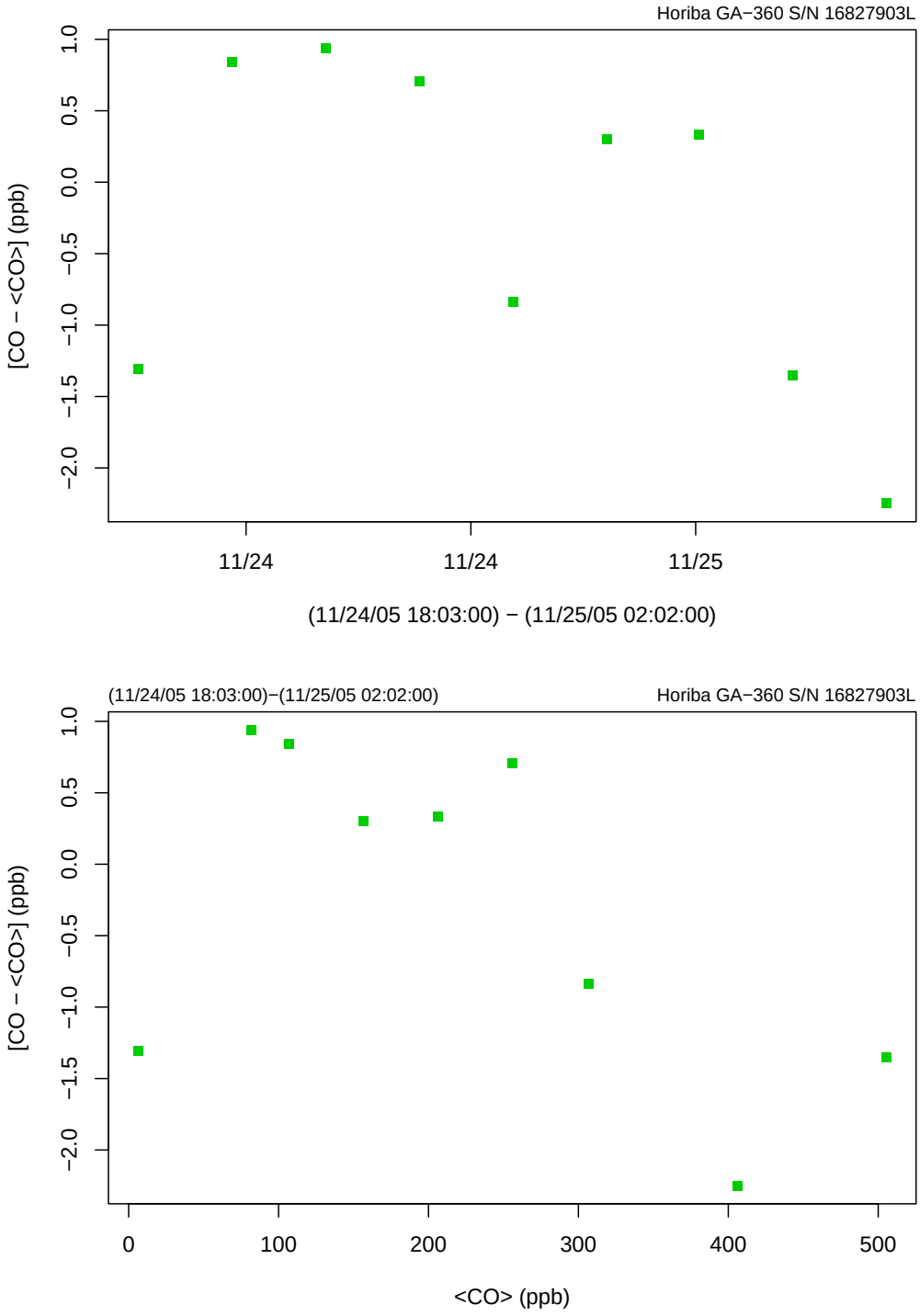

Figure 7. Regression residuals of the RYO carbon monoxide analyser. Points represent averages of valid 1'-aggregates. Upper panel: time dependence; Lower panel: concentration dependence.

Methane Measurements

On-going measurement of methane at Ryori commenced in 1990, and continuous data series have been available since then. Methane measurements at Ryori are made using NDIR technique. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning
The air-conditioning is identical to the one for surface ozone as described above.

Air Inlet System
Same as for CO.

Instrumentation
The analytical system for methane at Ryori consists of an NDIR monitor. The whole system was purchased from Horiba in 1990, and is integrated in a rack together with the carbon monoxide monitor. The system is fully automated. Instrumental details are listed in **Table 10** below.

Standards and Calibration
The standard methane scale, to which the Ryori CH_4 measurements are referenced, is based on standards obtained from Taiyonissan Co. Ltd. These are gravimetric standards containing natural purified air in 48 l aluminium cylinders. Calibration of the station standards is done at JMA against the JMA gravimetric scale purchased from Taiyonissan. The JMA standards were prepared in analogy to the Tohoku University (TU) method. The comparability of the TU scale to NOAA04 is described in [*Dlugokencky, et al.*, 2005], and is on the order of 0.5 nmol mol^{-1} at ambient values. Usually two station standards are available at the site. Table 6 gives details of the cylinders currently available at the station.

Calibration procedure: see carbon monoxide.

Table 9. Methane standards available at RYO station

Manufacturer, S/N, Use	CH_4 Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Taiyonissan CQB 13439	1699.0±1.7 ppb, CH_4 in natural purified air		JMA	2004/08	2005/11
Taiyonissan CQB 13442	2001.0±2.0 ppb, CH_4 in natural purified air		JMA	2004/08	2005/11
Taiyonissan CQB 13437	1703.0±2.0 ppb, CH_4 in natural purified air		JMA	2005/11	continues
Taiyonissan CQB 06942	2001.0±2.0 ppb, CH_4 in natural purified air		JMA	2005/11	continues

Operation and Maintenance
Same as for CO.

Data Acquisition and Data Transfer
Same as for CO.

Data Treatment
See CO.

Data Submission
Data is submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA shortly after validation. Submissions delays are short (a few months maximum).

Documentation
Hand-written instrument specific check lists and instrument manuals are available at the site. The check lists are sufficiently comprehensive and up-to-date.

Inter-Comparison of Methane Analysers
All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standard to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 16 below.

Setup and Connections
Table 10 shows details of the experimental setup during the inter-comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the RYO data acquisition system, and no further corrections were applied.

Table 10. Experimental details of the methane inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Field instrument	Model, S/N	Horiba GA-360S S/N 16827903L
	Principle	NDIR, Cross Flow Modulation Technique
	Modification	None
	Range	0 - 3 ppm
Connection of TS to field instrument		Sample inlet
Data Acquisition		30-second aggregates from RYO data acquisition
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 050419_FA02482 / 1772.54 / 0.21 2 / 050701_FA02505 / 1832.65 / 0.24 3 / 050419_FA02488 / 1841.22 / 0.49 4 / 050419_FA02479 / 1879.59 / 0.21 5 / 050415_FA02466 / 2004.49 / 0.25
Duration per level (min)		5 min
Sequence of levels		Randomised sequence
Runs		6 runs (23 November, 2005)

Results

Each methane level was applied for >5 minutes, which resulted in 10 useable 30 second averages per level and run for the Horiba 360-GA instrument. These were further aggregated by level before use in the assessment (cf. Table 11).

Table 11. CH_4 aggregates computed from 30''' averages (mean and standard uncertainty of mean) for each level during the inter-comparison of the RYO methane analyzer with the WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	CH_4 (ppb)	sd CH_4 (ppb)	No. 30'' av.
(11/23/05 11:40:30)	1841.22	0.49	1851.13	1.21	10
(11/23/05 11:45:30)	1841.22	0.49	1842.04	0.93	10
(11/23/05 11:56:30)	2004.49	0.25	2008.04	1.10	10
(11/23/05 12:01:30)	2004.49	0.25	2005.55	1.35	10
(11/23/05 12:12:30)	1772.54	0.21	1764.87	0.81	10
(11/23/05 12:17:30)	1772.54	0.21	1770.86	1.16	10
(11/23/05 12:26:30)	1879.59	0.21	1876.86	1.39	10
(11/23/05 12:31:30)	1879.59	0.21	1882.28	1.04	10
(11/23/05 12:43:30)	1832.65	0.24	1831.65	0.90	10
(11/23/05 12:48:30)	1832.65	0.24	1832.67	1.37	10
(11/23/05 13:03:45)	1772.54	0.21	1766.89	1.02	10
(11/23/05 13:08:45)	1772.54	0.21	1768.84	0.87	10
(11/23/05 13:21:45)	1832.65	0.24	1832.80	1.03	10
(11/23/05 13:26:45)	1832.65	0.24	1830.89	1.02	10
(11/23/05 13:41:45)	1841.22	0.49	1838.53	1.16	10
(11/23/05 13:46:45)	1841.22	0.49	1841.57	1.21	10
(11/23/05 14:01:45)	1879.59	0.21	1877.46	0.90	10
(11/23/05 14:06:45)	1879.59	0.21	1882.14	1.09	10
(11/23/05 14:20:45)	2004.49	0.25	2005.07	1.45	10
(11/23/05 14:25:45)	2004.49	0.25	2003.88	0.99	10
(11/23/05 14:45:45)	1879.59	0.21	1877.23	1.12	10
(11/23/05 14:50:45)	1879.59	0.21	1883.01	1.21	10
(11/23/05 15:10:15)	1841.22	0.49	1838.33	1.75	10
(11/23/05 15:15:15)	1841.22	0.49	1843.74	1.14	10
(11/23/05 15:34:45)	1832.65	0.24	1833.34	0.80	10
(11/23/05 15:39:45)	1832.65	0.24	1832.35	1.03	10
(11/23/05 15:52:45)	1772.54	0.21	1772.75	0.57	10
(11/23/05 15:57:45)	1772.54	0.21	1769.75	0.71	10
(11/23/05 16:18:15)	2004.49	0.25	2007.15	1.39	10
(11/23/05 16:23:15)	2004.49	0.25	2003.95	0.79	10

Figure 7 shows the regression residuals of the Horiba GA-360 plotted against time and concentration. The absence of a temporal trend (upper panel) indicates stable instrument conditions. The absence of concentration dependence (lower pane) indicates linearity of the instrument, even though the data is noisy.

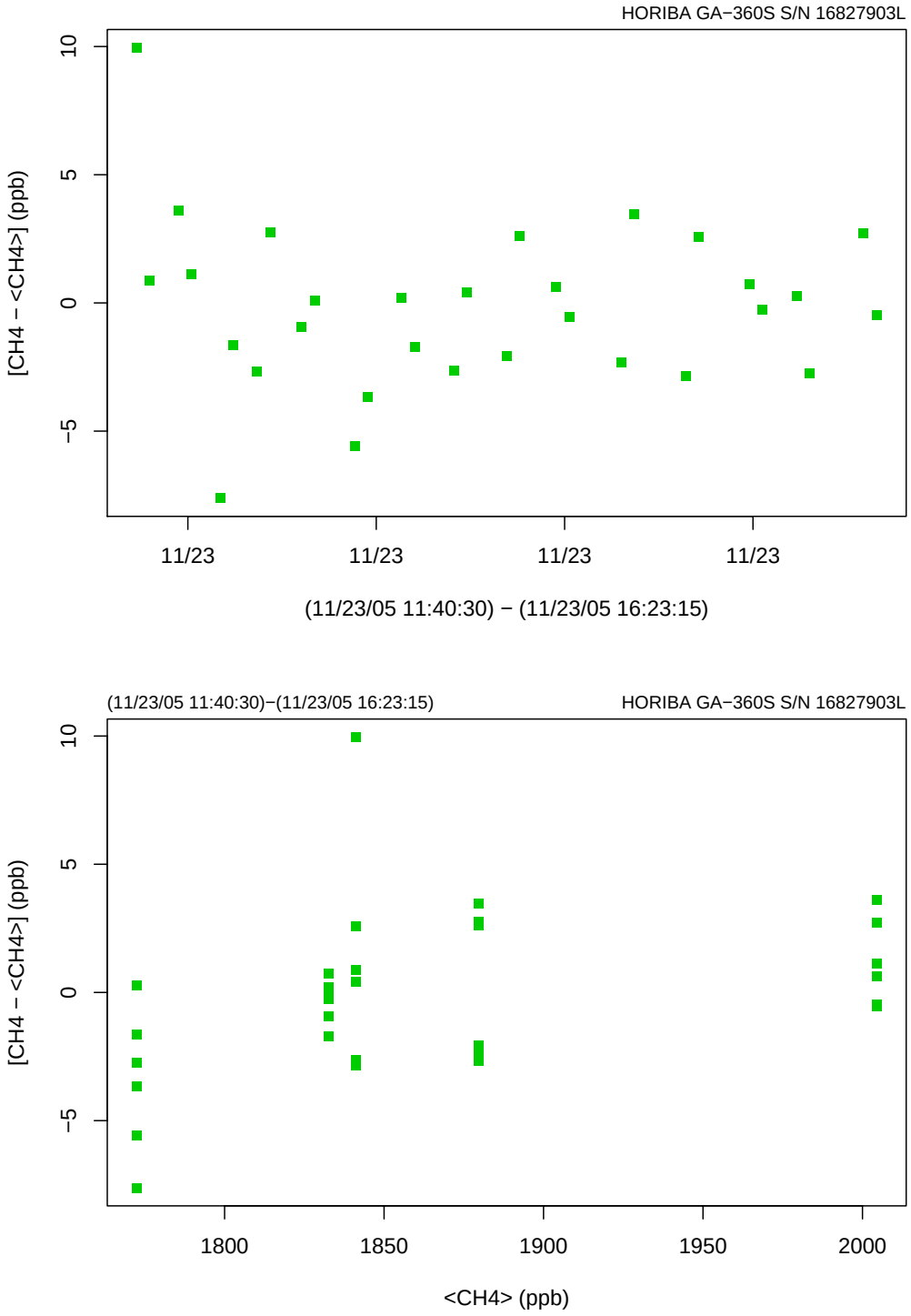

Figure 8. Regression residuals of the RYO methane analyser. Points represent averages of valid 30''-aggregates. Upper panel: time dependence; Lower panel: Concentration dependence.

Based on these inter-comparison results, unbiased methane volume mixing ratios of the Horiba GA-360 analyser X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed from the 30'' inter-comparison data using equation (3).

$$\mathbf{X_{CH4}\ (ppb) = (CH_4) / 0.99997}$$

$$\mathbf{u_{CH4}\ (ppb) = sqrt(10.4\ ppb^2 + 1.10e\text{-}07 * X_{CH4}^2)} \quad (3)$$

Conclusions

The good result of the inter-comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. The repeatability of five minute average values was sufficiently good, with an average standard deviation of 0.14% of six values. This value is comparable to GC/FID systems. Therefore no further technical recommendations are made by WCC-Empa.

WCC-Empa Transfer Standards

Ozone

The WCC-Empa transfer standard (TS) was compared with the Standard Reference Photometer before and after use during the field audit. Details of these inter-comparisons at the Empa calibration laboratory are summarized in Table 12, the inter-comparison data is given in Table 13.

Table 12. Experimental details of the inter-comparison of transfer standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.012
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (4 August, 2005) 3 runs after return of TS (13 December, 2005)

Table 13. Five-minute aggregates computed from 10 valid 30-second values for the inter-comparison of the Standard Reference Photometer (SRP) with the WCC-Empa transfer standard (TS).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2005-08-04	1	0	-0.15	0.29	-0.21	0.33
2005-08-04	1	140	137.28	0.24	136.49	0.18
2005-08-04	1	90	87.73	0.33	87.22	0.07
2005-08-04	1	30	29.26	0.34	29.04	0.07
2005-08-04	1	190	187.69	0.46	187.1	0.31
2005-08-04	1	60	58.49	0.37	58.06	0.09
2005-08-04	1	0	0.02	0.55	-0.31	0.1
2005-08-04	2	0	0.09	0.23	-0.24	0.1
2005-08-04	2	90	88.28	0.36	88.12	0.09
2005-08-04	2	190	188.67	0.37	188.4	0.14
2005-08-04	2	60	59.14	0.36	58.82	0.13
2005-08-04	2	140	138.91	0.32	138.83	0.11
2005-08-04	2	30	29.82	0.42	30.01	0.04
2005-08-04	2	0	-0.11	0.42	-0.09	0.06
2005-08-04	3	0	-0.19	0.55	0	0.08
2005-08-04	3	30	29.87	0.28	29.71	0.09
2005-08-04	3	190	188.62	0.48	188.58	0.13
2005-08-04	3	90	88.91	0.37	88.99	0.09
2005-08-04	3	140	138.93	0.27	139.04	0.05
2005-08-04	3	60	58.97	0.37	59.21	0.08
2005-12-13	4	0	0.14	0.23	-0.02	0.07
2005-12-13	4	0	0.22	0.36	-0.16	0.06
2005-12-13	4	140	140.13	0.37	139.53	0.1
2005-12-13	4	90	89.89	0.27	89.63	0.18
2005-12-13	4	30	30.12	0.26	30.2	0.12
2005-12-13	4	190	188.67	0.2	188.55	0.08
2005-12-13	4	60	60.29	0.16	60.14	0.12
2005-12-13	4	0	-0.09	0.26	-0.14	0.06
2005-12-13	5	0	0.05	0.25	-0.01	0.04
2005-12-13	5	90	89.52	0.37	89.58	0.1
2005-12-13	5	190	188.53	0.39	188.41	0.14
2005-12-13	5	60	59.98	0.34	60.18	0.07
2005-12-13	5	140	139.42	0.36	139.23	0.12
2005-12-13	5	30	30.4	0.32	30.37	0.09
2005-12-13	5	0	-0.1	0.21	-0.13	0.07
2005-12-13	6	0	-0.08	0.28	-0.13	0.06
2005-12-13	6	30	30.22	0.26	30	0.09
2005-12-13	6	190	188.68	0.21	188.31	0.09
2005-12-13	6	90	89.61	0.26	89.69	0.08
2005-12-13	6	140	139.3	0.33	139.21	0.11
2005-12-13	6	60	60.17	0.21	60.22	0.05
2005-12-13	6	0	-0.05	0.29	-0.01	0.08

[#]The level is only indicative.

The transfer standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 9). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (equation 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [*Klausen, et al.*, 2003]).

$$\mathbf{X_{TS}\ (ppb) = ([TS] + 0.07\ ppb) / 0.9991}$$

$$\mathbf{u_{TS}\ (ppb) = sqrt((0.43\ ppb)^2 + (0.0034 * X)^2)} \quad (4)$$

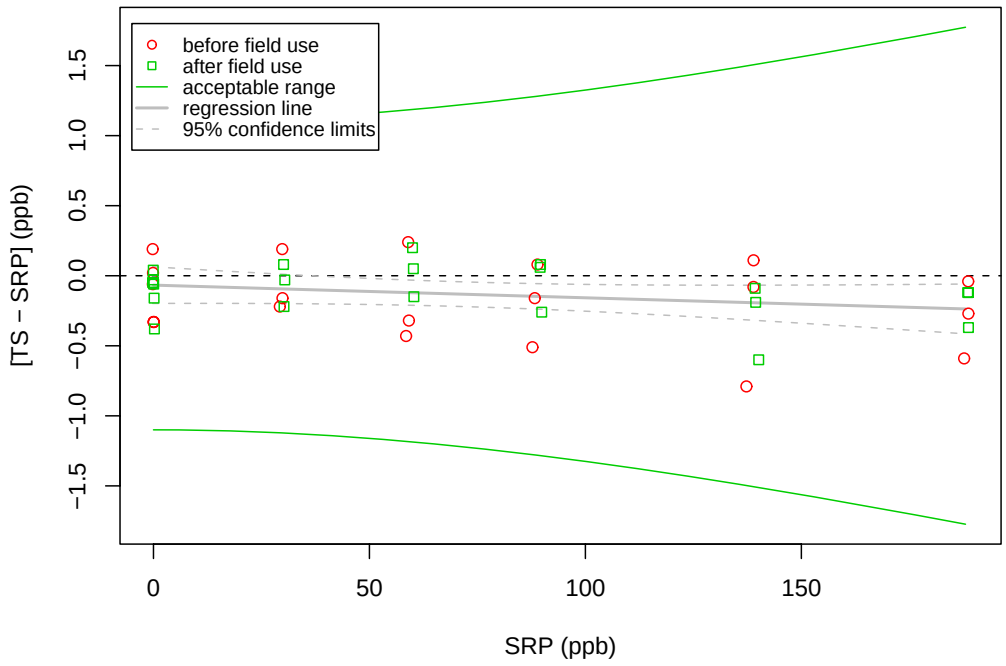

Figure 9. Deviations between transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly inter-compared with the CCL by way of travelling standards. The scale was transferred to the travelling standard using an AL5001 vacuum-fluorescence analyzer (Aerolaser), an instrument with high precision and proven linearity. Details are given in Table 14.

Table 14. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the travelling standard (TS) used during the field inter-comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale is based on two specific cylinders, CA02859 (194.7±1.9 ppb) CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Travelling standard (TS)		Dilution unit: zero air (1) and a high concentration carbon monoxide cylinder (2), in combination with a dilution unit (3)
(1) Zero air supply		Ambient air – Silicagel drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		040818_0646B, 50182±176 ppb in synthetic air.
(3) Dilution unit		Breitfuss MGM #2262/91/1. The levels used were calibrated before and after the field inter-comparison against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851).
Connection between instruments		Ca. 2 m 6 mm PTFE
Data acquisition		Aerolaser 1-min averages
Levels (ppb)		0, 75, 100, 150, 200, 250, 300, 400, 500
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 15. Calibration of the Breitfuss dilution system and carbon monoxide mixing ratios at different levels determined with WCC-Empa reference before and after the audit.

	Mass Flow Controller MFC 1 (mL min^{-1})		Mass Flow Controller MFC 2 (mL min^{-1})		Carbon Monoxide Mixing Ratio (ppb)	
Date	**Set**	**Measured#**	**Set**	**Measured**	**Calc.**	**Measured#**
2005-10-11	4000.0	3995.8 ± 4.1	0.000	0.209 ± 0.009	0.0	0.3 ± 0.5
2005-10-11	3992.0	4001.2 ± 2.3	7.981	8.109 ± 0.011	101.5	101.5 ± 0.7
2005-10-11	3994.0	4007.1 ± 0.7	5.986	6.105 ± 0.013	76.3	76.7 ± 1.0
2005-10-11	3980.0	3994.3 ± 0.3	19.953	20.141 ± 0.010	251.8	253.0 ± 0.8
2005-10-11	3976.1	3991.0 ± 0.6	23.944	24.164 ± 0.008	302.0	301.7 ± 0.9
2005-10-11	3988.0	4002.4 ± 0.5	11.972	12.119 ± 0.006	151.5	151.6 ± 1.7
2005-10-11	3984.0	3999.3 ± 0.3	15.963	16.123 ± 0.010	201.5	201.1 ± 1.2
2005-10-11	3960.1	3976.6 ± 0.7	39.907	40.245 ± 0.007	502.8	502.5 ± 1.4
2005-10-11	3968.1	3984.2 ± 0.4	31.925	32.184 ± 0.010	402.1	403.1 ± 1.5
2005-12-13	4000.0	4008.2 ± 2.6	0.000	0.195 ± 0.009	0.0	0.2 ± 1.1
2005-12-13	3992.0	4007.1 ± 1.0	7.981	8.129 ± 0.012	101.6	101.7 ± 0.8
2005-12-13	3994.0	4008.2 ± 0.9	5.986	6.121 ± 0.012	76.5	76.1 ± 0.8
2005-12-13	3980.0	3992.4 ± 0.6	19.953	20.141 ± 0.010	251.9	251.9 ± 1.5
2005-12-13	3976.1	3988.0 ± 0.6	23.944	24.152 ± 0.006	302.1	302.6 ± 1.4
2005-12-13	3988.0	3998.4 ± 0.5	11.972	12.122 ± 0.007	151.7	151.4 ± 1.5
2005-12-13	3984.0	3994.0 ± 0.5	15.963	16.125 ± 0.010	201.8	202.1 ± 1.2
2005-12-13	3960.1	3970.3 ± 0.5	39.907	40.203 ± 0.008	503.0	503.4 ± 1.3
2005-12-13	3968.1	3977.7 ± 0.5	31.925	32.160 ± 0.009	402.5	402.6 ± 1.2

#Average±sd (n =10)

Methane

WCC-Empa refers to the latest WMO/GAW methane scale (hereafter: NOAA04 scale) [*Dlugokencky, et al.*, 2005] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 16). The scale was transferred to the travelling standards using a Varian 3400 gas chromatograph with an FID detector. Details of the travelling standards are given in Table 17.

Table 16. NOAA/GMD CH_4 laboratory standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Cylinder#	Methane [ppb]* (NOAA04)
CA05316	1712.5 ± 0.30 ppb
CA04462	1817.4 ± 0.19 ppb
CA04580	1905.1 ± 0.24 ppb

* Certificates (CMDL83) from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316). Values were converted to NOAA04 scale by applying a factor of 1.0124.

Table 17. Calibration of the methane travelling standards with the WCC-Empa reference before and after the audit.

Date	2005-06-14	2005-10-04	2005-12-14
Cylinder identification	CH_4 (ppb)#	CH_4 (ppb)#	CH_4 (ppb)#
050419_FA02482	1772.5 ± 0.9		1772.6 ± 0.9
050701_FA02505		1832.7 ± 1.9	1832.6 ± 1.9
050419_FA02488		1841.5 ± 1.2	1840.9 ± 1.2
050419_FA02479		1879.6 ± 1.4	1879.6 ± 1.4
050415_FA02466		2004.6 ± 1.8	2004.4 ± 1.8

#Average±sd (n = 10)

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Ozone Audit Executive Summary (RYO)

0.1	Station Name:	Ryori
0.2	GAW ID:	RYO
0.3	Coordinates/Elevation:	39.033°N, 141.833°E (260 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	24 November, 2005
1.2	Auditors:	Dr. C. Zellweger, Dr. J. Klausen
1.3	Station staff involved in audit:	K. Tsuboi (JMA), K. Kimura (Ryori)
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS #54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	$(0.9991\pm0.0010) \times [SRP] - (0.07\pm0.09)$
1.6	Ozone Analyser [OA]	
1.6.1	Model:	Ebara Jitsugyo EG-2001 FTP #3453069
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset -1.5, Span 0.948
1.6.4	Calibration at start of audit (ppb):	$[OA] = (0.9968\pm0.0000) \times [SRP] - (0.52\pm0.04)$
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] + 0.52) / 0.9968$
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.62e\text{-}5 \times X^2)^{1/2}$
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 05/4 – Part A

[OA]: Instrument readings; [SRP]: SRP readings; X: mixing ratios on SRP scale

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Carbon Monoxide Audit Executive Summary (RYO)

0.1	Station Name:	Ryori
0.2	GAW ID:	RYO
0.3	Coordinates/Elevation:	39.033°N, 141.833°E (260 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	24 – 25 November, 2005
1.2	Auditors:	Dr. C. Zellweger, Dr. J. Klausen
1.3	Station staff involved in audit:	K. Tsuboi (JMA), K. Kimura (Ryori)
1.4	CO Reference:	WMO-2000
1.5	CO Transfer Standard [TS]	
1.5.1	CO Cylinder:	040818_0646B, 50182±176 ppb (α=0.05)
1.5.2	Zero Air:	Ambient Air, Purafil, Sofnocat, filter (WCC-Empa)
1.5.3	Dilution unit:	Breitfuss MGM #2262/91
1.5.4	Range of calibration:	0 – 500 ppb
1.6	CO analyzer [CA]	
1.6.1	Model:	Horiba GA-360 S/N 16827903L
1.6.2	Range of calibration:	0 – 500 ppb
1.6.3	Coefficients at start of audit	not applicable
1.6.4	Calibration at start of audit (ppb):	$CO = (0.992 \pm 0.002) \times X + (6.5 \pm 0.5)$
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 6.5) / 0.992$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (1.6\ ppb^2 + 2.94e\text{-}05 \times X^2)^{1/2}$
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 05/4 – Part A

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 CO scale.

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Methane Audit Executive Summary (RYO)

0.1	Station Name:	Ryori
0.2	GAW ID:	RYO
0.3	Coordinates/Elevation:	39.033°N, 141.833°E (260 m a.s.l)
Parameter:		Methane

1.1	Date of Audit:	23 November, 2005
1.2	Auditors:	Dr. C. Zellweger, Dr. J. Klausen
1.3	Station staff involved in audit:	K. Tsuboi (JMA), K. Kimura (Ryori)
1.4	CH_4 Reference:	NOAA04
1.5	CH_4 Transfer Standard [TS]	
1.5.1	CH_4 Cylinders: 050701_FA02505, 1832.65±0.24 ppb 050419_FA02488, 1841.22±0.49 ppb 050419_FA02479, 1879.59±0.21 ppb 050415_FA02466, 2004.49±0.25 ppb	050419_FA02482, 1772.54±0.21 ppb
1.6	CH_4 analyzer [CA]	
1.6.1	Model:	Horiba GA-360 S/N 16827903L
1.6.2	Range of calibration:	1770 –2005 ppb
1.6.3	Coefficients at start of audit	not applicable
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99997 \pm 0.00031) \times X$
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = CH_4 / 0.99997$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (10.5\ ppb^2 + 1.10e\text{-}07 \times X^2)^{1/2}$
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 05/4 – Part A

[CH_4]: Instrument readings; X: mixing ratios on the NOAA04 CH_4 scale.

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