8. NOAA-ICP

8.1. Round-robin cylinders (NOAA-ICP)

The WMO Central Calibration Laboratory for CO at NOAA proposed a comparison of CO measurements to the JMA and other laboratories in Japan as well as the WMO/WCC for CO at the Swiss Federal Laboratories for Materials Science and Technology (Empa) in Zurich (Novelli, 2016). This NOAA InterComParison (NOAA-ICP) experiment, which took place in 2013–2014, provided a good opportunity for the iceGGO program to compare results directly with the WMO CO scale (Novelli et al., 2003). NOAA prepared six round-robin cylinders for the NOAA-ICP experiment. Two cylinders (CB10067, CB09973) were also assayed as part of the WMO/IAEA Round Robin Comparison Experiment (RR 6), not only for CO but also for CO_2 and its isotopes, CH_4, N_2O, and other trace gases (SF_6, H_2, O_2/N_2) (www.esrl.noaa.gov/gmd/ccgg/wmorr/index.html).

Details of the six round-robin cylinders and the CO results have been reported elsewhere (Novelli, 2016). The cylinders (29.5 L AL) with tapered valves were filled with ambient dry air at Niwot Ridge in Colorado, USA. They were modified from ambient levels to higher or lower concentrations by adding aliquots of either 5 ppm CO or Ultra High Purity zero-air. The air in the cylinders contained final CO concentrations that ranged from ~50 to ~350 ppb. Dedicated two-stage regulators were prepared for CO measurements by NOAA.

To examine the isotope effect of the NDIR CO_2 measurements, the $\delta^{13}C$ and $\delta^{18}O$ of the CO_2 in the six cylinders were precisely measured by IRMS by the AIST and TU and

found to be about –8.6 to –9 ‰ and –1 to –24 ‰, respectively (Table 22). This isotopic composition is similar to that of natural air, but it is very different from that of the combusted petroleum CO_2 (around –30 ‰ for $\delta^{13}C$) used for the measurements by all Japanese participants.

Table 22. Isotopic composition of the CO_2 in the six round-robin gases prepared for the NOAA-ICP experiment.

Cylinder Identification	$\delta^{13}C(CO_2)$* ‰	$\delta^{13}C(CO_2)$** ‰	$\delta^{18}O(CO_2)$* ‰	$\delta^{18}O(CO_2)$** ‰
CB09739	-9.025 ±0.027	-8.949 ±0.009	-24.072 ±0.170	-24.255 ±0.011
CB10067$	-8.806 ±0.013	-8.758 ±0.009	-9.607 ±0.060	-9.797 ±0.006
CB09997	-8.679 ±0.026	-8.655 ±0.011	-1.278 ±0.027	-1.431 ±0.011
CB09977	-8.673 ±0.014	-8.645 ±0.007	-1.347 ±0.033	-1.479 ±0.010
CB09973$	-8.719 ±0.024	-8.678 ±0.014	-2.091 ±0.042	-2.214 ±0.006
CB10036	-8.772 ±0.004	-8.720 ±0.011	-3.510 ±0.009	-3.582 ±0.017

*Measured by IRMS of TU

**Measured by IRMS of AIST

$Used for the WMO Round Robin 6

8.2. Measurement methods (NOAA-ICP)

Six laboratories (NOAA, Empa, JMA, MRI, NIES, and TU) participated in the comparison of CO measurements for the NOAA-ICP experiment from May 2013 to September 2014. Table 23 lists the participating laboratories and details about their CO

analytical methods. NOAA and Empa measured the CO concentrations at the beginning and end of the experiment to evaluate CO drift.

Six instruments from as many manufacturers and five different analytical methods were used. NOAA and Empa reported their measurements in 2013 on the WMO X2004 scale. The measurements made in 2014 were reported on the transitional X2014 scale. That scale has since been finalized and was released in December 2015 as the WMO X2014A. The standards for CO concentrations, first assigned in 1993, were revised to X2014A and are available at www.esrl.noaa.gov/gmd/ccl/refgas.html. NOAA, Empa, and the JMA also reported their results with respect to the X2014A. The three other laboratories, MRI, NIES, and TU, used their own standard gas scales: MRI, NIES09, and TU2010, respectively.

Table 23. The six laboratories that participated in the NOAA-ICP and their CO analytical methods, instruments, and calibration scales.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
NOAA	ICOS	ICOS, N2O/CO, Los Gatos Inc	WMO X2004 & X2014 Scales			May 2013
Empa	QLC	QLC, mini-cw Aerodyne Research	WMO X2004 & X2014 Scales			June 2013
JMA	GC/HgO	TRA-1, Round Science Inc.	WMO X2004 & X2014A Scales	50 ppb - 350 ppb	4	October 11, 2013 & June 5, 2014
MRI	GC/FID	AG-1F (FID), Yanaco	MRI Scale	50 ppb - 500 ppb	5	December 3-7, 2013
NIES	VURF	AL5002 Aero-Laser, GmbH	NIES09 Scale	0 ppb - 5000 ppb	4	February 1-2, 2014
TU	GC/HgO	RGA Trace Analytical Inc.	TU2010 Scale	50 ppb - 320 ppb	4	March 17-18, 2014
Empa	QLC	QLC, mini-cw Aerodyne Research	WMO X2014A Scale			August 2014
NOAA	ICOS	ICOS, N2O/CO, Los Gatos Inc	WMO X2014A Scale			September 2014

The five Japanese laboratories (JMA, MRI, AIST, NIES, and TU) measured not only the CO concentrations but also the CO_2, CH_4, and N_2O concentrations in the NOAA-ICP

cylinders. The participating laboratories and their detailed analytical methods for measuring CO_2, CH_4, and N_2O are provided in Tables 24, 25, and 26, respectively.

Table 24. The five Japanese laboratories that participated in the NOAA-ICP for CO_2 and their CO_2 analytical methods, instruments, and calibration scales.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
JMA	NDIR	VIA-510R, Horiba	WMO X2007 Scale	350 ppm - 440 ppm	7	October 23, 2013 & May 30, 2014
MRI	NDIR	LI-6252, Licor	MRI 1987 Scale	350 ppm - 430 ppm	6	November 19-22, 2013
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	340 ppm - 430 ppm	6	December 27, 2013-January 19,2014
NIES	NDIR	LI-6252, Licor	NIES09 Scale	340 ppm - 450 ppm	8	January 28-29, 2014
TU	NDIR	VIA-500R, Horiba	TU2010 Scale	350 ppm - 430 ppm	6	February 19-March 6, 2014

Table 25. The five Japanese laboratories that participated in the NOAA-ICP for CH_4 and their CH_4 analytical methods, instruments, and calibration scales.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
JMA	GC/FID	GC-14BPF (FID), Shimadzu	WMO X2004 Scale	1610 ppb - 2170 ppb	5	October 19, 2013 & May 28, 2014
MRI	CRDS	CRDS, Piccaro	MRI Scale	1600 ppb - 2100 ppb	5	November 26-30, 2013
AIST	GC/FID	GC-14BPF (FID), Shimadzu	AIST Scale	1010 ppb - 2530 ppb	4	January 6-21, 2014
NIES	GC/FID	HP5890 (FID), Agilent	NIES94 Scale	1250 ppb - 2500 ppb	6	February 1-2, 2014
TU	GC/FID	6890NF (FID), HP	TU2008 Scale	1300 ppb - 2800 ppb	4	March 5-10, 2014

Table 26. The three Japanese laboratories that participated in the NOAA-ICP for N_2O and their N_2O analytical methods, instruments, and calibration scales.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
JMA	GC/ECD	GC-2014 (ECD), Shimadzu	WMO X2006A Scale	280 ppb - 340 ppb	5	October 2, 2013 & July 2, 2014
NIES	GC/ECD	Agilent 6890 (ECD), Agilent	NIES 96 Scale	250 ppb - 400 ppb	4	February 1-2, 2014
TU	GC/ECD	Agilent 6890 (ECD), Agilent	TU2006 Scale	320 ppb - 370 ppb	3	February 25-26, 2014

8.3. Results of NOAA-ICP

8.3.1. Results for CO (NOAA-ICP)

Table 27 provides the CO results for the six round-robin cylinders assayed by the six laboratories. The analytical precision of most of the measurements in all the laboratories was less than 0.8 ppb, although the MRI precision was larger due to the different analytical method (GC/FID).

NOAA and Empa reported measurements on three versions of the WMO CO scale. The results were sensitive to the version of the scale and the date of calibration. The results of these two laboratories agreed within ~1.3 ppb on the 2014A scale, although the differences between the JMA and NOAA ranged from ~1 to ~5 ppb.

CO concentrations in high-pressure cylinders are known to drift at rates of <1 ppb/yr. Empa and NOAA measured the air mixtures at the beginning and end of the experiment to evaluate possible changes in the standards. However, the results were inconclusive. Changes in the NOAA concentrations between the first and last measurements were ~1 to ~1.6 ppb/yr. The Empa data indicated increases of ~0.6 to ~1.3 ppb/yr.

Table 27. CO concentrations (ppb) measured during the NOAA-ICP experiment. The reported analytical precisions are indicated in parentheses.

	Cylinder Identifications					
Laboratory	CB09739	CB10067	CB09997	CB09977	CB09973	CB10036
NOAA *	51.9 (0.1)	99.1 (0.1)	153.4 (0.1)	176.2 (0.1)	236.0 (0.1)	346.7 (0.2)
NOAA ***	53.8 (0.2)	101.5 (0.2)	156.3 (0.1)	179.3 (0.1)	239.6 (0.1)	352.2 (0.2)
Empa *	51.8 (0.1)	99.0 (0.0)	153.2 (0.1)	175.7 (0.1)	235.7 (0.1)	346.8 (0.1)
Empa ***	54.7 (0.1)	102.3 (0.0)	156.9 (0.1)	179.6 (0.0)	239.9 (0.1)	351.7 (0.1)
JMA *	53.7 (0.2)	100.9 (0.2)	156.4 (0.2)	179.6 (0.2)	240.3 (0.3)	348.9 (0.3)
JMA ***	55.9 (0.2)	102.9 (0.2)	158.4 (0.2)	181.8 (0.2)	243.2 (0.3)	354.5 (0.3)
MRI	55.7 (3.0)	105.8 (1.8)	159.5 (3.6)	182.4 (1.5)	245.6 (1.2)	359.8 (1.5)
NIES	57.9 (0.0)	106.0 (0.0)	158.9 (0.6)	181.8 (0.4)	243.3 (0.1)	355.0 (0.8)
TU	51.9 (0.3)	103.8 (0.4)	162.2 (0.4)	185.9 (0.3)	245.5 (0.4)	354.6 (0.8)
JMA *	54.4 (0.4)	101.4 (0.5)	157.2 (0.6)	180.6 (0.3)	242.3 (0.4)	348.7 (0.7)
JMA ***	56.9 (0.4)	103.3 (0.5)	158.7 (0.6)	182.2 (0.3)	244.4 (0.4)	354.3 (0.7)
Empa **	55.2 (0.1)	101.8 (0.1)	155.5 (0.0)	177.9 (0.0)	237.6 (0.1)	348.2 (0.1)
Empa ***	55.1 (0.1)	102.4 (0.1)	156.9 (0.0)	179.6 (0.0)	240.2 (0.1)	352.4 (0.1)
NOAA **	54.6 (0.0)	101.6 (0.0)	155.9 (0.0)	178.6 (0.1)	239.5 (0.0)	352.4 (0.5)
NOAA ***	56.1 (0.0)	103.4 (0.0)	157.9 (0.0)	180.6 (0.1)	241.2 (0.0)	353.7 (0.4)

* Reported on the WMO X2004 scale
** Reported on the WMO X2014 scale
***Revised on the WMO X2014A scale

Figure 8 shows the differences in the CO concentrations measured by each laboratory (Laboratory X) and NOAA for the six cylinders. The concentrations of the NOAA, Empa, and JMA experiments are based on the WMO X2014A scale in Figure 8. The differences (Laboratory X minus NOAA) for these six cylinders ranged from –2 ppb to +8 ppb and often exceeded the WMO compatibility criterion of ±2 ppb.

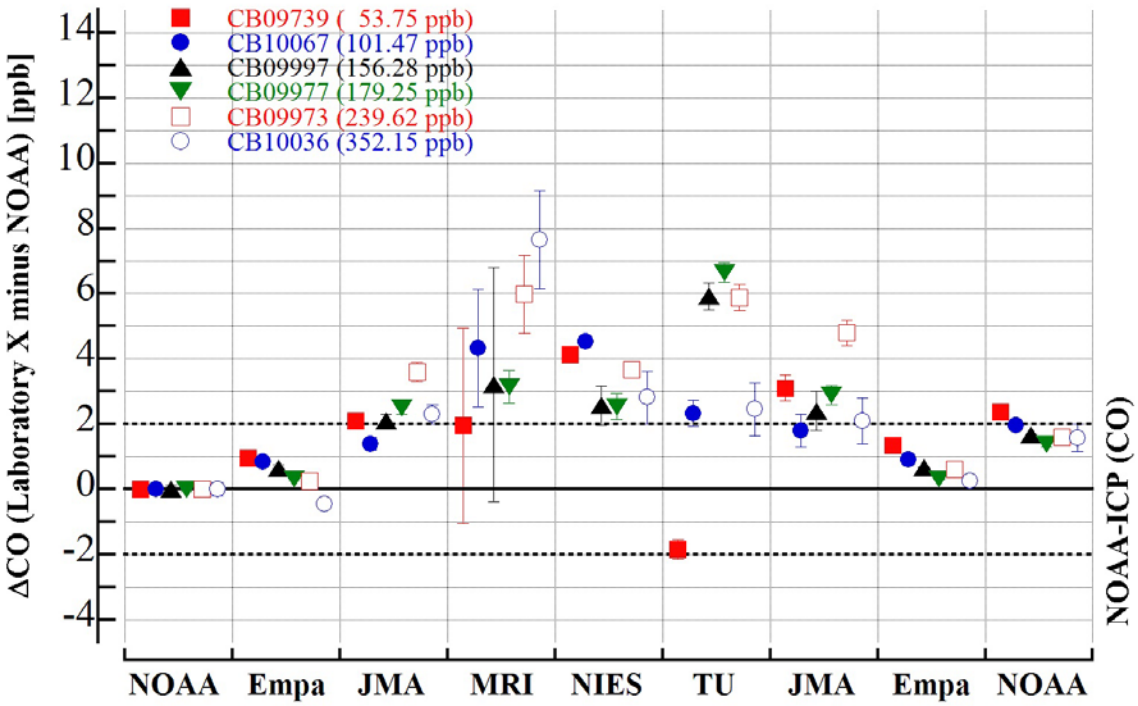

Figure 8. Differences (Laboratory X minus NOAA) of CO concentrations in six round-robin cylinders assayed for the NOAA-ICP. The error bars represent the ± measurement uncertainty reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CO measurement compatibility.

8.3.2. Results for CO_2 (NOAA-ICP)

Table 28 summarizes the CO_2 results for the six cylinders assayed by the five Japanese laboratories that participated in the NOAA-ICP experiment. Figure 9 shows the differences of the CO_2 concentrations measured by each laboratory (Laboratory X) and the NIES for the six cylinders. The results of the NOAA assays of two cylinders used at the WMO/IAEA RR-6 experiment are also plotted. The differences (Laboratory X minus NIES) ranged from –0.2 ppm to +0.3 ppm for these six cylinders.

Table 28. CO_2 concentrations (ppm) measured during the NOAA-ICP experiment. The reported analytical precisions are indicated in parentheses.

	Cylinder Identifications					
Laboratory	CB09739	CB10067	CB09997	CB09977	CB09973	CB10036
JMA	355.21 (0.012)	376.25 (0.014)	389.88 (0.007)	397.28 (0.012)	404.91 (0.009)	419.66 (0.011)
MRI	354.90 (0.007)	376.14 (0.015)	389.82 (0.014)	397.24 (0.015)	404.81 (0.008)	419.49 (0.012)
AIST	355.21 (0.008)	376.42 (0.008)	390.10 (0.011)	397.50 (0.008)	405.13 (0.008)	419.85 (0.013)
NIES	355.08 (0.00)* (+0.05)**	376.20 (0.01)* (+0.05)**	389.90 (0.01)* (+0.06)**	397.29 (0.00)* (+0.06)**	404.91 (0.01)* (+0.06)**	419.64 (0.00)* (+0.05)**
TU	355.24 (0.01)	376.45 (0.01)	390.16 (0.00)	397.56 (0.01)	405.20 (0.01)	419.87 (0.01)
JMA	355.22 (0.020)	376.28 (0.011)	389.89 (0.012)	397.29 (0.012)	404.92 (0.015)	419.67 (0.016)

*Corrected by isotope effect
**Isotope effect

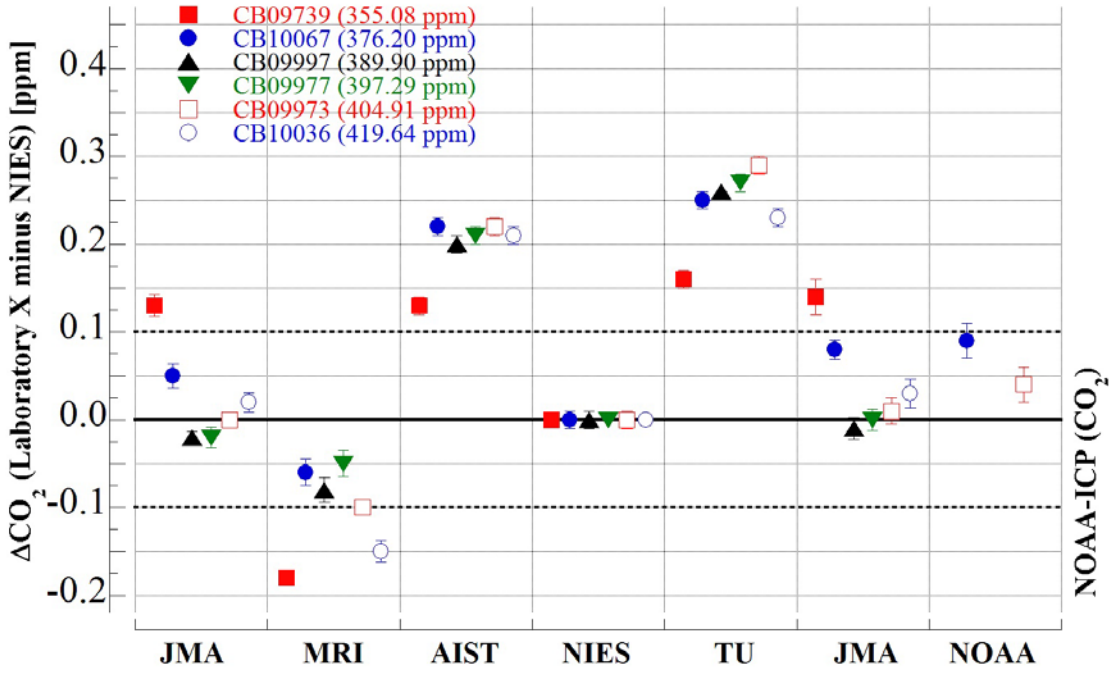

Figure 9. Differences (Laboratory X minus NIES) of CO_2 concentrations for six round-robin cylinders assayed for the NOAA-ICP study. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±0.1 ppm) for network compatibility in the Northern Hemisphere.

8.3.3. Results for CH_4 (NOAA-ICP)

Table 29 summarizes the CH_4 results for the six cylinders assayed by the five Japanese laboratories that participated in the NOAA-ICP experiment. Figure 10 shows the differences of the CH_4 concentrations measured by each laboratory (Laboratory X) and the JMA for the six cylinders. The NOAA results for two cylinders used in the WMO/IAEA RR-6 experiment are also plotted. The differences (Laboratory X minus NIES) for these six cylinders ranged from –2 ppb to +6 ppb.

Table 29. CH_4 concentrations (ppb) measured during the NOAA-ICP experiment. The reported analytical precisions are indicated in parentheses.

	Cylinder Identifications					
Laboratory	CB09739	CB10067	CB09997	CB09977	CB09973	CB10036
JMA	1569.8 (1.3)	1733.6 (1.2)	1841.1 (1.4)	1879.9 (1.8)	1937.4 (1.4)	2021.3 (0.7)
MRI	1569.7 (0.2)	1734.3 (0.2)	1843.7 (0.2)	1882.7 (0.2)	1940.2 (0.3)	2025.7 (0.2)
AIST	1570.4 (1.3)	1735.2 (1.4)	1843.9 (1.6)	1883.8 (1.7)	1940.1 (1.8)	2025.4 (1.5)
NIES	1571.3 (0.7)	1736.3 (0.3)	1845.6 (0.0)	1884.8 (0.3)	1941.9 (1.4)	2027.2 (0.5)
TU	1570.7 (1.2)	1734.7 (1.5)	1843.0 (1.4)	1882.7 (1.1)	1939.0 (1.6)	2022.6 (1.1)
JMA	1570.3 (1.2)	1732.7 (1.4)	1840.7 (1.1)	1879.5 (1.5)	1935.9 (1.6)	2020.7 (1.2)

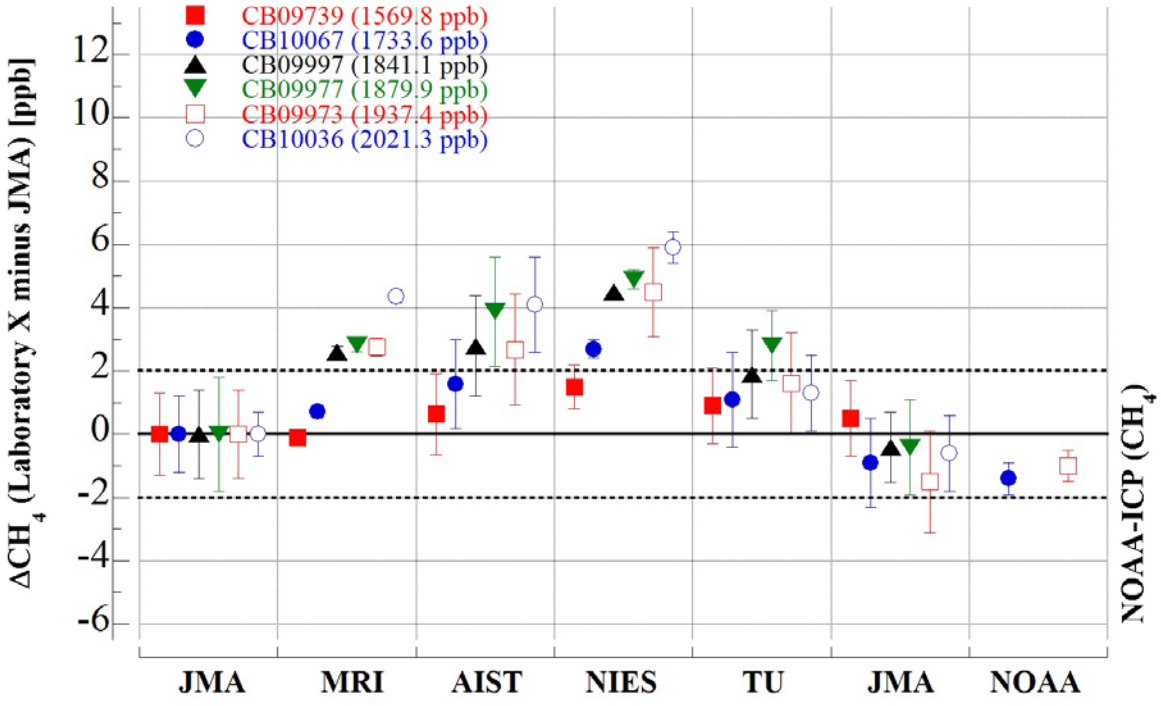

Figure 10. Differences (Laboratory X minus JMA) of CH_4 concentrations in six round-robin cylinders assayed during the NOAA-ICP experiment. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CH_4 measurement compatibility.

8.3.4. Results for N_2O (NOAA-ICP)

Table 30 summarizes the N_2O results for the six cylinders assayed by the three Japanese laboratories that participated in the NOAA-ICP N_2O experiment. Figure 11 shows differences in N_2O concentrations measured by each laboratory (Laboratory X) and the JMA for the six cylinders. The NOAA results for two cylinders used in the WMO/IAEA RR-6 experiment are also plotted. The differences (Laboratory X minus NIES) for these six cylinders ranged from –1.5 ppb to +0.6 ppb.

Table 30. N_2O concentrations (ppb) measured during the NOAA-ICP experiment.The reported precisions are shown in parentheses.

	Cylinder Identifications					
Laboratory	CB09739	CB10067	CB09997	CB09977	CB09973	CB10036
JMA	320.6 (0.3)	327.0 (0.5)	327.0 (0.4)	326.4 (0.3)	327.5 (0.4)	329.3 (0.3)
NIES	318.7 (0.0)	325.2 (0.1)	324.9 (0.1)	324.4 (0.2)	325.8 (0.3)	327.3 (0.2)
TU	319.6 (0.2)	326.3 (0.2)	326.0 (0.2)	325.7 (0.2)	327.0 (0.4)	328.7 (0.3)
JMA	320.5 (0.2)	327.1 (0.5)	326.8 (0.4)	326.8 (0.5)	327.8 (0.3)	329.0 (0.2)

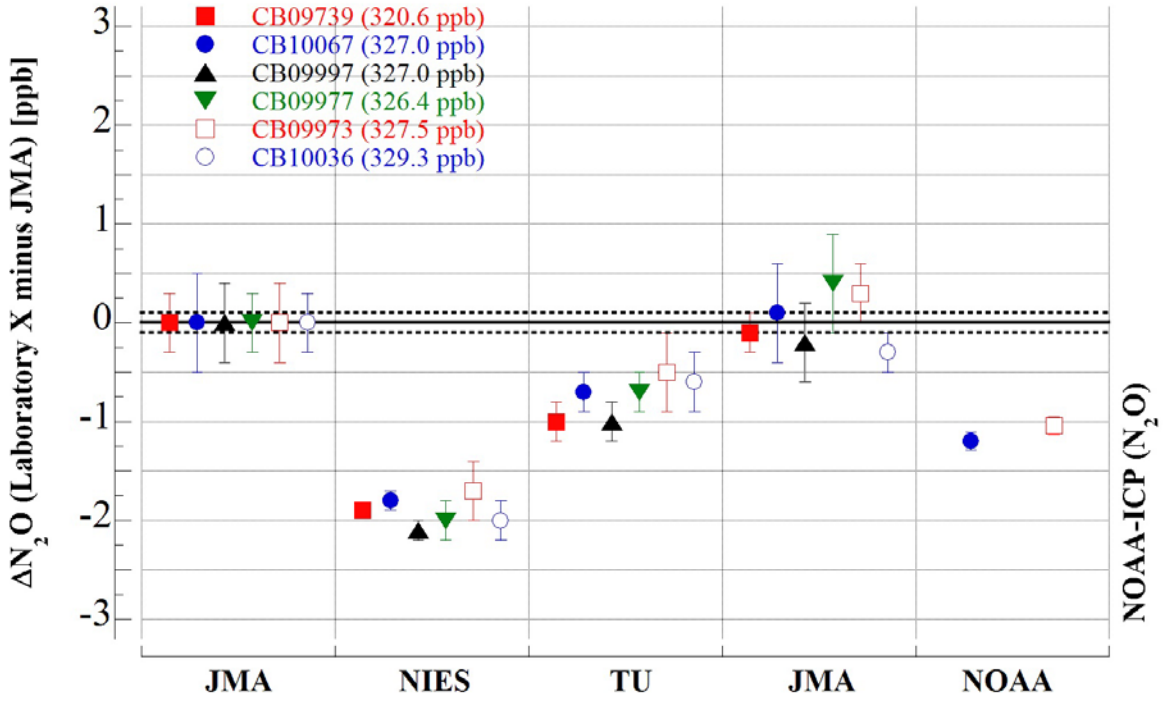

Figure 11. Differences (Laboratory X minus JMA) of N_2O concentrations in six round-robin cylinders assayed for the NOAA-ICP study. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±0.1 ppb) for N_2O measurement compatibility.