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気象研究所技術報告

第79号

2012年から2016年に実施された温室効果ガス観測に関する相互比較実験（iceGGO）

坪井一寛、中澤高清、松枝秀和、町田敏暢、青木周司、森本真司
後藤大輔、下坂琢哉、加藤健次、青木伸行、渡邉卓朗、向井人史
遠嶋康徳、勝又啓一、村山昌平、石戸谷重之、藤谷徳之助、小出寛
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気象研究所
METEOROLOGICAL RESEARCH INSTITUTE, JAPAN
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InterComparison Experiments for Greenhouse Gases Observation (iceGGO) in 2012–2016

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序

気象研究所海洋・地球化学研究部は、大気・海洋に存在する各種の化学物質の時間的・空間的な変動を把握し、地球環境変動を化学的に解明するための研究を行っている。特に、大気中の二酸化炭素等の温室効果ガスの長期観測を重点課題の一つとして実施し、その変動を正確に捉えるための基準となる標準ガスに基づく観測スケールの開発と維持管理手法の確立も行ってきた。これまでの研究実績を活用し、気象庁が実施する温室効果ガス観測や較正業務の向上を図ってきた。観測スケールの運用や観測データの品質管理に対して技術支援を行い、より精度の高い定常観測の運営に貢献している。

平成22年度に地球観測連携拠点（温暖化分野）の枠組みの下、気象研究所等温室効果ガス観測を実施する国内研究機関や現業観測を行っている気象庁に加えて、国家計量機関も参画した「温室効果ガス観測データ標準化ワーキンググループ」が設置された。この活動では、国内各機関の観測データを統合し解析するための第一歩として、相互の観測スケールの差異を把握することを目的として、標準ガスの巡回比較実験を行うことが合意された。実験は、平成24年度から約5年間にかけて7つの機関が参加して行われた。これら一連の実験では、国内の観測スケールの比較に留まらず、気象庁が維持する世界気象機関（WMO）スケールとの差異を示す新たな知見も得られ、国内外の学会でも発表された。また、測定原理や分析計機種の違いによる測定誤差についても精密な評価を行い、観測データの品質向上に繋がる重要な研究成果が得られた。

本技術報告は、国内観測機関と計量機関の連携による標準ガス巡回比較実験の詳細とその結果を取りまとめたものである。今後、各機関の観測データを比較・統合し、データ標準化を図る際の有益な指針となることが期待される。

気象研究所海洋・地球化学研究部長

倉賀野　連

2012年から2016年に実施された温室効果ガス観測に関する相互比較実験（iceGGO）

坪井一寛[1], 中澤高清[2], 松枝秀和[1], 町田敏暢[3], 青木周司[2], 森本真司[2], 後藤大輔[4], 下坂琢哉[5], 加藤健次[5], 青木伸行[5], 渡邉卓朗[5], 向井人史[3],遠嶋康徳[3], 勝又啓一[3], 村山昌平[6], 石戸谷重之[6], 藤谷徳之助[7], 小出寛[8], 髙橋正臣[8], 川﨑照夫[8], 滝沢厚詩[8], 澤庸介[1]

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地球温暖化観測を実施している日本の主要な研究・行政機関は「地球観測連携拠点（温暖化分野）」の活動に参画し、この枠組みのもと「温室効果ガス観測データ標準化ワーキンググループ」が発足し、国内において標準ガス比較実験を共同実施することが合意された。比較実験は、長期の観測データの品質向上と高精度の統合データベース化を達成することを目指して、各機関が保有する標準ガス・スケールの差異を明らかにすることを主要な目的とした。この活動には国家計量機関である産業技術総合研究所の計量標準総合センター（NMIJ: National Metrology Institute of Japan）も参加し、2012年から総合的なプロジェクト「温室効果ガス観測に関する相互比較実験」(InterComparison Experiments for Greenhouse Gases Observation: iceGGO）が実現することになった。気象庁（JMA: Japan Meteorological Agency）は世界気象機関（WMO: World Meteorological Organization）の全球大気監視（GAW: Global Atmosphere Watch）計画の下で運営している全球大気監視較正センター（WCC: World Calibration Center）の活動の一環として、 アジア及び南西太平洋地区のメタン巡回比較実験を継続的に実施しており、iceGGOとも連携し国内における比較実験を行った。

iceGGOにはNMIJとJMAのほか、東北大学（TU: Tohoku University)、国立極地研究所（NIPR: National Institute of Polar Research)、国立環境研究所（NIES: National

Institute for Environmental Studies）、産業技術総合研究所（AIST: National Institute of Advanced Industrial Science and Technology）、気象研究所（MRI: Meteorological Research Institute）を含めて合計7つの機関が参加した。また、実験の立案・実行と結果のとりまとめについては、「地球観測連携拠点（温暖化分野）」の活動の一部として、連携拠点を運営する地球温暖化観測推進事務局（OCCCO: Office for Coordination of Climate Change Observation）の全面的な協力を受けた。このようなオール・ジャパン体制による本格的な共同実験は初めての試みであり、その成果は国内外の研究集会や論文として発表すると同時に、JMAを通してWMOにも報告された。本報告は、2012年から2016年の5年間に実施された実験結果の詳細をまとめたもので、今後の地球温暖化の研究や温暖化対策の立案の基盤となる情報として有効に活用されることが期待される。

iceGGOでは、地球温暖化観測にとって重要な二酸化炭素（CO_2）、メタン（CH_4）、一酸化炭素（CO）、一酸化二窒素（N_2O）の4種類の微量気体を対象ガスとし、それらを大気濃度レベルに充填した高圧ガス容器を巡回して、各機関で測定を行い、結果を比較する手法を採用した。実験は6回のシリーズに分けて実施し、それぞれiceGGO-1(CH_4)、iceGGO-2(CO_2)、iceGGO-3(CO_2)、iceGGO-4(CO)、iceGGO-5(N_2O)、iceGGO-6(CH_4)とした。さらに7回目の実験として、米国海洋大気庁（NOAA: the National Oceanic and Atmospheric Administration）からCO測定比較のために輸入された6本の高圧ガス容器についてもiceGGOの一環として測定を実施したことから、NOAA-ICP（InterComParison）として本報告に加えることとした。なお、NOAA-ICPの2本の容器は、WMO/IAEAが主催する第6回国際巡回比較実験（http://www.esrl.noaa.gov/gmd/ccgg/wmorr/index.html）としても位置付けられた。

本研究で実施された合計 7 回のシリーズの実験概要を下記の表にまとめた。巡回した比較ガス容器は合計 36 本で、その内の 10 本は NMIJ において ISO-6142 に基づいた質量比混合法で調製された。

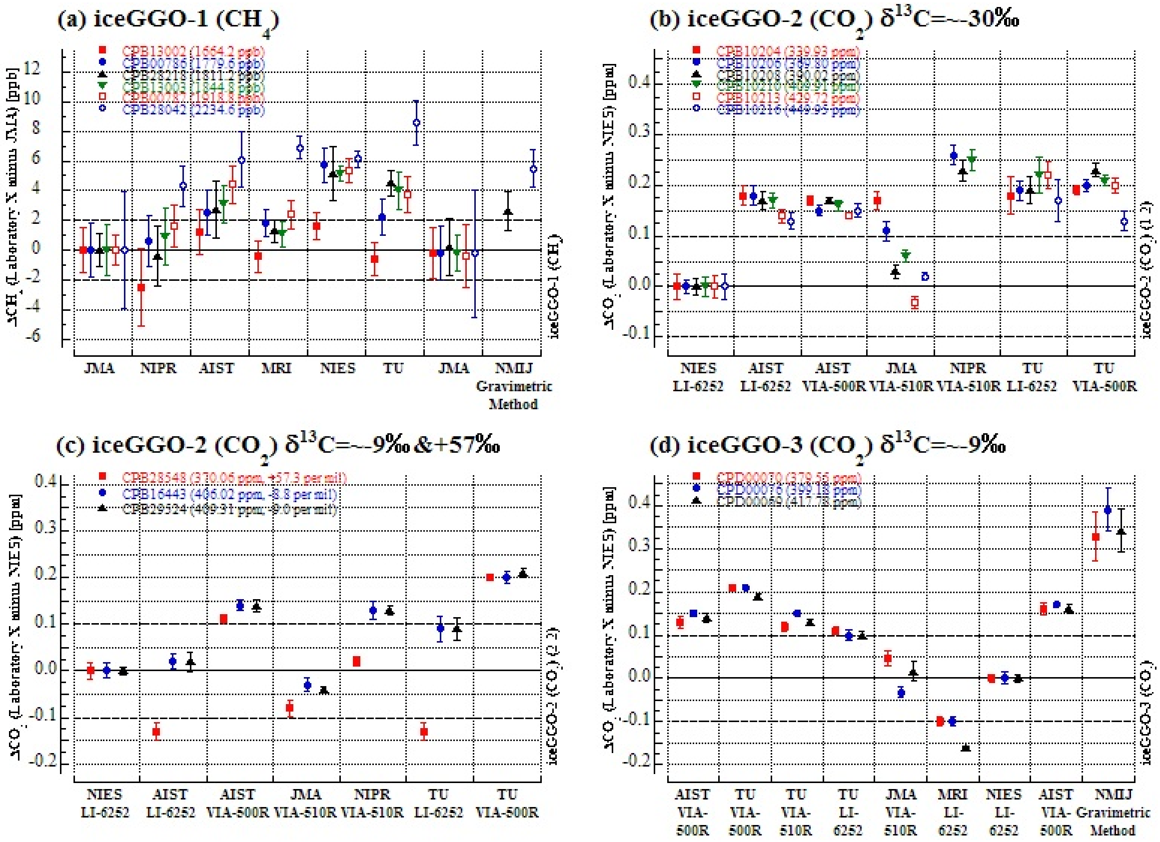
表ーI. iceGGO で実施された合計7回のシリーズの比較実験の概要。

	Total (NMIJ)	Range of concentration	Analytical method	Laboratories (Standard scale)
iceGGO-1 (CH_4)	6	1660 – 2240 ppb CH_4	GC/FID	AIST,JMA,MRI,NIES,NIPR,TU,NMIJ
	(2)			(AIST, MRI, NIES94, NIPR, TU2008, WMO X2004)
iceGGO-2 (CO_2)	9	340 – 450 ppm CO_2	NDIR	AIST,JMA,NIES,NIPR,TU
		(δ^{13}C÷−9‰ & +55‰)	(LI6252, VIA500R,VIA510R)	(NIES09, TU2010, WMO X2007)
iceGGO-3 (CO_2)	3	380 – 420 ppm CO_2	NDIR	AIST,JMA,MRI,NIES,TU,NMIJ
	(3)	(δ^{13}C÷-9‰, δ18O÷−13%	(LI6252, VIA500R,VIA510R)	(NIES09, MRI1987,TU2010, WMO X2007)
iceGGO-4 (CO)	2	250 & 350 ppb CO	GC/HgO, GC/FID, VURF	JMA,MRI,NIES,TU,NMIJ
	(2)			(NIES09, MRI, TU2010, WMO X2004)
iceGGO-5 (N_2O)	6	280 – 340 ppb N_2O	GC/ECD, ICOS	AIST,JMA,MRI,NIES,TU,NMIJ
	(1)			(AIST, MRI2014, NIES96, TU2006, WMOX2006A)
iceGGO-6 (CH_4)	4	1800 – 2200 ppb CH_4	GC/FID, CRDS	AIST,JMA,MRI,NIES,TU,NMIJ
	(2)			(AIST, MRI, NIES94, TU2008, WMO X2004)
NOAA-ICP	6	50 – 350 ppb CO		NOAA, Empa, AIST,JMA,MRI,NIES,TU
(CO, CO_2, CH_4, N_2O)		355 – 420 ppm CO_2		
		1570 – 2030 ppb CH_4		
		320 – 328 ppb N_2O		
Total	36			
	(10)			

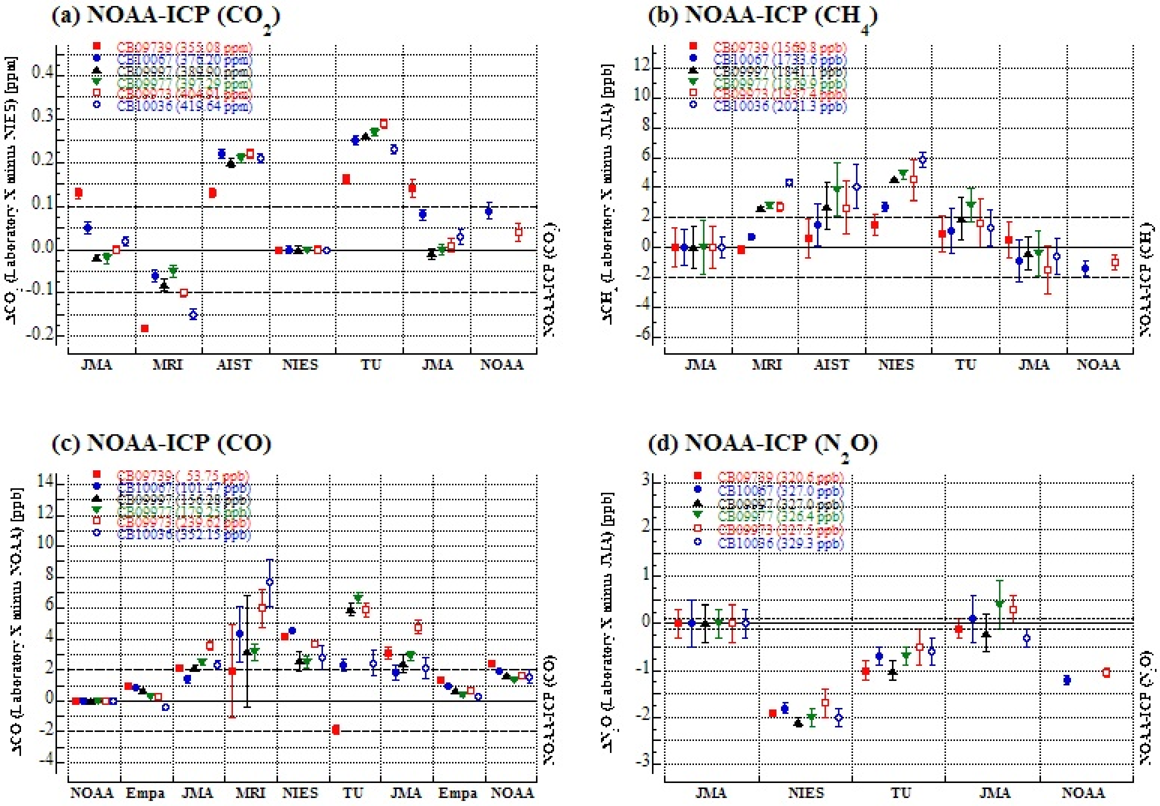
実験全体を通して、オール・ジャパン体制による連携により明らかにできた主要な成果について以下に要約する。

１）比較実験の結果

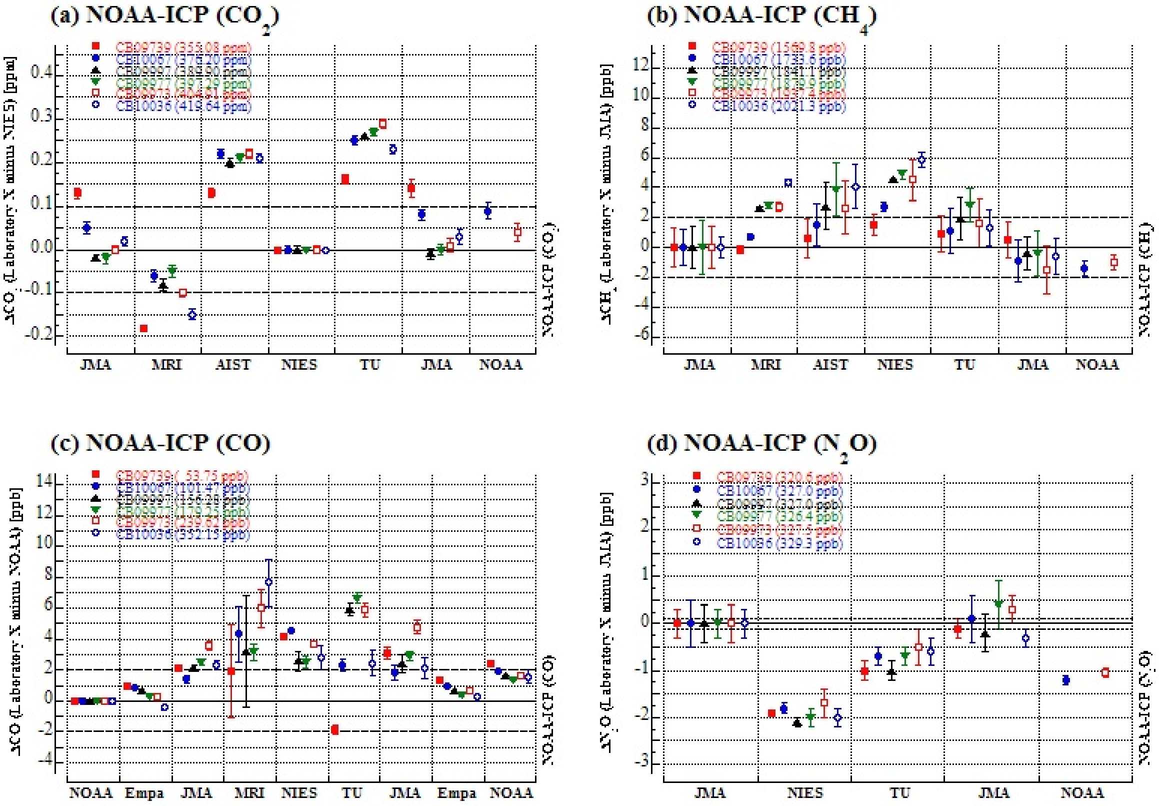
合計 7 回のシリーズの比較実験結果を図―I、図―II、図―III に示す。図の濃度値は、基準となる機関との測定濃度の差（偏差）を示し、観測機関のエラー・バーは各機関の測定誤差（1σ）を±の幅で示し、NMIJ のエラー・バーは質量比混合法の拡張不確かさ（*k* = 2）を示す。図中の点線は、WMO による観測データの統合目標の濃度範囲を表わしている。



図ーI a) iceGGO-1 実験の CH_4 濃度の比較結果。JMA の測定値からの偏差。 b) iceGGO-2 実験の軽い炭素同位体比(～ −30‰)をもつ 6 本の CO_2 濃度の比較結果。NIES の測定値からの偏差。 c) iceGGO-2 実験の重い炭素同位体比(−9‰ & +57‰)をもつ 3 本の CO_2 濃度の比較結果。NIES の測定値からの偏差。d) iceGGO-3 実験の CO_2 濃度測定の結果。NIES の測定値からの偏差。



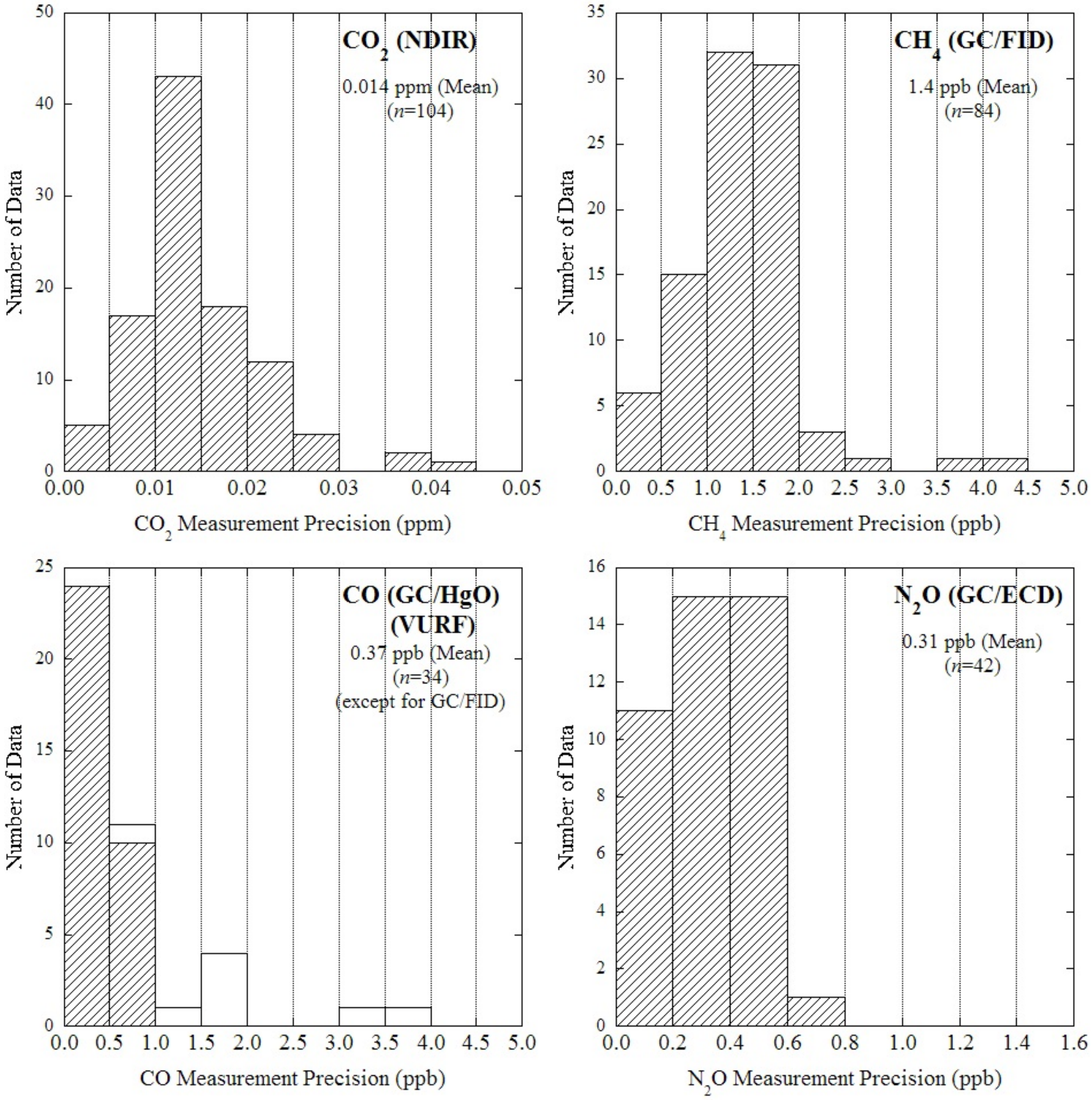
図－Ⅱ　a）iceGGO-4 実験の CO 濃度の比較結果。NMIJ の質量比混合法値からの偏差。 b）iceGGO-5 実験の N_2O 濃度の比較結果。NMIJ の質量比混合法値と NOAA の測定値からの偏差。 c）iceGGO-6 実験の CH_4 濃度の比較結果。NMIJ の質量比混合法値と NOAA の測定値からの偏差。



図－III a) NOAA-ICP 実験の CO_2 濃度の比較結果。NIES の測定値からの偏差。b) NOAA-ICP 実験の CH_4 濃度の比較結果。JMA の測定値からの偏差。c) NOAA-ICP 実験の CO 濃度の比較結果。NOAA の測定値からの偏差。d) NOAA-ICP 実験の N_2O 濃度の比較結果。JMA の測定値からの偏差。

２）測定精度の評価

報告された全濃度測定データの分析誤差の平均は、CO_2 で 0.014ppm（*n*=104）、CH_4 で 1.4ppb（*n*=84）、CO で 0.37ppb（*n*=34）、N_2O で 0.31ppb（*n*=42）であった（図－IV）。本研究の実験に参加したすべての観測機関の測定は高い精度で実施され、観測精度は世界トップレベルの水準で維持されていることが分かった。測定に用いられた主な分析計は以下の通りである。CO_2 は非分散型赤外分析計（NDIR）、CH_4 は水素炎イオン化型検出器を備えたガスクロマトグラフ（GC/FID）、CO は還元ガス型検出器を備えたガスクロマトグラフ（GC/RGD）と真空紫外共鳴蛍光法（VURF）、N_2O は電子捕獲型検出器を備えたガスクロマトグラフ（GC/ECD）であった。

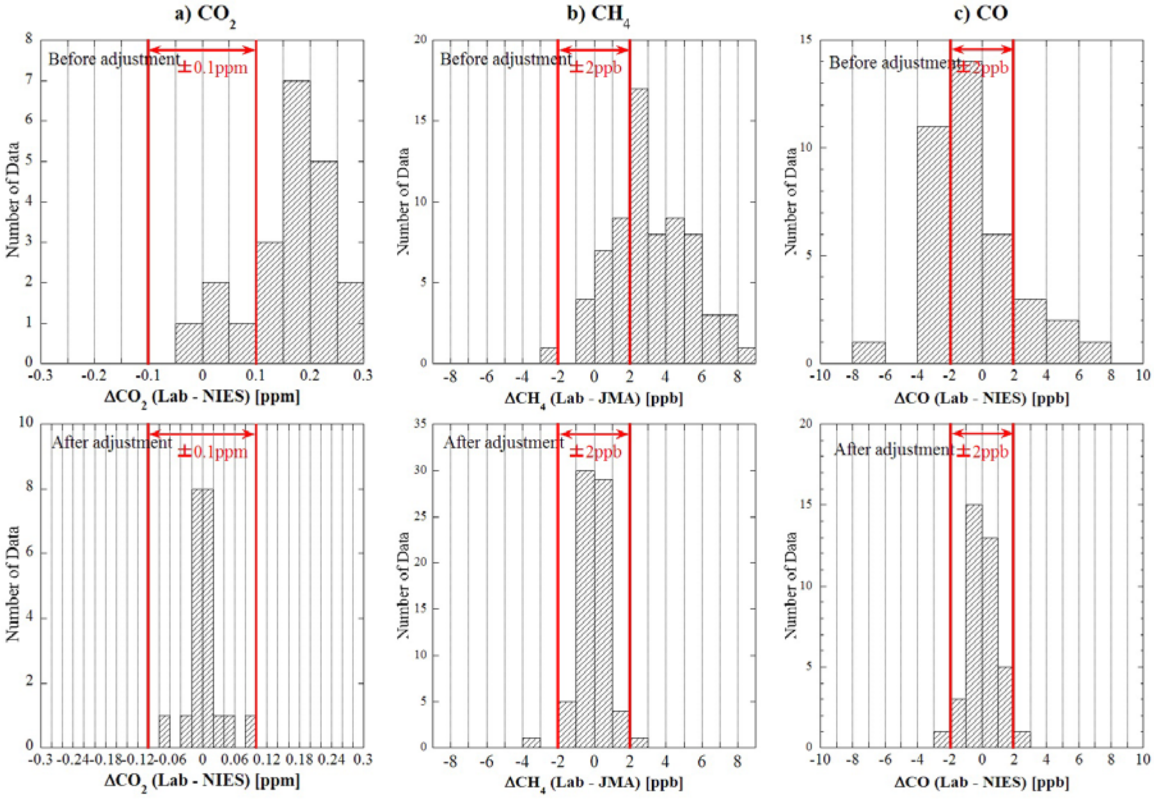


図ーIV CO_2、CH_4、CO 及び N_2O の測定精度。図の頻度分布は、合計 7 回のシリーズの実験における全機関のすべての測定値について報告された測定誤差を用いた。CO の白抜きのカラムは GC/FID 法の測定誤差分布を示す。

３）濃度スケール差とその補正

CO_2、CH_4、CO の測定値は機関間に大きな違いがあり、WMO によるデータの統合目標の濃度範囲（CO_2 は± 0.1ppm、CH_4 は± 2ppb、CO は± 2ppb）を超える差が認められ

た（図―V の上段）。これらの差は日本の各機関が独自に保有する濃度標準スケールの違いを主に反映しており、機関間の測定値の違いを比較解析することによって濃度スケール差に系統的な関係があることが把握できた。これらの関係を用いて、基準となるスケールの差を補正した結果、 各機関の測定濃度が WMO のデータ統合目標の範囲内にほぼ収束することが分かった（図―V の下段）。これによって、日本の主要な観測機関の観測データを高精度で統合する方法が確立できた。



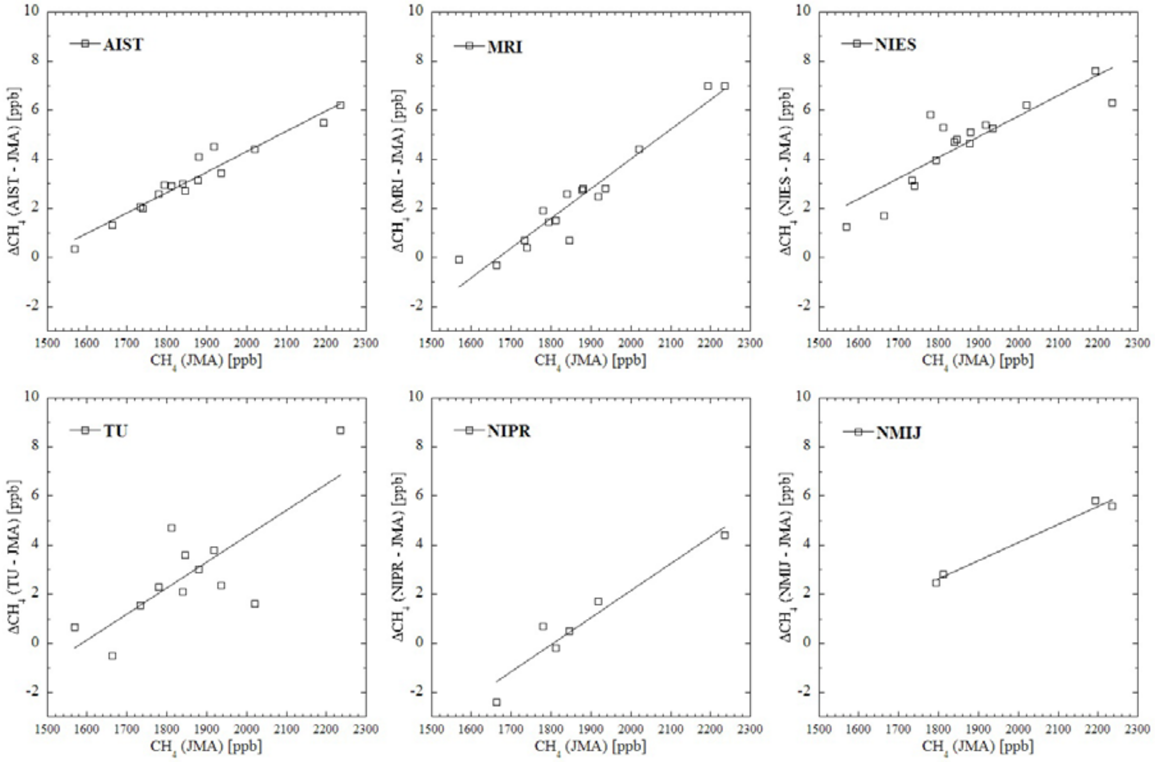
図ーV CO_2、CH_4、CO のスケール補正前（上段）と補正後（下段）の測定データの差の分布。赤線は、WMO が目標とするデータの統合目標の濃度範囲（CO_2 は± 0.1ppm、CH_4 は± 2ppb、CO は±2ppb）。

N_2O については、従来の GC/ECD 法による比較実験では、WMO が掲げる観測データの統合目標（± 0.1ppb）で、濃度スケールの差を正確に補正するのは困難であることが確認された。これは世界の観測ネットワークでも十分に達成されていない重要な課題であ

る。今回の実験では、次世代の高精度 N_2O 観測装置である中赤外レーザー分光型分析計による試験的な測定も報告された。さらに、N_2O 測定精度向上に向けた日本の連携した取組みの継続が期待される。

４）メタン・スケールの妥当性

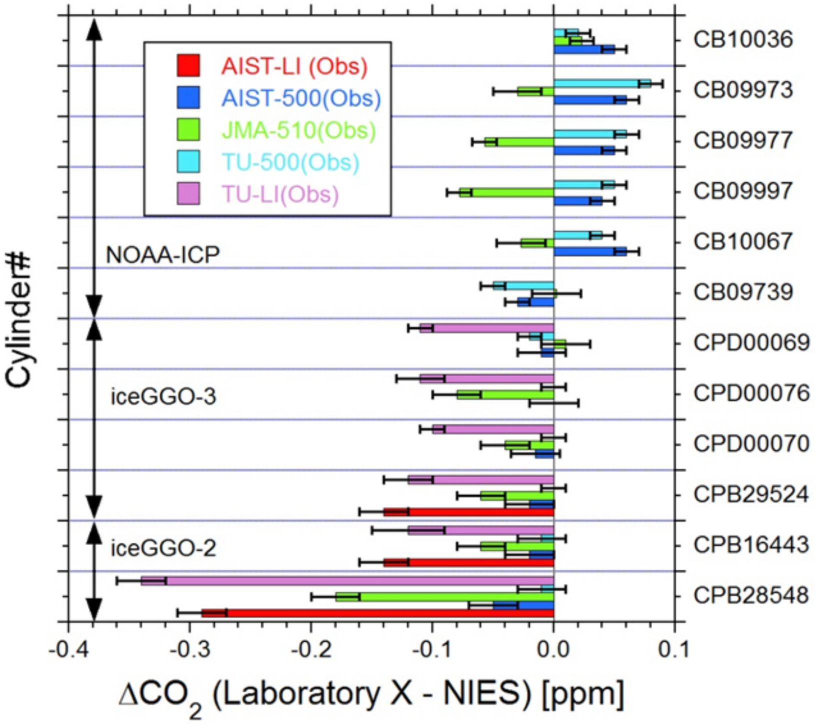
　日本の各機関が独自に保有する CH_4 の濃度スケールは、WMO の世界基準（WMO X2004 スケール）に依る JMA の値に対して濃度依存性をもった違いがあることが明瞭に示された（図―VI）。この傾向は、NMIJ による質量比混合法で決定された標準ガス濃度とも整合的であった。濃度スケールの差異は、1800-1900ppb の濃度範囲で 2～4ppb、2000-2300ppb の濃度範囲で 4～6ppb 程度と評価された。この結果は、世界基準となっている WMO スケールのより確度の高い改訂が必要であることを示す重要な知見と言える。



図ーVI　WMO X2004 スケールに依る JMA と各機関の CH_4 測定値の差と濃度の関係。図中のデータは、iceGGO-1(CH_4)、iceGGO-6(CH_4)、NOAA-ICP(CH_4)における測定結果を用いた。

５）二酸化炭素測定の器差（同位体効果）

全参加機関が採用している化石燃料起源 CO_2 から調製した標準ガスを用いて大気試料の CO_2 濃度を測定する際、NDIR 分析計固有の器差が生じ、その幅は-0.18ppm～+0.08ppm と評価された（図—VII）。器差の主な要因の一つとして、標準ガスと測定試料の同位体組成の違いが影響を与えていることが解析された。各機関の NDIR については $^{13}CO_2$ の測定結果が得られ、器差を低減するためのデータ補正に有効に活用できることが分かった。



図－VII　CO_2 測定における NDIR の器差評価の結果。器差は、各機関の濃度スケールを NIES スケールに変換した CO_2 測定値を算出した後、同位体補正をした NIES の測定値と比較した際に生じる濃度差と定義した。

Abstract

The Office for Coordination of Climate Change Observation in Japan has established a national alliance of the laboratories of seven organizations: the Japan Meteorological Agency, the Tohoku University, the National Institute for Environmental Studies, the National Institute of Advanced Industrial Science and Technology, the National Institute of Polar Research, the Meteorological Research Institute, and the National Metrology Institute of Japan. The mission of the alliance is to compare the standard gas scales used for measurements of atmospheric greenhouse gases (GHGs). Within the framework of this alliance, a working group committee (Chair: T. Nakazawa from Tohoku University) has organized and initiated a plan: InterComparison Experiments for Greenhouse Gases Observation (iceGGO). The purpose of the iceGGO is to examine the differences between the GHG standard gas scales used for atmospheric observations as well as to evaluate the consistency of the scales with the International System of Units traceable standard gases prepared by the gravimetric method of the National Metrology Institute of Japan. The iceGGO program performed six round-robin experiments for carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), and nitrous oxide (N_2O) during the period 2012–2016. An additional iceGGO experiment was also carried out using round-robin cylinders provided by the National Oceanic and Atmospheric Administration. Details of experimental methods and results for all experiments are reported herein. Throughout the seven experiments, the iceGGO program was successful in precisely determining the differences between the GHG standard gas scales. This report provides information that will facilitate combining atmospheric GHG measurements made by different Japanese laboratories into an integrated observation database based on a common standard gas scale consistent with the compatibility criteria recommended by the World Meteorological Organization.

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1. Introduction

Carbon dioxide (CO_2) and other greenhouse gases (GHGs) in the atmosphere have been increasing since the beginning of the industrial age due to the rapid growth of human activities. There is now sufficient scientific evidence to show that this increase in atmospheric GHGs is the main cause of the observed global warming and changes in climate. How well we can predict the future state of the earth therefore depends very much on how well we understand the global cycle of GHGs. The major approach of this study has been to examine the detailed temporal and spatial variations of the concentrations of GHGs in the atmosphere.

Monitoring of the atmospheric burden of CO_2 was initiated at Mauna Loa on Hawaii and at the South Pole on Antarctica more than half a century ago. Since then, the observing system has been expanded to include other GHGs and many sites worldwide (e.g., WMO, 2016a). Estimating sources and sinks with various top-down inverse calculation methodologies is an essential use of the observation data, and for that purpose, measurements made by different laboratories must be combined into an integrated measurement database to expand spatial and temporal coverage. A fundamental requirement for the GHG observations is careful and continuous calibration of measuring devices, including intercomparisons of calibration scales among different laboratories.

To compare the standard gas scales used for measurements of GHGs in Japan, the Office for Coordination of Climate Change Observation (OCCCO) established a national alliance with six observation laboratories of the Japan Meteorological Agency (JMA), Tohoku University (TU), National Institute for Environmental Studies (NIES), National Institute of Advanced Industrial Science and Technology (AIST), National Institute of Polar Research (NIPR), and the Meteorological Research Institute (MRI). The National Metrology Institute of Japan (NMIJ), which is part of the AIST, also participated this alliance under the collaboration with two international organizations, the World Meteorological Organization (WMO) and le Comité International des Poids et Mesures (CIPM). Within the framework of this alliance, a working group committee (Chair: T. Nakazawa from TU) was organized in 2012 and has initiated a program designated InterComparison Experiments for Greenhouse Gases Observation (iceGGO). The purpose of the iceGGO is to compare the standard gas scales used by observation laboratories as well as to evaluate their consistency with the International System of Units (SI) traceable standard gases. For this purpose, the NMIJ prepared standard gases with a gravimetric method according to ISO 6142:2001; the concentrations of the standard gases are calculated from the weight of the filled gases, the concentrations of the components in the filled gases, and the molar masses of the components. The uncertainties of the fractions computed with the gravimetric method are calculated based on propagation of uncertainty.

Six round-robin experiments for CO_2, methane (CH_4), carbon monoxide (CO), and nitrous oxide (N_2O) were performed for the iceGGO program during 2012–2016. An additional intercomparison experiment was made using round-robin cylinders provided by Dr. Paul Novelli of the National Oceanic and Atmospheric Administration (NOAA) (Novelli, 2016). Details of the experimental methods and results for all experiments are reported here, although some of them have been published elsewhere (Takahashi et al., 2013, 2014; Kawasaki et al, 2016; Tsuboi et al., 2016). More information about analytical method is available on referring to publications of TU (Tanaka et al., 1983; Aoki et al., 1992; Machida et al., 1995; Yashiro et al., 2009), AIST (Aoki et al., 1992; Murayama et al., 2003; Murayama et al., 2010), NIES (Machida et al., 2008; Machida et al., 2011; Katsumata et al., 2011), JMA (Matsueda et al., 2004a; Matsueda et al., 2004b; Tsuboi et al., 2013), and MRI (Matsueda, 1993; Matsueda and Inoue, 1996; Matsueda et al., 1998). Throughout the seven iceGGO experiments, our aim has been to achieve the WMO recommended compatibility goal of measurements within ±0.1 ppm for CO_2 (Northern Hemisphere), ±2 ppb for CH_4, ±2 ppb for CO, and ±0.1 ppb for N_2O (WMO, 2016b).

In accord with a report of the WMO (2016b), the following definitions and units have been used throughout this document. Mole fractions of substances in dry air (dry air includes ALL gaseous species except water):

ppm = μmol/mol = 10^{-6} mole of trace substance per mole of dry air

ppb = nmol/mol = 10^{-9} mole of trace substance per mole of dry air

In addition, we have used the term “concentration” instead of “amount-of-substance fraction” because we are concerned about communicating with the general public, and the latter term is unfamiliar to most members of the general public. We have reported concentrations and their associated analytical precisions from all laboratories in all tables to the same number of figures; in some cases this was accomplished by rounding off.

Isotopic ratio measurement results are here expressed as deviations from an agreed-upon international reference measurement standard in per mil (‰) units. δ^{13}C and δ^{18}O of CO_2 are defined as follows:

$$\delta^{13}C = \left\{ \frac{\left({}^{13}C / {}^{12}C \right)_{\mathrm{sa}}}{\left({}^{13}C / {}^{12}C \right)_{\mathrm{st}}} - 1 \right\} \times 1000 \ , \qquad (1)$$

$$\delta^{18}O = \left\{ \frac{\left({}^{18}O / {}^{16}O \right)_{\mathrm{sa}}}{\left({}^{18}O / {}^{16}O \right)_{\mathrm{st}}} - 1 \right\} \times 1000 \ , \qquad (2)$$

where the subscripts sa and st denote the sample and the standard, respectively. In this study, all measured δ^{13}C and δ^{18}O values of CO_2 are reported based on the Vienna Pee Dee Belemnite (VPDB) scale.

2. iceGGO-1 (CH_4)

2.1. Round-robin cylinders (iceGGO-1)

The first experiment (2012–2013), the iceGGO-1, focused on a comparison of CH_4 standard gas scales by circulating high-pressure gas cylinders. Details of the six sample cylinders used in this round-robin experiment are listed in Table 1. Four cylinders were commercially available CH_4 standard gases, which were filled by Japan Fine Products (JFP;

formerly Nippon Sanso Corporation, Japan). These four gases were prepared using purified natural air as a matrix gas, and their CH_4 concentrations ranged from ~1660 ppb to ~1920 ppb. Two of the four cylinders (CPB13002 and CPB13003) had been used previously by the JMA during 2008–2011 for the third round-robin experiment of the Global Atmosphere Watch (GAW) World Calibration Centre (WCC) for CH_4 in Asia and the southwest Pacific region (http://ds.data.jma.go.jp/wcc/ch4/rusult_3rd.html). The other two standard gases (CPB28218 and CPB28042), with CH_4 concentrations of about 1810 ppb and 2240 ppb, were prepared gravimetrically with a four-step dilution from pure N_2, O_2, Ar, and CO_2, and CH_4 (Table 2). These gases are SI-traceable standards prepared by the gravimetric method of the NMIJ. The expanded uncertainties of the gravimetric values, ~1.3 ppb ($k = 2$), were associated mainly with the determination of the concentration of CH_4 in the matrix gases (pure O_2 and N_2). Details of the NMIJ gravimetric method have been reported elsewhere (Flores et al., 2015).

Table 1. The six cylinders used for the iceGGO-1.

Cylinder Identification	CH_4 Concentration (ppb)	Matrix gas	Manufacturer	Filling method	Date of filling
CPB13002	1664.2*	Purified natural air	JFP	Gravimetric	April, 1, 2008
CPB00786	1779.6*	Purified natural air	JFP	Gravimetric	November 16, 1999
CPB13003	1844.8*	Purified natural air	JFP	Gravimetric	April, 1, 2008
CPB00787	1918.8*	Purified natural air	JFP	Gravimetric	November 16, 1999
CPB28218	1813.8**	Synthetic air$	NMIJ	Gravimetric	May 31 - June 1, 2012
CPB28042	2240.1**	Synthetic air$	NMIJ	Gravimetric	September 4-6, 2012

*Measured by JMA

**Gravimetric value from NMIJ

$Detailed composition in Table 2

Table 2. Details of the compositions of two cylinders prepared with the NMIJ gravimetric method. These values were calculated according to ISO-6142:2001. The numbers after the ± symbols indicate the expanded uncertainty (*k* = 2).

Cylinder Identification	CH_4 ppm	CO_2 ppm	N_2 ppm	O_2 ppm	Ar ppm
CPB28218	1.81381 ±0.00133	390.209 ±0.092	774381 ±6.68	215882 ±6.82	9344.69 ±0.7579
CPB28042	2.24013 ±0.00134	390.677 ±0.087	773710 ±6.31	216277 ±6.43	9619.48 ±0.7198

2.2. Measurement methods (iceGGO-1)

Six laboratories (JMA, NIPR, AIST, MRI, NIES, and TU) participated in the iceGGO-1 round-robin experiment from October 2012 to February 2013. Table 3 provides details of the CH_4 analytical methods used by the six laboratories. All participants used a gas chromatograph equipped with a flame ionization detector (GC/FID) to measure CH_4 concentrations; the instruments, however, differed between laboratories. Five laboratories carried out the measurements using different standard gas scales (NIPR, AIST, MRI, NIES94, and TU2008), which were independently developed and maintained for a long period of time. In contrast, the JMA measurements were based on the WMO X2004 scale, which has been propagated from the Global Monitoring Division (GMD) of the NOAA Earth System Research Laboratory (Dlugokencky et al., 2005; Tsuboi et al., 2016). The calibration gases used by the NIPR, AIST, NIES, and TU cover a relatively wide range of CH_4 concentrations, whereas the range of the JMA and MRI calibration gases was not wide enough to measure the highest concentration in the round-robin cylinder. To evaluate the drift of the CH_4 concentration during the experimental period, the JMA measured all cylinders at the beginning and end of the round-robin experiment.

2.3. Results of iceGGO-1

The CH_4 concentrations in the six gas cylinders reported by the six laboratories are given in Table 4. The analytical precision of most of the measurements from all laboratories was less than ~2 ppb. The relatively large analytical precision reported by the JMA for the cylinder with the highest CH_4 concentration reflects extrapolation of the calibration curve. The JMA measurements showed that the differences in concentrations between the beginning and end of the experiment for all four cylinders were less than 0.8 ppb, which is smaller than the JMA analytical precision. Thus, no correction for drift during the experimental period has been applied to the concentrations reported by the laboratories.

Table 3. The six laboratories and the analytical methods, instruments, and calibration scales they used to measure CH_4 during the iceGGO-1 experiment.

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	1620 ppb - 2110 ppb	5	October 11-12, 2012
NIPR	GC/FID	GC-8A (FID), Shimadzu	NIPR Scale	1390 ppb - 2280 ppb	4	October 18-23, 2012
AIST	GC/FID	GC-14BPF (FID), Shimadzu	AIST Scale	1010 ppb - 2530 ppb	4	November 11-17, 2012
MRI	GC/FID	AG-1F (FID), Yanaco	MRI Scale	1600 ppb - 2100 ppb	5	November 2 - December 6, 2012
NIES	GC/FID	HP5890 (FID), Agilent	NIES94 Scale	1250 ppb - 2500ppb	6	December 14-17, 2012
TU	GC/FID	6890NF (FID), HP	TU2008 Scale	900 ppb - 2500 ppb	5	January 12-24, 2013
JMA	GC/FID	GC-14BPF (FID), Shimadzu	WMO X2004 Scale	1620 ppb - 2110 ppb	5	February 7-20, 2013

Table 4. CH_4 concentrations (ppb) reported by the indicated laboratories as a part of the iceGGO-1. Reported analytical precisions are indicated in parentheses.

	Cylinder Identifications					
Laboratory	CPB13002	CPB00786	CPB13003	CPB00787	CPB28218	CPB28042
JMA	1664.2 (1.5)	1779.6 (1.8)	1844.8 (1.1)	1918.8 (1.7)	1811.2 (1.0)	2234.6 (3.9)
NIPR	1661.7 (2.6)	1780.2 (1.7)	1845.7 (1.9)	1920.4 (1.4)	1810.8 (2.0)	2238.9 (1.4)
AIST	1665.4 (1.5)	1782.1 (1.5)	1847.9 (1.3)	1923.2 (1.3)	1813.9 (1.9)	2240.7 (1.9)
MRI	1663.8 (1.1)	1781.4 (0.9)	1845.9 (0.8)	1921.2 (1.0)	1812.5 (0.8)	2241.5 (0.8)
NIES	1665.8 (0.9)	1785.3 (1.2)	1850.0 (0.5)	1924.1 (0.8)	1816.3 (1.8)	2240.8 (0.6)
TU	1663.6 (1.1)	1781.8 (1.2)	1848.8 (1.3)	1922.5 (1.2)	1815.7 (0.9)	2243.2 (1.5)
JMA	1664.0 (1.7)	1779.4 (1.8)	1845.6 (1.9)	1918.6 (1.2)	1810.8 (2.1)	2234.4 (4.3)
NMIJ	-	-	-	-	1813.8 (1.3)*	2240.1 (1.3)*

*Gravimetric value (Expanded uncertainty of gravimetric method (k = 2))

Figure 1 shows the differences between the CH_4 concentrations measured in the six round-robin cylinders by each laboratory (Laboratory X) and by the JMA. The differences (Laboratory X minus JMA) among the laboratories ranged from –2 ppb to +9 ppb. This range of differences reflects mainly differences in the reference CH_4 standard scales among the laboratories. The differences of the concentrations reported by all five laboratories and the JMA concentrations clearly increased with increasing CH_4 concentration. These increased differences often exceeded the criterion for compatibility of CH_4 measurements (±2 ppb) recommended by the WMO (WMO, 2016b). The gravimetric values determined by ISO 6142:2001 for the two cylinders were higher than the JMA measurements based on the WMO X2004 scale. The differences between the two gravimetric scales tended to increase with increasing CH_4 concentration. These results agree well with the difference between the NMIJ and WMO X2004 scales for the CCQM-K82 comparison as a part of the CIPM program (Flores et al., 2015). Tsuboi et al. (2016) have reported more details about the differences between the two scales.

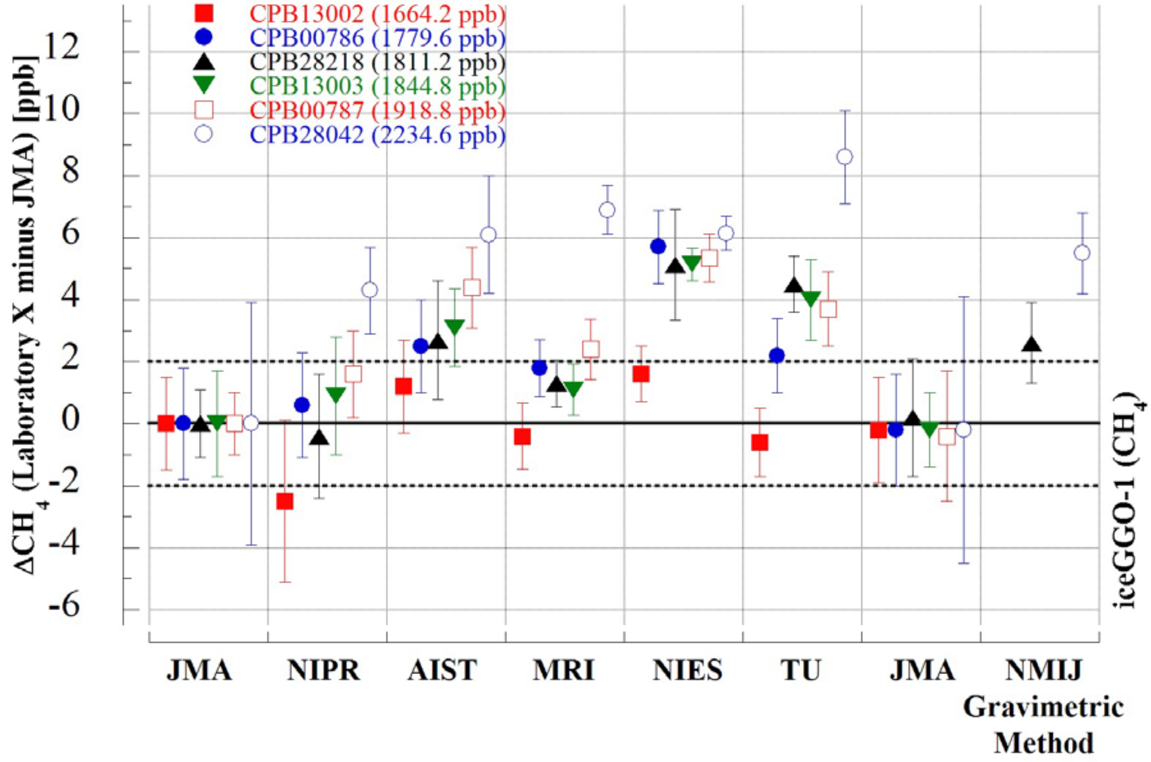

Figure 1. Differences (Laboratory X minus the JMA) of CH_4 concentrations for each round-robin cylinder measured as a part of the iceGGO-1. The error bars represent the ± measurement precision reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method ($k = 2$). The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CH_4 measurement compatibility.

3. iceGGO-2 (CO_2)

3.1. Round-robin cylinders (iceGGO-2)

The second experiment (2012), the iceGGO-2, focused on a comparison of CO_2 standard gas scales by circulating high-pressure cylinders. Details of the nine sample cylinders used for this round-robin experiment are listed in Table 5. Six cylinders filled by JFP using a volumetric method were provided by TU for the iceGGO-2 experiment. These six cylinders were prepared using purified natural air as a matrix gas, and their CO_2 concentrations ranged from about 340 ppm to 409 ppm. The parent CO_2 gas in these cylinders was derived from combusted petroleum; the $\delta^{13}C$ values of their CO_2 were deduced to be around –30 ‰.

Three other cylinders containing relatively high $^{13}CO_2$ concentrations were provided by NIES to examine isotope effects of CO_2 analyzers, because such effects would confound interpretation of apparent differences in the isotopic compositions of round-robin samples and calibration gases. Two cylinders (CPB16443 and CPB29524) were filled with dry natural air, including CO_2 at concentrations of about 405 ppm and 410 ppm, respectively. The $\delta^{13}C$ values of the CO_2 in these cylinders were measured by the NIES to be –8.8 ‰ and –9.0 ‰, respectively. A third cylinder (CPB28548) was specially prepared using an enriched $^{13}CO_2$ gas ($\delta^{13}C$ = +57.3 ‰) in purified natural air with a CO_2 concentration of ~370 ppm (Tohjima et al., 2009).

Table 5. The nine cylinders used in the iceGGO-2 experiment.

Cylinder Identification	CO_2 Concentration* (ppm)	Matrix gas	Manufacturer	Filling method	$\delta^{13}C$ of CO_2 (‰)
CPB10204	339.93	Purified natural air	JFP	Volumetric	
CPB10206	369.80	Purified natural air	JFP	Volumetric	
CPB10208	390.02	Purified natural air	JFP	Volumetric	
CPB10210	409.91	Purified natural air	JFP	Volumetric	
CPB10213	429.72	Purified natural air	JFP	Volumetric	
CPB10216	449.95	Purified natural air	JFP	Volumetric	
CPB28548	370.06	Purified natural air	NIES		+57.3&
CPB16443	406.02	Dry natural air	NIES		-8.8#
CPB29524	409.31	Dry natural air	NIES		-9.0#

*Measured by NIES

#Measured by Cavity Ring-Down Spectroscopy (CRDS) of NIES

&Measured by isotope ratio mass spectrometry (IRMS) of NIES (Tohjima et al., 2009)

3.2. Measurement methods (iceGGO-2)

Five laboratories (AIST, NIES, JMA, NIPR, and TU) participated in the iceGGO-2 round-robin experiment from May to August 2012. Table 6 provides details of the CO_2 analytical methods used by the five laboratories. All participants used a non-dispersive infrared (NDIR) analyzer to measure CO_2 concentrations. However, the models of the NDIR instruments differed: the AIST, NIES, and TU used a LI-6252 model (LI-COR); the AIST and TU used a model VIA-500R (Horiba); and the JMA and NIPR used a model VIA-510R (Horiba).

The JMA measurements were based on the WMO X2007 scale (Zhao and Tans, 2006), which has been propagated from the NOAA/GMD. The NDIR analyzers differ from the JMA and NOAA, although no consideration is given to associated isotope effects on the WMO scale transfer from the NOAA to the JMA. Three laboratories, TU, AIST, and NIPR, used the same TU2010 scale, which was developed recently by the TU. The NIES09 scale was based on eight cylinders prepared by a one-step dilution method with a precision of 0.04 ppm (Machida et al., 2011). All laboratories used a gas mixture that included CO_2 derived from combustion of fossil fuel (δ^{13}C of about –30 ‰) in purified natural air as a calibration gas.

Table 6. The five laboratories and the analytical methods, instruments, and calibration scales they used to measure CO_2 during the iceGGO-2 experiment.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
AIST	NDIR	LI-6252, Licor	TU2010 Scale	340 ppm - 450 ppm	6	May 20-25, 2012
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	340 ppm - 450 ppm	5 or 6	May 15-17, 2012
NIES	NDIR	LI-6252, Licor	NIES09 Scale	340 ppm - 450 ppm	8	April 29-May 1, 2012
JMA	NDIR	VIA-510R, Horiba	WMO X2007 Scale	320 ppm - 480 ppm	9	June 12-15, 2012
NIPR	NDIR	VIA-510R, Horiba	TU2010 Scale	370 ppm - 420 ppm	6	October 18-24, 2012
TU	NDIR	LI-6252, Licor	TU2010 Scale	380 ppm - 450 ppm	7	July 25- August 1, 2012
TU	NDIR	VIA-500R, Horiba	TU2010 Scale	380 ppm - 450 ppm	7	July 25- August 1, 2012

3.3. Results of iceGGO-2

Table 7 summarizes the CO_2 concentrations measured in the nine round-robin cylinders by five laboratories using three different NDIR models. The analytical precision of most of the measurements in all laboratories was less than 0.04 ppm, although the TU and AIST results indicated that the precision was higher for measurements made with the VIA-500R than with the LI-6252. The TU assayed six cylinders containing combusted petroleum CO_2 at both the beginning and the end of the experiment to evaluate the stabilities of the CO_2 contents during the experimental period. No significant drift of CO_2 concentration was observed in any of the six cylinders. The results for three other cylinders examined by the NIES were found to be stable during the experimental period. Thus, no correction for drift has been applied to the measurement results reported by any of the laboratories. The CO_2 concentrations of three cylinders reported by the NIES were corrected for isotope effects of +0.06 ppm for CPB16443 and CPB29524 and of +0.29 ppm for CPB28548 in accord with the method of Tohjima et al. (2009). The reported values from all other laboratories, however, were not corrected for isotope effects.

Table 7. CO_2 concentrations (ppm) and reported analytical precisions in parentheses during the iceGGO-2.

	Cylinder Identifications								
Laboratory	CPB10204	CPB10206	CPB10208	CPB10210	CPB10213	CPB10216	CPB28548	CPB16443	CPB29524
AIST (LI-6252)	340.11 (0.020)	369.98 (0.019)	390.19 (0.017)	410.08 (0.016)	429.86 (0.013)	450.08 (0.016)	369.93 (0.018)	406.04 (0.013)	409.33 (0.021)
AIST (VIA-500R)	340.10 (0.009)	369.95 (0.011)	390.19 (0.006)	410.07 (0.011)	429.86 (0.006)	450.10 (0.013)	370.17 (0.010)	406.16 (0.011)	409.45 (0.013)
NIES (LI-6252)	339.93 (0.024)	369.80 (0.014)	390.02 (0.017)	409.91 (0.018)	429.72 (0.023)	449.95 (0.024)	370.06*(0.017) (+0.29)**	406.02*(0.016) (+0.06)**	409.31*(0.008) (+0.06)**
JMA (VIA-510R)	340.10 (0.018)	369.91 (0.020)	390.05 (0.013)	409.97 (0.012)	429.69 (0.012)	449.97 (0.007)	369.98 (0.018)	405.99 (0.014)	409.27 (0.006)
NIPR (VIA-510R)	-	370.06 (0.020)	390.25 (0.020)	410.16 (0.020)	-	-	370.08 (0.010)	406.15 (0.020)	409.44 (0.010)
TU (LI-6252)	340.11 (0.037)	369.99 (0.020)	390.21 (0.026)	410.13 (0.035)	429.94 (0.026)	450.12 (0.042)	369.93 (0.018)	406.11 (0.028)	409.40 (0.025)
TU (VIA-500R)	340.12 (0.009)	370.00 (0.012)	390.25 (0.014)	410.12 (0.011)	429.92 (0.015)	450.08 (0.018)	370.26 (0.013)	406.22 (0.009)	409.52 (0.011)

*Corrected by isotope effect
**Isotope effect

Figure 2 shows differences in CO_2 concentrations measured by each laboratory (Laboratory X) and NIES for the six cylinders containing combusted petroleum CO_2. The differences (Laboratory X minus NIES) among the laboratories ranged from –0.03 ppm to +0.26 ppm. The differences for the TU, AIST, and NIPR exceeded +0.1 ppm, whereas the difference between the JMA and NIES depended largely on the CO_2 concentration. The concentrations measured with the two different instruments (VIA-500R and LI-6252) by the TU and AIST were in good agreement, although there was a small systematic difference (less than ~0.05ppm) between the two laboratories. These results mainly reflect differences in the standard gas scales for the CO_2 calibrations among the laboratories. Isotope effects are ruled out because the same combusted petroleum CO_2 was the CO_2 source in both the round-robin samples and the calibration gas cylinders.

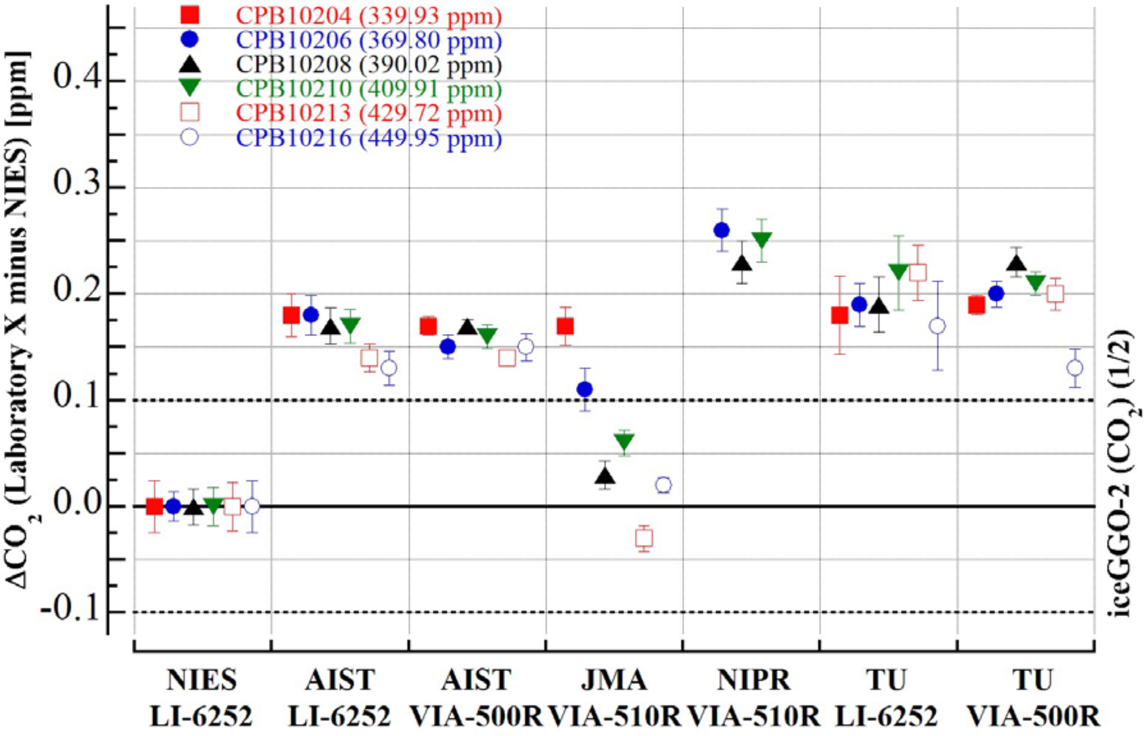

Figure 2. Differences (Laboratory X minus NIES) of CO_2 concentrations for six round-robin cylinders measured for the iceGGO-2. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

Figure 3 shows differences in CO_2 concentrations measured by each laboratory (Laboratory X) and the NIES for natural air samples in the CPB16443 and CPB29524 cylinders and the CPB28548 ($^{13}CO_2$ enriched) cylinder. The isotopic compositions of CO_2 in these three cylinders were different from those in the CO_2 calibration gases used in all laboratories to examine the isotope effect on the NDIR analysis. The differences (Laboratory X minus NIES) among the laboratories and NDIR models ranged from –0.15 ppm to +0.21 ppm in these three cylinders. The measurements of the two natural air sample cylinders agreed well within the analytical precision in all laboratories. However, there was a large difference (±0.1 ppm) between the concentrations determined with the VIA-500R and LI-6252 analyzers for two natural air samples analyzed by the TU and AIST. The deviations of the analyses were larger for the enriched $^{13}CO_2$ sample cylinder than for the two natural air sample cylinders. These results reflect not only differences in CO_2 calibration standard scales but also isotope effects associated with the NDIR models.

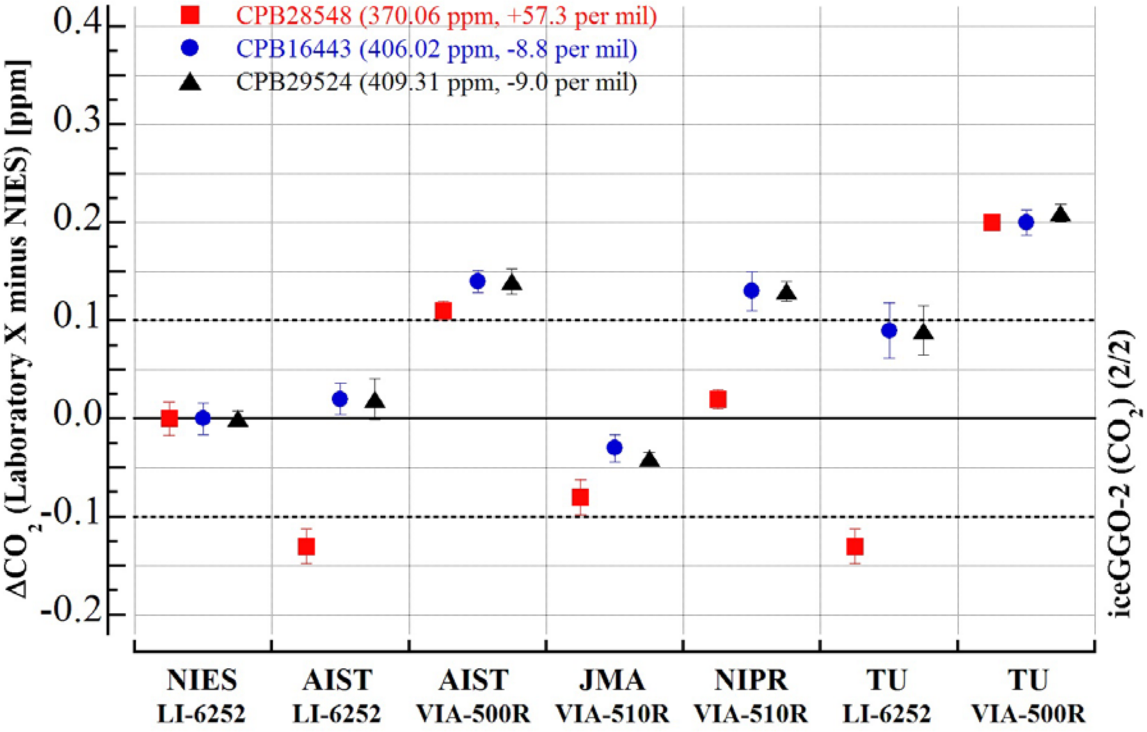

Figure 3. Differences (Laboratory X minus NIES) of CO_2 concentrations for three round-robin cylinders measured for the iceGGO-2. The error bars represent the ± measurement precisions reported by each laboratory. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

4. iceGGO-3 (CO_2)

4.1. Round-robin cylinders (iceGGO-3)

The third experiment (iceGGO-3), which took place in 2014, was a comparison of CO_2 concentrations in high-pressure cylinders. Table 8 provides details about the three sample cylinders used in the round-robin experiment. The samples in these three cylinders contained CO_2 at concentrations of about 380 ppm, 400 ppm, and 418 ppm, respectively. The samples were prepared from pure CO_2 and purified natural air with a three-step dilution by the gravimetric method in accordance with ISO 6142:2001 during the time interval from November 28, 2013, to December 19, 2013. At each step of the dilution, three mixtures were prepared. The CO_2 concentrations at each step were 60000 ppm, 5000 ppm, and 400 ppm. The purity of the CO_2 and the concentrations of N_2, O_2, and Ar in the purified natural air were determined by gas chromatography, Fourier-transform infrared spectrometry and so on. The expanded uncertainty of the CO_2 gravimetric values, about 0.05 ppm, was associated mainly with weighing the filling gas. The δ^{13}C and δ^{18}O values of the pure CO_2 used to prepare these gases, determined precisely by isotope ratio mass spectrometry (IRMS) at the AIST and TU, were about –8.9 ‰ and –13 ‰, respectively. This isotopic composition differed from that of the calibration gases prepared with combusted petroleum CO_2 (around –30 ‰ for $\delta^{13}CO_2$) that was used for measurements by all participants.

Table 8. Mean concentrations of gases in the three cylinders used for CO_2 analyses during the iceGGO-3. The numbers after the ± symbols indicate the expanded uncertainty ($k = 2$).

Cylinder Identification	CO_2 ppm	N_2 ppm	O_2 ppm	Ar ppm	$\delta^{13}C(CO_2)$* ‰	$\delta^{13}C(CO_2)$** ‰	$\delta^{18}O(CO_2)$* ‰	$\delta^{18}O(CO_2)$** ‰
CPD00070	379.88 ±0.056	781049 ±24	209214 ±16	9357 ±18	-8.907 ±0.012	-8.881 ±0.024	-13.099 ±0.011	-13.006 ±0.056
CPD00076	399.57 ±0.049	781044 ±29	209209 ±16	9347 ±24	-8.964 ±0.012	-8.874 ±0.024	-13.173 ±0.022	-13.064 ±0.027
CPD00069	418.12 ±0.051	781017 ±24	209209 ±15	9356 ±18	-8.908 ±0.006	-8.897 ±0.018	-13.088 ±0.012	-13.048 ±0.011

*Measured by IRMS of AIST

**Measured by IRMS of TU

4.2. Measurement methods (iceGGO-3)

Five laboratories (AIST, TU, JMA, MRI, and NIES) participated in the iceGGO-3 round-robin experiment from January to September 2014. Table 9 lists the participating laboratories and details of their CO_2 analytical methods.

All participants used a NDIR analyzer to measure CO_2 concentrations, but the models of the NDIR instruments differed. The TU used three different NDIR models: VIA-500R (Horiba), VIA-510R (Horiba), and LI-6252 (LI-COR). The other laboratories used only one NDIR model for the CO_2 measurements. The CO_2 scales were different from each other (Table 9). To check for CO_2 concentration drift during the experimental period, the AIST measured the CO_2 concentrations in all cylinders at both the beginning and the end of the round-robin experiment.

Table 9. The five laboratories and their analytical methods, instruments, and calibration scales for CO_2 during the iceGGO-3.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of Measurements
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	370 ppm - 450 ppm	6	January 22 - March 12, 2014
TU	NDIR	VIA-500R, Horiba	TU2010 Scale	370 ppm - 430 ppm	4	March 25 - 27, 2014
TU	NDIR	VIA-510R, Horiba	TU2010 Scale	370 ppm - 430 ppm	4	March 26, 2014
TU	NDIR	LI-6252, Licor	TU2010 Scale	370 ppm - 430 ppm	4	March 25 - 27, 2014
JMA	NDIR	VIA-510R, Horiba	WMO X2007 Scale	350 ppm - 440 ppm	7	June 4 - 5, 2014
MRI	NDIR	LI-6252, Licor	MRI 1987 Scale	350 ppm - 430 ppm	6	July 30 - August 1, 2014
NIES	NDIR	LI-6252, Licor	NIES09 Scale	340 ppm - 450 ppm	8	August 11-12, 2014
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	360 ppm - 450 ppm	6	September 2 - 5, 2014

4.3. Results of iceGGO-3

Table 10 shows results of the CO_2 analyses of the three round-robin cylinders by five laboratories using several NDIR models together with the gravimetric values. The precision of most of the results was less than 0.02 ppm. The AIST measurements at both the beginning and the end of the round-robin experiment revealed a slight increase for all three cylinders of 0.02–0.03 ppm, but this drift was not significant compared to the measurement precisions. Thus, no correction for drift was applied to the measurement results reported by the laboratories. The NIES measurements were corrected by the isotope effect (+0.066 ppm) in accord with Tohjima et al. (2009), but the isotope effect was not considered in the measurements made by other laboratories.

Table 10. CO_2 concentrations (ppm) determined during the iceGGO-3. The reported precisions are shown in parentheses.

	Cylinder Identifications		
Laboratory	CPD00070	CPD00076	CPD00069
AIST (VIA-500R)	379.68 (0.013)	399.33 (0.008)	417.92 (0.013)
TU (VIA-500R)	379.76 (0.007)	399.39 (0.005)	417.97 (0.005)
TU (VIA-510R)	379.67 (0.010)	399.33 (0.008)	417.91 (0.007)
TU (LI-6252)	379.66 (0.008)	399.28 (0.011)	417.88 (0.008)
JMA (VIA-510R)	379.60 (0.017)	399.15 (0.012)	417.80 (0.022)
MRI (LI-6252)	379.45 (0.011)	399.08 (0.008)	417.62 (0.002)
NIES (LI-6252)	379.55* (0.009) (+0.066)**	399.18* (0.014) (+0.066)**	417.78*(0.010) (+0.066)**
AIST (VIA-500R)	379.71 (0.013)	399.35 (0.006)	417.94 (0.011)
NMIJ	379.88# (0.056)##	399.57# (0.049)##	418.12# (0.051)##

*Corrected by isotope effect

**Isotope effect

#Gravimetric value

##Expanded uncertainty of gravimetric value (k = 2)

Figure 4 shows differences in the CO2 concentrations measured in the three cylinders by each laboratory (Laboratory X) and the NIES. The differences (Laboratory X minus NIES) among the laboratories and NDIR models ranged from –0.15 ppm to +0.2 ppm for the three cylinders. The gravimetric values from the NMIJ were higher than the CO2 concentrations measured by all the laboratories, but the reason for this difference is unknown. The TU measurements clearly showed a difference among the concentrations determined with the three NDIR models; the concentrations differed by about 0.1 ppm. These results strongly reflect not only differences in the CO2 calibration standard scales but also isotope effects between the NDIR models. Details of the isotope effect are described in section 9.5.

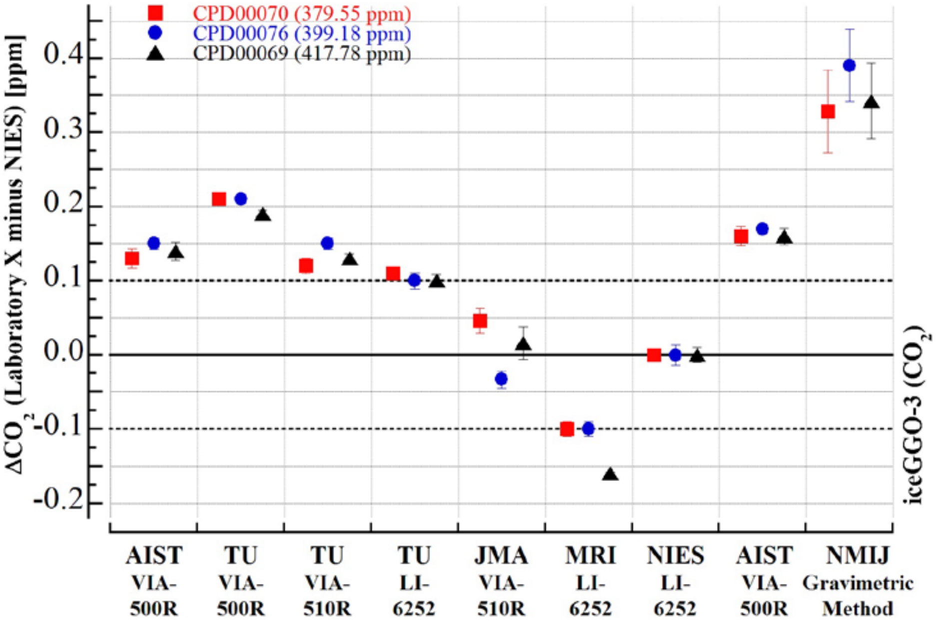

Figure 4. Differences (Laboratory X minus NIES) of CO_2 concentrations in three round-robin cylinders measured during the iceGGO-3. The error bars represent the ± measurement uncertainty reported by each laboratory, although the error bar for the NMIJ indicates the ± expanded uncertainty of the gravimetric method. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

5. iceGGO-4 (CO)

5.1. Round-robin cylinders (iceGGO-4)

The fourth experiment (iceGGO-4), which took place in 2013-2014, focused on comparison of CO standard gas scales by circulating high-pressure cylinders. Table 11 provides details about the two sample cylinders used for this round-robin experiment. The samples in these two cylinders contained CO at concentrations of about 346 ppb and 249 ppb, respectively. The samples were prepared from pure CO, N_2, and O_2 with a four-step dilution by the gravimetric method in accord with ISO 6142:2001. The CO concentrations at each step were 23,000–29,000 ppm, 610–670 ppm, 13–16 ppm, and 250–350 ppb. The expanded uncertainty of the CO gravimetric values ($k = 2$), about 0.3 ppb, was associated mainly with the determination of the CO concentrations in pure N_2 and O_2. Before the gravimetric preparation at the NMIJ, the inner walls of the high-pressure aluminum cylinders were treated in a special way by the Iwatani Corporation in Japan to minimize the drift of CO.

Table 11. The two cylinders used for CO analyses during the iceGGO-4.

Cylinder Identification	Matrix gas	Manufacturer	Filling method	Date of Filling	CO ppb	N_2 ppm	O_2 ppm
CPB16249	Synthetic air	NMIJ	Gravimetric	September 4, 2013	346.1 ± 0.31	791215 ± 6.1	208784 ± 6.1
CPB28680	Synthetic air	NMIJ	Gravimetric	August 27, 2013	248.7 ± 0.30	788013 ± 6.2	211986 ± 6.3

5.2. Measurement methods (iceGGO-4)

Four laboratories (NIES, MRI, TU, and JMA) participated from October 2013 to August 2014 in the iceGGO-4 round-robin measurements. Table 12 lists the participating laboratories and provides details about their CO analytical methods. To monitor for CO drift during the experimental period, the NIES measured all cylinders three times with a vacuum ultraviolet resonance fluorescence (VURF) analyzer. The TU and JMA used a gas chromatograph equipped with a reduction gas detector (GC/RGD) to measure CO concentrations, whereas the MRI used a GC/FID after conversion of CO to CH_4.

The JMA measurements were based on the WMO X2014A scale, which has been propagated from the NOAA/GMD (Novelli et al., 2003). The other three laboratories used different standard gas scales (NIES09, MRI, and TU2010), which were independently developed and maintained for a long period.

Table 12. The four laboratories and their analytical methods, instruments, and calibration scales for CO during the iceGGO-4.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
NIES	VURF	VURF, AL5002 Aero-Laser, GmbH	NIES09 Scale	0 ppb - 5000 ppb	4	October 18, 2013
MRI	GC/FID	AG-1F (FID), Yanaco	MRI Scale	50 ppb - 500 ppb	5	December 9-11, 2013
NIES	VURF	VURF, AL5002 Aero-Laser, GmbH	NIES09 Scale	0 ppb - 5000 ppb	4	January 29, 2014
TU	GC/HgO	RGA Trace Analytical Inc.	TU2010 Scale	50 ppb - 320 ppb	4	March 18, 2014
JMA	GC/HgO	TRA-1, Round Science Inc.	WMO X2014A Scale	50 ppb - 350 ppb	4	May 27, 2014
NIES	VURF	VURF, AL5002 Aero-Laser, GmbH	NIES09 Scale	0 ppb - 5000 ppb	4	August 13, 2014

5.3. Results of iceGGO-4

Table 13 shows the CO concentrations measured in the two round-robin cylinders by the four laboratories using different methods together with NMIJ’s gravimetric values. The analytical precision of most of the measurements from the four laboratories was less than 1 ppb, although the precision was larger for the GC/FID method used by the MRI. The NIES measurements, which were made three times during this experimental period of about one year, revealed a CO concentration increase in both cylinders. After the drifts had been estimated and the difference of CO standard scales examined, the measured values were corrected as discussed in section 9.3. Thus, the concentrations in Table 13 reported by the four laboratories reflect not only the differences of CO standard scales but also the CO drift effect.

Table 13. CO concentrations (ppb) during the iceGGO-4. The reported precisions are shown in parentheses.

	Cylinder Identifications	
Laboratory	CPB16249	CPB28680
NIES	348.0 (0.8)	249.8 (0.7)
MRI	355.0 (0.8)	251.1 (1.8)
NIES	349.1 (0.1)	251.4 (0.1)
TU	346.4 (0.5)	251.2 (0.6)
JMA	348.9 (0.4)	251.4 (0.4)
NIES	351.7 (0.2)	252.6 (0.3)
NMIJ	346.1 (0.3)*	248.7 (0.3)*

*Gravimetric value (Expanded uncertainty of gravimetric method (k = 2))

Figure 5 shows the differences in the CO concentrations measured by each laboratory (Laboratory X) and the gravimetric value of the NMIJ for the two round-robin cylinders. The concentrations measured by the NIES clearly increased with time due to the CO drifts in both the cylinders; none of the measured values was corrected. The differences

(Laboratory X minus NMIJ) among the laboratories ranged from 0 ppb to +8 ppb for the two cylinders. When the CO drifts are taken into consideration, the measurements of both the TU, JMA, and NIES are almost in agreement with the NMIJ gravimetric values to within the WMO recommended compatibility criterion (±2 ppb). In contrast, relatively large deviations from the NMIJ gravimetric values were observed for the high-CO-concentration cylinder assayed by the MRI. These results mainly reflect differences in the CO calibration standard scales used by the MRI and JMA.

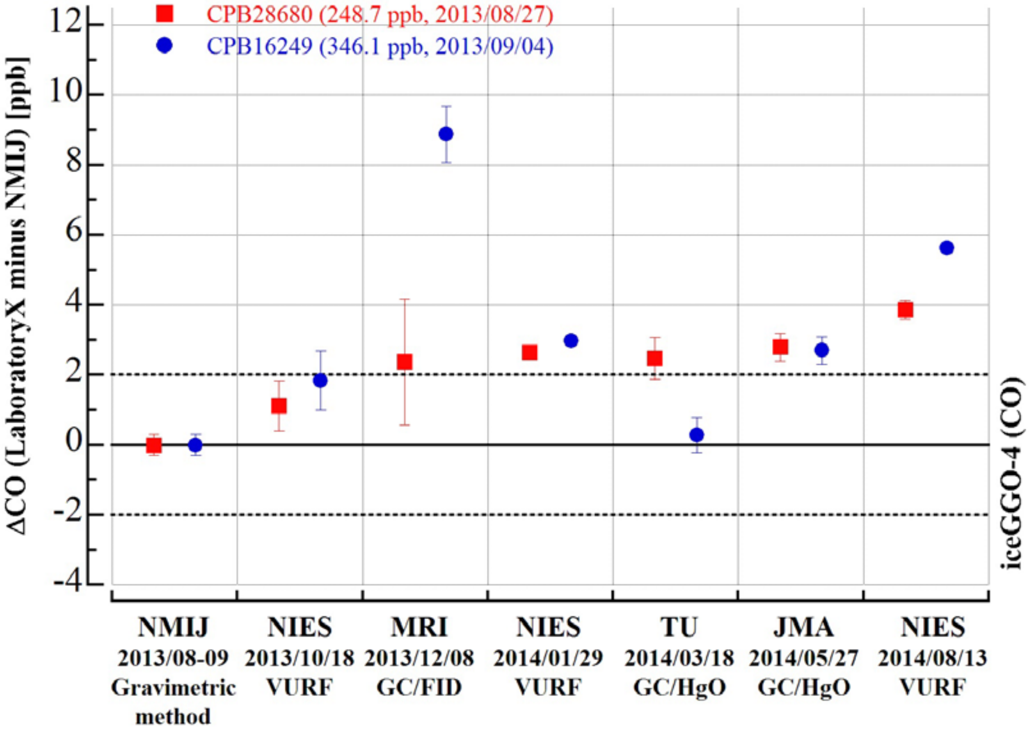

Figure 5. Differences (Laboratory X minus NMIJ) of CO concentrations for the two round-robin cylinders assayed for the iceGGO-4. The error bars represent the ± measurement precision reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method (k = 2). The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CO measurement compatibility.

6. iceGGO-5 (N_2O)

6.1. Round-robin cylinders (iceGGO-5)

The focus of the fifth experiment (iceGGO-5), which took place in 2016, was on a comparison of N_2O standard gas scales by circulating high-pressure gas cylinders. Table 14 provides details about the six sample cylinders used for this round-robin experiment. Five cylinders contained commercially available N_2O standard gases, which were filled by the JFP. The five gases were prepared using purified natural air as a matrix gas; their N_2O concentrations ranged from about 280 ppb to 340 ppb. The N_2O concentrations in the five cylinders had been previously calibrated twice by using the WMO X2006A scale (Hall et al., 2007) at NOAA in December 2006 and during September–October 2010. Their values have been published on the NOAA website (http://www.esrl.noaa.gov/gmd/ccl/refgas.html). Another cylinder (CPB31357) with a N_2O concentration of about 334 ppb was prepared from pure N_2O and purified natural air by the NMIJ gravimetric method. A four-step dilution was used to make the mixtures. The N_2O concentrations at each step were 19,000 ppm, 443 ppm, 14 ppm, and 330 ppb. Pure N_2 gas was used as the dilution gas in the first and second steps, and purified natural air was used as the dilution gas in the third and fourth steps. Three mixtures were prepared at each step. Table 15 lists the concentrations of the gases (N_2, O_2, Ar, and CO_2) in the mixtures. The expanded uncertainty of the gravimetric value ($k = 2$), ~0.18 ppb, was mainly associated with the determination of the N_2O concentration in the purified natural air.

Table 14. The six cylinders used for the iceGGO-5.

Cylinder Identification	N_2O Concentration (ppb)	Matrix gas	Manufacturer	Filling method	Date of filling
CQC00239	280.62 ±0.64*	Purified natural air	JFP	Volmetric	July, 27, 2006
CQC00238	295.69 ±0.18*	Purified natural air	JFP	Volmetric	July, 27, 2006
CQC00237	310.62 ±0.04*	Purified natural air	JFP	Volmetric	July, 27, 2006
CQC00236	325.88 ±0.25*	Purified natural air	JFP	Volmetric	July, 27, 2006
CQC00235	340.60 ±0.70*	Purified natural air	JFP	Volmetric	July, 27, 2006
CPB31357	333.88 ±0.18**	Purified natural air$	NMIJ	Gravimetric	March 4, 2016

*Averaged value measured in 2006 and 2010 by NOAA

**Gravimetric value from NMIJ with the expanded uncertainty (k = 2) after the ± symbols

$Detailed composition in Table 15

Table 15. Concentrations of gases in the iceGGO-5 cylinder prepared by the NMIJ gravimetric method. The numbers after the ± symbols indicate the expanded uncertainty (k = 2).

Cylinder Identification	N_2O ppb	CO_2 ppm	N_2 ppm	O_2 ppm	Ar ppm
CPB31357	333.88 ±0.18	398.38 ±0.08	780890 ±47.7	209389 ±41.7	9321.7 ±23.2

6.2. Measurement methods (iceGGO-5)

Five laboratories (JMA, AIST, MRI, NIES, and TU) participated in the iceGGO-5 round-robin measurements from March to October 2016. Table 16 provides details of the N_2O analytical methods used by the five laboratories. Three laboratories (JMA, NIES, and TU) used a gas chromatograph with an electron capture detector (GC/ECD) to measure N_2O concentrations, whereas three laboratories (JMA, AIST, and MRI) used a laser-based analyzer of Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS, LGR Inc.). The JMA measurements were based on the WMO X2006A scale (Hall et al., 2007), which has been propagated from the NOAA. The other four laboratories carried out their measurements using different standard gas scales (AIST, MRI2014, NIES96, and TU2006) that were developed independently. The calibration gases for the AIST, NIES, and TU covered a relatively wide range of N_2O concentrations, whereas the range of concentrations in the calibration gases used by the JMA and MRI was not wide enough to include the lowest concentration in one of the round-robin cylinders. To evaluate the stability of N_2O concentrations during the experimental period, the AIST assayed the NMIJ cylinder at the beginning and end of the experiment.

Table 16. The five laboratories that participated in the iceGGO-5 and their analytical methods, instruments, and calibration scales for N_2O.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
AIST(Laser)	ICOS	ICOS 907-0015, LGR	AIST Scale	270 ppb - 380 ppb	5	April 10-17, 2016
MRI(Laser)	ICOS	N2O/COAnalyzer, LGR	MRI 2014 Scale	300 ppb - 350 ppb	5	March 9, 2016
NIES(GC)	GC/ECD	Agilent 6890 (ECD), Agilent	NIES 96 Scale	250 ppb - 400 ppb	4	June 4-5, 2016
TU(GC)	GC/ECD	Agilent 6890 (ECD), Agilent	TU2006 Scale	120 ppb - 370 ppb	3	June 17 - July 20, 2016
JMA (GC)	GC/ECD	GC-2014 (ECD), Shimadzu	WMO X2006A Scale	300 ppb - 360 ppb	5	August 9 & October 13-14, 2016
JMA(Laser)	ICOS	DLT-100 Fast, LGR	WMO X2006A Scale	300 ppb - 360 ppb	5	August 19-20, 2016

6.3. Results of iceGGO-5

Table 17 lists the N_2O concentrations measured in the six round-robin cylinders by the five laboratories that used the GC/ECD and laser-based analyzers together with NMIJ's gravimetric value. No corrections for drift have been applied to the concentrations reported by any of the laboratories. The analytical precision of most of the measurements by four of the laboratories was less than 0.5 ppb; the precision of the JMA measurements made by the GC/ECD method was larger. In general, the precision of the laser-based analyzer, ICOS, was better than that of the GC/ECD. The JMA concentrations differed between the two analytical methods, although the same calibration standard gases were used for both of the methods.

Table 17. N_2O concentrations (ppb) during the iceGGO-5. The reported analytical precisions are shown in parentheses.

	Cylinder Identifications					
Laboratory	CPB31357	CQC00239	CQC00238	CQC00237	CQC00236	CQC00235
AIST (ICOS)	333.54 (0.03)	280.43 (0.06)	295.17 (0.05)	310.12 (0.05)	325.30 (0.05)	339.94 (0.05)
MRI (ICOS)	-	280.58 (0.25)	295.87 (0.53)	310.55 (0.03)	325.99 (0.34)	339.97 (0.04)
NIES (GC/ECD)	332.97 (0.13)	279.72 (0.20)	294.25 (0.16)	309.17 (0.18)	324.26 (0.18)	338.87 (0.01)
TU (GC/ECD)	334.37 (0.27)	280.79 (0.53)	295.54 (0.48)	310.05 (0.23)	325.55 (0.36)	339.79 (0.23)
JMA (GC/ECD)	335.15 (0.53)	280.92 (0.67)	295.61 (0.56)	310.65 (0.42)	325.95 (0.28)	340.56 (0.39)
JMA (ICOS)	333.84 (0.08)	280.59 (0.21)	295.41 (0.14)	310.52 (0.10)	325.84 (0.11)	340.54 (0.19)
NMIJ	333.88 (0.18)*	-	-	-	-	-

*Gravimetric value (Expanded uncertainty of gravimetric method (k = 2))

Figure 6 shows the differences in the N_2O concentrations measured by each laboratory (Laboratory X) and the NMIJ or NOAA for the six cylinders. The differences (Laboratory X minus NMIJ/NOAA) among the laboratories ranged from –1.7 ppb to +1.5 ppb. The differences from the NOAA values clearly depended on the N_2O concentrations for the measurements made by the AIST, NIES, and TU. In contrast, the values measured with ICOS analyzers by the MRI and JMA were similar to the NOAA values. These results reflect mainly differences in the N_2O calibration standard gas scales among the laboratories. The NMIJ gravimetric value was within ±1 ppb of the region of most of the N_2O measurements, except for the JMA measurement made with the GC/ECD.

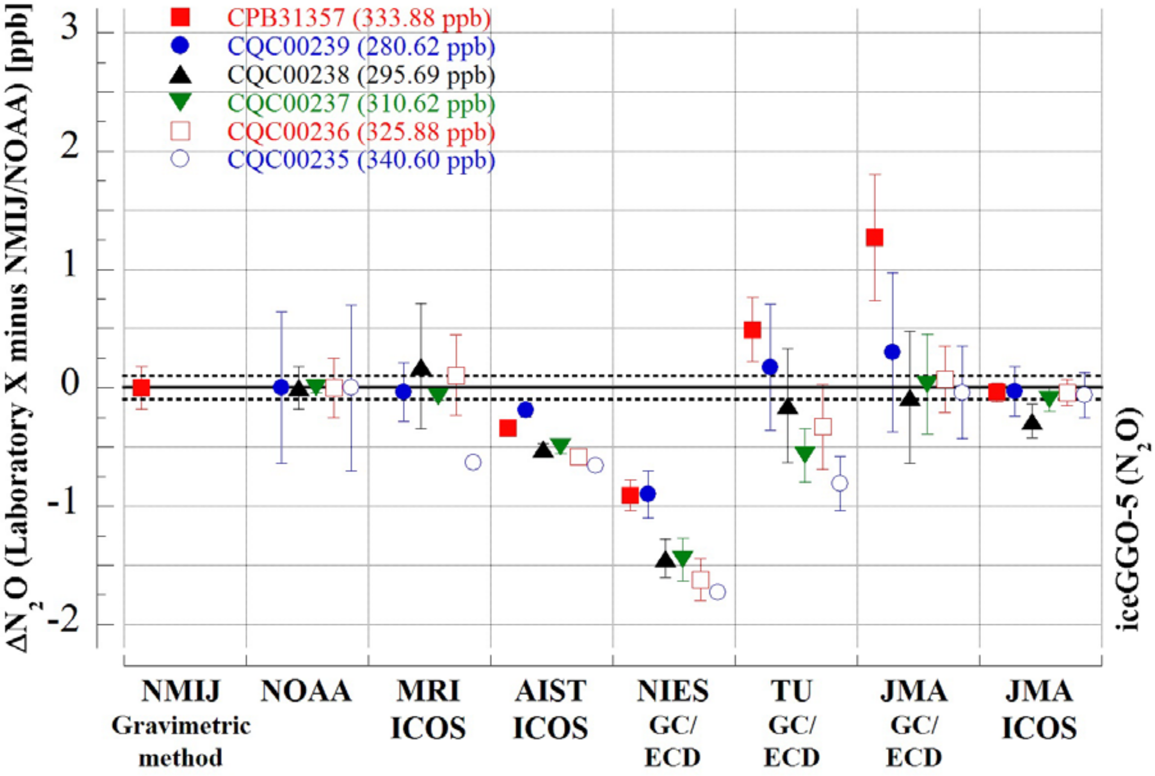

Figure 6. Differences (Laboratory X minus NOAA/NMIJ) of N_2O concentrations for each round-robin cylinder assayed during the iceGGO-5. The error bars represent the ± measurement uncertainty reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method (*k* = 2). The dashed lines around the zero line identify the WMO recommended criterion (±0.1 ppb) for N_2O measurement compatibility.

7. iceGGO-6 (CH_4)

7.1. Round-robin cylinders (iceGGO-6)

The sixth experiment (iceGGO-6), which took place in 2016, focused on a comparison of CH_4 standard gas scales by circulating high-pressure gas cylinders. Table 18 provides details about the four sample cylinders used in this round-robin experiment. Two cylinders contained commercially available CH_4 standard gases and were filled by the JFP. These two gas samples were prepared using purified natural air as the matrix gas, and the CH_4 concentrations were about 1738 ppb and 1877 ppb, respectively. They had previously been used for the fourth round-robin experiment of the GAW/WCC for CH_4 in Asia and the southwest Pacific region during 2011–2014 (http://ds.data.jma.go.jp/wcc/ch4/rusult_4th.html). The other two cylinders (CPB28035 and CPB28219) contained samples with CH_4 concentrations of about 1797 ppb and 2198 ppb, respectively. The samples were prepared by the NMIJ gravimetric method during the CIPM CCQM-K82 experiment. The cylinders were filled using a synthetic air diluent consisting of a mixture of pure N_2, O_2, Ar, and CO_2 (Table 19). The expanded uncertainty of the gravimetric values (k = 2), ±1.3 ppb, was associated mainly with the determination of the CH_4 in the matrix gases (pure O_2 and N_2). The details of the NMIJ gravimetric method have been reported elsewhere (Flores et al., 2015).

Table 18. The four cylinders used for the iceGGO-6.

Cylinder Identification	CH_4 Concentration (ppb)	Matrix gas	Manufacturer	Filling method	Date of filling
CPB28035	1797.3*	Synthetic air$	NMIJ	Gravimetric	August 28, 2012
CPB28219	2198.3*	Synthetic air$	NMIJ	Gravimetric	June 6, 2012
CPB31288	1740.1**	Purified natural air	JFP	Gravimetric	February 25, 2011
CPB31289	1878.6**	Purified natural air	JFP	Gravimetric	February 25, 2011

*Gravimetric value from NMIJ

**Measured by JMA/CRDS

$Detailed composition in Table 19

Table 19. Details of the compositions of the two cylinders prepared by the NMIJ gravimetric method. The numbers after the ± symbols indicate the expanded uncertainty (k = 2).

Cylinder Identification	CH_4 ppb	CO_2 ppm	N_2 ppm	O_2 ppm	Ar ppm
CPB28035	1797.3	386.66	779814	210538	9259.76
	±1.32	±0.091	±6.33	±6.45	±0.715
CPB28219	2198.3	383.39	780898	209276	9439.93
	±1.33	±0.087	±6.55	±6.68	±0.757

7.2. Measurement methods (iceGGO-6)

Four laboratories (JMA, AIST, MRI, and NIES) participated in the iceGGO-6 round-robin measurements from February 2016 to September 2016. Table 20 provides details of the CH_4 analytical methods used by the five laboratories. The JMA and MRI used a laser-based analyzer and wavelength-scanned cavity ring-down spectroscopy (WS-CRDS, Picarro Inc.) to measure CH_4 concentrations. Three laboratories (JMA, AIST, and NIES) used a GC/FID, although the instruments they used differed. The JMA measurements were based on the WMO X2004A scale, which has been propagated from the NOAA

(Dlugokencky et al., 2005). The other three laboratories carried out their measurements using different standard gas scales (AIST, MRI, and NIES94), which were developed independently. The calibration gases used by the AIST and NIES covered a relatively wide range of CH_4 concentrations, whereas the range of concentrations in the calibration gases used by the JMA and MIR was not wide enough to measure the highest concentration in the round-robin cylinder. To assess the gases for drift during the experimental period, the AIST measured the CH_4 concentrations in the two NMIJ cylinders at the beginning and end of the round-robin experiment.

Table 20. The four laboratories that participated in the iceGGO-6 and their analytical methods, instruments, and calibration scales for CH_4.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
AIST	GC/FID	GC-14BPF (FID), Shimadzu	AIST Scale	1010 ppb - 2530 ppb	4	April 2-9, 2016
MRI	CRDS	G2301 (CRDS), Picarro	MRI Scale	1600 ppb - 2100 ppb	5	February 12, 2016
NIES	GC/FID	HP7890 (FID), Agilent	NIES94 Scale	1250 ppb - 2500 ppb	6	May 18-19, 2016
JMA	GC/FID	GC-14BPF (FID), Shimadzu	WMO X2004A Scale	1620 ppb - 2110 ppb	5	August 15, 2016
JMA	CRDS	G2301 (CRDS), Picarro	WMO X2004A Scale	1610 ppb - 2160 ppb	5	August 4, 2016

7.3. Results of iceGGO-6

Table 21 lists the CH_4 concentrations measured in the four gas cylinders by the four laboratories. The AIST measurements at the end of the experiment revealed no change of CH_4 concentration in the two NMIJ cylinders. Thus, no correction for drift during the experimental period was applied to the concentrations reported by the laboratories. The analytical precision of most of the measurements in all the laboratories was less than ~2 ppb. The measurement precision of the laser-based analyzer, CRDS, was generally better than that of the GC/FID.

Table 21. CH_4 concentrations (ppb) measured during the iceGGO-6. The reported analytical precisions are indicated in parentheses.

	Cylinder Identifications			
Laboratory	CPB28035	CPB28219	CPB31288	CPB31289
AIST (GC/FID)	1797.8 (1.3)	2198.0 (1.4)	1741.1 (1.8)	1880.9 (1.7)
MRI (CRDS)	1796.3 (0.1)	2199.5 (0.1)	1739.5 (0.1)	1880.5 (0.1)
NIES (GC/FID)	1798.8 (0.6)	2200.1 (0.3)	1742.0 (0.1)	1882.4 (0.2)
JMA (GC/FID)	1793.3 (1.0)	2192.8 (2.0)	1738.1 (1.5)	1876.9 (1.6)
JMA (CRDS)	1796.4 (0.1)	2192.2 (0.2)	1740.1 (0.5)	1878.6 (0.3)
NMIJ	1797.3 (1.3)*	2198.3 (1.3)*	-	-

*Gravimetric value (Expanded uncertainty of gravimetric method (k = 2))

Figure 7 shows the differences between the CH_4 concentrations in the four cylinders measured by each laboratory (Laboratory X) and the NMIJ or NOAA. The NMIJ values for the two cylinders are based on the gravimetric method, whereas the NOAA values for the other two cylinders at 1740.0 ± 0.7 ppb (CPB31288) and 1879.7 ± 1.0 ppb (CPB31289) were measured during the fourth round-robin experiment of the JMA/WCC for CH_4 from

January to February 2014 (http://ds.data.jma.go.jp/wcc/ch4/rusult_4th.html). The differences (Laboratory X minus NMIJ/NOAA) among the laboratories ranged from –6 ppb to +7 ppb.

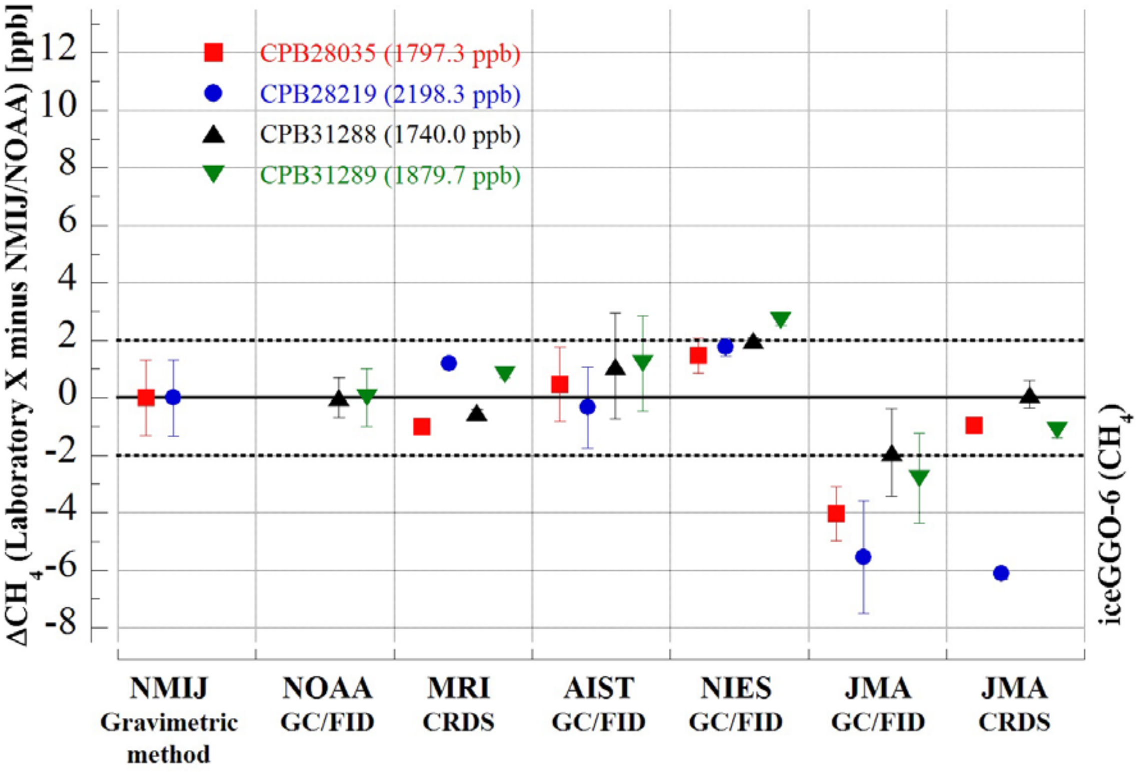

Figure 7. Differences (Laboratory X minus NOAA/NMIJ) of CH_4 concentrations for each round-robin cylinder measured during the iceGGO-6. The error bars represent the ± measurement precision reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method ($k = 2$). The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CH_4 measurement compatibility.

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.

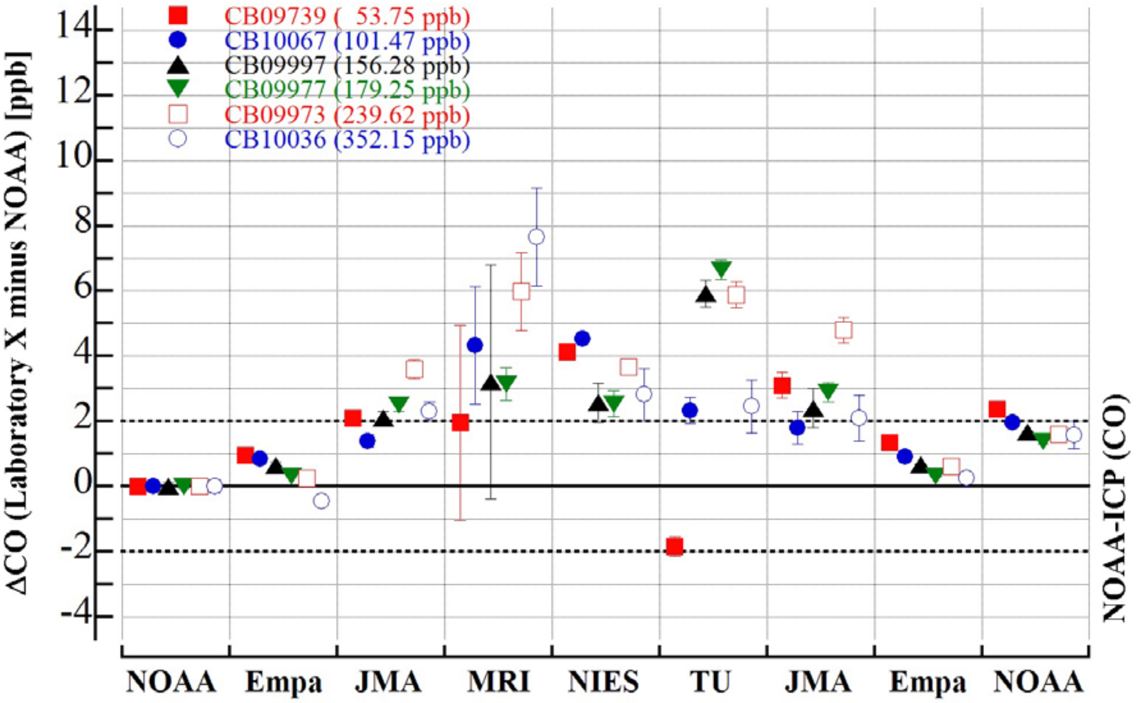

Figure 8. Differences (Laboratory X minus NOAA) of CO concentrations in six round-robin cylinders assayed for the NOAA-ICP. The error bars represent the ± measurement uncertainty reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CO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

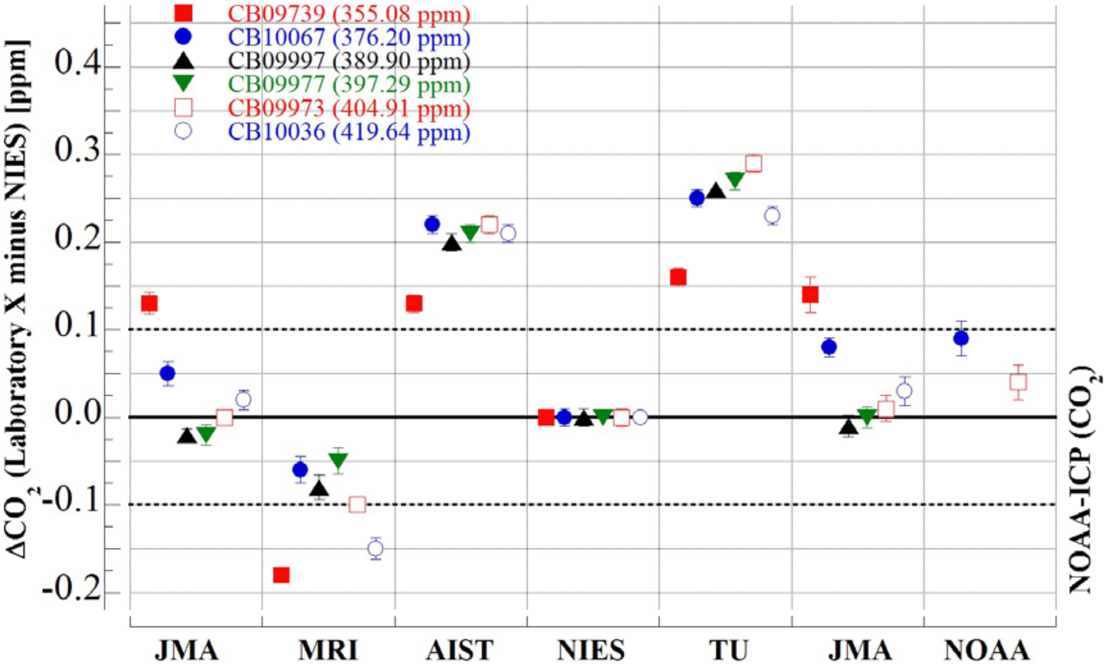

Figure 9. Differences (Laboratory X minus NIES) of CO_2 concentrations for six round-robin cylinders assayed for the NOAA-ICP study. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±0.1 ppm)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

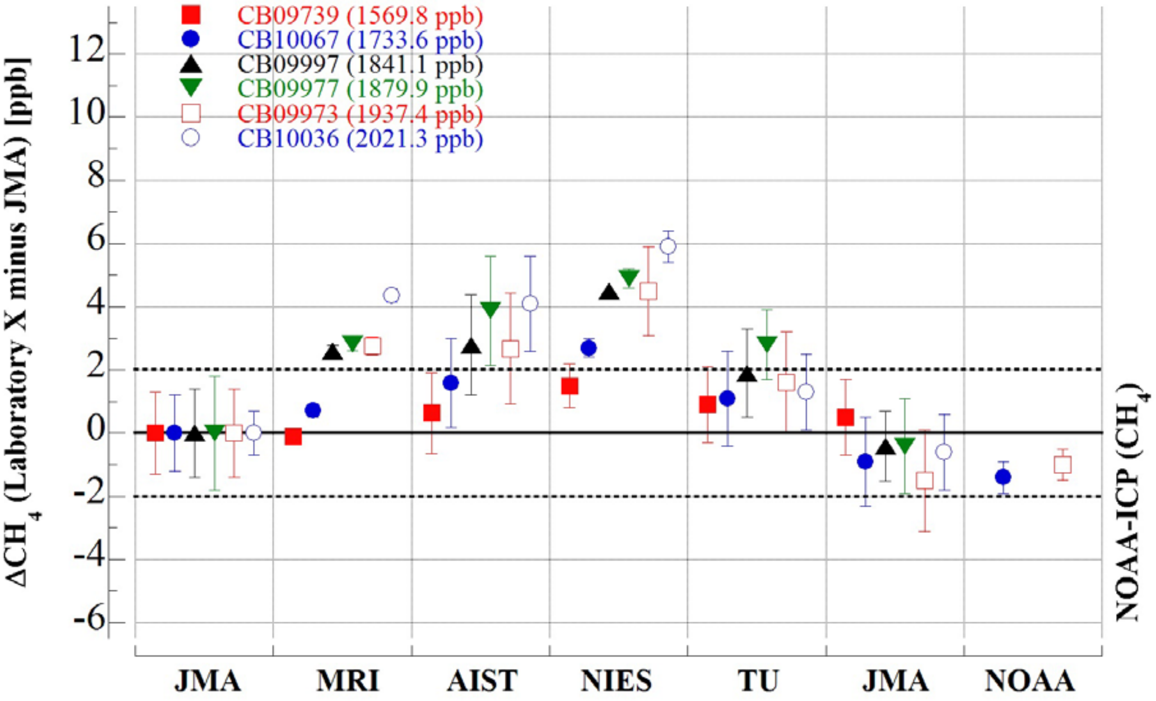

Figure 10. Differences (Laboratory X minus JMA) of CH_4 concentrations in six round-robin cylinders assayed during the NOAA-ICP experiment. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±2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

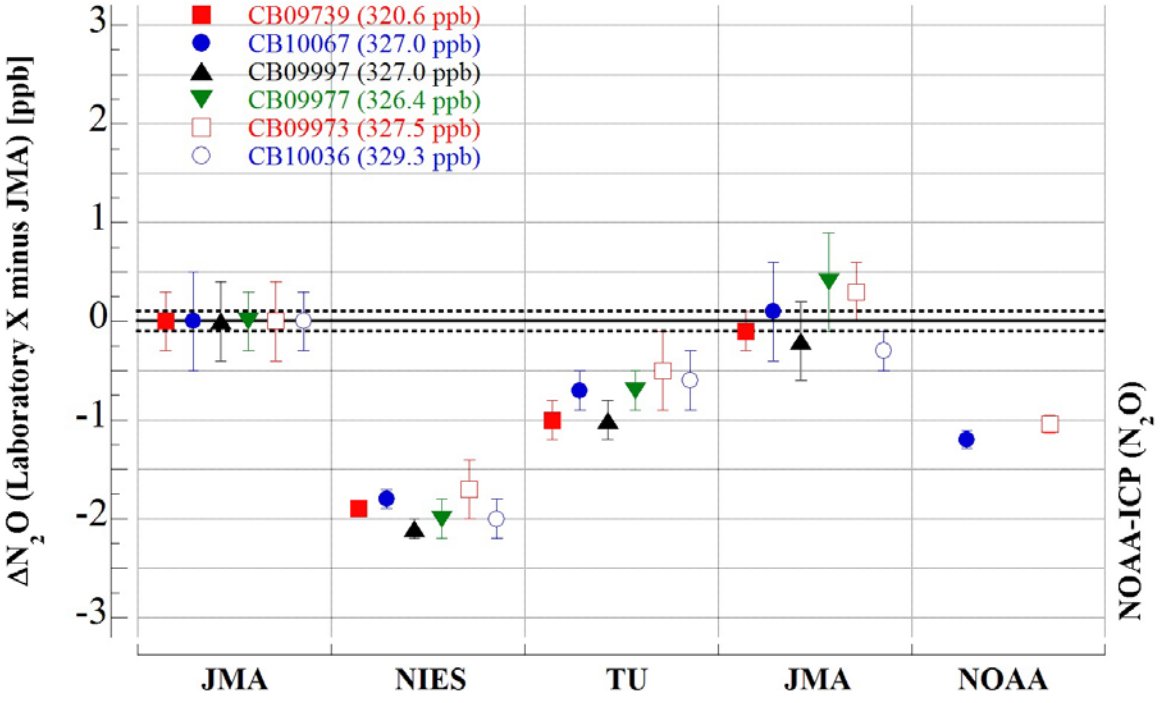

Figure 11. Differences (Laboratory X minus JMA) of N_2O concentrations in six round-robin cylinders assayed for the NOAA-ICP study. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO recommended criterion (±0.1 ppb)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

9. Discussion

9.1. Measurement precisions

In the iceGGO and NOAA-ICP experiments, all participating laboratories reported measurement precisions, although their estimation methods differed. Figure 12 shows frequency distributions of the measurement precisions reported by all participating laboratories in Japan for CO_2 with NDIR, CH_4 with GC/FID, CO with GC/RGD and VURF, and N_2O with GC/ECD.

The CO_2 analyses with NDIRs were very precise. The precisions were less than 0.045 ppm for all of the laboratories, although different types of NDIRs were used. The mean of all reported precisions for the CO_2 measurements was 0.014 ppm (n = 104). Most of the CH_4 measurement errors were less than 2 ppb, although several precisions greater than 3.5 ppb were derived from the extrapolated calibrations of the JMA. The mean of all reported precisions for the CH_4 measurements was 1.4 ppb (n = 84), which was similar to the overall precision of less than 1.5 ppb for the NOAA study, which involved use of a GC/FID (Dlugokencky et al., 2005). The CO measurement precisions for the GC/RGD and VURF methods were less than 1 ppb, but the precision of the GC/FID method used by the MRI was larger. All reported precisions for the CO measurements were high, the mean being 0.37 ppb (n = 34). The precision for the GC/FID method was especially large. Most of the N_2O measurement precisions with the GC/ECD method used by the NIES and TU were less than 0.3 ppb, but larger precisions were often observed for the JMA measurements. The mean of all reported errors for the N_2O measurements made by these three laboratories was 0.31 ppb (*n* = 42).

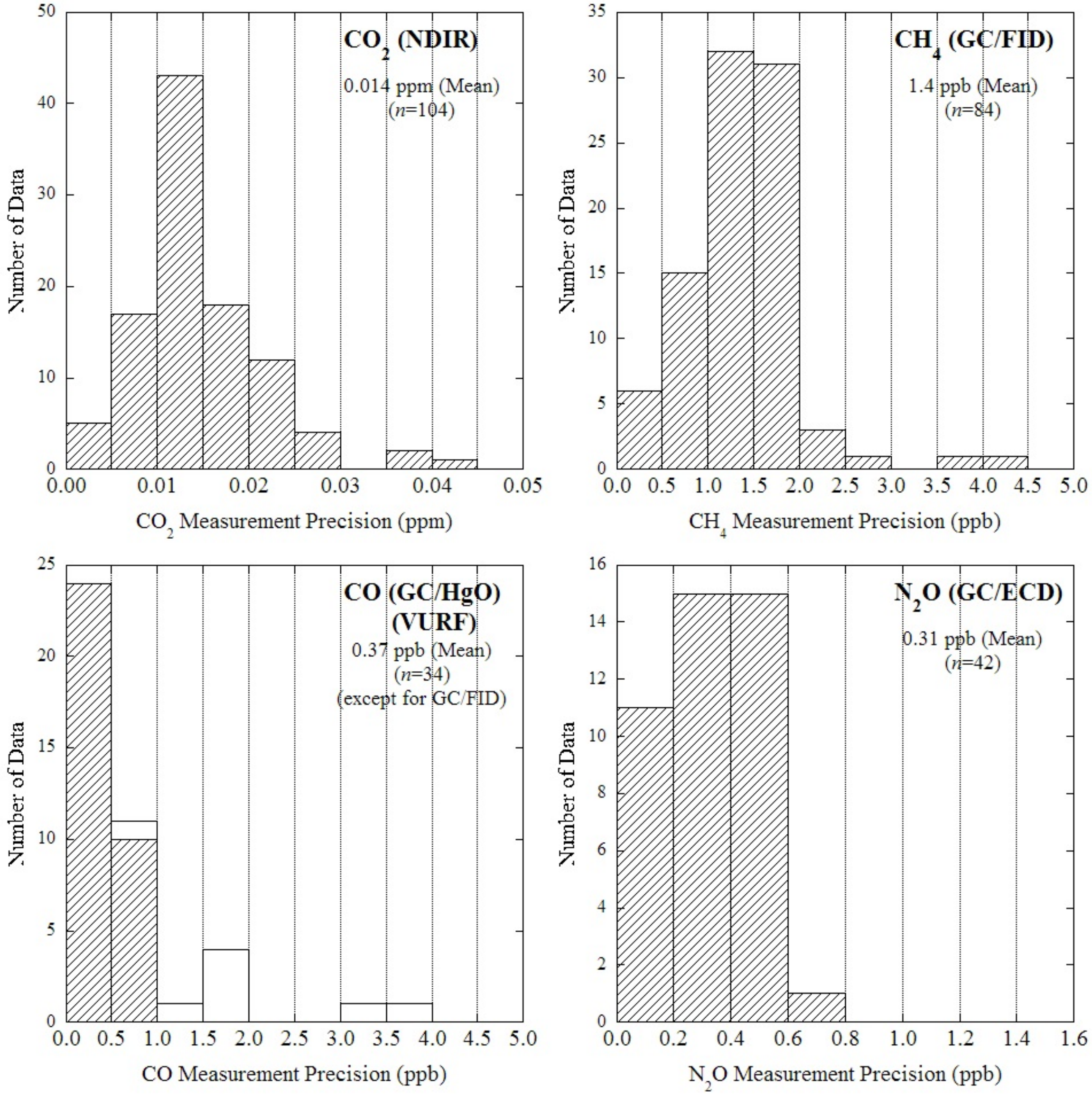

Figure 12. Frequency distributions of measurement precisions reported by all participating laboratories for CO_2, CH_4, CO, and N_2O. Open bars in the case of CO represent the precisions of the GC/FID measurements.

9.2. CH_4 scale adjustment

CH_4 comparative data were collected from three experiments, iceGGO-1, iceGGO-6, and NOAA-ICP, to address differences of CH_4 standard gas scales. These experiments revealed a difference of ~ 12 ppb in the CH_4 concentrations measured by the participating laboratories. It was clearly apparent that the differences of the CH_4 concentrations from the JMA values (Laboratory X minus JMA) increase with an increase of the concentrations for all the other laboratories (Figure 13).

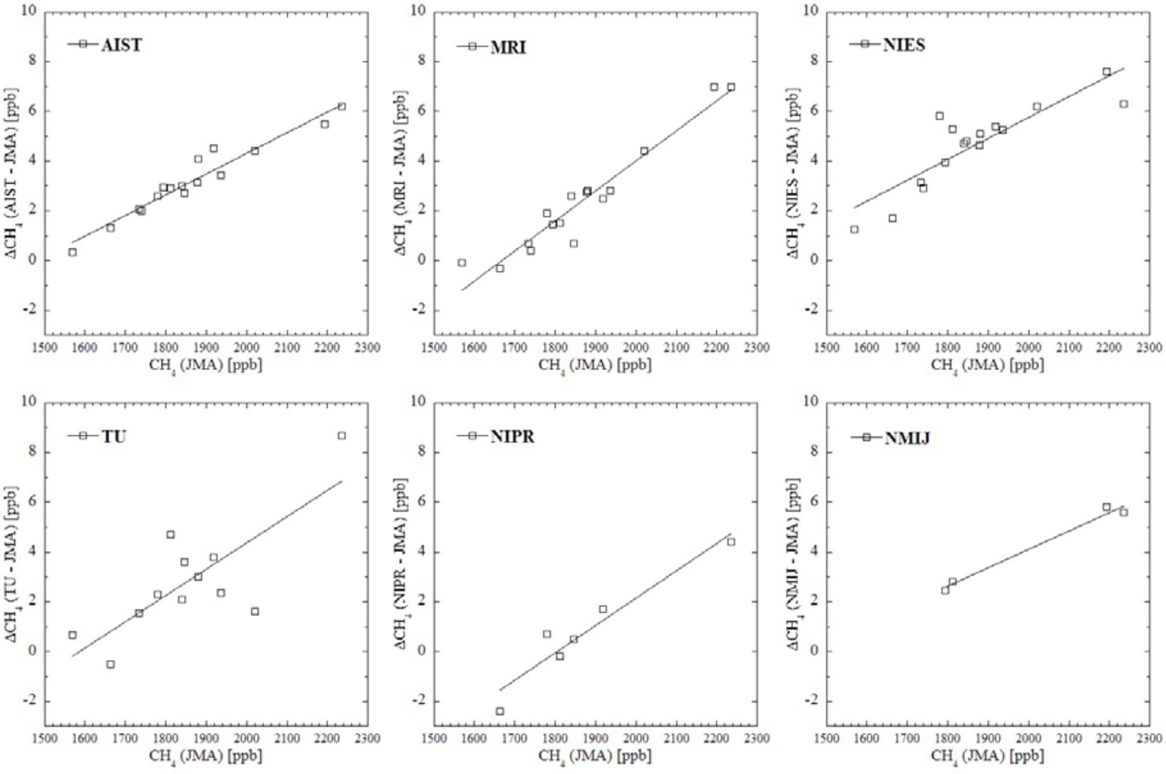

Figure 13. Differences of the measured CH_4 concentrations between participating laboratory and the JMA values as a function of CH_4 concentrations for the AIST, MRI, NIES, TU, NIPR, and NMIJ. The solid line represents the least-squares fit to all data points from three experiments: iceGGO-1, iceGGO-6, and NOAA-ICP.

The differences were therefore fitted with a linear regression line to examine their empirical relationship as follows:

$$C_{\mathrm{X}} - C_{\mathrm{JMA}} = a + b(C_{\mathrm{JMA}}), \qquad (3)$$

where C_{X} and C_{JMA} are the measured CH_4 concentrations of Laboratory X and JMA, respectively. Table 31 lists the coefficients from the best fits of Eq. (3) for the six laboratories. These linear relationships clearly revealed that the differences of the CH_4 concentrations, which ranged from about 1550 to 2250 ppb, were well described by a straight line. The correlation coefficients (r) exceeded 0.78 (Table 31). These results indicate that all measured CH_4 concentrations from the six laboratories could be re-calculated with a simple linear relationship to adjust the values to the same standard gas scale.

Table 31. Coefficients obtained with linear least square fits of Eq. (3) to the differences of the CH_4 concentrations from the JMA values for the six laboratories.

Laboratory	*a*	*b*	*r*
AIST	-12.3	0.00833	0.97
MRI	-20.3	0.01215	0.96
NIES	-11.1	0.00846	0.87
TU	-16.8	0.01059	0.78
NIPR	-19.9	0.01102	0.96
NMIJ	-10.8	0.00744	0.99

Figure 14 shows a frequency distribution of the differences of all CH_4 concentrations (n = 70) from the JMA values for the three intercomparison experiments. The differences were widely distributed from –3 ppb to 9 ppb, and they often exceeded the criterion for compatibility of CH_4 measurements (± 2 ppb) recommended by the WMO. This result strongly reflects differences in the CH_4 standard gas scales among the participating laboratories. These differences were therefore re-calculated based on the linear fit of Eq. (3) using the coefficients in Table 31, and their frequencies are shown in Figure 14. After a scale adjustment, the frequency distribution of the re-calculated differences covered a relatively narrow range, from –2 ppb to +2 ppb with a mean near zero, with the caveat that two data points deviated from this range. This result indicates that the re-calculation of fits from our comparison experiments was suitable for making datasets consistent by adjusting for differences of the standard gas scales by all participating laboratories.

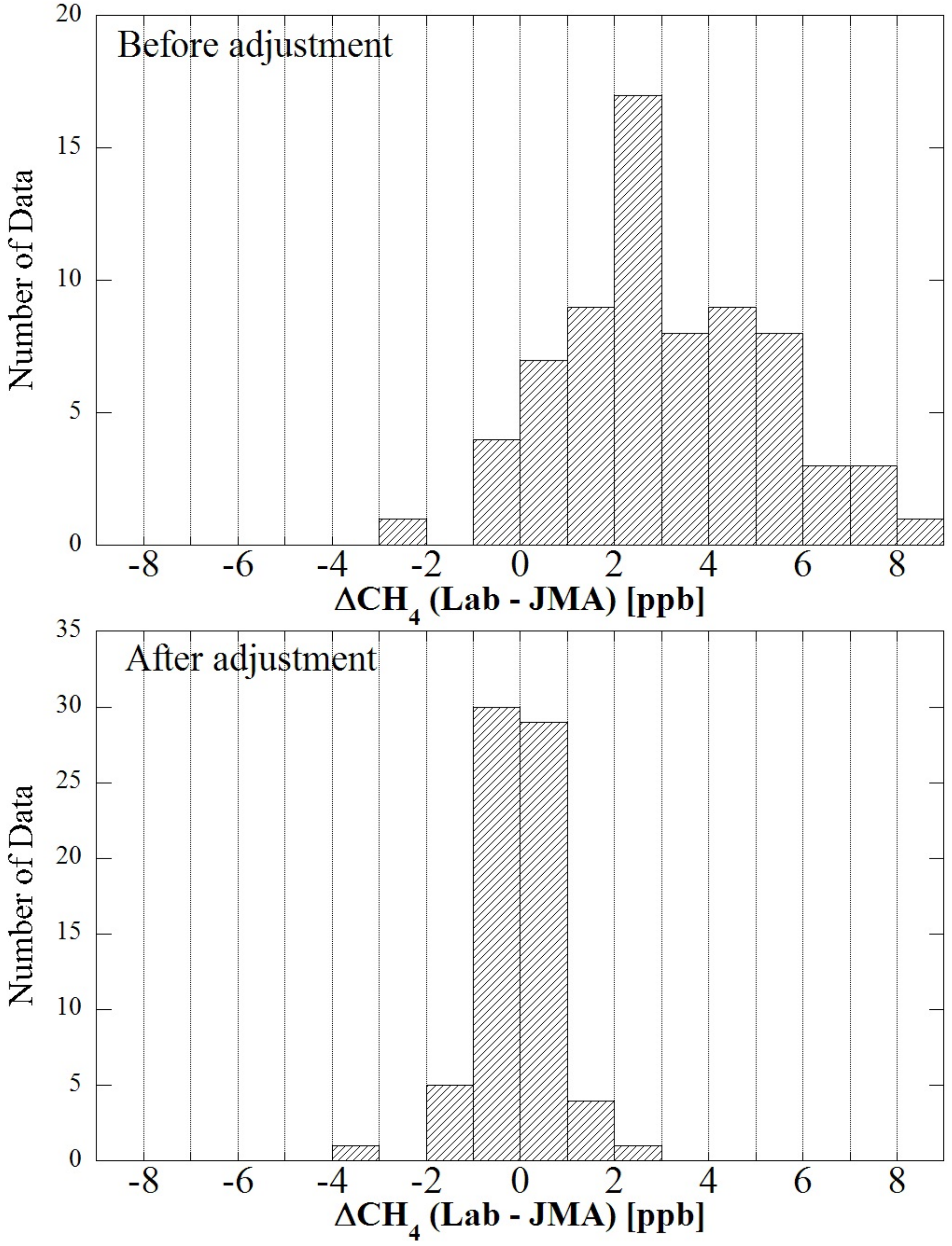

Figure 14. Frequency distributions of differences of all CH_4 measurements (n = 70) from the JMA for the three intercomparison experiments before and after scale adjustments.

9.3. CO scale adjustment

The CO comparison data were collected from two experiments, iceGGO-4 and NOAA-ICP, to focus on the difference of CO standard gas scales. For the iceGGO-4, CO concentrations in the two cylinders were found to increase with time during the experimental period of about one year. These CO increases were described rather well by linear regressions based on the three NIES measurements (Figure 15). The linear drift of CO concentrations was estimated to be about +3.2 ppb/yr for the CPB28680 cylinder and +4.7 ppb/yr for the CPB16249 cylinder. A similar CO concentration increase was also found in all six cylinders during the NOAA-ICP experiment when the measurements of the NOAA and Empa at the beginning and the end of the experiment were compared (Figure 8). The average linear drift of the CO concentrations for the NOAA-ICP experiment was estimated to be about 1 ppb/yr, which was smaller than the drift for the iceGGO-4 experiment, probably due to the difference of cylinder volume.

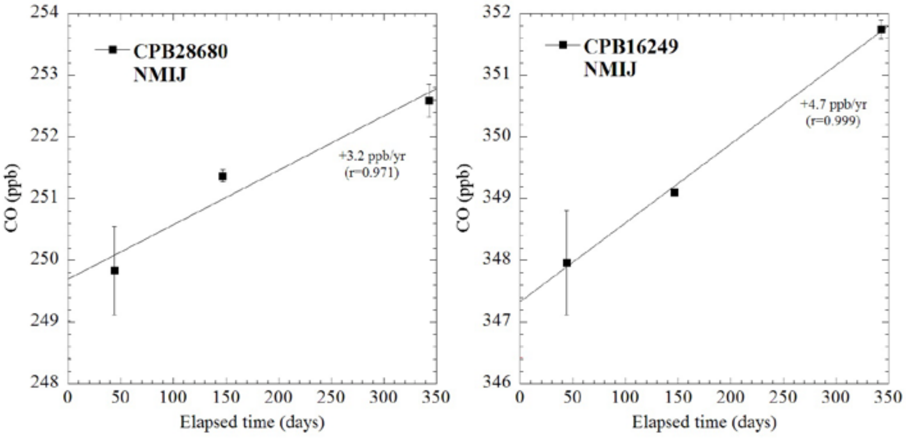

Figure 15. Changes of CO concentrations in the two cylinders (CPB28680 and CPB16249) with elapsed time during the iceGGO-4 experiment. The slopes of the linear regression lines represent CO drifts of +3.2 ppb/yr and +4.7 ppb/yr.

All reported CO values were therefore corrected based on the estimated drifts as stated above, and they were then compared to calculate the differences of CO concentrations among the participating laboratories. These results revealed a difference of ~16 ppb for the corrected CO measurements among all the laboratories. It was apparent that the differences of the CO concentrations from the NIES values (Laboratory X minus NIES) were rather well described by a linear regression line, although the TU and NIES relationships were described by two regression lines (Figure 16).

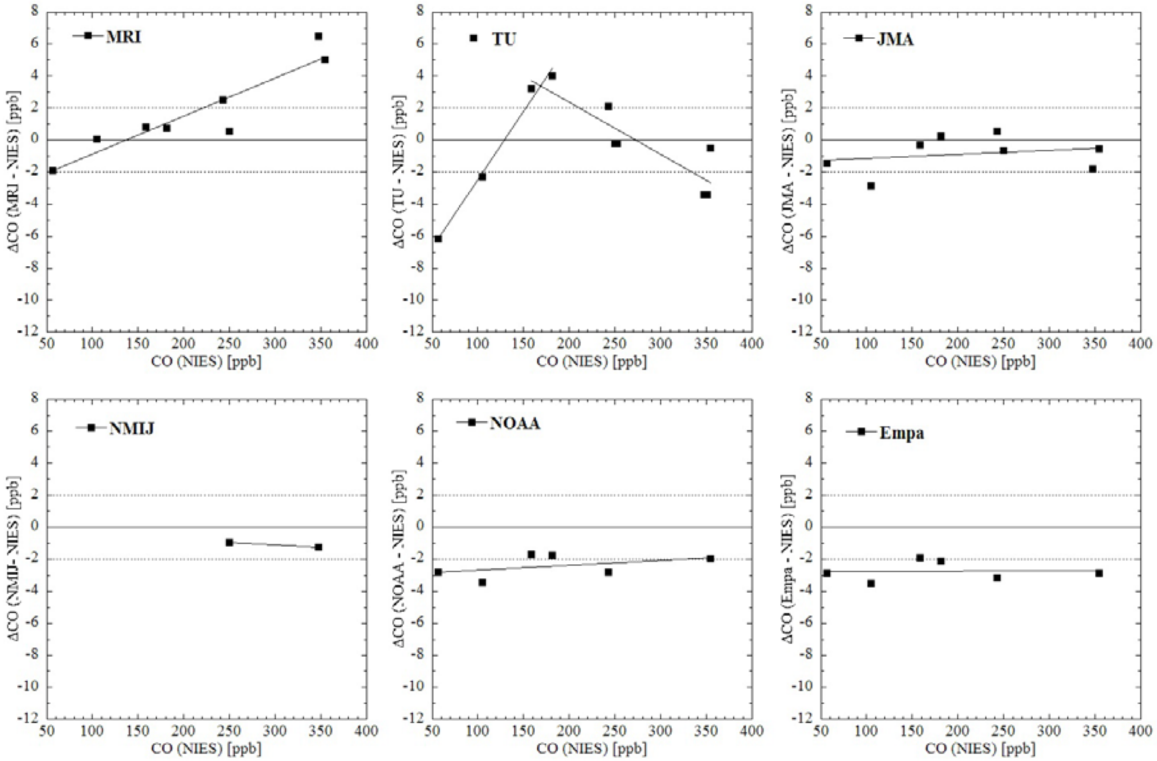

Figure 16. Differences of the measured CO concentrations between participating laboratory and the NIES values as a function of CO concentrations for the MRI, TU, JMA, NMIJ, NOAA, and Empa. The solid line represents a least-squares fit to all data points from two experiments, iceGGO-4, and NOAA-ICP. The TU-NIES relationships, however, were described by two regression lines.

The differences for each laboratory were fitted by a linear regression line to examine their empirical relationships as follows:

$$C_X - C_{NIES} = a + b(C_{NIES}), \qquad (4)$$

where C_X and C_{NIES} are the corrected CO concentrations of Laboratory X and the NIES, respectively. Table 32 lists the coefficients from the best fits of Eq. (4) for the six laboratories. These linear relationships clearly revealed that the differences of the CO concentrations, which ranged from about 50 ppb to 350 ppb, depended on the CO concentrations. These results indicate that all of the CO measurements from the six laboratories could be re-calculated with a simple linear relationship to adjust the values to a common standard gas scale.

Table 32. Coefficients obtained by linear least-squares fits of Eq. (4) to the differences of the drift of the corrected CO concentrations from the NIES values for the six laboratories.

Laboratory	a	b	r	Range of CO (ppb)
MRI	-3.25	0.024	0.93	50-350
TU	-11.03	-0.086	0.99	50-170
TU	8.84	-0.032	0.90	170-350
JMA	-1.38	-0.003	0.24	50-350
NMIJ	-0.16	-0.003	1.00	250-350
NOAA	-2.95	0.003	0.45	50-350
Empa	-2.77	0.002	0.03	50-350

Figure 17 shows frequency distributions of the differences of all CO measurements (n = 38) from the NIES values for the two intercomparison experiments before and after scale adjustments. The differences before the scale adjustments were widely distributed, from –8 ppb to +8 ppb, and they often exceeded the criterion for compatibility of CO measurements (±2 ppb) recommended by the WMO. This result strongly reflects differences in the reference CO standard gas scales among the participating laboratories. The differences were therefore re-calculated based on the linear fit of Eq. (4) using the coefficients in Table 32, and their frequency distribution is shown in Figure 17. The frequency distribution after the scale adjustment was narrower, the range of differences being –2 ppb to +2 ppb with a mean near zero, with the caveat that several data points deviated from this range. This result indicates that the re-calculated fits from our comparison experiments are suitable for making consistent datasets from the observed CO concentrations from all the laboratories by adjusting the difference of the CO standard scales.

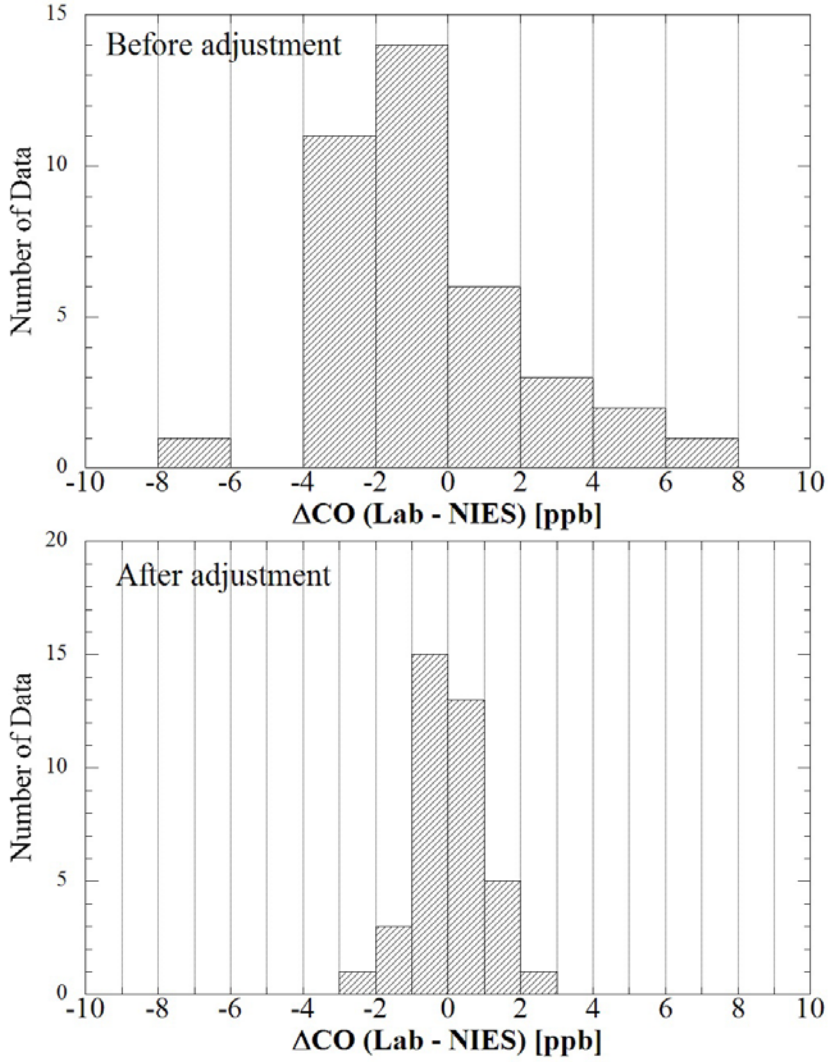

Figure 17. Frequency distributions of the differences of all the CO measurements (n = 38) from the NIES values for the two intercomparison experiments before and after scale adjustments.

9.4. CO_2 scale adjustment

The CO_2 measurement biases from the NIES values, estimated from Figure 18 using the results of the iceGGO-2 experiment, were 0.21 ppm for the TU, 0.16 ppm for the AIST, and 0.25 ppm for the NIPR. In contrast, the difference between the JMA and NIES values clearly decreased with increasing CO_2 concentration. The relationship could be fitted according to the linear equation $C_{JMA} – C_{NIES} = 0.867 + 0.0020602(C_{JMA})$, where C_{JMA} and C_{NIES} are the CO_2 concentrations measured by the JMA and NIES, respectively.

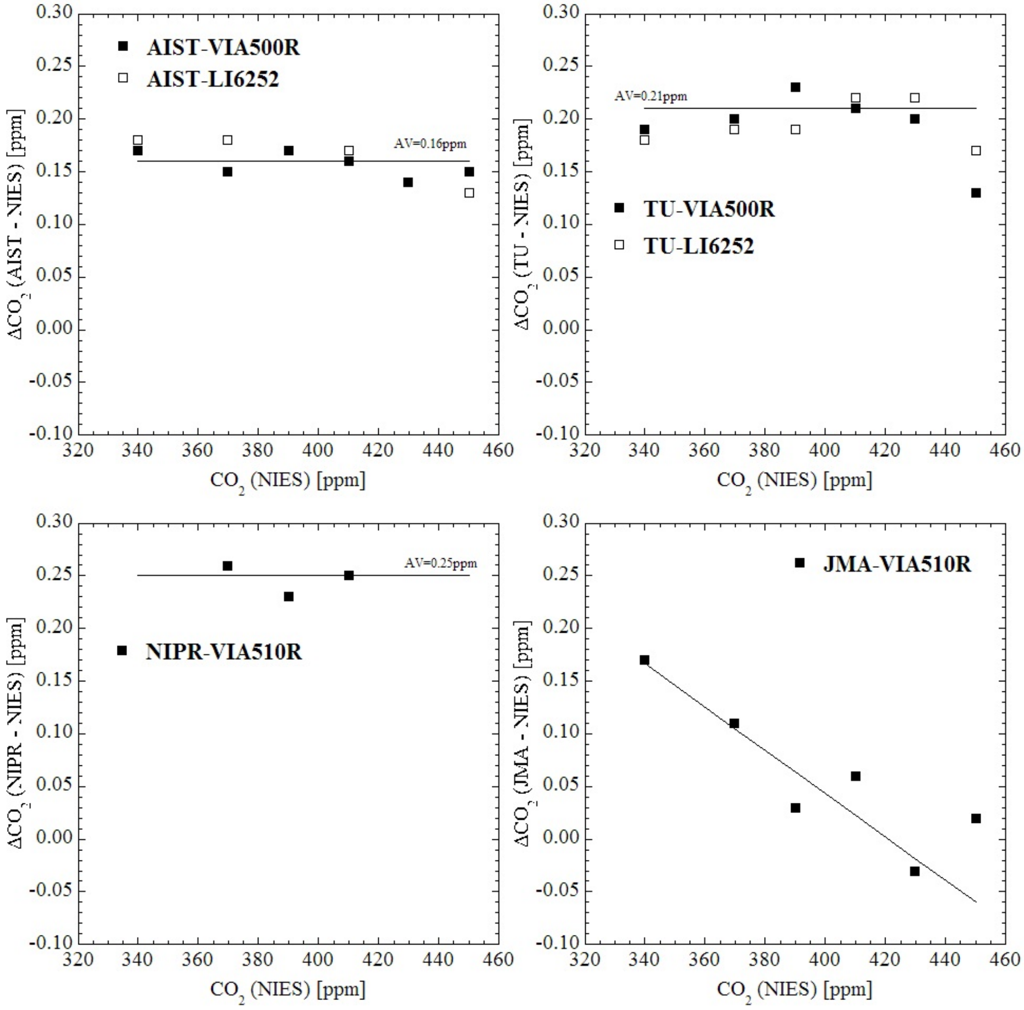

Figure 18. Differences of the measured CO_2 concentrations between participating laboratories and the NIES values as a function of CO_2 concentrations for the AIST, TU, NIPR, and JMA. The AIST and TU used two different analyzers. The solid line represents the estimated scale bias based on all data points from the iceGGO-2 experiment, which was based on six round-robin cylinders with isotopically lighter CO_2 derived from combusted petroleum.

Taking into consideration these estimated biases, the differences from the NIES values were re-calculated, and the values were then compared before and after the scale adjustment (Figure 19). The large deviations of the differences among the laboratories were significantly reduced after re-calculation, and the averaged differences were smaller. It was apparent that most of the CO_2 measurements from all six laboratories could be adjusted to within ±0.02 ppm based on the measurement scale biases from the iceGGO-2 experiment.

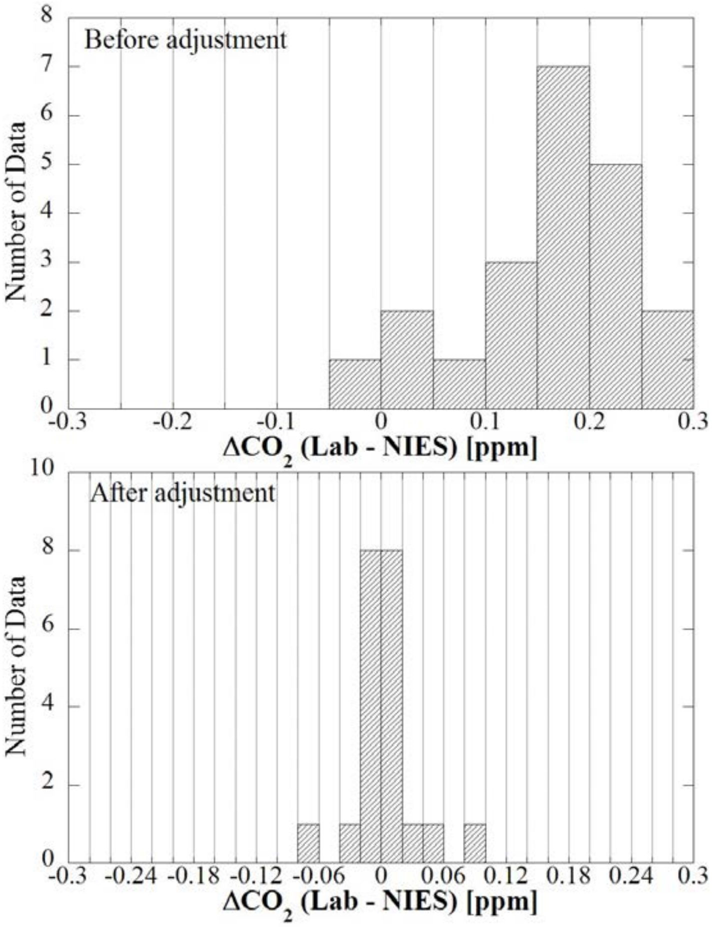

Figure 19. Frequency distributions of differences of all CO_2 measurements (n = 21) from the NIES values for the iceGGO-2 experiment before and after scale adjustments.

9.5. CO_2 isotope effect

In general, the NDIR analyzers used for the CO_2 measurements have mechanisms to reduce the interference effects from other infrared-active species. In the case of the LI-COR NDIR analyzers, including the LI-6252, optical bandpass filters designed to transmit wavelengths for a fundamental absorption band of $^{12}C^{16}O_2$ are placed between the sample cell and the detector to enhance the selective sensitivity to the CO_2. Unfortunately, the bandpass filter blocks a substantial part of the absorption band of $^{13}C^{16}O_2$, because the absorption region for $^{13}C^{16}O_2$ in substantial part overlaps those of N_2O and CO. Therefore, the LI-COR NDIR analyzer has different relative molar sensitivities to the different CO_2 isotopologues ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O^{16}O$, etc) that could potentially result in different responses to CO_2-in-air samples with the same bulk CO_2 mixing ratio but different isotopic compositions (Tohjima et al., 2009). This feature of the LI-COR NDIR analyzer resulted in significant errors in the measurement of the CO_2 mixing ratio of the ambient air sample because the CO_2 standard gases of all the laboratories participating in the iceGGO experiments were mixtures of purified natural air and isotopically light CO_2 gases derived from combusted petroleum.

In the iceGGO-2 and iceGGO-3 interlaboratory comparison experiments and the NOAA-ICP, three types of NDIR analyzers, VIA-500R, VIA-510R, and LI-6265, were used to measure the round-robin gas concentrations with a wide range of CO_2 isotopic compositions. We thus evaluated the isotope effects of the NDIR analyzers by using the results of the 12 cylinders for which the CO_2 isotopic compositions were significantly different from those of the CO_2 standard gases used in each laboratory (Table 33). The apparent differences in the measured CO_2 mixing ratios caused by the NDIR isotope effect were evaluated as follows. First, the CO_2 mixing ratios for the 12 cylinders determined by the AIST, JMA, and TU were converted to values based on the NIES CO_2 scale by using the adjustment factors described in section 9.4. Then, the differences of the adjusted CO_2 mixing ratios from the NIES values were computed (Table 33). Because the CO_2 mixing ratios determined by the LI-6252 at the NIES were precisely (within ±0.01 ppm) corrected for the isotope effect by adopting the approach of Tohjima et al. (2009), we considered these apparent differences to be due mainly to the isotope effect of the NDIR analyzers.

Table 33. Summary of CO_2 mixing ratios and isotopic values ($\delta^{13}C$ and $\delta^{18}O$) for the 12 round-robin cylinders used to evaluate the isotope effect of the five NDIR analyzers[a].

Cylinder #	$CO_{2,NIES}$	$\delta^{13}C^{c}$	$\delta^{18}O^{c}$			$CO_{2,X}-CO_{2,NIES}$[b]		
	NIES(6252)	‰,VPDB		AIST(6252)	AIST(500R)	JMA(510R)	TU(500R)	TU(6252)
iceGGO-2								
CPB28548	370.06(2)	57.3	-28.4	-0.29(2)	-0.05(2)	-0.18(2)	-0.01(2)	-0.34(2)
CPB16443	406.02(1)	-8.8	0.4[d]	-0.14(2)	-0.02(2)	-0.06(2)	-0.01(2)	-0.12(3)
CPB29524	409.31(1)	-9.0	0.4[d]	-0.14(2)	-0.02(2)	-0.06(1)	0.00(1)	-0.12(2)
iceGGO-3								
CPD00070	379.55(1)	-8.9	-13.0	-	-0.03(2)	-0.04(2)	0.00(1)	-0.10(1)
CPD00076	399.18(1)	-9.0	-13.2	-	-0.01(2)	-0.08(2)	0.00(1)	-0.11(2)
CPD00069	417.78(1)	-8.9	-13.1	-	-0.02(2)	0.01(2)	-0.02(1)	-0.11(1)
NOAA-ICP								
CB09739	355.08(0)	-8.9	-24.3	-	-0.03(1)	0.00(2)	-0.05(1)	-
CB10067	376.20(1)	-8.8	-9.8	-	0.06(1)	-0.03(2)	0.04(1)	-
CB09997	389.90(1)	-8.7	-1.4	-	0.04(1)	-0.08(1)	0.05(1)	-
CB09977	397.29(0)	-8.6	-1.5	-	0.05(1)	-0.06(1)	0.06(1)	-
CB09973	404.91(1)	-8.7	-2.2	-	0.06(1)	-0.03(2)	0.08(1)	-
CB10036	419.64(0)	-8.7	-3.6	-	0.05(1)	0.02(1)	0.02(1)	-

[a] Uncertainty of the last digit is expressed by parentheses.

[b] Calculated after the CO_2 mixing ratios for the individual laboratories are adjusted to the NIES standard scale by using the adjustment factors described in section 9.4.

[c] Isotope ratios are measured by AIST except CPB28548, CPB16443, and CPB29524, which are measured by NIES.

[d] Assumed to be the same as the values for the atmospheric CO_2 given in Tohjima et al. (2009).

Figure 20 shows the apparent differences in the CO_2 mixing ratios of the 12 round-robin cylinders determined by the five NDIR analyzers. It is of interest that the apparent differences for the two VIA-500R analyzers used at TU and AIST were within ±0.1 ppm, even when the ^{13}C-enriched CO_2-in-air mixture in the CPB28548 cylinder ($\delta^{13}C$ = +57.3 ‰) was measured. This result indicates that correction for the isotope effect was unnecessary for the CO_2 measurements made with the VIA-500R analyzers. In contrast, the VAI-510R and LI-6252 analyzers clearly showed negative differences (Laboratory X – NIES) due to the isotope effect, whereas the magnitudes of the differences for the LI-6252 were twice those for the VAI-510R.

We evaluated the observed isotope effects by adopting the approach used by Tohjima et al. (2009). We assumed that the VIA-500R and VIA-510R analyzers also used the same type of bandpass filter as the LI-COR analyzer. First, a gravimetric mixture of pure $^{13}CO_2$ gas and purified natural air was measured by each NDIR analyzer. All the NDIR analyzers gave $^{13}CO_2$ mixing ratios that were substantially lower than the gravimetric values of about 380 ppm and 400 ppm (Table 34), and the apparent $^{13}CO_2$ mixing ratios were related to the overlap between the absorption band of $^{13}CO_2$ and the wavelength transmitted by the bandpass filters for the NDIR analyzers. Thus, the position of the bandpass filter in the wavenumber domain was determined from the apparent $^{13}CO_2$ mixing ratio for each NDIR analyzer.

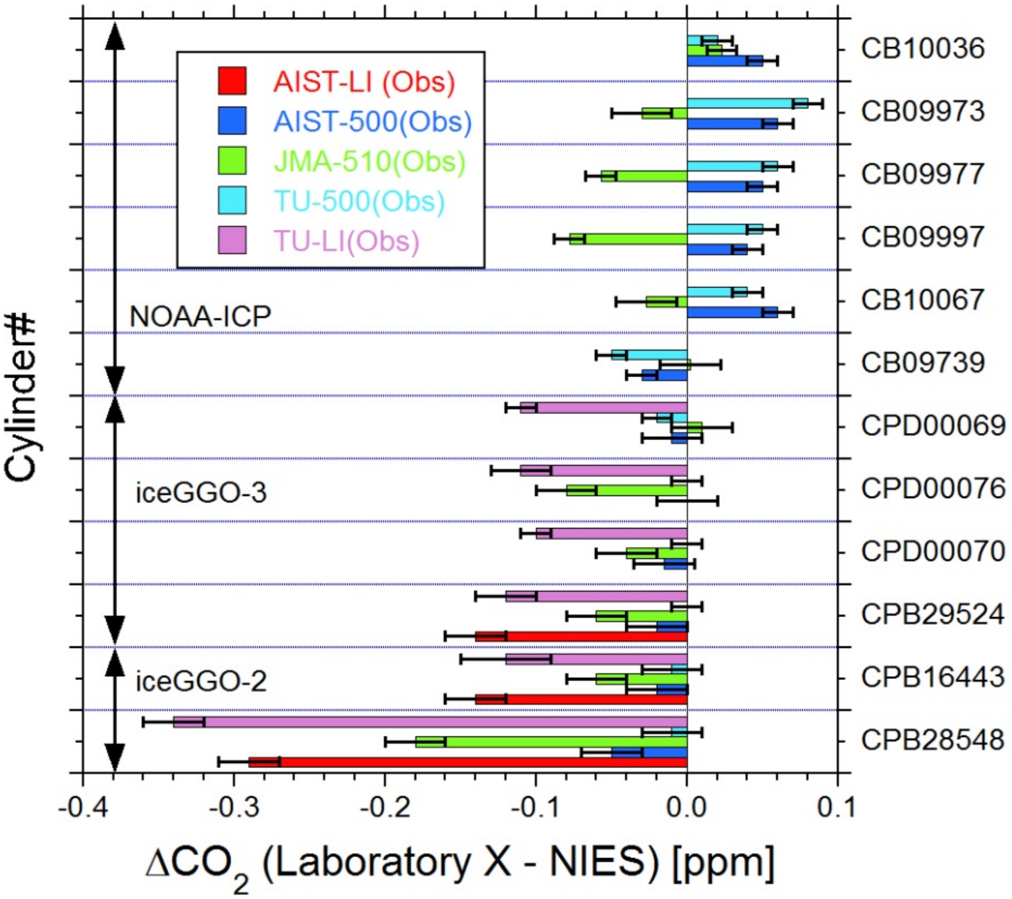

Figure 20. Differences of CO_2 mixing ratios determined by the five NDIR analyzers at the three laboratories from those determined by the LI-6252 analyzer at the NIES for the 12 round-robin cylinders. The differences in the CO_2 standard scales between the laboratories were adjusted to the NIES scale, and the CO_2 mixing ratios given by the NIES were corrected for the isotope effect of the NDIR analyzer. The plotted CO_2 differences are thus considered to reflect mainly the isotope effect of the individual NDIR analyzers.

Table 34. Apparent mixing ratios of gravimetric $^{13}CO_2$-in-air mixture determined by NDIR analyzers.

Laboratory	NDIR	NDIR Detector	Measurement date	$^{13}CO_2$ (ppm)	Measured $^{13}CO_2$ (ppm)
AIST	Beckman880	microphone condenser	2008/12/10	380.13	23.54
AIST	LI6252_IRG2-408*	semiconductor	2012/5/27	400.11	32.50
AIST	LI6262-1237	semiconductor	2008/12/2	380.13	39.41
AIST	BINOS MLT3.1	flow sensor	2008/12/9	380.13	51.97
AIST	LI6262-1333	semiconductor	2008/12/1	380.13	61.14
AIST	LI6262-452	semiconductor	2008/12/1	380.13	72.44
AIST	VIA-500R*	microphone condenser	2008/12/1	380.13	76.07
MRI	LI7000_IRG4-0768	semiconductor	2011/10/4	380.13	16.35
MRI	LI6252_IRG2-0568*	semiconductor	2011/10/4-5	380.13	30.47
MRI	LI7000_IRG4-0799	semiconductor	2011/10/5	380.13	30.56
MRI	Binos 4.1b	flow sensor	2008/2/1	380.13	67.67
MRI	VIA-510R	microphone condenser	2008/11/15	380.13	73.10
NIES	LI6252_IRG3-645	semiconductor	Tohjima et al. (2009)	380.00	27.34
NIES	LI6252_IRG2-654*	semiconductor	Tohjima et al. (2009)	380.00	45.68
NIES	LI6252_IRG2-246	semiconductor	Tohjima et al. (2009)	380.00	93.66
TU	LI6252*	semiconductor	2012/12/13	380.13	29.72
TU	VIA-500R*	microphone condenser	2012/12/13	380.13	82.59
JMA	VIA-510R*	microphone condenser	2013/05/01&06/04	380.13	50.52
JMA	LI7000_IRG4-0767	semiconductor	2013/5/1	380.13	19.97
JMA	LI7000_IRG4-0926	semiconductor	2013/6/4	380.13	24.19

*NDIR instruments used for the iceGGO experiments

Finally, we could evaluate the isotope effect of each NDIR analyzer for any CO_2-in-air mixture by taking into account the fractional abundances of CO_2 isotopologues, which are easily calculated from $\delta^{13}C$ and $\delta^{18}O$ values (Tohjima et al., 2009). The calculated apparent differences of the CO_2 mixing ratios for the round-robin cylinders for the individual NDIR analyzers are plotted in Figure 21. In the calculations we assumed that the isotopic compositions of the CO_2 standard gases used by the AIST, JMA, and TU were the same as those used by the NIES. As is apparent, the data for the LI-6252 analyzers, shown as circles and triangles in the figure, were scattered around the 1:1 line of the relationship, the indication being that the isotope effect of the LI-6252 analyzer could be rather well predicted with the approach of Tohjima et al. (2009). However, this approach cannot necessarily evaluate the isotope effects of the other NDIR analyzers satisfactorily, especially the VIA-500R.

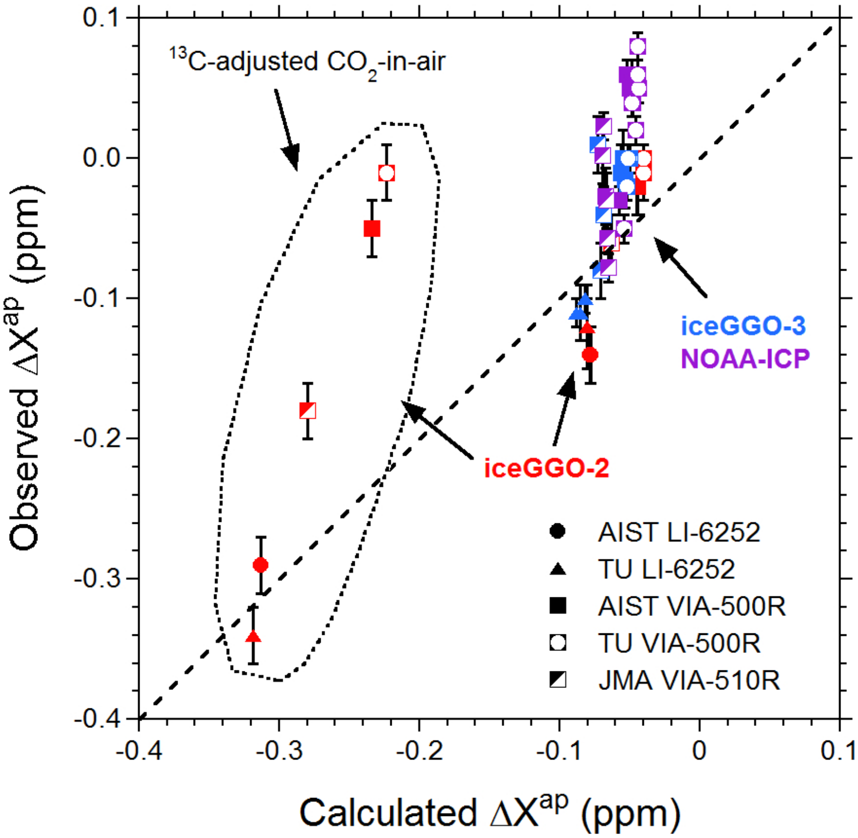

Figure 21. Relationship between the observed and calculated apparent differences in the CO_2 mixing ratios for the 12 round-robin cylinders caused by the isotope effects of the five NDIR analyzers. The observed values are the differences of the CO_2 mixing ratios determined by the AIST, TU, and JMA from those determined by the NIES (Laboratory X – NIES) after the standard scales of the three laboratories were adjusted to that of the NIES. The straight line represents the 1:1 relationship.

9.6. N_2O scale adjustment

The N_2O comparison data were collected from two experiments, iceGGO-5 and NOAA-ICP, to focus on the difference of the N_2O standard gas scales. Figure 22 shows the differences of the measured N_2O concentrations between the participating laboratories and the NIES as a function of the N_2O concentrations. The concentrations measured by the TU and AIST were higher by about 1 ppb than those measured by the NIES using the GC/ECD method. The values measured by the MRI and JMA with the ICOS were also higher than those measured by the NIES. These results indicate that all measured N_2O concentrations from the five laboratories could be re-calculated with simple linear relationships that would greatly reduce the standard scale differences. However, the reduced differences often exceeded the compatibility criterion for N_2O measurements (±0.1 ppb) recommended by the WMO because that goal is not easily achieved. The relationship between the NOAA and NIES values revealed a systematic difference between the iceGGO-5 and NOAA-ICP experiments. This difference was not observed in the relationship between the JMA and NIES concentrations measured via GC/ECD. Because the relatively large uncertainty of the GC/ECD analysis remained, further and more accurate comparisons using a high-precision mid-IR laser-based instrument will be needed to validate the differences of the N_2O standard gas scales.

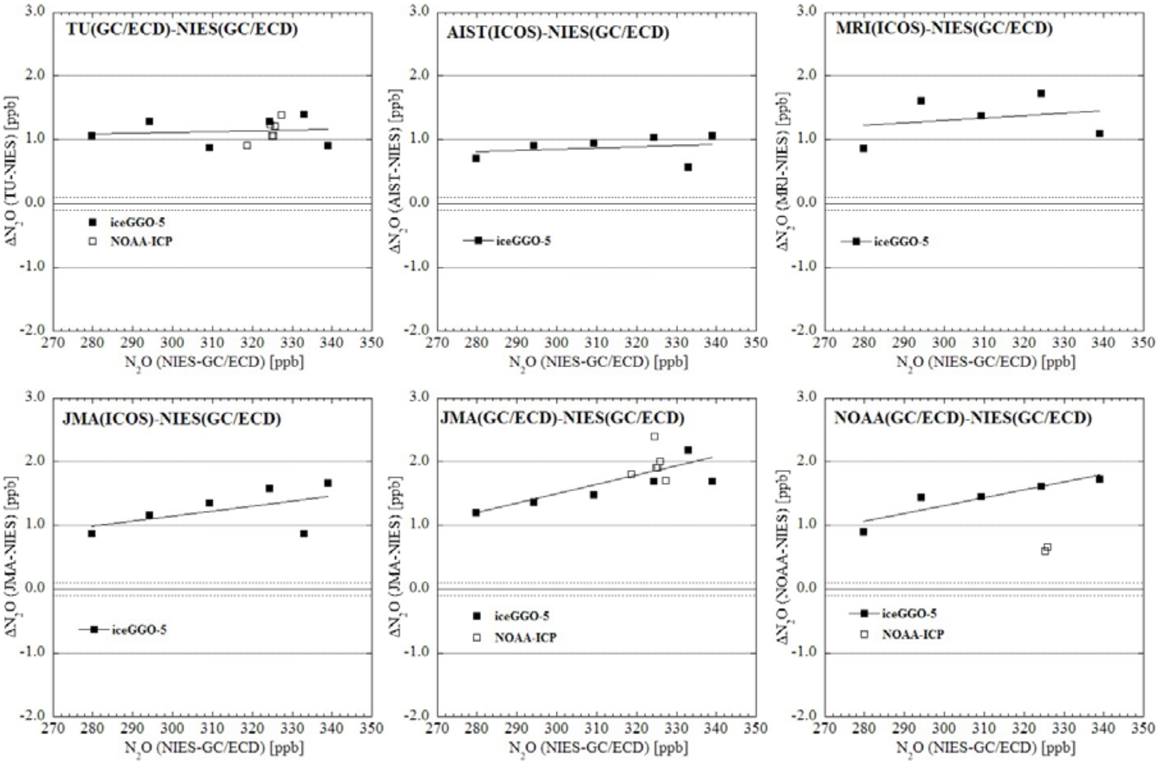

Figure 22. Differences of the measured N_2O concentration between participating laboratories and the NIES as a function of N_2O concentrations for the TU, AIST, MRI, JMA, and NOAA datasets. The solid line represents a least-squares fit to all data points from the iceGGO-5 and NOAA-ICP experiments.

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気象研究所技術報告は、1978（昭和53）年の初刊以来、気象研究所が必要の都度発行する刊行物であり、気象研究所の研究計画に基づき実施した研究に関する手法、データ、結果等についてのまとめ、または、すでに公表した研究論文類をとりまとめ総合的報告としたものを掲載する。

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