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;