



Results from the International Halocarbons in Air Comparison Experiment (IHALACE)

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Abstract. The International Halocarbons in Air Comparison Experiment (IHALACE) was conducted to document relationships between calibration scales among various laboratories that measure atmospheric greenhouse and ozone depleting gases. This study included trace gases such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs), as well as nitrous oxide, methane, sulfur hexafluoride, very short-lived halocompounds, and carbonyl sulfide. Many of these gases are present in the unpolluted atmosphere at pmol mol^{-1} (parts per trillion) or nmol mol^{-1} (parts per billion) levels. Six stainless steel cylinders containing natural and modified

natural air samples were circulated among 19 laboratories. Results from this experiment reveal relatively good agreement (within a few percent) among commonly used calibration scales. Scale relationships for some gases, such as CFC-12 and CCl_4 , were found to be consistent with those derived from estimates of global mean mole fractions, while others, such as halon-1211 and CH_3Br , revealed discrepancies. The transfer of calibration scales among laboratories was problematic in many cases, meaning that measurements tied to a particular scale may not, in fact, be compatible. Large scale transfer errors were observed for CH_3CCl_3 (10–100 %) and CCl_4 (2–30 %), while much smaller scale transfer

errors ($< 1\%$) were observed for halon-1211, HCFC-22, and HCFC-142b. These results reveal substantial improvements in calibration over previous comparisons. However, there is room for improvement in communication and coordination of calibration activities with respect to the measurement of halogenated and related trace gases.

1 Introduction

Halogenated trace gases, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and chlorinated solvents, are involved in stratospheric ozone depletion (Montzka et al., 2011). Some of these, along with hydrofluorocarbons (HFCs), are strong greenhouse gases. In an effort to characterize global distributions and sources/sinks of these gases, several international research groups measure the atmospheric abundance of CFCs, HCFCs, HFCs, and halogenated solvents on a routine basis.

Collaborative efforts utilizing measurements from multiple groups have led to more robust estimates of the global distributions and emissions of N_2O (Huang et al., 2008; Saikawa et al., 2013), CCl_4 (Xiao et al., 2010a), CH_3Cl (Xiao et al., 2010b), HCFC-22 (Saikawa et al., 2012) and SF_6 (Rigby et al., 2010). Integrating results from different research groups to produce a consistent picture of the global or regional atmospheric distribution can be challenging. There are many factors that can lead to differences in the data records collected by different groups (e.g., sampling or analytical artifacts, calibration differences, site selection). Perhaps the most fundamental of these is the calibration scale upon which the measurements are based.

Nearly all measurements of ozone-depleting and greenhouse gases are made on a relative basis. That is, abundances are determined relative to reference standards measured in a similar manner. Most reference standards used for calibration consist of mixtures of trace gases stored in compressed gas cylinders with known mole fractions. Reference standards are typically designed to match the atmospheric composition in order to minimize interference or bias. The term “scale” is often used to define the reference standard(s) used over a particular range of mole fractions. Some laboratories develop and maintain scales internally, while others adopt existing scales. Throughout this paper we refer to laboratories that develop scales as a “scale origin”. Scale adoption typically involves sending one or more reference standards to another laboratory for analysis. Issues important to both scale development and adoption include scale stability (are the reference standards or methods stable over time?) and scale propagation (can standards developed or evaluated using a particular instrument be reliably transferred to a different instrument or laboratory, and can the adopting laboratory maintain the adopted scale?).

The larger CO_2 measurement community, under the auspices of the World Meteorological Organization – Global Atmosphere Watch (WMO/GAW) program, has adopted a single reference scale for CO_2 measurements (WMO/GAW, 2009; Zhao et al., 1997). This ensures that all WMO/GAW CO_2 measurements are traceable to the same calibration scale. On-going efforts to compare laboratory CO_2 measurements and assess how well cooperating laboratories are linked to the WMO/GAW CO_2 calibration scale are fundamental to the WMO/GAW program (WMO/GAW, 2009). Protocols for CH_4 , N_2O , CO , SF_6 , and H_2 are also in place (WMO/GAW, 2011). Experiments have also been designed to assess calibration and analytical differences for select hydrocarbons (Apel et al., 1994; Plass-Dülmer et al., 2006; Apel et al., 2003). However, there have been few efforts to characterize differences between calibration scales and measurement programs for halogenated gases. Early comparison studies (Rasmussen, 1978; Fraser, 1979) found large differences in mole fractions of the most abundant ozone-depleting gases (CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CH_3CCl_3 , and CCl_4). For example, standard deviations of 10–25% were found among independent laboratories for CFC-12 and CCl_4 . Prinn et al. (1998) reported differences less than 1% for CFC-12 and CH_3Cl , 8–10% for CFC-11, and 20–35% for CH_3CCl_3 and HCFC-142b (CH_3CClF_2). Aside from a study by Jones et al. (2011) that focused on very short-lived halo-compounds, such as CH_2Br_2 and $CHBr_3$, much of the recent research in this area has been carried out on a bi-lateral or ad-hoc basis.

While the existence of independent calibration scales is important for verifying trends and estimating uncertainties, it is critically important to understand the relationships between independent scales. The International Halocarbon in Air Comparison Experiment (IHALACE) was conceived as a first step toward assessing the variability of calibration scales associated with the measurement of halogenated trace gases.

The goals of IHALACE were (1) to establish a calibration matrix that relates the calibration scales among different laboratories at a specific point in time, and (2) to enhance communication and cooperation among laboratories in order to improve data quality (e.g., through regular comparisons). We do not explore analytical or scale development uncertainties in depth. Typical scale uncertainties at ambient mole fractions are about 1–5% (95% confidence level). While it is possible that comparison results might agree within these uncertainties, small differences between measurement programs can be important for gases with small spatial or temporal gradients. It is important to understand even small differences between scales rather than to treat scales as equivalent based on agreement within uncertainties.

2 Methods

Six electro-polished stainless steel cylinders (Essex Cryogenics, St. Louis, MO), divided into two sets, were distributed among the participants (Table 1). These cylinders were selected because they have shown good stability for many halogenated gases at pmol mol^{-1} (parts per trillion, ppt) level. Each group received three cylinders, two at ambient mole fraction and one a mixture of 80 % ambient air and 20 % ultra-pure zero air (Table 2). Mole fractions were not disclosed at the time of distribution. To the extent possible, groups that develop their own calibration scales received the same set of three samples (set 1), while those groups that adopt scales from other laboratories received set 2.

2.1 Air sample preparation

Cylinders were filled at the NOAA/GMD (Earth System Research Laboratory, Global Monitoring Division) air sampling facility at Niwot Ridge, Colorado. This facility (40.03° N, 105.55° W) is located at an altitude of 3022 m in a sub-alpine forest approximately 50 km northwest of Denver. Airflow to the site is predominately westerly, bringing clean continental background air to the site.

Cylinders (34-L empty volume) initially contained ~ 100 hPa dry nitrogen upon receipt from the manufacturer. They were evacuated to 2 Pa and then filled with 6.2 MPa dry (dewpoint ~ -78 °C) natural air via transfer from a pressurized cylinder (filled previously at Niwot Ridge). Approximately 0.65 mL HPLC grade water was added to each cylinder to humidify the air. Cylinders were conditioned with this humidified air for one month, then evacuated to 6 Pa and re-humidified by adding 0.65 mL HPLC-grade water and ~ 0.3 MPa dry natural air as before. Dry synthetic zero-grade air was added to two cylinders to create mixtures with mole fractions ~ 20 % below those of the ambient air samples. The zero-grade air (Linweld, Lincoln, NE) was scrubbed for residual contamination by passing it through molecular sieve 5 Å and activated charcoal at -78 °C. Final pressurization to 6.2 MPa was performed at Niwot Ridge using an oil-free, breathing-air compressor (model SA6, Rix Industries, Benicia, CA). Distilled de-ionized water was added to the air stream at the pump inlet to cool and cleanse the first stage of the compressor. Experience has shown that cooling the compressor heads by adding 8–12 cc/min H_2O and blowing air across aluminum cooling fins mounted to the compressor heads greatly reduces the levels of contaminants generated by the compressor. Moisture was removed using Rix moisture separators and by passing the air through a stainless steel tube containing 350 g magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$). By combining 0.65 mL H_2O with ~ 2600 g dry air, the resulting water vapor mole fraction in each cylinder was ~ 400 ppm. Cylinders were filled on 17 March 2004 and 8 July 2004 (Table 2). Because mole fractions of some gases vary seasonally, the full range of mole fractions among

all six samples was greater than 20 % for some gases (CH_3Br for example) (see Supplement).

2.2 Analysis and data reporting

Each participant was instructed to analyze the air samples in a manner similar to other air samples from their measurement program. Most participants employ gas chromatography with electron-capture, mass-selective, or flame ionization detection. A dedicated pressure regulator was supplied with each cylinder (Veriflo 959TDR, Veriflo Division of Parker Hannifin, Richmond, CA) along with 1 m lengths of 1/16" stainless steel tubing. Participants were instructed to use the regulators provided unless their analysis method required a different procedure.

Each laboratory was instructed to forward the cylinders to the next laboratory according to a pre-determined schedule. Cylinders were initially distributed in September 2004. One set of cylinders was returned to Boulder for final analysis in 2006. The second set was returned a year later, taking an additional year to complete the circuit. Each cylinder was analyzed at NOAA at the beginning and end of the distribution period. At the end of the experiment, four of the six cylinders remained at high pressure (~ 5 MPa) while two were accidentally partially vented during the final weeks of the experiment. The final analysis at NOAA was performed while all cylinders still contained > 70 % of the initial air. These results represent the state of the art in halocarbon measurements around 2007.

Data were submitted to two referees and held until all analyses were complete. At that point, data were released to participants in anonymous form with laboratories identified by number. While IHALACE was operated as a "blind" comparison, one of the referees also acted as a participant. Although this is not generally considered protocol for a blind comparison, all participants were informed in advance and agreed with the protocol. The participant/referee submitted results to the other referee and to another participant (B. Hall). Furthermore, the participant/referee ensured that handling and analysis were performed by laboratory personnel not associated with the role of IHALACE referee.

It was requested that all data be properly identified with the corresponding calibration scale (see Supplement, Table S1). Data submitted on obsolete scales were converted to more recent scales according to known conversion factors (e.g., CH_4 on the CMDL-93 scale was converted to NOAA-04, Dlugokencky et al., 2005; CFC-12 on the NOAA-2001 scale was converted to NOAA-2008; HCFC-22 (CHClF_2) on the NOAA-92 scale was converted to NOAA-2006; CCl_4 on the NOAA-2002 scale was converted to NOAA-2008; N_2O on the NOAA-2000 scale was converted to NOAA-2006). In other cases, scale differences were small and do not significantly affect the results. For example, some data were submitted on SIO-98 scales even though SIO-05 is more recent. The conversion from SIO-98 to SIO-05 for CFC-12

Table 1. List of participants and sample set analyzed (three cylinders in each set).

Lab. #	Institution	Acronym	P.I.	Country	Set	Ref.
1	National Oceanic and Atmospheric Administration	NOAA	J. Elkins	USA	1, 2	f, m
2	Scripps Institution of Oceanography	SIO	R. Weiss	USA	1	l, n
3	South African Weather Service	SAWS	E.-G. Brunke	South Africa	2	d
4	Italian National Agency for New Technologies, Energy and Sustainable Economic Development	ENEA	F. Artuso	Italy	2	a
5	Environment Canada	EC	D. Worthy	Canada	2	s
6	University of Miami	UM-1	J. Happell	USA	2	h
7	National Institute of Standards and Technology	NIST	G. Rhoderick	USA	1	o
8	Karlsruhe Institute of Technology	KIT	H. E. Scheel	Germany	2	r
9	University of Bristol	UB	S. O'Doherty	United Kingdom	1	l, n, q
10	University of California Irvine	UCI-1	E. S. Salzman	USA	2	b
11	University of Urbino	UU	M. Maione	Italy	2	k
12	J. W. Goethe University of Frankfurt	UF	A. Engel	Germany	2	e
13	University of Heidelberg	UH	I. Levin	Germany	2	g, i
14	Swiss Federal Laboratories for Materials Science and Technology	Empa	S. Reimann	Switzerland	2	n, q
15	University of Miami	UM-2	E. Atlas	USA	1	p
16	National Institute for Environmental Studies	NIES	Y. Yokouchi	Japan	1	t
17	Commonwealth Scientific and Industrial Research Organization; and Cape Grim Baseline Air Pollution Station	CSIRO	P. Fraser	Australia	1	l, n
18	NASA Ames Research Center	NASA	M. Loewenstein	USA	2	j
19	University of California, Irvine	UCI-2	D. Blake	USA	2	c

^a Artuso et al. (2010), ^b Saltzman et al. (2009), ^c Blake et al. (2003), ^d Brunke et al. (1990), ^e Engel et al. (1997), ^f Hall et al. (2007), ^g Hammer (2008), ^h Happell and Wallace (1997), ⁱ Levin et al. (2010), ^j Loewenstein et al. (2002), ^k Maione et al. (2004), ^l Miller et al. (2008), ^m Montzka et al. (1993), ⁿ Prinn et al. (2000), ^o Rhoderick and Dorko (2004), ^p Schauffler et al. (1999), ^q Simmonds et al. (1995), ^r WMO/GAW (2011), ^s Worthy et al. (2003), ^t Yokouchi et al. (2002).

was estimated from SIO results submitted on both scales by the same laboratory. The scale ratio for CFC-12 (SIO-05/SIO-98 = 0.9999 at ~ 545 ppt) is sufficiently close to 1.0 that results reported on the SIO-98 scale can be compared directly to those submitted on SIO-05. Likewise, conversion from N₂O scale NOAA-2006 to NOAA-2006A is not necessary for comparative purposes. Finally, some laboratories reported data on more than one scale or from more than one analytical instrument. Some laboratories maintain multiple instruments, such as gas chromatographs with electron-capture detector (ECD) and mass-selective detector (MS). These results are presented in tables as non-integer laboratory numbers, and offset from the laboratory number in figures. See Table S1 for additional laboratory information.

3 Results and discussion

To examine the results, we focus first on laboratories that prepare their own scales. This provides an indication of how well atmospheric mole fractions are known on an absolute basis and avoids scale propagation issues. For each trace gas, we report the variation of results (one standard deviation) exclusively from laboratories that maintain independent scales (Table 5). While no calibration scale is known absolutely, good agreement among a number of scales would suggest

that errors in determining the atmospheric mole fraction of a particular trace gas are likely small. Next we examine how well laboratories reporting on the same scales compare, since two laboratories using the same scale should agree to the level at which the scale can be propagated (typically twice the analytical uncertainty of laboratory of scale origin). Finally, we compare the results of select gases from this experiment (collected over a period of a few weeks at each laboratory) with those derived from estimates of global mean mole fractions (based on measurements made over the course of a year or more).

We have separated results by the season during which the cylinders were filled (late winter versus early summer) as seasonal mole fraction differences are expected for some gases. For most comparisons, we focus on the undiluted air samples since calibration and analysis procedures are likely to be optimized for ambient samples. We use the NOAA results as the basis for many of the comparisons because all six cylinders were analyzed at NOAA. Initial and final mole fractions determined by NOAA agreed within analytical uncertainties for all gases except CH₂Br₂. Hence, initial mole fractions assigned by NOAA were used for comparison, except for CH₂Br₂ (adjusted for drift) and CFC-12 (described later). For gases not measured by NOAA, we assume no drift. This is a reasonable assumption given previous experience

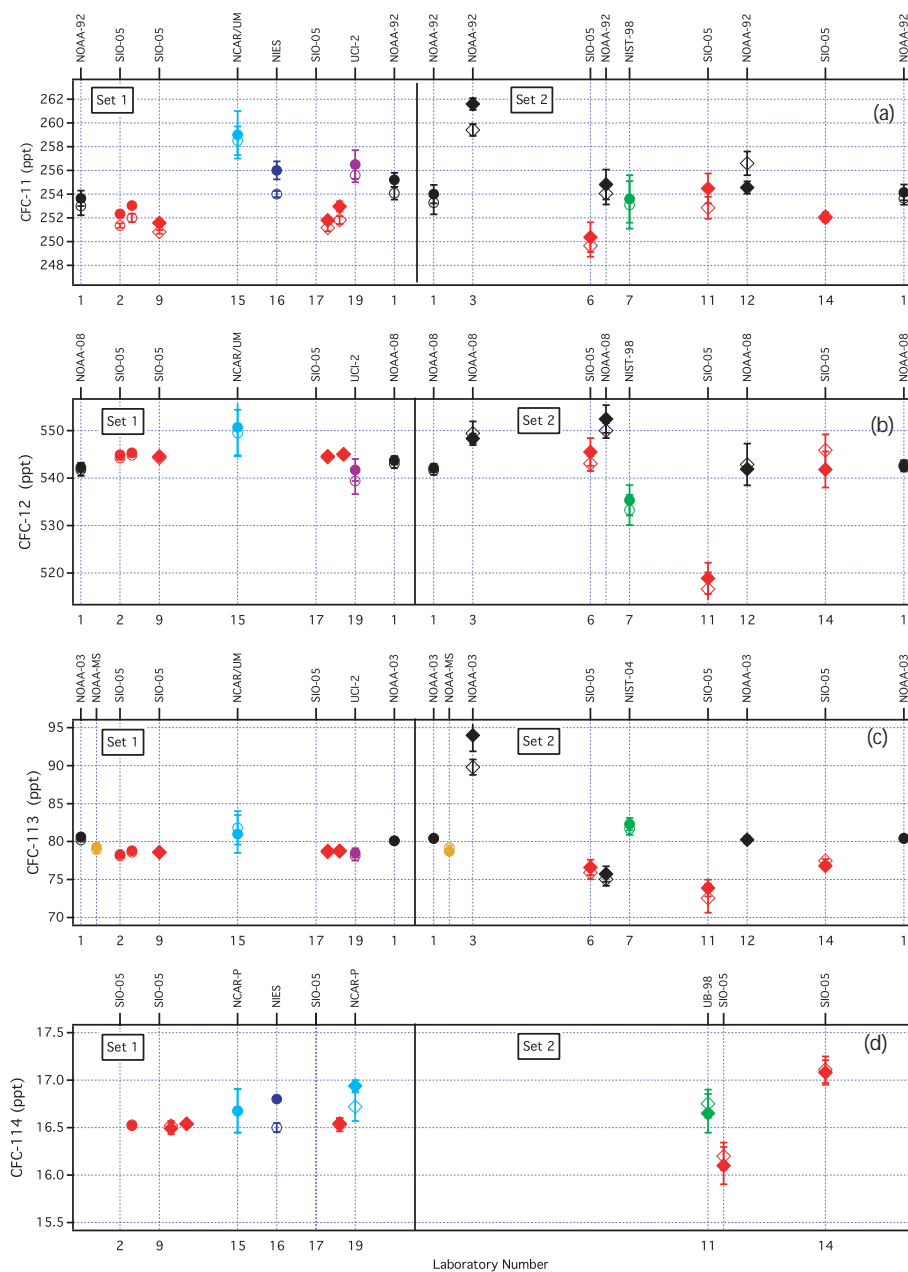


Fig. 1. Results from undiluted samples for (a) CFC-11, (b) CFC-12, (c) CFC-113, (d) CFC-114, (mole fraction, ppt = pmol mol⁻¹, parts per trillion) color-coded by calibration scale with scale identifiers shown along the top axis: open (closed) symbols correspond to cylinders filled in winter (summer); circles denote laboratories that develop scales and serve as a scale origin, diamonds denote laboratories that adopt existing scales. Errors bars are one standard deviation as reported. Results that appear offset from the integer laboratory numbers on the *x* axis indicate additional results submitted by the corresponding laboratory (different instruments, different calibration scales, etc.). For example, for CFC-11 laboratory 2 submitted data from two instruments on the same scale, while laboratory 6 submitted data on two different scales. Note that because some laboratories adopt scales from others, the scale identifier (top axis) and the laboratory (identified by number on the bottom axis) may differ (see Table 1). For example, in (c), laboratory 19 (UCI-2) reports CFC-113 on the UCI-2 scale, but in (d), reports CFC-114 on the NCAR-P scale.

with these cylinders under similar conditions. Differences between initial and final mole fractions (when available) can be seen in Figs. 1–6 and Tables 3 and 4 (columns 1a, 1b). Finally, we compare results for undiluted and diluted

samples. Results from both diluted and undiluted samples, taken together, may shed light on non-linearities associated with analysis or scale development, which could impact how data sets compare over the long term.

Table 2. Air samples distributed to labs.

Cylinder No.	Set No.	Fill date	Type
SX-3526	1	March 2004	diluted
SX-3528	1	March 2004	undiluted
SX-3537	1	July 2004	undiluted
SX-3536	2	July 2004	diluted
SX-3527	2	March 2004	undiluted
SX-3538	2	July 2004	undiluted

The full complement of results is available as supplemental material (see Supplement). Average differences (%) compared to NOAA for select gases are shown in Tables 3 and 4.

3.1 Chlorofluorocarbons (CFCs)

Both CFC-11 and CFC-12 have a long history of measurement and scale development over the years. For CFC-11, the standard deviation among six scales for the undiluted air samples was 1% (Table 5, Fig. 1a). There was some clustering, with three scales (developed by laboratories 1, 2, 7) at lower values and three scales (developed by laboratories 15, 16, 19) ~ 4 ppt higher, but in general, the relative differences among scales are smaller than those reported previously (Prinn et al., 1998). The average difference between laboratories 1 (NOAA) and 7 (NIST) was 0.1%. This is similar, within reported uncertainties, to the average difference of 0.9% reported by Rhoderick and Dorko (2004).

Scale relationships among three laboratories (NOAA, SIO, and UCI-2) were compared to those derived from 2004 and 2007–2008 global tropospheric mean mole fraction estimates reported in Montzka et al. (2011) (Table 6). Although scale relationships derived as such can be influenced by other factors, such as sampling issues, or the number and locations of measurement sites, it is useful to examine the consistency of scale factors since the 2004 comparisons are based on the analysis of air collected around the same time as the IHALACE samples. For CFC-11, the SIO/NOAA ratio derived from this experiment (0.9942) is nearly the same as that derived from estimates of global means in 2004 based on their different sampling networks (0.9921). However, global mean estimates from both networks indicate that this ratio has not been constant (Montzka et al., 2011). The UCI-2/NOAA factor based on this work (1.0108) is 1% larger than those based on global means in 2004 (0.9996) and 2007–2008 (0.9970).

Five CFC-12 calibration scales show a dispersion of 1% (Fig. 1b, Table 5). The final NOAA analysis of IHALACE cylinders suggests that initial NOAA assignments were ~ 0.8 ppt too low for unknown reasons (the average of the second NOAA analysis was 0.8 ppt higher than the first) and this was confirmed by analysis of additional standards at NOAA. All CFC-12 comparisons shown in Tables 3–6 are based on the final NOAA analysis.

CFC-12 scale factors derived from undiluted IHALACE cylinders for SIO/NOAA and UCI-2/NOAA are nearly identical to those derived from global mean mole fraction estimates (Table 6). Rhoderick and Dorko (2004) reported excellent agreement (< 1 ppt) between NOAA and NIST for CFC-12, but those results were based on an older NOAA CFC-12 scale (NOAA-2001), which is 7 ppt (1.3%) lower than the NOAA-2008 scale. IHALACE results show the NIST-NOAA average difference (Table 3) to be -8.3 ppt (-1.5%) on current scales.

While the standard deviations of CFC-11 and CFC-12 results on independent scales are not large ($\sim 1\%$), scale propagation could be improved. Some differences among laboratories reported to be on the same CFC-12 scale are nearly as large as differences among scales. Laboratories 3, 6, and 11 reported CFC-12 results that differ significantly from the laboratories that developed the scales (scale origin, shown as circles for each scale color in Figs. 1–6). This is an important finding also observed for other trace gases. Measurements that are supposedly comparable (traceable to the same scale) may not be compatible (see JCGM 200, 2008, 2007; WMO/GAW, 2011) due to scale propagation or sampling/measurement issues. This could impact the utility of combining data from different networks/sites even when the programs are linked to common scales. One likely reason is the lack of regular communication between laboratories regarding calibration scale changes. Equally important are efforts to verify that mole fractions of calibration standards are not changing over time. Efforts to ensure data quality and scale transfer are needed on a continuing basis to minimize potential bias. Examples of efforts to address these issues include routine comparison of standards or air samples, and co-located sampling, whereby measurements are taken by independent groups at the same site and time.

It is important to note that with regard to potential scale transfer errors, some groups within this study are more closely linked than others. For example, laboratories 2, 9, 14, and 17 are affiliated with the Advanced Global Atmospheric Gases Experiment (AGAGE) (Prinn et al., 2000). Standard preparation, scale propagation, and data processing are likely more centralized within this group than between other groups operating on common scales. Scale transfer errors between AGAGE-affiliated laboratories should be smaller than those between laboratories with little or no formal cooperative ties. The same would be expected from other measurement facilities operating within one agency. In general, transfer errors are indeed smaller for AGAGE-affiliated laboratories, but not in all cases.

CFC-113 ($\text{CCl}_2\text{FCClF}_2$) results are similar to those for CFC-11. The standard deviation of results from five scales is 1.7 ppt, or 2.1%. Again, scale propagation is problematic in some cases (Fig. 1c). Laboratory 12 agrees with laboratory 1 (scale origin) very well, and laboratories 9 and 17 agree with laboratory 2 (scale origin), but laboratory 3 shows a large difference relative to laboratory 1. Scale conversion

Table 3. Average differences (%) between each laboratory and laboratory 1 (NOAA) for selected compounds (average of both undiluted samples). Each result is compared to the initial NOAA result, except for CFC-12 (final) and CH₂Br₂ (average of initial and final).

	NOAA	Laboratory Number											
		2 MD	2.1 MS	3	4	5	6	6.1	7	8	9 MD	9.1 MS1	9.2 MS2
CFC-12	543	0.2	0.3	1.2			0.3	1.6	-1.5		0.2		
CFC-11	253	-0.6	-0.3	2.7			-1.4	0.3	-0.1		-0.8		
CFC-113	80	-2.8	-2.1	14.3			-5.2	-6.3	2.0		-2.2		
CH ₃ CCl ₃	23	-5.4	-2.6	184			-13.0	-11.0	2.8		-3.0	-3.0	
CCl ₄	95	-2.7	-3.1	34			-4.2	-0.7	2.2		-2.4	-3.9	
CHCl ₃	12	-5.2	-4.3						-23.5		-	-7.0	-3.6
HCFC-22	174		-0.7		0.0							-0.6	-1.1
HCFC-141b	19		1.2		3.1							0.4	1.0
HCFC-142b	16		3.7		-0.9							2.7	3.5
HFC-134a	33.1		0.8		-0.9							1.4	0.6
HFC-152a	5.2		-8.4									-11.5	-8.5
CH ₂ Cl ₂	32											-6.6	
C ₂ Cl ₄	3.6											-6.0	
CH ₃ Cl	564		-0.8									-1.1	-0.9
CH ₃ Br	9.4		-0.2									3.3	-0.4
CH ₃ I	0.18												
CH ₂ Br ₂	0.7												
CHBr ₃	0.5												
halon-1211	4.4		2.0									1.7	1.6
halon-1301	2.9		5.8									4.4	6.1
halon-2402	0.5												
CH ₄	1821	-0.1		0.01		0.05			0.34		0.0		
N ₂ O	318.3	-0.02		-0.34		-0.01			0.43	0.02	-0.01		
SF ₆	5.5		-0.1		2.4	-0.7						-0.7	-0.4
COS	570												

	Laboratory Number													
	10	11	12	13	14	15	16	17	17.1 MD	17.2 MS	18	19	1A	1B
CFC-12		-4.6	0.0		0.2	1.2			0.2	0.3		-0.5	0.0	0.0
CFC-11		0.0	0.8		-0.6	2.1	0.7		-0.7	-0.4		1.1	0.5	0.1
CFC-113		-9.0	-0.2		-4.1	1.2			-2.1	-2.1		-2.6	-0.4	0.0
CH ₃ CCl ₃		-10.6	-1.2		-11.7	-0.7	-2.5		-1.9	-2.3		4.8	1.1	-0.1
CCl ₄		-11.1	-0.8		-5.5	-2.7			-2.5	-4.3		-0.6	0.1	0.1
CHCl ₃		-4.6	-3.3		-6.2	7.9	-2.1		-4.9	-3.5		10.5	1.5	-0.4
HCFC-22		-4.0	-1.1		0.0	0.3	-3.8			-0.4		-2.8	-0.5	-0.3
HCFC-141b		-3.9	-3.7		-0.3	3.4	1.2			1.0		-5.5	0.2	0.6
HCFC-142b		0.2	0.5		3.3	8.7	2.4			3.6		-2.5	2.8	-0.5
HFC-134a		-4.6	-0.2		0.2	8.0	-0.2			1.0		-4.1	1.6	0.1
HFC-152a		-13.5			-7.7		-1.8			-8.6			-0.8	-0.5
CH ₂ Cl ₂		-14.0	-13.0		-10.5	-16.2				-6.9		-14.2	1.8	-0.1
C ₂ Cl ₄		-1.1			6.5	-1.3				5.3		28	2.9	2.8
CH ₃ Cl	3.7					-2.6	-0.7					-2.2	0.9	
CH ₃ Br	-3.1				3.6	1.5	1.8			1.3		-5.4	1.1	-0.1
CH ₃ I			0			109	13					19	0.6	2.6
CH ₂ Br ₂			15			17						18	21	9
CHBr ₃			12			27						10	-3	14
halon-1211		0.9	0.5		2.4	-2.8				2.0		-3.7	-0.1	0.1
halon-1301		0.4	1.0		8.5	-9.9				5.8			0.2	1.9
halon-2402					107.6	-10.0				93.6		-3.4	0.0	-0.4
CH ₄				0.04	-0.02	-0.6		0.0	0.0		0.03		-0.02	-0.01
N ₂ O			-0.41	0.23	-0.09	-0.1		0.23	-0.04				0.00	-0.01
SF ₆		-10.3	-1.1	-0.5	-2.7				0.0	-3.0			0.3	-0.1
COS	0.6					-4.2						-7.6	0.5	1.9

NOAA result: Mole fractions in ppt (except N₂O and CH₄, ppb). CFC-12, CFC-11, CFC-113, CH₃CCl₃, CCl₄, halon-1211, N₂O, and SF₆ based on ECD analysis. All others based on MS analysis. MD: multidetector (ECD or FID); MS: mass selective detector.

1A, 1B: % difference between final and initial NOAA results for sets 1 and 2, respectively.

Table 4. Same as Table 3 but for diluted samples.

	NOAA	Laboratory Number											
		2 MD	2.1 MS	3	4	5	6	6.1	7	8	9 MD	9.1 MS1	9.2 MS2
CFC-12	439	2.4	0.9	2.9			0.4	2.0	-1.7		1.7		
CFC-11	204	-0.1	0.4	4.4			-0.5	1.2	1.7		0.4		
CFC-113	64		-0.3	20.2			-4.0	-5.1	4.0		0.3		
CH ₃ CCl ₃	18	-4.7	-3.5	70.2			-20.1	-18.3	8.1		-4.3	-2.9	
CCl ₄	76		-3.6	34.4			-4.1	-0.5	2.8		-2.5	-3.3	
CHCl ₃	7.6	-3.7	-3.0						-1.6		-13.2	-5.7	-2.6
HCFC-22	141		0.1		0.5							0.0	-0.1
HCFC-141b	15.0		0.5		5.2							-2.0	0.1
HCFC-142b	12.5		1.7		1.8							0.9	2.0
HFC-134a	27		0.3		2.4							1.4	0.6
HFC-152a	27		-5.8									-9.4	-5.0
CH ₂ Cl ₂	26											-10.5	
C ₂ Cl ₄	2.8												5.4
CH ₃ Cl	456		-1.2									-1.1	-0.4
CH ₃ Br	7.8		-1.1									5.0	0.7
CH ₃ I	0.14												
CH ₂ Br ₂	0.6												
CHBr ₃	0.3												
halon-1211	141		1.7									2.0	2.0
halon-1301	2.3		7.8									7.8	10.0
halon-2402	0.4												
CH ₄	1480	0.0		-0.45		0.04			0.33		0.0		
N ₂ O	259.2	-1.77		-0.96		0.18			-0.14	0.08	-0.08		
SF ₆	4.5		-0.4		5.6	0.2						-3.8	-0.7
COS	451												

	Laboratory Number														
	10	11	12	13	14	15	16	17	17.1 MD	17.2 MS	18	19	1A	1B	
CFC-12		-3.4	0.4		0.2	1.2			1.0	1.1		0.6	0.0	0.0	
CFC-11		0.7	2.6		0.0	0.8	1.8		-0.3	0.4		1.7	0.4	0.3	
CFC-113		-10.1			-2.4	1.1			-0.1	-0.2		0.2	-1.4	0.0	
CH ₃ CCl ₃		-13.7			-13.2	-2.6	-3.1		-3.1	-3.8		3.6	0.7	-1.4	
CCl ₄		-10.8			-8.7	-3.9			-2.4	-3.8		-1.3	0.4	0.0	
CHCl ₃		-0.3			-4.7	8.0	1.2		-2.7	-1.6		13.5	6.1	1.6	
HCFC-22		-3.7			-0.6	0.3	-2.4			0.1		-2.2	0.0	-0.7	
HCFC-141b		-5.8			-0.5	0.9	1.6			0.0		-5.1	-0.1	0.7	
HCFC-142b		-0.2			4.0	6.2	2.2			1.9		-2.4	1.0	0.4	
HFC-134a		-3.9			-0.2	4.3	-0.8			0.5		-2.5	0.8	0.7	
HFC-152a		-14.4			-10.3		4.7			-6.3			4.4	0.6	
CH ₂ Cl ₂		-11.5			-10.4	-15.5				-6.7		-14.2	2.1	1.3	
C ₂ Cl ₄					3.3	-0.6	-6.3			6.5		36.1	2.8	3.3	
CH ₃ Cl	3.1	-4.5			12.2	-2.7	-1.0					-3.3	-0.1	0.3	
CH ₃ Br	-3.5	9.4			1.7	0.4	-2.1			1.0		-9.9	-1.1	-0.2	
CH ₃ I						93	33					26	13	0	
CH ₂ Br ₂						21						34	21	24	
CHBr ₃						36						26	2	0	
halon-1211		1.6			0.9	-2.5				2.2		-4.2	-0.3	-0.6	
halon-1301		2.1			2.1	-4.8				10.0			5.2	3.0	
halon-2402					130.2	-7.5				96.5		-1.5	-2.5	6.3	
CH ₄				0.20	-0.09	-0.4		0.1	-0.1		0.24		0.11	0.12	
N ₂ O			-0.31	-1.11	1.16	-0.02		-0.58	-0.59				-0.09	-0.18	
SF ₆		-10.2		-0.2	-2.4				-0.2	-1.4			0.4	1.1	
COS	-0.2						-4.5						-8.9	-1.1	0.7

NOAA result: Mole fractions in ppt (except N₂O and CH₄, ppb). CFC-12, CFC-11, CFC-113, CH₃CCl₃, CCl₄, halon-1211, N₂O, and SF₆ based on ECD analysis.

1A, 1B: % difference between final and initial NOAA results for sets 1 and 2, respectively. All others based on MS analysis. MD: multidetector (ECD or FID) MS: mass selective detector

Table 5. Analysis statistics for undiluted samples based on results from laboratories that develop calibration scales. Results from laboratories that adopt scales are not included here because we do not want to introduce potential scale transfer errors. Gases with large differences between winter (W) and summer (S) fillings were treated separately. All mole fractions are pmol mol^{-1} (ppt) unless indicated.

Trace Gas	Mean	Std Dev	Std Dev (%)	# Scales
CFC-11	254.7	2.6	1.0	6
CFC-12	542.6	5.5	1.0	5
CFC-113	80.1	1.7	2.1	5
CFC-114	16.6	0.1	0.7	4
CFC-115	8.2	0.3	4.1	3
CCl_4	94.4	1.8	1.9	5
halon-1211	4.36	0.10	2.2	4
halon-1301	2.90	0.21	7.3	3
halon-2402	0.48	0.04	7.4	2
CH_4 (W) (ppb)	1836.9	3.5	0.19	3
CH_4 (S) (ppb)	1808.8	4.3	0.24	3
N_2O (W) (ppb)	318.90	0.87	0.27	3
N_2O (S) (ppb)	318.57	0.72	0.23	3
CH_3CCl_3 (W)	23.4	0.8	3.4	6
CH_3CCl_3 (S)	22.1	1.0	4.7	6
HCFC-22 (W)	169.3	2.9	1.7	4
HCFC-22 (S)	174.3	3.7	2.1	4
HCFC-141b (W)	18.7	0.3	1.8	4
HCFC-141b (S)	18.9	0.2	1.0	4
HCFC-142b (W)	15.7	0.6	3.7	4
HCFC-142b (S)	17.0	0.6	3.4	4
HFC-134a (W)	32.1	1.6	4.9	4
HFC-134a (S)	35.4	1.0	2.7	4
HFC-152a (W)	4.48	0.26	5.9	3
HFC-152a (S)	5.49	0.26	4.8	3
SF_6 (W)	5.50	0.02	0.4	3
SF_6 (S)	5.56	0.01	0.2	3
CH_3Br (W)	8.82	0.20	2.2	5
CH_3Br (S)	10.05	0.16	1.6	5
CHCl_3 (W)	14.2	2.2	15.3	5
CHCl_3 (S)	9.0	0.4	4.3	5
CH_2Cl_2 (W)	32.7	2.9	8.7	3
CH_2Cl_2 (S)	26.8	2.4	9.0	3
C_2Cl_4 (W)	4.2	0.2	4.7	3
C_2Cl_4 (S)	2.7	0.1	3.6	3
CH_3Cl (W)	567.2	14.2	2.5	5
CH_3Cl (S)	559.5	12.0	2.2	5

factors derived from undiluted samples are consistent with those derived from global mean mole fraction estimates in 2004 (Table 6). The SIO/NOAA ratio is 0.972 compared with 0.975 from 2004 global mean estimates while the UCI-2/NOAA ratio is 0.974 compared to 0.978 based on global mean estimates. There are small differences between results from the same laboratory using different instruments. About half of the 1 % CFC-113 difference observed between ECD and MS results for laboratory 1 is due to reference standards (ECD and MS results are not based on the same standards). When the same reference standards are used, the difference is ~ 0.5 %. Laboratory 2 reported a similar difference (~ 0.6 %) between ECD and MS results. ECD results from both

laboratories 1 and 2 are likely affected by an interfering compound (co-elution). However, there is no difference between ECD and MS results for laboratory 17. While these differences are small, they suggest that CFC-113 results may be influenced by co-elution, matrix effects, or analytical nonlinearities. Instrument-specific differences of similar magnitude are also evident for CFC-11 and CFC-12 (Fig. 1a and b).

Results for CFC-114 ($\text{CClF}_2\text{CClF}_2$) and CFC-115 (CClF_2CF_3) were reported by eight and six laboratories, respectively. The variability reported for CFC-114 (Fig. 1d) was only 0.7 % among four scales, while that for CFC-115 was 4.1 % among three scales (figure not shown). Scale propagation errors were < 1 % for some AGAGE-affiliated laboratories. However, scale propagation errors for CFC-114 and CFC-115 cannot be fully addressed because cylinders in set 2 were not analyzed by SIO (scale origin). Furthermore, some of the CFC-114 differences could result from chromatographic co-elution of CFC-114 and CFC-114a (CCl_2FCF_3) since most laboratories measure the sum of CFC-114 and CFC-114a, and relative amounts of CFC-114 and CFC-114a in laboratory standards may differ from those in IHALACE samples.

3.2 Chlorinated solvents: CCl_4 , CH_3CCl_3 , CHCl_3 , CH_2Cl_2 , and C_2Cl_4

Carbon tetrachloride (CCl_4) was reported by 12 laboratories on five independent scales (Fig. 2a). The standard deviation of results among five scales was 1.8 ppt (1.9 %). The difference between the NOAA scale (laboratory 1) and the SIO-05 scale (laboratory 2, ECD results) was 2.7 %. This is comparable to both the 2.6 % difference reported by Xiao et al. (2010a) based on co-located sampling results, and the 2.6 % difference based on 2007–2008 global means (Table 6).

There remains a discrepancy between bottom-up inventories and top-down measurement-based estimates of global CCl_4 emissions (UNEP, 2007; Montzka et al., 2011). From the IHALACE study, the largest difference between scales (laboratory 2 versus laboratory 7) is 4.8 ppt, or 5 % of the average northern hemispheric mole fraction in 2004. If we assume that this represents the full range of calibration uncertainty, then top-down estimates of CCl_4 emissions could be subject to 5 % uncertainty due to calibration alone. This relatively small uncertainty is not enough to explain the discrepancy between top-down and bottom-up emissions estimates.

Comparison results for CH_3CCl_3 from 12 laboratories on six calibration scales are shown in Fig. 2b. Results on six scales show a variation of 0.8 ppt (3.4 %) for winter samples, and 1.0 ppt (4.7 %) for summer samples. The fact that all scales agree within a few ppt is remarkable considering that it has been difficult to obtain samples of pure CH_3CCl_3 in the past. A prior calibration scale developed by NOAA in

Table 6. Scale factors (relative to NOAA) derived from tropospheric global mean mole fractions reported in Table 1.1 of Montzka et al. (2011) for 2004 and 2007–2008, and from undiluted IHALACE samples (mean and standard deviation) for representative laboratories. Factors derived from AGAGE and UCI (University of California Irvine) global mean estimates can be compared with IHALACE factors from SIO and UCI-2, respectively. Unless otherwise specified, ratios were derived relative to NOAA ECD results.

		global mean 2004	global mean 2007–2008	this work
CFC-11	AGAGE, SIO ^a	0.9921	0.9939	0.9942 (0.0009)
	UCI, UCI-2	0.9996	0.9970	1.0108 (0.0007)
CFC-12	AGAGE, SIO ^a	1.0028	1.0034	1.0022 (0.0002)
	UCI, UCI-2	0.9952	0.9949	0.9948 (0.0020)
CFC-113	AGAGE, SIO ^a	0.9753	0.9777	0.9724 (0.0017)
	UCI, UCI-2	0.9778	0.9874	0.9737 (0.0001)
	NOAA ^c	0.9753	0.9854	0.9827 (0.0025)
CH ₃ CCl ₃	AGAGE, SIO ^a	0.967	0.950	0.946 (0.009)
	UCI, UCI-2	1.062	1.023	1.048 (0.008)
	NOAA ^c	0.978	0.962	0.982 (0.004)
CCl ₄	AGAGE, SIO ^a	0.969	0.974	0.973 (0.001)
	UCI, UCI-2	0.994	1.005	0.995 (0.001)
HCFC-22*	AGAGE, SIO ^b	1.003	1.000	0.993 (0.002)
	UCI, UCI-2	0.982	0.983	0.972 (0.013)
HCFC-141b*	AGAGE, SIO ^b	1.017	1.011	1.012 (0.001)
	UCI, UCI-2	–	0.976	0.945 (0.016)
HCFC-142b*	AGAGE, SIO ^b	1.041	1.028	1.037 (0.004)
	UCI, UCI-2	–	0.978	0.975 (0.010)
halon-1211	AGAGE, SIO ^b	1.014	1.012	1.021 (0.007)
	UCI, UCI-2	–	0.999	0.963 (0.008)
	NOAA ^c	0.963	0.958	0.974 (0.008)
halon-1301*	AGAGE, SIO ^b	1.041	1.027	1.058 (0.005)
CH ₃ Br*	AGAGE, SIO ^b	1.038	1.020	0.998 (0.003)

* Ratios derived relative to NOAA MS results. ^a AGAGE, SIO MD. ^b AGAGE, SIO MS. ^c NOAA MS.

the late 1990s was based on a CH₃CCl₃ reagent that contained as much as 7 % impurities.

Like CFC-113, instruments can give different results for CCl₄ and CH₃CCl₃ even when the same standards are used to define the scale. Laboratories 1, 2, 9, and 17 all reported CH₃CCl₃ results from both ECD and MS instruments. CH₃CCl₃ differences, generally less than 0.5 ppt (2–3 %), are evident in each case. Laboratories 2, 9, and 17 reported both ECD and MS results for CCl₄ on the SIO-05 scale and are aware of a systematic problem in their MS method, probably due to the chromatographic column. These results imply that one needs to be careful when using data collected by different instruments. Small analytical differences can lead to discrepancies even within the same measurement program, and differences need to be assessed on an instrument-by-instrument basis.

Despite relatively small scale differences among independent scales, there are some substantial scale propagation issues for both CH₃CCl₃ and CCl₄. While some laboratories were able to reproduce results on existing scales, others were not. CCl₄ results reported by laboratory 3 were ~30 ppt (34 %) larger than laboratory 1, from which the scale is derived (outlier in Fig. 2a). This could be caused by

a downward drift of CCl₄ in one or more standards used by laboratory 3 since CCl₄, at ppt levels, can decrease with time in some types of cylinders. Laboratory 3 also reported mole fractions of CH₃CCl₃ that were 70 % and 184 % larger than those of laboratory 1 (see Table 3). Here, downward drift of CH₃CCl₃ in standards used by laboratory 3 would also lead to higher reported mole fractions, but would not explain the large difference in mole fractions reported by laboratory 3 for the two undiluted samples (see Supplement).

Results for CHCl₃ are shown in Fig. 2c. The dispersion of five scales was 4.5 % and 15.5 % from summer and winter samples, respectively. The large standard deviation for the winter samples reflects a low mole fraction reported by laboratory 7. Excluding laboratory 7, results on four scales show a variability of ~5 % for both summer and winter samples. Differences due to scale transfer and analytical methods are on the order of 3 %, except for the MD (ECD) measurements from laboratory 9, which are 10 % lower than laboratory 2 (scale origin).

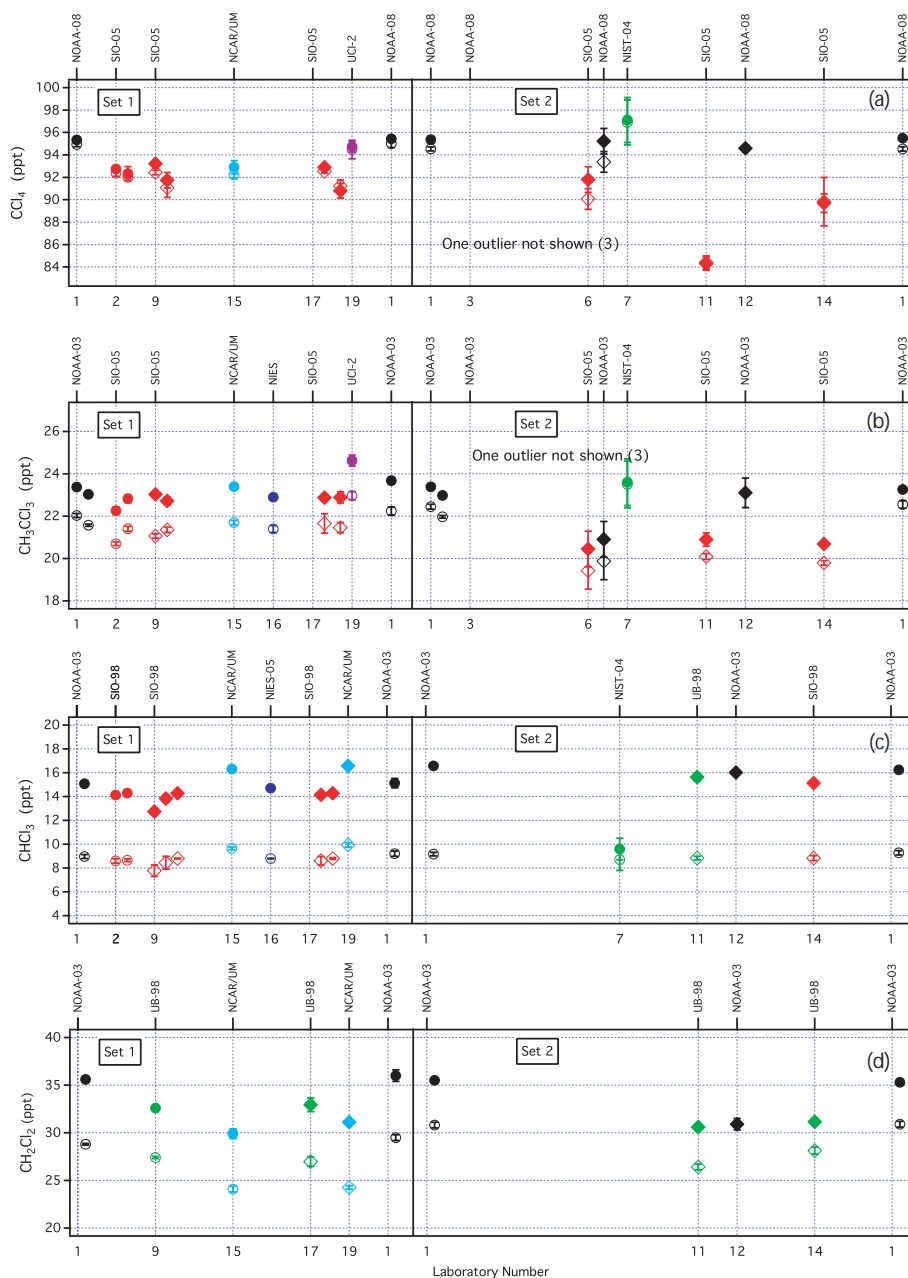


Fig. 2. Same as Fig. 1 for trace gases (a) CCl_4 , (b) CH_3CCl_3 , (c) CHCl_3 , (d) CH_2Cl_2 .

CH_2Cl_2 was measured by eight laboratories on three scales (Fig. 2d). The standard deviation of results on three scales was $\sim 9\%$. Scale transfer errors are of similar magnitude, with all laboratories agreeing with the laboratory of scale origin within 10% .

C_2Cl_4 (figure not shown) showed better agreement than CH_2Cl_2 , with a variation of $< 5\%$ among three scales, and scale transfer differences less than 7% in all cases except for laboratory 19, which showed differences of $30\text{--}35\%$ relative to laboratory 15 (scale origin) (see Supplement).

3.3 HCFCs and HFCs

The measurement histories of HCFCs and HFCs (1st and 2nd generation replacement for CFCs) are not as extensive as those of CFCs. Therefore, one might expect that development of measurement scales for HCFCs and HFCs is less advanced. Scale variations range from $1\text{--}2\%$ for HCFC-22 and HCFC-141b (four scales) to 4% for HCFC-142b (four scales), and $3\text{--}6\%$ for HFC-152a and HFC-134a (three scales) (Figs. 3 and 4a). While the relative scale differences are larger than those for CFC-11 and -12, the fact that HCFC

and HFCs require more advanced measurement techniques compared to CFCs, yet still show relatively good agreement among scales, is encouraging. It is likely that efforts to develop and improve CFC calibration scales through the years have translated into improved scales for HCFCs and HFCs.

The dispersion of HCFC-22 results on four scales was 1.7% for winter samples and 2.1% for summer samples. Scales developed by laboratories 1, 2, and 15 agree within 1%, while the scale developed by laboratory 16 is 4% lower. Scale transfer was excellent for some laboratories, with three of the AGAGE-affiliated laboratories demonstrating agreement within 0.5% of the SIO scale, and laboratory 4 only 0.1% different from the NOAA scale. Both SIO/NOAA and UCI-2/NOAA ratios are comparable to those based on global mean estimates.

Results for HCFC-141b and -142b are similar to those of HCFC-22. Agreement among four independent scales was 1–2% for HCFC-141b and ~3% for HCFC-142b. Transfer of SIO and NOAA scales to other laboratories was excellent (< 1%) for HCFC-142b in most cases, but an average difference of 10% was observed between laboratories 15 and 19. Results for HCFC-141b were similar, except that scale transfer differences were larger (~3%) for both SIO and NOAA scales, and about the same (9%) between laboratories 15 and 19. Observed SIO/NOAA ratios for HCFC-141b (1.012) and HCFC-142b (1.037) are similar to those derived from global mean estimates (Table 6).

Four scales for HFC-134a vary by 2.7 and 4.9% for summer and winter samples, respectively (Fig. 3d). Three scales (SIO, NOAA, NIES) are close to each other, and vary by only 0.5%. Scale transfer is very good (< 1%) among AGAGE laboratories (2, 9, 14, 17) and among those linked to the NOAA-04 scale (1, 4, 12). Laboratories 15 and 19 show an 11% discrepancy.

It is encouraging that nearly all laboratories detected a mole fraction difference between cylinders filled in winter and summer. In most cases the seasonal differences were similar among all labs, except for HCFC-141b (Fig. 3b). For HCFC-141b laboratories 1, 2, 4, and 17 observed a 1.0–1.5% difference between summer and winter samples, while laboratories 14 and 16 observed smaller differences, and laboratories 11 and 19 observed differences with opposite sign.

3.4 Halons

Halon results were reported on up to four independent scales with several other laboratories reporting on adopted scales. Halon-1211 was measured by nine laboratories (Fig. 4b). The standard deviation of halon-1211 results on four scales was 2.2%. In contrast to many other trace gases measured in this experiment, scale transfer is excellent (< 1% in most cases). Only one result, from laboratory 11 (cylinder SX-3538), shows a scale transfer discrepancy greater than 1%, and this difference is within the uncertainty reported by laboratory 11. This is impressive considering that the mole fractions of

halon-1211 in the undiluted samples were only 4.4 ppt. Scale factors derived based on global mean estimates (Table 6) are consistent with IHALACE results for SIO, but show a 4% discrepancy for UCI-2.

The dispersion of results reported for halon-1301 (Fig. 4c) was larger than that for halon-1211 (7% versus 2.2%). Scale transfer differences were similar in magnitude to the reported uncertainties. Note that SX-3537 was not analyzed for halon-1301 at NOAA. A NOAA value was estimated from SX-3538 (filled at the same time) using the summer/winter ratio from cylinders SX-3527 and SX-3538. This estimate does not affect the above conclusions because the mole fractions of all undiluted samples were similar for this gas.

Halon-2402 mole fractions, reported on two scales, agree within 0.05 ppt (10%) (Fig. 4d). While SX-3537 was not analyzed by NOAA, no attempt was made to estimate halon-2402 in this cylinder because both undiluted cylinders contained similar mole fractions according to results from laboratories 15, 17, and 19. Two laboratories (14 and 17) reported halon-2402 results based on provisional scales. Provisional scales are those adopted using indirect methods, such as the analysis of a subsample of a compressed gas standard, or by making measurements at a common location. These halon-2402 results differ from the scale origin (laboratory 1) by up to a factor of two. Results from laboratories 15 and 19, which are on the NCAR/UM scale, agree within 0.03 ppt (6.5%).

3.5 Methyl Bromide and Methyl Chloride

Results for CH₃Br from different laboratories differ by only a few percent. The standard deviations among five laboratories with independent scales were 2.2% and 1.6% for winter and summer samples, respectively (Table 5). Results on the UB-98 scale are not considered independent because the scale was adopted, not developed, by laboratory 11. Differences between summer and winter samples were detected by all laboratories (Fig. 5a). Scale transfer differences range from < 2% (laboratories 12 and 17) to ~10% (laboratory 19). The 7% instrument-specific differences for laboratory 9 are related to a drifting calibration standard, which has led to the first set of results being overestimated. The seasonal difference in CH₃Br mole fractions allows scales to be compared over a broad range. The five independent scales represented are, for the most part, linearly related to each other (Fig. 7). The SIO/NOAA ratio (0.998) is 4% lower than that based on 2004 global mean estimates (1.038) (Table 6). This discrepancy may reflect errors in the global mean estimates rather than actual scale differences and does not appear to be caused by analytical non-linearities.

CH₃Cl results are similar to those of CH₃Br, with relatively small differences among five independent scales (standard deviation ~2.5%) (Fig. 5b). The large apparent scale difference between SIO-05 and UB-98 (compare laboratories 2 and 11) is complicated by the similarly large scale propagation error between laboratories 2 and 11 for the SIO-05

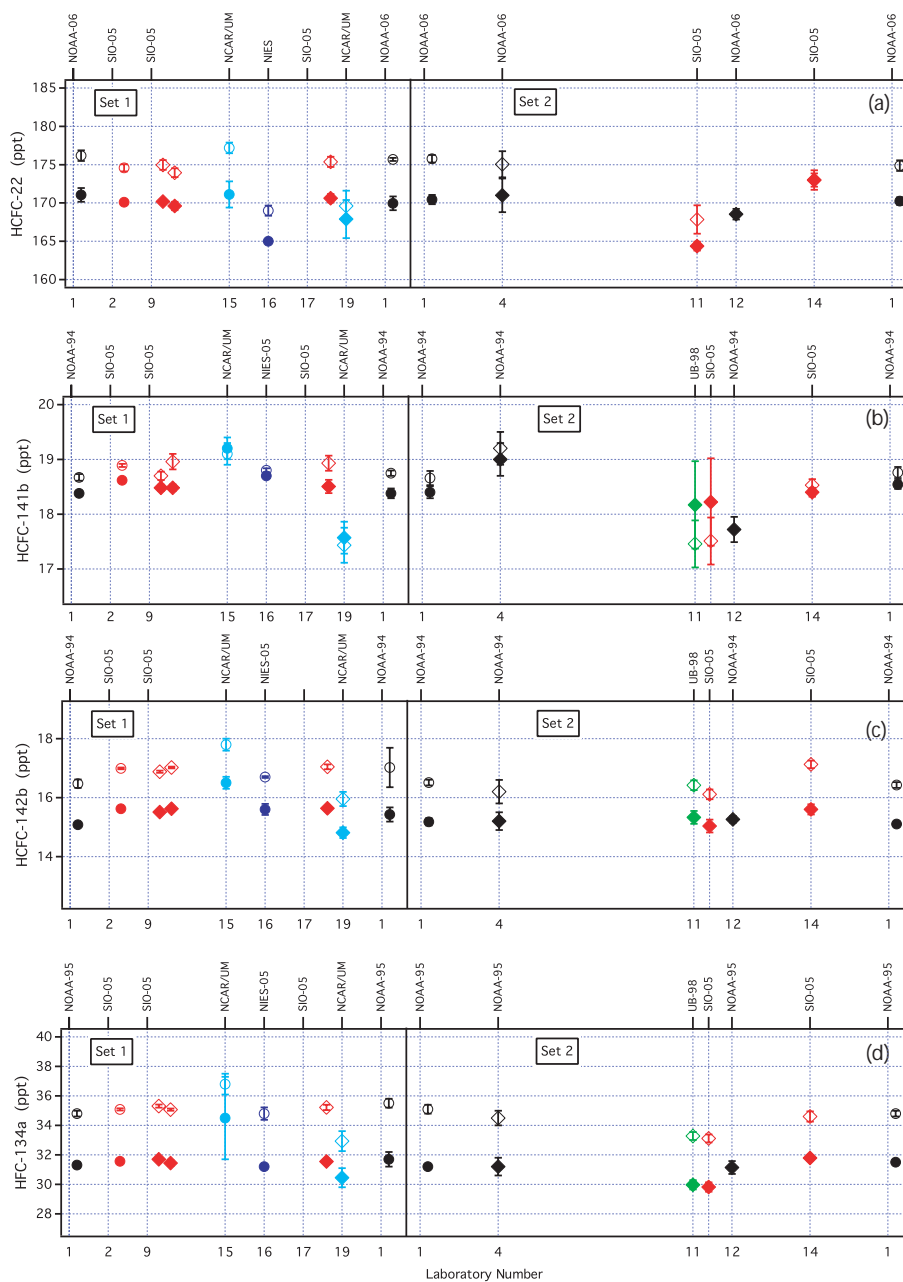


Fig. 3. Same as Fig. 1 for trace gases (a) HCFC-22, (b) HCFC-141b, (c) HCFC-142b, (d) HFC-134a.

scale. NOAA results indicate that undiluted cylinders from sets 1 and 2 had similar mole fractions, which is inconsistent with results from laboratory 11. Other laboratory comparisons (P. K. Salameh, personal communication, 2010) indicate that the UB-98 scale is 1.5 % higher than SIO-05, which then implies that the laboratory 11 results are ~ 25 ppt too low. The difference between the NOAA scale and the SIO-05 scale (laboratories 1 and 2) is 0.8 %, similar to the difference of 1.01 % used by Xiao et al. (2010b) based on co-located sampling.

3.6 Very short-lived halocompounds

Few laboratories reported results for very short-lived halocompounds, such as CHBr_3 , CH_2Br_2 , and CH_3I . However, recent interest in these gases (Read et al., 2008; Carpenter et al., 2009; Jones et al., 2011) warrants their inclusion. For CH_2Br_2 and CHBr_3 , only laboratories 1 and 15 provided results on independent scales, and laboratory 12 provided results on scales obtained from laboratory 1. There does not appear to have been a significant change in the mole fractions of CHBr_3 and CH_3I in the IHALACE cylinders during

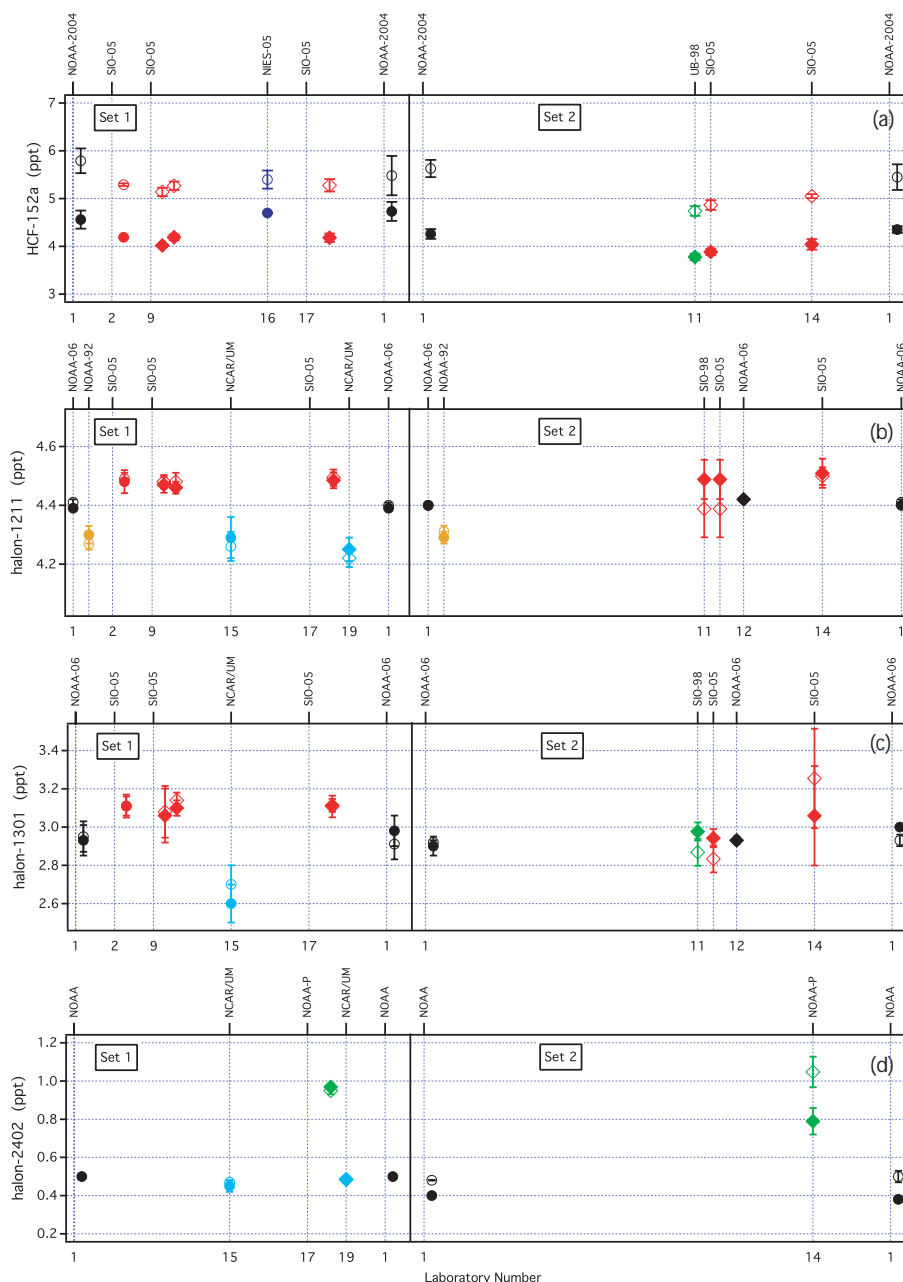


Fig. 4. Same as Fig. 1 for trace gases (a) HFC-152a, (b) halon-1211, (c) halon-1301, (d) halon-2402.

the experiment. An upward drift of 10–20 % over three years is suggested for CH_2Br_2 .

For CH_2Br_2 , differences between scales (laboratories 1 and 15) averaged 16 % (0.12 ppt) (Fig. 5d) after adjusting for possible drift in CH_2Br_2 . Scale transfer differences were 15 % between laboratories 1 and 12, but only 5 % between laboratories 15 and 19. Jones et al. (2011) reported scale differences of 20–70 % and relatively small transfer differences (less than 3 %).

For CHBr_3 , the difference between laboratories 1 and 15 was 30 % while the difference between laboratories 1 and 12 (same scale) was 6 % (Fig. 6a). Jones et al. (2011) reported scale differences as high as 70 % and scale transfer differences of ~ 15 %.

For CH_3I , results from most laboratories agreed within 20 %, with the exception of laboratory 15, which was a factor of 2 higher than the rest. Jones et al. (2011) also reported factor of 2 differences for CH_3I .

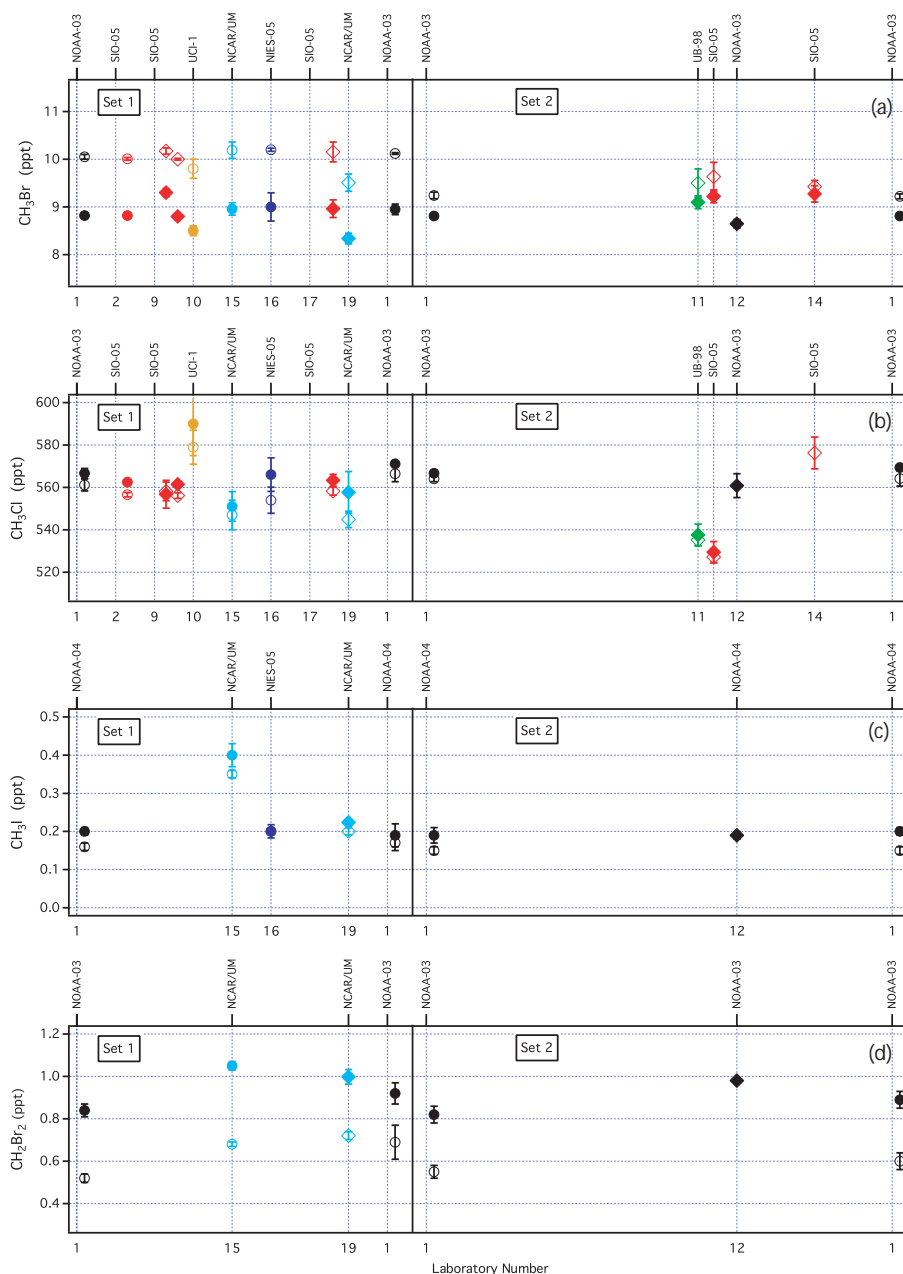


Fig. 5. Same as Fig. 1 for trace gases (a) CH₃Br, (b) CH₃Cl, (c) CH₃I, (d) CH₂Br₂.

Overall, the comparison of CH₂Br₂, CHBr₃, and CH₃I scales is promising considering that these gases are typically more difficult to measure compared to CFCs and HCFCs, and mole fractions in the IHALACE cylinders were less than 1 ppt. Comparisons carried out at higher mole fractions (2–5 ppt) might make quantifying scale differences easier for these gases.

3.7 Nitrous Oxide, SF₆, Methane, and Carbonyl Sulfide

The long atmospheric lifetime and small spatial gradients of nitrous oxide (N₂O) mean that compatibility requirements

are high. For multiple data sets to be optimally useful in inverse modeling, data should be compatible to within 0.1 ppb (WMO/GAW, 2009). This level of compatibility is often not met using ECD-based methods (WMO/GAW, 2011). However, progress has been made in recent years and studies involving multiple data sets have been performed (Hirsch et al., 2006; Huang et al., 2008; Nevison et al., 2011; Saikawa et al., 2013).

Nitrous oxide results varied by 0.72–0.87 ppb (0.23–0.27 %) among three scales (Fig. 6b). The average difference between NOAA and SIO (undiluted samples) was

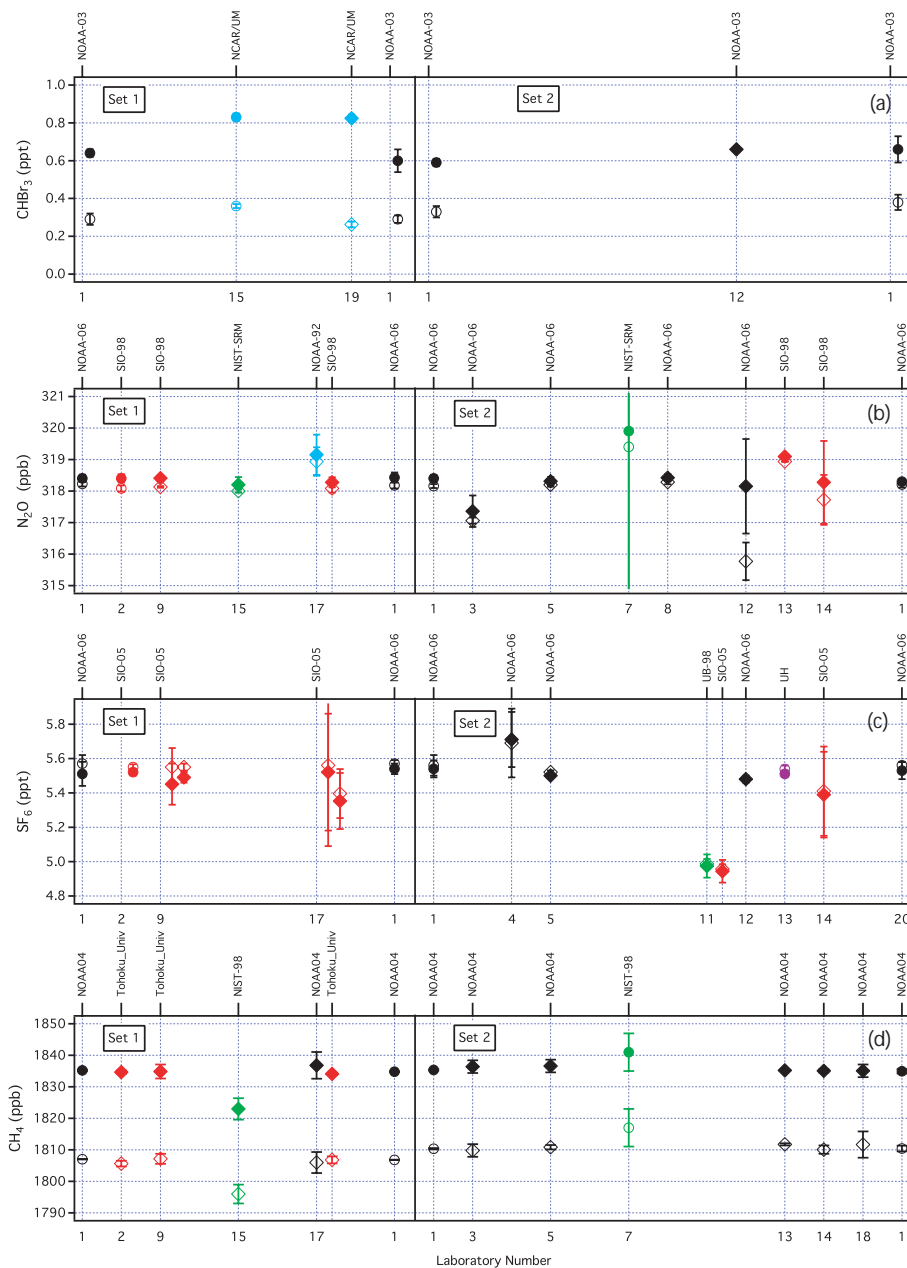


Fig. 6. Same as Fig. 1 for trace gases (a) CHBr_3 , (b) N_2O , (c) SF_6 , (d) CH_4 (N_2O and CH_4 in $\text{nmol mol}^{-1} = \text{ppb}$).

0.08 ppb, which is comparable to differences reported by Hall et al. (2007) and Huang et al. (2008). The relative difference between laboratory 17 (CSIRO) and laboratory 2 (SIO) was $0.02 \pm 0.03 \%$, which differs slightly from the 0.17% reported by Huang et al. (2008). There also appears to be good agreement between these scales and the NIST scale, except that the best agreement is shown by laboratory 15 (UM-2, adopted scale) and not laboratory 7 (NIST, scale origin). The difference between NIST and NOAA based on undiluted samples is 1.37 ppb, or 0.4%. This is larger and of opposite sign compared to that reported by Hall et al. (2007)

(-0.2%), but is within the uncertainties reported by NIST. A new scale has recently been developed by NIST, and a subsequent NIST-NOAA comparison has shown much better agreement (Kelley et al., 2013). Among laboratories on the same scale, compatibility is excellent for some (1, 5, 8; 2, 9, 17) and not so good for others (1, 3; 2, 13). We note that laboratory 13 recently adopted the NOAA-2006 N_2O scale, and that compatibility is much improved. The average difference between laboratories 1 and 8 (KIT) is < 0.1 ppb for undiluted samples. This is an important result because of the roles served by these laboratories within the WMO/GAW

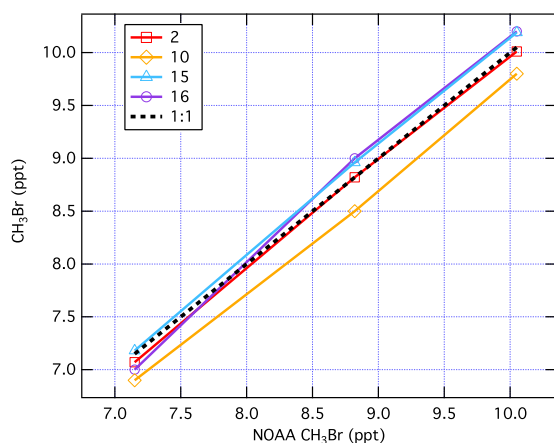


Fig. 7. Results from both diluted and undiluted samples for CH_3Br for five laboratories plotted against NOAA results. Five CH_3Br scales show a near-linear relationship over the range of mole fractions sampled.

program (NOAA as the Central Calibration Laboratory for N_2O , and KIT as the World Calibration Center). It is essential that these laboratories remain closely linked. Finally, summer/winter differences between the two undiluted cylinders (~ -0.2 ppb) were detected by most laboratories (1, 2, 3, 5, 8, 9, 13, 15, 17) and overestimated by some (laboratories 7, 12, 14). While the results are encouraging overall, there is room for improvement in inter-laboratory compatibility.

SF_6 was reported on four scales (Fig. 6c). Three of these are in excellent agreement. Ratios of commonly used scales relative to the NOAA-2006 scale are 0.9954 (University of Heidelberg) and 0.9991 (SIO) based on undiluted samples. The SIO/NOAA ratio is close to the mean scale factor of 0.998 ± 0.005 reported by Rigby et al. (2010) based on co-located sampling at five stations. While the three primary scales in use by the atmospheric science community show good agreement, scale transfer issues exist. Relatively large differences between laboratories 1 and 4 (NOAA scale) and laboratories 2, 11, and 14 (SIO scale) are apparent. However, it is encouraging that the precision reported by some laboratories is excellent. The average difference between summer and winter samples measured by laboratory 1 was 0.03 ppt. This difference, as measured by laboratories 2, 5, 6, 9, 13, and 14 was 0.03, 0.02, 0.06, 0.03, and 0.02 ppt, respectively. Thus, some laboratories are capable of resolving very small mole fraction differences.

Twelve laboratories reported CH_4 mole fractions on three scales (Fig. 6d). Scale differences are small ($< 0.3\%$). The relationship between the NOAA04 scale and the Tohoku University scale, 1.0003 as derived by Dlugokencky et al. (2005), is confirmed here. The average ratio of four laboratories on the Tohoku University scale relative to the NOAA results is 1.0003 ± 0.0002 . Both the NOAA04 and Tohoku University scales appear to have been propagated to within 2 ppb, which

is the WMO/GAW compatibility goal for measurements on the same scale (WMO/GAW, 2009). All laboratories also detected a 24–28 ppb summer/winter difference to within a few ppb. The only disagreement is between laboratories 7 and 15, which reported data on the NIST scale. The average result from laboratory 7 is 0.3 % higher than laboratory 1, which agrees with previous comparisons between NIST and NOAA (Dlugokencky et al., 2005). Thus, the laboratory 15 results are likely too low.

Carbonyl sulfide (COS) data were not part of the original data submission and are not shown. However, scale comparison information is of interest, particularly since measurements of COS may be useful as a tracer of photosynthesis (Montzka et al., 2007; Campbell et al., 2008). The standard deviation of COS data from four independent scales (winter samples) was 25 ppt (3.9 %). Two scales (1, 10) showed higher COS amounts, while two scales (15, 19) tended to be lower. All laboratories detected a large difference between summer and winter samples, consistent with the seasonal drawdown of COS over the continental US in summer (Montzka et al., 2007) (Supplement). The average difference between winter and summer values was 169 ppt (laboratories 1, 10, 19). This large seasonal difference, combined with results from the diluted sample, allows linear relationships among COS scales to be estimated. Here we compare to the NOAA scale as: $Y = aX + b$, where X is NOAA and Y is another scale: [Laboratory Number, a , b], (10, 1.064, -33), (15, 0.928, 17), (19, 0.985, -35). For example, the relationship between laboratory 10 and NOAA is $Y_{10} = 1.064 \cdot \text{NOAA} - 33$ ppt.

3.8 Linearity issues

The atmospheric mole fractions of most of the trace gases studied in this experiment have not been constant over time. CFC mole fractions increased rapidly in the 1980s and have been declining slowly over the last decade, and mole fractions of HCFCs continue to increase (Montzka et al., 2009; O'Doherty et al., 2004). Thus, a scale comparison based on air samples at one point in time may not be valid for other time periods. Furthermore, the analysis method, particularly an ECD, may exhibit a non-linear response, whereby calibration using reference standards over a particular range of mole fractions might lead to errors outside that range. We address this briefly by comparing results for diluted and undiluted samples. We focus on gases for which sampling issues and precision are less likely to influence the results. To simplify the analysis, we define a linearity factor (LF) as:

$$\text{LF} = \frac{(X_i/X_1)_{\text{diluted}}}{(X_i/X_1)_{\text{undiluted}}}, \quad (1)$$

where X_i is the result from laboratory i , and X_1 is the NOAA result, for diluted and undiluted samples. This factor provides an indication of whether or not a constant scale factor might be applied over a 20–30 % mole fraction range. An LF of 1.0

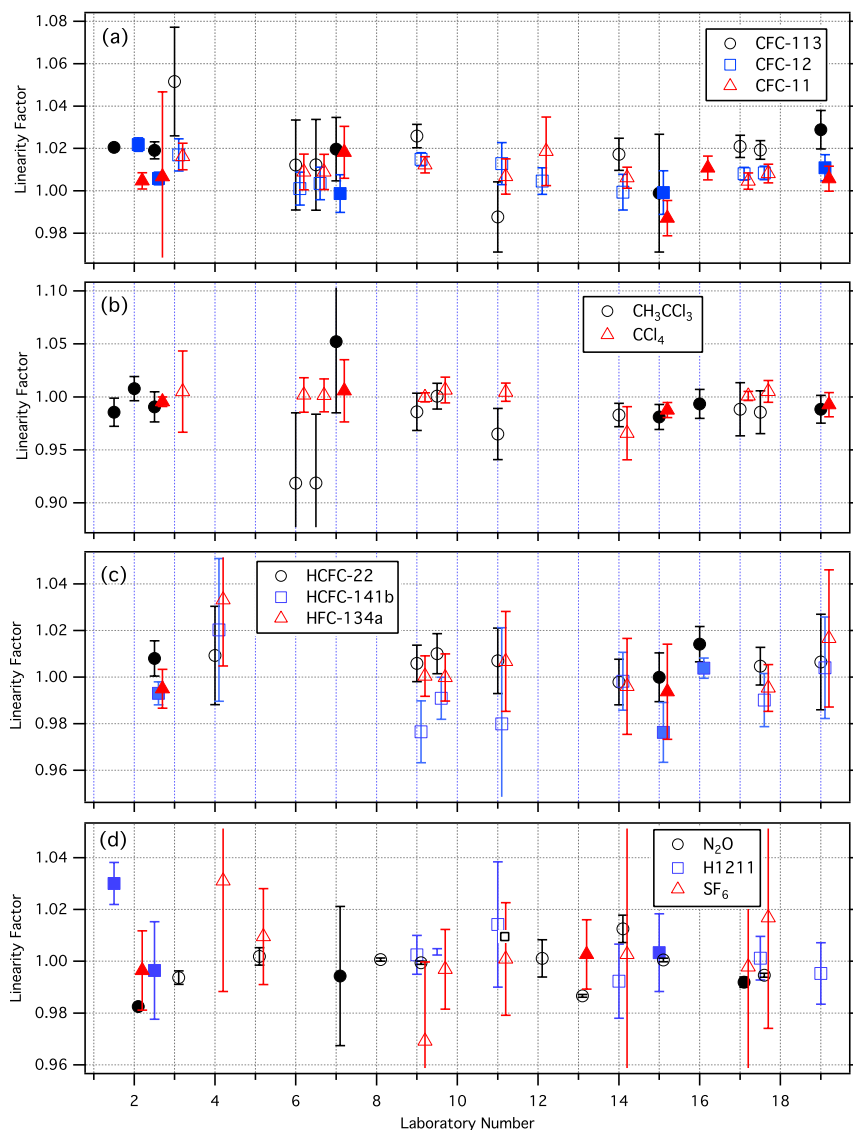


Fig. 8. Linearity factors relative to NOAA for select gases. A linearity factor of 1.0 corresponds to scale factors that are the same for both diluted and undiluted samples (NOAA results used for comparison are 1.0 by default and are not shown). Filled symbols denote laboratories that develop calibration scales, while open symbols denote those that adopt existing scales (see Table S1 for scale definitions). Note that symbol colors do not indicate common scales, as was the case in Figs. 1–6. Data have been shifted on the x axis for clarity. Error bars are 1 s.d. Linearity factors are relative to NOAA ECD results in panels (a), (b), and (d), and to NOAA MS results in panel (c).

results when scales differ by a constant factor at both ambient and sub-ambient mole fractions.

Linearity factors for CFC-113, CFC-12, and CFC-11 are shown in Fig. 8a. For CFC-113, linearity factors from four laboratories that prepare primary standards are close to the same value (1.02) and one laboratory (15) shows a ratio close to 1.00. Because a number of laboratories show similar results compared to the NOAA ECD-based CFC-113, it seems that the NOAA ECD-based CFC-113 scale may be subject to a co-elution or perhaps the non-linear response of the NOAA ECD was not fully characterized.

CFC-12 ECD results from NOAA and SIO differ by only 1 ppt at 535 ppt, but differ by 10 ppt at 448 ppt ($LF = 1.0218 \pm 0.0032$, 1 s.d.). This suggests that long-term records based on NOAA and SIO measurements might diverge at lower mole fractions. While these are relatively small differences on a percentage basis, they are larger than the typical analytical precision. SIO MS results are more consistent with NOAA ECD results over a 20 % mole fraction range ($LF = 1.0058 \pm 0.0030$). Similarly, mole fraction-dependent differences were also small for laboratories 7, 15, and 19 compared to NOAA ECD results.

We can use the LF results to estimate potential errors introduced by the use of fixed scale factors to adjust calibration scales over a 20 % mole fraction range. For example, LFs derived for CFC-11 are within 1 % of 1.0 for most laboratories, but the difference between laboratories 7 and 15 is nearly 3 %. Thus, if CFC-11 results on the NIST scale were adjusted to the NCAR/UM scale using a fixed scale factor based on undiluted samples from this experiment, errors up to 3 % could result in mole fractions 20 % lower than that upon which the fixed factor was derived. In contrast, results from laboratories 2 and 19 would likely be subject to much less uncertainty when adjusted by fixed scale factors over this range, since LFs from these laboratories are nearly identical.

Linearity factors for CH_3CCl_3 are close to 1.0 for most laboratories (Fig. 8b). However, LFs for several laboratories are less than 1.0, with an average of 0.986 for laboratories 9, 11, 14, 15, 16, 17, 19. This is likely due to the choice of reference values (NOAA ECD) used to calculate LFs. If NOAA MS results are used as reference values instead, LF factors increase by an average of 1.2 %. The same group of laboratories would then show an average LF of 0.999. This suggests a non-linearity or co-elution that affects the NOAA ECD data. Linearity of CH_3CCl_3 response could be important when interpreting historical CH_3CCl_3 data because of the rapid decline in CH_3CCl_3 mole fraction that has occurred over the last two decades.

Linearity factors for CCl_4 (Fig. 8b) show little variation among laboratories that prepare primary standards (1, 2, 7, 15, 19), with most LFs within 1 % of 1.00. This suggests that non-linear effects are not a major factor contributing to the observed 5 % scale differences discussed earlier.

Only small mole-fraction-dependent scale differences were observed for HCFC-141b, HCFC-22 (Fig. 8c), and HCFC-142b (not shown). Therefore application of a constant scale factor for these gases is unlikely to result in large errors over a limited mole fraction range. Linearity factors for HCFC-22 are nearly all within 1 % of 1.00, and many are not different from 1.00 given reported uncertainties. The LF factors for HCFC-141b range from 0.98 to 1.02, but in most cases differences between undiluted and diluted samples are about the same as the analytical precision. HFC-134a also shows good linearity in this comparison with most LFs within 1 s.d. of 1.0. Better scale transfers and linearity factors close to 1.0 for HCFCs may be partly due to the fact that MS instruments are more commonly used to measure HCFCs, and their response tends to be more linear than that of an ECD.

Nitrous oxide, which is typically measured using ECDs, showed discrepancies in scale relationship and scale transfer in some cases (Fig. 6b). While the NOAA-NIST (1, 7) difference is consistent for both diluted and undiluted samples, the NOAA-SIO (1, 2) difference increases substantially at the lower mole fractions, and this difference is not consistent among other laboratories linked to the SIO-98 scale (2, 9, 13, 14, 17). Laboratories 9 and 17 show LFs close to 1.0

on the SIO-98 N_2O scale, but laboratory 2 (scale origin) does not (Fig. 8d). This discrepancy could be due to the fact that the SIO-98 N_2O scale was developed over a limited mole fraction range, and the diluted samples measured here are outside the range of the SIO-98 scale.

For halon-1211, scale transfer was excellent for both diluted and undiluted samples (Fig. 8d), with linearity factors remarkably consistent near 1.0. Similarly, most LFs for SF_6 are not significantly different from 1.0. This is important because SF_6 mole fractions are increasing at ~ 0.25 ppt yr^{-1} (Levin et al., 2010; Rigby et al., 2010) and any comparison among laboratories will soon be obsolete unless linearity can be demonstrated. The same is true for other gases with rapidly changing mole fractions, such as HFC-134a.

Linearity factors shown here are based on a limited data set, and do not include time-dependent sampling issues that might influence real-world data. Long-term data records from similar locations should always be considered when applying scale factor adjustments across changes in mole fraction and time. Furthermore, agencies responsible for collecting the original data should be consulted whenever the application of scale factors is considered.

4 Summary

A comparison of numerous halogenated and other trace gases was carried out among 19 laboratories. These results reveal substantial improvements in calibration over previous comparisons (Rasmussen, 1978; Fraser, 1979; Prinn et al., 1998). However, scale differences for many compounds are large compared to atmospheric surface gradients, and merging data on independent scales without regard for scale differences is not advised. Furthermore, differences due to scale propagation were found to be as large or larger than differences between independent scales in many cases.

Scale differences ranged from 2 % for CFC-11 and CFC-12 to a factor of two for CH_3I . Depending on how data from different measurement networks are used, even differences on the order of 2 % could be important. Relatively large discrepancies among calibration scales were identified for CHCl_3 , CH_2Cl_2 , CH_3I , and CHBr_3 , with standard deviations of results on independent scales of 15 %, 9 %, 12 %, and 13 %, respectively. These gases could be important sources of halogen to the upper troposphere and lower stratosphere and calibration scale differences could influence estimates of their abundance in these regions. The standard deviation of CCl_4 results on five scales was 1.9 %, and the largest difference between any two scales was 5 %. Thus, uncertainties in top-down CCl_4 emissions estimates solely due to calibration uncertainties are likely less than 5 %. Scale differences for CH_4 , N_2O , and SF_6 reported previously were confirmed.

Scale propagation errors were relatively small for some gases (< 1 % for halon-1211, < 1 % for HFC-134a, < 0.05 % for CH_4) and larger for others (10 % for CFC-113, factor of

2 for CH_3CCl_3) and varied among laboratories. Scale propagation errors are considered large when they are larger than twice the typical analytical precision. In general, laboratories associated with the AGAGE network showed smaller scale transfer differences than others, but not in all cases. Differences between measurement methods (ECD versus MS) are apparent, suggesting that co-elution or matrix effects may be important for some gases.

As a result of this experiment, cooperation among laboratories making similar measurements has improved. These results, available to participants since 2008, have stimulated the exchange of calibrated air samples and data in efforts to understand some of the observed differences on a bi-lateral or multi-lateral basis. While these results provide a framework for relating calibration scales and measurement results among measurement programs, they should not be the sole basis upon which such relationships are derived. A one-time assessment of measurement differences is not sufficient to fully characterize all aspects of the measurement of these and other trace gases.

Supplementary material related to this article is available online at <http://www.atmos-meas-tech.net/7/469/2014/amt-7-469-2014-supplement.zip>.

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