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# 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. Six stainless steel cylinders containing natural and modified natural air samples were circulated among 19 laboratories. Results from this experiment reveal relatively good agreement among commonly used calibration scales for a number of trace gases present in the unpolluted atmosphere at  $\text{pmol mol}^{-1}$  (parts per trillion) levels, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs). Some scale relationships were found to be consistent with those derived from bi-lateral experiments or from analysis of atmospheric data, while others revealed discrepancies. The transfer of calibration scales among laboratories was found to be problematic in many cases, meaning that measurements tied to a common scale may not, in fact, be compatible. 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 and Reimann, 2011). Some of these, along with hydrofluorocarbons (HFCs), are also 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.

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Collaborative efforts utilizing measurements from multiple groups have led to more robust estimates of the global distributions and emissions of  $\text{N}_2\text{O}$  (Huang et al., 2008; Saikawa et al., 2013),  $\text{CCl}_4$  (Xiao et al., 2010a),  $\text{CH}_3\text{Cl}$  (Xiao et al., 2010b), HCFC-22 (Saikawa et al., 2012) and  $\text{SF}_6$  (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, the abundance is determined relative to a calibration standard measured in a similar manner. Most calibration standards consist of mixtures of trace gases stored in compressed gas cylinders with known mole fractions. Calibration standards are typically designed to match the atmospheric composition in order to minimize interference or bias.

The larger  $\text{CO}_2$  measurement community, under the auspices of the World Meteorological Organization – Global Atmosphere Watch (WMO/GAW) program, has adopted a single reference scale for WMO/GAW  $\text{CO}_2$  measurements (WMO/GAW, 2009; Zhao et al., 1997). On-going efforts to compare laboratory measurements and assess how well cooperating laboratories are linked to the calibration scale are fundamental to the WMO/GAW program (WMO/GAW, 2009). Protocols for  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{SF}_6$ , and  $\text{H}_2$  are also in place. 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 major ozone-depleting gases (CFC-11, CFC-12,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CCl}_4$ ) related to analytic methods and calibration. These studies revealed standard deviations of 10–25 % among independent laboratory scales, but showed good agreement (3 %) for CFC-12 and  $\text{CCl}_4$  among laboratories using commonly derived standards. In recent years, most of the research in this area has been carried out on a bi-lateral or ad-hoc basis. While a few scale differences can be calculated from global mean esti-

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mates (Clerbaux and Cunbold, 2007; Montzka and Reimann, 2011), these represent only a subset of research groups involved in the measurement of these trace gases, and do not differentiate between fundamental calibration scale differences and those associated with sampling, measurement location, or analytical technique.

5 The International Halocarbon in Air Comparison Experiment (IHALACE) was conceived as a first step toward assessing the variability of a number of common calibration scales for halogenated trace species measured in the atmosphere. While the existence of independent calibration scales is important for verifying trends and estimating uncertainties, it is also important to understand the relationships between independent scales. Experiments designed to assess calibration and analytical differences have been conducted for greenhouse gases (WMO, 2011) and select hydrocarbons (Apel et al., 1994; Slemr et al., 2002; Apel et al., 2003). Only a limited number of such experiments have been conducted with a focus on halocarbons (Rasmussen, 1978; Fraser, 1979; Prinn and Zander, 1998; Jones et al., 2011).

15 The goals of IHALACE were (1) establish a calibration matrix that relates the calibration scales among different laboratories at a specific point in time, and (2) 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 1–4 % (95 % C. L.). 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 gradients. As a result, it is important to understand even small differences between scales rather than treat scales as equivalent based on agreement within uncertainties.

## 25 **2 Methods**

Six electro-polished stainless steel cylinders (Essex Cryogenics, St. Louis, MO), divided in two sets, were distributed among the participants (Table 1). Each group re-

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ceived 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, while those groups that adopt scales from other laboratories received the other set of three samples.

### **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.

10 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 natural air via transfer from a pressurized Aculife-treated aluminum 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, evacuated to 6 Pa, and humidified by adding 0.65 mL HPLC-grade water and ~ 100 L dry natural air as before. Dry synthetic zero-grade air was added to two cylinders to create sub-ambient air samples. The zero-grade air (Linweld, Lincoln, NE) was scrubbed for residual contamination by passing it through molecular sieve 5Å 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). At Niwot Ridge, air was pumped through a 6-m stainless steel inlet line (2.54 cm O. D.). 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<sup>–1</sup> H<sub>2</sub>O and blowing air across aluminum cooling fins mounted to the compressor heads reduces the levels of contaminants generated by the compressor. Moisture was removed using Rix

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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  $\text{H}_2\text{O}$  with  $\sim 2600$  g dry natural air, the resulting water vapor mole fraction in each cylinder was  $\sim 400$  ppm. Three stainless steel cylinders (one diluted, two undiluted) were filled sequentially on 17 March 2004 during strong westerly synoptic flow. A second set of three cylinders was filled on 8 July 2004. 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 ( $\text{CH}_3\text{Br}$  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. While laser-based systems have been developed for some species (e.g.,  $\text{N}_2\text{O}$  and  $\text{CH}_4$ ), they were not widely used at the time of this experiment. A dedicated pressure regulator was supplied with each cylinder (Veriflow 959TDR, Veriflow 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 (4–5 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 large amounts of air, thus differences between initial and final mole fractions are not

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expected to be related to changes in cylinder pressure. Only minor differences were observed between initial and final analysis.

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. Participants were informed only of their laboratory 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 blind comparison, all participants were informed in advance, and there were no strong objections. The participant/referee submitted results to the other referee and to another participant (B. Hall). Further, 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 Table S1 in the Supplement). Data submitted on obsolete scales were converted to more recent scales according to known conversion factors (e.g.,  $\text{CH}_4$  on the CMDL-93 scale were converted to NOAA-04, Dlugokencky et al., 2005; CFC-12 on the NOAA-2001 scale were converted to NOAA-2008; HCFC-22 on the NOAA-92 scale were converted to NOAA-2006;  $\text{CCl}_4$  on the NOAA-2002 scale were converted to NOAA-2008;  $\text{N}_2\text{O}$  on the NOAA-2000 scale were 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 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  $\sim 545$  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  $\text{N}_2\text{O}$  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 figures and tables as non-integer labora-

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tory numbers. For example, additional results submitted by laboratory 2 are presented as laboratory 2.1. See Table S1 in the Supplement 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 prepare their own standards (Table 5). Of course, no calibration scale is known absolutely, but 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 the extent to which certain scales are propagated among different laboratories, as two laboratories on the same scale should agree to the level at which the scale can be propagated (typically  $2\sigma$  from the laboratory of scale origin). We also separate results by the season during which the cylinders were filled (late winter vs. 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. 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 standards development, which could impact how datasets compare over the long term.

We focus primarily on the results for major halogenated species (CFCs, HCFCs, HFCs, etc.), and other greenhouse gases such as  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ , and  $\text{CH}_4$ . We limit the analysis primarily to trace gases for which three or more laboratories provided results and at least two scales are represented. The full complement of results is available

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as Supplement (see Table S2). Average differences (%) compared to NOAA for select trace gases are shown in Tables 3 and 4.

#### 3.1 Chlorofluorocarbons (CFCs)

Both CFC-11 and CFC-12 have a long history of measurement in the atmosphere and extensive work on scale development has been done over the years. For CFC-11, good agreement was observed across six scales for the undiluted air samples, with a variation of only 1 % (one standard deviation) (Table 5, Fig. 1a). There was some clustering, with three scales (1, 2, 7) at lower values and three scales (15, 16, 19)  $\sim 4$  ppt higher, but in general there is good agreement among scales (recall that the variability among scales is based only on laboratories that prepare their own standards, and not on those that derive scales from others). The difference between laboratories 1 (NOAA) and 7 (NIST) was 0.1 %. This is less than the average difference of 0.9 % reported by Rhoderick and Dorko (2004) based on a comparison of two compressed gas standards.

Scale relationships for three commonly-used scales (NOAA, SIO, and UCI-2) were compared to those derived from 2004 and 2007–2008 global tropospheric mean mole fractions reported in Montzka and Reimann (2011) (Table 6). Although scale relationships derived as such can be influenced by other factors, such as the number and locations of measurement sites, and sampling issues not present with comparisons based on cylinder exchanges, 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, subsequent comparisons between NOAA and SIO scales at common sites indicate that this ratio is not constant in time. 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).

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Like CFC-11, the five CFC-12 calibration scales represented show a dispersion of 1 % (Fig. 1b, Table 5). NOAA re-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 were 0.8 ppt higher than the first) and this was confirmed by further analysis at NOAA. All CFC-12 comparisons shown in Tables 3–6 are based on the second NOAA analysis.

CFC-12 scale factors derived from undiluted IHALACE cylinders for SIO/NOAA and UCI-2/NOAA are nearly identical with those derived from global mean mole fraction estimates (Table 6). The NIST-NOAA average difference (Table 3) was –8.3 ppt (–1.5 %). The NIST results are more consistent with the NOAA-2001 CFC-12 scale (Rhoderic and Dorko, 2004). The NOAA-2001 scale is 7 ppt lower than the NOAA-2008 scale.

While the overall scale differences for CFC-11 and CFC-12 are not large, scale propagation could be improved. Differences among laboratories reported to be on the same scale are nearly as large as differences among scales. Some laboratories (3, 11) reported results more than 10 ppt higher than the laboratory that developed the scale (scale origin). This is an important finding also observed for other trace gases. Measurements which 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, where measurements are taken by independent groups at the same site.

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,

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14, and 17 are members of or 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. Select members of the AGAGE group were included in the experiment because of past experience with calibration scale development and trace gas records at important long-term sites (e.g., Cape Grim, Australia operated by the Australian Bureau of Meteorology in collaboration with CSIRO; and Mace Head, Ireland operated by University of Bristol).

CFC-113 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 origin). Scale conversion 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 means while the UCI-2/NOAA ratio is 0.974 compared to 0.978 based on global means. There are small differences between results from the same laboratory using different instruments. Laboratory 2 reported a difference of ~0.5 ppt between ECD and MS results, with the ECD results likely being affected by a co-elution. However, there is no difference between ECD and MS results for laboratory 17. Differences between ECD and MS results from laboratory 1 are partially traceable to standards used to define the scale. When the same standards are used on both ECD and MS instruments, agreement is within 0.5 % for these air samples. While these differences are small, they suggest that CFC-113 results may be influenced by co-elution, matrix effects, or analytical non-linearities.

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Fewer laboratories reported results for two additional CFCs: CFC-114 ( $\text{CClF}_2\text{CClF}_2$ ) and CFC-115 ( $\text{CClF}_2\text{CF}_3$ ). The variability among four scales reported for CFC-114 was 0.7%. While differences among primary scales were small, overall differences between laboratories were larger, with differences due to scale propagation larger than differences between primary scales (Fig. 1d). Some of the CFC-114 differences could result from chromatographic co-elution of CFC-114 and CFC-114a ( $\text{CCl}_2\text{FCF}_3$ ) and relative amounts of CFC-114 and CFC-114a in laboratory standards compared to IHALACE samples. The variability among three scales reported for CFC-115 was 4.1 % with comparable differences due to scale propagation (Fig. 2a).

### 3.2 Chlorinated solvents: $\text{CCl}_4$ , $\text{CH}_3\text{CCl}_3$ , and $\text{CHCl}_3$

Carbon tetrachloride ( $\text{CCl}_4$ ) was reported by 12 laboratories on five independent scales (Fig. 2b). 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 mean estimates (Table 6).

There remains a discrepancy between bottom-up inventories and top-down measurement-based inventories of global  $\text{CCl}_4$  emissions (UNEP, 2007; Montzka and Reimann, 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  $\text{CCl}_4$  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 emission estimates.

Comparison results for  $\text{CH}_3\text{CCl}_3$  from 12 laboratories on six calibration scales are shown in Fig. 2c. Results from laboratories that prepare primary standards 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

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been difficult to obtain samples of pure  $\text{CH}_3\text{CCl}_3$  in the past. A prior calibration scale developed by NOAA in the late 1990s was based on a  $\text{CH}_3\text{CCl}_3$  reagent that contained as much as 7 % impurities.

Like CFC-113, instruments can give different results for  $\text{CCl}_4$  and  $\text{CH}_3\text{CCl}_3$  even when the same standards are used to define the scale. Laboratories 1, 2, 9, and 17 all reported  $\text{CH}_3\text{CCl}_3$  results from both ECD and MS instruments. Small 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  $\text{CCl}_4$  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 accessing 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.

Results for  $\text{CHCl}_3$  are shown in Fig. 2d. 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 for the winter sample. Excluding laboratory 7, results on four scales show a variability of ~ 5 % for both summer and winter samples. Scale transfer issues appear to be relatively minor. Differences due to analytical methods are on the order of 2–3 %, similar to  $\text{CH}_3\text{CCl}_3$  and  $\text{CCl}_4$ .

Despite relatively small scale differences among independent scales, there are some substantial scale propagation issues for both  $\text{CH}_3\text{CCl}_3$  and  $\text{CCl}_4$ . While some laboratories were able to reproduce results on existing scales, others were not.  $\text{CCl}_4$  results reported by laboratory 3 were ~ 30 ppt higher than laboratory 1, from which the scale is derived (outlier in Fig. 2c). This could be caused by downward drift of  $\text{CCl}_4$  in standards used by laboratory 3 as  $\text{CCl}_4$  is known to drift in some types of cylinders (untreated aluminum, for example). A smaller, but still significant difference is evident for laboratory 11, with their scale derived from laboratory 2. Laboratory 3 reported mole fractions of  $\text{CH}_3\text{CCl}_3$  that were 18 and 65 ppt larger than those of laboratory 1 (see Table 3). A

large positive offset could be related to downward drift of  $\text{CH}_3\text{CCl}_3$  in standards used by laboratory 3, but would not explain the large difference in mole fractions reported for the two un-diluted samples.

### 3.3 HCFCs and HFCs

- 5 The atmospheric abundances of HCFCs and HFCs (1st and 2nd generation replacement for CFCs) are lower than those of the major CFCs and their measurement history is not as extensive. Thus, one might not expect the development of measurement scales to be as advanced as those for CFCs. Scale variations range from 1–2 % for HCFC-22 and HCFC-141b (four scales) to 4 % for HCFC-142b (four scales), and 3–  
10 6 % for HFC-152a and HFC-134a (three scales) (Figs. 3a–d and 4a).

While the overall 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 major scales is encouraging. It is likely that efforts to develop and improve CFC calibration scales through the years have  
15 translated into improved scales for HCFCs and HFCs as well. Once again, however, scale propagation is problematic in some cases, e.g., propagation errors for HFC-152a are as large as 10 %.

Four scales for HFC-134a vary by 2.7 and 4.9 % for summer and winter samples, respectively. A fifth scale (UB-98) also agrees with other scales (Fig. 3d), but is not  
20 included in Table 5 because laboratory 11 is not the scale origin for UB-98. Scale transfer is very good 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 based on undiluted samples.

It is encouraging that nearly all laboratories detected a mole fraction difference between cylinders filled in winter and summer, and that this was true for nearly all HCFCs and HFCs. In most cases the seasonal differences were similar among all labs, except  
25 for HCFC-141b (Fig. 3b). 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

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differences, and laboratories 11 and 19 observed differences with opposite sign. Thus, while there is generally good agreement among scales for HCFC-141b, there is room for improvement in analytical techniques.

- 5 Observed SIO/NOAA ratios for HCFC-141b (1.012) and HCFC-142b (1.037) are similar to those derived from global means (Table 6). Likewise, SIO/NOAA and UCI-2/NOAA ratios for HCFC-22 are comparable to those based on global means.

### 3.4 Halons

- Halon results are reported on two to three independent scales with several other laboratories reporting on dependent scales. Halon-1211 was measured by nine laboratories  
10 (Fig. 4b) on four scales with a standard deviation of 2.2 %. In contrast to most other trace gases measured in this experiment, scale transfer is excellent (< 1 % in most cases). Results on two different scales are shown for laboratory 1, one determined by ECD, the other one by MS.

- The range of values reported for halon-1301 (Fig. 4c) was larger than that for halon-1211 (7 % versus 2 %), but scale transfer issues were also relatively minor. Note that  
15 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.

- 20 Halon-2402 mole fractions, reported on two scales, show good agreement 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 values based on provisional scales (i.e.,  
25 scales adopted in a non-traditional manner, such as through the exchange of a sub-sample of a compressed gas standard, or through some second-order method, such as a limited period of co-located sampling). These halon-2402 values 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  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  for winter and summer samples, respectively (Table 5). Differences between summer and winter samples were detected by all laboratories (Fig. 5a). Scale transfer issues were minor in most cases, although a  $\sim 7\%$  difference between laboratories 15 and 19 is apparent. The SIO/NOAA ratio (0.998) differs by a few percent from those based on global mean estimates (Table 6). For laboratory 9, one set of results (9.1 in Fig. 5a) is known to be overestimated because of a drifting calibration standard. Standard drift was taken into account in the second set of results (9.2 in Fig. 5a), which explains why this group of results is in better agreement with laboratory 2 (scale origin) than the first group. The seasonal difference in  $\text{CH}_3\text{Br}$  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).

$\text{CH}_3\text{Cl}$  results are similar to those of  $\text{CH}_3\text{Br}$ , with relatively small differences among six scales (standard deviation  $\sim 2.5\%$ ) (Fig. 5b). The large apparent scale difference between SIO-05 and UB-98 (compare laboratories 2 and 11) is complicated by the scale propagation error between laboratories 2 and 11 (SIO-05 scale). 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  $\sim 25$  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.

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### 3.6 Short-lived organo-halides

Few laboratories reported results for short-lived halogens, such as  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ , and  $\text{CH}_3\text{I}$ . However, recent interest in these gases (Read et al., 2008; Carpenter et al., 2009; Jones et al., 2011) warrants their inclusion. For  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ , only laboratories 1 and 15 provided results on independent scales, and laboratory 12 provided results on scales obtained from laboratory 1. Because the mole fractions of these gases in the IHALACE cylinders were low ( $< 1$  ppt, consistent with continental background air) and the relative analytical precisions were larger than those of many other gases, we compare laboratories 15 and 12 to the average of the initial and final NOAA analysis. There does not appear to have been a significant change in the mole fractions of  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  in the IHALACE cylinders during the experiment. An upward drift of  $\sim 10\%$  is suggested for  $\text{CH}_2\text{Br}_2$ , although this is within the range of uncertainties.

For  $\text{CH}_2\text{Br}_2$ , differences between scales (laboratories 1 and 15) averaged 15 % (0.13 ppt) (Fig. 5d). Scale transfer differences (laboratories 1–12, 15–19) were as high as 19 %. Jones et al. (2011) reported scale differences of 20–70 % but much smaller scale transfer differences (less than 3 %).

For  $\text{CHBr}_3$ , 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  $\sim 15\%$ .

For  $\text{CH}_3\text{I}$ , results from most laboratories were in good agreement, with the exception of laboratory 15, which was a factor of 2 higher than the rest (Fig. 5c). Jones et al. (2011) also reported factors of 2 differences for  $\text{CH}_3\text{I}$ .

Overall, the comparison of  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CH}_3\text{I}$  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.

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### 3.7 Nitrous oxide, SF<sub>6</sub>, methane, and carbonyl sulfide

The long atmospheric lifetime and small spatial gradients of nitrous oxide (N<sub>2</sub>O) mean that compatibility requirements are high. For multiple datasets to be optimally useful in inverse modeling, data should be compatible to within 0.1 ppb (WMO/GAW, 2009).

5 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 datasets 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 0.08 ppb, which is comparable to differences reported by Hall et al. (2007) and Huang et al. (2008). The calibration ratio between laboratory 17 (CSIRO) and laboratory 2 (SIO) was 1.0025 (0.0002), which differs only slightly from the ratio 1.0017 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<sub>2</sub>O 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 program (NOAA as the Central Calibration Laboratory for N<sub>2</sub>O, 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

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(~ –0.2 ppb) were detected by most laboratories (1, 2, 3, 5, 8, 9, 13, 15, 17) and over-estimated by some (laboratories 7, 12, 14). While the results are encouraging overall, there is room for improvement in inter-laboratory compatibility.

SF<sub>6</sub> 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  $0.998 \pm 0.005$  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-2006) and laboratories 2, 11, and 14 (SIO-05) 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.

Although methane was not a focus of IHALACE, twelve laboratories reported CH<sub>4</sub> mole fractions on three scales (Fig. 6d). Scale differences are small. 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  $1.0003 \pm 0.0002$ . 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.

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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) (Table S2, 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  $Y_{10} = 1.064 \cdot X_{\text{NOAA}} - 33$  ppt.

### 3.8 Linearity issues

The atmospheric mole fractions of the majority of 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. Atmospheric mole fractions of some HCFCs (CFC replacements) 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. 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:

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

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. A LF of 1.0 results when scales differ by a constant factor at both ambient and sub-ambient mole fractions.

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 (Fig. 8a). 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, CFC-11 LF results are generally within 1 % of 1.0, but the difference between laboratories 7 and 15 is nearly 3%. Thus, if results on scale 7 (NIST) were adjusted to scale 15 (UM-2) using a fixed scale factor based on undiluted samples from this experiment, errors up to 3 % could result at 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.

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Linearity factors for  $\text{CH}_3\text{CCl}_3$  are close to 1.0 for most laboratories. 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 (Fig. 8b). This is likely due to the choice of reference values (NOAA ECD) used to calculate LF. If NOAA MS results are used 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 slight non-linearity in the NOAA ECD data. Linearity of  $\text{CH}_3\text{CCl}_3$  response could be important when interpreting historical  $\text{CH}_3\text{CCl}_3$  data because of the rapid decline in  $\text{CH}_3\text{CCl}_3$  mole fraction that has occurred over the last two decades.

Linearity factors for  $\text{CCl}_4$  (Fig. 8b) show little variation among laboratories that prepare primary standards (1, 2, 7, 15, 19) with most LF within 1 % of 1.00. This suggests that non-linear effects are not a major factor contributing to the observed 5 % scale differences.

Only small concentration-dependent scale differences were observed for HCFC-141b, HCFC-22 (Fig. 8c), and HCFC-142b (not shown) between commonly used scales (laboratories 1, 2, 15, 16). 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. The LF factors for HCFC-141b range from 0.98 to 1.02 but in most cases differences between undiluted and undiluted samples is of the same order as the analytical precision. HFC-134a also shows good linearity in this comparison with most LF 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).

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Laboratories 9 and 17 show LF's close to 1.0 on the SIO-98  $\text{N}_2\text{O}$  scale, but laboratory 2 (scale origin) does not (Fig. 8). This discrepancy could be due to the fact that the SIO-98  $\text{N}_2\text{O}$  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 appears to be excellent for both diluted and undiluted samples (Fig. 8d), with linearity factors remarkably consistent near 1.0. Good scale comparability and transfer was also realized for  $\text{CH}_4$  (not shown).  $\text{CH}_4$  is commonly measured using a flame ionization detector, which typically has a linear response. While relative uncertainties are larger for  $\text{SF}_6$  compared to  $\text{N}_2\text{O}$  and halon-1211, most linearity factors are close to 1.0. This is important because  $\text{SF}_6$  mole fractions are increasing at  $\sim 0.25 \text{ ppt yr}^{-1}$  (Levin et al., 2010; Rigby et al., 2010) and any comparison among laboratories will soon be obsolete unless linearity can be demonstrated.

Linearity factors shown here are based on a limited dataset, 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. Further, agencies responsible for collecting the original data should be consulted whenever the application of scale factors are considered.

#### 4 Summary

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

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Scale differences range from 2 % for CFC-11 and CFC-12 to a factor of two for CH<sub>3</sub>I. Relatively large discrepancies among major scales were identified for CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>I, CH<sub>2</sub>Br<sub>2</sub>, and CHBr<sub>3</sub>. The standard deviation of CCl<sub>4</sub> results on 5 scales was 1.9 %. Uncertainties in top-down CCl<sub>4</sub> emission estimates solely due to calibration uncertainties are less than 5 %. Scale differences for CH<sub>4</sub>, N<sub>2</sub>O, and SF<sub>6</sub> reported previously appear to be robust. Scale propagation errors are relatively small for some gases (halon-1211, HFC-134a) and larger for others (CH<sub>3</sub>CCl<sub>3</sub>). 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 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-discuss.net/6/8021/2013/](http://www.atmos-meas-tech-discuss.net/6/8021/2013/amtd-6-8021-2013-supplement.zip)  
**amtd-6-8021-2013-supplement.zip.**

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**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 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	UK	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

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

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**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

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**Table 3.** Average differences (%) between each laboratory and laboratory 1 (NOAA) for selected compounds (average of both undiluted 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	542.0	0.2	0.3	1.2			0.3	1.6	-1.5		0.2		
CFC-11	253.3	-0.6	-0.3	2.7			-1.4	0.3	-0.1		-0.8		
CFC-113	80.4	-2.8	-2.1	14.3			-5.2	-6.3	2.0		-2.2		
CH <sub>2</sub> CCl <sub>3</sub>	22.7	-5.4	-2.6	184			-13.0	-11.0	2.8		-3.0	-3.0	
CCl <sub>4</sub>	95.1	-2.7	-3.1	34			-4.2	-0.7	2.2		-2.4	-3.9	
CHCl <sub>3</sub>	12.0	-5.2	-4.3						-23.5		-14.4	-7.0	-3.6
HCFC-22	173.6		-0.7		0.0							-0.6	-1.1
HCFC-141b	18.5		1.2		3.1							0.4	1.0
HCFC-142b	15.8		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 <sub>2</sub> Cl <sub>2</sub>	32.2											-6.6	
CH <sub>3</sub> Cl	563.9		-0.8									-1.1	-0.9
CH <sub>3</sub> Br	9.4		-0.2									3.3	-0.4
CH <sub>3</sub> I	0.18												
CH <sub>2</sub> Br <sub>2</sub>	0.68												
CHBr <sub>3</sub>	0.47												
halon-1211	4.4		2.0									1.7	1.6
halon-1301	2.9		5.8									4.4	6.1
halon-2402	0.50												
CH <sub>4</sub>	1821.1	-0.1		0.01		0.05			0.34		0.0		
N <sub>2</sub> O	318.32	-0.02		-0.34		-0.01			0.43	0.02	-0.01		
SF <sub>6</sub>	5.54		-0.1		2.4	-0.7						-0.7	-0.4
COS	569.7												

NOAA result: Mole fractions in ppt (except N<sub>2</sub>O and CH<sub>4</sub>, ppb). CFC-12, CFC-11, CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, h1211, N<sub>2</sub>O, and SF<sub>6</sub> based on ECD analysis. All others based on MS analysis.

20(1), 20(2) % difference between final and initial NOAA analysis results for sets (1) and (2)

MD: multidetector (ECD or FID)

MS: mass selective detector.

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Table 3. Continued.

	Laboratory number								17.1 MD	17.2 MS	18	19	20 (1)	20 (2)	
	10	11	12	13	14	15	16	17							
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 <sub>3</sub> CCl <sub>3</sub>		-10.6	-1.2		-11.7	-0.7	-2.5		-1.9	-2.3		4.8	1.1	-0.1	
CCl <sub>4</sub>		-11.1	-0.8		-5.5	-2.7			-2.5	-4.3		-0.6	0.1	0.1	
CHCl <sub>3</sub>		-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 <sub>2</sub> Cl <sub>2</sub>		-14.0	-13.0		-10.5	-16.2				-6.9		-14.2	1.8	-0.1	
CH <sub>3</sub> Cl	3.7					-2.6	-0.7					-2.2	0.9		
CH <sub>3</sub> Br	-3.1				3.6	1.5	1.8			1.3		-5.4	1.1	-0.1	
CH <sub>3</sub> I			0.0			109	12.5					18.5	0.6	2.6	
CH <sub>2</sub> Br <sub>2</sub>			19.5			27.9						28.7	21.1	8.8	
CHBr <sub>3</sub>			11.9			26.9						9.7	-3.1	13.5	
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 <sub>4</sub>				0.04	-0.02	-0.6		0.0	0.0		0.03		-0.02	-0.01	
N <sub>2</sub> O			-0.41	0.23	-0.09	-0.1		0.23	-0.04				0.00	-0.01	
SF <sub>6</sub>		-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	

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Table 4. Average differences (%) between each laboratory and laboratory 1 (NOAA) for selected compounds (diluted samples).

	NOAA	Laboratory number										9 MD	9.1 MS1	9.2 MS2
		2 MD	2.1 MS	3	4	5	6	6.1	7	8				
CFC-12	438.7	2.4	0.9	2.9			0.4	2.0	-1.7		1.7			
CFC-11	203.8	-0.1	0.4	4.4			-0.5	1.2	1.7		0.4			
CFC-113	63.7		-0.3	20.2			-4.0	-5.1	4.0		0.3			
CH <sub>3</sub> CCl <sub>3</sub>	18.3	-4.7	-3.5	70.2			-20.1	-18.3	8.1		-4.3	-2.9		
CCl <sub>4</sub>	76.4		-3.6	34.4			-4.1	-0.5	2.8		-2.5	-3.3		
CHCl <sub>3</sub>	7.6	-3.7	-3.0						-1.6		-13.2	-5.7	-2.6	
HCFC-22	141.0		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	27.1		0.3		2.4							1.4	0.6	
HFC-152a	27.1		-5.8									-9.4	-5.0	
CH <sub>2</sub> Cl <sub>2</sub>	25.9											-10.5		
CH <sub>3</sub> Cl	456.5		-1.2									-1.1	-0.4	
CH <sub>3</sub> Br	7.8		-1.1									5.0	0.7	
CH <sub>3</sub> I	0.14													
CH <sub>2</sub> Br <sub>2</sub>	0.51													
CHBr <sub>3</sub>	0.32													
halon-1211	141.0		1.7									2.0	2.0	
halon-1301	2.3		7.8									7.8	10.0	
halon-2402	0.44													
CH <sub>4</sub>	1479.3	0.0		-0.45	0.04			0.33		0.0				
N <sub>2</sub> O	259.16	-1.77		-0.96	0.18			-0.14	0.08	-0.08				
SF <sub>6</sub>	4.49		-0.4	5.6	0.2							-3.8	-0.7	
COS	450.7													

NOAA result: Mole fractions in ppt (except N<sub>2</sub>O and CH<sub>4</sub>, ppb). CFC-12, CFC-11, CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, h1211, N<sub>2</sub>O, and SF<sub>6</sub> based on ECD analysis. All others based on MS analysis.

20(1), 20(2): % difference between final and initial NOAA analysis results for sets (1) and (2).

MD: multidetector (ECD or FID).

MS: mass selective detector.

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Table 4. Continued.

	Laboratory number								17.1 MD	17.2 MS	18	19	20 (1)	20 (2)
	10	11	12	13	14	15	16	17						
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 <sub>3</sub> CCl <sub>3</sub>		-13.7			-13.2	-2.6	-3.1		-3.1	-3.8		3.6	0.7	-1.4
CCl <sub>4</sub>		-10.8			-8.7	-3.9			-2.4	-3.8		-1.3	0.4	0.0
CHCl <sub>3</sub>		-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 <sub>2</sub> Cl <sub>2</sub>		-11.5			-10.4	-15.5				-6.7		-14.2	2.1	1.3
CH <sub>3</sub> Cl	3.1	-4.5			12.2	-2.7	-1.0					-3.3	-0.1	0.3
CH <sub>3</sub> Br	-3.5	9.4			1.7	0.4	-2.1			1.0		-9.9	-1.1	-0.2
CH <sub>3</sub> I						93.3	33.3					26.0	13.3	0.0
CH <sub>2</sub> Br <sub>2</sub>						31.7						44.0	20.6	23.7
CHBr <sub>3</sub>						36.4						26.4	2.3	0.0
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 <sub>4</sub>				0.20	-0.09	-0.4		0.1	-0.1		0.24		0.11	0.12
N <sub>2</sub> O			-0.31	-1.11	1.16	-0.02		-0.58	-0.59				-0.09	-0.18
SF <sub>6</sub>		-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

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**Table 5.** Analysis statistics for undiluted samples based on scale origin (only laboratories that prepare their own primary standards). Samples from set #2 were scaled to match sample set #1 based on NOAA analysis. Gases with large differences between winter (W) and summer (S) fillings were treated separately. All mole fractions are pmol mol<sup>-1</sup> (ppt) unless indicated.

Trace gas	Mean	Std. dev.	Std. dev. (%)	# Scales
CFC-11	254.7	2.6	1.0	5
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 <sub>4</sub>	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 <sub>4</sub> (W) (ppb)	1836.9	3.5	0.19	3
CH <sub>4</sub> (S) (ppb)	1808.8	4.3	0.24	3
N <sub>2</sub> O (W) (ppb)	318.90	0.87	0.27	3
N <sub>2</sub> O (S) (ppb)	318.57	0.72	0.23	3
CH <sub>3</sub> CCl <sub>3</sub> (W)	23.4	0.8	3.4	6
CH <sub>3</sub> CCl <sub>3</sub> (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 <sub>6</sub> (W)	5.50	0.02	0.4	3
SF <sub>6</sub> (S)	5.56	0.01	0.2	3
CH <sub>3</sub> Br (W)	8.82	0.20	2.2	5
CH <sub>3</sub> Br (S)	10.05	0.16	1.6	5
CHCl <sub>3</sub> (W)	14.2	2.2	15.3	5
CHCl <sub>3</sub> (S)	9.0	0.4	4.3	5
CH <sub>2</sub> Cl <sub>2</sub> (W)	32.7	2.9	8.7	3
CH <sub>2</sub> Cl <sub>2</sub> (S)	26.8	2.4	9.0	3
CH <sub>3</sub> Cl (W)	567.2	14.2	2.5	5
CH <sub>3</sub> Cl (S)	559.5	12.0	2.2	5

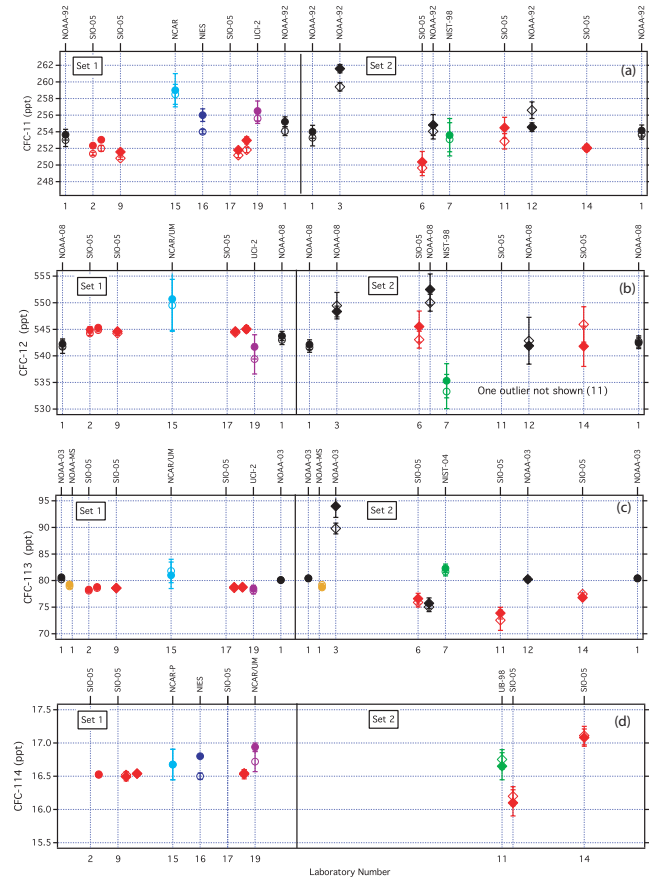
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**Table 6.** Scale factors (relative to NOAA) derived from tropospheric global mean mole fractions reported in Table 1.1 of Montzka and Reimann (2011) for 2004 and 2007–2008, and from undiluted IHALACE samples (mean and standard deviation) for representative laboratories. From these data we can compare global mean factors from AGAGE and UCI (University of California Irvine) 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 <sup>1</sup>	0.9921	0.9939	0.9942 (0.0009)
	UCI, UCI-2	0.9996	0.9970	1.0108 (0.0007)
CFC-12	AGAGE, SIO <sup>1</sup>	1.0028	1.0034	1.0022 (0.0002)
	UCI, UCI-2	0.9952	0.9949	0.9948 (0.0020)
CFC-113	AGAGE, SIO <sup>1</sup>	0.9753	0.9777	0.9724 (0.0017)
	UCI, UCI-2	0.9778	0.9874	0.9737 (0.0001)
	NOAA <sup>3</sup>	0.9753	0.9854	0.9827 (0.0025)
CH <sub>3</sub> CCl <sub>3</sub>	AGAGE, SIO <sup>1</sup>	0.967	0.950	0.946 (0.009)
	UCI, UCI-2	1.062	1.023	1.048 (0.008)
	NOAA <sup>3</sup>	0.978	0.962	0.982 (0.004)
CCl <sub>4</sub>	AGAGE, SIO <sup>1</sup>	0.969	0.974	0.973 (0.001)
	UCI, UCI-2	0.994	1.005	0.995 (0.001)
HCFC-22*	AGAGE, SIO <sup>2</sup>	1.003	1.000	0.993 (0.002)
	UCI, UCI-2	0.982	0.983	0.972 (0.013)
HCFC-141b*	AGAGE, SIO <sup>2</sup>	1.017	1.011	1.012 (0.001)
	UCI, UCI-2	–	0.976	0.945 (0.016)
HCFC-142b*	AGAGE, SIO <sup>2</sup>	1.041	1.028	1.037 (0.004)
	UCI, UCI-2	–	0.978	0.975 (0.010)
halon-1211	AGAGE, SIO <sup>2</sup>	1.014	1.012	1.021 (0.007)
	UCI, UCI-2	–	0.999	0.963 (0.008)
	NOAA <sup>3</sup>	0.963	0.958	0.974 (0.008)
halon-1301*	AGAGE, SIO <sup>2</sup>	1.041	1.027	1.058 (0.005)
CH <sub>3</sub> Br*	AGAGE, SIO <sup>2</sup>	1.038	1.020	0.998 (0.003)

\* Ratios derived relative to NOAA MS results; <sup>1</sup> AGAGE, SIO MD; <sup>2</sup> AGAGE, SIO MS; <sup>3</sup> NOAA MS.

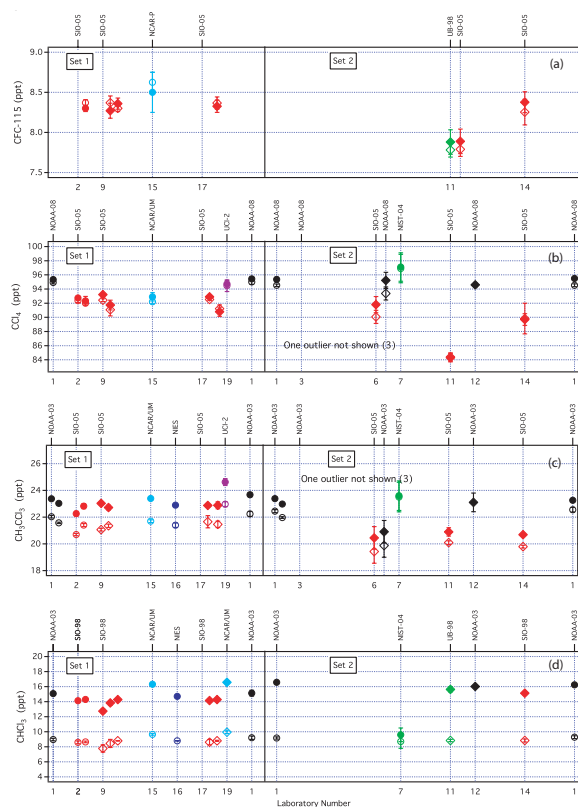
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**Fig. 1.** Results from undiluted samples for **(a)** CFC-11, **(b)** CFC-12, **(c)** CFC-113, **(d)** CFC-114, (mole fraction, ppt = pmol mol<sup>-1</sup>, parts per trillion) color-coded by calibration scale with scale identifiers shown along the top axis: similar colors denote similar scales; open (closed) symbols correspond to cylinders filled in winter (summer); circles denote laboratories that prepare primary standards, diamonds denote laboratories that adopt existing scales. Non-integer laboratory numbers indicate additional results submitted by or associated with 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.

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**Fig. 2.** Same as Fig. 1 for trace gases **(a)** CFC-115, **(b)** CCl<sub>4</sub>, **(c)** CH<sub>3</sub>CCl<sub>3</sub>, **(d)** CHCl<sub>3</sub>.

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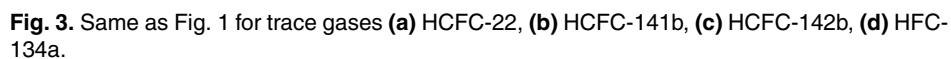


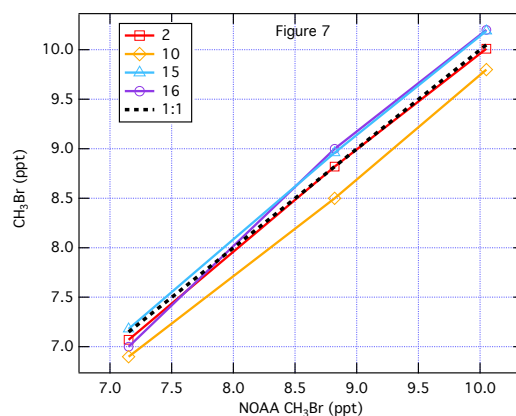
Figure 1 consists of four scatter plots (a, b, c, d) showing the relationship between laboratory number and various chemical concentrations. Each plot includes data points for different laboratories and a vertical line indicating the laboratory number.

- (a) HCF-152a (ppt):** The y-axis ranges from 3 to 7. The x-axis shows laboratory numbers 1, 2, 9, 16, 17, 1, 1. Data points are labeled with laboratory numbers and chemical names (HCF-152a, HCB-1211, HCB-1301, HCB-2402). A vertical line is at laboratory number 16.
- (b) HCB-1211 (ppt):** The y-axis ranges from 4.2 to 4.6. The x-axis shows laboratory numbers 1, 2, 9, 15, 17, 19, 1, 1. Data points are labeled with laboratory numbers and chemical names. A vertical line is at laboratory number 15.
- (c) HCB-1301 (ppt):** The y-axis ranges from 2.6 to 3.4. The x-axis shows laboratory numbers 1, 2, 9, 15, 17, 1, 1. Data points are labeled with laboratory numbers and chemical names. A vertical line is at laboratory number 15.
- (d) HCB-2402 (ppt):** The y-axis ranges from 0.2 to 1.2. The x-axis shows laboratory numbers 1, 15, 17, 19, 1, 1. Data points are labeled with laboratory numbers and chemical names. A vertical line is at laboratory number 15.

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

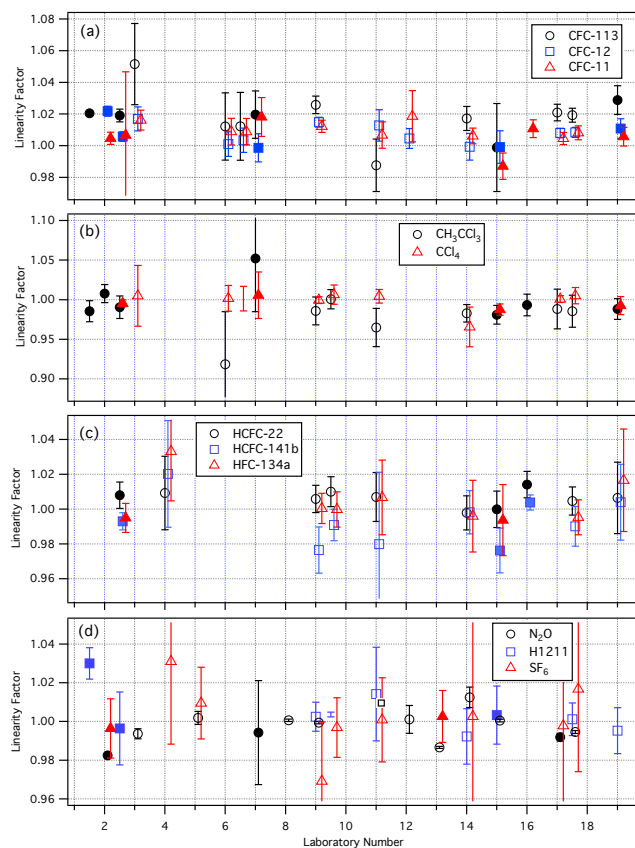
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**Fig. 7.** Results from both diluted and undiluted samples for  $\text{CH}_3\text{Br}$  for 5 laboratories plotted against NOAA results. Five  $\text{CH}_3\text{Br}$  scales show a near-linear relationship over the range of mole fractions sampled.

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**Fig. 8.** Linearity factors relative to NOAA for select gases. Filled symbols denote laboratories that prepare their own standards, while open symbols denote those that derive scales from others (see Table S1 in the Supplement 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. A ratio 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). Error bars are 1 s.d. Linearity factors are relative to NOAA ECD results in **(a)**, **(b)**, **(d)**, and to NOAA MS results in **(c)**.