The International Halocarbons in Air Comparison Experiment: First Results

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Introduction

Halocarbons and other atmospheric trace gases are measured by several laboratories around the world. These measurements are reported on a number of independent calibration scales. Few multi-laboratory comparisons have been conducted to assess the relative agreement among calibration scales.

In 2004, six 34-L stainless steel cylinders containing natural air were distributed among 22 laboratories. NOAA/ESRL served as the coordinating laboratory and analyzed all six cylinders at the beginning and end of the experiment. The goal of IHALACE was to provide a much needed comparison of calibration scales and atmospheric measurement records.

The experiment was completed in 2007. Initial results for a subset of trace gases are presented here. At this time, laboratories and calibration scales have not been identified.

Each lab measured two cylinders at near-ambient concentration and one at sub-ambient concentrations. Here we show only the near-ambient results. Not all species were measured by all labs. The figures show data reported for ambient-level cylinders, color coded by calibration scale. The symbols represent different cylinders.

Participants

NOAA/ESRL Global Monitoring Division
Scripps Institution of Oceanography
NIST Gas Metrology Group
Univ. California Irvine (2 labs)
Oregon Graduate Institute
CSIRO (Australia)
NIES (Japan)
Meteorological Service Canada
Univ. Miami (2 labs)
Univ. East Anglia (United Kingdom)
Bristol Univ. (United Kingdom)
Univ. Heidelberg (Germany)
Univ. Frankfurt (Germany)
ENEA (Italy)
Univ. Urbino (Italy)
EMPA (Switzerland)
South African Weather Service
IMK-FZK (Germany)
NASA-Ames

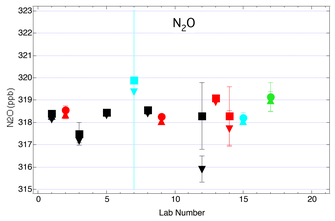
Discussion

Scale Differences: Results show that scale differences are modest for most species. For example, five CFC-12 scales agree to within ~2% (2 std. dev.).

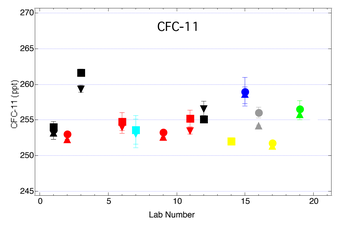
Several labs reported good precision, such that small conentration differences between cylinders were observed by most labs. Each pair of ambient-level cylinders distributed contained cylinders filled in opposite seasons. Seasonal features were observed in almost all of the HCFC-22 and HCFC-142b data.

Scale Propagation: Scale propagation appears to be problematic in some cases. For N_2O, there are four labs reporting on one scale and five reporting on another. Symbols of similar color should agree if the data are truly on the same scale. Although differences are small, some are large with respect to atmospheric gradients, and would limit the utility of merged data-sets if left uncorrected. CFC-12 results suggest that some labs may be using scales that are out of date. CCl_4 results show some large differences, which may be the result of drifting standards.

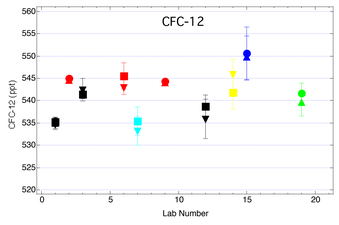
Logistics: The IHALACE experiment began in August 2004 and was completed in August 2007. Improvements in logistics and sample handling will be needed if experiments like these are to be completed in a more reasonable time frame.



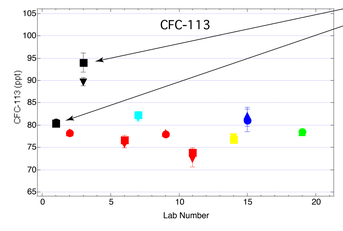
Twelve labs reported N_2O on four scales. There is good agreement among scales, but there appear to be some problems with scale propagation.



Thirteen labs reported CFC-11 on seven scales. There is good agreement among scales, and scale propagation appears to be good in most cases.

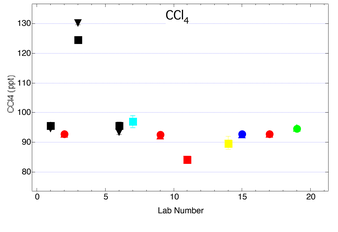


Ten labs reported CFC-12 on six scales. Scale differences of 2-3% are evident.

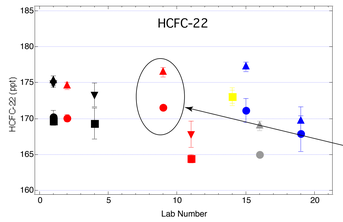


These data were reported on the same scale. Clearly there is a problem with scale propagation or analysis.

Ten labs reported CFC-113 on six scales. Agreement is reasonable, but there are some issues with scale propagation.

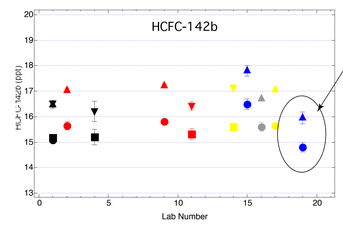


Eleven labs reported CCl_4 on six scales. Agreement is generally good.

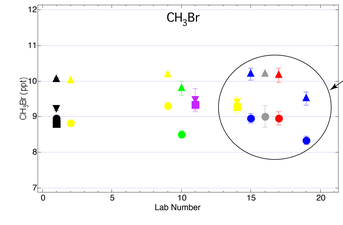


Nine labs reported HCFC-22 on five scales. Agreement is quite good.

Cylinders were filled five months out of season. Seasonal affects and atmospheric growth can be seen in nearly all measurements.



Surprisingly good agreement was observed from ten labs reporting HCFC-142b on five scales.



Most labs observed a 0.2 or 1.2 ppt difference between cylinders filled in summer and winter. There is also good agreement among CH_3Br scales even though the long-term storage of CH_3Br in cylinders can be problematic.

Statistics for major scales (ie. from labs reporting data on scales developed "in house"). Note that some labs reported data on more than one scale. Only the first reported scales were considered here.

Trace Gas	Mean (ppt)	Std Dev (ppt)	Std Dev (%)	Number of Scales
N_2O (ppb)	318.86	0.39	0.12%	4
CFC-11	254.8	2.3	0.9%	6
CFC-12	540.9	5.8	1.1%	5
CFC-113	80.1	1.7	2.1%	5
CCl_4	94.5	1.0	1.1%	5
HCFC-22 (winter)	168.8	2.5	1.5%	5
HCFC-22 (summer)	173.1	3.6	2.1%	5
HCFC-142b (winter)	15.7	0.6	3.8%	4
HCFC-142b (summer)	17.0	0.6	3.5%	4
CH_3Br (winter)	8.91	0.27	3.0%	6
CH_3Br (summer)	10.05	0.16	1.6%	5

Conclusions

1. Differences between scales are modest for most trace gases.
2. Laboratory precision was good in many cases. Small differences in trace gas concentration among cylinders were resolved by most labs.
3. Scale propagation is problematic in some cases. Laboratories that distribute scales need to improve communication of scale updates. Timely re-calibrations should be performed.
4. Data users who wish to merge data sets should exercise caution, even with data that are reported to be on the same scale.
5. IHALACE results should lead to improved regional and global data sets.