

Interactive comment on “Results from the International Halocarbons in Air Comparison Experiment (IHALACE)” by B. D. Hall et al.

Anonymous Referee #3

Received and published: 28 October 2013

This extensive comparison of calibration scales and inter-laboratory differences is unprecedented for halogenated trace gases. The substantial amount of new data presented is very valuable for the respective measurement community. There is however a number of concerns regarding this manuscript as expressed below.

The main concern is with respect to the non-quantitative nature of language used in the manuscript. In many cases statements are not backed up with quantitative evidence such as whether a “good agreement” is significant within (and along with) a certain level of confidence. Definitions of statistical terms used are missing, e.g. how are “scale propagation errors” defined and derived? Both the abstract and the introduction are rather vague. Given the quantity of trace gases in the atmosphere it would help the reader to know, which ones are being addressed here. Some guidance on the relative

C3088

importance/abundance would be useful, too. A general structural comment is, that large blocks of text make the manuscript hard to read in places – more sub-sections might help here. Also, the discussion order between compounds is inconsistent in places. Finally, and with regard to methods, little analytical detail is provided, especially for the primary reference lab (e.g. which detector was the NOAA analysis done on for the individual compounds)? A number of more specific points can be found below.

Abstract

Which scale relationships were found to be consistent with those derived from bi-lateral experiments and which were not? And why are there no quantitative statements at all in this abstract? How big are the discrepancies and the “substantial improvements”?

P8024, I24 please give formulas

P8025, I8 The “existence of independent calibration scales” is initially important for verifying abundances with trends being secondary. The “relationships between independent scales” are probably also of importance for trends.

P8025, I11 Which greenhouse gases? Preferably not halogenated ones?

P8025, I20 please explain abbreviation

P8025, I22 And small temporal gradients. It might be worth mentioning a clarifying example here, e.g. the importance of small changes for ozone recovery dates.

P8026, I14 define “dry”; Was a drying agent used at this stage?

P8027, I27 please quantify “large amounts”

P8028, I1 please quantify “minor differences”

P8028, I8 Does that mean there were objections? If so, how were these addressed?

P8029, I8 Why is Table 5 the third table referred to in the manuscript?

P8029, I13 How are these 2 sigma defined?

C3089

P8029, I23 Which compounds exactly? And which compounds are included but have been considered to be of less importance (and why)?

P8030, I11-14 Do these scales actually compare better (and if they do, is there a reason?) or is this merely a statistical coincidence?

P8030, I23 and 26 “nearly the same” and “1 % larger “ Are these statistically significant differences?

P8030, I24-26 This is a discussion of unpublished data that is not included in this paper.

P8031, I2-6 This is a difference of 0.15 %. Even if it is significant within the 2 sigma uncertainties of the NOAA analysis the initial results should not be rejected without evidence that they were flawed and that the cause for the discrepancy has been eliminated.

P8031, I14-19 Are 10 ppt significant? Generally, and also relevant for the whole manuscript: It is impossible to decide whether measurements are compatible or not without quantifying the analysis uncertainties for each of the instruments involved in this comparison.

P8032, I4-6 It is important to know, that differences should be smaller between some of the labs, but it would also be good to know, whether they actually are.

P8032, I21 Is this significant?

P8032, I22 “co-elution” An interfering compound perhaps? Also, why are differences between ECD and MS results not mentioned/discussed for all compounds?

P8032, I26 The discussion is sometimes jumping back and forth between percentage and ppt differences making it very hard to follow for the reader.

P8033, I1-4 “Fewer” “small” “larger” Please quantify.

P8033, I5-8 It might be worth explaining that most labs actually report the sum of CFC-

C3090

114 and 114a. Also, why are CFC-114 and 115 not listed in Table 3?

P8033, I17-18 “bottom-up” inventories might also be based on measurements (of emission factors).

P8033, I21-24 This is only true if there is no temporal drift between scales which could significantly affect growth rates and thus have a large effect on emission estimates.

P8034, I8 Jumping back to CCl4 at the end of the CH3CCl3 discussion.

P8034, I18 “minor” please quantify

P8034, I25 “drift” Is this a “drift in mole fraction”, and if yes, what is causing it?

P8035, I2-3 Could the type of detector play a role here?

P8035, I5-6 This is not true. HCFC-22 is almost as abundant as CFC-11 and HFC-134a very close to CFC-113.

P8035, I19-20 Could you please make this statement clearer? Why is UB-98 included in the figure but not in the table?

P8036, I8-10 The first two sentences contradict each other on the number of independent scales.

P8036, I20-23 It is not made clear, why “good agreement” means 1 % for CFC-11 but 10 % for Halon-2402.

P8036, I23-27 This is the first place in the manuscript where the reader actually learns about differences in calibration procedures. I understand that giving details of all the different calibration procedures would make this a very long manuscript. But only few experts will understand the term “non-traditional manner” if it is not explained at all.

P8037, I4, 9, 15, 18 “a few percent”, “a broad range”, “large” Please quantify.

P8039, I13 An uncertainty is only given for one of the two ratios discussed.

C3091

P8040, I15 These laboratories would only be “capable of resolving very small mole fraction differences” if precisions were sufficient, but these are not provided here.

P8041, I1-2 Why are data shown for all other compounds (including CH₄ which “was not a focus of IHALACE”) but not for COS? Also, a more correct abbreviation would be OCS, as carbon is the central atom in this molecule.

P8041, I10-12 Other molecules (such as CH₃Br or CHCl₃) show large seasonal differences. Why are linear relationships only inferred for OCS? And why is only one of these relationships mentioned?

P8041, I16 This section could use a brief introduction to linearity and connected problems (e.g. possibly explaining differences between detectors in the beginning. Few readers know about the non-linear character of an ECD measurement.).

P8041, I17 “majority of” should be “all”

P8041, I20 “the three major” might be better than “some”; “CFC replacements” is a repetition

P8042, I4-5 Is this factor meant to evaluate different scales as well as linearity within one scale?

P8042, I6 Why does the discussion start with CFC-113?

P8043, I6 Why does this only suggest “a slight non-linearity” and not “a co-elution” as for CFC-113?

P8043, I14 “small” Please quantify. Were any of these differences significant?

P8044, I10-12 Why is this only important for SF₆? It is not the only compound that is increasing.

P8044, I19 This section is not very well structured. Important differences should be clearly identified, quantified and put into context with the respective atmospheric im-

C3092

portance, abundance, and trend. Parts of this summary are repetitive of the abstract.

P8044, I20, 21,22, 24 “numerous”, “modest”, “substantial”, “large” Please quantify

Table 3 It is not possible to evaluate these differences without knowledge of the scale uncertainties and analysis uncertainties.

Figure 1 Axis labels are too small. It would help if labs on the same scale were adjacent to each other (making clustering effects more apparent). Error bars, and Set 1 and 2 are not explained in the caption. Although mentioned in the caption, there are no “non-integer laboratory numbers” in the figures.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 8021, 2013.

C3093