Atmos. Meas. Tech. Discuss., 5, C2203–C2209, 2012
www.atmos-meas-tech-discuss.net/5/C2203/2012/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Maintaining consistent traceability in high precision isotope measurements of CO_2: verifying atmospheric trends of $\delta^{13}C$" *by* L. Huang et al.

Anonymous Referee #2

Received and published: 17 September 2012

General comments:

This paper presents results from atmospheric isotopic content of CO_2 obtained over the last 10 years by analyzing air flasks samples. It is mainly focusing on the method developed at SIRL (Environment Canada) to ensure high precision of the analysis over long time period and how to apply it to get consistent and long term traceability of the measurement. The ultimate goal is to derive very weak but significant atmospheric trends from the data both for $\delta^{13}C$. In the paper, the authors mentioned several time about $\delta^{18}O$ but there is very little results nor examples presented about that isotope

(in particular the record and associated trend of $\delta^{18}O$ is not shown, page 4012 they choose a dry period favorable for calibration of ^{18}O but nothing is shown !). This could be a valuable addition to the paper as this isotope is even more sensitive than $\delta^{13}C$ to drift and to measure with a high precision.

This paper represents a very good experimental contribution to the increase of high precision carbon dioxide isotopic ratio measurement and traceability. It is providing valuable and robust methods and suggestions to do so. Therefore I would recommend publication of this paper, but only after revision as the present version is full of small errors (see below). Some parts would also benefit to be written on a more concise and simple manner. More specific comments and a few questions are listed below.

Specific comments:

In general, the paper would require andcareful proof reading as there is a lot of typing, spelling, used abbreviations or misunderstanding errors and mistakes. In some cases these might be problematic for a good understanding of the paper (in particular for non-specialists). On the contrary, it is sometimes may be too detailed (acid digestion part for example).

I'm not sure the Appendix at the end of the paper are fully useful (except may be appendix A). The second one is more a recipe and the last one can be found elsewhere about error propagation method.

Below are detailed errors I have noticed and a few questions regarding the manuscript?

The mentioned pages referred to a printer-friendly version of the paper.

Page 4005:

Line 7 and 8: the significance of mbl is not straightforward! Please explicit marine boundary layer.

Line 22: That's why, please reword properly for example "this is the reason why"

Page 4006:

Line 12: The time span . . . is derived, please reword that sentence, this is not clear!

Line 18-19: style a bit too telegraphic! Please reword in a more “written style”

Line 22, 26: Years instead of yr !

Line 25 miss one opening parenthesis before “directly”.

Page 4007:

Line 11: Add“is defined as THE “property . . . ”

Line 18-19: please add a reference for the NBS19/VPD values cited here.

Line 22: what is an “instrument liberality”? Not clear what the authors are meaning here.

Page 4008:

Line 2-3: “the other ARE secondary” there are three standards mentioned just after.

Line 7: NBS instead of NBA !

Line 13: “. . . discussed later. As shown on the . . . “

Page 4009:

Line 5: delete the “closing parenthesis”

Line 15: “to decreasesor increases OF the magnitude . . . ”

Line 16: The authors claim about “ideal clean conditions” for IRMS but without precision. What are those ideal clean conditions? How to evaluate them? When and how do you say it is clean? This is an important point for readers that would like to apply and evaluate this method elsewhere.

Page 4010:

Line 2-4: There are inconsistencies between the “constant values” given in the text and in the table A1 page 4033 (example: Cal1-CO2 about -46 per mil given in the text and about -45 per mil ! What is the exact value used at the end ?). Same for Cal2.

Line 8: QA/QC

Line 10: add reference(s) for the NBS18 literature value!

Page 4012:

Line 14: “between February AND April”

Line 21: delete “that” which is double

Line 25 delete of before greater

Page 4013:

Line 15: delete are at the end of the line !

Line 23: I’m not sure I understand well, for me there is only one term on the left side of equation 3: [R_{sam}/$R_{VPDB-CO2}$]

Line 25: Finnigan

Page 4014:

Line 2-5: consider rewording, the sentence is quite a bit difficult to follow. Is there a physical explanation for this effect in the machine?

Line 10-14: sentence starting with “as mentioned . . . is not fully readable, there is a t alone in the middle of the sentence . . . not self-understanding.

Line 15-17: Couldn’t this effect be linked with the fact the Cal2 is the most used standard and then the one where the air is the most circulating then potentially minimizing fractionation or mixing effect that might arise in the manometer, or inlet lines ?

Page 4015

Line 19: delete and after “time”

Page 4016:

Line 1 : here the IRMS uncertainty is given as 0.01 whereas it was shown and written to be 0.02 in the previous sections of the paper. This is not coherent.

Line 7 : Yr !

Line 10: Could you please add a reference as “it is known”.

Line 13-15: consider rewording this sentence which is difficult to follow.

Line 27: Yr !

Page 4017:

Line 20: yr

Page 4018:

Line 3 and 25: QA/QC

Page 4020 :

Line 9 : passed

Line 16 : delete will and correct associated

Page 4021:

Line 4: QA/QC

Line 5-8 : sentence not understandable !

Page 4025:

Line 14, 22: yr

Page 4029: Table 1

Could it be possible to add and compare some of the reported literature values for NBS18. This could give more strength to the table and section.

Page 4031: Table 3

Columns are not well aligned in the ave for IRMS.

Page 4032: Table 4

It seems to me that there is a little drift of the big deltas toward larger values over time and for both instruments. This seems correlated with the cleanliness of the Mat 252. What about the IsoPrime? Is there any other explanation for this? Is it surprising that in the meantime there is no drift when cal1 or cal2 are calibrated against NBS19 or NBS18.

Page 4033: Table A1: inconsistencies between the “constant values” given in the text and in the table. Measurement order 5, please delete the second “and” on the purpose text. In the figure caption, “the batch of APB2”, APB2 is not defined and is this information useful that way?

Table A2: Again there are different and incoherent values for Cal1 (-4 !!! instead of -45 !) and Cal2 (-2 instead of -2.6 initially in the text).

In measurement order 4 from table A2, what happens to the samples QC if the Big Delta values are not within the 2 standard deviation range? Are they invalidated ?

There are inconsistency in the notations WRG or WR ! Are those gases the same (I suppose they are all WRG)?

Page 4036:

Figure 2 and caption: the WR is not defined in the legend and is referred too as WRG in the textpage 4008, line 19 (working reference gas). Why not adding the relative position of $\delta^{18}O_{VPDB-CO2}$? The figure on the left panel is not easy to follow and the caption doesn't help too much (too more details and not enough description and explanation of

the figure itself).

Page 4038: figure 3:

Why not adding big delta 46. Replace C by c in coefficient.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 4003, 2012.