

# Carbon dioxide measurements by the Scripps O<sub>2</sub> program. 2020 Update

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April 2021

## Abstract

This report documents changes to the CO<sub>2</sub> calibration scale of the Scripps O<sub>2</sub> program to bring it in line with the SIO X12 scale. The update involves new assignments on six primary CO<sub>2</sub> reference gases used by the O<sub>2</sub> program, which were used to assign cubic coefficients to the instrument response function for the Siemens CO<sub>2</sub> analyzer used by the O<sub>2</sub> program. The new assignments correct for drift in the CO<sub>2</sub> concentration of these cylinders which is now well resolved. The update also entails changing the functional form for the instrument response function for the Licor CO<sub>2</sub> analyzer, also used by the Scripps O<sub>2</sub> program, from a cubic to a double inverse hyperbole. This update impacts all data from the Scripps O<sub>2</sub> program from program inception onwards. We designate the updated CO<sub>2</sub> scale as the VH344-2020 scale. The previous scale, which had no designation, is now called the VH344-2015 scale. The changes from the VH344-2015 to VH433-2020 scales involve changes at the level of a few tenths of a ppm, typically towards higher CO<sub>2</sub>. This report also compares the VH344-2020 scale to the NOAA X2007 scale based on tanks provided by Britt Stephens of the National Center of Atmospheric Research.

## Introduction

Since the program inception in 1989, the Scripps O<sub>2</sub> Program has measured CO<sub>2</sub> mole fractions as a geochemical complement to the O<sub>2</sub> measurements and also to correct for CO<sub>2</sub> interferences on the interferometric O<sub>2</sub> analyzer. The primary CO<sub>2</sub> instrument has always been a Siemens non-dispersive infrared analyzer.

In 2000, an Isoprime mass spectrometer was added to the instrument suite in the Scripps O<sub>2</sub> lab, which provided additional capability for measuring O<sub>2</sub>/N<sub>2</sub> (32/28) and Ar/N<sub>2</sub> (40/28) ratios. The Isoprime was plumbed downstream of a second CO<sub>2</sub> analyzer (Licor). The Licor/Isoprime and Siemens/Interferometer systems were plumbed in parallel, allowing simultaneous measurements of all tanks and 5-liter (round-bottom) flasks on both systems. The Licor/Isoprime system allowed measurements on flasks of smaller volume (referred to as B-flasks) than could be measured on the Siemens/Interferometer system. The analysis rack for B-flasks was plumbed upstream of the Siemens analyzer, allowing B-flasks to be analyzed only on the Licor/Isoprime system but not the Siemens/Interferometer system.

The CO<sub>2</sub> concentrations on both the Siemens and Licor analyzers have been based on a set of six steel primary tanks that were prepared by the Scripps CO<sub>2</sub> program led by CD Keeling in the late 1980s. Prior to this update, the CO<sub>2</sub> concentrations in these tanks were assumed to be constant at the concentrations reported in these tanks by the Scripps CO<sub>2</sub> program in the late 1980s. In the O<sub>2</sub> lab, these primary cylinder's are used to generate time-varying instrument response functions for the Siemens and Licor analyzers. These six cylinders were subsequently remeasured many times by the Scripps CO<sub>2</sub> lab, but these additional measurements had not been used as part of the calibration in the O<sub>2</sub> lab. The steel primary tanks range from about 300 to 420 ppm and thus are not sufficient to constrain CO<sub>2</sub> mole fractions outside this range.

Measurements from the Siemens and Licor instruments are initially reported on a preliminary (S1) scale that is linearly related to each instrument's response (Keeling et al, 1998) and which may also drift slowly with time due to assignment errors or drift in secondary reference gases. The S1 scales on the Siemens and Licor instruments are independent of each other. These S1 scales are then adjusted to a calibrated (S2) scale, where the calibration has relied on the set of six steel primary cylinders filled with natural air but with a range of CO<sub>2</sub> concentrations. The S1 to S2 conversion has taken the form of a time-varying cubic function. The value of the cubic coefficients are determined periodically through measurement of the suite of six primary cylinders.

The CO<sub>2</sub> scale that resulted from this previous calibration procedure was not explicitly named, but for the purpose of clarity, we now designate this as the VH344-2015 scale, where VH344 designates the room number (Vaughan Hall room 344) and 2015 is an arbitrary recent date prior to this update. As the VH344 measurements have been made simultaneously on both a Siemens and Licor analyzer (while sharing the same calibration gases), we can also distinguish between Licor and Siemens versions of this scale. Note that this lab was relocated in 1999 from Ritter Hall but we retrospectively use the VH341-2015 designator also for measurements in Ritter Hall.

With this update, we provide revised assignments of the CO<sub>2</sub> mole fractions in the primary six cylinders, allowing for an update of the CO<sub>2</sub> mole fractions to the SIO X12 scale (Keeling et al., 2016). We also explicitly allow for drift in the CO<sub>2</sub> mole fractions of these tanks, as resolved by repeated measurements of these tanks in the Scripps CO<sub>2</sub> lab. We further transition to using a new instrument response function for the Licor CO<sub>2</sub> analyzer, which allows for more precise extrapolation to higher CO<sub>2</sub> concentrations. We assess the precision of this extrapolation based on comparisons to tanks with concentrations of over 500 ppm that had independent determinations of CO<sub>2</sub> mole fraction provided by NOAA. This updated scale is called the VH344-2020 scale.

## Primary Cylinder Drift

As described above, the cubic adjustments which bring the S1 scale into alignment with S2 are based on periodic analysis of the six primary steel tanks. Until this revision, the assigned values were based on values reported by the CO<sub>2</sub> lab in the late 1980s as detailed in Table 1.

Cylinder ID	Assigned Value ppm
635862-19890101	354.46
635864-19890101	339.50
635866-19890101	381.79
635867-19890101	367.11
635868-19890101	301.40
635870-19890101	419.73

Table 1: List of Steel primary CO<sub>2</sub> cylinders and previously assigned values, ppm

Until this revision, these declared values have remained unchanged since the program inception.

Many additional cylinders have been analyzed in the O<sub>2</sub> lab since 1990. These cylinders can be classed based on the type of cylinder or size and their CO<sub>2</sub> concentrations. Siemens measurements of these suites on the VH344-2015 scale

are shown in Figure 1.

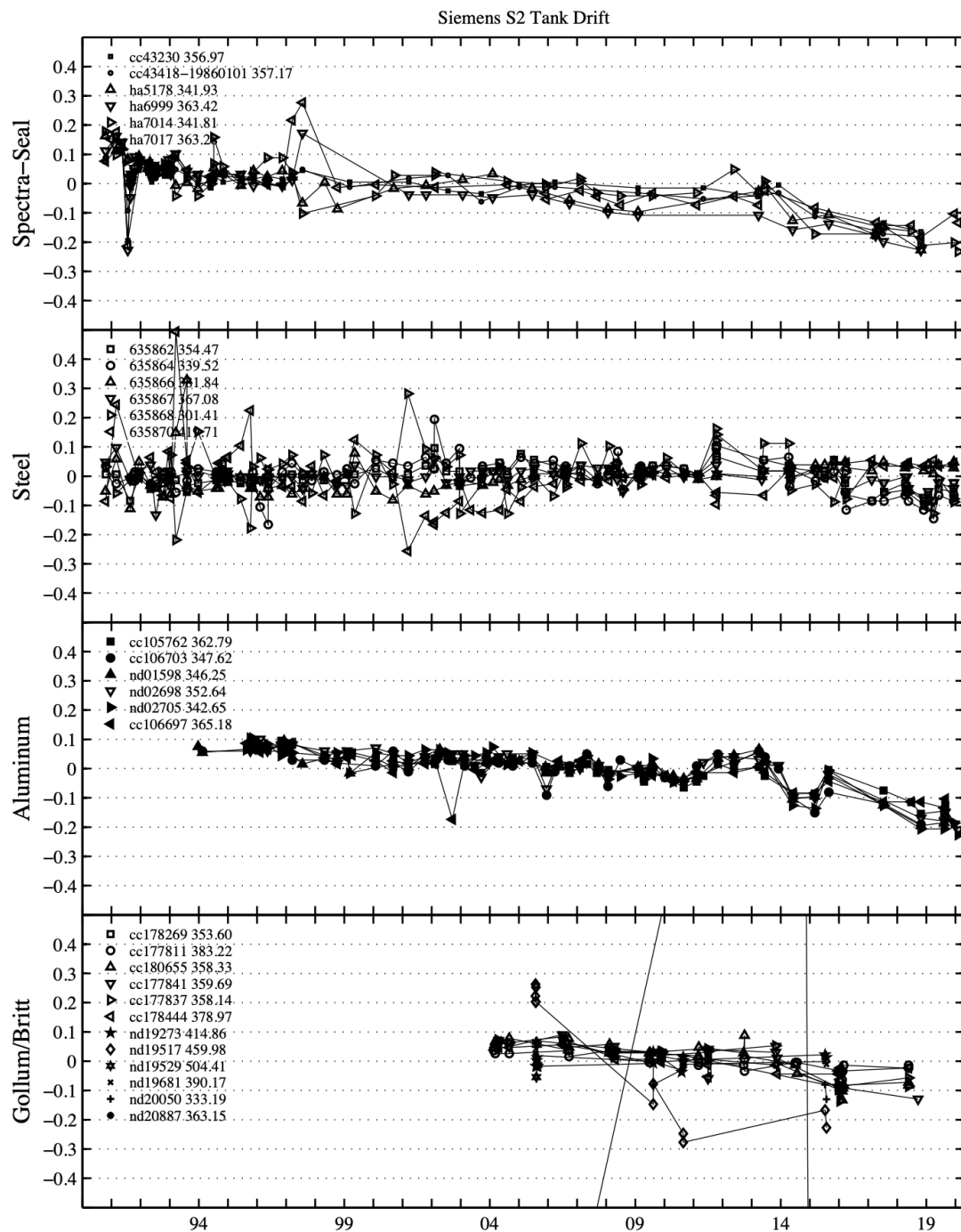


Figure 1: S2 concentrations on the VH344-2015 scale for 4 suites of cylinders measured on the Siemens analyzer. Y-axis represents the deviation of each cylinder's observed value from its long term average. With the exception of the CO<sub>2</sub> Primary "Steel" cylinders, which anchor the scale, all other suites, which comprise aluminum tanks, appear to drift downward in CO<sub>2</sub> by roughly 0.1ppm/decade.

In Figure 1, the CO<sub>2</sub> Primary cylinders from Table 1 are labeled “Steel”. Since the S2 scale is anchored to these cylinders, this group on average shows no drift over time. In contrast each of the other suites shows some small drift *downward* in CO<sub>2</sub>. The magnitude of the drift down is roughly 0.1 ppm/decade. Cylinders which apparently drift downward include the group of aluminum cylinders which, experience suggests, should maintain the most stable CO<sub>2</sub> values over time.

The CO<sub>2</sub> Primary cylinders have also been analyzed in the CO<sub>2</sub> lab (originally led by CD Keeling and previously designated as the CDRG lab) several times over the last 3 decades. The CO<sub>2</sub> concentrations measured in this lab were recently updated to reflect updated manometry and reported on a scale designated as the SIO X12 scale. Time series of the X12 values and the VH344-2015 are shown in Figure 2:

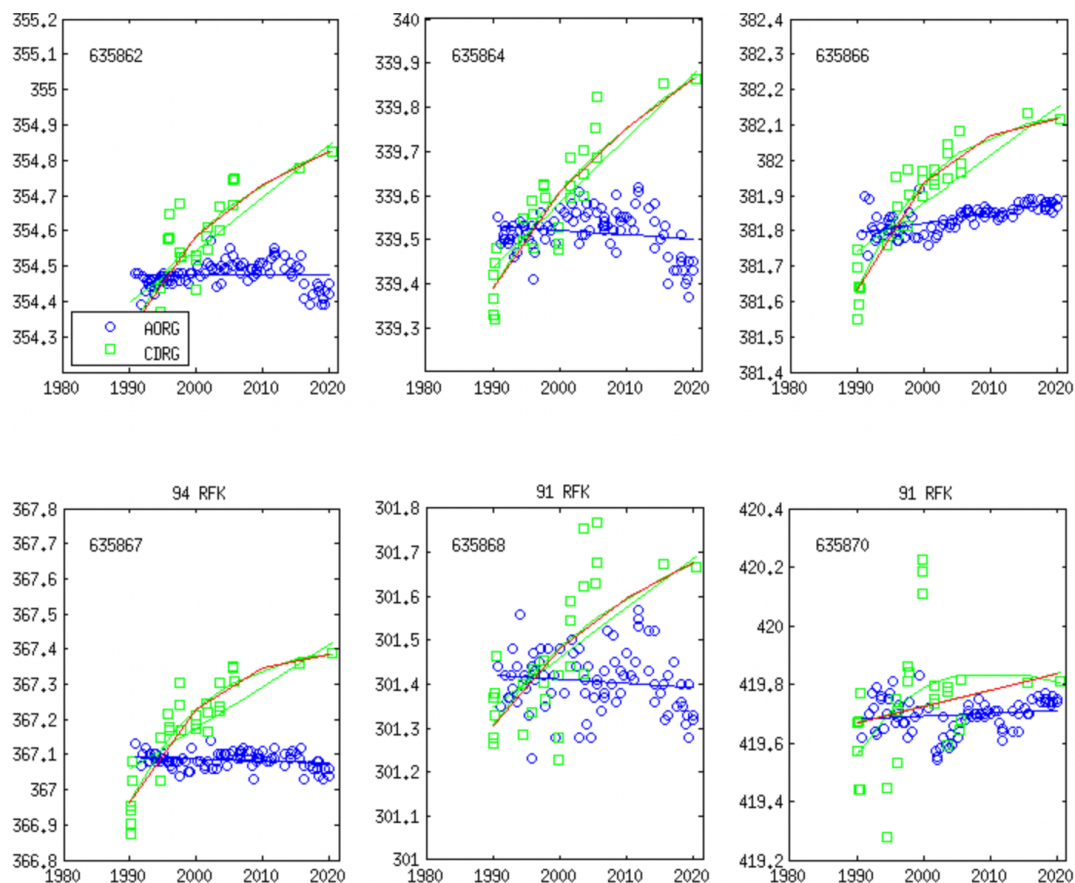


Figure 2: CO<sub>2</sub> Primary cylinders analysis results on the VH344-2015 scale (blue circles) and the SIO-X12 scale (green squares). By definition the VH344-2015 values maintain an average close to zero over time while the independent SIO-X12 measurements suggest cylinder drift.

From these results we conclude that each of the 6 CO<sub>2</sub> Primary cylinders have drifted upward in CO<sub>2</sub> and that the rate of drift has diminished over time. Figure 2 shows a least squares fit to the drift in which drift is expressed as a function of the square root of time. The plots also show, as red lines, linear segments that join points of the square root fit that have been evaluated at each decade. These straight line segments approximate the cylinder drift quite well. For the purpose of updating the CO<sub>2</sub> calibration of the Scripps O<sub>2</sub> program, we now assume that the CO<sub>2</sub> Primary cylinders have drifted from the declared values with time along the linear segments shown in this figure. These corrections have been implemented in matlab code and the drift rate of each segment is listed in the file

[http://bluemoon.ucsd.edu/protected/beta/database\\_active/input/tankdrift.csv](http://bluemoon.ucsd.edu/protected/beta/database_active/input/tankdrift.csv)

the pertinent section of which is included below. The last two columns represent initial and final adjustments over each relevant time period, which are added to the previously declared values in Table 1. Intermediate values are derived by linear interpolation in time.

```
% Licor, Siemens, 44/28
635862-19890101, 1990-01-01, 2000-01-01, 123, -0.15, +0.12,
635862-19890101, 2000-01-01, 2010-01-01, 123, +0.12, +0.26,
635862-19890101, 2010-01-01, 2020-01-01, 123, +0.26, +0.32,
635862-19890101, 2020-01-01, 2100-01-01, 123, +0.32, +0.32,
%
635864-19890101, 1990-01-01, 2000-01-01, 123, -0.11, +0.11,
635864-19890101, 2000-01-01, 2010-01-01, 123, +0.11, +0.24,
635864-19890101, 2010-01-01, 2020-01-01, 123, +0.24, +0.32,
635864-19890101, 2020-01-01, 2100-01-01, 123, +0.32, +0.32,
%
635866-19890101, 1990-01-01, 2000-01-01, 123, -0.15, +0.14,
635866-19890101, 2000-01-01, 2010-01-01, 123, +0.14, +0.29,
635866-19890101, 2010-01-01, 2020-01-01, 123, +0.29, +0.36,
635866-19890101, 2020-01-01, 2100-01-01, 123, +0.36, +0.36,
%
635867-19890101, 1990-01-01, 2000-01-01, 123, -0.15, +0.12,
635867-19890101, 2000-01-01, 2010-01-01, 123, +0.12, +0.23,
635867-19890101, 2010-01-01, 2020-01-01, 123, +0.23, +0.26,
635867-19890101, 2020-01-01, 2100-01-01, 123, +0.26, +0.26,
%
635868-19890101, 1990-01-01, 2000-01-01, 123, -0.10, +0.08,
635868-19890101, 2000-01-01, 2010-01-01, 123, +0.08, +0.17,
635868-19890101, 2010-01-01, 2020-01-01, 123, +0.17, +0.21,
635868-19890101, 2020-01-01, 2100-01-01, 123, +0.21, +0.21,
%
```

635870-19890101, 1990-01-01, 2000-01-01, 123, -0.17, +0.05,  
635870-19890101, 2000-01-01, 2010-01-01, 123, +0.05, +0.10,  
635870-19890101, 2010-01-01, 2020-01-01, 123, +0.10, +0.11,  
635870-19890101, 2020-01-01, 2100-01-01, 123, +0.11, +0.11,

## Re-Calculation of Cubics

The six CO<sub>2</sub> Primaries have continued to be analyzed on the Siemens and Licor roughly every 6 months. Workup of these data for analyses since March 2001 has been carried out via Matlab.

For the previous VH344-2015 scale, cubic coefficients were averaged over specific periods of time, and the averaged coefficients used in a stepwise manner over those periods. The breaks included the lab move from Colorado to Scripps in 1993, the transition from the Access to Matlab workup in 2001, and the replacement of the Siemens analyzer for a new Siemens analyzer in 2006.

For the VH344-2020 scale, we now interpolate the cubic coefficients linearly in time between the dates the cubics were defined from measurement and the date of analysis for which cubic terms are required. An exception is when there is an *a priori* reason to believe there might have been a stepwise change, such as when an analyzer is switched to a different unit.

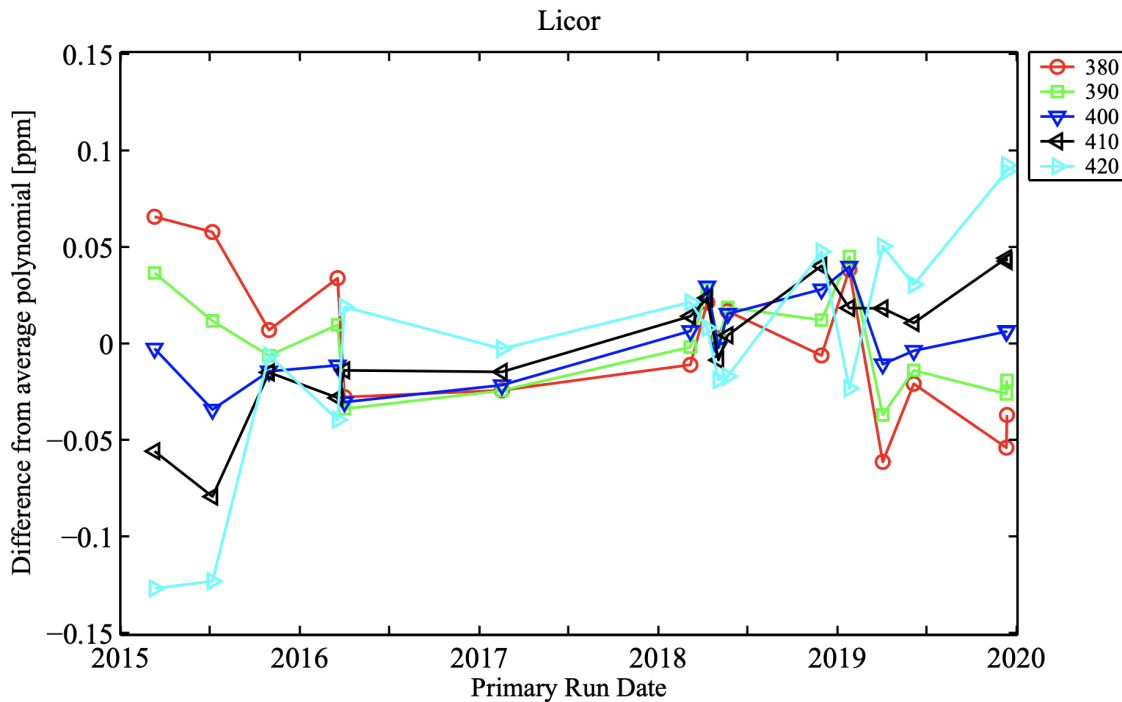
In matlab, the following method is used to obtain and interpolate cubic correction coefficients:

- 1) Time windows for averaging cubic coefficients are defined. These are usually 5 year periods beginning Jan-2000. However these windows are adjusted so that cubics are not linearly interpolated over dates when step changes are expected in the instrument's behaviour. Any time an analyzer is switched to a different unit, as occurred in July 2006 and April 2014 a stepwise change must be adopted. Time windows for cubic averaging are defined in the following file:  
[http://bluemoon.ucsd.edu/protected/beta/database\\_active/input/cubic\\_breaks.csv](http://bluemoon.ucsd.edu/protected/beta/database_active/input/cubic_breaks.csv)  
and are listed at the end of this report
- 2) All primary cylinder analyses occurring in the time windows defined above are sorted into groups separated by not more than 2 days. For each of these groups of analyses, cubic coefficients are obtained which relate S2 to S1. Individually calculated cubic coefficient for every grouped primary analysis date are listed in the file:  
[http://bluemoon.ucsd.edu/protected/beta/database\\_active/output/log/calco2siemens.out](http://bluemoon.ucsd.edu/protected/beta/database_active/output/log/calco2siemens.out)

- 3) Average cubic coefficients are calculated for all groups of primary analyses occurring in each time window. The average cubic coefficients are assumed to be valid at the mid point of its time window. Average cubic coefficients and mid-windows dates are recorded in the file:  
[http://bluemoon.ucsd.edu/protected/beta/database\\_active/output/log/cubics\\_bin\\_ned\\_siemens.csv](http://bluemoon.ucsd.edu/protected/beta/database_active/output/log/cubics_bin_ned_siemens.csv)
- 4) Cubic coefficients on any given analysis date are then linearly interpolated from the values listed in the file of 3).

## Example of averaging cubic coefficients

Figure 3 summarizes the behavior of each of the measured cubics in the last currently defined time window, 2015 to 2020, illustrating changes in the non-linearity during the time period. Cubics have been calculated on each date indicated on the x-axis from 2015 through 2020 that the CO<sub>2</sub> Primary cylinders were run, and these cubics have been evaluated at 5 specific S1 values of 380, 390, 400, 410 and 420 ppm. The average of all cubics during this interval is applied to the reference point of July 1st, 2017 which is the mid point of the x-axis.



/home/matlab/TMP/jibinpolynomials.m 03-Aug-2020 16:23:22



Figure 3: Illustration of how individually calculated sets of polynomial curves differ from the average all curves in the five-year 2015-2020 time window. Individual cubics have been evaluated on 11 dates on which CO<sub>2</sub> Primary cylinders were run from 2015 to 2020. The y-axis represents the difference between each individual cubic's value and the value of the mean of all 11 cubics which is assumed to be valid at the mid point of the time axis, July-2017. Cubics have been evaluated at 380, 390, 400, 410 and 420 ppm.

The y-axis in Figure 3 shows the difference between each evaluated cubic and the mean values for all cubics. The plot shows that only 2 points deviate by more than 0.1 ppm and that the differences vary systematically with time. This systematic drift is itself largely corrected for by the interpolation from the previous reference point.

During this interval, the S1 to S2 corrections are seen to drift upwards over time. This implies that the S1 scale drifted downwards over this interval, which could be due to drift in the CO<sub>2</sub> concentration of the secondary tanks which define the S1 scale, or due to random errors in their initial assignments.

Similar figures for other time windows are available in

[http://bluemoon.ucsd.edu/protected/beta/database\\_active/figures/diagnostic/](http://bluemoon.ucsd.edu/protected/beta/database_active/figures/diagnostic/)

## Licor Calibration for High CO<sub>2</sub>

The highest CO<sub>2</sub> concentration of the six CO<sub>2</sub> primary cylinders is 420 ppm so that the cubic coefficients for both the Licor and Siemens are unconstrained above that concentration. S2 values have nevertheless been reported above 420 ppm based on extrapolation of the cubic functions. As currently configured, the Siemens analyzer tends to saturate below 500 ppm, so even these extrapolated readings are not very useful. In contrast, the Licor has a well defined response function extending to very high CO<sub>2</sub> values that, in principle, could serve as the basis of an approximate extension of the record.

To assess the validity of such an extrapolation for the Licor, we examine results from cylinders from Britt Stephens of NCAR that were analyzed at NOAA and also in VH344. These NCAR cylinders cover a range of concentrations from ~330 to 510 ppm. A full listing of the NCAR cylinders with NOAA's assigned CO<sub>2</sub> concentration (on their X2007 scale) is included in the Appendix. A comparison of the CO<sub>2</sub> values reported by NOAA and VH344-2015 licor values for these cylinders is show in Figure 4:

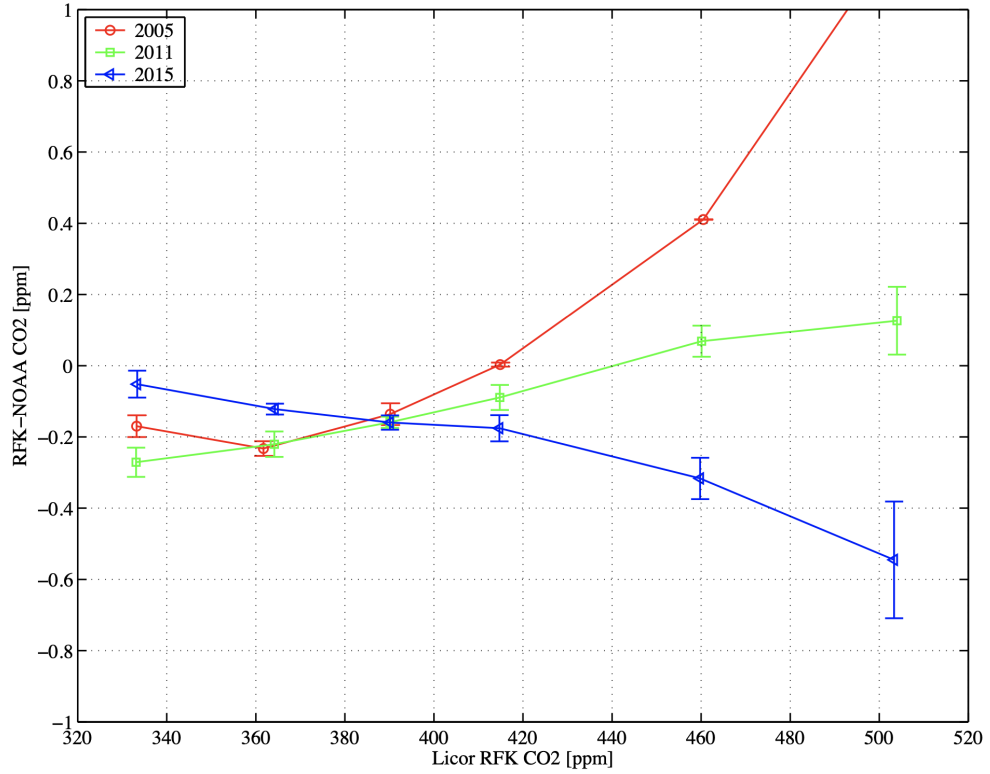


Figure 4: Concentration difference for a suite of NCAR cylinders. Y value is difference in concentration as VH344-2015 - NOAA value, grouped into time windows covering 5 years of analyses.

In making these comparisons the calculated differences between the NOAA and VH344-2015 scale have been grouped by analysis dates. Analyses have been averaged over approximately 5 year time windows that approximate the windows for the binned cubics. We note the NOAA and VH344-2015 scales show a positive offset of approximately 0.2 ppm below 420 ppm, but then diverge by as much as 0.5 to 1 ppm at higher concentrations, depending on which time period is chosen. This indicates that the extrapolation of the cubic functions has errors of this magnitude over this higher CO<sub>2</sub> range.

One limitation of these extrapolations is that a cubic relationship is known to be a poor description for the Licor response curve at high concentrations. Based on recommendations of Georbe Burba of Licor Instruments, we therefore also explored using an inverse double rectangular hyperbolae to relate the Licor S1 to S2 scales:

$$S1 = \frac{a1 S2}{a2 + S2} + \frac{a3 S2}{a4 + S2} \quad (1)$$

This form is also recommended in the LI-840A Instruction Manual (equation B-14). We thus apply this functional form to fit the S1 values of the six primary gases against their drift-corrected assignments (per Recalculation of Cubics, above),

replacing the cubic form. (We do not use the NCAR tanks to inform this fit, but these tanks remain useful for assessing the stability of the extrapolation to higher CO<sub>2</sub> value, as discussed below.)

Since Equation 1 is not linear in the parameters  $a_2$  and  $a_4$ , a non-linear optimization method is used to find these coefficients rather than the more usual linear least squares technique. These hyperbola fits now are calculated for the Licor (but not Siemens) in the modified matlab function *primayrcal.m* and a list of the fit parameters  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  are tabulated in:

[http://bluemoon.ucsd.edu/protected/beta/database\\_active/output/log/hyperbolic.csv](http://bluemoon.ucsd.edu/protected/beta/database_active/output/log/hyperbolic.csv)

Equation 1 expresses  $S_1$  as a function of  $S_2$ , which is not convenient for calculating  $S_2$  corrections as a function of  $S_1$ . It would be possible to invert the hyperbolae and obtain  $S_2$  as a function of  $S_1$ . However, to obtain a more simple analytic relationship from  $S_1$  to  $S_2$  and to make the Matlab code more consistent with the Siemens workup, it was decided to model the inverted hyperbola fits using a quartic polynomial. To do this each hyperbolic function was evaluated from 320 to 500 ppm. A quartic polynomial was then fit over this same concentration range giving a direct  $S_1$  to  $S_2$  correction. These quartics were then averaged in an identical manner to the cubics as described in “Recalculation of the Cubics” above, effectively replacing the cubics. The averaged quartics for use in the matlab codes  $S_1$  to  $S_2$  corrections are stored in:

[http://bluemoon.ucsd.edu/protected/beta/database\\_active/output/log/quartics\\_binned\\_licor.csv](http://bluemoon.ucsd.edu/protected/beta/database_active/output/log/quartics_binned_licor.csv)

We use the designator VH344-2020 to refer to this quartic-based version of the revised Licor calibration. An updated plot of NCAR tanks in Figure 5 shows a consistent relationship between the NOAA values and the VH344-2020 values of these NCAR tanks. In the range from 320 to 420 ppm, this consistency is largely attributed to having now corrected for drift in the six CO<sub>2</sub> Primaries, and the residual differences in this range presumably mostly reflect systematic offsets between the Scripps X12 scale and the NOAA scale. Above 420 ppm, this consistency evidently results from the improved ability to extrapolate to higher CO<sub>2</sub> concentrations using the double inverse hyperbolic functional form.

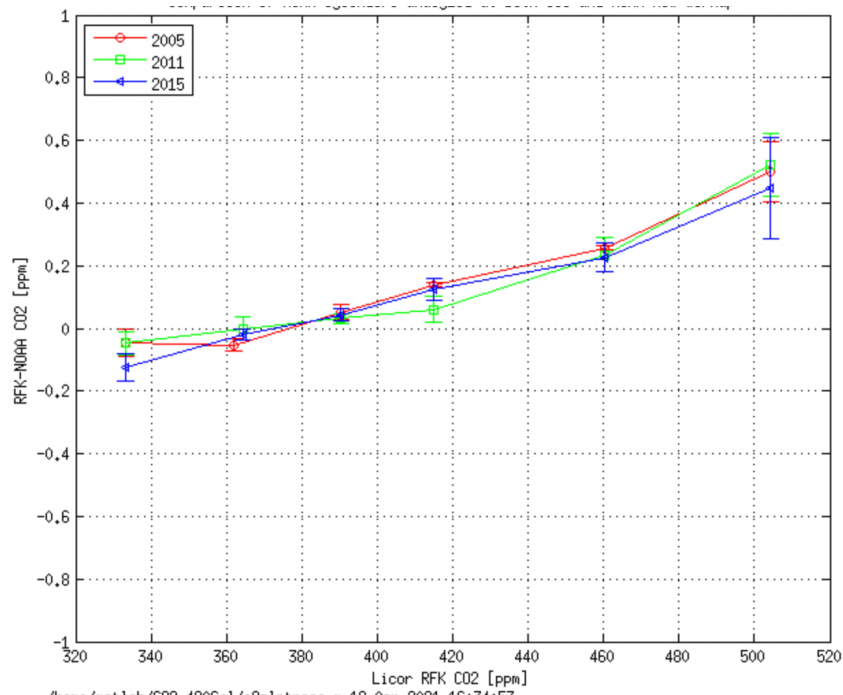


Figure 5: Concentration difference for a suite of NCAR cylinders. Y value is difference in concentration as VH344-2020 - NOAA value, grouped into time windows covering 5 years of analyses.

We note that the VH344-2020 Scale differences are now very consistent over time. Analyses in all periods show a steady trend of offset from NOAA with concentration.

## Special considerations for data prior to March 2001

Prior to 2001, the Siemens and Interferometer data were worked up using an MS Access database. The CO<sub>2</sub> workup used two sets of cubics to correct from S1 to S2, with the first covering analyses to 20-Feb-1993 and the second analyses from 9-Aug-1994 through 11-May-1999 (see Lab notebook #9 Pg 10). Previously, cubics calculated in each of these periods were averaged and each average used to make S1-S2 corrections in the associated periods. Here we have recalculated these cubics while allowing for the declared values of the CO<sub>2</sub> Primaries to drift as defined above, and this analysis is carried out using a matlab function *rwaccesscubics*.

In addition, a 3rd group of primary runs were identified in the Access database covering the period from Sep-2000 to Dec-2002. Addition of the 3rd set of cubics allows us to better capture the drift of the CO<sub>2</sub> Primaries with the Access workup. From these we calculated 3 sets of averaged cubics centered on midpoints of the three analysis windows. S1-S2 corrections are now calculated by linearly

interpolating the cubics at each analysis date rather than using stepwise cubic corrections as was done for the VH344-2015 scale.

Revised values for each individual cubic and the associated average values are tabulated below. These results can be compared to previous compilations (Lab notebook #9 pg 10).

19-Oct-1990	+2.73872e-07	+3.36127e-04	-3.43347e-01	+6.73310e+01
02-Mar-1991	+3.76807e-07	+1.93546e-04	-2.84619e-01	+5.98567e+01
04-May-1992	+2.48257e-07	+3.40248e-04	-3.38098e-01	+6.61705e+01
09-Jul-1992	-2.64896e-07	+8.86873e-04	-5.30049e-01	+8.84180e+01
07-Oct-1992	+1.43918e-07	+4.63945e-04	-3.84655e-01	+7.17842e+0
17-Dec-1992	+1.57671e-07	+4.33978e-04	-3.70036e-01	+6.97521e+01
15-Jan-1993	+2.69687e-07	+3.21586e-04	-3.30932e-01	+6.50307e+01
Average	+1.72188e-07	+4.25186e-04	-3.68819e-01	+6.97633e+01

09-Aug-1994	+1.33746e-07	+4.91089e-04	-3.95811e-01	+7.28347e+01
08-Sep-1994	+9.91934e-09	+6.16498e-04	-4.37898e-01	+7.75077e+01
03-Nov-1994	+1.77815e-07	+4.36765e-04	-3.74274e-01	+7.00595e+01
21-Dec-1994	+1.77690e-07	+4.34295e-04	-3.72691e-01	+6.98212e+01
30-Dec-1994	+2.17881e-07	+3.93843e-04	-3.59535e-01	+6.84562e+01
08-Jun-1995	+4.51717e-08	+5.78426e-04	-4.25459e-01	+7.63438e+01
09-Oct-1995	-7.42266e-07	+1.41804e-03	-7.22972e-01	+1.11396e+02
10-Nov-1995	+2.33405e-07	+3.81436e-04	-3.55392e-01	+6.78788e+01
09-Feb-1996	+8.88981e-07	-3.43176e-04	-9.08137e-02	+3.60023e+01
20-May-1996	+7.66059e-07	-2.09962e-04	-1.39197e-01	+4.19064e+01
15-Nov-1996	+2.44386e-07	+3.66722e-04	-3.49008e-01	+6.69961e+01
13-Mar-1997	-1.36934e-07	+7.73771e-04	-4.92190e-01	+8.35871e+01
29-Jul-1997	+2.45897e-07	+3.70480e-04	-3.52113e-01	+6.75929e+01
19-Nov-1997	+2.32126e-07	+3.83883e-04	-3.57936e-01	+6.85798e+01
20-Apr-1998	+5.54454e-07	+3.02555e-05	-2.27818e-01	+5.25437e+01
01-Oct-1998	-2.21013e-07	+8.64437e-04	-5.25470e-01	+8.78075e+01
03-Feb-1999	-3.64649e-07	+1.01402e-03	-5.76690e-01	+9.35590e+01
11-May-1999	+3.85289e-07	+2.19028e-04	-3.00601e-01	+6.21726e+01
Average	+1.58220e-07	+4.56658e-04	-3.80882e-01	+7.08359e+01

01-Sep-2000	-7.40169e-07	+1.42192e-03	-7.23411e-01	+1.11059e+02
09-Mar-2001	+1.23313e-06	-7.06576e-04	+4.00497e-02	+2.00070e+01
18-Oct-2001	-5.59116e-08	+6.94936e-04	-4.66018e-01	+8.06856e+01
03-Jul-2002	+3.04138e-08	+6.06552e-04	-4.36893e-01	+7.76443e+01
17-Dec-2002	-1.64890e-07	+8.09653e-04	-5.06515e-01	+8.54842e+01
20-Dec-2002	+1.47665e-08	+6.20850e-04	-4.43385e-01	+7.88895e+01
Average	+5.28907e-08	+5.74556e-04	-4.22696e-01	+7.56282e+01

These three averaged cubic coefficients are used to re-work the old access others and chart table, creating new versions of results.csv and others.csv files that are merged with the ongoing matlab data series. The rework of Access tables is conducted in Matlab, using modified versions of code that was originally written to

recalculate the interferometer span. The functions used are *rwchart.m*, *rwothers.m*. The new CO<sub>2</sub> cubics are stored in *rwco2s2.m*.

## Results

Figure 6 and 7 show the change in CO<sub>2</sub> for cylinders and interferometer flasks respectively as measured on the Siemens analyzer

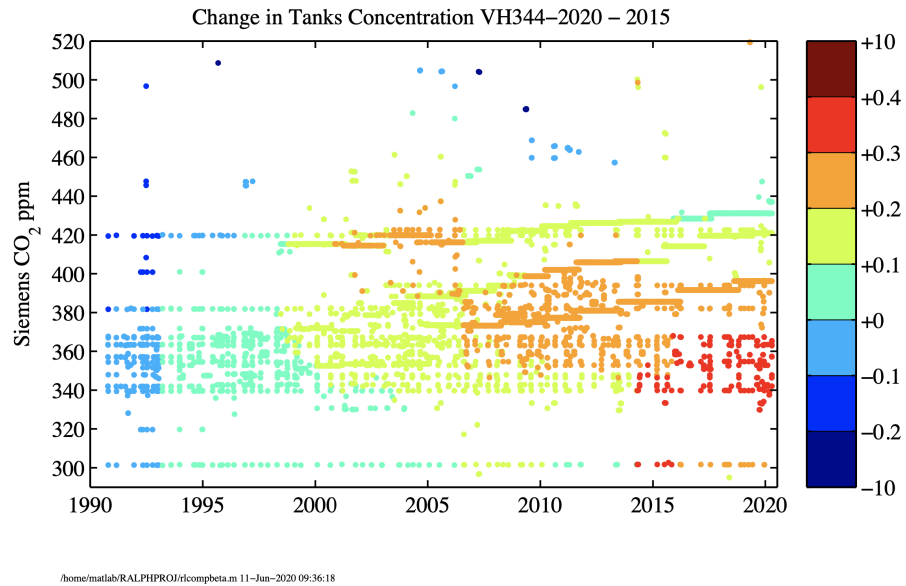


Figure 6: Change in cylinder concentration, VH344-2020 - VH344-2015, as measured on the Siemens analyzer.

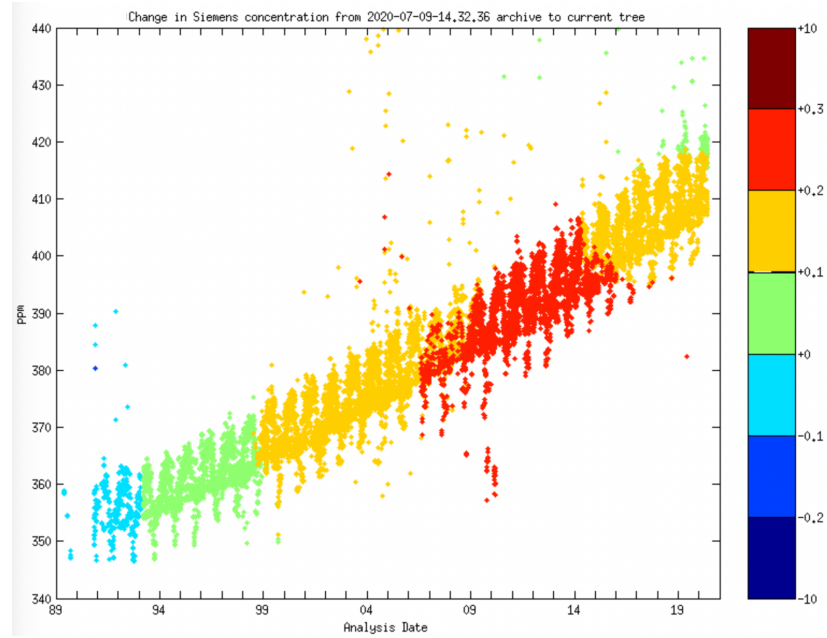


Figure 7: Change in interferometer flask CO<sub>2</sub> values from the Siemens analyzer, VH344-X2020 - VH344-X2015

A similar plot show the change in flask concentration as measured on the Licor is shown in Figure 8:

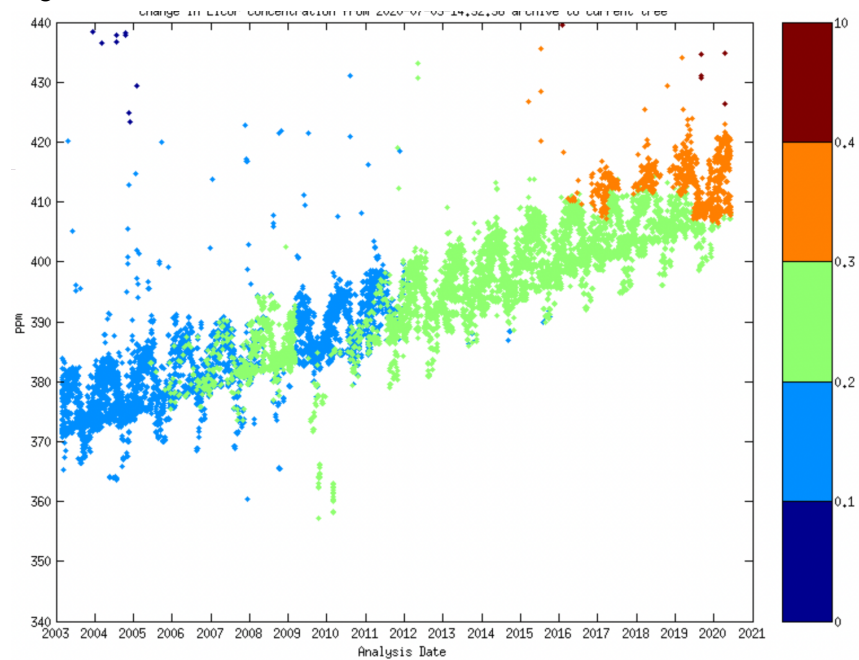


Figure 8: Change in interferometer flask CO<sub>2</sub> values from the Licor analyzer, VH344-X2020 - VH344-X2015

These revised CO<sub>2</sub> values impact oxygen results due to the effect of CO<sub>2</sub> interference in the interferometer. Calculated changes in O<sub>2</sub> as a result of the revised CO<sub>2</sub> values are illustrated in Figure 9

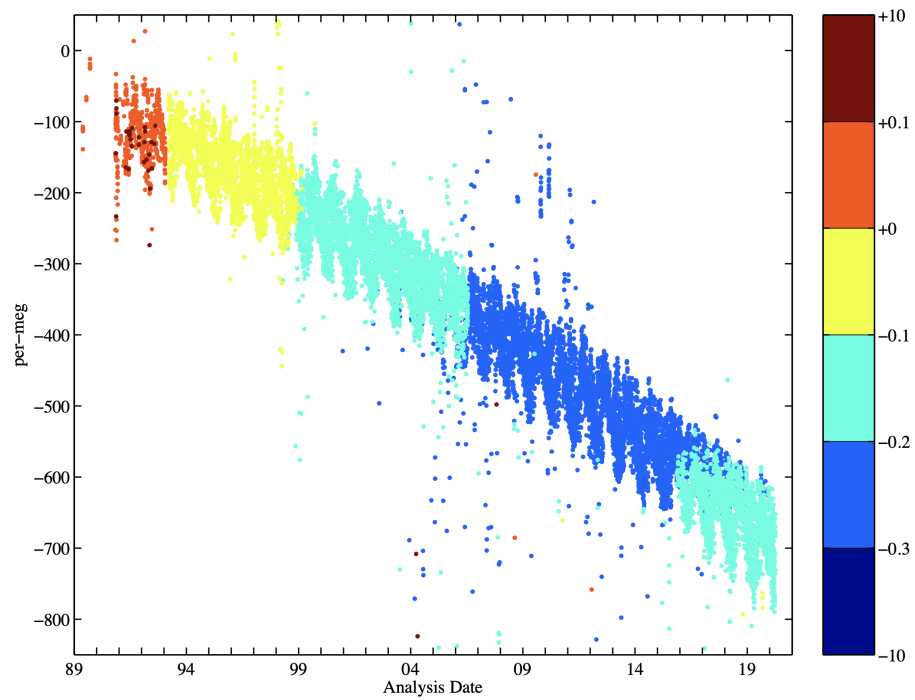


Figure 9: Change in  $d(O_2/N_2)$  reported for Interferometer flasks produced by revision of the S2 CO<sub>2</sub> value

Figure 10 Shows how CO<sub>2</sub> values differ on the Siemens and Licor on VH344-2020 and VH344-2015



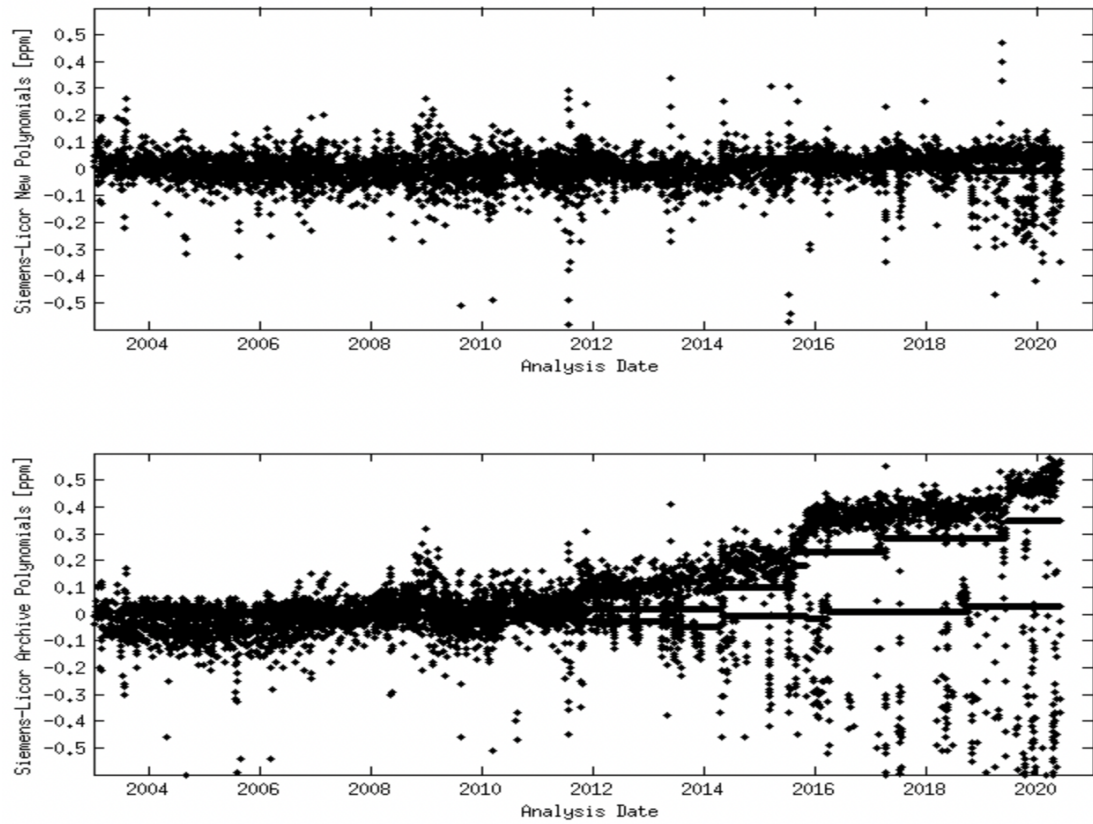


Figure 10: Difference in Siemens and Licor  $\text{CO}_2$  value for flasks samples. Top panel is for the VH344-2020 scales, the bottom panel for the VH344-2016 scales.

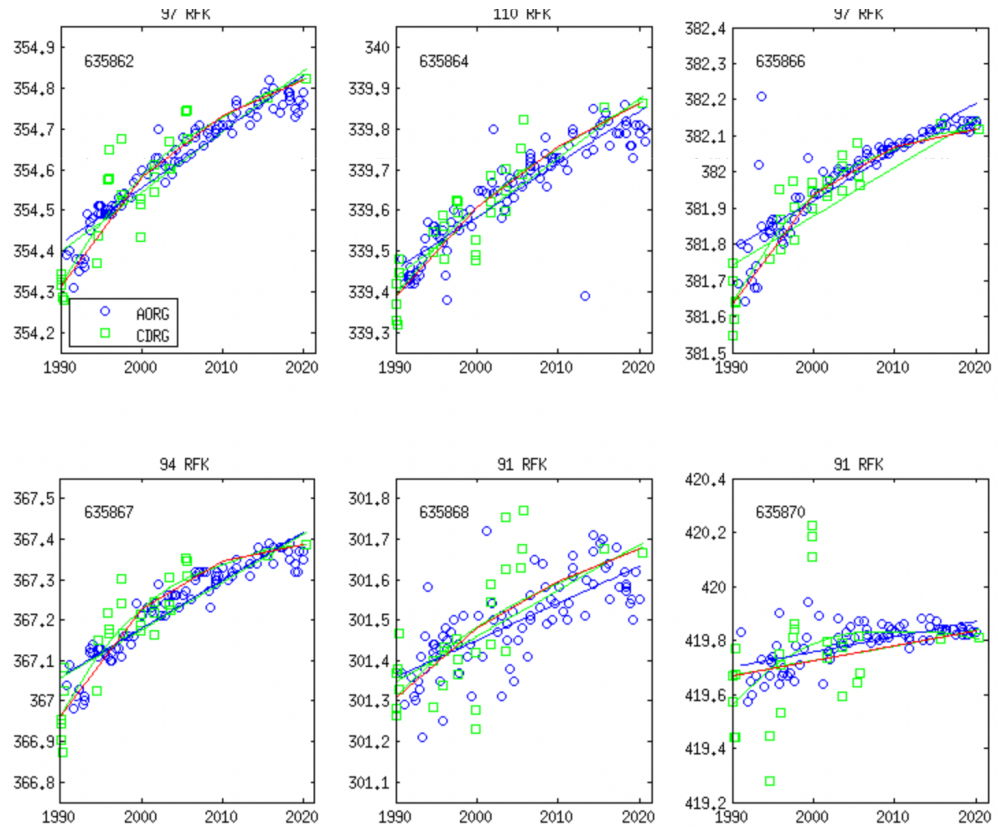


Figure 11: Time histories of the six primary CO<sub>2</sub> cylinders on the VH344-2020 scale (blue circles) and the SIOX12 scale (green squares). The plots demonstrate the successful convergence of these scales.

A revised plot of the Siemens S2 values calculated with the revised cubic coefficients for the 4 suites of tanks previously shown in Figure 1 are shown in Figure 11. All suites are seen to drift upwards, with the steel suite, which comprises the six CO<sub>2</sub> Primaries, showing the greatest drift.

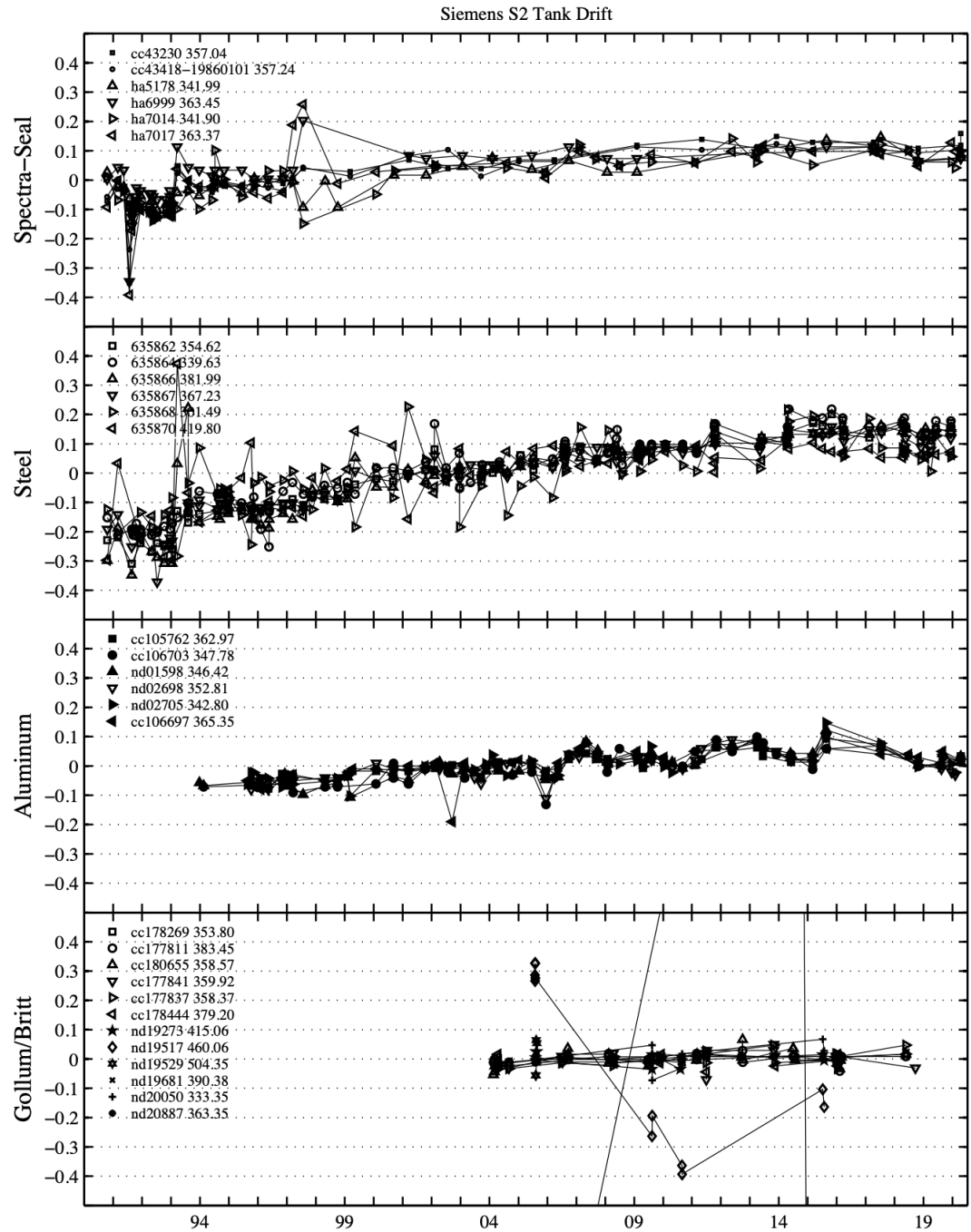


Figure 11: S2 concentrations measured on the Siemens VH344-2020 scale for the same cylinders shown in Figure 1. In comparison to Figure 1, the aluminum tanks are seen to be much more stable over time on the VH344-2020 scale.

# References

Keeling, R. F., A. C. Manning, E. M. McEvoy and S. R. Shertz (1998). "Methods for measuring changes in atmospheric O<sub>2</sub> concentration and their application in southern hemisphere air." *Journal of Geophysical Research-Atmospheres* 103(D3): 3381-3397.

Keeling, R.F., P. R. Guenther, S.J. Walker and D. Moss, "Scripps Reference Gas System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-Air Standards: Revision of 2012, Scripps Institution of Oceanography: 2016.

## Appendix

List of Britt Stephen's NCAR cylinders with associated CO<sub>2</sub> values assigned by NOAA on their X2007 scale. File obtained by email to Ralph Keeling from Britt Stephens, 16-March-2020. Filename GMDresults\_200316.txt

CylID	Date	Loc	Inst	Pressure	Conc	SD	Flag
ND20050	2006-04-13	BLD	S5	2000	333.409	0.005	.
ND20050	2006-04-19	BLD	S5	2000	333.401	0.013	.
ND20050	2006-04-25	BLD	S5	2000	333.402	0.023	.
ND20050	2010-12-13	BLD	L9	2150	333.405	0.004	.
ND20050	2011-01-26	BLD	L9	2050	333.383	0.012	.
ND20050	2011-01-27	BLD	L9	2050	333.38	0.014	.
ND20050	2011-02-02	BLD	L9	2040	333.383	0.012	.
ND20050	2015-11-05	BLD	L9	1750	333.423	0.013	.
ND20050	2015-11-12	BLD	L9	1775	333.414	0.004	.
ND20887	2006-04-20	BLD	S5	2000	361.944	0.014	.
ND20887	2006-04-26	BLD	S5	2000	361.94	0.008	.
ND20887	2006-05-02	BLD	S5	2000	361.95	0.008	.
ND20887	2011-03-14	BLD	L9	2000	364.413	0.008	.
ND20887	2011-03-22	BLD	L9	2000	364.391	0.016	.
ND20887	2011-03-24	BLD	L9	2150	364.36	0.007	.
ND20887	2011-04-06	BLD	L9	2150	364.378	0.005	.
ND20887	2015-11-06	BLD	L9	1925	364.419	0.013	.
ND20887	2015-11-16	BLD	L9	1900	364.398	0.005	.
ND19681	2006-04-07	BLD	S5	2000	390.296	0.009	.
ND19681	2006-04-13	BLD	S5	2000	390.311	0.01	.
ND19681	2006-04-17	BLD	S5	2000	390.311	0.008	.
ND19681	2010-12-30	BLD	L9	2000	390.292	0.007	.
ND19681	2011-02-03	BLD	L9	2000	390.045	0.102	*
ND19681	2011-02-08	BLD	L9	2000	390.122	0.043	*

ND19681	2011-02-22	BLD	L9	1950	390.185	0.046	*
ND19681	2011-03-01	BLD	L9	2000	390.286	0.012	.
ND19681	2011-03-04	BLD	L9	1900	390.289	0.009	.
ND19681	2015-10-30	BLD	L9	1625	390.289	0.01	.
ND19681	2015-11-03	BLD	L9	1625	390.297	0.02	.
ND19273	2006-04-07	BLD	S5	2000	414.886	0.012	.
ND19273	2006-04-13	BLD	S5	2000	414.866	0.011	.
ND19273	2006-04-19	BLD	S5	2000	414.909	0.003	.
ND19273	2011-02-04	BLD	L9	1950	414.898	0.011	.
ND19273	2011-02-09	BLD	L9	1950	403.922	0.015	*
ND19273	2011-02-26	BLD	L9	1950	414.894	0.014	.
ND19273	2015-10-30	BLD	L9	1775	414.89	0.004	.
ND19273	2015-11-03	BLD	L9	1750	414.888	0.008	.
ND19517	2006-04-07	BLD	S5	2000	460.197	0.088	*
ND19517	2006-04-14	BLD	S5	2000	460.077	0.009	.
ND19517	2006-04-21	BLD	S5	2000	460.058	0.014	.
ND19517	2006-04-24	BLD	S5	2000	460.097	0.016	.
ND19517	2011-01-27	BLD	L9	2050	460.115	0.009	*
ND19517	2011-01-28	BLD	L9	2050	460.061	0.01	.
ND19517	2011-01-31	BLD	L9	2050	460.059	0.014	.
ND19517	2011-02-10	BLD	L9	2000	460.034	0.007	.
ND19517	2015-10-30	BLD	L9	2000	460.096	0.015	.
ND19517	2015-11-03	BLD	L9	2000	460.097	0.002	.
ND19529	2006-04-07	BLD	S5	2000	503.922	0.053	.
ND19529	2006-04-14	BLD	S5	2000	503.842	0.003	.
ND19529	2006-04-21	BLD	S5	2000	503.869	0.019	.
ND19529	2010-12-23	BLD	L9	2000	503.875	0.034	.
ND19529	2011-02-11	BLD	L9	1450	503.758	0.012	*
ND19529	2011-02-28	BLD	L9	1900	503.734	0.031	*
ND19529	2011-03-09	BLD	L9	1900	503.835	0.017	.
ND19529	2011-03-17	BLD	L9	1900	503.851	0.018	.
ND19529	2015-10-30	BLD	L9	1600	503.882	0.014	.
ND19529	2015-11-03	BLD	L9	1600	503.875	0.024	.
ND12480	2000-05-30	BLD	S2	2000	336.767	0.043	.
ND12536	2000-05-25	BLD	S2	2000	427.942	0.026	.
ND12653	2000-05-26	BLD	S2	2000	369.41	0.063	.
ND12653	2000-09-29	BLD	L1	1800	371.185	0.01	.
ND12653	2001-01-17	BLD	L1	2000	372.486	0.011	.
ND12653	2001-04-12	BLD	L2	2000	377.88	0.006	.
ND12653	2001-09-06	BLD	L2	2000	369.158	0.014	.
ND12793	2000-05-26	BLD	S2	2000	369.12	0.017	.
ND12793	2000-09-14	BLD	L1	2000	364.049	0.025	.
ND12793	2001-01-17	BLD	L1	2000	372.4	0.006	.

ND12793	2001-06-06	BLD	L2	200	372.91	0.014	.
ND12793	2001-11-29	BLD	L9	2000	372.458	0.008	.
ND12793	2001-11-30	BLD	L9	2000	372.46	0.009	.
ND12795	2000-05-26	BLD	S2	2000	389.004	0.012	.