Special considerations for updating the primary *in situ* Mauna Loa record to the X12 scale

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We report here on several details that apply to updating the primary *in situ* Mauna Loa CO_2 record from the Scripps CO_2 program to the X12 calibration scale from the previous X08A scale. The update incorporates revised determinations of the primary reference gases on the constant-volume mercury-column manometer (CMM) based on improved assessments of manometer volumes and other parameters (Keeling et al., 2016). The changes, which impact data only after 1974, are typically of order 0.1 to 0.2 ppm or less at ambient concentrations.

In this update, we also incorporate two changes that are unrelated to the revised manometric determinations and are relevant only for the *in situ* Mauna Loa record but not relevant for flask data from Mauna Loa or other stations. The first involves a reassignment of a secondary calibration cylinder used for the *in situ* Mauna Loa measurements starting April 2015. The second involves eliminating a +0.12 ppm adjustment that had been applied only to the *in situ* Mauna Loa record to correct for offset between flasks and the continuous analyzer.

Correcting secondary calibration tank declaration in 2012

The measurement of flasks and calibration gases at Scripps depends on a single analyzer located in the lab at Scripps. In 2012, this analyzer was upgraded from the original Applied Physics Corporation (APC) instrument to a newer Picarro instrument. A pair of secondary calibration cylinders, with CO_2 concentrations determined using the APC, were used to initially establish the CO_2 scale on the Picarro. Based on later diagnostics, it subsequently became clear the actual concentration of one of these cylinders, the ambient calibration tank ID 4289, was lower by 0.15 ppm than initially determined. Correcting this assignment had the effect of shifting ambient flask and cylinder CO_2 concentrations measured on the Picarro down by 0.15 ppm. This correction was implemented in recent versions of X08A flask data. The change was not propagated, however, to secondary calibration cylinder JA02199 which has been in use at Mauna Loa since April 2015. With this update, we also correct the assigned value of JA02199, which has the effect of shifting the *in situ* Mauna Loa record downward by about 0.15 ppm since April-2015.

Removing additive correction to the Mauna Loa record since 1984

The Fortran code that produced the *in situ* Mauna Loa record included adjustments for several time periods during which additive corrections were made to CO_2 values (Walker et al, 2016). Pertinent sections of the code are included in Figure 1 and 2.

```
C
C  MAKE PERIOD CORRECTIONS
      DO 299 I=1,ICOR
      IF(IDAT.GE.IDAT1(I).AND.IDAT.LE.IDAT2(I))CMAN2=CMAN2+PECOR(I)
  299 CONTINUE
C
C  READ SPLINE COEFFICIENTS FROM FIT TO FLASK-ANALYZER DIFFERENCES
C  FOR MLO (FIT AR'71-DC'86); SPLINE CORRECTION APPLIED FROM LAST
C  DETECTOR CHANGE (JAN 1975) TO END OF N2 TANK USAGE (DEC 1983)
C
      IF(IDAT.GT.870930)GOTO 105
      IF(IDAT.LT.750130)GOTO 109
C
C     IF(IDAT.LT.750130.OR.IDAT.GE.831207)GOTO 109   ! prev
c
      T=YEAR(NALDT)
      CALL INTSPL(T,C2)
c
      GOTO 107
  105 C2=.12       ! from end of spline (see intspl coeffs)
  107 CMAN2=CMAN2 + C2
C
  109 CONTINUE
C
C..CONVERT J TO X
C...NOW AS OF 87SP13 NO LONGER OMIT SOURCE BLOCK CORRECTION; USE
C... CAL85 (GAS='A') OR  CAL87 (GAS='A') SINCE CORRECTING ANALYZER
C... TO FLASKS DURING 1970'S
C... [OMIT SOURCE BLOCK CORRECTION: USE FJ INPUT TO ACUB83 INSTEAD.
```

Period Corrections
Fixed adjustment in range of dates

Flask/Analyzer Spline Diffs

+0.12ppm after 30-Sep-1987

Figure 1: Fortran code from the main code, mauna5monx03A.F

```
      subroutine intspl(tt,cc)
C-------------------------------------------------------------------------------
c computes values of spline fit at times tt
c  spline coefficients from interpolated spline at 4 month intervals
c  through spline fit to flask-anlyzr diffs (1971-1987);
c       file:    FLANZJBSPCR.FIN   input to pgm  PLFLANSPL2.FOR
c       generated the spline coefficients used below
c
c       tt       input time at which to calc value of spline     input
c       cc       spline value to use in period correction       output
c
C-------------------------------------------------------------------------------
```

Figure 2: Heading of intspl Fortran subroutine that imposes correction for flask/continuous analyzer differences.

Prior to this update, these corrections from the Fortran code were carried through without modification to the Matlab code that is currently used to process the Mauna Loa record. These adjustments were:

- Period corrections for the early years (ending 1976) applied in a stepwise manner over time and stored in a data array named PECOR.
- Spline corrections[1], adjusting for differences between the flask and in situ record at Mauna Loa between Jan-1975 and Sep-1987.

[1] The physical basis for these spline corrections was not documented in the original Fortran code. We believe the corrections were intended to reduce calibration error associated with using CO_2-in-N_2 calibration gases at Mauna Loa, a practice which ended in Jan. 1984 in favor of using CO_2 in air. This view is supported by the fact that the corrections were designed to be constant after that.

The spline corrections, shown in Figure 3, were variable from 1975 to Dec-1983 and then essentially constant at -0.128 ppm from Jan-1984 to Sep-1987. In Sep-1987, the correction jumps from -0.128 to +0.12, which appears to represent a coding error. (This feature was confirmed by making test runs using mauna5monx03A.F with fixed input J values for the year 1987, as stored in */cdrgsun/mp0/whorf/mlo/mlodta/walker/*). We believe that the Fortan code was intended to maintain the last value of the spline correction, made in 1987, but the correction was implemented with the wrong sign after Sept 1987 (see Figure 2).

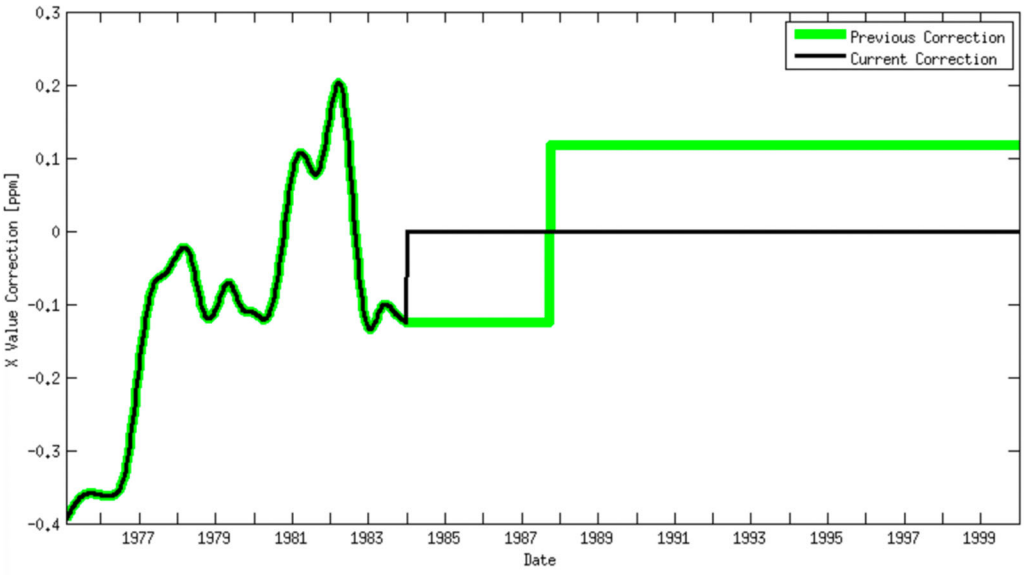

Figure 3: The green line represents the correction that was added to X values prior to this update. For data through Sep-1987 this was implemented in the function intspl and is based upon observed flask-analyzer differences. After Sep-1987 the correction was incorrectly hard wired in the main code at +0.12 ppm. The black line represents corrections that are now added to X values following this update. For data through 1984 these follow the previous adjustments based upon flask/analyzer differences. After 1984 the correction is held constant at 0.0 ppm.

For this update, we maintain the period corrections and modify the spline corrections to set them to zero abruptly starting Jan 1984, because we lack justification for their continued use after that time. The update thus has the effect of adjusting the Mauna Loa record from Jan 1984 to Jan 1987 by +0.12 ppm and adjusting the record after Jan 1987 by −0.12 ppm. This additive change is on top of changes associated with the redetermination of the secondary reference gas and the X08A-to-X12 update.

References

Keeling, R. F., P. Guenther, S. Walker and D. Moss (2016). Scripps Reference Gas Calibration System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-Air Standards: Revision of 2012. La Jolla, California, Scripps Institution of Oceanography: 1-173.

Walker, S. J., R. F. Keeling and S. C. Piper (2016). Reconstruction of the Mauna Loa Carbon Dioxide Record using High Frequency APC Data from 1958 through 2004. La Jolla, California, Scripps Institution of Oceanography: 1-17.