Assessment of the stability and relationships between the NIES-09, SIO-X12, and WMO-X2019 CO_2 scales

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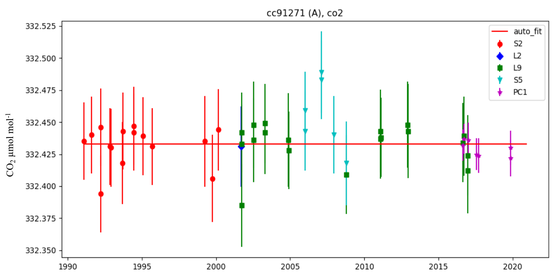
1. Introduction

Long-term monitoring of atmospheric CO_2 requires stable reference scales to ensure observed trends and spatial gradients are not influenced by changes in the underlying scale. The National Institute for Environmental Studies (NIES), the Scripps Institution of Oceanography (SIO), and the National Oceanic and Atmospheric Administration (NOAA) have maintained independent CO_2 in air scales for decades. The relationships between these three scales are important indicators of the relative stability of the scales and are becoming increasingly important as data traceable to the three scales are being combined in models.

2. Independent CO_2 Scales

	NIES-09	SIO-X12 CO_2 program	WMO-X2019
Institution	NIES	SIO	NOAA
Range	270-520 ppm	200-500 ppm	250 – 800 ppm
N primary standards	10 (scale held by 14 secondary)	12	19
Basis	Gravimetric	Manometric	Manometric
URL	https://db.cger.nies.go.jp	https://scrippsco2.ucsd.edu	https://gml.noaa.gov

- Scales are independent
- Used for decades for atmospheric monitoring.
- Based on two primary techniques



NOAA long-term target tank with 30 year record. Average value = 332.43 ± 0.02 ppm. Symbols indicate different analyzers used for CO_2 calibrations over time. Symbols indicate individual analyzers used on the calibration system.

Priority placed on ensuring long-term stability of scales

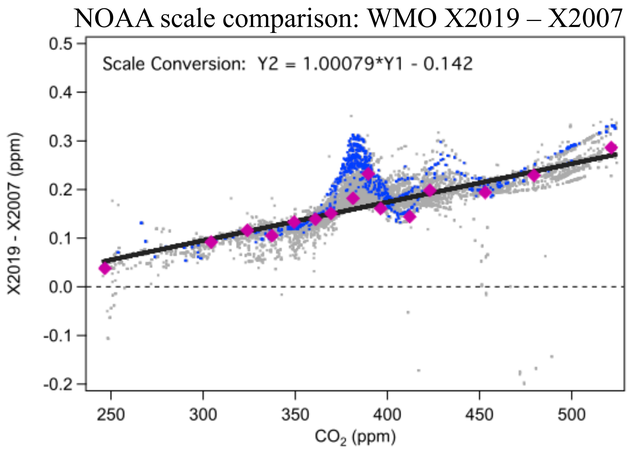
3. Motivation for work

X2019 revision impacts on GlobalView+ ObsPack

- Data distribution package for global modeling studies
  - ObsPack framework - consistent format for data and metadata
  - Latest release (V8, Aug 2022) - 66 institutions, 587 unique datasets
  - https://gml.noaa.gov/ccgg/obspack/index.html

- **How to handle independent scales?**
  - Data traceable to SIO and NIES scales are included
  - X2019 moved significantly - introduces biases
  - Solution: provide original submitted value and value converted to WMO X2019
    - Need scale conversion functions

NOAA scale comparison: WMO X2019 – X2007



Differences between X2019 and X2007 tertiary assignments from 1995 to 2017, (NDIR only) showing 2008 analysis in blue, all others in gray. A linear scale conversion derived from primary standards (pink) is shown as the black line. Hall et. al, 2021.

4. Comparison Activities

MLO co-located sampling:
- SIO since 1958
- NOAA since 1969
- NIES since 2010

Long term co-located monitoring sites
- Sensitive to sampling and measurement effects
- Sensitive to atmospheric conditions
- Need scale relationship first to understand other potential problems

WMO Round Robin experiments
- 2-3 cylinders over narrow mole fraction range
- Difficult to assess full scale range

Scale comparisons through exchange of suites of cylinders
- Cover large mole fraction range with multiple exchanged cylinders
- Preferred method for making a scale conversion
- Infrequent

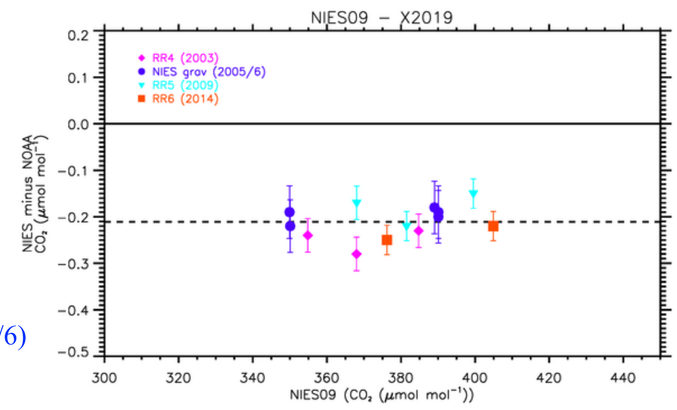
5. NIES-09 vs WMO-X2019

Extensive scale comparison currently in progress:

8 cylinders, 340 – 480 ppm

Historical cylinder exchanges:
- Round Robin #4 - RR4 (2003)
- Round Robin #5 - RR5 (2009)
- Round Robin #6 - RR6 (2014)
- 5 NIES gravimetric standards - NIES grav (2005/6)
  - Isotopically depleted
  - -0.06 ± 0.03 ppm correction to NOAA NDIR measurements

Cylinder offset = -0.21 ± 0.04 ppm

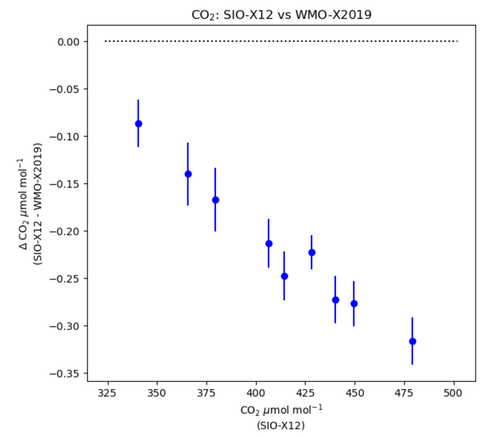


NIES-09 minus WMO-X2019 differences for exchanged cylinders.

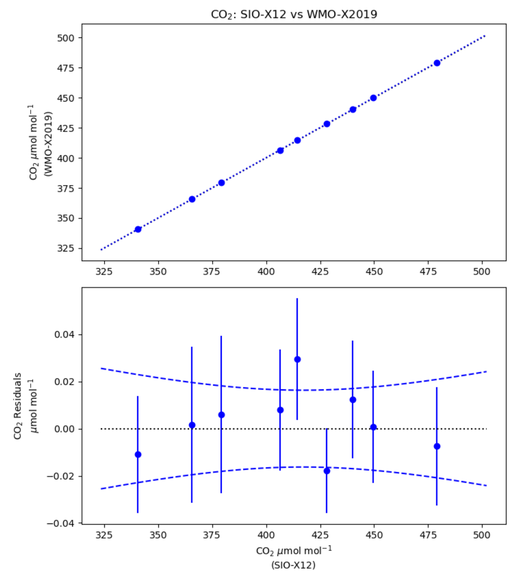
6. SIO-X12 vs WMO-X2019 scale comparison

2020 scale comparison episode:
- 9 cylinders (340 – 480 ppm)
- Measured by laser spectroscopic methods at both labs

Shows a mole fraction dependent offset



SIO-X12 minus WMO-X2019 differences vs SIO-X12 CO_2 values for 2020 comparison tanks.



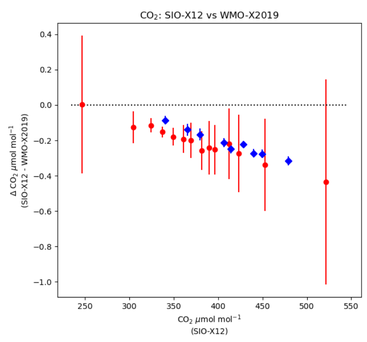
SIO-X12 to WMO-X2019 scale relationship:

[WMO_X2019] = -0.459 + 1.001634 * [SIO_X12]
Uncertainty ~ 0.02 ppm

Top panel, WMO-X2019 values verses the SIO-X12 values for 2020 comparison tanks with a linear ODR fit to the data. The bottom panel shows the residuals to the fit, the error bars are the combined uncertainty of the difference. We estimate the uncertainty of the scale conversion as the prediction interval of the fit, shown by the dashed lines.

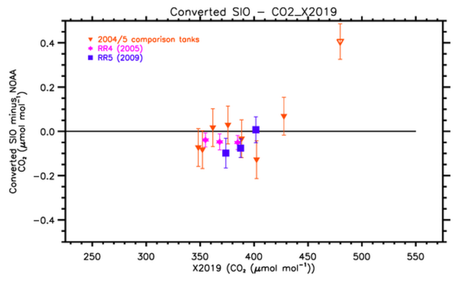
7. Can we use the scale relationship derived in 2020 for earlier data?

1992-1999 scale comparison:
- SIO calibrations of the NOAA primary standards
  - 5 episodes
  - Measured by NDIR at SIO
  - Measurements outside 1990's ambient range are noisy
- Relatively consistent scale differences over 25 years for 320 – 400 ppm range



SIO-X12 minus WMO-X2019 differences: 2020 comparison set in (blue), 1992-1999 averages for NOAA primary standards (red)

- **Test scale conversion with other exchanged cylinders**
  - 2004/5 exchange cylinders
  - WMO Round Robin #4 – 2005
  - WMO Round Robin #5 – 2009
  - SIO – NOAA after conversion = -0.04 ± 0.06 ppm



SIO – NOAA differences AFTER applying scale conversion.

8. Conclusion

Going forward there will be a need to better define relationships between independent CO_2 scales, both to evaluate scale stability and to allow independent data sets to be merged in models. There is an initiative through the CCQM Gas Analysis Working Group to have BIPM run on-going scale comparisons to meet this need. The current work of direct bi-lateral comparisons will serve as a valuable check on this process.

9. References

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