EPA Protocol Gas

Ambient Air Protocol Gas Verification Program

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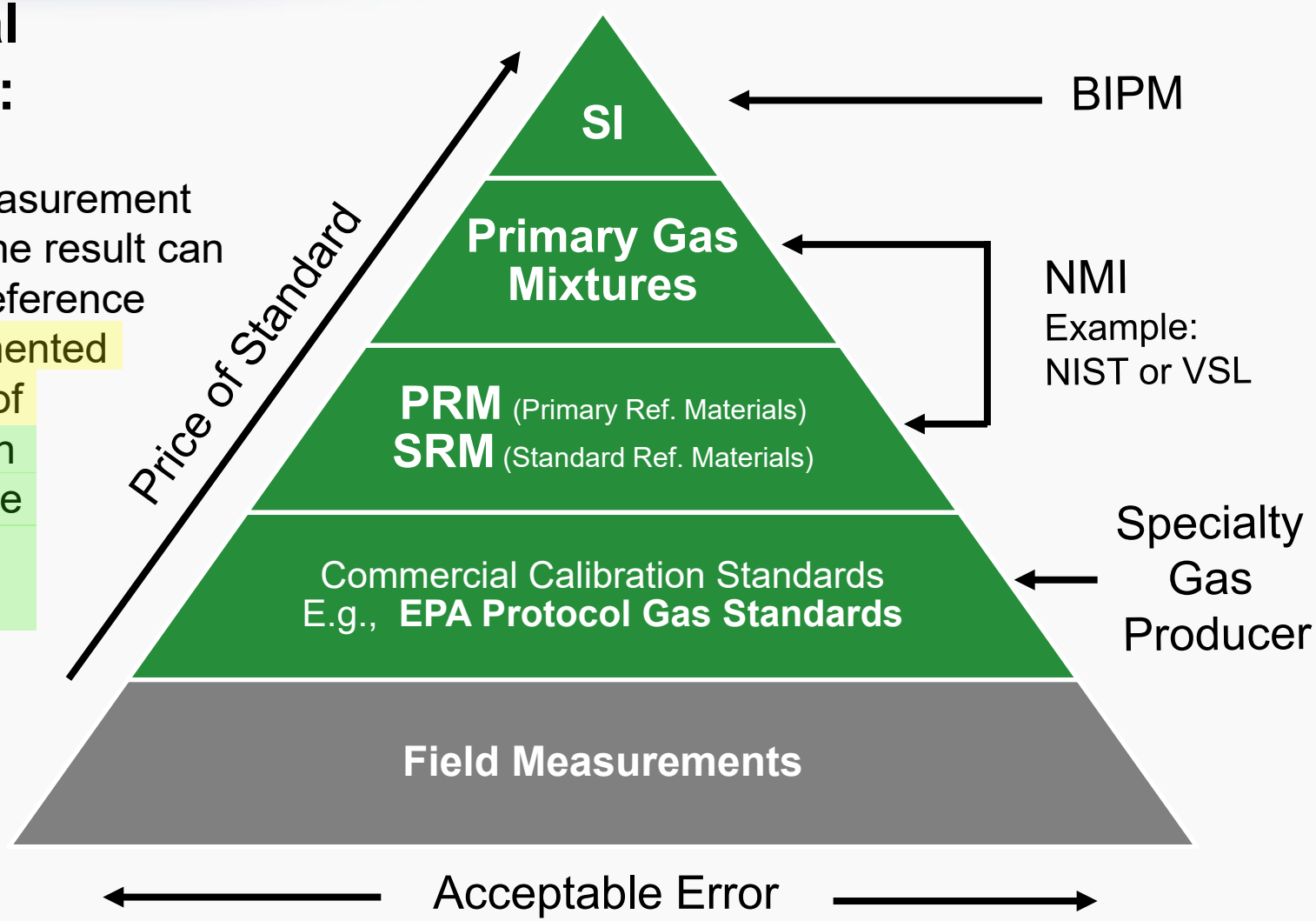
Metrological Traceability

Metrological Traceability:

property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.



Early History of Regulatory Gas Standards

1970: Clean Air Act

- New regulatory requirements for emission testing
  - Inspection and Maintenance (I&M) programs
  - Automotive Industry emission testing requirements, etc.
- Need for calibration gases to ensure measurements are traceable and of known accuracy

1972: Standard Reference Materials (SRM) for Compressed Gas Standards

- SRMs developed to address this regulatory testing need

1972-1977: Certified Standards for NAAQS monitoring are observed not to be of uniform quality

- NIST/NBS is selling SRMs to Specialty Gas Producers
- SRMs in high demand, NIST has difficulty keeping up with demand for SRMs
- EPA and SLTs have traceability to the SI via NIST, but this isn't a complete solution
- Causes varying quality:
  - Cylinder passivation techniques differ between specialty gas producers
  - Certification procedures differ
  - Methodology for estimating expanded uncertainty differ

Early History of Regulatory Gas Standards (continued)

1978: EPA Traceability Protocol for Assay Certification
- Provides uniform methodology for performing assay verification and certification
- Defines prescriptive procedure for declaring uncertainty of the standard

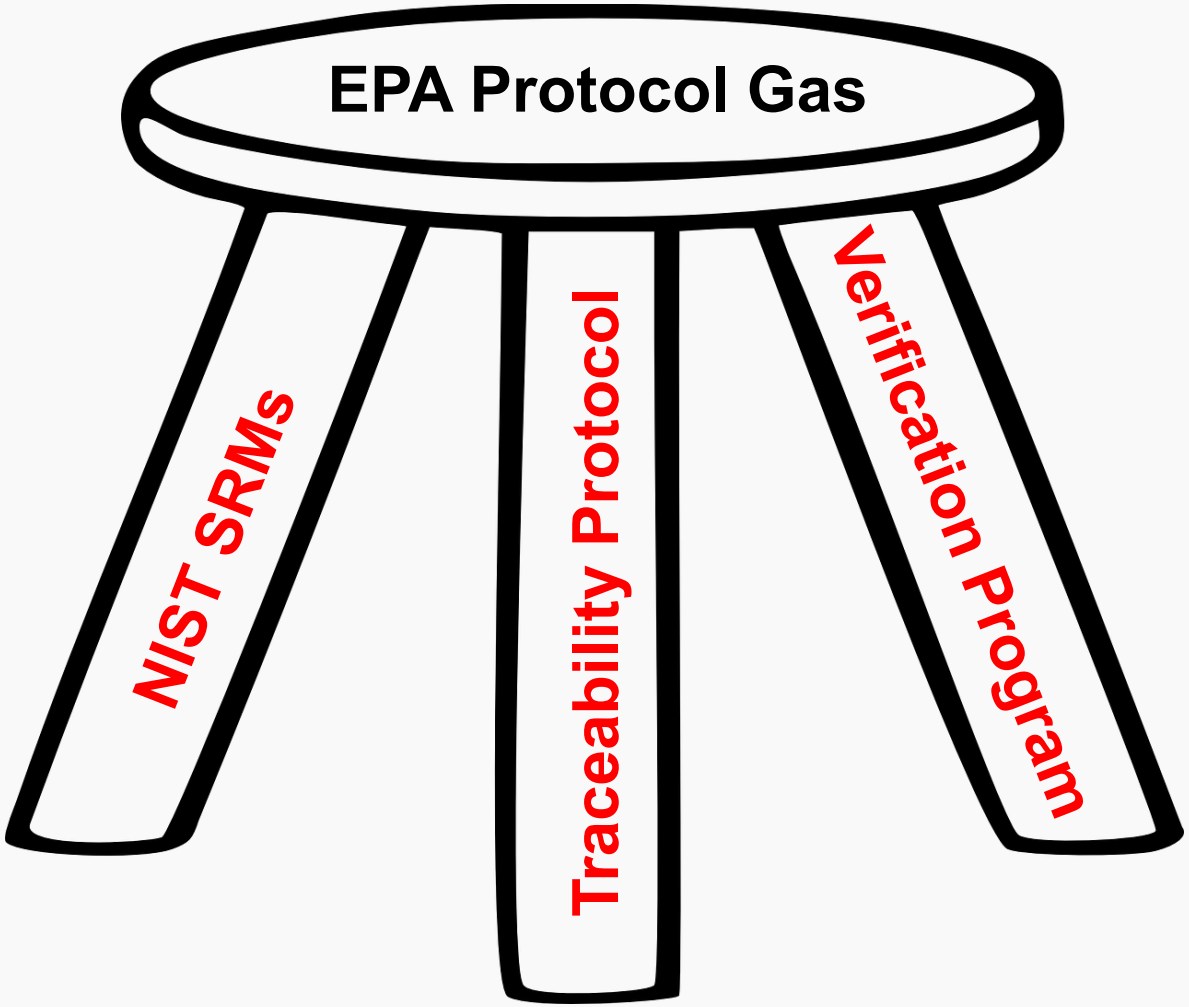
1985: EPA ORD Verification Audits of Protocol Gas Standards
- Specialty Gas Producers begin adoption of EPA Protocol Gas Standards for NAAQS ambient air monitoring

~1993-2006: EPA Protocol Gas Standards
- incorporated in Regs by Reference

2007-Present: EPA Protocol Gas Standards
- incorporated in Regs by Reference and EPA Protocol Gas Standards explicitly stated

So by 1985 we have this fixed and dialed-in, right?
almost…

Components of the EPA Protocol Gas Program



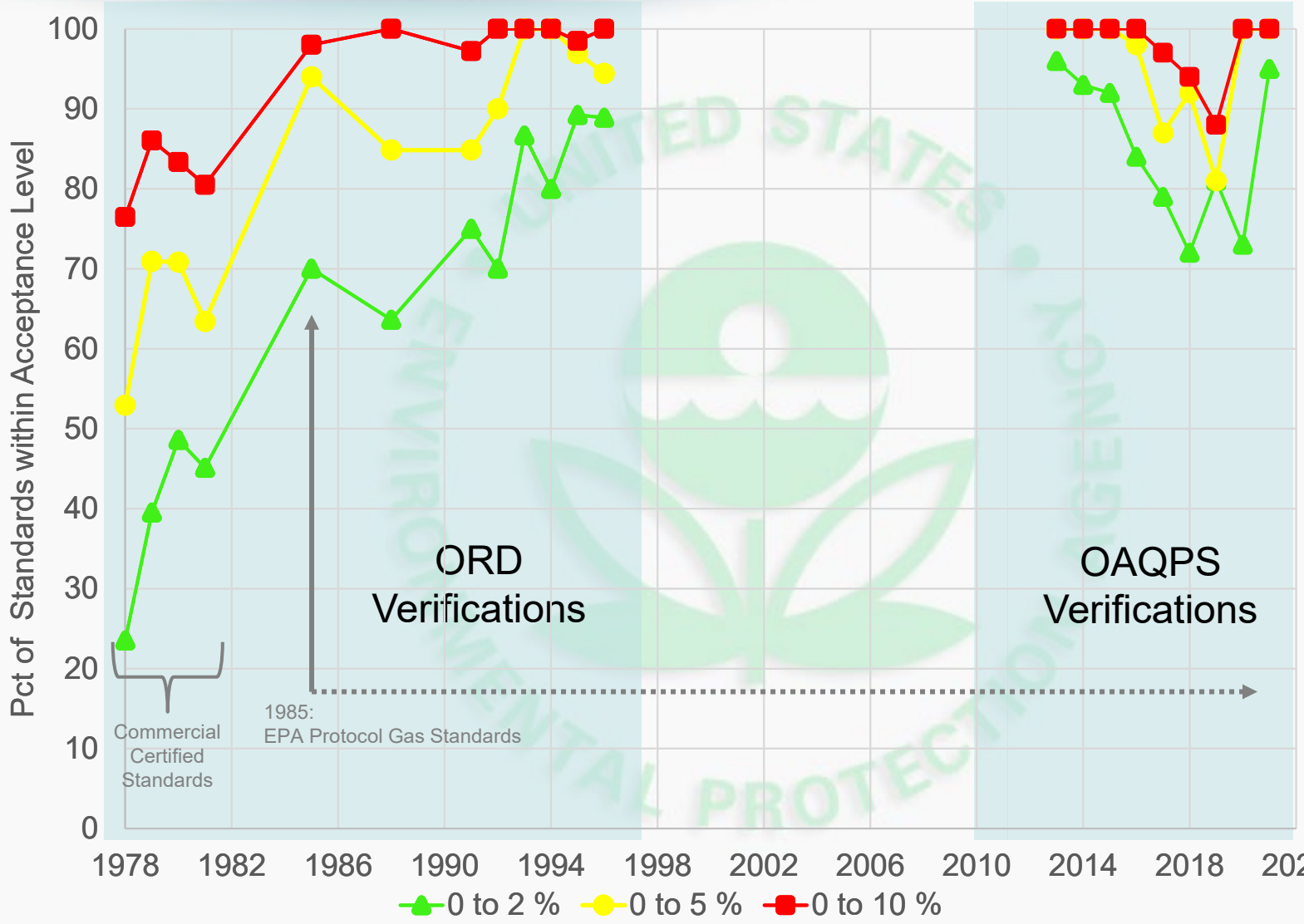
The Verification Program:

- is a critical component of the EPA Protocol Gas Program

Reminder:

- Calibration Standards for Ambient Air Monitoring are required to be EPA Protocol Gas Standards
- Calibration Standards cannot just be Certified NIST Traceable Standards

Percentage of Gas Standards within a Given Accuracy Range

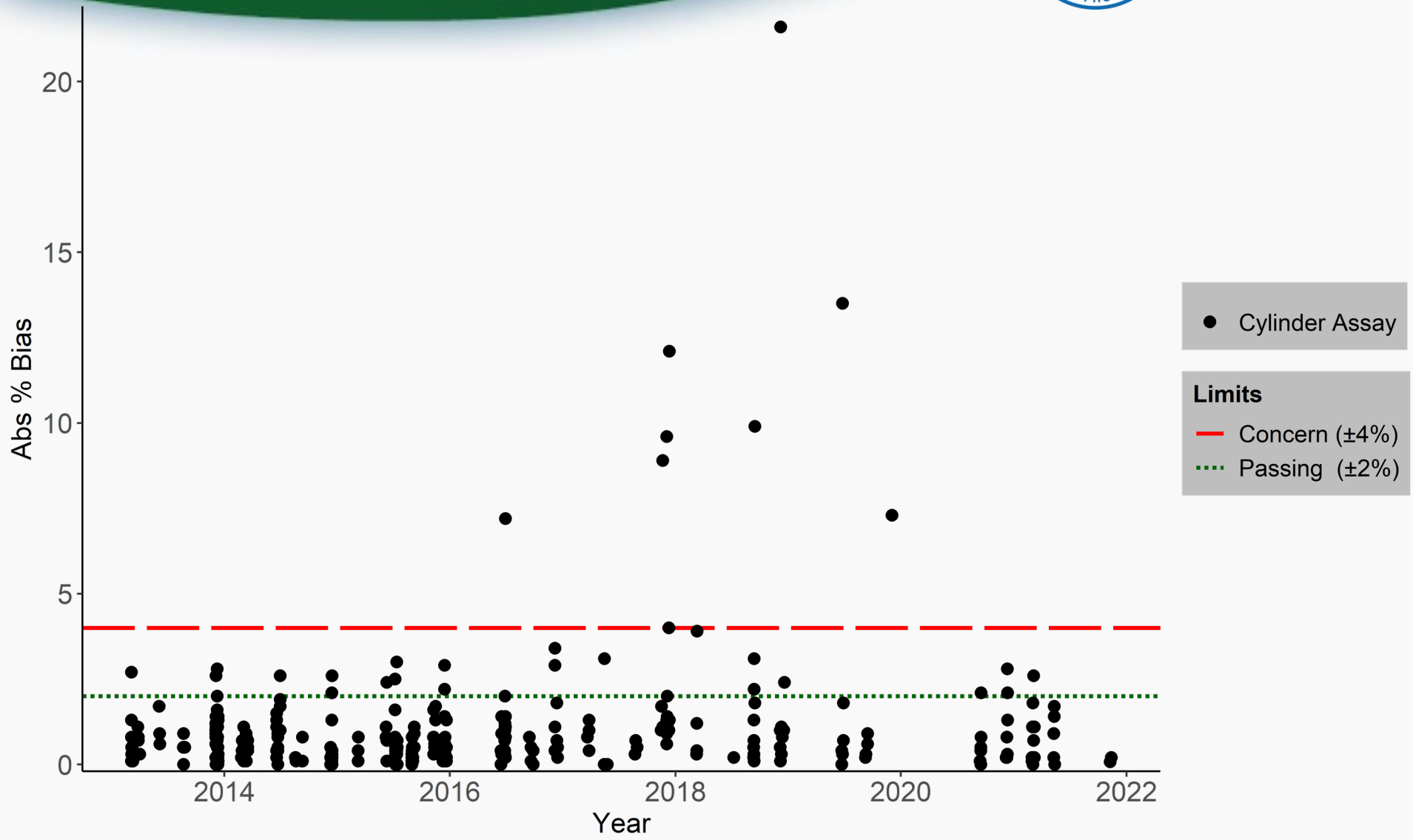


Milestones:

- 1978 EPA Traceability Protocol ***(2012 is current rev.)***
- 1985: EPA Protocol Gas Standards
- 1996: Hiatus in Verification Prog.
- EPA OAP Verifications ~ about every 3yr from 2010-2018 ***(not shown in Fig)***
- EPA OAQPS Verifications quarterly from 2010 – present **(2013 – present in fig)**

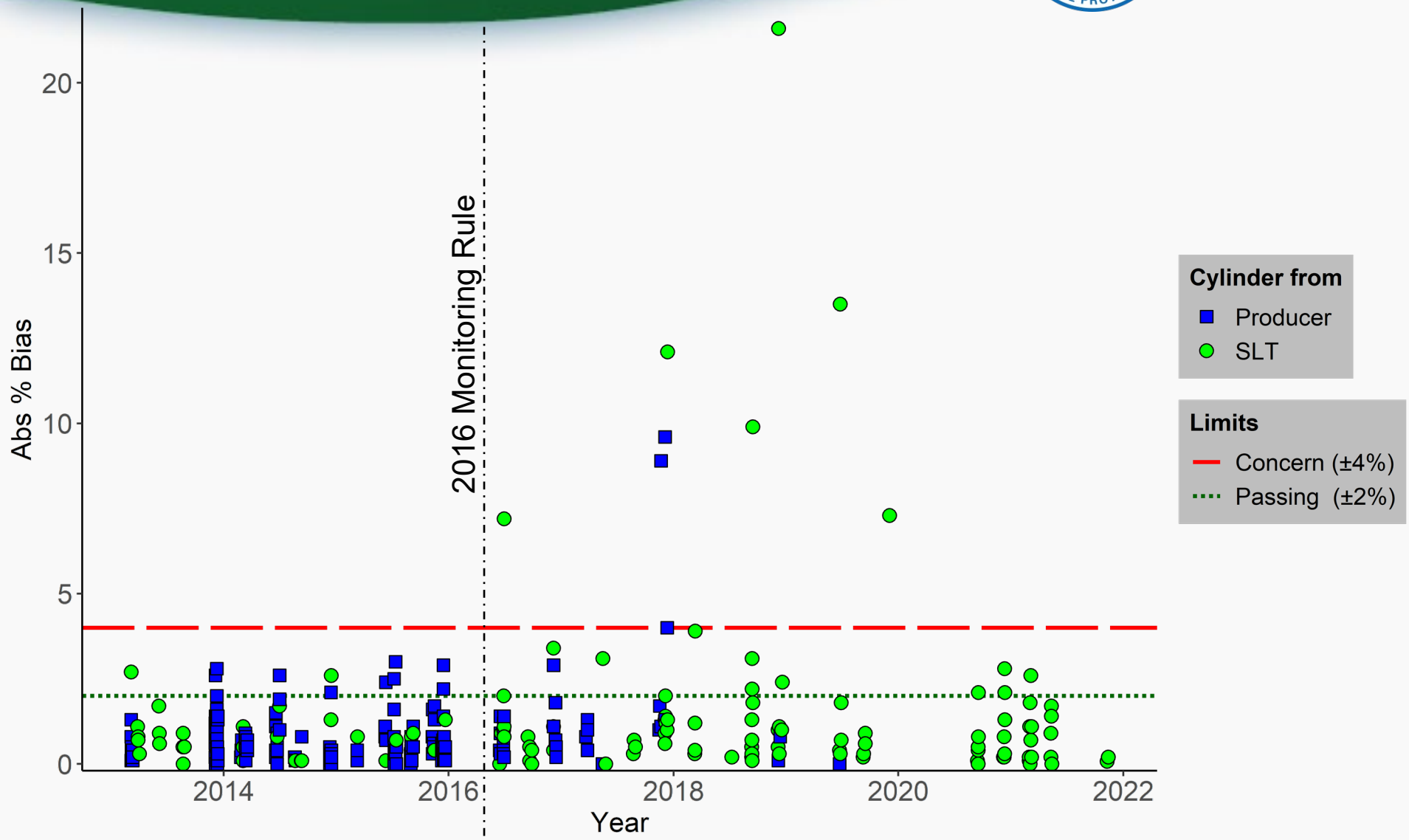
AA-PGVP Verfication Results

Timeseries 2013-2021



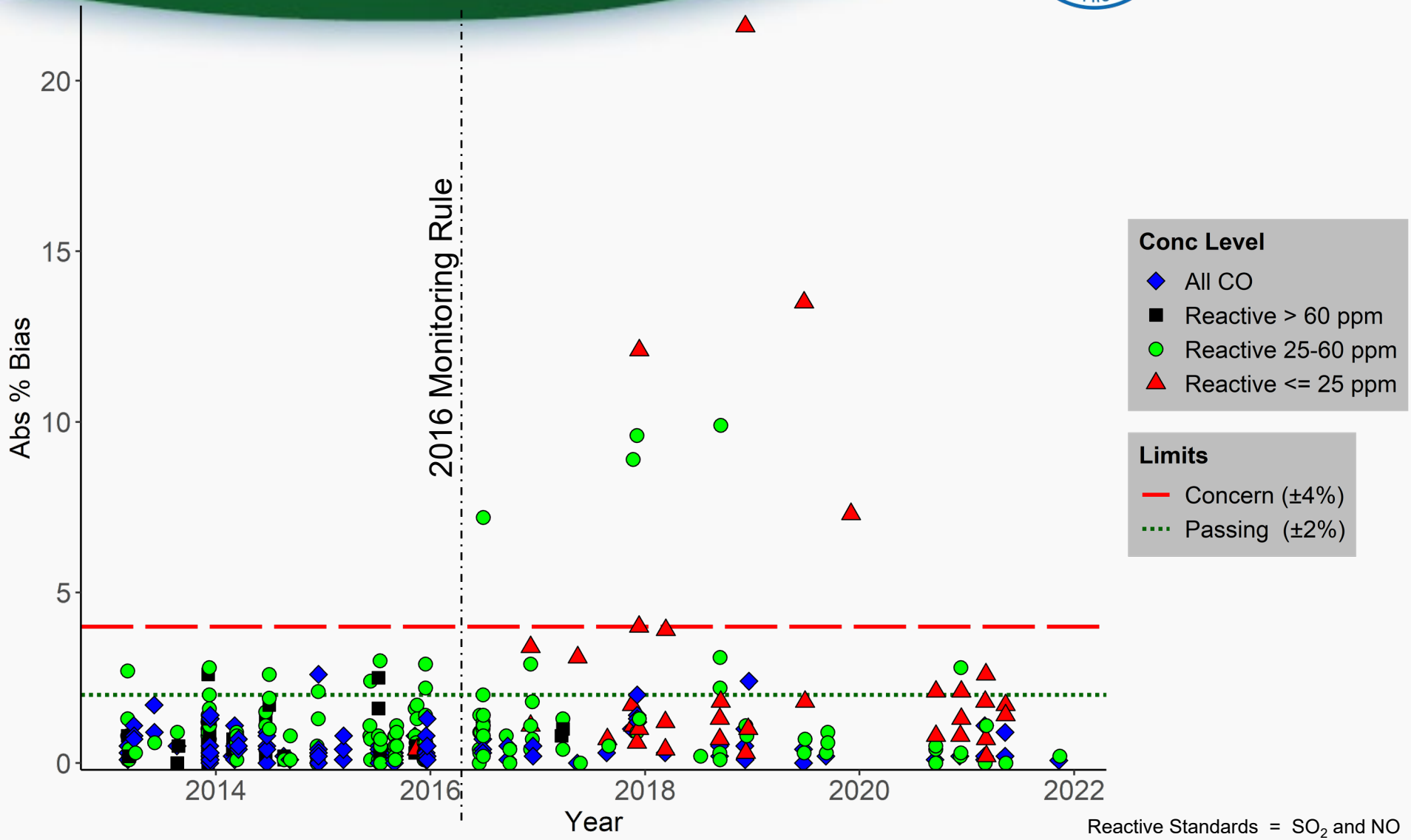
AA-PGVP Verfication Results

Timeseries 2013-2021 (by Cylinder Owner)



AA-PGVP Verfication Results

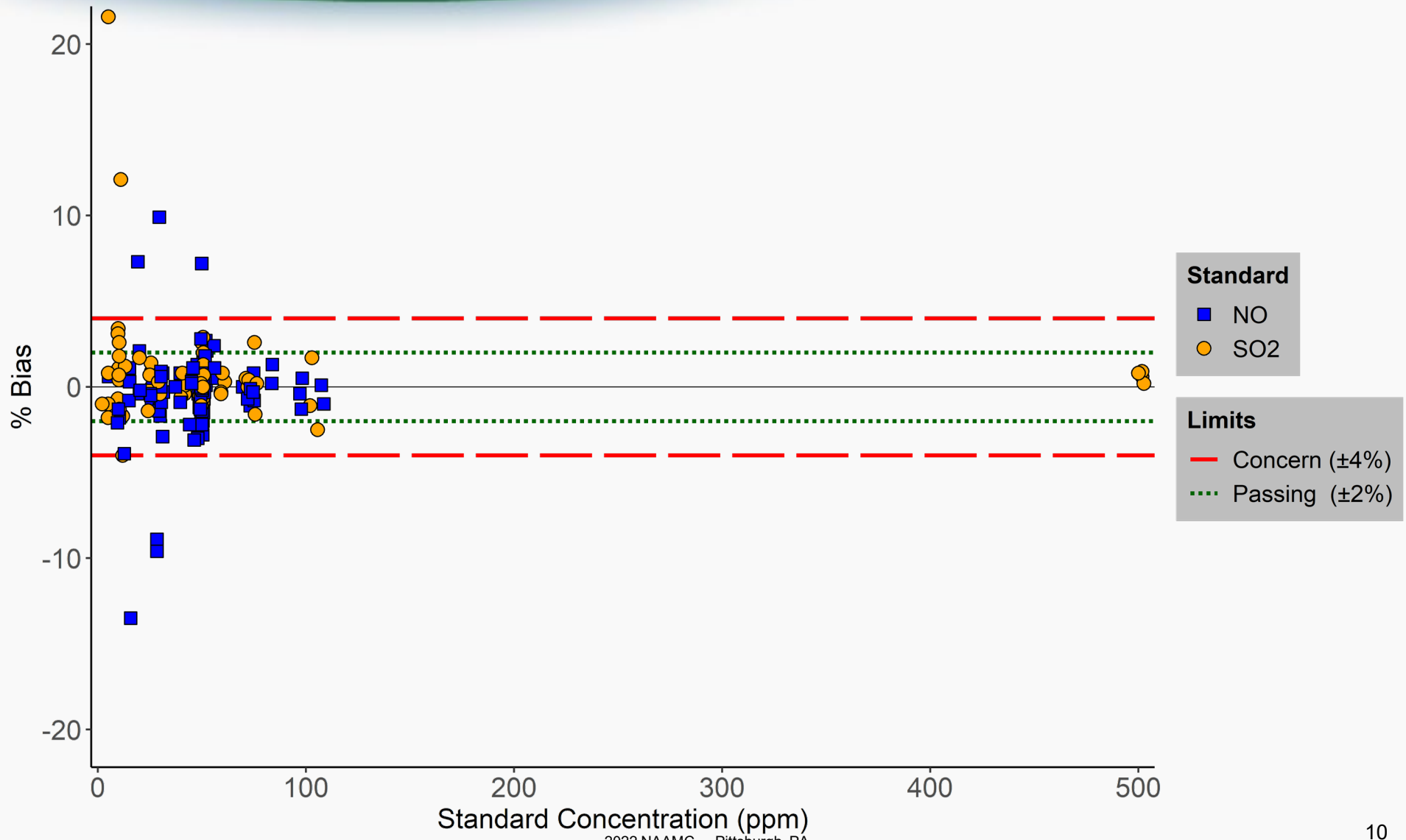
Timeseries 2013-2021 (by Cylinder Standard Type)



Reactive Standards = SO_2 and NO

AA-PGVP Verfication Results

Bias in NO & SO_2 gas standards by concentration



NO_2 Stability Concerns

Long term stability of standard in compressed gas cylinders

- **OAQPS 2/25/2022 Memo:**
  EPA Protocol Gas Long-Term Stability Requirements
  - **Clarifies that NO_2 is not currently a Protocol Gas Standards until further notice.**

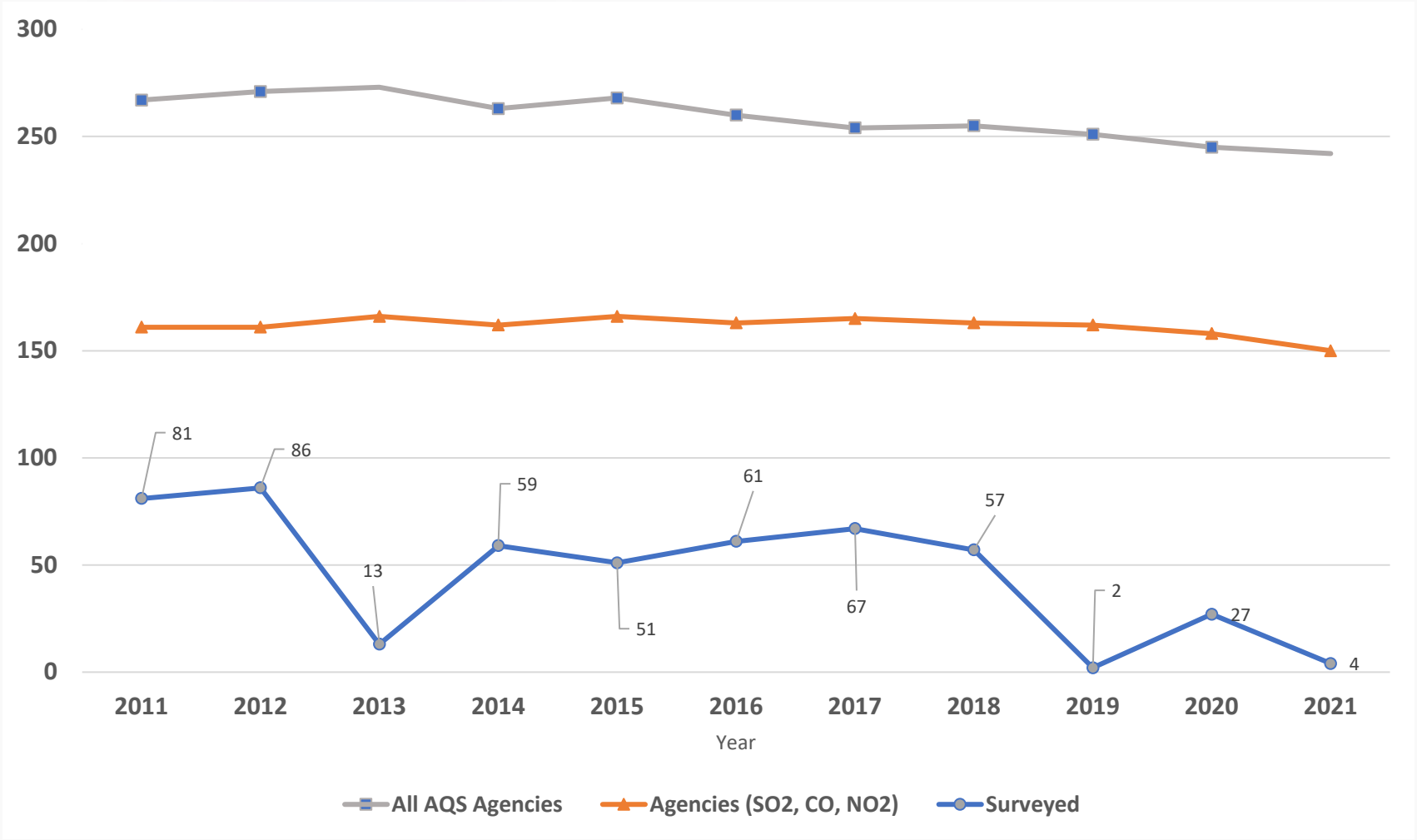
- **EURAMET study in 2021 (*Metrology for Nitrogen Dioxide*) determines NO_2 standards from National Metrology Institutes vary in quality and are not stable.**

- **2012 Traceability Protocol lacks stability data to establish the maximum certification period for NO_2.**
- **NIST SRMs not available for NO_2. Must obtain PRMs from VSL (Netherlands)**
- **EPA Verification:**
  - **NPAP does not assess performance of Direct Read NO_2 FEMs.**
  - **AA-PGVP currently lacks equipment and standards needed for performing verification assays.**

- **EPA ORD is actively working to revise the Traceability Protocol to establish testing and assay procedures for reactive gas standards like NO_2.**

AA-PGVP Annual Survey

Agency Participation



AA-PGVP Annual Survey

Agency Participation (Continued)

Problem:

- Survey historically hosted and maintained on a server and database separate from AQS
- Data from survey is difficult to relate back to monitoring networks in AQS
- Lack of validation on required data fields
- Lack of participation in survey

Solution:

- Enhance AQS to gather this data to support the AA-PGVP
- And discontinue the auxiliary annual survey mechanism

- EPA is very close to having this implemented.

AQS Enhancements for AA-PGVP
Timeline for Implementation

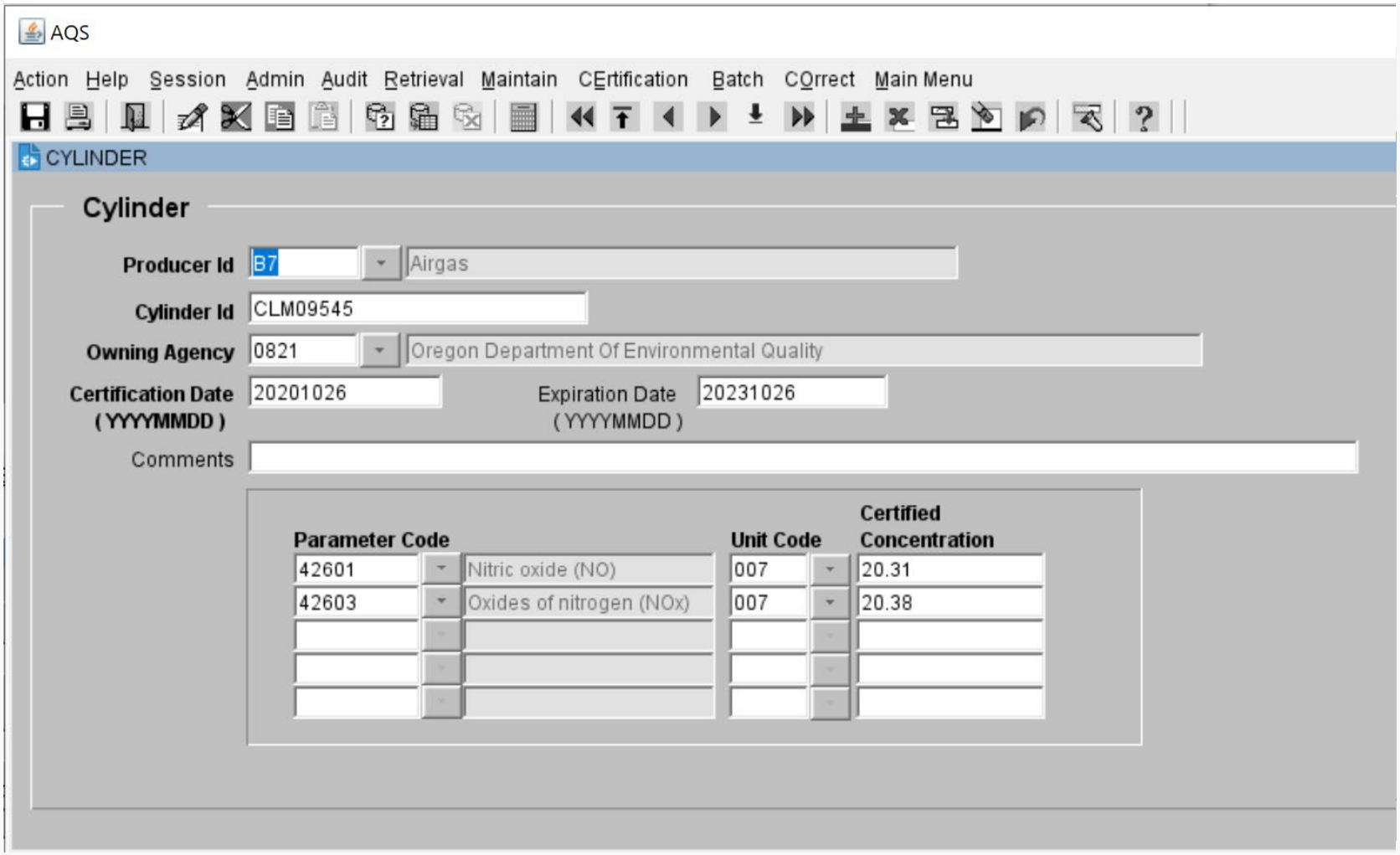
Ready Now	Soon	~August 2023
Cylinder Form	**Modify QA-Transaction** add Cyl-ID field to APE & 1pt Prec.	**Cylinder IDs become required for AQS QA-Transaction files**

- Currently 'Optional'
- but usage recommended
- EPA will be reaching out to SLTs through their Regional Offices to get the word out on this new AQS capability

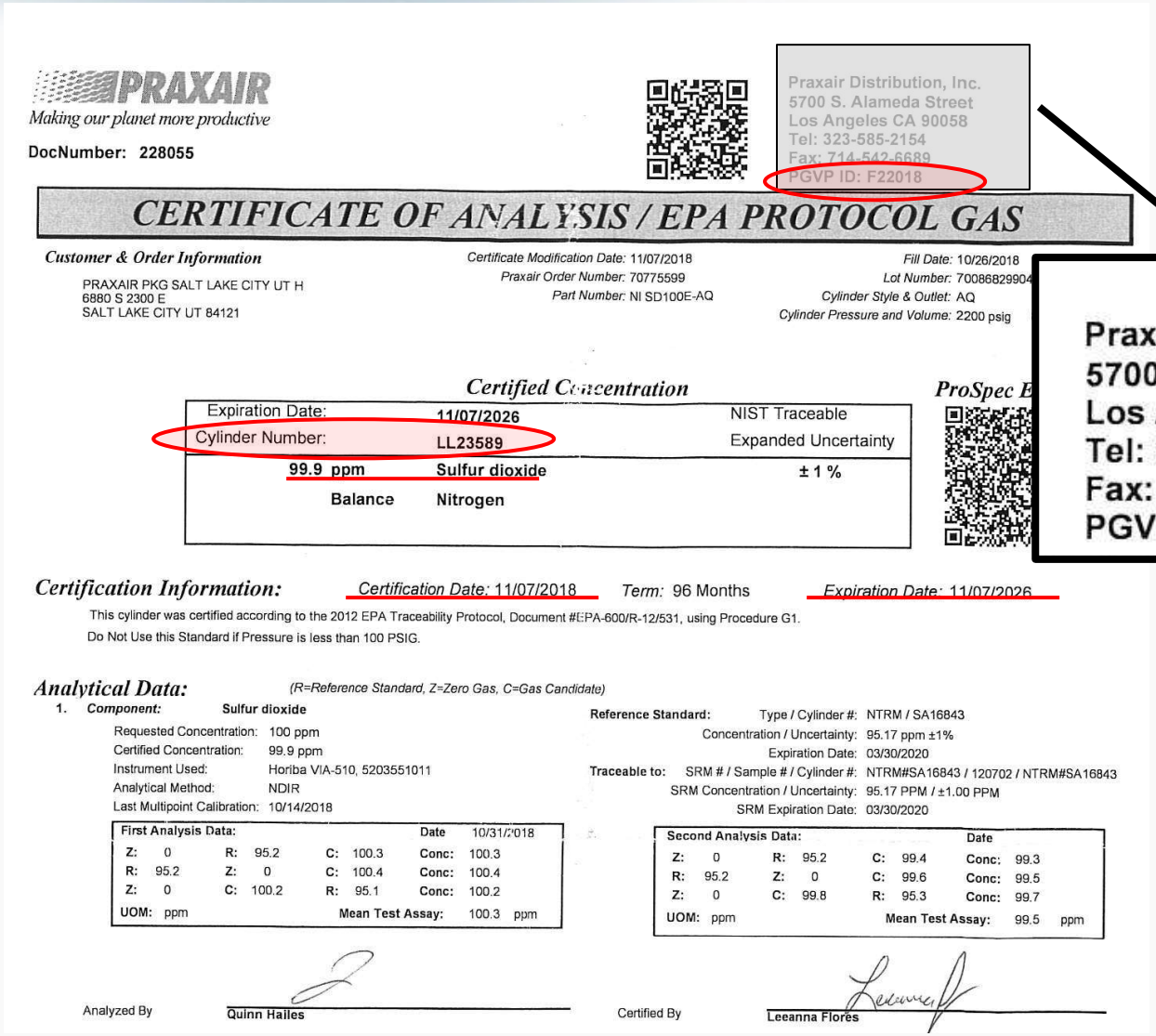
- Append field to QA-Trans. to accept Cyl-ID for APE & 1pt Prec.
- Cyl-ID field on QA-Trans. will be 'Optional' for 9mo to 1yr
- AQS will report 'warning' if Cyl-ID is not present

- Cyl-ID required on Cylinder Form and QA-Trans. for APE and 1pt Prec.
- AQS will report an 'error' and not load APE and 1pt Prec. QA-Transaction records where the Cyl-ID is not present

AQS Enhancements for AA-PGVP
*Maintain * Cylinder Form*



Certificate of Analysis (COA) showing *fields needed on AQS Cylinder Form*



PRAXAIR
Making our planet more productive

DocNumber: 228055

Praxair Distribution, Inc.
5700 S. Alameda Street
Los Angeles CA 90058
Tel: 323-585-2154
Fax: 714-542-6689
PGVP ID: F22018

CERTIFICATE OF ANALYSIS / EPA PROTOCOL GAS

Customer & Order Information

PRAXAIR PKG SALT LAKE CITY UT H
6880 S 2300 E
SALT LAKE CITY UT 84121

Certificate Modification Date: 11/07/2018
Praxair Order Number: 70775599
Part Number: NI SD100E-AQ

Fill Date: 10/26/2018
Lot Number: 70086829904
Cylinder Style & Outlet: AQ
Cylinder Pressure and Volume: 2200 psig

Certified Concentration

Expiration Date:	11/07/2026	NIST Traceable
Cylinder Number:	LL23589	Expanded Uncertainty
99.9 ppm	Sulfur dioxide	± 1 %
Balance	Nitrogen	

ProSpec E

Praxair Distribution, Inc.
5700 S. Alameda Street
Los Angeles CA 90058
Tel: 323-585-2154
Fax: 714-542-6689
PGVP ID: F22018

Certification Information: *Certification Date:* 11/07/2018 *Term:* 96 Months *Expiration Date:* 11/07/2026

This cylinder was certified according to the 2012 EPA Traceability Protocol, Document #EPA-600/R-12/531, using Procedure G1.
Do Not Use this Standard if Pressure is less than 100 PSIG.

Analytical Data: *(R=Reference Standard, Z=Zero Gas, C=Gas Candidate)*

1. *Component:* Sulfur dioxide

Requested Concentration: 100 ppm
Certified Concentration: 99.9 ppm
Instrument Used: Horiba VIA-510, 5203551011
Analytical Method: NDIR
Last Multipoint Calibration: 10/14/2018

First Analysis Data:					Date	10/31/2018
Z: 0	R: 95.2	C: 100.3	Conc: 100.3			
R: 95.2	Z: 0	C: 100.4	Conc: 100.4			
Z: 0	C: 100.2	R: 95.1	Conc: 100.2			
UOM: ppm			Mean Test Assay:	100.3	ppm	

Reference Standard: Type / Cylinder #: NTRM / SA16843
Concentration / Uncertainty: 95.17 ppm ±1%
Expiration Date: 03/30/2020
Traceable to: SRM # / Sample # / Cylinder #: NTRM#SA16843 / 120702 / NTRM#SA16843
SRM Concentration / Uncertainty: 95.17 PPM / ±1.00 PPM
SRM Expiration Date: 03/30/2020

Second Analysis Data:					Date	
Z: 0	R: 95.2	C: 99.4	Conc: 99.3			
R: 95.2	Z: 0	C: 99.6	Conc: 99.5			
Z: 0	C: 99.8	R: 95.3	Conc: 99.7			
UOM: ppm			Mean Test Assay:	99.5	ppm	

Analyzed By: Quinn Hailes
Certified By: Leeanna Flores

For this Certificate enter PGVP ID = "F2" On the AQS Maintain Cylinder Form

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Questions?