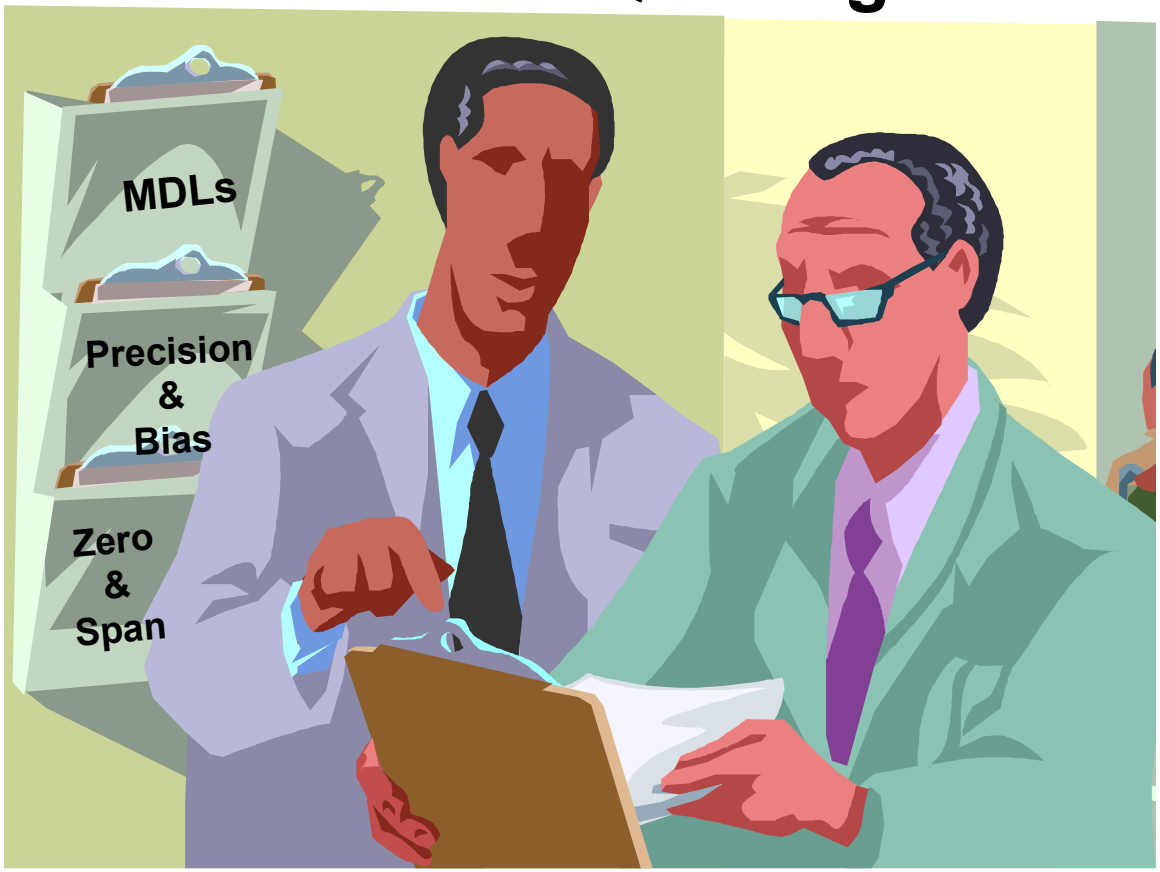
Precursor Gas QA Program



Mike Papp, November Ambient Air Monitoring Meeting, Las Vegas NV

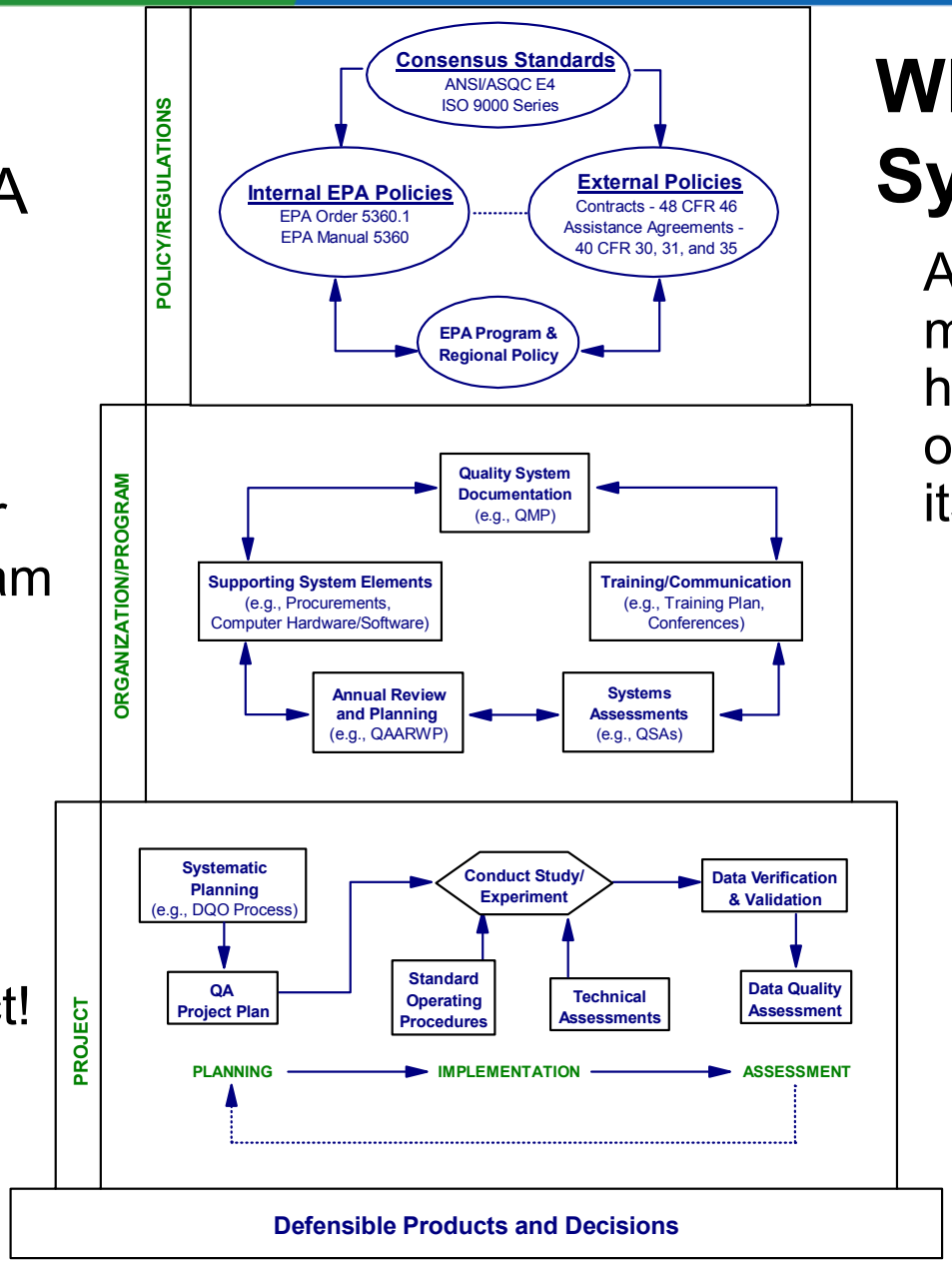
Outline

- Quality System Development
  - Data Quality Objectives
  - Measurement Quality Objectives & Calculations
  - Assessment Activities
    - Precision and Bias
    - NCore Linkage with NPAP TTP
- Monitoring Org QA responsibilities
  - Preliminary Data Collection
  - QAPP/SOP Development
- Timetable

EPA

Your Program

The Project!



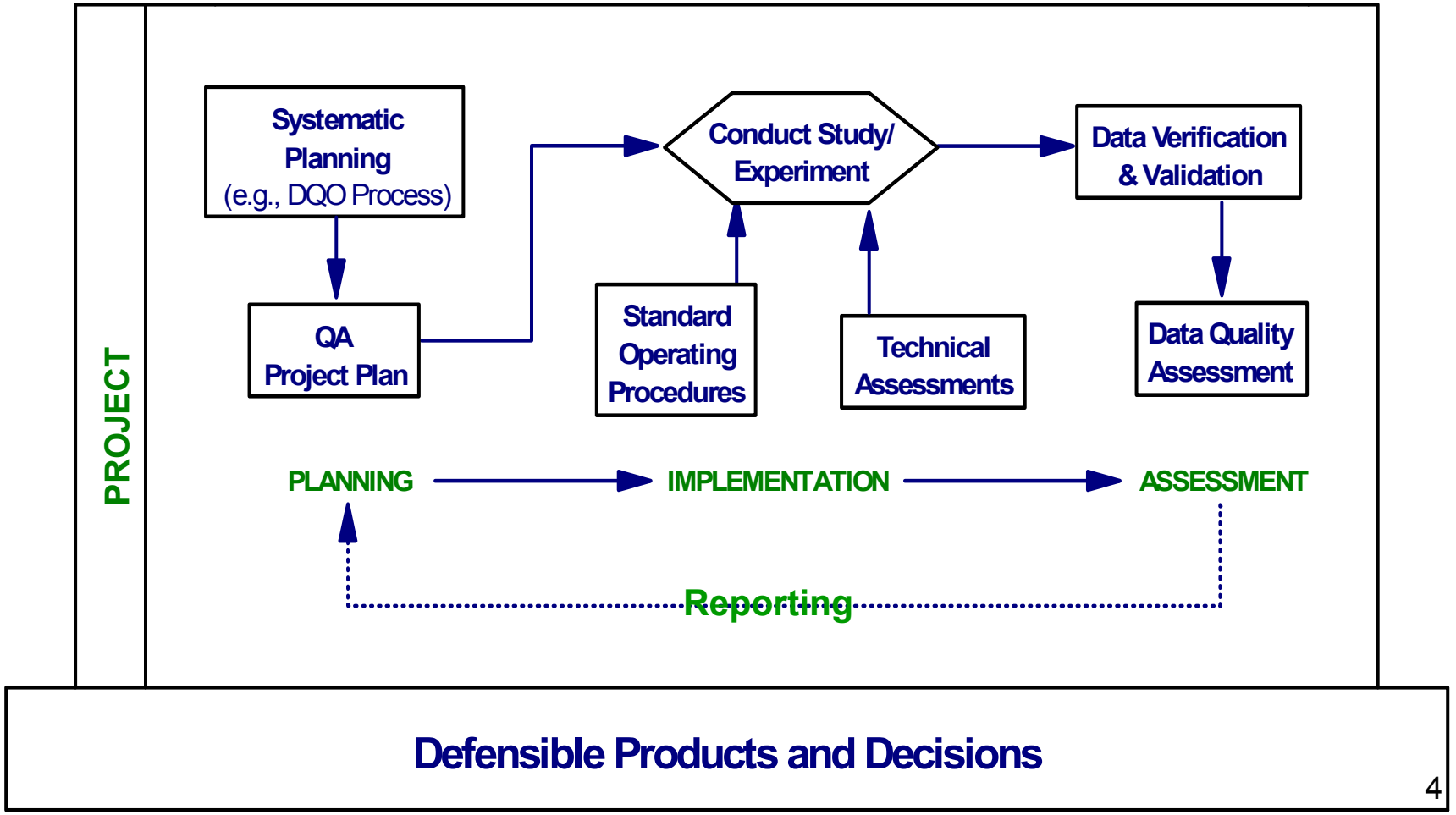
What is a Quality System ?

A structured and documented management system describing how and by whom an organization assures quality in its work.

Quality System Goals

- Make correct decisions
- Optimize resource use

Where are we?


PROJECT
Systematic Planning (e.g., DQO Process)
QA Project Plan
Conduct Study/ Experiment
Standard Operating Procedures
Technical Assessments
Data Verification & Validation
Data Quality Assessment
PLANNING
IMPLEMENTATION
ASSESSMENT
Reporting
Defensible Products and Decisions

1st Stop Systematic Planning The DQOs

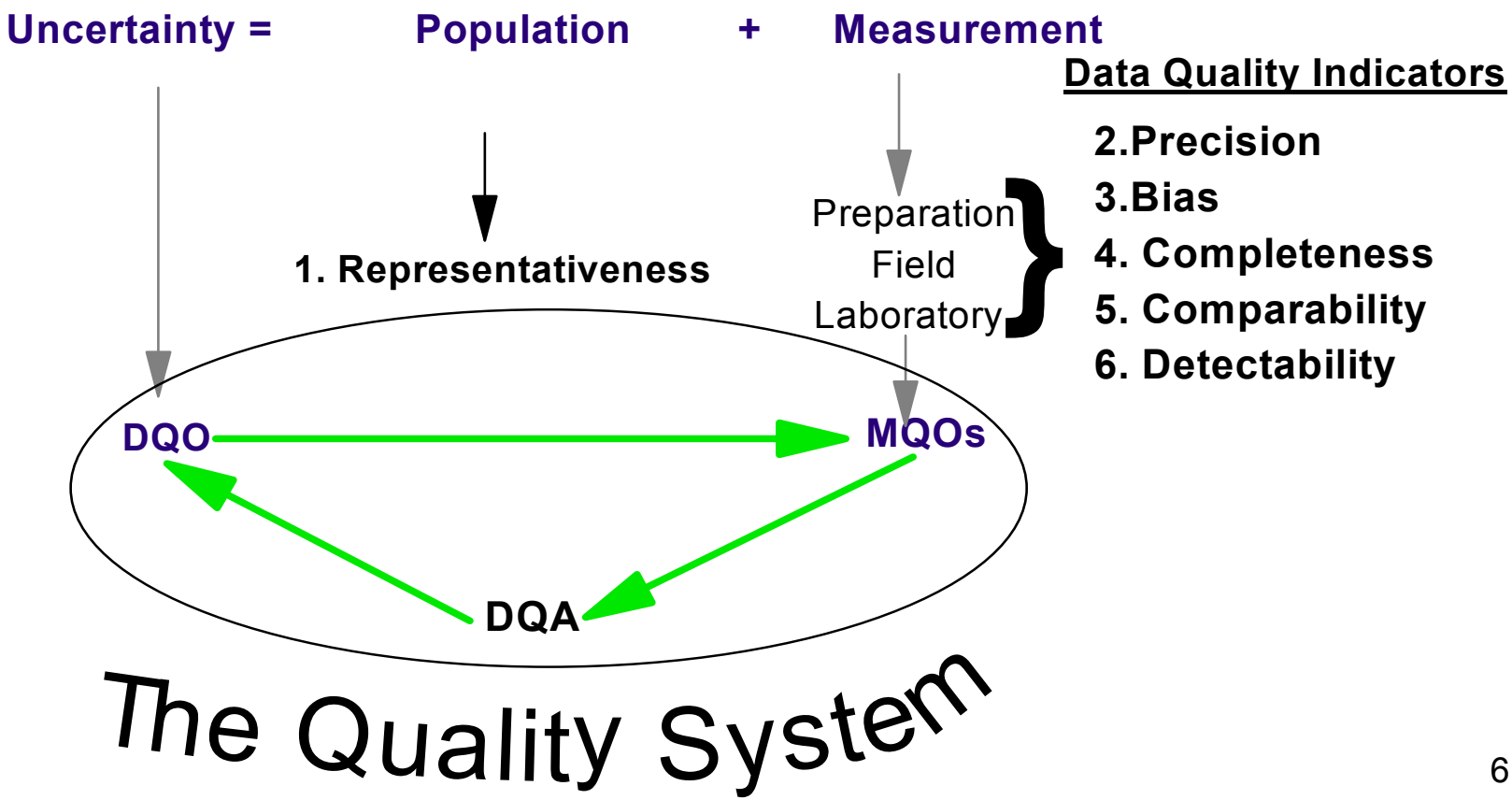
Designed to answer:

- What do you need?
- Why do you need it?
- How will you use it?
- What is your tolerance for errors?

Underlying Principles:

- All collected data have error.
- Nobody can afford absolute certainty.

Understanding and Controlling Uncertainty in Order to Minimize Decision Errors



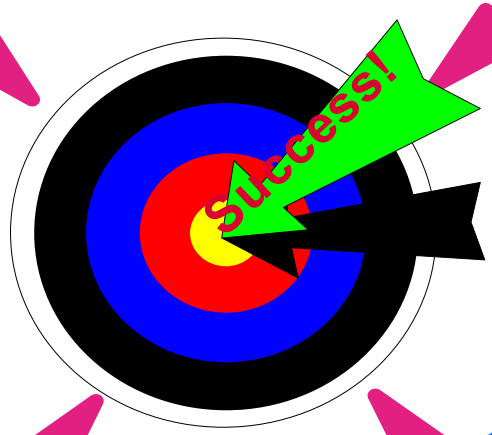
DQO Promotes Communication

Decision Maker

Problem
Decision
Error Tolerance
Resources
Time

Technical Expert

Methods
Expertise
Logistics
Implementation



QA Expert

DQOs
Quality system development
Measurement quality

Uncertainties
Statistical sample design
Achievable error limits

DQO Game Plan

- Formed Workgroup – May, 2005
  - Moved through steps 1-5
- 3-Primary Objectives Identified
  - Trends/Accountability- progress on pollution reduction
  - CMAQ model comparison
  - Health evaluations
- Steps 6 & 7 Evaluation/Optimization
  - Gathered data on population and measurement uncertainty
  - Evaluated population and measurement uncertainty parameters
  - Played the “what-if” games

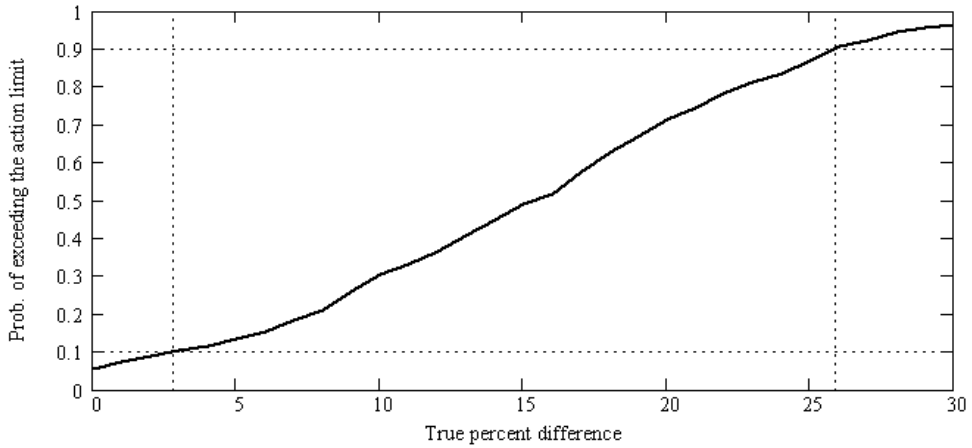
DQO Games

Table 3.1.1 DQO input parameters for benzene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.5	85%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.044	0.128

Table 3.1.2 DQO output parameters for benzene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
6%	3%	3% - 26%



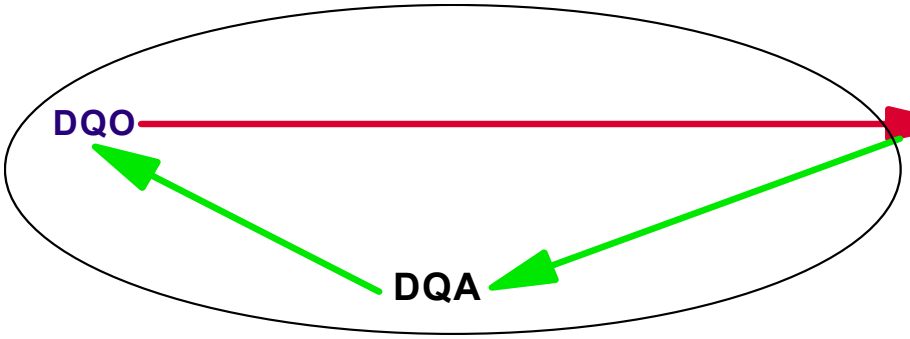
Example of the NATTS DQOs

Figure 3.1.1 Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in urban locations of the Pilot Study

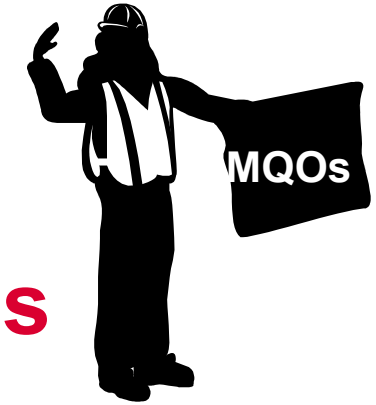
DQO Table for Precursor Gas Parameters

			Power to detect at an individual stite		Power to detect at multiple rural or urban sites		Multiplicative half-width for a 95% daily prediction interval at an individual site.
Annual ompleteness	Hourly Measurement Precision (CV)	Measurement bias	5% Annual Trend	10% Annual Trend	5% Annual Trend	10% Annual Trend	
90%	7%	5%					
		10%					
		20%					
	10%	5%					
		10%					
		20%					
	15%	5%					
		10%					
		20%					
	20%	5%					
		10%					
		20%					
75%	7%	5%					
		10%					
		20%					
	10%	5%					
		10%					
		20%					
	15%	5%					
		10%					
		20%					
	20%	5%					
		10%					
		20%					

2nd Stop of Systematic Planning Measurement Quality Objectives



MQOs



MQOs-The quality control samples and/or performance criteria that provide for an estimate of a data quality indicator for:

- the overall data collection effort
- a measurement phase

Performance criteria is established to:

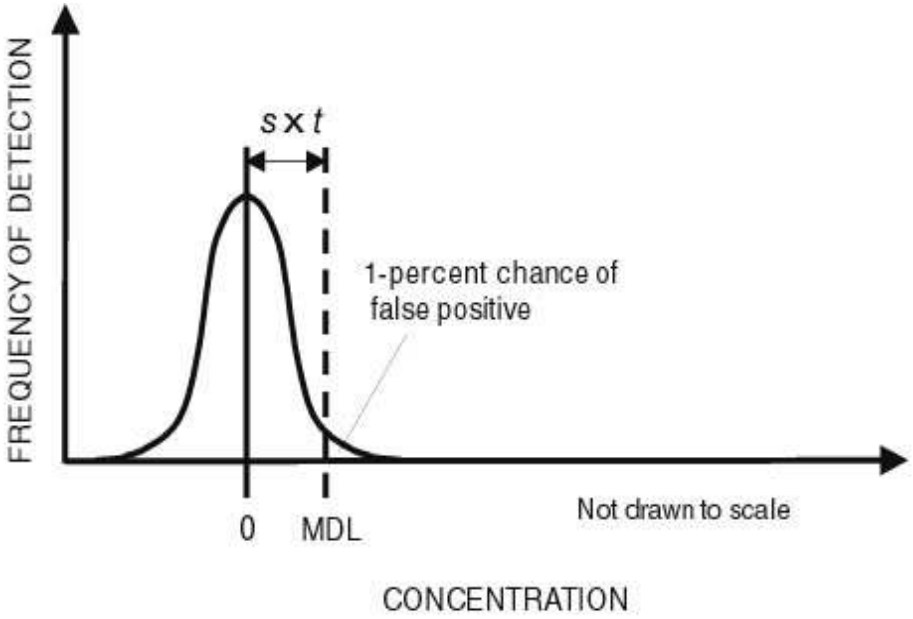
- control data quality
- to meet program DQOs
- can be used to develop validation templates

Data quality indicators used to establish the MQOs

Data Quality Indicator	QC Type	Comment
Detectability	MDL standard	40 CFR Part 136 App B
Precision	1 Point QC Check	90% Upper Confidence Limit of CV
Bias	1 Point QC Check	95% Upper Confidence Limit Absolute Value
Completeness	Routine Data	Percentage Collected from Expected

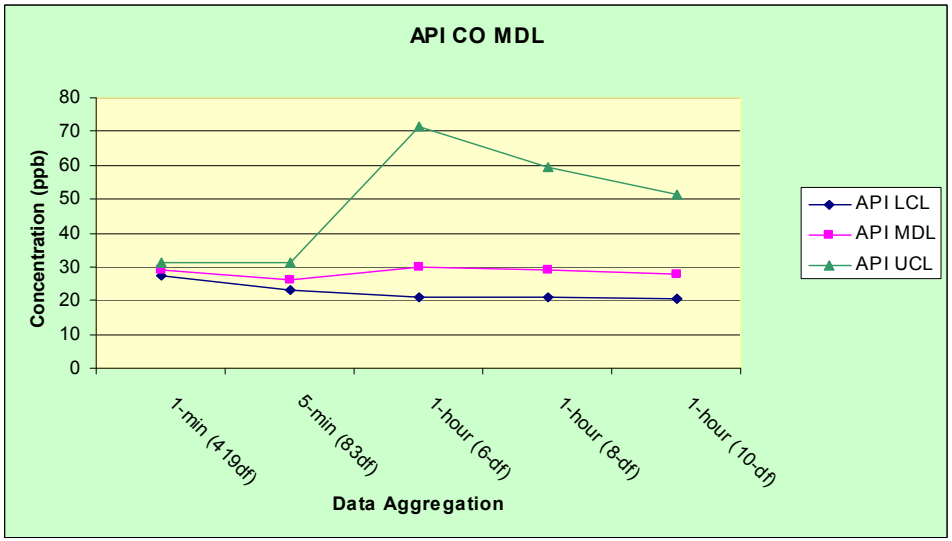
Detectability

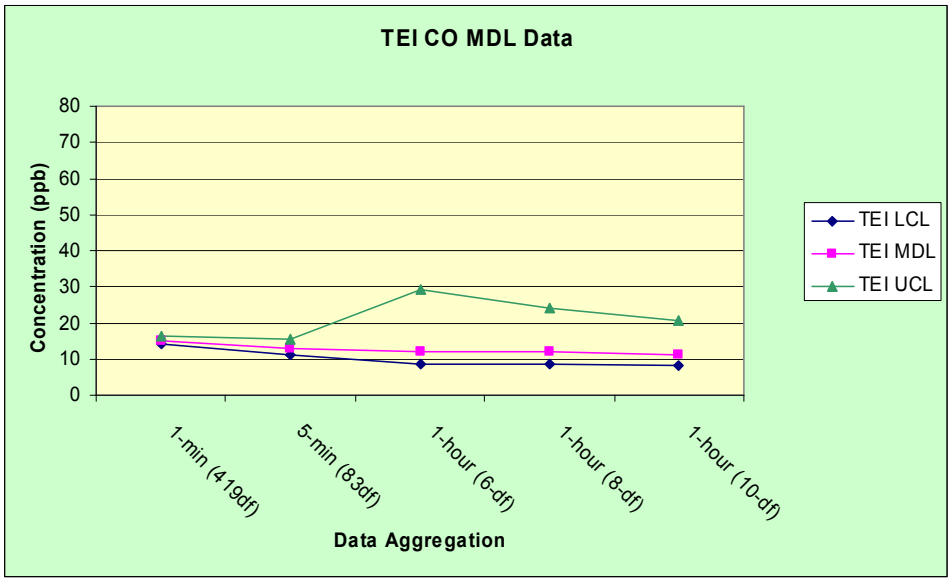
- Detection limit is important for this program
- EPA recommends that monitoring orgs. perform MDLs
  - Using 40 CFR Part 136 App B as a start
  - MDL under routine conditions
  - Minimum of 7 values
  - Consistency in method implementation is key for comparison



MDL: *the minimum concentration of a substance that can be measured and reported with 99% confidence that the concentration is greater than zero*

CO MDL Data





- Collected 1 hour data over 7 days (1-minute values)
- Developed MDL estimates on:
  - 1 minute (420 values)
  - 5 minute (84 values)
  - 1 hour (7 values)
- Conclusions
  - Suggest using 1-hour MDLs
  - Degrees of freedom important.
    - More 1-hour values over more days provide better confidence in MDL.

Precision and Bias

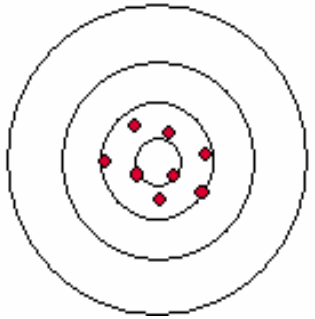
Estimates start the same way &
both use the 1-point QC check

Y_i: Monitor value

X : Target concentration (standard)

d_i : Percent Difference (individual bias)

$$d_i = \frac{Y_i - X}{X} \cdot 100$$



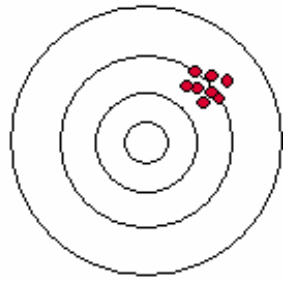
Precision

"A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions"

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1,n-1}}}$$

** Where $\chi^2_{0.10,(n-1)}$ is the 10th percentile of a Chi-Squared Distribution*

This represents a 90% upper confidence limit on the CV estimate



Bias

"A systematic or persistent distortion of a measurement process which causes errors in one direction"

Absolute Bias Point Estimate:

$$m_{abs} = \frac{1}{n} \cdot \sum_{i=1}^{n} |d_i|$$

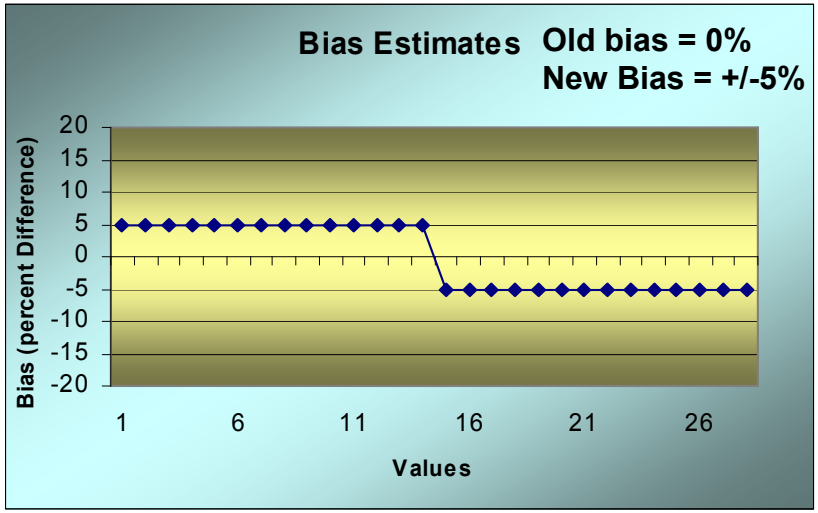
Absolute Bias Upper Bound:

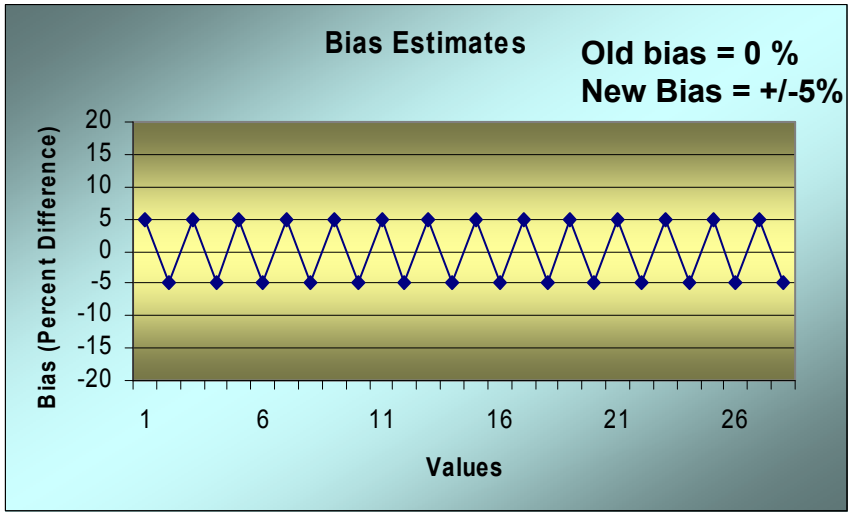
$$bias = m_{abs} + t_{0.95,(n-1)} \cdot \frac{s_{d\_abs}}{\sqrt{n}}$$

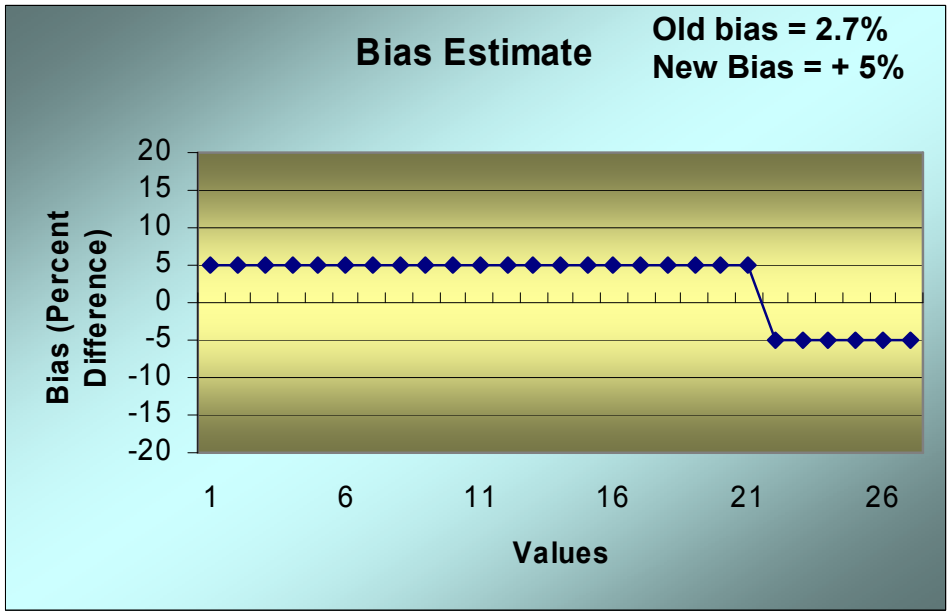
Where $t_{0.95,(n-1)}$ is the 95th quantile of a Student's t distribution with n-1 df and s_{d_abs} is the standard deviation of the absolute value of the relative percent differences

This represents a 95% upper confidence limit on the Bias estimate

Bias Illustrations

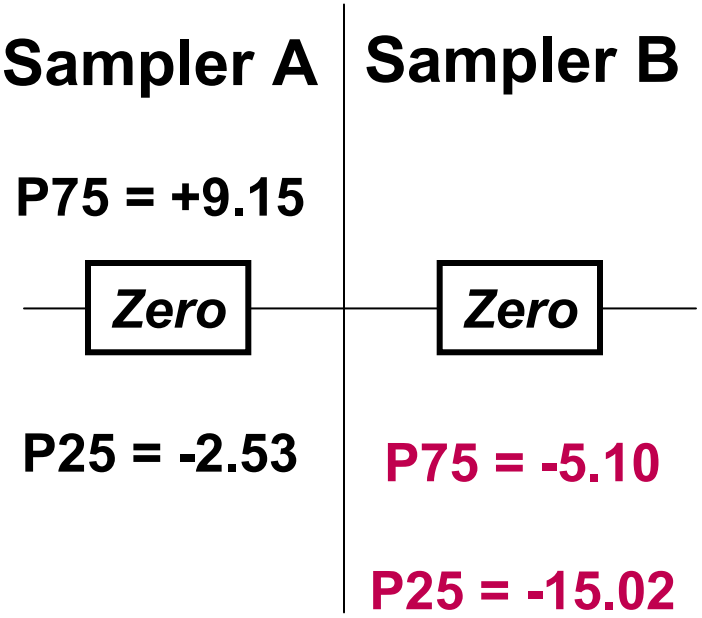






Associating a Sign to the Absolute Bias

A sign (+/-) is associated with the absolute bias only if the 25th and 75th percentiles of the percent differences have the ***same sign***



BIAS (%)

CO (Sampler A):	
OLD BIAS	**NEW BIAS**
3.91	**+/- 8.03**
CO (Sampler B):	
OLD BIAS	**NEW BIAS**
-10.36	**-11.35**

Not to Worry

- OAQPS has developed:
  - A guidance document of the statistics
    - Rationale for the statistics
    - Excel spreadsheets (DASC) and examples
  - AMP 255 Report
  - Calculated in the DAS systems?

EPA United States Environmental Protection Agency

Office of Air Quality Planning and Standards

DASC (Data Assessment Statistical Calculator)

P&B Guidance and Data Assessment Statistical Calculator (DASC) Software

Gaseous Assessments

Site: *{Enter Site ID or Name Here}*

Step 1	Step 2
Pick a Pollutant	*Pick a Statistic to Calculate*
Automated Methods	(•) Precision Estimate
(•) SO2	( ) Bias Estimate
( ) NO2	( ) Absolute Bias Estimate
( ) O3	( ) Semi-Annual Flow Rate
( ) CO	( ) One-Point Flow Rate
( ) PM 2.5	
( ) PM10	
( ) PM 10-2.5	
Manual Methods	***Step 3***
( ) PM 2.5	
( ) PM 10	Go To Worksheet
( ) PM 10-2.5	
( ) Lead	

Site ID: Burdens | **Pollutant type: NOy API** | **CV_ub (%)** | **Bias (%)**

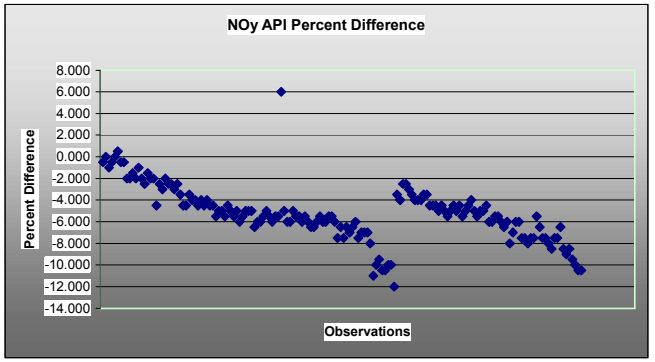
Meas Val (Y)	Audit Val (X)	d (Eqn. 1)	25th Percentile	d_sqrd	d_abs	d_abs ^2
19.9	20	-0.500	-6.500	0.250	0.500	0.250
20	20	0.000	75th Percentile	0.000	0.000	0.000
19.8	20	-1.000	-4.000	1.000	1.000	1.000
19.9	20	-0.500		0.250	0.500	0.250
20	20	0.000		0.000	0.000	0.000
20.1	20	0.500		0.250	0.500	0.250
19.9	20	-0.500		0.250	0.500	0.250
19.9	20	-0.500		0.250	0.500	0.250
19.6	20	-2.000		4.000	2.000	4.000
19.6	20	-2.000		4.000	2.000	4.000
19.7	20	-1.500		2.250	1.500	2.250
19.6	20	-2.000		4.000	2.000	4.000
19.8	20	-1.000		1.000	1.000	1.000
19.6	20	-2.000		4.000	2.000	4.000
19.5	20	-2.500		6.250	2.500	6.250
19.7	20	-1.500		2.250	1.500	2.250
19.6	20	-2.000		4.000	2.000	4.000
19.6	20	-2.000		4.000	2.000	4.000
19.1	20	-4.500		20.250	4.500	20.250
19.5	20	-2.500		6.250	2.500	6.250
19.4	20	-3.000		9.000	3.000	9.000
19.6	20	-2.000		4.000	2.000	4.000
19.5	20	-2.500		6.250	2.500	6.250
19.5	20	-2.500		6.250	2.500	6.250
19.4	20	-3.000		9.000	3.000	9.000
19.5	20	-2.500		6.250	2.500	6.250
19.3	20	-3.500		12.250	3.500	12.250
19.1	20	-4.500		20.250	4.500	20.250
19.1	20	-4.500		20.250	4.500	20.250
19.3	20	-3.500		12.250	3.500	12.250
19.2	20	-4.000		16.000	4.000	16.000
19.2	20	-4.000		16.000	4.000	16.000
19.1	20	-4.500		20.250	4.500	20.250
19.2	20	-4.000		16.000	4.000	16.000

n	st dev(d)	st dev (d^2)	sum(d_abs)	"AB" (Eqn 3a)
162	2.544	27.349	863.500	5.330
n-1	**sum(d)**	**sum(d^2)**	**sum(d_abs^2)**	**"AS" (Eqn 3b)**
161	-850.500	5507.250	5507.250	2.370

Bias (%) (Eqn 3)	Both Signs Positive
5.64	FALSE
Signed Bias (%)	**Both Signs Negative**
-5.64	TRUE

CV (%) (Eqn 2): 2.74

Upper Probability Limit	Lower Probability Limit
-0.26	-10.24



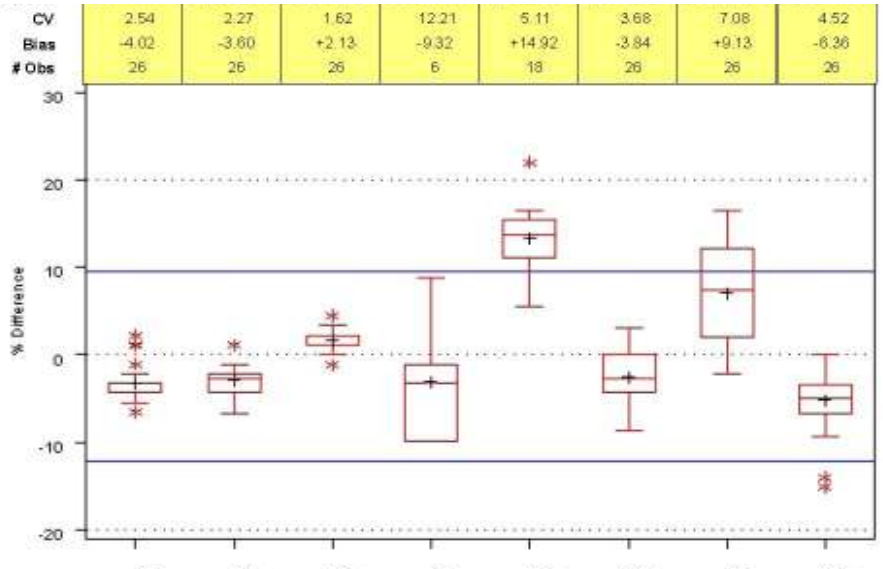
AMP 255 Report

Region	State	Agency	Site	CFR Lower Limit	CFR Upper Limit	Bias UB	CV UB
01	CT	0251	090010017	NA	NA	-2.17	0.77
01	CT	0251	090011123	NA	NA	4.15	4.88
01	CT	0251	090013007	NA	NA	-4.35	2.17
01	CT	0251	090019003	NA	NA	2.98	3.13
01	CT	0251	090031003	NA	NA	1.62	1.92
01	CT	0251	090070007	NA	NA	-3.95	1.96
01	CT	0251	090090027	NA	NA	0.60	0.84
01	CT	0251	090093002	NA	NA	-3.75	1.98
01	CT	0251	090110008	NA	NA	2.11	2.52
01	CT	0251	090131001	NA	NA	-4.04	1.22
01	CT	0251	All - NSP	-6.72	+3.53	-2.73	2.77
01	MA	0660	250010002	NA	NA	-1.61	1.35
01	MA	0660	250034002	NA	NA	+1.80	1.52
01	MA	0660	250051002	NA	NA	-2.99	0.61
01	MA	0660	250092006	NA	NA	-4.49	4.14
01	MA	0660	250094004	NA	NA	3.50	4.41
01	MA	0660	250095005	NA	NA	-1.64	1.9
01	MA	0660	250130008	NA	NA	1.73	2.11
01	MA	0660	250150103	NA	NA	+2.64	1.85
01	MA	0660	250154002	NA	NA	-4.84	2.14
01	MA	0660	250171102	NA	NA	-1.31	0.49
01	MA	0660	250213003	NA	NA	-1.32	1.13

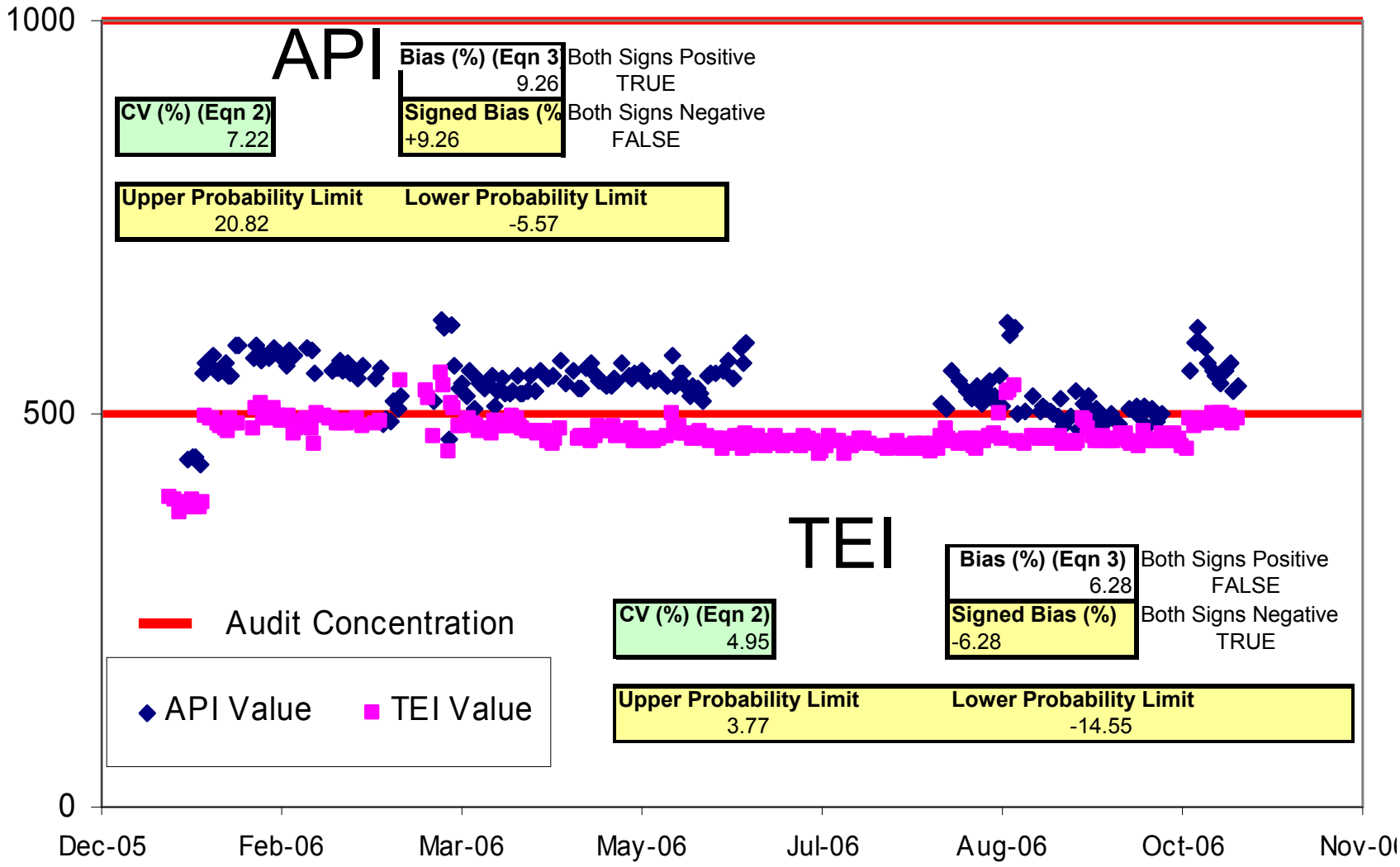
http://www.epa.gov/ttn/amtic/parslist.html

- Monitoring Orgs. Can run this as often as they wish
- OAQPS will run annually
- Box–and-whisker plots included in annual summary

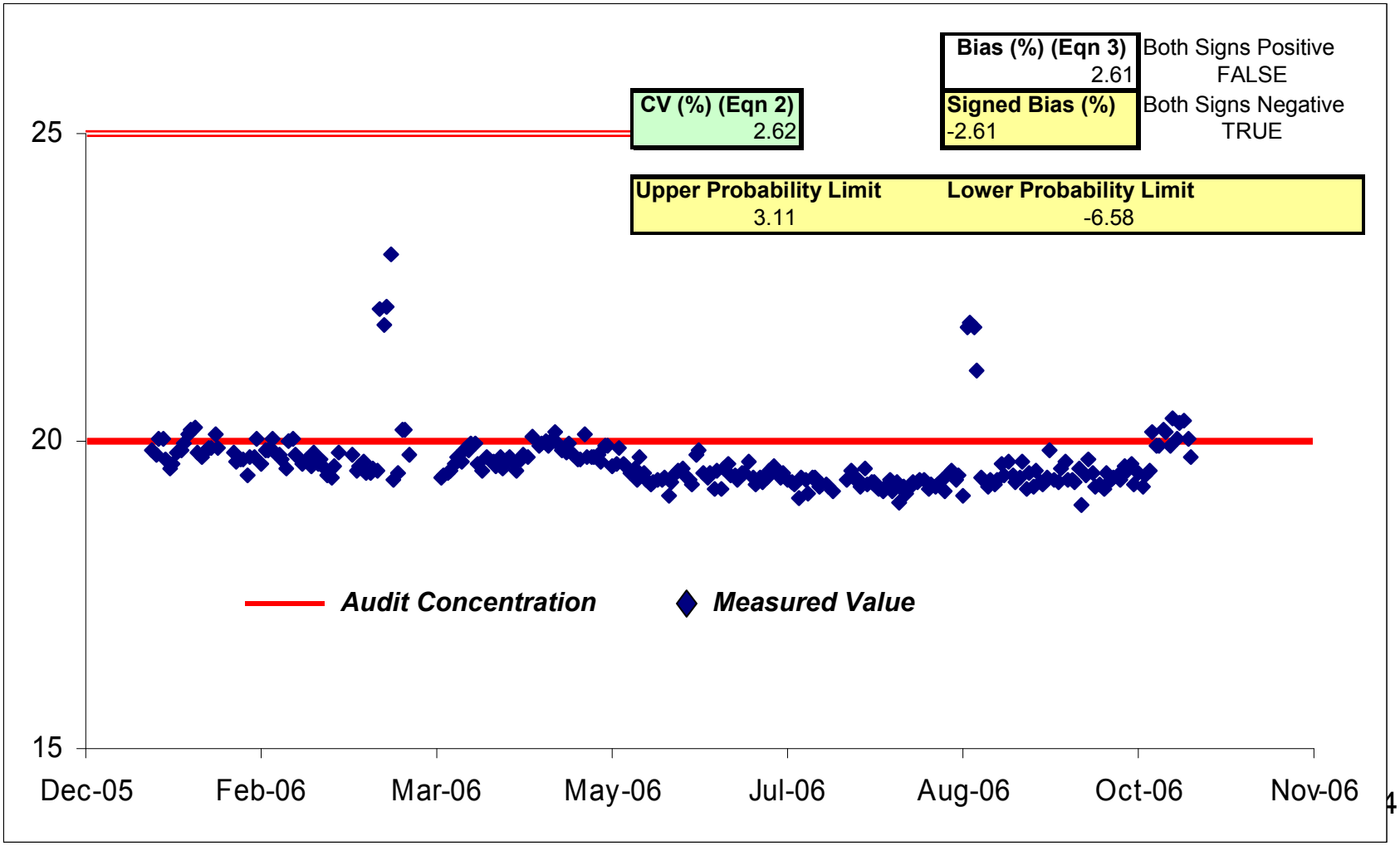
Box-& Whisker Plots



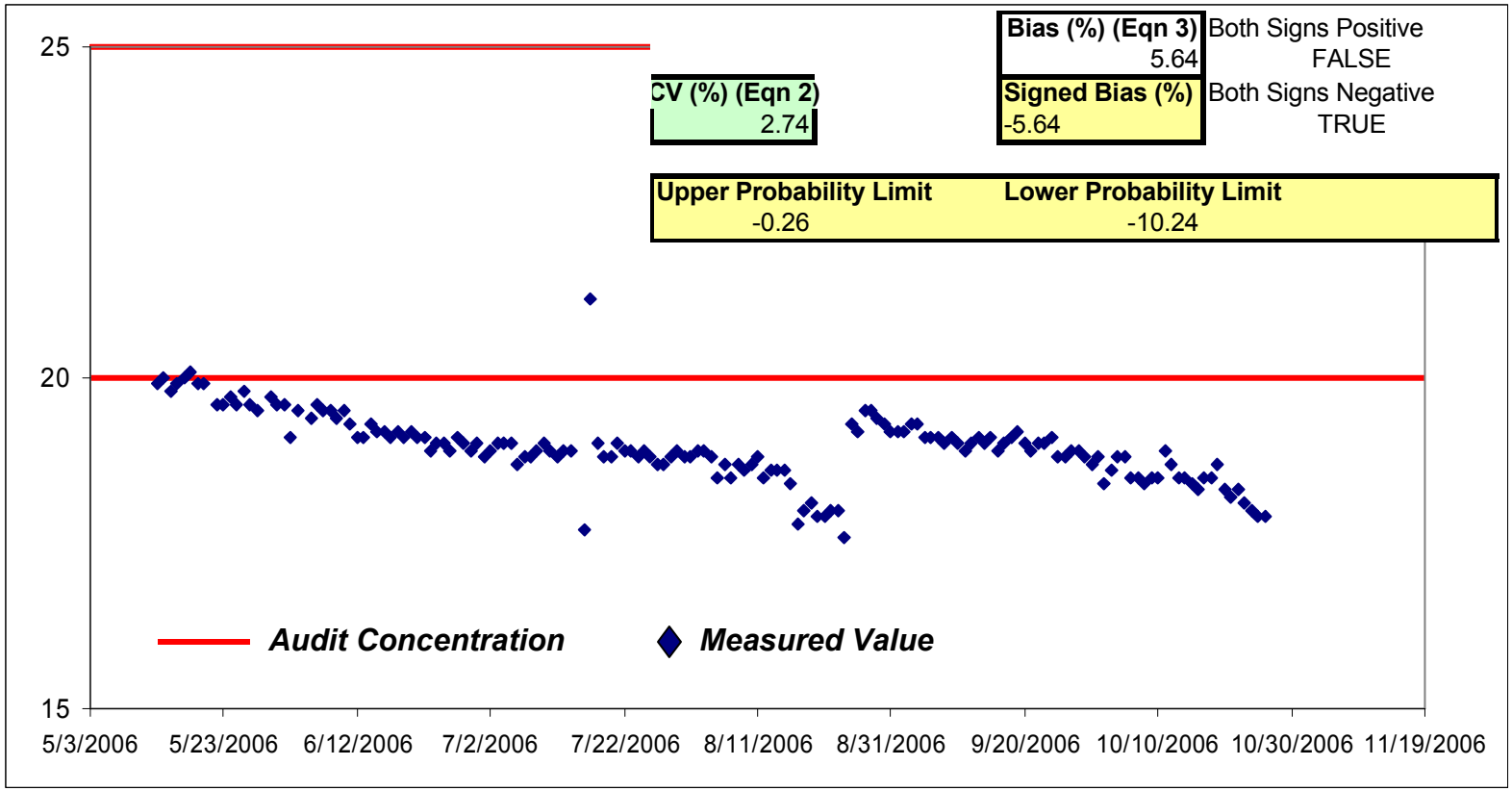
CO One-Point QC Checks



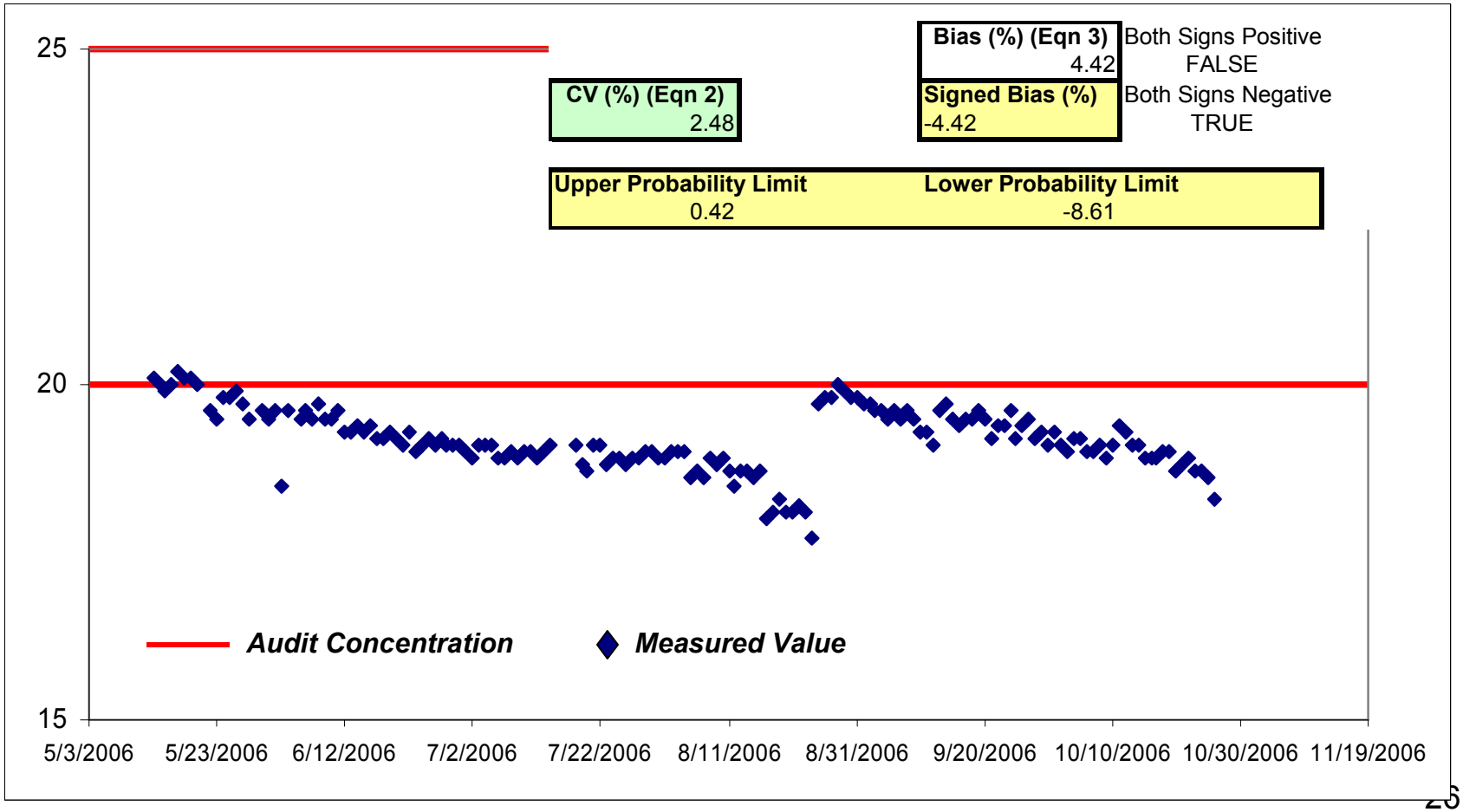
SO_2 - TEI
One-Point QC Check



NOy-API
One-Point QC Check



NO-API
One-Point QC Check



OAQPS Field Estimates (CY2006)

Make/ Model	API (CO)	TEI (CO)	TEI (SO_2)	TEI (NO_y)	API (NO_y)
MDL Obs.	**30ppb (20-59 ppb CL)**	**12 ppb (8-29 ppb CL)**	**0.055 ppb (0.038-0.148 ppb CL)**	**0.050 ppb (0.03-013 ppb CL)**	**0.058 ppb (0.04-011 ppb CL)**
Precision Obs.	***7.22%***	***4.95%***	***2.62%***	***1.49%***	***2.48%***
Bias Obs.	***+9.26%***	***-6.28%***	***+/-2.61%***	***+/-1.19%***	***-4.42%***

Monitoring Organization QA Responsibilities

- Phase 1 –Gaining Operational Experience
  - Help develop data set to get a handle on the data quality indicators.
    - Submission of routine and QC data to AQS
    - Compare to the MQOs
    - Provides for 2nd DQO review
- QA Project Plan Development
  - Once DQOs/MQOs developed
  - Revision of QAPP to include precursor gas data quality requirements.
  - SOPs are part of QAPP development

MQOs to Data Validation

- In 2000 QA Strategy Workgroup created a Validation Template from the PM2.5 MQO Table
- 2003-05 the Workgroup similarly revised the gaseous MQOs. These are going in next QA Handbook revision
- This can be done with the precursor gas MQOs

NPAP for Precursor Gas Sites?

- Precursor monitoring will be part of NPAP
- Monitoring organization are responsible for implementing adequate and independent audits
  - Allows for continued Federal implementation with STAG funds
- NPAP program testing TTP capabilities for precursor gasses at Burdens Creek
  - Some equipment still being purchased
  - Expected testing in 1st quarter 2007

EPA Assessment Activities

- National Performance Audit Program –Through The Probe (TTP)
  - DQO/MQO will determine need and frequency of TTP
  - Plan to develop one audit vehicle to test technical capability.
- Technical Systems Audits
  - Will occur at Regional level
- National Standards Certification
  - Proposal on table to certify precursor gas standards through ORIA
  - Should we buy 1 or 2 MDL standards for national use?
- Annual P and B Assessments
  - On AQS but data has to get there

Sequence of QA Events