Chapter 13

Quality Assessment and Statistical Analysis of Air Monitoring Data

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1.0 Introduction

The USEPA's Ambient Air Quality Monitoring Program is implemented under the authority of the Clean Air Act to provide air quality data for the three following objectives:

- Provide air pollution data to the general public in a timely manner
- Support compliance with air quality standards and emissions strategy development
- Support air pollution research studies

In order to support these objectives the monitoring networks are designed to measure ambient air concentrations for one or more of the following purposes:

1. determine the highest concentrations expected to occur in the area covered by the network;

2. determine typical concentrations in areas of high population density;

3. determine the impact on ambient pollution levels from significant sources or source categories;

4. determine the general background concentration levels;

5. determine the extent of regional pollutant transport among populated areas; and

6. measure air pollution impacts on visibility, vegetation damage, or other welfare-based impacts.

USEPA recognized the importance of collecting data of acceptable and consistent quality. In the late 1970's USEPA started developing consistent techniques to identify the objectives that required the highest quality data and then to develop requirements to collect and assess this measurement quality information. The USEPA embarked on the process very similar to what is now called the Data Quality Objectives (DQO) Process and determined that the comparison of data to the National Ambient Air Quality Standards (NAAQS) was the highest priority objective and that data would be collected in a manner that minimized the uncertainty in making attainment decisions. The primary data quality indicators for the ambient air program were identified as precision and accuracy (P&A). The early precision and accuracy statistics represented a compromise between theoretical statistical exactness and simplicity and uniformity in computational procedures. The P&A statistics were aggregated by reporting organization over various time periods and combined into a probability limit estimate. As the DQO process has matured, additional quality assurance objectives and statistical tests have come forth.

1.1 Data Quality Objectives

In order to provide data users with data of acceptable quality, USEPA uses the DQO process to determine data quality requirements for the ambient air criteria pollutants. Data quality objectives (DQOs) are a full set of performance constraints needed to design an environmental data collection operation, including a specification of the level of uncertainty (error) that a data user is willing to accept in the data to which a decision will apply. The data users are individuals that may be responsible for

- setting the NAAQS
- developing a quality system
- evaluating the data, or
- comparing data to the NAAQS

The data used in these decisions are never error free and always contain some level of uncertainty. Because of these uncertainties or errors, there is a possibility that data users may declare an area "nonattainment" when the area is actually in "attainment" or "attainment" when actually the area is in "nonattainment." Figures 1 and 2 illustrate how errors can affect a NAAQS attainment/nonattainment decision based on a hypothetical annual standard concentration value of 15.

Figure 1

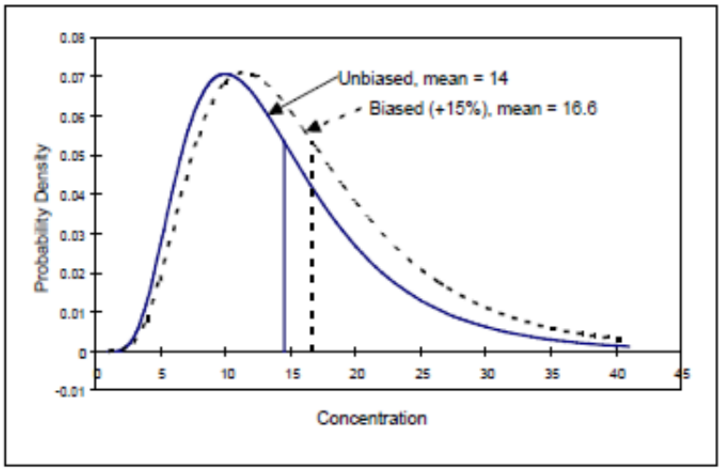

Figure 1. Effect of positive bias on the annual average estimate resulting in an incorrect declaration of non-attainment (from Guideline on the Meaning and the Use of Precision and Bias Data Required by 40 CFR Part 58 Appendix A, EPA-454/B-07-001, October 2007)

Figure 2

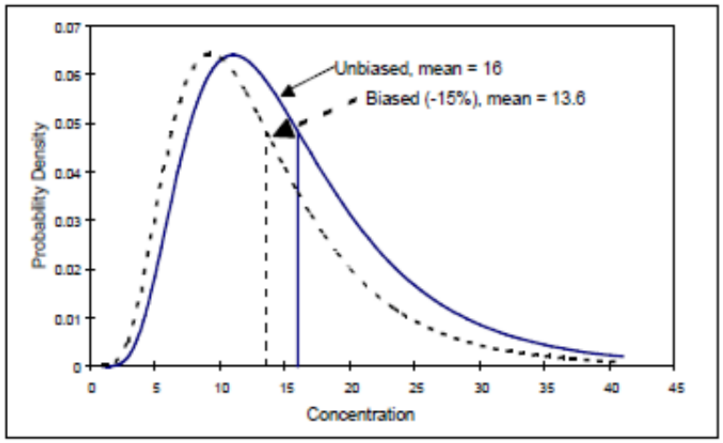

Figure 2. Effect of negative bias on the annual average estimate resulting in an incorrect declaration of attainment (from Guideline on the Meaning and the Use of Precision and Bias Data Required by 40 CFR Part 58 Appendix A, EPA-454/B-07-001, October 2007)

There are serious political, economic and health consequences of making such decision errors. Therefore data users need to understand and set limits on the probabilities of making incorrect decisions with these data.

In order to set probability limits on decision errors, one needs to understand and attempt to control uncertainty. Uncertainty is used as a generic term to describe the sum of all sources of error associated with an environmental data collection. Uncertainty can be illustrated as follows:

$$S_o^2 = S_p^2 + S_m^2$$

Where:

S_o = overall uncertainty
S_p = population uncertainty (spatial and temporal)
S_m = measurement uncertainty (data collection)

The estimate of overall uncertainty is an important component in the DQO process. Both population and measurement uncertainties must be understood. The DQOs are assessed through the use of data quality indicators (DQIs), which are the quantitative statistics and the qualitative descriptors used to interpret the degree of acceptability or utility of data to the user. The DQIs can then be used to establish the Measurement Quality Objectives (MQOs). Once the MQOs are established and monitoring is implemented, data quality assessments (DQAs) are performed to determine whether the DQOs were achieved. If not, the monitoring program should take steps to identify the major sources of uncertainty and find ways to reduce these uncertainties to the acceptable levels.

1.2 Data Quality Indicators

Data Quality Indicators (DQIs) are qualitative and quantitative descriptors used in interpreting the degree of acceptability or utility of data. Establishing acceptance criteria for the DQIs sets quantitative goals for the quality of data generated in the analytical measurement process. Data quality indicators typically used in ambient air monitoring include:

Representativeness – the degree in which data accurately and precisely represents a characteristic of a population, parameter variation at a sampling point, a process condition, or an environmental condition.

Precision – a measure of mutual agreement among individual measurements of the same property usually under prescribed conditions. This is the random component of error. Precision is estimated by various statistical techniques using some derivation of the standard deviation.

Bias – the systematic or persistent distortion of a measurement process which causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (imprecision) and systematic error (bias) components that are due to sampling and analytical operations.

Detectability – the determination of the low range critical value of a characteristic that a method specific procedure can reliably discern.

Completeness – a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions.

Comparability – a measure of confidence with which one data set can be compared to another.

The quality system for the ambient air monitoring program focuses on understanding and controlling (as much as possible) measurement uncertainty and because of that, mainly focuses on the data quality indicators of precision, bias, accuracy, detectability, completeness and comparability. Representativeness, which is a measure of the degree which data accurately and precisely represent parameter variations (spatial and temporal) at a sampling point, is addressed through network designs and is not something that the quality system can control through better measurements.

Of the six principal DQIs, precision, accuracy, detectability and bias are the quantitative measures, comparability is qualitative, and completeness is a combination of both quantitative and qualitative measures. DQIs are discussed at length in EPA QA/G-5I, *Guidance on Data Quality Indicators*.

1.2.1 Representativeness

Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population parameter at a sampling point or environmental condition. It is a qualitative term that should be evaluated to determine whether ambient air measurements and particulate and toxic samples are collected in such a manner that the resulting data appropriately reflect the ambient air and pollutant concentrations measured or studied.

1.2.2 Precision

Precision is a measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions. This is the random component of error. Precision is estimated by various statistical techniques typically using some derivation of the standard deviation. In ambient air monitoring, precision is calculated from the bi-weekly one-point quality control checks for the gaseous parameters or by collocated measurements for particulates.

1.2.3 Bias

Bias is the systematic or persistent distortion of a measurement process which causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value. In ambient air monitoring, bias is calculated from the bi-weekly one-point quality control checks for the gaseous parameters. For particulate parameters, bias is calculated from comparison to the EPA proficiency audits or flow verifications.

1.2.4 Accuracy

Accuracy is a measure of the closeness of an individual measurement or the average of a number of measurements to the true value. Accuracy includes a combination of variability (precision) and systematic error (bias) components that result from sampling and analytical operations. Accuracy is determined by analyzing a reference material of known pollutant concentration or by analyzing a sample to which a material of known concentration or amount of pollutant has been added.

1.2.5 Detectability

Detectability refers to the lowest concentration or amount of the target analyte that can be determined by a single measurement at a stated level of probability to be different from the zero contaminant concentration. Recent guidance documents suggest that monitoring organizations develop method detection limits (MDLs) for continuous instruments and or analytical methods. Many monitoring organizations use the default MDL listed in the EPA Air Quality system for a particular method. These default MDLs come from instrument vendor advertisements and/or method manuals. Monitoring organizations should not rely on instrument vendor's documentation on detection limits but determine the detection limits that are being achieved in the field during routine operations.

1.2.6 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected (i.e., measurements that were planned to be collected). Completeness is not intended to be a measure of representativeness; that is, it does not describe how closely the measured results reflect the actual concentration or distribution of the pollutant in the media sampled. The degree to which lack of completeness affects the outcome of the study is a function of many variables ranging from deficiencies in the number of field samples acquired to failure to analyze as many replications as deemed necessary by the QAPP and DQOs. The intensity of effect due to incompleteness of data is sometimes best expressed as a qualitative measure and not just as a quantitative percentage. Insufficient completeness will decrease the power of the statistical tests and may require reconsideration of the limits for the false negative and positive error rates. Ambient data completeness requirements are included in the reference methods (40 CFR Part 50).

1.2.7 Comparability

Comparability is the qualitative term that expresses the confidence that two data sets can contribute to a common analysis and interpolation. Comparability must be carefully evaluated to establish whether two data sets can be considered equivalent in regard to the measurement of a specific variable or groups of variables. In a laboratory analysis, the term comparability focuses on method type comparison, holding times, stability issues, and aspects of overall analytical quantitation. Comparability is a measure of the confidence with which one data set or method can be compared to another, considering the units of measurement and applicability to standard statistical techniques. Comparability of datasets is critical to evaluating their measurement uncertainty and usefulness. The various National Performance Evaluation Programs implemented in the Ambient Air Monitoring Program help EPA evaluate data comparability among PQAOs.

1.3 Measurement Quality Objectives

For each DQI a level of uncertainty or error that is acceptable and will achieve the DQO must be identified. Measurement Quality Objectives (MQOs) are designed to evaluate and control various phases (sampling, preparation, analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the DQOs. Appendix A of 40 CFR Part 58 establishes the various quality control checks, like the one-point quality control check for the gaseous pollutants or the particulate matter collocated instruments. These checks help quantify a data quality indicator and their acceptance criteria are the MQOs. Table 1 provides a listing of the required measurement quality checks and the MQOs as they are currently defined in Appendix A.

Table 1
Ambient Air Monitoring Quality Objectives

Method	CFR Reference 40CFR58 App A	Coverage	Minimum Frequency	MQOs
Automated Methods				
One-point QC: SO_2, NO_2, O_3, CO	Section 3.2.1	Each analyzer	Once per 2 weeks	O_3 Precision 7%, bias ±7%; SO_2, CO Precision 10%, Bias ±10%; NO_2 Precision 15%, Bias ±15%
Annual Performance Evaluation: SO_2, NO_2, O_3, CO	Section 3.2.2	Each analyzer	Once per year	O_3, SO_2, NO_2 Audit Levels 3 – 10 ≤ ±15%, Audit Levels 1 & 2 ± 1.5 ppb or ≤ ±15% CO Audit Levels 3 – 10 ≤ 15% Audit Levels 1 & 2 ±0.3 ppm or ≤ ±15%
NPAP audit SO_2, NO_2, O_3, CO	Section 2.4	20% of each parameter analyzers per year	Over all four quarters	O_3 Audit Levels 3 – 10 ≤ ±10%, Audit Levels 1 & 2 ± 1.5 ppb SO_2, NO_2 Audit Levels 3 – 10 ≤ ±15%, Audit Levels 1 & 2 ± 1.5 ppb CO Audit Levels 3 – 10 ≤ 15%, Audit Levels 1 & 2 ±0.3 ppm
Flow rate verification: $PM_{2.5}$, PM_{10}, $PM_{10-2.5}$	Section 3.2.3	Each monitor	Once per month	≤ ±4% of flow standard ≤ ±5% of design flow
Semi-annual flow rate audit $PM_{2.5}$, PM_{10}, $PM_{10-2.5}$	Section 3.2.4	Each monitor	Once every 6 months	≤ ±4% of flow standard ≤ ±5% of design flow
Collocated sampling $PM_{2.5}$, $PM_{10-2.5}$	Section 3.2.5	15% within the PQAO	Every 12 days	$PM_{2.5}$ – 10% precision $PM_{10-2.5}$ – 15% precision
Performance evaluation program $PM_{2.5}$, $PM_{10-2.5}$	Section 3.2.7	a. 5 valid audit for PQAO ≤ 5 sites b. 8 valid audits for PQAO > 5 sites c. All monitors in 6 years	Over all four quarters	$PM_{2.5}$ – ±10% bias $PM_{10-2.5}$ – 15% bias

Table 1 (continued)
Ambient Air Monitoring Quality Objectives

Method	CFR Reference 40CFR58 App A	Coverage	Minimum Frequency	MQOs
Manual Methods				
Collocated Sampling PM_{10}, $PM_{10-2.5}$, $PM_{2.5}$, Pb-TSP, Pb-PM_{10}	Section 3.3.1 and 3.3.5	15% within PQAO	Every 12 days	PM_{10}, $PM_{2.5}$ Pb-TSP – 10% precision $PM_{10-2.5}$ – 15% precision
Flow rate verification PM_{10} (low vol), $PM_{10-2.5}$, $PM_{2.5}$, Pb-TSP, Pb-PM_{10}	Section 3.3.2	Each sampler	Once per month	≤ ±4% of flow standard ≤ ±5% of design flow
Flow rate verification PM_{10} (hi vol), Pb-TSP	Section 3.3.2	Each sampler	Once per month	≤ ±7% of flow standard and design flow
Semi-annual flow rate audit PM_{10}(low vol), $PM_{10-2.5}$, $PM_{2.5}$	Section 3.3.3	Each sampler	Once per 6 months	≤ ±4% of flow standard ≤ ±5% of design flow
Semi-annual flow rate audit PM_{10}(hi vol), Pb-TSP	Section 3.3.3	Each sampler	Once per 6 months [IDEM: quarterly]	≤ ±7% of flow standard
Pb Analysis Audits Pb-TSP, Pb-PM_{10}	Section 3.3.4	Each sampler Analytical (lead strips)	Each quarter IDEM: quarterly	≤ ±10% bias
Performance evaluation program $PM_{2.5}$, $PM_{10-2.5}$	Section 3.3.7 and 3.3.8	5 valid audit for PQAO ≤ 5 sites 8 valid audits for PQAO > 5 sites All monitors in 6 years	Over all 4 quarters	$PM_{2.5}$ – ±10% bias $PM_{10-2.5}$ – 15% bias

1.4 Primary Quality Assurance Organization (PQAO)

Monitoring data are collected and submitted to the EPA Air Quality System (AQS) by the reporting organization. Quality assurance data (e.g., 1-point quality control audits, flow rate verifications) are submitted to AQS by the Primary Quality Assurance Organization. A primary quality assurance organization is defined as a monitoring organization or a coordinated aggregation of such organizations that is responsible for a set of monitoring and for which data quality assessments can logically be pooled. Each criteria pollutant sampler/monitor at a monitoring station in the SLAMS network must be associated with one, and only one, primary quality assurance organization. Under the above definitions it is possible to have a PQAO with more than one reporting organization associated with it.

Each primary quality assurance organization shall be defined such that measurement uncertainty among all stations in the organization can be expected to be reasonably homogeneous, as a result of common factors. Common factors that should be considered by monitoring organizations in defining primary quality assurance organizations include:

a. Operation by a common team of field operators according to a common set of procedures
b. Use of a common QAPP or standard operating procedures
c. Common calibration facilities and standards
d. Oversight by a common quality assurance organization; and
e. Support by a common management, laboratory or headquarters

Primary quality assurance organizations are not necessarily related to the organization reporting data to the AQS.

1.5 Air Quality System (AQS)

The Air Quality System is a database administered by the U.S. Environmental Protection Agency (USEPA) to assess the status of the Nation's air quality. The system includes a repository of ambient concentrations of air pollutants and associated meteorological data, as well as software used to provide statistical analysis of this data. In addition to the ambient air data, measurement quality checks (e.g., bi-weekly 1-point quality control checks of gaseous parameters, quarterly performance evaluations of gas analyzers, monthly flow verifications), which are used to statistically assess the quality of the air pollutant data is contained in the AQS.

1.6 Data Submission

Ambient data must be submitted to the IDEM Ambient Monitoring Section within 60 days after the end of the quarter. This will allow sufficient time for review before the AQS submittal deadline of 90 days after the end of each reporting calendar quarter. All ambient and quality assurance data submittals to AQS are done electronically via the Internet.

The Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Section (IDEM, OAQ, QAS), must submit to the USEPA - AQS, within 90 days after the end of each quarter, the results of all required valid precision, bias, and accuracy checks conducted within the state during that quarter. This data is from monitoring networks operated by industries, consultants, and IDEM. In order to meet the 90-day deadline, all precision, bias, and accuracy data from each reporting agency in Indiana must be submitted to the OAQ/QAS within 60 days after the end of each quarter.

EPA has prepared a stand-alone MS Windows application, the AQS QA Transaction Generator, which provides a mechanism to manually enter AQS QA transactions or import an AQS QA transaction and generate a valid AQS QA transaction file for uploading to AQS. The transaction is validated against AQS Reference data and will generate warnings or errors for incorrect data. The AQS QA Transaction Generator can be downloaded from the following EPA site:

http://www.epa.gov/ttn/airs/airsaqs/downloads.htm

1.7 National Performance Evaluations and Technical Systems Audit

The Indiana Department of Environmental Management, Office of Air Quality participates in USEPA's National Performance Audit Program (NPAP) and the PM Performance Evaluation Program (PEP) program. The NPAP/PEP is a quality assurance audit program required under Section 2.4 of 40 Code of Federal Regulations Part 58, Appendix A

The NPAP through-the-probe (TTP) audit is a QA activity that is used to independently evaluate the measurement system bias of the gaseous parameter monitoring network from the sample inlet through the sampling system to the analyzer. The NPAP auditor utilizes a mobile laboratory containing a carefully assembled system of high quality and high capacity (volume/flow) audit gas support, generation, and analysis equipment. The stability and ranges of the concentrations are independently certified to be traceable to NIST standards. NPAP auditors generate pollutant concentrations and flowing air streams, which they analyze onsite with independent analyzers calibrated onsite using NIST-traceable standards. The TTP audit system generates enough audit test gas to challenge most ambient air monitoring stations starting at the sample inlets. This larger test flow capacity can go up to a high of 20 or 30 lpm, enabling evaluation of the entire sampling flow path, from the sampling station inlet up to and through the back of the analyzer into the analyzer. If the on-board analysis and recording system document the stability and correct concentration of the generated gases, the NPAP auditor tells the site operator to start analyzing the TTP gases using the site's monitors and procedures. The gaseous TTP pollutant concentrations are unknown to the audit participants. The concentration outputs from the site analyzers are compared to the concentrations that were generated by the TTP audit system and reported to EPA.

The PEP is a QA activity that is used to independently evaluate the measurement system bias of the $PM_{2.5}$ FRM/FEM monitoring network, which includes measurement uncertainties from field

and laboratory activities. The pertinent regulations for the PEP audit are outlined in 40 CFR Part 58, Appendix A, Section 3.2.7. The strategy is for an independent PEP Auditor to collocate a portable FRM/FEM $PM_{2.5}$ air sampling instrument within 1–4 meters of a routine SLAMS/NCore air monitoring instrument. Both monitors operate simultaneously and the PEP filter is analyzed by an independent gravimetric laboratory. The gravimetric results that are derived from the two samplers are compared. A valid PE audit means that both the primary monitor and PEP audit concentrations have not been invalidated and are greater than 3 micrograms per cubic meter (µg/m3). For primary quality assurance organizations (PQAOs) with less than or equal to five monitoring sites, five valid PE audits must be collected and reported each year. For PQAOs with greater than five monitoring sites, eight valid PE audits must be collected and reported each year. Additionally, each year, every designated FRM or FEM within a PQAO must have each method designation evaluated each year; and all FRM or FEM samplers subjected to a PEP audit at least once every 6 years; which equates to approximately 15% of the monitoring sites audited each year.

Technical audits are systematic and objective examinations of a program or project to determine whether environmental data collection activities and related results comply with the project's Quality Assurance Project Plan and other planning documents, are implemented effectively, and are suitable to achieve its data quality goals. Technical systems audits by USEPA Region 5 are conducted at least every three years and results are reported to the AQS.

2.0 Gas Parameter Assessments

The assessments performed in this section pertain to continuous analyzers that monitor for SO_2, NO_2, O_3, and CO.

2.1 One-Point Quality Control Check

A one point precision check must be carried out a minimum of once every two weeks on each automated analyzer used to measure SO_2, NO_2, O_3 and CO. The precision check is made by challenging the analyzer with a check gas of known concentration between 0.01 and 0.10 ppm for SO_2, NO_2, and O_3 analyzers, and between 1 and 10 ppm for CO analyzers. The ranges allow for appropriate check gas selection for sites that may be sampling for different objectives, i.e., NCORE trace gas monitoring versus comparison to National Ambient Air Quality Standards (NAAQS). Ideally, the precision gas concentration selected should be related to the routine concentration normally measured at sites in the network. The Indiana Department of Environmental Management has increased the frequency of its QC checks to once per week due to outfitting all of its air monitoring stations with automated calibration systems.
Analyzers must operate in their normal sampling mode during the precision check, and the test atmosphere must pass through all filters, scrubbers, conditioners or other components used during normal ambient sampling and as much of the ambient air inlet system as practicable. If a precision check is made in conjunction with a zero or span adjustment, it must be made prior to such zero or span adjustments. [Note: some models of CO analyzers can be temporarily modified during the precision check to reduce vent or purge flows, or the test atmosphere may

enter the analyzer at a point other than the normal sample inlet, provided that the analyzer's response is not likely to be altered by these deviations from the normal operation mode.]

The actual concentration of the 1-point QC check gas and the corresponding indicated concentration (analyzer response) are reported and will be used in calculations of the measurement quality objectives.

2.2 One-Point Quality Control Statistic

The comparison statistic for the one-point QC audit, which is the comparison of an audit concentration to the concentration measured by the analyzer, is the percent difference, d_i. For each single point QC audit, the calculation of the percent difference is described in Equation 1:

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas = concentration indicated by the monitoring organization's analyzer and
audit = audit concentration of the standard used in the precision (QC) check

2.3 Precision Estimate

The precision estimator is used to assess the one-point precision (QC) checks for SO_2, NO_2, O_3, or CO. The precision estimator is the 90% upper control limit of the coefficient of variation and is calculated using Equation 2.

Equation 2:

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

Where,

n = number of one-point QC checks
$\mathbf{X^2_{0.1,\,n-1}}$ = 10th percentile of a chi-squared distribution with n-1 degrees of freedom.

2.4 Bias

The bias estimate is calculated from the results of the one-point QC checks for SO_2, NO_2, O_3, or CO. The bias estimator is a 95% upper control limit of the mean absolute value of the percent differences as described in Equation 3:

Equation 3:

$$|bias| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where,

n = number of single point checks being aggregated
$\boldsymbol{t_{0.95,\,n-1}}$ = 95th quartile of a t-distribution with n-1 degrees of freedom
AB = mean absolute value of all d_i calculated using Equation 4
AS = standard deviation of the absolute value of all d_i calculated using Equation 5

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i-1}^{n} |d_i|$$

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |d_i|^2 - \left(\sum_{i=1}^{n} |d_i|\right)^2}{n(n-1)}}$$

Since the bias statistic as calculate in Equation 3 uses absolute values, it does not have a tendency (negative or positive bias) associated with it. To assign a sign to the absolute bias, a rank ordering of the percent differences of the 1-point QC check results from a single analyzer for a particular assessment interval is undertaken and then reviewing the sign of the 25th and 75th percentile values. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs.

2.5 Performance Evaluations (Accuracy Audits)

Each calendar quarter, the primary quality assurance organization is required to conduct a performance evaluation on 25 percent or more of the SLAMS analyzers that are monitoring for SO_2, NO_2, O_3 and CO during that quarter. The IDEM Air Monitoring Branch conducts a performance evaluation on all network analyzers that monitor for SO_2, NO_2, O_3, or CO each quarter. A trained experienced auditor other than the site operator who performs routine monitoring, calibration, or analysis must conduct the performance evaluation. Transfer standards and equipment used for the performance evaluation must not be the same as the standards and equipment used for calibration and spans, but they may be referenced to the same NIST SRM, CRM, or primary UV photometer.

The audit is made by challenging the analyzer with audit gas concentrations from at least three audit levels shown in Table 3. The selected audit levels should represent or bracket 80 percent of ambient concentrations measured by the analyzer. An additional fourth level is encouraged for those analyzers that have the potential to exceed the concentration ranges described by the initial three audit levels selected. A November 10, 2010, memo from OAQPS expanded the accuracy audit levels from five to ten. The new accuracy audit levels incorporate trace level NCORE analyzer ranges along with the traditional ambient level analyzer ranges.
The new audit levels in Table 2 were promulgated in the following EPA memo:

http://www.epa.gov/ttn/amtic/files/ambient/pm25/datamang/TechMemoforPEAuditLevels.pdf .

Table 2. Accuracy Audit Concentration Levels

	Concentration Range (ppm)							
Audit	Ozone O_3		Sulfur dioxide SO_2		Nitrogen dioxide NO_2		Carbon monoxide CO	
Level	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
1	0.0040	0.0059	0.0003	0.0029	0.0003	0.0029	0.020	0.059
2	0.0060	0.0190	0.0030	0.0049	0.0030	0.0049	0.600	0.199
3	0.0200	0.0390	0.0050	0.0079	0.0050	0.0079	0.200	0.899
4	0.0400	0.0690	0.0080	0.0199	0.0080	0.0199	0.900	2.999
5	0.0700	0.0890	0.0200	0.0499	0.0200	0.0499	3.000	7.999
6	0.0900	0.1190	0.0500	0.0999	0.0500	0.0999	8.000	15.999
7	0.1200	0.1390	0.1000	0.1499	0.1000	0.2999	16.000	30.999
8	0.1400	0.1690	0.1500	0.2599	0.3000	0.4999	31.000	39.999
9	0.1700	0.1890	0.2600	0.7999	0.5000	0.7999	40.000	50.000
10	0.1900	0.2590	0.8000	1.0000	0.8000	1.0000	50.000	60.000

The analyzer should be audited through its normal sampling mode such that the test atmosphere passes through all filters, scrubbers, conditioners, and other sample inlet components used during normal ambient sampling and as much of the ambient air inlet system as is practicable. The exception given for certain CO analyzers in 1-point QC checks does not apply for performance evaluation audits. Note: NO_2 audit gas for chemiluminescence-type NO_2 analyzers must also contain residual NO gas concentration of at least 0.080 ppm and not greater than 0.120 ppm.

Both the audit test concentrations and the corresponding concentration measurements indicated by the analyzer for each concentration level being tested shall be reported. The percent difference, d_i, for each audit level of the performance evaluation is calculated using Equation 1 and can be compared to the probability intervals for the respective monitoring site.

2.6 Annual Probability Limits

The annual performance evaluations for SO_2, NO_2, O_3, or CO are used to verify the results obtained from the one-point QC checks and to validate those results across a range of concentration levels. Annual probability limits can be calculated from the one-point QC checks using Equations 6 and 7:

Equation 6:

$$\text{Upper Probability Limit} = m + 1.96S$$

Equation 7:

$$\text{Lower Probability Limit} = m - 1.96S$$

Where,

m = mean of the all one-point checks being aggregated over the evaluation period calculated using Equation 8 and;

S = standard deviation of the all one-point checks being aggregated over the evaluation period calculated using Equation 9.

Equation 8:

$$m = \frac{1}{k} \cdot \sum_{i-1}^{k} d_i$$

Equation 9:

$$S = \sqrt{\frac{k \cdot \sum_{i=1}^{k} d_i^{\,2} - \left(\sum_{i=1}^{k} d_i\right)^2}{k(k-1)}}$$

Where,

k = total number of one point QC checks performed during the evaluation period

Ninety-five percent of the individual percent differences (all audit concentration levels) for the performance evaluations should be captured within the probability intervals for the monitoring site.

2.7 Single Analyzer Statistics

The precision and bias statistics for a single analyzer can be calculated on a quarterly, annual, and triennial basis. The calculation of the probability limits is performed on an annual basis.

2.8 Primary Quality Assurance Organization Statistics

The precision and bias statistics for a single parameter (SO_2, NO_2, O_3, CO) aggregated over the PQAO can be calculated on a quarterly, annual, and triennial basis. The calculation of the probability limits is performed on a triennial basis.

3.0 Particulate Parameter Assessments

Because of the difficulty in developing a standard concentration for particulates, the statistics for particulates are based on comparison to collocated sampling or to flow rate verifications. Precision is estimated via duplicate measurements from collocated samplers. For each pair of collocated samplers, one sampler is designated as the sampler that will report the air quality for the site (“reporting”) and the other is designated as the duplicate sampler (“collocated”).The number and type of monitors required for collocated sampling is complex and requires a thorough review of the appropriate sections of Appendix A.

Parameter	Collocated Samplers	Reference
PM_{10}	Collocated samplers of the same type	§3.3.1, §4.2.1
$PM_{2.5}$	Collocated samplers of the same type or different method	§3.2.5, §3.3.5,
$PM_{10\text{-}2.5}$	Collocated samplers of the same type or different method	§3.2.6, §3.3.6
Pb-TSP	Collocated samplers of the same type	§3.3.4.3

Monthly flow rate verifications are required for both automated and manual $PM_{2.5}$, PM_{10} (low volume), and $PM_{10\text{-}2.5}$ instruments. Quarterly flow rate verifications are required for high volume PM_{10} and Pb-TSP instruments, but monthly flow verifications are encouraged. Estimates for the PM_{10} bias are calculated from the monthly flow verifications (Appendix A §4.2.2). Performance Evaluation Program (PEP) audits are performed on a certain number of instruments in $PM_{2.5}$, $PM_{10\text{-}2.5}$, and Pb-TSP networks to estimate the total measurement system bias.

3.1 Precision Estimates from Collocated Samples ($PM_{2.5}$, PM_{10}, $PM_{10\text{-}2.5}$, Pb)

At low concentrations, agreement between the measurements of collocated samplers, expressed as relative percent difference or percent difference, may be relatively poor. For this reason, collocated measurement pairs are selected for use in the precision calculations only when both reporting and collocated sampler measurements are above the concentrations listed in Table 3.

Table 3. Minimum Concentration Levels for Particulate Matter Precision Assessments

Parameter	Limit ($\mu g/m^3$)
$PM_{2.5}$	3
$PM10_{10\text{-}2.5}$	3
PM_{10} (Lo-Vol)	3
PM_{10} (Hi-Vol)	15
Pb	0.02

For each collocated data pair that exceed the minimum concentrations in Table 3, the relative percent difference, d_i, is calculated by Equation 10.

Equation 10:

$$d_i = \frac{y_i - x_i}{\frac{1}{2}\left(y_i + x_i\right)}$$

Where

$\boldsymbol{x_i}$ = concentration of the primary sampler and
$\boldsymbol{y_i}$ = concentration value from the audit sampler

The precision upper bound statistic, CV_{ub} is a standard deviation on d_i with a 90 percent upper confidence limit (Equation 11).

Equation 11:

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

Where,

n = number of valid data pairs being aggregated, and
$\mathbf{X^2_{0.1,\,n-1}}$ = 10th percentile of a chi-squared distribution with n-1 degrees of freedom

The factor of 2 in the denominator adjusts for the fact that each d_i is calculated from two values with error.

3.2 PM_{10} Flow Bias

The PM_{10} bias calculation begins with the percent difference result (d_i) from the monthly flow verifications.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas = flow measurement indicated by the sampler and
audit = flow measurement indicating by audit transfer standard used in the monthly flow verification

The bias estimator is a 95% upper control limit of the mean absolute value of the percent differences as described in Equation 3:

Equation 3:

$$|bias| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where,

n = number of monthly flow rate verifications being aggregated
$\boldsymbol{t_{0.95,\,n-1}}$ = 95th quantile of a t-distribution with n-1 degrees of freedom
AB = mean absolute value of all d_i and is calculated using Equation 4
AS = standard deviation of the absolute value of all d_i calculated using Equation 5

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i-1}^{n} |d_i|$$

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |d_i|^2 - \left(\sum_{i=1}^{n} |d_i|\right)^2}{n(n-1)}}$$

Since the bias statistic as calculate in Equation 3 uses absolute values, it does not have a tendency (negative or positive bias) associated with it. To assign a sign to the absolute bias, a rank ordering of the percent differences of the monthly flow rate verification results from a single instrument for a particular assessment interval is undertaken and then reviewing the sign of the 25th and 75th percentile values. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs.

While not required by Appendix A, the flow bias calculation can be applied to the $PM_{2.5}$ monthly flow verifications.

3.3 Bias Assessment for $PM_{10-2.5}$ and $PM_{2.5}$

At the PQAO level, the bias estimate is calculated using the Performance Evaluation Program (PEP) audit results and begins with the percent difference results described in Equation 1. Only collocated measurement pairs that are both above the concentrations listed in Table 3 are selected for use in the percent difference calculation.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas = concentration from the agency's primary monitor and
audit = concentration from the PEP monitor

The bias estimator is an upper 95th quantile on the mean absolute value of the percent differences (Equation 1), as described in Equation 3 as follows:

Equation 3:

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where,

n = number of valid paired concentrations being aggregated
$\boldsymbol{t_{0.95, n-1}}$ = 95th quantile of a t-distribution with n-1 degrees of freedom;
AB = mean absolute value of all d_i and is calculated using Equation 4
AS = standard deviation of the absolute value of all d_i calculated using Equation 5

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i-1}^{n} |d_i|$$

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |d_i|^2 - \left(\sum_{i=1}^{n} |d_i|\right)^2}{n(n-1)}}$$

Since the bias statistic as calculate in Equation 3 uses absolute values, it does not have a tendency (negative or positive bias) associated with it. To assign a sign to the absolute bias, a rank ordering of the percent differences of the valid paired concentration results for a particular assessment interval is undertaken and then reviewing the sign of the 25th and 75th percentile values. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs.

3.4 $PM_{2.5}$ Bias 90% Confidence Intervals

At the PQAO level, the bias estimate is calculated using the Performance Evaluation Program (PEP) audit results and begins with the percent difference (d_i) results described in Equation 1. Only collocated measurement pairs that are both above the concentrations listed in Table 3 are selected for use in the percent difference calculation.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas = concentration from the agency's primary monitor and
audit = concentration from the PEP monitor

The bias estimator is based on the upper and lower probability limits of the mean percent difference (Equation 12). The mean percent difference, *D*, is calculated by Equation 12 below.

Equation 12:

$$D = \frac{1}{n_j} \cdot \sum_{i-1}^{n_j} d_i$$

Where

$\mathbf{n_j}$ = number of valid concentration pairs

Confidence intervals can be constructed for the average bias estimate calculated by Equation 12 using Equations 13 and 14:

Equation 13:

$$Upper\ 90\%\ Confidence\ Interval = D + t_{0.95,df} * \frac{s_d}{\sqrt{n_j}}$$

Equation 14:

$$Lower\ 90\%\ Confidence\ Interval = D - t_{0.95,df} * \frac{s_d}{\sqrt{n_j}}$$

Where,

$\mathbf{t_{0.95,df}}$ = the 95th quantile of a t-distribution with degrees of freedom df = n_j-1 and
$\mathbf{s_d}$ = an estimate of the variability of the average bias calculated using Equation 15

Equation 15:

$$s_d = \sqrt{\frac{\sum_{i=1}^{n_j} (d_i - D)^2}{(n_j - 1)}}$$

3.5 Semi-Annual Flow Rate Audits

Flow rate audits are required to be performed on a semi-annual frequency spaced no closer than three months apart and no more than 9 months apart. The results of the flow rate audits are calculated using Equation 1 below. The Indiana Department of Environmental Management performs flow rate audits each calendar quarter (4 per year) using the same spacing criteria.

The flow rate audits are used to assess the results obtained from the one-point flow rate verifications and to provide an estimate of flow rate acceptability. For each monthly flow rate verification, calculate the percent difference in flow rate using Equation 1

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas = flow measurement indicated by the sampler and
audit = flow measurement indicating by audit transfer standard used in the monthly flow verification.

The semi-annual flow rate audits are used to verify the results obtained from the monthly flow rate verifications and to validate those results across a range of results. Annual probability limits can be calculated from the monthly flow verifications using Equations 6 and 7:

Equation 6:

Upper Probability Limit = m + 1.96S

Equation 7:

Lower Probability Limit = m − 1.96S

Where,

m = the mean (Equation 8)
S = standard deviation of the percent differences using Equation 9

Equation 8:

$$m = \frac{1}{k} \cdot \sum_{i-1}^{k} d_i$$

Where,

k = total number of flow rate verifications performed for the interval being evaluated and

Equation 9:

$$S = \sqrt{\frac{k \cdot \sum_{i=1}^{k_j} d_i^{\,2} - \left(\sum_{i=1}^{k} d_i\right)^2}{k(k-1)}}$$

Similar to the gas parameter performance evaluations, ninety five percent of all semi-annual flow rate audits should be captured within the upper and lower probability limits for the PQAO.

4.0 Lead Bias Assessments

The lead (Pb) bias assessment is composed of two biases, the flow bias determined by flow verifications and the mass bias from the lead strip analysis. The absolute bias estimates should be done on annual and 3-year levels. The flow rate audits are site-specific, so the absolute bias upper bound estimate can be done and treated as a site-level statistic.

4.1 Lead Strips

Each calendar month, the Pb Reference Method analytical procedure is audited using glass fiber filter strips containing a known quantity of Pb. These audit sample strips are prepared by depositing a Pb solution on unexposed glass fiber filter strips of dimensions 1.9 centimeters (cm) by 20.3 cm (3/4 inch by 8 inch) and allowing them to dry thoroughly. Audit samples must be extracted using the same extraction procedure used for exposed filters. The measured and actual results from Range 1 and 2 are reported to AQS.

Range	Pb concentration µg/strip	(Equivalent ambient Pb concentration, µg/m^3)[1]
0	0	0
1	9-30	.045-0.15
2	60-90	0.3-0.45

[1] Equivalent ambient Pb concentration in µg/m^3 is based on sampling at 1.7 m^3/min for 24 hours on a 20.3 cm x 25.4 cm (8 inch x 10 inch) glass fiber filter.

4.2 Absolute Lead Mass Bias

For each lead strip mass measurement pair (excluding the zero strips), the percent difference, d_i in mass is calculated using Equation 1.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas = value indicated by the mass measurement and
audit = actual lead mass on the audit strip

The absolute "mass bias" upper bound is then calculated using Equation 3

Equation 3:

$$|\,mass\ bias\,| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where

n = the number of analyzed lead strip pairs being aggregated
$\mathbf{t}_{\mathbf{0.95,n-1}}$ = the 95th quantile of a t-distribution with n-1 degrees of freedom
AB = the mean of the absolute values of all d_i (calculated using Equation 4)
AS = the standard deviation of the absolute value of all d_i (calculated using Equation 5)

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i-1}^{n} |\,d_i\,|$$

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |\,d_i\,|^2 - \left(\sum_{i=1}^{n} |\,d_i\,|\right)^2}{n(n-1)}}$$

4.3 Absolute Lead Flow Volume Bias

For each flow rate verification performed in the aggregate interval, calculate the percent difference, d_i in volume using Equation 1.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where,

meas is the value indicated by the sampler's flow measurement and
audit is the actual flow indicated by the auditing flow meter

The absolute "volume bias" upper bound is then calculated using Equation 3 below

Equation 3:

$$|\,volume\ bias\,| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where

n = the number of flow verifications being aggregated
$\mathbf{t_{0.95,n-1}}$ = the 95th quantile of a t-distribution with n-1 degrees of freedom
AB = the mean of the absolute values of all d_i (calculated by Equation 4 below)
AS = the standard deviation of the absolute value of all d_i (Equation 5 below)

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i-1}^{n} |\,d_i\,|$$

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |\,d_i\,|^2 - \left(\sum_{i=1}^{n} |\,d_i\,|\right)^2}{n(n-1)}}$$

4.4 Overall Absolute Lead Bias

Finally, the absolute bias upper bound is given by combining the absolute bias estimates of the flow rate and Pb strips using Equation 16:

Equation 16:

$$|Pb\ bias| \leq \frac{|mass\ bias| + |volume\ bias|}{100 - |volume\ bias|}$$

Where mass bias is the bias calculated for the Pb strips, and vol is the bias calculated for the flow rate audits.

5.0 PAMS Volatile Organic Compounds (VOC)

Consult Chapter 8 of the Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Manual for details on precision and accuracy requirements.