

**GUIDANCE IN IMPLEMENTATION OF PROFICIENCY TESTING
AND PERFORMANCE EVALUATION STUDIES**



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Section 1 Introduction to Data Quality, Proficiency Testing and Performance Evaluations Studies

1.0 Quality in Analytical Chemistry

There is some confusion as to what is meant by QUALITY. The dictionary definition of quality is the degree or grade of excellence possessed by an item. However, in analytical chemistry this definition needs to be expanded, just as in the case of judging quality in relation to everyday life. All successful manufacturers have to produce goods they can sell. So for example, car manufacturers have a range of products to suit their customers' needs. This can be compared with an analytical laboratory. An analytical chemist's product is the result which is produced at the end of the analysis and a comment on the use to which it can be put.

Quality in the analytical laboratory is all about providing results which:

- Meet the specific needs of the customer;
- Attract the confidence of the customer and all others who make use of the results;
- Represent value for money.

This is often referred to as *fitness for purpose*.

Data quality is meaningful only when it relates to intended use of data. Some data are good ("high quality") for some purposes but are bad ("low quality") for others.

The following factors need to be considered to ensure a "quality result"

- Knowledge of customer needs
- Acceptable level of uncertainty
- Correct sampling method
- Appropriate analytical method
- Experimental procedure fully recorded
- Report to the customer
- Maintenance of equipment to specification
- Proper methodology for the recording of results
- Proper management of laboratory materials
- All staff are competent to do the job in hand

Introduction to Proficiency Testing and Performance Evaluation

Quality control (QC) checks are essential for evaluating the reliability of data produced by a laboratory and for producing technically defensible data. Many quality control checks are done internally, such as the use of method blanks, matrix spikes, and laboratory control samples. However, a good quality assurance program will periodically utilize an independent third-party to evaluate the proficiency of its laboratory through participation in Proficiency Testing (PT) or Performance Evaluation (PE) studies. Proficiency Testing and Performance Evaluation studies are both independent objective studies used to evaluate the quality of data produced by a laboratory through analysis of blind samples provided by an outside source. For our purpose, PTs refer to the testing studies organized by the National Environmental Laboratory Accreditation Conference (NELAC), and PEs refers to similar testing studies organized by others (e.g., USGS, Environment Canada, QUASIMEME and Florida Department of Environmental Protection). PT/PE studies essentially adhere to the following process:

1. An outside source (or provider) provides a sample to the laboratory in which the sample composition is unknown to the laboratory
2. The laboratory analyzes the sample as part of its normal testing procedure or Standard Operating Procedure (SOP)
3. The results from the lab is sent back to the provider who evaluates the results using statistical methods
4. The provider then sends the laboratory (and accrediting authorities) the evaluation that includes a performance index or score, upon which a laboratory's accreditation is partly dependent
5. Based on the results of the test, the laboratory will evaluate its performance, which may include any necessary implementation and corrective actions.

A regular assessment of the technical performance of a laboratory is an important means of assuring the validity of analytical measurements as a part of an overall quality strategy. The main objectives of PT/PE studies include (i) assessing the accuracy of test results and (ii) meeting NELAC requirements for laboratory accreditation. However, successful implementation of PT and PE studies does not stop at obtaining passing or satisfactory scores. It is also used as a tool in identifying improvement areas in laboratory operation.

1.1 What PT/PE Studies Tell Us

Participation in PT/PE studies gives a laboratory an objective means of assessing and demonstrating the reliability of the data it produces. PT/PE studies are useful for revealing the strengths and weaknesses in

laboratory performance. The following lists information that may be garnered from the results of PT/PE studies:

1. The accuracy of the data produced by the laboratory
2. Identification of deficiencies within the laboratory's test methods (Do biases and error exist within the current test procedure?)
3. Whether or not corrective action is necessary
4. The current status of the laboratory compared to past performance (Is the lab performance getting better or worse?)
5. How the laboratory compares with other laboratories that participated in the study

1.2 Benefits of Participation

Periodic participation in PT/PE studies should be a natural part of a laboratory's routine check of quality control measures. Regular participation in PT/PE studies can help:

1. Identify deficiencies early and demonstrates a good quality assurance program which is important for the maintenance of laboratory accreditation.
2. Positive evaluations by reputable PT/PE studies validate the technical competency of a laboratory. This provides data end-users with confidence in the data's accuracy.
3. Comparative information about method and instrument performance
4. Overview of the quality of specific analyses in a sector, country or region

Section 2 Purpose and Scope

2.0 Purpose and Scope

Proficiency Test (PT) studies are scheduled at a program specified interval to ensure that the laboratory meets the frequency and quality criteria for each certification type (SDWA, NPW and Solids and Chemical Materials). Blind PT samples are acquired from a NELAC approved provider and are analyzed by the laboratory in accordance with routine Standard Operating Procedures. The results from the PT are submitted to the vendor who in turn directly submits the evaluation of the PT to the state NELAC accrediting authority, the Florida Department of Health (FDOH), or third party. These performance studies are required as a part of the certification procedures for the State of Florida. Requirements for the PT studies are based upon the current NELAC Standard.

The SFWMD laboratory participates in studies when the Performance Evaluation (PE) study provider meets the Guidelines for the Requirements for the Competence of Providers of Proficiency Testing (comprising ISO Guide 43-1:1997, as well as relevant elements of ISO/IEC 17025:2005 applicable to characterization, homogeneity and stability testing of proficiency testing materials), and the management system requirements of ISO/IEC 17025:2005, which includes the principles of ISO 9000:2005.

Ideally, PE samples are similar in nature to routine samples, and sufficiently homogeneous and stable not to influence the evaluation of participants' performance.

The goal of the SFWMD Chemistry Laboratory's "Guidance in Implementation of Proficiency Testing (PT) and Performance Evaluation (PE) Studies" is to give guidance for the selection of PT/PE providers, the protocol and process for study participation, the interpretation of study results, method improvement and corrective action.

Section 3 Proficiency Testing (PT) Studies

3.0 Proficiency Testing Studies

The State of Florida requires participation in Proficiency Testing studies for the purpose of certification. PT studies are organized by The National Environmental Laboratory Accreditation Conference (NELAC). NELAC maintains stringent criteria for the approval of PT Providers, test design and the accuracy of values assigned to test samples. The 2003 NELAC Standard (Section 2.4-Proficiency Testing) provides the protocol for participation upon which this section is based.

3.1 Process for Selection of PT Providers

The Proficiency Testing Oversight Body (PTOB)/Proficiency Test Provider Accreditor (PTPA) is responsible for approving PT sample providers. PT study samples must be obtained from a (PTOB)/ (PTPA) approved PT Provider. The PTOB/PTPA, The American Association for Laboratory Accreditation (A2LA), maintains a list of NELAC PT Providers at: <http://www.a2la.org/dirsearchnew/nelacptproviders.cfm>

Participating laboratories should choose a sample for each field of accreditation (matrix, technology/method, or analyte/analyte group). The SFWMD Chemistry Laboratory participates in the Non-Potable Water (NPW) study. The District laboratory is presently certified for 42 analytes, which are listed in Appendix B.

The selection of a PT Provider should be carefully chosen based on several criteria. First, locate a PT Provider with a testing scheme that is most similar to the routine analyses performed by the laboratory. Then select a PT Provider by considering the following:

1. Research the size of test study. How many laboratories participate in the study? Participation size is important for inter-laboratory comparison.
2. Research the quality of the PT Provider's test samples. This should include reviewing the Provider's history of sample value accuracy, homogeneity and stability.
3. Find out what kind of information is provided in the PT Provider's study evaluation. NELAC only requires the PT provider to report acceptable/not acceptable status for each analyte analyzed. However, some PT Providers also provide a summary of the individual laboratory's performance, usually based on a z-score, and a summary of the laboratory's performance compared to other laboratories that participated.

4. Based on the above criteria, evaluate if the cost of samples and program participation is reasonable.

3.2 Scheduling of PT Studies

To maintain accreditation, NELAC requires that a laboratory participate in two PT studies per year for each field of proficiency testing. The SFWMD Chemistry Laboratory currently participates in the Non-Potable Water (NPW) Accreditation every April and October (see Appendix C- 2006-2007 Schedule for Performance Testing and Inter-laboratory Studies).

3.3 Distribution and Analysis of PT Samples

The Laboratory Quality Assurance (QA) Officer is responsible for oversight of the PT Studies. Responsibilities include: selection of PT vendors, determination of testing frequency, and reporting of study results.

3.3.1 NELAC Requirements

Upon receipt of the PT Samples, the samples must be treated as if they were real environmental samples. Analysis of PT Samples shall utilize the normal:

1. Staff
2. Methods used in SOPs for that analyte
3. Procedure (including quality control checks)
4. Equipment and facilities
5. Frequency of analysis

Staff shall abide by the restrictions on exchange of information outlined in Section 2.5.1 of the NELAC Standard. The lab must keep copies of all written, printed, and electronic records (e.g., bench sheets, instrument strip charts or printouts, data calculations, and data reports) related to PT sample analysis for five years or for as long as required by the program. A copy of the PT study report form used to record PT results must also be included in the records. Samples must be analyzed and the results returned to the PT Provider by the study close date.

3.3.2 Laboratory Analysis

The following is an overview of the procedures followed by the SFWMD Chemistry Laboratory during a PT Study.

1. On arrival, PT Samples are inspected for shipment damage and contents.
2. Per standard operating procedure, samples are then logged into the Laboratory Information Management System (LIMS), and the labels and header sheets are printed.
3. The laboratory supervisors are notified that the samples are available for analysis.

4. The supervisors prepare the samples for analysis according to the sample instructions.
5. After preparation, the samples are analyzed along with quality controls, which are purchased from the PT Provider.

3.4 Review/Tabulation of Data and Submittal of Results

After analysis, the PT Samples are approved by the Laboratory Supervisors and the results of all PT and QC samples are submitted to the QA Officer for evaluation. The QA Officer completes the study's reporting forms and prepares the reports. Study results can be reported by three methods: online, mail or fax.

3.5 Evaluation of PT Lab Performance

3.5.1 Performance indicators

The z-score is a useful tool generated during a PT study that can be used as a performance indicator. A z-score is a measure of the deviation of the result (X_i) from the assigned value (X) for that determinant and are calculated as: $z = (X_i - X)/\sigma$, where σ is a standard deviation (EURACHEM). PT Sample results are evaluated using some form of parametric or nonparametric statistics to determine the mean and standard deviation. Determination of the method used to calculate the z-score is up to the PT Provider. NELAC does not prescribe a method for determining z-scores. Once a z-score has been determined, the performance is evaluated using a scale. The following is an example of the scale used by the SFWMD Chemistry Laboratory to evaluate its performance:

<u>Absolute Z-score</u>	<u>Rating</u>
0.00 to 0.50	Excellent
0.51 to 1.00	Good
1.01 to 2.00	Satisfactory
2.01 to 2.99	Questionable
≥ 3.00	Unacceptable

An example of a PT Study performance evaluation can be found in Appendix D. Other performance indicators include absolute t-value and relative bias.

3.5.2 Failed PT Study

Proficiency test acceptance limits, documented in the USEPA "National Standards for Water Proficiency Testing, Criteria Document", are used to determine the pass/fail evaluation of each analyte. For group PT samples, "acceptable" results must be obtained for 80% of the analytes in that group to receive a score of "Pass". Otherwise, greater than 20% "Not

Acceptable” results will receive a score of “Fail” for that PT analyte group. Failure to meet the semi-annual schedule for PT testing is also regarded as a failed study.

If the SFWMD Chemistry laboratory fails a PT Study, the Laboratory QA Officer will initiate the investigative process according to Section 2.7.4 of the NELAC Standard.

3.5.3 Failing Two PT Studies

If a lab fails two out of the most recent three PT studies, the lab may lose accreditation for the laboratory’s field of accreditation(s). In this case, a lab may participate in a Supplemental PT Study for Demonstrating Corrective Action (NELAC Standard 2.7.3) and meet the requirements for initial accreditation (NELAC Standard 2.7.2). Under these circumstances, the Laboratory QA Officer initiates an investigation on the cause of failure and documents the corrective action taken. The Laboratory QA Officer shall submit both the results of the investigation and the corrective measures taken to the Primary Accrediting Authority. The Florida Department of Health, Bureau of Laboratories is the Accrediting Authority for the SFWMD.

3.5.4 Long-Term Evaluation

If the laboratory performance during a PT Study is unsatisfactory then corrective action should be made:

1. After two consecutive, questionable, or marginal results;
2. If the results for any analysis show a clear trend towards unsatisfactory performance over three or more rounds; or
3. If a clear bias is observed in the results

A plot of collected performance test data may be used to assess performance over time. This is a very useful approach in the identification of trends. A laboratory’s internal quality control procedure is normally expected to identify trends. Trends may be used to identify improper instrument calibration or maintenance, or poor use of reagents. Monitoring PT performance over time acts as a backup system. A plot of the historical laboratory PT performance can be found in Appendix E- Historical Laboratory Performance.

Section 4

Performance Evaluation (PE) Studies

4.0 Performance Evaluation Studies

Performance Evaluation Studies are voluntary inter-laboratory studies also known as a “round robins”. PE Studies analyze real environmental samples, unlike PT Studies which use synthetic samples, which are similar in concentration to routine laboratory samples. The SFWMD Chemistry Laboratory currently participates in 3 such studies.

4.1 Process for Selection of PE Studies

The SFWMD Chemistry Laboratory chooses PE Studies based on the field of testing (matrix, method, or analyte). The following is a description of each study in which the laboratory participates.

4.1.1 USGS Round Robin

Biannually, the U.S. Geological Survey disseminates Standard Reference Samples (SRSs) to participating laboratories for a round-robin laboratory performance comparison study. The SRSs are typically prepared from natural-matrix water sources. The laboratories are evaluated based on their analytical performance on the measurement of inorganic and nutrient constituents. Laboratory results within the round determine the statistical parameters used for the performance evaluation.

4.1.2 National Water Research Institute (NWRI) Environment Canada

Environment Canada provides natural water samples with inorganic constituents for the evaluation of analytical methods. All results are evaluated for two important aspects of data: systematic bias and precision. Their services include semiannual sets of intercalibration and intercomparison proficiency testing samples and comprehensive data quality performance analysis reports.

4.1.3 QUASIMEME

QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) is hosted by Wageningen University and Research Centre, Wageningen, The Netherlands. QUASIMEME is a proficiency-testing study which provides seawater and estuarine samples for nutrient, DOC chlorophylls analyses and mercury in biological tissue. They also host conferences and workshops in support of participating laboratories.

4.2 Scheduling of PE Studies

The SFWMD Chemistry Laboratory attempts to evaluate every parameter every 3 months. This is reflected in the PT/PE testing schedule (Appendix C).

4.3 Distribution and Analysis of PE Samples

The process for the distribution and analysis of PE samples is the same as that described in Section 3.3.2 for PT Samples.

4.4 Review/Tabulation of Data and Submittal of Results

The Laboratory QA Officer is responsible for the compilation, evaluation, and submittal of all PE Sample and QC sample results. Study results can be submitted by three methods: online, mail or fax.

4.5 Evaluation of PE Lab Performance

Evaluation of PE Lab performance will be based on the performance index used by the PE study. Refer to Section 3.5.1 for explanation of the Z-score. The Laboratory QA Officer will determine the course of action in cases of poor performance. An example of a PE Study performance evaluation can be found in Appendix D.

4.5.1 Corrective Actions

One failed PE Study does not necessarily indicate a problem with laboratory performance. It is important to study the overall performance of all participants for a given scheme. Unsatisfactory performance in a round where a majority of the laboratories performed satisfactory may indicate a problem with the laboratory methodology used to test the sample. However, unsatisfactory performance in a round where the majority of the participants also performed poorly may suggest that the criteria for satisfactory performance were incorrectly set.

If the laboratory performance is unsatisfactory then corrective action should be made:

1. After one unsatisfactory result or Z-score on one round, if the analysis is a key component of the laboratory's business (TPO₄, OPO₄, TKN, NO_x, NH₄); or
2. If at least two unsatisfactory results or Z-scores are reported in one round, particularly if the analyses are linked; or
3. After two consecutive, questionable, or marginal results; or
4. If the results for any analysis show a clear trend towards unsatisfactory performance over two or more rounds; or
5. If results for any analysis over two rounds show clear and consistent bias, of at least one standard deviation above or below the assigned value, even if the results are satisfactory, or if the bias slope is >5%, or for five flagged values (Environmental Canada Study).

If one or more of the above criteria are met, a laboratory should identify and document the problem and decide whether corrective action is necessary. Below are possible corrective actions.

1. Analyze the quality problem based on the results of successive inter-laboratory studies, internal quality control data, and relevant measurements
2. Make a plan for corrective action
3. Execute and record the corrective action
4. Check whether the corrective action was successful

The procedure for the corrective action is described in SFWMD-LAB-SOP-5600-001.

4.5.2 Long-Term Evaluation

A plot of collected performance test data may be used to assess performance over time. This is a very useful approach in the identification of trends. A laboratory's internal quality control procedure is expected to identify trends. Trends may be used to identify improper instrument calibration or maintenance, or reagents preparation error. Monitoring PT performance over time can be used as a backup system to monitor QC procedures.

To this end, all performance scores for each PE study in which the SFWMD Chemistry laboratory participates are maintained in a central database. The stored data will be used to generate charts which show the distribution of Z-scores and laboratory performance trend line. The historical trend in laboratory PE performance can be found in Appendix E-Historical Laboratory Performance.

Section 5 Blind Studies

5.0 Blind Studies

A blind study is another example of a laboratory quality control check. Blind samples are inserted into the batch of routine samples unbeknownst to the analyst. Samples may be purchased from any reputable company that provides the certificate of analysis. After analysis, the results are examined by the Laboratory QA Officer for acceptability. Blind studies are used for investigations when additional information is needed or for confirmation of a problem.

Section 6

Overall Evaluation of Lab Performance

6.0 Overall Evaluation of Lab Performance

The SFWMD Chemistry Laboratory will monitor the overall Z-score performance of each PT/PE Study. An overall evaluation of lab performance will be based on all available results. PT/PE study results will be used for:

1. Regular, objective and independent assessment of the quality of routine analyses
2. Statistical evaluation that aids improvement of the technical work
3. Information used to evaluate methods and instrument performance

The overall historical laboratory performance in each study is presented on individual charts showing the distribution of z-scores and trend of lab performance (Appendix E).

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Appendix A Glossary

Accreditation: the process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of the National Environmental Laboratory Accreditation Program (NELAP), this process is a voluntary one. (NELAC)

Accrediting Authority: the Territorial, State, or federal agency having responsibility and accountability for environmental laboratory accreditation and which grants accreditation. (NELAC)[1.5.2.3]

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)

Analyte: a chemical compound that is the subject of a chemical analysis. (Merriam-Webster Dictionary)

Assessment Criteria: the measures established by NELAC and applied in establishing the extent to which an applicant is in conformance with NELAC requirements. (NELAC)

Bias: a systematic displacement of all the observations divided by their number. (AOAC)

Blind Sample: a sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process. (NELAC)

Certified Reference Material: a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO Guide 30-2.2)

Corrective Action: the action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)

Data Audit: a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the

resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria). (NELAC)

Error: the chance deviation between an observation and its expected or average value. (AOAC)

Everglades Round Robin: an interlaboratory comparison program initiated by the Florida Department of Environmental Protection (FDEP) for the purpose of assessing the comparability of phosphorus or total and methyl mercury data from laboratories engaged in the analysis of water samples. (FDEP)

Homogeneity: The degree to which a property or substance is randomly distributed throughout a material. (Taylor, J.)

Matrix: the component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:

Aqueous: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts.

Drinking Water: any aqueous sample that has been designated a potable or potential potable water source.

Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.

Non-aqueous Liquid: any organic liquid with <15% settleable solids.

Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.

Solids: includes soils, sediments, sludges and other matrices with >15% settleable solids.

Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.

Air: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device. (NELAC)

National Environmental Laboratory Accreditation Conference (NELAC): a voluntary organization of State and Federal environmental officials and interest groups purposed primarily to establish mutually acceptable standards for accrediting environmental laboratories. A subset of NELAP. (NELAC)

National Environmental Laboratory Accreditation Program (NELAP): the overall National Laboratory Accreditation Program of which NELAC is a part. (NELAC)

Performance Evaluation Studies (PE): Proficiency testing studies (other than NELAC) in which the SFWMD participates

Performance Index: an evaluation of multiple sets of data compiled into an overall measure.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC)

Proficiency Testing (PT): a means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (NELAC)[2.1]

Proficiency Testing Oversight Body/Proficiency Testing Provider Accreditor (PTOB/PTPA): an organization with technical expertise, administrative capacity and financial resources sufficient to implement and operate a national program of PT provider evaluation and oversight that meets the responsibilities and requirements established by NELAC Standard. (NELAC)

Proficiency Testing Program: the aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories. (NELAC)

Proficiency Testing Study Provider: any person, private party, or government entity that meets stringent criteria to produce and distribute NELAC PT samples, evaluate study results against published performance criteria and report the results to the laboratories, primary accrediting authorities, PTOB/PTPA, and NELAP. (NELAC)

Proficiency Test Sample: a sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (QAMS)

Protocol: a detailed written procedure for field and/or laboratory operation (e.g., sampling, analysis) which must be strictly followed. (EPA-QAD)

PT Fields of Testing: NELAC's approach to offering proficiency testing by regulatory or environmental program, matrix type, and analyte. (NELAC)

Quality Assurance: an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)

Quality Control: the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. (QAMS)

Reliability: the ability of an item or a system to perform a required function under stated conditions for a stated period of time (AOAC)

Standard Deviation: A statistic used as a measure of the dispersion or variation in a distribution, equal to the square root of the arithmetic mean of the squares of the deviations from the arithmetic mean. (American Heritage Dictionary)

Standard Operating Procedures (SOPs): a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks. (QAMS)

Test Method: Adoptions of a scientific technique for a specific measurement problem, as documented in a laboratory SOP. (NELAC)

Validation: the process of substantiating specified performance criteria. (EPA-QAD)

Variance: the square of the standard deviation, σ^2 . (American Heritage Dictionary)

Z-Score: a measure of the deviation of the result from the assigned value for that determinant (calculated as: $z = (X_i - X)/\sigma$ where σ is a standard deviation). (EURACHEM)

Sources:

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Florida Department of Environmental Protection

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US EPA Quality Assurance Division (QAD)

US EPA Quality Assurance Management Section (QAMS), Glossary of Terms of Quality Assurance Terms, 8/31//92 and 12/6/95.

Appendix B List of Analytes in which the SFWMD is Accredited

Charlie Crist
Governor



Ana M. Viamonte Ros, M.D., M.P.H.
State Surgeon General

Laboratory Scope of Accreditation

Page 1 of 3

Attachment to Certificate #: E46077-11, expiration date June 30, 2010. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E46077 EPA Lab Code: FL00103 (561) 681-2500

E46077
South Florida Water Management District Chemistry Laboratory
1480 Skees Road, Building 9
West Palm Beach, FL 33411

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Alkalinity as CaCO ₃	SM 2320 B	General Chemistry	NELAP	5/9/2007
Aluminum	SM 3120 B	Metals	NELAP	5/1/2002
Ammonia as N	SM 4500-NH ₃ H	General Chemistry	NELAP	5/1/2002
Arsenic	SM 3113 B	Metals	NELAP	5/9/2007
Cadmium	SM 3113 B	Metals	NELAP	5/9/2007
Calcium	SM 3120 B	Metals	NELAP	5/1/2002
Chloride	EPA 300.0	General Chemistry	NELAP	5/1/2002
Chlorophylls	SM 10200 H	General Chemistry	NELAP	5/1/2002
Chromium	SM 3120 B	Metals	NELAP	5/1/2002
Color	SM 2120 C	General Chemistry	NELAP	5/9/2007
Conductivity	SM 2510 B	General Chemistry	NELAP	5/1/2002
Copper	SM 3120 B	Metals	NELAP	5/1/2002
Fluoride	EPA 300.0	General Chemistry	NELAP	5/1/2002
Hardness	SM 2340 B	General Chemistry	NELAP	5/1/2002
Iron	SM 3120 B	Metals	NELAP	5/1/2002
Kjeldahl nitrogen - total	EPA 351.2	General Chemistry	NELAP	5/1/2002
Lead	SM 3113 B	Metals	NELAP	5/9/2007
Magnesium	SM 3120 B	Metals	NELAP	5/1/2002
Nitrate as N	SM 4500-NO ₃ F	General Chemistry	NELAP	5/1/2002
Nitrate-nitrite	SM 4500-NO ₃ F	General Chemistry	NELAP	5/1/2002
Nitrite as N	SM 4500-NO ₃ F	General Chemistry	NELAP	5/9/2007
Orthophosphate as P	SM 4500-P F	General Chemistry	NELAP	5/1/2002
pH	SM 4500-H+-B	General Chemistry	NELAP	5/1/2002
Phosphorus, total	SM 4500-P F	General Chemistry	NELAP	5/1/2002
Potassium	SM 3120 B	Metals	NELAP	5/1/2002
Residue-filterable (TDS)	SM 2540 C	General Chemistry	NELAP	5/1/2002
Residue-nonfilterable (TSS)	SM 2540 D	General Chemistry	NELAP	5/9/2007
Residue-volatile	EPA 160.4	General Chemistry	NELAP	5/1/2002
Silica-dissolved	SFWMD SOP 3120.1	General Chemistry	NELAP	1/4/2007
Sodium	SM 3120 B	Metals	NELAP	5/1/2002
Strontium	SM 3120 B	Metals	NELAP	4/7/2005
Sulfate	EPA 300.0	General Chemistry	NELAP	5/1/2002
Total organic carbon	SM 5310B	General Chemistry	NELAP	5/9/2007
Turbidity	SM 2130 B	General Chemistry	NELAP	5/1/2002
Zinc	SM 3120 B	Metals	NELAP	5/1/2002

Clients and Customers are urged to verify the laboratory's current certification status with the Environmental Laboratory Certification Program.

Issue Date: 7/1/2009

Expiration Date: 6/30/2010

Charlie Crist
Governor



Ana M. Viamonte Ros, M.D., M.P.H.
State Surgeon General

Laboratory Scope of Accreditation

Page 3 of 3

Attachment to Certificate #: E46077-11, expiration date June 30, 2010. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E46077 EPA Lab Code: FL00103 (561) 681-2500

E46077
South Florida Water Management District Chemistry Laboratory
1480 Skees Road, Building 9
West Palm Beach, FL 33411

Matrix: Biological Tissue

Analyte	Method/Tech	Category	Certification Type	Effective Date
Mercury	EPA 7473	Metals	NELAP	1/4/2007

Clients and Customers are urged to verify the laboratory's current certification status with the Environmental Laboratory Certification Program.

Issue Date: 7/1/2009

Expiration Date: 6/30/2010

Appendix C
Schedule for Performance Testing and Inter-laboratory Studies

2010 Schedule for Performance Testing and Performance Evaluation Studies

SCHEDULE												
Data Period ==>	January	February	March	April	May	June	July	August	September	October	November	December
Certification PT Study (ERA)				■	■					■	■	
USGS Round Robin		■	■					■	■			
Environment Canada (NRWI)	■					■	■					■
QUASIMEME (Wageningen University)	■	■	■				■	■	■			

STANDARD REFERENCE SAMPE Type																	
Sample Type	MATRIX																
	Surface Water				Sediments	Synthetic							Seawater			Estuarine	Fish Tissue
Standard Reference Sample Provider	Trace Elements	Major ions	Total Phosphorus in Fortified Water	Nutrients		Trace Metal	Minerals	Nutrients	Solids	Demand	Fluoride	Turbidity	Nutrients	DOC	Chlorophylls	Nutrients	Mercury
Certification PT					■	■	■	■	■	■	■						
USGS	■	■					■										
Environmental Canada	■	■	■														
QUASIMEME (Wageningen University)												■	■	■	■	■	■

Appendix D Examples of PT/PE Study Performance Evaluation

Proficiency Testing, NELAP Certification Study

Proficiency Testing (PT) is defined as a means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.

REQUIREMENTS FOR LABORATORY TESTING OF PT STUDY SAMPLES

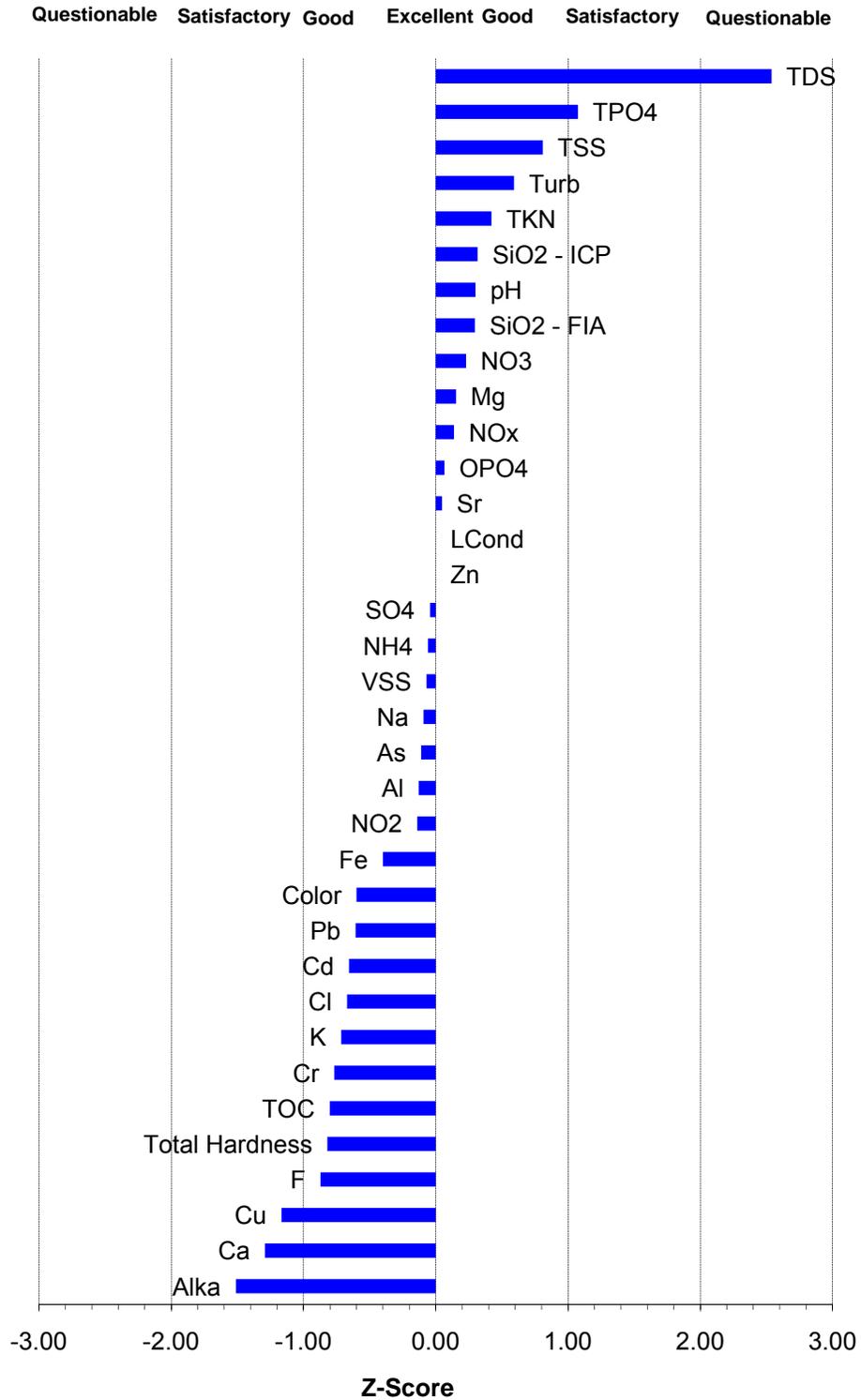
The samples shall be analyzed and the results returned to the PT Provider no later than 45 calendar days from the opening of the study (i.e., first day that samples are shipped or available to laboratories. The laboratory's management and all analysts shall ensure that all PT samples are handled (i.e., managed, analyzed, and reported) in the same manner as real environmental samples utilizing the same staff, methods as used for routine analysis of that analyte, procedures, equipment, facilities, and frequency of analysis. When analyzing a PT sample, a laboratory shall employ the same calibration, laboratory quality control and acceptance criteria, sequence of analytical steps, number of replicates and other procedures as used when analyzing routine samples.

Fields of Proficiency Testing (FoPTs) - the matrices, analytes, concentration ranges, and acceptance limits adopted for the PT program.

The [PT Expert Committee](#) of the NELAC Institute develops a standard for laboratory proficiency testing and proficiency testing samples, including: criteria for selection of the providers of the samples; protocols for the use of proficiency test samples and data in the accreditation of laboratories; and criteria for Proficiency Test Provider Accreditors (PTPAs).

Performance Testing Certification Results WP-177 October - November 2009

Unacceptable $Z \geq \pm 3$



Environment Canada Proficiency Testing Program

DESCRIPTION and PURPOSE

Environment Canada (EC) provides accredited proficiency testing studies for a wide range of inorganic constituents in water. These PE Studies are designed to quantify laboratory performance and improve the quality of environmental data.

DATA EVALUATION

Laboratory evaluations and performance statistics are calculated using a robust analysis for the number of usable test results.

Laboratory bias (ISO 13528:2005{E}, Section 7.1.1) is calculated as $D = x - X$, where D is the deviation, x is the test result and X is the assigned value. This deviation, normalized with the robust standard deviation (Annex C, Robust Analysis) is evaluated with the z-score calculation (ISO 13528:2005{E}, Section 7.4).

Systemic bias is indicated when the analytical results of a parameter are ranked, by the Youden non-parametric analysis, to be consistently and significantly higher or lower than the assigned value. Systemic bias may be indicated by the Youden rankings even when the test results have not been flagged for deviation from the assigned value.

Laboratory performance is ranked in terms of biased parameters (systemic bias) and flagged results (precision of measurement). Laboratories are assigned a 'rating' based on the sum of biased parameters and flagged results expressed as a *percentage*: Good: 0 to 5%; Satisfactory: >5 to 12.5%; Moderate: >12.5 to 30% or Poor: >30%.

2010-03-11

Program Name: FPMI

Number of Labs: 37

Study Code: 0095

Range of Samples: 1 to 10

Table 2a Laboratory Performance Scores - EC PT for Major Ions & Nutrients

Lab Code	Systemic Bias			Flagged Results			% Score (Sum of Parameters Biased & Results Flagged)
	No. of Parameters Analyzed	No. of Parameters Biased	Parameters Biased (50%)	No. of Results Reported	No. of Flags Assigned	Results Flagged (50%)	
F003	19	0	0.00	190	0	0.00	0.00
F004	5	0	0.00	50	0	0.00	0.00
F006	1	0	0.00	10	0	0.00	0.00
F014	1	0	0.00	10	0	0.00	0.00
F015b	2	0	0.00	20	0	0.00	0.00
F032	18	0	0.00	180	0	0.00	0.00
F036	16	0	0.00	160	0	0.00	0.00
F090	3	0	0.00	30	0	0.00	0.00
F304	3	0	0.00	30	0	0.00	0.00
F207	17	0	0.00	170	3	0.88	0.88
F009	11	0	0.00	110	2	0.91	0.91
F248	10	0	0.00	100	3	1.50	1.50
F158b	8	0	0.00	80	3	1.88	1.88
F026	15	1	3.33	148	2	0.68	4.01
F021	14	1	3.57	140	5	1.79	5.36
F158	19	2	5.26	190	4	1.05	6.32
F169	3	0	0.00	30	4	6.67	6.67
F183	18	1	2.78	180	15	4.17	6.94
F144	16	1	3.13	160	14	4.38	7.50
F042	16	2	6.25	160	7	2.19	8.44
F154b	1	0	0.00	10	2	10.00	10.00
F221	6	1	8.33	60	2	1.67	10.00
F010	16	3	9.38	160	5	1.56	10.94
F015	19	3	7.89	190	14	3.68	11.58
F074	16	2	6.25	160	27	8.44	14.69
F026b	4	1	12.50	39	2	2.56	15.06
F011	18	1	2.78	180	47	13.06	15.83
F022	18	4	11.11	180	22	6.11	17.22
F113	18	3	8.33	180	32	8.89	17.22
F266	12	2	8.33	120	35	14.58	22.92
F094	3	1	16.67	30	6	10.00	26.67
F154	20	6	15.00	200	49	12.25	27.25
F144b	2	1	25.00	20	1	2.50	27.50
F193	14	1	3.57	140	71	25.36	28.93
F159	10	3	15.00	94	38	20.21	35.21
F291b	2	1	25.00	20	15	37.50	62.50
F291	4	2	25.00	40	35	43.75	68.75

Laboratory Performance Rating

Rating	% Score*
Good	0 - 5
Satisfactory	> 5 - 12.5
Moderate	> 12.5 - 30
Poor	> 30

*Sum of Parameters Biased & Results Flagged

Program Name: FPMI

2010-03-12

Study Code: 0095

Table 3a Five-Year Historical Laboratory Performance - EC PT for Major Ions & Nutrients

LAB CODE	% Score Per Study (Sum of Parameters Biased & Results Flagged)										MEDIAN	RATING		
	0086		0087		0088		0089		0090				0091	
	Summer 2005	Winter 2005	Summer 2006	Winter 2006	Summer 2007	Winter 2007	Summer 2008	Winter 2008	Summer 2009	Winter 2009				
F003	3.6	5.8	0.5	0.3	2.5	0.8	0.8	2.5	0.8	2.5	0.0	1.6	Good	
F004	0.0	0.0	0.0	0.8	0.0	0.8	0.8	0.8	0.8	0.0	0.0	0.0	Good	
F006				10.0	15.0	0.0	0.0	0.0	0.0	15.0	0.0	0.0	Good	
F009	35.2	7.9	12.9	4.6	14.1	18.6	0.9	6.4	0.9	0.9	0.9	7.1	Satisfactory	
F010	25.8	20.1	15.6	15.9	11.7	9.6	10.9	18.4	10.3	10.9	13.6		Moderate	
F011	10.9	23.6	23.9	21.1	19.4	22.5	15.6	35.6	16.5	15.8	20.3		Moderate	
F014	16.5	6.2	7.1	5.3	9.4	10.0	8.8	0.0	7.2	0.0	7.1		Satisfactory	
F015	14.4	9.0	14.7	15.0	3.4	20.5	2.4	12.4	5.5	11.6	12.0		Satisfactory	
F015b						0.0	100.0	27.5	2.5	0.0	2.5		Good	
F021	4.7	10.7	6.3	11.3	12.0	8.3	5.3	1.3	11.3	5.4	7.3		Satisfactory	
F022	16.1	8.1	8.6	11.4	6.7	1.9	1.4	1.4	5.6	17.2	7.4		Satisfactory	
F028	1.7	0.9	22.6	3.8	7.5	5.3	0.3	8.8	0.3	4.0	3.9		Good	
F028b	5.0	1.7		0.0	37.5	0.0	27.5	17.5	0.0	15.1	5.0		Good	
F032	0.0	3.0	2.9	12.8	9.2	23.0	6.1	0.0	1.4	0.0	2.9		Good	
F038	50.0	6.9	4.1	2.5	8.1	4.4	15.9	16.6	1.9	0.0	5.6		Satisfactory	
F042	11.7	20.3	5.3	6.1	13.7	21.5	23.6	8.4	23.5	8.4	12.7		Moderate	
F074	16.7	5.0	12.8			4.0		16.8		14.7	13.7		Moderate	
F090							25.0	0.0	6.7	0.0	3.3		Good	
F094	2.7	12.1	2.1	9.5	9.3	15.5	14.3	11.0	0.0	26.7	10.3		Satisfactory	
F113	2.2	11.4	8.3	10.0	9.4	13.8	11.7	5.0	10.9	17.2	10.4		Satisfactory	
F144	10.0	17.5	15.0	5.4	9.2	12.9	12.9	2.1		7.5	10.0		Satisfactory	
F144b										27.5	27.5		Moderate	
F154									33.1	27.3	30.2		Poor	
F154b									25.0	10.0	17.5		Moderate	
F158	9.6	6.3	8.3	3.0	2.4	3.8	7.9	8.7	8.2	6.3	7.1		Satisfactory	
F158b		8.0	5.0	15.0	2.0	0.0	16.3	12.1	11.9	1.9	8.0		Satisfactory	
F159	42.5		43.2	24.2	58.2	39.2	12.0			35.2	39.2		Poor	

Laboratory Performance Rating
Rating % Score
Good 0 -5
Satisfactory > 5 - 12.5
Moderate > 12.5 - 30
Poor >30

PARAMETER: 15092 Total Phosphorus mg/L P

WATER SCIENCE & TECHNOLOGY
ENVIRONMENT CANADA

EC PT for Total Phosphorus in Water

SAMPLE	1=	2=	3=	4=	5=	6=	7=	8=	9=	10=
LAB NO	TP95-1 LAB RESULT	TP95-2 LAB RESULT	TP95-3 LAB RESULT	TP95-4 LAB RESULT	TP95-5 LAB RESULT	TP95-6 LAB RESULT	TP95-7 LAB RESULT	TP95-8 LAB RESULT	TP95-9 LAB RESULT	TP95-10 LAB RESULT
F003	0.001	0.011	0.033	0.117	0.067	0.274	0.004	0.337	0.466	0.913
F004	<0.002	0.006	0.031	0.120	0.071	0.272	<0.002	0.354	0.492	0.922
F007	<0.002	0.011	0.035	0.123	0.069	0.283	0.004	0.350	0.490	0.952
F010	0.0024	0.0125	0.0368	0.130 WH	0.0707	0.291	0.0056	0.351	0.508	0.959
F011	<0.01	<0.01	0.02 AL	0.11 WL	0.06	0.26	<0.01	0.28 AL	0.63 AH	1.17 AH
F015	<0.002	0.006	0.025 WL	0.104 AL	0.054 WL	0.24 WL	0.002	0.34	0.47	0.92
F021	<0.002	0.011	0.034	0.122	0.068	0.280	0.004	0.345	0.481	0.918
F022	<0.002	0.009	0.033	0.119	0.065	0.284	0.0041	0.333	0.481	0.963
F026	<0.001	0.0102	0.033	0.117	0.065	0.257	0.003	0.335	0.454	0.896
F026b	<0.02	<0.02	0.036	0.122	0.066	0.261	<0.02	0.331	0.458	0.894
F032	<0.01	<0.01	0.033	0.124	0.071	0.257	<0.01	0.322	0.475	0.921
F036	0.001	0.01	0.033	0.129 WH	0.066	0.284	0.003	0.347	0.49	0.929
F069	<0.008	0.011	0.034	0.121	0.068	0.273	<0.008	0.33	0.478	0.95
F069b	<0.02	<0.02	0.03	0.12	0.06	0.27	<0.02	0.33	0.47	0.92
F074	0.001	0.011	0.033	0.121	0.069	0.266	0.004	0.339	0.468	0.957
F112	<0.001	0.010	0.034	0.120	0.066	0.273	0.003	0.342	0.474	0.930
F113	<0.005	0.008	0.034	0.113	0.062	0.266	<0.005	0.332	0.454	0.878
F154	<0.010	<0.010	0.0336	0.117	0.0644	0.273	<0.010	0.338	0.474	0.909
F158	<0.005	0.006	0.024 AL	0.114	0.047 AL	0.246 WL	<0.005	0.323	0.450	0.928
F170	0.001	0.009	0.033	0.117	0.064	0.267	0.003	0.344	0.486	0.958
F183	<0.010	0.011	0.036	0.127	0.068	0.289	<0.010	0.365 WH	0.499	0.982
F202	0.004	0.013	0.036	0.123	0.070	0.280	0.006	0.347	0.488	0.944
F207	<0.002	0.009	0.034	0.117	0.069	0.278	0.004	0.339	0.483	0.932
F221	<0.001	0.010	0.033	0.119	0.066	0.269	0.003	0.335	0.465	0.927
F248	0.004	0.014	0.054 AH	0.118	0.071	0.27	0.007 WH	0.33	0.46	0.90
F304	<0.002	0.004 WL	0.028	0.117	0.062	0.275	<0.002	0.358	0.502	0.974
ASSIGNED VALUE *	0.0010	0.0100	0.0330	0.120	0.0660	0.272	0.0040	0.339	0.475	0.928
MEAN	0.0021	0.0097	0.0331	0.119	0.0654	0.271	0.0040	0.338	0.483	0.940
R-STD DEV *	0.00000	0.00260	0.00267	0.0046	0.00420	0.0116	0.00129	0.0114	0.0181	0.0296
RSD (%)	0.	26.	8.	4.	6.	4.	32.	3.	4.	3.
ACCEPTABLE LIMITS(+ -) *	0.00000	0.00520	0.00534	0.0092	0.00840	0.0232	0.00258	0.0228	0.0362	0.0592
WARNING LIMITS(+ -) *	.00000 .0000	.00520 .0078	.00534 .0080	.0092 .0138	.00840 .0126	.0232 .0348	.00258 .0038	.0228 .0342	.0362 .0543	.0592 .0888
ACTION LIMITS(< >) *	0.00000	0.00780	0.00801	0.0138	0.01260	0.0348	0.00387	0.0342	0.0543	0.0888
N *	7	21	26	26	26	26	15	26	26	26

* NOTE: SEE GLOSSARY FOR DEFINITIONS

The U.S. Geological Survey (USGS) Inter-laboratory Comparison Study

The U.S. Geological Survey (USGS) conducts an inter-laboratory comparison study semiannually. This project provides a variety of Standard Reference Samples (SRSs) for laboratory quality assurance testing and are available to purchase for internal quality control. The majority of samples are prepared with water from Colorado streams.

The objectives of the project have been to accomplish the following:

- Evaluate and improve the performance of participating laboratories;
- Provide a homogeneous, stable reference materials to laboratories;
- Identify analytical problem areas;
- Identify quality assurance needs with respect to environmental analyses and develop new reference materials to meet these needs; and
- Ascertain the bias and variability of analytical methods

STATISTICAL PRESENTATION OF DATA

Data are evaluated using nonparametric statistics. This statistical approach is a resistant statistic because outliers have less influence on the median, than on the mean in traditional parametric statistics. Statistical data for each sample analyte and for each laboratory are presented in tabular and graphical forms. Tabulated data includes the laboratory identification number; analytical method; reported values; most probable value (MPV); number of reported analyses, excluding less than values, (n); F-pseudo sigma; upper and lower hinges; percent difference; and the Z-value. The Z-value is equivalent to the Z-score of traditional statistics. The percent difference is a comparison between the reported value and the MPV (median). The F-pseudo sigma approximates the standard deviation of traditional statistics when the data has a Gaussian distribution. Less than values are not evaluated or used in the statistics but are identified if they are determined to be false negatives.

MPV = median value (excluding less than values)

F-pseudo sigma = $(U_h - L_h) / 1.349$

U_h = median of the upper half of the reported values (excluding less than values)

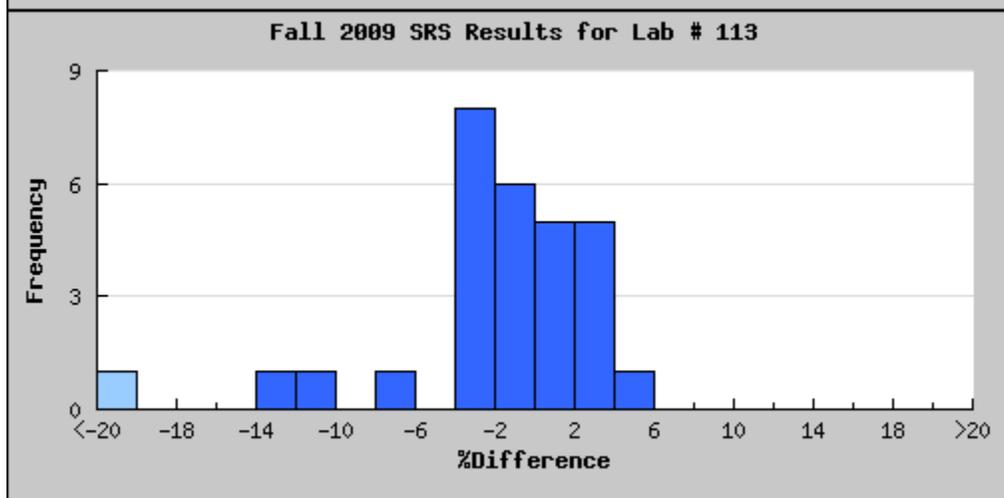
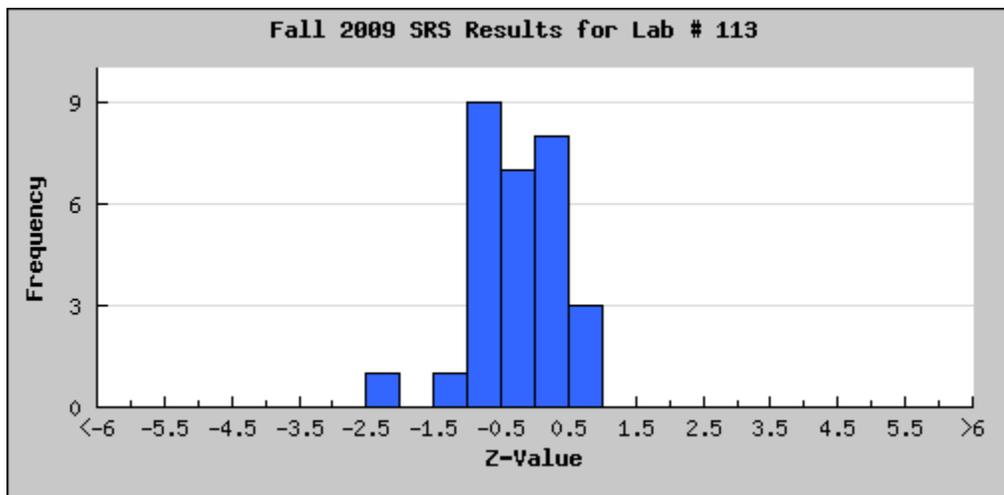
L_h = median of the lower half of the reported values (excluding less than values)

Z-value = $(\text{reported value} - \text{MPV}) / \text{F-pseudo sigma}$

%difference = $[(RV - \text{MPV}) / \text{MPV}] \times 100$



USGS Fall 2009 SRS Results for Lab # 113



Number of data points per sample	NUTRIENT (LOW)	MAJOR	TRACE
	5	13	13

SRS	Analyte	Method	RV	MPV	Fps	Z-value	% difference
N-103	Ammonia + Organic Nitrogen as N	22 Colorimetric	0.310 mg/L	0.354	0.067	-0.66	-12.43
N-103	Ammonia as N	22 Colorimetric	0.320 mg/L	0.320	0.017	0.00	0.00
N-103	Nitrite + Nitrate as N	22 Colorimetric	0.279 mg/L	0.272	0.010	0.70	2.57
N-103	Orthophosphate as P	22 Colorimetric	0.273 mg/L	0.277	0.009	-0.44	-1.44
N-103	Total Phosphorus as P	22 Colorimetric	0.299 mg/L	0.293	0.013	0.46	2.05
M-192	Alkalinity as CaCO3	21 Titration: electrometric	23 mg/L	23.9	1.19	-0.76	-3.77

M-192	Calcium	04 Inductively coupled plasma	4.8 mg/L	4.92	0.230	-0.52	-2.44
M-192	Chloride	07 Ion chromatography	12.6 mg/L	12.9	0.519	-0.58	-2.33
M-192	Fluoride	07 Ion chromatography	0.1 mg/L	0.129	0.026	-1.12	-22.48
M-192	Magnesium	04 Inductively coupled plasma	2.8 mg/L	2.72	0.111	0.72	2.94
M-192	Potassium	04 Inductively coupled plasma	0.9 mg/L	1.00	0.049	-2.04	-10.00
M-192	Residue on Evaporation	50 Gravimetric	60 mg/L	58.0	8.90	0.22	3.45
M-192	Silica	00 Other	7.82 mg/L	7.72	0.382	0.26	1.30
M-192	Sodium	04 Inductively coupled plasma	9.9 mg/L	9.88	0.374	0.05	0.20
M-192	Specific Conductance	41 Electrometric	102 µS/cm	102	2.97	0.00	0.00
M-192	Strontium	04 Inductively coupled plasma	156 µg/L	155	6.08	0.16	0.65
M-192	Sulfate	07 Ion chromatography	4.4 mg/L	4.54	0.278	-0.50	-3.08
M-192	Total Phosphorus as P	22 Colorimetric	0.075 mg/L	0.072	0.007	0.43	4.17
T-199	Aluminum	04 Inductively coupled plasma	93 µg/L	91.6	5.56	0.25	1.53
T-199	Arsenic	03 Atomic absorption: graphite furnace	<1 µg/L	0.203	0.064	--	--
T-199	Cadmium	03 Atomic absorption: graphite furnace	1.4 µg/L	1.50	0.111	-0.90	-6.67
T-199	Calcium	04 Inductively coupled plasma	3.7 mg/L	3.80	0.200	-0.50	-2.63
T-199	Chromium	04 Inductively coupled plasma	1.3 µg/L	1.28	0.130	0.15	1.56
T-199	Copper	04 Inductively coupled plasma	<2 µg/L	1.98	0.219	--	--
T-199	Iron	04 Inductively coupled plasma	169 µg/L	171	9.49	-0.21	-1.17
T-199	Lead	03 Atomic absorption: graphite furnace	1.4 µg/L	1.44	0.070	-0.57	-2.78
T-199	Magnesium	04 Inductively coupled plasma	6.4 mg/L	6.20	0.315	0.63	3.23
T-199	Potassium	04 Inductively coupled plasma	1.8 mg/L	1.87	0.111	-0.63	-3.74
T-199	Sodium	04 Inductively coupled plasma	7.7 mg/L	7.72	0.285	-0.07	-0.26
T-199	Strontium	04 Inductively coupled plasma	20.5 µg/L	20.7	0.964	-0.21	-0.97
T-199	Zinc	04 Inductively coupled plasma	6 µg/L	6.23	0.749	-0.31	-3.69

QUASIMEME EVALUATION STUDY

The acronym QUASIMEME comes from its EU project name "Quality Assurance of Information for Marine Environmental Monitoring in Europe" which was founded in 1993. The project has since kept this acronym. Its aim was to develop a holistic quality assurance program for marine environmental monitoring information in Europe.

Data Assessment

All data received from participants are entered into the QUASIMEME database and assessed using a standard procedure to allow direct comparison between participants in each round and between rounds. The approach to the assessment is based on the standard, ISO 135281, the IUPAC International Harmonized Protocol for Proficiency Testing. The summary statistics are based on Robust Statistics following DIN 38402, the AMC method and the Cofino Model. However, the assigned value and the laboratory assessment using the z-score are based on the Cofino Model.

The Cofino model has been developed for the routine QUASIMEME assessments. The Cofino model uses a Normal Distribution Assumption (NDA). The assigned value is based on the Cofino NDA model without any trimming of the data. This approach includes all data in the evaluation and no subjective truncation is made. This model has been further developed to include Left Censored Values (LCV). The development of these models has been fully documented and published.

The details of the Cofino Model approach are as follows:

- All data included in the assessment
- No data trimmed or down weighted
- Assigned values (AV) based on Cofino NDA model
- All LCV are also included, provided certain criteria are met

Following usual practices e.g. ISO 43, the z-scores can be interpreted as follows for laboratories which take part in Quasimeme to assure the quality of their data for use in international marine monitoring programs:

$|Z| < 2$ Satisfactory performance

$2 < |Z| < 3$ Questionable performance

$|Z| > 3$ Unsatisfactory performance

$|z| > 6$ frequently points to gross errors (mistakes with units during reporting, calculation or dilution errors, and so on).

LCV key: C – Consistent

I – Inconsistent

No data: B - Blanc

It is not possible to calculate a z-score for left censored values (LCV's). Quasimeme provides a simple quality criterion:

$LCV/2 <$ (concentration corresponding to $|z|=3$) : LCV consistent with assigned value

$LCV/2 >$ (concentration corresponding to $|z|=3$) : LCV inconsistent with assigned value, i.e. LCV reported by laboratory much higher than numerical values reported by other laboratories.

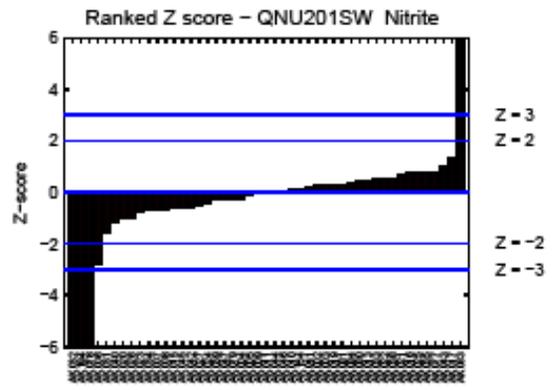
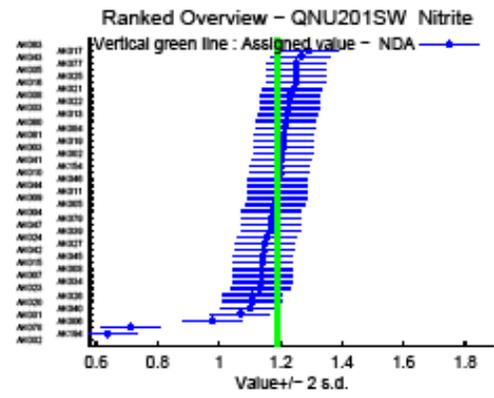
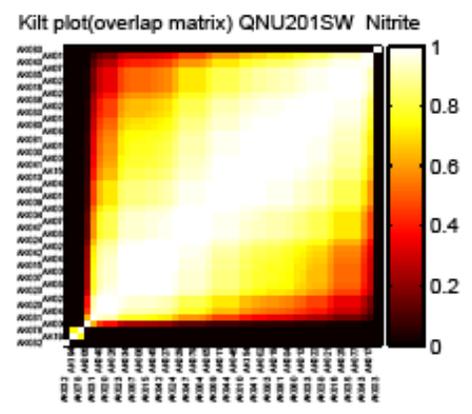
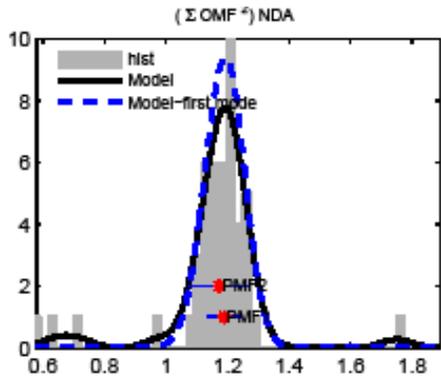
Quasimeme Database

Q763A South Florida Water Management District
Zdzislaw Kolasinski
U.S.A.

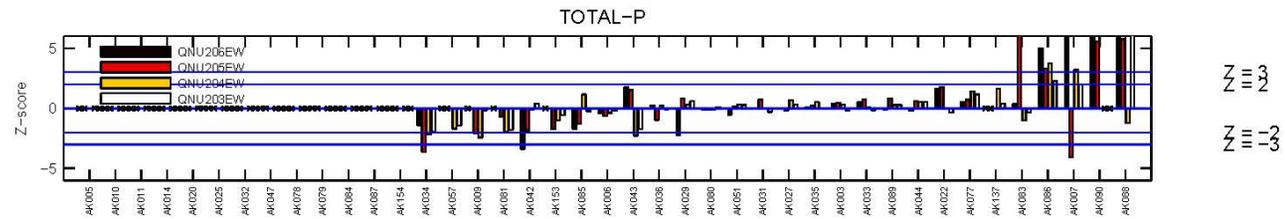
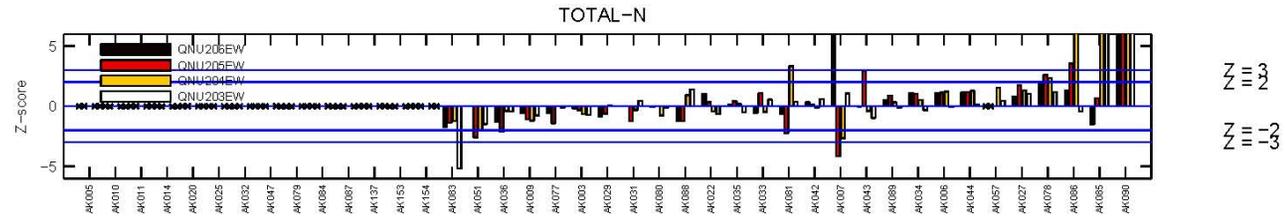
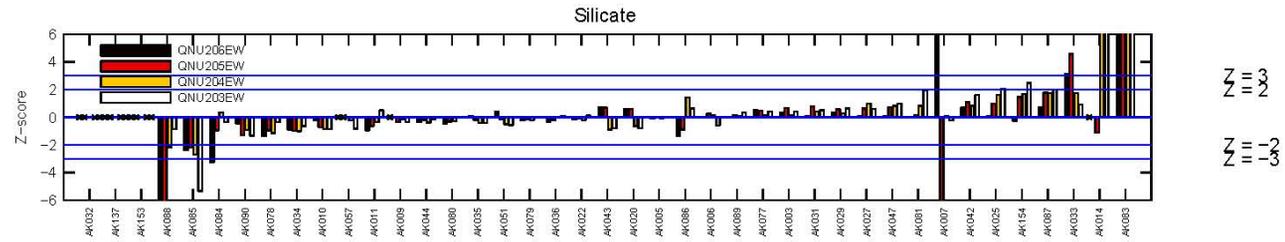
Exercise 854 – R58 Nutrients in Estuarine and low salinity open
water: Jul – Oct 2009

<i>Matrix</i>	<i>Determinand</i>	<i>Mean</i>	<i>Units</i>	<i>Assigned Value</i>	<i>Total Error</i>	<i>Z Score</i>	<i>z</i>	<i>Total Dupl.</i>
QNU203EW	TOxN	77.30	µmol/l	76.11	4.592	0.3	S	1
QNU203EW	Nitrite	8.070	µmol/l	8.488	0.514	-0.8	S	1
QNU203EW	Ammonia	19.80	µmol/l	19.94	1.246	-0.1	S	1
QNU203EW	Phosphate	8.200	µmol/l	8.368	0.527	-0.3	S	1
QNU203EW	Silicate	37.90	µmol/l	36.76	2.256	0.5	S	1
QNU203EW	TOTAL-N	102.0	µmol/l	99.08	6.195	0.5	S	1
QNU203EW	TOTAL-P	8.300	µmol/l	8.465	0.533	-0.3	S	1
QNU204EW	TOxN	34.10	µmol/l	33.52	2.036	0.3	S	1
QNU204EW	Nitrite	3.570	µmol/l	3.742	0.229	-0.7	S	1
QNU204EW	Ammonia	11.80	µmol/l	11.83	0.760	0.0	S	1
QNU204EW	Phosphate	4.550	µmol/l	4.660	0.305	-0.4	S	1
QNU204EW	Silicate	23.60	µmol/l	23.00	1.430	0.4	S	1
QNU204EW	TOTAL-N	45.50	µmol/l	46.48	3.039	-0.3	S	1
QNU204EW	TOTAL-P	4.650	µmol/l	4.670	0.305	-0.1	S	1
QNU204EW	DOC	5.800	C mg/L	6.211	0.423	-1.0	S	1
QNU205EW	TOxN	4.210	µmol/l	4.639	0.303	-1.4	S	1
QNU205EW	Nitrite	0.928	µmol/l	0.928	0.061	0.0	S	1
QNU205EW	Ammonia	1.780	µmol/l	1.250	0.125	4.2	U	1
QNU205EW	Phosphate	0.840	µmol/l	0.868	0.077	-0.4	S	1
QNU205EW	Silicate	7.200	µmol/l	6.843	0.461	0.8	S	1
QNU205EW	TOTAL-N	19.20	µmol/l	21.07	1.514	-1.2	S	1
QNU205EW	TOTAL-P	1.070	µmol/l	1.009	0.086	0.7	S	1
QNU206EW	TOxN	<0.357	µmol/l	0.087	0.036		C	1
QNU206EW	Nitrite	<0.143	µmol/l	0.015	0.007		I	1
QNU206EW	Ammonia	1.710	µmol/l	1.294	0.212	2.0	S	1
QNU206EW	Phosphate	0.130	µmol/l	0.153	0.044	-0.5	S	1
QNU206EW	Silicate	2.700	µmol/l	2.665	0.383	0.1	S	1
QNU206EW	TOTAL-N	15.70	µmol/l	15.73	2.216	0.0	S	1
QNU206EW	TOTAL-P	0.323	µmol/l	0.324	0.065	0.0	S	1

The letters in the z column indicate: S – Satisfactory, Q – Questionable,
U – Unsatisfactory, C – Consistent, I – Inconsistent, B - Blanc.



Summary Plots



Appendix E
Historical Laboratory Performance

The historical laboratory performance for each parameter can be access on the laboratory website at the following address:
https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_eraint/pg_sfwmd_eraint_chemistrylab?piref2074_4650556_2074_4650553_4650553.tabstring=tab20736398

Analyte:

Begin Date:
 e.g., Jun-2001

End Date:
 e.g., Dec-2006

PT/PE Provider:
 Select * for all providers

Z-scores Above 3.0	
Z-Score	Testing Date
4.7	Jan-2007

