Appendix 2A-1: Guidelines for Selecting Laboratories for Everglades Phosphorus Measurements

Florida Department of Environmental Protection
Bureau of Laboratories

BACKGROUND

Phosphorus has been identified in the Everglades Forever Act as the chemical agent responsible for undesirable ecological changes in the Everglades. Studies focused on establishing and quantifying ecological impacts due to phosphorus inputs have revealed the importance of accurately detecting and measuring phosphorus at very low concentrations. Typically, decisions for Everglades ecological preservation and restoration projects require that detection limits for total phosphorus be established at levels near or below marsh background concentrations.

Some of the historical Everglades data sets have been found to be inadequate for quantifying ecological change, primarily because the phosphorus measurements generated for those studies lacked sufficient sensitivity, accuracy and/or precision. The intent of this paper is to establish guidelines for procuring laboratory services with reasonable assurance that all phosphorus data generated will meet or exceed data quality objectives for Everglades restoration projects.

LABORATORY ACCREDITATION

All analytical work for Everglades restoration projects must be performed by a laboratory that maintains accreditation under the National Environmental Laboratory Accreditation Program (NELAP). NELAP provides for a minimum set of standards to ensure: (1) a documentation history of all essential data elements necessary to reconstruct reported results is maintained, (2) analyst training and demonstration of proficiency has been performed and documented, and (3) satisfactory analytical performance has been achieved on proficiency testing samples. NELAP accreditation must be obtained for all test methods that support Everglades restorations projects and must be maintained for the duration of the project.

METHODOLOGY

All methodology used must be accredited under NELAP for the duration of the project and must comply with FAC 62-160. Methods must be based on EPA or AWWA Standard Methods or validation data for Performance Based Measurement Systems (PBMS) must have been submitted to the Florida Department of Environmental Protection (FDEP) and approved. All method validation exercises must be performed using field matrix samples from the area of study and equivalency must be demonstrated vis-à-vis standardized EPA or AWWA methodologies (refer to *New and Alternative Analytical Methods*, DEP-QA-001/01). All preservation techniques and holding times must comply with guidelines published in 40 CFR Part 136 Table 2.

METHOD DETECTION LIMITS

Laboratories participating in Everglades restoration projects must maintain, and have documented, routinely achievable detection limits for total phosphorus of less than 5 µg/L. All detection limits must be calculated on an ongoing basis using data collected from each analytical run. All detection limits studies must have been conducted in accordance with FAC 62-160. Validation data for initial detection limit studies must have been submitted to the FDEP and approved.

PRACTICAL QUANTITATION LIMITS

Practical quantitation limits (PQLs) are defined in FAC 62-4 as the lowest measured value that can be quantified within specified limits of accuracy and precision. At values above the detection limit, the relative precision of a series of measurements (the measurement precision divided by the measured mean value) increases greatly as the detection limit is approached. For Everglades restoration projects, accuracy within 70 to 130 percent and long-term precision of less than 15 percent relative standard deviation (RSD) must be documented and maintained for total phosphorus concentrations of 10 µg/L or less in laboratory check standards. The accuracy at 10 µg/L must be evaluated at least once during each analytical run. Any data reported below the laboratory's practical quantitation limit must be qualified, as specified in FAC 62-160.

QUALITY CONTROL REQUIREMENTS

All quality control requirements, specified in NELAP Chapter 5, must be documented and maintained. For total phosphorus, a minimum of 5 calibration standards (excluding any calibration blank) must be included in analytical calibration curves. For background marsh samples, it is highly recommended that the upper calibration range not exceed 200 µg/L. Analytical sensitivity must be evaluated using a check standard prepared at the practical quantitation limit for each analytical run as described above. Analytical sensitivity evaluations must pass the criterion for accuracy specified for PQLs (70 to 130 percent recovery). Sample matrix spikes, using actual Everglades samples, must be evaluated with each analytical batch. Spike fortification should target a final concentration of 2 to 5 times the amount of phosphorus expected in the samples. Control limits for sample matrix spikes must not exceed 85 to 115 percent accuracy. If control limits for any measurements specified in NELAP Chapter 5 are exceeded (including control limits for sample matrix spikes), either the analysis must be repeated or all data reported for the associated analytical or preparation batch must be appropriately qualified as specified in F.A.C. 62-160. Data deemed to be inappropriate for project data quality objectives are subject to rejection by project managers.

PERFORMANCE DEMONSTRATIONS

Prior to performing any analytical work on Everglades restoration projects, laboratories must have demonstrated acceptable performance for total phosphorus measurements. Acceptable performance for initial consideration is either: (1) adequate performance (an overall rating of 3 or better) in at least one recent exercises of the Everglades Phosphorus Round Robin program, or (2) an average score of 2.0 or greater for total phosphorus on two or more consecutive, recent proficiency evaluation studies sponsored by the U.S. Geological Survey, Branch of Quality Systems (Standard Reference Sample Project, Nutrient Series), with no individual score for any total phosphorus measurement to be less than 1.0 .

In addition to the initial demonstration of performance, laboratories must agree to continue to participate and achieve acceptable performance (as described above) in the ongoing Everglades Phosphorus Round Robin program and in the USGS Standard Reference Sample Project). In the event that laboratory performance is unacceptable in a proficiency study (as described above), the project manager must be notified and the laboratory must take appropriate corrective action. Laboratories must agree to work with other participating laboratories to solve performance problems in a reasonable period of time. The laboratory and the project manager will undertake remedial action with regard to data reported during a period of poor performance.

DATA USABILITY

It is incumbent on laboratories to understand programmatic data quality objectives. Laboratories must perform an ongoing review of all aspects of data generation to ensure data are of sufficient quality to meet or exceed program objectives. Data review must include, at a minimum, an assessment of: (1) calibration curve, (2) results for all quality control samples specified in this document, (3) analytical detection limits and blank sample results, (4) potential analytical interferences, (5) field quality control sample results (blanks, duplicates, filtered and unfiltered sample results, etc.), (6) holding time requirements, and (7) comparison of reported analytical results versus historical values for the area under study (when available). Laboratories must take appropriate corrective action and notify their project manager whenever any aspect of the analysis fails to conform to requirements specified in the analytical method, this document or in NELAP Chapter 5.

AUDITS

Prior to beginning any analytical work for Everglades restoration projects, laboratories must be audited by the FDEP (or by a delegated representative from a contracting agency) for the purpose of determining their suitability to perform the analytical work. The FDEP audit will consist of a data validation audit and/or on-site performance audit. Electronic data must be available to FDEP from participating laboratories. Any critical deficiencies noted in audits must be corrected prior to performing analytical work on an Everglades restoration project.

EVERGLADES ROUND ROBIN PROGRAM

FDEP will conduct an Everglades Round Robin program twice annually. The program will consist of samples collected at Everglades marsh and canal sites as well as independent reference standards. The samples will be sent to participating laboratories for total phosphorus analysis and the results will be evaluated by FDEP using statistical methods recommended by the Florida State University Statistics Department for this exercise.