Florida Department of Environmental Protection

Bob Martinez Center
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Charlie Crist
Governor

Jeff Kottkamp
Lt. Governor

Michael W. Sole
Secretary

VIA EMAIL
January 8, 2008

Dr. Laurie E. Trenholm
Dr. John L. Cisar
Dr. J. Bryan Unruh
Mr. Peter Straub
University of Florida IFAS

SUBJECT: Performance and Records Audits conducted on work completed under WM869 at the Ft. Lauderdale Research and Education Center; The Plant Science Research and Education Unit in Citra; West Florida Research and Demonstration Site in Jay and the Analytical Research Laboratory in Gainesville – July and August 2007 – Final Audit Report

Audit Outcome

We have evaluated your responses to the preliminary audit report of referenced sites. The proposed corrective actions are acceptable with these comments:

- Field filtration is only required if the analysis of o-phosphorus continues to be part of this study. The nitrate samples must not be filtered, but must be preserved with sulfuric acid and placed in ice immediately after collection.
- The Ft. Lauderdale response did not discuss how the nitrate spike data are to be used. Further, the response to finding 14 of the records audit seems to imply that vials are reused. This is acceptable, but a non-phosphate detergent must be used. Further cleaning (acid rinsing) may be required if the levels in the blanks continue to be a significant factor.
- The field notes must identify the method of preservation (including acid, ice and freezing).
- Freezing is not mentioned as an acceptable practice in the DEP SOPs. It is mentioned in the QAPP, but the implication was that it would be used only if the samples could not meet the holding time. This was interpreted by the DEP QA reviewers to be the exception, not the routine procedure. If freezing continue to be the practice, a holding time study that compares results of properly preserved samples with frozen samples must be submitted to DEP for review and approval. If freezing is determined to be an acceptable practice, a conventional freezer should be used. A frost-free freezer may be acceptable if it can be demonstrated through continuous monitoring that the temperature of the freezer compartment does not exceed -10°C at any time during the freezing cycle.
- It is not clear how the laboratory intends to control values that are excessively negative, what the acceptance limit will be, or how these samples will be evaluated and treated. These items must be part of an SOP that clearly outlines what steps will be taken to evaluate negative values. In addition, as stated before, negative values cannot be set to zero. The lowest value that can be assigned to a negative number is the corresponding method detection limit.

- The laboratory must note in the analytical records the justification for dropped standard. This may be a reference to a specific section of an SOP that addresses dropped standards.
- In order to ensure the comparability of the data from the three locations, cross training as well as regularly scheduled teleconferences that involve all the sample teams should be implemented. The teams should discuss all aspects related to field activities including containers, preservation procedures, documentation and records, and actual sampling procedures.
- Unless an extensive comparability study is performed concerning the effects of filtering, freezing and extended holding times, data sets that use proper preservation techniques and are analyzed within holding times should not be compared with data sets from previously generated data.
- Researchers are again cautioned against setting negative results to zero. The reporting conventions for reporting non-detects and values between detection and the quantitation limits must be observed and used when evaluating data sets.
- In comparing the laboratory data from Ft. Lauderdale with the field records, it appears that many samples may have been mislabeled or switched. We have data for field blanks with hits of o-P as high as 1809 ppb, hits in samples identified as rain water as high as 8100 ppb, and nitrate spikes with no recovery. There are also notes in the field records that seem to indicate that sets of samples may not be properly identified. In observing the samplers during the field audit, it appears that they rely heavily on the "grid approach" rather than identifying each sample with a label. This practice can produce the types of mislabeling that were observed in the project audit. Samplers must ensure that the label **on the sample container** accurately identifies the sample location.

Appropriate corrective actions must be implemented for each of the items mentioned above.

The attached executive summary will be posted on the DEP Website, and this letter with our recommendations for data use will be forwarded to Michael Thomas and Eric Livingston.

Future Activities

Your response included a memo to Eric Livingston and Silky Labie that discussed several scenarios and proposals. Eric and Michael Thomas will need to make the final decision on the benefits and improvements of each of your proposals, however these comments are offered on two of your suggestions:

- A preservation study to demonstrate the difference between freezing and acidifying must be reviewed and approved by EAS. If the intent is to demonstrate no differences between properly preserved and analyzed samples as past data, all field treatment scenarios including filtration and long and short-term freezing must be included
- If an independent QA officer is hired to facilitate the QA process, that individual must be fully knowledgeable in QA and QC concepts as they relate to environmental analyses, and be willing to follow the already established procedures of the Gainesville Laboratory. Auditors noted that many analytical and quality control problems were identified and corrected as a result of the current procedures.

If you have any questions concerning these actions, please call Jessica Patronis or Silky Labie. We can be reached at (850) 245-8065. If you prefer email, the following email addresses may be used: silky.labie@dep.state.fl.us, or jessica.patronis@dep.state.fl.us.

Sincerely,

Silky S. Labie
Jessica Patronis
Environmental Assessment Section

Attachment: Executive Summary

cc (via email): Russ Frydenborg, EAS
Tom Frick, EAS
Jessica Patronis, EAS
Danny Wardell, EAS
Michael Thomas, DEP
Eric Livingston, DEP
Basil Wetherington, IFAS
Karen Williams, IFAS
Phil Moon, IFAS

Executive Summary
Audit of IFAS activities related to WM869

Audited Organizations:
IFAS Plant Science Research and Education Unit
2556 West Highway 318,
Citra, Florida 32113

UF / IFAS Analytical Research Laboratory
631 Wallace Building
Gainesville, FL 32611

Ft. Lauderdale Research & Education Center

West Florida Research and Education Center
4253 Experiment Drive
Highway 182
Jay, FL 32565-9524

Audit Dates: July and August 2007

Audit Location: Citra, Gainesville, Davie and Jay Florida

DEP Auditors:
Jessica Patronis
Silky S. Labie
Tom Frick
Danny Wardell
Environmental Assessment Section
2600 Blair Stone Road, MS 6511
Tallahassee, FL
(850) 245-8065

This audit was conducted to evaluate data generated under direct contract (WM869) to DEP. This study involved three different researchers at different geographic locations in the Florida whose samples were submitted to the IFAS laboratory in Gainesville, Fl. The purpose of the audit was to determine whether or not the generated data could be used to support decisions concerning levels of nitrates in fertilizer and to build a background data set for concentrations of o-phosphorus.

Two types of audits were performed. Performance audits were conducted at each site to evaluate current field procedures. The field teams were evaluated based on the requirements of the DEP Standard Operating Procedures for Field Activities. Project audits were performed using criteria that were developed to meet specific data quality objectives of the project. Selected records from the field stations and the laboratory were reviewed to determine if sufficient information was available to verify the quality of the data, with emphasis on calibration, quality control procedures, and documentation. The purpose of the audit was to determine data usability and was not intended as a regulatory action against the audited party.

The Environmental Assessment Section (EAS) determined that that field procedures were significantly different in the three locations, including whether samples were filtered, the immediacy of preservation and completeness of information that was recorded for each sampling event. None of the samples were preserved according to the DEP SOPs requirements, nor were samples analyzed within the holding times specified in the SOPs. All samples were frozen (some in frost free refrigerators) for various lengths of time before analysis; and no sample met the required 48-hour holding time. In at least one location, there was a noticeable problem with misidentifying samples. The field records did not contain sufficient

information to allow verification of actual sampling events or subsequent storage conditions and the results of field blanks indicate significant levels of o-phosphorus in some of the blanks.

The analytical records from the laboratory were complete, with the exception of sample receipt, storage and temperature logs and the fact that numerous samples were reported with negatives values that were exceeded the value of the reported method detection limit.

Based on the observations, and the responses to the observations, the EAS makes the following recommendations concerning data use:

1. All data generated to from samples that were frozen, should not be used to make definitive conclusions concerning the leaching rate of phosphorus or nitrates. The data can be used to determine relative differences at the three different locations.
2. The data from the three sites cannot be used as a single data set because of the differences in preservation procedures and filtration unless it can be demonstrated through a comprehensive comparability study that various filtration and freezing techniques do not significantly bias the data. If such a study is attempted, the principle investigators must work closely with the EAS to ensure that the study would provide useful information.
3. The data for o-phosphorus from the Jay and Ft. Lauderdale sites cannot be considered representative of the concentrations in the leachate since these samples were not filtered in the field.
4. The o-phosphorus data must be assessed relative to the contamination in the associated field blanks. Any data that are used must be greater than 10 times the concentration of the associated field blank.

Other supporting information is available upon request.