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Annual Summary Quality Assessment Report for the Coastal Water Quality Monitoring Network

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ANNUAL SUMMARY
Quality Assessment Report for the Coastal Water Quality Monitoring Network
(Agreement 4600000352)

For the period
January - December 2007

Submitted to the
Environmental Resource Assessment Department
Water Quality Analysis Division
South Florida Water Management District
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INTRODUCTION

This report is a summary of the assessment of the Southeast Environmental Research Center at Florida International University (SERC) field sampling and laboratory analysis project for the South Florida Water management District (SFWMD or District) funded Coastal Water Quality Monitoring Network, primarily for the following projects: Florida Bay (FLAB), Whitewater Bay (WWB), Biscayne Bay (BB), Ten Thousand Islands (TTI), and Rookery Bay (ROOK), from January 1, 2007 through December 31, 2007.

Water quality parameters monitored at each station include the dissolved nutrients nitrate + nitrite (NO_x^-), nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), inorganic nitrogen (DIN), and soluble reactive phosphorus (SRP). Total concentrations of nitrogen (TN), organic nitrogen (TON), phosphorus (TP), and organic carbon (TOC) were also measured. All concentrations for each of these parameters are reported as parts per million (ppm) except where noted. Phytoplankton biomass was measured using chlorophyll *a* (CHLA, $\mu g\ l^{-1}$). Field parameters measured at both surface and bottom of the water column include salinity, dissolved oxygen (DO; $mg\ l^{-1}$), and temperature (^oC). Turbidity (NTU) and pH were measure in surface water only.

Because field quality control (QC) samples are collected for trips that include multiple project samples for the stations of interest, the report may also cover information on stations or projects other than those in the above list. For 191-199 all samples were collected with duplicates; for surveys 200 to 202 and as requested by the SFWMD, field duplicates were collected but no sample duplicates were taken.

The SERC *Field Sampling Quality Manual*[1] provides the minimum requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual*[2] provides the minimum requirements followed in preparing and analyzing laboratory samples, as well as data verification and validation. The *Field Sampling Quality Assessment* and *Laboratory Analysis Quality Assessment* sections in this report provide the field and laboratory QC results during this quarter. The SERC Laboratory Information Management System provided the data used in this report. These data are considered preliminary until release into the District's DBHYDRO database.

This report is therefore a quality assurance QA/QC summary of collective efforts contributing from both field and laboratory staff. Its contents have been reviewed by the Quality Assurance Officer of the SERC laboratory.

[1]SERC-FIU. 2006. Field Sampling Quality Manual, Version X. Southeast Environmental Research Center, Florida International University, Miami, FL.
[2]SERC-FIU. 2008. Chemistry Laboratory Quality Manual, Version X. Southeast Environmental Research Center, Florida International University, Miami, FL

GLOSSARY

Accuracy. The agreement between the actual obtained result and the expected result. QC-check samples, having known or "true" values, are used to test for the accuracy of a measurement system.

Equipment Blank (EB). A general terminology used for analyte-free water that is processed onsite through all sampling equipment used in routine sample processing. May be an assessment of effectiveness of laboratory decontamination or on-site (field) decontamination (FCEB).

Field Blank (FB). Analyte-free water that is poured directly into the sample container on site during routine collection, preserved and kept open until sample collection is completed for the routine sample at that site. FB values are indicative of environmental contamination on site.

Field Cleaned Equipment Blank (FCEB). Analyte-free water that is processed on-site, after the first sampling site, through all sampling equipment used in routine sample processing. EB values are indicative of the effectiveness of the decontamination process.

Method Detection Limit (MDL). The smallest concentration of an analyte of interest that can be measured and reported with 99 percent confidence that the concentration is greater than zero. The MDLs are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in section 40 CFR, Part 136, Appendix B, as established by the U.S. Environmental Protection Agency.

Practical Quantitation Limit (PQL). The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the MDL, or can be assumed to be four times the MDL.

Precision. The agreement or closeness between two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical systems over a given time and field sampling period.

Relative Percent Difference (RPD). A measure of precision, used when comparing two values. It is calculated as %RPD = [Value1–Value2]/Mean*100.

Relative Standard Deviation (RSD). A measurement of precision, used when comparing more than two results. It is calculated as %RSD = [Std. Deviation/Mean]*100.

Replicate Sample (RS). A second sample collected from the same source as the routine sample, using the same sampling equipment. RS data are compared to routine sample to evaluate sampling precision.

Split Sample (SS). A second sample collected from the same sample obtained from the same sampling device. Results for SS are compared with routine sample results; agreement between these two results is mostly an indication of laboratory precision.

Z-Value. A measure of the deviation of the result (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi–X)/\sigma$, where σ is a standard deviation) (EURACHEM).

SUMMARY

For the period January-March 2007
Surveys 191-193

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

This period had no major procedural updates related to field data collection or to grab sample collection.

MISSING FIELD DATA

Survey 191 - Samples 456-460 and 479 have no salinity, DO, temperature, turbidity, and pH due to field meter malfunction.

Shelf 47 – Samples 375,376,383-395, and 397-399 had no salinity, DO, and temperature due to malfunction of CTD.

Corrective action: All field equipment that had problems during Survey 191 and Shelf 47 were repaired.

QUALITY CONTROL

All filtered samples were collected and filtered with a 0.7 um pore size filter.

Corrective Action: As per previous agreement with SFWMD, as long as SERC notifies or flags samples, there will be no need for variance request.

Field QC measures: Field QC measures consist of Equipment Blanks (EB), Field-Cleaned Equipment Blanks (FCEB), and Replicate Samples (RS). Table 1 summarizes EB, and FCEB collected for projects of interest to SFWMD.

Type of Blank	Project	Number of Blanks Collected
EB= C1_1 and C2_1 Where C= control 1_1 = day one EB and 2_1 = day two EB	191	9
	192	9
	193	10
FCEB = C1_2 and C2_2 Where C = Control 1_2= day one FCEB 2_2 = day two FCEB	191	9
	192	10

	193	8
	Shelf 047	2 EB, 2FCEB

Table 1. Field and equipment blank results for Surveys 191-193. Acceptance criteria is < MDL. Each set of controls have unfiltered and filtered bottles (for nutrients and totals respectively).

Total of controls > MDL:
53 for TN, all below PQL
59 for TOC, see note in appendix A
54 for NO2, all below 4* MDL
38 for TP, all below 3* MDL, mostly < 2*MDL

Summary Field QC measures: TN and TOC are not linked to the LIMS system. As such, all TN and TOC EBs and FCEBs results submitted as ADaPT Electronic Data Deliverables (EDD) do not include a correction (only for TN and TOC field controls) as established in 2002 by the former SERC Laboratory Director under approval by SFWMD. Based on SERC established procedure the TN and TOC field control data is within acceptance criteria, but this criterion will not be reflected (included) in the final report.

Corrective action: SERC will connect the TN and TOC instruments to the LIMS by December 2008.

FIELD PRECISION

A total of 592 duplicates have an RPD > 20%. Out of these 737 duplicates, 37 samples were below MDL and 332 were between MDL and PQL

LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

No analytical procedures were change during this reporting period.

TOTAL NUMBER OF RESULTS

Lab_Analysis_Ref_Method_ID	ACODE	Total Number of Results
SM18 10200 H	CHLA	878
EPA 360.2	DO_B	421
EPA 360.2	DO_S	421
EPA 350.1	NH4	874
EPA 353.3	NN	875
EPA 353.2	NO2	875
EPA 150.1	PH_B	439
EPA 150.1	PH_S	439
SM18 2520 B	SAL_B	421
SM18 2520 B	SAL_S	421
EPA 370.1	SI	357
EPA 365.1	SRP	876
EPA 170.1	TEMP_B	421
EPA 170.1	TEMP_S	421
ASTM D5176-91	TN	878
EPA 415.1	TOC	878
EPA 365.1 (Phosphorus - Total)	TP	878
EPA 180.1	TURB	438

Table 2. Total Number of results for surveys 191-193

MISSING DATA

Missing Data

FB191	NH4	12a,12b, 23b,24a
FB191	NO2	12a,12b, 23b
FB191	NN	12a,12b,
FB191	SRP	12a,12b,
FB193	NN	1b
S047	DO_S	(375-376, 383-399)
S047	SAL_S	(375-376, 383-399)
S047	TEMP_S	(375-376, 383-399)
S047	DO_B	(375-376, 383-399)
S047	SAL_B	(375-376, 383-399)
S047	TEMP_B	(375-376, 383-399)
S047	TURB	site 396

Table 3. Missing data for surveys 191-193

Corrective action: N/A

PREPARATION BATCH COUNT

ACODE	Number of batches with > 20 samples	Note
NH4	18	but <24 samples
NN	23	but <26 samples
NO2	24	but <26 samples
SRP	24	but <26 samples
TOC	3	but <36 samples
TP	21	but <24 samples

Table 4. Preparation Batch Count of more than 20 samples for surveys 191-193

*All CHLA counts per batch are under 20 samples, but batches IDs were not available for this report. CHLA is analyzed against a calibration curve of 8 points generated in an annual basis. All CHLA are run with a method blank at the beginning and a working standard (LCS), at least,

every 20 samples. CHLA sample result data is entered manually, but no format is currently established to enter the QC information in the LIMS system.

Corrective action: Batch ID and QC information will be incorporated in future reports.

The remainders of the runs in prep-batch-count are mostly nutrients which are analyzed using a 4 channel RFA (NN, NO2, NH4, and SRP). When the technician prepares a batch over 20, all the 4 analysis will have the same number of samples. All reagents and QC standards, including matrix spikes, were prepared with the preparation batch which is also the analysis batch.

Corrective action: All technicians were instructed to prepare and run batches of 20 samples only.

HOLDING TIMES

Holding times greater than 28 days: Holding times greater than 28 days occurred in only two occasions for TP Samples were initially analyzed within holding time, but the reruns were analyzed out of holding time due to the technician's error.

Corrective Action: A reminder/re-training to the TP and nutrients tech that all runs must be analyzed within 28 days, including reruns.

Holding times greater than 48 hours from collection time for NO2 and SRP: All NO2 and SRP are analyzed within 48 hours upon laboratory arrival. If samples are not going to be analyzed within the 48 hour window, receiving tech proceeds to freeze samples immediately and then they are analyzed within 48 hours after been thawed, with a maximum of 28 days. Some reruns were analyzed OHT.

Corrective Action: As of survey 207, samples are going to be frozen within 24 hours of collection time and will be analyzed within 48 hours of been thawed. Proper training will apply. SERC, as per January 2008 audit response, SERC will apply for the analysis preservation and holding time variances by December 2008.

METHOD BLANKS AND MDLS

The number of batches that have a MB > MDL are:

- NH4 1
- NN 2
- NO2 46
- TP 2

The total numbers of samples per analyte per surveys 191-193 that are linked to a run with a MB > MDL, but that their results are lower than the MB times 5 are 554 as follows:

NO2	554	(Note that NO2 MDL is very low)
NN	49	

Corrective Action: As of survey 203, NO2 new calculated MDL is higher, still NO2 MB vs MDL is been monitored more closely.

PERCENT RECOVERIES

These MS, MSD, and LCS are out of 85-115%, but all are within 30% of the expected value, and most within 20%.

Percent recovery failures on MS and MSD per analyte

- Ammonia 3
- TOC 4
- NN 2
- SRP 8
- TP 11
- Silica 11

Percent recovery failures on LCS per analyte

- NH4 2
- TOC 2
- NO2 4
- SRP 2
- Silica 1

These MS, MSD, and LCS are out of 85-115%, but all except one, Silica, are within 30% of the expected value, most within 20%.

Corrective Action: N/A

SUMMARY

For the period April-June 2007
Surveys 194-196

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

This period had no major procedural updates related to field data collection or to grab sample collection.

MISSING FIELD DATA

Survey 194 - Samples 378 and 379 had no salinity, DO, or temperature due to field equipment malfunction.
Survey 195 – Station 460 was not collected because water was too shallow to reach by boat.
Stations 70,72-75 had no pH data reported.

Corrective action: All field equipment that had problems during Survey 194 were repaired. Field technicians were informed of missing samples and warned to be more careful.

QUALITY CONTROL

All filtered samples were collected and filtered with a 0.7 um pore size filter.

Corrective Action: As per previous agreement with SFWMD, as long as SERC notifies or flags samples, there will be no need for variance request.

Field QC measures: Field QC measures consist of Equipment Blanks (EB), Field-Cleaned Equipment Blanks (FCEB), and Replicate Samples (RS). Table 5 summarizes EB, and FCEB collected for projects of interest to SFWMD.

Type of Blank	Project	Number of Blanks Collected
EB= C1_1 and C2_1 Where C= control 1_1 = day one EB and 2_1 = day two EB	194	9
	195	10
	196	8
FCEB = C1_2 and C2_2 Where C = Control 1_2= day one FCEB 2_2 = day two FCEB	194	9
	195	10

	196	8
	Shelf 048	1 EB, 1FCEB

Table 5. Field and equipment blank results for surveys 194-196. Acceptance criteria is < MDL. Each set of controls have unfiltered and filtered bottles (for nutrients and totals respectively).

Total of controls > MDL:

- 49 for TN, all below PQL
- 53 for TOC, all below 4 times MDL
- 27 for NO2, all below 3 times MDL
- 3 for NH4 all below 2 times MDL
- 36 for TP, all below 4 times MDL

Summary Field QC measures: TN and TOC are not linked to the LIMS system. As such, all TN and TOC EBs and FCEBs results submitted as ADaPT Electronic Data Deliverables (EDD) do not include a correction (only for TN and TOC field controls) as established in 2002 by the former SERC Laboratory Director under approval by SFWMD. Based on SERC established procedure the TN and TOC field control data is within acceptance criteria, but this criterion will not be reflected (included) in the final report.

Corrective action: SERC will connect the TN and TOC instruments to the LIMS by December 2008.

FIELD PRECISION

Field Precision Results with RPD > 20%: A total of 737 duplicates have an RPD > 20%. Out of these 737 duplicates, 56 samples were below MDL and 357 samples were between MDL and PQL.

LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

No analytical procedures were change during this reporting period.

TOTAL NUMBER OF RESULTS

Lab_Analysis_Ref_Method_ID	ACODE	Total # of Results	Total by site	comments
SM18 10200 H	CHLA	865*	437	No 459, 479
EPA 360.2	DO_B	439	437	No 378, 379 results
EPA 360.2	DO_S	439	437	No 378, 379 results
EPA 350.1	NH4	866*	437	No 7 460 results
EPA 353.3	NN	877*	438	No 460
EPA 353.2	NO2	876*	438	No 460
EPA 150.1	PH_B	434	433	No 70, 72-76 (6)
EPA 150.1	PH_S	433	433	No 70, 72-76 (6)
SM18 2520 B	SAL_B	439	437	No 378, 379 results
SM18 2520 B	SAL_S	439	437	No 378, 379 results
EPA 370.1	SI	357*	179	
EPA 365.1	SRP	876*	436	No 460
EPA 170.1	TEMP_B	439	437	No 378, 379 results
EPA 170.1	TEMP_S	439	437	No 378, 379 results
ASTM D5176-91	TN	866*	437	No 399, no 460
EPA 415.1	TOC	873*	438	No 460
EPA 365.1	TP	875*	437	No site 463, 460
EPA 180.1 * # includes bottle A and B	TURB	436	437	no 479, 396

Table 6. Total Number of results for surveys 194-196

MISSING DATA

There is no data missing

Corrective action: N/A

PREPARATION BATCH COUNT

ACODE	Number of batches with > 20 samples	Note
NH4	19	but <27 samples
NN	19	but <29 samples
NO2	21	but <29 samples
SRP	20	but <29 samples
TN	4	but <47 samples
TOC	6	but <31 samples
TP	19	but <23 samples

Table 7. Preparation Batch Count of more than 20 samples for surveys 194-196

All CHLA counts per batch are under 20 samples, but batches IDs were not available for this report. CHLA is analyzed against a calibration curve of 8 points generated in an annual basis. All CHLA are run with a method blank at the beginning and a working standard (LCS), at least, every 20 samples. CHLA sample result data is entered manually, but no format is currently established to enter the QC information in the LIMS system.

Corrective action: Batch ID and QC information will be incorporated in future reports.

The remainders of the runs in prep-batch-count are mostly nutrients which are analyzed using a 4 channel RFA (NN, NO2, NH4, and SRP). When the technician prepares a batch over 20, all the 4 analysis will have the same number of samples. All reagents and QC standards, including matrix spikes, were prepared with the preparation batch which is also the analysis batch.

Corrective action: All technicians were instructed to prepare and run batches of 20 samples only.

HOLDING TIMES

Holding times greater than 28 days: Holding timers greater than 28 days occurred in 28 occasions for NN analysis. Samples were initially analyzed within holding time, but the reruns were analyzed out of holding time due to the technician's error.

Corrective Action: A reminder/re-training to the TP and nutrients tech that all runs must be analyzed within 28 days, including reruns.

Holding times greater than 48 hours from collection time for NO2 and SRP: All NO2 and SRP are analyzed within 48 hours upon laboratory arrival. If samples are not going to be analyzed within the 48 hour window, receiving tech proceeds to freeze samples immediately and then they are analyzed within 48 hours after been thawed, with a maximum of 28 days. Some reruns were analyzed OHT.

Corrective Action: As of survey 207, samples are going to be frozen within 24 hours of collection time and will be analyzed within 48 hours of been thawed. Proper training will apply. SERC, as per January 2008 audit response, will apply for the analysis preservation and holding time variances by December 2008.

METHOD BLANKS AND MDLS

The number of batches that have a MB > MDL are:

- NN 1
- NO2 40

The total numbers of samples per analyte per surveys 194-196 that are linked to a run with a MB > MDL, but that their results are lower than the MB times 5 are 505 as follows:

- NO2 492 (Note that NO2 MDL is very low)
- NN 13

Corrective Action: As of survey 203, NO2 new calculated MDL is higher, still NO2 MB vs MDL is been monitored more closely.

PERCENT RECOVERIES

These MS, MSD, and LCS are out of 85-115%, but all are within 30% of the expected value, and most within 20%.

Percent recovery failures on MS and MSD per analyte

- Ammonia 4
- TOC 12
- NN 4
- SRP 2
- TP 11
- Silica 8

Percent recovery failures on LCS per analyte

- NN 2
- SRP 2
- TP 2

Percent RPD > 20 per analyte

Silica 3 (below 30%)

Corrective Action: N/A

SUMMARY

For the period July-September 2007
Surveys 197-199

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES :

This period had no major procedural updates related to field data collection or to grab sample collection.

MISSING FIELD DATA

Site 357 was missing filtered nutrients bottle.

Corrective Action: Field technicians told to be more careful.

QUALITY CONTROL

All filtered samples were collected and filtered with a 0.7 um pore size filter.

Corrective Action: As per previous agreement with SFWMD, as long as SERC notifies or flags samples, there will be no need for variance request.

Field QC measures: Field QC measures consist of Equipment Blanks (EB), Field-Cleaned Equipment Blanks (FCEB), and Replicate Samples (RS). Table 8 summarizes EB, and FCEB collected for projects of interest to SFWMD.

Type of Blank	Project	Number of Blanks Collected
EB= C1_1 and C2_1 Where C= control 1_1 = day one EB and 2_1 = day two EB	197	8
	198	9
	199	9
FCEB = C1_2 and C2_2 Where C = Control 1_2= day one FCEB 2_2 = day two FCEB	197	8
	198	9
	199	9

	Shelf 049	1 EB, 1FCEB

Table 8. Field and equipment blank results for surveys 197-199. Acceptance criteria is < MDL. Each set of controls have unfiltered and filtered bottles (for nutrients and totals respectively).

Total of controls > MDL:

- 43 for TN, all below PQL
- 50 for TOC, all below 3 times MDL
- 40 for NO2, all below 3 times MDL
- 36 for TP, all below 3 times MDL
- 1 for NN, below 2 times MDL

Summary Field QC measures: TN and TOC are not linked to the LIMS system. As such, all TN and TOC EBs and FCEBs results submitted as ADaPT Electronic Data Deliverables (EDD) do not include a correction (only for TN and TOC field controls) as established in 2002 by the former SERC Laboratory Director under approval by SFWMD. Based on SERC established procedure the TN and TOC field control data is within acceptance criteria, but this criterion will not be reflected (included) in the final report.

Corrective action: SERC will connect the TN and TOC instruments to the LIMS by December 2008.

FIELD PRECISION

Field Precision Results with RPD > 20%: A total of 629 duplicates have an RPD > 20%. Out of these 629 duplicates, 42 samples were below MDL and 298 samples were between MDL and PQL.

LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

No analytical procedures were change during this reporting period.

TOTAL NUMBER OF RESULTS

Lab_Analysis_Ref_Method_ID	ACODE	Total # of Results
SM18 10200 H	CHLA	878*
EPA 360.2	DO_B	439
EPA 360.2	DO_S	439
EPA 350.1	NH4	876*
EPA 353.3	NN	876*
EPA 353.2	NO2	876*
EPA 150.1	PH_B	390
EPA 150.1	PH_S	439
SM18 2520 B	SAL_B	439
SM18 2520 B	SAL_S	439
EPA 370.1	SI	356*
EPA 365.1	SRP	876*
EPA 170.1	TEMP_B	439
EPA 170.1	TEMP_S	439
ASTM D5176-91	TN	878*
EPA 415.1	TOC	878*
EPA 365.1	TP	878*
EPA 180.1	TURB	439

* includes bottle A and B (duplicates)

Table 9. Total Number of results for surveys 197-199

MISSING DATA

One case for nutrients (NN, NO2, NH4 and SRP): no filtered bottle A or B collected for site 357 from S 049.

Corrective action: N/A

PREPARATION BATCH COUNT

ACODE	Number of batches with > 20 samples	Note
NH4	21	but < 26 samples
NN	21	but < 26 samples
NO2	22	but < 26 samples
SRP	23	but < 26 samples
TN	4	but < 38 samples
TOC	2	but < 31 samples
TP	7	but < 23 samples

Table 10. Preparation Batch Count of more than 20 samples for surveys 197-199

All CHLA counts per batch are under 20 samples, but batches IDs were not available for this report. CHLA is analyzed against a calibration curve of 8 points generated in an annual basis. All CHLA are run with a method blank at the beginning and a working standard (LCS), at least, every 20 samples. CHLA sample result data is entered manually, but no format is currently established to enter the QC information in the LIMS system.

Corrective action: Batch ID and QC information will be incorporated in future reports.

The remainders of the runs in prep-batch-count are mostly nutrients which are analyzed using a 4 channel RFA (NN, NO2, NH4, and SRP). When the technician prepares a batch over 20, all the 4 analysis will have the same number of samples. All reagents and QC standards, including matrix spikes, were prepared with the preparation batch which is also the analysis batch.

Corrective action: All technicians were instructed to prepare and run batches of 20 samples only.

HOLDING TIMES

Holding times greater than 28 days: Sample 23 A & B from FB197 were initially analyzed for TN within holding time, but the reruns were analyzed out of holding time due to the technician's error.

Corrective Action: A reminder/re-training to the TP and nutrients technician that all runs must be analyzed within 28 days, including reruns.

Holding times greater than 48 hours from collection time for NO2 and SRP: All NO2 and SRP are going to be out of 48 hours from collection time, but all NO2 and SRP are analyzed within 48 hours upon laboratory arrival. If samples are not going to be analyzed within the 48 hour window, receiving tech proceeds to freeze samples immediately and then they are analyzed within 48 hours after been thawed, with a maximum of 28 days. Some reruns were analyzed OHT.

Corrective Action: As of survey 207, samples will be frozen within 24 hours of collection time and will be analyzed within 48 hours of being thawed. Proper training will apply. SERC, as per January 2008 audit response, will apply for the analysis preservation and holding time variances by December 2008.

METHOD BLANKS AND MDLS

The number of batches that have a MB > MDL are:

- NH4 2
- NN 3
- NO2 47
- SRP 2
- TP 2

The total numbers of samples per analyte per surveys 197-199 that are linked to a run with a MB > MDL, but that their results are lower than the MB times 5 are 540 as follows:

- NO2 496 (Note that NO2 MDL is very low)
- NN 7
- NH4 20
- SRP 16
- TP 1

Corrective Action: As of survey 203, NO2 new calculated MDL is higher, still NO2 MB vs MDL is been monitored more closely.

PERCENT RECOVERIES

These MS, MSD, and LCS are out of 85-115%, but all are within 30% of the expected value, and most within 20%.

Percent recovery failures on MS and MSD per analyte

- Ammonia 4

- TOC 4
- NN 1
- TP 15
- Silica 3
- TN 1

Percent recovery failures on LCS per analyte

- Ammonia 1
- NN 1
- SRP 1
- TP 1

Percent RPD > 20 per analyte

Silica 3 (below 30%)

Corrective Action: N/A

SUMMARY

For the period October–December 2007
Surveys 200-202

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

This period had no major procedural updates related to field data collection or to grab sample collection.

MISSING FIELD DATA

Salinity, DO, and Temperature for site 467 bottom for RB 202 was not collected due to site being too shallow to access by boat.

Corrective action: none

QUALITY CONTROL

All filtered samples were collected and filtered with a 0.7 um pore size filter.

Corrective Action: As per previous agreement with SFWMD, as long as SERC notifies or flags samples, there will be no need for variance request.

Field QC measures: Field QC measures consist of Equipment Blanks (EB), Field-Cleaned Equipment Blanks (FCEB), and Replicate Samples (RS). Table 11 summarizes EB, and FCEB collected for projects of interest to SFWMD.

Type of Blank	Project	Number of Blanks Collected
EB= C1_1 and C2_1 Where C= control 1_1 = day one EB and 2_1 = day two EB	200	8
	201	9
	202	9
FCEB = C1_2 and C2_2 Where C = Control 1_2= day one FCEB 2_2 = day two FCEB	200	9
	201	9
	202	9

Table 11. Field and equipment blank results for surveys 200-202. Acceptance criteria is < MDL. Each set of controls have unfiltered and filtered bottles (for nutrients and totals respectively).

Total of controls > MDL:

- 44 for TN, all below PQL
- 22 for TOC, all below 3 times MDL
- 13 for NO2, all below 3 times MDL
- 1 for SRP, all below 3 times MDL

Summary Field QC measures: TN and TOC are not linked to the LIMS system. As such, all TN and TOC EBs and FCEBs results submitted as ADaPT Electronic Data Deliverables (EDD) do not include a correction (only for TN and TOC field controls) as established in 2002 by the former SERC Laboratory Director under approval by SFWMD. Based on SERC established procedure the TN and TOC field control data is within acceptance criteria, but this criterion will not be reflected in the final report.

Corrective action: SERC will connect the TN and TOC instruments to the LIMS by December 2008.

FIELD PRECISION

All Field Precision Results met the criteria of RPD < 20%:

LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

No analytical procedures were change during this reporting period.

TOTAL NUMBER OF RESULTS

Lab_Analysis_Ref_Method_ID	ACODE	# results
EPA 180.1	TURB	341
EPA 365.1	TP_B	21
EPA 365.1 (TP))	TP	340
EPA 415.1	TOC_B	20
EPA 415.1	TOC	321
ASTM D5176-91	TN_B	21
ASTM D5176-91	TN	341
EPA 170.1	TEMP_S	341
EPA 170.1	TEMP_B	340
EPA 365.1	SRP_B	21
EPA 365.1	SRP	341
SM18 2520 B	SAL_S	341
SM18 2520 B	SAL_B	340
EPA 150.1	PH_S	341
EPA 150.1	PH_B	340
EPA 353.2	NO2_B	21
EPA 353.2	NO2	341
EPA 353.3	NN_B	21
EPA 353.3	NN	341
EPA 350.1	NH4_B	21
EPA 350.1	NH4	341
EPA 360.2	DO_S	341
EPA 360.2	DO_B	340
SM18 10200 H	CHLA_B	18
SM18 10200 H	CHLA	340

Table 12. Total Number of results for surveys 200-202

MISSING DATA

CHLA: Sample # 17 survey 200, lid broken, sample spilled.
CHLA: 3 duplicates not received
TN, TOC, TP: Sample # 67 from TTI20, unfiltered bottle was not collected.
TOC: Samples 49, 58, 65 from TTI 201 rerun were not done.
TOC: The following samples were not reported due to chemical interference. Suspected contamination with acetone during bottle rinsing.

- FB 201: 4,5,6,8,9,11
- WWB 201: 30, 35, 40B, 41, 49
- TTI 201: 52, 61
- WWB 202: 29a, 34
- BB 202: 101, 123,128,129,130
- RB 201: 457
- RB 202: 466a, 478a
- TTI 202 61, 64b

Corrective action: Both Laboratory and field technicians were made aware of need for careful attention to detail. Possible bottle contamination problem alleviated by elimination of bottle washing. We will use new bottles for each future survey.

PREPARATION BATCH COUNT

ACODE	Number of batches with > 20 samples	Note
NH4	4	but <23 samples
NN	5	but <23 samples
NO2	5	but <23 samples
SRP	4	but <23 samples
TP	1	but <22 samples

Table 13. Prep Batch Count for more than 20 samples for surveys 200-202

All CHLA counts per batch are under 20 samples, but batches IDs were not available for this report. CHLA is analyzed against a calibration curve of 8 points generated in an annual basis. All CHLA are run with a method blank at the beginning and a working standard (LCS), at least, every 20 samples. CHLA sample result data is entered manually, but no format is currently established to enter the QC information in the LIMS system.

Corrective action: Batch ID and QC information will be incorporated in future reports.

The remainders of the runs in prep-batch-count are mostly nutrients which are analyzed using a 4 channel RFA (NN, NO2, NH4, and SRP). When the technician prepares a batch over 20, all the 4 analysis will have the same number of samples. All reagents and QC standards, including matrix spikes, were prepared with the preparation batch which is also the analysis batch.

Corrective action: All technicians were instructed to prepare and run batches of 20 samples only.

HOLDING TIMES

Holding times greater than 28 days: Holding timers greater than 28 days occurred in 11 occasions for NN analysis. Samples were initially analyzed within holding time, but the reruns were analyzed out of holding time due to the technician's error.

Corrective Action: A reminder/re-training to the TP and nutrients tech that all runs must be analyzed within 28 days, including reruns.

Holding times greater than 48 hours from collection time for NO2 and SRP: Holding timers greater than 48 days occurred in 384 occasions for NN and SRP analysis All NO2 and SRP are analyzed within 48 hours upon laboratory arrival. If samples are not going to be analyzed within the 48 hour window, receiving tech proceeds to freeze samples immediately and then they are analyzed within 48 hours after been thawed, with a maximum of 28 days. Some reruns were analyzed OHT.

Corrective Action: As of survey 207, samples are going to be frozen within 24 hours of collection time and will be analyzed within 48 hours of been thawed. Proper training will apply. SERC, as per January 2008 audit response, SERC will apply for the analysis preservation and holding time variances by December 2008.

METHOD BLANKS AND MDLS

The number of batches that have a MB > MDL are:

- NN 1
- NO2 22

The total numbers of samples per analyte per surveys 200-202 that are linked to a run with a MB > MDL, but that their results are lower than the MB times 5 are 232 as follows:

- NO2 195 (Note that NO2 MDL is very low)
- NN 3
- NH4 27
- SRP 6
- TP 1

Corrective Action: As of survey 203, NO2 new calculated MDL is higher, still NO2 MB vs MDL is been monitored more closely.

PERCENT RECOVERIES

These MS, MSD, and LCS are out of 85-115%, but are within 80-120%, with the exception of 2 cases where the tech used a lower concentration yielding a lower number.

Percent recovery failures on MS and MSD per analyte

- Ammonia 5
- TOC 5
- NN 1
- SRP 2
- TP 1

Percent recovery failures on LCS per analyte

- NO2 2

Corrective Action: Regarding the two samples that read lower than the 80-120 % range, the tech was instructed not to use a different concentration or deviate from established procedure.