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Analytical

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3.1 Laboratory Responsibilities

Laboratory analyses will be performed by laboratories with NELAC certification (for analyses in this QAPP that specify such certification) and methods will be appropriate for samples with a wide range of salinities (i.e., from 0 to about 70 practical salinity units [PSU]). Laboratory audits performed by FPL (or their designee) will be allowed for any facility analyzing samples from this monitoring program and will respond to the recommended corrective actions in a timely manner.

The laboratory selected to conduct the tritium analysis for this project (see Appendix B) is an active participant in the International Atomic Energy Agency's (IAEA) Tritium Inter-Laboratory Comparison (TRIC) Study conducted every four years. The laboratory participated in the 2004 study and the IAEA TRIC 2004 report is available in Appendix B, Isotope Analysis. Results for the 2008 study, in which the laboratory also participated, were not available at the time of this version of the QAPP. The laboratory will provide FPL and the agencies a copy of the TRIC 2008 report when it becomes available.

Any laboratory conducting sample analysis is responsible for reviewing this QAPP to ensure that they are capable of generating data that will meet the project objectives. The laboratory shall notify FPL immediately when any NELAC certification applicable to this project has been lost or revoked. FPL will inform SFWMD and take steps to subcontract another NELAC lab certified for the particular analysis if the current lab can not obtain recertification prior to the next scheduled sampling.

The project analytical/measurement quality objectives are specified in the following sections. The laboratory can propose that the contractor modify these default objectives (e.g., laboratory QC control limits, method detection limits [MDLs]), based upon the laboratory's routine analytical performance for the specified methods and matrices; however, all proposed modifications must be approved in advance by both FPL and the SFWMD and the QAPP revised to document the approved changes. If the QAPP does not contain the information needed by the laboratory, the laboratory will contact the contractor.

The laboratory's responsibilities associated with data review are included in Section 4.1.3.1 of this QAPP, and the laboratory's responsibility for project-specific reporting procedures is specified in Section 4.1.3.2 of this QAPP.

3.2 Laboratory Methods

Groundwater, surface water, and rain samples will be collected quarterly. Quarterly monitoring at each groundwater cluster and surface water station shall consist of field parameters, ions, TDS, and the CCS tracer suite, as listed in Table 3.2-1. Semiannual monitoring at each groundwater cluster and surface water station shall consist of all of the above, plus the nutrient parameters in a subset of clusters/stations.

In addition to the analyses listed above, groundwater shall be monitored for trace elements semiannually for one year in a subset of groundwater clusters and all surface water stations located within the CCS shall be measured for total count of alpha particle radioactivity (Gross Alpha) semiannually for one year. Rainfall will be sampled quarterly via collectors located at stations surrounding the CCS and analyzed for the tritium.

For both groundwater and surface water samples, field measurements of conductivity and/or salinity will be logged and accompany all samples analyzed at laboratories to ensure appropriate methods are used to analyze saline and/or hypersaline samples. All contract laboratories will be made aware of and be capable of analyzing constituents in saline and/or hypersaline waters. For trace metal analysis, the high concentration of certain salts in hypersaline samples are interferences and cause increased detection limits for other analytes. Hypersaline samples may need to be precipitated before analysis by Method SW846-1640.

During the initial ecological condition characterization, porewater will be collected from sediments in freshwater and saline wetlands adjacent to the CCS, as well as Biscayne Bay and Card Sound, and analyzed for the CCS tracer suite.

Ecological monitoring of the same areas will include porewater, soil/sediment, and biotic (leaf) sample collection. Porewater shall be analyzed for nutrients (total phosphorus [TP], soluble reactive phosphorus [SRP], ammonium [NH₄], nitrogen oxide [NO_x], and total Kjeldahl nitrogen [TKN]) and the CCS tracer suite as prescribed in the Monitoring Plan. Soil samples will be analyzed for nutrients (TP, TN, TC), ash free dry weight, % moisture and bulk density, as listed in Table 3.2-2. Leaf samples will be analyzed for total C, N, and P contents, as well for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios, listed in Table 3.2-3.

If FPL authorizes the laboratory to use an analytical method other than those reference methods published by a nationally recognized organization (i.e., isotope analysis), the laboratory

data package will include all available data documenting that the non-reference method can produce data of known quality to meet the project objectives for each chemical of interest specified in this QAPP. Any analyses that are not EPA or FDEP approved methods may be required to undergo additional approval procedures by FDEP.

If the laboratory cites a reference method which is published by the FDEP or a nationally recognized organization and deviates from that method beyond the modifications allowed in that method, then the data generated by that method are considered suspect until the laboratory validates the data against the reference method. The data package will include the performance data demonstrating that the modified method meets the QC performance criteria of the reference method. The data package will include the comparison of the results obtained from the proposed method with those obtained for the approved reference method, interference studies, method and instrument detection limit studies, multiple-level matrix spikes studies of representative sample types, and precision and accuracy determinations, as applicable to the modifications being made.

Table 3.2-1 presents analytical methods and the MDL requirements for aqueous samples. Table 3.2-2 presents analytical methods and the MDL requirements for soil and sediment samples. Table 3.2-3 presents analytical methods and the MDL requirements for biota (vegetation) samples.

The first column in Tables 3.2-1, 3.2-2, and 3.2-3 lists the project required method for the analyte of interest. These methods are further detailed in the following subsections and Appendix B. The MDL requirements are based on applicable water quality criteria, method capabilities, the MDLs listed in ADaPT Solid Waste Library, and F.A.C 62-4.246(3). The water quality criteria include state surface water Class III standards for fresh and marine waters, potable (G-1) groundwater standards and cleanup target levels (CTLs), and state drinking water primary and secondary standards. The classification of surface water between fresh and marine water is based on the chloride concentration. When chloride levels in a sample are <1500 mg/L, they are considered fresh; ≥mg/L is considered marine. The last column in Tables 3.2-1, 3.2-2, and 3.2-3 indicate historical concentrations detected of the analyte as greater than or less than 20 times the project required MDL.

Table 3.2-1. Analytical Methods and Default QA/QC Targets for Groundwater, Surface Water, Porewater, and Rainfall

Method	Matrix	Analyte	Units	Surface Water Standards ¹		Groundwater Standards		Drinking Water Standards		Project Required MDL ⁶	Exp Conc. Range
				Fresh Water (Class III)	Marine (Class III)	GW (G-1) ²	CTLs ³	MCL ⁴	Secondary ⁵		
IONS											
EPA 6010B	SW, GW	Calcium (Ca ²⁺)	mg/L	--	--	--	--	--	--	0.17	>20x
EPA 6010B	SW, GW	Sodium (Na ⁺)	mg/L	--	--	160	primary	160	--	0.2	N/A
EPA 6010B	SW, GW	Magnesium (Mg ²⁺)	mg/L	--	--	--	--	--	--	0.1	>20x
EPA 6010B	SW, GW	Potassium (K ⁺)	mg/L	--	--	--	--	--	--	0.33	>20x
EPA 6010B	SW, GW	Strontium (Sr ²⁺)	mg/L	--	--	--	4.2	--	--	0.0005	<20x
EPA 6010B	SW, GW	Boron (B ⁺)	mg/L	--	--	--	1.4	--	--	0.05	N/A
EPA 300.0	SW, GW	Chloride (Cl ⁻)	mg/L	--	≤ 10% ⁸	500 ⁷	secondary	--	250	0.5	>>20x
EPA 300.0	SW, GW	Bromide (Br ⁻)	mg/L	--	--	--	--	--	--	0.05	N/A
EPA 300.0	SW, GW	Sulfate SO ₄ ²⁻	mg/L	--	--	--	--	--	250	0.5	>20x
EPA 300.0	SW, GW	Fluoride (F ⁻)	mg/L	≤ 10	≤ 5	1.4 as F	secondary	4	2	0.05	<20x
SM2320B	SW, GW	Alkalinity as CaCO ₃	mg/L	> ≤ 20	--	--	--	--	--	1.0	N/A

Table 3.2-1. Analytical Methods and Default QA/QC Targets for Groundwater, Surface Water, Porewater, and Rainfall

Method	Matrix	Analyte	Units	Surface Water Standards ¹		Groundwater Standards		Drinking Water Standards		Project Required MDL ⁶	Exp Conc. Range
				Fresh Water (Class III)	Marine (Class III)	GW (G-1) ²	CTLs ³	MCL ⁴	Secondary ⁵		
SM2320B	SW, GW	Bicarbonate (HCO ₃ ⁻)	mg/L	--	--	--	--	--	--	1.0	N/A
SM 4500S2 F	SW, GW	Sulfides	mg/L	--	--	0.2	--	--	--	0.2	N/A
NUTRIENTS											
SM 4500 NH ₃ G	SW, GW, PW	Ammonia (as N)	mg/L	--	--	0.5	2.8	--	--	0.02	<20x
DEP SOP (NH ₃)	SW, GW, PW	Unionized Ammonia - calculated	mg /L	≤ 0.02	--	--	--	--	--	not applicable ¹⁶	N/A
DEP SOP (NH ₃)	SW, GW, PW	Ammonium - calculated	mg /L	--	--	--	--	--	--	not applicable ¹⁶	N/A
EPA 353.2	SW, GW, PW	Nitrate+Nitrite (NO _x)	mg/L	--	--	10	primary	10	--	0.01	>20x
EPA 353.2	SW, GW, PW	Nitrite (NO ₂)	mg/L	--	--	1	primary	1	--	0.01	>20x
EPA 353.2	SW, GW, PW	Nitrate - calculated	mg/L	--	--	10	primary	10	--	0.01	
EPA 351.2	SW, GW, PW	Total Kjeldahl Nitrogen	mg/L	--	--	--	--	--	--	0.2	>20x

Table 3.2-1. Analytical Methods and Default QA/QC Targets for Groundwater, Surface Water, Porewater, and Rainfall

Method	Matrix	Analyte	Units	Surface Water Standards ¹		Groundwater Standards		Drinking Water Standards		Project Required MDL ⁶	Exp Conc. Range
				Fresh Water (Class III)	Marine (Class III)	GW (G-1) ²	CTLs ³	MCL ⁴	Secondary ⁵		
EPA 353.2 & EPA 351.2	SW, GW, PW	Total Nitrogen (TN) – calculated	mg/L	--	--	--	--	--	--	not applicable ¹⁶	>20x
EPA 365.1	SW, GW, PW	Total Phosphorous (TP)	mg/L	--	--	--	--	--	--	0.005	>20x
SM-4500 P-E	SW, GW, PW	Soluble Reactive Phosphorous (SRP)	mg/L	--	--	--	--	--	--	0.002	N/A
EPA 200.7	SW, PW	Silica	mg/L	--	--	--	--	--	--	0.5	N/A
TRACE ELEMENTS											
EPA 200.7	GW	Arsenic	mg/L	≤ 0.05	≤ 0.05	0.01	--	0.01	--	0.002	>20x
EPA 200.7	GW	Barium	mg/L			2	primary	2		0.005	N/A
EPA 200.7	GW	Beryllium	mg/L	≤ 0.00013 ⁹	≤ 0.00013 ⁹	0.004	primary	0.004	--	0.00015	N/A
EPA 200.7	GW	Cadmium	mg/L	Cadmium ¹⁰	< 0.0088	0.005	primary	0.005	--	0.0002	<20x
EPA 200.7	GW	Copper	mg/L	Copper ¹³	≤ 0.0037	--	secondary	--	1	0.002	<20x
EPA 200.7	GW	Iron	mg/L	≤ 1.0	≤ 0.3	0.3	secondary	--	0.3	0.044	<20x
EPA 200.7	GW	Lead	mg/L	Lead ¹⁴	≤ 0.0085	0.015	primary	0.0015		0.001	<20x
EPA 200.7	GW	Manganese	mg/L	--	--	--	secondary	--	0.05	0.005	N/A
EPA 200.7	GW	Molybdenum	mg/L	--	--	--	0.035	--	--	0.005	N/A
EPA 200.7	GW	Nickel	mg/L	Nickel ¹¹	≤ 0.0083	0.1	primary	0.1	--	0.005	N/A
EPA 200.7	GW	Selenium	mg/L	≤ 0.005	≤ 0.071	0.05	primary	0.05	--	0.002	N/A
EPA 200.7	GW	Thallium	mg/L	< 0.0063	< 0.0063	0.002	primary	0.002	--	0.001	N/A

Table 3.2-1. Analytical Methods and Default QA/QC Targets for Groundwater, Surface Water, Porewater, and Rainfall

Method	Matrix	Analyte	Units	Surface Water Standards ¹		Groundwater Standards		Drinking Water Standards		Project Required MDL ⁶	Exp Conc. Range
				Fresh Water (Class III)	Marine (Class III)	GW (G-1) ²	CTLs ³	MCL ⁴	Secondary ⁵		
EPA 200.7	GW	Vanadium	mg/L	--	--	--	0.049	--	--	0.01	N/A
EPA 200.7	GW	Zinc	mg/L	Zinc ¹⁵	≤ 0.086	--	secondary	--	5	0.02	<20x
SM-3500 CR-B	GW	Chromium (CrVI)	mg/L	≤ 0.011	≤ 0.05	--	primary	0.1 (total)	--	0.002	N/A
EPA 245.1	GW	Mercury	mg/L	0.000012	0.000025	--	primary	0.002	--	0.0001	N/A
CCS TRACER SUITE - ISOTOPES											
See Appendix B	SW, GW, PW	Hydrogen (² H) [Deuterium]	‰	--	--	--	--	--	--	--	N/A
See Appendix B	SW, GW, RW, PW	Hydrogen (³ H) [Tritium]	pCi/L	--	--	--	--	20,000	--	10	N/A
See Appendix B	SW, GW, PW	Oxygen (¹⁸ O, ¹⁶ O)	‰	--	--	--	--	--	--	--	N/A
See Appendix B	SW, GW, PW	Strontium (⁸⁷ Sr, ⁸⁶ Sr)	‰	--	--	--	--	--	--	--	N/A
See Appendix B	SW, GW, PW	Carbon (¹³ C, ¹² C)	‰	--	--	--	--	--	--	--	N/A

Table 3.2-1. Analytical Methods and Default QA/QC Targets for Groundwater, Surface Water, Porewater, and Rainfall

Method	Matrix	Analyte	Units	Surface Water Standards ¹		Groundwater Standards		Drinking Water Standards		Project Required MDL ⁶	Exp Conc. Range
				Fresh Water (Class III)	Marine (Class III)	GW (G-1) ²	CTLs ³	MCL ⁴	Secondary ⁵		
OTHER PARAMETERS											
EPA 900.0 ¹²	SW (CCS)	Gross Alpha	pCi/L	≤15	≤15	--	--	≤15	--	3	N/A
EPA 9060A		Dissolved Carbon (DC)									
EPA 9060A	SW, GW, PW	Dissolved Inorganic Carbon (DIC) - calculated	mg/L	--	--	--	--	--	--	not applicable ¹⁶	N/A
SM 2540 C	GW	Total Dissolved Solids (TDS)	mg/L	--	--	--	--	500	secondary	10	N/A

Key:

N/A - not available

GW – groundwater

SW – Surface water, may include samples within the cooling canal system (CCS)

PW – porewater

RW - Rainwater

“EPA” Series method reference: Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983, with the exception of Gross Alpha

“SW” Series method reference: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, Final Update III.

“SM” Series method reference: Standard Methods for the Examination of Water and Wastewater, 19th Edition

Notes:

While some standards listed above are not directly applicable to all aspects of the project, they are provided as partial rational for project MDL requirements

1 = Class III: Recreation Propagation and Maintenance of a Healthy Well - Balanced Population of Fish and Wildlife (Fresh or Marine Surface Water) FAC 62-302.530

2 = Class G-I: Potable Ground Water Supply

3 = FAC 62-777 Table 1, Groundwater Clean-up Target Levels http://www.dep.state.fl.us/waste/quick_topics/rules/documents/62-777/TableIGroundwaterCTLs4-17-05.pdf

4 = Maximum Contaminant Levels for Drinking Water in Florida, <http://www.dep.state.fl.us/water/drinkingwater/standard.htm>

5 = Secondary FL Drinking Water Standards

6 = Project Required MDL's based on applicable criteria, MDLs listed in ADaPT, FAC 62-4.246(3), and laboratory capabilities. MDLs based on analytical detection limits and the sample matrix (i.e., salt content)

Table 3.2-1. Analytical Methods and Default QA/QC Targets for Groundwater, Surface Water, Porewater, and Rainfall

Method	Matrix	Analyte	Units	Surface Water Standards ¹		Groundwater Standards		Drinking Water Standards		Project Required MDL ⁶	Exp Conc. Range
				Fresh Water (Class III)	Marine (Class III)	GW (G-1) ²	CTLs ³	MCL ⁴	Secondary ⁵		

7 = Waste shall not increase natural background more than 10%

8 = ≤10% above normal back-ground normal daily and seasonal fluctuations shall be maintained

9 = Beryllium, annual average not MDL based.

10 = $Cd < (e(0.7409[lnH]-4.719))/1000$

11 = $Ni \leq (e(0.846[lnH]+0.0584))/1000$

12 = EPA 900 reference: Prescribed Procedures for Measurement of Radioactivity in Drinking Waters, EPA-600/4-80-032 (Aug, 1980).

13 = $Cu \leq e(0.8545[lnH]-1.702)$

14 = $Pb \leq e(1.273[lnH]-4.705)$

15 = $Zn \leq e(0.8473[lnH]+0.884)$

16 = MDLs are not applicable for calculated parameters

17 = Salinity may vary from fresh to hypersaline and different methods may be necessary to achieve MDLs

Table 3.2-2. Analytical Methods and Default QA/QC Targets for Soil and Sediment Samples

Method	Matrix	Analyte	Units	Project Required MDL	Expected Concentration Range
EPA 440.0	SO	Total Nitrogen (TN)	mg/kg	1.0	>20.0
EPA 365.4	SO	Total Phosphorus (TP)	mg/kg	20	>100
SM 10300	SO	Ash-Free Dry Weight	g	0.1	N/A
EPA 440.0	SO	Total Carbon (TC)	%	1	>10
ASTM D5057-90	SO	Bulk Density	g/cm ³	0.01	>0.05
D2216	SO	Percent Moisture	%	0.1	>5

Key:

1 = Analysis via EPA 365.1 after Dry Ash/Acid Extraction procedures per Allen et al. (1974) and Jones et al. (1990).

Allen, S. E., Grimshaw, H.M., Parkinson, J.A. and Quarmby, C. 1974. Chemical Analysis of Ecological Materials. John Wiley and Sons, New York.

Jones, J. B. Jr., B. Wolf and H. A. Mills. 1990. Organic matter destruction procedures. *In: Plant Analysis Handbook*. Micro-Macro Publishing, Inc., Athens, GA. pp.195-6.

Table 3.2-3. Analytical Methods and Default QA/QC Targets for Biota Samples

Method	Matrix	Analyte	Units	Project Required MDL	Expected Concentration Range
EPA 440.0	VG	TN	mg/g	5	>20
EPA 365.4	VG	TP	mg/kg	20	>50
EA-IRMS ²	VG	Nitrogen (¹⁵ N/ ¹⁴ N)	Per mille units (‰)	N/A	N/A
EA-IRMS ²	VG	Carbon (¹³ C/ ¹² C)	‰	N/A	N/A

Key:

N/A - Not applicable.

¹ = Analysis via EPA 365.1 after Dry Ash/Acid Extraction procedures per Allen et al. (1974) and Jones et al. (1990).

² = Analysis via EPA 440.0 (Elemental Analyzer (EA)) followed by Isotope-Ratio Mass Spectrometer (IRMS).

Allen, S. E., Grimshaw, H.M., Parkinson, J.A. and Quarmby, C. 1974. Chemical Analysis of Ecological Materials. John Wiley and Sons, New York.

Jones, J. B. Jr., B. Wolf and H. A. Mills. 1990. Organic matter destruction procedures. *In: Plant Analysis Handbook*. Micro-Macro Publishing, Inc., Athens, GA. pp.195-6.

3.2.1 Laboratory Sample Handling and Custody

The laboratory QA manual and associated laboratory SOPs will specify the laboratory sample handling and custody requirements to be followed. These requirements will be consistent with NELAC and 40 Code of Federal Regulations [CFR] Part 136. In addition, the following procedures will be adhered to:

- Once the samples reach the laboratory, they will be checked for anomalies against information on the COC form accompanying the samples. Each cooler containing samples must have a COC seal and tape. The receiving laboratory will reject any sample cooler that shows evidence of tampering with the COC seal and tape. The condition, temperature, and appropriate preservation of samples will be checked and

documented on the COC form. Appropriate measuring methods include measurement of a temperature blank contained in the cooler. Infrared temperature measurement of an aqueous sample is also acceptable. If ice is found to be present in the cooler upon receipt, the laboratory will also note this on the COC form and may consider this an adequate indication that the cooler temperature is not above the acceptance criterion of 6°C. Checking an aliquot of the sample using pH paper is an acceptable procedure for checking acid/base preservation. The occurrence of any anomalies in the received samples and the resolution of these anomalies will be documented in laboratory records, a sample receipt log, and the case narrative submitted with the laboratory data package. All sample information will be entered into a Laboratory Information Management System (LIMS) tracking system, and unique laboratory analytical sample identifiers will be assigned. A copy of this information will be reviewed by the laboratory for accuracy.

- Procedures ensuring internal laboratory COC will also be implemented and documented by the laboratory. Specific instructions concerning the analysis specified for each sample will be communicated to the analysts. Analytical batches will be created, and laboratory QC samples will be introduced into each batch.

While in the laboratory, samples will be stored in limited-access, temperature-controlled areas. Refrigerators, coolers, and freezers will be monitored for temperature daily. The acceptance criterion for the temperatures of the refrigerators and coolers is 0.1 to 6°C. Acceptance criteria for the temperatures of the freezers will be less than 0°C. All of the cold storage areas will be monitored by thermometers or other temperature monitoring devices that have been calibrated against a NIST-traceable thermometer. As indicated by the findings of the calibration, correction factors will be applied to each thermometer. Records that include acceptance criteria will be maintained. All samples will be stored separately from standards. Samples will be stored after analysis until they can be disposed of in accordance with applicable local, state, and federal regulations. Prior to disposal, the laboratory will contact FPL. Disposal records will be maintained by the laboratory

3.2.2 Preparative Methods

The following inorganic sample preparation methods are from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (EPA SW-846, Chapter 3). These are applicable to the metals and cation analysis.

For the determination of total metals, the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in SW-846. Method 3005A is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids, Method 3010, is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all samples types. The digestions indicated may not be suitable for all samples. Differences in salinity may require alternate methods be tested and used to meet project DQOs

- **Method 3005A:** Acid Digestion of Waters for Total Recoverable Metals for Analysis by Flame Atomic Absorption Spectroscopy (FLAAS) or Inductively Coupled Plasma (ICP) Spectroscopy (6000 Series). This method may be used for the preparation of groundwater and surface water samples for total recoverable metal

determinations by FLAAS, ICP-atomic emission spectroscopy (AES), or ICP-mass spectroscopy (MS). The unfiltered (total) or filtered (dissolved) sample is vigorously heated nitric acid (HNO₃) prior to metal determination.

- **Method 3010A:** Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAAS or ICP Spectroscopy. This method may be used for the preparation of waste samples for total recoverable metal determinations by FLAAS, ICP-AES, or ICP-MS. The samples are digested with HNO₃ followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Preparation techniques and procedures specific to the other analyses performed in Section 3.2.3 are detailed in the respective method. Some of the methods necessitate filtration of the water through a 0.45-micron membrane filter. Following filtration of the sample, the referenced procedure must be followed.

Proprietary or non-standard preparation techniques may be required for certain analyses (i.e., some of the CCS tracer suite parameters). Any method employed that is not EPA approved, must be approved by the Agencies before it is used on project samples. A description of the preparation method employed will be documented by the laboratory and submitted for approval. Once approved, the laboratory will use the specific procedures described, without variation, for the duration of the project. If any modifications are required, FPL must document the changes and reasoning for review by the Agencies before the procedure is to be used on project samples.

3.2.3 Analytical Methods

The following section and its sub-elements contain information for some commonly used analytical procedures.

3.2.3.1 EPA Method 200.7 – Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)

Project samples are analyzed for metals (with the exception of cations, boron, and strontium) using EPA Method 200.7. This method utilizes ICP-AES in the determination of trace level concentrations of elements in water samples and in waste extracts or digests. Similar standard methods include SW846-6010 and SM3110.

For the determination of total recoverable silica in aqueous samples, samples (100 mL) are not filtered, but acidified with (1+1) nitric and hydrochloric acid to pH <2. Preservation may be done at the time of collection. The sample is then digested at 85°C to a final volume of 50 mL and analyzed.

When determining silica in aqueous samples, only plastic, polytetrafluoroethylene (PTFE, or Teflon[®]), or quartz labware shall be used from the time of sample collection to completion of analysis. Borosilicate glass must be avoided to prevent contamination of this analyte.

The ICP-AES measures characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch.

Element specific emission spectra are produced by a radio frequency (RF) ICP. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device.

A background correction technique is required to compensate for variable background contribution to the determination of the analytes. A primary disadvantage of ICP-AES is the occurrence of background radiation from other elements and the plasma gases. Although all ICP-AES instruments utilize high-resolution optics and background correction to minimize these interferences, analysis of trace levels of inorganic analytes in the presence of a large excess of a single analyte (i.e., chloride) is difficult.

Table 3.2-4 provides a summary of QC procedures for EPA Method 200.7. Method QC includes a method blank, an LCS, an Instrument Performance Check standard, a spectral interference check standard, and matrix spikes. Optional method QC techniques include the addition test and dilution test. MDLs are listed in Tables 3.2-1, 3.2-2, and 3.2-3.

Table 3.2-4. Summary of Calibration and QC Procedures for Method 200.7

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Multipoint calibration curve (minimum five standards and a blank)	Initial calibration prior to sample analysis.	Correlation coefficient > 0.995 for linear regression	Correct problem then repeat initial calibration
Instrument Performance Check (IPC) Standard (Calibration verification)	After each initial calibration, every 10 th sample, and at the end of the run	After initial calibration, mean concentration of four or more analyses within $\pm 5\%$ of true value, RSD<3%. Subsequent analyses shall be within 10%.	Reanalyze or correct problem and reanalyze samples run after last acceptable IPC
Calibration Blank	After each initial calibration, every 10 th sample, and at the end of the run		
Method blank	One per analytical batch	No analyte detected > MDL.	When blank values >10% sample values, re-prepare and analyze method blank and all samples processed with the contaminated blank
LCS	One LCS per analytical batch	Recovery within 85-115% of expected results	Correct problem then re-prepare and analyze the LCS and all samples in the affected analytical batch
MS/MSD	One MS/MSD per every 10 project samples per matrix	70-130% Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration	Describe in case narrative
Analyte Addition Test	When dilution test fails	Recovery within 85-115% of expected results	If analyte addition <20% sample analyte concentration, perform dilution test

Table 3.2-4. Summary of Calibration and QC Procedures for Method 200.7

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Dilution test	Each new sample matrix (i.e., soil or water)	1:4 dilution must agree within $\pm 10\%$ of the original determination for analyte concentration greater than 50x IDL	Perform post-digestion spike addition for failed analytes
Quality Control Sample	Quarterly to verify calibration standards, from second source	Mean concentration of three analyses within $\pm 5\%$ of true value	Recalculate results; locate and fix problem with system and then rerun
MDL study	Once per 12-month period, seven replicates	Detection limits in Table 3.2-1	None

3.2.3.2 EPA Method 6010B –Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Project samples are analyzed for cations, boron, and strontium by EPA SW-846-6010B. Samples are analyzed for trace elements or metals using Method SW6010B. Analysis for most metals requires digestion of the sample. Following digestion, the trace elements are determined simultaneously or sequentially using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Similar standard methods include EPA 200.7 and SM3120.

ICP-AES allows simultaneous or rapid sequential determination of many elements in a short time. Aerosol samples are introduced into an extremely hot plasma source which vaporizes, atomizes, ionizes and electronically excites the sample components. Upon exiting the plasma, the electronically excited analytes emit characteristic photons that are detected via emission spectrometry. A primary disadvantage of ICP-AES is the occurrence of background radiation from other elements and the plasma gases. Although all ICP-AES instruments utilize high-resolution optics and background correction to minimize these interferences, analysis of trace levels of inorganic analytes in the presence of a large excess of a single analyte (i.e., chloride) is difficult.

Table 3.2-5. Summary of Calibration and QC Procedures for Method SW6010B

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Multipoint calibration curve (minimum three standards and a blank)	Initial calibration prior to sample analysis.	Correlation coefficient > 0.995 for linear regression	Correct problem then repeat initial calibration
Second-source calibration verification	After each initial calibration	Analytes within $\pm 10\%$ of expected value	Correct problem then repeat initial calibration
Calibration verification	After every 10 samples and at the end of the analysis sequence	Analytes within $\pm 10\%$ of expected value	Correct problem then repeat initial calibration and reanalyze all samples since last successful calibration

Table 3.2-5. Summary of Calibration and QC Procedures for Method SW6010B

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Method blank	One per analytical batch	No analyte detected > MQL	When blank values >10% sample values, re-prepare and analyze method blank and all samples processed with the contaminated blank
LCS	One LCS per analytical batch	Recovery within 80-120% of expected results	Correct problem then re-prepare and analyze the LCS and all samples in the affected analytical batch
MS/MSD	One MS/MSD per every 20 project samples per matrix	Recovery within 75-125% of expected results - calculations are not required if the concentration added is less than 30% of the sample background concentration	Describe in case narrative
Dilution test	Each new sample matrix (i.e., soil or water)	1:5 dilution must agree within $\pm 10\%$ of the original determination for analyte concentration greater than 10x IDL	Perform post digestion spike addition for failed analytes
Post Digestion Spike Addition	When dilution test fails	Recovery within 80-120% of expected results	Correct problem then reanalyze post digestion spike addition
MDL study	Once per 12-month period	Detection limits in Table 3.2-1	None

3.2.3.3 .

3.2.3.3 Method SW1640 – Determination of Trace Metals in Water by Preconcentration and ICP-MS

Saline samples analyzed by ICP-MS may be pre-concentrated following Method 1640, or similar method, before analysis if necessary to meet project DQO's. Method 1640 is applicable for pre-concentration of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), and zinc (Zn). However, this method is not applicable for iron (Fe), manganese (Mn), molybdenum (Mo), and vanadium (V). A more appropriate pre-concentration method for Fe and Mn is a modified isotope dilution magnesium induced co-precipitation. A chelating resin such as Chelex-100 could be used to pre-concentrate Mo and V samples. The method for Fe, Mn, MO and V has not been provided in this QAPP and will require a subsequent QAPP modification as described in Section 8 if deemed necessary to meet project DQO's. Assessment procedures and criteria shall also be addressed if a QAPP modification is required. The pre-concentration techniques must be chosen based on the analytes of interest, and tested on samples representing the broad range of expected salinities encountered in this project, which may vary from nearly fresh to in excess of 70 psu and include potential interferences. A pre-concentration technique

meeting project DQOs for the analysis of one target analyte may not be suitable for the analysis of another target analyte. The pre-concentration procedure using reductive precipitation by sodium tetrahydroborate may be a suitable pre-concentration procedure for the analysis of As, Cd, Cu, Pb, Ni, and Zn for some project samples. However, this procedure is not suitable for the analysis of Ag. If recoveries do not meet project DQOs for any samples or analytes, it will be necessary to use an alternative preconcentration system or use a combination of pre-concentration methods to achieve project QA/QC standards and meet DQOs. In addition, to assure that the pre-concentration and analytical method used results in accurate determination of trace metal content in the sample, a certified reference material must be included in the analysis. Since the groundwater samples may have salinity levels from fresh to hypersaline, the following reference materials will be used as a check on accuracy: NASS-6 (seawater reference material for trace metals), CASS-5 (nearshore seawater reference materials for trace metals), or SLEW-3 (estuarine water reference material).

3.2.3.4 Method SM 3500-Cr B– Colorimetric Method for Hexavalent Chromium

Project samples are analyzed for Cr(VI) using Method SM 3500 CrB(21st Ed.). Cr(VI), in the absence of interfering amounts of substances such as molybdenum (Mb), Va, and Hg, may be determined colorimetrically. Diphenylcarbazide reacts with Cr(VI) in acid solution to form a colored (540 nm) complex.

Table 3.2-6 provides a summary of QC procedures for Method SM 3500 Cr D. Method QC includes a method blank, a LCS, and matrix spikes. MDLs are listed in Tables 3.2-1, 3.2-2, and 3.2-3.

Table 3.2-6. Summary of Calibration and QC Procedures for Method SM 3500-Cr B

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration curve (minimum one standard and a blank)	Initial calibration prior to sample analysis, standards treated as samples	Correlation coefficient > 0.995 for linear regression	Correct problem then repeat initial calibration
Calibration Verification	After every 10 samples and at the end of the analysis sequence	Analytes within $\pm 10\%$ of expected value	Correct problem then repeat initial calibration and reanalyze all samples since last successful calibration
Method blank	One per analytical batch	No analyte detected in the MB above the MDL-	
LCS	One LCS per analytical batch	Recovery within 85-115% of expected results	Correct problem then reprep and analyze the LCS and all samples in the affected analytical batch
MS/MSD	One MS/MSD per every 20 project samples per matrix	Recovery within 85-115% of expected results - calculations are not required if the concentration added is less than 30% of	Describe in case narrative

Table 3.2-6. Summary of Calibration and QC Procedures for Method SM 3500-Cr B

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
		the sample background concentration	

3.2.3.5 Method EPA 245.1 – Determination of Mercury in Water by Cold-Vapor Atomic Absorption Spectrometry

Project samples are analyzed for Hg using EPA Method 245.1. This method is a cold-vapor, flameless, AA technique based on the absorption of radiation by mercury vapor. Sample is digested in diluted potassium permanganate-potassium persulfate solutions and oxidized for two hours at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured using AA spectrophotometer at 253.7 nm. Mercury concentration is measured as a function of absorbance.

Table 3.2-7 provides a summary of QC procedures for EPA Method 245.1. Method QC includes a method blank, an LCS, and matrix spikes along with the use of internal standards. MDLs are listed in Tables 3.2-1, 3.2-2, and 3.2-3.

Table 3.2-7. Summary of Calibration and QC Procedures for EPA Method 245.1

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial multipoint calibration (minimum 5 standards and a blank)	Daily initial calibration prior to sample analysis	Correlation coefficient >0.995 for linear or non-linear regression	Correct problem then repeat initial calibration
Instrument Performance Check (IPC) Standard (Calibration verification)	After each initial calibration, every 10 th sample, and at the end of the run	After initial calibration, mean concentration of four or more analyses within $\pm 5\%$ of true value, RSD < 3%. Subsequent analyses shall be within 10%.	Reanalyze or correct problem and reanalyze samples run after last acceptable IPC
Calibration blank	Once per initial daily multipoint calibration	No analyte detected > MDL	Correct problem then reanalyze calibration blank and all samples associated with blank
Method blank	One per analytical batch	No analyte detected > MDL	When blank values > 10% sample values, re-prepare and analyze method blank and all samples processed with the contaminated blank
LCS	One LCS per analytical batch	85-115% Recovery	Correct problem then re-prepare and analyze the LCS and all samples in the affected analytical batch
MS/MSD	One MS/MSD per every 10 project samples per matrix	70-130% Recovery	Describe in case narrative

Table 3.2-7. Summary of Calibration and QC Procedures for EPA Method 245.1

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Quality Control Sample	Quarterly to verify calibration standards, from second source	mean concentration of three analyses within $\pm 10\%$ of true value	Recalculate results; locate and fix problem with system and then rerun
MDL study	Once per 12-month period	Detection limits in Table 3.2-1	None

3.2.3.6 EPA Method 300.0 – Determination of Inorganic Anions by Ion Chromatography

Project samples are analyzed for chloride, fluoride, bromide, and sulfate by EPA Method 300.0. This method addresses the sequential determination of anions in aqueous samples.

A small volume of water sample is injected into an ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of effluent. The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn (guard) column, and a separator column, are packed with a low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

Table 3.2-8 provides a summary of QC procedures for EPA Method 300.0. Method QC includes a method blank, an LCS, and matrix spikes along with the use of internal standards. MDLs are listed in Tables 3.2-1, 3.2-2, and 3.2-3.

Table 3.2-8. Summary of Calibration and QC Procedures for EPA Method 300.0

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial multipoint calibration (minimum 3 standards and a blank)	Initial calibration prior to sample analysis	Correlation coefficient > 0.995 for linear or non-linear regression	Correct problem then repeat initial calibration
Instrument Performance Check (IPC) Standard (Calibration verification)	After each initial calibration, every 10 th sample, and at the end of the run	All analytes within $\pm 10\%$ of expected value	Reanalyze or correct problem and reanalyze samples run after last acceptable IPC
Method blank	One per analytical batch	No analyte detected $> \text{MDL}$	When blank values $> 10\%$ sample values, re-prepare and analyze method blank and all samples processed with the contaminated blank

Table 3.2-8. Summary of Calibration and QC Procedures for EPA Method 300.0

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
LCS	One LCS per analytical batch	90-110%R	Correct problem then re-prepare and analyze the LCS and all samples in the affected analytical batch
MS/MSD	One MS/MSD per every 20 project samples per matrix	80-120%R	Describe in case narrative
Quality Control Sample	Quarterly to verify calibration standards, from second source	mean concentration of three analyses within $\pm 10\%$ of true value	Recalculate results; locate and fix problem with system and then rerun
MDL study	Once per 12 month period	Detection limits in Table 3.2-1	None

3.2.3.7 SM 2450 C – Total Dissolved Solids (TDS)

Project samples are analyzed for TDS by method SM 2540 C. TDS is defined as the portion of solids that passes through a filter of 2.0 microns nominal pore size. This method is applicable to drinking, surface, and saline waters. The MDL for this method is listed in Table 3.2-1.

3.2.3.8 SM 2320 B – Alkalinity

Project samples are analyzed for alkalinity by method SM 2320 B. In this method, an unaltered sample is titrated to an end point of pH 4.5 using hydrochloric (HCl) or sulfuric acid. The sample must not be filtered, diluted, concentrated, or altered in any way. The MDL for this method is listed in Table 3.2-1.

3.2.3.9 SM 4500 S2 F – Sulfides by Iodometric Method

Project samples are analyzed for sulfide by method SM 4500 S2 F. Iodine and HCl are added to the sample until blue color remains. The sample is back-titrated with sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) until the blue color disappears. The MDL for this method is listed in Table 3.2-1.

3.2.3.10 SM 4500 NH3-G – Nitrogen (Ammonia) by the Automated Phenate Method

Project samples are analyzed for ammonia by Method SM 4500 NH3 D. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The color is intensified with the addition of sodium nitroprusside. Calcium and magnesium in saline samples may cause interference by precipitation during the analysis. The addition of ethylenediaminetetraacetic acid EDTA and sodium potassium tartrate to the sample reduces the interference. Samples will be filtered as turbidity can cause additional interference. Additionally, the sample pH must be uniform as the intensity of the color produced is pH-dependant. Samples are analyzed using a colorimeter measuring 630 to 660 nm. The MDL for this method is listed in Table 3.2-1.

3.2.3.11. EPA Method 351.2– Determination of Total (Kjeldahl) Nitrogen by Semi-Automated Colorimetry

Project samples are analyzed for TKN by EPA Method 351.2. The sample is heated in the presence of sulfuric acid (H_2SO_4) for 2.5 hours. The residue is cooled, diluted to 25 mL and analyzed for ammonia. This digested sample may also be used for phosphorus determination. TKN is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, under the conditions of digestion described. Organic nitrogen is the difference obtained by subtracting the free-ammonia value from the TKN value. The MDL for this method is listed in Table 3.2-1.

3.2.3.12 EPA Method 353.2 – Determination of Nitrite-Nitrate Nitrogen by Automated Colorimetry

Project samples are analyzed for nitrite/nitrate nitrogen by EPA Method 353.2. Specifically, nitrite and nitrate combined are measured as well as nitrite individually; nitrate is then calculated as the difference. A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that was originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined, nitrate-nitrite values are readily obtained by carrying out the procedure first with, and then without, the copper-cadmium reduction step. The MDL for this method is listed in Table 3.2-1.

3.2.3.13 Total Nitrogen (calculated)

Project samples are analyzed for nitrate/nitrite and TKN by EPA Methods 353.2 and 351.2, respectively. The total nitrogen determination is made by the summation of the results for nitrate/nitrite and TKN. The MDL for this method is listed in Table 3.2-1.

3.2.3.14 EPA Method 365.1– Determination of Phosphorous by Semi-Automated Colorimetry

Aqueous project samples are analyzed for TP by EPA Method 365.1. Soil project samples are analyzed by 365.4. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration. Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion. The MDL for this method is listed in Table 3.2-1.

3.2.3.15 SM 4500-P E–Soluble Reactive Phosphorous by Ascorbic Acid Method

Project samples are analyzed for soluble reactive phosphorous by Method SM 4500 P E. There are several forms of phosphorus which can be measured. TP is a measure of all the forms of phosphorus, dissolved or particulate, that are found in a sample. SRP is a measure of orthophosphate, the filterable (soluble, inorganic) fraction of phosphorus, the form directly taken up by plant cells. This Standard Method follows the same procedures in EPA Method 365.1 above. The MDL for this method is listed in Table 3.2-1.

The SRP method will apply an additional step as suggested by the SFWMD. In some samples, the natural color of the sample may interfere with the analysis causing a high bias. The additional step analyzes the sample without color reagent to establish the amount contributed by the sample, and then with the color reagent as specified in the Method. The difference between the two results are reported as the SRP value.

3.2.3.16 EPA Method 9060A – Dissolved Inorganic Carbon (calculated)

Project samples are analyzed for dissolved carbon (DC) and dissolved organic carbon (DOC) by Method 9060A and the dissolved inorganic carbon (DIC) is calculated as the difference. While the method is stated as measuring total carbon, the method can be adapted to measure all forms of carbon in a sample. As dissolved carbon is being analyzed for, the sample must be filtered prior to analysis. Organic carbon is measured by purging with nitrogen acid-preserved samples to remove inorganic carbon. Total carbon is measured using sample that has not been preserved or purged. The sample is then converted to carbon dioxide (CO₂) by catalytic combustion or wet chemical oxidation. The CO₂ formed can be measured directly by an infrared detector. The MDL for this method is listed in Table 3.2-1.

3.2.3.17 EPA Method 900.0–Gross Alpha (with optional EPA Method 00-02)

Project samples are analyzed for gross alpha by EPA Method 900 (equivalent to SM 7110 B). An aliquot of a water sample is evaporated to a small volume and transferred quantitatively to a tared 2-inch stainless steel counting planchet. The sample residue is dried to constant weight, reweighed to determine dry residue weight, and then counted for alpha and/or beta radioactivity. Counting efficiencies for both alpha and beta particle activities are selected according to the amount of sample solids from counting efficiency versus sample solids standard curves.

In this method for gross alpha measurement, the radioactivity of the sample is not separated from the solids of the sample; therefore, the solids concentration is very much a limiting factor in the sensitivity of the method for any given water sample. A co-precipitation procedure can be employed that precipitates all alpha emitting actinides. The procedure, EPA 520/5-84-006, Method 00-02 – “Radiochemical Determination of Gross Alpha Activity in Drinking Water by Co-Precipitation” uses barium sulfate and ferric hydroxide to precipitate all alpha emitting actinides from the sample. The MDL for this method is listed in Table 3.2-1.

3.2.3.18 EPA Method 440.0 – Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis

Project samples are analyzed for total carbon and total nitrogen by EPA Method 440.0. A dried and weighed sediment sample is combusted in an elemental analyzer. The combustion products are passed over a copper reduction tube to convert the nitrogen oxides to elemental nitrogen. The sample is mixed with carbon dioxide and water then passed to a thermal conductivity detector for analysis. The matrix based MDL's for this method are listed in Tables 3.2-2 and 3.2-3.

Table 3.2-9. Summary of Calibration and QC Procedures for EPA Method 440.0

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
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Table 3.2-9. Summary of Calibration and QC Procedures for EPA Method 440.0

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial multipoint calibration (minimum 3 standards and a blank)	Initial calibration prior to sample analysis	Correlation coefficient >0.995 for linear or non-linear regression	Correct problem then repeat initial calibration
Instrument Performance Check (IPC) Standard (Calibration verification)	After each initial calibration, every 10 th sample, and at the end of the run	All analytes within $\pm 10\%$ of expected value	Reanalyze or correct problem and reanalyze samples run after last acceptable IPC
Method blank	One per analytical batch	No analyte detected > MDL	When blank values >10% sample values, reprep and analyze method blank and all samples processed with the contaminated blank
LCS	One LCS per analytical batch	85-115% Recovery	Correct problem then reprep and analyze the LCS and all samples in the affected analytical batch
Quality Control Sample	Quarterly to verify calibration standards, from second source	mean concentration of three analyses within $\pm 10\%$ of true value	Recalculate results; locate and fix problem with system and then rerun
MDL study	Once per 12 month period	Detection limits in Table 3.2-1	None

3.2.3.19 CCS Tracer Suite Analysis - Isotopes

Project samples are analyzed for barium, total iron, and DIC by the standard methods discussed above (see Table 3.2-1). The other analytes in the suite, ^3H , $^2\text{H} / ^1\text{H}$, $^{86}\text{Sr} / ^{87}\text{Sr}$, $^{18}\text{O} / ^{16}\text{O}$, and $^{13}\text{C} / ^{12}\text{C}$, will be analyzed by proprietary methods reviewed and approved for use by FDEP for this project. These methods are summarized below and detailed further in Appendix B.

Briefly, the analysis for stable isotope ratios is almost exclusively performed by mass spectrometry. For tritium, samples are distilled, electrolytically enriched, and analyzed by liquid scintillation counting (LSC). For hydrogen and oxygen isotopes, the water samples will be equilibrated in the presence of CO_2 for 12 hours prior to analysis on the isotope-ratio mass spectrometer (IRMS) for $\delta^{18}\text{O}$ and δD signatures. Carbon and nitrogen samples are first combusted and the gas analyzed on an elemental analyzer connected to an IRMS; this method allows for simultaneous determination of sample %C and %N followed by the measurement of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Samples for strontium analysis will be analyzed using a thermal ionization mass spectrometer (TIMS) system where the samples are dried on rhenium or tantalum filaments that will then be heated to combustion prior to analysis on a mass spectrometer.

3.3 Laboratory Quality Control

The purpose of this QC program is to produce data of known quality that satisfy the project objectives and that meet or exceed the requirements of the standard methods of analysis.

This program provides a mechanism for ongoing control and evaluation of data quality measurements through the use of QC materials.

3.3.1 Internal Quality Control Checks

QC data are necessary to determine precision and accuracy and to demonstrate the absence of interferences and/or contamination of glassware and reagents.

Field QC is specified in Section 2.6.1 and in the Monitoring Plan. . Field QC samples will be preserved, documented, and transported in the same manner as the samples they represent. Field duplicates and blanks will be analyzed by the laboratory as samples and will be numbered as described in Section 2.2.

Laboratory QC of standard methods will consist of standards, replicates, spikes, and blanks. Laboratory QC of non-standard methods is detailed in Appendix B. Laboratory QC samples will be included in the preparation batch with the field samples. A preparation batch is a number of samples (dependant on method requirements, not to exceed 20 environmental samples) that are similar in matrix and that are extracted or digested at the same time and with the same reagents. The term “analytical batch” also extends to cover samples that do not need separate extraction or digestion and is the number of samples (dependant on method requirements, not to exceed 20 environmental samples) that are similar in matrix and analyzed sequentially. The identity of each analytical batch will be unambiguously cross-referenced and reported with the associated sample analyses so that a reviewer can identify the QC samples and the associated environmental samples. It should be noted the analytical batch requirements may differ for the non-standard isotope analyses, detailed in Appendix B. Some of these analyses report batches larger than 20 samples.

The type of QC samples and the frequency of use of these samples are discussed below and in the method specific SOPs.

3.3.2 Blanks

Three types of blanks routinely analyzed in the laboratory are field blanks, method blanks, and reagent blanks. Typical field QC samples are described in Section 2.6.1. They are analyzed in the laboratory as samples, and their purpose is to access the sampling and transport procedures as possible sources of sample contamination. Method blanks and reagent blanks are used to access laboratory procedures as possible sources of sample contamination:

- Method blanks for all samples consist of deionized water (or Ottawa sand or other similar matrix to the environmental samples being analyzed determined to be analyte free) which is subjected to the entire analytical procedure, including extraction, distillation, and digestion (whatever is appropriate for the analytical method being utilized); and
- Reagent/solvent blanks consist of analyte-free water or solvents which are not processed. They are used to indicate instrument drift or contamination apart from that which may arise in sample processing.

The presence of analytes in the method blank at concentrations equal to or greater than the MDL indicates a need for corrective action for samples in which the reported concentration is

less than or equal to 10 times the associated blank concentration. The data qualifier code “V” applies to samples meeting these criteria. Corrective action will be performed to eliminate the source of contamination prior to proceeding with the analysis of these samples. After the source has been identified and corrected, all samples in the analytical batch will be re-extracted/re-digested and re-analyzed. No analytical data will be corrected for the presence of analytes in blanks. When an analyte is detected in the method blank and in the associated samples, the data validator will evaluate the effect of the potential laboratory contamination on the quality of the data.

3.3.3 Calibration Standards

Calibration standards are prepared in the laboratory by dissolving a known amount of a pure compound in an appropriate matrix. The final concentration calculated from the known quantities is the true value of the standard. The number of standards and the suggested concentration ranges are based on the method employed. The results obtained from these standards are used to generate a standard curve and thereby quantitate the compound in the environmental sample.

3.3.4 QC Check Standards

QC check standards can be prepared by the laboratory or may be obtained from an approved source. A check standard is not carried through the same process used for the environmental samples, but is analyzed without digestion or extraction. A check standard result is used to validate an existing concentration calibration standard file or calibration curve. The check standard provides information on the accuracy of the instrumental analytical method, independent of various sample matrices. Accuracy is expressed as %R and is calculated using the formula in Section 5.2.

3.3.5 Interference Check Samples (ICS)

The interference check sample (ICS), used in analyses only, contains both interfering and analyte elements of known concentrations. The ICS is used to verify background and interelement correction factors.

3.3.6 Laboratory Control Samples (LCS)

The LCS is analyte-free water (for aqueous analyses) or other solid matrix demonstrated to be analyte-free (for soil analyses) which, at a minimum, is spiked with all the chemicals of concern identified in the Monitoring Plan. The LCS will be spiked at a level less than or equal to the midpoint of the calibration curve for each analyte. The LCS will be carried through the complete sample preparation and analysis procedure. The LCS is used to evaluate each analytical batch and to determine if the method is in control. The LCS cannot be used as the continuing calibration verification. Acceptance criteria for LCSs are presented in the analytical summary tables in Section 3.2.

3.3.7 Matrix Spikes

A sample matrix spike (MS) is prepared by adding known amounts of all chemicals of concern to be analyzed in the environmental samples before processing. The spiking occurs prior to sample preparation and analysis. The MS will be spiked at a level less than or equal to the midpoint of the calibration curve for each analyte. Spike levels are only considered

appropriate for assessing accuracy if they are less than four times the native sample concentration. The sample to be used for MS/matrix spike duplicate (MSD) will be designated on the COC and extra volume of sample will be supplied for the additional analyses. The MS/MSD is used to document the bias of a method due to sample matrix. When there is negligible change in volume due to the spike, it is calculated as follows:

$$\%R = (SSR - SR) / SA \times 100$$

SSR = Measured concentration of the analyte in the spiked sample.

SR = Measured concentration of the analyte concentration in the sample before the spike was added.

SA = Concentration of added spike.

Acceptance criteria for matrix spikes are presented in the analytical summary tables in Section 3.2..

3.3.8 Laboratory Duplicates (sample duplicates, LCSD, MSD)

Laboratory duplicates are aliquots of a single sample that is split on arrival at the laboratory or upon analysis. An additional sample portion provided by the field sampling team may be required. Significant differences between laboratory duplicate samples are generally due to analytical technique or sample non-homogeneity.

MSD samples are aliquots split in the laboratory from the same sample, and each aliquot is treated exactly the same throughout the analytical method. The RPD between the values of the MS/MSD (organic analyses) or between the sample and duplicate (inorganic analyses), is taken as a measure of the precision of the analytical method. The formula for calculating precision as RPD is given in Section 1.3.

Acceptance criteria for laboratory duplicates are $\leq 20\%$ for aqueous samples and $\leq 40\%$ for soil/sediment samples..

3.3.9 Serial Dilution

Serial dilution analysis may be pertinent to metals analysis by ICP-AES, ICP/MS, and graphite furnace/atomic absorption (GFAAS). The ICP serial dilutions are run to help evaluate whether or not significant physical or chemical interferences exist due to the sample matrix. When analyte concentrations are sufficiently high (the concentration in the original sample is minimally a factor of 50 above the instrument detection limit), the results obtained from a five-fold dilution of the original sample are compared to the original results by means of a percent difference (%D).

3.3.10 Post Digestion Spike Data

Post digestion spike analysis may be pertinent to metals analysis by ICP-AES, ICP/MS, and GFAAS. The analyte recoveries obtained for post-digestion spike analyses will be compared to the acceptance range for accuracy contained in the analytical summary tables in Section 3.2. Under some circumstances, laboratories will quantify results by the method of standard additions (MSA) to compensate for low post-digestion spike recovery. Calculations by MSA should be

discussed in the analytical report narrative. The low spike recovery will not compromise the accuracy of the results, as the standards used in the MSA analysis are spiked directly into the sample.

3.3.11 Method Detection Limit (MDL) and Reporting Limit (RL)

For reporting purposes, analytical sensitivity is expressed by the MDL. MDLs are set such that the minimum concentration of an analyte is reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined according to procedures outlined in 40 CFR Part 136, Appendix B. Information about the determination of MDLs, IDLs, and RLs will be available for review to the agencies upon request.

MDLs are being developed for parameters, where absent, using the procedures references above. MDLs are determined at least yearly. Results from the annual studies are used to verify the MDL levels following procedures outlined in SOP-QA-013, Standard Operating Procedures for Performing MDL Studies.

Some MDLs may be set higher than experimentally determined MDLs to avoid interferences from matrix effects.

The Reporting Limit (RL) is equal to the lowest non-zero standard concentration in the laboratory's initial calibration curve based on the final volume or weight used by the laboratory. The PQL should be five to ten times the MDL for the majority of target analytes but no lower than three times the MDL.

As outlined in the FDEP Guidance for Selection of Analytical Methods and the Evaluation of MDLs and RLs, whenever an analyte is not detected at or above the MDL, the MDL for the measurement must be reported along with the qualifier code "U," indicating that the analyte was not detected at the reported detection limit. If an analyte was detected at or above the MDL but was below the RL, the result must be reported with the qualifier code "I," indicating the quantity is estimated.

Analyses not requiring MDLs, precision, or accuracy that will be parameters for surface and groundwater characterization include:

- pH;
- Temperature;
- Salinity;
- TDS;
- Specific conductance; and
- DO.

3.4 Laboratory Instrument / Equipment Testing, Inspection, and Maintenance

A preventive maintenance program will be in place to promote the timely and effective completion of a measurement effort. The preventive maintenance program is designed to minimize the downtime of crucial sampling and/or analytical equipment due to unexpected component failure. In implementing this program, efforts are focused in three primary areas: (1) establishment of maintenance responsibilities; (2) establishment of maintenance schedules for major and/or critical instrumentation and apparatus; and (3) establishment of an adequate inventory of critical spare parts and equipment.

Maintenance and repair of major laboratory equipment will be recorded in laboratory logbooks. These records will document the serial numbers of the equipment, the person performing the maintenance or repairs, the date of the repair, the procedures used during the repair, and proof of successful repair prior to the use of the equipment.

3.5 Instrument Calibration and Frequency per Method

Instruments and equipment used to generate or measure environmental data will be maintained and calibrated according to the manufacturers' specifications, the requirements of the analytical method, and the QC requirements specified in Section 3.2. Section 3.2.3 includes a discussion of required quality, calibration and tuning criteria, control checks, frequencies, acceptance criteria, and corrective actions associated with routine analytical methods. Calibration and tuning of laboratory instruments is the responsibility of the laboratory.

Field instrument calibration and frequency requirements for water level, pH, temperature, specific conductance, DO, redox potential, and turbidity measurements are addressed in Table 2.5-2 of this QAPP. Specific requirements for other field instrumentation for the project are specified in the Monitoring Plan.

Data that have been qualified as "rejected" will be reanalyzed if enough sample remains and it is still within holding time. If the sample has been depleted or is beyond the holding time, then FPL will direct the laboratory to provide additional sample containers and the matrix shall be re-sampled for the qualified parameter(s) as soon as practical unless SFWMD determines re-sampling is not necessary.

3.6 Inspection and Acceptance of Supplies

Any laboratory consumables or supplies that come into contact with samples must be documented to be free of contamination ("clean"). Examples of laboratory consumables and supplies include gloves, glassware, soaps, sample bottles, reagent-grade water, reagents, and pipettes. Documentation that laboratory consumables and supplies are clean may be achieved through several methods as follows:

- Collection of QC samples, such as bottle blank, water blank, or reagent blank samples. Bottle blanks may be used to demonstrate that bottles are free of contamination. Water blanks may be used to demonstrate that deionized or distilled water does not contain contamination. Reagent blank samples may be used to demonstrate that reagents are free from contamination.
- Certifications from manufacturers or laboratories may be used to show that bottles, consumable equipment, and other supplies are free of contamination.
- Purchasing through reliable and frequently used sources. A restricted list of common items may be assumed to be “clean,” until proven otherwise, if purchased from reliable commercial sources. This restricted list includes gloves and other personal protective equipment, paper towels, plastic bags, aluminum foil, or other similar items. If the “clean” certification provided by the vendor has been compromised (e.g., tears in the packaging), decontamination should be performed prior to use or the item should be discarded if it cannot be adequately decontaminated. Items which are purchased through commercial sources, and which are not documented to be “clean,” should not be used in direct contact with samples.

The laboratory must have documentation on file showing the procedure or process by which laboratory consumables and supplies are documented “clean.” This documentation must be available to FPL upon request. The laboratory Quality Assurance Manual should clearly identify other critical supplies, such as calibration gases or standards, the inspection or acceptance testing requirements, and the acceptance criteria. Critical field supplies, the inspection or acceptance testing requirements, and the acceptance criteria are addressed in Section 2.

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