Marshall Steam Station In-Stream Monitoring Plan

I. Introduction

In-Stream Monitoring Requirement

A requirement to semi-annually sample water quality at locations in Lake Norman upstream and downstream of the Marshall Steam Station (MSS) ash basin discharge was implemented in 2011 under section Part I # 26 (In-stream Monitoring) of the MSS National Pollutant Discharge Elimination System permit.

The following discussion describes the specific analyses, methods and analytical results of this monitoring program for the period 2011 – 2013.

II. Sampling and Methodology

Lake Norman Sampling Locations

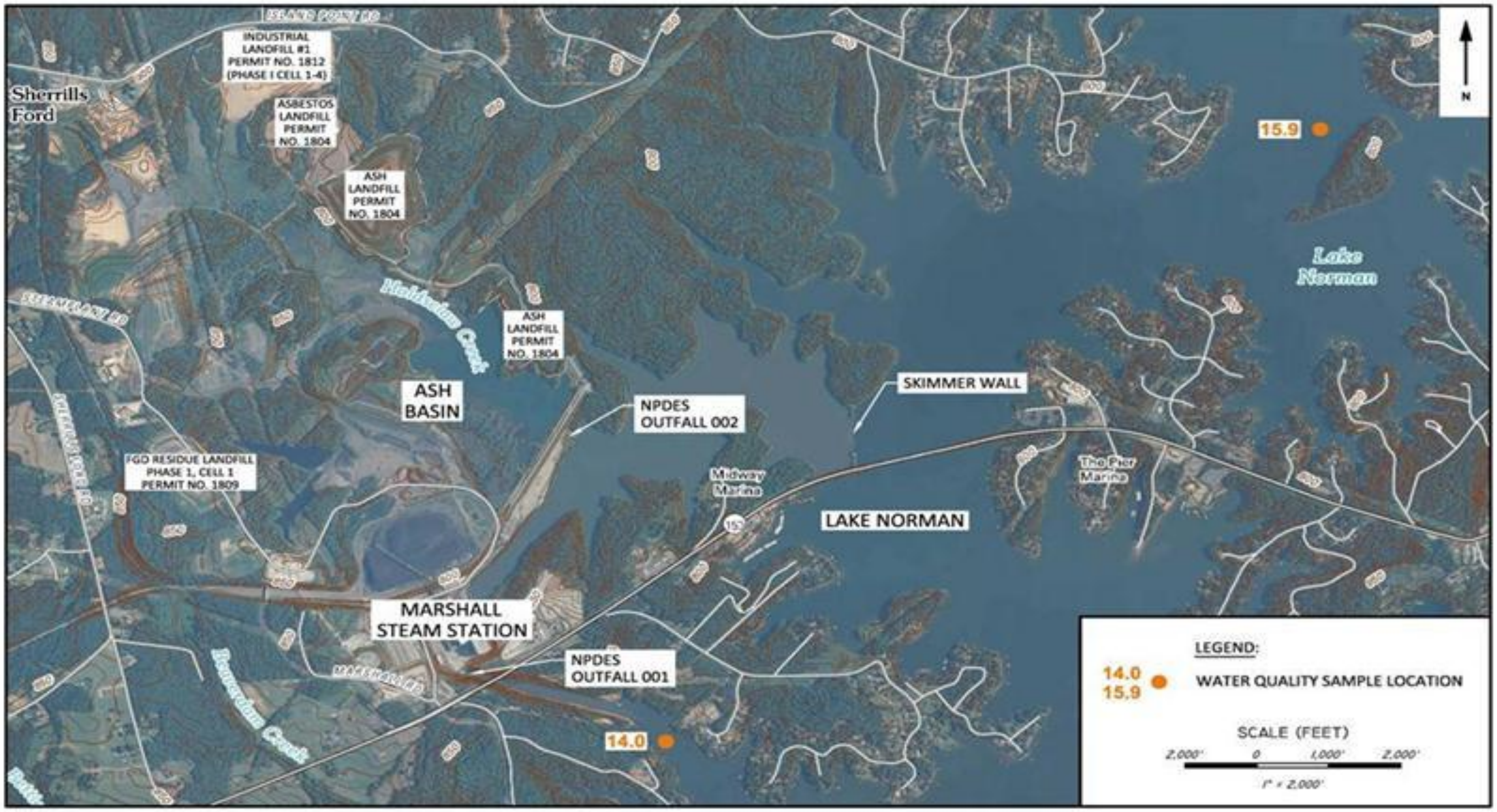
The water quality sampling locations associated with this monitoring plan are depicted in Figure 1. The upstream location (15.9) is approximately 2.5 miles upstream of where the MSS ash basin discharges into the MSS condenser cooling water (CCW) intake cove. The downstream location (14.0) is approximately 0.5 miles downstream of the MSS CCW discharge into Lake Norman.

Sampling and Analytical Methods

Grab samples collected from the surface (0.3 m) at both locations in Lake Norman were analyzed for the following parameters: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), zinc (Zn), and total dissolved solids (TDS). Storage and preservation techniques of the samples after collection and prior to analyses were followed according to Appendix A. Methods of analysis and results for each parameter are presented in Table 1. Analyses were conducted by Duke Energy's Huntersville analytical laboratory (NC Wastewater Certification #248).

III. Results & Recommendations

All trace metal results were low, with most values either tabulated as less than the analytical reporting limit (RL) for the method or close to the RL (Table 1). For example, all samples for arsenic, cadmium, chromium, mercury, lead and selenium were reported as less than the RL, whereas only four zinc values were greater than the RL of 1.0 µg/L. All zinc values were below the water quality standard (50 µg/L). Most of the copper values were above the RL, but only marginally so, and all values were also well below the water quality standard (7.0 µg/L). Total dissolved solids (TDS) values were low, and reflective of the low ionic strength and conductivity of waters in Lake Norman and the Catawba River Basin . All values for the nine water quality parameters monitored were below NC water quality standards. Duke Energy proposes that the in-stream monitoring frequency be reduced from semi-annually to annually.



NOTES:
1. WATER QUALITY SAMPLE LOCATIONS WERE PROVIDED BY DUKE ENERGY AND ARE APPROXIMATE.
2. MAP SOURCE: USGS TOPOGRAPHIC MAP - LAKE NORMAN NORTH QUADRANGLE, CREATED 1993, UPDATED 2011.

HDR

WATER QUALITY SAMPLE LOCATION MAP
MARSHALL STEAM STATION ASH BASIN
DUKE ENERGY CAROLINAS, LLC
CATAWBA COUNTY, NC

DATE
JUNE 17, 2014
FIGURE
1

Figure 1. Marshall Steam Station in-stream water quality monitoring locations.

Table 1. MSS in-stream monitoring analytical results and methodology. Locations 15.9 and 14.0 represents the upstream and downstream, respectively, sampling sites.

			Method	**EPA 200.8**		**EPA 200.8**		**EPA 200.8**		**EPA 200.8**		**EPA 245.1**		**EPA 200.8**		**EPA 200.8**		**EPA 200.8**		**SM2540C**	
Facility	**Date**	**Location**	**Depth (m)**	**<**	**Arsenic (µg/L)**	**<**	**Cadmium (µg/L)**	**<**	**Chromium (µg/L)**	**<**	**Copper (µg/L)**	**<**	**Mercury (µg/L)**	**<**	**Lead (µg/L)**	**<**	**Selenium (µg/L)**	**<**	**Zinc (µg/L)**	**<**	**TDS (mg/L)**
MSS	2/7/2011	15.9	0.3	<	1.00	<	1.00	<	1.00		2.09	<	0.05	<	1.00	<	1.00	<	2.00		50
MSS	2/7/2011	14.0	0.3	<	1.00	<	1.00	<	1.00		3.59	<	0.05	<	1.00	<	1.00	<	2.16		55
MSS	8/1/2011	15.9	0.3	<	1.00	<	1.00	<	1.00		1.69	<	0.05	<	1.00	<	1.00	<	2.00		37
MSS	8/1/2011	14.0	0.3	<	1.00	<	1.00	<	1.00		5.31	<	0.05	<	1.00	<	1.00	<	2.00		47
MSS	2/6/2012	15.9	0.3	<	1.00	<	1.00	<	1.00		1.31	<	0.05	<	1.00	<	1.00	<	2.00		51
MSS	2/6/2012	14.0	0.3	<	1.00	<	1.00	<	1.00		2.31	<	0.05	<	1.00	<	1.00	<	2.00		64
MSS	8/6/2012	15.9	0.3	<	1.00	<	1.00	<	1.00	<	1.00	<	0.05	<	1.00	<	1.00	<	1.00		50
MSS	8/6/2012	14.0	0.3	<	1.00	<	1.00	<	1.00	<	1.00	<	0.05	<	1.00	<	1.00	<	1.00		56
MSS	2/4/2013	15.9	0.3	<	1.00	<	1.00	<	1.00		1.12	<	0.05	<	1.00	<	1.00		2.67		47
MSS	2/4/2013	14.0	0.3	<	1.00	<	1.00	<	1.00		2.46	<	0.05	<	1.00	<	1.00		3.56		47
MSS	8/5/2013	15.9	0.3	<	1.00	<	1.00	<	1.00		2.46	<	0.05	<	1.00	<	1.00	<	1.00		40
MSS	8/5/2013	14.0	0.3	<	1.00	<	1.00	<	1.00		5.06	<	0.05	<	1.00	<	1.00		2.23		60
MSS	8/6/2012	15.9	0.3	<	1.00	<	1.00	<	1.00	<	1.00	<	0.05	<	1.00	<	1.00	<	1.00		50
MSS	8/6/2012	14.0	0.3	<	1.00	<	1.00	<	1.00	<	1.00	<	0.05	<	1.00	<	1.00	<	1.00		56

Appendix A

Sample Preservation and Hold times

Parameter name	Container1	Preservation[2] [3]	Maximum holding time[4]
Table IB—Inorganic Tests:			
1. Acidity	P, FP, G	Cool, ≤6 °C[18]	14 days.
2. Alkalinity	P, FP, G	Cool, ≤6 °C[18]	14 days.
4. Ammonia	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C[18]	48 hours.
10. Boron	P, FP, or Quartz	HNO_3 to pH <2	6 months.
11. Bromide	P, FP, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, FP G	Cool, ≤6 °C[18]	48 hours.
15. Chemical oxygen demand	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2	28 days.
16. Chloride	P, FP, G	None required	28 days.
17. Chlorine, total residual	P, G	None required	Analyze within 15 minutes.
21. Color	P, FP, G	Cool, ≤6 °C[18]	48 hours.
23-24. Cyanide, total or available (or CATC) and free	P, FP, G	Cool, ≤6 °C[18], NaOH to pH >10[5] [6], reducing agent if oxidizer present	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO_3 or H_2SO_4 to pH <2	6 months.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
31, 43. Kjeldahl and organic N	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2	28 days.
Table IB—Metals:[7]			
18. Chromium VI	P, FP, G	Cool, ≤6 °C[18], pH = 9.3-9.7[20]	28 days.
35. Mercury (CVAA)	P, FP, G	HNO_3 to pH <2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-lined cap[17]	5 mL/L 12N HCl or 5 mL/L BrCl[17]	90 days.[17]
3, 5-8, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75. Metals, except boron, chromium VI, and mercury	P, FP, G	HNO_3 to pH <2, or at least 24 hours prior to analysis[19]	6 months.
38. Nitrate	P, FP, G	Cool, ≤6 °C[18]	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2	28 days.
40. Nitrite	P, FP, G	Cool, ≤6 °C[18]	48 hours.
41. Oil and grease	G	Cool to ≤6 °C[18], HCl or H_2SO_4 to pH <2	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6 °C[18], HCl, H_2SO_4, or H_3PO_4 to pH <2	28 days.
44. Orthophosphate	P, FP, G	Cool, to ≤6 °C[18] [24]	Filter within 15 minutes; Analyze within 48 hours.
46. Oxygen, Dissolved Probe	G, Bottle and top	None required	Analyze within 15 minutes.
47. Winkler	G, Bottle and top	Fix on site and store in dark	8 hours.
48. Phenols	G	Cool, ≤6 °C[18], H_2SO_4 to pH <2	28 days.
49. Phosphorous (elemental)	G	Cool, ≤6 °C[18]	48 hours.
50. Phosphorous, total	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2	28 days.
53. Residue, total	P, FP, G	Cool, ≤6 °C[18]	7 days.
54. Residue, Filterable	P, FP, G	Cool, ≤6 °C[18]	7 days.
55. Residue, Nonfilterable (TSS)	P, FP, G	Cool, ≤6 °C[18]	7 days.
56. Residue, Settleable	P, FP, G	Cool, ≤6 °C[18]	48 hours.
57. Residue, Volatile	P, FP, G	Cool, ≤6 °C[18]	7 days.
61. Silica	P or Quartz	Cool, ≤6 °C[18]	28 days.
64. Specific conductance	P, FP, G	Cool, ≤6 °C[18]	28 days.
65. Sulfate	P, FP, G	Cool, ≤6 °C[18]	28 days.
66. Sulfide	P, FP, G	Cool, ≤6 °C[18], add zinc acetate plus sodium hydroxide to pH >9	7 days.
67. Sulfite	P, FP, G	None required	Analyze within 15 minutes.
68. Surfactants	P, FP, G	Cool, ≤6 °C[18]	48 hours.
69. Temperature	P, FP, G	None required	Analyze.
73. Turbidity	P, FP, G	Cool, ≤6 °C[18]	48 hours.

[1] “P” is for polyethylene; “FP” is fluoropolymer (polytetrafluoroethylene (PTFE); Teflon®), or other fluoropolymer, unless stated otherwise in this Table II; “G” is glass; “PA” is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); “LDPE” is low density polyethylene.

[2] Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sample (e.g., using a 24-hour composite sample; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), refrigerate the sample at ≤6 °C during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the

sample at ≤6 °C, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or aliquot split from a composite sample within 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (e.g., 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664 Rev. A (oil and grease) and the procedures at 40 CFR 141.34(f)(14)(iv) and (v) (volatile organics).

[3] When any sample is to be shipped by common carrier or sent via the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirement of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater; Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[4] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid. Samples may be held for longer periods only if the permittee or monitoring laboratory has data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under Sec. 136.3(e). For a grab sample, the holding time begins at the time of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, Appendix E), the holding time begins at the time of the end of collection of the composite sample. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See 136.3(e) for details. The date and time of collection of an individual grab sample is the date and time at which the sample is collected. For a set of grab samples to be composited, and that are all collected on the same calendar date, the date of collection is the date on which the samples are collected. For a set of grab samples to be composited, and that are collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14-15. For a composite sample collected automatically on a given date, the date of collection is the date on which the sample is collected. For a composite sample collected automatically, and that is collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14-15. For static-renewal toxicity tests, each grab or composite sample may also be used to prepare test solutions for renewal at 24 h, 48 h, and/or 72 h after first use, if stored at 0-6 °C, with minimum head space.

[5] ASTM D7365-09a specifies treatment options for samples containing oxidants (e.g*.,* chlorine). Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures.

[6] Sampling, preservation and mitigating interferences in water samples for analysis of cyanide are described in ASTM D7365-09a. There may be interferences that are not mitigated by the analytical test methods or D7365-09a. Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal or suppression technique not described in D7365-09a or the analytical test method must be documented along with supporting data.

[7] For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically.

[8] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

[9] If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.

[10] The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

[11] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity (*i.e.,* use all necessary preservatives and hold for the shortest time listed). When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to ≤6 °C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (regarding the requirement for thiosulfate reduction), and footnotes 12, 13 (regarding the analysis of benzidine).

[12] If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ±0.2 to prevent rearrangement to benzidine.

[13] Extracts may be stored up to 30 days at <0 °C.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

[15] The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

[16] Place sufficient ice with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, immediately measure the temperature of the samples and confirm that the preservation temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature cannot be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of

the increased holding temperature. Aqueous samples must not be frozen. Hand-delivered samples used on the day of collection do not need to be cooled to 0 to 6 °C prior to test initiation.

[17] Samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.

[18] Aqueous samples must be preserved at ≤6 °C, and should not be frozen unless data demonstrating that sample does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of "≤°C" is used in place of the "4 °C" and "<4 °C" sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that rounding down to 6 °C may not be used to meet the ≤6 °C requirement. Them preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).

[19] An aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately (see footnote 2). Soil and sediment samples do not need to be preserved with acid. The allowances in this footnote supersede the preservation and holding time requirements in the approved metals methods.

[20] To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

[21] Holding time is calculated from time of sample collection to elution for samples shipped to the laboratory in bulk and calculated from the time of sample filtration to elution for samples filtered in the field.

[22] Sample analysis should begin as soon as possible after receipt; sample incubation must be started no later than 8 hours from time of collection.

[23] For fecal coliform samples for sewage sludge (biosolids) only, the holding time is extended to 24 hours for the following sample types using either EPA Method 1680 (LTB-EC) or 1681 (A-1): Class A composted, Class B aerobically digested, and Class B anaerobically digested.

[24] The immediate filtration requirement in orthophosphate measurement is to assess the dissolved or bio-available form of orthophosphorus (*i.e.,* that which passes through a 0.45-micron filter), hence the requirement to filter the sample immediately upon collection (*i.e.,* within 15 minutes of collection). [38 FR 28758, Oct. 16, 1973