Phosphorus Reduction Analysis for Brickyard Pond

Barrington, Rhode Island

PREPARED FOR:
Department of Public Works
Town of Barrington
84 Upland Way
Barrington, Rhode Island 02806-2406

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ESS Project No.B439-002

June 2017

www.essgroup.com

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1.0 PURPOSE AND BACKGROUND

The purpose of this report is to evaluate conditions in Brickyard Pond, examine a variety of in-pond and shoreline phosphorus management actions, and develop a conceptual green infrastructure retrofit plan for phosphorus reduction.

Brickyard Pond is an approximately 84-acre pond located entirely in the Town of Barrington, Rhode Island. Originally excavated as a source of clay for brick-making operations, Brickyard Pond is now the key feature of the Town-owned Brickyard Pond Conservation Area and serves as a natural refuge within the developed suburban landscape. It also an important public recreational resource and present a highly visible landmark along the East Bay Bike Path. Unfortunately, water quality in the pond is steadily degrading and needs improvement for the pond to achieve its water quality goals under the federal Clean Water Act and Rhode Island Water Quality Regulations.

In 2007, the Rhode Island Department of Environmental Management (RIDEM) prepared a total maximum daily load (TMDL) study for Brickyard Pond to determine sources of phosphorus impairments and initiate development of an action plan to mitigate them. The TMDL indicates that the major sources of phosphorus to Brickyard Pond include waterfowl, shoreline erosion, stormwater, and internal cycling (RIDEM 2007).

What is a TMDL?

A TMDL, or total maximum daily load, is a watershed-based study of the level of pollution that a waterbody can receive on a daily basis and continue to meet water quality standards under the US Clean Water Act. TMDLs are approved by US Environmental Protection Agency and become enforceable through various policies and programs.

Following issuance of the TMDL, the Town prepared a TMDL implementation plan. The TMDL implementation plan, which was required to be developed within 180 days of TMDL approval, includes an acknowledgement of potential sources listed in the TMDL and describes a general approach for mitigating them; however, the plan also notes that additional water quality data would be needed to develop a cost-effective management strategy.

This report discusses:

- Collection of additional water quality data for the purposes of developing a management strategy.
- Initial (i.e., conceptual) design work focused on green infrastructure stormwater BMPs for the Brickyard Pond.
- Strategies to alleviate pollution from waterfowl, shoreline erosion, and internal cycling.

1.1 State and Federal Regulatory Context

On December 8, 1999, the U.S. Environmental Protection Agency (USEPA) promulgated Phase II of its National Pollution Discharge Elimination System (NPDES) storm water regulations. Among other tenets, Phase I of the USEPA storm water program established regulations for storm water discharge from municipal separate storm sewer systems (MS4s) in municipalities with populations of 100,000 or greater.

The Phase II Final Rule expands on the Phase I program by requiring smaller communities (e.g., with populations of 10,000 or more) in urbanized areas (UA) to implement stormwater management programs. Urbanized areas are based on the decennial census. Rhode Island is one of approximately 25 states delegated by USEPA to administer Phase II of NPDES. RIDEM implements the program as part of the Rhode Island Pollution Discharge Elimination System (RIPDES) in accordance with the *General Permit for the Rhode Island Pollutant Discharge Elimination System Storm Water Discharge from Small Municipal Separate Storm Sewer Systems and from Industrial Activity at Eligible Facilities Operated by Regulated Small MS4s* (MS4 GP).

The MS4 GP, which was adopted in February 5, 2003, requires each municipality in UAs to develop storm water management program plans (SWMPP). Generally speaking, SWMPPs must address six minimum control measures:

- Public Education and Outreach
- Public Participation/Involvement
- Illicit Discharge Detection and Elimination
- Construction Site Runoff Control
- Post-Construction Runoff Control
- Good Housekeeping/Pollution Prevention

Beyond the six minimum control measures, MS4 operators are also required to meet storm water provisions of approved total maximum daily load studies (TMDLs). A TMDL is a watershed study of one or more impaired waters. Impaired waters are waters of the state that do not meet water quality standards for one or more parameters in the *Rhode Island Water Quality Regulations*. TMDLs determine pollution reduction requirements needed to bring subject waters back into compliance with water quality standards. RIDEM formally approved a TMDL for Brickyard Pond in 2007 to address impairments due to excessive phosphorus and, therefore, Brickyard Pond is regulated under the MS4 GP.

2.0 AVAILABLE WATER QUALITY DATA

The discussion that follows in sections 2.1 and 2.2 is adapted from Barrington's *Stormwater Program Plan for Brickyard Pond*. Brickyard Pond has been the subject of a number of stormwater studies in recent years. This section of our report focuses on the following sources of data:

- Brickyard Pond TMDL
- Dry-weather sampling data

2.1 TMDL Data

According to the TMDL the major sources of phosphorus to Brickyard Pond, include stormwater, waterfowl, internal cycling and perhaps wastewater. Pollution sources were identified based on physical observation. The TMDL does not attempt to set the relative significance of these sources or quantify the level of pollution that each contributes.

2.1.1 Stormwater

The TMDL identifies 24 storm drains and three areas of concentrated flow discharging to Brickyard Pond, its tributary, or hydrologically connected wetlands. Eight of these outfalls are 18 inches in diameter or greater. Those identified in the TMDL as the "most significant" outfalls are listed in Table 2.1.

Table 2.1. Priority Outfalls for Brickyard Pond

Outfall ID	Diameter (in)	Location	Ownership[a]
BrP-E	24" x 48" box culvert	Bike path near Maple Av.	Town of Barrington
BrP-C	36	Bike path near Maple Av	Town of Barrington
BrP-I and BrP-J	Twin 24" culverts	Maple Av.	Town of Barrington
BrP-D	18	Ferncliffe Rd.	Town of Barrington
BrP-X	18	Broadview Dr.	Town of Barrington
BrP-O	24	South of Half Mile Rd.	Town of Barrington
BrP-Q	24	Near Nyatt Elementary	RIDOT
BrP-S	24	Woodhaven Rd.	Town of Barrington

Notes:
a. The TMDL infers ownership from ownership of nearest roadway. Although this provides a useful starting point, we recommend confirming ownership data through state and local records.

The TMDL sets general pollution abatement priority for these outfalls based on their anticipated quantity of discharge. The TMDL does not state whether this relative quantification was based on size of pipe, size of discharge area, or other approximation. Regardless, discharge quantity provides at best an indirect measure of pollutant contribution. Pollutant load quantification based on field sampling during wet weather provides a much more reliable and accurate estimation of actual level of contribution.

Nevertheless, the TMDL does provide a number of valuable observations from the field:

- Outfall BrP-E is a 24 x 48-inch box culvert that discharges directly into the pond at the bike path at the pond's northwestern end.
- Outfall BrP-C is a 36-inch outfall discharges directly into the pond at the bike path at the pond's northeastern end.
- Outfalls BrP-I and BrP-J are twin 24-inch culverts that discharge to a ditch just south of Maple Avenue, which discharges to the ditch alongside the bike path.
- Other outfalls include two 18-inch culverts (BrP-D and BrP-X) that discharge directly to the pond from a residential area at its southern shore, and three 24-inch culverts (BrP-O, BrP-Q, and BrP-S) that drain into the eastern tributary.

2.1.2 Waterfowl

The TMDL indicates that waterfowl may be a significant source of phosphorus to Brickyard Pond. The TMDL finds that significant numbers of waterfowl were observed on the pond during each of two site visits. TMDL staff observed approximately 25 Mute Swans on the pond during both site visits. The TMDL speculates that swans may congregate near shore in the grassed area along the bike path at the northern edge of the lake or on the many islands dotting the pond, although all of the swans observed during the shoreline survey were in the water. Approximately 55 gulls were observed on the pond during the first TMDL field inspection. During the second site visit approximately 125 gulls and 30 ducks were observed on the pond. Residents report that up to 1000 geese and 500 cormorants inhabit the pond, especially in the winter months. The TMDL indicates that cormorants typically congregate on the islands within the pond; however, it is unclear whether or not this was based on direct observation.

2.1.3 Soil Erosion

The TMDL indicates that soil erosion may be a significant source of phosphorus to Brickyard Pond and states that:

> Erosion is a significant problem at the northern shore of the pond along the bike path and to a lesser extent the northeastern shore in the general vicinity of the YMCA. Portions of the northern shoreline are characterized by vertical and undercut banks up to 1.5 m high, which is resulting in the undercutting of several large trees in the area. The ongoing erosion problems along the northern shore are probably the result of unstable vertical banks left by the historic clay-mining operation, fine-textured soils that are particularly susceptible to erosion and transport, and the orientation of the shoreline relative to prevailing winds. The clay soils in the area also have the potential to adsorb significantly more phosphorus than coarser sandy soils.

During a meeting with Town staff including the DPW director and planner on March 17, 2008, observations regarding shoreline erosion were discussed. Town staff believe that the erosion indicated in the TMDL are misstated. There is no known erosion near the YMCA. Brickyard Pond is manmade and the instability of the clay on northern shore is natural rather than the result of mining activity. This was confirmed during field review conducted as part of this study.

2.1.4 Internal Cycling

The TMDL classifies Brickyard Pond as a deep pond (i.e., >15 feet). The pond has been monitored by University of Rhode Island Watershed Watch since 1994. Phosphorus samples have been taken at two depths—surface and 4 meters (approximately 13 feet). Sampling data reveals significant difference in surface and deep sampling. The mean concentration of surface samples is approximately 22 ug/l. The mean concentration of deep samples is approximately 111 ug/l. The TMDL opines:

> It appears that internal cycling is a significant source of phosphorus for Brickyard Pond. The mean concentration of total phosphorus at the pond bottom was about 5 times greater than the concentration at the surface. The disparity in phosphorus concentrations becomes even more pronounced during the summer and fall. The phosphorus concentrations at the surface and at depth are similar in the spring, but differ by about an order of magnitude in the summer and early fall, when the pond is stratified.

2.2 Dry-Weather Survey for Illicit Discharges to the Town's Storm Sewer System

The Town received a grant from DEM to conduct dry-weather surveys, which have been completed and were documented in a 2008 report, entitled *Barrington Illicit Discharge Detection and Elimination Plan Dry-Weather Sampling* (Fuss & O'Neill). The report recommended further resampling of four outfalls for potential illicit discharge. The Town conducted resample of each and found no further evidence of illicit discharge. None of the four outfalls is within the watershed of Brickyard Pond. This work is a requirement of the MS4 GP.

2.3 Other Data

In-pond monitoring data for Brickyard Pond from 1994 to 2009 were obtained from URI Watershed Watch (2017). The data include transparency (Secchi disk), chlorophyll a, total phosphorus, and total nitrogen.

3.0 SAMPLING PROGRAM AND FIELD ANALYSIS

This section provides a discussion of the sampling done. Available sampling data is inconclusive regarding sources of phosphorus and the types of watershed conditions that may contribute to higher concentrations. ESS Group, Inc. (ESS) developed a sampling program that was designed to help determine conditions that contribute to phosphorus accumulation in Brickyard Pond and to confirm or dismiss suspected sources of pollution.

The ESS sampling program was developed in collaboration with the Town and documented in a QAPP. The QAPP is provided as Appendix A to this report.

The study approach included characterization of water quality through in-pond and shoreline runoff sampling. Additionally, Brickyard Pond sediments were sampled to further characterize the degree of internal nutrient loading. Lastly, surveys of resident waterfowl were completed to identify whether they were likely to constitute a significant source of nutrients to the pond.

In-pond work was completed on September 21 and November 3 of 2016. This included two rounds of water quality measurements and waterfowl observations, as well as one round of sediment sampling (during the November event).

During the September 21, 2016 field visit, the pond shoreline was also investigated to identify areas of runoff-driven erosion that could serve as conduits for sediment and nutrient loading to the pond. These areas were revisited on April 4, 2017 during a 1.51-inch storm event with the objective of collecting direct runoff into the pond.

Additional details on the sampling methods are provided in the project-specific QAPP (Appendix A).

3.1 Waterfowl

Resident waterbirds, including Canada Goose and Mute Swan were observed at Brickyard Pond during each field visit. However, neither species was observed at extreme densities (Table 3.1). All waterfowl observed were adults. The most frequent behaviors observed were swimming and loafing.

Waterfowl grazing habitat (mown lawn) is accessible from the pond in multiple locations; however, the extent of available forage is primarily limited to grassy areas along the East Bay Bike Path, Legion Way, and residences on Broadview Drive.

Other waterbirds and birds of prey observed include Double-Crested Cormorant, Mallard, Great Blue Heron, Green Heron, Osprey, Bald Eagle, and Spotted Sandpiper.

Table 3.1. Resident Waterfowl Assessment Results

Date	Species	Total Count	Count by Life Stage		Count by Dominant Behavior			
			Adult	Juvenile	Swimming	Foraging	Loafing	Flying
9/21/16	Canada Goose	6	6	0	4	0	2	0
	Mute Swan	3	3	0	3	0	0	0
	Mallard	2	2	0	2	0	0	0
	Double-crested Cormorant	10	10	0	0	0	10	0
	Great Blue Heron	1	1	0	0	1	0	0
	Gull sp.	28	10	18	28	0	0	0

Date	Species	Total Count	Count by Life Stage		Count by Dominant Behavior			
			Adult	Juvenile	Swimming	Foraging	Loafing	Flying
	Osprey	1	1	0	0	0	0	1
	Bald Eagle	1	0	1	0	0	0	1
11/3/16	Canada Goose	30	30	0	28	0	2	0
	Mute Swan	7	7	0	7	0	0	0
	Mallard	10	10	0	10	0	0	0
	Double-crested Cormorant	8	8	0	0	0	8	0
	Great Blue Heron	1	1	0	0	1	0	0
	Osprey	1	1	0	0	1	0	0
	Bald Eagle	1	0	1	0	0	0	1

3.2 Sampling Program Findings

The field sampling program findings are presented in the following sections. Site locations are depicted in Figure 3.1.

3.2.1 In-Pond Water Quality

Secchi Depth

The Secchi disk depths measured by ESS ranged from 0.75 m to 1.10 m, indicating very low water clarity. Previous data from Brickyard Pond indicate median Secchi disk readings near three meters in the early 1990s, declining to less than one meter by 2001 (URI Watershed Watch 2017). Although the current dataset is limited, Secchi transparency does not appear to have substantially changed since 2001.

Dissolved Oxygen, Temperature, Salinity

Based on the September 21 and November 3 sampling events, Brickyard Pond was strongly stratified during both the summer and autumn (see Table 3.2 and Figure 3.2). Under stratified conditions, mixing between surface and bottom waters is limited. Bottom waters were more saline, approaching 13 ppt, which is consistent with brackish water (approximate salinity of 0.5 – 30 ppt). During the summer event warmer, fresher water was found at the surface. During the autumn event, surface water was colder and fresher than water at the pond bottom.

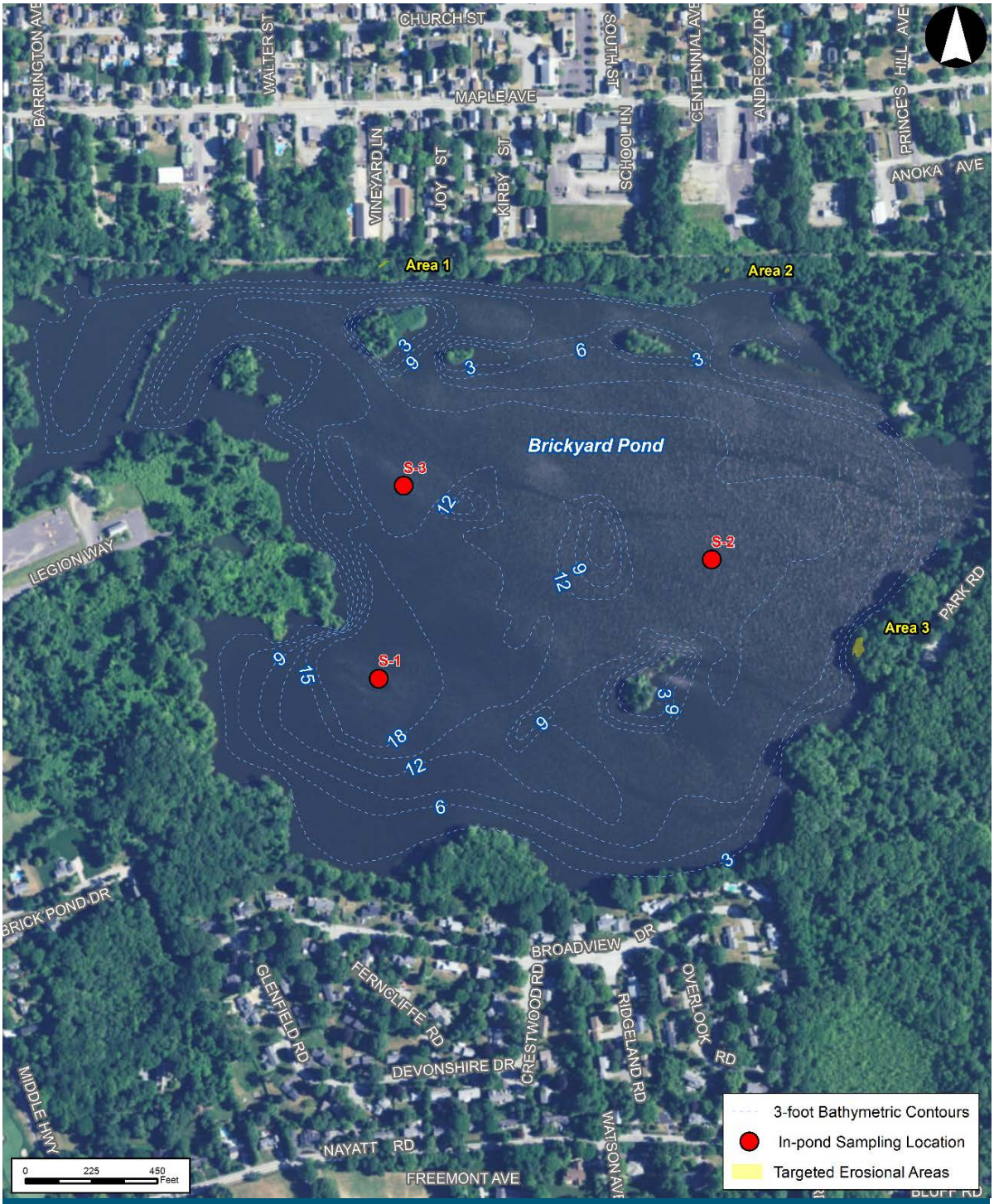

Figure 3.1 — In-pond Sampling Locations and Shoreline Erosional Areas

Table 3.2. Water Quality – Field Parameters

Date	Depth (m)	Depth (ft)	Water Temperature (°C)	Dissolved Oxygen		Salinity (ppt)
				(%)	(mg/L)	
9/21/2016	Surface	Surface	23.9	89.6	7.3	6.1
	0.5	1.6	23.9	88.3	7.3	6.1
	1.0	3.3	23.6	86.8	7.1	6.1
	1.5	4.9	23.4	86.1	7.2	6.1
	2.0	6.6	23.0	77.0	6.4	6.1
	2.5	8.2	22.3	1.2	0.1	8.3
	3.0	9.8	21.4	0.0	0.0	10.1
	3.5	11.5	20.8	0.0	0.0	10.8
	4.0	13.1	20.1	0.0	0.0	11.7
	4.5	14.8	19.3	0.0	0.0	12.2
	5.0	16.4	18.7	0.0	0.0	12.8
	5.5	18.0	18.6	0.0	0.0	12.8
11/3/2016	Surface	Surface	12.8	129.5	13.5	7.0
	0.5	1.6	12.7	127.5	13.0	7.0
	1.0	3.3	12.4	123.0	12.6	7.0
	1.5	4.9	12.1	120.3	12.4	7.0
	2.0	6.6	11.9	115.9	12.0	7.0
	2.5	8.2	11.5	113.0	11.8	7.0
	3.0	9.8	12.5	3.5	0.4	7.6
	3.5	11.5	15.2	0.0	0.0	10.5
	4.0	13.1	16.8	0.0	0.0	11.8
	4.5	14.8	17.2	0.0	0.0	12.4
	5.0	16.4	16.7	0.0	0.0	12.8
	5.5	18.0	16.7	0.0	0.0	12.4

In a typical New England freshwater pond, stratification is driven primarily by temperature, with water at the bottom approaching 4°C (the temperature at which water is densest). Surface water may be warmer or colder. Cooling autumn weather and warming spring weather result in overturn and mixing of surface and bottom waters. This allows oxygen from the surface to mix down to the bottom of the pond, while nutrients from the bottom are mixed up to the surface. At 18 feet deep (i.e., the depth of Brickyard Pond), freshwater ponds are generally too shallow to completely stratify; however, because Brickyard Pond is brackish (at least some of the time) stratification appears to be driven primarily by salinity, with water at the bottom being more saline and water at the surface being fresher.

This type of stratification may endure for multiple seasons before the pond turns over and mixes. The result appears to be a persistent loss of dissolved oxygen in the bottom waters of the pond (i.e., anoxia). Subsequently, anaerobic biological processes (i.e., those that can proceed in the absence of oxygen) dominate and gases like hydrogen sulfide are produced. Strong odors characteristic of hydrogen sulfide were observed during in-pond sampling at lower depths in both September and November. These conditions prevent the use of bottom waters by fish, invertebrates, or other aquatic life.

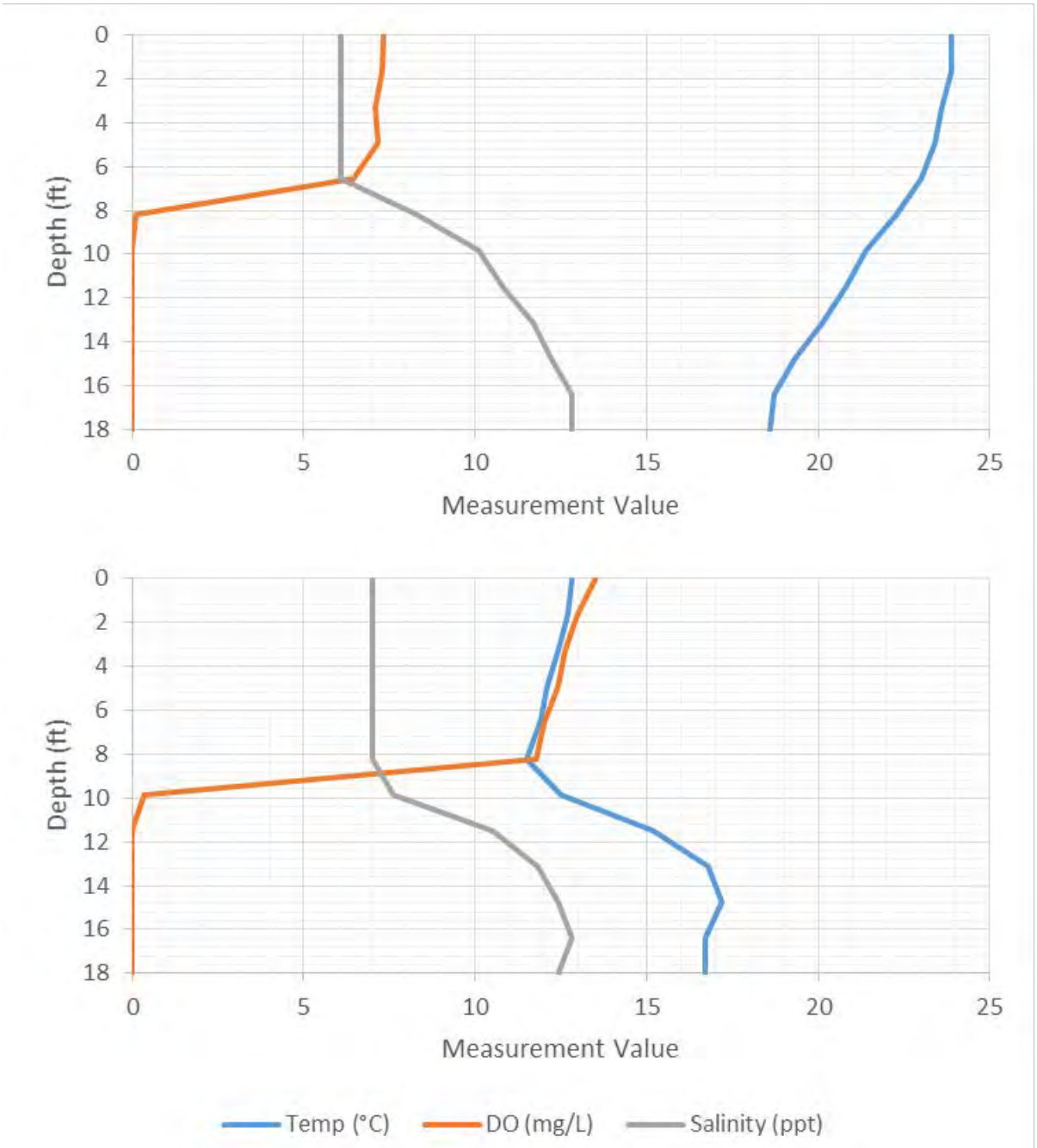

Figure 3.2— Temperature, Dissolved Oxygen, and Salinity Profiles in Brickyard Pond on September 21, 2017 (top) and November 3, 2017 (bottom)

Nutrients and Metals

A summary of nutrients and metals results is presented in this section. Full laboratory results are available in Appendix B.

Table 3.3. Water Quality – Lab Analytes

Date	Location	Aluminum (mg/L)	Iron (mg/L)	Alkalinity (mg $CaCO_3$/L)	TSS (mg/L)	Total N (mg/L)	Nitrate +Nitrite – N (mg/L)	TKN (mg/L)	TP (mg/L)	Soluble P (mg/L)
9/21/16	S1 surface	0.036	0.030	72.6	<5.0	1.09	0.081	1.01	0.023	0.041
	S1 bottom	0.027	0.061	247.0	8.7	6.15	<0.019	6.14	0.696	0.820
11/3/16	S1 surface	0.030	0.030	76.3	6.4	1.45	0.090	1.36	0.043	0.033
	S1 bottom	0.040	0.070	199.0	8.4	6.51	0.042	6.47	0.719	0.568

Phosphorus

Total phosphorus levels at Brickyard Pond averaged ranged from 0.023 mg/L at the surface in September to 0.719 mg/L at the bottom in November (Table 3.3). Dissolved phosphorus concentrations exhibited a very similar pattern to total phosphorus during both sampling events. In all cases, phosphorus concentrations were substantially higher near the bottom of the pond. This pattern is consistent with release of phosphorus from the sediments.

Prior data from Brickyard Pond indicate annual mean total phosphorus concentrations of approximately 0.035 mg/L to just over 0.040 mg/L from 2001 to 2008, the most recent period of observation (URI Watershed Watch 2017). These levels are consistent with those observed by the current study; therefore, total phosphorus concentrations at the surface do not appear to have changed significantly since 2008.

In freshwater ponds, phosphorus is typically the limiting nutrient for algal production, so even a small change could impact the frequency and severity of algae blooms. Given the small watershed-to-pond ratio at Brickyard Pond (just over 10:1) and average depth in excess of 10 feet, detention time is likely to be moderately long (on the order of several months), meaning that phosphorus may not be efficiently flushed from the system. Adsorption or chemical binding in sediments may be an important mechanism for phosphorus removal. The efficiency of this mechanism in sequestering phosphorus is dependent on a number of factors, including but not limited to the availability of dissolved oxygen and metals, such as aluminum and iron, each of which was also monitored as part of the current study (see “metals and alkalinity,” below).

Nitrogen

Total nitrogen levels at Brickyard Pond ranged from 1.09 mg/L at the surface in September to more than 6.50 mg/L at the bottom in November (Table 3.3). As with phosphorus, nitrogen was substantially higher in bottom waters.

Total Kjeldahl nitrogen (TKN), which includes both ammonia and organically bound nitrogen, was the primary species of nitrogen (>90%) documented in the pond. TKN concentrations were highest in bottom waters during both sampling events. Nitrate-plus-nitrite nitrogen was also present but concentrations were highest in surface waters during both sampling events.

Prior data from Brickyard Pond indicate annual mean total nitrogen concentrations of just under 0.500 mg/L to approximately 0.920 mg/L from 2001 to 2008, the most recent period of observation (URI Watershed Watch 2017). This suggests that total nitrogen has increased somewhat since 2008.

Metals and Alkalinity

Aluminum and iron concentrations at the surface of Brickyard Pond were similar to each other and fairly consistent between sampling events (Table 3.3). Aluminum was somewhat lower at the pond bottom in September, but somewhat higher in November. In contrast, iron was higher at the pond bottom during both sampling events.

Under aerobic conditions, iron combines complexes with phosphorus and precipitates out of solution. However, under anoxic conditions, such as those observed in the deeper waters of Brickyard Pond, iron releases phosphorus. Aluminum tends to hold its bond on phosphorus under low oxygen conditions. Where iron and aluminum concentrations are high relative to phosphorus, these processes are typically able to efficiently capture phosphorus and prevent it from being released into the surface waters of the pond. Typically, iron- and aluminum-to-phosphorus ratios of 16:1 and 10:1, respectively, are suggestive of systems with sufficient capacity to capture and sequester phosphorus. At Brickyard Pond, these ratios are generally less than 1:1, suggesting that iron and aluminum levels are generally insufficient to remove much of the phosphorus present in the water column.

In contrast, alkalinity levels in Brickyard Pond indicated substantial buffering capacity, particularly in bottom waters, where concentrations approached or exceeded 200 mg $CaCO_3$/L. ESS did not find previous alkalinity data for the pond; however, the alkalinity levels observed at Brickyard Pond are known to be toward the higher end of the range for ponds in Rhode Island (RIDEM 2012).

3.2.2 Shoreline Runoff Water Quality

Although shoreline runoff volume was insufficient to allow sampling for water quality purposes, observations made during the sampling event did provide some useful information. For example, no downslope mobilization of soils was observed at either of the two smaller areas of shoreline erosion on the northern periphery of the pond. These two areas were characterized by a more cohesive soil matrix; however, very small rills developed in the more severely eroded area on the eastern shoreline of the pond (Area 3), coinciding with sandy soils. Despite resulting in the development of rills, the medium to high intensity rainfall of the April 4, 2017 event was unable to generate surface runoff that reached the pond. Additionally, the amount of material mobilized toward the pond was minimal.

3.2.3 Sediment Analysis

A summary of sediment analysis results is presented in this section. Full laboratory results are available in Appendix B.

Sediment quality results indicated that phosphorus and total Kjeldahl nitrogen were present at detectable concentrations (Table 3.4). Nitrite-plus-nitrate levels were below detectable limits. There are no applicable state standards for nutrients in sediment; however, for context, total phosphorus concentrations in sediments from multiple waterbodies in Rhode Island and eastern Massachusetts were found to range from approximately 200 mg/kg to just over 2,000 mg/kg. Total nitrogen in the same ponds ranged from 3,500 mg/kg to near 6,000 mg/kg (ESS unpublished data). The total phosphorus levels found in Brickyard Pond sediments were within this range for phosphorus, although the total nitrogen concentration was above this range at S1.

Table 3.4. Sediment Analysis Results

Location	Total Solids (%)	Aluminum (mg/kg)	Iron (mg/kg)	Total N (mg/L)	Nitrate + Nitrite – N (mg/L)	TKN (mg/L)	TP (mg/L)
S1	14.6	17,000	30,000	9,500	<1.8	9,500	2,000
S2	20.2	13,000	22,000	5,000	<1.2	5,000	1,800
S3	20.2	12,000	21,000	4,400	<1.4	4,400	1,400

Ratios of iron to total phosphorus in Brickyard Pond sediments varied from 12:1 to 15:1. Typically, ratios of 16:1 are sufficient to capture and sequester phosphorus in the sediments under aerobic conditions. Under anaerobic conditions, some of the sediment phosphorus, particularly the portion complexed with iron, may be released into the water column. The production of hydrogen sulfide by anaerobic bacteria can also result in capture of iron and formation of insoluble iron sulfide. Over time, this may lead to iron depletion, effectively interrupting iron cycling and facilitating the presence of dissolved phosphorus in the water column, even under well-aerated conditions.

Ratios of aluminum to total phosphorus in Brickyard Pond sediments varied from 7:1 to 9:1. Although there are no applicable state standards for nutrients in sediment, an aluminum to iron ratio of 10:1 is frequently targeted for phosphorus management purposes. Aluminum is more effective than iron at capturing and sequestering phosphorus, even under anaerobic conditions.

3.3 Sampling and Field Analysis Conclusions

ESS recommends that key portions of this baseline assessment study be repeated on a periodic basis to monitor the condition of Brickyard Pond over time. These include a continuation of water quality sampling, and additional sediment sampling. Additional sediment sampling is also recommended, although changes to the scope of the program are encouraged to address questions that emerged from the results of the current study (as described in the following discussion).

With regard to shoreline erosion, ESS recommends slope stabilization as a minimum measure to prevent further degradation. Redesign of trail access to the eroded areas and revegetation are also recommended as options to enhance these areas.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

Field-measured Water Quality

No hold times were exceeded on field-measured water quality parameters. Additionally, one field duplicate measurement (10% rate) was made for each water quality parameter, which satisfies the 5% rate required in the QAPP. All measured duplicate values agreed within 10%. Therefore, no corrective measures were deemed necessary and field-measured water quality results were considered to be acceptable for use in this study.

Laboratory Water Quality and Sediment Analyses

All water quality and sediment samples arrived at the analytical laboratory in good condition and within hold times. Additionally, all laboratory analytical results conformed with internal laboratory QA/QC requirements. Therefore, no corrective measures were deemed necessary and laboratory sediment quality results were considered to be valid for use in this study.

Waterfowl Surveys

Duplicate waterfowl count data were collected during the September sampling event. Counts between observers were comparable and met QA/QC requirements.

Other Field Data Collection

No substantive data quality problems affected other field data collection efforts associated with this study. Therefore, the data collected were considered to be valid for use in this study.

5.0 CONDITIONS IN THE SURROUNDING WATERSHED

Section 5.0 provides a discussion of watershed data that may influence BMP design, including land use, habitat and cultural resources, and soils. The section also discusses stormwater infrastructure data that is available from the Town. The purpose of this discussion is to provide information to support the conceptual design of BMPs.

5.1 Land Use

Stormwater BMPs will be selected to best fit the environmental and land use constraints of the watershed. Land use and impervious surface data were obtained from the Rhode Island Geographic Information System (RIGIS) and the Town. Figure 4.1 shows land-use distribution in the Brickyard Pond watershed. The area of land surrounding Brickyard Pond is primarily forested with some residential area. Forested land makes up approximately 30% of the watershed. The remaining area is mostly residential and commercial development.

A forested perimeter is generally preferred from a water quality standpoint as forest vegetation helps to take up pollutants in runoff and provides habitat value. That said, the forested area around Brickyard Pond is not particularly wide, which may minimize its benefit.

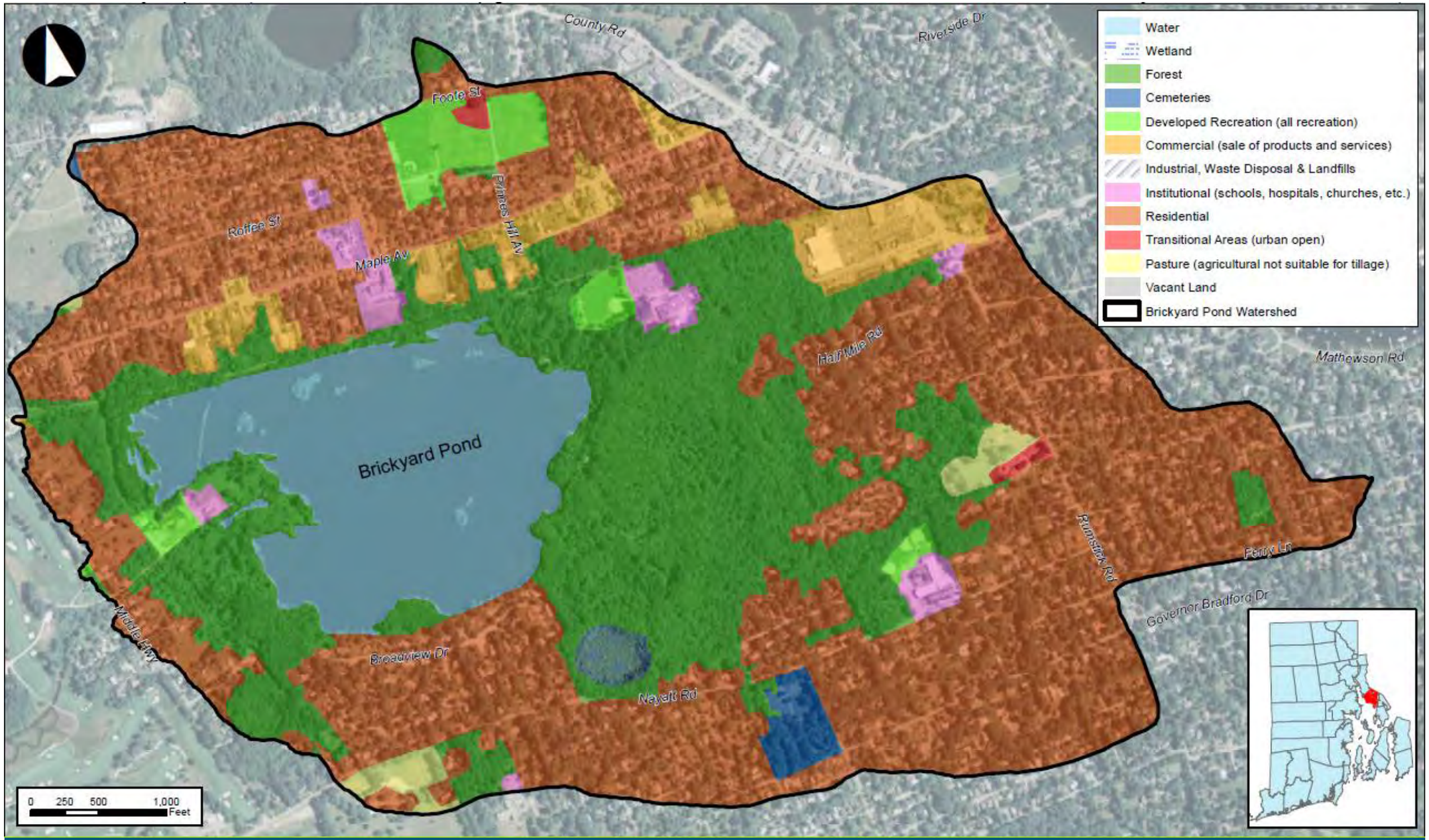

Figure 5.1—Land Use in the Brickyard Pond Watershed

5.2 Habitat and Cultural Resources

Disturbance of areas with sensitive cultural and habitat resources should be avoided when siting BMPs. To determine the existence of cultural and habitat resources within the watershed the following sources were consulted:

- The National Register of Historic Places database
- Rhode Island Advisory Commission on Historical Cemeteries
- Rhode Island Historic Preservation Commission
- Candidate State Historic Sites and Districts
- State Conservation and Recreational Open Space

Figure 5.2 shows the approximate locations of known habitat and cultural resources. The study area includes distribution of wetland types found within the Brickyard Pond watershed.

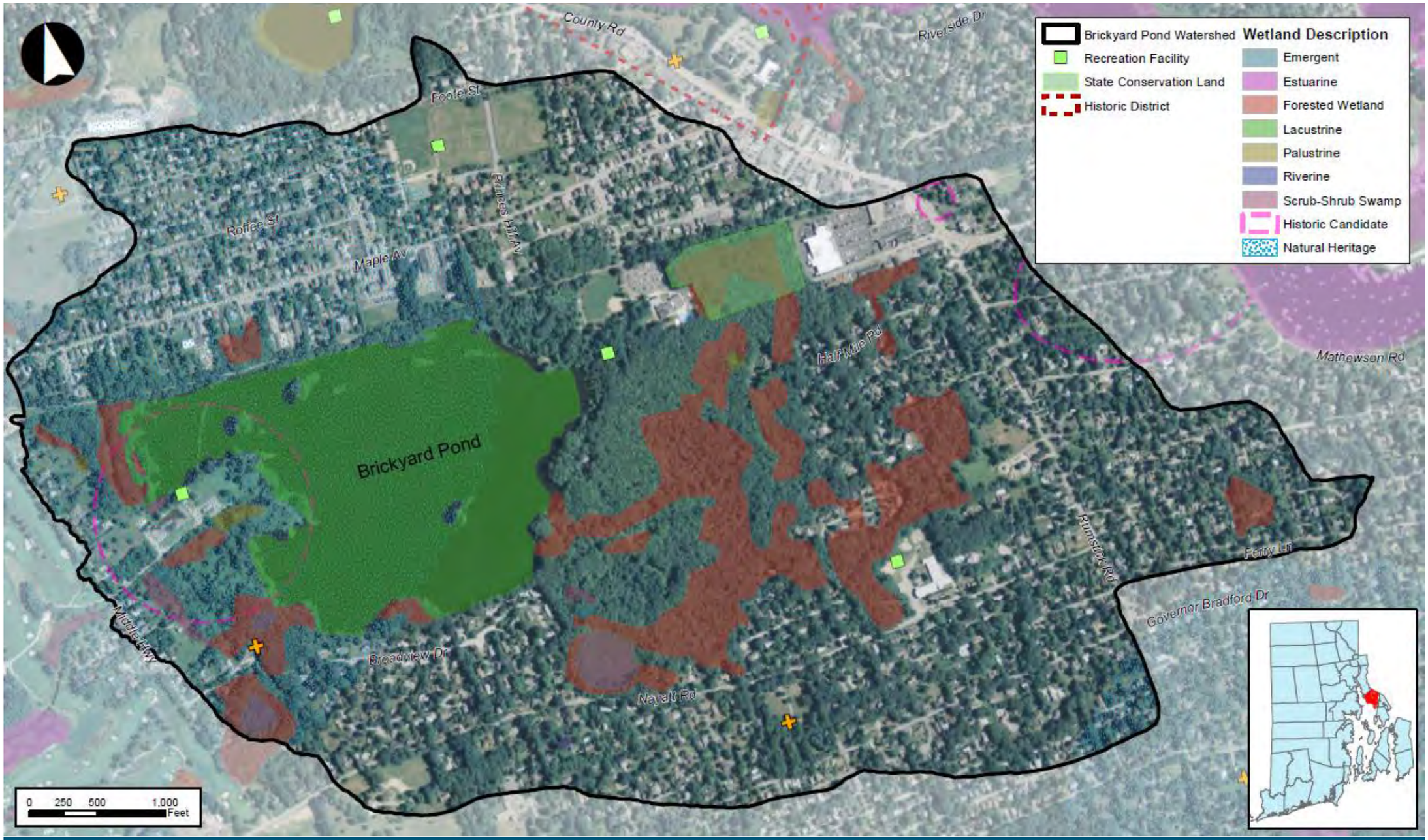

Figure 5.2—Habitat and Cultural Resources in the Brickyard Pond Watershed

5.3 Soils

Many stormwater BMPs rely on the infiltrative capacity of soil. Soil composition and structure affects its capacity to infiltrate runoff and filter pollutants. U.S. Department of Agriculture, Natural Resources Conservation Service (NRCS) has established four hydrologic soil groups (HSG types A, B, C, and D). Hydrologic Soil Groups A and B are preferred for infiltration BMP practices, which are especially effective at pollutant removal.

To determine approximate soil types within the watershed area, a SSURGO-certified data layer published by RIGIS and the Town originally from the U.S. Department of Agriculture, Natural Resources Conservation Service was consulted. With regard to stormwater design, hydrologic soil types are of particular interest within the watershed. General distribution of hydrologic soil ratings within the watershed are depicted in Figure 5.3.

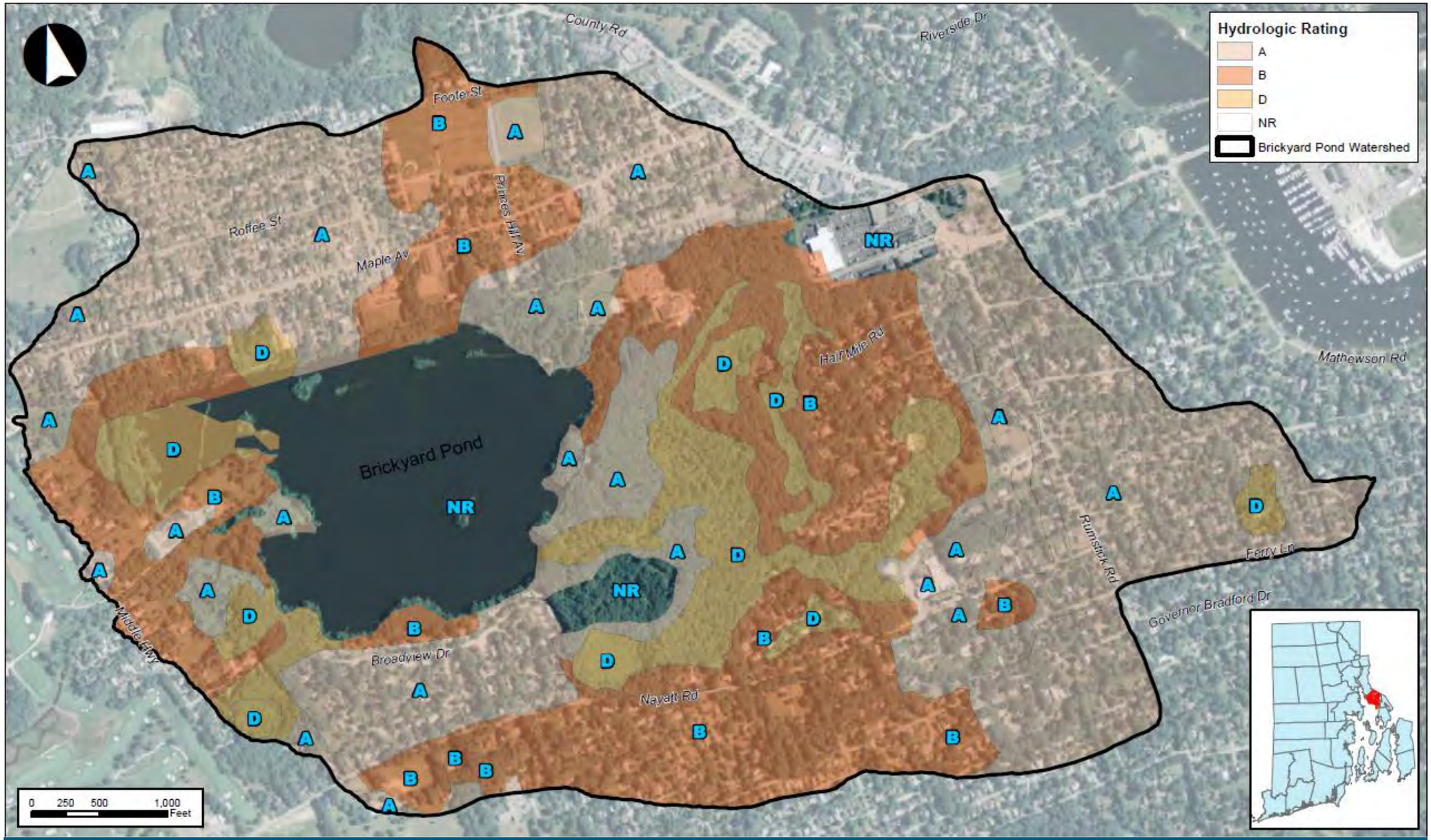

Figure 5.3 — Hydrologic Soil Groups in the Brickyard Pond Watershed

5.4 Impervious Surface

Stormwater runoff is a part of the hydrologic cycle (the movement of water between the earth's atmosphere, land, and waterbodies). (See Figure 5.4.)

When land is developed with buildings and roads, that development interrupts the natural hydrologic cycle by blocking water from uptake by plants and infiltration into soil. Pavement and other surfaces that prevent precipitation from draining into the soil are collectively referred to as impervious surface. Figure 5.4 below illustrates how increasing degrees urbanization may disrupt the natural water cycle and reduce the land's capacity to retain stormwater.

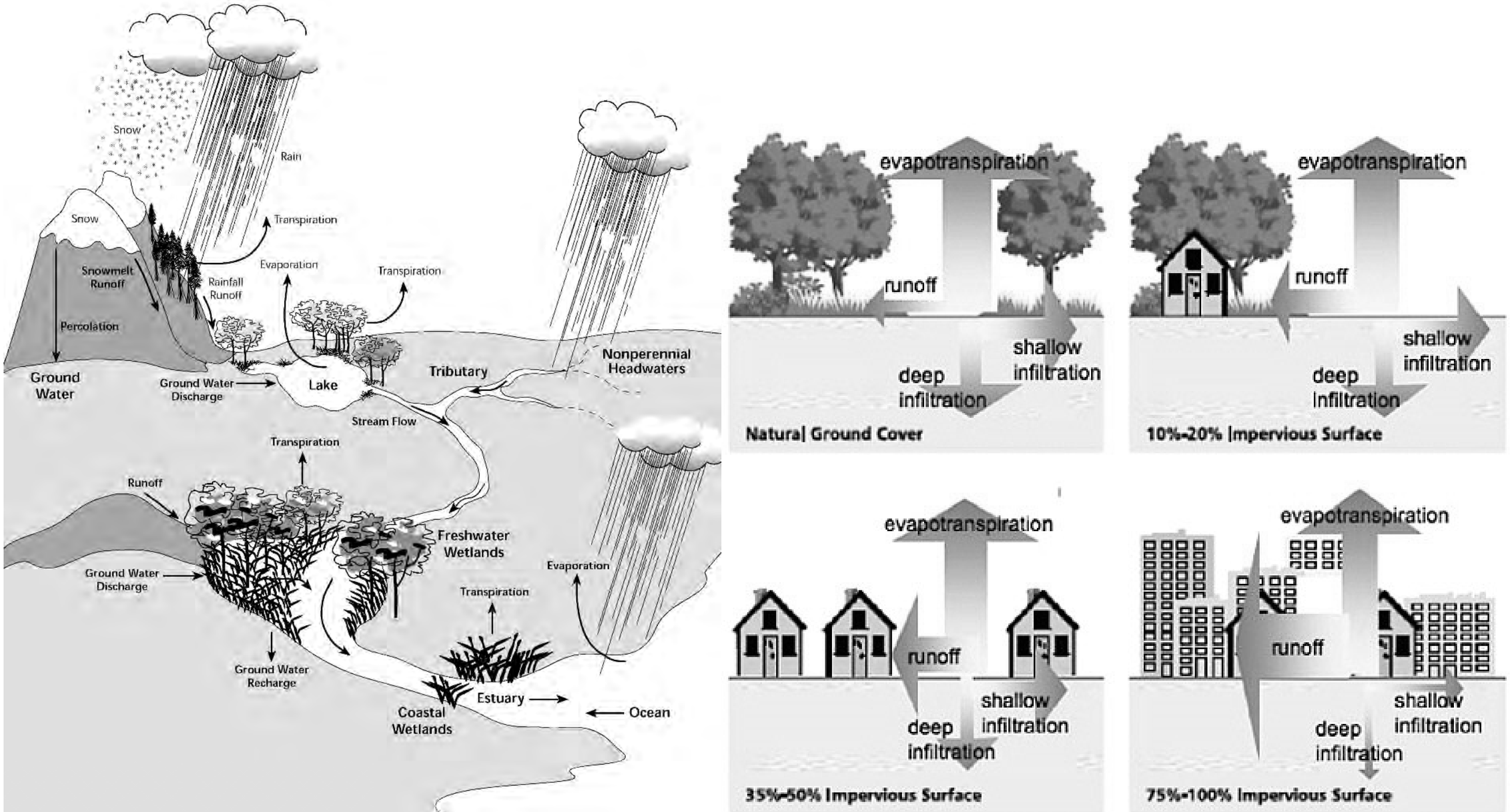

Figure 5.4—Stormwater Runoff and Urban Development
Stormwater runoff is a natural part of the hydrologic (i.e., water) cycle, but urban development and dense areas of impervious surface increase stormwater runoff to the extent that it causes floods and degrades water resources.

Impervious cover and intensity of development provide good metrics for the expected adverse effect of stormwater and the overall health of a watershed. Numerous studies have documented the cumulative effects of urbanization on stream and watershed ecology (Schueler 1995, Booth and Reinelt 1993, Arnold and Gibbons 1996, Brant 1999, Shaver and Maxted 1996). Research has shown that when impervious cover in a watershed reaches between 10 and 25 percent, ecological stress becomes clearly apparent. Beyond 25 percent impervious cover water quality becomes degraded and biological diversity decreases (NRDC, May 1999).

Total imperviousness in the study area is approximately 26 percent or approximately 200 acres of the 766-acre watershed. Figure 5.5 below depicts impervious surface in the Brickyard Pond Watershed. The amount of imperviousness within each drainage catchment will be determined for proper BMP siting. Table 5.1 (below) lists impervious surface by drainage area.

Table 5.1. Drainage Areas and Impervious Surface

	Drainage Area (acres)	Impervious Surface (acres)	Percent Impervious Surface (%)
BrP-E	34.06	11.50	34%
BrP-C	18.07	8.00	44%
BrP-I/J	42.80	22.32	52%
BrP-D	33.36	9.25	28%
BrP-X	19.08	6.74	35%
BrP-O	8.61	2.34	27%
BrP-Q	64.08	21.71	34%
BrP-S	2.88	1.46	51%
TOTAL	222.94	83.32	37%

Because of the close correlation of impervious surface to water quality, the *Rhode Island Stormwater Design and Installation Standards Manual* relies on impervious surface to determine water quality volume and sizing of water quality features in best management practice design. Our approach to sizing BMPs is discussed in Section 6.2.

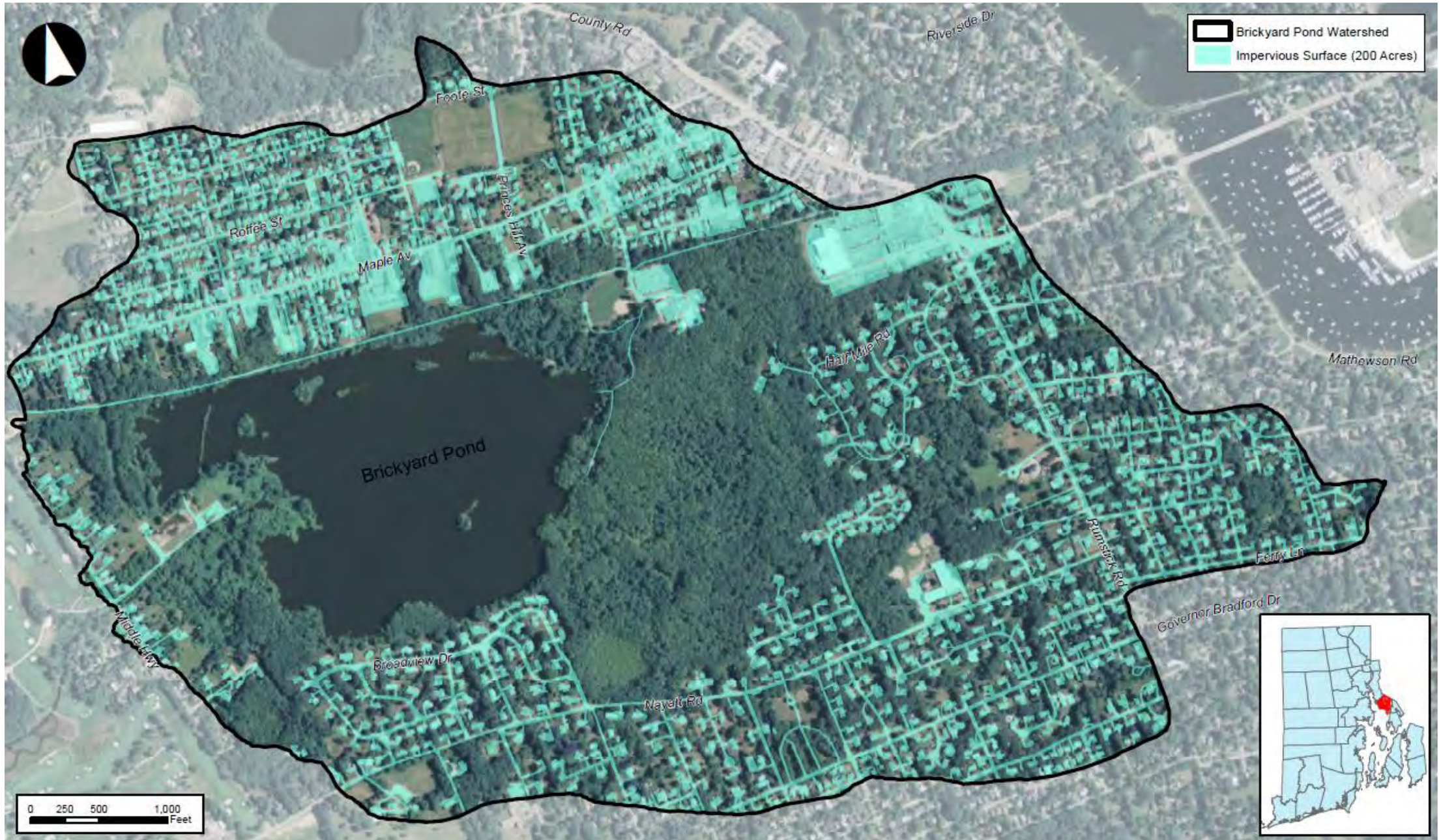

Figure 5.5 — Impervious Surface in the Brickyard Pond Watershed

6.0 STRUCTURAL ALTERNATIVES FOR PHOSPHORUS REDUCTION

A primary objective of this study is to select several suitable sites for conceptual stormwater BMP design. The following section discusses conceptual BMP alternatives.

6.1 Candidate Structural Alternatives

For this conceptual design study, we considered BMPs (i.e., structural alternatives) with significant capacity to treat phosphorous and based on information available in the *Rhode Island Stormwater Design and Installation Standards Manual*. Stormwater treatment mechanisms that work well to remove these pollutants include vegetated treatment, filtration, and infiltration. We considered but generally avoided use of BMPs that treat stormwater primarily by detention and sedimentation since a number of field studies have shown such BMPs to export pollutants such as nutrients. Appendix C provides a description of each type of BMP considered for this study as well as a discussion of their general application, advantages, and limitations. Appendix C also provides schematics and photographs of the candidate BMPs. The tables below provide a summary of information in Appendix C.

We selected BMPs primarily for their capacity to remove phosphorus and to function appropriately in the subject setting. We used 30 percent removal of phosphorus as our low-end limits for preferred BMPs. We consider BMPs with vegetative treatment process to be preferred as these processes are generally more reliable for nutrient removal and because vegetated BMPs are more likely to fit in well in residential areas, which are by far the dominant land use in the subject watershed area. We limited our selection of preferred BMPs to those that have the capacity to treat large areas (i.e., five acres or more) or roadways since we are focusing on retrofits to address community areas as opposed to individual private properties.

The following BMPs have been selected as preferred for further consideration. This is not intended to preclude the use of other BMPs, but instead to provide guidance in selecting BMPs for conceptual consideration and further study:

Table 6.1. Candidate BMPs Selected for Further Consideration

Preferred BMPs (Any Setting)	Secondary Consideration (Any Setting)	BMPs (Roadways Only)	Removed from Consideration in this Study
• **Bioretention**	• Water Quality Swale • Gravel Wetland	• **Subsurface Infiltration**	• Dry Wells • Green Roofs et al • Constructed Stormwater Wetland[a] • Wet Retention Pond[a] • Vegetated Filter Strip • Vegetated Drainage Ways • Planter and Tree Box Filters • Porous Pavement • Proprietary Media Filter • Infiltration Trenches • Sand Filters

Notes

a. Removed due to the presence of standing water, which is inappropriate for this application.

6.2 Sizing and Siting Methodology

To site BMPs we conducted a desktop evaluation using RIGIS and available Town data. BMP locations were selected using the following siting criteria:

- Site BMPs on Town or publically owned property to the extent practicable. The Town maintains parcel mapping through the Office of the Tax Assessor. The assessor's data was used to determine ownership and approximate the locations of property boundaries in order to identify Town-owned properties that are located in advantageous areas for BMP installation (e.g., near outfalls and stormwater sewer mains).
- Maximize potential stormwater capture and treatment based on hydrologic location and existing drainage patterns.
- Avoid disturbance of cultural and historic resources as well as wetlands and other sensitive receptors.
- Review hydrologic soil groups (HSG) to determine whether infiltration would be feasible and assume HSG soil types A and B would support infiltration and HSG type C soils would require noninfiltrating BMPs (e.g., wet vegetated treatment systems and sand filters).

Once potential BMPs locations were selected, these locations were evaluated for their capacity to fit BMPs that would manage the water quality volume (i.e., one inch over the impervious surface). The *Rhode Island Stormwater Design Manual* was utilized

- Subsurface infiltration provides six cubic feet of water quality storage per linear foot based on three-foot storage depth, six-foot bottom width on a road shoulder or up to 80% of a property footprint and storage bed material porosity of 0.33.
- Bioswales will have 3:1 (horizontal:vertical) side slopes and provide 6-inch depth of storage to allow for appropriate bottom surface area. Bioswales will be eight feet wide and provide five cubic feet of water quality volume per linear foot.

Conceptual BMP designs are shown, below, in Figure 6.1.

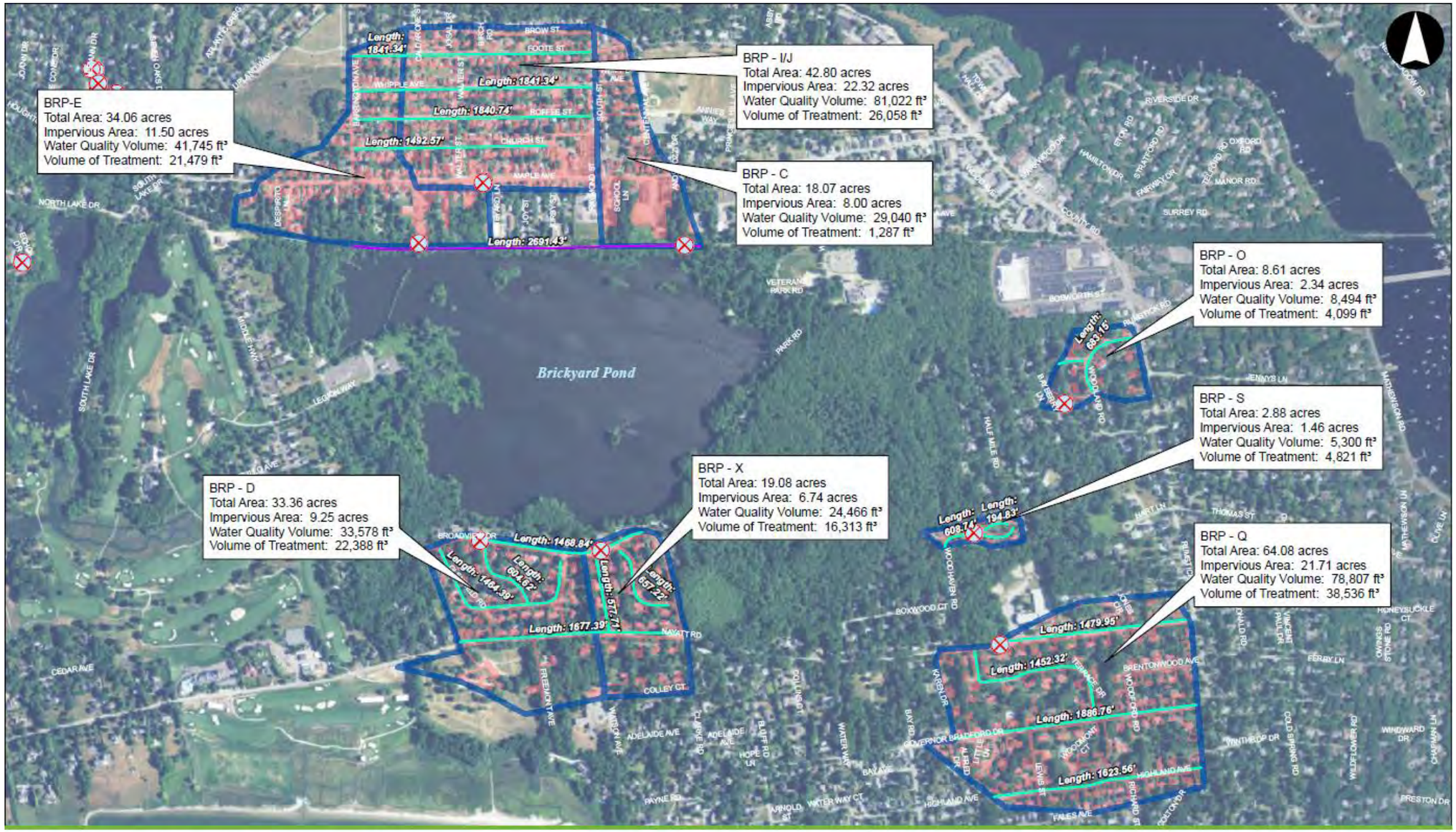

Figure 6.1 — Conceptual Stormwater Best Management Practices for the Brickyard Pond Watershed

6.3 Opinions of Cost

Order-of-magnitude opinions of cost for construction were developed based on unit cost of treatment (i.e., cost per cubic foot of treatment capacity; $29 per cubic foot for biorention and $33 per cubic foot for subsurface infiltration). Table 6.2 provides cost on a per-catchment basis for the alternatives recommended for each catchment.

Table 6.2. Cost of Selected BMPs and Probable Cost Based on Unit Pricing

Drainage Area	BMP Treatment Capacity (cu ft)	Cost of BMPs Based on Unit Price (nearest $1,000)		Cost per Treatment Site Based on Unit Price
		Bioretention ($29/cu ft)	Subsurface Infiltration ($33/cu ft)	
BrP-E	21,479	$63,000	$648,000	$711,000
BrP-C	1,287	$44,000	None Proposed	$44,000
BrP-I/J	26,058	$123,000	$741,000	$864,000
BrP-D	22,388	None Proposed	$739,000	$739,000
BrP-X	16,313	None Proposed	$538,000	$538,000
BrP-O	4,099	None Proposed	$135,000	$135,000
BrP-Q	38,536	None Proposed	$1,272,000	$1,272,000
BrP-S	4,821	None Proposed	$159,000	$159,000
Total	134,981	$230,000	$4,232,000	$4,462,000

Table 6.3. Probable Range of BMP Costs Based on Unit Pricing

Drainage Area	Most Probable Cost per Drainage Area	Probable Range of Cost	
		Low Range Cost per Treatment Site at -30%	High Range Cost per Treatment Site at +50%
BrP-E	$711,000	$497,700	$1,066,500
BrP-C	$44,000	$30,800	$66,000
BrP-I/J	$864,000	$604,800	$1,296,000
BrP-D	$739,000	$517,300	$1,108,500
BrP-X	$538,000	$376,600	$807,000
BrP-O	$135,000	$94,500	$202,500
BrP-Q	$1,272,000	$890,400	$1,908,000
BrP-S	$159,000	$111,300	$238,500

6.4 Anticipated Water Quality Benefits

Utilizing the *Rhode Island Stormwater Design and Installation* Standards Manual (March 2015) a pollutant loading analysis using the Simple Method was conducted. This approach was described and documented in the QAPP provided in Appendix A. The tables below summarize the estimated annual phosphorus loads and cost-benefit for each outfall point using structural BMPs identified in the previous section.

Table 6.4. Cost of Reducing Total Phosphorus ($/lbs/year) Using Structural BMPs

Drainage Area	Phosphorus Reduction		Anticipated Cost of BMPs		Cost per Pound Phosphorus Reduced	
	Percent Reduction	Mass Reduction (lbs/year)	Low Cost	High Cost	Low Estimate	High Estimate
BrP-E (Bioswale)	1.3	0.1	$44,100	$94,500	$441,000	$945,000
BrP-E (Subsurface Infiltration)	24.7	1.2	$453,600	$972,000	$378,000	$810,000
BrP-C (Bioswale)	1.3	0.0[a]	$30,800	$66,000	U/D[b]	U/D
BrP-I/J (Bioswale)	1.3	0.1	$86,100	$184,500	$861,000	$1,845,000
BrP-I/J (Subsurface Infiltration)	15.3	0.7	$518,700	$1,111,500	$741,000	$1,587,857
BrP-D (Subsurface Infiltration)	36.0	1.6	$517,300	$1,108,500	$323,313	$692,813
BrP-X (Subsurface Infiltration)	36.7	1.0	$376,600	$807,000	$376,600	$807,000
BrP-O (Subsurface Infiltration)	26.5	0.3	$94,500	$202,500	$315,000	$675,000
BrP-Q (Subsurface Infiltration)	26.9	2.5	$890,400	$1,908,000	$356,160	$763,200
BrP-S (Subsurface Infiltration)	49.9	0.2	$111,300	$238,500	$556,500	$1,192,500
Total	N/A[c]	7.7	$3,123,400	$6,693,000	N/A	N/A

Notes:
a. Zero due to rounding. Actual reduction was found to be less than 0.05 lbs per year.
b. "U/D" means undetermined due to division by zero.
c. "N/A" means not applicable.

6.5 Rationale for Selection of Structural Alternatives

For this conceptual design study, BMPs with significant capacity to treat bacteria and phosphorus were considered.

7.0 SUMMARY OF RECOMMENDATIONS

The follow discussion provides our recommendations for structural and nonstructural BMPs in the Brickyard Pond Watershed.

7.1 Structural

ESS recommends proceeding with design and implementation work at BrP-E, BrP-C, and BrP-J/I with a focus on the bioretention swale along the north side of the bike path. ESS gives an opinion of cost of $230,000 with a probable cost range of $161,000 to $345,000. The cost of these BMPs would be reduced if the Town provides construction services through its Department of Public Works.

If the Town wishes to proceed with additional BMPs, ESS recommends the subsurface infiltration systems proposed in the BrP-E and BrP-J/I catchments as this is the largest catchment and has direct discharges to the pond. ESS gives an opinion of cost of $1,389,000 with a probable cost range of $972,300 to $2,083,500. This would also allow for an excellent opportunity to measure BMP effectiveness.

7.2 Nonstructural Recommendations

The following are recommended nonstructural approaches.

Watershed: Animal Waste Management

Although resident waterfowl populations at Brickyard Pond did not appear to be excessive during project field visits, there are a number of locations where waterfowl can easily access grazing area (i.e., mown lawns). This could encourage resident Canada Goose populations to expand in future years. Therefore, we recommend developing an outreach and education program targeted to pond abutters. The program could include publications or a community workshop on both passive and active resident waterfowl deterrence techniques. Such a program could be developed for $2,500 to $5,000, depending on the level of outreach desired.

In-pond: Long-term Monitoring Program

Although in-pond management could potentially be used to reduce phosphorus loading to Brickyard Pond, additional study is needed before a feasible approach can be recommended. This is because the most appropriate management approach for Brickyard Pond will depend on the salinity regime, which can significantly influence nutrient cycling in the pond.

Brickyard Pond was previously determined to be a freshwater system by RIDEM (2007). However, the pond was observed to be brackish during both field visits by ESS in 2016. It is currently unclear whether the brackish conditions were the result of, or exacerbated by, ongoing severe drought conditions. Therefore, additional monitoring is needed to better establish the pond salinity and mixing regimes over multiple seasons and potentially years.

Elements that should be included in the monitoring program are summarized in Table 7.1.

Table 7.1. Minimum Elements for In-pond Monitoring Program at Brickyard Pond

Activity	Location	Frequency	Time of Year
Shoreline Erosion Monitoring	Shoreline areas 1, 2, and 3, as well as any new areas noted	Annually	Late fall to early spring (avoid periods with snow cover)
In-situ Water Quality – Temperature Dissolved Oxygen Salinity pH Transparency (Secchi)	Deep hole (at least every meter, except for transparency)	At least once per season	Once each season
Water Quality Sampling – Phosphorus (total and soluble) Nitrogen (TKN, nitrate-nitrite, ammonia)	Deep hole (surface and bottom, at a minimum)	At least twice annually	Once in spring/early summer Once in late summer

The costs for a monitoring program of this scope (including an annual monitoring report) would be expected to range from approximately $8,000 to $10,000 per year.

Depending on the results of the monitoring program, additional sediment testing may be warranted to develop a cost estimate for reducing phosphorus release from the sediments (i.e., internal recycling of phosphorus) through aeration, nutrient inactivation, or other in-pond management approach.

8.0 REFERENCES

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Appendix A

Brickyard Pond Phosphorus Reduction Analysis
Quality Assurance Project Plan

Brickyard Pond Phosphorus Reduction Analysis
Quality Assurance Project Plan

Prepared by:

ESS Group
10 Hemingway Drive
East Providence, RI 02915

August 8, 2016

Prepared in cooperation with the:

New England Interstate Water Pollution Control Commission, Narragansett Bay Estuary Program and the U.S. Environmental Protection Agency
EPA Grant # CE00A00004

Questions concerning this QAPP should be directed to:

Joseph Piccerelli
Acting Director
Department of Public Works
84 Upland Way
Barrington, RI 02806-2406
(401) 247-9107
jpiccerelli@barrington.ri.gov

SECTION A: PROJECT MANAGEMENT

A1 Approval Page:

Grant Project Manager:
8/15/16
Joseph Piccerelli, Acting Director — Date
Town of Barrington, RI

NEIWPCC QA Manager:
8/17/16
Michael Jennings, NEIWPCC — Date
Senior Program Manager

NBEP Project Manager:
8/18/2016
for Heather Radcliffe
Heather Radcliffe, NEIWPCC/NBEP — Date
Environmental Analyst and Staff Attorney

Contractor Project Manager:
8/8/16
James Riordan, ESS Group — Date
Principal Scientist

Contractor Lead Modeler:
8/8/16
Jessica Lajoie, ESS Group — Date
Scientist

Contractor QA Officer:
8/8/16
Carl Nielsen, ESS Group — Date
Vice President

EPA Project Officer:
8/29/16
Caitlyn Whittle, USEPA Region 1 — Date
Project Officer

EPA QA Reviewer:
9/1/2016
Nora Conlen, USEPA Region 1 — Date
QA Reviewer

A2 Table of Contents

Tables

Figures

Appendices

A3 Distribution List

Table A3.1 presents a list of people who will receive the approved QAPP, the QAPP revisions, and amendments as well as their role and project responsibilities.

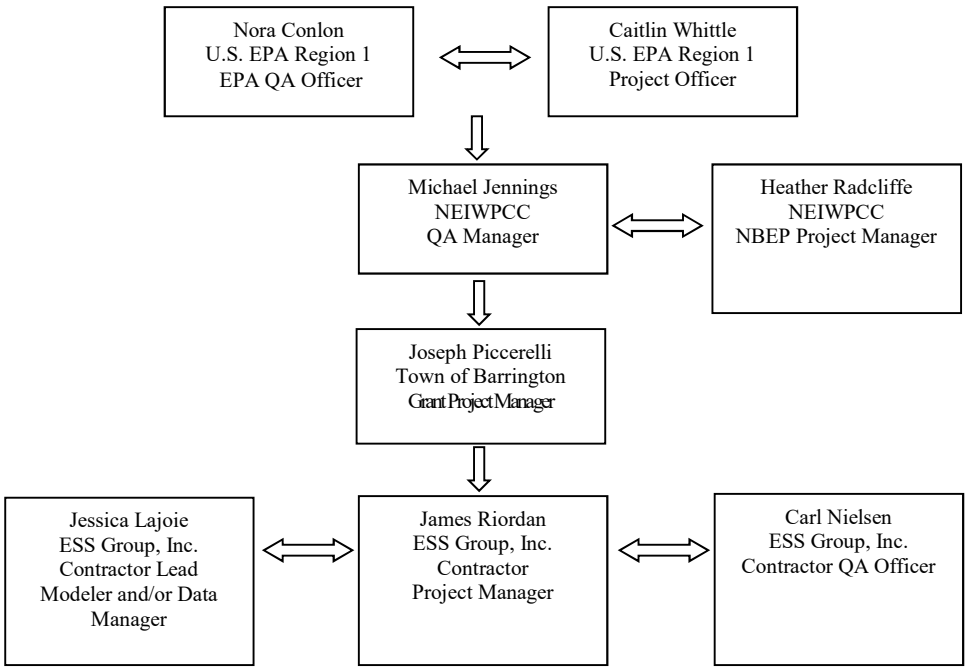
Table A3.1 - QAPP Distribution List and Project Roles and Responsibilities

QAPP Recipient and Affiliation	Project Role	Responsibility	Telephone Number and Email
Joseph Piccerelli Town of Barrington Barrington, RI	Grant Project Manager	Oversight and management of the project grant and contractor	(401) 247-1907 jpiccerelli@barrington.ri.gov
Michael Jennings NEIWPCC	NEIWPCC QA Manager	Management of quality assurance and control for NEIWPCC	(978) 323-7929 mjennings@neiwpcc.org
Heather Radcliffe NEIWPCC/NBEP	NBEP Project Manager	Management of this NBEP project	(978) 349-2522 hradcliffe@neiwpcc.org
James Riordan ESS Group	Contractor Project Manager	Oversee management of the project for ESS Group	(401) 330-1221 jriordan@essgroup.com
Jessica Lajoie ESS Group	Contractor Lead Modeler	Conduct modeling	(401) 330- 1230 jlajoie@essgroup.com
Carl Nielsen ESS Group	Contractor QA Officer	Provide quality assurance and control for ESS Group	(401) 330-1224 cnielsen@essgroup.com
Caitlyn Whittle USEPA Region 1	EPA Project Officer	Administer fiscal and technical aspects of the grant project for EPA	(617) 918-1748 whittle.caitlyn@epa.gov
Nora Conlon	EPA QA Officer	Management of quality assurance and control for EPA	(617) 918-8335 conlon.nora@epa.gov

A4 Project/Task Organization

The following section provides the names, duties, and responsibilities of key project participants as well as an organizational chart.

Figure A4.1 - Organization Chart - Lines of Communication



Town of Barrington, Rhode Island
Barrington applied for and received federal grant funds from NEIWPCC to assist in conducting this project. Barrington will oversee project work related to construction and subcontracting. Barrington is working in partnership with ESS Group and will oversee ESS's work and deliverables as they relate to the grant.

NEIWPCC
NEIWPCC was the grantor of grant monies being used for this project to the Town of Barrington. NEIWPCC will administer fiscal and technical aspects of the grant project as they relate to the grant from NEIWPCC to Barrington.

ESS Group
ESS Group is a partner with the Town of Barrington and will provide technical services including field sampling, modeling, water quality science and engineering for this project.

USEPA Region 1
EPA was the initial grantor to NEIWPCC/NBEP for grant monies that are being used for this project. USEPA Region 1 will administer fiscal and technical aspects of the grant project as they relate to the grant from EPA to NEIWPCC.

A5 Problem Definition/Background
The purpose of the QAPP is to clearly delineate the quality assurance policy, management structure and procedures to implement the requirements necessary to verify, calibrate, and validate the output of the modeling process associated with this project. This QAPP is reviewed by the NEIWPCC and EPA to help ensure that the outputs and data generated for the purposes described within are scientifically valid and legally defensible. This process will facilitate the use of project outputs and data by the NBEP and other programs deemed appropriate by the NEIWPCC and EPA.

Brickyard Pond is an approximately 84-acre pond located entirely in the Town of Barrington, Rhode Island. Originally excavated as a source of clay for brick-making operations, Brickyard Pond is now the key feature of the Town-owned Brickyard Pond Conservation Area and serves as a natural refuge within the developed suburban landscape. It also doubles as a public recreational and aesthetic amenity and is a highly visible landmark along the East Bay Bike Path. However, water quality in the pond is in need of restoration.

URI-Watershed Watch data from 1994 to 2008 demonstrate that water quality in Brickyard Pond declined over the period, with reductions in clarity and corresponding increases in chlorophyll *a* (algae) and nutrients (URIWW 2015). In 2007, the Rhode Island Department of Environmental Management (RIDEM) prepared a TMDL for Brickyard Pond to address impairments due to excessive phosphorus. According to the TMDL, the major sources of phosphorus to Brickyard Pond include waterfowl, shoreline erosion, stormwater and internal cycling (RIDEM 2007). Despite impairments, Brickyard Pond is a critically important ecological resource. Connected to Narragansett Bay through Mussachuck Creek, the pond hosts an annual run of anadromous river herring (a complex of species in regional decline), a diverse recreational fishery and multiple state-listed avian species of Concern (RINHS 2009).

The goals for this project include design of structural BMPs as well as collection of sediment, water quality, and biological data for the purpose of determining the relative magnitude of each type of nutrient source. This data will be used to select BMPs and to calibrate modeling to predict anticipated water quality improvement from stormwater BMP installation. The project will prioritize management actions to address stormwater and non-stormwater sources of phosphorus. The actions proposed will be planned to improve water quality of Brickyard Pond as well as ensure its ecological value.

A6 Project/Task Description and Schedule

The table below summarizes the tasks, deliverables, and timeline for the phosphorus reduction modeling and sampling scope of work. The text following the table provides a narrative description of the scope of work.

Table A6.1 - Project Schedule and Timeline

Task	Deliverable	Timeline
Develop Quality Assurance Project Plan (QAPP)	Approved QAPP	July 15, 2016- July 15, 2016
Collect and Analyze Data	Collection of field data in accordance with approved QAPP	July 15, 2016 – August 2016
Measure and Document Results	Modeling of anticipated load reduction from green infrastructure BMPs	February 2017
Final Reports	Final Report	May 31, 2017

Develop a QAPP: The overall grant project includes water quality modeling and sampling and, therefore, involves environmental data operations. All environmental data operations will strictly adhere to the method set forth in this QAPP. The NEIWPCC Quality Management Plan requires that quality assurance project plans are developed and approved for all projects involving environmental data operations (i.e., collection, analysis, and/or manipulation of environmental data). The timeline in Table A6.1 assumes 60 days for the development of the QAPP and 90 days for the review and approval of the QAPP by NEIWPCC and U.S. EPA QA officers and up to 60 days to complete revisions that may be needed for approval.

Collect and Analyze Data: This project will make use of existing in-pond water quality data from URI Watershed Watch (collected and analyzed under the EPA-approved URIWW Ambient Field Assays QAPP and the URIWW Analytical Lab QAPP) and the RIDEM Office of Water Resources (EPA-approved RIDEM TMDL 2007). Additional water quality data will also be collected to characterize phosphorus loading from shoreline runoff, three select stormwater outfalls, sediments (internal loading), and waterfowl (See Appendix B, which provides a detailed description of ESS field sampling methods to be used).

Measure and Document Results: We will measure water quality benefits for nutrient and pathogen load reduction using the Simple Method as defined in the 2015 *Rhode Island Stormwater Design and Installation Manual*. (See Appendix A, which provides a detailed description of the method to be used.)

The Simple Method was selected for this project because it can efficiently simulate pollutant loadings of nutrients, total suspended solids (TSS), and pathogens associated with stormwater runoff. The Simple Method also provides the ability to model pollutant removals associated with best management practices in urbanized settings and to develop relative cost-benefit analysis of BMPs using an Excel spreadsheet. This method was previously accepted by NEIWPCC and EPA as part of QAPP that was developed for a similar project for West Warwick, Rhode Island. A cost opinion will be developed based on the updated design using standard engineering costing methods.

Final Reporting: We will develop a project final grant report in accordance with NEIWPCC grant guidance, which will include the field sampling results, modeling results, and a description of QAPP process.

A7 Quality Objectives and Criteria

Field collection procedures focus on collecting accurate water quality data including shoreline runoff, stormwater outfall, internal loading, and waterfowl survey data at Brickyard Pond. Quality control requirements are the system of technical activities that measure the performance of a process and will be utilized for field and laboratory analysis. A summary of quality controls to be utilized in the present study is provided in the following section. Collection procedures and measurement criteria can be found in the applicable ESS SOGs (Appendix B).

In-Pond Water Quality Sampling

By ensuring that the field sampling plan is followed, proper sampling techniques are used, and proper analytical procedures are followed, and that sample hold times are not exceeded, ESS will be certain to collect and report data that are representative of actual in-pond water quality conditions.

Stormwater and Shoreline Runoff Sampling

By ensuring that the field sampling plan is followed, proper sampling techniques are used, and proper analytical procedures are followed, ESS will be certain to collect and report data that are representative of actual stormwater and shoreline runoff conditions.

Sediment Sampling

By ensuring that the field sampling plan is followed, proper sampling techniques are used, proper analytical procedures are followed, and that sample holding times are not exceeded, ESS will be certain to collect and report data that are representative of actual sediment conditions.

Waterfowl Survey

Waterfowl identification and counts will only be conducted by qualified observers. A minimum of two observers should conduct each survey together and record data independently. Survey counts can then be checked against each other and against photographs from the field for accuracy.

Laboratory Analyses

Laboratory analysis procedures focus on measuring water samples for total and soluble phosphorus, total nitrogen (TKN, Nitrate/Nitrite), TSS, key metals (iron and aluminum), and alkalinity and total phosphorus, total nitrogen, and key metals (iron and aluminum) for sediment samples. Alpha Analytical Laboratory of Westborough, Massachusetts will conduct the laboratory analysis required under this project. The accuracy, precision, and sensitivity of laboratory analytical data are critical to achieving the QC acceptance criteria of the analytical protocols. With respect to parameters tested in the laboratory, QC requirements will be implemented according to Alpha Analytical SOPs (Appendix D).

Modeling

The modeling procedure focuses on estimating relative nutrient contributions from the Brickyard Pond watershed and on modeling green infrastructure BMPs that could result in substantial and cost-effective nutrient load reduction. Substantial and cost-effective nutrient load reduction, for purposes of this project, means BMPs that are anticipated to have a removal efficiency of 50% or more for phosphorus.

We will run the model for the 1.2-inch, Type III, 24-hour wet-weather event, which is anticipated to generate one inch of runoff using the predictive methods of the Natural Resource Conservation Service's *Urban Hydrology for Small Watersheds* (TR-55). This is also known as the water quality event since it is the statistical 24-hour storm that generates runoff equal to the water quality volume. The primary goal of the model is to evaluate the relative cost effectiveness of various BMPs in reducing pollutant loads while targeting specific pollutant sources. Appendix A provides a thorough description of the modeling approach, data to be used and parameters. Generally speaking, input and output data include the parameters listed in Table A7.1.

Table A7.1 - Simple Method Model Input and Output Data

Input	Data Source	Data Range	Output
Annual Rainfall (inches/year)	Figure H-8, RISWM[a]	45 – 47 inches/year[b]	Total phosphorus pre and post implementation (lbs/year)
Mean Pollutant Contributions in Runoff (mg/l)	Table H-2, RISWM	1.74 – 2.1 mg/l	
Impervious Area (acres)	RIGIS Impervious Surface Coverage	Commonly 1 – 50 acres	
Drainage Area (acres)	LiDAR and topographic contours	Commonly 5 – 100 acres	
Percent Impervious	Calculated (divide impervious area by drainage area)	10 – 70%	
Pollutant Removal Rate of BMPs	Table H-3, RISWM	30% – 65%	

Notes:

a. "RISWM" means the 2015 *Rhode Island Stormwater Design and Installation Standards Manual*.
b. The Simple Method Model is run on annual rainfall data as provided in the RISWM. Since the purpose of the modeling for this project is to determine the relative effectiveness of BMPs for cost-benefit, updating the annual rainfall will not substantively affect outcome.

A8 Special Training Requirements/Certification

This field sampling effort requires experience in water quality, sediment sampling, and avian field surveys. Technicians have received prior training in limnological field methods, including water quality and sediment sampling, as well as wildlife field survey methods from previous academic study, routine participation at conferences on the subject of lake management, as well as during informal ESS in-house training associated with a variety of similar projects throughout New England. The appropriate ESS SOGs provided in Appendix B will be used to guide the field data collection process. The ESS QA Officer will ensure that all technicians employed for this project will be properly trained.

This modeling effort requires proficient knowledge, experience and understanding of the pollutant loading/land use interactions and receiving-water-response dynamics to phosphorus inputs. The scientists overseeing the modeling calculations and the related water quality interpretations of findings are experienced senior level scientists having 20 or more years of experience in surface water impact analysis, pollutant loading and water quality investigations. The appropriate user guides and manuals provided with the models described in Section A6 will be used to guide the modeling process.

A9 Documentation and Records

The field data, laboratory analysis results, modeling methods, assumptions and results will be presented in the final report for this project. Results will be presented in a tabular format as generated by use of an Excel spreadsheet with modeling algorithms. Upon conclusion of the project, NEIWPCC will retain its project files for three years following the close of the EPA funding agreement supporting the project. Spreadsheets and final report will be kept by ESS Group as part of the project files for three years. ESS Group electronic documents are backed up on a daily basis. The ESS Group Project Manager, James Riordan, will be responsible for maintenance and distribution of the approved QAPP and updates to it. These will be provided electronically as needed. No other modeling documents are anticipated.

SECTION B: MEASUREMENT AND DATA ACQUISITION

B1 Sampling Process Design

Water quality data will be collected directly as part of this study to support a more precise identification of sources and annualized loads. Specifically, water quality data will be collected to characterize phosphorus loading from shoreline runoff, select stormwater outfalls, internal loading, and waterfowl.

Shoreline Runoff

Field reconnaissance will be completed along the shorelines of the pond to document and map specific areas of erosion. ESS will then coordinate with the Town to select three priority sampling locations based on the field reconnaissance for one round of shoreline runoff data collection. The selected sampling locations will be targeted for direct measurement of water quality from sheet or rill flows during runoff (wet-weather) conditions, when eroded soils and nutrients are most likely to be mobilized into the pond.

Stormwater Outfalls

ESS will collect wet-weather samples from three stormwater outfalls known to discharge into Brickyard Pond (Figure B1-1). The outfalls will be selected in consultation with the Town prior to wet-weather sampling based on available GIS and field data.

Internal Loading

Internal loading of phosphorus will also be assessed using in-pond water quality profiles and sediment sampling. Two in-pond water quality profile surveys will be conducted at the deep hole (Figure B1.1) during summer water column stratification to measure the extent and duration of anoxia (oxygen poor-conditions) in the water column. Additionally, three sediment samples will be collected from the pond bottom during one of the water quality profile surveys. The locations of the sediment samples will depend on the results of the in-pond water quality profile measurements and will correspond to areas of the pond with most severe anoxia, as internal nutrient cycling is most likely to be problematic under these conditions.

Waterfowl Survey

Waterfowl phosphorus inputs will be assessed, with a primary focus on nuisance resident species, including Canada Goose and Mute Swan. Field surveys will be conducted twice, once during nesting in the spring of 2017 (March to May) and once during fledging in the summer of 2016 (June to August), to estimate the size of resident populations, identify potential nesting sites, and assess annual recruitment levels.

ess group
environmental consulting & engineering services

Brickyard Pond
Phosphorus Reduction Analysis
Barrington, Rhode Island

1 inch = 450 feet
Source: 1) RIGIS, Roads, 2010
2) Adapted from RIDEM, Bathymetry, Undated

Legend
3-foot Bathymetric Contours
In-pond Sampling Location

Bathymetry and Proposed In-pond Sampling

Figure B1.1

B2 Sampling Methods

All sampling will be conducted in accordance with ESS SOGs (see Appendix B for specifics). ESS employs the use of SOGs in Appendix B for all projects dealing with water analysis and collection; therefore they are fully vetted.

Shoreline Runoff

Three unattended samplers will be temporarily installed in the selected locations just prior to a runoff-generating storm event. Following the storm, ESS will collect the samplers and transfer the water into approved laboratory bottles. The samples will be submitted to Alpha Analytical Laboratory for analysis. Laboratory analysis will include total and soluble phosphorus, total nitrogen (TKN, Nitrate/Nitrite), and TSS. Please refer to the sampler specification sheet in Appendix B.

Stormwater Outfalls

ESS will collect wet-weather water samples from three stormwater outfalls that discharge into the pond. Samples will be collected in approved laboratory bottles. The samples will be submitted to Alpha Analytical Laboratory for analysis. Laboratory analysis will include total and soluble phosphorus, total nitrogen (TKN, Nitrate/Nitrite), and TSS. Additionally, ESS will record approximate discharge rate, temperature, specific conductance, and pH at each outfall. Please refer to associated ESS SOGs in Appendix B.

Internal Loading

Temperature, dissolved oxygen, specific conductance will be measured and recorded from the surface to the bottom of the pond at one-meter increments. Secchi disk transparency, a measure of water clarity, will also be obtained at this time. Surface and bottom water samples will be collected in approved laboratory bottles. Sediment samples will be taken from the bottom of the pond and collected in approved laboratory bottles. The samples will be submitted to Alpha Analytical Laboratory. Laboratory analysis will include total and soluble phosphorus, total nitrogen (TKN, Nitrate/Nitrite), key metals (iron and aluminum), and alkalinity for water samples and total phosphorus, total nitrogen (TKN, Nitrate/Nitrite), and key metals (iron and aluminum) for sediment samples. Please refer to associated ESS SOGs in Appendix B.

Waterfowl Survey

Waterfowl surveys will be conducted by foot and by boat using visual observations. Samplers in the boat will survey the entire perimeter of the pond and will also include the perimeters of any islands. The locations of waterfowl will be recorded on a handheld GPS. Species type (goose or swan), age classes (adult, juvenile, or fledgling), and total numbers will be recorded for each siting location. Potential nesting locations will also be recorded via handheld GPS. Please refer to associated ESS SOGs in Appendix B.

B3 Sampling Handling and Custody

All water quality measurements including discharge rate, temperature, specific conductance, pH, and water clarity will be recorded in a field notebook or on field data sheets for each sampling event. Additionally, waterfowl counts and observations will be recorded in a field notebook or on field data sheets for each survey event. ESS field technicians will scan and save field notes and data sheets to the ESS project folder after each field day. Data will be transcribed into a Microsoft Excel spreadsheet for analysis and reporting.

Sample bottles will be provided by Alpha Analytical Laboratory. All samples will be labeled with date and time, project identifier, sample location, analytes needed, and technician's initials. Chain of custody forms are provided by the laboratories and completed by ESS technicians in the field. An example of the chain of custody form can be found in Appendix C.

Hold times and methods for each laboratory analysis are listed below in Table B3.1 for solid samples and Table B3.2 for aqueous samples. Soluble phosphorus must be filtered by Alpha Analytical Laboratory staff within 24 hours of collection. ESS field technicians will store the samples on ice until arrival at Alpha Analytical Laboratory. Either an ESS field technician or an Alpha Analytical courier will pick up the samples and return to the Alpha Analytical Laboratory within the 24 hour window.

Table B3.1 - Laboratory Soil/Sediment/Solid Sample Reference Guide (Alpha Analytical)

Parameter	Sample Matrix	Volume Needed	Sample Container	Sample Preservation	Maximum Hold Time	Method
TKN	Sediment	4 oz	Glass	Ice (4°C)	28 Days	SM4500N_{org}-C
Nitrate/Nitrite	Sediment	4 oz	Glass	Ice (4°C)	28 Days	SM4500N_{org}-C
Phosphorous, Total	Sediment	8 oz	Glass	Ice (4°C)	28 Days	4500P-E
Aluminum, Total	Sediment	2 oz	Glass	Ice (4°C)	180 Days	6010C
Iron, Total	Sediment	2 oz	Glass	Ice (4°C)	180 Days	6010C

Table B3.2 - Laboratory Aqueous Sample Reference Guide (Alpha Analytical)

Parameter	Sample Matrix	Volume Needed	Sample Container	Sample Preservation	Maximum Hold Time	Method
Nitrogen, Total Kjeldahl	Surface Water	500mL	Plastic	H_2SO_4 Ice (4°C)	28 Days	4500N-C
Nitrogen, Nitrate/Nitrite	Surface Water	250mL	Plastic	H_2SO_4 Ice (4°C)	28 Days	4500NO3-F
Phosphorous, Soluble	Surface Water	500mL	Plastic	H_2SO_4 Ice (4°C)	28 Days	4500P-E
Phosphorous, Total	Surface Water	500mL	Plastic	H_2SO_4 Ice (4°C)	28 Days	4500P-E
Solids, Total Suspended (TSS)	Surface Water	950mL	Plastic	Ice (4°C)	7 Days	2540D
Alkalinity, Total	Surface Water	250mL	Plastic	Ice (4°C)	14 Days`	2320B
Aluminum, Total	Surface Water	500mL	Plastic	HNO_3 Ice (4°C)	180 Days	6010C
Iron, Total	Surface Water	500mL	Plastic	HNO_3 Ice (4°C)	180 Days	6010C

B4 Analytical Methods

All field sampling will follow a streamlined approach comparable to that outlined in the appropriate SOGs (Appendix B).

Water and sediment samples will be collected in the field by ESS personnel using the appropriate containers and preserved as required by the laboratory method.

Physical and chemical water quality parameters to be tested by ESS personnel in the field will include the following: discharge rate, pH, specific conductance, turbidity, dissolved oxygen, water clarity (secchi disk transparency), and temperature.

Table B4.1 summarizes the parameters to be measured in the field with respective EPA methods. Specific conductance, dissolved oxygen, temperature, pH, and water clarity (secchi disk transparency) will be measured directly in the water column. Turbidity samples will be collected in an instrument-specific container and measured immediately in the field.

Table B4.1 Description of Field-measured Water Quality Parameters, Including Precision and Accuracy

Parameter	Specific Conductance	Dissolved Oxygen	Turbidity	pH	Water Clarity (Secchi)	Temperature
Sample Matrix	Water	Water	Water	Water	Water	Water
Number of Sampling Locations*	1	1	1	1	1	1
Sample Container	Instrument	Instrument	Glass Cuvette	Instrument	Instrument	Instrument
Hold Time	In Field	In Field	In Field	In Field	In Field	In Field
Expected Range of Field Measurements	0 to 1,000 µS/cm	0 to 15 mg/L 0 to 150 % saturation	0 to 100 NTU	4 - 10 SU	0 – 10 m	-2 to 30 ^{o}C
Precision	0.1 µS/cm	0.01 mg/L and % saturation	0.01 NTU	0.1 SU	0.25 m	0.1 ^{o}C
Accuracy	± 2 % reading or 1.0 µS/cm, whichever is greater	± 2 % of the reading or ± 0.2 mg/L, whichever is greater	± 2 %	± 0.1 SU	+ 10% of the reading, subject to individual depth perception	± 0.3 ^{o}C

*Does not include field duplicates

Water samples will be analyzed by Alpha Analytical Laboratory for alkalinity, metals (iron and aluminum), total nitrogen (TKN, Nitrate/Nitrite), soluble phosphorus, total phosphorus, and TSS. Sediment samples will be analyzed by Alpha Analytical Laboratory for metals (iron and aluminum), total nitrogen (TKN, Nitrate/Nitrite), and total phosphorus. SOPs from Alpha Analytical for all analyses and methods are provided in Appendix D. See Table B3.1 and Table B3.2 above for a list of analytical methods for each parameter.

B5 Quality ControlDue to the sensitive nature of measuring physical and chemical parameters in water and sediment samples, quality control is important. Duplicate measurements will be collected in the field at a 5% rate and should agree within 10% for QC purposes. In general, if a discrepancy of greater than 10% is observed between the sample and its duplicate, the piece of equipment will be recalibrated and the sample will be reassessed. See SOGs in Appendix B for more information on field measurement QC.

Quality control and equipment testing and maintenance measures are taken for all laboratory analyses. The measures taken are described in detail in the Alpha Analytical SOPs provided in Appendix D.

B6 Instrument/Equipment Testing, Inspection and Maintenance

Due to the sensitive nature of the samples collected as part of this project, measures are taken for inspection and maintenance of laboratory equipment. The measures taken are described in more detail in the Alpha Analytical SOPs provided in Appendix D.

Field equipment is tested, inspected, and maintained in accordance with applicable ESS SOGs provided in Appendix B.

B7 Calibration and Frequency

Calibration of field instruments is completed in accordance with the manufacturer's recommendations for optimal function of the instrument and addressed in more detail in Appendix B. Given the short duration of water quality field measurement activities for this project, instruments will be calibrated, as needed, just prior to the water quality sampling event. No additional calibration of field instruments is anticipated.

Laboratory calibration methods are described in the Alpha Analytical SOPs provided in Appendix D. Calibrations are documented at the laboratory.

Calibration for the study area will be completed as part of the initial setup of the model as discussed in Appendix A. Model setup is limited to data input into a spreadsheet of such parameters as annual precipitation, study area land use, and study area size. The Simple Model is not available commercially and formulae to run the model will need to be entered manually. We will confirm that the model is working by running the example data provided in Appendix A. The model will be run on a personal computer with Excel spreadsheet software. Initiating and running the model will require no other special tools, instruments, or certified equipment.

It is recognized that the algorithms used to develop this model are relatively simplistic and provide a somewhat limited representation of actual loading and reduction. However, sampling is being conducted as well and can be used to verify the results.

B8 Inspection/Acceptance for Supplies and Consumables

All bottles will be supplied by Alpha Analytical Laboratory. The field technician will be responsible for checking that all bottles are in acceptable conditions (i.e., closing and opening properly, tight seal, no holes). All bottles are stored on ice in coolers until arrival at the laboratory.

B9 Non-Direct Measurements (Data Acquisition Requirements)

This project will use existing in-pond water quality data from URI Watershed Watch (collected and analyzed under the EPA approved URIWW Ambient Field Assays QAPP and the URIWW Analytical Lab QAPP) and the RIDEM Office of Water Resources (EPA approved RIDEM TMDL 2007).

This project will use GIS data layers from RIGIS, the Town of Barrington, and ESS Group including watershed boundary, land use, soil type, hydrology, roads, drainage layers, topography, LiDAR, and orthophotos. Data collected during this project will be used to determine effectiveness of BMP designs, prioritize sites for future BMP implementation and used for comparison with future water quality monitoring efforts.

The algorithms used to develop this model are relatively simplistic and provide a somewhat limited representation of loading and reduction that may occur in the field. Also, the literature values used are based on other watersheds and may not reliably depict the subject watershed. However, these limitations are balanced by the simplicity of the model's implementation.

B10 Data Management and Hardware/Software Configuration

Data collected by field technicians for this study will be documented and discussed in the final report. Additionally, data collected by the Contractor Lead Modeler and used in the modeling process will be documented in the final report. All data will be kept by ESS Group as computer files for three years and will be available to the Town of Barrington, NEIWPCC, and USEPA upon request. ESS will store the data on its computer network in the format that it is in when it is collected. Files on the network are stored by project, exclusively, under a folder named by the project number and project name. Data collected will be stored in the "resources" subfolder of the project folder.

SECTION C: ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

The QA Officer will provide oversight for each field data collection effort to ensure that protocols described in this QAPP are being followed. This duty includes ensuring that field equipment is properly calibrated, data are recorded in a consistent manner, and samples arrive at the laboratory in a timely fashion.

The Project Manager will review the final report to ensure that appropriate methodology is adhered to and reported data is within the accepted range for each parameter. Any "outlier" data discovered will be identified in the final report, and potential sources of error will be described.

Modeling runs will be reviewed by the Contractor Project Manager for quality assurance regarding the model input and output and particularly to ensure that the model output reasonably reflects existing conditions or the expected results in evaluating various BMP measures. The Contractor Lead Modeler will be responsible for data entry. The Project Manager will review the data entry and computations, by checking each data cell. The Project Manager will use a calculator to manually check the accuracy of computed data. Final model summary sheets will be reviewed by the project QA Officer prior to distribution to the QAPP project team. Also, as laboratory results become available the Contractor Project Manager will assess all samples for completeness and accuracy of result. Laboratory results will be assessed by reviewing the reports generated by the laboratories.

NEIWPCC may implement, at their discretion, various audits or reviews of this project to assess conformance and compliance to the quality assurance project plan in accordance with the NEIWPCC Quality Management Plan.

The Project Manager will consult with the QA Manager to include a description of QA activities, any QA issues noted, and corrective actions taken in quarterly reports, to be reviewed by the NEIWPCC Program Manager.

C2 Reports to Management

The project status and preliminary results will be presented as part of quarterly reporting, which will be developed by ESS Group and the Town. Baseline and preliminary modeling results will be presented on or before December 2016 (or as part of the quarterly report following QAPP approval). Also included will be results from the water and sediment samples. If corrective actions are needed they will be addressed as part of the Final Project Plan. If uncertainties arise in the input or output data, related decisions will be made by the Town, in consultation with the key project participants. The Final Project Plan is scheduled for completion in March 2017.

SECTION D: DATA VALIDATION AND USABILITY

D1 Departures from Validation Criteria

The modeling results will be reviewed by the Contractor Project Manager for completeness and reasonableness based on best professional judgement and review of spreadsheet calculations. Both the Contractor Project Manager and Contractor QA Officer will review the water quality, biological, and sediment sample results for completeness and reasonableness based on best professional judgement and review of laboratory results.

D2 Validation Methods

As described above in section C1, modeling runs will be reviewed by the Contractor Project Manager for quality assurance regarding the model input and output and particularly to ensure that the model output reasonably reflects existing conditions or the expected results in evaluating various BMP measures. As described in B7, we will confirm that the model is working by running the example data provided in Appendix A of this QAPP. The model will be run on a personal computer with Excel spreadsheet software. There is no anticipated need for data validation software for this project. Final model summary sheets will be reviewed by ESS Group's QA Officer and provided as part of the final project report. The ESS Group Project Manager, James Riordan, will be responsible for distribution of the report electronically to the distribution list.

As described above in section C1, laboratory data and field data entries will be reviewed by the Contractor Project Manager for quality assurance regarding completeness of data generated as well as accuracy. As discussed in B6 extensive measures are taken by the laboratory to ensure that the results are as representative of the actual conditions as possible.

Success of the project will be measured in nutrient pollution reduction. Because there is both pre and post BMP implementation monitoring the success of the project will be easily assessed.

D3 Reconciliation with User Requirements

The quarterly reports will be the mechanism by which data users will be able to have input on the results. In compiling the reports, ESS Group will assess anomalies or departures from assumptions. The modeling design is quite simple. The eventual use of the data will document the success of the implementation of BMPs at Brickyard Pond which will be discussed in the final report. Additionally, any remaining data uncertainty or limitation on the use of project data will be document in the final report.

Appendix A
Rhode Island Stormwater Design and Installation Standards Manual
Pollutant Loading Analysis (Simple Method)

Appendix B
ESS Standard Operating Guidelines

Included:

- Conductivity SOG
- Dissolved Oxygen SOG
- Flow Rate SOG
- pH SOG
- Secchi Disc SOG
- Sediment Collection SOG
- Surface Water SOG
- Temperature SOG
- Waterfowl Survey SOG
- Wet Weather Sampling SOG
- Shoreline Runoff GKY First-Flush Sampler Specification Sheet

Appendix C
Chain of Custody Example and Instructions
(Alpha Analytical Laboratory)

Appendix D
Alpha Analytical Laboratory Standard Operating Procedures
Aqueous Samples and Solid Samples

Included:

- Alkalinity, Titration Method (Wet Chemistry)
- Hot Block Digestion for Aqueous Samples (Metals Digestion)
- Inductively Coupled Plasma – Atomic Emission Spectrometry (Metals Analysis)
- Nitrate, Nitrite and Nitrate/Nitrite Nitrogen (Wet Chemistry)
- Total Phosphorous, Dissolved Phosphorus- Colorimetric, Combined Reagent (Wet Chemistry)
- Acid Digestion of Sediments, Sludges, and Soils (Metals Digestion)
- Nitrogen, Total Kjeldahl (Wet Chemistry)
- Total Solids in Solid and Semisolid Samples- Percent Solids (Wet Chemistry)
- Total Suspended Solids Dried at 103-105°C and Total Volatile Suspended Solids Dried at 500°C (Wet Chemistry)

H.3 POLLUTANT LOADING ANALYSES

H.3.1 Introduction

On a case by case basis, the permitting agency may require applicants to document that a particular project does not unduly contribute to, or cause, water resource degradation (generally for sensitive resource areas or where an elevated concern for water quality exists) or to document a reduction in pollutant load (generally, as a consequence of a TMDL requirement). In these cases, applicants may be required to calculate potential stormwater pollutant loadings for projects for pre-development and post-development conditions.

When such an analysis is required of the applicant, the Simple Method (Schueler, 1987) can be used to demonstrate urban stormwater pollutant loadings. The Simple Method requires estimates of annual rainfall, site percent impervious cover, land use type, and pollutant loading coefficients based on land use.

For a more detailed description of this method refer to Controlling Urban Runoff: A practical manual for planning and designing urban BMPs (Schueler, 1987). Table H-2 provides event mean concentrations (EMCs) in milligrams per liter (mg/L) for typical pollutants of concern associated with stormwater runoff (# col/100ml for bacteria). There may be an interest in calculating the loading rates of other pollutants not listed in this table. If this is necessary, an applicant shall use EMC data from a reliable source, as approved by the permitting agency, based on the land use category. These EMCs must be documented by scientific studies and referenced by the applicant.

The method outlined in this section is most often applied to calculating loadings to surface water bodies. Other pollutant loading methods may be acceptable, provided the applicant submits the methodology and data used along with the reasoning for the chosen method. All information supplied by the applicant will be reviewed by the permitting agency to determine the relevance of the model to the situation.

H.3.2 Overview of the Simple Method

Stormwater pollutant export load (L, in pounds or billion colonies) from a development site can be determined by solving the following equation:

(Eq 1.) $L = [(P)(Pj)(Rv)/12](C)(A)(2.72)$

Where:

P = rainfall depth (inches)
Pj = rainfall correction factor
Rv = runoff coefficient expressing the fraction of rainfall converted to runoff
C = flow-weighted mean concentration of the pollutant in urban runoff (mg/L)
A = contributing drainage area of development site (acres)
12, and 2.72 are unit conversion factors

For bacteria, the conversion factor is modified, so the loading equation is:

(Eq 1a.) $L = 1.03(10^{-3})[(P)(Pj)(Rv)](C')(A)$

Where:

P = rainfall depth (inches)
Pj = rainfall correction factor
Rv = runoff coefficient expressing the fraction of rainfall converted to runoff
C' = flow-weighted mean bacteria concentration (#col/100 ml)
A = contributing drainage area of development site (acres)
1.03 is a unit conversion factor

Table H-2 Median EMC Values for Differing Land Use Categories

Pollutant (mg/l)	Land Use Category				
	Residential	Commercial	Industrial	Highways	Undeveloped/Rural[3]
TSS	100[1]	75[1]	120[1]	150[1]	51
TP	0.3	0.2	0.25	0.25	0.11
TN	2.1	2.1	2.1	2.3	1.74
Cu	.005	.096	.002	.001	-
Pb	.012	.018	.026	.035	-
Zn	.073	.059	.112	.051	-
BOD	9.0	11.0	9.0	8.0	3.0
COD	54.5	58.0	58.6	100.0	27.0
Bacteria*	7000	4600	2400	1700	300

Sources:

1 Caraco (2001); default values from Watershed Treatment Model, from several individual assessments

2 (shaded) Maestre and Pitt (2005); National Stormwater Quality Database, v 1.1

3 CDM (2004) Merrimack River Watershed Assessment Study, Screening Level Model

* Bacteria concentration in #col/100 ml.

P (depth of rainfall)

The value of P selected depends on the time interval over which loading estimates are necessary (usually annual rainfall – See Figure H-8).

Appropriate annual rainfall values for a site specific location can be interpolated from Figure H-8 or obtained from the Northeast Regional Climate Center. If a load estimate is desired for a specific design storm (e.g., 10-year 24-hour, Type III storm), the user can supply the relevant value of P derived from Table 3-1. Caution is required as EMCs vary as a function of rainfall amount and intensity and those presented in Table H-2 are median values from a range of storms more representative of long-term loading. If a load is desired from a larger storm such as the 10-year, 24 hour, Type III storm, applicants shall provide appropriate documentation of the source of the EMC used. All rainfall data used in the analysis must be applicable to site location and referenced for review.

Pj (correction factor)
Use a value of 0.9 for Pj. This represents the percentage of annual rainfall that produces runoff. When solving the equation for individual storms, a value of 1.0 should be used for Pj.

Rv (runoff coefficient)
Rv is the measure of site response to rainfall events and is calculated as:

(Eq 2.) $Rv = r/p$

Where:
r = storm runoff (inches)
p = storm rainfall (inches)

The Rv for a site depends on soil type, topography, and vegetative cover. However, for annual pollutant loading assessments, the primary influence on Rv is the degree of watershed imperviousness. The following equation has been empirically derived from the Nationwide Urban Runoff Program studies (USEPA, 1983) and is used to establish a value for Rv.

(Eq 3.) $Rv = 0.05 + 0.009(\%I)$

Where:
%I = the percent of site imperviousness

A value for I can be calculated by summing the areas of all impervious surfaces (e.g., buildings, driveways, roads, parking lots, sidewalks, etc.) and dividing this area by the total contributing drainage area. If more than one land use is present at the site, divide the impervious portion of each land use by its respective total area.

A (drainage area)
The total contributing drainage area (acres) can be obtained from site plans.

C (pollutant concentration)
Choose the appropriate value of C from Table H-2.

Sample calculations:

A 30-acre undeveloped parcel is to be developed into a residential subdivision with the remaining 10 acres converted to a commercial plaza. Assume the commercial land use area has impervious surfaces covering 85% of the area, while the residential subdivision has 35% impervious surfaces. Also assume the entire 30-acre site has all drainage directed to one outlet (into a coastal pond). This site is located in an area that receives approximately 45 inches of precipitation per year, say Providence. What would be the potential annual loading rate of total nitrogen (TN) to the coastal salt pond from this site without the installation of onsite BMPs; compare pre- and post-development scenarios.

Pre-development conditions

Undeveloped site: (Eq.3) Rv = 0.05 + 0.009(%I) = 0.05 + 0.009(0) = 0.05

(Eq.1) L = [(P)(Pj)(Rv)/(12)](C)(A)(2.72); from Table H-2, C = 1.74 mg/l

L = [(45)(0.9)(0.05)/12](1.74)(30)2.72 = ***24.0 lbs TN/year***

Post-development conditions

Residential: (Eq.3) Rv = 0.05 + 0.009(%I) = 0.05 + 0.009(35) = 0.365

(Eq.1) L = [(P)(Pj)(Rv)/(12)](C)(A)(2.72); from Table H-2, C = 2.1 mg/l

L = [(45)(0.9)(0.365)/12](2.1)(20)2.72 = ***140.7 lbs TN/year***

Commercial: (Eq.3) Rv = 0.05 + 0.009(%I) = 0.05 + 0.009(85) = 0.815

(Eq. 1) L = [(P)(Pj)(Rv)/(12)](C)(A)(2.72); from Table H-2, C = 2.1 mg/l

L = [(45)(0.9)(0.815)/12](2.1)(10)2.72 = ***157.1 lbs TN/year***

Total annual nitrogen loading from the developed site = 140.7 + 157.1 = ***297.8 lbs TN/year***

Conclusion: Development of the site results in a net increase of 273.8 lbs of nitrogen (297.8 – 24.0) into the coastal salt pond per year.

Now evaluate the same example except for Bacteria:

Pre-development conditions

Undeveloped site: (Eq.3) Rv = 0.05 + 0.009(%I) = 0.05 + 0.009(0) = 0.05

(Eq 1a.) $L = 1.03(10^{-3})[(P)(Pj)(Rv)](C')(A))$; from Table H-2, C' = 300 col/100 ml

L = [1.03(10^{-3})(45)(0.9)(0.05)](300)(30) = ***18.8 Billion Colonies/year***

Post-development conditions

Residential: (Eq.3) Rv = 0.05 + 0.009(%I) = 0.05 + 0.009(35) = 0.365

(Eq 1a.) $L = 1.03(10^{-3})[(P)(Pj)(Rv)](C')(A))$; from Table H-2, C' = 7,000 col/100 ml

L = [1.03(10^{-3})(45)(0.9)(0.365)](7,000)(20) = ***2,131.6 Billion Colonies/year***

Commercial: (Eq.3) Rv = 0.05 + 0.009(%I) = 0.05 + 0.009(85) = 0.815

(Eq 1a.) L = 1.03(10^{-3})[(P)(Pj)(Rv)](C')(A)); from Table H-2, C' = 4,600 col/100 ml

L = [1.03(10^{-3})(45)(0.9)(0.815)](4,600)(10) = ***1,563.9 Billion Colonies/year***

Total annual bacteria loading from the developed site = 2,131.6 + 1563.9 = ***3,695.5 Billion Colonies/year***

Conclusion: Development of the site results in a net increase of ***3,676.7 Billion Colonies/year*** *(3695.5 – 18.8) into the coastal salt pond per year.*

Applicants will frequently need to evaluate the potential pollutant removal effectiveness of stormwater practices when conducting a pollutant loading analysis. To do this, applicants can use the rated pollutant removal effectiveness as listed in Tables H-3 and H-4 as a basis of estimating pollutant removal. These values have been derived from a variety of sources based on actual monitoring data and modified, where appropriate, to reflect the specific design and sizing criteria contained in Chapters Five, Six, and Seven.

In some cases, the pollutant removal rating values use median values from prior monitoring studies when the studies included a significant number of facilities of similar design criteria as those required in this manual. In other cases, the 75th quartile values (or high end) are reported where it is recognized that the prior monitoring was of insufficient sample size or was of practices with design criteria not as robust as those required in this manual. Lastly, in many cases, there is insufficient prior monitoring of practices for some or all of the reported pollutants, but primary pollutant removal mechanisms are similar to other practices; thus, a removal value is assigned, based on general literature values and/or as a policy decision. In addition, most of the design criteria for water quality BMPs incorporate pre-treatment requirements, such as the requirement for a forebay or grass channel prior to infiltration. In these cases, the rated removal efficiency of the practice is for the total system. For example, the gravel WVTS has a rated TSS removal of 86%; this accounts for the TSS removal of both the required forebay and the gravel bed/permanent pool.

In general, where pollutant loading assessments are requested, applicants may use the rated removal values as a basis for estimating pollutant load. However, other pollutant removal estimates may be acceptable, provided the applicant submits the source of these estimates and data used. All information supplied by the applicant will be reviewed by the permitting agency to determine the relevance of the removal estimates to the situation.

Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs

Water Quality BMPs (those meeting Min. Std 3)		Median Pollutant Removal Efficiency (%)			
		TSS	TP	TN	Bacteria
WVTS	Shallow WVTS	85%[2]	48%[3]	30%[2]	60%[2]
	Gravel WVTS	86%[3]	53%[1]	55%[3]	85%[2]
Infiltration Practices	Infiltration Basin	90%[2]	65%[3]	65%[2]	95%[2]
	Infiltration Trench	90%[2]	65%[3]	65%[2]	95%[2]
	Subsurface Chambers	90%[2]	55%[2]	40%[2]	90%[2]
	Dry Well	90%[2]	55%[2]	40%[2]	90%[2]
	Permeable Paving	90%[1]	40%[1]	40%[2]	95%[2]
Filters	Sand Filter	86%[3]	59%[3]	32%[3]	70%[2]
	Organic Filter	90%[2]	65%[2]	50%[2]	70%[2]
	Bioretention	90%[1]	30%[2]	55%[2]	70%[2]
	Tree Filter	90%[1]	30%[2]	55%[2]	70%[2]
Green Roofs	Extensive	90%[4]	30%[4]	55%[4]	70%[4]
	Intensive	90%[4]	30%[4]	55%[4]	70%[4]
Open Channels	Dry Swale	90%[1]	30%[2]	55%[2]	70%[2,6]
	Wet Swale	85%[3]	48%[3]	30%[2]	60%[2]

Table H-4 BMP Pollutant Removal Rating Values for Other BMPs

Other BMPs		Median Pollutant Removal Efficiency (%)			
		TSS	TP	TN	Bacteria
Pretreatment BMPs	Grass Channel	70%[1,2]	24%[3]	40%[2]	NT
	Sediment Forebay	25%[4]	8%[5]	3%[5]	12%[5]
	Filter Strip	25%[4]	ND	ND	ND
	Deep Sump Catch Basin	25%[4]	NT	NT	NT
	Hydrodynamic Device	25%[1]	NT	NT	NT
	Oil and Grit Separator	25%[4]	NT	NT	NT
Storage BMPs	Dry Extended Detention Basin	50%[2]	20%[2]	25%[2]	35%[2]
	Wet Extended Detention Basin	80%[3]	52%[3]	31%[3]	70%[3]
	Underground Storage Vault[2]	20%[2]	15%[2]	5%[2]	25%[2]

"ND" Specifies No Data
"NT" Specifies No Treatment
References
1 (UNHSC, 2007b)
2 (CWP, 2007)
3 (Fraley-McNeal, et al., 2007)
4 (prescribed value based on general literature values and/or policy decision)
5 (50% of reported values of low end for extended detention basins)
6 Presumed equivalent to bioretention; will require diligent pollutant source control to manage pet wastes in residential areas

Estimating Pollutant Removal of BMPs

Using the rated efficiencies from Tables H-3 and H-4, applicants can reduce post-development loadings to receiving waters when BMPs are designed, installed, and maintained in accordance with the provisions of this manual.

Example Calculation

The 10-acre commercial project (annual TN load = 157.1 #) is designed to be managed by a gravel WVTS.

The load reduced by the BMP is: 157.1 (.55) = 86.4 lbs TN/year.

The net loading to the bay is: 157.1 – 86.4 = ***70.7 lbs TN/year****.*

Estimating Pollutant Removal of BMPs in Series

In some cases, applicants may have one or more BMPs installed in a series as a so-called "treatment train." In these cases, available research has shown that the pollutant removal efficiency of specific BMPs, for specific pollutants, is reduced for subsequent BMPs in the treatment train arrangement. As stormwater migrates through the treatment train, coarser-grained particles are preferentially removed by the prior BMP, leaving progressively finer particles for practices down the line. The result is that for pollutants associated with fine particulates, removal efficiency drops off significantly (e.g., TSS and TP, in particular).

To account for this phenomenon, a widely applied and generally accepted method has been to discount the rated removal efficiency of the second BMP by a factor of between 75% and 50%, with subsequent BMPs being reduced accordingly (see ARC, 2001).

The Georgia Manual Method applies BMP removals as follows:

- 100% of the rated TSS removal efficiency (E_{TSS}) to the first BMP
  - If E_{TSS} > 80% for the first BMP; E for the second BMP = 50% (regardless of the pollutant constituent).
  - IF E_{TSS} <80% for the first BMP; E for the second BMP = 75% (regardless of the pollutant constituent).
- For succeeding BMPs, E is applied at either 50% or 75% depending on the equivalent E_{TSS} for the preceding BMPs (regardless of the pollutant constituent).

This method does not apply to bacteria, where removal is more a function of die-off than settling/attenuation; thus, the full efficiency is applied to subsequent BMPs.

Example Calculation

Using the example from above, the 10-acre commercial site first drains through a grass channel (designed in accordance with the guidance in Chapter Six) prior to a gravel WVTS (designed in accordance with the guidance in Chapter Five).

Removal efficiencies:
Grass channel: E_{TSS} = 70%; E_{TN} = 40%
Gravel WVTS: E_{TSS} = 86%; E_{TN} = 55%

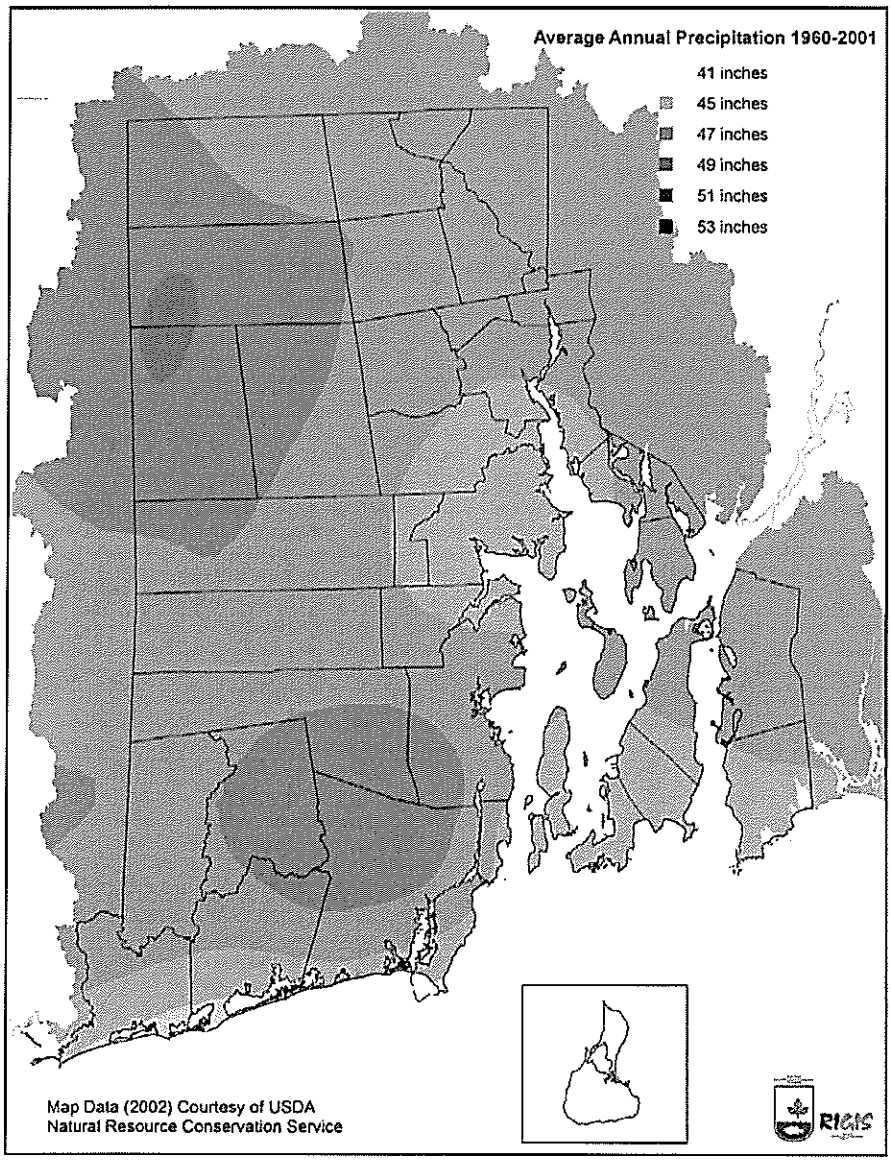
Since treatment train goes from grass channel to gravel WVTS, and E_{TSS} is <80% for the grass channel, reduce the rated TN removal of the second BMP by 25% (E_{TN} = 75% of the rated value). The new net loading reduction can be calculated:

Load reduced by grass channel: 157.1 (.40) = 62.8 lbs/yr;
remaining load = 157.1 – 62.8 = 94.3 lbs TN/year

Load reduced by gravel WVTS: 94.3 [(.75)(.55)] = 38.9 lbs/yr;

The net loading to the bay: 94.3 – 38.9 = ***55.4 lbs TN/year***

Figure H-8 Average Annual Precipitation Values for Rhode Island



H.4 TR-55 "SHORT-CUT" SIZING TECHNIQUE

This section presents a modified version of the TR-55 short-cut sizing approach. The method was modified by Harrington (1987), for applications where the peak discharge is very small compared with the uncontrolled discharge. This often occurs in the 1-year, 24-hour Type III detention sizing.

Using TR-55 guidance (NRCS, 1986), the unit peak discharge (q_u) can be determined based on the curve number and time of concentration. Knowing q_u and T (extended detention time), q_O/q_I (peak outflow discharge/peak inflow discharge) can be estimated from Figure 9.9.

Figure H-10 can also be used to estimate V_s/V_r. When q_O/q_I is <0.1 and off the graph, V_s/V_r can also be calculated using the following equation for Type II/III rainfall distributions:

$$V_s/V_r = 0.682 - 1.43\,(q_O/q_I) + 1.64\,(q_O/q_I)^2 - 0.804\,(q_O/q_I)^3$$

Where: V_s = required storage volume (acre-feet)
V_r = runoff volume (acre-feet)
q_O = peak outflow discharge (cfs)
q_I = peak inflow discharge (cfs)

Figure H-9 Detention Time vs. Discharge Ratios (Source: MDE, 2000)

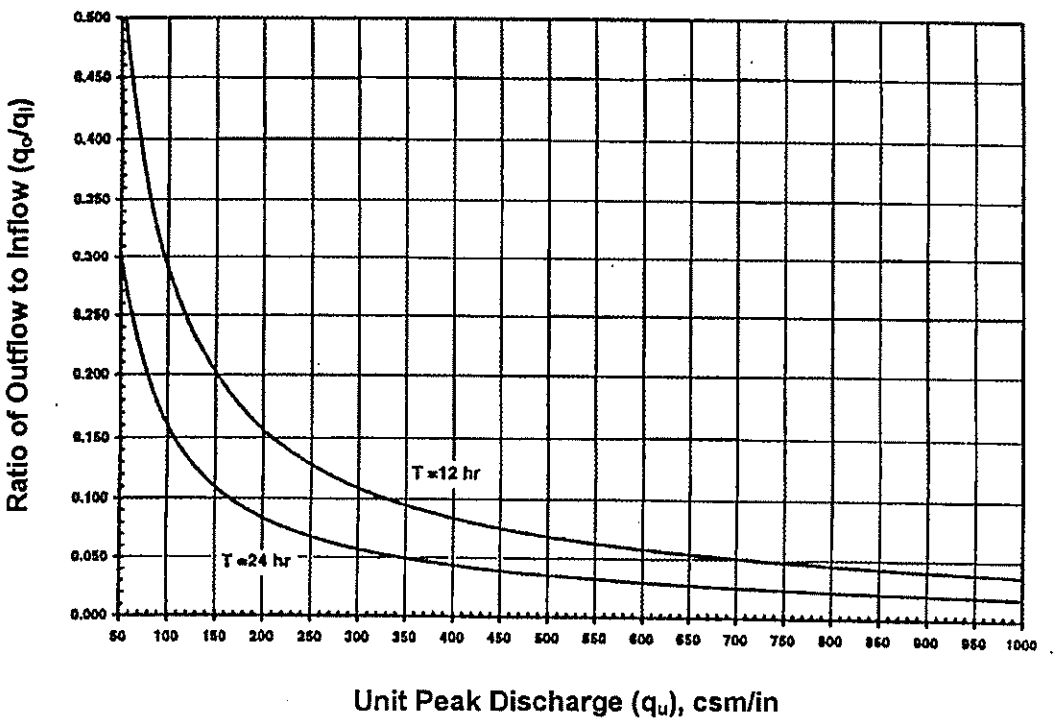
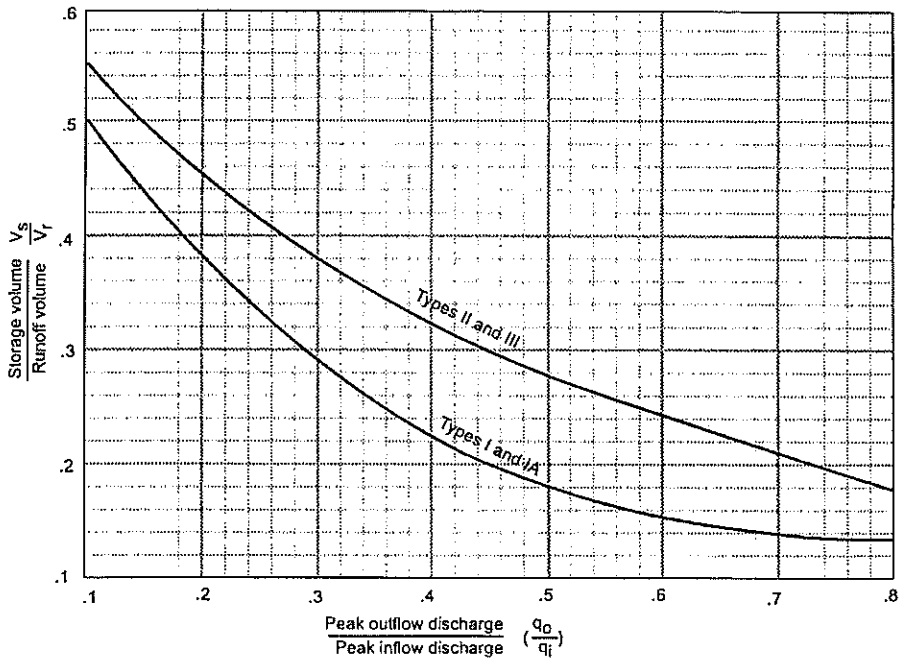


Figure H-10 Approximate Detention Basin Routing For Rainfall Types I, IA, II, and III. (Source: TR-55, 1986)



Example for calculating channel protection volume (CP_v):

For this example, the 1-year runoff from a hypothetical project in Providence County is 1.173 ac-ft = 51,096 ft^3, the composite CN for the project drainage area is 68, and the t_c is 15.1 minutes (0.25 hr).

Thus, the Initial abstraction (I_a) = 0.941, the 1-year precipitation (P) = 3.1"; I_a/P = 0.304.

From Exhibit 4-III of NRCS TR-55, read q_u = 450 csm/in (csm = cfs/mi^2). From Figure H-9, for T= 24 hours, read ratio of q_o/q_i = 0.04. Since q_o/q_i < 0.1 and off the graph shown in Figure H-10, use the equation provided above to find V_s/V_r where $V_s = CP_v$.

$$CP_v / V_r = 0.682 - 1.43 (q_O/q_I) + 1.64 (q_O/q_I)^2 - 0.804 (q_O/q_I)^3$$
$$CP_v / V_r = 0.682 - 1.43 (0.04) + 1.64 (0.04)^2 - 0.804 (0.04)^3 = 0.627.$$

$$CP_v = 0.627 * V_r = 0.627 (51{,}096\ ft^3) = \mathbf{32{,}037\ ft^3}$$

Notice that the "short-cut" routing equation from Section 3.3.4 uses a CP_v / V_r = 0.65 and 0.65 > 0.627 that we calculated here; this is because the short-cut method calculates the maximum detention volume required.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF SPECIFIC CONDUCTANCE

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine calibration and operation of a variety of specific conductance meters. Although this meter measures additional parameters (e.g., temperature, TDS), this SOG addresses specific conductance measurement only (other capabilities are outlined in the appropriate SOG and manufacturer's individual instrument manuals). This SOG is designed specifically for the measurement of specific conductance in accordance with EPA Method 120.1 and Standard Method 2510 B which address specific conductance measurements of drinking, surface, and saline waters, domestic and industrial wastes, and acid rain.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (OAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- The analyst is responsible for verifying that the specific conductance meter is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Specific conductance meter
- Specific conductance meter manufacturer's instruction manual
- Deionized water
- KCl standard at concentration that approximates sample concentrations
- Lint-free tissues
- National Institute of Standards and Technology (NIST)-traceable thermometer
- Calibration sheets or logbook
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

- Specific conductance measurements should be taken soon after sample collection since temperature changes, precipitation reactions, and absorption of carbon from the air can affect the specific conductance. If specific conductance measurements cannot be taken immediately (within 24 hours), samples should be filtered through a 0.45 μm filter, stored at 4°C and analyzed within 28 days.
- Report results as specific conductance, μmhos/cm at 25°C.

- As temperature can affect the specific conductance measurements obtained, record both the specific conductance and the temperature of the sample. The Cole-Parmer Portable Conductivity Meter and YSI Model 85 have the ability to compensate for temperature.
- Secondary standards may be purchased as a solution from commercial vendors. These standards should not be used after their expiration dates as provided by the manufacturer. An expiration date of one year should be used if the manufacturer does not supply an expiration date or if the standards are prepared from various salts (e.g., KCl).

4.2 Calibration and Measurement Procedures

- The specific conductance meter must be calibrated daily (or the calibration checked) before any analyses are performed.
- Set up the instrument according to the manufacturer's instructions.
- Rinse the probe with deionized water and dry with a lint-free tissue.
- Dip the probe into the calibration standard. Immerse the probe tip beyond the upper steel band. Stir the probe gently to create a homogenous sample.
- Record the stabilized specific conductance reading of the standard and the temperature. Enter the calibration mode (according to manufacturer's instructions) and change the value on the primary display to match the value of the calibration standard. The meter can be adjusted to $\pm$20% from the default setting. If the measurement differs by more than $\pm$20%, the probe should be cleaned or replaced as needed. If the meter does not have automatic temperature compensation (ATC), correct all measurements to 25°C by adding 2% of the reading per degree if the temperature is below 25°C or by subtracting 2% of the reading per degree if the temperature is above 25°C.
- An additional check may be performed, if required by the project plan, by placing the probe into an additional KCl standard. This standard should be from a different source than the standard used for the initial calibration. This standard should read within 5% of the true value.
- Verify the calibration every 15 samples and at the end of the day. Recalibrate or replace the instrument if the check value is not within 15% of the true value.
- The probe will be rinsed with deionized water and wiped gently with a lint-free tissue between sample analyses.
- The meter must be recalibrated following any maintenance activities and prior to the next use.
- Conductivity data may be post calibrated using any of a variety of calibration data including, but not limited to field calibration points, manufacturer calibration data, and analytical results from samples collected during field deployment of the sensors. The decision criteria for post calibration, and the technique used will be specified in the project plan, and will be consistent with the manufacturer's recommendations.

4.3 Troubleshooting Information

If there are any performance problems with any of the specific conductance meters which result in inability to achieve the acceptance criteria presented in Section 5.0, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

- Instrument maintenance should be performed according to the procedures and frequencies required by the manufacturer.
- The probe must be stored and maintained according to the manufacturer's instructions.
- If an instrument with ATC is being used, the meter should be checked annually for accuracy with an NIST thermometer.

5.0 QUALITY CONTROL

- The meter must be calibrated daily before sampling and recalibrated every 12 hours, and will not be used for sample determinations of specific conductance unless the initial check standard value is within 5% of the true value.
- Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within 10%.
- The temperature readout of the meter will be checked against an NIST traceable thermometer at least quarterly. If the difference is greater than 0.2°C, the instrument manufacturer will be consulted for instructions. Temperature measurements will be compensated for any difference with the reference thermometer.
- Some agencies may require the analysis of USEPA Water Pollution (WP) performance evaluation samples. These performance evaluation samples will be analyzed as required.

6.0 DOCUMENTATION

- All specific conductance meter calibration, temperature check, and maintenance information will be recorded on the daily calibration sheet (an example is presented as Figure 1). Specific conductivity data may be recorded on the appropriate laboratory or field data sheets or logbooks.
- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
    - Date and time of calibration
    - Signature or initials of person performing the measurement
    - Instrument identification number/model
    - Expiration dates and batch numbers for all standards
    - Reading for standard before and after meter adjustment
    - Readings for all continuing calibration checks
    - Temperature of standards (corrected for any difference with reference thermometer)
    - Comments
- Documentation for recorded data must include a minimum of the following:
    - Date and time of analysis
    - Signature or initials of person performing the measurement
    - Instrument identification number/model

- Sample identification/station location
- Temperature (corrected for any difference with reference thermometer) and conductance of sample (including units and duplicate measurements) Note: show all calculations for converting instrument reading to μmhos/cm if the instrument provides readings in any other units. Useful conversions: 1 mS/m = 10 μmho/cm or 1 μmho/cm = 0.1 mS/m.
- Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform specific conductance measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that specific conductance measurements be taken in the field by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF DISSOLVED OXYGEN

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of dissolved oxygen using a polarographic sensor equipped dissolved oxygen meter with a digital read-out (e.g., YSI Model 55 Handheld Dissolved Oxygen System). Measurements are made in accordance with EPA Standard Methods that addresses dissolved oxygen measurement of drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- The analyst is responsible for verifying that the dissolved oxygen measuring device is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Dissolved oxygen meter with digital read-out device
- Manufacturer's instruction manual for the instrument
- YSI Model 5775 Standard Membrane Kit with KCl solution and O-rings
- NIST-traceable thermometer
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

To achieve accurate dissolved oxygen measurements, samples should be analyzed *in situ*. Measurements in flowing waters should be made in relatively turbulent free areas. Measurements in standing waters will require probe agitation to create water movement around the probe.

4.2 Calibration and Measurement Procedures

To accurately calibrate most dissolved oxygen meters, you will need to know the approximate altitude of the region in which you are located and the approximate salinity of the water you will be analyzing. Fresh water has a salinity of approximately zero. Seawater has an approximate salinity of 35 parts per thousand (ppt). If uncertain, measure salinity with an appropriate device. The instructions below are applicable to the YSI Model 55; for other instruments, consult the instruction manual.

- Ensure that the sponge inside the instrument's calibration chamber is wet then insert the probe into the chamber. Turn the instrument on and wait for readings to stabilize (approximately 15 minutes).
- To calibrate, enter the calibration menu by pressing and releasing both the up and down arrow keys at the same time. Enter the altitude (in hundreds of feet) at the prompt by using the arrow keys to increase or decrease the altitude (example: 12 = 1,200 feet). Press enter when correct altitude is shown.
- The meter should display CAL in the lower left of the display with the calibration value in the lower right of the display and the current D.O. reading (before calibration) should be on the main display. Once the D.O. reading is stable, press ENTER. Enter the salinity at the prompt by using the arrow keys. Press ENTER when finished and the instrument will return to normal operation.
- Calibration should be performed at a temperature within ± 10°C of the sample temperature. Verify the calibration every 15 samples and at the end of the day.
- If erratic readings occur, replace membrane as per the manufacturer's manual. The average replacement interval is two to four weeks.
- Replace the membrane as per the manufacturer's manual if bubbles appear (>1/8 inch diameter), or if the membrane becomes damaged, wrinkled, or fouled.
- Avoid contact with any environment which contains substances that may attack the probe materials (e.g. acids, caustics, and strong solvents).
- The meter must be re-calibrated following any maintenance activities and prior to the next use.

4.3 Troubleshooting Information

If there are any performance problems with the dissolved oxygen-measuring device, consult the appropriate section of the instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

Instrument maintenance for meter-type dissolved oxygen measuring devices should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within ± 0.2 mg/L.

The temperature readout of the meter will be checked regularly (at least weekly) against a NIST-traceable thermometer. If the difference is greater than 0.5°C, the instrument manufacturer will be consulted for instructions. Temperature measurements will be compensated for any difference with the reference thermometer.

6.0 DOCUMENTATION

All dissolved oxygen meter calibration, checks, and maintenance information will be recorded on the daily calibration sheet or logbook. Dissolved oxygen data may be recorded on the appropriate laboratory or field data sheets or logbooks.

- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
    - Date and time of calibration

  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Expiration dates and batch numbers for all standard solutions
  - Readings for all continuing calibration checks
  - Comments
- Documentation for recorded data must include a minimum of the following:
  - Date and time of analysis
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Sample identification/station location
  - Dissolved oxygen, both in mg/L and percent saturation (corrected for any difference with reference thermometer) and temperature of sample (including units and duplicate measurements)
  - Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform dissolved oxygen measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that dissolved oxygen measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF FLOW RATE

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of flow rate in bodies of running water. The two techniques under consideration are the Time of Travel Method and the Global Flow Probe Procedure.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- The analyst is responsible for verifying that the instrumentation is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for the Global Flow Probe Procedure:

- Global Flow Probe (version FP101 or newer), Global Water, Gold River, CA
- LCD computer display
- Radio Shack 675 HP or equivalent batteries
- Manufacturer's instruction manual for the instrument
- Laboratory or field data sheets or logbooks

The following materials are necessary for the Time of Travel Method:

- A neutral buoyancy floating object, such as a cracked ping-pong ball
- Twine or other heavy-duty string material (optional)
- Water proof yard-stick to measure stream depth
- Stop-watch
- Permanent marker (e.g., sharpie) (optional)
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 General Measurement Procedures for Global Flow Probe Procedure

To achieve accurate flow measurements samples must be analyzed in the field. Flow measurements may be taken in small and large streams, rivers and within pipes.

- The average velocity of stream flow multiplied by the cross-sectional area is equal to the flow rate (Q=VxA). The cross sectional area is determined manually by measuring the depth of the water at several points across the channel. The cross section in square feet times the average velocity in feet per second gives the cubic feet per second (c.f.s.).
- When sampling within round pipes, one needs only to measure the water depth and then refer to the tables in the Global Flow Probe Instruction Manual to determine the cross-sectional area.

4.2 Calibration and Measurement Procedures for Global Flow Probe Procedure

The Flow Probe is set up and calibrated at the factory. The calibration sequence is entered automatically when the batteries are changed or by holding down both Right and Left buttons simultaneously for 8 seconds. Calibration should be checked annually.

- To change between English and Metric units and to enter the calibration sequence, hold down both Left and Right buttons simultaneously for 8 seconds. The Left button scrolls between English “mi” and Metric “km”.
- To check the calibration push the Right button to “CAL”. For “mi” calibration set Probe calibration to 33.31. For “km” calibration set Probe calibration to 1603. The Left button increases the number when the arrow points up and decreases the number when the arrow points down.
- The Flow Probe computer has a simple 2 – button operation. The Right button changes between Function and the Left button picks the Option. Pushing both buttons simultaneously for 1 second zeros the displayed value.
- By pushing the Right button you may scroll through the following functions. Velocity Function: “V” is instantaneous velocity to the nearest 0.1 feet per second. Push the Left button to scroll between “AV” (average velocity) and “MX” (maximum velocity) which reads out to the nearest 0.01 feet per second. Stop Watch / Clock Function: Push the Left button to start and stop watch.
- Make sure the prop turns freely and point the prop directly into the flow with the arrow on the bottom of the probe pointing down-stream.
- Press the Right button until the “V” for velocity appears and select the desired velocity parameters to be measured by pushing the Left button. Average velocity readings “AV” must be collected for flow rate measurements (c.f.s.).
- Put the probe at your measuring point and press both Right and Left buttons simultaneously and release to re-zero and begin recording. Hold in the flow for several seconds until you have steady average velocity.
- When sampling in small streams and within pipes, the probe should be moved slowly and smoothly along a vertical plane throughout the flow to ensure that the probe evenly samples the cross-sectional area of the flow.
- When sampling larger streams and rivers divide the stream into subsections (e.g. 2-3 feet in width). At the center of each subsection, insert the probe and sample vertically from the surface to the bottom smoothly to obtain a vertical average velocity profile. The Average Velocity times the Area of the subsection is the Flow for the subsection. Add all the subsection flows to obtain the Total Stream Flow.
- Repeat procedure three times in at least three different locations, recording data in field notebook. The flow rate should be calculated as an average of the three measurements taken at different locations within the channel or pipe.
- Calculate discharge (Q) from the measured data, as follows:

- Measure and calculate the cross-sectional area of your flow stream in square feet and multiply this by the average velocity in feet / second to obtain discharge in cubic feet per second (c.f.s.).
- Cross-sectional area (ft^2) x AV (ft/sec) = Q (ft^3/sec)

4.3 Calibration and Measurement Procedures for the Time of Travel Method

To measure travel time, the length of time taken for the floating object to travel 3 feet will be measured as follows:

1. Select an appropriate stream cross section with relatively uniform and uninterrupted flow
2. Securely attach 3 feet of string to floating object (i.e., cracked ping-pong ball). Alternately, identify a neutrally-buoyant floating object in the water.
3. Release the tethered floating object in the water and activate timer, or orient the yard stick above the un-tethered object, taking care not to disturb the flow.
4. Record time (T) from when the floating object is released to the time when the string goes taut, indicating that the object has traversed 3 feet, or the time it takes for the un-tethered object to travel 3 feet as measured by the yard stick.
5. Repeat procedure three times at three different locations, recording data in a field notebook. The flow rate should be calculated as an average of the three measurements taken at different locations within the stream channel. Flow rate = 3 feet/T (seconds) = X feet / second
6. Measure stream average width and average depth at sampling location

- Calculate discharge (Q) from the measured data, as follows:

1. Calculate cross-sectional area (A) of the stream, by multiplying average width and average depth
2. Select a coefficient or correction factor (C): 0.8 for rocky bottom streams, 0.9 for muddy bottom streams. The coefficient allows correction for the fact that water travels faster at the surface than at the stream bottom, due to resistance from bottom materials
3. Calculate Q as:

   Q = (A*C*L) / T

   Where L= 3 feet and T= time of travel (seconds) and units of Q are typically cubic feet per second.

4.4 Troubleshooting Information for Global Flow Probe Procedure

If there are any performance problems with the Global Flow Probe, consult the appropriate section of the instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department at (916) 638-3429 immediately for further instructions.

4.5 Maintenance for Global Flow Probe Procedure

Instrument maintenance for the Global Flow Probe should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

5.1 Quality Control for Global Flow Probe Procedure

The Global Flow Probe calibration should be checked annually to ensure that the Flow Probe is operating up to factory specifications.

5.2 Quality Control for the Time of Travel Method

To ensure a quality measurement, a minimum of three times of travel measurements will be obtained and recorded at each sampling point. An average value will be used to measure flow rate / discharge.

6.0 DOCUMENTATION

6.1 Documentation for Global Flow Probe Procedure

All Global Flow Probe calibration, checks, and maintenance information will be recorded on the daily calibration sheet or logbook. Flow data may be recorded on the appropriate laboratory or field data sheets or logbooks.

- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
  - Date and time of calibration
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Readings for all continuing calibration checks
  - Comments
- Documentation for recorded data must include a minimum of the following:
  - Date and time of analysis
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Sample identification/station location
  - Flow Rate in cubic feet per second (c.f.s.), average water velocity and maximum water velocity
  - Comments

6.2 Documentation for the Time of Travel Method

All data will be recorded in a field logbook. Documentation for recorded data must include a minimum of the following:

- Date, time and location of measurement
- Time of travel and distance traveled
- Comments, if any

7.0 TRAINING/QUALIFICATIONS

- To properly perform Global Flow Probe measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.
- Certain state certification programs require that flow measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.
- No special training is required to implement the Time of Travel Method; however, the analyst must be familiar with the calibration and measurement techniques stated in this SOG.

8.0 REFERENCES

Volunteer Stream Monitoring: A Methods Manual. EPA 841-B-97-003, November 1997.

Global Flow Probe Instruction Manual.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF PH

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine calibration and operation of a variety of pH meters, including the YSI Model 55, Hydac Multimeter Probe and the pHep pH Testers. Although these meters may measure additional parameters (e.g., temperature, specific conductivity, etc.), this SOG addresses pH measurement only (other capabilities are outlined in the appropriate SOG and manufacturer's individual instrument manuals). This SOG is designed specifically for the measurement of pH in accordance with EPA Method 150.1 and Standard Method 4500-H B which address electrometric pH measurements of drinking, surface, and saline waters, domestic and industrial wastes, and acid rain.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- The analyst is responsible for verifying that the pH meter is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials may be necessary for this procedure:

- pH meter
- pH meter manufacturer's instruction manual
- Deionized water
- 4.0, 7.0, and 10.0 buffer solutions
- Lint-free tissues
- Mild detergent
- 10% hydrochloric acid
- National Institute of Standards and Technology (NIST)-traceable thermometer
- Calibration sheets or logbook
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

- To achieve accurate pH measurements, samples should be analyzed in the field (preferably within 15 minutes), or as soon as possible after collection. Sample should be collected in plastic or glass containers.
- After measuring a sample containing oily material or particulate matter, the electrode must be cleaned by carefully wiping with a lint-free cloth, or washing gently in a mild detergent, followed by a deionized water rinse. If this does not suffice, an additional rinse with 10% hydrochloric acid (followed by deionized water) may be needed.
- As temperature can affect the pH measurements obtained, both the pH and the temperature of the sample must be recorded. Both the Hydac Multimeter and the pHep Tester that will be used in this study have the ability to compensate for temperature.
- Calibration must include a minimum of two points that bracket the expected pH of the samples to be measured. Calibration measurements must be recorded in logbook.
- Primary standard buffer salts available from NIST can be purchased and are necessary for situations where extreme accuracy is required. Secondary standard buffers may be purchased as a solution from commercial vendors and are recommended for routine use. Buffers should not be used after their expiration dates as provided by the manufacturer. An expiration date of one year should be used if the manufacturer does not supply an expiration date or if the buffers are prepared from pH powder pillows, etc.
- When using the meter in the laboratory, always place the buffer/sample beaker on the magnetic stirrer, and make sure the stirring bar is rotating during measurements. Rinse the stirring bar as well as the beaker between buffers/samples.

  EXCEPTION: Do not use the magnetic stirrer for acid rain samples. It is crucial not to induce dissolved gases into the sample to be absorbed or desorbed, as this will alter the pH. Stir the sample gently for a few seconds after introducing the electrode, then allow the electrode to equilibrate prior to recording temperature and pH readings.
- When the meter is being used in the field, move the probe in a way that creates sufficient sample movement across the sensor; this insures homogeneity of the sample and suspension of solids. If sufficient movement has occurred, the readings will not drift (<0.l pH units). Rinse the electrode with deionized water between samples and wipe gently with a lint-free tissue.
- When measuring the pH of hot liquids, wait for the liquid to cool to 160°F or below.
- Fluctuating readings may indicate more frequent instrument calibrations are necessary.

4.2 Calibration and Measurement Procedures

- The pH meter must be calibrated daily before any analyses are performed. The meter should be re-calibrated every 12 hours or at the frequency specified in the project plan.
- Connect the electrode to the meter. Choose either 7.0 and 10.0 (high range) or 4.0 and 7.0 (low range) buffers, whichever will bracket the expected sample range. Place the buffer in a clean glass beaker. If the pH is being measured in a laboratory, place the beaker on the magnetic

stirrer and place the stirring bar in the beaker. Measure and record the temperatures of the buffers using a calibrated thermometer or automatic temperature compensation (ATC).

- Place the electrode into the 10.0 buffer or into the 7.0 buffer.
- Adjust the instrument calibration according to the manufacturer's instructions. Discard the buffer and rinse the beaker and stirring bar thoroughly with deionized water.
- Refill the beaker with the 7.0 buffer or the 4.0 buffer. Rinse the electrode, gently wipe with a lint-free tissue, and place it in the selected buffer solution. If the pH is being measured in a laboratory, place the beaker on the magnetic stirrer and place the stirring bar in the beaker. Continue adjusting the instrument calibration according to the manufacturer's instructions. Record the electrode slope (if provided by the instrument) on the calibration sheet (an acceptable slope is between 92 and 102 percent). Measure and record the temperature of the buffer using a calibrated thermometer or ATC. Discard the buffer and rinse the beaker and stirring bar thoroughly with deionized water.
- An additional check may be performed, if required by the project plan, by placing the electrode into an additional buffer solution. This buffer should be from a different source than the buffers used for the initial calibration. This buffer should read within +0.2 pH units of the buffer's true pH value.
- Verify the calibration every 15 samples and at the end of the day. Recalibrate the instrument if the check value varies more than 0.2 pH units from the true value.
- The electrode will be rinsed with deionized water and wiped gently with a lint-free tissue between sample analysis.
- Recalibrate the instrument if the buffers do not bracket the pH of the samples.
- The meter must be re-calibrated following any maintenance activities and prior to the next use.

4.3 Troubleshooting Information

If there are any performance problems with any of the pH meters which result in the inability to achieve the acceptance criteria presented in Section 5.0, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

- Instrument maintenance should be performed according to the procedures and frequencies required by the manufacturer.
- The electrode must be stored and maintained according to the manufacturer's instructions.
- If an instrument with ATC is being used, the device should be checked on a quarterly basis for accuracy with an NIST thermometer.

5.0 QUALITY CONTROL

- Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within ±0.l pH units.

- The temperature readout of the meter will be checked annually against an NIST-traceable thermometer. If the difference is greater than 0.2°C, the instrument manufacturer will be consulted for instructions. Temperature measurements will be compensated for any difference with the reference thermometer.
- Some regulatory agencies may require the analysis of USEPA Water Supply (WS) or Water Pollution (WP) performance evaluation samples. These performance evaluation samples will be analyzed as required.

6.0 DOCUMENTATION

- All pH meter calibration, temperature check, and maintenance information will be recorded on the daily calibration sheet (Figure 1). pH data may be recorded on the appropriate laboratory or field data sheets or logbooks.
- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
  - Date and time of calibration
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Expiration dates and batch numbers for all buffer solutions
  - Reading for pH 7.0 buffer before and after meter adjustment
  - Reading for pH 4.0 or 10.0 buffer before and after meter adjustment
  - Readings for all continuing calibration checks
  - Temperature of buffers (corrected for any difference with reference thermometer), including units
  - Comments
- Documentation for recorded data must include a minimum of the following:
  - Date and time of analysis
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Sample identification/station location
  - Temperature (corrected for any difference with reference thermometer) and pH of sample (including units and duplicate measurements)
  - Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform pH measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that pH measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF WATER CLARITY WITH A SECCHI DISC

1.0 INTRODUCTION

This Standard Operating Guideline (SOG) provides basic instructions for the routine measurement of water clarity in lakes and ponds with a Secchi disc. Water clarity is a function of the number of particles in the water (algae, sediment, etc) and the color of the water, which both have an impact on the depth of light penetration. The transparency of the water column can be used as an indicator of water body productivity, with certain exceptions (e.g., naturally sediment laden waterbodies). Generally, the more productive a system is the more algae in the water column, and the lower the transparency. Water transparency can also be affected by erosionally-suspended particles which are related to water depth and wave action. Thus on any given day the turbidity of a water body may be affected by its productivity, the season, wind speed and level of sunlight. The methods outlined below are intended (1) to standardize the use of a Secchi disc in the measurement of turbidity; (2) to standardize recording of field data to assure proper documentation of weekly, monthly and seasonal patterns in turbidity.

2.0 REQUIRED MATERIALS

The following materials are necessary for the measurement of turbidity with a Secchi disc:

- Weighted Secchi disc with attached length of rope marked off in 0.1-meter increments with indelible ink.
- Field data sheets

3.0 METHODS

- A location will be selected from which to measure turbidity. This location will stay constant throughout the study.
- The date, weather conditions, and personnel conducting the measurement will be recorded on the field sheet.
- The Secchi disc will be lowered slowly into the water by the rope so that the weight enters the water first and the disc follows, flat side parallel to the water surface.
- The disc will continue to be lowered through the water column until it is no longer visible.
- A note will be made of the depth of the disc at this point to the nearest 0.1 meter by reading where the surface of the water touches the rope.
- The disc will then be slowly raised until it is just visible again.
- Once again a note will be made of the depth of the disc at this point.
- An average of these two depths will be calculated to give the “Secchi depth”, i.e. a measure of the turbidity of the water.

4.0 DOCUMENTATION

Secchi depth data will be reported on field data sheets for every day that a measurement is taken. Documentation for recorded data must include a minimum of the following:

- The date
- The time
- Weather conditions
- Signature or initials of person performing the measurement

- Depth measurements and average Secchi depth
- Field comments/observations on anything that may influence the Secchi depth measurement that day.

5.0 QUALITY CONTROL

- Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project specific criteria, duplicate measurements should agree within ±0.25 meters.
- The Secchi disk rope should be checked at least annually against a tape measure to ensure the units of measurement are accurate.

STANDARD OPERATING GUIDELINES FOR COLLECTION OF SEDIMENTS FROM FRESHWATER ENVIRONMENTS

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOGs) provide basic instructions for the collection of bottom sediments from freshwater environments. Collections are to be performed in accordance with methodologies generally accepted by the Massachusetts Department of Environmental Protection (MADEP). Laboratory analysis of sediment samples should be performed by a state certified laboratory with the detection limits for analysis specified on the project's Chain of Custody as per MADEP's Interim Policy # COMM-94-007 and their subsequent Technical Update for freshwater sediment screening (May 2002).

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements may be defined in a site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- Field personnel are responsible for verifying that all sampling equipment is in proper operating condition prior to use and for implementing the sampling procedures in accordance with this SOG and any specific project plan.

3.0 REQUIRED MATERIALS

The following materials may be necessary for this procedure:

- Sediment coring or grab sampling device
- Stainless steel mixing bowl
- Stainless steel mixing spoon or tool
- Nitrile gloves
- Alconox
- Pre-cleaned sample jars provided by laboratory
- Pencil and labeling marker or pen
- Field data sheets or logbooks
- GPS receiver and/or map of target waterbody to record sample locations

4.0 METHOD

Field personnel are to collect sediment cores or grabs in accordance with the instructions provided with each specific sampling device deployed. Nitrile gloves should be worn at all times during these procedures. At each sampling location, a pre-cleaned grab sample dredge or corer is to be deployed, typically from a boat. All equipment is to be decontaminated using alconox and fresh water before the collection of each discrete sample. If specified by the project plan, samples may be composited in a pre-cleaned stainless steel mixing bowl and mixed thoroughly with a pre-cleaned stainless steel spoon before being transferred to the glass sampling jars provided by the laboratory. However, volatile organic compound (VOC) samples should be collected from cores prior to compositing.

The sample jar should be labeled with the sample identification, date, and any other project specific requirements. This information should be recorded in a field book at the time of sampling along with other

essential information such as water depth, sample coordinates (or the location should be mapped on a figure at the time of sampling), and any other general notes on the nature of the sediment collected.

5.0 QUALITY CONTROL

Duplicate field samples or split samples may be collected if specified by the project plan. Once samples have been retrieved and placed into jars, the samples should be kept on ice or refrigerated until the laboratory can analyze them. Specific sample volumes, holding times, and detection limits for each parameter to be analyzed (Table 1) should be adhered to unless the project plan has outlined project-specific requirements.

TABLE 1. SEDIMENT ANALYSIS

PARAMETER	Volume Needed (ml)	Sample Container	Sample Preservation	Maximum Hold Time (hours)	Detection Limits (mg/Kg)	EPA #
Arsenic	100 g	Amber Glass	Ice	6 months	0.5	200.7
Cadmium	100 g	Amber Glass	Ice	6 months	0.1	200.7
Chromium	100 g	Amber Glass	Ice	6 months	1.0	200.7
Copper	100 g	Amber Glass	Ice	6 months	1.0	200.7
Lead	100 g	Amber Glass	Ice	6 months	1.0	200.7
Mercury	100 g	Amber Glass	Ice	6 months	0.02	245.1
Nickel	100 g	Amber Glass	Ice	6 months	1.0	200.7
Zinc	100 g	Amber Glass	Ice	6 months	1.0	200.7
PCBs	100 g	Amber Glass	Ice	7 days	0.01	8082
PAHs	100 g	Amber Glass	Ice	7 days	0.02	8270
EPH	100 g	Amber Glass	Ice	14 days	25	418.1
VOCs	100 g	Amber Glass	Methanol, Ice	7 days	0.1	EPA/ACE 8260
% Organic Content	100 g	Amber Glass	Ice	7 days	1.0%	160.4
% Ash Content	100g	Amber Glass	Ice	7 days	1.0%	160.4
Grain Size Analysis (Sieve and Hydrometer)	1,000g	Plastic Bag/Glass	None Required	Indefinite	0.1%	ASTMD 2216

% Water	100g	Amber Glass	Ice	14 days	1.0%	160.3

6.0 DOCUMENTATION

Documentation for recorded data must include a minimum of the following:

- Date and time of collection and analysis
- Signature or initials of person performing the collection or measurement
- Sample identification/station location
- Pertinent comments

7.0 TRAINING/QUALIFICATIONS

To properly perform sediment collections, the field personnel must be familiar with the techniques stated in this SOG and experienced in the operation of the sampling equipment.

8.0 REFERENCES

MADEP Interim Policy # COMM-94-007

MADEP 2002. Technical Update: Freshwater Sediment Screening Benchmarks for Use under the Massachusetts Contingency Plan. May 2002.

STANDARD OPERATING GUIDELINES FOR THE ACQUISITION OF SURFACE WATER

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the routine acquisition of surface water. The methods outlined below are intended (1) to standardize water sample collection methods used by ESS Group, Inc. (ESS) field personnel; (2) to ensure that samples delivered to the laboratory represent field conditions as accurately as possible; (3) to standardize recording of field data to assure proper documentation of sample collection; (4) to minimize cross contamination between sampling sites.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- The analyst is responsible for verifying that the sampling bottles are appropriately sanitized and contain the appropriate preservative for the desired laboratory analyses. Sample bottle caps should be securely in place to ensure that no contamination has occurred and that preservative has not been released.

3.0 REQUIRED MATERIALS

The following materials are necessary for the acquisition of surface water:

- Nitrile gloves
- Labeled sampling container provided from contracted laboratory, which is appropriately sanitized and contains the appropriate preservative for the desired analyses
- Laboratory or field data sheets or logbooks
- List of sites or locations of each site to be sampled

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

- Unless noted otherwise, surface water samples will be collected via direct grab methods.
- Upon entering a sampling location, ESS field personnel shall minimize disturbance to upstream waters and shall always sample water from the undisturbed upstream region. In addition, when wading in waterbodies, field personnel will try and disturb as little bottom sediment as possible.
- Sample collection shall precede the measurement of physical field parameters (such as turbidity, conductivity, dissolved oxygen, etc.) in order to minimize the risk of sediment disturbance and/or contamination.
- Clean rubber gloves shall be worn at each sampling location. Gloves shall be rinsed with distilled water prior to subsequent sample collection. When sampling multiple sites on the same date, gloves may be rinsed in the immediate downstream reaches of the waterbody to be sampled, before sample

collection, in order to minimize the risk of cross-contamination. When warranted by the sensitivity of the laboratory analyses under investigation or at the Clients request, new, sterile rubber gloves shall be worn at each different sampling location.

- In absence of a project specific sampling protocol, grab samples are to be collected from beneath the water surface (at approximately 8 to 12 inches beneath the surface or mid-way between the surface and the bottom if the waterbody is shallow, (EPA 1997)). Samples will be collected at an appropriate distance from the stream bank or lake shoreline and away from submerged obstacles. For small streams (i.e., 10-20 feet wide with a maximum depth of less than 2 feet) the appropriate distance to collect a sample would be the center, while within larger streams the sample would be taken at a location where water depth is 2-3 feet.
- When collecting samples, ESS field personnel shall stand downstream of the desired sampling location, hold the bottle near its base and plunge it below the water surface with the opening (mouth) downward. The opening of sample bottles shall always be directed away from field personnel in an upstream direction.
- Sample containers with preservatives should not be used to collect surface water samples. If using containers with preservatives, a pre-cleaned container of similar type should be used to collect the sample with subsequent transfer to the preserved container.
- ESS personnel shall leave an approximate 1-inch air space (except for dissolved oxygen and BOD samples) in sample bottles, so that bottles may be shaken (if needed) before analyses (EPA, 1997).
- ESS personnel shall place sample bottles and temperature blanks (if required by project plan or QAM) in a cooler filled with ice (if required by project plan or QAM).
- The testing or analytical method and sample containers, preservation technique, and sample volumes should be selected in consultation with the laboratory to ensure that the samples obtained will provide the desired results.

5.0 QUALITY CONTROL

5.1 Field Duplicates

Field duplicate measurements of a single sample will be performed at the frequency specified in the project plan. Collection of duplicates will adhere to the surface water acquisition methods described above. Field duplicates will be collected immediately following initial sample collection.

6.0 DOCUMENTATION

Surface water quality field data will be reported in field notebooks by ESS personnel. Surface water quality laboratory data will be reported by contracted laboratories on official laboratory letterhead. Any unanticipated site-specific information, which requires ESS field personnel to deviate from the above SOG will be reported in an ESS field notebook. Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Signature or initials of person performing the measurement
- Sample identification/station location
- Comments/observations

7.0 TRAINING/QUALIFICATIONS

To properly perform the acquisition of surface water, the analyst must be familiar with the sampling protocols as stated in this SOG.

8.0 REFERENCES

EPA, 1997. Volunteer Stream Monitoring: A Methods Manual. United States Environmental Protection Agency. Office of Water. EPA 841-B-97-003.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF TEMPERATURE

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of temperature using any high quality mercury-filled thermometer or thermistor with analog or digital read-out device (e.g., Hydac Multimeter Probe and YSI Model 55. Multimeter instruments). Instruments used for temperature measurement may measure additional parameters (e.g., dissolved oxygen, conductivity, pH, etc.). This SOG addresses temperature measurement only (other capabilities are outlined in the appropriate SOG). This SOG is designed specifically for the measurement of temperature in accordance with EPA Method 170.1 and Standard Method 2550 B which address thermometric temperature measurement of drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.
- The analyst is responsible for verifying that the temperature measuring device is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Thermometer or thermistor with analog or digital read-out device
- Manufacturer's instruction manual for the instrument
- National Institute of Standards and Technology (NIST)-traceable thermometer
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

To achieve accurate temperature measurements, samples should be analyzed immediately upon collection (preferably within 15 minutes). Samples should be collected in glass or plastic containers.

4.2 Calibration and Measurement Procedures

- ESS-owned temperature measuring devices will, at a minimum, be checked annually as described in Section 5.0. The device will be checked against an NIST-traceable thermometer and the necessary compensation made for the difference in temperature between the two. Rental equipment will be checked by the manufacturer and documentation provided to ESS.
- Immerse the thermometer or temperature measuring device into the sample.

- Swirl and take a reading when the value stabilizes.
- Record the temperature reading to the nearest 0.50 for a thermometer or 0.10 for digital meter-type instruments. Compensate for any difference with the NIST-traceable thermometer.
- Temperature data may be post-calibrated using any of a variety of calibration data including, but not limited to, field calibration points, manufacturer calibration data, and analytical results from samples collected during field deployment of the sensors. The decision criteria for post calibration, and the technique used, will be specified in the project plan, and will be consistent with the manufacturer's recommendations.

4.3 Troubleshooting Information

If there are any performance problems with any of the meter-type temperature measuring devices, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions. If a performance problem exists with the thermometer, discard the thermometer and replace.

4.4 Maintenance

Instrument maintenance for meter-type temperature measuring devices should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

- The temperature measuring devices will, at a minimum, be checked against an NIST-traceable thermometer at the frequency stated in Section 4.2. This verification procedure will be performed as follows:
    - Immerse the thermometer or temperature sensor and the NIST-traceable thermometer into a sample.
    - Allow the readings to stabilize.
    - Record the readings and document the difference.
    - Label the thermometer or temperature sensor with the correction value/adjustment and the date the accuracy check was performed.
    - Compensate for the difference when sample measurements are taken.
- Duplicate measurements of a single sample will be performed at the frequency stated in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within $\pm$0.50°C or approximately $\pm$1.00°F.

6.0 DOCUMENTATION

- Records for checking the accuracy of the thermometer or temperature measuring device (where applicable) will include:
    - Date
    - Thermometer or meter-type temperature measuring device checked
    - Reference thermometer number

- Readings for reference thermometer and thermometer being checked
- Adjustment made for difference in readings
- Initials of analyst

- Documentation for recorded data must include a minimum of the following:
  - Date and time of analysis
  - Signature or initials of person performing the measurement
  - Thermometer ID # or instrument identification number/model
  - Sample identification/station location
  - Temperature of sample (including units and duplicate measurements) compensated for any difference with the reference thermometer if applicable
  - Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform temperature measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that temperature measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR WATERFOWL SURVEYS

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the assessment of resident waterfowl in and adjacent to inland waterbodies. The methods outlined below are intended to do the following: (1) standardize waterfowl survey techniques used by ESS Group, Inc. (ESS) field personnel; and (2) standardize recording of field data.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the survey in accordance with this SOG and the project plan.
- The surveyors are responsible for properly identifying and enumerating resident waterfowl (including Canada Goose, Mute Swan, and Mallard, unless otherwise defined in the project-specific scope of work).

3.0 REQUIRED MATERIALS

The following materials are necessary:

- Boat (if conducting surveys from the water) and safety gear
- Waders (if needed for traversing areas of emergent plant growth)
- Binoculars
- Digital camera
- Site map (enlarged outline of the waterbody on water resistant paper)
- Field notebook/ pen/ pencil/ marker
- GPS unit
- Field guide (e.g., Sibley Field Guide to Birds of Eastern North America)

4.0 METHOD

Depending on the goals of the project, surveys be based on a stationary, fixed-transect, or meander approach. These survey types are not discussed in greater detail in this SOG, as they will be highly project-specific.

In general, survey locations should be recorded, either on a field map or GPS. For each location where waterfowl are observed, the following data (at a minimum) should be recorded: species, life stage (adult, juvenile, egg), counts, and where observed (water, land, or air). Areas of shoreline accessible to molting waterfowl (e.g., unobstructed lawns that slope gently to the water) should also be noted. Where possible, photographs should be taken of the waterfowl observed.

Where boats are used in the survey, the boat will be driven slowly and far enough from shore to minimize waterfowl disturbance, when possible.

In spring surveys, potential nesting locations will also be recorded as a separate data point. Photographs of nest sites will be taken, when possible.

Large numbers of waterfowl may need to be estimated using standard avian counting techniques. In general, this involves breaking the group into subsets (e.g., groups of 10 or 100). The recorded values

should be in line with the level of precision of the count. For example, if counting subsets of 100, the final count should be a multiple of 100.

The survey will be complete when the project-specific goals are achieved.

5.0 QUALITY CONTROL

Waterfowl identification and counts will only be conducted by qualified observers. When the project allows, a minimum of two observers should conduct each survey together and record data independently. Survey counts can then be checked against each other and against photographs from the field for accuracy.

6.0 DOCUMENTATION

Waterfowl observations will be recorded by ESS personnel in field notebooks, on field maps, or in a GPS data dictionary. Documentation should include a tally of species counts by life stage and location. Waterfowl locations will be recorded on a map outline of the waterbody that has been printed on weatherproof paper or in a GPS database. Any unanticipated site-specific information, which requires ESS field personnel to deviate from the above SOG will be reported to the project manager and documented electronically. Documentation for recorded data must include a minimum of the following:

- Survey date
- Weather conditions
- Name(s) or initials of person(s) performing the survey
- Waterfowl and nest site locations
- Species identifications and counts by life stage for each location
- Comments /observations

7.0 TRAINING/QUALIFICATIONS

To properly complete an assessment of waterfowl within a waterbody, the analyst must be familiar with the sampling protocols as stated in this SOG and must have familiarity with identifying and counting waterfowl.

STANDARD OPERATING GUIDELINES FOR STORM WATER SAMPLING

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the routine acquisition of storm water. The methods outlined below are intended (1) to standardize storm water sample collection methods used by ESS Group, Inc. (ESS) field personnel; (2) to ensure that samples delivered to the laboratory represent field conditions as accurately as possible; (3) to standardize recording of field data to assure proper documentation of sample collection; (4) to minimize cross contamination between sampling sites.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan. The project manager will directly coordinate storm water sampling events or designate a task coordinator on the project team.
- Field personnel are responsible for obtaining a correct bottle order from the laboratory and verifying that the sampling bottles are appropriately sanitized (or new) and contain the appropriate preservative for the desired laboratory analyses. Sample bottle caps should be securely in place to ensure that no contamination has occurred and that preservative has not been released. Field staff must completely fill out all required chains of custody and observe proper hold times for all samples.
- Field personnel are also responsible for ensuring that all meters and equipment are functional and calibrated prior to use.
- Field personnel are responsible for communicating with the project manager or task coordinator to confirm that an event will be sampled prior to departure for the project site. They are also responsible for documenting precipitation extent, intensity, and total amounts through photographs, field notes, and/or online weather reports and maps.

3.0 REQUIRED MATERIALS AND EQUIPMENT

The following equipment and materials are required for storm water sampling:

- Nitrile gloves
- Labeled sampling container provided from contracted laboratory, which is appropriately sanitized and contains the appropriate preservative for the desired analyses
- Appropriately maintained and calibrated meters (see individual SOGs for water quality measurements)
- Weatherproof field data sheets or field books

- Weatherproof pen
- List of sites or locations of each site to be sampled

Additionally, the following equipment and materials may be necessary for certain projects:

- Stopwatch
- Collapsible ruler
- Extendible grab sampler
- Cut off bottle or cup (for collecting overland runoff samples)
- DGPS (pre-loaded with sampling locations, if necessary)
- Pry bar, hook, shovel, or other tools (for opening manhole covers, grates, etc.)
- Loppers or other pruning tool (for clearing vegetation)
- Waders or hip boots

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

4.1.1 Selecting the Storm

- The target of storm water sampling is typically the "first flush" of a storm event. To obtain a sample representative of this first flush, sampling should only be conducted after a significant dry period, typically 72 hours (although the recommended dry period may be more or less depending on the project and/or state). Dry weather is usually defined as a period of 0.1 inch of precipitation or less and no measurable snow cover. Storm water sampling events may require a minimum storm event size of at least 0.5 inches of precipitation. Compliance with the minimum period of antecedent dry weather and storm event size is especially important on projects where sampling needs to be conducted in accordance with state regulations. Other regulations may also apply and field personnel should check with the project manager prior to sampling if the requirements of the storm water sampling program are unclear.
- Storms should be screened for a high probability of producing a sufficient amount of rain over the entire watershed area. Storms that meet this criterion should be tracked on a daily basis until the day of the storm. On the day of the storm, the storm watcher will use radar, precipitation total maps, forecast discussions, and any other evidence that is available and useful to track the storm. Remember that forecast and radar ***trends*** are at least as important as the latest forecast or radar map. Declining probabilities of precipitation or forecasted storm amounts are generally signs of a storm that is not likely to produce satisfactory results. It is important to check the scientific forecaster discussion (available as a link from most weather websites), which provides background information on the forecast reasoning. Changes to the going forecast may emerge in this discussion several hours before the daily or hourly forecasts for individual locations are altered.
- The project manager should track storm systems to assess the potential of each storm to produce conditions adequate for storm water sampling and communicate expectations to field personnel. Field staff should be notified as far in advance as possible, preferably two to five days, that sampling may be necessary for a particular event. This will reduce the number of missed events.

- Field personnel should have all equipment and materials (including bottles) prepped well in advance of the targeted storm event. Prior to leaving for the project site, field personnel should confirm with the project manager that storm water sampling is authorized. This will minimize the number of false starts. Field personnel should also notify the analytical laboratory of the sampling schedule for the day to ensure that samples will be received within holding times and that lab personnel will be available to log samples in a timely manner. This is particularly important when collected samples with short hold times, such as bacteria.
- See Figure 1 for a flow chart of project manager and field personnel responsibilities during the storm selection and sampling process.

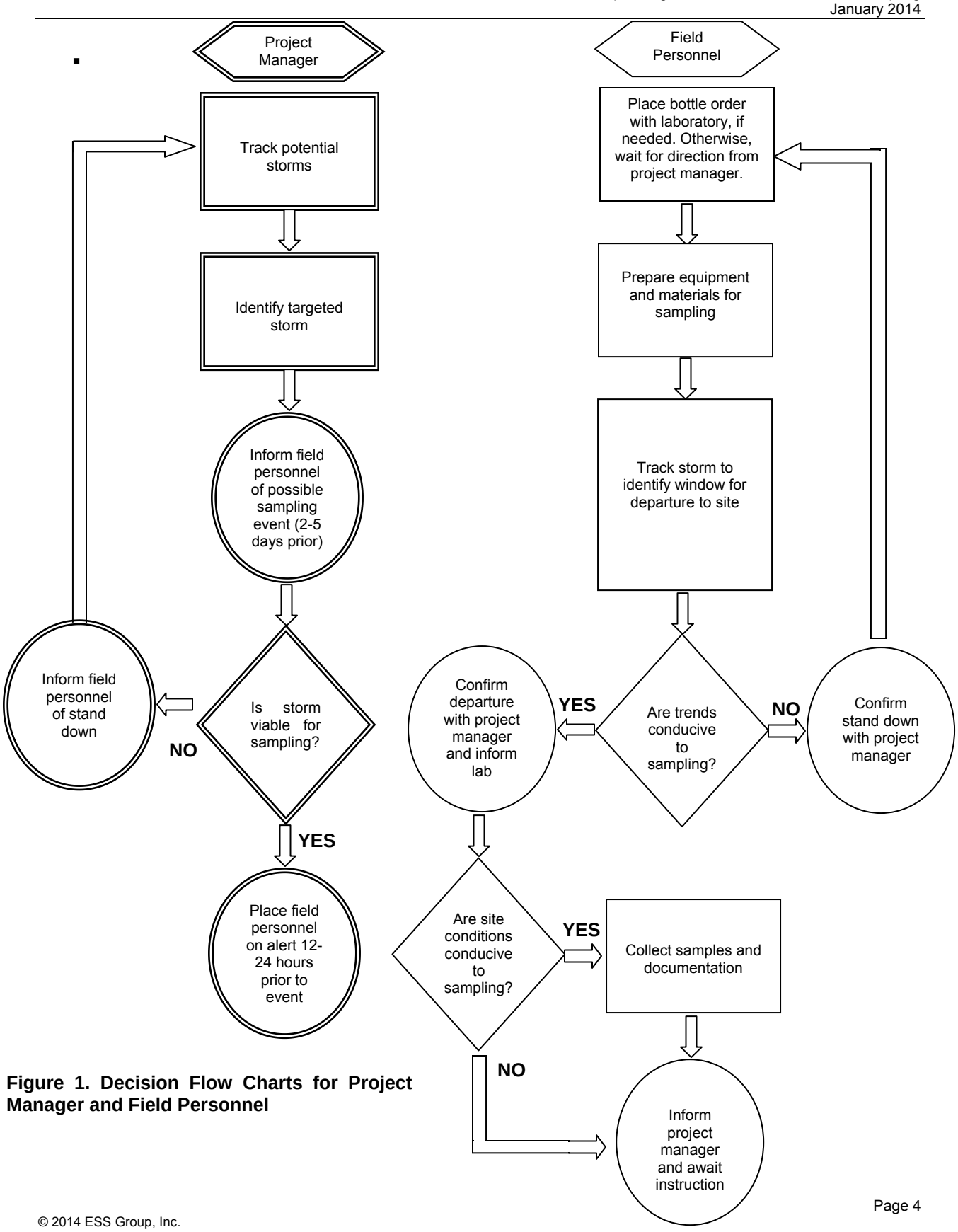


Figure 1. Decision Flow Charts for Project Manager and Field Personnel

4.1.2 Field Methods

General Guidelines

- The testing or analytical method and sample containers, preservation technique, and sample volumes should be selected in consultation with the laboratory to ensure that the samples obtained will provide the desired results.
- Unless noted otherwise, storm water samples will be collected via direct grab methods.
- New disposable gloves shall be worn at each sampling location to prevent cross-contamination.
- The opening of sample bottles shall always be directed away from field personnel in an upstream direction.
- Sample containers with preservatives should not be used to collect storm water samples. If using containers with preservatives, a pre-cleaned container of similar type should be used to collect the sample with subsequent transfer to the preserved container.
- Field personnel shall leave an approximate one-inch air space in sample bottles (except for dissolved oxygen, BOD, and alkalinity samples, unless otherwise directed by the lab), so that bottles may be shaken (if needed) or frozen before analyses.
- Field personnel shall place sample bottles and temperature blanks (if required by project plan or QAM) in a cooler filled with ice.

Guidelines for Stream Sampling

- Sample once the duration and amount of rain is sufficient to produce runoff.
- Field personnel shall minimize disturbance to upstream waters and shall always sample water from the undisturbed upstream region. In addition, when wading in waterbodies, field personnel will try and disturb as little bottom sediment as possible.
- Sample collection shall precede the measurement of physical field parameters (such as turbidity, conductivity, dissolved oxygen, etc.) in order to minimize the risk of sediment disturbance and/or contamination.
- In absence of a project specific sampling protocol, stream grab samples are to be collected from beneath the water surface (at approximately 8 to 12 inches beneath the surface or mid-way between the surface and the bottom if the waterbody is shallow, (EPA 1997)). Samples will be collected at an appropriate distance from the stream bank (generally midstream) and away from submerged obstacles. Field personnel shall stand downstream of the desired sampling location, hold the bottle near its base, and plunge it below the water surface with the opening (mouth) downward.

5.0 QUALITY CONTROL

5.1 Field Duplicates

Field duplicate measurements of a single sample will be performed at the frequency specified in the project plan. Collection of duplicates will adhere to the methods described above. Field duplicates will be collected immediately following initial sample collection. Not all projects require field duplicates. If unsure, check with the project manager prior to placing a bottle order.

6.0 DOCUMENTATION

Storm water field data will be reported on field sheets or in field notebooks by ESS personnel. Laboratory data will be reported on official laboratory letterhead. Any unanticipated site-specific information, which requires field personnel to deviate from the above SOG will be reported on field sheets or in a field notebook. Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Name or initials of person conducting the measurement or collection
- Sample identification/station location
- Comments/observations

Photographic evidence of storm water flows is also desirable and may be required for certain projects. Additionally, storm total maps and/or hourly precipitation records should be saved to the project folder for a period extending from 72 hours prior to end of the selected storm event.

7.0 TRAINING/QUALIFICATIONS

To properly perform the storm water sampling, the analyst must be familiar with the sampling protocols as stated in this SOG.

8.0 REFERENCES

EPA, 1997. Volunteer Stream Monitoring: A Methods Manual. United States Environmental Protection Agency. Office of Water. EPA 841-B-97-003.

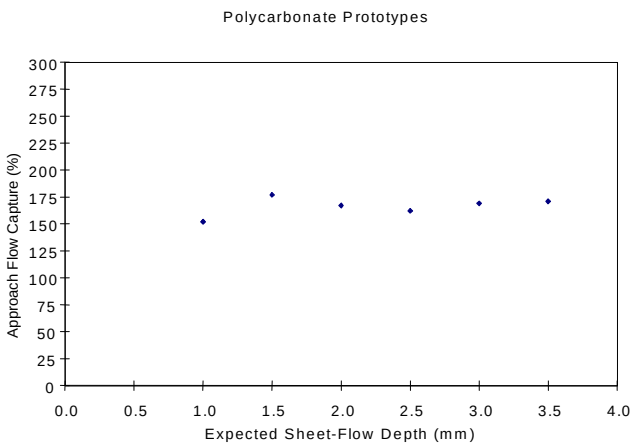
GKY FirstFlush *Sampler*

U.S. Patent Number 5,847,292 dated December 8, 1998

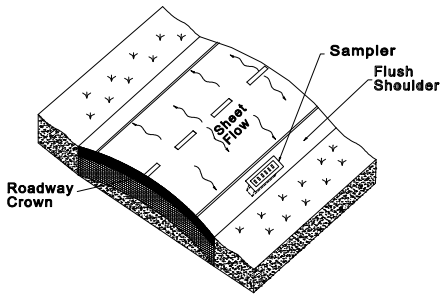
Inventors: G. Ken Young, Frank R. Graziano, Stuart M. Stein

Developed under the Small Business Innovative Research Program (SBIR) in conjunction with the Federal Highway Administration (FHWA), the **GKY FirstFlush Sampler** will make compliance with NPDES regulations easier and at much less expense than current sampling methods. Consider the following advantages of the **GKY FirstFlush Sampler**:

- It's small (roughly 230 mm x 430 mm x 150 mm), inexpensive, and expendable;
- It can be easily configured to capture different runoff volumes that are *exactly representative* of the entire pavement section (not a sample of the runoff);
- It captures runoff at a relatively constant rate regardless of the sheetflow depth (within expected ranges);
- Because of the constant rate of capture, our sampler also provides a theoretical estimate of the rainfall depth based on the captured volume;
- It is unobtrusive and entirely passive;
- The collection vessel is itself the sample container for shipment to the lab for analysis; and
- It requires no calibration or special skills to install and maintain.



Measured Capture Efficiency



Typical Application

The **GKY FirstFlush Sampler** is made entirely of plastic, keeping costs low. The grate and insert sections are manufactured from glass-filled polycarbonate (strong and durable) and the sample receptacle from high-density polyethylene (HDPE), a chemically compatible material that will not compromise the analytical results.

The principle of operation is simple; the constant capture efficiency (developed through extensive laboratory testing), allows the volume of the captured sample to be easily estimated:

$$Vol. = 6.35 D_{Runoff} L_{Flow} N_{Ports} Eff_{Ports}$$

Where :

Vol. = Required volume of sample, ml

D_{runoff} = Desired runoff capture depth, mm (i.e. 13 mm)

L_{Flow} = Runoff flow length, m

N_{ports} = Number of sample-ports

Eff_{Ports} = Sample-port capture efficiency

6.35 = Conversion factor

Given the length of the roadway section, you can simply select the number of sample-ports to leave open (maximum of 5) to tailor the sampling to meet your specific requirements. The included look-up charts will enable you to quickly and easily approximate how much volume is captured for a given rainfall depth and length of roadway.

For pricing or more information, call **(703) 870-7000** or e-mail **scoldren@gky.com**

CHAIN OF CUSTODY

PAGE_____ OF _____

WESTBORO, MA
TEL: 508-898-9220
FAX: 508-898-9193

MANSFIELD, MA
TEL: 508-822-9300
FAX: 508-822-3288

Date Rec'd in Lab:

ALPHA Job #:

Client Information

Client:

Address:

Phone:

Fax:

Email:

❑ These samples have been previously analyzed by Alpha

Project Information

Project Name:

Project Location:

Project #:

Project Manager:

ALPHA Quote #:

Turn-Around Time

❑ Standard ❑ RUSH *(only confirmed if pre-approved!)*

Date Due: **Time:**

Report Information - Data Deliverables

❑ FAX ❑ EMAIL

❑ ADEx ❑ Add'l Deliverables

Billing Information

❑ Same as Client info PO #:

Regulatory Requirements/Report Limits

State /Fed Program	*Criteria*

Other Project Specific Requirements/Comments/Detection Limits:

ANALYSIS

SAMPLE HANDLING

*Filtration*_____
❑ Done
❑ Not needed
❑ Lab to do

Preservation
❑ Lab to do
(Please specify below)

TOTAL # BOTTLES

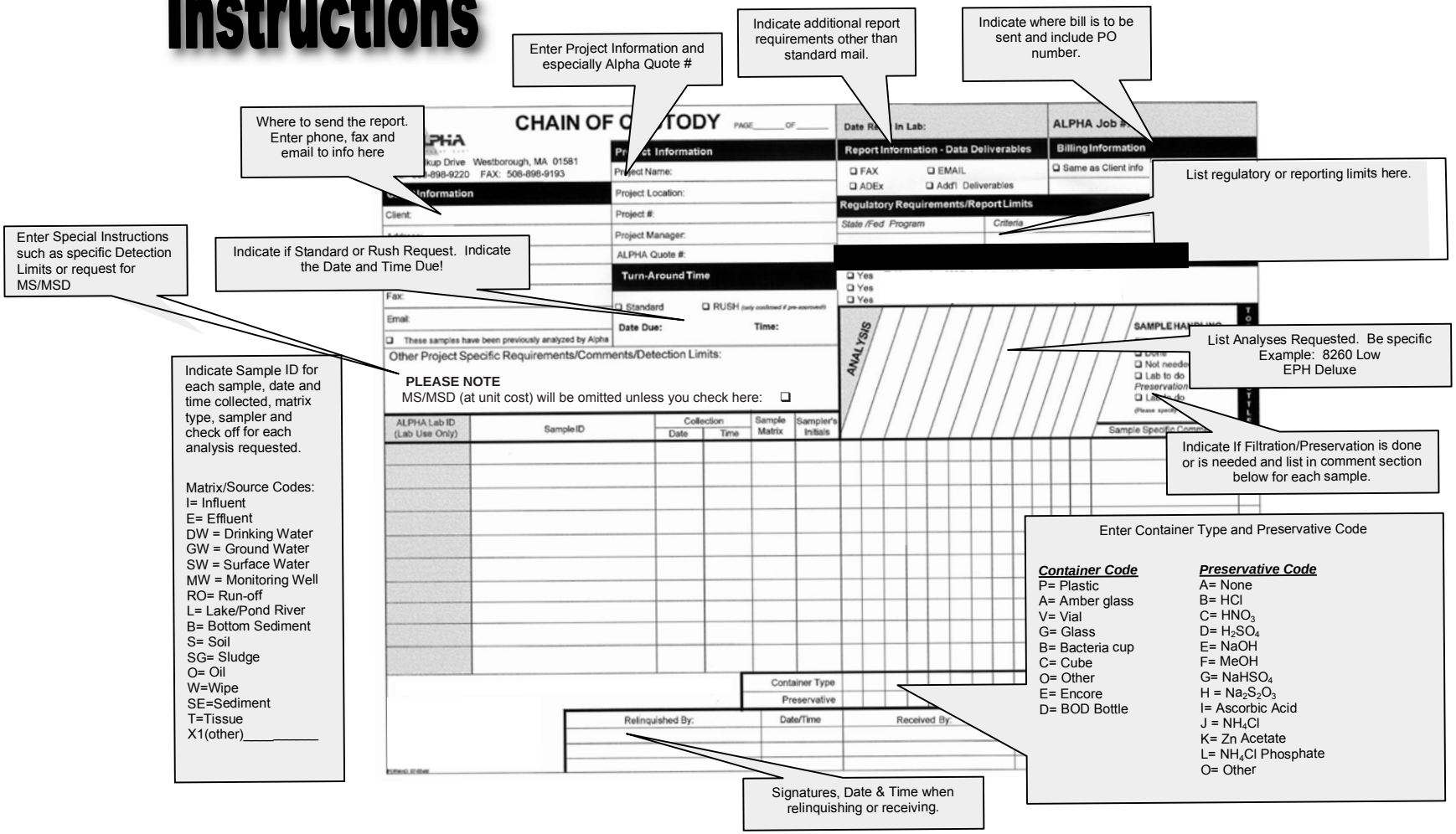
ALPHA Lab ID (Lab Use Only)	Sample ID	Collection Date	Collection Time	Sample Matrix	Sampler's Initials	Sample Specific Comments

Container Type	
Preservative	

Relinquished By:	Date/Time	Received By:	Date/Time

Please print clearly, legibly and completely. Samples can not be logged in and turnaround time clock will not start until any ambiguities are resolved. All samples submitted are subject to Alpha's Terms and Conditions. See reverse side.

Instructions



Terms & Conditions: In the absence of a written agreement to the contrary, this order constitutes an acceptance by the Client of Alpha Analytical, Inc. (ALPHA)'s offer to do business under these Terms and Conditions, and agrees to be bound by these conditions. Any terms and conditions from Client's that do not conform to the terms and conditions contained herein shall be deemed invalid and unenforceable, unless accepted in writing by ALPHA. This order shall not be valid unless it contains sufficient specifications to enable ALPHA to carry out the Client's requirements. Samples must be accompanied by: a) adequate instruction as to the quantity and type of analysis requested, and b) reporting and billing address information. Upon timely delivery of samples, ALPHA will use its best efforts to meet mutually agreed turnaround times, calculated from the point in time when ALPHA has determined that it can proceed with the defined work to be done (Sample Delivery Acceptance). ALPHA reserves the right, to refuse or revoke Sample Delivery Acceptance for any sample which in the sole judgment of ALPHA: a) is unsuitable volume; b) may pose a risk or become unsuitable for handling, transport or processing for any health , safety, environmental or any other reason; c) holding times cannot be met.

Client agrees to pay for all applicable charges to process this order. Payment in advance is required for all Clients except those whose credit has been established with ALPHA. For Clients with approved credit, payment terms are Net 30 days from the date of the invoice by ALPHA. All overdue payments are subject to an interest and service charge of one and one half percent (1.5%) (Or the maximum rate permissible by law, whichever is lesser) per month or portion thereof from the due date until the date of payment. ALPHA may suspend work and withhold delivery of data under this order at any time in the event that the Client fails to make timely payment of its invoices. Client shall be responsible for all costs and expenses of collection including reasonable attorney's fees. Data or information provided to ALPHA or generated by services performed under this agreement shall only become the property of the Client upon receipt in full by ALPHA of payment for the entire Order.

In no event shall ALPHA have any responsibility or liability to the Client for any failure or delay in performance by ALPHA which results, directly or indirectly in whole or in part, from any cause or circumstance beyond the reasonable control of ALPHA.

ALPHA shall dispose of the Client's samples 30 days after the analytical report is issued, unless instructed to store them for an alternate period of time or return such samples to the Client. The return of samples will be at the Client's own expense.

Total Solids in Solid and Semisolid Samples

(Percent Solids)

Reference Method: **SM 2540 G,** Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

1. Scope and Application

Matrices: Soils, solids and sludges.

Definitions: See Alpha Analytical Quality Manual

This method is applicable to the determination of total solids in such solid and semisolid samples as river and lake sediments, sludges separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other sludge dewatering processes.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results by completing an initial demonstration of capability

2. Summary of Method

A homogenized aliquot of sample is weighed in a tared dish and set in a 103° - 105°C oven until dry. The sample and dish are cooled and re-weighed, thus the percent of solids in the original sample can be calculated.

2.1 Method Modifications from Reference

Aluminum pans are used instead of porcelain dishes. However, if the sample is corrosive, then the porcelain dishes are used.

3. Reporting Limits

The Reported Detection Limit is 0.1%.

4. Interferences

4.1 Humidity: Humidity in the laboratory may cause samples to pick up moisture. When not being weighed, samples should be kept tightly capped or in a dessicator.

4.2 Large rocks / debris: Large rocks or debris may cause false high results and therefore should not be included in the sample aliquot.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents. Personal protective equipment is to be worn at all times within the laboratory areas. At a minimum, a labcoat, gloves and safety glasses are worn.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in glass or plastic containers with minimal headspace. Containers are covered immediately to minimize the loss of sample moisture.

6.2 Sample Preservation

Samples are refrigerated at 4 °C.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are kept refrigerated at 4 °C until the time of analysis.

For samples received, marked and commented as **Foreign Soils** reference SOP 2296 Treatment of Foreign Soils.

For samples received, marked and commented as **Containing or May contain Asbestos** reference WI 2535 Asbestos Handling Procedures.

7. Equipment and Supplies

7.1 Analytical Balance: Capable of weighing to 0.01g

7.2 Aluminum Weighing Dishes or Pans

7.3 Porcelain Evaporation Dishes

7.4 Dessicator: With a color-indicator dessicant.

7.5 Drying Oven: Capable of maintaining 103 – 105 °C.

7.6 Oven Trays

7.7 Computer: with connection to LIMS and the Analytical Balance (Sect. 7.1)

8. Reagents and Standards

None.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Not applicable.

9.2 Laboratory Control Sample (LCS)

Not applicable.

9.3 Initial Calibration Verification (ICV)

Not applicable.

9.4 Continuing Calibration Verification (CCV)

Not applicable.

9.5 Matrix Spike

Not applicable.

9.6 Laboratory Duplicate

One duplicate is analyzed per batch of 20 samples or less. Duplicate determinations must agree within 20%. If this criterion is not met, the sample and it's duplicate are reanalyzed.

If sample, used for batch duplicate, is non-homogeneous, then data may be reported with a narrative.

9.7 Method-specific Quality Control Samples

Not applicable.

9.8 Method Sequence

- Prepare evaporation dishes, if necessary.
- Generate a LIMS Batch
- Open the appropriate Excel Spreadsheet
- Record the Tare weights
- Homogenize sample
- Record the Gross weights
- Dry samples in the oven 2+ hours (samples logged with product ME-TS-2540 must be dried overnight.
- Cool samples in the dessicator
- Record the Net Weight (1)
- Dry samples again for 1+ hours unless samples were originally dried overnight.

Note: if samples are dried overnight, then one weight is used; drying overnight should be noted on excel format. This statement can be applied to all samples, except samples with state of origin ME.

- Cool samples in the dessicator
- Record the Net Weight (2)

- Save to LIMS

Note: Samples with state of origin ME must be logged using product ME-TS-2540; two weights are required to prove constant weight, all samples must be dried overnight.

10. Procedure

10.1 Equipment Set-up

10.1.1 LIMS Knowledge: Prior to utilizing this SOP, the analyst must first be familiar with the operation of the Laboratory Information Management System (LIMS) and the generation of a sample batch or workgroup.

10.1.2 Porcelain Dish Preparation: Porcelain evaporation dishes are used only if a sample is corrosive to aluminum. To prepare the porcelain dishes, bake them in the 103 – 105 °C drying oven for a minimum of 1 hour before placing them in the dessicator. Cool in the dessicator for a minimum of one hour.

10.2 Initial Calibration

Not applicable.

10.3 Equipment Operation and Sample Processing

10.3.1 Generating a LIMS Batch

Utilizing the computer (Sect. 7.7), generate a LIMS batch of samples and assign a Workgroup (WG) number to the batch. When generating the batch, choose a sample that will be duplicated. Print out a copy of the LIMS batchsheet.

10.3.2 Using the Excel Spreadsheet

10.3.2.1 Ensure that the Balance Software Wedge is open. Do this by clicking on the "Balance" icon on the Desktop, and then minimize the window that appears. This will open the lines of communication between the balance and the computer.

10.3.2.2 To open the WetChem Excel sheets, click on the the "Shortcut to Wetchem" icon on the Desktop.

10.3.2.3 Open the sheet entitled "TS_S.xlt.

10.3.2.4 Input the following information into the appropriate spaces on the Excel sheet: The WG number (as assigned in Section 10.3.1), the Chemist's initials, the date and the time.

10.3.2.5 Click on the "Get Samples" button on the Excel Sheet.

10.3.2.6 The Samples assigned to the WG number will be uploaded onto the Excel Sheet. However, verify that the Samples uploaded are the same samples that were printed on the LIMS batchsheet in Section 10.3.1.

10.3.3 Write the sample ID's on the weighing dishes (either aluminum or prepared porcelain dishes).

10.3.4 Taking the Tare Weight

10.3.4.1 On the Excel Sheet, click on the cell for the "Tare" weight for the appropriate sample.

10.3.4.2 Weigh the corresponding empty dish on a tared balance. When the weight is stable, push the "Print" button on the balance. This will transfer the weight of the empty dish into the Excel Sheet.

10.3.4.3 Repeat Sections 10.3.4.1 and 10.3.4.2 until the weight of all of the empty dishes has been recorded on the Excel Sheet.

10.3.5 Taking the Gross Weight

10.3.5.1 Homogenize the sample by mixing with a spatula or spoon.

10.3.5.2 Remove a 5 – 10g aliquot of soil sample or 20 – 25g of a sludge sample and place it in the weighing dish.

10.3.5.3 Click on the cell for the "Gross Weight" corresponding to the sample to be weighed.

10.3.5.4 Zero the balance. Weigh the dish plus the sample. When the weight is stable, push the "Print" button on the balance. This will transfer the weight into the Excel Sheet.

10.3.5.5 Place the dish onto an oven tray.

10.3.5.6 Repeat Sections 10.3.5.1 through 10.3.5.5 until all of the samples have been weighed.

10.3.5.7 Once the samples have all been weighed and the weights recorded in the Excel Sheet, click on "File" then on "Save As". Type in the WG number from the LIMS batchsheet (generated in Section 10.3.1) as the filename. Then click "OK". The batch has been saved under the WG number in the "My Documents" folder.

10.3.6 Drying the Samples : Phase I

10.3.6.1 Place the oven tray in the 103 – 105 °C drying oven.

10.3.6.2 After a minimum of two hours (samples with state of origin ME must be dried overnight), if samples appear dry, move the oven tray of dried samples to a dessicator. Allow to cool completely.

10.3.7 Taking the First Net Weight

10.3.7.1 Open the "My Documents" folder by clicking on the icon on the Desktop.

10.3.7.2 Select the WG number of the batch you are going to weigh. This will open the Excel Sheet. Verify that the correct batch sheet has been opened.

10.3.7.3 Click on the cell for the "Net Weight(1)" corresponding to the sample to be weighed.

10.3.7.4 Zero the balance. Weigh the dish plus the sample. When the weight is stable, push the "Print" button on the balance. This will transfer the weight into the Excel Sheet.

10.3.7.5 Repeat Sections 10.3.7.3 and10.3.7.4 until the Net Weight (1) for all samples has been recorded.

10.3.7.6 Click on the "Save" button to save the weights.

10.3.7.7 If samples have been dried overnight, type "Dried Overnight" in the comments field and proceed to Section 10.3.10.

10.3.8 Drying the samples : Phase II

10.3.8.1 If the Net Weight of the samples is taken on the same day as the Gross Weight, the tray of samples must be placed back in the 103 – 105 °C drying oven for a minimum of one hour.

10.3.8.2 After drying, move the oven tray of samples to a dessicator. Allow to cool completely.

10.3.9 Taking the Second Net Weight

10.3.9.1 Open the "My Documents" folder by clicking on the icon on the Desktop.

10.3.9.2 Click on the WG number of the batch you are going to weigh. This will open the Excel Sheet. Verify that the correct batch sheet has been opened.

10.3.9.3 Click on the cell for the "Net Weight(2)" corresponding to the sample to be weighed.

10.3.9.4 Zero the balance. Weigh the dish plus the sample. When the weight is stable, push the "Print" button on the balance. This will transfer the weight into the Excel Sheet.

10.3.9.5 Repeat Sections 10.3.9.3 and 10.3.9.4 until the Net Weight (2) for all samples has been recorded.

10.3.9.6 Click on the "Save" button to save the weights.

10.3.9.7 If Net Weight (1) and Net Weight (2) are within 4% or 50mg, the Excel Spreadsheet will display the word "Acceptable" in the far right column next to the appropriate sample. If "Acceptable" is displayed for all samples in the batch, proceed to Section 10.3.10.

10.3.9.8 If Net Weight (1) and Net Weight (2) are <u>not</u> within 4% or 50mg, repeat Sections 10.3.8 and 10.3.9 for those samples. This will allow the chemist to record a Net Weight (3), (4) or (5), until the word "Acceptable" is displayed in the far right column next to the appropriate sample.

If the samples have been dried $\geq$ 24 hours, and the weights are still not within 4% or 50mg, consult the Department Supervisor as to how to proceed.

10.3.10 Saving the Batch

10.3.10.1 Click on the "Save" button to save the weights in the Excel sheet.

10.3.10.2 Click on the "Save to LIMS" button on the spreadsheet.

10.4 Continuing Calibration

Not applicable.

10.5 Preventative Maintenance

The temperature of the laboratory ovens is recorded constantly on a circular chart recorder. The chart recorder and the laboratory ovens are calibrated on an annual basis by an instrument service company. Certificates are kept on file.

Analytical balances are calibrated on a semi-annual basis by an instrument service company. Certificates are kept on file. The calibration of the balances is verified on a daily basis and records are kept in a Logbook.

11. Data Evaluation, Calculations and Reporting

The Excel Spreadsheet is programmed to calculate the Percent Solids results. This is the formula that is used for calculation:

$$\% \text{ Total Solids} = \frac{(A - B)}{(C - B)} \times 100$$

Where: A = Final Net Weight (weight of dried residue + dish, g)
B = Tare weight (weight of dish, g)
C = Initial Gross Weight (weight of wet sample + dish, g)

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Improper preservation is noted on the Sample Delivery Group form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Unless the containers are labeled as hazardous material (i.e. low flashpoint, ignitable, containing asbestos or high levels of toxic materials), the dried samples are disposed of into the trash.

If sample containers are labeled as hazardous, refer to the Chemical Hygiene Plan for waste handling and disposal instructions.

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

WI 2535 Asbestos Handling Procedures

SOP 2296 Treatment of Foreign Soils

16. Attachments

None.

Alkalinity, Titration Method

Reference Methods: **Method 2320 B.** Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

1. Scope and Application

Matrices: This method is applicable to water matrices.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

The alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000mg calcium carbonate ($CaCO_3$)/L.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used, and for total alkalinity a pH of 4.5 is used for the end-point.

When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. Carbon dioxide concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. "Phenolphthalein alkalinity" is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator used in the determination.

The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids.

It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations, especially at a pH > 10.

2.1 Method Modifications from Reference

The reporting limit for this method is less than that in the Reference Method.

0.02N NaOH (Sodium Hydroxide) is used for LCS instead of 0.05N Na_2CO_3 (potassium carbonate) for LCS. All reagents are commercially prepped and have certificate of analysis.

3. Detection Limits

The laboratory follows the procedure found in 40CFR Part 136 to determine the MDL on an annual basis. The method detection limits determined by the laboratory are on file for review.

The reported detection limit is 2.0 mg/L.

4. Interferences

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let the electrode come to equilibrium or clean the electrode between samples.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Samples for alkalinity analysis are collected in exclusive plastic or glass bottles, with alkalinity as the only analysis from the bottle. The bottles are filled completely, without any headspace, and capped tightly. The sample container is not opened until the time of analysis.

6.2 Sample Preservation

Store at 4 ± 2°C.

6.3 Sample Handling

The sample holding time is 14 days from collection. Initial sample pH measurement is documented during the beginning of alkalinity analysis. The pH results are included on the printout with the Alkalinity data.

7. Equipment and Supplies

7.1 T70 Mettler Toledo Titrator: With InMotion Flex Autosampler, terminal, and dosing units

7.2 Mettler Toledo Combination Electrode: Incorporates measuring and referenced functions; solid, gel-type filling material

7.3 Computer: with related accessories: LabX2014 software, version 6.1.0

7.4 Pipets: 1 mL, 5 mL glass volumetric

7.5 Plastic Cups: Mettler Toledo brand, 100 mL volume

7.6 KCl 3 mol/L electrolyte solution: Mettler Toledo brand for electrode or equivalent

7.7 50 mL conical centrifuge tubes

8. Standards and Reagents

8.1 Standard Sulfuric Acid, 0.1N: A commercially prepared standard solution which has been standardized against a NIST standard. A certificate of analysis is kept on file. Store at room temperature. Expires upon manufacturer's specified date.

8.2 Standard Sulfuric Acid, 0.02N: A commercially prepared standard solution which has been standardized against a NIST standard. A certificate of analysis is kept on file. Store at room temperature. Expires upon manufacturer's specified date.

8.3 Sodium Hydroxide Solution, 0.1N: A commercially prepared solution. A certificate of analysis is kept on file. Store at room temperature. Expires upon manufacturer's specified date.

8.4 Sodium Hydroxide Solution, 0.02N: A commercially prepared solution. A certificate of analysis is kept on file. Store at room temperature. Expires upon manufacturer's specified date.

8.5 pH Buffer Solutions: pH 4 and pH 10; two sources/Lot numbers of pH 7. Use to calibrate pH meter. Store at room temperature. Expires upon manufacturer's specified date.

8.6 Reagent Water: All reference to water in this method refer to Deionized Water (DI) from Alpha's water treatment system.

9. Procedure

9.1 Set-up

Calibrate the pH meter of the Mettler Toledo titrator each day prior to use. Follow the manufacturer's instructions for calibration, using pH 4, pH 7, and pH 10, buffer solutions, using method 1 in LabX2014 software. Validate the calibration by using a second source pH 7 buffer, using method 2 in LabX2014 software. The results must be within ± 0.05 pH units, otherwise recalibration is necessary.

9.2 Equipment Operation and Sample Analysis

9.2.1 Ensure rinse bottle is filled with DI water and the standard acid container is filled with sulfuric acid (8.2).

9.2.2 Open LabX2014 software and calibrate according to 9.1.

9.2.3 Record standards and reagents in log book and write down the analytical sequence.

9.2.4 After the calibration and pH check, purge any old acid and air bubbles from the burette using the "burette" tab by rinsing out the burette twice, using the LabX2014 software.

9.2.5 Using method 3 for total alkalinity or using method 4 for 2 step alkalinity, type in the sequence for analytical run. Right click on the appropriate method and click on create task. Name the sequence using the date and add the correct number of samples.

9.2.5.1 Always start analytical run with rinse, blank, and LCS and following with all samples, duplicate and matrix spike.

9.2.6 Label plastic cups (7.5) with marker in correct analytical sequence.

9.2.7 Shake samples and measure out 50 mL of sample into centrifuge tubes and then transfer to label cup and place them in the auto sampler.

9.2.8 Under tasks, click start to begin the analytical run.

9.2.9 After the analytical run is complete, print out results. The initial sample pH results are included on the data print out and are available upon request.

9.2.10 NOTE: Only 30 mL of titrant (8.2) may be used. If samples use more than 30 mL of titrant, sample dilution and reanalysis are required. Dilutions are prepared by using a known amount of standard acid (8.2) and then titration a smaller volume of sample.

9.3 Preventative Maintenance

9.3.1 The pH electrode is filled with electrolyte (7.7) and is replaced as necessary.

9.3.2 Prior to each analytical run, the auto titrator burette is checked and purged of any air bubbles present.

9.3.3 Auto titrator burette is checked quarterly by the QA department to ensure accuracy.

9.4 Calculations

9.4.1 Alkalinity, mg $CaCO_3$/L = $\frac{\mathbf{A} \times \mathbf{N} \times 50{,}000}{\text{mL sample}}$

where:

A = mL of the standard acid titrated
N = normality of the standard acid

9.4.2 **Calculation of Alkalinity Relationships:** The mathematical conversion of the results is shown in Table 1.

9.4.2.1 **Carbonate (CO_3) Alkalinity** is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

9.4.2.2 **Hydroxide (OH) Alkalinity** is present if phenolphthalein alkalinity is more than half the total alkalinity.

9.4.2.3 **Bicarbonate (HCO_3) Alkalinity** is present if phenolphthalein alkalinity is less than half the total alkalinity.

9.4.2.4 Carbon Dioxide (CO_2)

9.4.2.4.1 **Free CO_2** is present if the total Alkalinity of a water is due almost entirely to hydroxides, carbonates or bicarbonates, and Total Dissolved Solids is not greater than 500mg/L.

mg Free CO_2/L = $2.0 \times B \times 10^{(6-pH)}$

Where:

B = Bicarbonate alkalinity, mg $CaCO_3$/L

9.4.2.4.2 **Total CO_2** is calculated from the Free CO_2, bicarbonate alkalinity and carbonate alkalinity.

mg Total CO_2/L = $[A + 0.44 (2B + C)]$

Where:

A = mg free CO_2/L (Section 9.4.2.4.1)

B = Bicarbonate alkalinity, mg $CaCO_3$/L

C = Carbonate alkalinity, mg $CaCO_3$/L

Table 1: Alkalinity Relationships

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
P = 0	0	0	T
P < ½ T	0	2P	T – 2P
P = ½ T	0	2P	0
P > ½ T	2P – T	2 (T – P)	0
P = T	T	0	0

Key: P = Phenolphthalein Alkalinity

T = Total Alkalinity

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When the parameter tested fails at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test.

10.2 Method Blank

Analyze one method blank per batch of 20 samples or less. The blank consists of 50 mL of DI water (8.6). The blank results must be less than the reported detection limit. No samples may be analyzed until an acceptable blank is obtained.

10.3 Laboratory Control Samples (LCS)

Analyze one LCS per batch of 20 samples or less. A 100 ppm LCS is prepared by adding 5 mL of 0.02N sodium hydroxide solution (8.4) to 45 mL of DI water (8.6). The LCS must be recovered within control limits generated by QA. If the LCS falls outside of acceptance criteria, it is reprepared and reanalyzed. If failure continues, the titrator is rinsed and the LCS analyzed again. No samples may be analyzed until an acceptable LCS recovery is obtained.

10.4 Matrix Spike (MS)

Analyze one matrix spike per batch of 20 samples or less. A 100 mg/L spike is prepared by adding 1.0 mL of 0.1 N sodium hydroxide solution (8.3) to 50 mL of sample. The MS recovery must be within control limits. If the MS is outside of acceptance criteria, the sample and its spike are reanalyzed. If failure continues, report the data with a narrative to be included on the final report.

10.5 Duplicates

Analyze one sample in duplicate per batch of 20 samples or less. The %RPD between the sample and its duplicate must within control limits. If %RPD is outside of acceptance criteria the sample and its duplicate are reanalyzed. If failure continues, report the data with a narrative to be included on the final report.

10.6 Continuing Calibration

A continuing calibration verification (CCV) (equivalent to the LCS) and a continuing calibration blank (CCB) (equivalent to method blank) pair is analyzed at the end of each analytical run to ensure that calibration is still valid.

Acceptance criteria for the CCV are 90-110% of the true value. If the CCV fails these criteria, all samples in the associated batch are reanalyzed.

The CCB must be less than the RL of 2.0 mg/L. If the CCB fails these criteria but the associated sample concentrations are non-detect, the sample results are reported with a narrative. If the CCB fails these criteria but the associated sample concentrations are greater than 10x the reporting limit, the sample results are reported with a narrative. Otherwise, if the CCB fails, all samples in the associated batch are reanalyzed.

10.7 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

10.8 Analytical Sequence

10.8.1 **Calibration** with pH 4, pH 7, and pH 10 buffers

10.8.2 **Calibration verification** with second source pH 7 buffer

10.8.3 **Rinse** burette with fresh acid

10.8.4 **Analytical Run** Rinse, Blank, LCS, Samples, Duplicate, Matrix Spike, CCV, CCB

10.8.5 **Titrate** to the pH end point on the auto titrator

10.8.6 **Calculate** the results

11. Method Performance

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data must be within the specifications of the reference method or the analysis is not continued until corrective action is completed.

12. Corrective Actions

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Review of LCSs, blanks, spikes and duplicates occur for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the LCS recovery falls outside the designated acceptance range, the laboratory performance is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan for waste handling and disposal.

Total Suspended Solids Dried at 103-105°C

Total Volatile Suspended Solids Dried at 500°C

References: **SM 2540 D (for TSS) and SM 2540 E (for TVSS)**, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

1. Scope and Application

Matrices: This method is suitable for the determination of Total Suspended Solids (TSS) and Total Volatile Suspended Solids (TVSS) in potable, surface, and saline waters, as well as domestic and industrial wastewaters.

Definitions: Refer to Alpha Analytical Quality Manual.

"Solids" refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

"Total solids" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include "total suspended solids," the portion of total solids retained by a filter, and "total dissolved solids," the portion that passes through the filter.

"Fixed solids" is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called "volatile solids." Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

A well-mixed sample is filtered through a weighed standard glass-fiber filter, and the residue retained on the filter is dried to a constant weight. The increase in the weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, the difference between the total solids and the total dissolved solids may provide an estimate of the total suspended solids. Samples submitted for Total Volatile Suspended Solids analysis are also dried at a higher temperature to a constant weight.

2.1 Method Modifications from Reference

Filters are prepared and analyzed at 500°C.

Method specifies that duplicate determination should agree within 5% of their average weight; Alpha is using in-house control limits.

3. Reporting Limits

The RDL for both TSS and TVSS analysis is 5mg/L using 1000mL of sample and an analytical balance sensitive to 0.1mg. A lower RDL may be achieved by using a larger sample (more volume) or the use of a more sensitive balance.

Note: TSS-low method should be used for samples where client requested reporting limit lower than 5 mg/L. Reporting limit for low TSS-LOW method is 1.0 mg/L. Analyst must use 5 digit balances in order to achieve low reporting limit.

4. Interferences

4.1 Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing.

4.2 Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with widebore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

4.3 Exclude large, floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

4.4 Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis.

4.5 Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200mg residue.

4.6 For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material.

4.7 Prolonged filtration times resulting from filter clogging may produce high results due to increased colloidal materials captured on the clogged filter.

4.8 If the sample has high sediment/sand content, it is necessary to use a smaller volume for analysis. This will allow for a smooth transfer of the filter to the drying tin.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in glass or plastic bottles, provided that the material in suspension does not adhere to container walls.

Sampling, subsampling, and pipetting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling.

6.2 Sample Preservation

None.

6.3 Sample Shipping

No specific requirements.

6.4 Sample Handling

Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4 ± 2°C up to the time of analysis to minimize microbiological decomposition of solids. In no case hold sample more than 7 days. Bring samples to room temperature before analysis.

7. Equipment and Supplies

7.1 Drying Tins: Aluminum.

7.1.1 50mm diameter: For use with 47mm filter disks (Section 7.2)

7.1.2 140mL capacity: For use with 90mm filter disks (Section 7.2)

7.2 Glass-Fiber Filter Disks: 90mm and 47mm diameter, without organic binder, Type A/B, size 1.0um; use with drying tins from Section 7.1.

7.3 Filtration Apparatus: With a membrane filter funnel.

7.4 Side-arm Flask: Of sufficient capacity for sample size selected.

7.5 Dessicator: With a dessicant containing a color indicator of moisture concentration.

7.6 Drying Oven: For operation at 103 - 105°C.

7.7 Analytical Balance: Capable of weighing to 0.1mg. % digit balances (capable of weighting 0.01 mg) must be used for TSS-LOW method.

7.8 Magnetic Stirrer: With TFE stirring bar.

7.9 Wide-bore Pipets: Various volumes.

7.10 Graduated Cylinders: Glass or plastic at 100mL, 500mL, 1000mL volumes.

7.11 Muffle Furnace: Capable of 500°C.

7.12 Porcelain Crucibles

7.13 Tweezers: Flat tip, non-piercing.

7.14 Wax crayon or Sharpie pen

7.15 Vacuum Pump for use at filtration station

8. Reagents and Standards

8.1 Reagent Water: Deionized (DI) water.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank

Filter one blank of 1000mL of DI water per batch of 20 samples or less. Results must be less than the Reporting Limit (RL). If Blank results are less than 10 times the RL and the sample results are greater than 10 times the RL, the data is reported. If Blank results are greater than 10 times the RL, and there is sufficient sample volume remaining, the entire batch is reset and reanalyzed. A narrative is included with the report.

9.2 Laboratory Control Sample (LCS)

Not Applicable.

9.3 Initial Calibration Verification (ICV)

Not Applicable.

9.4 Continuing Calibration Verification (CCV)

Not Applicable.

9.5 Matrix Spike

Not Applicable.

9.6 Laboratory Duplicate

Filter one sample in duplicate per batch of 10 samples or less. Duplicate determinations should be within in-house control limits. Current control limits are ≤ 11% and may be re-evaluated. If acceptance criteria are not met, and there is sufficient sample volume remaining and sample is within holding time, the sample is reset. Otherwise, the data is submitted a narrative is included with the final report.

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- Prepare the filters.
- Weigh the clean filters, and/or drying tins.
- Filter the appropriate volumes of sample, and QC samples.
- Rinse the filter with DI water.
- Transfer the filter into to its corresponding drying tin.
- Total Suspended Solids are dried for a minimum of 2 hours in a 103 – 105 °C oven.
- Cool in a dessicator until temperature is constant.
- Weigh the filters until the weight change is less than 4% of the previous weight or 0.5mg, whichever is less.
- Total Volatile Suspended Solids are also dried for a minimum of 2 hours in a 500 °C muffle furnace.
- Cool in a dessicator until temperature is constant.
- Weigh the filters until the weight change is less than 4% of the previous weight or 0.5mg, whichever is less.
- Calculate results.

10. Procedure

10.1 Equipment Set-up

10.1.1 Preparation of Glass-Fiber Filter Disk

10.1.1.1 Attach a side-arm flask to the filtration apparatus.

10.1.1.2 Insert a glass-fiber filter disk (Section 7.2) with the wrinkled side up into the filtration apparatus.

Note: Record the manufacturer and lot number of the filter in the logbook.

10.1.1.3 Apply the vacuum, and wash the disk with three successive 20mL portions of DI water.

10.1.1.4 Continue the suction to thoroughly remove all traces of water, and discard washings.

10.1.1.5 Using tweezers, remove the filter from filtration apparatus and transfer to a drying tin (Section 7.1).

10.1.1.6 Dry the filter and tin in an oven at 103-105°C for at least two hours.

Note: For TVSS filters must be pre-washed and dried at 500°C for at least 2 hours.

10.1.1.7 Cool in a dessicator to a constant temperature, and weigh. Record the weights on the computer worksheet. Print a copy of the worksheet for later use in Section 10.3.

10.1.1.8 The dried filters may be used immediately, or stored in a dessicator until needed. Proceed to Section 10.3.

10.2 Initial Calibration

Not Applicable.

10.3 Equipment Operation and Sample Processing

10.3.1 Label drying tins with sample IDs. At the beginning of analysis, record the date/time/analyst's initials in the TSS Logbook. Write all the sample numbers to be analyzed into the TSS Logbook for use when sample filtration begins (from Section 10.3.4).

10.3.2 Assemble filtering apparatus with a prepared filter from Section 10.1.1, attach a side-arm flask and apply vacuum. Wet filter with a small volume of DI water to seat it

10.3.3 Selection of Sample Sizes

Choose a sample volume to yield between 10 and 200mg dried residue. If more than 10 minutes are required to complete filtration, it is necessary to use another prepped filter (from Section 10.1.1) with a decreased sample volume.

If Total Dissolved Solids are to be determined, collect the filtrate into a clean side-arm flask. Refer to SOP/2219.

10.3.3.1 **Clean samples:** Shake sample container to ensure a well-mixed solution prior to pouring. Use a graduated cylinder to measure sample volume. Begin with a sample volume of 100mL. Continue filtering successive volumes of 100mL until the desired volume of 1000mL is reached. However, if the filtration begins to slow in efficiency during this time, do not add any more additional sample.

10.3.3.2 **Samples containing sediment or other material:** Begin with a smaller sample volume. (An initially large volume of these types of samples will likely clog the filter and require reanalysis.)

10.3.3.2.1 These types of samples require initial stirring on a magnetic stirrer. While stirring, withdraw a volume of sample using a wide-bore pipet (Section 7.9). Pipet the sample onto the filter, and then while holding the pipet over the filter, rinse the pipet with DI water and filter this rinseate as well. This will ensure that all of the solid material is transferred to the filter.

10.3.3.3 **Sludge samples:** These samples are always pipetted to the filter as stated above in Section 10.3.3.2.1. A small sample size is desirable to prevent crust formation and filter curling during the drying step of the procedure.

10.3.4 Write the volume of sample filtered on the computer worksheet that was printed in Section 10.1.1.7. Write the volume of sample filtered in the Logbook next to the corresponding sample number, along with any necessary comments regarding matrix interference, limited volume, etc.

10.3.5 Wash with three successive 10mL volumes of DI water, allowing complete drainage between washings, and continue suction for about 3 minutes after filtration is complete.

10.3.6 Samples with high dissolved solids may require additional washings.

10.3.7 Using tweezers, carefully remove the filter from filtration apparatus and transfer to the corresponding, labeled drying tin.

10.3.8 Place the filter in the tin into a 103-105°C oven to dry for a minimum of 2 hours. Record the date, time in and the oven temperature in the laboratory notebook.

10.3.9 After drying, remove tin from the oven to cool in a dessicator to a constant temperature. Record the date, time out and the oven temperature in the laboratory notebook.

10.3.10 Weigh the tin on an analytical balance. Record the weights on the computer worksheet, and the sample volumes filtered as written down from Section 10.3.3. Enter the sample volumes from the logbook onto the computer worksheet discussed in Section 10.1.1.7.

10.3.11 Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5mg, whichever is less. Record each weight on the computer worksheet.

10.3.12 Total Volatile Suspended Solids

10.3.12.1 If TVSS analysis is requested, using tweezers, transfer the filter from the drying tin to a labeled crucible.

10.3.12.2 Place the crucible into a 500°C muffle furnace for a minimum of 2 hours, and record the date, time in, and the oven temperature in the laboratory notebook. Following removal from muffle furnace, place in a dessicator to cool to a constant temperature. Record the date, time out and the oven temperature in the laboratory notebook.

10.3.12.3 Using an analytical balance, tare a clean drying tin. Remove the filter from the crucible with tweezers and transfer the filter to the drying tin.

10.3.12.4 Record the weights on the computer worksheet.

10.3.12.5 Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight c

10.3.12.6 wehange is less than 4% of the previous weight or 0.5mg, whichever is less. Record each weight on the computer worksheet.

10.4 Continuing Calibration

Not Applicable.

10.5 Preventive Maintenance

10.5.1 Prior to each use, the filtering apparatus is rinsed thoroughly with DI water.

10.5.2 As needed, the filtering apparatus is washed in the industrial dishwasher.

10.5.3 As necessary, wipe the inside of the filtering apparatus with a paper towel and then rinse thoroughly with DI water

10.5.4 Ensure that there is an adequate supply of oil in the vacuum pump.

10.5.5 Monitor automated data logger system twice daily for temperature of oven.

11. Calculations

$$\text{mg TSS / L} = \frac{(\mathbf{A} - \mathbf{B}) \times 1000}{\text{sample volume, (mL)}}$$

where:

A = Final weight (weight of filter + dried residue, g)
B = Initial weight (weight of clean filter, g)

$$\text{mg TVSS / L} = \frac{(\mathbf{G} - \mathbf{N}) \times 1000}{\text{sample volume, (mL)}}$$

where:

G = Final Weight at 105 °C (weight of dish + dried residue, g)
N = Weight at 500 °C (weight of dish + dried residue, g)

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance as outlined in Section 10.5.

Review of blanks and duplicate samples for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

The MDL for TSS and TVSS is a calculated value; therefore, the MDL studies are not performed.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734 and 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

Analysis of a weight-bearing, real-world sample is chosen to run four times in duplicate between two analysts (one of which must be a trained analyst), and the results must be within 10%.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

Analysis of a weight-bearing, real-world sample is chosen to run four times in duplicate between two analysts (one of which must be a trained analyst), and the results must be within 10%.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1734, 1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

16. Attachments

None.

Hot Block Digestion

For Aqueous Samples

Reference Methods: **EPA 200.7,** Code of Federal Regulations 40, Part 141 and Part 136, Revision 4.4, May 1994; **EPA 200.8,** Environmental Monitoring Systems Laboratory Office of Research and Development U.S. EPA Cincinnati, OH Rev 5.4; **Method 3005A,** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update I, 1992. **EPA 6010B,** SM2340B, Hardness by Calculation, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WPCF, 18th Edition. 1992; Method **6020** Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846 Draft Update UVA, May 1998.

1. Scope and Application

Matrices: This method is appropriate for the digestion of all influents, effluents, surface waters, monitoring wells, liquids, drinking waters, furnace metals and soluble metals.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

Aqueous samples and appropriate QC samples are poured into 50mL digestion cups. Acid is added to the cup and the samples are reduced at 90-95 °C. The samples are then brought up to a final volume of 50mL, and are ready for analysis by ICP or ICP-MS.

2.1 Method Modifications from Reference

Using 50mL for sample volume and final volume, not 100mL.

3. Reporting Limits

Reporting Limit information may be found in the analytical method SOPs.

4. Interferences

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents. This includes wearing personal protective equipment such as a lab coat, safety glasses, gloves and respirator (as necessary).

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in plastic bottles.

6.2 Sample Preservation

If samples are for soluble metals analysis, filtration must take place prior to preservation with 1:1 HNO_3 to a pH < 2. Soluble samples must be held at pH < 2 for at least 24 hours prior to digestion if not preserved at the time of filtration.

Samples for total metals analysis are preserved with 1:1 HNO_3 to a pH < 2. Non-potable water samples must be held at pH <2 for at least 24 hours prior to digestion if not preserved at the time of collection.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are stored at room temperature. Samples for soluble metals analysis should be filtered and preserved within 24 hours of collection.

6.4.1 **Sample Filtration for soluble metals:** Obtain a 250mL plastic bottle for each sample to be filtered plus one for the filter blank. Put preprinted labels on each bottle and place in glass jars of filtration apparatus. Screw caps on and attach filter funnel. Pour desired amount of sample into filter funnel and turn vacuum on. Filter blank uses DI water. Preserve samples and blank with 1:1HNO3 to a pH<2. Record in Sample Handling logbook.

7. Equipment and Supplies

7.1 Hot Block Apparatus: Calibrated annually by outside vendor to maintain sample temperature of 95°C.

7.2 Digestion cups: 50mL volume, polypropylene

7.3 Watch Glass: Polypropylene to cover the digestion cups during digestion.

7.4 Threaded Caps: To cover digestate following digestion

7.5 Volumetric Glassware: Various sizes of class A volumetric flasks and pipets, as needed

7.6 Whatman 41 Filters

7.7 pH Indicator Strips

7.8 Vacuum Filtration Apparatus: For filtering samples for soluble metals

7.9 0.45um Filter Funnel: 100mL volume

7.10 250mL plastic bottles

8. Reagents and Standards

8.1 Analytical Standards: All standards shall be prepared according to the appropriate method of analysis.

8.2 Trace Nitric Acid ($tHNO_3$)

8.2.1 Trace-grade $tHNO_3$: Store at room temperature in hood. Manufacturer's recommend expiration, if none then no expiration.

8.2.2 1:1$tHNO_3$: 500mL $tHNO_3$ diluted to 1 liter with DI water. Store at room temperature in hood. Manufacturer's recommend expiration, if none then no expiration.

8.3 Trace Hydrochloric Acid (tHCl)

8.3.1 Trace-grade tHCl: Store at room temperature in hood. Manufacturer's recommend expiration, if none then no expiration.

8.4 1:1tHCl: 500mL tHCl diluted to 1 liter with DI water. Store at room temperature in hood. Manufacturer's recommend expiration, if none then no expiration.

8.5 Deionized Water (DI)

8.6 Standard Spiking Solutions

Store at room temperature. Standards expire upon manufacturer's specified date.

8.6.1 IPS: To a 500mL volumetric flask, add 100mL DI water and 25mL of tHNO3. Add 50.0mL of the well-shaken, room temperature, ICP Spike Standard #1 (Section 8.5.5), 25.0mL of 1000ppm Antimony standard, and 2.5mL of 1000ppm Cadmium standard. Bring to volume with DI water.

0.5mL of this solution per 50mL of sample volume will yield the following concentrations in the spiked sample: 2ppm Aluminum, 2ppm Barium, 0.05ppm Beryllium, 0.2ppm Chromium, 0.5ppm Cobalt, 0.25ppm Copper, 1.0ppm Iron, 0.5ppm Manganese, 0.5ppm Nickel, 0.05ppm Silver, 0.5ppm Vanadium, 0.5ppm Zinc.

8.6.2 **FPS**: To a 500mL volumetric flask, add 200mL of DI water and 25mL of tHNO3. Add 3mL of the well-shaken, room temperature ICP Spike Standard #3 (Section 8.5.6) and add 25mL of1000ppm Lead standard. Bring to volume with DI water.

0.5mL of this solution per 50mL of sample volume will yield the following concentrations in the spiked sample: 0.12ppm Arsenic, 0.05ppm Cadmium, 0.12ppm Selenium, 0.12ppm Thallium, and 0.51ppm Lead.

8.6.3 **MIX:** To a 500mL volumetric flask add 50mL of DI water and 25mL of tHNO3. Add50mL of each of the following stock standards: 1000ppm Boron, 10,000ppm Calcium, 10,000ppm Magnesium, 1000ppm Molybdenum, 10,000ppm Potassium, 1000ppm Strontium, 10,000ppm Sodium, 1000ppm Titanium, and 1000ppm Tin. Bring to volume with DI water.

0.5mL of this solution per 50mL of sample volume will yield the following concentrations in the spike sample: 1.0ppm Boron, 10ppm Calcium, 10ppm Magnesium, 1.0ppm Molybdenum, 5ppm Potassium, 1.0ppm Strontium, 10ppm Sodium, 1.0 Titanium.

8.6.4 **1000ppm Standards of individual metals**

8.6.5 ICP Spike Standard #1: Purchased commercially prepared, with a certificate of analysis. Contains the following: 2000ppm Aluminum, 2000ppm Barium, 50ppm Beryllium, 200ppm Chromium, 500ppm Cobalt, 250ppm Copper, 1000ppm Iron, 500ppm Manganese, 500ppm Nickel, 50ppm Silver, 500ppm Vanadium, 500ppm Zinc.

8.6.6 ICP Spike Standard #3: Purchased commercially prepared, with a certificate of analysis. Contains the following 2000ppm Arsenic, 50ppm Cadmium, 500ppm Lead, 2000ppm Selenium, 2000ppm Thallium.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A minimum of one blank must be digested for every sample batch of 20 samples or less.

9.2 Laboratory Control Sample (LCS)

Use 50mL of DI water. Add 0.5mL each of IPS Spiking Solution (Section 8.5.1), FPS Spiking Solution (Section 8.5.2), and MIX Spiking Solution (Section 8.5.3). If the desired metal is not included in the spiking solution, add 50uL of desired metal standard stock 1000ppm solution. An LCS must be digested for every sample batch of 20 samples or less.

9.3 Initial Calibration Verification (ICV)

Not applicable to this preparatory method.

9.4 Continuing Calibration Verification (CCV)

Not applicable to this preparatory method.

9.5 Matrix Spike

A matrix spike is performed for each sample matrix. A minimum of one matrix spike must be analyzed for each batch of ten (10) or less wastewater or drinking water samples to be digested for methods 200.7 and 200.8. A minimum of one matrix spike shall be performed for each batch of twenty (20) or less groundwater or monitoring well samples. Add 0.5mL each of IPS Spiking Solution (Section 8.5.1), FPS Spiking Solution (Section 8.5.2), and MIX Spiking Solution (Section 8.5.3). If the desired metal is not included in the spiking solution, add 50uL of desired metal standard stock 1000ppm solution.

9.6 Laboratory Duplicate

Each batch of ten (10) or less wastewater or drinking water samples to be digested for methods 200.7 and 200.8 will include a duplicate sample. A minimum of one sample duplicate shall be performed for each batch of twenty (20) or less groundwater or monitoring well samples.

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- Determine which samples will be used for batch QC
- Record sample pH adjustments if applicable for those samples to be analyzed for Methods 200.7 and/or 200.8
- Pour 50mL sample into a digestion cup
- Add spike solution to samples, as appropriate
- Add 1 mL of 1:1 tHNO_3 and 0.5 mL of 1:1 tHCl
- Heat on hot block at 90-95 °C until the volume evaporates down to 45mL and there is no further color change.
- Bring samples to 50mL volume with DI water. Filter any digestates containing sediment.

10. Procedure

10.1 Equipment Set-Up

10.1.1 Inspect all samples and determine QC duplicate (DUP) and matrix spike (MS). This decision is normally based upon client sample content history and analytes requested. The ideal sample for QC is one that has both ample volume and the most requested analytes of all the samples in the batch. Known field blanks or equipment blanks must be avoided for use as QC samples.

10.1.2 One spike and one duplicate must be performed per batch of twenty (20) or less groundwater or monitoring well samples. One spike and one duplicate must be performed for every ten (10) or less samples to be digested for Methods 200.7 and 200.8.

10.1.3 Each batch must have a Prep Blank Water (PBW) and a Laboratory Control Sample Water (LCS).

10.1.4 Sample Preparation for Digestion

10.1.4.1 Obtain one 50mL polypropylene digestion vessel for each sample and QC sample to be digested. Labelling of the the vessels at the time of digestion processing with the last 5 digits of the sample number across the top 1/3 of the cup and below write "T" for total metals, "S" for soluble metals. Additionally, if the sample is being re-prepped, note this on the vessel. All matrix spikes and LCSs get a black line on top of tube to indicate that it will be spiked.

10.1.4.2 Using the Electronic Lab Notebook (ELN), fill in appropriate spaces for date, analyst, products, acid type(s), MS/LCS spiking information. Place a pre-printed label with the lot numbers on the top right hand corner.

10.1.4.2.1 Place all samples on a lab cart, lined up in the order recorded in the logbook. Samples to be analyzed by Methods 200.7 and 200.8 must have the pH verified in the original container as being <2. Using a clean disposable transfer pipet, place a drop of sample onto a pH strip.

The pH results are recoded in the logbook with a mark be those below 2 and "no" for those that are above 2. If the sample pH is >2 preserve the sample in the original bottle with 1:1 HNO3 and hold for 24 hours before continuing with this method digestion.

10.1.4.2.2 Individually label a digestion vessel, shake and pour 50mL of each sample into a vessel. 50mL of DI water is used for the Blank (PBW) and LCS.

Any sample dilutions must be performed based upon initial knowledge of sample concentration or if the sample is soapy, opaque, darkly colored or foamy. Dilutions up to 10x are prepared directly in the digestion cup, utilizing the graduated markings as a guide. Otherwise, for dilutions > 10x, volumetric glassware is used.

10.1.4.2.3 Note the Color and Clarity of each sample in the appropriate columns in the laboratory notebook. Clarity is used to describe any sediment the sample may contain cloudiness or opaqueness.

10.1.4.2.4 Add 1 mL of 1:1 HNO3 and 0.5 mL of 1:1 HCl and place the sample in the digestion block preheated at 90-95 °C.

10.1.4.2.5 Hardness: If samples require Hardness analysis then perform the following:

10.1.4.2.5.1 Determine if there is any sediment in the sample. If there is none, then simply decant the sample into the cup without shaking.

10.1.4.2.5.2 If the sample does contain sediment and the only requested analyte is Hardness, then let the sample settle and decant only the top layer, avoiding the sedimentary layer.

10.1.4.2.5.3 If other analytes are requested on the sample, first decant 50mL off the top layer into a tube marked with the sample number and

"Ha" below. Then shake the sample and pour it into a second tube labeled with the sample number. The first tube will be used for the Hardness analysis, and the second tube will be used for the analysis of the other analytes requested.

10.1.4.2.6 Spike all matrix spikes and LCS samples with 0.5 mL of each IPS, FPS, and MIX spiking solutions. Additionally, 50µL of the any individual 1000ppm metal standard is added if the requested metal is not included in the spiking solutions.

10.1.4.2.7 Heat samples at evaporate the samples down to 45 mL and there is no further color change.

10.1.4.2.8 All Hot Block samples are brought up to a 50mL final volume.

10.2 Initial Calibration

Not applicable to this preparatory method.

10.3 Equipment Operation and Sample Processing

10.3.1 Sample Digestion

10.3.1.1 The sample cups are placed on the hot block set to a temperature of 95 +/-3 °C. Each cup is covered with a ribbed polypropylene watch glass and remains on the hot block until the volume evaporates down to 45mL and there no further color change. Record in the laboratory notebook the time sample digestion began and the time the samples are taken off the hot block unit. Record the hot block temperature in the logbook.

10.3.1.2 Upon completion of the digestion, the samples are removed from the hot block and allowed to cool to room temperature. For each tube, the ribbed watch glass cover must be rinsed with a small amount of DI water to incorporate any condensate back into the digestate. Samples are then brought up to a final volume of 50mL using DI water.

All digestates that are suspended sediment-free are capped and are ready for instrumental analysis. If any samples contain suspended sediment, they are filtered using a Whatman 41 filter. The sample is then capped and is ready for instrumental analysis.

10.4 Continuing Calibration

Not applicable to this preparatory method.

10.5 Preventative Maintenance

The Hot Block temperature is calibrated on an annual basis by an instrument service company. Certificates are kept on file.

11. Data Evaluation, Calculations and Reporting

Refer to the analytical method SOPs.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If any QC parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP #1732 MDL/LOD/LOQ Generation

SOP# 1739 IDC/DOC Generation

SOP# 1728 Waste Management and Disposal

16. Attachments

None.

Nitrate, Nitrite and Nitrate/Nitrite Nitrogen

Automated Cadmium Reduction Method

References: **Methods 353.2:** Methods for the Determination of Inorganic Substances in Environmental Samples, EPA 600/ R-93/ 100. August, 1993.

Methods 4500NO_3-F, 4500NO_2-B: Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

Method 10-107-04-1, Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, 1992.

1. Scope and Application

Matrices: This method is limited to optically clear water samples with a total concentration of nitrite and nitrate below 8mg N/L.

Definitions: See Alpha Laboratories Quality Manual Appendix A

In waters and wastewaters, the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas (N_2), are biochemically interconvertible and are components of the nitrogen cycle. They are of interest for many reasons.

Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. It does not include all organic nitrogen compounds. Analytically, organic nitrogen and ammonia can be determined together and have been referred to as "kjeldahl nitrogen," a term that reflects the technique used in their determination. Organic nitrogen includes such natural materials as proteins and peptides, nucleic acids and urea. Numerous concentrations vary from a few hundred micrograms per liter in some lakes to more than 20mg/L in raw sewage.

Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen. Nitrate generally occurs in trace quantities in surface water but many attain high levels in some groundwater. In excessive amounts, it contributes to the illness known as methemoglobinemia in infants. A limit of 10mg nitrate as nitrogen/L has been imposed on drinking water to prevent this disorder. Nitrate is found only in small amounts in fresh domestic wastewater but in the effluent of nitrifying biological treatment plants, nitrate may be found in concentrations of up to 30mg nitrate as nitrogen/L. It is an essential nutrient for many photosynthetic autotrophs and has been identified as a growth-limiting nutrient.

Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Such oxidation and reduction may occur in wastewater treatment plants, water distribution systems, and natural waters. Nitrite can enter a water supply system through its use as a corrosion inhibitor in industrial process water. Nitrite is the actual etiologic agent of methemoglobinemia. Nitrous acid, which is formed from nitrite in acidic solution, can react with secondary amines (RR'NH) to form nitrosamines (RR'N-NO), many of which are known to be carcinogens. The toxicologic significance of nitrosation reactions in vivo and in the natural environment is the subject of much current concern and research.

Within this SOP, organic nitrogen is referred to as organic N, nitrate nitrogen as NO_3^--N, and nitrite nitrogen as NO_2^--N.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the

laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Lachat Analyzer and in the interpretation of Lachat data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water-soluble dye has a magenta color, which is read at 520nm. Nitrite alone can be determined by removing the cadmium column. The nitrate is calculated as the difference between the reduced and non-reduced sample.

2.1 Method Modifications from Reference

Soils can be analyzed using 1:10 ratio soil to water extraction, following filtration.

3. Detection Limits

This method has an analytical range of 0.1 to 8.0mg N/L in the form of nitrate, and 0.05 to 8.0mg N/L in the form of nitrite.

The Reporting Limit is 0.1mg/L for Nitrate and 0.05 mg/L for Nitrite. Reporting limit is 1.0 mg/kg for soils.

4. Interferences

4.1 Suspended matter in the column will restrict sample flow.

4.2 For turbid samples, filter through 0.45µm membrane filter prior to analysis.

4.3 Low results would be obtained for samples that contain high concentrations of iron, copper or other metals. In this method, EDTA is added to the buffer to reduce this interference.

4.4 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. In this case, only the water phase of the sample is used for analysis and a narrative is submitted with the data. Dilutions are performed as necessary.

4.5 Residual chlorine can interfere by oxidizing the Cd column, reducing its efficiency. Prior to analysis, check wastewater and drinking water samples for residual chlorine and record results in the Laboratory Notebook. If residual chlorine is present, and the samples are preserved with H_2SO_4, the sample may be analyzed for NO_3/NO_2 determination. However, NO_2 must be performed by a manual method. If it is not possible to analyze NO_2 by a manual method, the result is reported as NA and a narrative is submitted.

4.6 Sample color interferes if it is absorbed at about 540nm.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Samples are collected in glass or plastic bottles; 250mL minimum volume. Soils can be collected in plastic or glass containers.

6.2 Sample Preservation

Refrigerate samples at 4 ± 2 °C.

For Nitrate/Nitrite analysis, the samples are preserved with 1:1 H_2SO_4.

6.3 Sample Handling

Begin NO_3^- and/or NO_2^- determinations promptly after sampling. If storage is necessary, store for up to 48 hours at 4 ± 2 °C.

NOTE: If the 48-hour hold time cannot be met, the sample is to be handled as follows, only in an emergency situation. These instructions are not to be used on a regular basis.

Prior to the expiration of the 48-hour hold time, the following three steps are executed:

1. A manually colored Nitrite test is performed by Method 354.2. Results are recorded in the Laboratory Notebook.
2. A 50mL aliquot of the sample is preserved to a pH of <2 with concentrated H_2SO_4. Preservation is recorded in the Laboratory Notebook.

Prior to analysis, within 14 days of preservation, the preserved sample is neutralized using 6N NaOH. The sample is analyzed using only the Lachat Instrument.

CAUTION! Samples must NOT be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

7. Equipment and Supplies

7.1 Lachat 8000 Automated Ion Analyzer or Lachat QuickChem 8500 Automated Ion Analyzer

7.2 Nitrate+Nitrite Lachat Board

7.3 Nitrite Lachat Board

7.4 Pre-packed Cadmium Columns: Available from Lachat.

7.5 Ottawa sand.

7.6 Disposable Culture Tubes 13x100 ml

7.7 Disposable pipettes.

8. Standards and Reagents

8.1 Stock Nitrate Standard, 1000mg N/L as NO_3^-: Purchased commercially prepared with certificate of analysis. Expires upon manufacturer's expiration date. There must be different manufacturers for calibration stock and ICV/LCS stock.

8.1.1 Stock Nitrate Standard, 200.0mg N/L as NO_3^-: Pipet 50mL of 1000ppm standard (Section 8.1) into 250mL volumetric flask and bring to volume with DI.

Alternately, in a 1L volumetric flask, dissolve 1.444g potassium nitrate (KNO_3) in about 600mL DI. Add 2mL chloroform. Dilute to the mark with DI and invert to mix. Refrigerate at 4±2°C. This solution is stable for six months.

8.2 Stock Nitrite Standard, 1000mg N/L as NO_2^-: Purchased commercially prepared with certificate of analysis. Expires upon manufacturer's expiration date. There must be different manufacturers for calibration stock and ICV/LCS stock.

8.2.1 Stock Nitrite Standard, 200.0mg N/L as NO_2^-: Pipet 50mL of 1000ppm standard (Section 8.2) into 250mL volumetric flask and bring to volume with DI.

Alternately, in a 1L volumetric flask, dissolve 0.986g sodium nitrite ($NaNO_2$) or 1.214g potassium nitrite (KNO_2) in approximately 800mL DI. Add 2mL chloroform. Dilute to the mark with DI and invert to mix. Refrigerate at 4±2°C. This solution is stable for six months.

8.3 Intermediate Nitrate Working Standard, 20 mg N/L as Nitrate: To a 250mL volumetric flask, add 25.0mL of the 200mg N/L NO_3^- stock standard. Dilute to the mark with DI and invert to mix. These solutions are stable for two weeks. Refrigerate at 4±2°C.

8.4 Intermediate Nitrite Working Standard, 20 mg N/L as Nitrite: To a 250mL volumetric flask, add 25.0mL of the 200mg N/L NO_2^- stock standard. Dilute to the mark with DI and invert to mix. These solutions are stable for two weeks. Refrigerate at 4±2°C.

8.5 Set of Six Calibration NO_3^- Standards, 8.0, 4.0, 1.00, 0.40, 0.20 and 0.1mg N/L as Nitrate: These standards are stable for 2 weeks. Refrigerate at 4±2°C.

To four 200mL volumetric flasks, add respectively: 8.0, 4.0, 1.0 and 0.4mL of the 200mg N/L NO_3^- stock standard. Bring to volume with DI water.

To two 200mL volumetric flasks, add respectively: 2.0 and 1.0mL of the 20mg N/L NO_3^- intermediate standard. Bring to volume with DI water.

Alternatively, an autodiluter can be used to make the standards during calibration, in which case only 8.0ppm and 1.0 ppm need to be manually prepared. If an autodiluter is used then it must be checked in an analytical tray by autodiluting 8.0mg N/L as Nitrite. The recovery for NO2 must be within 10% of the true value.

8.6 Set of Six Calibration NO_2^- Standards, 8.0, 4.0, 1.00, 0.40, 0.10 and 0.05mg N/L as Nitrite: These standards are stable for 2 weeks. Refrigerate at 4±2°C.

To three 200mL volumetric flasks, add respectively: 8.0, 4.0 and 1.0 of the 200mg N/L NO_2^- stock standard. Bring to volume with DI water.

To three 200mL volumetric flasks, add respectively:4.0, 1.0mL and 0.5mL of the 20mg N/L NO_2^- intermediate standard. Bring to volume with DI water.

Alternatively, an autodiluter can be used to make the standards during calibration, in which case only 8.0ppm and 1.0 ppm need to be manually prepared.

8.7 Ammonium Chloride Buffer, pH 8.5: In a 2L volumetric flask, dissolve 170g ammonium chloride (NH_4Cl) and 2.0g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA•2H_2O$) in about 800mL water. Dilute to the mark with DI water and invert to mix. Adjust the pH to 8.5 with concentrated ammonium hydroxide. This solution is prepared monthly and stored at room temperature.

8.8 Sulfanilamide Color Reagent: To a 2L volumetric flask add about 1200mL water. Then add 200mL of 85% phosphoric acid (H_3PO_4), 80.0g sulfanilamide, and 2.0g N-(1-naphthyl)ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark with DI water and invert to mix. Store in a dark bottle. This solution is stable for one month. Store at room temperature.

8.9 200ppm Nitrate Stock Standard, (for ICV/LCS): Pipet 50mL of 1000ppm standard (Section 8.1) into 250mL volumetric flask and bring to volume with DI. Store refrigerated at 4±2°C. Expires six months from preparation or upon manufacturer's expiration date.

8.10 200ppm Nitrite Stock Standard: Pipet 50mL of 1000ppm standard (Section 8.2) into 250mL volumetric flask and bring to volume with DI. Store refrigerated at 4±2°C. Expires six months from preparation or upon manufacturer's expiration date.

8.11 Initial Calibration Verification Standard (ICV)/Laboratory Control Sample (LCS): Store refrigerated at 4±2°C. Expiration is 2 weeks from date of preparation.

8.11.1 Nitrate LCS, 5.0ppm: Pipet 5.0mL of 200ppm stock (Section 8.9) into a 200mL volumetric flask and bring to volume with DI.

8.11.2 Nitrate ICV, 0.5ppm: Pipet 10.0mL of 5.0ppm standard (Section 8.11.1) into a 100mL volumetric flask and bring to volume with DI.

8.11.3 Nitrite LCS, 5.0ppm: Pipet 5.0mL of 200ppm stock (Section 8.9) into a 200mL volumetric flask and bring to volume with DI.

8.11.4 Nitrite ICV, 0.5ppm: Pipet 10.0mL of 5.0ppm standard (Section 8.11.3) into a 100mL volumetric flask and bring to volume with DI.

8.12 DPD Free Chlorine Reagent Powder Pillows: HACH brand, for 25mL sample. Store at room temperature. Expires upon manufacturer's expiration date.

8.13 1N Hydrochloric acid (HCL): To a 1L volumetric flask add about 600mL DI. Then add 83mL of concentrated hydrochloric acid (HCL) Stir to dissolve. Dilute to the mark with DI water and invert to mix. This solution is stable for six month. Store at room temperature.

8.14 1N Sodium Hydroxide (NaOH): To a 1L volumetric flask add about 600mL DI. Then add 40 g of sodium Hydroxide. Stir to dissolve. Dilute to the mark with DI water and invert to mix. This solution is stable for six month. Store at room temperature

9. Procedure

9.1 SET-UP

9.1.1 Preparation

9.1.1.1 Place the Nitrate+Nitrite board (containing the cadmium column) in Channel 1. Place the Nitrite board in Channel 2. Make sure the valve to the cadmium column is closed prior to starting to pump the reagents.

9.1.1.2 Commence pumping of reagents.

9.1.1.3 Once the lines are full of reagent and free of gas bubbles, open the valve to allow reagent to flow through the cadmium column.

NOTE: Be sure to switch the valve back before rinsing the manifold with DI water at the completion of the run.

NOTE: DO NOT LET AIR ENTER THE CADMIUM COLUMN.

9.1.2 Column Efficiency Procedure

9.1.2.1 Visually inspect the column. Check for air bubbles in the column or lines, gaps in the column or any change in the cadmium surface characteristics, (cadmium granules should be dark gray). If air bubbles are present in column, connect the column into the manifold, turn the pump on maximum and tap firmly with a screwdriver handle, being careful not to break the column, working up the column until all air is removed. If air cannot be removed, the column should be repacked. Cadmium columns should be stored filled with buffer. If air enters the column, efficiency will decrease. Check the flow efficiency by disconnecting the cadmium column from the manifold and reconnecting to a green pump tube. Pump buffer through the packed column and collect in a graduated cylinder. The flow rate with the column connected should be greater than 4.0 mL/minute.

9.1.2.2 **Column Efficiency – Slope Ratio Method:** Calibrate with the mid-range NO_3 –N standards. Calibrate with a matching concentration range of NO_2–N standards. The column efficiency is determined by the equation:

$$E = \frac{S_{NO3\text{-}N}}{S_{NO2\text{-}N}} \times 100$$

where:

$S_{NO3\text{-}N}$ = slope of NO_3 calibration
$S_{NO2\text{-}N}$ = slope of NO_2 calibration
E = % efficiency

9.1.2.3 Column Efficiency – Concentration Ratio Method: Calibrate with the mid-range NO_2-N and NO_3-N standards. Run a known concentration NO_2-N standard. Run a matching concentration NO_3-N standard. The column efficiency is determined by the following equation:

$$E = \frac{C_{NO3\text{-}N}}{C_{NO2\text{-}N}} \times 100$$

where:

$C_{NO3\text{-}N}$ = concentration of NO_3 standard
$C_{NO2\text{-}N}$ = concentration of NO_2 standard
E = % efficiency

9.1.2.4 Column Efficiency Result: If the efficiency is <75%, the column is repacked. All results are recorded and maintained on file in the QC department.

9.1.3 Residual Chlorine Screening

Check all wastewater and drinking water samples for residual chlorine prior to analysis.

9.1.3.1 Add 1 DPD Free Chlorine powder pillow (Section 8.12) to 25mL of sample in a centrifuge tube. An immediate color change to pink indicates residual chlorine is present. If residual chlorine is present, add a small amount of ascorbic acid to a sample aliquot (record this in logbook) and check for residual chlorine presence again. If residual chlorine remains, notify the Department Manager and/or the Laboratory Director. Results will be reported as Not Applicable (N/A).

If residual chlorine is not present, continue with sample analysis.

9.2 Initial Calibration

Calibrate the Lachat ion analyzer according to manufacturer's instructions.

9.2.1 Calibration

Two boards are used to calibrate the Lachat instrument. Each curve has seven calibration points. The correlation coefficient of each curve must be $\geq$0.995, otherwise recalibration is necessary. Prepare standard curves by plotting the peak areas of standards processed through the manifold against NO_3+NO_2 as N and NO_2 as N concentrations in standards.

9.2.1.1 Channel 1 is used to generate a calibration curve for Nitrate/Nitrite ranging from 0 to 8.0ppm.

9.2.1.2 Channel 2 is used to generate a calibration curve for Nitrite ranging from 0 to 8.0ppm.

Note: Instrument is calibrated daily, fixed calibration range is used; linearity is verified daily; three standards are used for linear calibration verification (low ICV (0.5 mg/l), High ICV (5.0 mg/l) and CCV (1.0 mg/l)). All standards must be within 10% of true value

9.2.2 Initial Calibration Verification (ICV)

9.2.2.1 Prior to sample analysis, the following ICVs must be analyzed to verify both calibration curves.

9.2.2.1.1 Nitrate ICV, 0.5ppm (Section 8.12.2)

9.2.2.1.2 Nitrate ICV, 5.0ppm (Section 8.12.1)
9.2.2.1.3 Nitrite ICV, 0.5ppm (Section 8.12.4)

9.2.2.1.4 Nitrite ICV, 5.0ppm (Section 8.12.3)

9.2.2.2 The results must be within ±10% of the true value, otherwise re-calibration is required.

9.3 Continuing Calibration Verification

9.3.1 Continuing Calibration Verification, (CCV) and Continuing Calibration Blank, (CCB)

9.3.1.1 At the beginning of the first tray, after every ten samples and at the end of every analytical sequence, a CCV and a CCB pair must be analyzed to verify both calibration curves.

9.3.1.1.1 1.0ppm Nitrate CCV (Section 8.5)

9.3.1.1.2 1.0ppm Nitrite ICV (Section 8.6)

9.3.1.1.3 Calibration Blank (DI)

9.3.1.2 The results of the CCVs must be within ±10% of the true value, otherwise re-calibration is required.

9.3.1.3 The results of the CCBs must be less than our standard limit of detection, otherwise the analysis is stopped and the problem corrected.

9.4 Equipment Operation and Sample Analysis

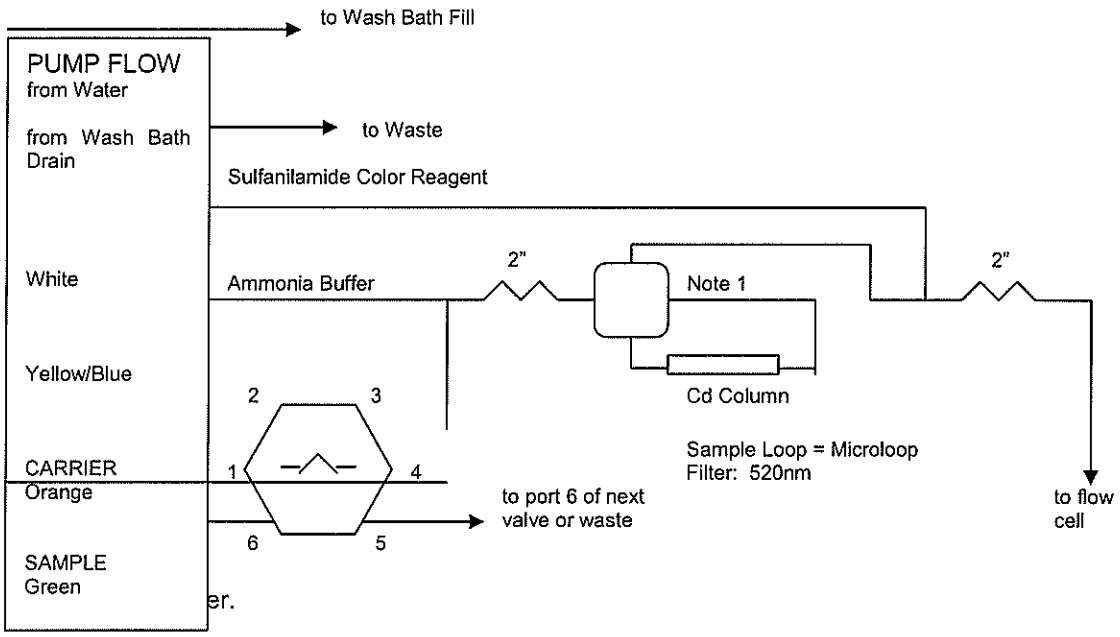
Follow the manufacturer's directions for the operation of the Lachat 8000.

All samples have to be inspected prior to analysis. Samples that are turbid or have sediment have to be filtered prior to analysis.
Check pH of the samples. If pH is less then 5 or greater then 9, then adjust pH using 1N Hydrochloric Acid (HCl) (8.13) or 1N Sodium Hydroxide (NaOH) (8.14). Record pH adjustment in the log book.

For soils: extract soils samples prior to analysis: take 5g of sample, add 50 ml of DI, extract for 30 min, then filter thorough 0.45 nm filter. Record all weights for calculations.

Note: if samples are filtered, then Method blank also have to be filtered

The Manifold Diagram follows:

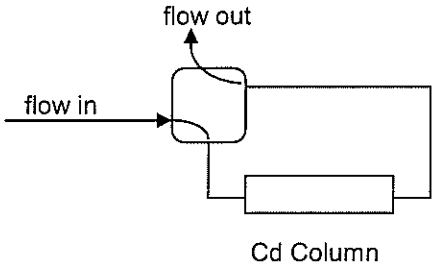


2" is 135cm of tubing on a 2-inch coil support.
APPARATUS: Standard valve, flow cell, and detector head modules are used.

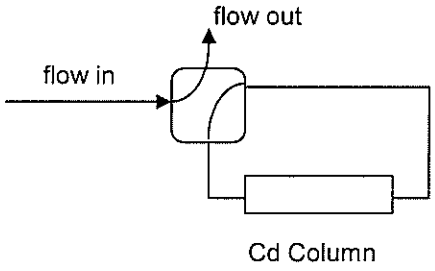
All manifold tubing is 0.8mm (0.032") i.d. This is 5.2µL/cm.

NOTE 1: This is a two-state switching valve used to place the cadmium column in line with the manifold.

State 1: Nitrate + Nitrite



State 2: Nitrite Only



9.5 Preventative Maintenance

Tubing is changed monthly or as needed.

At the end of each analytical sequence, the valve to the column is closed. DI is rinsed through the Lachat for five minutes followed by five minutes of air.

All maintenance is documented in the Instrument Maintenance Logbook.

9.6 Calculations

9.6.1 **Nitrate/Nitrite:** When the software is set up according to the manufacturer's recommendations, the concentration of nitrate plus nitrite in mg NO_3/NO_2-N/L is reported directly when the Cd column is included in the sample train in Channel 1.

9.6.2 **Nitrite:** When the software is set up according to the manufacturer's recommendations, the concentration nitrite in mg NO_2-N/L is reported directly when the Cd is not included in the sample train in Channel 2.

9.6.3 **Nitrate:** The concentration of nitrate is determined by the subtraction of the nitrite concentration, (Section 9.6.2 above), from the nitrate-nitrite concentration, (Section 9.6.1 above).

9.6.3.1 If the sample was preserved initially as described in Section 6.3, subtract the Nitrite value generated manually from the Nitrate/Nitrite value generated by the Lachat Instrument. This value is reported as the Nitrate result.

When the sample is preserved initially as described in Section 6.3, the value generated by the Lachat instrument for Nitrite is invalid and therefore disregarded.

9.6.4 If any sample exceeds a concentration of 8.0 mg/L, the sample must be diluted and re-analyzed. All sample concentrations must fall within the calibration curve.

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

10.2 Method Blank

One Method Blank is analyzed per batch of 20 samples or less The Method Blank consists of DI.

For soils: 5g of Ottawa sand extracted with 50 ml of DI. Results must be < 0.1mg/L. If this criterion is not met, the blank is re-analyzed. If there is still failure, the problem must be found and corrected prior to any sample analysis.

10.3 Calibration Verification and Laboratory Control Samples (LCS)

Two ICVs are analyzed at the beginning of the analytical sequence. One is at a concentration of 0.5ppm, and the other is at a concentration of 5.0ppm.

Both must be recovered within ± 10% of the true value. If these criteria are not met, the ICVs must be re-analyzed. If failure continues, the ICVs are to be re-made and/or a new calibration curve is to be generated.

The 5ppm ICV is reported as the LCS for the batch.

For soil LCS: 5g of Ottawa sand extracted with 0.25 ml of 1000 mg/l nitrate (8.1) (or 1000 mg/l Nitrite standard (8.2)) and 50 ml DI. The nitrate standard is used for spikes for Nitrate-N as well as Nitrate/Nitrite-N. LCS recoveries must be recovered within ± 10% of the true value. If these criteria are not met, LCS's must be re-analyzed. If failure continues, the batch has to be re-extracted and re-analyzed.

10.4 Matrix Spike

One Matrix Spike is analyzed per batch of 20 samples or less. Separate spikes are performed for Nitrate and Nitrite. In a 25mL volumetric flask, 0.5mL of 200ppm stock calibration standard (Section 8.1 or 8.2) is added to the sample. The final concentration of the matrix spike is 4.0ppm. The nitrate standard is used for spikes for Nitrate-N as well as Nitrate/Nitrite-N. The nitrite standard is used for spikes for Nitrite-N.

For soils: weigh 5.0 g of sample, add 2.0 ml of 200 mg/l Nitrate or Nitrite standard and 48 ml of DI. The final concentration of the matrix spike is 80.0 mg/kg. The nitrate standard is used for spikes for Nitrate-N as well as Nitrate/Nitrite-N. The nitrite standard is used for spikes for Nitrite-N.

% Recovery for the Matrix Spike must be within in-house control limits. If acceptance criteria are not met, the Matrix Spike is reanalyzed. If failure continues, a narrative is included with the data for inclusion on the Client report.

Note: For samples, analyzed by method **353.2** (NO2-353 and NO3-353) maximum batch size is 10 samples; every 10 samples required separate matrix spike (MS) to be analyzed. % Recovery for the Matrix Spike must be within +/- 10% of true value. If acceptance criteria are not met, the Matrix Spike is reanalyzed. If failure continues, a narrative is included with the data for inclusion on the Client report.

10.5 Duplicates

One Duplicate sample is analyzed per batch of 20 samples or less. A separate aliquot of the sample is analyzed for this purpose.

% RPD for the Duplicate must be within in-house control limits. If acceptance criteria are not met, the Duplicate is reanalyzed. If failure continues, a narrative is included with the data for inclusion on the Client report.

10.6 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

10.7 Analytical Sequence

- Calibration
- ICV/LCS – both levels
- Sample analysis
- CCV – every ten samples and at the end of the analytical sequence

11. Method Performance

11.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

11.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734 and 1739 for further information regarding IDC/DOC Generation.

11.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

11.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

12. Corrective Actions

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan for waste management and disposal.

Inductively Coupled Plasma - Atomic Emission Spectrometry

Reference Methods: **Method 6010C** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, February 2007.

SM 2340B, Hardness by Calculation, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

1. Scope and Application

Matrices: Digestates from all matrices.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludge, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion unless chemical interferants are suspected. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Metals Preparation SOPs for the appropriate digestion procedures.

Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths for the elements in clean aqueous matrices. Table 3 lists the Reported Detection Limits. The reported detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 9) is demonstrated.

Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is made by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic 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 inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used must be as free as possible from spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 4.0 must also be recognized and appropriate corrections made; tests for their presence are described in Section 9.4.4. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

This SOP includes the manual calculations for Total Hardness and Calcium Hardness, according to SM 2340B.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Refer to Table 3 for method Reporting Limits.

4. Interferences

4.1 Spectral

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans must be included in the correction algorithm. Off-line

spectral interferences are handled by including spectra on interfering species in the algorithm.

4.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

4.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that each instrument may exhibit somewhat different levels of interference. The interference effects must be evaluated for each individual instrument since the intensities will vary.

Major known interferences are Fe, Al, Ca, Mg, V, Ni, Cu, and Cr. To minimize any of these interferences, every analyte is analyzed on each instrument at or near its linear range and corrected for these interferences. This is done on an annual basis, and data is kept on file.

4.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending

upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear must be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users must not forget that some samples may contain uncommon elements that could contribute spectral interferences.

4.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

4.1.7 The primary wavelength for each analyte is based upon the instrument manufacturer's recommendations. An alternate wavelength is chosen if there is an indication of elevated background or overlap of another spectral wavelength. The wavelength for each analyte must be as free from interferences as possible.

4.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution must fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change must be determined and corrected and the correction factor updated. The interference check solutions must be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.1.9 When interelement corrections are applied, their accuracy must be verified, daily, by analyzing spectral interference check solutions. If the correction factor or multivariate correction matrices tested on a daily basis (by running a check solution on each analytical run) are found to be within 20% criteria for 5 consecutive days, analysis may be extended to a weekly basis. Also, if the nature of the samples analyzed is such that they do not contain concentrations of the interfering elements greater than the reported detection limit, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices are verified and updated on an annual basis or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. The standard solution must be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

4.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits, files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte

instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

4.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is >20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

4.2 Physical

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, using a peristaltic pump, use of an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 10.3.4.1 will help determine if a physical interference is present.

4.3 Chemical

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Additionally, if filtered samples are found to have an organic or sulfur like odor they are processed by heating after the addition of the acids to matrix match. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences must be recognized within an analytical run and suitable rinse times must be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample must be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit must be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse

period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

4.5 Other Interferences

4.5.1 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations must be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

4.5.2 **Silver** is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, spiked sample matrices and spiked blanks that do not undergo a complete digestion followed by analysis performed in a timely manner. Therefore, care should be taken when evaluating the sample digestate for silver chloride precipitation; if present a smaller sample aliquot should be selected for re-digestion and analysis.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in plastic bottles.

6.2 Sample Preservation

Samples for Total Metals are preserved with 1:1 Nitric acid to a pH of <2.

If samples are for Soluble Metals, they must not be preserved prior to filtration. They are preserved with 1:1 Nitric acid to a pH of <2 post-filter.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples to be analyzed for soluble metals, that have not been filtered, must be filtered and preserved within 24 hours of sample collection.

Preserved samples have a hold time of 6 months, and are stored at ambient temperature.

7. Equipment and Supplies

7.1 Inductively coupled argon plasma emission spectrometer:

- **Thermo Scientific ICAP Duo 6500 (Trace4, Trace5, Trace6)**

7.1.1 Computer-controlled emission spectrometer with background correction.

7.1.2 Radio-frequency generator compliant with FCC regulations.

7.1.3 Optional mass flow controller for argon nebulizer gas supply.

7.1.4 Optional peristaltic pump.

7.1.5 Optional Autosampler.

7.1.6 Argon gas supply - high purity.

7.2 Volumetric flasks of suitable precision and accuracy.

7.3 Volumetric pipets of suitable precision and accuracy.

8. Standards and Reagents

Reagent semiconductor and/or trace grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

8.1 Hydrochloric acid (conc), HCl. Stored at room temperature in acid resistant cabinet. Expiration date if defined by vendor.

8.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker. Stored at room temperature in polypropylene bottle, expiration date if defined by vendor..

8.3 Nitric acid (conc), HNO_3. Stored at room temperature in acid resistant cabinet. Expiration date if defined by vendor.

8.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker. Stored at room temperature in polypropylene bottle, expiration date if defined by vendor..

8.5 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

8.6 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All stock standards are ordered through ISO and American Association for Lab Accreditation vendors. All standards are in aqueous solutions and are generally at concentrations of 1000ppm and 10,000ppm.

8.7 Mixed calibration standard solutions

Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards must be prepared, as needed, with the realization that concentration can change on aging.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration must be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.
Additionally, sulfur standards are stand-alone single element standards and therefore are not to be combined in a mixed calibration standard solution.

8.8 Blanks

Two types of blanks are required for the analysis for samples. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

8.8.1 **The calibration blank** is prepared by acidifying reagent water to the same concentrations of the acids found in the standards. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations (see Sections 10.2 and 10.4). Refer to Section 10.4.1.2 for acceptance criteria and/or corrective actions.

8.8.2 **The method blank** must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. Refer to Section 9.1 for acceptance criteria and/or corrective actions.

8.9 The Initial Calibration Verification Standard (ICV) and the Continuing Calibration Verification Standard (CCV)

These ICV is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard. The CCV is prepared from the same source as the calibration standards and must be at a concentration near the mid-point of the calibration curve. At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV must be at a concentration near the mid-point of the calibration curve.

8.9.1 Low Level Initial Calibration Verification Standard (LLICV) and the Low Level Continuing Calibration Verification Standard (LLCCV)

These standards are actually a series of standards (typically 3) that are at or below the RL for the respective elements included in the calibration sequence. They are prepared from the same source as the calibration standards but at the laboratory's discretion may be from a second source from the calibration.

8.10 Interference Check Solution

These solutions are prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8.11 CRI

The CRI is an ICP standard that is analyzed at a concentration of 2 - 5 times each element's RDL. The CRI must be recovered within 70-130% of its true value. If the CRI does not meet these criteria, it is remade and reanalyzed. If the CRI fails a second time, the analysis is terminated, the problem determined and corrected. The instrument is then recalibrated.

CRI solutions are made for each type of instrument.

8.11.1 CRI Stock Standard Solution, for the TJA Trace instruments

To a 500mL volumetric flask, add 200mL DI water and 50mL of 1:1 HNO_3. Add the following volumes of each certified 1000ppm stock standard:

Pb	0.9 mL	Ni	1.6 mL
Se	0.4 mL	Ag	0.4 mL
Sb	2.0 mL	Tl	0.4 mL
As	0.4 mL	V	2.0 mL
Ba	0.8 mL	Zn	0.8 mL
Be	0.2 mL	Al	8.0 mL
Cd	0.2 mL	Ca	8.0 mL
Co	2.0 mL	Mg	8.0 mL
Cr	0.4 mL	B	2.0 mL
Cu	1.0 mL	Sr	0.4 mL
Fe	4.0 mL	Ti	0.4 mL

Mn	0.6 mL	Sn	0.4 mL
Mo	2.0 mL		

And the following volumes of each certified 10000ppm stock standard:

K	10.0 mL
Na	10.0 mL
Si	2.0 mL
S	2.0 mL

Bring to volume of 500mL with DI water. This solution expires 12 months after the date of preparation.

8.11.1.1 CRI Working Standard Solution

To a 1L volumetric flask, add 25mL of CRI Stock Standard Solution (Section 8.11.1). Bring to volume with DI water. This solution will contain elements in the following concentrations:

Pb	0.045 ppm	Ag	0.02 ppm
Se	0.02 ppm	Tl	0.02 ppm
Sb	0.10 ppm	V	0.10 ppm
As	0.02 ppm	Zn	0.04 ppm
Ba	0.04 ppm	Al	0.40 ppm
Be	0.01 ppm	Ca	0.40 ppm
Cd	0.01 ppm	Mg	0.40 ppm
Co	0.10 ppm	B	0.10 ppm
Cr	0.02 ppm	Sr	0.02 ppm
Cu	0.05 ppm	Ti	0.02 ppm
Fe	0.20 ppm	Sn	0.02 ppm
Mn	0.03 ppm	K	5.0 ppm
Mo	0.10 ppm	Na	5.0 ppm
Ni	0.08 ppm	Si	1.0 ppm
S	1.0 ppm		

8.12 Reporting Limit (RL) Verification Standard (LLICV/LLCCV)

The RL standard consists of a series of standards that are analyzed after the initial calibration verification (LLICV) and at the end of each run (LLCCV). Optionally, the LLCCV may be run every 10 samples with the CCV, CCB pair to eliminate the need for excessive reruns when low level instrument stability is questioned. These standards are at or below the RL included in the multi-point calibration sequence. The acceptance criteria are 70-130% to establish the RL for each analyte. The following standards are analyzed.

0.005 mg/L	Ag, As, Be, Cd
0.010 mg/L	B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sn, Sr, Ti, Tl, V
0.050 mg/L	Al, Sb, Fe, Zn, Ca, Mg, K, Na

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample.

The method blank results must be less than the reported detection limit (RDL) for all analytes of concern. If the results of the method blank exceed the RDL for any analyte, perform re-analysis of a new aliquot of the method blank.

If the results continue to exceed the RDL, proceed as follows:

If all of the samples for the analyte are non-detected, and the method blank is at or above the RDL, no action is required.

If one or more associated samples for that analyte have positive results at or above the RDL, those samples must be considered to be out of control, and are re-digested and reanalyzed.

9.2 Laboratory Control Sample (LCS)

Analyze one LCSW/SRM per sample batch. A LCS/SRM sample is a spiked volume of reagent water that is brought through the entire preparation and analytical process. The LCSW must have a % Recovery of ± 20% within the actual value or within vendor control limits (95% confidence limits) for the solid SRM.

If the LCSW or SRM % Recovery is outside the acceptable limits as stated in Table 2, or outside any vendor control limits, the LCS is rerun once. If upon reanalysis the LCS is still out of control, the failed analytes are re-prepped and re-analyzed. Otherwise, a nonconformance report form is raised to document the exact problem and this form is then authorized by the QA/QC Director and/or the Laboratory Manager(s).

9.3 Initial Calibration Verification (ICV)

For all analytes and determinations, the laboratory must analyze an ICV (Section 8.9), and a calibration blank (ICB, Section 8.8.1), immediately following daily calibration. The results of the ICV are to agree within 10% of the expected value; if not, re-analyze once, if still failing terminate the analysis, correct the problem, and recalibrate the instrument.

9.4 Continuing Calibration Verification (CCV)

A calibration blank (CCB, Section 8.8.1) and a calibration verification standard (CCV, Section 8.9) must be analyzed after every tenth sample and at the end of the sample run. Analysis of the calibration verification (CCV) must verify that the instrument is within 10% of the calibration with the relative standard deviation < 5% from replicate (minimum of two) integrations.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The batch sheet is noted. If the standard fails again, instrument maintenance must be performed and the CCV/CCB standard is reanalyzed. If the standard passes, then all samples run after the last passing CCV/CCB pair must be re-analyzed.

If the standard fails after instrument maintenance, the instrument is recalibrated. A new ICV/ICB is performed, and all previous data after the last passing CCV/CCB is reanalyzed.

9.5 Matrix Spike

Analyze matrix spike samples at a frequency of one per matrix batch. A matrix spike sample is a sample brought through the entire sample preparation and analytical process.

9.5.1 The percent recovery is to be calculated as follows:

$$\% \text{ Recovery} = \frac{MS - S}{C} \times 100$$

where:

MS = Matrix Spike value
S = Sample value.
C = Concentration of the Spiking solution.

9.5.2 If the Matrix Spike falls outside of the limits as stated in Table 2, or outside any historical documentation for analytes of interest a post analytical spike is performed for the failed analytes. The same sample from which the MS/MSD aliquots were prepared should be spiked with a post digestion spike at a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. The acceptable % Recovery of the post analytical spike is 80-120%. A nonconformance is noted in the LIMS and approved in secondary peer review and/or by the Metals Manager.

9.5.3 If the Post Spike fails the dilution test should be performed. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

9.6 Laboratory Duplicate

A duplicate sample is analyzed once per matrix batch. This sample is brought through the entire sample preparation and analytical process.

9.6.1 The relative percent difference between duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

9.6.2 If the Duplicate falls outside of the limits as stated in Table 2, or outside any historical documentation and the concentrations of the failing analytes are less than 5x the RL or a matrix interference is found a nonconformance is noted in the LIMS and approved in secondary peer review and/or by the Metals Manager.

9.7 Method-specific Quality Control Samples

9.7.1 Interference Check Standards

A check solution is analyzed once daily. One solution (ICSA) has only elevated concentrations of Fe, Al, Ca, Mg to ensure no interferences occur. The concentrations of the analytes of interest must have an absolute value of <2X RL. The other check solution (ICSAB) is the same solution spiked with a known amount of each analyte. These solutions are analyzed at the beginning of the first analytical run of the day.

If the analytes of interest in the ICSAB solution falls outside the acceptable limits of 80 – 120% of the true value, the solutions may be rerun once. The high level interferences are not evaluated for recovery just as in the ICSA. If the problem persists take corrective action which may include re-evaluation of the inter-element correction values (IECs). The instrument calibration routine must then be performed and confirmed by the ICV/ICB pair and the ICSA/ICSAB re-analyzed before proceeding with analysis. Otherwise, the nonconformance issue is raised to the Department Supervisor and/or the QA Department.

9.7.2 Reporting Limit (RL) Verification Standard (LLICV/LLCCV)

The RL standards are actually a series of standards that are analyzed at the beginning and at the end of each run. The lowest of the RL standards may be used to evaluate the sensitivity of reportable elements under method 6010C. This may be a low level client-specific analysis, or it may be the standard reporting limits for an aqueous sample or a soil/solid material. The standards must have a percent recovery of 70-130%. If an element fails the acceptance criteria to establish a specific RL, the RL standard may be re-analyzed. If the element failure continues, then either re-calibrate the instrument and rerun the affected samples or analyze the affected samples on another instrument with a passing RL verification standard for the element(s) of interest.

9.8 Method Sequence

- Calibration of instrument
- Initial Calibration Verification Standard
- Initial Calibration Blank
- LLICV
- Interference Check Solution A
- Interference Check Solution AB
- CRI
- Continuing Calibration Verification Standard
- Continuing Calibration Blank
- samples
- Continuing Calibration Verification Standard
- Continuing Calibration Blank
- Samples
- LLCCV
- Continuing Calibration Verification Standard
- Continuing Calibration Blank

10. Procedure

10.1 Equipment Set-up

10.1.1 Sample Preparation

Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards.

10.1.2 Instrument Set-Up

Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

Startup Procedures

For iCAP Duo 6500

- Turn on power to the chiller
- Click on ThermoSpec Icon; enter analyst initials in login screen
- Click on Plasma icon to start instrument
- Allow to warm up for 30 minutes
- Enter analytical workgroup number (obtained from LIMS) globally under the Instrument menu by selecting Tools, then Options, then Analyst.
- Click on the Sequence tab and enter the sequence by selecting New Autosampler Table, Add Sequence, Add # of spaces.
- Enter the sample locations and IDs
- Press Run Auto-Session button (►) in menu bar.

10.1.2.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user.

Operating conditions for axial plasma will vary from 1100 – 1500 watts forward power, 15-19 Liters/min argon coolant flow, 0.5 – 0.7 L/min argon nebulizer flow, 140 – 200 rpm pump rate and a default 1 minute preflush time and 10 second measurement time is recommended for all simultaneous instruments.

10.1.2.2 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array.

The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

10.1.2.2.1 The Thermo ICP's typically use a Meinhard Nebulizer. The nebulizer flow for each instrument is 1.0 +/- 0.2 mL/min.

10.1.2.2.2 The 6500 Duo instruments automatically perform a wavelength check at start up without user interaction.

10.1.2.2.3 The instrument operating condition finally selected as being optimum must provide the lowest reliable instrument detection limits and method detection limits.

10.1.2.2.4 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and argon pressures must be reoptimized.

10.1.2.2.5 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± the RDL. The upper control limit is the analyte instrument detection limit. Once established, the entire routine is periodically verified annually. In between that time, IEC's are done on a need be basis per analyte. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine must be kept on file. Special cases where continual verification is required are described elsewhere.

10.1.2.3 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

10.1.2.3.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit.

10.1.2.3.2 Determination of limits using reagent water MDLs represent a best case situation and do not represent possible matrix effects of real world samples.

10.1.2.3.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non-consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate.

10.1.2.3.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these must be near the upper limit of the range. The ranges which may be used for the analysis of samples must be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made must be documented and kept on file. The upper range limit must be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst must also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges must be determined whenever there is a significant change in instrument response. The linear dynamic range is checked on an annual basis. For those analytes that are known interferences, and are present at above the linear range, the analyst must ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit must have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves must be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and must be checked whenever there have been moderate equipment changes.

10.1.2.4 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

10.2 Initial Calibration

Calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 8.7. Flush the system with the calibration blank (Section 8.8.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve consists of a calibration blank, RL standard and a high level standard. Calibration curve verification is accomplished through the analysis of the ICV, LLICV and CRI standards.

10.3 Equipment Operation and Sample Processing

10.3.1 For all analytes and determinations, the laboratory must analyze an ICV (Section 8.9), and a calibration blank (ICB, Section 8.8.1), immediately following daily calibration.

A calibration blank (CCB, Section 8.8.1) and a calibration verification standard (CCV, Section 8.9) must be analyzed after every tenth sample and at the end of the sample run. Analysis of the calibration verification (CCV) must verify that the instrument is within 10%

of the calibration with the relative standard deviation < 5% from replicate (minimum of three) integrations.

If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICB, ICV, CRI, CCV or CCB must be reanalyzed. The analysis data for the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

10.3.2 Rinse the system with the calibration blank solution (Section 8.8.1) before the analysis of each sample. The suggested default rinse time is one minute. Each ICP instrument may establish a reduction in this rinse time through a suitable demonstration.

10.3.3 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

10.3.4 If less than acceptable accuracy and precision data are generated a series of tests are performed prior to reporting concentration data for analyte elements. At a minimum, these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests, as outlined in Sections 10.3.4.1 and 10.3.4.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

10.3.4.1 Post Digestion Spike Addition: If the matrix spike recoveries are unacceptable an analyte spike added to a portion of a prepared sample, or its dilution, must be run, recovery limits equal to 80% to 120% of the known spike value. The spike addition must produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a dilution test (10.3.4.2) should be performed. If both the MS/MSD and post spike fail then a matrix effect must be suspected.

10.3.4.2 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution must agree within ± 10% of the original determination. If not, a chemical or physical interference effect must be suspected.

10.3.5 **CAUTION:** If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

10.4 Continuing Calibration

10.4.1 Check calibration with an ICV following the initial calibration (Section 8.9). Verify calibration with the Continuing Calibration Verification (CCV) Standard (Section 8.9) at the end of the initial calibration sequence (ICV, ICB, ICSA, ICSAB, CRI, project specific RDL standards), after every ten samples, and at the end of an analytical run. At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV must be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 8.8.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

A CRI (Section 8.11) must be analyzed after the ICSAB. The concentration of the CRI is 2 – 5 times that of each element's RDL. The linearity of the instrument is confirmed on an annual basis by an LDR standard at +/-10% recovery.

10.4.1.1 The results of the ICV are to agree within 10% of the expected value, and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

10.4.1.2 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

10.4.1.3 The results of the CRI must be within 30% of the true value. If they are not, correct the problem and recalibrate the instrument. (Any element may be analyzed on a different ICP that has passed the CRI.)

10.4.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the ICSA/ICSAB (Section 8.10). Results must be within 80 – 120% of the true value for the analytes of interest in the ICSAB.

10.4.3 When low-level sensitivity is required, a check standard at the requested limit of quantitation is analyzed to confirm the reported detection limit (RDL). This is performed on a project-by-project basis.

10.5 Preventive Maintenance

Whenever instrument maintenance is performed, it is noted in the instrument's Maintenance Logbook.

10.5.1 Daily

Inspect the nebulizer pump tubing from the Autosampler to the Nebulizer. Replace if necessary.

10.5.2 Monthly or as needed

Remove the torch, "shot glass", nebulizer and spray chamber. Clean each with 10% Nitric Acid and rinse with tap water. Coat the inside of the spray chamber and shot glass with concentrated Sulfuric Acid and soak for one hour, then rinse well with DI water. Soak the torch and nebulizer in aqua regia overnight, then rinse with DI water.

10.5.3 Every 6 months

Preventive Maintenance is performed by the Vendor or in-house personnel as follows:

- check the cooling system
- flush/refill the chiller with distilled water and antibacterial conditioner
- clean the instrument to regain intensity
- clean/replace air filters.

11. Data Evaluation, Calculations and Reporting

11.1 If dilutions were performed, the appropriate factors must be applied to sample values. All results must be reported with up to three significant figures.

11.2 Soil samples

Soil samples are calculated as follows:

$$A = \frac{\text{Sample weight (grams)}}{\text{Final Volume (mL)}}$$

$$\text{B (concentration in mg/Kg)} = \frac{\text{Concentration of analyte (mg/L)}}{A}$$

11.2.1 Dry weight correction

The LIMS calculates the dry weight correction, however it is calculated as follows:

$$\text{Final concentration in mg/Kg dry weight} = \frac{B}{\text{\% Solids}}$$

11.3 Liquid samples

Liquid samples are calculated as follows:

$$\text{Dilution Factor} = \frac{\text{Final Volume (mL)}}{\text{Sample Volume (mL)}}$$

$$\text{Final concentration in mg/L} = \text{Concentration of analyte (mg/L)} \times \text{Dilution Factor}$$

11.4 Calculations for Hardness

The method for determining hardness is to compute it from the results of separate determinations of Calcium and Magnesium on aqueous samples.

11.4.1 Total Hardness

Total Hardness, mg equivalent $CaCO_3/L$ = [2.497 (Ca, mg/L)] + [4.118 (Mg, mg/L)]

11.4.2 Calcium Hardness

Calcium Hardness, mg equivalent $CaCO_3/L$ = [2.497 (Ca, mg/L)]

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Also refer to Section 9 for Quality Control and acceptance criteria.

If the ICSA or ICSAB is outside of the 80 – 120% recovery window, then the standard is reanalyzed. If the standard failure continues, the IECs for the element/elements in question are reviewed and recalculated if necessary.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The raw data is noted. If the standard fails again, the problem must be found and corrected. The CCV/CCB standard is remade and reanalyzed. If the standard passes, then the data that had failed up to the previous passing standard is reanalyzed.

If the standard fails after instrument maintenance, the instrument is recalibrated. A new ICV/ICB is performed, and all previous data that had failed up to the previous passing CCV/CCB is reanalyzed.

The procedure outline above is also conducted for a failing LCS or Method Blank.

If the Matrix Spike does not meet acceptance criteria, a Post Spike is performed. The recovery must be within 80-120% of the true value for aqueous samples and within 80-120% of the true value for soil samples. If these criteria are met, then the Matrix Spike data is reported, with the post spike narrated on the final report. If the post spike fails the acceptance criteria, the Department Manager is notified to determine what type of matrix interference is present, and whether a serial dilution must be performed.

If sample Duplicates are outside of the acceptance criteria, the analyst examines the sample for homogeneity. If the sample is not homogenous, this is narrated on the final report. Clean, homogenous samples are redistilled and reanalyzed within holding time.

Sample nonconformance regarding a Matrix Spike recovery or a duplicate %RSD is narrated on the final report along with the corrective action(s) taken.

If the ICSA or the ICSAB are outside of the 80-120% window then the standard in question must be re-analyzed. If the standard failure continues, then check the IECs for the element(s) in question and re-calculate and recalibrate the instrument. The instrument is recalibrated, verified with the ICV/ICB and the ICSA/ICSAB are then re-analyzed. If the standard failure repeats, then a fresh standard is prepared and re-analyzed. If failure continues notify the Department Supervisor.

The RL standards must have a % Recovery of 70-130%. If an element fails the acceptance criteria, the RL standards may be re-analyzed if the element must be included in the analytical event. If the element failure continues, then either re-calibrate the instrument and rerun the affected samples or analyze the sample on another instrument.

If the CRI (low level check standard), is recovered outside of the 70-130% window, the standard may be re-analyzed if the element must be included in the analytical event. If the element failure continues, then either re-calibrate the instrument or analyze the sample on another instrument.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP #1732 MDL/LOD/LOQ Generation

SOP# 1739 IDC/DOC Generation

SOP# 1728 Waste Management and Disposal

16. Attachments

TABLE 1: Element Wavelengths

TABLE 2: Precision and Accuracy Acceptance Criteria

TABLE 3: Reporting Limits

TABLE 1
ELEMENT WAVELENGTHS

Element	6500 Duo wavelength (nm)
Pb	220.3
Se	196.0
Sb	206.8
As	189.0
Ba	455.4
Be	313.0
Cd	214.4
Co	228.6
Cu	324.7
Cr	267.7
Fe	259.9
Mn	257.6
Mo	202.0
Ni	231.6
Ag	328.0
Tl	190.8
V	292.4
Zn	206.2
Al	396.1
Ca	315.8
Mg	279.0
B	208.9
Si	212.9
Sn	189.9
Sr	421.5
Ti	334.9
Bi	223.0
Na	589.5
K	766.4
S	180.7

TABLE 2
PRECISION AND ACCURACY ACCEPTANCE CRITERIA

	% Recovery LCS		Aqueous % Recovery MS		Soil % Recovery SRM		Duplicate	
Element	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Aqueous %RPD**	**Soil %RPD**
Aluminum	80	120	75	125	29	171	20	20
Antimony	80	120	75	125	4	196	20	20
Arsenic	80	120	75	125	81	119	20	20
Barium	80	120	75	125	83	118	20	20
Beryllium	80	120	75	125	83	117	20	20
Boron	80	120	75	125	70	129	20	20
Cadmium	80	120	75	125	82	117	20	20
Calcium	80	120	75	125	83	117	20	20
Chromium	80	120	75	125	80	119	20	20
Cobalt	80	120	75	125	83	117	20	20
Copper	80	120	75	125	83	117	20	20
Iron	80	120	75	125	51	150	20	20
Lead	80	120	75	125	80	120	20	20
Magnesium	80	120	75	125	74	126	20	20
Manganese	80	120	75	125	83	117	20	20
Molybdenum	80	120	75	125	81	119	20	20
Nickel	80	120	75	125	82	117	20	20
Potassium	80	120	75	125	74	126	20	20
Sulfur	80	120	75	125	NA	NA	20	20
Selenium	80	120	75	125	80	120	20	20
Silica (SiO_2)	80	120	75	125	NA	NA	20	20
Silver	80	120	75	125	66	134	20	20
Sodium	80	120	75	125	74	127	20	20
Strontium	80	120	75	125	80	120	20	20
Thallium	80	120	75	125	79	120	20	20
Tin	80	120	75	125	69	131	20	20
Titanium	80	120	75	125	82	118	20	20
Vanadium	80	120	75	125	79	121	20	20
Zinc	80	120	75	125	82	119	20	20

TABLE 3
REPORTING LIMITS

Element	Aqueous (mg/L)	Soil (mg/Kg)
ALUMINUM	0.10	4.0
ANTIMONY	0.05	2.0
ARSENIC	0.005	0.40
BARIUM	0.01	0.40
BERYLLIUM	0.005	0.20
BORON	0.03	1.2
CADMIUM	0.005	0.40
CALCIUM	0.10	4.0
CHROMIUM	0.01	0.40
COBALT	0.02	0.80
COPPER	0.01	0.40
IRON	0.05	2.0
LEAD	0.01	2.0
MAGNESIUM	0.10	4.0
MANGANESE	0.01	0.40
MOLYBDENUM	0.05	2.0
NICKEL	0.025	1.0
POTASSIUM	2.5	100
SULFUR	0.25	10
SELENIUM	0.01	0.80
SILICON	0.50	20
SILVER	0.007	0.40
SODIUM	2.0	80
STRONTIUM	0.01	2.0
THALLIUM	0.02	0.80
TIN	0.05	4.0
TITANIUM	0.01	0.40
VANADIUM	0.01	0.40
ZINC	0.05	2.0

Total Phosphorous

Dissolved Phosphorus

Colorimetric, Combined Reagent

References: **SM 4500P-E,** Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

SM4500P-B, Section 5 (Persulfate Digestion), Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

AQ2 method: **EPA-119-A** Rev. 7, equivalent to EPA 365.1, version 2(1993) **SM4500-P-B, F**(18-20)

1. Scope and Application

Matrices: Water and wastewater samples and soils.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms.

These forms of phosphate arise from a variety of sources. Small amounts of certain condensed phosphates are added to some water supplies during treatment. Larger quantities of the same compounds may be added when the water is used for laundering or other cleaning, because these materials are major constituents of many commercial cleaning preparations. Phosphates are used extensively in the treatment of boiler waters. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with storm run-off and to a lesser extent with melting snow. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body wastes and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving water biota.

Phosphorus is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. In instances where phosphate is a growth-limiting nutrient, the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro- and macro-organisms in nuisance quantities.

Phosphates also occur in bottom sediments and in biological sludges, both as precipitated inorganic forms and incorporated into organic compounds.

Phosphorus analyses embody two general procedural steps: (a) conversion of the phosphorus form of interest to dissolved orthophosphate, and (b) colorimetric determination of dissolved orthophosphate. The separation of phosphorus into its various forms is defined analytically but the analytical differentiations have been selected so that they may be used for interpretive purposes.

Filtration through a 0.45-µm-pore-diameter membrane filter separates dissolved from suspended forms of phosphorus. No claim is made that filtration through 0.45-µm filters is a true separation of suspended and dissolved forms of phosphorus; it is merely a convenient and replicable analytical technique designed to make a gross separation.

Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample are termed "reactive phosphorus." While reactive phosphorus is largely a measure of orthophosphate, a small fraction of any condensed phosphate present usually is hydrolyzed unavoidably in the procedure. Reactive phosphorus occurs in both dissolved and suspended forms.

Acid hydrolysis at boiling-water temperature converts dissolved and particulate condensed phosphates to dissolved orthophosphates. The hydrolysis unavoidably releases some phosphate from organic compounds, but this may be reduced to a minimum by judicious selection of acid strength and hydrolysis time and temperature. The term "acid-hydrolyzable phosphorus" is preferred over "condensed phosphate" for this fraction.

The phosphate fractions that are converted to orthophosphate only by oxidation destruction of the organic matter present are considered "organic" or "organically bound" phosphorous. The severity of the oxidation required for this conversion depends on the form of, and to some extent on the amount of, the organic phosphorus present. Like reactive phosphorus and acid hydrolyzable phosphorus, organic phosphorus occurs both in the dissolved and suspended fractions.

The total phosphorus as well as the dissolved and suspended phosphorus fractions each may be divided analytically into the three chemical types that have been described: reactive, acid hydrolyzable, and organic phosphorus. Determinations usually are conducted only on the unfiltered and filtered samples. Suspended fractions generally are determined by difference.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

Digestion Method: Because phosphorus may occur in combination with organic matter, a digestion method to determine total phosphorus must be able to oxidize organic matter effectively to release phosphorus as orthophosphate. This digestion is performed by using the persulfate oxidation technique.

Colorimetric Method: The ascorbic acid method is used for the determination of orthophosphate in environmental samples. An extraction step is recommended for the lower levels and when interferences must be overcome. Ammonium molybdate and potassium antimonyl tartrates react in acid medium with orthophosphate to form a heteropoly acid-phosphomolybdic acid that is reduced to intensely colored molybdenum blue by ascorbic acid. The absorbance of this complex is measured photometrically at 880nm.

2.1 Method Modifications from Reference

Glassware is acid rinsed with room temperature 1:1 HCl, instead of hot dilute HCl.

Initial testing of samples with phenophthalein has been eliminated since samples are received already preserved with H_2SO_4 and are pH checked by the Login Department upon receipt.
Soil samples are analyzed using the same digestive procedure.

3. Reporting Limits

The Reported Detection Limit is 0.01mg/L for waters and 5.0mg/kg for soils

4. Interferences

Correction for Turbidity or Interfering Color: The natural color of water generally does not interfere at the high wavelength used. For highly colored or turbid waters, prepare a blank by adding all reagents except ascorbic acid and potassium antimonyl tartrate to the digested sample aliquot. Subtract the blank absorbance from the absorbance of each sample.

Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1mg As/L interfere with the phosphate determination.

Hexavalent chromium and NO_2 interfere to give results about 3% low at concentrations of 1mg/L and 10 to 15% low at 10mg/L.

Sulfide (Na_2S) and silicate do not interfere at concentrations of 1.0 and 10mg/L.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Water samples are collected in 500mL plastic bottles, soil samples may be collected in plastic or glass jars.

6.2 Sample Preservation

If samples are for Dissolved Phosphorus analysis, filtration must take place prior to preservation with H_2SO_4 to a pH < 2.

All samples are preserved with H_2SO_4.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are stored under refrigeration at 4 ± 2 °C. Analysis must be performed within 28 days of collection. All samples should be analyzed as soon as possible after digestion. If a prolonged period passes in between, sample extracts are refrigerated at 4 ± 2 °C.

7. Equipment and Supplies

7.1 Spectrophotometer, with infrared phototube for use at 880nm, providing a light path of 2.5cm.

7.2 Acid-washed Glassware: Use acid-washed glassware for determining low concentration of phosphorus. Phosphate contamination is common because of its absorption on glass surfaces. Avoid using commercial detergents containing phosphate. Clean all glassware with 1:1 HCl two times followed by two DI water rinses. Preferably, reserve the glassware only for phosphate determination. Only disposable syringes and filters are to be used for filtering samples for Dissolved Phosphorus analysis.

7.3 Centrifuge Tubes: 50mL volume. (Must be new and disposable.)

7.4 Hot Plate: A 30cm x 50cm heating surface is adequate.

7.5 Scoop, 0.5gm To hold required amounts of persulfate crystals.

7.6 Erlenmeyer Flasks: 125mL volume.

7.7 0.45µm membrane filters: For Dissolved Phosphorus sample preparation.

7.8 Borosilicate Glass beads

7.9 SEAL AQ2 Discrete Analyzer, with all associated reagent wedges, sample tubes, and reaction segments. The SEAL has a light and filter capable of maintaining a 880nm wavelength.

7.10 Boiling Chips ultra-pure, non-reactive.

7.11 Syringes to use with membrane filters.

7.12 Pipettes Class A glass or automated.

8. Reagents and Standards

8.1 Calibration Curve and Spike, Stock Complex Phosphate Standard: 1000 mgP/L This stock solution is certified and purchased commercially prepared. Store at 4 ± 2°C. Expires upon manufacturer's specified date.

8.2 Calibration Curve and Spike, Intermediate Complex Phosphate Standard: 50 mgP/L Dilute 5.0mL stock complex phosphate solution to 100mL with DI water. Store at 4 ± 2°C. Expires 6 months after date of preparation.

8.3 Calibration Curve, Working Standard: 1.0 mgP/L Add 2mL of 50 mgP/L intermediate standard (Section 8.2) to 100mL volumetric flask and dilute to volume with DI water. Prepare fresh on each day of use.

8.4 Calibration Standards: Follow table below. Prepare fresh on each day of use.

Volume of 1.0 mg/L Working Standard (Section 8.3)	Final Volume (mL)	Calibration Standard Final Concentration (mgP/L)
0 mL	50	0
0.5 mL	50	0.010
2 mL	50	0.040
5 mL	50	0.100
25mL	50	0.500
50mL	50	1.000

8.5 ICV-LCS-CCV Stock Complex Phosphate Standard: 1000 mgP/L Second, independent, source standard. Store at 4 ± 2°C. Expires upon manufacturer's specified date.

8.6 ICV-LCS-CCV Intermediate Complex Phosphate Standard: 50 mgP/L Add 5mL of 1000 mgP/L stock standard (Section 8.5) to 100mL volumetric flask and dilute to volume with DI water. Store at 4 ± 2°C. Expires 6 months after date of preparation.

8.7 ICV-LCS-CCV Working Standard: Prepare fresh each day of use.

8.7.1 **0.5 mgP/L:** Add 0.5mL of 50 mg/L intermediate standard (Section 8.6) to 50mL centrifuge tube and dilute to the 50mL mark with DI water.

8.8 Matrix Spike: Intermediate Phosphate Standard (Section 8.2) is utilized for matrix spike solution. Pipet 0.5mL of the 50 mgP/L standard into 50mL of sample to result in a 0.5mg/L spike concentration.

8.9 Sulfuric Acid, H_2SO_4, 5N: Dilute 140mL concentrated sulfuric acid to 1L with DI. Store at room temperature. Expires 6 months from date of preparation.

8.10 Potassium Antimonyl Tartrate Solution: Dissolve 1.3715g K(SbO) $C_4H_4O_6 \cdot \frac{1}{2}H_2O$ in 400mL DI water in a 500mL volumetric flask and dilute to volume. Store at 4 ± 2°C. Expires one month from date of preparation.

8.11 Ammonium Molybdate Solution: Dissolve 10g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 250mL distilled water. Store at 4 ± 2°C. Expires one month from date of preparation.

8.12 Ascorbic Acid, 0.1M: Dissolve 3.52g ascorbic acid in 200mL DI water. The solution is stable for about 1 week at 4 ± 2°C.

8.13 Orthophosphate 1000ppm solution Independent, source standard. Store at 4 ± 2°C. Expires upon manufacturer's specified date.

8.14 Orthophosphate 25ppm spike solution Add 2.5mLs 1000ppm Orthophosphate solution to a clean, glass 100mL volumetric and dilute to volume with DI. Store at 4 ± 2°C. Expires 6 months from date of preparation.

8.15 SEAL Working Ascorbic Acid, 15g/L (with orthophosphate spike): Dissolve 1.5g of ascorbic acid in about 80mL DI water. Spike with .1mL 25ppm Orthophosphate standard to produce a spike level of .025mg P/L. Dilute to 100mL and mix well. The solution is stable for one week if stored at 4 ± 2°C. Discard if the solution becomes yellowed.

8.16 Combined Reagent: Mix 8.9, 8.10, 8.11, and 8.12 in the following proportions for 100mL of the combined reagent: 50mL 5N H_2SO_4 (Section 8.9), 5mL potassium antimonyl tartrate solution (Section 8.10), 15mL ammonium molybdate solution (Section 8.11), and 30mL ascorbic acid solution (section 8.12). Mix after addition of each reagent. Let all reagents reach room temperature before they are mixed and mix in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until turbidity disappears before proceeding. The reagent is stable for 4 hours. Discard reagent if it turns blue or black in color.

8.17 SEAL Working Coloring Reagent: To a clean 100mL volumetric flask, add 40mL sulfuric acid (8.9), followed by 6.5 mL antimony potassium tartrate (8.10) and swirl to mix. Then, add 20 mL ammonium molybdate (8.11). Swirl the contents, fill the flask up to the mark with DI water and mix well. Expires three weeks from day of preparation if stored at 4 ± 2°C. Discard if the reagent turns blue or becomes turbid.

8.18 Sodium Hydroxide, 6N: Dissolve 240 grams of NaOH pellets in 1000mL of DI water. Store at room temperature. Expires one month from date of preparation.

8.19 Phenolphthalein Indicator: Aqueous solution, commercially available. Store at room temperature. Expires upon manufacturer's specified date.

8.20 11N Sulfuric Acid Solution: Dilute 308mL concentrated sulfuric acid to 1000mL with DI. Store at room temperature. Expires 6 months from date of preparation.

8.21 Potassium Persulfate ($K_2S_2O_8$): Commercially available. Store at room temperature. Expires upon manufacturer's specified date.

8.22 Deionized Water

8.23 Soil LCS/SRM ERA Standard Reference Material for Nutrients in soil, catalog no. 542

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Method Blank/Calibration Blank - One method blank, which consists of DI water brought through the entire method, must be analyzed per batch of 20 samples or less. The CCB is analyzed after every 10 samples and at the end of the sequence.

Results of the Blanks must be less than the reporting limit. Otherwise the entire batch of samples must be re-prepared and reanalyzed. Exceptions are samples with results of more than 10 times the positive blank value.

Soil blanks are made with 0.1gm boiling chips and 50mLs of DI water and are analyzed like water blanks.

9.2 Laboratory Control Sample (LCS)

Analyze one per batch of 20 samples or less. The calibration curve must be verified by a second source standard prior to performing any sample analysis. For Total and Dissolved Phosphorus, the LCS is the ICV.

The ICV/LCS must be recovered within 85-115% of the true value. If the ICV/LCS fails, re-analyze. If failure continues, stop analysis, correct problem and re-calibrate.

Soil LCS's are made with approximately 0.15g of Standard Reference Material (SRM) brought up to 50mL with DI water.

9.3 Initial Calibration Verification (ICV)

Analyze one per batch of 20 samples or less. The calibration curve must be verified by a second source standard prior to performing any sample analysis. For Total and Dissolved Phosphorus, the ICV is the LCS.

The ICV/LCS must be recovered within 85-115% of the true value for water samples and be within vendor criteria for SRM. If the ICV/LCS fails, re-analyze. If failure continues, stop analysis, correct problem and re-calibrate.

9.4 Continuing Calibration Verification (CCV)

Analyze one per batch of 20 samples or less. The calibration curve must be verified by a second source standard. The CCV is analyzed after every 10 samples and at the end of the sequence to verify the curve.

The CCV must be recovered within 85-115% of the true value. If the CCV fails, re-analyze. If failure continues, stop analysis, correct problem and re-calibrate.

9.5 Matrix Spike

Analyze one per batch of 20 samples or less. Concentration is 0.5 mgP/L. The matrix spike must be recovered within 75 – 125% of the true value. If the matrix spike recovery is outside acceptance criteria, and the LCS is acceptable, a narrative is submitted with the data for inclusion on the client report.

9.6 Laboratory Duplicate

Analyze one sample in duplicate per batch of 20 samples or less. The RPD must be ≤ 20%. If this criterion is not met, a narrative is submitted with the data for inclusion on the client report.

9.7 Method-specific Quality Control Samples

Not applicable.

9.8 Method Sequence

9.8.1 Using spectrophotometer:

- Acid-rinse all glassware
- Calibration curve generation.
- Filter samples if analysis is for Dissolved Phosphorus, then preserve with H_2SO_4.
- Add 50mL of water sample or 0.1g of soil sample and 50mL DI water to an Erlenmeyer flask.
- Add 1mL H_2SO_4 solution and scoop solid $K_2S_2O_8$ and glass beads
- Boil down to 10mL or less.
- Cool and dilute to 30mL with DI.
- Add 1 drop phenolphthalein indicator solution.
- Neutralize to faint pink color with NaOH.
- Add sample aliquot to a new centrifuge tube and bring up to 50mL with DI.
- Add 4 mL combined reagent to a 25mL aliquot of sample.
- Read sample absorbance after 10-30 minutes.
- Analyze CCV and CCB after every 10 samples to verify curve.
- End sequence with CCV and CCB.
- Calculate results.

9.8.2 Using SEAL AQ2 analyzer:

- Acid-rinse all glassware
- Calibration curve generation.
- Filter samples if analysis is for Dissolved Phosphorus, then preserve with H_2SO_4.
- Add 50mL of water sample (soils are not done on the SEAL) to an Erlenmeyer flask.
- Add 1mL H_2SO_4 solution and scoop solid $K_2S_2O_8$ and glass beads
- Boil down to 10mL or less.
- Cool and dilute to 50mL with DI.
- Turn on the SEAL AQ2 analyzer.
- Fill out a run sequence and save it.
- Fill cups, including a cup of 1.0ppm digested standard for the curve
- Start the analysis.
- Change names of blank and LCS to be what the LIMS will recognize (ie, what is on the batch sheet).
- Export the data to LIMS by dropping it into the "SEAL on bowzer" folder.

10. Procedure

10.1 Equipment Set-up

10.1.1 Sample Preparation for Dissolved Phosphorus Analysis

Prior to preservation, samples to be analyzed for dissolved phosphorus are filtered using new disposable syringes and new 0.45um filter discs. 100mL of sample is filtered, poured into two new centrifuge tubes and preserved with H_2SO_4.

10.2 Initial Calibration

10.2.1:

Preparation of calibration curve, with spectrophotometer: Prepare individual calibration curve from a series of six digested standards (0 mgP/L to 1.0 mgP/L) on each day of analysis. The curve must be digested. Use DI water without the combined reagent to zero the Spectrophotometer. Plot absorbance vs. phosphate concentration to give a straight line. The correlation coefficient must be 0.995 or greater for the cure to be considered valid. Analyze at least one phosphate standard with each batch of 20 samples or less.

10.2.2:

Preparation of calibration curve, with SEAL AQ2 analyzer: Prepare and digest a 1.0 mgP/L standard and put it into the first slot in the auto-sampler. When prompted, click on "Auto-calibrate" to start calibration. Once the curve is finished, it may be checked in the "calibration" section. The correlation coefficient must be 0.995 or greater for the curve to be considered valid.

10.3 Equipment Operation and Sample Processing, with spectrophotometer

10.3.1 Add 50mL or a suitable portion of thoroughly mixed sample to a prepared (Section 7.2) 125mL Erlenmeyer flask. Use 0.1g of soil sample with 50 ml of DI for soil samples.

10.3.2 Add 1mL H_2SO_4 solution, one scoop solid $K_2S_2O_8$ and 3 to 5 glass beads.

10.3.3 Boil gently on a preheated hot plate until a final volume of 10mL or less is reached. Organophosphorus compounds such as AMP may require as much as 1-1/2 to 2 hours for complete digestion.

10.3.4 Cool, dilute to 30mL with DI water.

10.3.5 Add 0.05mL (1 drop) phenolphthalein indicator solution.

10.3.6 Neutralize to a faint pink color with NaOH.

10.3.7 Pour pink liquid sample into a new (unused) centrifuge tube and bring volume to 50mL with DI. Pour back into a 125mL Erlenmeyer flask.

10.3.8 Swirl the sample to mix and pour off 25mL digested sample into centrifuge tube.

10.3.9 Add 4.0mL combined reagent to all 25mL sample and QC sample aliquots and mix thoroughly.

10.3.10 After at least 10 minutes but no more than 30 minutes, use DI as the reference solution to zero the spectrophotometer at 880nm. Measure absorbance of each sample and record in the electronic laboratory notebook. If samples seem to have high background color before the addition of the coloring reagent, a background color may be checked for (see section 4).

If the sample concentration is greater than the highest concentration of the calibration curve (1.0mg/L), the digested sample is diluted with DI water to a concentration within the range of the calibration curve.

10.4 Equipment Operation and Sample Processing, with SEAL AQ2 Analyzer

10.4.1 Acid rinse all glassware twice with 1:1 hydrochloric acid and then twice with DI water.

10.4.2 Pour out 50mLs of mixed samples and QC samples, including a 1.0ppm calibration standard.

10.4.3 Add 1mL H_2SO_4 solution, one scoop solid $K_2S_2O_8$ and 3 to 5 glass beads.

10.4.4 Boil gently on a preheated hot plate until a final volume of 10mL or less is reached. Organophosphorus compounds such as AMP may require as much as 1-1/2 to 2 hours for complete digestion.

10.4.5 Cool and dilute to 50mLs.

10.4.6 Turn on SEAL AQ2 analyzer by flipping first the small, and then the large switch in the back.

10.4.7 Give the instrument at least half an hour to warm up.

10.4.8 If it has not yet been done that day, go through daily start-up, check voltages, and test aspiration.

10.4.9 Double click on scheduling to open the schedule form, and insert samples, Method Blanks, LCSs, Duplicates, and Matrix Spikes (the CCVs and CCBs populate automatically) NB: leave the first spot for the calibration curve.

10.4.10 Pour a small (approximately 1 mL) aliquot into small tubes and put them into the instrument. Put the 1.0ppm standard into the first spot.

10.4.11 Check to see that all the reagent wedges are in the correct spots and that there are sufficient reaction segments.

10.4.12 Save the sequence and double click on "run"; check the boxes for curve analysis.

10.4.13 Once the instrument is done analyzing the run, check and approve the results in the Data Review section. Then, change the Blank and LCS names to be whatever they are on the batch sheet (ex: WG123456-1) and save the run in the "out" folder.

10.4.14 Open the "SEAL on bowzer" folder and drop the run into it from the "out" folder. This saves the data to LIMS.

10.5 Continuing Calibration

The method blank and LCS are used as the CCB/CCV and should be read after every ten samples and at the end of the batch. Recovery for the CCV must be between 85-115% of the true value. Recovery for the CCB must be between the RL and its negative, (i.e: within -.01mg/L and .01mg/L for waters).

10.5 Preventative Maintenance

The Spectrophotometers are calibrated on a semi-annual basis by an instrument service company. Certificates are kept on file.

11. Data Evaluation, Calculations and Reporting

Calculate the concentration value of the sample directly from the standard curve. (Section 10.2).

$$\text{mg } P_{Total}/L = \frac{\text{absorbance} - \text{y-intercept}}{\text{slope}} \times \text{Dilution factor}$$

If samples were filtered prior to preservation, report as mg $P_{Dissolved}$ / L.

For soil samples, convert results to mg/kg, by multiplying result in mg/l by extraction volume and dividing by weight. All results must by reported based on dry weight.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedances or improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CCV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

16. Attachments

None.

Nitrogen, Total Kjeldahl

References: **Method 351.1,** Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020, U.S. Environmental Protection agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268 (March 1979)

Method SM 4500N_{org}-C, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

Method 10-107-06-2-D, Methods for Automated Ion Analyzers, May 20, 1998.

1. Scope and Application

Matrices: Total Kjeldahl nitrogen can be determined in potable, surface, and saline waters as well as domestic and industrial wastewaters.

Definitions: See Alpha Laboratories Quality Manual Appendix A

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Tecator and/or Lachat Instrument and in the interpretation of Lachat data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

This method covers the determination of total kjeldahl nitrogen in drinking, surface and saline waters, and domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

In waters and wastewaters the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas (N_2), are biochemically interconvertible and are components of the nitrogen cycle. They are of interest for many reasons.

Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. It does not include all organic nitrogen compounds. Analytically, organic nitrogen and ammonia can be determined together and have been referred to as "Kjeldahl nitrogen", a term that reflects the technique used in their determination. Organic nitrogen includes such natural materials as proteins and peptides, nucleic acids and urea, and numerous synthetic organic materials. Typical organic nitrogen concentrations vary from a few hundred micrograms per liter in some lakes to more than 20mg/L in raw sewage.

Ammonia is present naturally in surface and wastewaters. Its concentration generally is low in groundwaters because it adsorbs to soil particles and clays and is not leached readily from soils. It is produced largely by deamination of organic nitrogen containing compounds and by hydrolysis of urea. At some water treatment plants ammonia is added to react with chlorine to form a combined chlorine residual.

In the chlorination of wastewater effluents containing ammonia, virtually no free residual chlorine is obtained until the ammonia has been oxidized. Rather, the chlorine reacts with ammonia to form mono- and dichloramines. Ammonia concentrations encountered in water vary from less than 10µg ammonia nitrogen/L in some natural surface and groundwaters to more than 30 mg/L in some wastewaters.

In this discussion, organic nitrogen is referred to as organic N, nitrate nitrogen as NO_3–N, nitrite nitrogen as NO_2 - - N, and ammonia nitrogen as NH_3–N.

Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

2. Summary of Method

The organic nitrogen is converted to ammonia via heating in the presence of concentrated sulfuric acid, K_2SO_4, $HgSO_4$, and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and treated and made alkaline with a hydroxide-thiosulfate solution. The digestate is distilled at high pH into a solution of boric acid. The ammonia in the distillate is determined colorimetrically by the phenate method.

The phenate method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630nm, and is directly proportional to the ammonia concentration in the digestate.

2.1 Method Modifications from Reference

This method has been modified for soil digestion, Section 9.4.1.

3. Detection Limits

The RDL is determined to be 0.3 mg/L for liquid samples and 150 mg/Kg for soil or solid samples.

4. Interferences

4.1 Instrumental

Samples with a high concentration of TKN may carry-over into the next sample and therefore yield false high results in that next sample. If a sample with a low concentration follows a sample with a high concentration, re-analyze the low sample to ensure results are accurate.

4.2 Parameters

High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever

means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

NOTE: Both Phenol and Mercury used in this method are hazardous and general laboratory safety practices must be observed. Due to the Mercury used in this procedure, digestion must be done under a hood.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

The most reliable results are obtained on fresh samples. Use plastic or glass containers.

6.2 Sample Preservation

Samples may be preserved by addition of 2mL of concentrated H_2SO_4 per liter if sample cannot be analyzed immediately. Refrigerate at 4°C.

6.3 Sample Handling

Even when properly preserved, conversion of organic nitrogen to ammonia may occur. Therefore samples should be analyzed as soon as possible.

7. Equipment and Supplies

7.1 Digestion apparatus: Kjeldahl Digestion System 20, Model 1015 Digester. Follow the instrument manufacturer's instructions.

7.2 Distillation apparatus: Tecator Instruments Automatic Distillation Unit: Follow the instrument manufacturer's instructions for proper operation.

7.3 Automated Ion Analyzer: Lachat Instruments

7.4 Disposable polypropylene cups: 250mL with covers.

7.5 Glass Tuttlecaps: For digestion.

7.6 Glass Pipets: Various volumes.

7.7 Auto-pipettor with tips: For 10mL capability.

8. Standards and Reagents

8.1 Sodium Phenolate: **CAUTION!** Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin. In a 1L volumetric flask, dissolve 88mL of 88% liquified phenol or 83g crystalline phenol (C_6H_5OH) in approximately 600mL DI water. While stirring, slowly add 32g sodium hydroxide (NaOH). Cool, dilute to the mark, and invert three times. Do **not** degas this reagent. Expires one month from date of preparation.

8.2 Sodium Hypochlorite (approximate 2.6%): In a 500mL volumetric flask, dilute 250mL Regular Chlorine bleach [5.25% sodium hypochlorite (NaOCl)] to the mark with DI water. Invert three times to mix. Expires one month from date of preparation.

8.3 Sodium Nitroprusside (coloring agent): In a 1L volumetric flask, dissolve 3.50g sodium nitroprusside (Sodium Nitroferricyanide $[Na_2Fe(CN)_5NO_2 \cdot H_2O]$) dilute to the mark with DI water. Degas with helium to prevent bubble formation. Use He at 140kPa (20 lb/in^2) through a helium degassing tube. Bubble He vigorously through the solution for one minute. Expires one month from date of preparation.

8.4 Boric 1.5% Boric Acid Solution: To a 1000mL volumetric flask add 15g Boric Acid. Dilute to the mark with DI water. Expires one month from date of preparation.

8.5 Mercuric Sulfate Solution: Dissolve 8g red mercuric oxide (HgO) in 50mL of I:4 sulfuric acid (10.0mL concentrated H_2SO_4 : 40mL distilled water) and dilute to 100mL with distilled water. Expires one month from date of preparation.

8.6 Digestion Solution (Sulfuric Acid-Mercuric Sulfate-Potassium Sulfate): Dissolve 267g K_2SO_4 in 1300mL distilled water and 400mL concentrated H_2SO_4. Add 50mL mercuric sulfate (Section 8.5) solution and dilute to 2L with distilled water. Expires one month from date of preparation.

8.7 Sodium Hydroxide-Sodium Thiosulfate Solution: Dissolve 500g NaOH and 25g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1L. Expires one month from date of preparation.

8.8 0.2% Boric Acid Solution (Carrier Solution): To a 2L volumetric flask, dissolve 4g Boric Acid (H_3BO_3) in DI water. Degas by bubbling vigorously with Helium for one minute. Expires one month from date of preparation.

8.9 Stock Standard, 1000ppm as NH_3 (for calibration solutions): Commercially prepared. Certificate of analysis is required.

8.9.1 Intermediate Calibration Stock Standard, 100ppm as NH_3: To a 100mL volumetric flask, add 10.0mL of Stock Standard (Section 8.9) and dilute to the mark with 0.2% Boric Acid solution (Section 8.8). Invert three times. Expires one month from date of preparation.

8.9.1.1 Nine Working Calibration Standards: Prepare the following standards in volumetric flasks:

8.9.1.1.1 20.0ppm: 40mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.2 10.0ppm: 20mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.3 8.00ppm: 8mL of 100ppm standard (Section 8.9.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.4 **4.00ppm:** 8mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.5 **2.00ppm:** 2mL of 100ppm standard (Section 8.9.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.6 **1.00ppm:** 1mL of 100ppm standard (Section 8.9.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.7 **0.400ppm:** 4mL of 20ppm standard (Section 8.9.1.1.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

8.9.1.1.8 **0.200ppm:** 1mL of 20ppm standard (Section 8.9.1.1.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Alternately, this standard may be prepared utilizing autodilution of the 20ppm standard on the autosampler. Prepare fresh each day of use.

8.9.1.1.9 **0.100ppm:** 1mL of 20ppm standard (Section 8.9.1.1.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Alternately, this standard may be prepared utilizing autodilution of the 20ppm standard on the autosampler. Prepare fresh each day of use.

8.9.1.1.10 **0.050ppm:** 20mL of 0.100ppm standard (Section 8.9.1.1.9) to 40mL with 0.2% Boric Acid solution (Section 8.8). Alternately, this standard may be prepared utilizing autodilution of the 20ppm standard on the autosampler. Prepare fresh each day of use.

8.9.1.2 Continuing Calibration Standards:

8.9.1.2.1 **0.400ppm Low CCV:** 4mL of 20ppm standard (Section 8.9.1.1.1) to 200mL with 0.2% Boric Acid solution (Section 8.8).

8.9.1.2.2 **4.00ppm Hi CCV:** 8mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8).

8.10 Stock Standard, 1000ppm as TKN (for spike): Commercially prepared. Certificate of analysis is required

8.10.1 Intermediate spike Stock Standard, 200ppm as TKN: To a 100mL volumetric flask, add 20.0mL of Stock Standard (Section 8.10) and dilute to the mark with 0.2% Boric Acid solution (Section 8.8). Invert three times. Expires one month from date of preparation.

8.11 Stock Standard Solution, 1000ppm as NH_3 (for ICV only): Commercially prepared. Certificate of analysis is required. This must be from a different source than that used for Stock Standard (Section 8.9).

8.11.1 Initial Calibration Verification Standards (ICV):

8.11.1.1 Hi ICV, 10ppm: To a 100mL volumetric flask add 1mL of 1000ppm standard (Section 8.11). Dilute to the mark with 0.2% Boric Acid Solution (Section 8.8). Expires one month from date of preparation.

8.11.1.2 Hi ICV, 8.0ppm: To a 100mL volumetric flask add 0.8mL of 1000ppm standard (Section 8.11). Dilute to the mark with 0.2% Boric Acid Solution (Section 8.8). Expires one month from date of preparation.

8.11.1.3 Low ICV, 1.0ppm: To a 100mL volumetric flask add 10mL of 10ppm ICV (Section 8.11.1.1). Dilute to the mark with 0.2% Boric Acid Solution (Section 8.8). Expires one month from date of preparation.

8.12 Stock Standard Solution, 1000ppm as TKN (for LCS): Commercially prepared. Certificate of analysis is required. This must be from a different independent source than that used for Stock Standard (Section 8.10).

8.12.1 LCS solution, 200ppm as TKN: To a 100mL volumetric flask add 20mL of 1000ppm Stock Standard (Section 8.12) and dilute to the mark with DI water. Expires one month from date of preparation.

9. Procedure

9.1 SET-UP

9.1.1 Clean 250mL Tecator tubes by rinsing twice with approximately 0.5mL of 6N NaOH solution and 100mL RO water. Rinse twice again with DI water.

9.1.2 Rinse glass tuttlecaps under the hood in a 1000mL beaker with approximately 500mL DI and 1.0 mL NaOH. Allow to sit in this solution until use.

9.2 Initial Calibration

Calibrate the Lachat ion analyzer according to manufacturer's instructions.

9.2.1 Calibration

Two boards are used to calibrate the Lachat instrument. Each curve has 7 calibration points. The correlation coefficient of each curve must be $\geq$ 0.995, otherwise re-calibration is necessary. Prepare standard curves by plotting the peak areas of standards processed through the manifold against NH_3-N concentrations in standards.

9.2.1.1 Channel 1 is used to generate a calibration curve on the low range from 0.00 – 2ppm.

9.2.1.2 Channel 2 is used to generate a calibration curve on the high range from 0 – 20ppm.

Alternative method: One board can be used to calibrate the Lachat instrument. !0 point calibration curve will be used with calibration standards 10.0, 8.0,4.0,2.0,1.0,04, 0.2, 0.1 , 0.05 mg/l each and blank. The correlation coefficient must be $\geq$ 0.995, otherwise re-calibration is necessary. Prepare standard curves by plotting the peak areas of standards processed through the manifold against NH_3-N concentrations in standards

9.2.2 Initial Calibration Verification (ICV)

Prior to sample analysis, an ICV is analyzed at 1.0ppm (Section 8.10.1.2) to verify the low calibration curve on Channel 1. Another ICV is analyzed at 10ppm (Section 8.10.1.1) to verify the high calibration curve on Channel 2. Both ICVs must yield results ± 10% of their true value, otherwise re-calibration is necessary.

Note: if instrument is calibrated using one board calibration, then both ICV's (Low and High), will be evaluated and high ICV will be 8.0 mg/l ICV standard (Section 8.11.1.2)

9.2.3 Initial Calibration Blank (ICB)
Following the ICV is the analysis of an ICB. The ICB consists of an aliquot of 0.2% Boric Acid (Section 8.8). Results must be less than < 0.05mg/L.

9.3 Standardization (Continuing Calibration Verification)

Analyze the following after every 10 samples and at the completion of analysis:

0.400ppm Low CCV, (Section 8.9.1.2.1)

4.0ppm Hi CCV, (Section 8.9.1.2.2)

Blank, 0.2% Boric Acid Solution. (Section 8.8)

9.4 Equipment Operation and Sample Analysis

9.4.1 Aqueous Sample Digestion: Add 50mL of sample or a portion diluted to 50mL with DI water, to pre-washed Tecator tubes that are numbered to correspond with the samples.

Soil/Solid Sample Digestion: Weigh 0.1g of soil/solid sample and record the weight in the laboratory notebook. Transfer to a pre-washed, pre-numbered Tecator tube and add 50mL of DI water.

In a similar manner, for each matrix, prepare the QC samples to be digested with the batch (refer to Sections 10.2.1, 10.3.1, 10.7 and 10.8)

Then add approximately 1g of black boiling chips to each tube. Move to hood before adding 10mL of Digestion Solution (Section 8.6) to each tube with a calibrated pipettor.

Rinse glass tuttlecaps with DI and place one onto the top of each Tecator tube. Place Tecator tube rack onto Tecator digestion block and turn temperature control knob to "4" which represents approximately 250°C. (Temperature should never exceed 300°C.) Cook for approximately 2 hours to SO_3 fumes. The remaining mixture will be clear or pale yellow in color. Remove tube from digestion block and allow to cool to ~80 °C before adding DI to the 90mL mark on the tube.

9.4.2 Distillation: To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation. Make the digestate alkaline by careful addition of 20mL of sodium hydroxide-thiosulfate solution (Section 8.7) without mixing. Do not mix until the digestion tube has been connected to the distillation apparatus. Connect the Tecator tube to the Tecator distillation unit's stopper as defined in the manual. Distill for 3 minutes 40 seconds as defined in the manual and collect distillate in 20mL boric acid solution (Section 8.4). Distill at maximum rate with the tip of the delivery tube below the surface of boric acid receiving solution. Collect at least 90mL distillate. Dilute to 150mL with DI water. Refrigerate at 0-4°C if Lachat analysis is delayed.

9.4.3 Ammonia analysis of distillate: Follow the manufacturer's instructions for the proper operation of the ion analyzer. The following are specific notes for this analysis.

Sample throughput:	90 samples/hr; 40 sec/sample
Pump speed:	35
Cycle period:	40 s
Inject to start of peak period:	25 s
Inject to end of peak period:	63 s

9.4.4 System Notes:

9.4.4.1 Allow 15 minutes for heating unit to warm up to 60°C.

9.4.4.2 System IV GAIN: 175 x 1.

9.4.4.3 If standards are not distilled, samples should be multiplied by procedure dilution (final volume 150mL) divided by initial volume.

9.4.4.4 If baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

9.4.4.4.1 Place all reagent lines in deionized water and pump to clear reagents (2-5 minutes).

9.4.4.4.2 Place reagent lines and carrier in 1M hydrochloric acid (1 volume concentrated HCl added to 11 volumes of deionized water) and pump for several minutes.

9.4.4.4.3 Place all lines in deionized water and pump until the HCl is thoroughly washed out.

9.4.4.4.4 Resume pumping reagents.

9.4.4.5 If samples are colored or are suspected to show a background absorbance, this interference should be subtracted. This can be done by diluting or by the following procedure:

9.4.4.5.1 Calibrate the system in the normal manner.

9.4.4.5.2 Disable the check standard or DQM features and analyze the samples.

9.4.4.5.3 Place reagent and carrier lines in DI water and allow the baseline to stabilize.

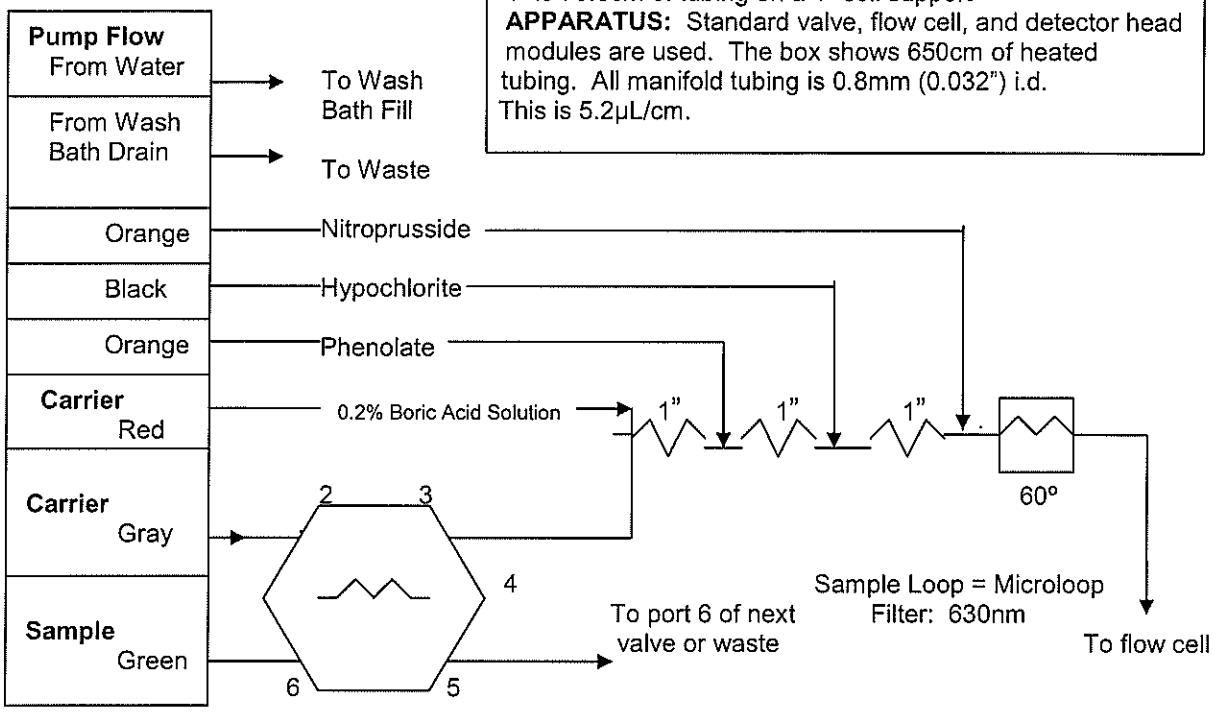
9.4.4.5.4 Inject samples again without recalibrating.

9.4.4.5.5 Subtract the "background" concentration from the original concentration to give the corrected concentration.

Original Concentration – Background Concentration = Corrected Concentration.

Manifold Diagram:

CARRIER is helium degassed 0.2% boric acid solution.
1" is 70.0cm of tubing on a 1" coil support
APPARATUS: Standard valve, flow cell, and detector head modules are used. The box shows 650cm of heated tubing. All manifold tubing is 0.8mm (0.032") i.d.
This is 5.2µL/cm.



9.5 Preventative Maintenance

9.5.1 All lines are flushed at the end of each run.

9.5.2 All equipment is kept clean.

9.6 Calculations

Prepare standard curves by plotting peak areas of standards processed through the manifold against NH_3 -N concentrations in standards. Compute sample NH_3 -N concentration by comparing sample peak areas with standard curve, as determined by the Lachat instrument software.

9.6.1 If the sample has a concentration of less than 2ppm, calculate results by using the low curve generated on Channel 1.

9.6.2 If the sample concentration is greater than 2ppm, calculate results by using the high curve generated on Channel 2.

To compute final results for aqueous samples, multiply the direct reading by the dilution factor based on the initial preparation volume.

TKN mg/L = mg/L direct reading x dilution factor

To compute results for soil/solid samples, multiply the direct reading by the extraction final volume (150mL) and then divide by the weight of the sample used for extraction (Section 9.4.1), and multiply by a dilution factor as necessary.

$$\text{TKN mg/Kg} = \left[\frac{\text{(mg/L direct reading) x extraction final volume (150mL)}}{\text{Sample weight (g)}}\right] \times \text{dilution factor}$$

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

10.2 Blank

10.2.1 The Distillation Blank is 50mL of DI. Distill two per batch of 20 samples or less, but only the lowest is reported. Subtract any blank greater than 0.3mg/L from all samples and QC.

10.2.2 The Analytical Blank (ICB) for the Lachat analysis is not distilled and is 0.2% Boric Acid Solution (Section 8.8).

The ICB is run after the initial calibration verification standards (ICV) and another is run after the continuing calibration standards (CCV).

10.3 Laboratory Control Samples (LCS)

10.3.1 Distillation: Distill a Low and a Hi LCS with each batch of 20 samples or less. The results from the Hi LCS are reported for the batch. The Low LCS is used to verify the low curve, but is not reported.

10.3.1.1 Low 4.0ppm LCS: Add 1mL of 200ppm LCS solution (Section 8.10.2) to 50 mL DI. This is used for the Low 0 - 6 ppm curve.

10.3.1.2 Hi 40ppm LCS: Add 10mL of 200ppm LCS solution (Section 8.10.2) to 50 mL DI. This is used for the Hi 0 - 60 ppm curve.

10.4 Initial Calibration Verification Standards

10.4.1 Lachat Analysis: The ICVs are not distilled. Analyze the following after calibration of the Lachat instrument. Recoveries must be within 10% of the true value, otherwise recalibration of the instrument is necessary.

10.4.1.1 Low ICV, 1.0ppm (Section 8.10.1.2)

10.4.1.2 Hi ICV, 10ppm (Section 8.10.1.1); **HI ICV** will be 8.0 ppm (Section 8.10.1.2) in case of one board calibration.

10.5 Continuing Calibration Verification Standards

10.5.1 Lachat Analysis: The CCVs are not distilled. Analyze the following after every ten samples and at the completion of analysis. Recoveries must be within 10% of the true value.

If recoveries fall outside of this range, the cause for the failure is determined and corrected, and the instrument is recalibrated. All samples that were analyzed since the last CCV that was within range are reanalyzed.

10.5.1.1 0.4ppm Low CCV (Section 8.9.1.2.1)

10.5.1.2 4.0ppm Hi CCV (Section 8.9.1.2.2)

10.6 Interference Check Standards

None.

10.7 Matrix Spike

One per batch of 20 samples or less. Prior to distillation, add 2mL of 200ppm Spiking Solution (Section 8.9.2) per 50mL of sample.

10.8 Duplicates

Distill one duplicate sample per batch of 20 samples or less.

10.9 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

10.10 Analytical Sequences

10.10.1 Distillation Sequence:

3 Rinse tubes
Blank 1
Blank 2
Low LCS
Hi LCS
Rinse
Samples (each sample must be followed by rinse, except between sample and its spike or sample and its duplicate)
Duplicate
Spike
Rinse
Shut-down

10.10.2 Lachat Analytical Sequence:

Instrument Calibration
DQM = Hi 4.0ppm CCV
Low 0.4ppm CCV
CC Blank
Low 1.0ppm ICV
Hi 10ppm ICV or 8.0 ppm ICV
IC Blank
Samples
DQM : Run after every 10 samples and at completion of analysis
Rinse reagent lines with 1M HCl for 5 to 10 minutes
DI water rinse for 5 to 10 minutes
Air rinse 5 to 10 minutes.
Shut-Down.

11. Method Performance

11.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732 These studies performed by the laboratory are maintained on file for review.

11.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734, 1739 for further information regarding IDC/DOC Generation.

11.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

11.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

12. Corrective Actions

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan SOP/1728 for waste handling and disposal.

NOTE: TKN Lachat waste contains Mercury and must be deposited into TKN/Lachat waste stream in the Waste Room.

Acid Digestion
of Sediments, Sludges and Soils

Reference Method: **EPA 3050B,** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, 1996.

1. Scope and Application

Matrices: Sediments, sludge, soils.

Definitions: See Alpha Laboratories Quality Manual Appendix A

This method provides two separate digestion procedures. Samples prepared by this method may be analyzed by ICP- AES or ICP-MS for all the listed metals, provided the detection limits are adequate for the analytical end use of the data.

Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be digested by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest.

The recommended determinative techniques for each element are listed below:

ICP- AES		
Aluminum	Antimony	Barium
Beryllium	Cadmium	Calcium
Chromium	Cobalt	Copper
Iron	Lead	Magnesium
Manganese	Molybdenum	Nickel
Potassium	Silver	Sodium
Thallium	Vanadium	Zinc

ICP-MS	
Arsenic	Beryllium
Cobalt	Cadmium
Chromium	Iron
Lead	Molybdenum
Selenium	Thallium

This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available". By design,

elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If total digestion is required, Method 3052 is preferable.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

A representative sample from 1.25g to 5g is digested in a solution of Aqua Regia (3:1 HCl:HNO_3) and further additions nitric acid (HNO_3 conc.) and heated in a heat source.

Samples digested in the Hot Block: Nitric acid and Hydrochloric acid are added to the sample and reflux for 30 minutes. 5-10 mL of DI water is added to wash down the walls of the digestion vessel and 1 mL of concentrated Nitric acid is added. The samples are again heated in the heat source and allowed to reflux at 90-100°C for an additional 30 minutes.

After digestion, the extract is brought to a final volume of 50mL and allowed to settle or filtered if necessary.

2.1 Method Modifications from Reference

Digestates are prepared in the same manner for both ICP-AES and ICP-MS determinative methods.

Method section 7.5 Aqua Regia digestion with optional filtration performed when settling is not feasible based on sample composition (i.e.: high suspended solids, precipitates or floatables).

3. Reporting Limits

The Reporting Limit is determined by the amount of sample used for preparation. Therefore, a review of Client requirements for Reporting Limits is necessary prior to sample preparation. Also refer to the analytical SOP.

4. Interferences

None.

5. Health and Safety

Caution must be used when handling the following:

- cHCL
- $cHNO_3$
- Aqua Regia

These chemicals are all corrosives and can cause harm to skin and eyes. When using these corrosives, the analyst must wear a lab coat, gloves, and protective eye wear.

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in glass or plastic jars

6.2 Sample Preservation

None.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are refrigerated at 4 ± 2 °C upon receipt, and are digested within 90 days of collection.

7. Equipment and Supplies

7.1 Polypropylene Digestion Vessel: 50mL volume, SCP Science

7.2 Reflux Cap, SCP Science

7.3 Weighing Tray

7.4 Spatula, Stainless Steel

7.5 Volumetric Flasks: 200mL volume, Class A

7.6 Whatman 40 or equivalent Filter Paper

7.7 Hot Block, thermostatically controlled, calibrated with correction factor application.

7.8 Balance: Capable of weighing to 0.001g.

7.9 Polypropylene Bottles: 250mL volume

8. Reagents and Standards

8.1 Hydrochloric Acid, concentrated (cHCl): 18M; store at room temperature.

8.2 Nitric Acid, concentrated ($cHNO_3$): 18M; store at room temperature.

8.3 Aqua Regia: Prepare a 3:1 solution of cHCl: $cHNO_3$. This solution is prepared fresh each day of use and discarded after use.

8.4 50% Hydrochloric Acid (HCl): 500mL cHCl diluted to 1 liter with DI water; store at room temperature.

8.5 10% Nitric Acid (HNO_3): 100mL $cHNO_3$ diluted to 1 liter with DI water; store at room temperature.

8.6 Reagent Water: Deionized water (DI) from Alpha's water treatment system.

8.7 1000ppm and 10,000ppm Single Element Stock Standards: All stock standards are commercially prepared and certified. All standards are in acidic aqueous solutions. Standards are stored at room temperature, and the vendors' expiration date is used.

8.8 10ppm Single Element Intermediate Standards: Intermediate standards are made from dilution 1:10 commercially prepared and certified stock standards (Section 8.9). All standards are in acidic aqueous solutions. Standards are stored at room temperature and the vendor's expiration date is used.

8.9 Multi-element Stock Standards: All stock standards are commercially prepared and certified. All standards are in acidic aqueous solution. Standards are stored at room temperature, and the vendors' expiration date is used.

8.9.1 IPS Stock Standard:

CLP ICP Standard #1: Al, Ba at 2000 µg/mL; Fe at 1000 µg/mL; Co, Mn, Ni, V, Zn at 500 µg/mL; Cu at 250 µg/mL; Cr at 200 µg/mL; Be and Ag at 50 µg/mL.

FPS Stock Standard:

CLP ICP Standard #3: As, Se, Tl at 2000 µg/mL; Pb at 500 µg/mL; Cd at 50 µg/mL.

Ag Spike Standard: 100 ug/mL prepared standard.

8.10 Working Standards: The working standards are prepared from the stock standards in 10% nitric acid and then brought to a 500mL final volume. Standards are stored at room temperature, this solution expires 12 months after the date of preparation or the expiration of the parent solution, whichever is earliest.

8.10.1 IPS Working Standard: To a 500mL Class A volumetric flask, add 250mL of DI water the add 25mL of $cHNO_3$ (Section 8.2), cap and mix by inverting. Add 50mL of CLP ICP Standard #1 stock (Section 8.11.1), 25mL of 1000ppm Sb Standard (Section 8.9), 2.5mL of 1000ppm Cd Standard (Section 8.9) and dilute to a final volume of 500mL with DI water.

The resulting concentration of this solution is: 200 mg/L of Al and Ba; 100 mg/L of Fe; 50 mg/L of Co, Mn, Ni, V and Zn; 25 mg/L of Cu; 20 mg/L of Cr; 5 mg/L of Be and Ag ; 50 mg/L of Sb; and 5 mg/L of Cd; 10% $cHNO_3$.

8.10.2 FPS Working Standard: To a 500mL Class A volumetric flask, add 250mL of DI water the add 25mL of $cHNO_3$ (Section 8.2), cap and mix by inverting. Add 3mL of CLP ICP Standard #3 stock (Section 8.11.2), 25mL of 1000ppm Pb Standard (Section 8.9) and dilute to a final volume of 500mL with DI water.

The resulting concentration of this solution is: 12 mg/L of As, Se and Tl; 53 mg/L of Pb; and 0.3 mg/L of Cd; 10% $cHNO_3$.

8.10.3 MIX Working Standard: To a 500mL Class A volumetric flask, add 50mL of DI water the add 25mL of $cHNO_3$ (Section 8.2), cap and mix by inverting. Add 50mL each 1000ppm of the following from Section 8.9: ICP Boron Standard, ICP Mo Standard, ICP Sr Standard, ICP Ti Standard. Add 50mL each 10,000ppm of: ICP Ca Standard, ICP Mg Standard, ICP K Standard, ICP Na Standard and dilute to a final volume of 500mL with DI water.

The resulting concentration of this solution is: 100 mg/L of B, Mo, Sr and Ti; 1000 mg/L of Ca, Mg, K, and Na.

8.10.4 Silver Spike Standard: To a 100mL Class A volumetric flask, add 50mL of DI water the add 5mL of $cHNO_3$ (Section 8.2), cap and mix by inverting. Add 10 mL of 1000 ug/mL Ag standard and dilute to the final 100 mL volume mark. Transfer to an amber glass 200 mL bottle.

The resulting concentration of this solution is: 100 mg/L of Ag.

8.11 Standard Reference Material (SRM)

A standard reference material is used for all solids and soil digestions as the LCS. The SRM is purchased from a vendor (ERA) and evaluated by the vendor control limits (95%confidence limits).

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

PBS, Prep blank for soil: Digest one PBS per batch of 20 samples or less. The Method Blank is carried through the complete preparation procedure and contains the same volume of reagents as the sample solutions. The Method Blank is used to assess contamination from the laboratory environment.

9.2 Laboratory Control Sample (LCS)

LCSS, Laboratory Control Sample for soil: Digest one LCSS per batch of 20 samples or less.

For samples that are prepared in the 50mL Polypropylene digestion vessel and utilize between 0.3 and 0.4 grams of Standard Reference Material (SRM): Environmental Resource Associates, Cat 540, lot number D0xx-540.

9.3 Initial Calibration Verification (ICV)

Not applicable.

9.4 Continuing Calibration Verification (CCV)

Not applicable.

9.5 Matrix Spike

Digest one MS per batch of 20 samples or less for MET-T products or upon client request.

For samples that are prepared in the 50mL Polypropylene digestion vessel and utilize between 0.3 and 0.4 grams of sample: To a second aliquot of the sample chosen for the MS, add 1.0mL of IPS (Section 8.9.2), FPS (Section 8.9.3), and MIX (Section 8.9.4) working stock standards and 0.25 mL of 100ppm Ag standard (Section 8.9.5). If the desired metal is not included in the spiking solution, then also add 50µL of 1000ppm desired metal stock standard (Section 8.9).

9.6 Laboratory Duplicate

One duplicate sample is digested per matrix batch of 20 or less for MET-T products or upon client request.

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- Mix the sample thoroughly to obtain a homogeneous and representative aliquot.
- Weigh the appropriate amount of sample, and QC samples.
- Add 1 mL $cHNO_3$ and 3 mL cHCl to the each sample vial.
- Cover flasks with a reflux cap and heat in the digestion block at 90-100 °C for 30 minutes.
- Raise and rotate each sample vessel to the elevated position in the sample rack and allow to cool slightly.
- Using 5-10 mL DI water, rinse down the inner walls of the sample vessel.
- Add 1 mL of $cHNO_{3\ to}$ each vessel.
- Rotate and lower each sample vessel to the heating position and heat at 90-100 °C for 30 minutes.
- Remove from samples from the digestion block. Bring samples to a 50 mL final volume with DI water and let settle or filter if necessary.

10. Procedure

10.1 Equipment Set-up

10.1.1 Turn on the heat source (Section 7.7) to a temperature of 95 °C ± 3 °C.

10.1.2 Set up the electronic laboratory notebook completing all fields including the following information:

- Date, Chemist's initials, Method
- Job number, Metals analysis requested
- Sample weight
- Type of acid used and its Lot#, Final Volume
- Comments on color of sample, texture of sample
- MS / LCSS used
- Time ON and OFF the heat source

10.2 Initial Calibration

Not applicable.

10.3 Equipment Operation and Sample Processing

10.3.1 Homogenization:

Homogenize the entire contents of the sample container to a consistent appearance to achieve a representative sample.

10.3.2 Duplicate: A second aliquot of the sample chosen to be duplicated.

10.3.3 Preparation Blank Solid (or Method Blank), (PBS):
The Method Blank is carried through the complete preparation procedure and contains the same volume of reagents as the sample solutions. The Method Blank is used to assess contamination from the laboratory environment.

10.3.4. Laboratory Control Sample Solid, (LCSS):

10.3.4.1: In the 50mL Polypropylene digestion vessel and utilize between 0.3 and 0.4 grams of SRM: Carry through entire process as a sample.

10.3.5 Matrix Spike, (MS):

10.3.5.1: To an aliquot of the sample designated for the MS, add 1.0mL each of IPS (Section 8.9.2), FPS (Section 8.9.3), and MIX (Section 8.9.4) working stock standards and 0.25 mL of 100ppm Ag standard (Section 8.9). If the desired metal is not included in the spiking solution, then also add 50µL of 1000ppm desired metal stock standard (Section 8.9).

10.3.6 Digestion Procedure:

Weigh a representative sample from 1.25g to 5g into a 50 mL digestion tube. Under a laboratory hood, slowly add 1 mL cHNO_3 (Section 8.2) followed immediately by the addition of 3 mL cHCl (Section 8.1) to each sample in the digestion vessel. Cover each vessel with a Reflux Cap.

NOTE: The acid combination used creates Aqua Regia, a powerful oxidizer which is a strong irritant; do not remove samples containing this concentrated form from the laboratory hood.

Heat the samples in the digestion vessel in the digestion block at 95 +/-3°C, and reflux for 30 minutes without boiling. Allow the samples to cool slightly by elevating the vessels in the rack-locks, add 1mL of cHNO_3, and reflux for another 30 minutes.

Ensure the sample is covered by the acid at all times during heating. Record in the laboratory notebook the time samples are placed in the digestion block and the time samples are taken out of the digestion block. The samples are brought up to a final volume of 50 mL. Instrumental analysts are to allow the sample to settle before decanting a sample aliquot.

10.3.6.1 Filtration Procedure:

If the sample has high suspended solids, precipitates upon cooling or floatables the sample filtration is performed as follows:

- Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 50-mL digestion tube. Wash the filter paper with no more than 5 mL of hot (~95 °C) HCl, then with 20 mL of hot (~95 °C) reagent water. Pre-heat the acid and reagent water in digestion tubes on the digestion heating block. Collect washings in the same 50-mL digestion vessel.
- Remove the filter and residue from the funnel, and place them back in the original digestion tube. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95 °C ± 3 °C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate and combine with the first filtrate in the 50-mL digestion vessel. Allow filtrate to cool.
- Bring to a final volume of 50mL with DI water, cap and mix by inverting a minimum of 3 times. Deliver to Instrument room with all appropriate batch paperwork.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume but add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water.

10.4 Continuing Calibration

Not applicable.

10.5 Preventive Maintenance

The Hot Block temperature is calibrated on an annual basis by an instrument service company. Certificates are kept on file.

11. Data Evaluation, Calculations and Reporting

Refer to analytical SOPs.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedances and improper preservation are noted on the batch sheet by the prep analyst and conveyed to the department supervisor or manager to include on nonconformance report.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the appropriate maintenance logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples; record any trends or unusual performance on a nonconformance action form.

If any QC parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP# 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP# 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP #1732 MDL/LOD/LOQ Generation

SOP# 1739 IDC/DOC Generation

SOP# 1728 Waste Management and Disposal SOP

16. Attachments

None.

Appendix B

Sampling Results

ANALYTICAL REPORT

Lab Number:	L1629859
Client:	ESS Group Incorporated 10 Hemingway Dr. 2nd Fl East Providence, RI 02915
ATTN:	Jim Riordan
Phone:	(401) 330-1233
Project Name:	BARRINGTON-BRICKYARD POND
Project Number:	B439-002
Report Date:	09/28/16

Certifications & Approvals: MA (M-MA086), NY (11148), CT (PH-0574), NH (2003), NJ NELAP (MA935), RI (LAO00065), ME (MA00086), PA (68-03671), VA (460195), MD (348), IL (200077), NC (666), TX (T104704476), DOD (L2217), USDA (Permit #P-330-11-00240).

Eight Walkup Drive, Westborough, MA 01581-1019
508-898-9220 (Fax) 508-898-9193 800-624-9220 - www.alphalab.com

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1629859
Report Date: 09/28/16

Alpha Sample ID	Client ID	Matrix	Sample Location	Collection Date/Time	Receive Date
L1629859-01	SURFACE	WATER	RI	09/21/16 11:30	09/21/16
L1629859-02	BOTTOM	WATER	RI	09/21/16 11:40	09/21/16

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1629859
Project Number: B439-002 **Report Date:** 09/28/16

Case Narrative

The samples were received in accordance with the Chain of Custody and no significant deviations were encountered during the preparation or analysis unless otherwise noted. Sample Receipt, Container Information, and the Chain of Custody are located at the back of the report.

Results contained within this report relate only to the samples submitted under this Alpha Lab Number and meet NELAP requirements for all NELAP accredited parameters unless otherwise noted in the following narrative. The data presented in this report is organized by parameter (i.e. VOC, SVOC, etc.). Sample specific Quality Control data (i.e. Surrogate Spike Recovery) is reported at the end of the target analyte list for each individual sample, followed by the Laboratory Batch Quality Control at the end of each parameter. Tentatively Identified Compounds (TICs), if requested, are reported for compounds identified to be present and are not part of the method/program Target Compound List, even if only a subset of the TCL are being reported. If a sample was re-analyzed or re-extracted due to a required quality control corrective action and if both sets of data are reported, the Laboratory ID of the re-analysis or re-extraction is designated with an "R" or "RE", respectively. When multiple Batch Quality Control elements are reported (e.g. more than one LCS), the associated samples for each element are noted in the grey shaded header line of each data table. Any Laboratory Batch, Sample Specific % recovery or RPD value that is outside the listed Acceptance Criteria is bolded in the report. All specific QC information is also incorporated in the Data Usability format of our Data Merger tool where it can be reviewed along with any associated usability implications. Soil/sediments, solids and tissues are reported on a dry weight basis unless otherwise noted. Definitions of all data qualifiers and acronyms used in this report are provided in the Glossary located at the back of the report.

In reference to questions H (CAM) or 4 (RCP) when "NO" is checked, the performance criteria for CAM and RCP methods allow for some quality control failures to occur and still be within method compliance. In these instances the specific failure is not narrated but noted in the associated QC table. The information is also incorporated in the Data Usability format of our Data Merger tool where it can be reviewed along with any associated usability implications.

Please see the associated ADEx data file for a comparison of laboratory reporting limits that were achieved with the regulatory Numerical Standards requested on the Chain of Custody.

HOLD POLICY
For samples submitted on hold, Alpha's policy is to hold samples (with the exception of Air canisters) free of charge for 21 calendar days from the date the project is completed. After 21 calendar days, we will dispose of all samples submitted including those put on hold unless you have contacted your Client Service Representative and made arrangements for Alpha to continue to hold the samples. Air canisters will be disposed after 3 business days from the date the project is completed.

Please contact Client Services at 800-624-9220 with any questions.

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1629859
Project Number: B439-002 **Report Date:** 09/28/16

Case Narrative (continued)

Report Submission

All non-detect (ND) or estimated concentrations (J-qualified) have been quantitated to the limit noted in the MDL column.

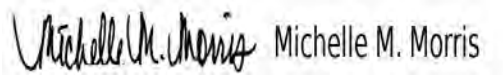
Phosphorus, Soluble

L1629859-02: The Soluble Phosphorus result is slightly higher than the Total Phosphorus result. The difference is within % RPD limits; therefore, no further action was taken.

Solids, Total Suspended

WG935560: A laboratory duplicate could not be performed due to insufficient sample volume available for analysis.

I, the undersigned, attest under the pains and penalties of perjury that, to the best of my knowledge and belief and based upon my personal inquiry of those responsible for providing the information contained in this analytical report, such information is accurate and complete. This certificate of analysis is not complete unless this page accompanies any and all pages of this report.

Authorized Signature:  Michelle M. Morris

Title: Technical Director/Representative Date: 09/28/16

METALS

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1629859
Project Number: B439-002
Report Date: 09/28/16

SAMPLE RESULTS

Lab ID: L1629859-01
Client ID: SURFACE
Sample Location: RI
Matrix: Water
Date Collected: 09/21/16 11:30
Date Received: 09/21/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	0.036	J	mg/l	0.10	0.020	1	09/23/16 14:00	09/23/16 23:31	EPA 3005A	1,6010C	FB
Iron, Total	0.030	J	mg/l	0.050	0.020	1	09/23/16 14:00	09/23/16 23:31	EPA 3005A	1,6010C	FB

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1629859
Project Number: B439-002
Report Date: 09/28/16

SAMPLE RESULTS

Lab ID: L1629859-02
Client ID: BOTTOM
Sample Location: RI
Matrix: Water

Date Collected: 09/21/16 11:40
Date Received: 09/21/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	0.027	J	mg/l	0.10	0.020	1	09/23/16 14:00	09/23/16 23:36	EPA 3005A	1,6010C	FB
Iron, Total	0.061		mg/l	0.050	0.020	1	09/23/16 14:00	09/23/16 23:36	EPA 3005A	1,6010C	FB

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1629859

Project Number: B439-002 **Report Date:** 09/28/16

Method Blank Analysis
Batch Quality Control

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
Total Metals - Mansfield Lab for sample(s): 01-02 Batch: WG935196-1										
Aluminum, Total	ND		mg/l	0.10	0.020	1	09/23/16 14:00	09/23/16 21:10	1,6010C	JH
Iron, Total	ND		mg/l	0.050	0.020	1	09/23/16 14:00	09/23/16 21:10	1,6010C	JH

Prep Information

Digestion Method: EPA 3005A

Lab Control Sample Analysis

Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND

Project Number: B439-002

Lab Number: L1629859

Report Date: 09/28/16

Parameter	LCS %Recovery	Qual	LCSD %Recovery	Qual	%Recovery Limits	RPD	Qual	RPD Limits
Total Metals - Mansfield Lab Associated sample(s): 01-02 Batch: WG935196-2								
Aluminum, Total	105		-		80-120	-		
Iron, Total	97		-		80-120	-		

Matrix Spike Analysis
Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1629859
Report Date: 09/28/16

Parameter	Native Sample	MS Added	MS Found	MS %Recovery	Qual	MSD Found	MSD %Recovery	Qual	Recovery Limits	RPD	Qual	RPD Limits
Total Metals - Mansfield Lab Associated sample(s): 01-02 QC Batch ID: WG935196-3 WG935196-4 QC Sample: L1629722-24 Client ID: MS Sample												
Aluminum, Total	ND	2	2.1	105		2.0	100		75-125	5		20
Iron, Total	0.12	1	1.1	98		1.0	88		75-125	10		20

INORGANICS
&
MISCELLANEOUS

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1629859
Report Date: 09/28/16

SAMPLE RESULTS

Lab ID: L1629859-01
Client ID: SURFACE
Sample Location: RI
Matrix: Water
Date Collected: 09/21/16 11:30
Date Received: 09/21/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Alkalinity, Total	72.6		mg CaCO3/L	2.00	NA	1	-	09/26/16 11:08	121,2320B	AW
Solids, Total Suspended	ND		mg/l	5.0	NA	1	-	09/25/16 16:30	121,2540D	SG
Nitrogen, Nitrate/Nitrite	0.081	J	mg/l	0.10	0.019	1	-	09/22/16 21:24	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	1.01		mg/l	0.300	0.066	1	09/22/16 01:00	09/26/16 22:25	121,4500N-C	AT
Phosphorus, Total	0.023		mg/l	0.010	0.003	1	09/26/16 09:25	09/27/16 10:05	121,4500P-E	SD
Phosphorus, Soluble	0.041		mg/l	0.010	0.004	1	09/27/16 12:15	09/27/16 15:45	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1629859
Report Date: 09/28/16

SAMPLE RESULTS

Lab ID: L1629859-02
Client ID: BOTTOM
Sample Location: RI
Matrix: Water

Date Collected: 09/21/16 11:40
Date Received: 09/21/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Alkalinity, Total	247.		mg CaCO3/L	2.00	NA	1	-	09/26/16 11:08	121,2320B	AW
Solids, Total Suspended	8.7		mg/l	5.0	NA	1	-	09/25/16 16:30	121,2540D	SG
Nitrogen, Nitrate/Nitrite	ND		mg/l	0.10	0.019	1	-	09/22/16 21:25	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	6.14		mg/l	0.300	0.066	1	09/22/16 01:00	09/26/16 22:26	121,4500N-C	AT
Phosphorus, Total	0.696		mg/l	0.010	0.003	1	09/26/16 09:25	09/27/16 10:06	121,4500P-E	SD
Phosphorus, Soluble	0.820		mg/l	0.020	0.008	2	09/27/16 12:15	09/27/16 15:45	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1629859

Project Number: B439-002 **Report Date:** 09/28/16

Method Blank Analysis
Batch Quality Control

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG934526-1										
Nitrogen, Total Kjeldahl	0.112	J	mg/l	0.300	0.022	1	09/22/16 01:00	09/26/16 22:18	121,4500N-C	AT
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG934866-1										
Nitrogen, Nitrate/Nitrite	ND		mg/l	0.10	0.019	1	-	09/22/16 20:35	121,4500NO3-F	MR
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG935560-1										
Solids, Total Suspended	ND		mg/l	5.0	NA	1	-	09/25/16 16:30	121,2540D	SG
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG935695-1										
Phosphorus, Total	ND		mg/l	0.010	0.003	1	09/26/16 09:25	09/27/16 09:35	121,4500P-E	SD
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG935784-1										
Alkalinity, Total	ND		mg CaCO3/L	2.00	NA	1	-	09/26/16 11:08	121,2320B	AW
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG936109-1										
Phosphorus, Soluble	0.005	J	mg/l	0.010	0.004	1	09/27/16 12:15	09/27/16 15:45	121,4500P-E	SD

Lab Control Sample Analysis

Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND

Project Number: B439-002

Lab Number: L1629859

Report Date: 09/28/16

Parameter	LCS %Recovery	Qual	LCSD %Recovery	Qual	%Recovery Limits	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG934526-2								
Nitrogen, Total Kjeldahl	94		-		78-122	-		
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG934866-2								
Nitrogen, Nitrate/Nitrite	98		-		90-110	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG935695-2								
Phosphorus, Total	100		-		80-120	-		
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG935784-2								
Alkalinity, Total	103		-		90-110	-		10
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG936109-2								
Phosphorus, Soluble	99		-		80-120	-		

Matrix Spike Analysis
Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1629859
Report Date: 09/28/16

Parameter	Native Sample	MS Added	MS Found	MS %Recovery	Qual	MSD Found	MSD %Recovery	Qual	Recovery Limits	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG934526-4 QC Sample: L1629827-01 Client ID: MS Sample												
Nitrogen, Total Kjeldahl	3.03	8	10.7	96		-	-		77-111	-		24
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG934866-4 QC Sample: L1629795-01 Client ID: MS Sample												
Nitrogen, Nitrate/Nitrite	33.	4	36	**75**	Q	-	-		80-120	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG935695-3 QC Sample: L1629120-01 Client ID: MS Sample												
Phosphorus, Total	0.004J	0.5	0.506	101		-	-		75-125	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG935784-4 QC Sample: L1629737-01 Client ID: MS Sample												
Alkalinity, Total	3970	500	4770	**160**	Q	-	-		86-116	-		10
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG936109-3 QC Sample: L1629778-04 Client ID: MS Sample												
Phosphorus, Soluble	0.041	0.5	0.477	87		-	-		75-125	-		20

Lab Duplicate Analysis
Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1629859
Report Date: 09/28/16

Parameter	Native Sample	Duplicate Sample	Units	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG934526-3 QC Sample: L1629827-01 Client ID: DUP Sample						
Nitrogen, Total Kjeldahl	3.03	3.13	mg/l	3		24
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG934866-3 QC Sample: L1629795-01 Client ID: DUP Sample						
Nitrogen, Nitrate/Nitrite	33.	32	mg/l	3		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG935695-4 QC Sample: L1629120-01 Client ID: DUP Sample						
Phosphorus, Total	0.004J	ND	mg/l	NC		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG935784-3 QC Sample: L1629737-01 Client ID: DUP Sample						
Alkalinity, Total	3970	4290	mg CaCO3/L	8		10
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG936109-4 QC Sample: L1629778-02 Client ID: DUP Sample						
Phosphorus, Soluble	0.632	0.674	mg/l	6		20

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1629859
Report Date: 09/28/16

Sample Receipt and Container Information

Were project specific reporting limits specified? YES

Cooler Information Custody Seal

Cooler	
A	Absent

Container Information

Container ID	Container Type	Cooler	pH	Temp deg C	Pres	Seal	Analysis(*)
L1629859-01A	Plastic 250ml unpreserved w/No H	A	N/A	4.5	Y	Absent	ALK-T-2320(14)
L1629859-01B	Plastic 500ml H2SO4 preserved	A	<2	4.5	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1629859-01C	Plastic 250ml unpreserved	A	7	4.5	Y	Absent	SPHOS-4500(28)
L1629859-01D	Plastic 250ml HNO3 preserved	A	<2	4.5	Y	Absent	AL-TI(180),FE-TI(180)
L1629859-01E	Plastic 950ml unpreserved	A	7	4.5	Y	Absent	TSS-2540(7)
L1629859-01X	Plastic 250ml H2SO4 preserved Fi	A	<2	4.5	Y	Absent	SPHOS-4500(28)
L1629859-02A	Plastic 250ml unpreserved w/No H	A	N/A	4.5	Y	Absent	ALK-T-2320(14)
L1629859-02B	Plastic 500ml H2SO4 preserved	A	<2	4.5	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1629859-02C	Plastic 250ml unpreserved	A	7	4.5	Y	Absent	SPHOS-4500(28)
L1629859-02D	Plastic 250ml HNO3 preserved	A	<2	4.5	Y	Absent	AL-TI(180),FE-TI(180)
L1629859-02E	Plastic 950ml unpreserved	A	7	4.5	Y	Absent	TSS-2540(7)
L1629859-02X	Plastic 250ml H2SO4 preserved Fi	A	<2	4.5	Y	Absent	SPHOS-4500(28)

*Values in parentheses indicate holding time in days

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1629859
Project Number:	B439-002	**Report Date:**	09/28/16

GLOSSARY

Acronyms

EDL	- Estimated Detection Limit: This value represents the level to which target analyte concentrations are reported as estimated values, when those target analyte concentrations are quantified below the reporting limit (RL). The EDL includes any adjustments from dilutions, concentrations or moisture content, where applicable. The use of EDLs is specific to the analysis of PAHs using Solid-Phase Microextraction (SPME).
EPA	- Environmental Protection Agency.
LCS	- Laboratory Control Sample: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes.
LCSD	- Laboratory Control Sample Duplicate: Refer to LCS.
LFB	- Laboratory Fortified Blank: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes.
MDL	- Method Detection Limit: This value represents the level to which target analyte concentrations are reported as estimated values, when those target analyte concentrations are quantified below the reporting limit (RL). The MDL includes any adjustments from dilutions, concentrations or moisture content, where applicable.
MS	- Matrix Spike Sample: A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.
MSD	- Matrix Spike Sample Duplicate: Refer to MS.
NA	- Not Applicable.
NC	- Not Calculated: Term is utilized when one or more of the results utilized in the calculation are non-detect at the parameter's reporting unit.
NDPA/DPA	- N-Nitrosodiphenylamine/Diphenylamine.
NI	- Not Ignitable.
NP	- Non-Plastic: Term is utilized for the analysis of Atterberg Limits in soil.
RL	- Reporting Limit: The value at which an instrument can accurately measure an analyte at a specific concentration. The RL includes any adjustments from dilutions, concentrations or moisture content, where applicable.
RPD	- Relative Percent Difference: The results from matrix and/or matrix spike duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). Values which are less than five times the reporting limit for any individual parameter are evaluated by utilizing the absolute difference between the values; although the RPD value will be provided in the report.
SRM	- Standard Reference Material: A reference sample of a known or certified value that is of the same or similar matrix as the associated field samples.
STLP	- Semi-dynamic Tank Leaching Procedure per EPA Method 1315.
TIC	- Tentatively Identified Compound: A compound that has been identified to be present and is not part of the target compound list (TCL) for the method and/or program. All TICs are qualitatively identified and reported as estimated concentrations.

Footnotes

1	- The reference for this analyte should be considered modified since this analyte is absent from the target analyte list of the original method.

Terms

Total: With respect to Organic analyses, a 'Total' result is defined as the summation of results for individual isomers or Aroclors. If a 'Total' result is requested, the results of its individual components will also be reported. This is applicable to 'Total' results for methods 8260, 8081 and 8082.

Analytical Method: Both the document from which the method originates and the analytical reference method. (Example: EPA 8260B is shown as 1,8260B.) The codes for the reference method documents are provided in the References section of the Addendum.

Data Qualifiers

A	- Spectra identified as "Aldol Condensation Product".
B	- The analyte was detected above the reporting limit in the associated method blank. Flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank. For MCP-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank. For DOD-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank AND the analyte was detected above one-half the reporting limit (or above the reporting limit for common lab contaminants) in the associated method blank. For NJ-Air-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte above the reporting limit. For NJ-related projects (excluding Air), flag only applies to associated field samples that have detectable concentrations of the analyte, which was detected above the reporting limit in the associated method blank or above five times the

Report Format: DU Report with 'J' Qualifiers

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1629859
Project Number:	B439-002	**Report Date:**	09/28/16

Data Qualifiers

reporting limit for common lab contaminants (Phthalates, Acetone, Methylene Chloride, 2-Butanone).

C - Co-elution: The target analyte co-elutes with a known lab standard (i.e. surrogate, internal standards, etc.) for co-extracted analyses.

D - Concentration of analyte was quantified from diluted analysis. Flag only applies to field samples that have detectable concentrations of the analyte.

E - Concentration of analyte exceeds the range of the calibration curve and/or linear range of the instrument.

G - The concentration may be biased high due to matrix interferences (i.e, co-elution) with non-target compound(s). The result should be considered estimated.

H - The analysis of pH was performed beyond the regulatory-required holding time of 15 minutes from the time of sample collection.

I - The lower value for the two columns has been reported due to obvious interference.

M - Reporting Limit (RL) exceeds the MCP CAM Reporting Limit for this analyte.

NJ - Presumptive evidence of compound. This represents an estimated concentration for Tentatively Identified Compounds (TICs), where the identification is based on a mass spectral library search.

P - The RPD between the results for the two columns exceeds the method-specified criteria.

Q - The quality control sample exceeds the associated acceptance criteria. For DOD-related projects, LCS and/or Continuing Calibration Standard exceedences are also qualified on all associated sample results. Note: This flag is not applicable for matrix spike recoveries when the sample concentration is greater than 4x the spike added or for batch duplicate RPD when the sample concentrations are less than 5x the RL. (Metals only.)

R - Analytical results are from sample re-analysis.

RE - Analytical results are from sample re-extraction.

S - Analytical results are from modified screening analysis.

J - Estimated value. The Target analyte concentration is below the quantitation limit (RL), but above the Method Detection Limit (MDL) or Estimated Detection Limit (EDL) for SPME-related analyses. This represents an estimated concentration for Tentatively Identified Compounds (TICs).

ND - Not detected at the method detection limit (MDL) for the sample, or estimated detection limit (EDL) for SPME-related analyses.

Report Format: DU Report with 'J' Qualifiers

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1629859
Project Number:	B439-002	**Report Date:**	09/28/16

REFERENCES

1 Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. EPA SW-846. Third Edition. Updates I - IV, 2007.

121 Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

LIMITATION OF LIABILITIES

Alpha Analytical performs services with reasonable care and diligence normal to the analytical testing laboratory industry. In the event of an error, the sole and exclusive responsibility of Alpha Analytical shall be to re-perform the work at it's own expense. In no event shall Alpha Analytical be held liable for any incidental, consequential or special damages, including but not limited to, damages in any way connected with the use of, interpretation of, information or analysis provided by Alpha Analytical.

We strongly urge our clients to comply with EPA protocol regarding sample volume, preservation, cooling, containers, sampling procedures, holding time and splitting of samples in the field.

Certification Information

The following analytes are not included in our Primary NELAP Scope of Accreditation:

Westborough Facility
EPA 624: m/p-xylene, o-xylene
EPA 8260C: NPW: 1,2,4,5-Tetramethylbenzene; 4-Ethyltoluene, Azobenzene; SCM: Iodomethane (methyl iodide), Methyl methacrylate, 1,2,4,5-Tetramethylbenzene; 4-Ethyltoluene.
EPA 8270D: NPW: Dimethylnaphthalene,1,4-Diphenylhydrazine; SCM: Dimethylnaphthalene,1,4-Diphenylhydrazine.
EPA 300: DW: Bromide
EPA 6860: NPW and SCM: Perchlorate
EPA 9010: NPW and SCM: Amenable Cyanide Distillation
EPA 9012B: NPW: Total Cyanide
EPA 9050A: NPW: Specific Conductance
SM3500: NPW: Ferrous Iron
SM4500: NPW: Amenable Cyanide, Dissolved Oxygen; SCM: Total Phosphorus, TKN, NO2, NO3.
SM5310C: DW: Dissolved Organic Carbon

Mansfield Facility
SM 2540D: TSS
EPA 3005A NPW
EPA 8082A: NPW: PCB: 1, 5, 31, 87,101, 110, 141, 151, 153, 180, 183, 187.
EPA TO-15: Halothane, 2,4,4-Trimethyl-2-pentene, 2,4,4-Trimethyl-1-pentene, Thiophene, 2-Methylthiophene, 3-Methylthiophene, 2-Ethylthiophene, 1,2,3-Trimethylbenzene, Indan, Indene, 1,2,4,5-Tetramethylbenzene, Benzothiophene, 1-Methylnaphthalene.
Biological Tissue Matrix: ***EPA 3050B***

The following analytes are included in our Massachusetts DEP Scope of Accreditation

Westborough Facility:

Drinking Water
EPA 300.0: Nitrate-N, Fluoride, Sulfate; **EPA 353.2**: Nitrate-N, Nitrite-N; **SM4500NO3-F**: Nitrate-N, Nitrite-N; **SM4500F-C, SM4500CN-CE, EPA 180.1, SM2130B, SM4500Cl-D, SM2320B, SM2540C, SM4500H-B**
EPA 332: Perchlorate; **EPA 524.2:** THMs and VOCs; **EPA 504.1:** EDB, DBCP.
Microbiology: **SM9215B; SM9223-P/A, SM9223B-Colilert-QT,SM9222D**.

Non-Potable Water
SM4500H,B, EPA 120.1, SM2510B, SM2540C, SM2320B, SM4500CL-E, SM4500F-BC, SM4500NH3-BH, **EPA 350.1**: Ammonia-N, **LACHAT 10-107-06-1-B**: Ammonia-N, **SM4500NO3-F, EPA 353.2**: Nitrate-N**, EPA 351.1, SM4500P-E, SM4500P-B, E, SM4500SO4-E, SM5220D, EPA 410.4, SM5210B, SM5310C, SM4500CL-D, EPA 1664, EPA 420.1, SM4500-CN-CE, SM2540D.**
EPA 624: Volatile Halocarbons & Aromatics,
EPA 608: Chlordane, Toxaphene, Aldrin, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, Dieldrin, DDD, DDE, DDT, Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin, Endrin Aldehyde, Heptachlor, Heptachlor Epoxide, PCBs
EPA 625: SVOC (Acid/Base/Neutral Extractables), **EPA 600/4-81-045**: PCB-Oil.
Microbiology: **SM9223B-Colilert-QT; Enterolert-QT, SM9222D-MF**.

Mansfield Facility:

Drinking Water
EPA 200.7: Ba, Be, Cd, Cr, Cu, Ni, Na, Ca. **EPA 200.8:** Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, TL. **EPA 245.1** Hg.

Non-Potable Water
EPA 200.7: Al, Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Sr, TL, Ti, V, Zn.
EPA 200.8: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, TL, Zn.
EPA 245.1 Hg.
SM2340B

For a complete listing of analytes and methods, please contact your Alpha Project Manager.

CHAIN OF CUSTODY

PAGE _____ OF _____

Date Rec'd in Lab: 9/21/16

ALPHA Job #: L1629859

ALPHA ANALYTICAL
8 Walkup Drive, Westboro, MA 01581, Tel: 508-898-9220
320 Forbes Blvd, Mansfield, MA 02048, Tel: 508-822-9300

Project Information

Project Name: BARRINGTON-BRICKYARD POND
Project Location: RI
Project #: B439-002
Project Manager: JIM RIORDAN
ALPHA Quote #:

Report Information - Data Deliverables

☐ ADEx ☑ EMAIL

Billing Information

☑ Same as Client info PO #:

Client Information

Client: ESS GROUP
Address:
Phone: 401-330-1204
Email: mladewig@essgroup.com

Regulatory Requirements & Project Information Requirements

☐ Yes ☑ No MA MCP Analytical Methods ☐ Yes ☑ No CT RCP Analytical Methods
☐ Yes ☑ No Matrix Spike Required on this SDG? (Required for MCP Inorganics)
☐ Yes ☑ No GW1 Standards (Info Required for Metals & EPH with Targets)
☐ Yes ☑ No NPDES RGP
☐ Other State /Fed Program _____ Criteria _____

Turn-Around Time

☑ Standard ☐ RUSH (only confirmed if pre-approved!)
Date Due:

Additional Project Information:

NOTE: PLEASE RUN LOW DETECT (0.01 mg/L) ON PHOSPHORUS OR BETTER + REPORT MDL
- LOW DETECT ALKALINITY

ANALYSIS: VOC: ☐ 8260 ☐ 624 ☐ 524.2 | SVOC: ☐ ABN ☐ PAH | METALS: ☐ MCP 13 ☐ MCP 14 ☐ RCP 15 | METALS: ☐ RCRA5 ☐ RCRA8 ☐ PP13 | EPH: ☐ Ranges & Targets ☐ Ranges Only | VPH: ☐ Ranges & Targets ☐ Ranges Only | ☐ PCB ☐ PEST | TPH: ☐ Quant Only ☐ Fingerprint | TKN | NO2/NO3 | TOTAL P** | TSS | SOLUBLE P** | ALKALINITY | METALS (Fe, Al)

SAMPLE INFO
Filtration
☐ Field
☑ Lab to do
Preservation
☐ Lab to do

ALPHA Lab ID (Lab Use Only)	Sample ID	Collection Date	Collection Time	Sample Matrix	Sampler Initials	Sample Comments	TOTAL # BOTTLES
29859-01	SURFACE	9/21/16	1130	SW	AC/ML		5
-02	BOTTOM	9/21/16	1140	SW	AC/ML		5

Container Type											P	P	P	P	P	P	P	
Preservative											D	D	D	A	A	A	C	

Container Type
P= Plastic
A= Amber glass
V= Vial
G= Glass
B= Bacteria cup
C= Cube
O= Other
E= Encore
D= BOD Bottle

Preservative
A= None
B= HCl
C= HNO_3
D= H_2SO_4
E= NaOH
F= MeOH
G= $NaHSO_4$
H = $Na_2S_2O_3$
I= Ascorbic Acid
J = NH_4Cl
K= Zn Acetate
O= Other

Relinquished By:	Date/Time	Received By:	Date/Time
John Sullivan RAL 9/21/16	9/21/16 15:50	RAL	9/21/16 14:27 9/21/16 1550

All samples submitted are subject to Alpha's Terms and Conditions. See reverse side.

FORM NO: 01-01 (rev. 12-Mar-2012)

ANALYTICAL REPORT

Lab Number:	L1635672
Client:	ESS Group Incorporated 10 Hemingway Dr. 2nd Fl East Providence, RI 02915
ATTN:	Jim Riordan
Phone:	(401) 330-1233
Project Name:	BARRINGTON-BRICKYARD POND
Project Number:	B439-002
Report Date:	11/09/16

Certifications & Approvals: MA (M-MA086), NY (11148), CT (PH-0574), NH (2003), NJ NELAP (MA935), RI (LAO00065), ME (MA00086), PA (68-03671), VA (460195), MD (348), IL (200077), NC (666), TX (T104704476), DOD (L2217), USDA (Permit #P-330-11-00240).

Eight Walkup Drive, Westborough, MA 01581-1019
508-898-9220 (Fax) 508-898-9193 800-624-9220 - www.alphalab.com

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1635672
Report Date: 11/09/16

Alpha Sample ID	Client ID	Matrix	Sample Location	Collection Date/Time	Receive Date
L1635672-01	SURFACE	WATER	RI	11/03/16 12:54	11/03/16
L1635672-02	BOTTOM	WATER	RI	11/03/16 12:42	11/03/16
L1635672-03	S1	SEDIMENT	RI	11/03/16 13:03	11/03/16
L1635672-04	S2	SEDIMENT	RI	11/03/16 11:28	11/03/16
L1635672-05	S3	SEDIMENT	RI	11/03/16 11:48	11/03/16

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1635672
Project Number: B439-002 **Report Date:** 11/09/16

Case Narrative

The samples were received in accordance with the Chain of Custody and no significant deviations were encountered during the preparation or analysis unless otherwise noted. Sample Receipt, Container Information, and the Chain of Custody are located at the back of the report.

Results contained within this report relate only to the samples submitted under this Alpha Lab Number and meet NELAP requirements for all NELAP accredited parameters unless otherwise noted in the following narrative. The data presented in this report is organized by parameter (i.e. VOC, SVOC, etc.). Sample specific Quality Control data (i.e. Surrogate Spike Recovery) is reported at the end of the target analyte list for each individual sample, followed by the Laboratory Batch Quality Control at the end of each parameter. Tentatively Identified Compounds (TICs), if requested, are reported for compounds identified to be present and are not part of the method/program Target Compound List, even if only a subset of the TCL are being reported. If a sample was re-analyzed or re-extracted due to a required quality control corrective action and if both sets of data are reported, the Laboratory ID of the re-analysis or re-extraction is designated with an "R" or "RE", respectively. When multiple Batch Quality Control elements are reported (e.g. more than one LCS), the associated samples for each element are noted in the grey shaded header line of each data table. Any Laboratory Batch, Sample Specific % recovery or RPD value that is outside the listed Acceptance Criteria is bolded in the report. All specific QC information is also incorporated in the Data Usability format of our Data Merger tool where it can be reviewed along with any associated usability implications. Soil/sediments, solids and tissues are reported on a dry weight basis unless otherwise noted. Definitions of all data qualifiers and acronyms used in this report are provided in the Glossary located at the back of the report.

In reference to questions H (CAM) or 4 (RCP) when "NO" is checked, the performance criteria for CAM and RCP methods allow for some quality control failures to occur and still be within method compliance. In these instances the specific failure is not narrated but noted in the associated QC table. The information is also incorporated in the Data Usability format of our Data Merger tool where it can be reviewed along with any associated usability implications.

Please see the associated ADEx data file for a comparison of laboratory reporting limits that were achieved with the regulatory Numerical Standards requested on the Chain of Custody.

HOLD POLICY
For samples submitted on hold, Alpha's policy is to hold samples (with the exception of Air canisters) free of charge for 21 calendar days from the date the project is completed. After 21 calendar days, we will dispose of all samples submitted including those put on hold unless you have contacted your Client Service Representative and made arrangements for Alpha to continue to hold the samples. Air canisters will be disposed after 3 business days from the date the project is completed.

Please contact Client Services at 800-624-9220 with any questions.

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1635672
Project Number:	B439-002	**Report Date:**	11/09/16

Case Narrative (continued)

Report Submission

All non-detect (ND) or estimated concentrations (J-qualified) have been quantitated to the limit noted in the MDL column.

Solids, Total Suspended

WG949416: A laboratory duplicate could not be performed due to insufficient sample volume available for analysis.

Phosphorus, Soluble

The WG949785-4 Laboratory Duplicate RPD (28%), performed on L1635672-01, is above the acceptance criteria; however, the sample and duplicate results are less than five times the reporting limit. Therefore, the RPD is valid.

I, the undersigned, attest under the pains and penalties of perjury that, to the best of my knowledge and belief and based upon my personal inquiry of those responsible for providing the information contained in this analytical report, such information is accurate and complete. This certificate of analysis is not complete unless this page accompanies any and all pages of this report.

Authorized Signature: Amita Naik

Title: Technical Director/Representative Date: 11/09/16

METALS

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1635672
Project Number: B439-002
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-01
Client ID: SURFACE
Sample Location: RI
Matrix: Water

Date Collected: 11/03/16 12:54
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	0.03	J	mg/l	0.10	0.03	1	11/08/16 08:30	11/08/16 22:05	EPA 3005A	1,6010C	AB
Iron, Total	0.03	J	mg/l	0.05	0.01	1	11/08/16 08:30	11/08/16 22:05	EPA 3005A	1,6010C	AB

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1635672
Project Number: B439-002
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-02
Client ID: BOTTOM
Sample Location: RI
Matrix: Water

Date Collected: 11/03/16 12:42
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	0.04	J	mg/l	0.10	0.03	1	11/08/16 08:30	11/08/16 22:09	EPA 3005A	1,6010C	AB
Iron, Total	0.07		mg/l	0.05	0.01	1	11/08/16 08:30	11/08/16 22:09	EPA 3005A	1,6010C	AB

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1635672
Project Number: B439-002
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-03
Client ID: S1
Sample Location: RI
Matrix: Sediment
Percent Solids: 15%

Date Collected: 11/03/16 13:03
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	17000		mg/kg	26	7.1	1	11/04/16 19:18	11/08/16 15:53	EPA 3050B	1,6010C	AB
Iron, Total	30000		mg/kg	13	2.4	1	11/04/16 19:18	11/08/16 15:53	EPA 3050B	1,6010C	AB

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1635672
Project Number: B439-002
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-04
Client ID: S2
Sample Location: RI
Matrix: Sediment
Percent Solids: 20%

Date Collected: 11/03/16 11:28
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	13000		mg/kg	20	5.3	1	11/04/16 19:18	11/08/16 16:12	EPA 3050B	1,6010C	AB
Iron, Total	22000		mg/kg	9.8	1.8	1	11/04/16 19:18	11/08/16 16:12	EPA 3050B	1,6010C	AB

Project Name: BARRINGTON-BRICKYARD POND
Lab Number: L1635672
Project Number: B439-002
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-05
Client ID: S3
Sample Location: RI
Matrix: Sediment
Percent Solids: 20%

Date Collected: 11/03/16 11:48
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Total Metals - Mansfield Lab											
Aluminum, Total	12000		mg/kg	19	5.2	1	11/04/16 19:18	11/08/16 16:16	EPA 3050B	1,6010C	AB
Iron, Total	21000		mg/kg	9.6	1.7	1	11/04/16 19:18	11/08/16 16:16	EPA 3050B	1,6010C	AB

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1635672

Project Number: B439-002 **Report Date:** 11/09/16

Method Blank Analysis
Batch Quality Control

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
Total Metals - Mansfield Lab for sample(s): 03-05 Batch: WG949368-1										
Aluminum, Total	ND		mg/kg	4.0	1.1	1	11/04/16 19:18	11/08/16 16:04	1,6010C	AB
Iron, Total	0.77	J	mg/kg	2.0	0.36	1	11/04/16 19:18	11/08/16 16:04	1,6010C	AB

Prep Information

Digestion Method: EPA 3050B

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
Total Metals - Mansfield Lab for sample(s): 01-02 Batch: WG950119-1										
Aluminum, Total	ND		mg/l	0.10	0.03	1	11/08/16 08:30	11/08/16 20:52	1,6010C	AB
Iron, Total	ND		mg/l	0.05	0.01	1	11/08/16 08:30	11/08/16 20:52	1,6010C	AB

Prep Information

Digestion Method: EPA 3005A

Lab Control Sample Analysis

Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND

Project Number: B439-002

Lab Number: L1635672

Report Date: 11/09/16

Parameter	LCS %Recovery	Qual	LCSD %Recovery	Qual	%Recovery Limits	RPD	Qual	RPD Limits
Total Metals - Mansfield Lab Associated sample(s): 03-05 Batch: WG949368-2 SRM Lot Number: D091-540								
Aluminum, Total	92		-		52-148	-		
Iron, Total	100		-		47-154	-		
Total Metals - Mansfield Lab Associated sample(s): 01-02 Batch: WG950119-2								
Aluminum, Total	95		-		80-120	-		
Iron, Total	87		-		80-120	-		

Matrix Spike Analysis
Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1635672
Report Date: 11/09/16

Parameter	Native Sample	MS Added	MS Found	MS %Recovery	Qual	MSD Found	MSD %Recovery	Qual	Recovery Limits	RPD	Qual	RPD Limits
Total Metals - Mansfield Lab Associated sample(s): 03-05 QC Batch ID: WG949368-3 QC Sample: L1635707-01 Client ID: MS Sample												
Aluminum, Total	12000	167	11000	**0**	Q	-	-		75-125	-		20
Iron, Total	24000	83.5	24000	**0**	Q	-	-		75-125	-		20
Total Metals - Mansfield Lab Associated sample(s): 01-02 QC Batch ID: WG950119-3 QC Sample: L1635420-03 Client ID: MS Sample												
Aluminum, Total	0.07J	2	2.0	100		-	-		75-125	-		20
Iron, Total	0.28	1	1.2	92		-	-		75-125	-		20

INORGANICS
&
MISCELLANEOUS

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1635672
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-01
Client ID: SURFACE
Sample Location: RI
Matrix: Water
Date Collected: 11/03/16 12:54
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Alkalinity, Total	76.3		mg CaCO3/L	2.00	NA	1	-	11/06/16 13:06	121,2320B	SG
Solids, Total Suspended	6.4		mg/l	5.0	NA	1	-	11/05/16 00:43	121,2540D	MC
Nitrogen, Nitrate/Nitrite	0.090	J	mg/l	0.10	0.019	1	-	11/04/16 20:29	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	1.36		mg/l	0.300	0.066	1	11/07/16 21:30	11/08/16 21:38	121,4500N-C	AT
Phosphorus, Total	0.043		mg/l	0.010	0.003	1	11/04/16 13:00	11/07/16 10:01	121,4500P-E	SD
Phosphorus, Soluble	0.033		mg/l	0.010	0.004	1	11/07/16 10:45	11/07/16 15:25	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1635672
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-02
Client ID: BOTTOM
Sample Location: RI
Matrix: Water

Date Collected: 11/03/16 12:42
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Alkalinity, Total	199.		mg CaCO3/L	2.00	NA	1	-	11/06/16 13:06	121,2320B	SG
Solids, Total Suspended	8.4		mg/l	5.0	NA	1	-	11/05/16 00:43	121,2540D	MC
Nitrogen, Nitrate/Nitrite	0.042	J	mg/l	0.10	0.019	1	-	11/04/16 20:31	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	6.47		mg/l	0.300	0.066	1	11/07/16 21:30	11/08/16 21:54	121,4500N-C	AT
Phosphorus, Total	0.719		mg/l	0.010	0.003	1	11/04/16 13:00	11/07/16 10:02	121,4500P-E	SD
Phosphorus, Soluble	0.568		mg/l	0.020	0.008	2	11/07/16 10:45	11/07/16 15:25	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1635672
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-03
Client ID: S1
Sample Location: RI
Matrix: Sediment
Date Collected: 11/03/16 13:03
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Solids, Total	14.6		%	0.100	NA	1	-	11/04/16 01:36	121,2540G	VB
Nitrogen, Nitrate/Nitrite	ND		mg/kg	6.4	1.8	1	-	11/04/16 20:51	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	9500		mg/kg	980	210	1	11/08/16 09:53	11/08/16 23:06	121,4500N-C	AT
Phosphorus, Total	2000		mg/kg	160	54.	4.7	-	11/07/16 12:30	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1635672
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-04
Client ID: S2
Sample Location: RI
Matrix: Sediment
Date Collected: 11/03/16 11:28
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Solids, Total	20.2		%	0.100	NA	1	-	11/04/16 01:36	121,2540G	VB
Nitrogen, Nitrate/Nitrite	ND		mg/kg	4.4	1.2	1	-	11/04/16 20:53	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	5000		mg/kg	670	140	1	11/08/16 09:53	11/08/16 23:08	121,4500N-C	AT
Phosphorus, Total	1800		mg/kg	130	44.	5.3	-	11/07/16 12:30	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002
Lab Number: L1635672
Report Date: 11/09/16

SAMPLE RESULTS

Lab ID: L1635672-05
Client ID: S3
Sample Location: RI
Matrix: Sediment

Date Collected: 11/03/16 11:48
Date Received: 11/03/16
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Solids, Total	20.2		%	0.100	NA	1	-	11/04/16 01:36	121,2540G	VB
Nitrogen, Nitrate/Nitrite	ND		mg/kg	4.8	1.4	1	-	11/04/16 20:54	121,4500NO3-F	MR
Nitrogen, Total Kjeldahl	4400		mg/kg	590	120	1	11/08/16 09:53	11/08/16 23:09	121,4500N-C	AT
Phosphorus, Total	1400		mg/kg	120	40.	4.9	-	11/07/16 12:30	121,4500P-E	SD

Project Name: BARRINGTON-BRICKYARD POND **Lab Number:** L1635672

Project Number: B439-002 **Report Date:** 11/09/16

Method Blank Analysis
Batch Quality Control

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG949232-1										
Phosphorus, Total	ND		mg/l	0.010	0.003	1	11/04/16 13:00	11/07/16 09:31	121,4500P-E	SD
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG949363-1										
Nitrogen, Nitrate/Nitrite	ND		mg/l	0.10	0.019	1	-	11/04/16 20:14	121,4500NO3-F	MR
General Chemistry - Westborough Lab for sample(s): 03-05 Batch: WG949367-1										
Nitrogen, Nitrate/Nitrite	ND		mg/kg	1.0	0.03	1	-	11/04/16 20:46	121,4500NO3-F	MR
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG949416-1										
Solids, Total Suspended	ND		mg/l	5.0	NA	1	-	11/05/16 00:43	121,2540D	MC
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG949621-1										
Alkalinity, Total	ND		mg CaCO3/L	2.00	NA	1	-	11/06/16 13:06	121,2320B	SG
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG949785-1										
Phosphorus, Soluble	ND		mg/l	0.010	0.004	1	11/07/16 10:45	11/07/16 15:25	121,4500P-E	SD
General Chemistry - Westborough Lab for sample(s): 03-05 Batch: WG949816-1										
Phosphorus, Total	ND		mg/kg	5.0	1.7	1	-	11/07/16 12:30	121,4500P-E	SD
General Chemistry - Westborough Lab for sample(s): 01-02 Batch: WG950000-1										
Nitrogen, Total Kjeldahl	0.067	J	mg/l	0.300	0.022	1	11/07/16 21:30	11/08/16 21:24	121,4500N-C	AT
General Chemistry - Westborough Lab for sample(s): 03-05 Batch: WG950202-1										
Nitrogen, Total Kjeldahl	0.07	J	mg/kg	0.30	0.02	1	11/08/16 09:53	11/08/16 23:04	121,4500N-C	AT

Lab Control Sample Analysis

Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1635672
Report Date: 11/09/16

Parameter	LCS %Recovery	Qual	LCSD %Recovery	Qual	%Recovery Limits	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG949232-2								
Phosphorus, Total	96		-		80-120	-		
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG949363-2								
Nitrogen, Nitrate/Nitrite	98		-		90-110	-		20
General Chemistry - Westborough Lab Associated sample(s): 03-05 Batch: WG949367-2								
Nitrogen, Nitrate/Nitrite	98		-		90-110	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG949621-3								
Alkalinity, Total	102		-		90-110	-		10
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG949785-2								
Phosphorus, Soluble	101		-		80-120	-		
General Chemistry - Westborough Lab Associated sample(s): 03-05 Batch: WG949816-2								
Phosphorus, Total	91		-		52-148	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 Batch: WG950000-2								
Nitrogen, Total Kjeldahl	99		-		78-122	-		

Lab Control Sample Analysis

Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND

Project Number: B439-002

Lab Number: L1635672

Report Date: 11/09/16

Parameter	LCS %Recovery	LCSD %Recovery	%Recovery Limits	RPD	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 03-05 Batch: WG950202-2					
Nitrogen, Total Kjeldahl	96	-	84-115	-	26

Matrix Spike Analysis
Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1635672
Report Date: 11/09/16

Parameter	Native Sample	MS Added	MS Found	MS %Recovery	Qual	MSD Found	MSD %Recovery	Qual	Recovery Limits	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949232-3 QC Sample: L1634644-01 Client ID: MS Sample												
Phosphorus, Total	37.8	1.25	39.7	**158**	Q	-	-		75-125	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949363-4 QC Sample: L1635722-06 Client ID: MS Sample												
Nitrogen, Nitrate/Nitrite	0.090J	4	3.8	95		-	-		80-120	-		20
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG949367-4 QC Sample: L1635565-01 Client ID: MS Sample												
Nitrogen, Nitrate/Nitrite	0.75J	185.8	160	86		-	-		80-120	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949621-4 QC Sample: L1635672-01 Client ID: SURFACE												
Alkalinity, Total	76.3	100	179	103		-	-		86-116	-		10
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949785-3 QC Sample: L1635672-02 Client ID: BOTTOM												
Phosphorus, Soluble	0.568	0.5	1.06	98		-	-		75-125	-		20
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG949816-3 QC Sample: L1635401-01 Client ID: MS Sample												
Phosphorus, Total	70.	246	350	110		-	-		75-125	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG950000-4 QC Sample: L1635672-01 Client ID: SURFACE												
Nitrogen, Total Kjeldahl	1.36	8	9.28	99		-	-		77-111	-		24
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG950202-4 QC Sample: L1635672-03 Client ID: S1												
Nitrogen, Total Kjeldahl	9500	24500	32000	94		-	-		43-160	-		26

Lab Duplicate Analysis
Batch Quality Control

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1635672
Report Date: 11/09/16

Parameter	Native Sample	Duplicate Sample	Units	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG949041-2 QC Sample: L1635152-01 Client ID: DUP Sample						
Solids, Total	73.5	75.1	%	2		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949232-4 QC Sample: L1634644-01 Client ID: DUP Sample						
Phosphorus, Total	37.8	38.8	mg/l	3		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949363-3 QC Sample: L1635722-06 Client ID: DUP Sample						
Nitrogen, Nitrate/Nitrite	0.090J	0.093J	mg/l	NC		20
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG949367-3 QC Sample: L1635565-01 Client ID: DUP Sample						
Nitrogen, Nitrate/Nitrite	0.75J	0.80J	mg/kg	NC		20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949621-2 QC Sample: L1635672-01 Client ID: SURFACE						
Alkalinity, Total	76.3	77.3	mg CaCO3/L	1		10
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG949785-4 QC Sample: L1635672-01 Client ID: SURFACE						
Phosphorus, Soluble	0.033	0.025	mg/l	**28**	Q	20
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG949816-4 QC Sample: L1635401-01 Client ID: DUP Sample						
Phosphorus, Total	70.	210	mg/kg	**100**	Q	20
General Chemistry - Westborough Lab Associated sample(s): 01-02 QC Batch ID: WG950000-3 QC Sample: L1635672-01 Client ID: SURFACE						
Nitrogen, Total Kjeldahl	1.36	1.20	mg/l	13		24
General Chemistry - Westborough Lab Associated sample(s): 03-05 QC Batch ID: WG950202-3 QC Sample: L1635672-03 Client ID: S1						
Nitrogen, Total Kjeldahl	9500	9400	mg/kg	1		26

Project Name: BARRINGTON-BRICKYARD POND
Project Number: B439-002

Lab Number: L1635672
Report Date: 11/09/16

Sample Receipt and Container Information

Were project specific reporting limits specified? YES

Cooler Information Custody Seal

Cooler	
A	Absent

Container Information

Container ID	Container Type	Cooler	pH	Temp deg C	Pres	Seal	Analysis(*)
L1635672-01A	Plastic 250ml unpreserved w/No H	A	N/A	2.6	Y	Absent	ALK-T-2320(14)
L1635672-01B	Plastic 500ml H2SO4 preserved	A	<2	2.6	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1635672-01C	Plastic 250ml unpreserved	A	7	2.6	Y	Absent	SPHOS-4500(28)
L1635672-01D	Plastic 250ml HNO3 preserved	A	<2	2.6	Y	Absent	AL-TI(180),FE-TI(180)
L1635672-01E	Plastic 950ml unpreserved	A	7	2.6	Y	Absent	TSS-2540(7)
L1635672-01X	Plastic 250ml H2SO4 preserved Fi	A	<2	2.6	Y	Absent	SPHOS-4500(28)
L1635672-02A	Plastic 250ml unpreserved w/No H	A	N/A	2.6	Y	Absent	ALK-T-2320(14)
L1635672-02B	Plastic 500ml H2SO4 preserved	A	<2	2.6	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1635672-02C	Plastic 250ml unpreserved	A	7	2.6	Y	Absent	SPHOS-4500(28)
L1635672-02D	Plastic 250ml HNO3 preserved	A	<2	2.6	Y	Absent	AL-TI(180),FE-TI(180)
L1635672-02E	Plastic 950ml unpreserved	A	7	2.6	Y	Absent	TSS-2540(7)
L1635672-02X	Plastic 250ml H2SO4 preserved Fi	A	<2	2.6	Y	Absent	SPHOS-4500(28)
L1635672-03A	Metals Only - Glass 60mL/2oz unp	A	N/A	2.6	Y	Absent	AL-TI(180),FE-TI(180)
L1635672-03B	Plastic 2oz unpreserved for TS	A	N/A	2.6	Y	Absent	TS(7)
L1635672-03C	Glass 60mL/2oz unpreserved	A	N/A	2.6	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1635672-04A	Metals Only - Glass 60mL/2oz unp	A	N/A	2.6	Y	Absent	AL-TI(180),FE-TI(180)
L1635672-04B	Plastic 2oz unpreserved for TS	A	N/A	2.6	Y	Absent	TS(7)
L1635672-04C	Glass 60mL/2oz unpreserved	A	N/A	2.6	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1635672-05A	Metals Only - Glass 60mL/2oz unp	A	N/A	2.6	Y	Absent	AL-TI(180),FE-TI(180)
L1635672-05B	Plastic 2oz unpreserved for TS	A	N/A	2.6	Y	Absent	TS(7)
L1635672-05C	Glass 60mL/2oz unpreserved	A	N/A	2.6	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)

*Values in parentheses indicate holding time in days

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1635672
Project Number:	B439-002	**Report Date:**	11/09/16

GLOSSARY

Acronyms

EDL	- Estimated Detection Limit: This value represents the level to which target analyte concentrations are reported as estimated values, when those target analyte concentrations are quantified below the reporting limit (RL). The EDL includes any adjustments from dilutions, concentrations or moisture content, where applicable. The use of EDLs is specific to the analysis of PAHs using Solid-Phase Microextraction (SPME).
EPA	- Environmental Protection Agency.
LCS	- Laboratory Control Sample: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes.
LCSD	- Laboratory Control Sample Duplicate: Refer to LCS.
LFB	- Laboratory Fortified Blank: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes.
MDL	- Method Detection Limit: This value represents the level to which target analyte concentrations are reported as estimated values, when those target analyte concentrations are quantified below the reporting limit (RL). The MDL includes any adjustments from dilutions, concentrations or moisture content, where applicable.
MS	- Matrix Spike Sample: A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.
MSD	- Matrix Spike Sample Duplicate: Refer to MS.
NA	- Not Applicable.
NC	- Not Calculated: Term is utilized when one or more of the results utilized in the calculation are non-detect at the parameter's reporting unit.
NDPA/DPA	- N-Nitrosodiphenylamine/Diphenylamine.
NI	- Not Ignitable.
NP	- Non-Plastic: Term is utilized for the analysis of Atterberg Limits in soil.
RL	- Reporting Limit: The value at which an instrument can accurately measure an analyte at a specific concentration. The RL includes any adjustments from dilutions, concentrations or moisture content, where applicable.
RPD	- Relative Percent Difference: The results from matrix and/or matrix spike duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). Values which are less than five times the reporting limit for any individual parameter are evaluated by utilizing the absolute difference between the values; although the RPD value will be provided in the report.
SRM	- Standard Reference Material: A reference sample of a known or certified value that is of the same or similar matrix as the associated field samples.
STLP	- Semi-dynamic Tank Leaching Procedure per EPA Method 1315.
TIC	- Tentatively Identified Compound: A compound that has been identified to be present and is not part of the target compound list (TCL) for the method and/or program. All TICs are qualitatively identified and reported as estimated concentrations.

Footnotes

1	- The reference for this analyte should be considered modified since this analyte is absent from the target analyte list of the original method.

Terms

Total: With respect to Organic analyses, a 'Total' result is defined as the summation of results for individual isomers or Aroclors. If a 'Total' result is requested, the results of its individual components will also be reported. This is applicable to 'Total' results for methods 8260, 8081 and 8082.

Analytical Method: Both the document from which the method originates and the analytical reference method. (Example: EPA 8260B is shown as 1,8260B.) The codes for the reference method documents are provided in the References section of the Addendum.

Data Qualifiers

A	- Spectra identified as "Aldol Condensation Product".
B	- The analyte was detected above the reporting limit in the associated method blank. Flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank. For MCP-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank. For DOD-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank AND the analyte was detected above one-half the reporting limit (or above the reporting limit for common lab contaminants) in the associated method blank. For NJ-Air-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte above the reporting limit. For NJ-related projects (excluding Air), flag only applies to associated field samples that have detectable concentrations of the analyte, which was detected above the reporting limit in the associated method blank or above five times the

Report Format: DU Report with 'J' Qualifiers

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1635672
Project Number:	B439-002	**Report Date:**	11/09/16

Data Qualifiers

reporting limit for common lab contaminants (Phthalates, Acetone, Methylene Chloride, 2-Butanone).

C - Co-elution: The target analyte co-elutes with a known lab standard (i.e. surrogate, internal standards, etc.) for co-extracted analyses.

D - Concentration of analyte was quantified from diluted analysis. Flag only applies to field samples that have detectable concentrations of the analyte.

E - Concentration of analyte exceeds the range of the calibration curve and/or linear range of the instrument.

G - The concentration may be biased high due to matrix interferences (i.e, co-elution) with non-target compound(s). The result should be considered estimated.

H - The analysis of pH was performed beyond the regulatory-required holding time of 15 minutes from the time of sample collection.

I - The lower value for the two columns has been reported due to obvious interference.

M - Reporting Limit (RL) exceeds the MCP CAM Reporting Limit for this analyte.

NJ - Presumptive evidence of compound. This represents an estimated concentration for Tentatively Identified Compounds (TICs), where the identification is based on a mass spectral library search.

P - The RPD between the results for the two columns exceeds the method-specified criteria.

Q - The quality control sample exceeds the associated acceptance criteria. For DOD-related projects, LCS and/or Continuing Calibration Standard exceedences are also qualified on all associated sample results. Note: This flag is not applicable for matrix spike recoveries when the sample concentration is greater than 4x the spike added or for batch duplicate RPD when the sample concentrations are less than 5x the RL. (Metals only.)

R - Analytical results are from sample re-analysis.

RE - Analytical results are from sample re-extraction.

S - Analytical results are from modified screening analysis.

J - Estimated value. The Target analyte concentration is below the quantitation limit (RL), but above the Method Detection Limit (MDL) or Estimated Detection Limit (EDL) for SPME-related analyses. This represents an estimated concentration for Tentatively Identified Compounds (TICs).

ND - Not detected at the method detection limit (MDL) for the sample, or estimated detection limit (EDL) for SPME-related analyses.

Report Format: DU Report with 'J' Qualifiers

Project Name:	BARRINGTON-BRICKYARD POND	**Lab Number:**	L1635672
Project Number:	B439-002	**Report Date:**	11/09/16

REFERENCES

1 Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. EPA SW-846. Third Edition. Updates I - IV, 2007.

121 Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

LIMITATION OF LIABILITIES

Alpha Analytical performs services with reasonable care and diligence normal to the analytical testing laboratory industry. In the event of an error, the sole and exclusive responsibility of Alpha Analytical shall be to re-perform the work at it's own expense. In no event shall Alpha Analytical be held liable for any incidental, consequential or special damages, including but not limited to, damages in any way connected with the use of, interpretation of, information or analysis provided by Alpha Analytical.

We strongly urge our clients to comply with EPA protocol regarding sample volume, preservation, cooling, containers, sampling procedures, holding time and splitting of samples in the field.

Certification Information

The following analytes are not included in our Primary NELAP Scope of Accreditation:

Westborough Facility
EPA 624: m/p-xylene, o-xylene
EPA 8260C: NPW: 1,2,4,5-Tetramethylbenzene; 4-Ethyltoluene, Azobenzene; SCM: Iodomethane (methyl iodide), Methyl methacrylate, 1,2,4,5-Tetramethylbenzene; 4-Ethyltoluene.
EPA 8270D: NPW: Dimethylnaphthalene,1,4-Diphenylhydrazine; SCM: Dimethylnaphthalene,1,4-Diphenylhydrazine.
EPA 300: DW: Bromide
EPA 6860: NPW and SCM: Perchlorate
EPA 9010: NPW and SCM: Amenable Cyanide Distillation
EPA 9012B: NPW: Total Cyanide
EPA 9050A: NPW: Specific Conductance
SM3500: NPW: Ferrous Iron
SM4500: NPW: Amenable Cyanide, Dissolved Oxygen; SCM: Total Phosphorus, TKN, NO2, NO3.
SM5310C: DW: Dissolved Organic Carbon

Mansfield Facility
SM 2540D: TSS
EPA 3005A NPW
EPA 8082A: NPW: PCB: 1, 5, 31, 87,101, 110, 141, 151, 153, 180, 183, 187.
EPA TO-15: Halothane, 2,4,4-Trimethyl-2-pentene, 2,4,4-Trimethyl-1-pentene, Thiophene, 2-Methylthiophene, 3-Methylthiophene, 2-Ethylthiophene, 1,2,3-Trimethylbenzene, Indan, Indene, 1,2,4,5-Tetramethylbenzene, Benzothiophene, 1-Methylnaphthalene.
Biological Tissue Matrix: ***EPA 3050B***

The following analytes are included in our Massachusetts DEP Scope of Accreditation

Westborough Facility:

Drinking Water
EPA 300.0: Nitrate-N, Fluoride, Sulfate; **EPA 353.2**: Nitrate-N, Nitrite-N; **SM4500NO3-F**: Nitrate-N, Nitrite-N; **SM4500F-C, SM4500CN-CE, EPA 180.1, SM2130B, SM4500Cl-D, SM2320B, SM2540C, SM4500H-B**
EPA 332: Perchlorate; **EPA 524.2:** THMs and VOCs; **EPA 504.1:** EDB, DBCP.
Microbiology: **SM9215B; SM9223-P/A, SM9223B-Colilert-QT,SM9222D**.

Non-Potable Water
SM4500H,B, EPA 120.1, SM2510B, SM2540C, SM2320B, SM4500CL-E, SM4500F-BC, SM4500NH3-BH, **EPA 350.1**: Ammonia-N, **LACHAT 10-107-06-1-B**: Ammonia-N, **SM4500NO3-F, EPA 353.2**: Nitrate-N**, EPA 351.1, SM4500P-E, SM4500P-B, E, SM4500SO4-E, SM5220D, EPA 410.4, SM5210B, SM5310C, SM4500CL-D, EPA 1664, EPA 420.1, SM4500-CN-CE, SM2540D.**
EPA 624: Volatile Halocarbons & Aromatics,
EPA 608: Chlordane, Toxaphene, Aldrin, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, Dieldrin, DDD, DDE, DDT, Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin, Endrin Aldehyde, Heptachlor, Heptachlor Epoxide, PCBs
EPA 625: SVOC (Acid/Base/Neutral Extractables), **EPA 600/4-81-045**: PCB-Oil.
Microbiology: **SM9223B-Colilert-QT; Enterolert-QT, SM9222D-MF**.

Mansfield Facility:

Drinking Water
EPA 200.7: Ba, Be, Cd, Cr, Cu, Ni, Na, Ca. **EPA 200.8:** Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, TL. **EPA 245.1** Hg.

Non-Potable Water
EPA 200.7: Al, Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Sr, TL, Ti, V, Zn.
EPA 200.8: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, TL, Zn.
EPA 245.1 Hg.
SM2340B

For a complete listing of analytes and methods, please contact your Alpha Project Manager.

CHAIN OF CUSTODY

PAGE ____ OF ____

Date Rec'd in Lab: 11/3/16

ALPHA Job #: L1635672

ALPHA ANALYTICAL
8 Walkup Drive, Westboro, MA 01581, Tel: 508-898-9220
320 Forbes Blvd, Mansfield, MA 02048, Tel: 508-822-9300

Project Information

Project Name: Barrington-Brickyard Pond
Project Location: RI
Project #: B439-002
Project Manager: Jim Riordan
ALPHA Quote #:

Report Information - Data Deliverables

☐ ADEx ☑ EMAIL

Billing Information

☑ Same as Client info PO #:

Client Information

Client: ESS Group
Address:
Phone: 401-330-1204
Email: mladewig@essgroup.com

Regulatory Requirements & Project Information Requirements

☐ Yes ☑ No MA MCP Analytical Methods ☐ Yes ☑ No CT RCP Analytical Methods
☐ Yes ☑ No Matrix Spike Required on this SDG? (Required for MCP Inorganics)
☐ Yes ☑ No GW1 Standards (Info Required for Metals & EPH with Targets)
☐ Yes ☑ No NPDES RGP
☐ Other State /Fed Program _____ Criteria _____

Turn-Around Time

☑ Standard ☐ RUSH (only confirmed if pre-approved!)
Date Due:

Additional Project Information:

Note: *Please Run low detect (0.01 mg/L or better) on Phosphorus and report MDL
- Low detect alkalinity

ANALYSIS: VOC: ☐ 8260 ☐ 624 ☐ 524.2; SVOC: ☐ ABN ☐ PAH; METALS: ☐ MCP 13 ☐ MCP 14 ☐ RCP 15; METALS: ☐ RCRA5 ☐ RCRA8 ☐ PP13; EPH: ☐ Ranges & Targets ☐ Ranges Only; VPH: ☐ Ranges & Targets ☐ Ranges Only; ☐ PCB ☐ PEST; TPH: ☐ Quant Only ☐ Fingerprint; TKN; NO3/NO2; Total P*; TSS; Soluble P*; ALKALINITY; METALS (FE/AL); Total solids

SAMPLE INFO
Filtration: ☐ Field ☑ Lab to do
Preservation: ☐ Lab to do

ALPHA Lab ID (Lab Use Only)	Sample ID	Collection Date	Collection Time	Sample Matrix	Sampler Initials	Sample Comments	TOTAL # BOTTLES
35(72.01)	Surface	11/3/16	12:54	SW			5
.02	Bottom	11/3/16	12:42	SW			5
.03	S1	11/3/16	13:03	SE			3
.04	S2	11/3/16	11:28	SE			3
.05	S3	11/3/16	11:48	SE			3

Container Type	P	P	P	P	P		P	P
Preservative	G	G	G	A	A	A	G	A
	D	D	D				C	
	A	A	A				A	

Container Type
P= Plastic
A= Amber glass
V= Vial
G= Glass
B= Bacteria cup
C= Cube
O= Other
E= Encore
D= BOD Bottle

Preservative
A= None
B= HCl
C= HNO_3
D= H_2SO_4
E= NaOH
F= MeOH
G= $NaHSO_4$
H = $Na_2S_2O_3$
I= Ascorbic Acid
J = NH_4Cl
K= Zn Acetate
O= Other

Relinquished By:	Date/Time	Received By:	Date/Time
Amy L. Elm	11/3/16		11/3/16 1503
	11/3/16 1727		11/3/16 1727

All samples submitted are subject to Alpha's Terms and Conditions. See reverse side.

FORM NO. 01-01 (rev. 12-Mar-2012)

ANALYTICAL REPORT

Lab Number:	L1710259
Client:	ESS Group Incorporated 10 Hemingway Dr. 2nd Fl East Providence, RI 02915
ATTN:	Matt Ladewig
Phone:	(401) 330-1204
Project Name:	BRICKYARD POND
Project Number:	B439-002
Report Date:	04/10/17

Certifications & Approvals: MA (M-MA086), NH NELAP (2064), NJ NELAP (MA935), CT (PH-0574), IL (200077), ME (MA00086), MD (348), NY (11148), NC (25700/666), PA (68-03671), RI (LAO00065), TX (T104704476), VT (VT-0935), VA (460195), USDA (Permit #P330-14-00197).

Eight Walkup Drive, Westborough, MA 01581-1019
508-898-9220 (Fax) 508-898-9193 800-624-9220 - www.alphalab.com

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

Alpha Sample ID	Client ID	Matrix	Sample Location	Collection Date/Time	Receive Date
L1710259-01	IJ	WATER	BARRINGTON, RI	04/04/17 09:00	04/04/17
L1710259-02	D	WATER	BARRINGTON, RI	04/04/17 09:30	04/04/17
L1710259-03	Q	WATER	BARRINGTON, RI	04/04/17 10:00	04/04/17

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

Case Narrative

The samples were received in accordance with the Chain of Custody and no significant deviations were encountered during the preparation or analysis unless otherwise noted. Sample Receipt, Container Information, and the Chain of Custody are located at the back of the report.

Results contained within this report relate only to the samples submitted under this Alpha Lab Number and meet NELAP requirements for all NELAP accredited parameters unless otherwise noted in the following narrative. The data presented in this report is organized by parameter (i.e. VOC, SVOC, etc.). Sample specific Quality Control data (i.e. Surrogate Spike Recovery) is reported at the end of the target analyte list for each individual sample, followed by the Laboratory Batch Quality Control at the end of each parameter. Tentatively Identified Compounds (TICs), if requested, are reported for compounds identified to be present and are not part of the method/program Target Compound List, even if only a subset of the TCL are being reported. If a sample was re-analyzed or re-extracted due to a required quality control corrective action and if both sets of data are reported, the Laboratory ID of the re-analysis or re-extraction is designated with an "R" or "RE", respectively. When multiple Batch Quality Control elements are reported (e.g. more than one LCS), the associated samples for each element are noted in the grey shaded header line of each data table. Any Laboratory Batch, Sample Specific % recovery or RPD value that is outside the listed Acceptance Criteria is bolded in the report. All specific QC information is also incorporated in the Data Usability format of our Data Merger tool where it can be reviewed along with any associated usability implications. Soil/sediments, solids and tissues are reported on a dry weight basis unless otherwise noted. Definitions of all data qualifiers and acronyms used in this report are provided in the Glossary located at the back of the report.

In reference to questions H (CAM) or 4 (RCP) when "NO" is checked, the performance criteria for CAM and RCP methods allow for some quality control failures to occur and still be within method compliance. In these instances the specific failure is not narrated but noted in the associated QC table. The information is also incorporated in the Data Usability format of our Data Merger tool where it can be reviewed along with any associated usability implications.

Please see the associated ADEx data file for a comparison of laboratory reporting limits that were achieved with the regulatory Numerical Standards requested on the Chain of Custody.

HOLD POLICY
For samples submitted on hold, Alpha's policy is to hold samples (with the exception of Air canisters) free of charge for 21 calendar days from the date the project is completed. After 21 calendar days, we will dispose of all samples submitted including those put on hold unless you have contacted your Client Service Representative and made arrangements for Alpha to continue to hold the samples. Air canisters will be disposed after 3 business days from the date the project is completed.

Please contact Client Services at 800-624-9220 with any questions.

Project Name: BRICKYARD POND **Lab Number:** L1710259
Project Number: B439-002 **Report Date:** 04/10/17

Case Narrative (continued)

Report Submission

All non-detect (ND) or estimated concentrations (J-qualified) have been quantitated to the limit noted in the MDL column.

Sample Receipt

The samples were received at the laboratory above the required temperature range. The samples were transported to the laboratory in a cooler with blue-ice and delivered directly from the sampling site.

I, the undersigned, attest under the pains and penalties of perjury that, to the best of my knowledge and belief and based upon my personal inquiry of those responsible for providing the information contained in this analytical report, such information is accurate and complete. This certificate of analysis is not complete unless this page accompanies any and all pages of this report.

Authorized Signature: Lisa Westerlind

Title: Technical Director/Representative Date: 04/10/17

INORGANICS
&
MISCELLANEOUS

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

SAMPLE RESULTS

Lab ID: L1710259-01
Client ID: IJ
Sample Location: BARRINGTON, RI
Matrix: Water

Date Collected: 04/04/17 09:00
Date Received: 04/04/17
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Specific Conductance	ND		umhos/cm	10	10.	1	-	04/05/17 07:59	4,120.1	KA
Solids, Total Suspended	130		mg/l	10	NA	2	-	04/07/17 10:55	121,2540D	DW
Nitrogen, Nitrate/Nitrite	0.080	J	mg/l	0.10	0.019	1	-	04/05/17 20:54	121,4500NO3-F	CW
Nitrogen, Total Kjeldahl	1.39		mg/l	0.300	0.066	1	04/04/17 22:30	04/06/17 21:43	121,4500NH3-H	AT
Phosphorus, Total	0.431		mg/l	0.020	0.006	2	04/06/17 10:55	04/07/17 10:06	121,4500P-E	SD
Phosphorus, Soluble	0.037		mg/l	0.010	0.004	1	04/07/17 10:15	04/07/17 14:45	121,4500P-E	SD

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

SAMPLE RESULTS

Lab ID: L1710259-02
Client ID: D
Sample Location: BARRINGTON, RI
Matrix: Water

Date Collected: 04/04/17 09:30
Date Received: 04/04/17
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Solids, Total Suspended	53.		mg/l	5.0	NA	1	-	04/07/17 10:55	121,2540D	DW
Nitrogen, Nitrate/Nitrite	0.24		mg/l	0.10	0.019	1	-	04/05/17 20:55	121,4500NO3-F	CW
Nitrogen, Total Kjeldahl	0.839		mg/l	0.300	0.066	1	04/04/17 22:30	04/06/17 21:44	121,4500NH3-H	AT
Phosphorus, Total	0.138		mg/l	0.010	0.003	1	04/06/17 10:55	04/07/17 10:07	121,4500P-E	SD
Phosphorus, Soluble	0.046		mg/l	0.010	0.004	1	04/07/17 10:15	04/07/17 14:45	121,4500P-E	SD

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

SAMPLE RESULTS

Lab ID: L1710259-03
Client ID: Q
Sample Location: BARRINGTON, RI
Matrix: Water

Date Collected: 04/04/17 10:00
Date Received: 04/04/17
Field Prep: Not Specified

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab										
Solids, Total Suspended	11.		mg/l	5.0	NA	1	-	04/07/17 10:55	121,2540D	DW
Nitrogen, Nitrate/Nitrite	0.070	J	mg/l	0.10	0.019	1	-	04/05/17 20:56	121,4500NO3-F	CW
Nitrogen, Total Kjeldahl	0.478		mg/l	0.300	0.066	1	04/04/17 22:30	04/06/17 21:45	121,4500NH3-H	AT
Phosphorus, Total	0.089		mg/l	0.010	0.003	1	04/06/17 10:55	04/07/17 10:08	121,4500P-E	SD
Phosphorus, Soluble	0.052		mg/l	0.010	0.004	1	04/07/17 10:15	04/07/17 14:45	121,4500P-E	SD

Project Name: BRICKYARD POND
Project Number: B439-002
Lab Number: L1710259
Report Date: 04/10/17

Method Blank Analysis
Batch Quality Control

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Analytical Method	Analyst
General Chemistry - Westborough Lab for sample(s): 01-03 Batch: WG991049-1										
Nitrogen, Total Kjeldahl	ND		mg/l	0.300	0.022	1	04/04/17 22:30	04/06/17 21:30	121,4500NH3-H	AT
General Chemistry - Westborough Lab for sample(s): 01-03 Batch: WG991430-1										
Nitrogen, Nitrate/Nitrite	ND		mg/l	0.10	0.019	1	-	04/05/17 19:45	121,4500NO3-F	CW
General Chemistry - Westborough Lab for sample(s): 01-03 Batch: WG991632-1										
Phosphorus, Total	0.009	J	mg/l	0.010	0.003	1	04/06/17 10:55	04/07/17 09:35	121,4500P-E	SD
General Chemistry - Westborough Lab for sample(s): 01-03 Batch: WG992027-1										
Solids, Total Suspended	ND		mg/l	5.0	NA	1	-	04/07/17 10:55	121,2540D	DW
General Chemistry - Westborough Lab for sample(s): 01-03 Batch: WG992173-1										
Phosphorus, Soluble	ND		mg/l	0.010	0.004	1	04/07/17 10:15	04/07/17 14:45	121,4500P-E	SD

Lab Control Sample Analysis

Batch Quality Control

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

Parameter	LCS %Recovery	Qual	LCSD %Recovery	Qual	%Recovery Limits	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-03 Batch: WG991049-2								
Nitrogen, Total Kjeldahl	96		-		78-122	-		
General Chemistry - Westborough Lab Associated sample(s): 01 Batch: WG991192-1								
Specific Conductance	99		-		99-101	-		
General Chemistry - Westborough Lab Associated sample(s): 01-03 Batch: WG991430-2								
Nitrogen, Nitrate/Nitrite	98		-		90-110	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-03 Batch: WG991632-2								
Phosphorus, Total	104		-		80-120	-		
General Chemistry - Westborough Lab Associated sample(s): 01-03 Batch: WG992173-2								
Phosphorus, Soluble	97		-		80-120	-		

Matrix Spike Analysis
Batch Quality Control

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

Parameter	Native Sample	MS Added	MS Found	MS %Recovery	Qual	MSD Found	MSD %Recovery	Qual	Recovery Limits	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG991049-4 QC Sample: L1710013-03 Client ID: MS Sample												
Nitrogen, Total Kjeldahl	1.35	8	8.42	88		-	-		77-111	-		24
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG991430-4 QC Sample: L1710259-03 Client ID: Q												
Nitrogen, Nitrate/Nitrite	0.070J	4	3.6	90		-	-		80-120	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG991632-3 QC Sample: L1710122-01 Client ID: MS Sample												
Phosphorus, Total	0.047	0.5	0.527	96		-	-		75-125	-		20
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG992173-3 QC Sample: L1710259-02 Client ID: D												
Phosphorus, Soluble	0.046	0.5	0.529	97		-	-		75-125	-		20

Lab Duplicate Analysis
Batch Quality Control

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

Parameter	Native Sample	Duplicate Sample	Units	RPD	Qual	RPD Limits
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG991049-3 QC Sample: L1710013-03 Client ID: DUP Sample						
Nitrogen, Total Kjeldahl	1.35	1.37	mg/l	1		24
General Chemistry - Westborough Lab Associated sample(s): 01 QC Batch ID: WG991192-2 QC Sample: L1710259-01 Client ID: IJ						
Specific Conductance	ND	11	umhos/cm	NC		20
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG991430-3 QC Sample: L1710259-03 Client ID: Q						
Nitrogen, Nitrate/Nitrite	0.070J	0.068J	mg/l	NC		20
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG991632-4 QC Sample: L1710122-01 Client ID: DUP Sample						
Phosphorus, Total	0.047	0.039	mg/l	19		20
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG992027-2 QC Sample: L1710214-01 Client ID: DUP Sample						
Solids, Total Suspended	750	600	mg/l	22		29
General Chemistry - Westborough Lab Associated sample(s): 01-03 QC Batch ID: WG992173-4 QC Sample: L1710259-01 Client ID: IJ						
Phosphorus, Soluble	0.037	0.036	mg/l	3		20

Project Name: BRICKYARD POND
Project Number: B439-002

Lab Number: L1710259
Report Date: 04/10/17

Sample Receipt and Container Information

Were project specific reporting limits specified? YES

Cooler Information Custody Seal

Cooler	
A	Absent

Container Information

Container ID	Container Type	Cooler	pH	Temp deg C	Pres	Seal	Analysis(*)
L1710259-01A	Plastic 250ml unpreserved	A	7	8.2	Y	Absent	COND-120(1),SPHOS-4500(28)
L1710259-01B	Plastic 500ml H2SO4 preserved	A	<2	8.2	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1710259-01C	Plastic 950ml unpreserved	A	7	8.2	Y	Absent	TSS-2540(7)
L1710259-01X	Plastic 250ml H2SO4 preserved Fi	A	N/A	8.2	Y	Absent	SPHOS-4500(28)
L1710259-02A	Plastic 250ml unpreserved	A	7	8.2	Y	Absent	SPHOS-4500(28)
L1710259-02B	Plastic 500ml H2SO4 preserved	A	<2	8.2	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1710259-02C	Plastic 950ml unpreserved	A	7	8.2	Y	Absent	TSS-2540(7)
L1710259-02X	Plastic 250ml H2SO4 preserved Fi	A	N/A	8.2	Y	Absent	SPHOS-4500(28)
L1710259-03A	Plastic 250ml unpreserved	A	7	8.2	Y	Absent	SPHOS-4500(28)
L1710259-03B	Plastic 500ml H2SO4 preserved	A	<2	8.2	Y	Absent	TKN-4500(28),TPHOS-4500(28),NO3/NO2-4500(28)
L1710259-03C	Plastic 950ml unpreserved	A	7	8.2	Y	Absent	TSS-2540(7)
L1710259-03X	Plastic 250ml H2SO4 preserved Fi	A	N/A	8.2	Y	Absent	SPHOS-4500(28)

*Values in parentheses indicate holding time in days

Project Name:	BRICKYARD POND	**Lab Number:**	L1710259
Project Number:	B439-002	**Report Date:**	04/10/17

GLOSSARY

Acronyms

EDL	- Estimated Detection Limit: This value represents the level to which target analyte concentrations are reported as estimated values, when those target analyte concentrations are quantified below the reporting limit (RL). The EDL includes any adjustments from dilutions, concentrations or moisture content, where applicable. The use of EDLs is specific to the analysis of PAHs using Solid-Phase Microextraction (SPME).
EPA	- Environmental Protection Agency.
LCS	- Laboratory Control Sample: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes.
LCSD	- Laboratory Control Sample Duplicate: Refer to LCS.
LFB	- Laboratory Fortified Blank: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes.
MDL	- Method Detection Limit: This value represents the level to which target analyte concentrations are reported as estimated values, when those target analyte concentrations are quantified below the reporting limit (RL). The MDL includes any adjustments from dilutions, concentrations or moisture content, where applicable.
MS	- Matrix Spike Sample: A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.
MSD	- Matrix Spike Sample Duplicate: Refer to MS.
NA	- Not Applicable.
NC	- Not Calculated: Term is utilized when one or more of the results utilized in the calculation are non-detect at the parameter's reporting unit.
NDPA/DPA	- N-Nitrosodiphenylamine/Diphenylamine.
NI	- Not Ignitable.
NP	- Non-Plastic: Term is utilized for the analysis of Atterberg Limits in soil.
RL	- Reporting Limit: The value at which an instrument can accurately measure an analyte at a specific concentration. The RL includes any adjustments from dilutions, concentrations or moisture content, where applicable.
RPD	- Relative Percent Difference: The results from matrix and/or matrix spike duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). Values which are less than five times the reporting limit for any individual parameter are evaluated by utilizing the absolute difference between the values; although the RPD value will be provided in the report.
SRM	- Standard Reference Material: A reference sample of a known or certified value that is of the same or similar matrix as the associated field samples.
STLP	- Semi-dynamic Tank Leaching Procedure per EPA Method 1315.
TIC	- Tentatively Identified Compound: A compound that has been identified to be present and is not part of the target compound list (TCL) for the method and/or program. All TICs are qualitatively identified and reported as estimated concentrations.

Footnotes

1	- The reference for this analyte should be considered modified since this analyte is absent from the target analyte list of the original method.

Terms

Total: With respect to Organic analyses, a 'Total' result is defined as the summation of results for individual isomers or Aroclors. If a 'Total' result is requested, the results of its individual components will also be reported. This is applicable to 'Total' results for methods 8260, 8081 and 8082.

Analytical Method: Both the document from which the method originates and the analytical reference method. (Example: EPA 8260B is shown as 1,8260B.) The codes for the reference method documents are provided in the References section of the Addendum.

Data Qualifiers

A	- Spectra identified as "Aldol Condensation Product".
B	- The analyte was detected above the reporting limit in the associated method blank. Flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank. For MCP-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank. For DOD-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte at less than ten times (10x) the concentration found in the blank AND the analyte was detected above one-half the reporting limit (or above the reporting limit for common lab contaminants) in the associated method blank. For NJ-Air-related projects, flag only applies to associated field samples that have detectable concentrations of the analyte above the reporting limit. For NJ-related projects (excluding Air), flag only applies to associated field samples that have detectable concentrations of the analyte, which was detected above the reporting limit in the associated method blank or above five times the

Report Format: DU Report with 'J' Qualifiers

Project Name:	BRICKYARD POND	**Lab Number:**	L1710259
Project Number:	B439-002	**Report Date:**	04/10/17

Data Qualifiers

reporting limit for common lab contaminants (Phthalates, Acetone, Methylene Chloride, 2-Butanone).

C - Co-elution: The target analyte co-elutes with a known lab standard (i.e. surrogate, internal standards, etc.) for co-extracted analyses.

D - Concentration of analyte was quantified from diluted analysis. Flag only applies to field samples that have detectable concentrations of the analyte.

E - Concentration of analyte exceeds the range of the calibration curve and/or linear range of the instrument.

G - The concentration may be biased high due to matrix interferences (i.e, co-elution) with non-target compound(s). The result should be considered estimated.

H - The analysis of pH was performed beyond the regulatory-required holding time of 15 minutes from the time of sample collection.

I - The lower value for the two columns has been reported due to obvious interference.

M - Reporting Limit (RL) exceeds the MCP CAM Reporting Limit for this analyte.

NJ - Presumptive evidence of compound. This represents an estimated concentration for Tentatively Identified Compounds (TICs), where the identification is based on a mass spectral library search.

P - The RPD between the results for the two columns exceeds the method-specified criteria.

Q - The quality control sample exceeds the associated acceptance criteria. For DOD-related projects, LCS and/or Continuing Calibration Standard exceedences are also qualified on all associated sample results. Note: This flag is not applicable for matrix spike recoveries when the sample concentration is greater than 4x the spike added or for batch duplicate RPD when the sample concentrations are less than 5x the RL. (Metals only.)

R - Analytical results are from sample re-analysis.

RE - Analytical results are from sample re-extraction.

S - Analytical results are from modified screening analysis.

J - Estimated value. The Target analyte concentration is below the quantitation limit (RL), but above the Method Detection Limit (MDL) or Estimated Detection Limit (EDL) for SPME-related analyses. This represents an estimated concentration for Tentatively Identified Compounds (TICs).

ND - Not detected at the method detection limit (MDL) for the sample, or estimated detection limit (EDL) for SPME-related analyses.

Report Format: DU Report with 'J' Qualifiers

Project Name:	BRICKYARD POND	**Lab Number:**	L1710259
Project Number:	B439-002	**Report Date:**	04/10/17

REFERENCES

4 Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020. Revised March 1983.

121 Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

LIMITATION OF LIABILITIES

Alpha Analytical performs services with reasonable care and diligence normal to the analytical testing laboratory industry. In the event of an error, the sole and exclusive responsibility of Alpha Analytical shall be to re-perform the work at it's own expense. In no event shall Alpha Analytical be held liable for any incidental, consequential or special damages, including but not limited to, damages in any way connected with the use of, interpretation of, information or analysis provided by Alpha Analytical.

We strongly urge our clients to comply with EPA protocol regarding sample volume, preservation, cooling, containers, sampling procedures, holding time and splitting of samples in the field.

Certification Information

The following analytes are not included in our Primary NELAP Scope of Accreditation:

Westborough Facility
EPA 624: m/p-xylene, o-xylene
EPA 8260C: NPW: 1,2,4,5-Tetramethylbenzene; 4-Ethyltoluene, Azobenzene; SCM: Iodomethane (methyl iodide), Methyl methacrylate, 1,2,4,5-Tetramethylbenzene; 4-Ethyltoluene.
EPA 8270D: NPW: Dimethylnaphthalene,1,4-Diphenylhydrazine; SCM: Dimethylnaphthalene,1,4-Diphenylhydrazine.
EPA 300: DW: Bromide
EPA 6860: NPW and SCM: Perchlorate
EPA 9010: NPW and SCM: Amenable Cyanide Distillation
EPA 9012B: NPW: Total Cyanide
EPA 9050A: NPW: Specific Conductance
SM3500: NPW: Ferrous Iron
SM4500: NPW: Amenable Cyanide, Dissolved Oxygen; SCM: Total Phosphorus, TKN, NO2, NO3.
SM5310C: DW: Dissolved Organic Carbon

Mansfield Facility
SM 2540D: TSS
EPA 3005A NPW
EPA 8082A: NPW: PCB: 1, 5, 31, 87,101, 110, 141, 151, 153, 180, 183, 187.
EPA TO-15: Halothane, 2,4,4-Trimethyl-2-pentene, 2,4,4-Trimethyl-1-pentene, Thiophene, 2-Methylthiophene, 3-Methylthiophene, 2-Ethylthiophene, 1,2,3-Trimethylbenzene, Indan, Indene, 1,2,4,5-Tetramethylbenzene, Benzothiophene, 1-Methylnaphthalene.
Biological Tissue Matrix: EPA 3050B

The following analytes are included in our Massachusetts DEP Scope of Accreditation

Westborough Facility:

Drinking Water
EPA 300.0: Nitrate-N, Fluoride, Sulfate; **EPA 353.2**: Nitrate-N, Nitrite-N; **SM4500NO3-F**: Nitrate-N, Nitrite-N; **SM4500F-C, SM4500CN-CE, EPA 180.1, SM2130B, SM4500Cl-D, SM2320B, SM2540C, SM4500H-B**
EPA 332: Perchlorate; **EPA 524.2:** THMs and VOCs; **EPA 504.1:** EDB, DBCP.
Microbiology: **SM9215B; SM9223-P/A, SM9223B-Colilert-QT,SM9222D**.

Non-Potable Water
SM4500H,B, EPA 120.1, SM2510B, SM2540C, SM2320B, SM4500CL-E, SM4500F-BC, SM4500NH3-BH, **EPA 350.1**: Ammonia-N, **LACHAT 10-107-06-1-B**: Ammonia-N, **SM4500NO3-F, EPA 353.2**: Nitrate-N**, EPA 351.1, SM4500P-E, SM4500P-B, E, SM4500SO4-E, SM5220D, EPA 410.4, SM5210B, SM5310C, SM4500CL-D, EPA 1664, EPA 420.1, SM4500-CN-CE, SM2540D.**
EPA 624: Volatile Halocarbons & Aromatics,
EPA 608: Chlordane, Toxaphene, Aldrin, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, Dieldrin, DDD, DDE, DDT, Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin, Endrin Aldehyde, Heptachlor, Heptachlor Epoxide, PCBs
EPA 625: SVOC (Acid/Base/Neutral Extractables), **EPA 600/4-81-045**: PCB-Oil.
Microbiology: **SM9223B-Colilert-QT; Enterolert-QT, SM9221E.**

Mansfield Facility:

Drinking Water
EPA 200.7: Ba, Be, Cd, Cr, Cu, Ni, Na, Ca. **EPA 200.8:** Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, TL. **EPA 245.1** Hg.

Non-Potable Water
EPA 200.7: Al, Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Sr, TL, Ti, V, Zn.
EPA 200.8: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, TL, Zn.
EPA 245.1 Hg.
SM2340B

For a complete listing of analytes and methods, please contact your Alpha Project Manager.

CHAIN OF CUSTODY

PAGE 1 OF 1

ALPHA ANALYTICAL
8 Walkup Drive
Westboro, MA 01581
Tel: 508-898-9220

320 Forbes Blvd
Mansfield, MA 02048
Tel: 508-822-9300

Date Rec'd in Lab: 4/4/17

ALPHA Job #: L1710259

Client Information

Client: ESS Group
Address: 10 Hemingway Dr.
East Providence RI 02915
Phone: (401) 330-1244
Email: mladewig@essgroup.com

Project Information

Project Name: Brickyard Pond
Project Location: Barrington, RI
Project #: B439-002
Project Manager: Matt Ladewig
ALPHA Quote #:

Turn-Around Time

☒ Standard ☐ RUSH (only confirmed if pre-approved!)
Date Due:

Report Information - Data Deliverables

☐ ADEx ☐ EMAIL

Billing Information

☐ Same as Client info PO #:

Regulatory Requirements & Project Information Requirements

☐ Yes ☐ No MA MCP Analytical Methods ☐ Yes ☐ No CT RCP Analytical Methods
☐ Yes ☐ No Matrix Spike Required on this SDG? (Required for MCP Inorganics)
☐ Yes ☐ No GW1 Standards (Info Required for Metals & EPH with Targets)
☐ Yes ☐ No NPDES RGP
☐ Other State /Fed Program _____ Criteria _____

Additional Project Information:
Note low detect on phosphorus 0.01 mg/L or better

ALPHA Lab ID (Lab Use Only)	Sample ID	Collection Date	Collection Time	Sample Matrix	Sampler Initials	VOC: ☐ 8260 ☐ 624 ☐ 524.2	SVOC: ☐ ABN ☐ PAH	METALS: ☐ MCP 13 ☐ MCP 14 ☐ RCP 15	METALS: ☐ RCRA5 ☐ RCRA8 ☐ PP13	EPH: ☐ Ranges & Targets ☐ Ranges Only	VPH: ☐ Ranges & Targets ☐ Ranges Only	☐ PCB ☐ PEST	TPH: ☐ Quant Only ☐ Fingerprint	5 Phos (4500P-E)	TSS (2540D)	NO3/NO2 (4500NO3-F)	TKN (4500N-C)	TPhos (4500P-E)	Specific Conductance (if Possible)	Sample Comments	TOTAL # BOTTLES
10259-01	IJ	4/4/17	0900	SW	MM									X	X	X	X	X	X		
-02	D	4/4/17	0930	SW	MM									X	X	X	X	X			
-03	Q	4/4/17	1000	SW	MM									X	X	X	X	X			
Container Type														P	P	P	P	P	P		
Preservative														A	A	D	D	D	A		

SAMPLE INFO
Filtration
☐ Field
☑ Lab to do
Preservation
☐ Lab to do

Container Type
P= Plastic
A= Amber glass
V= Vial
G= Glass
B= Bacteria cup
C= Cube
O= Other
E= Encore
D= BOD Bottle

Preservative
A= None
B= HCl
C= HNO_3
D= H_2SO_4
E= NaOH
F= MeOH
G= $NaHSO_4$
H = $Na_2S_2O_3$
I= Ascorbic Acid
J = NH_4Cl
K= Zn Acetate
O= Other

Relinquished By:	Date/Time	Received By:	Date/Time
	4/4/17 1420	AAL	4/4/17 1420
	4/4/17		4/4/17 19:15
	4/4/17 2015		4/4/17 2015

All samples submitted are subject to Alpha's Terms and Conditions. See reverse side.

FORM NO. 01-01 (rev. 12-Mar-2012)

Appendix C

Candidate Best Management Practices and Model Spreadsheet

INTRODUCTION

The following text provides a description of best management practices (BMPs) that are used to treat stormwater at end-of-pipe and in the upland areas of drainage catchments. The text provides a general description of each BMP as well as an assessment of pollutant removal capacity, treatment processes provided, and applications, advantages and limitations. The following BMPs are included in alphabetical order:

- Bioretention, Rain Gardens, Stormwater Planters
- Constructed Stormwater Wetland (Including Gravel Wetlands)
- Dry Wells
- Green Roofs, Blue Roofs and Facades
- Infiltration Basin
- Infiltration Trenches
- Planter and Tree Box Filters
- Porous Pavement
- Proprietary Media Filter
- Sand Filters
- Subsurface Infiltration (Including Leaching Catch Basins)
- Vegetated Drainage Ways
- Water Quality Swale
- Wet Vegetated Treatment System (Gravel)

For the most part, BMP types are based on BMPs listed in the Rhode Island Stormwater Design and Installation Standards Manual (RIDEM, 2010). In certain instances (e.g., leaching catch basins), we have adapted BMPs from other standards documents such as the Boston Water and Sewer Commission's Stormwater Best Management Practices: Guidance Document (2013).

Knowledge of pollutant removal capacity in conjunction with BMP treatment mechanisms is important to understanding the capacity of BMPs to improve stormwater quality. Removal capacities have been adapted from the Rhode Island Stormwater Design and Installation Standards Manual and were taken from either Appendix H or the "Key Considerations" text boxes. Treatment processes have been adapted from the Boston Water and Sewer Commission's Stormwater Best Management Practices: Guidance Document. Percent removal data is not available for metals in either of these documents; however, Rhode Island Stormwater Design and Installation Standards Manual qualifies BMPs as to whether they are able to achieve "good" metals removal or not.

A tabular summary of BMP application, advantages and limitations is provided to help ensure that BMPs selected are appropriately suited to the surrounding land use and other watershed conditions. This information was taken from several sources including the Rhode Island Stormwater Design and Installation Standards Manual and the Stormwater Best Management Practices: Guidance Document. We have also included our general knowledge of BMPs.

Summary of Candidate Best Management Practices for Selection of Retrofits

BMP Type	Pollutant Removal Capacity		Treatment Process		Application		
	Bacteria (+70%)	TN (+20%)	Infiltration Filtration	Vegetative Treatment	Common Areas	Roads	Drainage Area (+5 acres)
Bioretention	✓	✓	✓	✓	Appropriate	Appropriate	Appropriate
Constructed Stormwater Wetland	✓	✓		✓	Appropriate	Appropriate	Appropriate
Dry Wells	✓		✓				
Green Roofs et al	✓	✓		✓			
Impervious Surface Disconnection			✓	✓	Appropriate	Appropriate	
Infiltration Basin	✓	✓	✓	✓	Appropriate	Appropriate	Appropriate
Infiltration Trenches	✓	✓	✓		Appropriate	Appropriate	Appropriate
Leach Catch Basin	✓	✓	✓	✓	Appropriate	Appropriate	
Planter and Tree Box Filters	✓	✓	✓	✓	Appropriate	Appropriate	
Porous Pavement	✓		✓			Appropriate	
Proprietary Media Filter	✓	✓	✓			Appropriate	
Sand Filters	✓	✓	✓		Appropriate	Appropriate	Appropriate
Subsurface Infiltration	✓		✓			Appropriate	Appropriate
Vegetated Filter Strip			✓	✓	Appropriate	Appropriate	
Vegetated Drainage Ways				✓	Appropriate	Appropriate	Appropriate
Water Quality Swale	✓	✓	✓		Appropriate	Appropriate	Appropriate
Wet Vegetated Treatment System (Gravel)	✓	✓	✓	✓	Appropriate	Appropriate	Appropriate

Bioretention, Rain Gardens, Stormwater Planters

Bioretention and rain gardens are shallow landscaped depressions designed to manage and treat stormwater runoff. Bioretention systems are a variation of a surface sand filter, where the sand filtration media is replaced with a planted soil bed designed to remove pollutants through physical and biological processes. The concept of bioretention originated with the Prince George's County, Maryland, Department of Environmental Resources in the early 1990s as an alternative to more traditional management practices. Stormwater flows into the bioretention area, ponds on the surface, and gradually infiltrates into the soil bed. Treated water is allowed to infiltrate into the surrounding soils or is collected by an underdrain system and discharged to the storm drain system or receiving waters. Small-scale bioretention applications (i.e., residential yards, median strips, parking lot islands) are commonly referred to as rain gardens. Tree box filters are essentially mini bioretention systems installed in concrete vaults. They are most often designed to fit in urban landscapes (e.g., sidewalks as part of street tree systems) where space is at a premium.

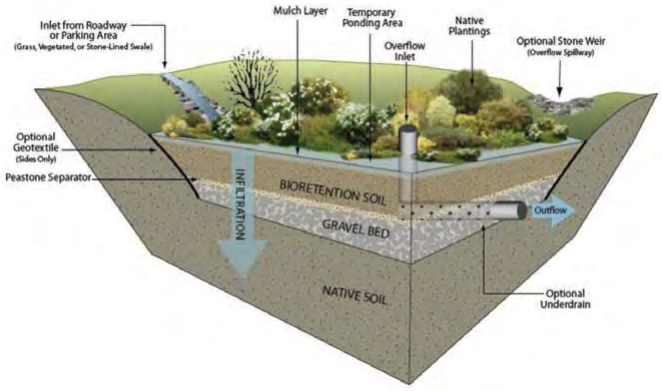


Figure A.1—Bioretention

Table A-1
Pollutant Removal Capacity
Bioretention, Rain Gardens, Stormwater Planters

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	70%
Total Phosphorus	30%
Total Nitrogen	30 - 50%
TSS	90%
Metals	Good

Notes:

a. Percent removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs and "Key Considerations" text boxes of the *Rhode Island Stormwater Design and Installation Standards Manual*.

Table A-2
Treatment Processes Provided by
Bioretention, Rain Gardens, Stormwater Planters

Treatment Processes[a]	Process Provided?
Biological Processes	✓
Infiltration	✓ (if designed to infiltrate)
Filtration	✓
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	✓

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-3
Advantages, Disadvantages and Limitations of
Bioretention, Rain Gardens, Stormwater Planters

Applications	Advantages	Limitations
• May be used in a wide variety of settings including residential, commercial, and industrial areas. • May be decentralized (e.g., as rain gardens on individual lots) or centralized in common areas to manage multiple properties. • May be lined and underdrained; or designed to infiltrate and recharge groundwater.	• Highly versatile and adaptable to size of watershed and type of land use. • High solids, metals, and bacteria removal efficiency. • Infiltrating bioretention can provide groundwater recharge. • Helps to mimic predevelopment runoff conditions. • Reduces need for end-of-pipe treatment.	• Bottom of the filter must be at or above the seasonal high groundwater table if infiltration is being used. • Generally requires approximately 3-foot depth for soil bed and ponding area.

Figure A.2—Photograph of tree box filter.

CONSTRUCTED STORMWATER WETLAND

Figure A.3—Photograph of constructed stormwater wetland.

A constructed stormwater wetland is a system designed to maximize pollutant removal through vegetative uptake, retention, and settling. A typical constructed wetland consists of a sediment forebay to provide pretreatment and dissipate energy, a base with shallow pockets planted with diverse emergent vegetation, deeper areas or micro-pools and a water quality outlet structure. In addition to water quality treatment, constructed wetlands are designed to control peak flow rates from the 2-and 10-year storm through extended detention above the permanent pool elevation. The interactions between the incoming stormwater runoff, aquatic vegetation, wetland soils, and associated physical, chemical, and biological processes are a fundamental part to reducing suspended soils, nutrients, metals, oils and grease, and trash. Site investigations must be conducted prior to design and construction to ensure proper soils, depth to groundwater and suitable land.

There are several types of Constructed Stormwater Wetlands. Common types of constructed stormwater wetland include shallow marsh, basin/wetland, extended detention, and pocket.

Table A-4
Pollutant Removal Capacity
Constructed Stormwater Wetland

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	90%
Total Phosphorus	48%
Total Nitrogen	20 - 55%
TSS	85%
Metals	Fair

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-5
Treatment Processes Provided by
Constructed Stormwater Wetland

Treatment Processes[a]	Process Provided?
Biological Processes	
Infiltration, if designed as such	
Filtration	✓
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-6
Advantages, Disadvantages and Limitations of
Constructed Stormwater Wetland

Applications	Advantages	Limitations
• May be used as regional detention and treatment • May be best for sites without space constraints	• Low maintenance cost • Treatment of large tributary areas • Provides wildlife habitat • Aesthetically pleasing	• High land requirement • High capital cost • Design affected by depth to groundwater and bedrock • Additional restrictions apply in cold-water fishery watershed based on distance from discharge point to streams (and any contiguous wetlands)

DRY WELLS

A dry well is a small, excavated pit, backfilled with stone aggregate. Dry wells function like infiltration systems to control roof runoff and are applicable for most types of buildings.

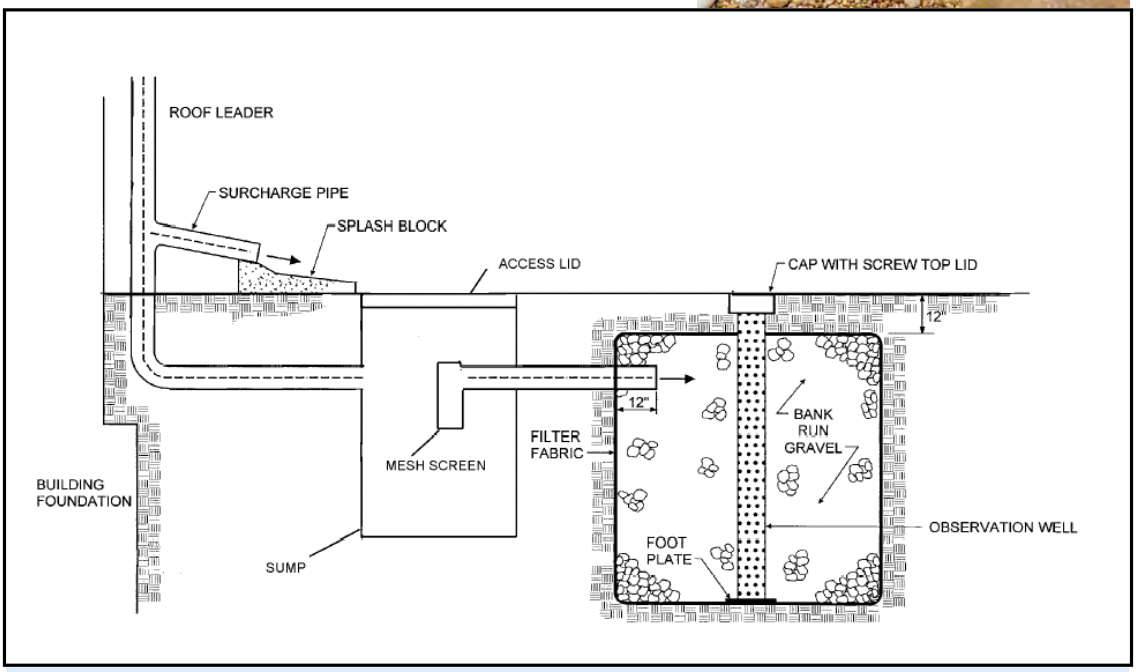


Figure A.4—Photograph and schematic of dry wells.

Table A-7
Pollutant Removal Capacity
Dry Wells

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	90%
Total Phosphorus	55%
Total Nitrogen	40%
TSS	90%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-8
Treatment Processes Provided by
Dry Wells

Treatment Processes[a]	Process Provided?
Biological Processes	
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	✓

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-9
Advantages, Disadvantages and Limitations of
Dry Wells

Applications	Advantages	Limitations
• Can be useful for disposing of roof runoff and reducing the overall runoff volume from a variety of building sites. (e.g., residential, commercial industrial, etc.).	• Low cost. • Provides retention of runoff from roofs. • Recharges groundwater. • Reduces need for end-of-pipe treatment.	• Clogging likely when used for runoff other than from rooftops • Only applicable in small drainage areas • When located near buildings, potential issues with water seeping into cellars or inducing cracking/heaving. • Two-foot minimum separation to groundwater • Minimum soil infiltration rate of 0.5 inches per hour • Infiltration of rooftop runoff from commercial or industrial buildings with pollution control, heating, cooling, or venting equipment may require UIC review and approval.

GREEN ROOFS, BLUE ROOFS AND FACADES

Figure A.5—Photograph of green roofs.

Green roofs are vegetated roof covers designed to reduce stormwater volumes through storage of precipitation in a soil media layer and increased evapotranspiration. Green roofs decrease the impervious footprint of buildings and help mimic pre-development hydrology. They are applicable in highly urbanized locations where land is limited and expensive. Due to an observed increase in nitrogen and phosphorous discharged from green roofs, they should not be used in nutrient sensitive waters, or locations where groundwater recharge is a priority due to low base flows. There are two types of green roofs: intensive green roofs and extensive green roofs. Extensive green roofs are lightweight systems requiring minimal maintenance and a shallow soil media, while intensive green roofs are larger and deeper systems requiring regular maintenance (irrigation, fertilizing, mowing) throughout the year.

Rooftop runoff management structures are modifications to conventional building design that attenuate runoff originating from roofs. The modifications include:

- Vegetated roof covers
- Roof gardens
- Vegetated building facades
- Roof ponding areas (e.g., blue roofs)

Roofs are significant sources of runoff from developed sites. If runoff is controlled at the source, the size of other BMPs throughout the site can be reduced. Rooftop runoff management practices influence the runoff hydrograph in two ways:

- Intercept rainfall during the early part of a storm.
- Limit the maximum release rate.

In addition to achieving specific stormwater runoff management objectives, rooftop runoff management can also be aesthetically and socially beneficial.

Design Variations

- Vegetated roof cover – Vegetated roof covers, also called green roofs and extensive roof gardens, involve blanketing roofs with a veneer of living vegetation. Vegetative roof covers are particularly effective when applied to extensive roofs, such as those that typify commercial and institutional buildings. The filtering effect of vegetated roof covers results in a roof discharge that is free of leaves and roof litter. Therefore, it is recommended where roof runoff will be directed to infiltration devices (see Standards for Infiltration Practices and Dry Wells).
- Because of recent advances in synthetic drainage materials, vegetated covers now are feasible on most conventional flat roofs. An efficient drainage layer is placed between the growth media and the roof surface. This layer rapidly conveys water off of the roof surface and prevents water from

"lying" on the roof. In fact, vegetated roof covers can be expected to protect roof materials and prolong their life.

- If materials are selected carefully to reduce the weight of the system, vegetated roof covers generally can be created on existing flat roofs without additional structural support. Drainage nets or sheet drains constructed from lightweight synthetic materials can be used as underlayments to carry away water and prevent ponding. The total load of a fully vegetated and saturated roof cover system can be less than the design load computed for gravel ballast on conventional tar roofs.
- Although vegetative roof covers are most effective during the growing season, they also are beneficial during the winter months as additional insulation if the vegetative matter from the dead or dormant plants is left in place and intact.
- Roof Gardens – Vegetated roof covers blanket an entire roof area and, although presenting an attractive vista, generally are not intended to accommodate routine traffic by people. Roof gardens, on the other hand, are landscaped environments, which may include planters and potted shrubs and trees. Roof gardens can be tailor-made natural areas, designed for outdoor recreation, and perched above congested city streets. Because of the special requirements for access, structural support, and drainage, roof gardens are found most frequently in new construction.
- Roof gardens generally are designed to achieve specific architectural objectives. The load and hydraulic requirements for roof gardens will vary according to the intended use of the space.
- Intensive roof gardens typically include design elements such as planters filled with topsoil, decorative gravel or stone, and containers for trees and shrubs. Complete designs also may detain runoff ponding in the form of water gardens or storage in gravel beds. A wide range of hydrologic principles may be exploited to achieve stormwater management objectives, including runoff peak attenuation and runoff volume control.
- Vegetated Building Facades – Vegetated facades provide many of the same benefits as vegetated roof covers and roof gardens, including the interception of precipitation and the retardation of runoff. However, their effectiveness is limited to small rainfall events.
- Vertical facades and walls of houses can be covered with the foliage of self-climbing plants that are rooted in the ground and reach heights in excess of 80 feet. Vines can be evergreen or prolific deciduous flowering plants. As for roof gardens, the designer must be judicial in selecting plant species that will prosper in the constructed environment. Planters and trellises can be installed so that vegetation can be placed strategically.
- Roof Ponding – Roof ponding, also known as blue roofs, is applicable where the increased load of impounded water on a roof will not increase the building costs significantly or require extensive reinforcement. Roof ponding generally is not viable for large-area commercial buildings where clear spans are required. Special consideration must be given to ensuring that the roof will remain watertight under a range of adverse weather conditions. Low-cost plastic membranes can be used to construct an impermeable lining for the containment area.

Tables A-10 and A-14 address green roofs only because currently available literature provides only limited pollutant removal and design standards information on blue roofs and vegetated facades.

Table A-10
Pollutant Removal Capacity
Extensive and Intensive Green Roofs

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	70%
Total Phosphorus	30%
Total Nitrogen	55%
TSS	90%
Metals	Good

Notes:
a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

There is no available data on pollutant removal capacity on blue roofs or facades.

Table A-11
Treatment Processes Provided by
Extensive and Intensive Green Roofs

Treatment Processes[a]	Process Provided?
Biological Processes	
Infiltration	
Filtration	
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	✓

Notes:
a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-12
Treatment Processes Provided by
Blue Roofs

Treatment Processes	Process Provided?
Biological Processes	
Infiltration	
Filtration	
Peak Flow Reduction	✓
Plant Uptake	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	✓

Notes:
a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-13
Treatment Processes Provided by Facades

Treatment Processes	Process Provided?
Biological Processes	✓
Infiltration	
Filtration	
Sedimentation	
Vegetated Treatment	✓
Volume Reduction	

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-14
Advantages, Disadvantages and Limitations of Extensive and Intensive Green Roofs

Applications	Advantages	Limitations
• Can use vegetative roofs on residential, commercial and light industrial buildings. • Vegetative roof systems are most appropriate on roofs with slopes of 12:1 to 4:1. • Vegetative roofs may be used on flatter slopes if an underdrain is installed.	• Rooftop runoff management techniques can be retrofitted to most conventionally constructed buildings. • Reduces energy consumption for heating and cooling. • Conserves space. • Reduces wear on roofs caused by UV damage, wind, and extremes of temperature. Vegetative roof covers can reduce bare roof temperatures in summer by as much as 40 percent. • Roof gardens, vegetated roof covers, and vegetated facades add aesthetic value to residential and commercial property that attract songbirds, bees, and butterflies. • Benefit water quality by reducing the acidity of runoff and trapping airborne particulates. • May reduce the size of onsite runoff attenuation BMPs.	• Maximum 20% roof slope, unless specific measures are provided to retain the system on steeper slopes. • Needs to be designed in accordance with weight loads and aesthetics and consideration of thermal performance.

INFILTRATION BASIN

An infiltration practice that stores the water in a surface depression before it is infiltrated into the underlying soils or substratum. Infiltration basins are stormwater impoundments, over permeable soils with vegetated bottoms and side slopes. Infiltration basins are designed to reduce stormwater volumes through exfiltration and groundwater recharge. Pretreatment is vital to ensuring successful performance. There are 2 types of infiltration basins: full exfiltration and partial or off-line exfiltration. Full exfiltration basins are designed to store, treat, and exfiltrate the full required water quality volume and attenuate peak flows. Partial or off-line exfiltration basins are designed to exfiltrate a portion of the runoff (usually the "first flush" or runoff from first 0.5 inches of precipitation), while diverting the remaining runoff to another BMP through flow splitters or weirs. The type of infiltration basin is chosen based upon site conditions and limitations.

Table A-15
Pollutant Removal Capacity
Infiltration Basin

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	90%
Total Phosphorus	65%
Total Nitrogen	50 - 60%
TSS	90%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-16
Treatment Processes Provided by
Infiltration Basin

Treatment Processes[a]	Process Provided?
Biological Processes	✓
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	✓

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

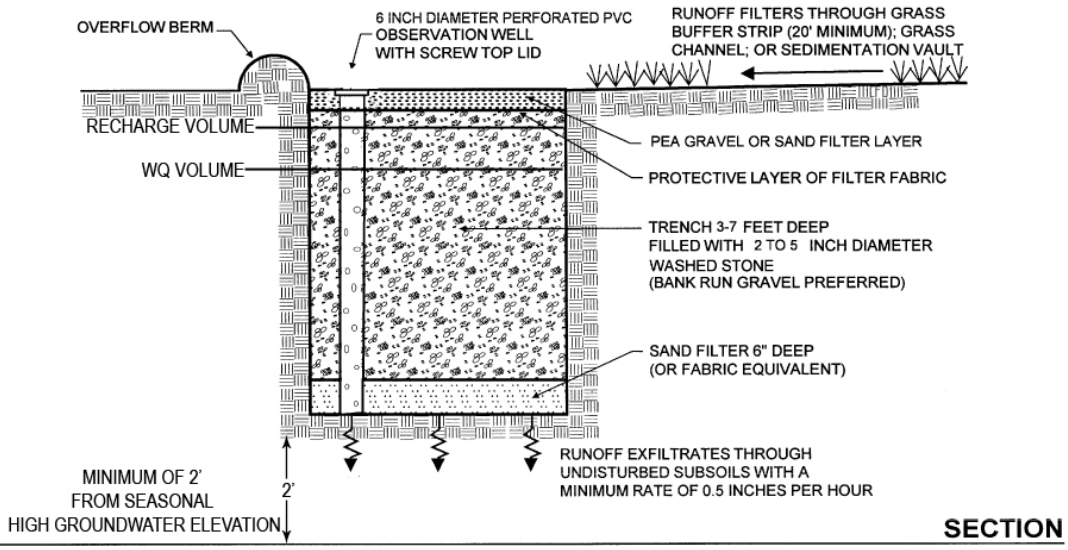
Table A-17
Advantages, Disadvantages and Limitations of
Infiltration Basin

Applications	Advantages	Limitations
• Contributing drainage area should be between 2 and 15 acres • Suitable for sites with gentle slopes, permeable soils, and relatively deep groundwater table	• Reduces local flooding • Can use near cold-water fisheries	• Requires pretreatment • Requires large pervious area • Clogging potential is high so high level of maintenance is necessary • Not suitable for treating high loads of sediment or other pollutants

INFILTRATION TRENCHES

Gravel trenches are long, narrow, gravel-filled trenches, which treat stormwater runoff from small drainage areas. Gravel trenches remove stormwater pollutants through infiltration, sedimentation and filtration. Reactive media (e.g., zeolite, activated carbon, oxide-coated sand, etc.) may be incorporated into the design to increase sorption capacity and target specific pollutants. Pretreatment may be provided to prevent clogging of the gravel bed and suA-grade.

Figure A.6—Photograph and schematic of infiltration trench.



Example of Infiltration Trench

Table A-18
Pollutant Removal Capacity
Infiltration Trenches

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	95%
Total Phosphorus	65%
Total Nitrogen	65%
TSS	90%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-19
Treatment Processes Provided by
Infiltration Trenches

Treatment Processes[a]	Process Provided?
Biological Processes	
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	✓

Notes:

a. Treatment processes are assumed to be same as Dry Wells and are identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-20
Advantages, Disadvantages and Limitations of
Infiltration Trenches

Applications	Advantages	Limitations
• Infiltration may be useful for disposing of roof runoff (e.g., dry wells), or runoff from parking lots and roadways. • Infiltration trenches generally have a longer life cycle when hydrologically proceeded by pretreatment such as a vegetated filter strip. • Infiltration generally requires UIC review and approval.	• Appropriate for installation directly adjacent to parking lots or other impervious surfaces • Applicable to small drainage areas, stormwater retrofits and highly developed sites. • High bacteria removal efficiency. • Infiltration provides groundwater recharge. • Helps to mimic predevelopment runoff conditions. • Reduces need for end-of-pipe treatment.	• Susceptible to clogging by sediment • Maintenance required approximately every six months • Minimum soil infiltration rate of 0.5 inches per hour • Natural slope less than 15% • Cannot accept LUHPPL runoff • Separation to high groundwater minimum of 2 feet

LEACHING CATCH BASINS

Leaching catch basins are pre-cast concrete structures with openings within the structure walls and an open bottom. The openings allow water to infiltrate into the surrounding soils. Preferable design of a leaching catch basin involves an offline system with a deep sump catch basin upstream for pretreatment.

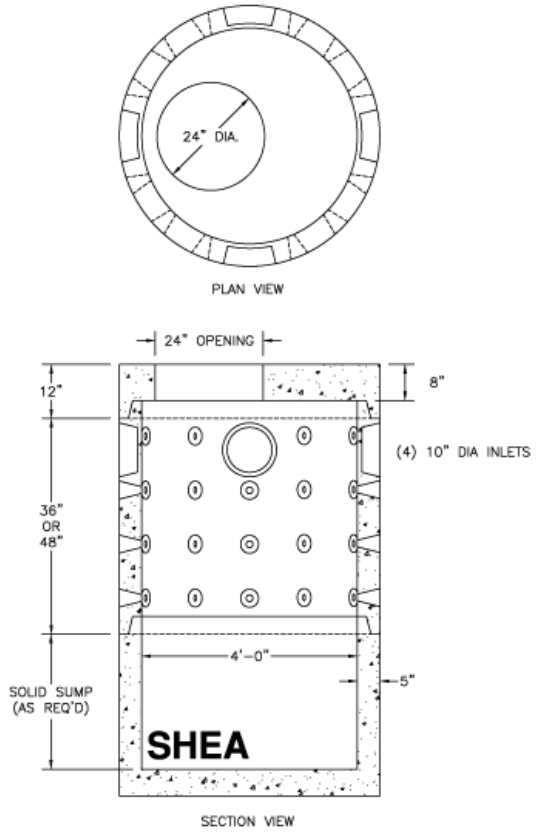


Figure A.7—Schematic of leaching catch basins.

Table A-21
Pollutant Removal Capacity
Leaching Catch Basins

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	90%
Total Phosphorus	55%
Total Nitrogen	40%
TSS	90%
Metals	Good

Notes:
a. Removal rates assumed to be the same as Dry Wells and taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-22
Treatment Processes Provided by
Leaching Catch Basins

Treatment Processes[a]	Process Provided?
Biological Processes	
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	✓

Notes:
a. Treatment processes are assumed to be same as Dry Wells and are identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-23
Advantages, Disadvantages and Limitations of
Leaching Catch Basins

Applications	Advantages	Limitations
• Can be implemented as a retrofit • May be useful in urban areas with land constraints	• Low cost per unit of treatment • Especially suitable retrofit for roads and parking lots • Relatively easy to repair/replace	• Susceptible to clogging by sediment

PLANTER AND TREE BOX FILTERS

Planter boxes are bioretention treatment control measures that are completely contained within an impermeable structure with an underdrain (they do not infiltrate). The boxes can be comprised of a variety of materials, such as brick or concrete, (usually chosen to be the same material as the adjacent building or sidewalk) and are filled with gravel on the bottom (to house an underdrain system), planting soil media, and vegetation. As stormwater passes down through the planting soil, pollutants are filtered, adsorbed, and biodegraded by the soil and plants.

Figure A.8—Photographs of planter and tree box filters.

Table A-24
Pollutant Removal Capacity
Planter and Tree Box Filters

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	70%
Total Phosphorus	30%
Total Nitrogen	55%
TSS	90%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-25
Treatment Processes Provided by
Planter and Tree Box Filters

Treatment Processes[a]	Process Provided?
Biological Processes	✓
Infiltration	
Filtration	✓
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	✓

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-26
Advantages, Disadvantages and Limitations of
Planter and Tree Box Filters

Applications	Advantages	Limitations
• Commonly used in densely urbanized areas such as along roads, highways, sidewalks and parking lots	• Reduces volume and rate of runoff • Smaller footprint required • May be used as pretreatment device • Provides decentralized stormwater treatment • Ideal for redevelopment or in ultra-urban settings	• Requires vegetative maintenance • Treats small volumes • Treats small tributary areas

POROUS PAVEMENT

Porous pavement is a permeable alternative to conventional asphalt and concrete and constructed in pedestrian, highly urbanized, or residential settings with low traffic speeds and volumes. A high surface void ratio allows precipitation to pass through the pavement and a stone base, where runoff is retained and sediments and metals are treated to some degree. Porous pavement is designed to achieve peak flow attenuation of small intensity storms and groundwater recharge through infiltration into underlying soils. Porous pavement includes porous asphalt and pervious concrete, which are poured in place, and paving stones and grass pavers, which are typically precast and installed in an interlocking array to create a surface.

Figure A.9—Photographs of porous pavement.

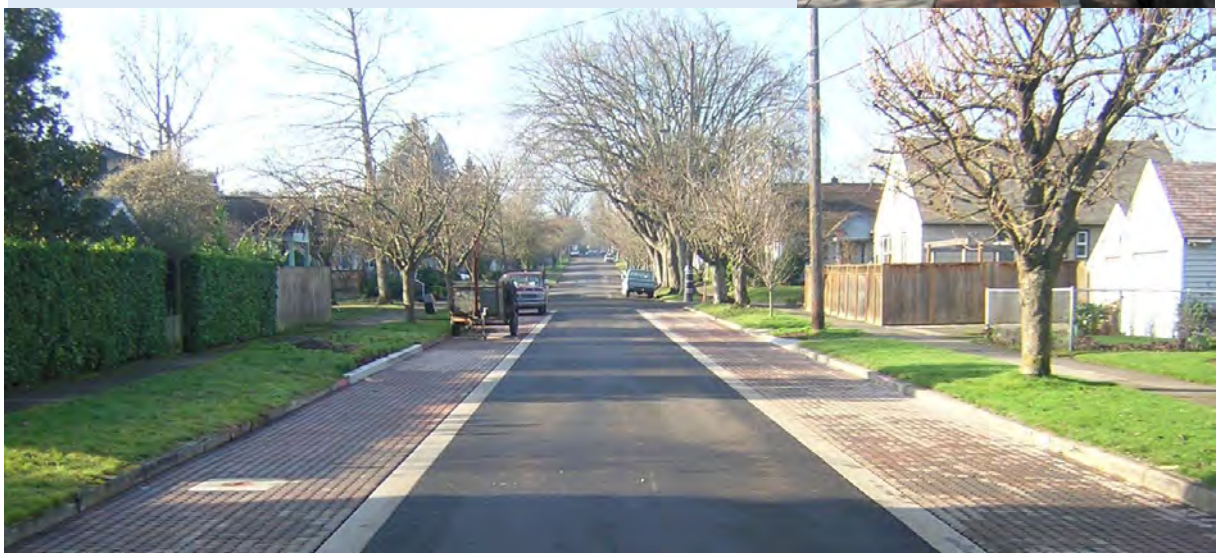


Table A-27
Pollutant Removal Capacity
Porous Pavement

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	95%
Total Phosphorus	40%
Total Nitrogen	40%
TSS	90%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-28
Treatment Processes Provided by
Porous Pavement

Treatment Processes[a]	Process Provided?
Biological Processes	✓
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	✓

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-29
Advantages, Disadvantages and Limitations of
Porous Pavement

Applications	Advantages	Limitations
• Good option for commercial and industrial parking lots • Can be used in urban and residential settings • Can be implemented as a retrofit • Preferable for low-volume, low-speed areas or pedestrian areas • Useful application to sidewalks	• Reduces sediment and particulate-bound pollutants • Reduces amount of impervious area needing water quality treatment	• Frequent clogging if not maintained • No sanding in winter • Compacting of underlying soils is common • Limited removal of dissolved constituents when underdrains are used

PROPRIETARY MEDIA FILTER

Proprietary Media Filters are typically underground structures that first settle out in an upstream structure and then flow through a specific filter media to reduce targeted pollutants.

Removal rates of pollutants vary depending on the filter media. Filtration is the main treatment process that all proprietary media filters provide.

Table A-30
Advantages, Disadvantages and Limitations of
Proprietary Media Filter

Applications	Advantages	Limitations
• Sites with space constraints • Ultra-urban areas	• Suitable for specialized applications, such as industrial sites, for specific target pollutants • Preferred for redevelopments or in the ultra-urban setting when LID or larger conventional practices are not practical	• Must be purchased from private sector firm • May require more maintenance • "Wet" systems that are designed to retain water can cause mosquito and vector problems unless access points are sealed

SAND FILTERS

Sand filters are engineered sand filled depressions that treat stormwater runoff from small tributary areas. Sand filters allow for the percolation of runoff through the void space within the sand before it is eventually released through an underdrain at the bottom of the filter. Stormwater runoff enters the filter from a pretreatment system (sediment forebay or vegetated filter strip) and spreads evenly over the surface. As flows increase, water backs up on the surface of the filter where it is held until it can percolate through the sand. As stormwater passes through the sand, pollutants are trapped in the small pore spaces between sand grains or are adsorbed to the sand surface. The effectiveness and efficiency of a sand filter depends heavily on the pretreatment BMPs performance to settle out sand, clay, and silt particles, which prevent clogging of the sand filter.

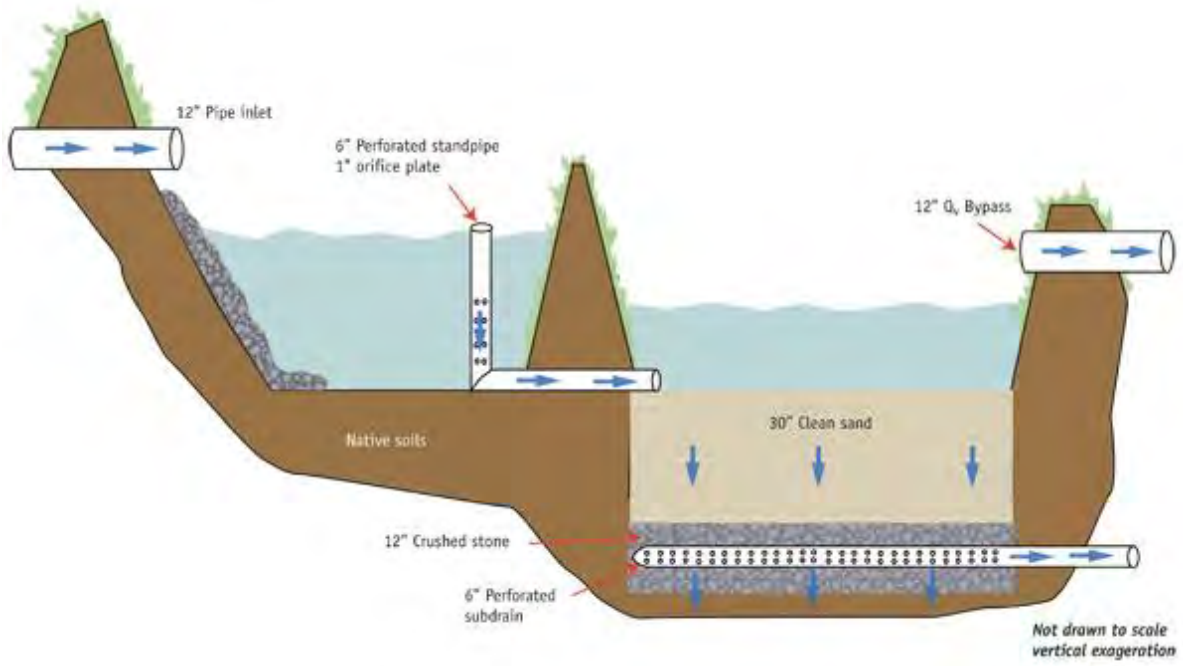


Figure A.10—Photographs and schematic of sand filters.

Table A-31
Pollutant Removal Capacity
Sand Filter

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	70%
Total Phosphorus	59%
Total Nitrogen	32%
TSS	86%
Metals	Good

Notes:
a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-32
Treatment Processes Provided by
Sand Filter

Treatment Processes[a]	Process Provided?
Biological Processes	✓
Infiltration	
Filtration	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	

Notes:
a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-33
Advantages, Disadvantages and Limitations of
Sand Filter

Applications	Advantages	Limitations
• Can be used in ultra-urban sites with small drainage areas • Drainage area can be 100% impervious like parking lots • May be useful as redevelopment / retrofit projects	• Long design life if properly maintained • Good for densely populated urban areas or parking lots • Relatively small footprint area	• Pretreatment required to prevent clogging • Frequent maintenance required • Costly to build and install • Limited removal of dissolved constituents • May not be effective in winter • Can be unattractive and create odors

SUBSURFACE INFILTRATION

Subsurface infiltration structures are underground systems that capture and infiltrate runoff into the groundwater through highly permeable rock and gravel. It is usually not practical to infiltrate runoff at the same rate that is generated; therefore, these facilities generally include both a storage component and a drainage component. Typical subsurface infiltration systems that can be installed to enhance groundwater recharge include pre-cast concrete or plastic pits, chambers (manufactured pipes), and perforated pipes.

Figure A.11—Rendering of subsurface infiltration structure.

Table A-34
Pollutant Removal Capacity
Subsurface Infiltration

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	90%
Total Phosphorus	55%
Total Nitrogen	40%
TSS	90%
Metals	Good

Notes:
a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-35
Treatment Processes Provided by
Subsurface Infiltration

Treatment Processes[a]	Process Provided?
Biological Processes	
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	
Volume Reduction	✓

Notes:
a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-36
Advantages, Disadvantages and Limitations of
Subsurface Infiltration

Applications	Advantages	Limitations
• Applicable for private and public projects, commercial and residential • Can be implemented as a retrofit • May be useful in urban areas adjacent to buildings	• Low cost per unit of treatment • Especially suitable retrofit for roads and parking lots	• Susceptible to clogging by sediment • Minimum soil rate of 0.5 inches per hour • Separation from seasonal high groundwater, minimum of 2 feet

VEGETATED DRAINAGE WAYS

Structural drainage systems and storm sewers are designed to be hydraulically efficient for removing stormwater from a site. However, in doing so, these systems tend to increase peak runoff discharges, flow velocities and the delivery of pollutants to downstream waters. An alternative is the use of natural drainage ways such as grass natural drainage systems.

The use of natural open channels allows for more storage of stormwater flows on-site, lower stormwater peak flows, a reduction in erosive runoff velocities, infiltration of a portion of the runoff volume, and the capture and treatment of stormwater pollutants.

Figure A.12—Photograph of vegetated drainage ways.

Table A-37
Pollutant Removal Capacity
Vegetated Drainage Ways

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	No Treatment
Total Phosphorus	No Data
Total Nitrogen	No Data
TSS	No Data
Metals	No Data

Notes:
a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-38
Treatment Processes Provided by
Vegetated Drainage Ways

Treatment Processes	Process Provided?
Biological Processes	
Infiltration	
Filtration	
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	

Notes:
a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-39

Advantages, Disadvantages and Limitations of Vegetated Drainage Ways

Applications	Advantages	Limitations
• Use vegetated open channels in the street right-of-way to convey and treat stormwater runoff from roadways, particularly for low-density development and residential subdivisions where density, topography, soils, slope, and safety issues permit. • Use vegetated open channels in place of curb and gutter to convey and treat stormwater runoff. • Design drainage systems and open channels to: ▪ Increase surface roughness to retard velocity. ▪ Include wide and flat channels to reduce velocity of flow and encourage sheet flow if possible. ▪ Increase channel flow path to increase time of concentration and travel time.	• Reduces or eliminates the cost of constructing storm sewers or other conveyances, and may reduce the need for land disturbance and grading. • Increases travel times and lower peak discharges. • Can be combined with buffer systems to enhance stormwater filtration and infiltration.	• Maximum longitudinal slope of 4%, without checkdams • Can erode during large storms • Treats small tributary areas

WATER QUALITY SWALE

Water quality swales are shallow, open conveyance channels with low-lying vegetation designed to settle out suspended pollutants due to shallow flow depths and slow velocities. Additional pollutant removal mechanisms include volume reduction through infiltration and evapotranspiration and biochemical processes that provide treatment of dissolved constituents. It is generally accepted that water quality swales have higher pollutant removal efficiencies than grass channels. An effective vegetated swale achieves uniform sheet flow through a vegetated area for at least 10 minutes.

Figure A.13—Photograph of water quality swale.

Vegetated open channels designed to treat and attenuate the water quality volume and convey excess stormwater runoff. Dry swales are primarily designed to receive drainage from small impervious areas and rural roads.

Wet swales are primarily used for highway runoff, small parking lots, rooftops, and pervious areas. Vegetated open channels designed to treat and attenuate the water quality volume and convey excess stormwater runoff. Dry swales are primarily designed to receive drainage from small impervious areas and rural roads. Wet swales are primarily used for highway runoff, small parking lots, rooftops, and pervious areas.

Table A-40
Pollutant Removal Capacity
Water Quality Swale

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	70%
Total Phosphorus	30%
Total Nitrogen	55%
TSS	90%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-41
Treatment Processes Provided by
Water Quality Swale

Treatment Processes[a]	Process Provided?
Biological Processes	✓
Infiltration	✓
Filtration	✓
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	✓

Notes:

a. Treatment processes identified from Boston Water and Sewer Commission (BWSC) *Stormwater Best Management Practices: Guidance Document*, January 2013.

Table A-42
Advantages, Disadvantages and Limitations of
Water Quality Swale

Applications	Advantages	Limitations
• Residential settings along roadways.	• Low capital cost • Low maintenance requirements	• Can erode during large storms • Treats small tributary areas • Not for areas with very flat grades, steep topography, or poorly drained soils • Higher degree of maintenance than curb and gutter systems

GRAVEL WETLAND

Gravel WVTS is a wet stormwater basin system designed to provide treatment primarily in a wet gravel bed with emergent vegetation. The SGW is designed as a series of horizontal flow-through treatment cells, preceded by a sedimentation basin (forebay) designs maintain a saturated gravel bed and provide treatment by stormwater movement through the gravel bed and plant/soil treatment processes.

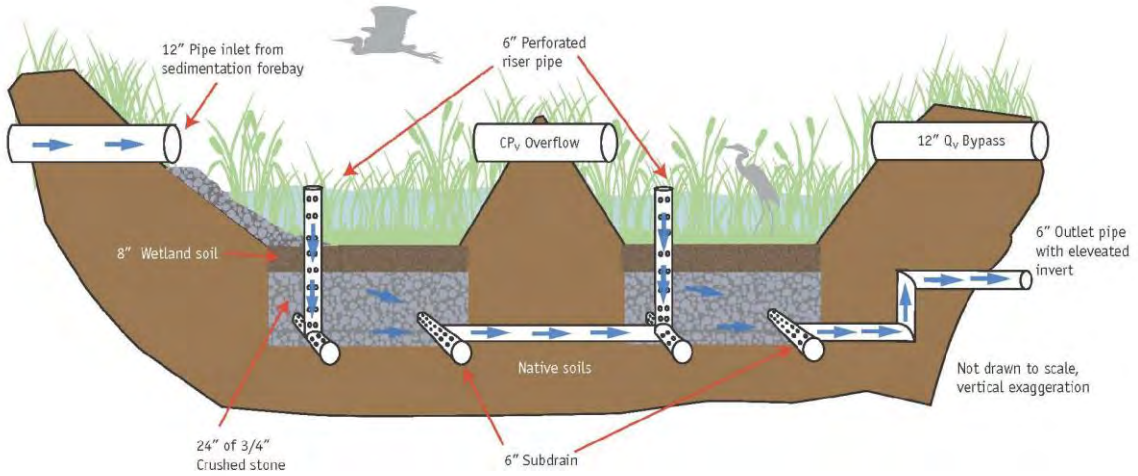


Figure A.14—Schematic of wet vegetated treatment system.

Table A-43
Pollutant Removal Capacity
Wet Vegetated Treatment System (Gravel)

Target Constituents	Removal Rates Based on the *Rhode Island Stormwater Design and Installation Standards Manual*[a]
Bacteria	85%
Total Phosphorus	53%
Total Nitrogen	55%
TSS	86%
Metals	Good

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-44
Treatment Processes Provided by
Wet Vegetated Treatment System (Gravel)

Treatment Processes	Process Provided?
Biological Processes	✓
Infiltration	
Filtration	✓
Sedimentation	✓
Vegetated Treatment	✓
Volume Reduction	

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

Table A-45
Advantages, Disadvantages and Limitations of
Wet Vegetated Treatment System (Gravel)

Applications	Advantages	Limitations
• May be used in a wide variety of settings including residential, commercial, and industrial areas; but are most commonly applied to commercial and industrial settings. • May be decentralized (e.g., bioretention) or centralized in common areas to manage multiple properties. • Must be lined and underdrained to ensure proper function.	• Desirable for small drainage areas, stormwater retrofits and highly developed sites. • High bacteria removal and nutrient removal efficiency. • Reduces need for end-of-pipe treatment. • Well-suited for water quality retrofit of existing storm drainage systems and stormwater ponds.	• High land requirement • High capital cost • Design needs to consider depth to groundwater and bedrock • Additional restrictions apply in cold-water fishery watershed based on distance from discharge point to streams (and any contiguous wetlands)

Notes:

a. Removal rates taken from Table H-3 Pollutant Removal Efficiency Rating Values for Water Quality BMPs of the *Rhode Island Stormwater Design and Installation Standards Manual*

REFERENCES

Boston Water and Sewer Commission. (2013). *Stormwater Best Management Practices: Guidance Document.*

RIDEM. (2010). *Rhode Island Stormwater Design and Installation Standards Manual*.

Land Use Class (restricted)	
Residential	
Commercial	
Industrial	
Highways	
Undeveloped/Rural	

Point of Analysis	Drainage Area (Acres) by LU Class	Impervious Acres in Drainage Area	Land Use Category	Percent Impervious in Drainage Area	Runoff Coefficient	Pollutant of Interest	Pollutant Concentration	Water Quality Volume	Pollutant Load Without Treatment (lbs/year)	BMP Treatment Option	Mass Reduction (lbs/yr)	Cost	Removal Cost (lbs/year)	Low Range Cost Per Treatment Site at -30%	High Range Cost Per Treatment Site at +50%
BRP-E	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Bioretention	0.0	$63,279	$1,000,886	$44,296	$94,919
BRP-E	32.36	10.93	Residential	33.8%	0.05	TP	0.3	39,676	4.7	Bioretention	0.1				
BRP-E	1.70	0.58	Undeveloped/Rural	34.1%	0.05	TP	0.11	2,105	0.1	Bioretention	0.0				
BRP-E	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Subsurface Chambers	0.0	$647,746	$716,333	$453,422	$971,619
BRP-E	32.36	10.93	Residential	33.8%	0.05	TP	0.3	39,676	4.7	Subsurface Chambers	1.2				
BRP-E	1.70	0.58	Undeveloped/Rural	34.1%	0.05	TP	0.11	2,105	0.1	Subsurface Chambers	0.0				
BRP-I/J	6.42	3.35	Commercial	0.0%	0.05	TP	0.2	12,161	0.6	Bioretention	0.0	$122,817	$1,537,943	$85,972	$184,226
BRP-I/J	36.38	18.97	Residential	52.1%	0.05	TP	0.3	68,861	5.5	Bioretention	0.1				
BRP-I/J	0.00	0.00	Undeveloped/Rural	0.0%	0.00	TP	0.11	0	0.0	Bioretention	0.0				
BRP-I/J	6.42	3.35	Commercial	0.0%	0.05	TP	0.2	12,161	0.6	Subsurface Chambers	0.0	$741,420	$909,477	$518,994	$1,112,130
BRP-I/J	36.38	18.97	Residential	52.1%	0.05	TP	0.3	68,861	5.5	Subsurface Chambers	0.7				
BRP-I/J	0.00	0.00	Undeveloped/Rural	0.0%	0.00	TP	0.11	0	0.0	Subsurface Chambers	0.0				
BRP-C	1.81	0.80	Commercial	0.0%	0.05	TP	0.2	2,904	0.2	Bioretention	0.0	$44,021	$2,125,688	$30,814	$66,031
BRP-C	5.42	2.40	Residential	44.3%	0.05	TP	0.3	8,712	0.8	Bioretention	0.0				
BRP-C	10.84	4.80	Undeveloped/Rural	44.3%	0.05	TP	0.11	17,424	0.6	Bioretention	0.0				
BRP-D	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Subsurface Chambers	0.0	$738,805	$661,372	$517,164	$1,108,208
BRP-D	31.69	8.97	Residential	28.3%	0.05	TP	0.3	32,561	4.6	Subsurface Chambers	1.6				
BRP-D	1.67	0.46	Undeveloped/Rural	27.5%	0.05	TP	0.11	1,670	0.1	Subsurface Chambers	0.0				
BRP-X	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Subsurface Chambers	0.0	$538,329	$829,456	$376,830	$807,494
BRP-X	19.08	6.74	Residential	35.3%	0.05	TP	0.3	24,466	2.8	Subsurface Chambers	1.0				
BRP-X	0.00	0.00	Undeveloped/Rural	0.0%	0.05	TP	0.11	0	0.0	Subsurface Chambers	0.0				
BRP-O	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Subsurface Chambers	0.0	$135,264	$558,263	$94,685	$202,896
BRP-O	8.61	2.34	Residential	27.2%	0.05	TP	0.3	8,494	1.2	Subsurface Chambers	0.3				
BRP-O	0.00	0.00	Undeveloped/Rural	0.0%	0.05	TP	0.11	0	0.0	Subsurface Chambers	0.0				
BRP-Q	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Subsurface Chambers	0.0	$1,271,673	$690,915	$890,171	$1,907,509
BRP-Q	64.08	21.71	Residential	33.9%	0.05	TP	0.3	78,807	9.4	Subsurface Chambers	2.5				
BRP-Q	0.00	0.00	Undeveloped/Rural	0.0%	0.05	TP	0.11	0	0.0	Subsurface Chambers	0.0				
BRP-S	0.00	0.00	Commercial	0.0%	0.05	TP	0.2	15	0.0	Subsurface Chambers	0.0	$159,107	$1,468,133	$111,375	$238,660
BRP-S	2.88	1.46	Residential	50.7%	0.05	TP	0.3	5,300	0.4	Subsurface Chambers	0.2				
BRP-S	0.00	0.00	Undeveloped/Rural	0.0%	0.05	TP	0.11	0	0.0	Subsurface Chambers	0.0				