CES INC

Engineers ◆ Environmental Scientists ◆ Surveyors

January 22, 2020

Richard Hull
US Environmental Protection Agency, Region I
5 Post Office Square, Suite 100
Boston, Massachusetts 02109-3912

Re: Stormwater Investigation Report – Response to Comments
Coakley Landfill – North Hampton and Greenland, New Hampshire

Dear Mr. Hull:

On behalf of the Coakley Landfill Group (CLG), CES, Inc. (CES) is hereby submitting the following Response to Comments provided by the United States Environmental Protection Agency (USEPA) in their November 22, 2019 letter to Peter Britz of the CLG. A revised Stormwater Investigation Report (Report) will be submitted following completion of the additional activities outlined in the enclosed scope of work and will incorporate the USEPA's proposed revisions as appropriate.

A summary of responses to comments is provided below:

USEPA

1. **Water infiltrating within Areas 1 and 2 is collected by the underdrain piping system while water infiltrating in Area 3 enters a gravel-filled toe drain system, but the ultimate discharge location for the toe drain system is not identified.**

CLG Response

The location and ultimate discharge locations for the toe drains will be identified on a revised Figure 1 – Stormwater Investigation Sampling Locations included with Attachment A of this letter and used in future reporting.

USEPA

2. **The Introduction briefly describes the stormwater sampling that was proactively conducted in spring 2018. The data from that sampling event should be provided in either its own table or included in Table 3 to allow for comparison of results over time.**

<u>CLG Response</u>
The data for the stormwater sampling completed in Spring 2018 were included with Table 3. These samples were collected from three locations (PD-2, OFP-2, and UP-2) and can be identified by their sampling date of 4/26/2018. Future presentation of these data will include notation to identify these as the initial samples collected in the Spring 2018.

USEPA

3. **Section 2 describes the perimeter drainage ditches and “rip-rap let-down structures” and cites Figure 1, but the figure does not have the let-down structures labeled. Given that the Stormwater Report references several rip-rap structures, it would be useful to specifically label the let-down structures and toe-drains in Figure 1.**

<u>CLG Response</u>
The referenced rip rap-lined letdown structures referenced in Section 2 will be included on a revised Figure 1 – Stormwater Investigation Sampling Locations included with this letter (Attachment A) and in final reporting efforts. For toe drain locations, see response to USEPA Comment No. 1.

USEPA

4. **First paragraph of Section 2 describes the “stormwater retained in the basins” as subsequently discharging to “adjacent wetland areas through infiltration and via an outlet structure in each basin…”. This description is a bit simplistic compared to the more accurate description provided throughout the rest of the Stormwater Report. Consider expanding the description here to explain the infiltration from the basins to shallow groundwater, and subsequently to adjacent wetland areas.**

<u>CLG Response</u>
The description included in the first paragraph of Section 2 (Background) was designed specifically to provide a more generalized description of the basins and infiltration with the more thorough description provided elsewhere in the report (e.g. Section 3.1). Future reporting will use a more consistent version of the description with an explanation offered to include the infiltration of stormwater within the basins to shallow groundwater and subsequent discharge to surface water.

USEPA

5. **Section 3.1 describes the landfill cap construction, including the “plastic drainage netting (geonet) with bonded geotextile fabric on top and textured flexible membrane liner (FML) located below the geonet.” Figure 2 describes the geonet as being bonded with geotextile on both sides, and as-built drawing 5-5 also describes the geonet as being bonded on top for the slopes up to 5% and bonded on both sides for side slopes.**

<u>*CLG Response*</u>

Multiple forms of geonet were used in the construction of the landfill cap based on landfill side slope. For example, Landfill Cap Types 1 and 3 (Drawing 5-5) do not include the use of a geonet, with Type 2 and Type 4 having geotextile bonded to the top and both surfaces of the geonet, respectively. Figure 2 was designed to reference the Cap Type selected for landfill cap sampling with other cap types referenced in Drawing 5-5.

USEPA

6. **Figure 2 presents a cross-section of the landfill cap based on the Type 4 model but does not provide cross-sections for the other cap types. It would be helpful to include cross- sections for landfill cap Types 1, 2 and 3 as figures, or to reference the cross-sections included in Landfill Cover System Design Report Drawing 5-5 in Appendix A in the text descriptions.**

<u>*CLG Response*</u>

The CLG concurs that a reference to the cross sections included in the Landfill Cover System Design Report – Drawing 5-5 (Appendix A; Stormwater Investigation Report) would be helpful to describe and/or reference the other landfill cap types. Future descriptions of the various landfill cap types will be accompanied by either a representative detail cross section or appropriate design drawing references as were included with Drawing 5-5 in Appendix A of the Stormwater Investigation Report as submitted on September 24, 2019.

USEPA

7. **In the description of the sources of the cover soil provided in Section 3.1.1, the term "topsoil" is used to describe the cover soil in that section.**

<u>*CLG Response*</u>

The term cover soil should have been used in the description of the cover soil source material instead of topsoil and will be corrected in subsequent reporting efforts described above.

USEPA

8. **Section 3.2, second paragraph should clarify that piezometers PZ-1 and PZ-2 were constructed of stainless steel and that PZ-3 was constructed of PVC.**

<u>*CLG Response*</u>

The CLG concurs that the second paragraph of Section 3.2 could clarify the variations in construction materials used in piezometer construction; however, we feel the description provided in the first paragraph of Section 3.2 and the provided piezometer construction diagrams are sufficient to establish the locations of PZ-1 and PZ-2 with regards to the construction materials outlined in the second paragraph. Future stormwater reporting efforts will include more detailed descriptions of piezometer construction.

USEPA

9. **Section 3.3 and Table 1 describe the surface and groundwater elevation and provide the data from fall 2018 and spring 2019 monitoring. Table 1 is confusing as both surface water and groundwater elevations are provided in the columns labeled as "GW. EL. FT." A map should be provided that includes all locations used for water elevation measurements (see Table 1). Not all the monitoring wells listed in Section 3.3 are shown on Figure 1; nor are all the surface water locations listed in Table 1.**

CLG Response

The CLG concurs that the column headers are confusing with respect to the static water levels being represented. A revised Table 1 has been provided with this response to comments letter (Attachment A) to clarify any misunderstanding related to the column headers. Any future figures generated in support of stormwater characterization or reporting activities will include all locations referenced or reported. This includes revising the scale of figures to encompass areas where these features are located.

USEPA

10. **Section 3.4.1 does not identify or describe the analytical methods used for the analysis of the various cap components. It is presumed that the varying sample types (soil, pipe, membrane) would require different analytical testing procedures. The laboratory methods and procedures should be described. Section 3.4.1 should also describe the methods for sampling the cap materials (hand auger, test pit, shovel, etc.) and the depths of the various samples and how those depths compared to the design drawings. The last paragraph of Section 3.4.1 states that the soil matrix samples were a 4-point composite, but only a single sampling location is shown on Figure 1, and that a 2-point composite was used for sampling the construction materials. The Stormwater Report should describe the sample collection methods and analytical preparation procedures for the cap soils and materials, and detail the analytical methods used.**

CLG Response

Analytical methods used in the analysis of stormwater investigation samples were included on corresponding tables. See response to comment 11, below. Relative to the laboratory methods and procedures used in the analysis of the cap components, based on correspondence with the contracted laboratories, that although different methods are often used in the analysis of materials, the primary difference is in sample preparation/extraction and not in the analytical method used. These preparation and extraction methods are typically a proprietary technique specific to the laboratory and only general information is provided by the lab specific to their analysis process. As per a response from Vista Analytical Laboratories (Vista), HDPE underdrain piping was "…sonicated in methanol - the methanol was then analyzed to determine the levels of the leached analytes." This was completed in accordance with Vista SOP 49, rev. 22. A redacted copy of this SOP, as supplied by Vista, has been included with this letter as Attachment A.

Cap construction materials were sampled using a stainless-steel bucket auger with notes made on materials encountered relative to those referenced on cap construction details provided in Drawing 5-5 of the Landfill Cover Design Report (Appendix A; Stormwater Investigation Report). It was observed that materials encountered matched in both composition and depth/thickness as provided in the Landfill Cover Design Report. In support of the text provided in the last paragraph of Section 3.4.1 describing the 2-point and 4-point composite techniques used, corresponding composite sample IDs were provided on Figure 1 in parentheses and accompanying explanation in the notes included with Figure 1.

USEPA

11. **Section 3.5 does not list the analytical methods used for the various samples, or even the laboratory used. Again, the Stormwater Report should specify the analytical methods used for all samples.**

CLG Response

Eastern Analytical was used for the analysis of 1,4-dioxane and general landfill chemistry parameters, with PFAS analysis completed by Vista Analytical under subcontract to Eastern Analytical. The analytical methods used for the various samples are specified in Tables 2, 3 and 4. Analyses were completed as per USEPA Method 537 in accordance with Vista SOP 49, rev. 22. A redacted copy of this SOP, as supplied by Vista, has been included with this letter (Attachment A). For additional information related to the analysis of cap components, please refer to the response of Comment No. 10, above.

USEPA

12. **Table 2 indicates that bold text denotes concentrations above reporting limits (Note 10), but the results in Table 2 that appear to be above the reporting limits and are not flagged, do not appear in bold text.**

CLG Response

The CLG concurs that those values above the reporting limits should be in bold. A revised Table 2 has been included with Attachment A of this letter and will be included as part of future stormwater reporting.

USEPA

13. **Section 4.1 discusses results for PFOA and PFOS but does not mention the distribution and types of the other PFAS compounds analyzed and detected.**

CLG Response

The discussion of PFAS compounds was specific to address those that were regulated in groundwater at the time of report submittal. Additional PFAS compounds detected within cap materials, if detected in groundwater, were not regulated and not included in the discussion of results. Future reporting and discussions of PFAS compounds in soil materials will include those regulated and will, at a minimum, include a list of detections.

USEPA

14. **Section 4.2.1 details the results from location L-1 as part of the stormwater investigation, but these results are not included in Table 3. While Table 4 presents the historical results for L-1, the results from samples collected as part of the stormwater investigation should also be provided in Table 3 for comparison with the results from the other locations sampled as part of the investigation.**

CLG Response
The CLG concurs that historical data for L-1 could be provided in Table 3 for comparison and will include this in future presentation of stormwater analytical data as referenced above.

USEPA

15. **Section 5.1 concludes that "some infiltration of shallow groundwater may be entering the annular space between the corrugated steel piping of the outfall system and surrounding bedding material during periods when shallow groundwater levels are high." Shallow groundwater levels would be high during wet periods when surface water may be present in the stormwater basin. Another conclusion could be that during high groundwater level conditions, stormwater discharging from the basin is leaking down around the overflow pipe and flowing through the bedding material and out into the L-1 area. The head driver for that pathway would be substantially higher than for shallow groundwater.**

CLG Response
The CLG concurs that the hydraulic head conditions present during wet conditions/increased shallow groundwater elevations could result in stormwater discharge via bypassing the overflow pipe and be transported through the overflow pipe bedding material.

USEPA

16. **Section 5.2 describes an "average annual precipitation" of 59.55 inches, based on NOAA precipitation data for 2018. The amount of water falling on the landfill in 2018 (39 million gallons) is described as calculated using the average annual precipitation value and the landfill area. If 59.55 inches of rainfall for 2018 is used in this calculation, wouldn't it be more accurately described as total rainfall for 2018 rather than average annual precipitation? And that the total amount of water falling on the landfill would be specifically for 2018 rather than an annual average?**

CLG Response
The CLG concurs that the amount of rainfall used in the calculation could be more accurately described as total rainfall for 2018 rather than average annual precipitation. The use of terminology (precipitation) was coincident to that referenced by source data used during modeling. Though the term precipitation accounts for all forms of recordable precipitation, including rainfall, clarification of the term precipitation and how the volume of water was calculated will be provided in future reporting.

USEPA

17. **If the average annual precipitation (46 inches) was used in the mass loading calculations rather than the 2018 precipitation (59 inches) as described in Section 5.2, then the model calculations for the average rainfall amount should be described in similar detail and the amounts for surface runoff, infiltration and evapotranspiration should be provided.**

CLG Response

The CLG agrees that future assessment of contaminant loading should incorporate a long-term "average" precipitation value and resultant components (surface runoff, infiltration, evapotranspiration) should be based on an average precipitation value. Any future model calculations using an "average" rainfall amount will be described in similar detail with the amounts used for surface runoff, infiltration, and evapotranspiration provided.

USEPA

18. **Section 5.2.2 - The area of impacted groundwater discharge to Berry's Brook (estimated at 40 acres) should be clearly demarcated and labeled on Figure 3. A legend should be added to indicate the meaning of the various line types (3) used on that figure. In addition, no reference is provided for the watershed boundaries shown in Figure 3 and they do not correspond to the boundaries shown in NH GRANIT, a statewide geographic information system clearinghouse http://www.granit.unh.edu/. These maps show a considerably different southern boundary of the Berry's Brook watershed near the landfill and does not show a Bailey Brook watershed but suggest Bailey Brook is included in Berry's Brook watershed.**

CLG Response

A revised Figure 3 has been generated and has been included with this submission. These revisions include a defined area of impacted groundwater to Berry's Brook, the addition of a legend to define the various line types used, and notes provided to indicate the source of watershed boundaries illustrated. The southern boundary of the Berry's Brook watershed illustrated on Figure 3 was based on information obtained from the GRANIT GIS database for Level 6 Hydrologic Boundaries, Figure 1 of the Berry's Brook Watershed Management Plan, the Berry's Brook Watershed Wetland Soils and Tax Parcels Map (Rockingham Planning Commission), and high-resolution LiDAR surface topography obtained from GRANIT. According to metadata provided by GRANIT for the Level 6 Boundaries and notes provided in the Wetland Soils and Tax Parcels Map, the watershed boundary layer (shapefile) in GRANIT was generated from topographic information obtained from 1:24,000 scale USGS topographic maps (1969-1984) and from existing Level 11 Sub-watershed Data. The more recent LiDAR data (based on collection of data from 2010-2014) includes topography for the southern portion of the landfill following the regrading and capping of the landfill in the late 1990's and is not believed to have been included with the original watershed delineation efforts completed during generation and digitization of the GRANIT shapefile. The interpreted Bailey Brook Watershed boundary is *interpreted from surface topography obtained from LiDAR data as contoured and illustrated on Figure 3. Notation has been added to Figure 3 to include this information.*

USEPA

19. **Section 5.2.2 – Why wasn't data from more wells (AE-3A, PZ-3) and L1 seep used in the representation of groundwater quality? How was the 40-acre groundwater discharge area defined, and why wasn't it defined using monitoring wells and groundwater contours?**

CLG Response

The primary purpose of the Stormwater Investigation was to evaluate potential PFAS loading to surface water (wetland complex and Berry's Brook) due to runoff from the landfill cover system. The HELP model is well-suited to estimate runoff volumes from the landfill cover surface and that analysis provide relatively detailed information with respect to stormwater runoff. Performing a detailed analysis of contaminant mass loading from groundwater to surface water was not specifically included in the investigation scope of work. However, it was determined that a rough estimate of contaminant loading from groundwater could provide a basis for a comparison to stormwater contaminant loading to determine if the stormwater PFAS loading was a "significant" contribution to contaminants in surface water compared to groundwater discharge.

The PFAS concentrations used in the groundwater loading estimate were based on isoconcentration contour maps provided in previous Annual Monitoring Reports and review of PFAS concentrations in shallow overburden wells that were judged to be representative of groundwater that would most likely be discharging to surface water at this point in time (i.e., for comparison to the 2018 HELP model results). The area of groundwater discharge was estimated to include much of the wetland area west of the landfill and extending north to Breakfast Hill Road. That area was determined to be approximately 40 acres in size. Because a surface water sampling location (SW-110) is present where Berry's Brook crosses Breakfast Hill Road, groundwater discharges north of Berry's Brook were not included.

We agree that more refined estimates of groundwater could be made, but based on the more generalized mass loading estimates, it is clear that stormwater runoff provides a significant PFAS loading to surface water. The purpose of this part of the evaluation was to verify this hypothesis, and the analysis performed was sufficient to do so. Following the completion of efforts outlined in the scope of work provided below, an evaluation of mass loading estimates will be performed, and comparisons made to initial estimates provided in the Stormwater Investigation Report. These efforts include the evaluation of additional sources of analytical data within a more refined discharge area.

USEPA

20. **Section 5.2.2 should more specifically describe the data set used to calculate the average concentration of PFAS.**

CLG Response
See response to comment 19.

USEPA

21. **Section 5.2.2 does not adequately explain how the PFAS mass discharge via groundwater from the landfill was calculated. It is not clear how the average value for recharge from precipitation (22.3") can be applied to a 'groundwater discharge area' in a wetland to estimate PFAS mass flux in groundwater from the landfill by applying an average PFAS concentration from monitoring wells.**

    A more traditional method would be to calculate the PFAS mass flux in groundwater at a series of transects perpendicular to the groundwater flow across the mapped plume. The groundwater flux is calculated via Darcy's Law and analytical results from monitoring wells located along the transect(s) are used for the PFAS concentration. This provides a reliable estimate of the PFAS mass leaving the landfill via the groundwater pathway.

CLG Response
The PFAS loading was a simplified assessment that assumed a steady state hydraulic condition where groundwater recharge is balanced by groundwater discharge. Given that no large scale groundwater withdrawals are known to be present within the immediate Berry's Brook watershed area discussed in the Stormwater Investigation Report, the approach assumed uniform recharge and used a pro-rated discharge area where groundwater impacts are known to occur as the basis for estimating a mass loading estimate.

We agree that more sophisticated methods could have been used to estimate mass flux of PFAS from groundwater to surface water. However, as noted in the response to Comment No. 19, the purpose was only to assess the overall significance of stormwater loading compared to groundwater loading.

Should any future remedial investigation work on this issue include assessment of shallow groundwater, a more rigorous assessment of PFAS loading will be warranted. However, the collection of additional data as outlined in the provided Scope of Work will provide for a more complete understanding of the interaction between shallow groundwater and surface water and allow for more accurate estimates of mass flux within the system. For additional efforts related to loading estimates, please see response to Comment No. 19, above.

USEPA

22. **Section 5.2.3 does not adequately explain how the PFAS mass discharge into Berry's Brook was calculated. It is unclear how an average surface water PFAS concentration based on limited sample results from a single location can be applied to groundwater recharge over the entire watershed to estimate the mass. Further, the resulting recharge mass is then assumed to equate to the mass in Berry's Brook.**

A more traditional method would be to calculate the PFAS mass flux in Berry's Brook using measured PFAS concentrations in the brook at the Breakfast Hill Road crossing and stream discharge rates from the USGS gauging station. The gauging station data can be adjusted to reflect the drainage area upstream from Breakfast Hill Road by applying the ratio method. This method is straightforward and accurate.

This will facilitate a comparison between the three pathways: 1) groundwater PFAS flux in the plume, 2) PFAS mass flux in the stormwater, and 3) PFAS mass flux in the brook. The relative impact of the stormwater on Berry's Brook can then be quantitatively assessed. However, it should be noted that there are other components of the PFAS mass flux that are not considered by this method; refer to Comment 24.

CLG Response
The estimated mass of PFAS leaving the Site via Berry's Brook assumed a baseflow condition. Surface water samples from location SW-110 historically have been collected during normal or low flow conditions rather than during high surface runoff events. As a result, a large component of flow is likely to be considered baseflow of the Brook.

We agree that the surface water sample set is limited, and it is not possible to determine PFAS concentration fluctuations with respect to varying surface water discharge volumes. It is likely that additional PFAS mass is discharged during high runoff events, but significant dilution due to freshwater input within the watershed will also be occurring. Assigning an average value under all discharge conditions that could be applied to an adjusted USGS downstream gauging station would include many assumptions that would be difficult to justify based on the limited data set. More refined mass discharge via Berry's Brook can be calculated as additional data is obtained. Following the collection of additional information related to shallow groundwater water and stormwater contribution to surface water as outlined in the Scope of Work provided below, a more complete data set will be available to facilitate comparisons between multiple pathways referenced above.

USEPA

23. **In Section 5.2.3, what is meant by "above Breakfast Hill Road"? The description of the watershed area seems to identify the area north of Breakfast Hill Road and SW-110, but it appears that the calculation is for the area providing water volume that is discharged across Breakfast Hill Road?**

CLG Response
The reference to "above Breakfast Hill Road" refers to the watershed area(s) south (upstream) of Breakfast Hill Road.

USEPA

24. **The analysis in Section 5.2.3 assumes that all groundwater impacted by the landfill discharges to Berry's Brook upstream of Breakfast Hill Road. This assumption is not accurate. Some overburden and bedrock groundwater containing PFAS migrates under Breakfast Hill Road and continues to flow downgradient. The analysis also ignores any migration of PFAS into the underlying bedrock, which we know takes place due to the detections noted in that unit. The PFAS mass flux for those pathways should be estimated to assess whether they are significant enough to be considered in the evaluation.**

CLG Response

The CLG concurs and this is consistent with the general conceptual site model for the Site. However, concentrations of PFAS detected at MW-20, residential well R-3 and the Breakfast Hill Golf Club drinking water supply well, are orders of magnitude lower than concentrations observed in monitoring wells near the landfill and wetland complex. This demonstrates a significant mass of PFAS is not migrating north of Breakfast Hill Road. It should also be noted that the golf club irrigation water contained higher concentrations of PFAS, when sampled by others in 2017 (24 ng/L PFOA), than those detected in the northernmost overburden well within the Coakley GMZ (<1 ng/L at MW-20S). These concentrations in the golf club irrigation well may affect groundwater and surface water concentrations of PFAS north of Breakfast Hill Road. PFAS detected in golf course irrigation water is believed to be unrelated to the Coakley Landfill as the irrigation well is constructed within overburden, is located side gradient of the golf club drinking water supply well, and is located across a watershed divide (located in Winnicut River Watershed) from the area located downstream from the Coakley Landfill and north of Breakfast Hill Road (located in Berry's Brook Watershed). In addition, water level monitoring of wells within the Coakley Landfill monitoring network and near the irrigation well completed during a well yield test performed on the irrigation well in 2017 resulted in no evidence of influence in the monitored wells during pumping. Continued monitoring of newly installed overburden and bedrock groundwater monitoring wells will aid in assessing migration of PFAS in the vicinity of Breakfast Hill Road.

USEPA

25. **A sensitivity analysis should be conducted for all calculations detailed in Sections 5.2.1, 5.2.2, and 5.2.3 by modifying the inputs and assumptions (volume of discharge, average concentration, discharge area, etc.) to allow for an evaluation of the inputs relative to outputs; which will allow the accuracy of the various components of the assessment to be estimated.**

CLG Response

The CLG concurs that a sensitivity analysis could provide additional accuracy of the various components and inputs used for calculations described in Sections 5.2.1 through 5.2.3. However, the scope of work that has been developed to further investigate the extent of contaminant loading to Berry's Brook will allow for more accurate information (inputs) to be used in additional calculations and modelling. The scope of work will be developed to include the collection and evaluation of data in the context of contaminant loading from the cap (stormwater contribution) *relative to that of shallow groundwater and to evaluate the interaction of surface water and shallow groundwater in Berry's Brook and the adjacent wetland complex. The information gathered as part of this effort will aid in the overall accuracy of these calculations and will be presented further in future reporting.*

USEPA

26. **One of the findings is that, based on 1,4-dioxane results from PZ-2 in fall 2018 (ND) and a detection in spring 2019, along with iron results from OFP-1, PZ-1, PZ-2 and PZ-3, shallow groundwater beyond the landfill boundary interacts with discharges from the northwest outfall pipe (OFP-2) during periods of high overburden groundwater levels. How are the iron results from OFP-1 and PZ-1 in the northeast basin related to the interaction between groundwater and the discharge from OFP-2? And how does the detection of 1,4-dioxane in PZ-2 relate to the discharge from OFP-2 when it is measuring shallow groundwater just beneath the basin?**

CLG Response
Based on the iron results at OFP-1 (3 mg/L) and PZ-1 (4.6 mg/L), there is likely an interaction between shallow groundwater and stormwater within the northeast basin (SB-1) similar to that believed to be occurring in the northwest basin (SB-2). This is supported by low levels (<1 mg/L) of iron in perimeter ditch and underdrain pipe samples (no supposed direct interaction with shallow groundwater) and concentrations similar to those observed from the same structure locations (i.e. UP) in the northwest corner of the landfill. It is reasonable to assume that shallow groundwater can migrate through the bedding material of the OFP structure at times when overburden groundwater reaches seasonal high levels. As iron was only analyzed for during the Spring 2019 sampling event, additional information on seasonal iron concentrations may be needed to generate a more comprehensive model for stormwater and shallow groundwater interaction. However, despite iron being an important indicator to landfill influence, it is a parameter that can be influenced by several environmental factors. As such, iron concentrations will be used with other general groundwater chemistry parameters to assist with evaluating the interaction between stormwater and shallow groundwater.

With regard to the detection of 1,4-dioxane in PZ-2 (5.7 ug/L) and OFP-2 (<0.2 ug/L) during Spring 2019, the relationship between shallow groundwater (as monitored by PZ-2) and discharge from OFP-2 may be a function of seasonal variations in water levels and/or changes in the amount of contact time the shallow groundwater has with refuse before migrating downgradient. As with the reported iron concentrations, additional information on seasonal 1,4-dioxane concentrations and hydraulics may be needed to generate a more comprehensive model for stormwater and shallow groundwater interaction.

USEPA

27. **Conclusions state that "stormwater and groundwater contribute significant percentages of PFAS to the wetland complex" while the annual contributions of PFAS from stormwater and groundwater discharge to surface water is described**

as exceeding the mass estimate of PFAS calculated in Berry's Brook by a factor of 2.5. The conclusions should more clearly represent this calculated relationship and summarize the potential causes of this discrepancy.

CLG Response
The CLG concurs that the conclusions stated in the report should more clearly represent the calculated relationship between stormwater and groundwater contributions of PFAS to the wetland complex. Future reporting will include revised conclusions relative to the discussion of the relationships and contribution of PFAS to the wetland complex by stormwater and shallow groundwater.

USEPA

28. **The Stormwater Report makes no mention of the underdrain system cleanouts. Were these inspected? Are these routinely checked? Is there any reason to believe that the system may not be functioning as designed due to the discharge piping being fouled?**

CLG Response
The underdrain cleanouts were visually inspected during the verification of the stormwater system components; however, these are not routinely inspected. Due to the photographic documentation of discharge of the underdrain piping during and immediately following precipitation events, there is no reason to suspect that the discharge piping has been fouled. In addition, water clarity (no visual evidence of soil particulates or iron fouling/staining) does not indicate the presence of material that would be characteristic of a blockage or fouling within the pipes.

USEPA

29. **The PFAS compositional plots included in Appendix D are not referenced or discussed anywhere in the document. They are only mentioned briefly in Section 6.1. A discussion of how the plots were prepared and what they represent should be included.**

CLG Response
The CLG concurs that additional reference to compositional plots included as Appendix D of the Stormwater Investigation Report should be made and will include this with future reporting efforts proposed. The plots were prepared for select locations using six PFAS compounds analyzed for during the Fall 2018 stormwater sampling event. The compositional plots were generated to visually illustrate a "signature" for PFAS composition within stormwater. This signature can be visually correlated to the composition of PFAS within shallow groundwater (e.g. MW-9) to illustrate the impact of stormwater to shallow groundwater in areas immediately adjacent to stormwater discharge locations.

CESINC

SENSIBLE SOLUTIONS

SURFACE WATER EVALUATION
SCOPE OF WORK
COAKLEY LANDFILL SUPERFUND SITE
NORTH HAMPTON
AND GREENLAND, NEW HAMPSHIRE

FOR

COAKLEY LANDFILL GROUP

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SURFACE WATER EVALUATION SCOPE OF WORK
COAKLEY LANDFILL SUPERFUND SITE
NORTH HAMPTON AND GREENLAND, NEW HAMPSHIRE

1.0 | INTRODUCTION

On behalf the Coakley Landfill Group (CLG), CES, Inc. (CES) has prepared the following Surface Water Evaluation Scope of Work (SOW) to provide an approach and protocols for the collection and analysis of additional information relative to migration of contaminants from stormwater and shallow groundwater to Berry's Brook. The intent of this investigation is to better understand contaminant distribution and migration as it relates to the interaction between surface water, stormwater discharge from the landfill, and shallow groundwater.

The sampling and investigation activities are being conducted by the CLG, at the request of the United States Environmental Protection Agency (USEPA) and New Hampshire Department of Environmental Services (NHDES) as outlined in a letter from the USEPA to the CLG dated November 22, 2019. This letter contained comments generated from a review of stormwater investigation activities presented in the *Stormwater Investigation Report* submitted to the Agencies on September 24, 2019. The SOW will include an assessment of options for limiting the contaminant loading to Berry's Brook and for the evaluation of collection and treatment options through pilot or treatability studies. These assessment actions will serve to address requirements included in New Hampshire House Bill 494 (HB494).

2.0 | PROJECT BACKGROUND AND DESCRIPTION

As part of Site remedy design and construction activities implemented in the mid and late 1990s and evaluated during the Stormwater Investigation completed in the Fall of 2019, the majority of stormwater runoff from the landfill surface is conveyed to two unlined stormwater retention basins. These basins are located in the northeast and northwest corners of the landfill and are designated as SB-1 and SB-2, respectively. The stormwater runoff (sheet flow) enters each basin via a series of perimeter drainage ditches and rip-rap let-down structures on the landfill (**Figure 1**). Stormwater retained in the basins is subsequently discharged to adjacent wetland areas via an outlet structure in each basin and associated corrugated metal piping or to shallow groundwater via infiltration.

In addition to surface stormwater runoff, precipitation that infiltrates through the landfill's vegetative layer and cover soil is collected in a drainage layer and geonet filtration layer placed immediately above the flexible membrane liner (FML) of the cap system. Water along the east side of the landfill is conveyed via underground perforated piping of the underdrain system to the northeast stormwater retention basin (SB-1), while water along the west side of the landfill is conveyed via similar underdrain piping to a rip rap lined discharge swale located west of SB-2 (**Figure 1)**.

As detailed in the September 24, 2019 Stormwater Investigation Report, a significant contribution of per- and polyfluoroalkyl substances (PFAS) to the adjacent wetland complex and shallow groundwater is from stormwater runoff and stormwater discharge from the landfill cover system. These components of contaminant input to surface water and shallow groundwater resulted in a request by the USEPA to further investigate the interaction between stormwater, groundwater and contaminant concentrations detected in Berry's Brook.

Concurrent with the completion of activities described in the Stormwater Investigation Report, the passage of HB494 in August of 2019 resulted in a requirement that the CLG work with the NHDES and USEPA to "…propose, under the applicable consent decree involving the Coakley Landfill superfund site, an appropriate remedy including a design solution and associated costs to ensure the substantial reduction of the contaminants entering Berry's Brook from the Coakley Landfill superfund site."

The CLG, NHDES, and USEPA have jointly worked to identify activities and remedies that can be implemented to address both the comments of the USEPA in its November 22, 2019 letter and the requirements of HB 494. This SOW provides details of activities to be completed that will assist in assessing options to reduce contaminant concentrations in Berry's Brook.

2.1 Study Objectives

The overall objective of this evaluation will be to further assess the extent of contaminant distribution and migration to Berry's Brook and shallow groundwater from stormwater discharge at the Coakley Landfill. This evaluation will allow for a better understanding of the interaction between stormwater, surface water discharging to the wetland complex, and groundwater that ultimately discharges to Berry's Brook. Results of the evaluation will also be used to assess potential mitigation measures to reduce contaminant concentrations in Berry's Brook.

3.0 | SAMPLING AND INVESTIGATION ACTIVITIES

The SOW is comprised of several efforts or phases and is designed to provide the information necessary to make informed decisions on subsequent investigation activities.

3.1 Piezometer Installation

A total of three piezometers (PZ-1, PZ-2, and PZ-3) were installed as part of the Stormwater Investigation completed in September 2019. PZ-1 was installed in the northeast stormwater retention basin (SB-1) and PZ-2 was installed in the northwest basin (SB-2) to monitor localized subsurface soil saturation conditions resulting from direct infiltration of stormwater through the bottom of the unlined basins. PZ-3 was installed in the vicinity of the L-1 seep sampling point to establish a discrete sampling location representative of shallow groundwater discharging to the wetlands in the area downgradient from the outfall discharge from stormwater retention basin SB-2. To supplement these existing monitoring locations, the installation of eight additional piezometers is proposed to further evaluate the relationships between surface water and shallow groundwater north and west of the landfill.

Piezometers will be installed at several existing surface water sampling locations (BB-2, SW-4, SW-103, and SW-110) and in areas where surface water is not currently being monitored as illustrated on **Figure 2**. These include areas immediately north of the landfill boundary and in an area west of the railroad easement between BB-1 and BB-2. As a result of a prolonged period of below average precipitation prior to the Fall 2019 Semiannual Sampling event, several surface water locations did not contain sufficient water (SW-4, SW-5, BB-1, and BB-2) to obtain a representative sample. SW-4 and BB-2, though dry during the Fall 2019 sampling event, represent locations where surface water is typically present and have been identified as locations that will be targeted in the monitoring of surface water as part of this evaluation. Locations SW-5 and BB-1 may not be representative of the natural surface water drainage network, but rather, more characteristic of localized ponded water areas isolated from the more direct surface water drainage network. Analytical results from these locations may not be typical of natural surface water where there is an established gradient allowing for the influx and passage of water through the system; however, availability of historical information from the location of SW-5 within the area of investigation makes it a suitable location for piezometer installation. A piezometer is not planned for installation at BB-1. However, a piezometer will be installed at an alternate location west of the railroad easement. Data from a piezometer in this location will be used in conjunction with data from several existing monitoring locations within the wetland complex west of the tracks and with data obtained from proposed porewater sampling efforts discussed below.

The installation of piezometers at BB-2, SW-4, SW-5, SW-103, SW-110, and SW-111 will allow for the monitoring of shallow groundwater at locations where historical data on surface water is available and allow for the monitoring of both surface water and shallow groundwater elevations at a single location. In addition, the installation of piezometers at locations immediately north of the landfill and in areas adjacent to existing wetlands (**Figure 1**) will provide a more comprehensive network of monitoring to develop a better understanding of interaction between shallow groundwater and surface water at areas of interest.

Monitoring of water levels within these piezometers will be performed on a monthly basis and will be combined with the gauging of overburden groundwater monitoring wells as identified on **Figure 2**. These wells include MW-9, MW-10, FPC-5A, FPC-6A, AE-3A, FPC-7A, FPC-9A, OP-2, and OP-5.

Piezometers will be constructed using either 1.25-inch diameter stainless steel drive point well screens or 1-inch diameter Schedule 40 PVC well screen and riser. Piezometer construction will be based on field conditions at the time of installation. Following installation, piezometers will be surveyed relative to existing surveyed locations that include survey pins, staff gauges, or monitoring wells surveyed during the Stormwater Investigation. This will allow for water level comparisons to existing surveyed monitoring wells in the vicinity of the piezometers.

3.2 Stormwater and Shallow Groundwater Sampling

To minimize duplication of sampling, surface water sampling locations that are part of the routine semiannual sampling program will continue to be sampled during regularly scheduled semiannual events separate from stormwater and shallow groundwater (piezometer) sampling outlined below. However, efforts will be made to schedule stormwater and shallow groundwater sampling in conjunction with routine sampling events to allow for more direct correlation of analytical results.

3.2.1 Stormwater Sampling Locations

Based on results of stormwater sampling completed during the stormwater investigation, select locations have been identified for continued sampling to establish a more extensive database of results. Due to similarities in PFAS composition and concentrations between samples from the northeast and northwest retention basins, locations proposed for continued sampling will be primarily from the northwest basin (SB-2) due to the proximity to the primary area of investigation (i.e., wetland complex and Berry's Brook). Shallow groundwater within PZ-1 and surface water within SB-1 (located in the northeast retention basin) will continue to be sampled due to the contribution of stormwater to the wetland area located immediately north of SB-1. Analytical data from these locations will be correlated with past results and data from shallow groundwater samples.

Sample designations (STM) will be consistent with those used for stormwater samples during the stormwater investigation. Samples related to the Northeast Stormwater Basin will have the designation of 1 while samples related to the Northwest Stormwater Basin will have the designation of 2. Stormwater samples will be collected from a total of six locations as illustrated in **Figure 1** and include:

- Landfill Seep (L-1)
- Northeast Stormwater Retention Basin (STM-SB-1)
- Northwest Stormwater Retention Basin (STM-SB-2)
- Northwest Outfall Pipe (STM-OFP-2)
- Northwest Perimeter Ditch (STM-PD-2)
- Northwest Underdrain Piping (STM-UP-2)

These locations will continue to be sampled for comparison with past and future analytical results. This analytical information will aid in the continued assessment of water quality of the landfill seep at L-1. Samples from L-1 will be collected during conditions where there is minimal or no discharge from the adjacent SB-2 outfall pipe (STM-OFP-2) or when the seep at L-1 is not visibly influenced by other stormwater discharge. These conditions ensure that the samples at L-1 are isolated and representative of the discharge of shallow groundwater to surface water.

The potential exists for some locations (e.g. STM-OFP-2) to be dry during sampling events, based on the absence or presence of water within the stormwater basin; however, these conditions will be noted and reported accordingly.

Surface water locations, as stated above, will continue to be collected during regularly scheduled groundwater monitoring events. Surface water locations SW-5 and SW-103 are locations in closest proximity to the stormwater control system locations in the northwest portion of the landfill and are approximately 75-ft and 300-ft north of L-1, respectively.

3.2.2 Groundwater Sampling

Shallow groundwater samples will be collected from proposed piezometer locations as identified in **Section 3.1** and will also include piezometers previously installed as part of the stormwater investigation. These samples are designed to be representative of groundwater water that is in direct communication with surface water. Results can be compared to co-located surface water sample results to more directly compare surface water results with shallow groundwater analytical results. These locations include PZ-1, PZ-2, PZ-3, PZ-4, PZ-5, PZ-6, PZ-7, PZ-8, PZ-9, PZ-103, and PZ-110.

In addition to groundwater samples collected from piezometers, overburden groundwater samples obtained from monitoring wells sampled during regular biannual sampling events will be used during data evaluation.

3.2.3 Porewater Sampling

In an effort to obtain samples representative of the interaction between shallow groundwater and surface water (Berry's Brook), porewater samples will be completed at up to 9 locations as illustrated on **Figure 3**. These locations have been identified based on the expected groundwater discharge to surface water as determined by surface water elevations and overburden groundwater potentiometric surfaces recorded during semiannual sampling events. These locations are designed to provide information between locations monitored by piezometers (existing and proposed). Porewater sample locations were selected to reduce the number of locations where permanent installations were needed that would require landowner approval. Samples will be collected using a push point sampler with water withdrawn using a syringe or peristaltic pump in accordance with Standard Operating Procedure #16 (SOP-16): *Groundwater/Surface Water Interface Sampling Using A Pore Water Sampler* included as **Attachment B**.

3.2.4 Sampling Schedule

The sampling of locations as outlined in **Section 3.2.1** will be completed in conjunction with the semiannual sampling events completed during the Spring and Fall; however, stormwater locations will be sampled based on the presence of a precipitation event sufficient to generate flow at selected stormwater locations. It is anticipated the sampling event will occur in the Spring 2020 with the installation and development of piezometers occurring prior to the sampling event to allow for the monitoring of water levels prior to spring precipitation. The Spring event will be completed during March and April, based on weather conditions, to coincide with the period of seasonal high groundwater flow and recharge as reported in the *Assessment of Ground-Water Resources in the Seacoast Region of New Hampshire* (Mack, 2009). A second sampling event will occur during Summer 2020 at a subset of piezometer and porewater locations based on results obtained during the Spring sampling event. The Summer sampling will be completed during July to coincide when the effective groundwater recharge in the area could be zero or negative based on precipitation and evapotranspiration rates (Mack, 2009). Additionally, this time period will coincide with base flow conditions within the Brook when there is direct contribution of groundwater to surface water.

3.2.5 Laboratory Analysis

Stormwater, porewater, and shallow groundwater samples (**Figure 1**) will be submitted for analysis of PFAS, 1,4-dioxane, and general landfill parameters (alkalinity, ammonia, nitrate, and iron) as shown on **Table 1**. Analysis of PFAS compounds will include an expanded list of analytes analyzed in previously completed sampling events at the Site. Samples will be submitted to Alpha Analytical of Westborough, Massachusetts (Alpha) following collection and in accordance with sample collection, handling, and chain of custody procedures documented in the project SAP.

3.3 Water Level Measurements

Water level measurements will be recorded from surface water staff gauges, piezometers and select overburden groundwater monitoring wells on a monthly basis to account for seasonal water level fluctuations. Several piezometers will be instrumented with continuously recording water level transducers to assess the rate and duration of influence on shallow groundwater levels following precipitation events and to monitor short term effects of beaver dam removal as discussed in **Section 3.5**. The correlation of this information with historic overburden and bedrock groundwater elevations will allow for a more comprehensive understanding of the interaction between groundwater and surface water.

In addition to providing surface water elevations at previously gauged locations, as detailed in the Stormwater Investigation Report, steel survey pins will be installed and used to monitor surface water elevations in wetland areas east of SW-103, south of GZ-114/GZ-115, east of MW-21S, and east of FPC-6A/6B. These steel pins will allow monitoring of surface water elevations in areas where shallow overburden groundwater is monitored and/or sampled as part of routine groundwater monitoring events. Surface water elevations will also be measured at piezometers installed at current surface water sampling locations (e.g. SW-4, SW-5, etc.) and referenced from the measuring point of the piezometer (top of riser).

3.4 Stage Discharge Rating Curve

The relationship between the depth of water within Berry's Brook and Brook discharge rate will be established through the development of a rating curve. Water depths are recorded during periods of base flow (dry conditions when groundwater is a primary source of water to the stream), periods of peak flow (immediately following precipitation events), and during seasonal periods (spring recharge periods) in conjunction with Brook flow rates measured with stream flow meters and channel configuration.

Stage discharge measurements will be completed using the velocity area method pursuant to USGS protocols. A minimum of 6-8 measurements will be recorded at a range of flow rates to adequately evaluate changes in flow during the monitoring period. It is proposed that these measurements be recorded during a minimum of three separate events at up to three locations along Berry’s Brook located between the headwaters south of Breakfast Hill Road and SW-111. The coordination of these events will coincide with the measurement of water levels detailed in Section 3.3.

3.5 Beaver Dam Removal

The presence of two beaver dams within the survey area (**Figure 3**) has created localized ponded areas north and west of the landfill. These areas had previously been monitored and/or controlled by the railroad due to the flooding conditions that resulted on the railroad bed and subsequent rail trail due to beaver dams. The ponding caused by beaver dams may affect the fate and transport of contaminants in the wetland complex serving as the headwaters to Berry’s Brook due to an altered distribution of contaminants being discharge via both groundwater and stormwater discharges. The removal of these dams will allow for the establishment of more defined surface water drainage conditions within the existing wetland complex and allow for better evaluation of groundwater and surface water interaction. It should be noted that the railroad easement has been purchased from PanAm Railways with plans for conversion to a recreational trail for use by the public. Beaver dam removal will aid in eliminating seasonal flooding observed along the trail. The establishment of more defined surface drainage conditions (hydraulic gradients and flow patterns) will be valuable in the assessment and monitoring of remedial alternatives evaluated/implemented as part of HB494.

3.6 Refined System Modeling

Following the collection and analysis of stormwater, surface water, and shallow groundwater information, additional/refined mass flux calculations will be completed. These efforts will be used to incorporate new information into the current understanding of mass flux within the surface water and shallow groundwater within the wetland complex and Berry’s Brook.

3.7 Remedial Alternatives Evaluation

Following the collection and analysis of data in accordance with this SOW, a list of remedial alternatives will be generated, and an initial qualitative assessment performed. This assessment will include identifying remedial alternatives that can be implemented with the goal of “…substantial reduction of the contaminants entering Berry's Brook from the Coakley Landfill superfund site.” As part of the assessment process, remedial alternatives suitable for bench-scale evaluation will be identified relative to design concepts and treatment effectiveness. This will enable determination of field-sensitive design parameters prior to scaling a design for a Pilot Study or direct field application. The assessment will include, but not be limited to, the evaluation of available “off the shelf” technologies used for the treatment of surface water and stormwater to identify an approach using new or proprietary technologies.

4.0 | REPORTING

Data transmittals, memoranda, and/or brief task-specific reports will be generated during the investigation as part of consultation with USEPA and NHDES regarding interpretations of data and subsequent modifications to investigation scope of work or schedule. Upon completion of the scope of work, a surface water evaluation report will be prepared for review by the Agencies. The report will include a narrative of activities completed, analytical data collected, interpretation of results, associated tables, figures and appendices, and recommendations for future activities, if any.

5.0 | REFERENCES

CES, Inc. (2017), Quality Assurance Project Plan (Revision 1), Coakley Landfill Superfund Site, North Hampton and Greenland, New Hampshire (September 2017). Prepared by CES, Inc. for The Coakley Landfill Group

CES, Inc. (2018), Sampling and Analysis Plan, Coakley Landfill Superfund Site, North Hampton and Greenland, New Hampshire (July 2018). Prepared by CES, Inc. for The Coakley Landfill Group

Golder Associates, Inc. (1996), Final (100%) Design Report, Coakley Landfill, North Hampton, New Hampshire (May 1996). Prepared by Golder Associates, Inc. for The Coakley Landfill Group

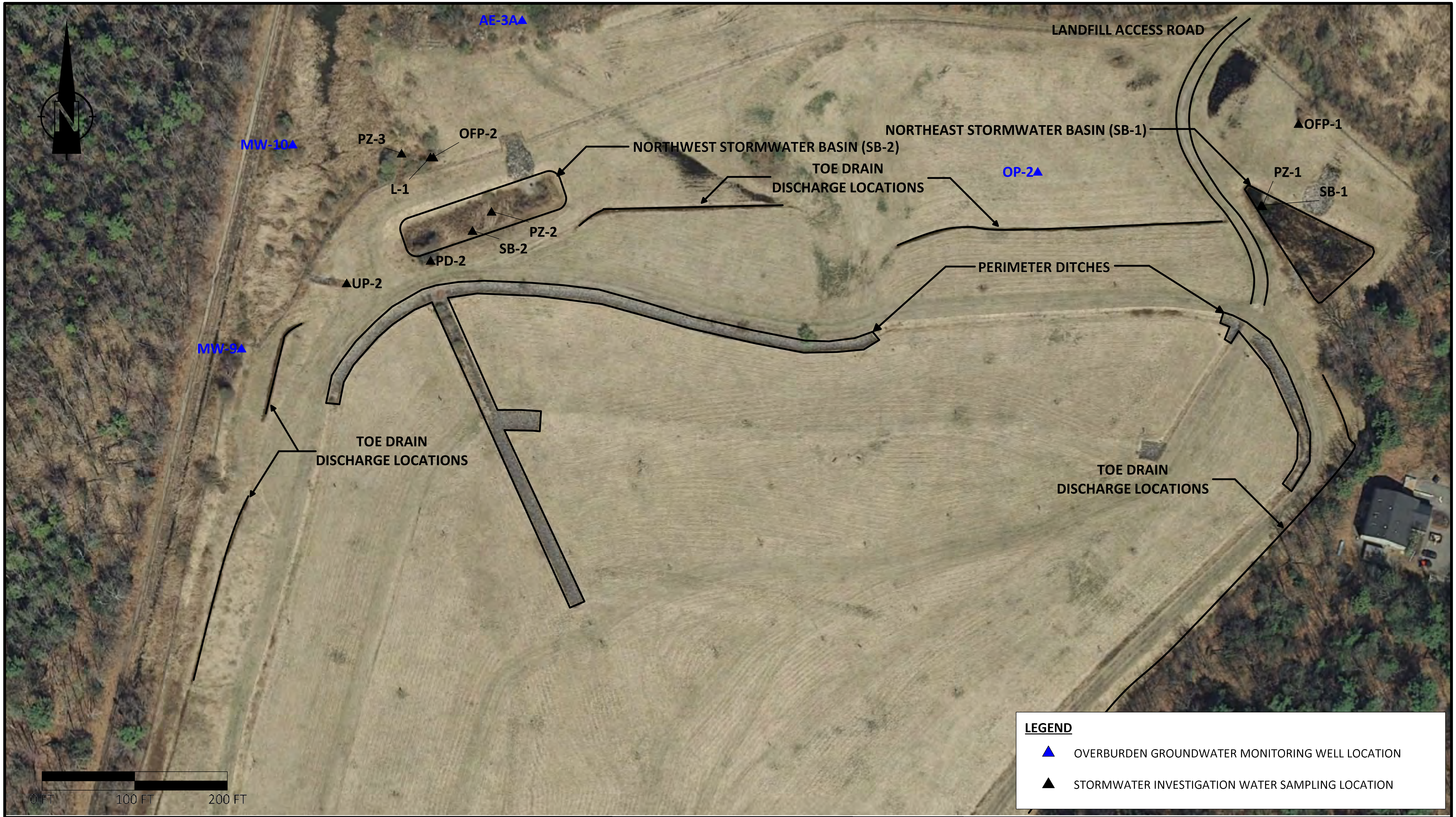
Mack, Thomas J., 2009, *Assessment of Ground-Water Resources in the Seacoast Region of New Hampshire*, United States Geological Survey Scientific Investigations Report 2008-5222

TABLE

TABLE 1
Summary of Proposed Analytical Parameters
Coakley Landfill Superfund Site - North Hampton and Greenland, New Hampshire

SAMPLE LOCATION ID	PFAS	1,4-DIOXANE	GENERAL LANDFILL PARAMETERS
STORMWATER			
L-1	X	X	X
SB-1	X	X	X
SB-2	X	X	X
OFP-2	X	X	X
PD-2	X	X	X
UP-2	X	X	X
PIEZOMETER			
PZ-1	X	X	X
PZ-2	X	X	X
PZ-3	X	X	X
PZ-4	X	X	
PZ-5	X	X	X
PZ-6	X	X	X
PZ-7	X	X	
PZ-8	X	X	X
PZ-9	X	X	
PZ-103	X	X	
PZ-110	X	X	X
POREWATER			
PW-1	X	X	X
PW-2	X	X	
PW-3	X	X	X
PW-4	X	X	
PW-5	X	X	
PW-6	X	X	X
PW-7	X	X	X
PW-8	X	X	
PW-9	X	X	X

FIGURES



PROJECT TITLE:
COAKLEY LANDFILL SUPERFUND SITE
NORTH HAMPTON & GREENLAND, NEW HAMPSHIRE

SHEET TITLE
STORMWATER SAMPLING AND GAUGING LOCATIONS

DWG
FIGURE 1

JN: 10424.020
SCALE AS SHOWN

BY: CFB
DATE 2020-01-20
APPROVED BY MAD
CHECKED BY CFB

REV:
REV DATE
ISSUE
ISSUE DATE

NOTE

EXISTING CONDITIONS BASEMAP FROM PLAN TITLED "AS-BUILT SURVEY OF THE COAKLEY LANDFILL, BREAKFAST HILL ROAD, NORTH HAMPTON, N.H." PREPARED BY RICHARD D. BARTLETT & ASSOCIATES, INC. DATED SEPT. 23, 1998.

COVER MATERIAL SAMPLE IDENTIFICATION NOMENCLATURE IS BASED ON SAMPLE MATERIAL AND LOCATION. STM-STORMWATER, SO-SOIL, SB-STORMWATER BASIN, UP-UNDERDRAIN PIPE, PD-PERIMETER DITCH, OFP-OUTFALL PIPE, TS-TOPSOIL, CM-CONSTRUCTION MATERIAL, DL- DRAINAGE LAYER, (1)-COMPOSITE SAMPLE NUMBER.

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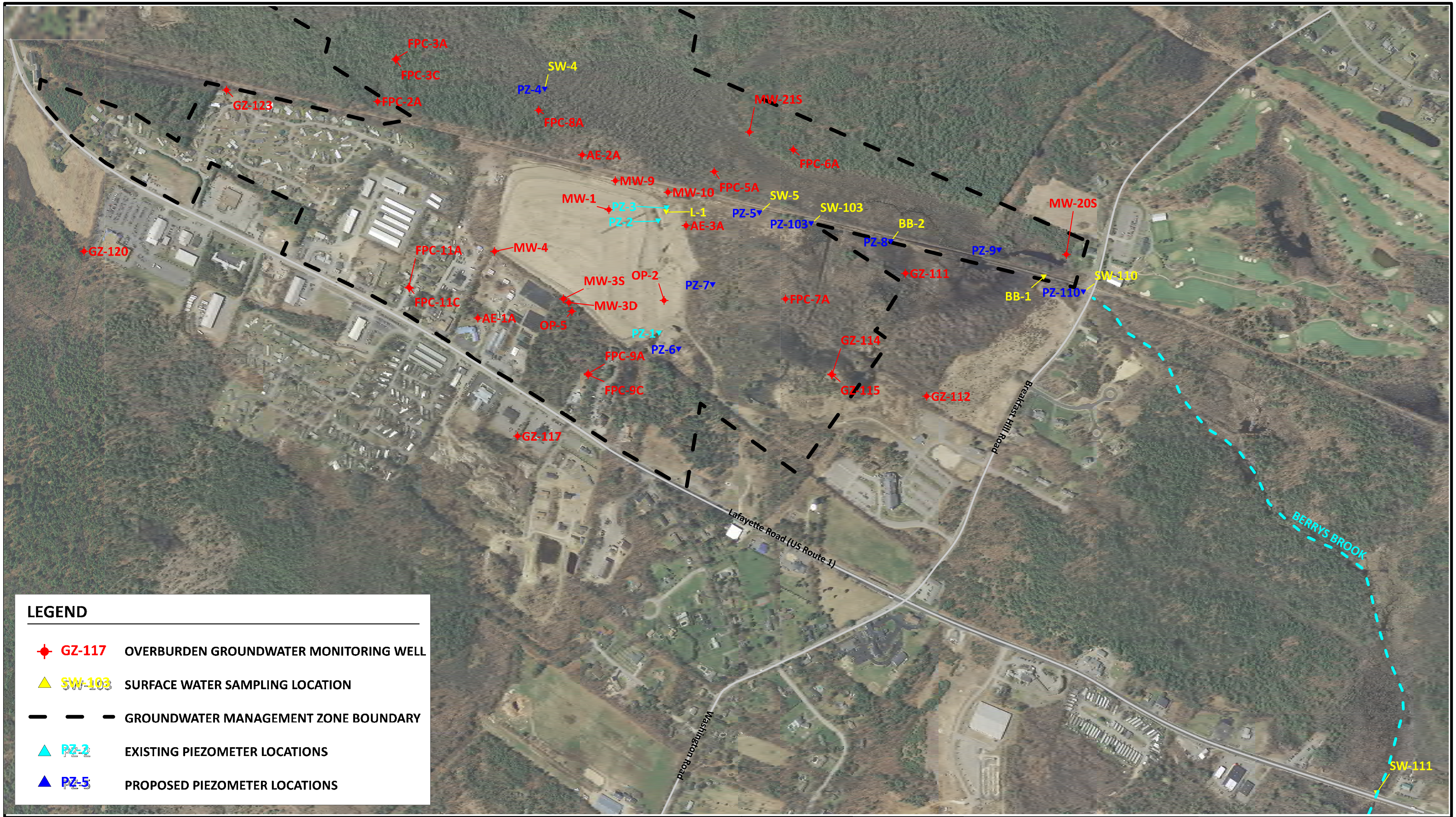

LEGEND

✦	GZ-117	OVERBURDEN GROUNDWATER MONITORING WELL
△	SW-103	SURFACE WATER SAMPLING LOCATION
— — —		GROUNDWATER MANAGEMENT ZONE BOUNDARY
▲	PZ-2	EXISTING PIEZOMETER LOCATIONS
▲	PZ-5	PROPOSED PIEZOMETER LOCATIONS

PROJECT TITLE: **COAKLEY LANDFILL SUPERFUND SITE NORTH HAMPTON & GREENLAND, NEW HAMPSHIRE**	DWG: **FIGURE 2**	BY: KWD	REV:	
		DATE: 2020-01-03	REV DATE:	
SHEET TITLE: **PROPOSED PIEZOMETER LOCATIONS**	JN: 10424.020	APPROVED BY: MAD	ISSUE:	
	SCALE: AS SHOWN	CHECKED BY: CFB	ISSUE DATE:	

NOTE:
1. THIS SITE PLAN IS BASED ON EXISTING SAMPLING LOCATIONS AS PER THE COAKLEY LANDFILL SUPERFUND SITE REVISED SAMPLING AND ANALYSIS PLAN DATED JULY 18, 2018.
2. GMZ BOUNDARY IS BASED UPON "GMZ BOUNDARY PLAN" DATED MAY 9, 2008 INCLUDED IN THE 2008 GMP APPLICATION PREPARED BY HANCOCK ASSOCIATES AND 2013 GMZ EXPANSION AREA ESTABLISHED BY THE 2013 GMP DATED JANUARY 7, 2014.
3. GIS DATA COURTESY OF NEW HAMPSHIRE ONLINE GRANITE DATABASE.
4. MAP IS PROJECTED USING THE NEW HAMPSHIRE STATE PLANE PROJECTION, US FEET AND REFERENCES THE NORTH AMERICAN VERTICAL DATUM OF 1983.

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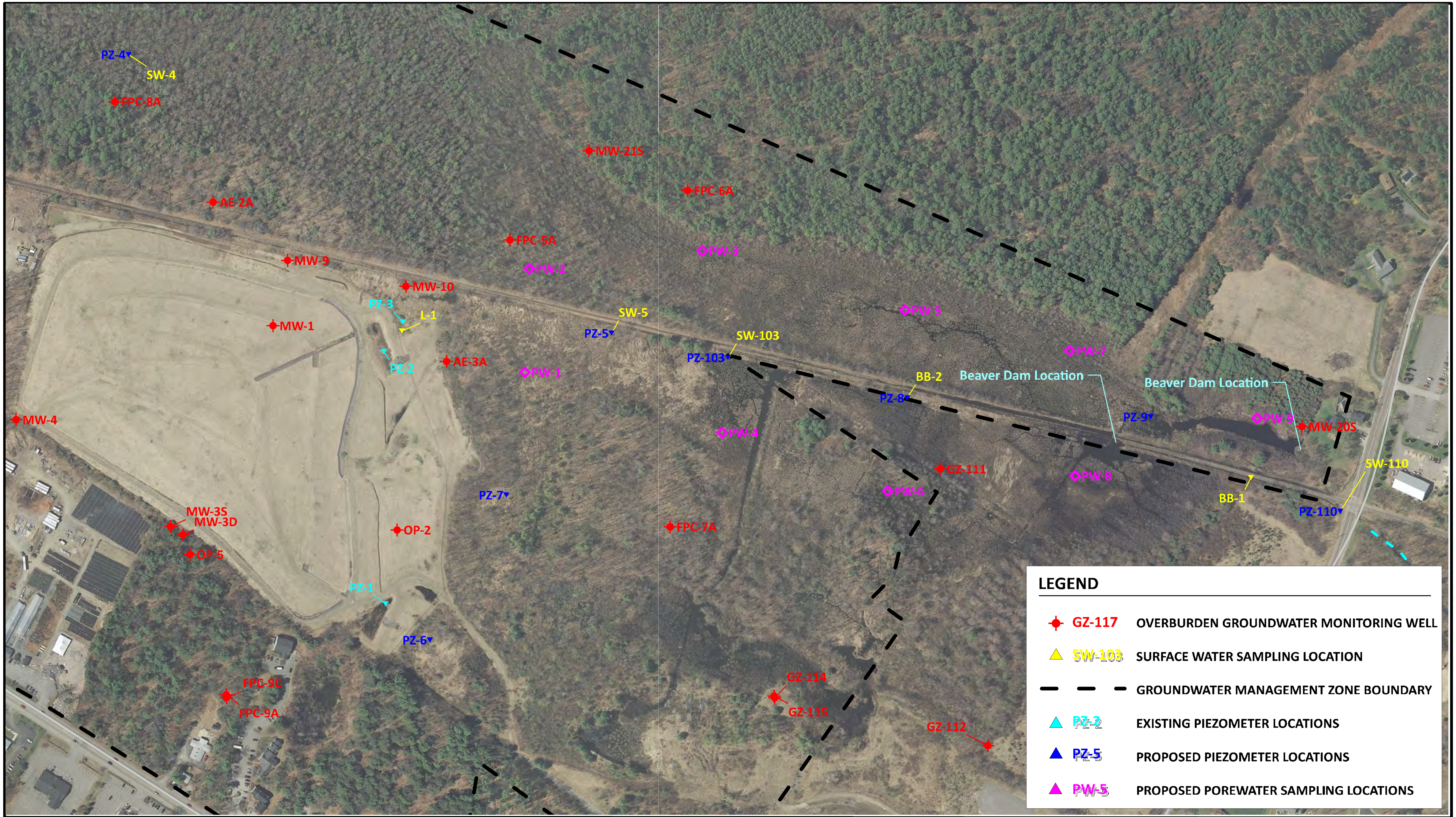

PROJECT TITLE:

COAKLEY LANDFILL SUPERFUND SITE
NORTH HAMPTON & GREENLAND, NEW HAMPSHIRE

SHEET TITLE:

PROPOSED POREWATER SAMPLING LOCATIONS

DWG: FIGURE 3	BY: KWD	REV:	
	DATE: 2020-01-10	REV DATE:	
JN: 10424.020	APPROVED BY: MAD	ISSUE:	
SCALE: AS SHOWN	CHECKED BY: CFB	ISSUE DATE:	

NOTE:

1. THIS SITE PLAN IS BASED ON EXISTING SAMPLING LOCATIONS AS PER THE COAKLEY LANDFILL SUPERFUND SITE REVISED SAMPLING AND ANALYSIS PLAN DATED JULY 18, 2018.
2. GMZ BOUNDARY IS BASED UPON "GMZ BOUNDARY PLAN" DATED MAY 9, 2008 INCLUDED IN THE 2008 GMP APPLICATION PREPARED BY HANCOCK ASSOCIATES AND 2013 GMZ EXPANSION AREA ESTABLISHED BY THE 2013 GMP DATED JANUARY 7, 2014.
3. GIS DATA COURTESY OF NEW HAMPSHIRE ONLINE GRANITE DATABASE.
4. MAP IS PROJECTED USING THE NEW HAMPSHIRE STATE PLANE PROJECTION, US FEET AND REFERENCES THE NORTH AMERICAN VERTICAL DATUM OF 1983.

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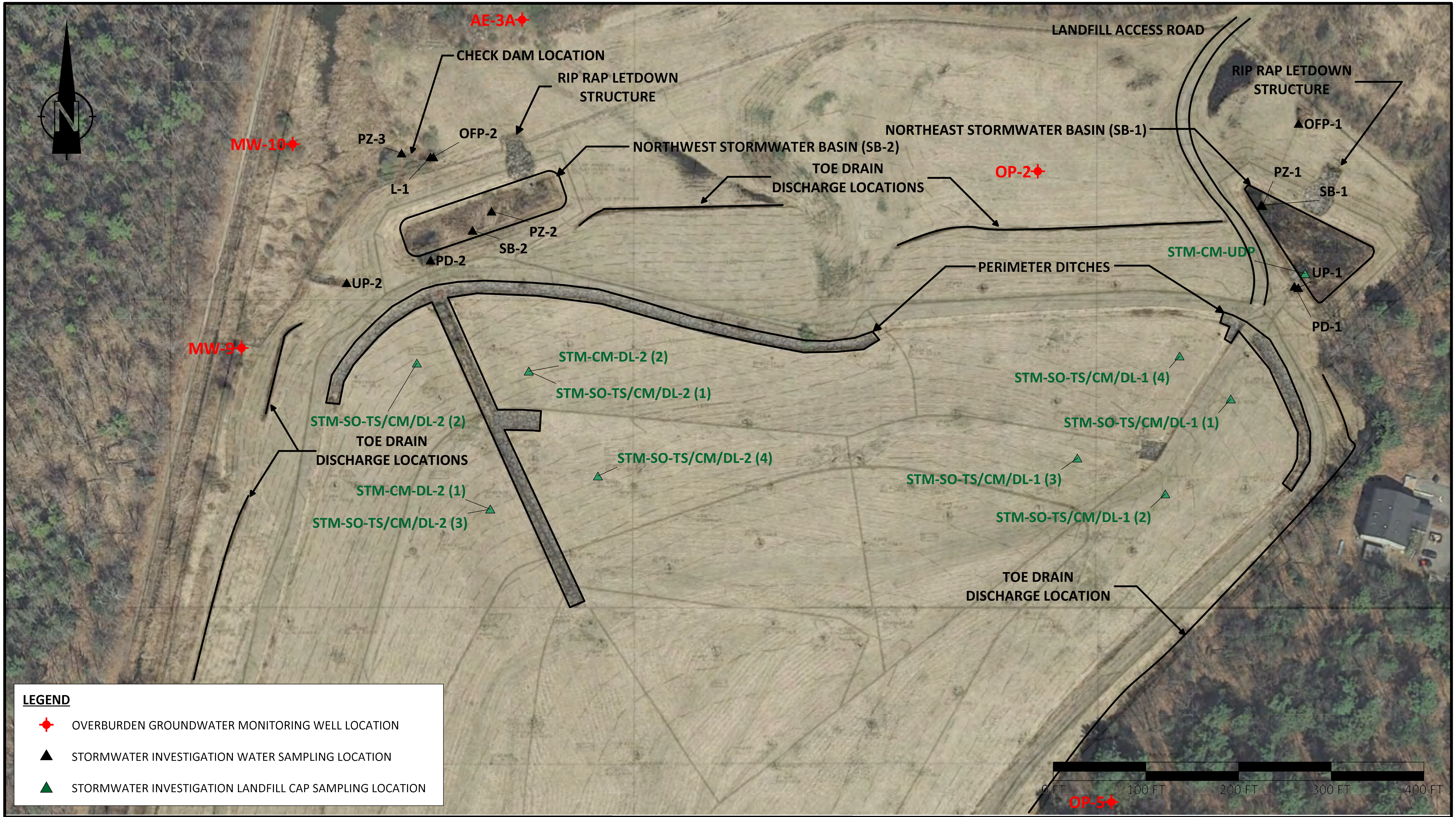
ATTACHMENT A

SELECT REVISED STORMWATER INVESTIGATION REPORT

TABLES, FIGURES, AND SOP



LEGEND

- ✦ OVERBURDEN GROUNDWATER MONITORING WELL LOCATION
- ▲ STORMWATER INVESTIGATION WATER SAMPLING LOCATION
- ▲ STORMWATER INVESTIGATION LANDFILL CAP SAMPLING LOCATION

PROJECT TITLE:
COAKLEY LANDFILL SUPERFUND SITE
NORTH HAMPTON & GREENLAND, NEW HAMPSHIRE

SHEET TITLE
STORMWATER SAMPLING AND GAUGING LOCATIONS

DWG **FIGURE 1**	BY: CFB	REV:		
	DATE 2019-09-24	REV DATE		
JN: 10424.020	APPROVED BY MAD	ISSUE		
SCALE AS SHOWN	CHECKED BY CFB	ISSUE DATE		

NOTE
EXISTING CONDITIONS BASEMAP FROM PLAN TITLED "AS-BUILT SURVEY OF THE COAKLEY LANDFILL, BREAKFAST HILL ROAD, NORTH HAMPTON, N.H." PREPARED BY RICHARD D. BARTLETT & ASSOCIATES, INC. DATED SEPT. 23, 1998.

COVER MATERIAL SAMPLE IDENTIFICATION NOMENCLATURE IS BASED ON SAMPLE MATERIAL AND LOCATION. STM-STORMWATER, SO-SOIL, SB-STORMWATER BASIN, UP-UNDERDRAIN PIPE, PD-PERIMETER DITCH, OFP-OUTFALL PIPE, TS-TOPSOIL, CM-CONSTRUCTION MATERIAL, DL- DRAINAGE LAYER, (1)-COMPOSITE SAMPLE NUMBER.

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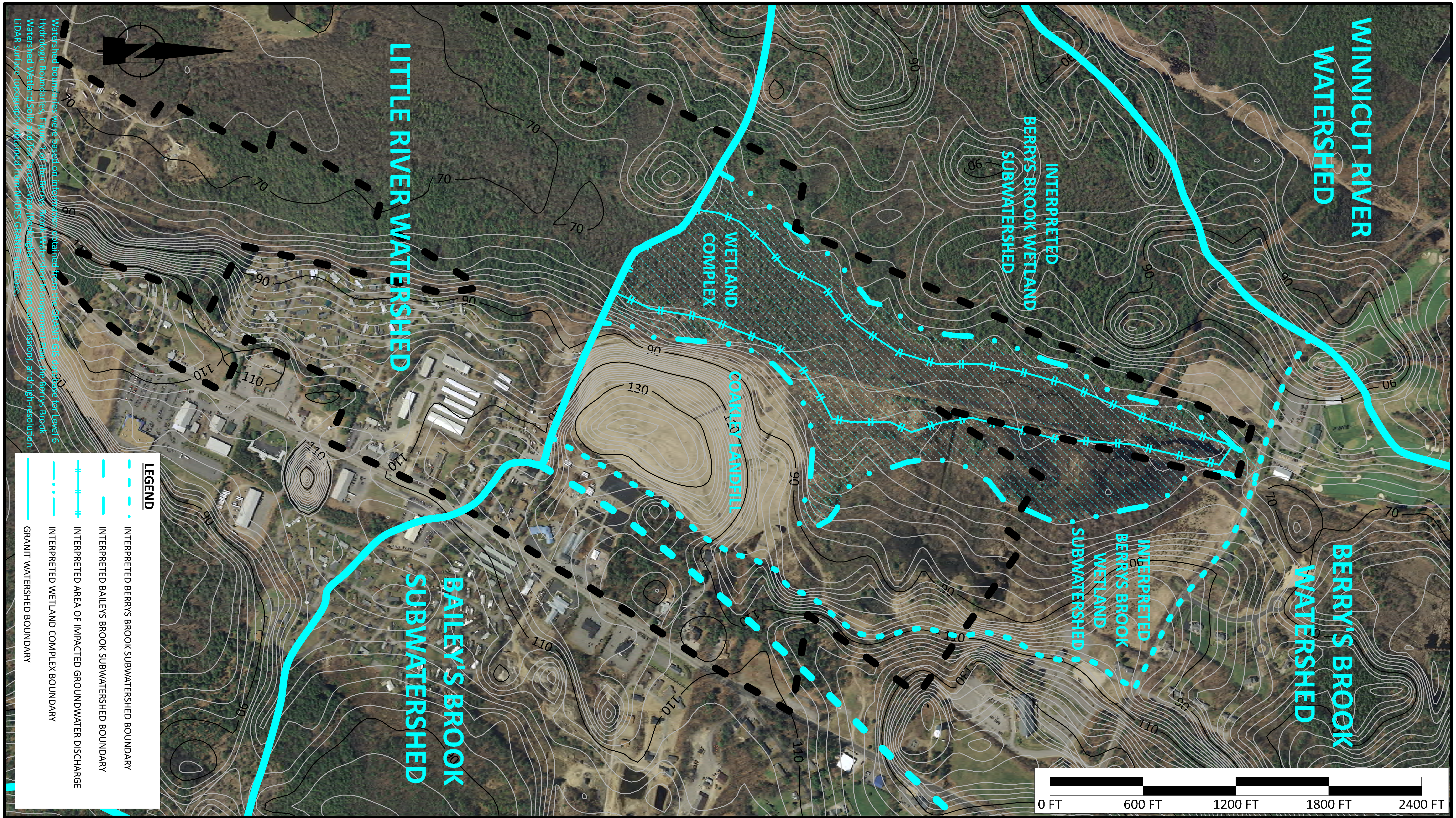

Watershed boundaries were based on information obtained from the GRANIT GIS database for Level 6 Hydrologic Boundaries, Figure 1 of the Berrys Brook Watershed Management Plan, the Berrys Brook Watershed Wetland Soils and Tax Parcels Map (Rockingham Planning Commission), and high-resolution LiDAR surface topography obtained from NHDES GRANIT database.

LEGEND

- INTERPRETED BERRYS BROOK SUBWATERSHED BOUNDARY
- INTERPRETED BAILEY'S BROOK SUBWATERSHED BOUNDARY
- INTERPRETED AREA OF IMPACTED GROUNDWATER DISCHARGE
- INTERPRETED WETLAND COMPLEX BOUNDARY
- GRANIT WATERSHED BOUNDARY

PROJECT TITLE:
COAKLEY LANDFILL SUPERFUND SITE
NORTH HAMPTON & GREENLAND, NEW HAMPSHIRE

SHEET TITLE:
COAKLEY LANDFILL WATERSHED BOUNDARY LOCATIONS

DWG: FIGURE 3
JN: 10424.020
SCALE: AS SHOWN

BY: CFB
DATE: 2020-01-14
APPROVED BY: MAD
CHECKED BY: CFB

REV:
REV DATE:
ISSUE:
ISSUE DATE:

NOTE:
1. GMZ BOUNDARY IS BASED UPON "GMZ BOUNDARY PLAN" DATED MAY 9, 2008 INCLUDED IN THE 2008 GMP APPLICATION PREPARED BY HANCOCK ASSOCIATES AND 2013 GMZ EXPANSION AREA ESTABLISHED BY THE 2013 GMP DATED JANUARY 7, 2014.
2. GIS DATA COURTESY OF NEW HAPSHIRE ONLINE GRANIT DATABASE.
3. MAP IS PROJECTED USING THE NEW HAMPSHIRE STATE PLANE PROJECTION, US FEET AND REFERENCES THE NORTH AMERICAN VERTICAL DATUM OF 1983.

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TABLE 1

Summary of Groundwater and Surface Water Elevation Data
Stormwater Investigation Report
Coakley Landfull Superfund Site
North Hampton and Greenland, New Hampshire

	Easting NH - State Plane NAD 1983 - Feet	Northing NH - State Plane NAD 1983 - Feet	Ref. Pt Elev. (FT. NGVD)	Fall 2018 Water Elev. FT.	Spring 2019 Water Elev. FT.	Comments
Operable Unit 1						
MW-9	1211077.36	183947.41	81.70	76.55	76.33	Top of Riser
MW-10	1211132.54	184167.68	79.10	73.46	73.62	Top of Riser
OP-2	1211936.99	184138.16	99.00	93.35	93.89	Top of Riser
OP-5	1212016.54	183457.15	108.40	93.39	94.29	Top of Riser
Operable Unit 2						
AE-3A	1211380.24	184301.83	85.00	77.18	76.83	Top of Riser
FPC-5A	1210979.69	184509.92	73.80	73.46	71.98	Top of Riser
FPC-6A	1210835.64	185063.10	78.19	72.43	74.33	Top of Riser
FPC-7A	1211925.71	185037.99	87.60	87.27	87.18	Top of Riser
FPC-9A	1212479.83	183576.85	114.10	93.85	94.28	Top of Riser
Stormwater						
PZ-1	1212179.59	184101.08	99.50	95.25	96.41	Top of Riser
PZ-2	1211347.26	184095.08	84.50	82.38	83.04	Top of Riser
PZ-3	1211250.12	184157.76	81.58	NA	78.60	Top of Riser
L-1	1211281.31	184153.70	78.50	77.19	77.94	Top of Staff Gauge
OFP-1	1212218.65	184189.78	93.20	NA	NA	Invert Elevation of Pipe
OFP-2	1211190.95	184018.72	76.90	NA	NA	Invert Elevation of Pipe
PD-1	1212214.11	184013.95	101.80	NA	NA	Invert Elevation of Pipe
PD-2	1211281.47	184042.12	87.10	NA	NA	Invert Elevation of Pipe
UP-1	1212218.32	184012.51	100.30	NA	NA	Invert Elevation of Pipe
UP-2	1211190.93	184017.80	83.20	NA	NA	Invert Elevation of Pipe
SB-1	1212178.05	184101.54	97.70	97.20	96.44	Top of Staff Gauge
SB-2	1211326.74	184074.27	84.00	81.74	80.93	Top of Staff Gauge
Surface Water						
SW-5	1211286.92	184845.04	75.00	74.04	74.20	Top of Staff Gauge
SW-103	1211367.44	185228.27	74.80	73.52	73.71	Top of Staff Gauge
SW-110	1211874.68	187243.98	68.70	67.21	67.15	Top of Staff Gauge
BB-1	1211763.51	186949.74	72.00	71.74	71.56	Top of Steel Pin
BB-2	1211500.44	185818.19	73.50	72.59	72.44	Top of Steel Pin
LRB - Little River	1208971.20	179648.17	68.90	65.32	64.69	Top of Concrtete Headwall

NOTES:
Elevations and locations of reference points were surveyed by TF Moran on 11/16/18 and 3/25/19.

TABLE 2
Landfill Cover Material Analytical Results
Stormwater Investigation Report
Coakley Landfill Superfund Site - North Hampton and Greenland, New Hampshire

SAMPLE IDENTIFICATION	**SOILS**						**CONSTRUCTION MATERIALS**	
	STM-SO-CM-01	**STM-SO-CM-02**	**STM-SO-TS-01**	**STM-SO-TS-02**	**STM-SO-DL-01**	**STM-SO-DL-02**	**STM-CM-DL-01**	**STM-CM-UDP**
MATERIAL TYPE	**Cover Soil**	**Cover Soil**	**Topsoil**	**Topsoil**	**Grading Fill/Sand**	**Grading Fill/Sand**	**Geotextile**	**HDPE Pipe**
DATE SAMPLED	**12/4/2018**	**12/4/2018**	**12/4/2018**	**12/4/2018**	**12/20/2018**	**12/20/2018**	**12/20/2018**	**12/4/2018**
PERFLUORINATED CHEMICALS BY MODIFIED 537 - (mg/kg)								
Perfluorobutanoic Acid (PFBA)	0.000139 U	0.000137 U	0.000416 J	0.000671 J	0.000134 U	0.000138 U	0.000131 U	0.000106 U
Perfluoropentanoic Acid (PFPeA)	0.000200 U	0.000198 U	0.000748 J	0.001090 J	0.000194 U	0.000199 U	0.000189 U	0.000153 U
Perfluorohexanoic Acid (PFHxA)	0.000201 U	0.000199 U	0.000639 J	0.000717 J	0.000194 U	0.000200 U	0.000190 U	0.000154 U
Perfluoroheptanoic Acid (PFHpA)	0.000203 U	0.000200 U	0.000994 J	0.001150 J	0.000196 U	0.000202 U	0.000192 U	0.000156 U
Perfluorohexane Sulfonate (PFHxS)	0.000307 U	0.000303 U	0.000455 J	0.000497 J	0.000297 U	0.000306 U	0.000290 U	0.000235 U
6:2 Fluorotelomer Sulfonic Acid (6:2 FTS)	0.000227 U	0.000224 U	0.000226 U	0.000229 U	0.000219 U	0.000226 U	0.000214 U	0.000174 U
Perfluoroheptane Sulfonic Acid (PFHpS)	0.000168 U	0.000166 U	0.000168 U	0.000170 U	0.000163 U	0.000168 U	0.000159 U	0.000129 U
Perfluorononanoic Acid (PFNA)	0.000579 J	0.001510 J	**0.00332**	**0.00408**	0.000171 U	0.000176 U	0.000313 J	0.000135 U
Perfluorooctane Sulfonamide (PFOSA)	0.000225 U	0.000222 U	**0.00388**	**0.00425**	0.000217 U	0.000390 J	0.000212 U	0.000172 U
Perfluorodecanoic Acid (PFDA)	**0.00275**	**0.00369**	**0.0115**	**0.0137**	0.000245 U	0.000253 U	0.000724 J	0.000194 U
8:2 Fluorotelomer Sulfonate (8:2 FTS)	0.000282 U	0.000279 U	**0.0024**	**0.00297**	0.000273 U	0.000281 U	0.000266 U	0.000216 U
N-Methyl Perfluorooctane Sulfonamidoacetic Acid (MeFOSAA)	0.000299 U	0.000295 U	0.000882 J	0.000739 J	0.000289 U	0.000298 U	0.000282 U	0.000229 U
N-Ethyl Perfluorooctane Sulfonamidoacetic Acid (EtFOSAA)	0.000318 U	0.000314 U	**0.00593**	**0.00682**	0.000308 U	0.000317 U	0.000300 U	0.000244 U
Perfluoroundecanoic Acid (PFUnA)	0.000928 J	0.000979 J	**0.0106**	**0.0107**	0.000339 U	0.000349 U	0.000528 J	0.000269 U
Perfluorodecane Sulfonate (PFDS)	0.000533 J	0.000524 J	**0.00592**	**0.00506**	0.000193 U	0.000198 U	0.000188 U	0.000153 U
Perfluorododecanoic Acid (PFDoA)	0.000314 J	0.000270 U	**0.00543**	**0.00588**	0.000264 U	0.000272 U	0.000315 J	0.000210 U
N-Methyl Perfluorooctane Sulfonamide (MeFOSA)	0.000934 U	0.000922 U	0.000931 U	0.000945 U	0.000903 U	0.000931 U	0.000881 U	0.000716 U
Perfluorotridecanoate (PFTrDA)	0.000121 U	0.000119 U	0.001060 J	0.001210 J	0.000117 U	0.000120 U	0.000114 U	0.0000926 U
Perfluorotetradecanoic Acid (PFTeDA)	0.000196 U	0.000194 U	0.001080 J	0.001000 J	0.000190 U	0.000195 U	0.000185 U	0.000150 U
N-Ethyl Perfluorooctane Sulfonamide (EtFOSA)	0.000133 U	0.001310 U	0.001320 U	0.001340 U	0.001280 U	0.001320 U	0.001250 U	0.001020 U
Perfluorohexadecanoic Acid (PFHxDA)	0.0000346 U	0.0000341 U	0.000148 J	0.000145 J	0.0000334 U	0.0000344 U	0.0000326 U	0.0000265 U
N-Methyl Perfluorooctane Sulfonamidoethanol (MeFOSE)	0.001930 U	0.001910 U	0.006210 J	0.006210 J	0.001870 U	0.001920 U	0.001820 U	0.001480 U
N-Ethyl Perfluorooctane Sulfonamidoethanol (EtFOSE)	0.001000 U	0.000988 U	0.001200 J	0.001040 J	0.000968 U	0.000997 U	0.000944 U	0.000767 U
Perfluorobutane Sulfonic Acid (PFBS)	0.000359 U	0.000355 U	0.000359 U	0.000364 U	0.000348 U	0.000358 U	0.000339 U	0.000276 U
Perfluorooctanoic Acid (PFOA)	0.000497 J	0.000755 J	**0.00365**	**0.00425**	0.000226 U	0.000233 U	0.000386 J	0.000179 U
Perfluorooctane Sulfonate (PFOS)	**0.00648**	**0.012**	**0.0279**	**0.0396**	0.000809 U	0.000834 U	**0.00317**	0.000642 U

NOTES:

1. J = Estimated concentration below the reporting limit.
2. Q = Ion ratio outside of the 70 - 130 % standard ratio.
3. U = Not detected above the reporting limit
4. ND = Not detected
5. STM-SO-CM =- Cover Soil Common Borrow (frost protection) Layer Soil Sample
6. STM-SO-TS - Top Soil (vegetative layer) Sample
7. STM-SO-DL = Grading Fill/Sand Drainage Layer Sample
8. STM-CM-UDP = Construction Material Under Drain Pipe (HDPE) Sample
9. STM-CM-DL = Construction Material Geotextile Fabric over Sand Drainage Layer
10. **Bold** denotes concentrations reported above the applicable reporting limit/Limit of Quantitation

SOP 49	**Revision: 22**	**Supersedes: 21**
PREPARATION AND ANALYSIS FOR THE DETERMINATION OF PER and POLY-FLUORINATED COMPOUNDS		
Analyst Review:		
Chemist Review:		
Management: Martha Maier		
Quality Assurance:		
Effective Date: October 28, 2019		

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Revision No.	Revision Date	Description of Revision
19	03/28/2019	Updated SOP to Newly released QSM 5.2 Updated glossary to include EIS Updated the following sections; 7.4, 10.5, 11.1.5, 11.1.7, 11.2.1.1, 11.2.2, 11.3.5, 11.4, 12.10.3, 12.11.7.1 Added the following sections; 10.2.1, 10.5.3, 11.2.3, 11.7, 12.1.1, 20.4 Revise Table B-15 to reflect changes in new QSM 5.2 Added Notes on Table 5 Reformatted section 12 tables.
20	04/24/2019	Added compounds to Scope table in section 2.1 Added note to section 12.10.1 Updated Tables 1, 2, and 3 with new compounds. Removed Table 4 Updated Appendix A and B
21	05/29/2019	Updated CAS No. for PFNS to the acid version. Corrected PFOA CAS No, typo. Corrected PFecHS CAS No. Updated from QSM 5.2 reference to QSM 5.3. and updated QSM 5.3 table with changes. Updated Table 1, 2, and 3
22	10/28/2019	Added Chemist review to sign-offs page Added section 2.2 Corrected PFDA IPR limit in Table 3 Removed sections 11.1.4 and 11.1.7.2 Revised sections 1.1, 9.3, 11.1.7, 11.1, 11.2.1.1

1. PURPOSE

1.1. This SOP outlines and describes the preparative and analytical techniques used for the determination of per and poly-fluorinated compounds (PFAS) in drinking water, aqueous, solid and tissue matrices.

2. SCOPE

2.1. Data determined to be out-of-control from criteria stated within this SOP, is handled according to procedures addressed within the applicable section.

2.2. For states that allow Drinking Water samples to be processed by Isotope Dilution, this method may be used, per client request. This method is not application for states that require Drinking Water samples to be processed by EPA 537 or 537.1.

Compound	CAS Registry No.*
Perfluorobutanesulfonic acid (PFBS)	375-73-5
Perfluoroheptanoic acid (PFHpA)	375-85-9
Perfluorohexanesulfonic acid (PFHxS)	355-46-4
Perfluorohexanoic acid (PFHxA)	307-24-4
Perfluorooctanesulfonic acid (PFOS)	1763-23-1
Perfluorooctanoic acid (PFOA)	335-67-1
Perfluorobutanoic acid (PFBA)	375-22-4
Perfluoroheptanesulfonic acid (PFHpS)	375-92-8
Perfluorodecane sulfonic acid (PFDS)	335-77-3
Perfluoropentanoic acid (PFPeA)	2706-90-3
Perfluorononanoic acid (PFNA)	375-95-1
Perfluoroundecanoic acid (PFUdA / PFUnA)	2058-94-8
Perfluorodecanoic acid (PFDA)	335-76-2
Perfluorododecanoic acid (PFDoA)	307-55-1
Perfluorotridecanoic acid (PFTrDA)	72629-94-8
Perfluorotetradecanoic acid (PFTeDA)	376-06-7
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5
Perfluorooctadecanoic acid (PFODA)	16517-11-6
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	757124-72-4
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	27619-97-2
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	39108-34-4
N-methylperfluoro-1-octanesulfonamide (N-MeFOSA)	31506-32-8
N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)	4151-50-2
Perfluorooctane sulfonamide (PFOSA)	754-91-6
N-methylperfluoro-1-octanesulfonamido ethanol (N-MeFOSE)	24448-09-7
N-ethylperfluoro-1-octanesulfonamido ethanol (N-EtFOSE)	1691-99-2
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	2355-31-9
Perfluoropentane sulfonic acid (PFPeS)	2706-91-4
Perfluorononane sulfonic acid (PFNS)	68259-12-1

Hexafluoropropylene oxide dimer acid (HFPO-DA)	13252-13-6
4,8-dioxa-3H-perfluorononanoic acid (ADONA)	919005-14-4
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F-53 Minor / 11Cl-PF3OUdS)	763051-92-9
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (F-53 Major / 9Cl-PF3ONS)	756426-58-1
10: 2 Fluorotelomer sulfonic acid (10:2 FTS)	120226-60-0
2H,2H,3H,3H-perfluorohexanoic acid (FPrPA or 3:3 FTCA)	356-02-5
2H,2H,3H,3H-perfluorooctanoic acid (FPePA or 5:3 FTCA)	914637-49-3
2H,2H,3H,3H-perfluorodecanoic acid (FHpPA or 7:3 FTCA)	812-70-4
Sodium perfluoro-1-propanesulfonate (PFPrS)	423-41-6
Pentacosafluorododecane-1-sulfonic acid (PFDoS)	79780-39-5
Potassium perfluoro-4-ethylcyclohexanesulfonate (PFecHS)	646-83-3

*Chemical Abstract Service

3. SUMMARY OF METHOD

3.1. This procedure uses ultra-performance liquid chromatography/tandem mass spectrometry (UPLC/MS/MS) for detection and quantitation of per and poly-fluorinated compounds, commonly referred to as PFAS.

4. CONTAMINATION AND INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All these materials must be demonstrated to be free from interfering substances under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using materials containing PTFE, where possible.

4.2. The use of high purity reagents and solvents helps to minimize interference problems.

4.3. Interferants co-extracted from the sample will vary considerably from matrix to matrix.

5. DEFINITIONS

5.1. Definitions are presented in the Glossary.

6. SAFETY

6.1. Procedures shall be carried out in a manner that protects the health and safety of all Vista employees.

6.2. Each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. All compounds or reagents should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

6.3. Additional health and safety information can be obtained from safety data sheets (SDS) available to all personnel involved in these analyses.

6.4. In the event of a known or potential compromise to the health and safety of a Vista associate, all work must stop, and the incident reported immediately to management.

6.5. Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood

6.6. The toxicity or carcinogenicity of each chemical used in this method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of SDS should also be made available to all personnel involved in these analyses.

7. APPARATUS AND MATERIALS

Note: All materials used should be suitable for LC work, and comparable brand materials can be substituted where specific brands are mentioned.

7.1. Analytical Balances, capable of reading to 0.01g and 0.0001g
7.2. Solid Phase Extraction Manifold
7.3. [redacted]
7.4. ENVI-Carb cartridges, or equivalent
7.5. Silicone tubing, 1/16" diameter, various lengths
7.6. Screw top polypropylene LC vials, 12x32mm
7.7. Screw top high recovery glass LC vials, 12x32mm
7.8. HDPE Bottle various sizes
7.9. Screw caps with pre-slit polypropylene septa, for 12x32mm vials
7.10. Disposable polypropylene Pasteur pipets, various sizes
7.11. Chlorine test strips
7.12. Organomation 24-Station N-Evaporator with water bath capable of heating to 65°C
7.13. Polypropylene centrifuge tubes, 13 mm x 100 mm
7.14. Wiretrol II Precision Disposable Micropipettes
7.15. Sonicator, VWR, Model 150T
7.16. Thermo Scientific Sorvall ST16 Centrifuge
7.17. Eppendorf Centrifuge Model 5804;
7.18. Eppendorf Centrifuge Model 5702
7.19. [redacted]
7.20. Acquity PFC Isolator Column
7.21. Acquity Ultra Performance LC
7.22. Computer work station(s) with MassLynx, Analyst and MultiQuant Software
7.23. Quattro Premier XE with Micromass Technology
7.24. Shimadzu Nexera X2 UHPLC LC System
7.25. 4000 Q Trap (Sciex)
7.26. AB SCIEX API 4000 Triple Quadrupole Mass Spectrometer
7.27. Waters Mass Spectrometer (TQS-m) MS/MS

8. REAGENTS, SOLVENTS AND STANDARDS

8.1. Reagents (HPLC grade or above)

8.1.1. Trizma pre-set crystals
8.1.2. Sodium Acetate, HPLC grade
8.1.3. Ammonium Acetate, HPLC grade
8.1.4. Ammonium Hydroxide, Concentrated
8.1.5. Formic Acid, Concentrated
8.1.6. Ultra-pure nitrogen gas
8.1.7. Ultra-pure argon gas
8.1.8. [redacted]
8.1.9. See SOP 15 for information about Reagents preparation

8.2. Solvents (HPLC Grade or above)

8.2.1. Reagent Water
8.2.2. Acetonitrile (ACN)
8.2.3. Hexane (for cleaning)
8.2.4. Methanol (MeOH)
8.2.5. Methylene chloride (DCM)
8.2.6. Acetone
8.2.7. Isopropyl Alcohol (IPA)

8.3. Standards

8.3.1. All analytical standards are obtained from an approved vendor.
8.3.2. See SOP 15 and Standards section in LIMS for information about Standards preparation.

9. COLLECTION, PRESERVATION, AND HANDLING

9.1. HDPE or polypropylene bottles and jars should be used for collection.
9.2. Trizma may be added to the sample bottles prior to the collection of chlorinated drinking water samples in the amount of 5.0g/L.
9.3. Drinking Water and Aqueous samples should be extracted within 14 days of collection and analyzed within 28 days of extraction.
9.4. Sample temperature should be ≤ 10°C when samples are received at the laboratory.
9.5. Solid and Tissue samples should be extracted within 60 days from collection and analyzed within 30 days of extraction. No hold times have been established for tissue samples.
9.6. All samples are stored at < 6°C.

10. QUALITY CONTROL

10.1. Each time a modification is made to this method and the detection limit will be affected by the change, the laboratory is required to demonstrate that the MDL is lower than one-third the regulatory compliance level or one-third the method reporting limit (MRL) in the method, whichever is higher.

10.2. Instrument Blank (DoD only): Instrument blank is analyzed immediately following the highest standard analyzed and daily prior to sample analysis.

10.2.1. Instrument Blank must contain the extracted Internal Standard Analytes (EIS) to enable quantitation of contamination.

10.2.2. Concentration of each analyte must be ≤ ½ the LOQ.

10.2.3. If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met.

10.3. Method Blank (MB): Method blank is a matrix preparation that is free of native analyte that has been prepared and analyzed using the same procedures followed for the rest of the analytical batch. Simulate as close as possible the matrix to be extracted.

10.3.1. Daily or with each extraction batch of up to 20 samples, (whichever is more frequent).

10.3.2. For the determination of native PFAS, the levels measured in the method blank of all method analytes must be below 1/2 the LOQ or less than 1/10th the amount measured in any sample or 1/10th the regulatory limit whichever is greater.

10.3.3. If amount found is greater than the minimum level or one-third the regulatory compliance limit, whichever is greater; or if any potentially interfering compound is found in the blank at or above the minimum level for each congener, the batch shall be re-extracted and reanalyzed. If there is no sample remining, the data must be qualified appropriately.

10.4. Ongoing Precision and Recovery Samples (OPR): An ongoing precision and recovery sample is prepared by adding a known quantity of native standards to an interferant free matrix and used to assess method performance (precision and recovery).

10.4.1. Add the appropriate amount of native spike. The native spikes contain the compounds listed in Table 1.

10.4.2. Native spike includes quantitative standards for PFOS, PFHxS, MeFOSAA and EtFOSAA containing both the linear and branched isomers.

10.4.3. An OPR is analyzed with every analytical batch.

10.4.4. The OPR % recoveries for native and internal standards should be within the limits shown in Table 3, except when the native recovery is high and the analyte is Non-Detect (ND) in the sample.

10.4.5. If the percent recovery of the native or, two or more of the internal standards of an isomer in the OPR is out of method limits, it is recommended that the sample(s) be re-extracted and/or re-analyzed.

10.5. Matrix Spike and Matrix Spike Duplicate (MS/MSD): A matrix spike sample, and its duplicate, are prepared by adding the appropriate quantity of native standards to a sample matrix prior to extraction. MS/MSD's are performed by client request. For DoD projects, MS and MSD samples are required per preparatory batch, unless project QAPP states otherwise.

10.5.1. The relative percent difference (RPD) between MS/MSD samples should be ≤ 50% for non-DoD projects, and ≤ 30% for DoD projects.

10.5.2. If RPD does not meet the acceptance criteria, the data are evaluated and qualified appropriately.

10.5.3. For DoD projects, MS/MSD recovery limits can be found in Table 3.

10.6. Duplicate Samples: Duplicate samples are two separate aliquots taken from the same source.

10.6.1. Duplicate samples are analyzed independently to assess laboratory precision. Duplicate samples are performed by client request and on all samples prepared by serial dilution.

10.6.1.1. Serial dilution is used when sample is known to be or expected to be significantly outside the calibration range.

10.6.1.2. MB and OPR are required per batch of ≤20 samples.

10.6.1.3. MS/MSD are not required.

10.6.1.4. For DoD projects, a post spike sample is required for aqueous samples that have a reported analyte value of "< LOQ."

10.6.1.4.1. For a Post Spike sample, the sample must be spiked at the LOQ level. The spike recovery must be between 70-130%.

10.6.2. The relative percent difference between duplicate samples should be ≤30%.

10.6.3. If the concentration is within a factor of 2 of the MRL, the relative percentage difference (RPD) must be ≤ 50%.

10.6.4. If the RPD does not meet the acceptance criteria, the data are evaluated and qualified appropriately.

10.7. Field Reagent Blank (FRB): A field reagent blank is a matrix preparation that is free of native analyte, transported to the field in sealed containers and returned with the samples. FRBs are opened in the field and transferred into another clean sample collection container. FRB's are performed upon client request.

10.8. Trip Blank: a trip blank is a matrix preparation that is free of native analyte transported to the field in sealed containers and returned with the samples. A trip blank is not opened in the field.

10.9. Initial Calibration Verification (ICV): Analytes from a different source than that of the calibration standards. This is prepared and analyzed in the same way as a CCC.

10.9.1. This is analyzed with every calibration curve.

10.9.2. The calculated value for the ICV must be within ±30% of the expected true value.

11. EXTRACTION PROCEDURES

11.1. Aqueous Samples (Including Drinking Water matrix)

11.1.1. Test pH and chlorine of each sample using pH and Chlorine strips.

11.1.1.1. If chlorine test is positive, add [redacted] to appropriate amount using [redacted]

11.1.2. For the method blank (MB) and OPR(s), transfer [redacted] or appropriate volume of reagent water into a bottle for each.

11.1.2.1. For MDL, LOQ/LOD, and IPRs [redacted] should be used.

11.1.3. Record the combined weight of the bottle, cap and sample for each sample to be extracted. After the sample has been removed from the bottle, allow it to drain overnight and reweigh it and the cap to determine the amount of sample extracted. For AQ samples 1g=1mL.

11.1.4. Add the appropriate volume of Internal Standard (IS) and Internal Supplement Standard (IS-SUP) solutions when appropriate. Add the appropriate volume of Native Standard (NS) solutions to OPR and/or MS/MSD.

11.1.5. Allow the spiked samples to equilibrate for at least 30 minutes before extraction.

11.1.6. Aqueous samples with visible particulate should be spiked with the appropriate volume of IS, IS-SUP, and NS and allowed to equilibrate for [redacted] minutes. Samples are then centrifuged for [redacted] in a refrigerated centrifuge. Decant sample back into the original container when complete.

11.1.6.1. Rinse sides of centrifuge tube with a small amount of methanol, vortex, and re-centrifuge. Decant methanol into original sample.

11.1.6.2. The MB and OPR(s) need to be centrifuged if any client sample is centrifuged.

NOTE: Centrifuging may be repeated if necessary.

11.2. **Solid/Tissue Samples**

11.2.1. Digestion

11.2.1.1. Weigh out approximately [redacted] of homogenized solid or well ground fish/tissue into a polypropylene test tube. (1g may be used for samples with known high concentration).

NOTE: project specific requirements for fish/tissue samples preparation should be followed.

11.2.1.2. Add [redacted]

11.2.1.3. Add the appropriate volume of Internal Standard (IS) solution and Supplement Standard (IS-Sup) solution (when appropriate) to all samples. Add the appropriate volume of Native Standard (NS) solution to OPR and/or MS/MSD.

11.2.1.4. Vortex

11.2.1.5. Sonicate

11.2.1.6. Incubate at ambient temperature.

11.2.2. Extraction

11.2.2.1. Add [redacted] vortex well so that sample homogenizes with solution.

11.2.2.2. Shake for [redacted] and centrifuge [redacted]

11.2.2.3. Decant [redacted]

11.2.2.4. Repeat the extraction process (11.2.2.1 – 11.2.2.3).

11.2.3. Neutralization

11.2.3.1. Add [redacted] of 1M Hydrochloric Acid.

11.2.3.2. [redacted]

11.3. SPE Extraction

11.3.1. Assemble the SPE apparatus and attach the SPE cartridges as shown in the Appendix A, Figure 1.

11.3.2. Condition the cartridges by eluting with [redacted] methanol. Discard eluant.

11.3.3. Condition the cartridge with [redacted] Discard eluant.

11.3.4. Load sample onto cartridge by way of siphon, maintain a flow rate

11.3.5. Upon completion of siphon wash cartridge with [redacted]

11.3.6. Dry the cartridge under vacuum

11.4. Cartridge Elution

11.4.1. If sample **does not** require ENVI-Carb, proceed by rinsing bottle with [redacted] of [redacted] Use these rinses to elute cartridge by gravity. Collect extracts eluted from the column into clean test tube containing the appropriate amount of RS.

11.4.1.1. Glass test tube for "B" analytes or polypropylene test tube for "A" analytes.

11.4.2. If sample **does** require ENVI-Carb clean up, elute as stated above (11.4.1) into polypropylene test tubes without the addition of RS. Proceed to 11.5.

11.5. ENVI-Carb Clean-up (on all DoD and tissue samples or when appropriate)

11.5.1. Condition cartridge with [redacted] of MeOH. Discard.

11.5.2. Load Sample.

11.5.3. Collect elution from the column into clean test tube containing the appropriate amount of RS.

11.5.3.1. Glass test tube for "B" analytes or polypropylene test tube for "A" analytes.

11.5.4. Rinse original test tube with [redacted] of methanol and load onto ENVI-Carb cartridge after all the sample has passed through. Collect elution.

11.6. Adjustment to Final Volume

11.6.1. Concentrate extract to [redacted]

11.6.2. Reconstitute to a Final Volume of [redacted]

11.6.3. [redacted]

11.7. Serial Dilution

11.7.1. **AFFF samples are prepared using serial dilution, each field sample must be prepared in duplicate (DoD Requirement).**

11.7.2. Determine what dilutions are needed.

11.7.3. For the method blank (MB) and OPR(s), transfer 1mL HPLC water into a conical glass vial.

11.7.4. Weigh out approximately 1g of sample and transfer to HDPE bottle. Dilute appropriately with HPLC water.

11.7.4.1. A Matrix Duplicate (MD) is required for each sample prepared by serial dilution.

11.7.5. After all dilutions are made transfer 1mL of each dilution into a separate conical glass vial.

11.7.6. Add the appropriate volume of Internal Standard (IS) and Internal Supplement Standard (IS-SUP) solutions when appropriate. Add the appropriate volume of Native Standard (NS) solutions to OPR.

11.7.7. Cap and Vortex.

11.7.8. Transfer samples into clean autoinjector vials.

12. LC/MS ANALYSIS

12.1. Full mass calibration is performed initially prior to use and after performing major maintenance, or at least annually.

12.1.1. The mass scale of the MS is calibrated with the compounds and procedures described by the manufacturer.

12.1.2. Mass calibration is verified after each mass calibration, prior to initial calibration.

12.2. All compounds are tuned during the set-up of the method. When masses fall outside of the ±0.5 amu of the true value, the compound must be re-tuned.

12.3. A minimum of 10 spectra scans are acquired across each chromatographic peak for all analytes, internal standards and recovery standards.

12.4. Establish the necessary conditions. The LC conditions may be optimized for compound separation and sensitivity. Once optimized, the same LC conditions must be used for the analysis of all standards, blanks, OPR aliquots, and samples. The following LC operating conditions are guidance and adjustments may be required.

12.5. Instrument: Aquity UPLC/ Waters Quattro Premier XE

Column: [redacted]
Ionization: [redacted]
Acquisition: MRM mode, unit resolution
Injection Volume: 5-15µL

<table>
<tr><th colspan="2"><i>General LC Conditions</i></th></tr>
<tr><td>[redacted]</td><td>[redacted]</td></tr>
<tr><td>[redacted]</td><td>[redacted]</td></tr>
<tr><td>[redacted]</td><td>[redacted]</td></tr>
<tr><th colspan="2"><i>MS Conditions</i></th></tr>
<tr><td>[redacted]</td><td>[redacted]</td></tr>
<tr><td>[redacted]</td><td>[redacted]</td></tr>
<tr><td>[redacted]</td><td>[redacted]</td></tr>
</table>

LC Gradient Program				
Time (min)	**Flow Mixture***		**LC Flow Rate (mL/min)**	**Gradient**
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

- [redacted]
- [redacted]
- [redacted]

12.6. Instrument: Shimadzu DGU-20Asr/Sciex 4000 Q trap

Column: [redacted]
Ionization: [redacted]
Acquisition: MRM mode, unit resolution
Injection Volume: 1-10 µL

General LC Conditions	
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]
MS Conditions	
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]
MS Conditions	
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]

LC Gradient Program				
Time (min)	**Flow Mixture***		**LC Flow Rate (mL/min)**	**Events**
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

- [redacted]
- [redacted]
- [redacted]

12.7. Instrument: Aquity UPLC/ Waters TQS-Micro

Column: [redacted]
Ionization: [redacted]
Acquisition: MRM mode, unit resolution
Injection Volume: 1-10 µL

General LC Conditions	
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]
MS Conditions	
[redacted]	[redacted]
[redacted]	[redacted]
[redacted]	[redacted]

LC Gradient Program Modified				
Time (min)	**Flow Mixture***		**Flow Rate (mL/min)**	**Gradient**
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

- [redacted]
- [redacted]
- [redacted]
- [redacted]

12.8. Initial Calibration (ICAL)

12.8.1. An initial calibration curve is created using either a linear or second order quadratic regression over the calibration range and consists of a minimum of 5 calibration points for linear and 6 for quadradic. An initial calibration is repeated at least annually, whenever a new set of spiking calibration standards is created or whenever the continuing calibration falls outside the acceptance criteria.

12.8.1.1. Establish the operating conditions suggested in Section 12.5 or 12.7

12.8.2. The retention time for 13C4-PFOS must be greater than 4 minutes.

12.8.3. The coefficient of determination for all native compounds must be ≥ to 0.99.

12.8.4. RSD area requirements are ≤20% for all internal standards

12.8.5. The following analyte recovery criteria must be met: each calibration point for each analyte must calculate to be with 70-130% of the assigned concentration.

12.8.6. The S/N Ratio must be ≥ 10:1 for all ions used for quantification. The S/N ratio for the confirmation ion for PFOA and PFOS must be ≥ 3:1. (See Table 5 for DoD ICAL)

12.9. Continuing Calibration

12.9.1. A continuing calibration verification (CCV) must be analyzed at the beginning, after every 10 field samples and at the end of each analytical run. For DoD projects, an instrument sensitivity check (ISC) must be ran as the beginning CCV at the LOQ level, and all subsequent CCVs should be at a midlevel concentration. Additionally, an ISC must be run every 12 hours.

12.9.2. The CCV is acceptable if the following criteria are met:

12.9.2.1. The LC peak representing each native ion used for quantification and each labeled compound must be present with a S/N ≥10.

12.9.2.2. The percent recovery for native standards and the internal standards must be within the limits shown in Table 3.

12.9.2.3. If the CCV fails because the calculated concentration is greater than 130% for a particular method analyte, and Field Sample extracts show no detection for that method analyte, non-detects may be reported without re-analysis.

12.10. Qualitative Determination

12.10.1. For samples, the signal to noise ratio (S/N) at the LC peak maximum for each native compound must be ≥ 10:1 for each quantification ion and ≥ 3:1 for confirmation ions detected in a sample extract.

NOTE: When DoD requirements are not necessary and a quantitative ion is present without a qualitative ion, exceptions can be made per analyst discretion for the following compounds: PFOSA, PFHxDA, and PFTrDA. These compounds are known to have a weak qualitative ion response and have been observed to consistently have the largest ion ratios of the monitored compounds.

12.10.2. The retention time (RT) of the peak for a native compound must be within 0.4 min of the predicted retention time established through the CCV or midpoint of the ICAL on days when a calibration is ran.

12.10.3. The quantitative/qualitative ion ratio shall be monitored and documented for all analytes except PFBA, PFPeA, PFODA, N-ETFOSE and N-MeFOSE. The ratios are compared to a midpoint continuing calibration verification or the midpoint of initial calibration if there is a calibration curve for that day. All analytes must be within ±50% of the parent/product ratio. Quantitation ions and confirmation ion peaks must be within ±2 seconds. Compounds that do not meet the criteria are flagged and reported.

12.11. Quantitative Determination

12.11.1. Calibration by Isotope Dilution: Isotope dilution calibration is used for the native PFAS for which labeled compounds are available. If an isotope is available and not used, the reason must be technically justified. For those compounds that an isotope is not available, internal standard calibration is used.

12.11.2. Native compounds should have a retention time within 0.1 mins. of its equivalent extracted internal standard.

12.11.3. Recovery of each extracted internal standard versus the injection internal standard should be within the limits shown in Table 3.

12.11.4. If injection internal standard recoveries are acceptable for QC samples, but not field samples, the field samples may be re-prepared and re-analyzed (greater dilution may be needed). If recoveries are unacceptable for QC samples, correct problem and reanalyze all associated failed field samples.

12.11.4.1. For DoD QSM 5.1 samples and associated QC, the injected internal standard peak areas must be within -50% to +50% of the area measured in the ICAL midpoint standard. On days when ICAL is not performed, the peak areas must be within -50% to +50% of the peak area measured in daily beginning CCV.

12.11.4.2. For DoD QSM 5.3 samples and associated QC, the extracted internal standard peak areas must be within -50% to +50% of the area measured in the ICAL midpoint standard. On days when ICAL is not performed, the peak areas must be within -50% to +50% of the peak area measured in daily beginning CCV.

12.11.5. Recoveries below the limits may be accepted if the signal to noise is >10:1. If the signal to noise is not >10:1, samples must be re-extracted and re-analyzed, or the data must be qualified.

12.11.6. If the concentration of any of the analytes exceeds the concentration of the highest calibration point, a dilution of the extract must be analyzed.

12.11.6.1. Dilutions are made at various dilution factors to bring a sample within the calibrated range of the instrument. Dilutions are made to match the composition of the extract at final volume.

12.11.7. PFHxS, PFOA, PFOS, N-MeFOSAA and N-EtFOSAA have native standards for linear and branched isomers. All chromatographic peaks for these compounds are integrated and the areas totaled. Technical mixtures are referenced during method development for retention times.

13. CALCULATIONS

13.1. The concentrations of native compounds are determined by quadratic regression:

$$\mathrm{NRR} = \frac{A_x}{A_y} Q_y$$

Where:

NRR = Normalized relative response

A_x = Area of the quantitation ion for the native compound in sample

A_y = Area of the quantitation ion for the labeled compound in sample

Q_y = Quantity of Internal Standard in sample

13.1.1. Determine the calibration equation for each compound by regressing the NRR against the native compound concentration (See Appendix B).

13.1.2. The curve may be concentration weighted based on the analyst's discretion.

13.2. Internal standard recoveries are calculated by using the formula:

$$\%\mathrm{REC} = \frac{(A_{IS})(Q_{RS}) \mathrm{X}\ 100}{(A_{rs})(Q_{IS})(RRF_{IS})}$$

Where:

A_{IS} = Area of the quantitation ion for the internal standard.

A_{RS} = Area of the quantitation ion for the recovery standard.

Q_{IS} = Quantity of the internal standard.

Q_{RS} = Quantity of the recovery standard.

RRF_{IS} = Calculated relative response factor for the internal std. analyte.

13.3. RRF for labeled analytes (RRF_{IS}):

$$RF_{IS} = \frac{(A_{IS})(Q_{RS})}{(Q_{IS})(A_{RS})}$$

Where:

A_{IS} = Area of the quantitation ion for the labeled standards
A_{RS} = Area of the quantitation ions for the labeled recovery standards
Q_{IS} = Quantity of internal standard injected (pg)
Q_{RS} = Quantity of recovery standard injected (pg)

14. POLLUTION PREVENTION

14.1. The solvent evaporation techniques used in this method are amenable to solvent recovery, and the laboratory shall recover solvents wherever feasible.

14.2. Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standard.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. Safety officer should be contacted if additional information is required.

15.2. The laboratory waste management is in compliance with all federal, state, and local regulations to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations

16. METHOD PERFORMANCE

16.1. This SOP is based on methods noted as references (Section 20).

17. EQUIPMENT/INSTRUMENT MAINTENANCE

17.1. Equipment/Instrument maintenance is performed in accordance with SOP 10 “Instrument Maintenance Logbooks and Schedule”.

17.2. Records of maintenance are kept in instrument logbooks.

18. COMPUTER HARDWARE AND SOFTWARE

18.1. MassLynx

18.2. Analyst 1.6.2

19. TROUBLESHOOTING

Troubleshooting is performed in accordance with Instrument Manuals:

19.1. ACQUITY UPLC system maintenance (Waters)
19.2. Waters Micromass Quattro Premier XE Mass Spectrometer Operator's guide
19.3. MassLynx 4.1 Manual and Documents
19.4. SHIMADZU LC-30AD Instruction Manual
19.5. SHIMADZU System Guide
19.6. SHIMADZU CTO-20A, 20AC Instruction Manual
19.7. SHIMADZU DGU-20A3R, 20A5R Instruction Manual
19.8. Line adjustment Transformer Instruction Manual
19.9. Thermo Scientific manual for centrifuge
19.10. Eppendorf operating manual for centrifuge
19.11. AB SCIEX API 4000 Triple Quadrupole Mass Spectrometer (Q-3) 2017
19.12. Waters Acquity Mass Spectrometer (TQTMS) MS/MS Q-4 2017

20. REFERENCES

20.1. ISO 25101:2009 – Water Quality – Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanonate (PFOA) – Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry, 1st edition, Dated March 2009.
20.2. EPA 821-R-11-007- Draft Procedure for Analysis of Perfluorinated Carboxylic Acids and Sulfonic Acids in Sewage Sludge and Biosolids by HPLC/MS/MS, Draft, December 2011.
20.3. EPA method 537 1.0, Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Version 1.0, November 2018.
20.4. QSM 5.1 - DoD Quality Systems Manual for Environmental Laboratories, Version 5.1, 2016
20.5. QSM 5.3 - DoD Quality Systems Manual for Environmental Laboratories, Version 5.3, 2019

Table 1
Calibration Curve Concentration (pg/µL)

Compound	CS (-2)	CS (-1)	CS0	CS1	CS2	CS3	CS4	CS5	CS6	CS7
PFBS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFHpA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFHxS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFHxA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFOS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFOA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFBA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFHpS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFDS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFPeA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFDA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFNA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFUdA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFDoA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFTrDA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFTeDA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFHxDA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFODA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
4:2 FTS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
6:2 FTS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
8:2 FTS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
N-MeFOSA	1.25	2.5	5.0	10	25	50	250	500	1250	2500
N-EtFOSA	1.25	2.5	5.0	10	25	50	250	500	1250	2500
PFOSA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
N-MeFOSE	1.25	2.5	5.0	10	25	50	250	500	1250	2500
N-EtFOSE	1.25	2.5	5.0	10	25	50	250	500	1250	2500
N-EtFOSAA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
N-MeFOSAA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFPeS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFNS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
HFPO-DA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
ADONA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
11Cl-PF3OUdS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500

Table 1 Continued
Calibration Curve Concentration (pg/µL)

Compound	CS (-2)	CS (-1)	CS0	CS1	CS2	CS3	CS4	CS5	CS6	CS7
9Cl-PF3ONS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
10:2 FTS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
FPrPA or 3:3 FTCA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
FPePA or 5:3 FTCA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
FHpPA or 7:3 FTCA	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFPrS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFDoS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500
PFecHS	0.25	0.5	1.0	2.0	5.0	10	50	100	250	500

Table 1 Continued
Calibration Curve Concentration (pg/μL)

Internal Standard	CS-2	CS-1	CS0	CS1	CS2	CS3	CS4	CS5	CS6	CS7
13C3-PFBA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C3-PFPeA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C3-PFBS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-PFHxA	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
13C2-PFDA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C4-PFHpA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C3-PFHxS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-6:2 FTS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-PFOA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C8-PFOS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C5-PFNA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-8:2 FTS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C8-PFOSA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-PFUdA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-PFDoA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
d3-N-MeFOSA	150	150	150	150	150	150	150	150	150	150
d7-N-MeFOSE	150	150	150	150	150	150	150	150	150	150
d9-N-EtFOSE	150	150	150	150	150	150	150	150	150	150
d5-N-EtFOSA	150	150	150	150	150	150	150	150	150	150
13C2-PFTeDA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-PFHxDA	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
d5-N-EtFOSAA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
d3-N-MeFOSAA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C3-HFPO-DA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5

Table 1 Continued
Calibration Curve Concentration (pg/μL)

Recovery Standard	CS-2	CS-1	CS0	CS1	CS2	CS3	CS4	CS5	CS6	CS7
13C6-PFDA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C4-PFBA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-4:2FTS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C5-PFHxA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
18O2-PFHxS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C8-PFOA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C4-PFOS	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C9-PFNA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C7-PFUdA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
13C2-FOUEA	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5

Table 2

Exact Masses Monitored Waters XEVO-TQSmicro

Compound	Native Parent-Daughter	Internal Standard	IS Parent-Daughter
PFBS	299 – 80	$^{13}C_3$-PFBS	302 – 99
	299 – 99		
PFHpA	363 – 319	$^{13}C_4$-PFHpA	367 – 322
	363 – 169		
PFHxS	399 – 80	$^{13}C_3$-PFHxS	402 - 80
	399 – 99		
PFHxA	313 – 269	$^{13}C_2$-PFHxA	315 – 269
	313 – 119		
PFOS	499 – 80	$^{13}C_8$-PFOS	507 – 80
	499 – 99		
PFOA	413 – 369	$^{13}C_2$-PFOA	415 – 370
	413 – 169		
PFBA	213 – 169	$^{13}C_3$-PFBA	216 – 179
PFHpS	449 – 99	$^{13}C_2$-PFOA	415 – 370
	449 – 80		
PFDS	599 – 99	$^{13}C_8$-PFOS	565 – 520
	599 – 80		
PFPeA	263 – 219	$^{13}C_3$-PFPeA	266 – 229
PFDA	513 – 469	$^{13}C_2$-PFDA	515 – 470
	513 – 219		
PFNA	463 – 419	$^{13}C_5$-PFNA	468 – 423
	463 – 219		
PFUdA	563 – 519	$^{13}C_2$-PFUdA	565 – 520
	563 – 269		
PFDoA	613 – 319	$^{13}C_2$-PFDoA	615 – 570
	613 – 569		
PFTrDA	663 – 619	$^{13}C_2$-PFDoA	615 – 570
	663 – 319	$^{13}C_2$-PFTeDA	715 – 670
PFTeDA	713 – 669	$^{13}C_2$-PFTeDA	715 – 670
	713 – 369		
PFHxDA	813 – 769	$^{13}C_2$-PFHxDA	815 – 770
	813 – 219		
PFODA	913 – 869	$^{13}C_2$-PFHxDA	815 – 770
6:2 FTS	427 – 407	$^{13}C_2$-6:2 FTS	429 – 409
	427 – 80		
8:2 FTS	527 – 507	$^{13}C_2$-8:2 FTS	529 – 509
	527 – 80		
N-MeFOSA	512 – 169	d_3-N-MeFOSA	515 – 169
	512 – 219		

Compound	Native Parent-Daughter	Internal Standard	IS Parent-Daughter
N-EtFOSA	526 – 169 526 – 219	d$_5$-N-EtFOSA	531 – 169
PFOSA	498 – 79 498 – 478	^{13}C$_8$-PFOSA	506 – 78
N-MeFOSE	616 – 59	d$_7$-N-MeFOSE	623 – 59
N-EtFOSE	630 – 59	d$_9$-N-EtFOSE	639 – 59
N-EtFOSAA	584 – 419 584 – 483	d$_5$-N-EtFOSAA	589 – 419
N-MeFOSAA	570 – 419 570 – 483	d$_3$-N-MeFOSAA	573 – 419
4:2 FTS	327.2 – 307.2 327.2 – 81.1	^{13}C$_2$-4:2FTS	329 – 309
PFPeS	349.1 – 80.0 349.1 – 99.0	^{13}C$_3$-PFBS	302 – 99
PFNS	549.1 – 80.1 549.1 – 99.1	^{13}C$_8$-PFOS	507 – 80
HFPO-DA	328.8 – 169 328.8 – 285	^{13}C$_3$-HFPO-DA	332.2 – 287
ADONA	376.8 – 250.9 376.8 – 85.0	^{13}C$_4$-PFHpA	367 – 322
11Cl-PF3OUdS	632.6 – 452.7 632.6 – 450.7	^{13}C$_2$-PFDoA	615 – 570
9Cl-PF3ONS	530.7 – 350.8 530.7 – 82.8	^{13}C$_8$-PFOS	507 – 80
PFPrS	248.9 – 79.9 248.9 – 98.9	^{13}C$_3$-PFBS	302 – 99
PFecHS	460.8 – 381.0 460.8 – 98.9	^{13}C$_2$-PFOA	415 – 370
10:2 FTS	627-606.9 627-80.9	^{13}C$_2$-PFDoA	615 – 570
FPrPA or 3:3 FTCA	240.9-176.9 240.9-116.9	^{13}C$_3$-PFPeA	266 – 229
FPePA or 5:3 FTCA	340.9-236.9 340.9-216.9	^{13}C$_4$-PFHpA	367 – 322
FHpPA or 7:3 FTCA	340.9-236.9 340.9-216.9	^{13}C$_5$-PFNA	468 – 423
PFDoS	698.8-79.9 698.8-98.9	^{13}C$_2$-PFTeDA	715 – 670
Recovery Standard			
^{13}C$_6$-PFDA	519 – 474	NA	NA
^{13}C$_2$-FOUEA	459 – 394	NA	NA
^{13}C$_4$-PFBA	217 – 179	NA	NA
^{13}C$_8$-PFOA	421 – 376	NA	NA

Compound	Native Parent-Daughter	Internal Standard	IS Parent-Daughter
$^{13}C_5$-PFHxA	318 – 273	NA	NA
$^{18}O_2$-PFHxS	403 – 103	NA	NA
$^{13}C_4$-PFOS	503 – 80	NA	NA
$^{13}C_9$-PFNA	472 – 427	NA	NA
$^{13}C_7$-PFUdA	570 – 525	NA	NA

Table 3
QSM 5.3 Acceptance Criteria for Performance Tests

Compound	CCV	IPR		OPR % MS/MSD %	Sample /OPR/IPR Labeled compound recovery in samples % QSM 5.3	Sample /OPR/IPR Labeled compound recovery in samples %
		RSD %	Ave %			
PFBA	70-130	20	70-130	73-129(1) 71-135(2) 70-130(4)	NA	NA
PFPeA	70-130	20	70-130	72-129(1) 69-132(2) 70-130(4)	NA	NA
PFBS	70-130	20	70-130	72-130(1) 72-128(2) 70-130(4)	NA	NA
PFHxA	70-130	20	70-130	72-129(1) 70-132(2) 70-130(4)	NA	NA
PFHpA	70-130	20	70-130	72-130(1) 71-131(2) 70-130(4)	NA	NA
PFHxS	70-130	20	70-130	68-131(1) 67-130(2) 70-130(4)	NA	NA
6:2 FTS	70-130	20	60-130	64-140(1) 64-140(2) 60-130(4)	NA	NA
PFOA	70-130	20	70-130	71-133(1) 69-133(2) 70-130(4)	NA	NA

Compound	CCV	IPR		OPR % MS/MSD %	Sample /OPR/IPR Labeled compound recovery in samples % QSM 5.3	Sample /OPR/IPR Labeled compound recovery in samples %
		RSD %	Ave %			
PFHpS	70-130	20	60-130	69-134(1) 70-132(2) 60-130(4)	NA	NA
PFOS	70-130	20	70-130	65-140(1) 68-136(2) 70-130(4)	NA	NA
PFNA	70-130	20	70-130	69-130(1) 72-129(2) 70-130(4)	NA	NA
PFDA	70-130	20	70-130	71-129(1) 69-133(2) 70-130(4)	NA	NA
8:2 FTS	70-130	20	60-130	67-138(1) 65-137(2) 60-130(4)	NA	NA
PFOSA	70-130	20	70-130	67-137(1) 67-137(2) 70-130(4)	NA	NA
PFDS	70-130	20	60-130	53-142(1) 59-134(2) 60-130(4)	NA	NA
PFUdA	70-130	20	70-130	69-133(1) 64-136(2) 70-130(4)	NA	NA

Compound	CCV	IPR		OPR % MS/MSD %	Sample /OPR/IPR Labeled compound recovery in samples % QSM 5.3	Sample /OPR/IPR Labeled compound recovery in samples %
		RSD %	Ave %			
PFDoA	70-130	20	70-130	72-134(1) 69-135(2) 70-130(4)	NA	NA
N-MeFOSA	70-130	20	70-130	68-141(1) 70-130(3) (4)	NA	NA
N-MeFOSE	70-130	20	70-130	70-130(3) (4)	NA	NA
PFTrDA	70-130	20	60-130	65-144(1) 66-139(2) 60-130(4)	NA	NA
N-EtFOSA	70-130	20	70-130	70-130(3) (4)	NA	NA
N-EtFOSE	70-130	20	70-130	70-130(3) (4)	NA	NA
PFTeDA	70-130	20	70-130	71-132(1) 69-133(2) 70-130(4)	NA	NA
PFHxDA	70-130	20	70-130	70-130(3) (4)	NA	NA
PFODA	70-130	20	40-130	40-130(3) (4)	NA	NA
N-EtFOSAA	70-130	20	70-130	61-135(1) 61-139(2) 70-130(4)	NA	NA
N-MeFOSAA	70-130	20	70-130	65-136(1) 63-144(2) 70-130(4)	NA	NA

Compound	CCV	IPR		OPR % MS/MSD %	Sample /OPR/IPR Labeled compound recovery in samples % QSM 5.3	Sample /OPR/IPR Labeled compound recovery in samples %
		RSD %	Ave %			
4:2 FTS	70-130	20	60-130	63-143(1) 62-145(2) 60-130(4)	NA	NA
PFPeS	70-130	20	70-130	71-127(1) 73-123(2) 70-130(4)	NA	NA
PFNS	70-130	20	70-130	69-127(1) 69-125(2) 70-130(4)	NA	NA
HFPO-DA	70-130	20	70-130	70-130(3) (4)	NA	NA
ADONA	70-130	20	70-130	70-130(3) (4)	NA	NA
11Cl-PF3OUdS	70-130	20	70-130	70-130(3) (4)	NA	NA
9Cl-PF3ONS	70-130	20	70-130	70-130(3) (4)	NA	NA
PFPrS	70-130	20	60-130	60-130(3) (4)	NA	NA
PFecHS	70-130	20	60-130	60-130(3) (4)	NA	NA
10:2 FTS	70-130	20	60-130	60-130(3) (4)	NA	NA
FPrPA or 3:3 FTCA	70-130	20	60-130	60-130(3) (4)	NA	NA
FPePA or 5:3 FTCA	70-130	20	60-130	60-130(3) (4)	NA	NA
FHpPA or 7:3 FTCA	70-130	20	60-130	60-130(3) (4)	NA	NA
PFDoS	70-130	20	60-130	60-130(3) (4)	NA	NA
Internal Standards					**QSM 5.3**	
$^{13}C_3$-PFBA	50-150	20	NA	NA	50-150	60 – 130

Compound	CCV	IPR		OPR % MS/MSD %	Sample /OPR/IPR Labeled compound recovery in samples % QSM 5.3	Sample /OPR/IPR Labeled compound recovery in samples %
		RSD %	Ave %			
$^{13}C_3$-PFPeA	50-150	20	NA	NA	50-150	60 – 150
$^{13}C_3$-PFBS	50-150	20	NA	NA	50-150	60 – 150
13C2-4:2FTS	50-150	20	NA	NA	50-150	40 – 150
$^{13}C_2$-PFHxA	50-150	20	NA	NA	50-150	70 – 130
$^{13}C_4$-PFHpA	50-150	20	NA	NA	50-150	60 – 150
$^{13}C_3$-PFHxS	50-150	20	NA	NA	50-150	60 – 130
$^{13}C_2$-6:2 FTS	50-150	20	NA	NA	50-150	40 – 150
$^{13}C_2$-PFOA	50-150	20	NA	NA	50-150	60 – 130
$^{13}C_8$-PFOS	50-150	20	NA	NA	50-150	60 – 130
$^{13}C_5$-PFNA	50-150	20	NA	NA	50-150	50 – 130
$^{13}C_2$-PFDA	50-150	20	NA	NA	50-150	60 – 130
$^{13}C_2$-8:2 FTS	50-150	20	NA	NA	50-150	40 – 150
$^{13}C_8$-PFOSA	50-150	20	NA	NA	50-150	20 – 150
$^{13}C_2$-PFUdA	50-150	20	NA	NA	50-150	60 – 130
$^{13}C_2$-PFDoA	50-150	20	NA	NA	50-150	30 – 130
$^{13}C_3$-HFPO-DA	50-150	20	NA	NA	50-150	60 – 150
d_3-N-MeFOSA	50-150	20	NA	NA	50-150	10 – 130
d_7-N-MeFOSE	50-150	20	NA	NA	50-150	10 – 150
d_9-N-EtFOSE	50-150	20	NA	NA	50-150	10 – 150
d_5-N-EtFOSA	50-150	20	NA	NA	50-150	10 – 150
$^{13}C_2$-PFTeDA	50-150	20	NA	NA	50-150	20 – 150

Compound	CCV	IPR		OPR % MS/MSD %	Sample /OPR/IPR Labeled compound recovery in samples % QSM 5.3	Sample /OPR/IPR Labeled compound recovery in samples %
		RSD %	Ave %			
$^{13}C_2$-PFHxDA	50-150	20	NA	NA	50-150	20 – 150
d_5-N-EtFOSAA	50-150	20	NA	NA	50-150	50 – 150
d_3-N-MeFOSAA	50-150	20	NA	NA	50-150	50 – 150

(1) DoD QSM 5.3; Aqueous Matrix

(2) DoD QSM 5.3; Solid Matrix

(3) All Matrices

(4) DoD QSM 5.1 limits, Non-DoD Limits (unless otherwise specified by client.)

Note Regarding Table 5:

As per client request, requirements from table B-15 from DoD QSM 5.1 may be applied. See below for a brief summary of the most impactful changes from QSM 5.1 to QSM 5.3. For any further specific request, see DoD QSM 5.1.

	EIS Recovery	**IIS Areas**	**LCS/LCSD Native Recovery Limits**	**Sample PFAS Indetification**
QSM 5.1	Processed by referencing each labeled EIS to an assigned IIS. Recovery limits for all EIS compounds are 50-150%.	50-150% recovery of all samples and CCVs.	70-130% for all compounds.	S/N ≥3:1 for both quantitation and confirmation ions.
QSM 5.3	Processed by referencing total peak area of each EIS to its corresponding total peak area in the midpoint of the ICAL or the first CCV on days when an ICAL is not run. Recovery limits for all EIS compounds are 50-150%.	No IIS requirements.	Specific to each compound; see Table 3 above.	S/N ≥10:1 for quantitation ion, S/N ≥3:1 for confirmation ion..

Table 5

5.3 QSM DoD Client Requirements Only

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Aqueous Sample Preparation Section 11.1	Each sample and associated batch QC samples.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g. Aqueous Film Forming Foam (AFFF) formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE	NA.	NA.	Samples with >1% solids may require centrifuge prior to SPE extraction. Pre-screening of separate aliquots or aqueous samples is recommended.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Soil Sample Preparation Section 11.2	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	NA.	NA.	NA.
Biota Sample Preparation Section 11.2	Each sample and associated batch QC samples.	Sample prepared as defined by the project (e.g. whole fish versus filleted fish).	NA.	NA.	NA.
AFFF and AFFF mixture samples, preparation Section 11.7	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate) Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	NA.	NA.	Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Sample Cleanup Procedure Section 11.3 (SPE Extraction) Section 11.5 (ENVI-Carb Cleanup)	Each sample and associated batch QC samples. Not applicable to AFFF formulation samples.	ENVI-Carb™ or equivalent must be used on each sample and batch QC sample	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix interferences.
Mass Calibration Section 12	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to initial calibration (ICAL),	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 amu of the true value by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer instructions on corrective maintenance.	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an as-needed basis (e.g. QC failures, ion masses fall outside of ±0.5 amu of the true value, major instrument maintenance is performed, or the instrument in moved).

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Mass Spectral Acquisition Rate Section 12.0	Each analyte, Extracted Internal Standard (EIS) Analyte.	A minimum of 10 spectra scans are acquired across each chromatographic peak.	NA.	Flagging is not appropriate.	NA.
Calibration, Calibration Verification, and Spiking Standards Section 12.9	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes.	NA.	Flagging is not appropriate.	Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for quantitative analysis.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
(Continued) **Calibration, Calibration Verification, and Spiking Standards** Section 12.9		For PFAS that do not have a quantitative branched or linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e. accounting for peaks that are identified as linear and branched isomers) and relying on the initial calibration that uses the linear isomer quantitative standard.			

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Sample PFAS identification Section 12.11	All Analytes detected in a sample.	The chemical derivation of the ion transition must be documented. A minimum of two ion transitions (Precursor →quant ion and precursor → confirmation ion) and the ion transition ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50-150%	NA.	PFAS identified, within ion ratios that fail acceptance criteria, must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as "estimated, biased high."	For example: Ion Ratio = (quant ion abundance/ confirm ion abundance) Calculate the average ratio (A) and standard deviation (SD) using the ICAL standards. An acceptance range of ratio could be within A± 3SD for confirmation of detection.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
(Continued…) **Sample PFAS identification**		Signal to Noise Ratio (S/N) must be ≥10 for all ion ratios used for quantification and must be ≥3 for all ions used for confirmation Quant ion and confirmation ion must be present and must maximize simultaneously (±2 seconds).			

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Ion Transitions (Precursor → Product)	Every field samples, standard, blank, and QC sample.	In order to avoid biasing results high due to known interferences for some transitions, the following transitions must be used for the quantification of the following analytes: PFOA: 413 ⟶ 369 PFOS: 499 ⟶ 80 PFHxS: 399 ⟶ 80 PFBS: 299 ⟶ 80 4:2 FTS: 327 ⟶ 307 *(continued next page)*	NA.	Flagging is not appropriate.	NA.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Ion Transitions (Parent-> Product) *(Continued)*		6:2 FTS: 427 —› 407 8:2 FTS: 527 —› 507 NEtFOSAA: 584 —› 419 NMeFOSAA: 570 —› 419 If these transitions are not used, the reason must be technically justified and documented (e.g., alternate transition was used due to observed interferences).			

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL) Section 12.8	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	The isotopically labeled analog of an analyte (Extracted Internal Standard Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts, are acceptable, providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number. If a labeled analog is not commercially available, the Extracted Internal Standard Analyte with the closest retention time or chemical stability to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70-130% of their true value for each calibration standard	Correct problem, then repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ICAL has passed. External Calibration is not allowed for any analyte. Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
(Continued…) **Initial Calibration (ICAL)** Section 12.8		ICAL must meet one of the two options below: Option 1: The RSD of the RFs for all analytes must by ≤20% Option 2: Linear or non-linear calibrations must have $r^2 \geq 0.99$ for each analyte.			
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and EIS.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Retention Time (RT) window width	Every field sample, standard, blank, and QC sample.	RT of each analyte and EIS analyte must fall with 0.4 minutes of the predicted retention times from the daily calibration verification of on days when ICAL is performed, from the midpoint standard of the ICAL.	Correct problem and reanalyze samples.	NA.	Calculate for each analyte and EIS.
Instrument Sensitivity Check (ISC)	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration Verification (ICV) Section 10.9	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true value.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV) Section 12.9 Table 1	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Instrument Sensitivity Check (ISC) can serve as a bracketing CCV.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Instrument Blanks Section 10.2	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument Blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (> ½ LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left.	No samples shall be analyzed until instrument blank has met acceptance criteria. Note: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it is used only to document a higher concentration at which carry over still does not occur.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Extracted Internal Standard (EIS) Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container, prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. Extracted Internal Standard Analyte recoveries must be within 50% to150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may by re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner.	Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, if the EIS is fortified at excessive concentrations.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Method Blank (MB) Section 10.3	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, re-extract and reanalyze MB and all QC samples and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid MB. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS) Section 10.4	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. (Table C-44 & C-45) If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-extract and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix Spike (MS) Section 10.5	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. (Table C-44 & C-45) If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD) Section 10.5	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample ≥ LOQ. The MD is a second aliquot of the field sample that has been prepared by serial dilution.

Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Post Spike Sample Section 10.6.1.4.	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of <LOQ for analyte(s).	Spike all analytes reported as <LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample as <LOQ. When analyte concentrations are calculated as <LOQ, the post spike for that analyte must recover within 70-130%of its true value.	When analyte concentrations are calculated as <LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.	Flagging is not appropriate.	When analyte concentrations are calculated as <LOQ, results may not be reported without acceptable post spike recoveries.

Glossary

Analyte – Compound of interest. The analytes are listed in Table 1.

Calibration Standard – A solution prepared from a stock solution and used to calibrate the response of the HPLC/MSMS.

Calibration Verification Standard (CCC) – Calibration Standard containing a known concentration of native analytes, internal standard and recovery standards. This is analyzed to verify the accuracy of the existing calibration for those analytes.

Extracted Internal Standard Analyte (EIS) – Isotopically labeled analogs of analytes of interest added to all standards, blanks and samples analyzed. Added to samples and batch QC samples prior to the first step of sample extraction and to standards and instrument blanks prior to analysis. Used for isotope dilution methods.

Field Reagent Blank – A field reagent blank is a matrix preparation that is free of native analyte transported to the field in sealed containers and returned with the samples

Internal Standard – A labeled compound used as a reference for quantitation of other labeled and native compounds.

IPR – Initial precision and recovery; four aliquots of a reference material spiked with analytes of interest are analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IPR is performed anytime the method or instrumentation is modified.

Isotope dilution quantitation – Determination of a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched. This method employs ^{2}H or ^{13}C labeled analogs which are spiked into each sample

LC – Liquid chromatography

Labeled Compound – A molecule in which one or more of the atoms is isotopically enriched, thereby increasing the mass of the molecule

Laboratory Blank – See method blank.

May – This action, activity, or procedural step is neither required nor prohibited.

May Not – This action, activity, or procedural step is prohibited.

Method Blank – An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Method Detection Limit (MDL) – The lowest concentration at which an analyte can be detected under routine operating conditions (see 40 CFR 136, Appendix B).

MS – Mass spectrometer or mass spectrometry.

Must – This action, activity, or procedural step is required.

Native Compound – A molecule in which all atoms have naturally occurring isotopic abundances

OPR – Ongoing precision and recovery sample (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Reagent Water – Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Recovery Standards (RS) – are equivalent to the DoD definition of Injection Internal Standards.

Relative Standard Deviation (RSD) – The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RPD – Relative Percent Difference shown

RF – Response factor.

RRF – Relative response factor.

Should – Although this action, activity, or procedural step is suggested, it is not required.

SICP – Selected ion current profile; the line described by the signal at an exact m/z.

Signal-to-noise ratio (S/N) – The height of the signal as measured from the mean of the noise to the peak maximum divided by the width of the noise.

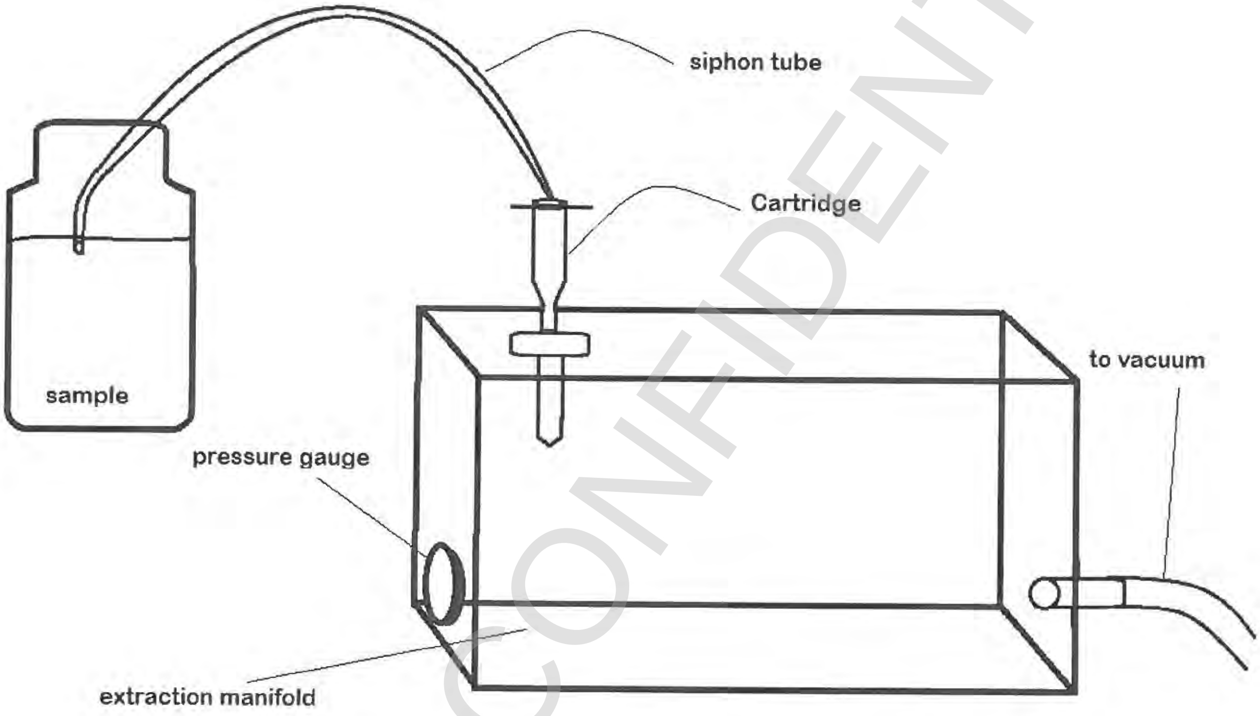
SPE – Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte.

Stock Solution – A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

UPLC – Ultra performance liquid chromatography

Appendix A

Figure 1. Extraction Manifold Set-up



Appendix B

Quadratic and Higher Order Curves

Masslynx uses a general Least Squares Fit algorithm to regress a polynomial of any order against the calibration points. The method used is outlined below.

Polynomial regression can be described as the fitting of m `independent' variables ($X_j$, $j$=0 to $m$ – 1) to a single `dependent' variable y. In other words:

$$y = Xb + e$$

Where:

- y is the n x 1 vector containing the n y values (y_i).
- X is the n x m matrix of x values (x_i^j).
- b is the m x 1 vector of regression coefficients (b_j).
- e is the n x 1 vector of residuals from the fit to each y_i value.

The familiar least squares solution for the regression coefficients is given by:

$$b = (X'X)^{-1}X'y$$

Where:

- $^{-1}$ indicates matrix inverse
- ' indicates matrix transpose

The above equation can then be solved using Gauss-Jordan elimination.

To implement weighted regression X and y are first multiplied by a diagonal n x n matrix P (in other words, X becomes PX and Y becomes PY), before the above equation is solved.

Where each element (p_{ij}) of P is given by:

$$p_{ij} = w_1½ \text{ for } i = j$$

$$p_{ij} = 0 \text{ for } i <> j$$

w_1 is weighting of ith calibration point, all set to 1 for no weighting.

ATTACHMENT B

STANDARD OPERATING PROCEDURE NO. 16 (SOP-16):

GROUNDWATER/SURFACE WATER INTERFACE SAMPLING USING A PORE WATER SAMPLER

GROUNDWATER/SURFACE WATER INTERFACE SAMPLING USING A POREWATER SAMPLER

PURPOSE

The purpose of this standard operating procedure (SOP) is to obtain pore water samples from a location of groundwater/surface water interface using a porewater sampler for analyses that are representative of environmental conditions at the Coakley Landfill Superfund Site in North Hampton and Greenland, New Hampshire. The collection of these samples using the following sampling procedures will be carried out at the locations identified in the Coakley Landfill Sampling and Analysis Plan (SAP).

Any modifications to this SOP shall be approved in advance by the New Hampshire Department of Environmental Services (NHDES) Project Manager and Quality Assurance (QA) Coordinator, in consultation with the United States Environmental Protection Agency (USEPA), documented in the site logbook, and presented in the final report.

It is assumed that sampling can be conducted either from the shore, or by a sampler standing in the water wearing boots or waders.

SAFETY

If a sample cannot be obtained safely, the sample should not be taken at all and the conditions documented in the sampler's field book. Potential dangers include, but are not limited to, uneven and rocky terrain that may cause a fall or other personal injury. All necessary precautionary measures should be heeded when performing these sampling techniques.

GENERAL INFORMATION

1. Each of the regular sampling locations is permanently marked in the field so that sampling points are consistent for each round. All porewater samples shall be located using a global positioning system (GPS) unit.
2. Digital photographs shall be taken at each sampling location, upstream and downstream from the same position. Consistency should be maintained between sampling rounds.
3. Porewater sampling will occur congruent to the groundwater sampling event. Based on weather reports, the sampling team will select the driest period during the Site sampling events to collect the samples, unless otherwise directed by the project manager.
4. Additional information to be recorded on the Porewater Worksheet includes the following:
    - Past 7 days of local meteorological data showing a minimum of daily precipitation totals and barometric pressure;
    - General physical description of the samples and sampling locations; and
    - Descriptions/ID’s of digital photographs

<u>POREWATER SAMPLING</u>

This SOP specifically describes the procedures for collecting porewater samples.

EQUIPMENT AND MATERIALS

- Informational materials for sampling event: A copy of the current approved site-specific Health and Safety Plan, site-specific SAP, location map(s), field data from prior sampling events, manuals for sampling, and the monitoring instrument’s operation and maintenance manuals, should be brought to the site.
- Appropriate personal protective equipment (PPE).
- New laboratory-supplied wide-mouth glass sample containers (jar) for each sampling location. Extras will be used as transfer vessels to fill pre-preserved sampling containers.
- 0.45-micron filters for each sampling location to collect dissolved metals, as required.
- Logbook, pencil/pen, calculator.
- Appropriate sample containers, pre-preserved as necessary by the laboratory.
- Re-sealable plastic bags to protect and store samples.
- Cooler and loose ice.
- Multi-parameter water quality parameter unit to take in-situ readings for pH, Specific Conductivity, Temperature, oxygen reduction potential (ORP) and dissolved oxygen (DO).
- Appropriate calibration solutions for the multi-parameter instrument.
- Turbidity Meter.
- Calibration solutions for the Turbidity meter.
- Field data from last sampling event, if available.
- Field data sheets, sample labels, chain of custody forms.
- The manufactures instruction manuals for all equipment.
- Paper towels.
- Trash bags to containerize used consumable field supplies.
- Toolbox to include general items such as large and small wrenches, pliers, screw drivers, 25’ measuring tape, hose connectors, sharp knife (locking blade), duct tape, at a minimum.
- Decontamination supplies as described in the Decontamination SOP included in the SAP.
- Digital camera.
- Adjustable rate Geotech Peristaltic Pump Series II Variable Speed pump 300 + 600 RPM with Easy Load Peristaltic Pump Heads (that allow 50 ml/minute) and a battery (marine, battery pack, etc)
- ¼” ID x 3/8” OD polyethylene tubing for sample collection – new tubing will be used at each sampling location and disposed.
- Pharmaceutical or surgical grade silicon tubing for pump. <u>For sampling</u>: Thin walled tubing #16 (1/8” x ¼” x 1/16”) and/or thin walled tubing #14 (1/16” x 3/16” x 1/16”) if necessary to reduce flow to 50 ml/min. <u>For connections</u>: thick walled tubing #15 (3/16” x 3/8” x 3/32” – new tubing will be used at each sampling location and disposed.
- A three way stop cock to divert sample flow (before the multi-parameter meter) to collect turbidity samples.
- Equipment to keep monitoring and sampling equipment off the ground (e.g. table, bucket or polyethylene sheeting).

PRELIMINARY PROCEDURES

1. In general, all instrumentation necessary for field monitoring and health and safety purposes shall be maintained, tested, and inspected according to the manufacturer's instructions. The manufacturer's instruction manuals for field equipment shall be kept on-site with the equipment.
2. All instruments will be successfully calibrated once by the sampling team prior to the sampling event. Instruments will be calibrated and checked according to the Calibration SOP in the SAP.
3. Sampling occurs sequentially from downstream to upstream. Each sampling location is entered from downgradient side.
4. Prepare sampling equipment and bottles on shore.

PROCEDURE USING THE PERISTALTIC PUMP

Preliminary Procedure

1. Set up sampling equipment on shore as if following the low flow sampling procedure. Refer to the attached set-up diagram from the low flow sampling procedure in the SAP. Low flow purging and protocol is not necessary for this procedure. Lay out sheet of clean polyethylene for monitoring and sampling equipment, unless equipment is elevated above the ground (e.g., on a table, bucket, etc.). Be sure to tilt the low flow cell in the ring stand with the outflow connection facing upward to eliminate and prevent air bubbles. Field parameters should be collected from the surface water body that is being recharged from the porewater to be sampled, which will be used to compare to field parameters collected from the porewater.
2. Carefully insert a porewater sampler into the river/stream bed to the desired depth, typically around eight inches in depth. After insertion, remove the strengthening rod from the porewater sampler.
3. Determine and cut the appropriate length of tubing needed to reach the porewater sampling location. Connect the tubing to the porewater sampler.

Sampling Procedure

1. Start the pump at its lowest speed setting and slowly increase the speed until discharge occurs. Continue purging until purge water is relatively clear. Once the purge water has cleared, connect the tubing to the flow through cell and allow parameters to stabilize for at least two minutes.
2. Once the readings have stabilized, record the pH (unit), Specific Conductivity (µS/cm), Temperature (°C), ORP (millivolts) and DO (mg/L) on the worksheet.
3. Collect an aliquot of water from the three way stop cock for the Hach and analyze the sample for turbidity. Record the NTU value on the Surface Water Worksheet.
4. Check the tubing; the water flow during sampling needs to be a laminar flow without air bubbles. If air bubbles are observed they can usually be removed by elevating the discharge tube and pump to allow the air to continue rising until discharged with the water.

5. Once a laminar flow is achieved, begin collecting the samples.
    a) Remove the cap from the sample container and place it on the plastic sheet or in a location where it won't become contaminated.
    b) Refer to the SAP for specific samples to be collected. The order in which samples should be collected from each well includes:
        - VOCs
        - 1,4-Dioxane, as applicable
        - PFAS - **(Refer to SOP-10 for specific sampling procedures related to PFAS sampling)**
        - Total metals (Dissolved metals, as required)
        - Other parameters, as required
    c) All sample containers should be filled by allowing the discharge to flow gently down the inside of the container with minimal turbulence. Cap sample containers securely after filling each bottle. Sample containers should be wiped dry.
    d) If dissolved metals are required, stop the pump, attach a one use only 0.45 micron in-line filter to the tubing, start the pump again, and allow water to rinse through the filter before collecting the sample.
    e) Field duplicate and matrix spike, matrix spike duplicate (MS/MSD) samples should be collected by filling a separate container for each analysis immediately following the actual field sample collection and should be in the same priority order as indicated above. Refer to SAP for specific QC sampling requirements and appropriate COC notations required for MS/MSD samples.
    f) Place samples in re-sealable plastic bags and then in loose ice within the cooler. Metals samples do not require cooling.

4. Once the samples have been collected, stop the pump.
5. Disconnect equipment and dispose of the sampling tubing.

REFERENCES

"Protocol for Groundwater/Surface Water Interface Sampling Using A Porewater Sampler", MEDEP Division of Remediation SOP No. RWM-DR-023, Revision 3, April 28, 2015

ATTACHMENTS

Porewater Sampling Worksheet

FIELD DATA INFORMATION
PORE WATER SAMPLING LOG

SITE INFORMATION	
Project:	Date:
Sample ID:	Job Number:
SURFACE WATER INFORMATION	**SAMPLE COLLECTION INFORMATION**
Channel Width: (ft/inches)	Sample Collection Method:
Depth at Center: (ft/inches)	Water Body/Location ID Sampled:
Approximate Flow Rate: (ft/second)	

SURFACE WATER PARAMETERS

TIME	pH (S.U.)	SP. COND. (μS/CM)	TURB. (NTU)	D.O. (MG/L)	TEMP. (°C)	OBSERVATIONS

PORE WATER PARAMETERS

TIME	pH (S.U.)	SP. COND. (μS/CM)	TURB. (NTU)	D.O. (MG/L)	TEMP. (°C)	OBSERVATIONS

Calibration Record	Date:	Type of Meter:
	Time:	Comments:

Notes:

<u>LOCATION SITE SKETCH</u>

Signature of CES Sampler:____

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