TNT/TNB-focused Bioremediation Pilot Study at Bangor Site F Source Area

FINAL Work Plan

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LIST OF ACRONYMS AND ABBREVIATIONS

AHA	Activity Hazard Analysis
BTC	breakthrough curve
COC	chain of custody
gpm	gallons per minute
HPLC	high performance liquid chromatography
IDW	investigation derived waste
ISB	*in situ* bioremediation
MDL	method detection limit
mg/L	milligram per liter
mM	millimolar
$NaHCO_3$	sodium bicarbonate
NAVFAC NW	Naval Facilities Engineering Command Northwest
P&T	Pump and treat
PPT	Push-pull test
PSOHP	Project Safety and Occupational Health Plan
PM	project manager
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RL	reporting limit
TOC	total organic carbon
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
UFP-QAPP	Uniform Federal Policy Quality Assurance Project Plan
µg/L	microgram per liter
USACE	The U.S. Army Corps of Engineers Seattle District and U.S. Army Engineer Research and Development Center

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1. INTRODUCTION

Naval Base Kitsap, Bangor Site F Operable Unit 2 (Site F, Figure 1) was used from approximately 1957-1972 for the disposal of wastewater produced from ordnance demilitarization. This disposal resulted in 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazine (RDX) contaminated groundwater which currently extends 4,900 feet downgradient of the former ordnance wastewater lagoon and overflow area. The groundwater pump-and-treat (P&T) remedy currently in place is not predicted to achieve explosives cleanup concentrations within a reasonable timeframe. In an effort to accelerate the Site F remedy, Naval Facilities Engineering Command Northwest (NAVFAC NW) has identified a cost-effective means to significantly expedite cleanup at Site F.

The U.S. Army Corps of Engineers Seattle District and U.S. Army Engineer Research and Development Center (collectively USACE) have completed multiple rounds of *in situ* bioremediation (ISB) pilot testing at Site F, which collectively show (1) that ISB is capable of achieving RDX cleanup concentrations, and (2) that implementing ISB could significantly reduce aquifer cleanup time and cost at Site F. While the degradation of RDX via anaerobic biostimulation has been proven at Site F, results on TNT and TNB degradation in the source area are still lacking. Therefore, NAVFAC NW has expressed interest in performing an ISB pilot study to simulate a portion of a full-scale ISB remedy in the Site F aquifer, which would provide (1) full-scale bioremediation performance information for the Navy and the Navy's remediation contractor to use when developing the full-scale ISB design, and (2) extended ISB performance monitoring to directly answer remaining questions regarding ISB performance specific to TNT in the Site F source area and longevity of treatment. This document describes materials and methods for USACE-performed injection of water amended with fructose and bicarbonate, as well as USACE-performed groundwater monitoring.

2. TEST OBJECTIVES

The ISB pilot study will first explore TNT and 1,3,5-trinitrobenzene (TNB) transport characteristics in the Site F source area by performing short duration push-pull tests (PPTs). A total of three PPTs will be performed in three separate wells near the source area (F-MW21, F-MW32, and F-MW33) using groundwater obtained from F-MW31, containing approximately 700 micrograms per liter (µg/L) TNT, and approximately 600 µg/L TNB, as of January 2021. The PPTs will yield aquifer dispersivity and TNT/TNB retardation factor estimates specific to the Site F aquifer, which will support bioremediation performance assessments during the biostimulation event and during future full-scale bioremediation efforts at Site F.

The pilot study will then establish an *in situ* bioreactor by injecting a large quantity of fructose-amended groundwater to stimulate growth and activity of indigenous explosives degrading microbes in the Site F aquifer. A portion of the water currently extracted from well F-EW3 will be diverted to the ISB test locations, fructose and bicarbonate will be added to F-EW3 groundwater, and then the amended groundwater will be injected into an existing monitoring well (F-MW33) and an existing extraction well (F-EW7). The ability to adjust and continuously record the rate of F-EW3 groundwater injected, and the ability to adjust and continuously record the rate of fructose and bicarbonate solution metered into the F-EW3 groundwater being injected is critical to test success.

After the amended groundwater injection has occurred, and after reducing geochemical conditions have been achieved in the interrogated portion of the aquifer, extended ISB performance monitoring data will be collected to answer questions regarding: (1) ISB performance specific to TNT and TNB in the Site F source area and (2) the longevity of bioremediation treatment. Although TNT and TNB are the target contaminants for this pilot study, information on how other explosives (e.g., RDX and 1,3-dinitrobenzene (DNB)) respond to biostimulation will also be gained. An additional goal of the study is to assess the ability to achieve TNT/TNB cleanup levels in site groundwater using ISB; however, the ability to achieve cleanup levels during the test will be subject to field conditions encountered. Any deleterious findings, though not anticipated, will empower Navy with required information to ensure the full-scale system is properly designed and implemented. Previous tests revealed aquifer acidification inhibited the degradation of RDX in the Site F aquifer. To ensure aquifer acidification has no negative impacts on biodegradation, the injected solution will be buffered with sodium bicarbonate. The buffer quantity required herein was based on excess acid production measured during previous biostimulation tests performed in the Site F aquifer.

Field materials, procedures, and analytical methods to be utilized to accomplish these objectives are described below.

3. LIST OF MATERIALS

1,500-gallon tanks	sump pumps and garden hose
sample containers	high-flow transfer pump and tubing
carbon substrate	step ladder
chloride bromide salts	plastic sheeting
generators	personal protective equipment
fuel and fuel containers	QED MicroPurge basics MP20 Flow Cell
flow cell calibration solutions	measurement forms
water level meter	Batteries
ferrous iron Hach Kits	distilled water
large graduated cylinder	1-gallon plastic Ziploc-type bags
coolers	Ice
packing tape	garbage bags
extension cord(s)	Sharpies
flow meters	field book
metering pumps	pump control box
submersible pumps and tubing	sodium bicarbonate (buffer)

4. METHODS

The Site F TNT/TNB Source Area Pilot Study will include push-pull tests, substrate injections, and long-term groundwater monitoring. The pilot study will proceed in the following two steps:

- 1. Preliminary Phase: Push-pull Tests (PPTs) will be carried out to determine site-specific estimates of aquifer dispersity and TNT/TNB retardation factors, which will support bioremediation performance assessments during Phase I ISB and in future pilot studies (e.g., a second round of injections - Phase II ISB - are planned for 2023) and full-scale bioremediation efforts at the site.
  - Groundwater monitoring for background conditions prior to start of PPTs
  - Injection of 150-gallons of groundwater obtained from F-MW31 (amended with 100 milligrams per liter (mg/L) bromide) per well
  - Extraction of 450-gallons of groundwater with samples taken every 30-gallons for explosives/anions analysis
- Phase I: *In-situ* Bioremediation (ISB) and performance monitoring
  - Groundwater monitoring for background conditions prior to start of ISB
  - Phase I injection of water obtained from F-EW3, amended with fructose and sodium bicarbonate
  - Flush with unamended groundwater to increase fructose footprint
  - Continued groundwater monitoring after injections in six test wells (F-EW1, F-EW3, F-MW31, F-MW32, F-MW35, and F-MW21) and the two injection wells (F-MW33 and F-EW7)

A summary of the field tests is provided in Table 1. The carbon substrate (fructose) concentration to be injected, as well as test volumes, are subject to revision prior to the test, including input from all collaborators. Fructose is the recommended bioremediation substrate of choice based on results of previous studies conducted at Site F; but also because of its ease of use in the field (rapidly dissolves to create uniform solution in field scale injection volumes; uniform composition and widely available). Field duplicates from the monitoring wells will be collected at 10% frequency and MS/MSD samples from the monitoring wells will be collected at 5% frequency in agreement with recommendations from the March 2005 UFP-QAPP Part 2B QA/QC Compendium.

Table 1. Groundwater Injections and Amendments by Test Phase

Test Field Work Phase	Groundwater Injection Amendments and Concentrations	Injection Volume	Injection Wells	Monitoring Wells
Push-Pull Tests	Water from F-MW31 Bromide (1.25 mM, 100 mg L^{-1})	150-gallons per well	F-MW32, F-MW33, and F-MW21	F-MW32, F-MW33, and F-MW21
Phase I ISB	Water from F-EW3 Fructose (25 mM) Bicarbonate (8 mM)	Approximately 3.5 million gallons total, split between two injection locations	F-MW33 and F-EW7	F-EW1, F-EW3, F-EW7, F-MW31, F-MW32, F-MW33, F-MW35, and F-MW21

4.1 Work Plans and Health and Safety Plans

USACE has prepared this Work Plan to detail USACE work for this project. USACE will prepare a Project Safety and Occupational Health Plan (PSOHP) according to EM 385-1-1 and an Activity Hazard Analysis (AHA) for work carried out by USACE employees.

4.2 Site Work

USACE shall complete earthwork necessary for the placement of tanks and equipment required for the injections; however, this shall be minimal due to the substrate metering system being located on an already existing concrete pad. The area is approximately 45 feet long by 25 feet wide and the approximate location is shown in Figures 2 and 4. The earthwork may include clearing, grading and preparing suitable subgrade as needed for amendment tanks and metering system. The clearing may include removing brush, logs and rocks. No tree removal will be allowed. All material removed must be placed on site in a location that does not obstruct access to existing roads or work areas. USACE will be responsible for determining the exact size of the area, grading necessary to level the area and type of rock, geofabric or other material necessary to create a suitable subgrade as needed. USACE shall also complete any clearing necessary to route water from F-EW3 to the substrate metering system, and from the substrate metering system to the injection wells.

4.3 Equipment Connections

4.3.1 F-EW3 Plumbing Connection

USACE shall connect to the effluent water line from F-EW3 (illustrated on Figure 4). USACE shall coordinate with the Navy and the Navy's contractors for access to F-EW3 and minimize disruptions to the operation F-EW3. The connection must allow a portion of F-EW3 effluent to be routed to the injection location and the remaining water to go to the treatment plant. The assumed constant flow rate out of F-EW3 is 40 gallons per minute (gpm). USACE must route the water to the mixing location and then the injection well and ensure the injection rate will remain constant. The piping or hose can remain above ground; however, it may cross an access road that must remain open. USACE shall plumb the injection piping or hose into the injection well while still allowing access for water level monitoring and the ability to lock the well head when not in use.

4.3.2 Electrical Connection

USACE shall provide power to the equipment used for the injections including pumps, mixing equipment and other miscellaneous equipment required for the injections. USACE shall determine the electrical load required and components necessary. USACE may connect to existing underground power at the site. USACE will be required to coordinate with the Navy and local utilities to use the existing power on site. USACE must use qualified electricians for all design and work and follow appropriate electrical codes and standards.

4.4 Injection Equipment

USACE will provide all equipment necessary to complete the injections. USACE will determine the equipment necessary to complete the nutrient injections based on the design requirements described in Section 4.7. USACE will provide a design in the work plan (Figure 3) that lists all the equipment and specifications for the equipment. The equipment will include:

- Buffer System – A mixing, storage, and metering system for dissolving sodium bicarbonate into solution and then metering it into the injected solution. The metering rate needs to be adjustable so that the final injected bicarbonate concentration remains ~ constant even if the injection rate changes during the injections.
- Fructose Injection System – A storage/metering system to inject fructose at the required rate per Section 4.7 into the injected water and record the rate of injection. The metering rate needs to be adjustable so that the final injected fructose concentration remains ~ constant even if the injection rate changes during injections.
- Injection Sampling Port – Piping and injection sample port equipment and flow meter at the well head to allow for sampling the injected solution.
- Monitoring Equipment – Flow meters on each component including F-EW3, and the fructose/sodium bicarbonate injection systems that can read both real time and total volumes injected. The flow meters must be rated for the injection ranges, specified in Section 4.7, and the viscosity of the material it will be measuring.
- Automatic shutoff – The goal is to continuously inject amended groundwater at a rate of 20 gpm for the duration of the test. However, if the aquifer cannot withstand this continuous injection rate, a high water switch in the injection well will turn the system off if water level in the injection well is between approximately 10 feet below ground surface.

4.5 Proof of Operability

USACE shall operate the system with only water to demonstrate the system performs as designed at ERDC's Waterways Experiment Station in Vicksburg, MS prior to transporting the system to the field site and prior to the injection of amended water. USACE shall install all components necessary for the injections and run the injection system at the designed flow rates and ratios of fructose, sodium bicarbonate, and water. Fructose and sodium bicarbonate will be used during the proof of operability test if available; otherwise, water will be used in place of fructose and the sodium bicarbonate solution. The proof of operability test need only be performed briefly (e.g. an hour or two as needed). The proof of operability test should simulate how to operate the system during the biostimulation event (i.e., Field Work Phase I ISB) using metering equipment to meter fructose/sodium bicarbonate solutions (or water as a stand in for fructose and sodium bicarbonate solutions if fructose/sodium bicarbonate are not available) into flowing water.

After the proof of operability test, USACE ERDC shall provide all other USACE personnel with training required to turn on the system (i.e., begin an injection) and to turn off the system when the injections are complete. Since the proof of operability test will be conducted at a remote location, tap water will be used as a substitute for F-EW3 groundwater and the test should occur only as long as needed to ensure operability.

4.6 Preliminary Phase: Push-Pull Tests

One background sample will be collected from up to three wells prior to the PPT using the low-flow techniques described in Section 4.9. PPTs will include a single injection of 150-gallons of water obtained from F-MW31 ([TNT] ~700 µg/L and [TNB] ~600 µg/L), and amended with 100 mg/L bromide tracer, followed by time-series groundwater sampling and analysis in that well. F-MW32, F-MW33, and F-MW21 have been selected as test locations. Prior to injection, water and bromide will be mixed thoroughly using a high-flow transfer pump, paddles, or other portable pumps (as necessary). Following mixing, the solution will be injected at approximately 5 gallons per minute; if that rate is not possible, then injection will occur via siphon. Water will be injected at the highest possible rate without the well overflowing so that post-injection sampling for monitoring will have the highest concentrations of explosives. During injection, three samples of the injection solution will be collected at each well (9 samples total). Following injection, three times the injection volume will be extracted from each well (i.e., 450-gal) as quickly as possible – with a target extraction rate of 2 gpm. During extraction, up to 15 groundwater samples will be collected from each well (up to 45 samples total); one sample for every 30 gallons extracted (Table 2). Each sample will be submitted for bromide and explosives analysis. Up to two samples per well (6 total) will also be submitted for TOC analysis. One of the TOC samples will be collected within the first 225-gallons and the second during the second 225-gallons.

USACE personnel will collect groundwater monitoring samples from the three wells used during the test (F-MW32, F-MW33, and F-MW21). USACE will collect samples for laboratory analysis of total organic carbon (TOC), explosives from the Method 8330B analytes list, and anions (bromide). Resulting breakthrough curves (BTC) can be analyzed using published methodologies to determine estimates for longitudinal dispersivity and TNT/TNB retardation factors (Schroth et al. 2001). Equations 1 and 2 can be used to determine the longitudinal dispersivity in the area near the test wells.

$$\hat{r}_{max} = \sqrt{\frac{V_{inj}}{\pi bnR} + r_w^2} \qquad \text{Equation 1}$$

where V_{inj} is the injected volume of PPT solution, b is the aquifer thickness, n is the effective porosity, R is the solute retardation factor, r_w is the well radius, and r_{max} is the final frontal position of the injection solution.

$$\frac{C}{C_0} = \frac{1}{2} erfc \left\{ \left(\frac{V_{ext}}{V_{inj}} - 1 \right) / \left[\frac{16}{3} \frac{\alpha_L}{\hat{r}_{max}} \left(2 - \left| 1 - \frac{V_{ext}}{V_{inj}} \right|^{\frac{1}{2}} * \left(1 - \frac{V_{ext}}{V_{inj}} \right) \right) \right]^{1/2} \right\} \qquad \text{Equation 2}$$

where V_{ext} is the cumulative extracted volume and α_L is the aquifer longitudinal dispersivity. According to Schroth et al. 2001, the tracer frontal position at the end of the injection phase, $r_{max,tr}$, is computed from Equation 1 based on know values for V_{inj}, b, n, and R = 1. Then, Equation 2, with $r_{max} = r_{max,tr}$ is fit to the tracer BTC to obtain and estimate for α_L. Then, Equation 3 can be used to determine an estimate for the retardation factor (R^*) for the sorbing solute:

$$R^* = \left(\frac{\hat{r}_{max,tr}}{\hat{r}_{max,sol}} \right)^2 \qquad \text{Equation 3}$$

The following method for estimating retardation factors for a sorbing solute from a PPT extraction BTC is thus: 1) determine $r_{max,tr}$ from Equation 1 and α_L from the tracer extraction phase BTC using Equation 2; 2) keeping α_L fixed in Equation 2, estimate the sorbing solute frontal position at the end of the injection phase $r_{max,sol}$ by fitting Equation 2 to the sorbing BTC; 3) use Equations 2 and 3 to estimate the explosive retardation factors.

Prior to and after the completion of the PPTs, nine (9) 1,500-gallon tanks located on site require cleaning. The tanks shall be pressure washed prior to being filled with 150-gallons of water obtained from F-MW31, and at the completion of the tests. The PPTs are expected to begin in September 2022 and estimated to take one day per well; however, the time may vary depending on the injection rate. The injection solution shall be injected in the morning and extracted immediately following injection.

Table 2. PPT Sample Quantities

Phase	Analytes	Number of sampling events	Number of sample location	Sample locations	Number of Field Samples (no FD or MS/MSD)	Number of Matrix Spike/Matrix Spike Duplicates (MS/MSD)	Number of Field Duplicates (FD)	Number of Total Samples (With FD and MS/MSD)
Background Sampling	Explosives	1	8	PPT Wells	8	1/1	1	11
	Anions	1	3	PPT Wells	3	1/1	1	6
	TOC	1	8	PPT Wells	8	1/1	1	11
PPT Injection Water Sampling	Explosives	3	3	PPT Wells	9	1/1	1	12
	Anions	3	3	PPT Wells	9	1/1	1	12
PPT Extraction Solution	Explosives	15	3	PPT Wells	45	3/3	5	56
	Anions	15	3	PPT Wells	45	3/3	5	56
	TOC	2	3	PPT Wells	6	1/1	1	9
Provisional Samples	Explosives	N/A	N/A	PPT Wells	N/A	N/A	N/A	4
	Anions	N/A	N/A	PPT Wells	N/A	N/A	N/A	4
	TOC	N/A	N/A	PPT Wells	N/A	N/A	N/A	1
							Total Explosives	**83**
							Total Anions	**78**
							Total TOC	**21**

1. Field Duplicate (FD) samples will be collected at a rate of 1 per every 10 field samples.
2. Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples will be collected at a rate of 1 pair per every 20 field samples.
3. PPT Wells are F-MW32, F-MW33, and F-MW21.

4.7 Phase I: *in situ* Bioremediation and Long-term Monitoring

The Phase I field work consists of an ISB pilot study and extended biostimulation performance monitoring. The ISB pilot study will biologically activate the aquifer by injecting a large quantity of fructose-amended groundwater to stimulate growth and activity of indigenous explosives degrading microbes in the Site F aquifer. Performance monitoring will occur before and after the biostimulation injection has occurred.

The goal is to inject approximately 3.5 million gallons of water amended with 25 mM fructose and 8 mM sodium bicarbonate at a rate of 20 gpm. The water used will originate from well F-EW3. Water from F-EW3 will be diverted from the extraction well to the substrate metering system (see Figure 4) for addition of fructose and sodium bicarbonate prior to injection. ISB injections will occur at two different locations: first at F-MW33 and then at F-EW7. The first injection, at F-MW33, is expected to last 56 calendar days. However, this is dependent on the injection rate and aquifer conditions. After injecting at the first location, non-amended groundwater will be injected for 6 days to further disperse fructose-amended groundwater. The second injection location, at F-EW7, is also expected to last 56 calendar days, with a 6 day post-injection flush. The intent is to split the total injection volume between both locations; however, F-MW33 (which has a smaller screened interval) may not be able to accommodate this volume due to the potential for biofouling. Therefore, a contingency plan is to inject as much into F-MW33 before changing injection locations to F-EW7. As an extraction well, F-EW7 is screened over a 30-ft interval (as opposed to F-MW33 which is screened over a 10-ft interval). Therefore, it is anticipated that any biofouling will be less pronounced at F-EW7. A remedy to the biofouling issue could then be initiated while injecting the fructose-amended groundwater at the alternative location.

Phase I is expected to begin in May 2023. The Phase I injections are expected to last a total of 139 calendar days; however, the time may vary depending on the injection rate/aquifer conditions. Phase I monitoring and sampling is expected to last up to one year after the injection is completed.

4.7.1 USACE Collection of F-EW3 Water for Phase I Injection Solution

Water from F-EW3 will be used for the Phase I ISB injection solution. USACE will install a spigot onto the already existing extraction system and route water from F-EW3 to the metering system for addition of fructose and bicarbonate.

4.7.2 USACE Purchase and Receipt of Fructose and Sodium Bicarbonate

USACE will be responsible for receiving fructose and sodium bicarbonate and preparing sodium bicarbonate solution to specific concentration. USACE shall purchase 12,000 gallons of 42% high fructose corn syrup. USACE shall purchase 8,500 kg (~19,000 pounds) of sodium bicarbonate ($NaHCO_3$).

4.7.3 Fructose and Sodium Bicarbonate Metering

USACE shall construct/install the fructose and sodium bicarbonate metering system as illustrated in Figure 3. Fructose will be metered into the F-EW3 obtained water at a rate of 0.075 gpm and sodium bicarbonate will be metered in at a rate of 0.170 gpm to achieve the desired concentrations of 25 mM fructose and 8 mM sodium bicarbonate. The fructose solution will be stored using six of the Navy's 1,500-gallon tanks near the injection locations as shown in Figure 4. Sodium bicarbonate solution will be stored in the Navy's three remaining 1,500-gallon tanks. Since a total of approximately 27,500-gallons of sodium bicarbonate solution will be required for buffering, these three tanks will require up to seven refills (roughly one refill every 16 days).

4.7.4 Personnel

USACE shall: 1) ensure the system remains operational during the injection including the continued supply of fructose and sodium bicarbonate and 2) be available to complete any necessary repairs. USACE shall be available for troubleshooting of the supplied equipment as needed. USACE shall be available to mobilize and complete maintenance/repairs on the required equipment within 24 hours of notification.

USACE will complete the day to day monitoring and manual adjustments of the system. A Contractor on-site field technician will not be required during the injections.

4.7.5 USACE Sampling and Groundwater Monitoring

Water Level Monitoring: USACE will install pressure transducers in the eight wells used during the test (F-EW1, F-EW3, F-MW31, F-MW32, F-MW35, F-MW21, and the injection wells F-MW33 and F-EW7), as well as two background wells outside the area of influence of the test (F-MW17 and F-MW24) and record the water level every 15 minutes to monitor the change in water level during the test. The pressure transducers will be installed a minimum of two weeks prior to injection starting to collect background water levels. The data loggers will be downloaded once a week during the injection and once a month during the monitoring period. Manual readings of the monitoring wells using an electronic water level indicator will be collected prior to installing the transducers and during every groundwater sampling event.

Injection Samples: USACE personnel will collect three water samples from the injection water periodically throughout injection (Table 4). USACE will perform field measurements of groundwater parameters: dissolved oxygen, conductivity, temperature, and pH, and will test water for Iron (II) with a Hach kit. USACE will collect samples for laboratory analysis of TOC, and explosives from the Method 8330B analytes list.

Groundwater Temperature Monitoring: USACE personnel will install temperature loggers in the screened portion of the injection and monitoring wells. The temperature loggers will be installed a minimum of two weeks prior to the injections in test wells (F-EW1, F-EW3, F-EW7, F-MW31, F-MW32, F-MW33, F-MW35, F-MW21, and the injection wells F-MW33 and F-EW7). The loggers will record the water temperature every 15 minutes and the data will be downloaded once a week during the injection and once a month during the monitoring period.

Groundwater Monitoring Samples: USACE personnel will collect groundwater monitoring samples from eight wells (F-MW31, F-MW32, F-MW35, F-MW21, F-EW1, F-EW3, and the injection wells F-MW33 and F-EW7) (Tables 3 and 4). A total of 13 rounds of samples, including one background round prior to injection, will be collected from all 8 wells over the course of Phase I ISB. USACE will collect samples for laboratory analysis of TOC and explosives from the Method 8330B analytes list.

The PPT and Phase I ISB sample schedules are based on USACE knowledge at the time of UFP-QAPP finalization. USACE does not anticipate any deviations to the PPT sample schedule. Learnings from PPT results could prompt optimization in the Phase I ISB sampling schedule to ensure the best data possible is obtained to meet data quality objectives. Any alterations to the Phase I ISB sampling schedule will be proposed to all UFP-QAPP recipients in advance of Phase I ISB sampling.

Groundwater Parameters: USACE personnel will collect groundwater parameters, using methods described in Section 4.9, from the test wells prior to collecting groundwater samples and several times during and after the injection. USACE personnel will perform field measurements of groundwater parameters: dissolved oxygen, conductivity, temperature, and pH, and will test groundwater for Iron (II) with a Hach kit.

Table 3. Phase I ISB Injection and Sampling Schedule

Phase	Start Date	End Date	GW Monitoring Sample Location and Analytes	Groundwater Quality Parameter Monitoring Performed?
GW Monitoring (Background Sampling – conducted during PPTs)	4/2023	4/2023	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Location 1 Injection	5/1/2023	6/30/2023	NA	NA
Location 1 Flush	6/30/2023	7/6/2023	NA	NA
Move metering system to Location 2	7/7/2023	7/10/2023	NA	NA
Location 2 Injection	7/10/2023	9/8/2023	NA	NA
Location 2 Flush	9/8/2023	9/14/2023	NA	NA
Sampling Event #1	9/15/2023	9/18/2023	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #2	10/16/2023	10/17/2023	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #3	11/20/2023	11/21/2023	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #4	12/18/2023	12/19/2023	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #5	1/15/2024	1/16/2024	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #6	2/19/2024	2/20/2024	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #7	3/18/2024	3/19/2024	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #8	4/15/2024	4/16/2024	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells
Sampling Event #9	5/23/2024	5/24/2024	Test and Injection Wells (TOC and Explosives)	Yes, Test and Injection Wells

1. Injection Wells: Location 1 is F-MW33 and Location 2 is F-EW7
2. Test Wells: F-MW31, F-MW32, F-MW35, F-MW21, F-EW1, F-EW3

Table 4. Phase I ISB Sample Quantities

Phase	Analytes	Number of sampling events	Number of sample location	Sample locations	Number of Field Samples (no FD or MS/MSD)	Number of Matrix Spike/Matrix Spike Duplicates (MS/MSD)	Number of Field Duplicates (FD)	Number of Total Samples (With FD and MS/MSD)
Injection Water Sampling	Explosives	3	1	Injection Sampling Port	3	1/1	1	6
	TOC	3	1	Injection Sampling Port	3	1/1	1	6
ISB Long-term GW Monitoring	Explosives	9	8	Test Wells, Injection Well	72	4/4	8	88
	TOC	9	8	Test Wells, Injection Well	72	4/4	8	88
Provisional Samples	Explosives	N/A	N/A	Test Wells, Injection Well	N/A	N/A	N/A	18
	TOC	N/A	N/A	Test Wells, Injection Well	N/A	N/A	N/A	18
							Total Explosives	**112**
							Total TOC	**112**

1. Field Duplicate (FD) samples will be collected at a rate of 1 per every 10 field samples.
2. Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples will be collected at a rate of 1 pair per every 20 field samples.
3. Injection Wells: F-MW33, F-EW7
3. Test Wells: F-MW31, F-MW32, F-MW35, F-MW21, F-EW1, F-EW3

4.8 Assessing Pilot Performance and TNT/TNB Degradation

Data will be evaluated using multiple approaches in order to accomplish project objectives. The first approach will involve using tracer-corrected time course TNT and TNB concentrations measured during PPTs and standard PPT data analysis methods (Istok et al. 1997, Haggerty et al. 1998) to extract localized TNT and TNB retardation coefficients to support bioremediation performance assessments during Phase I ISB. After Phase I injections, extended ISB performance monitoring data will be collected to answer questions regarding: (1) ISB performance specific to TNT and TNB in the Site F source area and (2) the longevity of bioremediation treatment. Collectively, this large-scale bioremediation pilot will provide additional performance data to inform design and performance monitoring of a future full-scale ISB system.

4.9 Per- and Polyfluoroalkyl Substances Assessment

The Navy's long term monitoring contractor will sample groundwater from Site F wells and analyze the samples for per-and polyfluoroalkyl substances (PFAS). The PFAS sampling occurred in April 2022 and will occur annually thereafter (CH2M Hill, 2021). The PFAS sampling is addressed in a separate Sampling and Analysis Plan (CH2M Hill). The Navy's contractor analyzed for 18 PFAS analytes (US EPA Method 537.1), including PFOS, PFOA, and PFBS, using liquid chromatography tandem mass spectrometry (LC-MS/MS) compliant with DoD Quality Systems Manual Table B-15. The contractor's laboratory holds DoD and state accreditation. Third party data validation was performed.

PFAS sampling is to be conducted in the test and injection wells before and after the pilot study by another contractor under another task order. USACE will compare the concentrations of the analyzed PFAS obtained from the Navy's contractor over the course of the test and will describe the results and any changes in concentrations over the course of the test. This analysis will be included in the final report.

Appendix B presents the PFAS analytical results, and Appendix C presents a map of wells where PFAS testing was conducted. Results from the April 2022 PFAS sampling event indicate very low levels of PFAS in the area of the pilot test. In F-MW21, the sum of all PFAS detections (two compounds) was 5.58 parts per trillion (ppt), and in F-MW54S, there was one PFAS compound detection (1.29 ppt). In F-MW31, five PFAS compounds were detected at a combined concentration of approximately 15 ppt. In F-MW31, the sum of PFOS and PFOA (Perfluorooctane sulfonic acid and Perfluoroctanoic acid) was 4.07 ppt, which is below the Environmental Protection Agency (EPA) Lifetime Health Advisory (LHA) of 70 ppt, and also below their respective Regional Screening Levels (RSLs) as recently promulgated by EPA. PFOS and PFOA were not detected in F-MW21 and F-MW54S. PFAS precursors N-Ethyl perfluorooctane sulfonamido acetic acid (EtFOSAA) and N-Methyl perfluorooctane sulfonamido acetic acid (MeFOSAA) were not detected in the Site F explosives source area; therefore, precursor biotransformation is not expected to pose an issue.

4.10 USACE Groundwater Collection and Analysis Procedures

Background samples will be collected using a submersible pump using low-flow sampling techniques. The low flow sampling will be conducted in accordance with the USEPA "*Low Stress (low flow) purging and sampling procedure for the collection of groundwater sampled from monitoring wells*" (EPA 2017). Water levels will be monitored during low-flow sampling. Stabilization parameters pH, specific conductivity, temperature, dissolved oxygen, and oxidation reduction potential will be measured using an in-line flow cell (QED MicroPurge® Flow Cell Model MP20 or similar instrument) that will be calibrated each morning prior to use. Turbidity, while not considered a stabilization parameter, will also be measured. Fe (II) will be measured using a Hach Iron (Ferrous) Color Disc Test Kit, Model IR-18C following stabilization.

The initial flow rates will be closely monitored during purging. Well purge flow rates will be calculated by dividing volume purged by elapsed time. After determining the optimum flow rate, the controller will be adjusted, or throttled to the desired pump flow rate. For low-flow sampling, the flow rate should be no greater than 500 milliliters/minute. Micropurge flow cell data will be recorded every two minutes while monitoring for stabilization prior to sample collection.

At each well, low-flow purging will continue until three consecutive measurements of the stabilization parameters meet stabilization requirements. Stabilization parameter requirements are as follows:

pH	+/- 0.2 units
Specific Conductivity	+/- 0.020 mS/cm
Temperature	+/- 0.2 ºC
DO	+/- 0.2 mg/l
ORP	+/- 20 mV

Samples of injected test solutions and groundwater for laboratory analysis will be collected in amber glass or HDPE bottles as appropriate, shipped on ice, and stored at 2-6 °C until analysis.

Explosives and transformation product concentrations will be determined by high performance liquid chromatography (HPLC) or gas chromatography using EPA Method 8330B. At a minimum, the laboratory required limit of detection shall be 0.25 µg/L and the limit of quantitation shall be 1.0 µg/L. Samples will be analyzed for bromide using EPA Method 300.0. Samples will be analyzed for TOC using SW-846 Test Method 9060A.

Samples will be packaged in insulated coolers for shipment to the lab. Each cooler will be lined with plastic bubble wrap for shock absorption, and sample bottles will be individually protected by bubble wrap to protect against breakage. Each sample bottle will be placed in its own plastic Ziploc bag. A large plastic garbage bag will be used inside the cooler to contain the sample bottles in case of breakage. All samples will be placed in the shipping coolers and denoted on the Chain of Custody (COC) form accompanying each cooler. A photo of each completed COC form will be taken. Completed COC forms will be taped to the inside of each cooler lid. The coolers will be shipped via standard overnight FedEx service to the analytical laboratory. The sampling team lead shall call or email the laboratory POC each day samples are shipped in order to alert the lab to samples to arrive the next day. The laboratory POC shall call or email USACE confirming receipt of each shipment.

The nearest FedEx shipment location is the FedEx Office Print and Ship Center in Silverdale, Washington at 10854 NW Myhre Pl, Silverdale, WA 98383. The business is open 8:00 AM to 8:00 PM during the week (except Wednesdays, the business is open 8:00 AM to 6:00 PM), with the latest drop-off time for express shipments at 4:05 PM. Coolers will be shipped to the appropriate lab cooled from 2-6 °C with wet ice, in a timeline that will meeting the sample holding times, under chain of custody control.

4.11 Standard Forms

Example chain of custody and purge log forms are provided in Appendix A. A field notebook will be maintained to document all field activities discussed in this work plan. The field notebook will be filled out in ink and dedicated to the project. Each page will be dated and numbered consecutively. Required information for each day field work is completed includes; onsite personnel, field activities completed (sampling, water levels, etc.), time onsite, off site and time of each field activity. A photo record of the field book will be maintained by taking photos of each days' field notes and archiving the photos.

5. PROJECT ORGANIZATION AND RESPONSIBILITIES

Key USACE personnel responsible for executing the pilot test are listed below.

USACE Project Manager: Briana Niestrom (206) 764-3498. The USACE Project Manager (PM) is the primary liaison with the Navy for this field program, and is responsible for keeping the USACE team and Navy informed of project schedule, budget, and changes. She has overall responsibility for achieving the technical objectives of this project. Responsibilities will also include adherence to data quality objectives, analytical methods and laboratories, and approval of QA/QC procedures.

Field Team Leader: Jeffrey Weiss (206) 764-3312. The Field Team Leader is responsible for the on-site performance of the injections and sample collection, packaging/shipment to lab, and ensuring the injections and sampling are completed correctly. He will confirm that all personnel have received the required health and safety training, ensure the necessary personal protective equipment and supplies are used, and correct any unsafe work practices (duties of the site safety officer). He will contribute to data analysis and report preparation.

Project Scientists: Jenny Phillippe (206) 764-6965 and Dan Carlson (206) 764-6899. The Project Scientists are responsible for maintaining the project schedule and ensuring on-time preparation of documents such as the Work Plan, Uniform Federal Policy Quality Assurance Project Plan (UFP-QAPP), and Final Report. They are responsible for preparing USACE equipment and supplies, coordinating fieldwork with the Field Team Leader, and coordinating with the full project team. They will work with the USACE chemist to ensure analytical data is of acceptable quality for use during data analysis. They will contribute to data analysis and report preparation.

Project Chemist: Alison Suess (206) 764-3264. The Project Chemist is responsible for leading preparation of the UFP-QAPP and for ensuring analytical data is of acceptable quality for use during data analysis. She will contribute to data analysis and report preparation.

Principal Investigator: Jacob Lalley (513) 368-2266. The Principal Investigator is responsible for overall project execution including injections, sampling, data analysis, and report preparation.

Senior Technical Advisor: Mandy Michalsen (206) 764-3324. The Senior Technical Advisor provides guidance to the project team for the field test execution, adaptive management, and data analysis and interpretation.

6. SCHEDULE

The pilot test project schedule is summarized below.

Task Name	Duration	Start	Finish	Notes
QAPP / Work Plan Preparation	**(Work Days)**			
DQO meeting	1	7/20/2021	7/20/2021	
Preliminary Draft QAPP / Work Plan	25	10/1/2021	11/5/2021	
Preliminary Draft QAPP / Work Plan Internal Review	5	11/8/2021	11/12/2021	QAPP will be reviewed by USACE internally.
Revision of Preliminary Draft QAPP / Work Plan	5	11/15/2021	11/19/2021	
Stakeholders (Navy, Ecology, and EPA) Review Draft QAPP / Work Plan	20	6/8/2022	7/6/2022	
Meeting with stakeholders	1	7/6/2022	7/6/2022	
Revision of Draft QAPP / Work Plan	5	7/6/2022	7/20/2022	
Stakeholders Backcheck	5	7/20/2022	7/27/2022	
Final QAPP / Work Plan	--	7/27/2022	2/9/2023	Unforeseeable issues resulted in substantial project delays
Laboratory Task Order Award	NA	3/2023	9/2024	
Field Work	**(Total Days)**			
Push-Pull Tests	5	3/20/2023	3/24/2023	
PPT monitoring and sampling	5	3/20/2023	3/24/2023	
Substrate metering system installation and background sampling	10	4/17/2023	4/28/2023	To include sodium bicarbonate and fructose tank preparation.

Task Name	Duration	Start	Finish	Notes
Phase I ISB Location 1 injection	60	5/1/2023	6/30/2023	
Location 1 flush	6	6/30/2023	7/6/2023	
Transition of substrate metering system	4	7/7/2023	7/10/2023	
Phase I ISB Location 2 injection	60	7/10/2023	9/8/2023	
Location 2 flush	6	9/8/2023	9/14/2023	
Phase I ISB sampling and monitoring	252	9/15/2023	5/24/2024	To include 9 monthly sampling events
Reporting	**(Work Days)**			
Preliminary Draft Report	30	5/24/2024	7/8/2024	The report will include a data usability assessment based on the data validation report received
Internal Review of Preliminary Draft Report	5	7/9/2024	7/15/2024	
Revise Preliminary Draft Report	5	7/16/2024	7/22/2024	
Stakeholders Review of Draft Report	21	7/23/2024	8/21/2024	
Revise Draft report	5	8/22/2024	8/28/2024	
Final Report	1	8/29/2024	8/30/2024	

7. REFERENCES

CH2M HILL (CH2M HILL, Inc.). 2021. Draft Sampling and Analysis Plan, Site Inspection of Per-and Polyfluoroalkyl Substances, Naval Base Kitsap, Bangor, Washington. Prepared for Naval Facilities Engineering Systems Command Northwest, Silverdale, Washington. September.

Schroth, M. H., Istok, J. D., and Haggerty, R., 2000. In situ evaluation of solute retardation using single-well push–pull tests. Advances in Water Resources, 24(1):105-117.

U.S. Environmental Protection Agency, 2017, *Low stress (low flow) purging and sampling procedure for the collection of groundwater samples from monitoring wells*; Washington, DC (EPA/ EQASOP-GW4).

FIGURES

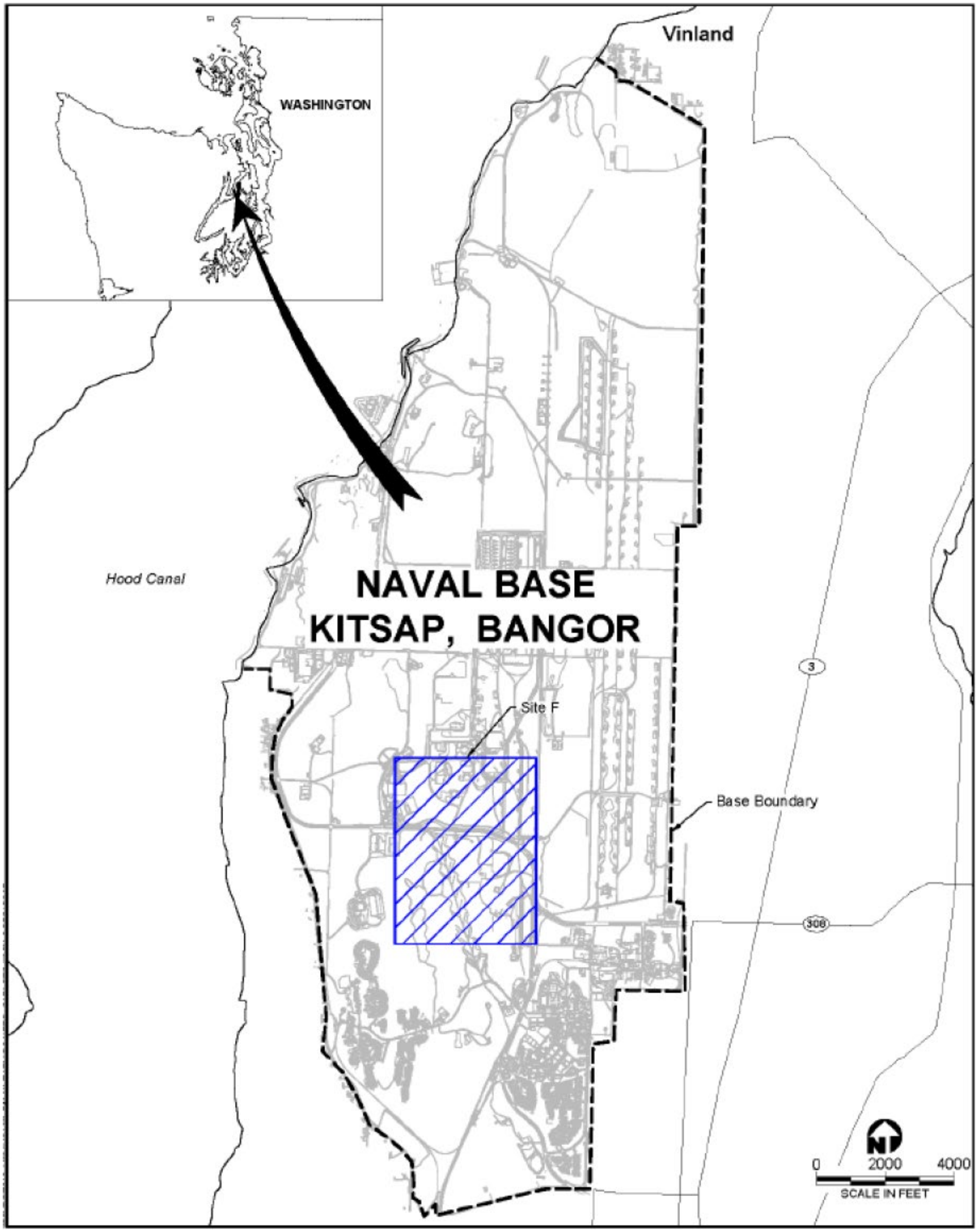

Figure 1. Bangor Site F Vicinity Map

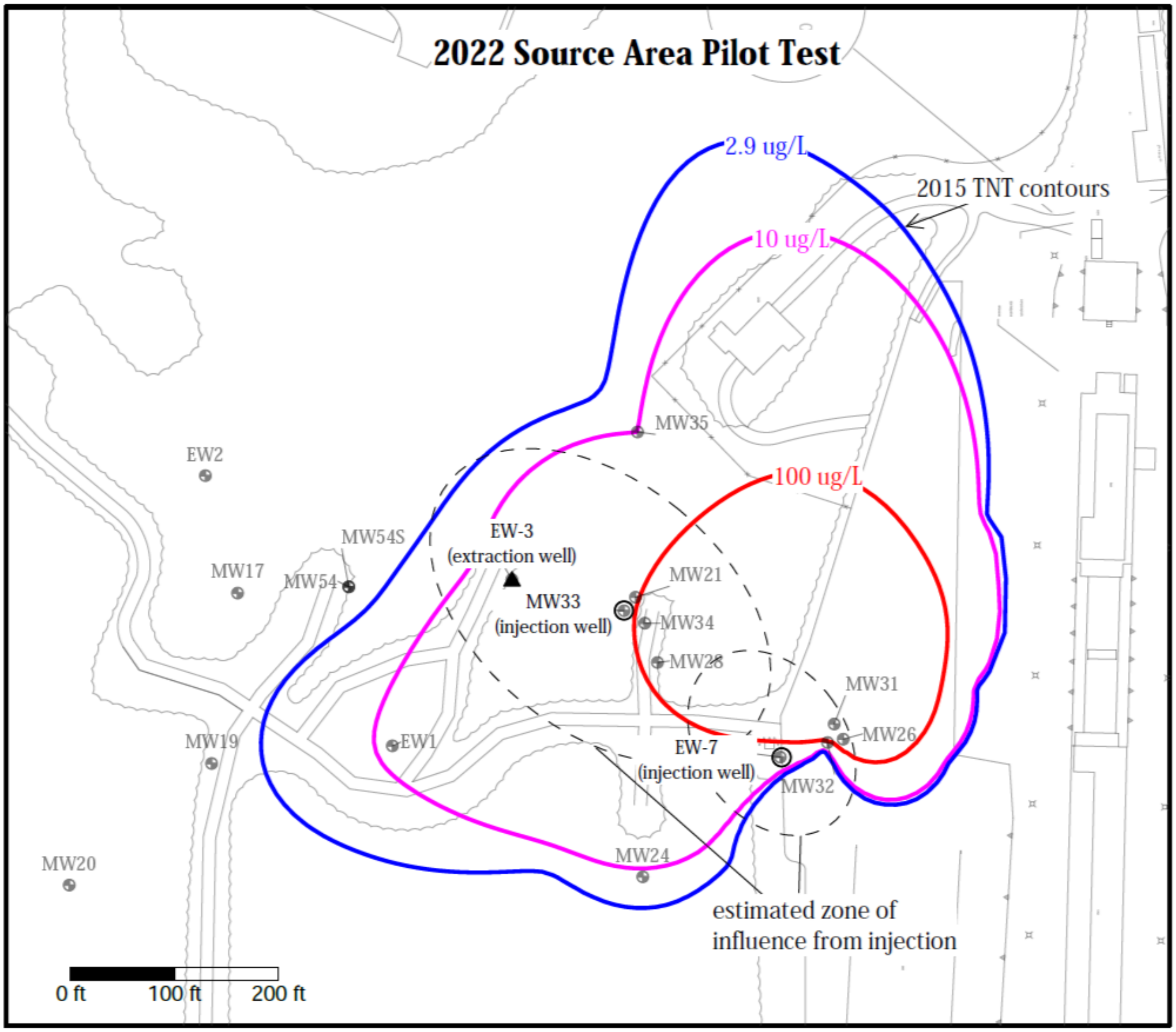

Figure 2. Pilot Test Wells and Anticipated Zones of Influence

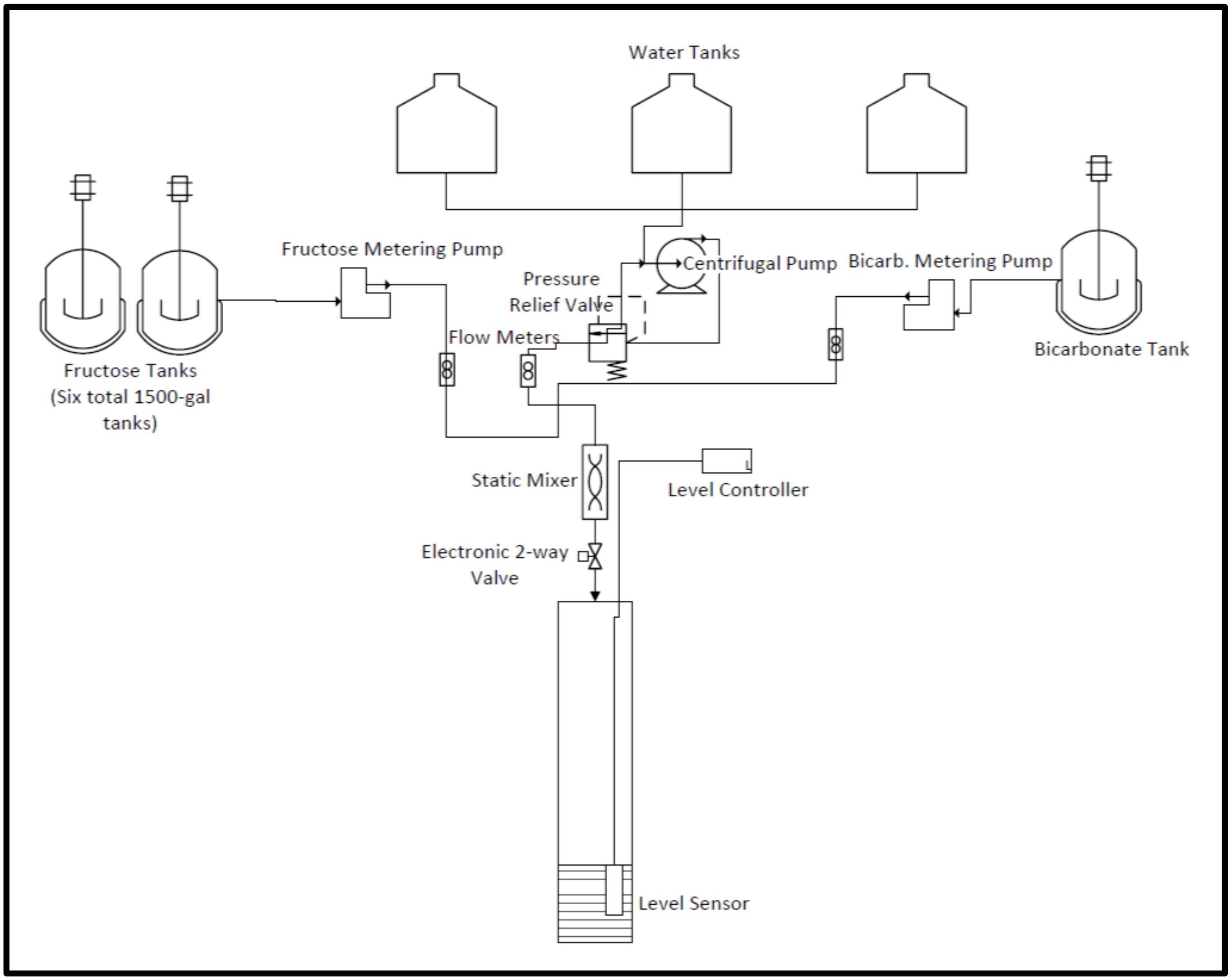

Figure 3. Schematic of Substrate Metering/Injection System

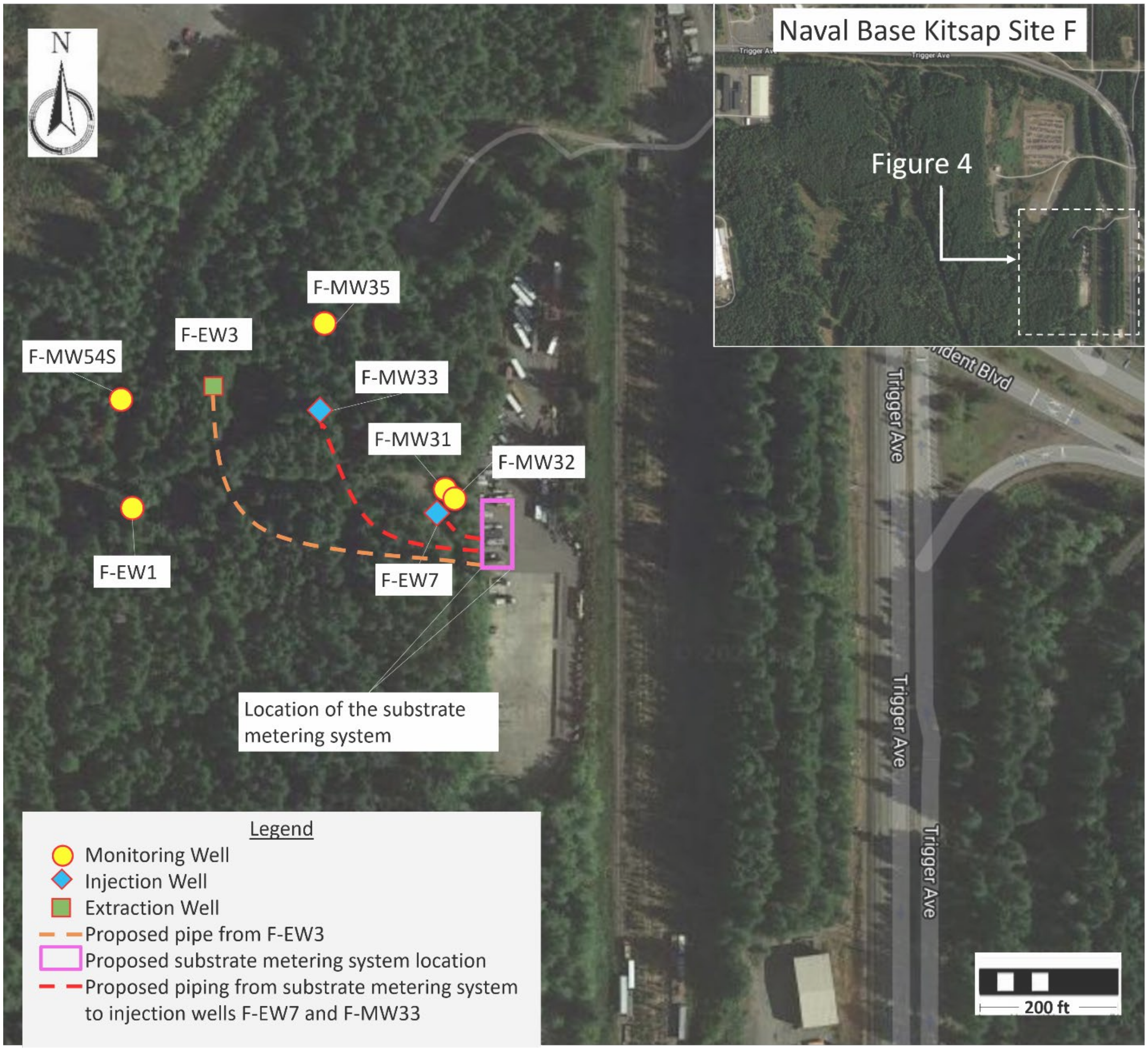

Figure 4. Injection Site Plan

APPENDIX A: Field Forms

US Army Corps of Engineers ® Seattle District

Chain of Custody Record--US Army Corps of Engineers

Project: Bangor Site F Pilot	Analytical Method and Preparation/Extraction	__1__ of __1__ COCs
Naval Base Kitsap, WA		Additional Lab Instructions:
LAB:	Sample collection and preservation information.	
Lab POC:		
Sampling Team:		
COOLER No.	[X] X indicates cooler is iced.	
Report Results To: [Project Chemist]		
Phone No.		

Sample Identification	Sample Date (2021)	Sample Time	Matrix	Collect Method	# of Cont.	Pres.														

FEDEX AIRBILL Tracking Number:

Possible Hazard Identification:
[ ] *Low-Level Contaminants* [ ] *Skin Irritant* [X] *Unknown*

Sample Disposal Options:
[ ] *Return To Site* [X] *Disposal By Lab* *Archive For* ____ *Months*

Special Instructions/QC Requirements & Comments: **Email COCs on day of receipt to [Project Chemist]** **Sample Collection Method - G = Grab.** **Field Team Leads:**

Relinquished by: (orignal signed)	Organization: USACE	Date/Time:	Received by:	Organization:	Date/Time:
Relinquished by:	Organization:	Date/Time:	Received by:	Organization:	Date/Time:
Relinquished by:	Organization:	Date/Time:	Received by:	Organization:	Date/Time:

Sheet _1__ of __1_

MICROPURGE/LOW-FLOW SAMPLING LOG

US Army Corps of Engineers® Seattle District

PROJECT: ______
Sample Round: ______
Task: ______
Date: ______
Weather: ______
Samplers: ______

Purge Method: Micropurge
Sample Collection Method: Low Flow
Sampling Device: Peristaltic Pump or portable bladder pump
Tubing: Bonded TLPE **Pump Intake Depth:** ______
Total Recovered Purge Water This Well: ______

WELL ID: ______
flush mount Y N
Well Condition: ______
Well Riser Dia. (ID): ______
Screened Interval: ______
S.W.L. Measuring Pnt: top of well riser

Well Bottom Depth: ______
STATIC WATER LEVEL: ______
Initial Purge Volume: ______
Approximate Pump Throttle Setting: ______

Groundwater Sample Data:

Sample ID	Analysis	Primary	QC	MS/MSD	Blank					

Instrumentation/Equipment Data:	**Calibration Date:** (Temperature is factory calibrated)
MP 20 Water Analyzer - probes for Temp., pH, Cond., ORP, D.O.,	
and Turbidity.	

Field Test Results:

Pump Flow Rate:

Comments: ______
Observations: Clarity: Odor: Floating Product: Sheen:

PURGE WATER DATA TABLES

Stabilization Parameters	Units	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes
Temperature	C								
Sp. Cond.	ms/cm								
D.O.	ppm								
pH									
ORP (Eh)	mV								
Turbidity	NTU								
Clock Time									
Static W.L.									
Flow Rate									

Stabilization Parameters	Units	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes	____ Minutes
Temperature	C								
Sp. Cond.	ms/cm								
D.O.	ppm								
pH									
ORP (Eh)	mV								
Turbidity	NTU								
Clock Time									
Static W.L.									
Flow Rate									

US Army Corps of Engineers Environmental Sampling Team

APPENDIX B: PFAS Analytical Results

Station ID	F-MW21		F-MW31		F-MW54S	
Sample ID	NBKB-F-MW21-0422		NBKB-F-MW31-0422		NBKB-F-MW54S-0422	
Sample Date	4/20/2022		4/21/2022		4/21/2022	
Chemical Name						
PFAS (NG/L)						
4,8-dioxa-3H-perfluorononanoic acid (ADONA)	2.6	U	2.22	U	2.65	U
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)	2.6	U	2.22	U	2.65	U
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	2.6	U	2.22	U	2.65	U
N-Ethyl Perfluorooctanesulfonamidoacetic Acid (NEtFOSAA)	2.6	U	2.22	U	2.65	U
N-Methyl Perfluorooctanesulfonamidoacetic Acid (NMeFOSAA)	2.6	U	2.22	U	2.65	U
Hexafluoropropylene oxide dimer acid (HFPO-DA)	2.6	U	2.22	U	2.65	U
Perfluorobutanesulfonic acid (PFBS)	2.6	U	2.22	U	1.29	J
Perfluorodecanoic Acid (PFDA)	2.6	U	2.22	U	2.65	U
Perfluorododecanoic Acid (PFDoA)	2.6	U	2.22	U	2.65	U
Perfluoroheptanoic acid (PFHpA)	2.6	U	1.68	J	2.65	U
Perfluorohexanesulfonic acid (PFHxS)	3.65	J	6.6		2.65	U
Perfluorohexanoic Acid (PFHxA)	2.6	U	2.47	J	2.65	U
Perfluorononanoic acid (PFNA)	2.6	U	2.22	U	2.65	U
Perfluorooctane sulfonic acid (PFOS)	2.6	U	1.21	J	2.65	U
Perfluorooctanoic acid (PFOA)	1.93	J	2.86	J	2.65	U
Perfluorotetradecanoic Acid (PFTeDA)	2.6	U	2.22	U	2.65	U
Perfluorotridecanoic Acid (PFTrDA)	2.6	U	2.22	U	2.65	U
Perfluoroundecanoic Acid (PFUnA)	2.6	U	2.22	U	2.65	U

Notes:

NA = Not analyzed

J = The analyte was positively identified: the associated numerical value is the approximate concentration of the analyte in the sample.

U = The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

APPENDIX C: PFAS Sampling Location Map

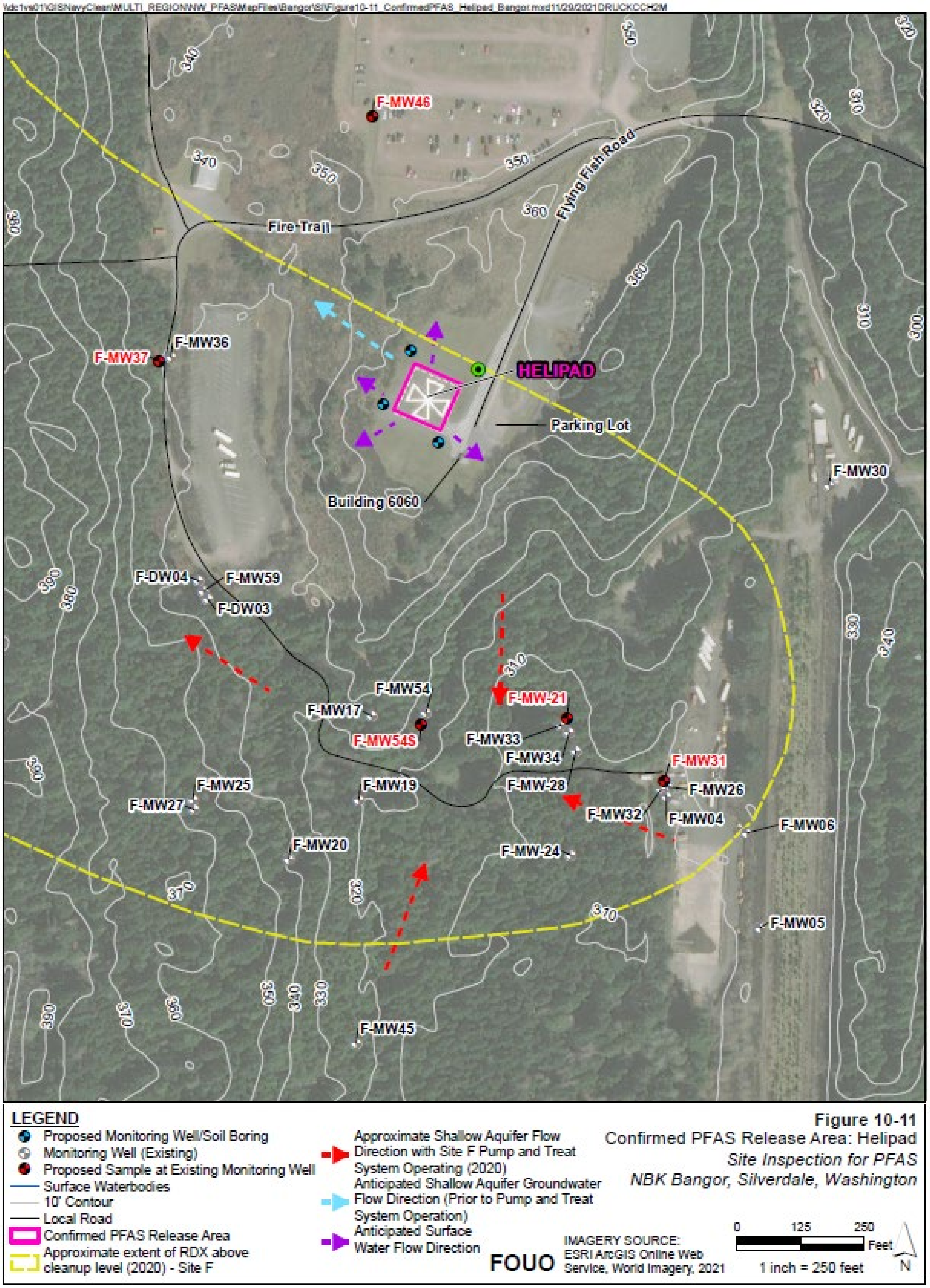

Figure 10-11
Confirmed PFAS Release Area: Helipad
Site Inspection for PFAS
NBK Bangor, Silverdale, Washington