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OU-1 Enhanced Attenuation Field Demonstration Sampling and Analysis Plan Mound, Ohio, Site

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Abbreviations

BVA	Buried Valley Aquifer
cVOC	chlorinated volatile organic compound
DCE	dichloroethene
EPA	U.S Environmental Protection Agency
MCL	maximum contaminant level
OU-1	Operable Unit 1
P&T	pump-and-treatment
PCE	perchloroethene
TCE	trichloroethene
VOC	volatile organic compound

1.0 Introduction

At the Mound, Ohio, Site, groundwater in Operable Unit 1 (OU-1) has been impacted by chlorinated volatile organic compounds (cVOCs) originating from the former solid waste landfill. Contaminated groundwater from the former landfill is currently being controlled using two extraction wells. Since the source materials have been removed from the landfill, the feasibility of switching from (1) the active remedy of a pump-and-treatment (P&T) system to capture contaminated groundwater originating beneath the former landfill to (2) a passive attenuation remedy is being considered as a viable alternative at the Mound site.

A field demonstration will be performed to determine whether discrete treatment zones can be established that will expedite the attenuation of cVOCs in the OU-1 groundwater. There are several areas in the OU-1 area that have elevated concentrations of cVOCs in groundwater and soil. A recent aquifer rebound study showed that the concentrations of cVOCs increase above the U.S Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) when the P&T system is shut off. In considering a transition to a passive remedy (i.e., monitored natural attenuation), the U.S. Department of Energy will conduct the field demonstration to evaluate the use of edible oils to enhance natural attenuation processes.

Sampling is being performed to support the field demonstration. A more detailed discussion of the field demonstration is presented in the *Field Demonstration Work Plan for Using Edible Oils to Achieve Enhanced Attenuation of cVOCs and a Groundwater Exit Strategy for the OU-1 Area, Mound, Ohio* (DOE 2013b).

1.1 Background

Industrial solvents (primarily trichloroethene [TCE]) and other cVOCs that originated from the former solid waste landfill have contaminated the groundwater in the Buried Valley Aquifer (BVA) beneath the Mound site. The landfill was used from 1948 to 1974 for the disposal of trash, debris, and liquid waste. In 1977, much of the waste was relocated and encapsulated onsite. The landfill site and surrounding OU-1 area occupy approximately 4 acres in the southwestern portion of the site.

The P&T system started operating in 1996. It is designed to control contaminated groundwater beneath the former landfill and to reduce contaminant concentrations to drinking water standards. Approximately 27 pounds of TCE were removed between December 1996 and April 2003. After April 2003, the mass removed by the P&T system was no longer calculated, as the mass was negligible. A soil vapor extraction system was installed and operated from 1997 to 2003 to accelerate the removal of cVOCs from the vadose zone. This extraction system removed approximately 4,105 pounds of TCE, with 90 percent of the removal occurring within the first 3 years.

Waste and contaminated soil removal activities were performed between 2007 and 2010. Approximately 99,500 cubic yards of material were removed from the OU-1 landfill area; the remaining soils in the OU-1 area meet the site cleanup objectives for future industrial/ commercial use. Excavation generally was limited to the unsaturated materials; however, in some cases, excavation proceeded to the water table. It was determined that excavating beyond the water table was not practicable, and in most cases the cleanup objectives were reached. It was

recognized that residual sources would still be present in the landfill footprint and would be addressed in future groundwater decisions.

After completion of the OU-1 excavation, the remaining sources that could continue to impact groundwater are secondary and tertiary sources. Tertiary sources are primarily present in the base of the former landfill excavation, with a lesser amount in the till materials downgradient of the landfill. Some secondary sources may be present within the southwestern corner of the landfill excavation and along the eastern side of the former sanitary landfill.

The distribution of cVOCs in groundwater, as illustrated from the TCE data (Figure 1), indicates there are three areas that have cVOC contamination greater than the MCL: (1) beneath the southwestern corner of the former landfill, (2) in the vicinity of wells 0410 and 0419, and (3) in the vicinity of wells 0451, 0452, and P060. The predominant migration pathway is to the southeast, parallel to the contact of the BVA with the bedrock to the east.

Several studies have been performed to evaluate the fate and transport of cVOCs in the OU-1 area. Based on these studies, the conceptual model for the OU-1 area consists of the following considerations:

- There are residually impacted vadose zone materials in the immediate vicinity of the former landfill, which results in downgradient contaminated groundwater in the outwash aquifer/BVA.
- The aquifer in the OU-1 area is comprised of unconsolidated materials and is mostly unconfined.
- The P&T system (when operating) creates a hydraulic barrier that bisects the aquifer downgradient of the southern landfill boundary. So long as this system remains active, the aquifer is separated into two components.
- When the P&T system is not operating, the average flow direction of the aquifer is to the southeast, generally parallel to the bedrock interface to the east.
- Although the aquifer is very transmissive, the flow rates are slow (50 to 80 feet per year) due to low hydraulic gradients.
- Aerobic conditions dominate the OU-1 groundwater system; however, reductive dechlorination of perchloroethene (PCE) to TCE to *cis*-1,2-dichloroethene (DCE) does occur within the central portions of the area of groundwater contamination.
- Cometabolic aerobic oxidation of TCE and *cis*-1,2-DCE is feasible along the margins of the area of groundwater contamination.

Since the source materials have been removed from the landfill, the feasibility of switching from the active remedy of a P&T system to capture contaminated groundwater originating beneath the former landfill to a passive attenuation remedy is being considered as a viable alternative. However, recent aquifer rebound studies show that the concentrations of cVOCs increase above the EPA MCLs when the P&T system is shut off. As part of the process of considering a transition to monitored natural attenuation, a field demonstration to evaluate the use of edible oils to enhance natural attenuation processes will be conducted.

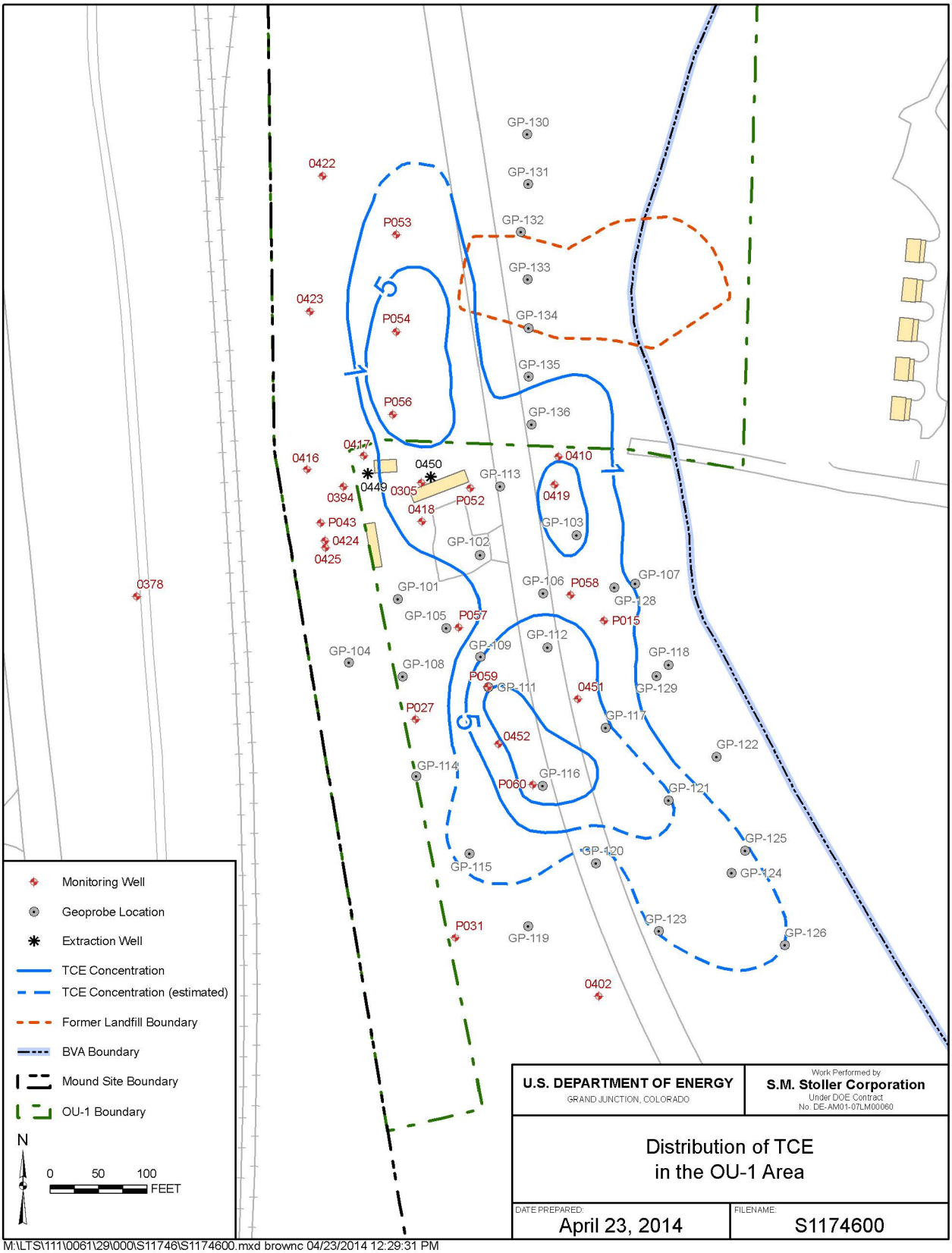

Figure 1. Distribution of TCE in the OU-1 Area

1.2 Objectives

Groundwater will be sampled to assess the performance of the deployment strategy for long-term attenuation of cVOCs in the OU-1 area. The objectives of the performance monitoring are to collect data to:

- Measure the effects of neat and emulsified oil emplacement within the treatment zones.
- Assess any changes in the size or location of anaerobic areas in the treatment zones.
- Measure cometabolic and abiotic conditions along the lateral and distal portions of the treatment zones.
- Determine if there is any reduction in PCE and TCE concentrations within the treatment zones.

After completion of the edible oil injection, static water levels will be measured and groundwater samples will be collected from selected wells throughout the OU-1 area. The objective of the post-deployment groundwater monitoring is to collect data to:

- Evaluate the performance of the attenuation by monitoring for the reduction of parent constituents (PCE/TCE), the presence of degradation (daughter) products, and the presence of anaerobic and aerobic geochemical zones.
- Determine degradation rates.
- Determine if there is any degradation in groundwater quality downgradient of the treatment zones.

2.0 Sampling Program

Sampling to support the field demonstration is separated into three programs: (1) baseline monitoring, (2) deployment monitoring, and (3) post-deployment monitoring. Each of these programs will provide data that will be used to evaluate establishment of the structured geochemical zones and the efficacy of edible oils to enhance natural attenuation processes in the OU-1 area.

2.1 Locations

Groundwater samples will be collected from wells in the OU-1 area (Figure 2). Monitoring wells are divided into the following categories:

- **Treatment zone wells:** Monitoring locations 0410, 0419, 0451, P054, P056, P059, and P060 are located within the source areas/treatment zones.
- **Upgradient/lateral area wells:** Well 0379 is located along the northern upgradient boundary of the OU-1 area. Monitoring location 0416 is located along the western edge of OU-1 where recharge from the Great Miami River enters the OU-1 area. Location 0422 is located immediately upgradient of the area of groundwater impact within the former landfill footprint.
- **Interior impact area wells:** Monitoring locations 0418, P057, and P058 are located between the treatment zone within the landfill footprint and the treatment zone in the OU-1 far-field area. These interior impact area wells can monitor any rebounding that might occur after the initial injection of the edible oils.
- **Downgradient/sentinel wells:** Monitoring locations 0402, P031, P061, P062, and P063 are located downgradient of the area of groundwater impact. Wells 0402 and P062 are terminal sentinel wells that will be used to verify that the groundwater quality in the BVA is not impacted by use of the edible oils for cVOC treatment or by unforeseen migration of cVOCs from the OU-1 area. Wells P031 and P061 are intermediate sentinel wells that will be used to monitor downgradient groundwater quality closer to the treatment zones. They will also provide early detection of plume expansion.
- **Other wells:** The remaining OU-1 Area wells (0305, 0417, 0423, 0424, 0425, 0452, P015, P027, P053), which are located throughout the OU-1 area, will be sampled periodically with the previously listed wells to provide a data set that covers the entire OU-1 area.
- **Extraction wells:** Monitoring locations 0449 and 0450 are located on the southern boundary of the former landfill. Monitoring location 0452 is located within the area of cVOC-impacted groundwater to the south.

During the neat and emulsified oil deployment phase, the wells used to evaluate the progression of the emulsified oil treatment will be sampled more frequently to monitor the cVOC concentrations and geochemical status of the aquifer while the attenuation zones are being established. This deployment phase of the monitoring is expected to occur for 3 to 4 months. After the zones have been established and it is determined that concentrations of the parent cVOCs have declined, post-deployment monitoring will be performed, and sampling frequencies will be decreased.

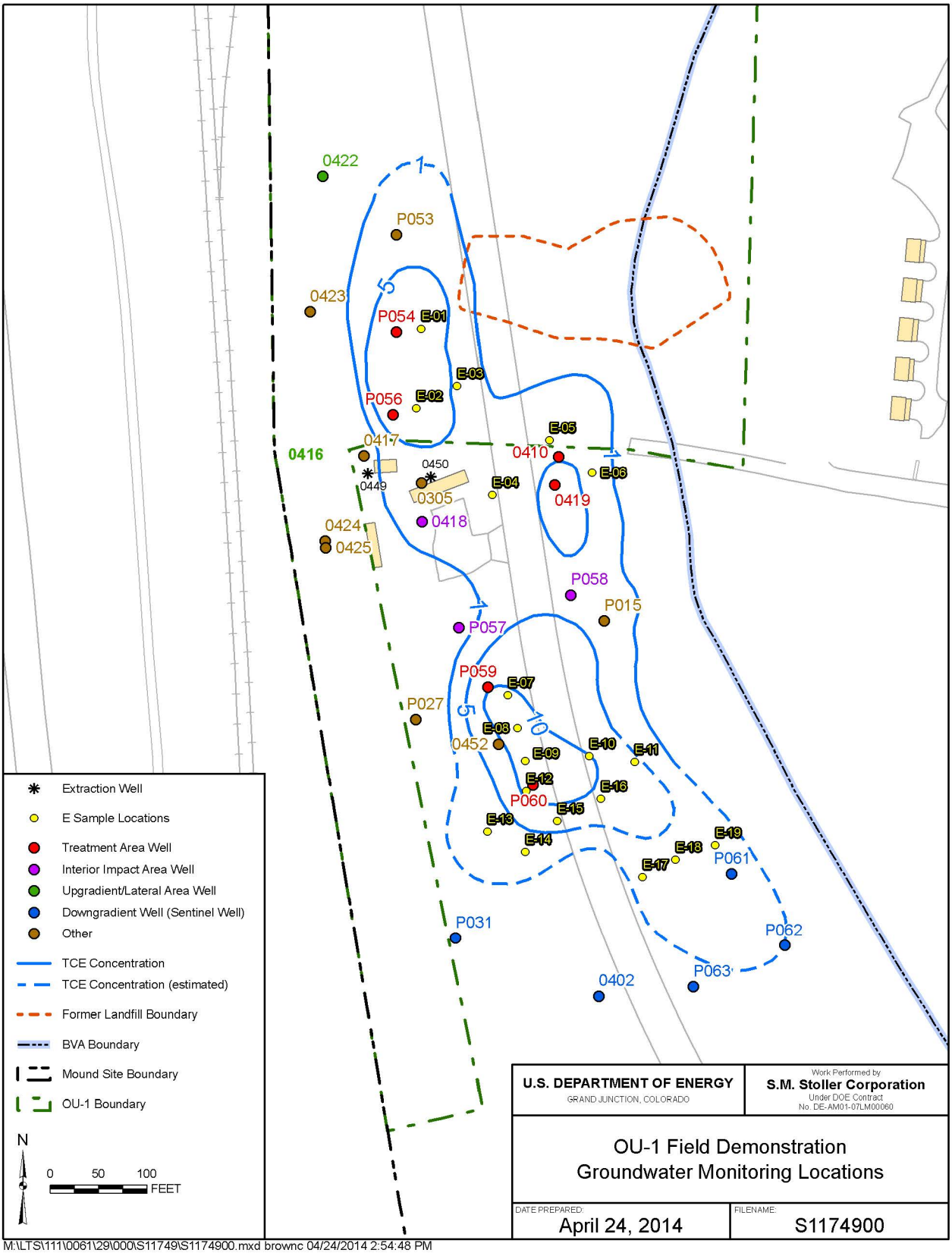

Figure 2. OU-1 Field Demonstration Groundwater Monitoring Locations

Operation of the P&T system using wells 0449, 0450, and 0452 will continue during the deployment of the emulsified oil and for a period of 3 to 4 months following the completion of injection. Extracting water from well 0452 during the deployment of the emulsified oil will help mitigate the potential to spread contamination downgradient, especially during the injection operations near well P060. However, if emulsion is observed in any of the extraction wells during the deployment phase, the well(s) in question will be removed from service to prevent damage to the P&T system and to prevent alteration of the structure of the structured treatment zone.

2.2 Analytes

Table 1 identifies the classes of samples and specific analytes that will be analyzed to evaluate the monitoring objectives.

Table 1. Sampling Class and Associated Analytes and Parameters

Sampling Class	Analytes and Parameters Measured
cVOCs	PCE, TCE, *cis*-1,2- DCE, *trans*-1,2-DCE, vinyl chloride
Indicator/field parameters	pH, conductivity, dissolved oxygen, oxidation-reduction potential, temperature, turbidity, alkalinity
Anions	Nitrate, sulfate, sulfide, phosphate, and chloride
Ammonia	Ammonia
Total organic carbon	Total organic carbon
Iron	Dissolved iron
Light hydrocarbons	Butane, propane, ethane, ethene, methane
Dissolved gases	Carbon dioxide, nitrogen
Appearance	Edible oil, color, odor
Microbial analysis	Quantitative polymerases chain reaction for fermentative, dechlorinating, and cometabolic bacteria

2.3 Baseline Sampling

The collection and analysis of baseline samples will be performed prior to injecting any edible oils in the OU-1 area. The objectives of the baseline sampling are:

- Establish the distribution of cVOCs in groundwater
- Assess the geochemistry of the aquifer
- Assess the presence of anaerobic and aerobic zones within the aquifer

The baseline sampling will consist of two sampling events performed at least 4 weeks apart. Samples will be collected as outlined in Table 2.

Table 2. Baseline Sampling Program

Category	Well IDs	Analytes	Frequency
Treatment Zone	0410 0419 0451 P054 P056 P059 P060	cVOCs Indicator/field parameters Anions Ammonia Total organic carbon Dissolved iron Light hydrocarbons Dissolved gases	2 times prior to oil deployment
Upgradient/Lateral Area	0379 0416 0422		
Interior Impact Area	0418 P057 P058		
Downgradient/Sentinel	0402 P031 P061 P062 P063		
Other	0305 0417 0423 0424 0425 0452 P015 P027 P053		

2.4 Deployment Sampling

During the deployment of the neat and emulsified oils, groundwater sampling will be performed to:

- Evaluate the oil distribution
- Assess the aerobic and anaerobic conditions in the aquifer
- Monitor for possible downgradient spread of cVOCs due to oil deployment

It is anticipated that the oil deployment will take approximately 45 days. Samples will be collected as outlined in Table 3.

Table 3. Monitoring Program During Oil Deployment

Category	Well IDs	Analytes	Frequency
Treatment Zone	0410 0419 0451 P054 P056 P059 P060	Indicator/field parameters Appearance	Weekly
Upgradient/Lateral Area	0379 0416 0422	Indicator/field parameters Appearance	Weekly
Interior Impact Area	0418 P057 P058	Indicator/field parameters Appearance	Weekly
Downgradient/Sentinel	0402 P031 P061 P062 P063	Indicator/field parameters Appearance	Weekly
		cVOCs	Biweekly
Extraction Wells	0449 0450 0452	Indicator/field parameters Appearance	Daily
		cVOCs	Biweekly

2.5 Post-Deployment Sampling

The current schedule is to continue the field demonstration for 3 years after the injection of the edible oils. During this period, monitoring will be performed to:

- Assess the changes in cVOC concentrations in groundwater
- Assess daughter products and their subsequent degradation
- Assess degradation pathways
- Assess the extent and changes in aerobic and anaerobic conditions in the aquifer
- Determine if additional means are needed to stimulate and/or maintain attenuation
- Monitor for downgradient spread of cVOCs

After completion of the oil deployment, it is anticipated that it may take 4 to 6 months before the data support the establishment of the structured geochemical zones. Sampling will be performed more frequently during that period to assess the changes in the aquifer system and to provide sufficient data to determine whether the zones have been maintained. After that time, sampling will continue until the end of the 3-year period. Samples will be collected as outlined in Table 4.

Table 4. Monitoring Program—Post-Deployment Monitoring

Category	Well IDs	Analytes	Frequency
Treatment Zone	0410 0419 0451 P054 P056 P059 P060	cVOCs Indicator/field parameters Anions Ammonia Dissolved iron Light hydrocarbons Dissolved gases Total organic carbon	First 6 months: monthly. Remainder of the 3-year period: quarterly.
Upgradient/Lateral Area	0379 0416 0422	cVOCs Indicator/field parameters Anions Dissolved iron	
Interior Impact Area	0418 P057 P058	cVOCs Indicator/field parameters Anions TOC Ammonia Dissolved iron Light hydrocarbons Dissolved gases	
Downgradient/Sentinel	0402 P031 P061 P062 P063	cVOCs Indicator/field parameters Anions TOC Ammonia Dissolved iron Total organic carbon Dissolved gases	
Emulsified Oil Deployment Points	E-01 through E-19	Indicator/field parameters Appearance	First month: weekly Remainder of 4 to 6 month period: biweekly

2.6 Other Sampling

Additional sampling will be performed during this period to provide supplemental data to support the field demonstration. These events include:

- Microbial analyses
- Routine sampling for cVOCs in the OU-1 area
- Groundwater elevation monitoring
- VOC analyses in emulsified oil deployment points

These sampling events will be performed as outlined in the following sections.

2.6.1 Microbial Analyses

Samples will be collected from a subset of the wells to measure the temporal type and abundance of the microbial community (fermentative, dechlorinating, and cometabolic) in the OU-1 area. Two sampling events will be performed:

- Prior to the deployment of the edible oils
- After data supports the establishment of the structured geochemical zones

Samples will be collected from wells 0419, P031, P056, P058, P060, and P061. These locations were selected to provide data in both the anaerobic and aerobic portions of the field demonstration area.

2.6.2 cVOC Sampling in OU-1 Area

Quarterly sampling for cVOCs will be performed in selected wells in the OU-1 area throughout the field demonstration. The wells 0305, 0417, 0423, 0424, 0425, 0452, P015, P027, and P053 will be sampled quarterly to provide a comprehensive data set for cVOCs that covers the entire OU-1 area. Efforts will be made to perform these sampling events in conjunction with other post-deployment sampling.

2.6.3 Water Level Monitoring

Static water levels will be measured monthly in the OU-1 monitoring network throughout the first year of the study. After the first year, a recommendation may be made to reduce the frequency of these measurements, if appropriate.

2.6.4 Sampling of Emulsified Oil Deployment Points

A one-time sampling of the emulsified oil deployment points E-01 through E-19 will be performed after the indicator parameters are stable (assumed to be approximately 1 month after injections) to evaluate the geochemistry of the aquifer within the treatment zones. These points will be sampled for VOCs, anions, ammonia, dissolved iron, light hydrocarbons, and dissolved gases.

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3.0 Quality Assurance/Quality Control

Quality assurance requirements and protocols for Mound site monitoring operations and environmental monitoring are contained in the *Operations and Maintenance (O&M) Plan for the U.S. Department of Energy, Miamisburg, Ohio*, *Site (Mound Site)* (DOE 2014).

Mound site-specific environmental sampling requirements are incorporated into the *Fernald Preserve and Mound, Ohio, Sites Environmental Monitoring Procedures* (DOE 2013a). This document is a compilation of the necessary performance and quality requirements associated with environmental monitoring activities at the Mound site. These procedures also provide instructions to ensure that data generated though the environmental sampling programs outlined in the O&M Plan are stored and maintained as records.

A comprehensive list of analytes, along with the required analytical methods, are listed in Table 5. The analytical methods are mostly from *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846) or *Methods for Chemical Analysis of Water and Wastes* (EPA 1983), or *Standard Methods for the Examination of Water and Wastewater* (APHA 1989).

Numerous quality-control samples will be collected in support of environmental monitoring activities. Samples also will be provided to the laboratory for internal laboratory quality-control evaluations specific to the samples media (matrix spikes, matrix spike duplicates, and matrix duplicate samples). The following is a summary of the various quality control samples that will be collected to support the environmental monitoring activities at the Mound site:

- **Field duplicate:** Collect 1 per 20 samples.
- **Equipment blank:** Collect 1 per 20 samples.
- **Matrix spike/matrix spike duplicate:** Collect 1 per 20 samples.
- **Matrix duplicate:** Collect 1 per 20 samples.
- **Trip blank:** Collect 1 for each cooler containing VOC samples.

Table 5. Analyte List for Groundwater

Analysis	Method	LIC	Container	Preservative	Holding Time
VOCs	SW-846 8260B (low level)	VOA-A-007	Glass polytetrafluoro-ethylene (PTFE) septum vial (zero headspace)	HCl, pH < 2, Cool 4ºC	14 days
Nitrate-N	SW-846 9056	MIS-A-041	Plastic	Cool 4ºC	48 hours
Sulfate		MIS-A-044	Plastic	Cool 4ºC	28 days
Chloride		MIS-A-039	Plastic	Cool 4ºC	28 days
Phosphate		MIS-A-XXX	Plastic	Cool 4ºC	28 days
Sulfide	SM4500-S-E	WCH-A-038	Plastic	2N zinc acetate + NaOH, to pH/9 Cool 4ºC	7 days
Ammonia	EPA 350.1	WCH-A-005	Plastic	H_2SO_4, pH<2, Cool 4ºC	28 days
Methane	RSK-175	VOA-A-021	Glass PTFE septum vial (zero headspace)	HCl < 2, Cool 4ºC	14 days
Butane		VOA-A-XXX			
Propane		VOA-A-XXX			
Ethane		VOA-A-XXX			
Ethene		VOA-A-XXX			
TOC	Standard Method (SM) 5310 B,C,D	WCH-B-025	Amber glass with PTFE-lined lid (zero headspace)	H_2SO_4, pH<2, Cool 4ºC	28 days
Iron, dissolved	SW-846 6010	MET-A-020	Plastic	HNO_3, pH<2	
Carbon dioxide	Hach Kit CA-23	NA	In situ	None	In situ
Conductivity	YSI	NA	In situ	None	In situ
Dissolved oxygen	YSI	NA	In situ	None	In situ
Oxidation-reduction potential	YSI	NA	In situ	None	In situ
pH	YSI	NA	In situ	None	In situ
Temperature	YSI	NA	In situ	None	In situ
Turbidity	Hach Kit 2100P	NA	Field Method	None	None
Alkalinity	SM 2320 B	WCH-A-002	Plastic	Cool 4ºC	14 days
Microbial analysis	quantitative polymerase chain reaction (qPCR)	TBD	Laboratory provided filter and container	Cool 4ºC	48 hours

Abbreviations:
PTFE = polytetrafluoroethylene
SM = Standard Method

4.0 References

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DOE (U.S. Department of Energy), 2013b. *Field Demonstration Work Plan for Using Edible Oils to Achieve Enhanced Attenuation of cVOCs and a Groundwater Exit Strategy for the OU-1 Area, Mound, Ohio*, LMS/MND/S11039, Office of Legacy Management, Grand Junction, Colorado, December.

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EPA (U.S. Environmental Protection Agency), 1983. *Methods for Chemical Analysis of Water and Wastes,* EPA-625-/6-74-003a, March.

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