

# 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

July 2014



U.S. DEPARTMENT OF  
**ENERGY**

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## Abbreviations

ATD	Authorization to Discharge
BVA	Buried Valley Aquifer
cVOC	chlorinated volatile organic compound
DCE	dichloroethene
DO	dissolved oxygen
EPA	U.S. Environmental Protection Agency
ft/day	feet per day
ft/yr	feet per year
MCL	maximum contaminant level
µg/L	micrograms per liter
mg/kg	milligrams per kilogram
MNA	monitored natural attenuation
ORP	oxidation-reduction potential
OU-1	Operable Unit 1
P&T	pump and treatment
PCE	tetrachloroethene (perchloroethene)
TCE	trichloroethene
TOC	total organic carbon
VOCs	volatile organic compounds

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## **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 the active remedy of pump-and-treatment (P&T) to capture contaminated groundwater originating beneath the former landfill to a more passive attenuation remedy is being considered as a viable alternative at the Mound site.

### **1.1 Purpose**

The purpose of the field demonstration is to determine whether discrete treatment zones can be established that expedite the attenuation of cVOCs in the OU-1 groundwater. Several areas having elevated concentrations of cVOCs in groundwater and soil are present in the OU-1 area. Results of a recent aquifer rebound study show 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 monitored natural attenuation (MNA), the U.S. Department of Energy will conduct the field demonstration to evaluate the use of edible oils to enhance natural attenuation processes.

### **1.2 Objective**

Edible oils (neat and emulsified) will be used to create treatment zones to reduce the concentrations of trichloroethene (TCE) and tetrachloroethene (PCE) in groundwater and enhance attenuation of these parent compounds and degradation (daughter) products. The goal of the field demonstration is to show that these treatment zones can be established and effectively maintained such that cVOC concentrations in groundwater can decrease to MCLs in a reasonable time frame. Ongoing groundwater monitoring will be included to ensure that groundwater quality does not degrade downgradient of these treatment zones.

Data will also be collected to evaluate the feasibility of MNA as a remedy to address cVOC contamination in the OU-1 groundwater. Factors to be evaluated include stability of the plume, degradation rates, and downgradient groundwater quality.

### **1.3 Background**

Industrial solvents (primarily 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 1.6 hectares (4 acres) in the southwestern portion of the site.

The P&T was started in 1996 and is used to control contaminated groundwater beneath the former landfill and 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.

### **1.3.1 Geology and Hydrology**

The geologic record preserved in the rocks underlying the site indicates that the area has been relatively stable since the beginning of the Paleozoic Era more than 500 million years ago. There is no evidence of subsurface structural folding, significant stratigraphic thinning, or subsurface faulting in the underlying bedrock. Limestone interbedded with shale layers comprises the uppermost bedrock units at the site. No evidence of solution cavities or cavern development has been observed in any borings or outcrops in the Miamisburg area.

The aquifer system at the Mound site consists of two different hydrogeologic environments: groundwater flow through the bedrock beneath the hills, and groundwater flow within the unconsolidated glacial deposits and alluvium associated within the BVA in the Great Miami River valley. The bedrock flow system is dominated by fracture flow and is not considered a highly productive aquifer. The BVA is dominated by porous flow with interbedded gravel deposits providing the major pathway for water movement. The unconsolidated deposits are Quaternary-age sediments consisting of both glacial and fluvial deposits. The BVA is a highly productive aquifer capable of yielding a significant quantity of water and is designated a sole-source aquifer. The general structure and flow characteristics for these two interconnected systems are depicted on Figure 1.

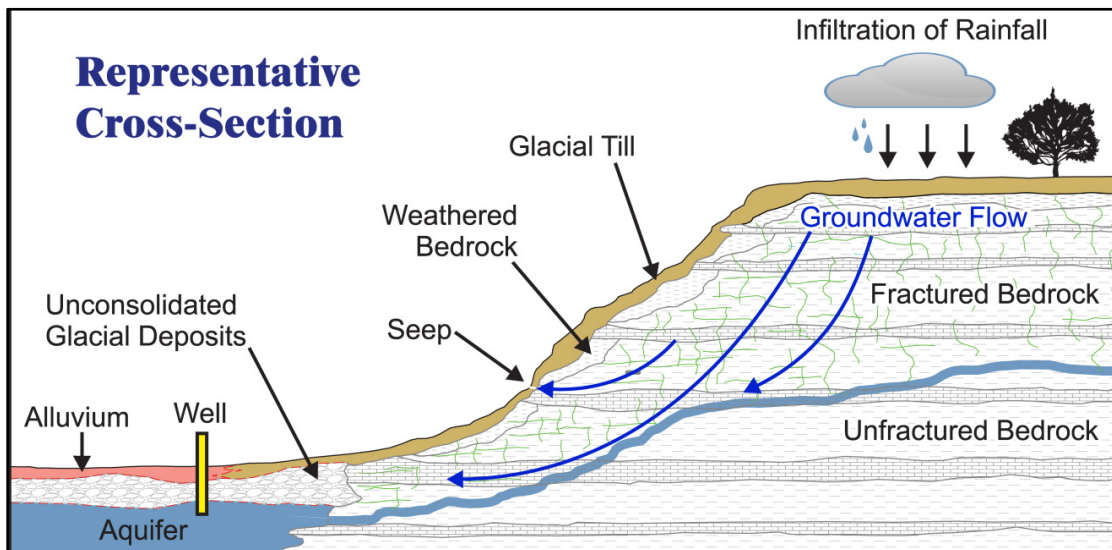


Figure 1. Generalized Cross Section Showing Bedrock Flow

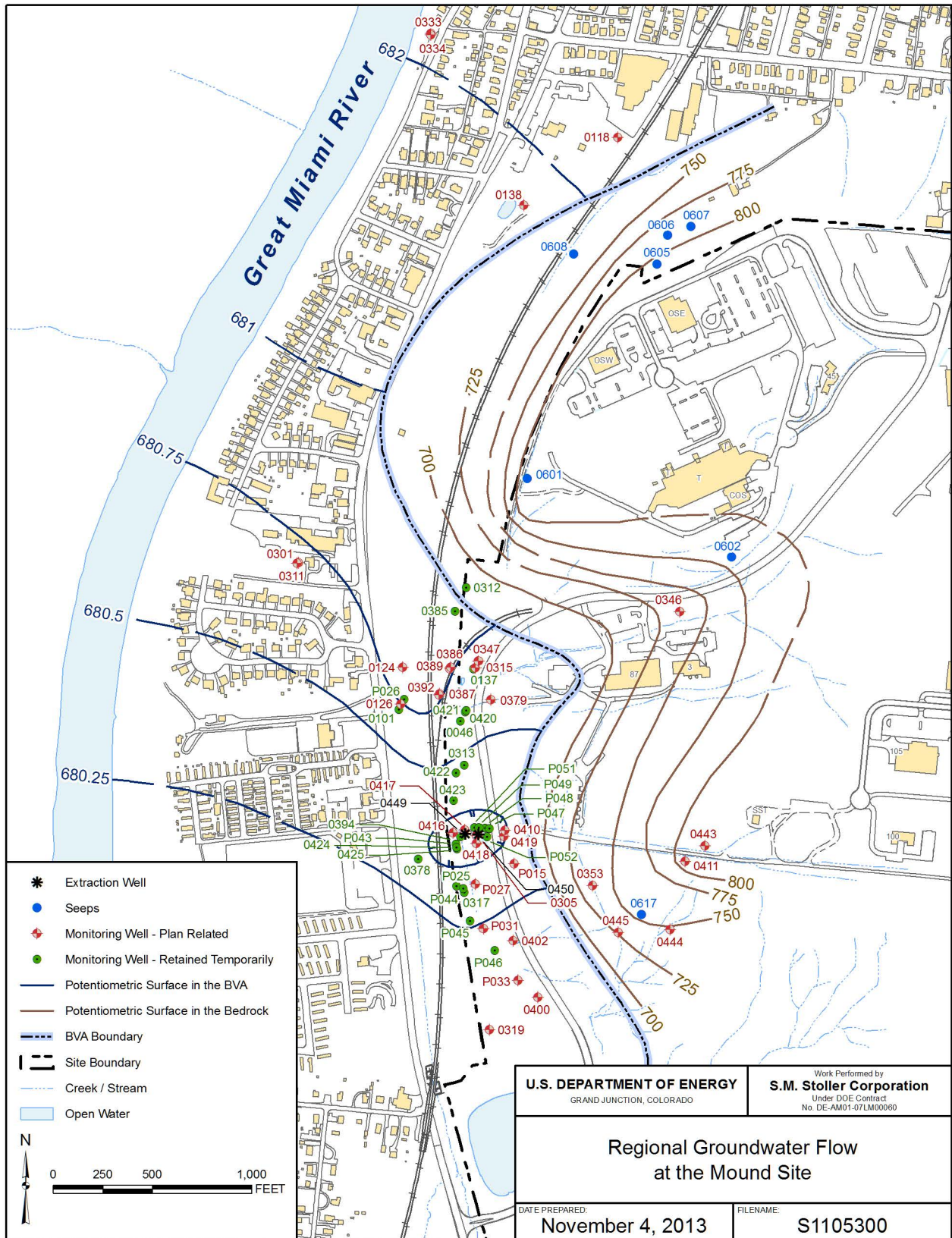
### 1.3.2 Groundwater Flow

Static water levels were measured during the May 2013 sampling event from wells in OU-1, Phase I, and Parcels 6, 7, and 8. Since these measurements were made within a short time frame, the data were used to depict the general groundwater flow in the area (Figure 2). Groundwater flow in the bedrock typically mimics surface topography; groundwater discharges to the BVA, or discharge from the upper bedrock occurs at seeps. Groundwater flow in the BVA near the Mound site is to the east and then south, following the downstream course of the Great Miami River.

Based on the lithology of the OU-1 area and the low barometric efficiencies of the monitoring wells, the outwash aquifer is considered to be unconfined. A representative hydraulic conductivity (K) value of 650 feet per day (ft/day) was determined by a constant-rate drawdown test. Based on a representative hydraulic conductivity value of 650 ft/day for the outwash aquifer and the average hydraulic gradient of 0.00024 ft/ft, a typical specific discharge (Darcy velocity or specific flux) would be 0.156 ft/day or about 57 feet per year (ft/yr). Assuming a porosity of 0.25, this is equivalent to a pore velocity of 228 ft/yr. The calculated flow direction of 152 degrees from north suggests the preferential groundwater flow pathway is to the southeast, paralleling the BVA bedrock boundary.

### 1.3.3 Aquifer Chemistry

Overall, aerobic and generally oxidizing conditions dominate the BVA groundwater system in the OU-1 area. Wells upgradient and along the fringes of the areas of VOC groundwater impact exhibit high dissolved oxygen (DO) levels and positive oxidation-reduction potential (ORP) values. This environment is maintained by recharge from the Great Miami River and infiltration of precipitation.



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Figure 2. Regional Groundwater Flow at the Mound Site

Groundwater quality data from wells within the contaminated parts of the aquifer depict lower DO concentrations and negative ORP values, indicating that anaerobic and more reducing environments occur locally (Figure 3).

#### **1.3.4 VOCs in Groundwater**

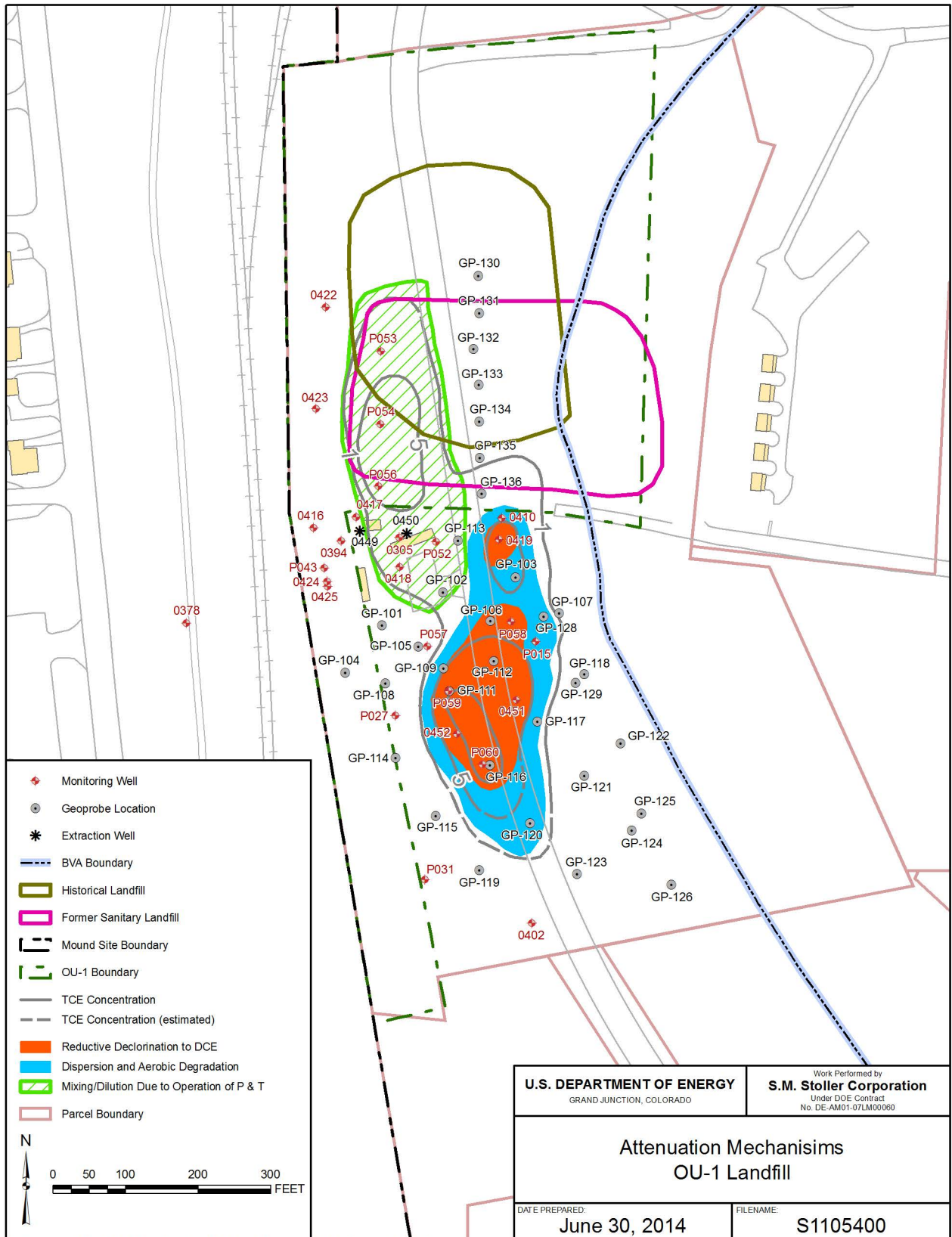
VOCs have been detected in OU-1 groundwater at concentrations greater than MCLs since routine sampling began in the 1980s. The contaminant source was determined to be the former landfill. Initially, groundwater originating beneath the landfill was influenced by the operation of the Mound Plant production wells, which resulted in the distribution of VOCs being skewed to the west as contaminated groundwater was captured by the production wells. The extent of TCE in groundwater when the P&T system started operating in 1997 is depicted in Figure 4.

The recent distribution of cVOCs (illustrated in Figure 5 using TCE data from May 2013) indicates three areas of cVOC contamination above the MCL: (1) beneath the southwest 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 zones of groundwater contamination result from the operation of the P&T system, which bisected the plume, and excavation of the former landfill, which left discrete residual source areas in the soil. The area of VOC groundwater impact downgradient of the hydraulic capture zone of the extraction wells has been held in place due to limited recharge and low hydraulic gradients.

Data collected since 1990 indicate the continued presence of cVOCs in the groundwater downgradient of OU-1, even after operation of the OU-1 P&T system (Figure 6). Concentrations of TCE have generally declined since the operation of the P&T system began in 1997. Periodic increases in TCE concentrations in some wells are linked to excavation phases and aquifer rebound following periodic P&T system shutdown.

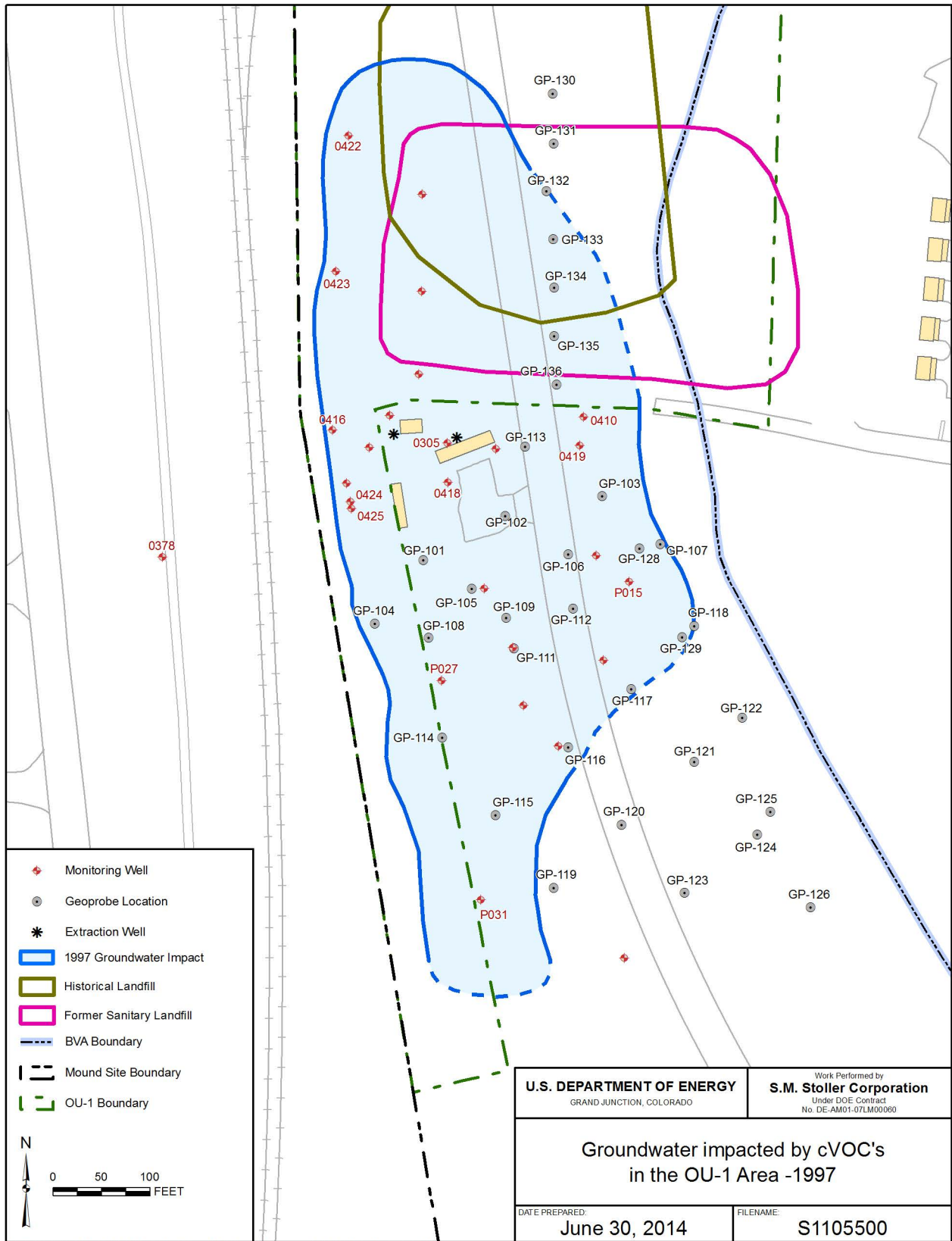
#### **1.3.5 VOCs in Soil**

From 2007 through 2010, approximately 99,500 cubic yards of materials were removed from the landfill area. The remaining soil in the OU-1 area meets the site cleanup objective for future industrial/commercial land use. The soil cleanup levels were risk-based in consideration of the industrial/commercial user and were not developed in consideration of the groundwater pathway; therefore, materials remain in the landfill footprint that may act as an ongoing source to groundwater impact. Figure 7 is a sketch of the soil concentrations measured at the completion of the OU-1 source removal activities. The areas with vadose zone TCE or PCE concentrations above 1 milligram per kilogram (mg/kg) are indicated.



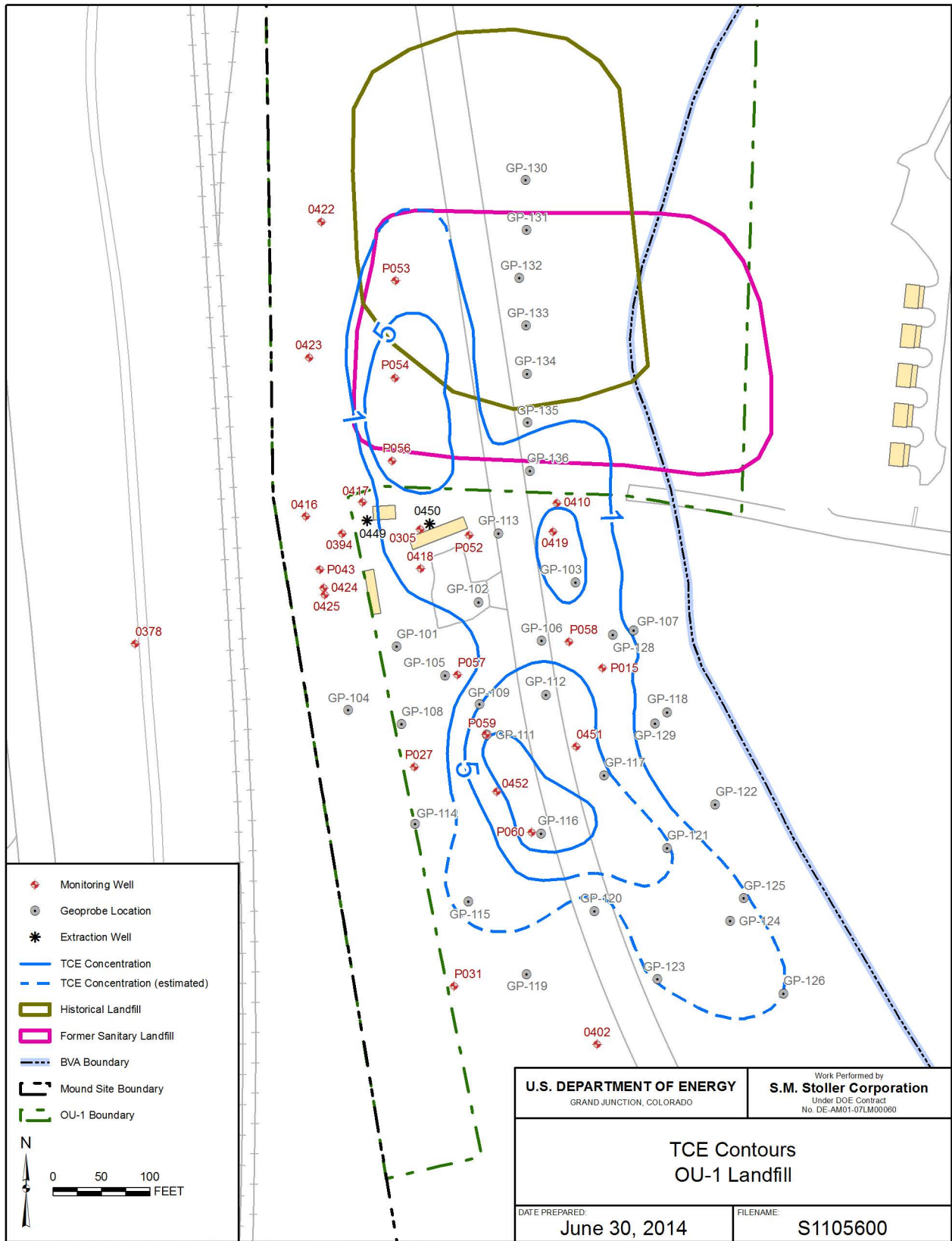
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Figure 3. Attenuation Mechanisms OU-1 Landfill



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Figure 4. Groundwater Impacted by VOCs in the OU-1 Area—1994



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Figure 5. Distribution of TCE in Groundwater in May 2013



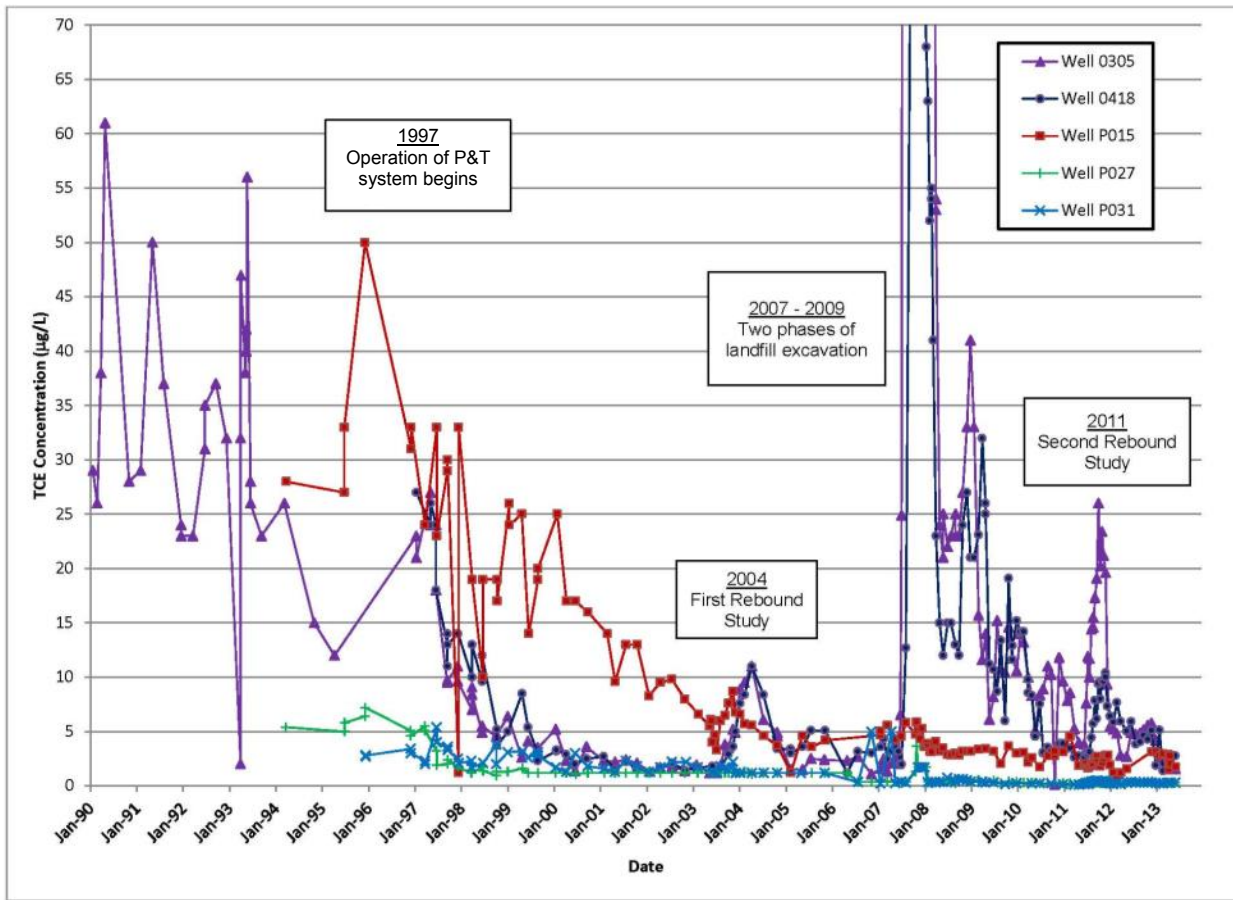
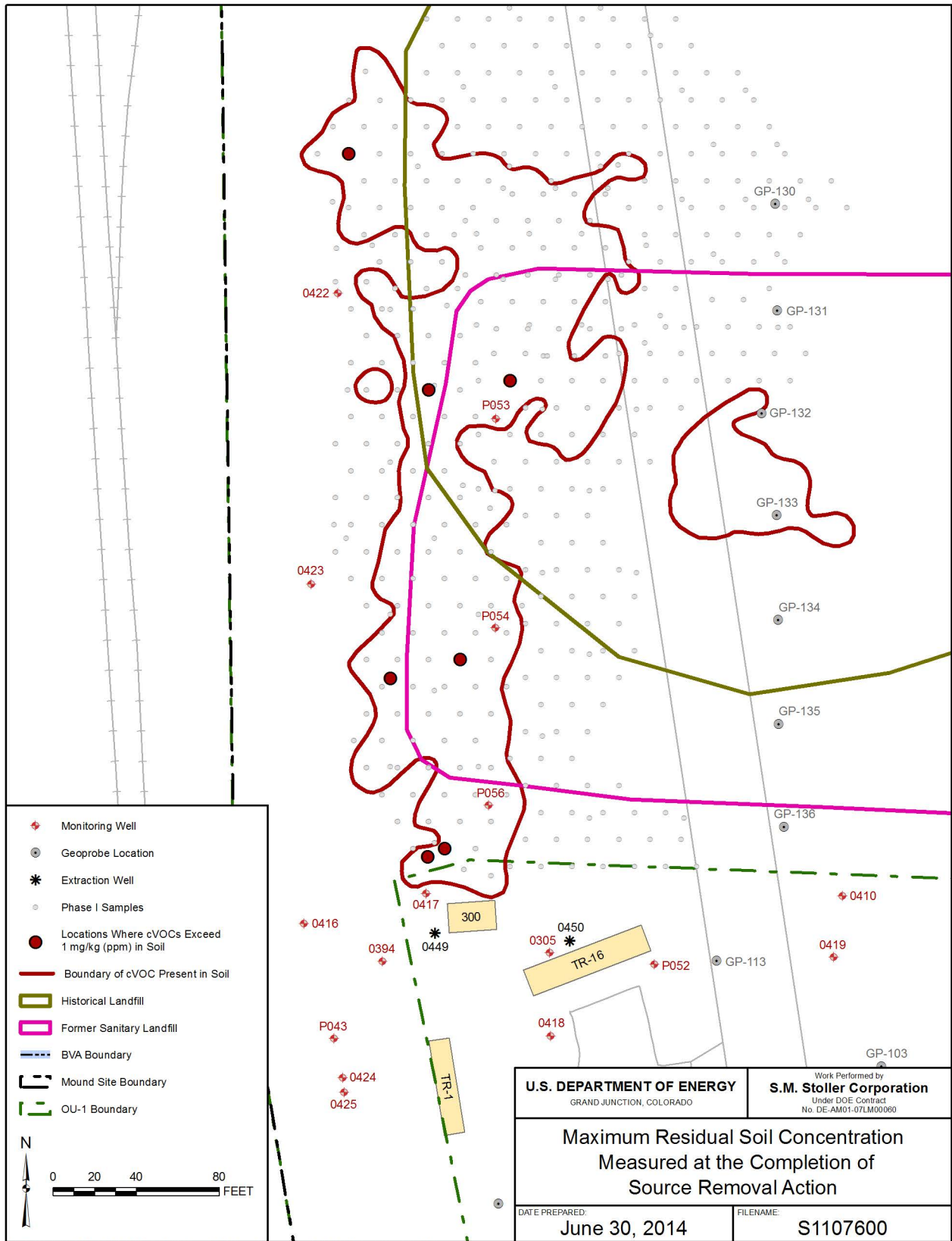


Figure 6. TCE Concentrations in Selected Wells in the OU-1 Area—1990 to 2013



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*Figure 7. Maximum Residual Soil Concentrations Measured at the Completion of the Source Removal Action*

## 1.4 Preliminary Analysis of Remedial Alternatives for OU-1 Groundwater

Information from historical investigations and the more recent testing led to the recommendation that more passive methods be considered to address the current cVOC impact in OU-1 groundwater. This could also include limited treatment of “hot spots” to reduce cVOC concentrations in portions of the soil or groundwater and to create an environment more conducive to the destruction of cVOCs.

### 1.4.1 Potential Remedial Alternatives

Three categories of alternatives for achieving remedial objectives at OU-1 are being considered to address the cVOC impact in groundwater: (1) passive methods, (2) semi-passive methods, and (3) active methods. Three remedial approaches being considered are:

- MNA: Monitoring of cVOCs and other indicator parameters to verify reduction of contaminant concentrations to MCLs in the existing attenuation zones.
- Enhanced Attenuation: Treatment of portions of the aquifer and possibly residual source areas to initially reduce cVOC concentrations and also enhance the existing attenuation zones. This treatment would be coupled with long-term monitoring of cVOCs and indicator parameters to verify reduction of contaminant concentrations to MCLs.
- P&T: Extraction of groundwater to establish hydraulic capture of cVOC-impacted groundwater and treatment until MCLs are attained. This method would be coupled with long-term monitoring of cVOCs to verify reduction of contaminant concentrations to MCLs.

Table 1 outlines remedial alternatives that would adequately address the cVOC impact in the OU-1 area as well as a baseline scenario of “no action.” Appendix A presents a summary of assumptions associated with each potential remedy and estimated durations.

*Table 1. Potential Remedial Alternatives for OU-1 Groundwater*

Alternative	Description
1. No action	No active remedy to address cVOC-impacted groundwater. Perform long-term monitoring of VOCs until concentrations meet MCLs.
2. Monitored natural attenuation	Rely on natural mechanisms (reductive dechlorination and aerobic oxidation) to decrease cVOC concentrations to MCLs. Monitor cVOCs until concentrations meet MCLs. Monitor for indicator parameters to verify that attenuation processes continue to reduce VOC concentrations. Develop contingency action of P&T using a downgradient well to address unacceptable increases in cVOCs.
3. Enhanced attenuation	Inject nutrients into the areas of higher cVOC contamination to stimulate reductive dechlorination of cVOCs in groundwater and rely on natural mechanisms (reductive dechlorination and aerobic oxidation) to further decrease cVOC concentrations to MCLs. Monitor cVOCs until concentrations meet MCLs. Monitor for indicator parameters to verify that attenuation processes continue to reduce cVOC concentrations. Develop contingency action of P&T using a downgradient well to address unacceptable downgradient increases in cVOCs.
4. P&T in OU-1 near-field	Extract cVOC-impacted groundwater in the OU-1 near-field using wells 0449 and 0450 and treat with air stripper in Building 300. Monitor cVOCs until concentrations meet MCLs.
5. P&T in OU-1 far-field	Extract cVOC-impacted groundwater in the OU-1 far-field using well 0452 and treat via air stripper in Building 300. Monitor cVOCs until concentrations meet MCLs.

## 1.4.2 Remedial Alternative Considered for the Field Demonstration

Consistent with the current conditions, *enhanced attenuation*—an engineering and regulatory strategy that has recently been developed by the Interstate Technology and Regulatory Council in a *Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation at Sites with Chlorinated Organic Plumes* (see Figure 17 in Section 6.1) is being considered to address the cVOC contamination in OU-1 groundwater. Enhanced attenuation uses active engineering solutions to alter the target site in such a way that the contaminant plume will passively stabilize and shrink; monitoring will verify that the action is effective, timely, and sustainable. The strategy recognizes that attenuation remedies are fundamentally based on a mass balance. Thus, long-term plume dynamics can be altered either by reducing the contaminant loading from the source or by increasing the rate of natural attenuation processes within all or part of the plume volume.

The combination of technologies that emerged for OU-1 includes (1) neat (pure) vegetable oil deployment in the deep vadose zone in the former source area, (2) emulsified vegetable oil deployment within the footprint of the groundwater plume, and (3) monitoring of concentration trends, attenuation mechanisms, and rates in the plume. In the first part, neat oil spreads laterally and forms a thin layer on the water table beneath presumptive soil sources to intercept and reduce future cVOC loading (via partitioning) and reduce oxygen inputs to the local groundwater (via biostimulation). In the second and third parts, emulsified oil forms active bioremediation reactor zones within the plume footprint to degrade existing groundwater contaminants (via reductive dechlorination and/or cometabolism) and stimulates long-term attenuation capacity in the distal plume (via cometabolism).

As depicted in Figure 8, edible oil deployment results in the development of structured geochemical zones and serves to decrease chlorinated compound concentrations in two ways: (1) physical sequestration, which reduces effective aqueous concentration and mobility, and (2) stimulation of anaerobic, abiotic, and cometabolic degradation processes. In the near-source deployment area, contaminants initially partition into the added oil phase. Biodegradation of the added organic substrate depletes the aquifer of oxygen and other terminal electron acceptors and creates conditions conducive to anaerobic degradation processes. The organic substrate is fermented to produce hydrogen, which is used as an electron donor for anaerobic dechlorination by organisms such as *Dehalococcoides*. Degradation (daughter) products leaving the treatment zone are amenable to aerobic oxidation and abiotic degradation. Further, the organic compounds leaving the deployment zone (e.g., methane and propane) stimulate and enhance downgradient aerobic cometabolism, which degrades both daughter compounds and several parent cVOCs. Figure 8 depicts TCE concentration reduction processes along with their corresponding breakdown products in a structured geochemical zone scenario.

The OU-1 area is uniquely suited for this type of remedial approach, given that the average linear velocity of groundwater is low and there are no nearby receptors. The low groundwater velocity allows for longer residence time for attenuation mechanisms within the treatment zones to reduce cVOC concentrations in groundwater and adequate time to react to changed conditions before groundwater could migrate offsite. It is estimated that the longevity of the oil in the OU-1 area will exceed the expected period of mass discharge of residual cVOCs from the vadose zone and upgradient residual sources. This estimation of the time frame before full utilization of the oil to

sequester and attenuate cVOCs in OU-1 groundwater is presented in Appendix B. Also, ICs restricting groundwater use eliminate the possibility of future onsite receptors.

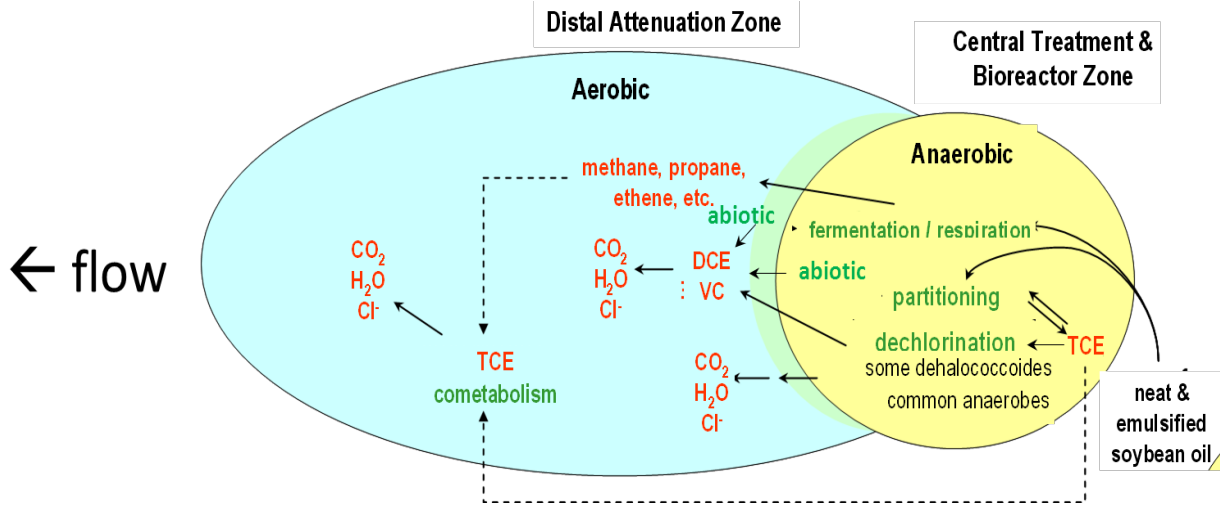


Figure 8. Schematic of TCE Concentration Reduction Processes

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## 2.0 Enhanced Attenuation Using Edible Oils

Edible oils have emerged as an effective treatment to enhance anaerobic bioremediation and sequestration of chlorinated solvent contamination in groundwater. Traditionally, active remedial approaches such as P&T have been applied, but active technologies are inefficient in achieving final remediation goals where mass transfer of contaminants from secondary and tertiary sources is occurring. Use of edible oils at sites with relatively low contaminant concentrations has proven to be a cost-effective alternative for treatment of residual contamination in the saturated zone. Edible oils can be deployed to form structured geochemical zones—a series of reaction zones that provide sequential anaerobic and aerobic conditions to maximize beneficial performance, constrain the amount of reagent addition, and minimize collateral impacts of the remediation.

A detailed document will be prepared that outlines the specific material and equipment requirements necessary to deploy the neat and emulsified oils in order to meet the design criteria presented in this document. The document will also include specific locations and construction details for the temporary wells that will deploy the edible oils.

### 2.1 Field Demonstration Objectives

The overall objectives of the field demonstration are to:

- Assess the performance and viability of attenuation using structured geochemical zones as a remediation strategy for OU-1 groundwater.
- Stabilize the plume and minimize/mitigate the potential for plume growth.
- Develop the biogeochemical conditions to accelerate progress to remedial objectives and transition the strategy to MNA.

Enabling objectives for the field demonstration include:

- Monitor oil and amendment emplacement along with responses in groundwater biogeochemistry.
- Determine cVOC degradation and degradation rates.
- Assess degradation (daughter) products and their subsequent degradation.
- Assess degradation pathways (reductive dechlorination, cometabolism, abiotic).
- Assess the recruitment of appropriate bacteria (i.e., fermentative, dechlorination, and cometabolic) and biomass.
- Assess the ability of the oil deployment to stabilize and shrink the groundwater plume and to provide a sustainable treatment to meet the cleanup level of 5 micrograms per liter TCE.
- Determine long-term operation, maintenance, and monitoring requirements.

### 2.2 Deployment Design

The design for this enhanced attenuation field demonstration focuses on transition from active remediation of cVOCs in OU-1 groundwater to an attenuation-based remedy. The design is derived from two mechanisms—partitioning and degradation—combined with standard

hydrology and engineering calculations. The current configuration of OU-1 influenced the assumptions used in developing this design, which is based on data from previous studies and from existing wells. The deployment will rely on these existing wells (along with strategic additional monitoring locations) for tracking the performance and progress of the cleanup.

Details of the injection point construction and oil deployment methods will be prepared that emphasize the strategic application of edible oils to address residual secondary cVOC sources in soil beneath the former landfill as well as downgradient tertiary sources. Further, the design of the injection points will consider site lithostratigraphy and the water table surface to assist in developing deployment zones that have the correct geometry to intercept contaminants and effectively treat the groundwater plume. During the deployment phase, the P&T system will continue to be operated. However, imperative to this field demonstration is that the P&T system will not be operated post-deployment (starting 3 to 4 months after injection), allowing for the natural movement of groundwater through the treatment areas. This will simulate the conditions that would be present during an MNA remedy. The P&T system will be placed on standby and considered as part of the contingency planning (Section 5).

The result of the conceptual design process is a two-part deployment: (1) neat (pure) vegetable oil at the water table beneath areas with the highest residual cVOC concentrations in soil and (2) emulsified vegetable oil substrate in the areas of highest concentrations of cVOCs in the groundwater plume. In the first part, neat oil injected into the vadose zone spreads laterally and forms a thin layer on the water table to intercept and reduce future cVOC input from residually contaminated soils in the vadose zone (Figure 9). In the second part, emulsified oil injected below the water table stimulates the formation of an active bioremediation treatment zone within the active plume footprint to degrade existing groundwater contamination and any future inputs (Figure 10).

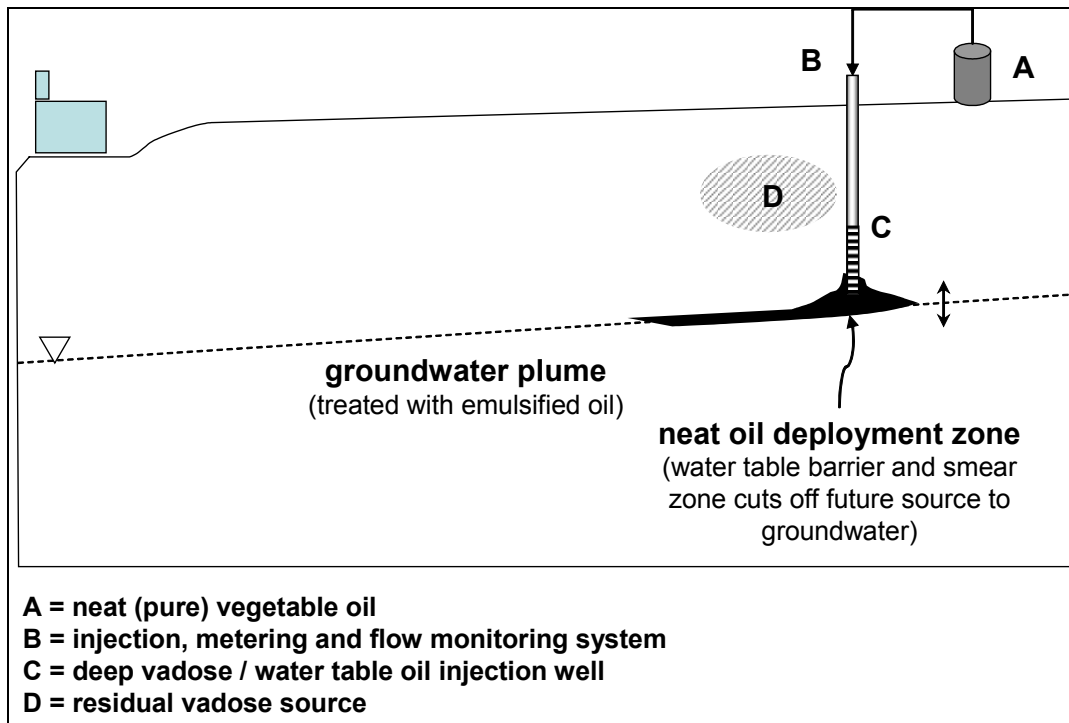


Figure 9. Schematic Diagram of Neat Oil Deployment



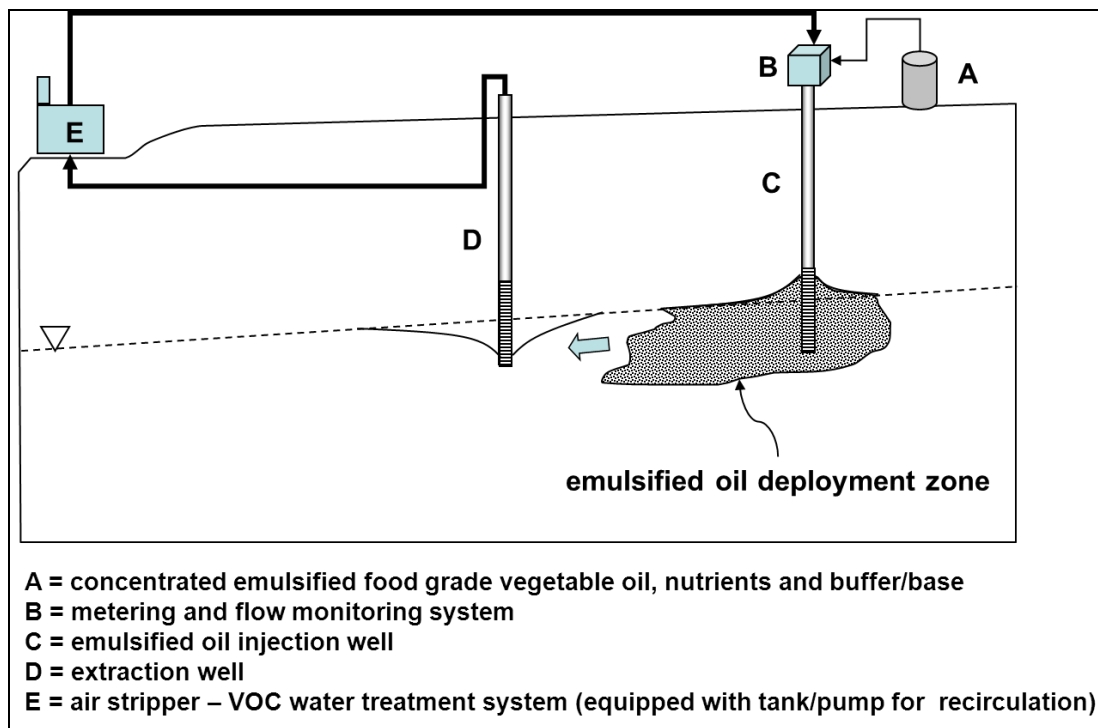


Figure 10. Schematic Diagram of Emulsified Oil Deployment

Key factors that will be considered in the site-specific implementation for the field demonstration are:

- Downgradient: Intensive emulsified oil injection in multiple locations to address the “downgradient” plume of cVOC groundwater contamination in the OU-1 far-field (i.e., near well P060). This will generate a number of anaerobic treatment zones that will promote biotreatment and partitioning and will further limit downgradient plume expansion.
- Former Source Area: Strategic infusion of neat oil into the lower portion of the vadose zone in the areas with “high” measured soil concentrations (e.g., the seven locations with measured concentrations above 1 mg/kg TCE or PCE). This oil will spread on the water table and form a barrier to reduce the mass discharge rates into the groundwater from the residual vadose zone secondary sources.
- Former Source Area: Strategic emulsified oil injection in the groundwater to form treatment zones that address key flow lines in the groundwater flowing beneath the former landfill area. These treatment zones will limit the rebound in cVOC concentrations between the P&T extraction wells and wells P015 and P027.
- All areas: The emulsified oil will be injected at locations that are a sufficient distance from existing P&T wells (0449 and 0450) and potential future recovery wells (0452) to allow these wells to operate in the future as a containment contingency.

## 2.3 Equipment and Materials

The logistics for the edible oil injection are summarized in Figure 11, which depicts the three major phases of this field demonstration—preparation, deployment, and monitoring. The Mound Core Team is integrated into the process during all three stages; initially as part of the design process (preparation of this work plan), then to assess the deployment monitoring data, and finally to periodically review progress and/or respond to changed conditions that may result in contingency actions.

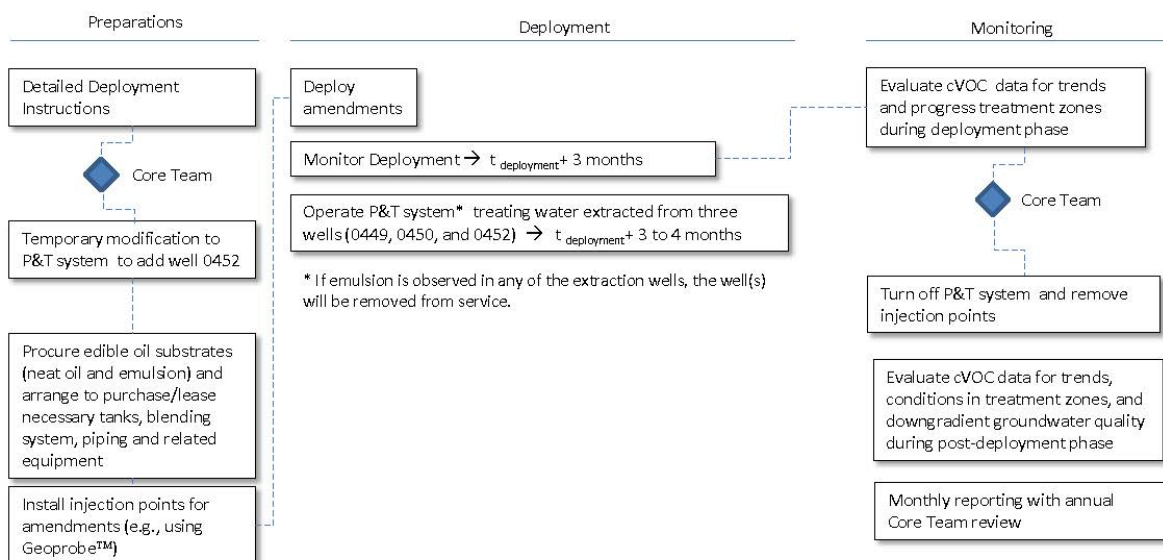


Figure 11. Deployment Project Planning and Implementation Schedule

The key steps for full-scale deployment are as follows:

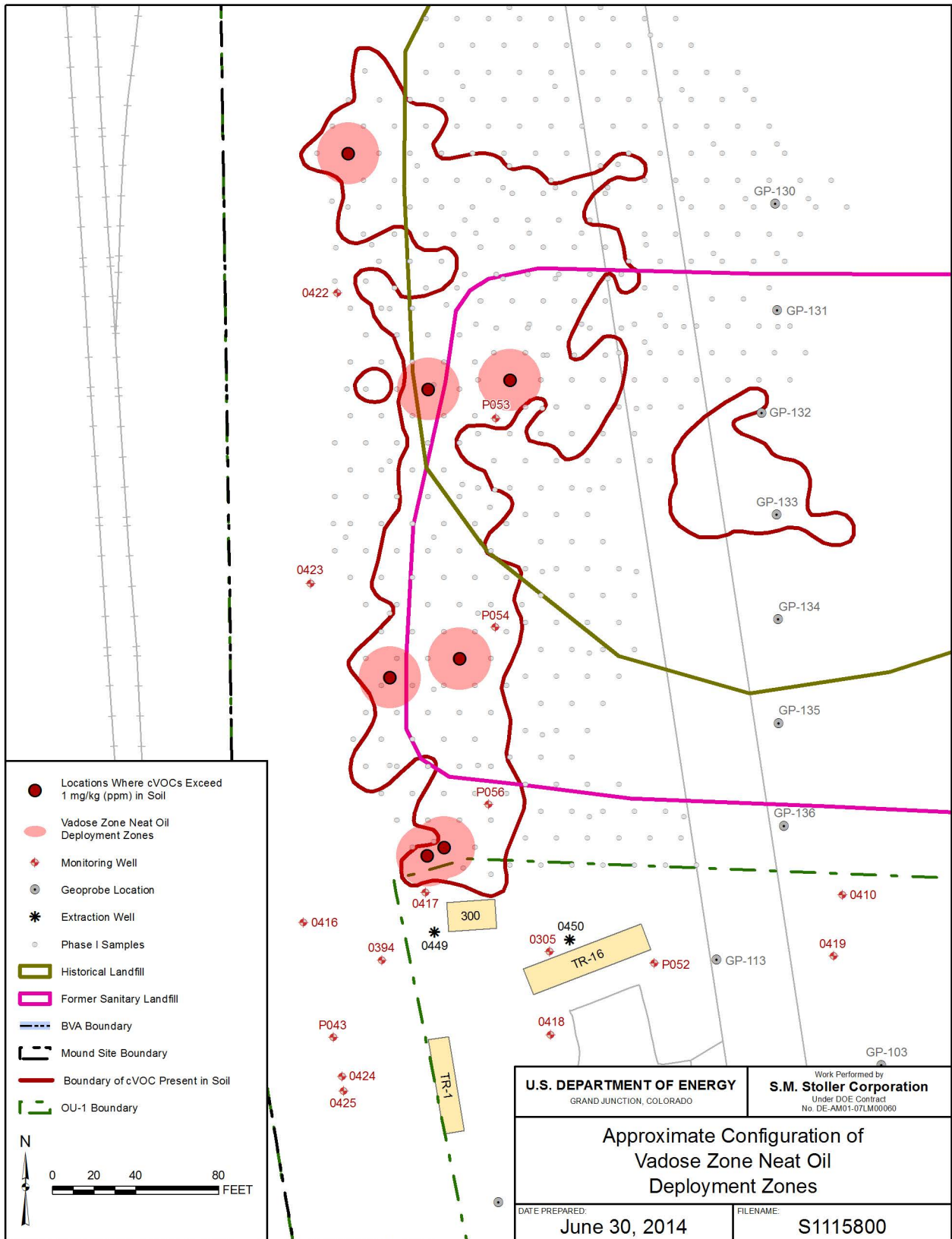
### Neat Oil at the Water Table

- Description of deployment:
  - Emplace a “sheet” of oil at the water table beneath residual vadose sources using a deep vadose zone well completed just above the water table in each of the six areas with soil contamination above 1 mg/kg (as measured following the waste removal activities).
  - Deployment method—Gravity feed with an assumed flow rate of 0.5 to 2.0 gallons per minute in each location.
  - Procure neat food-grade soybean oil and stage onsite using “farm wagons” or flatbed trailers (to elevate the containers/totes above ground level).
  - The subsurface deployment relies on the characteristics of the oil (density and transport properties) and interactions with the water table and capillary fringe to generate the desired thin, laterally distributed configuration.
- Quantity of oil: approximately 4,800 gallons of food-grade soybean oil—approximately 800 gallons per location.

- Zone of influence: approximately 30 to 35 ft diameter assuming listed oil volume and approximate porosity = 0.25, residual oil saturation after stabilization = 0.1, stabilized thickness of oil layer = 1 ft (Figure 12).
- Approximate field time needed for deployment: 5 to 10 days.

#### Emulsified Oil in the Groundwater Plume

- Description of deployment:
  - Modify P&T system to add well 0452. This will help mitigate the potential to spread contamination downgradient during the injection operations near well P060. Use treated water from the P&T system to provide treated water for use in deploying the emulsified oil amendment.
  - Procure emulsified oil amendment (see further description below).
  - Lease amendment blending and distribution equipment (e.g., mechanical proportioning valve and distribution manifold) to allow simultaneous deployment in multiple locations.
  - Operate P&T system using wells 0449, 0450, and 0452 during deployment and until treatment zones are confirmed (approximately 3 months after injection is completed).
  - Deployment method: Mechanical proportioning system (e.g., Dosatron) to deliver emulsion and dilution water in a ratio of approximately 50:1 (water:std emulsion).
- Total quantities of emulsion and water: Emulsion—approximately 5,700 gallons (47,000 pounds) distributed to approximately 19 locations (335 gallons of emulsion per location). Total treated groundwater for blending—approximately 285,000 gallons distributed to approximately 19 locations (16,750 gallons per location).
- Emulsion characteristics prior to dilution—factory-prepared emulsion containing approximately 45 percent soybean oil, carbon substrate initiators (e.g., lactate), appropriate emulsifiers, vitamin B1, and nutrients (e.g., yeast extract). Emulsion shall have median droplet size  $\leq 1$  micrometer and be commercially available reagent with a documented record of successful use.
- Approximate field time needed for deployment: 30 to 45 days.
- Zone of influence: deployment zone diameter approximately 20 ft calculated two ways: (1) based on oil retention of approximately 0.1 pound oil per cubic foot of aquifer, and (2) based on total injected water/emulsion volume, a 20 to 30 ft screen length, and a porosity of 0.25 (Figure 13).



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Figure 12. Approximate Configuration of Vadose Zone Neat Oil Deployment Zones

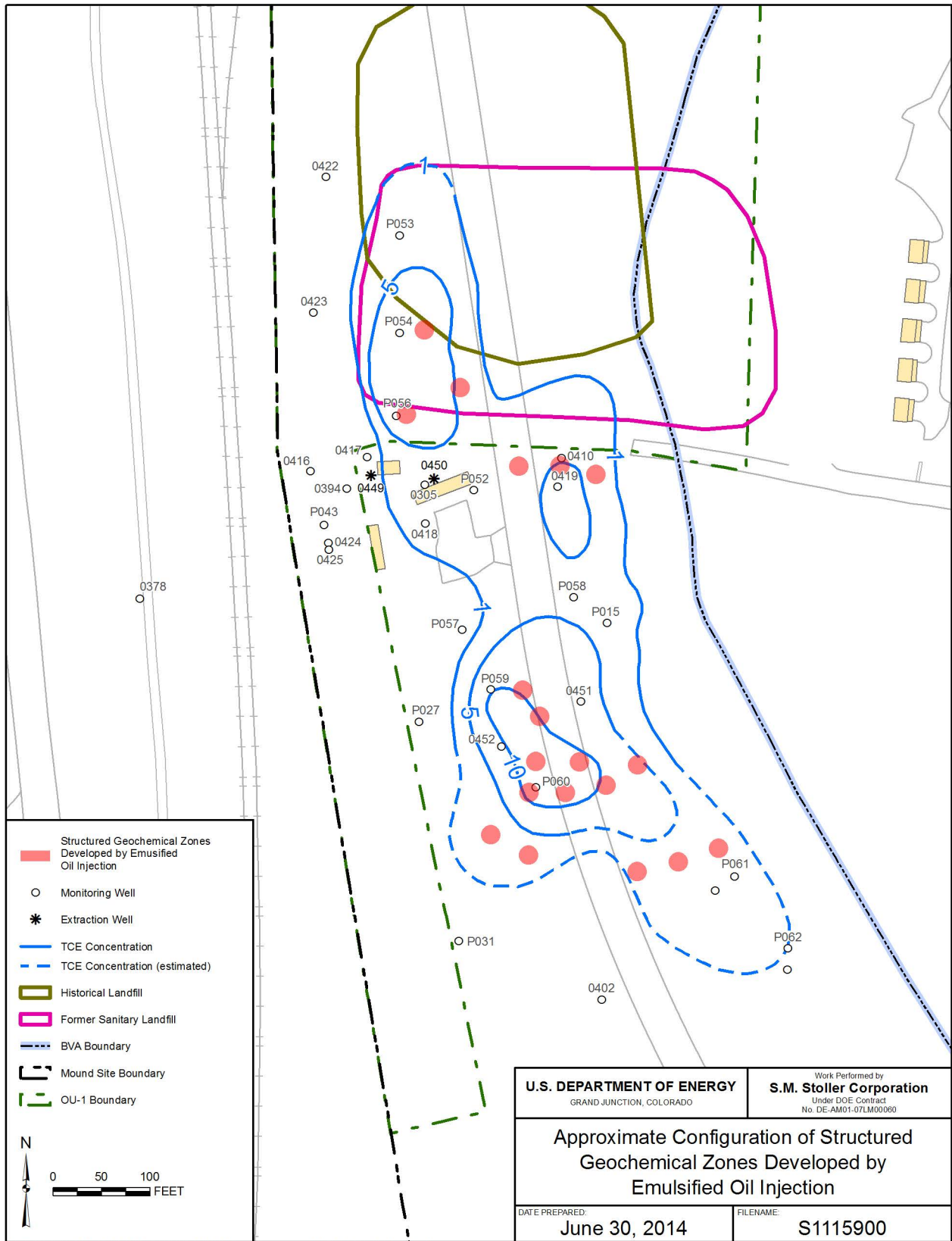


Figure 13. Approximate Configuration of Structured Geochemical Zones Developed by Emulsified Oil Injection

The deployment zones are distributed throughout the plume to achieve the following objectives:

- Former landfill area (three locations): provide treatment of existing groundwater contamination and future mass discharge into the groundwater beneath the residual soil sources.
- Mid plume (three locations): limit the magnitude of rebound within the plume.
- Downgradient contaminated zone (eight locations): provide treatment of the contaminated groundwater near well P060.
- Distal zone (five locations): provide additional protection to limit plume expansion.

## 3.0 Groundwater Monitoring Approach

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:

- Demonstrate neat and emulsified oil emplacement within the treatment zones.
- Indicate changes in the treatment zones to anaerobic.
- Indicate cometabolic and abiotic conditions along the lateral and distal portions of the treatment zones.
- Reduce 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 groundwater monitoring is to collect data to:

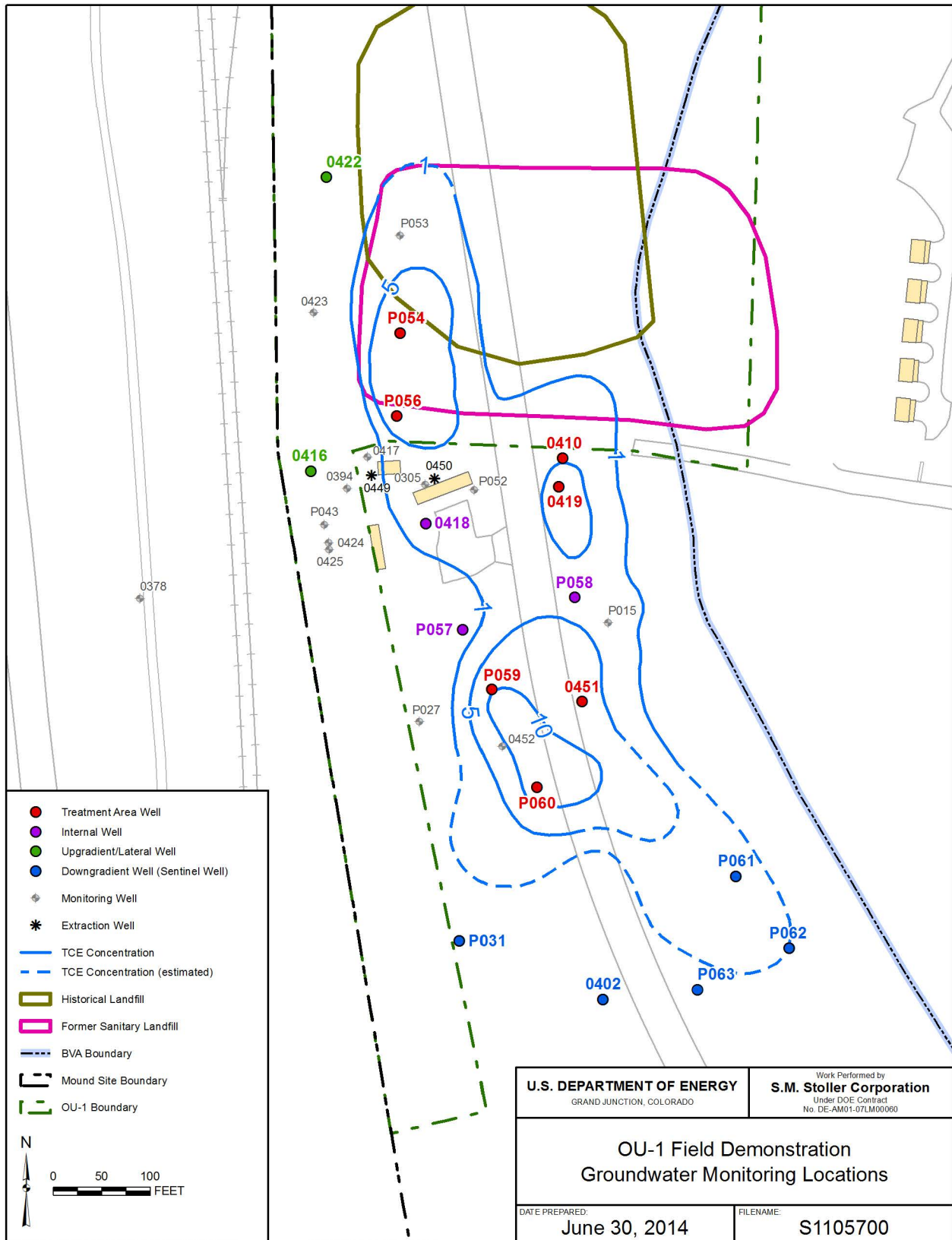
- Evaluate the performance of the attenuation-reduction of parent constituents, presence of degradation (daughter) products, and presence of anaerobic and aerobic geochemical zones.
- Determine degradation rates.
- Ensure that groundwater quality does not degrade downgradient of the treatment zones.

Evaluation of the data is outlined in Section 4, and contingency actions are outlined in Section 5. A Sampling and Analysis Plan will be prepared in advance of this fieldwork that will describe sample collection and analysis to support this field demonstration.

### 3.1 Sampling Locations

Groundwater samples will be collected from 17 wells in the OU-1 area (Figure 14). Monitoring wells will be divided into the following categories:

- Treatment area 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; location 0422 is located immediately upgradient of the area of groundwater impact within the former landfill footprint. Monitoring location 0416 is located along the western edge of OU-1 where recharge from the Great Miami River enters the OU-1 area.
- 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 wells are used to monitor rebound that may 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, P062, and P063 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 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 and provide early detection of plume expansion.



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Figure 14. Groundwater Monitoring Locations



The remaining OU-1 Area wells (0305, 0417, 0423, 0424, 0425, 0452, P015, P027, P031, 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.

### 3.2 Analytes and Sampling Frequencies

Table 2 shows the classes of samples and specific analytes that will be analyzed to evaluate the monitoring objectives.

Table 2. Sampling Class and Measured Parameters

Sampling Class	Analytes and Parameters Measured
VOCs	PCE, TCE, <i>cis</i> -1,2-dichloroethene (DCE), <i>trans</i> -1,2-DCE, vinyl chloride,
Indicator parameters	pH, conductivity, DO, ORP, temperature, turbidity, alkalinity
Anions	Nitrate, sulfate, chloride, bromide
Light hydrocarbons	Ethane, ethene, methane
Dissolved gases	Carbon dioxide, nitrogen
Other	Total organic carbon, ammonia, iron
Neat oil	Floating oil location and thickness
Microbial analysis	Quantitative polymerases chain reaction for fermentative, dechlorinating, and cometabolic bacteria

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 it is determined that the zones have been established and concentrations of the parent cVOCs have declined, post-deployment monitoring will be performed, and sampling frequencies will be decreased. The details for both phases of monitoring (deployment and post-deployment) will be outlined in the Sampling and Analysis Plan.

### 3.3 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, recommendation may be made to further reduce the frequency of these measurements, if appropriate.

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## 4.0 Data Evaluation

The sampling strategy was designed to provide sufficient data to meet the field demonstration objectives. As described in Section 3, measurements will be made in a representative set of wells within and outside the treatment zones and downgradient of the treatment zones. The data generated from the sampling events will be evaluated as outlined in the following sections.

### 4.1 Effectiveness of the Enhanced Attenuation Zones

The goal of the field demonstration is to create treatment zones by injecting edible oil (neat and emulsified) into the subsurface, initially reducing the concentrations of PCE and TCE and over time stimulating existing attenuation processes to further degrade cVOCs. Data collected from selected monitoring wells will be evaluated to determine if the use of emulsified oils to enhance the attenuation processes is viable in OU-1.

The effectiveness of the oil treatment will be discussed in terms of lines of evidence similar to those outlined in EPA's document *Use of Monitored Natural Attenuation at Superfund, RCRA, Corrective Action, and Underground Storage Tank Sites* (OSWER 9200.4-17P) to evaluate the use of MNA as a remedy. The lines of evidence are:

First Line of Evidence: Historical groundwater data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time and the presence of degradation (daughter) products at appropriate monitoring points. This typically includes graphical techniques using the VOC data and statistical tests, such as the Mann-Kendall test.

Second Line of Evidence: Hydrogeologic and geochemical data that can be used to demonstrate indirectly the types of natural attenuation processes at the site and the rate at which such processes will reduce contaminant concentrations to required levels. Example analytes include competing electron acceptors (e.g., oxygen, sulfate, and nitrate), helpful electron donors (e.g., hydrocarbons and hydrogen), and diagnostic indicators/byproducts (e.g., methane and iron).

Third Line of Evidence: Other information, such as data from field or microcosm studies, which directly demonstrate or quantify the occurrence of a particular natural attenuation process and ability to degrade contaminants of concern.

#### 4.1.1 First Line of Evidence: Mass and Concentration Plots

Plume stability is an important concept to an MNA remedy. Some rebound in the middle part of the plume (between the P&T extraction wells and wells P015 and P027) is expected in the first year of the field demonstration following shutdown of the P&T system and may result in transient increases in overall plume mass or local concentration increases. These increases are expected to stabilize and then follow a decreasing trend. Time-series concentration data at individual wells and plume-wide trends will be used to evaluate the stability of the area of cVOC impact in groundwater. These data trends will be evaluated using approaches similar to those in the decision-support software MAROS (developed by Aziz et al.). An overview of the MAROS approaches used for data evaluation is provided in Appendix B.

## Individual Well Trends

Concentrations of cVOCs over time will be plotted to assess the changes in concentrations after treatment with neat and emulsified oils. Nonparametric tests such as the Mann-Kendall test are suitable for analyzing data that do not follow a normal distribution. Nonparametric methods focus on the location of the probability distribution of the sampled population rather than the specific parameters of the population. The Mann-Kendall test for trend is a nonparametric test that has no distribution assumptions, and irregularly spaced measurement periods and missing data are permitted. The advantage of this approach involves the cases where outliers in the data would produce biased estimates when using parametric trend tests (such as a least squares estimated slope). The Mann-Kendall statistic (S) measures the trend in the data and can indicate the potential presence of increasing or decreasing concentrations at a given location. A confidence in the contaminant trends, which represents the probability that the contaminant concentrations are increasing or decreasing, can be estimated.

## Plume Stability

Confirmation of the effective performance of MNA requires the demonstration of a stable or shrinking plume based on historical and performance monitoring data. Moment analysis is used to estimate:

Zero-th Moment: A mass estimate of a contaminant for a sampling event. The estimated mass is used to evaluate the change in the total mass of the area of groundwater impact over time. These estimated masses can be trended to evaluate the change in mass over time.

First Moment: An estimate of the center of mass of a contaminant plume ( $x$  and  $y$  coordinates) for a sampling event. The center of mass locations indicate the movement of the center of mass over time. The locations can be trended to evaluate the movement of the center of mass from a baseline center of mass location.

Second Moment: An estimate of distance of contamination from the center of mass. The distance represents the spread of the plume over time. These distances from the center of mass can be trended to evaluate the change in plume spread over time.

### **4.1.2 Second Line of Evidence: Geochemical Footprint**

Geochemical data will be used to indicate the presence of appropriate geochemical conditions in the different areas within the structured geochemical zones. In the anaerobic areas, conditions must be conducive to reductive dechlorination, and surrounding and distal plume aerobic zone conditions must be appropriate for cometabolism and oxidation.

## Reducing Conditions in the Area of Deployment

Reductive dechlorination of PCE and TCE generally requires conditions reducing enough to promote methanogenesis (anaerobic respiration). Measurements that may indicate redox conditions include ORP, DO, dissolved iron, nitrate, ammonia, and sulfate.

Data collected in the OU-1 area will be evaluated for the following to determine the presence of a reducing environment in the anaerobic treatment zones:

ORP	Low ORP is being maintained in the anaerobic treatment zones
Dissolved Oxygen	Low DO is being maintained in the anaerobic treatment zones
Methane	Methane has reached saturation levels in some wells in the anaerobic treatment zones
Dissolved Iron	High dissolved iron concentrations are indicative of reducing conditions
Ammonia/Nitrate	Under strongly reducing conditions, microbial reactions will convert nitrate to ammonia
Sulfate	Dissolved sulfate in groundwater may inhibit reductive dechlorination of solvents
Appearance	Groundwater from wells within the anaerobic treatment zones may have an odor and orange-colored water, which are indicative of reducing conditions

#### Cometabolic Conditions Surround and Distal from Deployment

Aerobic cometabolism has the ability to remediate low solvent concentrations in groundwater to nontoxic end products (CO<sub>2</sub> and Cl<sup>-</sup>). Cometabolic bioremediation relies on an appropriate primary substrate (light hydrocarbon or aromatic organic compounds), DO (electron acceptor), nutrients, and the appropriate microorganisms. Cometabolic organisms for TCE destruction use other growth substrates (total organic carbon [TOC], methane, propane, butane, ethene, aromatic natural organic matter, and ammonia) to produce enzymes capable of degrading TCE to the end products.

Data collected in the OU-1 area will be evaluated for the following to determine the occurrence of cometabolism in the aerobic treatment zones:

TOC	Increasing TOC concentrations in the downgradient aerobic zones
Methane	Increasing methane concentrations in the downgradient aerobic zones
Ethene	Increasing concentrations in the downgradient aerobic zones
Ammonia	Increasing ammonia concentrations in the downgradient aerobic zones
Dissolved Oxygen	Decreasing DO concentrations are expected in the downgradient aerobic zones

#### **4.1.3 Third Line of Evidence: Demonstration of Attenuation Processes**

The third line of evidence uses data from groundwater sampling events or microcosm studies that directly demonstrate or quantify the occurrence of a particular attenuation process and/or the ability to degrade the VOCs.

## Reductive Dechlorination

The following data will be evaluated to determine if reductive dechlorination is occurring in the deployment zones:

VOC degradation products	Presence of degradation products (namely <i>cis</i> -1,2-DCE) in the anaerobic treatment zones
Microorganisms	Presence of methanogenic and methanotrophic bacteria in the anaerobic treatment zones

## Cometabolism

The following data will be evaluated to determine if cometabolism is occurring:

Microorganisms	Presence of bacteria that are capable of producing oxygenase enzymes such as methane mono-oxygenase, toluene mono-oxygenase, toluene dioxygenase
Other	Limited extent of anaerobic VOC degradation products in areas outside of anaerobic treatment zones

## **4.2 Degradation Rates**

The overall impact of natural attenuation processes can be assessed by evaluating the rate at which contaminant concentrations are decreasing either spatially or temporally. First-order attenuation rate constants can be important tools for evaluating natural attenuation processes for groundwater contamination and can aid in determining remediation time frames. These attenuation rates can be used in characterizing plume behavior or the time required for achieving MCLs. Data can be evaluated in two ways to determine attenuation rates: (1) concentration versus time and (2) concentration versus distance. Attenuation rates will be determined using EPA's *Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies*.

### **4.2.1 Concentrations vs. Time Attenuation Rate Constant**

Concentration versus time rate constants ( $k_{\text{point}}$ ) are used for estimating how quickly remediation goals will be met at a specific location within the area of impact. This attenuation rate constant, in units of inverse time, is derived as the slope of the natural log of the concentration versus time curve measured at a selected monitoring location. Attenuation rates will be determined for the following wells (Figure 15): 0410, 0419, 0451, P054, P056, P059, and P060.

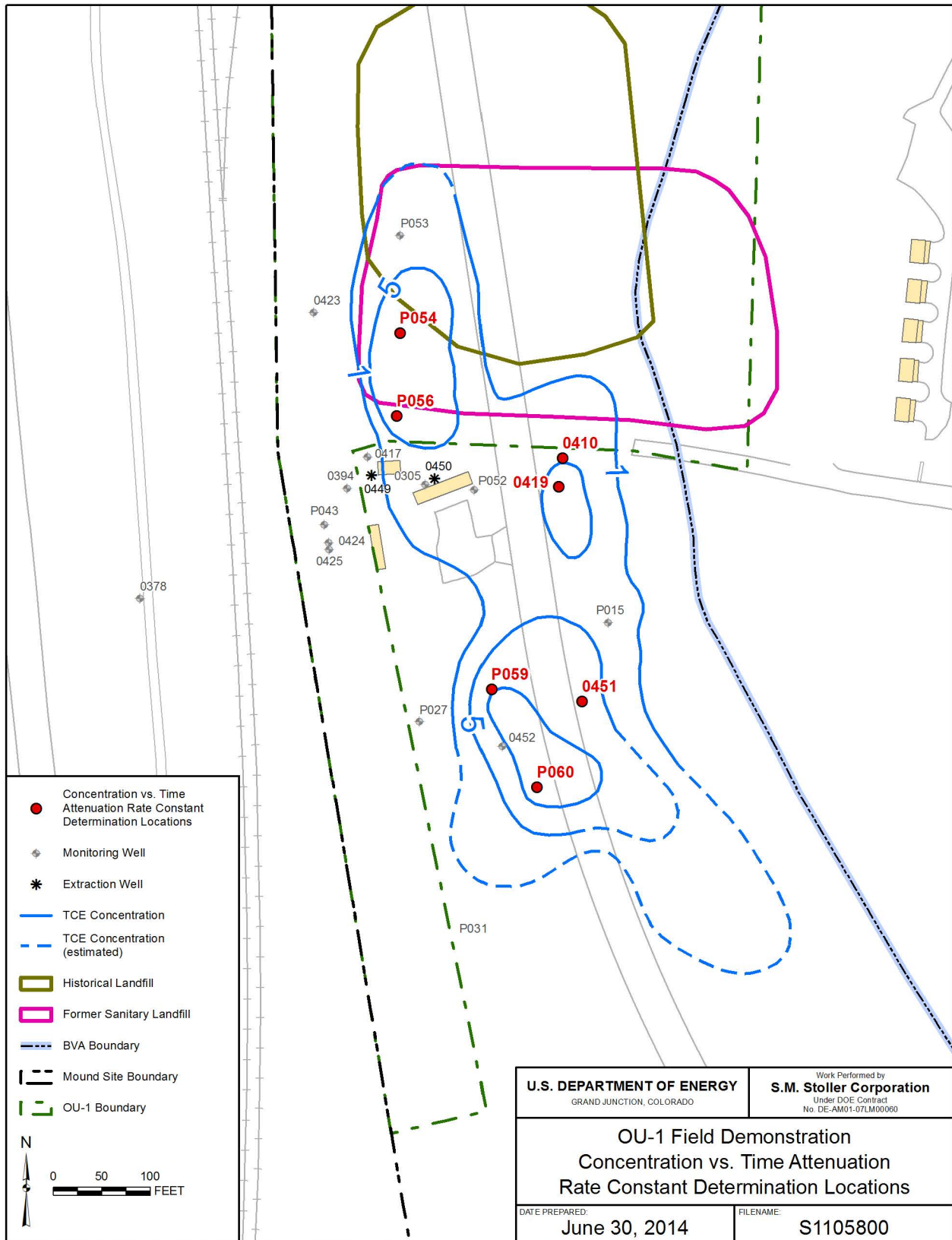


Figure 15. Concentrations vs. Time Attenuation Rate Constant Locations

#### **4.2.2 Concentration vs. Distance Attenuation Rate Constant**

Concentration versus distance bulk attenuation rate constants ( $k$ ) are used for estimating whether a plume is expanding, showing little change, or shrinking due to the combined effects of attenuation processes. This attenuation rate is used to characterize the distribution of contaminant mass within space at a given point in time. This attenuation rate constant, in units of inverse time, is derived by plotting the natural log of the concentration versus distance and calculating the rate as the product of the slope of the transformed data plot and the groundwater seepage velocity. Attenuation rates will be determined for transects depicted on Figure 16.

#### **4.3 Downgradient Groundwater Quality**

Results from routine groundwater samples will be reviewed for the presence of cVOCs, namely PCE, TCE, and their degradation products, to determine if there are any changes in water quality throughout the field demonstration. If cVOCs are present, trends will be evaluated, primarily in the sentinel wells (0402, P031, P061, and P062).

#### **4.4 Groundwater Elevations and Flow**

Periodic static water level measurements will be used to construct potentiometric surface maps of the aquifer in the OU-1 area. Information will be used to determine groundwater gradients and flow directions in the study area.



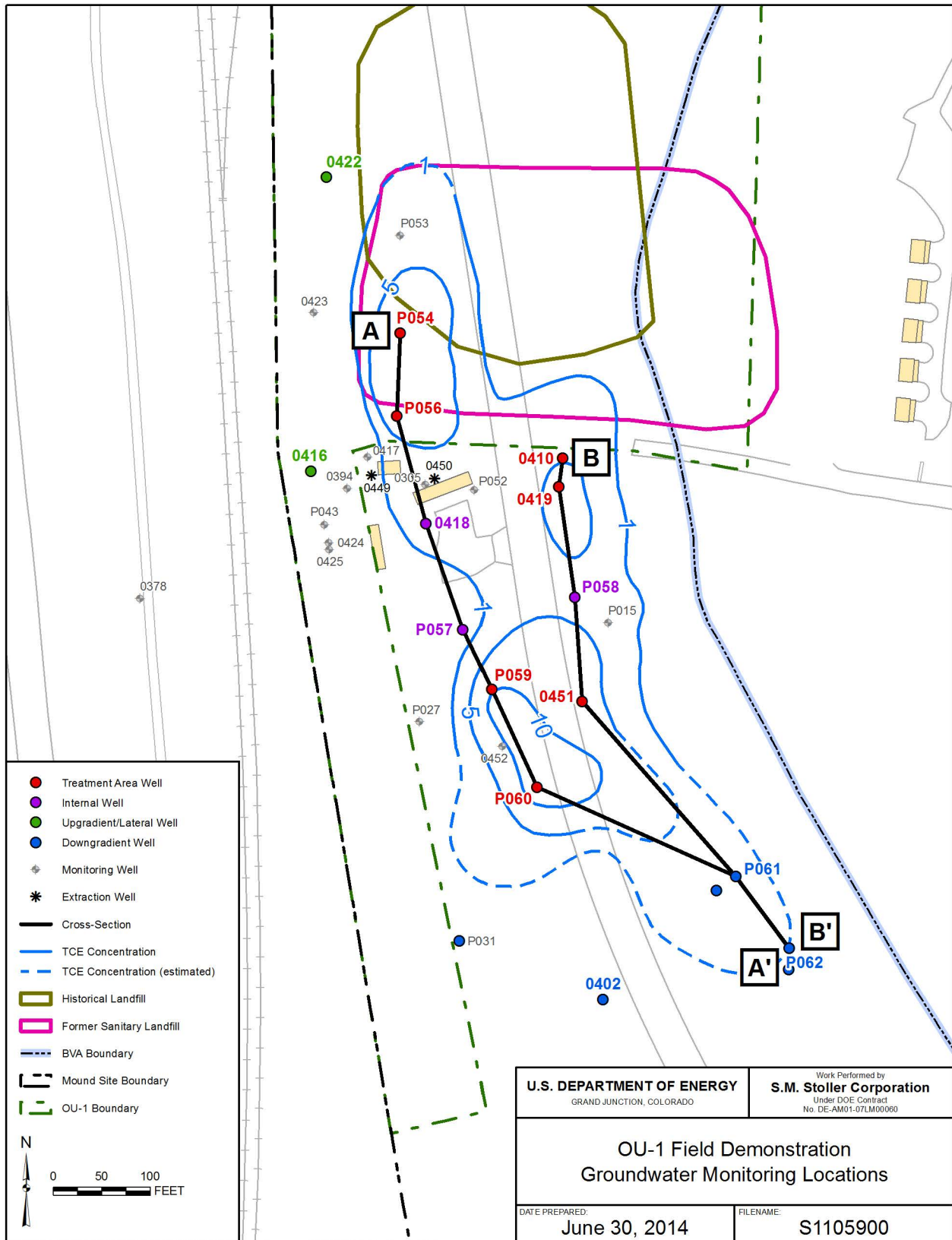


Figure 16. Concentrations vs. Distance Attenuation Rate Constant Determination Locations

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## 5.0 Contingency Planning

Monitoring data collected as part of this field demonstration will be used to determine if the treatment (structured geochemical) zones are established and are adequately reducing VOC concentrations in the OU-1 groundwater and to verify that unforeseen impact to the downgradient groundwater is not occurring.

During the deployment phase, the P&T system will continue to be operated. However, imperative to this field demonstration is that the P&T system will not be operated during the post-deployment phase (starting 3 to 4 months after injection), allowing for the natural movement of groundwater through the treatment areas. This will simulate the conditions that would be present during an MNA remedy. The P&T system will be placed on standby and considered as part of the contingency planning.

Contingency actions that may be implemented in response to changing aquifer conditions or contamination concentrations include:

- Resampling to verify reported data.
- Increased sampling frequencies.
- Analysis for additional parameters.
- Additional sampling locations.
- Strategic injection in treatment zones.
- Restarting the P&T system.

The data from wells monitoring the structured geochemical zones (treatment area and internal wells), the intermediate sentinel wells, and the terminal sentinel wells (see Figure 14) will be evaluated to determine if cVOC concentrations and aquifer geochemistry are responding as designed or anticipated. Table 3 presents possible combinations of anticipated or unanticipated behaviors in each of these wells groups and outlines the most likely contingency actions that would be considered. Table 4 outlines the factors that will be considered to determine if the data indicate anticipated or unanticipated behavior in each of these well groupings.

The primary indication of unanticipated performance of the field demonstration would be sustained increases of cVOC concentrations above threshold levels. The threshold levels for the sentinel wells are:

- Intermediate sentinel wells (P031 and P061):  $2 \times$  MCL for TCE and PCE
- Terminal sentinel wells (0402, P052, and P063): MCL for TCE and PCE

TCE and PCE results will be compared to threshold values outlined above and in Table 2. An exceedence of a threshold value will result in resampling the well to confirm that it does not exceed the value. Resampling will be performed within 10 days of discovery of the exceedence. The data will be submitted for accelerated analysis, with a minimum turnaround time of 7 days.

A sustained increase or exceedence is defined as concentrations of TCE or PCE greater than the threshold value for two consecutive scheduled post-deployment sampling events **and** an upward trend in the data at that location. The upward trend will be determined by statistical analysis of

time-series data using the Mann-Kendall statistic, as well as the MAROS Mann-Kendall analysis decision matrix to determine the confidence in the trend, as outlined in Appendix C.

Throughout the process, the Groundwater Technical Team will have a significant role in reviewing and evaluating performance data to determine if field demonstration goals are being met and to verify that downgradient water quality is not being degraded by the use of edible oils. If it is determined that the field demonstration is not performing as anticipated or designed based on data from the terminal sentinel wells, this team will recommend whether contingency measures should be implemented and whether the field demonstration should continue. These recommendations will be provided to the Core Team for final approval.

*Table 3. OU-1 Field Demonstration Contingency Planning Scenarios*

<b>Geochemical Structured Zones</b>	<b>Intermediate Sentinel Wells</b>	<b>Terminal Sentinel Wells</b>	<b>Action</b>
+	+	+	Continue monitoring.
-	+	+	Evaluate whether the demonstration goals are being met and, if necessary, identify which goal is not being attained. Continue monitoring.
-	-	+	Evaluate whether the demonstration goals are being met and, if necessary, identify which goal is not being attained. Continue monitoring—consider modifications to monitoring approach. Consider strategic re-injection of edible oils.
-	-	-	Evaluate whether the demonstration goals are being met and, if necessary, identify which goal is not being attained. Continue monitoring—consider modifications to monitoring approach. Consider strategic re-injection of edible oils. Consider re-starting P&T at a downgradient location to provide hydraulic capture of groundwater.
+	-	+	Continue monitoring. Evaluate groundwater flow for possible bypass of treatment zones. Consider strategic re-injection if bypass is identified.
+	+	-	Continue monitoring—consider modification to monitoring approach. Evaluate groundwater flow for possible bypass of treatment zones. Consider strategic re-injection if bypass is identified.
+	-	-	Continue monitoring—consider modification to monitoring approach. Evaluate groundwater flow for possible bypass of treatment zones. Consider strategic re-injection if bypass is identified. Consider re-starting P&T at a downgradient location to provide hydraulic capture of groundwater.

+ = Behavior is as designed/anticipated

- = Behavior is not as designed/anticipated

*Table 4. Indicators of Anticipated/Unanticipated Performance in Treatment and Downgradient Monitoring Areas*

<b>Area</b>	<b>Indicators of Anticipated Performance</b>	<b>Indicators of Unanticipated Performance</b>
Structured Geochemical Zones	Reducing conditions at injection points Aerobic conditions along downgradient and lateral fringes Decrease in cVOC concentrations Increase in cVOC daughter products Stability or shrinking of the plume	Lack of reducing conditions at injection points. Lack of aerobic conditions along downgradient and lateral fringes. No change in cVOC concentrations. Lack of cVOC daughter products. Expansion of the plume.
Intermediate Sentinel Wells	Stable or decreasing cVOC concentrations Aerobic conditions	Upward trends in cVOC concentrations. Sustained exceedance of 2× MCL for TCE or PCE. Appearance of significant daughter products. Indication of geochemical change.
Terminal Sentinel Wells	Stable or decreasing cVOC concentrations Aerobic conditions	Sustained exceedance of MCL. Upward trends in cVOC concentrations.

If the P&T system must be re-activated, the composition of the extracted groundwater could potentially be altered by the injection of the edible oils in the OU-1 area. As part of the Authorization to Discharge (ATD) of the P&T system, any significant change in character of the discharge that may occur should be reported and may constitute cause for modification of the ATD. An evaluation of treatment options for the extracted water was performed to account for the potential that prolonged pumping might extract emulsified edible oils. Appendix D presents this evaluation.

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## 6.0 Groundwater Exit Strategy

Groundwater in OU-1 has been impacted by cVOCs originating in the former landfill, and the migration of contaminated groundwater from the former landfill is being controlled using two extraction wells that create a hydraulic barrier. Since the source materials have been removed from the landfill, the feasibility of switching from the active remedy of P&T to a more passive remedy is being considered as a viable alternative at the Mound site.

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 and to a limited extent in the glacial till 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 goal of the field demonstration is to create treatment zones by injecting emulsified oil into the subsurface to initially reduce the concentrations of PCE and TCE and over time to stimulate existing attenuation processes that will further degrade cVOCs. Data collected during this field demonstration will be used to determine if treatment using emulsified oil to enhance the attenuation processes is a viable remedy in OU-1.

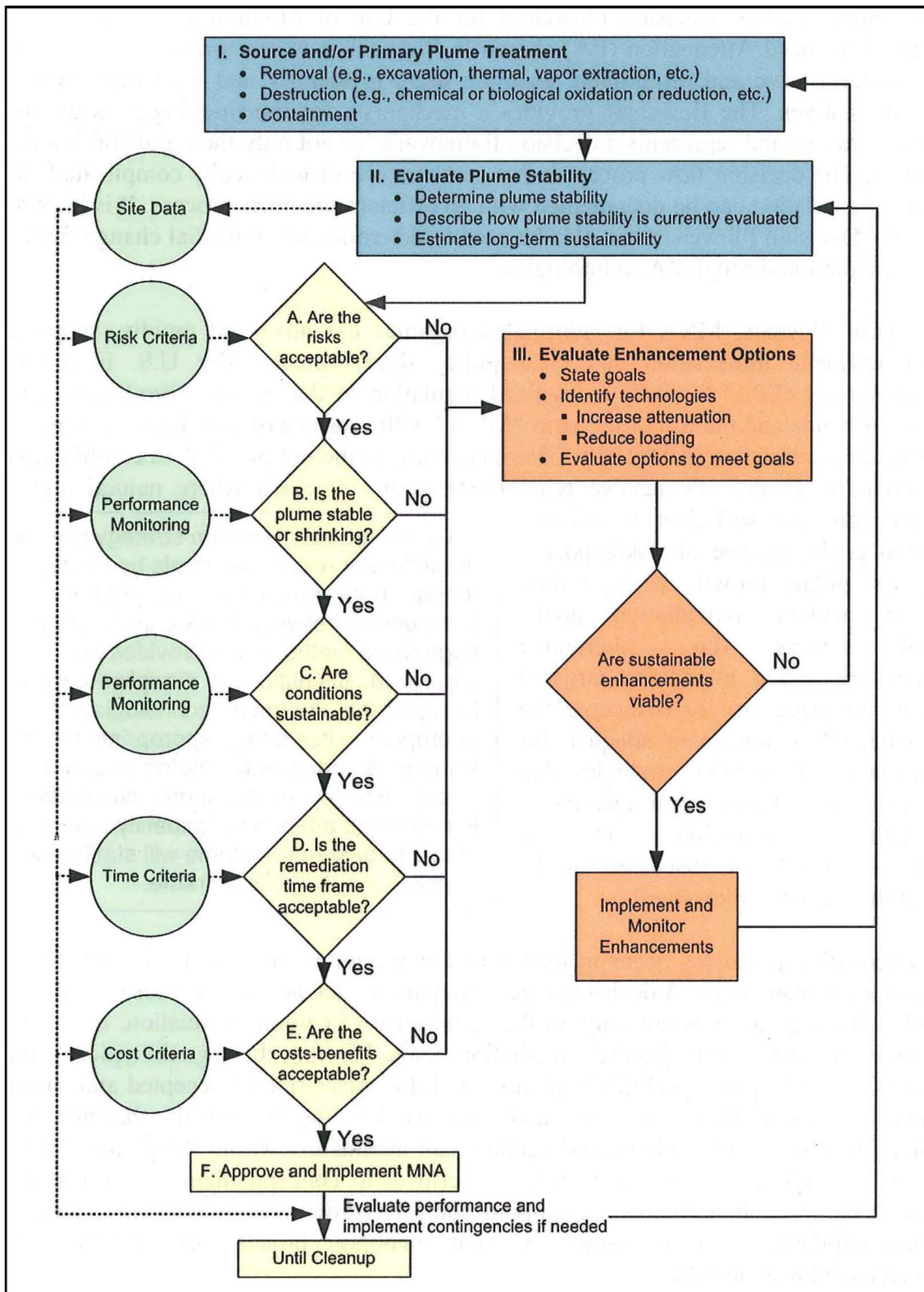
### 6.1 Consideration of the MNA Remedy

The consideration of MNA as a remedy to address cVOCs in groundwater in the OU-1 area will be based on the effectiveness of the emulsified oil treatment to reduce VOCs in groundwater and stimulate (enhance) the natural attenuation processes in the treatment zones. The following factors are outlined in EPA's *Use of Monitored Natural Attenuation at Superfund, RCRA, Corrective Action, and Underground Storage Tank Sites* (OSWER 9200.4-17P) and are used when considering MNA as a remedy.

- The cVOCs in groundwater can be effectively remediated by natural attenuation processes.
- The contaminant plume is stable, and the potential for the environmental conditions that influence plume stability will not change over time.
- Downgradient groundwater will not be adversely impacted as a consequence of selecting MNA as a remedy.
- Estimated time frame of remediation is reasonable compared to time frames of other, more active methods.
- Nature and distribution of sources can be controlled.
- Resulting transformation products do not pose a greater risk than the parent contaminants.

Of the above factors, the most important considerations regarding the suitability of MNA as a remedy include whether the contaminants are likely to be effectively addressed by natural attenuation process, the stability of the contaminant plume and its potential for migration, and the potential for unacceptable risk from the contamination.

The flowchart depicted in Figure 17 provides a mechanism for systematically evaluating data and information obtained during the field demonstration. The decision flow process is consistent with the factors outlined above and will be used to determine whether MNA can be implemented at OU-1.



Source: Interstate Technology and Regulatory Council (2007)

Figure 17. Data Evaluation Flowchart for Enhanced Attenuation and MNA



## 6.2 Period of Performance

The current schedule is to continue the field demonstration for 3 years after injection of the edible oils. The terminal sentinel wells 0402, P062, and P063 are located approximately 175 ft from the downgradient treatment cell and is within the maximum distance (228 ft) that groundwater could travel from that zone after 1 year. Continued monitoring for 2 additional years will allow monitoring for changes in groundwater velocity, changes in aquifer chemistry, and establishment of the treatment zones.

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## 7.0 Reporting

The groundwater quality, sampling frequencies, and static water level measurements will be documented in a monthly report. This report will also document any changes made to the monitoring program as the study progresses.

Annual reports will be prepared describing the status of the field demonstration and results from the evaluation of data collected for the performance of the attenuation zones. It is anticipated that interim reports will be prepared during the first 2 years of the demonstration, and a final report will be made 3 years after the injections. The interim reports will provide an evaluation of each of the test goals and determine if contingency measures need to be implemented and/or if the field demonstration should continue. The final report will evaluate the considerations of an MNA remedy for the OU-1 area as described in Section 6.1.

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## **Appendix A**

### **Potential Remedial Alternatives for OU-1 Groundwater**

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Option	Duration (years)	Assumptions
1. <u>No Action</u> : No P&T and long-term monitoring for VOCs	26	<p>A. Monitoring for VOCs at 10 to 20 locations.</p> <p>B. Cost for removal of P&amp;T system (wells, equipment, and building) are not included.</p>
2. <u>Passive</u> : Monitored Natural Attenuation with P&T contingency (well 0452)	26	<p>A. Monitoring for VOCs and other geochemical constituents at 10 to 20 locations.</p> <p>B. P&amp;T system in Bldg. 300 would be placed in stand-by (first year cost), periodic maintenance of the system, and utilities.</p> <p>C. Cost for operating the P&amp;T contingency not included; however, these costs would be similar to those reflected in Option 5. It is anticipated that well 0452 would be used for the contingency action.</p> <p>D. Cost for engineering/planning for operation of P&amp;T contingency will be incurred during the first year. This includes identifying necessary equipment planning for hook-up to Bldg. 300.</p>
3. <u>Passive</u> : Enhanced Attenuation (with Biostimulation) and P&T contingency (well 0452)	13	<p>A. One time injection of nutrients in hot spots followed by supplemental MNA sampling at 10 to 20 locations. First year costs for monitoring are for the supplemental monitoring and would add to the normal annual monitoring costs.</p> <p>B. Cost estimate for the nutrient injection based upon \$100K for electron donor amendment plus planning, equipment and field labor.</p> <p>C. P&amp;T system in Bldg. 300 would be placed in stand-by (first year cost), periodic maintenance of the system, and utilities.</p> <p>D. Cost for operating the P&amp;T contingency not included; however, these costs would be similar to those reflected in Option 5. It is anticipated that well 0452 would be used for the contingency action.</p> <p>E. Cost for engineering/planning for operation of P&amp;T contingency will be incurred during the first year. This includes identifying necessary equipment planning for hook-up to Bldg. 300.</p>
4. <u>Active</u> : P&T using wells 0449 and 0450	26	<p>A. Operation of P&amp;T system using 0449 and 0450.</p> <p>B. Monitoring for VOCs at 7 to 10 locations and NPDES sampling.</p>
5. <u>Active</u> : P&T using downgradient well (0452)	13	<p>A. Operation of P&amp;T system using 0452 (requires hook up).</p> <p>B. 0452 hook-up includes labor and materials.</p> <p>C. 0452 design includes engineering/planning to identify necessary equipment and drawings for installation and hookup.</p> <p>D. Monitoring for VOCs at 7 to 10 locations and NPDES sampling.</p> <p>E. Cost for removal of existing extraction wells (0449 and 0450) are not included.</p>

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## **Appendix B**

### **Estimation of Oil Longevity**

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A scoping calculation was performed to assess the potential longevity of the deployed oil. This calculation is based on the oxidation of the oil by inflow of electron acceptors (e.g., oxygen, nitrate, and sulfate) delivered into the deployment zone from upgradient, oil utilization by reduction of minerals in the deployment zone (e.g., Fe(III)-containing minerals converted to dissolved Fe(II)), and oil converted to light hydrocarbons (e.g., methane) or into soluble carbon compounds. The “oxidation” calculation is performed by multiplying the estimated total volumetric flow of the groundwater (liters per year) times the concentrations of the various electron acceptors and adjusting the result based on molecular weight and reaction stoichiometry (see Newell and Aziz 2004). The output is converted to an equivalent rate of oil loss in kilograms of oil per year. This result is added to similar estimates for the oil lost from the subsurface due to methane generation and Fe(III) mineral reduction, and loss of soluble carbon species (these calculations are based on assumed post-deployment downgradient concentrations of methane, Fe(II), and dissolved organic carbon, respectively). As shown in the tabulated information below, the projected time frame for complete utilization of the deployed oil is calculated to be 44 years. This estimate is approximate (most values are rounded to 1 or 2 significant figures). The results suggest that the proposed deployment volume should provide sufficient longevity to sequester and attenuate TCE and other solvents beyond the expected period of mass discharge from the residual OU1 vadose zone and upgradient source area. As an additional check, the proposed oil mass, the calculated time frame, and the overall deployment zone geometry were used to estimate a normalized oil utilization rate (see EPA 1995). The result, 0.03 milligram oil per kilogram soil per day ( $\text{mg kg}^{-1} \text{day}^{-1}$ ), is in the expected range for a transitional (aerobic/anaerobic) environment. In fully aerobic settings, the normalized oil utilization rates are typically in the range of 1 to 100  $\text{mg kg}^{-1} \text{day}^{-1}$  in the vadose zone and 0.01 to 1  $\text{mg kg}^{-1} \text{day}^{-1}$  in the saturated zone. In general, aerobic oil degradation rates are significantly higher than anaerobic rates due to the higher energy gain and more favorable kinetics or carbon utilization in the presence of oxygen. In anaerobic settings, oil degradation rates are typically 0.01  $\text{mg kg}^{-1} \text{day}^{-1}$  or less.

<b>Assumptions:</b>		<b>Basis:</b>	
Plume width:	200 ft	Plume maps	
Plume thickness:	10 ft	Cross sections	
Darcy Velocity:	70 ft/yr	LMS/MND/S10323	
Dissolved Oxygen	4 mg/L	GEMS (approx 3rd quartile)	
Nitrate	3 mg/L	GEMS (approx 3rd quartile)	
Sulfate	150 mg/L	GEMS (approx 3rd quartile)	
Deployment Zone (total size):	200 ft x 200 ft x 10 ft		
<b>Design Information:</b>			
Emulsion:	5700 gallons emulsion		
Soyben Oil Deployed:	2500 gallons soybean oil (at approx @ 45% soybean oil by volume)		
	8700 Kg soybean oil		
<b>Stoichiometric Balance and Time Calculation:</b>		<b>Basis:</b>	
Volumetric water flow through plume:	4000000 L/yr	Darcy Velocity and Plume geometry	
Soyben Oil Consumption:		--- see Newell and Aziz (2004)*	
Dissolved Oxygen	5 Kg oil / yr	Concentration, stoichiometry and flow	
Nitrate	5 Kg oil / yr	Concentration, stoichiometry and flow	
Sulfate	130 Kg oil / yr	Concentration, stoichiometry and flow	
Iron reduction (post deployment)	5 Kg oil / yr	Assumed Fe(II) = 25 mg/L, stoichiometry and flow	
methane production (post deployment)	25 Kg oil / yr	Assumed methane = 5 mg/L, stoichiometry and flow	
organic washout	30 Kg oil / yr	Assumed 5 mg DOC / L, volumetric flow rate and stoichiometry	
Total.....	200 Kg oil / yr	---	
Scoping Oil lifetime.....	44 yr	oil deployment mass / consumption rate	
Deployment zone volume:	400000 cu ft	WxLxH	
Deployment zone sediment mass:	20000000 Kg	dry bulk density approx 1.7 Kg/L	
Normalized oil utilization rate	0.03 mg oil / Kg soil / day	calculated by formula = (oil used / soil mass / time)	

References:

EPA (U.S. Environmental Protection Agency), 1995. *Manual: Bioventing Principles and Practices, Volume 1*, EPA/540/R-95/534A, U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., September, 80 pp.

Newell, C.J., and C.E. Aziz, 2004. "Long-Term sustainability of reductive dechlorination reactions at chlorinated solvents sites," *Bioremediation*, 15:387–394.

## **Appendix C**

### **MAROS Data Evaluation Methods—Statistical Trend Analysis and Spatial Moment Analysis**

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## APPENDIX A.2: STATISTICAL TREND ANALYSIS METHODS

**Authors:** Newell, C.J. and Aziz, J.J., Groundwater Services, Inc.

This appendix details the data evaluation and remedy selection procedures employed by the Monitoring and Remediation Optimization System (MAROS) Software. The procedures outlined below were developed to assess appropriate response measures for affected groundwater plumes based on scientifically sound quantitative analyses of current and historical site groundwater conditions.

### Initial Site Investigation

Evaluation of groundwater plume conditions and appropriate response measures requires adequate site characterization, including plume delineation. Therefore, for the compliance monitoring evaluation, the minimum required site information includes:

- *Constituents of Concern (COCs):* Individual constituents must be identified along with their relevant source areas and transport mechanisms.
- *Site Hydrogeology:* Site stratigraphy and groundwater flow velocity and direction must be identified.
- *Affected Groundwater:* Plume must be completely delineated for each COC to ensure that the results of the compliance monitoring assessment are reliable and not erroneously influenced by a migrating plume.
- *Time-Series Groundwater Monitoring Data:* Historical record must be compiled for each COC and meet the minimum data requirements described below.
- *Actual and Potential Groundwater Receptors:* Well locations, groundwater-to-surface water discharge locations, underground utilities, or other points of exposure must be identified.
- *Current or Near-Term Impact?:* Any current or near-term receptor impact (defined for this evaluation as occurring in zero to two years) must be assessed. Plumes posing current or near-term impact on applicable receptors are referred for immediate evaluation of appropriate risk management measures.

### Site Conceptual Model

The EPA recommends the use of conceptual site models to integrate data and guide both investigative and remedial actions (e.g., see EPA, 1999). A conceptual site model (CSM) is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. In the context of the MAROS software, conceptual model development prior to software use would allow the user to better utilize the information gained through the various software modules as well as provide guidance for assessing the data that would best typify historical site conditions.

It is recommended that available site characterization data should be used to develop a conceptual model for the site prior to the use of the MAROS software. The conceptual model should include a three-dimensional representation of the source area as a NAPL or region of highly contaminated ground water, of the surrounding uncontaminated area, of ground water flow properties, and of the solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data for the site (EPA, 1998). Data on the contaminant levels and aquifer characteristics should be obtained from wells and boreholes which will provide a clear three-dimensional picture of the hydrologic and geochemical characteristics of the site. High concentrations of dissolved contaminants can be the result of leachates, rinse waters and rupture of water conveyance lines, and are not necessarily associated with NAPLs.

This type of conceptual model differs from the more generic conceptual site models commonly used by risk assessors that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. However, the conceptual model of the ground water system facilitates identification of these risk-assessment elements for the exposure pathways analysis. After development, the conceptual model can be used to help determine optimal placement of additional data collection points, as necessary, to aid in the natural attenuation investigation and to develop the solute fate and transport model. Contracting and management controls must be flexible enough to allow for the potential for revisions to the conceptual model and thus the data collection effort.

Successful conceptual model development involves (EPA, 1998):

- Definition of the problem to be solved (generally the three dimensional nature, magnitude, and extent of existing and future contamination).
- Identification of the core or cores of the plume in three dimensions. The core or cores contain the highest concentration of contaminants.
- Integration and presentation of available data, including:
  - Local geologic and topographic maps,
  - Geologic data,
  - Hydraulic data,
  - Biological data,
  - Geochemical data, and
  - Contaminant concentration and distribution data.
- Determination of additional data requirements, including:
  - Vertical profiling locations, boring locations and monitoring well spacing in three dimensions,
  - A sampling and analysis plan (SAP), and
  - Other data requirements.

Conceptual model development prior to use of the MAROS software will allow more accurate site evaluation through quality data input (i.e. identification of source and tail wells, etc.), as well as viewing the MAROS results in light of site-specific conditions. The conceptual model will also allow the user to gain insight into the type and extent of site data that is needed to fulfill minimum data requirements in order to fully utilize the MAROS software.



## Minimum Data Requirements

Compliance Monitoring data evaluation must be based on data from a consistent set of wells over a series of periodic sampling events. Statistical validity of the constituent trend analysis requires constraints on the minimum data input. To ensure a meaningful comparison of COC concentrations over time and space, the following minimum requirements were imposed on the time-series groundwater monitoring data:

- *Number of Wells:* Evaluation should include data from at least four wells (ASTM , 1998) in which COCs have been detected. May include up to two wells which have not exhibited COCs during more recent sampling events being analyzed, but in which COCs were previously detected. As many wells should be included in the evaluation as possible, subject to the other minimum data requirements.
- *Minimum Data per Well:* Data for each well should include at least four measured concentrations over six sampling events during the time period being analyzed. For any well, data may not be missing from more than two consecutive sampling events. Guidelines given by ASTM, 1998 notes that a minimum of more than one year of quarterly monitoring data of 4 or 5 wells is needed to establish a trend.
- *Number of Sampling Events:* Evaluation should include at least six most-recent sampling events which satisfy the minimum groundwater data requirements specified above. For this evaluation, it is suggested that the user consolidate multiple sampling dates within a single quarter to consider them to be a single sampling event, with multiple measurements of the same constituent subject to a user defined consolidation (e.g. average). The sampling events do not need to be the same for each well.

**Sufficient Data:** At least four wells with four or more independent sampling events per well are available

**Insufficient Data:** Fewer than four wells or fewer than 4 independent sampling events per well are available.

Although the software will calculate trends for fewer than four wells and a minimum of 4 sampling events, the above criteria will ensure a meaningful evaluation of COC trends over time. The minimum requirements described would apply only to “well behaved” sites, for most sites more data is required to obtain an accurate representation of COC trends. Sites with significant variability in groundwater monitoring data (due to water table fluctuation, variations in groundwater flow direction, etc.) will require more data to obtain meaningful stability trends. Essentially, the plume you are evaluating should be delineated with adequate consecutive sampling data to accurately evaluate the concentration trend with time.

## Plume Stability Analysis

Confirmation of the effective performance of monitored natural attenuation as a stand-alone remedial measure requires the demonstration of *primary lines of evidence*, i.e., actual measurement of stable or shrinking plume conditions based on evaluation of historical groundwater monitoring data. For a delineated plume, a stable or shrinking condition can be identified by a stable or decreasing concentration trends over time. For this analysis, an overall plume condition was determined for each COC based on a statistical trend analysis of concentrations at each well, as described below.

## STATISTICAL TREND ANALYSIS: CONCENTRATION VS. TIME

Under optimal conditions, the natural attenuation of organic COCs at any site is expected to approximate a first-order exponential decay for compliance monitoring groundwater data. With actual site measurements, apparent concentration trends may often be obscured by data scatter arising from non-ideal hydrogeologic conditions, sampling and analysis conditions. However, even though the scatter may be of such magnitude as to yield a poor goodness of fit (typically characterized by a low correlation coefficient, e.g.,  $R^2 \ll 1$ ) for the first-order relationship, parametric and nonparametric methods can be utilized to obtain *confidence intervals* on the estimated first-order coefficient, i.e., the slope of the log-transformed data.

Nonparametric tests such as the Mann-Kendall test for trend are suitable for analyzing data that do not follow a normal distribution. Nonparametric methods focus on the location of the probability distribution of the sampled population, rather than specific parameters of the population. The outcome of the test is not determined by the overall magnitude of the data points, but depends on the ranking of individual data points. Assumptions on the distribution of the data are not necessary for nonparametric tests. The Mann-Kendall test for trend is a nonparametric test which has no distributional assumptions and irregularly spaced measurement periods are permitted. The advantage gained by this approach involves the cases where outliers in the data would produce biased estimates of the least squares estimated slope. Parametric tests such as first-order regression analysis make assumptions on the normality of the data distribution, allowing results to be affected by outliers in the data in some cases. However, the advantage of parametric methods involve more accurate trend assessments result from data where there is a normal distribution of the residuals. Therefore, when the data is normally distributed the nonparametric method, the Mann-Kendall test, is not as efficient. Both tests are utilized in the MAROS software.

## Primary Line of Evidence 1: Mann-Kendall Analysis

### GENERAL

The Mann-Kendall test is a non-parametric statistical procedure that is well suited for analyzing trends in data over time (Gilbert, 1987). The Mann-Kendall test can be viewed as a nonparametric test for zero slope of the first-order regression of time-ordered concentration data versus time. The AFCEE MAROS Tool includes this test to assist in the analysis of groundwater plume stability. The Mann-Kendall test does not require any assumptions as to the statistical distribution of the data (e.g. normal, lognormal, etc.) and can be used with data sets which include irregular sampling intervals and missing data. The Mann-Kendall test is designed for analyzing a single groundwater constituent, multiple constituents are analyzed separately.

For this evaluation, a decision matrix was used to determine the "Concentration Trend" category for each well, as presented on Table 2.

### MANN-KENDALL STATISTIC (S)

The Mann-Kendall statistic (S) measures the trend in the data. Positive values indicate an increase in constituent concentrations over time, whereas negative values indicate a decrease in constituent concentrations over time. The strength of the trend is proportional to the magnitude of the Mann-Kendall Statistic (i.e., large magnitudes indicate a strong trend).

Data for performing the Mann-Kendall Analysis should be in time sequential order. The first step is to determine the sign of the difference between consecutive sample results.  $Sgn(x_i - x_{i-1})$  is an

indicator function that results in the values 1, 0, or -1 according to the sign of  $x_j - x_k$  where  $j > k$ , the function is calculated as follows

$$\begin{aligned} \text{sgn}(x_j - x_k) &= 1 && \text{if } x_j - x_k > 0 \\ \text{sgn}(x_j - x_k) &= 0 && \text{if } x_j - x_k = 0 \\ \text{sgn}(x_j - x_k) &= -1 && \text{if } x_j - x_k < 0 \end{aligned}$$

The Mann-Kendall statistic (S) is defined as the sum of the number of positive differences minus the number of negative differences or

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(x_j - x_k).$$

The *confidence in the trend* for the Mann-Kendall statistic is calculated using a Kendall probability table (e.g. Hollander, M. and Wolfe, D.A., 1973, incorporated into the software). By assessing the S result along with the number of samples, n, the Kendall table provides the probability of rejecting the null hypothesis ( $H_0$  = no trend) for a given level of significance. MAROS calculates a 'confidence level' percentage by subtracting the probability from 1. Confidence of 90% represents a significance level of  $\alpha = 0.1$  and 95% corresponds to  $\alpha = 0.05$ . The resulting confidence in the trend is applied in the Mann Kendall trend analysis as outlined in Table A.2.1. The Mann-Kendall test used in MAROS is limited to 40 sample events.

#### **AVERAGE**

The arithmetic mean of a sample of n values of a variable is the average of all the sample values written as

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

#### **STANDARD DEVIATION**

The standard deviation is the square root of the average of the square of the deviations from the sample mean written as

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}.$$

The standard deviation is a measure of how the value fluctuates about the arithmetic mean of the data.

#### **COEFFICIENT OF VARIATION (COV)**

The Coefficient of Variation (COV) is a statistical measure of how the individual data points vary about the mean value. The coefficient of variation, defined as the standard deviation divided by the average or

$$C.O.V. = \frac{s}{\bar{x}}$$

Values less than or near 1.00 indicate that the data form a relatively close group about the mean value. Values larger than 1.00 indicate that the data show a greater degree of scatter about the mean.

**RESULTS AND INTERPRETATION OF RESULTS: MANN-KENDALL ANALYSIS**

The Constituent Trend Analysis results are presented in the *Mann-Kendall Analysis* Screen (accessed from the *Plume Analysis Menu*). The software uses the input data to calculate the Coefficient of Variation (COV) and the Mann-Kendall statistic (S) for each well with at least four sampling events (see Figure A.2.1). A “Concentration Trend” and “Confidence in Trend” are reported for each well with at least four sampling events. If there is insufficient data for the well trend analysis, N/A (Not Applicable) will be displayed in the “Concentration Trend” column.

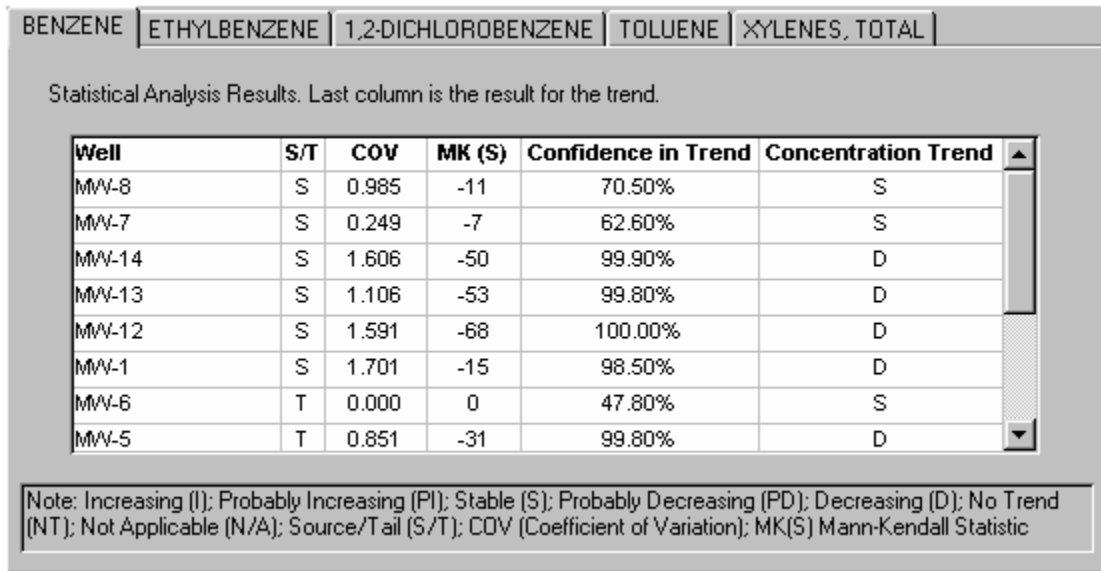


FIGURE A.2.1 MANN-KENDALL ANALYSIS RESULTS

- The Coefficient of Variation (COV) is a statistical measure of how the individual data points vary about the mean value. Values less than or near 1.00 indicate that the data form a relatively close group about the mean value. Values larger than 1.00 indicate that the data show a greater degree of scatter about the mean.
- The Mann-Kendall statistic (MK (S)) measures the trend in the data. Positive values indicate an increase in constituent concentrations over time, whereas negative values indicate a decrease in constituent concentrations over time. The strength of the trend is proportional to the magnitude of the Mann-Kendall Statistic (i.e., large magnitudes indicate a strong trend).
- The “Confidence in Trend” is the statistical probability that the constituent concentration is increasing (S>0) or decreasing (S<0).
- The “Concentration Trend” for each well is determined according to the following rules, where COV is the coefficient of variation:

TABLE A.2.1 MAROS MANN-KENDALL ANALYSIS DECISION MATRIX

Mann-Kendall Statistic	Confidence in Trend	Concentration Trend
S > 0	> 95%	Increasing
S > 0	90 - 95%	Probably Increasing
S > 0	< 90%	No Trend
S ≤ 0	< 90% and COV ≥ 1	No Trend
S ≤ 0	< 90% and COV < 1	Stable
S < 0	90 - 95%	Probably Decreasing
S < 0	95%	Decreasing

The MAROS Mann-Kendall Analysis Decision Matrix was developed in-house by Groundwater Services Inc. Strongly Increasing or Decreasing trends indicate a higher level of statistical significance. The confidence can be used as a qualitative measure of the statistical strength of the trend when evaluating the overall stability of the plume. The user can choose not to apply one of the two statistical plume analysis decision matrices. Choose “Not Used” in the Trend Result weighting screen. If the user would like to use another decision matrix to determine stability of the plume, they would need to do this outside the software.

## Statistical Plume Analysis 2: Linear Regression Analysis

### GENERAL

Linear Regression is a parametric statistical procedure that is typically used for analyzing trends in data over time. However, with the usual approach of interpreting the log slope of the regression line, concentration trends may often be obscured by data scatter arising from non-ideal hydrogeologic conditions, sampling and analysis conditions, etc. Even though the scatter may be of such magnitude as to yield a poor goodness of fit (typically characterized by a low correlation coefficient, e.g.,  $R^2 \ll 1$ ) for the first-order relationship, *confidence intervals* can nonetheless be constructed on the estimated first-order coefficient, i.e., the slope of the log-transformed data. Using this type of analysis, a higher degree of scatter simply corresponds to a wider confidence interval about the average log-slope. Assuming the *sign* (i.e., positive or negative) of the estimated log-slope is correct, a level of confidence that the slope is not zero can be easily determined. Thus, despite a poor goodness of fit, the overall *trend* in the data may still be ascertained, where low levels of confidence correspond to “Stable” or “No Trend” conditions (depending on the degree of scatter) and higher levels of confidence indicate the stronger likelihood of a trend. The coefficient of variation, defined as the standard deviation divided by the average, is used as a secondary measure of scatter to distinguish between “Stable” or “No Trend” conditions for negative slopes. The Linear Regression Analysis is designed for analyzing a single groundwater constituent, multiple constituents are analyzed separately. The MAROS software includes this test to assist in the analysis of groundwater plume stability.

For this evaluation, a decision matrix was used to determine the “Concentration Trend” category for each well, as presented on Table A.2.2.

**LINEAR REGRESSION**

The objective of linear regression analysis is to find the trend in the data through the estimation of the log slope as well as placing confidence limits on the log slope of the trend. Regression begins with the specification of a model to be fitted. A linear relationship is one expressed by a linear equation. The Linear Regression analysis in MAROS is performed on Ln (COC Concentration) versus Time. The regression model assumes that for a fixed value of x (sample date) the expected value of y (log COC concentration) is some function. For a particular value,  $x_i$  or sample date the predicted value for y (log COC concentration) is given by

$$\hat{y}_i = a + bx_i .$$

The fit of the predicted values to the observed values ( $x_i, y_i$ ) are summarized by the difference between the observed value  $y_i$  and the predicted value  $\hat{y}_i$  (the residual value.) A reasonable fit to the line is found by making the residual values as small as possible. The method of least squares is used to obtain estimates of the model parameters (a, b) that minimize the sum of the squared residuals,  $S^2$  or the measure of the distance between the estimate and the values we want to predict (the y's).

$$S^2 = \sum_{i=1}^n (y_i - \hat{y}_i)^2$$

The values for the intercept (a) and the slope (b) of the line that minimize the sum of the squared residuals ( $S^2$ ), are given by

$$b = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2} \quad \text{and} \quad a = \bar{y} - b\bar{x}$$

where  $\bar{x}$  and  $\bar{y}$  are the mean x and y (log COC concentration) values in the dataset.

In order to test the confidence on the regression trend, there is a need to place confidence limits on the slope of the regression line. In this stage of the trend analysis, it is assumed that for each x value, the y-distribution is normal. A t-test may be used to test that the true slope is different from zero. This t-test is preferentially used on data that is not serially correlated or seasonally cyclic or skewed.

The variance of  $y_i$  ( $\sigma^2$ ) is estimated by the quantity  $S_{y,x}^2$  where this quantity is defined as

$$S_{y|x}^2 = \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n - 2}$$

where n is the number of samples.

The estimation of the standard deviation or standard error of the slope (s.e.b.) is defined as

$$s.e.b. = \sqrt{\frac{S_{y|x}^2}{\sum_{i=1}^n (x_i - \bar{x}_i)^2}}$$

To test significance of the slope calculated, the following t-test result can be used to find the confidence interval for the slope.

$$t = \frac{b}{s.e.b.}$$

The t result along with the degrees of freedom (n-2) are used to find the confidence in the trend by utilizing a t-distribution table found in most statistical textbooks (e.g. Fisher, L.D. and van Belle, G., 1993). The resulting confidence in the trend is utilized in the linear regression trend analysis as outlined in Table A.2.2.

**RESULTS AND INTERPRETATION OF RESULTS: LINEAR REGRESSION ANALYSIS**

The Constituent Trend Analysis Results are presented in the Linear Regression Analysis Screen (accessed from the Mann-Kendall Analysis screen). The software uses the input data to calculate the Coefficient of Variation (COV) and the first-order coefficient (Ln Slope) for each well with at least four sampling events. A "Concentration Trend" and "Confidence in Trend" are reported for each well with at least four sampling events. If there is insufficient data for the well trend analysis, N/A (Not Applicable) will be displayed in the "Concentration Trend" column (Figure A.2.2)

BENZENE | ETHYLBENZENE | 1,2-DICHLOROBENZENE | TOLUENE | XYLENES, TOTAL

Statistical Analysis Results. Last column is the result for the trend.

Well	S/T	Average	Ln Slope	COV	Confidence in Trend	Concentration Trend
MVV-8	S	6.8E-04	-9.5E-05	9.8E-01	82.2%	S
MVV-7	S	5.4E-04	-3.1E-05	2.5E-01	78.1%	S
MVV-14	S	9.5E-03	-1.0E-03	1.6E+00	99.6%	D
MVV-13	S	1.7E-02	-1.5E-03	1.1E+00	100.0%	D
MVV-12	S	3.6E-02	-1.7E-03	1.6E+00	100.0%	D
MVV-1	S	3.6E-01	-1.4E-03	1.7E+00	99.6%	D
MVV-6	T	5.0E-04	0.0E+00	0.0E+00	100.0%	S

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Applicable (N/A); Source/Tail (S/T); COV (Coefficient of Variation)

FIGURE A.2.2 LINEAR REGRESSION ANALYSIS RESULTS

- The Coefficient of Variation (COV) is a statistical measure of how the individual data points vary about the mean value. Values less than or near 1.00 indicate that the data form a

relatively close group about the mean value. Values larger than 1.00 indicate that the data show a greater degree of scatter about the mean.

- The Log Slope (Ln Slope) measures the trend in the data. Positive values indicate an increase in constituent concentrations over time, whereas negative values indicate a decrease in constituent concentrations over time.
- The “Confidence in Trend” is the statistical probability that the constituent concentration is increasing (ln slope>0) or decreasing (ln slope<0).
- The “Concentration Trend” for each well is determined according to the following rules, where COV is the coefficient of variation:

TABLE A.2.2 MAROS LINEAR REGRESSION ANALYSIS DECISION MATRIX

Confidence in Trend	Ln Slope	
	Positive	Negative
<90%	No Trend	COV < 1 Stable COV > 1 No Trend
90% - 95%	Probably Increasing	Probably Decreasing
> 95%	Increasing	Decreasing

COV = Coefficient of Variation

The MAROS Linear Regression Analysis Decision Matrix was developed in-house by Groundwater Services Inc. The user can choose not to apply one of the two statistical plume analysis decision matrices. Choose “Not Used” in the Trend Results weighting screen. If the user would like to use another decision matrix to determine stability of the plume, they would need to do this outside the software.

### Further Considerations

The results of a constituent concentration trend analysis form just one component of a plume stability analysis. Additional considerations in determining the over-all plume stability include:

- Multiple constituent concentration trend analyses;
- Time-frame over which the trend is evaluated;
- Adequate delineation of the plume;
- Status of the COC as a parent or daughter product;
- Proximity of monitoring wells with stable or decreasing constituent trends to the downgradient edge of the plume.

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## APPENDIX A.5 SPATIAL MOMENT ANALYSIS

Authors: Aziz, J. J. and Newell, C. J., Groundwater Services, Inc.

This appendix details the moment analysis procedures employed by the Monitoring and Remediation Optimization System (MAROS) Software. The procedures outlined below were developed to assess plume stability for groundwater plumes based on scientifically sound quantitative analyses of current and historical site groundwater conditions. The moment analysis results can also be used to further assess possible information loss due to eliminating sample locations in the long-term monitoring network.

### Plume Stability Analysis

Confirmation of the effective performance of monitored natural attenuation as a stand-alone remedial measure requires the demonstration of actual measurement of stable or shrinking plume conditions based on evaluation of historical groundwater monitoring data. For this analysis, an overall plume condition was determined for each COC based on a statistical trend analysis of moments for each sample event, as described below. The function that describes residence time of mass in a field is difficult to characterize exactly. An infinite set of parameters are needed to fully characterize the distribution and the mean residence time and variance are often inadequate, as well. It is more convenient to characterize the approximate distribution rather than the exact distribution, in terms of the moments. (Rasmuson 1985). The moment calculations can predict how the plume will change in the future if further statistical analysis is applied to the moments to identify a trend (in this case, Mann Kendall Trend Analysis is applied). The role of moment analysis in MAROS is to provide a relative measure of plume stability and condition, but can also assist the user in evaluating the impact on plume delineation in future sampling events by removing identified "redundant" wells from a long-term monitoring program.

Plume stability may vary by constituent, therefore the MAROS Moment analysis can be used to evaluate multiple COCs simultaneously which can be used to provide a quick way of comparing individual plume parameters to determine the size and movement of constituents relative to one another.

To estimate the mass, center of mass, and the spread of the plume at each sample event, spatial moment analysis of the discrete groundwater monitoring data was performed. The  $ijk$ th moment of the 2-D concentration distribution in space  $M_{ijk}(t)$  is defined as (Freyburg, 1986):

$$M_{ijk}(t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \eta C(x, y, z, t) x^i y^j z^k dx dy dz$$

where  $C(x,y,z)$  is the concentration at a monitoring point;  $\eta$  is the total porosity; and  $x, y, z$  are the spatial coordinates. The zeroth, first, and second moments ( $i+j+k = 0, 1, \text{ or } 2$ , respectively) provide measures of the mass, location of the center of mass, and relative distribution of the plume.

The moment trends over time can be assessed by the Mann-Kendall test, which is a non-parametric statistical procedure that is well suited for analyzing trends in data over time (Gilbert, 1987). The Mann-Kendall test can be viewed as a nonparametric test for zero slope of the first-order regression of time-ordered concentration data versus time. The AFCEE MAROS Tool

includes this test to assist in the analysis of groundwater plume stability and plume changes over time. The Mann-Kendall test does not require any assumptions as to the statistical distribution of the data (e.g. normal, lognormal, etc.) and can be used with data sets which include irregular sampling intervals and missing data. The Mann-Kendall test is designed for analyzing a single groundwater constituent, multiple constituents are analyzed separately. For more details on the Mann-Kendall Trend Analysis refer to Appendix A.2 *Statistical Trend Analysis Methods*.

**ZEROth MOMENT: SHOWS CHANGE IN MASS OVER TIME**

The zeroth moment is the sum of concentrations for all monitoring wells and is an estimate of the total dissolved mass in the plume. The zeroth moment calculation can show high variability over time, largely due to the fluctuating concentrations at the most contaminated wells as well as the varying number and identity of wells in the network. Plume analysis and delineation based exclusively on concentration can exhibit temporal and spatial variability. The mass estimate is also sensitive to the extent of the site monitoring well network over time. Therefore, the plume should be adequately delineated for the mass estimates to be considered.

The 3-D Zeroth Moment or Mass estimate was calculated using the following formula:

$$M_{0,0,0} = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \eta C_i dx dy dz$$

where  $C_i$  is the concentration of the COC,  $\eta$  is the total porosity; and  $x, y, z$  are the spatial coordinates.

Because the data are spatially discontinuous, a numerical approximation to this equation is required. To conduct the numerical integration the horizontal plane ( $x,y$ ) was divided into contiguous triangular regions with the apex of each triangle defined by a well sampling location with an associated COC concentration and saturated thickness at each sample location. A spatial interpolation method over these triangles allows the zeroth moment calculations using Delaunay Triangulation (see Appendix A.2 for methodology). An approximation of the mass is obtained from calculating:

$$Mass_{Estimated} \cong \sum \eta V_i C_{i\ avg}$$

where  $C_{i\ avg}$  is the geometric mean concentration of each triangle for a particular COC(i) ,  $V_i$  is the volume of the triangle (calculated by  $d \cdot A_i$ , where  $d$  is the averaged saturated thickness and  $A_i$  is the area of the triangle) and  $\eta$  is an estimate of the total porosity for the site.

**Zeroth Moment Trend:** The Zeroth Moment trend over time is determined by using the Mann-Kendall Trend Methodology. The “Zeroth Moment” Trend for each COC is determined according to the rules outlined in Appendix A.1. The Zeroth Moment trend test will allow the user to understand how the plume mass has changed over time. Results for the trend include: Increasing, Probably Increasing, No Trend, Stable, Probably Decreasing, Decreasing or Not Applicable (Insufficient Data).

**Mann-Kendall Statistic (S):** The Mann-Kendall Statistic (S) measures the trend in the data. Positive values indicate an increase in estimated mass over time, whereas negative values indicate a decrease in estimated mass over time. The strength of the trend is proportional to the magnitude of the Mann-Kendall Statistic (i.e., large magnitudes indicate a strong trend). However, the zeroth moment calculation can show high variability over time, largely due to the

fluctuating concentrations at the most contaminated wells as well as varying monitoring well network sampling.

**Confidence in Trend:** The “Confidence in Trend” is the statistical confidence that the estimate of total dissolved mass is increasing ( $S>0$ ) or decreasing ( $S<0$ ) over time.

**COV:** The Coefficient of Variation (COV) is a statistical measure of how the individual data points (estimates of total dissolved mass) vary about the mean value. The coefficient of variation is defined as the standard deviation of mass estimates divided by the average. Values near 1.00 indicate that the data form a relatively close group about the mean value. Values either larger or smaller than 1.00 indicate that the data show a greater degree of scatter about the mean.

**FIRST MOMENT: SHOWS CHANGE IN CENTER OF MASS OVER TIME**

The first moment estimates the center of mass, coordinates ( $X_c$  and  $Y_c$ ) for each sample event and COC. The changing center of mass locations indicate the movement of the center of mass over time. Whereas, the distance from the original source location to the center of mass locations indicate the movement of the center of mass over time relative to the original source.

The 2-D coordinates for the center of mass of the plume for a given sample event can be calculated from:

$$X_c = \frac{M_{1,0,0}}{M_{0,0,0}} = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \eta C_i x dx dy dz}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \eta C_i dx dy dz} \quad Y_c = \frac{M_{0,1}}{M_{0,0}} = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \eta C_i y dx dy dz}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \eta C_i dx dy dz}$$

where  $C_i$  is the concentration of the COC,  $\eta$  is the total porosity; and  $x, y$  are the spatial coordinates.

Similar to the Zeroth Moment calculation, the data are spatially discontinuous therefore a numerical approximation to this equation is required. To conduct the numerical integration the horizontal plane ( $x,y$ ) was divided into contiguous triangular regions with the apex of each triangle defined by a well sampling location with an associated COC concentration at each sample location. A spatial interpolation method over these triangles allows the first moment calculations using Delaunay Triangulation (see Appendix A.3 for methodology). The Delaunay triangulation is a rough way to discretize the domain. The following formulas represent the 2-D approximation of the center of mass:

$$X_c \cong \frac{\sum X_i V_i C_{iavg}}{\sum V_i C_{iavg}} \quad Y_c \cong \frac{\sum Y_i V_i C_{iavg}}{\sum V_i C_{iavg}}$$

where  $C_{iavg}$  is the geometric mean concentration of the each triangle for a particular COC(i) ,  $X_i, Y_i$  are the spatial coordinates of the center of each triangle,  $V_i$  is the volume of the triangle (calculated by  $d \cdot A_i$ , where  $d$  is the averaged saturated thickness and  $A_i$  is the area of the triangle) and  $X_c, Y_c$  are the coordinates of the center of mass.

Calculation of the first moment normalizes the spread by the concentration indicating the center of mass. Analysis of the movement of mass should be viewed as it relates to 1) the original source location of contamination and 2) the direction of groundwater flow. Spatial and temporal trends in the center of mass can indicate spreading or shrinking or transient movement based on season variation in rainfall or other hydraulic considerations. No appreciable movement or a neutral trend in center of mass would indicate plume stability.

**Distance from Source to Center of Mass:**

To calculate the distance from the center of mass of the plume for a particular COC and sample event to the source location, the following formula is used:

$$D_{\text{fromcenter}} = \sqrt{(X_{\text{source}} - X_c)^2 + (Y_{\text{source}} - Y_c)^2}$$

where  $D_{\text{fromcenter}}$  is the distance from the source location to the center of mass for a particular COC(i) and sample event,  $X_c, Y_c$  are the coordinates of the center of mass,  $X_{\text{source}}, Y_{\text{source}}$  are the coordinates of the source location for a particular COC.

**First Moment Trend:** The First Moment trend of the distance to the center of mass over time is determined by using the Mann-Kendall Trend Methodology. The “First Moment” trend for each COC is determined according to the rules outlined in Appendix A.1. Results for the trend include: Increasing, Probably Increasing, No Trend, Stable, Probably Decreasing, Decreasing or Not Applicable (Insufficient Data).

**MK (S):** The Mann-Kendall Statistic (S) measures the trend in the data, in this case the trend in the distance from the source area to the center of mass. Positive values indicate an increase in the distance from the source to the center of mass over time, whereas negative values indicate a decrease in the distance from the source to the center of mass over time. The strength of the trend is proportional to the magnitude of the Mann-Kendall Statistic (i.e., large magnitudes indicate a strong trend).

**Confidence in Trend:** The “Confidence in Trend” is the statistical confidence that the distance from the source to the center of mass is increasing ( $S > 0$ ) or decreasing ( $S < 0$ ).

**COV:** The Coefficient of Variation (COV) is a statistical measure of how the individual data points vary about the mean value. The coefficient of variation, defined as the standard deviation divided by the average distance between the source and mass center. Values near 1.00 indicate that the data form a relatively close group about the mean value. Values either larger or smaller than 1.00 indicate that the data show a greater degree of scatter about the mean.

**SECOND MOMENT: SHOWS SPREAD OF THE PLUME OVER TIME**

The second moment indicates the distribution of the contaminant about the center of mass ( $\sigma_{xx}$  and  $\sigma_{yy}$  or equivalently  $S_{xx}$  and  $S_{yy}$ ), or the distance of contamination from the center of mass for a particular COC and sample event. The Second Moment represents the spread of the plume over time in the x and y directions with x-axis representing its major migration direction. Freyberg (1986) describes the second moment about the center of mass as the “spatial covariance tensor”.

The components of the covariance tensor are indicative of the spreading of the contaminant plume about the center of mass. The components of the covariance tensor can be described in terms of an ellipse (x the major axis and y the minor axis). The values of  $\sigma_{xx}$  and  $\sigma_{yy}$  represent the axes of the covariance ellipse.

The 2-D covariance or second moment equations (axial terms) are as follows:

$$\sigma_{xx} = \frac{M_{2,0,0}}{M_{0,0,0}} - X_c^2 \qquad \sigma_{yy} = \frac{M_{2,0,0}}{M_{0,0,0}} - Y_c^2$$

where  $\sigma_{xx}$  and  $\sigma_{yy}$  are the second moments for a particular COC (i) and sample event,  $X_c$ ,  $Y_c$  are the coordinates of the center of mass.

Similar to the other Moment calculations, the data are spatially discontinuous therefore a numerical approximation to this equation is required. To conduct the numerical integration the horizontal plane (x, y) was divided into contiguous triangular regions with the apex of each triangle defined by a well sampling location with an associated COC concentration at each sample location. A spatial interpolation method over these triangles allows the first moment calculations using Delaunay Triangulation (see Appendix A.2 for methodology). The Delaunay triangulation is a rough way to discretize the domain. The following formulas represent the 2-D approximation of the spatial covariance tensors:

$$S_{xx} \cong \frac{\sum (X_i - X_c)^2 V_i C_{iavg}}{\sum V_i C_{iavg}} \qquad S_{yy} \cong \frac{\sum (Y_i - Y_c)^2 V_i C_{iavg}}{\sum V_i C_{iavg}}$$

$$S_{xy} \cong \frac{\sum (X_i - X_c)(Y_i - Y_c) V_i C_{iavg}}{\sum V_i C_{iavg}}$$

Where  $S_{xx}$ ,  $S_{yy}$ , and  $S_{xy}$  (the diagonal term) are the spatial covariance tensors for a particular COC(i) and sample event, where  $C_{iavg}$  is the geometric mean concentration of each triangle for a particular COC(i),  $X_i$  and  $Y_i$  are the spatial coordinates (the easting-northing coordinates) of the center of each triangle,  $V_i$  is the volume of the triangle (calculated by  $d \cdot A_i$ , where  $d$  is the averaged saturated thickness and  $A_i$  is the area of the triangle).

In order to analyze the behavior of the plume, the values of the spatial covariance tensors need to be adjusted relative to the orientation of the plume elliptical axes. It is assumed that the major elliptical axis ( $x'$ ) is parallel to the estimated mean groundwater velocity vector and the minor elliptical axis ( $y'$ ) is perpendicular to the groundwater direction. The components are estimated using the field coordinate system and then rotated counterclockwise using the standard Cartesian tensor rotational transformation with the following formulas:

$$S_{xx}' = S_{xx} (\cos \theta)^2 + 2S_{xy} \sin \theta \cos \theta + S_{yy} (\sin \theta)^2$$

$$S_{yy}' = S_{xx} (\sin \theta)^2 - 2S_{xy} \sin \theta \cos \theta + S_{yy} (\cos \theta)^2$$

where  $\theta$  is the representative groundwater direction measured anti-clockwise from the X-axis field coordinate system. These are the actual values reported as second moments in MAROS.

**Second Moment Trend:** The Second Moment trend of the Spread of the Plume in the X or Y direction over time is determined by using the Mann-Kendall Trend Methodology. The “Second Moment” trend for each COC is determined according to the rules outlined in Appendix A.1. Results for the trend include: Increasing, Probably Increasing, No Trend, Stable, Probably Decreasing, Decreasing or Not Applicable (Insufficient Data).

**MK (S):** The Mann-Kendall Statistic (S) measures the trend in the data. Positive values indicate an increase in the spread of the plume over time (expanding plume), whereas negative values indicate a decrease in the spread of the plume over time (shrinking plume). The strength of the trend is proportional to the magnitude of the Mann-Kendall Statistic (i.e., large magnitudes indicate a strong trend).

**Confidence in Trend:** The “Confidence in Trend” is the statistical confidence that the spread of the plume in the x or y direction is increasing ( $S > 0$ ) or decreasing ( $S < 0$ ).

**COV:** The Coefficient of Variation (COV) is a statistical measure of how the individual data points vary about the mean value. The coefficient of variation, defined as the standard deviation divided by the average. Values near 1.00 indicate that the data form a relatively close group about the mean value. Values either larger or smaller than 1.00 indicate that the data show a greater degree of scatter about the mean.

**RESULTS AND INTERPRETATION OF RESULTS: MOMENT TREND ANALYSIS**

The Moment Trend Analysis results are presented in the *Spatial Moment Analysis Results* screen (accessed from the *Moment Analysis Site Details* screen). The software uses the input data to calculate the Zeroth, First, and Second Moments for each sampling event (see Figure A-5.1).

Effective Date	0th Moment	1st Moment (Center of Mass)		2nd Moment (Spread)	
	Estimated Mass (Kg)	Xc (ft)	Yc (ft)	Sxx (sq ft)	Syy (sq ft)
10/4/1988	1.1E-02	-15	-39	5	0
11/17/1989	4.1E-02	7	-17	1,299	11,517
3/1/1990	6.6E-03	54	-1	1,695	11,576
5/31/1990	4.5E-02	18	-19	797	2,568
9/13/1990	8.2E-03	25	-17	1,692	5,020
4/3/1991	2.6E-02	17	-22	410	706

Note: Xc and Yc are the Centers of Mass; Sxx and Syy are the Second Moments, which represent the plume spread; the Estimated Mass is the Zero Moment.

Figure A.5.1 Moment Analysis Results

**RESULTS AND INTERPRETATION:**

The role of moment analysis in MAROS is to provide a relative measure of plume stability and condition over time, but can also assist the user in evaluating the impact on plume delineation in future sampling events by removing identified “redundant” wells from a long-term monitoring program.

Plume stability may vary by constituent, therefore the MAROS Moment analysis can be used to evaluate multiple COCs simultaneously which can be used to provide a quick way of comparing individual plume parameters to determine the size and movement of constituents relative to one another.

**Zerorth Moment Trend:** The Zerorth Moment trend over time will allow the user to understand how the plume mass has changed historically. A “Concentration Trend” and “Confidence in Trend” are reported for each sample event (see Figure A.5.2).

Zerorth moment calculations can show high variability over time, largely due to the fluctuating concentrations at the most contaminated wells. Field data can be highly variable due to changes in physical factors such as aquifer recharge and temperature. Plume analysis and delineation based exclusively on concentration can exhibit a large degree of temporal and spatial variability. When considering the results of the Zerorth moment trend, take into consideration the following factors which could effect the calculation and interpretation of the plume mass over time: 1) Change in the spatial distribution of the wells sampled historically 2) Different wells sampled within the well network over time (addition and subtraction of well within the network). 3) Adequate versus inadequate delineation of the plume over time

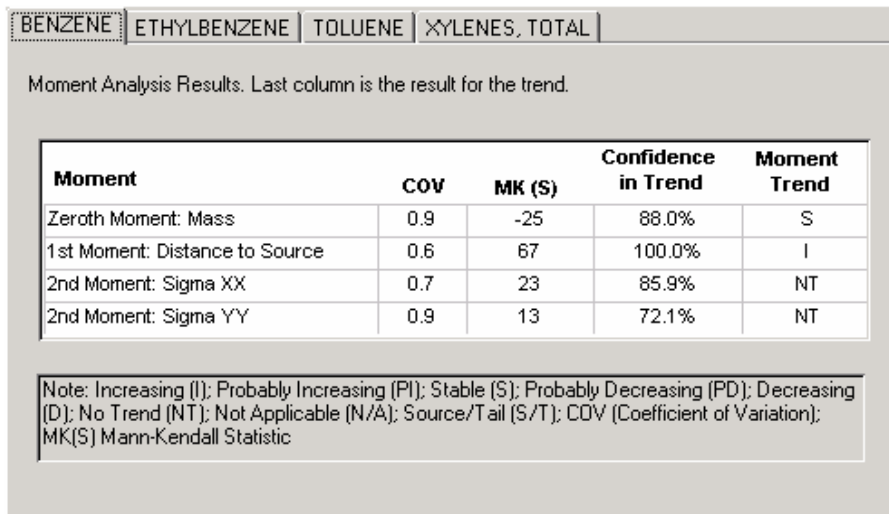


Figure A.5.2 Moment Analysis Mann-Kendall Trend Results

**First Moment Trend:** The First Moment trend of the distance to the center of mass over time is shows movement of the plume in relation to the original source location over time. Analysis of the movement of mass should be viewed as it relates to 1) the original source location of contamination 2) the direction of groundwater flow and/or 3) source removal or remediation. Spatial and temporal trends in the center of mass can indicate spreading or shrinking or transient



movement based on season variation in rainfall or other hydraulic considerations. No appreciable movement or a neutral trend in the center of mass would indicate plume stability. However, changes in the first moment over time do not necessarily completely characterize the changes in the concentration distribution (and the mass) over time. Therefore, in order to fully characterize the plume the First Moment trend should be compared to the Zeroth moment trend (mass change over time), refer to Figures A.5.3 – A.5.5.

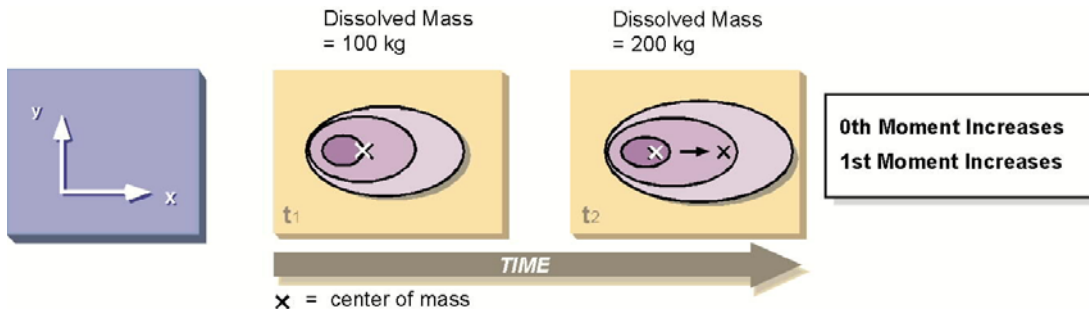


Figure A.5.3 Moment Analysis Mann-Kendall First Moment Trend Results: Zeroth Moment (Dissolved Mass) Increases over time and the First Moment Increases over time.

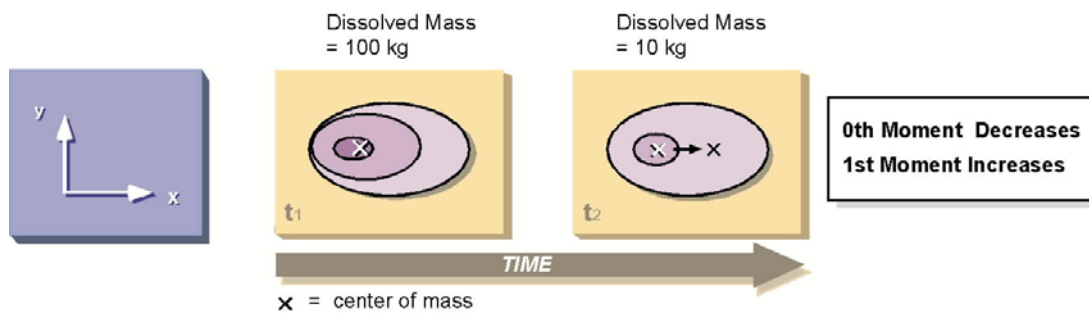
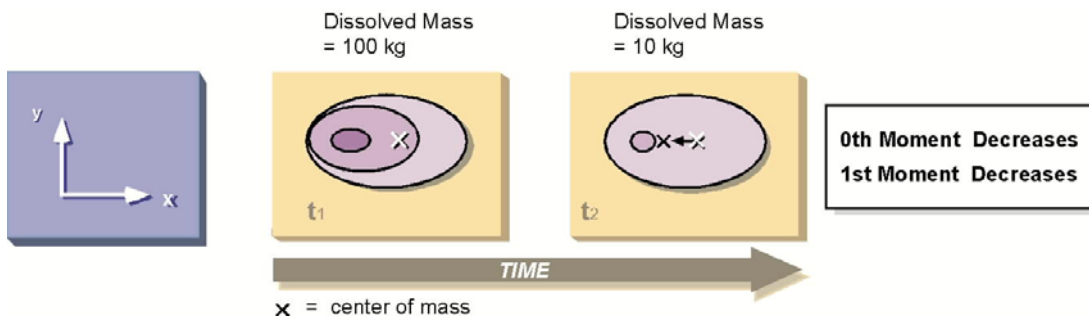


Figure A.5.4 Moment Analysis Mann-Kendall First Moment Trend Results: Zeroth Moment (Dissolved Mass) Decreases over time and the First Moment Increases over time.

Figure A.5.5 Moment Analysis Mann-Kendall First Moment Trend Results: Zeroth Moment



(Dissolved Mass) Decreases over time and the First Moment Decreases over time.

**Second Moment Trend:** The Second Moment trend indicates the spread of the plume about the center of mass. Analysis of the spread of the plume should be viewed as it relates to the direction of groundwater flow. An increasing trend in the second moment indicates an expanding plume, whereas a declining trend in the plume indicates a shrinking plume. No appreciable movement or a neutral trend in the center of mass would indicate plume stability. The second moment provides a measure of the spread of the concentration distribution about the plume's center of mass. However, changes in the second moment over time do not necessarily completely characterize the changes in the concentration distribution (and the mass) over time. Therefore, in order to fully characterize the plume the Second Moment trend should be compared to the Zeroth moment trend (mass change over time), refer to Figures A.5.6 - A.5.8.

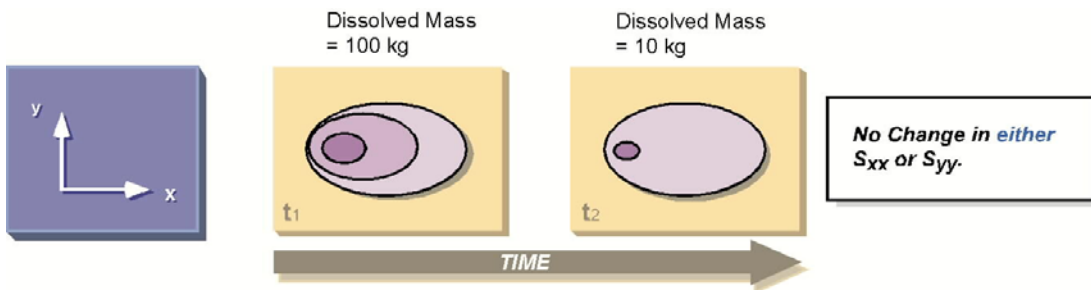


Figure A.5.6 Moment Analysis Mann-Kendall Second Moment Trend Results: No Change in trend of either  $S_{xx}$  or  $S_{yy}$  (both parallel and perpendicular to the plume center line), Mass Decreases over time.

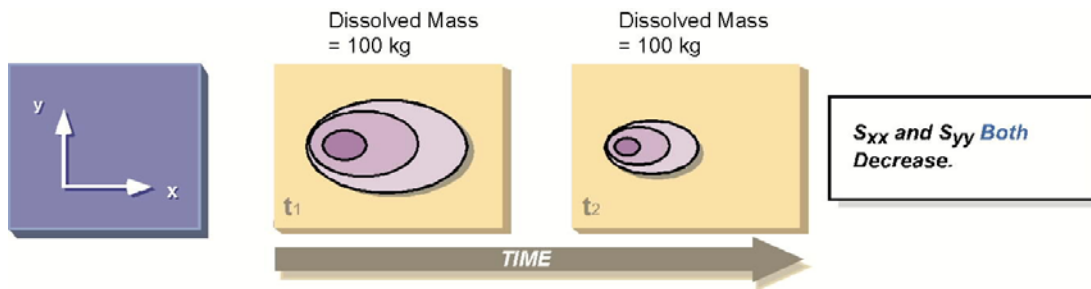


Figure A.5.7 Moment Analysis Mann-Kendall Second Moment Trend Results: Decreasing Trend in both  $S_{xx}$  and  $S_{yy}$  (both parallel and perpendicular to the plume center line), no change in Mass over time.

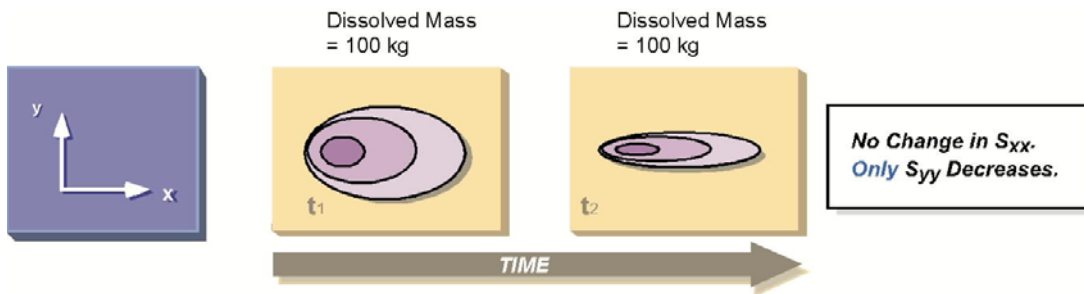


Figure A.5.8 Moment Analysis Mann-Kendall Second Moment Trend Results: Decreasing Trend in  $S_{yy}$  (perpendicular to the plume center line), no change in mass over time.

### Redundant Well Removal

Moment analysis can also be used to evaluate the effect of removing wells from a monitoring program. The question this analysis answers is whether or not removing a well from the well network will appreciably effect future plume delineation. The application of this technique involves analyzing how the moments would change if wells were removed from historical data sets.

Historical data used in plume delineation is evaluated for zeroth, first and second moments including all wells in a monitoring program and then again, excluding the wells proposed for elimination. The values determined for mass, center of mass and spread of mass can be compared to determine how plume delineation would change if wells are removed. If removal of a well has significant impact on plume delineation, then the well should be maintained in the monitoring program.

For example, if one were to choose a candidate (or several) well to remove from the monitoring program, you could go back into the historic data and perform moment analysis on the data set minus the candidate well. If similar zeroth, first and second moments were generated, then removing the wells would be not significantly effect the future delineation of the plume through a revised groundwater sampling network. Validation of removing a well from a monitoring program can be especially helpful when the water analysis alternates between non-detect and detection of very low concentrations.

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## **Appendix D**

### **Treatment Options to Address Emulsified Oil in P&T Discharge Water**

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If the P&T system must be reactivated, the injection of the edible oils in the OU-1 area could potentially alter the composition of the extracted groundwater. As part of the Authorization to Discharge (ATD) of the P&T system, any significant change in character of the discharge that may occur should be reported and may constitute cause for modification of the ATD. Treatment options for the extracted water have been evaluated to account for the potential that prolonged pumping might extract emulsified edible oils.

Two alternatives are being considered to deal with influent to the P&T system that may have emulsified oils. The two alternatives are:

- Treatment through existing air stripper with additional equipment to address emulsified oils prior to discharge to the river
- Treatment through the P&T system and discharge to the City of Miamisburg publicly owned treatment works (POTW)

The first alternative consists of adding equipment to remove the oil and total organic carbon from the influent prior to going through the air stripper. The proposed treatment system will comprise three vessels (Siemens PV2000 tanks or equivalent brand) connected in series containing two types of filtration absorption media to ensure that constituents of interest are removed and the run length of the system is maximized. The first two vessels (primary and secondary tanks) will contain a zeolite-impregnated media, which is effective for removing oil, grease, and hydrocarbons. The third and final tank will contain reactivated carbon and will be used as a final stage to remove the total organic carbon species. Last, the water will go through the existing air stripper to aerate the water prior to discharge into the river.

This proposed alternative would be relatively quick to implement, as the equipment and media are readily available from several vendors. The time required to have the equipment installed and operating is estimated to be about 30 days after DOE is notified that the P&T system must be restarted.

The second alternative would be to connect the P&T system directly to the Miamisburg POTW. The emulsified oils are food-grade materials that typically are treated in most wastewater treatment facilities. Historical discharge monitoring data indicate that cVOC levels are minimal after the influent has passed through the air stripper.

This proposed alternative would require more time to implement due to the need to acquire permission from the City of Miamisburg to connect to the sanitary sewage system. The physical connection of the effluent would be relatively quick to implement, as the sanitary sewer is close to Building 300, where the P&T system is housed.

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