### Progress toward Cleanup of Operable Unit 1 Groundwater at the US DOE Mound, Ohio, Site: Success of a Phased-Combined Remedy - 15310

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## ABSTRACT

Industrial solvents (primarily trichloroethene) and other volatile organic compounds (VOCs) that originated from the former solid waste landfill contaminated the groundwater in the Buried Valley Aquifer beneath the Mound, Ohio, 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 area (Operable Unit 1 [OU-1]) occupy approximately 1.6 hectares (4 acres) in the southwestern portion of the site. The historical pathway of concern consisted of leaching of contaminants from site soils or disposed wastes down into the groundwater, entrainment in the flowing groundwater, and migration toward former Mound site water-production wells.

A groundwater pump-and-treat (P&T) system was initiated in 1996 to interdict the plume and a soil vapor extraction system was installed and operated from 1997 to 2003 to remove the bulk of the VOC sources from the vadose zone. Physical removal of the landfill waste and contaminated soil was performed between 2006 and 2010. Approximately 76,000 cubic meters (99,400 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 or commercial use. Operation of the groundwater P&T system continued throughout this period.

During the remediation time frame, groundwater monitoring and a number of innovative characterization campaigns were completed to assess the contaminant and biogeochemical conditions in the subsurface at OU-1. For example, in 2013 an integral pumping test was performed to characterize the amount (mass) of the low-level VOCs in groundwater. Soil and groundwater were also collected to obtain site-specific data to identify if geochemical conditions support natural attenuation reactions. Contaminant and hydrogeologic data collected from this test, as well as historical data, were evaluated to identify the distribution and potential sources of VOCs, refine the hydrogeologic description, update the conceptual model of VOC fate and transport, and determine if monitored natural attenuation remains a viable option to address VOCs in groundwater.

To date, the performance of the phased-combined remedy has resulted in significant reductions in the concentrations of VOCs in the groundwater. For example, in 2013 the trichloroethene in all wells was less than 40 micrograms per liter, with a plurality of the wells near or below maximum contaminant levels. The generally observed declining concentration trends and the low

concentrations for 2013 represent the net impact of source removal actions, P&T operation, and natural attenuation.

In accordance with the current conditions, the joint US DOE and regulator Core Team is proceeding with a field demonstration of enhanced attenuation-an engineering and regulatory strategy that was recently developed by the Interstate Technology and Regulatory Council. Enhanced attenuation strategies focus on altering a target site in such a way that it can transition to natural attenuation. The combination of technologies to be deployed includes neat (pure) vegetable oil deployment in the deep vadose zone of the former landfill area and emulsified vegetable oil deployment within the footprint of the groundwater plume. In the first part of the deployment, neat oil spreads laterally and forms a thin layer on the water table beneath residual soil sources to intercept and reduce future VOC loading and to reduce oxygen inputs to the local groundwater. In the second part of the deployment, emulsified oil forms active bioremediation treatment zones within the plume footprint to degrade existing groundwater contaminants (via reductive dechlorination, cometabolism, or both) and stimulates long-term attenuation capacity in the downgradient plume (via cometabolism). If the proposed activities are successful, they will accelerate the progress of the Mound OU-1 toward remedial goals and convert the current active P&T remedy into a passive attenuation-based remedy that represents a cost-effective final step in a phased remediation.

# INTRODUCTION

At the Mound, Ohio, Site, groundwater in Operable Unit 1 (OU-1) has been impacted by volatile organic compound (VOC)-contaminated materials in the former solid waste landfill. The present selected remedy for controlling contamination from residual soil and groundwater at OU-1 is the collection, treatment, and disposal of groundwater. Monitored natural attenuation (MNA) is being considered as a viable alternative to hydraulic containment for the following reasons:

- The majority of the source term has been removed from the former landfill.
- Concentrations of VOCs in groundwater have decreased since the removal the source.
- Attenuation mechanisms, such as dilution, dispersion, and reductive dechlorination of trichloroethene (TCE), have been observed in OU-1 groundwater.

The performance of phased-combined remedies has resulted in significant reductions in the concentrations of VOCs in the groundwater. Initially, a large amount of VOCs were removed through the extraction of contaminated groundwater and operation of a soil vapor extraction (SVE) system within the former landfill footprint. Later, residually contaminated soil and debris were excavated from OU-1 area to support future site redevelopment. Since the source materials have been removed from the landfill, one final phase is being implemented to move away from an active remedy to a more passive remedy, namely MNA, to address groundwater contamination in OU-1.

## Background

The Mound site is located in Miamisburg, Ohio, approximately 10 miles southwest of Dayton, Ohio. The Mound site was established by the US Atomic Energy Commission, a predecessor to

DOE, as an integrated research, development, and production facility that supported the nation's weapons and energy programs. In 1995, the US DOE Mound site, named after the Miamisburg Indian Mound that is adjacent to the site, was comprised of 120 buildings on 306 acres. The Great Miami River located west of the site flows from northeast to southwest through Miamisburg and dominates the geography of the region surrounding the Mound site.

As part of the national DOE reconfiguration and consolidation of activities, the Mound site shifted into environmental cleanup with the goal of redevelopment as both an industrial and commercial site. After VOCs were discovered in the groundwater, the Mound site was placed on the National Priorities List in 1989. DOE remediated the former DOE Mound site property to the US Environmental Protection Agency's risk-based standards for both industrial and commercial use, and institutional controls are used to control land and groundwater use on the remediated property.

OU-1 occupies approximately 1.6 hectares (4 acres) in the southwestern portion of the Mound site and includes a former landfill site that was used from 1948 to 1974 for the disposal of general trash and liquid waste (Figure 1). Much of the waste was later relocated and encapsulated in the site's sanitary landfill constructed in 1977. There were known releases of VOCs from OU-1 into the adjacent buried valley aquifer (BVA), a sole-source aquifer. The pathway of concern consists of leaching of contaminants from site soils or disposed wastes into the groundwater and withdrawal by future wells. The OU-1 remedial action was designed to control groundwater contamination (primarily low-level VOCs) to prevent migration of contamination toward the plant production wells, and to minimize exposure to potential receptors.

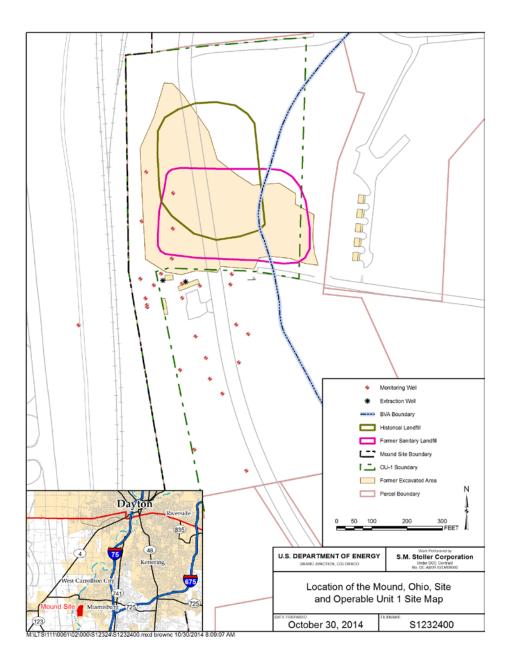


Fig. 1. This map shows the location of the Mound, Ohio, Site and layout of Operable Unit 1 (OU-1).

Periodic water sampling for VOCs in OU-1 started in 1984. Groundwater sampling data from the *Operable Unit 1 Remedial Investigation Report* [1] identified VOCs in the groundwater beneath OU-1 at levels greater than proposed or established regulatory limits. Data from 1997 were used to indicate the occurrence of VOCs in groundwater at the time the pump-and-treat (P&T) system was started (Figure 2).

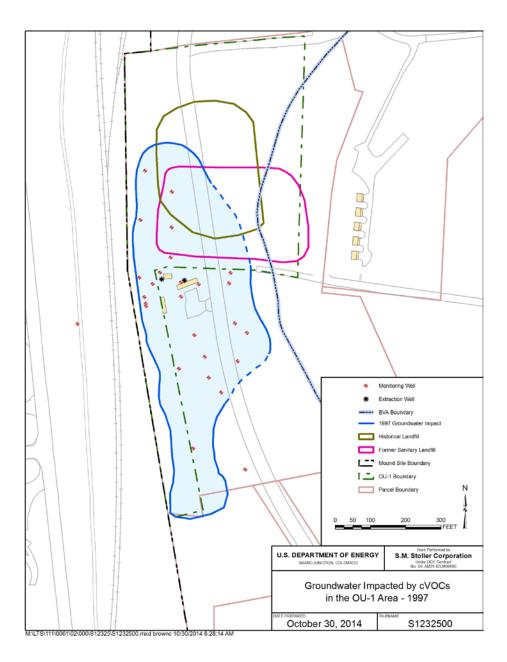


Fig. 2. This figure shows groundwater impacted by cVOCs in the OU-1 Area during 1997.

### **Phase-Combined Remedy Approach:**

#### Groundwater Extraction and SVE (1996–2007)

The goal of the OU-1 remedy was to capture the VOC-contaminated groundwater beneath the OU-1 landfill and reduce concentrations to drinking water standards and prohibit VOC-contaminant movement in the BVA, a sole-source aquifer. The agencies determined the soils within the OU-1 area would not pose an unacceptable risk to future outdoor industrial workers with appropriate institutional controls in place. At the time the Record of Decisionwas signed,

excavation and treatment of the residual subsurface contaminants within the OU-1 area was not considered practicable given the diffuse nature of contamination and lack of any identifiable contamination hot spots.

The P&T system was started in 1996. Approximately 12 kilograms 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. An SVE system was installed and operated from 1997 to 2003 to accelerate the removal of chlorinated volatile organic compounds (VOCs) from the vadose zone. This extraction system removed approximately 1862 kilograms of TCE, with 90 percent of the removal occurring within the first 3 years.

A contaminant rebound test was performed from May 2003 through February 2004, and the system was restarted because predetermined VOC threshold concentrations were measured in a nearby downgradient well. The 2003 test was performed prior to the removal of the landfill; therefore, materials were present that provided a VOC source to groundwater. It was concluded from this initial rebound test that increases and decreases in the VOC concentrations in groundwater may have been linked to rises in the groundwater table rather than being caused by a classical rebound of concentrations over time. During the test period, high groundwater levels were measured and were due to exceptionally high river stages. Increases in VOCs were observed in the wells coincident with the high groundwater levels and resulted from groundwater coming in contact with impacted material in the landfill.

## Landfill Excavation (2007–2011)

Although the P&T remedy for OU-1 is protective of human health and the environment, the group responsible for the development and management of the Mound site property remained concerned over the potential impact of the OU-1 landfill area on future plans to expand an adjacent road and to construct buildings in the OU-1 area. In response to these concerns, DOE took additional action to remove as much of the remaining waste and debris as possible using the funds provided.

In 2007 and 2008, approximately 50,000 cubic meters (65,000 cubic yards) of waste were removed. In 2009 and 2010, additional excavation was performed and approximately 26,375 cubic meters (34,500 cubic yards) of waste was removed. Excavation generally was limited to the unsaturated materials; however, in some cases, excavation proceeded to the water table. 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 act as an ongoing source to groundwater impact. These areas are small and located in the southwestern corner of the landfill excavation.

After completion of the landfill excavation, a second contaminant rebound test was performed from June to December 2011. Data were collected to evaluate the changes in VOC concentrations in the monitoring network and changes in groundwater flow when the P&T system was not operating. These data were also to be used to determine if the existing monitoring network was adequate to detect migration of the VOC impacted groundwater.

The rebound test was stopped in December 2011 when VOC concentrations in two downgradient boundary locations exceeded the MCL (i.e., the pre-determined threshold). The results from this most recent test indicated that impact greater than the MCL is present downgradient of the hydraulic barrier created by the extraction well system. Concentrations of VOCs in wells near the landfill increased gradually but did not reach threshold values that would have prompted restarting the P&T system.

## **Enhanced Attenuation Field Demonstration (2012–2014)**

Information from historical investigations and the studies performed after the second rebound test led to the recommendation that more passive methods should be considered to address the current VOC impact in OU-1 groundwater. The recommendation suggested that the methods could also include limited treatment of "hot spots" to reduce VOC concentrations in portions of the soil or groundwater and to create an environment more conducive to the destruction of VOCs.

As determined from the integral pumping test , which is a constant rate pumping test used to quantify the contaminant mass flow rates and mean contaminant concentrations within the plume, the impact downgradient of the hydraulic boundary is residual dissolved phase VOC in groundwater with no additional sources of VOC impact. Also, it was determined the migration rate of the plume is slow due to small hydraulic gradients. Within the areas of impact, characterization data indicate that reductive dechlorination of perchloroethene (PCE) to TCE occurs; however, subsequent reductive dechlorination of TCE to *cis*-1,2-Dichloroethene (DCE) is limited. Overall, aerobic conditions dominate the OU-1 groundwater system indicating cometabolic aerobic oxidation of TCE and *cis*-1,2-DCE is feasible based on organic carbon and dissolved oxygen results.

The combination of technologies that emerged for OU-1 included (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 attenuation rates in the plume. The goal of the edible oil deployment is to develop structured geochemical zones, which serve 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 VOCs. Figure 3 depicts TCE concentration reduction processes along with their corresponding breakdown products in a structured geochemical zone scenario.

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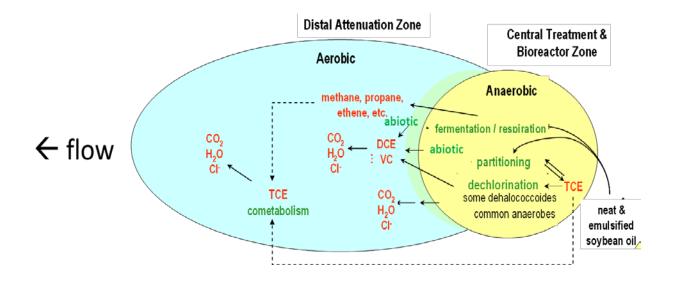


Fig. 3. This is a schematic of TCE concentration reduction processes.

The OU-1 area is uniquely suited for this type of remedial approach, given the aquifer chemistry supports the presence of structured geochemical zones (Figure 4), the low average linear velocity of groundwater (less than 100 feet per year), and are no nearby receptors. The low groundwater velocity allows for longer residence time for attenuation mechanisms within the treatment zones to reduce VOC concentrations in groundwater and adequate time to react to changed conditions before groundwater could migrate offsite. Also, institutional controls restricting groundwater use eliminate the possibility of future onsite receptors.

The design for the enhanced attenuation field demonstration focused on transition from active remediation of VOCs in OU-1 groundwater to an attenuation-based remedy. The design was derived from two mechanisms—partitioning and degradation—combined with standard hydrology and engineering calculations. The deployment relies on existing wells along with strategic additional monitoring locations for tracking the performance and progress of the cleanup.

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 VOC concentrations in soil and (2) emulsified vegetable oil substrate in the areas of highest concentrations of VOCs in the groundwater plume. In the first part, neat oil (Figure 5) spreads laterally and forms a thin layer on the water table beneath residually contaminated soil sources in the vadose zone to intercept and reduce future VOC loading (via partitioning) and reduce oxygen inputs to the local groundwater (via biostimulation). In the second part (Figure 6), emulsified oil injected below the water table 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).

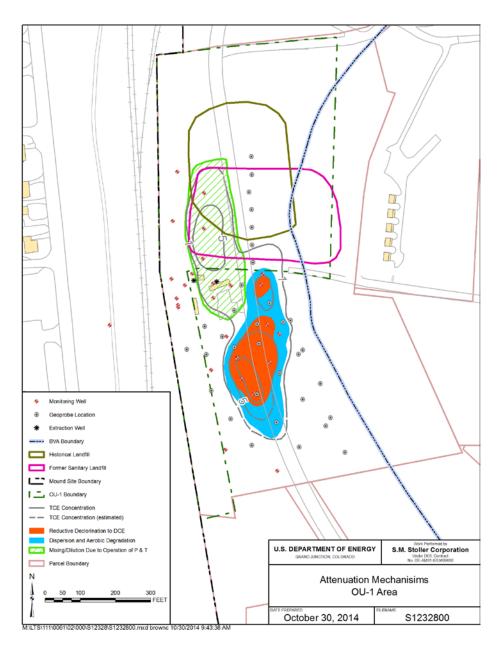


Fig. 4. This map illustrates attenuation mechanisms at OU-1 landfill.

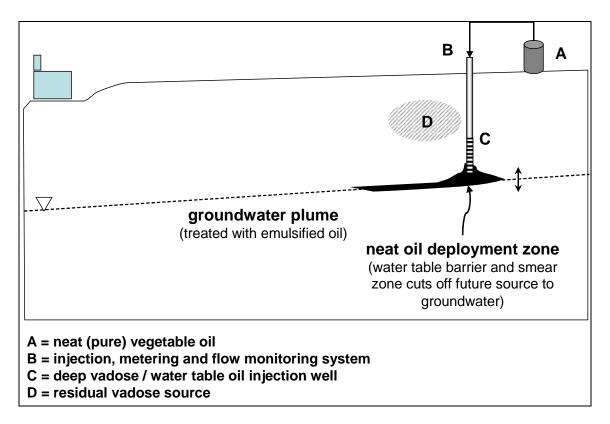


Fig. 5. Here is a schematic illustrating the neat oil deployment.

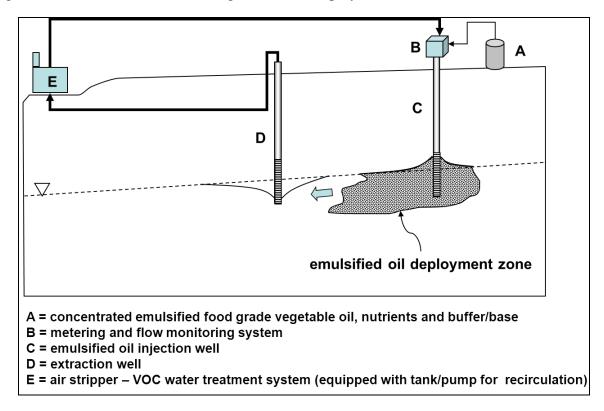


Fig. 6. Here is a schematic illustrating the emulsified oil deployment.

The final deployment design (Figure 7) consisted of neat oil injection at 6 locations within the OU-1 landfill footprint and emulsified oil injection at 19 locations throughout the OU-1 area. The key factors considered in the site-specific implementation for the field demonstration were:

- 1. <u>Former Source Area—Soil:</u> Strategic deployment of neat oil into the lower portion of the vadose zone in the areas with elevated measured soil concentrations of TCE or PCE greater than 1 mg/kg.
- 2. <u>Former Source Area—Groundwater:</u> Strategic emulsified oil injection in the groundwater to form treatment zones that address key flow lines in the aquifer beneath the former landfill area.
- 3. <u>Downgradient of Former OU-1 Landfill—Groundwater:</u> Intensive emulsified oil injection in multiple locations to address the cVOC-impacted groundwater downgradient of the former landfill.

On-going monitoring of VOC concentrations and geochemical indicators as well as microbial type and abundance indicate the formation of discrete zones conducive to the reduction of PCE and TCE and support increased microbial activity (Figure 8). These zones display:

- Increased concentrations of *cis*-1,2-DCE.
- Negative oxidation-reduction potential values and declining dissolved oxygen concentrations.
- Increased concentrations in metabolic by-products (acetone, 2-butanone, and alkalinity).
- Wells exhibiting foul odor and changes in water color that are indicative of reduced conditions.
- Increased bacterial count.

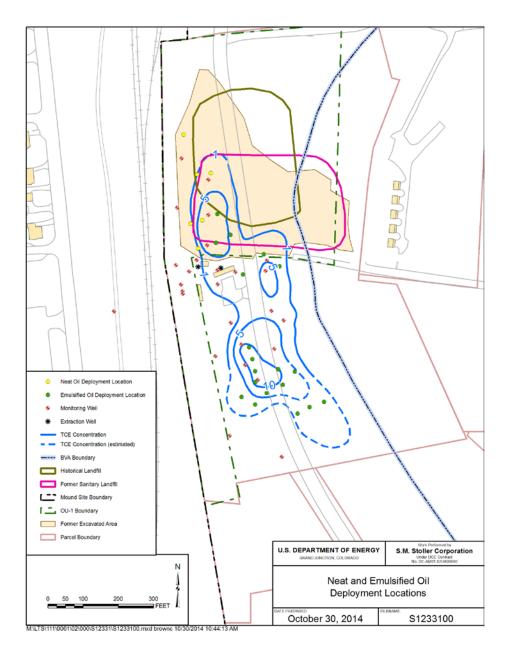


Fig. 7. This map shows the deployment locations of neat and emulsified oil.

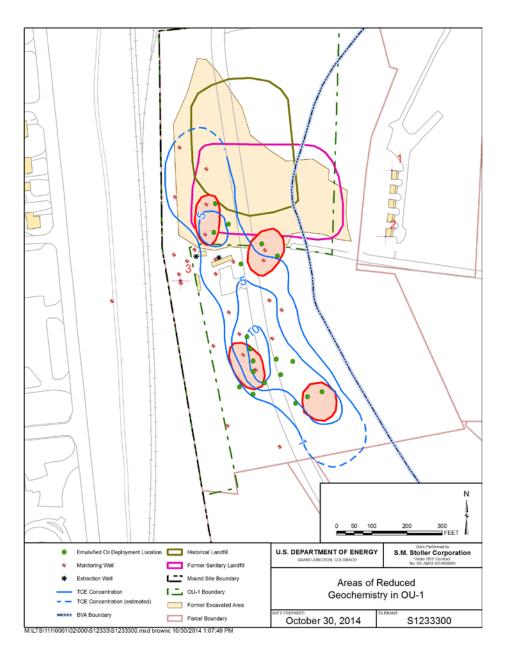


Fig. 8. Here are the areas of reduced geochemistry in OU-1.

## CONCLUSIONS

The performance of phased-combined remedies has resulted in significant reductions in the concentrations of PCE and TCE in the groundwater. VOCs have been detected in OU-1 groundwater at concentrations greater than the MCLs since routine sampling began in the 1980s. A large amount of VOCs were removed through the extraction of contaminated groundwater and operation of a soil vapor extraction system within the former landfill footprint. Later, contaminated soil and debris were excavated from OU-1 area removing additional residual sources to future groundwater impact. Figure 9 shows that concentrations of TCE have generally declined since the operation of the P&T system was started in 1997 and the excavation of VOC-impacted material from the landfill. Periodic increases in concentrations in wells are linked to excavation phases and rebound studies. Data collected since the injection of edible oil in the OU-1 area continue to show decreased TCE concentrations in the groundwater in the OU-1 area.

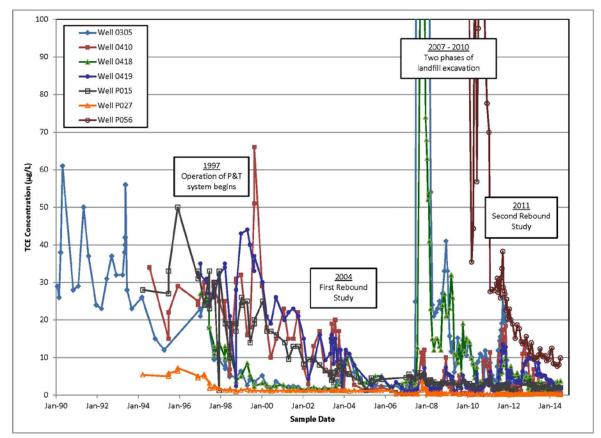


Fig. 9. This chart illustrates the TCE concentrations in select wells in the OU-1 Area from 1990 through 2014.

### REFERENCES

1. US DOE, *Operable Unit 1 Remedial Investigation Report*, Miamisburg, Ohio: U.S. Department of Energy Albuquerque Operations Office (May 1994).