LMS/MND/S37026

Evaluation of the Occurrence of Methane in Operable Unit 1 of the Mound, Ohio, Site

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Contents

Figures

Appendixes

Abbreviations

bgs	below ground surface
BVA	Buried Valley Aquifer
cDCE	*cis*-1,2-dichloroethene
cm	centimeters
CSM	conceptual site model
EA	enhanced attenuation
ft	feet
LEL	lower explosive limit
mg/L	milligrams per liter
µg/g/h	micrograms per gram per hour
MMO	methane monooxygenase
Ohio EPA	Ohio Environmental Protection Agency
OU-1	Operable Unit 1
PCE	tetrachloroethene
ppm	parts per million
TCE	trichloroethene
VC	vinyl chloride
VI	vapor intrusion
VOC	volatile organic compound

1.0 Introduction

This report provides information regarding the measured levels of methane in the vadose zone in Operable Unit 1 (OU-1) of the Mound, Ohio, Site in 2020. Field screening during a soil-gas sampling event performed by the Ohio Environmental Protection Agency (Ohio EPA) identified elevated levels of methane (as determined by the exceedance of the lower explosive limit [LEL]) in the vadose zone in OU-1.

1.1 Purpose and Scope

The purpose of this report is to evaluate why elevated levels of methane have been measured in the vadose zone in OU-1 and to determine if methane should be included as a vapor intrusion (VI) contaminant of potential concern in the addendum to the focused Feasibility Study for OU-1.

This report will discuss the available data, including data from previous investigations in the OU-1 and field screening obtained in early 2020. Included in this report are the following:

- Background information
- Occurrence, fate, and transport of methane in subsurface in OU-1
- Conceptual site model (CSM) for VI of methane in OU-1
- Conclusions and recommendations

1.2 Background

Ohio EPA performed a sampling event in February 2020 that would be used to compare the results from passive and active soil-gas sampling methods to determine if the two sampling methods produced comparable results (Ohio EPA 2020a). Ohio EPA had questioned the use of the passive samplers by DOE as part of a VI sampling plan because of the limited use of passive samplers at Ohio projects and the uncertainty related to the reproducibility of results compared to active sampling methods. Ohio EPA selected OU-1 as the area to test the two sampling methodologies because this area has had the highest historical concentrations of volatile organic compounds (VOCs) in soil and groundwater; the sampling was not meant to produce data for decision-making purposes about OU-1.

The Ohio EPA comparative sampling focused on areas in OU-1 known to have elevated concentrations of VOCs in soil, soil gas, and groundwater. These areas are typically in the vadose zone immediately above the groundwater table at depths ranging from 20 to 30 feet (ft) below ground surface (bgs). As part of the soil-gas sampling, a gas meter was used to purge the tubing before sampling. Measurements were recorded for oxygen (in percent), methane (percent of the LEL), and photoionization detector readings (for VOC detection). Decreasing trends in oxygen levels to subatmospheric levels were used to verify that leakage was not occurring within the sampling apparatus and tubing. The other parameters are measured as general practice to evaluate subsurface conditions. It was noted while reviewing the purge data that methane LEL values at or near 100% were reported for many of the locations. Results are provided in the *Vapor Intrusion Comparative Soil Gas Sampling Event at Former DOE Mound Facility Field and Data Analysis Report* (Ohio EPA 2020b).

2.0 Occurrence, Fate, and Transport of Methane in OU-1

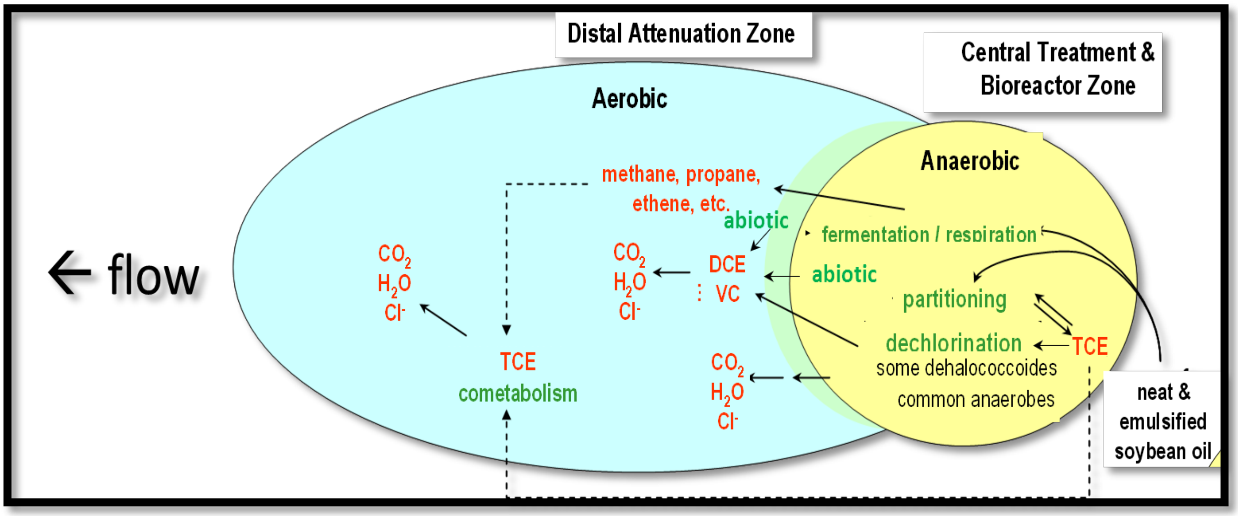
Although methane is considered nontoxic and does not have any known long-term human health risk due to exposure (EPA 2015), it can pose a risk of fire or explosion if present in the atmosphere or indoor air at concentrations between the LEL of 5% (50,000 parts per million [ppm]) and the upper explosive limit of 15% (150,000 ppm). For such events to occur, both oxygen and an ignition source must be present in conjunction with methane within the explosive range in a confined space. Methane is identified as a vapor-forming chemical due to its potential to pose an explosion hazard as documented in the *OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* (EPA 2015). It should be noted that methane will not explode in situ in the vadose zone because there is insufficient volume of methane and oxygen in the pore spaces and because soil also acts as a flame arrestor, preventing ignition (Eklund 2010).

A general fate and transport model for biogenic methane (i.e., methane generated by organisms) in the vadose zone is that methane can be generated in the subsurface by microbes called methanogens in anaerobic conditions, and methane can also be consumed by microbes called methanotrophs in the presence of oxygen. Within the vadose zone, methane might be produced at depths where anaerobic conditions are more prevalent, and any methane migrating upward to the ground surface is rapidly attenuated by oxidation within the shallower aerobic portions of the vadose zone. The biogas produced by microbes in the subsurface consists of roughly 50% methane and 50% carbon dioxide; therefore, it can be common for soil-gas readings taken near the biogas generation to contain relatively high concentrations of methane. The soil gases will not explode in situ in the subsurface soils, but, if a sufficient volume of gases is produced, there could be a potential for migration of biogases.

In the vadose zone, methane generated in the subsurface moves upward into the near-surface aerobic environments because methane is lighter than air. The rate that methane diffuses upward is dependent upon the physical properties of materials within the vadose zone (Gebert et al. 2011). Coarse-grained material (i.e., sands and gravels) typically have more interconnected pore volume that allows for diffusion of gases, while fine-grained materials (silts and clays) generally have more tortuous interconnected pore volume, resulting in slower diffusion of gases. As methane moves vertically through the vadose zone, it is oxidized by contact with oxygen or microbes, with the greatest amount of oxidation occurring within the upper 20 centimeters (cm) via microbial oxidation (Scheutz et al. 2004). There is significant documentation regarding the emission of methane through landfill covers and oxidation rates ranging between 40 micrograms per gram per hour (µg/g/h) and 128 µg/g/h (Scheutz et al. 2004).

In groundwater, methane can be dissolved or in a gaseous state. Methane is typically insoluble in water; however, with increasing pressure, it may become soluble and can be transported in groundwater. It can also become soluble in groundwater when it reaches equilibrium with methane in the overlying vadose zone. In an aquifer, methane can be confined by overlying fine-grained deposits, and methane concentrations can reach saturation concentrations, which can range between 28 milligrams per liter (mg/L) (USGS 2012) and 35 mg/L (Eklund 2010) at atmospheric pressure. In shallower aquifers, methane will typically convert to a gaseous state and migrate vertically through the vadose zone.

The methane present in the vadose zone and groundwater in OU-1 is the result of the OU-1 Enhanced Attenuation (EA) Field Demonstration performed from 2014 to 2018. Edible oils were injected into the vadose zone at the groundwater interface and into the groundwater itself to enhance the microbial activity to degrade VOCs in groundwater and reduce infiltration of VOCs from the vadose zone to the underlying groundwater. Methane is generated through the microbial reductive dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE), and its presence was expected and is necessary to create and maintain the series of structured (anaerobic and aerobic) geochemical zones as shown in Figure 1. As illustrated in this figure, methane generated by microbes in the treatment zones as TCE and also PCE are degraded and then subsequently utilized by other microbes as a substrate in the aerobic cometabolic degradation of *cis*-1,2-dichloroethene (cDCE) and vinyl chloride (VC). Results from the field demonstration are available in three annual status reports and the final completion report (DOE 2016; DOE 2017; DOE 2019; DOE 2020).

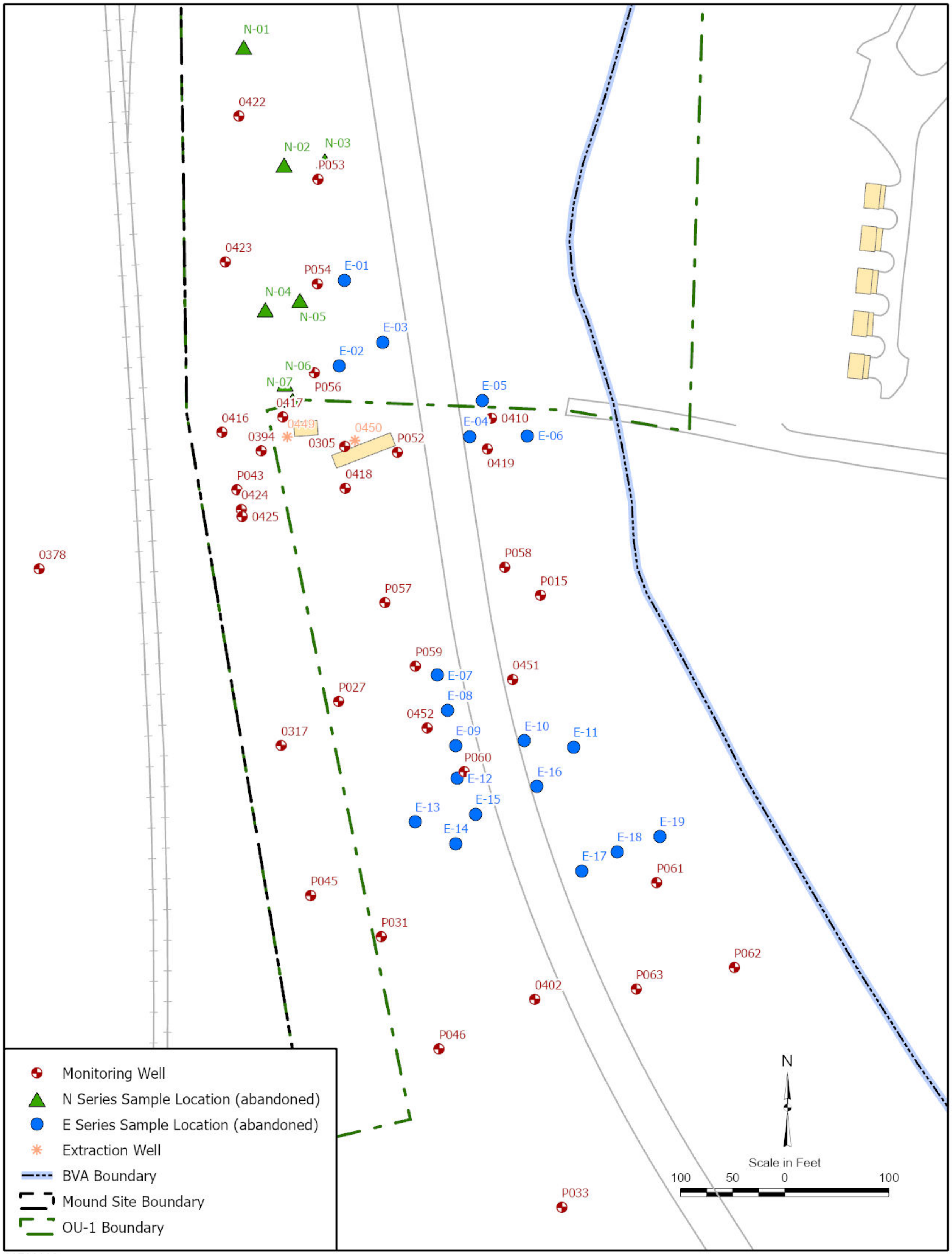


Abbreviations: Cl^- = chloride, CO_2 = carbon dioxide, DCE = dichloroethene, H_2O = water

Figure 1. General Anaerobic and Aerobic Treatment Zone Processes

The final deployment design (Figure 2) consisted of neat oil injection at six 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:

- **Former Source Area—Soil:** 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 milligram per kilogram.
- **Former Source Area—Groundwater:** Strategic emulsified oil injection in the groundwater to form treatment zones that address key flow lines in the aquifer beneath the former landfill area.
- **Downgradient of Former OU-1 Landfill—Groundwater:** Intensive emulsified oil injection in multiple locations to address the VOC-impacted groundwater downgradient of the former landfill.



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Abbreviation: BVA = Buried Valley Aquifer

Figure 2. OU-1 Field Demonstration Injection Point and Monitoring Well Locations

Groundwater samples are collected from selected wells in the OU-1 area (Figure 2). Monitoring wells are divided into different categories based on their location within the treatment area. These categories are:

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

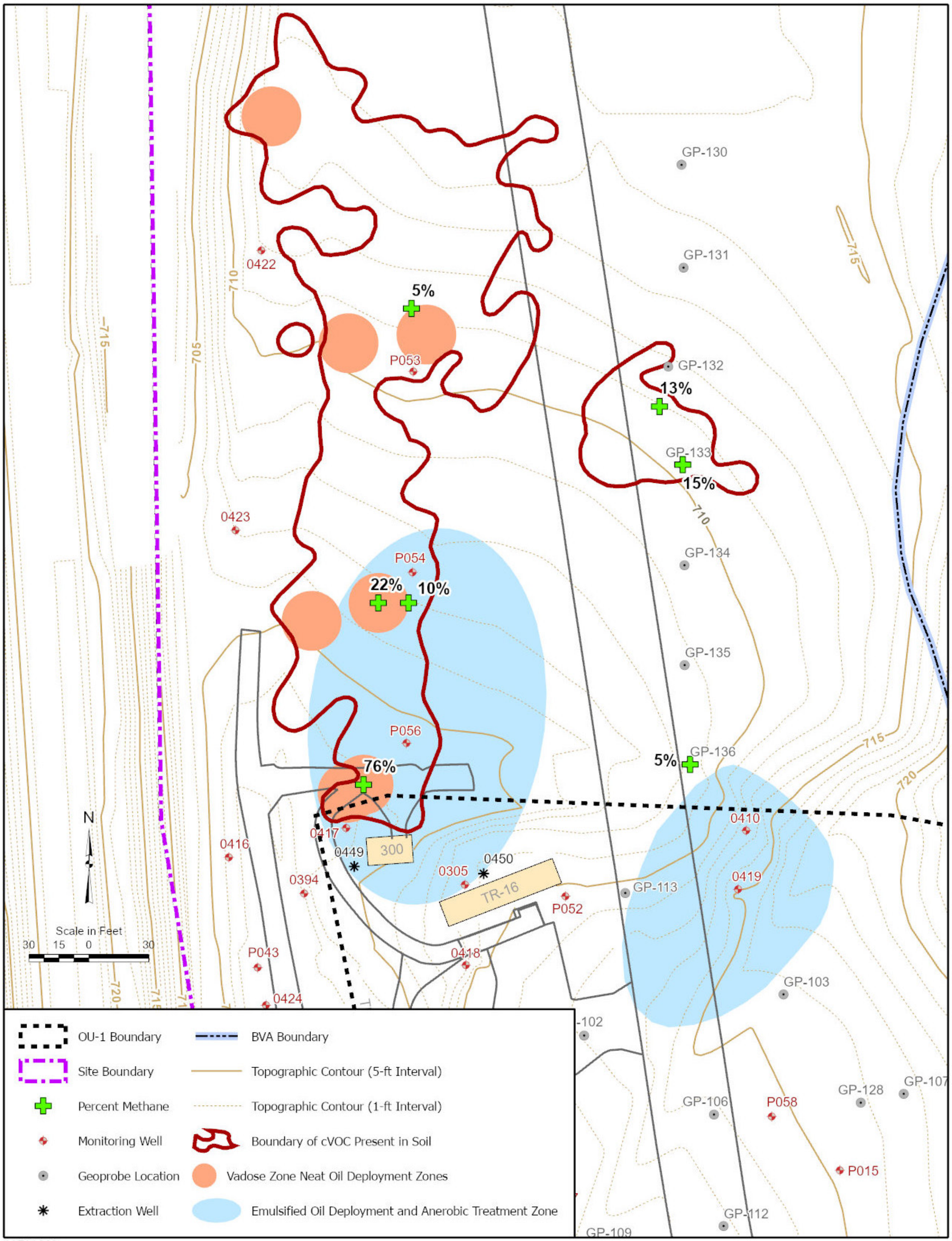
VI of methane is fundamentally different than VI of VOCs for several reasons. For VOCs, the concentration present in soil gas can be directly related to the potential risk; higher concentrations equate to greater potential for risk from VI. This correlation can be made because the primary transport mechanism is diffusion—transport is primarily driven by differences in concentration. For methane, the concentration does not correlate to the amount of methane present in the subsurface or its rate of generation. Even in areas with low microbial activity, concentrations of methane in soil gas can approach 50% or more at the point of generation. The primary transport mechanism of concern for methane is advective flow—transport is primarily driven by differences in pressure. For VI of methane to lead to an explosion, large volumes of soil gas need to migrate into a building or confined space in a relatively short time and accumulate until concentrations reach or exceed 5% (Eklund 2010). The rate of generation of methane promotes transport in the subsurface to the surface or to buildings or preferential flow paths. Since methane is lighter than air, it tends to migrate vertically in the subsurface; however, if the production of methane is sufficiently high, differential pressure can induce flow along preferential flow paths, such as a permeable conduit (i.e., buildings, utility corridors, or geological zones) or beneath an impermeable barrier. For in situ bioremediation projects, the generation rates of methane are insufficient to create the volumes and pressures needed to create significant transport of methane, and diffusion of methane becomes the primary mechanism for movement.

2.1 Methane in Subsurface Vapors in OU-1

In November 2020, DOE performed methane screening using the same locations and depths as the Ohio EPA comparative sampling event, which was performed in February 2020. A meter to measure total percent methane present was used rather than a meter that only recorded the amount of methane present with respect to its LEL. Results from the screening were similar to those from the Ohio EPA comparative sampling, with locations exhibiting methane readings at or near 100% of the LEL still having elevated methane values. Appendix A contains the summary prepared by the Legacy Management Support subcontractor for this work.

In December 2020, the methane screening results and information about the OU-1 EA Field Demonstration were provided for review to Weiss Associates, a consulting firm with vast experience in VI. Weiss Associates indicated that the results were typical for bioremediation-type projects where elevated methane was present within injection and treatment areas. Samples collected near the point of biogas production (i.e., injection sites) typically contain high levels of methane, as biogases are roughly composed of 50% methane and 50% carbon dioxide.

Comparison of data from the methane screening to current conditions (i.e., VOC distribution and aquifer geochemistry data) in OU-1 resulting from the OU-1 EA Field Demonstration shows that the highest methane measurements are colocated with the treatment zone in the southwest corner of the landfill footprint where neat oil was also deployed at select locations (Figure 3). TCE is very low in this area, and the geochemistry of the area is reduced (anaerobic), which is conducive for microbial reductive dechlorination of PCE and TCE and generation of methane. Higher methane measurements were also associated with a known area of VOC impact in the vadose zone along the eastern boundary of the landfill as identified from 2012 soil-gas results (DOE 2014).



Abbreviation: cVOC = chlorinated volatile organic compound

Figure 3. Locations of Elevated Methane Readings—March 2020

2.2 Methane in Groundwater in OU-1

Methane concentrations in groundwater before the start of the OU-1 EA Field Demonstration in 2014 were reported as nondetect (less than 10 mg/L) (DOE 2016). Small areas exhibiting reducing environments and evidence of some biological reduction of TCE were observed but were generally not robust; therefore, there was little methane production.

During the first 18 to 24 months of the OU-1 EA Field Demonstration, methane concentrations in groundwater increased significantly within the treatment zones as microbial populations increased in response to the added substrate and then concentrations subsequently decreased. Figure 4 and Figure 5 show the concentrations of methane in wells in the two treatment zones in the OU-1 area. Biogenic methane production was the highest during this period in response to the injection of oils in the vadose zone and the aquifer. Methane concentrations were highest in wells P056 and P060, reaching saturation in water during the first 12 months of the field demonstration. Methane can reach saturation at 28 mg/L (USGS 2012) to 35 mg/L (Eklund 2010) at atmospheric pressure. It is likely that the methane was confined beneath the neat oil remaining on the surface of the water table and the clayey till and backfill materials in the vadose zone, resulting in methane becoming saturated during this period in the groundwater. Methane biodegradation is expected to occur rapidly in the presence of oxygen (DOD 2006), and the rate of methane production in the anaerobic treatment zone would generally be expected to decrease as the substrate was consumed. As the field demonstration progressed, the concentrations of methane in groundwater decreased in the treatment zones as substrate was consumed and as the microbial community declined in response to the decreasing mass of PCE and TCE in the treatment zones.

Figure 6 shows the concentrations of methane in the interior transition zone between the two treatment zones. Concentrations of methane in groundwater were highest during the first few years of the field demonstration but were not as high as those within the treatment zones where methane production occurred. It was expected that methane generated during the anaerobic respiration process would be consumed as part of the cometabolism of VOCs in this interior (aerobic) zone between the two treatment zones. The concentrations of methane in the wells along the downgradient edge of the transition zones are lower than those in the upgradient treatment and interior transition zone shown in Figure 7.

Historical methane distributions during the field demonstration can be found in Appendix B. The distributions of methane in groundwater indicate that the areas of biogas generation are in or near the treatment zones, as would be expected. Concentrations of methane decrease substantially downgradient of the treatment zones due to consumption of methane by microbes or conversion of methane to a gaseous state and vertical migration into the vadose zone.

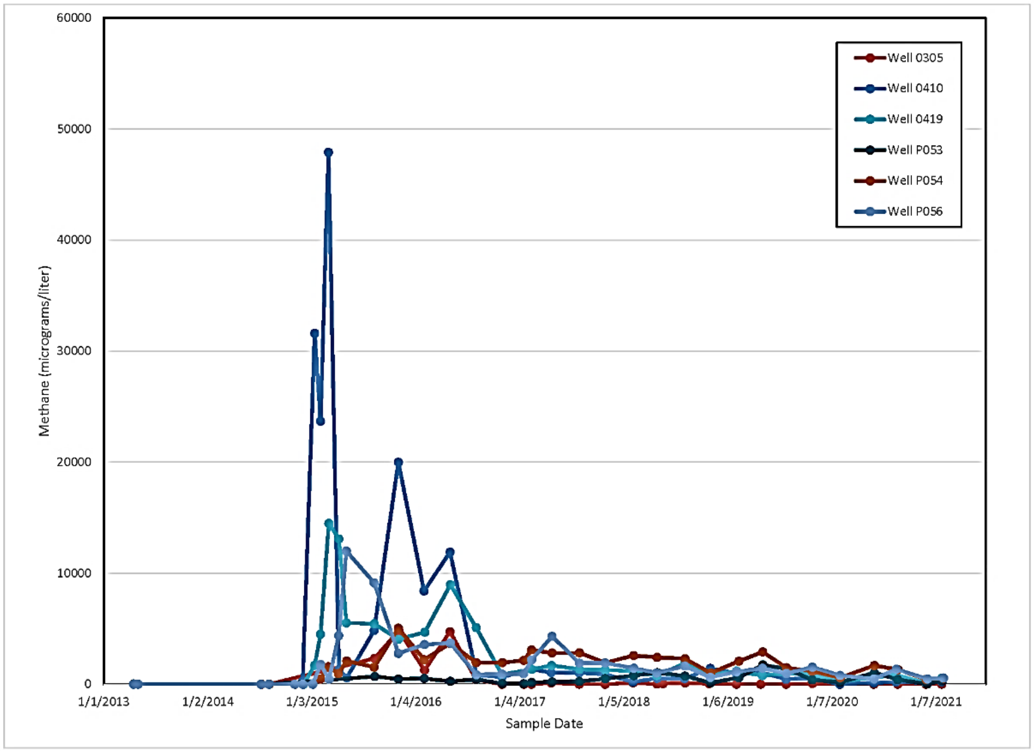


Figure 4. Methane in Groundwater—Treatment Zone 1 (North)

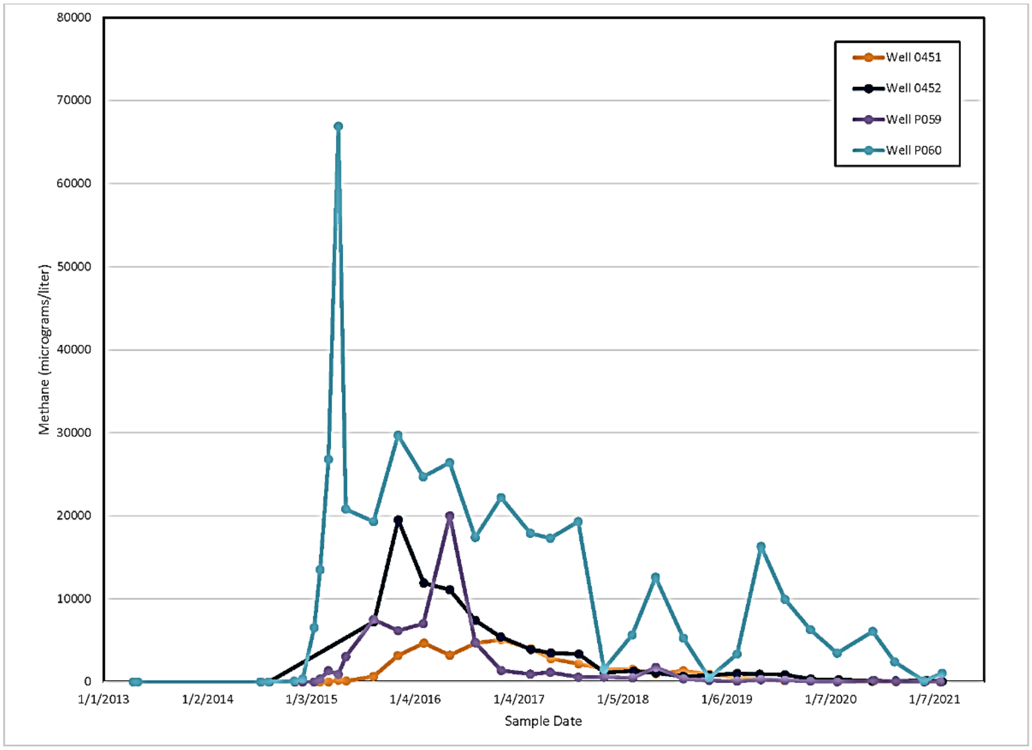


Figure 5. Methane in Groundwater—Treatment Zone 2 (South)

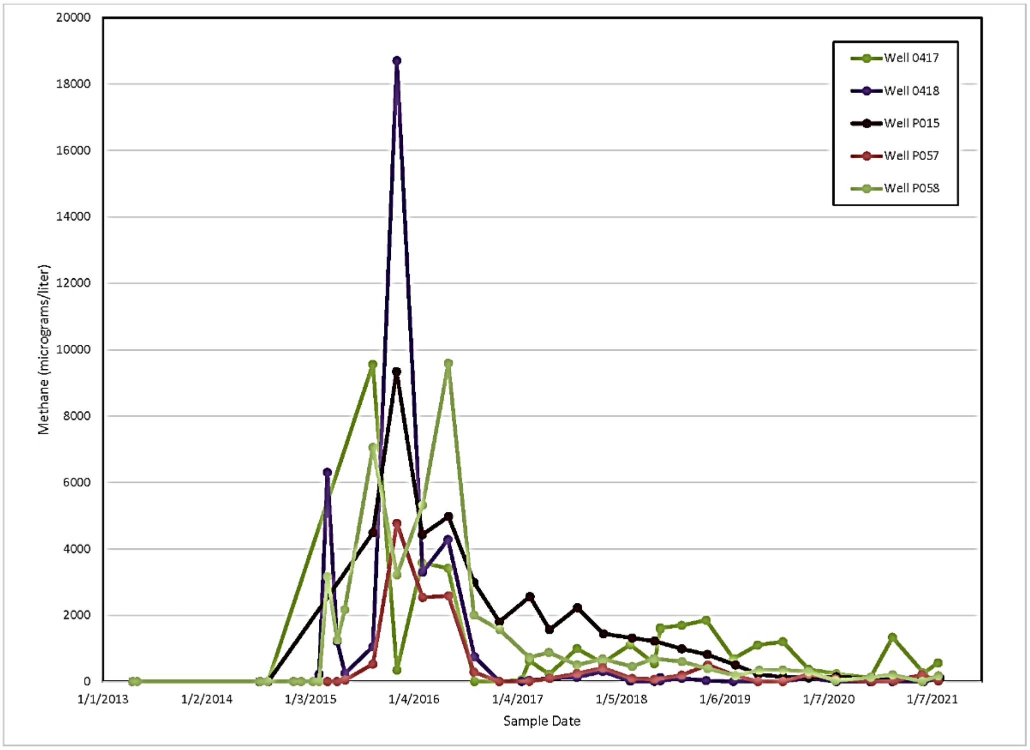


Figure 6. Methane in Groundwater—Interior Transition Zone

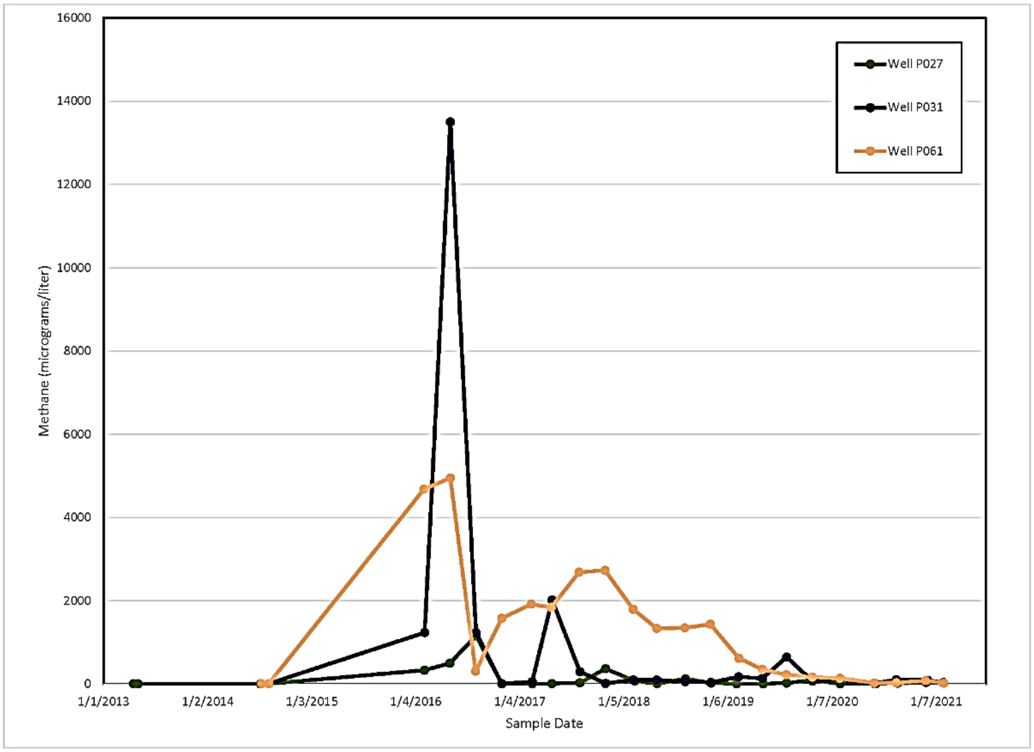


Figure 7. Methane Groundwater—Downgradient of Interior Transition Zone

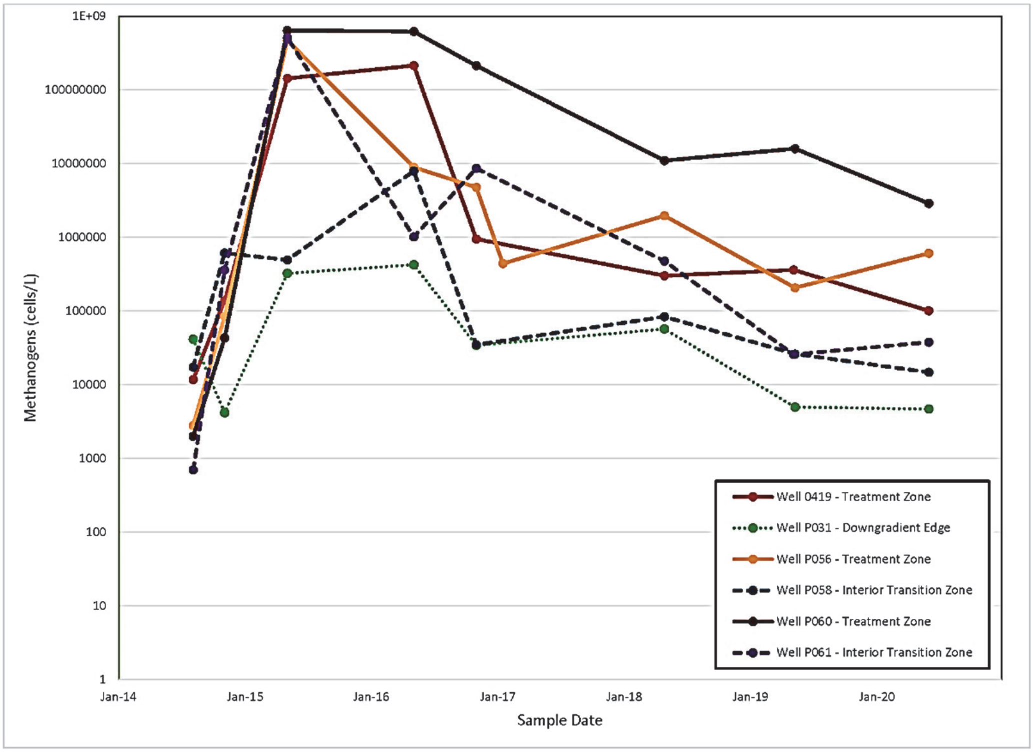
2.3 Methane Generated and Consumed by Microbial Action in OU-1

The soil-gas screening data collected in OU-1 show that the highest methane values generally coincide with the locations where neat oil was deployed beneath known VOC "hot spots" at the base of the landfill excavation (Figure 3). This neat oil was deployed at the water table to reduce the mass flux of residual VOCs from the vadose zone into the groundwater by creating a zone where VOCs would be sequestered into the oil and slowly released over time. The neat oil also is used as a substrate for microbial activity, and degradation of released VOCs in the anaerobic environment near the neat oil zones further limits infiltration into the aquifer. These neat oil zones were designed to be about 30 to 35 ft in diameter; therefore, they cover just a limited portion of the aquifer near the injection points.

The occurrence of elevated methane in groundwater is limited; the highest concentrations in groundwater are associated with the treatment zones created by the injection of emulsified oil into the aquifer. Microbial activity is highest in these zones, and methane is produced as the emulsified oils are consumed and fermentation persists. Methane gas has a greater affinity to migrate vertically through saturated and unsaturated media because it is lighter than air. Any methane gas that does become soluble in water can move laterally with groundwater flow where it is consumed by microbes that cometabolize VOCs in the aerobic portions of the aquifer downgradient of the anaerobic treatment zones.

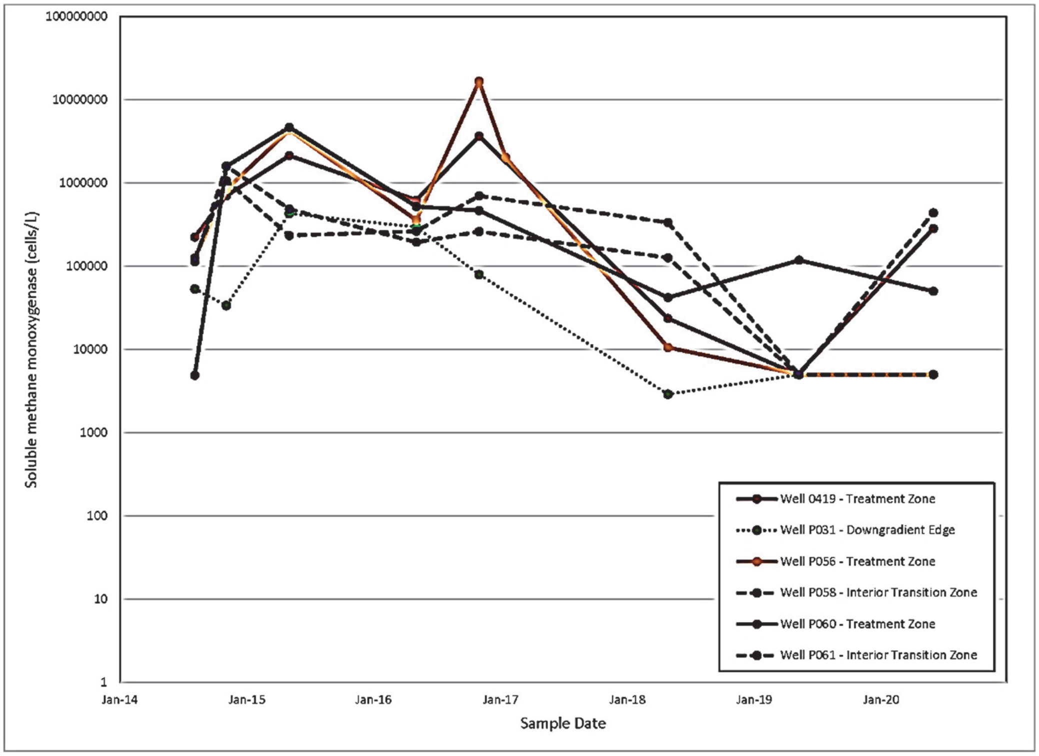
The microbial data collected during and after completion of the OU-1 EA Field Demonstration were reviewed to evaluate the generation and consumption of methane within the treatment zones. The following observations have been noted:

- Methanogen counts in groundwater indicate that the largest communities are present within the treatment zones (depicted as solid lines in Figure *8*). Methanogens are microbes that produce methane as part of the metabolic process as they consume organic materials (neat and emulsified oil).
- Soluble methane monooxygenase (MMO) counts in groundwater indicate that the largest methanotrophs (organisms that consume methane) have been variable, but, in general, the counts have been higher in the interior transition zone (depicted as dashed lines in Figure *9*) later in the field demonstration. MMO is an enzyme produced by methanotrophs, and this enzyme plays a key role in the aerobic cometabolism process for TCE, cDCE, and VC.



Abbreviation: cells/L = cells per liter

Figure 8. Methanogens in Groundwater



Abbreviation: cells/L = cells per liter

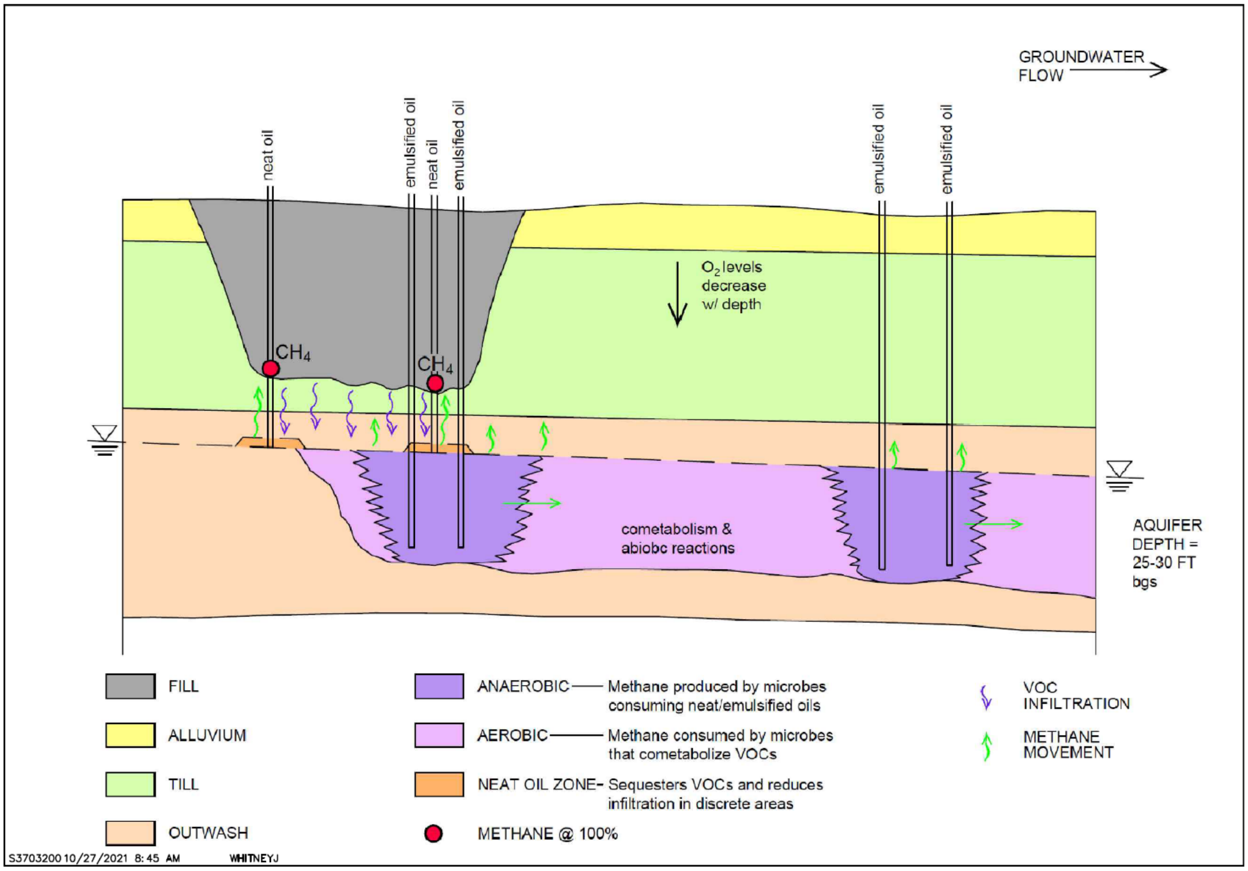
Figure 9. Soluble MMO Representing Methanotrophs in Groundwater

3.0 Conceptual Site Model for VI Regarding Methane in OU-1

The methane present in the vadose zone and groundwater is the result of the OU-1 EA Field Demonstration study. Methane is generated by enhanced microbial reductive dechlorination of PCE and TCE within the treatment zones. The rate of methane production for bioremediation projects are generally low; therefore, diffusion becomes the primary transport mechanism because there are insufficient pressure differentials for advective flow to occur. The methane that is present in the groundwater either converts to a gaseous state and diffuses vertically through the vadose zone or is transported in the groundwater where it is then subsequently utilized by other microbes as a substrate in the aerobic cometabolic degradation of cDCE and VC. The primary source for VOCs in the OU-1 area are residually impacted vadose zone materials remaining within the bottom of the excavation of the former landfill and, to a lesser extent, the underlying and downgradient groundwater in the BVA (outwash aquifer). Based on the types of affected media (soil and groundwater), the following methane transport mechanisms should be considered:

- Movement of methane through the vadose zone within the former landfill area
- Release of methane from groundwater
- Migration of methane through preferential pathways

Figure 10 is a CSM of methane in the OU-1 area. The areas of methane generation and migration are depicted using a cross section through the former landfill area. The cross section depicts the material types in the vadose zone, depth to groundwater in the area, EA treatment zones, and known areas with elevated methane results.



Abbreviations: CH_4 = methane, O_2 = oxygen

Figure 10. CSM for Methane and Generalized Cross Section Through OU-1 Landfill

3.1 Movement of Methane Through the Vadose Zone in Former Landfill Area

Methane generated in the vadose zone and groundwater within the landfill footprint will primarily move upward (vertically) through the vadose zone because methane is lighter than air. Some methane that has become soluble in the groundwater will move laterally until transitioning to a gaseous phase from the groundwater or being consumed by microbes (i.e., MMOs) as part of the cometabolism process of VOCs. For methane in soil gas, transport is influenced by the physical properties of the soil (e.g., grain size and structure), the rate that methane is generated in the subsurface, and how deep the methane is generated.

Unconsolidated materials in the OU-1 area consist primarily of artificial fill, recent alluvial deposits, glacial till, and glacial outwash. The following is a general summary of each unit:

- The fill material is typically composed of compacted clean soil materials composed of silt and clay. Depending upon compaction, fill material may have a moderate to low permeability.
- The alluvium is mostly overbank deposits consisting of stratified fine sands, silts, and clays.

- The till is composed of an unsorted, unstratified mixture of clay, silt, sand, and coarser materials. These materials typically have low permeability.
- The outwash is composed of well-sorted to moderately well-sorted sand and gravel and, in the OU-1 area, can be interstratified with till. The outwash is generally saturated and makes up the bulk of the BVA of the Great Miami River.

Elevated methane levels were encountered at depths ranging between 18 and 28 ft bgs (Terran 2020). As methane moves upward through the vadose zone, it is attenuated via aerobic degradation in the shallow portions of the vadose zone where oxygen is present. Since the unconsolidated materials are generally heterogenous, there is less likelihood for preferential movement through zones of permeable materials.

3.2 Release of Methane from Groundwater

Migration of methane in groundwater is influenced by groundwater flow direction and pathways, as well as the properties of the overlying vadose zone materials. Groundwater flow in OU-1 occurs within the unconsolidated glacial deposits (i.e., till and outwash) in OU-1. The groundwater surface is relatively flat and changes in groundwater elevation in the unconfined aquifer across OU-1 are approximately 1 ft, resulting in low hydraulic gradients (average 0.0002 ft/ft). The typical flow rate of the aquifer is about 57 ft per year (DOE 2014).

The low flow rate within the aquifer limits the lateral distance that soluble methane can move downgradient of the points of generation within the treatment zone before being consumed by microbes (MMOs) as part of the cometabolic degradation of VOCs or transitioning to a gaseous form and moving vertically through the vadose zone.

3.3 Migration of Vapors in Preferential Pathways

If sufficient volumes are generated, methane can migrate distances through either natural or man-made pathways with high gas permeability via advective flow. There are active and abandoned utility conduits present within the OU-1 area that could act as conduits into future buildings. Figure 11 shows the locations of underground utilities, both active and inactive, within OU-1/Parcel 9. These utilities are present about 10 ft to 15 ft bgs.

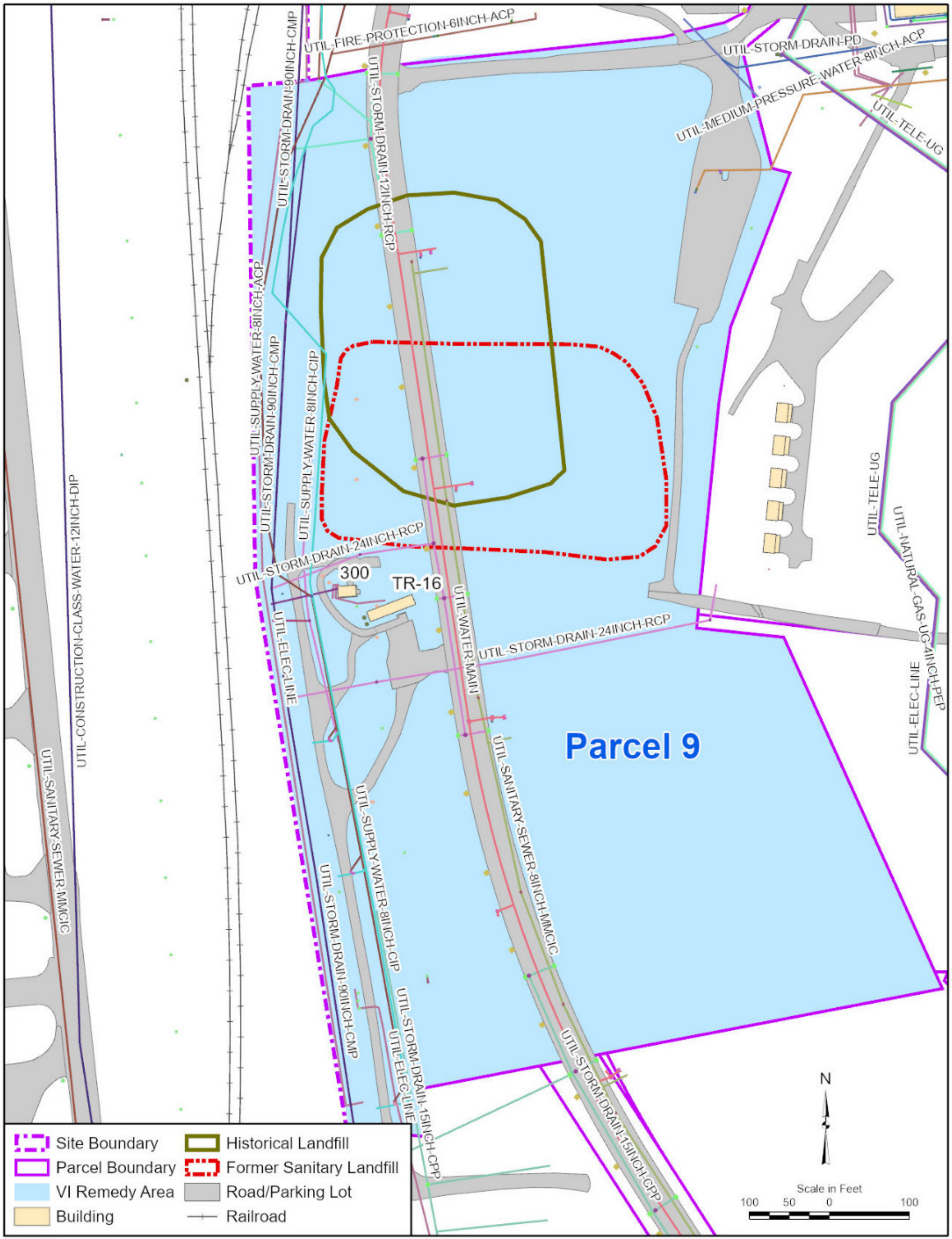


Figure 11. Location of Underground Utilities in OU-1/Parcel 9

4.0 Review of Potential Risk from Methane in OU-1 Landfill Area

This section provides general recommendations about risk pertaining to methane in the subsurface in the former OU-1 landfill area. The risk review is supported by the CSM presented in Section 3.0, which has been supported by several lines of site-specific data and the assumption that subsurface sources of methane have been sufficiently identified (as presented in Section 2.0) to support the risk management decisions for the site.

4.1 Site-Specific Lines of Data

VI pathways are generally assessed using multiple lines of evidence. As discussed in the EPA VI guidance (EPA 2015), appropriate lines of evidence to support development of the CSM and evaluate the VI pathway may include the following:

- Identifying subsurface vapor sources
- Determining vapor migration pathways
- Determining potential attenuation processes for vapors in the subsurface
- Identifying the susceptibility of a building for vapor entry

4.1.1 Subsurface Vapor (Methane) Sources

In the OU-1 area, subsurface conditions were enhanced through the injection of edible oils to promote anaerobic conditions at and below the water table to stimulate existing microbial communities and promote anaerobic reductive dechlorination of PCE and TCE in the aquifer. Additional neat oil was injected in discrete locations within the footprint of the former landfill to sequester VOCs that may infiltrate from the remaining residually contaminated soils in the bottom of the landfill excavation and then slowly release into the underlying groundwater and ultimately be attenuated. The injection patterns and design of the treatment zones were done so the methane generated during the reductive degradation of PCE and TCE was used as a substrate for the downgradient aerobic cometabolism of the daughter products, cDCE and VC. The generation of methane by microbes consuming the injected oils was expected and necessary to enhance the attenuation of VOCs using a series of anerobic and aerobic treatment zones. The microbial processes typically proceed slowly with peak microbial activity and production of methane occurring shortly after injection of the substrates, which was performed in fall 2014.

Methane production was highest during the first 12 to 18 months of the field demonstration when microbial activity was at its highest and ample substrate was available; several lines of evidence support that the generation of methane has since decreased. These lines of evidence are:

- The microbial communities have reduced in number due to the decreasing mass of PCE and TCE in the treatment zones (DOE 2020) resulting in less methane generation.
- Methane concentrations in groundwater decreased significantly within the treatment zones after the initial increases that occurred after the injection of the neat and emulsified oils.

4.1.2 Vapor (Methane) Migration and Attenuation

The rate of generation of methane affects the propensity for methane to move away from its production source via advective flow rather than diffusion. Advective (pressure-driven) transport is the transport mechanism of primary concern with respect to VI of methane. The decrease in microbial community counts have resulted in a decrease in methane generation, thereby limiting pressure driving forces that could be created within the treatment zones. Since the decline in the production of methane within the treatment zone, it can be concluded that the primary migration route for methane is not lateral movement via advective flow, but rather vertical diffusion through the overlying vadose zone.

Because the primary migration direction of methane is vertical through the overlying soil and backfill material in the former landfill area, methane is attenuated as oxygen and microbes that oxidize methane are encountered in the vadose zone. The greatest amount of microbial oxidation typically occurs within the upper 20 cm of the vadose zone. The depth where methane is produced in the former landfill area is approximately 25 ft bgs or deeper based on the location of the neat oil treatment zones or the emulsified oil treatment zones in the aquifer. The vadose materials are generally silt and clay that comprise both the till unit and the clean backfill that was compacted within the landfill excavation. These materials have relatively low permeabilities meaning vertical migration should be considered slow.

Preferential pathways consisting of new and abandoned utilities are present in the OU-1 area. However, these utilities are generally no more than 10 ft bgs. Because methane is typically generated greater than 20 ft bgs and vadose zone materials have a low permeability, it is unlikely that a large volume of methane could diffuse through the vadose zone materials and accumulate within the bedding materials associated with the utilities or migrate within the bedding materials within the utility excavation that would result in an explosive hazard.

4.1.3 Entry of Vapors (Methane) into Buildings

Currently, there are no buildings in Parcel 9, but the area is zoned as commercial/industrial and construction and occupancy of buildings is likely in the near future. Because the generation of methane should continue to decrease as the parent compounds of PCE and TCE are degraded in the aquifer and methane that is currently present, as well as any methane generated should continue to be consumed as part of the attenuation of daughter products, it is unlikely that methane will be generated at a rate in the future that could result in advective transport of methane into current or future utility corridors or future buildings.

4.2 VI Pathway Assessment (complete or incomplete)

A complete pathway indicates that there is an opportunity for human exposure, which warrants further analysis to determine whether there is a basis for undertaking a response action. Specifically, a complete exposure pathway does not necessarily mean that an unacceptable human health risk exists due to VI. Rather, specific exposure conditions, such as the magnitude, frequency, and duration of exposures, or the contribution from background concentrations warrant examination. It is then recommended that additional analyses be conducted to assess and characterize human health risk to building occupants where the VI pathway is determined to be complete. Alternatively, human exposure and health risk from the VI pathway will not exist if the pathway is not complete. As outlined in the EPA VI Guidance (EPA 2015), a VI pathway is referred to as "complete" for a specific building or collection of buildings when the following five conditions are met under current conditions:

- A subsurface source of vapor-forming chemicals is present underneath or near the building(s)
- Vapors form and have a route along which to migrate toward the building(s)
- The buildings are susceptible to soil-gas entry, which means openings exist for the vapors to enter the building and driving forces exist to draw the vapors from the subsurface through the openings into the building(s)
- One or more vapor-forming chemicals comprising the subsurface vapor source(s) is (or are) present in the indoor environment
- The building is occupied by one or more individuals when the vapor-forming chemical(s) is (or are) present indoors

In the case of properties like OU-1/Parcel 9 where buildings are not present but will likely be constructed in the future, the EPA VI Guidance suggests that evaluations consider whether the VI pathway is "potentially complete" under reasonably expected future conditions. The VI pathway is referred to as "potentially complete" for a building when the following conditions could be met in the future:

- A subsurface source of vapor-forming chemicals is present underneath or near an existing building or a building that is reasonably expected to be constructed in the future
- Vapors can form from this source(s) and have a route along which to migrate toward the building
- The three additional conditions are reasonably expected to all be met in the future:
    - The building is susceptible to soil-gas entry, which means openings exist for the vapors to enter the building and driving forces exist to draw the vapors from the subsurface through the openings into the building
    - One or more vapor-forming chemicals comprising the subsurface vapor source(s) is (or will be) present in the indoor environment
    - The building is or will be occupied by one or more individuals when the vapor-forming chemical(s) is (or are) present indoors.

It has been determined that "potentially complete" exposure pathways for methane do not exist in OU-1/Parcel 9 using the above-listed conditions. The second condition is not met because there is not a route for methane to migrate toward the buildings. Even though there is a subsurface source of methane in the former landfill area, there is insufficient generation of methane occurring or that will occur in the future that would result in the advective transport of methane into future buildings or existing or future utility corridors and result in the accumulation of methane that could result in an explosion hazard.

5.0 Conclusions

The review of available data and information compiled in the CSM supports that methane should not be considered a VI hazard in OU-1. In general, high methane levels alone are not enough to indicate a potential explosion risk, and other factors, such as sufficient generation of methane, attenuation of methane in the subsurface, and opportunities for accumulation, need to be considered. Methane was generated by microbes consuming the oils injected as part of the OU-1 EA Field Demonstration in 2014. Injections were performed at the water table that is approximately 25 ft bgs. Methane production was highest during the first 12 to 18 months of the field demonstration and then significantly decreased. The decrease in methane generation limited any pressure driving forces that could be created in the treatment zones, thereby reducing lateral migration. It was concluded that the primary migration route for methane is vertical diffusion. Because the primary migration direction of methane is vertical, it is attenuated as oxygen, and microbes that oxidize methane are encountered in the vadose zone. All these lines of evidence result in the elimination of methane as a VI hazard in OU-1.

6.0 References

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Appendix A

Methane Field Screening Performed by Terran Corporation in November 2020

Terran Corporation

Environmental Services

Becky Cato
Via email (Becky.Cato@lm.doe.gov) December 1, 2020

Re: Methane Soil Vapor Testing Task 1 Results

Becky,

Terran was tasked to perform soil gas testing at the Mound OU-1 area for methane concentrations as well as volatile organic compounds (VOCs) and oxygen content. Terran completed the testing over a two day period at 16 sampling locations on November 23 and 24, 2020. The methane and oxygen content was measured using a GEM-2000 landfill gas monitor while the VOCs were measured using a MiniRae-3000 photoionization detector (PID). Both instruments were calibrated on November 19, 2020 and checked with reference gases each morning prior to use.

When using the MiniRae, the unit faulted at locations SP-2, 4, 5, 6, 7, and 8 due to increased vacuum while connected to the sample tube causing the pump to shut off. The unit was generally turned back on a couple times to capture a relative reading. The PID readings at those locations were estimated and not to be considered accurate. The logical conclusion was that the sample location depth was below the current groundwater level. There was standing surface water noted along the west side of the area due to some recent rainfall.

The data is presented in the table below. Methane results ranged up to 75% (SP-11) along the foot of the old landfill. The VOC data indicated the highest amounts in SP-3, 4 and 6 with no measurable VOCs in the locations that had the highest methane. Previous testing by the Ohio EPA in early 2020 showed much that same trend with SP-4 having by far the highest PID reading and the locations along the landfill having the highest methane readings.

Based on these results, it is obvious there are still some VOCs in the soil gas in the vicinity of the lactate injection area as well as high methane concentrations near the foot of the old landfill that was removed. It is recommended that the phase 2 sampling with Tedlar bags and in-lab analysis be postponed until the water table drops or there becomes an urgent need for more precise data.

Please let us know if you have any questions or concerns.

Best Regards,

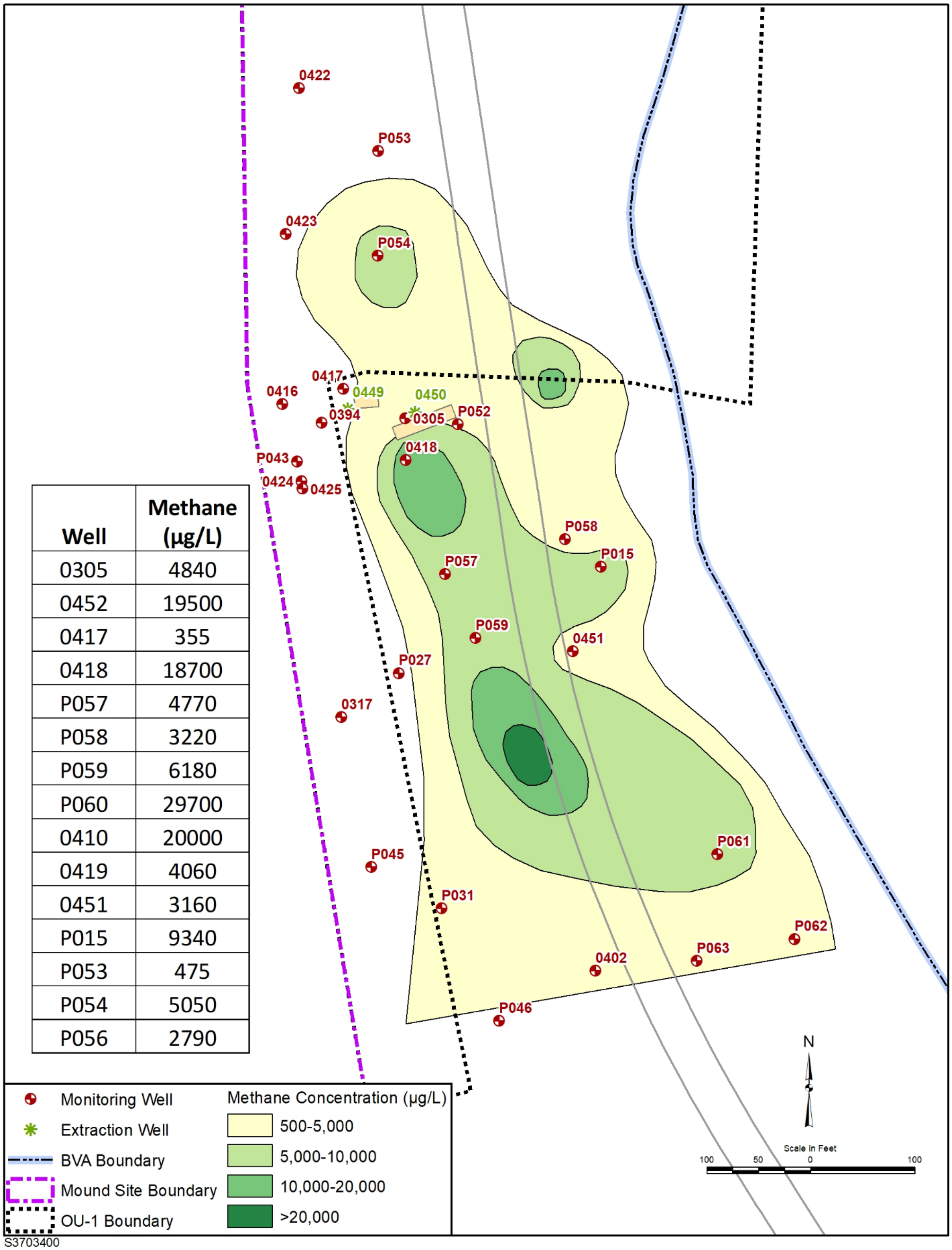
Chris Athmer – Terran Corporation

Table 1. Methane, O2 and VOC Soil Gas Measurements for November 2020.

Sampling Location	**Date**	**Time**	**Multi-Gas Meter**[1]		**PID**[2]	**Comments**	Sample Depth (bgs)
			CH4 (%)	**O2 (%)**	**VOC (ppm)**		
SP-1	11/23-24/2020	1009/0829	1.1	21.4	0.8	W.L. = 12.39' below TOC	25 ft
SP-2	11/23-24/2020	1001/0828	0.6	20.2	1.0	Appears to be pulling against a vacuum. W.L. = 19.79' below TOC	18 ft
SP-3	11/23-24/2020	0956/0825	5.4	8.7	57.6		20 ft
SP-4	11/23-24/2020	0940/0822	0.7	20.1	228	Appears to be pulling against a vacuum.	19 ft
SP-5	11/23-24/2020	0932/0840	1.4	18.4	0.8	Appears to be pulling against a vacuum. W.L. = Dry	21.5ft
SP-6	11/23-24/2020	0921/0832	0.0	15.4	14.5	Appears to be pulling against a vacuum. W.L. = 18.67' below TOC	18.5 ft
SP-7	11/23-24/2020	0926/0833	1.7	13.1	3.1	Appears to be pulling against a vacuum.	19 ft
SP-8	11/23-24/2020	0915/0837	0.0	22.0	0.0	Appears to be pulling against a vacuum. W.L. = 15.16' below TOC	19.5 ft
SP-9	11/23-24/2020	0906/0836	21.5	15.8	0.0		27 ft
SP-10	11/23-24/2020	0858/0835	10.1	18.2	0.0	W.L. = Dry	26 ft
SP-11	11/23-24/2020	0850/0838	75.8	0.0	0.0	W.L. = Dry	18.5 ft
SP-12	11/23-24/2020	1016/0841	12.9	1.8	0.0		28 ft
SP-13	11/23-24/2020	1021/0842	14.6	0.0	0.0		26 ft
SP-14	11/23-24/2020	1025/0843	4.6	0.8	0.0		20 ft
SP-15	11/23-24/2020	1034/0846	0.5	0.0	0.0		20 ft
SP-16	11/23-24/2020	1031/0845	0.4	5.3	0.5		16 ft

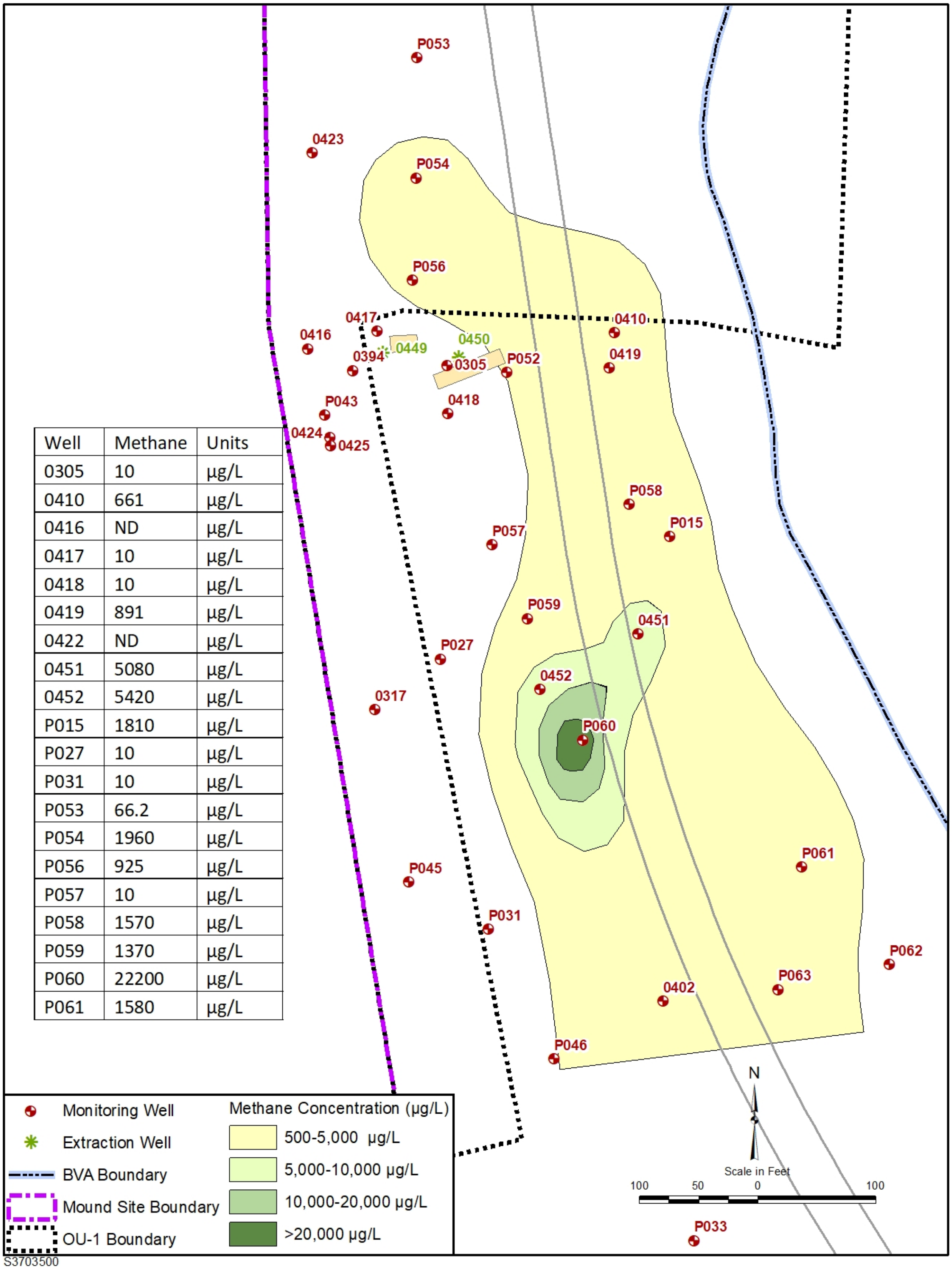
Appendix B

Distribution of Methane in OU-1 During the OU-1 EA Field Demonstration



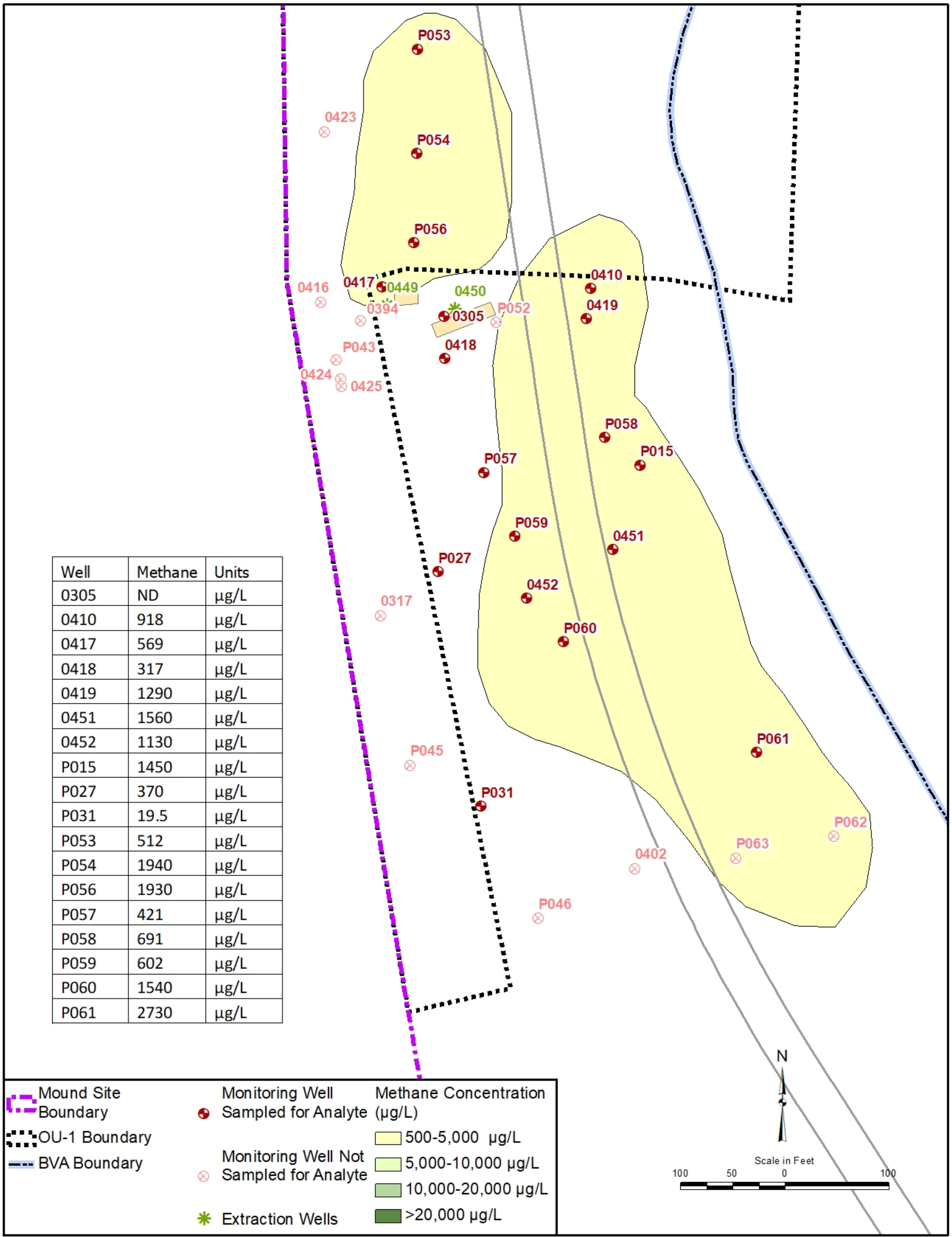
Well	Methane (µg/L)
0305	4840
0452	19500
0417	355
0418	18700
P057	4770
P058	3220
P059	6180
P060	29700
0410	20000
0419	4060
0451	3160
P015	9340
P053	475
P054	5050
P056	2790

Figure B-1 Methane Distribution in OU-1 – November 2015



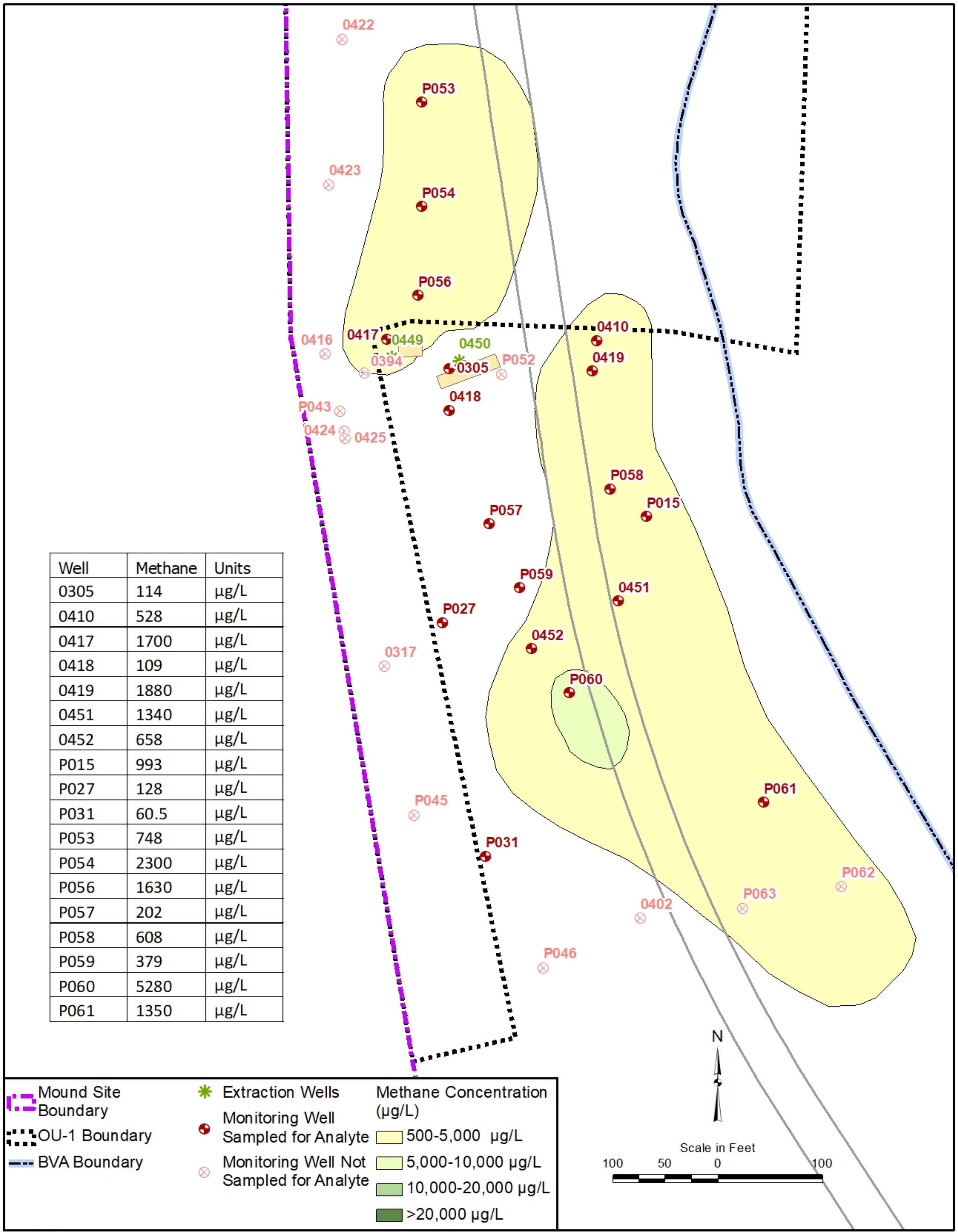
Well	Methane	Units
0305	10	µg/L
0410	661	µg/L
0416	ND	µg/L
0417	10	µg/L
0418	10	µg/L
0419	891	µg/L
0422	ND	µg/L
0451	5080	µg/L
0452	5420	µg/L
P015	1810	µg/L
P027	10	µg/L
P031	10	µg/L
P053	66.2	µg/L
P054	1960	µg/L
P056	925	µg/L
P057	10	µg/L
P058	1570	µg/L
P059	1370	µg/L
P060	22200	µg/L
P061	1580	µg/L

Figure B-2 Methane Distribution in OU-1 – November 2016



Well	Methane	Units
0305	ND	µg/L
0410	918	µg/L
0417	569	µg/L
0418	317	µg/L
0419	1290	µg/L
0451	1560	µg/L
0452	1130	µg/L
P015	1450	µg/L
P027	370	µg/L
P031	19.5	µg/L
P053	512	µg/L
P054	1940	µg/L
P056	1930	µg/L
P057	421	µg/L
P058	691	µg/L
P059	602	µg/L
P060	1540	µg/L
P061	2730	µg/L

Figure B-3 Methane Distribution in OU-1 – November 2017



Well	Methane	Units
0305	114	µg/L
0410	528	µg/L
0417	1700	µg/L
0418	109	µg/L
0419	1880	µg/L
0451	1340	µg/L
0452	658	µg/L
P015	993	µg/L
P027	128	µg/L
P031	60.5	µg/L
P053	748	µg/L
P054	2300	µg/L
P056	1630	µg/L
P057	202	µg/L
P058	608	µg/L
P059	379	µg/L
P060	5280	µg/L
P061	1350	µg/L

S3703700

Figure B-4 Methane Distribution in OU-1 – August 2018