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In Situ Treatment and Management Strategies for 1,4-Dioxane-Contaminated Groundwater

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The presence of 1,4-dioxane in groundwater at DoD sites is significantly impacting the DoD's understanding of its environmental liabilities. The overall objective of this project was to examine management strategies for sites contaminated with 1,4-dioxane through applied research on novel in situ treatment technologies, modifications to existing technologies, and a better understanding of plume transport and attenuation characteristics. The goal is to use these findings to develop a more informed basis for managing these sites.

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ABSTRACT

OBJECTIVES: The presence of 1,4-dioxane in groundwater at DoD sites is significantly impacting the DoD's understanding of its environmental liabilities. The overall objective of this project was to examine management strategies for sites contaminated with 1,4-dioxane through applied research on novel in situ treatment technologies, modifications to existing technologies, and a better understanding of plume transport and attenuation characteristics. The goal is to use these findings to develop a more informed basis for managing these sites.

TECHNICAL APPROACH: The overall technical approach for the project focused on tasks that tested a number of hypotheses about fate and transport of 1,4-dioxane and what constitutes an effective treatment strategy for contaminated sites.

In Task 1, a "big data" study was used to identify the typical scale and conditions within 1,4-dioxane and/or CVOC sites. Site information was largely compiled from the state of California's GeoTracker database, supplemented with analyses of data from the Air Force. Included in the evaluation were plume size estimates, detection frequency and concentration relationships between co-contaminants, attenuation rates, and identifying factors that influenced attenuation.

In Task 2, the goal was to assess metal catalysis as a novel 1,4-dioxane treatment approach. The task addressed the hypotheses that metal catalysts can degrade dioxane (and/or its oxidized by-products) catalytically under mild conditions and that a metal-on-metal nanostructure leads to enhanced reaction rates. Bench-scale treatability studies were used to screen a wide variety of metal catalysts and quantify each catalyst's relative efficiency of 1,4-dioxane removal.

In Task 3, remediation technologies including chemical oxidation, catalysis, and biodegradation processes were evaluated to understand the potential advantages of combined "treatment trains" on 1,4-dioxane degradation kinetics. During these bench-scale tests, the effect of common co-contaminants at various concentrations was also evaluated. 1,4-Dioxane biodegradation biomarker genes were quantified, and metagenomics were applied to analyze the structure of microbial community and biodiversity.

In Task 4, the potential contribution of matrix diffusion processes on 1,4-dioxane fate and transport were investigated using two different approaches. The first involved comprehensive modeling of typical 1,4-dioxane release scenarios as a "proof of concept" study. The second was a field investigation that looked at the relationship between 1,4-dioxane concentrations and site hydrostratigraphy at two different contaminated groundwater sites.

RESULTS: As part of the big data study, it was determined that 1,4-dioxane plumes were generally dilute (median of site maximum concentration = 365 ug/L) but not as large as expected (median length = 269 m). At sites where both 1,4-dioxane and chlorinated solvents were detected (n= 105), the chlorinated solvent plume (typically 1,1-DCE and/or TCE) was longer at 56%. 1,4-dioxane was detected at 193 sites (of 589) where it was analyzed, with TCE being the most frequently detected co-occurring contaminant (93%), followed by 1,1-DCE (86%) and TCA (58%). At sites where 1,4-dioxane was measured, it was detected at 52% of sites containing TCE, 70% of sites containing 1,1,1-TCA, and 69% of sites containing 1,1-DCE (69%). This

study identified hundreds of sites with chlorinated solvents where 1,4-dioxane has not been analyzed, ranging from 67% to 85% for this set of constituents. Statistically-significant positive source attenuation rates for 1,4-dioxane were confirmed at 22 sites (median equivalent half-life = 20 months). At sites where chlorinated solvents and 1,4-dioxane were both present, the median value of all statistically-significant dioxane source attenuation rates was similar to 1,1-DCE and TCE (but lower than 1,1,1-TCA). A supplemental study on Air Force well data established that attenuation was positively correlated with increasing oxygen concentrations and negatively correlated with increasing CVOC and metals concentrations.

In the catalysis treatability tests, several catalysts were able to degrade > 50% of the added 1,4-dioxane within 48 hours in mild oxidizing conditions. Of the catalysts tested during further optimization studies, 1,4-dioxane degradation was greatest using WO_x/ZrO_2, then CuO, then ZrO_2, and finally TiO_2. Though CuO appeared to be slightly more efficient that the WO_x/ZrO_2 (i.e., it uses less H_2O_2 per 1,4-dioxane degraded), WO_x/ZrO_2 was selected for further evaluation in the treatment train studies due to its high activity and to avoid potential toxicity issues from the leaching of Cu^{2+} from the CuO catalyst.

The most promising treatment train was in situ oxidation followed by bioaugmentation with a 1,4-dioxane degrading culture. Pre-treatment using chemical oxidation degraded a portion of the 1,4-dioxane, but importantly, degraded the chlorinated solvents. By removing these inhibitors of 1,4-dioxane biodegradation, the bioaugmentation culture thrived and continued to degrade 1,4-dioxane indefinitely. In the absence of chemical oxidation, the undegraded chlorinated solvents completely inhibited 1,4-dioxane biodegradation. Biomarker analysis determined that 1,4-dioxane biomarkers (DXMO and ALDH) were absent in the native soil and groundwater supporting the lack of dioxane-degrading bacteria in the natural microbial community. Metagenomic analyses showed that biodiversity was inhibited by the oxidation process, but was able to recover and thrive in the following biodegradation phase, even greater than the original level, attributed to peroxide-tolerance and potential horizontal gene transfer. Catalysis also inhibited biodiversity, but the community recovered during the biodegradation phase.

The modeling results confirmed that diffusion of 1,4-dioxane mass in and out of lower-permeability soils (e.g., silts, clays) can be an important fate and process for this compound. During a typical release scenario, 1,4-dioxane actively loaded the low-k layer within the source zone for only a short period (<3 years) relative to 1,1,1-TCA due to 1,4-dioxane's high solubility. However, the mass of 1,4-dioxane in the low-k source zone, as well as the groundwater concentration from back diffusion, was consistently larger than that for 1,1,1-TCA. Even 80 years after release, the 1,4-dioxane concentration resulting from back diffusion (> 100 µg/L) was still orders-of-magnitude higher than regulatory levels. Diffusion also contributed to higher concentrations and enhanced penetration of 1,4-dioxane into the low-k zones relative to 1,1,1-TCA in the downgradient plume. Data from focused characterization studies at two different field sites confirmed that a significant amount of the 1,4-dioxane mass was associated with lower-k zones within and adjacent to the more transmissive portions of the aquifers.

BENEFITS: The results of this project identified several important elements that will help site managers develop more appropriate conceptual models and treatment strategies for 1,4-dioxane sites. First, dilute plumes and matrix diffusion were confirmed as challenges to using conventional treatment technologies 1,4-dioxane sites; these processes mean that 1,4-dioxane sites may lack a easily-targeted source zone for active treatment. In combination with the evidence of 1,4-dioxane attenuation and shorter plumes, the project findings highlight the potential utility of natural attenuation as a site management option. The corroboration between field and lab data collected during this project suggests that biological degradation of 1,4-dioxane is promising at sites that do require active treatment.

OBJECTIVES

1.1 General Objectives

The overall objective of this project was to develop integrated, site-specific management approaches for sites contaminated with 1,4-dioxane (dioxane) through applied research on novel in situ treatment technologies, modifications to existing technologies, and a better understanding of plume transport and attenuation characteristics. ***By evaluating how innovative and conventional technologies might address the specific challenges of sites with 1,4-dioxane and chlorinated volatile organic compound (CVOC) contamination, the goal is to develop a more informed basis for managing these sites.***

1.2 Project Hypotheses

The study was designed to test several hypotheses:

1. *1,4-Dioxane plumes are typically considered large and dilute, which should be reflected during the development of treatment strategies.* Due to its migration potential, 1,4-dioxane may tend to form large but dilute plumes. Migration of plumes relative to co-occurring chlorinated solvents has implications for drinking water and surface water receptors. However, attenuation of these contaminants should also be evaluated in order to understand the applicability of monitored natural attenuation (MNA) as a management option for 1,4-dioxane sites.
2. *Catalysis offers a rapid robust method for degrading a wide variety compounds (Heck et al., 2009; Wong et al., 2009), including 1,4-dioxane potentially through a ring opening and oxidative pathway.* Catalysts could also be used in conjunction with conventional oxidants to promote more rapid and complete degradation, or as a pre-treatment step prior to in situ biodegradation. Basic research on material selection and formulations is needed to demonstrate their utility for in situ 1,4-dioxane applications.
3. *Combining treatment technologies may enhance 1,4-dioxane removal.* Chlorinated solvents—and strategies for their removal—can either inhibit or enhance apparent 1,4-dioxane removal, meaning that combinations of technologies may be necessary. The presence of 1,1,1-trichloroethane (TCA) and other chlorinated solvents has been shown to significantly reduce 1,4-dioxane biodegradation rate (Mahendra et al., 2013; Zhang et al., 2016). Enhanced in situ bioremediation of co-contaminants can lead to anaerobic or anoxic conditions that are generally less favorable for 1,4-dioxane degradation (Mahendra and Alvarez-Cohen, 2006; 2007). In situ chemical oxidation may have short-term negative impacts on microbial activity due to the oxidants and the introduction of competing electron acceptors, although some chemical reagents could potentially stimulate aerobic pathways (via increased oxygen availability).
4. *1,4-dioxane is subject to matrix diffusion processes that should be accounted for during site management*. Diffusion of chlorinated solvents into low-permeability layers within an aquifer is known to limit the effectiveness of conventional in situ treatment

approaches. The impact of matrix diffusion on 1,4-dioxane has yet to be explored, and there are properties that would both mitigate and exacerbate the potential for matrix diffusion.

1.3 Specific Objectives

To test these hypotheses and to develop integrated site-specific management approaches for 1,4-dioxane, the specific technical objectives of this proposed project are as follows:

a) Use modeling and data mining of existing 1,4-dioxane site records to better understand plume and site characteristics, and to inform a conceptual model of 1,4-plume dynamics relative to co-located CVOC plumes

b) Determine reaction pathways, rates, and efficacy of catalyst-based oxidation and reduction of 1,4-dioxane, and develop potential in situ approaches for this process in the presence of CVOC co-contaminants.

c) Evaluate biodegradation potential of 1,4-dioxane under a range of natural and engineered geochemical conditions, including in tandem with other methods (both conventional and innovative) for treating 1,4-dioxane and CVOC co-contaminants.

d) Understand how matrix diffusion processes impact 1,4-dioxane and chlorinated solvents through a combination of modeling and field characterization.

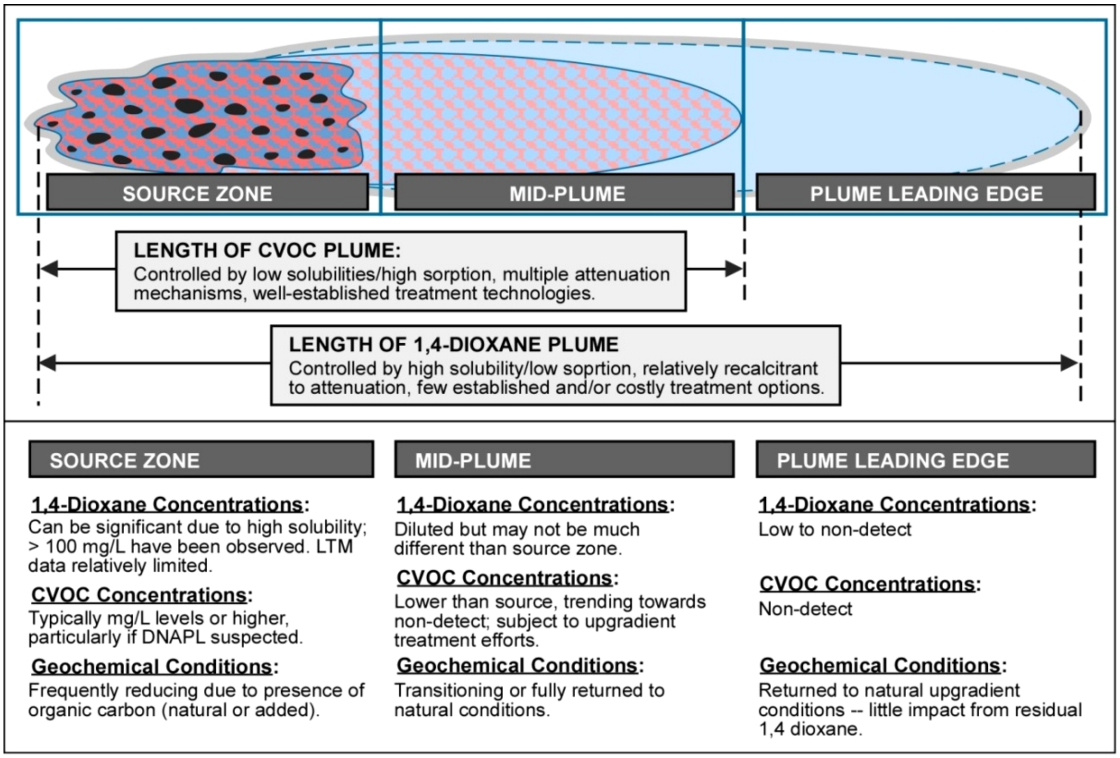
2. BACKGROUND

The DoD has a significant need to develop low-cost and green remedial solutions for long-term management of environmental liabilities at contaminated sites. As a result, their focus is to effectively close-out sites in a way that most efficiently handles the significant financial burdens associated with these sites while eliminating both short-term and long-term risk. As of FY2009, the Cost-to-Complete remedial activities associated with closure goals at DoD sites was estimated to be $12.1 billion. In its 2013 report, the National Research Council stated that the DoD had already spent approximately $30 billion to clean up hazardous wastes associated with historical operations (NRC, 2013).

However, there has been an increasing realization that so-called “emerging contaminants”, such as 1,4-dioxane, will have a significant impact on the scope of DoD’s environmental liabilities. This includes sites where no or limited remediation has been implemented, such that selection of an appropriate and cost-effective remedy is necessary to ensure that emerging contaminants are being treated. Further, it includes sites where remediation is on-going or may have already been completed to address one or more primary constituents (e.g., chlorinated volatile organic compounds (CVOCs)), but where the impacts or effectiveness of these efforts on emerging contaminants are unknown or have not been investigated. Finally, it includes sites where intensive remediation efforts have already been completed and have resulted in very low residual levels of primary contaminants as well as the emerging contaminants. Continued management of this residual contamination is often required, and it is important to know if typical strategies for these “low-risk sites” are applicable for management of emerging contaminants as well. Importantly, the presence of emerging contaminants, such as 1,4-dioxane, at these sites increases the uncertainty in the closure cost and timeframe estimates. Given that 1,4-dioxane frequently co-occurs with chlorinated solvents, an opportunity exists to identify in situ remediation processes or management strategies that will adequately address both sets of co-contaminants.

The need to address 1,4-dioxane contamination is being driven by the potential health risks associated with exposure to this emerging contaminant. This includes ingestion of 1,4-dioxane in drinking water, which is largely assumed to be associated with releases to groundwater and discharges of 1,4-dioxane in groundwater to surface water. Currently, there is no federally-enforceable limit in drinking water limit for 1,4-dioxane. A recent study using data from the USEPA’s Third Unregulated Contaminant Monitoring Rule showed that 1,4-dioxane was detected in 21% of U.S. public water systems, and that detection rates were higher in groundwater than surface water (Adamson et al., 2017). When released to groundwater, 1,4-dioxane has distinct properties (e.g., high solubility, low sorption) that contribute to plume development. Understanding the implications of these properties in relation to those of commonly-released co-contaminants is important in designing effective treatment solutions for all compounds present.

Figure 1 displays the conventional conceptual model of the primary issues that are expected in managing a 1,4-dioxane plume in the presence of co-contaminants. Because the characteristics of each contaminant class can lead to significantly different plume dimensions, it is critical to evaluate the treatment options within the context of the expected geochemical conditions of the 1,4-dioxane and CVOC plumes. For example, while 1,4-dioxane is present in small amounts in new 1,1,1-TCA preparations, many facilities use activated carbon for 1,1,1-TCA reclamation before waste disposal, potentially enriching the 1,4-dioxane levels in the mixed waste streams. The hydrophilic nature of 1,4-dioxane allows it to mix rapidly with groundwater, and 1,4-dioxane plumes have the potential to extend much beyond chlorinated solvent plumes. Consequently, the concentration ratios of 1,4-dioxane and the chlorinated co-contaminants may vary greatly within aquifers, and must be measured and modeled accurately to inform remediation of both contaminants.



LENGTH OF CVOC PLUME: Controlled by low solubilities/high sorption, multiple attenuation mechanisms, well-established treatment technologies.

LENGTH OF 1,4-DIOXANE PLUME Controlled by high solubility/low soprtion, relatively recalcitrant to attenuation, few established and/or costly treatment options.

SOURCE ZONE

1,4-Dioxane Concentrations: Can be significant due to high solubility; > 100 mg/L have been observed. LTM data relatively limited.

CVOC Concentrations: Typically mg/L levels or higher, particularly if DNAPL suspected.

Geochemical Conditions: Frequently reducing due to presence of organic carbon (natural or added).

MID-PLUME

1,4-Dioxane Concentrations: Diluted but may not be much different than source zone.

CVOC Concentrations: Lower than source, trending towards non-detect; subject to upgradient treatment efforts.

Geochemical Conditions: Transitioning or fully returned to natural conditions.

PLUME LEADING EDGE

1,4-Dioxane Concentrations: Low to non-detect

CVOC Concentrations: Non-detect

Geochemical Conditions: Returned to natural upgradient conditions -- little impact from residual 1,4 dioxane.

Figure 1. Traditional Conceptual Model of a 1,4-Dioxane Contaminated Site with CVOCs Present

However, there is limited technical information on the actual scale and conditions within 1,4-dioxane sites, as well as the efficacy of various natural and engineered attenuation processes for 1,4-dioxane. Based on the project team's experience at several 1,4-dioxane sites, groundwater concentrations in excess of 1 mg/L of 1,4-dioxane can be encountered in source areas. While it is reasonable to make assumptions about source and plume characteristics based on the chemical properties of 1,4-dioxane as described above, detailed multi-site data have yet to be compiled. At the outset of this project, the only reported initial attempt at quantifying the scale of 1,4-dioxane contamination issues has been made by AFCEC using the ERPIMS database (Anderson, 2012), where nearly 6,000 wells (from 49 installations) with 1,4-dioxane analyses were evaluated. Of those wells where 1,4-dioxane was present above reporting limits (approximately 18%), nearly all (94%) also contained TCE and/or 1,1,1,-TCA.

The properties of 1,4-dioxane also have important implications for the potential efficacy of engineered or enhanced remedial approaches. Treatment of 1,4-dioxane impacted water using conventional technologies has proven challenging (Zenker et al., 2003; Otto and Nagaraja, 2007; Pintenich, 2008; Stepian et al., 2014; USEPA, 2006; USEPA, 2013). In terms of in situ treatment options, 1,4-dioxane is subject to chemical oxidation as long as the radical species being generated has sufficiently high oxidation potential (e.g., hydroxyl radical) (Adams et al, 1994; Tsitonaki et al., 2010). Enhanced anaerobic bioremediation has proven to be a successful strategy for addressing many chlorinated solvents, but there are very limited data to date to suggest that 1,4-dioxane is subject to degradation via anaerobic (reductive) mechanisms (Shen et al., 2008). However, there is increasing evidence that biological oxidation of 1,4-dioxane is a relevant attenuation pathway (Mahendra and Alvarez-Cohn, 2006; Mahendra et al., 2007; Kim et al., 2009; Li et al., 2010; Sei et al., 2010; Sales et al., 2013; Sei et al., 2013; Li et al., 2013; Pornwongthong et al., 2014; Huang et al., 2014; Hand et al., 2014; Zhang et al., 2016). A number of organisms and enzymes that degrade 1,4-dioxane as a carbon/energy source or co-metabolically have been identified, but the prevalence of these degradative capabilities in the environment is only starting to be investigated (Li et al., 2013; Li et al., 2014; Li et al., 2015; Gedalanga et al., 2014; Gedalanga et al., 2016).

1,4-dioxane biodegradation strategies are based on understanding the rates of contaminant degradation under natural or engineered conditions, but inherently these processes involve a wide range of organisms. Therefore, shifts in the structure and function of the microbial community could affect the fate and transport of contaminants in the environment (Zhang et al., 2016). Because more than 99% of environmental microorganisms are thought to be uncultivable or difficult to culture in a lab and primers used for specific PCR are also limited, it is clear that many of the mysteries associated with environmental bacteria are far from solved (Miao et al., 2015, Stewart et al., 2012). Metagenomics is defined as the study of environmental microbial communities using a suite of genomic tools to directly access their genetic content, and help to gain insight into functional aspects in addition to species composition (Shah et al., 2013; Zafra et al., 2016; Gillan et al., 2015; Kao et al., 2016). Compared with conventional molecular biotechnology, metagenomic approaches based on next generation sequencing (NGS) technology can directly sequence genomic DNA or RNA. Consequently, this methodology is designed to overcome the biases and limits of culture-dependent approaches and PCR-based methods (Fang et al., 2013) while revealing previously-inaccessible environmental microbiomes in their whole complexity (Gillan et al., 2015). Metagenomics could improve our understanding of taxonomic and enzymatic diversity both pre- and post-contamination, which will expand our understanding of microbial processes involved in bioremediation as well as the impact of various response strategies for contaminant cleanup (Chakraborty et al., 2012). Moreover, metagenomics applications in bioremediation will answer questions about how microorganisms respond to the disturbance created by the contaminant (Bell et al., 2015), and provide information on how microbial communities respond to changes in a variety of environmental factors (Miao et al., 2015).

Monooxygenase enzymes play an important role in 1,4-dioxane biodegradation process

(Mahendra and Alvarez-Cohen, 2006). Derived from the whole genome sequence of a well-characterized 1,4-dioxane biodegrading strain, *Pseudonocardia dioxanivorans* CB1190, primers to amplify 1,4-dioxane biomarkers have been developed based on conventional PCR-based methods, then used as indicators for potential contaminant biodegradation (Gedalanga et al., 2014; Li et al., 2014). The DXMO biomarker genes respond to the presence of 1,4-dioxane while ALDH is associated with 1,4-dioxane breakdown products in the form of aldehydes (e.g., hydroxylethoxyacetaldehyde). In addition to the DXMO and ALDH biomarkers associated with 1,4-dioxane metabolism, other monooxygenase enzymes could catalyze 1,4-dioxane in cometabolic pathways, including methane (MMO), propane (PrMO), phenol (PHE), tetrahydrofuran (THFMO), and toluene (TOL, T4MO, RMO) monooxygenases (Masuda et al., 2012; Fishman et al., 204; Mahendra and Alvarez-Cohen, 2005; Ryan et al., 2007; Vainberg et al., 2006).

The recent development of biomarkers that can be used to assess aerobic 1,4-dioxane degradative activity is likely to be a valuable tool in validating natural attenuation at field sites (e.g., Li et al., 2013; Gedalanga et al., 2014). These and other diagnostic tools have been used as part of a small yet growing number of studies that have documented 1,4-dioxane degradation capabilities at specific sites in aerobic conditions (Li et al., 2010; Li et al., 2014; Li et al., 2015; Chiang et al., 2008; Chiang et al., 2012). For example, Li et al. (2015) demonstrated significant indigenous degradation activity in lab microcosms using material from three 1,4-dioxane-impacted sites, particularly in samples collected from source areas. A parallel study by the same research group showed that the amount of 1,4-dioxane degraded in microcosms from these same three sites (as well as two others) correlated well with increases in the abundance of specific oxygenase-encoding genes (thmA/dxmA) that are known to degrade 1,4-dioxane (Li et al., 2014). In a recent study by Gedalanga et al. (2016), 1,4-Dioxane biomarkers were detected and quantified in a historical 1,4-dioxane plume and were highly associated with monitored levels of 1,4-dioxane indicating the potential for natural attenuation (Gedalanga et al., 2016). However, there is a critical need to expand the number of sites where 1,4-dioxane attenuation can be documented to ensure that these are not isolated cases and to provide a more quantitative basis for the potential range of field rates.

These types of studies also highlight the 1,4-dioxane treatment needs to be addressed within the context of co-contaminants, and they should be expanded in order to better identify site conditions that are conducive to natural attenuation or engineered remediation. This fundamental lack of knowledge has slowed development and implementation of suitable remedial technologies. Mass present in high-concentration source areas may be the primary target for remedial efforts, and there are several treatment methods that may achieve significant mass reductions in source areas, such as ex situ or in situ chemical oxidation. However, given 1,4-dioxane's ability to move rapidly following release, the apparent footprint of the 1,4-dioxane source area may not coincide well with that of any CVOC co-contaminants. A relatively higher percentage of the 1,4-dioxane mass may be present in the middle and downgradient edge of the plume, making it difficult to cost-effectively implement many treatment efforts.

As such, it is prudent to develop treatment technologies that are suitable for source zones or can be modified as lower intensity approaches for the leading edge of a plume. This includes:

1. Chemical oxidation, which is likely the most commonly-used treatment technology for 1,4-dioxane. Due to its stable ring structure, 1,4-dioxane is relatively resistant to chemical breakdown and needs the oxidation potential (eV) to be greater than 2 V for efficient degradation (Mohr et al., 2010). Advanced oxidation processes (AOPs), which use the hydroxyl radical as an oxidant, can achieve substantial reduction in 1,4-dioxane groundwater concentrations. with the advantage of a short reactive period and high removal efficiency. Various sites in the United States with 1,4-dioxane concentrations ranging from 4.6 μg/L to 320 μg/L were successful in remediating the compound to their respective target levels using the APTWater (Sacramento, CA) HiPOx system (Otto and Nagaraja, 2007). A similar method has been successfully applied to remove 1,4-dioxane at the Pall-Gelman Sciences site in Michigan where more than 100,000 gallons of 1,4-dioxane-contaminated water from the aquifer have been treated, leading to significant reductions in plume concentrations. The goal should be to move away from ex situ treatment of extracted groundwater using chemical oxidants and instead refine existing methods for in situ treatment, while at the same time ensuring that co-contaminants are treated and other long-term attenuation processes are not negatively impacted. the aquifer have been treated, leading to significant reductions in plume concentrations (Fotouhi et al., 2006).
2. In situ biodegradation, which is generally implemented for a variety of organic and inorganic contaminants using established and relatively economical methods. As discussed above, there have been several recent advances in laboratory studies demonstrating that 1,4-dioxane can be biologically degraded, but there have been very few demonstrations that these processes are viable under conditions encountered in the field, or that they are sustainable when other co-contaminants are present and/or being remediated.
3. Novel approaches, such as metals-mediated catalysis, which can be specifically tailored to remove a wide variety of compounds. Catalysis has been widely evaluated for a variety of organics such as TCE reduction (Fang et al., 2011), and metal catalysts are known to generate oxidants (H2O2) and radical oxygen species in aerobic conditions (Yalfani et al., 2009; Edwards et al, 2013; Merhi and Kochkar, 2014) The anticipated fast degradation rates from newly designed materials motivates the development and testing of catalyst-based methods for treating a problematic compound such as 1,4-dioxane is an important step in advancing our understanding of processes that are not typically considered. Research on catalytic degradation of 1,4-dioxane is especially limited. Recently, only a few studies documented photocatalytic degradation using titanium dioxide (Nakajima et al., 2004; Hill et al., 1997). It was shown that photocatalytic degradation by titanium dioxide could readily mineralize 1,4-dioxane with ethylene diformate as the major intermediate (Hill et al., 1997).

A critical limitation in the evolving conceptual model for 1,4-dioxane source zones is that it ignores the contribution of matrix diffusion processes to elevated 1,4-dioxane concentrations within the source zone and the downgradient plume. This has significant implications on the appropriateness of various treatment options for a particular site. Matrix diffusion is a term used to describe the diffusion of contaminants both into and out of lower-permeability zones (e.g., clays, silts, bedrock) within a heterogeneous or fractured groundwater-bearing unit (Sale et al., 2013). Because advective forces in these low-k zones are very limited, this causes mass to be stored for long period of time, particularly if sorption is also occurring. Release of these contaminants (i.e., “back diffusion”) and into adjacent transmissive zones occurs at later stages once the concentration gradient reverses, and this mass has the potential to serve as significant and persistence secondary source, even after the primary source (e.g., NAPL) has been depleted or removed (Parker et al., 2008).

Matrix diffusion has been recognized to have important implications on source and/or plume longevity (Sudicky et al., 1985; Ball et al., 1997; Liu and Ball, 2002; Parker et al., 2004; Chapman and Parker, 2005; Parker et al., 2008; Payne et al., 2008; West and Kueper, 2010; Rasa et al., 2011; Seyedabbasi et al., 2012; Chapman et al., 2012; Leeson et al., 2013; Brown et al., 2012; McDade et al., 2013; Suthersan et al., 2013; Sale et al., 2013; Hadley and Newell, 2014; Matthieu et al., 2014; Yang et al., 2015). The 2013 report by the National Research Council emphasized the need to better understand how matrix diffusion processes impact conceptual site models and projected remediation timeframes at “complex and difficult” sites (NRC, 2013). There has been considerable research on matrix diffusion processes (much of it sponsored by SERDP and ESTCP), but it has primarily focused on chlorinated solvents. These solvents have relatively limited aqueous solubitilies (generally ranging from low hundreds to low thousands of mg per L), and as a result, the period during which a chlorinated solvent source can diffuse into adjacent low-permeability zones (i.e., the loading period) can be quite long. Studies that focus on compounds with higher solubility and less sorptive capacity are more rare (Rasa et al., 2011; Yang et al., 2015). Rasa et al. (2011) examined a gasoline spill site using modeling and field data and demonstrated that diffusion of methyl tert-butyl ether and tert-butyl alcohol mass into and out of lower-permeability silt layers contributed to persistence of these compounds in transmissive zones, including the period after the source was depleted.

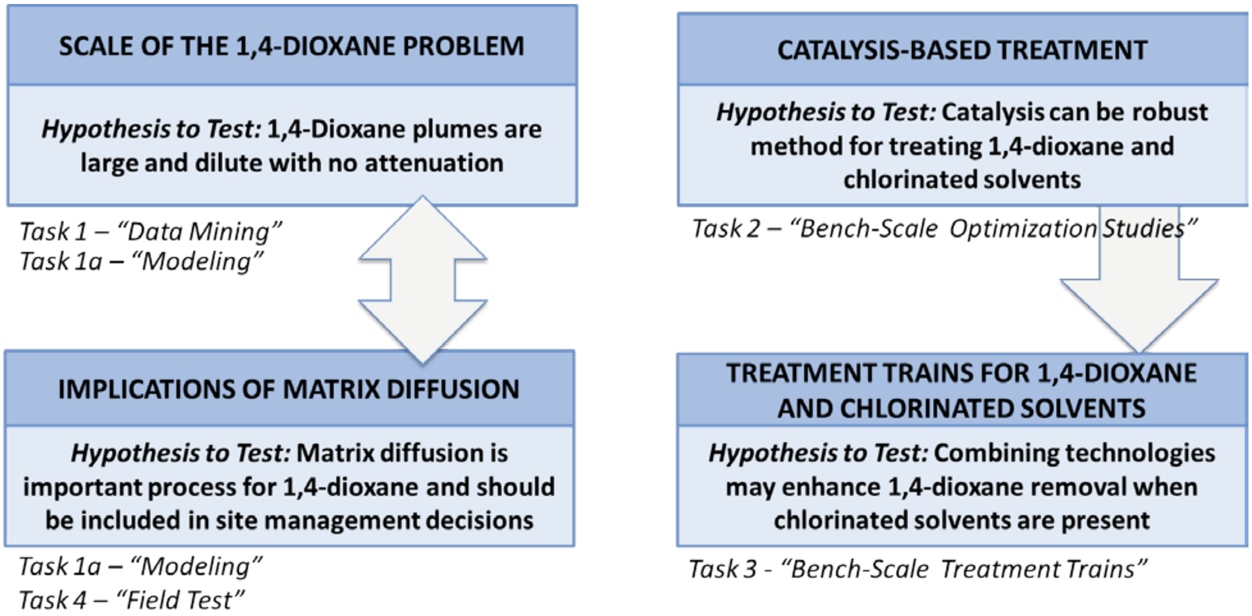
1,4-Dioxane is highly soluble, meaning that immediately after its release, there will be a significant concentration gradient to drive diffusion processes within heterogeneous formations (Mohr et al., 2010). However, this solubility also promotes rapid depletion of the source, such that it is uncertain if the 1,4-dioxane loading period is sufficiently long to promote significant mass storage due to diffusion. Therefore, this project also looked to test the hypothesis that storage of 1,4-dioxane mass within low-permeability zones is significant and can contribute to concentrations in that are likely to be above acceptable limits for decades or longer. Sites where matrix diffusion is active will be harder to clean up using conventional (injection-based) in situ technologies that rely on distribution of amendments. These sites may be more cost-effectively managed using containment-based or natural attenuation processes.

3. MATERIALS AND METHODS

3.1 Overall Approach

The overall technical approach for the project focused on testing a number of hypotheses about what constitutes effective treatment strategies for 1,4-dioxane-contaminanted groundwater. This hypothesis-based approach is designed to enhance our understanding of fundamental fate and transport issues for 1,4-dioxane in the presence of co-contaminants, and then develop and evaluate more appropriate in situ remedial options for managing sites with these compounds.

As shown in **Figure 2** below, a series of project tasks were developed to generate information to test these hypotheses. There was some evolution in the task list as the project progressed. In particular, Task 4 was modified to field test an important concept that was identified in Task 1a (matrix diffusion).



Hypothesis to Test: **1,4-Dioxane plumes are large and dilute with no attenuation**

Hypothesis to Test: **Catalysis can be robust method for treating 1,4-dioxane and chlorinated solvents**

Hypothesis to Test: **Matrix diffusion is important process for 1,4-dioxane and should be included in site management decisions**

Hypothesis to Test: **Combining technologies may enhance 1,4-dioxane removal when chlorinated solvents are present**

Figure 2. Primary Research Hypotheses

The individual sections of this report, including the descriptions of materials and methods, are organized based on these research hypotheses (i.e., as opposed to specific task numbers). Note that Task 1a (modeling) was used to support two separate hypotheses, but for the purposes of this report will be primarily discussed within the "matrix diffusion" section (along with Task 4).

3.2 Scale of the 1,4-Dioxane Problem

A comprehensive “big data” study was used to identify the typical scale and conditions within 1,4-dioxane sites, particularly those with CVOC co-contaminants. Efforts were geared toward testing the general hypothesis that the chemical properties of 1,4-dioxane result in plumes that are generally classifiable as large, dilute, and poorly characterized, particularly relative to co-occurring chlorinated solvent plumes. The goal is to evaluate the extent to which actual 1,4-dioxane site characteristics reflect these assumptions, and how this will dictate the appropriate remedy selection. Significant work has been done on classifying other contaminant plumes based on mass discharge (e.g., the plume magnitude classification system for CVOCs described in Newell et al., 2011) and plume length (e.g., MTBE and BTEX in Kamath et al., 2012 and Connor et al., 2014), but information is currently lacking for 1,4-dioxane. Initial efforts, such as those being undertaken by AFCEC (Anderson, 2012), need to be built upon to better understand the scope of the 1,4-dioxane problem.

These types of big data studies are also known as “data mining” because they attempt to sift through large amounts of data to identify patterns and make predictions. They are based on the simple principle that the more data that are available to be compiled and analyzed, the more powerful are the conclusions that can be made. Big data studies allow a user to test a hypothesis, or alternatively, to develop new hypotheses based on patterns that may not have been previously apparent. This approach has been successfully employed as part of other SERDP and ESTCP projects, including the Source Depletion Support System for ESTCP ER-201120. As part of these projects, the project team compiled a detailed historical database on the performance and costs of source depletion technologies that represents the highest quality dataset assembled to date (based on the data density and publication of peer-reviewed papers).

For this project, the approach involved identifying a series of sites with concentration records and other data to support the assessment, including temporal records to the extent possible. Various data have been examined at either the entire set of sites, or a subset of sites, including:

- Maximum concentrations of 1,4-dioxane and other co-contaminants;
- Spatial footprint/length of 1,4-dioxane plumes relative to co-located CVOC plumes;
- Frequency of 1,4-dioxane detection in monitoring wells, and frequency of co-detection of 1,4-dioxane with other co-contaminants;
- Adequacy of characterization including sites where 1,4-dioxane would be expected to be present but has not yet been analyzed
- Geochemical conditions in 1,4-dioxane plumes;
- Hydrogeologic setting, particularly features that might contribute to matrix diffusion effects;
- Attenuation rates and/or plume stability trends; and
- Frequency and influence of any remediation efforts; including in situ treatment and containment-focused methods.

The overall goal of this evaluation was to determine whether these data from contaminated sites confirm the conventional conceptual model for 1,4-dioxane behavior in the environment. As noted in Section 2, the existing conceptual model is based on the distinct properties of 1,4-dioxane (e.g., high solubility, low sorption, suspected recalcitrance) that contribute to groundwater plume development following its release to the subsurface. These properties allow 1,4-dioxane to mix rapidly with groundwater, and 1,4-dioxane plumes have the potential to extend much beyond chlorinated solvent plumes. Because the characteristics of each contaminant class can lead to significantly different plume dimensions and/or concentration ratios, it is critical to evaluate the treatment options within the context of the conditions of the 1,4-dioxane and CVOC plumes. The concentration ratios of 1,4-dioxane and the chlorinated co-contaminants may vary greatly within aquifers, and must be measured and modeled accurately to inform remediation of both contaminants. Therefore, the data mining was designed to test several of the underlying hypotheses of the existing conceptual model, as outlined in **Table 1**.

Table 1. Tested Hypotheses that are Associated with 1,4-Dioxane Conceptual Model

Hypotheses
Dioxane usually forms "large, dilute" plumes at sites
Dioxane plumes are longer than co-occurring chlorinated solvent plumes
Dioxane plumes are poorly delineated
Dioxane is not attenuating
Dioxane plume development is influenced by site characteristics and the presence of co-occurring chlorinated solvents

A portion of the results from this task were published in two peer-reviewed articles (Adamson et al., 2014; Adamson et al., 2015). The following sections provide further detail on methods as well as more comprehensive results.

3.2.1 Sources of Data

To date, the project has relied primarily on data contained in the state of California's GeoTracker database (GeoTracker, 2013). Groundwater-impacted sites regulated by the California State Water Resources Control Board are mandated to provide specific information to include within this publicly-accessible database. Individual sites within the corrective action program (including commercial/industrial and military sites) are assigned a unique identification number, such that relevant information associated with each site can be queried and sorted. Based on the number of different identification numbers, GeoTracker contains data for greater 12,000 sites (with the number of records approaching 100 million). As an example, over 6000 of these sites have analytical data for 1,1,1-TCA. In addition to analytical and various descriptive data fields, GeoTracker also contains various site reports (e.g., monitoring reports, remedial action plans) that can be downloaded and reviewed.

Selected data from the Air Force ERPIMS database was included in an evaluation of 1,4-dioxane attenuation. These data were analyzed by Hunter Anderson at AFCEC and served as key material in a publication on 1,4-dioxane attenuation (Adamson et al., 2015). The findings of this attenuation study are presented here, but it should be understood that these Air Force data were not part of the dataset used for other project-specific evaluations.

3.2.2 Data Compilation

All data were loaded to a SQL server that was then linked to various Microsoft Access databases. For the purposes of this evaluation, relevant information fields included site name, location (e.g., county), identification number, geographic coordinates, site status, remedial measures, monitoring well identification numbers, sampling dates for each well, analytes for each well and sampling date, and concentration results for each analyte well, and sampling date. Other site information and environmental data provided in GeoTracker were also collected but were not part of the study described here.

Several sites contained data for 1,4-dioxane (or one of the other target constituents) but were removed from the database because it was determined that they were not groundwater sites. These deletions were generally based on the information stored in the “Field Point Class” in GeoTracker. For example, sites were eliminated if all analyses and/or detections were associated with leachate sampling points, QC samples, surface water, or treatment plant influent/effluent samples.

The source database that was used as part of this evaluation typically contained complete data for the fields described above. In addition, there were several types of site data characteristics that were not part of the source database that were deemed valuable for further evaluation (soil type, hydraulic conductivity/groundwater velocity, redox state), such that portions of the project database had to be constructed manually through review of site documents. Given that manual compilation of data was a time intensive process, it focused necessarily on sites where 1,4-dioxane was detected (and particularly those where either a plume length estimate or attenuation rate/trend could be estimated). As was expected, site documents were often incomplete, such that many sites in the resulting project database are missing data for one or more fields.

The data query focused on sites with groundwater concentration data for the period between February 2000 - December 2013 for at least one of the following constituents: 1,4-dioxane, 1,1,1-TCA, TCE, 1,1-dichloroethene (1,1-DCE), 1,1-dichloroethane, cis-1,2-dichloroethene (cDCE), vinyl chloride (VC). 1,1-DCE was included as a potential by-product of 1,1,1-TCA and TCE; by-products that are specific to TCE (e.g., cis-1,2-dichloroethene) was not included in this focused evaluation. The start date reflects the first recorded analysis for any constituent in GeoTracker database; the first 1,4-dioxane analysis was recorded in September 2001. For most sites, the latest data available is from approximately July 2013, as monitoring data from the second half of 2013 was generally not uploaded to GeoTracker until after the early January 2014 reporting period.

3.2.3 Data Evaluation Methods

Data evaluation proceeded along the following three paths:

1. ***Exploratory Data Analysis (EDA):*** Large datasets were evaluated to identify relationships between various constituents in terms of frequency and concentration, as well as to establish general plume characteristics. This was accomplished primarily using graphical techniques (bivariate scatter plots, box-and-whisker, histograms) to display the overarching structures of the data.
2. ***Statistical-Based Testing*****:** This was a more focused evaluation of the various datasets, with the goal of testing specific hypotheses and establishing the significance of various parameters and/or differences between groups. These build on the graphic methods used in EDA but typically used smaller datasets that may have been log-transformed to improve normality
3. ***Case Studies for Detailed Evaluation:*** Nine different sites were evaluated in more detail to provide thorough yet site-specific examples of how 1,4-dioxane might be expected to behave. A variety of different types of sites were selected, including those that both fit the standard conceptual model for 1,4-dioxane (i.e., 1,4-dioxane plume longer than that for co-occurring chlorinated solvents) and those that did not fit this conceptual model. Inherent in this evaluation is documenting temporal changes in plume dynamics and how site-specific factors have influenced the current plume conditions.

The goal was to develop metrics that would allow for comparisons between sites and constituents. Thus, potential biases were minimized by calculating the metrics for each constituent identically.

Order-of-Magnitude Reduction (OoM). OoM reduction was used as an indicator of attenuation of 1,4-dioxane and other constituents. The OoM metric is simple metric for describing concentration changes or remediation performance over time. It is analogous to percent reduction but is more useful across wider ranges of concentration changes (e.g., those often required to reach cleanup objectives). OoM reduction was estimated as:

$$OoM = -\log\left({}^{C_t}/_{C_0}\right)$$

where C_t is the recent concentration (C_t) and C_0 is the maximum concentration for a given monitoring period. OoM reductions were calculated for multiple constituents. For the purposes of this project, two different OoM reductions were calculated as described in **Table 2**.

Table 2. Different Methods for Calculating OoM Reduction

OoM Reduction Method	C_0	C_t
Method 1	Maximum historic concentration measured at the site at any well	Maximum concentration measured at the site since 2013
Method 2	Maximum historic concentration measured at the site at any well	Most recent concentration at well where historic maximum concentration was recorded

Source Attenuation Rates: First-order rate coefficients were calculated from temporal monitoring data for each constituent for each site. These site-wide values were considered more representative of source attenuation rates (and less subject to purely transport-related phenomena) and thus of more interest to understanding timeframes for site management (Newell et al., 2002). The methods for estimating site-wide attenuation rate followed those described in McHugh et al. (2013) which also involved a GeoTracker-derived dataset. Briefly, the maximum concentration recorded at a site over each 6-month period of monitoring was used as part of a linear regression analysis:

$$C = C_0 \, e^{-k_{source} \times t}$$

where C is the maximum concentration for a given 6-month period, C_0 is the initial concentration, k_{source} is the source attenuation rate coefficient (obtained through the best-fit regression equation), and t is the length of the monitoring period. A minimum of 4 distinct concentration measurements was the used as the cut-off for performing the rate coefficient estimation (note that not all sites were measured during each 6-month period). In addition, a p-value was calculated (using ANOVA in Microsoft Excel) for each rate coefficient, with values less 0.05 used to establish that the rate coefficient was statistically significant (i.e., different than zero).

Trend Analysis (Mann-Kendall): To compensate for datasets that were potentially not normally distributed, non-parametric trend analysis was also performed on temporal monitoring data using the Mann-Kendall test. This is a widely-used non-parametric test that assigns a trend to temporal data (Increasing/Probably Increasing, Stable, Decreasing/Probably Decreasing, or No Trend) based on a calculated test statistic, coefficient of variation, and confidence factor (1-p) (Connor et al., 2014). All analyses were completed using either the GSI Mann-Kendall Toolkit (Connor et al., 2014; www.gsi-net.com/en/software/free-software/gsi-mannkendall-toolkit.html) or MAROS (Aziz et al.; 2003; http://www.gsi-net.com/software/free-software/maros.html).

Plume Length Estimates: A GIS-based algorithm for estimating plume lengths from the spatial coordinates for each well was developed. For each site, the straight-line Euclidian distance (based on Pythagorean theorem) between each possible well pair with detections of the relevant constituent (e.g., 1,4-dioxane) over the entire monitoring period was calculated using location coordinate data. The plume length for that constituent was estimated as the maximum distance of all possible well pairs (**Figure 3**). The process was then repeated for each constituent. In general, this process yielded the maximum historic extent of the plume for each constituent. In certain cases, additional plume length estimates for specific points in time were made by reviewing historical plume maps and/or monitoring data. Because monitoring data listed in GeoTracker is segregated by site (based on how the state and federal regulatory agencies decide identify and manage sites), the plume length estimates are as representative as possible of individual sites. However, it is acknowledged that wells that are outside of the property or plume boundary for a specific site may also be included in the records for that site because they were being monitored jointly. For this reason, the plume lengths generated by this approach may be overestimates in some cases (i.e., conservative).

Indeterminate Plumes: To evaluate whether plumes were well-delineated, the same GIS-based algorithm was used to determine the maximum distance between any two wells where samples were collected (regardless of detections). If this maximum potential distance for a given site was equal to the plume length estimate, then the plume length for that site was categorized as "indeterminate" because the maximum constituent plume length is at least as long as the maximum potential plume that could be cleanly delineated by the existing well network. In other words, the plume length estimate for that site was negatively influenced by the lack of clean boundary wells. Sites with indeterminate plume lengths were retained in this evaluation in order to compare the frequency of occurrence for the various constituents. However, plume lengths could not be estimated for all sites, primarily due to sparse monitoring well networks and/or lack of spatially-distinct detections.

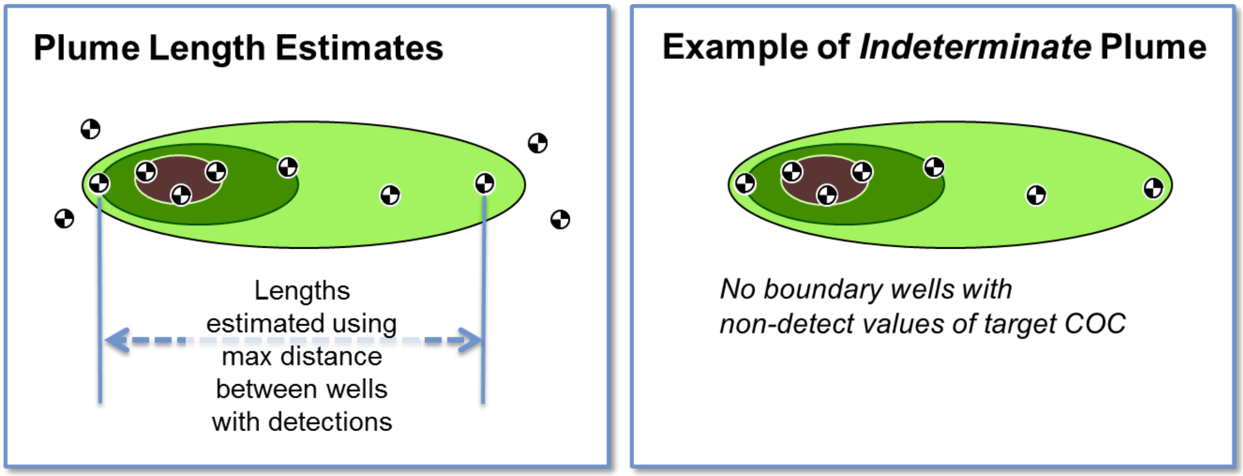


Figure 3. Plume Length Estimation Methods.

Relationships Between Parameters – Parametric: Linear regression was the primary parametric method for establishing correlations between various parameters (e.g., maximum concentration vs. plume length). In general, all parameter values were log-transformed prior to performing regressions. In addition to a slope and correlation coefficient for each regression, the potential significance of each relationship (i.e., that the slope of the regression line was greater than zero) was established if p-value were < 0.05. Multiple regression was used in certain cases to determine if stronger predictive models could be established by including multiple independent variables. When performing multiple regressions, variables were added one at a time, and only those variables whose inclusion resulted in a smaller p-value were considered relevant.

Relationships Between Parameters – Non-parametric: To account for non-normal data, Spearman rank correlation was also used as a non-parametric means for evaluating relationships between various parameters. The test yields a correlation coefficient (rho) that ranges from +1 (perfect positive correlation to -1 (perfect negative correlation). The hypothesis that the correlation did not occur by chance was checked using significance tables and an appropriate p value (0.05).

Differences Between Groups - Parametric: Standard t tests were used to determine if there was a statistically significant difference (based on $p<0.05$, two-tailed test) between two groups of independent values. Because datasets were typically log-transformed, the null hypthosis of each test was the median values of each group were identical. In certain cases where there were more than two groups of data being compared, ANOVA was used to evaluate differences.

Differences Between Groups – Non-parametric: The Wilcoxon Rank Sum test was used as a supplemental non-parametric method because the project datasets frequently did not meet the requirements for parametric tests (i.e., normal distribution). The Wilcoxon Rank Sum test is applicable for non-paired data (i.e., comparisons between data sets containing different numbers of data points are possible). Significance was evaluated using the two-tailed test and $p<0.05$.

Categorical Variables: There were several variables that could not be evaluated as strictly quantitative (numerical) variables. This included: 1) variables such as redox state where no single value could be considered representative of the entire site; and 2) variables that are non-numerical and instead reflect a designation (e.g., soil type) or presence or absence of a particular characteristic (e.g., pump-and-treat system). Instead, the data had to be converted to categorical data, as described in **Table 3**, prior to evaluating the potential relationship between these parameters with other parameters. For instance, dummy coding was used for regression models. Sites were assigned to categories based on review and interpretation of information and data from site documents, including boring logs and field sampling. Precedence was given to specific references within site reports, e.g., a site was classified as aerobic for the purposes of the project database if the introduction or background of a report classified it as such.

Table 3. Categorical Variables Used in Statistical Evaluations

Categorical Variable	Category and Dummy Coding	Comments
Redox State	Anaerobic = 0 Mildly aerobic to mildly anaerobic = 1 Aerobic = 2	Aerobic if majority of groundwater samples D.O. > 2.0 mg/L and ORP > 0 mV; Anaerobic if majority of groundwater samples D.O < 1.0 mg/L and ORP < -100 mV; otherwise categorized as mildly aerobic to mildly anaerobic
Soil type	Silt-clay = 0 Sand w/ silt-clay = 1 Sand/gravel = 2	Categorization based on boring logs or hydrogeologic description in reports
Pump-and-Treat	No pump-and-treat present = 0 Pump-and-treat present = 1	Pump-and-treat was considered present even if it was no longer active
Mann-Kendall Trend	Decreasing/Probably Decreasing = 0 Stable = 1 Increasing/Probably Increasing = 2	Trend assigned using Mann-Kendall test

Reporting Limits: GeoTracker includes reporting limits and/or analytical methods for only a subset of the analytical data (i.e., stakeholders are not required to enter this information). However, it was necessary to use reporting limit data to determine suitable values to substitute for non-detections when calculating attenuation rates and other metrics. In the absence of reporting limits for each individual sampling event, the median value of all constituent-specific reporting limits for sample concentrations labeled as non-detect in GeoTracker were used (**Table 4**). Given the large number of data points for each constituent, this substitution likely represents a reasonable approximation.

Table 4. Reporting Limits for Non-Detect Samples

Constituent	**No. of Non-Detect Samples with Reporting Limits** (% of all non-detect samples)	**Median Value of Reporting Limits** (used to calculate default substitution value for non-detects) (µg/L)
1,4-Dioxane	2,720 (10%)	2
TCE	52,149 (13%)	1
TCA	65,116 (12%)	1
1,1-DCE	59,277 (12%)	1
1,1-DCA	53,555 (12%)	1
cDCE	50,955 (13%)	1
VC	51,805 (11%)	0.5

For the purposes of this project, non-detect values for each constituent were generally substituted with one-half of the median value listed in **Table 4**.

3.3 Catalysis-Based Treatment

The objective for this project task was to assess metal catalysis as a novel dioxane treatment approach. The research task addressed the hypotheses that metal catalysts can degrade dioxane (and/or its oxidized by-products) catalytically under mild conditions and that a metal-on-metal nanostructure leads to enhanced reaction rates. The results can provide guidance on the most appropriate ways to deploy the catalytic treatment technology, e.g., as a standalone pump-and-treat system or as part of a treatment train. Note that a Go/No-Go decision point for the catalytic treatment approach was included at the end of the first year of the project based on the following performance objectives: i) degradation extent of 1,4-dioxane (% degraded < 50%); ii) degradation kinetics of 1,4- dioxane (half-life of months instead of days (or less)); or iii) required experimental conditions (reaction will not proceed at temperatures < 25°C), the catalytic approach will be curtailed.

3.3.1 Catalyst Screening for 1,4-Dioxane Degradation

A wide variety of heterogeneous catalysts were screened for the degradation of dioxane. The first phase involved several commercial-available catalysts and was designed to ensure that the Go/No-Go performance objectives were met. These tests were then expanded in a second phase that included additional catalysts (including combinations of metals). In total, the following catalysts were screened for 1,4-dioxane degradation:

- CuO
- Fe_2O_3
- TiO_2,
- Pd/Al_2O_3
- Ni(III) Oxide
- $PdAu/Al_2O_3$
- Au/Al_2O_3
- Ag/Al_2O_3
- ZrO_2,
- WO_x/ZrO_2 (20 wt%),
- CeO_2
- Al_2O_3
- H^+-exchanged zeolite Y
- SiO_2
- WO_3

All bench-scale tests were conducted using a similar protocol. Briefly, 171 g of water was added to a 250 mL glass reactor bottle. To mimic possible project configurations (e.g. in situ), the bottles were covered in aluminum foil to block ambient light (**Figure 4a)**. The reactor was then spiked with 0.4 µL of 1,4-dioxane (for a concentration of 27 µM) and 300 µL of H_2O_2 (for a concentration of 15 mM). Approximately 2 mL of reactor solution was sampled as a baseline. The catalyst powder was then added to start the reaction. The amount of catalyst added was based on the specific surface area of the catalyst, and chosen such that the surface area of exposed catalyst (and presumed active sites) was constant between reactors (475 m^2 L^{-1}). The catalyst powder was kept in suspension by magnetic stirring. To determine the 1,4-dioxane concentration, ~2 mL aliquots were taken from the reactor and filtered to remove the suspended catalyst and stop the reaction. Reactions were repeated in triplicate. Control experiments were also performed where no H_2O_2 was added, and no 1,4-dioxane degradation was observed.

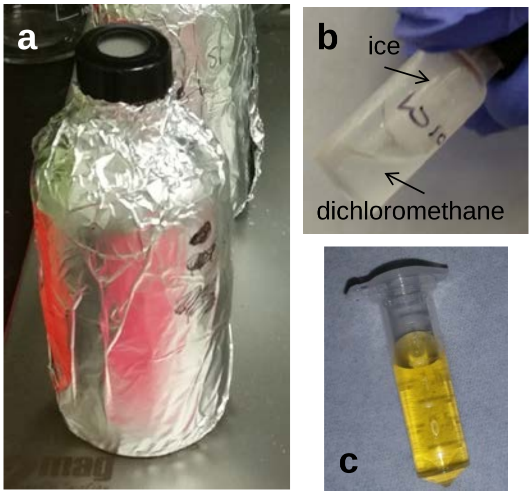


Figure 4. **Typical batch reactor used in catalyst screening studies:** (a); example of separation of water from 1,4-dioxane containing dichloromethane phase via the frozen extraction method (b); yellow-colored perititanic acid formed from the reaction of a solution containing hydrogen peroxide with titanium oxysulfate (c).

3.3.2 Catalyst screening for the degradation of 1,4-dioxane in the presence of CVOCs

Because CVOCs are often co-contaminants with 1,4-dioxane, we also tested the performance of the catalysts identified in the previous section for the degradation of 1,4-dioxane in the presence of trichloroethylene (TCE) as a model CVOC co-contaminant. The reaction set-up is similar to that described in the first section: 171 mL H_2O was added to a 250 mL batch reactor, and acidified to pH 3 with H_3PO_4. 250 mg of catalyst (either Fe(III) oxide, Cu(II) oxide, or TiO_2) and a stir bar was added and the reactor sealed with a septum. 0.4 µL of 1,4-dioxane and 4 µL of TCE were injected into the reactor. Because of the low solubility of TCE, the reactors were stirred rapidly and allowed to equilibrate for at least 3 hours. The reaction was initiated by injecting 300 µL of 30 wt% H_2O_2 into the reactor. A baseline sample of the liquid phase was taken and ~1 mL aliquots of solution were taken over time, and analyzed as indicated previously. The reactions using TiO_2 were performed in an amber bottle covered with aluminum foil to shield the contents from ambient light.

3.3.3 Catalyst screening for the degradation of 1,4-dioxane in the presence of CVOCs under reductive conditions

Because the presence of co-occurring CVOCs may results in the formation of reducing conditions, additional tests were focused on dioxane degradation in the presence of H_2 as a reducing agent. Experiments were performed at acidic pH following the methods described in Nutt et al (2006). Briefly, 171 g of water was added to a 250 mL glass reactor bottle, and acidified with 171 µL of the H_3PO_4 solution. A stir bar was added and the reactor sealed with a cap containing a rubber septum. The solution and headspace was then saturated with H_2 gas by bubbling for ~15 min. 4 µL of TCE, 0.4 µL of 1,4-dioxane, and 0.2 µL of pentane (as an internal standard) were injected into the reactor. Because of the low solubility of TCE, the reactors were stirred rapidly and allowed to equilibrate for at least 3 hours. To start the reaction, 25 mg of 1 wt% Pd/Al_2O_3 suspended in 2 mL of water was injected into the reactor. TCE concentration was monitored via GC analysis of headspace samples. 1,4-Dioxane concentration was determined by taking 1 mL aliquots of reactor fluid, filtering, and analyzed via the method described in the previous section. Control experiments omitting the acid and 1,4-dioxane were also performed to determine the effect of these on TCE hydrodechlorination.

3.3.4 Analytical Methods

1,4-Dioxane Quantification: 1,4-dioxane was quantified by the frozen extraction method reported by Li et al. Briefly, 500 µL of the reaction sample was mixed with 500 µL of dichloromethane in an autosampler vial to extract the 1,4-dioxane, agitated for at least 30 seconds, and placed in a -20°C freezer for at least 1 hour to freeze the water phase. The dichloromethane was then decanted into a clean autosampler vial and analyzed via GC-MS. 1,4-dioxane was quantified using a calibration curve prepared using known amounts of 1,4-dioxane in deionized water.

H_2O_2 Quantification: Titanium oxysulfate (~15 wt% in dilute H_2SO_4) was used to quantify unreacted H_2O_2. This species forms peritinanic acid upon reaction with H_2O_2, a yellow colored compound which can be quantified via UV-vis spectroscopy. A calibration curve was prepared for concentrations of 0-80 µM H_2O_2 to ensure maximum extinction (at λ=405 nm) was less than 1. Reaction aliquots were diluted from 0-20x to ensure that the extinction at λ=405 nm fell within the calibration curve.

3.4 Treatment Trains for 1,4-Dioxane and Chlorinated Solvents

3.4.1 Procurement of Site Materials for Treatability Testing

Site Identification and Description: In collaboration with AECOM, soil and groundwater for laboratory microcosm studies were collected from former Air Force Plant 3 in Tulsa, Oklahoma. Former AFP 3 is located northeast of Tulsa, Oklahoma, adjacent to the Tulsa International Airport. Former AFP 3 is bounded to the south, west, and north by the airport and to the east by N Mingo Road / N 97th E Avenue. Mingo Creek is located approximately 0.25 miles east of former AFP 3 property. Currently, the Tulsa Airport Authority (TAA) and the City of Tulsa own the AFP 3 property and lease building space to Spirit Aerosystems, Inc. and Navistar. The study area for an AFCEC-funded technology demonstration involving the Mahendra lab was located in AOC 1 (on the eastern side of Building 1) and this area was deemed suitable for this study as well. Historically, two vapor degreasers were housed within (or near) Building 1 for solvent reuse; the former TCE degreaser was located sub-grade within a sump while the former TCA degreaser was above grade. Environmental investigations conducted to date have identified VOCs and 1,4-dioxane groundwater plumes originating from the former vapor degreaser locations and migrating east-northeast in the direction of groundwater flow towards Mingo Creek.

The shallow groundwater zone at former AFP 3 is perched above the Nowata Shale formation, a black clay shale that was encountered at depths of 12 to 27 feet below ground surface (ft bgs) across the site. Based on a hydraulic gradient of 0.01 foot per vertical foot (ft/ft), hydraulic conductivities for former AFP 3 range from 7.6 x 10^{-5} to 1.12 x 10^{-3} centimeters per second (cm/s) and effective porosities range from 0.1 to 0.3 (AECOM, 2012). Average linear groundwater velocities across former AFP 3 were estimated to range from 2.6 to 116 feet per year (ft/yr).

Based on previous investigations performed at the site, the subsurface at AOC 1 consists of a thin gravel bed and reworked soils (from past construction activities), followed by native clay and silty clay deposits to depths ranging from approximately 10 feet bgs to 12 feet bgs. At AOC 1, groundwater was typically encountered at depths of 10 ft bgs to 14 ft bgs and flows in an east-northeastern direction towards Mingo Creek. Specific groundwater velocities near AOC 1 have not been calculated but are assumed to fall in the range cited above far AFP 3.

Site Contaminants: Previous environmental investigations have identified soil and groundwater impacts at AOC 1, east of Building 1, where the two former vapor degreasers were located. Contaminants of concern (COCs) include TCE and TCA, their degradation intermediates (1,1-dichloroethane [1,1-DCA], 1,2-dichloroethane [1,2-DCA], 1,1-dichloroethene [1,1-DCE], and cis-1,2-dichloroethene [cis-DCE]), and 1,4-dioxane. Concentrations of COCs at temporary and permanent monitoring wells in the vicinity of the proposed demonstration area are summarized in **Table 5**.

Table 5. Groundwater Concentrations in the Vicinity of the Demonstration Area
(Courtesy:AECOM, 2014)

COC	Groundwater Concentrations (July-August 2013) (µg/L)					
	TW43	**TW44**	**TW45**	**8MNW17**	**8MNW20**	**8MNW54***
TCE	14,700/15,700	486 J	7.12	7,080	17,400/17,000	1,310
TCA	164/156	<0.5	<0.5	67.3	4.23/4.18	91.5
1,4-DX	620/680	91	62/63	270	147/145	351 J
cDCE	120/119	0.822 F	19.9/18.9	69.1	31.4/30.6	105 M
1,1-DCE	3,600/3,630	7.07	18.6/17.1	1,720	2,330/2,910 J	296 F
1,1-DCA	7.26/6.54	5.77	68.2/65	8.59	3.96/3.87	6.81
1,2-DCA	<5	4.04 F	<5	13.2	37.3/36.3	24.4

Notes: (1) *Monitoring well 8MNW54 installed adjacent to location of temporary well TW43; /denotes duplicate sample; (2) Data qualifiers: F= qualifier indicating concentration in excess of detection limit and below reporting limit; J = qualifier indicating estimated concentration; M = qualifier indicating matrix effect.

Field Sample Collection and Analysis: Grab samples of groundwater were collected from a specific screen depth at three wells: temporary well TW43 is located in source zone, monitoring well 8MNW20 is located mid-plume, and 8MNW17 is located upgradient but close to source zone. Typically, 10 L groundwater and 2 kg soil were collected from each location in polypropylene containers for laboratory studies (additional groundwater samples for volatile organic analysis in 40 mL glass vials with Teflon-lined septa).

1,4-Dioxane was measured in field groundwater samples at UCLA by using frozen micro-extraction method described in Li et al. (2011), followed by a modified 8270-SIM using gas chromatograph-mass spectrometer. Select VOCs were also measured using a GC equipped with FID or ECD.

3.4.2 Treatment Technologies and Amendment Formulations

Biodegradation treatment involved incubation of unamended site material under aerobic conditions. Microcosm bottles were maintained in a shaking incubator at 30˚C and 150 rpm shaking for more than 10 weeks. During this process, 1,4-dioxane was spiked to ensure concentrations were consistent with site conditions. Aseptic techniques were used throughout the experiment to prevent contamination. In addition to active microcosm treatments, a sterile control to correct for abiotic losses of 1,4-dioxane, and a positive control bioaugmented with *Pseudonocardia dioxanivorans* CB1190 was also tested.

Oxidation treatment involved amending site materials with hydrogen peroxide and permanganate. With hydrogen peroxide as oxidant, microcosm bottles were prepared with 50 ml groundwater and 10 g soil, as well as 100 mg $FeSO_4 \cdot 7H_2O$. 10% sulfuric acid was added to achieve a pH at 4.5. Bottles were incubated at room temperature and rotated with 100 rpm. After 12 hours, the H_2O_2 oxidation process was quenched with NaOH. With permanganate as oxidant, 211 mM sodium permanganate was added before sealing the bottles and incubating them at room temperature and 100 rpm in a bench top rotating shaker. After 18 hours, the reactors were quenched using $Na_2O_3S_2$ (5 times the molar concentration of permanganate used).

Catalysis treatment involved amending site materials with WO_x/ZrO_2. For the catalysis step in treatment trains with no prior oxidation steps, 400 mg of 20 wt% WO_x/ZrO_2 was added to each microcosm along with 1600 µL of 30 % H_2O_2 as determined from the optimization experiments, and the reactors stirred overnight.

For the catalysis step in trains with a preceding oxidation step, the possibility of the $FeSO_4$ retaining H_2O_2 activity was considered. As such, while 400 mg of 20 wt% WO_x/ZrO_2 was still added to each microcosm, 12 or 52 µL of 3% H_2O_2 was added to the reactors instead of the 1600 µL of 30 % H_2O_2, and the reactors were stirred overnight. If little degradation was observed the next day, a subsequent dose of 1600 µL 30% H_2O_2 was added and the reactors were stirred overnight.

3.4.3 Treatment Trains

The treatment trains included biodegradation only (B), oxidation and biodegradation (OB), biodegradation and catalysis and oxidation (BCO), oxidation and catalysis (OC), and catalysis and biodegradation (CB). Bioaugmentation was included in the B microcosms, as well as all of the treatments trains, which are described in more detail below:

1. ***Oxidation and Biodegradation process (OB):*** Both steps of this process were completed at UCLA. H_2O_2 and permanganate oxidation processes were processed as described above and slurry samples were collected before (Control) and after (OB1) oxidation. Then the same microcosms were continuously incubated at optimal conditions with 30˚C, 150 rpm shaking for more than 10 weeks. During biodegradation process, 1,4-dioxane and *Pseudonocardia dioxanivorans* CB1190 (1:10) was added in bioaugmentation microcosms to ensure concentrations are consistent with site conditions. Slurry samples were collected after first time bioaugmentation (OB2), and after 10 weeks (OB3).
2. ***Oxidation, Biodegradation, and Catalysis process (OBC):*** The OB microcosms were sent from UCLA to Rice for treatment using an additional catalysis step. This was possible because little 1,4-dioxane and CVOC removal was observed during biodegrdation step (with the exception of bioaugmented microcosms), such that conditions did not change in the interim period between the B and C steps.
3. ***Biodegradation, Catalysis and Oxidation process (BCO):*** Microcosms were incubated for 10 weeks at UCLA as described in biodegradation only process, then sent to Rice University for the catalysis process and subsequent oxidation treatment. Slurry samples were collected before (Control) and after (BCO1) catalysis as well as after oxidation (BCO2).
4. ***Oxidation and Catalysis process (OC):*** This treatment train was conducted at Rice University, Slurry samples were collected before (Control) and after (OC1) oxidation, and after catalysis (OC2).
5. ***Catalysis and Biodegradation process (CB):*** Catalysis process was conducted at Rice University. Slurry samples were collected before (Control) and after (CB1) catalysis. Then the same microcosms were send to UCLA, and continuously incubated at optimal conditions with 30˚C, 150 rpm shaking for more than 10 weeks. During biodegradation process, 1,4-dioxane and *Pseudonocardia dioxanivorans* CB1190 (1:10) was added in bioaugmentation microcosms to ensure concentrations are consistent with site conditions. Slurry samples were collected after first time bioaugmentation (CB2), and after 10 weeks (CB3).

3.4.4 Microcosm Construction

All microcosms were constructed by filling 500 milliliter (mL) (nominal volume) glass bottles with approximately 50 mL of groundwater and 10 grams (g) of site soil leaving headspace for maintenance of aerobic conditions. Contaminant mixtures concentrations were spiked to natural conditions and are listed in **Table 6**.

Table 6. Experimental Conditions and Target Concentrations of Contaminant Mixtures in Treatment Trains

Experimental Conditions	**1,4-Dioxane (µg/L)**	**TCE (µg/L)**	**TCA (µg/L)**	**1,1-DCE (µg/L)**	**cDCE (µg/L)**
High DX/High cVOC	5	5	5	5	5
High DX/Low cVOC	5	0.5	0.5	0.5	0.5
Low DX/Low cVOC	0.5	0.5	0.5	0.5	0.5
Low DX Only	0.5	0	0	0	0
Abiotic High DX/High cVOC	5	5	5	5	5
Abiotic High DX/Low cVOC	5	0.5	0.5	0.5	0.5
Abiotic Low DX/Low cVOC	0.5	0.5	0.5	0.5	0.5
Abiotic Low DX Only	0.5	0	0	0	0
Bioaugmentation	5	0.5	0.5	0.5	0.5

Microcosms were sealed with screw-cap Mininert™ valves to allow repetitive sampling of each microcosm, and to allow the addition of amendments to sustain metabolic/biodegradation activities. Within 24 hours after microcosm construction, 1,4-dioxane concentrations were measured in the bottles and if necessary, the microcosms were spiked with 1,4-dioxane to ensure concentrations were consistent with site conditions. Microcosms and controls were maintained under aerobic conditions for up to 10 weeks (as needed depending upon 1,4-dioxane biodegradation kinetics) in an incubator shaker at 30˚C with150 rpm shaking. Aseptic techniques were used throughout the experiment to prevent contamination. As noted above, a sterile control to correct for abiotic losses of 1,4-dioxane, and a positive control bioaugmented with *Pseudonocardia dioxanivorans* CB1190 were tested in addition to the active microcosm treatments. Detailed microcosm conditions for different treatments are described in **Table 7** below.

Table 7. Microcosm Amendments for Treatment Train Studies

No.	**Test Condition**	**Amendments**
1	Autoclaved (-) Control *(correct for abiotic losses)*	None, sterilized at 121˚C for 15 minutes
2	Active Condition for B (=BC), CB, OB	Air
3	Bioaugmentation (+) Control	CB1190, air, and NMS (if needed)

3.4.5 Monitoring Program

During the microcosm study, the following parameters were periodically analyzed:

- 1,4-Dioxane and CVOCs (by GC-FID or GC-MS)
- ORP, DO, pH (using bench scale electrodes)
- Microbial community analysis using direct 16SrRNA gene sequencing at Laragen, Inc.
- Gene abundance by qPCR using recently-developed primers by the Mahendra laboratory as evidence of 1,4-dioxane-degrading monooxygenase activity.

The change in 1,4-dioxane concentration over time was measured for each combination of treatments. Gene abundance was quantified using qPCR for different bacterial populations and RT-qPCR for monooxygenase genes involved in 1,4-dioxane biodegradation.

3.4.5 Analytical Methods

Organ***ic compounds:*** 1,4-Dioxane and chlorinated solvent concentrations in samples from microcosms were measured using a GC equipped with an FID or a GC-MS. Aliquots of samples (200 µL) were collected from microcosms and transferred to screw top vials. Degradation of 1,4-dioxane in samples were suspended by acidifying with 12.1 N hydrochloric acid prior to storing at -20˚C for subsequent extractions. For concentrations of 1,4-dioxane higher than 1 mg/L, samples were filtered using 0.2 µm Nylon syringe filters, and 2 µl injected directly on-column into the gas chromatograph. For low concentrations of 1,4-dioxane, preserved samples were extracted using frozen micro-extraction method described in Li et al. (2011). Briefly, methylene chloride (200 µL) was added into samples along with 200 µg/L 1,4-dioxane-d8 internal standard. After mixing vigorously, the vials were placed in a vial tray at a temperature of -80 ˚C at a 45˚ angle for 45 minutes. Methylene chloride extract was removed from the vial and transferred to a clean instrumental vial with an insert. Sodium sulfate (0.05 g) was added into the vial to remove water residue in the extract. Extracted samples (5 µL) were injected into a Hewlett-Packard 6890 Chromatograph Plus coupled with a mass spectrometer detector and Supelco SPB-1 column (30 m x 0.53 mm id x 1 µm) by a 7693A ALS autosampler under pulse splitless mode. The oven program was set as 40 °C (1 min), ramped at 10 °C/min to 120 °C (1 min). All other GC-MS parameters and method details were used according to Isaacson et al. (2006).

Total Nucleic Acids: Total nucleic acids were extracted from samples using a modified phenol-chloroform extraction method as described previously (Zhang et al., 2016). Briefly, 500 µL of cell cultures was centrifuged at 13000g for 3 min, and the supernatant was discarded. The cells were lysed by adding 250 µL of lysis buffer (50 mM sodium acetate, 10 mM EDTA [pH 5.1]), 100 µL 10% sodium dodecyl sulfate, 1.0 mL pH 8.0 buffer-equilibrated phenol, and 1 g of 100 µm-diameter zirconia−silica beads (Biospec Products, Bartlesville, OK), followed by heating at 65 °C for 2 min, bead beating for 2 min with a Mini-Beadbeater 16 (Biospec Products, Bartlesville, OK), incubating for 8 min at 65 °C, and bead beating again for 2 min. The lysate was collected by centrifugation at 13000g for 5 min, followed by phenol−chloroform−isoamyl alcohol purification and chloroform−isoamyl alcohol purification. Precipitation of total nucleic acids was performed by addition of 0.1 volume of 3 M sodium acetate and 1 volume of isopropanol followed by incubation at −20 °C overnight. Nucleic acid pellets were collected by centrifugation at 4 °C for 30 min at 20000g. The precipitate was washed with 70% ethanol and resuspended in 100 µL of DNase- and RNase-free water. The concentrations of DNA and RNA were determined by a Nanodrop 2000C spectrophotometer (Thermo Scientific, Wilmington, DE).

Quantitative Polymerase Chain Reaction (qPCR): All reactions were run on a StepOnePlus thermocycler (Life Technologies, Carlsbad, CA) using a total volume of 20 µL containing 1× Luminaris Color HiGreen-HiROX qPCR Master Mix (Thermo Scientific, Waltham, MA), 0.5

mM primers, and 2 µL of DNA (1-10 ng/µL) template. Primer sequences and annealing temperatures are listed in **Table 8** (Gedalanga et al., 2014). All reactions were accompanied by a melt- curve analysis to confirm the specificity of quantitative polymerase chain reaction (qPCR) products.

Table 8. Primer Sequences and Annealing Temperatures

Gene	**Forward Primer (5’ → 3’)**	**Reverse Primer (3’ → 5’)**	**Annealing Temperature (°C)**
Universal 16S rRNA	ATGGCTGTCGTCAGCT	ACGGGCGGTGTGTAC	45
CB1190-like 16S rRNA	ACGGTCTCGCAGCCCTCTGT	AGCGGGTTATGCCGGGGACT	60
dxmB/dioxane monooxygenase (DXMO)	CCAAACGGGCGTCAGTCAT	AGAACGTGCGCTCCCAAAG	60
sad/aldehyde dehydrogenase (ALDH)	ACCAAGGACCTCACCTCGTA	AACGGATGCGCGTTGTTC	60
16S rRNA gene V3-V4 region	TCGTCGGCAGCGTCAGATGTGTATAAGAGACAGCCTACGGGNGGCWGCAG	GTCTCGTGGGCTCGGAGATGTGTATAAGAGACAGGACTACHVGGGTATCTAATCC	55

Microbial community analysis (MCA): The extracted DNA samples were amplified with a set of primers targeting the hypervariable V3-V4 region of 16S rRNA gene (Klindworth et al., 2013) (**Table 8**). Barcodes and adapters were incorporated between the adapter and forward primers. The PCR amplification was conducted in a 50 µL reaction system containing 2 µL forward primer (10 M) and 2 µL reverse primer (10 M), 25 µL 2 × EasyTaq® PCR SuperMix, 40 ng template DNA and 21 µL ddH$_2$O. The PCR was conducted under following protocol: 95°C for 3min; 25 cycles of 95°C for 30s, 55°C for 30s, 72°C for 30s, and a final extension at 72°C for 5 min; Hold at 4 °C. PCR products were purified and added with adapters and dual-index barcodes, then mixed and sent to Laragen, Inc (Culver City, CA) for Illumina Miseq sequencing. Using paired 300-bp reads, and MiSeq v3 reagents, the ends of each read were overlapped to generate high-quality, full-length reads of the V3 and V4 region in a single 65-hour run.

3.4.6 Data Analysis

Data treatment and bioinformatics analysis: After sequencing, we used Mothur (http://www.mothur.org/) to sort sequences exactly matching the specific barcodes into different samples following commands ‘fastq.info’, ‘trim.seqs’ and ‘make.fastq’. Then, the separated forward and reverse reads were merged by using the commands ‘make.contigs’. An initial denoising step was used to reduce sequencing and PCR errors with command ‘screen.seqs’, then command ‘chimera.uchime’ was used to process improved sequences. Denoised reads were extracted from raw datasets by using commands ‘get.seqs’ for downstream analyses. Taxonomic classification of each or couples of samples was conducted by ‘classify.seqs’ with confidence threshold at 80% and aligned with Silva database. Then ‘cluster.split’ was applied to cluster sequences into OTUs. Biodiversity was evaluated using the species diversity in specific samples based on OTUs including species types and abundance. This diversity was then displayed using rarefaction curves, which provided a way of comparing the diversity observed in different samples. The diversity takes into account the species richness and their abundance distribution. The value of the measured diversity was then plotted against the number of sequenced reads, estimating the 1) trend of diversity in different samples, and 2) whether all species in the sample had been detected (Gotelli and Colwell, 2001). On the rarefaction curves, the y-axis represents the number of OTUs, and the x-axis indicates trimmed number of sequenced reads. Moreover, an evaluation of beta diversity was conducted via OTU-based approaches (Schloss et al., 2009), with membership and structure shown using a combination of heat maps and Venn diagrams.

Statistical analysis: Statistical analyses and plotting were performed in R language (V 3.3.2) with packages of ggplot2, factoextra, vegan, heatmaply, etc.

3.5 Implications of Matrix Diffusion

The potential contribution of matrix diffusion processes on 1,4-dioxane fate and transport were investigated using two different approaches. The first was based on comprehensive modeling of typical 1,4-dioxane release scenarios. This was essentially a “proof of concept” study. The second was a field investigation that looked at the relationship between 1,4-dioxane concentrations and site hydrostratigraphy at two different contaminated groundwater sites. Note that majority of the methods and results of the modeling task were already published in Adamson et al. (2016).

3.5.1 Modeling Study

Simulations were performed with the help of the Matrix Diffusion Toolkit, a publicly-available free software tool developed for the Department of Defense to evaluate the potential impact of these processes on site trends (Farhat et al., 2012). This tool provides a set of analytical solutions to common matrix diffusion models, such that Concentrations and mass in the lower-permeability and transmissive zones for different scenarios can be easily evaluated. Simple dissolution models (described below) were used to generate input values for representative concentrations and loading periods for the individual release scenarios.

Matrix Diffusion Models: Two different analytical models that have been coded into the Matrix Diffusion Toolkit were used to assess the impact of matrix diffusion on contaminant mass, concentration.

1. <u>Square-Root Model:</u> This first of these models (commonly referred to as the “Square-root model”) was originally developed by Parker et al. (1994) and expanded in a guidance document for the Air Force (AFCEE, 2007). It relies on a simplified conceptual model of a two-layer aquifer system (a transmissive layer overlying a low-k layer) and considers

two distinct time periods: (1) a **loading period** where there is a constant concentration of contaminants (e.g., NAPL) in the transmissive zone that drives contaminants into the low-k zone; and (2) A **release period**, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated. The source is configured as a horizontal plane that covers a defined source area. It is assumed that the low-permeability layer is at least 1 meter thick and that degradation does not occur within this zone. Mass discharge related to the transverse diffusion of contaminants into the low-permeability layer underlying the source is then estimated at any time *t* using the equation:

$$M_d(t,t') = \varphi C_s A\left(\sqrt{\frac{RD_e}{\pi t}} - \sqrt{\frac{RD_e}{\pi(t-t')}}\right) \qquad (1)$$

where *M*d is the mass discharge (M/T), *t* is the time since the source was introduced (T), *t'* is the time at which source was removed/depleted from the high-permeability compartment (T), *Φ* is the porosity of low-permeability zone (unitless), C_s *is the* representative concentration above the low-permeability compartment during the loading period (M/L^3), *A* is the area of low-permeability compartment beneath the transmissive zone plume (L), *R* is the retardation factor for the low-permeability compartment (unitless), and D_e is the effective aqueous-phase diffusion coefficient in the low-k compartment (L^2/T). D_e can be estimated as the product of the molecular diffusion coefficient in free water (L^2/T) and Φ^p, where *p* is the apparent tortuosity factor exponent (unitless) (Pankow and Cherry, 1996, Charbeneau, 2000).

The total mass can be estimated from the mass discharge by integrating Eq. (1):

$$M_d(t,t') = 2\varphi C_s\sqrt{\frac{RD_e}{\pi}}\left(\sqrt{t} - \sqrt{t-t'}\right) \qquad (2)$$

The transmissive zone concentration is estimated by including a 10-ft screened interval located at the interface between the source and plume (with the assumption that the well capture the entire mass discharge):

$$C(t) = \frac{M_d}{V_d H W} \qquad (3)$$

where *C(t)* is the concentration in the transmissive zone at time t (M/L^3), V_d is the Darcy velocity of the transmissive compartment (L/T), *H* is the thickness of screened interval of the hypothetical well (L), and *W* is the width of the modeled area (L).

2. Dandy-Sale Model: A second, more sophisticated, analytical solution for the same two-layer system was also used. This method was developed by Sale et al. (2008) and further described in Bolhari et al. (2012). The source configuration is a vertical plane source that is introduced and results in a constant concentration during the loading period followed by a release period during which the transmissive zone is assumed to have no concentration as a boundary condition. A primary assumption is that both layers are uniform, homogeneous, isotropic, and infinite in the vertical (z) direction. Concentrations are calculated starting at the chosen interface between the source and the plume. One primary advantage of the application of this solution is that it provides a means for estimating the concentration at any point in time or space within the low-permeability zone downgradient of the source area:

This model was used to generate two-dimensional estimates of concentration within the low-permeability portion of the plume at various time points. A more complete description of the model, including assumptions and boundary conditions, can be found in the guidance manual for the Matrix Diffusion Toolkit (Farhat et al., 2012).

Source Depletion Model: Both matrix diffusion models described above require information on representative source concentration (C_s) and the loading period. For the purposes of this study, it was assumed that (1) 1,4-dioxane was initially released as part of a chlorinated solvent NAPL; and (2) the effective solubility of 1,4-dioxane could be approximated using Raoult's Law. To select representative values, a multi-component compositional NAPL dissolution model was adapted using the semi-analytical approach described by Charbeneau (2000). In this model, the source area is presumed to be a box of length L_0 in the direction of groundwater flow, with an arbitrary width and height, and containing a uniformly distributed NAPL at a volumetric content θ_N. A mass balance on the source box gives the following expressions for the change in constituent mass and NAPL saturation:

$$\begin{aligned} L_0 \frac{dm_i}{dt} = J_i = q_w C_{wi} \quad &\Rightarrow \quad m_i^{n+1} = m_i^n - \frac{\Delta t}{L_0} q_w C_{wi} \\ L_0 \frac{d\theta_N}{dt} = \sum \frac{J_i}{\rho_i} \quad &\Rightarrow \theta_N^{n+1} = \theta_N^n - \frac{\Delta t}{L_0} \sum \frac{J_i}{\rho_i} \end{aligned} \qquad (4)$$

where m_i it the mass of constituent i per bulk volume of porous medium, J_i is the flux of constituent i out of the source area, q_w is the specific discharge out of the source area, C_{wi} is the aqueous concentration of constituent i in the source area, and the superscripts n+1 and n refer to the next and current time step, respectively. At each time step, the mass of constituent i in the source box is:

$$m_i = (\theta_w + \rho_b K_{di})C_{wi} + \theta_N C_{Ni} \qquad (5)$$

where θ_w is the volumetric water content, ρ_b is the soil bulk density, K_{di} is the linear soil/water partitioning coefficient of constituent i, and C_{Ni} is the concentration of constituent i in the NAPL. The aqueous concentration and the NAPL concentration of constituent i are related through Raoult's Law:

$$C_{wi} = S_i \frac{C_{Ni} / MW_i}{\sum \left(C_{Nj} / MW_j \right)} \qquad (6)$$

where S_i is the pure phase solubility of NAPL constituent i, and MW is molecular weight.
Combining equations 5 and 6 leads to:

$$C_{Ni} = \frac{m_i}{(\theta_w + \rho_b K_d) \dfrac{S_i / MW_i}{\sum \left(C_{Nj} / MW_j \right)} + \theta_N} \qquad (7)$$

This equation can be solved iteratively at each time step to find C_{Ni}. The aqueous concentrations can then be calculated using Eq. 5, and the change in NAPL mass and NAPL saturation are determined with Eq. 4. The change in permeability of the porous medium in the source zone is estimated by calculating a relative permeability based on the Mualem model (Mualem, 1976; van Genuchten, 1980):

$$k_{rw} = \sqrt{\Theta}\left(1 - \left[1 - \Theta^{1/M}\right]^{M}\right)^{2} \qquad (8)$$

where k_{rw} is the water relative permeability, Θ is the reduced water content, and M is the van Genuchten (1980) soil characteristic curve parameter.

The model provides aqueous concentration vs. time data for the period until all mass is depleted from the NAPL for a given mixture of 1,4-dioxane and chlorinated solvents. A representative loading period for each compound was selected as the time required for depletion of 99.9% of the initial NAPL mass. The representative source concentration during that loading period (as an input for the matrix diffusion model) was set as the average concentration during that loading period (based on the data generated by the dissolution model).

Scenarios Evaluated: Two different release scenarios were developed and evaluated in detail using the models described above (**Figure 5**).

1. Scenario 1: The release of 1,4-dioxane as a secondary component of a TCA DNAPL within a well-delineated on-site source zone was evaluated (i.e., “on-site source”). This scenario simulates the expected behavior of 1,4-dioxane and a typical co-occurring chlorinated solvent following a historic release (circa 1970). An equivalent of 13 drums of spent solvent was selected as the volume released. Initial mole fractions of 0.20 for 1,4-dioxane and 0.55 for TCA were selected to represent the relative ratio of these compounds in spent solvent waste as described in Table 3.10 of Mohr et al. (2010). For the purposes of this study, NAPL components other than TCA and 1,4-dioxane were handled as follows: (1) mass of all other compounds were used to select the initial mole fractions of TCA and 1,4-dioxane; (2) dissolution of other stabilizers (e.g., 1,3-dioxalane) were not explicitly included in the model but were assumed to occur on the same timeframe as 1,4-dioxane based on their relatively similar solubilities and molecular weights; (3) cutting oils were included in the dissolution model using estimated parameter values provided by Mohr et al. (2010). Within the source zone, the mass and post-loading period concentrations were modeled using Eq(1) – Eq(3). As part of this evaluation, a range of 1,4-dioxane and TCA C_s values were evaluated to better demonstrate the sensitivity of the results to this parameter. Within the downgradient plume, mass and concentrations were calculated using Eqs(1-3). The full set of input parameters for this scenario is provided in **Table 9**.

2. Scenario 2: the migration of a lower-level 1,4-dioxane plume from an upgradient source was simulated (i.e., “off-site source”). For this case, it was assumed that 1,4-dioxane concentrations had decreased to 1 mg/L (through attenuation, dispersion, and/or diffusion) by the time they had entered a site with similar hydrogeologic characteristics as modeled in Scenario 1 (**Table 9**). The year 2000 was selected as the start date for Scenario 2. A larger area (50 m length, or approximately a 1 year travel time for 1,4-dioxane) was modeled to represent plume-wide conditions after a pulse of 1,4-dioxane

has moved through a site where no 1,4-dioxane source was released. A range of loading times was investigated to demonstrate how decisions about when to remediate the upgradient 1,4-dioxane source impacted 1,4-dioxane trends within the plume.

Table 9 lists the values selected for various input parameters that are associated with the hydrogeological characteristics of the subsurface, as well as values for representative concentrations and loading periods that are described in more detail in Section 4.5. In general, the remaining input values correspond to the default values for the Matrix Diffusion Toolkit, which were based on mid-range values from available literature compilations. For the purposes of the 1,4-dioxane release scenarios, default values were chosen to ensure that the results could be considered representative of a "typical" site. A full description of how these default values were chosen can be found in Farhat et al. (2013).

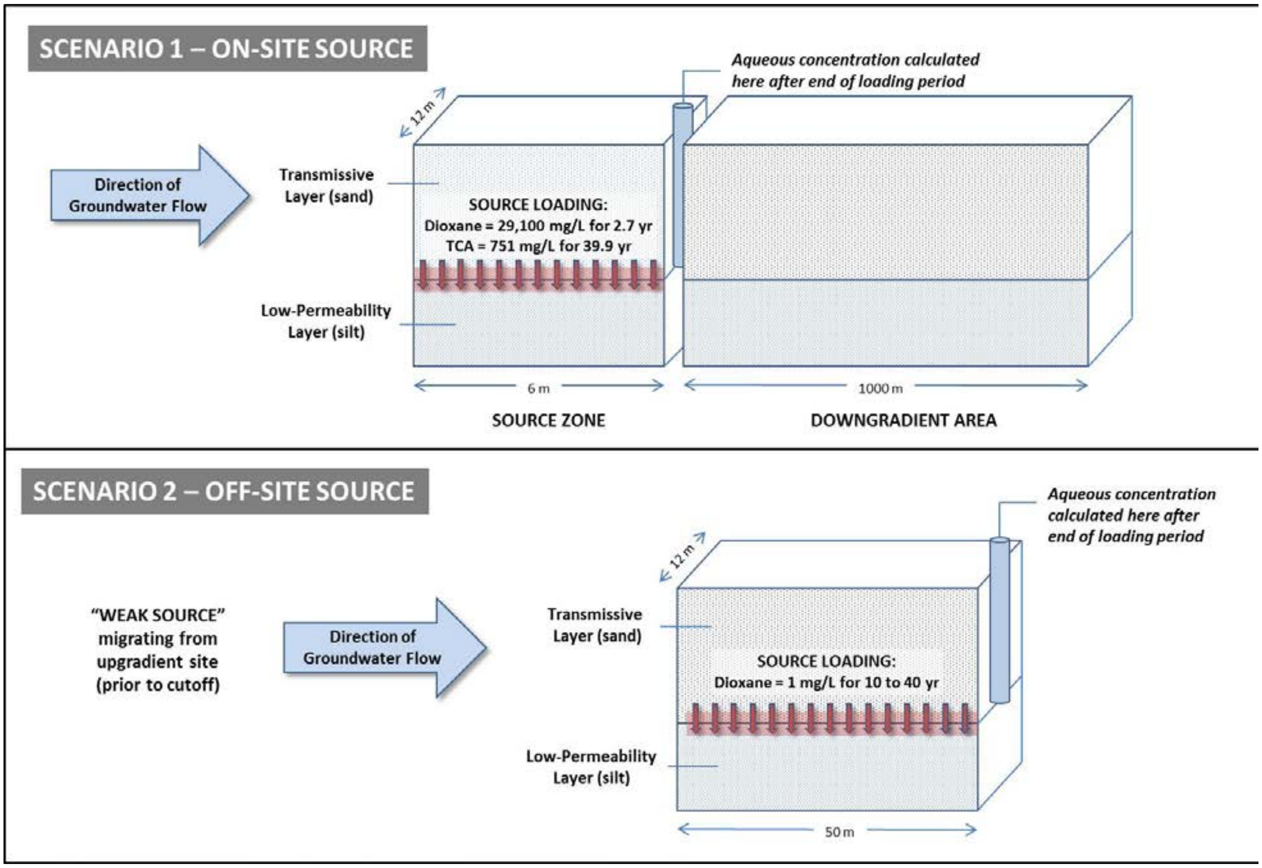


Figure 5. 1,4-Dioxane Release Scenarios Evaluated During Matrix Diffusion Modeling Study

Table 9. Input Parameters for Modeling.

Parameter	Value [a,c]
Source length	12
Source width	6
Source zone depth	1 m
Low-k zone depth	>1 m
Low-k zone soil type	Silt
Low-k zone porosity (ϕ)	0.43
Low-k zone fraction of organic carbon (f_{oc})	0.005
Low-k zone tortuosity factor exponent (p)	0.42
Low-k zone hydraulic conductivity (K)	3.05 m/d
Transmissive zone soil type	Sand
Transmissive zone porosity (ϕ)	0.37
Transmissive zone fraction of organic carbon (f_{oc})	0.0001
Transmissive zone hydraulic conductivity (K)	0.0036 cm/s
Transmissive zone seepage velocity, (v)	50 m/yr
Molecular diffusion coefficient (D_o)	Dioxane = 1.06 x 10^{-9} m^2/s; TCA = 0.88 x 10^{-9} m^2/s
Organic carbon partitioning coefficient (K_{oc})	Dioxane = 17 L/kg TCA = 110 L/kg
Retardation factor	Dioxane = 1.01; TCA = 3.17
Loading period [b]	Scenario 1: 1,4-dioxane = 2.7 yr; TCA = 39.9 yr Scenario 2: 1,4-dioxane = 1 yr
Representative concentration during loading period (C_s) [b]	Scenario 1: 1,4-dioxane = 28,900 mg/L; TCA = 751 mg/L Scenario 2: 1,4-dioxane = 1 mg/L
Attenuation/degradation processes?	None

[a] Values for site and hydrogeological parameters based on hypothetical site characteristics. Baseline values for C_s and loading period based on dissolution modeling (see Figure 2).

[b] Baseline values are listed, but range of values were evaluated to test parameter sensitivity (dioxane C_s in Scenario 1; TCA loading period durations in Scenario 1; 1,4-dioxane loading period durations in Scenario 2).

[c] Values for hydrogeological input parameters were chosen based on default values in the Matrix Diffusion Toolkit. These values represent mid-range values for literature compilations. See Farhat et al., (2012) for more information.

3.5.2 Field Study

To further advance the preliminary findings of the modeling study, a high-resolution characterization program specifically designed to evaluate the issue of matrix diffusion was performed at 2 sites with significant geologic heterogeneity. The aim would be to establish the distribution of contaminant mass within zones of differing permeability to determine the extent to which storage (and release) of mass from low permeability intervals influence the long-term fate and transport of 1,4-dioxane and co-occurring chlorinated solvents. A secondary goal was to determine if there is evidence for degradation within low-permeability intervals, as well as rates associated with these degradation reactions.

Site Selection: Three sites were selected as candidates based on their initial interest in the project. This included Cape Canaveral Air Force Station (CCAFS), Joint Base Cape Cod, and Naval Air Station (NAS) Whidbey Island. Both Joint Base Cape Cod and NAS Whidbey Island were eliminated based on the depth of contamination as well the depth of potential low-k zones. The sites selected for the demonstration was **Cape Canaveral Air Force Station (with separate investigations completed at Facility 1381 and Space Launch Complex 16).**

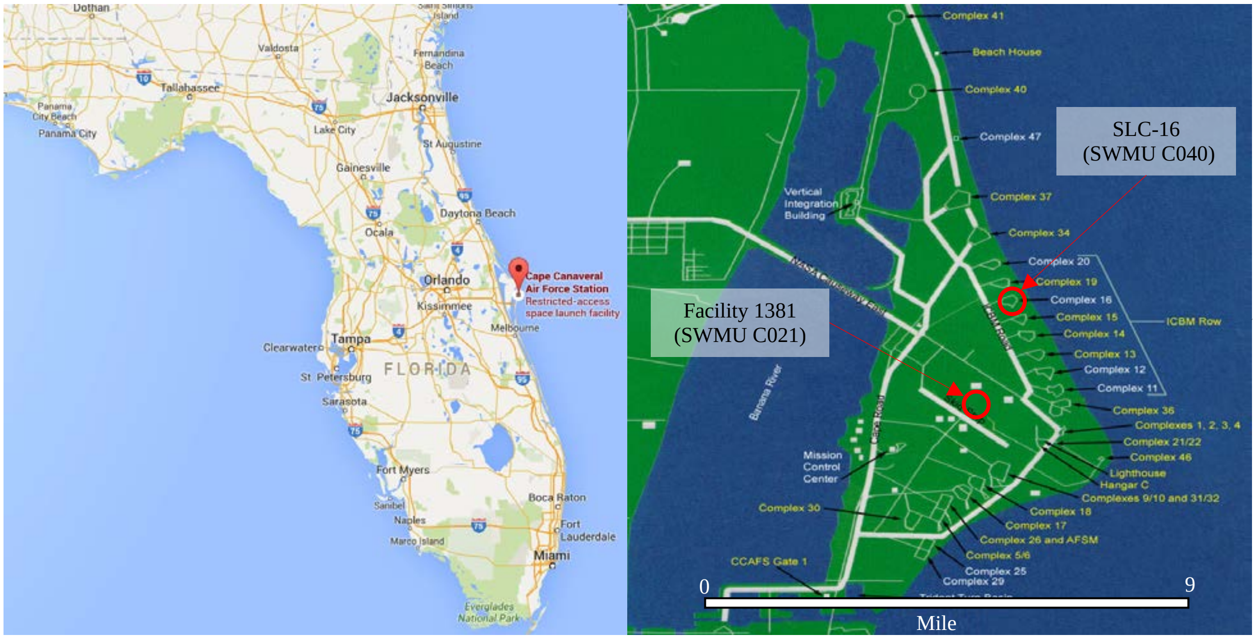


Figure 6. Location of Cape Canaveral Air Force Station (left panel) and Field Sites (right panel).

Site History and Characteristics: Relevant site characteristics are summarized below. Note that the following descriptions are based on information provided by site personnel in early 2016.

1. <u>Space Launch Complex 16 (SLC-16):</u> SLC-16 is located in the eastern portion of CCAFS, immediately adjacent to the Atlantic coast (**Figure 6**). SLC-16 was constructed in 1959 for the Titan I missile program and subsequently used to launch Titan II, Pershing IA, and Pershing II missiles. Site reports suggest that TCE and other organic compounds were used in limited quantities for cleaning small parts (but not the missiles

themselves). Under the Resource Conservation and Recovery Act (RCRA), it is designated as Solid Waste Management Unit (SWMU) C040.

A long-term monitoring (LTM) program at SLC-16 was initiated in January 2001 for a dissolved chlorinated solvent plume detected during the RCRA Facility Investigation (RFI). Results indicated that solvent concentrations have been relatively stable since the initiation of the LTM program. To address recommendations in the five-year review completed in 2008, a multi-phase direct push technology (DPT) sampling approach was used to assess the intermediate groundwater zone at SLC-16. Additional DPT investigations have been completed during the subsequent period to further define the horizontal and vertical extent of the CVOC plumes.1,4-dioxane was recently added to the sampling program and has been measured in existing monitoring wells since 2012. This site is scheduled to undergo extensive remediation in the near future, and the performance-based contractor is currently preparing a Corrective Measures Study to address this site.

Based on available site reports, the geology and hydrogeology at SLC-16 consist primarily of fine to course sand with shells to a depth of approximately 20 ft bgs. Below this is a 20-ft or more layer that has been described as very fine sands with shells. A boring log from a well installed in the source area (MW-43) suggests that there is an apparent transition to finer-grained soils with higher silt and clay content below 20 ft, but this is not reflected in the geologic cross-sections (which do not extend past 40 ft bgs). Select stratigraphic logs (collected in 2015 using the Hydraulic Profiling Tool) show a lower-permeability layer from approximately 40 to 45 ft. This may correspond to the silt-rich unit described in the boring log for MW-43. However, this lower-permeability layer is not apparent in all stratigraphic profiles, and it is possible that any such layer is discontinuous. Note that a more defined clay-rich unit is present at Facility 1381 (less than 3 miles from SLC-16) at a depth of approximately 50 ft bgs. Regardless of whether this unit extends to the SLC-16 area, the available stratigraphic information suggests that considerable heterogeneity in the SLC-16 geology that could be influencing contaminant mass storage at this site.

Groundwater is encountered within the shallow soils and the groundwater-bearing unit extends at least to 90 ft bgs. Wells have been installed in shallow (5 to 25 ft bgs), intermediate (30 to 43 ft bgs), and deep (49 to 90 ft bgs) portions of the groundwater-bearing unit. Flow is generally to the south, and the gradient in the shallow soils has been reported as 0.0009 ft/ft.

A comprehensive DPT investigation completed in late 2015 established the distribution of CVOCs in 10-ft vertical intervals (to 90 ft bgs) throughout the entire site. Based on the results of this investigation, the CVOC plume extends for approximately 600 ft from a source area that is located in the western portion of the site. Elevated CVOCs are encountered to at least 90 ft bgs. However, the plume footprint is relatively large in the depth intervals from 10 to 40 ft bgs but does not extend more than approximately 100 ft from the apparent source area in the depth intervals from 40 to 90 ft bgs. The highest concentrations of TCE, ranging from 100 to 500 mg/L are generally encountered in the 10 to 30 ft bgs intervals (with higher concentrations at certain locations). Elevated levels of daughter products are also encountered throughout the site, with the highest concentrations of cis-1,2-DCE (450 mg/L) and VC (34 mg/L) found in areas where TCE is also elevated.

Limited 1,4-dioxane data are available because the 2015 DPT investigation did not include 1,4-dioxane as an analyte. Groundwater samples collected from permanent wells indicate that 1,4-dioxane is present at low to moderate levels from depths ranging between 10 and 50 ft bgs. The highest reported concentration is 2.4 mg/L in well MW-43 in August 2015 (screened from 40 to 50 ft bgs). This is near the apparent source area for CVOCs. Lower concentrations have been measured in wells extending downgradient (e.g., MW-36, MW-37, MW-39, MW-42) at varying depths. Based on available data, the 1,4-dioxane plume occupies a similar footprint to the CVOC plume. Samples from deeper wells (screened below 50 ft bgs) are typically above reporting limits for 1,4-dioxane. A similar pattern was observed with the CVOC data (lower concentrations below 50 ft), suggesting that there is a barrier to vertical migration (e.g., a lower-permeability confining unit) at depths of approximately 40 to 50 ft bgs in the area south of the source area.

Groundwater geochemical data, along with the elevated concentrations of dechlorination products, indicate that reducing conditions prevail throughout the site. Sulfate and other electron acceptors are generally low, and pH values are near neutral. Field measurements of electrical conductivity fall in a relatively high range (1 to 10 mS/cm) but are consistent with the coastal location.

2. <u>Facility 1381:</u> This site is located in the central portion of CCAFS, southwest of SLC-16 and southeast of Armory Road (**Figure 6**). The facility was constructed in 1958, and the property included an acid neutralization pit that received a variety of spent solvents. The U.S. Coast Guard has been using the site as an Ordnance Support Facility since 1979. Under, it is designated as Solid Waste Management Unit (SWMU) C021. A drainage canal is located along the southwest boundary and separates the site from a large landfill (SWMU C019, Landfill No. 2).

   Assessment and investigation of the site under RCRA was initiated in 1993. An RFI was completed in 1998 and determined that dense non-aqueous phase liquid (DNAPL) was present and required remediation to address groundwater contamination. A subsequent Corrective Measures Study (CMS) recommended that soil mixing enhanced with steam and iron be used in the source area. This corrective action was completed in 2007 and treated over 44,000 cubic yards of soil and removed an estimated 11,000 lb of contaminants. Monitored natural attenuation has been used during the subsequent period, and there is no evidence that concentrations have rebounded following soil mixing. In addition to the primary measure, a number of Interim Measures have been completed in (or near) the source area, including air sparging, phytoremediation, groundwater recirculation, enhanced anaerobic bioremediation, and aeration diffusers (in the canal). A passive interceptor basin has been constructed immediately upgradient of the canal and will eventually replace the diffusers as a means for treating contaminant discharge.

Extensive remediation has occurred in the vicinity of Facility 1381, including soil mixing and the installation of an interceptor trench. As a result of these efforts (which included the use of bentonite to greatly reduce the overall permeability of the treatment zone), the native hydrogeology of the site has been altered significantly. The current demonstration will focus on an area outside of the soil mixing zone, such that unaltered soils are expected to be encountered.

The geology and hydrogeology at Facility 1381 have been well studied, in part to support the design of the interceptor basin. Predominantly sandy soils are present to 110 ft bgs and are classified as a surficial aquifer system. The shell and fine content (silts and clays) generally increase with depth. Within this aquifer, a competent plastic marine clay unit is encountered at between 48 and 50 ft bgs and is approximately 10 ft thick beneath the site. This low-permeability layer appears to be serving as a barrier to further vertical migration to underlying soils (which consist primarily of sands).

Groundwater is encountered within the first 5 to 10 ft bgs of the surficial aquifer and is considered unconfined. Wells are installed in shallow, intermediate, and deep portions of the first 50 ft of the groundwater-bearing unit. The facility itself represents a topographic high for the water table. Within the shallow and intermediate zones, groundwater flows south (where it is intercepted prior to reaching the canal) but also has been shown to move in north, west, and east directions relative to the facility. In part, groundwater direction varies considerably in response to rainfall events. Flow within the aquifer is considered "very slow" due to shallow gradients. Hydraulic conductivities have been defined for modeling purposes and ranges from 10 to 200 ft/d in the shallowest layer to 0.0001 ft/d in the clay layer. The layers immediately above the clay (approximately 24 ft thick) are considered slightly less permeable ($K = 1.2$ to 1.9 ft/d) than the shallower zones.

CVOC concentrations have decreased significantly in the presumed source areas (which underlie the facility) as a result of extensive treatment efforts. Based on a combination of field data and modeling, the projected maximum length of the cis-1,2-DCE plume (based on the compliance level of 70 µg/L) was approximately 1000 ft, while the size of the VC plume (based on the compliance level of 2 µg/L) was much larger (tens of acres). TCE has occupied a relatively small footprint in the vicinity of the facility. Contaminant levels were treated to low levels by soil mixing except for a few hotspots northeast of the soil mixing area where concentrations in excess of 1 mg/L of TCE (along with daughter products) were present; this area has recently been treated using enhanced anaerobic bioremediation such that most CVOCs are below detection levels at all wells. Historically, CVOC concentrations have been generally higher in shallow zones than in intermediate and deep zones.

Like SLC-16, 1,4-dioxane data at Facility 1381 are relatively limited. Groundwater samples from monitoring wells have been analyzed for 1,4-dioxane periodically since 2009. In general, 1,4-dioxane concentrations have been relatively low, with the maximum concentration to-date of 26 μg/L in well BN01I in July 2014. While the highest concentrations are present in an area immediately northwest of the primary treatment area, 1,4-dioxane has been detected in wells extending at least 700 ft north of this area, suggesting that a large, dilute plume is present. There is insufficient data to evaluate whether 1,4-dioxane is predominantly present in shallow vs. intermediate zone wells and no data exists for wells in deeper zones (including below the clay unit). 1,4-dioxane has been infrequently detected at low levels in the interceptor basin and in the canal downgradient. In addition, several wells installed at the periphery of the adjacent landfill have also observed minor detections of 1,4-dioxane. There is no evidence that groundwater beneath Facility 1381 is hydraulically connected to groundwater beneath the landfill.

The groundwater geochemistry at Facility 1381 is similar to SLC-16 (i.e., predominantly reducing and favorable for biological activity).

Experimental Design: The field program was designed to collect high-resolution depth-discrete data from low permeability zones at multiple sites. A similar protocol was followed at each site (see **Figure 7** for an example of the conceptual design). Specifically, multiple locations were characterized at each site to generate several vertical soil profiles. This allowed for a more comprehensive assessment of spatial differences in historical source loading as well as location-specific influences related to advection, sorption, degradation, and other processes. At each location, soil sub-sampling was preceded by detailed vertical stratigraphic profiling to optimize the selection of soil sampling depths, as well as to provide groundwater data to refine conceptual and quantitative modeling at each location. The sampling and analysis plans are detailed in **Table 10** and **Table 11**.

Membrane Interface Probe/Hydraulic Profiling Tool: A detailed vertical characterization of each test location at each site was completed using the Hydraulic Profiling Tool (HPT) equipped with a membrane interface probe (MIP). This is a subsurface data acquisition system developed by GeoProbe that collects anintegrated set of companion data in a single, continuous direct push. The MIP-HPT is capable of collecting data at close vertical spacings to capture small-scale changes in site stratigraphy. Integrated sensors provide hydrostratigraphic data displayed graphically as the tooling is advanced, allowing real-time identification of optimum sampling locations. In particular this tool allows field identification of lower permeability zones in real time using a direct-push platform for advancement. The primary depth-discrete data collected during advancement of the HPT include: 1) electrical conductivity (EC) as an indicator of permeability; and 2) an estimated hydraulic conductivity value based on the corrected hydraulic pressures encountered during tool advancement.

High-Resolution Vertical Soil Sub-Sampling: A parallel vertical characterization was completed at all selected test locations by collecting high-resolution soil concentration data. This involved the collection of relatively undisturbed soil cores from the saturated soil intervals located above the low permeability units and within the low permeability units themselves. The objective was to quantitatively establish the amount of mass present in each of these layers using refined sampling and analytical techniques appropriate to analysis of contamination in fine-grained material. Soil cores were obtained using a direct push rig within several feet of location(s) where HPT characterization was completed to ensure that highly similar subsurface conditions are encountered. Continuous coring is anticipated from an interval from the surface to a depth several feet within the targeted low permeability unit at each location. To prevent the vertical migration of contamination to deeper intervals (i.e., “drag down”), the tooling was not advanced through the entirely of the low-permeability units (i.e., to prevent communication between shallow and deeper groundwater bearing units). In addition, the step-wise advancement/collection process minimizes cross contamination from occurring.

Approximately 10 soil samples were collected from each core at closely-spaced vertical intervals with a sampling frequency based on data obtain during the HPT characterization and visual inspection of cores. Samples were collected from the center of split cores using TerraCore samplers and immediately transferred to vials containing a known amount of preservative. Soil samples were analyzed for 1,4-dioxane, CVOC concentrations, and soil organic carbon at an accredited laboratory (ESC Labs). Investigation-derived waste was analyzed and disposed of in a manner appropriate for its characteristics. Following completion, the borehole was abandoned by site personnel per standard protocols for the site.

Vertical Groundwater Sampling: A parallel characterization was completed at all test locations by collecting groundwater concentration data. The primary objective of the groundwater sampling and testing program was to generate data for confirmation of groundwater concentrations in the zones where soil sampling has occurred. In addition, several analytes are more easily obtained using groundwater samples than soil samples. To accomplish these objectives, up to three groundwater samples were collected from the same locations where soil samples have been collected, including at least one sample from within the lower-permeability zone. Depth intervals will be selected based on the results of the HPT investigation (as well as existing site characterization data).

Samples were collected using one of the following methods: 1) using the direct-push rig to collect grab samples from exposed screens during advancement; or 2) by first installing temporary piezometers. The specific groundwater collection method was based on contractor experience and field conditions encountered during the investigation (particularly well yield in low-k zones). In each case, method-appropriate and depth-appropriate pumping methods (e.g., bladder pumps, peristaltic) were selected to collect the sample. Low-flow techniques will be used if possible except in cases where sample volumes are limited. For low-flow samples, general water quality parameters will be measured during groundwater purging. Groundwater samples were analyzed at laboratories according to standard methods for 1,4-dioxane, VOCs, biomarkers, isotopes, major anions, dissolved gases, and total organic carbon (as detailed in **Table 11**)

Table 10. Summary of Sampling Plan for Field Demonstration

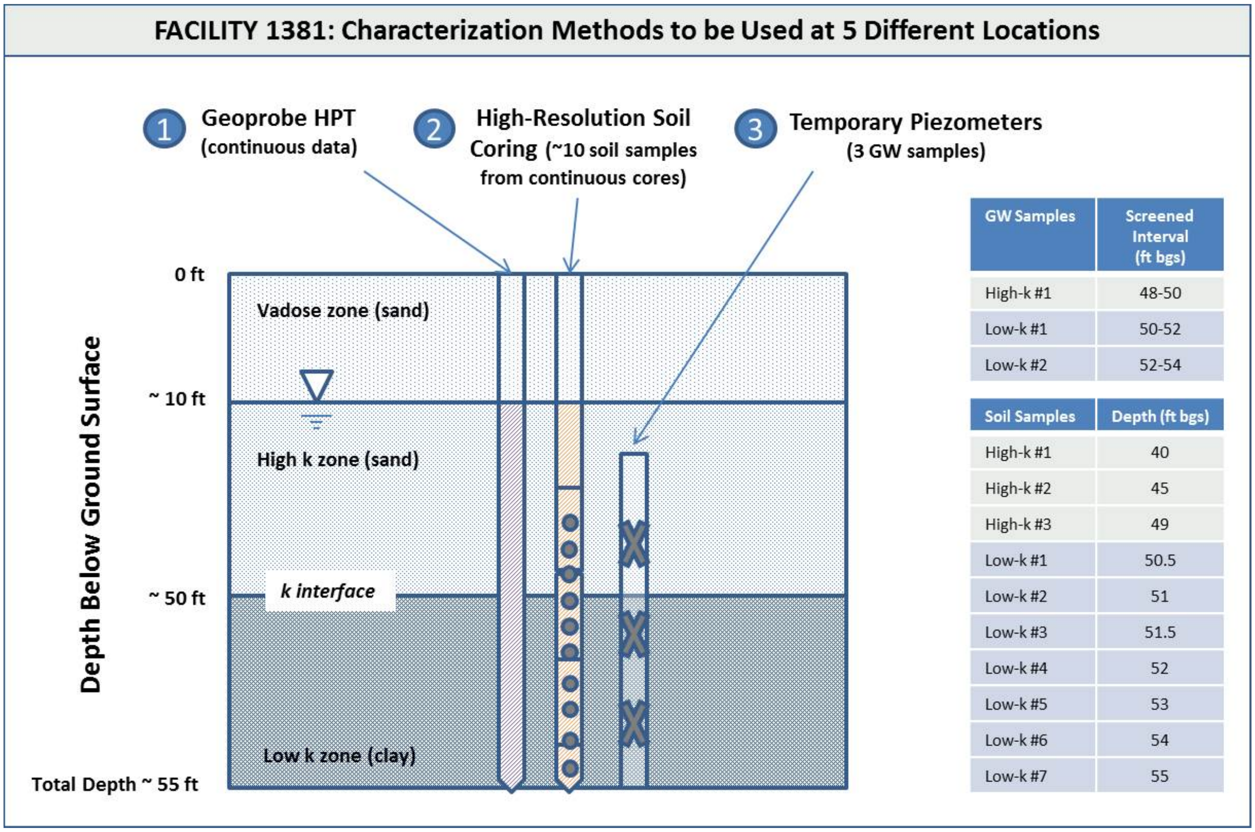
Project Component	Matrix	Collection Method	Number of Samples	Analyte(s) (listed in order of priority)	Location
Membrane Interface Probe-Hydraulic Profiling Tool (MIP-HPT)	--	Downhole tooling	Continuous	Electrical conductivity (EC), estimated hydraulic conductivity (K); Detector response(s) (PID/FID/ECD)	Same locations (4 to 5 per site) where high-resolution soil sub-sampling/analyses is to be completed
High-Resolution Soil Sub-Sampling	Soil	Geoprobe w/ liner for core; TerraCore for soil samples	8 to 12 per location	1,4-dioxane, CVOCs, biomarkers	Same locations (4 to 5 per site) where HPT is performed and confirms lower-k layer(s) present
			4 to 6 per location	organic carbon, moisture content	
Groundwater Sampling	Groundwater	Temporary piezometer or Geoprobe grab sample	Up to 3 per location	1,4-dioxane, CVOCs, field parameters, biomarkers, major anions, dissolved gases	Same locations (4 to 5 per site) where HPT is performed and confirms lower-k layer(s) present
			Up to 2 per location	TOC, isotopes	

Notes: (1) Additional analytes may be added to provide additional information on attenuation mechanisms; (2) Field parameters for groundwater include temperature, pH, oxidation-reduction potential, electrical conductivity, and dissolved oxygen; (3) Number of samples is approximate; actual number of samples collected and/or analyzed may be lower; (4) CVOCs = chlorinated volatile organic compounds; TOC = total organic carbon.

Table 11. Summary of Analytical Methods for Samples Collected During Field Demonstration

Matrix	Analyte	Method(s)	Container and Preservative	Laboratory
Soil	CVOCs	EPA 8260B	2 40-mL VOA vials per sample, each containing 5 g soil transferred using TerraCore samplers; 1 VOA vial contains methanol as preservative, other 2 VOA vials contain deionized water	ESC Lab
	1,4-Dioxane	EPA8260B “Low-level”	40-mL VOA vials per sample, containing 5 g soil transferred using TerraCore samplers; VOA vial contains deionized water but no preservative	ESC Lab
	Organic carbon	ASTM D2974	4-oz wide-mouth glass; no preservative	ESC Lab
Groundwater	CVOCs	EPA 8260B	2 40-mL VOA vials; HCl to pH < 2	ESC Lab
	1,4-Dioxane	EPA 8260B “Low-level”	2 40-mL VOA vials; HCl to pH < 2	ESC Lab
	Biomarkers	Proprietary qPCR-based method	TBD	UCLA
	1,4-Dioxane Isotopes (^{13}C, ^{2}H)	Proprietary	2 40-mL VOA vials; HCl to pH < 2	University of Waterloo
	TOC	EPA 9060A	250-mL amber; field preserve with HCl	ESC Lab
	Major anions	EPA 9056A	250-mL plastic	ESC Lab
	Dissolved gases	RSK175	3 40-mL VOA vials; HCl to pH < 2	ESC Lab
	Field parameters (dissolved oxygen, electrical conductivity, oxidation-reduction potential, pH, temperature)	YSI Mulitmeter (or equivalent)	> 100 mL; no preservative	Not applicable (field measurement)

Notes: (1) All samples shipped to commercial labs were packed in ice to ensure that sample arrived at 4°C within method-specific holding times; (2) CVOCs = chlorinated volatile organic compounds; TOC = total organic carbon; VOA = volatile organic analysis (standard amber bottle with Teflon seal)



GW Samples	Screened Interval (ft bgs)
High-k #1	48-50
Low-k #1	50-52
Low-k #2	52-54

Soil Samples	Depth (ft bgs)
High-k #1	40
High-k #2	45
High-k #3	49
Low-k #1	50.5
Low-k #2	51
Low-k #3	51.5
Low-k #4	52
Low-k #5	53
Low-k #6	54
Low-k #7	55

Figure 7. Conceptual Overview of Characterization at Facility 1381. Depths are approximate and were based on available site information at the time the Demonstration Plan was developed. Actual depths were established during field investigation; total depth and sampling depth(s) varied slightly from location to location within the site. Sample collection (number, method) was also adjusted based on field conditions. Not all analyses were performed at all depths.

4. RESULTS AND DISCUSSION

4.1 Scale of the 1,4-Dioxane Problem

Overall hypothesis that was tested: 1,4-dioxane plumes are large, dilute, and do not attenuate

Note: The bulk of the findings in this section were published in Adamson et al. 2014 and Adamson et al. 2015. Due to the evolution and refinement of the database, the results have changed slightly (by a few %) in some cases from those published previously.

4.1.1 General Plume Characteristics

The focus of this section is general characteristics of sites where 1,4-dioxane has been detected, including concentration and plume lengths. For comparative purposes, the same characteristics for sites with chlorinated solvents are also shown, but without considering the issue of co-occurrence of chlorinated solvents and 1,4-dioxane (which is addressed in the next section).

By the end of 2013, 1,4-dioxane analyses were completed at 582 individual sites, and 1,4-dioxane was detected at 191 of these sites. This is a much smaller number of sites than those where TCE was detected (2322 sites), TCA (477 sites), 1,1-DCE (1063 sites), 1,1-DCA (1082 sites), cDCE (1893 sites), and VC (1022 sites). **Figure 8** shows the wide geographical distribution of the California sites where 1,4-dioxane and several of the chlorinated solvents were detected. The median value of the range of maximum historical 1,4-dioxane concentrations at these sites was 130 μg/L (10th percentile = 5.8 μg/L; 90th percentile = 9,800 μg/L), this value is approximately two and a half orders of magnitude higher than the health-based reference concentration used by USEPA in UCMR3 monitoring of public water supplies.

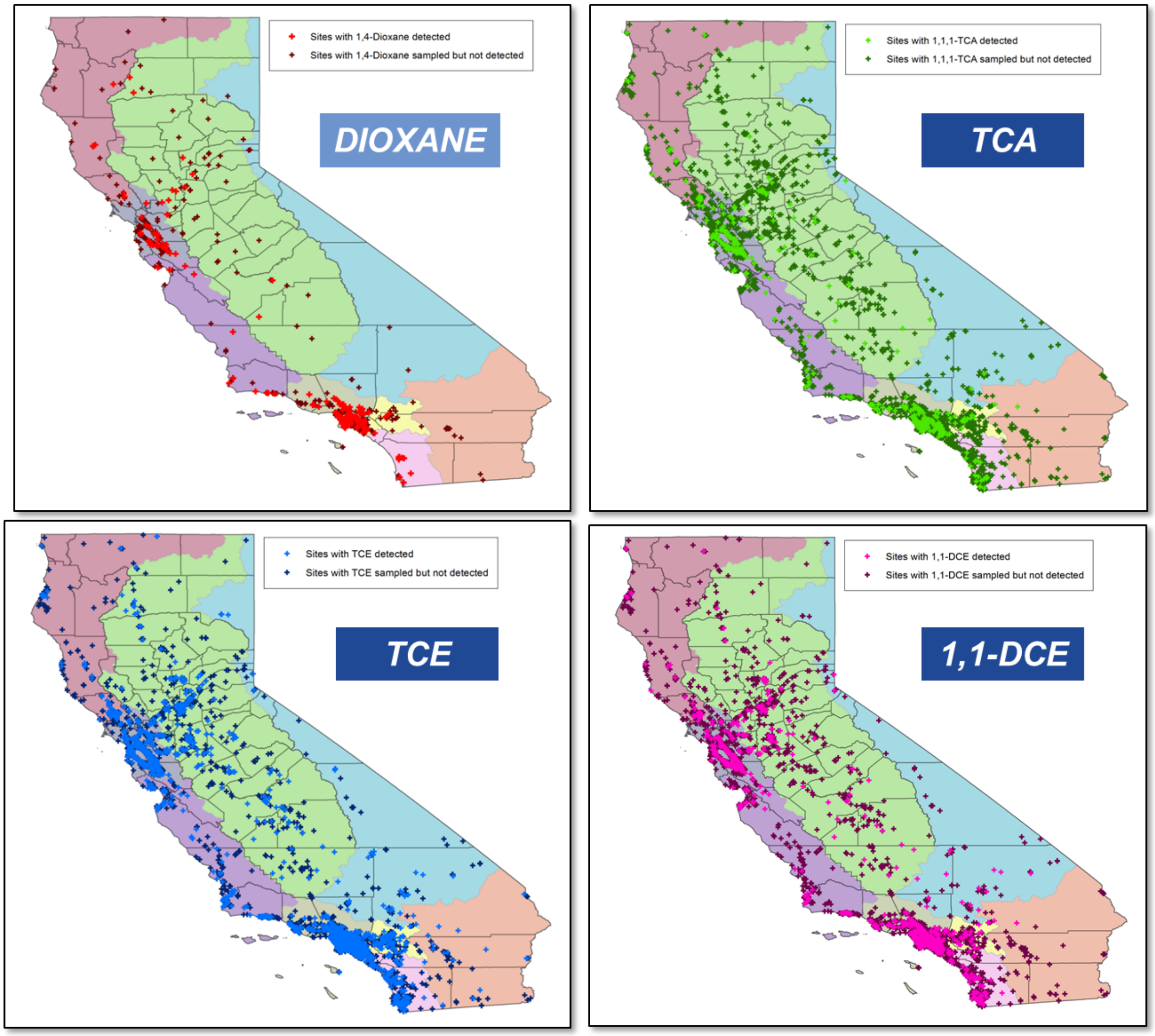


Figure 8. Geographic Locations of California Sites with 1,4-Dioxane and Several Chlorinated Solvents

Of the sites where 1,4-dioxane was detected, plume lengths could be estimated at 109 of these sites (for sites where a plume length could not be established, the typical reason was a lack of multiple monitoring points with detections). One or more chlorinated solvents was also detected at 95% of these sites, confirming the importance of co-occurrence (see next section). The median value of the range of maximum historical 1,4-dioxane concentrations at sites with 1,4-dioxane plume length estimates was 365 µg/L (10th percentile = 9 µg/L; 90th percentile = 13,460 µg/L). Again, this value is multiple orders of magnitude higher than the drinking water reference concentration of 0.35 µg/L for 1,4-dioxane issued by the USEPA for UCMR3 purposes. The median 1,4-dioxane plume length was 275 m (the full distribution of plume length estimates is shown in **Figure 9**).

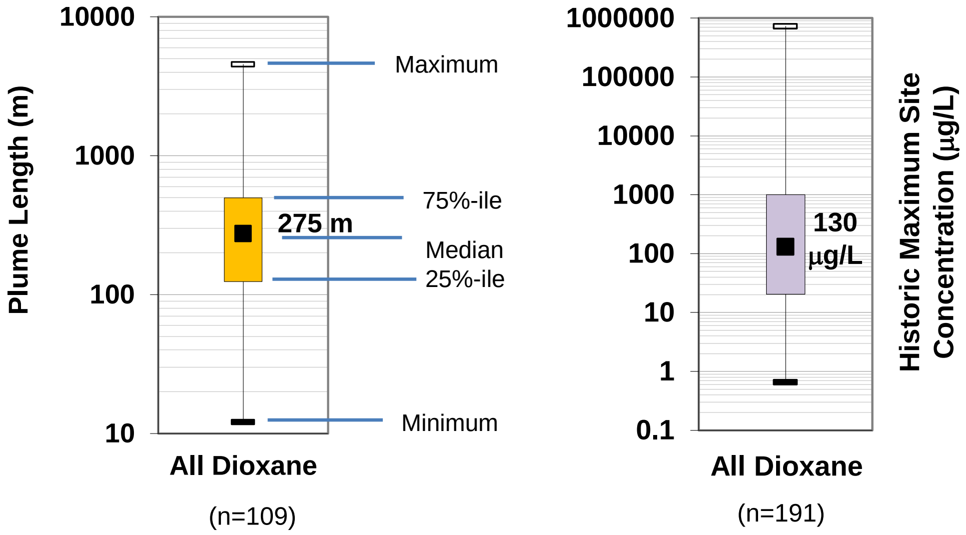


Figure 9. Distribution of Maximum Historic Concentration and Plume Length Estimates for 1,4-Dioxane. Median value is shown in bold text.

Table 12 displays the plume characteristics of 1,4-dioxane relative to various metrics that can be used to evaluate the incidence of large, dilute plume formation. These types of sites pose significant problems for stakeholders because of the cost and technical challenges associated with remediating large areas where dilute concentrations reduce the efficiency of mass removal processes. Informal definitions refer to plumes of relatively low concentration with lengths that extend for kilometers or miles (FRTR, 2013). This was used to develop the criteria shown in **Table 12**. For comparison purposes, **Table 12** also displays the same plume characteristics for TCE, which is the most prevalent chlorinated solvent at sites in the database (detected at 2322 sites). The results indicate that only 7% of the 1,4-dioxane plumes were classifiable as large and dilute. The large majority of plumes were relatively dilute, but only 11% were longer than 1 km. Overall, the percentages of 1,4-dioxane sites meeting each of the individual criteria in **Table 12** were similar to those for TCE, despite chemical properties that encourage migration of 1,4-dioxane relative to TCE.

Table 12. Comparison Between 1,4-dioxane and TCE Sites Relative to Typical Large, Dilute Plume Characteristics

	Constituent	
	Dioxane (n=109)	**TCE (n=1208)**
% Plumes > 1 km	11%	8%
% of Plumes with majority of detections < 100 μg/L	86%	91%
% of Plumes with majority of detections < 50 μg/L	72%	84%
% of Plumes > 1 km and majority of detections < 50 μg/L	7%	6%

A comparison of the distributions of historic maximum site concentrations and plume lengths for 1,4-dioxane and several different chlorinated solvents are presented in **Figure 10**. When the entire set of sites are considered (i.e., without regard to co-occurrence), the results indicate that a typical 1,4-dioxane plume is longer than a typical chlorinated solvent plume (**Figure 10**). The median 1,4-dioxane plume length of 275 m (n=109) was significantly larger ($p < 0.05$) than that of 1,1,1-TCA (115 m; n=208), TCE (95 m; n=1209), and 1,1-DCE (121 m; n=542) based on both parametric and non-parametric tests. As a group, the three chlorinated solvents had plume length distributions that were relatively similar, but because of the large number of sites available for evaluation, statistically significant differences were able to be established between 1,1,1-TCA, TCE, and 1,1-DCE plume lengths ($p<0.05$). The median plume lengths for the chlorinated solvents obtained during this study were smaller than those reported in Newell et al (1990) for chlorinated ethenes (median =305 m; n = 88) and chlorinated ethanes (median = 152 m; n = 29).

Of the 109 sites where a 1,4-dioxane plume estimate was generated, 26 of these plumes (24%) were considered indeterminate in length. For 1,1,1-TCA, TCE, and 1,1-DCE, the percentage of plumes that fell into this category was 13%, 33%, and 22%, respectively. Given the large number of chlorinated solvents sites included in this analysis, the range for chlorinated solvents is likely representative and useful as a basis of comparison for other less-investigated compounds. The data indicate that, on a site-by-site basis, the adequacy of 1,4-dioxane plume delineation is similar to chlorinated solvents. This means that at a site where 1,4-dioxane has already been identified, there is little indication that the 1,4-dioxane plume has yet to be delineated.

The maximum historical site concentrations for 1,4-dioxane relative to six different chlorinated solvents are also shown in **Figure 10**. Note that these concentration distributions include all sites where one or more of these compounds were detected, regardless of whether the plume length could be estimated (i.e, includes a larger number of sites). When comparing the concentration distributions, the 1,4-dioxane concentrations are higher than those for each of these compounds ($p<0.05$ based on both parametric and non-parametric tests). This demonstrates that most chlorinated solvent sites are characterized by low source strength and that few have concentrations that are greater than conventional operational definitions of DNAPL sites (i.e., > 1% – 10% of solubility). A closer look at concentration relationships between co-occurring 1,4-dioxane and chlorinated solvents is provided in the next section.

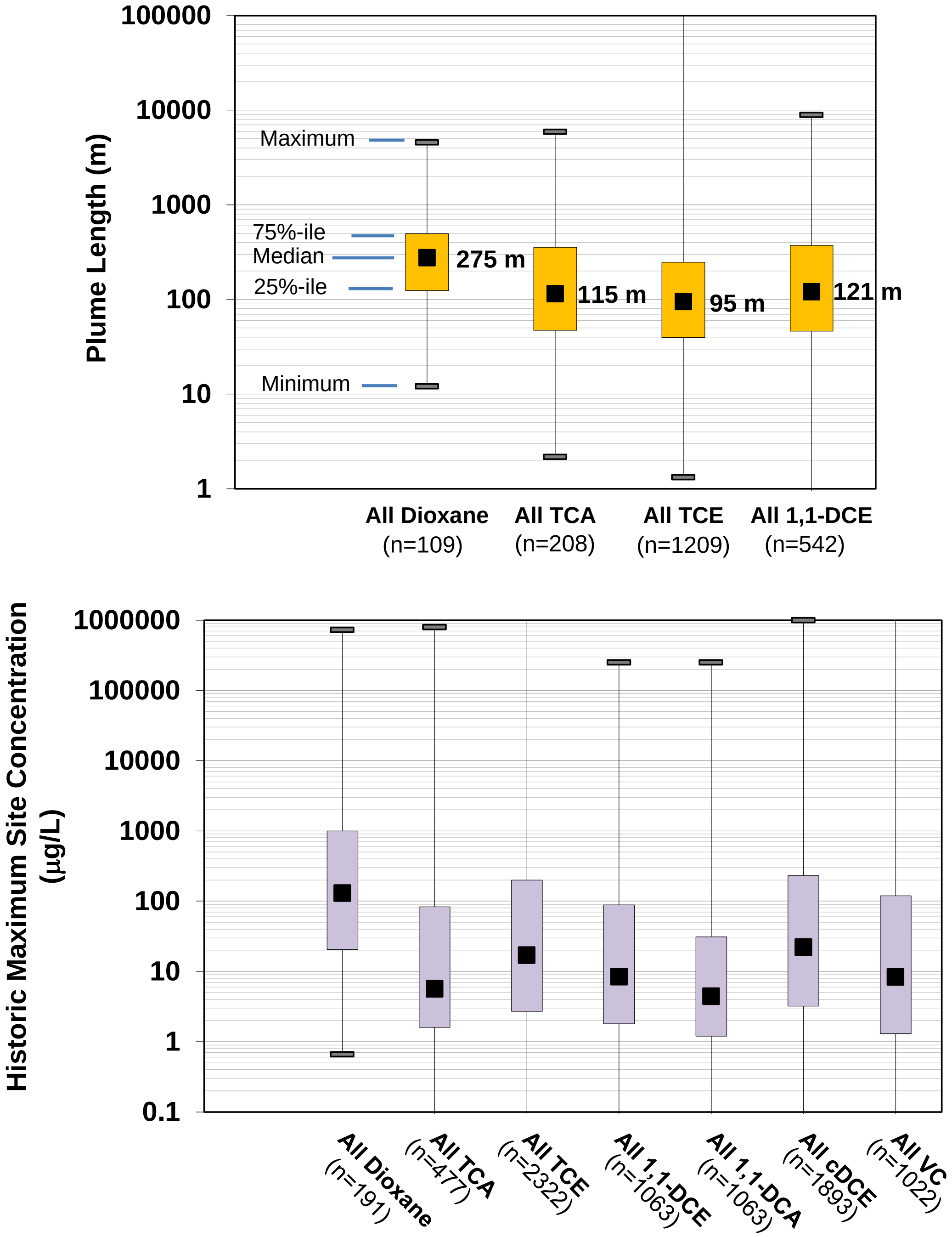


Figure 10. Distribution of Plume Length Estimates and Maximum Hstorical Site Concentrations for 1,4-Dioxane and Several Chlorinated Solvents. Includes all sites where each compound has been detected without regard to co-occurrence.

4.1.2 Characteristics of Co-Occurring Plumes

The probability that 1,4-dioxane will co-occur with chlorinated solvents is an important consideration in developing an accurate conceptual site model and selecting an appropriate long-term management strategy. If a release of 1,4-dioxane is associated with TCA, for which it served as a widespread stabilizer (Mohr et al., 2010; ATSDR, 2012), then the relatively high solubility and low sorption of 1,4-dioxane could presumably lead to longer 1,4-dioxane plumes than co-occurring chlorinated solvent plumes. Typical concentrations of 1,4-dioxane in TCA formulations have been reported as 3 to 5% by volume (Mohr et al., 2010, Anderson et al., 2012), but the concentration released to subsurface would likely be higher due to preferential stripping of TCA during vapor degreasing. Furthermore, the concentration encountered in groundwater would be strongly influenced by attenuation, particularly given the presumed recalcitrance of 1,4-dioxane. At many sites where TCA was used, TCE may have also been used as a solvent during earlier periods (i.e., prior to the widespread shift to TCA in the early 1970s) or later periods (i.e., after TCA usage began to decline in the late 1980s and 1990s). Finally, by-products of TCA and PCE/TCE may also be present at these sites as a result of various attenuation processes. For example, TCA is subject to abiotic hydrolysis which results in the formation of 1,1-DCE and acetate. The co-occurring chlorinated solvents have a range of chemical characteristics that can contribute to different behaviors in the subsurface, especially when combined with release histories.

Anderson et al. (2012) presented results from a study where nearly 6,000 wells (from 49 installations) with 1,4-dioxane analyses were evaluated. Of those wells where 1,4-dioxane was present above reporting limits (approximately 18%), nearly all (94%) also contained TCA and/or TCE. The study confirmed that the majority of 1,4-dioxane detection occurred in samples where TCE was present but TCA was absent, and a strong relationship between the concentration of 1,4-dioxane and TCE was confirmed.

One of the goals of the current project was to expand on these earlier findings using a larger dataset, including an evaluation of the frequency of co-occurrence of additional by-products of the typical chlorinated solvents as well as plume length estimates. As a first step, aggregated data for all sites was used to determine the frequency that each compound was detected in individual samples. The results are summarized in **Table 13**, which is organized similarly to a table presented in Anderson et al. (2012). The primary differences are the size of the dataset (approximately 43,000 samples relative to the approximately 6000 samples reported in Anderson et al., 2012) and the inclusion of 1,1-DCE as a potential by-product of TCA (and to a lesser extent TCE). Odds ratios (OR) were calculated using aggregated data and confirmed statistically significant associations ($p<0.05$) between 1,4-dioxane and TCE (OR=6.3), 1,4-dioxane and TCA (OR=10.0), and 1,4-dioxane and 1,1-DCE (10.3). For samples where 1,4-dioxane was detected, the high OR between TCA and TCE detections (4.84) suggested a significant nonrandom association between TCA and TCE.

Table 13. Frequency of 1,4-dioxane Co-Occurrence with TCE, TCA, and 1,1-DCE in All Sample Records

			Dioxane			
TCE	**TCA**	**1,1-DCE**	**# Analyzed**	**Non-detect**	**Detect**	**% Detect**
Non-detect	Non-detect	Non-detect	21,336	18,060	3276	15%
Non-detect	Non-detect	Detect	1443	595	848	59%
Non-detect	Detect	Detect	320	56	264	83%
Non-detect	Detect	Non-detect	104	50	54	52%
Detect	Detect	Detect	3756	552	3204	85%
Detect	Detect	Non-detect	168	74	94	56%
Detect	Non-detect	Non-detect	7439	4808	2631	35%
Detect	Non-detect	Detect	8877	2677	6200	70%
		Total	43,443	26,872	16,571	38%

There are several key findings based on the co-occurrence data presented in **Table 13**:

- Dioxane was present in the majority of samples where one or more chlorinated solvents were present, with the highest 1,4-dioxane detection rate (85%) in samples where all three chlorinated solvents were detected. In samples where TCE was the only one of these three chlorinated solvents that was detected, 1,4-dioxane was present in 35%, while 1,4-dioxane was present in 52% of samples where TCA was the only solvent detected. This lower percentage is consistent with the assumption that 1,4-dioxane was not used as a stabilizer for TCE, though this is a subject of continuing debate (Anderson et al., 2012).
- Dioxane was detected in only 15% of samples where all three chlorinated solvents were not detected, but these detections represented 20% of all 1,4-dioxane detections. Both of these are higher than the percentages reported by Anderson et al. (2012), where 3% of samples with non-detectable levels of TCE and TCA contained 1,4-dioxane (representing 6% of all 1,4-dioxane detections).
- The number of samples where TCA and 1,4-dioxane were both detected (3616) was smaller than the number of samples where TCA was absent but 1,4-dioxane and TCE and/or 1,1-DCE were present (9679). The latter group represented 58% of all 1,4-dioxane detections, a rate that is similar to that reported by Anderson et al. (2012) for 1,4-dioxane detections independently associated with TCE (64%). This confirms that the lack of TCA is not a suitable line of evidence that 1,4-dioxane will not be present.
- Similarly, 1,4-dioxane was detected in a significant number of samples (848; detection rate of 59%) where 1,1-DCE was present but TCE and TCA were not. Consequently, the absence of TCA and TCE does not rule out the presence of 1,4-dioxane because these compounds may have been transformed preferentially to 1,4-dioxane. Instead, the presence of 1,1-DCE (as a product of TCA hydrolysis) should also be used as an indicator that 1,4-dioxane may be present.
- As a further confirmation that 1,1-DCE is a more reliable indicator than TCA, only 4% of samples with TCA contained no 1,1-DCE, while 72% of samples with 1,1-DCE contained no TCA.

- There are very few samples where TCA is detected in the absence of TCE (10%), suggesting that TCA was also used at some point at most sites where TCE was used.

In addition to documenting the frequency of co-occurrence on a sample-by-sample basis, the data were organized by site. This had the added advantage of documenting sites where 1,4-dioxane has not been part of the historical analytical program but would be suspected to be present based on detections of one or more chlorinated solvents.

Figure 11 illustrates that 1,4-dioxane has been monitored at a high percentage of sites where samples (to-date) have not contained 1,4-dioxane above reporting limits. This argues a significant level of precaution has been incorporated into site-specific decisions about analytical program. However, as discussed below, it is clear that the total number of sites where 1,4-dioxane has been analyzed is significantly lower than for chlorinated solvents. On a site basis, TCE is the most frequently detected co-occurring contaminant with 1,4-dioxane (93%), followed by 1,1-DCE (86%) and TCA (58%). These data are consistent with those presented on a sample-by-sample basis in **Table 13**.

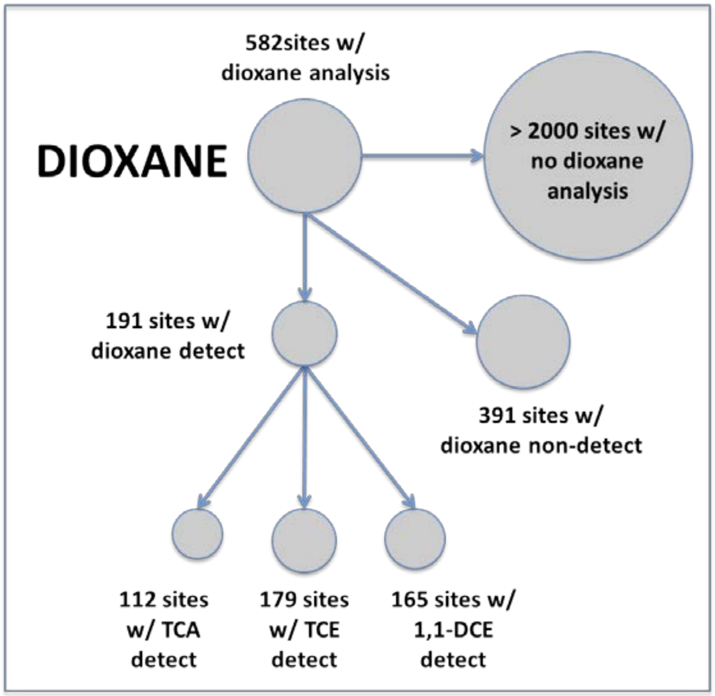


Figure 11. Frequency of 1,4-Dioxane Detections on a Site-by-Site Basis. For each category, the area of the circle is proportional to the number of sites in that category.

The number of sites with detections of TCE, TCA, and 1,1-DCE are presented in **Figure 12**, along with a breakdown of these sites to show where : i) 1,4-dioxane was detected; ii) 1,4-dioxane was not detected (i.e., analyzed but below reporting limits); iii) 1,4-dioxane was not analyzed. A similar breakdown for cDCE, 1,1-DCA, and VC are shown in **Figure 13**.

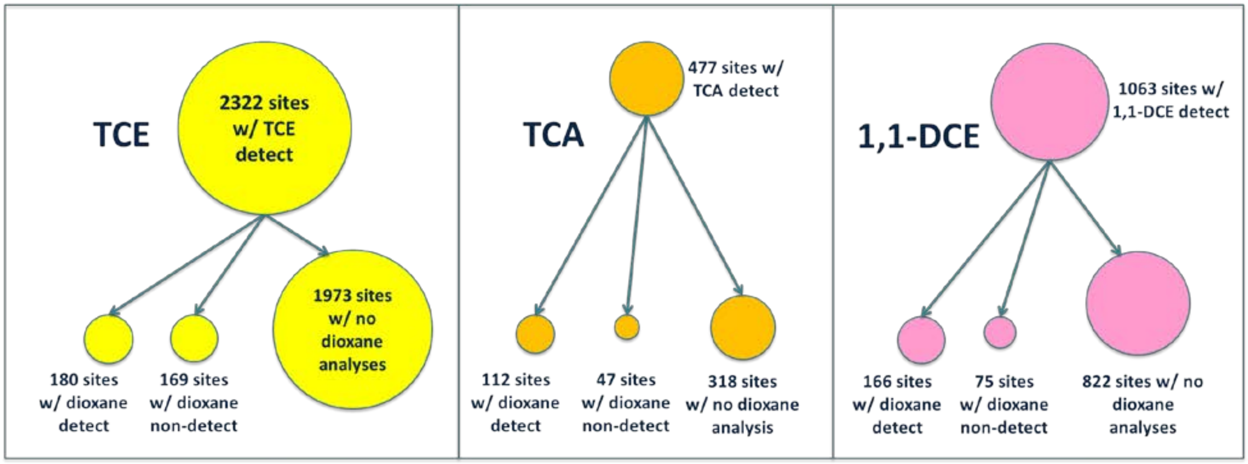


Figure 12. Frequency of 1,4-Dioxane Detections on a Site-by-Site Basis with TCE, TCA, and 1,1-DCE. For each category, the area of the circle is proportional to the number of sites in that category.

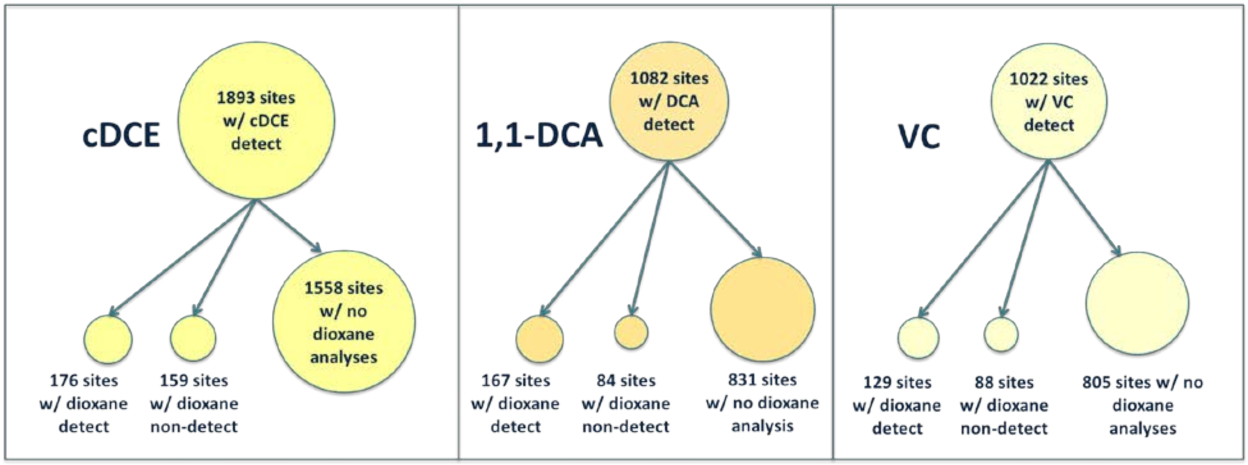


Figure 13. Frequency of 1,4-Dioxane Detections on a Site-by-Site Basis with cDCE, 1,1-DCA, and VC. For each category, the area of the circle is proportional to the number of sites in that category.

Key findings based on the site-by-site co-occurrence data shown in **Figure 12** and **Figure 13** include the following:

- On a site-by-site basis, the frequency that 1,4-dioxane co-occurs with TCE (52%), TCA (70%), and 1,1-DCE (69%) is similar to the frequencies observed using all sample records (**Table 13**; TCE = 60%, TCA = 83%; 1,1-DCE = 73%).
- As expected based on the degradation pathways, the frequency that 1,4-dioxane co-occurs with 1,1-DCA (64%) is similar to TCA and 1,1-DCE, while the frequency that 1,4-dioxane co-occurs with cDCE (53%) and VC (59%) is similar to TCE.
- For all chlorinated solvents, the percentage of sites where 1,4-dioxane has not been analyzed is large, ranging from 67% to 85% for this set of constituents. While there may be a technical justification for this at a site with TCE, it is clearly an oversight at sites where one or more of the remaining compounds have been detected.
- Dioxane has not been analyzed at 318 sites where TCA has been detected. At sites where 1,4-dioxane analysis was part of the monitoring program, 70% of the sites with 1,1,1-TCA detections contained detectable levels of 1,4-dioxane. While not all 1,1,1-TCA formulations contained 1,4-dioxane, the frequency of 1,4-dioxane detections at sites and/or monitoring wells where 1,1,1-TCA has been detected suggests that 1,4-dioxane was a constituent of the majority of 1,1,1-TCA releases. If the value from the current study (70%) is extrapolated to the 318 sites where 1,1,1-TCA has been detected but 1,4-dioxane has not been analyzed, then this would represent an additional 222 sites with 1,4-dioxane-impacted groundwater. The finding that this number is greater than the number of sites where 1,4-dioxane was definitively identified (191) is evidence of the scale of the problem.
- The 1,1-DCE and 1,1-DCA data provide further evidence of additional unrecognized 1,4-dioxane-impacted sites (**Figure 14**). Of the 61 sites where 1,1-DCE was detected but 1,1,1-TCA and TCE were not detected, 59 (or 97%) had no analyses for 1,4-dioxane. Similarly, there were 572 sites with 1,1-DCA but non-detectable levels of TCA where no 1,4-dioxane analyses had been completed. These are problematic numbers given that 1,4-dioxane was detected at 69% of the sites where 1,1-DCE was detected and 1,4-dioxane was analyzed, as well as 64% of the sites where 1,1-DCA was detected and 1,4-dioxane was analyzed. If these percentages are applied to the sites without 1,4-dioxane analyses, the result is an additional 366 1,1-DCA sites and 41 1,1-DCE sites where 1,4-dioxane-impacted groundwater would be suspected.
- 1,1-DCA is a reductive dechlorination product of TCA, while 1,1-DCE is a frequent hydrolysis product of 1,1,1-TCA (as well as a potential intermediate during reductive dechlorination of chlorinated ethenes) (Vogel and McCarty, 1987; Freedman and Gossett, 1989). Therefore, the absence of 1,1,1-TCA and TCE should not be considered proof-positive that 1,4-dioxane will also be absent; the presence of 1,1-DCE and 1,1-DCA as surrogates should also be evaluated.

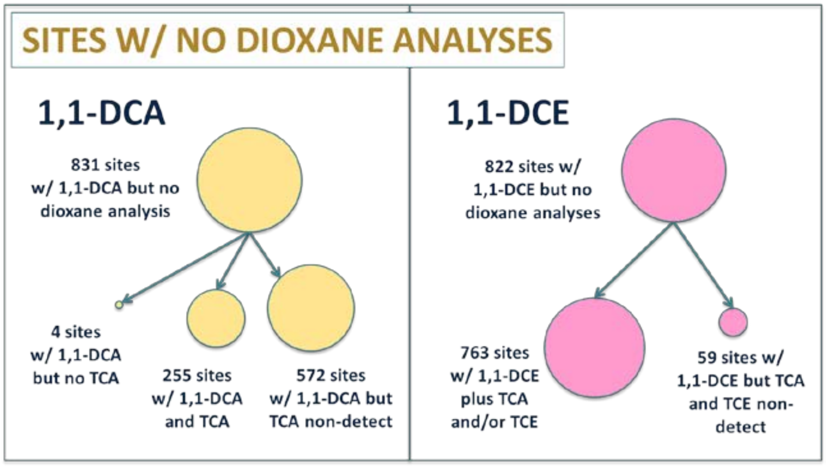


Figure 14. Evidence of Unrecognized 1,4-Dioxane at Sites with 1,1-DCA and 1,1-DCE. For each category, the area of the circle is proportional to the number of sites in that category.

As a second step to evaluate co-occurrence of 1,4-dioxane and chlorinated solvents, scatter plots of the concentration of 1,4-dioxane vs. the concentration of individual chlorinated solvents were generated using data from each discrete sampling record (**Figure 15**). Only those wells where both constituent were above reporting limits were included. Linear regression was used to screen these concentration relationships for significance, with the understanding that the data (even log-transformed) were not necessarily normally distributed. Non-parametric tests were not attempted due to the large number of data points. However, the size of the dataset also resulted in very low p-values following regression, such that further sorting of the data was not attempted.

Using linear regression, a statistically significant relationship ($p<0.05$) was established between 1,4-dioxane and each of the six chlorinated solvents. The strongest predictive relationships and least variability were established for 1,1-DCE, TCA, and 1,1-DCA. The R^2 values were similar for the regression lines for 1,4-dioxane and each of these 3 compounds (0.32 - 0.37). Lower R^2 values were obtained for regressions with TCE, cDCE, and VC (0.07-0.10). This pattern is not surprising given that 1,4-dioxane was present in many TCA formulations but was presumably not used in TCE solvent formulations. The slopes of the regression lines for 1,1-DCE, TCA, and 1,1-DCA were uniformly higher than those for TCE, cDCE, and VC, suggesting a stronger concentration relationship with 1,4-dioxane. However, it should be noted that the slope of all regression lines were less than one while the y-intercepts for all regression lines were significantly higher than one. This is indicative of a high chlorinated solvent-to-dioxane ratio at high chlorinated solvent concentrations, and a low chlorinated solvent-to-dioxane ratio at low chlorinated solvent concentrations. The pattern suggests that as attenuation proceeds (i.e., moving from the upper right of each scatter plot to the lower left), 1,4-dioxane is more persistent than each of the co-occurring chlorinated solvents.

This pattern can also be used as a line of evidence for evaluating attenuation of a parent compound and its degradation by-products, as shown in **Figure 16a** using TCA as an example. For both 1,1-DCE and 1,1-DCA, strong relationships with TCA were observed, but the significant y-intercept values are associated with the persistence of these by-products relative to TCA. This is reflected in the increased variability (spread) in the by-product concentration(s) as TCA attenuation proceeds.

The potential impact of 1,4-dioxane on the observed concentration relationships for chlorinated solvents and their by-products was evaluated for TCA/1,1-DCA and TCE/cDCE (**Figure 16b**). The distribution of TCA and 1,1-DCA data appears to be little impacted by the presence of 1,4-dioxane, with the exception that a narrower concentration range for 1,1-DCA was generally observed in samples with 1,4-dioxane. For TCE, samples with 1,4-dioxane exhibited a similar trend but fell into a narrow concentration range for both TCE and cDCE. This is consistent with 1,4-dioxane's absence as a stabilizer in TCE, in that 1,4-dioxane is not detected in samples with high TCE concentrations that would more likely be associated with DNAPL or newer releases. For both TCA and TCE, the data suggest that 1,4-dioxane exhibits a slight negative impact on chlorinated solvent attenuation.

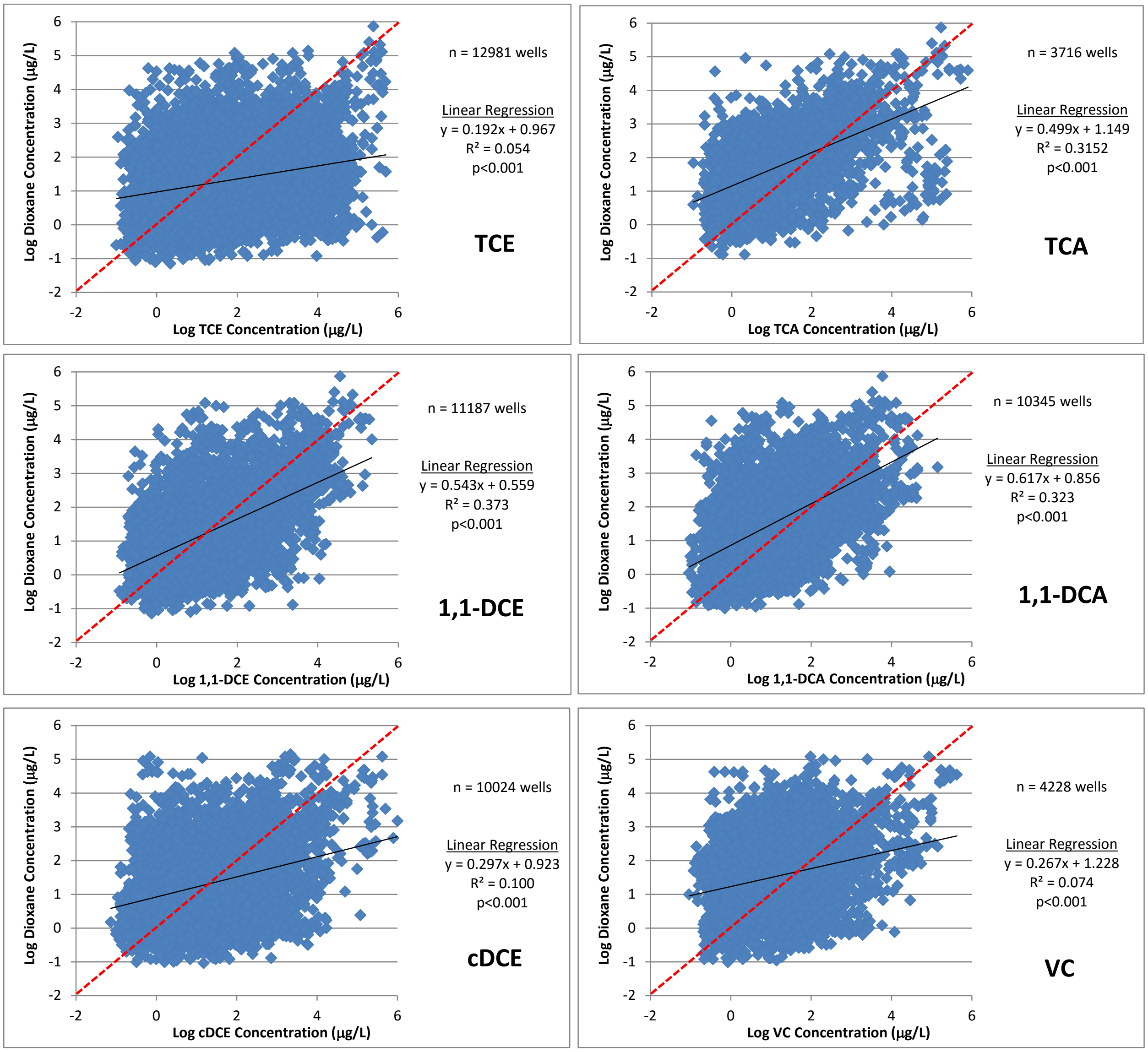


Figure 15. Concentration Relationships Between 1,4-Dioxane and Co-Occurring Chlorinated Solvents. Each plot shows all records from all wells where both constituents were detected. Black line is the best fit from linear regression. Red line is 1:1 relationship.

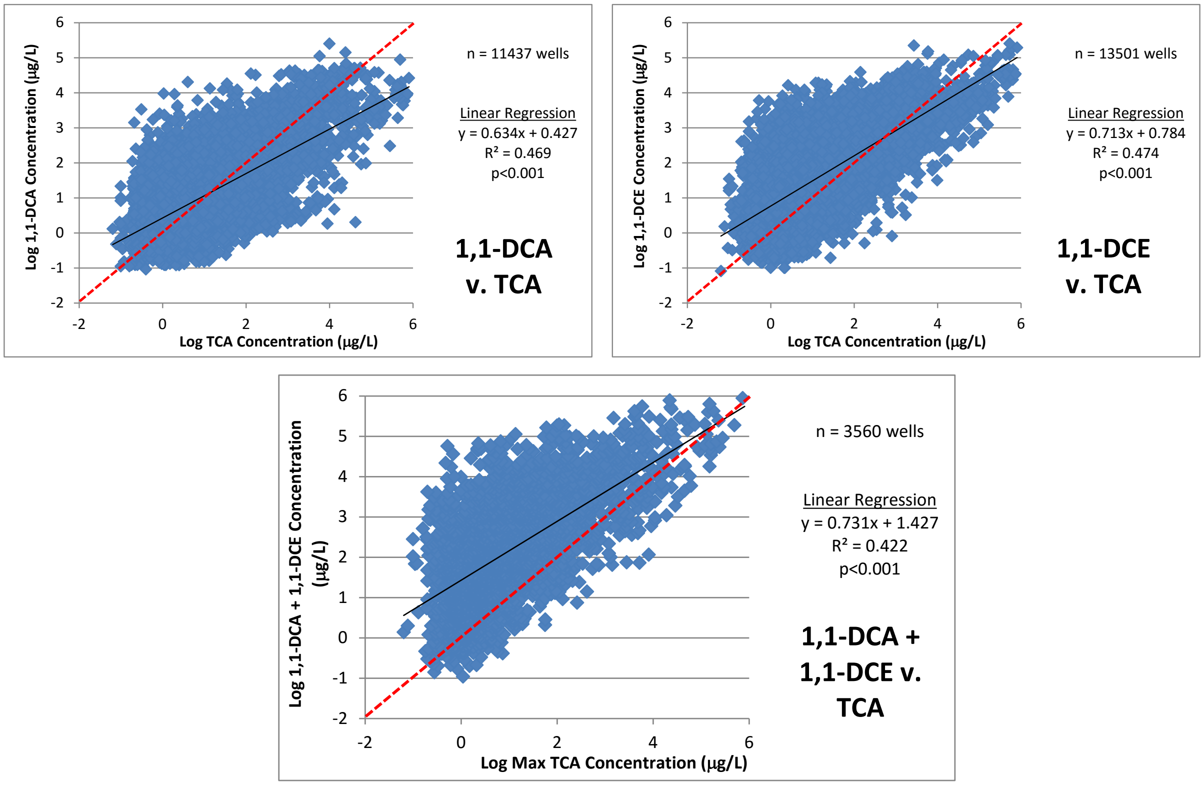


Figure 16a. Concentration Relationships Between TCA and Its Degradation By-Products. The top two plots show all records from all wells where both constituents were detected. The bottom plot shows maximum TCA concentration record from all wells where 1,1-DCA and/or 1,1-DCE were detected. Black line is the best fit from linear regression. Red line is 1:1 relationship.

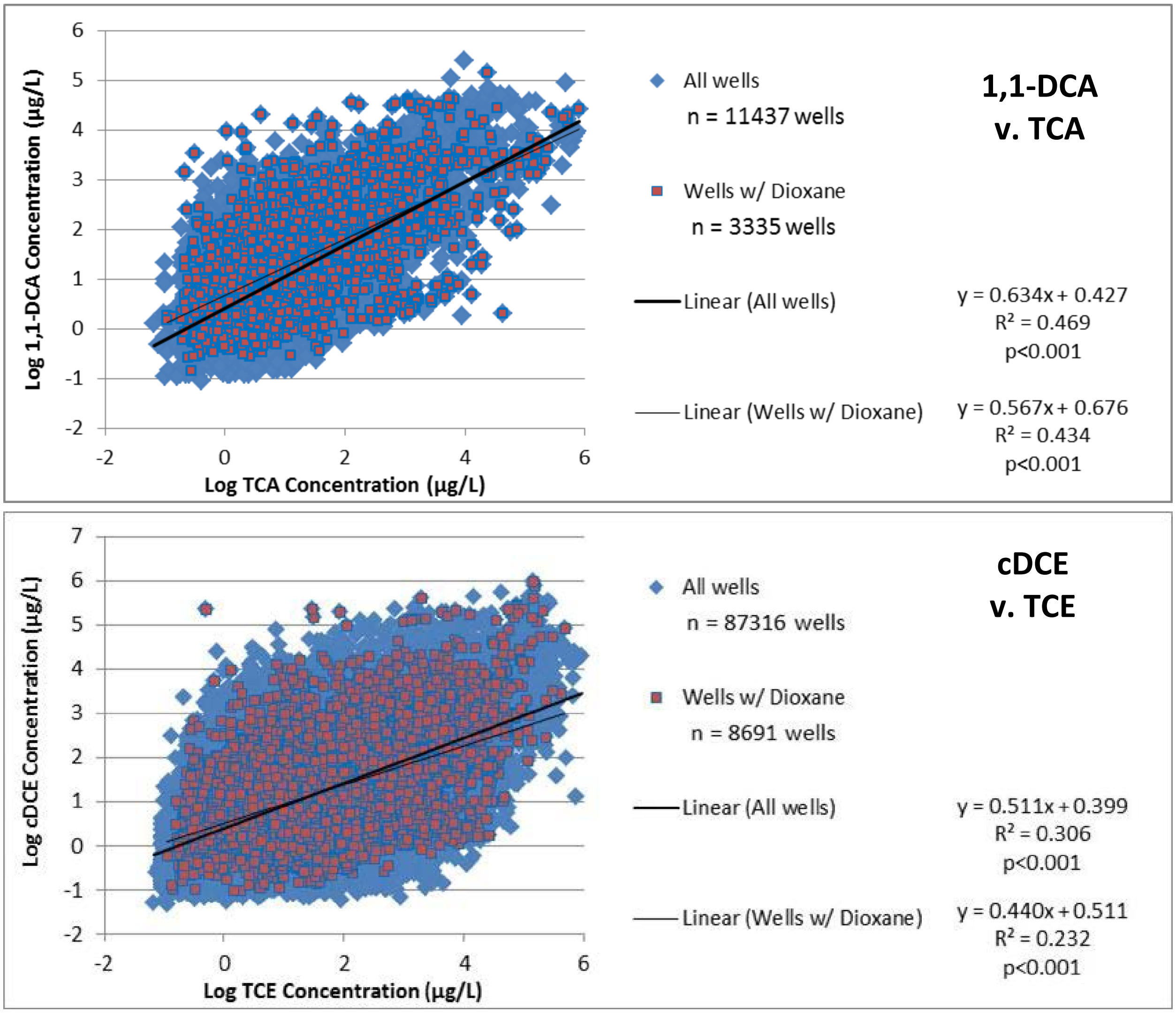


Figure 16b. Concentration Relationships Between TCA and 1,1-DCA (top panel) and TCE and cDCE (bottom panel) in the Presence of 1,4-dioxane. Each plot shows all records from all wells where both constituents were detected. Black lines are the best fits from linear regression.

Finally, the issue was co-occurrence was evaluated by estimating plume lengths for sites where chlorinated solvents were present with 1,4-dioxane.

As shown in **Figure 10**, the plume length distributions generated for 1,4-dioxane and several different chlorinated solvents indicated that 1,4-dioxane plumes are longer when the entire set of sites was considered. However, a comparison of the plume lengths at sites where 1,4-dioxane and chlorinated solvents are co-occurring provides a more direct and meaningful test of the prevailing conceptual model. Of the 109 sites where a 1,4-dioxane plume length could be estimated, 105 sites contained detectable levels of one or more chlorinated solvent. For this subset, the 1,4-dioxane plume was longer than the corresponding chlorinated solvent plume(s) at only 21% of the sites (**Figure 17**). At 56% of the sites where both compound classes were detected, the chlorinated solvent plume was longer.

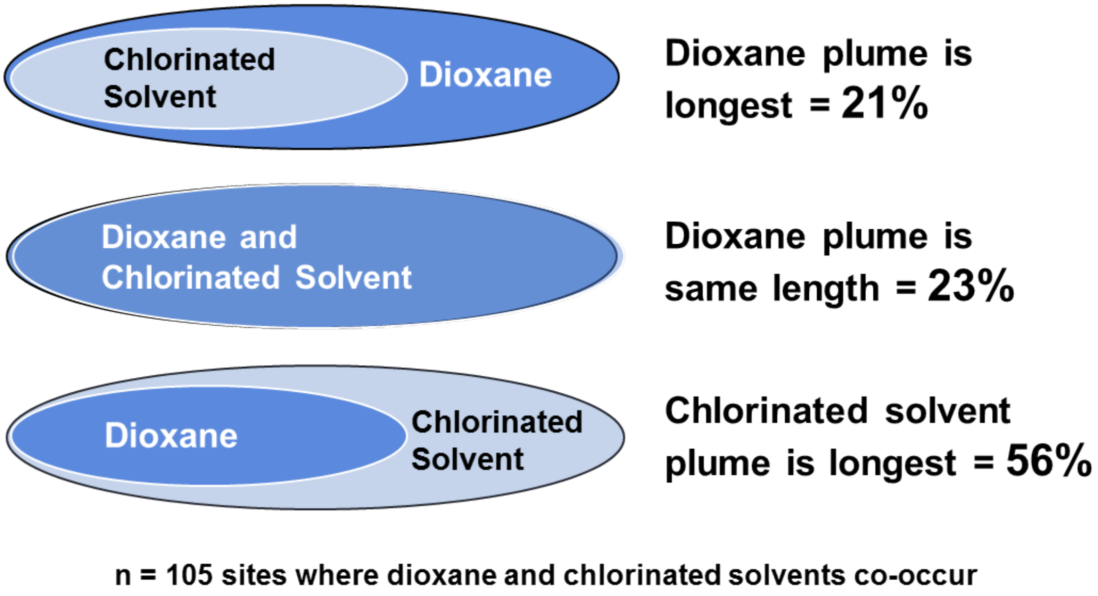


Figure 17. Frequency of 1,4-Dioxane Plume Lengths Exceeding Chlorinated Solvent Plume Lengths at Sites with Co-Occurring Compounds.

Plume length estimates were aggregated by compound for the 62 sites where 1,4-dioxane is present with 1,1,1-TCA, TCE, and 1,1-DCE (**Figure 18**). The resulting plume length distributions for the four compounds appear much more similar than when the data were not filtered using co-occurrence (**Figure 10**), with median plume lengths that fell between 319 m and 439 m. For this set of sites, 1,4-dioxane plume lengths were determined to be shorter than those for TCE and longer than those for 1,1,1-TCA ($p<0.05$) (**Table 14**). No statistically significant difference could be established between 1,4-dioxane and 1,1-DCE plume lengths ($p=0.09$).

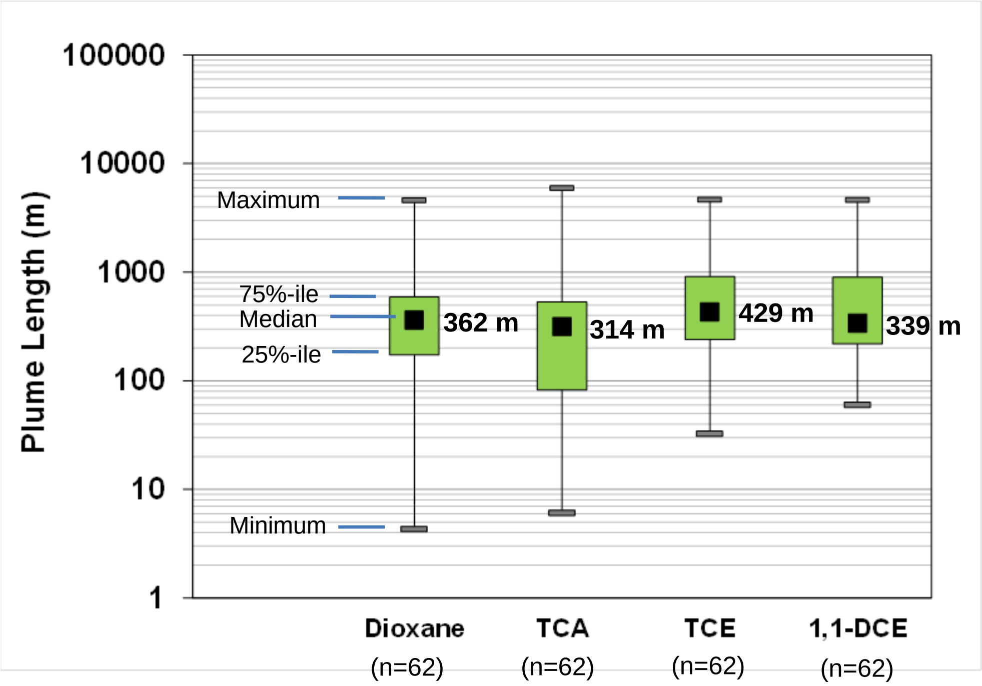


Figure 18. Distribution of Plume Length Estimates for 1,4-Dioxane, TCA, TCE, and 1,1-DCE at Sites Where All Four Compounds are Detected.

Table 14. Statistical Evaluation of Differences Between Plume Length Estimates for 1,4-dioxane, TCA, TCE, and 1,1-DCE at Sites where all Four Compounds are Detected.

	Dioxane		**TCA**		**TCE**		**1,1-DCE**	
	p-value		**p-value**		**p-value**		**p-value**	
	t-test	**WSR**	**t-test**	**WSR**	**t-test**	**WSR**	**t-test**	**WSR**
Dioxane	--	--	0.79	**0.002**	**0.002**	**0.001**	0.09	0.10
TCA	0.79	**0.002**	--	--	**0.03**	**<0.0001**	**0.0008**	**<0.0001**
TCE	**0.002**	**0.001**	**0.03**	**<0.0001**	--	--	0.49	**0.001**
1,1-DCE	0.09	0.10	**0.0008**	**<0.0001**	0.49	**0.001**	--	--

Notes: (1) Bold values indicate statistically-significant differences between plume length distributions between pair of compounds ($p<0.05$).

The comparisons between sites where 1,4-dioxane is detected along with chlorinated solvents provide a more representative picture of the behavior of co-occurring contaminants. At these sites, releases to the subsurface are expected to have occurred from the same point or points. Biases resulting from differences between subsurface hydrogeological characteristics are thus minimized because each contaminant follows similar flowpaths after being released. Consequently, each compound would be subject to similar geochemical environments and other factors impacting fate and transport (e.g., reactive mineral species, organic carbon). The relative similarity between the plume lengths for the various compound types suggests that transport-related factors, such as advection, may be more important than factors associated with plume attenuation. A confounding factor is the solvent usage history at this set of sites, with TCE usage likely predating 1,1,1-TCA usage, although a switch back to TCE may have occurred at some sites (Mohr et al., 2010; Anderson et al., 2012). Only 1,1,1-TCA was likely to contain 1,4-dioxane (Mohr et al., 2010). The finding that TCE plumes are slightly but statistically-significantly longer than 1,4-dioxane ($p<0.05$) and much longer than 1,1,1-TCA plumes ($p<0.05$) is consistent with the presumed timing of solvent usage. As of this date, there is no evidence that the 1,4-dioxane plumes have "caught up" to the TCE plumes. Collectively, these plume length data demonstrate that the spatial scale of 1,4-dioxane plumes is relatively similar to that of chlorinated solvents at sites where both compound types were released.

The results also show that the estimated chlorinated solvent plume lengths increased when 1,4-dioxane was present (**Figure 19**). Statistically significant differences ($p<0.05$ using Wilcoxon Rank Sum test) were observed for both TCA plume lengths and TCE plume lengths when 1,4-dioxane was present. In addition, statistically significant increases in TCA plumes were observed when TCE and 1,1-DCE were present, as well as increases in TCE plumes when TCA and 1,1-DCE plumes were present. The increase in chlorinated solvent plume lengths in the presence of other chlorinated solvents is consistent with the known inhibitory nature of compounds like TCA towards reductive dechlorination of chlorinated ethenes (Adamson et al., 2000, Grostern and Edwards, 2006; Chan et al., 2011). The potential impact of 1,4-dioxane on chlorinated solvent degradation is not well documented in the literature, but there is evidence of competitive inhibition between 1,4-dioxane, TCA, and 1,1-DCE during the cometabolic degradation of these compounds by *Pseudonomas mendocina KR1* and toluene monooxygenase-expressing *E. coli* (Mahendra et al., 2013). However, it is likely that factors unrelated to natural attenuation processes are also influencing the plume length distributions shown in **Figure 19**. For example, sites where only a single contaminant has been reported may have been characterized and/or managed differently than more complex sites with multiple known contaminant types. This is particularly relevant for the TCA sites; 1,4-dioxane is likely to be present at many of these sites even if it has yet to be included in the analytical programs. Consequently, it is more likely that inhibition is influencing the observed TCE plume length distributions than the TCA plume length distributions.

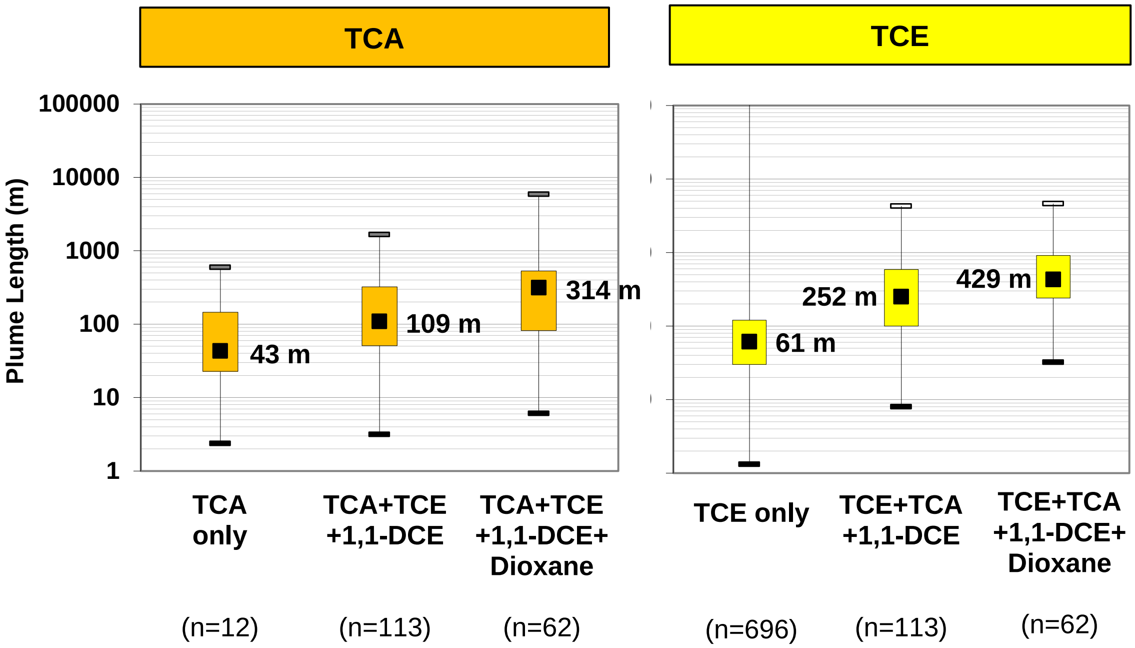


Figure 19. Distribution of Plume Length Estimates for TCA and TCE at Sites Where One or More Compounds are Detected.

4.1.3 Evidence of Attenuation – 1,4-Dioxane and Chlorinated Solvents

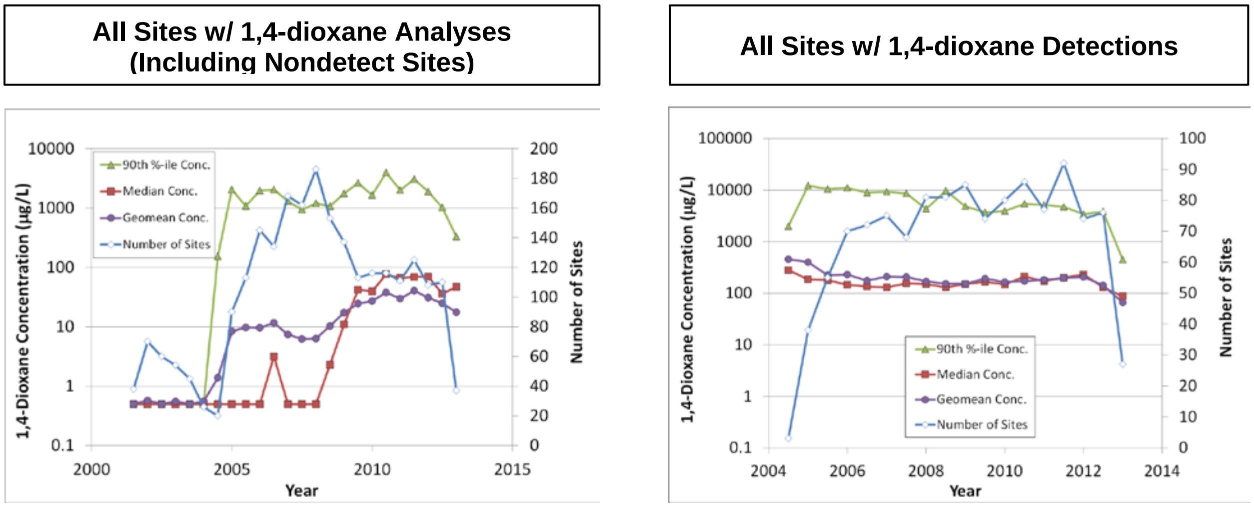
The chemical properties of 1,4-dioxane tend to make it more recalcitrant to attenuation than co-occurring chlorinated solvents. This is important in terms of how it will attenuate in the environment, as well as the potential efficacy of engineered or enhanced remedial approaches. In terms of in situ options, 1,4-dioxane is subject to chemical oxidation as long as the radical species being generated has sufficiently high oxidation potential (e.g., hydroxyl radical). Enhanced anaerobic bioremediation has proven to be a successful strategy for addressing many chlorinated solvents, but there is no indication (to date) that 1,4-dioxane is subject to degradation via anaerobic (reductive). However, there is increasing evidence that biological oxidation of 1,4-dioxane is a relevant attenuation pathway. A number of organisms that degrade 1,4-dioxane as a carbon/energy source or cometabolically have been identified. The recent development of biomarkers that can be used to assess 1,4-dioxane degradative activity is likely to be a valuable tool in documenting natural attenuation at field sites (Li et al., 2013; Gedalanga et al., 2014).

For the purposes of this project, data mining was used to investigate changes in concentration over time in the 1,4-dioxane data sets, following a lines of evidence approach: 1) aggregated concentration vs. time data for all sites; 2) comparison of historic maximum concentration vs.

recent maximum concentrations for sites/wells; and 3) estimates of attenuation rate coefficients (k_{source}) for all sites.

Line of Evidence #1 – Changes in Concentration in Aggregated Site Data. Using 6-month intervals, **Figure 20** shows several general trends in aggregated monitoring data for 1,4-dioxane, including the median and 90th percentile values in the distribution of maximum site concentrations for all sites. This is repeated for a case where only sites where 1,4-dioxane has been detected were included (right panel in **Figure 20a**). Including the non-detects in the plot illustrates that the majority of sites where 1,4-dioxane was analyzed were generally characterized by low or non-detectable levels of 1,4-dioxane up until approximately 2008. However, this shift to higher concentration sites over time also biases any assessment of attenuation. Therefore, only the data for sites where 1,4-dioxane was detected were included in the subsequent trend analysis. **Figure 20b** shows similar temporal data for sites where TCA, TCE and 1,1,-DCE were detected; only detections were plotted for these compounds because including nondetects yielded no discernible trends.

In addition, a striking trend indicated on the plot for 1,4-dioxane (all detections) is the inconsistency in number of sites monitored for each 6-month interval (blue line). The first spike can be attributed to adoption of the GeoTracker database as a medium for data storage, and the last drop to incomplete data for the first half of 2013. Similar spikes in the early 2000s and drops in 2013 can be seen in the plots for the other contaminants (**Figure 20b**). To compensate for this bias, data from the first and last monitoring period were excluded from the trend analysis for 1,4-dioxane, and only 2005—2012 data were used for analyzing the chlorinated solvent trends.



All Sites w/ 1,4-dioxane Analyses (Including Nondetect Sites)

All Sites w/ 1,4-dioxane Detections

Figure 20a. Maximum Site Concentrations vs. Time for 1,4-Dioxane.

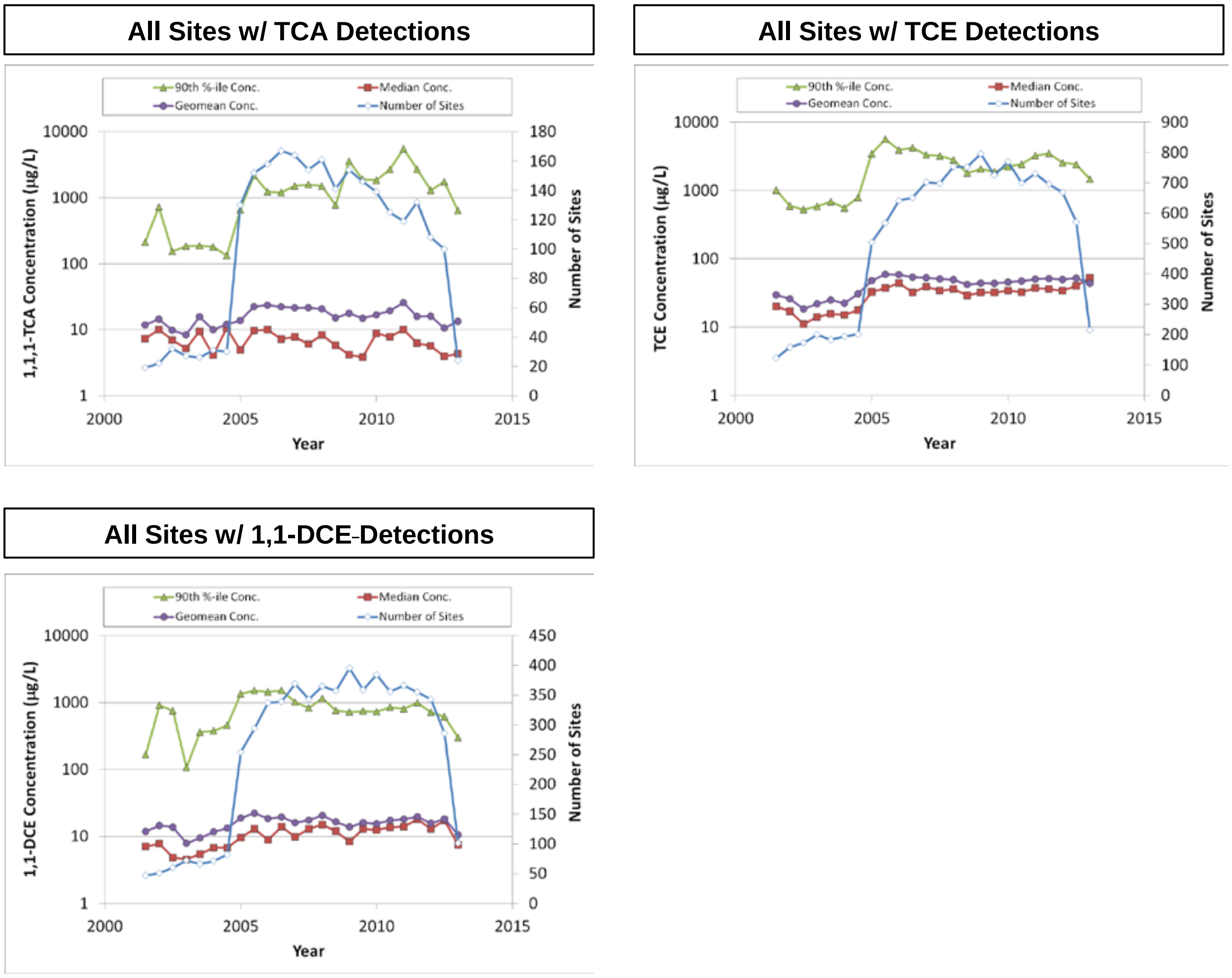


Figure 20b. Maximum Site Concentrations vs. Time for TCA, TCE, and 1,1-DCE.

Based on a Mann-Kendall analysis, 1,4-dioxane exhibited a statistically significant decreasing trend for the 90th percentile and geomean concentrations (**Table 15**). No trend could be established using the median value of all maximum 1,4-dioxane concentration for each site. These results serve as a promising line of evidence that 1,4-dioxane sources are attenuating over time. 1,4-dioxane generally exhibited the same or better trend than the chlorinated solvents that were evaluated. For example, both TCE and 1,1-DCE exhibited decreasing trends for the 90th percentile and stable trends for the geomean concentration, but either no trend (TCE) or increasing trend (1,1-DCE) for the median concentration. Mixed results were observed TCA, including an increasing trend for the 90th percentile concentration. As will be discussed in the next section, TCA is subject to relatively rapid attenuation, such that the increasing trend for the 90th percentile concentration is likely due to a shift over time in the types of sites that were included in the trend evaluation. As can be seen in **Figure 20b**, there were progressively fewer

TCA sites in GeoTracker over time, and a few complex sites (with high source concentrations that fell in the 90th percentile) may have been over-represented in the later years.

Table 15. Mann-Kendall Trend Analysis for Aggregated Maximum Site Concentration vs. Time Data for 1,4-Dioxane, TCA, TCE, and 1,1-DCE.

Compound	Data Set	Trend	Confidence Factor (1-p)
Dioxane	90th Percentile Concentration	Decreasing	>99.9%
	Geomean Concentration	Decreasing	97.9%
	Median Concentration	No Trend	77.5%
TCA	90th Percentile Concentration	Increasing	96.8%
	Geomean Concentration	Decreasing	96.8%
	Median Concentration	Stable	86.7%
TCE	90th Percentile Concentration	Decreasing	96.8%
	Geomean Concentration	Stable	82.5%
	Median Concentration	No Trend	58.8%
1,1-DCE	90th Percentile Concentration	Decreasing	99.9%
	Geomean Concentration	Stable	88.6%
	Median Concentration	Increasing	98.2%

Notes: (1) Test was run on data from 2005 – 2012 shown in Figure 20a (dioxane) and Figure 20b (TCA, TCE, 1,1-DCE); (2) Only sites with detections were included.

Line of Evidence #2 – Concentration Reductions. The reduction in concentration from historical maximum values to recent maximum values was calculated on a site-by-site basis and well-by-well basis for 1,4-dioxane and multiple chlorinated solvents. In each case, an OoM reduction was calculated for sites using two different methods which differed in how the "recent" concentration value was queried. While the results of each of these methods can be used as indicators of attenuation, it should be noted that there are primary benefits to each method.

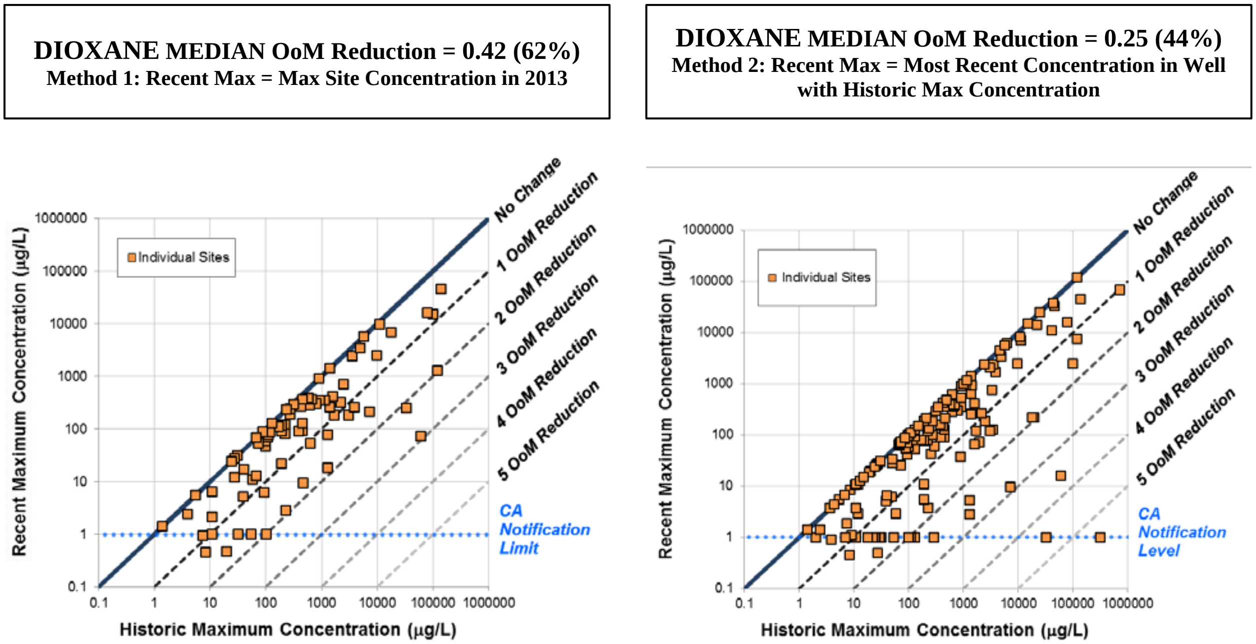
- In ***Method #1***, the recent maximum value was the maximum concentration recorded at the site in 2013. This method ensures a longer monitoring period for each individual site than Method #2.
- Because not all sites (or wells) were sampled in 2013, ***Method #2*** used the latest concentration measured in the same well where the historical maximum concentration was obtained as the "recent" value. This second method generates OoM reduction estimates for a larger number of sites than Method #1.

Both methods suggest that significant 1,4-dioxane attenuation has occurred at sites where it has been detected, with a median OoM reduction of 0.42 for Method 1 and 0.25 for Method 2 (**Figure 21**, **Table 16**). For this evaluation, the time elapsed since the historic maximum 1,4-dioxane concentration was recorded was generally very short (median value = 2.0 years for Method 1; median value = 1.0 years for Method 2). These durations are considerably shorter than the total monitoring periods (median value = 6.8 years for Method 1; median value = 5.0 years for Method 2). These differences have several implications: 1) during the early stages of monitoring, sites were not adequately identifying or assessing the areas of high 1,4-dioxane concentration; such that 2) the OoM reductions for 1,4-dioxane (**Table 16**) are conservative.

The median OoM reduction values for 1,4-dioxane were comparable to the OoM reductions for TCE, 1,1-DCE, and 1,1-DCA when all sites were considered, although the differences were not statistically significant in all cases. The OoM reductions for TCA were larger than those for 1,4-dioxane (with a statistically-significant difference using both methods for calculating the OoM reduction). These results indicate that 1,4-dioxane is attenuating to a similar extent as those chlorinated solvents that typically co-occur with 1,4-dioxane, with the exception of TCA.

OoM reductions were also calculated for those sites where chlorinated solvents and 1,4-dioxane were present (i.e., sites where 1,4-dioxane has yet to be analyzed were omitted). Again, there were no significant differences between 1,4-dioxane OoM reductions and OoM reductions for TCE, 1,1-DCE, and 1,1-DCA. TCA OoM reductions were significantly greater than 1,4-dioxane. These findings support the hypothesis that 1,4-dioxane is less prone to attenuate than TCA, but they also provide evidence that 1,4-dioxane attenuation should be comparable to that observed for degradation products of TCA (1,1-DCE and 1,1-DCA) and other parent compounds (TCE).

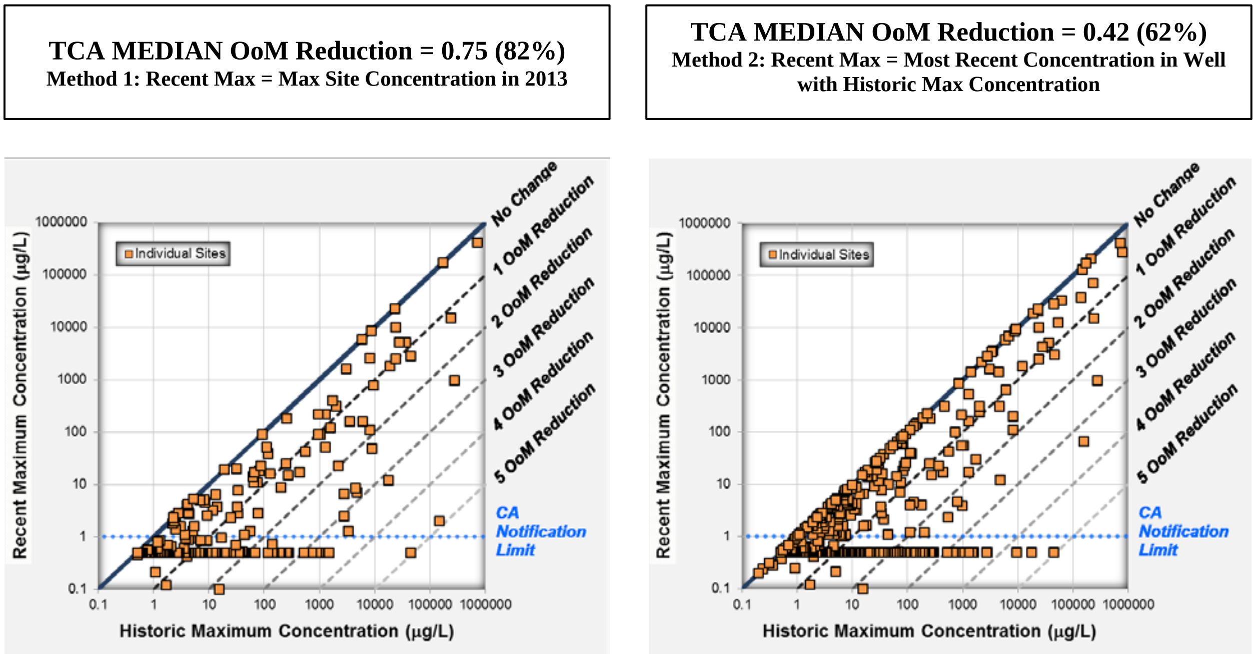
The triangle plots shown in **Figure 21** also highlight that temporal concentration reductions of more than 1-2 orders of magnitude are relatively uncommon for 1,4-dioxane and the individual chlorinated solvents. For each compound, the most recent maximum concentration at the majority of sites is well above any potentially-applicable regulatory level (which are generally 1 μg/L or less).



DIOXANE MEDIAN OoM Reduction = 0.42 (62%)
Method 1: Recent Max = Max Site Concentration in 2013

DIOXANE MEDIAN OoM Reduction = 0.25 (44%)
Method 2: Recent Max = Most Recent Concentration in Well with Historic Max Concentration

Figure 21a. Recent vs. Historical Maximum Site Concentrations for 1,4-Dioxane.



TCA MEDIAN OoM Reduction = 0.75 (82%)
Method 1: Recent Max = Max Site Concentration in 2013

TCA MEDIAN OoM Reduction = 0.42 (62%)
Method 2: Recent Max = Most Recent Concentration in Well with Historic Max Concentration

Figure 21b. Recent vs. Historical Maximum Site Concentrations for TCA. Includes sites with and without 1,4-dioxane detections.

TCE MEDIAN OoM Reduction = 0.35 (55%)
Method 1: Recent Max = Max Site Concentration in 2013

TCE MEDIAN OoM Reduction = 0.23 (41%)
Method 2: Recent Max = Most Recent Concentration in Well with Historic Max Concentration

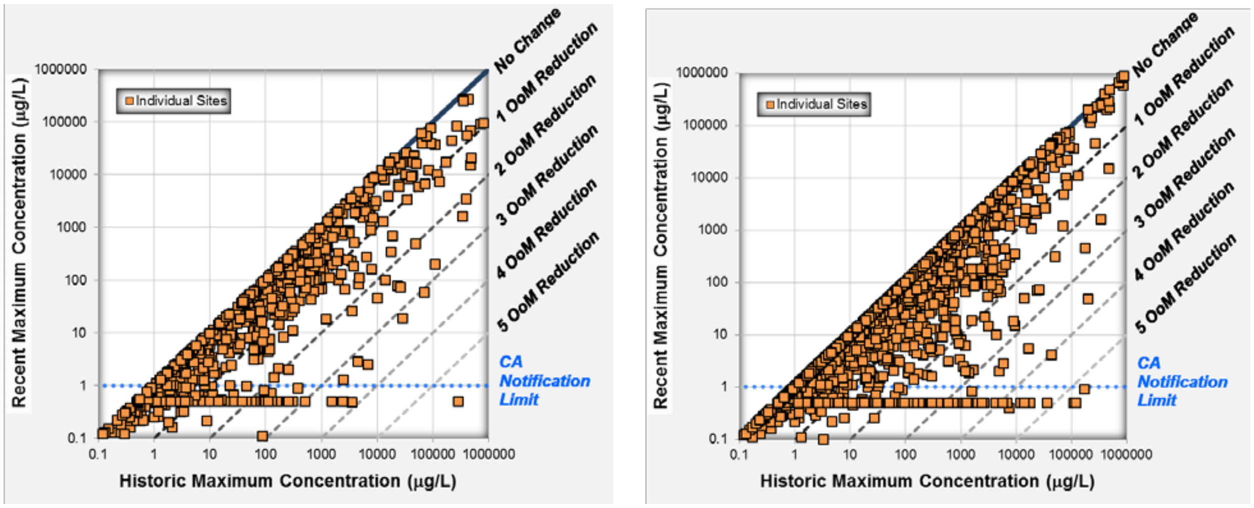


Figure 21c. Recent vs. Historical Maximum Site Concentrations for TCE. Includes sites with and without 1,4-dioxane detections.

1,1-DCE MEDIAN OoM Reduction = 0.37 (57%)
Method 1: Recent Max = Max Site Concentration in 2013

1,1-DCE MEDIAN OoM Reduction = 0.31 (51%)
Method 2: Recent Max = Most Recent Concentration in Well with Historic Max Concentration

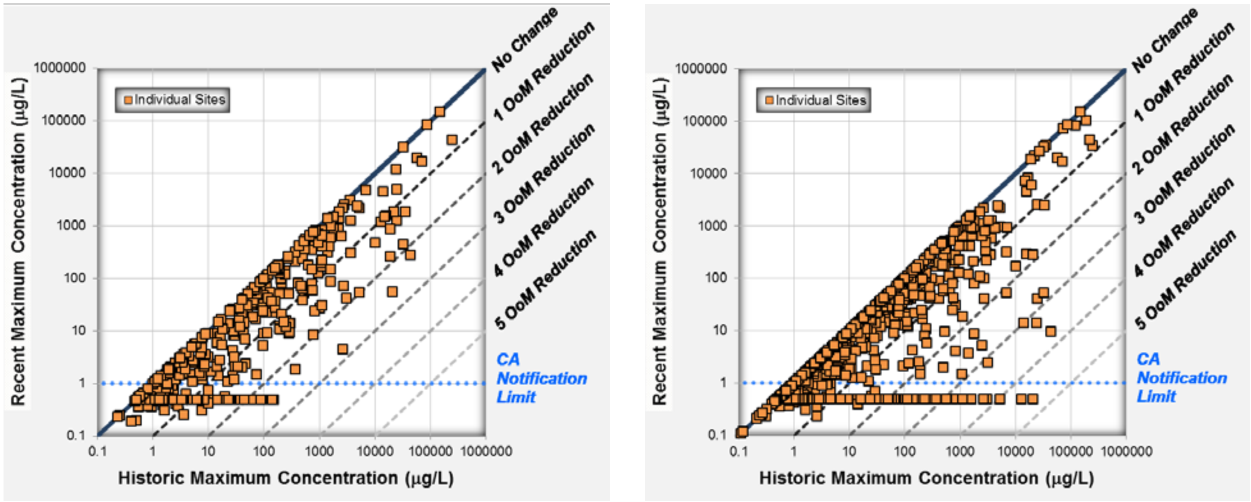


Figure 21d. Recent vs. Historical Maximum Site Concentrations for 1,1-DCE. Includes sites with and without 1,4-dioxane detections.

Table 16. Summary of Order of Magnitude Reductions Over Time for Sites with 1,4-Dioxane, TCA, TCE, 1,1-DCE, and 1,1-DCA.

Compound	**OoM Reduction**			
	Median for Method 1 (no. of sites)	**Comparisons to OoM Reduction for 1,4-dioxane (p-value)**	**Median for Method 2 (no. of sites)**	**Comparisons to OoM Reduction for 1,4-dioxane (p-value)**
ALL SITES				
Dioxane	0.42 (n=80)	--	0.25 (n=155)	--
TCA	0.75 (n=191)	Larger than 1,4-dioxane (p=0.0004)	0.42 (n=419)	Larger than 1,4-dioxane (p=0.03)
TCE	0.35 (n=826)	Not different than 1,4-dioxane (p=0.38)	0.23 (n=1908)	Not different than 1,4-dioxane (p=0.67)
1,1-DCE	0.37 (n=441)	Not different than 1,4-dioxane (p=0.52)	0.31 (n=918)	Not different than 1,4-dioxane (p=0.59)
1,1-DCA	0.34 (n=456)	Not different than 1,4-dioxane (p=0.36)	0.26 (n=923)	Not different than 1,4-dioxane (p=0.71)
SITES WITH 1,4-dioxane				
Dioxane	0.42 (n=80)	--	0.25 (n=155)	--
TCA	0.98 (n=70)	Larger than 1,4-dioxane (p=0.0003)	0.83 (n=108)	Larger than 1,4-dioxane (p=0.0003)
TCE	0.37 (n=107)	Not different than 1,4-dioxane (p=0.42)	0.30 (n=168)	Not different than 1,4-dioxane (p=0.70)
1,1-DCE	0.32 (n=103)	Not different than 1,4-dioxane (p=0.58)	0.37 (n=155)	Not different than 1,4-dioxane (p=0.10)
1,1-DCA	0.41 (n=105)	Not different than 1,4-dioxane (p=0.77)	0.24 (n=158)	Not different than 1,4-dioxane (p=0.63)

Notes: (1) Method 1 uses the maximum site concentration measured in 2013 as the recent maximum concentration; Method 2 uses the most recent concentration measured in the well with the historic maximum concentration as the recent maximum concentration; (2) Does not include sites where well with historic maximum concentration was only sampled once; (3) Differences between groups evaluated using Wilcoxon Rank Sum test (non-parametric; two-tailed; significance based on p-value < 0.05); (4) For sites where the most recent maximum concentration is nondetect, a value equal to half the median reporting limit was substituted (see Table 4).

For 1,4-dioxane, the same two methods were used to calculate OoM reductions for all individual wells by comparing the maximum historical concentration for a well relative to a "recent" concentration (**Figure 22**). Due to the inclusion of a larger set of wells (in this case, including wells that were only sampled once), the median OoM reductions for 1,4-dioxane (0.0.16-0.31-0.45) using this approach were smaller than those obtained when a single maximum well was used to represent the site (0.25-0.42). However, the results provide further confirmation that attenuation has contributed to substantial reductions in 1,4-dioxane concentrations. For this evaluation, the time elapsed since the historic maximum concentration was generally much shorter (median value = 1.3 years for Method 1; median value = 0.92 years for Method 2) because many of the wells had only been sampled once.

DIOXANE MEDIAN OoM Reduction = 0.35 (55%)
Method 1: Recent Max = Max Concentration in 2013

DIOXANE MEDIAN OoM Reduction = 0.16 (31%)
Method 2: Recent Max = Most Recent Concentration

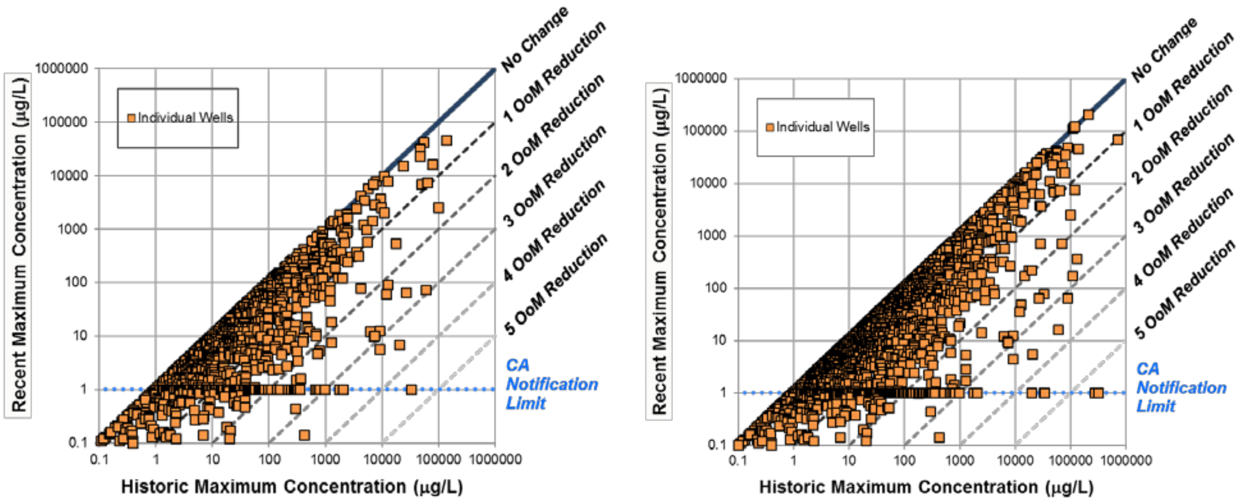


Figure 22. Recent vs. Historical Maximum Concentrations in Wells with 1,4-Dioxane Detections.

Line of Evidence #3 – Site-Specific Attenuation Rates (GeoTracker sites). First-order rate coefficients (k_{source}) were calculated for 1,4-dioxane and chlorinated solvents on a site-by-site basis for the GeoTracker dataset. A first-order relationship was selected on the basis on modeling attenuation based on degradative pathways. It should be noted that zero-order rate coefficients could also be estimated using the OoM reduction values (described above) and the length of the monitoring period, but this was not attempted.

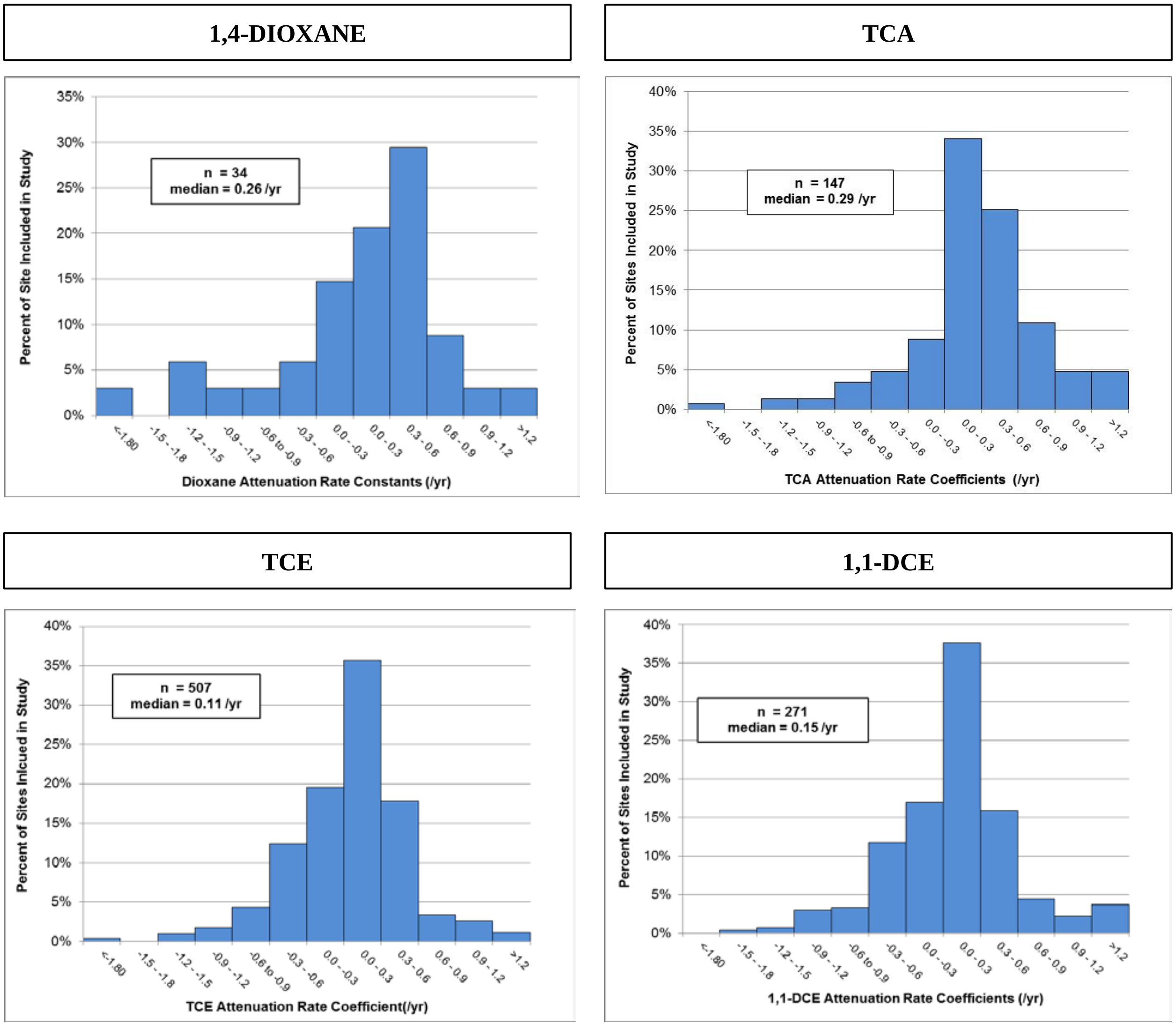
Results of this evaluation are summarized in **Table 17**, and histograms of the distribution of rate coefficients for each compound are presented in **Figure 23**. Key findings include the following:

- Statistically-significant positive k_{source} values for 1,4-dioxane could be established at 22 sites. This serves as unequivocal evidence of 1,4-dioxane attenuation at these sites.
- The mean (0.08/yr) and median (0.26/yr) of the entire set of statistically-significant k_{source} values for 1,4-dioxane (n=34) were both positive, suggesting that measurable attenuation is occurring at these sites. The median k_{source} of 0.26/yr corresponds to a 1,4-dioxane half-life of approximately 2.6 yr.
- It could not be established that the rate coefficients for 1,4-dioxane were significantly different than zero, although the p-value for the non-parametric test ($p=0.07$) nearly met the threshold for significance ($p<0.05$). This can be attributed to two inter-related issues: 1) the length of monitoring periods for 1,4-dioxane has been relatively short (typically <3 years), meaning that there was frequently insufficient data to establish a significant k_{source} value at many sites where 1,4-dioxane was detected; and 2) the number of sites with significant k_{source} values was small (particularly relative to the number of sites for chlorinated solvents), which makes it more difficult to establish significant differences using hypothesis testing.
- A smaller number of sites had negative k_{source} values for 1,4-dioxane. There are no realistic mechanisms that would cause 1,4-dioxane to accumulate at a site. Therefore, negative k_{source} values are likely to be associated with sites where changes in site characterization and/or monitoring over time resulted in better identification of 1,4-dioxane hotspots. It is important to note that the percentage of 1,4-dioxane sites with negative k_{source} values is relatively similar to the percentages for TCE and 1,1-DCE sites.
- The results of hypothesis testing for the chlorinated solvents confirm that the attenuation rate constants for those contaminants are greater than zero. The impact of the larger sample sizes is clearly illustrated by the smaller confidence intervals, even though the histograms show that the distribution for 1,4-dioxane is relatively similar to that for the chlorinated solvents.
- The median k_{source} value for 1,4-dioxane was higher than those for TCE and 1,1-DCE, while the mean k_{source} value for 1,4-dioxane fell between those TCE and 1,1-DCE. The corresponding values for TCA were both higher than those for 1,4-dioxane. No statistically significant difference between 1,4-dioxane and the other compounds could be established, suggesting similar attenuation rates for 1,4-dioxane and the chlorinated solvents. However, this is likely influenced by the small sample size for 1,4-dioxane.

Table 17. Summary of Site Attenuation Rate Coefficients (k_{source}) for 1,4-Dioxane, TCA, TCE, and 1,1-DCE.

	Dioxane	TCA	TCE	1,1-DCE
Total No. of k_{source} Values	113	401	1453	763
No. of Significant k_{source} Values ($p<0.1$)	34	147	507	271
No. of Positive Significant k_{source} Values	22 (63%)	117 (80%)	309 (61%)	173 (68%)
Mean k_{source} (± 95% Confidence Interval)	0.08 (± 0.23) yr^{-1}	0.27 (± 0.095) yr^{-1}	0.044 (± 0.041) yr^{-1}	0.11 (± 0.073) yr^{-1}
Median k_{source}	0.26 yr^{-1}	0.29 yr^{-1}	0.11 yr^{-1}	0.15 yr^{-1}
k_{source} Different Than 1,4-dioxane? (*p*-value)	--	No (p=0.43)	No (p=0.09)	No (p=0.17)
k_{source} Different Than Zero? (*p*-value)	No (p=0.49)	Yes (p<0.001)	Yes (p=0.04)	Yes (p=0.005)

Notes: (1) Statistically significant k_{source} values were based on $p<0.1$ to ensure that an adequate sample size for 1,4-dioxane was available for evaluation; (2) Differences between groups computed using the Wilcoxon Rank Sum test as a non-parametric method (two-tailed; significance based on p-value < 0.05); (3) Differences from zero computed using the one-sided t-test as a parametric method (significance based on p-value < 0.05); (4) When evaluating if k_{source} values for each compound were different than 1,4-dioxane or zero, all significant k_{source} values (positive and negative) were included.



1,4-DIOXANE

TCA

TCE

1,1-DCE

Figure 23. Histograms of Site Attenuation Rate Coefficients (k_{source}) for 1,4-Dioxane, TCA, TCE, and 1,1-DCE. Includes all statistically-significant values.

As described earlier, the evaluation of 1,4-dioxane attenuation rates was supplemented with a parallel set of monitoring data from Air Force sites. For the purposes of this supplemental evaluation (performed by Hunter Anderson at AFCEC and detailed in Adamson et al. (2015)), it was generally not feasible to segregate the Air Force data to individual "sites" due to the complexity of each installation (e.g., multiple operating units with different sources) as well as the fact that historic data loading omitted any reference to potential or known sources and, thus, focused on individual sampling locations.

Therefore, 1,4-dioxane rate coefficients (either zero-order or first-order based on fit) were estimated on a well-specific basis for the Air Force dataset. There were 441 wells that had sufficient data to evaluate, and 269 (61%) of these had with no significant trend. Forty-one (9%) were observed with significantly increasing trends while significantly decreasing trends were observed at 131 wells (30%).

The positive rate coefficients were converted to empirical half-lives for 1,4-dioxane (i.e., negative rate coefficients cannot be expressed as a half-life). The distribution of values from the Air Force dataset and the GeoTracker dataset are shown side-by-side in Figure is shown in **Figure 24**. The general shapes of the two distributions are similar, although the median half life for the GeoTracker dataset (20 months) is shorter than the median half life for the Air Force dataset (48 months). In addition, there is a clear tail on the right side of the Air Force distribution that represents wells with longer half-lives for 1,4-dioxane. Both datasets provide evidence that significant attenuation of 1,4-dioxane has occurred at some sites within meaningful timeframes. Given that the rate coefficients were calculated using two different (but perhaps equally representative) methods, they also confirm that attenuation occurs on a well-by-well basis and within the source.

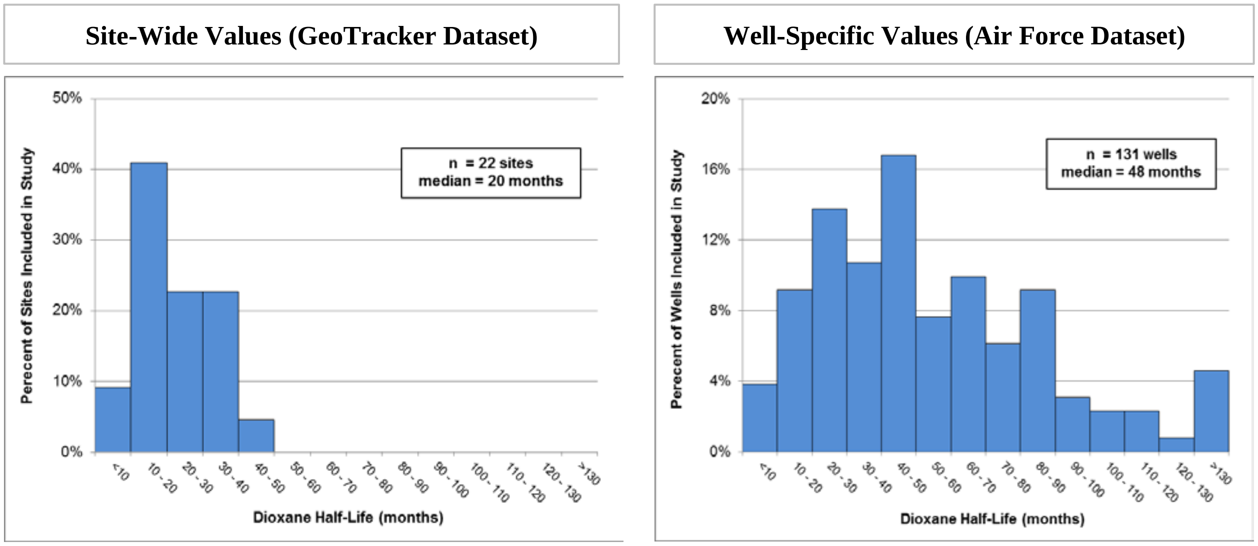


Figure 24. Histogram of Site-Wide Attenuation Half-Lives and Well-Specific Attenuation Half-Lives for 1,4-Dioxane. Includes only those sites/wells where statistically-significant positive rate could be established.

Line of Evidence #4 – Trend Analysis. Concentration trends over time were evaluated using the Mann-Kendall test. For each compound, this non-parametric test was performed on all sites with data from 4 or more sampling events. The distribution of the trends established during these tests is shown in **Figure 25**.

For 1,4-dioxane, 21% of the site concentration trends could be categorized as decreasing, 25% were stable, 42% had no trend, and only 12% were increasing. There is a striking similarly between the trend distribution for 1,4-dioxane and the distributions for the three chlorinated solvents. In particuar, 1,4-dioxane, TCE, and 1,1-DCE had nearly identical percentages of sites categorized as decreasing (21-23%), stable (25-26%), and increasing (12-13%). The pattern is consistent with the similarity in k_{source} values for these three compounds, and it provides further evidence that 1,4-dioxane is behaving similarly to TCE and 1,1-DCE at contaminated groundwater sites. The trend analysis confirmed that TCA concentrations are significantly decreasing at a larger percentage of sites (33%) than 1,4-dioxane or other co-occurring chlorinated solvents. However, it is important to note that there is still a large percentage of sites where: 1) no trend for TCA can be established (36%), highlighting the inherent variability in monitoring data; and 2) a stable or increasing TCA trend was established (31%).

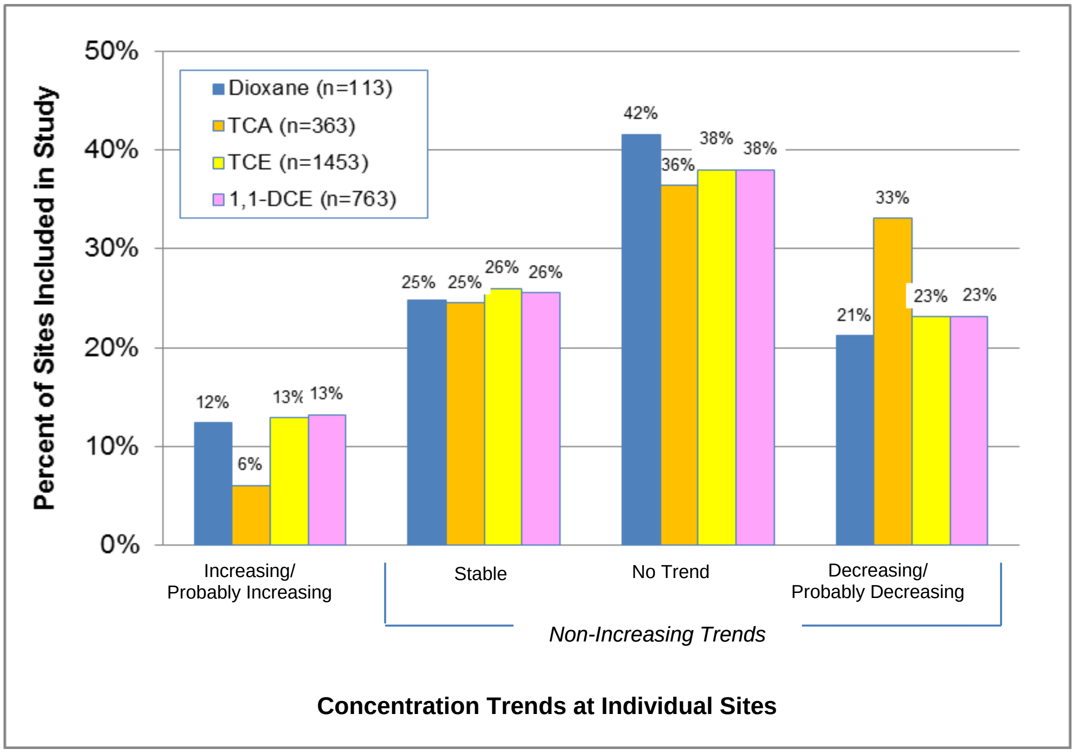


Figure 25. Comparison of Concentration Trends for Sites with 1,4-Dioxane, TCA, TCE, and 1,1-DCE. Trends established using Mann-Kendall test.

4.1.4 Evaluation of Factors Influencing Plume Length

Based on the plume length estimation procedure described in Section 2.4.2, 1,4-dioxane plumes were generally similar to those for co-occurring chlorinated solvents. Since this pattern was different than the conventional conceptual site model, a number of factors that potentially influence plume length were cataloged from the database. The evaluation of these factors used parametric and non-parametric correlation methods to determine if there was a statistically-significant relationship with the 1,4-dioxane plume length. Given that neither the independent variables nor the dependent variable are normally distributed (even after log-transformation), the non-parametric test results are considered more applicable. For the Spearman's test, the Rho value serves as a correlation coefficient that measures the strength of the relationship (absolute value: 0.0-0.2 very weak; 0.2-0.4 weak; 0.4-0.6 moderate; 0.6-0.8 strong; 0.8-1.0 very strong).

A summary of the results of this evaluation are provided in **Table 18** and **Table 19**. Key findings from this evaluation include the following:

- There were several variables that proved to be significantly correlated with 1,4-dioxane plume length. However, with a few exceptions, the R^2 values for linear regression and Spearman's Rho values were generally low. This pattern suggests that the predictive power of these factors is typically not very strong and that there are a number of unidentified factors that influence the plume length estimates.
- The 1,4-dioxane plume length was highly correlated with chlorinated solvent plume length, especially 1,1-DCE (Rho = 0.81; R^2=0.55; **Figure 26**). This is consistent with the 1,4-dioxane and chlorinated solvent releases for a particular site occurring from similar locations following similar flowpaths. It is also consistent with the assumption that the lengths of the 1,4-dioxane and chlorinated solvent plumes are being delineated and monitored using the same well networks.
- Of the remaining significant variables, the strongest correlation was obtained with the hydraulic conductivity of the groundwater-bearing unit. This supports the conceptual model that plume lengths should increase with the ability for the formation to transmit fluid. Similarly, there was a significant (though weaker) correlation with soil type, with longer plumes associated with gravel and sand dominated units than silt and clay units. There were relatively few sites with reported values for hydraulic conductivity (28 of 109), and there was insufficient data to evaluate groundwater velocity.
- The maximum concentration of 1,4-dioxane and the maximum concentration of chlorinated solvents (as well as the maximum concentration of TCA) showed significant correlations. This relationship is consistent with the principles of contaminant transport.
- The presence of a pump-and-treat system was significantly correlated with longer 1,4-dioxane plumes. Depending on the location of extraction wells, a pump-and-treat system could have a range of impacts on plume length. The fact that plume lengths were positively correlated with pump-and-treat systems suggests that the majority of systems in this study have been focused on downgradient containment rather than solely on

source control (which might shorten plumes). The finding that plume lengths for 1,4-dioxane and chlorinated solvents are relatively similar is consistent with containment-focused systems. Placing extraction wells along a downgradient transect would “cut off” plumes and thus effectively equalize plume distance among different compounds, regardless of their individual transport properties. For sites where 1,4-dioxane, TCE, TCA, and 1,1-DCE were all present, the median plume lengths for each compound were significantly longer at sites with pump-and-treat systems than those without (**Figure 27).**

- The redox state for a site was assumed to be an important factor for 1,4-dioxane plume lengths, given reports of aerobic (but not anaerobic) biodegradation. While the median 1,4-dioxane plume length was smaller at aerobic sites (236 m) than at mildly aerobic to mildly anaerobic sites (454 m) and anaerobic sites (413 m), no significant relationship could be established between redox state and plume length. Furthermore, the plume lengths for chlorinated solvents were generally smaller at aerobic sites than at sites with more anaerobic redox states (**Figure 28**). Each of these chlorinated solvents has well-documented anaerobic degradation pathways, although there are viable aerobic degradation pathways for each as well, including TCA hydrolysis. A potential contributing factor to shorter plumes at aerobic sites is higher percentage of the sand/gravel soil type at anaerobic sites (48%) compared to aerobic sites (28%).
- No statistically-significant relationship could be established between the 1,4-dioxane plume length and any of the attenuation metrics, including k_{source} values, OoM reductions, and the Mann-Kendall trend. In most cases, positive attenuation metrics (e.g., decreasing trend by Mann-Kendall) was associated with shorter plumes, but these were not statistically significant effects. To a certain extent, attenuation of the source would be expected to lead to shorter plumes. However, these changes in concentration may occur slowly relative to groundwater transport, such that considerable plume expansion can still occur. Releases often precede any remedial efforts by several decades, such that concentration reductions that result from remedial activities may have little impact on the plume length at an older site. As stated above, in situ remediation was typically associated with longer plumes.
- Sites where in situ bioremediation was used had longer 1,4-dioxane plume lengths than sites without in situ bioremediation, although this effect was statistically significant. For chlorinated solvents, the effect was significant in only a few cases (TCA and TCE via linear regression; and TCE via Spearman’s correlation). While in situ bioremediation would be expected to shorten plumes via treatment of the source (or plume), this result suggests that in situ bioremediation is either having limited impact or has been used preferentially on sites where longer plumes already existed.
- Sites where in situ chemical oxidation was used had shorter 1,4-dioxane plume lengths than sites without in situ chemical oxidation, but again, this effect was not statistically significant. Further, this effect was statistically significant in only a single chlorinated solvent (TCA via linear regression). In situ chemical oxidation would also be expected to shorten plumes and these data are consistent with that assumption, though it is possible that there is some inherent bias in the types of sites selected for this treatment.

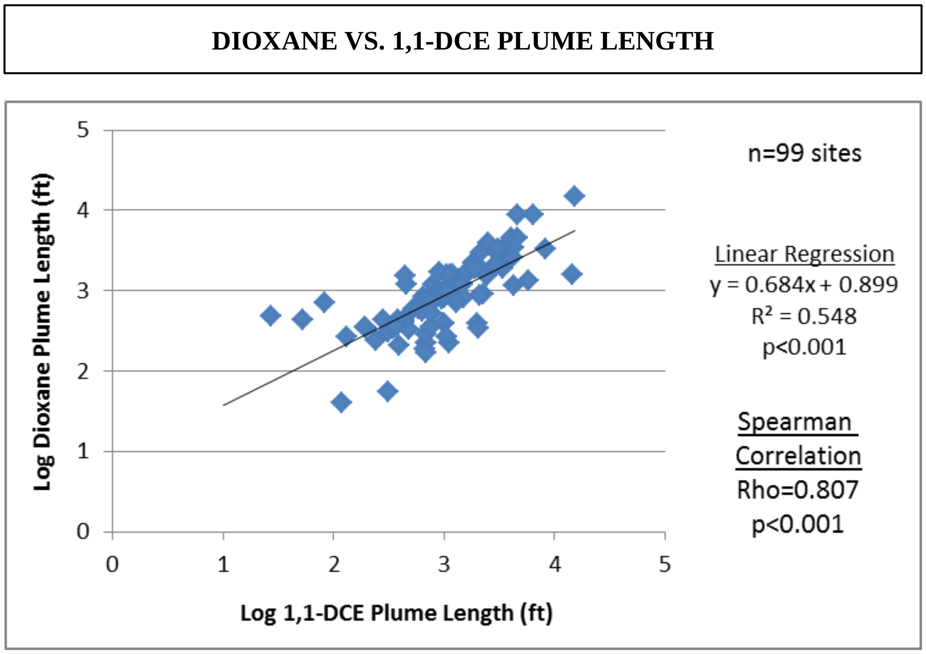


Figure 26. Correlation Between 1,1-DCE and 1,4-Dioxane Plume Length.

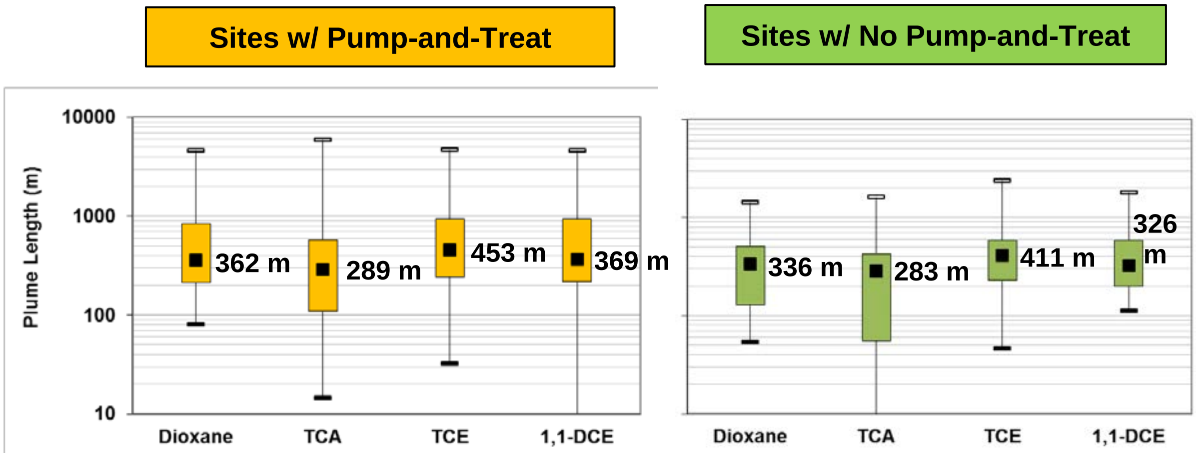


Figure 27. Impact of the Presence of a Pump-and-Treat System on the Distribution of Plume Length Estimates for Sites with Detections of 1,4-Dioxane, TCA, TCE, and 1,1-DCE. For chlorinated solvents, graph includes only those sites where 1,4-dioxane plume lengths and/or attenuation rates were established.

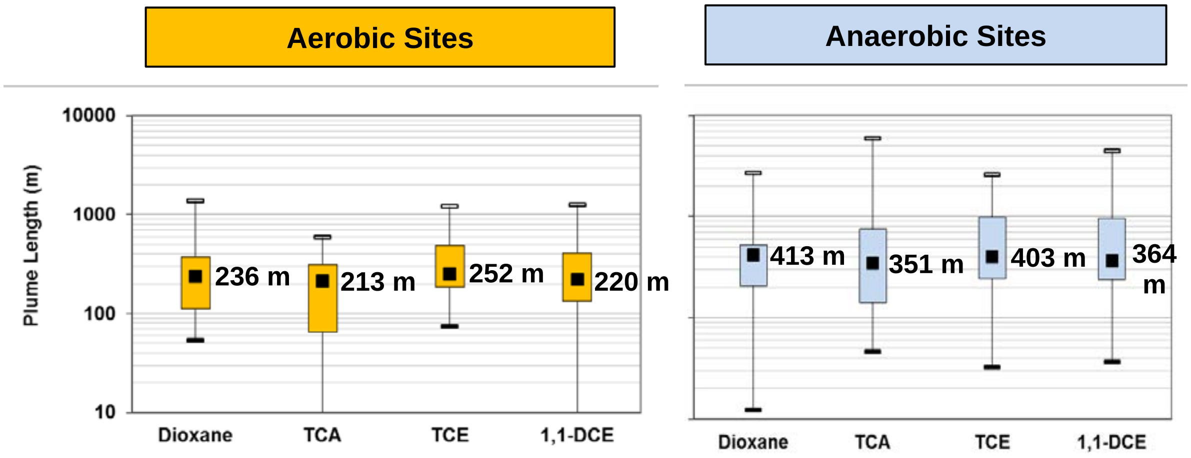


Figure 28. Impact of Redox State on the Distribution of Plume Length Estimates for Sites with Detections of 1,4-Dioxane, TCA, TCE, and 1,1-DCE. For chlorinated solvents, graph includes only those sites where 1,4-dioxane plume lengths and/or attenuation rates were established.

Table 18. Results of Correlation Analyses for 1,4-Dioxane Plume Length

Independent Variable	Units	Log Transform?	n	Linear Regression (parametric)				Spearman's Test (non-parametric)	
				R^2	Slope	p-value	y-intercept	Rho	p-value
Hydraulic conductivity	ft/d	Yes	28	0.18	0.145	**0.024**	2.94	0.40	**0.034**
Max. 1,4-dioxane Conc.	µg/L	Yes	109	0.06	0.096	**0.010**	2.71	0.22	**0.022**
Max. TCA Conc.	µg/L	Yes	75	0.08	0.071	**0.012**	2.87	0.28	**0.014**
Max. Chlorinated Solvent Conc.	µg/L	Yes	109	0.04	0.067	**0.035**	2.72	0.23	**0.018**
TCA Plume Length	ft	Yes	61	0.51	0.472	**<0.0001**	1.70	0.76	**<0.0001**
TCE Plume Length	ft	Yes	102	0.52	0.700	**<0.0001**	0.82	0.75	**<0.0001**
DCE Plume Length	ft	Yes	99	0.55	0.684	**<0.0001**	0.90	0.81	**<0.0001**
Dioxane k_{source} (all values)	yr^{-1}	No	88	0.03	0.167	0.126	2.99	0.12	0.289
Dioxane k_{source} (all significant values)	yr^{-1}	No	26	0.04	0.146	0.341	2.95	0.16	0.433
Dioxane k_{source} (all positive significant values)	yr^{-1}	No	19	0.002	0.073	0.850	2.97	0.12	0.632
OoM Reduction (Method 1)	--	No	74	0.009	0.076	0.508	2.97	0.09	0.523
Time Between Historic Max and Recent Max Conc. (Method 1)	yr	Yes	74	0.032	0.205	0.217	2.94	0.22	0.117
OoM Reduction (Method 1)	--	No	50	0.000	0.006	0.930	2.98	0.01	0.945
Time Between Historic Max and Recent Max Conc. (Method 1)	yr	Yes	50	0.018	0.157	0.256	2.93	0.15	0.198

Notes: (1) Bold values with yellow shading indicate that the statistical test indicates a significant relationship using one or more test; (2) Dependent variable (dioxane plume length) was log-transformed with units of ft.

Table 19. Relationship Between Selected Categorical Parameters and 1,4-Dioxane Plume Length.

Independent Variable	Units	n	ANOVA (parametric)		Kruskal-Wallis (non-parametric)	
			Evidence of Significant Association?	**p-value**	**Evidence of Significant Association?**	**p-value**
Redox State	(Categorical)	86	No	0.40	No	0.34
Soil Type	(Categorical)	98	Yes (more permeable soils increase plume length)	**0.017**	Yes (more permeable soils increase plume length)	**0.019**
P&T System Present	(Categorical)	109	Yes (increases plume length)	**0.014**	Yes (increases plume length)	**0.029**
In Situ Bioremed.	(Categorical)	109	0.12	0.	No	0.18
In Situ Chem. Ox.	(Categorical)	109	No	0.12	No	0.52
Mann-Kendall Trend	(Categorical)	53	No	0.26	No	0.31

Notes: (1) Bold values with blue shading indicate relationships that are significant based on one or more test (p-value<0.05); (2) Independent variables are categorical and evaluated using the following assigned categories: redox state (0=anaerobic; 1=mixed; 2=aerobic); soil type (0=clay/silt; 1=sand w/ silt/clay; 2=sand/gravel; pump-and-treat system present (0=absent; 1=present); in situ bioremediation performed (0=not performed; 1=performed), in situ chemical oxidation performed (0=not performed; 1=performed) and Mann-Kendal Trend (0=Decreasing/Probably Decreasing; 1=Stable; 2=Increasing/Probably Increasing.

Table 20. Relationship Between Selected Categorical Parameters and Chlorinated Solvent Plume Length.

			ANOVA (parametric)		Kruskal-Wallis (non-parametric)	
Independent Variable	**Units**	**n**	**Evidence of Significant Association?**	**p-value**	**Evidence of Significant Association?**	**p-value**
Redox State (TCA Plume Length)	(Categorical)	64	No	0.099	No	0.11
Redox State (TCE Plume Length)	(Categorical)	114	No	0.25	No	0.19
Redox State (DCE Plume Length)	(Categorical)	109	Yes (aerobic decreases plume length)	**0.007**	Yes (aerobic decreases plume length)	**0.005**
P&T System Present (TCA Plume Length	(Categorical)	64	No	0.089	No	0.17
P&T System Present (TCE Plume Length	(Categorical)	114	Yes (increases plume length)	**0.009**	Yes (increases plume length)	**0.006**
P&T System Present (DCE Plume Length	(Categorical)	109	No	0.079	Yes (increases plume length)	**0.018**
In Situ Chem. Ox. (TCA Plume Length)	(Categorical)	64	Yes (decreases plume length)	**0.018**	No	0.061
In Situ Chem. Ox. (TCE Plume Length)	(Categorical)	114	No	0.87	No	0.76
In Situ Chem. Ox. (DCE Plume Length)	(Categorical)	109	No	0.15	No	0.23
In Situ Bioremed. (TCA Plume Length)	(Categorical)	64	Yes (increases plume length)	**0.024**	No	**0.065**
In Situ Bioremed. (TCE Plume Length)	(Categorical)	114	Yes (increases plume length)	**0.021**	Yes (increases plume length)	**0.033**
In Situ Bioremed. (DCE Plume Length)	(Categorical)	109	No	0.055	No	0.11

Notes: (1) Bold values with blue shading indicate relationships that are significant based on one or more test ($p\text{-value} < 0.05$); (2) Independent variables are categorical and evaluated using the following assigned categories: redox state (0=anaerobic; 1=mixed; 2=aerobic); pump-and-treat system present (0=absent; 1=present); in situ bioremediation performed (0=not performed; 1=performed), and in situ chemical oxidation performed (0=not performed; 1=performed).

Several attempts were made at constructing a multiple regression model that improved the predictive power of the correlations. This involved using two or more independent variables and regressing against the 1,4-dioxane plume length. Independent variables were retained only when they were significant (i.e., slope > 0 based on $p<0.05$ for F-test). Because not all independent variables had values for all sites, this typically resulted in a smaller sample sizes for multiple regression than it did for simple regression (i.e., with a single variable). For this reason, multiple regression models using hydraulic conductivity (which had relatively high R^2 values for simple regression but only 28 data points) did not improve the correlations.

The strongest set of correlations for 1,4-dioxane plume length were obtained using plume lengths from one or more of the chlorinated solvents. The strongest used DCE and TCE plume lengths, which was slight improvement over TCA and TCE plume lengths. Regressing with plume lengths for all three chlorinated solvents resulted in a higher R^2 but not all variables were significant. Given the multicollinearity between these independent variables, there is little expectation that an improved model can be built with these variables. Furthermore, no stronger multiple regression models could be constructed using plume length in combination with other independent variables.

Log 1,4-dioxane Plume Length =
0.465*(**Log DCE Plume Length**) + 0.336*(**Log TCE Plume Length**) + 0.520

$R^2 = 0.62$;
Significance of Regression = $2.0\text{x}10^{-20}$;
p-value for DCE Plume Length = 0.0001;
p-value for TCE Plume Length = 0.005

For multiple regressions that did not include plume length, the strongest correlations were obtained using a combination of Soil Type, P&T System, and Maximum Chlorinated Solvent Concentrations as the independent variables.

Log 1,4-dioxane Plume Length =
0.10*(**Maximum Chlorinated Solvent Concentration**) + 0.131*(**Soil Type**)
+ 0.23*(**P&T System Present**) + 2.59

$R^2 = 0.23$;
Significance of Regression = $2.0\text{x}10^{-5}$;
p-value for Max. Chlorinates Solvent Conc. = 0.002;
p-value for Soil Type = 0.012
p-value for P&T System Present = 0.012

This represented a slight improvement over the simple regression model with hydraulic conductivity as the independent variable, which was the strongest correlation with 1,4-dioxane plume length among those where the chlorinated solvent plume was omitted.

4.1.5 Evaluation of Factors Influencing Attenuation

Based on the various metrics for attenuation described in Section 2.4.3, 1,4-dioxane plumes were generally attenuating to a similar extent as TCE and 1,1-DCE but less than TCA. A further evaluation of a number of factors that potentially influence 1,4-dioxane attenuation was performed using a combination of methods. This included a separate evaluation of the GeoTracker dataset (which involved sites and thus relied on categorical variables to describe site parameters like redox state) as well as a supplemental evaluation of the Air Force dataset (which involved well data and thus could use continuous variables for parameters like dissolved oxygen). The latter evaluation was performed by Hunter Anderson (AFCEC) to support the findings published in Adamson et al. (2015).

GeoTracker dataset: A summary of the evaluation using the GeoTracker dataset are provided in **Table 21** (OoM reductions) and **Table 22** (k_{source} values). As with the plume length evaluations, the results from the non-parametric methods are given greater weight since the independent variables and dependent variable are not necessarily normally distributed. Key findings from this evaluation include the following:

- For the 1,4-dioxane OoM reductions, there was little evidence for significant correlations between any of the factors evaluated, with the exception of the k_{source} values and the Mann-Kendall trends. These latter metrics are estimated using the same data as the OoM reductions (temporal concentration records) and thus are not truly independent variables.
- Other variables that showed a significant relationship with 1,4-dioxane OoM reduction using one or more tests were hydraulic conductivity and the maximum TCA concentration. However, the relationships were not significant for all tests and the correlation coefficients were low. It is worth noting that 1,4-dioxane OoM reduction showed a positive correlation with the maximum TCA concentration (i.e., greater 1,4-dioxane reductions were observed at sites with higher maximum TCA concentrations).
- While the relationship was not statistically significant, there was a positive correlation between more oxidizing conditions and greater 1,4-dioxane OoM reductions.
- There was no clear indication that the types of remediation that were evaluated had any impact on 1,4-dioxane OoM reductions. Sites with P&T showed mixed results, sites in situ bioremediation were associated with lower 1,4-dioxane OoM reductions, and sites with in situ chemical oxidation were associated with higher 1,4-dioxane OoM reductions. The latter relationship would have been significant if the p-value threshold for hypothesis testing was set at 0.1, and it is consistent with the assumption that 1,4-dioxane is more subject to oxidative degradation.
- There was also little evidence for significant correlations between the 1,4-dioxane k_{source} values and any of the factors evaluated, with the exception of the k_{source} values for other co-occurring chlorinates solvents (discussed below). To increase the sample size, the evaluation was performed with all k_{source} values prior to repeating the evaluation using the smaller set of statistically-significant k_{source} values.

- A significant but weak positive correlation between higher 1,4-dioxane k_{source} values and the presence of P&T using one or more of the tests.
- There was no positive correlation between more oxidizing conditions and greater 1,4-dioxane k_{source} values.
- There was evidence that the 1,4-dioxane k_{source} values were positively correlated with k_{source} values for TCE and—in particular—1,1-DCE (**Table 22a**, **Figure 29**). Based on the slope of regression curves in **Figure 29**, 1,4-dioxane is attenuating at approximately 32% of the rate of TCE and at approximately 44% of the rate of 1,1-DCE.
- The predictive strength of each of these relationships increased when only statistically-significant k_{source} values for 1,4-dioxane and TCE and 1,1-DCE were included (**Table 22b**, **Figure 30).** Based on the slope of regression curves in **Figure 23**, 1,4-dioxane is attenuating at approximately 45% of the rate of TCE and at approximately 82% of the rate of 1,1-DCE.
- No correlation between the k_{source} values for 1,4-dioxane and TCA could be established. This confirms that at the large majority of sites, TCA is attenuating much more rapidly than 1,4-dioxane.
- **Figure 29** also shows that there was a significant and strong correlation among the attenuation rates for chlorinated solvents at sites where more than one of these compounds are present. The slopes of the regression lines suggest that TCA attenuates at a more rapid rate than both TCE and 1,1-DCE, and that TCE attenuates more rapidly than 1,1-DCE.

The influence of the maximum historical 1,4-dioxane concentration on the estimated k_{source} values from the GeoTracker dataset was also evaluated. This was accomplished by distributing the sites into quartile groups based on the maximum historical 1,4-dioxane concentration, and then comparing the distribution of k_{source} values within each quartile with the other quartile groups. The same exercise was repeated with TCA, TCE, and 1,1-DCE, with the results summarized in **Table 23**.

No significant difference among the 1,4-dioxane k_{source} values for the different groups could be established (using single-factor ANOVA, $p<0.05$). Similar mean values were observed for each group (0.43 to 0.5 yr^{-1}, corresponding to 1,4-dioxane half-lives of approximately 1.5 yr), suggesting that the maximum 1,4-dioxane concentration has little influence on 1,4-dioxane attenuation. Using the median values, there was an indication that faster 1,4-dioxane attenuation was occurring at the low and high end of the initial concentration ranges. A similar effect was noted in the Air Force dataset (described later in this section), but in this case, the effect was not statistically significant. Similarly, no relationship could be established between the historical maximum 1,1-DCE concentration and the k_{source} values for 1,1-DCE. However, there was a significant positive correlation between higher TCE concentrations and TCA concentrations with their respective k_{source} values. It is important to note that the first-order rate coefficient should not be influenced by the maximum concentration unless there are external factors influencing the reaction rate. In the case of TCA and TCE, there is the potential that higher concentrations support preferential and/or growth-supporting biodegradation that might be less favorable at lower concentrations. The k_{source} values are also influenced by site-specific remedial decisions, including a higher incidence of aggressive remediation at sites with higher concentrations that would also be reflected in higher k_{source} values. However, this effect should have been noticed at 1,1-DCE sites since 1,1-DCE co-occurrence and concentration are highly correlated with TCA. Therefore, the concentration effect for TCA and perhaps TCE may reflect an influence of higher concentrations on in situ degradative mechanisms.

A final evaluation performed using the GeoTracker dataset focused on the potential impact of the presence of co-occurring chlorinated solvents on 1,4-dioxane attenuation. This was accomplished using the OoM reductions for 1,4-dioxane on a well-by-well basis. For individual chlorinated solvents, the distribution of 1,4-dioxane OoM reductions were compiled for wells where the chlorinated solvent was present (i.e., above reporting levels) and for wells where the chlorinated solvent was absent (either not detected or not analyzed). The median values for each case are presented in **Table 24**, along with the p-value from a non-parametric test to establish if the presence of each chlorinated solvent was significant. In this evaluation, wells that met the following conditions were excluded: 1) wells that were sampled only once; 2) wells where the maximum concentration occurred during the final event. This change was made to ensure that the evaluation focused on wells where an actual change in concentration was occurring, such that the effect of a co-contaminant on this change could actually be assessed.

Based on this evaluation, the following conclusions were reached for each compound:

- ***TCE:*** The presence of TCE had no apparent impact on 1,4-dioxane attenuation, meaning that similar OoM reductions (for both methods) were obtained for wells where this compound was absent.
- ***1,1-DCE:*** Like TCE, the presence of 1,1-DCE had no apparent impact on 1,4-dioxane attenuation. Slightly larger median OoM reductions (for both methods) were obtained for wells where 1,1-DCE was present, though this effect was not statistically significant. 1,1-DCE is a known inhibitor of 1,4-dioxane biodegradation (both growth-supporting and cometabolic; Mahendra et al., 2013; Zhang et al., 2016), meaning that this pattern would not be expected if biodegradation was the dominant attenuation mechanism.
- ***1,1-DCA:*** A higher median 1,4-dioxane OoM reduction was observed when 1,1-DCA was present. However, this effect was only statistically significant using data from one of the two methods for calculating the OoM reduction in 1,4-dioxane.
- ***VC:*** The presence of VC had a significantly negative impact on 1,4-dioxane attenuation. Of the compounds that were evaluated, it was the only one that resulted in lower 1,4-dioxane OoM reductions when it was present. The fact that this effect was also statistically significant serves as evidence that it offsets any bias that site-specific management decisions have on these datasets (e.g., sites where a compound has been detected are more likely to spur aggressive remedial action and thus lead to higher OoM reductions). There are at least two possible explanations for the negative effect of VC: (1) inhibition of 1,4-dioxane biodegradation by VC; and (2) VC presence is associated

with anaerobic conditions (via reductive dechlorination), which are unlikely to support 1,4-dioxane attenuation based on known degradation pathways (aerobic). The latter explanation is consistent with the existing conceptual model for 1,4-dioxane attenuation; the former explanation has yet to be established in the scientific literature but would not be unexpected based on 1,4-dioxane inhibition by other chlorinated solvents.

- ***TCA:*** Higher 1,4-dioxane OoM reductions were observed in wells where TCA was present, and this effect was statistically significant. This pattern conflicts with known evidence that TCA inhibits several aerobic biodegradation pathways for 1,4-dioxane (Mahendra et al., 2013). Based on existing evidence, it is unlikely that the presence of TCA provides any benefit or stimulation of 1,4-dioxane biodegradation. The presence (or absence) of degradation products at these TCA sites is also unlikely to be a significant contributor, based on the relatively minor impact of 1,1-DCA and 1,1-DCE on 1,4-dioxane OoM reductions. More likely explanations lie with differences between sites where TCA is present and sites where TCA is absent. For example, anaerobic conditions may predominate at wells where TCA is absent; these conditions would support reductive dechlorination (and hydrolysis) of TCA but would not support 1,4-dioxane attenuation.

Air Force dataset: As noted above, the Air Force dataset provided a unique ability to evaluate factors that influenced attenuation because it contained extensive well-specific information that was not available for the GeoTracker dataset. Linear discriminant analysis was used to screen parameters and ultimately quantify significant canonical correlation between several factors and the presence of 1,4-dioxane attenuation. In this case, a linear combination of dissolved oxygen, all metals evaluated, and the chlorinated ethenes resulted in the most significant discriminant function ($p = 0.022$). **Figure 31** shows the standardized canonical structure. The largest effect was observed for dissolved oxygen and resulted in a positive correlation (i.e., 1,4-dioxane attenuation was correlated with increasing dissolved oxygen concentrations). CVOCs and metals were both negatively correlated and were the second and third-ranked effects, respectively. In this evaluation, excluding the chlorinated ethanes from the CVOCs improved the magnitude and statistical-significance of the effect.

Given that similar effects have been noted in lab-based studies (e.g., Pornwongthong e al., 2014), the results provide field-based evidence that support expected fate and transport patterns for 1,4-dioxane. **In particular, the results suggest that the biological degradation is a major contributor to the observed attenuation.** This is because higher dissolved oxygen concentrations serve to promote aerobic biodegradation of 1,4-dioxane, while there is little evidence that anaerobic pathways exist. In addition, metals and CVOCs have been shown to inhibit 1,4-dioxane biodegradation, meaning that the presence of 1,4-dioxane attenuation would be expected to be negatively correlated to higher concentrations of these compounds. It was surprising to note that the negative correlation for CVOCs was improved by excluding the chlorinated ethanes. Several studies have shown that TCA can inhibit both cometabolic and metabolic 1,4-dioxane degradation pathways (Mahendra et al., 2013; Zhang et al., 2016). No negative association between the presence of TCA and site-wide attenuation metrics could be established using the GeoTracker dataset either. The initial TCA concentrations (C_0) at the wells included in this study were generally lower than reported values for the TCA inhibition coefficient (K_I) for 1,4-dioxane degradation (approximately 30 to 500 μg/L based Mahendra et al., 2013 and Zhang et al., 2016). This minimized the potential inhibitory effects of TCA (and potentially other chlorinated solvents like 1,1-DCE). Further, Zhang et al. (2016) confirmed that TCA was much less inhibitory to 1,4-dioxane biodegradation than the chlorinated ethenes (particularly 1,1-DCE) when CVOCs and 1,4-dioxane are both present.

Significant differences in mean half-life values were also observed, including a significant main effect was observed for the 1,4-dioxane C_0 values as categorized by quartile ($p = 0.030$). **Figure 32** shows the mean half-lives among the C_0 quartiles. Slower attenuation (larger half-lives) occurred within the inner-quartile concentration range (4.6 to 16 μg/L), while faster 1,4-dioxane attenuation (smaller half-lives) was observed at the lowest (first quartile) and highest (fourth quartile) C_0 values, whereas. This pattern suggests that low and high concentration environments favor the development of 1,4-dioxane attenuation capabilities is associated with high and low concentration environments. If biodegradation was assumed to be the responsible attenuation mechanism, then only the concentrations falling in the highest quartile range would the estimated saturation coefficient (K_S) value that has been reported for *P. dioxanivorans* strain CB1190 (approximately 160 mg/L based on Mahendra et al., 2006) Saturation coefficients for 1,4-dioxane co-metabolizing organisms are reportedly one order of magnitude lower than for the 1,4-dioxane-metabolizing *P. dioxanivorans* strain CB1190 (Mahendra et al., 2013). Based on the available information, the concentration effect noted in the Air Force data may be associated preferential growth and activity of these different indigenous 1,4-dioxane-degrading populations. Note that these results differ from those in Table 23, where no concentration effect was noted for 1,4-dioxane in the GeoTracker data. However, the 1,4-dioxane concentrations in the latter evaluation were much larger than those in the Air Force evaluation, and this may have masked any effect that occurs nearer to threshold values.

Table 21a. Results of Correlation Analyses for OoM Reduction (Method 1)

				Linear Regression (parametric)				**Spearman's Test (non-parametric)**	
Independent Variable	**Units**	**Log Transform ?**	**n**	**R^2**	**Slope**	**p-value**	**y-intercept**	**Rho**	**p-value**
Hydraulic conductivity	ft/d	Yes	14	0.18	0.299	0.129	0.423	0.12	0.680
Max. 1,4-dioxane Conc.	µg/L	Yes	59	0.003	0.027	0.704	0.612	0.08	0.552
Max. TCA Conc.	µg/L	Yes	46	0.05	0.075	0.129	0.567	0.28	0.057
Max. Chlorinated Solvent Conc.	µg/L	Yes	58	0.03	0.085	0.217	0.444	0.18	0.172
Redox State	(Categorical)	No	44	0.008	0.059	0.573	0.611	0.10	0.499
Soil Type	(Categorical)	No	54	0.01	-0.084	0.383	0.817	-0.13	0.339
P&T System Present	(Categorical)	No	59	0.007	-0.095	0.519	0.728	-0.05	0.716
In Situ Bioremed.	(Categorical)	No	59	0.04	-0.303	0.116	0.712	-0.22	0.084
In Situ Chem. Ox.	(Categorical)	No	59	0.0008	0.040	0.827	0.646	0.09	0.484
Dioxane k_{source} (all values)	yr^{-1}	No	52	0.10	-0.545	**0.025**	0.629	0.36	**0.008**
Dioxane k_{source} (all significant values)	yr^{-1}	No	16	0.23	-0.563	0.057	0.787	0.60	**0.014**
Dioxane k_{source} (all positive significant values)	yr^{-1}	No	12	0.49	2.739	**0.016**	0.041	0.61	**0.036**
Mann-Kendall Trend	(Categorical)	No	32	0.19	-0.271	**0.013**	0.917	-0.48	**0.006**
Time Between Historic Max and Recent Max Conc. (Method 1)	yr	Yes	59	0.009	0.132	0.482	0.638	0.28	**0.031**
Dioxane Plume Length	ft	Yes	50	0.009	0.121	0.508	0.338	0.09	0.523

Notes: (1) Bold values with yellow shading indicate that the statistical test indicates a significant relationship using one or more test; (2) Dependent variable is Order of Magnitude (OoM) Reduction estimated using Method 1 (see Table 2 for description of methods).

Table 21b. Results of Correlation Analyses for OoM Reduction (Method 2)

Independent Variable	Units	Log Transform ?	n	Linear Regression (parametric)				Spearman's Test (non-parametric)	
				R^2	Slope	p-value	y-intercept	Rho	p-value
Hydraulic conductivity	ft/d	Yes	23	0.17	0.313	**0.048**	0.563	0.30	0.168
Max. 1,4-dioxane Conc.	µg/L	Yes	95	0.02	0.092	0.154	0.581	0.03	0.806
Max. TCA Conc.	µg/L	Yes	70	0.02	0.064	0.218	0.709	0.28	**0.018**
Max. Chlorinated Solvent Conc.	µg/L	Yes	94	0.0008	0.017	0.782	0.773	0.09	0.392
Redox State	(Categorical)	No	74	0.0008	0.027	0.815	0.804	-0.03	0.807
Soil Type	(Categorical)	No	88	0.0009	-0.029	0.779	0.880	0.02	0.891
P&T System Present	(Categorical)	No	95	0.02	0.214	0.182	0.749	0.15	0.135
In Situ Bioremed.	(Categorical)	No	95	0.02	-0.241	0.208	0.825	-0.02	0.815
In Situ Chem. Ox.	(Categorical)	No	95	0.03	0.336	0.078	0.734	0.18	0.082
Dioxane k_{source} (all values)	yr^{-1}	No	80	0.03	0.429	0.135	0.804	0.29	**0.009**
Dioxane k_{source} (all significant values)	yr^{-1}	No	23	0.01	0.260	0.629	1.168	0.37	0.080
Dioxane k_{source} (all positive significant values)	yr^{-1}	No	17	0.11	1.338	0.199	0.731	0.44	0.070
Mann-Kendall Trend	(Categorical)	No	52	0.01	-0.126	0.449	1.000	-0.34	**0.013**
Time Between Historic Max and Recent Max Conc. (Method 2)	yr	Yes	95	0.04	0.366	0.056	0.714	0.30	**0.0028**
Dioxane Plume Length	ft	Yes	74	0.0001	0.017	0.930	0.775	0.009	0.936

Notes: (1) Bold values with yellow shading indicate that the statistical test indicates a significant relationship using one or more test; (2) Dependent variable is Order of Magnitude (OoM) Reduction estimated using Method 2 (see Table 2 for description of methods).

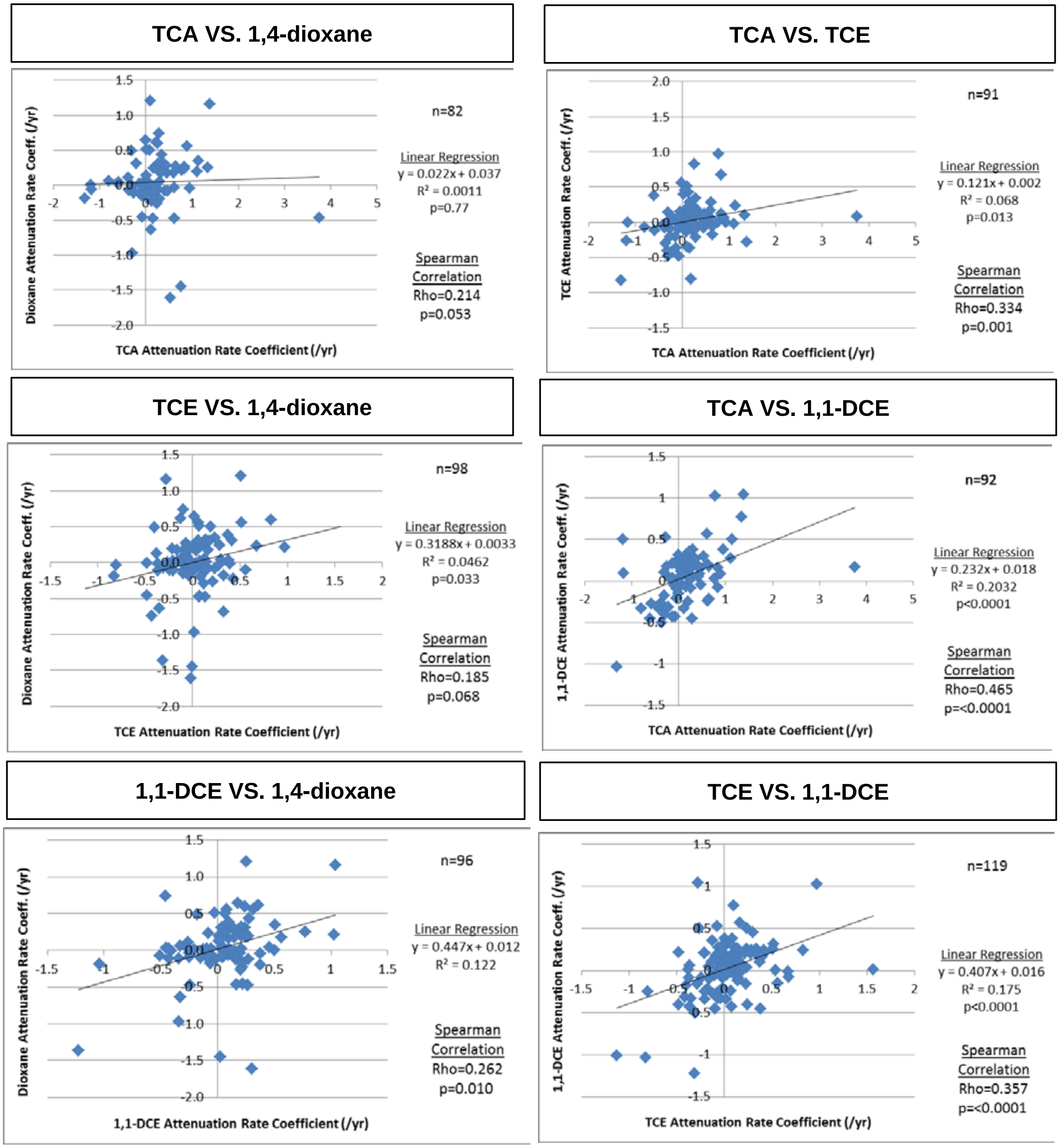
Table 22a. Results of Selected Correlation Analyses for All 1,4-Dioxane Source Attenuation Rate Coefficients (k_{source})

Independent Variable	Units	Log Transform ?	n	Linear Regression (parametric)				Spearman's Test (non-parametric)	
				R^2	Slope	p-value	y-intercept	Rho	p-value
Hydraulic conductivity	ft/d	Yes	25	0.005	0.031	0.741	-0.117	-0.22	0.282
Max. 1,4-dioxane Conc.	µg/L	Yes	104	0.01	0.040	0.290	-0.084	0.09	0.375
Max. TCA Conc.	µg/L	Yes	80	0.00002	0.047	0.966	0.047	0.07	0.551
Max. Chlorinated Solvent Conc.	µg/L	Yes	105	0.0003	-0.006	0.868	0.038	0.02	**0.850**
Redox State	(Categorical)	No	80	4E-07	-0.0004	0.995	0.002	-0.06	0.616
Soil Type	(Categorical)	No	95	0.00008	0.0045	0.930	-0.022	0.06	0.576
P&T System Present	(Categorical)	No	104	0.05	0.183	**0.030**	-0.056	0.17	0.080
In Situ Bioremed.	(Categorical)	No	104	0.03	-0.160	0.102	0.042	-0.08	0.398
In Situ Chem. Ox.	(Categorical)	No	104	0.02	0.136	0.205	-0.017	0.05	0.585
TCA k_{source} (all values)	yr^{-1}	No	82	0.001	0.022	0.771	0.037	0.21	0.053
TCE k_{source} (all values)	yr^{-1}	No	98	0.05	0.319	**0.034**	0.003	0.18	0.068
1,1-DCE k_{source} (all values)	yr^{-1}	No	96	0.12	0.447	**0.0005**	0.012	0.26	**0.010**

Table 22b. Results of Selected Correlation Analyses for Statistically-Significant 1,4-Dioxane Source Attenuation Rate Coefficients (k_{source})

Independent Variable	Units	Log Transform ?	n	Linear Regression (parametric)				Spearman's Test (non-parametric)	
				R^2	Slope	p-value	y-intercept	Rho	p-value
Max. TCA Conc.	µg/L	Yes	28	0.07	0.088	0.171	0.044	0.20	0.311
Redox State	(Categorical)	No	25	1.3E-7	0.0003	0.999	0.161	-0.06	0.773
Soil Type	(Categorical)	No	25	0.014	-0.074	0.579	0.162	0.06	0.759
TCA k_{source} (all values)	yr^{-1}	No	28	0.003	-0.037	0.768	0.259	0.04	0.842
TCA k_{source} (all significant values)	yr^{-1}	No	13	0.034	-0.136	0.544	0.433	-0.31	0.297
TCE k_{source} (all values)	yr^{-1}	No	30	0.085	0.490	0.117	0.151	0.20	0.296
TCE k_{source} (all significant values)	yr^{-1}	No	15	0.19	0.446	0.106	0.1274	0.45	0.092
1,1-DCE k_{source} (all values)	yr^{-1}	No	31	0.32	0.775	**0.0009**	0.098	0.31	0.090
1,1-DCE k_{source} (all signif. values)	yr^{-1}	No	20	0.44	0.811	**0.001**	-0.026	0.42	0.063

Notes: (1) Bold values with yellow shading indicate that the statistical test indicates a significant relationship using one or more test; (2) Dependent variable is k_{source} values for 1,4-dioxane.


TCA VS. 1,4-dioxane

TCA VS. TCE

TCE VS. 1,4-dioxane

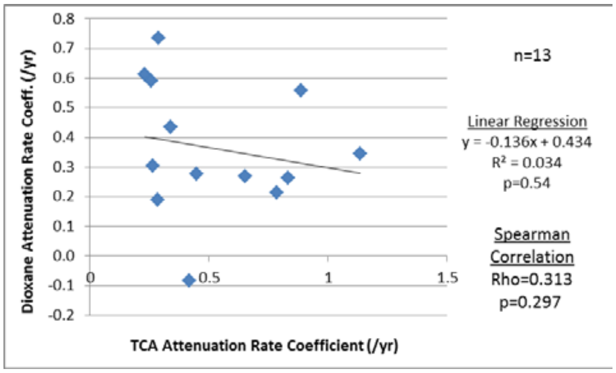
TCA VS. 1,1-DCE

1,1-DCE VS. 1,4-dioxane

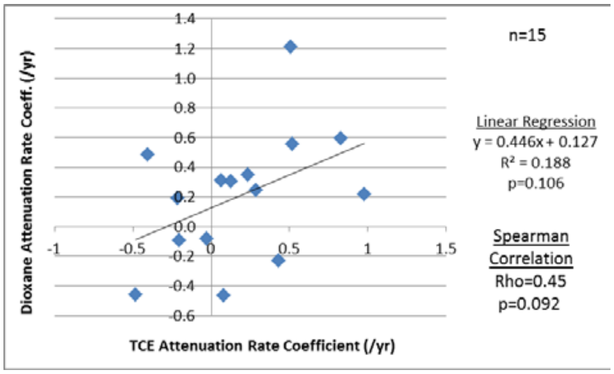
TCE VS. 1,1-DCE

Figure 29. Correlations Between Paired Site Attenuation Rate Coefficients (k_{source}) for 1,4-Dioxane, TCA, TCE, and 1,1-DCE

TCA VS. 1,4-dioxane



TCE VS. 1,4-dioxane



1,1-DCE VS. 1,4-dioxane

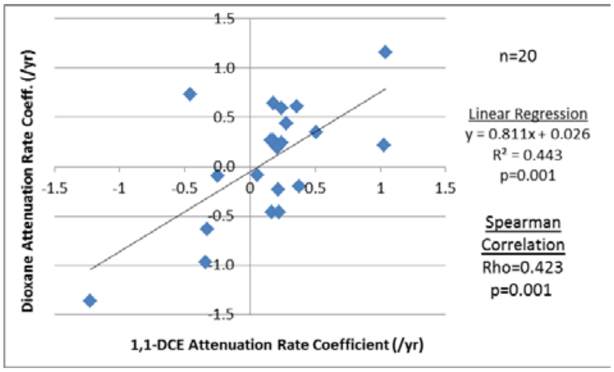


Figure 30. Correlations Between Paired, Statistically-Significant Site Attenuation Rate Coefficients (k_{source}) for 1,4-Dioxane, TCA, TCE, and 1,1-DCE

Table 23. Evaluation of Concentration Effects on Site Attenuation Rate Coefficients (k_{source}) for 1,4-Dioxane, TCA, TCE, and 1,1-DCE

Compound	**Median Concentration for Quartile Range (µg/L)**	**k_{source} (yr^{-1})**		**p-value for single-factor ANOVA** (**bold** if significant at $p<0.05$)
		Mean	**Median**	
Dioxane (n=22 sites)				
1st Quartile Concentrations	110	0.49	0.55	0.98
2nd Quartile Concentrations	1140	0.49	0.34	
3rd Quartile Concentrations	2750	0.50	0.31	
4th Quartile Concentrations	80,000	0.43	0.49	
TCA (n=113 sites)				
1st Quartile Concentrations	2.3	0.32	0.21	**0.000003**
2nd Quartile Concentrations	7.7	0.33	0.30	
3rd Quartile Concentrations	50	0.44	0.42	
4th Quartile Concentrations	905	0.81	0.65	
TCE (n=307 sites)				
1st Quartile Concentrations	3.1	0.24	0.22	**0.0006**
2nd Quartile Concentrations	25	0.33	0.24	
3rd Quartile Concentrations	220	0.31	0.24	
4th Quartile Concentrations	5000	0.43	0.33	
1,1-DCE (n=173 sites)				
1st Quartile Concentrations	1.8	0.26	0.19	0.18
2nd Quartile Concentrations	9.4	0.51	0.30	
3rd Quartile Concentrations	109	0.41	0.24	
4th Quartile Concentrations	2140	0.44	0.29	

Notes: (1) Evalulation included only statistically-significant positive k_{source} values for each compound; (2) Concentration ranges are based on the maximum historic concentration reported for each compound.

Table 24. Impact of Co-Occurring Chlorinated Solvents on OoM Reductions for 1,4-dioxane

	OoM Reduction: Method 1			**OoM Reduction: Method 2**		
	n	**Median OoM**	**p-value**	**n**	**Median OoM**	**p-value**
VC	414 wells	0.46	0.72	759 wells	0.42	**0.022**
No VC	553 wells	0.51		1157 wells	0.47	
1,1-DCA	713 wells	0.51	0.31	1344 wells	0.48	**0.042**
No 1,1-DCA	254 wells	0.45		571 wells	0.40	
TCA	296 wells	0.60	**0.0001**	659 wells	0.59	**7.2E-6**
No TCA	666 wells	0.45		1246 wells	0.40	
TCE	798 wells	0.49	0.87	1549 wells	0.46	0.57
No TCE	169 wells	0.45		367 wells	0.43	
1,1-DCE	723 wells	0.51	0.51	1430 wells	0.46	0.26
No 1,1-DCE	239 wells	0.45		473 wells	0.43	

Notes: (1) Differences between groups evaluated using Wilcoxon Rank Sum test as a non-parametric method (two-tailed; significance based on p-value < 0.05); (2) Method 1 uses the concentration measured in 2013 as the recent concentration; Method 2 uses the most recent concentration measured (2013 or earlier) as the recent concentration; (3) Include no wells that were only sampled once or where the maximum concentration was the most recent concentration; (4) For wells where the most recent concentration is nondetect, a value equal to half the median reporting limit was substituted (see Table 4).

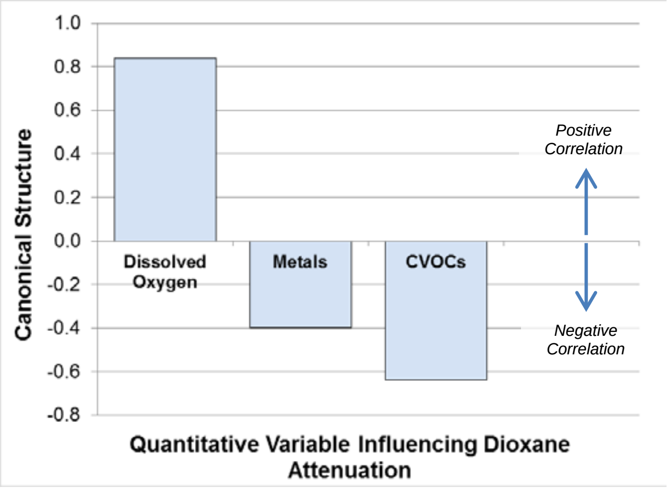


Figure 31. Linear Discriminant Analysis of Variables Influencing 1,4-dioxane Attenuation. Categorical response variable was wells with significant 1,4-dioxane attenuation vs. wells with no significant trend. Relative order of magnitude for this set of wells was concentrations of dissolved oxygen, CVOCs, and metals. Analysis completed on Air Force dataset by Hunter Anderson (AFCEC). Originally published in Adamson et al. (2015).

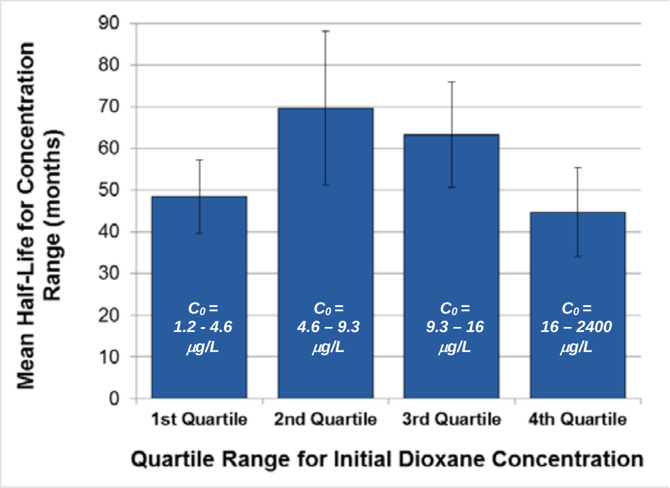


Figure 32. Influence of Initial 1,4-Dioxane Concentration on Attenuation Half-Lives for 1,4-Dioxane. Includes only those wells where statistically-significant positive rate could be established. Error bars display standard error. Analysis completed on Air Force dataset by Hunter Anderson (AFCEC). Originally published in Adamson et al. (2015).

4.1.6 Case Studies

Graphical presentations of the nine different case studies are presented in **Figures 33** through **Figure 40** (sites SL209154190 and SL0607396081 are combined because they are adjacent properties). In each case, the plume extent, individual well stability trends, and attenuation patterns are documented. A summary of the concentration trends for the entire set of monitoring wells at these sites is included in **Table 25**. Mass and plume trends are summarized in **Table 26**; this table includes trends for 11 different groundwater-bearing units at the nine different sites that were evaluated.

This evaluation included a wide range of different sites, including: 1) sites with and without apparent 1,4-dioxane attenuation; 2) sites with 1,4-dioxane plumes that are shorter, longer, or the same as chlorinated solvent plumes; 3) sites with 1,4-dioxane and/or chlorinated solvent plume shrinkage over time; and 4) sites with remediation efforts that have helped to manage 1,4-dioxane contamination.

While these nine sites are not intended to be representative of all sites with 1,4-dioxane, they do illustrate that 1,4-dioxane behavior in the environment can vary and may not necessarily follow expected patterns based on its physical-chemical properties. For example, the trend data in **Table 25** demonstrate that 1,4-dioxane well trends are largely similar to those for 1,1-DCE and relatively similar to those for TCE. In wells where trends could be established, the majority were characterized by stable or decreasing 1,4-dioxane concentration trends.

Table 25. Summary of Individual Well Concentration Trends for Sites Included in 1,4-Dioxane Case Studies

Trend	Total Number of Wells			
	Dioxane	**TCA**	**TCE**	**1,1-DCE**
Decreasing/Probably Decreasing	41	29	39	55
Increasing/Probably Decreasing	12	4	15	9
Stable	57	29	87	47
No Trend	44	29	36	45
Non-Detect	22	102	39	49
Not Applicable/Insufficient Data	62	50	61	59

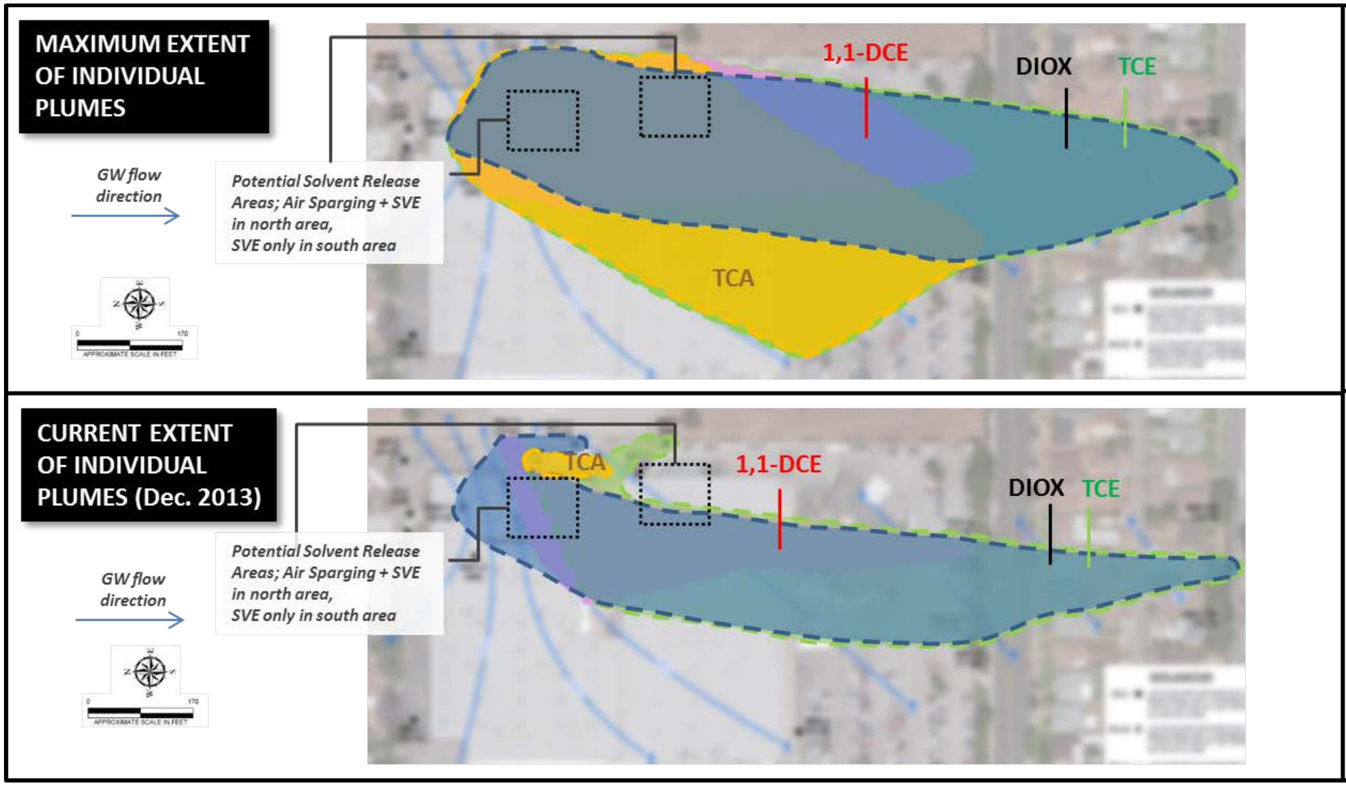
Notes: (1) All trend analyses represent the results of Mann-Kendall analysis completed using MAROS v. 3.0 (AFCEC, 2013); (2) Four or more data records are needed to complete the analysis; wells that did not meet this criteria are included in “Not Applicable/Insufficient Data” along with well where the compound was not analyzed.

Table 26. Summary of Site-Wide Trends for Sites Included in 1,4-Dioxane Case Studies

Trend	Total Number of Sites			
	Dioxane	**TCA**	**TCE**	**1,1-DCE**
Change in Mass Over Time (Zero Moment)				
Decreasing/Probably Decreasing	2	1	4	3
Increasing/Probably Decreasing	1	1	0	1
Stable	4	4	5	7
No Trend	4	3	2	0
Change in Center of Mass Over Time (Zero Moment)				
Decreasing/Probably Decreasing	4	2	2	4
Increasing/Probably Decreasing	2	1	3	2
Stable	3	2	4	1
No Trend	2	4	2	4
Spread of Plume Over Time (Second Moment, x-direction)				
Decreasing/Probably Decreasing	2	3	3	1
Increasing/Probably Decreasing	2	3	2	5
Stable	4	2	3	2
No Trend	3	1	3	3
Spread of Plume Over Time (Second Moment, x-direction)				
Decreasing/Probably Decreasing	1	3	1	0
Increasing/Probably Decreasing	3	4	7	6
Stable	4	0	1	1
No Trend	3	2	3	4

Notes: (1) For the 9 sites included as case studies, 2 had sufficient data to complete trend analyses for 2 different groundwater-bearing zones. Therefore, the total lists results for 11 sites; (2) All trend analyses represent the results of Mann-Kendall analysis completed using MAROS v. 3.0 (AFCEC, 2013).

Site SL184321415: This represents a site where the 1,4-dioxane plume is similar to the TCE plume, with little or no shrinkage over time, but where there is evidence of 1,4-dioxane attenuation. The other chlorinated solvents that were evaluated (TCA and 1,1-DCE) had smaller plume footprints, with the current TCA plume much smaller than the historical extent of TCA detections. There is evidence that the 1,4-dioxane plume has been expanding (its arrival was only recently noted at the farthest downgradient well), such that it has "caught up" with TCE that was likely part of an earlier release. However, 1,4-dioxane appears to be attenuating based on the decreasing mass trend and numerous wells with decreasing concentration trends. This may be attributable to the implementation of air sparging in the source area in 2011. The large k_{source} value for 1,4-dioxane, along with the decreasing 1,4-dioxane concentration trends noted in the center of the plume, are consistent with treatment of the 1,4-dioxane source.. The current maximum 1,4-dioxane concentration is no longer encountered in the source area. Outside of the air sparging area, redox conditions are largely anaerobic. This includes areas where decreasing concentration trends can be established. As noted above, these trends are likely attributable to source treatment, such that they do not necessarily provide evidence of 1,4-dioxane attenuation in anaerobic conditions. Relative to the predominantly decreasing trends for 1,4-dioxane, a larger percentage of the TCE concentration trends are stable.



MASS TRENDS (Mann-Kendall)

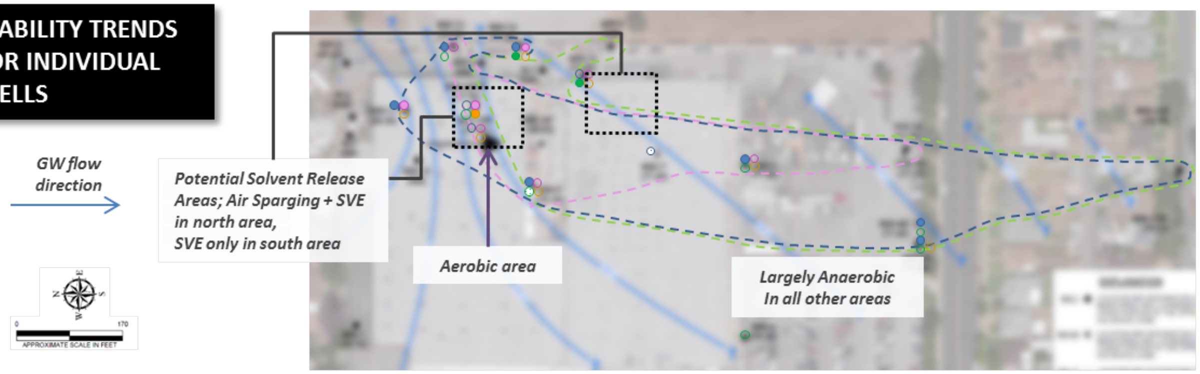
DIOXANE = DECREASING
1,1-DCE = STABLE
TCE = NO TREND
TCA = STABLE

KEY FINDINGS

- Dioxane and TCE plumes similar in size and exhibit only moderate shrinkage relative to other chlorinated solvents.
- Recent dioxane arrival (< 1 µg/L) at far downgradient well (2013).
- Decreasing dioxane mass trend suggests dioxane may be attenuating.
- Stable TCA mass trend is due to very low initial TCA mass.

Figure 33a. Summary of Site SL184321415: Plume Extent

STABILITY TRENDS FOR INDIVIDUAL WELLS



GW flow direction

Potential Solvent Release Areas; Air Sparging + SVE in north area, SVE only in south area

Aerobic area

Largely Anaerobic In all other areas

TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (7 wells)
- ○ Stable (2 wells) or No Trend (1 well)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (10 wells)

TCE:
- ● Decreasing (2 wells)
- ○ Stable (5 wells) or No Trend (3 wells)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (16 wells)

TCA:
- ● Decreasing (1 well)
- ○ Stable (4 wells) or No Trend (4 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (18 wells)

1,1-DCE:
- ● Decreasing (3 wells)
- ○ Stable (3 wells) or No Trend (3 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (18 wells)

KEY FINDINGS

- Decreasing dioxane trends throughout majority of site.
- Insufficient data to assess dioxane stability at two downgradient wells where concentrations have been recently increasing.
- Chlorinated solvents trends are more stable than dioxane.
- Increasing dioxane trend in well in center of plume is associated with deeper unit (not included in air sparging design).
- Air sparging (2011--) targets CVOCs but may have also reduced dioxane concentrations as evidenced by declining trends in center of plume.
- Insufficient data to establish trends in air sparigng wells but short-term CVOC concentration reduction have been observed.
- Redox state is still largely anaerobic outside of air sparging area.

Figure 33b. Summary of Site SL184321415: Stability Trends

ATTENUATION PATTERNS

Only wells screened across entire shallow unit were considered

SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 1.2

k_{source} (based on C vs. t) = 0.27 yr^{-1}

$k_{distance}$ (based on C vs. d) = 0.0095 ft^{-1}

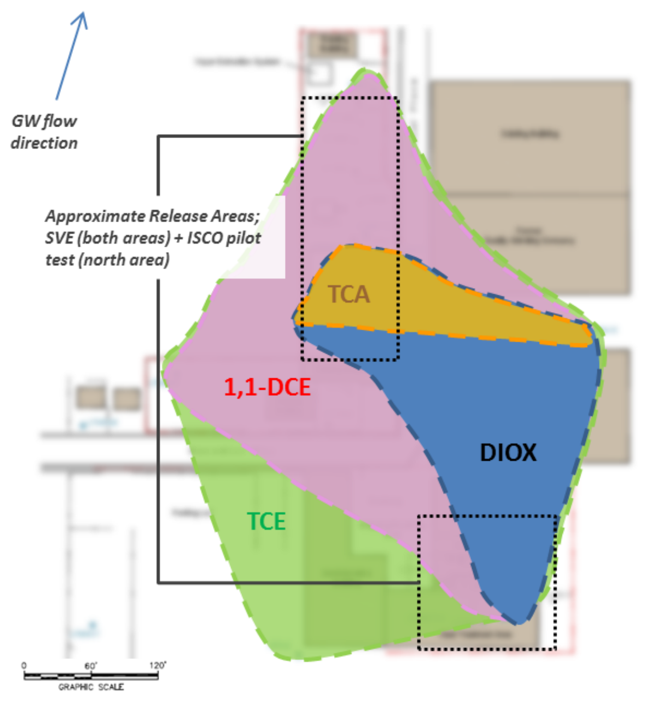
KEY FINDINGS

- Significant dioxane attenuation with time and distance is apparent.
- Current maximum concentration for dioxane is located farther downgradient from historic maximum concentration, suggesting that either: 1) treatment has reduced dioxane source concentrations; or 2) elevated concentration "pulse" may be moving downgradient.
- Significant attenuation of chlorinated solvents has also been observed .

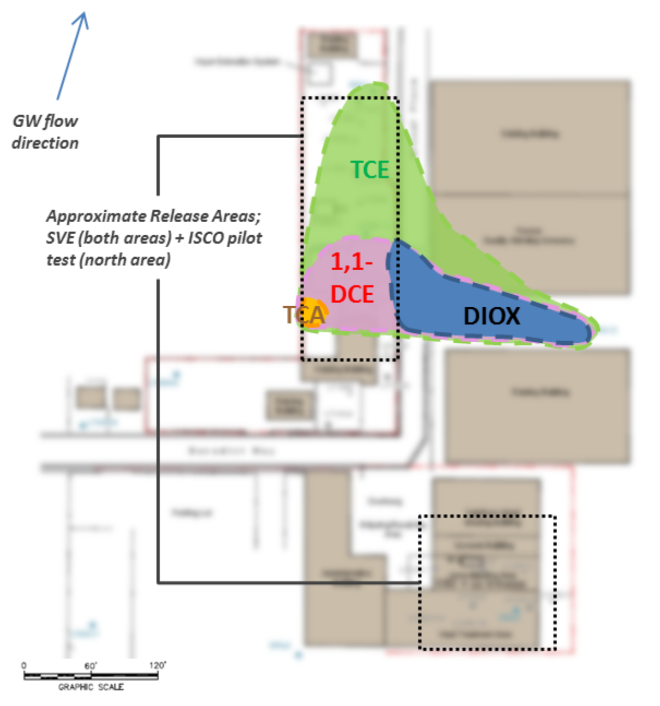
Figure 33c. Summary of Site SL184321415: Attenuation Patterns.

Site SL2043A1558: This represents a site where shrinkage of the 1,4-dioxane plume has been observed, with historic and current 1,4-dioxane plume footprints that are smaller than other chlorinated solvents. However, there is little evidence of potential 1,4-dioxane attenuation based on mass trends, rate coefficients, and individual well stability trends. It is likely that there are two source areas at the site, with possible influence from additional upgradient (off-site) sources. Because 1,4-dioxane concentrations have declined in the upgradient portions of the site at the same time that 1,4-dioxane concentrations were increasing (and then decreasing) in downgradient areas (along the eastern boundary). Therefore, it appears that 1,4-dioxane may be migrating, and that this migration may be responsible for the observed plume shrinkage. However, this has not resulted in downgradient expansion of the 1,4-dioxane plume, suggesting some degree of attenuation with distance. The chlorinated solvents are more clearly attenuating due to the decreasing mass trends that can be established for 1,1-DCE and TCE. Remediation efforts at this site (SVE and limited pilot-testing of ISCO) were not expected to have a significant impact on contaminant trends. As such, the observed patterns are largely attributable to natural attenuation. Redox conditions were not reported but are assumed to be largely anaerobic based on the presence of reductive dechlorination products throughout the site.

MAXIMUM EXTENT OF INDIVIDUAL PLUMES



CURRENT EXTENT OF INDIVIDUAL PLUMES (Dec. 2013)



MASS TRENDS (Mann-Kendall)

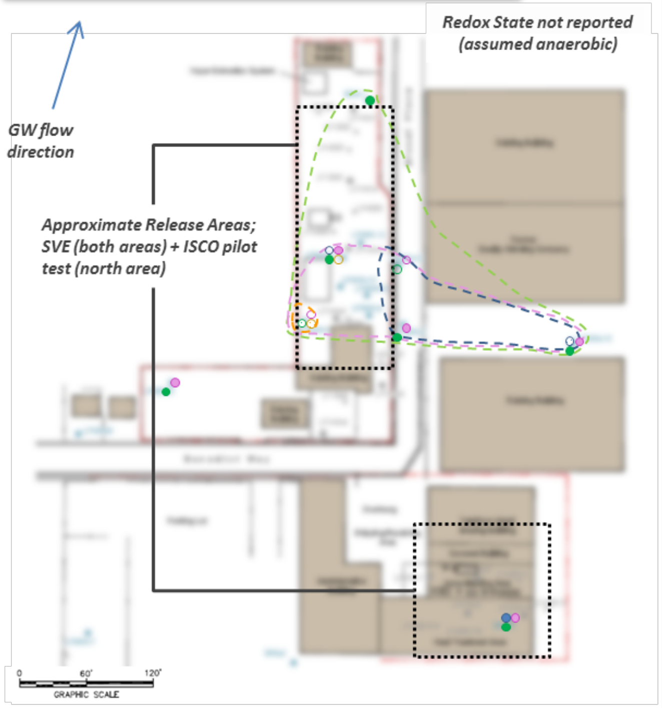
DIOXANE = STABLE
1,1-DCE = DECREASING
TCE = DECREASING
TCA = INCREASING

KEY FINDINGS

- Significant plume shrinkage of dioxane as well as chlorinated solvents.
- Stable dioxane mass trend suggests that dioxane plume shrinkage may not be attributable to destructive mechanisms.
- Increasing TCA mass trend is due to very low initial TCA mass.

Figure 34a. **Summary of Site SL2043A1558: Plume Extent**

STABILITY TRENDS FOR INDIVIDUAL WELLS



TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (1 well)
- ○ Stable (1 well) or No Trend (2 wells)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (6 wells)

TCA:
- ● Decreasing (0 wells)
- ○ Stable (1 well) or No Trend (0 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (9wells)

TCE:
- ● Decreasing (5 wells)
- ○ Stable (2 wells) or No Trend (0 wells)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (3 wells)

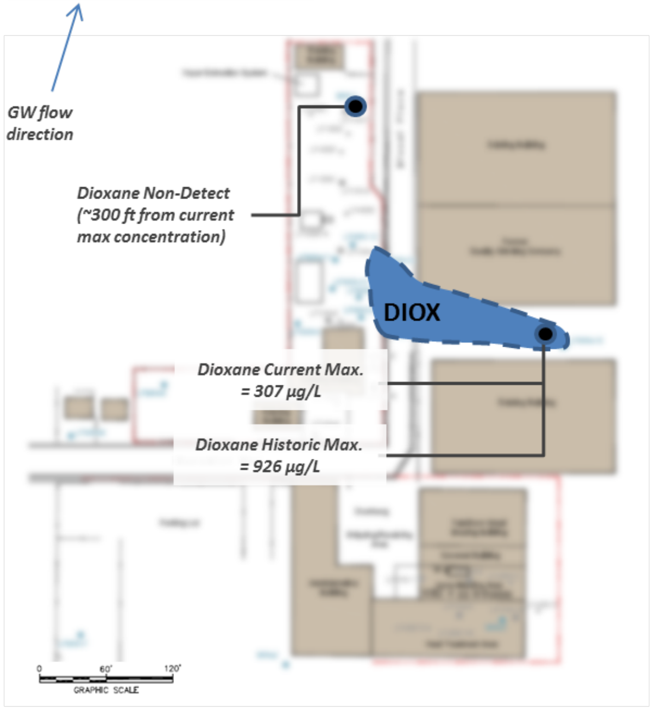
1,1-DCE:
- ● Decreasing (5 wells)
- ○ Stable (2 wells) or No Trend (0 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (4 wells)

KEY FINDINGS

- Decreasing dioxane and chlorinated solvent trends in upgradient areas.
- Increasing dioxane trend in well in eastern edge of plume appears to result from dioxane plume migrating through that portion of site. Concentrations have more recently begun to decline (consistent with decreasing trend observed in upgradient well).
- TCA detections are infrequent and low concentration—difficult to establish trends.
- TCE and 1,1-DCE are generally decreasing throughout the site.
- Limited impact expected from remediation—trends are likely related to natural attenuation
- Redox state not reported but assumed to be at least mildly anaerobic due to: 1) presence of 1,1-DCA and cDCE; and 2) reports that ISCO pilot test did not have lasting impact on redox.

Figure 34b. Summary of Site SL2043A1558: Stability Trends

ATTENUATION PATTERNS



GW flow direction

Dioxane Non-Detect (~300 ft from current max concentration)

Dioxane Current Max. = 307 µg/L

Dioxane Historic Max. = 926 µg/L

SUMMARY RESULTS FOR DIOXANE

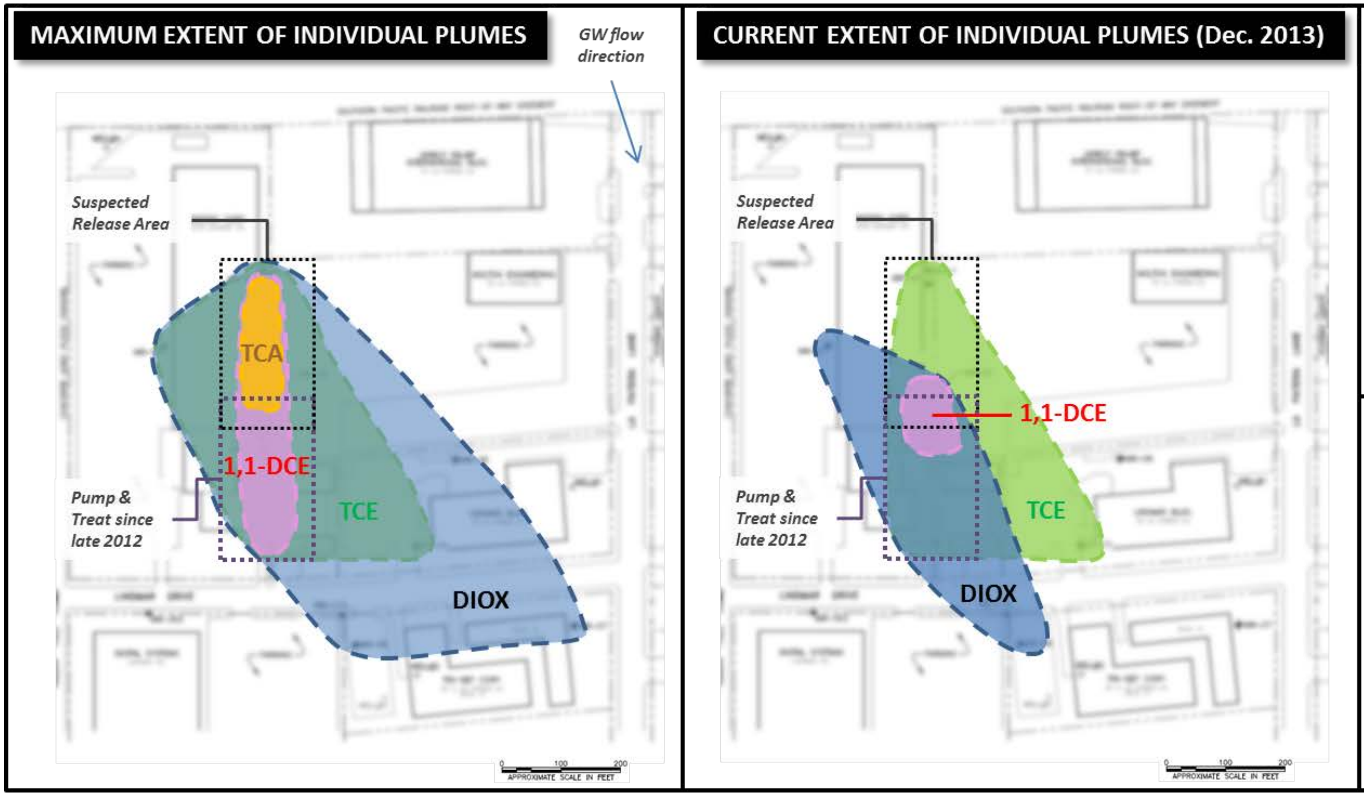
OoM Reduction = 0.47
k_{source} (based on C vs. t)
= -0.04 yr^{-1} (still increasing)
$k_{distance}$ (based on C vs. d)
= 0.012 ft^{-1}

KEY FINDINGS

- **Migration of dioxane plume through eastern portion of site resulted in slow increase in concentration followed by slow decrease in this area.**
- **Negative k_{source} value also reflects the initial rise in concentration at well with historic and current max.**
- **Significant dioxane attenuation with distance is apparent.**

Figure 34c. Summary of Site SL2043A1558: Attenuation Patterns

Site SL0608334912: This represents a site where the 1,4-dioxane plume has expanded farther than the co-occurring chlorinated solvents plume, with continued migration beyond a recently-installed pump-and-treat system. Only small amounts of TCA and 1,1-DCE were ever detected at the site, and the plumes for these compounds have either disappeared or shrunk considerably. The current extent of the TCE and 1,4-dioxane plumes is relatively similar with only moderate shrinkage. The temporal monitoring data are relatively limited, and the resulting attenuation parameters (mass trend, well stability, rate coefficients) provide little evidence of 1,4-dioxane attenuation. A decreasing trend for 1,4-dioxane is noted at the far downgradient monitoring well. However, the maximum historic and maximum current 1,4-dioxane concentrations are encountered in the toe of the current 1,4-dioxane plume. This suggests some additional migration of the plume but is consistent with the location of this monitoring well outside of the capture zone for the extraction wells. While the pump-and-treat system appears to be contributing to slow plume shrinkage, it is clear that a portion of the 1,4-dioxane mass will not be addressed by this remedial effort.



MAXIMUM EXTENT OF INDIVIDUAL PLUMES

CURRENT EXTENT OF INDIVIDUAL PLUMES (Dec. 2013)

MASS TRENDS (Mann-Kendall)

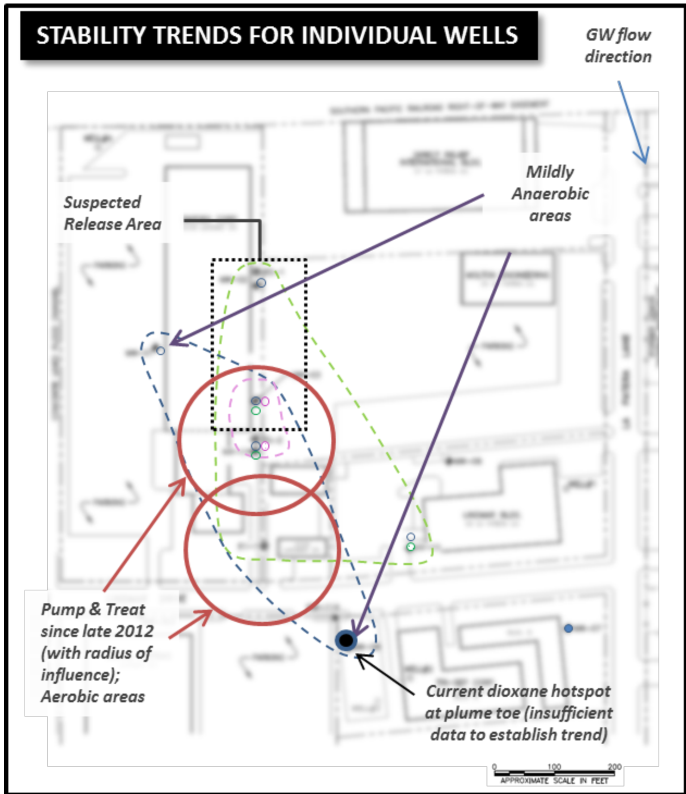
DIOXANE = NO TREND
1,1-DCE = INCREASING
TCE = STABLE
TCA = NON-DETECT/ INSUFFICIENT DATA

KEY FINDINGS

- Moderate plume shrinkage observed for dioxane and chlorinated solvents.
- No dioxane mass trend could be established but pump-and-treat may have contributed to plume shrinkage.
- Increasing 1,1-DCE mass trend is due to very low initial 1,1-DCE mass.

Figure 35a. **Summary of Site SL0608334912: Plume Extent**

STABILITY TRENDS FOR INDIVIDUAL WELLS



TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (1 well)
- ○ Stable (2 wells) or No Trend (3 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (5 wells)

TCA:
- (Not shown) Non-detect/insufficient data (all wells)

TCE:
- ● Decreasing (0 wells)
- ○ Stable (1 wells) or No Trend (1 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (8 wells)

1,1-DCE:
- ● Decreasing (0 wells)
- ○ Stable (0 wells) or No Trend (1 wells)
- ○ Increasing (1 wells)
- (Not shown) Non-detect/insufficient data (9 wells)

KEY FINDINGS

- Trends are largely stable for dioxane and chlorinated solvent in plume core areas. Temporal data are relatively limited.
- Decreasing trend for dioxane noted in far downgradient well.
- Current extent of dioxane plume outside of capture zone for pump & treat system and does not include dioxane hotspot.
- Increasing trend for TCE at toe of plume and increasing trend for 1,1-DCE near plume core.
- Plume core is aerobic (consistent with operation of pump & treat system), but upgradient and downgradient are at least mildly anaerobic.

Figure 35b. Summary of Site SL0608334912: Stability Trends

ATTENUATION PATTERNS

SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.0
k_{source} (based on C vs. t)
= 0.008 yr^{-1}
$k_{distance}$ (based on C vs. d)
= 0.00 ft^{-1}

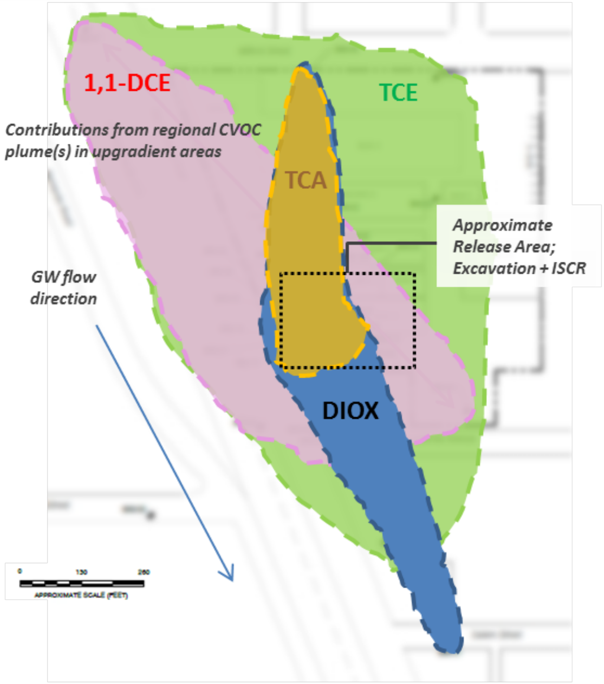
KEY FINDINGS

- No dioxane attenuation with time or distance is apparent.
- Concentrations at farthest downgradient monitoring point are slightly increasing over time.
- Dioxane hotspot is outside of pump & treat capture zone and may be migrating off-site

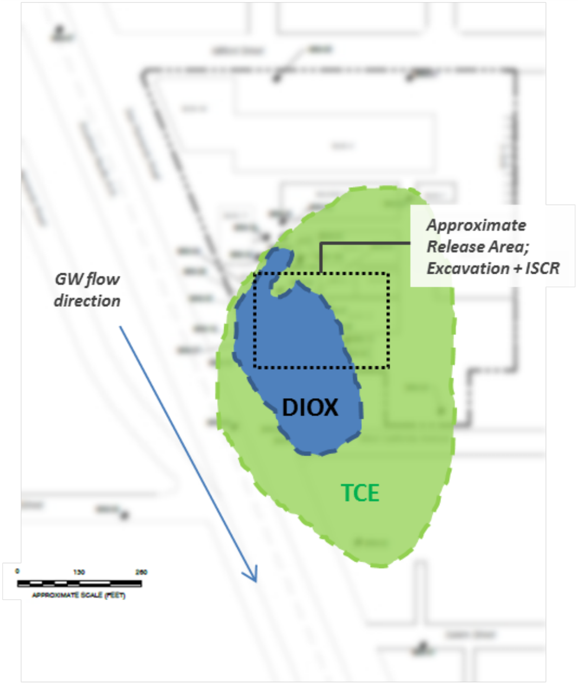
Figure 35c. Summary of Site SL0608334912: Attenuation Patterns

Site T0603704937: This represents a site where attenuation of 1,4-dioxane and chlorinated solvents appears to be occurring, but the potential contribution from off-site sources complicates interpretation of plume behavior. Historically, 1,4-dioxane has occupied a similar footprint to the TCE and 1,1-DCE plumes, with a much smaller TCA plume (suggesting rapid attenuation of TCA). Currently, the TCA and 1,1-DCE plumes are no longer present, and the 1,4-dioxane plume has shrunk to the extent that it is now shorter than the TCE plume. While the presence of off-site sources of these compounds are suspected because of historic detections far upgradient of the on-site release area, these off-site sources appear to have diminished based on the changes in the plume footprints and the decreasing concentration trends in upgradient areas. A decreasing mass trend was established for both 1,4-dioxane and 1,1-DCE, indicating that attenuation may have contributed to the plume shrinkage. Decreasing concentration trends for 1,4-dioxane and chlorinated solvents are also observed in a large number of wells in the source area. In situ chemical reduction has been implemented in an effort to treat the chlorinated solvents, and it appears that this has contributed to attenuation of 1,4-dioxane as well. Historically, 1,4-dioxane concentrations have been low at the site but the historic and current maximum concentrations are from wells located near the suspected on-site source. This argues that source treatment has played a role in the observed attenuation (i.e., it is not solely attributable to diminishing strength of the upgradient source). ISCR is not thought to be a viable technology for degrading 1,4-dioxane, so the benefit may be in reducing inhibition through the removal of co-occurring chlorinated solvents. Groundwater entering the site is aerobic, but reducing conditions have been established in the source/treatment zone and are largely maintained throughout the downgradient monitoring network.

MAXIMUM EXTENT OF INDIVIDUAL PLUMES



CURRENT EXTENT OF INDIVIDUAL PLUMES (Dec. 2013)



MASS TRENDS (Mann-Kendall)

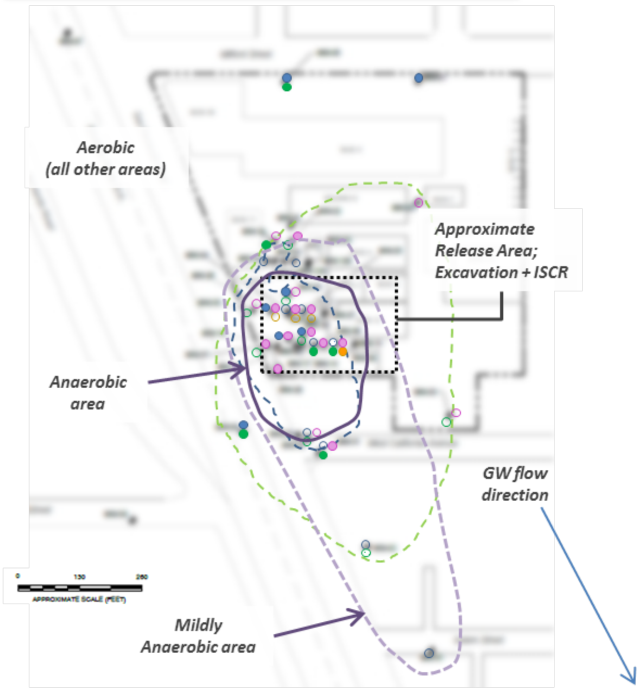
DIOXANE = DECREASING
1,1-DCE = DECREASING
TCE = STABLE
TCA = NO TREND

KEY FINDINGS

- Significant dioxane plume shrinkage as well as chlorinated solvents.
- Stable dioxane mass trend suggests that dioxane plume shrinkage may be due to destructive mechanisms.
- Stable TCA mass trend is due to very low initial TCA mass.
- Regional plumes contribute in areas up- and side-gradient

Figure 36a. Summary of Site T0603704937: Plume Extent

STABILITY TRENDS FOR INDIVIDUAL WELLS



TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (7 wells)
- ○ Stable (10 wells) or No Trend (9 wells)
- ○ Increasing (7 wells)
- (Not shown) Non-detect/insufficient data (2 wells)

TCA:
- ● Decreasing (1 wells)
- ○ Stable (3 wells) or No Trend (7 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (13 wells)

TCE:
- ● Decreasing (5 wells)
- ○ Stable (8 wells) or No Trend (5 wells)
- ○ Increasing (1 wells)
- (Not shown) Non-detect/insufficient data (4 wells)

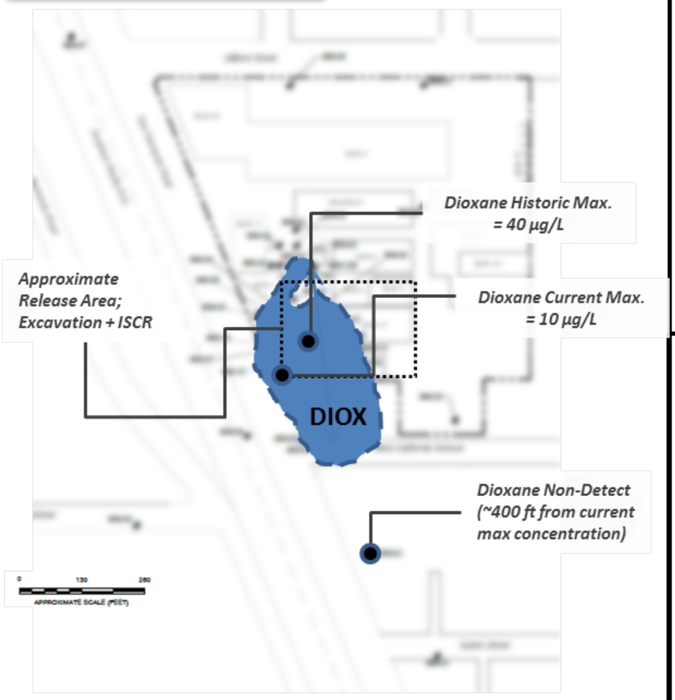
1,1-DCE:
- ● Decreasing (11 wells)
- ○ Stable (5 wells) or No Trend (1 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (7 wells)

KEY FINDINGS

- Decreasing dioxane and chlorianted solvent trends in upgradient and plume core areas.
- Higher incidence of stable and/or decreasing wells in downgradient area.
- Trends for dioxane are similar to those for chlorinated solvents in ISCR treatment area (largely decreasing).
- ISCR likely contributed to observed shrinkage in chlorinated solvent plumes. ISCR possibly contributed to dioxane plume shrinkage but decline in upgradient sources is a factor.
- Remaining plume cores associated with anaerobic area.

Figure 36b. Summary of Site T0603704937: Stability Trends.

ATTENUATION PATTERNS



SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.6

k_{source} (based on C vs. t) = 0.02 yr^{-1}

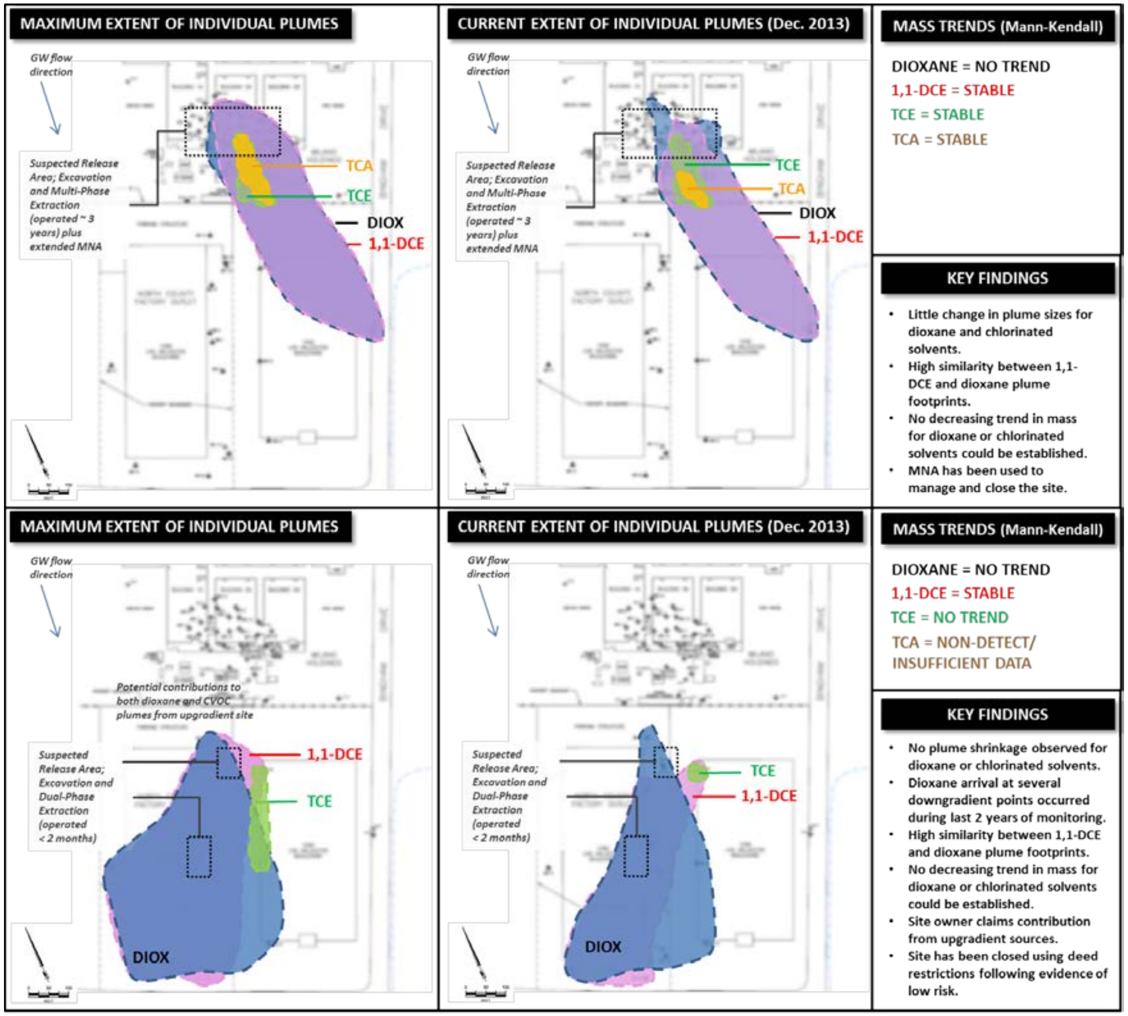
$k_{distance}$ (based on C vs. d) = 0.0068 ft^{-1}

KEY FINDINGS

- Significant dioxane attenuation with time and distance is apparent.

Figure 36c. Summary of Site T0603704937: Attenuation Patterns.

Site SL209154190 and Site SL0607396081: These two adjoining sites represent an example of sites with 1,4-dioxane in groundwater that were eventually closed. The sites share a boundary (SL209154190 to the north, SL0607396081 to the south and downgradient in the direction of groundwater flow) but have distinct ownership and operating histories. The northern site has generally had higher 1,4-dioxane concentrations and there was likely some downgradient migration of 1,4-dioxane that contributed to issues at the southern site. However, TCA was used at the southern site (though it has attenuated completely), such that there was likely a separate 1,4-dioxane source at this site. At both sites, the mass trend for 1,4-dioxane is stable, the individual well stability trends are largely stable, and changes in the source concentrations over time have been relatively modest. Despite this, there is significant evidence for attenuation with distance, such that 1,4-dioxane concentrations decrease to levels at or below reporting limits within the delineated downgradient areas. It is noteworthy that at both sites, the 1,4-dioxane plume extent is similar to the chlorinated solvent plumes, and that attenuation of the 1,4-dioxane plume occurs within a largely anaerobic area. Site reports for the northern site have documented 1,4-dioxane degradation in aerobic and anaerobic microcosms (with the latter attributed to abiotic and/or biotic mechanisms). While both sites used excavation and multi-phase/dual-phase extraction as source remedies, MNA was used to manage the plumes. The performance of this remedy was confirmed using the stability trends, although there is some evidence that the 1,4-dioxane plume has recently expanded at the southern site (dioxane detections at downgradient locations occurred in the last 2 years). Deed restrictions on groundwater consumption were established to ensure that any potential risk would be eliminated, and both sites were successfully closed in the past year with no further action required.



MASS TRENDS (Mann-Kendall)

DIOXANE = NO TREND
1,1-DCE = STABLE
TCE = STABLE
TCA = STABLE

KEY FINDINGS

- Little change in plume sizes for dioxane and chlorinated solvents.
- High similarity between 1,1-DCE and dioxane plume footprints.
- No decreasing trend in mass for dioxane or chlorinated solvents could be established.
- MNA has been used to manage and close the site.

MASS TRENDS (Mann-Kendall)

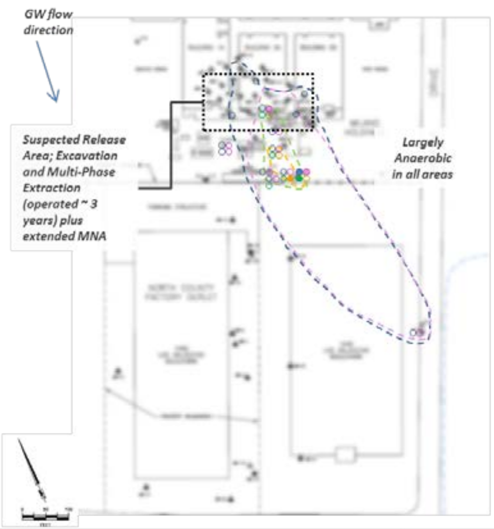
DIOXANE = NO TREND
1,1-DCE = STABLE
TCE = NO TREND
TCA = NON-DETECT/ INSUFFICIENT DATA

KEY FINDINGS

- No plume shrinkage observed for dioxane or chlorinated solvents.
- Dioxane arrival at several downgradient points occurred during last 2 years of monitoring.
- High similarity between 1,1-DCE and dioxane plume footprints.
- No decreasing trend in mass for dioxane or chlorinated solvents could be established.
- Site owner claims contribution from upgradient sources.
- Site has been closed using deed restrictions following evidence of low risk.

Figure 37a. Summary of Site SL209154190 and Site SL0607396081: Plume Extent.

STABILITY TRENDS FOR INDIVIDUAL WELLS



TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (1 well)
- ○ Stable (8 wells) or No Trend (5 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (20 wells)

TCA:
- ● Decreasing (1 well)
- ○ Stable (1 well) or No Trend (1 well)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (32 wells)

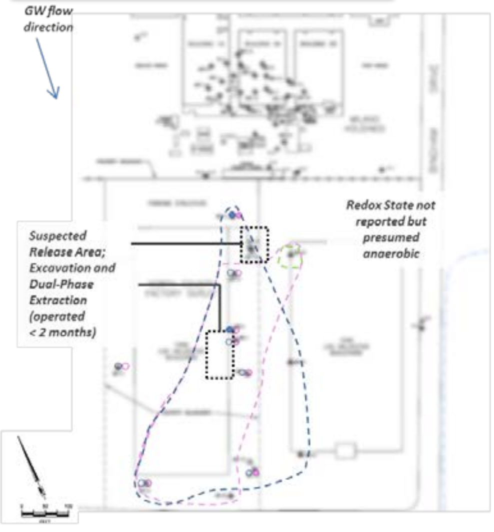
TCE:
- ● Decreasing (1 wells)
- ○ Stable (1 wells) or No Trend (2 wells)
- ○ Increasing (1 wells)
- (Not shown) Non-detect/insufficient data (31 wells)

1,1-DCE:
- ● Decreasing (2 wells)
- ○ Stable (3 wells) or No Trend (5 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (30 wells)

KEY FINDINGS

- Trends are largely stable or decreasing for dioxane and chlorinated solvents in source area.
- Stable trends for dioxane and 1,1-DCE noted in far downgradient well, consistent with plume stability.
- MNA has been used to manage and close site; remedy performance is confirmed by stability trends.
- Little impact on dioxane from other historic remedial efforts was expected or observed.
- Shallow groundwater bearing unit is largely anaerobic (particularly in source area) with methane detected. Deep unit is also largely anaerobic. Conditions are favorable for natural attenuation of chlorinated solvents.
- Site reports claim evidence for both aerobic and anaerobic degradation of dioxane (using 14C-labeled dioxane in bench-scale treatability tests).

STABILITY TRENDS FOR INDIVIDUAL WELLS



TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (2well)
- ○ Stable (3 wells) or No Trend (3 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (5 wells)

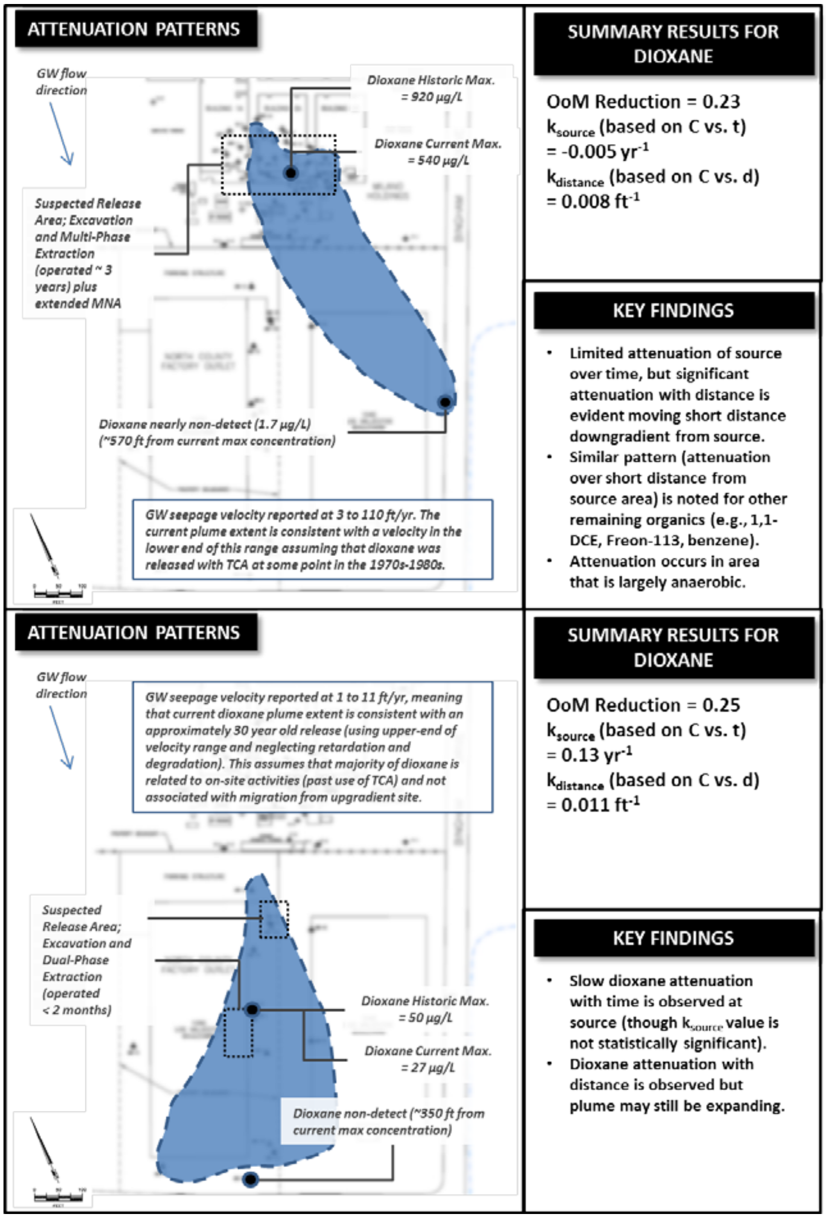
TCE:
- ● Decreasing (0 wells)
- ○ Stable (0 wells) or No Trend (0 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (13 wells)

1,1-DCE:
- ● Decreasing (2 wells)
- ○ Stable (5 wells) or No Trend (1 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (5 wells)

KEY FINDINGS

- Trends are largely stable or decreasing for dioxane and chlorinated solvent in source areas.
- Decreasing trends in upgradient areas suggest that any contributions from upgradient site are declining as well.
- Appropriateness of site closure is confirmed by stability trends, though no trend could be established at most downgradient wells.
- Little impact on dioxane from other historic remedial efforts was expected or observed.
- Reports contain no information on redox state but it is assumed that site is anaerobic due to proximity to another anaerobic site (to the north).
- TCA was used at site but is not detected. Low levels of 1,1-DCA are present. 1,1-DCE was not used at site but believed to originate from TCA degradation.

Figure 37b. **Summary of Site SL209154190 and Site SL0607396081: Stability Trends.**



GW seepage velocity reported at 3 to 110 ft/yr. The current plume extent is consistent with a velocity in the lower end of this range assuming that dioxane was released with TCA at some point in the 1970s-1980s.

SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.23

k_{source} (based on C vs. t) = $-0.005\ yr^{-1}$

$k_{distance}$ (based on C vs. d) = $0.008\ ft^{-1}$

KEY FINDINGS

- Limited attenuation of source over time, but significant attenuation with distance is evident moving short distance downgradient from source.
- Similar pattern (attenuation over short distance from source area) is noted for other remaining organics (e.g., 1,1-DCE, Freon-113, benzene).
- Attenuation occurs in area that is largely anaerobic.

GW seepage velocity reported at 1 to 11 ft/yr, meaning that current dioxane plume extent is consistent with an approximately 30 year old release (using upper-end of velocity range and neglecting retardation and degradation). This assumes that majority of dioxane is related to on-site activities (past use of TCA) and not associated with migration from upgradient site.

SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.25

k_{source} (based on C vs. t) = $0.13\ yr^{-1}$

$k_{distance}$ (based on C vs. d) = $0.011\ ft^{-1}$

KEY FINDINGS

- Slow dioxane attenuation with time is observed at source (though k_{source} value is not statistically significant).
- Dioxane attenuation with distance is observed but plume may still be expanding.

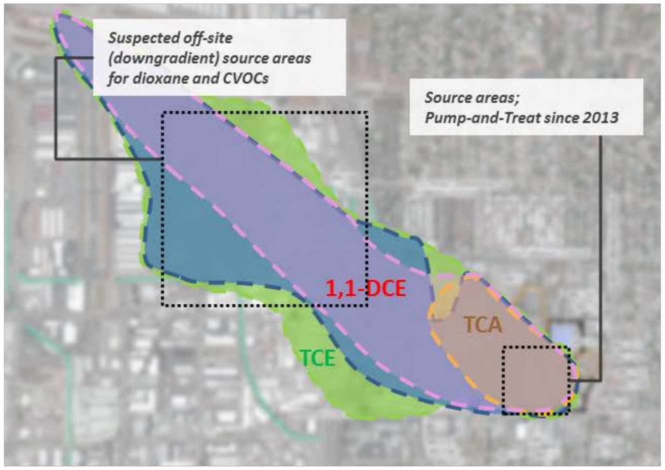
Figure 37c. Summary of Site SL209154190 and Site SL0607396081: Attenuation Patterns.

Site SL209234198: This represents a site where attenuation of 1,4-dioxane and chlorinated solvents in the source area appears to be occurring, but contribution from a suspected downgradient source contributes to a lack of plume shrinkage. The 1,4-dioxane plume extent is largely similar to those for TCE and 1,1-DCE, and all are currently at their historic maximum length. However, there is separate site located several thousand feet downgradient of the source area for this site that appears to have released 1,4-dioxane and chlorinated solvents. Despite evidence for source area attenuation at Site SL209234198 (based on the individual stability trends for wells located in the source area), the downgradient extent of the plume from this site overlaps with the source area of the off-site (downgradient) property. Consequently, it will be more difficult to establish plume shrinkage over time. A pump-and-treat has been operating within the source area of the site for the past year, but the decreasing trends for chlorinated solvents and 1,4-dioxane were established even before this system came on-line. There is little evidence for attenuation and/or decreasing trends in the off-site (downgradient) source, but slow 1,4-dioxane attenuation can be observed with both time and distance in the on-site source. Because the number of wells where 1,4-dioxane is being analyzed has increased over time, the mass trend for 1,4-dioxane was increasing.

MAXIMUM EXTENT OF INDIVIDUAL PLUMES

Shallow unit only

GW flow direction



Suspected off-site (downgradient) source areas for dioxane and CVOCs

Source areas; Pump-and-Treat since 2013

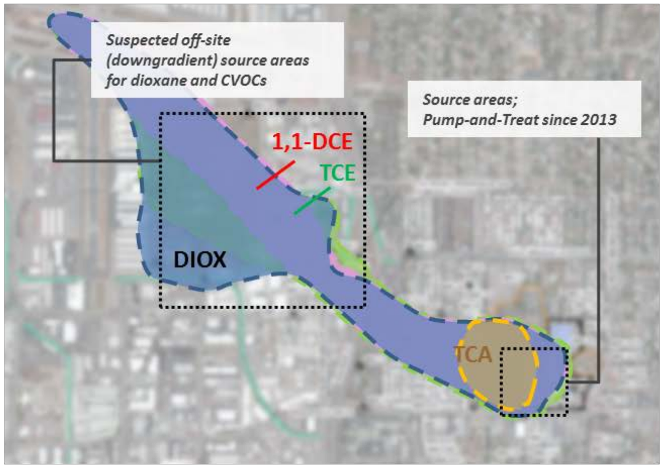
MASS TRENDS (Mann-Kendall)

DIOXANE = INCREASING
1,1-DCE = STABLE
TCE = DECREASING
TCA = STABLE

CURRENT EXTENT OF INDIVIDUAL PLUMES (Jan. 2014)

Shallow unit only

GW flow direction



Suspected off-site (downgradient) source areas for dioxane and CVOCs

Source areas; Pump-and-Treat since 2013

KEY FINDINGS

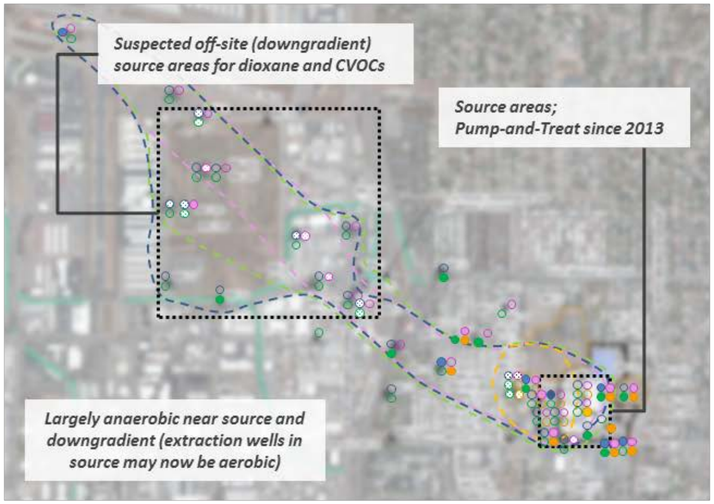
- Dioxane plume size is similar to TCE and 1,1-DCE plumes with little evidence of plume shrinkage over time.
- Evaluation of downgradient plume extent is hindered by suspected presence of off-site source.
- TCA plume is much smaller than other plumes. TCA mass trend is stable over period of evaluation (2004--), but data from earlier periods suggest decreasing trend.
- Increasing dioxane mass trend is artifact associated with higher number of wells included in more recent monitoring events.

Figure 38a. **Summary of Site SL209234198: Plume Extent.**

STABILITY TRENDS FOR INDIVIDUAL WELLS

Includes selected wells from all units (but not all wells)

GW flow direction



TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (10 wells)
- ○ Stable (24 wells) or No Trend (11 wells)
- ○ Increasing (6 well)
- (Not shown) Non-detect/insufficient data (18 wells)

TCE:
- ● Decreasing (13 wells)
- ○ Stable (25 wells) or No Trend (14 wells)
- ○ Increasing (7 wells)
- (Not shown) Non-detect/insufficient data (11 wells)

TCA:
- ● Decreasing (16 wells)
- ○ Stable (8 wells) or No Trend (5 wells)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (39 wells)

1,1-DCE:
- ● Decreasing (11 wells)
- ○ Stable (14 wells) or No Trend (13 wells)
- ○ Increasing (6 wells)
- (Not shown) Non-detect/insufficient data (25 wells)

KEY FINDINGS

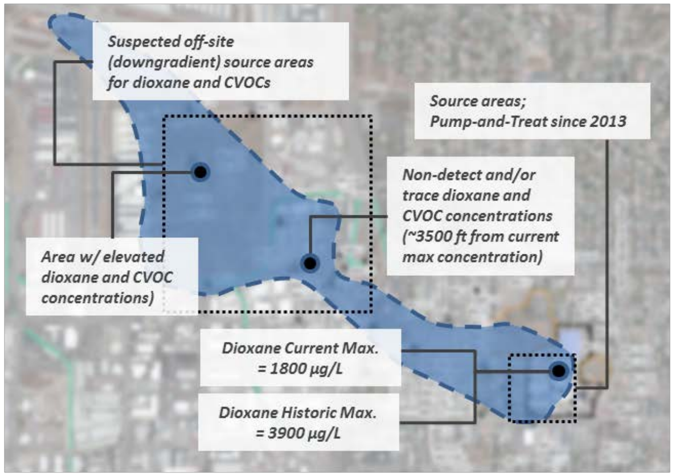
- Decreasing dioxane and chlorinated solvent trends throughout majority of source area.
- Increasing dioxane and chlorinated solvent trends are largely associated with downgradient off-site source areas that are unrelated to site activities. The exception are a few deeper wells (screened into underlying bedrock) in the on-site source area that show increasing trends for dioxane and chlorinated solvents.
- Stable trends tend to be observed outside of source areas.
- Trends were established prior to current remediation (full-scale pump-and-treat started in 2013).
- Near source and downgradient areas are anaerobic and has clearly contributed to TCA attenuation and possibly to attenuation of other chlorinated solvents.
- Source area near extraction wells may now be aerobic following startup of pump-and-treat system.

Figure 38b. **Summary of Site SL209234198: Stability Trends.**

ATTENUATION PATTERNS

Shallow unit only

GW flow direction



SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.3

k_{source} (based on C vs. t) = 0.13 yr^{-1}

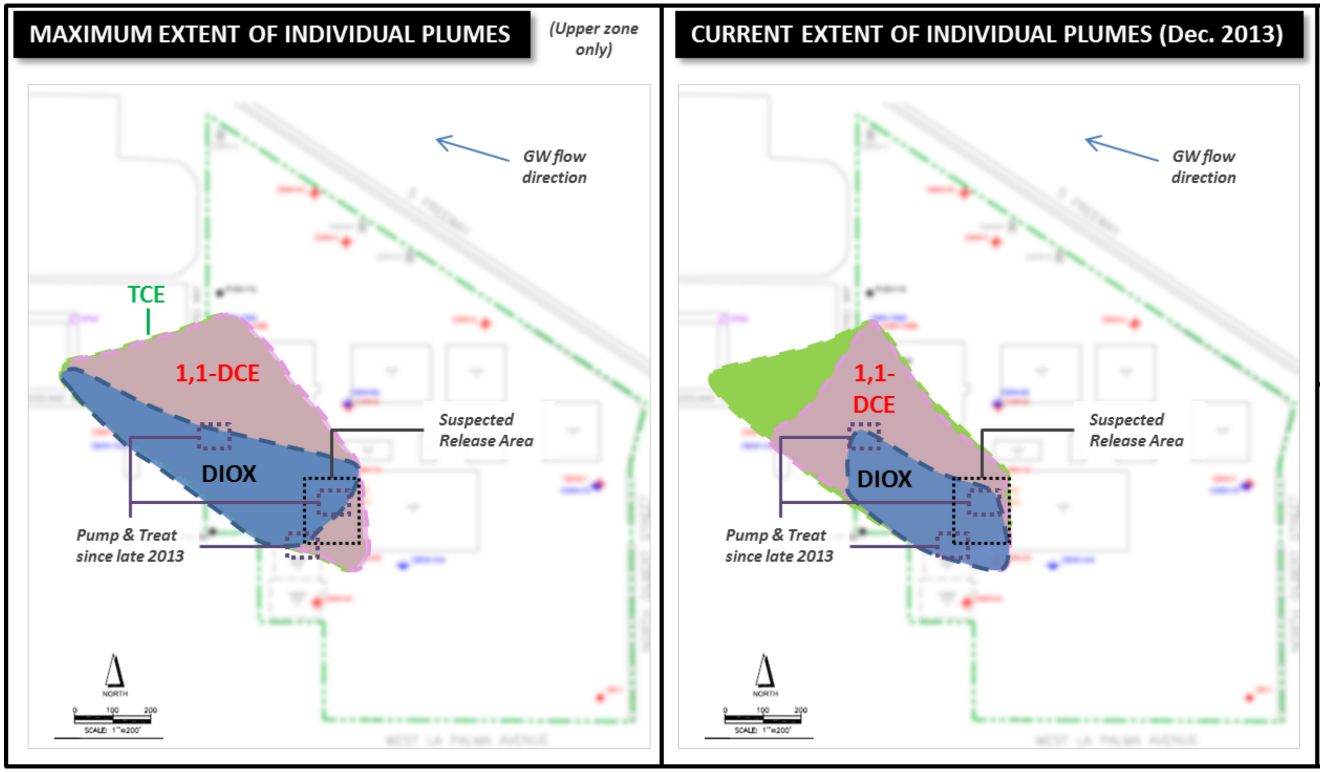
$k_{distance}$ (based on C vs. d) = 0.0015 ft^{-1}

KEY FINDINGS

- Slow dioxane attenuation with time and distance from on-site source area.
- Non-detect and/or trace levels of dioxane and most chlorinated solvents within 3000 ft of on-site source area.
- Higher dioxane and chlorinated solvent concentrations are observed downgradient in area where off-site source is suspected.

Figure 38c. Summary of Site SL209234198: Attenuation Patterns.

Site SL0605979737: This represents a site where shrinkage of the 1,4-dioxane plume has been observed to the point that it now occupies a smaller footprint than the existing chlorinated solvent plumes. While the downgradient extent of site impacts have not been particularly well-documented, the TCE, 1,1-DCE, and 1,4-dioxane plumes originally extended the same distance from the source area. The 1,4-dioxane has since shrunk while the chlorinated solvents are still detected at the farthest downgradient monitoring well. There is evidence of decreasing mass trends for 1,1-DCE (in the upper zone) and TCE (in the lower zone), but this has yet to manifest in shrinking chlorinated solvent plumes (with the exception of TCA, which has historically been below reporting levels). The 1,4-dioxane mass trend is stable, but there are a large number of wells with decreasing concentration trends, particularly in the downgradient area. Similar well trends are noted for the chlorinated solvents. A pump-and-treat system has been operating for less than 1 year in the source area (2013), meaning that these trends were established prior to this remedial effort. Aerobic conditions are noted in the vicinity of the extraction wells, but anaerobic conditions exist in the downgradient wells where decreasing trends for both 1,4-dioxane and chlorinated solvents have been established. In the source area, attenuation of 1,4-dioxane with time and distance are apparent. The historic maximum 1,4-dioxane concentration was relatively large (1500 µg/L) but was measured within a few months of the current maximum concentration (470 µg/L). These concentrations were recorded following the startup of the pump-and-treat system in the same area, and likely reflect the change in groundwater flow conditions.


MAXIMUM EXTENT OF INDIVIDUAL PLUMES *(Upper zone only)*

CURRENT EXTENT OF INDIVIDUAL PLUMES (Dec. 2013)

MASS TRENDS (Mann-Kendall)

Upper Zone:

DIOXANE = STABLE

1,1-DCE = DECREASING

TCE = STABLE

Lower Zone:

DIOXANE = STABLE

1,1-DCE = STABLE

TCE = DECREASING

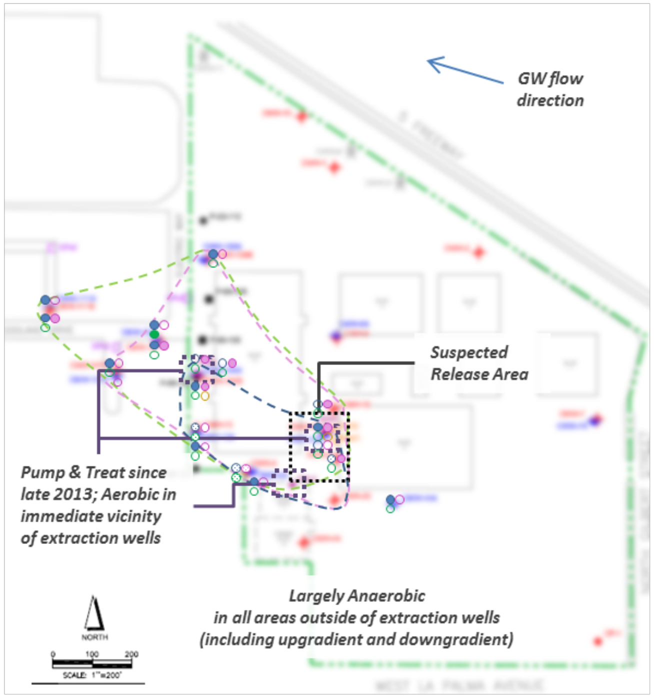
KEY FINDINGS

- Moderate plume shrinkage observed for dioxane.
- Chlorinated solvent plumes are slightly longer and not yet shrinking but show some evidence of mass loss.
- No dioxane mass trend but pump-and-treat may have contributed to plume shrinkage.
- Plumes not well-delineated in downgradient direction

Figure 39a. Summary of Site SL0605979737: Plume Extent.

STABILITY TRENDS FOR INDIVIDUAL WELLS

(Upper and lower zones)



GW flow direction

Suspected Release Area

Pump & Treat since late 2013; Aerobic in immediate vicinity of extraction wells

Largely Anaerobic in all areas outside of extraction wells (including upgradient and downgradient)

TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (10 wells)
- ○ Stable (4 wells) or No Trend (1 well)
- ○ Increasing (3 wells)
- (Not shown) Non-detect/insufficient data (3 wells)

TCA:
- ● Decreasing (0 wells)
- ○ Stable (0 wells) or No Trend (2 wells)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (18 wells)

TCE:
- ● Decreasing (1 well)
- ○ Stable (11 wells) or No Trend (0 wells)
- ○ Increasing (2 wells)
- (Not shown) Non-detect/insufficient data (6 wells)

1,1-DCE:
- ● Decreasing (8 wells)
- ● Stable (3wells) or No Trend (7 wells)
- ○ Increasing (1 wells)
- (Not shown) Non-detect/insufficient data (1 well)

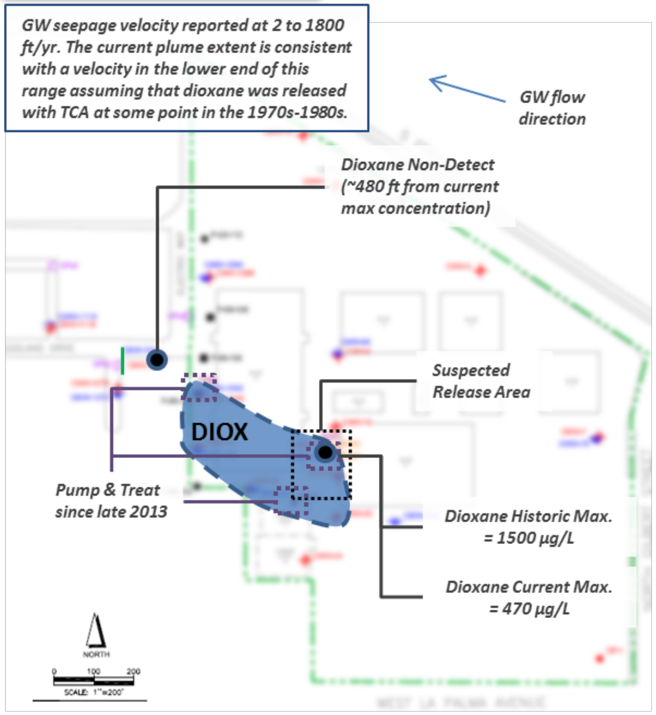
KEY FINDINGS

- Trends are largely decreasing for dioxane and 1,1-DCE, particularly along toe of plume. Stable wells are mostly located near source zone.
- Increasing trends are solely in shallow zone and sidegradient of extraction wells for that zone.
- Pump-and-treat has been operating for < 1 yr so trends are not solely attributable to remediation.
- Source area is aerobic (consistent with operation of pump-and-treat system), but upgradient and downgradient are anaerobic. Dioxane plume does not extend past chlorinated solvent plume despite anaerobic conditions downgradient of source area.

Figure 39b. **Summary of Site SL0605979737: Stability Trends.**

ATTENUATION PATTERNS

GW seepage velocity reported at 2 to 1800 ft/yr. The current plume extent is consistent with a velocity in the lower end of this range assuming that dioxane was released with TCA at some point in the 1970s-1980s.



SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.5

k_{source} (based on C vs. t) = 0.019 yr^{-1}

$k_{distance}$ (based on C vs. d) = 0.018 ft^{-1}

KEY FINDINGS

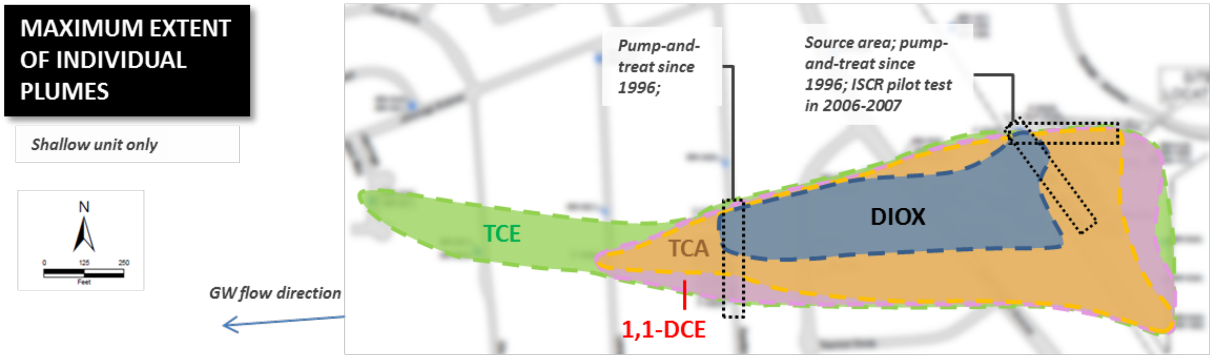
- **Dioxane attenuation with time and distance is apparent.**
- **Historically, only trace dioxane levels present at downgradient boundary, indicating significant attenuation with distance even prior to pump-and-treat.**
- **Current maximum and historic maximum were recorded within several months, indicating influence of recent startup of pump-and-treat system.**

Figure 39c. Summary of Site SL0605979737: Attenuation Patterns.

Site T0609791288: This represents a site where trace levels of 1,4-dioxane are present and may not be related to significant on-site releases. Regardless, 1,4-dioxane contamination has been successfully managed by the pump-and-treat system that has been operating at the site since 1996. This system consists of separate transects of extraction wells in the source area as well as in a downgradient area. It captures water from multiple units; 1,4-dioxane is primarily detected in wells screened in the shallow and intermediate groundwater-bearing units. Long-term extraction of groundwater appears to have contributed to shrinkage of the chlorinated solvent plumes towards the downgradient transect of extraction wells, and the 1,4-dioxane plume has been cut off by the downgradient transect. Additional remedial efforts include a pilot test of in situ chemical reduction was completed in the source area in 2006-2007; this technology was ultimately not implemented at full-scale. 1,4-dioxane is now largely absent in the source area, and there are a number of wells with decreasing trends for chlorinated solvents and 1,4-dioxane in the source area. However, decreasing mass trends for these compounds could not be established, in part because the period of evaluation (post-2000 based on GeoTracker data) did not include historic data that would suggest significant chlorinated solvent attenuation. In addition, 1,4-dioxane has been monitored for a relatively short period and in a smaller number of monitoring wells. As a result, no significant temporal trend in the site-wide maximum 1,4-dioxane concentration could be established (although the current maximum concentration is nearly an order-of-magnitude lower than the historical maximum concentration). The field parameter data were not consistent with either a predominantly aerobic or a predominantly anaerobic site. Therefore, there was little to suggest that aerobic conditions (that would presumably favor 1,4-dioxane biodegradation) were present, although it is reasonable to assume that there was significant dissolved oxygen in the vicinity of the groundwater extraction wells.

MAXIMUM EXTENT OF INDIVIDUAL PLUMES

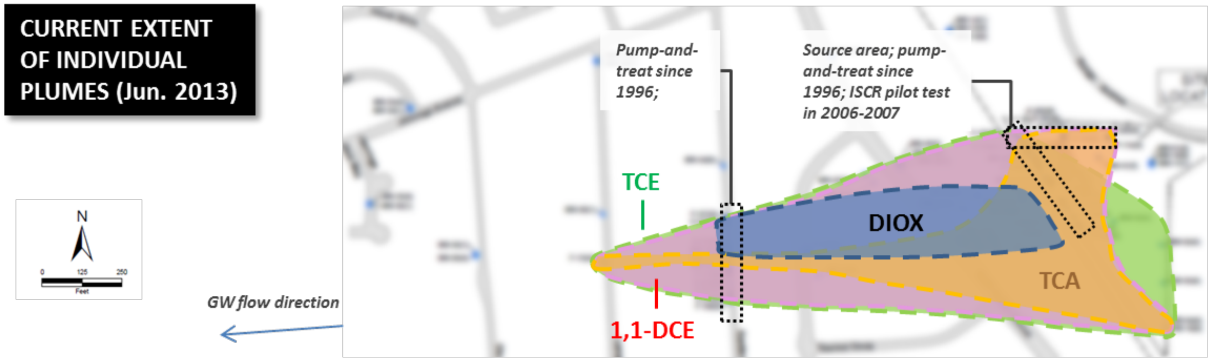
Shallow unit only



MASS TRENDS (Mann-Kendall)

DIOXANE = STABLE
1,1-DCE = STABLE
TCE = STABLE
TCA = STABLE

CURRENT EXTENT OF INDIVIDUAL PLUMES (Jun. 2013)



KEY FINDINGS

- Chlorinated solvent plumes longer than dioxane plume.
- Chlorinated solvent plumes have begun to recede toward downgradient extraction well transect.
- Several wells have been monitored since late 80s; extending evaluation period may have resulted in decreasing mass trends for chlorinated solvents.

Figure 40a. Summary of Site T0609791288: Plume Extent

STABILITY TRENDS FOR INDIVIDUAL WELLS

TREND SUMMARY (Mann-Kendall)

DIOXANE:
- ● Decreasing (2 wells)
- ○ Stable (3 wells) or No Trend (9 well)
- ○ Increasing (0 wells)
- (Not shown) Non-detect/insufficient data (9 wells)

TCE:
- ● Decreasing (12 wells)
- ○ Stable (22 wells) or No Trend (10 wells)
- ○ Increasing (1 well)
- (Not shown) Non-detect/insufficient data (3 wells)

TCA:
- ● Decreasing (10 wells)
- ○ Stable (10 wells) or No Trend (9 wells)
- ○ Increasing (2 wells)
- (Not shown) Non-detect/insufficient data (17 wells)

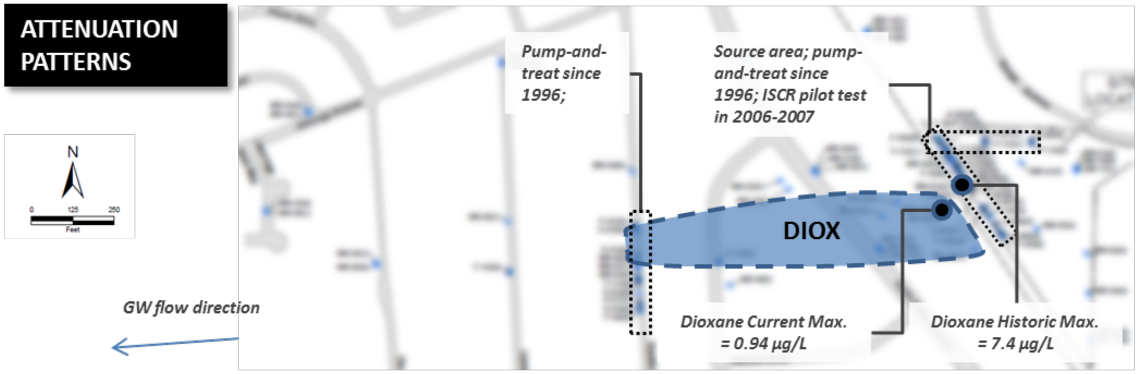
1,1-DCE:
- ● Decreasing (12 wells)
- ○ Stable (13 wells) or No Trend (13 wells)
- ○ Increasing (1 wells)
- (Not shown) Non-detect/insufficient data (9 wells)

KEY FINDINGS

- Stable dioxane trends throughout majority of site.
- Decreasing or stable trends are generally observed for chlorinated solvents, particularly near extraction wells. Chlorinated solvents trends are more stable than dioxane.
- Trends are similar in shallow and deeper groundwater-bearing units.
- Decreasing chlorinated solvent trends are consistent with long-term operation of pump-and-treat system and shrinkage of chlorinated solvent plumes.
- Dioxane largely absent from source area extraction wells.
- Redox state is difficult to assign based on field parameter data (higher D.O. generally associated with lower ORP readings). Likely mildly anaerobic to mildly aerobic, with aerobic conditions in immediate vicinity of extraction wells.

Figure 40b. **Summary of Site T0609791288: Stability Trends.**

ATTENUATION PATTERNS



SUMMARY RESULTS FOR DIOXANE

OoM Reduction = 0.9

k_{source} (based on C vs. t) = -0.09 yr^{-1}

$k_{distance}$ (based on C vs. d) = N/A

KEY FINDINGS

- No evidence of dioxane attenuation with time.
- Evaluation of attenuation with distance is prevented by: 1) low levels of dioxane; 2) inconsistent sampling program; and 3) multiple groundwater bearing units.
- Attenuation of chlorinated solvents with time and distance has been observed (historic max concentrations range from 10-100 mg/L; current max range from 0.1 – 10 mg/L).
- Historic and current maximum concentrations for dioxane are near chlorinated solvent source area (in intermediate B zone). Trace dioxane levels suggest that dioxane was not a major component of solvent used at site.

Figure 40c. Summary of Site T0609791288: Attenuation Patterns.

4.1.7 Discussion

The results obtaining during this task provided a sufficient basis for evaluating the hypotheses presented in Section 3.2 (**Table 1**). The findings of this "big data" evaluation are presented in **Table 27**.

Table 27. Summary of Findings from "Big Data" Task

Hypotheses	Findings
1,4-Dioxane usually forms "large, dilute" plumes at sites	**NO** • Percentage of 1,4-dioxane plumes classifiable as large and dilute (7%) was similar to TCE (6%)
1,4-Dioxane plumes are longer than co-occurring chlorinated solvent plumes	**NO** • 1,4-Dioxane frequently shorter than TCE and/or 1,1-DCE plumes at sites where compounds co-occur • Typically longer than TCA plumes
1,4-Dioxane plumes are poorly delineated	**MIXED** • Plume dimensions are delineated to similar extent as chlorinated solvent plumes; • Lack of 1,4-dioxane analyses at many sites with chlorinated solvents present suggests many unidentified 1,4-dioxane plumes
1,4-Dioxane is not attenuating	**NO** • Evidence for 1,4-dioxane attenuation at some but not majority of sites; • Magnitude is similar to 1,1-DCE and TCE; less than TCA
1,4-Dioxane plume development is influenced by the presence of co-occurring chlorinated solvents and by site characteristics that can be identified	**YES** • 1,4-Dioxane plume length correlated more w/ hydrogeologic factors (hydraulic conductivity, soil type); • 1,4-Dioxane attenuation correlated more w/ attenuation of co-occurring chlorinated solvents; • 1,4-Dioxane attenuation also positively correlated to dissolved oxygen concentration and negatively correlated to increasing CVOC concentrations and metals concentrations

The findings suggest that several of the hypotheses associated with the conceptual model for 1,4-dioxane contaminated sites are not entirely validated. For the purposes of managing these sites, these findings are positive because they indicate that 1,4-dioxane plumes are relatively similar to those for certain chlorinated solvents (with the exception of TCA). This suggests that current efforts for managing chlorinated solvents have been effective for containing 1,4-dioxane plumes or at least have not exacerbated them. This is not necessarily attributable to in situ treatment efforts that have removed 1,4-dioxane along with chlorinated solvents. Instead, it more likely related to natural attenuation and containment of decades-old releases of chlorinated solvents and 1,4-dioxane that have been migrating along similar flowpaths and environments. Because TCE usage at a site will typically predate any release of 1,4-dioxane, continued long-term monitoring of 1,4-dioxane is important even at sites with relatively short plumes to ensure that 1,4-dioxane does not eventually outpace TCE (or other chlorinated solvent) plumes. The large number of concentration datasets evaluated for this project provide evidence of attenuation of 1,4-dioxane at a similar numbers of sites as TCE and 1,1-DCE. Source attenuation rates for 1,4-dioxane and these compound are correlated and of similar magnitude, although the mechanisms are not necessarily the same. Collectively, these data support the use of monitored natural attenuation to help manage sites with 1,4-dioxane and chlorinated solvent sites. They also suggest that biological degradation processes (either natural or enhanced) can be an important contributor to 1,4-dioxane treatment strategies.

These findings, along with the finding that matrix diffusion is an important fate and transport process for 1,4-dioxane, support an improved conceptual model for 1,4-dioxane in contaminated groundwater. How these findings support more informed management strategies for 1,4-dioxane-contaminated sites is discussed in detail in Section 5 of this report.

4.2 Catalysis-Based Treatment

Overall hypothesis that was tested: Metal catalysts can degrade dioxane catalytically under environmentally-relevant conditions and at rates that are compatible with in situ treatment approaches.

4.2.1 Catalyst Screening for 1,4-Dioxane Degradation – Phase I

As noted previously, catalyst screening was completed in phases. Results from the screening tests for the initial sets of catalysts are shown in **Figure 41** after 20 hours and 100 hours. As can be seen, Cu(II) oxide and Fe(III) oxide showed the most activity of all the catalysts, completely removing 1,4-dioxane in less than 100 hours, though the more noble metal catalysts of 1 wt% Pd/Al_2O_3, 3 wt% Ag/Al_2O_3 and 1wt% Au/Al_2O_3 did show slight degradation capability after 100 hours. Interestingly, even under dark conditions, commercially available TiO_2 also shows activity. Titanosilicate zeolites have shown the ability to degrade 1,4-dioxane (Fan et al., 2008). One possibility for its activity may be that there are some of the same type of active sites present on the zeolite that may also be presen in bulk TiO_2.

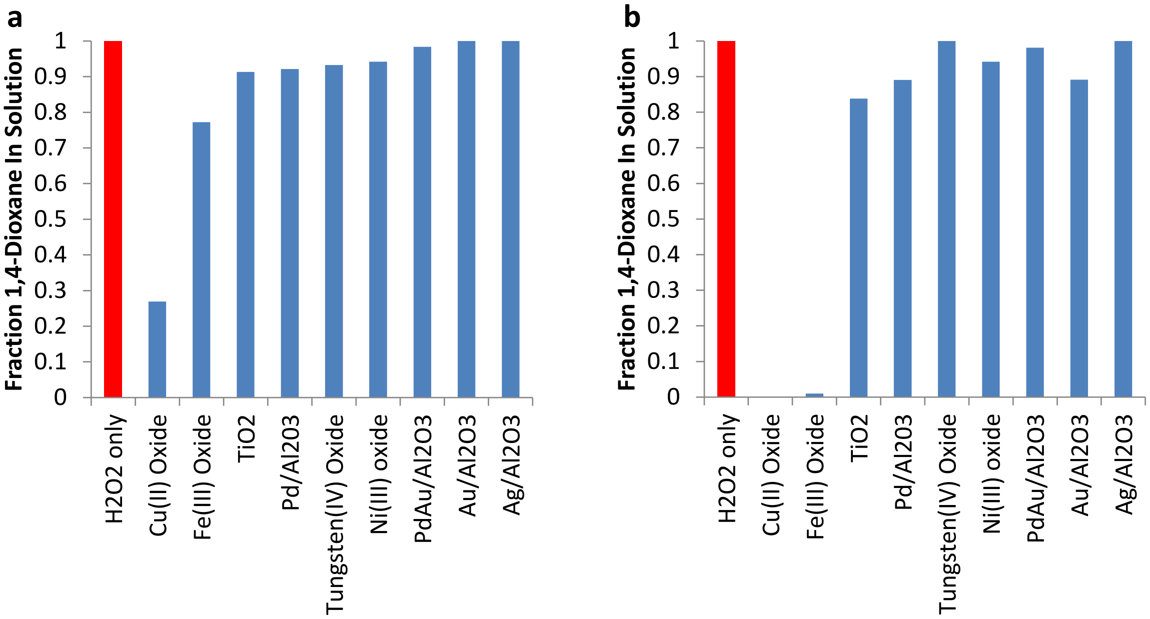


Figure 41. Fraction of 1,4-Dioxane Remaining in Solution after a) 20 Hours and b) 100 Hours. Reaction conditions: pH 3, initial dioxane concentration of 27 µM, initial H_2O_2 concentration of 30.6 mM, 25 mg catalyst.

To better assess the degradation activity of the Cu(II)oxide, TiO_2, and Fe(III)oxide catalysts, we increased the amount of catalyst added to decrease the analysis time. **Figure 42** shows the results of these experiments.

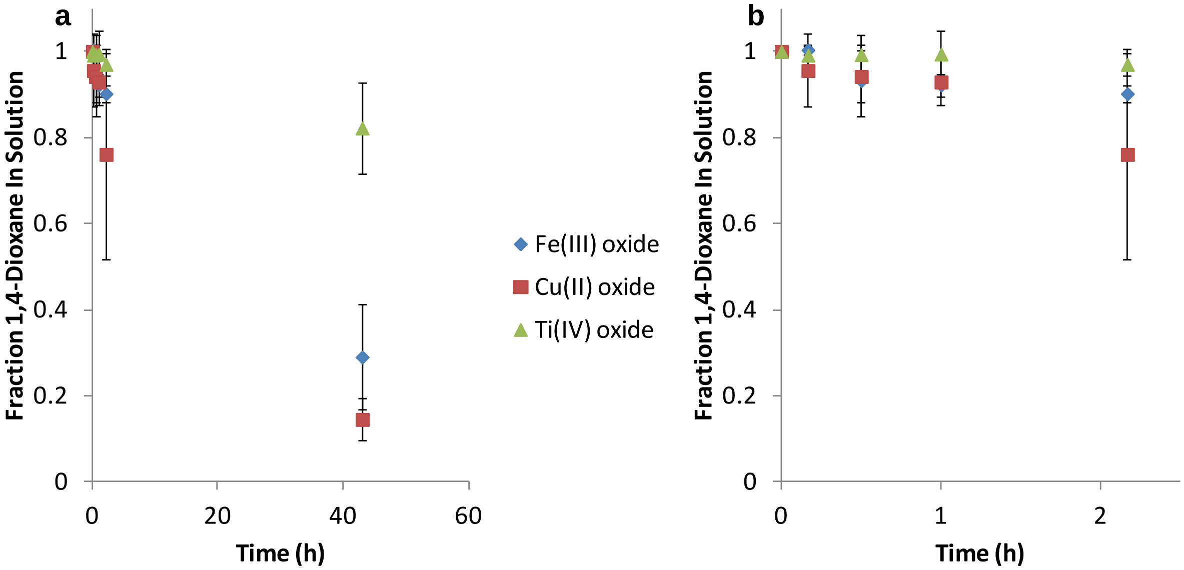


Figure 42. Degradation of 1,4-Dioxane Over Time by Active Catalysts: a) full time period of analysis, b) first two hours of analysis. Reaction conditions: pH 3, initial dioxane concentration of 27 µM, initial H_2O_2 concentration of 15.3 mM, 250 mg catalyst, room temperature. Error bars are one standard deviation of three experiments.

Cu(II) oxide is the most active of these materials, degrading 85% of the dioxane over 43 hours. Fe(III) oxide is active as well, degrading 71% of the dioxane in 43 hours. TiO_2 showed some activity as well under dark conditions, degrading 18% of the initial dioxane.

It should be noted that the reaction curves for Fe(III) oxide and Cu(II) oxide do not exhibit typical first order behavior, but rather accelerate over time. The reason for this effect may be due to the possible dissolution of the iron and copper catalysts; liberating Fe and Cu ions into solution, which may act as Fenton-like homogeneous catalysts for the degradation of H_2O_2.

Note that these catalysts fit the criteria for a go decision as discussed in the proposal, as shown in **Table 28**.

Table 28. Summary of Go/No-Go Decision Points For Catalysis Task (Task 2)

Go/No-Go Decision Point	Findings
Extent of 1,4-dioxane degradation > 50%	Several materials identified that are capable of degrading 1,4-dioxane Most active material able to degrade 85% of initial 1,4-dioxane over 2 days
Degradation kinetics; half-life of days rather than months	Most active material had a half-life of ~25 hours
Required reaction temperature of < 25°C	All reactions conducted at 22°C

4.2.2 Catalyst Screening for 1,4-Dioxane Degradation – Phase II

To determine if the poor rates demonstrated by the TiO_2 could be improved upon, we additionally screened other non-toxic metal oxide catalysts of varying surface Lewis acidity, including SiO_2, Al_2O_3, WO_3 and 20 wt% WO_x/ZrO_2.

Figure 43 shows the activity screening results for these additional catalysts, along with the catalysts from Phase I testing for comparison purposes.

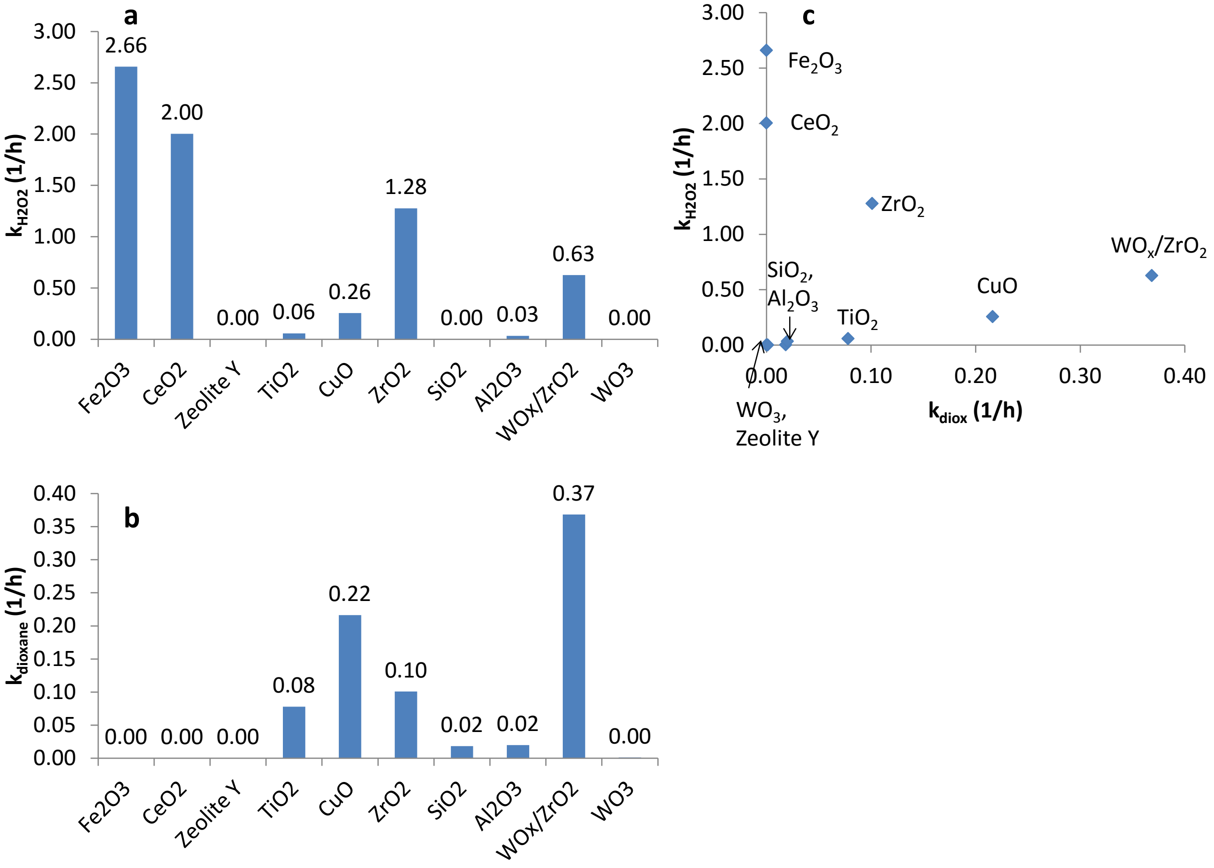


Figure 43. Decay Rates During Catalysis: (a) H_2O_2 Decay (B) 1,4-dioxane decay (c) Rate of H_2O_2 Decay vs. Rate of 1,4-Dioxane Decay for the Catalysts Screened.

As can be seen from **Figure 43b**, the WO_x/ZrO_2 catalyst demonstrates the best activity for 1,4-dioxane degradation. We hypothesize that this is due to the high Lewis acidity of WO_x groups on the ZrO_2 support, which are likely more capable of binding 1,4-dioxane and increasing the likelihood of reaction with surface bound hydroxyl radicals, which are presumably activated by the ZrO_2 support (bare ZrO_2 has a k_{H2O2} of 1.28 h^{-1}, **Figure 43a**). Indeed, a control experiment using WO_3 showed that WO_3 alone has negligible 1,4-dioxane degradation activity (**Figure 43b**), presumably due to its inability to degrade H_2O_2 (**Figure 43a**).

Figure 44 shows the efficiency of the catalysts in terms of mmoles 1,4-dioxane degraded per mole H_2O_2 consumed. In general, catalyst efficiency seems to be related to equal rates of 1,4-dioxane degradation and H_2O_2 consumption.

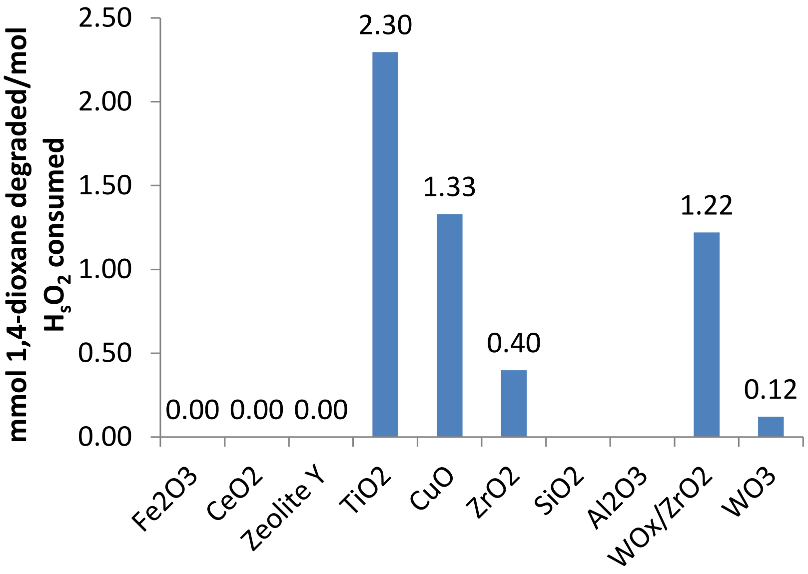


Figure 44. Efficiency of Catalysts in terms of 1,4-Dioxane Degraded vs. H_2O_2 Consumed.

As can be seen in **Figure 44**, the WO_x/ZrO_2 catalyst shows a reasonably close efficiency to the previous best catalyst, TiO_2. Since its activity is over 4.5 x greater than TiO_2 alone, this catalyst is a much better candidate for use in the treatment train studies.

Figure 45 summarizes the pseudo-first order H_2O_2 and 1,4-dioxane degradation activities of the catalysts screened. In this semi-log plot, the pseudo-first order surface normalized rate constant for the activation of H_2O_2 is plotted against the rate constant for the degradation of 1,4-dioxane to show the relative efficiencies of the various catalytic materials for 1,4-dioxane degradation. Ideally, one would desire a catalyst that rapidly degrades 1,4-dioxane (high k_{diox}) while using the least amount of H_2O_2 possible (low k_{H2O2}), thus the overall “best” catalysts are those closest to the lower right hand corner.

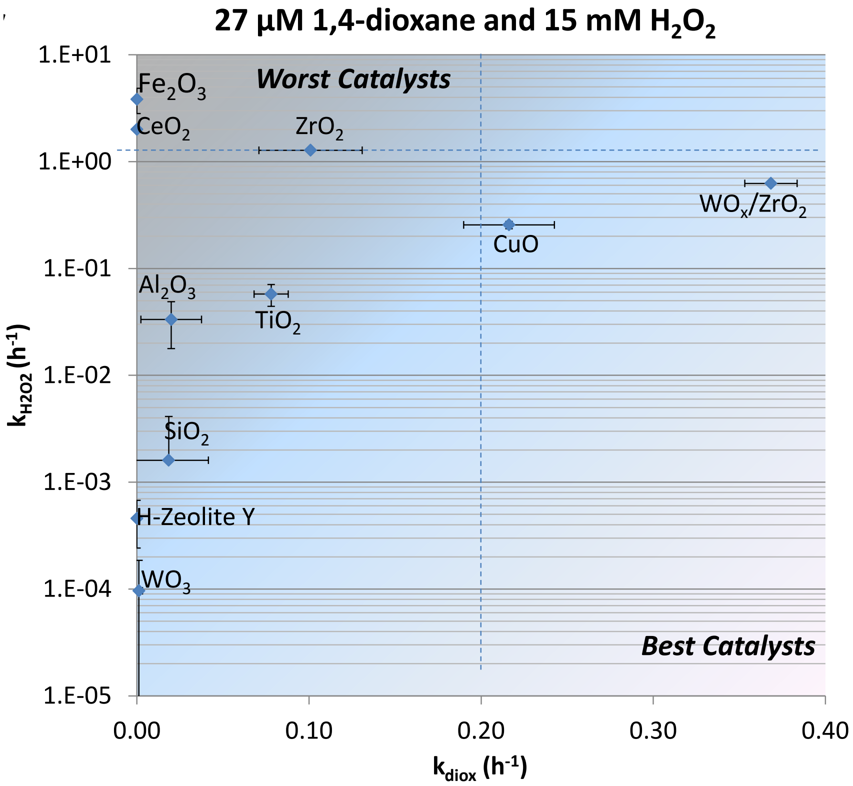


Figure 45. Surface-Normalized Pseudo-First Order Rate Constant for H_2O_2 Activation vs. Rate Constant for Degradation of 1,4-Dioxane

From this plot, we observe that of the catalysts tested, $WO_x/ZrO_2 > CuO > ZrO_2 > TiO_2$ for the degradation of 1,4-dioxane. Though CuO appears to be slightly more efficient that the WO_x/ZrO_2 (e.g. uses less H_2O_2 per 1,4-dioxane degraded), we chose to use WO_x/ZrO_2 for the treatment train studies due to its high activity and to avoid potential toxicity issues from the leaching of Cu^{2+} from the CuO.

4.2.2 Catalyst screening for the degradation of 1,4-dioxane in the presence of CVOCS

Because CVOCs are co-contaminants with dioxane, we also tested the activity of the active catalysts found in the previous section for dioxane degradation with added TCE, which may compete with dioxane for hydroxyl radicals. **Figure 46** shows preliminary results of these experiments.

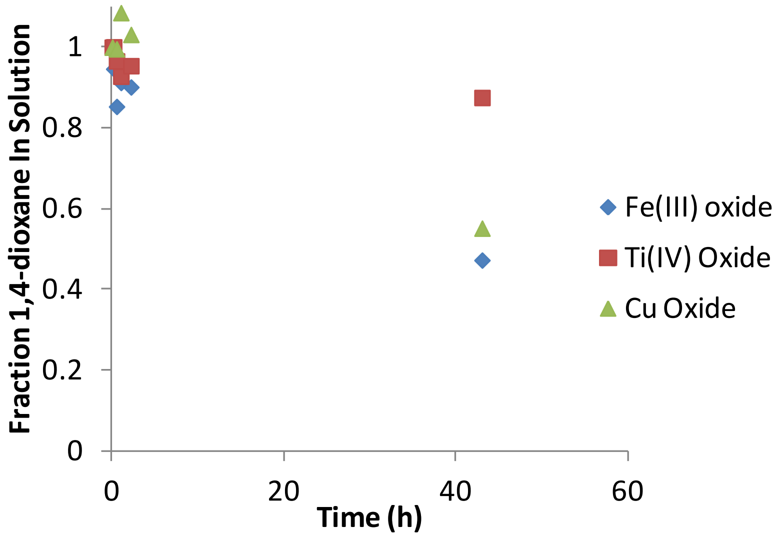


Figure 46. Degradation of 1,4-Dioxane over Time by Active Catalysts. Reaction conditions: pH 3, initial 1,4-dioxane concentration of 27 µM, initial TCE concentration of 261 µM, initial H_2O_2 concentration of 15.3 mM, 250 mg catalyst, room temperature.

The catalysts all still exhibited activity for dioxane degradation. After 43 hours, under these conditions the Fe(III) oxide catalyst was most active, degrading 53% of the initial dioxane. The Cu (II) oxide and TiO_2 catalyst were also active, degrading 45% and 13% of the initial dioxane. The presence of TCE inhibited the degradation of 1,4-dioxane for all catalysts, the Fe (III) oxide, Cu(II) oxide and TiO_2 degraded 18%, 40% and 5% less 1,4-dioxane respectively, corresponding to a decrease in activity of 25%, 40%, and 27% respectively compared to the case where no TCE is present.

One possible reason for the decrease could be from competition of TCE with 1,4-dioxane for hydroxyl radicals which are presumed to be generated by the catalysts. However, even though there is 10 fold more TCE present than 1,4-dioxane, the decrease in activity for the Fe (III) oxide and TiO_2 catalysts only drops by approximately 25%, suggesting that dioxane is preferentially oxidized compared to TCE. The reason for the larger decrease in the activity of the Cu (II) oxide catalyst (~40%) is unknown, but may be due to possible poisoning of the Cu (II) oxide by TCE. This plus the possibility of microbial toxicity from Cu ions may limit the applicability of Cu(II) oxide for field deployment.

4.2.3 Catalyst screening for the degradation of 1,4-dioxane in the presence of CVOCS under reductive conditions

Despite their apparent inactivity for the degradation of 1,4-dioxane via the decomposition of H_2O_2 to hydroxyl radicals, to assess whether they would be useful in conjunction with either biodegradation and/or ISCO techniques, Pd catalysts were tested for their activity for dioxane degradation and/or TCE hydrodechlorination with hydrogen gas and at an acidic pH required for the ISCO process. The latter point in particular is important to assess since previous studies have indicated lower pHs lead to the deactivation of Pd catalysts.

A commercial 1 wt% Pd/Al_2O_3 catalyst for the hydrodechlorination of TCE was tested under three conditions: unbuffered (neutral pH) and without added 1,4-dioxane, unbuffered with 1,4-dioxane, and buffered to a pH of 3 using phosphoric acid and with 1,4-dioxane. The catalyst was effective in converting all of the TCE present to over 95% inert products (ethane, ethene, and trace amounts of butene/butanes) in all three cases.

While unfortunately no degradation of 1,4-dioxane was observed, on the other hand, the presence of 1,4-dioxane did not inhibit the rate of degradation of TCE. Because the degradation of TCE at these relatively high concentrations is a non-first-order process (Heck et al., 2009), the activity was characterized by taking the initial slope of the concentration vs time curve, then dividing by the amount of catalyst, which in this case the active phase consists only of Pd. The initial rate of degradation, then, is 55 mM-TCE $min^{-1}g\text{-}Pd^{-1}$ for the catalysts with and without dioxane. Encouragingly, buffering the solution to pH 3 with phosphoric acid only inhibited the reaction slightly, decreasing the reaction rate constant by ~18% to 46 mM-TCE $min^{-1}g\text{-}Pd^{-1}$.

Thus, at the very least, it should be possible to selectively convert TCE to harmless products using Pd catalysts. Pd catalysts may be able to work with Task 3 by eliminating the chlorinated contaminants, which can inhibit bacterial degradation of 1,4-dioxane (Li et al, 2010; Mahendra et al., 2013), and also require much more resources for in situ chemical oxidation (ISCO) processes, which also can oxidize chlorinated contaminants to more harmful species.

4.2.4 Cost and Performance Evaluation for In Situ 1,4-Dioxane Treatment Using Catalysis

Based on the results of the initial catalyst screening, the project team compiled a list of advantages and disadvantages of the various catalysts, along with a detailed cost evaluation. This evaluation, which is included as **Appendix A**, determined that catalysis could provide cost-effective treatment for 1,4-dioxane as part of permeable reactive barrier for 1,4-dioxane treatment. Based on detailed cost modeling, it was likely that a catalyst PRB would be effective and less costly than a conventional ISCO treatment (consistent with the lower unit costs associated with passive methods like PRBs). However, using a catalyst as a supplement for ISCO (i.e., as an injected amendment to reduce the H_2O_2 dosage) would not provide a significant reduction in cost relative to conventional ISCO

While this summary did not include the Phase II catalysts (e.g., WO_x/ZrO_2), it should be noted that the cost model is not particularly sensitive to the catalyst cost (because the catalyst mass requirements are relatively low). Therefore, these costs are considered representative for the technology.

4.3 Treatment Trains for 1,4-Dioxane and Chlorinated Solvents

Overall hypothesis that was tested: Combining technologies may enhance 1,4-dioxane removal when chlorinated solvents are present.

4.3.1 Biodegradation Process Only (B only)

Removal performance and biomarker genes: Under each condition, 1,4-dioxane was not removed after 10 weeks of the biodegradation test had elapsed (**Figure 47** and **Figure 48**). This indicates that the native microbial populations were not able to degrade 1,4-dioxane in the natural conditions. Moreover, even in the bioaugmented microcosms, CB1190 was not able to measurably degrade 1,4-dioxane within the 10 week period. We attributed this to the inhibition from CVOCs in the system, which remained persistent throughout the test (**Table 29**). This inhibition could delay ATP production and down-regulate both *dxmB* and *aldH* genes (Zhang et al., 2016). This was also consistent with the biomarker genes abundances in bioaugmented microcosms showing that both DXMO (**Figure 49**) and ALDH (**Figure 50**) were decreasing with time. Moreover, total abundance of microorganisms was relatively unchanged in 8MNW54 for all conditions except bioaugmentation, indicating the resilience of native microbial populations (**Figure 51**). However, there was some evidence that microorganism abundance steadily decreased with time in 8MNW17 under low DX/low CVOCs, low DX, and bioaugmentation conditions (**Figure 51**). This was likely related to a microbial community that was more sensitive to the energy depletion under CVOCs stress (Zhang et al., 2016), but it was not universally observed in these microcosms.

Table 29. CVOC concentrations after biodegradation process (B only).

Wells	Microcosms Conditions	TCE (µg/L)	1,1-DCE (µg/L)	cis-DCE (µg/L)	TCA (µg/L)
8MNW17	High DX/High CVOCs	30046.51	21295.84	30855.88	10246.13
	High DX/Low CVOCs	2986.23	1595.92	1999.68	668.74
	Low DX/Low CVOCs	N	N	N	N
8MNW54	High DX/High CVOCs	15446.32	9190.61	6404.08	4603.02
	High DX/Low CVOCs	3146.24	1682.73	3096.7	928.84
	Low DX/Low CVOCs	200.68	0	119.14	0

Notes: N = No measurement.

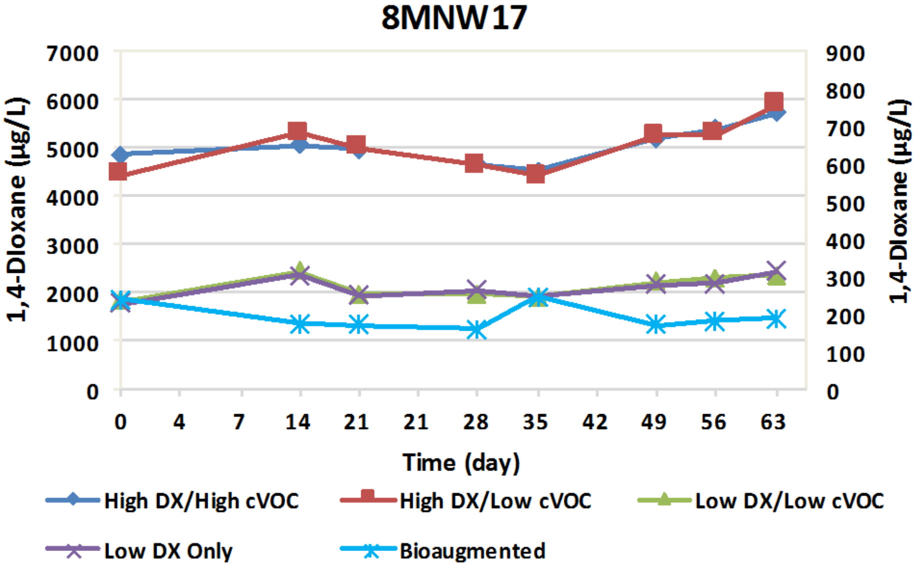


Figure 47. Removal performances of 1,4-dioxane in microcosms constructed from well 8MNW17 during biodegradation process under different 1,4-dioxane and CVOC concentrations (B only).

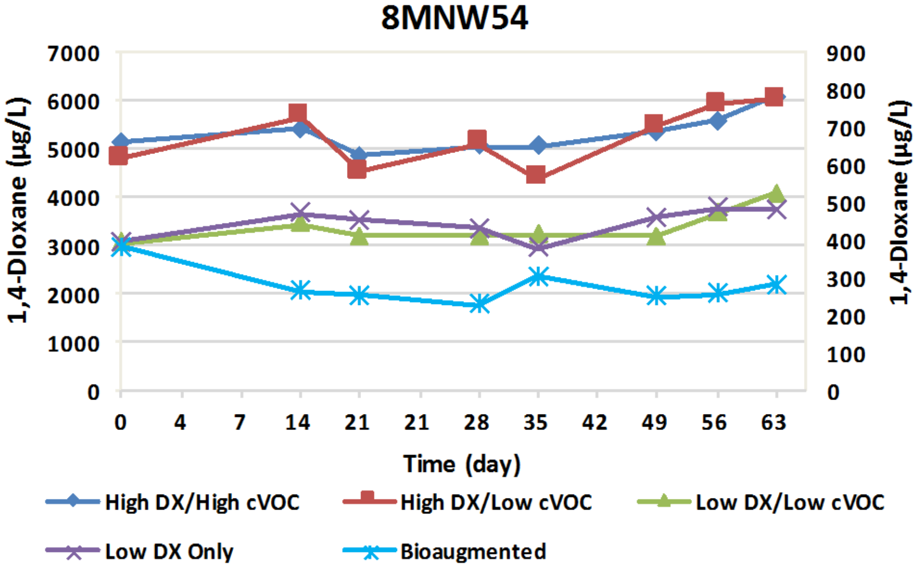


Figure 48. Removal performances of 1,4-dioxane in microcosms constructed from well 8MNW54 during biodegradation process under different 1,4-dioxane and CVOC concentrations (B only).

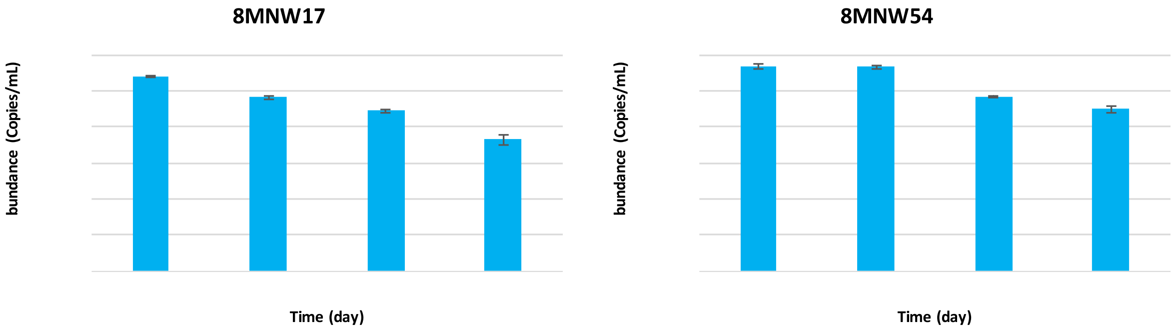


Figure 49. DXMO gene abundance under bioaugmentation condition during biodegradation process (B only).

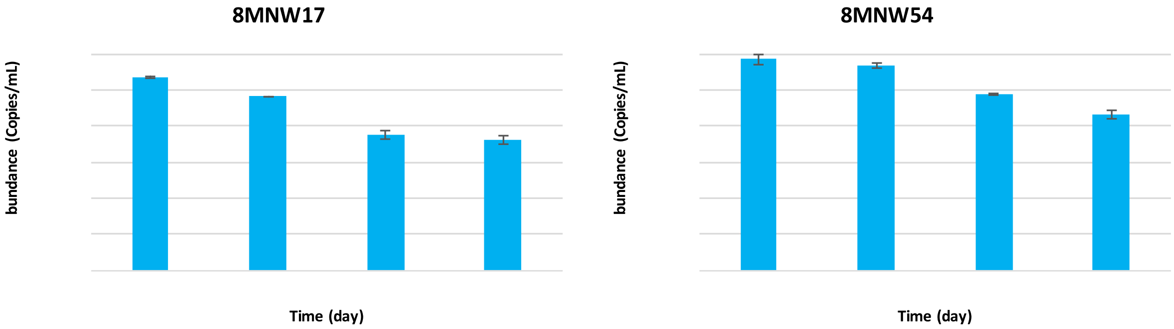


Figure 50. ALDH gene abundance under bioaugmentation condition during biodegradation process (B only).

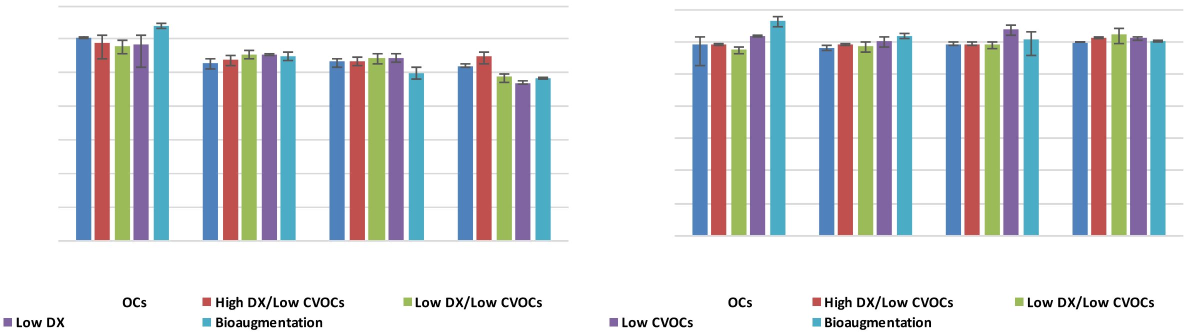


Figure 51. Total bacterial 16S rRNA gene abundance under different conditions during biodegradation process (B only).

Microbial community analysis: Samples for microbial community analysis were collected from the well 8MNW54 microcosms under five conditions: high 1,4-dioxane/high CVOCs (High/High), high 1,4-dioxane/low CVOCs (High/low), low 1,4-dioxane/low CVOCs (Low/Low), low 1,4-dioxane (Low) and bioaugmentation (Bioaug) Sample were collected at four sampling points: before biodegradation (Control), after 7 days (B3), after 14 days (B5), and end of biodegradation (B10). Sequencing for metagenomics analysis was completed on an Illumina Miseq platform.

Pseudomonas was the dominant genus with slight decreasing trend under all conditions except for the bioaugmentation condition. However, exposure to different concentrations of 1,4-dioxane and CVOCs influenced how the microbial community changed over time (**Figure 52**). Genus *Pseudonocardia* increased after spiking in the bioaugmentation condition, but its abundance then decreased along over time. This indicated that *Pseudonocardia* was weak in terms of its ability to compete with other natural microbiomes, and/or that its exhibited poor tolerance to CVOCs, which is consistent with the low 1,4-dioxane removals.

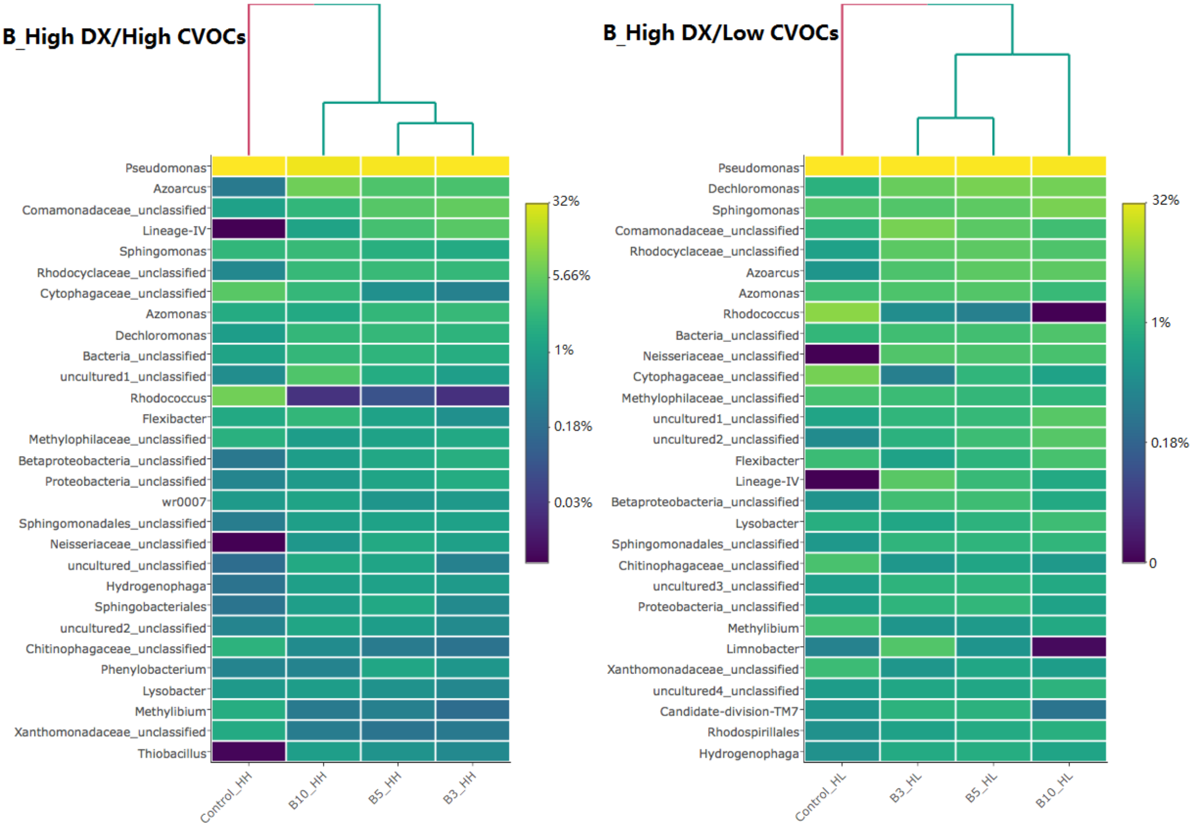


Figure 52 (continued on next page). Microbial community analysis under different conditions during biodegradation process (B only). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before biodegradation (Control), after 7 days (B3), after 14 days (B5), and end of biodegradation (B10). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

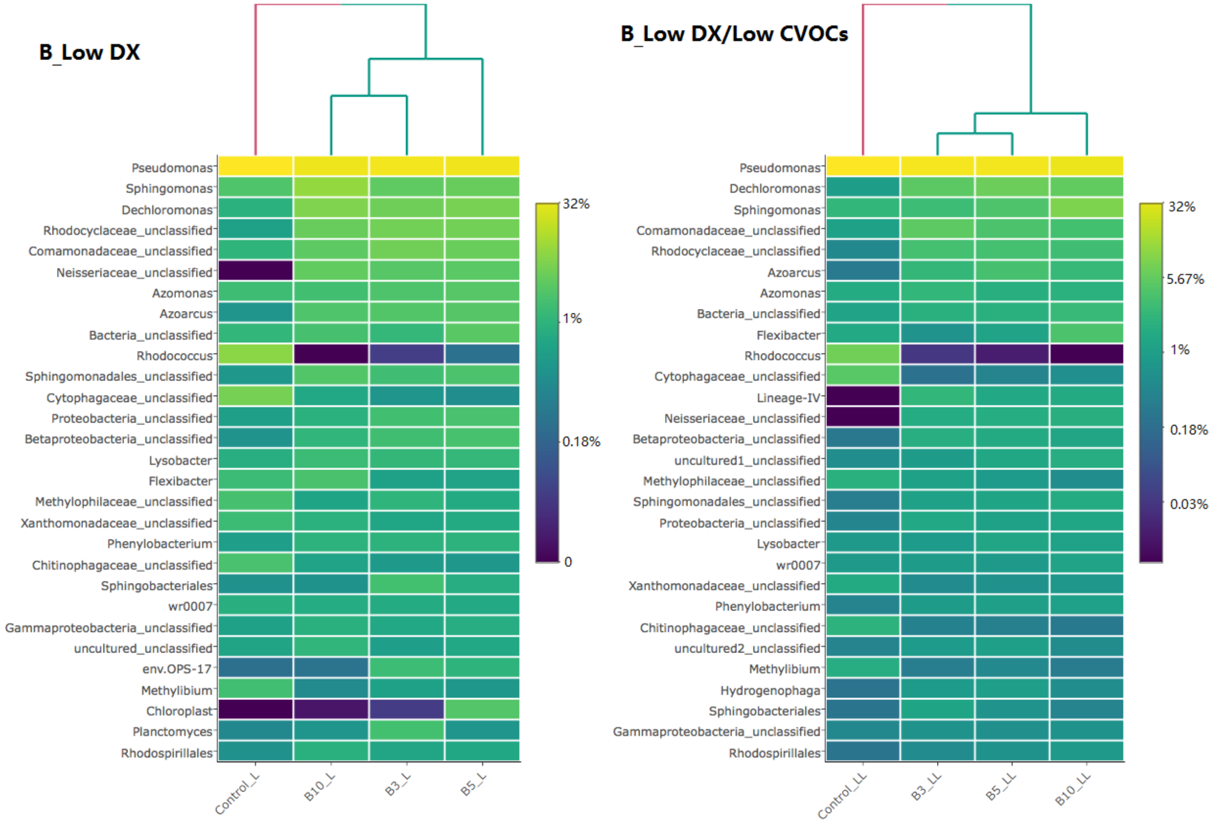


Figure 52 (continued from previous page; continued on next page). Microbial community analysis under different conditions during biodegradation process (B only). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before biodegradation (Control), after 7 days (B3), after 14 days (B5), and end of biodegradation (B10). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

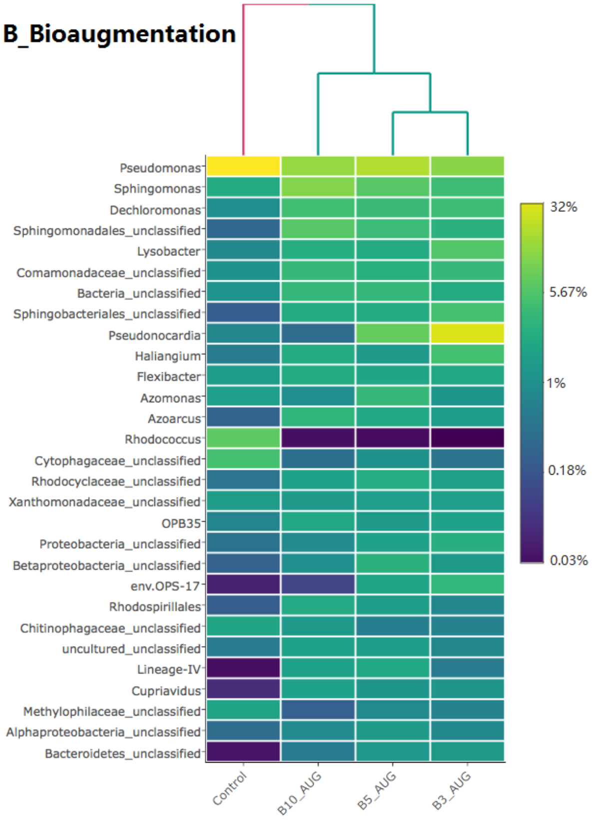


Figure 52 (continued from previous page). Microbial community analysis under different conditions during biodegradation process (B only). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before biodegradation (Control), after 7 days (B3), after 14 days (B5), and end of biodegradation (B10). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

4.3.2 Oxidation and Biodegradation (OB)

Hydrogen peroxide dose determination: For in-situ chemical oxidation (ISCO) treatment, hydrogen peroxide (H_2O_2) was the primary oxidant used to degrade 1,4-dioxane and CVOCs. In all cases where oxidation was used as one of the treatment steps, the goal was to achieve 50% 1,4-dioxane degradation (i.e., to achieve partial removal so that 1,4-dioxane remained for the subsequent step(s) in the treatment train. The initial aqueous 1,4-dioxane concentrations were 206.9 ppb (8MNW17 groundwater and TW5 soil) and 404.7 ppb (8MNW54 groundwater and TW1 soil), respectively. The results of these dose tests for the samples from each site are summarized in **Table 30**. The optimal doses of H_2O_2 were 0.24 mM for 8MNW17 groundwater and TW5 soil and 0.96 mM for 8MNW54 groundwater and TW1 soil, respectively.

Table 30. Optimization test for hydrogen peroxide dosage

8MNW17 + TW5		8MNW54 + TW1	
Hydrogen Peroxide Added	**% Degradation**	**Hydrogen Peroxide Added**	**% Degradation**
77.62 mM	Full	77.62 mM	Full
38.81 mM	Full	38.81 mM	Full
19.40 mM	Full	19.40 mM	Full
9.55 mM	Full	9.55 mM	Full
4.78 mM	Full	4.78 mM	Full
1.19 mM	90.0%	1.19 mM	90.0%
0.96 mM	76.4%	1.07 mM	Full
0.48 mM	53.0%	0.96 mM	71.4%
0.36 mM	55.2%	0.96 mM	59.4%
0.24 mM	43.3%	0.84 mM	47.7%
0.12 mM	18.1%	0.48 mM	30.8%
0.06 mM	None	0.06 mM	None

Permanganate dose determination: Permanganate was also tested, and the required dose was determined by using a range of permanganate additions for several different bottles under the same soil, water, and pH conditions as previously discussed. A 1,4-dioxane concentration of approximately 500 µg/L was used, and the permanganate doses that were tested were 12 mM, 23 mM, 46 mM, 70 mM, and 211 mM. Bottles were sampled after 12, 20, 24, and 36 hours. For 12and 23 mM permanganate, approximately 10% of initial 1,4-dioxane was transformed after 36 hours. 46 mM permanganate was able to remove more 1,4-dioxane (~25%) after 36 hours. With the addition of 70 mM permanganate, about 40% of initial 1,4-dioxane was removed after 36 hours. 211 mM permanganate removed 60% of initial 1,4-dioxane after 36 hours. Based on this data, the optimal dose was determined to be 211 mM permanganate by mass, with a contact time of 18 hours to achieve approximately 50% 1,4-dioxane oxidation (**Figure 53**).

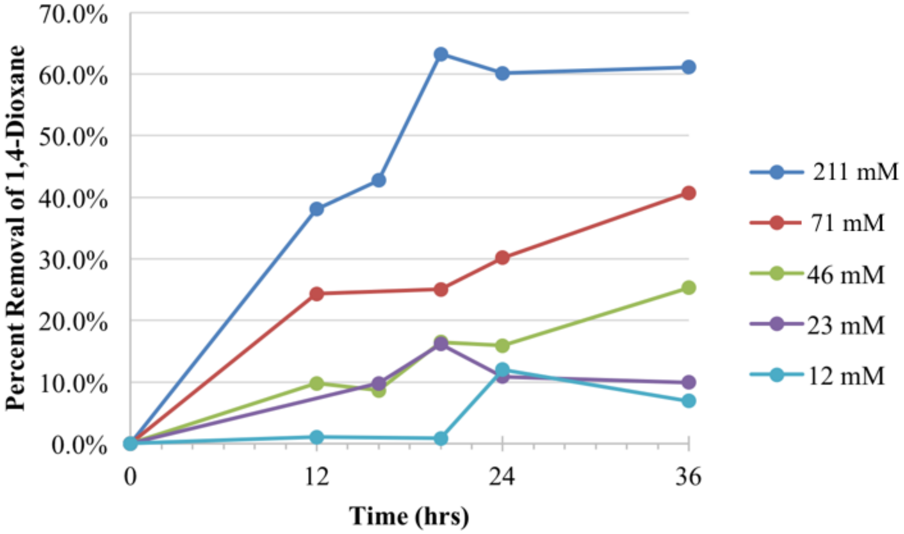


Figure 53. **Removal kinetics for 1,4-dioxane when subjected to permanganate as an initial chemical oxidation step.** Each series represents a different dose of sodium permanganate.

Removal performance and biomarker genes: After oxidation using H_2O_2 was allowed to proceed for 12 hours, 1,4-dioxane was reduced 37%-89% in soils from 8MNW17 and 8MNW54, and chlorinated solvents were completely removed (**Figure 54** and **Figure 55**). This was consistent with previous study that AOPs can efficiently degrade many SVOCs and VOCs commonly found in contaminated groundwater (Ikehata et al., 2016). The low dosages of H_2O_2 were necessary to obtain approximately 50% 1,4-dioxane removal and to ensure that there was still sufficient 1,4-dioxane for the second step in the treatment train (biodegradation). During the biodegradation phase, the native microbial community was not able to significantly remove 1,4-dioxane within 10 weeks of monitoring (**Figure 54** and **Figure 55**). Biomarker analysis determined that DXMO and ALDH were absent in the native microbial community. In recent study at AFP 3 completed by the Mahendra lab, both biomarker gene targets were detected at locations that tracked the 1,4-dioxane plume with reasonable accuracy, suggesting a strong association between biomarkers and potential biodegradation of 1,4-dioxane in natural environments (Gedalanga et al., 2016). Interestingly in the current study, only the microcosms augmented with CB1190 demonstrated continuing 1,4-dioxane biodegradation activity during the post-ISCO period (**Figure 54** and **Figure 55**). Enrichment of DXMO and ALDH in bioaugmentation microcosms indicated that CB1190 was able to thrive in these ISCO-treated environments (**Figure 56** and **Figure 57**). This study confirms bioaugmentation with CB1190 can be used for continued 1,4-dioxane degradation after chemical oxidation.

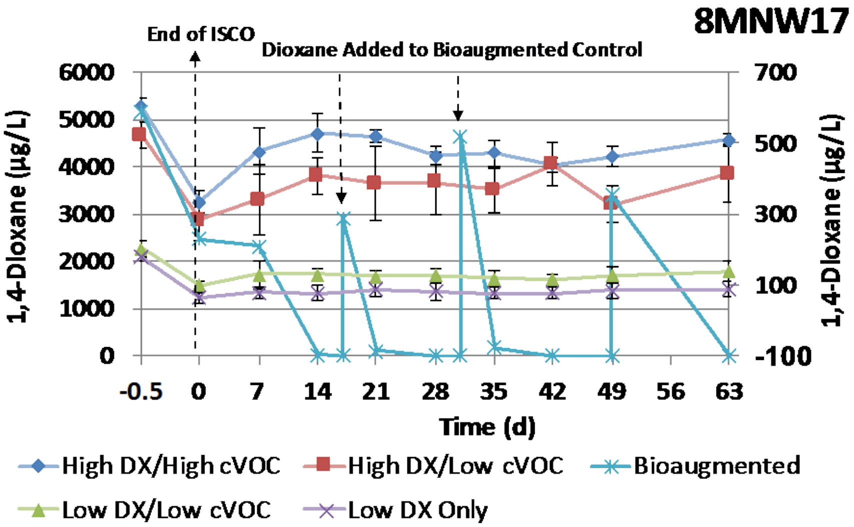


Figure 54. Removal performance of 1,4-dioxane in microcosms constructed from well 8MNW17 during oxidation-biodegradation process under different 1,4-dioxane and CVOC concentrations (OB). Hydrogen peroxide was used as the oxidant. Chlorinated compounds were completely removed after oxidation process.

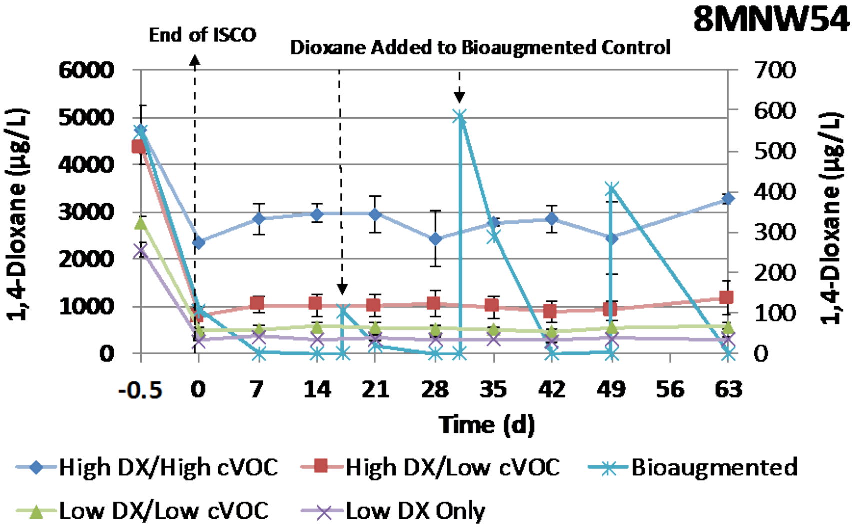


Figure 55. Removal performances of 1,4-dioxane in microcosms constructed from well 8MNW54 during oxidation-biodegradation process under different 1,4-dioxane and CVOC concentrations (OB). Hydrogen peroxide was used as the oxidant. Chlorinated compounds were completely removed after oxidation process.

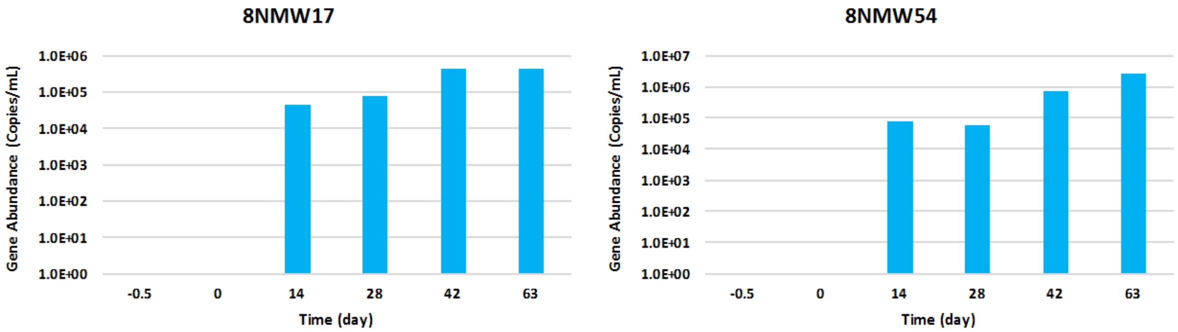


Figure 56. DXMO gene abundance under bioaugmentation condition during oxidation-biodegradation process (OB).

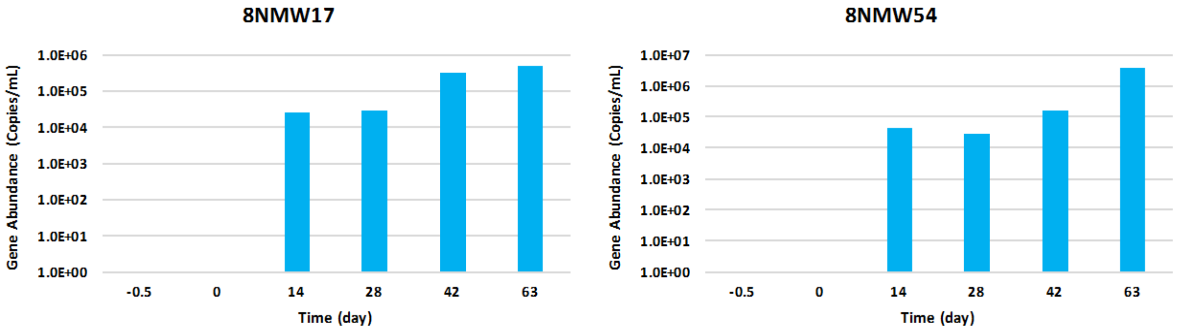


Figure 57. ALDH gene abundance under bioaugmentation condition during oxidation-biodegradation process (OB).

Following rapid 1,4-dioxane transformation during the ISCO treatment with permanganate, no significant 1,4-dioxane removal was noted in the post-quenching biodegradation phase. Even the positive control that was bioaugmented with known 1,4-dioxane-degrading bacterium P. dioxanivorans CB1190 showed no significant 1,4-dioxane removal during the biodegradation phase (**Figure 58**). The overall 1,4-dioxane removal percentages for the total duration of the experiment are shown in **Figure 59**. All reactors, with the exception of abiotic high dioxane/high CVOCs demonstrated a similar level of 1,4-dioxane removal. Small discrepancies between some abiotic reactors and their experimental counterparts is likely due to 1,4-dioxane losses during sterilization (**Figure 59**).

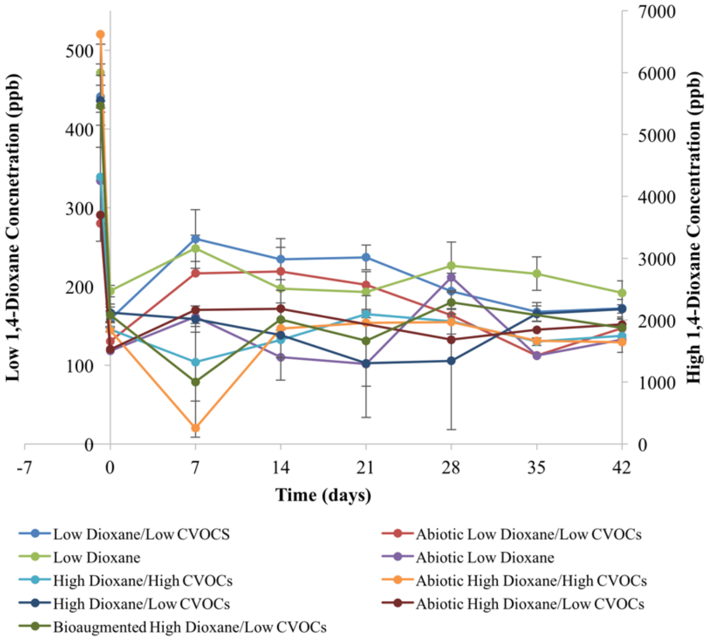


Figure 58. Removal performance of 1,4-Dioxane in microcosms during OB treatment with permanganate as the oxidant. No significant 1,4-dioxane removal was observed after permanganate treatment. Error bars for low dioxane/low CVOCs, low dioxane, high dioxane/high CVOCs, and high dioxane/low CVOCs represent the standard deviation of three parallel replicate reactors. Error bars for the bioaugmented condition represent the standard deviation of three analytical replicates. CVOCs were not measured in permanganate experiments.

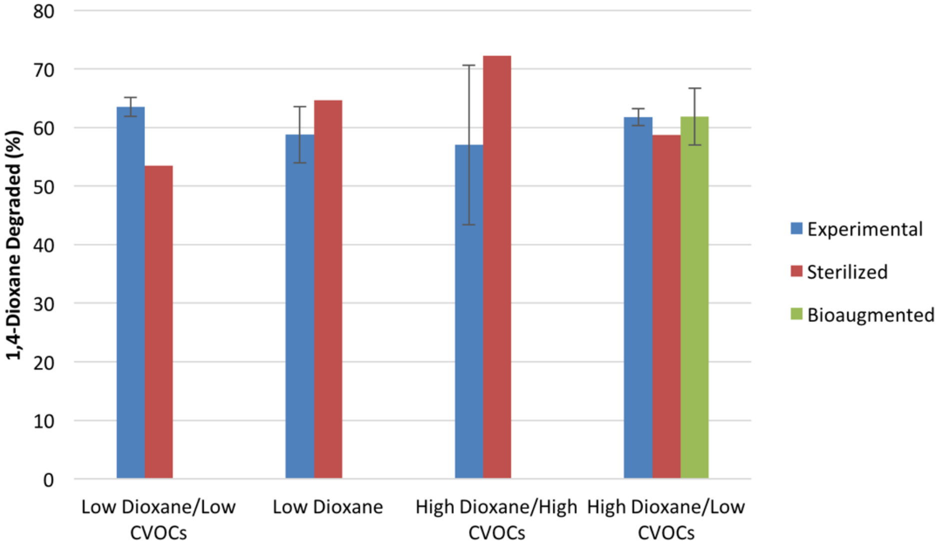


Figure 59. 1,4-Dioxane removal over the entire duration of the OB treatment with permanganate as the oxidant. No significant difference was observed for the high dioxane/low CVOC condition between experiment, abiotic, and bioaugmented reactors. Some abiotic reactors demonstrated higher 1,4-dioxane removal than the experimental counterpart, which is likely due to lower initial starting concentrations because of losses during autoclaving. Error bars for the experimental bottles represent the standard deviation of three parallel replicate reactors. The error bars for the bioaugmented reactor represent three analytical replicates.

Microbial community analysis: Samples from well 8MNW54 under five conditions, high 1,4-dioxane/high CVOCs (High/High), high 1,4-dioxane/low CVOCs (High/low), low 1,4-dioxane/low CVOCs (Low/Low), low 1,4-dioxane (Low) and bioaugmentation (Bioaug) were collected at four sampling time points, before oxidation (Control), after oxidation (OB1), middle of biodegradation (14 days, OB2), and end of biodegradation (70 days, OB3). Sequencing for metagenomics analysis was completed on an Illumina Miseq platform.

Rarefaction curves were used to compare taxon diversity observed in different samples. The curves for the different conditions used during the OB process were similar in the respect that biodiversity was reduced as a result of oxidation with peroxide and recovered by 14 days to levels similar to those that were observed prior to oxidation treatment. Finally, the biodiversity thrived relative to initial conditions (**Figure 60**). The main reason was that the majority of species were eliminated after oxidation, while some minor peroxide-tolerant species survived, then thrived under biodegradation process without competitions. The higher biodiversity observed in the Low 1,4-Dioxane only condition relative to those with CVOCs present also demonstrated the negative impact of CVOCs on diversity. The fact that all microcosms exhibited an initially decreasing trend in biodiversity followed by increasing trend is also consistent with the qPCR results (**Figure 61**). Total bacteria concentrations decreased in abundance after oxidation and then exhibited a steady increase in abundance during the subsequent biodegradation phase (**Figure 61**). Laurent et al. (2012) found that although Fenton oxidation caused a decrease in density of cultivable bacteria and 16S rDNA gene copy numbers, a rebound of microbial populations in oxidized soil was observed after 5 weeks of biodegradation. Interestingly, increased bacterial abundances may be attributed to the ability of bacteria to metabolize the byproducts of ISCO treatment in these samples. Stefan and Bolton (1998) reported that ISCO byproducts, such as methoxyacetic acid, 1,2-ethanediol mono(di)formate, formic acid, acetic acid, oxalic acid, glycolic acid, acetaldehyde, and formaldehyde, were more biodegradable than 1,4-dioxane. Our results show that ISCO treatment led to the proliferation of H_2O_2-tolerant species (**Figure 62**) as discussed below. This subgroup became dominant during the 10 weeks biodegradation phase that followed the oxidation step and resulted in an increase the overall biodiversity.

Species richness is the number of different species represented in an ecological community, and a Venn diagram was used to indicate the kind of species in different samples under different conditions, as well as the richness connections among different samples (**Figure 63**). The results illustrated that for each condition, samples from week 2 (OB2) and week 10 (OB3) have many connections with high amounts of shared species, and samples from week 10 (OB3) contain the highest number of different species (OTUs), which corresponds with the diversity analysis (**Figure 60**). Even when a low dose of H_2O_2 was applied to the microcosms, the redox conditions would change and induce the cell differentiation (Handsberg and Aguirre, 1990).

Taxonomic classification (**Figure 62**) showed that members of the genus *Pseudomonas* were initially the most dominant group for all conditions with relative abundance of 21.71-28.77%. Following oxidation, genus *Pseudomonas* significantly decreased, indicating that this group was vulnerable to the oxidation process and either recovered poorly or were outcompeted. In the microcosms that were bioaugmented with with CB1190, there was an initial increase in the relative abundance of *Pseudonocardia*. However, *Pseudonocardia* levels decreased after extended periods, suggesting a relatively weak competitive ability with other bacteria. Members of the genus *Pseudonocardia* were also detected in other conditions in addition to the bioaugmentation control.

A native minor genus, *Cupriavidus*, was also ubiquitous in all conditions except for those with high CVOCs; its abundance stabilized after oxidation and but increased within the biodegradation phase. Members of this genus have been studied for their ability to accumulate large amount of polyhydroxyalkanoates (PHA) and poly(3-hydroxybutyrate) (PHB) using different carbon sources (Obruca et al., 2010a), particularly as a stress response to H_2O_2 (Obruca et al., 2010b). The presence of *Cupriavidus* in all conditions may be attributed to the accumulation of carbon and energy in the form of PHAs and/or PHBs (Passanha et al., 2014), leading to increased biodiversity in these microcosms. Genus *Variibacter* showed similar response with *Cupriavidus*, which was not detectable under high CVOCs condition, suggesting evidence of 1,4-dioxane and H_2O_2 tolerance. However, under high DX/high CVOCs condition, the other two main genera, *Bacillus* and *Bradyrhizobium*, were found to increase over time after oxidation. This is the first report of *Bradyrhizobium* displaying an oxidative stress response to H_2O_2, which was previously described to be activated by the indole-3-acetic acid (IAA) (Donati et al., 2013). Additionally, genus *Lysobacter* displayed a similar trend (i.e., increase rapidly only under high DX/low CVOCs condition), indicating that1,4-dioxane or its degradation byproducts may have stimulated these bacteria in the microcosms without elevated chlorinated solvent stress. Additionally, genus *Novosphingobium* was found under low DX condition and could only increase over time in the absence of chlorinated compounds.

More major genera were found to be inhibited and eliminated after oxidation and within the biodegradation phase, indicating an abundance of native microbiomes were vulnerable to oxidative stress. Interestingly, certain genera survived during oxidation process, and occupied dominant positions with higher abundance compared to vulnerable ones after oxidation. However, their competitive ability during the extended biodegradation phase was weak and some of these bacteria were overwhelmed during this process. Genus *Ralstonia* was the best example of this trend and these bacteria were detected in all conditions. The genome of *Ralstonia sp.* contains multiple reactive oxygen species (ROS) scavenging enzymes, indirectly indicating their response to intense oxidative stress in their evolution (Flores-Cruz and Allen, 2009).

A cluster analysis using Partitioning Around Medoids (PAM) algorithms was performed on all samples at four time points under five conditions. PAM algorithms split all samples into different groups to check the similarity of the microbial community in each sample at the genus level (**Figure 64**). The results for the PAM analysis demonstrate that all OB3 samples at different 1,4-dioxane and CVOC exposures do not cluster with any other time points and conditions (**Figure 61**). This finding suggests that the concentration of 1,4-dioxane and CVOCs is a major determinant of microbial community structure after oxidation treatment, but effects were seen only after an extended incubation time (3 weeks). This was consistent with the biodiversity trends that lots of species thrived at the end of biodegradation, indicating that oxidation process would initially change the microbial community, and they needed longer time to grow separately. Moreover, different 1,4-dioxane and CVOCs concentrations would induce different responses of microbiomes under these conditions, then induce the various growing trends. Additionally, the community at the end of the biodegradation phase under bioaugmentation condition (Bioaug OB3) was more similar to previous conditions (The Rest), demonstrating that augmentation with CB1190 could help to stabilize community.

Correlation calculations were conducted for the different conditions at all time points, to identify connections of different genera (**Figure 65**) across differing DX and CVOC exposures. Since microcosms were set up independently, nonparametric statistic was used among different conditions, which represented by Spearman’s rank correlation coefficient. We found that the dominant genus *Pseudomonas* significantly correlated with genera *Variovorax*, *Variibacter* under some conditions. Additionally, the correlation analysis highlights the potential peroxide-tolerant genera which showed positive correlations with each other over time (*Cupriavidus*, *Ralstonia*, *Bradyrhizobium*, etc.).

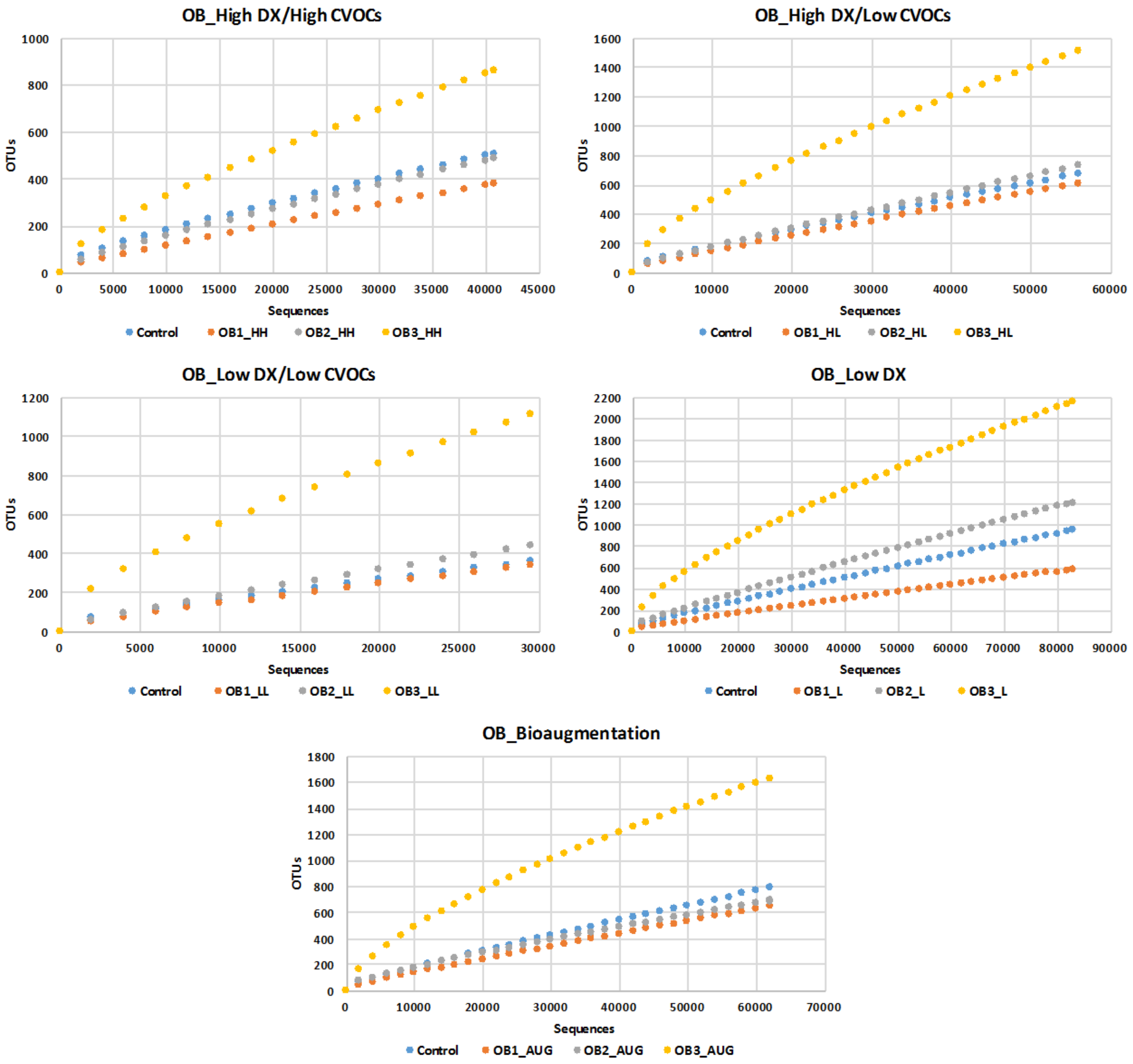


Figure 60. Rarefaction curves during oxidation- biodegradation process under different 1,4-dioxane and CVOC concentrations (OB). Rarefaction was plotted as the value of the measured diversity against the number of sequenced reads, estimating the 1) trend of diversity in different samples, and 2) whether all species in the sample had been detected. On the rarefaction curves, the y-axis represents the number of OTUs, and x-axis indicates the trimmed number of sequenced reads.

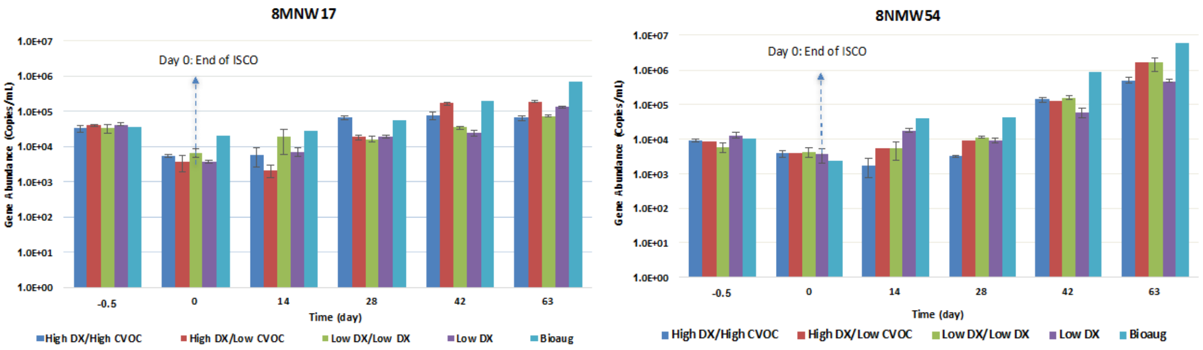


Figure 61. Total bacterial 16S rRNA gene abundance under different conditions during oxidation-biodegradation process (OB).

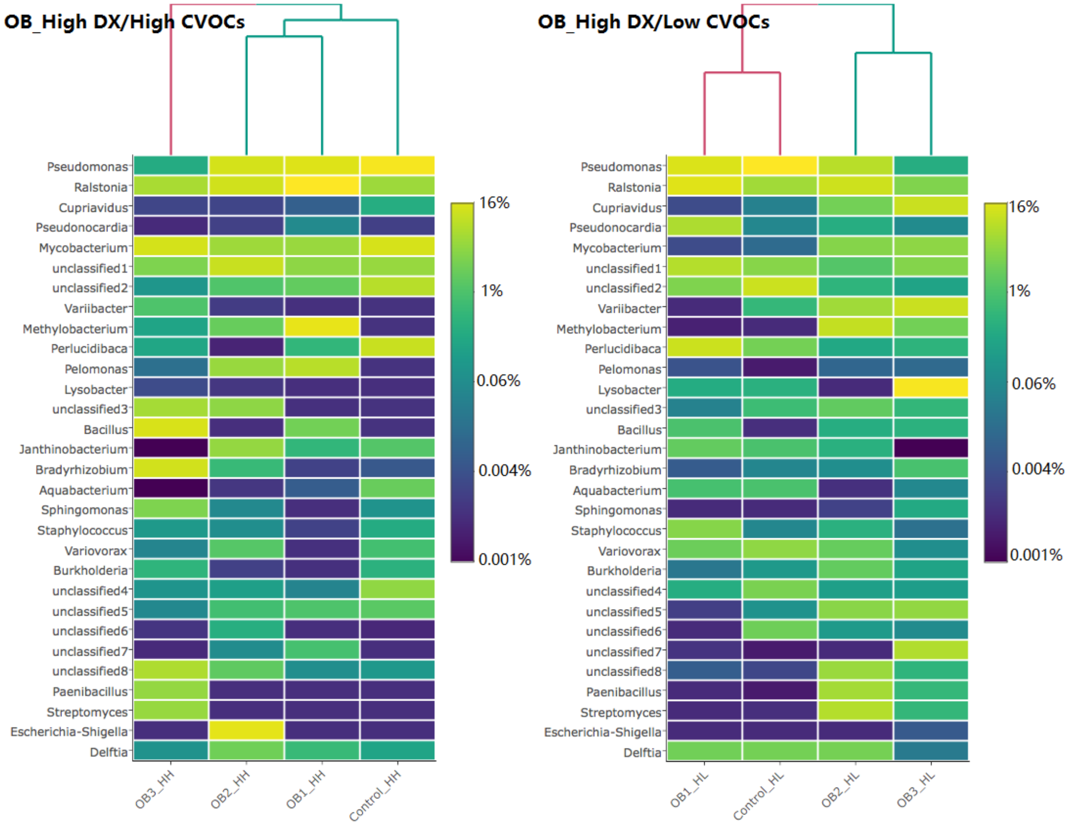


Figure 62 (continued on next page). Microbial community analysis under different conditions during oxidation-biodegradation process (OB). Each column represents the relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before oxidation (Control), after oxidation (OB1), middle of biodegradation (14 days, OB2), and end of biodegradation (70 days, OB3). Relative abundance (%) was the ratio that number of reads belonging to specific genus versus total number of reads in one sample.

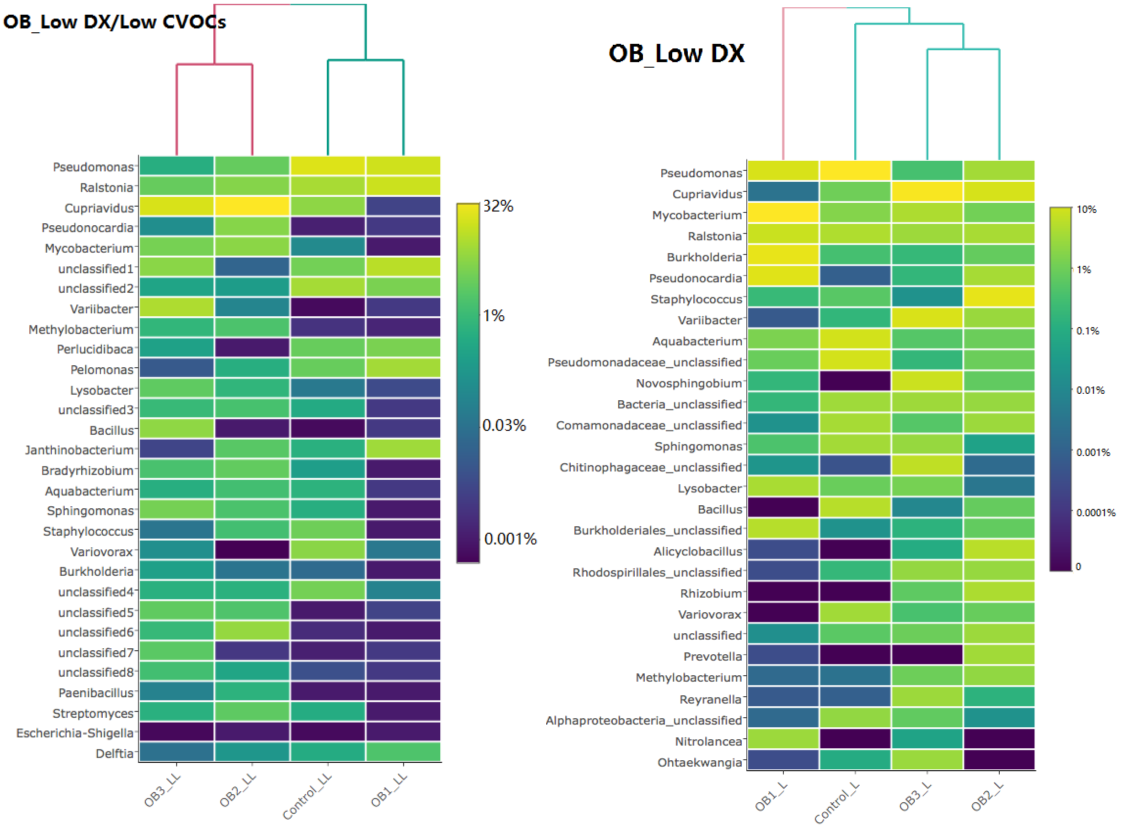


Figure 62 (continued from previous page; continued on next page). Microbial community analysis under different conditions during oxidation-biodegradation process (OB). Each column represents the relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before oxidation (Control), after oxidation (OB1), middle of biodegradation (14 days, OB2), and end of biodegradation (70 days, OB3). Relative abundance (%) was the ratio that number of reads belonging to specific genus versus total number of reads in one sample.

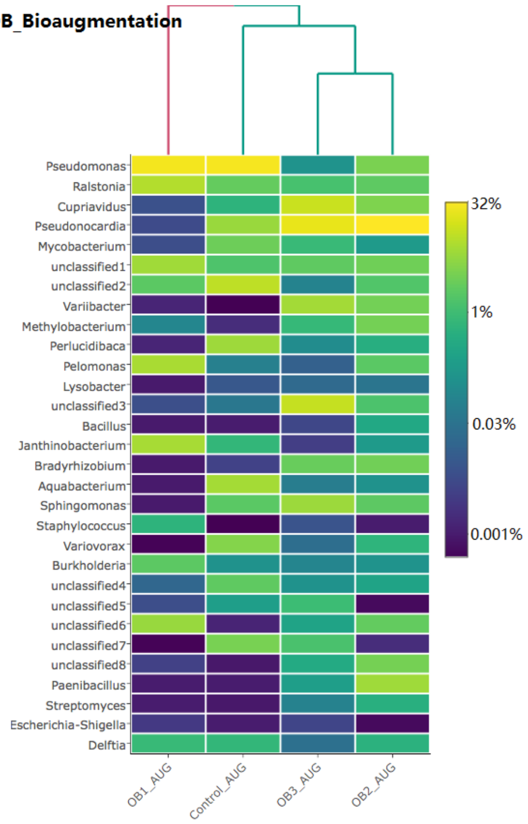


Figure 62 (continued from previous page). Microbial community analysis under different conditions during oxidation-biodegradation process (OB). Each column represents the relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before oxidation (Control), after oxidation (OB1), middle of biodegradation (14 days, OB2), and end of biodegradation (70 days, OB3). Relative abundance (%) was the ratio that number of reads belonging to specific genus versus total number of reads in one sample.

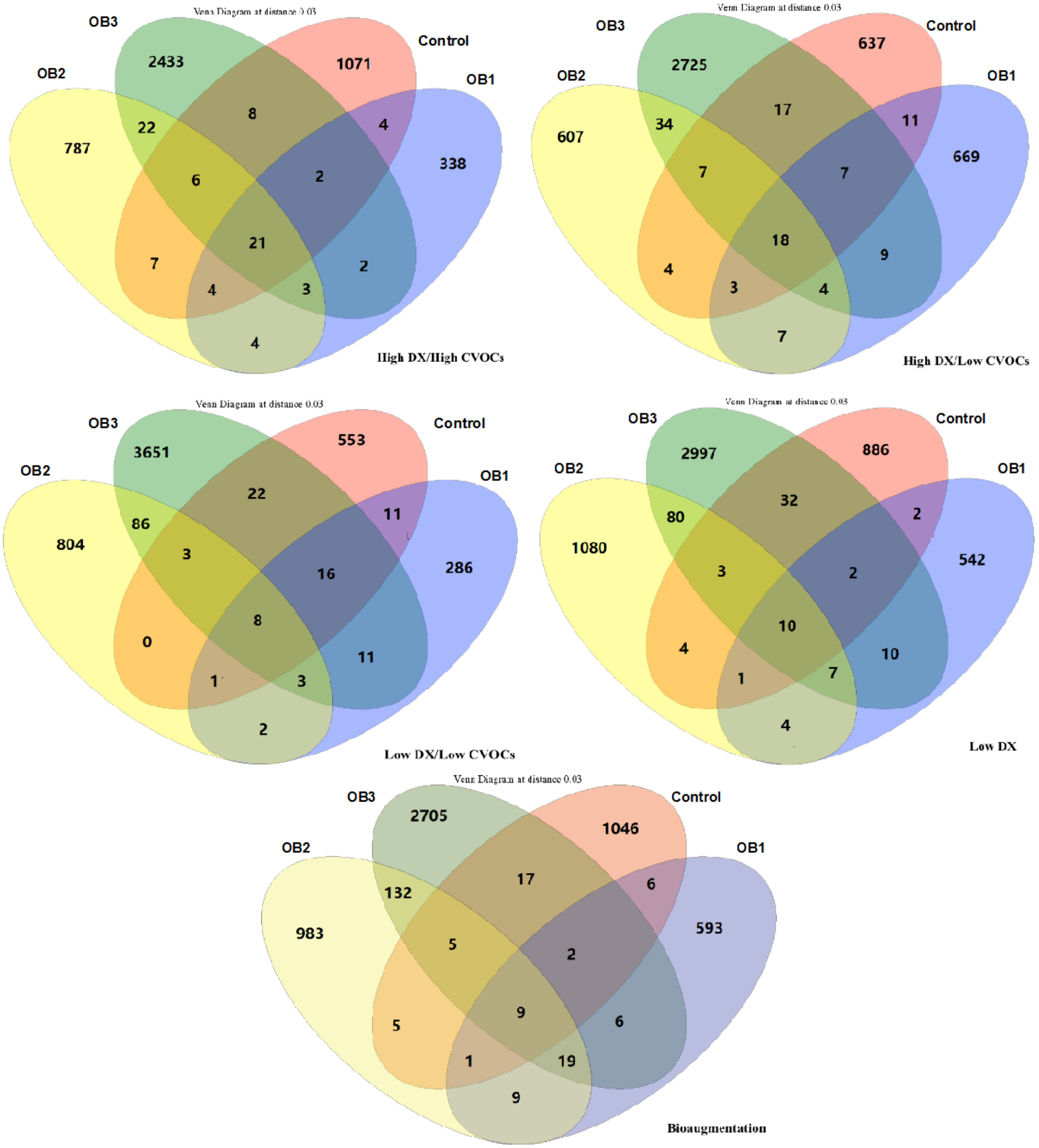


Figure 63. Venn diagrams under different conditions during oxidation-biodegradation process (OB). The ellipses represent the number of OTUs in different samples, and the overlaps of two, three, and four circles indicate the number of shared OTUs among samples.

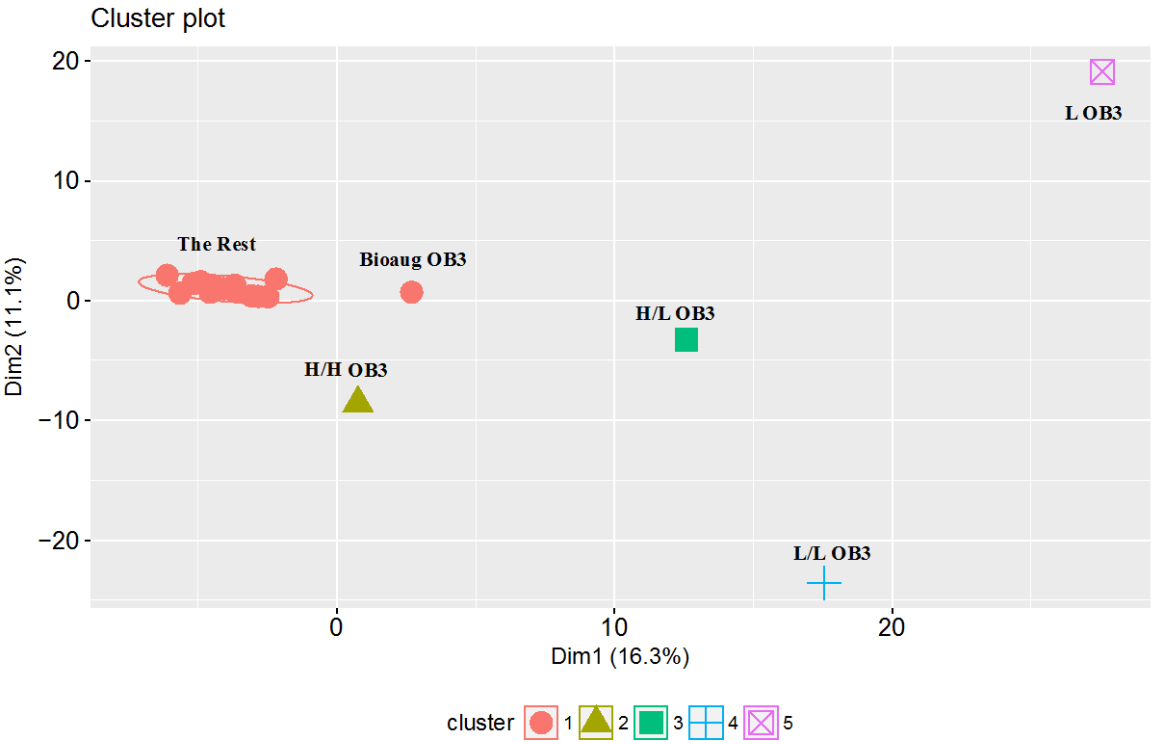
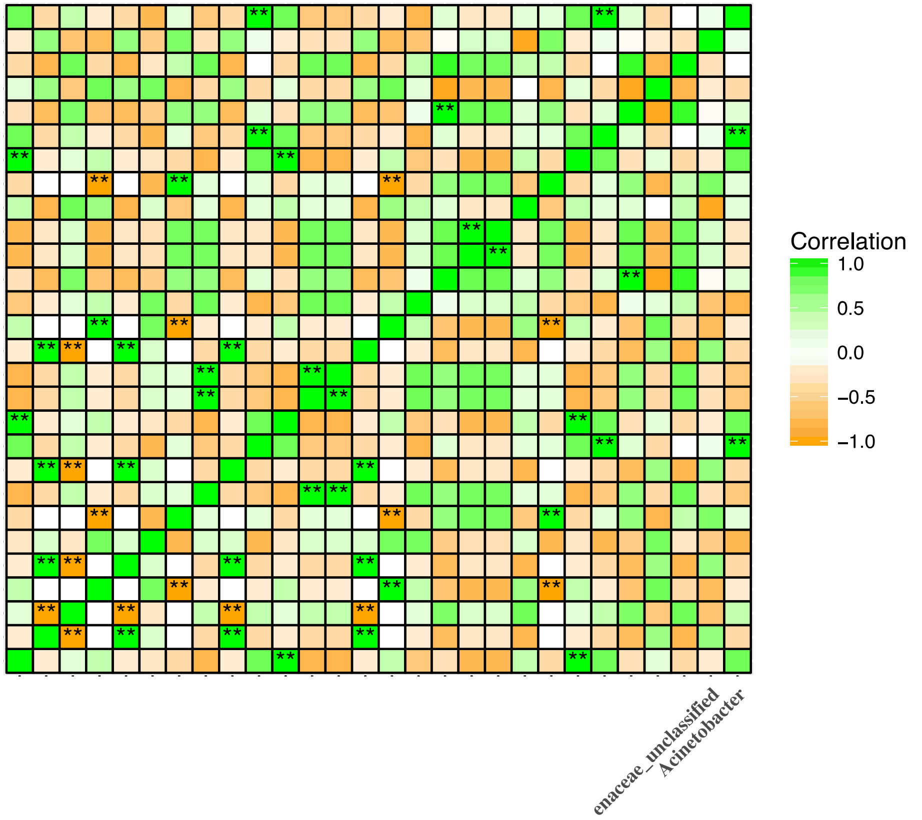
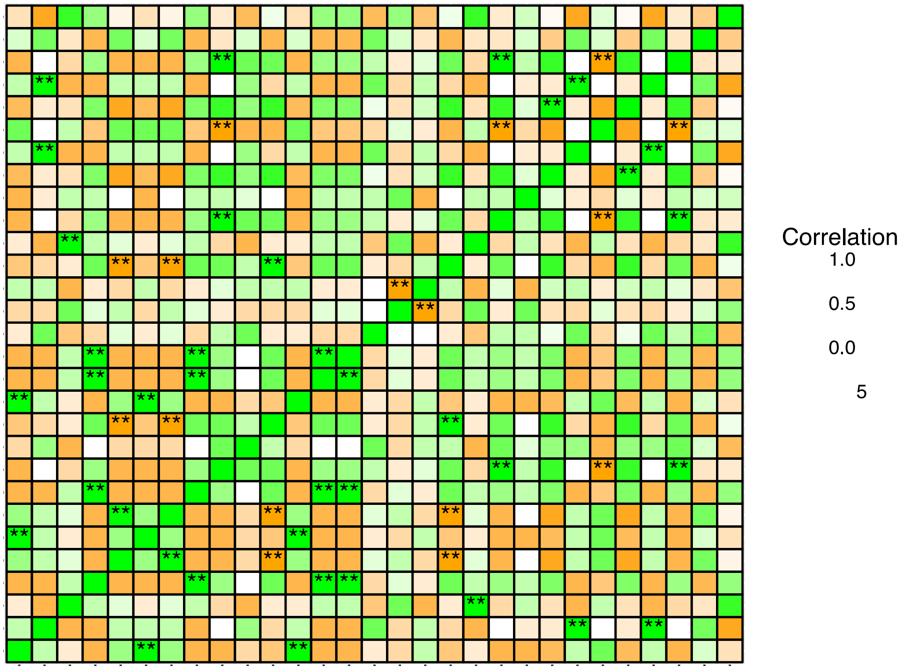


Figure 64. Cluster analysis pooling all samples at different time points under different conditions during oxidation-biodegradation process (OB). The cluster analysis based on relative abundance of all genera was performed using Partitioning Around Medoids (PAM) algorithms on all samples at four time points under five conditions. PAM algorithms split all samples into five different groups to check the similarity of the microbial community in each sample at the genus level. Each cluster was constructed by assigning each genus to the nearest medoid.



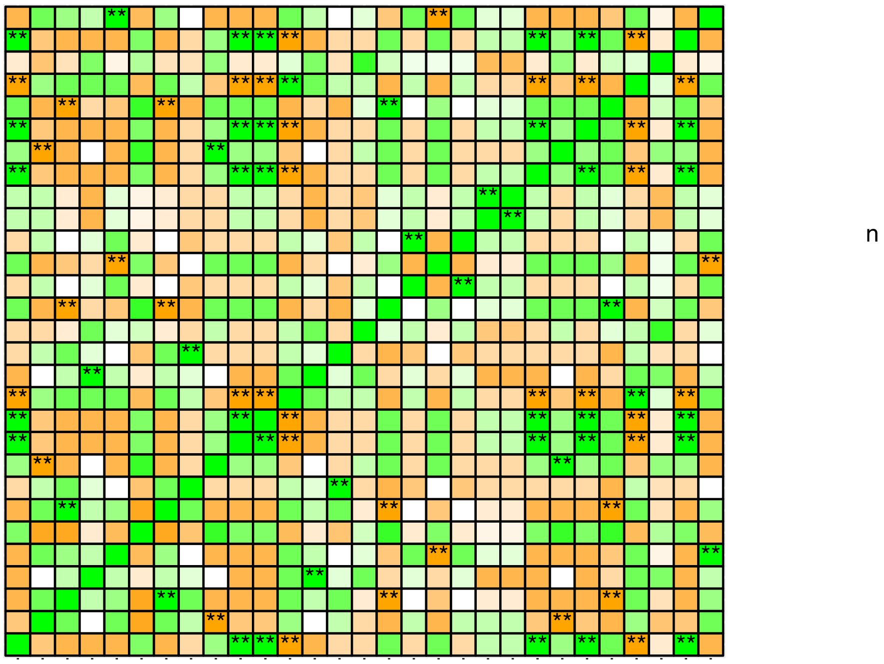
High DX/High CVOCs

Figure 65 (continued on next page). Significance of correlation among genera under different conditions during oxidation-biodegradation process (OB). * indicates *p*<0.05, and ** indicated *p*<0.01. The top 30 abundant genera in each sample were pooling together and calculated with Spearman's rank correlation coefficient.



High DX/Low CVOCs

Figure 65 (continued from previous page; continued on next page). Significance of correlation among genera under different condition during oxidation-biodegradation process (OB). * indicates *p*<0.05, and ** indicated *p*<0.01. The top 30 abundant genera in each sample were pooling together and calculated with Spearman’s rank correlation coefficient.



Low DX/Low CVOCs

Figure 65 (continued from previous page; continued on next page). Significance of correlation among genera under different conditions during oxidation-biodegradation process (OB). * indicates *p*<0.05, and ** indicated *p*<0.01. The top 30 abundant genera in each sample were pooling together and calculated with Spearman's rank correlation coefficient.

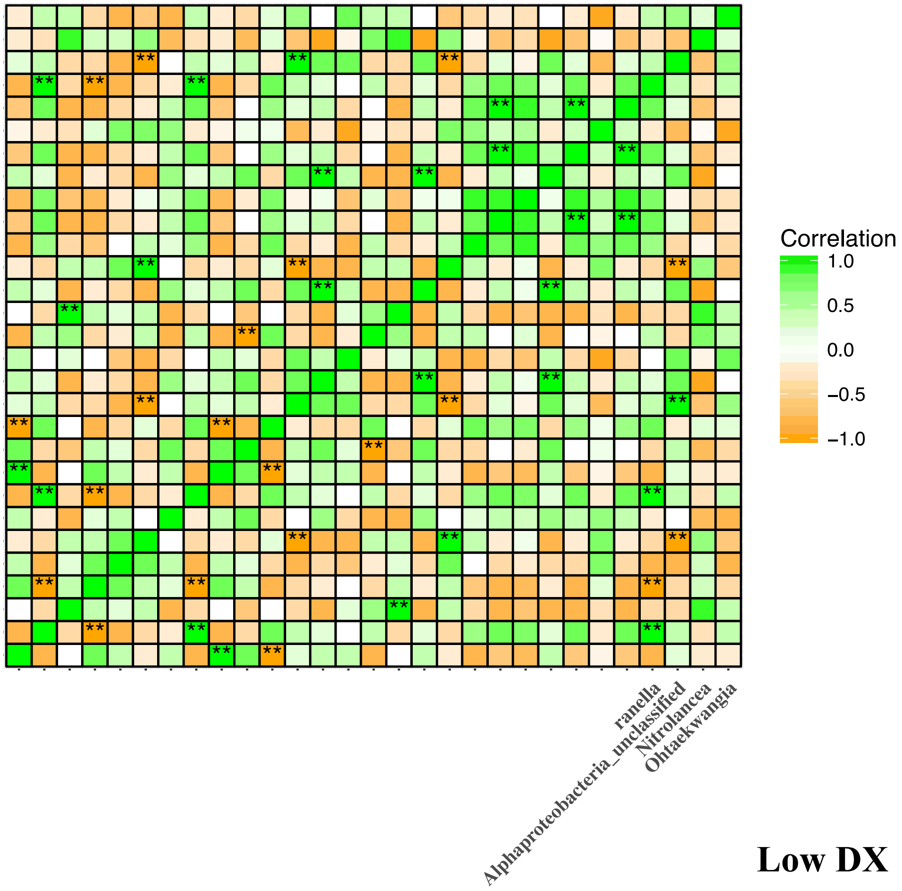
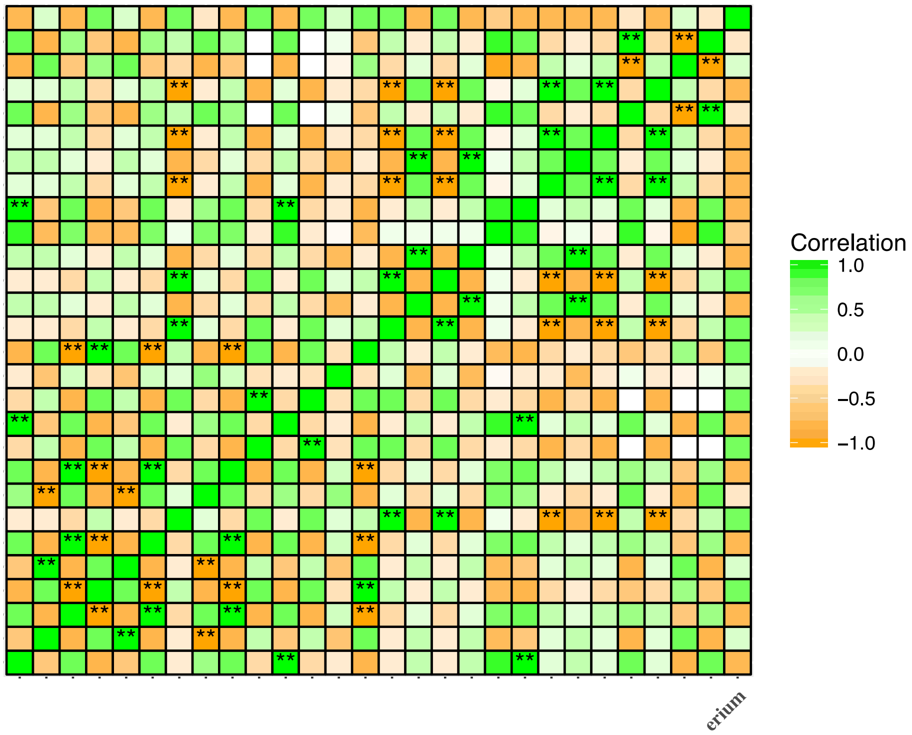


Figure 65 (continued from previous page; continued on next page). Significance of correlation among genera under different conditions during oxidation-biodegradation process (OB). * indicates *p*<0.05, and ** indicated *p*<0.01. The top 30 abundant genera in each sample were pooling together and calculated with Spearman's rank correlation coefficient.



Bioaugmentation

Figure 65 (continued from previous page). Significance of correlation among genera under different conditions during oxidation-biodegradation process (OB). * indicates *p*<0.05, and ** indicated *p*<0.01. The top 30 abundant genera in each sample were pooling together and calculated with Spearman's rank correlation coefficient.

4.3.3 Catalysis and Biodegradation (CB)

Screening of Catalyst Doses: The results for the screening experiments are shown in **Table 31** and **Table 32** for the 8MNW54 and 8MNW17 systems respectively.

Table 31. Catalyst and Hydrogen Peroxide H_2O_2 Dosing Tests for 8MNW54

[H_2O_2] (mM)	**[20 wt% WO_x/ZrO_2] (g_{cat} L^{-1})**		
	2	**4**	**8**
0	0%		
0.12	3%		
0.24	6%		
0.36	0%		
0.48	1%		
0.96	3%		
1.19	-2%		
4.78	2%		
9.55	-5%		
19.4	4%		
38.81	2%		
77.62	6%	5%	
155	16%	11%	
310	19%		19%

Table 32. Catalyst and Hydrogen Peroxide Dosing Tests for 8MNW17

[H_2O_2] (mM)	**[20 wt% WO_x/ZrO_2] (g_{cat} L^{-1})**		
	2	**4**	**8**
0	0%		
4.78	7%		
9.55	9%		
19.4	7%		
38.81	7%		
77.62	4%		
155	13%	11%	11%
310	13%		21%

In general, small doses of H_2O_2 only degraded trace amounts of the 1,4-dioxane present. Only when [H_2O_2] was over 155 mM was significant (>10%) 1,4-dioxane degradation observed.

Additionally, higher catalyst concentrations seemed to be more effective for 1,4-dioxane degradation, particularly for the TW5-8MNW17 microcosm. Therefore, to simplify the furture experiments, a catalyst dose of 8 g_{cat} L^{-1} and H_2O_2 dose of 310 mM was chosen for both microcosms, where ~20% of the 1,4-dioxane was degraded in each, respectively.

The relatively large amount of H_2O_2 required vs. that used in the initial catalyst screening experiments (15 mM) is likely due to the presence of many different species in the groundwater/soil microcosms vs the deionized water used for the initial screening experiments. Catalytic site poisoning could occur through the irreversible chemisorption of cations, anions, or other organic species present in the microcosms. Deactivation of the catalysts could also be due to the physical fouling of the catalyst surface or blockage of pores by large molecules or sediment in the microcosms.

Removal performance and biomarker genes: The catalysis process was designed to achieve partial removal of 1,4-dioxane, Observed removal ranged between 8.42-23.75% 1,4-dioxane under high 1,4-dioxane/high CVOCs and high 1,4-dioxane/high CVOCs conditions in 8MNW17, while the remaining conditions experienced removals between 7.33-13.15% (**Figure 66**). Moreover, 1,4-dioxane continuously decreased in the first two weeks of biodegradation phase in 8MNW54 indicating the residual catalysts in the system, while native microbiomes could not degrade 1,4-dioxane during biodegradation phase (**Figure 67**). However, bioaugmentation with CB1190 improved 1,4-dioxane removal, which confirmed the activity of CB1190 in the post-catalysis environment. Note that residual CVOCs were present at the start of the biodegradation step (**Table 33**).

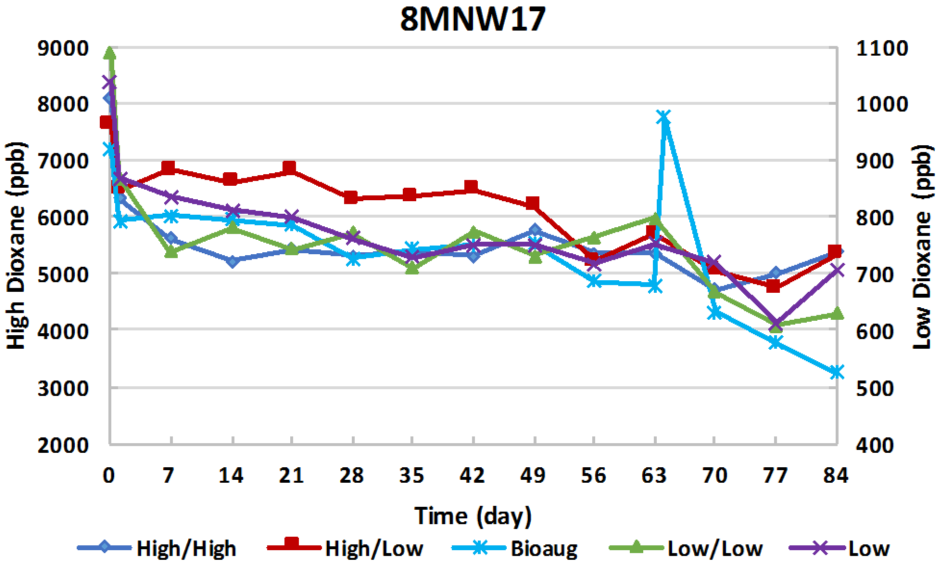


Figure 66. Removal performance of 1,4-dioxane in microcosms constructed from well 8MNW17 during catalysis-biodegradation process under different 1,4-dioxane and CVOC concentrations (CB).

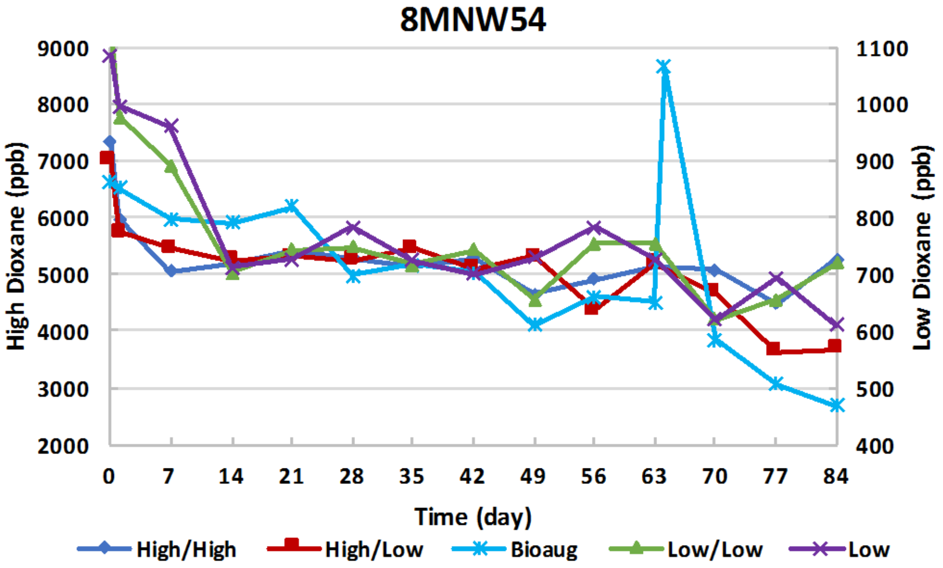


Figure 67. Removal performance of 1,4-dioxane in microcosms constructed from well 8MNW54 during catalysis-biodegradation process under different 1,4-dioxane and CVOC concentrations (CB).

Table 33. CVOC concentrations after catalysis in catalysis-biodegradation process (CB).

Wells	Microcosm Conditions	TCE (µg/L)		1,1-DCE (µg/L)		cis-DCE (µg/L)	
		Average	STDEV	Average	STDEV	Average	STDEV
8MNW17	High DX/High CVOCs	1054.51	76.26	8202.93	315.42	1976.83	208.17
	High DX/Low CVOCs	34.99	25.63	44.49	35.02	14.49	4.93
	Low DX/Low CVOCs	115.74	63.60	174.74	100.24	272.15	118.71
8MNW54	High DX/High CVOCs	1127.40	234.43	10208.50	956.20	2169.61	295.80
	High DX/Low CVOCs	216.63	101.93	1307.31	585.07	244.21	103.11
	Low DX/Low CVOCs	158.27	29.11	942.63	72.72	233.43	25.28

Biomarker genes DXMO and ALDH were detected at relatively low levels until the end of biodegradation phase after bioaugmentation (**Figure 68** and **Figure 69**). Interestingly, total bacteria and CB1190-like bacteria abundance immediately decreased after the catalysis process (**Figure 70** and **Figure 71**). The surviving microorganisms that were tolerant of catalysis treatment were able to thrive in the post-catalysis biodegradation phase, indicating the resilient composition of natural and bioaugmented microbiomes.

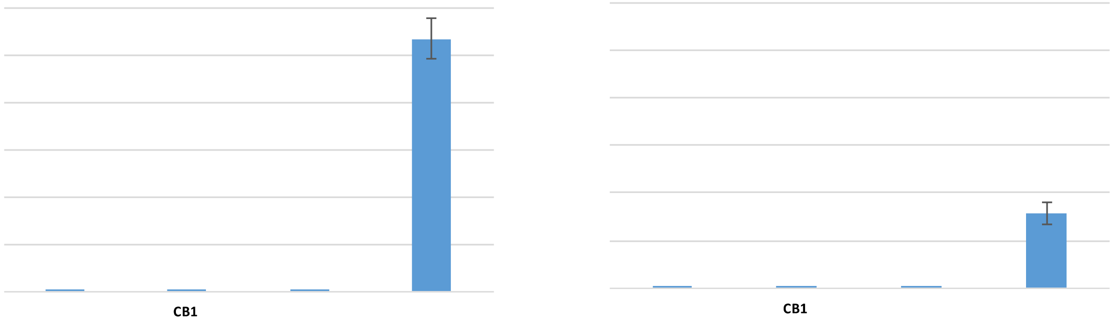


Figure 68. DXMO gene abundance under bioaugmentation condition during catalysis-biodegradation process (CB). Samples were collected at four sampling points: before catalysis (CB0), after catalysis (CB1), middle of biodegradation phase (CB2), and end of the biodegradation phase (CB3).

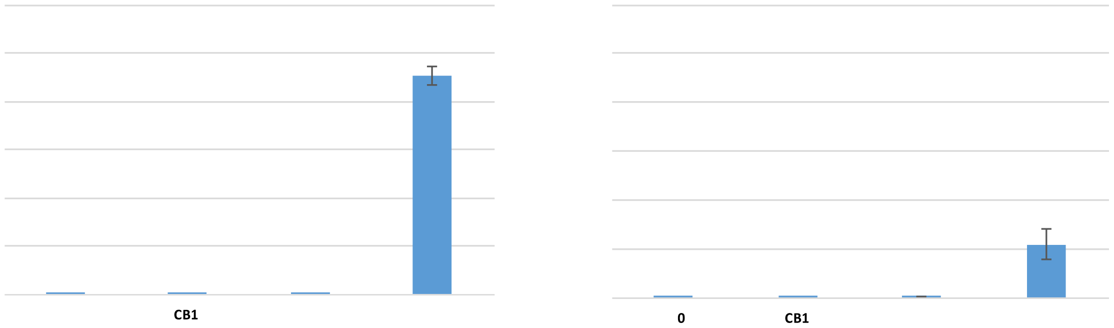


Figure 69. ALDH gene abundance under bioaugmentation condition during catalysis-biodegradation process (CB). Samples were collected at four sampling points: before catalysis (CB0), after catalysis (CB1), middle of biodegradation phase (CB2), and end of the biodegradation phase (CB3).

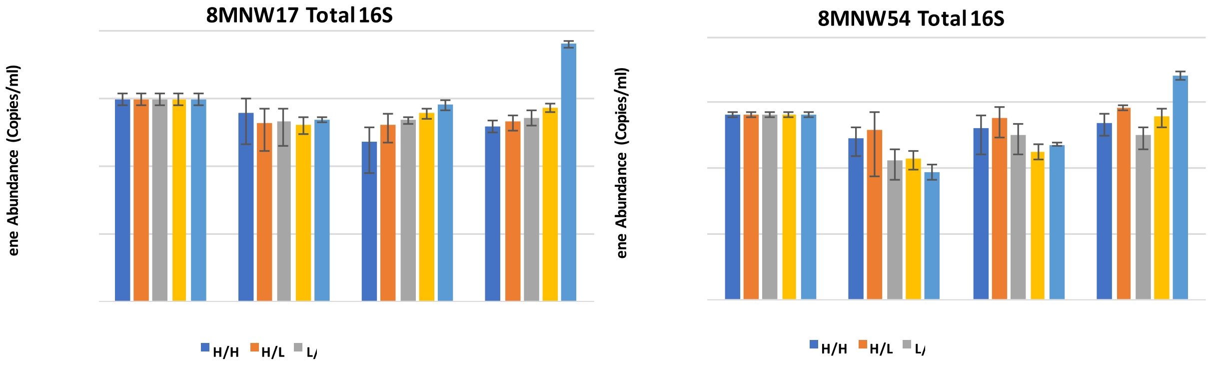


Figure 70. Total bacterial 16S rRNA gene abundance under different conditions during catalysis- biodegradation process.

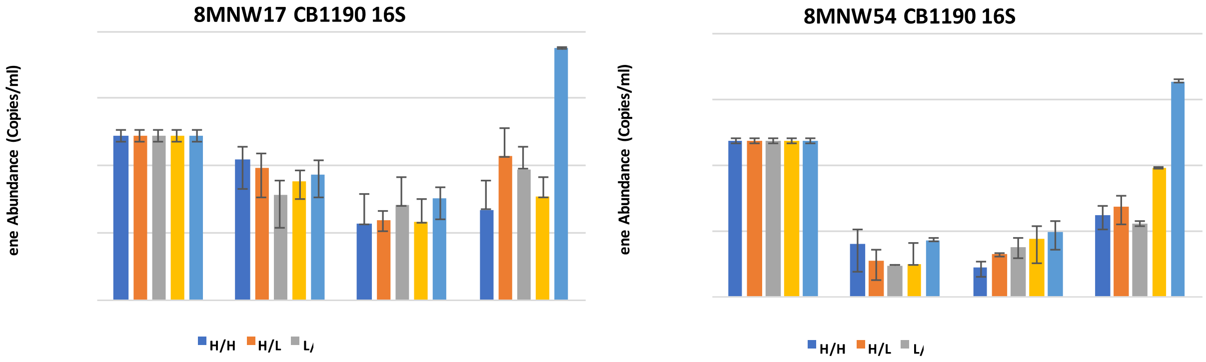


Figure 71. CB1190-like bacterial 16S rRNA gene abundance under different conditions during catalysis- biodegradation process.

Microbial community analysis: Samples from well 8MNW54 under five conditions, high 1,4-dioxane/high CVOCs (High/High), high 1,4-dioxane/low CVOCs (High/low), low 1,4-dioxane/low CVOCs (Low/Low), low 1,4-dioxane (Low) and bioaugmentation (Bioaug) were collected at four sampling points: before catalysis (CB0), after catalysis (CB1), middle of biodegradation phase (CB2), and end of the biodegradation phase (CB3). Sequencing for metagenomics analysis was completed on an Illumina Miseq platform.

Genus *Pseudomonas* was predominant before catalysis, and it was inhibited after the catalysis process (**Figure 72**). Genus *Rhodococcus* and genera in family Cytophagaceae were also inhibited by catalysis. However, genera *Sphingomonas* and *Methylibium* were found to increase immediately after catalysis, which indicates some members of these genera were able to resist catalyst-based stress relative to other genera. Indeed, a previous study selected *Sphingomonas* to inoculate bioreactors in combination with the TiO_2-photocatalytic ozonation ($TiO_2/UV/O_3$) process to treat 1-amino- 4-bromoanthraquinone-2- sulfonic acid (ABAS) (Wang et al., 2013). After the catalysis process, genus *Pseudomonas* recovered in the middle of the biodegradation phase, with the potential influence of residual catalysis in the microcosms. At the end of the biodegradation phase, a genus belonging to family Comamonadaceae increased to become the majority in the microcosms, indicating its ability to outcompete other microorganisms in these microcosms (**Figure 72**).

Biodiversity decreased after catalysis indicating a high impact of this treatment to the microbial community (**Figure 73**). However, surviving microorganisms thrived during the biodegradation process. This was consistent with oxidation process that biodiversity was inhibited by the chemical reaction. Interestingly, biodiversity gradually returned to the original level under lower CVOCs conditions, while biodiversity was stimulated to surpass the beginning level in the middle of biodegradation and descended at the very end when exposed to higher concentration of CVOCs. The main reason for the different diversity trends in biodegradation process between CB and OB was that residual CVOCs were detected after catalysis, which could stimulate microbiomes during the biodegradation process. However, CVOCs was probably degraded, inducing the recovery of biodiversity to the original level, especially under lower CVOCs conditions. This phenomenon demonstrated the impact of CVOCs on biodiversity along with catalysis-biodegradation process (**Figure 73**).

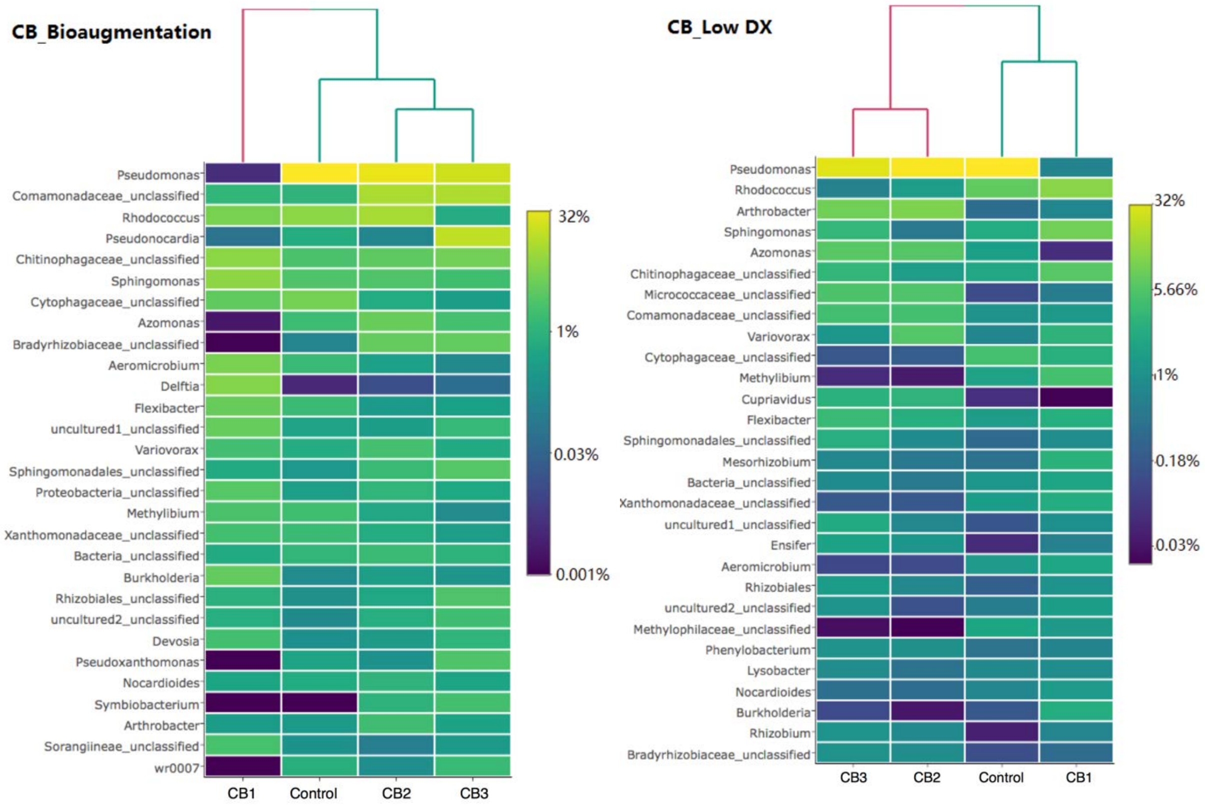


Figure 72 (continued on next page). Microbial community analysis under different conditions during catalysis-biodegradation process (CB). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before catalysis (Control), after catalysis (CB1), middle of biodegradation phase (CB2), and end of the biodegradation phase (CB3). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

Figure 72 (continued from previous page; continued on next page). Microbial community analysis under different conditions during catalysis-biodegradation process (CB). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before catalysis (Control), after catalysis (CB1), middle of biodegradation phase (CB2), and end of the biodegradation phase (CB3). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

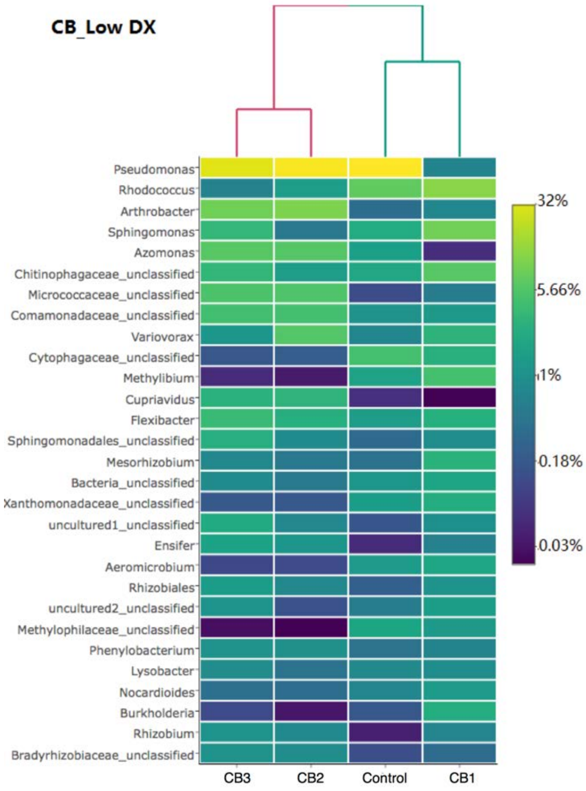


Figure 72 (continued from previous page). Microbial community analysis under different conditions during catalysis-biodegradation process (CB). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before catalysis (Control), after catalysis (CB1), middle of biodegradation phase (CB2), and end of the biodegradation phase (CB3). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

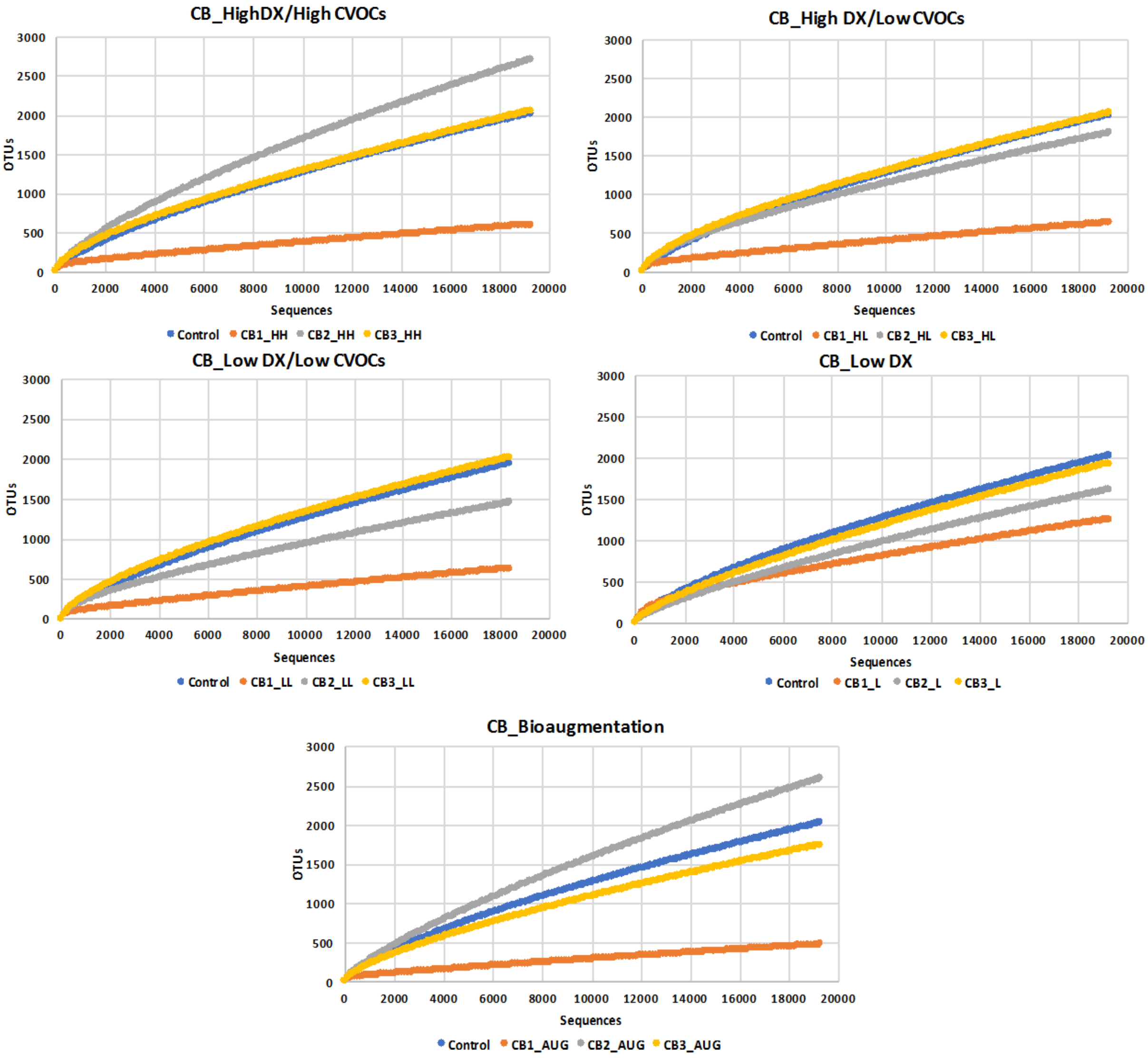


Figure 73. Rarefaction curves during catalysis- biodegradation process under different 1,4-dioxane and CVOC concentrations (CB). Rarefaction was plotted as the value of the measured diversity against the number of sequenced reads, estimating the 1) trend of diversity in different samples, and 2) whether all species in the sample had been detected. On the rarefaction curves, the y-axis represents the number of OTUs, and the x-axis indicates the trimmed number of sequenced reads.

4.3.4 Oxidation and Catalysis (OC)

Removal performance: The fraction of 1,4-dioxane degraded in the microcosms after the oxidation step is shown in **Figure 74**.

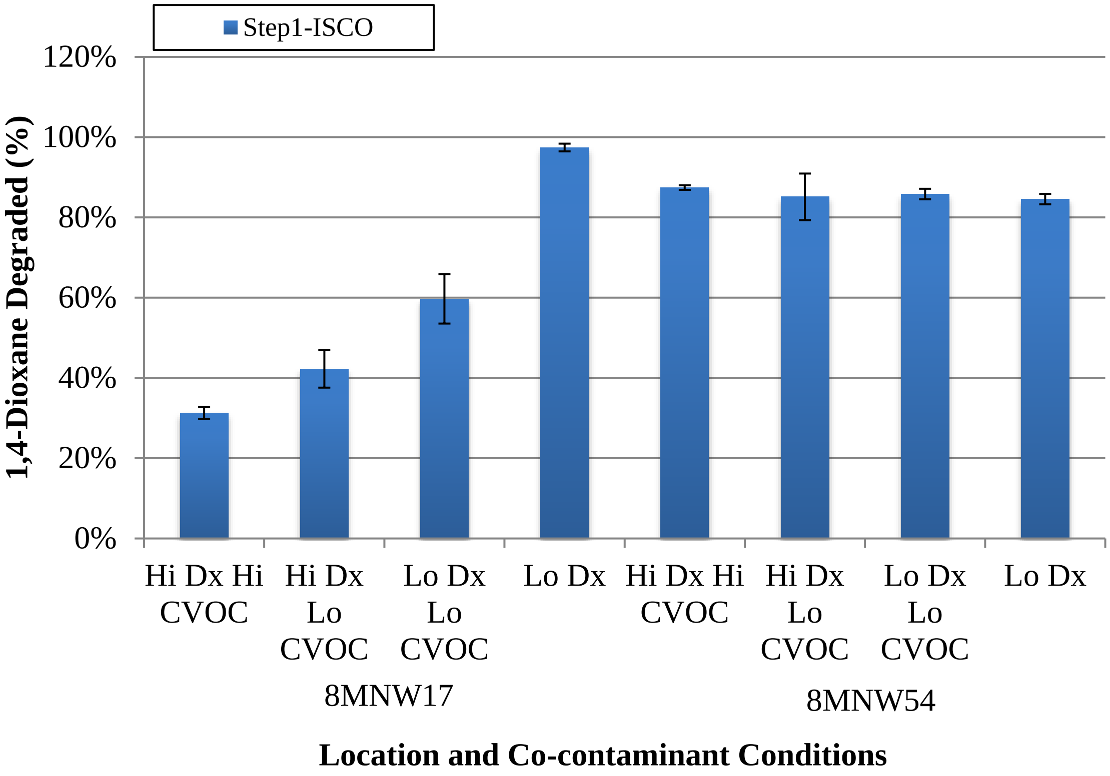


Figure 74. Percent of 1,4-dioxane degraded following oxidation step of OC treatment train.

The amount of 1,4-dioxane degraded in the 8MNW54 site was generally higher (up to ~90%) than the amount targeted (50%) as determined by the dosage screening studies, but reasonably match what was established in microcosms. The amount of 1,4-dioxane degraded in the 8MNW17 microcosms ranged from 35% to almost 90%. For this location, it appears that the presence of the CVOC co-contaminant did inhibit the degradation somewhat as the ones containing CVOC showed less 1,4-dioxane degradation than the low dioxane only condition, and the one containing a high CVOC condition showing less degradation than those with the low CVOC condition.

To test the effect of the catalysis step, the catalyst was then added, and a small dose of H_2O_2 was added to take into consideration the possibility that the $FeSO_4$ retained activity. The residual 1,4-dioxane degraded is defined as

$$residual\ 1{,}4 - dioxane = \left(1 - {C_n}/{C_{n-1}}\right) x100\%$$

where n is the concentration of 1,4-dioxane after the current step and n-1 is the concentration of 1,4-dioxane after the preceding step or right before the current step. In this case, C_n is the concentration of 1,4-dioxane after the catalysis low H_2O_2 treatment, and C_{n-1} is the concentration of 1,4-dioxane after the oxidation step. The residual 1,4-dioxane concentration for this step is shown in **Figure 75**.

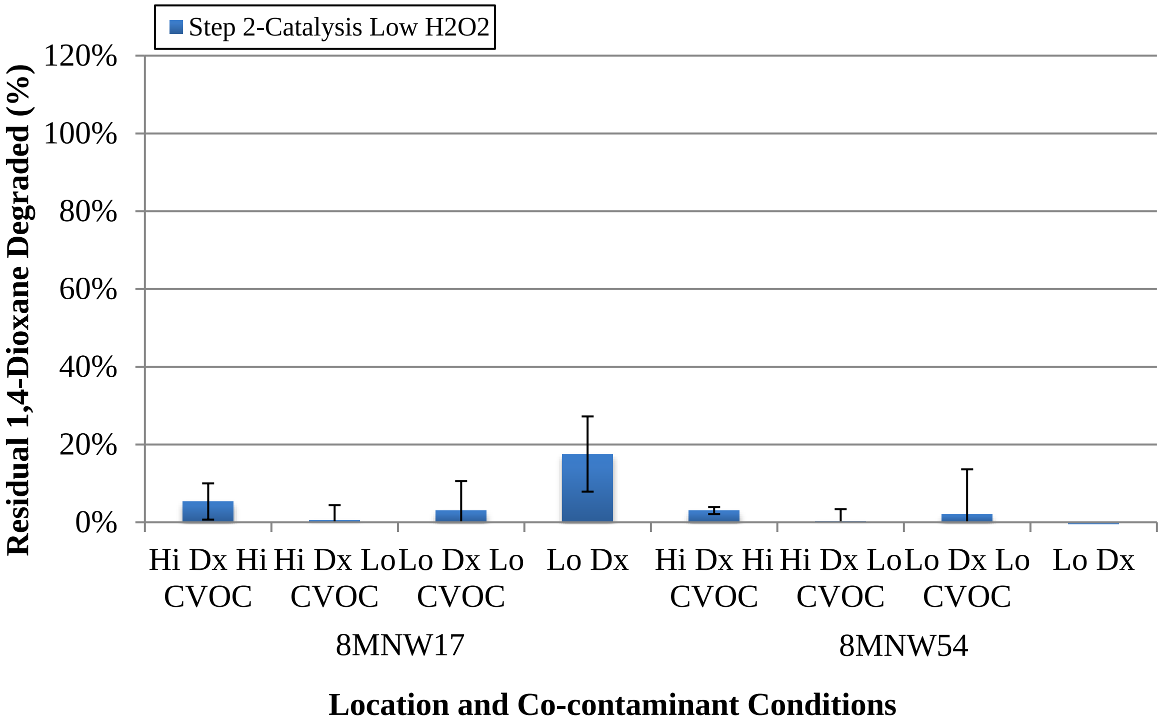


Figure 75. Fraction of residual 1,4-dioxane remaining after catalysis step 1 (low H_2O_2) of OC treatment train.

As can be seen, only a small fraction of the residual 1,4-dioxane remaining was degraded following the low dose of H_2O_2, with most microcosms showing less than 5% degradation. The exception is the low 1,4-dioxane only condition in 8MNW17, but it should be noted that the 1,4-dioxane in this microcosm was almost fully degraded in the oxidation step, so the absolute amount of 1,4-dioxane degraded was very small (~3 µg/L). It is not clear why the degradation in the microcosms was so small given the presence of both the catalyst and $FeSO_4$; the pH of the microcosms was verified to remain ~4, meaning the iron should have remained in solution, though it may be that the Fe(II) was oxidized to a less active Fe(III) species.

Because of the small observed dose, an additional 1600 µL of H_2O_2 was added to the microcosms to simulate the catalysis step performed in the CB train. The residual amount of 1,4-dioxane degraded by this step is shown in **Figure 76**.

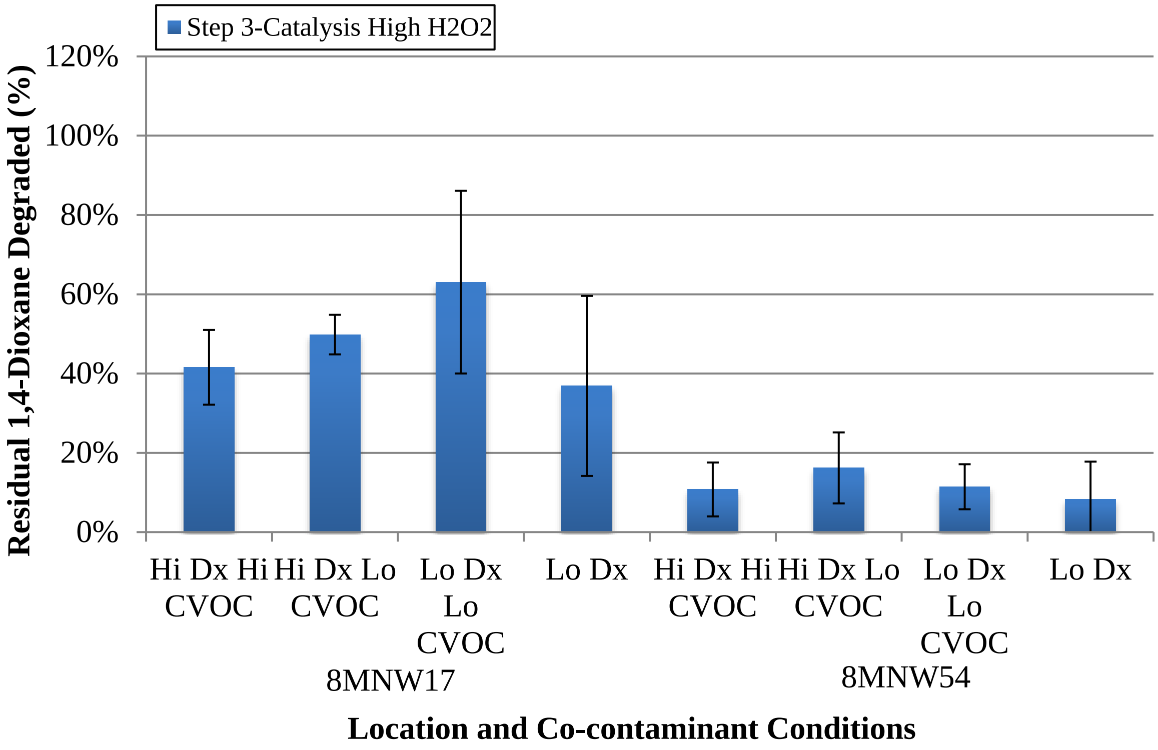


Figure 76. Fraction of residual 1,4-dioxane remaining after catalysis step 2 (high H_2O_2) of OC treatment train.

For 8MNW54, the fraction of remaining 1,4-dioxane that was degraded was similar to that achieved in the catalysis (C) portion of the CB train, with all of these microcosms exhibiting between 10-20% degradation, with the effect of CVOC co-contaminant unclear. For well 8MNW17, however, a much larger fraction of 1,4-dioxane was degraded, between 38-62% depending on the site conditions. For this site, it appears that the CVOC co-contaminant may have an effect. If one compares the high 1,4-dioxane conditions, the one with lower CVOC content does appear to have more 1,4-dioxane degradation, which may imply that CVOC is inhibiting the reaction. The effect is less clear for the low 1,4-dioxane conditions, which may be due to the unexpectedly high degradation of 1,4-dioxane following the oxidation step (see **Figure 74**).

The overall change in 1,4-dioxane concentration as it relates to the different treatment steps is shown in **Figure 77**. As previously mentioned, one reason for the much smaller relative drop in 1,4-dioxane concentration for well 8MNW54 relative to well 8MNW17 site in the final catalysis step may have been due to the fact that the oxidation step degraded significantly more 1,4-dioxane in this site compared to well 8MNW17.

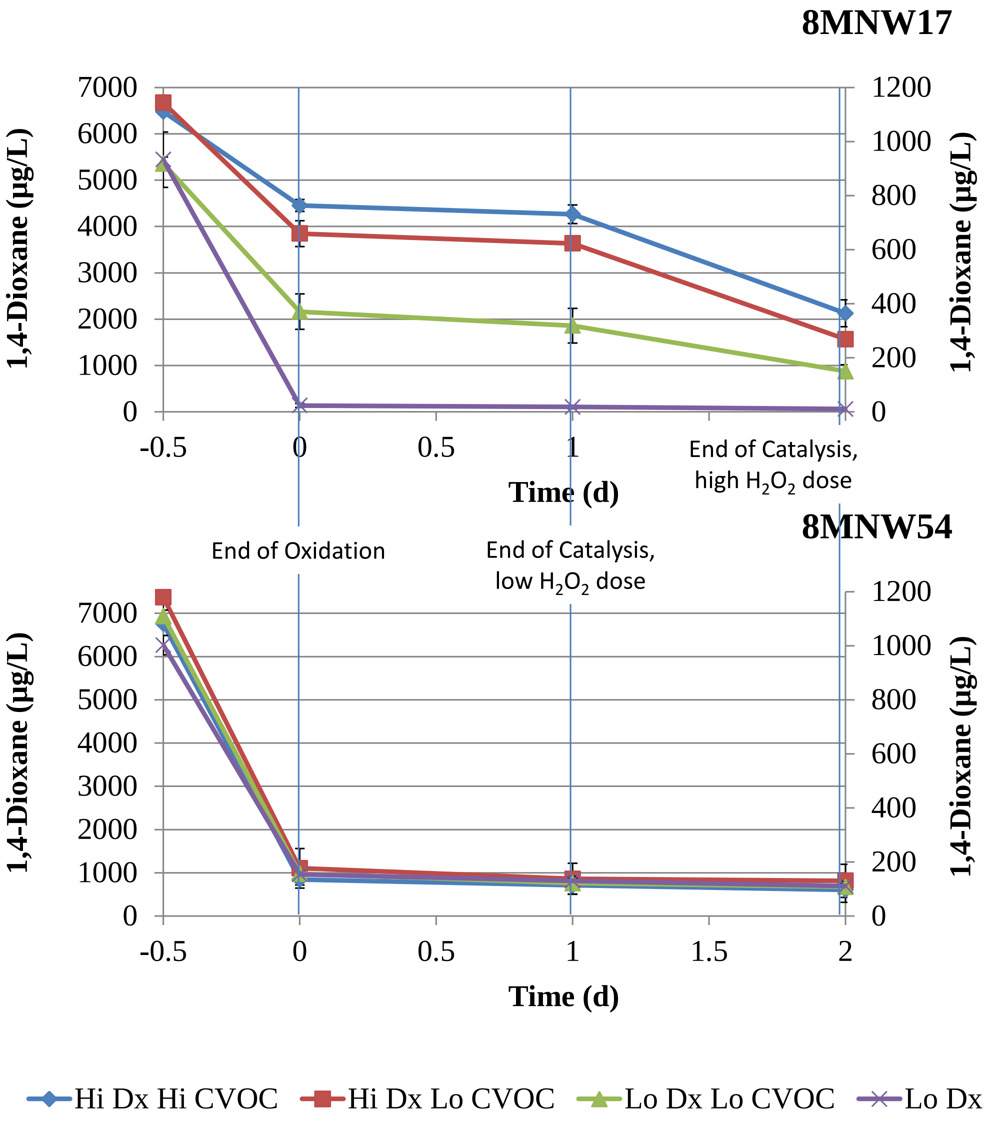


Figure 77. 1,4-dioxane concentration profiles of microcosms after OC treatment train.

Regardless, the combination of treatments resulted in greater degradation of the 1,4-dioxane than catalysis or oxidation alone. **Table 34** summarizes the amount of 1,4-dioxane degraded after the different treatments for the two locations and the different microcosm conditions.

Table 34. 1,4-dioxane degraded in O and C alone, and overall in OC Process

Location	**Condition**	**1,4-dioxane degraded (µg)**			
		Oxidation Only[a]	**Catalysis Only[b]**	**Catalysis step of OC train[c]**	**Overall OC**
8MNW17	High 1,4-dioxane, high CVOC	101.2	34.1	106.9	217.55
	High 1,4-dioxane, low CVOC	141.15	90.45	103.25	255.1
	Low 1,4-dioxane, low CVOC	27.35	4	8.45	38.4
	Low 1,4-dioxane	45.45	6.7	0.4	46.1
8MNW54	High 1,4-dioxane, high CVOC	295.5	61.15	5.25	307.5
	High 1,4-dioxane, low CVOC	313.2	38.85	2.35	327.7
	Low 1,4-dioxane, low CVOC	47.6	7.4	0.7	50.05
	Low 1,4-dioxane	42.35	6.45	1	44.55

[a] As determined by oxidation experiments in section 4.4.2

[b] As determined by catalysis experiment in section 4.4.1

[c] Note that this is 1,4-dioxane degraded in catalysis step only

In general, the amount of 1,4-dioxane degraded after the catalysis step in the OC train is much higher than the catalysis step alone for the 8MNW17 location. It appears to be much less effective for the 8MNW54 location and the low 1,4-dioxane case of the 8MNW17 location, however, these microcosms had significantly more 1,4-dioxane degraded in the oxidation step than anticipated (~90% as compared to ~50% for the target experiments). As can be seen, the combination of oxidation and catalysis in general degrades twice as much as the oxidation step alone, and anywhere from 3-10 times as much as the catalysis step alone, suggesting that this combination of treatment technologies could be effective for 1,4-dioxane degradation regardless of the presence of CVOC or initial concentration of 1,4-dioxane.

The enhancement of the catalysis step following the oxidation step vs the catalysis step alone could be due to a variety of reasons. The oxidation step involved lowering the pH of the microcosm to ~4, which could possibly promote the activity of the WO_x/ZrO_2. Additionally, the oxidation step could have potentially mineralized some would-be catalyst poisons (such as thiols) present in the microcosms to less deactivating species.

Biomarker genes: Treatment trains that included oxidation followed by catalysis showed different microbial responses depending on the AFP 3 well where microcosm material was obtained. In 8MNW17, total bacteria concentrations slightly decreased after oxidation and catalysis treatments (**Figure 78**). Moreover, CB1190-like bacteria were inhibited by the oxidation process, while the following catalysis step did not exhibit a strong inhibitory impact on CB1190-like bacteria (**Figure 79**). However, in well 8MNW54, inhibitory impacts of chemical reactions were clear under high DX/high CVOCs condition, while under low DX/low CVOCs and low DX conditions, more microorganisms survived after catalysis, indicating that higher concentration of 1,4-dioxane along with catalysis treatment exhibited more pressure on microbiomes in 8MNW54. In addition, CB1190-like bacteria were eliminated after oxidation process, showing their sensitive response to oxidation. The initial concentration of H_2O_2 oxidant, which was up to 0.96 mM in 8MNW54 compared to 0.24 mM in 8MNW17, in the samples both locations may have contributed to the observed difference in bacterial abundances.

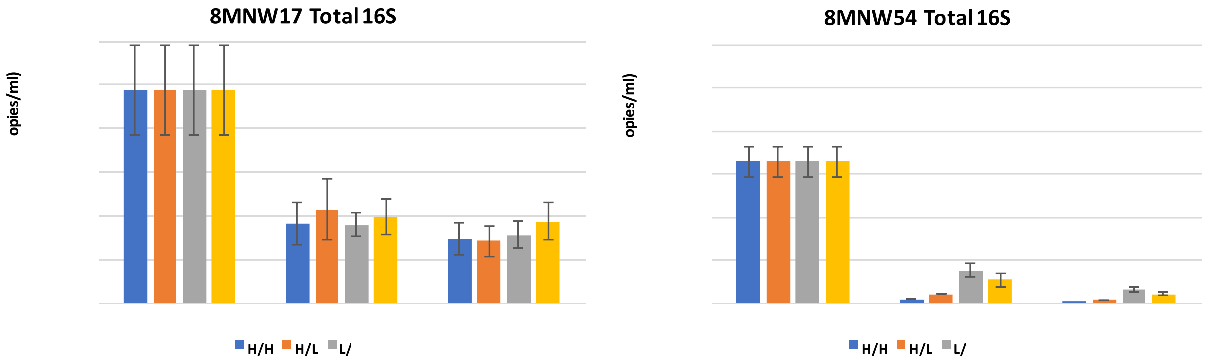


Figure 78. Total bacterial 16S rRNA gene abundance under different conditions during oxidation-catalysis process (OC).

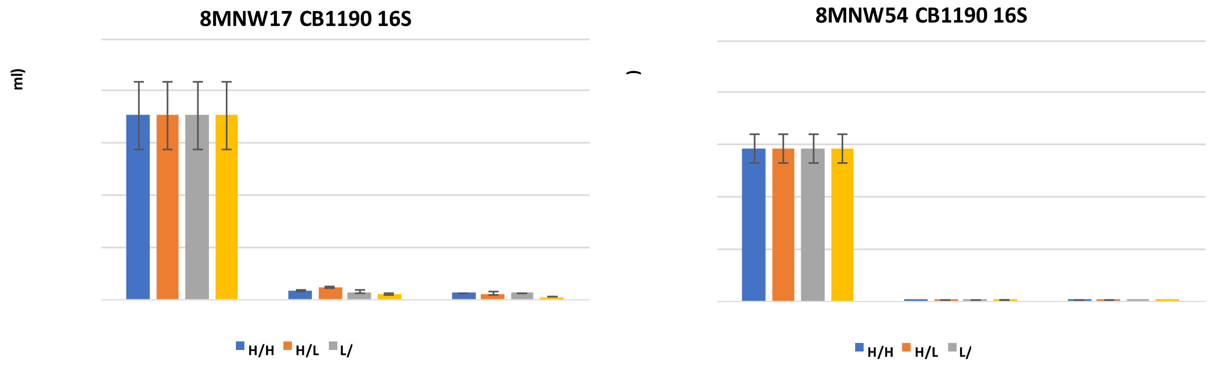


Figure 79. CB1190-like bacterial 16S rRNA gene abundance under different conditions during oxidation-catalysis process (OC).

Microbial community analysis: Samples from well 8MNW54 under five conditions, high 1,4-dioxane/high CVOCs (High/High), high 1,4-dioxane/low CVOCs (High/low), low 1,4-dioxane/low CVOCs (Low/Low), low 1,4-dioxane (Low) were collected at three sampling points, before biodegradation (Control), after oxidation (OC1), and after catalysis (OC2). Sequencing for metagenomics analysis was completed on an Illumina Miseq platform.

Pseudomonas was the dominant genus prior to chemical treatment (**Figure 80**). This genus was inhibited by the oxidation process and could not recover during the subsequent catalysis step. However, genus *Massilia* thrived after oxidation under all conditions, except for low DX condition, which was replaced by other genera in the same family Oxalobacteraceae, indicating the tolerance and/or recovery capabilities of *Massilia* to CVOCs. The other genus *Rhodococcus* also thrived except at high DX/high CVOCs condition, indicating its weak tolerance to CVOCs but peroxide-tolerance, which was reported to use hydrogen peroxide as sole oxygen source (Tarasov et al., 2004). Moreover, genus *Sphingomonas* showed catalyst-tolerance through an increased abundance during catalysis process, except high DX/high CVOCs condition, which was occupied by other genera belonging to the same family Sphingomonadales (**Figure 80**).

For the biodiversity analysis, in the high DX/high CVOCs condition, the diversity was slightly inhibited during oxidation and catalysis processes (**Figure 81**). Under other conditions, the oxidation step increased the biodiversity, then the catalysis step inhibited again, indicating that chemical reactions along with high CVOCs levels had widely-varying impacts on microorganisms. Specifically, under low DX condition, the final biodiversity was higher than that observed originally, which also demonstrates the associated impacts of CVOCs and catalysis on microorganisms (**Figure 81**).

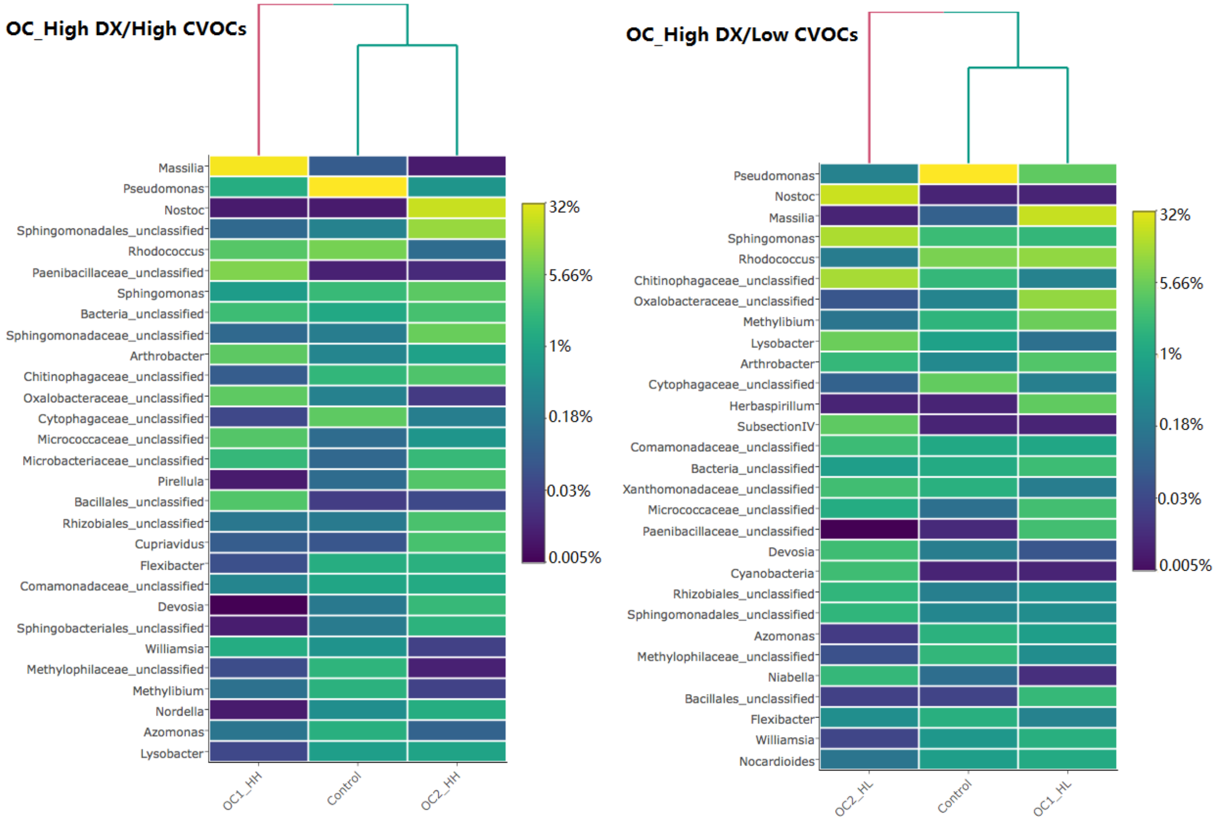


Figure 80 (continued next page). Microbial community analysis under different conditions during oxidation-catalysis process (OC). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at three sampling points: before biodegradation (Control), after oxidation (OC1), and after catalysis (OC2). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

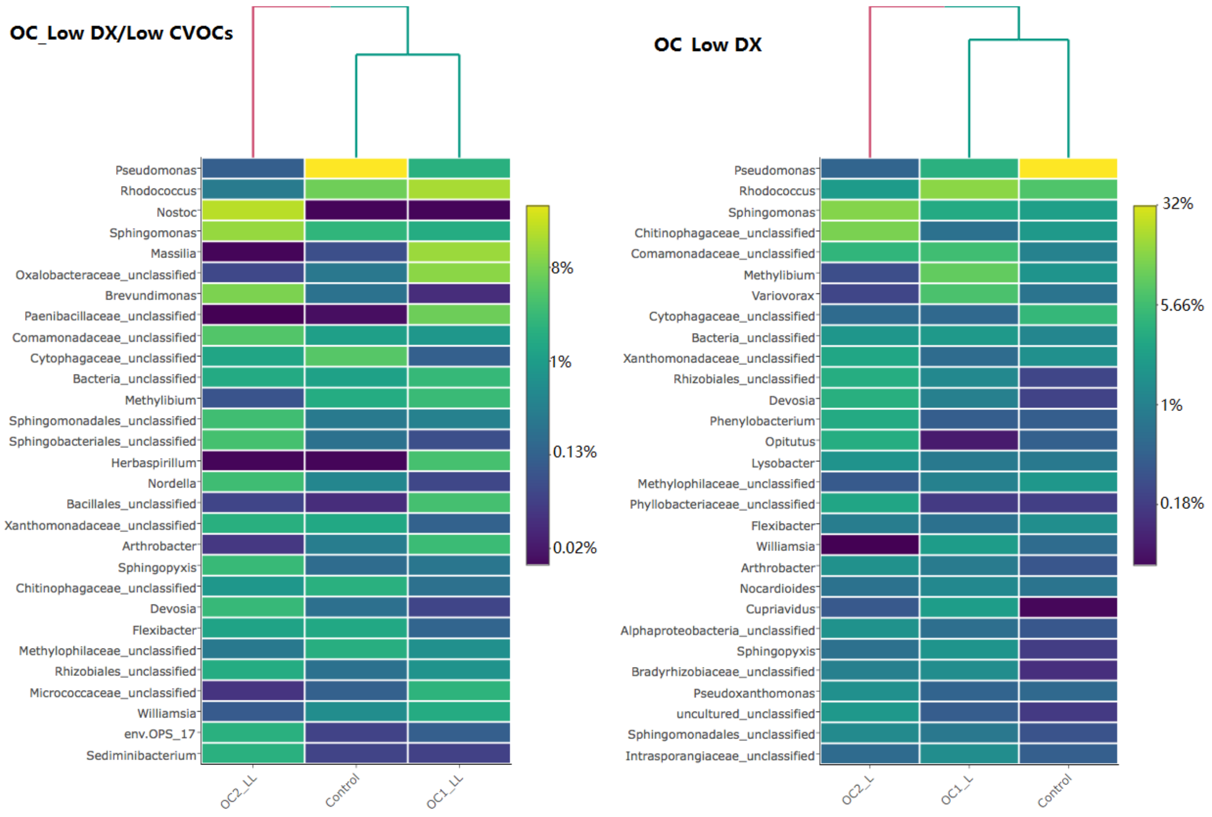


Figure 80 (continued from previous page). Microbial community analysis under different conditions during oxidation-catalysis process (OC). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at three sampling points: before biodegradation (Control), after oxidation (OC1), and after catalysis (OC2). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

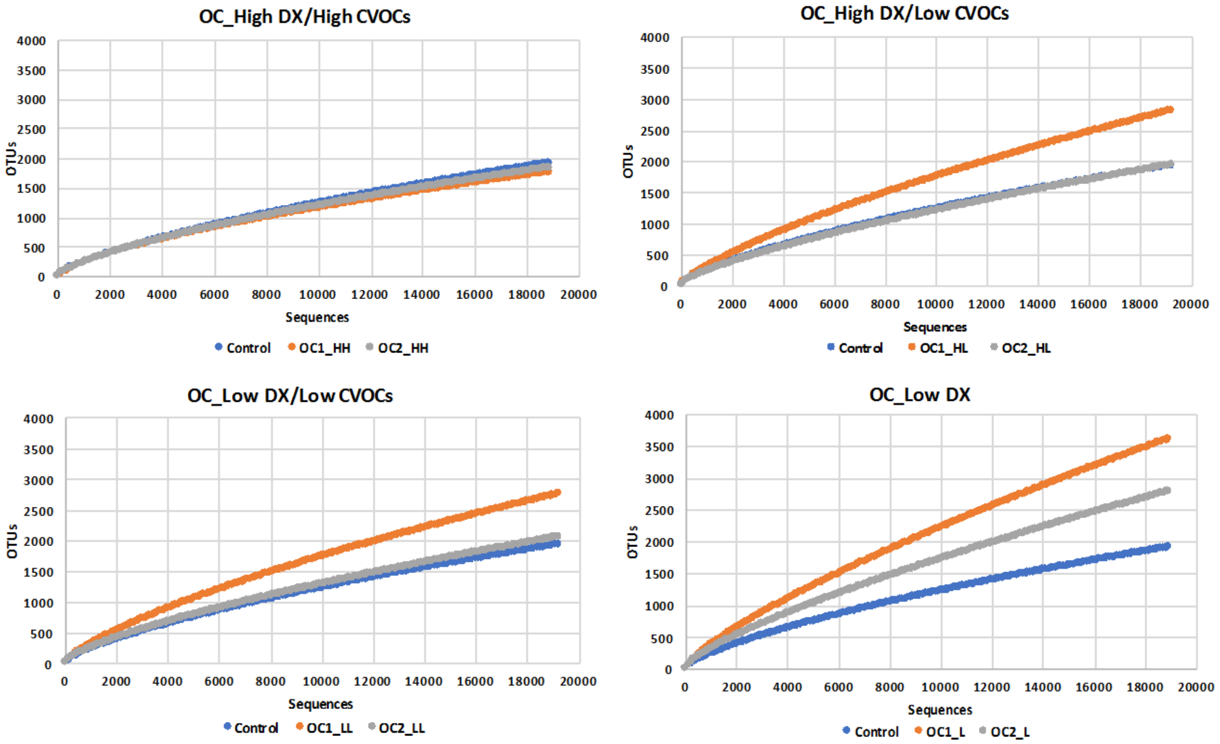


Figure 81. Rarefaction curves during oxidation-catalysis process under different 1,4-dioxane and CVOC concentrations (OC). Rarefaction was plotted as the value of the measured diversity against the number of sequenced reads, estimating the 1) trend of diversity in different samples, and 2) whether all species in the sample had been detected. On the rarefaction curves, the y-axis represented the number of OTUs, and the x-axis was indicating trimmed number of sequenced reads.

4.3.5 Oxidation, Biodegradation, and Catalysis (OBC)

Removal Performance: An extra catalysis step was also performed on the initial oxidation-bioremediation (OB) train. Like the oxidation-catalysis train, an initial low dose of H_2O_2 was added with the presumption that there would be some still active $FeSO_4$ in the microcosms. The residual 1,4-dioxane degraded is shown in **Figure 82**.

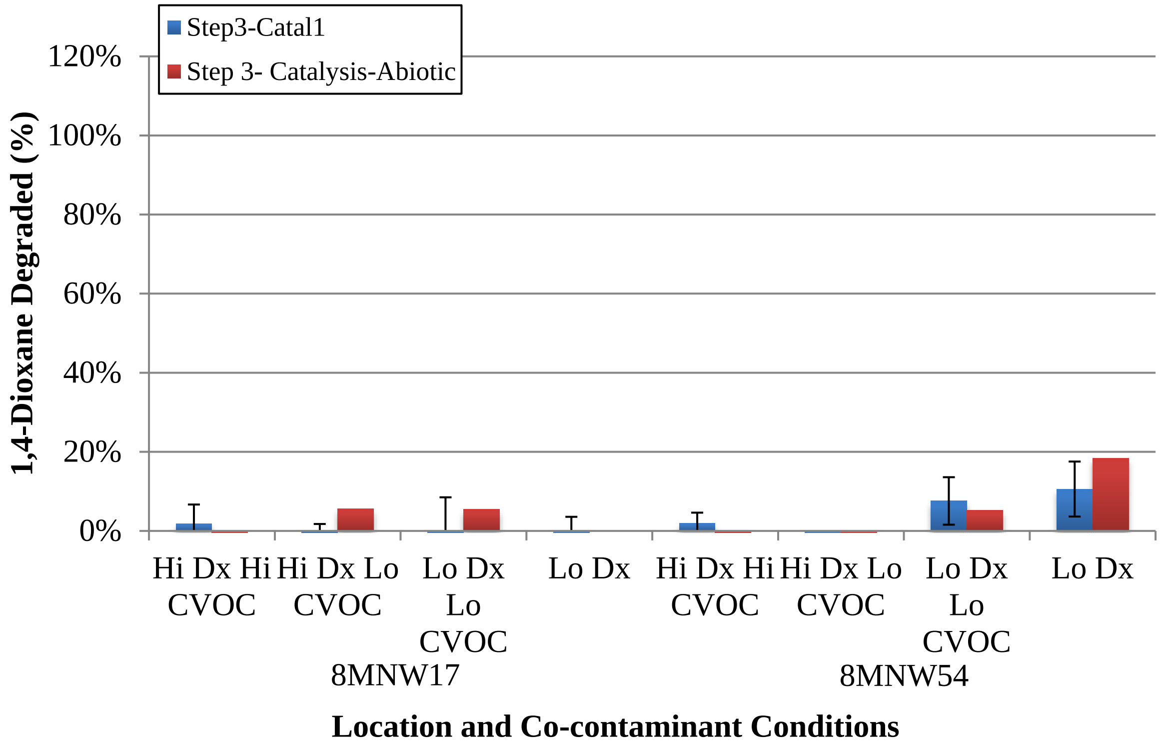


Figure 82. Fraction of residual 1,4-dioxane remaining after catalysis step 1(low H_2O_2) of OBC treatment train.

As was the case for the OC train, negligible 1,4-dioxane degradation was observed in all cases when the small dose of H_2O_2 was added. Because of this, an additional high dose of H_2O_2 was added as determined by the initial screening case. The residual fraction of 1,4-dioxane degraded is shown in **Figure 83**.

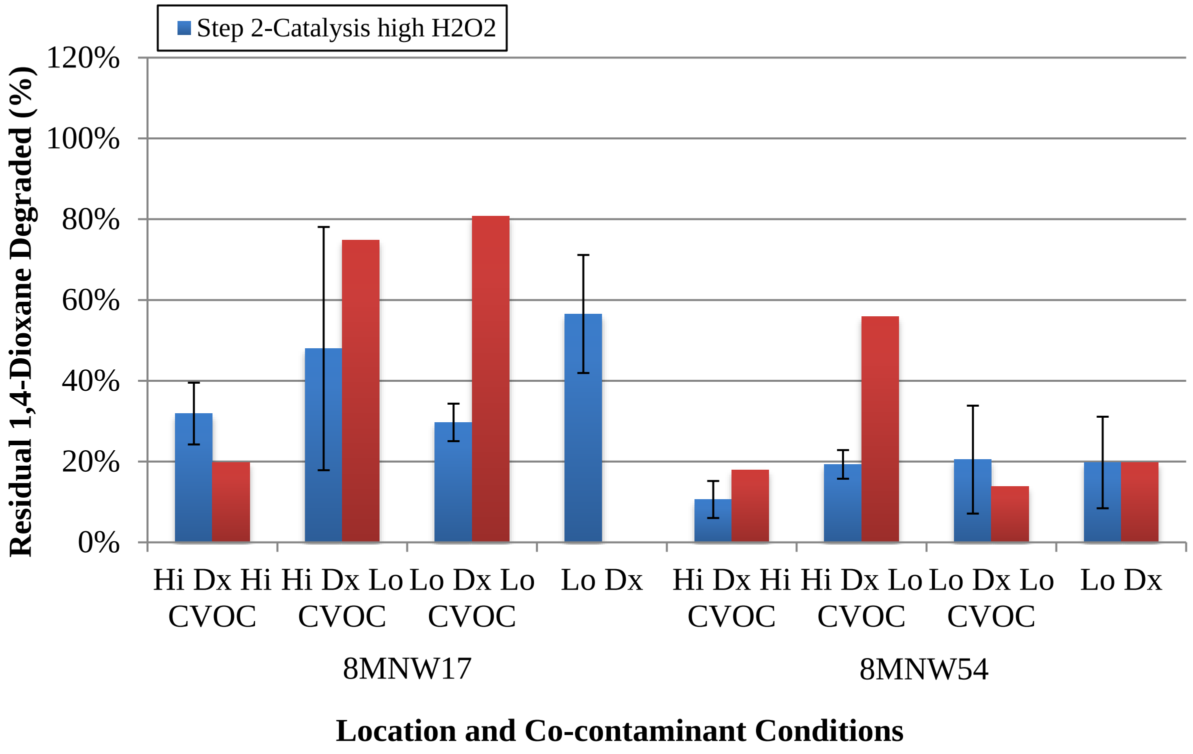


Figure 83. Fraction of residual 1,4-dioxane remaining after catalysis step 2 (high H_2O_2) of OBC treatment train.

The results are similar to those observed in the OC case, with more degradation observed in well 8MNW17 (~30-55%) than well 8MNW54 (10-20%). In both of these cases, there does seem to be an effect of the CVOC co-contaminant, with the high CVOC condition showing much less degradation than the low or no CVOC conditions. The effect of the lower concentration of CVOC was not as apparent, particularly at well 8MNW54.

The concentration of 1,4-dioxane in the microcosms for the two catalysis steps of the OBC train is shown in **Figure 84**.

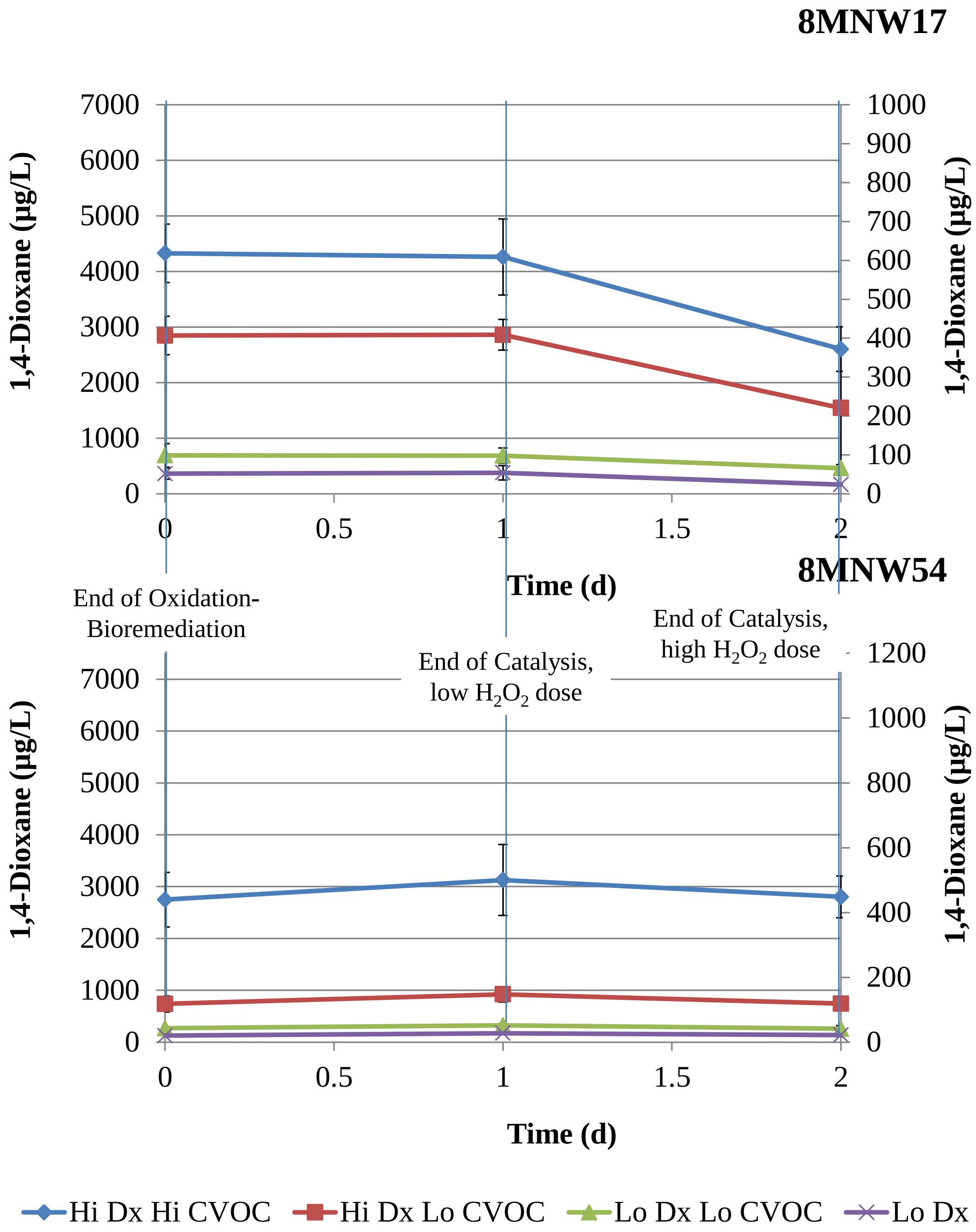


Figure 84. 1,4-dioxane concentration profiles of microcosms during catalysis steps of OBC treatment train.

Like the OC train, the final concentration of remaining 1,4-dioxane was much lower than the catalysis or oxidation step alone. **Table 35** summarizes the amount of 1,4-dioxane degraded after the different treatments for the two sites and the different microcosm conditions.

Table 35. 1,4-Dioxane degraded in O and C alone, and in catalysis steps for OC and OBC processes

Location	Condition	1,4-dioxane degraded (µg)				
		Oxidation Only[a]	Catalysis Only[b]	Catalysis step of OC train[c]	Catalysis step of OBC train[c]	Total in OC train
8MNW17	High 1,4-dioxane, high CVOC	101.2	34.1	106.9	83.0	217.6
	High 1,4-dioxane, low CVOC	141.2	90.5	103.3	65.9	255.1
	Low 1,4-dioxane, low CVOC	27.4	4.0	8.5	1.6	38.4
	Low 1,4-dioxane	45.5	6.7	0.4	1.5	46.1
8MNW54	High 1,4-dioxane, high CVOC	295.5	61.2	5.3	16.2	307.5
	High 1,4-dioxane, low CVOC	313.2	38.9	2.4	9.0	327.7
	Low 1,4-dioxane, low CVOC	47.6	7.4	0.7	0.5	50.1
	Low 1,4-dioxane	42.4	6.5	1.0	0.3	44.6

[a] As determined by oxidation experiments in section 3.2
[b] As determined by catalysis experiment in section 3.1
[c] Note that this is 1,4-dioxane degraded in catalysis step only

In general, the amount of 1,4-dioxane degraded after the catalysis step in the OC train is much higher than the catalysis step alone for well 8MNW17. It appears to be much less effective for the 8MNW54microcosms, however, it should be noted that these microcosms had a much lower starting concentration due to higher than anticipated degradation in the oxidation step. The difference in the amount of 1,4-dioxane degraded between the OC and OBC train can be due to similar arguments, well 8MNW17 had a lower pre-catalysis concentration for the OBC train than in the OC train, while well 8MNW54 generally had higher pre-catalysis 1,4-dioxane concentration (see **Figures 81** and **Figure 84**). Once again, it appeared that high CVOC concentrations slightly inhibited the 1,4-dioxane degradation, with lower CVOC concentrations having less of an effect.

Note that no additional biomarker or microbial community analyses were performed for this set of microcosms.

4.3.6 Biodegradation, Catalysis, and Oxidation (BCO)

Removal performance: 1,4-dioxane degradation during the catalysis step of the BCO train is shown in **Figure 85.**

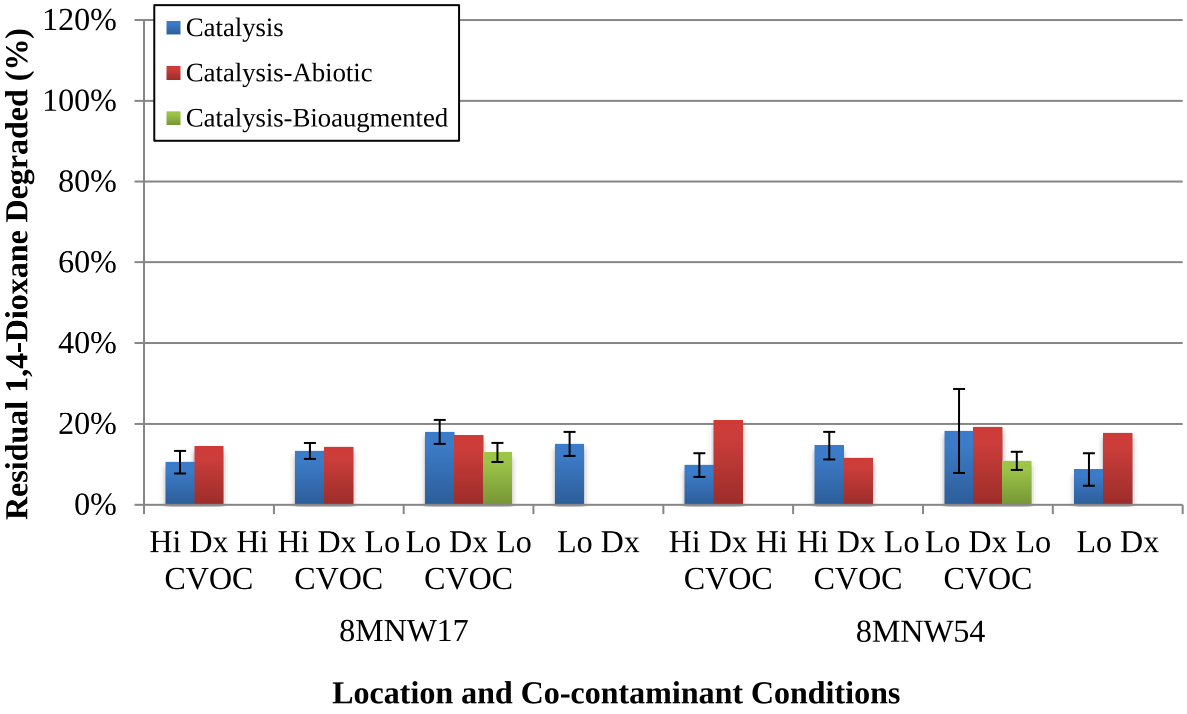


Figure 85. Fraction of residual 1,4-dioxane remaining after catalysis step of BCO treatment train. Note that abiotic 8MNW17 low 1,4-dioxane microcosm was broken during transport.

As can be seen, ~10-20% of the 1,4-dioxane was degraded following the catalysis step, which is consistent with both the screening experiments (**Table 31** and **Table 32**) and the results after the catalysis step in the CB train (**Figure 66 and Figure 67**). As in previous cases, there was no clear effect of CVOC co-contaminant.

Figure 86 shows the 1,4-dioxane degraded following the supplemental oxidation step of the BCO train.

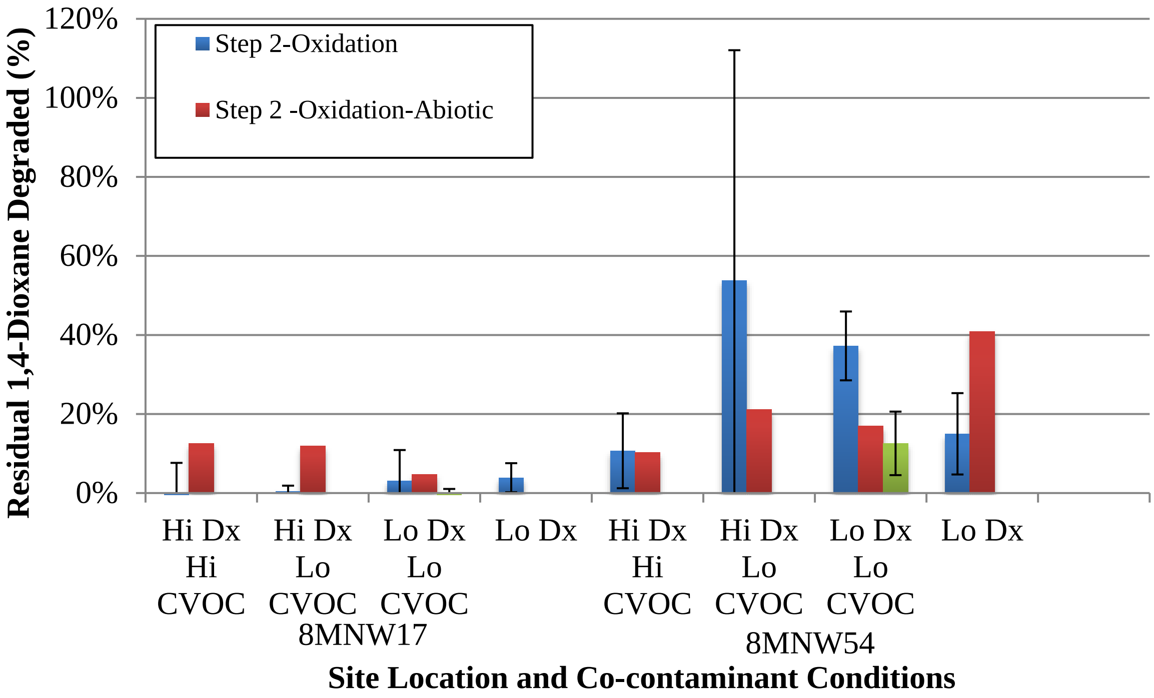


Figure 86. Fraction of residual 1,4-dioxane remaining after supplemental oxidation step of BCO treatment train. Note that abiotic 8MNW17 low 1,4-dioxane microcosm was broken during transport.

For well 8MNW54, there was a wide variation in the amount of 1,4-dioxane degraded, from 10-50%. The oxidation step was less effective for well 8MNW17, where only trace amounts of 1,4-dioxane was degraded. This trend matches the results from the oxidation step for other microcosms, where in general more 1,4-dioxane is degraded in well 8MNW54 microcosms site than well 8MNW17. However, it is noted that much less 1,4-dioxane was degraded following the O step in the BCO train than the OC train, which could possibly be due to a number of factors, such as nonspecific degradation of H_2O_2 on the additional catalytic material.

The concentration of 1,4-dioxane in the microcosms for the catalysis and oxidation steps for the BCO train is shown in **Figure 87**.

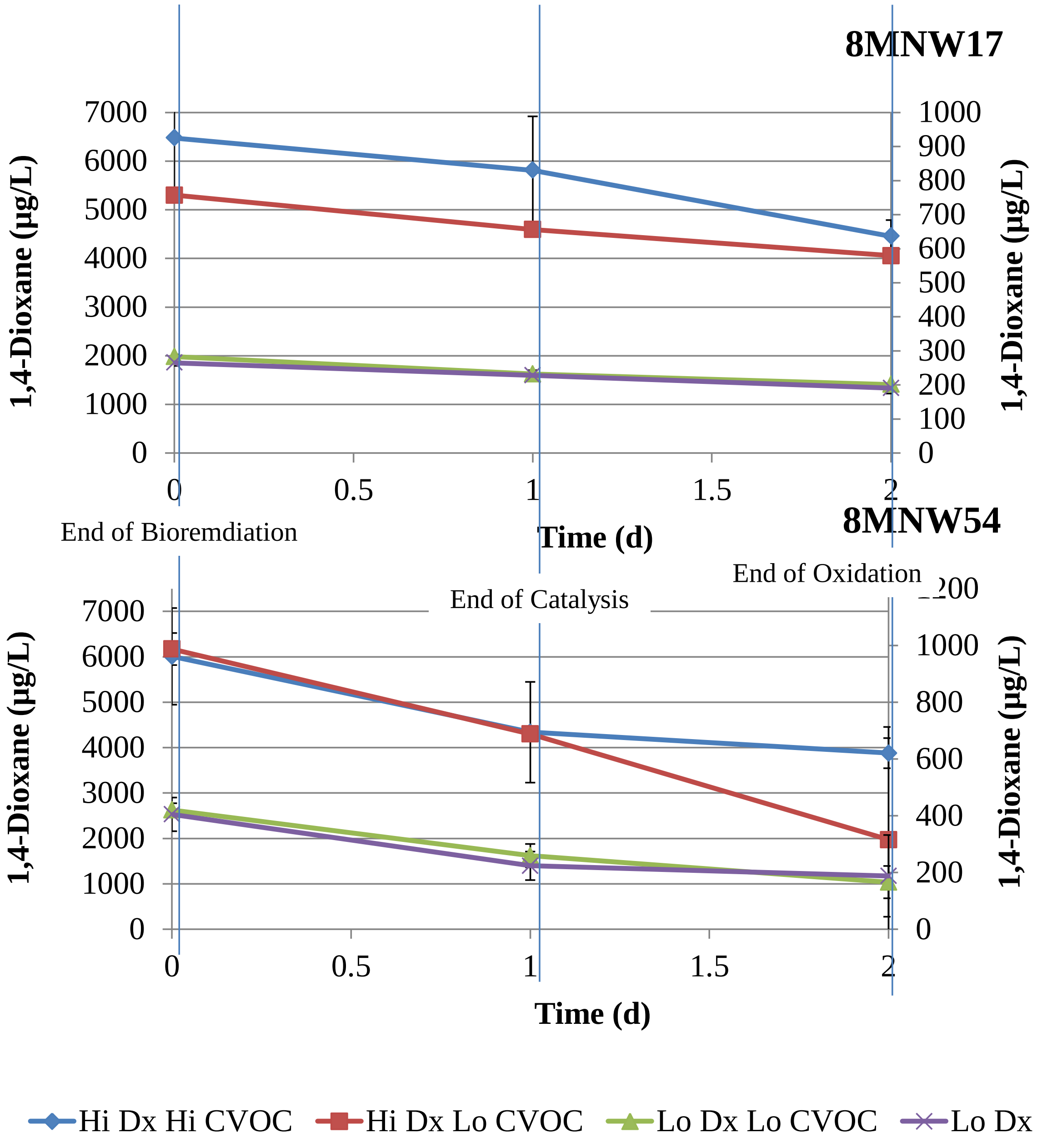


Figure 87. 1,4-dioxane concentration profiles of microcosms during catalysis and supplemental oxidation steps of BCO treatment train.

While the oxidation step following the catalysis step did not seem to be as effective as the catalysis step following the oxidation step, more degradation was observed regardless of microcosm when the combination of technologies was employed.

Biomarker genes: In the microcosms from well 8MNW17, total bacteria were stable after the chemical catalysis and oxidation steps, while total bacteria under low DX/low CVOCs and low DX conditions in the microcosms from well 8MNW54 were inhibited by both catalysis and oxidation (**Figure 88**). However, CB1190-like bacteria were inhibited under all conditions in the two wells (**Figure 89**). Biomarker genes DXMO and ALDH were only detected under bioaugmentation condition and these genes decreased in well 8MNW17 (**Figure 90** and **Figure 91**), which was consistent with the change of CB1190-like bacteria.

Microbial community analysis: Samples from well 8MNW54 under five conditions, high 1,4-dioxane/high CVOCs (High/High), high 1,4-dioxane/low CVOCs (High/low), low 1,4-dioxane/low CVOCs (Low/Low), low 1,4-dioxane (Low) and bioaugmentation (Bioaug) were collected and sequenced at four sampling points: before biodegradation phase (Control), after biodegradation phase (BCO1), after catalysis (BCO2), and after oxidation (BCO3).

The dominant genus *Pseudomonas* was inhibited under all conditions during the biodegradation phase, indicating the associated impact of 1,4-dioxane and chlorinated solvents on *Pseudomonas*, whose members could not degrade 1,4-dioane and CVOCs in the two wells (**Figure 92**). However, the abundance of *Pseudomonas* recovered after oxidation process under all conditions except for high DX/high CVOCs condition. This thriving process indicated that peroxide-tolerant members of *Pseudomonas* were present and abundant during the biodegradation phase. However, under high DX/high CVOCs condition, *Pseudomonas* was not recovered at the end, demonstrating the inhibitory effect of high level CVOCs on it. Moreover, this study is one of the first to our knowledge that reports on the dominance of genus *Sphingomonas* after catalysis treatment. In addition, genera *Ensifer* and *Cupriavidus* thrived after oxidation process indicating peroxide tolerance. Many members of these genera were also previously reported to overexpress *flavodoxin* to resist oxidative stress (Coba de la Pena et al., 2013).

During the biodegradation phase, microorganisms were able to grow in relatively suitable conditions and thus more species thrived after biodegradation. However, the subsequent catalysis and oxidation processes inhibited biodiversity, which eliminated vulnerable species in the microcosms. Interestingly, CVOC levels also had an apparent effect on the measured biodiversity. In the presence of lower CVOC concentrations, the biodiversity returned to the original level, while under higher CVOCs or no CVOCs conditions, the biodiversity eventually exceeded the original level, indicating the complicated composition of microorganisms responding to CVOCs (**Figure 93**).

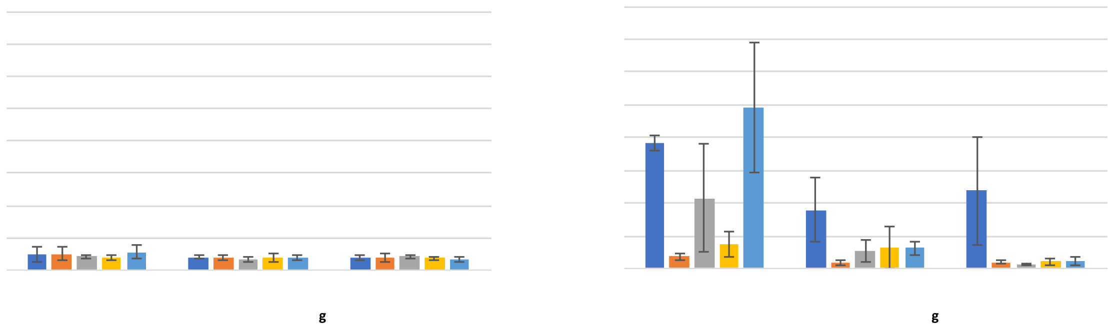


Figure 88. Total bacterial 16S rRNA gene abundance under different conditions during biodegradation-catalysis-oxidation process (BCO)

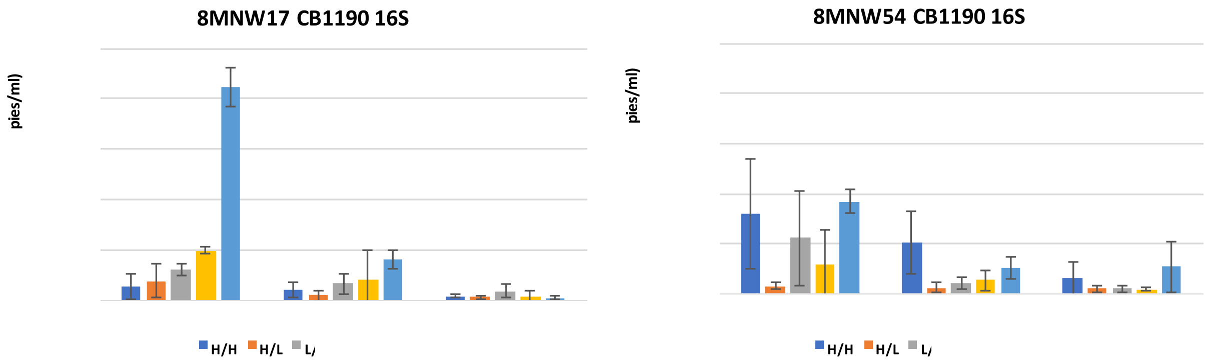


Figure 89. CB1190-like bacterial 16S rRNA gene abundance under different conditions during biodegradation-catalysis-oxidation process (BCO).

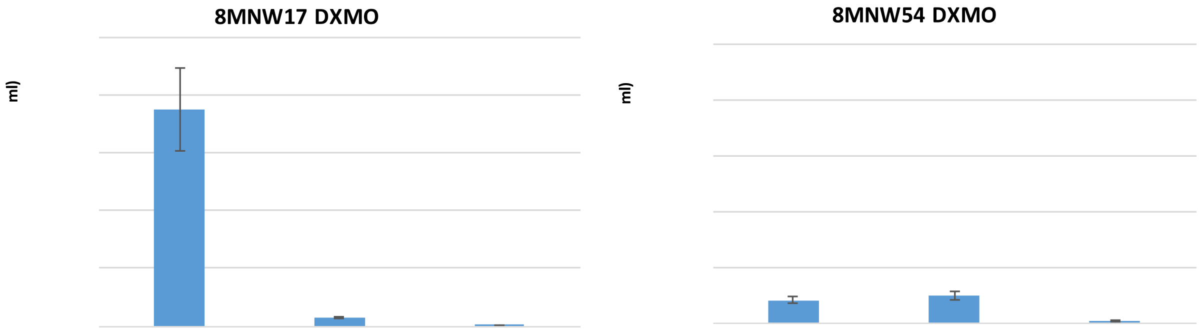


Figure 90. DXMO gene abundance under bioaugmentation condition during biodegradation-catalysis-oxidation process (BCO).

Figure 91. ALDH gene abundance under bioaugmentation condition during biodegradation-catalysis-oxidation process (BCO).

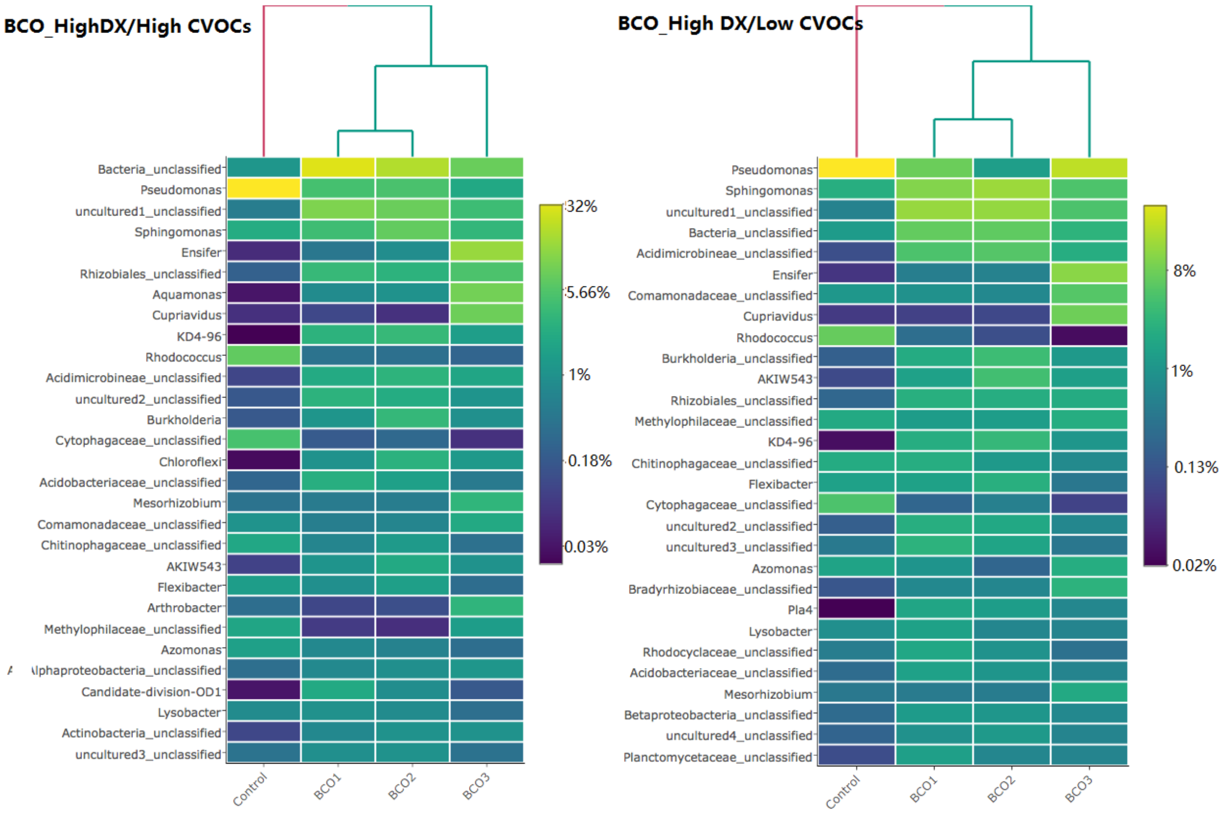


Figure 92 (continued on next page). Microbial community analysis under different conditions during biodegradation-catalysis-oxidation process (BCO). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before biodegradation phase (Control), after biodegradation phase (BCO1), after catalysis (BCO2), and after oxidation (BCO3). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

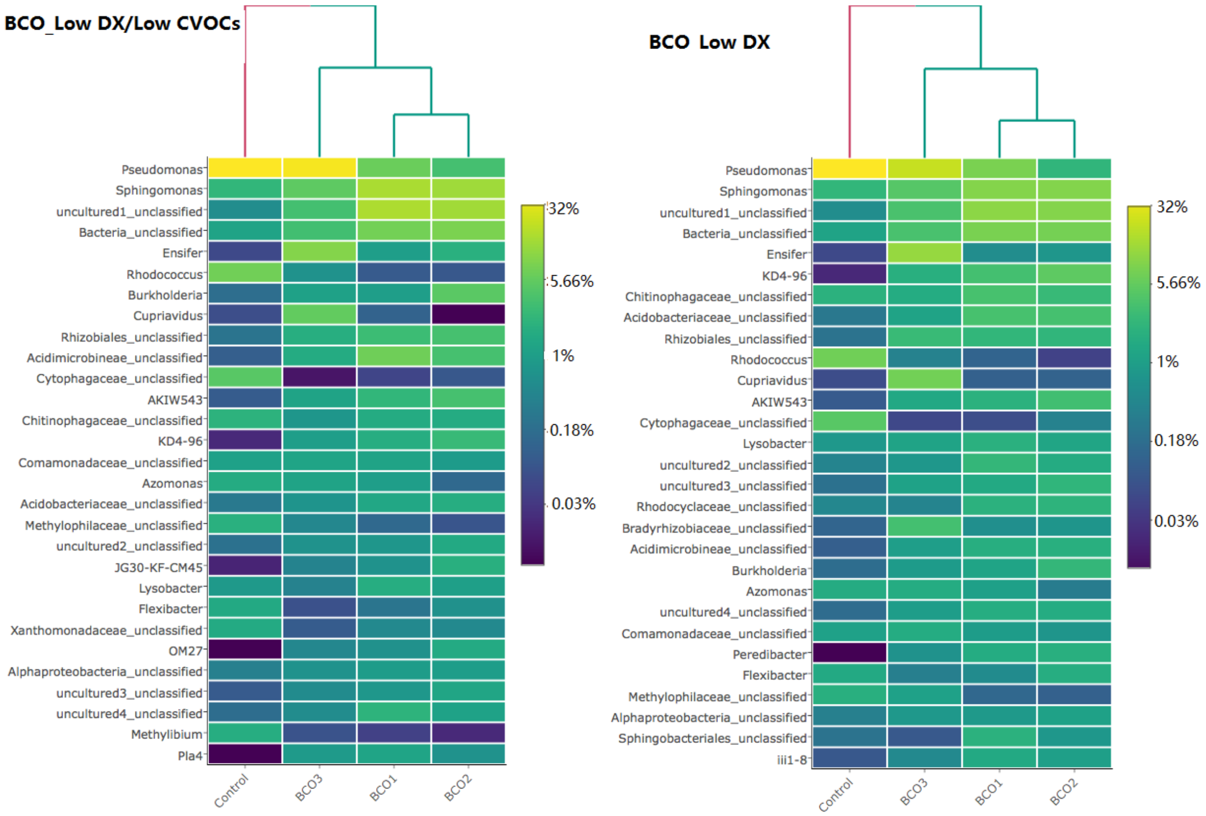


Figure 92 (continued from pervious page; continued on next page). Microbial community analysis under different conditions during biodegradation-catalysis-oxidation process (BCO). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before biodegradation phase (Control), after biodegradation phase (BCO1), after catalysis (BCO2), and after oxidation (BCO3). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.

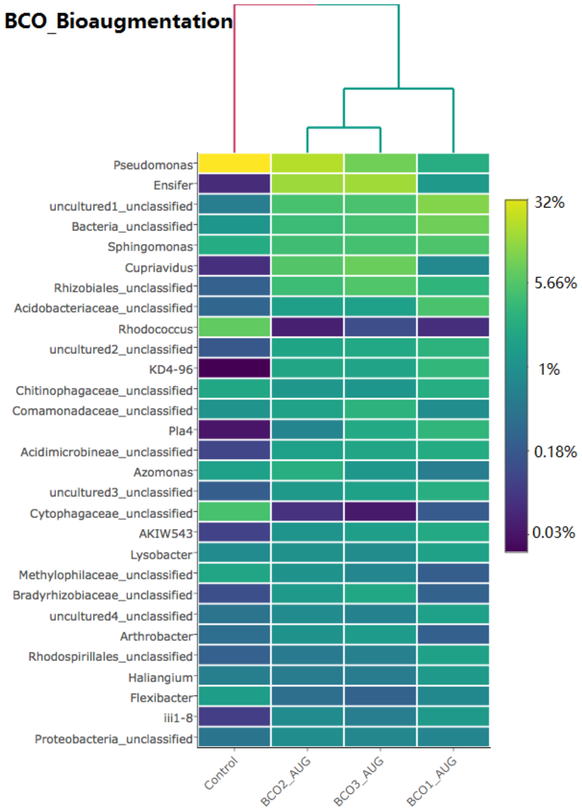
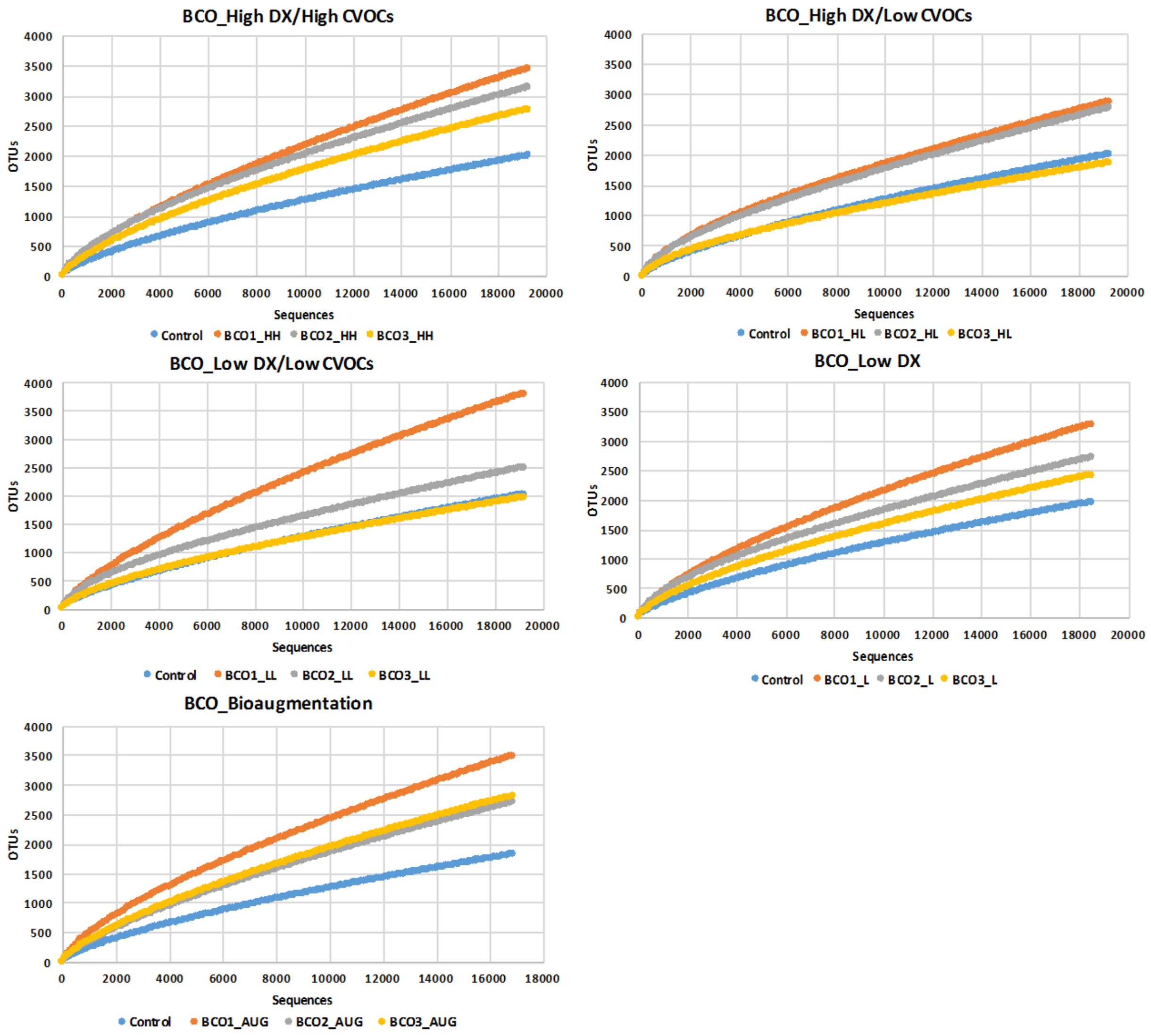


Figure 92 (continued from previous page). Microbial community analysis under different conditions during biodegradation-catalysis-oxidation process (BCO). Each column represents relative abundance (%) of top 30 abundant genera in each sample. Samples were collected at four sampling points: before biodegradation phase (Control), after biodegradation phase (BCO1), after catalysis (BCO2), and after oxidation (BCO3). Relative abundance (%) was the ratio that number of reads belonged specific genus versus total number of reads in one sample.


BCO_High DX/High CVOCs

BCO_High DX/Low CVOCs

BCO_Low DX/Low CVOCs

BCO_Low DX

BCO_Bioaugmentation

Figure 93. Rarefaction curves during biodegradation-catalysis-oxidation process under different 1,4-dioxane and CVOC concentrations (BCO). Rarefaction was plotted as the value of the measured diversity against the number of sequenced reads, estimating the 1) trend of diversity in different samples, and 2) whether all species in the sample had been detected. On the rarefaction curves, the y-axis represents the number of OTUs, and the x-axis indicates the trimmed number of sequenced reads.

4.3.7 Treatment Train Summary

This task served as the foundation for developing improved engineered 1,4-dioxane bioremediation technologies under chlorinated solvents co-contaminants stress. The combined chemical and biological treatment technologies has the potential to provide effective cost-friendly solutions to treat 1,4-dioxane and CVOCs contaminated areas. In addition, the actual environmental microbial community structure and 1,4-dioxane biodegradation related functional gene encoding enzymes were identified in this study.

Co-occurring chlorinated solvents were shown to impose time- and dose-dependent inhibition on 1,4-dioxane biodegradation, via energy depletion, reduced functional gene abundance, and decreased expression carried by 1,4-dioxane metabolizers. Thus, bioaugmentation with CB1190 could not remove 1,4-dioxane efficiently in the biodegradation only treatment. In this study, the use of chemical oxidation followed by bioaugmentation resulted in complete 1,4-dioxane removal with 5 μg/L contaminant mixtures. A similar removal performance was observed in the catalysis-bioaugmentation treatment trains where 1,4-dioxane concentrations decreased more than in unamended catalysis-biodegradation microcosms. The chemical reactions were able to break the structure of co-contaminants and improve the biodegradability of the target compound (1,4-dioxane), which could be further utilized by the microorganisms used for bioaugmentation. Moreover, advanced oxidation process might provide oxygen for aerobic biodegradation and produce bioavailable oxidized daughter compounds. Thus, bioaugmentation in conjunction with *in situ* chemical oxidation or catalysis might be a promising and applicable strategy for the engineered 1,4-dioxane remediation. The amount of 1,4-dioxane and CVOCs degraded by the catalysis step was generally lower than for chemical oxidation. Therefore, chemical oxidation is likely to be the preferred initial step for treatment trains

Analyses of the microbial community structure and biodiversity indicated that there were shifts in the microbiomes in different treatment train combinations under high or low contaminant mixtures stress. Genus *Pseudomonas* was detected as the dominant genus in the original native population, but it exhibited a different response to each combination of treatments. Chemical processes would inhibit *Pseudomonas*, and it could not recover in the subsequent biodegradation step. However, in the BCO train, *Pseudomonas* could grow up in the biodegradation phase prior to catalysis and oxidation treatments. Moreover, some peroxide-tolerant or catalyst-tolerant genera were found after chemical treatments, such as *Ralstonia*, *Methylobacterium*, *Perlucidibaca*, *Janthinobacterium*, *Sphingomonas*, *Ensifer* and *Cupriavidus*, etc. Biodiversity demonstrated the abundances and types of microbiomes dynamics that were associated with each phase of the combined treatments. Chemical processes prior to the biodegradation phase would reduce the biodiversity, and tolerant members of the microbial community were able to thrive during the biodegradation phase, indicating a diverse and resilient microbiome after chemical processes.

Overall, this study evaluated the efficiency of combined treatment technologies and highlighted the viability of a treatment approach based on oxidation/bioaugmentation. Metagenomics provided comprehensive insights into the microbial communities, which expanded our understanding of the functional microorganisms found in 1,4-dioxane contaminated environments and revealed the potential for further optimization of engineered 1,4-dioxane bioremediation under co-contaminants stress.

4.4 Implications of Matrix Diffusion

Overall hypothesis that was tested: Matrix diffusion is an important process for 1,4-dioxane and should be included in site management decisions

4.4.1 Modeling Study

Dissolution Modeling: The dissolution model was used to estimate the representative source concentration (C_s = 29,100 mg/L) and the loading period (2.7 years) for Scenario 1. As shown in **Figure 94**, high 1,4-dioxane concentrations are present in the source zone immediately following release but would be expected decline rapidly within a short period, such that the period for back diffusion is much longer than the leading period in this case. TCA concentrations increase slightly during the period when the 1,4-dioxane source is depleting, then remain relatively constant near saturation levels for several decades until the TCA NAPL is depleted. For matrix diffusion modeling of TCA, this yielded a C_s value of 751 mg/L and a loading period of 39.9 years.

Note that this scenario involved a release date of 1970 (i.e., during a period when TCA usage was relatively high), which pre-dates most monitoring programs for 1,4-dioxane by several decades. Since the loading period appears to be very short based on these results, they suggest that the recent monitoring programs for 1,4-dioxane are measuring concentrations that are far from representative of the historic source concentrations. As described in the next section, it also indicates that 1,4-dioxane concentrations in this range (well below solubility) may be strongly influenced by back diffusion processes.

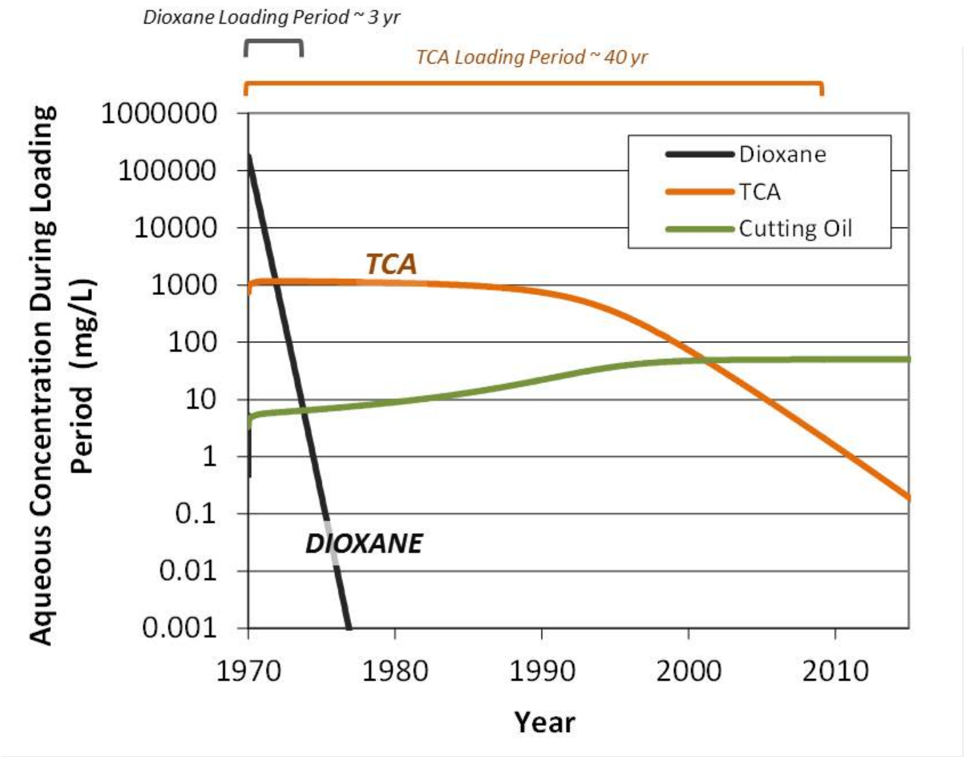


Figure 94. Predicted Source Concentration vs. Time for 1,4-dioxane and TCA from NAPL Dissolution. Loading periods defined by dissolution of 99.9% of initial mass for each constituent. Cutting oil included in NAPL dissolution model for purpose of adjusting mole fractions of 1,4-dioxane and TCA.

Matrix Diffusion in On-Site Source Zone (Scenario 1): The impact of matrix diffusion on mass distribution over time within the low-permeability and transmissive portions of the source zone was calculated using the “Square-Root Model” (i.e., Eq (2)). **Figure 95** displays the results for the 80-year period following the release (1971-2050) for both 1,4-dioxane and TCA. At the end of the loading period for 1,4-dioxane (1973), the total mass of 1,4-dioxane in the low-permeability interval within the source zone peaked at 270 kg for the baseline case. This was followed by a decline in the 1,4-dioxane mass in this layer due to a switch in the concentration gradient. For TCA, mass accumulated in the low-permeability zone for a longer period due to its lower effective solubility. At the end of the TCA loading period in 2010, a a maximum value of 41 kg was reached. This is slightly higher than the 1,4-dioxane mass present in 2010. However, there is a noticeably flatter “tail” in the 1,4-dioxane mass trend by this point, and the TCA mass in the low-permeability zone decreases to a level well below that for 1,4-dioxane within a few years after the end of the loading period. By the end of the simulation in 2050, there is nearly twice as much 1,4-dioxane (26 kg) as TCA (17 kg) predicted to remain in the low-permeability zone.

The shaded areas on the curves in **Figure 95** show the mass distributions for 1,4-dioxane and TCA using a larger range of source concentrations for each compound. The mass that diffuses into the low-permeability zone is linearly proportional to C_s in these models, and results reflect this pattern. For 1,4-dioxane, the lower end (3000 mg/L) and upper end (300,000 mg/L) of C_s values that were simulated cover a wide range of initial source concentrations. For TCA, an upper limit of 1330 mg/L was set to match the aqueous solubility of this compound. These results highlight the impact of weaker and stronger source strengths on diffusion of these compounds during the selected loading periods. For example, a NAPL with a higher mole fraction of 1,4-dioxane would be associated with a higher source concentration. In this case, the higher mass dissolution rate for 1,4-dioxane compensates for the larger mass present in the NAPL, such that the loading period (i.e., diffusion into the low-permeability zone due to the presence of an active source) is relatively unaffected by the change in mole fraction.

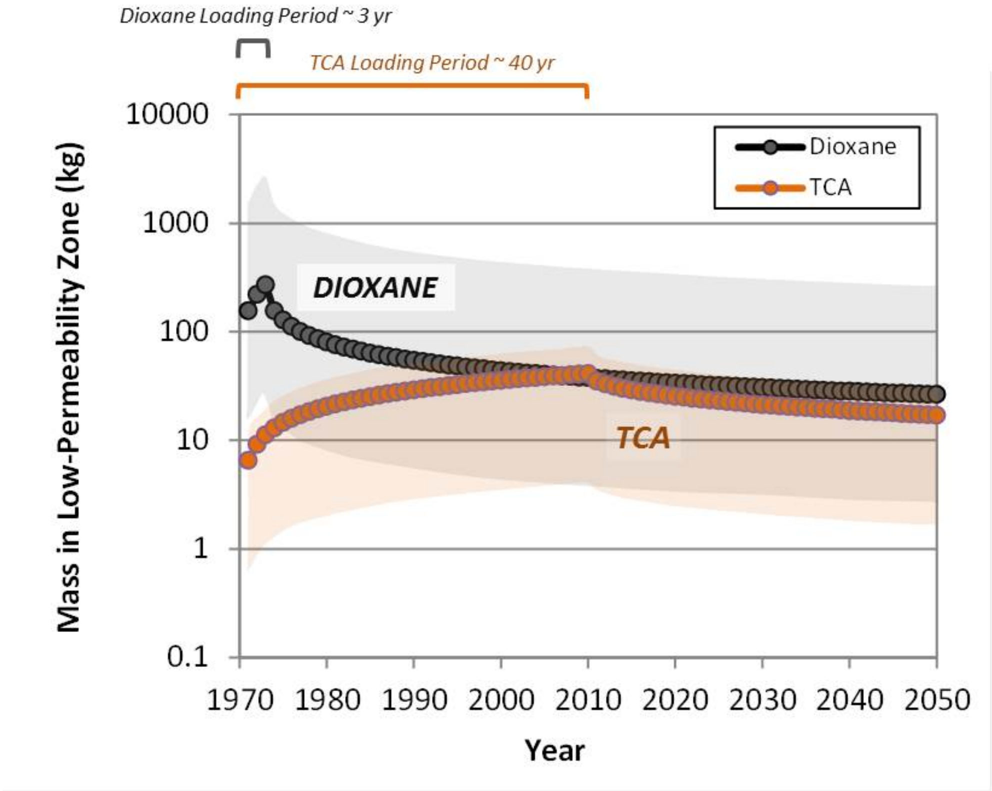


Figure 95. 1,4-dioxane and TCA Masses in Low-Permeability Interval within Source Zone for On-Site Source Scenario (Scenario 1). Assumed release of 1,4-dioxane and TCA in NAPL using loading scenario described in Table 9. Shaded areas for each constituent represent results for sensitivity analysis (dioxane C_s = 30,000 – 300,000 mg/L; TCA C_s = 75 mg/L – 1330 mg/L).

Figure 96 shows the predicted aqueous concentrations of 1,4-dioxane and TCA resulting from diffusion of these compounds from the low-permeability zone to the transmissive zone. The initial 1,4-dioxane concentration exceeded 100 mg/L immediately following depletion of the source, and this directly reflects the significant mass stored within the low-permeability layer. During the next 80 years when back diffusion was occurring, concentrations in the transmissive zone declined by over two-orders of magnitude. However, the 1,4-dioxane concentration remained significantly higher than potentially-applicable action levels even after this extended period. For reference purposes, the California notification level of 0.001 mg/L is shown on **Figure 96**. This illustrates that regulatory drivers would require a concentration reduction of several additional orders-of-magnitude before compliance could be achieved. Based on the C_s sensitivity analysis (shaded areas in **Figure 96**), even the lowest C_s value during the loading period would still result in 1,4-dioxane concentrations that exceeded the 0.001 mg/L level by several orders of magnitude for several centuries. It should be understood that this is an idealized scenario, meaning that it assumes that compliance within a source zone monitoring well would be required. Regardless, these results establish that diffusion of 1,4-dioxane can contribute to elevated aqueous concentrations long after the source in the transmissive zone is depleted.

The trend in the predicted aqueous concentrations of TCA in the transmissive zone reflected that there was less TCA mass stored in the low-permeability zone relative to 1,4-dioxane. Diffusion of TCA from the low-permeability zone resulted in an initial post-loading concentration of approximately 10 mg/L. By the end of the simulation period (2050), the concentration for the baseline case had declined below that of 1,4-dioxane at the same timepoint. For cases where a lower TCA C_s was assumed during the loading period, the TCA concentration resulting from diffusion eventually decreased below the MCL (0.2 mg/L). These results illustrate that TCA is generally less persistent than 1,4-dioxane, despite the higher potential for sorption of TCA within the low-permeability zone.

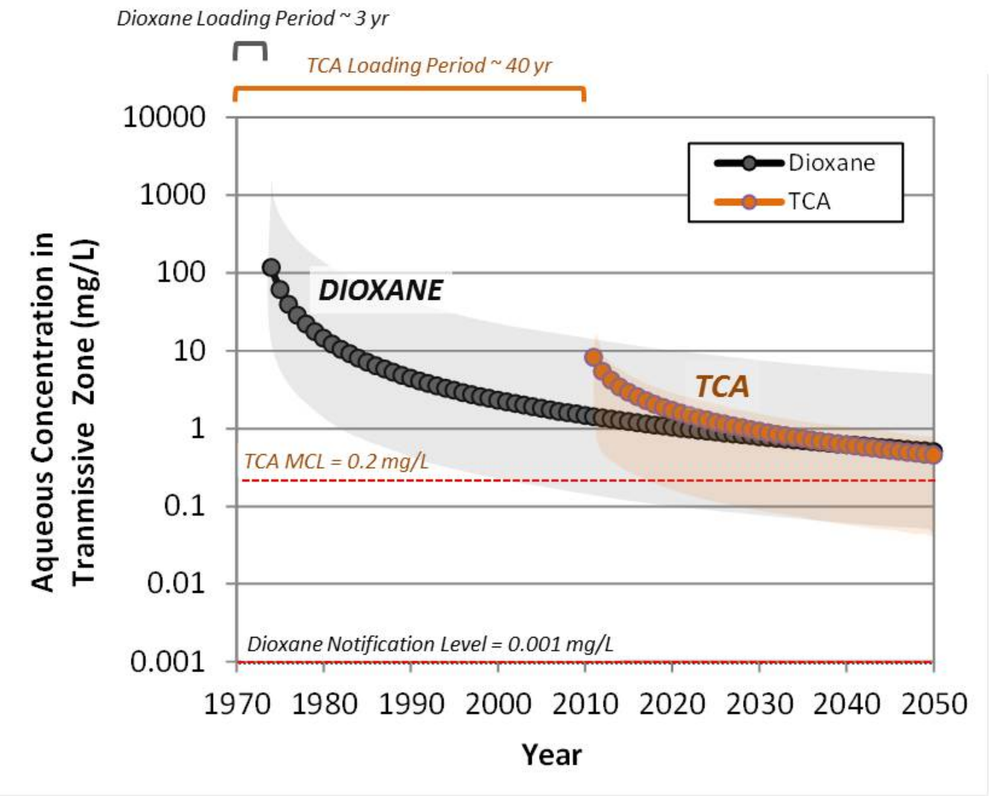


Figure 96. 1,4-Dioxane and TCA Concentration in Transmissive Zone Monitoring Well within Source Zone for On-Site Source Scenario (Scenario 1). Shaded areas for each constituent represent results for sensitivity analysis (dioxane C_s = 30,000 – 300,000 mg/L; TCA C_s = 75 mg/L – 1330 mg/L).

For this scenario, the lengths of the loading periods were based on the expected NAPL dissolution under idealized conditions. By simulating shorting loading periods for TCA, it was also possible to evaluate how remediation impacted mass and concentration trends (**Figure 97**). Note that it was not practical to perform the same evaluation for 1,4-dioxane for this on-site release scenario for two simple reasons: 1) the 1,4-dioxane loading period is already expected to be short; and 2) for decades-old releases, the loading period for 1,4-dioxane would be expected to end prior to the implementation of source zone remediation. In the case of TCA, there was a obvious benefit associated with decreasing the loading period. By removing the source within the transmissive zone in 1990 (i.e., shortening the loading period to 20 years), a reduction of approximately one order-of-magnitude in the aqueous concentration was achieved by the end of the simulation. Removing the source in 1990 would also reduce the aqueous concentration from diffusion to a level below the TCA MCL by 2043, while source removal in 2010 would extend this period of non-attainment for another 47 years. Given that source zone remediation of chlorinated solvents was infrequent prior to the 1990s (NRC, 2013), these simulations illustrate the expected impact of early remediation efforts.

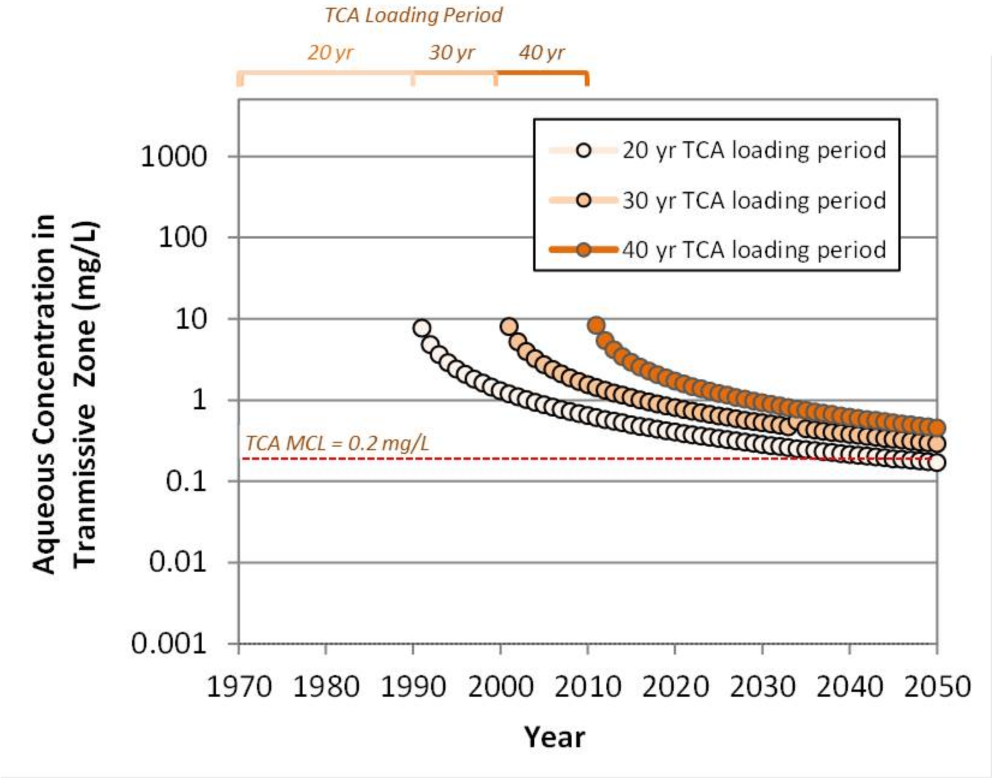


Figure 97. Effect of Loading Period on TCA Concentration in Transmissive Zone Monitoring Well within Source Zone for On-Site Source Scenario (Scenario 1).

Matrix Diffusion Within Downgradient Plume (Scenario 1): The Dandy-Sale model was used to perform a parallel simulation of the diffusion-based storage and release of mass within the downgradient plume for Scenario 1. This model predicts the total concentration of 1,4-dioxane and TCA at any distance and depth downgradient of the source zone, though it is important to note that the model is not directly coupled to the source zone results. the primary assumption is that the downgradient plume response is based on the isolation of a source at the end of a specified loading period (i.e., back diffusion from the source zone no longer contributes to downgradient plume). As with the source zone model described previously, the loading period was specified as 1970 to 1973 for 1,4-dioxane, and 1970 to 2010 for TCA. Mass and concentration of each compound within the plume were modeled for the first 1000 m downgradient of the source.

A total mass of 470 kg of 1,4-dioxane was predicted to remain within the low-permeability portion of the plume immediately after the end of the 1,4-dioxane loading period (1973) **(Figure 95**). This was significantly higher than the TCA mass within the low-permeability compartment at the same time point (9.5 kg), in large part due to the higher source concentration for 1,4-dioxane during this period. At the end of the loading period, a maximum 1,4-dioxane concentration of 7300 mg/kg was predicted at the interface between the low-permeability and transmissive layers immediately downgradient of the source zone (i.e., the origin in **Figure 98a**). Concentrations in excess of 1 mg/kg were observed approximately 1.4 m into the low permeability zone and 150 m downgradient of the source zone. This pattern reflects the greater transport of 1,4-dioxane relative to TCA within both the transmissive zone (driven by advection) and the low-permeability zone (driven by diffusion).

The TCA loading period continued until 2010 when the source was depleted (or otherwise isolated (**Figure 98b**). A total mass of 160 kg of TCA was predicted to diffuse into low-permeability zone within the plume after 40 years of source, and the maximum concentration of 590 mg/kg occurred at the interface (i.e., depth of 0 m). This is smaller than the total mass of 1,4-dioxane 630 kg) of 1,4-dioxane that was associated with the low-permeability zone by 2010, a significant increase over the mass at the end of the loading period (470 kg). During this later period, further penetration of 1,4-dioxane to deeper intervals was also predicted, with a maximum concentration of 137 mg/kg encountered at a depth of 1.3 m. In terms of penetration of lower concentrations, greater than 1 mg/kg of 1,4-dioxane were predicted 4.8 m into the low-permeability interval. The 1,4-dioxane concentration at the interface was greater than 1 mg/kg for the entire 1000 m modeling domain downgradient of the source zone. Because 1,4-dioxane has a very low retardation factor, the remnant signal of the 1,4-dioxane source following source isolation (i.e., the maximum aqueous concentration of 1,4-dioxane in the transmissive zone) had already been transported outside of the modeling domain via advection, while the TCA source signal was still present (due to slower dissolution). As a result, continued diffusion of TCA into the low-permeability zone would be expected at downgradient locations, while diffusion of 1,4-dioxane into the low-permeability zone (at least within the modeling domain) was largely complete.

Eighty years after the initial release (2050), there was still significant amount of 1,4-dioxane and TCA mass stored within the low-permeability zone (**Figure 98c**). The total mass of TCA had increased to 200 kg by 2050, in part because the presence of a remnant source signal within the modeling domain contributed to continued diffusion into the low-permeability zones within the portions of the downgradient plume between 2010 and 2050. While back diffusion of 1,4-dioxane from the low-permeability zones had been occurring for a much longer period than for TCA, the TCA mass in the low-permeability zones was still predicted to be lower than the total mass of 1,4-dioxane in the low-permeability zone (370 kg). Increased penetration of 1,4-dioxane into the low-permeability zone had occurred during this period, as evidenced by 1,4-dioxane concentrations greater than 1 mg/kg extending to a depth of 6.5 m). The peak 1,4-dioxane concentration (encountered at a depth of 2 m) had declined to approximately 67 mg/kg.

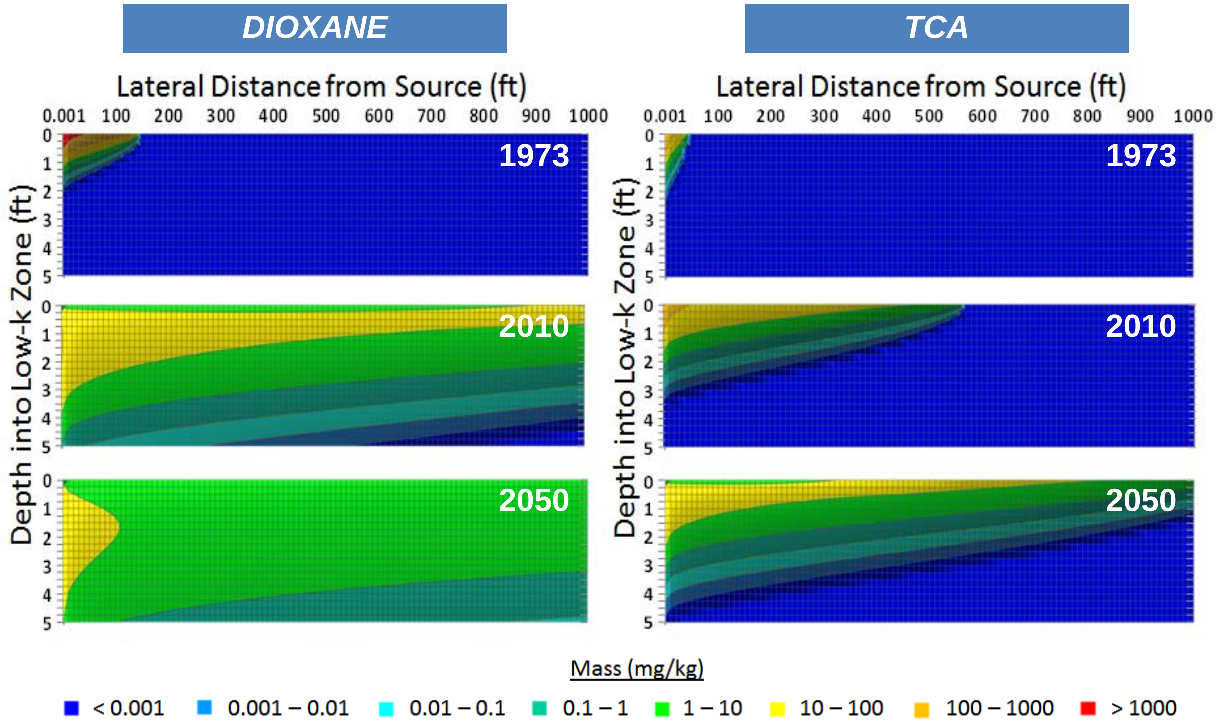


Figure 98. 1,4-dioxane and TCA Masses in Low-Permeability Interval in the Downgradient Area for On-Site Source Scenario (Scenario 1): (A) In 1973 after the end of the 1,4-dioxane loading period; (B) In 2010 after the end of the TCA loading period; and (C) In 2050.

Matrix Diffusion Caused by Off-Site Weak Source (Scenario 2): As confirmed by the Scenario 1 results, 1,4-dioxane's migration potential can pose significant risks to off-site areas that are located hydraulically downgradient. At these downgradient sites, knowledge of operational history may be incomplete (or non-existent), such that there may be some uncertainty about whether or not any on-site releases of 1,4-dioxane have occurred. This may make it difficult to identify the cause or extent of 1,4-dioxane contamination at downgradient sites, especially since identifying and delineating a source zone (at least in the traditional sense) may not be effective. Therefore, the purpose of this scenario was to highlight how 1,4-dioxane being stored and released via matrix diffusion may serve as a "source" of low but persistent levels of 1,4-dioxane at these downgradient sites.

For Scenario 2, temporal patterns in the mass in the low-permeability zone were predicted based on 10 year, 20 year, and 40 year loading periods that started in 2000 (to account for travel time from an upgradient source where a 1,4-dioxane release occurred several decades ago (**Figure 99**). While these loading times are significantly longer than those used in Scenario 1, they represent cases where the source strength is no longer dictated by the presence of NAPL at the upgradient location. Instead, back diffusion of 1,4-dioxane from a depleted source at the upgradient site (or alternatively, from dispersion of the upgradient source) was assumed to be responsible for the source concentration entering the downgradient site. Because this scenario specifically focused on the contribution from back diffusion (a process that can occur over decades), this scenario used longer loading periods for 1,4-dioxane entering the off-site area, as well as a longer total simulation period (100 years). This off-site scenario also used a lower C_s value for 1,4-dioxane (1 mg/L) to account for diminishment of the source strength due to NAPL depletion and/or transport-driven processes.

Based on these input values and assumptions, the model predicted that the mass diffusing into low-permeability zone at the downgradient location (**Figure 99**) would be markedly lower than was observed when an on-site source zone was simulated. The maximum mass stored in the low-permeability zone (at the end of the respective loading periods) ranged from 0.07 to 0.14 kg, with the upper end representing the 40 year loading period. By the end of the simulation period (2100), the mass remaining in the low-permeability zone (following extended back diffusion) had decreased by 64% (40 year loading period), 76% (30 year loading period), and 84% (10 year loading period).

The aqueous concentrations in the transmissive zones that were predicted to result from diffusion of 1,4-dioxane from the low-permeability zones are displayed in **Figure 100.** In this scenario, the initial aqueous concentration was not highly sensitive to the length of the loading period and thus similar (0.23 to 0.28 mg/L). While these concentrations are above potentially-applicable regulatory levels for 1,4-dioxane (typically 0.001 mg/L or less) they are clearly lower than would be expected if NAPL was the source of 1,4-dioxane during the loading period. Over the range of simulated loading periods, the aqueous concentrations were observed to decline below the 0.001 mg/L level between 2030 (10 year loading period) and at the latest by 2100 (40 year loading period). The results of the sensitivity analysis (based on varying the C_s values) are shown in the shaded areas in **Figure 100.** Decreasing the source concentration to 0.1 mg/L resulted in an aqueous concentration of 1,4-dioxane below 0.001 mg/L by within a few years of back diffusion for each case (e.g., by 2013 for the case where loading was assumed from 2000 to 2010).

Note that Scenario 2 is based on an assumption that the loading periods for 1,4-dioxane would eventually end. This is equivalent to assuming that 1,4-dioxane was no longer entering the site (and subject to back diffusion) because of remediation, isolation, or natural attenuation of the upgradient (off-site) source. Another alternative would be some means of plume control (e.g., extraction wells, permeable reactive barrier) that prevented migration of the plume onto the downgradient site. The results in **Figure 100** help to demonstrate that the potential benefit that these types of efforts in terms of improving the remedial timeframe for 1,4-dioxane. Simply decreasing the loading period from 20 years to 10 years decreases the time required for the 1,4-dioxane aqueous concentration to fall below 0.001 mg/L by 23 years (i.e., achieved in 2036 as opposed to 2059).

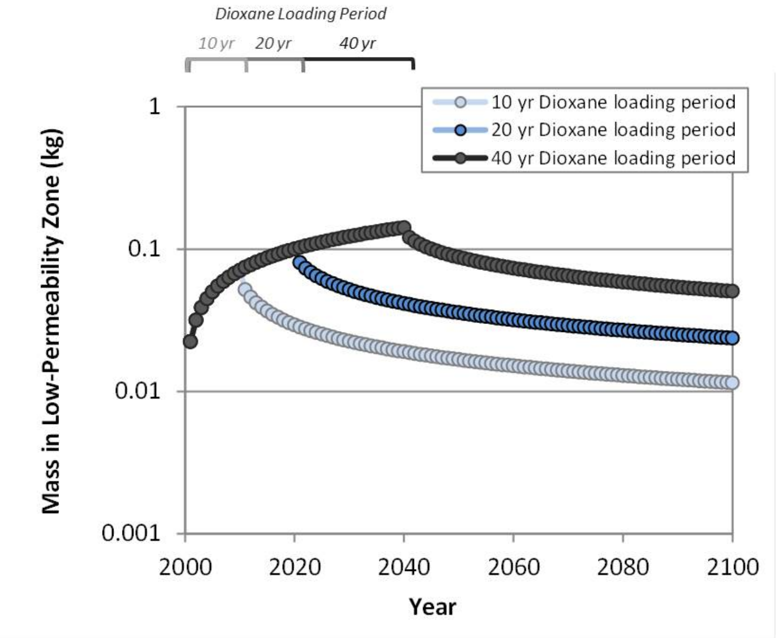


Figure 99. 1,4-Dioxane Mass in Low-Permeability Interval within Source Zone for Off-Site Source Scenario (Scenario 2). Assumed release of 1,4-dioxane from off-site (upgradient) site using loading scenario described in Table 9.

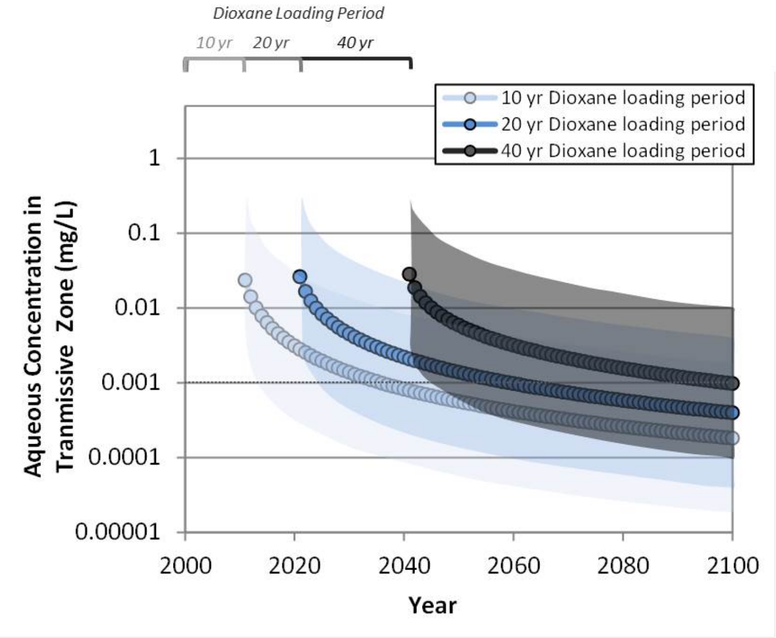


Figure 100. 1,4-Dioxane Concentration in Transmissive Zone Monitoring Well within Source Zone for Off-Site Source Scenario (Scenario 2). Shaded areas represent results for sensitivity analysis (dioxane C_S = 0.1 – 10 mg/L).

4.5.2 Field Study

To further evaluate the processes identified during the modeling study, two different sites were investigated using high resolution characterization methods to understand mass distribution relative to low permeability zones. Investigation points are shown in **Figure 101** (Facility 1381) and **Figure 102** (SLC-16).

Figure 101. Locations for Investigation Points at Facility 1381, Cape Canaveral Air Force Station. At each location, vertical profiling, soil sub-sampling, and groundwater sampling was completed. Source area is in vicinity of location 1381-SB1. Groundwater flows in multiple directions from source area, including both northwest and southwest (toward canal and newly-installed interceptor trench).

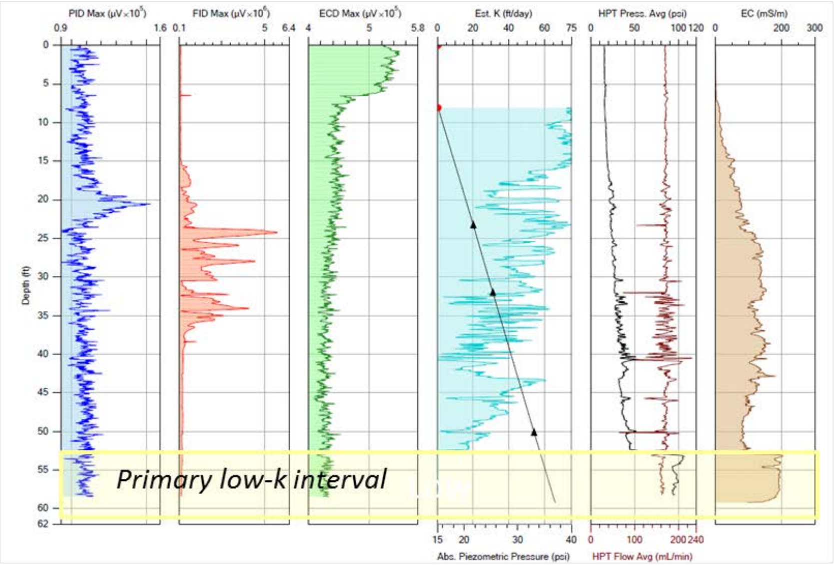
Figure 102. Locations for Investigation Points at SLC-16, Cape Canaveral Air Force Station. At each location, vertical profiling, soil sub-sampling, and groundwater sampling was completed. Source area is in vicinity of locations SLC16-SB1 and SLC16-SB2. Groundwater generally flows in southeast direction.

MIP-HPT Characterization: Screening-level stratigraphic data were collected at 4 different locations at Facility 1381 and 5 different locations at SLC-16. These data largely confirmed known site characteristics, with the understanding that there was much more pre-existing characterization data at Facility 1381 than SLC-16 at the time of this investigation.

At Facility 1381, HPT data confirmed that a distinct low-permeability interval was present starting at between 48 and 52 ft bgs. **Figure 103** shows an example profile from this site (the remaining MIP-HPT profiles can be found in **Appendix A**). This low-permeability interval was generally at least 5 ft thick and essentially had no measurable permeability (as noted by the estimated K values in the HPT estimated K profile). The overlying soils were generally fairly permeable (estimated K = 20 to 75 ft/day), although the profiles suggested that a thinner layer of reduced permeability 0 to 10 ft/day) were encountered at a depth of approximately 40 ft. Regardless, considerable heterogeneity (as evidenced by the sharp changes in the estimated K values over short vertical intervals) was apparent at all locations. The MIP FID profiles suggested that low levels of organics were present in intervals ranging from approximately 15 to 35 ft bgs. The PID and ECD signals were relatively flat; both of these detectors are more sensitive to highly chlorinated solvents. Collectively, the MIP results suggest that only minor levels of organics (and primarily less chlorinated compounds) are present in shallow permeable soils but not the low-permeability intervals. This is consistent with the extensive remedial efforts that have been completed to address chlorinated solvent contamination at the site. It is important to note that none of these detectors are sensitive to 1,4-dioxane and cannot be used to establish its presence and/or distribution at these locations..

At SLC-16, the profiles suggested an even higher degree of heterogeneity with less evidence for distinct low-permeability intervals. Instead, the stratigraphy at each location was characterized by thinner sub-intervals of varying permeability that changed every few feet (i.e., more “peaks and valleys”) (see **Figure 103** for example; **Appendix A** for all profiles). The sub-intervals of high permeability had estimated K values in a range (20 to 75 ft/day) that were relatively similar to the K-values estimated at Facility 1381. However, a higher percentage of the profile exhibited K values below 20 ft/day. The intervals with the lowest apparent permeability were generally found in 1 to 3 ft intervals at depths starting at 49 to 52 ft bgs. The exception was location SLC-SB5, where a more distinct and thicker (5 ft) low-k layer was encountered between 40 and 45 ft bgs. The MIP profiles suggested elevated levels of organics were present at SLC16-SB1 and (to a lesser extent) SLC16-SB2. These two locations are closest to the suspected source, and the ECD profiles indicated that highly chlorinated hydrocarbons were present. The profile at SLC16-SB1 suggested that these high concentrations of these contaminants were present throughout the soil column staring at 15 ft bgs, while the profile at SLC16-SB2 was consistent with high levels at the surface (i.e., the interval between 0 to 15 ft bgs) followed by lower concentrations starting at approximately 30 ft bgs. However, it was later determined that the apparent surface contamination at SLC16-SB2 was associated with carryover from the previous location (SLC16-SB1), such that the deeper contamination was more representative of that location.

(a) Facility 1381:
Location 1381-SB1



(b) SLC-16:
Location SLC16-SB1

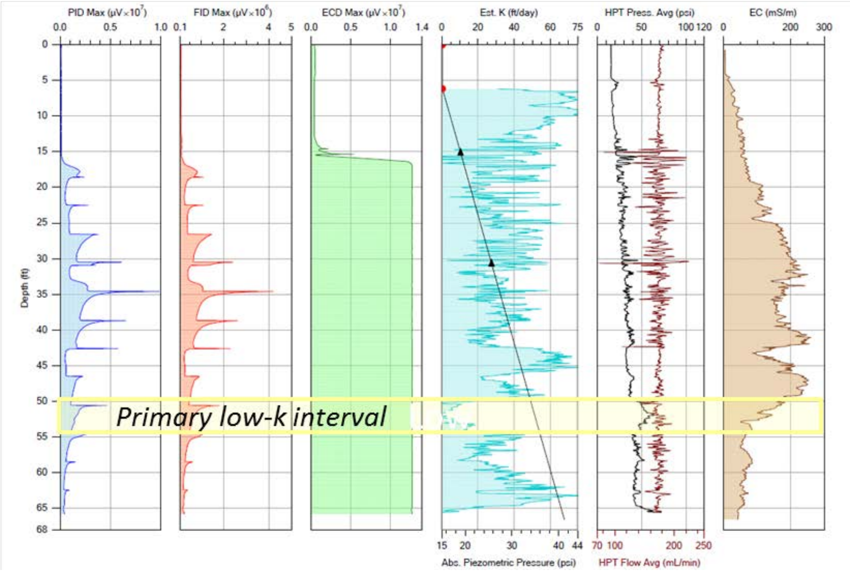


Figure 103. Example MIP-HPT Profiles from (a) Facility 1381 and (b) SLC-16. At each location, left three profiles show MIP data for 3 different detectors (PID, FID, EC) and right three profiles show HPT data, including estimated hydraulic conductivity ("Est. K"). Graphics are modified versions of data compilations provided by Columbia Technologies.

Soil Characterization: Soil cores were collected at the same four locations at Facility 1381 and five locations at SLC-16 where MIP-HPT characterization was performed. Inspection of the cores confirmed that the stratigraphy data generated by the HPT generally matched the soil type encountered during continuous coring (boring logs are included in **Appendix A**). In other words, the higher permeability intervals were dominated by sands (with a large content of shells), and that slight decreases in permeability (as indicated by the HPT data) were associated with higher percentages of fine-grained material (primarily silts but occasionally clays) within the sand unit. At Facility 1381, a distinct clay layer was identified at the depth where the HPT indicated that estimated K values became negligible (approximately 50 ft bgs). Soil organic carbon ranged from 0.4 to 2%, with higher percentages generally associated with the lower-permeability intervals.

At SLC16, there was generally a higher clay content within the shallow sandy soils than was encountered at Facility 1381, and this was consistent with the apparent heterogeneity in permeability that was indicated by the HPT data. At most SLC16 locations, a clay layer was encountered within the interval with the lowest estimated K values. However, this layer was generally only 1 to 2 ft thick. At one location (SLC16-SB4), no clay was observed, but the majority of the interval between 25 and 50 ft bgs was classified as a sandy silt. This finding was consistent with the estimated K profile for this location, which generally showed lower overall permeability throughout a wide interval. Organic carbon in soil samples ranged from 0.2 to 1.6% and were generally lower than those observed at Facility 1381.

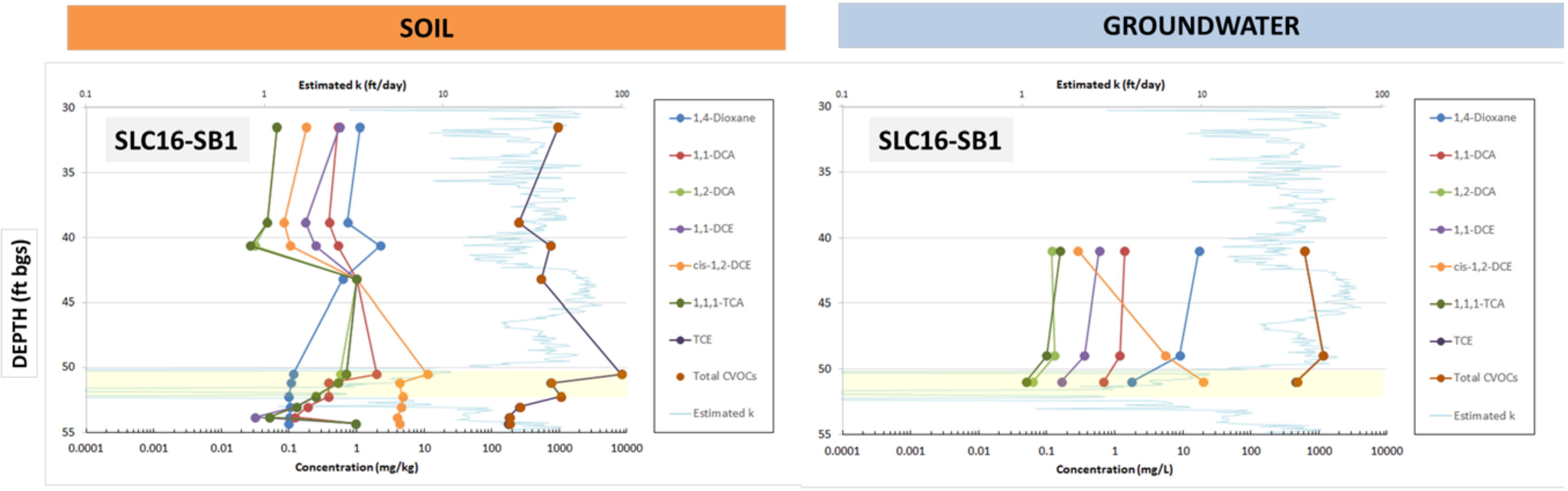
Soil chemical data revealed distinctly different patterns at the two sites. Analysis of soil cores collected at Facility 1381 indicated that individual organic compounds were infrequently present above reporting limits (see **Appendix A** for complete data tables). This included 42 samples from 4 different locations, covering both the high-permeability sands and the low-permeability clay. 1,4-dioxane was detected at trace levels in two samples from 1381-SB4, including one sample from the low-permeability clay. The investigation points were largely present in an area that has been intensively remediated. The soil results support the current conceptual site model that these remediation efforts have successfully reduced the chlorinated solvent concentrations across the site. Furthermore, the soil results suggest that any 1,4-dioxane that was released or migrated into this area is not stored within low-permeability soils.

At SLC-16, the soil data confirmed that significant CVOC and 1,4-dioxane concentrations are present at this non-remediated site (**Figure 104**; see **Appendix A** for complete data tables). The highest concentrations were encountered at the location nearest to the presumed source (SLC16-SB1), with maximum concentrations of 2.33 mg/kg 1,4-dioxane and 1055 mg/kg total CVOCs. TCE represented > 99% of the mass. However, there was a difference between the vertical distribution associated with each of these two compound types at this location. The peak CVOC concentrations were found within the clay layer at a depth immediately below the interface with the overlying sands (SLC16-SB1-50.5 FT). CVOC concentrations generally declined with depth into the clay. For 1,4-dioxane, the peak concentration occurred within the more transmissive sands (SLC16-SB1-40.6 FT) but no 1,4-dioxane was detected in samples from the clay unit.

Unfortunately, no samples were collected from the sandy soils immediately above the clay unit (closest sample was SLC16-SB1-43.2 FT), but further evidence was obtained using groundwater data (described below). SLC16-SB2 was also located within the presumed source zone (within 10 m of SLC16-SB2) and was characterized by slightly lower concentrations but a similar vertical distribution. At SLC16-SB2, 1,4-dioxane was present in the high-k soils but not the low-k soils, while CVOC concentrations peaked at 51ft bgs, near the interface between two zones of differing permeability.

The remaining three SLC-16 borings, all of which were located farther from the presumed source area, were characterized by trace or non-detectable levels of 1,4-dioxane CVOCs in the majority of samples. At two of the three locations, peak concentrations were encountered in intervals that were lower in permeability than adjacent soil layers. It should be noted that the current investigation was primarily focused on relatively deep intervals (> 25 ft bgs) to understand the potential impact on lower-permeability soils known to be present in these zones. Based on existing site data, it is possible that higher concentrations would have been detected in shallower sand-dominated soils (< 25 ft bgs) had they been included in this investigation. Regardless, the soil results collected during this project suggest minimal impact on the deeper low-permeability soils outside of the source zone.

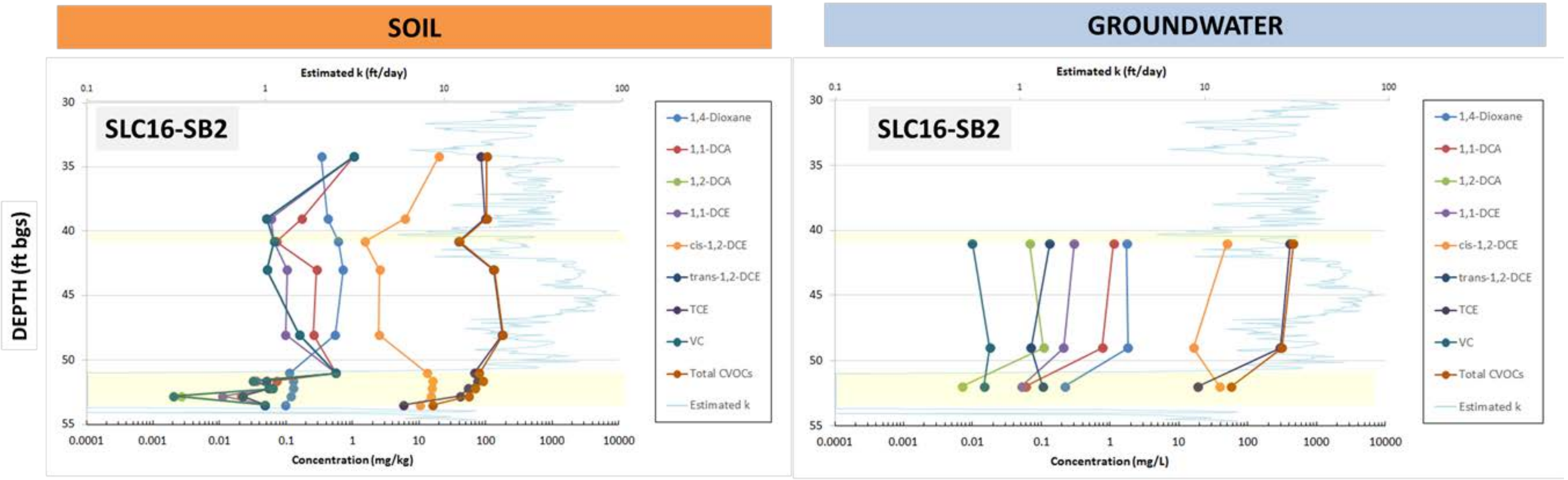
Groundwater Characterization: A total of 10 groundwater samples were collected at the same 4 locations at Facility 1381 where soil coring was completed (**Figure 105**). Given the relatively consistent low-k unit present at this site, it was possible to screen separately between high-k units (1 sample per location) and the low-k unit (2 samples per location; with the exception of 1381-SB4 which did not produce water from the low-k unit). Groundwater was moderately reducing (based on ORP readings) with relatively low levels of anions except for chloride. Geochemical conditions were generally favorable for biological activity, and the presence of elevated methane (up to 16 mg/L) confirmed that anaerobic activity was occurring (despite relatively low TOC at most locations). Only trace levels of CVOCs (3 µg/L or less) were detected in any sample. At the two locations near the source zone (1381-SB1 and 1381-SB2), CVOCs were detected in the low-k zone but not in the overlying sands. The opposite was observed at 1381-SB3, albeit in the form of a 0.2 ug/L detection of VC in the sands. No CVOCs were present at the downgradient location. 1,4-dioxane was not detected in any groundwater samples from these four locations, although the relatively high reporting limit (3 µg/L) did not preclude the possibility that trace levels of 1,4-dioxane were present. Overall, the low contaminant concentrations detected in groundwater at the Facility 1381 were consistent with the soil results from these same locations. However, the groundwater data do suggest that a significant portion of the remaining CVOC contaminant mass is associated with the lower-permeability interval at this site.



Depth (ft bgs)	1,4-Dioxane	1,1-DCA	1,2-DCA	1,1-DCE	cis-1,2-DCE	1,1,1-TCA	TCE	Total CVOCs
31.5	**1.12**	**0.527**	0.0665	**0.56**	**0.181**	0.0665	**952**	**953.268**
38.8	**0.734**	**0.392**	0.0474	**0.177**	**0.0839 J**	0.0474	**251**	**251.6529 J**
40.6	**2.23**	**0.53**	**0.0313 J**	**0.248**	**0.105**	0.02675	**738**	**738.9143 J**
43.2	**0.621**	1	1	1	1	1	**539**	**539**
50.5	0.115	**1.99**	0.575	**0.708 J**	**11.2**	**0.709 J**	**8330**	**8344.607 J**
51.2	0.1075	**0.382 J**	0.54	0.54	**4.3**	0.54	**752**	**756.682 J**
52.2	0.099	**0.387 J**	0.248	0.248	**4.81**	0.248	**1050**	**1055.197 J**
53	0.103	**0.189 J**	0.1285	0.1285	**4.64**	0.1285	**256**	**260.829 J**
53.8	0.102	**0.124**	0.051	**0.0316 J**	**4**	0.051	**180**	**184.1556 J**
54.3	0.098	0.98	0.98	0.98	**4.36**	0.98	**178**	**183.34 J**

Depth (ft bgs)	1,4-Dioxane	1,1-DCA	1,2-DCA	1,1-DCE	cis-1,2-DCE	1,1,1-TCA	TCE	Total CVOCs
41	**17.2**	**1.4**	**0.118**	**0.588**	**0.287**	**0.158**	**607**	**609.275**
49	**9**	**1.18**	**0.131**	**0.359**	**5.58**	0.1	**1150**	**1157.119 J**
51	**1.77**	**0.688**	**0.0628 J**	**0.164**	**20**	0.05	**459**	**479.9148 J**

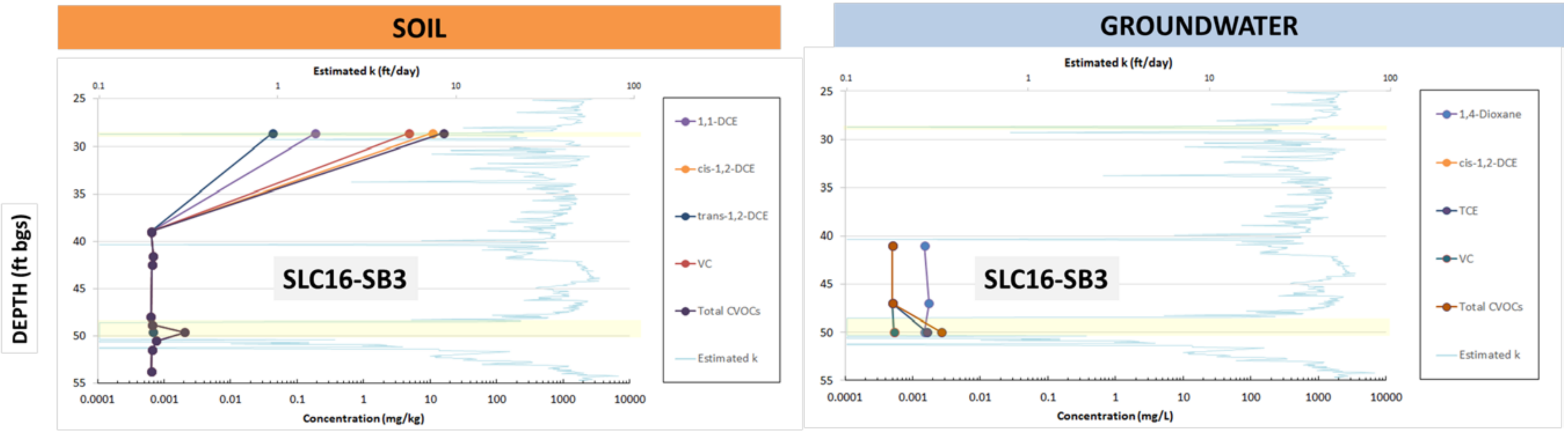
Figure 104a. Soil and Groundwater Data from Location SLC16-SB1. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).



Depth (ft bgs)	1,4-Dioxane	1,1-DCA	1,2-DCA	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE	TCE	VC	Total CVOCs
34.2	**0.34**	1.04	1.04	1.04	**19.6**	1.04	**84.7**	1.04	**104.3**
39	**0.421**	**0.174**	0.051	**0.0589 J**	**6.23**	0.051	**98.1**	0.051	**104.5629 J**
40.8	**0.613**	**0.0718 J**	0.066	0.066	**1.52**	0.066	**38.8**	0.066	**40.3918 J**
43	**0.722**	**0.289**	0.052	**0.103 J**	**2.56**	0.052	**132**	0.052	**134.952 J**
48	**0.545**	**0.259 J**	0.158	**0.0977 J**	**2.49**	0.158	**178**	0.158	**180.8467 J**
51	0.113	0.565	0.565	0.565	**13.2**	0.565	**67.6**	0.565	**80.8**
51.6	0.1275	**0.0715**	0.0319	**0.0357 J**	**16**	**0.0503 J**	**76.2**	0.0319	**92.3575 J**
52.2	0.1275	**0.0549 J**	0.0635	0.0635	**15.6**	**0.0554 J**	**54.8**	0.0635	**70.5103 J**
52.8	0.1195	**0.0209**	**0.0027**	**0.0111**	**15.3**	**0.0222**	**41.3**	**0.00201**	**56.65891**
53.5	0.097	0.04855	0.04855	0.04855	**10.2**	0.04855	**5.78**	0.04855	**15.98**

Depth (ft bgs)	1,4-Dioxane	1,1-DCA	1,2-DCA	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE	TCE	VC	Total CVOCs
41	**1.75**	**1.12**	**0.0676**	**0.302**	**50**	**0.132**	**410**	**0.00992**	**461.63152**
49	**1.82**	**0.766**	**0.108**	**0.211 J**	**16.4**	**0.0706**	**298**	**0.0178**	**315.5734**
52	**0.22**	**0.0589 J**	**0.00711**	**0.0519**	**38.8**	**0.105**	**18.9**	**0.0148**	**57.93771**

Figure 104b. Soil and Groundwater Data from Location SLC16-SB2. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).

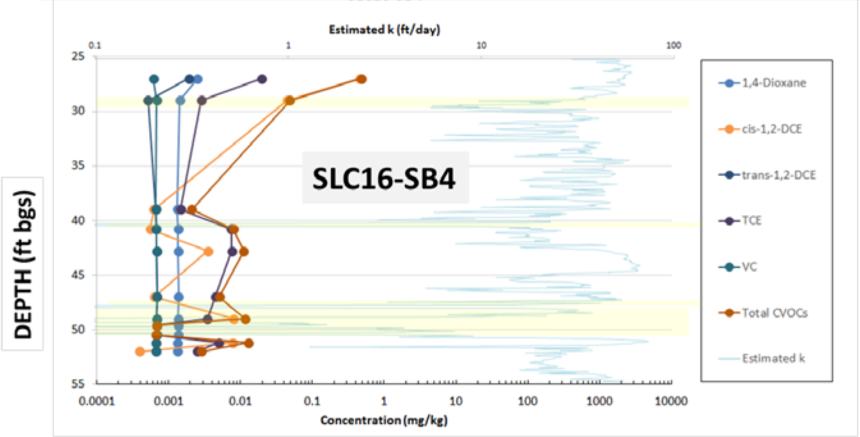


Depth (ft bgs)	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE	VC	Total CVOCs
28.6	**0.188**	**10.8**	**0.0428 J**	**4.87**	**15.9008 J**
39	0.00064	0.00064	0.00064	0.00064	0.00064
41.6	0.00069	0.00069	0.00069	0.00069	0.00069
42.5	0.000655	0.000655	0.000655	0.000655	0.000655
48	0.00063	0.00063	0.00063	0.00063	0.00063
48.8	0.000665	0.000665	0.000665	0.000665	0.000665
49.6	0.00068	0.00068	0.00068	**0.00205**	**0.00205**
50.5	0.00077	0.00077	0.00077	0.00077	0.00077
51.5	0.000655	0.000655	0.000655	0.000655	0.000655
53.7	0.00064	0.00064	0.00064	0.00064	0.00064

Depth (ft bgs)	1,4-Dioxane	cis-1,2-DCE	TCE	VC	Total CVOCs
41	0.0015	0.0005	0.0005 J	0.0005	**0.0005 J**
47	**0.00173**	0.0005	0.0005	0.0005	**0.0005 J**
50	0.0015	**0.000531**	**0.00164**	**0.000528**	**0.002699 J**

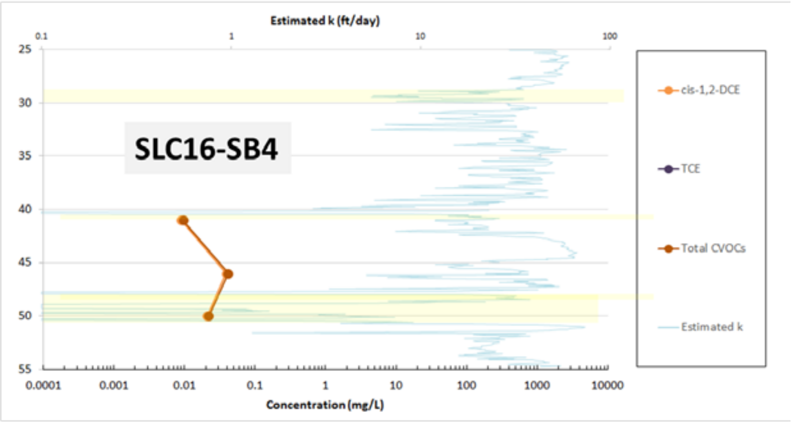
Figure 104c. Soil and Groundwater Data from Location SLC16-SB3. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).

SOIL



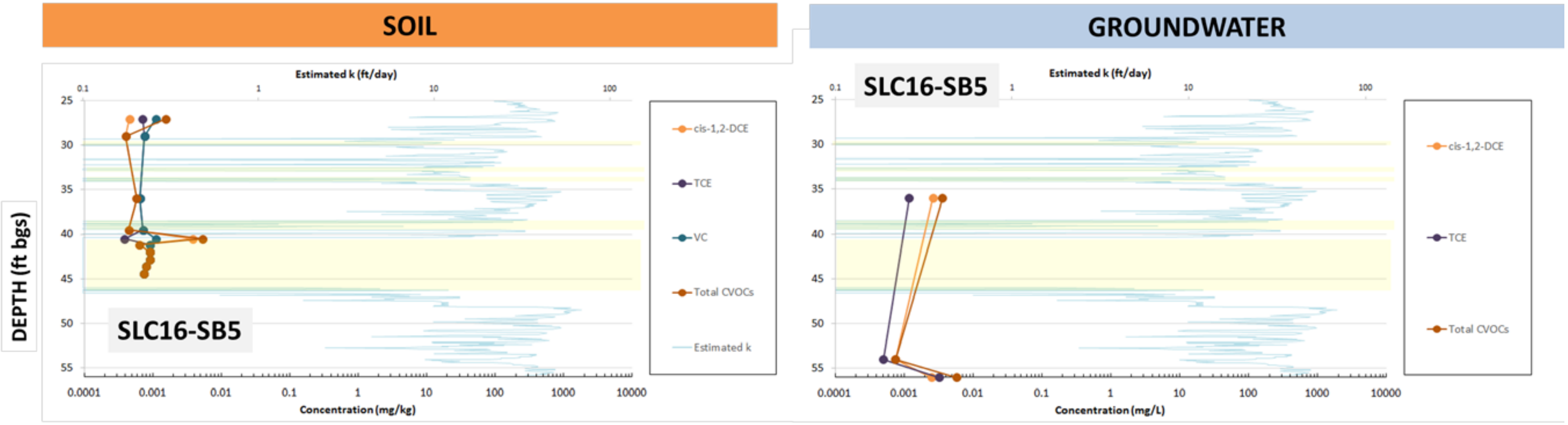
Depth (ft bgs)	1,4-Dioxane	cis-1,2-DCE	trans-1,2-DCE	TCE	VC	Total CVOCs
27	**0.00254**	**0.461**	**0.0019**	**0.0199 J**	**0.000611 J**	**0.483411 J**
29	0.001425	**0.0447**	**0.000519 J**	**0.00284**	**0.000686 J**	**0.048745 J**
39	0.00132	**0.000621 J**	0.00066	**0.00147**	0.00066	**0.002091 J**
40.8	0.00135	**0.000549 J**	0.000675	**0.00743**	0.000675	**0.007979 J**
42.8	0.00136	**0.00352**	0.00068	**0.00755**	0.00068	**0.01107 J**
47	0.00138	**0.000631 J**	0.00069	**0.00444**	0.00069	**0.005071 J**
49	0.001355	**0.00803**	0.00068	**0.00345**	0.00068	**0.01148 J**
49.6	0.00138	0.00069	0.00069	0.00069	0.00069	0.00069
50.5	0.001375	0.000685	0.000685	**0.000675 J**	0.000685	**0.000675 J**
51.2	0.001325	**0.00786**	0.00066	**0.00494**	0.00066	**0.0128**
52	0.001345	**0.000398 J**	0.00067	**0.00248**	0.00067	**0.002878 J**

GROUNDWATER



Depth (ft bgs)	cis-1,2-DCE	TCE	Total CVOCs
41	**0.000586**	**0.00897 J**	**0.009556 J**
46	**0.00291**	**0.0388**	**0.04171 J**
50	**0.00108 J**	**0.0209**	**0.02198 J**

Figure 104d. Soil and Groundwater Data from Location SLC16-SB4. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).

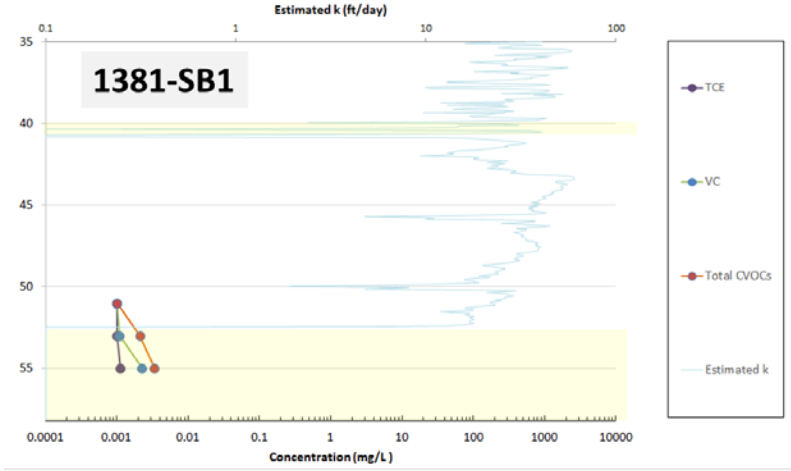


Depth (ft bgs)	cis-1,2-DCE	TCE	VC	Total CVOCs
27	**0.000456**	0.00071	**0.00111 J**	**0.001566 J**
29	**0.000405 J**	0.000755	0.000755	**0.000405 J**
36	**0.000583 J**	0.00065	0.00065	**0.000583 J**
39.5	**0.000448 J**	0.00072	0.00072	**0.000448 J**
40.5	**0.00384**	**0.000386 J**	**0.00111 J**	**0.005336 J**
41.2	**0.000645 J**	0.000905	0.000905	**0.000645 J**
42	0.0009	0.0009	0.0009	0.0009
42.8	0.00091	0.00091	0.00091	0.00091
43.6	0.000795	0.000795	0.000795	0.000795
44.4	0.000735	0.000735	0.000735	0.000735

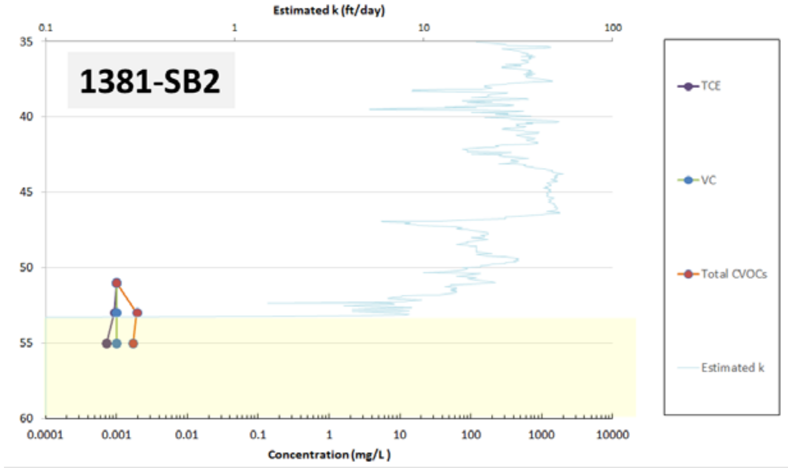
Depth (ft bgs)	cis-1,2-DCE	TCE	VC	Total CVOCs
36	**0.00261**	**0.00118**	0.001	**0.00361 J**
54	**0.000749 J**	0.0005	0.001	**0.000749 J**
56	**0.00249 J**	**0.00322**	0.001	**0.00571 J**

Figure 104e. Soil and Groundwater Data from Location SLC16-SB5. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).

GROUNDWATER

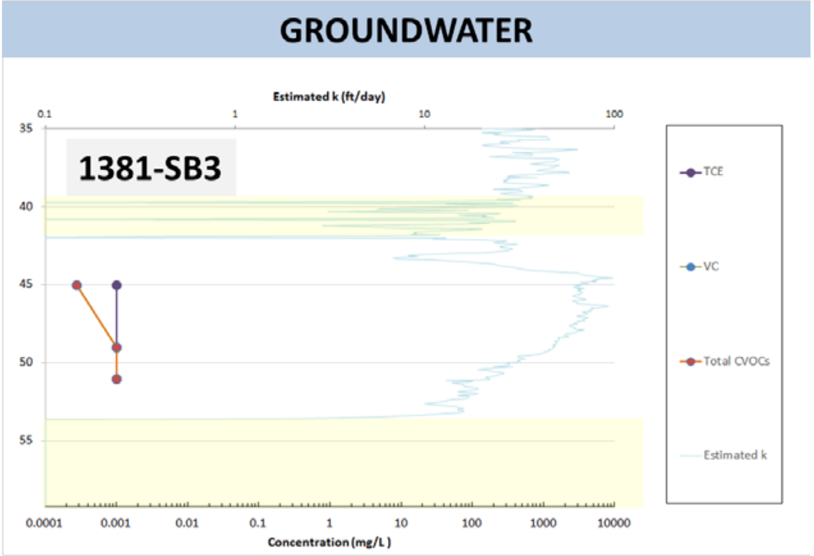


Depth (ft bgs)	TCE	VC	Total CVOCs
51	0.001	0.001	0.001
53	**0.001**	**0.00109**	**0.00209**
55	**0.00111**	**0.00225**	**0.00336**

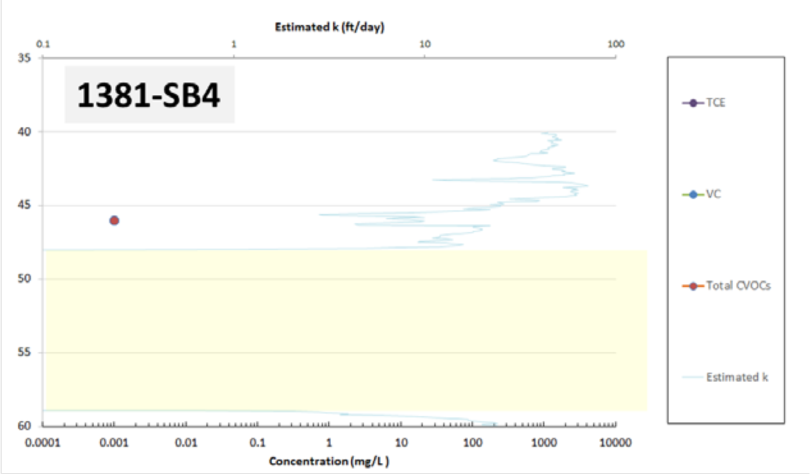


Depth (ft bgs)	TCE	VC	Total CVOCs
51	0.001	0.001	0.001
53	**0.000941**	0.001	**0.001941**
55	**0.000726**	0.001	**0.001726**

Figure 105a. Groundwater Data from Locations 1381-SB1 and 1381-SB2. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations (mg/L) above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).



Depth (ft bgs)	TCE	VC	Total CVOCs
45	0.001	**0.000277**	**0.000277**
49	0.001	0.001	0.001
51	0.001	0.001	0.001



Depth (ft bgs)	TCE	VC	Total CVOCs
46	0.001	0.001	0.001

Figure 105b. Groundwater Data from Locations 1381-SB3 and 1381-SB4. Yellow-shaded areas represent primary low-permeability intervals. Bold values in data tables are concentrations (mg/L) above reporting limits while unbolded values represent reporting limits (i.e., non-detects). Only those constituents that were above reporting limits in one or more samples are displayed (see **Appendix A** for complete dataset for all SLC-16 locations).

At SLC-16, a total of 15 groundwater samples were collected from the 5 investigation points (**Figure 104**). Due to the relatively thin clay/silt layers encountered at this site, it was generally possible to collect only a single sample per location from a low-permeability zone. At one downgradient location, no groundwater could be collected from the low-permeability interval. Geochemical conditions displayed some similarities to those encountered at Facility 1381 (i.e., moderately reducing, near neutral pH) but there were notable exceptions. This included significantly higher nitrate at one location (SLC16-SB1) and generally higher levels of sulfate and conductivity throughout the site. Methane was detected at low concentrations (<1 mg/L) except at the far downgradient location (SLC16-SB5).

In the two SLC-16 locations within the presumed source zone, high concentrations of CVOCs (> 100 mg/L) were detected in all samples from the sandy soils immediately above the interface with the primary low-permeability zone. TCE was the major constituent and was present at levels approaching solubility (although no evidence of NAPL was observed during the collection of soil or groundwater samples). At these two source zone locations, CVOC concentrations were lower in the samples collected from the low-k zone (although cDCE did increase in both cases). In contrast to the soil data, 1,4-dioxane was detected in all groundwater samples collected from these source zone locations. Like the CVOCs, 1,4-dioxane concentrations decreased moving from the sandy soils into the underlying lower-permeability interval. It should be noted that the 1,4-dioxane concentrations reported for this set of samples (ranging from 1 – 17 mg/L) were biased high due to the presence of high concentrations of the CVOCs (which interfere with quantitation). Therefore, the relative concentrations among the various samples (particularly with respect to the vertical intervals where they were collected) are more important than the actual magnitude of the concentrations.

At the three SLC-16 locations that were outside of the source zone, the CVOC and 1,4-dioxane concentrations in groundwater samples were relatively low or below reporting limits. Of the three locations, the highest concentrations were observed at SLC16-SB4, but these were still several orders of magnitude lower than observed in samples from the source zone locations. Consistent with the soil data, slightly higher concentrations were encountered in samples from lower-permeability units than high-permeability units in at least one location. But as noted previously, it is highly likely that higher CVOC concentrations would have been encountered if the shallower sandy soils were included in this investigation.

Evidence for Degradation: In addition to collecting data on contaminant concentrations and geochemical conditions, the field program also used compound-specific isotope analysis and biomarker quantification to assess degradation. These were particularly important analytes for 1,4-dioxane, given that this compound does not have readily-detectable metabolites. For this particularly study, the goal was to determine if there was evidence for degradation in lower-k layers that would help mitigate the long-term impacts of matrix diffusion.

Stable isotope analysis was performed on 17 groundwater samples. This included quantification of the 13C isotopic ratio ($\delta^{13}C$) on 17 samples and the ^{2}H isotopic ratio ($\delta^{2}H$) on

4 samples (there was insufficient sample volume to analyze ^{2}H in samples). Methods for analyzing isotopes in 1,4-dioxane in soil are in development but were not used in this study.

The isotope results are summarized in **Table 36a**. Of the 10 samples where δ^{13}C was above analytical limits, the values ranged between -30.61‰ to -22.39‰ in samples from Facility 1381 and -33.80‰ to -23.39‰ in samples from SLC-16. In the 4 samples where δ^2H was quantified, the values ranged from -70.61‰ to -9.97‰. Degradation of 1,4-dioxane results in isotopic fractionation, or enrichment of the heavier ^{13}C and ^{2}H isotopes (i.e., increasing δ^{13}C and δ^2H values) While CSIA of 1,4-dioxane is still an emerging area of research, there have been several groups that have been investigating representative isotopic values for commercial 1,4-dioxane. A summary of these values is provided in **Figure 106**. Based on this compilation, it is clear that multiple samples from Facility 1381 and at least one sample from SLC-16 show evidence of fractionation based on the carbon isotope data. Although the hydrogen isotopic data are more limited (and the ranges for commercial sources vary significantly depending on the research group performing the analyses), there is at least one sample from SLC-16 (SLC16-SB1-48-50') that is clearly enriched in ^{2}H.

Based on known pathways for 1,4-dioxane attenuation, there is evidence that the observed fractionation is related to 1,4-dioxane biodegradation. Pornwongthong (2014b) reported relatively modest enrichment factors for biodegradation of 1,4-dioxane (ε = - 1.38 to -1.06 for carbon and ε = -51.7 to -45.1 for hydrogen), with indistinguishable values for cometabolic and metabolic degradation. Pornwongthong (2014b) also reported that fractionation patterns and enrichment factors for biodegradation were clearly different than those for abiotic processes (e.g., sonication and aeration) that did not result in carbon fractionation. Therefore, it is reasonable to conclude that the isotopic patterns noted in several CCAFS samples are consistent with 1,4-dioxane biodegradation.

Other important findings related to the isotopic data include the following:

- The majority of samples from Facility 1381 showed evidence of degradation, despite 1,4-dioxane concentrations that were actually below the reporting limit. This suggests that there may be trace levels of dissolved 1,4-dioxane in these depth intervals but that it is highly degraded across the site. A lower percentage of SLC-16 samples showed evidence of degradation.
- The majority of the isotope data are from groundwater collected from relatively high-permeability intervals (due to highly-limited sample volumes from low-permeability intervals). Of the three samples from lower-permeability intervals that were analyzed, two were below analytical limits and one showed little evidence of fractionation (1381-SB3-48-50'). However, the samples from the higher-permeability intervals were collected within a few vertical feet of the low-permeability intervals, suggesting that degradation is occurring in close proximity. This is important for mitigating the effect of any 1,4-dioxane mass that may diffuse into the aquifer from the lower-permeability intervals.

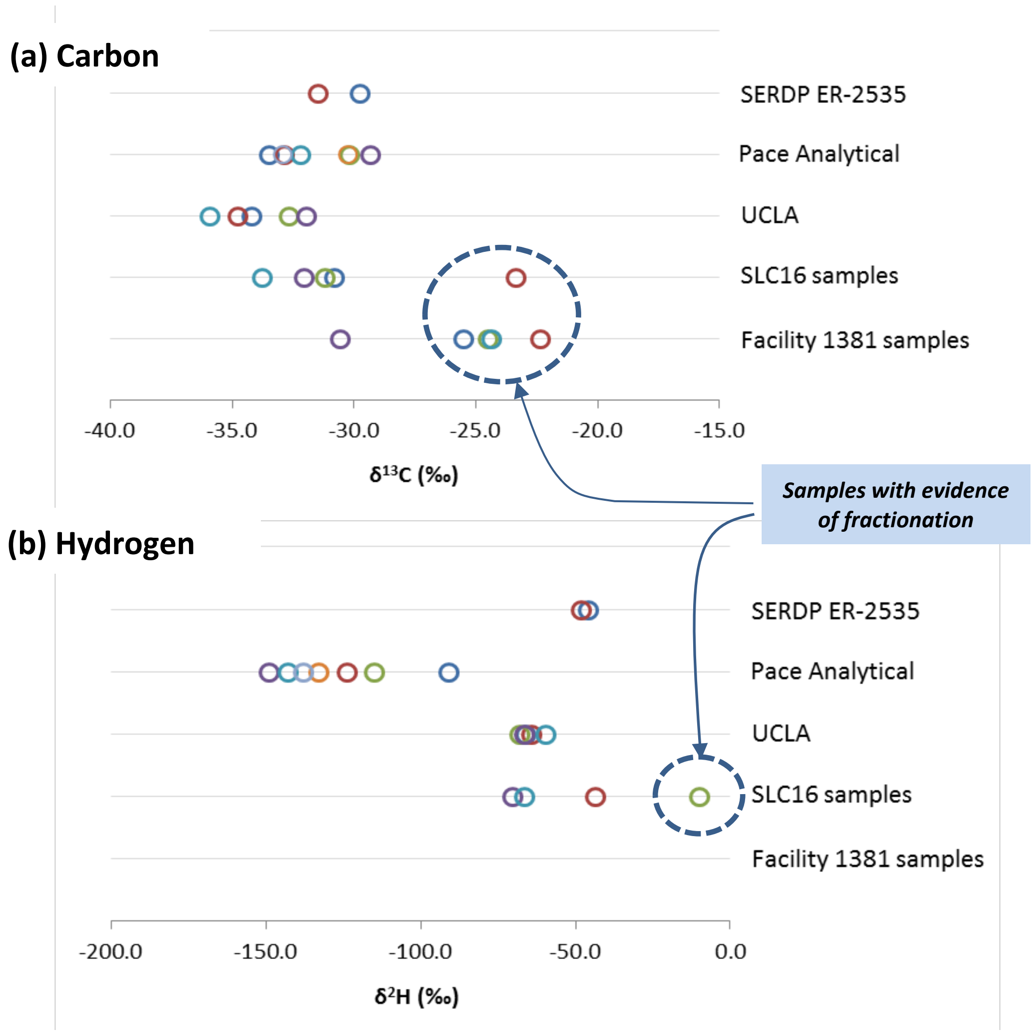


Figure 106. Comparison of Isotopic Data for Groundwater Samples from Facility 1381 and SLC-16 with Reported Values for Commercial 1,4-Dioxane. Each dot represents value associated with individual sample (or set of samples). Top three are commercial 1,4-dioxane while bottom two are groundwater samples collected during this investigation. Sources for data: 1) SERDP ER-2535 values are based on personal communication with project PI (Peter Bennett, Haley & Aldrich); 2) Pace Analytical values are based on conference presentation (Yi Wang, Pace Analytical); 3) UCLA values are based on Ph.D. dissertation (Pornwongthong, 2014b). There was insufficient sample volume to analyze samples from Facility 1381 for δ^2H.

Biomarker and microbial community analysis was performed on 9 groundwater samples and 16 soil samples. This included quantification (based on qPCR of 16S rRNA encoding genes) of total bacteria, *Pseudonocardia* sp., 1,4-dioxane monooxygenase (DXMO), and aldehyde dehydrogenase (ALDH). The latter three gene targets are associated with 1,4-dioxane degradation capabilities. The genera *Pseudonocardia* includes several known 1,4-dioxane degrading species, while DXMO and ALDH both encode for enzymes responsible for 1,4-dioxane degradation. The key difference is that ALDH has been implicated in growth-supporting (metabolic) pathways, while DXMO can be associated with both cometabolic and metabolic degradation pathways.

The biomarker dataset is presented in **Table 36a** (groundwater samples) and **Table 36b** (soil samples), along with the isotope data for the same set of groundwater samples. Microbial populations could be quantified in all samples, regardless of the depth interval or location where they were collected. The detection frequencies and mean biomarker concentrations are summarized in **Table 37**. Key points from the biomarker analysis include the following:

- The total population exhibited no apparent relationship with the 1,4-dioxane concentration. Similarly, the presence (or absence) of biomarkers for 1,4-dioxane degradation did not appear to correlate with high (or low) concentrations of 1,4-dioxane. This is surprising given that the abundance of these biomarkers is generally correlated with the amount of 1,4-dioxane consumed (i.e., upregulation of genes). However, it is also likely that trace levels of 1,4-dioxane (below the reporting limit) are present or have been present in the past at many of these locations, such that there would be a reason for 1,4-dioxane degrading organisms to express these genes and grow. Furthermore, biomarkers for 1,4-dioxane degradation were more frequently detected in samples from near the presumed release area at Facility 1381 (locations 1381-SB1 and 1381-SB2) than in a sample collected outside the release area (location 1381-SB4).
- The total microbial population was slightly higher at SLC-16 than Facility 1381. The detection frequencies for 1,4-dioxane biomarkers were slightly higher at SLC-16 but exhibited similar patterns.
- *Pseudonocardia* sp. were detected in all samples, while the more specific 1,4-dioxane biomarkers were generally detected in a smaller percentage of samples. It is important to note that there are likely to be a significant number of 1,4-dioxane-degrading genes beyond those that can be identified using DXMO and ALDH. Assaying for *Pseudonorcdia* sp. helps to bridge this gap (although it is also clear that not all Pseudonocardia sp. are 1,4-dioxane degraders). Therefore, the lack of DXMO and ALDH in a particular sample does not necessarily mean that no 1,4-dioxane degrading capabilities exist at that location.
- DXMO was detected more frequently than ALDH. Given the importance of the latter gene target in the metabolic 1,4-dioxane degradation pathway, this finding suggests that 1,4-dioxane degradation is occurring due to a combination of cometabolic and metabolic pathways.
- DXMO was detected in the majority of samples collected from lower-permeability intervals. This indicates that even if long-term storage of 1,4-dioxane mass is occurring due to matrix diffusion, 1,4-dioxane-degrading capabilities are relatively widespread within these low-permeability intervals.

- In general, a greater abundance of both total bacteria and 1,4-dioxane biomarkers was observed in samples collected from lower-permeability intervals than samples collected from higher-permeability intervals. This was particularly evident at Facility 1381. This is promising with respect to long-term attenuation of any mass that diffuses into these lower-permeability soils.

Collectively, the biomarker data suggest that significant 1,4-dioxane degradation capabilities are present at these sites, and the isotopic data suggest that 1,4-dioxane degradation has already occurred (particularly at Facility 1381). However, there is no clear indication that the locations where biomarkers for 1,4-dioxane degradation are abundant are also locations where isotopic fractionation has occurred. This is based on a comparison of the depth-discrete data shown in **Table 36a**. For example, three samples with evidence for carbon fractionation (1381-SB1-50-52'; 1381-SB4-45-47'; SLC16-SB1-48-50') were also analyzed for biomarkers, but DXMO and ALDH were not detected in any of these samples. In addition, DXMO was detected in two samples where there was little or no evidence of fractionation. It is unclear if this lack of a correlation is related to the relatively small number of samples where both isotopic and biomarker analyses were performed and generated interpretable results. Note that it was not possible to analyze all samples for all analytes, given that there were sample volume restrictions and no protocol for isotopic analysis of soil. This was particular limitation in evaluating patterns in low-permeability zones (i.e., little isotopic data from these intervals).

Summary: **Table 38** lists the key findings from this field study. At each site, there was evidence that matrix diffusion of 1,4-dioxane and/or chlorinated solvents was occurring. As discussed in Section 4.4.3, the long-term implications of matrix diffusion are more pronounced at SLC-16, but there is a potential to mitigate these effects if short-term remedial efforts are implemented.

Table 36a. Concentration of Stable Isotopes and Selected Biomarkers in Groundwater

Sample ID	1,4-Dioxane Concentration	$\delta^{13}C$ 1,4-Dioxane	$\delta^{2}H$ 1,4-Dioxane	Pseudonocardia 16S (copies/mL)		Total 16S (copies/mL)		DXMO (copies/mL)		ALDH (copies/mL)	
	(mg/L)	PDB ± 0.3‰	VSMOW ± 0.5‰	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1381-SB1 (50-52')	<0.003	-25.54	NES	2.4E+03	1.4E+03	1.5E+07	8.3E+06	ND		ND	
1381-SB1 (52-54'')	<0.003	BAL	NES								
1381-SB2 (50-52')	<0.003	-22.39	NES								
1381-SB2 (52-54')	<0.003	BAL	NES	2.8E+03	1.7E+03	2.1E+07	4.3E+06	1.9E+03	4.3E+02	2.3E+03	2.4E+02
1381-SB3 (44-46’)	<0.003	-24.53	NES								
1381-SB3 (48-50’)	<0.003	-30.61	NES								
1381-SB4 (45-47')	<0.003	-24.37	NES	3.6E+02	2.9E+02	2.0E+06	9.3E+05	ND		ND	
SLC16-SB1 (40-42')	17.2	-30.85	-43.62	9.1E+03	5.2E+03	6.2E+04	1.4E+04	ND		ND	
SLC16-SB1 (48-50')	9.0	-23.39	-9.97	2.5E+03	1.3E+03	4.3E+03	2.7E+03	ND		ND	
SLC16-SB2 (40-42')	1.75	-31.21	-70.61	3.8E+03	1.8E+03	2.8E+06	8.1E+05	1.3E+03	3.6E+02	ND	
SLC16-SB2 (48-50')	1.82	-32.06	-66.70	6.1E+03	2.3E+03	9.2E+06	2.7E+06	ND		ND	
SLC16-SB3 (40-42’)	<0.003	BAL	NES								
SLC16-SB3 (46-48’)	0.00173	BAL	NES								
SLC16-SB4 (40-42’)	<0.003	BAL	NES								
SLC16-SB4 (45-47’)	<0.003	BAL	NES								
SLC16-SB5 (35-27')	<0.003	-33.80	NES	3.3E+04	2.0E+04	1.0E+07	4.5E+06	1.9E+03	1.5E+03	1.9E+03	7.6E+02
SLC16-SB5 (53-55')	<0.003	BAL	NES	3.1E+04	1.5E+04	4.3E+07	1.6E+07	6.7E+03	3.2E+03	1.3E+04	2.7E+03

Notes: (1) Yellow shaded samples were collected from low-permeability interval; (2) Biomarker detection limit in groundwater: 1.47E+02 copies/mL;(3) ND = non-detect; (3) BAL; (4) NES = not enough sample available for analysis; (5) DXMO = 1,4-dioxane monooxgenase; (6) ALDH = aldehyde dehydrogenase.

Table 36b. Concentration of Selected Biomarkers in Soil

Sample ID	1,4-Dioxane Concentration (mg/kg)	δ13C 1,4-Dioxane PDB ± 0.3‰	δ2H 1,4-Dioxane VSMOW ± 0.5‰	Pseudonocardia 16S (copies/g)		Total 16S (copies/g)		DXMO (copies/g)		ALDH (copies/g)	
				Mean	SD	Mean	SD	Mean	SD	Mean	SD
1381-SB1 (38')	<0.00286	--	--	7.5E+03	1.7E+03	5.9E+02	4.6E+02	6.2E+01	3.4E+01	ND	
1381-SB1 (57')	<0.002	--	--	3.5E+03	2.7E+03	3.9E+04	2.6E+04	4.1E+00	1.8E-01	3.7E+02	6.7E+01
1381-SB2 (37.5')	<0.00266	--	--	7.2E+03	1.4E+03	5.2E+02	3.1E+02	5.4E+01	6.7E+01	ND	
1381-SB2 (56')	<0.002	--	--	1.5E+04	1.1E+04	3.1E+05	1.1E+05	2.2E+02	2.9E+02	2.3E+02	2.1E+02
1381-SB4 (44.5')	<0.0026	--	--	1.2E+03	1.0E+03	4.5E+02	1.9E+02	ND		ND	
1381-SB4 (56.3')	<0.002	--	--	4.9E+03	4.1E+03	1.7E+04	4.6E+03	ND		ND	
SLC16-SB1 (43.2')	0.621	--	--	6.6E+02	2.4E+02	8.9E+03	3.7E+03	ND		ND	
SLC16-SB1 (50.5')	<0.23	--	--	4.4E+03	2.0E+03	4.4E+04	2.0E+04	ND		ND	
SLC16-SB1 (53')	<0.206	--	--	8.9E+03	4.9E+03	1.1E+04	7.3E+03	ND		ND	
SLC16-SB1 (54.3')	<0.196	--	--	5.5E+03	2.1E+03	3.1E+05	2.4E+05	1.9E+02	1.4E+02	ND	
SLC16-SB2 (43')	0.722	--	--	7.3E+02	3.2E+02	6.5E+03	4.2E+03	ND		ND	
SLC16-SB2 (51')	<0.226	--	--	1.2E+04	3.6E+03	2.3E+05	1.7E+05	4.6E+01	2.3E+01	ND	
SLC16-SB2 (52.2')	<0.255	--	--	8.2E+03	2.8E+03	8.7E+05	3.1E+05	2.3E+02	2.3E+02	ND	
SLC16-SB2 (53.5')	<0.194	--	--	4.4E+03	2.0E+03	2.8E+06	2.5E+06	2.6E+02	3.6E+02	ND	
SLC16-SB5 (36')	<0.00261	--	--	1.0E+03	5.1E+02	2.1E+04	1.4E+04	2.5E+02	3.3E+02	1.5E+02	7.2E+01
SLC16-SB5 (41.2')	<0.00363	--	--	5.2E+03	4.1E+03	1.0E+05	5.3E+04	ND		ND	

Notes: (1) Yellow shaded samples were collected from low-permeability interval; (2) Biomarker detection limit in soil: 2.9E+02 copies/g;(3) ND = non-detect; (4) BAL; (5) NES = not enough sample available for analysis; (6) DXMO = 1,4-dioxane monooxgenase; (7) ALDH = aldehyde dehydrogenase.

Table 37. Summary of Biomarker Detection Frequencies

Location	Soil Type	Mean of Total Population (based on 16S)	Pseudonocardia detected? (mean of detections)	DXMO detected? (mean of detections)	ALDH detected? (mean of detections)
Facility 1381	High-k (sands)	5.2x10^{2} copies/g	3 of 3 Soil samples (5.2x10^{3} copies/g)	2 of 3 Soil samples (5.8x10^{1} copies/g)	0 of 3 Soil samples
		8.5x10^{6} copies/mL	2 of 2 GW samples (1.4x10^{3} copies/mL)	0 of 2 GW samples	0 of 2 GW samples
	Low-k (clays)	4.7x10^{5} copies/g	10 of 10 Soil samples (7.2x10^{3} copies/g)	6 of 10 Soil samples (1.2x10^{2} copies/g)	2 of 10 Soil samples (3.0x10^{2} copies/g)
		2.1x10^{7} copies/mL	1 of 1 GW samples (2.8x10^{3} copies/mL)	1 of 1 GW samples (1.9x10^{3} copies/mL)	1 of 1 GW samples (2.3x10^{3} copies/mL)
SLC-16	High-k (sands)	1.2x10^{4} copies/g	3 of 3 Soil samples (8.0x10^{2} copies/g)	1 of 3 Soil samples (2.5x10^{2} copies/g)	1 of 3 Soil samples (1.5x10^{2} copies/g)
		1.1x10^{7} copies/mL	6 of 6 GW samples (1.4x10^{4} copies/mL)	3 of 6 GW samples (3.3x10^{3} copies/mL)	2 of 6 GW samples (7.5x10^{2} copies/mL)
	Low-k (clays)	6.2x10^{5} copies/g	7 of 7 Soil samples (6.9x10^{3} copies/g)	4 of 7 Soil samples (1.5x10^{2} copies/g)	0 of 7 Soil samples
		--	--	--	--

Notes: (1) Blue shading used to represent the relative detection frequency; (2) Detection limit in groundwater: 1.47E+02 copies/mL; (3) detection limit in soil: 2.9E+02 copies/g; (4) DXMO = 1,4-dioxane monooxgenase; (5) ALDH = aldehyde dehydrogenase.

Table 38. Summary of Findings from Field Investigation

	SLC-16	Facility 1381
Stratigraphy	• Heterogeneous sandy unit with thin (2 ft or less), discontinuous low-k layer (silty clay) present at ~50 ft bgs • Very thin (1 ft or less) lower-k sub-intervals also present at shallower depths	• Sands underlain by well-defined and continuous low-k layer (clay) present at ~50 ft bgs; • Low-k layer is generally > 3 ft thick
1,4-Dioxane Distribution	• Moderate to high 1,4-dioxane concentrations present in apparent source area • Little or no 1,4-dioxane in downgradient or outside of source area	• Little or no 1,4-dioxane present at majority of locations (1 location with trace levels in soil) • Consistent with dilute plume
CVOC Distribution	• High CVOC concentrations (nearing solubility) present in apparent source zone	• Low CVOC concentrations in deeper portions of aquifer and in low-k layer throughout the site
Evidence for Matrix Diffusion?	• **STRONG** – elevated CVOC and 1,4-dioxane concentrations in low-k samples confirm mass storage	• **MODERATE** – CVOC and 1,4-dioxane concentrations are generally low but tend to be slightly higher in low-k zone than overlying high k zone
Current "Direction" of Diffusion Processes?	• Dominated by **"forward diffusion"** • 1,4-dioxane and CVOC concentrations decrease from higher-k layers to lower-k layers, suggesting continued loading of low-k layers	• Dominated by **"back diffusion"** • 1,4-dioxane and CVOC concentrations generally increase from high-k layer to low-k layer, suggesting release into overlying aquifer
Apparent Impact of Historic Remediation Efforts?	• No major remedial efforts performed yet	• Historic remediation efforts have reduced CVOCs and did not leave significant residual 1,4-dioxane mass
Geochemical Conditions	• Groundwater is reducing and generally supportive of biological activity, but elevated conductivity and competing electron acceptors	• Groundwater is reducing and generally supportive of biological activity (neutral pH, no competing electron acceptors, elevated methane)
Evidence for 1,4-Dioxane Degradation?	• High k zone: **YES** (isotope fractionation in at least 1 sample) • Low k zone: **POSSIBLE** (biomarkers for 1,4-dioxane degradation frequently detected; more biomass than in high-k zone)	• High k zone: **YES** (isotope fractionation in multiple samples) • Low k zone: **POSSIBLE** (biomarkers for 1,4-dioxane degradation frequently detected; more biomass than in high-k zone)
Evidence for CVOC Degradation?	• High k zone: **YES BUT LIMITED** (high levels of parent compounds; low ratios of by-products to parents) • Low k zone: **POSSIBLE** (elevated ratios of by-products to parents in some low-k samples; elevated biomass)	• High k zone: **YES** (low level of parent compounds; high ratios of by-products to parents) • Low k zone: **POSSIBLE** (elevated ratios of by-products to parents in some low-k samples; elevated biomass)

4.4.3 Discussion

The results of this study suggest that matrix diffusion can be a key process driving the long-term fate of 1,4-dioxane in the subsurface. The modeling study used an idealized approach to demonstrate the potential implications of matrix diffusion, while the field study gathered evidence at two different sites to show how matrix diffusion was playing a role at these sites.

In the modeling portion of this study, a significant amount of contaminant mass was predicted to be stored in low-permeability zones within both a theoretical source zone and the downgradient plume. Even after the source was depleted, this mass was enough to contribute to aqueous concentrations in the adjacent transmissive layer that exceeded regulatory levels by several orders-of-magnitude for long timeframes (i.e., centuries). This finding is consistent with previous studies that focused on the matrix diffusion of chlorinated solvents and confirmed that, like chlorinated solvents, the potential for matrix diffusion should be considered when developing a conceptual site model for 1,4-dioxane contamination.

A key finding from the modeling study was that the risk posed by 1,4-dioxane matrix diffusion is perhaps even more significant than for TCA. A higher mass of 1,4-dioxane diffused into the low-permeability interval than TCA prior to source depletion. After source depletion, aqueous concentrations of 1,4-dioxane in the transmissive zone plateaued at a level above that predicted for TCA. This poses a particular problem for 1,4-dioxane because of the lower regulatory levels that are likely to be applicable for 1,4-dioxane (i.e., 1 μg/L or less) when compared to TCA (MCL = 200 μg/L). The total mass of 1,4-dioxane was also higher than that predicted for TCA at each time point within the downgradient plume.

The predicted persistence of 1,4-dioxane due to matrix diffusion highlights how several characteristics of this compound enhance mass storage within low-k soils. First, the high effective solubility of 1,4-dioxane creates an initial concentration gradient that drives large amounts of mass into the low-permeability zone. Given that 1,4-dioxane sorbs poorly, significant penetration into the low-permeability layer is promoted during the period when the transmissive zone is still active. This vertical penetration continues after the transmissive zone source has been depleted. As a result, back diffusion of 1,4-dioxane mass occurs across a much deeper interval (e.g., > 6 m eighty years after the release) than was predicted for TCA. Similarly, rapid migration of 1,4-dioxane was predicted to impact a larger downgradient area than TCA. The influence of compound-specific chemical properties on diffusion-influenced contaminant transport can be complex (Brown et al., 2012). In the release scenarios that were modeled during this study, the minimal source longevity of 1,4-dioxane within the transmissive portions of the release area were not enough to offset the characteristics of 1,4-dioxane that favored mass storage within the low-permeability zones.

The modeling results provide evidence that at some sites, source zones for 1,4-dioxane may be difficult to identify and delineate. Rapid dissolution of any 1,4-dioxane associated with a decades-old chlorinated solvent NAPL would greatly complicate any present-day source characterization efforts. For the theoretical release modeled during this study, the original 1,4-dioxane source was depleted from the transmissive portions of the source zone within a few years—long before there would have been any attempt to delineate the source zone. The migration potential of 1,4-dioxane in groundwater presents a further challenge to identifying the source. It may be more productive to simply delineate the traces of the chlorinated solvent source zone and then use this to approximate the area where 1,4-dioxane was released.

This has significant implications for remedial decision-making. Source removal and control is one of the primary elements of most remedies, but the results of the modeling study suggest it has limited application at some sites for 1,4-dioxane, at least in the conventional sense. The majority of 1,4-dioxane mass would have already exited the transmissive portions of the source zone, and the mass that remained in the low-permeability zone would not be addressed by any attempt to treat the transmissive layer within the perceived source zone (e.g., via injection of reagents that will promote 1,4-dioxane degradation). As a result, source zone treatment would do little to prevent recontamination of the transmissive zone via back diffusion once the treatment has concluded. Furthermore, continued migration of 1,4-dioxane mass that had already been transported downgradient in the decades since the release occurred would be difficult to prevent through source treatment. The mass in the plume serves as additional reservoir of material that can serve to load the low-permeability zones across large areas during advective transport. However, accounting for the entire area contaminated by 1,4-dioxane during the design of a treatment system may be technically impractical.

The modeling results predict that back diffusion of mass from the low-permeability zone represents a “secondary source” of 1,4-dioxane that becomes particuarly relevant after source material in the transmissive zone has been depleted. Back diffusion processes were predicted to result in maximum (i.e., source zone) aqueous concentrations in the range of 0.1 to 10 mg/L by the mid-2010s based on the release scenarios that were evaluated. These concentrations may be fairly representative of a “typical” 1,4-dioxane site based on the survey results presented in Section 4.1. In that study, it was estimated that the maximum site-wide 1,4-dioxane concentration frequently fell within a similar range (10th percentile = 0.009 mg/L; 90th percentile = 13 mg/L) (Adamson et al., 2014). The consistency between the predicted and observed concentration ranges suggests that diffusion-driven processes may be significantly contributing to currently-measured 1,4-dioxane concentrations at field sites.

The field study did demonstrate that matrix diffusion and mass storage of 1,4-dioxane were occurring at the two sites that were investigated. However, the results did not conclusively show that the 1,4-dioxane present at these two sites fit the “secondary source” hypothesis suggested by the modeling study. At the SLC-16 site at CCAFS, there was still significant 1,4-dioxane mass present in the transmissive zones, and it was generally higher than the amounts measured in the low-permeability sub-intervals. The release area for 1,4-dioxane is unknown at this site has not been established, but the locations and depth intervals with elevated 1,4-dioxane concentration tended to match those where elevated CVOC concentrations are encountered. In other words, this means that there is a 1,4-dioxane source zone remaining and that is reasonably co-located with the CVOC source zone. This finding was unexpected based on 1,4-dioxane's properties, but there are at least two potential mitigating factors: (1) it is possible that TCE was being released for an extended period prior to 1,4-dioxane releases (which were more likely associated with 1,1,1-TCA); (2) there may be NAPL remaining (based on the high TCE concentrations in groundwater) that is controlling contaminant transport in unexpected ways (particularly if it is poorly-accessible pore space).

The mass distribution of 1,4-dioxane at SLC-16 suggest that there is still a 1,4-dioxane source zone that could be targeted using conventional treatment methods that are generally more effective in transmissive formations. This would not necessarily address the significant amount of 1,4-dioxane that has already diffused into the low-k intervals at this site. However, it would clearly be effective at reducing the longer-term impacts of matrix diffusion. This is because the source appears to be still actively loading the low-k zone (i.e., "forward diffusion" due to a positive concentration gradient). Eliminating the source would prevent further mass storage both in the source zone and in the downgradient plume. Attention would then shift to managing the mass in the low-k zones. It should be noted that no major remedial efforts have been undertaken at this site (at the date of this report), and site management strategies will have to account for 1,4-dioxane as well as the high CVOCs that are present.

Results from the second field site at CCAFS (Facility 1381) suggest a different conceptual model for 1,4-dioxane at this site. Specifically, there was no clear source zone for 1,4-dioxane, at least within the deeper portions of the aquifer that were part of the investigation. Instead, there were minor amounts of 1,4-dioxane in a few soil samples, and the majority of the site had no 1,4-dioxane above the reporting limit. This is consistent with a "dilute plume" where there is no distinct release area and/or the 1,4-dioxane is coming from off-site (similar to Scenario 2 in the modeling study). Given 1,4-dioxane's potential to migrate, it is possible that a significant percentage of 1,4-dioxane sites fit this conceptual model. In the case of Facility 1381, there was an indication that a portion of the remaining mass is associated with the distinct low-k zone at the site. This confirmed that matrix diffusion has occurred, and it appears (based on the concentration gradient) that back diffusion is now the dominant diffusion process. However, the important finding is that the mass in the low-k zone is currently very low. This means that the historical loading (i.e., 1,4-dioxane source strength) was likely very low as well, and it suggests that the long-term impact of this mass from back diffusion should be relatively limited. In terms of remedial decision-making, it also means that is no true "source zone" that could be cost-effectively targeted to improve the remediation timeframe (at least at the locations that were part of this investigation. It is important to note that extensive remediation has already been performed at Facility 1381 to address CVOCs. While the impact of these efforts on 1,4-dioxane cannot be established, the study results confirmed that CVOC remediation did not appear to leave behind a large amount of 1,4-dioxane.

While the data suggest that 1,4-dioxane concentrations have been historically low at Facility 1381 and have not driven significant mass into the low-k interval, there was also evidence that 1,4-dioxane degradation contributed to the current site conditions. In particular, carbon isotope fractionation in multiple samples suggests that much of the 1,4-dioxane that remains at the site is highly degraded. To a lesser extent, the biomarker data also demonstrate that degradative capabilities are present. The aquifer is largely anaerobic, although like most heterogeneous formations, there are certainly areas where dissolved oxygen may be present to support aerobic 1,4-dioxane biodegradation. The removal of high concentrations of chlorinated solvents through earlier remediation efforts would have helped alleviate the inhibitory effects of these compounds on 1,4-dioxane biodegradation.

There was also evidence for 1,4-dioxane degradation at SLC-16 but it was relatively limited. This may be attributable to the relatively high CVOC concentrations at locations where 1,4-dioxane was detected. In addition, SLC-16 has several characteristics that are associated with "early-stage" sites (potential NAPL, on-going loading of low-k zones) as opposed to "late-stage" sites (Sale and Newell, 2005). 1,4-dioxane biodegradation is known to be relatively slow and not necessarily ubiquitous, and it may be that biodegrdation capabilities are still developing at this early-stage site.

Collectively, the results of this study emphasize that for 1,4-dioxane-contaminated sites, there are multiple different types of conceptual site models that may be appropriate. In each case, matrix diffusion can be important component, and its contribution to the fate and transport of 1,4-dioxane has a range of potential implications. In the worst case, matrix diffusion of 1,4-dioxane may limit the effectiveness of conventional treatment strategies and hinder the goal of short-term site closure. As discussed in the next section, stronger consideration would need to be given to the development of alternative end-points and/or longer-term management at these types of sites.

Assuming that the potential for matrix diffusion of 1,4-dioxane has been included in the conceptual model for a contaminated groundwater site, it becomes imperative to develop remediation strategies that appropriately address long-term storage and release from low-permeability zones.

5. CONCLUSIONS AND IMPLICATIONS FOR SITE MANAGEMENT

The following section summarizes the main findings from this study as they relate to improved decision making and management of 1,4-dioxane contaminated sites.

FINDING #1: 1,4-Dioxane plumes are not as large as expected. 1,4-dioxane is highly soluble and does not strongly sorb. These properties have led to a concern that 1,4-dioxane plumes will be long, particularly when compared to chlorinated solvents that may co-occur at these sites. Using geospatial analysis of groundwater monitoring data from the California GeoTracker database, a median 1,4-dioxane plume length of 269 m was established (n = 108 sites). At sites where both 1,4-dioxane and chlorinated solvents were detected (n= 105), the 1,4-dioxane plume was estimated to be longer than the chlorinated solvent plume(s) at only 21% of the sites. At 56% of the sites, the chlorinated solvent plume (typically 1,1-DCE and/or TCE) was longer.

IMPLICATIONS FOR SITE MANAGEMENT: The data suggest that 1,4-dioxane plumes are less likely to extend beyond current monitoring networks (which were designed for chlorinated solvents) than originally feared. This finding is likely related to natural attenuation and containment of decades-old releases of chlorinated solvents and 1,4-dioxane that have been migrating along similar flowpaths and environments. Also, TCE usage at many sites likely predates the release of 1,4-dioxane, giving TCE (and its by-products) a potential “head-start”. However, careful long-term monitoring of 1,4-dioxane plume stability is important, even at sites with relatively short plumes. Given 1,4-dioxane’s high migration potential, there is a possibility that 1,4-dioxane plumes at some sites will eventually “catch up” to the chlorinated solvent plumes.

FINDING #2: Based on the observed co-occurrence of 1,4-dioxane and chlorinated solvents, there are probably many “unidentified” 1,4-dioxane plumes. 1,4-dioxane is expected to co-occur with chlorinated solvents based on its use as a stabilizer (for 1,1,1-TCA) and the historic switching between various solvents (e.g., TCE to 1,1,1-TCA, then back to TCE) that occurred at many sites. During the site survey, 1,4-dioxane was detected at 193 sites (of 589) where it was analyzed, with TCE being the most frequently detected co-occurring contaminant (93%), followed by 1,1-DCE (86%) and TCA (58%). At sites where 1,4-dioxane was included in the analytical program, it was detected at 52% of sites containing TCE, 70% of sites containing 1,1,1-TCA, and 69% of sites containing 1,1-DCE (69%). The project results confirmed earlier studies on contaminant co-occurrence (Anderson et al., 2012). However, a key difference was that this study identified a large number of sites with chlorinated solvents where 1,4-dioxane has not been analyzed, ranging from 67% to 85% for this set of constituents. For example, no 1,4-dioxane analyses were conducted at 318 (67%) of the sites where 1,1,1-TCA was detected. Similarly, there were 572 sites with 1,1-DCA but non-detectable levels of TCA where no dioxane analyses had been completed. Based on the co-occurrence data, this means that (at the time of this study) there were several hundred sites in California alone where 1,4-dioxane plumes had yet to be identified and characterized.

IMPLICATIONS FOR SITE MANAGEMENT. There is a high likelihood that 1,4-dioxane is present at many sites where chlorinated solvents have been detected in groundwater. The data suggest that the majority of sites have yet to include 1,4-dioxane in monitoring programs. While there may be a technical justification for not measuring 1,4-dioxane at a site with mostly TCE, there may be limited historical records of site-specific chlorinated solvent usage. Therefore, prudence would suggest that 1,4-dioxane be included in monitoring programs at all chlorinated solvent sites, particularly those where 1,1,1-TCA degradation products (e.g., 1,1-DCA, 1,1-DCE) are present. Given the potential for sub-ppb regulatory action levels, implementing a thorough characterization and monitoring program is key to eliminating any potential risk to receptors.

FINDING #3: Most 1,4-dioxane sites are dilute. 1,4-dioxane was detected at 193 individual sites included in the survey. The median maximum historical 1,4-dioxane concentrations at these sites was 365 μg/L (10th percentile = 9 μg/L; 90th percentile = 13,460 μg/L). This value is approximately three orders of magnitude higher than the drinking water screening level of 0.67 μg/L for 1,4-dioxane. These results supported the conventional conceptual model that the large majority of plumes a relatively dilute, but only 11% were longer than 1 km. Similar results were found for TCE.

IMPLICATIONS FOR SITE MANAGEMENT: The results support the conventional conceptual model that 1,4-dioxane plumes are dilute (though not necessarily long). As a result, it is more difficult to identify a “high-value” target for aggressive source treatment, and in fact it may be difficult to identify the source itself at some sites. The cost-effectiveness of 1,4-dioxane source treatment (e.g., mass removed per dollar spent) is likely to be poor in most cases, and alternative approaches are likely to be preferable where possible.

FINDING #4: Storage of 1,4-dioxane in lower permeability soils likely contributes to its long-term persistence. Modeling was used to establish that, like chlorinated solvents, diffusion of 1,4-dioxane mass in and out of lower-permeability (low-k) soils (e.g., silts, clays) can be an important fate and process for this compound. During a typical release scenario, 1,4-dioxane was actively loading the low-k layer within the source zone for only a short period (<3 years) relative to 1,1,1-TCA due to 1,4-dioxane’s high effective solubility. Despite this short loading period, the mass of 1,4-dioxane stored within the low-k source zone, as well as the groundwater concentration resulting from back diffusion, was consistently larger than that predicted for 1,1,1-TCA. Even 80 years after release, the 1,4-dioxane concentration resulting from back diffusion (> 100 μg/L) was still orders-of-magnitude higher than potentially-applicable criteria. Diffusion also contributed to higher concentrations and enhanced penetration of 1,4-dioxane into the low-k zones relative to 1,1,1-TCA within the downgradient plume. Data from focused characterization studies at two different field sites confirmed that a significant amount of the 1,4-dioxane mass was associated with lower-k zones within and adjacent to the more transmissive portions of the aquifers.

IMPLICATIONS FOR SITE MANAGEMENT: The results indicate that 1,4-dioxane within transmissive portions of the source zone can be depleted quickly due to characteristics that favor both diffusion-based storage and groundwater transport. The modeling results also highlight the potential differences between 1,4-dioxane and chlorinated solvent source zones. For 1,4-dioxane, there may be much less mass in a defined source zone, and the remaining mass will be harder to treat using conventional means. Instead, many sites may be dominated by long-term back diffusion of 1,4-dioxane mass from these "secondary sources". At a minimum, characterization efforts and conceptual site models for 1,4-dioxane must include this mass in lower-k zones.

FINDING #5: There is extensive evidence for 1,4-dioxane attenuation at field sites. The conventional conceptual model for 1,4-dioxane is that it is persistent and that limited attenuation would be expected to occur in groundwater. Temporal concentration changes were used to estimate attenuation rates at California GeoTracker sites and monitoring wells at Air Force installations. Statistically-significant positive source attenuation rates for 1,4-dioxane were confirmed at 22 sites (median equivalent half-life = 20 months). At sites where chlorinated solvents and 1,4-dioxane were both present, the median value of all statistically-significant dioxane source attenuation rates was similar to 1,1-DCE and TCE (but lower than 1,1,1-TCA). Attenuation rates based on well-specific records from the Air Force dataset confirmed significant 1,4-dioxane attenuation (131 out of 441 wells) at a similar frequency and extent (median equivalent half-life = 48 months) as observed at the California sites.

IMPLICATIONS FOR SITE MANAGEMENT: While 1,4-dioxane attenuation was not observed at all sites (in part due to fairly short monitoring records for 1,4-dioxane), the evidence was sufficient enough to question the common belief that 1,4-dioxane is recalcitrant. These findings support the potential viability of natural attenuation as a long-term site management strategy. At a minimum, remedial decision-making should consider the use of recently-developed biomarkers to assess aerobic 1,4-dioxane degradation because it may be an important contributor to site-specific natural attenuation capacity.

FINDING #6: Several factors influencing 1,4-dioxane attenuation at field sites have been confirmed. Based on the analysis of California sites, there was little indication that chlorinated solvent remedial efforts (e.g., chemical oxidation, enhanced bioremediation) impacted 1,4-dioxane attenuation. However, a statistical analysis of different factors that could potentially impact 1,4-dioxane attenuation found a positive correlation between increasing concentrations of dissolved oxygen and 1,4-dioxane attenuation at the Air Force wells. This same analysis found that 1,4-dioxane attenuation negatively correlated with higher metals and CVOC concentrations.

IMPLICATIONS FOR SITE MANAGEMENT: These results indicate that significant 1,4-dioxane attenuation is more likely to occur at sites where aerobic conditions are present. However, these same conditions are generally unfavorable for reductive dechlorination, and the persistence of chlorinated solvents would negatively impact 1,4-dioxane attenuation rates. This highlights the complexity of removing both 1,4-dioxane and chlorinated solvents at the same site but suggests that treatment trains may be a useful approach.

FINDING #7: Biodegradation was implicated as a contributor to 1,4-dioxane attenuation at field sites. The correlations between 1,4-dioxane attenuation and the concentration of oxygen, chlorinated solvents, and metals corroborate the results of extensive lab-based research on 1,4-dioxane biodegradation. This suggests that aerobic biodegradation of 1,4-dioxane was contributing to the observed attenuation at the sites that were evaluated as part of the big data study. Isotope and biomarker data from the field investigation indicated that there was evidence for 1,4-dioxane biodegradation capacity at these demonstration sites.

IMPLICATIONS FOR SITE MANAGEMENT: The results highlight that biodegradation is a potential attenuation mechanism for 1,4-dioxane and that it can be incorporated into treatment approaches. Removal of inhibitory compounds such as CVOCs and metals may be key to promoting 1,4-dioxane attenuation at field sites and should be considered as part of the site management strategy.

FINDING #8: If 1,4-dioxane treatment is necessary, then treatment trains may provide a more effective approach. 1,4-dioxane's structure makes it resistant to reductive-based degradation mechanisms, but it is subject to oxidative attack. In situ oxidation technologies (e.g., chemical oxidation, enhanced aerobic biodegradation) should degrade 1,4-dioxane but each has inherent limitations. This study looked at overcoming these limitations by using combinations of technologies, or "treatment trains" that were tested in a series of bench-scale treatability assays. Based on these results, the most promising treatment train was in situ oxidation followed by bioaugmentation with a 1,4-dioxane degrading culture (**Figure 5**). Pre-treatment using chemical oxidation degraded a portion of the 1,4-dioxane, but importantly, degraded the chlorinated solvents. By removing these inhibitors of 1,4-dioxane biodegradation, the bioaugmentation culture thrived and continued to degrade 1,4-dioxane indefinitely. In the absence of chemical oxidation, the undegraded chlorinated solvents completely inhibited 1,4-dioxane biodegradation.

IMPLICATIONS FOR SITE MANAGEMENT: For sites where high-concentration source zones have been identified, or where regulatory and risk drivers exist, active treatment of 1,4-dioxane may be a necessary step. For these cases, treatment trains should be considered as a viable approach for co-occurring 1,4-dioxane and chlorinated solvents. Targeted chemical oxidation may prove beneficial for subsequent biologically-based approaches, including both enhanced bioremediation and natural attenuation.

FINDING #9: 1,4-dioxane contaminated sites likely require different management strategies than typical contaminated sites. This project confirmed the dilute nature of most 1,4-dioxane plumes and identified the potential contribution of matrix diffusion. As described above, treatment of the transmissive portion of the source zone may not be practical at some sites because most of the 1,4-dioxane mass is no longer present in this subsurface compartment. These efforts may benefit off-site locations if the source area is treated and/or hydraulically isolated to minimize diffusion-driven loading as contamination moves downgradient (Sale et al., 2008). An example of this impact is shown in the modeling results (see Section 4.5). In Scenario 2 of this evaluation, the time to achieve an assumed regulatory threshold was significantly shortened when the upgradient source was isolated after 20 years as opposed to waiting until 40 years to isolate. In cases where this type of opportunity to address the source still exists, the simulation results suggest that the impacts of a low-strength 1,4-dioxane plume moving onto a downgradient site could be relatively moderate. This is beneficial because the timeframe for remedial decision-making is likely to be more favorable at downgradient sites than at source areas. In other words, present-day decisions are much more likely to occur during the loading period for these downgradient sites than in areas where 1,4-dioxane was released, and thus may actually limit further diffusion of 1,4-dioxane mass into low-permeability zones.

IMPLICATIONS FOR SITE MANAGEMENT: At sites where mass storage is an issue and migration of a relatively dilute 1,4-dioxane plume is a concern, source isolation and/or plume control measures may also be a viable 1,4-dioxane treatment strategy for transmissive zones. Such measures would effectively cut off the upgradient source and protect off-site areas from suffering the same degree of diffusion-related issues that would be expected in the release area. The drawbacks to this strategy is that it would require installation of a pump-and-treat system or a similar cost-and time-intensive measure, and this would need to be implemented in time to protect downgradient areas (Chapman and Parker, 2005; Mattieu et al., 2014). Alternatively, a remedial design that focuses on direct treatment of the mass in low-permeability zones could be attempted. However, many conventional in situ technologies have difficulties in delivering amendments to the types of fine-grained units where matrix diffusion is favored (i.e., silts, clays, rock) (Hønning et al., 2007; Leeson et al., 2013; Sale et al., 2013). Given these challenges, management of these secondary 1,4-dioxane sources using less-intensive methods such as natural attenuation and institutional controls may be more feasible. There is increasing evidence that 1,4-dioxane can attenuate, but there needs to be additional research on whether the conditions to support attenuation are present in low-permeability zones.

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APPENDICES

APPENDIX A. SUPPORTING DATA

A.1 White Paper on 1,4-Dioxane Catalysis

A.2 Results of Field Investigation

APPENDIX A.1

White Paper on 1,4-Dioxane Catalysis – *submitted to program office in February 2016*

WHITE PAPER

TO: Andrea Leeson, ESTCP Program Manager, Environmental Restoration

FROM: David Adamson (GSI Environmental Inc.), Michael Wong, and Kimberley Heck (Rice University)

RE: Response to In-Progress Review Comments for SERDP ER-2307

For our research project entitled *In Situ Treatment and Management Strategies for 1,4-Dioxane Contaminated Groundwater* (SERDP ER-2307), we presented progress to-date at the November 2014 in-progress review (IPR). This included results from the proof-of-concept catalysis studies (Task 2). Following the IPR, comments from the program office included the following as an Action Item:

> *The Program Office is concerned about the cost and performance implications of implementing catalysis (Task 2) as a remedy. Please submit a White Paper by* ***15 February 2015*** *highlighting and comparing the advantages and disadvantages of using the various promising catalysts being tested and compare to an established treatment technology (i.e., ISCO). Please ensure that in the comparison, implementation cost is considered.*

This White Paper addresses these issues and provides the requested cost comparison.

1.0 COMPARISON OF PROMISING CATALYSTS

A variety of catalysts were tested at the bench-scale for their ability to degrade 1,4-dioxane in groundwater. Three of the catalysts tested during this screening phase showed significant activity: Cu(II) oxide, Fe(III) oxide, and TiO_2. A comparison of the advantages and disadvantages of each these catalysts is provided in **Table 1**.

Note that testing of other catalyst combinations is on-going, and results from these optimization studies may provide additional benefits to those described in **Table 1** (or the interim report for this project).

Table 1: Comparison of Promising Catalysts from Task 2 Bench-Scale Testing

Catalyst	Primary Advantages	Primary Disadvantages
Cu(II) oxide	• demonstrates highest reaction rates (5479 μM/lb/hr) • has been shown to be an effective catalyst for hydrogen peroxide, so it should work well in tandem with ISCO • catalytic activity is less sensitive to pH and works well at neutral pH	• highest cost of materials tested (~$8.70 per lb) • has been shown to be an effective catalyst for hydrogen peroxide, so it should work well in tandem with ISCO • known inhibitory effects on biodegradation activity (including inhibition of dioxane degraders) • dioxane oxidation competitively inhibited by TCE when both dioxane and TCE are present • precipitation may slow reaction • subject to dissolution over time
Fe(III) oxide	• most inexpensive of materials tested (~$3.00 per lb) • demonstrates moderate reaction rates (2245 μM/lb/hr) • lowest cost on a $-per-lb degraded basis • iron chemistry is well studied • little impact on biological activity expected • should compliment ISCO • less subject to competitive inhibition by TCE than Cu(II) oxide	• pH sensitivity • precipitation may slow reaction • subject to dissolution over time
TiO_2	• moderate material costs (~$4.70 per lb) • increasingly well studied for water treatment applications (e.g., sorption of arsenic, photocatalytic oxidation of PPCPs, nitrate, MTBE, etc.) • should compliment ISCO • less subject to competitive inhibition by TCE than other catalysts	• demonstrates slowest reaction rates of materials tested (689 μM/lb/hr) • possible toxic effects • precipitation may slow reaction • subject to dissolution over time

2.0 PERFORMANCE AND IMPLEMENTATION ISSUES

The purpose of Task 2 is to determine the reactivity of various catalysts for degradation of 1,4-dioxane. Nonetheless, we recognize that the results of this testing should support the larger goal of developing treatment approaches that can be implemented in the field. It is preferable that catalytic approaches can be adaptable to in situ approaches to avoid the issues associated with ex situ treatment of contaminated groundwater. Currently, however, there are no catalytic in situ processes that have been fully developed and implemented. As part of ESTCP ER-0012, researchers from Stanford and the Navy developed and tested a catalytic technology for treating chlorinated volatile organic compounds, but the field testing was completed in an ex situ reactor using pumped groundwater. As such, there is relatively limited basis for designing and estimating the costs associated with any in situ processes.

It is envisioned that catalysts would work best as part of a permeable reactive barrier (PRB) design for treating dioxane-impacted groundwater. This is because the catalysts are solid materials that are well-suited for emplacement within a permeable barrier. PRB designs typically are aimed at plume contaminant, but barriers can also be installed in source zones in an effort to reduce the remediation timeframe. Given that the initial testing has confirmed that the masses of catalysts required for effective dioxane removal are relatively small (0.01 – 1% by weight), there is also the possibility that catalysts could be injected directly into the groundwater as a slurry.

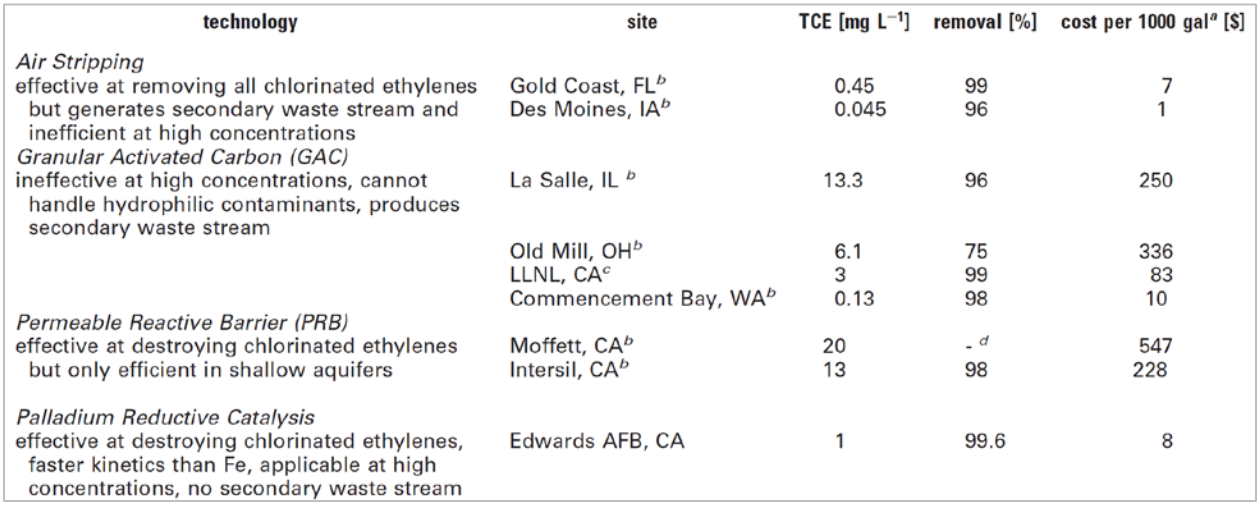
Based on the initial results from Task 2, the reaction rates for the catalysts ranged from 689 to 5479 μM dioxane per hour per pound of catalyst. These rates are far higher than those required to degrade moderate to high concentrations of dioxane (e.g., 0.1 to 100 mg/L) within the residence time typically provided by a PRB (e.g., 0.5 to 5 days in a 2-ft thick barrier installed within a transmissive zone with a seepage velocity of 100 to 500 ft/yr). This suggests that performance is sufficient for in situ applications.

For comparison to an established technology like ISCO, it is important to note that catalyst-based treatment could serve as a replacement for ISCO or as a complement to ISCO. For the former case, a catalyst-containing PRB is the most practical design choice. While this has significant advantages in terms of ensuring compliance at downgradient receptors and minimizing long-term O&M obligations, it may not be as effective at reducing remediation timeframes. Therefore, it is anticipated that installing a series of PRBs, including one that focuses on the source zone (or area of highest concentration) may be necessary if a true replacement for ISCO is required. In terms of complementing an ISCO-based treatment, it is anticipated that catalysis can be used to reduce the amount of oxidant needed. This is because the bench-scale treatability tests demonstrated that dioxane degradation could be accomplished using small volume ratios of oxidant (<0.0004% H_2O_2) relative to typical ISCO applications (where 1 to 30% H_2O_2 is injected).

3.0 COST EVALUATION

As noted previously, there is little basis for estimating costs associated with in situ treatment of groundwater using catalysts. To provide context, cost studies for the treatment of contaminated groundwater in conjunction with ex situ pump-and-treat processes have been published for the case of TCE (McNab et al., 2000; Davie et al., 2008). **Table 2** shows the comparative costs analysis for the treatment of water contaminated by TCE using air stripping, granular activated carbon, PRB, and palladium reductive catalysis treatment methods developed as part of ESTCP ER-0012.

Table 2: Previously-Published Cost Comparison of Catalysis vs. Competing Technologies for Groundwater Remediation (reproduced from Davie et al., 2008)



technology	site	TCE [mg L^{-1}]	removal [%]	cost per 1000 gal[a] [$]
Air Stripping effective at removing all chlorinated ethylenes but generates secondary waste stream and inefficient at high concentrations	Gold Coast, FL[b]	0.45	99	7
	Des Moines, IA[b]	0.045	96	1
Granular Activated Carbon (GAC) ineffective at high concentrations, cannot handle hydrophilic contaminants, produces secondary waste stream	La Salle, IL [b]	13.3	96	250
	Old Mill, OH[b]	6.1	75	336
	LLNL, CA[c]	3	99	83
	Commencement Bay, WA[b]	0.13	98	10
Permeable Reactive Barrier (PRB) effective at destroying chlorinated ethylenes but only efficient in shallow aquifers	Moffett, CA[b]	20	- [d]	547
	Intersil, CA[b]	13	98	228
Palladium Reductive Catalysis effective at destroying chlorinated ethylenes, faster kinetics than Fe, applicable at high concentrations, no secondary waste stream	Edwards AFB, CA	1	99.6	8

[a] All costs amortized for 10 year operation. [b] Data taken from EPA report no. 542-R-99-006. [c] Data taken from McNab (2000). [d] Data not given.

The economic analysis presented in **Table 2** suggests that, except for very small concentrations of contaminant, ex situ catalytic treatment is competitive with or more cost effective than other established treatment technologies, especially if concentrations are in the mg/L range. Indeed, while air stripping water with low levels of contaminant may appear cost effective, it must be noted that the cost analysis does not take into account the treatment of the secondary waste stream generated by this method. Most striking is that the cost for PRB—and in situ method—is almost 70X higher than than ex situ catalysis.

However, the details of this cost model were not provided in this publication (and were also difficult to discern from the project report). In addition, there may be some bias associated with a “cost per 1000 gallons treated” metric for comparing the study’s catalyst approach (in which high pumping rates could be exploited without affecting performance) with a PRB design (where treatment is passive and the flow rate is controlled by aquifer characteristics).

For the purposes of evaluating the costs associated with catalysis of dioxane relative to ISCO, two different scenarios were created:

- ***Scenario 1: Catalyst-based PRB vs. Conventional ISCO***. In this case, a series of PRBs containing catalysts are installed and operated for 10 years. This includes a PRB within the source zone and a PRB that covers a downgradient boundary to ensure containment. This option was compared to a "conventional" ISCO application using H_2O_2 injected in a grid across a treatment zone.

- ***Scenario 2: Catalyst-Supplemented ISCO vs. Conventional ISCO.*** In this case, a conventional ISCO application is compared to an application where the catalyst is used to reduce the oxidant concentration in the injected reagent. For both cases, the size of the treatment area and number of injections is assumed to be the same. The catalyst is injected as part of a low-concentration slurry based scaling up the mass/volume ratios that were effective in bench-scale testing.

Other assumptions used to develop the cost model and generate cost estimates for the scenarios included the following:

- Generic site characteristics and treatment requirements as listed in **Table 3a** (Scenario 1) and **Table 3b** (Scenario 2) were used.
- The treatment area for ISCO was set as equivalent to the same pore volume that would be treated in 1 year via advective transport through the PRB.
- Costs include design, implementation, reporting, O&M, and routine process monitoring but do not include initial site characterization.
- Typical unit costs for each technology were used. For PRB installation, a mid-point value of $400 per linear ft was used based on the range cited in ITRC's recent guidance document on PRBs (ITRC, 2011). Additional design and reporting costs were estimated as 50% of the installation costs based on past experience. For ISCO, a unit cost of $125 per cubic yard was selected using the source treatment costs compiled as part of SERDP CU-1292 (and reported in McDade et al., 2005) and ESTCP ER-201120 (results not yet published) as a basis. These unit costs for ISCO generally included design and reporting obligations.
- Material quantities were based on mass/volume ratios used in bench-scale testing. For Scenario 2, it was assumed that supplementing with catalyst would reduce the required H_2O_2 concentration from 30% to 10%.
- Materials costs were based on the following unit costs: catalyst = $5 per pound; H_2O_2 = $0.25 per pound.
- No adjustment was made to the PRB installation cost based on using catalyst material. This is because the cost for the required amount of catalyst ($2000) is small relative to the installation cost. It is likely that the catalyst would be mixed with native soil for installation purposes, and thus the costs associated with catalyst-based PRB might be lower than typical PRB media (e.g., ZVI, mulch).
- A 10-year lifecycle was used for Scenario 1. Over that time period, annual O&M costs were estimated to be $40,000 due to a combination of process monitoring and minor reconditioning of the catalyst. No catalyst replacement was required since catalyst lifetime was assumed to be 10 years. Dissolved oxygen in the groundwater was assumed to serve as a sufficient oxidant source for the reaction. Therefore, these scenarios necessarily involve an aerobic aquifer.
- Net present value was not used for cost estimation. This results in a conservative estimate for catalysis in Scenario 1 (because it has extended O&M requirements).

Table 3a: Cost Comparison for Catalysis vs. Competing Technologies for Dioxane Remediation – Scenario 1

Catalyst PRB	Conventional ISCO
Treatment area = 300 ft length x 20 ft depth x 2 ft width (of PRB)	**Treatment area** = 300 ft x 100 ft width x 20 ft depth
Groundwater seepage velocity = 300 ft/yr	**Groundwater seepage velocity** = 300 ft/yr
Porosity = 0.3	**Porosity** = 0.3
Number of PRBs = 2; • source PRB = 50 ft length; • downgradient PRB = 300 ft length	**Number of injection events** = 3
Volume of groundwater treated = 1.4 x 10^7 gallons	**Total treatment volume** = 4.5 x 10^6 gallons **Volume of groundwater treated** = 1.4 x 10^6 gallons
Pore volumes treated = 10	**Pore volumes treated** = 1
Unit costs: • $400/ft installation + 50% for design and reporting • $40,000 annual O&M	**Unit costs:** • $125 per cubic yard of treatment volume • Unit cost includes costs associated with all injection events
Total Cost = $610,000	**Total Cost = $2,780,000**
Cost per 1000 gallons of groundwater treated = $45	**Cost per 1000 gallons of groundwater treated = $2000**

Table 3b: Cost Comparison for Catalysis vs. Competing Technologies for Dioxane Remediation – Scenario 2

Conventional ISCO	Catalyst-Supplemented ISCO
Treatment area = 300 ft x 100 ft width x 20 ft depth	**Treatment area** = 300 ft x 100 ft width
Groundwater seepage velocity = 300 ft/yr	**Groundwater seepage velocity** = 300 ft/yr
Porosity = 0.3	**Porosity** = 0.3
Number of injection events = 3	**Number of injection events** = 3
Total treatment volume = 4.5 x 10^6 gallons	**Total treatment volume** = 4.5 x 10^6 gallons
Volume of groundwater treated = 1.4 x 10^6 gallons	**Volume of groundwater treated** = 1.4 x 10^6 gallons
Pore volumes treated = 1	**Pore volumes treated** = 1
Unit costs: • $125 per cubic yard of treatment volume • Unit cost includes costs associated with all injection events	**Unit costs:** • $125 per cubic yard of treatment volume **Adjustment to material costs (relative to baseline)** = decrease of 47,000 lb of H_2O_2 + 1640 lb of catalyst = $3500
Total Cost = $2,780,000	**Total Cost = $2,777,000**
Cost per 1000 gallons of groundwater treated = $2000	**Cost per 1000 gallons of groundwater treated = $2000**

The results of the cost evaluation for Scenario 1 indicate that the catalyst-based PRB approach would achieve significant cost savings relative to the established technology of injection-based ISCO. This is due primarily to two factors: (1) material costs for the catalyst are low and would not significantly increase costs related to PRB installation; (2) PRB designs are often more cost-efficient than injection-based designs at large sites with reasonably high groundwater flow rates. In particular, the generic site characteristics selected for this evaluation were likely more favorable for a cost-efficient PRB design than those reported by Davie et al. (2008). However, we feel that the assumptions made for the current evaluation are representative of a “typical” site and thus are valuable for comparing to ISCO. As noted above, expressing the cost per 1000 gallons treated” provides additional insight, but it should be understood that PRB has a distinct advantage in that higher volumes are treated over the project lifetime.

The results of the cost evaluation for Scenario 2 indicate that the catalyst-supplemented ISCO approach would achieve very modest cost savings relative to conventional ISCO. This is due primarily to the fact that material costs do not represent a significant cost driver for the model developed for this evaluation. Most of the costs associated with ISCO are related to engineering (both design and reporting), equipment, and labor during field implementation. However, it is possible that more significant savings would be achieved for larger projects with correspondingly higher material costs. In addition, the costs associated with shipping materials were not included in this model. Given the quantities of H_2O_2 that are typically used (several tons or more), reducing the H_2O_2 required for effective dioxane degradation could represent a significant cost savings.

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W.W. McNab, R. Ruiz and M. Reinhard (2000). In-situ destruction of chlorinated hydrocarbons in groundwater using catalytic reductive dehalogenation in a reactive well: Testing and operational experiences. Environ. Sci. Technol., 34: 149-153.

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APPENDIX A.2

Results of Field Investigation

1. Location Maps for Facility 1381 and SLC-16

2. MIP-HPT Logs for Facility 1381 and SLC 16

3. Soil and Groundwater Analytical Data for Facility 1381 and SLC-16

4. Boring Logs for Facility 1381 and SLC-16

N

LEGEND

● Sample location

PRELIMINARY

Notes

Background Imagery: Area extracted from GoogleEarth Pro, dated February 13, 2016. Resolution: Current (1662 x 1074).

Feet
0 50 100

Projected Coordinate System
Datum: NAD 1983
UTM: Zone 17N (m)

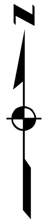
GSI
ENVIRONMENTAL

SITE 1381

Cape Canaveral AFS, Cape Canaveral, Florida

GSI Job No.	G-3926	Drawn By:	CDM
Issued:	21-Apr-2016	Chk'd By:	JAL
Map ID:	**001_02**	Appv'd By:	

FIGURE 2



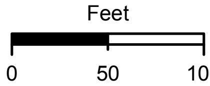
LEGEND

● Sample location

PRELIMINARY

Notes

Background Imagery: Area extracted from GoogleEarth Pro, dated February 13, 2016. Resolution: Current (1662 x 1074).



Projected Coordinate System
Datum: NAD 1983
UTM: Zone 17N (m)

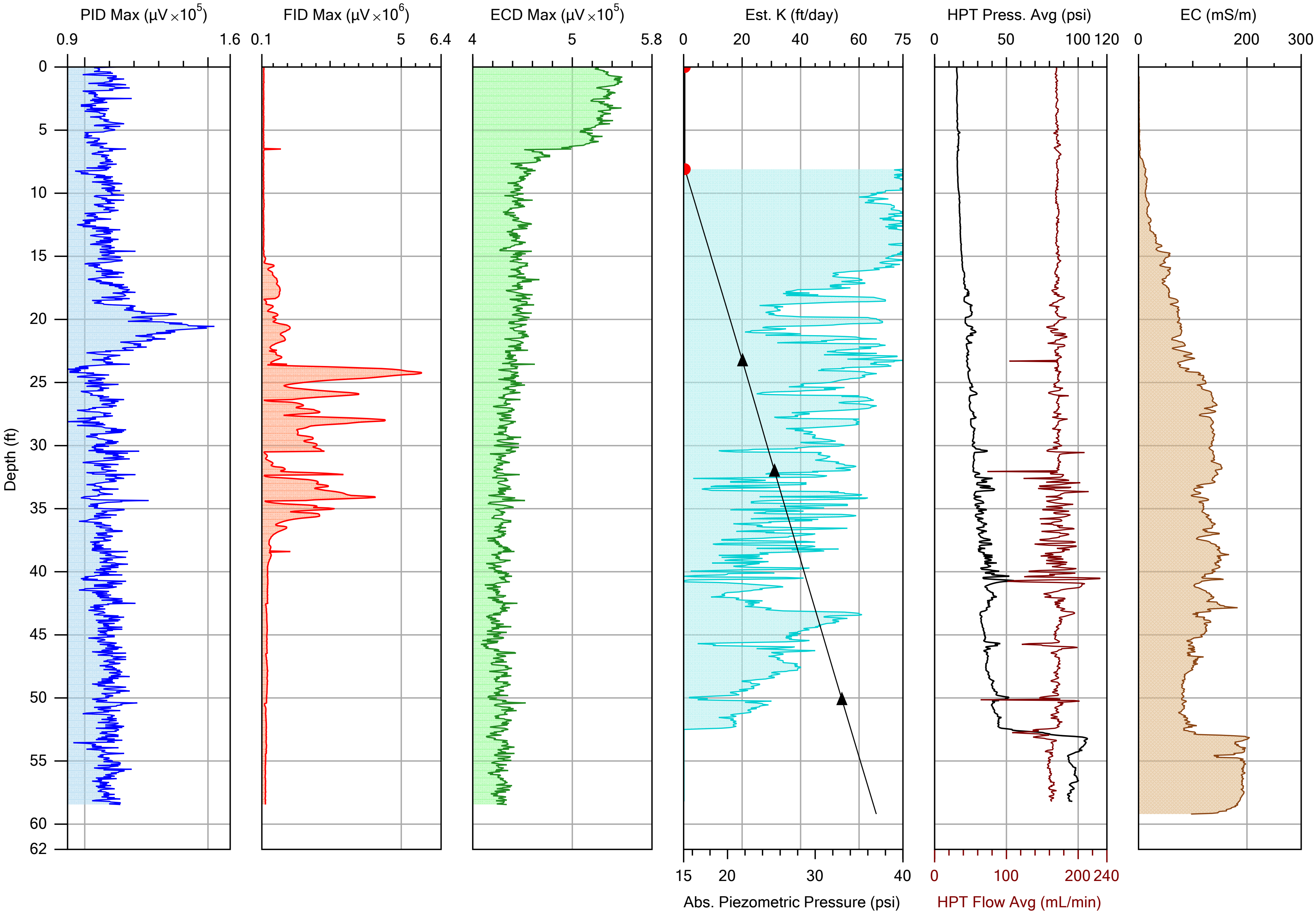
GSI
ENVIRONMENTAL

SITE SLC16

Cape Canaveral AFS, Cape Canaveral, Florida

GSI Job No.	G-3926	Drawn By:	CDM
Issued:	21-Apr-2016	Chk'd By:	JAL
Map ID:	**001_01**	Appv'd By:	

FIGURE 1



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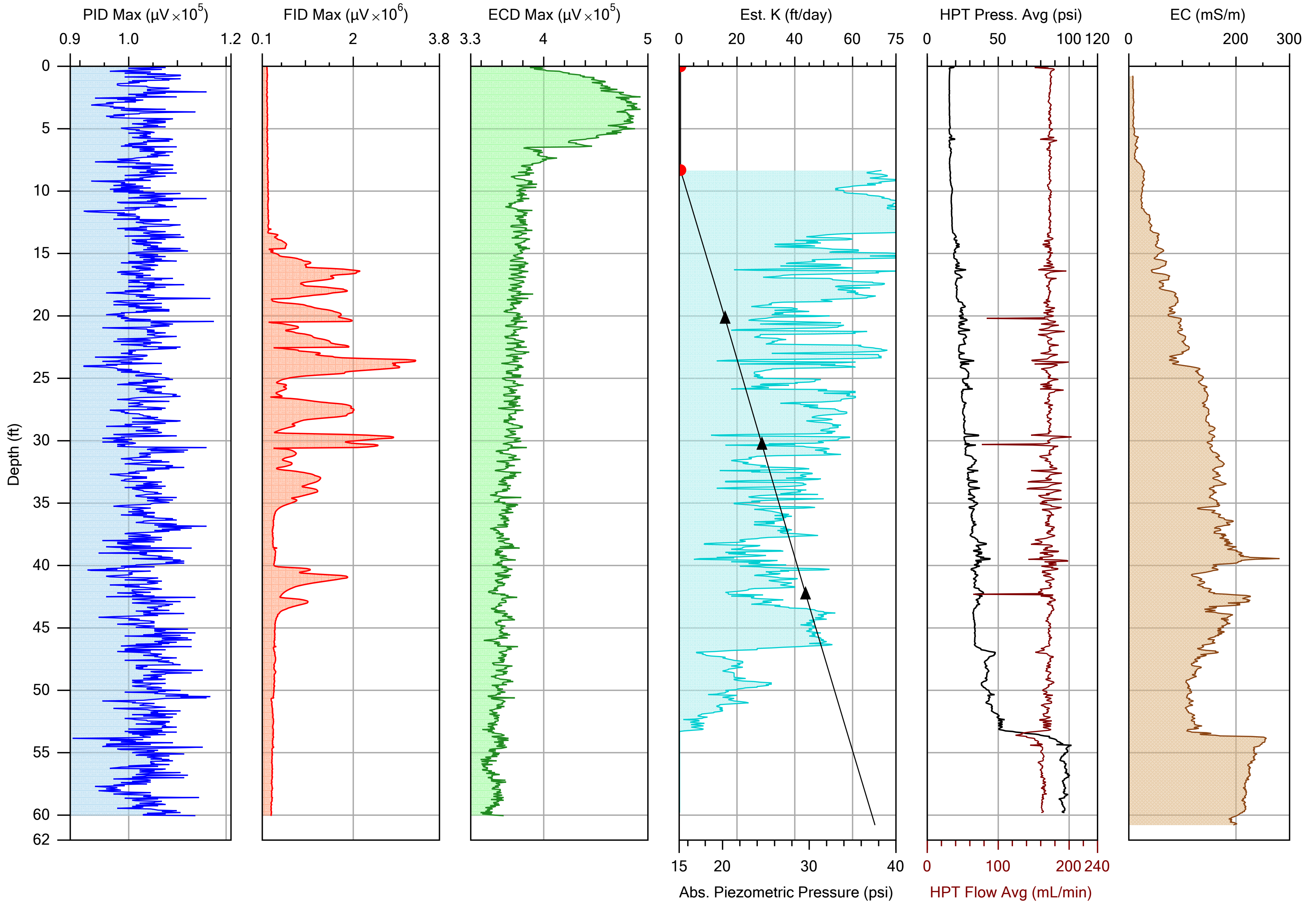

COLUMBIA TECHNOLOGIES

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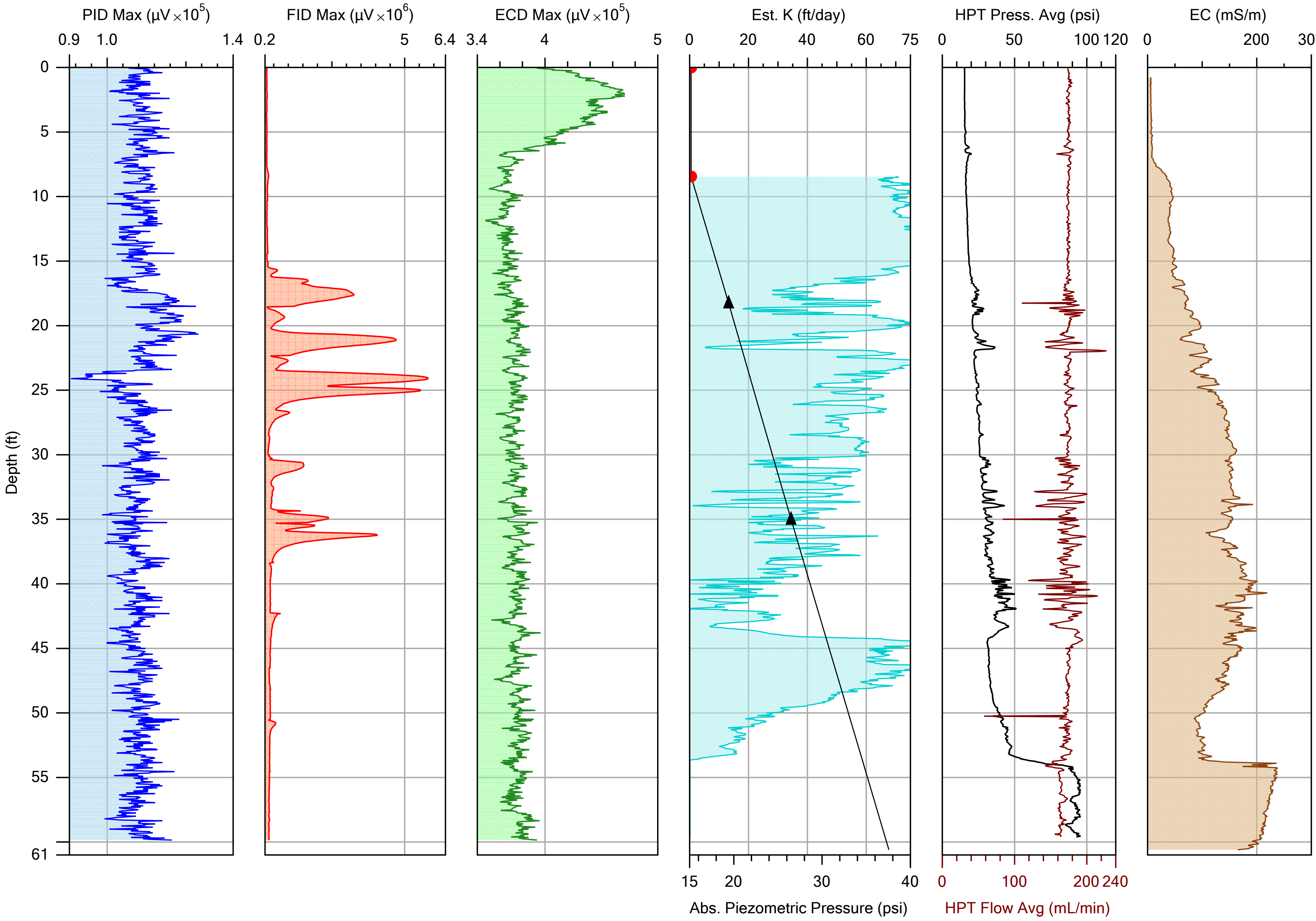

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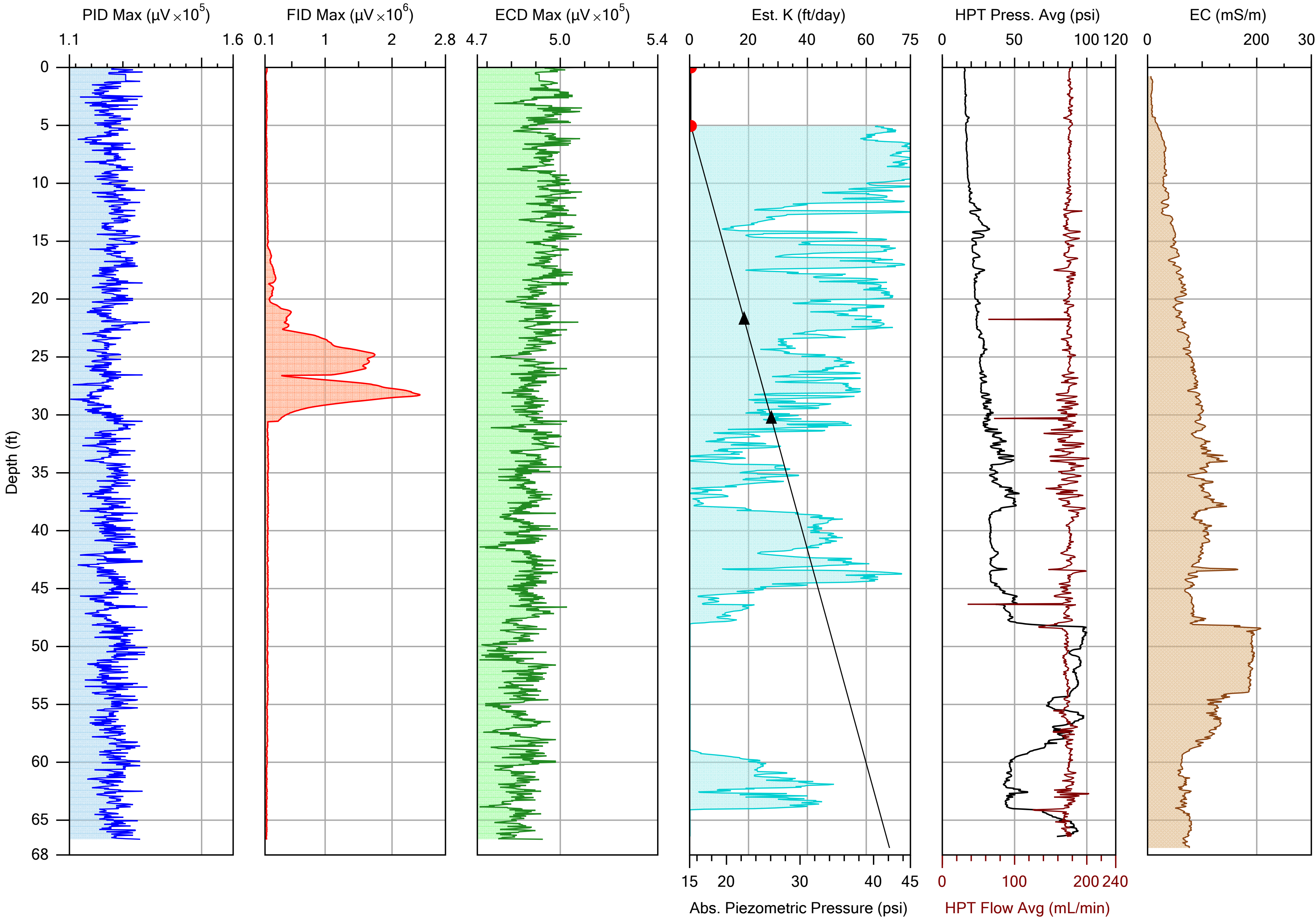

COLUMBIA TECHNOLOGIES

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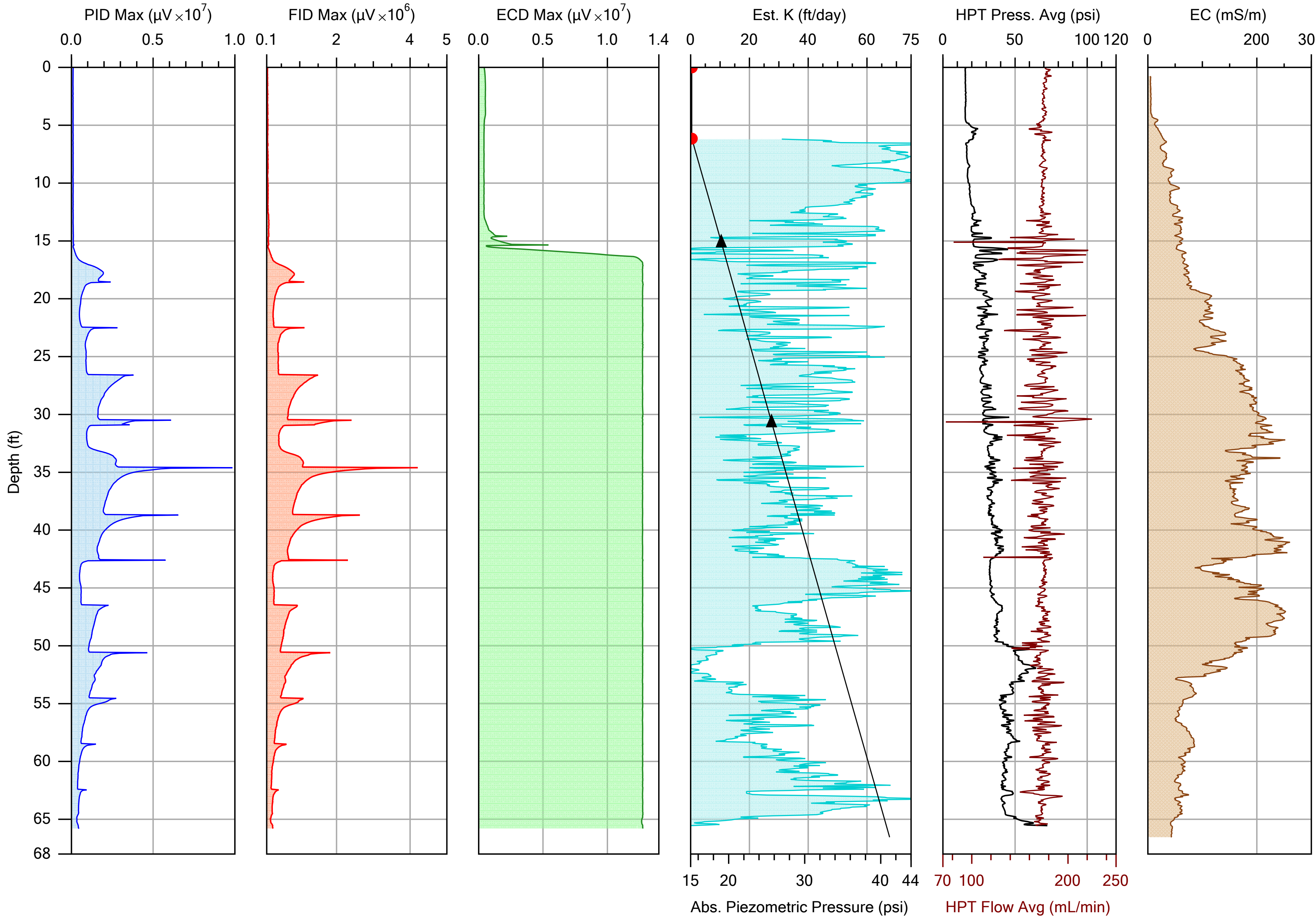

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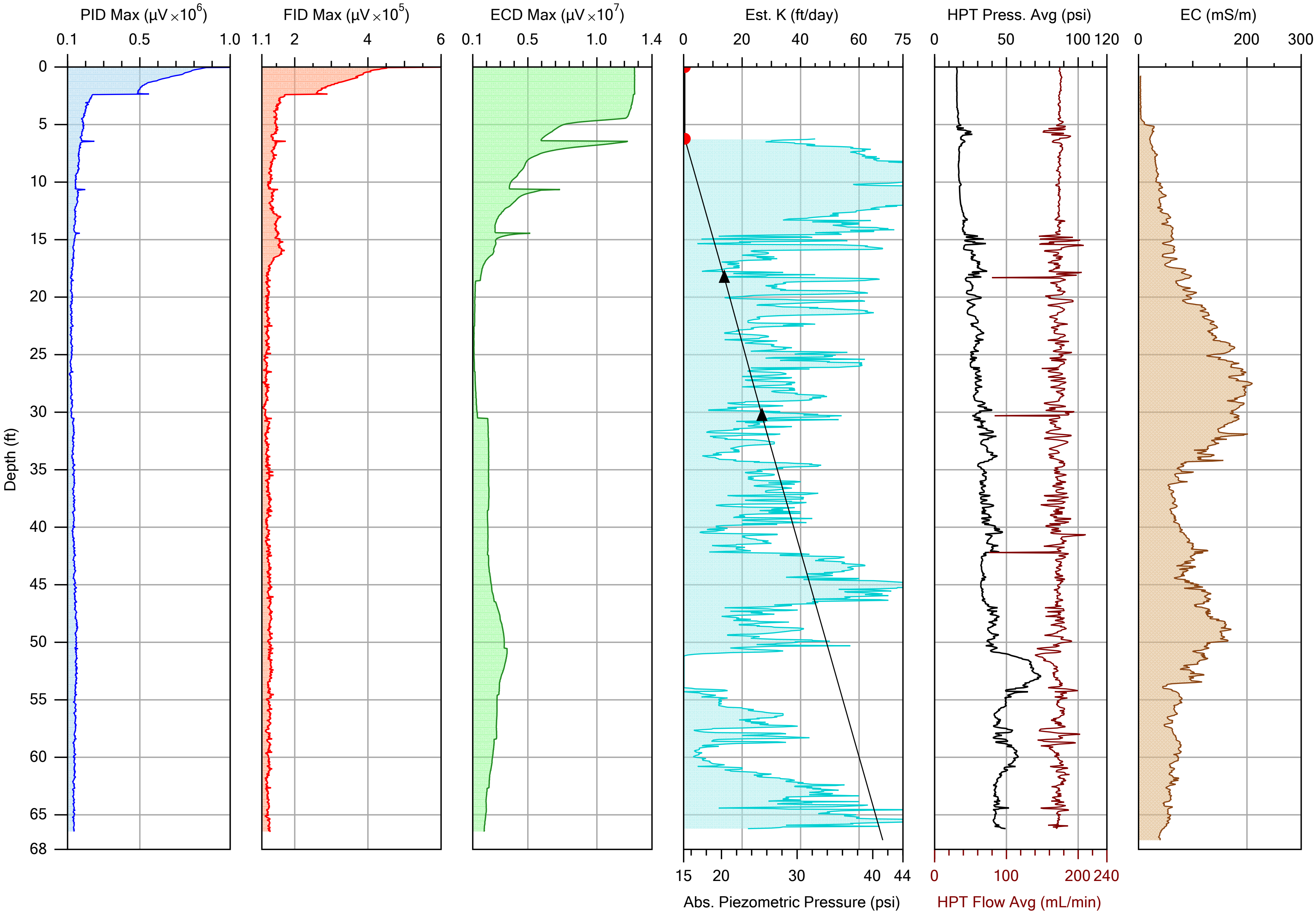
Project ID:	Client:	Location:



COLUMBIA TECHNOLOGIES

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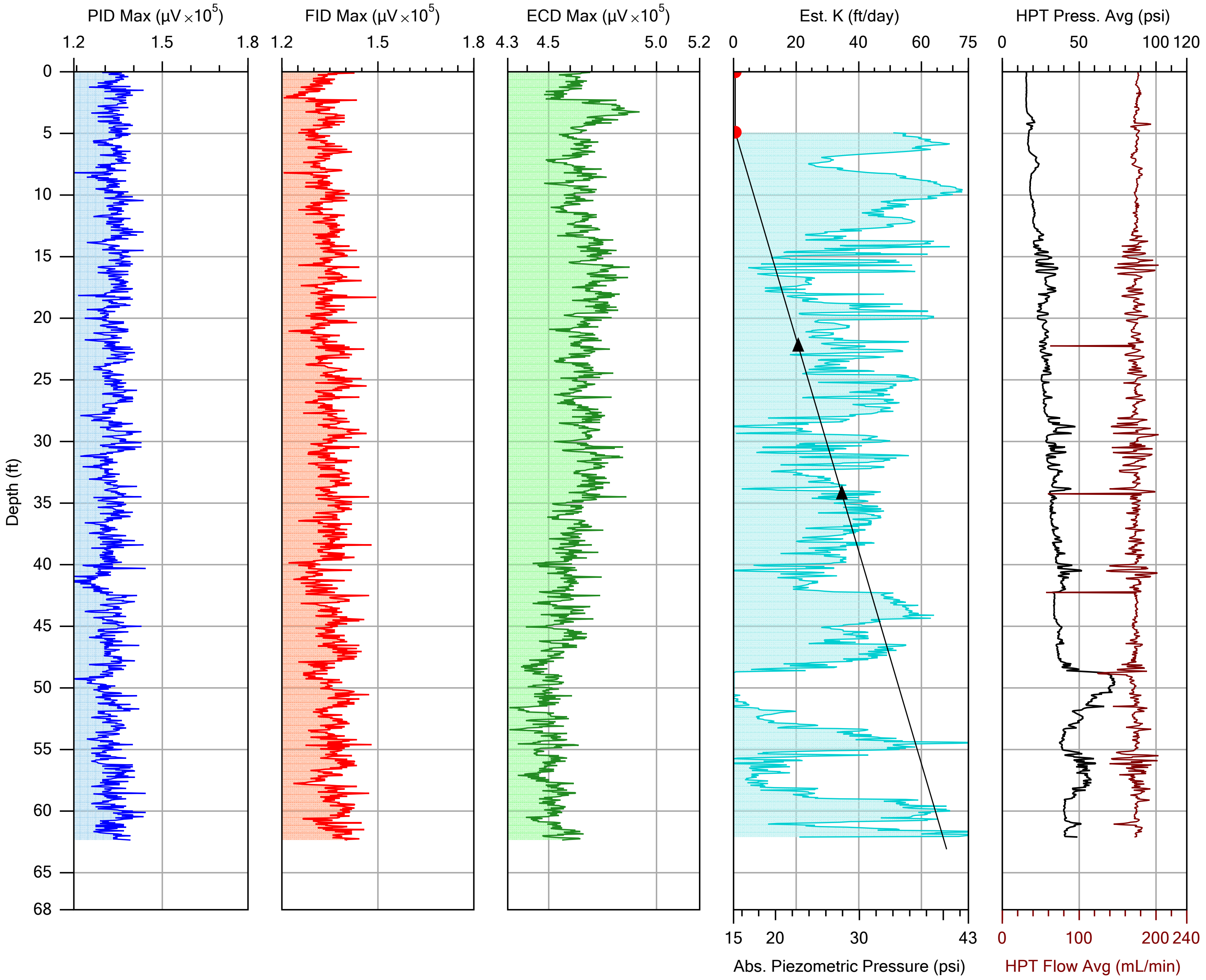

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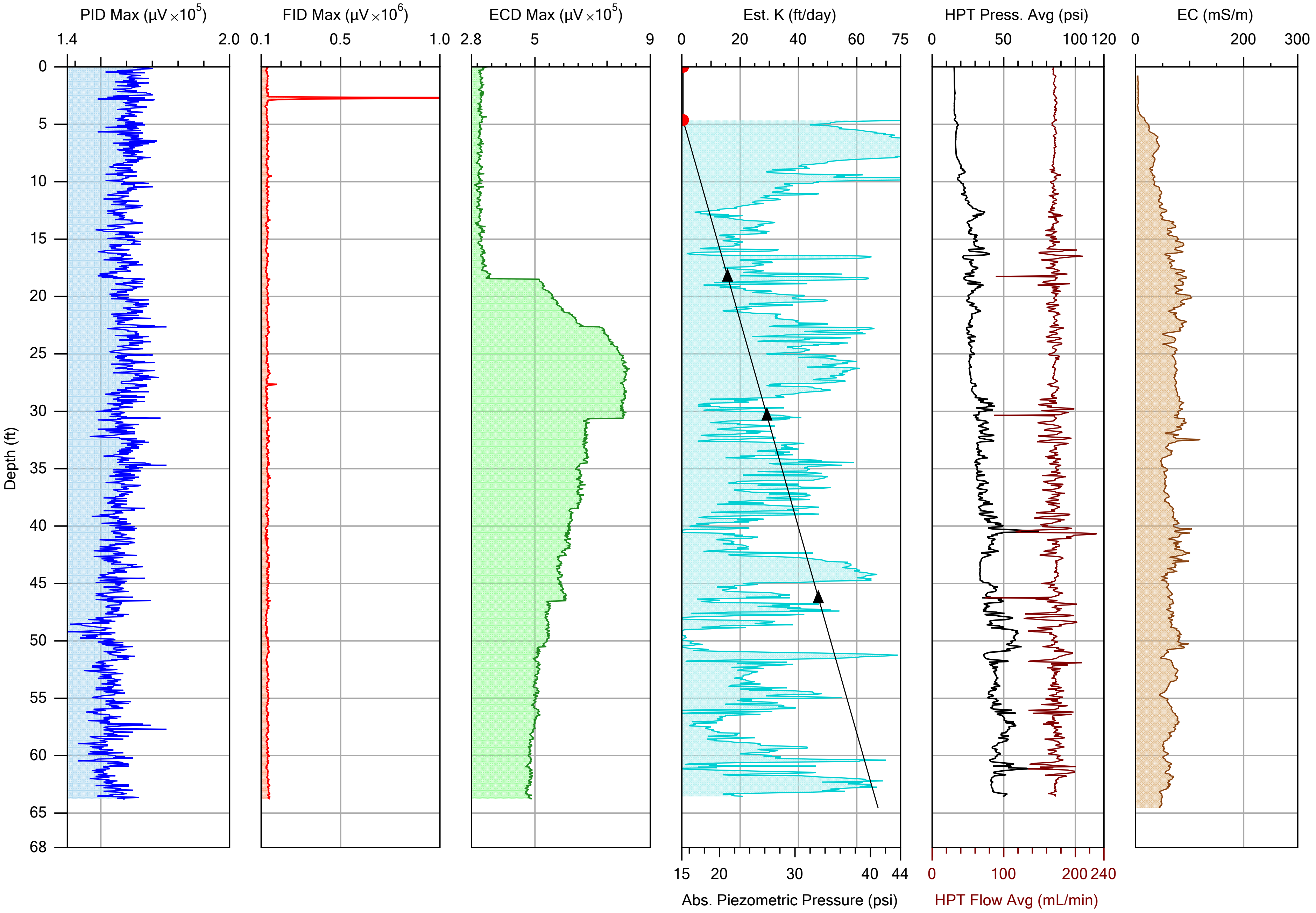

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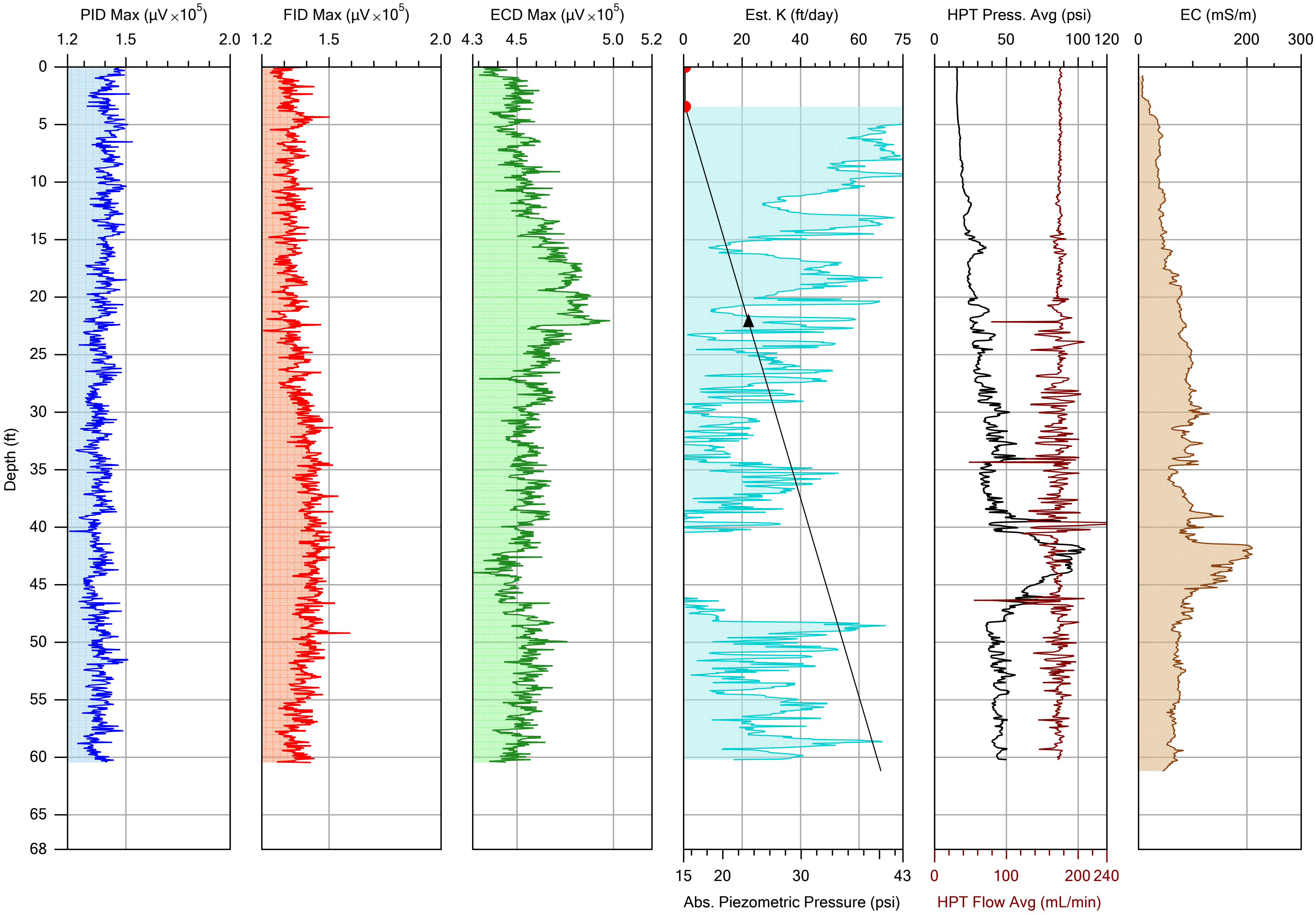

COLUMBIA
TECHNOLOGIES

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Project ID: Cape Canaveral AFS: SERP Field Study	Client: GSI Environmental	Location:

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB1	1381-SB1	1381-SB1	1381-SB1	1381-SB1
SAMPLE ID:		1381-SB1 38FT	1381-SB1 40FT	1381-SB1 43FT	1381-SB1 51FT	1381-SB1 52FT
SAMPLE DEPTH:		38 FT	40 FT	43 FT	51 FT	52 FT
PERMIABILITY ZONE:		High k	Low k	High k	High k	Low k
SAMPLE DATE:		05/12/2016	05/12/2016	05/12/2016	05/12/2016	05/12/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00286	<0.002	<0.002	<0.00265	<0.00356
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Bromoform	75-25-2	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Bromomethane	74-83-9	<0.00714	<0.005	<0.005	<0.00665	<0.0089
Carbon tetrachloride	56-23-5	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Chlorobenzene	108-90-7	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Chlorodibromomethane	124-48-1	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Chloroethane	75-00-3	<0.00714	<0.005	<0.005	<0.00665	<0.0089
2-Chloroethyl vinyl ether	110-75-8	<0.0714 J3	<0.05	<0.05	<0.0665	<0.089
Chloroform	67-66-3	<0.00714	<0.005	<0.005	<0.00665	<0.0089
Chloromethane	74-87-3	<0.00357	<0.0025	<0.0025	<0.00333	<0.00445
1,2-Dichlorobenzene	95-50-1	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,3-Dichlorobenzene	541-73-1	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,4-Dichlorobenzene	106-46-7	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Dichlorodifluoromethane	75-71-8	<0.00714	<0.005	<0.005	<0.00665	<0.0089
1,1-Dichloroethane	75-34-3	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,2-Dichloroethane	107-06-2	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,1-Dichloroethene	75-35-4	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Cis-1,2-dichloroethene	156-59-2	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Trans-1,2-dichloroethene	156-60-5	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,2-Dichloropropane	78-87-5	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Cis-1,3-dichloropropene	10061-01-5	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Trans-1,3-dichloropropene	10061-02-6	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Methylene chloride	75-09-2	<0.00714	<0.005	<0.005	<0.00665	<0.0089
1,1,2,2-Tetrachloroethane	79-34-5	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Tetrachloroethene	127-18-4	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,1,1-Trichloroethane	71-55-6	<0.00143	<0.001	<0.001	<0.00133	<0.00178
1,1,2-Trichloroethane	79-00-5	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Trichloroethene	79-01-6	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Trichlorofluoromethane	75-69-4	<0.00714	<0.005	<0.005	<0.00665	<0.0089
Vinyl chloride	75-01-4	<0.00143	<0.001	<0.001	<0.00133	<0.00178
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00553**	--	--	**0.00812**	**0.0156**
Fractional organic matter, %	--	**0.953**	--	--	**1.4**	**2.68**
Total Solids by Method 2540 G-2011						
Total solids	--	**70**	--	--	**75.2**	**56.2**

Notes:

1. Detections are shown in **bold**.
2. < = Constituent not detected at specified Sample Quantitation Limit.
   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB1	1381-SB1	1381-SB1	1381-SB1	1381-SB1
SAMPLE ID:		1381-SB1 52.7FT	1381-SB1 53.5FT	1381-SB1 54.3FT	1381-SB1 56FT	1381-SB1 57FT
SAMPLE DEPTH:		52.7 FT	53.5 FT	54.3 FT	56 FT	57 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/12/2016	05/12/2016	05/12/2016	05/12/2016	05/12/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.002	<0.0035	<0.002	<0.00369	<0.002
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.00175	<0.001	<0.00185	<0.001
Bromoform	75-25-2	<0.001	<0.00175	<0.001	<0.00185	<0.001
Bromomethane	74-83-9	<0.005	<0.00873	<0.005	<0.00923	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.00175	<0.001	<0.00185	<0.001
Chlorobenzene	108-90-7	<0.001	<0.00175	<0.001	<0.00185	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.00175	<0.001	<0.00185	<0.001
Chloroethane	75-00-3	<0.005	<0.00873	<0.005	<0.00923	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.0873	<0.05	<0.0923	<0.05
Chloroform	67-66-3	<0.005	<0.00873	<0.005	<0.00923	<0.005
Chloromethane	74-87-3	<0.0025	<0.00437	<0.0025	<0.00461	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.00175	<0.001	<0.00185	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.00873	<0.005	<0.00923	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.00175	<0.001	<0.00185	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.00175	<0.001	**0.000791 J**	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.00175	<0.001	<0.00185	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.00175	<0.001	<0.00185	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.00175	<0.001	<0.00185	<0.001
Methylene chloride	75-09-2	<0.005	<0.00873	<0.005	<0.00923	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.00175	<0.001	<0.00185	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.00175	<0.001	<0.00185	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.00175	<0.001	<0.00185	<0.001
Trichloroethene	79-01-6	<0.001	<0.00175	<0.001	<0.00185	<0.001
Trichlorofluoromethane	75-69-4	<0.005	<0.00873	<0.005	<0.00923	<0.005
Vinyl chloride	75-01-4	<0.001	<0.00175	<0.001	**0.00468**	**0.000782 J**
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	--	**0.018**	--	**0.0155**	--
Fractional organic matter, %	--	--	**3.1**	--	**2.67**	--
Total Solids by Method 2540 G-2011						
Total solids	--	--	**57.2**	--	**54.2**	--

Notes:
1. Detections are shown in **bold**.
2. < = Constituent not detected at specified Sample Quantitation Limit.
   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB2	1381-SB2	1381-SB2	1381-SB2	1381-SB2
SAMPLE ID:		1381-SB2 37.5FT	1381-SB2 40FT	1381-SB2 41FT	1381-SB2 51FT	1381-SB2 52FT
SAMPLE DEPTH:		37.5 FT	40 FT	41 FT	51 FT	52 FT
PERMIABILITY ZONE:		High k	Low k	High k	High k	Low k
SAMPLE DATE:		05/12/2016	05/12/2016	05/12/2016	05/12/2016	05/12/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00266	<0.002	<0.00251	<0.002	<0.00353
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Bromoform	75-25-2	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Bromomethane	74-83-9	<0.00665	<0.005	<0.00627	<0.005	<0.00883
Carbon tetrachloride	56-23-5	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Chlorobenzene	108-90-7	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Chlorodibromomethane	124-48-1	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Chloroethane	75-00-3	<0.00665	<0.005	<0.00627	<0.005	<0.00883
2-Chloroethyl vinyl ether	110-75-8	<0.0665	<0.05	<0.0627	<0.05	<0.0883
Chloroform	67-66-3	<0.00665	<0.005	<0.00627	<0.005	<0.00883
Chloromethane	74-87-3	<0.00333	<0.0025	<0.00314	<0.0025	<0.00442
1,2-Dichlorobenzene	95-50-1	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,3-Dichlorobenzene	541-73-1	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,4-Dichlorobenzene	106-46-7	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Dichlorodifluoromethane	75-71-8	<0.00665	<0.005	<0.00627	<0.005	<0.00883
1,1-Dichloroethane	75-34-3	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,2-Dichloroethane	107-06-2	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,1-Dichloroethene	75-35-4	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Cis-1,2-dichloroethene	156-59-2	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Trans-1,2-dichloroethene	156-60-5	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,2-Dichloropropane	78-87-5	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Cis-1,3-dichloropropene	10061-01-5	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Trans-1,3-dichloropropene	10061-02-6	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Methylene chloride	75-09-2	<0.00665	<0.005	<0.00627	<0.005	<0.00883
1,1,2,2-Tetrachloroethane	79-34-5	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Tetrachloroethene	127-18-4	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,1,1-Trichloroethane	71-55-6	<0.00133	<0.001	<0.00125	<0.001	<0.00177
1,1,2-Trichloroethane	79-00-5	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Trichloroethene	79-01-6	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Trichlorofluoromethane	75-69-4	<0.00665	<0.005	<0.00627	<0.005	<0.00883
Vinyl chloride	75-01-4	<0.00133	<0.001	<0.00125	<0.001	<0.00177
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00507**	--	**0.00509**	--	**0.0121**
Fractional organic matter, %	--	**0.874**	--	**0.878**	--	**2.09**
Total Solids by Method 2540 G-2011						
Total solids	--	**75.2**	--	**79.7**	--	**56.6**

Notes:
1. Detections are shown in **bold**.
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   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB2	1381-SB2	1381-SB2	1381-SB2	1381-SB2
SAMPLE ID:		1381-SB2 52.7FT	1381-SB2 53.5FT	1381-SB2 54.3FT	1381-SB2 55.1FT	1381-SB2 56FT
SAMPLE DEPTH:		52.7 FT	53.5 FT	54.3 FT	55.1 FT	56 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/12/2016	05/12/2016	05/12/2016	05/12/2016	05/12/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.002	<0.0035	<0.002	<0.00352	<0.002
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.00175	<0.001	<0.00176	<0.001
Bromoform	75-25-2	<0.001	<0.00175	<0.001	<0.00176	<0.001
Bromomethane	74-83-9	<0.005	<0.00874	<0.005	<0.0088	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.00175	<0.001	<0.00176	<0.001
Chlorobenzene	108-90-7	<0.001	<0.00175	<0.001	<0.00176	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.00175	<0.001	<0.00176	<0.001
Chloroethane	75-00-3	<0.005	<0.00874	<0.005	<0.0088	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.0874	<0.05	<0.088	<0.05
Chloroform	67-66-3	<0.005	<0.00874	<0.005	<0.0088	<0.005
Chloromethane	74-87-3	<0.0025	<0.00437	<0.0025	<0.0044	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.00175	<0.001	<0.00176	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.00874	<0.005	<0.0088	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.00175	<0.001	<0.00176	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.00175	<0.001	<0.00176	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.00175	<0.001	<0.00176	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.00175	<0.001	<0.00176	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.00175	<0.001	<0.00176	<0.001
Methylene chloride	75-09-2	<0.005	<0.00874	<0.005	<0.0088	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.00175	<0.001	<0.00176	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.00175	<0.001	<0.00176	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.00175	<0.001	<0.00176	<0.001
Trichloroethene	79-01-6	<0.001	<0.00175	<0.001	<0.00176	<0.001
Trichlorofluoromethane	75-69-4	<0.005	<0.00874	<0.005	<0.0088	<0.005
Vinyl chloride	75-01-4	<0.001	<0.00175	<0.001	<0.00176	<0.001
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	--	**0.0195**	--	**0.0194**	--
Fractional organic matter, %	--	--	**3.36**	--	**3.34**	--
Total Solids by Method 2540 G-2011						
Total solids	--	--	**57.2**	--	**56.8**	--

Notes:
1. Detections are shown in **bold**.
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   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J3 = The associated batch QC was outside the established quality control range for precision.
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   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB3	1381-SB3	1381-SB3	1381-SB3	1381-SB3
SAMPLE ID:		1381-SB3 34 FT	1381-SB3 41 FT	1381-SB3 46 FT	1381-SB3 50 FT	1381-SB3 52 FT
SAMPLE DEPTH:		34 FT	41 FT	46 FT	50 FT	52 FT
PERMIABILITY ZONE:		High k	High k	High k	Low k	Low k
SAMPLE DATE:		05/13/2016	05/13/2016	05/13/2016	05/13/2016	05/13/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00255 J3	<0.002	<0.00275	<0.002	<0.00282
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Bromoform	75-25-2	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Bromomethane	74-83-9	<0.00639	<0.005	<0.00686	<0.005	<0.00704
Carbon tetrachloride	56-23-5	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Chlorobenzene	108-90-7	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Chlorodibromomethane	124-48-1	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Chloroethane	75-00-3	<0.00639	<0.005	<0.00686	<0.005	<0.00704
2-Chloroethyl vinyl ether	110-75-8	<0.0639	<0.05	<0.0686	<0.05	<0.0704
Chloroform	67-66-3	<0.00639	<0.005	<0.00686	<0.005	<0.00704
Chloromethane	74-87-3	<0.00319	<0.0025	<0.00343	<0.0025	<0.00352
1,2-Dichlorobenzene	95-50-1	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,3-Dichlorobenzene	541-73-1	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,4-Dichlorobenzene	106-46-7	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Dichlorodifluoromethane	75-71-8	<0.00639	<0.005	<0.00686	<0.005	<0.00704
1,1-Dichloroethane	75-34-3	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,2-Dichloroethane	107-06-2	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,1-Dichloroethene	75-35-4	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Cis-1,2-dichloroethene	156-59-2	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Trans-1,2-dichloroethene	156-60-5	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,2-Dichloropropane	78-87-5	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Cis-1,3-dichloropropene	10061-01-5	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Trans-1,3-dichloropropene	10061-02-6	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Methylene chloride	75-09-2	<0.00639	<0.005	<0.00686	<0.005	<0.00704
1,1,2,2-Tetrachloroethane	79-34-5	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Tetrachloroethene	127-18-4	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,1,1-Trichloroethane	71-55-6	<0.00128	<0.001	<0.00137	<0.001	<0.00141
1,1,2-Trichloroethane	79-00-5	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Trichloroethene	79-01-6	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Trichlorofluoromethane	75-69-4	<0.00639	<0.005	<0.00686	<0.005	<0.00704
Vinyl chloride	75-01-4	<0.00128	<0.001	<0.00137	<0.001	<0.00141
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00332**	--	**0.00801**	--	**0.00929**
Fractional organic matter, %	--	**0.572**	--	**1.38**	--	**1.6**
Total Solids by Method 2540 G-2011						
Total solids	--	**78.3**	--	**72.8**	--	**71**

Notes:
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   J3 = The associated batch QC was outside the established quality control range for precision.
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   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB3	1381-SB3	1381-SB3	1381-SB3	1381-SB3
SAMPLE ID:		1381-SB3 52.5 FT	1381-SB3 53 FT	1381-SB3 56.3 FT	1381-SB3 57.1 FT	1381-SB3 58 FT
SAMPLE DEPTH:		52.5 FT	53 FT	56.3 FT	57.1 FT	58 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/13/2016	05/13/2016	05/13/2016	05/13/2016	05/13/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.002	<0.00348	<0.002	<0.00375	<0.002
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.00174	<0.001	<0.00195	<0.001
Bromoform	75-25-2	<0.001	<0.00174	<0.001	<0.00195	<0.001
Bromomethane	74-83-9	<0.005	<0.00872	<0.005	<0.00973	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.00174	<0.001	<0.00195	<0.001
Chlorobenzene	108-90-7	<0.001	<0.00174	<0.001	<0.00195	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.00174	<0.001	<0.00195	<0.001
Chloroethane	75-00-3	<0.005	<0.00872	<0.005	<0.00973	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.0872	<0.05	<0.0973	<0.05
Chloroform	67-66-3	<0.005	<0.00872	<0.005	<0.00973	<0.005
Chloromethane	74-87-3	<0.0025	<0.00436	<0.0025	<0.00487	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.00174	<0.001	<0.00195	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.00872	<0.005	<0.00973	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.00174	<0.001	<0.00195	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.00174	<0.001	<0.00195	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.00174	<0.001	<0.00195	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.00174	<0.001	<0.00195	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.00174	<0.001	<0.00195	<0.001
Methylene chloride	75-09-2	<0.005	<0.00872	<0.005	<0.00973	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.00174	<0.001	<0.00195	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.00174	<0.001	<0.00195	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.00174	<0.001	<0.00195	<0.001
Trichloroethene	79-01-6	<0.001	<0.00174	<0.001	<0.00195	<0.001
Trichlorofluoromethane	75-69-4	<0.005	<0.00872	<0.005	<0.00973	<0.005
Vinyl chloride	75-01-4	<0.001	<0.00174	<0.001	<0.00195	<0.001
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	--	**0.0155**	--	**0.0146**	--
Fractional organic matter, %	--	--	**2.67**	--	**2.51**	--
Total Solids by Method 2540 G-2011						
Total solids	--	--	**57.4**	--	**53.4**	--

Notes:
1. Detections are shown in **bold**.
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   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB4	1381-SB4	1381-SB4	1381-SB4	1381-SB4
SAMPLE ID:		1381-SB4 42.2 FT	1381-SB4 42.8 FT	1381-SB4 44.5 FT	1381-SB4 53 FT	1381-SB4 54 FT
SAMPLE DEPTH:		42.2 FT	42.8 FT	44.5 FT	53 FT	54 FT
PERMIABILITY ZONE:		High k	Low k	High k	Low k	Low k
SAMPLE DATE:		05/13/2016	05/13/2016	05/13/2016	05/13/2016	05/13/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	**0.000753 J**	<0.002	<0.0026	**0.00795**	<0.00353
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Bromoform	75-25-2	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Bromomethane	74-83-9	<0.00714	<0.005	<0.0065	<0.005	<0.00884
Carbon tetrachloride	56-23-5	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J6
Chlorobenzene	108-90-7	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Chlorodibromomethane	124-48-1	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Chloroethane	75-00-3	<0.00714	<0.005	<0.0065	<0.005	<0.00884
2-Chloroethyl vinyl ether	110-75-8	<0.0714	<0.05	<0.065	<0.05	<0.0884 J3 J6
Chloroform	67-66-3	<0.00714	<0.005	<0.0065	<0.005	<0.00884 J3 J6
Chloromethane	74-87-3	<0.00357	<0.0025	<0.00325	<0.0025	<0.00442 J6
1,2-Dichlorobenzene	95-50-1	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,3-Dichlorobenzene	541-73-1	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,4-Dichlorobenzene	106-46-7	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Dichlorodifluoromethane	75-71-8	<0.00714	<0.005	<0.0065	<0.005	<0.00884 J3 J6
1,1-Dichloroethane	75-34-3	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,2-Dichloroethane	107-06-2	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,1-Dichloroethene	75-35-4	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J6
Cis-1,2-dichloroethene	156-59-2	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Trans-1,2-dichloroethene	156-60-5	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,2-Dichloropropane	78-87-5	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Cis-1,3-dichloropropene	10061-01-5	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Trans-1,3-dichloropropene	10061-02-6	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Methylene chloride	75-09-2	<0.00714	<0.005	<0.0065	<0.005	<0.00884 J3 J6
1,1,2,2-Tetrachloroethane	79-34-5	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Tetrachloroethene	127-18-4	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,1,1-Trichloroethane	71-55-6	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
1,1,2-Trichloroethane	79-00-5	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Trichloroethene	79-01-6	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J3 J6
Trichlorofluoromethane	75-69-4	<0.00714	<0.005	<0.0065	<0.005	<0.00884 J3 J6
Vinyl chloride	75-01-4	<0.00143	<0.001	<0.0013	<0.001	<0.00177 J6
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00737**	--	**0.00607**	--	**0.0169**
Fractional organic matter, %	--	**1.27**	--	**1.05**	--	**2.92**
Total Solids by Method 2540 G-2011						
Total solids	--	**70.1**	--	**76.9**	--	**56.6**

Notes:
1. Detections are shown in **bold**.
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   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB4	1381-SB4	1381-SB4	1381-SB4	1381-SB4
SAMPLE ID:		1381-SB4 54.7 FT	1381-SB4 55.5 FT	1381-SB4 56.3 FT	1381-SB4 57.1 FT	1381-SB4 58 FT
SAMPLE DEPTH:		54.7 FT	55.5 FT	56.3 FT	57.1 FT	58 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/13/2016	05/13/2016	05/13/2016	05/13/2016	05/13/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.002	<0.00275	<0.002	<0.00249	<0.002
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.00137	<0.001	<0.00125	<0.001
Bromoform	75-25-2	<0.001	<0.00137	<0.001	<0.00125	<0.001
Bromomethane	74-83-9	<0.005	<0.00686	<0.005	<0.00624	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.00137	<0.001	<0.00125	<0.001
Chlorobenzene	108-90-7	<0.001	<0.00137	<0.001	<0.00125	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.00137	<0.001	<0.00125	<0.001
Chloroethane	75-00-3	<0.005	<0.00686	<0.005	<0.00624	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.0686	<0.05	<0.0624	<0.05
Chloroform	67-66-3	<0.005	<0.00686	<0.005	<0.00624	<0.005
Chloromethane	74-87-3	<0.0025	<0.00343	<0.0025	<0.00312	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.00137	<0.001	<0.00125	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.00686	<0.005	<0.00624	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.00137	<0.001	<0.00125	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.00137	<0.001	<0.00125	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.00137	<0.001	<0.00125	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.00137	<0.001	<0.00125	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.00137	<0.001	<0.00125	<0.001
Methylene chloride	75-09-2	<0.005	<0.00686	<0.005	<0.00624	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.00137	<0.001	<0.00125	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.00137	<0.001	<0.00125	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.00137	<0.001	<0.00125	<0.001
Trichloroethene	79-01-6	<0.001	<0.00137	<0.001	<0.00125	<0.001
Trichlorofluoromethane	75-69-4	<0.005	<0.00686	<0.005	<0.00624	<0.005
Vinyl chloride	75-01-4	<0.001	<0.00137	<0.001	<0.00125	<0.001
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	--	**0.00854**	--	**0.00365**	--
Fractional organic matter, %	--	--	**1.47**	--	**0.63**	--
Total Solids by Method 2540 G-2011						
Total solids	--	--	**72.8**	--	**80.2**	--

Notes:
1. Detections are shown in **bold**.
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TABLE 1
SOIL SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB4	1381-SB4
SAMPLE ID:		DUP1 42.8 FT	DUP2 56.3 FT
SAMPLE DEPTH:		42.8 FT	56.3 FT
PERMIABILITY ZONE:		Low k	Low k
SAMPLE DATE:		05/13/2016	05/13/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM			
1,4-Dioxane	123-91-1	<0.002	<0.002
Volatile Organic Compounds by Method 8260B			
Bromodichloromethane	75-27-4	<0.001	<0.001
Bromoform	75-25-2	<0.001	<0.001
Bromomethane	74-83-9	<0.005	<0.005 J4
Carbon tetrachloride	56-23-5	<0.001	<0.001
Chlorobenzene	108-90-7	<0.001	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.001
Chloroethane	75-00-3	<0.005	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.05
Chloroform	67-66-3	<0.005	<0.005
Chloromethane	74-87-3	<0.0025	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.001
Methylene chloride	75-09-2	<0.005	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.001
Trichloroethene	79-01-6	<0.001	<0.001
Trichlorofluoromethane	75-69-4	<0.005	<0.005
Vinyl chloride	75-01-4	<0.001	<0.001
Fractional Organic Carbon by Method D2974			
Fractional organic carbon, g C/g soil	--	--	--
Fractional organic matter, %	--	--	--
Total Solids by Method 2540 G-2011			
Total solids	--	--	--

Notes:
1. Detections are shown in **bold**.
2. < = Constituent not detected at specified Sample Quantitation Limit.
   -- = Not analyzed or not applicable.
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TABLE 2
GROUNDWATER SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB1	1381-SB1	1381-SB1	1381-SB2	1381-SB2
SAMPLE ID:		1381-SB1 50-52FT	1381-SB1 52-54FT	1381-SB1 54-56FT	1381-SB2 50-52 FT	1381-SB2 52-54FT
SAMPLE DEPTH:		50-52 FT	52-54 FT	54-56 FT	50-52 FT	52-54 FT
PERMIABILITY ZONE:		High k	Low k	Low k	High k	Low k
SAMPLE DATE:		05/12/2016	5/20/2016	5/20/2016	5/13/2016	5/20/2016
ANALYTE	CAS No.	mg/L	mg/L	mg/L	mg/L	mg/L
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.003	<0.003	<0.003	<0.003	<0.003
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.001	<0.001	<0.001	<0.001
Bromoform	75-25-2	<0.001	<0.001	<0.001	<0.001	<0.001
Bromomethane	74-83-9	<0.005	<0.005	<0.005	<0.005	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorobenzene	108-90-7	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.001	<0.001	<0.001	<0.001
Chloroethane	75-00-3	<0.005	<0.005	<0.005	<0.005	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.05	<0.05	<0.05 J3 J4	<0.05
Chloroform	67-66-3	<0.005	<0.005	<0.005	<0.005	<0.005
Chloromethane	74-87-3	<0.0025 J3 J4	<0.0025	<0.0025	<0.0025	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.001	<0.001	<0.001	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.005	<0.005	<0.005	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.001	<0.001	<0.001	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.001	<0.001	<0.001	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.001	<0.001	<0.001	<0.001
Methylene chloride	75-09-2	<0.005	<0.005	<0.005	<0.005	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.001	<0.001	<0.001	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trichloroethene	79-01-6	<0.001	**0.001**	**0.00111**	<0.001	**0.000941 J**
Trichlorofluoromethane	75-69-4	<0.005	<0.005	<0.005	<0.005	<0.005
Vinyl chloride	75-01-4	<0.001	**0.00109**	**0.00225**	<0.001	<0.001
Anions by Method 9056A						
Chloride	16887-00-6	**734**	**--**	**--**	**1180**	**1190**
Nitrate	14797-55-8	<0.1	**--**	**--**	<0.1	<0.1
Sulfate	14808-79-8	**1.11 J**	**--**	**--**	<5	**8.14**
Total Organic Carbon by Method 9060A						
TOC (Total organic carbon)	--	**4.59**	**89.1**	**--**	**7.79**	**10.8**
Dissolved Gases By Method RSK 175						
Methane	74-82-8	**2.06**	**2.97**	**2.81**	**15**	**1.52**
Ethane	74-84-0	<0.013	**0.0106 J**	**0.0105 J**	**0.00873 J**	**0.00877 J**
Ethene	74-85-1	<0.013	**0.00997 J**	**0.011 J**	<0.013	**0.00987 J**
Acetylene	74-86-2	<0.208	<0.0208	<0.0208	<0.0208	<0.0208
Field Parameters - Before Sampling						
Temperature (°F)	--	87.2	--	--	77.3	81.3
Specific Conductivity (mS/cm)	--	2.85	--	--	4.36	4.58
Turbidity (NTU)	--	>1000	--	--	>1000	>1000
Redox (mV)	--	-190	--	--	-117	40
Dissolved Oxygen (mg/L)	--	3.33	--	--	2.33	3.66
pH	--	7.14	--	--	7.41	6.8
Field Parameters - After Sampling						
Temperature (°F)	--	86.6	--	--	77.6	80.3
Specific Conductivity (mS/cm)	--	2.79	--	--	4.36	4.49
Turbidity (NTU)	--	>1000	--	--	127	857
Redox (mV)	--	-187	--	--	-157	-98
Dissolved Oxygen (mg/L)	--	2.62	--	--	2.32	3.53
pH	--	7.35	--	--	7.57	7.33

Notes:
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   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy

TABLE 2
GROUNDWATER SAMPLING AND TESTING RESULTS: FACILITY 1381

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		1381-SB2	1381-SB3	1381-SB3	1381-SB3	1381-SB4
SAMPLE ID:		1381-SB2 54-56FT	1381-SB3 44-46 FT	1381-SB3 48-50FT	1381-SB3 50-52FT	1381-SB4 45-47 FT
SAMPLE DEPTH:		54-56 FT	44-46 FT	48-50 FT	50-52 FT	45-47 FT
PERMIABILITY ZONE:		Low k	High k	Low k	Low k	High k
SAMPLE DATE:		5/20/2016	5/13/2016	5/20/2016	5/20/2016	5/13/2016
ANALYTE	CAS No.	mg/L	mg/L	mg/L	mg/L	mg/L
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.003	<0.003	<0.003	<0.003	<0.003
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.001	<0.001	<0.001	<0.001
Bromoform	75-25-2	<0.001	<0.001	<0.001	<0.001	<0.001
Bromomethane	74-83-9	<0.005	<0.005	<0.005	<0.005	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorobenzene	108-90-7	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.001	<0.001	<0.001	<0.001
Chloroethane	75-00-3	<0.005	<0.005	<0.005	<0.005	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.05 J3 J4	<0.05	<0.05	<0.05 J3 J4
Chloroform	67-66-3	<0.005	<0.005	<0.005	<0.005	<0.005
Chloromethane	74-87-3	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.001	<0.001	<0.001	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.005	<0.005	<0.005	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.001	<0.001	<0.001	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.001	<0.001	<0.001	<0.001	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.001	<0.001	<0.001	<0.001
Methylene chloride	75-09-2	<0.005	<0.005	<0.005	<0.005	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001 J4	<0.001	<0.001 J4	<0.001 J4	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trichloroethene	79-01-6	**0.000726 J**	<0.001	<0.001	<0.001	<0.001
Trichlorofluoromethane	75-69-4	<0.005	<0.005	<0.005	<0.005	<0.005
Vinyl chloride	75-01-4	<0.001	**0.000277 J**	<0.001	<0.001	<0.001
Anions by Method 9056A						
Chloride	16887-00-6	**--**	**1410**	**1250**	**1110**	**741**
Nitrate	14797-55-8	**--**	<0.1	<0.1	<0.1	<0.1
Sulfate	14808-79-8	**--**	<5	**0.559 J**	**4.81 J**	<5
Total Organic Carbon by Method 9060A						
TOC (Total organic carbon)	--	**--**	**9.34**	**7.27**	**--**	**6.89**
Dissolved Gases By Method RSK 175						
Methane	74-82-8	**--**	**10.1**	**9.82**	**8.89**	**15.6**
Ethane	74-84-0	**--**	**0.00817 J**	<0.065	<0.013	<0.013
Ethene	74-85-1	--	**0.00847 J**	<0.065	<0.013	<0.013
Acetylene	74-86-2	--	<0.0208	<0.104	<0.0208	<0.0208
Field Parameters - Before Sampling						
Temperature (°F)	--	--	89	85.5	86.8	89.8
Specific Conductivity (mS/cm)	--	--	5.33	4.49	4.14	2.88
Turbidity (NTU)	--	--	>1000	916	>1000	431
Redox (mV)	--	--	-21	-135	-131	-50
Dissolved Oxygen (mg/L)	--	--	5.16	2.86	2.44	5.13
pH	--	--	7.87	7.5	7.46	7.97
Field Parameters - After Sampling						
Temperature (°F)	--	--	86.8	83	83.3	83.9
Specific Conductivity (mS/cm)	--	--	5.32	4.59	4.21	2.87
Turbidity (NTU)	--	--	>1000	405	258	691
Redox (mV)	--	--	-99	-109	-114	-93
Dissolved Oxygen (mg/L)	--	--	2.54	2.19	2.34	2.16
pH	--	--	7.74	7.41	7.41	7.59

Notes:
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   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB1	SLC16-SB1	SLC16-SB1	SLC16-SB1	SLC16-SB1
SAMPLE ID:		SLC16-SB1 31.5FT	SLC16-SB1 38.8FT	SLC16-SB1 40.6FT	SLC16-SB1 43.2FT	SLC16-SB1 50.5FT
SAMPLE DEPTH:		31.5 FT	38.8 FT	40.6 FT	43.2 FT	50.5 FT
PERMIABILITY ZONE:		High K	High K	High K	High K	Low k
SAMPLE DATE:		05/16/2016	05/16/2016	05/16/2016	05/16/2016	05/16/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	**1.12**	**0.734**	**2.23**	**0.621**	<0.23
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.133	<0.0948	<0.0535	<2	<1.15
Bromoform	75-25-2	<0.133	<0.0948	<0.0535	<2	<1.15
Bromomethane	74-83-9	<0.665	<0.474	<0.268	<10	<5.75
Carbon tetrachloride	56-23-5	<0.133	<0.0948	<0.0535	<2	<1.15
Chlorobenzene	108-90-7	<0.133	<0.0948	<0.0535	<2	<1.15
Chlorodibromomethane	124-48-1	<0.133	<0.0948	<0.0535	<2	<1.15
Chloroethane	75-00-3	<0.665	<0.474	<0.268	<10	<5.75
2-Chloroethyl vinyl ether	110-75-8	<6.65 J4	<4.74 J4	<2.68 J4	<100 J4	<57.5 J4
Chloroform	67-66-3	<0.665	<0.474	<0.268	<10	<5.75
Chloromethane	74-87-3	<0.332	<0.237	<0.134	<5	<2.87
1,2-Dichlorobenzene	95-50-1	<0.133	<0.0948	<0.0535	<2	<1.15
1,3-Dichlorobenzene	541-73-1	<0.133	<0.0948	<0.0535	<2	<1.15
1,4-Dichlorobenzene	106-46-7	<0.133	<0.0948	<0.0535	<2	<1.15
Dichlorodifluoromethane	75-71-8	<0.665	<0.474	<0.268	<10	<5.75
1,1-Dichloroethane	75-34-3	**0.527**	**0.392**	**0.53**	<2	**1.99**
1,2-Dichloroethane	107-06-2	<0.133	<0.0948	**0.0313 J**	<2	<1.15
1,1-Dichloroethene	75-35-4	**0.56**	**0.177**	**0.248**	<2	**0.708 J**
Cis-1,2-dichloroethene	156-59-2	**0.181**	**0.0839 J**	**0.105**	<2	**11.2**
Trans-1,2-dichloroethene	156-60-5	<0.133	<0.0948	<0.0535	<2	<1.15
1,2-Dichloropropane	78-87-5	<0.133	<0.0948	<0.0535	<2	<1.15
Cis-1,3-dichloropropene	10061-01-5	<0.133	<0.0948	<0.0535	<2	<1.15
Trans-1,3-dichloropropene	10061-02-6	<0.133	<0.0948	<0.0535	<2	<1.15
Methylene chloride	75-09-2	<0.665	<0.474	<0.268	<10	<5.75
1,1,2,2-Tetrachloroethane	79-34-5	<0.133	<0.0948	<0.0535	<2	<1.15
Tetrachloroethene	127-18-4	<0.133	<0.0948	<0.0535	<2	<1.15
1,1,1-Trichloroethane	71-55-6	<0.133	<0.0948	<0.0535	<2	**0.709 J**
1,1,2-Trichloroethane	79-00-5	<0.133	<0.0948	<0.0535	<2	<1.15
Trichloroethene	79-01-6	**952**	**251**	**738**	**539**	**8330**
Trichlorofluoromethane	75-69-4	<0.665	<0.474	<0.268	<10	<5.75
Vinyl chloride	75-01-4	<0.133	<0.0948	<0.0535	<2	<1.15
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**--**	**0.00391**	**0.00951**	**--**	**--**
Fractional organic matter, %	--	**--**	**0.674**	**1.64**	**--**	**--**
Total Solids by Method 2540 G-2011						
Total solids	--	**70.7**	**76**	**74.7**	**76**	**71.3**

Notes:
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   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high. BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB1	SLC16-SB1	SLC16-SB1	SLC16-SB1	SLC16-SB1
SAMPLE ID:		SLC16-SB1 51.2FT	SLC16-SB1 52.2FT	SLC16-SB1 53FT	SLC16-SB1 53.8FT	SLC16-SB1 54.3FT
SAMPLE DEPTH:		51.2 FT	52.2 FT	53 FT	53.8 FT	54.3 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/16/2016	05/16/2016	05/16/2016	05/16/2016	05/16/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.215	<0.198	<0.206	<0.204	<0.196
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<1.08	<0.496	<0.257	<0.102	<1.96
Bromoform	75-25-2	<1.08	<0.496	<0.257	<0.102	<1.96
Bromomethane	74-83-9	<5.38	<2.48	<1.28	<0.511	<9.8
Carbon tetrachloride	56-23-5	<1.08	<0.496	<0.257	<0.102	<1.96
Chlorobenzene	108-90-7	<1.08	<0.496	<0.257	<0.102	<1.96
Chlorodibromomethane	124-48-1	<1.08	<0.496	<0.257	<0.102	<1.96
Chloroethane	75-00-3	<5.38	<2.48	<1.28	<0.511	<9.8
2-Chloroethyl vinyl ether	110-75-8	<53.8 J4	<24.8 J4	<12.8 J4	<5.11 J4	<98
Chloroform	67-66-3	<5.38	<2.48	<1.28	<0.511	<9.8
Chloromethane	74-87-3	<2.69	<1.24	<0.642	<0.256	<4.9
1,2-Dichlorobenzene	95-50-1	<1.08	<0.496	<0.257	<0.102	<1.96
1,3-Dichlorobenzene	541-73-1	<1.08	<0.496	<0.257	<0.102	<1.96
1,4-Dichlorobenzene	106-46-7	<1.08	<0.496	<0.257	<0.102	<1.96
Dichlorodifluoromethane	75-71-8	<5.38	<2.48	<1.28	<0.511	<9.8 J3
1,1-Dichloroethane	75-34-3	**0.382 J**	**0.387 J**	**0.189 J**	**0.124**	<1.96
1,2-Dichloroethane	107-06-2	<1.08	<0.496	<0.257	<0.102	<1.96
1,1-Dichloroethene	75-35-4	<1.08	<0.496	<0.257	**0.0316 J**	<1.96
Cis-1,2-dichloroethene	156-59-2	**4.3**	**4.81**	**4.64**	**4**	**4.36**
Trans-1,2-dichloroethene	156-60-5	<1.08	<0.496	<0.257	<0.102	<1.96
1,2-Dichloropropane	78-87-5	<1.08	<0.496	<0.257	<0.102	<1.96
Cis-1,3-dichloropropene	10061-01-5	<1.08	<0.496	<0.257	<0.102	<1.96
Trans-1,3-dichloropropene	10061-02-6	<1.08	<0.496	<0.257	<0.102	<1.96
Methylene chloride	75-09-2	<5.38	<2.48	<1.28	<0.511	<9.8
1,1,2,2-Tetrachloroethane	79-34-5	<1.08	<0.496	<0.257	<0.102	<1.96
Tetrachloroethene	127-18-4	<1.08	<0.496	<0.257	<0.102	<1.96
1,1,1-Trichloroethane	71-55-6	<1.08	<0.496	<0.257	<0.102	<1.96
1,1,2-Trichloroethane	79-00-5	<1.08	<0.496	<0.257	<0.102	<1.96
Trichloroethene	79-01-6	**752**	**1050**	**256**	**180**	**178**
Trichlorofluoromethane	75-69-4	<5.38	<2.48	<1.28	<0.511	<9.8
Vinyl chloride	75-01-4	<1.08	<0.496	<0.257	<0.102	<1.96
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00998**	**0.00357**	**--**	**0.00365**	**--**
Fractional organic matter, %	--	**1.72**	**0.615**	**--**	**0.629**	**--**
Total Solids by Method 2540 G-2011						
Total solids	--	**70.6**	**77.6**	**75.9**	**73.4**	**79.6**

Notes:
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    J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
    V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high.
    BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB2	SLC16-SB2	SLC16-SB2	SLC16-SB2	SLC16-SB2
SAMPLE ID:		SLC16-SB2 34.2FT	SLC16-SB2 39FT	SLC16-SB2 40.8FT	SLC16-SB2 43FT	SLC16-SB2 48FT
SAMPLE DEPTH:		34.2 FT	39 FT	40.8 FT	43 FT	48 FT
PERMIABILITY ZONE:		High K	High k	Lower k	High k	High k
SAMPLE DATE:		05/16/2016	05/16/2016	05/16/2016	05/16/2016	05/17/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	**0.34**	**0.421**	**0.613**	**0.722**	**0.545**
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<2.08	<0.102	<0.132	<0.104	<0.316
Bromoform	75-25-2	<2.08	<0.102	<0.132	<0.104	<0.316
Bromomethane	74-83-9	<10.4	<0.508	<0.659	<0.518	<1.58
Carbon tetrachloride	56-23-5	<2.08	<0.102	<0.132	<0.104	<0.316
Chlorobenzene	108-90-7	<2.08	<0.102	<0.132	<0.104	<0.316
Chlorodibromomethane	124-48-1	<2.08	<0.102	<0.132	<0.104	<0.316
Chloroethane	75-00-3	<10.4	<0.508	<0.659	<0.518	<1.58
2-Chloroethyl vinyl ether	110-75-8	<104	<5.08 J4	<6.59 J4	<5.18 J4	<15.8
Chloroform	67-66-3	<10.4	<0.508	<0.659	<0.518	<1.58
Chloromethane	74-87-3	<5.2	<0.254	<0.33	<0.259	<0.789
1,2-Dichlorobenzene	95-50-1	<2.08	<0.102	<0.132	<0.104	<0.316
1,3-Dichlorobenzene	541-73-1	<2.08	<0.102	<0.132	<0.104	<0.316
1,4-Dichlorobenzene	106-46-7	<2.08	<0.102	<0.132	<0.104	<0.316
Dichlorodifluoromethane	75-71-8	<10.4 J3	<0.508	<0.659	<0.518	<1.58
1,1-Dichloroethane	75-34-3	<2.08	**0.174**	**0.0718 J**	**0.289**	**0.259 J**
1,2-Dichloroethane	107-06-2	<2.08	<0.102	<0.132	<0.104	<0.316
1,1-Dichloroethene	75-35-4	<2.08	**0.0589 J**	<0.132	**0.103 J**	**0.0977 J**
Cis-1,2-dichloroethene	156-59-2	**19.6**	**6.23**	**1.52**	**2.56**	**2.49**
Trans-1,2-dichloroethene	156-60-5	<2.08	<0.102	<0.132	<0.104	<0.316
1,2-Dichloropropane	78-87-5	<2.08	<0.102	<0.132	<0.104	<0.316
Cis-1,3-dichloropropene	10061-01-5	<2.08	<0.102	<0.132	<0.104	<0.316
Trans-1,3-dichloropropene	10061-02-6	<2.08	<0.102	<0.132	<0.104	<0.316
Methylene chloride	75-09-2	<10.4	<0.508	<0.659	<0.518	<1.58
1,1,2,2-Tetrachloroethane	79-34-5	<2.08	<0.102	<0.132	<0.104	<0.316
Tetrachloroethene	127-18-4	<2.08	<0.102	<0.132	<0.104	<0.316
1,1,1-Trichloroethane	71-55-6	<2.08	<0.102	<0.132	<0.104	<0.316
1,1,2-Trichloroethane	79-00-5	<2.08	<0.102	<0.132	<0.104	<0.316
Trichloroethene	79-01-6	**84.7**	**98.1**	**38.8**	**132**	**178**
Trichlorofluoromethane	75-69-4	<10.4	<0.508	<0.659	<0.518	<1.58
Vinyl chloride	75-01-4	<2.08	<0.102	<0.132	<0.104	<0.316
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**--**	**0.00307**	**0.00448**	**--**	**0.00506**
Fractional organic matter, %	--	**--**	**0.529**	**0.772**	**--**	**0.873**
Total Solids by Method 2540 G-2011						
Total solids	--	**74**	**78.7**	**75.9**	**76.2**	**72.9**

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   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
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TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB2	SLC16-SB2	SLC16-SB2	SLC16-SB2	SLC16-SB2
SAMPLE ID:		SLC16-SB2 51FT	SLC16-SB2 51.6FT	SLC16-SB2 52.2FT	SLC16-SB2 52.8FT	SLC16-SB2 53.5FT
SAMPLE DEPTH:		51 FT	51.6 FT	52.2 FT	52.8 FT	53.5 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/17/2016	05/17/2016	05/17/2016	05/17/2016	05/17/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.226	<0.255	<0.255	<0.239	<0.194
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<1.13	<0.0638	<0.127	<0.00133 J3 J6	<0.0971
Bromoform	75-25-2	<1.13	<0.0638	<0.127	<0.00133	<0.0971
Bromomethane	74-83-9	<5.64	<0.319	<0.637	<0.00663 J3	<0.485
Carbon tetrachloride	56-23-5	<1.13	<0.0638	<0.127	<0.00133 J3	<0.0971
Chlorobenzene	108-90-7	<1.13	<0.0638	<0.127	<0.00133	<0.0971
Chlorodibromomethane	124-48-1	<1.13	<0.0638	<0.127	<0.00133	<0.0971
Chloroethane	75-00-3	<5.64	<0.319	<0.637	<0.00663 J3	<0.485
2-Chloroethyl vinyl ether	110-75-8	<56.4 J4	<3.19	<6.37	<0.0663 J3 J6	<4.85 J4
Chloroform	67-66-3	<5.64	<0.319	<0.637	<0.00663 J3	<0.485
Chloromethane	74-87-3	<2.82	<0.159	<0.318	<0.00332 J3 J5	<0.243
1,2-Dichlorobenzene	95-50-1	<1.13	<0.0638	<0.127	<0.00133	<0.0971
1,3-Dichlorobenzene	541-73-1	<1.13	<0.0638	<0.127	<0.00133	<0.0971
1,4-Dichlorobenzene	106-46-7	<1.13	<0.0638	<0.127	<0.00133	<0.0971
Dichlorodifluoromethane	75-71-8	<5.64	<0.319	<0.637	<0.00663 J3 J5	<0.485
1,1-Dichloroethane	75-34-3	<1.13	**0.0715**	**0.0549 J**	**0.0209 J3 J6**	<0.0971
1,2-Dichloroethane	107-06-2	<1.13	<0.0638	<0.127	**0.0027 J3**	<0.0971
1,1-Dichloroethene	75-35-4	<1.13	**0.0357 J**	<0.127	**0.0111 J3**	<0.0971
Cis-1,2-dichloroethene	156-59-2	**13.2**	**16**	**15.6**	**15.3**	**10.2**
Trans-1,2-dichloroethene	156-60-5	<1.13	**0.0503 J**	**0.0554 J**	**0.0222 J3 J6**	<0.0971
1,2-Dichloropropane	78-87-5	<1.13	<0.0638	<0.127	<0.00133 J3 J6	<0.0971
Cis-1,3-dichloropropene	10061-01-5	<1.13	<0.0638	<0.127	<0.00133 J3 J6	<0.0971
Trans-1,3-dichloropropene	10061-02-6	<1.13	<0.0638	<0.127	<0.00133 J3 J6	<0.0971
Methylene chloride	75-09-2	<5.64	<0.319	<0.637	<0.00663 J3	<0.485
1,1,2,2-Tetrachloroethane	79-34-5	<1.13	<0.0638	<0.127	<0.00133	<0.0971
Tetrachloroethene	127-18-4	<1.13	<0.0638	<0.127	<0.00133	<0.0971
1,1,1-Trichloroethane	71-55-6	<1.13	<0.0638	<0.127	<0.00133 J3	<0.0971
1,1,2-Trichloroethane	79-00-5	<1.13	<0.0638	<0.127	<0.00133	<0.0971
Trichloroethene	79-01-6	**67.6**	**76.2**	**54.8**	**41.3**	**5.78**
Trichlorofluoromethane	75-69-4	<5.64	<0.319	<0.637	<0.00663 J3	<0.485
Vinyl chloride	75-01-4	<1.13	<0.0638	<0.127	**0.00201 J3 J5**	<0.0971
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**--**	**0.00829**	**--**	**0.00573**	**--**
Fractional organic matter, %	--	**--**	**1.43**	**--**	**0.988**	**--**
Total Solids by Method 2540 G-2011						
Total solids	--	**73.6**	**70.6**	**73.8**	**75.4**	**78.3**

Notes:

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V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high. BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB3	SLC16-SB3	SLC16-SB3	SLC16-SB3	SLC16-SB3
SAMPLE ID:		SLC16-SB3 28.6FT	SLC16-SB3 39FT	SLC16-SB3 41.6FT	SLC16-SB3 42.5FT	SLC16-SB3 48FT
SAMPLE DEPTH:		28.6 FT	39 FT	41.6 FT	42.5 FT	48 FT
PERMIABILITY ZONE:		Low k	High k	High K	High k	High k
SAMPLE DATE:		05/18/2016	05/18/2016	05/18/2016	05/18/2016	05/18/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00277	<0.00255	<0.00275	<0.00262	<0.00253
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Bromoform	75-25-2	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Bromomethane	74-83-9	<0.608	<0.00638	<0.00688	<0.00656	<0.00631
Carbon tetrachloride	56-23-5	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Chlorobenzene	108-90-7	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Chlorodibromomethane	124-48-1	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Chloroethane	75-00-3	<0.608	<0.00638	<0.00688	<0.00656	<0.00631
2-Chloroethyl vinyl ether	110-75-8	<6.08	<0.0638	<0.0688	<0.0656	<0.0631
Chloroform	67-66-3	<0.608	<0.00638	<0.00688	<0.00656	<0.00631
Chloromethane	74-87-3	<0.304	<0.00319	<0.00344	<0.00328	<0.00316
1,2-Dichlorobenzene	95-50-1	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
1,3-Dichlorobenzene	541-73-1	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
1,4-Dichlorobenzene	106-46-7	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Dichlorodifluoromethane	75-71-8	<0.608	<0.00638	<0.00688	<0.00656	<0.00631
1,1-Dichloroethane	75-34-3	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
1,2-Dichloroethane	107-06-2	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
1,1-Dichloroethene	75-35-4	**0.188**	<0.00128	<0.00138	<0.00131	<0.00126
Cis-1,2-dichloroethene	156-59-2	**10.8**	<0.00128	<0.00138	<0.00131	<0.00126
Trans-1,2-dichloroethene	156-60-5	**0.0428 J**	<0.00128	<0.00138	<0.00131	<0.00126
1,2-Dichloropropane	78-87-5	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Cis-1,3-dichloropropene	10061-01-5	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Trans-1,3-dichloropropene	10061-02-6	**0.0834 J**	<0.00128	<0.00138	<0.00131	<0.00126
Methylene chloride	75-09-2	<0.608	<0.00638	<0.00688	<0.00656	<0.00631
1,1,2,2-Tetrachloroethane	79-34-5	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Tetrachloroethene	127-18-4	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
1,1,1-Trichloroethane	71-55-6	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
1,1,2-Trichloroethane	79-00-5	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Trichloroethene	79-01-6	<0.122	<0.00128	<0.00138	<0.00131	<0.00126
Trichlorofluoromethane	75-69-4	<0.608	<0.00638	<0.00688	<0.00656	<0.00631
Vinyl chloride	75-01-4	**4.87**	<0.00128	<0.00138	<0.00131	<0.00126
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00398**	**0.00463**	**--**	**--**	**0.00317**
Fractional organic matter, %	--	**0.685**	**0.798**	**--**	**--**	**0.547**
Total Solids by Method 2540 G-2011						
Total solids	--	**72.3**	**78.4**	**72.7**	**76.2**	**79.2**

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   BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB3	SLC16-SB3	SLC16-SB3	SLC16-SB3	SLC16-SB3
SAMPLE ID:		SLC16-SB3 48.8FT	SLC16-SB3 49.6FT	SLC16-SB3 50.5FT	SLC16-SB3 51.5FT	SLC16-SB3 53.7FT
SAMPLE DEPTH:		48.8 FT	49.6 FT	50.5 FT	51.5 FT	53.7 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	High k	High k
SAMPLE DATE:		05/18/2016	05/18/2016	05/18/2016	05/18/2016	05/18/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00266	<0.00273	<0.00308	<0.00262	<0.00256
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Bromoform	75-25-2	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Bromomethane	74-83-9	<0.00664	<0.00682	<0.00771	<0.00655	<0.0064
Carbon tetrachloride	56-23-5	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Chlorobenzene	108-90-7	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Chlorodibromomethane	124-48-1	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Chloroethane	75-00-3	<0.00664	<0.00682	<0.00771	<0.00655	<0.0064
2-Chloroethyl vinyl ether	110-75-8	<0.0664	<0.0682	<0.0771	<0.0655	<0.064
Chloroform	67-66-3	<0.00664	<0.00682	<0.00771	<0.00655	<0.0064
Chloromethane	74-87-3	<0.00332	<0.00341	<0.00385	<0.00328	<0.0032
1,2-Dichlorobenzene	95-50-1	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,3-Dichlorobenzene	541-73-1	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,4-Dichlorobenzene	106-46-7	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Dichlorodifluoromethane	75-71-8	<0.00664	<0.00682	<0.00771	<0.00655	<0.0064
1,1-Dichloroethane	75-34-3	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,2-Dichloroethane	107-06-2	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,1-Dichloroethene	75-35-4	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Cis-1,2-dichloroethene	156-59-2	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Trans-1,2-dichloroethene	156-60-5	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,2-Dichloropropane	78-87-5	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Cis-1,3-dichloropropene	10061-01-5	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Trans-1,3-dichloropropene	10061-02-6	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Methylene chloride	75-09-2	<0.00664	<0.00682	<0.00771	<0.00655	<0.0064
1,1,2,2-Tetrachloroethane	79-34-5	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Tetrachloroethene	127-18-4	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,1,1-Trichloroethane	71-55-6	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
1,1,2-Trichloroethane	79-00-5	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Trichloroethene	79-01-6	<0.00133	<0.00136	<0.00154	<0.00131	<0.00128
Trichlorofluoromethane	75-69-4	<0.00664	<0.00682	<0.00771	<0.00655	<0.0064
Vinyl chloride	75-01-4	<0.00133	**0.00205**	<0.00154	<0.00131	<0.00128
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**--**	**0.00664**	**--**	**0.00385**	**--**
Fractional organic matter, %	--	**--**	**1.15**	**--**	**0.664**	**--**
Total Solids by Method 2540 G-2011						
Total solids	--	**75.3**	**73.3**	**64.9**	**76.3**	**78.1**

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   BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB4	SLC16-SB4	SLC16-SB4	SLC16-SB4	SLC16-SB4
SAMPLE ID:		SLC16-SB4 27FT	SLC16-SB4 29FT	SLC16-SB4 39FT	SLC16-SB4 40.8FT	SLC16-SB4 42.8FT
SAMPLE DEPTH:		27 FT	29 FT	39 FT	40.8 FT	42.8 FT
PERMIABILITY ZONE:		High k	Lower k	High k	Low k	High k
SAMPLE DATE:		05/17/2016	05/17/2016	05/17/2016	05/17/2016	05/17/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	**0.00254 J**	<0.00285	<0.00264	<0.0027	<0.00272
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Bromoform	75-25-2	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Bromomethane	74-83-9	<0.00672	<0.00713	<0.00659	<0.00674	<0.00681
Carbon tetrachloride	56-23-5	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Chlorobenzene	108-90-7	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Chlorodibromomethane	124-48-1	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Chloroethane	75-00-3	<0.00672	<0.00713	<0.00659	<0.00674	<0.00681
2-Chloroethyl vinyl ether	110-75-8	<0.0672	<0.0713	<0.0659	<0.0674 J4	<0.0681
Chloroform	67-66-3	<0.00672	<0.00713	<0.00659	<0.00674	<0.00681
Chloromethane	74-87-3	<0.00336	<0.00356	<0.0033	<0.00337	<0.0034
1,2-Dichlorobenzene	95-50-1	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
1,3-Dichlorobenzene	541-73-1	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
1,4-Dichlorobenzene	106-46-7	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Dichlorodifluoromethane	75-71-8	<0.00672	<0.00713	<0.00659	<0.00674	<0.00681
1,1-Dichloroethane	75-34-3	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
1,2-Dichloroethane	107-06-2	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
1,1-Dichloroethene	75-35-4	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Cis-1,2-dichloroethene	156-59-2	**0.461**	**0.0447**	**0.000621 J**	**0.000549 J V3**	**0.00352**
Trans-1,2-dichloroethene	156-60-5	**0.0019**	**0.000519 J**	<0.00132	<0.00135	<0.00136
1,2-Dichloropropane	78-87-5	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Cis-1,3-dichloropropene	10061-01-5	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Trans-1,3-dichloropropene	10061-02-6	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Methylene chloride	75-09-2	<0.00672	<0.00713	<0.00659	<0.00674	<0.00681
1,1,2,2-Tetrachloroethane	79-34-5	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Tetrachloroethene	127-18-4	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
1,1,1-Trichloroethane	71-55-6	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
1,1,2-Trichloroethane	79-00-5	<0.00134	<0.00143	<0.00132	<0.00135	<0.00136
Trichloroethene	79-01-6	**0.0199 J**	**0.00284**	**0.00147**	**0.00743 V3**	**0.00755**
Trichlorofluoromethane	75-69-4	<0.00672	<0.00713	<0.00659	<0.00674	<0.00681
Vinyl chloride	75-01-4	**0.000611 J**	**0.000686 J**	<0.00132	<0.00135	<0.00136
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00217**	**0.00423**	**--**	**--**	**0.00409**
Fractional organic matter, %	--	**0.374**	**0.729**	**--**	**--**	**0.705**
Total Solids by Method 2540 G-2011						
Total solids	--	**74.4**	**70.2**	**75.8**	**74.2**	**73.5**

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TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB4	SLC16-SB4	SLC16-SB4	SLC16-SB4	SLC16-SB4
SAMPLE ID:		SLC16-SB4 47FT	SLC16-SB4 49FT	SLC16-SB4 49.6FT	SLC16-SB4 50.5FT	SLC16-SB4 51.2FT
SAMPLE DEPTH:		47 FT	49 FT	49.6 FT	50.5 FT	51.2 FT
PERMIABILITY ZONE:		Lower K	Low k	Low k	Low k	High K
SAMPLE DATE:		05/17/2016	05/17/2016	05/17/2016	05/17/2016	05/17/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00276	<0.00271	<0.00276	<0.00275	<0.00265
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Bromoform	75-25-2	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Bromomethane	74-83-9	<0.0069	<0.00678	<0.0069	<0.00686	<0.00661
Carbon tetrachloride	56-23-5	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Chlorobenzene	108-90-7	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Chlorodibromomethane	124-48-1	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Chloroethane	75-00-3	<0.0069	<0.00678	<0.0069	<0.00686	<0.00661
2-Chloroethyl vinyl ether	110-75-8	<0.069	<0.0678	<0.069 J4	<0.0686 J4	<0.0661
Chloroform	67-66-3	<0.0069	<0.00678	<0.0069	<0.00686	<0.00661
Chloromethane	74-87-3	<0.00345	<0.00339	<0.00345	<0.00343	<0.00331
1,2-Dichlorobenzene	95-50-1	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,3-Dichlorobenzene	541-73-1	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,4-Dichlorobenzene	106-46-7	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Dichlorodifluoromethane	75-71-8	<0.0069	<0.00678	<0.0069	<0.00686	<0.00661
1,1-Dichloroethane	75-34-3	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,2-Dichloroethane	107-06-2	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,1-Dichloroethene	75-35-4	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Cis-1,2-dichloroethene	156-59-2	**0.000631 J**	**0.00803**	<0.00138	<0.00137	**0.00786**
Trans-1,2-dichloroethene	156-60-5	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,2-Dichloropropane	78-87-5	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Cis-1,3-dichloropropene	10061-01-5	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Trans-1,3-dichloropropene	10061-02-6	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Methylene chloride	75-09-2	<0.0069	<0.00678	<0.0069	<0.00686	<0.00661
1,1,2,2-Tetrachloroethane	79-34-5	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Tetrachloroethene	127-18-4	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,1,1-Trichloroethane	71-55-6	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
1,1,2-Trichloroethane	79-00-5	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Trichloroethene	79-01-6	**0.00444**	**0.00345**	<0.00138	**0.000675 J**	**0.00494**
Trichlorofluoromethane	75-69-4	<0.0069	<0.00678	<0.0069	<0.00686	<0.00661
Vinyl chloride	75-01-4	<0.00138	<0.00136	<0.00138	<0.00137	<0.00132
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**--**	**--**	**0.00548**	**--**	**0.00408**
Fractional organic matter, %	--	**--**	**--**	**0.946**	**--**	**0.704**
Total Solids by Method 2540 G-2011						
Total solids	--	**72.4**	**73.8**	**72.5**	**72.9**	**75.6**

Notes:
1. Detections are shown in **bold**.
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   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J3 = The associated batch QC was outside the established quality control range for precision.
   J4 = The associated batch QC was outside the established quality control range for accuracy
   J5 = The sample matrix interfered with the ability to make any accurate determination; spike value is high
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high.
   BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB4	SLC16-SB5	SLC16-SB5	SLC16-SB5	SLC16-SB5
SAMPLE ID:		SLC16-SB4 52	SLC16-SB5 27FT	SLC16-SB5 29FT	SLC16-SB5 36FT	SLC16-SB5 39.5FT
SAMPLE DEPTH:		52 FT	27 FT	29 FT	36 FT	39.5 FT
PERMIABILITY ZONE:		High K	High k	Lower k	High k	Low K
SAMPLE DATE:		05/17/2016	05/18/2016	05/18/2016	05/18/2016	05/18/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00269	<0.00284	<0.00303	<0.00261	<0.00288
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Bromoform	75-25-2	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Bromomethane	74-83-9	<0.00672	<0.0071	<0.00756	<0.00652	<0.0072
Carbon tetrachloride	56-23-5	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Chlorobenzene	108-90-7	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Chlorodibromomethane	124-48-1	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Chloroethane	75-00-3	<0.00672	<0.0071	<0.00756	<0.00652	<0.0072
2-Chloroethyl vinyl ether	110-75-8	<0.0672	<0.071	<0.0756	<0.0652	<0.072
Chloroform	67-66-3	<0.00672	<0.0071	<0.00756	<0.00652	<0.0072
Chloromethane	74-87-3	<0.00336	<0.00355	<0.00378	<0.00326	<0.0036
1,2-Dichlorobenzene	95-50-1	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,3-Dichlorobenzene	541-73-1	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,4-Dichlorobenzene	106-46-7	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Dichlorodifluoromethane	75-71-8	<0.00672	<0.0071	<0.00756	<0.00652	<0.0072
1,1-Dichloroethane	75-34-3	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,2-Dichloroethane	107-06-2	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,1-Dichloroethene	75-35-4	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Cis-1,2-dichloroethene	156-59-2	**0.000398 J**	**0.000456 J**	**0.000405 J**	**0.000583 J**	**0.000448 J**
Trans-1,2-dichloroethene	156-60-5	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,2-Dichloropropane	78-87-5	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Cis-1,3-dichloropropene	10061-01-5	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Trans-1,3-dichloropropene	10061-02-6	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Methylene chloride	75-09-2	<0.00672	<0.0071	<0.00756	<0.00652	<0.0072
1,1,2,2-Tetrachloroethane	79-34-5	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Tetrachloroethene	127-18-4	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,1,1-Trichloroethane	71-55-6	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
1,1,2-Trichloroethane	79-00-5	<0.00134	<0.00142	<0.00151	<0.0013	<0.00144
Trichloroethene	79-01-6	**0.00248**	<0.00142	<0.00151	<0.0013	<0.00144
Trichlorofluoromethane	75-69-4	<0.00672	<0.0071	<0.00756	<0.00652	<0.0072
Vinyl chloride	75-01-4	<0.00134	**0.00111 J**	<0.00151	<0.0013	<0.00144
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**--**	**0.00242**	**--**	**--**	**0.00848**
Fractional organic matter, %	--	**--**	**0.417**	**--**	**--**	**1.46**
Total Solids by Method 2540 G-2011						
Total solids	--	**74.4**	**70.4**	**66.1**	**76.7**	**69.4**

Notes:

1. Detections are shown in **bold**.
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   J5 = The sample matrix interfered with the ability to make any accurate determination; spike value is high
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high.
   BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB5	SLC16-SB5	SLC16-SB5	SLC16-SB5	SLC16-SB5
SAMPLE ID:		SLC16-SB5 40.5FT	SLC16-SB5 41.2FT	SLC16-SB5 42FT	SLC16-SB5 42.8FT	SLC16-SB5 43.6FT
SAMPLE DEPTH:		40.5 FT	41.2 FT	42 FT	42.8 FT	43.6 FT
PERMIABILITY ZONE:		Low k	Low k	Low k	Low k	Low k
SAMPLE DATE:		05/18/2016	05/18/2016	05/18/2016	05/18/2016	05/18/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg		
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.00274	<0.00363	<0.00361	<0.00364	<0.00317
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Bromoform	75-25-2	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Bromomethane	74-83-9	<0.00684	<0.00907	<0.00902	<0.00908	<0.00793
Carbon tetrachloride	56-23-5	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Chlorobenzene	108-90-7	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Chlorodibromomethane	124-48-1	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Chloroethane	75-00-3	<0.00684	<0.00907	<0.00902	<0.00908	<0.00793
2-Chloroethyl vinyl ether	110-75-8	<0.0684	<0.0907	<0.0902	<0.0908	<0.0793
Chloroform	67-66-3	<0.00684	<0.00907	<0.00902	<0.00908	<0.00793
Chloromethane	74-87-3	<0.00342	<0.00454	<0.00451	<0.00454	<0.00396
1,2-Dichlorobenzene	95-50-1	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,3-Dichlorobenzene	541-73-1	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,4-Dichlorobenzene	106-46-7	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Dichlorodifluoromethane	75-71-8	<0.00684	<0.00907	<0.00902	<0.00908	<0.00793
1,1-Dichloroethane	75-34-3	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,2-Dichloroethane	107-06-2	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,1-Dichloroethene	75-35-4	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Cis-1,2-dichloroethene	156-59-2	**0.00384**	**0.000645 J**	<0.0018	<0.00182	<0.00159
Trans-1,2-dichloroethene	156-60-5	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,2-Dichloropropane	78-87-5	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Cis-1,3-dichloropropene	10061-01-5	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Trans-1,3-dichloropropene	10061-02-6	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Methylene chloride	75-09-2	<0.00684	<0.00907	<0.00902	<0.00908	<0.00793
1,1,2,2-Tetrachloroethane	79-34-5	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Tetrachloroethene	127-18-4	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,1,1-Trichloroethane	71-55-6	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
1,1,2-Trichloroethane	79-00-5	<0.00137	<0.00181	<0.0018	<0.00182	<0.00159
Trichloroethene	79-01-6	**0.000386 J**	<0.00181	<0.0018	<0.00182	<0.00159
Trichlorofluoromethane	75-69-4	<0.00684	<0.00907	<0.00902	<0.00908	<0.00793
Vinyl chloride	75-01-4	**0.00111 J**	<0.00181	<0.0018	<0.00182	<0.00159
Fractional Organic Carbon by Method D2974						
Fractional organic carbon, g C/g soil	--	**0.00743**	**--**	**0.0164**	**--**	**0.0123**
Fractional organic matter, %	--	**1.28**	**--**	**2.82**	**--**	**2.12**
Total Solids by Method 2540 G-2011						
Total solids	--	**73.1**	**55.1**	**55.4**	**55**	**63.1**

Notes:
1. Detections are shown in **bold**.
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   J5 = The sample matrix interfered with the ability to make any accurate determination; spike value is high
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high.
   BDL results will be unaffected.

TABLE 1
SOIL SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB5	SLC16-SB5	SLC16-SB5
SAMPLE ID:		SLC16-SB5 44.4FT	DUP 3	DUP 4
SAMPLE DEPTH:		44.4 FT	27 FT	39.5 FT
PERMIABILITY ZONE:		Low k	High k	High k
SAMPLE DATE:		05/18/2016	05/18/2016	05/18/2016
ANALYTE	CAS No.	mg/Kg	mg/Kg	mg/Kg
1,4-Dioxane by Method 8260B-SIM				
1,4-Dioxane	123-91-1	<0.00295	<0.002	<0.002
Volatile Organic Compounds by Method 8260B				
Bromodichloromethane	75-27-4	<0.00147	<0.001	<0.001
Bromoform	75-25-2	<0.00147	<0.001	<0.001
Bromomethane	74-83-9	<0.00736	<0.005	<0.005
Carbon tetrachloride	56-23-5	<0.00147	<0.001	<0.001
Chlorobenzene	108-90-7	<0.00147	<0.001	<0.001
Chlorodibromomethane	124-48-1	<0.00147	<0.001	<0.001
Chloroethane	75-00-3	<0.00736	<0.005	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.0736	<0.05	<0.05
Chloroform	67-66-3	<0.00736	<0.005	<0.005
Chloromethane	74-87-3	<0.00368	<0.0025	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.00147	<0.001	<0.001
1,3-Dichlorobenzene	541-73-1	<0.00147	<0.001	<0.001
1,4-Dichlorobenzene	106-46-7	<0.00147	<0.001	<0.001
Dichlorodifluoromethane	75-71-8	<0.00736	<0.005	<0.005
1,1-Dichloroethane	75-34-3	<0.00147	<0.001	<0.001
1,2-Dichloroethane	107-06-2	<0.00147	<0.001	<0.001
1,1-Dichloroethene	75-35-4	<0.00147	<0.001	<0.001
Cis-1,2-dichloroethene	156-59-2	<0.00147	**0.00104**	<0.001
Trans-1,2-dichloroethene	156-60-5	<0.00147	<0.001	<0.001
1,2-Dichloropropane	78-87-5	<0.00147	<0.001	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.00147	<0.001	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.00147	<0.001	<0.001
Methylene chloride	75-09-2	<0.00736	<0.005	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.00147	<0.001	<0.001
Tetrachloroethene	127-18-4	<0.00147	<0.001	<0.001
1,1,1-Trichloroethane	71-55-6	<0.00147	<0.001	<0.001
1,1,2-Trichloroethane	79-00-5	<0.00147	<0.001	<0.001
Trichloroethene	79-01-6	<0.00147	<0.001	<0.001
Trichlorofluoromethane	75-69-4	<0.00736	<0.005	<0.005
Vinyl chloride	75-01-4	<0.00147	**0.00111**	<0.001
Fractional Organic Carbon by Method D2974				
Fractional organic carbon, g C/g soil	--	**--**	**--**	**--**
Fractional organic matter, %	--	**--**	**--**	**--**
Total Solids by Method 2540 G-2011				
Total solids	--	**67.9**	**--**	**--**

Notes:
1. Detections are shown in **bold**.
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   J5 = The sample matrix interfered with the ability to make any accurate determination; spike value is high
   J6 = The sample matrix interfered with the ability to make any accurate determination; spike value is low
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high.
   BDL results will be unaffected.

TABLE 2
GROUNDWATER SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB1	SLC16-SB1	SLC16-SB1	SLC16-SB2	SLC16-SB2
SAMPLE ID:		SLC16-SB1 40-42FT	SLC16-SB1 48-50FT	SLC16-SB1 50-52FT	SLC16-SB2 40-42FT	SLC16-SB2 48-50FT
SAMPLE DEPTH:		40-42 FT	48-50 FT	50-52 FT	40-42 FT	48-50 FT
PERMIABILITY ZONE:		High k	High k	Low k	High k	High k
SAMPLE DATE:		05/16/2016	05/16/2016	05/16/2016	05/17/2016	05/17/2016
ANALYTE	CAS No.	mg/L	mg/L	mg/L	mg/L	mg/L
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	**17.2 V3**	**9 V3**	**1.77 V3**	**1.75 J**	**1.82 J**
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.1	<0.2	<0.1	<0.025	<0.025
Bromoform	75-25-2	<0.1	<0.2	<0.1	<0.025	<0.025
Bromomethane	74-83-9	<0.5	<1	<0.5	<0.125	<0.125
Carbon tetrachloride	56-23-5	<0.1	<0.2	<0.1	<0.025	<0.025
Chlorobenzene	108-90-7	<0.1	<0.2	<0.1	<0.025	<0.025
Chlorodibromomethane	124-48-1	<0.1	<0.2	<0.1	<0.025	<0.025
Chloroethane	75-00-3	<0.5	<1	<0.5	<0.125	<0.125
2-Chloroethyl vinyl ether	110-75-8	<5 J4	<10 J4	<5 J4	<1.25	<1.25
Chloroform	67-66-3	<0.5	<1	<0.5	<0.125	<0.125
Chloromethane	74-87-3	<0.25	<0.5	<0.25	<0.0625	<0.0625
1,2-Dichlorobenzene	95-50-1	<0.1	<0.2	<0.1	<0.025	<0.025
1,3-Dichlorobenzene	541-73-1	<0.1	<0.2	<0.1	<0.025	<0.025
1,4-Dichlorobenzene	106-46-7	<0.1	<0.2	<0.1	<0.025	<0.025
Dichlorodifluoromethane	75-71-8	<0.5	<1	<0.5	<0.125	<0.125
1,1-Dichloroethane	75-34-3	**1.4**	**1.18**	**0.688**	**1.12**	**0.766**
1,2-Dichloroethane	107-06-2	**0.118**	**0.131 J**	**0.0628 J**	**0.0676**	**0.108**
1,1-Dichloroethene	75-35-4	**0.588**	**0.359**	**0.164**	**0.302**	**0.211**
Cis-1,2-dichloroethene	156-59-2	**0.287**	**5.58**	**20**	<100	**16.4 J**
Trans-1,2-dichloroethene	156-60-5	<0.1	<0.2	**0.0844 J**	**0.132**	**0.0706**
1,2-Dichloropropane	78-87-5	<0.1	<0.2	<0.1	<0.025	**0.514**
Cis-1,3-dichloropropene	10061-01-5	<0.1	<0.2	<0.1	<0.025	<0.025
Trans-1,3-dichloropropene	10061-02-6	<0.1	<0.2	<0.1	<0.025	<0.025
Methylene chloride	75-09-2	<0.5	<1	<0.5	<0.125	<0.125
1,1,2,2-Tetrachloroethane	79-34-5	<0.1	<0.2	<0.1	<0.025	<0.025
Tetrachloroethene	127-18-4	<0.1	<0.2	<0.1	<0.025	<0.025
1,1,1-Trichloroethane	71-55-6	**0.158**	<0.2	<0.1	<0.025	<0.025
1,1,2-Trichloroethane	79-00-5	<0.1	<0.2	<0.1	<0.025	<0.025
Trichloroethene	79-01-6	**607**	**1150**	**459**	**410**	**298**
Trichlorofluoromethane	75-69-4	<0.5	<1	<0.5	<0.125	<0.125
Vinyl chloride	75-01-4	<0.1	<0.2	<0.1	**0.00992 J**	**0.0178 J**
Anions by Method 9056A						
Chloride	16887-00-6	**1370**	**1110**	**698**	**1130**	**1110**
Nitrate	14797-55-8	**802**	**568**	**95.5**	**70.7**	<0.1
Sulfate	14808-79-8	**70.4**	**149**	**87.7**	**358**	**594**
Total Organic Carbon by Method 9060A						
TOC (Total organic carbon)	--	**34.1**	**23.2**	--	**13.3**	**41.4**
Dissolved Gases By Method RSK 175						
Methane	74-82-8	**0.00583 J**	**0.0109**	**0.011**	**0.0138**	**0.00974 J**
Ethane	74-84-0	**0.00847 J**	**0.00937 J**	**0.00833 J**	**0.00985 J**	**0.00909 J**
Ethene	74-85-1	**0.0109 J**	**0.0168**	**0.0204**	**0.014**	**0.0118 J**
Acetylene	74-86-2	<0.0208	**0.0174 J**	**0.0103 J**	<0.0208	**0.0163 J**
Field Parameters - Before Sampling						
Temperature (°F)	--	84.3	88.6	87.1	78.7	80.6
Specific Conductivity (mS/cm)	--	9	6.5	3.51	4.68	5.09
Turbidity (NTU)	--	>1000	>1000	>1000	800	936
Redox (mV)	--	-91	-159	-116	-38	-201
Dissolved Oxygen (mg/L)	--	3.43	2.38	3.25	2.45	2.33
pH	--	6.87	7.6	7.88	7.99	7.86
Field Parameters - After Sampling						
Temperature (°F)	--	82.3	86.4	85.1	78.1	80.4
Specific Conductivity (mS/cm)	--	8.87	7.17	3.31	4.6	5.74
Turbidity (NTU)	--	900	552	138	>1000	>1000
Redox (mV)	--	-150	-152	-95	-143	-214
Dissolved Oxygen (mg/L)	--	2.43	2.4	2.37	2.05	1.28
pH	--	7.56	7.47	7.85	7.96	7.82

Notes:
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   J4 = The associated batch QC was outside the established quality control range for accuracy
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high. BDL results will be unaffected.

TABLE 2
GROUNDWATER SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB2	SLC16-SB3	SLC16-SB3	SLC16-SB3	SLC16-SB4
SAMPLE ID:		SLC16-SB2 51-53FT	SLC16-SB3 40-42FT	SLC16-SB3 46-48FT	SLC16-SB3 49-51FT	SLC16-SB4 40-42FT
SAMPLE DEPTH:		51-53 FT	40-42 FT	46-48 FT	49-51 FT	40-42 FT
PERMIABILITY ZONE:		Low k	High k	High k	Low k	High k
SAMPLE DATE:		05/17/2016	5/18/2016	5/18/2016	5/18/2016	05/17/2016
ANALYTE	CAS No.	mg/L	mg/L	mg/L	mg/L	mg/L
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	**0.22 V3**	<0.003	**0.00173 J**	<0.003	<0.003
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.001	<0.001	<0.001	<0.001
Bromoform	75-25-2	<0.001	<0.001	<0.001	<0.001	<0.001
Bromomethane	74-83-9	<0.005	<0.005	<0.005	<0.005	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorobenzene	108-90-7	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.001	<0.001	<0.001	<0.001
Chloroethane	75-00-3	**0.000592 J**	<0.005	<0.005	<0.005	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.05	<0.05	<0.05	<0.05
Chloroform	67-66-3	<0.005	<0.005	<0.005	<0.005	<0.005
Chloromethane	74-87-3	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.001	<0.001	<0.001	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.005	<0.005	<0.005	<0.005
1,1-Dichloroethane	75-34-3	**0.0589**	<0.001	<0.001	<0.001	<0.001
1,2-Dichloroethane	107-06-2	**0.00711**	<0.001	<0.001	<0.001	<0.001
1,1-Dichloroethene	75-35-4	**0.0519**	<0.001	<0.001	<0.001	<0.001
Cis-1,2-dichloroethene	156-59-2	**38.8**	<0.001	<0.001	**0.000531 J**	**0.000586 J**
Trans-1,2-dichloroethene	156-60-5	**0.105**	<0.001	<0.001	<0.001	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.001	<0.001	<0.001	<0.001
Methylene chloride	75-09-2	<0.005	**0.00135 J**	**0.00136 J**	<0.005	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.001	<0.001	<0.001	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trichloroethene	79-01-6	**18.9**	<0.001	<0.001	**0.00164**	**0.00897**
Trichlorofluoromethane	75-69-4	<0.005	<0.005	<0.005	<0.005	<0.005
Vinyl chloride	75-01-4	**0.0148**	<0.001	<0.001	**0.000528 J**	<0.001
Anions by Method 9056A						
Chloride	16887-00-6	**634**	**565**	**556**	**579**	**605**
Nitrate	14797-55-8	**0.542**	<0.1	<0.1	<0.1	<0.1
Sulfate	14808-79-8	**113**	**70.2**	**72.7**	**76.7**	**78.3**
Total Organic Carbon by Method 9060A						
TOC (Total organic carbon)	--	--	**2.65**	**2.97**	--	**3.12**
Dissolved Gases By Method RSK 175						
Methane	74-82-8	**0.0144**	**0.00904 J**	**0.0252**	**0.0286**	**0.0267**
Ethane	74-84-0	**0.0075 J**	<0.013	**0.00825 J**	<0.013	<0.013
Ethene	74-85-1	**0.00979 J**	<0.013	<0.013	<0.013	<0.013
Acetylene	74-86-2	<0.0208	<0.0208	<0.0208	<0.0208	<0.0208
Field Parameters - Before Sampling						
Temperature (°F)	--	83	78.7	80.8	84.5	85.9
Specific Conductivity (mS/cm)	--	2.51	2.36	2.32	2.35	2.21
Turbidity (NTU)	--	>1000	>1000	>1000	>1000	213
Redox (mV)	--	-39	-136	-221	-207	-209
Dissolved Oxygen (mg/L)	--	2.82	3.19	2.99	3	4.71
pH	--	7.94	7.19	7.73	7.68	7.88
Field Parameters - After Sampling						
Temperature (°F)	--	81.2	79.3	79.5	79.7	83.3
Specific Conductivity (mS/cm)	--	2.49	2.31	2.33	2.38	2.17
Turbidity (NTU)	--	187	665	>1000	81.6	>1000
Redox (mV)	--	-34	-194	-197	-187	-227
Dissolved Oxygen (mg/L)	--	2.6	4.19	3.54	3.62	2.08
pH	--	7.86	7.65	7.74	7.73	7.89

Notes:
1. Detections are shown in **bold**.
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   -- = Not analyzed or not applicable.
   J = The identification of the analyte is acceptable; the reported value is an estimate.
   J4 = The associated batch QC was outside the established quality control range for accuracy
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high. BDL results will be unaffected.

TABLE 2
GROUNDWATER SAMPLING AND TESTING RESULTS: SPACE LAUNCH COMPLEX 16

Cape Canaveral Air Force Station
Cape Canaveral, Florida

SAMPLE LOCATION:		SLC16-SB4	SLC16-SB4	SLC16-SB5	SLC16-SB5	SLC16-SB5
SAMPLE ID:		SLC16-SB4 45-47FT	SLC16-SB4 49-51FT	SLC16-SB5 35-37FT	SLC16-SB5 53-55FT	SLC16-SB5 55-57FT
SAMPLE DEPTH:		45-47 FT	49-51 FT	35-37 FT	53-55 FT	55-57 FT
PERMIABILITY ZONE:		High k	Low k	High k	High k	High k
SAMPLE DATE:		05/17/2016	05/17/2016	5/18/2016	5/18/2016	5/18/2016
ANALYTE	CAS No.	mg/L	mg/L	mg/L	mg/L	mg/L
1,4-Dioxane by Method 8260B-SIM						
1,4-Dioxane	123-91-1	<0.003	<0.003	<0.003	<0.003	<0.003
Volatile Organic Compounds by Method 8260B						
Bromodichloromethane	75-27-4	<0.001	<0.001	<0.001	<0.001	<0.001
Bromoform	75-25-2	<0.001	<0.001	<0.001	<0.001 J4	<0.001 J4
Bromomethane	74-83-9	<0.005	<0.005	<0.005	<0.005	<0.005
Carbon tetrachloride	56-23-5	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorobenzene	108-90-7	<0.001	<0.001	<0.001	<0.001	<0.001
Chlorodibromomethane	124-48-1	<0.001	<0.001	<0.001	<0.001	<0.001
Chloroethane	75-00-3	<0.005	<0.005	<0.005	<0.005	<0.005
2-Chloroethyl vinyl ether	110-75-8	<0.05	<0.05	<0.05	<0.05	<0.05
Chloroform	67-66-3	<0.005	<0.005	<0.005	<0.005	<0.005
Chloromethane	74-87-3	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025
1,2-Dichlorobenzene	95-50-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,3-Dichlorobenzene	541-73-1	<0.001	<0.001	<0.001	<0.001	<0.001
1,4-Dichlorobenzene	106-46-7	<0.001	<0.001	<0.001	<0.001	<0.001
Dichlorodifluoromethane	75-71-8	<0.005	<0.005	<0.005	<0.005	<0.005
1,1-Dichloroethane	75-34-3	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloroethane	107-06-2	<0.001	<0.001	<0.001	<0.001	<0.001
1,1-Dichloroethene	75-35-4	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,2-dichloroethene	156-59-2	**0.00291**	**0.00108**	**0.000261 J**	**0.000749 J**	**0.00249**
Trans-1,2-dichloroethene	156-60-5	<0.001	<0.001	<0.001	<0.001	<0.001
1,2-Dichloropropane	78-87-5	<0.001	<0.001	<0.001	<0.001	<0.001
Cis-1,3-dichloropropene	10061-01-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trans-1,3-dichloropropene	10061-02-6	<0.001	<0.001	<0.001	<0.001	<0.001
Methylene chloride	75-09-2	<0.005	<0.005	<0.005	<0.005	<0.005
1,1,2,2-Tetrachloroethane	79-34-5	<0.001	<0.001	<0.001	<0.001	<0.001
Tetrachloroethene	127-18-4	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,1-Trichloroethane	71-55-6	<0.001	<0.001	<0.001	<0.001	<0.001
1,1,2-Trichloroethane	79-00-5	<0.001	<0.001	<0.001	<0.001	<0.001
Trichloroethene	79-01-6	**0.0388**	**0.0209**	**0.00118**	<0.001	**0.00322**
Trichlorofluoromethane	75-69-4	<0.005	<0.005	<0.005	<0.005	<0.005
Vinyl chloride	75-01-4	<0.001	<0.001	<0.001	<0.001	<0.001
Anions by Method 9056A						
Chloride	16887-00-6	**556**	**572**	**635**	**675**	**652**
Nitrate	14797-55-8	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfate	14808-79-8	**82.9**	**82.4**	**0.205 J**	**15.8**	**33.8**
Total Organic Carbon by Method 9060A						
TOC (Total organic carbon)	--	**4.47**	--	**6.2**	**4.59**	--
Dissolved Gases By Method RSK 175						
Methane	74-82-8	**0.0234**	**0.0248**	**13**	**2.01**	**0.344**
Ethane	74-84-0	**0.00768 J**	**0.00784 J**	<0.013	<0.013	<0.013
Ethene	74-85-1	<0.013	<0.013	<0.013	<0.013	<0.013
Acetylene	74-86-2	<0.0208	<0.0208	<0.0208	<0.0208	<0.0208
Field Parameters - Before Sampling						
Temperature (°F)	--	83.4	84.2	90	92.1	92.5
Specific Conductivity (mS/cm)	--	2.28	2.29	2.88	2.7	2.6
Turbidity (NTU)	--	>1000	>1000	>1000	>1000	>1000
Redox (mV)	--	-244	-170	-122	-298	-281
Dissolved Oxygen (mg/L)	--	1.59	5.23	3.23	1.98	1.54
pH	--	7.97	8.05	7.78	7.85	7.84
Field Parameters - After Sampling						
Temperature (°F)	--	79.1	82.4	84.4	84.6	84.8
Specific Conductivity (mS/cm)	--	2.23	2.28	2.86	2.74	2.64
Turbidity (NTU)	--	>1000	752	392	797	730
Redox (mV)	--	-184	-209	-91	-260	-260
Dissolved Oxygen (mg/L)	--	2.69	2.34	4.8	4.21	5.05
pH	--	7.92	7.91	7.79	7.77	7.86

Notes:
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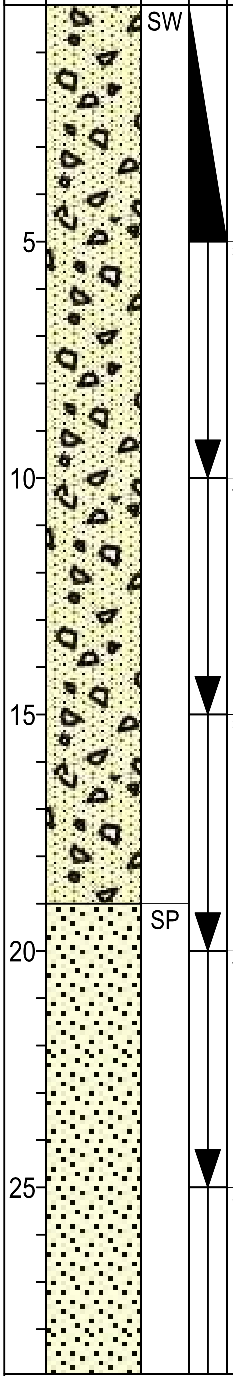
   V3 = The internal standard exhibited poor recovery due to sample matrix interference. The analytical results will be biased high. BDL results will be unaffected.

BORING ID: **1381-SB1**

LOGGED BY: Luz Rocha
DRILLING COMPANY: Groundwater Protection
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT
BORING DIAMETER (in): 2.0

COMPLETION DATE: 5/12/2016
GROUND SURFACE ELEVATION: Not surveyed
LATITUDE: 3149532 LONGITUDE: 543044
COORDINATE SYSTEM: UTM Zone 17N
SATURATION ENCOUNTERED: 10.0 ft bgs



Depth (ft bgs)	USCS	% Recovery	Soil Lab Sample	GW Lab Sample	PID (ppm)	Water Level	Soil Description
							GROUND SURFACE
	SW						White to light brown medium to fine SAND (SW), dry, soft, no odor
					0.0		
5		3/5					-moist below 5 ft -light brown with gravel throughout from 5 to 10 ft, shells present at 10 ft
10		4/5			0.6	▽	-very moist to saturated below 10 ft -shells present below 10 ft
							-gray below 12 ft
15		3.5/5			0.3		-medium to fine grained below 15 ft
	SP						Light gray fine SAND (SP), soft, saturated, no odor
20		4/5			75.7		
							-seam with shells from 23.5 to 23.8 ft
25		5/5			5.1		-gray with slight to very slight odor from 25-31 ft

GSI ENVIRONMENTAL

LOG OF SOIL BORING
1381-SB1

Cape Canaveral Air Force Station
Facility 1381

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Depth (ft bgs)	USCS	% Recovery	PID (ppm)	Soil Description
	SP	5/5		Light gray fine SAND (SP), soft, saturated, no odor -gray with slight to very slight odor from 25-31 ft
30		5/5	0.1	
35	SW/ SP	5/5	0.0	Light gray SAND with fine sand and shells present (SW/SP), minor clay towards bottom and last 0.5 ft increased clay content
			0.0	
40	SW	5/5		Gray SAND (SW), saturated, soft, slight odor -minor clay from 40 to 42.8 ft -shell present from 42.8 to 45 ft
45	GM	5/5	0.0	Gray coastal deposits/ shells with silt (GM), saturated, coarse, slight odor -increased sand content below 49 ft
50		5/5	0.8	
	CH			Gray CLAY (CH), iron oxide nodules/ staining throughout, soft, high moisture content, no odor
55		4/5	0.0	-minor dark gray mottling and few iron oxide nodules from 55 to 60 ft -medium stiff with medium moisture content below 55 ft
			0.0	
	ML			Greenish gray clayey SILT (ML), soft, moist, shell pieces present, no odor
60			0.0	**TOTAL DEPTH = 60.0 FT BGS**

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LOG OF SOIL BORING

1381-SB1

Cape Canaveral Air Force Station
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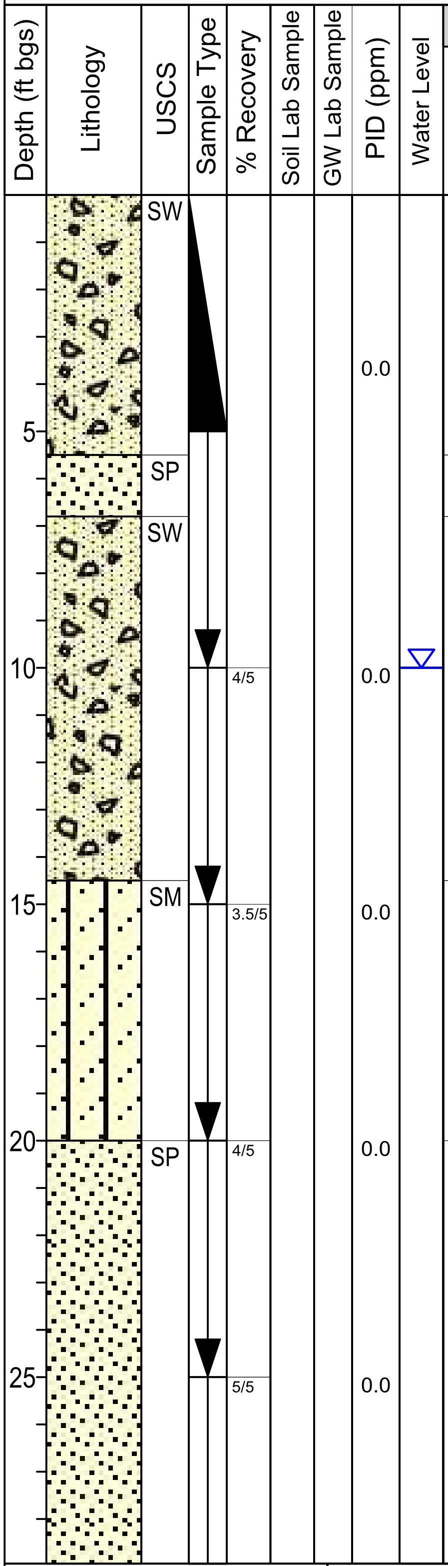
GSI Job No. 3926

Issued: 2 June 2016

BORING ID: **1381-SB2**

LOGGED BY: Luz Rocha	COMPLETION DATE: 5/12/2016
DRILLING COMPANY: Groundwater Protection	GROUND SURFACE ELEVATION: Not surveyed
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT	LATITUDE: 3149512 LONGITUDE: 543002
BORING DIAMETER (in): 2.0	COORDINATE SYSTEM: UTM Zone 17N
	SATURATION ENCOUNTERED: 10.0 ft bgs



Depth (ft bgs)	USCS	% Recovery	PID (ppm)	Soil Description
				GROUND SURFACE
	SW			Brown to dark brown SAND (SW), medium grained, dry, soft, no odor
			0.0	
5				
	SP			White fine SAND (SP), soft, dry, no odor
	SW			Light brown SAND (SW), coarse, moist, soft, no odor
10		4/5	0.0	-shell pieces and very moist to saturated below 10 ft
				-gray shells from 14 to 15 ft
15	SM	3.5/5	0.0	Gray SAND with silt (SM), fine to medium grained, saturated, soft, very slight odor towards 15 ft
				-seam of coarse sand of 2 inches at 18 ft
20	SP	4/5	0.0	Gray fine SAND (SP), saturated, soft, odor
25		5/5	0.0	

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LOG OF SOIL BORING
1381-SB2

Cape Canaveral Air Force Station
Facility 1381

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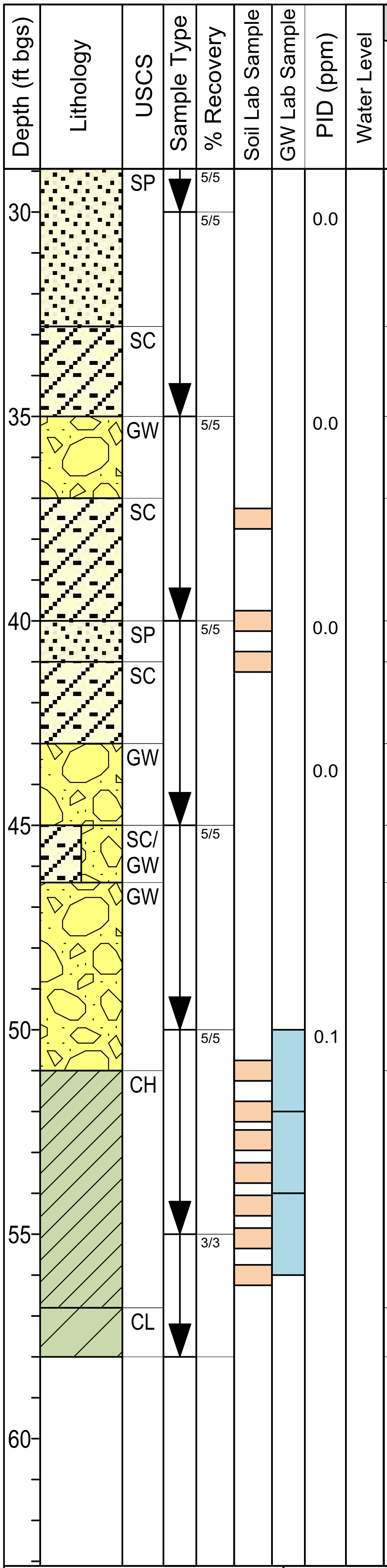

Soil Description

Gray fine SAND (SP), saturated, soft, odor

Gray fine SAND with clay (SC), saturated, soft, no odor

Coastal deposits/ shells (GW) with little gray sand, saturated, no odor

Light gray clayey SAND (SC), saturated, soft, no odor

-medium stiff and high moisture content from 38.6 to 40 ft

Gray fine SAND (SP), saturated, soft, odor

Light gray clayey SAND (SC), medium stiff, high moisture content, no odor

Coastal deposits/ shells (GW) with little gray sand, saturated, slight odor

Coastal deposits/ shells with clay and sand (SC/GW), saturated, soft, no odor

Coastal deposits/ shells with minor fine sand and silt (GW), saturated, no odor

Gray CLAY (CH), low moisture content, stiff, iron oxide staining, no odor

Gray silty CLAY (CL) with rocks, medium stiff, medium moisture content, no odor

TOTAL DEPTH = 58.0 FT BGS

GSI ENVIRONMENTAL

LOG OF SOIL BORING
1381-SB2

Cape Canaveral Air Force Station
Facility 1381

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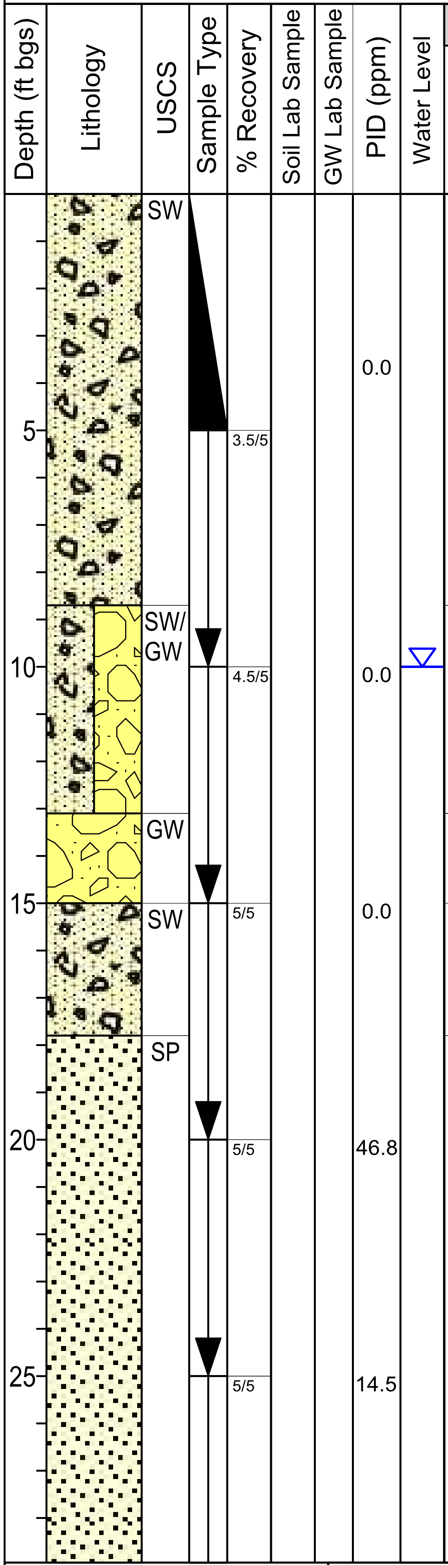
BORING ID: **1381-SB3**

LOGGED BY: Luz Rocha
DRILLING COMPANY: Groundwater Protection
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT
BORING DIAMETER (in): 2.0

COMPLETION DATE: 5/13/2016
GROUND SURFACE ELEVATION: Not surveyed
LATITUDE: 3149563 LONGITUDE: 543093
COORDINATE SYSTEM: UTM Zone 17N
SATURATION ENCOUNTERED: 10.0 ft bgs



Soil Description

GROUND SURFACE

Light brown to dark brown SAND (SW), dry, soft, rocks on top foot, medium grained, no odor

Light gray medium SAND and GRAVEL with shells (SW/GW), moist, soft, no odor

-very moist to saturated below 10 ft

Dark gray coastal deposits/ shells (GW), very moist to saturated, soft, no odor

Light gray SAND (SW), saturated, soft, shells and coarse to medium sand, no odor

Light gray to gray fine SAND (SP), saturated, soft, no odor

-seam of shells of 3 inches at 23.5 ft

-very slight odor from 25 to 30 ft

GSI ENVIRONMENTAL

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1381-SB3

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Facility 1381

GSI Job No. 3926

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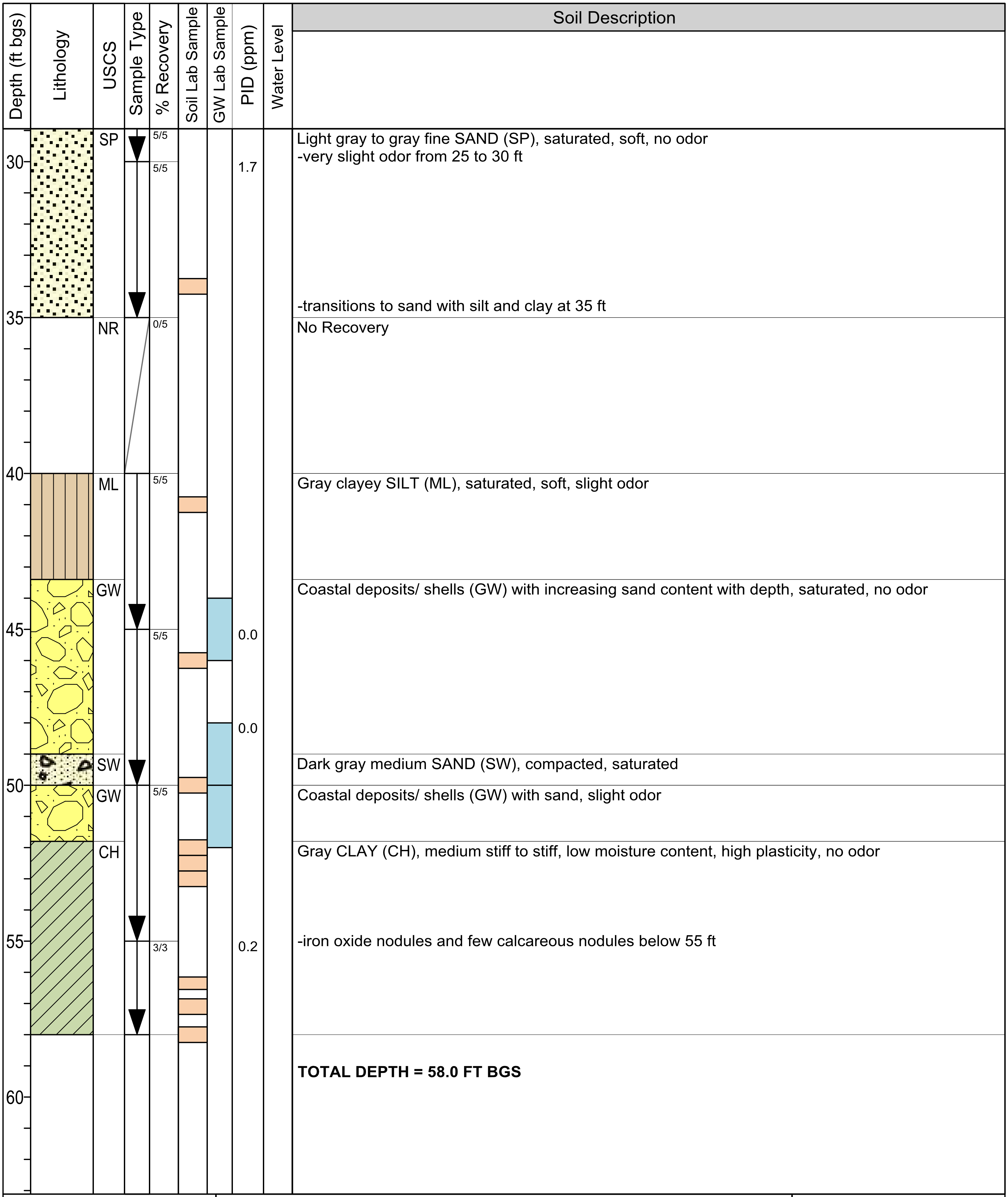

Depth (ft bgs)	Lithology	USCS	Sample Type	% Recovery	Soil Lab Sample	GW Lab Sample	PID (ppm)	Water Level	Soil Description
		SP		5/5					Light gray to gray fine SAND (SP), saturated, soft, no odor -very slight odor from 25 to 30 ft
30				5/5			1.7		
									-transitions to sand with silt and clay at 35 ft
35		NR		0/5					No Recovery
40		ML		5/5					Gray clayey SILT (ML), saturated, soft, slight odor
		GW							Coastal deposits/ shells (GW) with increasing sand content with depth, saturated, no odor
45				5/5			0.0		
							0.0		
		SW							Dark gray medium SAND (SW), compacted, saturated
50		GW		5/5					Coastal deposits/ shells (GW) with sand, slight odor
		CH							Gray CLAY (CH), medium stiff to stiff, low moisture content, high plasticity, no odor
55				3/3			0.2		-iron oxide nodules and few calcareous nodules below 55 ft
									TOTAL DEPTH = 58.0 FT BGS
60									

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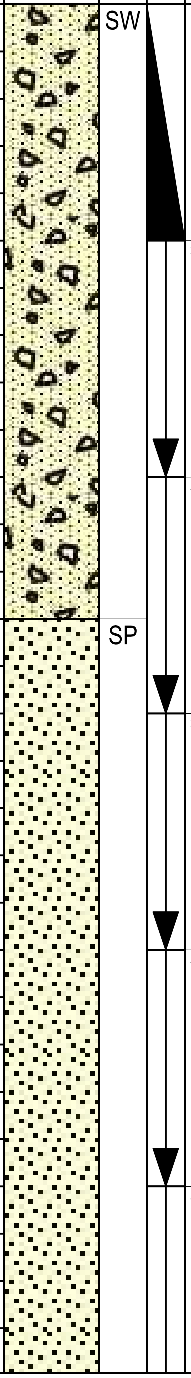
BORING ID: **1381-SB4**

LOGGED BY: Luz Rocha
DRILLING COMPANY: Groundwater Protection
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT
BORING DIAMETER (in): 2.0

COMPLETION DATE: 5/13/2016
GROUND SURFACE ELEVATION: Not surveyed
LATITUDE: 3152959 LONGITUDE: 543322
COORDINATE SYSTEM: UTM Zone 17N
SATURATION ENCOUNTERED: 10.0 ft bgs



Depth (ft bgs)	Lithology	USCS	Sample Type	% Recovery	Soil Lab Sample	GW Lab Sample	PID (ppm)	Water Level	Soil Description
									GROUND SURFACE
		SW							White to light brown SAND (SW), coarse to medium grained, dry, soft, no odor
							0.0		
5				3/5					-moist below 5 ft -transitions to moist gray sand below 5.5 ft -lots of shells present from 5 to 10 ft
10				5/5			1.3	▽	-very moist to saturated below 10 ft
		SP							Gray fine to medium SAND (SP), saturated, soft, no odor
15				3.5/5			0.8		
20				5/5			0.0		-shells present from 20 to 25 ft
25				5/5			0.0		

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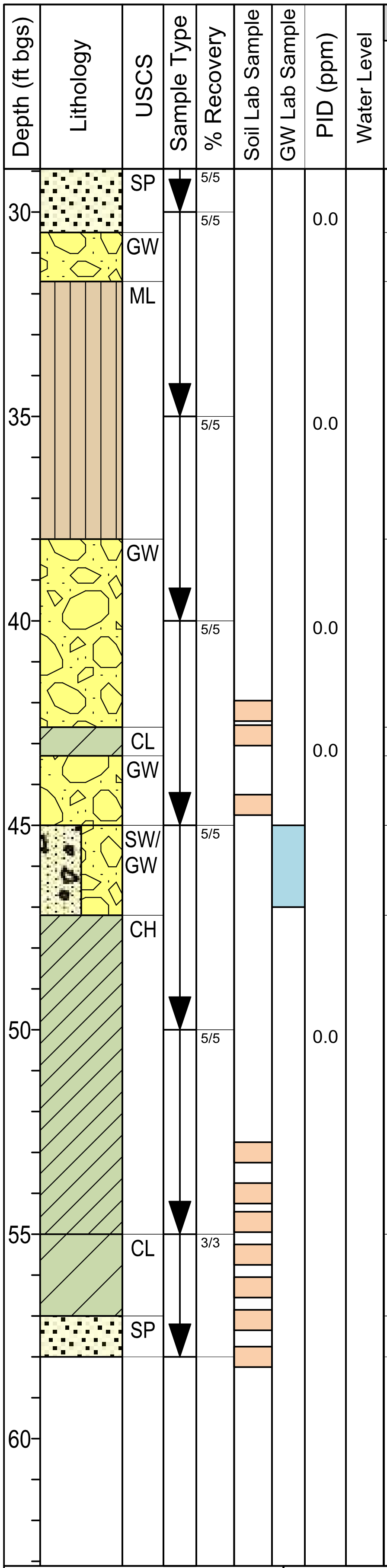

Soil Description

Gray fine to medium SAND (SP), saturated, soft, no odor

Coastal deposits/ shells with minor sand and silt (GW), saturated, no odor

Gray SILT with minor clay and sand (ML), saturated, soft, no odor

-seam of shells from 35 to 35.3 ft

Coastal deposits/ shells (GW) with little to no sand, saturated, no odor

Gray silty CLAY (CL), high moisture content, soft, no odor

Coastal deposits/ shells (GW) with sand, saturated, no odor

Gray medium to fine SAND and coastal deposits/ shells (SW/GW), saturated, soft, no odor

Gray CLAY (CH), medium to low moisture content, medium stiff to stiff, high plasticity, no odor

-some iron oxide nodules from 50 to 55 ft

Greenish gray sandy silty CLAY (CL), medium moisture content, very stiff, some orange mottling towards the top, and increasing silt content with depth

Greenish gray SAND (SP), fine to medium grained, saturated, shells present, no odor

TOTAL DEPTH = 58.0 FT BGS

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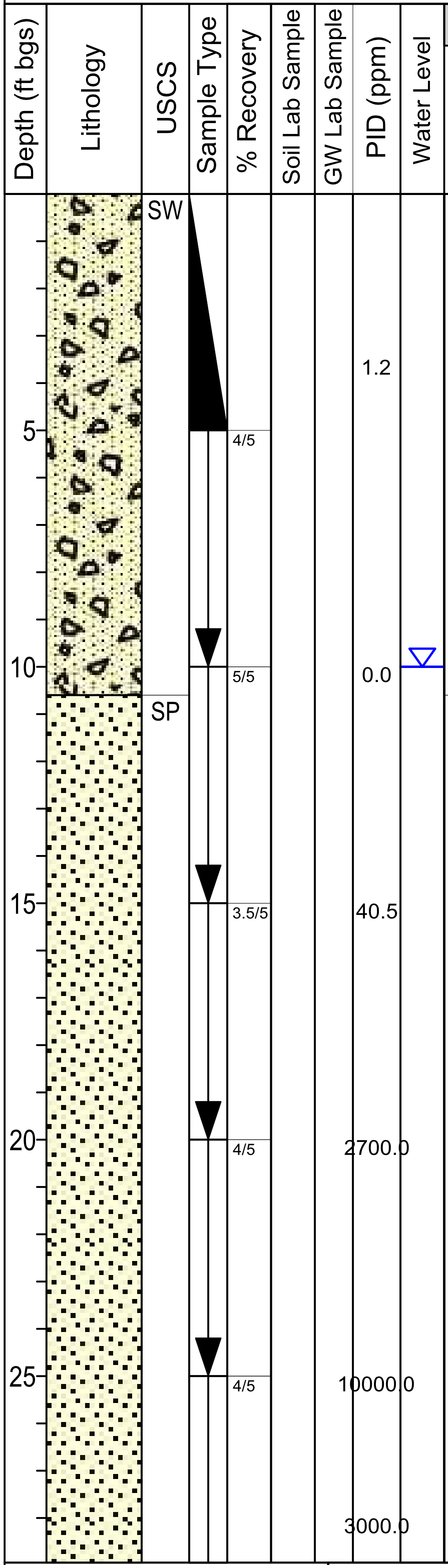
BORING ID: **SLC16-SB1**

LOGGED BY: Luz Rocha
DRILLING COMPANY: Groundwater Protection
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT
BORING DIAMETER (in): 2.0

COMPLETION DATE: 5/16/2016
GROUND SURFACE ELEVATION: Not surveyed
LATITUDE: 3153069 LONGITUDE: 543270
COORDINATE SYSTEM: UTM Zone 17N
SATURATION ENCOUNTERED: 10.0 ft bgs



Depth (ft bgs)	USCS	% Recovery	PID (ppm)	Water Level	Soil Description
					GROUND SURFACE
0	SW				Light brown to gray medium fine SAND (SW), dry, soft, no odor
			1.2		-seam of shells with light gray fine to medium sand from 3.7 to 4 ft -Gray below 4 ft
5		4/5			-medium to coarse sand, moist below 5 ft
10		5/5	0.0	▽	-seam of shells with little sand from 10 to 10.6 ft
	SP				Gray fine to medium SAND (SP), saturated, soft, no odor
					-seam of shells with sand from 12.5-13 ft
15		3.5/5	40.5		-shell pieces present throughout 15 to 25 ft
20		4/5	2700.0		
25		4/5	10000.0		-increasing silt content below 25 ft
			3000.0		

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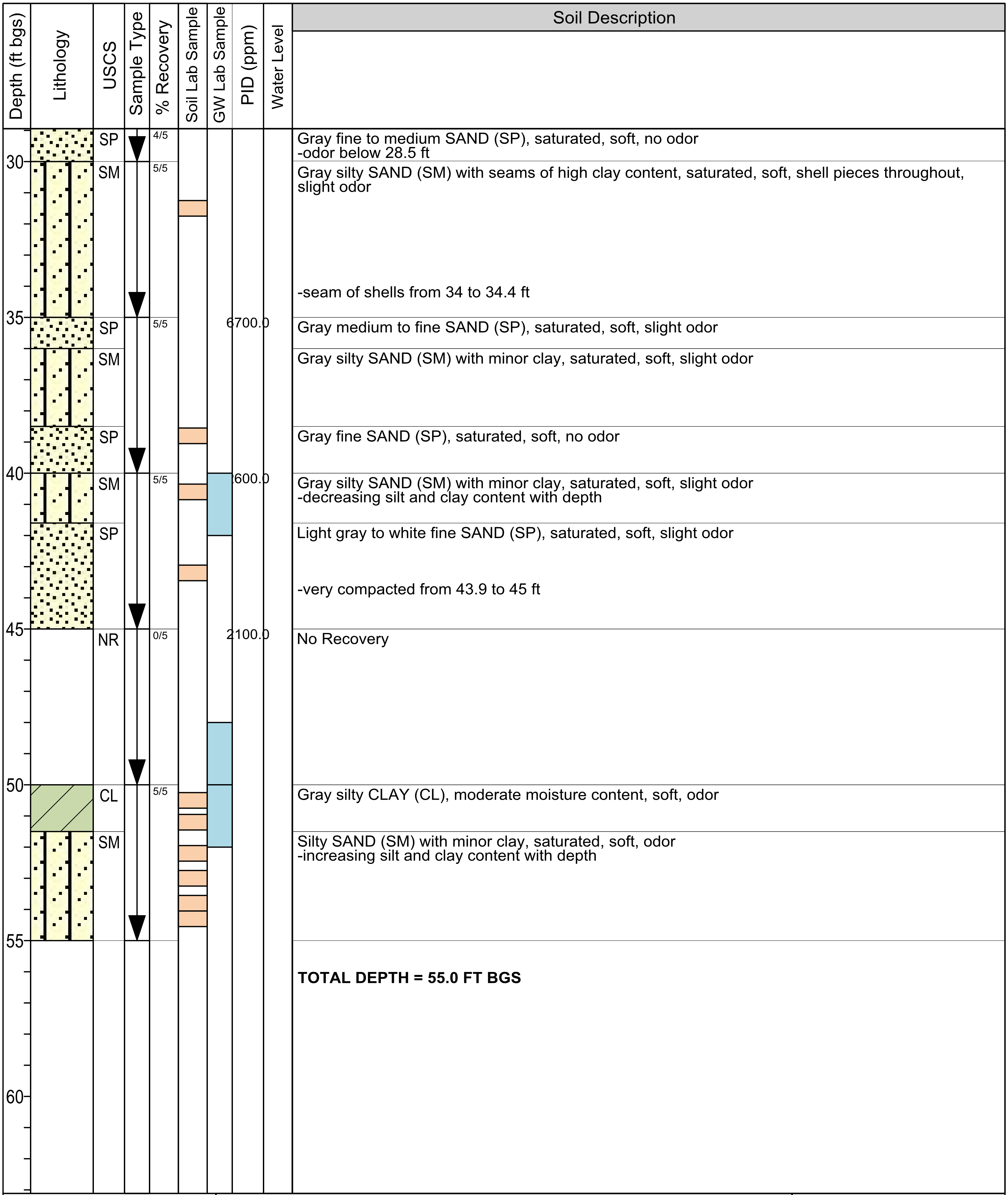

Depth (ft bgs)	Lithology	USCS	Sample Type	% Recovery	Soil Lab Sample	GW Lab Sample	PID (ppm)	Water Level	Soil Description
		SP		4/5					Gray fine to medium SAND (SP), saturated, soft, no odor -odor below 28.5 ft
30		SM		5/5					Gray silty SAND (SM) with seams of high clay content, saturated, soft, shell pieces throughout, slight odor -seam of shells from 34 to 34.4 ft
35		SP		5/5			6700.0		Gray medium to fine SAND (SP), saturated, soft, slight odor
		SM							Gray silty SAND (SM) with minor clay, saturated, soft, slight odor
		SP							Gray fine SAND (SP), saturated, soft, no odor
40		SM		5/5			2600.0		Gray silty SAND (SM) with minor clay, saturated, soft, slight odor -decreasing silt and clay content with depth
		SP							Light gray to white fine SAND (SP), saturated, soft, slight odor -very compacted from 43.9 to 45 ft
45		NR		0/5			2100.0		No Recovery
50		CL		5/5					Gray silty CLAY (CL), moderate moisture content, soft, odor
		SM							Silty SAND (SM) with minor clay, saturated, soft, odor -increasing silt and clay content with depth
55									**TOTAL DEPTH = 55.0 FT BGS**

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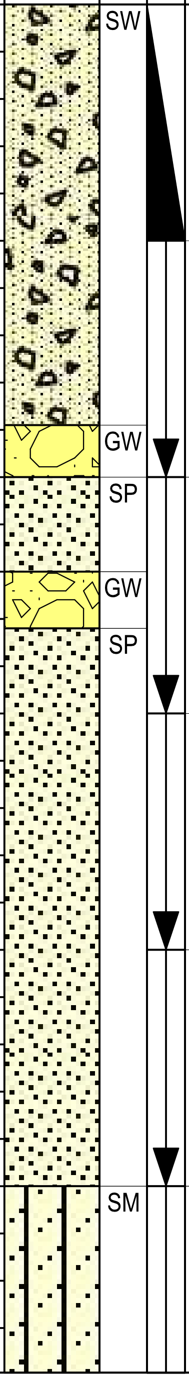
BORING ID: **SLC16-SB2**

LOGGED BY: Luz Rocha
DRILLING COMPANY: Groundwater Protection
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT
BORING DIAMETER (in): 2.0

COMPLETION DATE: 5/17/2016
GROUND SURFACE ELEVATION: Not surveyed
LATITUDE: 3153065 LONGITUDE: 543264
COORDINATE SYSTEM: UTM Zone 17N
SATURATION ENCOUNTERED: 9.0 ft bgs



Depth (ft bgs)	Lithology	USCS	Sample Type	% Recovery	Soil Lab Sample	GW Lab Sample	PID (ppm)	Water Level	Soil Description
									GROUND SURFACE
		SW							Light brown to gray SAND (SW), medium to fine grained, dry, soft, no odor
							0.5		
5				3.5/5					
									-seam of medium to fine sand (SP), moist to saturated from 8 to 8.9 ft
								▽	
		GW							Coastal deposits/ shells (GW) with light brown to gray sand, saturated, no odor
10		SP		5/5			0.7		Brown fine SAND (SP), saturated, soft, no odor -few shell pieces from 10 to 12 ft
		GW							Coastal deposits/ shells (GW) with gray sand, saturated, no odor
		SP							Gray fine SAND (SP) with shell pieces, saturated, soft, no odor
15				3.5/5			1.0		
20				3.5/5			23.9		-fewer shell pieces below 20 ft
25		SM		4.5/5			500.8		Gray silty SAND (SM), saturated, soft, very few shell pieces, slight odor

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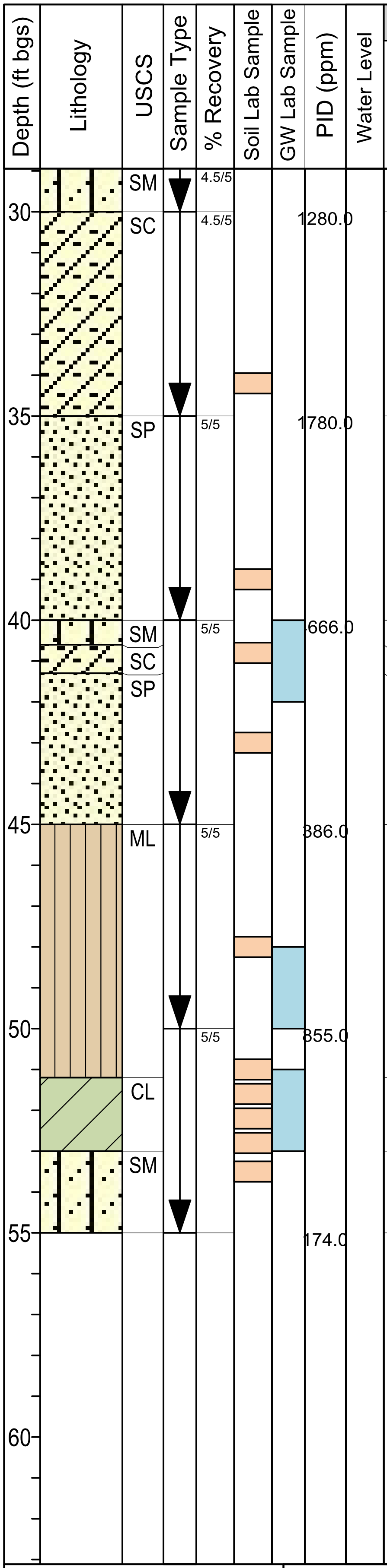

Soil Description
Gray silty SAND (SM), saturated, soft, very few shell pieces, slight odor
Gray silty clayey SAND (SC), saturated, soft, odor -seam with shells at 33.3 ft -increased clay content below 33.7 ft -seam with shells at 34.6 ft
Gray fine SAND with silt and minor clay (SP), saturated, soft, odor
Gray silty SAND (SM), moist, medium stiff, odor
Gray clayey SAND (SC), high moisture content, soft, odor
Gray fine SAND with silt and minor clay (SP), saturated, soft, odor -compacted stiff sand from 44 to 45 ft
Greenish gray sandy SILT (ML), saturated, soft, odor -yellowish-orange mottling from 45 to 48.6 ft -seam of clayey sandy silt from 48.6 to 49.4 ft -shells with silt below 49.4 ft -gray clayey silt below 50 ft
Gray silty CLAY (CL), high moisture content, soft, odor
Gray silty SAND (SM), saturated, soft, odor
TOTAL DEPTH = 55.0 FT BGS

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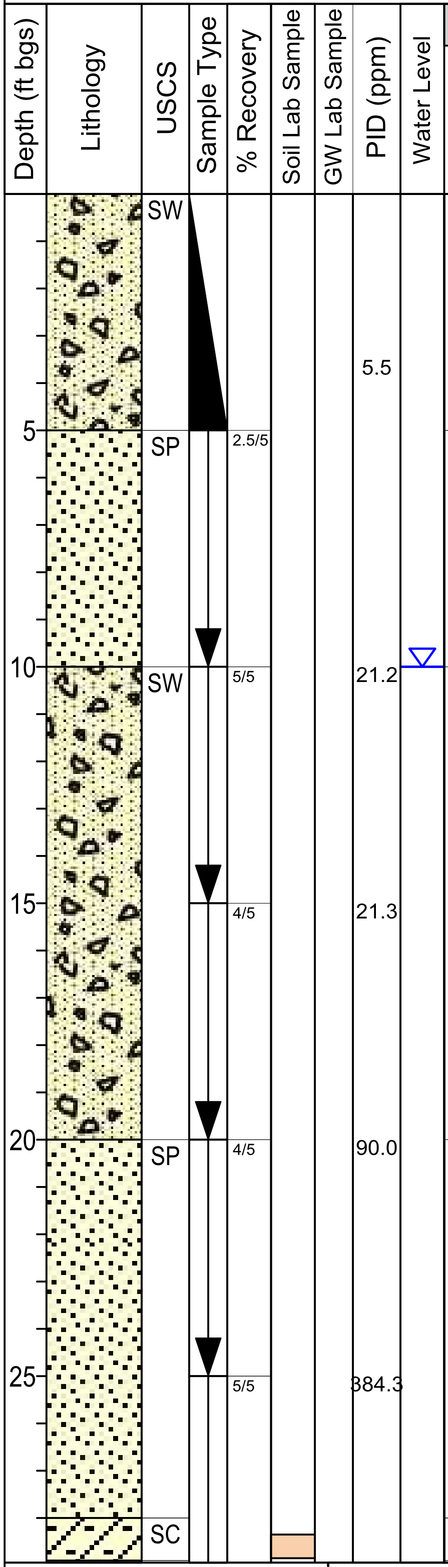
BORING ID: **SLC16-SB3**

LOGGED BY: Luz Rocha	COMPLETION DATE: 5/17/2016
DRILLING COMPANY: Groundwater Protection	GROUND SURFACE ELEVATION: Not surveyed
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT	LATITUDE: 3153088 LONGITUDE: 543307
BORING DIAMETER (in): 2.0	COORDINATE SYSTEM: UTM Zone 17N
	SATURATION ENCOUNTERED: 10.0 ft bgs



Soil Description

GROUND SURFACE

Depth (ft bgs)	USCS	% Recovery	PID (ppm)	Soil Description
	SW		5.5	Light brown to dark brown coarse to fine SAND (SW), moist , soft, no odor
5	SP	2.5/5		Yellowish brown medium to fine SAND (SP), moist to saturated, soft, no odor -shells with little sand below 9.2 ft
10	SW	5/5	21.2	Gray medium to fine SAND (SW) with shells, saturated, soft, no odor -light brown mottling from 10 to 12 ft
15		4/5	21.3	-fewer shells below 15 ft
20	SP	4/5	90.0	Gray SAND (SP), saturated, soft
25		5/5	384.3	-slight odor below 25 ft
	SC			Gray clayey SAND (SC) with silt, saturated, soft, slight odor

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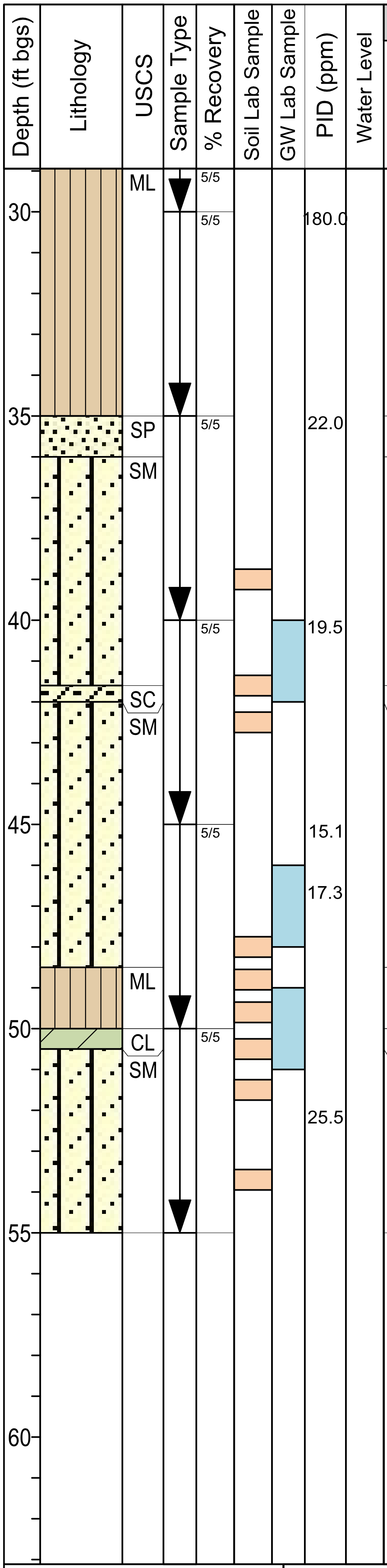

Soil Description

Gray clayey sandy SILT (ML), saturated, soft, some shells present, no odor
-slight odor below 30 ft

-seam of clayey silt of 3 inches at 31.3 ft and 33.2 ft
-several shells from 31.5 to 33.4 ft

Gray fine SAND (SP), saturated, soft, odor

Gray silty SAND (SM), saturated, soft, few shells throughout, odor

-compacted from 39.5 to 40 ft
-gravel/shells present from 40 to 41.6 ft

Gray clayey SAND (SC), saturated, soft, odor

Gray silty SAND (SM), saturated, soft, few shells throughout, odor

-gray/light gray transitions to white with orange mottling/staining from 43.5 to 45 ft

Gray sandy SILT (ML), saturated, soft, few shells throughout, no odor

Gray silty CLAY (CL), soft, high moisture content

Gray silty SAND (SM), saturated, soft

-slightly compacted from 54 to 55 ft

TOTAL DEPTH = 55.0 FT BGS

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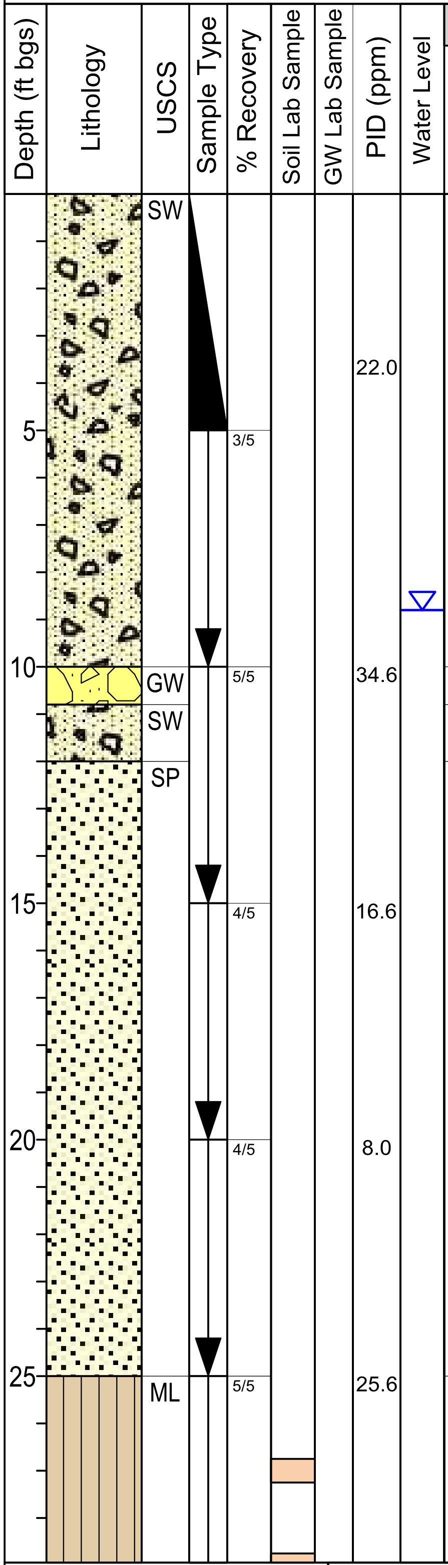
BORING ID: **SLC16-SB4**

LOGGED BY: Luz Rocha	COMPLETION DATE: 5/17/2016
DRILLING COMPANY: Groundwater Protection	GROUND SURFACE ELEVATION: Not surveyed
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT	LATITUDE: 3153044 LONGITUDE: 543280
BORING DIAMETER (in): 2.0	COORDINATE SYSTEM: UTM Zone 17N
	SATURATION ENCOUNTERED: 8.8 ft bgs



Soil Description

GROUND SURFACE

White to light brown medium SAND (SW), soft, dry, no odor

-moist to saturated with very slight odor below 5 ft

-seam of shells between 7.8 and 8.8 ft

-saturated and gray medium to fine sand below 8.8 ft

Light brown coastal deposits/ shells with little sand (GW), saturated, slight odor

Gray medium SAND (SW), saturated, soft, slight odor

Light gray fine to medium SAND (SP), saturated, soft, slight odor

-shell pieces below 15 ft

-seam of shells at 17 ft

Gray sandy SILT (ML), saturated, soft, increasing clay content with depth, odor

-clayey silt with sand below 28.3 ft

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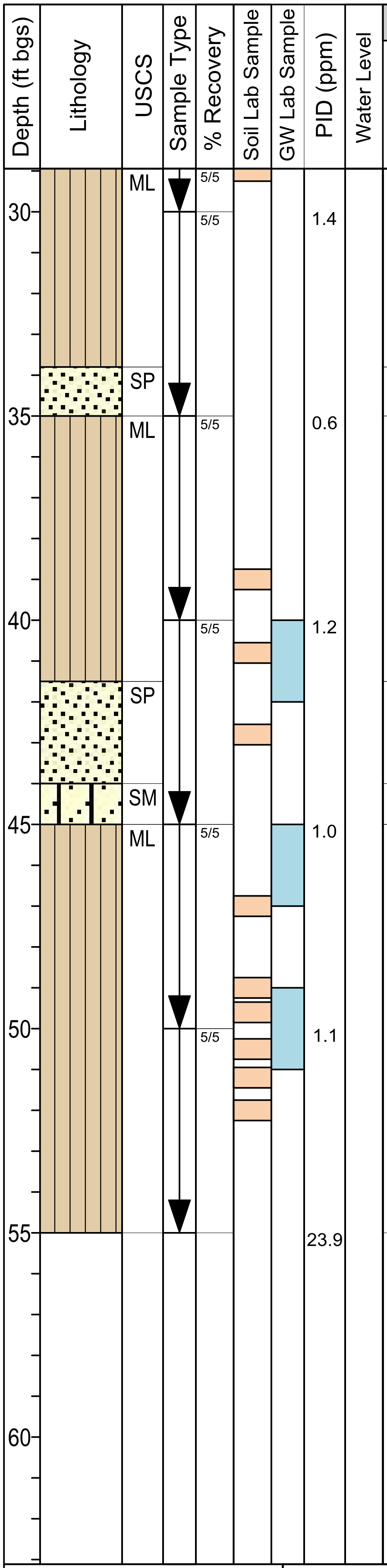

Soil Description

Gray sandy SILT (ML), saturated, soft, increasing clay content with depth, odor

-seam of shells at 31.5 ft

-seam of shells at 32.9 ft

Gray medium SAND (SP), saturated, soft, no odor

Gray sandy SILT (ML), saturated, soft, with fine sand, very slight odor
-compacted from 35-35.8 ft

-clayey silt below 39.6 ft

Light gray to greenish gray fine SAND (SP), saturated, soft, very slight odor

-seam of rocks from 42.8 to 43.3 ft

Light gray silty SAND (SM), compacted/ stiff, saturated

Gray sandy SILT (ML), soft, saturated, no odor

-increasing clay content with depth below 47 ft

-clayey silt from 48 to 50 ft

-odor below 50 ft
-sandy silt with clay from 50 to 53.3 ft

-no clay content below 53.3 ft

TOTAL DEPTH = 55.0 FT BGS

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BORING ID: **SLC16-SB5**

LOGGED BY: Luz Rocha
DRILLING COMPANY: Groundwater Protection
DRILLING METHOD AND EQUIPMENT: Geoprobe - 7822 DT
BORING DIAMETER (in): 2.0

COMPLETION DATE: 5/18/2016
GROUND SURFACE ELEVATION: Not surveyed
LATITUDE: 3149795 LONGITUDE: 543021
COORDINATE SYSTEM: UTM Zone 17N
SATURATION ENCOUNTERED: 5.0 ft bgs

Depth (ft bgs)	Lithology	USCS	Sample Type	% Recovery	Soil Lab Sample	GW Lab Sample	PID (ppm)	Water Level	Soil Description
									GROUND SURFACE
		SW							Light brown coarse to medium SAND (SW), soft, moist, no odor
							4.3		
5				4.5/5				▽	
									-medium sand with lots of shells, odor, and saturated below 7 ft
10				3.5/5			65.5		-gray medium to fine sand below 10 ft
									-lots of shells below 13.5 ft
15		SP		3.5/5			114.0		Gray medium to fine SAND (SP), saturated, soft, odor
									-seam of shells at 18 ft and 18.8 ft
20				3.5/5			238.0		
25		SM		5/5			38.9		Gray silty SAND (SM), fine sand, saturated, soft, odor
					▨				
									-clayey silty sand with increasing clay content below 28 ft
					▨				

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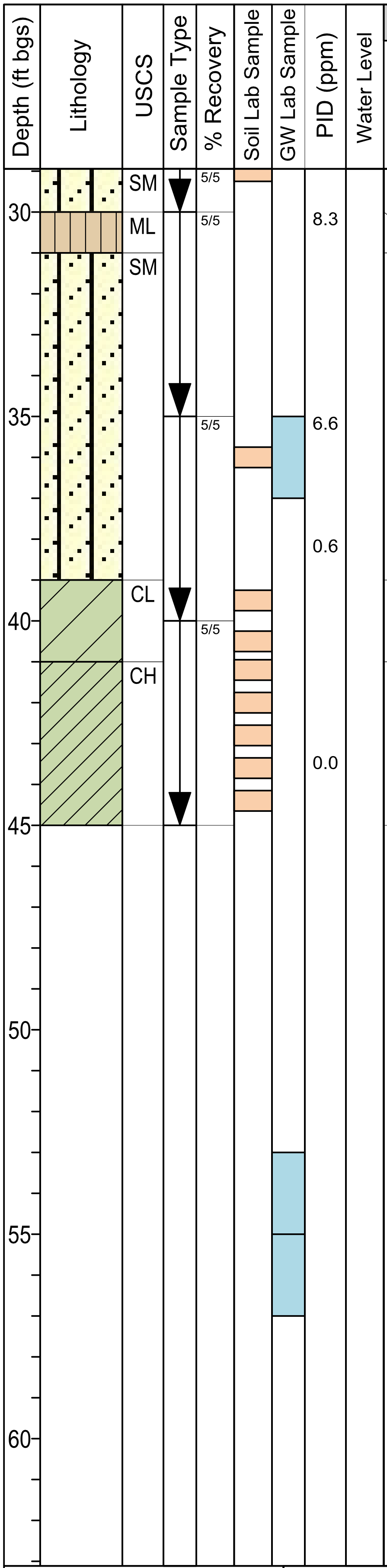

Soil Description

Gray silty SAND (SM), fine sand, saturated, soft, odor
-clayey silty sand with increasing clay content below 28 ft

Gray clayey sandy SILT (ML), saturated, soft, slight odor

Gray silty SAND (SM), saturated, soft, gravel and shell pieces throughout, slight odor
-increasing clay content below 32 ft

-seam of clayey SILT (ML) from 33 to 33.5 ft

Gray silty CLAY (CL) with sand and some shells, soft to medium stiff, high moisture content, very slight odor

Gray CLAY (CH) with silt, moderate plasticity, medium stiff, low moisture content, no odor

-shells present at 43.8 ft and below

TOTAL DEPTH = 45.0 FT BGS

GSI ENVIRONMENTAL

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APPENDIX B. LIST OF PUBLICATIONS

Published

- Adamson, D.T., Mahendra, S., Walker, K., Rauch, S., Sengupta, S., and Newell, C.J., 2014. A Multi-Site Survey to Identify the Scale of the 1, 4-Dioxane Problem at Contaminated Groundwater Sites. *Environmental Science & Technology Letters*, 1(5): 254-258.
- Adamson, D.T., Anderson, R.H., Mahendra, S. and Newell, C.J., 2015. Evidence of 1, 4-dioxane attenuation at groundwater sites contaminated with chlorinated solvents and 1, 4-dioxane. *Environmental science & technology*, *49*(11): 6510-6518.
- Adamson D.T., de Blanc P.C., Farhat S.K., Newell C.J., 2016. Implications of matrix diffusion on 1, 4-dioxane persistence at contaminated groundwater sites. *Science of The Total Environment*, 562:98-107.

In Preparation

- One manuscript by Rice research group
- Two manuscripts by UCLA research group

Conference Presentations

- Battelle 2014 (Adamson; poster)
- Battelle 2015 (Adamson)
- Emerging Contaminants 2016 (Adamson)
- RemTEC 2015 (Adamson)
- RemTEC 2017 (Wong)