

ESTCP Cost and Performance Report

(ER-200828)



Field Demonstration of Propane Biosparging for *In Situ* Remediation of N- Nitrosodimethylamine (NDMA) in Groundwater

December 2015

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14. ABSTRACT This ESTCP demonstration evaluated the technical effectiveness and cost of in situ propane biosparging for treating N-nitrosodimethylamine (NDMA) in groundwater. The demonstration site was the Aerojet Superfund Site in Rancho Cordova, CA. The propane sparging system, which consisted of three biosparging wells connected to an air compressor and propane gas feed, supplied approximately 1.8 lbs of propane to the in situ test plot per day to stimulate native bacteria to biodegrade NDMA. Over the 374 day operational period of the system, NDMA concentrations were reduced by > 99.7% in the treatment area, declining from as high as 25,000 ng/L to < 3 ng/L in one system monitoring well. Over the same time period, NDMA concentrations in a sidegradient control well declined by only 14%. There were no negative impacts to groundwater geochemistry. A full-scale biosparging system was determined to be approximately 40% less expensive to build, install, and operate than a comparable ultraviolet system over a 30 year remedial time frame.					
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ACRONYMS AND ABBREVIATIONS

µg	microgram(s)
Aerojet	Aerojet Superfund Site, Rancho Cordova, CA
AFB	Air Force Base
AS	air sparging
bgs	below ground surface
BMW	background monitoring well
BW	biosparge well
C	carbon
°C	degree(s) Celsius
CB&I	CB&I Federal Services, LLC
C ₃ H ₈	propane gas
CO ₂	carbon dioxide
DO	dissolved oxygen
DoD	U.S. Department of Defense
EDB	1,2-dibromoethane
ENV425	propanotroph <i>Rhodococcus ruber</i> ENV425
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EW	extraction (downgradient pumping) well
FBR	fluidized bed reactor
Freon-113	1,1,2-trichloro-1,2,2-trifluoroethane
ft	foot/feet
GET	groundwater extraction and treatment
GET A	Groundwater Extraction and Treatment System A at Aerojet
gpm	gallon(s) per minute
K	hydraulic conductivity
L	liter(s)
lb	pound
LEL	lower explosive limit
LRTA	liquid rocket test area
MCL	Maximum Contaminant Level
mg	milligram(s)
min	minute(s)
mL	milliliter(s)

mV	millivolt(s)
MW	monitoring well
NASA	National Aeronautics and Space Administration
NDMA	N-nitrosodimethylamine
ng	nanogram(s)
NO ₃	nitrate
NPV	Net Present Value
O ₂	oxygen gas
O&M	operations and maintenance
OEHHA	Office of Environmental Health Hazard Assessment
ORP	oxidation-reduction potential
OU	Operable Unit
P&T	pump and treat
PJKS	Peter J. Kiewit and Sons (Air Force Plant)
PLC	Programmable Logic Controller
PMW	performance monitoring well
PQL	practical quantitation limit
qPCR	quantitative polymerase chain reaction
SCADA	supervisory control and data acquisition
SCFM	standard cubic foot/feet per minute
SU	standard unit(s)
SVE	soil vapor extraction
SWRCB	State Water Resources Control Board
TCE	1,1,2-trichloroethene
TPA	Test Plot Area
UDMH	unsymmetrical dimethylhydrazine or 1,1- dimethylhydrazine
U.S.	United States
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
VOC	volatile organic compound

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EXECUTIVE SUMMARY

OBJECTIVE

N-Nitrosodimethylamine (NDMA) is present in groundwater and drinking water from industrial, agricultural, water treatment, and military/aerospace sources. NDMA is a suspected human carcinogen and an emerging groundwater contaminant that has been detected at a number of U.S. Department of Defense (DoD) and National Aeronautics and Space Administration (NASA) sites involved in the production, testing, or disposal of liquid propellants containing unsymmetrical dimethylhydrazine (UDMH). NDMA was a common contaminant in UDMH-containing fuels (e.g., Aerozine-50) and is also produced when these fuels enter the environment through natural oxidation processes. Currently, the most effective treatment technology for NDMA in groundwater is pump-and-treat (P&T) with ultraviolet (UV) irradiation. However, this approach is expensive because it requires high energy input to effectively reduce the levels of NDMA to meet regulatory requirements. The objective of this Environmental Security Technology Certification Program (ESTCP) project was to demonstrate and validate the application of *in situ* propane biosparging for treatment of NDMA in groundwater.

TECHNOLOGY DESCRIPTION

Previous laboratory studies revealed that natural propanotrophs in many aquifers are capable of biodegrading NDMA to low nanogram per liter (ng/L) concentrations while growing aerobically on propane. During this *in situ* demonstration, propane gas and oxygen were added to groundwater via three biosparging wells to stimulate this process. The demonstration was performed at the Aerojet Superfund Site (Aerojet) in Rancho Cordova, CA, in a location downgradient of a site where liquid rocket engines were developed and tested. The groundwater in this area has NDMA concentrations ranging from ~2,000 to >30,000 ng/L. Currently, the groundwater in this region is captured by a groundwater extraction and treatment (GET) system and NDMA is removed by UV irradiation.

To evaluate effectiveness of biosparging, NDMA concentrations in groundwater were monitored in a series of performance monitoring wells (PMWs) placed within a Test Plot Area (TPA), three of which (PMW-2, PMW-3, PMW-4) were within or slightly downgradient of the expected zone of influence of three biosparge wells (BW-6, BW-7, PMW-1). It should be noted that PMW-1 was used as both a biosparge well and a PMW throughout the demonstration. Monitoring wells PMW-5 and PMW-6 were downgradient of the plot and expected to be influenced later in the demonstration, as treated water reached this region. Background Monitoring Well (BMW)-1, which was side-gradient (~75 feet [ft] west of the center of the biosparge zone), was used as a control well to monitor NDMA concentrations outside of the treatment zone. The biosparging system was operated for a period of 374 days from start-up to shut-down. Full rounds of groundwater sampling were conducted on 12 occasions. This included two baseline sampling rounds on Day -84 and -70, nine performance sampling events during active sparging (Days 42, 84, 161, 185, 213, 241, 287, 311, and 353), and two rebound events after biosparging ceased (Day 385 and 430). The variables that were adjusted and optimized throughout the demonstration included (1) the percentage of propane in the air-propane feed, (2) the length of sparging cycles, (3) the number of sparging cycles per day, and (4) the breakdown of the sparge cycle, which was composed of an initial air sparge, a period of combined air-propane sparging, and then a final air sparge to clear the sparge lines of propane gas.

When the system was optimized, the percent propane in the sparge gas set at 40% of the lower explosive limit (LEL) (which equated to ~0.84% propane in the feed gas) and the system was operated for 12 cycles per day with propane being added for 40 minutes (min) during each cycle. The amount of propane added to the TPA after optimization was ~1.83 pounds (lbs)/day, and a total of approximately 475 lbs of propane was injected throughout the demonstration.

RESULTS

The biosparging approach was highly effective for the removal of NDMA from the aquifer. From baseline sampling (average concentrations from Day -70 and Day -84) to the final day of sampling during active biosparging (Day 353), concentrations of NDMA declined by 99.7%, to >99.9% in the four PMWs within the zone of influence of the biosparge system (PMW-1–PMW-4). Baseline concentrations of NDMA, which averaged $25,000 \pm 6000$ ng/L (seven test plot monitoring wells [MWs], two baseline events) declined to between 2.7 and 72 ng/L by Day 353 (mean value 40 ± 30 ng/L). The NDMA concentration at well PMW-2 was <3 ng/L on Day 353. By comparison, the NDMA concentration in the side-gradient control well (BMW-1) averaged 36,000 ng/L during baseline sampling and was 31,000 ng/L on Day 353—a decline of only 14%. Concentrations of NDMA in the far downgradient wells PMW-5 and PMW-6 began to show measurable declines near the end of the demonstration, presumably as treated water from the biosparge plot began to reach this region of the aquifer. NDMA in PMW-5 declined to 5,400 ng/L on Day 430 (from an initial average of 26,000 ng/L) and NDMA in PMW-6 fell to 13,000 ng/L on Day 430 (from an initial average of 22,500 ng/L). The rate of NDMA biodegradation in the TPA was calculated in wells PMW-2, PMW-3, and PMW-4. First-order rate constants were determined using data from Day 84 to Day 353. The degradation rates were 0.019 day^{-1} for PMW-3 ($R^2 = 0.95$), 0.031 day^{-1} for PMW-4 ($R^2 = 0.82$), and 0.037 day^{-1} for PMW-2 ($R^2 = 0.68$). These rates equate to NDMA half-lives ranging from 19 to 36 days.

IMPLEMENTATION AND COST

This biosparging technology is ready for full-scale application. The expected cost drivers for installation and operation of a full-scale propane biosparging delivery system for the remediation of NDMA-contaminated groundwater, and those that will determine the cost/selection of this technology over other options, include the following:

- Depth of the plume below ground surface (bgs);
- Width, length, and thickness of the plume;
- Aquifer lithology and the presence or absence of impervious layers that would impede sparging;
- Regulatory/acceptance of alternatives to sparging that include groundwater extraction and re-injection;
- Length of time for clean-up (e.g., necessity for accelerated clean-up);
- The presence of indigenous propanotrophic bacteria capable of degrading NDMA;
- Presence of co-contaminants such as chloroform, chlorinated ethenes, and chlorinated ethanes;
- The radius of influence that can be achieved via sparging; and
- Operations and maintenance (O&M) costs.

Based on a cost analysis for treatment of a shallow groundwater plume (~10–40 ft bgs) of ~400 ft in width, a propane biosparge barrier was determined to be the most cost-effective option compared to current alternatives, which included P&T with either UV or biological (via fluidized bed bioreactor [FBR]) removal of NDMA. Under this scenario, and assuming a 30-year operational period with equivalent costs for groundwater monitoring, the *in situ* barrier approach was >40% less expensive than either of the *ex situ* alternatives. The primary cost difference between the alternatives was the high capital cost of building an *ex situ* water conveyance and treatment facility, which is required for the UV or FBR system, but not for the *in situ* biosparge barrier. The capital costs for the *ex situ* options were approximately three times those for the *in situ* biobarrier.

In summary, the data from this ESTCP field test clearly indicate that propane biosparging can be an effective approach to reduce the concentrations of NDMA in a groundwater aquifer by 3–4 orders of magnitude, and that concentrations in the low ng/L range can be achieved with continuous treatment. These results are consistent with data achieved in pure culture studies as well as with various bioreactor tests. Moreover, for many applications, a propane biosparging system is expected to be significantly less expensive to install and operate than a conventional P&T system for NDMA removal from groundwater.

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1.0 INTRODUCTION

1.1 BACKGROUND

The origin of N-Nitrosodimethylamine (NDMA) in groundwater and drinking water includes industrial, water treatment, and military sources. Contamination of military installations, National Aeronautics and Space Administration (NASA) facilities, and aerospace contractors with NDMA has occurred largely from the former use and disposal of liquid rocket propellants containing unsymmetrical dimethylhydrazine (UDMH). This compound, which is a major component of the propellant Aerozine-50, contains NDMA as a chemical impurity and has also been observed to oxidize to NDMA in natural environments (Fleming et al., 1996; Mitch et al., 2003). Military and NASA sites reporting NDMA in groundwater include the Rocky Mountain Arsenal (CO), former Air Force Plant Peter J. Kiewit and Sons (PJKS) (CO), White Sands Missile Range (NM), Aerojet (multiple locations in CA), Jet Propulsion Labs (CA), and Edwards Air Force Base (AFB) (CA). Testing conducted during the past decade has also revealed that NDMA is present in reclaimed wastewater and in numerous drinking water supplies as a disinfection byproduct (Mitch and Sedlak, 2002a, b; Mitch et al., 2003; Sedlak et al., 2005). Both Los Angeles and Orange Counties (CA) have reported NDMA in groundwater supply wells (SWRCB, 2015a).

The most effective treatment technology currently available for removing NDMA from groundwater to required levels is *ex situ* treatment with ultraviolet (UV) irradiation, which breaks the N-N bond, yielding nitrite and dimethylamine as primary products (Mitch et al., 2003). Although effective, this *ex situ* approach is expensive because the energy required to reduce aqueous NDMA concentrations by one order of magnitude is approximately ten times that used for standard disinfection of viruses and other water-borne pathogens (Mitch et al., 2003), and large-scale pump-and-treat (P&T) systems are generally required to contain NDMA plumes derived from rocket testing activities.

1.2 OBJECTIVE

The objective of this Environmental Security Technology Certification Program (ESTCP) project was to demonstrate and validate the application of propane biosparging for the aerobic *in situ* biological treatment of NDMA-contaminated groundwater to nanogram per liter (ng/L) concentrations.

1.3 REGULATORY DRIVERS

Historically, NDMA was not thought to be a significant groundwater contaminant, so no Federal Maximum Contaminant Level (MCL) currently exists for drinking water in the United States. However, according to the U.S. Environmental Protection Agency (USEPA), a safe level of NDMA in drinking water based on lifetime *de minimis* risk calculations ($<10^{-6}$ risk of developing cancer) is only 0.7 ng/L (USEPA, 2011), which is below the current practical quantitation limit (PQL) for the compound. Due to the carcinogenicity of NDMA, the California Office of Environmental Health Hazard Assessment (OEHHA) established a public health goal (PHG) for NDMA in drinking water of 3 ng/L (OEHHA, 2006). This is lower than the State of California's current *notification level* for NDMA in groundwater, which is 10 ng/L (SWRCB, 2015b). Massachusetts also has an action level of 10 ng/L for NDMA in drinking water (MADEP, 2015).

The USEPA also recently added NDMA to its current Contaminant Candidate List 3 (CCL 3; USEPA, 2008), which is a possible step toward regulation under the Safe Drinking Water Act. At many military bases and installations, local government water agencies set the P&T discharge limits of NDMA. As the presence of NDMA in groundwater aquifers continues to be discovered and potentially impacts drinking water sources, future State and Federal regulations will likely be enhanced further.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The objective of this project was to demonstrate an effective *in situ* biological remediation option for the treatment of NDMA. The technology chosen—co-metabolic biosparging—relies on the use of an inexpensive alkane substrate, propane, and oxygen to stimulate the growth and degradative activity of native bacteria. The native propane-oxidizing bacteria are able to use propane as a growth substrate while degrading NDMA (Sharp et al., 2005, 2007; Hatzinger et al., 2008; Fournier et al., 2009). Propane and oxygen (from air) were added to an NDMA-contaminated aquifer to stimulate these bacteria to biodegrade NDMA from >20 micrograms per liter ($\mu\text{g/L}$) to low ng/L concentrations. To our knowledge, this represents the first *in situ* approach for NDMA remediation that is likely to have wide applicability. There are a variety of different ways to supply propane and oxygen to an aquifer, including (1) air- and propane-biosparging, (2) groundwater recirculation with above-ground propane and oxygen addition, (3) bubble-free gas injection systems, and (4) trenches with air and propane injection lines (Steffan et al., 2003). The applicability of these different approaches depends primarily on site geology/hydrogeology and plume characteristics. The key objective is to evenly distribute propane and oxygen gas throughout the desired treatment area in the safest and most cost-effective manner. During this demonstration, oxygen and propane were supplied to a contaminated aquifer using a biosparging approach (see **Figure 2.1**). This approach is mature, cost effective, and can be safely applied in a number of different configurations based on site conditions.

The addition of alkanes, including propane, methane, and butane, has been used in the past to treat contaminants including chlorinated solvents and fuel oxygenates (Battelle, 2001; Semprini and McCarty, 1991; Semprini et al., 1994; Hazen et al., 1994; Steffan et al., 1997, 2003). The main challenges with these earlier applications were the competitive inhibition between the alkane and target substrates, the inability of specialized organisms to compete with native organisms, and the production of toxic metabolites (e.g., 1,1,2-trichloroethene [TCE] epoxide) that can poison the process. However, recent laboratory studies suggest that these factors should not limit NDMA treatment via this approach (Hatzinger et al., 2008; Sharp et al., 2010).

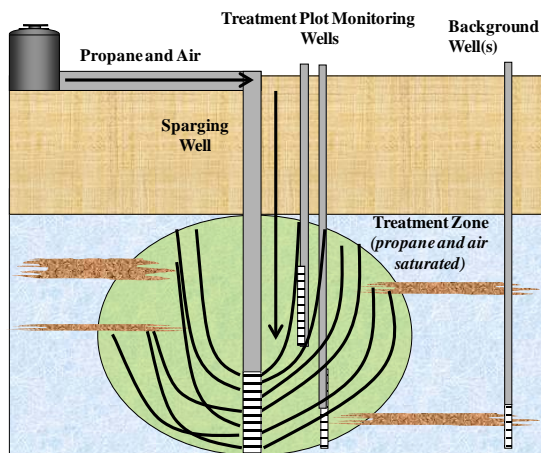


Figure 2.1. Basic Layout of the Air and Propane Biosparging System.

Propane and oxygen (from air) were supplied intermittently to groundwater through sparge wells.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

As previously discussed, the most effective technology for removing NDMA from water is currently UV irradiation. However, this *ex situ* technology is expensive, requiring the installation of P&T infrastructure and banks of UV lights that require significant energy to reduce NDMA to required levels. Propane biosparging for co-metabolic biodegradation of NDMA has several advantages over the current P&T technology. Importantly, the technology is destructive and it can be applied *in situ*, thereby reducing the risk of contaminant exposure, reducing contaminant/media disposal costs, and eliminating groundwater recovery costs. Unlike bioremediation processes that require the degradative bacteria to metabolize and grow on the target contaminant, the co-metabolic approach allows bacteria to grow on the available co-substrate (i.e., propane), allowing it to degrade the contaminant (NDMA) to sub-ng/L concentrations (e.g., Fournier et al., 2009; Hatzinger et al., 2011; Webster et al., 2013). Such low treatment levels are typically not attainable with metabolic systems because there is insufficient carbon (C) and energy for growth at low contaminant concentrations (Alexander, 1994; Schmidt et al., 1985). Furthermore, the technology is very flexible and can be applied in a wide range of configurations (source area treatment, *in situ* permeable barriers, recirculation systems, etc.), and it relies on the use of a very low-cost substrate (e.g., propane). It also may allow the simultaneous treatment of multiple co-contaminants at low concentrations (chlorinated ethenes, chlorinated ethanes, 1,4-dioxane, etc.) (Tovanabootr et al., 2001; Battelle, 2001; Lippincott et al., 2015).

In addition to its many advantages, the technology may have some disadvantages. For example, successful application of the technology requires the presence of propane oxidizing bacteria that can degrade the target contaminant. At some sites, indigenous bacteria able to degrade propane and NDMA may not be abundant. In these cases, bioaugmentation with exogenous organisms such as propanotroph *Rhodococcus ruber* ENV425 (ENV425) may be required (e.g., Lippincott et al., 2015; Fournier et al., 2009). Likewise, at some sites, achieving and demonstrating adequate distribution of injected gases (propane and oxygen) may be challenged by site hydrogeology. These same conditions, however, would likely also limit the implementation of other *in situ*, and possibly *ex situ*, technologies. Finally, successful application of the technology could be inhibited by the presence of high concentrations of some co-contaminants. In particular, high concentrations (in milligrams per liter [mg/L]) of chlorinated ethenes could poison the propanotrophic bacteria via the formation of toxic metabolites, such as TCE-epoxide, as was observed in a bioreactor study (Hatzinger et al., 2011). However, with a longer residence time in the field, it may be possible to treat both NDMA and various chlorinated solvents with this approach, despite the formation of metabolites, as was observed in a treatability study from a New Jersey aquifer (Hatzinger et al., 2008). The potential for treatment of co-contaminants using this approach can be assessed by performing site-specific treatability testing.

3.0 PERFORMANCE OBJECTIVES

The performance objectives for the field demonstration are summarized in **Table 3.1**.

Table 3.1. Performance Objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Determine effectiveness of NDMA treatment	<ul style="list-style-type: none"> Pre- and post-treatment contaminant concentrations in groundwater MWs using EPA Method 521 	<ul style="list-style-type: none"> Reduction to <3 ng/L (OEHHA PHG) in one or more treatment zone or downgradient (performance) groundwater MWs Overall NDMA reduction in treatment zone and closest downgradient MWs of >99% Comparison of treatment zone, downgradient, and background groundwater MW data 	<ul style="list-style-type: none"> Degradation of NDMA to <3 ng/L was achieved in one of the monitoring wells (PMW-2), which had baseline concentrations as high as 25,000 µg/L. Overall reduction in NDMA of >99.7% was achieved in the closest treatment zone MWs.
Adequate distribution of gases in groundwater	<ul style="list-style-type: none"> Pre-demonstration tracer studies using air sparging (AS) (measure increases in dissolved oxygen [DO]). Initial concentrations of propane in treatment wells at system start-up. Measurements of propane via EPA 3810, RSK-175, and DO via field meter in groundwater MWs 	<ul style="list-style-type: none"> Increased DO in expected treatment zone during preliminary biosparge tests Increased DO and propane in first row of treatment zone groundwater MWs during demonstration start-up Declining concentrations of both gases in downgradient wells as predicted based on site model and laboratory treatability tests 	<ul style="list-style-type: none"> Adequate gas distribution was documented at a 12.5-foot (ft) radius of influence in preliminary testing. DO increases in local MWs were documented. Propane consumption in treatment zone MWs was documented.
Minimal negative impacts to groundwater geochemistry	<ul style="list-style-type: none"> Measurements of DO, pH, oxidation-reduction potential (ORP), nitrate, sulfate 	<ul style="list-style-type: none"> DO >2 mg/L pH varying by <1 standard unit (SU) ORP >+100 millivolts (mV) 	<ul style="list-style-type: none"> No negative impacts to groundwater geochemistry were observed.
Increase in propanotroph population	<ul style="list-style-type: none"> quantitative polymerase chain reaction (qPCR) 	<ul style="list-style-type: none"> Increase in total propanotrophs by >1 log order in treatment plot wells 	<ul style="list-style-type: none"> >1 log order increase in total propanotrophs was observed by qPCR.
Qualitative Performance Objectives			
System reliability	<ul style="list-style-type: none"> Feedback from field technician PLC data logs, maintenance logs, and time 	<ul style="list-style-type: none"> System operates with minimal shut-down time (<10%) and necessity for unplanned maintenance/repair 	<ul style="list-style-type: none"> After initial optimization, system proved to be reliable.

MW – monitoring well; PLC – Programmable Logic Controller

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4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

The Aerojet facility is located in eastern Sacramento County, CA, approximately 15 miles east of Sacramento. Approximately 5,900 acres of the 8,500-acre site are included in the Aerojet Superfund Site, which has been used to develop rocket propulsion systems in support of national defense, space exploration, and satellite deployment since the 1950s (Tetra Tech, 2008). Industrial activities that supported and continue to support this work include solid rocket motor manufacturing and testing, liquid rocket engine manufacturing and testing, chemical manufacturing, and disposal of materials (Tetra Tech, 2008). During the development of rocket propulsion systems, various chemicals were used, including solvents, propellants, fuels, oxidizers, metals, and explosives. Historic operations at the facility resulted in the discharge of some of these chemicals to the subsurface.

The selected Test Pilot Area (TPA) is in the northeast corner (Zone 4) of the Eastern Operable Unit (OU). The general location for the demonstration was based on discussions with Mr. Scott Neville, an Environmental Project Manager at Aerojet. Several different locations were considered for the TPA, and soil cores and groundwater samples were collected at three locations from two separate areas (see Locations 1 and 2 in **Figure 4.1**) during site selection work. Based on existing site data and the ESTCP site characterization activities, the TPA was located in the vicinity of Alder Creek, just south of Extraction Well 4125 (EW 4125). **Figure 4.1** shows the different TPA locations that were evaluated for the demonstration.

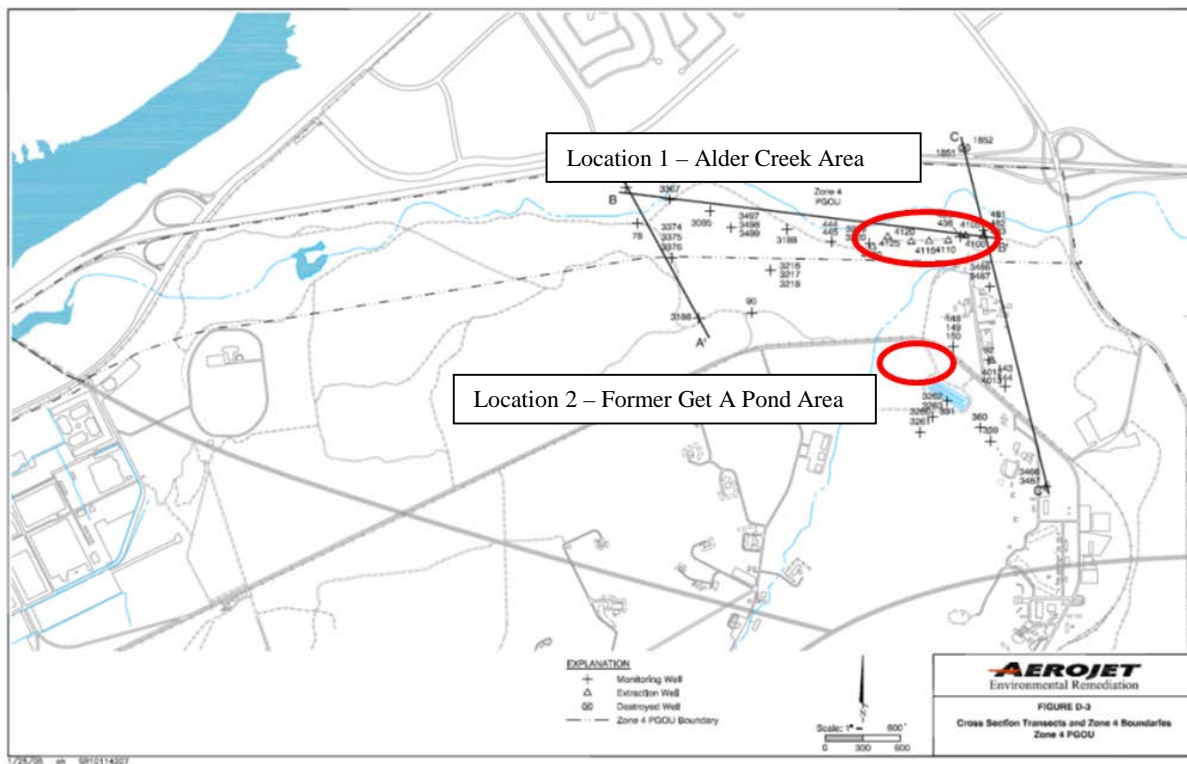


Figure 4.1. Locations of Site Investigation Work Conducted to Determine the Best Location for the Test Plot Area (indicated by the red circles).

The following criteria were favorable and led to the selection of this test location near EW 4125:

1. This region had historically high concentrations of NDMA (~20–30 µg/L) due to previous testing of liquid rocket propellants.
2. Contaminated groundwater was relatively shallow (approximately 50–80 feet [ft] below ground surface [bgs]).
3. Electrical service was installed and available.
4. Access was year round and not subject to flooding.
5. The site was secure.
6. TCE and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) were not present as co-contaminants in this region.
7. The downgradient groundwater was being captured by the GET System A at Aerojet (GET A).

Some of the difficulties with this area include the following characteristics:

1. Downgradient of steep terrain, so space was limited.
2. Upgradient of active extraction well (but well only operating at 5 gallons per minute [gpm]).
3. Complex geology.
4. Potential for high rate of groundwater flow in regional aquifer.
5. Relatively low groundwater dissolved oxygen (DO) (<1 mg/L) and oxidation-reduction potential (ORP) (-100 millivolts [mV]), although nitrate and sulfate were present suggesting the aquifer was merely anoxic (rather than highly anaerobic).

4.2 SITE GEOLOGY/HYDROGEOLOGY

The Aerojet site is located in eastern Sacramento County near the transition zone between the Great Valley and Sierra Nevada geomorphic provinces. The geology of the Great Valley, as summarized by Hackel (1966), can be described as a large, elongate, northwest-trending, asymmetric trough. This trough is filled with a very thick sequence (up to 60,000 ft) of sediments of primarily marine origin ranging in age from Jurassic to recent. The sediments that compose the eastern flank of the Great Valley (where Aerojet is situated) thin dramatically as they approach the foothills of the Sierra Nevada and eventually thin out completely, exposing the underlying crystalline basement rocks of pre-Tertiary-age igneous and metamorphic rocks that make up the Sierra Nevada Mountain Range.

Aerojet is underlain by fluvial and marine sedimentary deposits ranging in age from Cretaceous to recent. These sedimentary deposits unconformably overlie Jurassic-aged metamorphic basement rocks that dip to the west. These sediments form a wedge, which thickens from east to west, across the Aerojet site. The easternmost sediments at the Aerojet site are about 60-ft-thick, while at its western boundary (a distance of six miles) the sediments are nearly 2,000-ft-thick. A geologic cross-section across the Aerojet facility is provided as **Figure 4.2**. Hydrostratigraphic layers identified in the Eastern OU model include Layers Q (Quaternary sediments), L (Tertiary Laguna Formation), M (Tertiary Mehrten Formation), VS (Tertiary Valley Springs Formation), and I (Tertiary Ione Formation).

The wells installed for this demonstration were screened in Layer M, which is composed of multiple sublayers of coarse-grained fluvial black sands, variegated gravels, and interbedded clays, tuffs, and breccia of the Mehrten Formation, and typically contains the first water-bearing sublayer encountered across the facility. The Mehrten Formation contains the most productive aquifers underlying the Aerojet site and serves as the principal source of water for private and public water supply wells in the area. The majority of the chemicals released to groundwater are found in the Mehrten Formation.

Groundwater flow direction is controlled by a local bedrock high, oriented east to west across the middle of the facility from the LRTA to the Central Disposal Area. Locally, a trough in the bedrock controls groundwater flow in the northern portion of the LRTA, toward Alder Creek. Successive deposition of the Ione, Valley Springs, Mehrten, and Laguna Formations draped thin sediments over the bedrock high and thick layers of sediment in the deep troughs north and south of the facility. Groundwater flow is radial from the center of the bedrock high to the north, west, and south, becoming more westerly with depth and distance from the bedrock high. First groundwater is typically encountered at a depth of 20 ft in the far eastern portion of the facility and 105 ft in the western portion of the facility. However, substantial dewatering and lowering of first water can occur near extraction well fields. Discontinuous lenses of shallow perched groundwater are commonly found across the Aerojet facility. Perched groundwater is most often encountered within dredge tailings (Layer Q) at depths ranging from 10 to 75 ft. Perched groundwater is affected by seasonal recharge and periods of drought, commonly disappearing during long drought periods and rebounding quickly when normal rainfall patterns return.

A hydrostratigraphic cross section through the southern portion of the demonstration area is presented in **Figure 4-3**. Groundwater elevations in Layers Q, M1 through M10, VS, and I demonstrate that there is substantial hydraulic communication between the layers with a vertical downward hydraulic potential. In general, water-bearing layers within the Valley Springs Formation and Ione Formation (west of LRTA) are confined and exhibit a vertical upward hydraulic potential. Reported hydraulic conductivities for the various hydrostratigraphic layers range from 1 to 350 ft/day, with an average of about 70 ft/day (Central Valley, 2005). Hydraulic gradients at the site range from 0.005 to 0.02. Slug testing performed by CB&I on three monitoring wells in February 2011 indicated hydraulic conductivities ranging from 0.18 to 5.2 ft/day (see details in the *Project Final Report*).

The geology of the Eastern OU consists of permeable sand and gravel which is well suited for the biosparging technology proposed for this ESTCP demonstration. Clay and silt interbeds are also present in many locations, but these were not expected to be a significant impediment to the project, and may in fact have aided in keeping injected oxygen and propane confined within the targeted treatment zone. During the site investigation work, each boring was logged to evaluate the local occurrence of these layers within the proposed TPA. Screen intervals and specific locations for gas injection and groundwater monitoring wells were subsequently designed based on site-specific geology.

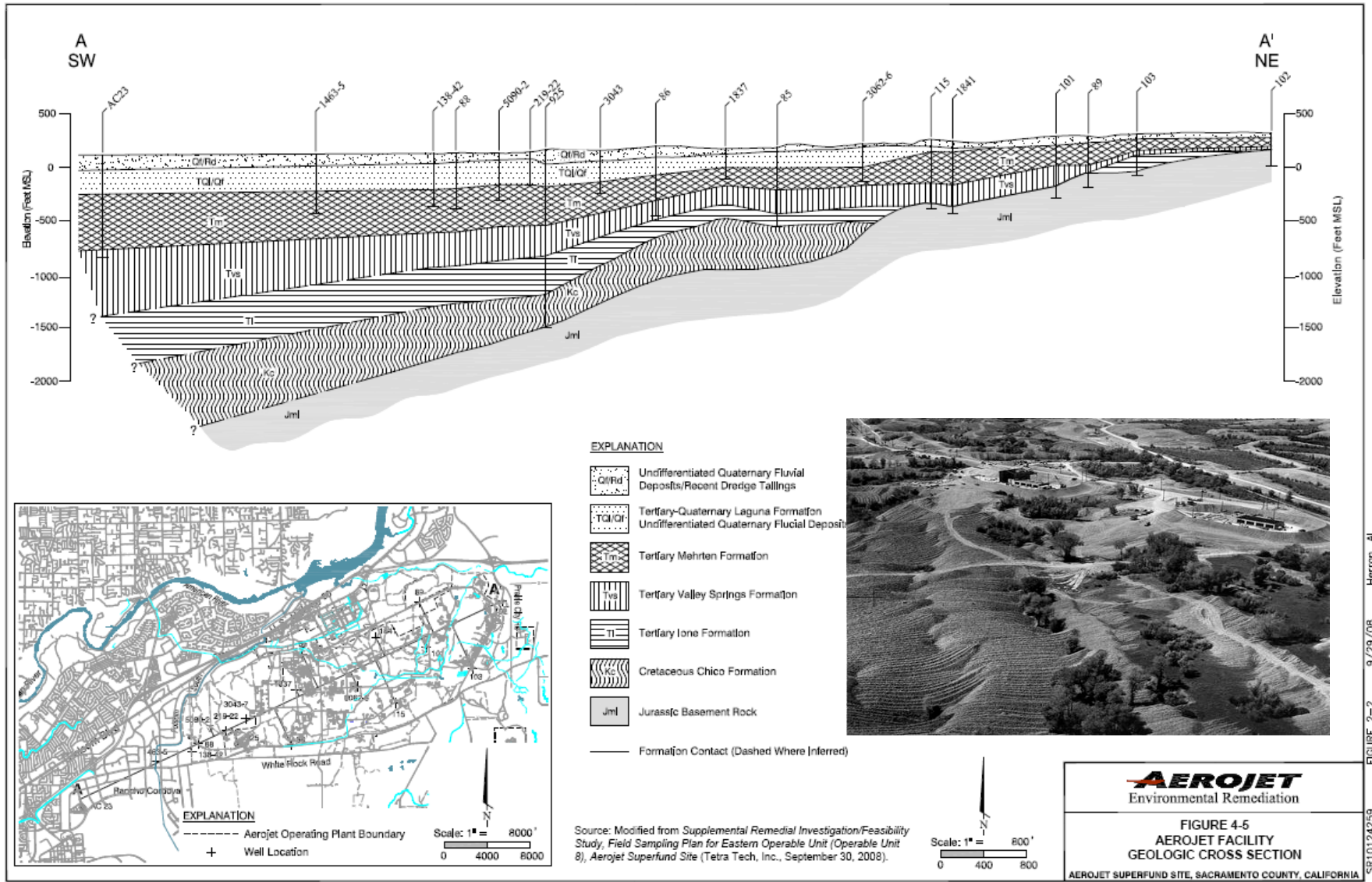


Figure 4.2. Aerogjet Facility Geological Cross Section.

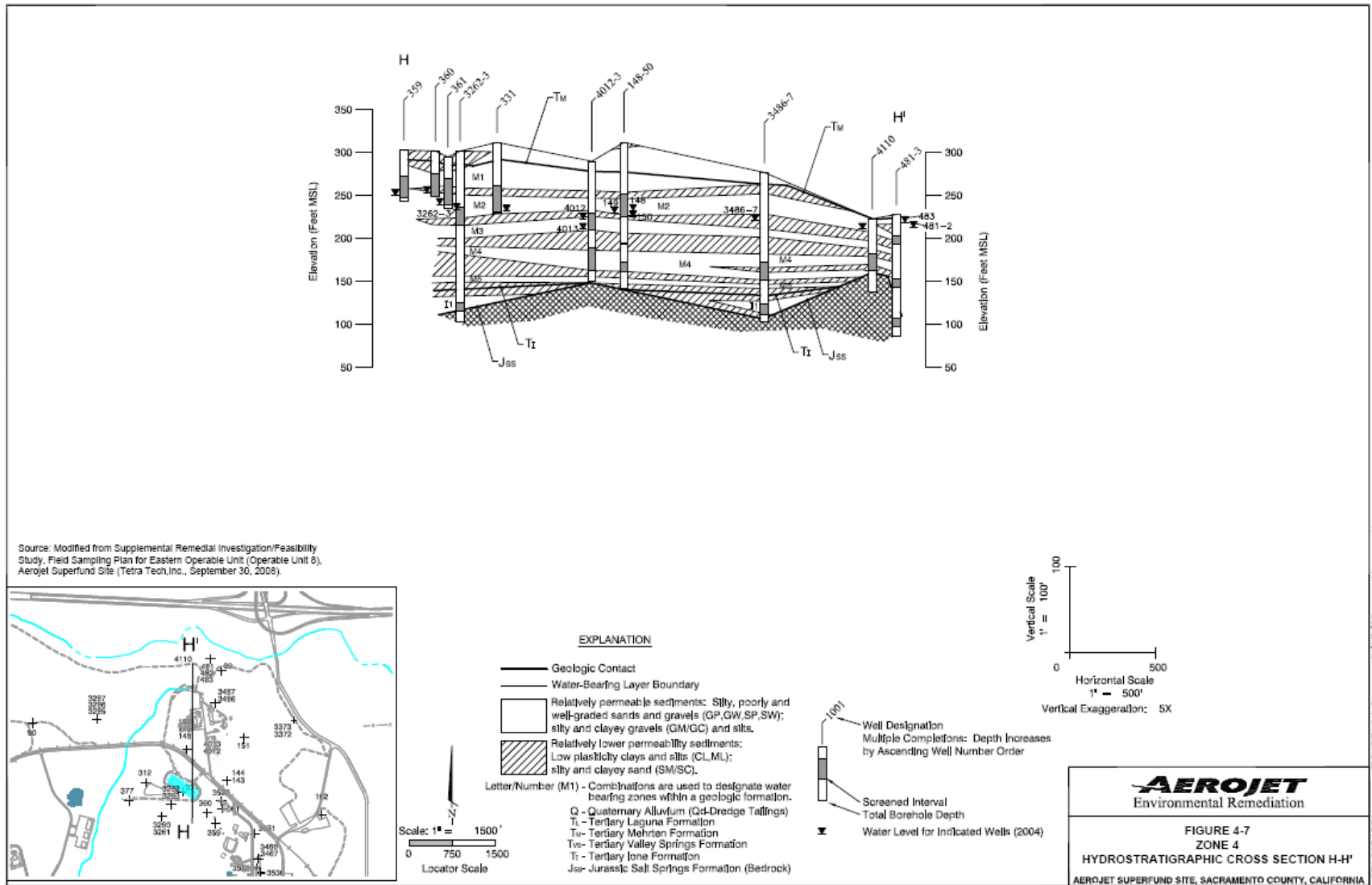


Figure 4.3. Hydrostratigraphic Cross Section through TPA.

The geology of the Eastern OU consists of permeable sand and gravel, which is well-suited for the biosparging technology proposed for this ESTCP demonstration. Clay and silt interbeds are also present in many locations, but these were not expected to be a significant impediment to the project, and may in fact have aided in keeping injected oxygen and propane confined within the targeted treatment zone. During the site investigation work, each boring was logged to evaluate the local occurrence of these layers within the proposed TPA. Screen intervals and specific locations for gas injection and groundwater MWs were subsequently designed based on site-specific geology.

4.3 CONTAMINANT DISTRIBUTION

A map of total volatile organic compounds (VOCs) and NDMA groundwater concentrations within the Mehrten Formation Fourth Water Bearing Layer (M4) hydrostratigraphic unit in Zone 4 is provided in **Figure 4.4**. The TPA area selected near EW 4125 and the other areas evaluated (near the former GET A Pond and EW 4100) are shown on this figure. Existing site data indicated that NDMA concentrations in each of these potential areas should be $>1 \mu\text{g/L}$, while total VOC concentrations could be variable. However, VOC concentrations were expected to be $<200 \mu\text{g/L}$ in both the GET A Pond area and near EW 4125. NDMA also exists in the M2 layer in this general area. However, this layer had lower NDMA concentrations based on initial site assessment work, and may not have been sufficiently saturated to serve as an effective water-bearing zone for the demonstration. Site characterization activities provided the necessary contaminant distribution information required to select the location and depth of the TPA well network.

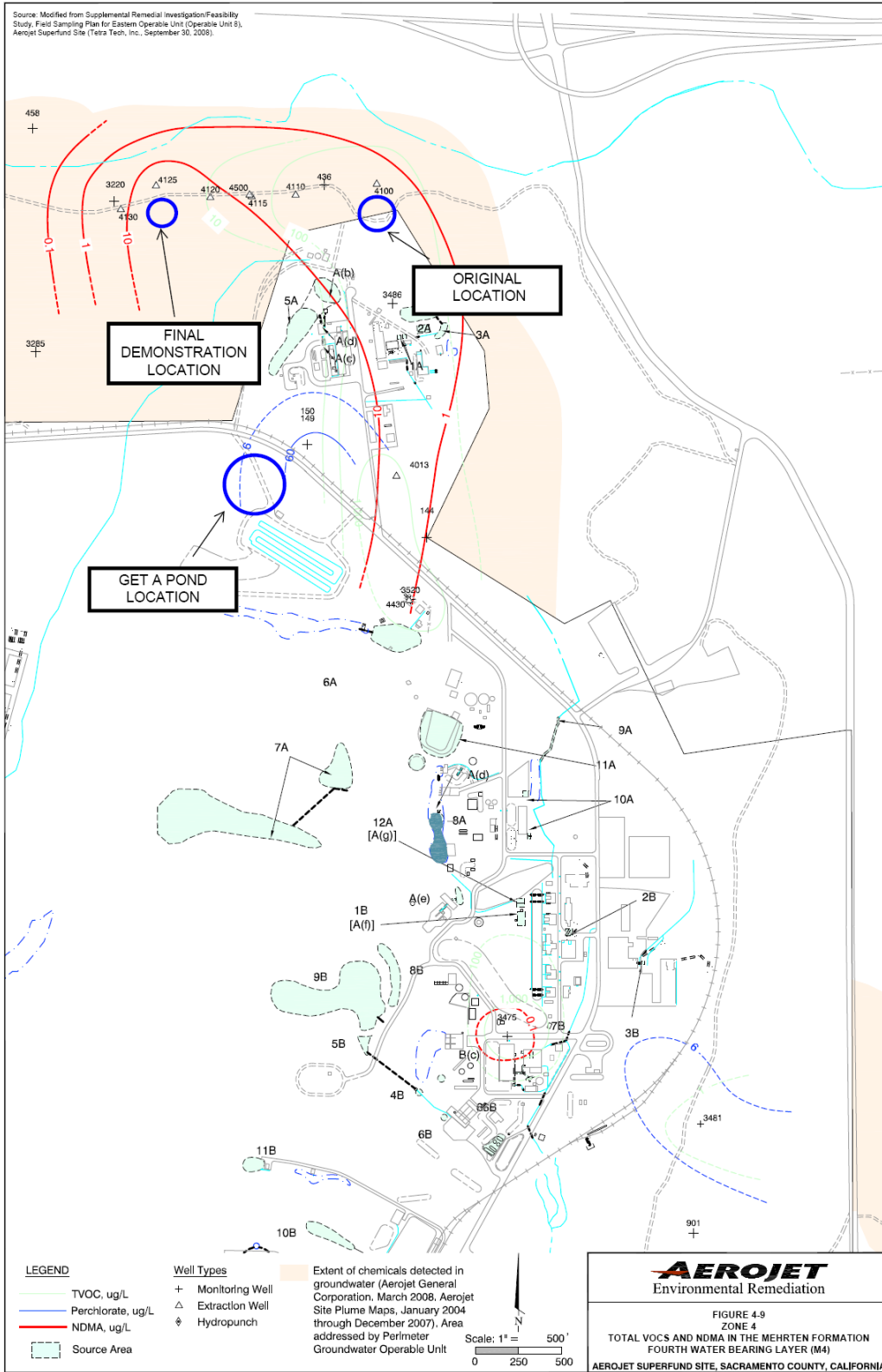


Figure 4.4. Zone 4 Total VOCs and NDMA in the Mehrten Formation Fourth Water Bearing Layer (M4).

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5.0 TEST DESIGN

The following subsections provide detailed descriptions of the system design and testing that were conducted to address the performance objectives described in **Section 3.0**.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

During this ESTCP demonstration, propane and oxygen (from air) were added to an NDMA-contaminated aquifer to stimulate indigenous propanotrophs to biodegrade the nitrosamine. The key objective was to evenly distribute propane and oxygen gas throughout the desired treatment area. This was accomplished using a biosparging approach (see **Figure 2.1**). This approach is mature, cost effective, and can be safely applied in a number of different configurations based on site conditions. A well network was installed for this purpose, which included a series of air and propane biosparging wells, a series of treatment zone groundwater MWs to evaluate the performance of propane and oxygen addition, one side-gradient MW installed in a zone outside the influence of the sparge wells, and two downgradient MWs. The system performance was evaluated by measuring propane, oxygen, and NDMA concentrations before and after propane and oxygen biosparging in all of the installed MWs. Geochemical parameters and propanotrophic bacteria also were measured.

Design of the *in situ* propane biosparging system required detailed site-specific knowledge of the contaminant distribution, aquifer lithology and hydrology, and microbiology. Specific system parameters directly influenced by these factors included amendment selection and addition rates, and the spacing and screen intervals of the biosparge and MWs. All available site characterization data was reviewed prior to selecting the location of the demonstration (see previous summary in **Section 4**). However, additional local characterization of the selected demonstration TPA was required to facilitate system design. The activities described within this section were conducted in order to attain the needed site-specific information required for final system design. Specific activities included laboratory microcosms and column experiments to evaluate biodegradation kinetics, MW and biosparge well installation, air-injection testing to determine biosparging radius of influence, supplemental groundwater investigation to confirm contaminant concentrations and delineate the dissolved contaminant plume, and passive flux meter testing to confirm groundwater flow rate. Further details and results of these activities are provided in the *Project Final Report*.

5.2 BASELINE CHARACTERIZATION

Prior to site selection, CB&I reviewed existing site investigation documents and all available hydrogeologic, contaminant concentration, and geochemical data for the Aerojet site. While these data were helpful in the selection of three potential TPAs in two different regions, additional data were required to effectively design the field demonstration. The following subsections describe baseline characterization activities that were performed.

In February 2011, after determining that the original TPA near EW 4100 was unsuitable for the demonstration (see **Figure 4.4**), CB&I performed site characterization activities in Zone 4 using existing site MWs that included:

- Groundwater elevation data collection,

- Groundwater sampling, and
- Hydrogeologic testing (i.e., slug tests).

Results of these activities led to the selection of the two potential locations for the demonstration (the Alder Creek Area near EW 4125, and the former GET A Pond Area; **Figure 4.4**). Additional site characterization activities conducted in each of these two locations in March and April 2011, included:

- Continuous soil core collection,
- Discrete groundwater sample collection,
- Monitoring and biosparging well installations, and
- Groundwater sampling of the new monitoring and biosparging wells.

Results of these activities were used to select the Alder Creek Area south of EW 4125 as the TPA. Additional site characterization activities conducted in this area included:

- Air sparge testing to determine radius of influence of biosparging wells and connectivity of the newly installed biosparging and MWs in the TPA;
- Passive flux meter (PFM) testing to verify groundwater velocity in the TPA; and
- Measurement of groundwater elevation in all new wells, and determination of gradient.

The results of these baseline activities are provided in the *Project Final Report*.

5.3 LABORATORY STUDY RESULTS

In preparation for the field demonstration, a series of laboratory batch and column studies were completed. The objectives of the treatability studies were as follows: (1) to determine if indigenous propanotrophs in the expected TPA could be stimulated via propane and oxygen addition to biodegrade NDMA, (2) to determine if these organisms could achieve low ng/L NDMA concentrations during biodegradation, (3) to estimate the kinetics of *in situ* NDMA biodegradation, and (4) to determine if the common co-contaminants TCE and Freon-113 affect NDMA biodegradation or if these contaminants are biodegraded by native propanotrophs. Extensive details of laboratory treatability testing results were submitted to ESTCP in the form of a *Treatability Study Report* (Hatzinger, 2010).

The conclusion of the treatability work for this project marked a go/no-go decision point for the field study. Overall, the treatability results revealed that propane- and methane-degrading bacteria are present at the Aerojet site, and that these bacteria can be stimulated to biodegrade NDMA from $\mu\text{g/L}$ to ng/L concentrations. Batch and column studies confirmed these observations. However, the batch data suggested that NDMA biodegradation can decline with time (which may be an artifact of the closed system), and the column results clearly showed that high concentrations of co-contaminants in the Aerojet water (TCE and Freon-113) can significantly reduce rates of NDMA degradation. Based on the treatability studies, it was proposed to move forward with the field study, but to either (1) use a modified field design to enable the removal of TCE and Freon-113 *in situ* with traditional air-sparging prior to stimulating NDMA biodegradation via propane addition or (2) evaluate alternate locations at Aerojet (but within the same general region where the treatability studies were conducted) that have NDMA, but lower levels of TCE and Freon-113 (<50 and 100 $\mu\text{g/L}$, respectively).

After significant additional site assessment work was conducted, the latter alternative was selected. A suitable location in the general region where samples were collected for the treatability studies was found with high NDMA concentrations ($>10 \mu\text{g/L}$) but with non-detectable levels of VOCs. The Alder Creek site north of MW 4125 (the “Final Demonstration Location”) is shown in **Figure 4.4**.

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

As previously discussed, *in situ* remediation of NDMA via co-metabolism requires the addition and distribution of propane gas and oxygen in groundwater. For this demonstration, an air- and propane-biosparging approach was used to deliver these gases to the subsurface (**Figure 2.1**). Although biosparging is a form of air sparging (AS), the focus is on providing the necessary gases for contaminant biodegradation while minimizing volatilization. The key objective is to evenly distribute propane and oxygen gas throughout the desired treatment area in the safest and most cost-effective manner. The following subsections detail the design and layout of the various demonstration components.

5.4.1 Demonstration Plot Layout

The original demonstration plot for this project included five biosparging wells and seven groundwater MWs. The breakout pressure in the five biosparging wells was much higher than anticipated due to apparent issues with the specialized sparge well screens, which may have collapsed upon installation due to a manufacturer defect or required too much pressure for breakout due to confining aquifer conditions (see *Project Final Report*). Because these wells could not be used, one of the central monitoring wells (PMW-1, built with a traditional screen) was initially used for biosparging and then two additional biosparge wells were installed approximately four months after the initial system start-up. The final demonstration plot design is provided in **Figure 5.1**. This was the demonstration plot layout for the majority of the demonstration, with PMW-1 used as the third system biosparge well, as well as a system MW.

The final demonstration plot included three biosparging wells and seven MWs. Monitoring wells were divided into three groups:

1. One side-gradient (or “background”) monitoring well (BMW-1) located ~ 75 ft side-gradient of the central part of the test plot;
2. Four treatment zone performance monitoring wells (PMW-1, PMW-2, PMW-3, PMW-4), located within (PMW-1, PMW-2), slightly upgradient (PMW-3, ~ 4 ft), and slightly downgradient (PMW-4, ~ 7 ft) of the triangulated propane sparge wells; and
3. Two downgradient monitoring wells (PMW-5 and PMW-6) located ~ 30 – 40 ft downgradient of the central region of the triangulated propane sparge wells.

The as-built well construction details are provided in **Table 5.1**. BMW-1 was located outside the influence of the biosparging system and was used to verify NDMA and other groundwater contaminant concentrations flowing side-gradient of the treatment area. Performance monitoring wells PMW-1–PMW-4 were used to verify propane and oxygen distribution, propanotroph numbers, and treatment effectiveness within the treatment zone. PMW-1 was also used as a biosparge well throughout the demonstration as previously described. Performance wells PMW-5 and PMW-6 were used to evaluate treatment effectiveness downgradient of the treatment zone.

The three biosparging wells were located in a triangle with distances ranging from ~12 ft to 18 ft apart as shown in **Figure 5.1**.

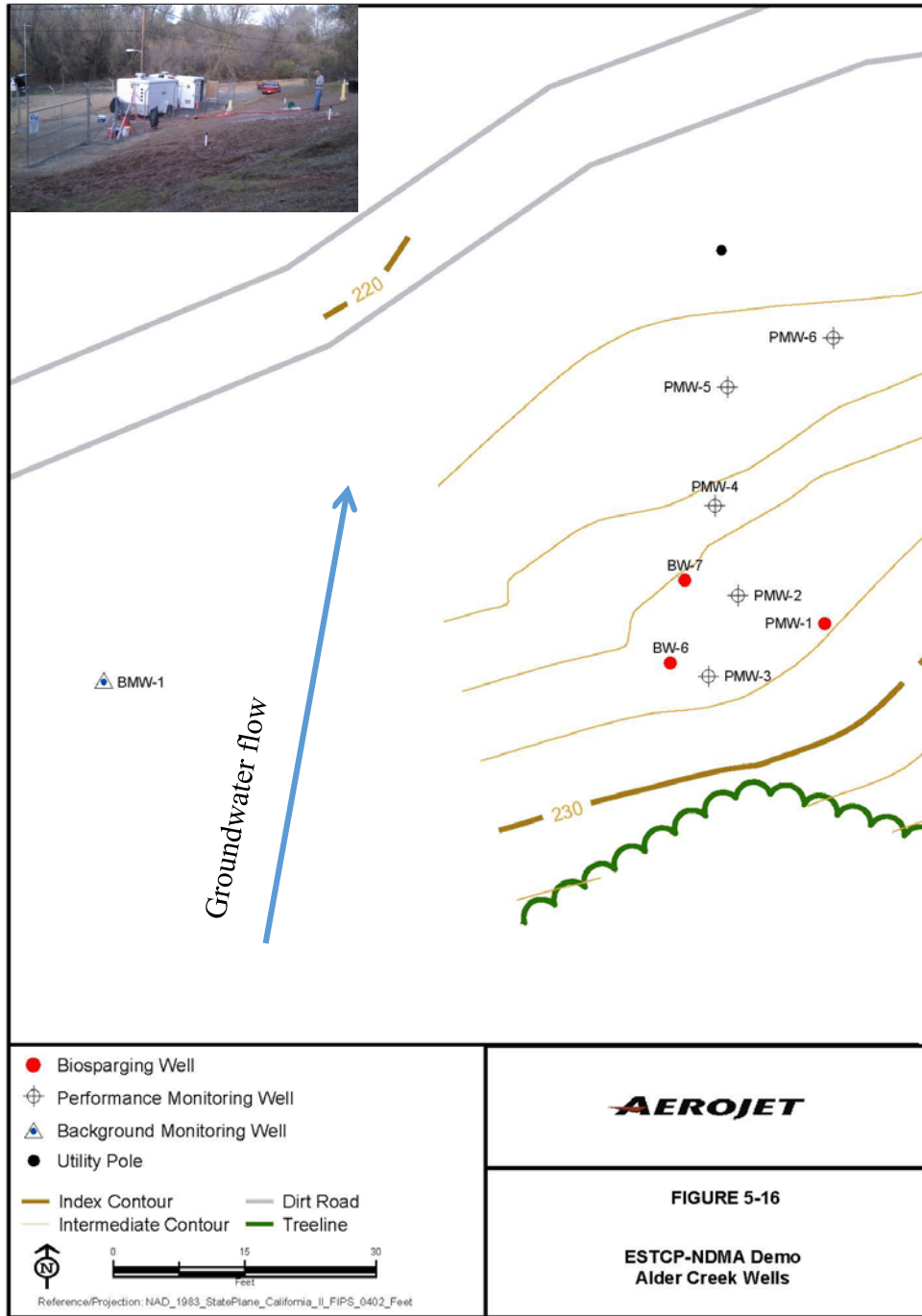


Figure 5.1. Final Layout of Demonstration Plot Biosparge and Monitoring Wells.

An inset of the demonstration plot looking northeast is provided.

Table 5.1. Summary of As-Built Well Construction Details.

Well ID	Date Installed	Well Diameter (inches)	Well Material	Screen Type	Elevations (ft. MSL)			Screen Intervals				Stick Up or Flushmount	Type of Stickup	Concrete Pad (Y/N)
					Top of PVC Casing	Top of Steel Casing or Flushmount	Ground Surface	Top of Screen (ft. bgs)	Bottom of Screen (ft. bgs)	Top of Screen (ft. MSL)	Bottom of Screen (ft. MSL)			
Sparge Wells														
BW-1	11/5/2011	2.0	PVC	SHUMASOIL	226.76	NA	225.41	57	62	168.41	163.41	Stick Up	PVC only	N
BW-2	11/4/2011	2.0	PVC	SHUMASOIL	229.44	NA	227.71	62	67	165.71	160.71	Stick Up	PVC only	N
BW-3	11/3/2011	2.0	PVC	SHUMASOIL	230.16	NA	228.57	63	68	165.57	160.57	Stick Up	PVC only	N
BW-4	11/1/2011	2.0	PVC	SHUMASOIL	226.66	NA	225.12	70	75	155.12	150.12	Stick Up	PVC only	N
BW-5	11/2/2011	2.0	PVC	SHUMASOIL	227.65	NA	226.55	63	68	163.55	158.55	Stick Up	PVC only	N
BW-6	6/20/2012	2.0	PVC	Slotted PVC	Not Surveyed			71	76	Not Surveyed		Stick Up	PVC only	N
BW-7	6/21/2012	2.0	PVC	Slotted PVC	Not Surveyed			67	77	Not Surveyed		Stick Up	PVC only	N
Monitoring Wells														
BMW-1	10/25/2011	2.0	PVC	Slotted PVC	224.13	224.59	222.20	45	50	177.20	172.20	Stick Up	6" Steel	Y
PMW-1	4/23/2011	2.0	PVC	Slotted PVC	230.22	230.72	227.80	60	65	167.80	162.80	Stick Up	6" Steel	Y
PMW-2	4/27/2011	2.0	PVC	Slotted PVC	226.50	226.85	226.47	60	65	166.47	161.47	Flushmount	NA	Y
PMW-3	4/26/2011	2.0	PVC	Slotted PVC	227.13	227.66	227.29	59	64	168.29	163.29	Flushmount	NA	Y
PMW-4	4/28/2011	2.0	PVC	Slotted PVC	226.25	226.88	224.54	60	65	164.54	159.54	Stick Up	6" Steel	Y
PMW-5	10/28/2011	2.0	PVC	Slotted PVC	221.40	221.97	221.86	57	62	164.86	159.86	Flushmount	NA	Y
PMW-6	10/27/2011	2.0	PVC	Slotted PVC	221.12	221.89	221.75	60	65	161.75	156.75	Flushmount	NA	Y

5.4.2 Biosparging System Design

CB&I refurbished an existing propane biosparging system for use during this demonstration. The trailers were shipped to CB&I’s engineering and equipment facility in Findlay, OH, where all components were inspected, adjusted, or replaced as necessary to ensure good operation in the field. The system consists of two mobile trailers (Trailer #1 and Trailer #2) housing equipment and controls (**Figure 5.2**). Trailer #1 (**Figure 5.3**) is electrically wired for a non-explosion proof atmosphere. It contains the main control panel and main electrical junction box as well as the air feed system. A 220 volts alternating current (VAC), single-phase power drop to the system is required to be hard-wired to the main electrical junction box located on the outside of Trailer #1. A Programmable Logic Controller (PLC) and user interface are located within the trailer in the main control panel. Electrical power and control is transferred via flexible cable to Trailer #2. A wireless system was installed to provide for call out when an operating fault was detected. The air feed system included a two-stage, duplex air compressor with 5 horsepower (HP) motors and a 120 gallon tank, capable of providing 34.2 standard cubic feet per minute (SCFM) at 175 pounds per square inch (psi). It also included two particulate filters, a 35 SCFM refrigerated air dryer, regulator, control solenoids, pressure switch, control valve, and a mass flow meter that was linked to the PLC. Air is transferred to Trailer #2 via flexible hose. A secondary airline with a regulator is also included to provide venting of the lower explosive limit (LEL) sampling line in Trailer #2 during non-injection periods.



Figure 5.2. Biosparge Trailer Units.



Figure 5.3. Inside of Trailer #1 – Controls and Air Supply System.

Trailer #2 (**Figure 5.4**) is electrically wired for an explosion-proof atmosphere. The trailer consists of a propane feed system, air/propane distribution system, and a soil vapor extraction (SVE) system (the SVE system was not utilized during this demonstration). The propane feed system consists of an external propane cylinder with regulator that transfers propane to the air/propane distribution system through a pressure switch to redundant solenoid control valves, through a flow indicator with a switch and ball valve. The propane joins the air feed downstream of its pair of check valves. The Propane Injection Panel Assembly is intrinsically safe and in full compliance with the liquefied petroleum (LP)-Gas Code, with barriers inside the main control panel.



Figure 5.4. Inside of Trailer # 2 – Propane Feed, and Distribution and SVE Equipment.

Propane gas was supplied by a 95-pound (lb) external propane cylinder that was secured within a vertical, metal gas storage cabinet immediately adjacent to Trailer #2. The cylinder was properly grounded and concrete barriers installed around the trailer for protection from vehicles. A gas pressure regulator and excess flow valve were installed on the cylinder. The excess flow valve automatically shuts off delivery of propane if it exceeds a preset limit (i.e., in the event of a leak or system malfunction). Appropriate tubing was used between the excess flow valve and the propane gas connection on the trailer. The entire propane system was insulated to ensure good operation in cold temperatures.

The air/propane distribution system in Trailer #2 includes dual check valves to prevent back flow of the air propane mixture, an LEL sampling system, pressure gauges, and a backpressure regulator. The system is designed to feed propane below the LEL (2.1%) and will automatically shut down in the event the LEL is exceeded. Propane feed concentrations for this demonstration were generally between 30% and 40% of the LEL (between 0.63% and 0.84% propane). The air/propane mixture is manifolded between five discharge points that include flow indicators with needle valves (i.e., maximum of five sparge wells). The LEL sampling system diverts a minor flow from the air/propane mixture to an LEL analyzer with flow cell. The sample is filtered and monitored for adequate flow via two indicators and a flow switch. The sample will discharge to the atmosphere through tubing that passes through the wall of the trailer. An air discharge permit is not required, as the mass of propane discharged daily has been calculated at approximately 0.07 lbs/day, well below the 2 lb/day limit.

5.5 FIELD TESTING

A timeline of system operation is provided as **Table 5.2**. The biosparging system was operated for a period of 374 days from start-up to shut-down. The operation entailed automated injections of air and propane into the TPA biosparging wells. Inorganic nutrients were not added. As described in **Section 5.4.2**, propane was fed into the air stream in Trailer #2, prior to being injected into the biosparging wells. With the exception of the first few weeks after start-up, propane feed concentrations were generally between 30% and 40% of the LEL (between ~0.63% and 0.84% propane; **Table 5.2**). The flow, divided evenly between the biosparging wells, was generally between 5 and 6 SCFM, and daily cycles varied from 30 to 50 minutes (min) in length and 2–12 times daily. Operational details are provided in the subsequent subsections.

During the active testing period (after background sampling and during active gas flow), groundwater samples were collected and analyzed for NDMA, VOCs, propane, dissolved oxygen, anions, total propanotrophic bacteria (select sampling events), and basic field parameters (temperature, pH, specific conductivity, dissolved oxygen (DO), and ORP). A total of 13 groundwater sampling events (including two baseline sampling events and two rebound sampling events) were conducted during the demonstration.

5.5.1 System Operation and Performance Monitoring

The biosparging system was operated for a period of 374 days from start-up to shut-down. As noted, PMW-1 was operated as the sole sparging well for the first 4 months of operation (with the exception of the first few weeks when BW-4 was also operating), and then wells BW-6, BW-7, and PMW-1 were operated together for the remaining 8.3 months of operation. The operational data are provided in **Table 5.2**. The variables that were adjusted and optimized throughout the demonstration included (1) the average LEL reading (measure of percentage propane in the air-propane feed); (2) the length of the sparging cycles; (3) the number of sparging cycles per day; and (4) the breakdown of the sparge cycle, which was composed of an initial air sparge, a period of combined air-propane sparging, and then a final air sparge to clear the sparge lines of propane gas. These variables were modified during the demonstration (as described below and in **Table 5.2**) based upon the levels of propane and NDMA observed during sampling events and during propane degradation testing.

The percent propane in the sparge gas was increased over the first few months of the demonstration, and eventually set at 40% of the LEL on Day 131, which equated to ~0.84% propane in the feed gas. The setting remained at this level through Day 374, when the sparge system was shut down. Similarly, the number of cycles per day was increased from 6 to 8 on Day 89, and then further to 12 on Day 217 through the end of operation on Day 374. The amount of time that propane was sparged to each of the wells per cycle was increased from 20 min to 26 min on Day 89, decreased slightly to 24 min on Day 134, and then increased to 40 min on Day 217 for the remainder of the 374-day sparging period. The amount of propane added to the TPA (1.83 lbs/day) was considered optimized on Day 217, and generally remained the same for the remaining five months of active sparging.

Full rounds of groundwater sampling were conducted on 13 occasions as shown in **Table 5.2**. This included two baseline sampling rounds on Day -84 and -70, nine performance sampling events during active sparging (Days 42, 84, 161, 185, 213, 241, 287, 311, and 353), and two rebound events after biosparging ceased (Day 385 and 430). Sampling generally consisted of seven wells (PMW-1–PMW-6 and BMW-1). An additional round of baseline sampling of all wells (excluding PMW-6) for propanotrophs was also conducted on Day -6. For the final three sampling events, wells BW-6 and BW-7 were also sampled. The sampling protocol and list of analytes are described in **Section 5.6**.

The supervisory control and data acquisition (SCADA) system connected to the PLC that controlled the biosparging system collected and stored readings of total system flow and LEL every 3 min. The wireless communications system connected to the SCADA allowed for remote access to the system, and downloading of the operational data. A system check form was completed when onsite field technicians evaluated system operation. Any system modifications were also documented on this form.

5.5.2 System Shutdown and Demobilization

The biosparging system was shut down on Day 374. The two biosparging trailers, along with the propane cylinders and all above-ground equipment, were subsequently removed from the site. All biosparging and MWs were abandoned according to California regulations on Day 520 (July 17, 2013).

5.6 SAMPLING METHODS

5.6.1 Groundwater Sampling and Analysis

Groundwater samples were collected by CB&I personnel utilizing low-flow purging in accordance with USEPA Low-Flow Ground-Water Sampling Procedures (Puls and Barcelona, 1996). Samples were obtained from each MW using a dedicated submersible bladder pump and Teflon™ tubing, and a flow-through cell with a YSI field meter (or equivalent) to allow measurement of field geochemical parameters (pH, ORP, temperature, specific conductivity, and DO). All field meters were calibrated at the beginning of each day.

Groundwater samples were analyzed for basic field parameters, NDMA (EPA Method 521), VOCs (EPA Method 8260), dissolved gases (methane, propane, ethane, ethene via EPA 3810, RSK-175), and anions (EPA 300.0) as detailed in **Table 5.3**. VOC sampling only occurred during the baseline sampling events since no compounds were detected by EPA 8260. Total propanotrophic bacteria were quantified during one baseline event prior to gas injection to establish background levels and four of the monthly events thereafter using quantitative polymerase chain reaction (qPCR) (see **Table 5.2**). The analysis of VOCs, anions, and dissolved gases was performed by CB&I's Analytical Laboratory in Lawrenceville, NJ. Total propanotrophs were quantified by qPCR at Microbial Insights (Knoxville, TN). Analysis of NDMA was performed by Weck Laboratories, City of Industry, CA. Weck Laboratories is a California Department of Public Health-approved laboratory and is listed under the State of California Environmental Laboratory Accreditation Program (ELAP). Prior to each sampling event, groundwater elevation measurements were collected using an electronic water level indicator. Measurements were obtained from the top-of-casing and recorded to the nearest 0.01-ft.

Table 5.2. Timeline of Sampling and System Operation.

Date	Duration	Day	Activity	Operational Wells				Average Total Flow (SCFM)	Average LEL Reading (percent)	No. of Cycles per Day	Cycle length (minutes)	Propane Cycle (minutes)	Cycle Breakdown (minutes)	Comments
				PMW-1	BW-4	BW-6	BW-7							
11/21/2011	1 day	-84	Baseline Sampling Event #1										7 wells: NDMA, anions, dissolved gases	
12/5/2011	1 day	-70	Baseline Sampling Event #2										7 wells: NDMA, anions, dissolved gases	
2/7/2012	1 day	-6	Baseline Sampling Event (propanotrophs)										6 wells for total propanotrophs	
2/8/2012	1 day	-5	Dissolved oxygen and propane distribution sampling (system testing)										Select wells sampled for field param & dissolved gases to determine gas distribution during system testing	
2/9/2012	1 day	-4	Dissolved oxygen and propane distribution sampling (system testing)										Select wells sampled for field param & dissolved gases to determine gas distribution during system testing	
2/13/2012	3 days	0	System startup & testing	X	X			5	2	2	50	30	10-30-10	
2/16/2012	15 days	3	Normal operation	X	X			5	5	2	30	20	5-20-5	Having problems with propane condensation at night due to low temperature and high pressure required to sparge at BW-4
3/2/2012	22 days	18	Restart operation: PMW-1 only, 2 cycles per day	X				5	30	2	30	20	5-20-5	BW-4 no longer operational, sparging at PMW-1 only
3/24/2012	41 days	40	Normal operation: 3 cycles during day-none at night	X				5	30	3	35	20	10-20-5	Intermittent problems with propane flow, due to cold temp - correct with heat tape and insulation
3/26/2012	1 day	42	Performance Sampling Event #1											7 wells: NDMA, anions, dissolved gases
5/4/2012	8 days	81	Normal operation: 6 cycles per day	X				5	35	6	35	20	10-20-5	Increase to 6 cycles per day
5/7/2012	1 day	84	Performance Sampling Event #2											7 wells: NDMA, anions, dissolved gases, total propanotrophs
5/12/2012	131 days	89	Normal operation: 8 cycles per day	X				6	40	8	32	26	2-26-4	Increase to 8 cycles per day
6/4/2012	1 day	112	Propane distribution sampling											5 wells for dissolved gases PMW-1 for NDMA.
6/18/2012	4 days	126	Installed new sparge wells BW-6 and BW-7											
6/26/2012	83 days	134	Normal operation: 3 wells, 8 cycles per day	X		X	X	6	40	8	34	24	4-24-6	
7/23/2012	1 day	161	Performance Sampling Event #3											7 wells: NDMA, anions, dissolved gases
8/16/2012	1 day	185	Performance Sampling Event #4											7 wells: NDMA, anions, dissolved gases
9/13/2012	1 day	213	Performance Sampling Event #5											7 wells: NDMA, anions, dissolved gases, total propanotrophs
9/17/2012	157 days	217	Normal operation: 3 wells, 12 cycles per day	X		X	X	6	40	12	48	40	4-40-4	Increased to 12 cycles per day
10/1/2012	1 day	231	Propane degradation test											PMW-3 & PMW-4. Two sparge cycles.
10/11/2012	1 day	241	Performance Sampling Event #6											7 wells: NDMA, anions, dissolved gases
11/26/2012	1 day	287	Performance Sampling Event #7											7 wells: NDMA, anions, dissolved gases
12/20/2012	1 day	311	Performance Sampling Event #8											7 wells: NDMA, anions, dissolved gases, total propanotrophs
1/31/2013	1 day	353	Performance Sampling Event #9											9 wells: NDMA, anions, dissolved gases
2/21/2013	1 day	374	System shutdown											all gas flow shut down
3/4/2013	1 day	385	Rebound Sampling Event #1											9 wells: NDMA, anions, dissolved gases
4/18/2013	1 day	430	Rebound Sampling Event #2											9 wells: NDMA, anions, dissolved gases, total propanotrophs
7/17/2013	2 days	520	Well abandonment											

Table 5.3. Analytical Methods for the Demonstration.

Analyte ¹	Method/ Laboratory	Preservative	Bottle	Hold time
NDMA	EPA 521/Weck	4°C with sodium thiosulfate	500 mL glass screw-cap x 2. Bottles provided by Weck Laboratory	14 days (extraction) 28 days (extract)
VOCs	EPA 8260/CB&I	4°C with HCl	40 mL VOA vial x2. No headspace	14 days
Anions	EPA 300.0/CB&I	4°C	100 mL polyethylene screw-cap	2 days (NO ₃ , PO ₄); 28 days all other
Total Propanotrophs	qPCR/Microbial Insights ²	4°C	950 mL sterile screw-cap bottle	NA ³
Dissolved Gases	EPA 3810, RSK-175/CB&I ²	4°C with HCl	40 mL VOA vial x 2. No headspace	14 days
Redox Potential	Field Meter	--	--	NA
DO	Field Meter	--	--	NA
pH	Field Meter	--	--	NA
Conductivity	Field Meter	--	--	NA

¹All analyses are in groundwater ²Not a standard EPA Method. ³NA = Not applicable; °C – degrees Celsius; HCl – hydrochloric acid; mL – milliliter(s); NO₃ – nitrate; PO₄ – phosphate; VOA – volatile organic analysis

5.6.2 Numbers and Types of Samples Collected

The numbers and types of groundwater samples collected are provided in **Table 5.4**. During site characterization activities, four bromide sampling events were performed at four wells (PMW-1–PMW-4) as part of a bromide tracer test that occurred over approximately one month. Two rounds of baseline groundwater sampling were conducted from the seven MWs in the TPA (PMW-1–PMW-6 and BMW-1) on Days -84 and -70 before system start-up (Day 0). Six wells were sampled on Day -6 to quantify baseline propanotroph numbers. There were nine rounds of sampling conducted during biosparging that included all seven PMWs (from Day 42 to Day 353 after start-up). Biosparge wells BW-6 and BW-7 were also sampled on Days 133 (after installation), 311, and 353. Samples for total propanotrophs were collected during three sampling rounds (Day 84, 213, and 353). Samples were collected from five wells (PMW-1–PMW-5) on Day 112 after a sparge cycle to evaluate propane distribution in the TPA during biosparging at PMW-1. A propane degradation test was conducted on Day 231 after system optimization to evaluate the propane concentrations in groundwater during biosparge cycles and the rate at which the propane was consumed by indigenous bacteria. Finally, two rebound sampling rounds were conducted after the biosparging system was shut down on Day 353 (Days 385 and 430). In addition to the seven wells typically sampled during the performance monitoring event, samples were collected from biosparging wells BW-6 and BW-7 during these events.

Table 5.4. Total Number and Types of Samples Collected During the Demonstration.

Event	Occurrence	Number of Samples	Analyte	Location
Bromide Tracer Testing	6 Events (Days -229, -227, -223, -217, -202, -200)	24	Anions (bromide)	4 Wells (PMW-1 through PMW-4)
Background Sampling	2 Events (Days -84 and -70)	14	NDMA, VOCs, anions, dissolved gases, field parameters	7 Wells. All performance monitoring wells (PMW-1 through PMW-6); background well (BMW-1)
	1 Event (Day -6)	6	Total propanotrophs	6 Wells. Performance monitoring wells (PMW-1 through PMW-5); background well (BMW-1) and
Technology Performance Sampling	9 Events (Days 42, 84, 161, 185, 213, 241, 287, 311, 353)	64	NDMA, anions, dissolved gases, field parameters	7 Wells. All performance monitoring wells (PMW-1 through PMW-6); background well (BMW-1) and wells BW-6, BW-7 (Day 133, 311, 353 only)
	1 Event (Day 133) for BW-6 and BW-7 only			
	3 Events (Days 84, 213, 311)	18	Total propanotrophs	6 Wells. Performance monitoring wells (PMW-1 through PMW-5); background well (BMW-1)
Propane Distribution Sampling	1 Event (Day 112)	5	Dissolved gases (propane)	PMW-1 through PMW-5 after sparge cycle
	1 Event (Day 231)	46	Dissolved gases (propane)	PMW-3 and PMW-4 23 samples each through two sparge cycles
Rebound Sampling	2 Events (Days 385 and 430)	18	NDMA, anions, dissolved gases, field parameters	9 Wells. All performance monitoring wells (PMW-1 through PMW-6); background well (BMW-1); Biosparge wells BW-6, BW-7
	1 Event (Day 430)	6	Total propanotrophs	6 Wells. Performance monitoring wells (PMW-1 through PMW-5); background well (BMW-1)

5.7 SAMPLING RESULTS

5.7.1 NDMA

From baseline sampling (average concentrations from Day -70 and Day -84) to the final day sampling during active biosparging (Day 353), concentrations of NDMA declined by 99.7%–>99.9% in the four PMWs within the zone of influence of the biosparge system (**Figure 5.5**). Baseline concentrations of NDMA, which averaged 25,000 ±6000 ng/L (seven TPA MWs, two baseline events) declined to between 2.7 and 72 ng/L by Day 353 (mean value 40 ±30 ng/L).

The NDMA concentration in well PMW-2 was <3 ng/L on Day 353. By comparison, the NDMA concentration in the side-gradient control well (BMW-1) averaged 36,000 ng/L during baseline sampling and was 31,000 ng/L on Day 353, a decline of only 14%. Concentrations of NDMA in the far downgradient wells PMW-5 and PMW-6 began to show measurable declines near the end of the demonstration (including after the biosparging system was shut down), presumably as clean water from the biosparge plot began to reach this region of the aquifer. NDMA in PMW-5 declined to 5,400 ng/L on Day 430 (from an initial average of 26,000 ng/L) and NDMA in PMW-6 fell to 13,000 ng/L on Day 430 (from an initial average of 22,500 ng/L).

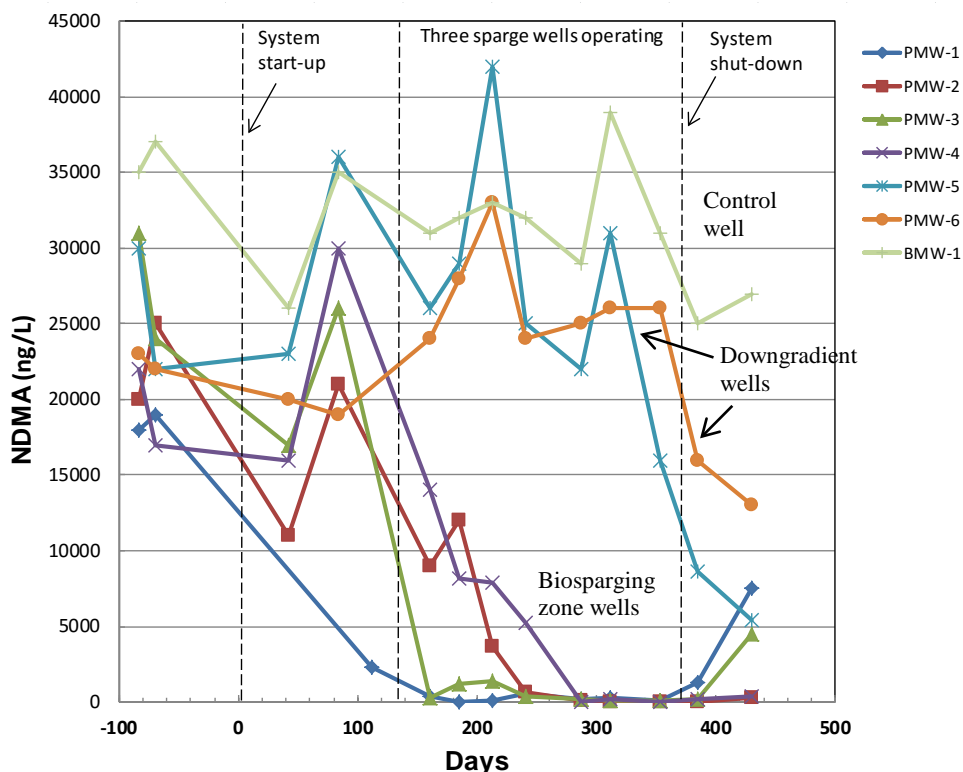


Figure 5.5. Concentrations of NDMA in the Demonstration Plot.

After the system was shut down on Day 373, increases in NDMA were observed in all four of the PMWs within the zone of influence of the biosparge well (**Figure 5.5**). This is consistent with a supply of propane gas being necessary for continued *in situ* biodegradation of NDMA in the aquifer.

The concentration of NDMA was also measured in biosparging wells BW-6 and BW-7 on Days 133 (immediately after installation), and on Days 311, 353, 385, and 430. As observed with the system MWs, NDMA declined significantly in each of these wells. NDMA in BW-6 declined from 25,000 ng/L on Day 133, to 5 ng/L on Day 353, and then rebounded after system shut-down to 340 ng/L on Day 430. NDMA in BW-7 declined more slowly, falling from 15,000 ng/L on Day 133, to 3,800 ng/L on Day 353. Interestingly, the concentration continued to decline in this well after the biosparge system was shut down, reaching 9.5 ng/L by Day 430. Propane concentrations in this well during the sampling events were also somewhat lower than in the other two wells used for sparging, reaching a maximum of only 37 $\mu\text{g/L}$ on Day 353. This may merely reflect the time between system shut-down and well sampling since the propane consumption in the aquifer was rapid, and the well appeared to operate properly as a sparge well, based on pressures and gas flow.

Despite the differences in NDMA degradation rates, losses of >99.9% were achieved in each well.

5.7.2 Volatile Organic Compounds (VOCs)

VOCs were analyzed by EPA Method 8260 during both of the background sampling events on Day -84 and Day -70 in each of the MWs. None of the 67 VOCs included in the EPA 8330 analyte list were detected at a concentration above the PQL of 5–10 µg/L based on the compound. Because no VOCs were detected in the TPA, this analysis was not performed during the remainder of the demonstration.

5.7.3 Dissolved Gases

5.7.3.1 Propane

Propane was detected at between 20 and 300 µg/L in PMW-1, PMW-2, PMW-3, and PMW-4, 14 days after the system start-up (**Figure 5.6**), indicating that the gas was being distributed throughout the demonstration plot. However, as noted previously, PMW-1 was primarily used for biosparging at the beginning of the demonstration due to issues with the original five sparge wells. New sparge wells BW-6 and BW-7 were installed approximately four months after start-up and run along with PMW-1 for the duration of the study. The addition of these wells significantly increased the propane concentrations in PMW-1, PMW-2, and PMW-3 (>500 µg/L) and the overall amount of propane supplied to the demonstration plot. PMW-4 also had detectable propane albeit at lower concentrations than the other three wells. Thus, good gas distribution in the treatment area was documented. The maximum concentration of propane in groundwater throughout the demonstration plot did not exceed 1 mg/L at any time, even in PMW-1, which was used as a biosparge well in addition to a MW. A desired ratio of at least 4 parts oxygen to 1 part propane (mg/L basis) was always exceeded (See **Section 6.2**).

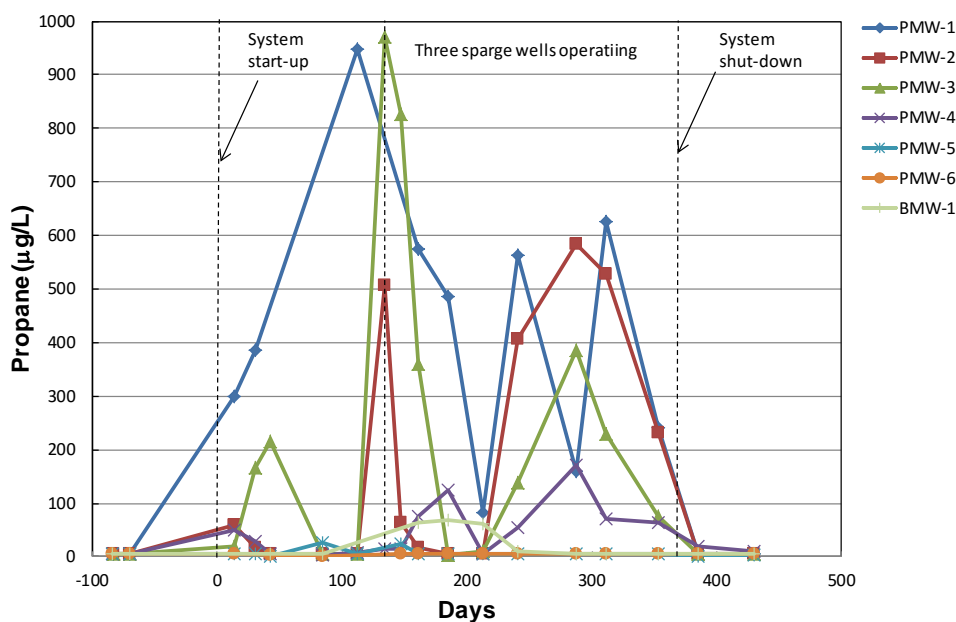


Figure 5.6. Concentrations of Propane in the Demonstration Plot.

It is interesting to note that low concentrations of propane (maximum of 70 $\mu\text{g/L}$) were detected in control well BMW-1 (which was ~ 75 ft away from the center of the demonstration plot) shortly after installation of BW-6 and BW-7. NDMA degradation was not indicated in this well, likely because the quantities of propane reaching this region were too low to stimulate bacterial activity. However, some of the sparged propane clearly traveled to this region of the aquifer. This may reflect the fact that the biosparging zone was in a confined region of the aquifer, which acted to enhance horizontal transport of propane.

A field test was conducted on Day 230 to evaluate the flux of propane in the aquifer during sparge cycles using PMW-1, BW-6, and BW-7 (i.e., wells that operated from Day 133 to Day 373). During this test, two 45-min sparge-cycles were conducted at 6 SCFM with propane at 40% of the LEL. Each sparge cycle was followed by a recovery period. The concentration of propane was measured in PMW-3 and PMW-4 before, during, and after each of the sparge cycles at 23 sample times. The results from this test are provided in **Figure 5.7**. At the time of testing, propane concentrations in PMW-3 and PMW-4 ranged from a high of ~ 225 $\mu\text{g/L}$, which occurred 30 min after the end of each sparge cycle, to < 50 $\mu\text{g/L}$ during the middle of each sparge interval. Presumably the delay in reaching a maximum concentration reflects time required for propane transport from the sparging wells to PMW-3 and PMW-4, as well as time required for propane dissolution. If it is assumed that the decline in concentration is due predominantly to biodegradation, the propane first order decay rates in these wells are on the order of 0.02 – 0.03 min^{-1} . These are in the range of rates observed for propane decay recently at Vandenberg AFB during a demonstration of cometabolic degradation of 1,4-dioxane (0.01 – 0.05 min^{-1}) (Lippincott et al., 2015).

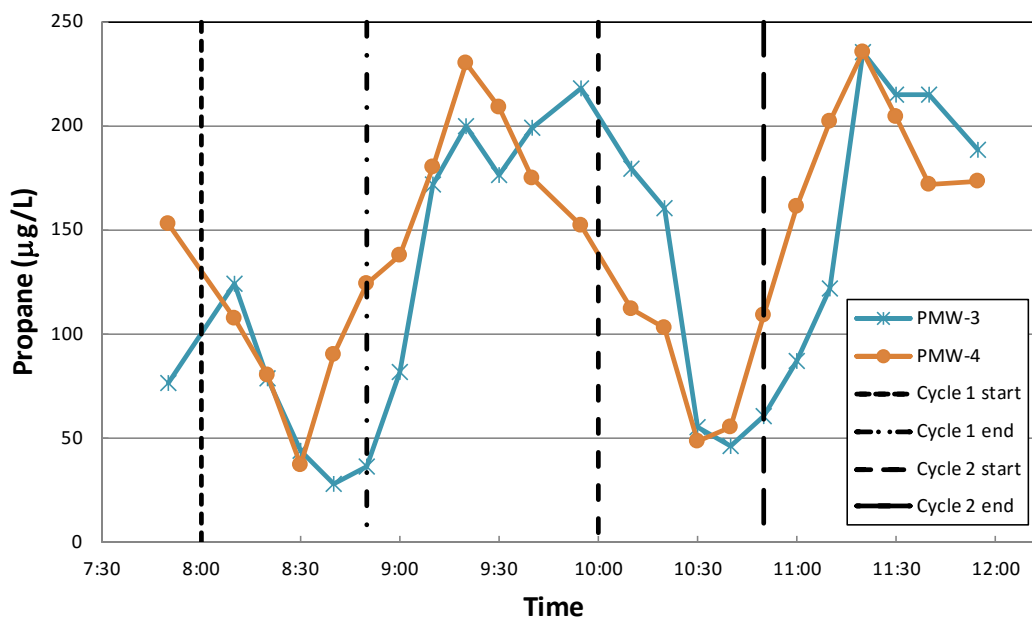


Figure 5.7. Concentrations of Propane in PMW-3 and PMW-4 During a Propane Biosparge Test.

The start and end of the two sparge cycles are provided as dashed lines as indicated.

5.7.3.2 Dissolved oxygen (DO)

DO in the TPA was generally <5 mg/L prior to the initiation of biosparging. DO increased throughout the demonstration area PMWs consistently to >10 mg/L during active sparging, even when only well PMW-1 was in operation as the lone biosparge well (**Figure 5.8**). DO increases of similar magnitude were observed in downgradient well PMW-5 after installation of additional biosparge wells (BW-6, BW-7), and DO in downgradient well PMW-6 also increased to near 10 mg/L by the end of the demonstration. Slight increases in DO were detected in control well BMW-1, but the maximum DO was 5 mg/L and the concentration decreased after Day 300. This may be due to seasonal variations, or indicates that, as with propane, a small amount of sparged air reached the side-gradient well. The objective of achieving DO values >10 mg/L throughout the TPA was achieved. There was clearly enough oxygen present in the TPA to support aerobic degradation of propane throughout the entire demonstration period.

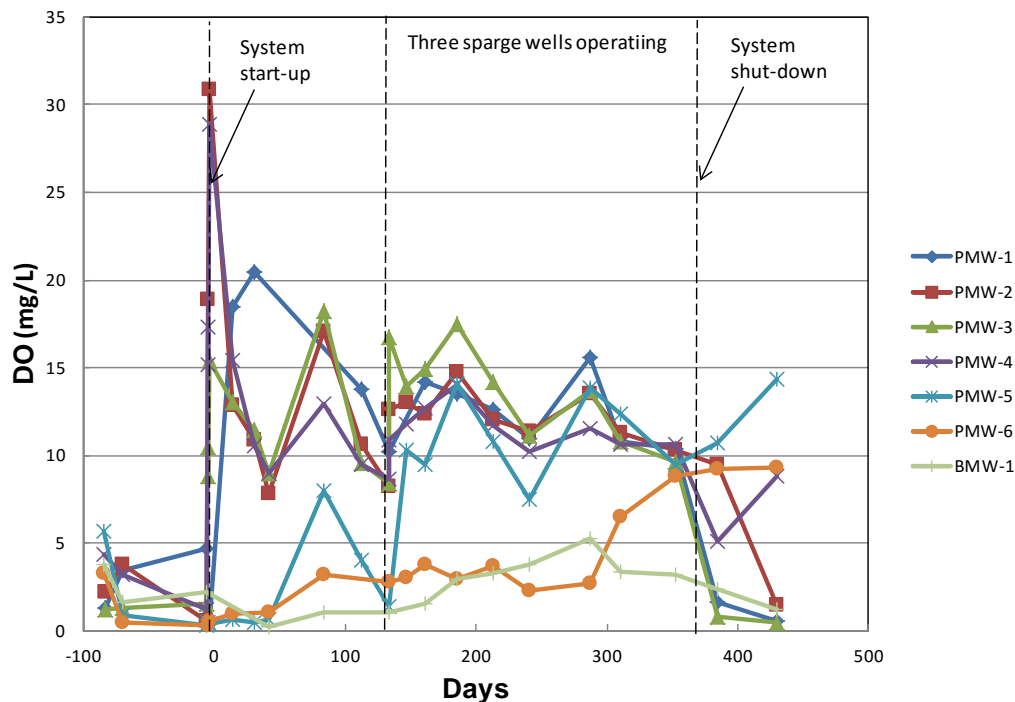


Figure 5.8. Concentrations of DO in the Demonstration Plot Wells.

5.7.3.3 Dissolved methane

Methane was detected in all of the MWs during the two baseline sampling events at measurable concentrations, but typically at <5 µg/L. Somewhat higher concentrations were detected in PMW-4 (212 µg/L on Day -84, and 145 µg/L on Day -70). This methane is most likely derived from methanogenic processes occurring in upgradient groundwater. Throughout the course of the demonstration, methane was detected sporadically at trace concentrations (typically <1 µg/L) in wells PMW-1–PMW-4, PMW-6, and BMW-1. Somewhat higher concentrations were detected in PMW-5, with concentrations of up to 100 µg/L observed during system operation and one measurement of 2,800 µg/L occurring on Day 385 after system shut-down. This well most likely intercepted a conductive layer with higher methane, due to current or past methanogenesis.

5.7.4 Oxidation-Reduction Potential (ORP)

The baseline ORP in the TPA ranged from ~ -100 mV to $+100$ mV prior to system start-up (**Figure 5.9**). With the exception of Day 161, when the ORP in three of the PMWs was negative, the ORP in the demonstration plot wells was generally $>+100$ mV, indicating that conditions were sufficiently oxidizing for an aerobic degradation process to occur. However, there was significant variation in ORP among the different sampling events, and most of the wells (including the background well BMW-1) tended to have similar ORP values at any given time point. For instance, on Day 241, most of the wells had an ORP value of $+100$ mV, whereas on Days 287 and 311, most wells were near $+400$ mV, before declining again to $\sim +150$ mV by Day 353. The reason for this co-variation, particularly between the background well and PMWs, is unclear, and is most likely due to inconsistencies often observed when collecting ORP readings in the field. The DO values in the wells were much more consistent over time.

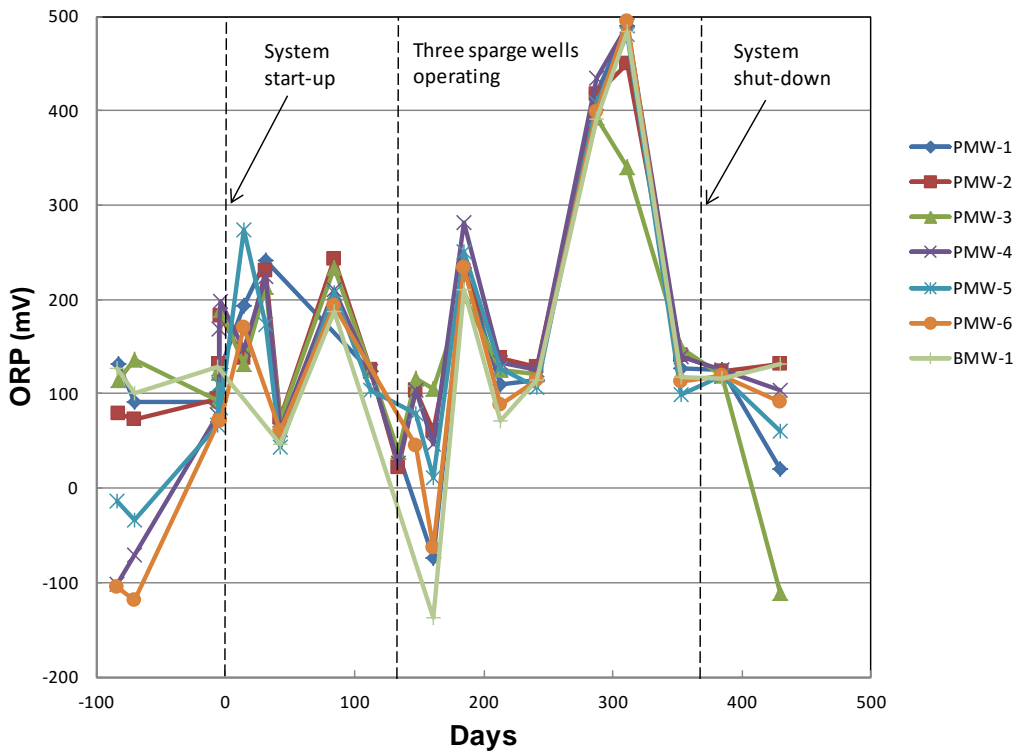


Figure 5.9. ORP in the Demonstration Plot Wells.

5.7.5 Anions

Nitrate: The primary anions of interest in the TPA were nitrate and sulfate. Nitrate concentrations in PMW-1–PMW-5 declined appreciably over the course of the demonstration (**Figure 5.10**). The background levels in most of the wells ranged from ~1.7 to 2.5 mg/L as NO₃-N, with slightly lower values in PMW-6. During system operation, NO₃-N in PMW-1–PMW-5 declined to <0.3 mg/L. A similar decline did not occur in BMW-1, and PMW-6 only showed a moderate decline toward the end of the demonstration. Nitrite was not detected in any of the wells. Because of the high DO and ORP, the loss of nitrate is likely not the result of denitrification, a process that is inhibited by oxygen. Rather, the consumption of nitrate is consistent with assimilation of N by propanotrophs in the aquifer as a required inorganic nutrient. No exogenous nutrients were added to the aquifer, so bacterial assimilation of existing nutrients is expected.

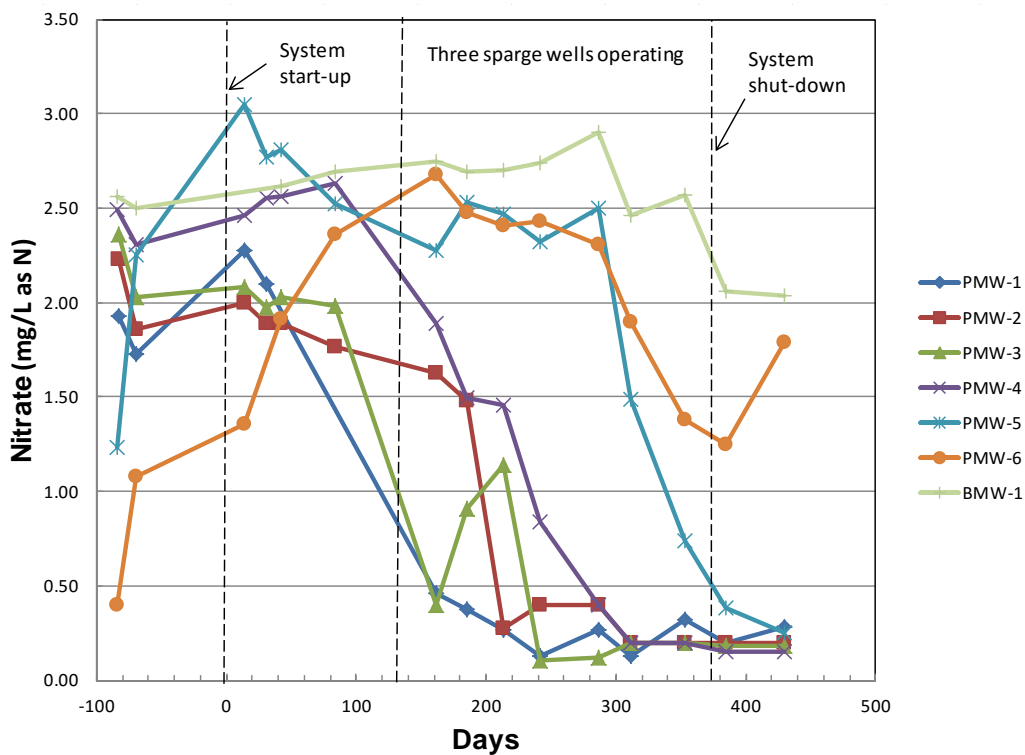


Figure 5.10. Concentration of Nitrate-N in the Demonstration Plot Wells.

Sulfate: Sulfate concentrations throughout the TPA ranged from ~13 to 20 mg/L during baseline sampling (**Figure 5.11**). These concentrations remained consistently in this range over the course of the demonstration as would be expected under the oxidizing conditions in the aquifer.

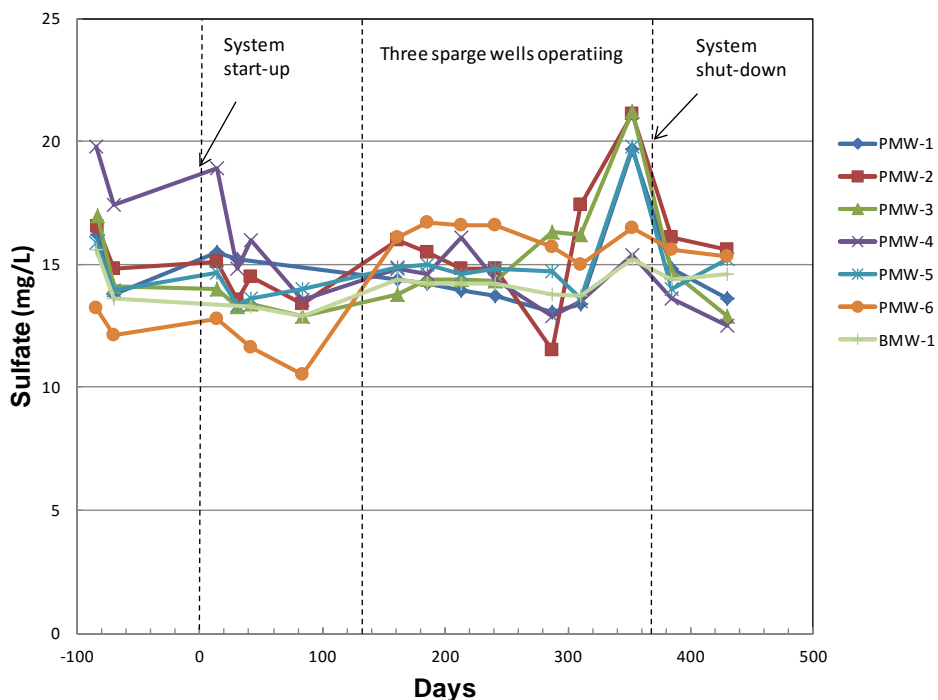


Figure 5.11. Concentration of Sulfate in the Demonstration Plot Wells.

Orthophosphate: Orthophosphate was not detected in the TPA groundwater at a minimum detection limit (MDL) of 0.2–1 mg/L. Bacteria require phosphorus for growth, but it is likely that this was obtained from insoluble forms of phosphate in the aquifer that would not be detected by the EPA 300 analytical method.

Chloride: Chloride concentrations in groundwater remained in the vicinity of 10 mg/L throughout the demonstration.

5.7.6 pH

The pH in the demonstration plot generally remained between 6.5 and 7 during the demonstration. The pH was slightly elevated in PMW-1 (which was used as both a sparge well and a MW) during some events, but did not exceed 7.5 standard units (SU).

5.7.7 Temperature

The mean groundwater temperature varied seasonally from ~14 degrees Celsius (°C) on Day -70 (December) to a maximum of ~19°C on Day 185 (August).

5.7.8 Total propanotrophs

The population of indigenous propanotrophs in wells PMW-2, PMW-3, and PMW-4 increased by >1 log order over the course of the demonstration (**Figure 5.12**). On Day 311, the final day of sampling during active biosparging, the propanotroph density in these three wells ranged from 2×10^5 to 6×10^5 cells/milliliter (mL). The propanotroph population in each of these wells remained reasonably constant thereafter even in the absence of propane addition for >100 days. By comparison, the cell density in BMW-1 declined from 2×10^4 to 6×10^3 cells/mL over the entire course of the demonstration. It should also be noted that only propanotrophs present as planktonic bacteria in groundwater were measured. It is possible—even likely—that the density of propanotrophs adsorbed to aquifer particles increased more significantly as some propanotrophs are known to form significant biofilms (Hatzinger et al., 2011; Webster et al., 2013; Lippincott et al., 2015).

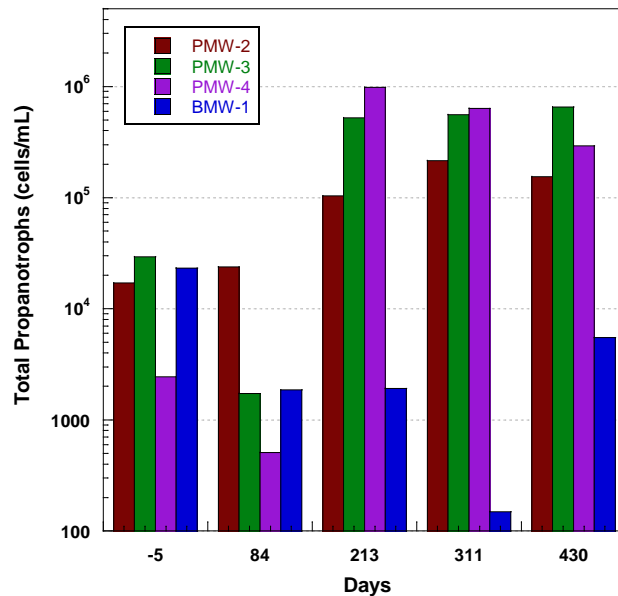


Figure 5.12. Total propanotrophs in Groundwater in the Demonstration Plot Wells.

6.0 PERFORMANCE ASSESSMENT

Performance objectives were established for this demonstration to provide a basis for evaluating the results of the *in situ* remediation approach for NDMA in groundwater. Performance criteria were selected based on factors that would likely be considered when bringing the proposed technology to full-scale application. The performance objectives are provided in **Table 3.1**. The data for each given objective are provided in **Section 5.7**. The critical performance objectives for this demonstration were achieved. The following subsections summarize the data collected and provide a summary and assessment of the data supporting performance objectives.

6.1 EFFECTIVENESS OF NDMA TREATMENT

The key performance objectives for *in situ* NDMA treatment were >99% overall reduction in NDMA concentrations throughout the local treatment plot from the pre-treatment to the post-treatment phase, and reduction of NDMA to <3 ng/L (the current California PHG for NDMA in water; OEHHA, 2006) in at least one of the PMWs. Both objectives were met. As presented in **Section 5.7.1**, NDMA declined by 99.7%–>99.9% in the four PMWs within the zone of influence of the biosparge system, an area of ~20 ft by 20 ft (**Figure 5.1**). Baseline concentrations of 25,000 ±6,000 ng/L NDMA declined to between 2.7 and 72 ng/L by Day 353 (mean value 40 ±30 ng/L; 99.8% reduction). Similar declines in NDMA also were observed in biosparge wells BW-6 and BW-7, with reductions >99.9%. The side-gradient control well (BMW-1; ~75 ft from the core of the demonstration plot) that was not appreciably influenced by the system declined only 14%. Downgradient wells PMW-5 and PMW-6 showed measurable declines near the end of the demonstration, presumably as treated water from the biosparge plot began to reach this region of the aquifer. NDMA in PMW-5 and PMW-6 declined to 5,400 ng/L and 13,000 ng/L, respectively, by Day 430, the final day of sample collection.

The rate of NDMA biodegradation in the TPA was calculated in wells PMW-2, PMW-3, and PMW-4. First-order rate constants were determined using data from Day 84 to Day 353 (**Figure 5.5**). The degradation rates were 0.019 day⁻¹ for PMW-3 ($R^2 = 0.95$), 0.031 day⁻¹ for PMW-4 ($R^2 = 0.82$), and 0.037 day⁻¹ for PMW-2 ($R^2 = 0.68$). These rates equate to NDMA half-lives ranging from 19 to 36 days. These rates are similar to those reported by Lippincott et al. (2015), for treatment of 1,4-dioxane using propane biosparging at a site in California, where degradation rates varied from 0.021 day⁻¹ to 0.036 day⁻¹.

The data from this field test clearly indicate that propane biosparging is an effective approach to reduce the concentrations of NDMA in a groundwater aquifer by 3 to 4 orders of magnitude, and that concentrations in the low ng/L range can be achieved with continuous treatment. These results are consistent with data achieved in pure culture studies (Fournier et al., 2009) as well as various bioreactor designs (Hatzinger et al., 2011; Webster et al., 2013). To our knowledge, this is the first report of successful *in situ* treatment of NDMA in groundwater using cometabolism or any other bioremediation approach. The application of propane biosparging for effective treatment of another U.S. Department of Defense (DoD) contaminant of concern, 1,4-dioxane, has also recently been reported (Lippincott et al., 2015).

6.2 ADEQUATE DISTRIBUTION OF GASES IN GROUNDWATER

Distribution of adequate propane and oxygen, and appropriate ratios of these two gases, was critical to the success of this remedial approach. Preliminary testing at the demonstration plot suggested that a gas sparging radius of at least 12.5 ft could be achieved in the TPA. When the system was started, with sparging primarily through well PMW-1 (and a low amount flow from BW-4 for approximately two weeks), dissolved propane was detected at between 5 and 50 µg/L in PMW-4, which was ~20 ft away from PMW-1 (**Figure 5.6**) showing that the gas was being distributed in the aquifer. However, based on analytical results for both dissolved propane and NDMA, the amount of propane provided by PMW-1 alone was not sufficient for stimulating NDMA degradation throughout the TPA, so biosparge wells BW-6 and BW-7 were installed. The addition of these wells significantly increased the dissolved propane concentrations in PMW-1, PMW-2, and PMW-3 (>500 µg/L) and the overall amount of propane supplied to the demonstration plot. PMW-4 also had detectable dissolved propane, albeit at lower concentrations than the other three wells. Thus, good gas distribution in the treatment area was documented.

The oxygen:propane ratio in the groundwater was also important to the success of this field demonstration. In particular, it was important to ensure that adequate oxygen was present to support propane biodegradation and not create anoxic conditions in the aquifer. Propane was used as the primary carbon source/electron donor for bacterial growth in the aquifer with oxygen as the electron acceptor. The required molar ratio of oxygen (O₂) to propane (C₃H₈) for complete oxidation of propane to carbon dioxide (CO₂; not accounting for microbial biomass incorporation of C) is ~5 mols O₂ to 1 mol C₃H₈ [**Eq. 1**]. When converted to mg/L, the above stoichiometry suggests that the oxygen requirement for bacteria to biodegrade 1 mg/L of C₃H₈ is ~3.6 mg/L O₂. Thus, on an mg/L basis, an oxygen:propane ratio of ~4:1 is required to ensure that anoxic conditions do not occur in the aquifer.



A desired ratio of oxygen:propane was always exceeded based on the analytical data generated during the project, with DO typically >10 mg/L (**Figure 5.8**) during system operation and dissolved propane never exceeding even 1 mg/L (**Figures 5.6** and **5.7**). During a sparging field test run under optimized conditions, two 45-min sparge-cycles were conducted at 6 SCFM with propane at 40% of the LEL, and propane was measured in PMW-3 and PMW-4 before, during, and after each of the sparge cycles (**Figure 5.7**). Propane concentrations in these wells, which reached ~225 µg/L, declined to 25–50 µg/L during ~1 hour, indicating rapid consumption of propane in the aquifer. If it is assumed that the decline in concentration is due predominantly to biodegradation, the propane first-order decay rates in these wells are 0.032 min⁻¹ (R² = 0.84) for PMW-3, and 0.021 min⁻¹ (R² = 0.94) for PMW-4. These propane decay rates are consistent with those observed recently at Vandenberg AFB during a demonstration of cometabolic degradation of 1,4-dioxane (0.01–0.05 min⁻¹) (Lippincott et al., 2015).

Between June 26, 2012, and September 16, 2012, normal system operation included a total biosparge injection rate of 6 SCFM (2 SCFM per biosparge well), for eight 34-min cycles per day. Propane was added at a concentration of approximately 0.84% (40% of the LEL) for 24 min during each cycle. During this period, an estimated 0.73 lbs of propane was added daily. Between September 17, 2012, and February 20, 2013, normal system operation included a total biosparge injection rate of 6 SCFM (2 SCFM per biosparge well), for twelve 48-min cycles per day.

Propane was added at a concentration of approximately 0.84% (40% of the LEL) for 40 min during each cycle. During this period, an estimated 1.83 lbs of propane was added daily. A total of approximately 475 lbs (5 cylinders) of propane was injected throughout the demonstration.

6.3 MINIMAL NEGATIVE IMPACTS TO GROUNDWATER GEOCHEMISTRY

One of the traditional issues with anaerobic bioremediation processes for many different contaminants is the general degradation in water quality in the vicinity of the treatment area. The addition of large quantities of organic substrates (e.g., to stimulate reduction of chlorinated solvents) often leads to the generation of organic byproducts (such as fatty acids), production of methane and hydrogen sulfide, and the mobilization of redox sensitive metals, such as iron, manganese, and arsenic among others (e.g., Leeson et al., 2004). The groundwater pH also can be affected in poorly buffered systems. When pumping wells are present downgradient of a treatment area (as is the case with OU 4 at Aerojet), the presence of organic byproducts and dissolved metals can lead to the chemical and biological fouling of both extraction wells and *ex situ* treatment systems. A previous injection of molasses at the Aerojet site caused such issues.¹

One of the advantages of aerobic treatment processes, such as that utilized during this demonstration, is minimal secondary impacts to groundwater geochemistry (provided that the groundwater environment is not naturally highly-reducing). Based on the metrics examined (DO, ORP, pH), negative impacts on groundwater geochemistry in the plot area were not observed. DO increased throughout the demonstration area PMWs from ≤ 1 mg/L to >10 mg/L during active sparging. DO increases of similar magnitude were observed in downgradient well PMW-5 after installation of additional sparge wells (BW-6, BW-7), and DO in downgradient well PMW-6 also increased to near 10 mg/L by the end of the demonstration. Slight increases in DO were detected in control well BMW-1, but the maximum DO was 5 mg/L and the concentration decreased after Day 300. This may be a seasonal change. Similarly, the ORP in the demonstration plot wells was near or $>+100$ mV for a majority of the demonstration. The pH in the demonstration plot generally remained between 6.5 and 7 during the demonstration. This pH was slightly elevated in PMW-1 (which was used as both a sparge well and a MW) during some events, but did not exceed 7.5 SU.

6.4 INCREASE IN PROPANOTROPH POPULATION

Propane-oxidizing bacteria increased by more than ten-fold in treatment wells (PMW-2, PMW-3, PMW-4) relative to pre-treatment concentrations (between 2×10^3 and 3×10^4 cells/mL). On Day 311, the final day of sampling during active biosparging, the propanotroph density in these three wells ranged from 2×10^5 to 6×10^5 cells/mL. The propanotroph population in each of the wells remained reasonably constant thereafter, even in the absence of propane addition for >80 days. By comparison, the cell density in BMW-1 declined from 2×10^4 to 6×10^3 cells/mL over the entire course of the demonstration. It is likely that even greater increases in indigenous propanotrophs occurred in the aquifer. The true extent of this increase is difficult to accurately measure without collecting and extracting cells from aquifer cores because only planktonic (free living) organisms are present in groundwater samples, and the number of cells present in biofilms are not typically or easily readily measured, even though they may be much higher than planktonic cells (Costerton et al., 1986).

¹ Personal communication, Mr. Scott Neville, Senior Geologist, Aerojet.

This may be particularly true for some propanotrophic cells, which have been observed to be largely present in biofilms in flow-through systems (Hatzinger et al., 2011, Webster et al., 2013). For example, Hatzinger et al. (2011) reported that nearly all cells of the ENV425 were adsorbed to surfaces in a membrane bioreactor study, and Lippincott et al. (2015) observed no significant increases in propanotroph density in groundwater during an *in situ* biosparging study despite rapid and increasing rates of propane consumption and 1,4-dioxane degradation. Thus, while the increase in propanotroph density in groundwater may be reflective of increases on solid surfaces, the overall cell numbers in the aquifer system may be much higher than reported, based solely on the planktonic cells in groundwater.

6.5 SYSTEM RELIABILITY

As discussed in **Section 2.1**, an air- and propane-biosparging approach was used for this demonstration. Although biosparging is a form of AS, the focus is on providing the necessary gases (usually oxygen) for contaminant biodegradation and minimizing volatilization (USEPA, 1994). Therefore, the proposed biosparging system used during this demonstration was expected to operate reliably with minimal requirement for maintenance after start-up.

The system reliability was evaluated qualitatively through discussions with field personnel, and quantitatively by evaluating operational data (flows and LEL) collected from the PLC on the biosparging system, total time down for unplanned maintenance/repair (documented in field book), and total costs of the unplanned maintenance/repair (tracked via personnel hours and replacement parts/materials).

Data collected by the PLC from June 26, 2012 (after additional sparging wells were installed), through February 20, 2013, showed that the system operated within design parameters (e.g., air flow and propane delivery) for 233 out of 240 days, or 97% of the time. Thus, system reliability exceeded the established performance objective of 90% as cited in **Table 3.1**. Additionally, no significant maintenance or repairs to the system were required during this period. Repairs to the system that were made during operation included the replacement of a needle valve, a solenoid valve, and the LEL meter (at the end of the demonstration). Considering the biosparging system used during the demonstration was >10 years old, these repairs were not unexpected. Maintenance to the system (beyond routine checks and flow adjustments) primarily included replacement of spent propane cylinders, the installation of a heating blanket for the propane cylinder, and the installation of heat trace tape to propane delivery lines on the system.

7.0 COST ASSESSMENT

7.1 COST MODEL

Costs associated with various aspects of the demonstration were tracked throughout the course of the project in order to evaluate the cost of a potential full-scale bioremediation program and compare it against other remedial approaches. **Table 7.1** summarizes the various cost elements and total cost of the demonstration project. The costs have been grouped by category as recommended in the Federal Remediation Technologies Roundtable Guide to Documenting Cost and Performance for Remediation Projects (FRTR, 1998). Many of the costs shown on this table are a product of the innovative and technology validation aspects of this project, and would not be applicable to a typical site application. Therefore, a separate “discounted costs” column that excludes or appropriately discounts these costs has been included in **Table 7.1** to provide a cost estimate for implementing this technology at the same scale as the demonstration (i.e., pilot scale).

Costs associated with the propane biosparging demonstration were tracked from September 2008 to November 2015. The total cost of the demonstration was \$897,000, which included \$313,000 in capital costs, \$181,000 in operations and maintenance (O&M) costs, and \$403,000 in demonstration-specific costs (cost related to ESTCP requirements, site selection, and characterization).

7.1.1 Capital Costs

Capital costs (primarily system design and installation) accounted for \$313,000 (or 35%) of the total demonstration costs. As indicated in **Table 7.1**, these costs exceed what would be expected during a typical remediation project due partially to the large number of PMWs (seven) installed within the relatively small (50 ft by 30 ft) demonstration area.

7.1.2 O&M Costs

O&M costs accounted for \$181,000 (or 20%) of the total demonstration cost. These costs consisted primarily of groundwater monitoring (including analytical), systems O&M, and reporting costs. System O&M costs were \$91,000, or 10% of total demonstration costs. The cost of the propane added during the demonstration was \$5,000, or 0.5% of total demonstration costs. The cost of consumable treatment components was minimal. Extensive performance monitoring activities were conducted to evaluate this technology including 13 groundwater sampling events (2 baseline and 11 performance).

7.1.3 Demonstration-Specific Costs

Other demonstration-specific costs include those not expected to be incurred during non-research-oriented remediation projects and accounted for \$403,000 (or 54%) of the total demonstration cost. These costs included site selection and characterization, laboratory treatability studies, column studies, ESTCP demonstration reporting, technology transfer, meeting requirements, demonstration and work plans, and preparation of detailed technical and cost and performance reports.

Table 7.1. Demonstration Cost Components.

Cost Element	Details	Tracked Demonstration Costs	Discounted Costs¹
CAPITAL COSTS			
Groundwater Modeling	Labor	\$1,000	\$0
System Design	Labor	\$13,000	\$13,000
Well Installation, Development & Surveying ²	Labor	\$70,000	\$35,000
	Materials	\$3,000	\$3,000
	Subcontracts (driller/surveyor)	\$59,000	\$30,000
System Installation (electrical service, biosparge trailers, system materials)	Labor	\$45,000	\$15,000
	Equipment & Materials	\$30,000	\$30,000
	Subcontracts	\$75,000	\$15,000
Sparge Testing	Labor and Materials	\$17,000	\$8,000
Subtotal		\$313,000	\$149,000
OPERATION AND MAINTENANCE COSTS			
Groundwater Sampling	Labor	\$30,000	\$5,000
	Materials	\$8,000	\$1,000
Analytical	In-House Labor	\$20,000	\$5,000
	Outside Labs	\$26,000	\$5,000
System O&M (including testing & start-up)	Labor	\$66,000	\$43,000
	Materials (propane and consumables)	\$5,000	\$5,000
Reporting & Data Management	Labor	\$24,000	\$6,000
Travel		\$2,000	\$2,000
Subtotal		\$181,000	\$72,000
OTHER TECHNOLOGY-SPECIFIC COSTS			
Site Selection	Labor	\$16,000	\$0
Site Characterization (drilling investigation, depth-dependent sampling, slug tests, pump tests)	Labor (including in-house analytical)	\$74,000	\$0
	Materials	\$1,000	\$0
	Subcontractor (driller)	\$14,000	\$0
Treatability Studies and Column Testing	Labor (including in-house analytical)	\$119,000	\$0
	Outside Lab	\$26,000	\$0
IPR Meeting & Reporting	Labor & Travel	\$21,000	\$0
Technology Transfer (presentations, papers)	Labor & Travel	\$23,000	\$0
Demonstration Plan/Work Plan	Labor	\$41,000	\$10,000
Final Report	Labor	\$52,000	\$10,000
Cost and Performance Report	Labor	\$16,000	\$0
Subtotal		\$403,000	\$20,000
TOTAL COSTS		\$897,000	\$241,000

Notes:

¹Discounted costs are defined as estimated costs to implement this technology at the same scale as the demonstration. These costs do not include the technology validation aspects of this ESTCP demonstrations, such as site selection, treatability studies, extensive groundwater sampling, ESTCP demonstration reporting and meeting (IPR) requirements, and preparation of technical and cost and performance reports.

7.2 COST DRIVERS

7.2.1 General Considerations

The expected cost drivers for installation and operation of a propane biosparging delivery system for the remediation of NDMA-contaminated groundwater, and those that will determine the cost/selection of this technology over other options, include the following:

- Depth of the plume bgs;
- Width, length, and thickness of the plume;
- Aquifer lithology and the presence or absence of impervious layers that would impede sparging;
- Regulatory approval/acceptance of alternatives to sparging that include groundwater extraction and re-injection;
- Length of time for clean-up (e.g., necessity for accelerated clean-up);
- The presence of indigenous propanotrophic bacteria capable of degrading NDMA;
- Presence of co-contaminants such as chloroform, chlorinated ethenes, and ethanes;
- The radius of influence that can be achieved via sparging; and
- O&M costs.

7.2.2 Competing Treatment Technologies

Two other technologies in addition to propane biosparging that have been proven to treat NDMA to below regulatory levels at the field scale include groundwater extraction (P&T) with either:

1. *Ex situ* UV treatment or
2. *Ex situ* fluidized bed reactor (FBR) treatment using cometabolic propanotrophs.

No other *in situ* technologies are known to have been demonstrated to consistently reduce concentrations of NDMA in groundwater aquifers to below regulatory levels of concern. P&T technologies provide capture of contaminated groundwater, and above-ground treatment of the extracted water prior to discharge or re-injection into the subsurface. While these systems can provide protection to downgradient receptors if designed properly, they are inefficient at removing contaminant mass from a plume or source zone, and often require operation for decades, leading to high overall costs.

7.3 COST ANALYSIS

A previous evaluation of cost for NDMA treatment technologies is provided in the Final Report for ESTCP Project 200829 titled “Treatment of N-Nitrosodimethylamine (NDMA) in Groundwater using a Fluidized Bed Bioreactor” (Hatzinger and Webster, 2014). The cost analysis included in that report includes both the UV and FBR treatment approaches, and the following cost analysis is based in part on the cost estimates developed for that project. A cost analysis for the base case was performed for the following technologies:

1. Propane biosparging barrier
2. P&T with UV treatment
3. P&T with FBR treatment

7.3.1 Base Case

A hypothetical base case was developed as a template for the cost analysis as presented in Krug et al. (2009). The base case presents a situation where a shallow aquifer consisting of homogeneous silty sands is contaminated with NDMA. The NDMA-contaminated groundwater extends from 10 to 40 ft bgs along the direction of groundwater flow for 800 ft, and is 400 ft in width (**Figure 7.1**). The specific base case site characteristics including aquifer characteristics and design parameters for each of the remedial approaches analyzed are summarized in **Table 7.2**.

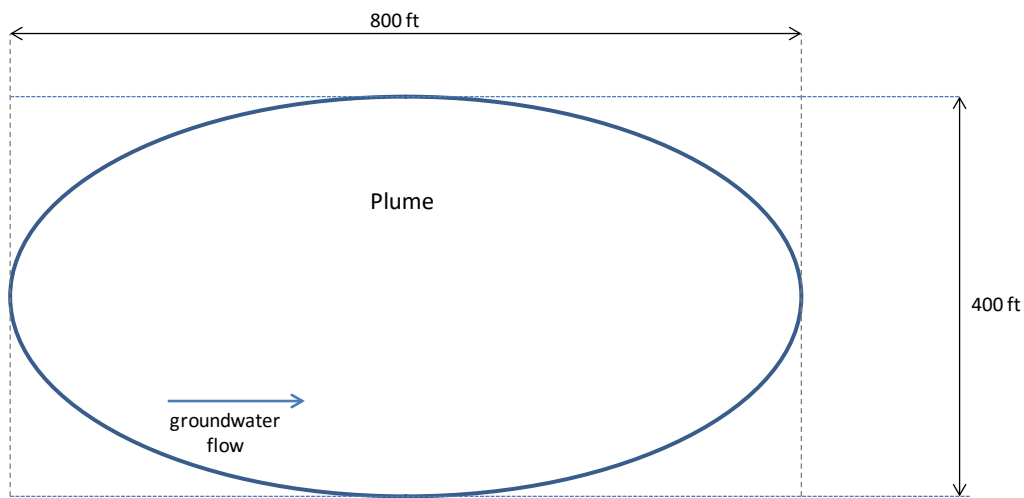


Figure 7.1 Base Case Plume Characteristics.

As indicated in **Table 7.2**, the base case assumes a groundwater seepage velocity of approximately 33 ft/year, and two pore volumes of clean water will need to flush through the impacted area to achieve the cleanup objectives. However, there are a number of factors, such as the degree of heterogeneity of the geological media that will determine the actual number of pore volumes of clean water required to flush through the subsurface to achieve target treatment objectives. Variations in K of the aquifer materials can allow a significant fraction of the total mass of contaminants to diffuse into low K layers, and then act as an ongoing source to the higher K zones. In most geological settings, it is likely that more than two pore volumes would be required to achieve treatment objectives, thus leading to longer treatment times (and costs) for passive and P&T approaches.

Table 7.2. Summary of Base Case Site Characteristics and Design Parameters.

Design Parameter	Units	Alternative		
		Propane Biosparge Barrier	Pump and Treat with UV Treatment	Pump and Treat with FBR Treatment
Width of Plume	feet	400	400	400
Length of Plume	feet	800	800	800
Depth to Water	feet	10	10	10
Vertical Saturated Thickness	feet	40	40	40
Porosity	dimensionless	0.25	0.25	0.25
Gradient	dimensionless	0.008	0.008	0.008
Hydraulic Conductivity	ft/day	2.8	2.8	2.8
Groundwater Seepage Velocity	ft/year	33	33	33
Nitrate Concentration	mg/L	15	15	15
Dissolved Oxygen Concentration	mg/L	5	5	5
Assumed Number of Pore Volumes to Flush Plume	each	2	2	2
Number of Barriers	each	NA	1	1
Number of Monitoring Wells	each	10	10	10
Number of Sparge Wells	each	32	0	0
Number of Extraction Wells	each	0	9	9

Groundwater Travel Time to Barrier	years	24	24	24
Years to Clean Up Groundwater	years	48	48	48

NA - Not Applicable

The following subsections provide cost estimates for implementation of each the three treatment approaches for the base case. The cost estimates provide insight into the comparative capital, O&M, and long-term monitoring costs to better identify cost drivers for each technology/approach. Total costs and the Net Present Value (NPV) of future costs were calculated for each treatment approach. Future costs (O&M and long-term monitoring costs) are discounted, using a 1.4% real discount rate to determine the NPV estimates of these costs (OMB, 2015). Specifically excluded from consideration are the costs of pre-remedial investigations and treatability studies, assuming the costs for these activities would be similar for each alternative. The cost analyses comparing the three approaches are presented below based on a 30-year operating scenario.

7.3.2 Propane Biosparge Barrier

The propane biosparge barrier alternative assumes that a series of sparge wells will be installed at the downgradient edge and perpendicular to the axis of the plume shown in **Figure 7.1**.

Spacing for the sparge wells is assumed to be 25 ft with both a shallow and deep sparge well installed at each of 16 locations for a total of 32 sparge wells. A propane injection system will be constructed including a compressor, controls, and associated piping. An enclosure will be installed to contain the above-ground components. The biosparge barrier will be operated for a period of 30 years, and this alternative assumes 30 years of associated O&M and long-term monitoring costs.

As summarized in **Table 7.3**, the estimated total costs for this alternative over 30 years are approximately \$2,881,000 with a total NPV of lifetime costs of approximately \$2,333,000. The capital cost is approximately \$481,000 including design, work plan, installation of sparge wells and construction of the propane injection system, along with start-up and testing. The NPV of the O&M is estimated at approximately \$1,451,000 for the 30 years of treatment. The O&M costs include the labor costs associated with operations, costs for equipment repair and replacement, and cost for propane.

Table 7.3. Cost Components for Biosparging.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	36,580	-	-	-	-	-	-	36,580	36,580
Well Installation	216,258	-	-	-	-	-	-	216,258	216,258
System Installation	210,186	-	-	-	-	-	-	210,186	210,186
Start-up and Testing	17,978	-	-	-	-	-	-	17,978	17,978
SUBCOST (\$)	481,002	-	-	-	-	-	-	481,002	481,002
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	62,557	63,557	63,557	63,557	63,557	63,557	63,557 every year	1,450,931	1,905,724
SUBCOST (\$)	62,557	63,557	63,557	63,557	63,557	63,557		1,450,931	1,905,724
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
SUBCOST (\$)	37,002	37,002	37,002	37,002	37,002	12,369		400,991	494,235
TOTAL COST (\$)	580,562	100,559	100,559	100,559	100,559	75,926		2,332,924	2,880,961

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately \$401,000.

This alternative ranks lowest in estimated total remedy cost and lowest in NPV of lifetime costs compared to the other alternatives (see **Table 7.6**) due to the relatively low equipment and ongoing maintenance requirements compared to the other alternatives evaluated.

7.3.3 P&T with UV Treatment

The P&T with UV Treatment alternative includes the design and construction of a groundwater extraction system and groundwater treatment plant. Groundwater is pumped from nine extraction wells to the treatment facility. This water is initially pumped into a double-walled, high-density polyethylene (HDPE) pipe that routes water to a surge tank in the treatment building.

Before entering the surge tank, the groundwater is injected with a polyphosphate scale control chemical, which is distributed on a flow-proportional basis. Water is pumped into particulate filters before entering the UV reactor where it is exposed to low pressure amalgam UV light lamps. The UV light provided by the lamps destroys the NDMA via direct photolysis leading to dimethylamine, nitrate, and nitrite (Stefan and Bolton, 2002). Treated groundwater exiting the UV reactor is then either recycled into a surge tank or proceeds to an infiltration basin.

As summarized in **Table 7.4**, the estimated total costs for this alternative over 30 years are approximately \$5,603,000 with a total NPV of lifetime costs of approximately \$4,637,000. The capital cost including design, work plan, installation of extraction wells, and treatment plant construction are approximately \$1,461,000. The NPV of the O&M is estimated at approximately \$2,775,000 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with equipment replacement and electrical requirements. Replacement of UV lamp components is assumed to occur every two years at a cost of \$27,000 per replacement event. Electrical consumption is the highest for this alternative due to the electrical requirement for the UV equipment. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately \$401,000. This alternative ranks highest in both total remedy cost and NPV of lifetime costs compared to the other alternatives evaluated (See **Table 7.6**).

Table 7.4. Cost Components for P&T with UV Treatment.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	95,142	-	-	-	-	-	-	95,142	95,142
Well Installation	108,738	-	-	-	-	-	-	108,738	108,738
System Installation	1,230,835	-	-	-	-	-	-	1,230,835	1,230,835
Start-up and Testing	26,250	-	-	-	-	-	-	26,250	26,250
SUBCOST (\$)	1,460,965	-	-	-	-	-	-	1,460,965	1,460,965
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	108,195	135,031	108,195	135,031	108,195	135,031	108,195 to 135,031	2,775,150	3,648,404
SUBCOST (\$)	108,195	135,031	108,195	135,031	108,195	135,031		2,775,150	3,648,404
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
SUBCOST (\$)	37,002	37,002	37,002	37,002	37,002	12,369		400,991	494,235
TOTAL COST (\$)	1,606,162	172,033	145,197	172,033	145,197	147,400		4,637,105	5,603,603

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

7.3.4 P&T with FBR Treatment

The P&T with FBR Treatment alternative also includes the design and construction of a groundwater extraction system and groundwater treatment plant (as does the P&T with UV Treatment alternative). The treatment system contains a full-scale FBR constructed with welded stainless steel with a closed-top design. Included with the FBR is a fluidization pump, an influent distribution system and effluent/biomass collection system, two biomass separators, 7,100 lbs of carbon media (coconut shell-based), oxygen generator, and a gas delivery system for both oxygen and propane. Provided for the entire plant is a systems controls package that includes a control panel with motor controls, a PLC system with operator interface, and necessary electrical power supply.

As summarized in **Table 7.5**, the estimated total cost for this alternative over 30 years is approximately \$5,139,000 with a total NPV of lifetime costs of approximately \$4,319,000. The capital cost including design, work plan, treatment system construction, and installation of extraction and MWs are approximately \$1,601,000. The NPV of the O&M is approximately \$2,317,000 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with routine operations. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately \$401,000. This alternative ranks second in both estimated total remedy cost and NPV of lifetime costs (see **Table 7.6**).

Table 7.5. Cost Components for P&T with FBR Treatment.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	95,142	-	-	-	-	-	-	95,142	95,142
Well Installation	108,738	-	-	-	-	-	-	108,738	108,738
System Installation	1,370,835	-	-	-	-	-	-	1,370,835	1,370,835
Start-up and Testing	26,250	-	-	-	-	-	-	26,250	26,250
SUBCOST (\$)	1,600,965							1,600,965	1,600,965
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	96,153	101,653	101,653	101,653	101,653	101,653	101,653 every year	2,316,711	3,044,104
SUBCOST (\$)	96,153	101,653	101,653	101,653	101,653	101,653		2,316,711	3,044,104
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
SUBCOST (\$)	37,002	37,002	37,002	37,002	37,002	12,369		400,991	494,235
TOTAL COST (\$)	1,734,120	138,655	138,655	138,655	138,655	114,022		4,318,666	5,139,303

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

Table 7.6. Summary of Capital Costs and NPV of Costs for O&M and Monitoring.

Alternative	Capital Costs	NPV of 30 Years of O&M Costs	NPV of 30 Years of Monitoring Costs	NPV of 30 Years of Total Remedy Costs	Total 30-Year Remedy Costs
Biosparge Barrier	\$290	\$600	\$400	\$1,290	\$1,570
Pump and Treat with UV Treatment	\$1,410	\$1,780	\$400	\$3,590	\$4,240
Pump and Treat with FBR Treatment	\$1,570	\$1,320	\$400	\$3,290	\$3,800

notes: All costs are in thousands of dollars

NPV - Net Present Value; current value of future costs based on a 2% annual discount rate

O&M - Operation and Maintenance

8.0 IMPLEMENTATION ISSUES

8.1 END-USER ISSUES

The primary end-users of the technology are expected to be DoD site managers and their contractors, consultants, and engineers. The general concerns of the end users are likely to include the following: (1) technology applicability and performance under local site conditions, (2) safety, (3) secondary groundwater impacts, and (4) technology cost compared to other remedial options. These implementation issues are addressed in the following sections.

8.1.1 Technology Applicability and Performance under Local Site Conditions

The primary objective of co-metabolic treatment for NDMA is to supply propane and oxygen to an aquifer for microbial growth. There are a number of different approaches to achieve this end whose applicability depends on site geology/hydrogeology and plume characteristics. These approaches consist of including (1) air- and propane-biosparging as applied in this demonstration, (2) groundwater recirculation with above-ground propane and oxygen addition, (3) bubble-free gas injection systems, and (4) trenches with air and propane injection lines, among others (Steffan et al., 2003). The critical objective with any of these approaches is to evenly and consistently distribute propane and oxygen gas throughout the desired treatment area.

A groundwater recirculation design for treatment of 1,2-dibromoethane (EDB) in groundwater was recently tested using ethane gas and pure oxygen (Hatzinger et al., 2015, Hatzinger and Begley, 2014). In this case, groundwater was pumped from an existing extraction well at 10–12 gpm, amended with oxygen, ethane gas, and inorganic nutrients, and then re-injected into an injection well (approximately 60 ft upgradient), forming a closed loop. Good gas distribution was observed in system MWs and the biodegradation of ethane and EDB were documented throughout the demonstration plot. EDB reached concentrations below the stringent Massachusetts MCL of 0.02 µg/L. The one potential O&M issue with this approach was the observation of biofouling in the injection well tubing when ethane concentrations were increased from 2 mg/L in the injected water to 4 mg/L during one phase of the study. A recent study also examined the use of bubble-free gas injection systems to supply oxygen and propane to a groundwater aquifer (Shaw Environmental, 2013). This approach was significantly less successful than either biosparging or groundwater recirculation for two main reasons: (1) the inability to adequately control the oxygen:propane ratio with the system used, and (2) the inability to supply and distribute enough oxygen in the aquifer to overcome the highly reducing geochemical conditions. Gas distribution can be a significant limitation with this type of system.

The biosparging technology utilized during this demonstration consisted of the injection of propane gas into a groundwater aquifer in a stream of air. This approach is both highly flexible and widely applicable under differing aquifer conditions. In this case, biosparging was conducted in a confined interval in the layered aquifer. One of the significant advantages of this approach is that groundwater does not have to be pumped from the subsurface, thus avoiding all of the common capital costs and O&M issues with groundwater extraction and reinjection. This approach can also be used cost-effectively in deep as well as shallow aquifers, and for aerially wide plumes. Aquifer depth is one of the limiting factors for fully passive designs, which become increasingly expensive due to close spacing of injection points, or technically impractical (e.g., for passive trench barriers) as the depth to the water table increases (Stroo and Ward, 2009).

A semi-passive pumping design has fewer limitations with depth. Similarly, wide plumes are more readily treated with active or semi-passive approaches than with fully passive designs, as a few wells (and high flow rates) can often be used to distribute co-substrate over a large area rather than closely spaced wells or injection points (see Stroo and Ward [2009] for further comparisons of different amendment designs).

8.1.2 Safety

Because propane is a flammable gas, specific safety measures must be considered when designing, installing, and monitoring an *in situ* propane biosparge system. However, it is very easy for a competent engineer to design a system that is safe for operation. All electrical equipment and wiring in the system trailer supplying propane should be intrinsically safe, and the propane cylinders/tanks should be stored outside of the trailer. During this demonstration, a two-trailer system was used—one that housed the system controls and compressor (non-explosion proof) and one that mixed the compressed air with propane gas (explosion proof). When operating properly, no propane gas should be released into the trailer housing the propane mixing equipment, and safeguards should be put in place to automatically shut the system down and vent the atmosphere in case of a catastrophic failure (e.g., rupture of a propane feed line). This can be achieved using an LEL meter that shuts down propane feed and activates a vented roof fan if a specific percentage of the LEL for propane is exceeded in room air. Communication systems should also be used to alert an operator if this safety system is activated.

Safety considerations should also be given to groundwater monitoring. If high concentrations of propane (i.e., higher than the LEL) are added to groundwater, there is the potential for levels above the LEL to exist in a sealed biosparge well or groundwater MW. To prevent this possibility, propane should be added to groundwater at concentrations significantly below the LEL. During this demonstration, a propane concentration of 40% of the LEL was not exceeded. Wells can also be designed with vents in the well caps so that sampling personnel can safely take an initial measure of the propane concentration in each well before sampling the groundwater (using a photo-ionization detector [PID] meter), and then vent the well with fresh air if necessary prior to sampling. In addition, the system should be shut down during sampling events, and signs specifying that a flammable gas is being used in the area and that smoking is not permitted should be clearly visible to all personnel. With these simple design and operational precautions, this type of system can be safely operated and sampled.

8.1.3 Secondary Impacts to the Local Aquifer

One of the significant advantages of an aerobic treatment system of this type is that there are typically very few negative impacts to groundwater geochemistry (provided that the groundwater environment is not naturally highly reducing), particularly in comparison to *in situ* anaerobic systems where large amounts of carbon substrate are applied to treat contaminants. As noted in **Section 6.3**, DO throughout the demonstration area typically increased from ≤ 1 mg/L to >10 mg/L over the course of this demonstration. Similarly, the ORP in the demonstration plot groundwater was near or greater than +100 mV, and the pH generally remained between 6.5 and 7. Thus, the water became highly aerobic and oxidizing, and remained neutral in pH. It should also be noted that propane never exceeded 1 mg/L in the site groundwater, and the half-life of the dissolved propane was on the order of minutes rather than days or weeks (see **Section 6.2**), so the presence of residual propane in the aquifer is highly unlikely.

8.1.4 Technology Cost Compared to Other Remedial Options

The expected cost drivers for the installation and operation of an *in situ* biosparging system for NDMA and comparisons to other remedial approaches are provided in **Section 7**.

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RWQCB – Regional Water Quality Control Board; SERDP – Strategic Environmental Research and Development Program



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