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Field demonstration of *N*-Nitrosodimethylamine (NDMA) treatment in groundwater using propane biosparging

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ABSTRACT

N-Nitrosodimethylamine (NDMA) is found in groundwater and drinking water from industrial, agricultural, water treatment, and military/aerospace sources, and it must often be treated to part-per-trillion (ng/L) concentrations. The most effective remedial technology for NDMA in groundwater is pump-and-treat with ultraviolet irradiation (UV), but this approach is expensive because it requires *ex situ* infrastructure and high energy input. The objective of this project was to evaluate an *in situ* biological treatment approach for NDMA. Previous laboratory studies have revealed that propane-oxidizing bacteria are capable of biodegrading NDMA from μg/L to low ng/L concentrations (Fournier et al., 2009; Webster et al., 2013). During this field study, air and propane gas were sparged into an NDMA-contaminated aquifer for more than 1 year. Groundwater samples were collected throughout the study from a series of monitoring wells within, downgradient, and sidegradient of the zone of influence of the biosparge system. Over the course of the study, NDMA concentrations declined by 99.7% to >99.9% in the four monitoring wells within the zone of influence of the biosparge system, reaching low ng/L concentrations whereas the control well declined by only 14%. Pseudo first-order degradation rate constants for NDMA in system monitoring wells ranged from ~0.019 day^{-1} to 0.037 day^{-1} equating to half-lives ranging from 19 to 36 days. Native propanotrophs increased by more than one order of magnitude in the propane-impacted wells but not in the control well. The field data show for the first time that propane biosparging can be an effective *in situ* approach to reduce the concentrations of NDMA in a groundwater to ng/L concentrations.

1. Introduction

N-nitrosodimethylamine (NDMA) contaminates groundwater and drinking water from industrial, water treatment, aerospace, and military sources among others (Mitch and Sedlak, 2002a,b; Mitch et al., 2003; Zhao et al., 2008; Sgroi et al., 2018). Potential industrial sources include tanneries, foundries, rubber and tire manufacturers, alkylamine producers and users, and fish processors (ASTDR, 1989). Its presence at military installations and aerospace facilities 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 form NDMA under oxidizing conditions (Lunn and Sansone, 1994; Fleming et al., 1996; Mitch et al., 2003). Testing has also revealed that NDMA is present in reclaimed wastewater and in numerous drinking water supplies as a disinfection byproduct formed during chlorination, particularly when chloramine reacts with dimethylamine or other organic-nitrogen precursors (Mitch and Sedlak, 2002a,b; Mitch et al., 2003; Sedlak et al., 2005; Sgroi et al., 2018; Krasner et al., 2018).

Because of its physiochemical properties, including high water solubility, low adsorption coefficient (log Kow = −0.57; ASTDR, 1989) and low Henry's Law constant (2.63×10^{-7} atm m^3/mol at 20 °C; ASTDR, 1989), NDMA is not readily removed from groundwater via traditional remediation technologies, such as adsorption to granular activated carbon or air-stripping (Mitch et al., 2003). The most effective treatment technology currently available for treating NDMA in groundwater is *ex situ* treatment with ultraviolet irradiation (UV) which breaks the N-N bond in NDMA at a wavelength of 225−250 nm, yielding nitrite and dimethylamine as primary products (Mitch et al., 2003; Stefan and Bolton, 2002). Although effective, this *ex situ* approach is expensive, because

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typical energy requirements for treating NDMA to ng/L concentrations are far greater than for pathogen removal, particularly when order-of-magnitude reductions are required and/or when other constituents in the water increase turbidity or otherwise reduce treatment efficiency (Mitch et al., 2003). Moreover, this approach requires the capital investment in typical pump-and-treat infrastructure (i.e., piping, pumps, control system, facility, water discharge system) in addition to the UV system.

Historically, NDMA was not considered to be an important water contaminant, so no federal maximum contaminant level (MCL) currently exists for drinking water in the U.S. 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 a mere 0.7 ng/L (USEPA, 1993). NDMA, along with several other nitrosamines, is listed on the USEPA's Contaminant Candidate List - 4 (CCL-4; USEPA, 2016). Large water utilities are required to analyze for CCL listed compounds, so that the USEPA can determine their prevalence and concentrations in drinking water sources nationwide. This is a possible step toward regulation under the Safe Drinking Water Act. A total of 15 states have established health-based guidance levels for NDMA in drinking water ranging from 0.7 to 18 ng/L (USEPA, 2017). Moreover, local or state regulatory bodies often set discharge limits for NDMA treated via *ex situ* processes under the Resource Conservation Recovery Act (RCRA) or other relevant legislation, and these limits are typically in the ng/L range (e.g., 4.2 ng/L for the NASA White Sands Test Facility; Hatzinger et al., 2017). The prospects of setting a Federal Maximum Contaminant Level (MCL) for NDMA in water is unclear, but with water resources becoming increasingly scarce and recharge and reuse of wastewater becoming more common, NDMA is likely to remain as a contaminant of concern in drinking water for the forseeable future.

The objective of this project was to demonstrate an effective, *in situ* biological remediation option for the treatment of NDMA. The technology chosen, cometabolic biosparging, relies on the use of an inexpensive alkane substrate, propane, and oxygen to stimulate the growth and degradative activity of propane-oxidizing bacteria (propanotrophs), a number of which have been observed to aerobically biodegrade NDMA while using propane as a substrate (Sharp et al., 2005, 2007, 2010; Fournier et al., 2009; Weidhaas et al., 2012; Homme and Sharp, 2013). Propane (and potentially other compounds) induces the enzyme propane monooxygenase (PrMO) in these microorganisms, which has been observed to catalyze the degradation of NDMA as well as numerous other persistent water pollutants (Sharp et al., 2007, 2010; Homme and Sharp, 2013; Steffan et al., 1997; Wackett et al., 1989). While growing on the propane, the bacteria fortuitously degrade NDMA via the PrMO enzyme without gain of carbon or energy, a process termed cometabolism (Alexander, 1994).

Unlike bioremediation processes that require the degradative bacteria to metabolize and grow on the target contaminant, the addition of a secondary growth substrate (e.g., propane) to support bacterial growth has been observed to allow cometabolic treatment of μg/L concentrations of some contaminants, such as NDMA and 1,2-dibromoethane, to low ng/L concentrations (e.g., Fournier et al., 2009; Hatzinger et al., 2015, 2017, 2018). Such treatment levels are typically not attainable with metabolic systems because there is insufficient carbon and energy for microbial growth (Alexander, 1994; Schmidt et al., 1985). This approach also may allow the simultaneous treatment of multiple co-contaminants at low concentrations (e.g., chlorinated ethenes, chlorinated ethanes, and 1,4-dioxane; Tovanabootr et al., 2001; Lippincott et al., 2015; Chu et al., 2018).

During this field demonstration, propane and oxygen (from air) were added to an NDMA-contaminated aquifer to stimulate native propanotrophs to biodegrade NDMA from >20 μg/L to low ng/L concentrations. To our knowledge, this represents the first *in situ* treatment approach for NDMA remediation that is likely to have wide applicability.

2. Materials and methods

2.1. Site geology and hydrogeology

The Aerojet General Corporation Superfund Site (Aerojet), where the demonstration was conducted, is located in eastern Sacramento County, California, USA 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 18,000 m) 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 18 m thick, while at its western boundary (a distance of 10 km) the sediments are nearly 600 m thick. Hydrostratigraphic layers identified at the site include Quaternary sediments, and the Tertiary-aged Laguna Formation, Mehrten Formation, Valley Springs Formation, and Ione Formation. A hydrostratigraphic cross section that passes through the demonstration area is presented in Supplementary Data, Figure S-1.

The wells installed for this demonstration were screened in Layer M4, a permeable zone in the Mehrten Formation which is composed of multiple sublayers of coarse-grained fluvial black sands, variegated gravels, and interbedded clays, tuffs, and breccia and often contains the first waterbearing sublayer encountered across the facility (Figure S-1). 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. Locally, a trough in the bedrock controls groundwater flow toward Alder Creek. Reported hydraulic conductivities for the various hydrostratigraphic layers range from 0.3 to 106 m/day, with an average of about 21 m/day (Central Valley Environmental, Inc, 2005). Slug testing performed on three monitoring wells prior to the demonstration indicated hydraulic conductivities ranging from 0.05 to 1.6 m/day in the chosen test plot area. A subsequent passive flux meter test (Annable et al., 2005) conducted in three of the installed test plot wells revealed Darcy velocities in each well ranging from ~0.12 to 0.17 m/day, with wells generally showing an increased velocity with depth in the interval tested. The average groundwater velocity was 0.14 m/day based on all measured values (Supplementary Data, Figure S-2 and accompanying text).

2.2. Demonstration plot design and operation

As previously discussed, *in situ* remediation of NDMA via cometabolism was undertaken via the addition and distribution of propane gas and oxygen in groundwater. For this demonstration, an air- and propane-biosparging approach was utilized to deliver these gases to the subsurface. The main advantage of this approach is that the necessary substrates can be supplied to a contaminated aquifer without pumping groundwater, which requires significant additional infrastructure and operation and maintenance concerns, such as biofouling. That being said, recirculation systems have been used successfully in recent years for cometabolic bioremediation of various contaminants, including 1,2-dibromoethane (Hatzinger et al., 2018), and mixtures of 1,4-dioxane and chlorinated organics (Chu et al., 2018). One of the disadvantages of biosparging is the potential for poor gas distribution in highly heterogenous formations, with primary gas flow channeling through the most conductive zones in a formation and bypassing other regions as has been observed for traditional high-flow air sparging applications (Leeson et al., 2002 and references therein). However, the focus of this demonstration on a confined, permeable region in a highly layered aquifer was thought to minimize the potential for significant short-circuiting of added air and propane.

2.2.1. Demonstration plot layout

An overhead view of the demonstration plot design is provided in Fig. 1 and a generalized test plot cross section and conceptual design is provided in Fig. 2. During the initial operation (~4 months) only one well was generally used as a propane sparge well (PMW-1), but for the duration of the project thereafter, three wells were utilized (PMW-1, BW-6, BW-7). The BW-6 and BW-7 wells were installed when the initial sparge well was observed to not provide sufficient propane to the treatment area. The final demonstration plot included 7 monitoring wells. Monitoring wells were divided into three groups: (1) One background monitoring well (BMW-1) located ~23 m sidegradient 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, ~1.2 m), and slightly downgradient (PMW-4, ~4.1 m) of the triangulated propane sparge wells, and (3) two downgradient monitoring wells (PMW-5 and PMW-6) located 9.1 m and 10.7 m downgradient of the central region the triangulated propane sparge wells, respectively. The final spacing of the biosparge and monitoring wells was determined based upon an initial field test in which air was injected into a temporary well over

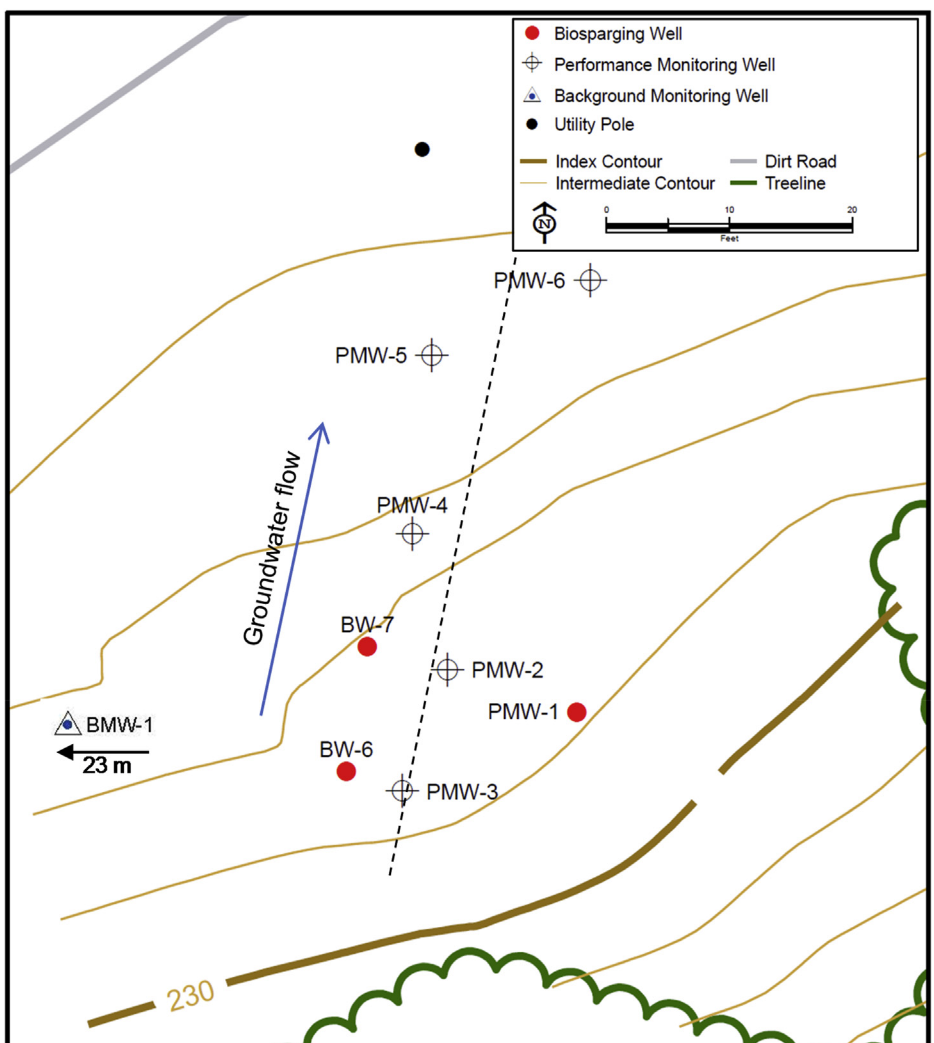

Fig. 1. Layout of demonstration plot biosparge and monitoring wells. The blue arrow indicates the general direction of groundwater flow, which is influenced by downgradient pumping wells. Well BMW-1 is located 23 m west of the location indicated on the figure. The contours represent the ground surface elevation (ft msl) with each minor contour representing a 2 ft (0.6 m) change in elevation (declining from south to north). The dotted line represents the generalized cross section shown in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

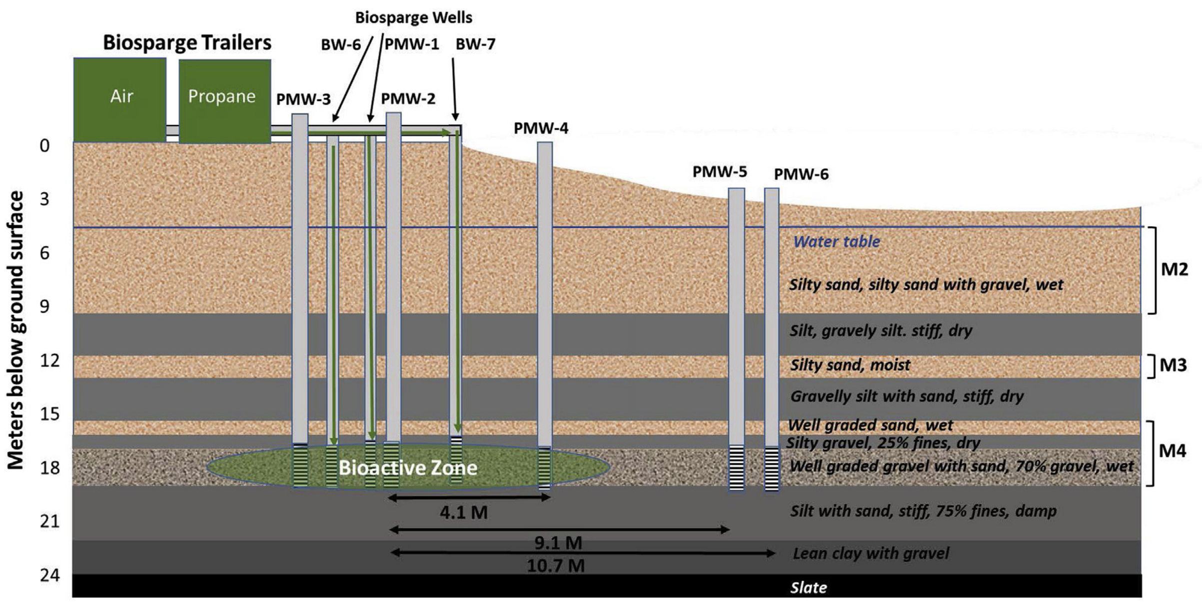

Fig. 2. Conceptual site model and generalized test plot cross section. The scale of the figure is approximate. The generalized cross section is indicated by the dotted line in Fig. 1. The water table elevation is indicated, and the direction of groundwater flow is left to right across the figure. The solid areas represent layers with lower conductivity and the mottled areas (M2 − M4) are more conductive regions. Side-gradient well BMW-1 is not indicated. Layers M2, M3 and M4 are also shown on Figure S-1.

time at differing flow rates (~0.014−0.14 cubic meters per minute; CMM) and dissolved oxygen (DO) and oxidation-reduction potential (ORP) were measured using a field meter (see Section 2.2.4) in wells installed from ~2.5 to 8 m from the biosparge well. The short-term tests indicated a radius of influence for a single sparge well of at least 3.8 m at a gas flow rate of 0.14 CMM (data not shown).

Background well BMW-1 was located outside of the expected influence of the biosparging system and was used to verify NDMA and other groundwater contaminant concentrations flowing through the treatment area. Because of the steep vertical grade of the test site, it was not possible to install a well upgradient of the test plot, but the test plot wells and the control well were all located within the central region of a large NDMA plume. Performance monitoring wells PMW-1 through 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.

Monitoring and biosparging wells were installed via rotosonic drilling. Continuous cores were initially collected from ground surface to the bottom of each boring. The lithology of each core was logged by a qualified geologist. An example of one of the boring logs is provided in Supplementary Data, Figure S-3 and a general schematic of the site geology is provided in Fig. 2. The wells were installed through the temporary casing placed via the rotosonic method, and were constructed with flush-threaded, 5-cm diameter, Schedule 40, PVC riser and screen. The monitoring wells and biosparging wells BW-6 and BW-7 were constructed with 1.5 m of 0.025-cm slotted well screen. Final screen lengths and intervals at each location were determined based on the lithology observed during drilling. Screen intervals were selected to ensure that the well screen was placed within the zone with highest overall NDMA concentrations, which was a highly conductive interval (Zone M4; Figure S-1) in the Mehrten Formation characterized by well-graded gravel and sand (Fig. 2). A previous investigation using depth-dependent groundwater sampling identified this general zone as having the highest NDMA concentrations among the conductive intervals encountered during drilling (data not shown). The depth to the top of the screen of each well varied from ~13.7 to 18.3 m below ground surface.

The filter pack for each well consisted of #2/12 sand (or equivalent) extending to 0.9 m above the top of screen. A minimum 0.9-m bentonite seal was placed above the filter pack. The remaining annular space was filled with cement-bentonite grout (no more than five percent bentonite by weight) emplaced to within 0.6 m of the surface via Tremie pipe. Well development was accomplished by pumping the groundwater until the water was clear and the well was sediment free to the extent practical. Wells were developed using a surge block (if necessary) and submersible pump. Water was not added to the well to aid in development, nor was any type of air-lift technique used. The pump, tubing, and surge block were decontaminated between locations.

2.2.2. Biosparging system design

The propane biosparging system used during this demonstration was described previously in Lippincott et al. (2015). In summary, the system consists of two trailers, one of which contains the main control panel and main electrical junction box as well as the air feed system; a two-stage, duplex air compressor w/5 HP motors and a 450 L tank, capable of providing 1 CMM @ 1200 kPa. The air flow from the initial trailer is transferred to the second trailer via flexible hose. The second trailer consists of the 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 is fed from an external propane cylinder with a two-stage regulator that delivers propane to the air/propane distribution system in the second trailer. The system is designed to feed propane below the lower explosive limit (LEL; 2.1%) and will automatically shut down in the event the LEL is exceeded. The propane used for this demonstration was purchased in 44 kg tanks and was >99% purity with no mercaptans added (Airgas, Sacramento, CA). Propane feed concentrations for this demonstration were generally between 30 and 40% (vol/vol; v/v) of the LEL (between 0.63% and 0.84% propane). The air/propane

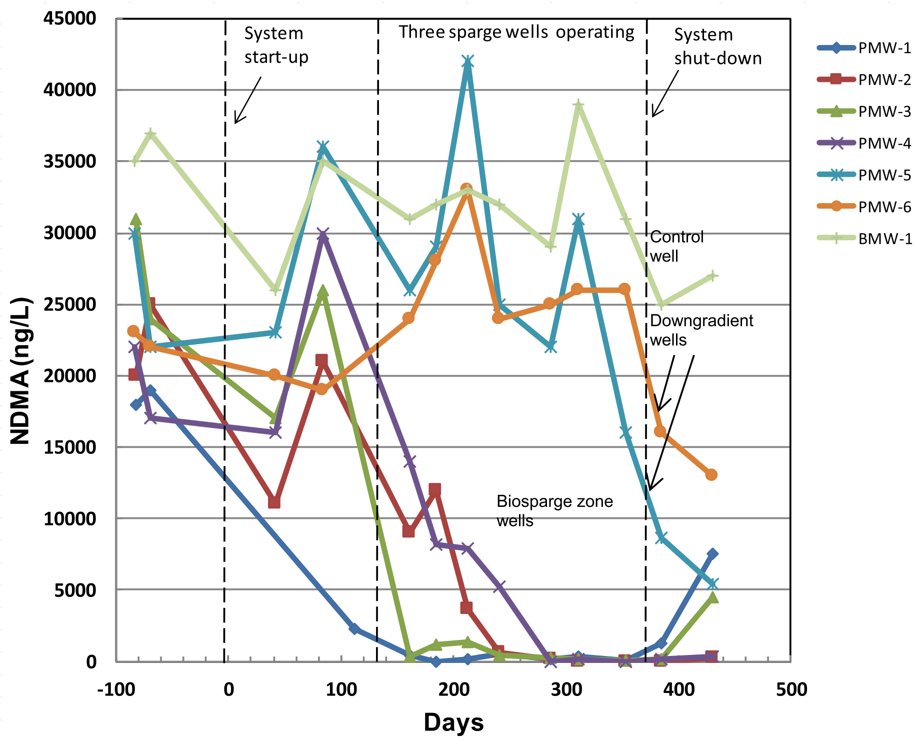

Fig. 3. Concentrations of NDMA in the demonstration plot monitoring wells. The dashed lines indicate different phases of system operation as indicated.

mixture exiting the second trailer is manifolded among 1–5 discharge points that include flow indicators with needle valves (i.e., maximum of 5 sparge wells).

2.2.3. Biosparging system operation & 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, and then wells BW-6, BW-7, and PMW-1 were operated together for the remaining period of operation. The operational data are provided in Supplementary Data, Table S-1. 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, and 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 S-1) 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 test plot wells (0.8 kg/day) was considered optimized on Day 217, and generally remained the same thereafter for the remaining 5 months of active sparging.

Full rounds of groundwater sampling were conducted on 13 occasions as shown on .Table S-1 This included two sampling rounds to establish baseline (i.e., pre-gas injection) conditions on Day −84 and −70 (with Day 0 being the beginning of system operation), 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 7 wells (PMW-1 to 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.

2.2.4. Groundwater sampling and analytical

Groundwater samples were collected by field personnel utilizing low-flow purging in accordance with USEPA Low-Flow Ground-Water Sampling protocol (Puls and Barcelona, 1996). Samples were obtained from each monitoring well using a dedicated submersible bladder pump and Teflon tubing. Groundwater was passed through a flow-through cell fitted with a YSI 600XL field meter (Yellow Springs, OH) that simultaneously measured pH, ORP, temperature, specific conductivity, and DO. The values for each parameter were recorded, and once all values were stable, based upon low-flow sampling protocol, groundwater samples were collected for laboratory analysis. All field meters were calibrated at the beginning of each day.

Groundwater samples were analyzed for basic field parameters, NDMA (USEPA Method 521), dissolved gases (methane, propane, ethane, ethene via EPA 3810, RSK175; Kampbell and Vandegrift, 1998) and anions (USEPA 300.0). Total propanotrophic bacteria were quantified during one baseline event prior to gas injection to establish background levels and four of the monthly events thereafter. The analysis of anions and dissolved gases was performed by Aptim's Analytical Laboratory in Lawrenceville, NJ. Total propanotrophs were quantified by qPCR at Microbial Insights (Knoxville, TN) by measuring the genes for PrMO using a set of proprietary primer and probe sequences derived from *Gordonia* sp. strain TY-5 (Kotani et al., 2003). Analysis of NDMA was performed by Weck Laboratories, City of Industry, CA. Weck Laboratories is a California Department of Public Health approved lab and is listed under the State of California Environmental Laboratory Accreditation Program (ELAP).

3. Results and discussion

3.1. NDMA

NDMA declined by 99.7% to >99.9% in the four monitoring wells within the zone of influence of the biosparge system (PMW-1 to PMW-4), an area of ~6 m by 6 m (Fig. 3). Baseline concentrations of 25,000 ± 6,000 ng/L NDMA (average groundwater concentrations in the 7 test plot wells from Day −70 and Day −84) 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 exceeding 99.9%. The sidegradient control well (BMW-1) that was not appreciably influenced by the system had an average NDMA concentration of 36,000 ng/L during baseline sampling and was 31,000 ng/L on Day 353, a decline of only 14%. The far 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.

Pseudo first-order degradation rate constants were determined for monitoring wells PMW-2 to PMW-6 and well BMW-1 using data from Day 84 to Day 353 (See Fig. 3 and Supplementary Data Table S-2 and Figure S-4 and accompanying text). A rate constant was not calculated for PMW-1, which also served as a sparge well. The rates assume that losses are due to biodegradation rather than volatile losses given the high water solubility and low Henry's Law constant for NDMA, the relatively low gas flow rates (i.e., compared to an air sparging application to volatize chemicals - which is typically designed with soil vapor extraction; SVE), and the fact that the geological interval where the gases were added was confined. Estimated rate constants for NDMA in treatment area monitoring wells PMW-2, PMW-3, and PMW-4 were 0.037 ± 0.011 day $^{-1}$, 0.019 ± 0.008 day $^{-1}$ and 0.031 ± 0.014 day $^{-1}$, respectively. These rates equate to NDMA half-lives ranging from 19 to 36 days and 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 0.02 day^{-1} to 0.04 day^{-1}. The rates are higher than those reported for the model-estimated biodegradation of NDMA (0.01 day^{-1}) in a California aquifer receiving recycled water for recharge (Zhao et al., 2008). It is likely that this process may also be cometabolic with substrates in the recycled wastewater supporting NDMA biodegradation, particularly since no organisms capable of growth-linked NDMA biodegradation have yet been reported. No other comparable *in situ* rate data for active NDMA treatment are available to our knowledge.

After the system was shut down on Day 373, increases in NDMA were observed in all four of the monitoring wells within the zone of influence of the biosparge wells (Fig. 3). This is consistent with a supply of propane gas being necessary for continued *in situ* biodegradation as NDMA enters the treatment zone in the aquifer from upgradient. For a full-scale application (e.g., as a downgradient biobarrier) the *in situ* system would be required to operate until NDMA concentrations in the upgradient region declined to below regulatory levels. This plume is currently captured via a series of extraction wells and the NDMA is treated in a central facility using a UV system.

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 3−4 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 using various bioreactor designs in both the laboratory and the field (Hatzinger et al., 2011, 2017; Webster et al., 2013). To our knowledge, this is the first report of successful *in situ* treatment of NDMA in groundwater to ng/L concentrations using cometabolism or any other bioremediation approach. The application of propane biosparging (Lippincott et al., 2015) and groundwater recirculation with propane (Chu et al., 2018) for effective treatment of another DoD contaminant of concern, 1,4-dioxane, have also recently been reported. A number of different co-mingled chlorinated aliphatics were simultaneously treated during each of these demonstrations.

3.2. Propane and oxygen

Distribution of adequate propane and oxygen, and appropriate ratios of these two gases, was critical to the success of this remedial approach. As previously noted, preliminary testing at the demonstration plot suggested that a gas sparging radius of at least 3.8 m could be achieved in the aquifer from a single sparge well. When the system was started initially, with sparging through well PMW-1, dissolved propane was detected at between 5 and 50 μg/L in PMW-4, which was located ~6.1 m from PMW-1, showing that the gas was being distributed in the aquifer (Fig. 4). 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, so biosparge wells BW-6 and BW-7 were added to the plot to increase propane distribution. 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.

It is interesting to note that low concentrations of propane (<70 μg/L) were detected in control well BMW-1 (which was ~23 m away from the center of the demonstration plot), for a few months after installation of BW-6 and BW-7. Significant NDMA degradation was not indicated in this well, likely because the quantities of propane reaching this region were too low to stimulate significant bacterial activity. However, some of the added propane clearly traveled this far in 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.

DO in the test plot was generally below 5 mg/L prior to the initiation of biosparging. DO increased throughout the treatment zone wells (PMW-1 to PMW-4) consistently to >10 mg/L during active sparging, even when only PMW-1 was in operation as the lone biosparge well (Fig. 5). 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 indicate that, as with propane, a small amount of sparged air reached the side-gradient well.

The oxygen:propane ratio in the groundwater was 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

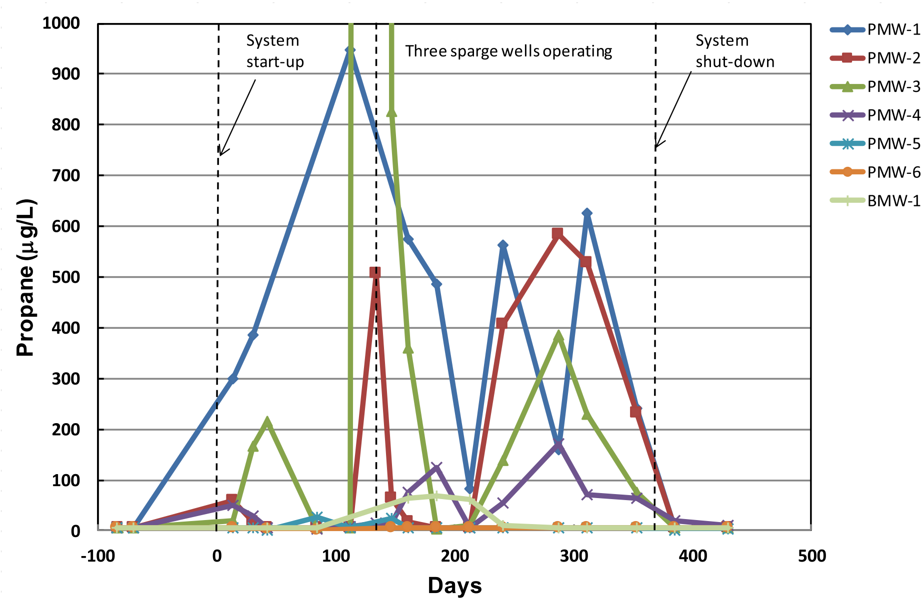

Fig. 4. Concentrations of propane in the demonstration plot monitoring wells. The dashed lines indicate different phases of system operation as indicated.

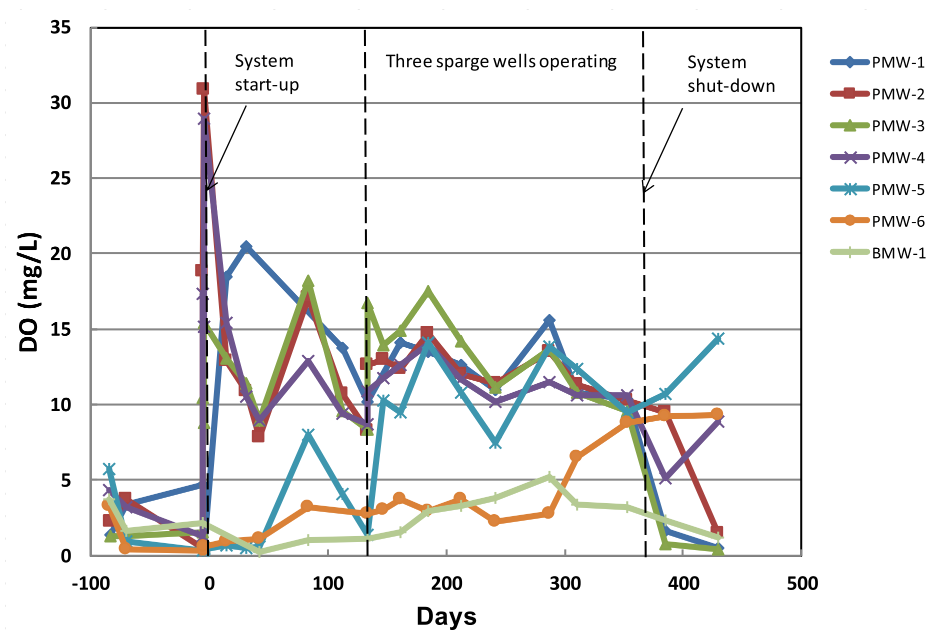

Fig. 5. Concentrations of dissolved oxygen in the demonstration plot monitoring wells. The dashed lines indicate different phases of system operation as indicated.

aquifer. The required molar ratio of oxygen (O_2) to propane (C_3H_8) for complete oxidation of propane to carbon dioxide (CO_2; not accounting for microbial biomass incorporation of C) is ~5 mols O_2 to 1 mol C_3H_8 [Eq. (1)]. When converted to mg/L, the above stoichiometry suggests that the oxygen requirement for bacteria to biodegrade 1 mg/L of C_3H_8 is ~3.6 mg/L O_2. Thus, on a mg/L basis, an oxygen to propane ratio of ~4:1 is required to ensure that anoxic conditions do not occur in the aquifer.

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad (1)$$

A desired ratio of oxygen to propane was always exceeded based on the analytical data generated during the project, with DO typically exceeding 10 mg/L (Fig. 5) during system operation and dissolved propane never exceeding 1 mg/L (Fig. 4).

During a sparging field test run under optimized conditions, two 45-min sparge-cycles were conducted at 0.17 CMM 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 (Fig. 6). Propane concentrations in these wells, which reached ~225 µg/L, declined to 25–50 µg/L during ~1 h, indicating rapid consumption of propane in the aquifer. If one assumes that the decline in concentration is due predominantly to biodegradation, the propane first order decay rates in these wells are 0.03 min^{-1} for PMW-3 and 0.02 min^{-1} for PMW-4. These propane decay rates are consistent with those observed recently at Vandenberg Air Force Base during a

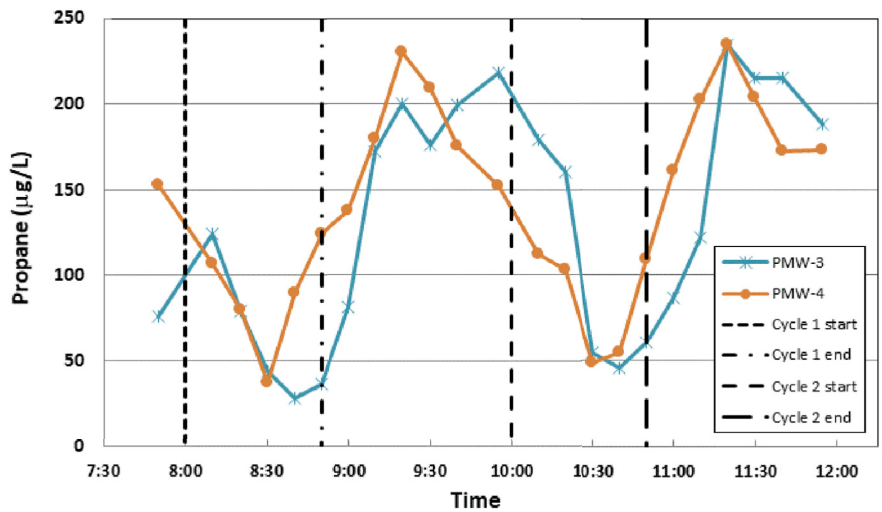

Fig. 6. Concentrations of propane in PMW-3 and PMW-4 during the propane biosparge test. The start and end of the two sparge cycles are provided as dashed lines as indicated.

demonstration of cometabolic degradation of 1,4-dioxane (0.01–0.05 min^{-1}) (Lippincott et al., 2015).

3.3. Nitrate and sulfate

Nitrate concentrations in PMW-1 through PMW-5 declined appreciably over the course of the demonstration (Fig. 7). The background levels in most of the wells ranged from ~1.7 to 2.5 mg/L as NO_3-N, with slightly lower values in PMW-6. During system operation, NO_3-N in PMW-1 to PMW-5 declined to <0.3 mg/L. A similar decline did not occur in background well 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, the loss of nitrate is likely not the result of denitrification, a process that is typically inhibited by oxygen (Ferguson, 1994). Rather, the consumption of nitrate is consistent with assimilation of N from NO_3^- by propanotrophs in the aquifer as a required inorganic nutrient. No exogenous inorganic nutrients were added to the aquifer, as is often required during cometabolic treatment (e.g., Lippincott et al., 2015; Hatzinger et al., 2018), so bacterial assimilation of existing inorganic nutrients is expected. As a general confirmation of this hypothesis, sulfate concentrations throughout the test plot ranged from ~13 to 20 mg/L during baseline sampling and remained consistently in this range over the course of the demonstration as would be expected under the oxidizing conditions in the aquifer (Supplementary Data, Figure S-5). Unlike N, most bacteria do not require significant quantities of S as a nutrient for growth.

3.4. Propanotrophic bacteria

The population of indigenous propanotrophs in wells PMW-2, PMW-3, and PMW-4 increased by greater than 1 log order over the course of the demonstration (Fig. 8). On Day 311, the final day of

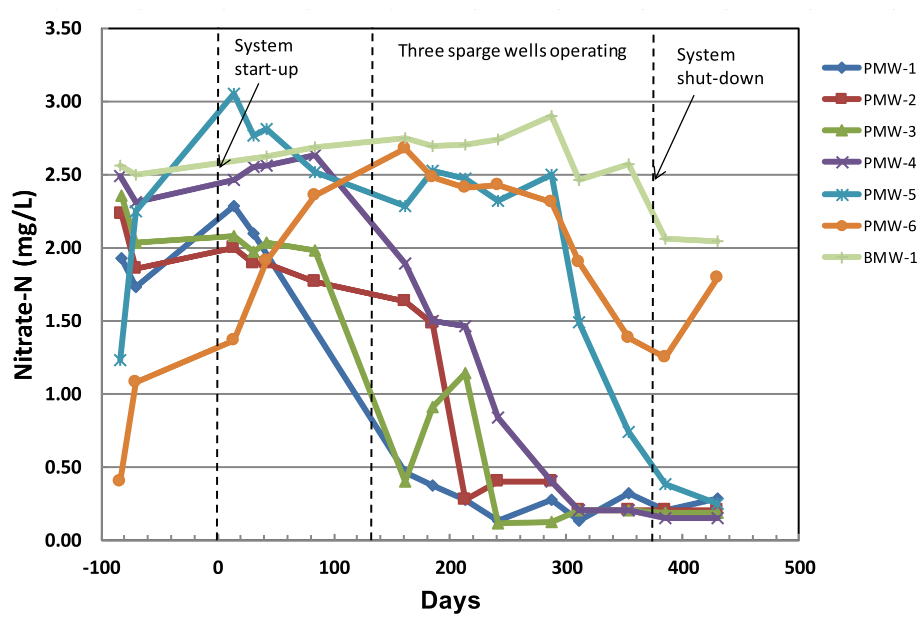

Fig. 7. Concentration of nitrate-N in the demonstration plot monitoring wells. The dashed lines indicate different phases of system operation as indicated.

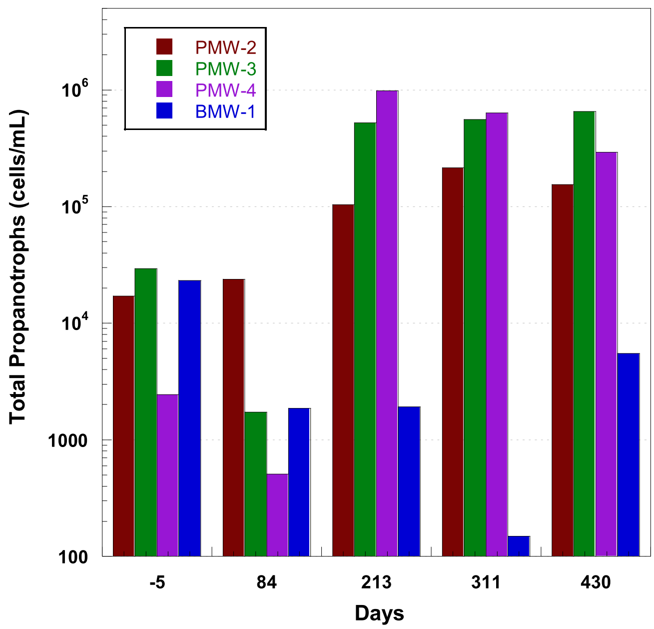

Fig. 8. Concentration of propanotrophs in the demonstration plot monitoring wells.

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 these wells remained reasonably constant thereafter even in the absence of propane addition for more than 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 of these organisms are known to form biofilms (Hatzinger et al., 2011, 2018; Webster et al., 2013; Lippincott et al., 2015).

3.5. pH and oxidation-reduction potential

The pH in the demonstration plot generally remained between 6.5 and 7 during the demonstration (Figure S-6). The pH was slightly elevated in PMW-1 (which was used as both a sparge well and a monitoring well) during some events, but did not exceed 7.5 SU. The baseline oxidation-reduction potential (ORP) in the plot ranged from ~ −100 mV to +100 mV prior to system start-up. 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 greater than +100 mV, indicating that conditions were sufficiently oxidizing for an aerobic degradation process to occur (Figure S-7).

3.6. Technology application

This field demonstration showed for the first time 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. The ability to reach ng/L concentrations of NDMA with cometabolism is consistent with data from previous laboratory studies with pure cultures as well as laboratory and field bioreactor testing (Fournier et al., 2009; Webster et al., 2013; Hatzinger et al., 2018). At the Aerojet site, as well as other large dilute NDMA plumes, the most effective full-scale application of cometabolic biosparging is likely to be a biobarrier to prevent further downgradient migration of contaminated groundwater. This type of barrier could be designed with either vertical or horizontal gas injection wells depending on site geology and economic considerations.

In order to optimize this approach, however, it is important to conduct initial testing in an aquifer to assess the distribution of gases from biosparge wells both horizontally and vertically in the aquifer. Like traditional air sparging (Leeson et al., 2002), biosparged gases can follow preferential flow paths which may impact their overall distribution in an aquifer. In addition, while secondary sinks for oxygen in the Aerojet aquifer were minimal, if conditions in an aquifer are highly anaerobic, a longer timeframe may be required to achieve desired levels of oxygen in an aquifer to support cometabolic bioremediation. Under such conditions, however, a biosparging approach would typically be favored over a design where gases are added to extracted groundwater and reinjected, because mineral and biological fouling of such systems is likely to limit their long-term effectiveness. Finally, in the absence of mg/L concentrations of nitrate-N in groundwater, it is likely that another source of N will need to be added during biosparging to maintain cell growth and contaminant degradation rates over time.

4. Conclusions

- Field data suggest that biosparging with propane in air can be an effective *in situ* approach to treat NDMA in groundwater to low ng/L concentrations.
- For large dilute plumes of NDMA such as that present at the Aerojet site, a biobarrier design to limit downgradient contaminant migration is likely to be the most effective application of this technology.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2019.114923.

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