

ESTCP Cost and Performance Report

(ER-200829)



Treatment of N-Nitrosodimethylamine (NDMA) in Groundwater Using a Fluidized Bed Bioreactor

January 2014

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TABLE OF CONTENTS

| | Page |
|--|-------------|
| EXECUTIVE SUMMARY | ES-1 |
| 1.0 INTRODUCTION | 1 |
| 1.1 BACKGROUND | 1 |
| 1.2 OBJECTIVE OF THE DEMONSTRATION | 2 |
| 1.3 REGULATORY DRIVERS | 2 |
| 2.0 TECHNOLOGY | 3 |
| 2.1 TECHNOLOGY DESCRIPTION | 3 |
| 2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY | 5 |
| 3.0 PERFORMANCE OBJECTIVES | 7 |
| 4.0 SITE DESCRIPTION | 9 |
| 4.1 SITE LOCATION AND HISTORY | 9 |
| 4.2 SITE GEOLOGY/HYDROGEOLOGY | 9 |
| 4.3 CONTAMINANT DISTRIBUTION | 10 |
| 5.0 TEST DESIGN | 13 |
| 5.1 CONCEPTUAL EXPERIMENTAL DESIGN | 13 |
| 5.2 BASELINE CHARACTERIZATION ACTIVITIES | 14 |
| 5.3 LABORATORY STUDY RESULTS | 14 |
| 5.3.1 Microcosms | 15 |
| 5.3.2 Laboratory FBR | 15 |
| 5.4 FIELD TESTING | 17 |
| 5.5 SAMPLING METHODS | 18 |
| 5.6 SAMPLING RESULTS | 21 |
| 5.6.1 NDMA and DMN | 21 |
| 5.6.1.1 Phase I to Phase III | 21 |
| 5.6.1.2 Phase IV Steady State Operation | 23 |
| 5.6.1.3 Phase V Challenge Experiments | 23 |
| 5.6.1.4 Phase VI Co-contaminant Treatment | 24 |
| 5.6.2 Oxygen and Propane | 25 |
| 6.0 PERFORMANCE ASSESSMENT | 27 |
| 6.1 QUANTITATIVE PERFORMANCE OBJECTIVES | 27 |
| 6.1.1 <i>R. ruber</i> ENV425 Adaptation | 27 |
| 6.1.2 Treat NDMA to Below Regulatory Limits/Produce Quality Data | 27 |
| 6.1.3 Effects of Interruptions on FBR Operation | 28 |
| 6.1.4 Effects of Co-Contaminants on NDMA Treatment | 28 |
| 6.1.5 Treatment of DMN | 29 |

TABLE OF CONTENTS (continued)

| | Page |
|------------|--|
| 6.2 | QUALITATIVE PERFORMANCE OBJECTIVES..... 29 |
| 6.2.1 | Ease of Use 29 |
| 6.2.2 | Reliability..... 29 |
| 6.2.3 | Reduction of Treatment Costs 30 |
| 7.0 | COST ASSESSMENT..... 31 |
| 7.1 | COST MODEL 31 |
| 7.1.1 | Treatability Study..... 32 |
| 7.1.2 | Project Management & Design..... 32 |
| 7.1.3 | Fabrication & Equipment..... 33 |
| 7.1.4 | Installation..... 33 |
| 7.1.5 | Operation and Maintenance 33 |
| 7.1.5.1 | Materials Required..... 33 |
| 7.1.5.2 | Labor 34 |
| 7.1.6 | Monitoring 34 |
| 7.2 | COST DRIVERS 34 |
| 7.3 | COST ANALYSIS..... 35 |
| 7.3.1 | FBR System 37 |
| 7.3.2 | UV Treatment System..... 38 |
| 7.3.3 | Cost Comparison of FBR versus UV 38 |
| 8.0 | IMPLEMENTATION ISSUES 41 |
| 8.1 | REGULATIONS..... 41 |
| 8.2 | END USER CONCERNS..... 42 |
| 9.0 | REFERENCES 45 |
| APPENDIX A | POINTS OF CONTACT..... A-1 |

LIST OF FIGURES

| | Page |
|------------|--|
| Figure 1. | Three full-scale FBR installations. 3 |
| Figure 2. | Schematic of fluidized bed bioreactor. 4 |
| Figure 3. | Hydraulic and biological expansion of media. 4 |
| Figure 4. | NASA WSTF MPITS UV System..... 9 |
| Figure 5. | NASA WSTF NDMA plume..... 11 |
| Figure 6. | NASA WSTF NDMA, TCE, and Freon 113 plumes..... 11 |
| Figure 7. | Conceptual set-up of pilot-scale FBR. 13 |
| Figure 8. | Removal of NDMA over the duration of the laboratory FBR study. 16 |
| Figure 9. | Photographs of the installed FBR system. 17 |
| Figure 10. | NDMA in the FBR influent and effluent over the duration of the study..... 22 |
| Figure 11. | DMN in the FBR influent and effluent over the duration of the study..... 22 |
| Figure 12. | DO in the influent and effluent of the FBR system over the duration of the study..... 25 |
| Figure 13. | Dissolved propane in the influent and effluent of the FBR system over the duration of the study. 26 |

LIST OF TABLES

| | Page |
|----------|--|
| Table 1. | Performance objectives. 7 |
| Table 2. | WSTF historical groundwater analyses from the mid-plume area (BLM-15)..... 10 |
| Table 3. | Operating conditions for the pilot-scale FBR treatment. 14 |
| Table 4. | WSTF representative groundwater analysis from MPITS (NASA, 2013). 14 |
| Table 5. | Gantt chart of NDMA pilot system schedule..... 19 |
| Table 6. | Monitoring program for the FBR treatment system. 20 |
| Table 7. | Analytical parameters and methods conducted during the pilot-scale experiment..... 21 |
| Table 8. | Cost model for small-scale FBR implementation (<5 gpm)..... 32 |
| Table 9. | FBR and UV full-scale treatment system cost at 125 gpm and NDMA at 1 µg/L..... 36 |

ACRONYMS AND ABBREVIATIONS

| | |
|--------------------------------|---|
| BLM | Bureau of Land Management |
| EC | degrees Celsius |
| C | carbon |
| CB&I | Chicago Bridge & Iron |
| CCL | Current Contaminant List |
| CDHS | California Department of Health Services |
| CDPH | California Department of Public Health |
| CFC | chlorofluorocarbon |
| DAP | Diammonium Phosphate |
| DGGE | denaturing gradient gel electrophoresis |
| DMN | N-nitrodimethylamine |
| DO | dissolved oxygen |
| DoD | U. S. Department of Defense |
| ESTCP | Environmental Security Technology Certification Program |
| ETI | Envirogen Technologies, Inc. |
| FBR | fluidized bed reactor |
| GAC | granulated activated carbon |
| GC | gas chromatograph |
| GC/MS | gas chromatography/mass spectroscopy |
| gpm | gallons per minute |
| HCL | hydrochloric acid |
| HDPE | high density polyethylene |
| HRMS | high-resolution mass spectrometry |
| HRT | hydraulic retention time |
| H ₂ SO ₄ | sulfuric acid |
| kW/hr | kilowatt hour |
| MBR | membrane bioreactor |
| MCL | maximum contaminant level |
| MDL | method detection limit |
| mg | milligram |
| mL | milliliter |
| µg/L | micrograms per liter |
| MPITS | Mid-Plume Interception and Treatment System |
| ng/L | nanograms per liter |
| NASA | National Aeronautics and Space Administration |
| NDMA | N-nitrosodimethylamine |

ACRONYMS AND ABBREVIATIONS (continued)

| | |
|-----------------|--|
| NEMA | National Electrical Manufacturers Association |
| NMED | New Mexico Environment Department |
| NPDES | National Pollutant Discharge Elimination System |
| O&M | operation & maintenance |
| OEHHA | Office of Environmental Health Hazard Assessment |
| OMB | Office of Management and Budget |
| PCE | tetrachloroethylene |
| PHG | public health goal |
| P&ID | piping and instrumentation diagram |
| PLC | programmable logic controller |
| ppm | part per million |
| PQL | practical quantitation limit |
| QA | quality assurance |
| QC | quality control |
| <i>R. ruber</i> | <i>Rhodococcus ruber</i> |
| QA | quality assurance |
| QC | quality control |
| QAPP | quality assurance project plan |
| SERDP | Strategic Environmental Research and Development Program |
| Shaw | Shaw Environmental, Inc. |
| SRI | Southwest Research Institute |
| TCE | trichloroethylene |
| TOC | total organic carbon |
| TSS | total suspended solids |
| UDMH | unsymmetrical dimethylhydrazine (1,1-dimethylhydrazine) |
| USEPA | U. S. Environmental Protection Agency |
| UV | ultraviolet |
| VOC | volatile organic compound |
| WSTF | White Sands Test Facility |

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

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 Department of Defense (DoD) and National Aeronautics and Space Administration (NASA) sites involved in the production, testing, and/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 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 use of an advanced bioreactor design, a fluidized bed bioreactor (FBR), in the field for the ex situ treatment of NDMA from part-per-billion (micrograms per liter [$\mu\text{g/L}$]) influent concentrations to low part-per trillion (nanograms per liter [ng/L]) effluent concentrations. The demonstration was conducted at the NASA White Sands Test Facility (WSTF) in Las Cruces, NM. The capital and operational costs of the FBR were subsequently compared to those of an existing UV system for NDMA treatment at the WSTF facility.

TECHNOLOGY DESCRIPTION

Previous studies in our laboratory revealed that the propanotroph *Rhodococcus ruber* ENV425 and other similar strains are capable of biodegrading NDMA to low ng/L concentrations while growing aerobically on propane. Based on this observation, and laboratory bioreactor tests, a field scale FBR was designed, constructed, and tested for NDMA treatment. The FBR is an efficient fixed-film bioreactor. It consists of a reactor vessel containing media with a high surface area (usually sand or granulated activated carbon [GAC]) to foster the growth of microbial biomass. The high biomass achievable within the FBR bed makes it appreciably more efficient for water treatment than many other types of biological reactor systems. This reduces the reactor size and, subsequently, the cost of treatment. The pilot-scale FBR (1-5 gallons per minute [gpm] influent flow) was operated for ~ 1 year on the actual site water using coconut shell based GAC media under various operating conditions. The FBR was seeded with ENV425 and subsequently fed propane, oxygen, and inorganic nutrients to promote cell growth and NDMA biodegradation. The treatment of a secondary contaminant from rocket fuel, N-nitrodimethylamine (DMN), within the FBR was also examined. The hydraulic retention time (HRT) of groundwater within the FBR was varied from 60 minutes to 10 minutes, and different challenge studies were conducted to assess the resiliency of the FBR to system upsets.

DEMONSTRATION RESULTS

Based on more than a year of operational data, the FBR treatment system was demonstrated to be an effective means to treat $\sim 1 \mu\text{g/L}$ concentrations of NDMA in WSTF groundwater to less than 10 ng/L at a 10 minute HRT and to less than 4.2 ng/L , the WSTF regulatory discharge limit, at a

20 minute HRT. The system also effectively treated DMN from ~ 0.6 µg/L to < 10 ng/L at an HRT as low as 10 minutes. The system was observed to be resilient to upsets, including power outages, interruptions in influent groundwater flow, shutdown of propane and nutrient feeds, and presence of low levels of volatile organic compounds (VOC) in the influent groundwater. In general, effluent NDMA and DMN concentrations either remained at < 10 ng/L during the system challenge studies (most of which were conducted at the 10 minute HRT), or recovered to this level within a few to several days. The system reliability was high, with a 94% uptime recorded over the duration of the study, and less than 10 hours per week of operator attention was required. In addition, a cost analysis suggested that the FBR would be ~ \$900,000 less expensive (roughly 35%) to treat NDMA than a comparable UV system at a 125 gpm flowrate, with the primary savings being related to lower electrical and maintenance costs over a 30 year remedial timeframe.

IMPLEMENTATION ISSUES

This FBR technology is currently ready for implementation. A full-scale system can be designed, constructed, and operated based on the results of this ESTCP demonstration. Although this is the first application of a field-scale propane-fed FBR, the basic FBR technology is mature and has been widely applied for treatment of other contaminants, including nitrate, perchlorate, tert-butyl alcohol and other organics. Systems are currently operating in the United States at groundwater flow rates as high as 5000 gpm. Moreover, the electrical demand of a FBR system is anticipated to be ~ 3x lower than a comparable UV system for groundwater treatment, making this biological approach more sustainable and energy efficient for NDMA. The implementation of this technology to treat contaminated groundwater, rather than simply relying on energy intensive alternatives, can serve as a new paradigm of water treatment for significantly impaired resources. With quality supplies of water rapidly declining throughout the United States, the implementation of such a biological treatment plant can be effectively used for NDMA contaminant removal. Technology transfer efforts for this project include presentation of the results at several national and international remediation and groundwater conferences, publication of a two peer-reviewed manuscripts on the technology, and presentation of the results directly to NASA, DoD, and commercial aerospace contractors with NDMA contamination in groundwater.

1.0 INTRODUCTION

The origin of N-nitrosodimethylamine (NDMA) in groundwater and drinking water includes 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, and/or disposal of liquid propellants containing unsymmetrical dimethylhydrazine (UDMH). NDMA is a known impurity in UDMH-based fuels (such as Aerozine-50) and it can be formed through oxidation of UDMH in the environment or after exposure to hydrogen peroxide (Fleming et al., 1996; Mitch et al., 2003; Lunn and Sansone, 1994). DoD and NASA Sites with NDMA in groundwater include former Air Force Plant PJKS¹ (CO); the White Sands Test Facility (NM); the Rocky Mountain Arsenal (CO); Jet Propulsion Labs (CA), and Edwards Air Force Base (CA). NDMA plumes have also been detected at aerospace contractor sites, such as Aerojet in CA (Girard, 2000). Both Los Angeles and Orange Counties in California have reported NDMA in groundwater supply wells (California Department of Public Health [CDPH], 2013).

Currently, the most effective treatment technology for NDMA in groundwater is pump-and-treat with ultraviolet irradiation (UV). However, this approach is expensive because it requires high energy input to effectively reduce the levels of NDMA. The objective of this ESTCP project was to demonstrate and validate the use of an advanced bioreactor design, a fluidized bed bioreactor (FBR), in the field for the treatment of NDMA to required regulatory levels. This ESTCP project was a collaborative effort among scientists and engineers at Shaw Environmental, Inc (Shaw) (a subsidiary of Chicago Bridge & Iron [CB&I], Lawrenceville, NJ), Envirogen Technologies, Inc. (ETI) (Rancho Cucamonga, CA), and the White Sands Test Facility (WSTF) (Las Cruces, NM).

1.1 BACKGROUND

The effective treatment of NDMA in groundwater requires that the concentrations of the compound be reduced from a few to several hundred micrograms per liter ($\mu\text{g/L}$) to low nanograms per liter (ng/L) concentrations. To date, no pure bacterial cultures have been isolated that can utilize NDMA as a sole source of carbon and energy. Moreover, in many instances, bacteria have been observed to have a lower threshold concentration for an organic substrate below which degradation ceases (Alexander, 1994; Schmidt et al., 1985). The absence of cultures that can use NDMA for growth and the aforementioned threshold phenomenon are both important considerations when evaluating bioremediation strategies for NDMA. These observations make it unlikely that a bacterial strain will be able to grow on a few $\mu\text{g/L}$ of NDMA and reduce its concentration to ng/L levels. However, the degradation of NDMA by a cometabolic process in which the bacterium actually grows on a secondary substrate (such as propane, toluene, butane, etc.) and degrades NDMA, may allow threshold limitations to be overcome, and low concentrations to be achieved.

This ESTCP project builds upon the successful results from Strategic Environmental Research and Development Program (SERDP) Project ER-1456, the objective of which was to examine the potential for in situ and ex situ biodegradation of NDMA using co-metabolic approaches.

¹ Air Force Plant: Peter J. Kiewit and Sons (PJKS)

The full results from this project are available in Hatzinger et al., (2008). The key findings of that project are as follows: (1) the propanotroph *Rhodococcus ruber* (*R. ruber*) EN425 is capable of degrading NDMA to innocuous products, including formate, nitrate, nitrite, methylamine, and carbon dioxide (Fournier et al., 2009); (2) *R. ruber* ENV425 can biodegrade NDMA from typical groundwater concentrations (e.g., 1-100 µg/L) to low part-per-trillion (ng/L) concentrations (Fournier et al., 2009; Hatzinger et al., 2011); (3) similar propanotrophs capable of degrading NDMA are indigenous to other groundwater environments, and these organisms can be stimulated to degrade NDMA through the addition of propane and oxygen; and (4) propane does not appear to be a significant inhibitor of NDMA biodegradation by many propanotrophs even though the reaction is cometabolic (Sharp et al., 2010).

Results from batch experiments and a laboratory bioreactor study with the propanotroph *R. ruber* ENV425 revealed that NDMA treatment to levels of < 10 ng/L were achievable through biodegradation (Hatzinger et al., 2011; Fournier et al., 2009). In the first phase of this ESTCP demonstration, a treatability study was conducted in which a bench-scale FBR was tested for NDMA removal from water (Webster et al., 2009; Webster et al., 2013). The FBR is an efficient fixed-film bioreactor in which a high concentration of biomass is attached onto fluidized medium and has been widely used for the treatment of groundwater contaminated with a variety of compounds. The bench-scale FBR clearly showed the potential for treating NDMA using this reactor design, so the field demonstration described herein was subsequently conducted.

1.2 OBJECTIVE OF THE DEMONSTRATION

The objective of this pilot-scale demonstration is to evaluate the cost and performance of a biological FBR for the treatment of NDMA in groundwater under field conditions.

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 U.S. However, according to the U.S. Environmental Protection Agency (USEPA), a safe level of NDMA in drinking water based on lifetime *de minimus* risk calculations (< 10⁻⁶ risk of developing cancer) is only 0.7 ng/L (USEPA, 2013), which is below the current practical quantitation limit 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 *action level* for NDMA in groundwater, which is 10 ng/L (California Department of Health Services [CDHS], 2008). The USEPA also recently added NDMA to its current Contaminant Candidate List (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 pump-and-treat discharge limits of NDMA. For example, NASA WSTF in New Mexico was regulated at 10 ng/L of NDMA for discharge of treated groundwater for surface deposition for a number of years. As of September 2011, the New Mexico Environmental Department (NMED) changed the NDMA concentration regulated by the discharge permit from 10 ng/L to 4.2 ng/L. The original objective of this study was to treat to 10 ng/L, but the system was later assessed to determine its ability to reduce the effluent NDMA concentrations below 4.2 ng/L.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

During this ESTCP project, the biodegradation of part-per-billion ($\mu\text{g/L}$) concentrations of NDMA was evaluated in a granular activated carbon (GAC) based FBR. The FBR is an efficient fixed-film bioreactor that was originally developed beginning in the 1970s as a means to increase the efficiency of traditional packed bed reactors (USEPA, 1993; Sutton and Mishra, 1994). Full-scale FBR systems (50 – 5,000 gallons per minute [gpm]) built by Shaw's Bioreactor Group (now ETI) are presently operating at several DoD and DoD-contractor facilities to remove perchlorate and nitrate from groundwater (Figure 1) (Hatzinger, 2005; Webster et al., 2009). The FBR consists of a reactor vessel containing media with a high surface area (usually sand or GAC) to foster the growth of microbial biomass (Sutton and Mishra, 1994; USEPA, 1993). The high biomass achievable within the FBR bed makes it appreciably more efficient for water treatment than many other types of biological reactor systems (USEPA, 1993). This reduces the reactor size and, subsequently, the cost of treatment.



Figure 1. Three full-scale FBR installations.

The media bed in the FBR is fluidized by passing influent groundwater through a distribution system at the bottom of the FBR vessel (Figure 2). This distribution system provides a consistent upflow velocity with a flow rate sufficient to achieve a 25-30% expansion of the media within the FBR (Figure 3). For this project, the FBR was inoculated with a known NDMA degrading propanotroph, *R. ruber* ENV425. Propane (electron donor and carbon source), oxygen, and inorganic nutrients were supplied to the reactor to support microbial growth. Utilizing the propane and inorganic nutrients, the microorganisms attach to the GAC media to create a biofilm, and perform an oxidation/reduction reaction in consuming the dissolved oxygen (DO) and propane. The NDMA is removed by *R. ruber* ENV425 and/or native propanotrophs through cometabolism (Fournier et al., 2009). As the microorganisms grow and attach to media particles in the FBR, the media bed expands such that longer hydraulic retention times (HRT) can be achieved for contaminant removal. The treated fluid flows into a submerged recycle collection header pipe and the effluent collection header pipe at the top of the reactor. A portion of the fluid exits the FBR system while the balance is recycled back to the suction of the influent pump. An in-bed biomass separation device controls bed height growth by physically separating biomass from the media particles. Typically, a bed expansion of 40-60% of the settled bed height is targeted. Any excess biomass that is separated from the media exits the system through the effluent collection system.

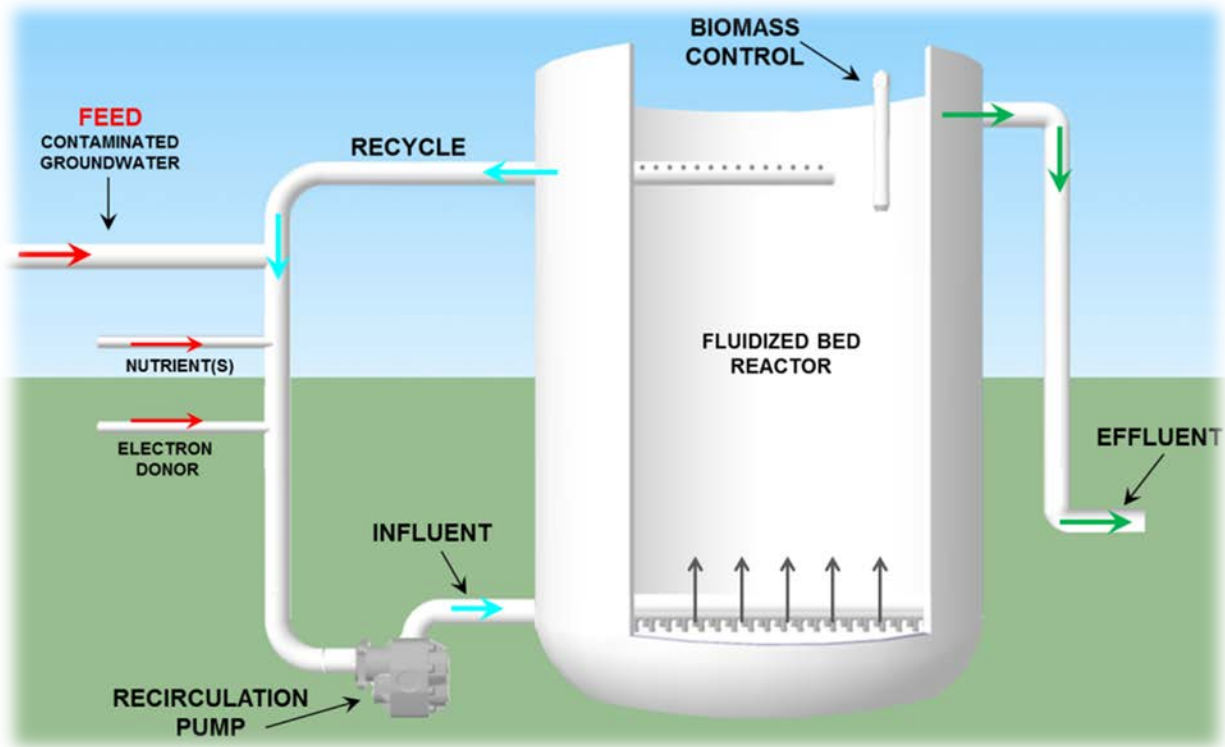


Figure 2. Schematic of fluidized bed bioreactor.

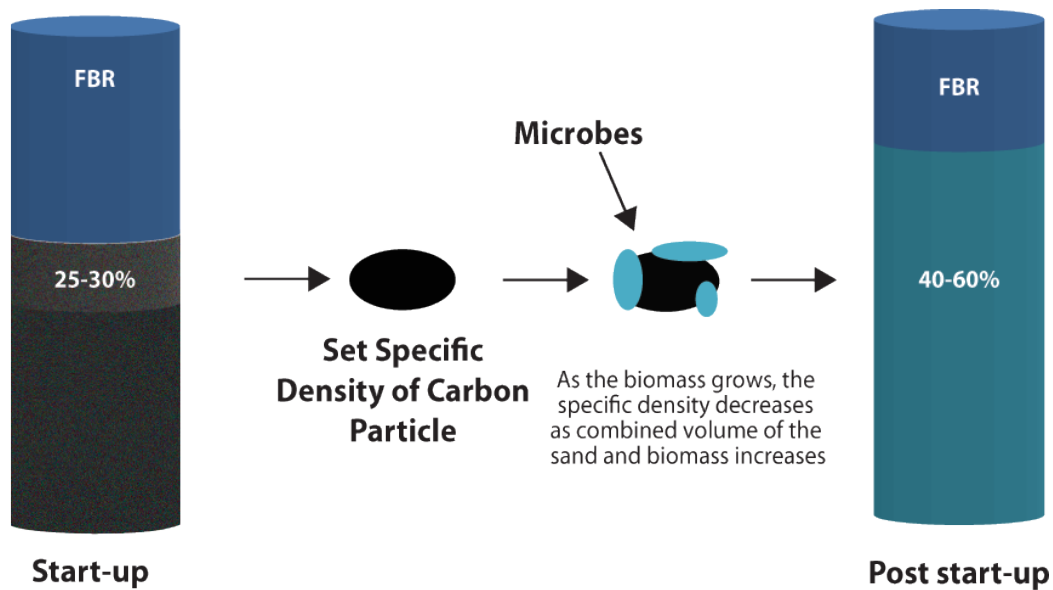


Figure 3. Hydraulic and biological expansion of media.
(from Webster et al., 2009)

The key challenges of this ESTCP demonstration were to (1) develop an FBR feed system capable of effectively and safely supplying propane and oxygen, and (2) optimize the FBR technology for the treatment of NDMA to ultra-low concentrations. To date, a field-scale propane-fed FBR has never been built or tested. With respect to the relevant microbiology, it has been demonstrated that NDMA can be biodegraded by a wide variety of propane-oxidizing bacteria, and that these strains can readily achieve NDMA levels below 10 ng/L in both batch experiments and in a laboratory bioreactor operated continuously for several months (Fournier et al., 2009; Hatzinger et al., 2008, 2011). In addition, it has been determined that NDMA degradation by *R. ruber* ENV425 follows a mixed denitration/ demethylation pathway producing low concentrations of innocuous products including methylamine nitrite, nitrate, and methanol (Fournier et al., 2009). The strain also mineralizes significant quantities of NDMA to carbon dioxide (> 60%). During the laboratory phase of this ESTCP study, at a 20-30 minute HRT using a bench-scale FBR system, effective removal of 10-20 µg/L of NDMA to levels less than 10 ng/L was demonstrated, suggesting that this approach has promise at the field scale (Section 5.3; Webster et al., 2013). Thus, the FBR is a mature technology and laboratory data to date suggest that this technology is applicable to treat NDMA to ng/L concentrations potentially at both the pilot- and full-scale.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The main advantages of utilizing an FBR for NDMA treatment are:

- Potentially reduced operating costs compared to traditional physical/chemical treatment technologies such as UV irradiation;
- Near complete destruction of the NDMA via a biological process with no harmful intermediates formed;
- Rapid and effective recovery from feed and power loss;
- An effective and safe means to deliver both oxygen and propane gas has been designed into such treatment systems.
- Potentially capable of treating multiple contaminants in the same reactor; and
- Limited space requirements for a complete treatment system.

Technical risks and limitations inherent to the system include:

- NDMA microbiological degradation in the laboratory has been demonstrated during the treatability study using a bench-scale FBR. Although it has been determined that laboratory bioreactor designs (membrane bioreactor [MBR] and FBR) could effectively treat NDMA to low concentrations, treatment at field scale and under field conditions has not been proven.
- Operator attention to the FBR may be at least as much as physical/chemical treatment technologies, such as UV irradiation.

- NDMA treatment may be inhibited by chlorinated organics, such as trichloroethylene (TCE), if concentrations are high enough. These compounds can easily be removed from the water prior to entering the FBR (e.g., via air-stripping).
- Biomass solids are generated that may require additional filtration prior to the water being reinjected or discharged to surface water.

Based on this successful demonstration, the DoD will have a widely applicable ex situ remediation approach for NDMA. UV treatment is presently the primary practical method used to remove NDMA from groundwater. Although this technology is effective, it is also very expensive. Operational costs for the FBR treatment system include chemical and electrical costs. Based on the low concentrations of NDMA (low contaminant loading rates), these operational costs are expected to be a fraction of the amount observed for a UV system for many applications (see Section 7.3). Because federal regulations for this carcinogen are likely in the future, it is important to evaluate potentially less expensive treatment options for NDMA. This demonstration assessed a biological treatment approach with the potential to be both effective and economical. Such a discovery provides both a cost- and environmental-benefit to a number of DoD installations and contractors that could apply this technology.

3.0 PERFORMANCE OBJECTIVES

Performance objectives were established for this demonstration to provide a basis for evaluating the performance and costs of NDMA treatment in an FBR. The primary performance objectives for this demonstration are summarized in Table 1.

Table 1. Performance objectives.

| Performance Objective | Data Requirements | Success Criteria | Results |
|---|--|---|--|
| Quantitative Performance Objectives | | | |
| Determine NDMA degradation effectiveness in FBR at start-up | Initial feed and effluent NDMA concentration data during first month of operation | Reduction of NDMA concentrations from $\mu\text{g/L}$ to low ng/L ($<100 \text{ ng/L}$) | NDMA was reduced to below 100 ng/L at a 60 minute HRT by the fourth week after inoculation |
| Assess pilot-scale FBR ability to treat NDMA to below regulatory limits (10 ng/L , later to 4.2 ng/L) | Feed and effluent NDMA concentration data at different HRTs by USEPA Method 607 and High-Resolution Mass Spectrometry (HRMS) by Southwest Research Institute (SRI) | Reduction of NDMA concentrations to less than 10 ng/L (then 4.2 ng/L) at a HRT less than 30 minutes Meet 95% completeness | At an HRT of 10 minutes, NDMA was reduced to less than 10 ng/L , and to below 4.2 ng/L at a 20 minute HRT. The 95% completeness measurement was achieved, with completeness at 98% for the NDMA samples |
| Effects of interruptions in plant operation | Feed and effluent co-contaminant concentration data at minimal HRT upon shutdown/restart | Reestablishment of FBR performance to less than 10 ng/L after feed restart | Within 24 hours to 4 days after feed restart, NDMA was reduced to less than 10 ng/L |
| Effects of co-contaminants on NDMA treatment | Feed and effluent co-contaminant concentration data at minimal HRT | $< 100 \text{ ng/L}$ in effluent during co-contaminant addition Any reduction in co-contaminants | At the 10 minute HRT, system achieved consistent removal below 10 ng/L but not 4.2 ng/L . Some reduction in chlorofluorocarbon (CFC) 11 and TCE was observed |
| Assess pilot-scale FBR treatment of N-nitrodimethylamine (DMN) | Feed and effluent DMN concentration data at different HRTs. HRMS by SRI. | Reduction of DMN concentrations to less than 10 ng/L | DMN was consistently reduced to $< 10 \text{ ng/L}$ at a 20 and 30 min HRT. $< 10 \text{ ng/L}$ DMN also was achieved at a 10 min HRT except during feed challenge |
| Qualitative Performance Objectives | | | |
| Ease of use | Feedback from field technician on usability of technology and time required | A single field technician able to effectively take measurements safely | System monitored by one field engineer effectively |
| Reliability | Uptime of system. Mechanical issues Daily measurements of operational data | Greater than 90% uptime Ability of electron donor system to consistently operate | Uptime was 94% No issues with the delivery of the electron donor were observed |
| Reduction of treatment costs | Feed flow, oxygen addition rates, and propane addition rates | Minimization of HRT and gaseous addition rates | At 20 minute HRT with oxygen addition rate of 176 mg/min and a propane addition rate of $35 \text{ milligrams per minute (mg/min)}$ ($28.6 \text{ mg carbon [C]/min}$) |

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4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

The NASA WSTF was chosen as the location for this demonstration because (1) they had an extensive groundwater plume with high levels of NDMA and typical co-contaminants found at NDMA sites from rocket testing applications (e.g., TCE and Freon-113); (2) they were installing a full-scale UV system that could provide an excellent comparison to the pilot-scale FBR plant at the demonstration site, (3) the site had the available infrastructure to host the pilot project, and (4) the WSTF management was interested in participating in the ESTCP demonstration and had on-site contractors to assist with system installation and non-routine maintenance issues (e.g., pump replacement).

WSTF is located 12 miles east of Las Cruces, New Mexico, six miles north of U.S. Highway 70 on the western flank of the San Andres Mountains and on the eastern edge of the Jonada del Muerto Basin. The facility is approximately 28 square miles situated on the U.S. Army's White Sands Missile Range. Historically, this test facility evaluated rocket engines, space flight components, and rocket propulsions systems. More recently, it continues to test such systems, but also serves other testing functions for NASA including materials assessment, hazard assessments, space flight system testing, and launch and landing system testing.

The pilot-scale FBR was located at the newly constructed full-scale Mid-Plume Intersection and Treatment System (MPITS) building. The MPITS is designed to treat 125 gpm of flow from various extraction wells located in the mid-plume area. Treatment of the water involves the use of an air stripper for volatile organic contaminants (primarily Freon-113, CFC-11 and TCE) followed by a low pressure lamp UV photolysis system for NDMA treatment (Figure 4). The pilot FBR was located in the MPITS building next to the air stripper, allowing feed water to the FBR to originate from either before or after the air stripper.



Figure 4. NASA WSTF MPITS UV System.

4.2 SITE GEOLOGY/HYDROGEOLOGY

WSTF is in the Mexican Highland Section of the Jonada del Muerto Basin and within the Rio Grande Rift Zone. WSTF is located along the western flank of the San Andres Mountains, with the uppermost alluvial layers consisting of silt, sand, gravel, boulders, and locally-cemented

conglomerates. These layers range from 400 to 700 feet thick adjacent to the mountains to 100 to 200 feet thick in the basin floor. The surface of the uppermost alluvium layer is a sandy-silt containing some gravel and occasional boulders (NMED, 2009). Groundwater is the primary water supply in the area for nearly all uses (i.e., potable, industrial, commercial, and agricultural). Runoff from the adjacent San Andres Mountains primarily provides recharge to the basin, with the majority (up to 75%) migrating offsite as surface runoff. The runoff that eventually reaches the alluvial fans at the base of the mountains is a small volume, but continuing source of ground water recharge in the area (NMED, 2009).

4.3 CONTAMINANT DISTRIBUTION

Between 1964 and the late 1970s, the oxidation of wastewater containing dimethylhydrazine resulted in the unintentional formation and release to grade of NDMA (Giles et al., 2004). In addition, a number of other (VOC) were utilized at the facility and released, migrating into the groundwater table. Characteristic groundwater concentrations in well Bureau of Land Management (BLM)-15 are provided in Table 2. The contamination resulted in a groundwater plume nearly 4 miles in length, 1.5 miles in width, and up to 700 feet thick (Figures 5 and 6). The FBR demonstration was set up to treat groundwater collected from extraction wells located within this plume.

Table 2. WSTF historical groundwater analyses from the mid-plume area (BLM-15).

| Analyte | Result (µg/L) |
|-----------|---------------|
| NDMA | 8.1-18.7 |
| TCE | 2.5-3.5 |
| CFC-21 | 2.3-4.7 |
| CFC-11 | 206-240 |
| Freon-113 | 51.2-154 |

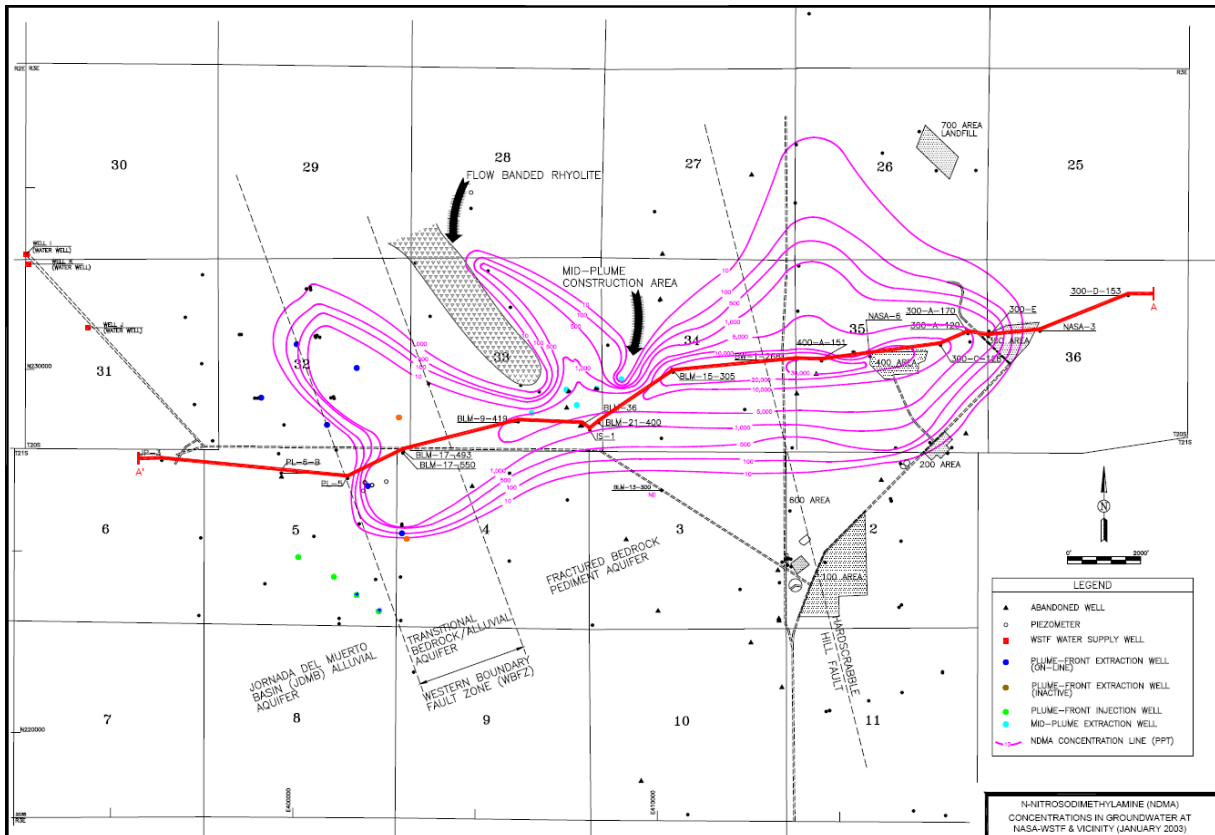


Figure 5. NASA WSTF NDMA plume.

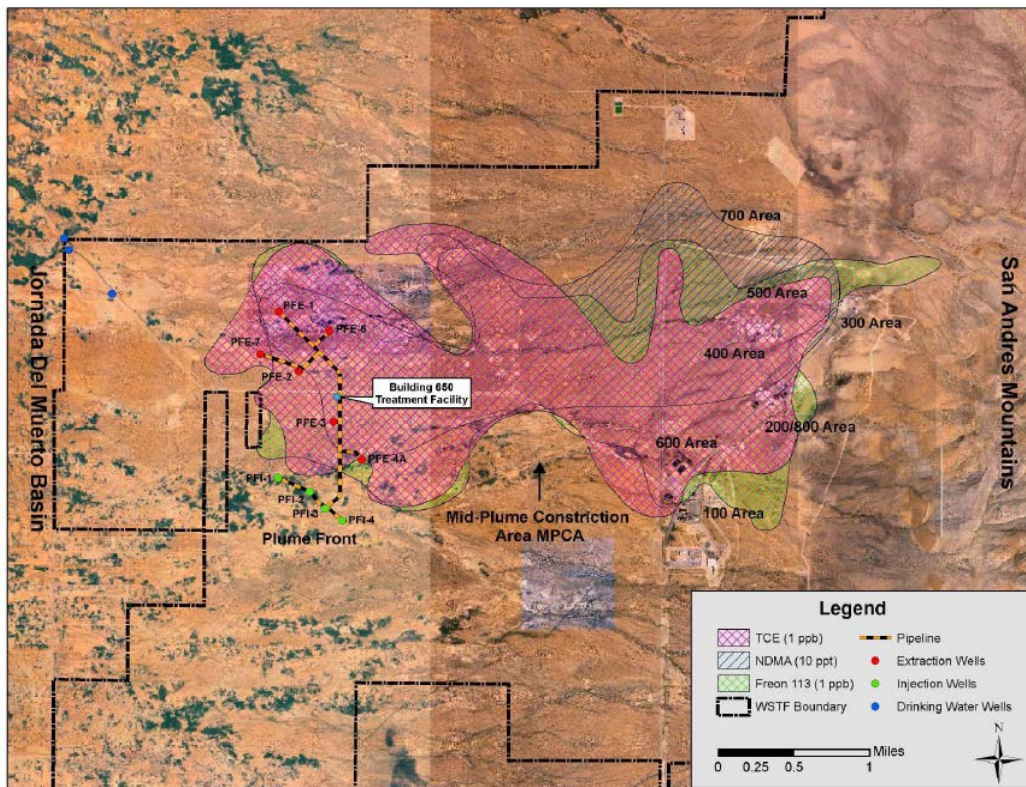


Figure 6. NASA WSTF NDMA, TCE, and Freon 113 plumes.

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5.0 TEST DESIGN

The objective of this ESTCP project was to demonstrate biological remediation of NDMA in groundwater using an aerobic, propane-fed FBR under field conditions.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

Based upon successful treatability study and bench-scale FBR results (Section 5.3; Webster et al., 2013), the pilot-scale FBR testing was conducted at the MPITS location at WSTF. The pilot-scale FBR was operated for ~1 year on the actual site water using coconut shell based GAC media under various operating conditions (Figure 7, Table 3). The design of this pilot-scale FBR system utilized separate pressure vessels to add propane and oxygen to the system recycle water. All necessary engineering precautions were taken to ensure that the two gases were added safely (lower explosive limit sensors, programmed alarms, etc.). The pilot-scale system was designed to treat 1-5 gpm of water.

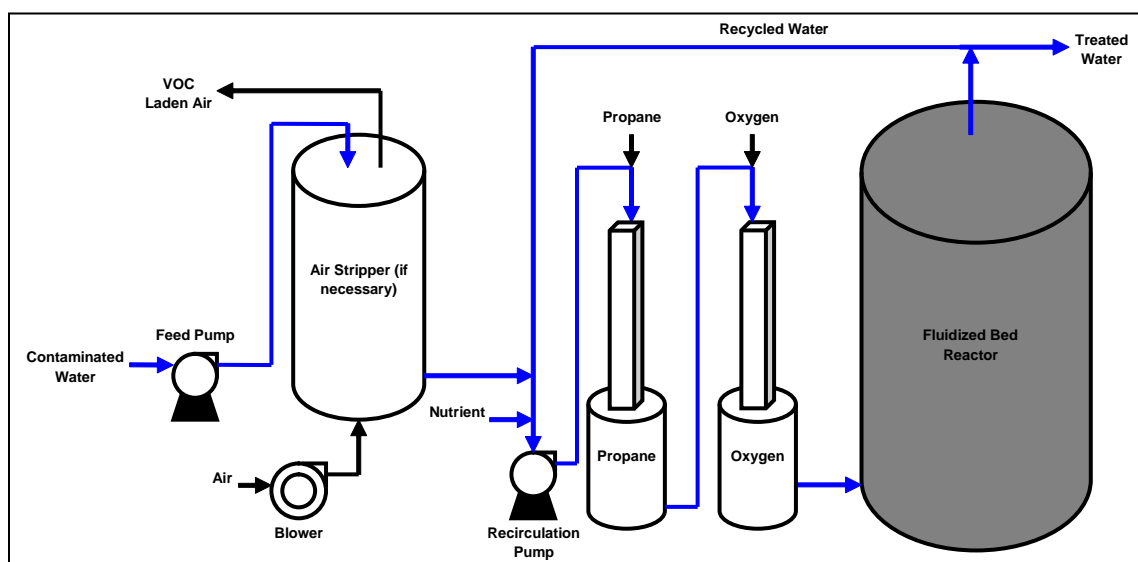


Figure 7. Conceptual set-up of pilot-scale FBR.

Operating parameters, such as HRT, propane and oxygen addition rates, and nutrient addition rates were adjusted based on system performance in order to optimize NDMA removal. The pilot-scale FBR system was tested with the actual site water with co-contaminants removed via air-stripper for the majority of the demonstration (i.e., the same water entering the UV system). At the end of the demonstration period, the air stripper was bypassed for 27 days to assess the effect of the presence of organic co-contaminants on NDMA biodegradation, simulating an air stripper failure. The unit was decommissioned after approximately 1 year of operation.

Table 3. Operating conditions for the pilot-scale FBR treatment.

| Phase | Duration | Purpose | Changes |
|-------|------------------------|--|--|
| I | 83 days (Days 0-83) | Conduct start-up/Determine abiotic losses | Mechanical Shakedown/30-60 minute HRT |
| II | 7 days (Days 83-90) | Recycle of <i>R. ruber</i> ENV425 inoculum | Oxygen/propane addition with residual |
| III | 90 days (Days 90-180) | Increase in <i>R. ruber</i> ENV425 within FBR | 30-60 minute HRT, oxygen/propane addition with residual |
| IV | 90 days (Days 180-270) | Demonstrate NDMA removal under steady-state conditions | 10-30 minute HRT |
| V | 80 days (Days 270-350) | Demonstrate NDMA removal under non-steady-state conditions | Feed shutdown/electrical shutdown/restart, nutrient interruption |
| VI | 27 days (Days 350-377) | Demonstrate NDMA and co-contaminant removal | Bypass of air stripper to allow co-contaminants in feed. |
| VII | 15 days (Days 377-392) | Decommissioning of Unit | Disconnect utilities/prepare for shipment |

5.2 BASELINE CHARACTERIZATION ACTIVITIES

The MPITS system was designed to treat a combined influent from several different wells in the NDMA plume at WSTF. Baseline groundwater characterization was initially conducted from well BLM-15 for treatability testing (Section 5.3). WSTF water from this well demonstrated a range for each contaminant (See Table 2). WSTF initiated operation of their new MPITS just months prior to the installation of the pilot-FBR system at the same location. Hence, significant water chemistry data was collected and analyzed by WSTF personnel from the MPITS influent. Representative values for NDMA and organics entering the MPITS are provided in Table 4 from this initial evaluation.

Table 4. WSTF representative groundwater analysis from MPITS.

| Analyte | Result (µg/L) |
|---------------------------|---------------|
| NDMA | 0.8-3.4 |
| TCE | 19-47 |
| Tetrachloroethylene (PCE) | 0.9-2.2 |
| CFC-11 | 30-75 |
| Freon-113 | 39-120 |

5.3 LABORATORY STUDY RESULTS

The treatability phase of this study entailed initial batch microcosm studies to evaluate the ability of *R. ruber* ENV425 to mineralize the NDMA in the WSTF water, followed by extensive FBR bench-scale testing to assess reactor performance and to evaluate different operating conditions (i.e., HRT, propane, and oxygen addition rates, etc.). The complete data from the treatability study are provided in the ESTCP treatability study report for this project (Hatzinger and Webster, 2009), and the laboratory-scale FBR results were published in Webster et al. (2013).

5.3.1 Microcosms

For the initial bench-scale microcosm study, *R. ruber* ENV425 rapidly mineralized 55-60% of the NDMA in a sample of WSTF water. Based on the extent of mineralization and evidence of cell growth, the WSTF water did not appear to be inhibitory to NDMA degradation by *R. ruber* ENV425 during growth on propane. In large-scale mesocosms prepared with WSTF groundwater and augmented with propane, oxygen, and *R. ruber* ENV425, NDMA was degraded from ~18 µg/L to ~10 ng/L in 3 days. The killed control and live control samples did not demonstrate a similar reduction in NDMA concentration. Hence, the presence of co-contaminants or other geochemical factors within the WSTF water did not appear inhibitory to *R. ruber* ENV425.

5.3.2 Laboratory FBR

Based upon successful results of the batch-scale microcosm tests, a laboratory-scale FBR was constructed at the Shaw Laboratory in Lawrenceville, New Jersey. Based on groundwater data, a synthetic blend of water was produced in the Shaw laboratory to mimic the site NDMA and other chemical constituent concentrations in groundwater. The bench-scale FBR was tested for 8 months on the synthetic site water, and then actual water was supplied at the end of the study. The design of the bench-scale FBR system incorporated adding propane and oxygen using separate pressure vessels to the recycle water. The bench-scale system was designed to treat up to 70 milliliters (mL)/min of NDMA-laden groundwater.

Initial operation of the bench-scale FBR allowed for the abiotic removal of NDMA through adsorption. Once breakthrough of the NDMA was achieved across the FBR and the steady-state operation of the system was reached, the FBR process was demonstrated to be an effective means to consistently treat 10-20 µg/L of NDMA to levels below 100 ng/L (Figure 8) (Webster et al., 2013). When conditions were further optimized, the FBR system demonstrated treatment of the NDMA to effluent concentrations of less than 10 ng/L under specific system operating parameters:

- A 20-30 minute HRT,
- An oxygen addition rate of 6-7 mL/min (7.9-9.2 mg/min)
- A propane addition rate of 0.6-0.8 mL/min (0.9-1.2 mg C/min)
- A diammonium phosphate addition rate of 0.58 mL/min at 88 mg/L,
- A urea addition rate 0.58 mL/min at 176 mg/L.

In summary, *R. ruber* ENV425 was demonstrated to biodegrade NDMA in NASA WSTF water from typical concentrations (10–20 µg/L) to less than 10 ng/L in both batch microcosms and in a laboratory pilot FBR. Based on these results, the “Go” decision to Phase 2 and Phase 3 for this project was recommended. Phase 2 involved the design and fabrication of the pilot-scale FBR for the treatment of NDMA-laden water from the WSTF site, while Phase 3 involved the operation the pilot-scale unit in the field for a one year evaluation, providing site operational experience while identifying the critical parameters for eventual full-scale design.

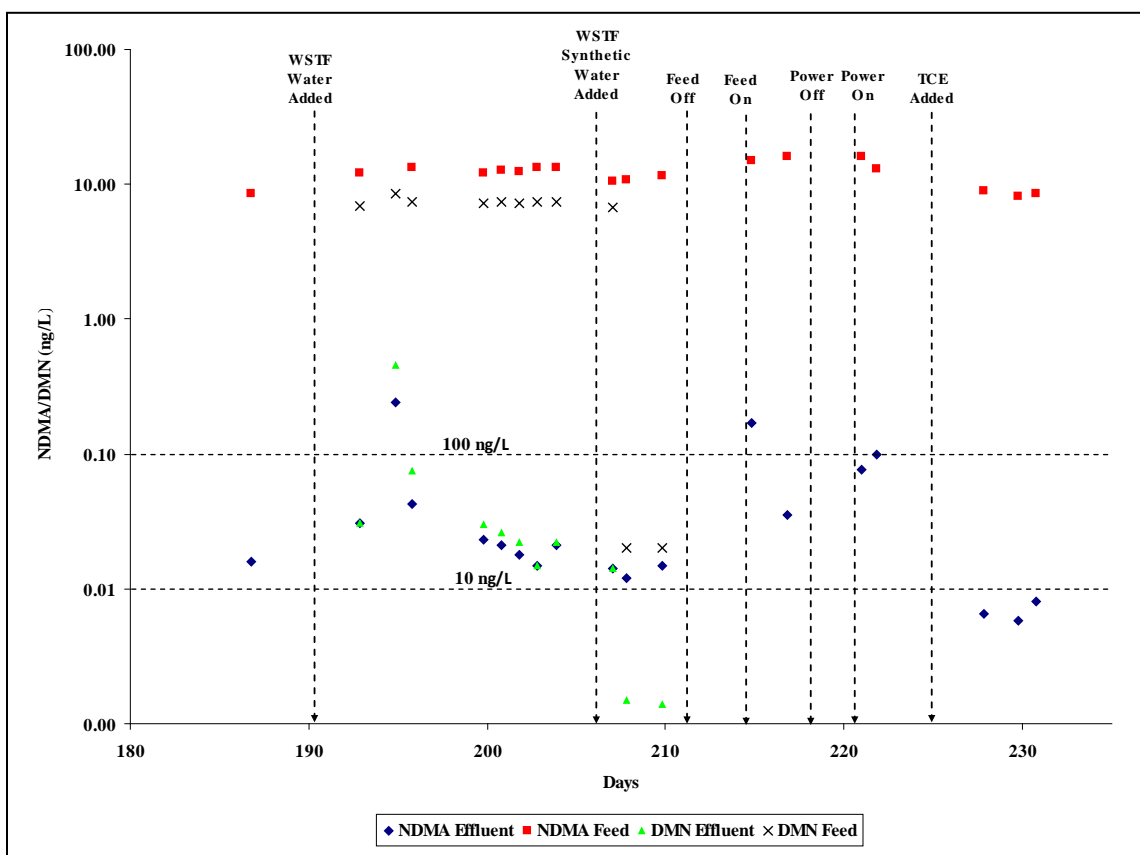
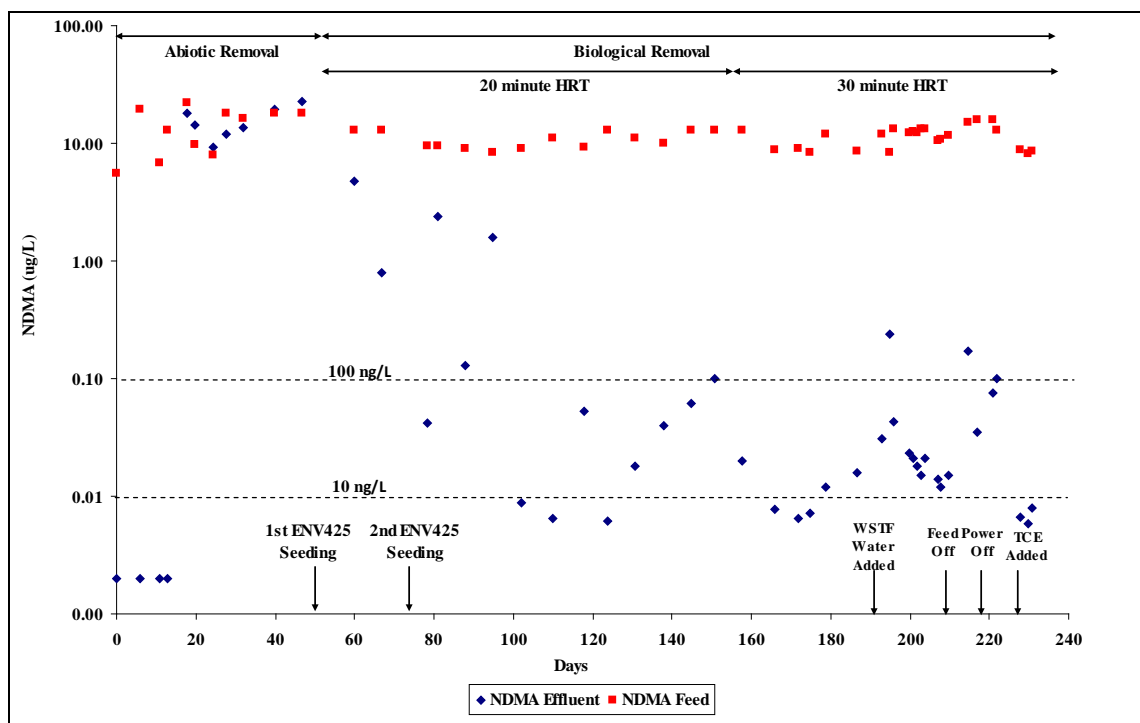


Figure 8. Removal of NDMA over the duration of the laboratory FBR study.
 Days 180-230 detailed in bottom panel (modified from Webster et al., 2013).

5.4 FIELD TESTING

The pilot-system arrived on site as a packaged, self-contained unit on a skid. It was unloaded and placed in the MPITS facility using a forklift. System photographs are provided in Figure 9. The utilities, including electrical, air, and feed and effluent water piping, were connected by qualified site personnel. Following the system installation, all equipment was checked for proper operation. The oxygen and propane cylinders were installed at the site, and all system alarms and interlocks were tested to ensure proper operation. After each piece of equipment on the FBR skid was verified to be working correctly, the feed water was turned on at 3 gpm and forward feed proceeded through the FBR treatment system to the gravity feed drain line. Any necessary repairs or improvements were conducted at this time prior to the carbon being added to the system. After all systems were tested, the carbon media was added to the FBR vessel, and the system was placed in recycle so that the media was hydraulically fluidized.



Figure 9. Photographs of the installed FBR system.

Several critical system and treatment operations were evaluated during the 1-year demonstration period. A number of experiments were conducted to test the robustness of the FBR technology while continuing to produce water with an NDMA concentration less than 10 ng/L. These experimental design components are discussed in detail in the project final report. All data was compiled and reviewed by the principal investigators as it became available. Weekly reports were generated by the system operator and provided to the principal investigators for review. Teleconferences were held among the principal investigators and staff to evaluate data and system performance and to discuss modifications. System modifications, including alterations in flow-rates, propane and oxygen dosage, nutrient addition, etc. were made during the demonstration. All input from WSTF staff was addressed by the Project Manager and changes were implemented as necessary.

The basic operational phases of this demonstration are presented in Table 5.1, and a schedule of these phases and other operational conditions is provided in a Gantt chart in Table 5.

5.5 SAMPLING METHODS

The primary matrix sampled during the demonstration was the raw feed groundwater (i.e., FBR feed) and the treated FBR effluent water. Sampling was carried out in accordance with the Quality Assurance Project Plan described in the ESTCP Demonstration Plan (Webster et al., 2010). The parameters, monitoring locations, sampling frequency, and the sample location for the 1-year period of operation for the different phases of the pilot-scale experiments are provided (Table 6). The analytical methods utilized are provided in Table 7. Grab samples were collected from the FBR feed and effluent streams. A piping and instrumentation diagram (P&ID) with sample points listed is provided in the project final report. Field measurements were conducted using hand-held and in-line instruments, as well as conventional methods.

For the on-site water quality analysis, various USEPA approved HACH[®] methods were utilized. For the off-site laboratory analysis, the selected methods represented standard USEPA procedures or modifications of these procedures for the analytes of concern. Grab samples were generally collected two times per week during Phase I and Phase III and Phases IV-VI for NDMA (See Table 3). All other water quality analyses were conducted weekly or as the experimental operation of the FBR system required. The sampling and analytical methods performed on the feed and effluent streams included NDMA analysis by USEPA Method 607 (all samples); by HRMS for samples below detection by USEPA Method 607 (10 ng/L practical quantitation limit [PQL]); and by USEPA Method 521 (quality assurance [QA]/quality control [QC] split samples), VOC analysis (USEPA 8260), propane analysis via gas chromatograph (GC) (USEPA 3810), total organic carbon (TOC) (USEPA 415.1), total suspended solids (TSS) (USEPA 160.2), ammonia (USEPA 350.2), and orthophosphate (USEPA 300.0). This sampling plan provided a thorough evaluation of the potential for an FBR to remove NDMA to required regulatory levels.

Analysis of NDMA was conducted using Southwest Research Institute (SRI) using USEPA method 607 and a HRMS method developed for NASA for samples that were below detection by USEPA Method 607 (< 10 ng/L). SRI is a contracted lab with NASA and conducts analysis to meet the discharge permit requirements at WSTF. For some batch samples with high NDMA concentration (e.g., adsorption studies, extractions of GAC and virgin GAC) analysis was conducted at the Shaw Biotechnology Development and Applications Laboratory (Lawrenceville, NJ) by gas chromatography/mass spectroscopy (GC/MS) according to the procedure described previously in Hatzinger et al. (2011). As a means for comparison of low level NDMA data between labs, the outside lab chosen for quality assurance comparison was Weck Laboratories, Inc. located in the City of Industry, CA. These samples were analyzed by USEPA Method 521. Results of the QA/QC sampling are provided in the final report for this project.

Table 6. Monitoring program for the FBR treatment system.

| Parameter | Typical Measurement Location | Method | Frequency (Start-up) | Frequency (At Steady-State) | Sample Location | Reason for Monitoring Parameter |
|---|------------------------------|---|--|--|--------------------------------|---|
| Ammonia | Field | HACH® Test Strip | 3x per week | 3x per week | FBR Effluent | Used to determine if adequate nutrients are available. Measurement greater than 1 part per million (ppm). |
| DO | Field | In-line Sensor Probe | Continuous (checked 5x per week) | 3x per week | FBR Feed FBR Effluent | Used to determine propane dosage. |
| FBR Bed Height | Field | Markland Model 10 Sludge Level Detector | 3x per week | 3x per week | FBR Vessel | Used to determine FBR bed height. |
| Fluidization Flow | Field | Mass Flow Indicator | Continuous (checked 5x per week) | Continuous (checked 3x per week) | FBR Skid | Used to determine bed expansion versus recycle flow. |
| Nutrient Flow | Field | Calibration Columns | 3x per week | 2x per week | FBR Skid | Used to determine amount of inorganic nutrients (P,N) fed to FBR. |
| pH - Fluidization | Field | Hand-held Sensor Probe | 3x per week | 1x per week | FBR Fluidization | Used to confirm in-line pH probe |
| pH - Fluidization | Field | System pH In-line Sensor Probe | Continuous (checked 3x per week) | Continuous (checked 3x per week) | FBR Skid | Used to determine system pH to maintain appropriate biological growth conditions |
| Ortho-phosphate (reactive) | Field | HACH® Test Strip | 3x per week | 3x per week | FBR Effluent | Used to determine if adequate nutrients are available. Measurement greater than 1 ppm. |
| Pressure Gauges | Field | System Pressure Gauges | Daily (5x per week) | 3x per week | FBR System | Used to determine normal operating line pressures. |
| System Feed Flow | Field | System Feed Mass Flow Indicator | Continuous (checked 5x per week) | 3x per week | FBR Skid | Used to determine load on reactor. |
| Temperature | Field | Sensor Probe/Thermometer | Continuous (checked 5x per week) | 3x per week | FBR Feed FBR Effluent | Used to monitor system temperature. |
| Microbial Analysis | Off-site Laboratory | denaturing gradient gel electrophoresis (DGGE) | Beginning, 1x | Middle and End, 1x | Upper Portion of Fluidized Bed | To determine microbial composition in the FBR over time |
| NDMA | Off-site Laboratory | USEPA 521.0 (QA/QC samples) USEPA 607 (Modified) HRMS (SRI) | 2x per week | 2x per week | FBR Feed FBR Effluent | Used to confirm FBR reactor performance. |
| Nitrate-N, Nitrite-N, Sulfate, Phosphate) | Off-site Laboratory | USEPA 300.0 | Weekly | Bi-weekly | FBR Effluent | Used to confirm field testing and nutrient addition rates. |
| Propane | Off-site Laboratory | GC Analysis/Henry's Law Calculation | 1x per week | 2x per week | FBR Effluent | Used to confirm residual propane concentration. |
| TSS | Off-site Laboratory | USEPA 160.2 | 1x per week | Bi-weekly | FBR Effluent | Provides potential loading characteristics on discharge basin and corroborates turbidity measurements. |
| VOCs | Off-site Laboratory | USEPA 8260 | 2x per week to 1x per week One time | 2x per week during bypass of air stripper | FBR Effluent | Provides co-contaminant concentrations |

Table 7. Analytical parameters and methods conducted during the pilot-scale experiment.

| Analytes | Method | Bottle Size | Bottle Type | Preservative ¹ | Field/Off-Site |
|---|---|-------------|----------------------------------|---|---------------------|
| VOCs | 8260 | 40 mL | Amber Glass | Hydrochloric acid (HCL) | off-site lab |
| Propane | 3810 | 40 mL | Amber glass | HCL | off-site lab |
| Ammonia | 350.2 | 500 mL | High density polyethylene (HDPE) | Sulfuric acid (H ₂ SO ₄) | field/ off-site lab |
| Anions (nitrate, nitrite, phosphate, sulfate) | 300 | 500 mL | HDPE | None | off-site lab |
| TSS | 160.2 | | | | off-site lab |
| NDMA | USEPA 607 Modified SRI HRMS USEPA 521 (QA/QC) | 1 L | Amber Glass | Filtration (all) Sodium Thiosulfate (only for method 521) | off-site lab |
| DO | Field Meter | 100 mL | HDPE | None | field |
| pH/Temperature | Field Meter | 100 mL | HDPE | None | field |

¹All samples were stored at 4°C and shipped on ice.

5.6 SAMPLING RESULTS

The sampling results for NDMA and DMN are summarized in the subsequent sections as are the results for oxygen and propane levels in the FBR. Other analyses and the complete dataset for the project are provided in the project final report.

5.6.1 NDMA and DMN

5.6.1.1 Phase I to Phase III

During Phase I (Days 0-83), NDMA-laden water was passed through the FBR to fully load the GAC prior to inoculation with *R. ruber* ENV425 and addition of propane and oxygen. This was conducted so that the biological treatment and adsorption removal mechanisms could be clearly delineated in the ensuing phases of the study. Prior to Day 0, the system had received intermittent flow of groundwater with NDMA but this addition was routinely interrupted. The results of the continuous abiotic loading at a 2.7-3.3 gpm flow rate demonstrated that after approximately 6 days, the influent and effluent NDMA concentrations were comparable (effluent at 0.91 µg/L and influent at 0.92 µg/L; Figure 10). The system was operated under this flow regime while mechanical optimization continued and the inoculum was prepared for the FBR system. Additional NDMA analyses repeatedly demonstrated that complete breakthrough of the contaminant occurred. Results for DMN were similar (Figure 11). Thus, throughout Phase I, influent and effluent concentrations of both NDMA and DMN were the same, suggesting that no abiotic removal of either compound was occurring.

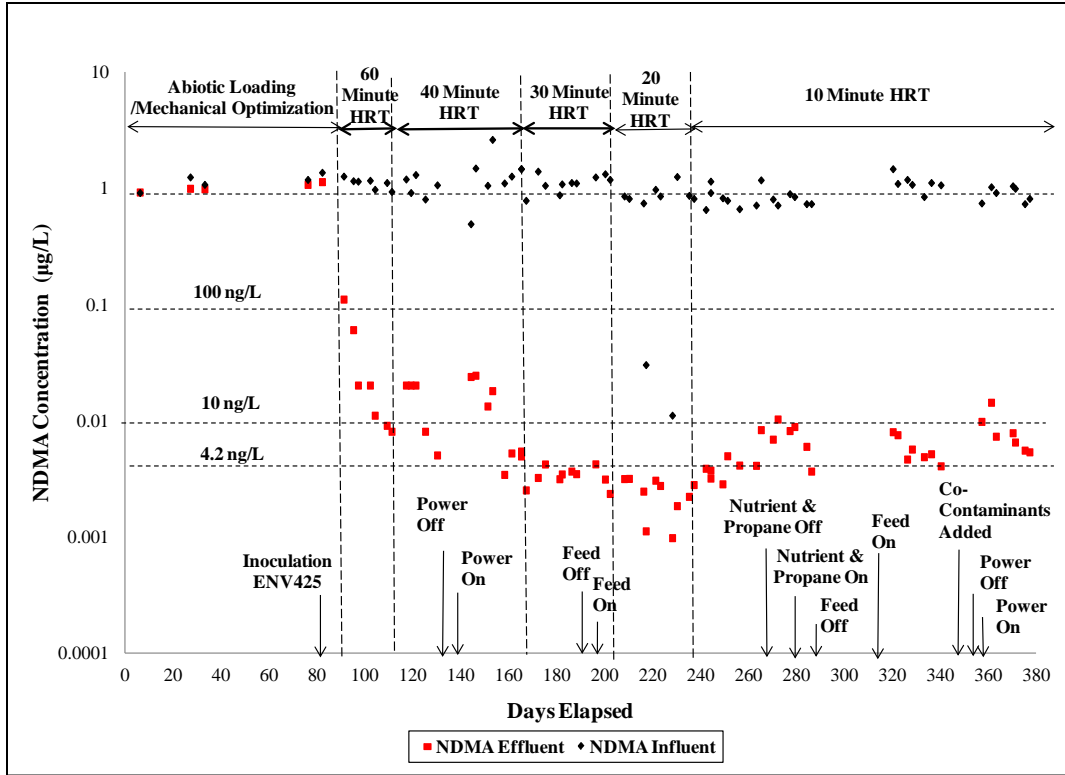


Figure 10. NDMA in the FBR influent and effluent over the duration of the study.

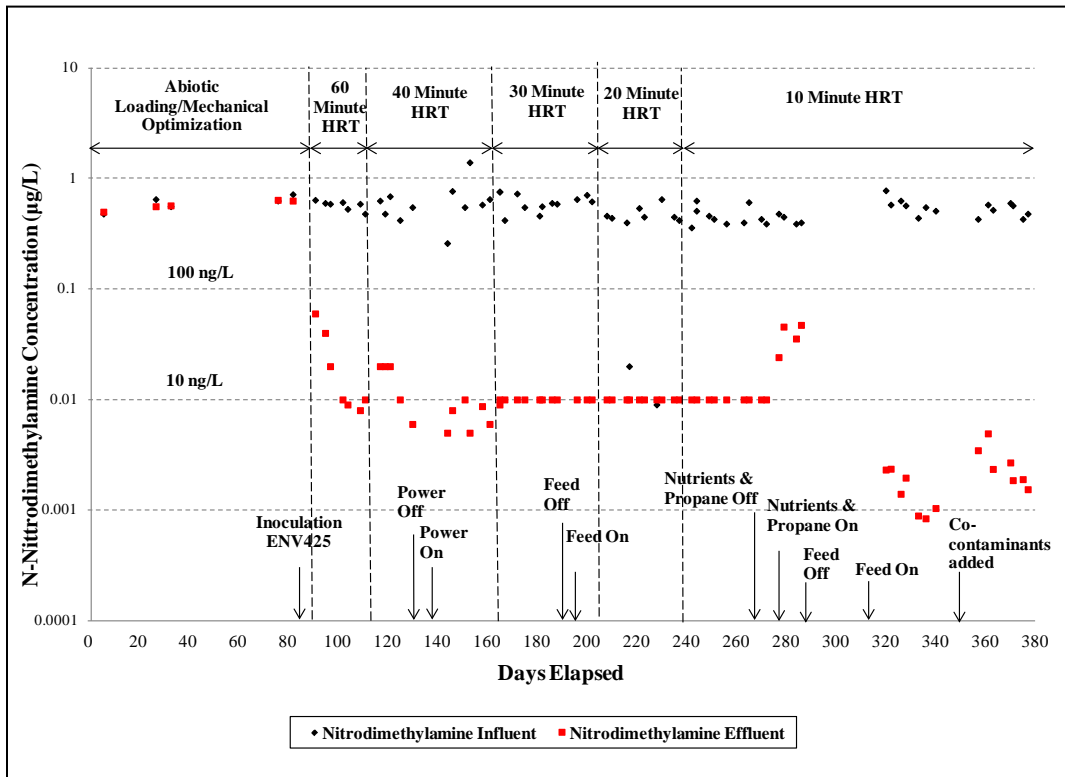


Figure 11. DMN in the FBR influent and effluent over the duration of the study.

Phase II, microbial inoculation and attachment, was conducted from Days 83-90. No NDMA or DMN data were collected during this time period, as the objective was to promote cell adsorption to the GAC media, and the system was placed in total recycle during this period with no groundwater being introduced. During Phase III (Days 90-180), the HRT was gradually decreased from 60 minutes to 30 minutes. The oxygen and propane flow rates were 200-300 mg/min and 40-70 mg/min, respectively. These levels of oxygen and propane were varied as efforts were conducted to optimize NDMA treatment and bed growth. NDMA degradation was apparent shortly after inoculation, with effluent concentrations declining from ~ 1 $\mu\text{g/L}$ to < 10 ng/L within 25 days after *R. ruber* ENV425 was introduced (Figure 10). When the HRT was decreased from 60 minutes to 40 minutes, the effluent NDMA concentrations increased to above 20 ng/L, but then declined again to < 10 ng/L by Day 165, when the HRT was reduced further to 30 minutes, where they remained for the duration of Phase III. Much like NDMA, DMN concentrations declined to < 10 ng/L during the first 25 days after inoculation with *R. ruber* ENV425, and then they increased marginally when the HRT was reduced from 60 minutes to 40 minutes (Figure 11). By the end of Phase III, DMN was consistently < 10 ng/L.

5.6.1.2 Phase IV Steady State Operation

Phase IV was conducted from days 180-270. At an HRT of 30 minutes during this period of steady-state operation (Days 180-204), the average influent NDMA was 1.13 ± 0.003 $\mu\text{g/L}$ and the effluent NDMA was 3.3 ± 0.6 ng/L utilizing an oxygen and propane addition rate of 200-260 mg/min and 40-50 mg/min, respectively. DMN averaged 0.58 ± 0.09 $\mu\text{g/L}$ in the influent, and the effluent was consistently < 10 ng/L (method detection limit [MDL]). With continually effective treatment at the 30 minute HRT from days 204-239, the feed flow was increased such that a 20 minute HRT was achieved. During this phase of the study, oxygen and propane feed rates were 175 mg/min and 35 mg/min, respectively. NDMA concentrations in the influent and effluent averaged 0.72 ± 0.39 $\mu\text{g/L}$ and 2.3 ± 0.8 ng/L, respectively. DMN averaged 0.38 ± 0.21 $\mu\text{g/L}$ in the influent, and the effluent was consistently < 10 ng/L (MDL). On Day 239 through Day 270, the system HRT was reduced further to 10 minutes. At this HRT, NDMA effluent values began to increase somewhat. NDMA concentrations in the influent and effluent averaged 0.85 ± 0.19 $\mu\text{g/L}$ and 4.6 ± 1.8 ng/L, respectively. DMN averaged 0.47 ± 0.10 $\mu\text{g/L}$ in the influent, and the effluent remained < 10 ng/L (MDL). The oxygen and propane feed rates were 130 mg/min and 40-50 mg/min, respectively.

The data during Phase IV clearly showed that the FBR was capable of reducing NDMA to below the WSTF regulatory limit of 4.2 ng/L at a 20 minute HRT. An effluent concentration < 10 ng/L was consistently met at the 10 minute HRT, but effluent concentrations exceeded the revised WSTF discharge limit of 4.2 ng/L after a few weeks of operation. The study also showed that concurrent NDMA and DMN removal by *R. ruber* ENV425 is possible within the same FBR system. Degradation of DMN as well as NDMA was previously observed in our laboratory for *R. ruber* ENV425 (Fournier et al., 2009).

5.6.1.3 Phase V Challenge Experiments

Propane and inorganic nutrients were shut off from Days 270-279 (10 minute HRT) to simulate the effects of a failure in these systems. NDMA concentrations in the effluent slightly exceeded 10 ng/L on Day 272, but values did not increase further toward the 1 $\mu\text{g/L}$ influent value. The

data suggest that the FBR is resilient to a shutdown of propane and/or nutrients over the short term. It is possible that the bacteria utilized dead cell mass for growth and to support NDMA degradation during this time. We previously observed significant NDMA mineralization in some environmental samples that were amended with yeast extract or lactate (Hatzinger et al., 2008). After the propane and nutrient feeds were reestablished, NDMA effluent concentrations below 10 ng/L were observed within 8 hours. After 7 days, the effluent NDMA concentrations were below 4.2 ng/L. The concentration of DMN increased to > 45 ng/L during the 9 day period when the propane and nutrient feed was off and remained in this vicinity through Day 287, when the system shutdown experiment was conducted.

During an unscheduled groundwater feed shutdown (Days 190-195), NDMA did not exceed 4.2 ng/L upon restart at a 30 minute HRT. Similarly, DMN remained < 10 ng/L. For a scheduled feed shutdown experiment on Days 287-315 (system was placed in total recycle with continuous feed of oxygen and propane, and batch nutrient addition), the feed was restarted after 28 days and NDMA samples were collected 5 days after restart. NDMA in the effluent was < 10 ng/L (influent concentration 1.46 µg/L) at the first collection point after restarting groundwater flow, with subsequent samples over the next 25 days slowly declining to below 4.2 ng/L even at the 10 minute HRT. It is anticipated that recovery would have been much more rapid at the 20 minute HRT for which effluent values < 4.2 ng/L were consistently achieved. DMN was < 10 ng/L upon restart of the system. Results from the nutrient and feed shutdown experiments indicated that the FBR could recover to treatment levels below 10 ng/L within hours to a few days after restart.

Other unplanned shutdowns occurred in addition to the planned studies, and the system generally recovered quickly. On Day 186, after the system was shut down for a day due to power outage caused by lightning, the effluent NDMA and DMN were both < 10 ng/L one day after restart. Similarly, on Day 354, after the system was shut off for about 3 days due to the air compressor and breaker failure, sampling occurred 3 days after system restart and the NDMA in the effluent was observed to be 9.7 ng/L and DMN was 5.9 ng/L. Hence, the short-term unplanned shutdowns did not hinder the reactor performance significantly.

5.6.1.4 Phase VI Co-contaminant Treatment

On Days 350-377, a limited study was conducted in which the air stripper was bypassed and water contaminated with TCE and Freon 11, in addition to NDMA, was allowed to enter the FBR. Treatment of NDMA to less than 100 ng/L in the presence of site co-contaminants was the objective. During the testing at an HRT of 10 minutes, influent Freon 11 and TCE concentrations averaged 28 ± 3 and 16 ± 1 µg/L, respectively. Effluent Freon 11 averaged 18 ± 2 µg/L and effluent TCE averaged 0.7 ± 0.2 µg/L. The observed decline in TCE may have been due to adsorption or biodegradation, or a combination of these processes. For Freon 11, adsorption is the most likely loss mechanism, as *R. ruber* ENV425 was observed to not biodegrade this compound in batch studies. The NDMA in the effluent increased slightly from 4 ng/L to 14 ng/L after the water with VOCs passed through the FBR (Figure 10). DMN remained < 5 ng/L during and after the addition of the VOCs (Figure 11). By Day 363, effluent NDMA concentrations were < 8 ng/L, declining to < 6 ng/L by Day 375. The data suggest that short-term contact with low concentrations of TCE and Freon 11 had no significant impact on NDMA treatment. Low TCE concentrations also were observed not to affect treatment of NDMA in the pilot FBR system (Freon 11 was not added) (Webster et al., 2013), although TCE at ~ 200 µg/L was

observed to affect NDMA degradation in a laboratory MBR system seeded with *R. ruber* ENV425 (Hatzinger et al., 2011). Thus, influent concentration and reactor configuration may determine the overall effect of TCE and other VOCs on NDMA degradation.

5.6.2 Oxygen and Propane

DO was measured using both an inline sensor and with a DO probe on grab samples throughout the several phases of operation. The inline sensor recorded concentrations of 4.2 ± 1.3 mg/L in the FBR during Phase I before DO, propane, and nutrient feed was initiated (Figure 12). The concentration thereafter averaged 6.4 ± 1.5 mg/L, with slight declines occurring as the HRT was intentionally decreased through the course of the study. The mass of DO added to the FBR per minute (oxygen load) was reduced over the course of the study to minimize total gas addition. Based on the external probe, the concentration of DO present in the influent water to the FBR was 4.2 ± 0.4 mg/L, throughout the duration of the FBR study (Day 100 to Day 377) (Figure 12). These results agree with the inline probe readings prior to adding additional oxygen gas. The effluent DO concentrations were generally higher than the influent (which was expected because DO was added to the recycle line of the FBR) throughout Phase II to Phase IV until ~ Day 239, when the influent HRT was reduced from 30 minutes to 20 minutes. The influent and effluent DO were generally similar during operation at the 10 minute HRT based on the DO probe measurements. When oxygen was added to the system, the inline probe measurements were generally higher than DO measurements taken on grab samples. This reflects differences in the sampling location, as the inline probe measured the DO at the top of the FBR after gas addition; whereas the effluent probe samples were collected downstream of the solids recovery tank but before additional DO was added. Most critically, it is clear that DO was not limiting microbial growth or NDMA degradation in the FBR through the course of the study.

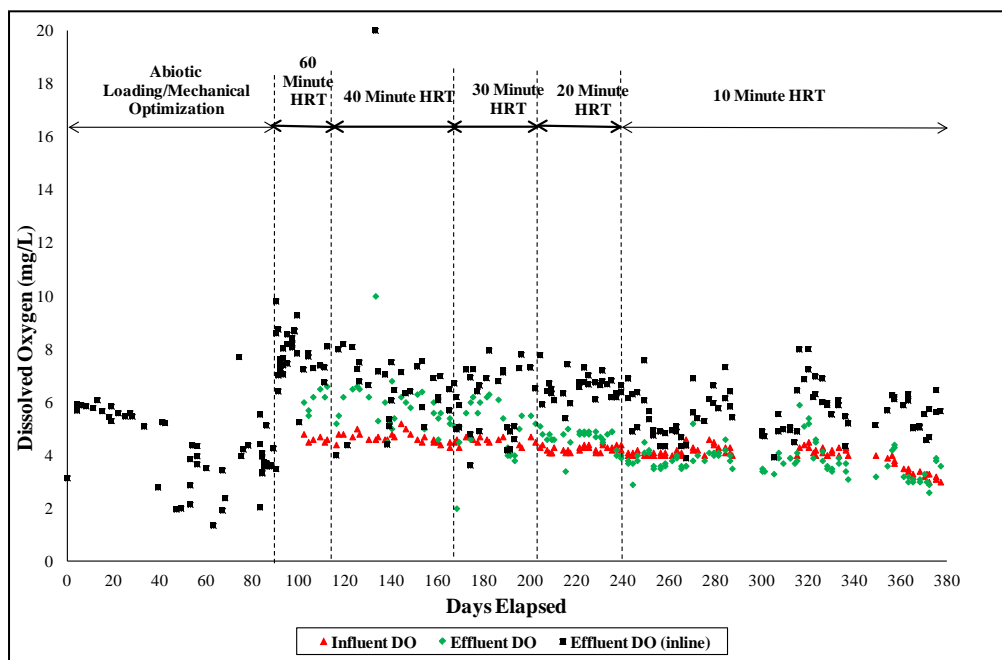


Figure 12. DO in the influent and effluent of the FBR system over the duration of the study.

The propane feed to the system was initiated on Day 83 at the beginning of Phase II, when the *R. ruber* ENV425 culture was inoculated. Influent propane measurements were not collected during the first few weeks of operation at the 60 minute HRT, although the propane system feed was on. From the beginning of the 40 minute HRT in Phase III until the propane was shut down on Day 287 for system challenge testing in Phase V, the propane concentration in the FBR averaged $634 \pm 384 \mu\text{g/L}$ (Figure 13). From Day 216-Day 230, no propane was detected in the FBR influent despite the flow controllers showing that it was being added to the system. The reason for this anomaly is unclear, particularly since residual propane was detected in the FBR effluent. The effluent propane concentrations from the FBR averaged $27 \pm 9 \mu\text{g/L}$ from the beginning of the 40 minute HRT in Phase III until the propane was shut down on Day 287. From the shutdown period in Phase V until the end of the study, the propane was reduced, such that the influent averaged $175 \pm 90 \mu\text{g/L}$. The effluent propane during this time averaged $5 \pm 3 \mu\text{g/L}$. The data show that the FBR system generally operated with a slight excess of propane, and that propane concentrations well below 1 mg/L were effective for treating NDMA to $< 4.2 \text{ ng/L}$ at the 20 minute HRT.

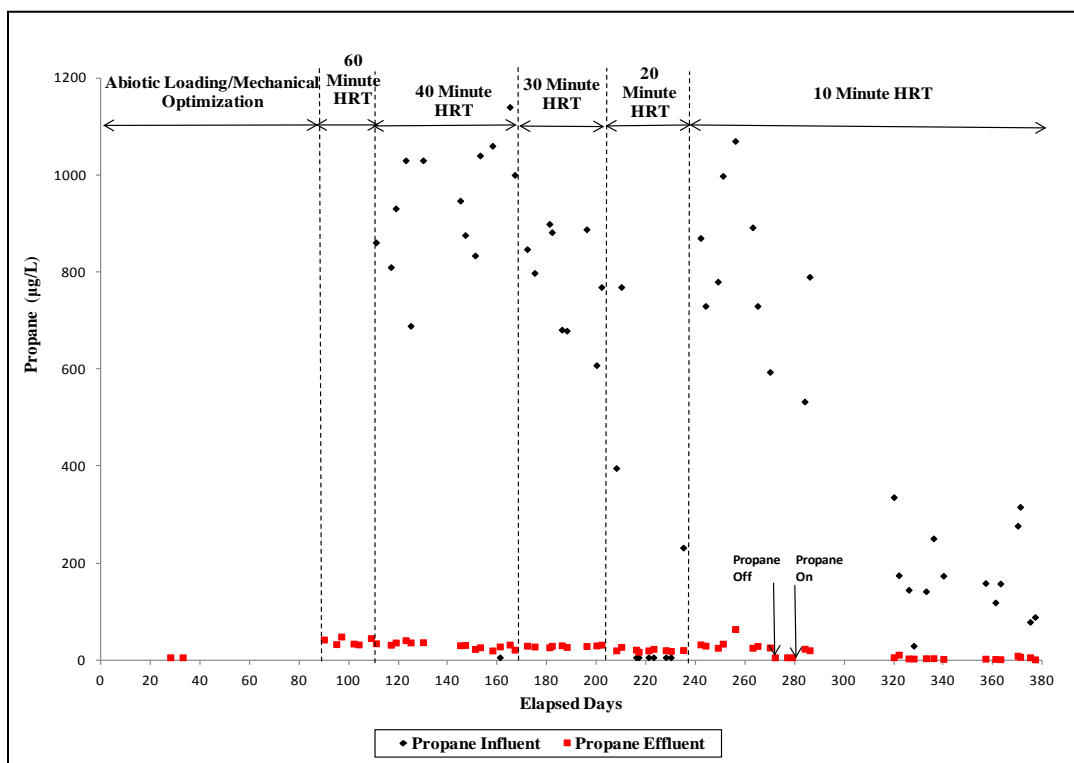


Figure 13. Dissolved propane in the influent and effluent of the FBR system over the duration of the study.

6.0 PERFORMANCE ASSESSMENT

The performance of the system during the demonstration included both qualitative and quantitative objectives as described in Section 3.0 and Table 1. Each of these objectives is assessed in this section and supported by the sample results provided in Section 5.6 and in the project final report.

The general objectives of this FBR treatment system study were to evaluate:

- The ability of *R. ruber* ENV425 to effectively colonize the fluidized bed media and achieve an initial NDMA reduction from $\mu\text{g/L}$ to low ng/L ($<10 \text{ ng/L}$) concentrations.
- The ability of the FBR under steady-state conditions to reduce the NDMA concentrations to less than 10 ng/L , and optimally less than 4.2 ng/L , at a HRT less than 30 minutes.
- The ability of the FBR to maintain performance after various system interruptions (feed flow, propane and nutrient flow, power, etc).
- The response to co-contaminant addition.

6.1 QUANTITATIVE PERFORMANCE OBJECTIVES

6.1.1 *R. ruber* ENV425 Adaptation

Over the initial 5 days of operation at a 60 minute HRT, the microbial community established within the FBR system was able to achieve treatment of NDMA to less than 100 ng/L in the system effluent (Figure 10). Within three weeks of start-up, NDMA was degraded from $\sim 1 \mu\text{g/L}$ down to $\sim 10 \text{ ng/L}$ in the FBR system. The FBR consistently treated NDMA to $< 10 \text{ ng/L}$ thereafter, with only minor exceedences during initial reduction in HRT and at the final HRT of 10 minutes during system challenge studies. Based on the results, a microbial community had adapted adequately to the conditions in the FBR during start-up. However, the data suggest that the microbial community in the FBR became increasingly diversified with time, and that several different *Mycobacterium* spp. became the dominant propanotrophs within the FBR, displacing *R. ruber* ENV425 (data not shown; see project final report).

6.1.2 Treat NDMA to Below Regulatory Limits/Produce Quality Data

Once steady-state operation of the pilot-scale FBR was achieved, NDMA was consistently treated to below 10 ng/L (Figure 10). Reductions in HRT occurred while optimizing the oxygen and propane addition rates. The reduction of NDMA concentrations from $1 \mu\text{g/L}$ to less than 10 ng/L was indicative of successful treatment. At the 20 and 30 minute HRTs, the FBR system was capable of treating to less than 4.2 ng/L (the current regulatory limit at the WSTF site), while at a 10 minute HRT the FBR could consistently achieve NDMA concentrations below 10 ng/L . Hence, the FBR treatment system was demonstrated to be an effective means to treat $1 \mu\text{g/L}$ concentrations of NDMA consistently to less than 10 ng/L and, when further optimized, concentrations below 4.2 ng/L were achieved.

During steady-state operation, the oxygen and propane residuals in the FBR effluent averaged greater than 4 mg/L and $\sim 30 \mu\text{g/L}$, respectively. The settings for oxygen and propane were

modified to ensure that an explosive environment was not produced in the headspace of the FBR, while still allowing for full treatment to occur. The levels of propane in the effluent were approximately an order of magnitude lower than those observed during bench scale FBR testing (Webster et al., 2013). Hence, lower residual propane addition rates were achievable. Details concerning the levels of oxygen and propane in the FBR over the duration of the study are provided in Section 5.6.2 and in the project final report.

To ensure that all the data collected and reported was valid in demonstrating that the plant met the NDMA regulatory standards, extensive quality QA/QC measures were undertaken. Per the QA project plan (QAPP) for this project, the completeness objective for all validated data was 95%. For the off-site laboratories, a total of 226 samples were submitted for analysis of NDMA. Of these 226 samples, two points on Day 27 were flagged (one influent and one effluent sample) because the sample hold time was exceeded by one day. The percentage completeness for the NDMA analysis was 98%. For all other chemical parameters measured, the completeness objective of 95% was met.

6.1.3 Effects of Interruptions on FBR Operation

Challenge experiments were conducted to determine the ability of the FBR technology to rebound from propane and nutrient feed interruptions, feed flow interruption, and system shutdowns. For all of the interruptions, re-establishment of FBR performance to less than 10 ng/L of NDMA at the plant effluent within 24 hours of system restart was targeted. When the plant reached steady-state, the interruption of electron donor and nutrients did not have any negative impact when the system was restarted 9 days later. NDMA effluent concentrations were below 4.2 ng/L at the first sample collection point. Presumably, the biomass was able to survive/thrive the shorter interruption by utilizing the supply of residual TOC, dead cells, and/or other nutrients available (nothing was added). If the experiment was conducted longer (i.e., 30 days), the same results may not have been observed. For the groundwater feed and system shutdowns during steady-state operation, results generally indicated that the FBR could recover to treatment levels below 10 ng/L in 24 hours to 4 days. During the 20-30 minute HRT, effluent concentrations < 4.2 ng/L of NDMA were observed consistently upon system restart. Again, this may be a function of the length of the interruption. However, even after 28 days of feed interruption, the system was capable of treatment to less than 10 ng/L within 5 days (when samples were first collected). The target objective of 24 hours was realized depending on the length of the shutdown and subsequent restart.

6.1.4 Effects of Co-Contaminants on NDMA Treatment

Treatment of NDMA to less than 100 ng/L in the presence of site co-contaminants was the objective. Before removing the air stripper bypass, NDMA effluent concentrations were approaching 4.2 ng/L at the 10 minute HRT (Figure 10). After removing the bypass, initial data demonstrated NDMA effluent concentrations increasing above 10 ng/L (to 14 ng/L at one point), but the effluent NDMA concentrations continued to decline over the course of the challenge experiment to approximately 5 ng/L. Some reduction in Freon 11 was observed during this experiment, but that likely reflects adsorption to the GAC matrix. TCE was reduced to < 1 µg/L, which may have been the result of a combination of adsorption and biodegradation. Treatment of TCE in aerobic environments has been previously observed via cometabolic pathways by other

researchers (Malachowsky et al., 1994; Alvarez-Cohen and McCarty, 1991; Wackett et al., 1989). However, during this experiment, the co-contaminants were added over a fairly short duration and at such low concentrations that adsorption to the carbon media bed may have been a contributing removal mechanism. These experiments provided data corroborating the treatability study results and demonstrating minimal effect from the presence of co-contaminants in the FBR feed water on NDMA treatment.

6.1.5 Treatment of DMN

Treatment of DMN to < 10 ng/L in the FBR at an HRT value of 20 to 30 minutes was the objective. The treatment objective was met. DMN was treated to < 10 ng/L from Day 97 to Day 270, when the propane and nutrient feed was shut off. DMN increased to 46 ng/L by Day 279, when the gas and nutrient addition was reinitiated. The concentration remained at 47 ng/L on Day 286, but declined thereafter, falling to < 10 ng/L from Day 320 to the end of the study on Day 377.

6.2 QUALITATIVE PERFORMANCE OBJECTIVES

6.2.1 Ease of Use

Operator attention of less than or equal to 10 hours per week was considered ideal for such a system. This included collecting operational data, filling chemical drums, and checking on basic water chemistry. Efforts (i.e., time required) of sample acquisition for this pilot-study beyond what would be required for a full-scale system were accounted for when determining if the success criteria were met. The minimal operator attention of about 10 hours a week (2-4 hours per day, 3 times a week) was maintained overall during the demonstration.

During the treatability study, one area of labor-sink in terms of the operator attention was manually limiting bed expansion, but this was not an issue in the pilot-study. A second labor-sink was the continual manual adjustment of the oxygen and propane addition rates to the system. This second action was minimized at the pilot-scale by the use of a flow controller that was temperature sensitive. Since more accurate, lower levels of oxygen and propane were added to the system, less biomass formed, which allowed for improved bed control. Thus, a key finding from this study is that the lower gas addition rates ultimately lead to less operator attention necessary for the system.

6.2.2 Reliability

The ability for the system to continuously operate is critical. Hence, greater than 90% uptime reliability was the target goal. In those circumstances when intentional interruptions or manual changes in system operation were encountered, such breeches in reliability were not incorporated into the system uptime calculation. The largest upsets to the system that occurred were caused by equipment failure from the fluidization pump and air compressor on Days 130 and 354, respectively. A secondary upset was when power outages were caused by lightning storms in the area (Day 186). A third upset was caused by UV shut down for maintenance causing system feed to be off (Day 195). Even with these system interruptions, quick resolutions to the problems were generally enacted and the system brought back on line. This resulted in 94% uptime being

achieved, demonstrating that the system was reliable. In terms of the full-scale, as a precaution, it is advisable to include a spare fluidization pump as a requirement since this item can have a long lead time to replace.

6.2.3 Reduction of Treatment Costs

As part of the demonstration, multiple FBR HRTs were evaluated to determine the limits of the system to achieve regulatory NDMA requirements. During this testing, nutrient/propane/oxygen addition rates were adjusted while still maintaining effluent NDMA concentrations of less than 10 ng/L at the effluent of the FBR. Every attempt was made to minimize these chemical addition rates, the system electricity requirements, and operator attention/maintenance. Based on the findings, a 20 minute HRT produced optimal conditions for the FBR system to meet regulations for NDMA treatment to below 10 ng/L, and even the more stringent 4.2 ng/L requirement that was instituted for WSTF after the initiation of this project. So, the optimal operating parameters were determined to be:

- 20 minute hydraulic retention time,
- An oxygen addition rate of 176 mg/min,
- A propane addition rate of 35 mg/min (28.6 mg C/min),
- A diammonium phosphate addition rate of 35 mL/min at 110 mg/L,
- A urea addition rate of 36 mL/min at 352 mg/L.

Using these optimal operating parameters, the FBR treatment costs have been developed and are provided in comparison with a competing technology in Section 7.0.

7.0 COST ASSESSMENT

The pilot-scale FBR treatment system operation was demonstrated for approximately a 1 year period (March 8, 2012 through March 20, 2013). The current technology of choice for NDMA treatment is UV irradiation. NASA WSTF has installed a 125 gpm MPITS with UV being the primary treatment mechanism. For the FBR technology, its cost-effectiveness is directly correlated to the system HRT. At the HRT of 20 minutes, the NDMA feed was treated effectively from feed concentration of ~ 1 $\mu\text{g/L}$ to an effluent concentration of < 4.2 ng/L . Hence, during the course of the demonstration, a number of variables were tracked to further understand their cost implication as the FBR technology would be scaled from 2.2 gpm (20 minute HRT) to 125 gpm.

7.1 COST MODEL

A cost model has been developed and is provided with the necessary cost elements of the FBR treatment system that are required for implementing the technology at full scale at < 5 gpm (Table 8). A number of assumptions and caveats are required. The installation costs provided are only applicable for systems in this size range (< 5 gpm) being implemented as a pilot-scale demonstration. For larger systems, though scaling of the costs may be directly proportional in some cases (i.e., electrical design), costing is not always directly scaled. For instance, for this demonstration, the concrete pad and building already existed as they formed the basis of the infrastructure for the MPITS. Hence, the costs for these items are not applicable in this specific case. The concrete pad and building requirements for a scaled-up FBR may be different than the existing UV system. For much larger installations, significantly more design, labor, and materials would be required. Although a cost reduction might be observed based on an economy of scale, this reduction may be offset by the need for larger delivery trucks, fuel fees, additional labor, etc. These differences are not accounted for in the cost model and are typically calculated on a case-by-case basis. A detailed cost comparison between a UV system and an FBR operated at 125 gpm over a 30 year life cycle is also presented (Section 7.3 and Table 9).

Additional caveats must be realized with the costs presented because the associated labor and monitoring costs were a direct result of the number of scientific experiments that were conducted specifically for the ESTCP evaluation. This level of labor and monitoring effort would not be required for a typical operating system of any scale. Finally, like all system plant start-ups, typically the initial 2 to 3 months of operation require more troubleshooting and are more labor intensive. Hence, the first year of labor required is greater than subsequent years of operation. For the cost model presented in Table 8, estimated costs for designing and operating an FBR at the scale of this demonstration (< 5 gpm) are presented. In several instances, the costs presented differ from those actually incurred during this project for a variety of reasons, including significant delays after system installation due to issues with the MPITS facility; the fact that the FBR pilot-unit used for the demonstration had been previously constructed, and was modified for this effort rather than built from scratch; and that a long-term study was performed with a laboratory-scale FBR before the field demonstration to establish operating conditions. Table 8 estimates the cost of designing and operating a new FBR at the scale provided, and relevant subsections discuss some of the differences between the costs in the ESTCP research project and those expected for a typical commercial application.

Table 8. Cost model for small-scale FBR implementation (<5 gpm).

| Element | Data Tracked During the Demonstration | Description | Cost |
|---|---|--|-------------|
| Treatability Study/Baseline Characterization | NDMA Treatment in WSTF water and in a bench-scale system | Year 1 of study | \$231,000 |
| Project Management | Coordination of system design, procurement, reporting, administrative | Inclusive for only the pilot-scale study | \$63,000 |
| Design Fabrication & Equipment | FBR system | Equipment cost-new unit | \$235,000 |
| Installation | Shipping cost, rigging, unloading (roundtrip) | Memphis, TN to Las Cruces, NM | \$6400 |
| | Travel and incidentals required to work on site | Hotels, per diem, mileage, rental vehicles | \$10,600 |
| | Labor and materials required for installation of reactor, piping and electrical | Multiple projects served at the site, two man crew | \$20,000 |
| Operation and Maintenance (O&M) | Chemicals and consumables required (propane, oxygen, nutrients) for plant operation | Chemicals, consumables | \$15,000 |
| | Laboratory supplies, analytical instrument supplies for monitoring | Test kits, glassware | \$5000 |
| | Labor required | Field Engineer, 10 hours/wk | \$31,000 |
| | | Project Manager, 4 hours/wk | \$19,000 |
| Electricity required | Not able to measure | \$1000 | |
| Monitoring | Laboratory analytical services | Analytical | \$107,000 |
| Waste Disposal | Trash service | Rental/haul away on monthly basis | \$1000 |

7.1.1 Treatability Study

Significant bench-scale treatability testing as conducted in support of this ESTCP demonstration, including various microcosm tests to evaluate NDMA degradation in batch and a long-term laboratory FBR study; the results of which were published separately in Webster et al., (2013). The estimated cost of this scale of laboratory study is \$231,000. For this ESTCP application, the laboratory FBR study was conducted to evaluate whether it would be possible to treat NDMA to < 10 ng/L in an FBR, and to assess optimal FBR operation, including gas addition rates, bed height growth and control, pH adjustment, nutrient requirements, etc. For future applications, it would likely not be necessary to conduct a similar study (although cost is included in Table 8), which would significantly reduce this cost element. Small-scale microcosm testing is always recommended, primarily to ensure that the geochemical conditions and/or co-contaminants are not toxic to propanotrophic bacteria. However, this testing would be anticipated not to exceed \$15,000.

7.1.2 Project Management & Design

This ESTCP demonstration involved designing, engineering, and fabricating a “first-of-its kind” complete biological NDMA treatment system using propane as a cometabolic substrate. Hence, project management and design costs are significantly influenced by the labor required to implement this initial system. In addition, a number of management tasks were associated with this project that were the result of delays in the start-up of the system. The equipment arrived in

August, 2010 but was not permitted to be operated until March 2012. Such delays required the retraining of personnel and additional oversight of activities at the site that were not planned. Thus, these costs were higher than would be expected for a typical application of this technology at a new site. The estimated \$63,000 for system design, procurement, reporting and administration presented in Table 8 represents estimated costs for design of a small-scale FBR, assuming knowledge of the results of this demonstration and none of the project delays that occurred during this effort.

7.1.3 Fabrication & Equipment

The associated costs for the fabrication of the FBR treatment system included both the use of in-house labor for the FBR and associated controls, as well as subcontracted vendors for programming and electrical. The pilot-test equipment already existed prior to this study, but significant overhaul of the unit was necessary to make it operable for this specific application. This overhaul included upgrading the programmable logic controller (PLC) computer, modifying the gas delivery systems, implementing gas monitoring safety considerations, and retrofitting many of the feed, fluidization, and metering pumps. Because this pilot-scale system already existed, the cost for fabrication is not directly scalable to larger systems. However, the estimated cost for a 1 foot diameter FBR system designed for < 5 gpm that is fabricated as a new unit, including all necessary controls, is \$235,000 (Table 8). In addition, the estimated cost for the fabrication of a full-scale system operating at 125 gpm is provided in Table 9 (Section 7.3).

7.1.4 Installation

The majority of the installation was conducted by the personnel at WSTF with supervision by ETI and Shaw personnel. Because a concrete pad, electrical, piping, and a building already existed at the MPITS, the costs to install the actual pilot-scale equipment were minimal in comparison. An estimate for installation of a newly fabricated system at the site is \$6400 for shipping, \$10,600 for travel and incidentals, and \$20,000 for all labor and installation materials. Estimates of similar costs for a full-scale FBR system designed to operate at 125 gpm are provided in Section 7.3, based on a number of prior installations.

7.1.5 Operation and Maintenance

7.1.5.1 Materials Required

During the course of the demonstration, the FBR treatment system was operated in continuous forward feed mode. Chemicals were continually added to the treatment process to ensure that the NDMA was treated to low levels. These chemicals included propane grade 2.0, 99% purity and zero-grade oxygen 2.8 in separate pressure vessels. In addition, diammonium phosphate (110 mg/L) and urea (352 mg/L) were added as inorganic nutrients. Usage was tracked on a monthly basis and the costs for the 1 year demonstration were reported. Chemical costs and consumables were approximately \$15,000, and field laboratory supplies for on-site monitoring were approximately \$5000. Presumably, significant cost reductions would be observed for larger quantity purchases. Volumes of chemicals can be considered linearly scaled with feed flow being treated, but the associated costs actually are reduced per kilogram of NDMA treated because of the reduction in bulk chemical costs.

7.1.5.2 Labor

A portion of the costs associated with the O&M of the 5 gpm plant are applicable to a plant of a much larger size (i.e., 125 gpm). The issues encountered at the demonstration plant during start-up and operation would likely be observed and resolved in a similar manner at a much larger scale plant. Hence, the manpower and time required during start-up can be considered conveyable at either scale of plant. The manpower utilized during this demonstration after start-up issues were resolved was primarily utilized for performing a variety of experiments that would not necessarily be required on a day-to-day operation of a much larger full-scale plant. For more routine operation of a 5 gpm plant, it is anticipated that the labor costs for system O&M would include 10 hours per week for a field technician (estimated at \$31,000 per year of operation) and 4 hours per week for a project manager (estimated at \$19,000 per year). For a scaled-up plant, O&M costs must be carefully evaluated on a case-by-case basis.

A few caveats must be noted regarding the O&M cost values presented:

- The start-up process of any water treatment plant will typically require significantly more labor until the mechanical, electrical, and process issues are addressed and remedied. From experience, this process can take from 2 to 4 months depending on the complexity of the process.
- The labor costs associated with the plant operation in the field are derived based on industry standards for a service contractor to conduct the operation. A licensed water treatment plant operator did not service this plant during the study. Rates for another facility will differ based on location, operator experience and requirements, and the level of system complexity.

7.1.6 Monitoring

The monitoring/analytical costs for the implementation of the technology, which were tracked during the demonstration, amounted to \$107,000. These costs are anticipated to be significantly higher than would be required for a typical similarly sized plant or as the plant is scaled-up for a number of reasons:

- The demonstration study that was conducted involved a number of scientific experiments to test the robustness of the technology. Hence, there was additional monitoring in frequency and the variety of analytes that would not be required under normal operation of any size FBR treatment system.
- In terms of monitoring, every National Pollutant Discharge Elimination System (NPDES) permit is unique with respect to the analytical requirements. Although an NPDES requirement is developed for the UV system at the MPITS, unique monitoring analysis may be required based the technology choice and on the location of the plant.

7.2 COST DRIVERS

The major anticipated cost drivers of the technology are the concentration of NDMA in the feed stream and the anticipated feed flow requiring treatment. Ultimately, this loading rate of NDMA

dictates the HRT required by the FBR to maintain effective treatment to a low level effluent requirement. As the load increases, the required bed volume to treat the NDMA increases based on the maximum NDMA elimination capacity. The larger the HRT requirement, the greater the capital investment in the equipment is necessary. This requirement results in greater tank/vessel size, larger pumps, and more filter bed media. Typically, the full-scale FBR reactors are provided at a minimum of 3-foot diameter up to a maximum of a 14-foot diameter bed. If more bed volume is required, multiple 14-foot diameter beds are provided. The major limitation for the 14-foot diameter bed size is based on a transportation permit limitation. As the reactors increase in diameter, an economy-of-scale factor is observed in the design and fabrication requirements. However, this economy-of-scale savings can be offset by the increase of material costs. In addition to the capital investment required for the larger equipment, installation costs will increase as more manpower, larger installation equipment (cranes, rigs, etc.), larger diameter pipe and run lengths, and greater electrical equipment complexities are necessary.

7.3 COST ANALYSIS

One of the reasons for selecting WSTF as the demonstration site was the existence of the MPITS with a UV treatment system for NDMA and a pre-treatment air stripper for VOCs. The technology cost analysis for this project compares the costs for the 125 gpm UV system at WSTF with an FBR system scaled to treat the same groundwater flow rate and load. The project assumptions are:

- 30 year remediation water project,
- 125 gpm design treatment,
- Existing extraction wells available
- NDMA feed concentration of 1 µg/L
- Temperature = 20EC,
- pH = 7.0-8.0 SU,
- Oxidation reduction potential > 100 mV, and
- Pre-treatment air stripper provided for both technologies

The life-cycle costs are estimated for the FBR water treatment production plant utilizing both the capital/investment and operating costs. The life-cycle costs are developed for the UV water treatment plant based on actual data provided by the operating facility (Zigmond, 2013). The assumptions are:

- Investment and operating costs based on 2013 dollars
- Well operation not included in costs
- Electrical energy costs at \$0.062 per kilowatt hour (kW/hr) (averaged for peaking and non-peaking use) and \$15.47/kW demand charge
- Amortized costs based on 30 years, 1.1 % real discount rate (Office of Management and Budget [OMB], 2012)
- FBR and UV Installation costs are comprised of the construction and engineering costs estimated based on USEPA Technology Design Panel Cost Model (USEPA, 2000) as 1.5X the capital cost;

- Oxygen generated on site using atmospheric air as source;
- Propane at \$2.32/gallon (U. S. Energy Information Administration, 2013);
- Nutrients of urea and DAP at \$0.11/lb and \$0.50/lb, respectively;
- UV polyphosphate addition, \$10.91/gallon; and
- Labor technician at \$100/hour (Routine labor assumed the same between FBR and UV).

The FBR treatment system (with oxygen generator) and the UV design, fabrication, installation, and operation costs are provided in Table 9.

Table 9. FBR and UV full-scale treatment system cost at 125 gpm and NDMA at 1 µg/L.

| Parameter | UV | FBR | Notes |
|--|--------------------|--------------------|--|
| Capital and Installation | | | |
| <i>Capital Costs</i> | \$317,000 | \$373,000 | |
| <i>Installation Costs (Engineering and Construction)</i> | \$475,500 | \$559,500 | |
| Total Capital and Installation Costs | \$792,000 | \$932,000 | |
| Capital/Install Cost Amortization (\$/yr) | \$31,139 | \$36,643 | 30 yrs, 1.1% real discount rate |
| Total for 30 year Remediation | \$934,170 | \$1,099,300 | 30 yrs, 1.1% real discount rate |
| Operating Costs | | | |
| <i>Annual Chemical Addition</i> | | | |
| Propane | NA | \$1263 | 6.31 lbs/day |
| Nutrient | NA | \$300 | DAP: (Diammonium Phosphate) 0.7 lbs/day, Urea: 2.3 lbs/day |
| Polyphosphate | \$1200 | NA | 110 gallons/yr |
| Total for 30 year Remediation | \$48,682 | \$63,408 | Includes 2% escalation/year |
| <i>Electricity Consideration</i> | | | |
| Electrical Demand (kW·hr/month) | 11,470 | 3600 | |
| Monthly Energy Cost | \$659 | \$223 | UV actual, FBR calculated |
| Monthly Demand Cost | \$279 | \$74 | UV 18 kW, FBR 5 kW |
| Total Monthly Cost | \$938 | \$297 | |
| Annual Cost | \$11,256 | \$3564 | |
| Total for 30 year Remediation | \$456,634 | \$144,584 | Includes 2% escalation/year |
| <i>Annual Equipment Replacement</i> | | | |
| UV Lamp Replacement | \$17,980 | NA | \$333/lamp changed out every 1.4 yrs, 12 hours labor |
| UV Quartz Sleeve Replacement | \$1976 | NA | \$115/sleeve changed out every 5 years, 16 hours labor |
| UV Lamp Ballast Replacement | \$5720 | NA | \$750/ballast changed out every 5 years, 16 hours labor |
| UV Wiper Insert Replacement | \$1160 | NA | \$10/wiper part, changed out every 2 years, 16 hours labor |
| FBR Media Replacement | NA | \$500 | 2% loss per year |
| FBR Equipment Repair, Maintenance | NA | \$5000 | O&M on pumps, valves, checking unit |
| Annual Cost | \$26,836 | \$5500 | |
| Total for 30 year Remediation | \$1,088,685 | \$324,545 | Includes 2% escalation/year |
| Overall Costs | | | |
| Grand Total for 30 Year Remediation | \$2,528,171 | \$1,631,837 | |

7.3.1 FBR System

The costs for a complete FBR treatment system to meet NDMA treatment requirements of reducing influent from 1 µg/L to below 4.2 ng/L are provided. Based on the WSTF water chemistry and associated HRT required, an FBR system to effectively treat 125 gpm of WSTF groundwater would need to be 5 feet in diameter with an expanded bed height of 20 feet (20% safety factor added). The plant would consist of one full-scale fluidized bed bioreactor, constructed with welded, 304 stainless steel to API-650 with sidewall anchor chairs; closed top design and full stainless steel flat floor plate with access ladder; and a deck grating and handrail on roof. Included with the FBR is a fluidization pump, an influent distribution system, and effluent/biomass collection system, two biomass separators, 7100 pounds of carbon media (coconut shell based), and oxygen generator and a gas delivery system (both oxygen and propane). Provided for the entire plant is a systems controls package that includes a National Electrical Manufacturers Association (NEMA) four control panel, with system motor controls, Allen-Bradley SLC Series PLC with operator interface, and any required transformers or power supply. The total capital and installation costs for the FBR is estimated at \$932,000 or \$1,099,300, if amortized over 30 yrs at a 1.1% discount rate.

During the demonstration, the level of solids at the effluent was equal or less than provided at the feed. Based on this level of solids generated (< 10 mg/L TSS), additional equipment for solids removal is not provided. It is anticipated that the effluent of the FBR would be discharged to an infiltration pond. Any accumulation of solids would occur regardless of the technology implemented such that dredging and removal may be required.

For the implementation of such a treatment plant, the documentation for the project includes:

1. Process description,
2. Process flow diagrams,
3. Material balance,
4. Piping and instrumentation diagrams,
5. Utility requirements,
6. Equipment and instrument cut sheets for ETI-supplied equipment/instruments,
7. General layout diagrams,
8. Detailed layouts for skidded equipment and vessels,
9. Electrical design drawings for the control panels,
10. Functional control specification and detailed process specification,
11. Equipment and instrument cut sheets, and
12. Project schedule.

The provided costs reflect all project administration, reporting, oversight of subcontracted services, preparation of O&M manuals and progress reports, installation supervision of major equipment, attendance at all project meetings, system mechanical shakedown and hydraulic testing, process start-up, and initial operational training. In addition, an estimate of system installation costs that will be required at a particular site are also provided. These costs include both in-house and subcontractor work.

7.3.2 UV Treatment System

The existing technology at the site (MPITS) is a groundwater pump and treat facility designed for 125 gpm using UV technology. Groundwater is pumped from five extraction wells to the treatment facility. This water is initially pumped into a surge tank in the treatment building. The surge tank enables a stable control volume of groundwater so that flow going into an air stripper can be regulated. Before entering the surge tank, the groundwater is injected with a polyphosphate scale control chemical, which is distributed on a feed flow proportional basis. The chemical cleaning system is not currently being used since it is only implemented when the system is processing high turbidity water. From the surge tank, groundwater is then pumped into a 5-micron filter bank before entering the air stripper. The air stripper removes VOCs from the groundwater by passing ambient air from a blower upward through perforated trays as water flows downward through the trays. The volatilized VOCs from groundwater are discharged from the roof of building into the atmosphere. Effluent water from the air stripper is pumped into 1-micron filter banks before entering the TrojanUVPhox™ reactor. The groundwater is exposed to low pressure, amalgam ultraviolet 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. The MPITs has been running for over 1 year. The total capital and installation costs for the UV system are estimated at \$792,000 or \$942,170, if amortized over 30 years at a 1.1% discount rate.

7.3.3 Cost Comparison of FBR versus UV

The life-cycle costs for the UV and FBR systems were based on the capital equipment costs, the engineering and installation costs, and the overall operating costs of chemicals, electricity, and parts replacement. Difficulties arise in comparing any technology costs for applications where all costs are not accounted or estimates need to be developed. A few issues require addressing when comparing the data provided in Table 9:

- Both the FBR and UV system were quoted as continually operating systems at 125 gpm. However, downtime for both processes will differ. Hence, although remediation times were developed equally for both technologies over 30 years, these technologies may require actual different timelines to provide the same mass removal of NDMA.
- Quoted costs assumed wellhead pumping, the air stripper and associated infrastructure, a building and associated infrastructure, the infiltration pond construction and maintenance, and overall operation (labor, expenses) were assumed similar for both units. Hence, in order to provide as close a cost comparison for the FBR and the UV technology as possible, these costs were not included in the evaluation of either technology. Still, these costs could differ depending on the technology. For instance, the FBR may not require a building while the UV system would.

For these reasons, all of the costs provided in Table 9 must not be considered an absolute comparison. However, a general analysis of the costs can be undertaken:

- Capital costs for UV are lower compared to the FBR treatment system at the NDMA concentration treated.
- Installation/engineering costs for both technologies used scaling factors (USEPA, 2000) that were a direct function of the capital cost. Hence, the UV installation/engineering cost by definition was less expensive than the FBR.
- Operating costs for chemicals favored the UV, but the difference over 30 years was not significant based on the overall treatment costs (less than \$15,000).
- Operating costs for the electricity and the parts replacement favor the FBR significantly over the UV system. The UV electrical demand is 3x higher than the FBR, while the need for UV lamp replacement every 1.4 years makes up over half the 30-year remediation cost for UV parts. If the replacement frequency of the lamps increases or decreases over time, the overall costs will change accordingly.
- Overall costs for the 30-year remediation project favor the FBR over the UV system by ~ \$900,000.

The costs in Table 9 are only comparable for the specific site conditions quoted. However, some general cost sensitivity analysis based on flow and NDMA concentration has been conducted to determine the applicability of the two technologies under different operating scenarios. In general, the trends are as follows:

- An increase in flow from 125 gpm up to 1000 gpm would result in a significant increase in both the UV and FBR capital costs to maintain adequate residence time to ensure NDMA treatment. The UV system would require more lamps to ensure sufficient exposure time to the NDMA is provided, with a linear increase versus flowrate in capital reflected in the number of additional lamps and quartz sleeves. The FBR would require a larger reactor so that the volume of biological active media was sufficient to react with the larger volume of water requiring treatment. The increase in the capital cost for the FBR system is not linear from 125 gpm to 1000 gpm, but instead is approximately 3x greater.
- An increase in flow from 125 gpm to 1000 gpm would require an increase in operating expenses for both systems. The operating costs of the UV would be expected to increase linearly with flow, with electrical demand per lamp being in proportion to the flow increase. The FBR would have an increase in oxygen in propane consumption on a linear rate with flow as well. However, lower dosing of the propane would be possible once an established biomass is created. This lower dosing requirement would minimize the impact of the cost increase of chemical addition with increasing flow.
- An increase in the NDMA concentration from 1 µg/L up to 5 µg/L would result in some level of capital cost increase with the UV system as longer residence times would be required for effective treatment of the NDMA. However, the amount of increase in capital expense would not be linearly proportional to the concentration as it is with flow. Concentration of NDMA entering the FBR was not varied during this pilot study. However, in prior bench-scale work, the residence time required to effectively treat up to 20 µg/L of NDMA was demonstrated to be 20-30 minutes, similar to that required to treat

1 µg/L in the field FBR. Such results indicate that a degree of robustness is afforded the FBR as the concentration of NDMA increases. Thus, an increase in FBR size is likely not required for moderate increases in NDMA influent concentrations (e.g., up to 20 µg/L).

- The electrical demand of a UV system follows a log-linear relationship. That is, to treat 1 µg/L to 1 ng/L (3 log order reduction) requires 3x the energy as treating 1 µg/L to 100 ng/L (1 log order reduction). Hence, as NDMA concentrations increase from 1 µg/L to 5 µg/L, or higher, electrical demand and O&M costs for the UV system will increase accordingly. For the FBR, bench-scale studies have demonstrated that an increase from 1 µg/L up to 20 µg/L of NDMA resulted in no increase in propane or oxygen consumption as the NDMA is treated cometabolically (i.e., cells are growing on propane not NDMA). Hence, unlike a UV system, the operating expenses for the FBR should not be affected by the increase in NDMA concentrations up to 20 µg/L.
- An increase in other factors, such as TSS in the groundwater, would not impact FBR costs as this type of biological system can effectively operate at TSS concentrations up to 100 mg/L. However, increasing TSS/turbidity would have a major detrimental effect on the ability of the UV lamps to provide sufficient energy to oxidize NDMA. Hence, a prefilter step may be required, raising capital and operating costs.

8.0 IMPLEMENTATION ISSUES

For this demonstration, the implementation of the FBR system to treat contaminated groundwater with NDMA has been shown to be possible and effective. Future implementation of the technology requires that the necessary permitting regulations are met, end user concerns are addressed, and lessons learned during the demonstration are implemented at the next scale.

8.1 REGULATIONS

Under current practice, statewide regulatory agencies are provided primacy to implement regulations that meet the federally mandated Clean Water Act standards for discharges of treated water to the environment. This is achieved by these regulatory agencies through the implementation of an NPDES permit. However, the statewide regulatory agencies also have the latitude to institute specific additional limitations on an effluent discharge based upon sensitivity of the receiving body of land or water. For instance, if downstream of the effluent discharge point, there exists a drinking water aquifer, more stringent requirements may be enacted. In the event that regulations do not exist for a particular contaminant or a state determines that a more restrictive regulation is required, such authority to develop new or more stringent regulations based on a health-based risk assessment or through other means is provided to each individual state by the federal government.

There is currently no federal MCL for NDMA in the U.S., but the USEPA recently added NDMA to its current CCL-3 (USEPA, 2008), which is a possible step toward regulation under the Safe Drinking Water Act. The NMED regulates the discharge of the NDMA in the effluent from WSTF. Originally, WSTF was regulated at 10 ng/L of NDMA for discharge of treated groundwater for surface deposition for a number of years. After further review of the health risks associated with the contaminant, the NDMA concentration in their discharge limit was reduced from 10 ng/L to 4.2 ng/L. As additional health effects are realized for contaminants such as NDMA, additional future limitations may be placed on the effluent discharge requirements. Hence, as NDMA treatment is implemented throughout the country, technologies should continually be striving to treat to near non-detect levels (i.e., < 2 ng/L) when possible.

In implementing a full-scale FBR treatment plant for WSTF, the NMED will require that an NPDES permit application be submitted and approved. This permit submittal will require a formal application and a technical report with sufficient information to demonstrate that the new treatment system can provide consistent, quality water meeting at least all of the requirements of the current NPDES permits for the discharge of NDMA treated water. Portions of this report generated for this demonstration study can be utilized to meet the requirements of the technical report submittal to the NMED. From such a submittal, the NMED will prepare an engineering evaluation report that will detail the water source, extent of contamination, contaminant migration, and effect on the receiving body of water. From this report, recommendations are developed for a permit that describe the treatment train, the specific operating regimes, and required monitoring program. Typical monitoring requirements may include 30-day average and maximum daily NDMA concentrations and general water chemistry parameters. However, because the specific FBR technology is a biological process, additional monitoring requirements may include such items as TSS, biochemical oxygen demand, chemical oxygen demand, TOC, and heterotrophic plate count analyses.

Finally, additional permits that will be required in the implementation of the treatment technology will include a publicly owned treatment works discharge permit (if required for solids removal) and typical construction permits with the local municipalities.

8.2 END USER CONCERNS

The primary end-users of this technology are expected to be industrial or military clients that have a history of NDMA usage or contamination at their facility. Additional stakeholders with interest in this FBR technology demonstration include the NMED, USEPA, and DoD. The general concerns for all of the end users include: (1) technology performance; (2) technology cost; (3) ease of operation; (4) technology robustness; and the (5) effluent water quality. These issues, with guidance from WSTF, were effectively addressed and demonstrated throughout the study. The concerns are reflected in the performance objectives that are described in Sections 3.0 and 6.0.

Considerable process development has been implemented to ensure that the FBR treatment plant supplied a consistent supply of NDMA treated water. The FBR treatment system has proven to be a robust, dependable treatment technology for NDMA treatment. The FBR treatment system technology is a custom built system and is not considered a commercially-off-the-shelf technology. However, numerous systems of varying size have been previously built and installed elsewhere treating more than 12 million gallons of organic and inorganic pollutants, to non-detect levels every day (e.g., Hatzinger, 2005). Thus, the future procurement of an expanded system should not be considered problematic and a typical environmental/civil engineering firm will be able to scale-up and apply this technology in the field. The FBR treatment technology is not considered proprietary. However, specific components of the FBR are considered proprietary or are patented by ETI. These components include the FBR vessel distribution headers, the biomass removal system, and the control logic for the propane and oxygen addition by the PLC.

In implementing the full-scale FBR treatment system, a number of typical project issues will need to be addressed by those stakeholders involved in the implementation of this remediation process. These include:

- Land acquisition for the site of plant;
- Site surveying and soil analysis;
- Project civil, electrical, and mechanical engineering for plant fabrication/installation;
- Preparation of sub-contractor bidding documents for fabrication/installation;
- Project management and engineering during fabrication/installation;
- Fabrication/installation labor, equipment, and materials
- Geotechnical engineering for production/reinjection well installation;
- Preparation of well and water conveyance subcontractor bidding documents;
- Drilling/installation of production and or reinjection wells (as necessary);
- Engineering design for water conveyance to/from the plant;
- Water conveyance system (piping, booster pumps, labor, etc.);
- Discharge water permitting (NPDES);
- Other permitting required for installation and water conveyance; and
- Operation and maintenance of the plant.

The implementation of such a “first-of-its-kind” technology to treat contaminated groundwater, rather than simply rely on energy intensive alternatives, to low-level water standards can serve as a new paradigm of water treatment for significantly impaired resources. With quality supplies of water rapidly declining throughout the United States, the implementation of such a biological treatment plant can be effectively used for NDMA contaminant removal.

In summary, the operational/process lessons include:

- For an FBR HRT of 20 minutes (at 2.2 gpm for the pilot-scale), the propane and oxygen requirements were established at 35 mg/min (28.6 mg C/min) and 175 mg/min, respectively. This quantity of propane incorporated an excess beyond stoichiometric requirements to account for abiotic loss and microbial biomass incorporation. During steady-state operation, the oxygen and propane residuals in the FBR effluent averaged greater than 4 mg/L and ~ 30 µg/L, respectively. The feed of diammonium phosphate and urea can be adjusted to provide only minimal excess ammonia and orthophosphate in the FBR effluent during steady-state operation (< 1 mg/L each). Higher effluent concentrations may initially be required during FBR bed growth, but at equilibrium, low concentrations were maintained (~ 0.8 mg/L orthophosphate as P and < 0.2 mg/L ammonia as N).
- The interruption of forward feed flow or power to the plant is more detrimental to the system performance in the early stages of bed biofilm maturation. In general, plant interruptions should be kept at a minimum in the first 60 days of operation in order to maximize NDMA removal performance. The ability of the system to recover from such interruptions may be a function of the frequency and duration of such events. For shorter periods (days), the system was able to rebound within hours to days. Longer shutdown periods may have resulted in a different response in treatment.
- A rapid bed expansion did not occur during the study period. Although it was assumed that the full fluidized bed was utilized for biological treatment of the NDMA (at a 20 minute HRT), it may be possible that an even shorter HRT (10 minutes) could be utilized and still provide effective treatment. At an HRT of 10 minutes, effluent NDMA concentrations below 10 µg/L were consistently achieved. However, although values less than 4.2 µg/L were achievable, this level was not consistently met.
- Although the FBR was inoculated with a specific propanotroph (*R. ruber* ENV425), that organism was not among the most dominant bacteria in the FBR by Day 249 of FBR operation. Rather, various *Mycobacterium* spp., among which are many different propanotrophs, dominated the FBR based on molecular analysis (see final report). Presumably, these native propanotrophs seeded the reactor from WSTF groundwater. Clearly, these propanotrophs were capable of degrading NDMA to low concentrations, which is consistent with our previous findings that this ability is widespread among propanotrophic bacteria. These data bring into question the necessity of inoculating an FBR with a specific microbe for NDMA treatment if the feed water contains indigenous propanotrophs. However, given that it is relatively inexpensive to inoculate a reactor, and that propanotrophs are not indigenous in all environments, seeding an FBR with *R. ruber* ENV425 or a similar propanotrophic culture is recommended.

- The grade of propane and oxygen were not laboratory quality, but instead an industrial quality with a lower level of purity. The presence of contamination in the gases provided did not appear to have a harmful effect on the microbes present. This is important as industrial grade propane is less expensive and more readily available. The oxygen can be generated on site using atmospheric air as the source gas.
- The presence of VOCs in the WSTF groundwater did not significantly hinder the performance of the FBR. This experiment was conducted for a short period of time, but no/minimal short-term negative effects were observed. Hence, if certain contaminants are not required to be treated per the NPDES permit and an FBR is to be implemented for NDMA treatment, the elimination of the upstream air stripper may be possible. However, long-term tests of FBR operation in the presence of the co-contaminants should be conducted, and potential increases in the co-contaminants should be considered, as increasing concentrations could have a detrimental effect on NDMA treatment based on previous studies (Hatzinger et al., 2011).

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