Permeable Reactive Barriers for Removal of Nitrate from Groundwater Through Injection of Emulsified Vegetable Oil

Engineering Design Manual

June 2023

Prepared For:

Southeast New England Program

Prepared By:

Woods Hole Oceanographic Inst.
86 Water Street
Woods Hole, MA 02543
www.whoi.edu

In-Situ Oxidative Technologies, Inc.
11 Princess Rd, STE A
Lawrenceville, NJ 08648
wwww.isotec-inc.com

Terra Systems, Inc.
130 Hickman Road, STE 1
Claymont, DE 19703
www.terrasystems.net

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ATTACHMENTS

ACKNOWLEDGEMENTS

This engineering design manual was prepared as part of the United States Environmental Protection Agency (USEPA) Southeast New England Program (SNEP) Watershed Grant SNEPWG19-12-WHOI.

The Woods Hole Oceanographic Institution (WHOI) is the lead organization on the grant. Partner Organizations include the Town of Falmouth and its Water Quality Management Committee and the Cape Cod Commission. Key contributions to the project planning, implementation, and assessment included In-Situ Oxidative Technologies, Inc. (ISOTEC), Terra Systems, Inc., and Science Wares, Inc.

This document is intended to assist coastal communities in Southeast New England and beyond in design for reduction of groundwater nitrogen transport to surface waters.

The authors of this design manual are:

- Paul M. Dombrowski, P.E., In-Situ Oxidative Technologies, Inc. (ISOTEC).
- Michael Lee, Ph.D., Terra Systems, Inc.
- Richard L. Raymond, Jr., Terra Systems, Inc.

The authors acknowledge the assistance of numerous individuals who participated in the field activities, data review, Water Quality Advisory Meetings, and provided review and input throughout the process of developing this manual:

- Matthew Charette, Ph.D., Woods Hole Oceanographic Institution (WHOI).
- Kristen Rathjen, Science Wares, Inc.
- Tim Pac, CPG, Terra Systems, Inc.
- James Begley, MT Environmental.
- Tim Pasakarnis, Cape Cod Commission.

ACRONYMS AND ABBREVIATIONS

NH_4^+	ammonium (ion)
BMP	best management practice
CWA	Clean Water Act
CLU-IN	Clean-Up Information (website – https://www.clu-in.org)
A_c	cross-sectional area
°C	degrees Centigrade
DOC	dissolved organic carbon
DO	dissolved oxygen
n_{eff}	effective porosity
EVO	emulsified vegetable oil
ESTCP	Environmental Security Technology Certification Program
g/L	grams per Liter
Q	groundwater flow (units of length/time)
HRSC	high resolution site characterization
K	hydraulic conductivity (units of length/time)
I	hydraulic gradient (unitless)
ISOTEC	In-Situ Oxidative Technologies, Inc.
ITRC	Interstate Technology and Regulatory Council
Fe	iron (metal)
LA	load allocations
Mn	manganese (metal)
MOS	margin of safety
MassDEP	Massachusetts Department of Environmental Protection
MEP	Massachusetts Estuaries Project
ug/L	micrograms per Liter
CH_4	methane
mg/L	milligrams per Liter
NO_3^-	nitrate (anion)
NAFO	nitrate-dependent anaerobic ferrous iron oxidation
NO	nitric oxide
NO_2^-	nitrite (anion)
N_2	nitrogen (gas)
N_2O	nitrous oxide
ORP	oxidation reduction potential
PRB	permeable reactive barrier
PO_4^{3-}	phosphate (anion)
n	porosity
v_s	seepage velocity (units of length/time)
SNEP	Southeast New England Program
SU	standard units (of pH)
SO_4^{2-}	sulfate (anion)
S^{2-}	sulfide (anion)
SRS®-NR	Terra Systems Inc.'s modified EVO formulation
PCE	tetrachloroethene

TMDL(s)	Total Maximum Daily Load(s)
TOC	total organic carbon
TKN	total Kjeldahl nitrogen
TCE	trichloroethene
TNT	trinitrotoluene
UIC	Underground Injection Control
USEPA	United States Environmental Protection Agency
USGS	United States Geologic Survey
UMass	University of Massachusetts
VOC(s)	Volatile Organic Compound(s)
WLA	wasteload allocations
WHOI	Woods Hole Oceanographic Institution

1.0 EXECUTIVE SUMMARY

Discharge of nitrogen-enriched groundwaters to coastal embayments can lead to eutrophication, a process whereby excess growth of algae negatively impacts water quality and ecology. Eutrophication also poses human health risks, as well as economic impacts. On Cape Cod, approximately 80% of the nitrogen that enters watersheds comes from septic systems, and as a result excessive nitrogen discharge from groundwater to surface water has significant financial impacts on in Southern New England and other coastal communities due to losses in commercial fishing, property taxes and tourism revenue streams.

Permeable Reactive Barriers(s) or PRBs are a widely used approach for removing and/or treating contaminants in groundwater. This engineering design manual is focused on design and installation of PRBs for the biological treatment of nitrate in groundwater through injection of carbon substrate electron donors. These donors stimulate indigenous anaerobic bacteria to perform denitrification, a biologically mediated degradation process also known as biodegradation.

Biodegradation is the natural process whereby indigenous microorganisms alter and break down organic molecules. Natural communities of microbes are amazingly versatile. They can carry out biodegradation in almost every type of environment and habitat, under both aerobic and anaerobic conditions. In-situ aerobic biodegradation in the cleanup of a gasoline contaminated groundwater was first demonstrated in 1970 by providing the indigenous bacteria with the missing components required for increased activity. Denitrifying PRBs use the same basic approach where indigenous denitrifying bacteria in soil are provided missing components needed to enhance the denitrifying process.

Compliance with the federal Clean Water Act (CWA) and state water quality standards are the primary regulatory drivers for nitrogen removal from groundwater. The high cost for construction and operation of centralized wastewater infrastructure has led to investigation of alternative solutions for coastal communities to reduce nitrogen discharges to surface water. PRBs can address multiple non-point sources of nitrogen, including septic systems, storm water, fertilizer, and atmospheric deposition.

For impaired watersheds, the level of effort and cost to achieve regulatory compliance can be significant. For example, the cost to bring Cape Cod communities in compliance with the CWA entirely through traditional wastewater treatment and sewering will cost billions of dollars. In addition, installation of sewer systems will not result in treatment of nitrogen already traveling in groundwater, such that any newly installed sewer system may take many years to have an impact on the discharge of nitrate. Installation of a denitrification PRB before the discharge to coastal embayments in combination with source reductions can treat the nitrate in the groundwater.

This manual utilizes best practices developed in the groundwater treatment industry, coupled with the results from four in-situ demonstration test biological PRBs for denitrification completed between 2016 and 2023. This manual summarizes relevant information on PRB design for nitrate removal and provides references to supplemental documents for additional detail.

The objectives of this design manual are to assist communities to cost effectively consider, plan, design, implement, and monitor denitrification PRBs to address nitrogen in groundwater. At full-scale, future installation may entail combined lengths of hundreds to thousands of linear feet of PRBs in municipalities on Cape Cod, Long Island, and other coastal areas as well as in agricultural areas where fertilizer use has resulted in elevated concentrations of nitrogen species to groundwater. This manual was developed with focus on engineering design of denitrification PRBs through injection of carbon substrate electron donor. The manual recognizes that PRBs may not be the solution for all locations; biological PRBs are one key tool in the "nitrate reduction toolbox." The use of this tool will depend on several variables which are described in this manual.

2.0 INTRODUCTION

Permeable Reactive Barriers(s) or PRBs are a widely used approach for removing and/or treating a range of different contaminant types in groundwater (ITRC, 2011). This engineering design manual is focused on design and installation of PRBs for treatment of nitrate in groundwater through injection of reagents to stimulate anaerobic bacteria to perform denitrification. PRBs installed via injection of liquid carbon substrate solutions, as detailed in this manual, can also effectively treat chlorinated volatile organic compounds (VOCs), including tetrachloroethene (PCE) and trichloroethene (TCE) (Borden 2008). This manual was developed utilizing best practices developed in the groundwater remediation industry along with observations from in-situ demonstration test PRBs for denitrification installed on Cape Cod, Massachusetts between 2016 and 2020 and subsequent monitoring. This engineering design manual was prepared with support of a Southeast New England Program (SNEP) Watershed Grant.

2.1 THE NITROGEN PROBLEM

Nitrogen-enriched groundwaters entering coastal embayments or other surface waters are negatively impacting the water quality and ecology of these water bodies due to eutrophication where growth of algae is stimulated by increases in available nitrogen and phosphorus. Water quality impacts include fluctuations in dissolved oxygen concentrations, increasing occurrences of fish kills, native eelgrass being replaced by macroalgae, unpleasant odors, visible scum, and accumulation of anoxic sediments which fosters a complete loss of benthic macroinvertebrates in some cases. Excessive nitrogen discharge from groundwater to surface water has a significant financial impact in Southern New England and other coastal communities due to losses in commercial fishing, property values, and tourism revenue streams. Further, nitrate levels in groundwater and surface water are elevated in many areas of the world due to applications of fertilizer and animal manure in agricultural areas.

Nitrate in drinking water is linked to various adverse health effects including infant methemoglobinemia (blue baby syndrome), specific cancers, and birth defects (Ward et al., 2018). The National Primary Drinking Water Standards for public water supplies limit the concentration of nitrate-N in drinking water to 10 milligrams per liter (mg/L).

Anthropogenic sources of nitrogen to groundwater include nitrogen-containing fertilizers, sewage sludge, manure from agriculture, discharge from septic tanks, and leaking sewers (Wakida & Lerner, 2005). In many coastal communities across the United States, notably on Cape Cod, Massachusetts, the primary source of nitrogen in groundwater is the widespread use of septic systems. Permitted septic systems were designed for removal of pathogens such as enteric bacteria, not removal of nutrients such as nitrate. Septic systems have created nitrate plumes in a hydrogeologic environment that allows relatively rapid transport to coastal waters with limited attenuation. Septic systems represent more than 90% of the total load of wastewater-derived nitrogen for the coastal watersheds in Cape Cod, and approximately 80% of the nitrogen that enters Cape Cod's watersheds comes from septic systems (Cape Cod Commission, 2015). Marine ecosystems can be impacted by nitrate-N levels as low as 0.5 mg/L (Bowen et al., 2007).

In septic systems, microorganisms decompose the organic nitrogen species to ammonium (NH_4^+) through a process known as ammonification. Upon entering the groundwater, NH_4^+ can be converted to nitrite (NO_2^-) and nitrate (NO_3^- by aerobic microorganisms, those using oxygen for respiration, through a two-step process referred to as nitrification. These nitrification reactions are performed by two different groups of bacteria (Metcalf and Eddy, 2003). The first step is performed by ammonia-oxidizing bacteria that oxidize NH_4^+ to NO_2; *Nitrosomonas* is the frequently identified genus of ammonia-oxidizing bacteria. In the second step nitrite-oxidizing bacteria oxidize NO_2^- to nitrate (NO_3^-); *Nitrobacter* is the frequently identified genus of nitrite-oxidizing bacteria. Once in groundwater, nitrate can be transported to surface water bodies including ponds, streams, estuaries, and embayments, where it can contribute to increased algae growth and eutrophication. The processes of nitrogen transformations and transport from septic systems to discharge via groundwater transport is shown in **Figure 1**.

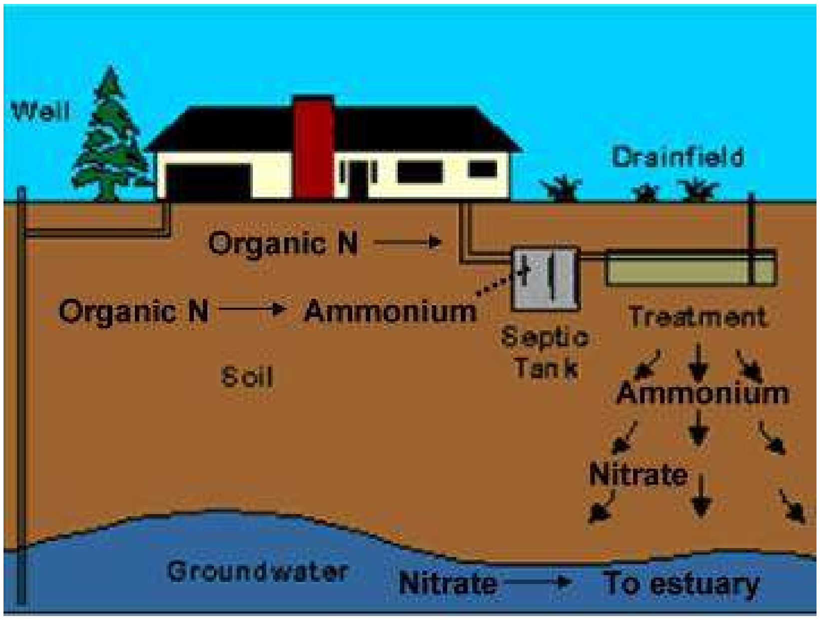


Figure 1. Nitrogen Transport from Homes to Groundwater to Surface Water.
(Source: Oyster Pond Environmental Trust, 2022)

2.2 Objectives for Using PRBs to Remove Nitrate from Groundwater

The United States Environmental Protection Agency (USEPA) has issued orders to reduce nitrogen discharge loading for numerous coastal embayments, including on Cape Cod and in other regions where loads of nitrogen are being transported by groundwater to surface water bodies. Through the CWA, attention is focused on priority water bodies with the aim of improving impaired waters through development of total maximum daily load (TMDLs) followed by permits, restoration plans, and monitoring (Section 2.3).

The high cost for construction and operation of centralized wastewater infrastructure in areas of relatively low development density has led to investigation of alternative solutions for coastal communities to reduce nitrogen discharges to surface water. PRBs have been identified as a promising Best Management Practice (BMP) for remediating nitrogen in groundwater before it enters marine systems, including within the 208 Plan Update. The 208 Plan Update was developed to address federal regulatory requirements and restore coastal water quality on Cape Cod using watershed-based approaches (Cape Cod Commission, 2015). PRBs can address multiple non-point sources of nitrogen that percolate into the aquifer, including septic systems, stormwater, fertilizer, and atmospheric deposition. PRBs can treat nitrogen at the source and/or near the point of discharge into the surface water bodies, which can result in immediate and long-term improvements to water quality and address historical nitrogen inputs still traveling in groundwater.

The objectives of this design manual are to assist communities to plan, design, implement, and monitor denitrification PRBs using data collected from previous denitrification PRBs and incorporating best practices from in-situ groundwater treatment processes. This manual can be used for planning PRB demonstrations/pilot-scale injections or a full-scale denitrification PRB. At full-scale, future installation may entail combined lengths of hundreds to thousands of linear feet of PRBs in municipalities on Cape Cod, Long Island, and other coastal areas.

2.3 REGULATORY DRIVERS AND STAKEHOLDER BENEFITS OF PRBS

Compliance with the federal CWA and state water quality standards are the primary regulatory drivers for installing PRBs for nitrogen removal from groundwater. In December 2013, USEPA announced a new framework for implementing the CWA Section 303(d) program with states titled A Long-Term Vision for Assessment, Restoration and Protection under the CWA Section 303(d) Program (U.S. Environmental Protection Agency, 2013). The program focuses attention on priority waters and extends flexibility to states in using available tools to attain water quality restoration and protection. The aim of the program is to advance impaired waters through a process of identification, determination of pollutant reduction requirements, development of TMDLs, followed by permits, restoration plans, and monitoring.

TMDL is a calculation of the maximum amount of a pollutant that can be accepted by a waterbody and still meets a state-determined Water Quality Standards for public health or environmental receptors. Under the federal CWA, states must identify waterbodies that do not meet state standards and develop TMDLs for them. TMDLs represent a dynamic or load based standard to achieve water quality restoration goals compared with a target concentration standard where a specified concentration of a contaminant must be attained. TMDLs incorporate the sum of wasteload allocations (WLA), sum of load allocations (LA), and margin of safety (MOS). WLA's include identified point sources, and LA's include nonpoint sources and background levels of the contaminant of concern. The flowrate or flux of the contaminant must be considered. For example, a highly concentrated waste stream at a slow flowrate may have little impact on a large receiving water body.

For impaired watersheds, the level of effort and cost to achieve compliance can be significant. For example, the cost to bring Cape Cod communities in compliance with the

CWA entirely through traditional wastewater treatment and sewering has been estimated to be $4.6 to $6.2 billion (Cape Cod Commission, 2015). In addition, due to extended travel times from the wasteload allocations (e.g., septic tanks) to the point of discharge in the surface waters, installation of sewer systems will not result in treatment of nitrogen already traveling in groundwater such that a newly installed sewer system may take many years to have an impact on the discharge of nitrate.

PRBs offer many benefits for communities for addressing nitrogen in groundwater and attaining TMDLs:

- Much smaller capital cost than traditional sewering and wastewater treatment.
- Minimal operations requirements or costs after installation beyond periodic groundwater sampling and laboratory analyses.
- Multiple point and non-point sources can be addressed together.
- Nitrogen can be treated nearer to a point of discharge, resulting in more immediate improvements to surface water quality and attaining TMDL.
- Scaling to treat the highest nitrogen load or flux areas thereby optimizing its overall size and cost.
- Small footprint and disturbance, which is largely limited to the installation and reinjection phases at the location of the PRB.
- Can be used in combination with other nitrogen removal technologies for achieving TMDLs at the watershed scale.
- Actively remove nitrogen, or other contaminants of concern for many years between substrate injections, depending on the selected reactive amendment and dosage and the flowrate of the groundwater.
- Provide nearly immediate removal of nitrogen from groundwater, while conventional wastewater treatment or other nitrogen removal approaches (e.g., shellfish aquaculture) are being designed, constructed, and brought online.

PRBs may not be applicable where nitrate impacted groundwater is deep (80 to 100 feet or deeper), immediately adjacent to surface water, and areas with many subsurface utilities, or where above ground features limits access.

This manual focuses on the design of PRBs installed via injection of liquid reagent solutions. Underground Injection Control (UIC) permitting by USEPA regions or by state, territory, or tribal entities with primacy for implementing USEPA approved UIC programs often have minimum set-back requirements from a body of water and may further influence siting beyond the above listed constraints.

The Massachusetts Estuaries Project (MEP) was created in 2001 to help determine current nitrogen loads to southeastern Massachusetts estuaries and evaluate reductions that would be necessary to support healthy ecosystems. The MEP is a collaborative effort between the Massachusetts Department of Environmental Protection (MassDEP), University of Massachusetts Dartmouth (UMass Dartmouth), and southern Massachusetts communities. MEP evaluations will be completed for approximately 70 coastal embayments in southern Massachusetts. The MEP model has helped to identify the sources and magnitudes of watershed nitrogen inputs and is used as a basis for establishment of TMDLs and other regulatory limits. Additional information about the MEP and TMDL reports for Massachusetts watersheds can be found at the following links:

- https://www.mass.gov/guides/the-massachusetts-estuaries-project-and-reports.
- https://www.mass.gov/lists/total-maximum-daily-loads-by-watershed.

3.0 DENITRIFICATION OVERVIEW

3.1 BRIEF HISTORY OF IN-SITU BIOLOGICAL DEGRADATION

Biodegradation is the natural process whereby microorganisms alter and break down organic molecules. Natural communities of microbes are amazingly versatile. They can carry out biodegradation in almost every type of environment and habitat, under both aerobic and anaerobic conditions.

Richard L. Raymond, Sr. first demonstrated the use of in-situ aerobic biodegradation in the cleanup of a gasoline contaminated drinking water well field in Whitemarsh Township, Pennsylvania in 1970. He later received a patent (Raymond, 1974) for this process which was named the Raymond Process by the USEPA. At the project, a bioreactor was created in the subsurface by providing the indigenous bacteria with the missing components they required for life including oxygen, nitrogen, and phosphorus. Petroleum hydrocarbon-degrading bacteria are ubiquitous in nature and can utilize these compounds as sources of carbon and energy. Bacteria displaying such capabilities are often utilized for the bioremediation of petroleum oil-contaminated environments (Xu, et al., 2018).

Mr. Raymond later contributed to the development of anaerobic biodegradation of chlorinated solvents in the late 1980s by which anaerobic bacteria are stimulated from the addition of an electron donor, which is most commonly an organic carbon substrate.

The use of PRBs for removing nitrogen from groundwater uses the same basic approach used by Mr. Raymond in that, the indigenous denitrifying bacteria are being provided with the missing components they need to conduct the denitrifying process.

3.2 DENITRIFICATION PROCESS

Denitrification is the process where nitrate (NO_3^-) is converted to nitrogen gas (N_2) through a series of sequential reactions. The reactions occur in steps, with the nitrogen atom gaining one electron in each step:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (1)$$

The nitrate reduction reaction can be written as a half equation:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \qquad (2)$$

Denitrification reactions are performed by bacteria in an anoxic environment, which is an environment with an absence of oxygen. The bacteria use nitrate as a terminal electron acceptor in their metabolic processes (Korom, 1992), as a substitute for oxygen. Denitrification reactions occur naturally in many environments with anaerobic conditions favorable for the denitrifying bacteria, and several genera of bacteria can perform these reactions including *Alcaligenese, Bacillus, Brevibacterium, Flavobacterium, Lactobacillus, Micrococcus, Proteus, Pseudomonas,* and *Spirillum*. Denitrifying bacteria are ubiquitous to most soil formations, and the populations of these bacteria are active in the absence of oxygen and the presence of nitrate. If oxygen is present, these bacteria preferentially use oxygen for metabolism before using nitrate. Therefore, promotion of the denitrification process requires the depletion of oxygen for the reactions to function. Advanced wastewater treatment for removal of nitrogen utilizes denitrifying bacteria in anoxic treatment tanks. Denitrifying PRBs use the same processes to accomplish denitrification in the subsurface.

Bacteria obtain energy through chemical reactions involving electron transfer. For denitrification bacteria, nitrate is the electron acceptor while organic carbon is typically the food source/electron donor that is oxidized. In the absence of oxygen, nitrogen is the second preferred electron acceptor for bacteria to perform organic carbon oxidation. Thus, denitrification occurs after the depletion of oxygen and in the presence of nitrate.

Denitrification involves four consecutive reduction steps, starting with nitrate and ending with dinitrogen as shown in **Figure 2**. An enzyme is necessary for each reduction reaction. The enzymes responsible for the complete denitrification and the genes related to each step are illustrated in the nitrogen cycle in **Figure 2**. The denitrification process generally is completed with production of inert nitrogen gas, which is the most abundant gas in the atmosphere. However, the reaction steps can be impeded at any of the intermediate stages and generate nitrite (NO_2^-), nitric oxide (NO), or nitrous oxide (N_2O). NO and N_2O gases contribute to acid rain, promote the formation of ground-level ozone, and contribute to global warming. However, complete denitrification results in nitrate yielding nitrogen gas (N_2).

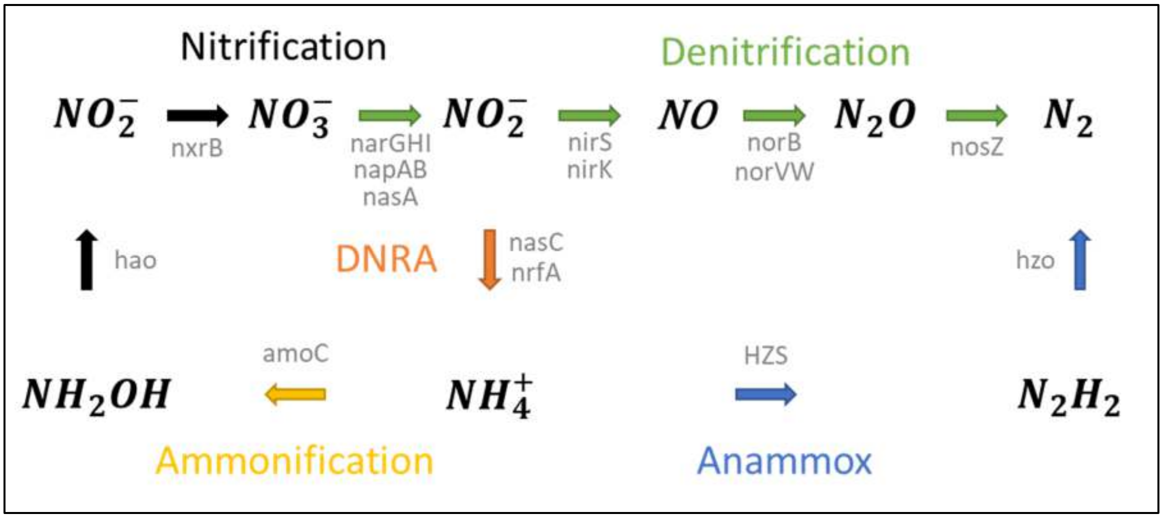


Figure 2 - Enzymatic Pathway for Nitrogen Compounds.
(Source: adapted from Alvarez et al., 2014)

3.3 CARBON SUBSTRATES FOR DENITRIFICATION

Many different substrates have been used for PRBs to treat nitrate. These include wood mulch, straw, or sawdust (Robertson and Cherry 1995); soluble substrates like starch and acetate (ITRC 2002); and emulsified vegetable oil (Silver et al., 2014). Wood mulch contains cellulose and hemicellulose that can be slowly biodegraded by many microbes.

Mulch is comparatively inexpensive and often can be derived from local sources. The main difficulty in using mulch or similar solid products is that it must be installed in a trench or open bioreactor, mixed into the soil with excavators, backhoes, or large diameter augers, or placed in a bioreactor through which the groundwater is pumped (Easton et al., 2018). While mulch cannot be easily injected, related compounds like carboxymethylcellulose can be injected (Johnson et al., 2013).

Soluble substrates are more rapidly consumed and/or transported out of the treatment zone but can be readily injected. Other carbon substrate electron donors that can enhance in-situ biological denitrification include lecithin, lactates, molasses, and cheese whey, (ITRC, 2011 and Lee et al., 1997). The disadvantages of using soluble electron donors in a PRB is that these materials may move away from injection zone with the groundwater flow and have shorter persistence, typically three to twelve months, and would require frequent reinjection.

Emulsified vegetable oil (EVO) and other hydrogen releasing compounds are widely used for groundwater treatment of a wide array of groundwater contaminants (Solutions-IES, 2006) and provides a longer lasting source of carbon due to partitioning of the oil onto the soil particles (Borden, 2008). This manual focuses on the design of PRBs installed via injection of liquid reagent solutions, notably EVO. Injection of liquid solutions of carbon substrates has been demonstrated to effectively enhance denitrification for a wide range of nitrate concentrations, including more than 3,000 micrograms per liter (ug/L) (Lazenby, et al, 2023).

EVO is often prepared with vegetable oil, surfactants, nutrients including yeast extract and other sources of nitrogen and phosphorus, vitamins, and often readily biodegradable substrates like sodium lactate or glycerol (Borden, 2008). Soybean oil is generally the least expensive and most readily available vegetable oil in the United States. Food grade surfactants are often used in the preparation of the emulsion. The surfactants can include lecithin, polysorbate 20, 21, 80, or 85, glycerol monooleate, mixtures of these surfactants, and others (Borden 2008). Nonionic (uncharged) surfactants will bind less to the soil particles and can enhance distribution. Charged surfactants like lecithin with both anionic and cationic functional groups or anionic surfactants can be added to enhance soil adsorption based on the soil type. The EVO droplet size will also impact the distribution. Larger droplets will tend to adsorb onto the soil particles more and smaller droplets will tend to move further from the point of injection. The type of mixer will also impact the particle size and distribution: blenders and high shear mixers with fewer passes tend to produce larger particles and a wider particle size distribution. Sonication and high shear mixers with more passes produce lower particle sizes and a narrower particle size distribution. A homogenizer will produce the finest droplets with few large droplets.

A modified EVO formulation (SRS®-NR) was developed to increase retention in coarse grained (sandy) soils typical to most areas of Cape Cod that incorporates anionic surfactants with larger EVO particle sizes (Lee et al., 2016 and Lee et al., 2019). SRS®-NR can be prepared with only soybean oil and surfactant or can also include a soluble substrate and/or nutrients. Column tests showed greater retention of the larger droplet, stickier surfactant SRS®-NR formulation compared to the standard small droplet EVO formulation (Dombrowski et al., 2017). This modified EVO formulation (SRS®-NR) has been used as the carbon substrate electron donor for the first four denitrification PRB demonstration tests on Cape Cod between 2016 and 2020.

4.0 PERMEABLE REACTIVE BARRIERS

4.1 PRB TECHNOLOGY SUMMARY

Biodegradation is the natural process whereby microorganisms alter, break down, or remove from water organic molecules. PRBs are a passive treatment approach for *in-situ* (in place in the ground) treatment of groundwater by intercepting groundwater before reaching a sensitive receptor (**Figure 3**). PRBs are ideally oriented perpendicular to the direction of groundwater flow and rely solely on the natural groundwater gradient to carry the contaminant(s) through the PRB (ITRC, 2011). The system is permeable to not interfere with or redirect groundwater flow.

PRBs are widely used for the treatment of a wide range of chemicals in groundwater, including chlorinated solvents, petroleum hydrocarbons, metals, and nitrogen compounds. The earliest groundwater treatment PRBs were installed in the early 1990s, and PRBs have been utilized at hundreds of sites over the past three decades (ITRC, 2011; ITRC, 2005; Thiruvenkatachari et al., 2008, USEPA et al., 1998).

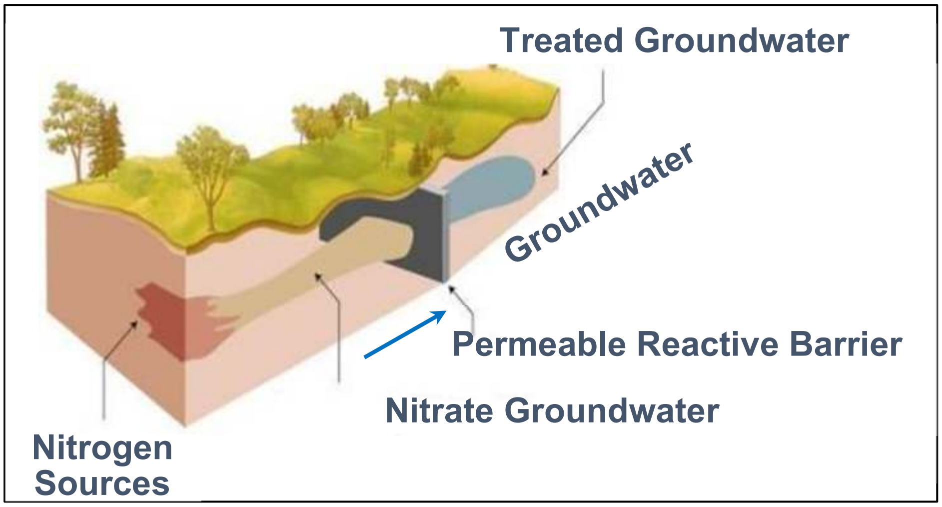


Figure 3. Permeable Reactive Barriers Schematic
(adapted from ITRC, 2011)

A denitrification PRB is designed to intercept and treat nitrate in groundwater by biological denitrification utilizing naturally occurring heterotrophic bacteria before groundwater reaches downgradient surface waters. Nitrate is removed as groundwater containing nitrate passes through the reactive zone of the PRB as provided by the carbon substrate. The introduced carbon serves as an energy source for soil bacteria, as an electron donor such that soil bacteria consume the carbon substrate. At the PRB front, aerobic bacteria consume oxygen in groundwater thus creating anoxic conditions favorable for denitrifying bacteria within, and downgradient of, the barrier. In-situ biological denitrification has long been identified as being an economical process for removal of nitrogen from groundwater (Hunter, 2001).

4.2 PRB INSTALLATION METHODS

PRBs have been implemented through several construction methods, including backfilling an excavated trench with reactive media (using standard construction excavators), continuous trenching using a one-pass trencher, drilling auger boreholes backfilled with reactive media, through the direct injection of reactive liquid solutions, and electroosmosis using electrochemical methods.

Site-specific factors determine the most appropriate construction method for a particular location. Pertinent factors include the depth and width of the PRB, the reactive media to be used, the quantity of reactive media, the site geology, and the surface/subsurface obstructions present (ITRC, 2011). The most common options for nitrate PRBs include trench installations with wood mulch or other solid carbon substrates, and direct injection (with or without permanent injection wells) of liquid organic carbon substrates such as emulsified vegetable oil. The benefits and drawbacks of these construction methods are provided in **Table 1**. As a discussion of all construction methods and substrates is infeasible, this manual focuses on design of PRBs installed via injection of liquid reagent solutions, notably EVO.

Table 1. Comparative Evaluation of Permeable Reactive Barrier Installation Methods (adapted from AECOM, 2016).

Conventional Excavator Installation Permeable Reactive Barrier (Mulch or Other Solid Carbon Substrate)	
Advantages	**Disadvantages**
● Mulch PRBs widely accepted groundwater treatment method. ● Construction equipment readily available. ● Carbon substrate (mulch) has no potential to migrate. ● In most cases, mulch-based carbon substrate will last longer than liquid substrate.	● Requires large construction equipment and the associated disruption of the surrounding environment. ● Requires soil handling and disposal plus area to stage soils. ● Reactive zone (residence time) limited to trench width (3-4 feet). ● Limited to depth of excavator arm (~20 feet), which limits depth of PRB treatment. One-pass trenching can allow deeper PRBs (35-50 feet). ● Alignment may be limited due to above and below ground site features. ● Biodegradation and compaction of mulch may lead to settling of ground surface of trench over time so cannot be placed near roadways.

Injection Permeable Reactive Barrier (Liquid Food-Grade Carbon Substrate)	
Advantages	**Disadvantages**
● PRB can be emplaced at any depth or distance from environmental resource areas. ● Carbon substrate injections widely accepted groundwater treatment method and equipment readily available. ● Small equipment footprint for installation (small drill rig, all pumps and mixing tanks contained to box truck/trailer). ● Can be installed under roadways. ● Limited impacts to traffic and adjacent properties. ● Orientation can be adjusted to accommodate above and below ground site features (utilities, curbs, trees, overhead power lines). ● Injection can generate a wider treatment zone (greater residence time) than a trench filled with solid reactive media. ● Shorter field construction time than trenching.	● Liquid amendments can be transported by groundwater flow (requires verification of stability). ● Injection PRBs likely would require replenishment sooner than mulch trenches.

A PRB would be most cost effective at locations where groundwater transport of nitrogen is significant; higher nitrate concentrations are present, and a moderate to relatively fast groundwater velocity (0.3 to >3 feet per day). Such locations result in a high mass flux of nitrate through a comparatively small treatment zone.

4.3 DENITRIFICATION PRBS AND TMDLS

Total Maximum Daily Load (TMDL) is a calculation of the maximum amount of a pollutant that a waterbody can accept and still meet the state's Water Quality Standards for public health and healthy ecosystems. The federal CWA requires all states to identify waterbodies that do not meet state standards and develop TMDLs for them, and if a TMDL is not achieved for a water body, the classification of that water body can be downgraded through a process within the CWA (MassDEP, 2022).

A TMDL is the sum of loads that are allowable from all contributing point and nonpoint sources of pollution. Point sources are primarily fixed facilities such as wastewater treatment plants that discharge to surface water or groundwater. Nonpoint sources are more diffuse discharges and include septic systems, stormwater discharges via runoff over the land surface or detention ponds, and fertilizer runoff from lawns and golf courses (MassDEP, 2022).

The amount of nitrate entering the surface water body will be determined for each embayment impacted by nitrate. Accordingly, a PRB does not have to remove the entirety of nitrate that travels through the barrier, or even reduce concentration below a concentration criterion, to support achieving a TMDL for a waterbody. For watersheds where a TMDL cannot be achieved with a PRB alone, a PRB can be used in conjunction with other nitrogen reducing approaches such as centralized wastewater treatment, innovative/alternative septic systems, and shellfish aquaculture. The PRB approach can be especially suited for treating lower housing density areas or neighborhoods that are far removed from an existing sewer network.

Quantification of nitrogen removal requirements necessitates a site-specific determination based on state or local regulatory requirements, watershed TMDL, location(s) of PRB, and anticipated longevity of PRB. Section 6.0 of this manual provides details on monitoring PRBs (which may be integral to nitrogen removal crediting); however, documenting nitrogen removal and credits will not be discussed in detail in this engineering design manual.

5.0 PRB KEY ENGINEERING DESIGN PARAMETERS

Section 5.0 describes key parameters and considerations for developing a design for a PRB to treat nitrate via injection of a liquid solution of carbon substrate electron donor. To support this engineering design manual, the ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** was developed. Each engineering design parameter described below will detail considerations for site-specific design use using the ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers.***

5.1 LOCATION FOR DENITRIFICATION PRBS

Selecting the location, or approximate location, of a PRB is the first step in the design process. There are three primary factors that need to be considered for locating a PRB. The first is to identify a location where reduction of nitrogen flux using a PRB will support attainment of a watershed-specific target (see Section 5.5 for details on estimating nitrogen flux). The second consideration is providing sufficient access to install a PRB considering property-ownership and land usage. The presence of a potable water well downgradient of the PRBs could prevent the placement of a PRB. Regulatory criteria for an underground injection control permits may specific off-set distances for approval. In addition, changes to water quality parameters because of the injection of a liquid solution of a carbon substrate may impact the potable water quality (see Section 5.6.1).

PRBs are typically oriented perpendicular to groundwater flow direction. Access and land usage may not allow the PRB to be oriented exactly perpendicular. For larger-scale PRBs (length greater than 500 feet), perpendicular orientation is less important as groundwater containing nitrate will flow into a reactive barrier zone across the length of the PRB such that nitrate will be removed by denitrifying bacteria. For example, in some communities PRB layout follows the path of a roadway. Section 5.3 below includes details regarding groundwater flow direction, including how flow direction can be affected by various features above and below ground, including drains, groundwater pumping, and surface water features. These features should be identified and considered when determining placement of a PRB.

5.2 CONCENTRATIONS OF NITROGEN SPECIES

Quantifying the groundwater concentrations of relevant nitrogen species is critical for PRB design. For denitrification PRBs, nitrate will be the primary groundwater contaminant to be treated. Nitrite is the first product in the denitrification process and may contribute to nitrogen demand.

Identifying if any other groundwater contaminants in addition to the nitrate that are present in the groundwater is important for selecting treatment reagent and dosage. The presence of ammonium and/or organic nitrogen are indications of a nearby nitrogen source, such as a landfill or leachfield(s). Section 6.1 provides additional details on analyses for nitrogen species. Ammonium will not be treated by a denitrification PRB unless it is first oxidized to nitrite and nitrate.

5.3 LOCAL GEOLOGY AND HYDROGEOLOGY

Understanding the subsurface conditions forms the basis for understanding the existing geologic and hydrogeologic conditions present across the study area, which are used in PRB design.

Geological parameters include soil type (i.e., percent of gravel, sand, silt, clay), consolidation (i.e., porous granular soil, unfractured rock, peat, sediment), porosity and other parameters (e.g., color, odor, stiffness, plasticity). Geology parameters should be identified with depth at multiple locations using existing data and/or new investigation where the PRB is being considered. Hydrogeology is determined from the degree of saturation and the depth of water, relative to the site datum or surface elevation.

The geology and hydrogeology conditions need to be understood both laterally and vertically in the subject area. Geology and hydrogeology influences groundwater flow rates, flow direction, nitrogen transport, and changes relative to other Site conditions (i.e., streams, wetlands, structures, basements, subsurface utilities or tanks, wells or previous investigations and land ownership and regulation) and will be incorporated into nearly all aspects of PRB design. Visually illustrating the order of geologic layers (stratigraphy), variability in geology (e.g., percentage of sand, silt or clay and the degree of heterogeneity), and nitrogen concentrations will support a thorough design. The importance of having a sufficient understanding of the site's conditions cannot be understated. Not adequately characterizing hydrogeology can result in a PRB that is ineffective for nitrogen treatment or less effective than desired, which can require additional injection activities and costs.

Local geology conditions will also affect PRB installation, including drilling rigs needed, method of injection (injection wells or temporary injection points), and injection flow rates. Additional details on selecting type of injection points are presented in Section 5.10. More permeable soils (sands and gravels) will allow higher injection flow rates than finer grained soils (silts, clay, glacial till). Pilot testing is the best method to determine site-specific injection flow rates.

A site investigation method known as High Resolution Site Characterization (HRSC) can be designed and implemented to collect environmental measurements at the appropriate scale of the heterogeneities in the subsurface to further define nitrate flow paths. Heterogeneities exist at scales that are often too small for conventional investigation strategies (e.g., monitoring wells) that typically assess heterogeneities that are on the scale of tens of meters, while heterogeneities that control contaminant transport are on the centimeter to meter scale. Additional details on planning and performing HRSC are available on the USEPA Clean-Up Information (CLU-IN) website (https://clu-in.org/characterization/technologies/hrsc/hrscintro.cfm).

The following subsection illustrates the importance of site geology, for an example site on Cape Cod.

5.3.1 Cape Cod Geology Example

The backbone of Cape Cod is a terminal moraine that consists of a ridge of pushed and piled soil deposited at the end of a glacier deposited more than 10,000 years ago. Moraine is the mixed debris that is pushed by the glacier typified by heterogenous mixtures of particles (sometimes referred to as till or drift) composed of crushed rock, sand, silt, clay, and/or boulders. The moraine is the ridge of till that forms at the margin of the glacier (i.e., the sides and/or end), and terminal moraines are particularly important in glacial geology as they mark the terminus of the ice for an extended time. These ice-contact ridges also form the elevated backbone of Long Island and the Islands (i.e., Block Island, Martha's Vineyard, and Nantucket) (USGS, 1976), as well as Cape Cod (Guswa et al., 1985). As moraine materials vary widely and may include significant thicknesses of silt and clay, permeability can be low rendering these aquifers undesirable for supplies of water.

Most of Cape Cod is composed of relatively coarse-grained sand and gravel outwash deposited in front of the moraines, extending outward miles across the Cape and into the Atlantic Ocean. These flat outwash plains may be 80 feet to more than 900 feet thick where underlying bedrock is located (Oldale, 1969). These thick deposits of permeable sand and gravel yield significant quantities of water and provide the sole source of water supply for Cape Cod communities.

The flat terrain has led to the belief that Cape Cod soils are simple and consist of homogenous medium sand. This belief is untrue, as the soils contain interbedded silts and clays, remnants from kettle ponds, buried river valleys (Mulligan et al., 2003), and shallow lakes. Local variations in topography, lithology, and depositional environment result in a complex and heterogenous assemblage of that may vary several orders of magnitude both laterally and vertically (see **Table 2**).

Table 2. Typical Hydraulic Conductivity on Cape Cod

Lithology	**Hydraulic Conductivity** *(feet/day)*	**Ratio of Horizontal to Vertical**
Silt and/or clay till	1 - 10	1:1 - 100:1
Glacial moraine	10 - 150	10:1 - 100:1
Sand	450	10:1
Sand and gravel	500	3:1
Gravel	600	3:1
Sources: *Guswa and LeBlanc (1985) and Masterson et al. (1997)*		

Hydraulic conductivity values can vary by more than an order of magnitude within soil types that are similarly labeled. Layers of finer grained soils (fine sands, silts, clays) can also be present within predominantly sandy soils on Cape Cod. These variabilities in stratigraphy and hydraulic conductivity can result in groundwater seepage velocities varying spatially and vertically at a given site as well as nitrogen mass flux in groundwater flow. This variation necessitates that any area be well characterized both laterally and vertically to understand the geologic and geochemical conditions, and associated effects on groundwater flow and nitrate concentration, prior to evaluating options to control nitrate.

5.4 HYDROGEOLOGY, GROUNDWATER FLOW AND DIRECTION

As part of site evaluation and PRB design groundwater elevation must be mapped across the entire study site using a network of monitoring wells. This network of wells can provide information on the direction of groundwater flow, the hydraulic gradient (change in groundwater elevation over distance), and groundwater velocity at a given site.

Groundwater seepage velocity (v_s) is calculated using hydraulic conductivity (K), hydraulic gradient (i), and porosity (n).

$$\mathbf{v_s = K * i / n}$$

- Hydraulic conductivity (K) is a measure of the capability of the soil material to transmit water and is also referred to as coefficient of permeability. Hydraulic conductivity has units similar to velocity (length over time such as ft/day or cm/sec). Hydraulic conductivity can be estimated using the soil type, and for sandy soils can be estimated using grain size distribution from soil cores using the Hazen method or other similar methods. Site-specific hydraulic conductivity should be evaluated using pumping tests or rising head/falling head tests. ASTM D2434-22 (Standard Test Methods for Measurement of Hydraulic Conductivity of Coarse-Grained Soils) provides additional details on measuring hydraulic conductivity. Soil zones with higher hydraulic conductivity (high permeability zones) can transport considerably more groundwater, and therefore nitrate.
- Hydraulic gradient (i) is the calculated change in hydraulic head over a horizontal distance in the direction of groundwater flow. Hydraulic gradient is determined from site-specific measurements of groundwater elevation in monitoring wells. Groundwater flows along gradient from high to low head. Hydraulic gradient is reported as unitless or with units of distance over distance (for example, change in head feet divided by horizontal distance in feet). Hydraulic gradient must be determined from a synoptic (at the same time) groundwater elevation event. Hydraulic gradient should never be estimated using groundwater elevation collected on different dates. In addition, on sites that may be tidally influenced groundwater elevation measurements must be collected in a short period of time (15 to 30 minutes).
- Porosity (n) is the volume of pore space within a soil material. Recognizing that not all pore space transmits groundwater (e.g., dead end pore space, immobile porosity) porosity is often measured as effective porosity (n_{eff}) or that pore space that is capable of groundwater flow ($n_{eff} < n$). Porosity can be estimated in the lab using soil collected from the site. Variability in porosity typically is less than a factor of two, with porosity ranging between 0.2 and 0.35 for most overburden porous media. At many sites a sensitivity analysis using a range of porosity values based on observed soil type is adequate. See Section 5.9 for additional information on porosity as related to PRB design.

A minimum of three wells, oriented as a triangle, are required to determine groundwater flow direction. However, more wells for measuring groundwater elevation will allow more precise determination of flow direction and hydraulic gradient and can also identify groundwater variability at a site. The minimum spacing between wells must be adequate to identify enough of a difference in groundwater elevation to define the surface of the groundwater (piezometric surface).

Groundwater flow direction and hydraulic gradient can vary spatially and seasonally across a site based on a variety of aboveground and below ground features including but not limited to storm drains/sewers, water discharge to the subsurface (e.g., gutter downspouts), stormwater detention features, nearby surface water features, and groundwater pumping wells for potable or irrigation water usage. Groundwater flow direction can change several tens of degrees over time (Gavaskar et al., 2000). It is also important to consider groundwater levels at the time of measurement relative to historic averages. A single groundwater measurement event at historic high or low groundwater elevation may result in overestimating or underestimating the groundwater flow velocities and/or show variation in groundwater flow direction. A higher number of monitoring wells is recommended for determination of groundwater direction and hydraulic gradient if any of these features are present.

5.5 NITROGEN FLUX

The mass flux of nitrate is the mass of nitrate flowing across an identified area per unit of time (units of mass per area-time). PRBs are best located where reduction of nitrogen flux will support attainment of a watershed-specific target, as noted in Section 5.1. Nitrate mass flux is determined using nitrate concentrations and groundwater flow (q) estimates. Since a mass flux quantifies mass of nitrate flowing across a thin cross-sectional area (A_c), porosity of the soil is not considered.

$$\mathbf{q = A_c * K * i}$$

As described in Section 5.4 groundwater flow uses hydraulic gradient (i) from change in groundwater elevation in the direction of groundwater flow and hydraulic conductivity (K, which is an aquifer soil specific property estimated through pumping tests).

Groundwater flow velocities may vary depending vertically upon the site stratigraphy. Nitrate concentration also varies vertically. It is important to understand the groundwater flow rate and flux of nitrate-N through the different stratigraphic layers, as it is critical that the PRB target the vertical zones with the highest nitrate-N flux.

For denitrification PRBs where nitrate mass reduction is the objective, there is not a minimum concentration of nitrate to consider for PRB design. Assessment of nitrogen flux at the PRB location, accounting for concentration and groundwater flow, is more important than only nitrate concentration.

5.6 GROUNDWATER GEOCHEMISTRY AND WATER QUALITY PARAMETERS

Soil chemistry includes other substances which normally would not be thought of as a contaminant but may interfere with treatment reactions. Soil and aqueous matrix chemistry includes other species and factors such as, major cations and anions, mineral content, physical parameters such as pH and oxidation reduction potential (ORP), soil buffering, ion exchange capacity, alkalinity, acidity, and salinity. The interaction of factors can be complex. Groundwater quality parameters such as mobilization of iron (Fe), manganese

(Mn), phosphate, and arsenic (As) may impact PRB performance and need to be considered as part of the PRB design (see Sections 5.6.1 and 6.1.4).

Groundwater quality parameters, such as dissolved oxygen (DO), pH, ORP, temperature, specific conductance, and turbidity are typically measured during well purging with a water quality meter prior to sampling. An evaluation of the impacts and need for characterization of the other matrix parameters will be determined on a case-specific basis.

5.6.1 Terminal Electron Acceptors

For denitrification PRBs, nitrate will be the primary groundwater contaminant to be treated. However, other terminal electron acceptors will impose a demand for carbon substrate electron donor (increase consumption of EVO in the subsurface).

DO is the primary competing electron acceptor for denitrification PRBs as DO must be significantly reduced or fully consumed (below 1 mg/L) before nitrate reduction can be initiated. Freshly recharged groundwater is rich in DO unless it passes through a layer of high organic matter like peat or marsh sediments. Deeper groundwater may also have lower oxygen levels due to the slow loss of oxygen to biological and physical processes over long travel distance and time. As such, shallower PRBs will tend to have more DO with more EVO being consumed than deeper installations.

Other terminal electron acceptors that can result in bacterial EVO consumption, listed in order of decreasing energy yield, include:

- Manganese (Mn^{4+}) will reduce to the form Mn^{2+}.
- Ferric iron (Fe^{3+}) will reduce to soluble ferrous iron (Fe^{2+}).
- Sulfate (SO_4^{2-}) will reduce to sulfide (S^{2-}).
- Carbon dioxide (CO_2) will reduce to methane (CH_4).

Other groundwater contaminants (e.g., volatile organic compounds), should they be present, can also exert a demand for EVO in the PRB. The presence of reduced compounds in the vicinity of the PRB may sustain denitrification for a significant period after EVO is completely consumed (see Section 5.11).

5.6.2 Groundwater pH

The pH of the groundwater can also impact denitrification rates (Gonsalez et al., 2023; Gonsalez, 2020) with significantly lower denitrification rates below pH 4.6 and above 8.3. Groundwater pH has been recorded between pH 4.0 and 5.0 in individual monitoring wells at sites where denitrification PRBs demonstration tests have been performed (Water Vision, 2016; AECOM, 2016; Gonsalez, 2020), and therefore existing groundwater pH may inhibit effective denitrification. Gonsalez et al. (2023) describes a framework for modeling the impacts of pH and EVO on denitrification PRB using the Activated Sludge Model.

Buffers such as sodium bicarbonate or calcium carbonate are inexpensive and can be injected along with the EVO solution to bring acidic pHs into a more favorable range. Sodium bicarbonate (baking soda) is significantly more soluble (96 grams per Liter (g/L) at 20 C) than calcium carbonate (0.01 g/L at 20º C under low carbon dioxide levels). The maximum pH that sodium bicarbonate will generate is 8.3 SU. Thus, calcium carbonate may maintain the pH in a favorable range for a longer period but will be more difficult to inject because of the low solubility. Other available buffers include potassium bicarbonate, sodium carbonate (soda ash), calcium oxide or calcium hydroxide, magnesium hydroxide or magnesium oxide, and sodium hydroxide. The drawback to many of these alternative buffers is that they can take the pH too high. Lee et al. (2010) used sodium carbonate to raise the pH of an aquifer from 4.8 to neutral.

5.7 DENITRIFICATION PRB DIMENSIONS

Three key dimensions need to be determined for all PRB designs. PRB length is the PRB dimensions perpendicular to groundwater flow direction. PRB height is the vertical treatment interval for the PRB. PRB width is the dimension parallel to groundwater flow direction (see **Figure 3**).

PRB length and PRB height are determined by identifying where treatment of nitrate concentrations/fluxes spatially and vertically will support attainment of a watershed-specific target and where access is available to employ injection.

Determining the PRB dimension parallel to groundwater flow direction (width) must provide adequate residence time for the denitrification reactions. Under favorable conditions, denitrification reactions occur rapidly. A column study by (Gonsalez, et al., 2022) operated at room temperature of about 21 ºC has shown that residence times as little as 0.07 days is sufficient to allow complete denitrification when EVO substrate is uniformly distributed. However, carbon substrate distribution cannot be assumed to be uniformly applied using injections. Subsurface temperatures are cooler than 21 ºC in many parts of the United States, including Southern New England which may impact biological reactions. In addition, groundwater does not flow uniformly through porous media, and preferential (faster) flow paths for nitrate will exist.

The overall PRB width is determined by the flow rate in the target zone(s) and the corresponding flux to provide an adequate residence time within the PRB. A typical rule of thumb is for the PRB to have a minimum of a 3-day residence time using average groundwater seepage velocity to allow complete denitrification to occur (Lee et al., 2016). Longer residence times of 7 to 14 days are recommended to ensure adequate contact of nitrate and other terminal electron acceptors with the EVO adsorbed to the soil. Groundwater flow direction can vary spatially and seasonally at a PRB, and hydraulic conductivity may vary by as much as a factor of 5 or 10 between estimated and actual field conditions, even with careful site characterization. With these uncertainties, designing a wider PRB will allow residence time and capture zone requirements to be met for an effective PRB (Gavaskar et al., 2000).

5.8 DOSAGE OF EVO FOR DENITRIFICATION PRBS

EVO dosages and longevity are important considerations for PRB injection. The required EVO dosage is dependent upon the following factors (Lee et al., 2016):

- Groundwater flow rate.

- Competing electron acceptors like DO, sulfate, ferric iron, manganese, and carbon dioxide.
- Treatment zone dimensions.

The initial distribution of the EVO will be dependent on the amount of EVO injected, the injection technique, and the amount of dilution water injected with the EVO. There will likely be some transport of the EVO downgradient with the groundwater, particularly with high groundwater flow rates and in sandy soils with little clay or organic matter. As a rule of thumb, sufficient EVO and dilution water should be added for a minimum of 15% of the effective pore volume in the PRB. Higher loadings up to 30% of the effective pore volume may be appropriate for high groundwater flow rate aquifers. Column studies described in Solutions IES et al. (2007) demonstrated a loss of up to 66% in hydraulic conductivity occurred during injection of a small droplet EVO, but the hydraulic conductivity returned to background levels during flushing with clean water. Larger EVO droplets had more impact on the hydraulic conductivity.

5.9 EVO INJECTION VOLUME FOR DENITRIFICATION PRBS

The volume of EVO solution injected is a critical design parameter for any in-situ groundwater treatment program, especially PRBs. Application of adequate volume of EVO solution is necessary to achieve distribution of the carbon substrate for the PRB. The EVO volume needs to both carry the carbon substrate mass dosage and deliver it outward from the injection point. Research and experience of more than 20 years of injection for groundwater treatment in the hazardous waste remediation industry, including by the authors of this manual, have observed that increasing the injection volume for in-situ groundwater treatment (oxidants, bioremediation agents, or other remediation reagent) can result in a larger radius of influence, the need for fewer injection events, and more effective concentration reduction of groundwater contaminant(s). A consideration when designing injection volume for a PRB is that volume impacts time to perform injection, which affects the overall PRB cost. For that reason, PRB design cannot be based upon injecting as much volume as possible while also not injecting too low EVO volume that results in inadequate performance for nitrogen removal. The PRB design must balance injecting sufficient EVO volume to maintain performance while keeping the injection duration and associated cost within the project budget and expectations. This section discusses factors to consider when selecting injection volume for an EVO PRB.

The emulsion component of EVO, which includes hydrophobic vegetable oil droplets surrounded by a surfactant, partitions onto soil particles within a short distance from the injection (Solutions-IES, 2006). Therefore, focus for an injection should be given to the immediate contact between the injected EVO and the aquifer media to establish the target treatment zone (Huling et al., 2017) and to minimize gaps in the PRB that would result in nitrogen impacted groundwater flowing through the PRB untreated. Post-injection transport of dissolved organic carbon in the downgradient direction can result in additional denitrification in the aquifer and will be dependent on hydrogeologic conditions and EVO loading. For example, in higher groundwater flow aquifers dispersion will be lower resulting in less lateral transport of injected carbon substrate after injection, and therefore at these sites distribution of EVO perpendicular to groundwater flow will almost be entirely a result of initial injection.

Within porous media aquifers, a fraction of the overall total porosity contributes to much of advective flow and transport of nitrogen in groundwater, and this is referred to as the mobile (or effective) porosity; the portion of the porosity void space that does not contribute to the advective flow of groundwater is immobile porosity (Payne et al., 2008). Standard aquifer testing protocols are used to calculate average hydraulic conductivity which combines mobile and immobile porosity, which can underestimate the actual groundwater flow velocities. Few sites collect data to determine mobile porosity. Mobile porosity of sand and gravel aquifers, as observed on Cape Cod, was estimated to be less than 0.1 with mobile porosity values ranging from 0.02 to 0.10 (Payne et al., 2008), compared to n_{eff} values of 0.20 to 0.35 for most aquifers with sandy soils.

Injection volumes based on targeting a fraction of the overall pore volume of the PRB is recommended for this design manual. As noted above a significant portion of groundwater flow, and nitrogen transport, occurs in the smaller fraction mobile porosity. However, higher transport in the mobile porosity will result in faster groundwater flow speeds for the aqueous nitrogen species than would be calculated using conventional methods to estimate hydraulic conductivity. Targeting the total n_{eff} provides a safety factor for establishing adequate residence time and in distributing EVO across the width of a PRB. Additionally, even though most sites do not specifically measure porosity, the value of this parameter will vary by a factor of less than 1.5 between most sites when the predominant soil type is known.

For injection of chemical oxidants, injection volumes range from less than 10 percent to more than 50 percent of total porosity (Battelle/NAVFAC, 2013); however, chemical oxidants are often applied in multiple injection events. For injection of emulsified reagents, a study recommended 10 percent to 30 percent of total porosity (Geosyntec, 2009). ISOTEC and Terra Systems generally recommend injection of 8 percent to 20 percent of total estimated pore volume for EVO injections and designing in the upper half of this range for PRB applications. Design injection volumes for denitrification PRB demonstration tests on Cape Cod between 2016 and 2020 were based on injecting 12% to 20% of effective pore volumes.

Increasing the injection volume can help to distribute EVO more uniformly within the PRB supporting establishment of reactive residence time and minimizing potential for nitrate containing groundwater to flow through untreated. Other site-specific factors need to be considered in determining injection volume. A higher design injection volume can be selected for sites with more permeable soils (sands, gravels), and a lower injection volume should be considered for soils with lower hydraulic conductivity (silts, clay, till) to minimize groundwater mounding and/or preferential flow. Lower design injection volumes should also be considered for sites with shallow depth to groundwater (especially 8 feet or less), subsurface utilities, or other sensitive receptors, such as surface water, potable water wells or catch basins.

5.10 EVO INJECTION POINTS FOR DENITRIFICATION PRBS

Injections to the groundwater are generally performed using a regular-spaced line of injection points. Injection using a row of closely spaced points is intended to establish a continuous barrier length to minimize potential for groundwater to flow through gaps in the reactive zone. Closely spaced points reduce the injection volume of EVO and dilution water at each point as well as increase the distribution of the EVO in the subsurface, which is intended to prolong the persistence of the EVO after injection.

Spacing of injection points for PRBs will be determined based on site features above and below ground. Injection points should be offset by at least five feet from any known underground utilities (10 feet from water mains) to minimize damage to utilities during drilling or monitoring wells to reduce the potential that the injected amendment could short circuit through the utility conduits or well sand packs. Clearance of injection points by DigSafe (Call 811) and/or ground penetrating radar (GPR) should be performed prior to the injection event to avoid impacting utilities or storm water drains. Closer spaced injection points will result in a PRB with overlap of injected reagents to minimize groundwater flowing through the barrier without reaction. However, closer spaced injection points require more drilling for installation of injection wells or advancing more temporary injection points. Spacing of injection points for denitrification PRB demonstration tests on Cape Cod between 2016 and 2020 was generally 10 feet.

Some injection PRBs utilize two rows of injection points to increase PRB residence time and reduce the potential for groundwater flowing through the PRB not contacting the reactive media or substrate. A double line of staggered injection points would likely provide for better distribution and longevity and a lower possibility for nitrate to flow through a PRB untreated than a single row of injection points. Increasing the injection volume can help to distribute EVO more uniformly. However, in the Orleans PRB example which compared one row of injection points to two rows of staggered injection points, there was no obvious difference in nitrate removal or dissolved organic carbon (DOC) distribution between the two configurations.

PRBs established using injection points can apply carbon substrates and other reagents through semi-permanent PVC wells or directly through direct-push (i.e., Geoprobe®) rods (**Figure 4**). The advantages of direct-push injections are that there is no well construction required so there is no added cost for well installation, maintenance, and abandonment. An additional advantage of direct-push injection points is the greater flexibility for target treatment of vertical intervals with higher nitrate flux. Injection can be performed across the entire vertical zone of a PRB using multiple injection intervals with injection screen raised or lowered (if using bottom-up or top-down injection, respectively).

The advantages of installed injection wells are that they can be used as monitoring points (if the substrate is adequately flushed out of the injection well) and can be used again for reinjections in the future. In some cases, injection wells can be installed to greater depths than direct push points or through formations such as cobbles or geological features that the direct push equipment cannot penetrate. Injection screen lengths are typically recommended to be less than 10 to 15 feet due to heterogeneities in hydrogeology (authors' experience and Huling, et al., 2017). Therefore, for a treatment interval of more than 15 feet, multiple injection well screens are recommended to be constructed at each point. For both injection wells and direct-push injection tooling, vertical injection interval should consider geologic stratigraphy and targeting observed soil layers. In addition, for injection well PRBs, it is recommended to apply a sufficient volume of chase water (minimum of 3 well volumes) after injection of carbon substrate to minimize biofouling to allow the injection wells to be used for an additional injections in the future.

Figure 4. Direct-push drill rig used to advance temporary injection points for a PRB, and injection PRB using PVC injection wells.

In summarizing this section, utilizing shorter injection intervals, a greater number of injection points, and smaller spacing in between injection points will increase the probability of applying evenly across the PRB treatment zone, reduce delivering excessive carbon substrate into preferential pathways, and prevent gaps in the PRB that would allow nitrate to flow through the barrier.

5.11 EVO INJECTION FREQUENCY

EVO and other slow-release carbon substrate electron donors have been demonstrated to enhance biodegradation for groundwater treatment of chlorinated VOCs such as tetrachloroethene and/or trichloroethene for 3 years to more than 5 years. At the demonstration test denitrification PRB in Orleans, MA reducing conditions and ongoing denitrification is occurring more than 7 years after initial injection of a modified EVO formulation (SRS®-NR) developed to increase retention in coarse grained (sandy) soils. Denitrification bench scale column studies have indicated that a minimum concentration of 2 mg/L total organic carbon (TOC) can sustain complete denitrification (Lee et al., 2016), which is lower than desired TOC concentration for biodegradation of chlorinated VOCs by reductive dechlorination (10 mg/L).

The longevity of denitrification PRBs is continuing to be monitored, including at the four demonstration tests implemented on Cape Cod from 2016 to 2020. It is anticipated that EVO injection PRB lifetimes of 5 years to more than 10 years can be expected based on observations of reduction of nitrate concentrations downgradient of denitrification PRB demonstration tests on Cape Cod and depletion of nitrate detected in groundwater downgradient of anthropogenically generated anoxic conditions (for example, EVO injections to enhance reductive dechlorination or fuel oil release from an underground storage tank). An EVO barrier to enhance denitrifying bacteria has been active for more than 10 years at a site in West Virginia for treatment of nitroaromatics including 2,4,6-trinitrotoluene (TNT); nitroaromatic compounds are also biodegraded by anaerobic denitrifying bacteria (Downey et al., 2023).

However, complete removal of nitrate entering a PRB may not be necessary for attainment of nitrate mass reduction objectives and watershed TMDLs. A management approach that does not target complete removal as a trigger for rejuvenation may significantly increase the time between reinjection events, resulting in a more cost effective PRB design.

The persistence of denitrification triggered by anaerobic PRB installation may also be extended by fortuitous nitrate-dependent anaerobic ferrous iron (Fe^{2+}) oxidation (NAFO). Outwash sands within Atlantic coastal plain aquifers, including on Cape Cod, are typically coated with iron oxide (ferric oxides) (Penn et al., 2001; Charette & Sholkovitz, 2002). The iron (Fe^{3+}) in iron oxides are electron acceptors, and the iron is reduced within the anaerobic PRB injection zone resulting in increased dissolved ferrous iron (Fe^{2+}) in groundwater. Concern regarding dissolved ferrous iron generated as a secondary water quality contaminant has led to assessment of the mobility and persistence of ferrous iron downgradient of PRBs. An in-depth study by Borden et al., 2015 found that generated ferrous iron during injection of a liquid carbon substrate does not migrate significant distances from the injection zone. Migration is limited because it is typically bound to soils downgradient of the injection point by chemical and physical processes. The soil bound ferrous iron may then act as a secondary permeable barrier, removing nitrate even after the injected carbon substrate is fully depleted (Borden et al., 2015). This secondary ferrous iron barrier relies on NAFO. The ferrous iron generated by the primary barrier is re-oxidized during denitrification by an autotrophic biological process. This process converts nitrate to nitrogen gas using ferrous iron as electron donor under anoxic conditions (Zhang et al., 2014). Confirmation of the NAFO pathway and quantification of the potential benefit of NAFO for extended nitrate reduction should be evaluated with a site-specific assessment and is not addressed in this design guidance.

Nitrate concentrations will be the primary analyte to monitor for effectiveness of a denitrification PRB. However, influent nitrate concentrations do fluctuate temporarily, and a single event detecting nitrate downgradient of a PRB may result. Other indicators of reducing conditions in groundwater favorable for denitrification should be evaluated when considering if re-injection is needed for an EVO PRB, notably DO (<1 mg/L desired) and oxidation-reduction potential (negative values desired). If DO, ORP, and nitrate are all observed to increase in more than one sampling event, denitrification may no longer be effective. TOC or DOC levels are important to monitor also. When they fall below 5 mg/L near the PRB, heterotrophic denitrification may slow.

5.12 DENITRIFICATION PRB DESIGN CALCULATOR

To support PRB design using this engineering design manual, the ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** was developed in Microsoft Excel. This subsection describes the tool and provides guidance on using the calculator. The groundwater flow rate is a function of soil properties such as hydraulic conductivity and porosity and the hydraulic gradient. Sandy soils with little clay and those with a steeper gradient will have higher groundwater flow rates.

DO concentrations range from 0 to 12 mg/L with colder waters holding more DO. DO is the primary competing electron acceptor for denitrification PRBs as DO must be significantly reduced (below 1 mg/L) before nitrate reduction can be initiated. Freshly recharged groundwater is rich in DO unless it passes through a layer of high organic matter like peat or marsh. As such, shallower PRBs will tend to have more DO than deeper installations with more EVO being consumed for DO reduction. Other electron acceptors that can result in bacterial EVO consumption include manganese and iron oxides, sulfate, and carbon dioxide (listed in order of energy yield). In most freshwater systems, sulfate is generally between 5 to 200 mg/L. Elevated concentrations of sulfate in groundwater may not adversely impact denitrification reactions but can reduce the longevity of the EVO PRB. Sulfate concentrations are highly elevated in saline environments such that PRB installation should be avoided where salt-water intrusion is a possibility. Without a previous injection of a similar organic substrate at the site, it is difficult to predetermine how much manganese and iron will be reduced, and how much carbon dioxide will be converted to methane. Lebron et al. (2005) presents a bioavailable ferric iron assay, but it has not been widely applied. Based upon data from many chlorinated solvent contaminated sites treated with EVO, a common rule of thumb is to assume the following will be produced:

- 5 mg/L manganese (Mn^{2+}).
- 50 mg/L ferrous iron (Fe^{2+}).
- 10 mg/L methane (CH_4).

In the four PRB pilot tests conducted on Cape Cod, maximum dissolved or ferrous iron concentrations ranged from 1.1 to 263 mg/L, maximum dissolved manganese from 8.2 to 29.7 mg/L, and maximum methane (where measured) from 6.6 to 18.1 mg/L (see **Attachment 1** with additional details on denitrification PRB demonstration tests on Cape Cod).

The treatment interval is another important factor. Nitrate-N concentrations are typically between 1 to 10 mg/L but were as high as 40 mg/L in the PRB pilots tests. Nitrate-N levels vary with depth, and it is important to make sure that the EVO is distributed in the zone that has the highest flux of nitrate due to the groundwater flow rate and nitrate-N concentrations.

The EVO dosage can be calculated using simple stoichiometric models like the ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** to estimate the substrate demand for the site. The ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** assumes an emulsified vegetable oil product with 60% vegetable oil will be applied. The electron donor contributions from the surfactants and any quick release substrates like 60% sodium lactate or glycerol are not included. The primary factors that control the substrate demand are the width of the plume, the groundwater flow rate, and the electron acceptor concentrations, including dissolved oxygen and nitrate. The ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** requires the user to enter the barrier length, barrier width, depth to top of PRB, depth to bottom of PRB, hydraulic conductivity, hydraulic gradient, porosity, injection target pore volume, injection grid spacing, number of injection rows, design period, design factor, and electron acceptors.

For denitrification PRBs, a minimum design period of 5 to 10 and a design factor of 3 are recommended (see Section 5.11). More conservative designs with a longer design period or larger design factor can be employed. Lee et al. (2013) reported organic carbon concentration over 10 mg/L for between 0.2 and greater than 6.9 years at chlorinated solvent impacted sites. Denitrifying bacteria require lower organic carbon concentrations (2 mg/L, Falmouth column study I in **Attachment 1**) and less reducing conditions, suggesting that an even longer period could be required for replenishing an EVO PRB for denitrification. Depending upon the groundwater flow rate, concentrations of competing electron acceptors, and distribution of EVO in the first injection, replenishment of the PRB may be required after 5 to more than 10 years.

Other bioremediation calculators for estimating carbon substrate electron donor quantities, including the ESTCP Substrate Estimating Tool for Enhanced Anaerobic Bioremediation of Chlorinated Solvents (ESTCP, 2010; Henry, 2010) can be used. Other parameters, in the ESTCP Substrate Estimating Tool including oxidation-reduction potential, temperature, pH, alkalinity, total dissolved solids, specific conductivity, chloride, pre-injection and post-injection sulfide, aquifer matrix total iron, cation-exchange capacity, neutralization potential, soil bulk density, soil fraction organic carbon (f_{oc}), and volatile organic constituents concentrations not included in the PRB EVO Dosage Calculator as they do not impact the carbon substrate demand calculations and are not included as input parameters in the ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** developed for use with this manual.

Use of column studies that simulate site-specific conditions and/or an in-situ demonstration studies can be used to confirm and modify carbon substrate loading estimating from a calculated dosage.

5.12.1 Denitrification PRB Design Calculator Input Parameters

User input parameters are listed in this section and summarized in **Table 3**. The input parameters are assembled in key groups. As detailed throughout Section 5.0, geology, hydrogeology, and nitrogen concentrations/flux vary spatially and vertically. Accordingly, the authors recommend developing separate ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** models for different zones of the PRB. For example, two different calculators may be prepared for different geologic strata where groundwater flow varies.

5.12.1.1 PRB Size and Location

Sections 5.1 and 5.7 describe locating and sizing a denitrification PRB, respectively. Input parameters for PRB size will be determined based on identifying where a reduction of nitrogen flux using a PRB will support attainment of a watershed-specific target, groundwater sampling results, and access. Key size parameters include:

- Barrier length (perpendicular to groundwater flow).
- Barrier width (parallel to groundwater flow).

- Depth of top of barrier (based on groundwater sampling).
- Depth of bottom of barrier (based on groundwater sampling).

5.12.1.2 Geology and Hydrogeology

Sections 5.3 and 5.4 provide details on geology and hydrogeology and relationship to PRB design and function. Key geologic parameters include:

- Hydraulic conductivity:
    - Field measurements for hydraulic conductivity are the best means for selecting a value. Authors experience with design of in-situ groundwater treatment has encountered that hydraulic conductivity values calculated using site-specific testing can differ by more than an order of magnitude from estimates of hydraulic conductivity by observed soil type.
- Hydraulic gradient (see Section 5.4).
- Effective porosity (see Section 5.4).

5.12.1.3 Groundwater Entering PRB

Sections 5.2 and 5.6 provide details on groundwater quality and important analytes for PRB design. The concentration of nitrate, dissolved oxygen, and sulfate should be determined from site-specific measurements to enter in the design calculator.

Total dissolved manganese, total ferrous iron, and methane are predicted values after the PRB zone is converted from aerobic to anaerobic. Values should be selected based on bench-scale or pilot-scale results for the site, or from a similar, nearby site, including:

- Nitrate + Nitrite ($NO_3^- + NO_2^-$).
- Dissolved oxygen (DO).
- Sulfate (SO_4^{2-}).
- Total Dissolved Manganese (Mn^{4+}).
- Total Ferrous Iron (Fe^{2+}).
- Methane (CH_4).

5.12.1.4 Injection Design Details

Sections 5.9 and 5.10 provide details on injection volume and injection points, respectively:

- Injection Target Pore Volume of the Barrier (8 to 20%, see Section 5.9).
- Injection Grid Spacing (8 to 15 feet, see Section 5.10).
- Number of Injection Rows (typically 1 or 2, see Section 5.10).
- PRB Design Time (desired duration for PRB to effectively remove nitrate):
    - Persistence will be determined by hydrogeology (longer persistence with lower groundwater seepage velocity), flux of nitrate and other terminal electron acceptors (e.g., dissolved oxygen), and overall EVO mass applied at the PRB.

- Design Factor:
    - This is a user-selected engineering safety factor. Authors recommend a range of 1 to 3.

Table 3. Denitrification PRB Design Tool Input Parameters

Parameter	Recommended Range	Relevant Manual Subsections
PRB Size and Location		
Barrier Length	Site-specific	5.1, 5.7
Barrier Width	Site-specific	
Depth of Top of PRB	Site-specific	
Depth of Bottom of PRB	Site-specific	
Geology and Hydrogeology		
Hydraulic Gradient (i)	Site-specific	5.3, 5.4
Hydraulic Conductivity (K)	Site-specific (K values based on observed soils can be used with sensitivity analysis)	
Effective Porosity (n_{eff})	0.2 – 0.35	
Groundwater Entering PRB		
Nitrate + Nitrite	Site-specific (use maximum value near the PRB)	5.2
Dissolved Oxygen (DO)		5.6
Sulfate (SO_4^{2-})		5.6
Manganese (Mn)	1 – 20 mg/L	5.6
Ferrous Iron (Fe^{2+})	5 – 50 mg/L	5.6
Methane (CH_4)	1 – 20 mg/L	5.6
Injection Design Details		
Injection Target Pore Volume	8 – 20+ percent of barrier pore volume	5.9
Injection Point Spacing	8 – 15 feet	5.10
Injection Rows	1 - 3 (2 off-set rows recommended to minimize groundwater flow through and increase residence time in PRB)	5.10
PRB Design Time	Site-specific (typically 5 – 10+ years)	5.11
Design Factor	1 – 1.3	5.11

6.0 MONITORING FOR DENITRIFICATION PRBS

Groundwater monitoring is a critical aspect of using PRBs to reduce nitrogen in groundwater. The analytical parameters, sampling frequency, and sampling locations will not be the same for all phases of the project. Evaluating locations for placing a PRB, PRB design, pilot/demonstration testing, and full-scale PRBs will each have different objectives for sampling. However, at a minimum, monitoring wells must be emplaced both upgradient as well as within and/or downgradient of the PRB. This section presents an overview of the important analytical parameters for monitoring for PRBs and considerations for analytes for different phases of PRB planning and assessment based on the authors' experience for design and evaluation of PRBs. Monitoring wells should be carefully constructed to prevent stormwater infiltration that would confound monitoring results and prevent cross contamination and groundwater mixing where multi-level monitoring wells are installed. The USEPA guidance document titles "Design and Installation of Monitoring Wells" can be consulted for procedures and methods to be used when installing permanent and temporary groundwater monitoring wells for collection of groundwater samples (USEPA, 2008). For additional details on developing a monitoring program, consult "Hydrologic Site Assessment for Passive Treatment of Groundwater Nitrogen With Permeable Reactive Barriers, Cape Cod, Massachusetts" that was jointly prepared by the USEPA, United States Geologic Survey (USGS), and the Cape Cod Commission (Barbaro, et al., 2019).

6.1 PRIMARY ANALYTES

Primary analytes for PRB monitoring include groundwater analyses to assess nitrate transformation (or reduction), distribution of the injected reagents, and key water quality indicators used to determine if conditions favorable for anoxic denitrification reactions are present. Additional information on primary analyses is included in **Table 4** below.

6.1.1 Nitrogen Species

Since the primary objective of a denitrification PRB is to reduce the mass load of nitrogen in groundwater, quantifying the concentration of nitrogen species is required. Nitrate and nitrite (or nitrate + nitrite) analyses should be included for all denitrification PRB associated groundwater sampling.

Analysis for ammonium (NH_4^+) and/or total Kjeldahl nitrogen (TKN, sum of NH_4^+ and organic nitrogen) will provide input on if reduced nitrogen sources may be present in the vicinity of the PRB (for example, leachfield(s) or a landfill). Quantifying NH_4^+ and/or TKN will be more important during initial site assessment and in baseline sampling to determine if reduced forms of nitrogen are present at a sampling location.

6.1.2 Total Organic Carbon or Dissolved Organic Carbon

Denitrification PRBs involve introduction of a carbon substrate to the subsurface to enhance activity of anaerobic denitrifying bacteria. EVO and mulch biowalls have been evaluated on Cape Cod, Massachusetts and elsewhere. Quantifying organic carbon in groundwater within and downgradient of a PRB will provide indication of the distribution of the added carbon substrate and if sufficient organic carbon is present to support denitrification. Bench scale column studies have indicated that a minimum concentration of 2 mg/L total organic carbon (TOC) can sustain complete denitrification of 20 to 27 mg/L nitrate-N at a flow rate of about 1.1 feet/day [Lee et al., 2016)]. TOC or dissolved organic carbon (DOC) are recommended analytes to quantify organic carbon. Both parameters do not need to be tested for in a sample. TOC will often be higher than DOC as filtration for the DOC measurements can remove EVO droplets or fine particle-bound carbon. Post injection the concentration of DOC will vary temporally and spatially. Immediately post injection DOC levels will increase significantly downgradient of the PRB. Once the biomass of heterotrophic bacteria increases in response to the presence of the substrate, the concentration of DOC will decrease to lower levels due to an equilibrium between DOC generated from the stationary oil droplets and DOC utilization by soil bacteria, including denitrifying bacteria. Long term monitoring of PRB performance should mainly rely on observed nitrate concentrations and the reduction/oxidation (redox) condition of groundwater.

6.1.3 Field Water Quality Parameters

Groundwater quality parameters are important parameters that are measured in the field using available water quality meters, including, but not limited to, those manufactured by Hanna Instruments, In-Situ, and YSI. These field parameters provide lines of evidence on redox conditions within the aquifer and if conditions are favorable for denitrification. The following sensor-based water quality parameters are recommended for measurement.

- <u>Dissolved oxygen (DO).</u> Denitrification is performed by anoxic bacteria which are most active where oxygen is low or not present (less than 0.5 mg/L). However, denitrification can occur in oxygen concentrations of 1 or 2 mg/L (Rivett et al., 2008), which are mostly due to micro-anaerobic environments formed by particulate organic matter, heterogeneous soil lenses with higher organic carbon content, or biofilms. DO should be measured in the field as DO can change in samples collected for laboratory analyses. DO concentrations, and comparison to pretreatment or upgradient locations, can be used to evaluate if anaerobic conditions are present. As DO can be difficult to measure, care should be taken to ensure that the DO meter is properly calibrated, groundwater is not exposed to air during collection, and that the DO readings are consistent with other measurements. For example, a negative ORP would not be expected with elevated DO (>2 mg/L).
- <u>Oxidation Reduction Potential (ORP).</u> This parameter provides indication of the groundwater redox condition, how oxidizing or reducing an environment is. Denitrifying bacteria are anaerobic and prefer reducing conditions. ORP values less than 0 millivolts (mV) are most favorable for denitrification. ORP values higher than this do not preclude denitrification, but denitrifying bacteria will be less active as conditions are more oxidizing.
- <u>pH.</u> This parameter provides an indication of how acidic or basic groundwater is. Bacterial activity can vary with pH. Denitrifying bacteria, like many bacterial types, grow optimally within one or two pH units of neutral pH (pH 7). Lab studies using Cape Cod soils amended with EVO observed limited denitrification below pH 5.0 (Gonsalez, 2020). It should be noted that acidic

groundwater pH (pH 5 and lower) is measured in groundwater collected in wells across Cape Cod. Groundwater pH has been recorded between pH 4.0 and 5.0 in individual monitoring wells at sites where denitrification PRBs demonstration tests have been performed (WaterVision, 2016; AECOM, 2016; Gonsalez, 2020).

- Temperature: Optimal temperatures for denitrification bacteria are between 15 degrees Centigrade) (ºC) and 35ºC, and incomplete denitrification as demonstrated by nitrite accumulation has been observed at temperatures below 10ºC (Liao, et al., 2018). Groundwater temperatures as observed from quarterly sampling of PRB demonstration tests at Orleans and Falmouth sites on Cape Cod ranged between 9ºC and 22ºC.
- Specific conductivity. This provides an indirect measurement of the concentration of dissolved ions in water. Specific conductance values can be higher where saltwater intrusion occurs in groundwater, near roads where salt is applied in winter, and where other inputs occur to groundwater. Denitrifying bacteria are present in marine environments so high specific conductivity is unlikely to have much impact on denitrification (Pajares and Ramos, 2019).

6.1.4 Secondary Analytes

Additional analyses can be performed to provide information about the PRB and its impact on nearby groundwater and additional information to evaluate redox conditions.

- Sulfate (SO_4^{2-}) is an electron acceptor used by sulfate-reducing bacteria under anaerobic conditions more reducing than those needed for nitrate-reducing bacteria. Under sulfate-reducing conditions, SO_4^{2-} is converted to sulfide (S^{2-}). Sulfide is not commonly detected in groundwater samples as the metal sulfide precipitates (commonly iron sulfides) are a sink for soluble sulfide. A reduction in sulfate concentrations within and downgradient of a PRB would indicate that conditions are adequately reducing to support denitrifying bacteria.
- Metals (Fe, Mn and As). Denitrifying PRBs are installed with the objective of converting aerobic groundwater to a reducing environment to enhance anaerobic bacteria. Some metals are more soluble under anaerobic conditions, including iron and manganese. The concentrations of these metals can increase under reducing conditions created by the injection of carbon substrates. Furthermore, their mobilization in groundwater can lead to increases in arsenic and phosphate, which are normally bound to metal oxides present in groundwater aquifers. Metals such as arsenic that have water quality criteria should be monitored when evaluating PRBs near potable water wells and surface water bodies.

  It should be noted that if baseline/upgradient conditions are aerobic these metals may have low concentrations or not be detected. Bench scale or field pilot studies where anaerobic conditions are created can evaluate if these metals concentrations would increase with installation of a PRB. Cape Cod PRB demonstrations and the SERDP assessment of impacts of reductive bioremediation have shown that the migration potential of these secondary contaminants is limited (Borden et al., 2015).

- Phosphate (PO_4^{3-}). Phosphate is a nutrient required by microbes and algae. In some waters (typically freshwater environments), phosphate availability can control eutrophication. Phosphate tends to bind to soils and is not as readily transported in groundwater as nitrate; however, phosphate can be mobilized during iron reduction as noted previously. The estuarine waters around Cape Cod are typically nitrogen limited.

6.1.5 Tertiary Analytes

Additional analyses have been performed in studying PRBs at the bench and pilot scale in researching the denitrification processes. These tertiary analytes are not necessary to design or evaluate the performance of a PRB; however, these can provide a deeper understanding of the functioning of a denitrification PRB, or these parameters may be incorporated into denitrification PRB design as more is learned through research on the impact of these parameters on PRB operations.

- Methane (CH_4). Under highly reducing conditions, methanogenic bacteria are active and produce CH_4 from CO_2. CH_4 is a greenhouse gas and generation of this species in groundwater can escape to the atmosphere. However, CH_4 generated below the water table is likely to be consumed by aerobic microbes in the unsaturated zone above the PRB zone (Lee et al., 2005). In addition, observation of CH_4 at a denitrification PRB may indicate overdosing of carbon substrate.

  It should be noted that denitrification PRBs are generally installed into aerobic aquifers. Methane as well as other byproducts of generation of anaerobic conditions to stimulate denitrification may only be detected months or years after initial carbon substrate injection as more reducing conditions establish from the lack of oxygen/aerobic conditions to the PRB and downgradient.
- Microbial Testing. Batch reactor testing performed by Gonsalez (2020) using soil samples collected from two Cape Cod sites observed different rates of nitrate reduction. A more detailed investigation of the biomass in each reactor using quantitative polymerase chain reaction (qPCR) quantified total bacteria and three target genes from the denitrification pathway: nirK, nirS and nosZ (**Figure 2**). Samples were collected at the end of the experiment after anaerobic conditions for denitrification were established. The final total biomass and functional genes associated with denitrification were measured at lower concentrations in the soil test with a lower nitrate reduction rate. This study highlights the importance of biomass and microbial characterization in site characterization and design for denitrification PRBs as well as recognizing the spatial variability in the subsurface and differences in biomass ecology. Future denitrification PRB studies should consider analyses of denitrification target genes to understand potential for incomplete denitrification. As many sites considered for denitrification PRBs have aerobic groundwater at baseline, microbiology assessments for denitrification may require batch reactors where a carbon substrate electron donor is applied to a soil-groundwater slurry. However, nitrite reductase (nirS) presence in baseline samples did appear to be an indicator of denitrification potential (Gonsalez, 2020).

Microbiological tools to assess NAFO (Section 5.11), may be beneficial to evaluating long-term performance of denitrifying PRBs for removing nitrate and when re-injection may be required.

- <u>Nitrogen greenhouse gases.</u> Incomplete denitrification can generate nitride oxide or nitrous oxide that are greenhouse gases. More research is needed to evaluate if this occurs and if these gaseous nitrogen species migrate upwards and reach the atmosphere.

6.2 DATA QUALITY OBJECTIVES

Prior to installing any monitoring wells or collecting groundwater or soil samples, data quality objectives need to be defined for the phase of the project.

Data quality objectives for PRB design can include, but not be limited to, the following:

- Identify locations with elevated nitrate (nitrogen) concentrations and/or flux in groundwater for PRB siting.
- Identify pre-treatment nitrate (nitrogen) concentrations and range of seasonal variation.
- Determine groundwater flow direction at a location being considered for a PRB, including if groundwater flow direction varies seasonally.
- Determine groundwater seepage velocity, including site-specific hydraulic conductivity measurements.

Examples of data quality objectives for post-injection monitoring can include, but not be limited to, the following:

- Demonstrate reduction in nitrate concentrations in groundwater in monitoring wells compared to baseline samples and/or wells upgradient of the PRB.
- Quantify horizontal distance traveled by EVO emulsion.
- Identify the extent of generated reducing conditions.
- Evaluate potential for reduction in aquifer permeability because of EVO application.
- Evaluate persistence of EVO emulsion and anaerobic conditions favorable for denitrifying bacteria after PRB installation.
- Quantify increases in metals and/or other redox sensitive parameters (e.g., iron, manganese, arsenic, hydrogen sulfide) because of EVO injection.
- Assess changes in groundwater monitoring parameters because of the PRB.

Table 4. Summary of Primary and Secondary Analyses for Groundwater Performance Evaluation

Parameter	Relevance to Denitrification PRBs
Nitrate (NO_3^-)	Primary groundwater compound targeted for treatment.
Nitrite (NO_2^-)	Intermediate nitrogen species from the aerobic nitrification of ammonia to nitrate.
Ammonium (NH_4^+)	Reduced inorganic nitrogen species that occurs in proximity of leach fields and landfills.
Total Kjeldahl Nitrogen (TKN)	TKN is the summation of NH_4^+ and organic nitrogen. TKN will be higher in groundwater in proximity of leachfields before nitrification converts nitrogen species to nitrite and nitrate.
Metals (Fe, Mn, As)	Mobility of metals can be impacted by groundwater geochemistry changes, notably pH and ORP. Arsenic may be included as a redox-sensitive metalloid; arsenic solubility is connected with iron solubility.
Total Organic Carbon (TOC)	Indicator of injection of EVO or other carbon substrate
Sulfate (SO_4^{2-})	Sulfate will decrease with generation of sufficiently anaerobic conditions favorable for sulfate-reducing bacteria.
pH	Denitrification is optimal at circumneutral conditions, and significantly lower denitrification rates have been observed below pH 4.6 and above 8.3 (Gonsalez, 2020). Groundwater pH can decrease because of fermentation of injected carbon substrates.
Oxidation Reduction Potential (ORP)	ORP will decrease with generation of reducing conditions following injection of carbon substrate.

6.3 WHERE TO MONITOR

The spatial location of monitoring will be determined based on objectives of the PRB. For a denitrification PRB, one of the primary objectives will be to quantify a reduction in nitrate and nitrogen concentrations because of the PRB. Groundwater monitoring locations for a denitrification PRB should be established upgradient and downgradient of the PRB to comparatively evaluate groundwater conditions entering the PRB compared to changes after water flows through the reactive barrier. Monitoring wells should be able to collect groundwater data associated with different vertical intervals across the PRB, depending on the PRB vertical thickness and geological layers observed.

Placement of upgradient and downgradient monitoring well locations along the length of the PRB needs to consider several factors, including total PRB length, groundwater flow direction, proximity to surface water bodies and other environmental receptors, and upgradient land usage. Spacing of wells parallel to the PRB could be as close as 50 feet for demonstration tests or for shorter PRB lengths (less than 400 feet). For longer PRBs (1,000 feet to longer than 5,000 feet), monitoring well spacing parallel to the injection line could be 200 to 1,000 feet. A minimum of three monitoring well locations (upgradient and downgradient) are recommended for all PRBs to quantify flux reduction and assess groundwater flow direction at the PRB. Where long PRBs are being considered (more than 200 feet), multiple sets of three monitoring wells each should be considered to assess flow direction in more than one area.

There will be differences in selecting groundwater monitoring locations for a denitrification PRB pilot test compared with a full-scale PRB. A demonstration test will be anticipated to have more wells to evaluate nitrate removal, injectate distribution (horizontally and vertically), and other groundwater quality changes (DO, ORP, pH, metals, and terminal electron acceptors like sulfate). A denitrification PRB demonstration test will have downgradient monitoring wells located near to the PRB injection points (5 to 15 feet downgradient) to monitor conditions immediately adjacent to the PRB and in shorter time after injection (2 to 12 months). Further downgradient monitoring wells should also be considered for a PRB demonstration test to assess impacts on the aquifer as groundwater moves away from the PRB. Denitrification PRB demonstration tests on Cape Cod have identified groundwater changes 50 to more than 90 feet downgradient of demonstration test PRBs injection points. Changes are anticipated to extend 200 to 400 feet downgradient.

The monitoring well network for a full-scale system should be designed to monitor representative locations along the PRB rather than monitoring the full length with closely spaced monitoring wells. For full-scale PRBs, downgradient monitoring wells are recommended to be located 10 to 30 feet from the row of injection. At this distance range lines of evidence of the PRB injection points will be evident, including reduction in nitrate concentration, DO, and ORP potential as well as changes in TOC or DOC. This distance range is based on observations from PRB demonstration tests on Cape Cod as well as EVO injection for other enhanced biodegradation applications. Downgradient monitoring well locations are recommended to be closer to the PRB for finer grained soils, including fine sands and silts.

Identifying the groundwater flow direction at the PRB location is important for placement of monitoring wells and should be determined before installation of performance monitoring wells. Local groundwater flow direction can vary at a property due to extraction wells, stormwater holding tanks, water discharges, and subsurface utilities. If groundwater flow direction varies from what is assumed, downgradient monitoring wells may not observe lines of evidence of the denitrification PRB. The concern of downgradient monitoring wells not being aligned with the PRB is higher for short PRBs (150 feet or shorter) as a longer PRB has a large aquifer cross-sectional area and will also influence a larger downgradient zone that a monitoring well may be placed within. Monitoring well installation may need to be performed in two phases, with groundwater elevations measured to reassess groundwater flow direction at the PRB location prior to installing the remaining monitoring wells. It should be noted that groundwater flow direction may vary across the length of a PRB based on features above and below ground. Groundwater particle tracking models are useful tools for both locating a PRB and identifying subsections within a PRB where higher nitrogen fluxes may be traveling. Such models can be used to aid in selecting placement of monitoring wells upgradient and downgradient of a PRB and for estimating the capture zone of the PRB for assessment of wastewater sources and the associated nitrogen load to be intercepted.

For PRBs with a vertical treatment zone of more than 15 to 20 feet, multi-level monitoring wells should be installed.

Vertical monitoring well sampling interval, either from a screen or a discrete sampling port, must consider geological layers. As noted above in Section 5, different vertical intervals vertically across the PRB can contribute more or less groundwater flow and transport of nitrogen or PRB injectate. Geological boring logs and/or in-situ measurements for aquifer permeability (e.g., hydraulic profiling tool, pumping tests, or slug rising/falling head measurements) should be evaluated to select monitoring well sampling elevations/screen intervals. It is recommended that monitoring well screens do not overlap two distinctly different geologic layers. Tracer tests with an inert compound like bromide, fluorescein dye, specific conductivity, and others will determine the groundwater flow rates and, if multiple vertical sampling points are installed, may help to identify high flux zones. Additionally, monitoring well screen lengths should be a maximum of 15 feet for sampling a relatively uniform soil type, with shorter well screens preferred (<5 feet to 10 feet long), especially for a heterogeneous formation.

6.4 WHEN TO MONITOR

This section focuses on performance monitoring after injection of EVO to install a denitrification PRB. EVO PRBs have been demonstrated to enhance biodegradation for removal of nitrate, as well as other contaminants in groundwater, for 2 to more than 5 years depending on groundwater seepage velocity and concentrations of terminal electron acceptors, primarily DO and nitrate. Primary considerations for frequency of monitoring will be to assess if the PRB is effectively removing nitrate and to determine if/when re-injection may be required. Monitoring for more than 5 years will typically be required for direct assessment of longevity. The specific groundwater monitoring frequency may be determined by the Underground Injection Control permit.

More frequent groundwater monitoring is recommended during the pilot testing phase for a denitrification PRB to collect appropriate site-specific information to support the design of a larger-scale PRB. Ideally, initial groundwater sampling is performed 2 to 6 weeks after injection; this initial event will provide observations on where EVO was distributed as a result of the injection activities. This initial sampling event may consider a limited subset of analyses of TOC (or DOC) and field water quality parameters (DO, ORP, pH, and conductivity) as anoxic conditions favorable for denitrification will be developing. Quarterly groundwater sampling for a period of two years after a pilot test injection is the minimum frequency recommended. Quarterly sampling will provide insight into development of denitrification conditions, migration of TOC (or DOC) and reducing conditions, and seasonal fluctuations in groundwater velocity, nitrate, and other parameters.

For a full-scale PRB, a monitoring frequency needs to be established based on the objectives of the PRB and to quantify reduction of nitrate concentrations and nitrogen flux. Full-scale PRBs will have a large area to sample and sampling frequency and number of wells to sample need to be considered. It is recommended that a minimum frequency of annual sampling be performed for wells upgradient and downgradient of a PRB to assess change in nitrogen concentrations downgradient of the PRB. If a pilot test was performed at the location of a full-scale PRB, it is assumed that more is known about hydrogeology and injection distribution of EVO. For full-scale PRBs where a pilot test was not performed, a higher sampling frequency for the first 12 to 24 months after injection is recommended to document initial distribution of the EVO and reduction in nitrate concentrations. For full-scale PRBs monitoring, frequency should consider when during the year nitrogen mass fluxes are determined to be highest.

Remote sensing is anticipated to be more commonly used for PRB monitoring in the future as sensors become less expensive. Remote sensing will allow for higher frequency sampling temporally (as well as other spatial dimensions depending on sensor and well construction). Remote sensing for nitrogen can provide input on nitrogen entering a PRB or if a PRB is still effectively enhancing denitrification.

6.5 BENCH SCALE STUDIES

Bench scale-testing is intended to provide data to support modifications to important design parameters under site-specific conditions. Design modifications may include EVO/carbon substrate dosage or pH buffer dosage.

Batch microcosm testing with site soil and groundwater can be used to confirm that a denitrifying microbial population is present and to evaluate different substrates or substrate loadings and impacts of pH buffering. The biodegradation kinetics for a batch test may not be representative of field conditions.

Column studies are a better representation of the field conditions. Column tests should utilize site soil as denitrifying bacteria inhabit the surface of soil grains, and other controlling factors are generally determined by soil (e.g., pH, metal content). Large volumes of water may be required based on the column test duration, and nitrate-spiked water may be required. The column is packed with soil and groundwater with nitrate-N is pumped through the column (Lee et al., 2009). Column studies can be used to compare different substrates, loadings, pH buffers, groundwater flowrates, etc. The influent and effluent from the column should be monitored for field parameters like DO, pH, and ORP; electron acceptors including nitrate-N and nitrite-N; and electron donors including TOC or DOC, chemical oxygen demand, and/or volatile fatty acids such as acetic, proprionic, butyric, formic, and lactic acids also can be collected to support evaluation of denitrification and bacteria activity within the column. Other analytes may include NO and N_2O, sulfate, metals (e.g., Fe, Mn, As), and methane. To our knowledge, NO and N_2O have not been quantified in column or field studies. A short-term column test can determine the presence of denitrifying bacteria at the site, confirm complete denitrification, and demonstrate distribution of the substrate. A longer-term column test can be run to evaluate persistence of the substrate including timing for replenishment and to look for secondary impacts like production of ferrous iron, manganese, or arsenic.

The soil or groundwater can be sampled and submitted to a laboratory such as SiREM or Microbial Insights to determine the presence and numbers of microbes with the functional genes to carry out denitrification. In most cases, denitrifying bacteria will be present. Barrett et al. (2013) reported nirS, nirK, and nosZ abundance of 1E1 to 1E4 gene copies per L in groundwater samples from four groundwater sites in Ireland. Counts of >1E3 gene copies per liter of groundwater or gram of soil likely indicate the presence of denitrifying population. Where lower counts (>1 copies per liter) are detected, cell counts may increase once a carbon substrate is added to create reducing conditions favorable for the growth of the denitrifying bacteria. Groundwater can easily be collected for microbial testing during the column study. However, many bacteria grow preferentially on solid surfaces and analyses of groundwater may underestimate the denitrification microbial population. Collection of soil samples may only be possible at the beginning and end of the column studies. Functional gene analyses for \denitrifying genes including nxrB, narGHI, napAB, and nasA, are not known to be commercially available from Microbial Insights or SiREM. Microbial Insights can measure norB, nor/nxr (nitrite oxidizing), and archael genes ADNFNIRK, ADNFNIRS, AMXNIRS, and AMXNIRK that convert nitrite to nitrous oxide, and AOA an archael gene for ammonia oxidation to nitrite. Next generation sequencing (NGS) may be useful in understanding denitrification.

In-situ microcosm studies offer an alternative to batch or column studies. A biotrap composed of specially formulated beads can be baited with EVO and placed into a monitoring well for 30 to 90 days. Another biotrap without EVO to evaluate monitored natural attenuation is recommended. The biotraps could be monitored for the geochemical parameters such as anions (nitrate-N, nitrite-N, sulfate, chloride, and ortho-phosphate), volatile fatty acids (acetate, butyrate, and lactate) or TOC, pH, dissolved gases (methane), and functional denitrifying genes such as *nirS* and *nirK*.

Soil core samples and groundwater samples should be collected from the site in question or representative site nearby.

6.6 QUALITY CONTROL/QUALITY ASSURANCE

Sample collection, custody, storage/holding times, and analysis will be conducted in accordance with laboratory protocols and as detailed in a sampling work plan and/or quality assurance project plan (QAPP). Field duplicates and bottle blanks need to be included in the sampling plan and budget, with one set assumed for each sampling event or at a frequency determined in the sampling work plan or QAPP.

7.0 CONCLUSIONS

Nitrate levels in groundwater and surface water are elevated in many areas of the world because of anthropogenic sources of nitrogen to groundwater, notably discharge from septic systems and nitrogen-containing fertilizers from agriculture. Discharge of nitrogen-enriched groundwaters to coastal embayments can lead to eutrophication, a process whereby excess growth of algae negatively impacts water quality and ecology. Eutrophication poses human health risks as well as economic impacts from reduction in tourism, commercial fishing, and property values. Nitrate in drinking water, which can be impacted surface water or groundwater, is also linked to various adverse health effects. In addition to reducing the human health risks, compliance with the federal CWA and state water quality standards is a key driver to finding methods for reducing nitrogen in the groundwater that feeds into surface water bodies.

Identifying economical and sustainable methods for reducing the nitrogen entering the surface water bodies from the groundwater is an objective for communities across the United States and globally. One such method is permeable reactive barriers(s) or PRBs that are a widely used approach for removing and/or treating contaminants in groundwater. PRBs can address multiple non-point sources of nitrogen that percolate into the aquifer and remove nitrogen from groundwater before discharging to surface water or a potable water extraction well. Denitrification PRBs rely on biodegradation where indigenous microorganisms convert nitrate to nitrogen gas (N_2) to remove nitrogen from the groundwater. There are numerous benefits of PRBs for communities for addressing nitrogen in groundwater and attaining water quality criteria:

- PRBs have a much smaller capital cost than traditional sewering and wastewater treatment.
- PRBs have minimal operations requirements or costs after installation beyond periodic groundwater sampling and laboratory analyses.
- PRBs can address multiple point and non-point sources of nitrogen that have already percolated into the aquifer, including septic systems, stormwater, and fertilizer usage.
- PRBs can treat nitrogen nearer to a point of discharge, which should result in more immediate improvements to surface water quality and attaining a TMDL.
- PRBs have a small footprint and disturbance is largely limited to the installation and reinjection phases at the location of the PRB.
- PRBs can be used in combination with other nitrogen removal technologies for achieving TMDLs at the watershed scale.

This engineering design manual is focused on design and installation of PRBs for the biological treatment of nitrate. The objective of this design manual is to assist communities to plan, design, implement, and monitor denitrification. Due to extended travel times from the wasteload allocations (e.g., septic tanks) to the point of discharge in the surface waters, installation of sewer systems will not result in treatment of nitrogen already traveling in groundwater and a newly installed sewer system may take many years to have an impact on the discharge of nitrate to receiving waters. The missing components required by the denitrifying bacteria are a renewable carbon source (vegetable oil) for energy and appropriate nutrients. Key factors in designing a PRB to treat nitrate via injection of a liquid solution of electron donor are detailed in Section 5.0, and a Denitrification PRB Design Tool based in Excel was developed to accompany this manual. Details on monitoring to support design and evaluation of PRB performance are detailed in Section 6.0.

This engineering design manual provides descriptions and details to support the design of denitrification PRBs, while acknowledging that design of denitrification PRBs needs to incorporate site-specific conditions and considerations.

8.0 REFERENCES

AECOM. (2016). Technical Memorandum Final for Preliminary Engineering Work Plan for Permeable Reactive Barriers. Prepared for Town of Orleans.

Alvarez, L., Bricio, C., Blesa, A., Hidalgo, A., & Berenguer, J. (2014). Transferable Denitrification Capability of Thermus thermophilus. Applied and Environmental Microbiology, 80(1), 19-28. https://doi.org/10.1128/AEM.02594-13

ASTM International. (2022). Standard Test Methods for Measurement of Hydraulic Conductivity of Coarse-Grained Soils, ASTM D2434-22. https://doi.org/10.1520/D2434-22

Barbaro, J.R., Belaval, M., Truslow, D.B., LeBlanc, D.R., Cambareri, T.C., & Michaud, S.C. (2019). Hydrologic Site Assessment for Passive Treatment of Groundwater Nitrogen With Permeable Reactive Barriers, Cape Cod, Massachusetts. U.S. Geological Survey (USGS) Scientific Investigations Report 2019–5047. https://doi.org/10.3133/sir20195047

Barrett, M., Jahangir, M.M.R., Lee, C., Smith, C., Bhreathnach, N., Collins, G., Richards, K., & O'Flaherty, V. (2013). Abundance of Denitrification Genes under Different Piezometer Depths in Four Irish Agricultural Groundwater Sites. Environmental Science and Pollution Research, 20, 6646-6657. https://doi.org/10.1007/s11356-013-1729-3

Battelle Memorial Institute (Battelle) and Naval Facilities Engineering Command (NAVFAC). (2013). Best Practices for Injection and Distribution of Amendments. Technical Report TR-NAVFAC-EXWC-EV-1303.

Borden, R.C. (2008). Final Report Development of Permeable Reactive Barriers (PRB) Using Edible Oils. Strategic Environmental Research and Development Program (SERDP) Project ER-1205.

Borden, R.C., Tillotson, J.M, Ng, G-H.C, Bekins, B.A., & Kent, D.B. (2015). Final Report Impacts of Enhanced Reductive Bioremediation on Post-Remediation Groundwater Quality. SERDP Project ER-2131.

Bowen, J.L., Kroeger, K.D., Tomasky, G., Pabich, W.J., Cole, M.L., Carmichael, R.H., & Valiela, I. (2007). A Review of Land–sea Coupling by Groundwater Discharge of Nitrogen to New England Estuaries: Mechanisms and Effects. Applied Geochemistry, 22(1), 175-191. https://doi.org/10.1016/j.apgeochem.2006.09.002

Cape Cod Commission. (2015). 208 Plan Cape Cod Area Wide Water Quality Management Plan Update.

Charette, M.A. & Sholkovitz, E.R. (2002). Oxidative Precipitation of Groundwater-derived Ferrous Iron in the Subterranean Estuary of a Coastal Bay. Geophysical Research Letters, 29(10), 85-1-85-4. https://doi.org/10.1029/2001GL014512

Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRCCARE). (2016). A Framework for Selecting, Designing and Implementing a Permeable Reactive Barrier System. Technical Report 25.

Dombrowski, P.M., Temple, M. Parece, T., Marrion, J., Shreve, B., Begley, J., Lee, M.D., Raymond, R., Jr., & Hostrop, F. (2017). Denitrifying Permeable Reactive Barriers on Cape Cod: Bench-Scale Studies and Implementation of the First In-Situ EVO PRB. A6-539. 4th International Symposium on Bioremediation and Sustainable Environmental Technologies.

Downey, S., Mayer, R., & Parham, Z. (2023) Bioaugmentation Design for Treatment of Munitions Constituents. 6th International Symposium on Bioremediation and Sustainable Environmental Technologies.

Easton, Z.M., Bock, E., & Stephenson, K. (2019). Feasibility of Using Woodchip Bioreactors to Treat Legacy Nitrogen to Meet Chesapeake Bay Water Quality Goals. Environ. Sci. Technol. 53(21), 12291-12299. https://doi.org/10.1021/acs.est.9b04919

Environmental Security Technology Certification Program (ESTCP). (2010). Substrate Estimating Tool for Enhanced Anaerobic Bioremediation of Chlorinated Solvents. Version 1.2. Accessed 1/19/2023.

Gavaskar, A., Gupta, N., Sass, B., Janosy, R., & Hicks, J., (2000). Final Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation. Battelle Memorial Institute, https://doi.org/10.21236/ada379980

Geosyntec. (2009). Emulsified Zero Valent Iron (ZVI) Treatment of Chlorinated Solvents. Remediation Innovative Technology Seminar (RITS). Prepared for the Naval Facilities Engineering Command (NAVFAC).

Gonsalez, V.L. (2020). Evaluating Denitrification in Microcosms for Application of Permeable Reactive Barriers (PRBs). Master of Science Thesis, Tufts University.

Gonsalez, V., Dombrowski, P.M., Lee, M.D., & Ramsburg, C.A. (2023). The Influence of pH on Subsurface Denitrification Stimulated with Emulsified Vegetable Oil. Water 2023:15(5), 883. https://doi.org/10.3390/w15050883

Gonsalez, V., Ramsburg, C.A., Dombrowski, P.M., Lee, M.D., & Muller, K. A. (2022). Process Based Modeling of Denitrification Stimulated and Sustained with Vegetable Oil. American Geophysics Union Fall Meeting Abstracts, 2022: H25H-1200.

Guswa, J.H. & LeBlanc, D.R. (1985). Digital Models of Ground-water Flow in the Cape Cod Aquifer System, Massachusetts. USGS Water Supply Paper 2209. https://doi.org/10.3133/ofr8067

Henry, B. (2010). Final Report Loading Rates and Impacts of Substrate Delivery for Enhanced Anaerobic Bioremediation. ESTCP Project ER-0627.

Huling, S.G., Ross, R.R., & Meeker Presbo, K. (2017). In Situ Chemical Oxidation: Permanganate Oxidant Volume Design Considerations. Ground Water Monitoring & Remediation, 37(2), 78-86. https://doi.org/10.1111/gwmr.12195

Hunter, W.J. (2001). Use of Vegetable Oil in a Pilot-scale Denitrifying Barrier, Journal of Contaminant Hydrology, 53, 119 – 131. https://doi.org/10.1016/S0169-7722(01)00137-1

Interstate Technology and Regulatory Council (ITRC). (2002). A Systematic Approach to In Situ Bioremediation in Groundwater, Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate (ISB-8).

ITRC. (2011). Permeable Reactive Barrier: Technology Update (PRB-5).

ITRC. (2005). Permeable Reactive Barriers: Lessons Learned/New Directions. Technical/Regulatory Guidelines (PRB-4).

Johnson, R.L., Nurmi, J.T., Johnson, G.S.O., Fan, D., Johnson, R.L.O., Shi, Z., Salter-Blanc, A.J., Tratnyek, P.G., & Lowry, G.V. (2013). Field-scale Transport and Transformation of Carboxymethylcellulose-Stabilized Nano Zero-Valent Iron. Environ. Sci. Technol., 47(3), 1573-1580. https://doi.org/10.1021/es304564q

Korom, S.F. (1992). Natural Denitrification in the Saturated Zone: A Review. Water Resources Research, 28(6), 1657–1668. https://doi.org/10.1029/92WR00252

Lebron, C., Evans, P., Trute, M., Olsen, R., Chappell, R., Wilson, J., Adair, C., Weber, E., Kenneke, J., Thomas, B.T., DiChristina, T., & Drexler, J. (2005). Cost and Performance Report. Bioavailable Ferric Iron (BAFeIII) Assay. ESTCP Project Number ER-200009.

Lazenby, B., Cosme, F., Konzuk, J., Phillips, K., Black., A., Howarth, B., McCollin, S., & Schultz, B. (2023) Bioaugmentation Design for Treatment of Munitions Constituents. 6th International Symposium on Bioremediation and Sustainable Environmental Technologies.

Lee, M.D., Borden, R.C., Lieberman, M.T., Becvar, E.K., & Haas P.E. (2005). TCE Plume Management Through Edible Oil Injection and Natural Attenuation. 3D-09. 4th International Conference on Remediation of Chlorinated and Recalcitrant Compounds.

Lee, M.D., Hauptmann, E., Raymond, R.L, Ochs, D., Lake, R., & Selover, M. (2010). Buffering Acidic Aquifers with Soluble Buffer to Promote Reductive Dechlorination. F-031. 7th International Conference on Remediation of Chlorinated and Recalcitrant Compounds.

Lee, M.D., Hostrop, F., Hauptmann, E., Raymond, R., Jr., & Begley. J.F. (2016). Column Studies to Evaluate EVO for Nitrate Removal in Permeable Reactive Barriers on Cape Cod, MA. G-106. 10th International Conference on Remediation of Chlorinated and Recalcitrant Compounds.

Lee, M.D., Hostrop, F., & Raymond, R.L Jr. (2019). Optimizing EVO Formulations. 5th International Symposium on Bioremediation and Sustainable Environmental Technologies.

Lee, M.D., Lee, J.E., & Raymond, R.L. Jr. (2013). EVO Carbon Footprint, Distribution, and Longevity: Summary of SRS® Case Histories. E-21. 2nd International Symposium on Bioremediation and Sustainable Environmental Technologies.

Lee, M.D., Quinton, G.E. Beeman, R.E. Biehle A.A., Liddle, R.L., Ellis, D.E. & Buchanan, R.J. (1997). Scale-up of an *In Situ* Anaerobic PCE Bioremediation Project. Journal of Industrial Microbiology and Biotechnology 18(2/3), 106-115. https://doi.org/10.1038/sj.jim.2900289

Lee, M.D., Raymond, R.L. Cole, S., Stenberg, L., Lyon, R., & Williams, D. (2009). Emulsified Vegetable Oil Transport Studies in Soil Columns. L-82. 10th International In Situ and On-Site Bioremediation Symposium.

Massachusetts Department of Environmental Protection (MassDEP). The Basics of Total Maximum Daily Loads (TMDLs). Accessed October 4, 2022.

Masterson, J.P., Stone, B.D., Walter, D.A., & Savoie, J. (1997). Hydrogeologic Framework of Western Cape Cod, Massachusetts. USGS Hydrologic Atlas 741. https://doi.org/10.3133/ha741

Metcalf & Eddy, Inc., Tchobanoglous, G., Burton, F.I., & Stensel, H.D. (2003). Wastewater Engineering: Treatment and Reuse. 4th Edition, McGraw-Hill. ISBN 0070418780, 9780070418783.

Mulligan, A. & Uchupi, E. (2003). New Interpretation of Glacial History of Cape Cod May Have Important Implications for Groundwater Contaminant Transport. Eos, 84(19), 177-188. https://doi.org/10.1029/2003EO190001

Oldale R.N. (1976). Generalized Geologic Map of Cape Cod. USGS Open-File Report 76-765. https://doi.org/10.3133/ofr76765

Oyster Pond Environmental Trust. (2022). Managing Nitrogen Pollution in Oyster Pond. Accessed August 1, 2022.

Pajares, S. Ramos, R. (2019). Processes and Microorganisms Involved in the Marine Nitrogen Cycle: Knowledge and Gaps. Front. Mar. Sci., 6, 739. https://doi.org/10.3389/fmars.2019.00739

Payne, F.C., Quinnan J.A., & Potter, S.T. (2008). Remediation Hydraulics. CRC Press. ISBN 9780849372490.

Penn, R.L, Zhu, C., Veblen, D.R., & Xu, H. (2001). Iron Oxide Coatings on Sand Grains From the Atlantic Coastal Plain: High-resolution Transmission Electron Microscopy Characterization. Geology, 29(9). https://doi.org/10.1130/0091-7613(2001)029%3C0843:IOCOSG%3E2.0.CO;2

Raymond, R.L. (1974). Reclamation of Hydrocarbon Contaminated Ground Water. United States Patent Office 3,846,290. Patented Nov. 5, 1974.

Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., & Bemment, C.D. (2008). Nitrate Attenuation in Groundwater: A Review of Biogeochemical Controlling Processes. Water Research, 42(16), 4215-4232. https://doi.org/10.1016/j.watres.2008.07.020

Robertson, W.D. & Cherry, J.A. (1995). In Situ Denitrification of Septic-system Nitrate using Reactive Porous Media Barriers: Field Trials. Ground Water 33(1), 99-111. https://doi.org/10.1111/j.1745-6584.1995.tb00266.x.

Silver, C.F., Bogosh, M., Sanderson, E. & Young, D. (2014). Nitrate Treatment in Falmouth, Massachusetts, (Cape Cod) Using Permeable Reactive Barriers. H-073. 9th International Conference on Remediation of Chlorinated and Recalcitrant Compounds.

Solutions-IES. (2006). Protocol for Enhanced In-Situ Bioremediation Using Emulsified Edible Oil. ESTCP ER-0221.

Solutions-IES, Terra Systems, Inc. & Parsons Infrastructure & Technology Group, Inc. (2007). Final Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil. Air Force Center for Engineering and the Environmental.

Thiruvenkatachari, R., Vigneswaran, S., & Naidu, R. (2008). Permeable Reactive Barrier for Groundwater Remediation. Journal of Industrial and Engineering Chemistry, 14(2), 145-156. https://doi.org/10.1016/j.jiec.2007.10.001.

U.S. Environmental Protection Agency (USEPA). (2013). A Long-Term Vision for Assessment, Restoration, and Protection under the Clean Water Act Section 303(d) Program.

U.S. Environmental Protection Agency (USEPA). (2008). Design and Installation of Monitoring Wells. SESDGUID-101-R0.

U.S. Environmental Protection Agency (USEPA), Powell, R.M, Puls, R.W., Blowes, D.W., Gillman, R.W., Powell, P.D., Schultz, D., Sivavec, T., & Landis, R. (1998). Permeable Reactive Barrier Technologies for Contaminant Remediation. EPA/600/R-98/125.

Wakida, F.T. & Lerner, D.N. (2005). Non-agricultural Sources of Groundwater Nitrate: A Review and Case Study. Water Research, 39, 3-16. https://doi.org/10.1016/j.watres.2004.07.026

Ward, M.H., Jones, R.R., Brender, J.D., De Kok, T.M., Weyer, P.J., Nolan, B.T., Villanueva, C.M., & Van Breda, S.G. (2018). Drinking Water Nitrate and Human Health: An Updated Review. Int J Environ Res Public Health, 15(7), 1557. https://doi.org/10.3390/ijerph15071557

WaterVision, LLC. (2016). Project Summary Memorandum, Site Characterization for Design of Pilot-Scale Permeable Reactive Barriers for Nitrogen Reduction in Groundwater on Cape Cod – Supplemental Fieldwork at Shorewood Drive, Falmouth, MA.

Xu X, Liu W, Tian S, Wang W, Qi Q, Jiang P, Gao X, Li F, Li H & Yu, H. (2018). Petroleum Hydrocarbon-Degrading Bacteria for the Remediation of Oil Pollution Under Aerobic Conditions: A Perspective Analysis. Frontiers of Microbiology. 9: 2885. https://doi.org: 10.3389/fmicb.2018.02885

Zhang, M., Zheng, P., Wang, R., Li, W., Lu, H., & Zhan, J. (2014). Nitrate-dependent Anaerobic Ferrous Oxidation (NAFO) by Denitrifying Bacteria: A Perspective Autotrophic Nitrogen Pollution Control Technology. Chemosphere 117, 604-609. https://doi.org/10.1016/j.chemosphere.2014.09.029

ATTACHMENT 1 – EVO LOADING EXPERIENCE FOR DENITRIFICATION PERMEABLE REACTIVE BARRIERS

Figures

Tables

4. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, Total N % Removal, pH Change, % Alkalinity Removal, %DO Consumed, % Sulfate Consumed, Maximum Dissolved Iron and Manganese, Maximum Methane, and Maximum Arsenic for Salt Pond Eastham, MA PRB
5. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, Total N % Removal, % Phosphate Removal, pH Change, % Alkalinity Removal, %DO Consumed, % Sulfate Consumed, Maximum Dissolved Iron and Manganese, and Maximum Arsenic for Falmouth 1 Year PRB
6. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, Total N % Removal, % Phosphate Removal, pH Change, % Alkalinity Removal, %DO Consumed, % Sulfate Consumed, Maximum Dissolved Iron and Manganese, and Maximum Arsenic for Falmouth 2 Year PRB

EVO LOADING EXPERIENCE FOR DENITRIFICATION PERMEABLE REACTIVE BARRIERS

A. COLUMN STUDIES

A.a. Terra Systems Inc. Falmouth MA Column Study I (2015-16)

Sand column studies were conducted by Terra Systems, Inc. with soil and groundwater from a site in Falmouth, Cape Cod to evaluate emulsified vegetable oil (EVO) to support denitrification (Lee et al., 2015; Dombrowski et al., 2017). Primary objectives of the bench scale testing were to assess effectiveness in removing nitrate, persistence of the EVO and denitrifying conditions, and migration of EVO. Three columns were tested with each column 3.8 feet (0.9 meters) long and 2 inches (0.78 cm) in diameter (**Figure 1**). Each column was constructed with 11.5 pounds soil and the total pore space was estimated to be 592 milliliters (mL).

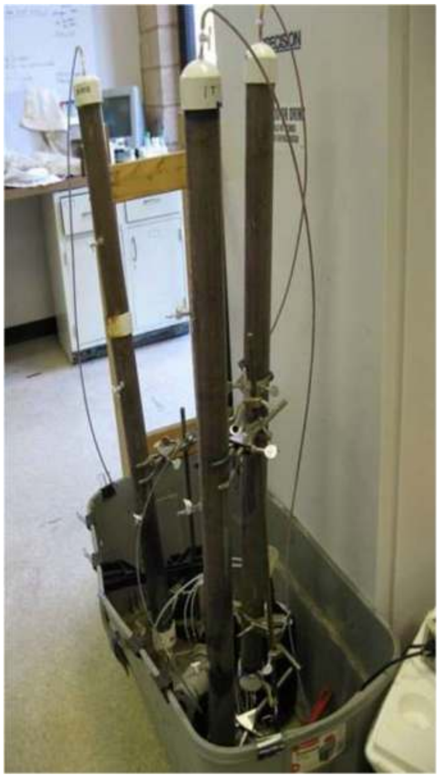


Figure 1. Sand Columns.

Column 1 and Column 2 received 30.8 grams and 61.6 grams, respectively, of a small droplet EVO (SRS®-SD, manufactured by Terra Systems, Inc., average droplet size of 0.6 µm). Column 3 received 61.6 g SRS$^{®}$-SD and 24.6 grams zero valent iron (ZVI). Water was pumped through each column at 1.2 feet per day (0.37 meters per day) with influent nitrate-Nitrogen (N) of approximately 19.5 to 26.9 milligrams per liter (mg/L). In addition, sulfate was included in the influent at concentrations of 10 to 43 mg/L. The pH of the influent ranged from 5.9 to 8.1 SU and the effluents from 4.6 to 8.8 SU.

The columns were operated for 354 days (98-109 pore volumes). After EVO was introduced, total organic carbon (TOC) was measured at between 626 to 3,900 mg/L in reactor effluents. Emulsion was observed, identified visually as a white color and by turbidity, in the effluents for the first 2 to 11 pore volumes, and emulsion was not visibly observed thereafter. All three columns achieved complete removal of nitrate-N in the effluent for over 310 days (87 to 92 pore volumes) as shown on **Figure 2A**. When TOC levels fell below 4.0 mg/L (**Figure 2B**), nitrate began to appear in effluent. Over the 374 days of operation of column 1 which received 30.8 g SRS®-SD or approximately 15.4 g TOC removed about 1.2 g of nitrate-N while 7.4 g of TOC was released or about 0.16 g nitrate-N/g TOC retained on the column. More nitrate-N would have been removed if the columns had been operated longer. Over the 354 days of operation of column 2 which received 61.6 g SRS®-SD or approximately 30.8 g TOC removed about 1.42 g of nitrate-N while 1.8 g of TOC was released or about 0.049 g nitrate-N/g TOC retained on the column. Over the 354 days of operation, column 3 which received 61.6 g SRS®-SD or approximately 30.8 g TOC removed about 1.3 g of nitrate-N while 3.4 g of TOC was released or about 0.047 g nitrate-N/g TOC retained on the column. More nitrate-N would have been removed if the columns had been operated longer. Sulfate removal on a mass balance basis ranged between 0.094 to 0.723 g. Based on the three columns, no obvious difference in effectiveness or longevity was measured with increased loading of SRS®-SD or with combination with ZVI.

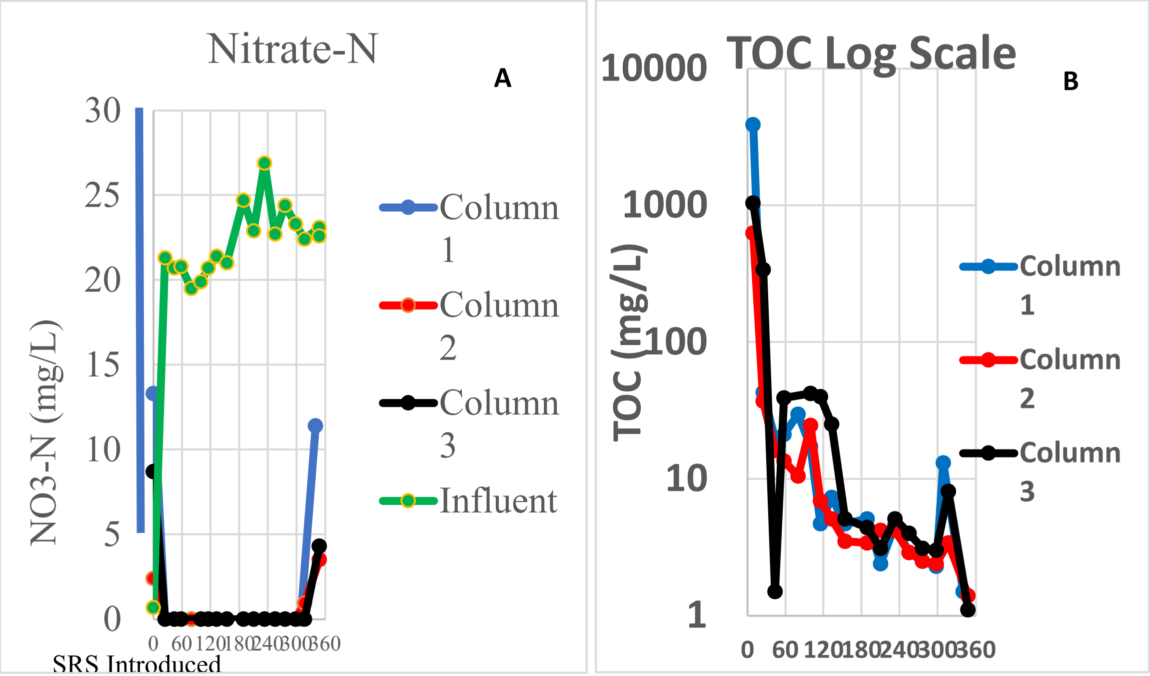


Figure 2. Bench Scale Testing Results Thru Day 354
A) Nitrate-N Concentrations, and B) TOC

Based on observation of nitrate breakthrough after less than one year and in consideration of field injection to medium-coarse sand aquifer on Cape Cod, modifications were contemplated to make an EVO solution that would better adhere to soil grains, minimize migration out of the PRB, and extend longevity of the EVO and denitrification. A modified

EVO formulation was created by Terra Systems, Inc. with larger EVO droplet (5 micron mean droplet), an anionic surfactant, and without lactate (most remediation EVO solutions contain ~4 percent sodium or potassium lactate by mass).

Additional bench scale column testing was performed with the new formulation. On Day 355 of the study, the three columns were connected in series into a single longer column set up (11.4 feet, 3.5 meters), and 31 grams (diluted 1:10) of the modified EVO formulation (SRS®-NR) or about 15.9 g TOC was applied to the influent of the column. Influent water had 21 to 24 mg/L nitrate-N and 25 to 32 mg/L sulfate. Average flow rate through the combined columns was increased to 301 mL/day (0.58 meters per day; 1.9 feet per day).

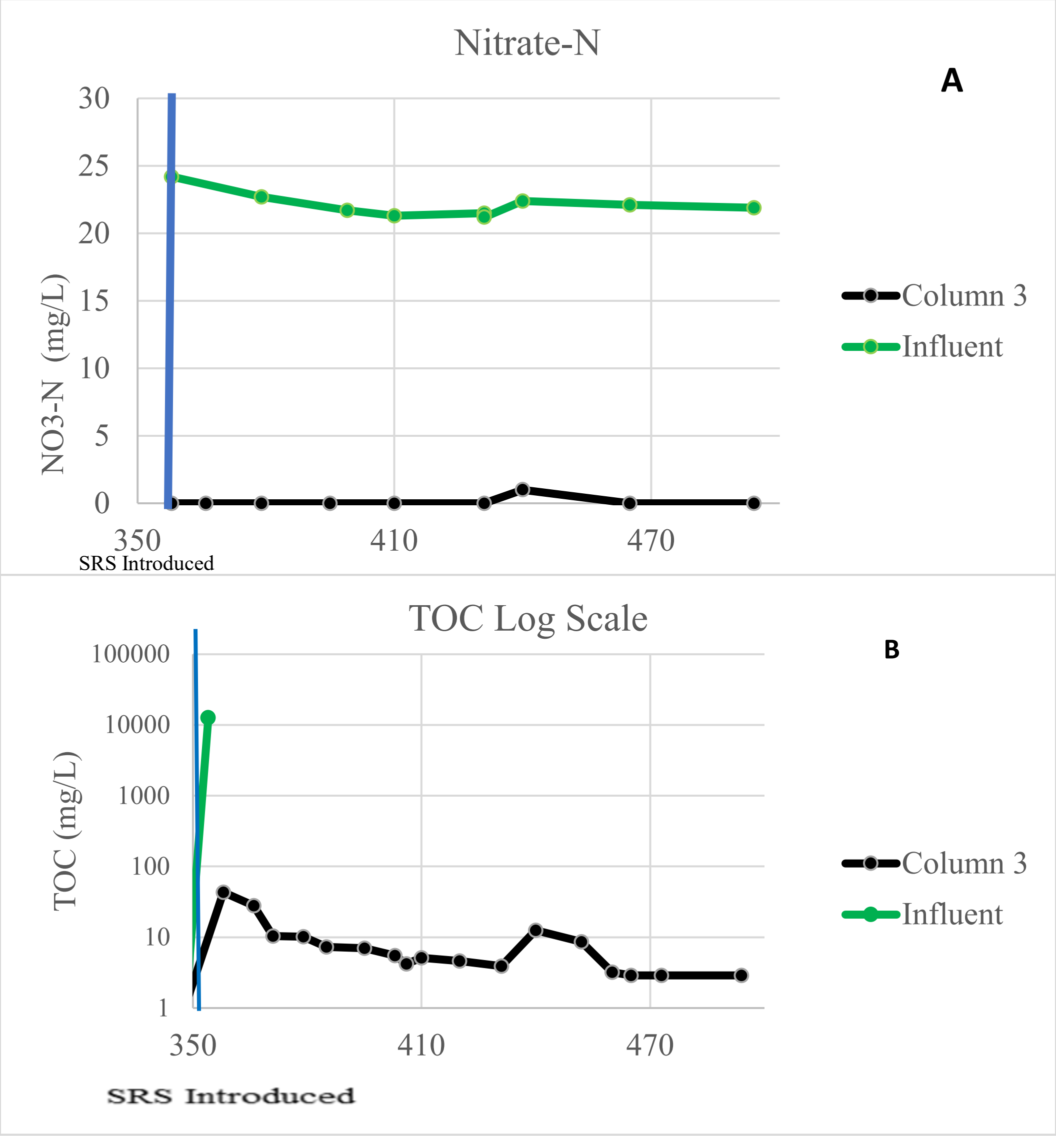


Figure 3. Bench Scale Testing Results with SRS®-NR
A) Nitrate-N Concentrations, and B) TOC

The column test was operated for an additional 140 days (69 additional pore volumes). The influent TOC was 12,600 mg/L. After injection, TOC reached 43 mg/L in column 3 effluent, which was significantly lower than the TOC observed in effluent of earlier column tests (compare **Figure 3B** with **Figure 2B**). Effective removal of nitrate-nitrogen in the effluent was achieved for the entire period of additional testing (**Figure 3A**) including sustained nitrate removal at 2.9 mg/L TOC in effluent (in contrast to earlier bench tests where nitrate breakthrough was observed when TOC in effluent was below 4 mg/L). In addition, the emulsion was not visually observed in the effluent and showed a maximum turbidity equivalent to 74 mg/L SRS®-NR in the effluent water, suggesting that little of the modified EVO formulation migrate 11.5 feet through the column in 140 days at an average flow rate of 1.9 ft per day water. Over the 140 days of operation, the combined columns which received 31 g SRS®-NR or approximately 15.9 g TOC removed about 0.9 g of nitrate-N while 0.3 g of TOC was released or about 0.054 g nitrate-N/g TOC retained on the columns. Nitrate had not broken through in the effluent so more nitrate removal would have occurred. An estimated 0.25 g of sulfate was removed during the second phase of testing. The SRS®-NR formulation with anionic surfactant was better retained on the soil matrix than the standard small droplet EVO amendment (SRS®-SD), while still supporting almost complete nitrate removal.

A.b. Falmouth Column Study II (2020)

A second column study for Falmouth was conducted to evaluate the impact of buffering on denitrification. The groundwater pH ranged from 5.3 to 5.5 SU. The influent pH was adjusted to as low as 3.2 SU. Three 48-inch long 2-inch diameter clear PVC columns were prepared with site soil and groundwater (**Figure 4**). The columns required 4.90, 4.95, and 5.00 kg of soil. Assuming 25% porosity as a typical porosity of a medium sand, the pore volumes were estimated to be between 661 and 666 mL. Column 1 received 300 g of a 1:10 SRS®-NR which filled the column to about 22 inches from the bottom. Column 2 received 0.05% by weight of a fine ground calcium carbonate powder (2.5 g of average 3.5 mm Specialty Minerals Vicron 15-15) mixed into 5.0 kg soil plus 300 mL of a 1:10 SRS®-NR solution which filled the column to about 22 inches from the bottom. Column 3 received 0.25% by weight of a fine ground calcium carbonate powder (12.75 g of average 3.5 mm Specialty Minerals Vicron 15-15) mixed into 5.1 kg soil plus 300 g of a 1:10 SRS®-NR solution which filled the column to about 22 inches from the bottom. The 300 mL of 1:10 SRS®-NR provided about 15.4 g TOC (based upon the theoretical TOC content).

The groundwater was pumped up through the columns using a peristaltic pump at a flow rate of about 4 ft/day based upon the estimated groundwater rate at the site. The effluents from the columns were collected in Tedlar bags. The residence time in the columns was about 1 day. Once the columns were filled with groundwater and pumped for two days, SRS®-NR diluted 1:10 was added to the columns. The flow to the columns was turned off for three days to allow the SRS®-NR to coat the soil and not advance further than the target distance up the columns. Once the initial groundwater volume supplied for the test was depleted, the influent was prepared with tap water and the pH adjusted with hydrochloric acid.

Figure 4. Falmouth II Columns

The columns were run for 83 days. Samples of the influent and effluents from the three columns were monitored one or two times per week for pH, ORP, DO using calibrated meters and probes, for turbidity using a Hach 890 colorimeter (as a measure of the SRS®-NR based upon a calibration curve prepared with diluted SRS®-NR). The volume of water collected in the Tedlar bags was determined by weighing the bags. Influent and effluent samples were analyzed for nitrate-N, nitrite-N, sulfate, dissolved iron and dissolved manganese, volatile fatty acids, and TOC by Eurofins Lancaster Laboratories.

The initial groundwater pH was 5.3 to 5.5 SU. The pH in the influent using site groundwater generally crept up from 5.4 to as high as 6.4 SU possibly as carbon dioxide was released (the influent was open to air). With the tap water amended with sodium nitrate and hydrochloric acid, the influent pHs ranged from as low as 3.2 up to 7.1 SU. The pH tended to creep up in the influent batches during incubation. **Figure 5** shows the pH in the influent and effluents from the columns.

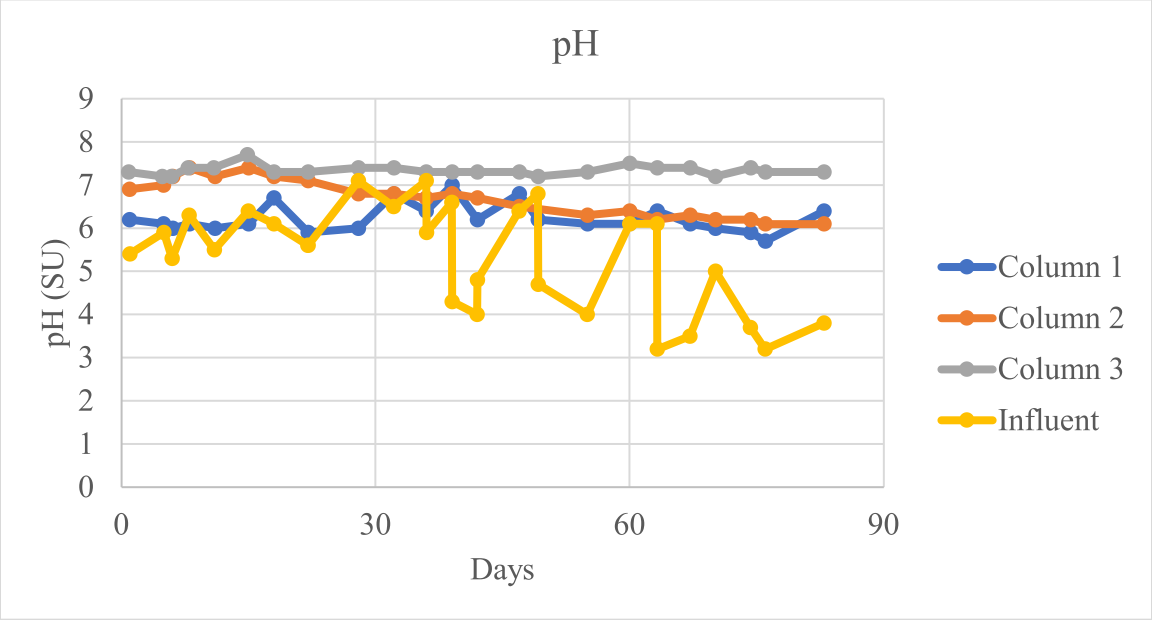


Figure 5. Falmouth II Columns pH

Column 1 with SRS®-NR only had a pH in the effluent of 5.7 to 7.0 with an average of 6.2 SU. Passage through the soil in the column and denitrification resulted in pH increases of -1.1 to 2.6 SU with an average increase of 0.7 SU. Nitrate-N analyses by ion chromatography at Eurofins Lancaster Laboratories showed no detectable nitrate in the effluent (**Figure 6**) through Day 76. Nitrite-N was also found on Day 55 and in this batch of influent. Based upon the flow rates and differences in nitrate-N between the influent and column 1 effluent, an estimated 0.30 g of nitrate-N was removed. Low levels of dissolved iron (0.04 mg/L), manganese (0.68 mg/L), acetic acid (1 mg/L) and propionic acid (13 mg/L) were detected on Day 55. The TOC in this column decreased from 35.3 mg/L on Day 8 to 9.8 on Day 42 and ranged from 11.2 to 19.2 mg/L from Day 55 to Day 76 (**Figure 7**). An estimated 0.71 g of TOC was released in this column. The nitrate-N removal was 0.020 g NO3-N/g TOC retained on the column. Breakthrough of the nitrate-N had not occurred, so the ratio underestimates the nitrate-N removal per g carbon. Sulfate removal was negligible.

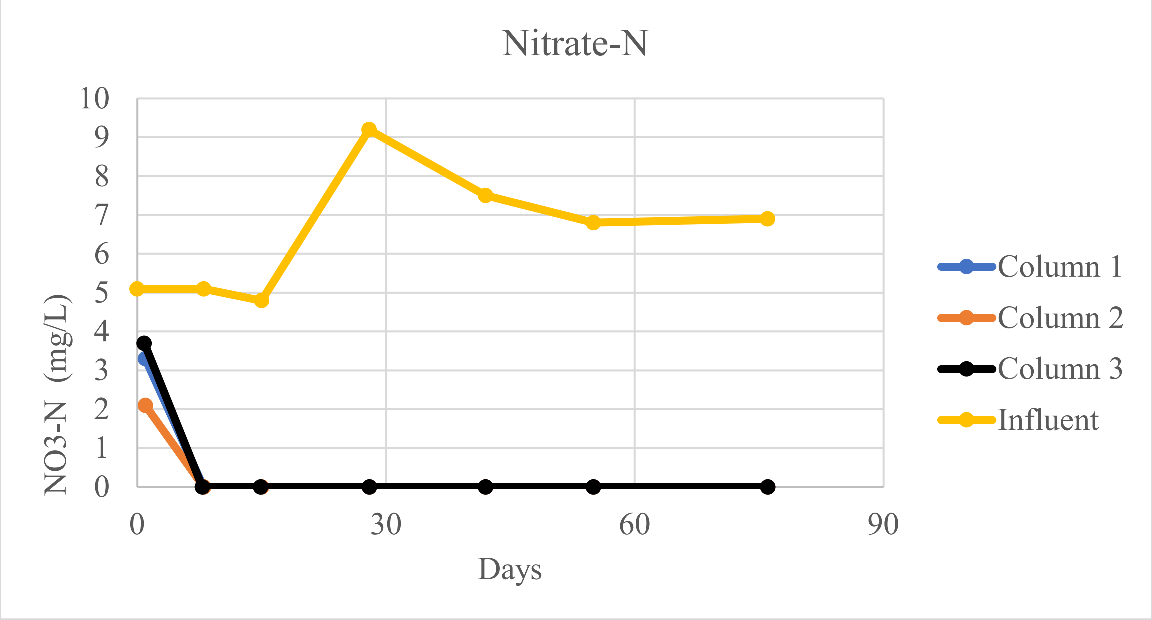


Figure 6. Falmouth II Columns NO3-N

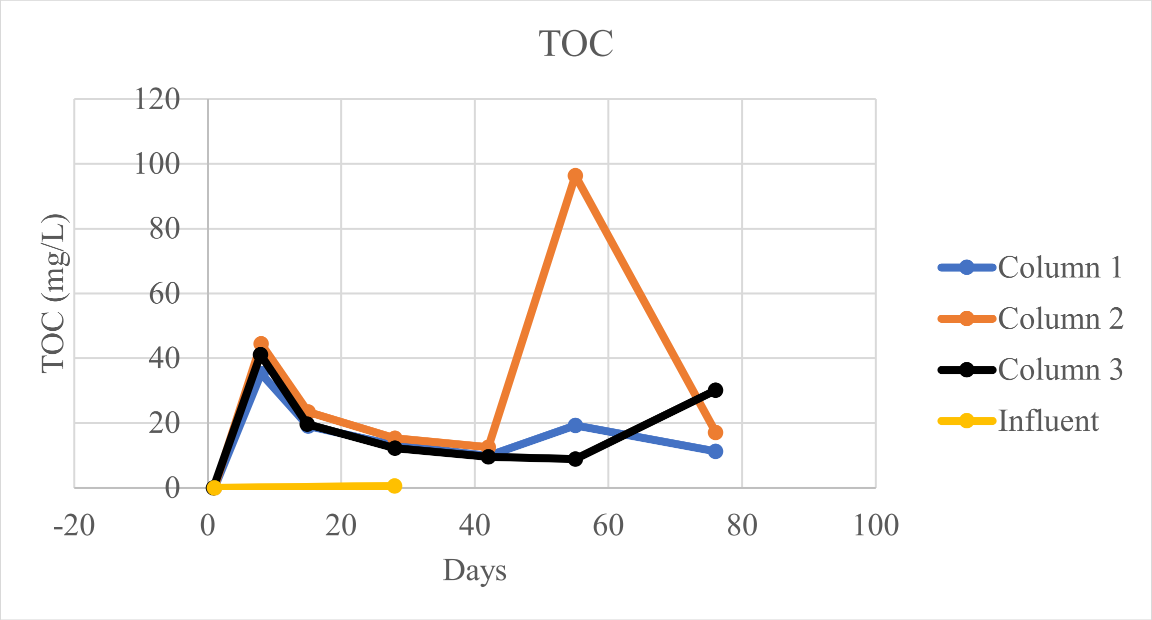


Figure 7. Falmouth II Columns TOC

The pH in the effluent from column 2 with 0.049% calcium carbonate and the SRS®-NR ranged from 6.1 to 7.4 with an average of 6.7. The effluent pH dropped from between 6.9 to 7.4 over the first 22 days of column operation to between 6.1 and 6.8 SU over the next 61 days. Passage through the soil in the column, treatment with the calcium carbonate buffer, and denitrification resulted in pH increases of -0.4 to 2.9 SU comparing the influent to the effluent with an average of 1.3 SU increase. Complete denitrification was observed within 4 days after resuming flow with 44.5 mg/L TOC on Day 8 to 12.5 mg/L on Day 42 and 17.1 mg/L on Day 76. An elevated TOC of 96.4 mg/L was found on Day 55. On a mass balance basis compared to the influent and based upon the flowrate, an estimated 0.27 g of nitrate-N and 0.19 g sulfate were removed. On Day 55, 0.98 mg/L nitrite-N was found in the effluent of column 2 but nitrite-N was not detected on Day 76. Nitrite-N was also found in this batch of influent. Moderate levels of dissolved iron (2.15 mg/L), manganese (0.72 mg/L), acetic acid (67 mg/L), propionic acid (64 mg/L) and pyruvic aid (0.38 mg/L) were detected on Day 55. The TOC in this column decreased from 35.3 mg/L on Day 8 to 9.8 on Day 42 and ranged from 11.2 to 19.2 mg/L from Day 55 to Day 76. An estimated 1.44 g of TOC was released. The nitrate-N removal was 0.019 g NO3-N/g TOC retained on the column. Breakthrough of nitrate-N had not occurred.

The pH in Column 3 with 0.24% calcium carbonate and the SRS®-NR ranged from 7.2 and 7.7 with an average of 7.3. Passage through the soil in the column, treatment with the calcium carbonate buffer, and denitrification resulted in pH increases of 0.2 to 4.1 SU with an average of 1.8 SU increase. Complete denitrification was observed within 4 days after resuming flow with 41.1 mg/L TOC on Day 8 and between 8.9 to 30.1 mg/L from Days 42 to 76. On a mass balance basis compared to the influent and based upon the flowrate, an estimated 0.35 g of nitrate-N and 0.05 g sulfate were removed. On Day 55, 1.1 mg/L nitrite-N was found in the effluent of column 3 but nitrite-N was not detected on Day 76. Nitrite-N was also found in this batch of influent. Low levels of dissolved iron (0.064 mg/L) and dissolved manganese (0.45 mg/L) were detected in the effluent on Day 55, but no volatile fatty acids. The TOC in this column decreased from 41.1 mg/L on Day 8 to 9.5 on Day 42 and ranged from 8.9 to 30.1 mg/L from Day 55 to Day 76. An estimated 0.78 g of TOC was released from this column. The nitrate-N removal was 0.025 g NO3-N/g TOC retained on the column. Breakthrough of nitrate-N had not occurred.

In conclusion, the column studies showed fast and complete denitrification rates with a 4 feet/day groundwater flow rate or retention times of about 1 day. The pH of the influent was not maintained as low as that measured in the groundwater initially. The influent pH ranged from 3.2 to 7.1 with the acidified tap water. No impact of acidic influent water on denitrification was observed in the 83 days of column operation even for column 1 without calcium carbonate buffer. Alkalinity in the influent and soil and denitrification likely neutralized the acidic influent. On a mass balance basis from the influent nitrate concentrations, between 0.27 and 0.36 mg of nitrate and 0 to 0.19 g sulfate were removed with release of 0.72 to 1.44 g of TOC. Nitrite-N was detected in the influent and effluents from all three columns on Day 55 but was not detected in the subsequent samples. Conditions were generally not so reducing that much of the sulfate was removed except in Column 2. Relatively little iron or manganese were reduced to ferrous (dissolved) iron or manganese (1V). Acetic, propionic, and pyruvic acids were found in the effluents of columns 1 and 2 on Day 55, but only accounted for 47.9 to 60.3% of the TOC. Only 4.6 to 9.4% of the TOC applied as SRS®-NR reached the effluent of the 4 feet columns operated at a groundwater flow rate of 4 ft/day.

Although these column studies did not shown inhibition of denitrification using low pHs influent in column 1 with no buffer, the intermediate loading of 0.049% calcium carbonate by weight soil was recommended for the Falmouth injections (see Section D below). The soil density is 1.73 g/cm^3 or about 108 pounds per cubic feet. With a 0.049% calcium carbonate loading, each cubic foot of soil would require 0.053 pounds calcium carbonate.

Assuming a 5-foot radius of influence and 24 feet target injection thickness, the soil surrounding each injection point would require about 100 pounds of calcium carbonate.

B. FIELD TRIALS

Field demonstration tests of denitrification PRBs using EVO are underway at the following locations four locations in Massachusetts:

- Eldredge Park, Orleans - two injection phases in November 2016 and June 2018 (Parece, 2022).
- Salt Pond, Eastham - injections in April 2020 (Verdantas and MT Environmental Restoration, 2023).
- Shoreham Drive, Falmouth - injections in July 2020 (Woods Hole Oceanographic Institute, 2022).
- Lagoon Pond, Martha's Vineyard - injections in November 20202 (Thomas, 2023).

Table 1 summarizes key parameters for each PRB. The pilot PRBs ranged from 110 to 200 feet perpendicular to groundwater flow direction, 10 to 22 feet parallel to groundwater flow direction, and 18 to 38 feet vertical thickness. The calculated groundwater flow rate ranged from 0.13 to 0.6 ft/day at the four locations. During the initial planning phases, faster seepage velocities (1 to 2 feet per day) were assumed at several of these locations prior to collection of additional hydrogeologic data (site-specific hydraulic conductivity and hydraulic gradients). The demonstration test PRBs were between 80 and 2,400 feet from the nearest water body. Similar spacing between injection points were used at the four sites (10 to 12.5 feet). The SRS$^{®}$-NR substate ranged from 2,620 to 6,600 gallons per site with loadings of 0.040 to 0.122 gallons of SRS$^{®}$-NR per cubic foot of the PRBs and an average of 0.072 gallons per cubic foot of PRB. The second phase of the Orleans injection and the Eastham PRB both received sodium lactate in addition to the 4.0-5.5% which is typically added to the SRS$^{®}$-NR to more rapidly generate reducing conditions. Between 350 to 550 pounds of sodium bicarbonate and 320 to 1,600 pounds of calcium carbonate were injected as buffers or between 0.0053 to 0.0492 pounds of buffer per cubic foot of the PRB and an average of 0.015 pounds per cubic foot of the PRB. The substrate was diluted with 72.2 to 84.1% dilution water and the injectate represented 8.6 to 27.2% of a pore volume.

The ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** developed for this Engineering Design Manual estimates for EVO were 0.56 lower to 1.19X higher than the SRS$^{®}$-NR volumes that were injected for the Eldredge Park Orleans and Eastham pilots. The ***Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers*** estimates for EVO were 0.05 to 0.062X lower than the SRS$^{®}$-NR injection volumes for the Shorewood Drive, Falmouth PRB. The design for the Shorewood Drive project was based upon a groundwater flow rate of 1 to 2 feet day; the actual groundwater flow rate was closer to 0.13 ft/day. Insufficient data was available for the Martha's Vineyard PRB to be able to run the Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers.

The buffers and denitrification raised the pH by a maximum of between 0.9 to 2.2 SU over the groundwater pH observed before EVO and buffer injections. The four pilots had 30.5 to 125 feet distance to the furthest impacted monitoring location. The longevity of substrate and effective denitrification was greater than 2 to 5.8 years based upon the pilot data. Later analyses at the Orleans pilot suggest that the substrate will last longer than 5.8 years. . In wells impacted by the substrate, maximum dissolved oxygen consumption ranged between 96.6 to 99.8%, with sulfate consumption of 1.1 to 100%, between 1.1 and 263 mg/L ferrous or dissolved iron was generated, and 82 to 29.7 mg/L of dissolved manganese, 6.6 to 16.7 mg/L methane (methane was not monitored for Falmouth or Martha's Vineyard), and 0.003 to 0.043 mg/L maximum arsenic.

Table 1. Cape Cod and the Islands Denitrification PRB Demonstration Tests Design Summaries

PRB Location	**Units**	**Orleans Phase I One Row**	**Orleans Phase I Two Rows Offset**	**Orleans Phase II Two Rows Offset**	**Eastham**	**Falmouth 1 Year PRB**	**Falmouth 2 Year PRB**	**Martha's Vineyard**
Barrier Length Perpendicular to GW Flow Direction	ft	60	50	110	200	60	60	150
Barrier Width Parallel to GW Flow Direction		10	20	22	12	10	10	12.5
Barrier Thickness	ft	32	32	38	43	24	24	18
Estimated Groundwater Flow Rate	ft/day	0.2-0.3	0.2-0.3	0.2-0.3	6	0.13	0.13	0.6
Distance to Water Body	Ft	2,400	2,400	2,400	131	330	330	80
Upgradient or Pre-Injection Nitrate-N Concentrations	mg/L	13.5	8.4	21.6	2.8	4.2	5.8	2.0
Number of Injection Wells	#	7	10	20	21	6	6	12
Spacing for Injection Wells	ft	10	10	10	10	10	10	10-15
Volume of SRS®-NR Substrate	gallons	1,079	1,541	3,696	6,600	1,001	1,751	3,432
Volume of Sodium Lactate	gallons			225	264			
Emulsified Vegetable Oil Loading Calculator for Denitrification Permeable Reactive Barriers Estimate	gallons	1,028	865	2,262	7,871	50	109	NA
Volume of Buffer	pounds	144 NaBC	206 NaBC	600 NaBC	550 NaBC 550 CaCO3	164 CaCO3	156 CaCO3	1600 CaCO3
Volume of Dilution Water	gallons	3,121	5,060	10,879	24,400	5,287	4,164	13,723
Percent Substrate of Injectate	%	25.7	23.3	26.5	21.3	15.9	27.8	20.0
Pore Volume Injected (Assuming 25% Porosity)	%	11.7	11.0	8.6	16.1	9.7	9.7	27.2
Buffer Loading Per Cubic Foot of PRB	Pounds/ft^3	0.0075	0.0064	0.0125	0.0053	0.014	0.0108	0.0492
SRS®-NR Loading	gallons/ft^3	0.056	0.048	0.040	0.064	0.070	0.122	0.102
Distance to Furthest Impacted Monitoring Location	ft	50	50	50	100	125	64	30.5
Longevity of Substrate	years			5.8	1.9	1.9	1.9	0.4
Effective Denitrification	years			5.8	1.9	1.9	1.9	0.4
Effective Denitrification Depth Interval	ft bgs			35	30	-14 to -35	-4.5 to -16.5	10-15
Maximum pH Increase	SU			1.8	1.2	0.9	2.2	NA
Maximum DO Consumption	%			99.4	96.6	99.8	98.1	NA
Maximum Sulfate Consumption	%			100	72.7	1.1	86.9	NA
Maximum Ferrous (Dissolved) Iron	mg/L			157	263	1.1	71.0	NA
Maximum Dissolved Manganese	mg/L			11.5	18.1	8.2	29.7	NA
Maximum Methane	mg/L			16.7	6.6	NA	NA	NA
Maximum Arsenic	mg/L			0.043	0.0425	0.003	0.020	NA

NA = not available

C. ELDREDGE PARK, ORLEANS, MA PILOT

The first liquid carbon substrate denitrification PRB demonstration test of Cape Cod was performed by the Town of Orleans with AECOM as the town's consulting engineer (Parece, 2022). For the demonstration test, it was desired to have the denitrification PRB attain an effective longevity of at least three years with an objective of the demonstration test to evaluate how long a PRB could enhance denitrification. EVO was the selected amendment based on the desire for extended PRB longevity and relative ease of injection. The Substrate Estimating Tool for Enhanced Anaerobic Bioremediation of Chlorinated Solvents developed for the ESTCP was used to support EVO quantities for the PRB Demonstration Tests. This tool estimates quantities of various carbon substrates to provide sufficient amendment for the sum of electron donor demand from electron acceptors (dissolved oxygen, nitrate, and sulfate) as well as volatile organic compounds if present. The primary sources of electron demand for the demonstration test PRB were dissolved oxygen in an aerobic aquifer and nitrate and the associated fluxes at assumed groundwater velocity of up to 2 feet per day. Initial dissolved oxygen ranged from 0 to 6.9 with an average of 1.5 mg/L. **Figure 8** shows the injection wells in one row monitored by wells in transect A MW-12A (18 feet upgradient), MW-12B (18 feet upgradient), MW-12C (17 and 8 feet upgradient), MW-1010C (9 and 16 feet downgradient), MW-2020B (9 and 80 feet downgradient), MW-2020C (21 and 26 feet downgradient), MW-1050A (45 and 91 feet downgradient), MW-1050B (44 and 93 feet downgradient), MW-1050C (44 and 94 feet downgradient), and MW-1075B (65 and 41 feet downgradient). Nitrate-N in these wells ranged from 0.78 to 37.0 mg/L with an average of 13.5 mg/L. Two injection rows were also used with monitoring wells in transect B: MW-BU2A (12 feet upgradient) MW-BU2B (13 feet upgradient), MW-BU2C (13 feet upgradient), MW-2010C (22 and 24 feet downgradient), MW-2020B (13 and 82 feet downgradient), MW-2020C (14 and 82 feet downgradient), MW-2050A (43 and 93 feet downgradient), MW-2050B (39 and 34 feet downgradient), MW-2050C (43 and 93 feet downgradient), MW-2075A (84 and 139 feet downgradient), and MW-2100C (82 and 141 feet downgradient). Nitrate-N in these wells ranged from 0.35 to 35 mg/L with an average of 8.4 mg/L. Initial sulfate concentrations ranged from <5 to 33.2 with an average of 11.7 mg/L.

Using the results of bench scale testing (see subsection A.a., Terra Systems Inc. Falmouth MA Column Study I (2016)), the modified, EVO formulation (SRS®-NR) was selected for injection for the demonstration test. The SRS®-NR formulation consists of 60 percent soybean oil with emulsifiers and an anionic surfactant. Sodium lactate was not added to SRS®-NR for Phase 1 injection. EVO dilution and injection volume were selected to establish residence time and longevity. A low dilution EVO solution (diluted 4.3:1, 14% soybean oil) was chosen to increase carbon loading. Total design injection volume was prescribed to be 14% of the effective pore volume at the PRB demonstration test. Groundwater pH on Cape Cod tends to be slightly acidic. Groundwater samples from the site have a pH range of 4.4 to 7.2 (average 6.1). Denitrifying bacteria are most active in circumneutral groundwater (pH 6 to 8). However, denitrification has been observed to be inhibited at less than pH 5 (Gonsalez, 2023). Sodium bicarbonate was selected as a pH buffer to raise groundwater pH near the PRB and/or minimize pH decrease because of fermentation of injected carbon substrate.

Injection of carbon substrates was elected to be performed using direct-push injections, as there is no added cost for well installation, maintenance, and abandonment and reduced on-site construction time adjacent to a school by not installing injection wells. The total length of the demonstration test was 110 feet with injection points closely spaced on a 10-foot spacing to establish a continuous barrier length to minimize potential for groundwater to flow through gaps in the reactive zone (see **Figure 8**). On the western half of the demonstration test PRB, seven injection points were set up in a single row (60 feet). On the east side, 10 injection points were laid out in two parallel rows of points (50 feet) to compare nitrate removal, longevity, and groundwater quality. Pre-injection groundwater monitoring indicated that nitrate concentrations were present at depths of 70 feet below ground surface (bgs). For the demonstration test, the vertical treatment interval was established to 36 to 68 feet bgs.

C.a. Demonstration Test Implementation

ISOTEC performed the first injection of SRS®-NR to establish the PRB from November 15 through 18, 2016 with oversight by AECOM. Injection of carbon substrate was performed directly through direct-push rods using the custom-designed ISOTEC proprietary laser-cut stainless steel injection screens. In total, 10,800 gallons of diluted EVO solution was injected, with 2,740 gallons of SRS®-NR and 350 pounds of sodium bicarbonate (3.9 g/L). The average injection flow rate was approximately 6.2 gallons per minute. The EVO solution was generally injected at pressures of 0 pounds per square inch (psi). Injection pressures of 10 to 28 psi were recorded for several intervals corresponding to locations and depths where silts and finer sands were observed in boring logs for monitoring wells. Field monitoring for turbidity, conductivity, pH, and visual observations were performed during the injection. On Day 3 of injection, groundwater samples were collected for laboratory analysis of dissolved organic carbon (DOC) and alkalinity. Negligible impact of EVO was observed based upon turbidity, pH, conductivity, alkalinity, and DOC were detected from monitoring wells approximately 7, 10, and 20 feet downgradient of the PRB injection points during the injection event.

Due to the impact of the wastewater infiltration and stormwater recharge basins , the groundwater flow was not consistently in the expected direction. A second 110 feet PRB was installed with 22 points on 10 feet spacing in a double row to the west of the Phase 1 PRB to intercept elevated nitrate concentrations emanating from a wastewater discharge associated with the nearby school. ISOTEC performed the second injection of SRS®-NR to establish the PRB from June 18 through 20, 2018 with oversight by AECOM. For the second phase, 14,830 gallons of diluted EVO solution were injected, with 3,696 gallons of SRS®-NR, 225 gallons of 60% sodium lactate, and 600 pounds of sodium bicarbonate (2.5 g/L). The 2016 and 2018 injection locations, monitoring wells, and transects are shown in **Figure 8**. Injection of carbon substrate was performed directly through direct-push rods using ISOTEC's proprietary laser-cut injection screens. In total for both phases, 25,630 gallons of diluted EVO solution were injected, with 6,436 gallons of SRS®-NR, 225 gallons of 60% sodium lactate, and 950 pounds of sodium bicarbonate (4.4 g/L). The average injection flow rate was approximately 4.7 gallons per minute. The EVO solution was generally injected at pressures of 0 pounds psi. Injection pressures of 10 to 70 psi were recorded for several intervals corresponding to locations and depths where silts and finer sands were observed in boring logs for monitoring wells.

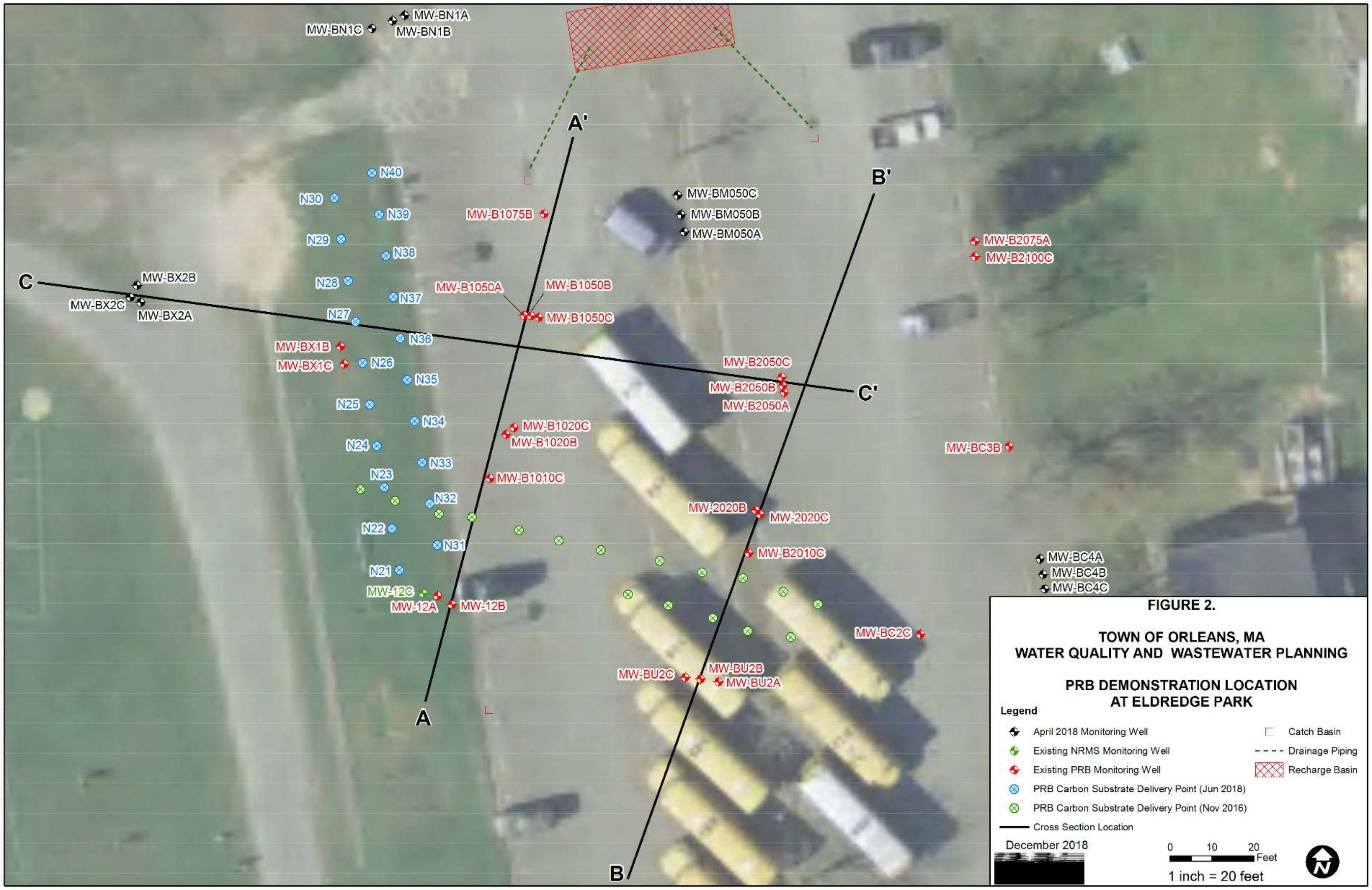
C.b. Results and Discussion

A monitoring well network was established to evaluate performance of the PRB Demonstration Test, which includes monitoring wells upgradient and downgradient of the PRB to evaluate changes to nitrate and groundwater quality. Monitoring wells downgradient of the PRB are located at various distances away from the PRB between 7 to 140 feet to assess distance of emulsion travel, extent of reducing conditions for denitrification away from the PRB, potential for metals mobilization, and groundwater flow velocity. Monitoring wells were installed at three depths; the A zone was from 70 to 80 feet bgs, the B zone from 55 to 65 feet bgs, and the C zone from 40 to 50 ft bgs.

Routine groundwater sampling by AECOM continued for a period of up to six years after the first injection. Periodic annual groundwater sampling is ongoing. A comprehensive suite of analyses was specified to assess denitrification performance, groundwater entering the PRB, and downgradient water quality. Quarterly sampling analyses include nitrate-N, nitrite-N, ammonia-N, Total Kjeldahl Nitrogen (TKN), Total Nitrogen, chloride, sulfate, dissolved iron, dissolved manganese, dissolved arsenic, boron, sodium, DOC, methane, and alkalinity. The primary objectives of the post-injection sampling were to assess reduction in nitrate concentrations, removal of nitrate flux from groundwater as it flows through the PRB, identify distance traveled by EVO emulsion and DOC, evaluate persistence of EVO emulsion and conditions favorable for denitrifying bacteria, and assess changes to other groundwater quality parameters including metals mobilization. It is anticipated the monitoring program would be dynamic and continuously evaluated to adjust the selected monitoring parameters and frequency of monitoring based on data collected and observations.

The groundwater flow direction is influenced by stormwater recharge, wastewater infiltration, and other factors. Estimating groundwater flow direction and velocity is complex as flow may be variable and intermittent due to temporary mounding during rain events. Additional wells were installed in March 2017 to evaluate the PRB performance and groundwater flow at the demonstration test site. The average groundwater flow rate was estimated to be 0.2 to 0.3 ft/day with an average of 0.25 ft/day.

In the A zone (deepest) shown in **Figures 9** (Transect A), **10** (Transect B), and **11** (Transect C) and Tables 2 and 3, the initial nitrate-N in the eight monitoring wells ranged from 0.35 to 37.0 mg/L with an average of 13.4 mg/L. Well MW-BC4A (54 feet crossgradient and 147 feet downgradient from the injection lines) is excluded from the initial average as it appeared to have been impacted by the substrate injections prior to the first sampling point in May 2018. The initial dissolved oxygen ranged from 0 to 4.1 mg/L with an average of 1.3 mg/L. The initial pH ranged from 4.7 to 7.2 SU with an average of 6.4 SU. In the line of wells in Transect A, well MW-12A was 18 feet upgradient and had little DOC or nitrate transformation. Good removal of nitrate in well MW-1050A (33 to 49 feet from the injection lines) which had 28 mg/L maximum DOC and 99.7% removal of the nitrate-N. Well MW-BN1A was 34 feet cross-gradient and had little DOC or nitrate removal. Transect B showed little DOC or denitrification in the well MW-BU2A (12 feet upgradient), moderate (86.5%) nitration reduction in MW-2050A (45 to 91 feet) with a maximum of 9.4 mg/L DOC in June 2021. Well MW-B2075A located between 84 and 139 feet from the nearest injection points and showed little DOC or denitrification. Transect C showed little DOC or nitrate removal in the upgradient wells MW-BX2A (52 feet upgradient) or MW-BM050A (68 to 72 feet downgradient). Well MW-BC4A was about 54 feet crossgradient and 147 feet downgradient for the second SRS®-NR injection and was not installed until September 2018. DOC reached 14 mg/L in well MW-BC4A (54 feet crossgradient and 147 feet downgradient) with good nitrate removals. DOC levels above 5 mg/L were observed in wells MW-B1050A (33 and 49 feet downgradient), MW-B2050A (45 and 91 feet), and MW-BC4A (54 and 147 feet downgradient) at the last sampling period in June 2021. The pH decreased by 0.2 to 1.6 SU in A-zone wells MW-12A (18 feet upgradient), MW-BU2A (12 feet upgradient), MW-B1050A (33 and 33 feet downgradient), MW-B2050A (45 and 91 feet downgradient), and MW-BM050A (68 and 72 feet downgradient) from the first monitoring period to the last sampling event but increased by 0.3 to 1.0 SU in wells MW-BX2A (52 feet upgradient), MW-BN1A (34 feet crossgradient), MW-B2075A (84 and 139 feet downgradient), and MW-BC4A (54 feet crossgradient and 147 feet downgradient). Dissolved oxygen consumption was observed in wells MW-2050A (45 and 91 feet downgradient), MWBM50A (68 and 72 feet downgradient), and MW2075A (84 and 139 feet downgradient) through June 2021. Sulfate was reduced to below detection limits in wells MW-BN1A (34 feet crossgradient) and MW-B1050A (68 and 72 feet downgradient) through June 2021, by 1.4% in MW-BU2A (12 feet upgradient) but increased in the other A zone wells. The maximum dissolved iron was 50.8 mg/L in well MW-B1050A (44 and 93 feet downgradient) with only wells MW-BU2A (12 feet upgradient), MW-B2050A (45 and 91 feet downgradient), and MW-BM050A (68 and 72 feet downgradient) having more than 1 mg/L dissolved iron. Dissolved manganese was above 1 mg/L only in wells MW-B1050A (44 and 93 feet downgradient) and MW-BC4A (54 and 147 feet downgradient). Methane and dissolved arsenic were not detected in the A-zone, with only well MW-BC4A (54 feet crossgradient and 147 feet downgradient) analyzed for dissolved arsenic.



P:\Jobs\Indl_Service\Project Files\Orleans\PRB_Cross_Sections\Site_Plan\MXD\PRB_Figure2_EldredgePark.mxd

Figure 8. Eldredge Park, Orleans Monitoring Wells and Transects

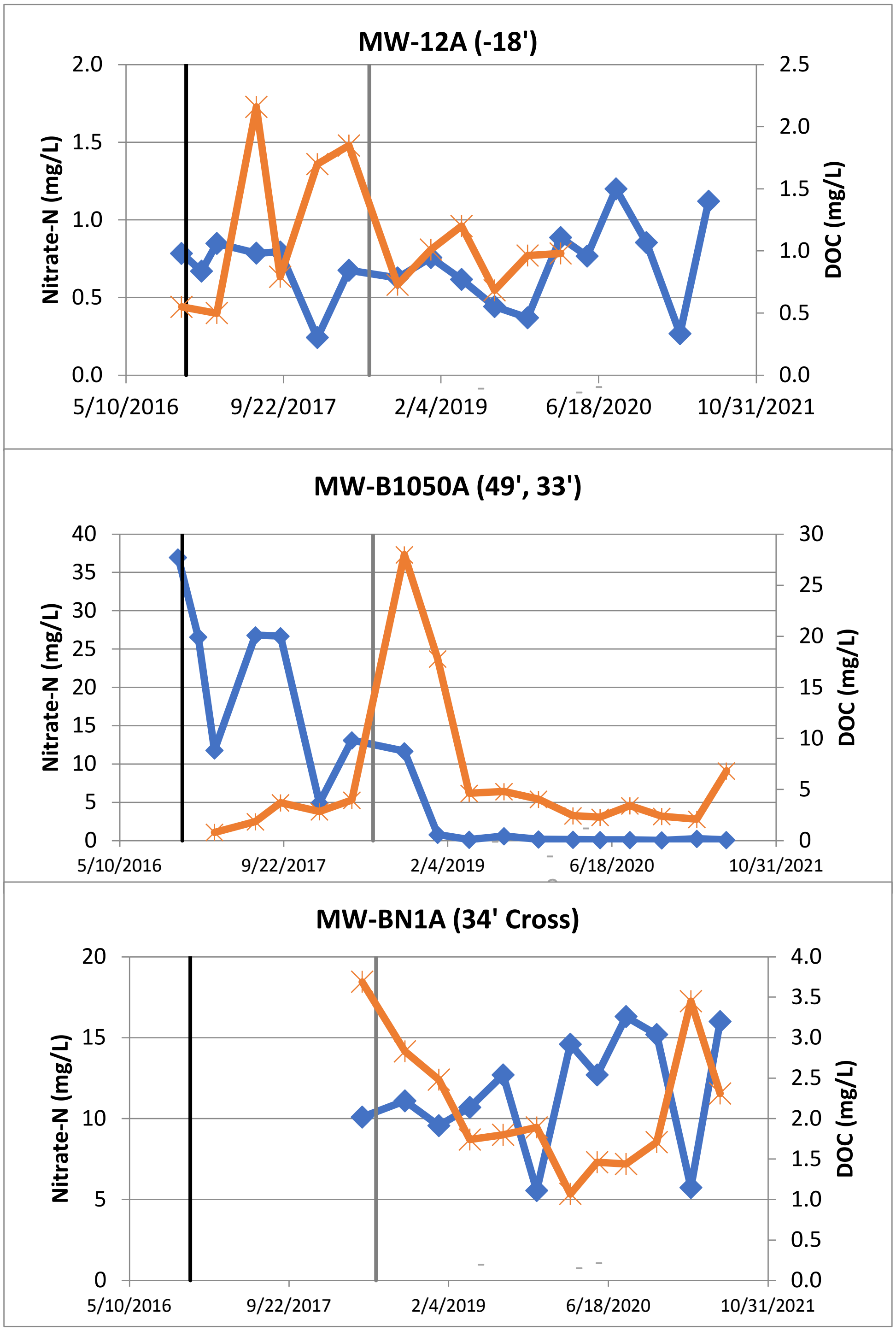


Figure 9. A Zone Wells Transect A

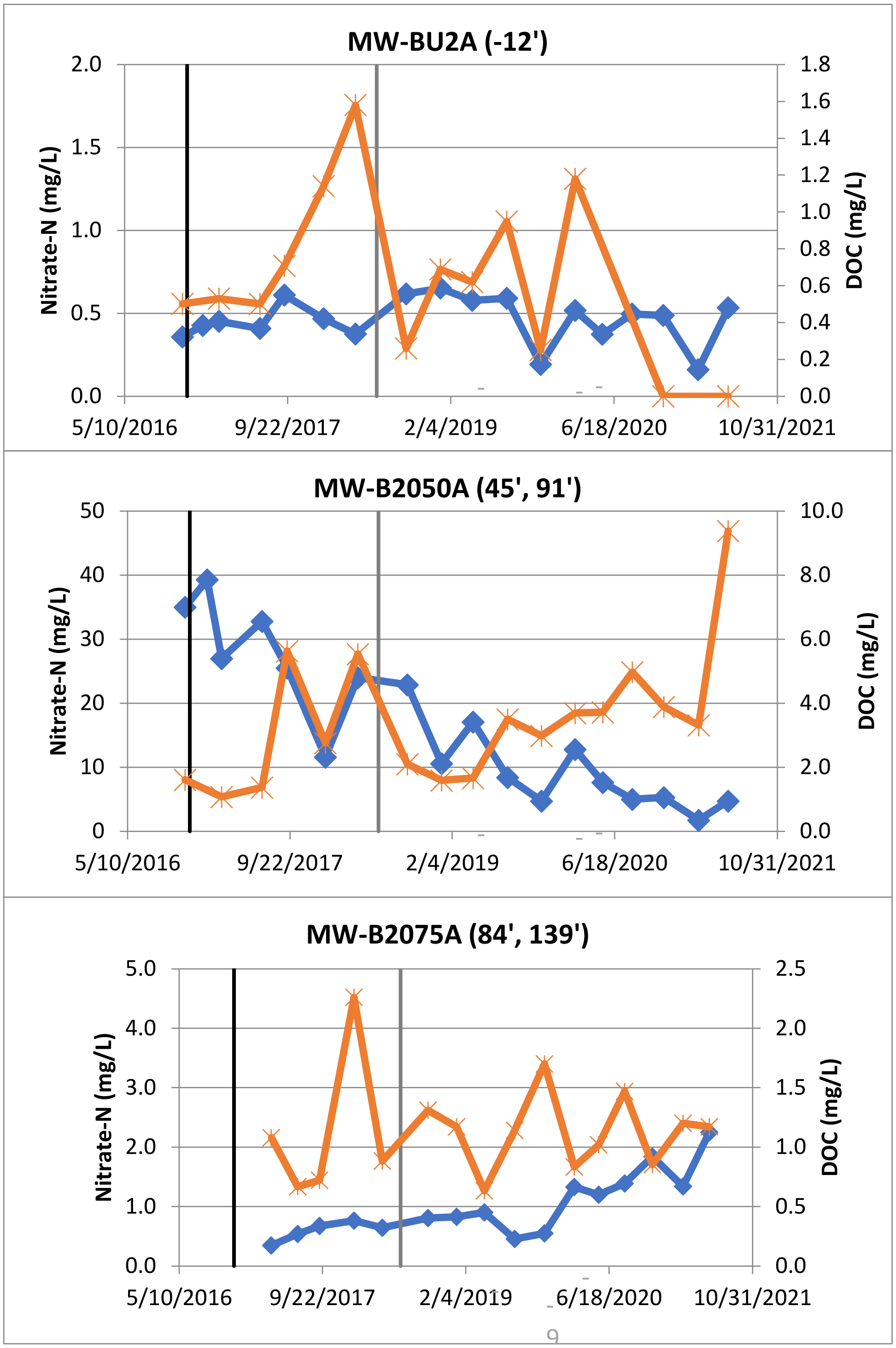


Figure 10. A Zone Wells Transect B

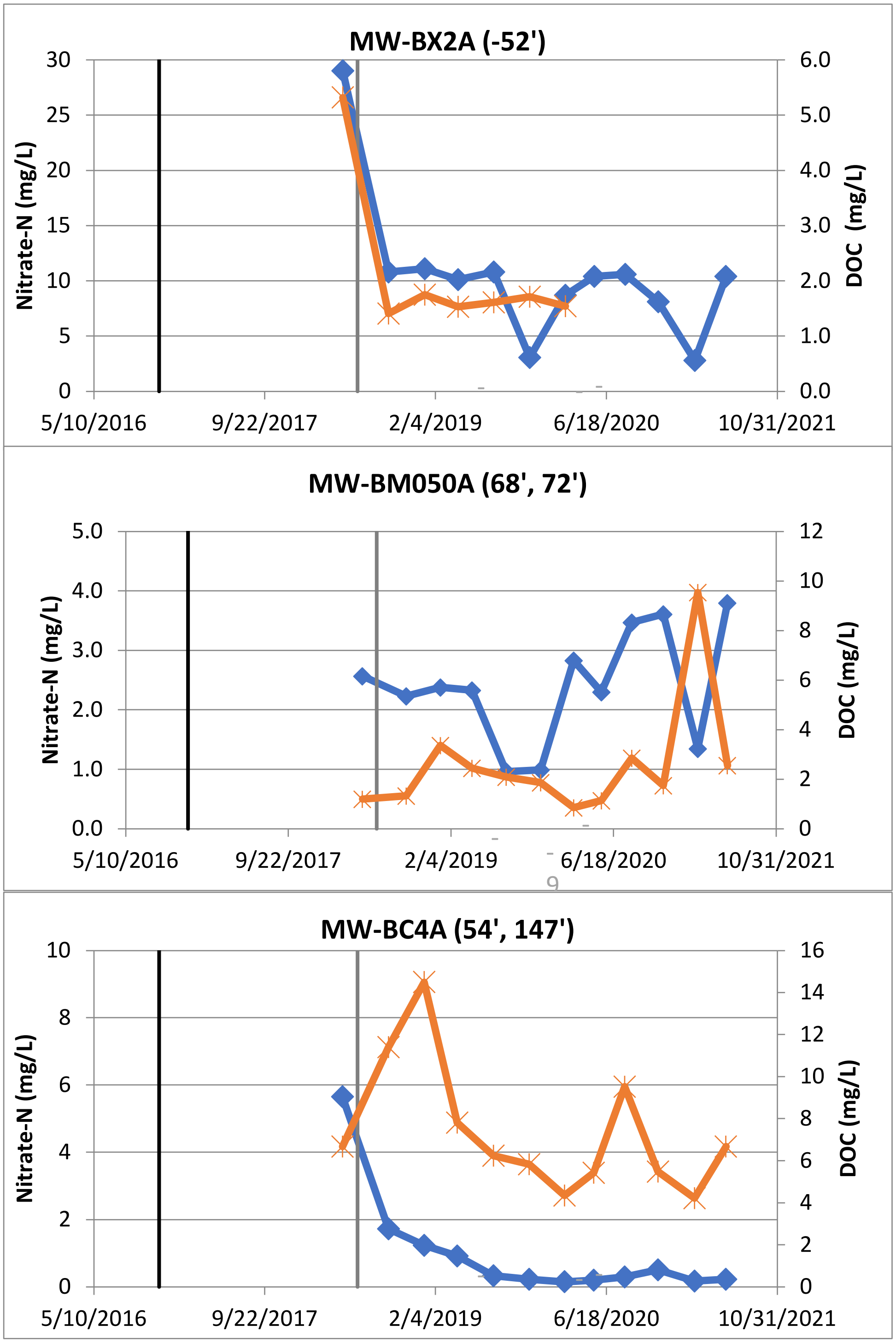


Figure 11. A Zone Wells Transect C

In the B zone (intermediate) shown in **Figure 12** (Transect A), **13** (Transect B), and **14** (Transect C) and Tables 2 and 3, the initial nitrate-N in the ten monitoring wells ranged from 1.1 to 28.4 mg/L with an average of 10.3 mg/L. Wells MW-BC4B (53 feet crossgradient and 145 feet downgradient), MW-4N1B (31 feet crossgradient), and MW-BX2B (52 feet upgradient) were not included in the initial averages as they were not sampled prior to the the second round of EVO injections and appeared to have been impacted by the substrate injections prior to the first round of samples being collected from these wells). The initial dissolved oxygen ranged from 0 to 2.5 mg/L with an average of 1.2 mg/L. The initial pH ranged from 4.7 to 7.2 SU with an average of 6.4 SU. In transect A, the upgradient well MW-12B (19 feet upgradient) showed little DOC (maximum 3.7 mg/L) and limited or no transformation of nitrate-N or total N. Wells MW-B1020B (19 and 82 feet downgradient) and MW-B1050B (7 and 25 feet downgradient) showed up to 668 mg/L DOC and complete denitrification. Well MW-B1075, 41 to 65 feet from the nearest injection wells, had only 11 mg/L DOC and limited denitrification. Well MW-BN1B was about 31 feet crossgradient from the nearest injection well and had little DOC or denitrification. For transect B, little DOC was found in well MW-BU2B (13 feet upgradient) and little nitrate consumption. While DOC reached a maximum of 30 mg/L in MW-B2020B (13 and 82 feet downgradient) in September 2017, nitrate rebounded in April 2019 when the DOC fell below 9 mg/L. Well MW-B2050B (34 and 39 feet downgradient) saw up to 7.4 mg/L DOC in June 2019 with good nitrate treatment. Well MW-BM050B (13 and 82 feet downgradient) had only limited DOC or nitrate treatment. In transect C, MW-BX2B was about 52 feet upgradient of the second injection but showed up to 28 mg/L DOC which supported 18.4 mg/L of nitrate-reduction. However, the DOC was rapidly consumed to below 5 mg/L and little further nitrate or total N was removed in well MW-BX2B (52 feet upgradient). Well MW-BX1B was about 6 feet from the nearest injection well and showed DOC levels up to 112 mg/L and removal of 84.3% of the nitrate-N and 78.3% total N. Well MW-BC3B (56 feet crossgradient) had limited DOC and denitrification. When the DOC reached 13 mg/L in well MW-BC4B (53 feet crossgradient and 145 feet downgradient) in May 2018, nitrate levels were 1.2 to 1.9 mg/L, but nitrate-N increased when DOC declined. DOC levels above 5 mg/L were found in the last sampling point for wells MW-BX1B (6 feet upgradient), MW-B1050B (7 and 25 feet downgradient), MW-B1075B (41 to 65 feet from the nearest injection wells), MW-B2050B (34 and 39 feet downgradient), MW-B2020B (13 and 82 feet downgradient), and MW-BC4B (53 feet crossgradient and 145 feet downgradient). Wells MW-BX1B (6 feet upgradient), MW-B1020B (19 and 82 feet downgradient), and MW-B1050B (44 and 93 feet downgradient) were last sampled in June or September 2022 and had 4.1 to 9.3 mg/L DOC and good denitrification. The pH decreased by 0.1 to 1.6 SU in B-zone wells MW-12B (19 feet upgradient), MW-BU2B (13 feet upgradient), MW-BC3B (56 feet crossgradient), MW-B1020B (19 and 82 feet downgradient), MW-B1050B (44 and 93 feet downgradient), MW-B1075B (41 and 65 feet downgradient), MWB2050B (34 and 39 feet downgradient), and MW-B2020B from the first monitoring period to the last sampling event but increased by 0.2 to 1.5 SU in wells MW-BX2B (52 feet upgradient), MW-BN1B (31 feet crossgradient), MW-BX1B (6 feet upgradient), MW-BM050B (71 and 73 feet downgradient), and MW-BC4B (53 and 145 feet crossgradient). Dissolved oxygen consumption greater than 90% was observed in wells MW-12B (19 feet upgradient), MW-BX1B (6 feet upgradient), MW-B1020B (19 and 82 feet downgradient), MW-B1050B (7 and 25 feet downgradient) , and MW-B2050B (34 and 39 feet downgradient) through June 2021. Sulfate was reduced to below detection limits in wells MW-BX2B (52 feet upgradient), MW-BX1B (6 feet upgradient), MW-B1020B (13 and 82 feet downgradient), and MW-B1050B (44 and 93 feet downgradient) and MW-B1050B (44 and 93 feet downgradient) through June 2021 but not in the other B zone wells. The maximum dissolved iron was 152 mg/L in well MW-BX1B (6 feet upgradient) and 151 mg/L in well MW-B1050B (44 and 93 feet downgradient) with wells MW-BC3B (56 feet crossgradient), MW-B1020B (19 and 82 feet downgradient), and MW-B2050B (34 and 39 feet downgradient) having more than 1 mg/L dissolved iron. Dissolved manganese was above 1 mg/L only in wells MW-BC3B (56 feet crossgradient), MW-BX1B (6 feet upgradient), MW-B1020B (19 and 82 feet downgradient), MW-B2050B (34 and 39 feet downgradient), and MW-B2020B (13 and 82 feet downgradient). The maximum methane detected in the B-zone wells was 16.6 mg/L in well MW-BX1B (6 feet upgradient) with wells MW-B1050B (44 and 93 feet downgradient) and MW-BC4B (53 feet crossgradient and 145 feet downgradient) having more than 1 mg/L methane. Only a limited number of wells were analyzed for methane. Dissolved arsenic was not detected in the B-Zone.

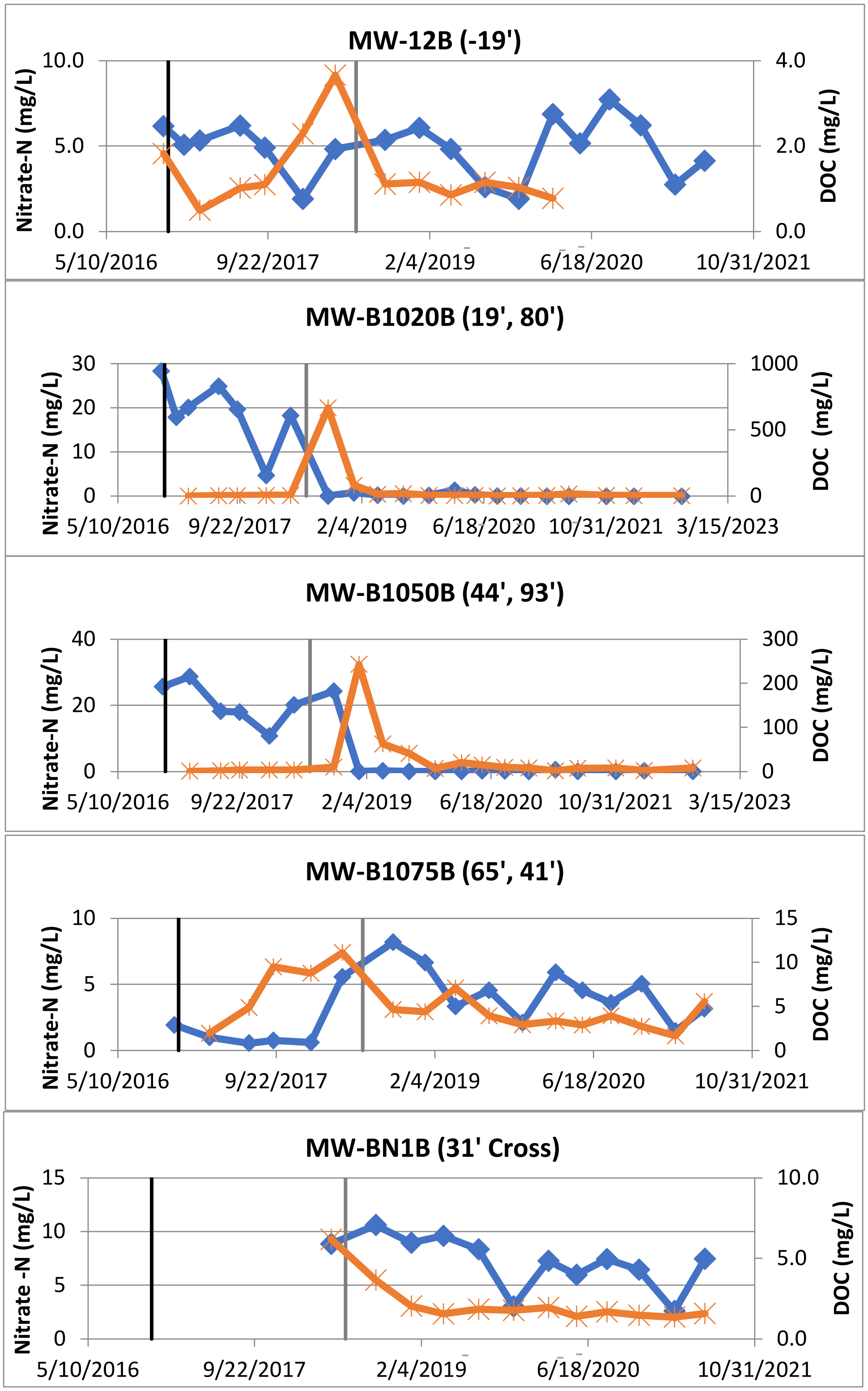


Figure 12. B Zone Wells Transect A

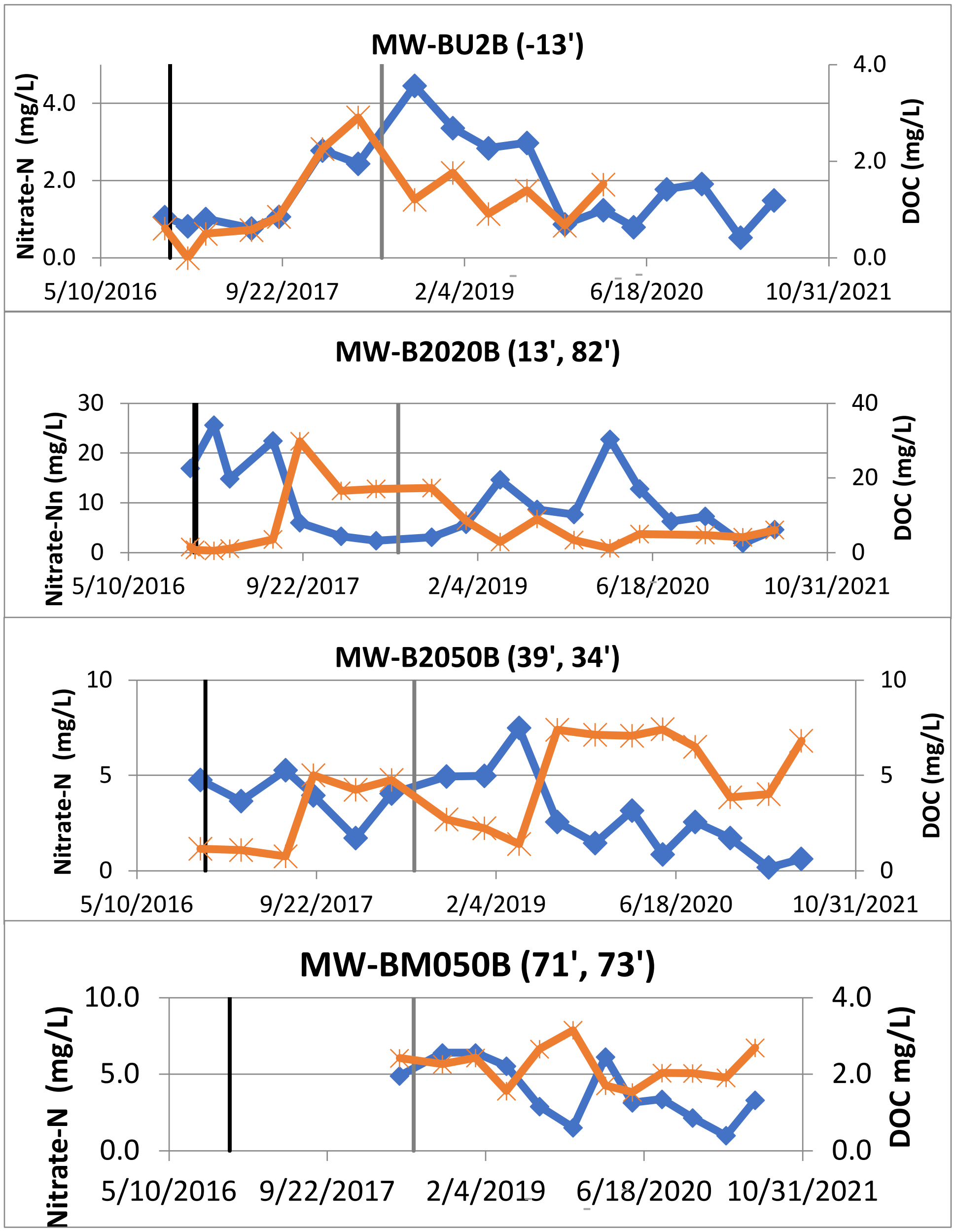


Figure 13. B Zone Wells Transect B

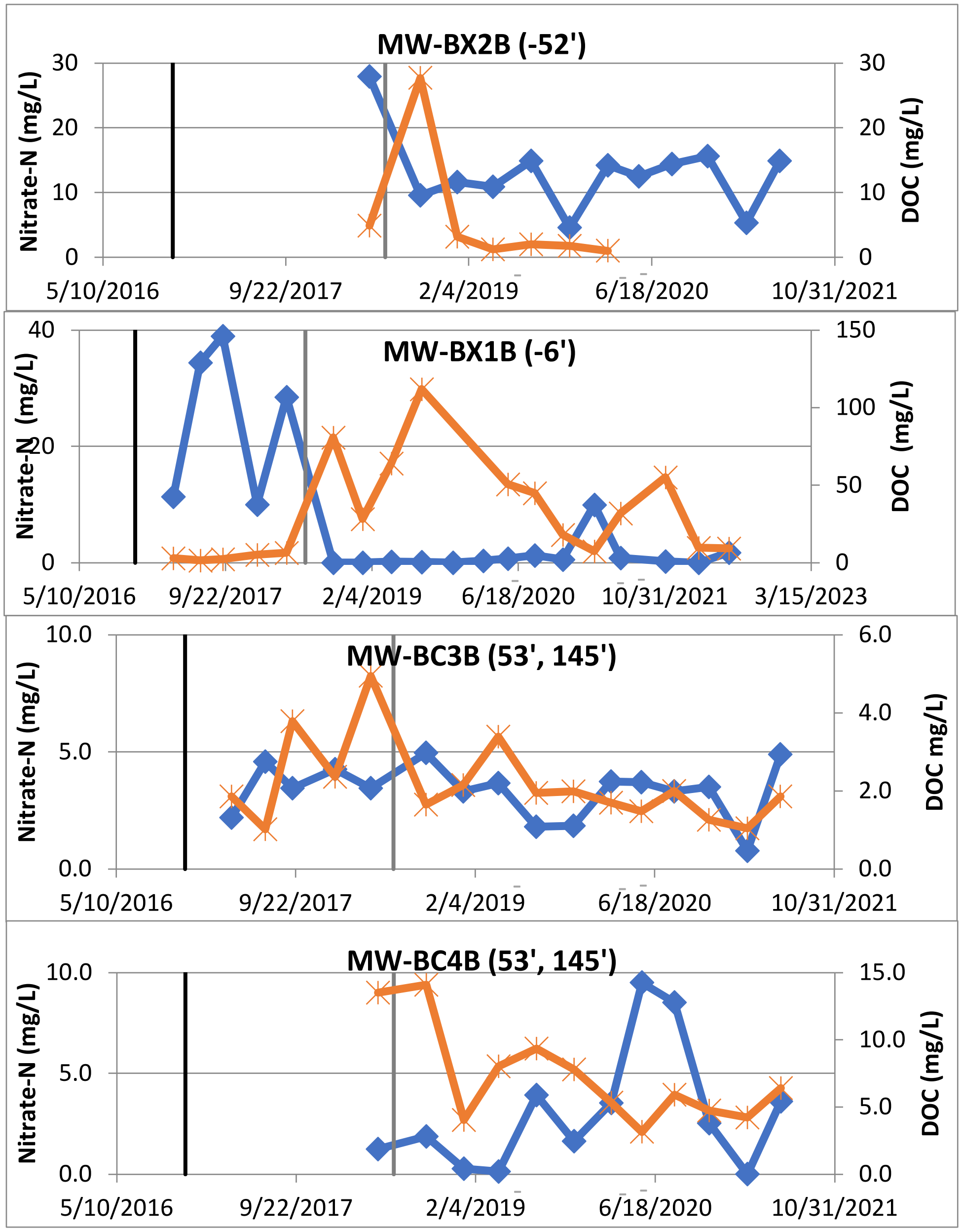


Figure 14. B Zone Wells Transect C

In the C zone (shallowest) shown in **Figures 15** (Transect A), **16** (Transect B), and **17** (Transect C) and **Tables 2** and **3**, the initial nitrate-N in the fourteen monitoring wells (excluding MW-BC4C (25 feet crossgradient and 121 feet downgradient) which appeared to have been impacted by the substrate injections prior to the first sampling point) ranged from 1.1 to 39.7 mg/L with an average of 11.6 mg/L. The initial dissolved oxygen ranged from 0.7 to 6.9 mg/L with an average of 2.4 mg/L. The initial pH ranged from 4.7 to 7.2 SU with an average of 6.2 SU. In Transect A, only low levels of DOC were found in the upgradient wells MW-12C (8 to 17 feet upgradient) with little denitrification. Wells MW-B1010C (9 and 16 feet downgradient), MW-B1020C (21 and 26 feet downgradient), and MW-B1050C located 44 and 94 feet downgradient from the injection barrier all showed elevated DOCs and good nitrate removals. Well MW-BN1C located 30 feet crossgradient showed only 4.2 mg/L DOC but nitrate-N decreased by 61.8%. In transect B, DOC was limited in wells MW-BU2C (13 feet upgradient) with little denitrification. Wells MW-B2010C (22 and 24 feet downgradient) and MW-B2020C (14 and 82 feet downgradient) had elevated DOCs and complete denitrification. Wells MW-B2050C (43 and 93 feet downgradient) and MW-B2100C (82 and 141 feet downgradient) had 5.2 to 2.3 mg/L DOC which did not support denitrification. For transect C, upgradient well MW-BX2C (54 feet upgradient) had a maximum of 4.2 mg/L with 48.4% nitrate removal. Well MW-BX1C, 6 feet upgradient of the barrier, had up to 79 mg/L DOC which supported denitrification for 17 months until the DOC dropped below 12 mg/L. Well MW-BM050C, 71 and 77 feet from the injection line, showed <3 mg/L DOC and little nitrate removal. Well MW-BC4C (25 feet crossgradient and 121 feet downgradient), had almost complete denitrification even with a maximum of 9.4 mg/L DOC.

DOC levels were above 5 mg/L at the last sampling event in June 2021 in C-Zone wells MW-BC4C (25 feet crossgradient and 121 feet downgradient), MW-BX1C (6 feet upgradient), MW-B1010C (9 and 16 feet downgradient), MW-B1020C (21 and 26 feet downgradient), MW-B2020C (14 and 84 feet downgradient), MW-B1050C (44 and 94 feet downgradient), and MW-B2050C (43 and 93 feet downgradient). The pH decreased by 0.1 to 1.6 SU in C-zone wells MW-BU2C (13 feet upgradient), MW-BC2C (24 feet crossgradient and 118 feet downgradient), MW-B1010C (9 and 16 feet downgradient), MW-B2010C (22 and 24 feet downgradient), MW-B1020C (21 and 26 feet downgradient), MW-B2020C (14 and 82 feet downgradient), MW-B1050C (44 and 94 feet downgradient), and MW-B2050C (43 and 93 feet downgradient) from the first monitoring period to the last sampling event but increased by 0.2 to 1.5 SU in wells MW-12C (8 to 17 feet upgradient), MW-BX2C (54 feet upgradient), MW-BN1C (30 feet crossgradient), MW-BC4C (25 feet crossgradient and 121 feet downgradient), MW-BX1C (6 feet upgradient), MW-BM050C (71 and 77 feet downgradient), and MW-B2100C (82 and 141 feet downgradient). Dissolved oxygen consumption greater than 90% was observed in wells MW-12C (8 and 17 feet upgradient), MW-BX1C (6 feet upgradient), MW-B1020C (21 and 26 feet downgradient), and MW-B2050C (43 and 93 feet downgradient) through June 2021. Sulfate was reduced to below detection limits in wells MW-12C (8 and 17 feet upgradient) and MW-BX2C (54 feet upgradient) through June 2021 but not in the other C zone wells. The maximum dissolved iron was 157 mg/L in well MW-B2010C (22 and 24 feet downgradient), 140 mg/L in well MW-B1020C (21 and 26 feet downgradient), 139 mg/L in well MW-B1010C (9 and 16 feet downgradient), and 103 mg/L in MW-B2020C (14 and 82 feet downgradient) with wells MW-12C (8 to 17 feet upgradient), MW-BC4C BC4C (25 feet crossgradient and 121 feet downgradient), MW-BX1C (6 feet upgradient), and MW-B1050C (44 and 94 feet downgradient) having more than 1 mg/L dissolved iron. Dissolved manganese was above 1 mg/L only in wells MW-BN1C (30 feet crossgradient), MW-BC4C (25 feet crossgradient and 121 feet downgradient), MW-B1010C (9 and 16 feet downgradient), MW-B2010C (22 and 24 feet downgradient), MW-B1020C (21 and 26 feet downgradient), MW-B2020C (14 and 82 feet downgradient), and MW-B1050C (44 and 94 feet downgradient). The maximum methane detected in the B-zone wells was 16.7 mg/L in well MW-MW-B1010C (9 and 16 feet downgradient) with wells MW-BX1C (6 feet upgradient), MW-B2010C (22 and 24 feet downgradient), MW-B1020C (21 and 26 feet downgradient), and MW-B2020C (14 and 82 feet downgradient) having more than 1 mg/L methane. Only a limited number of wells were analyzed for methane. Dissolved arsenic was found at a maximum of 0.043 mg/L in well MW-B2010C (22 and 24 feet downgradient) with 0.036 mg/L in well MW-B1020C (21 and 26 feet downgradient).

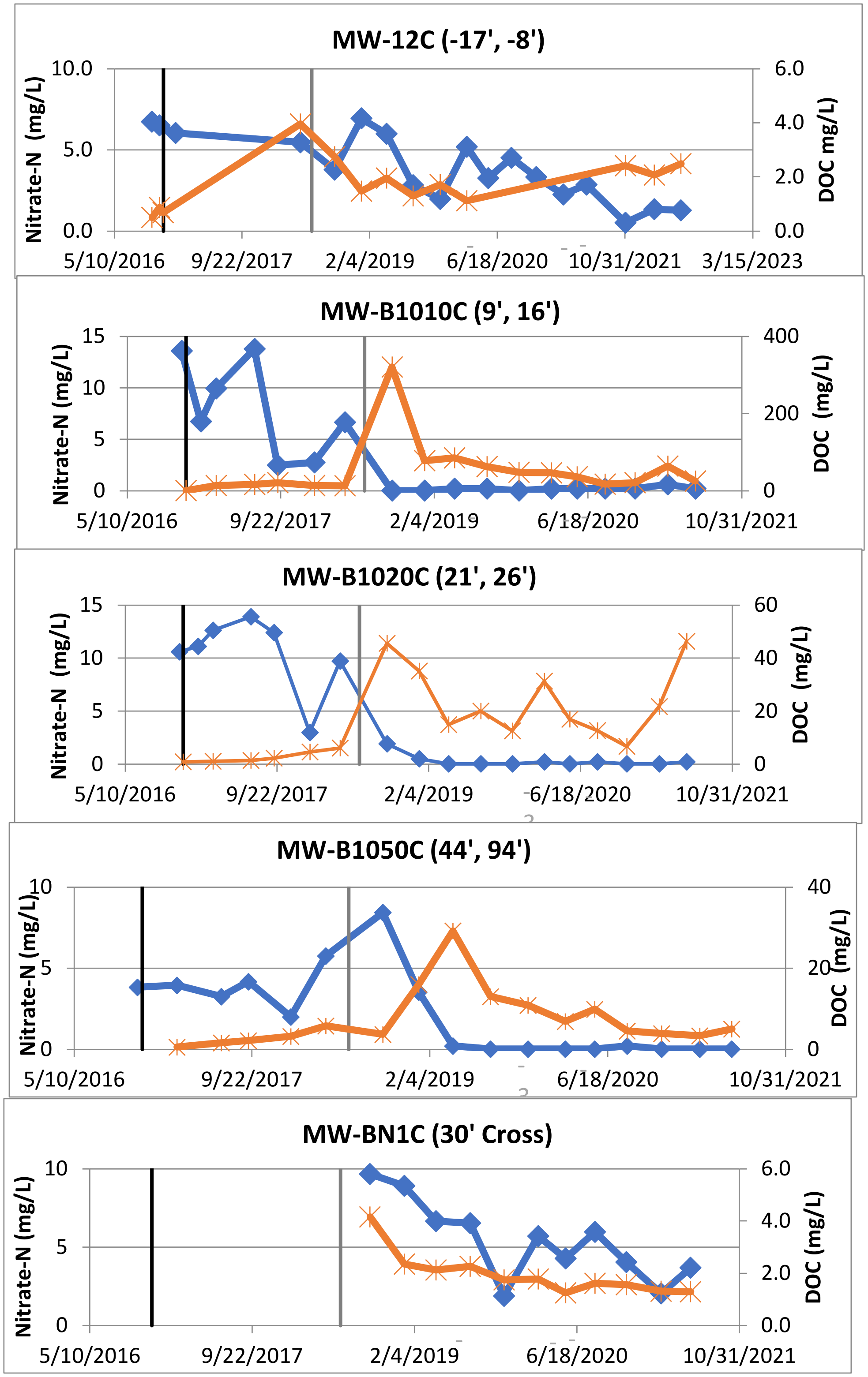


Figure 15. C Zone Wells Transect A

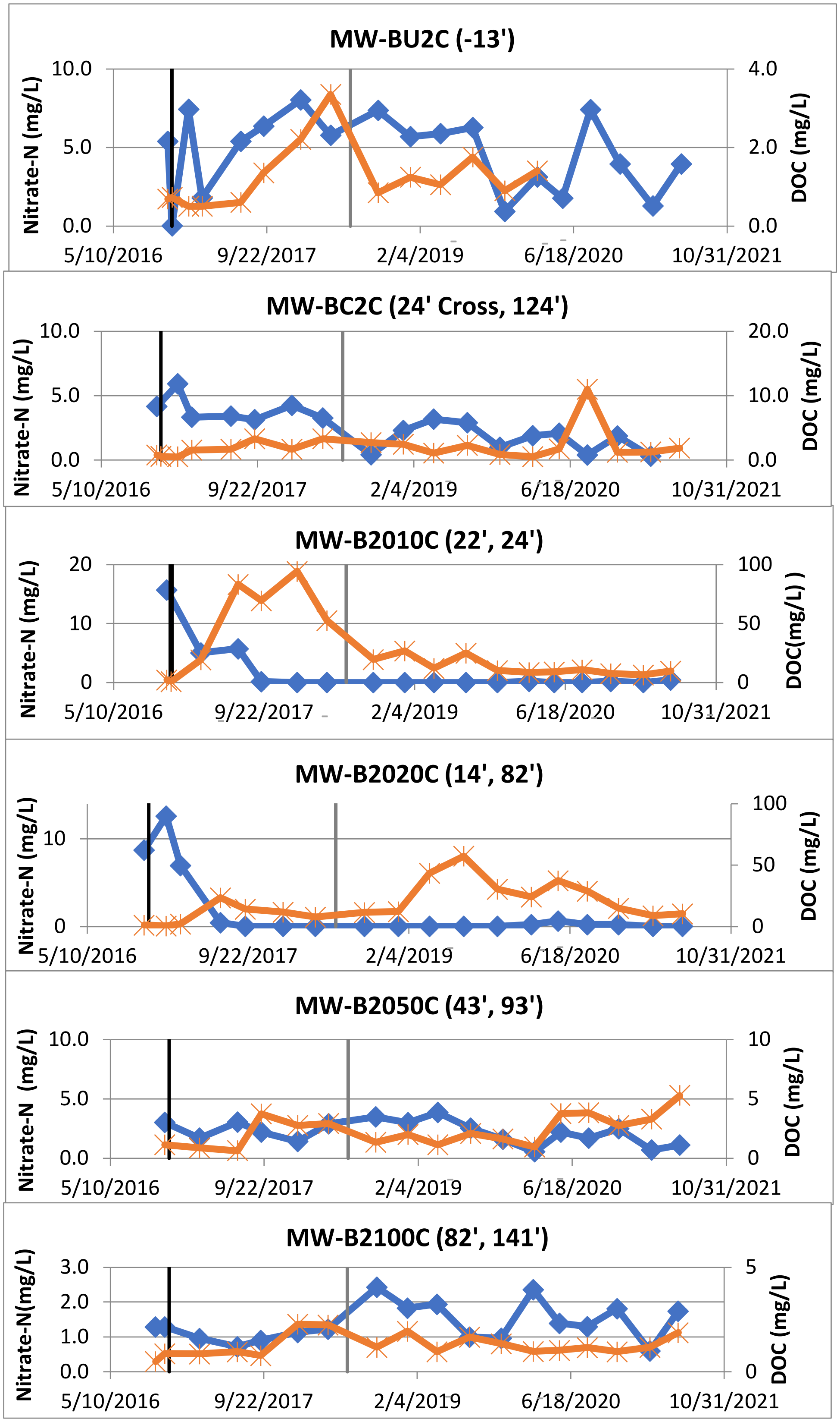


Figure 16. C Zone Wells Transect B

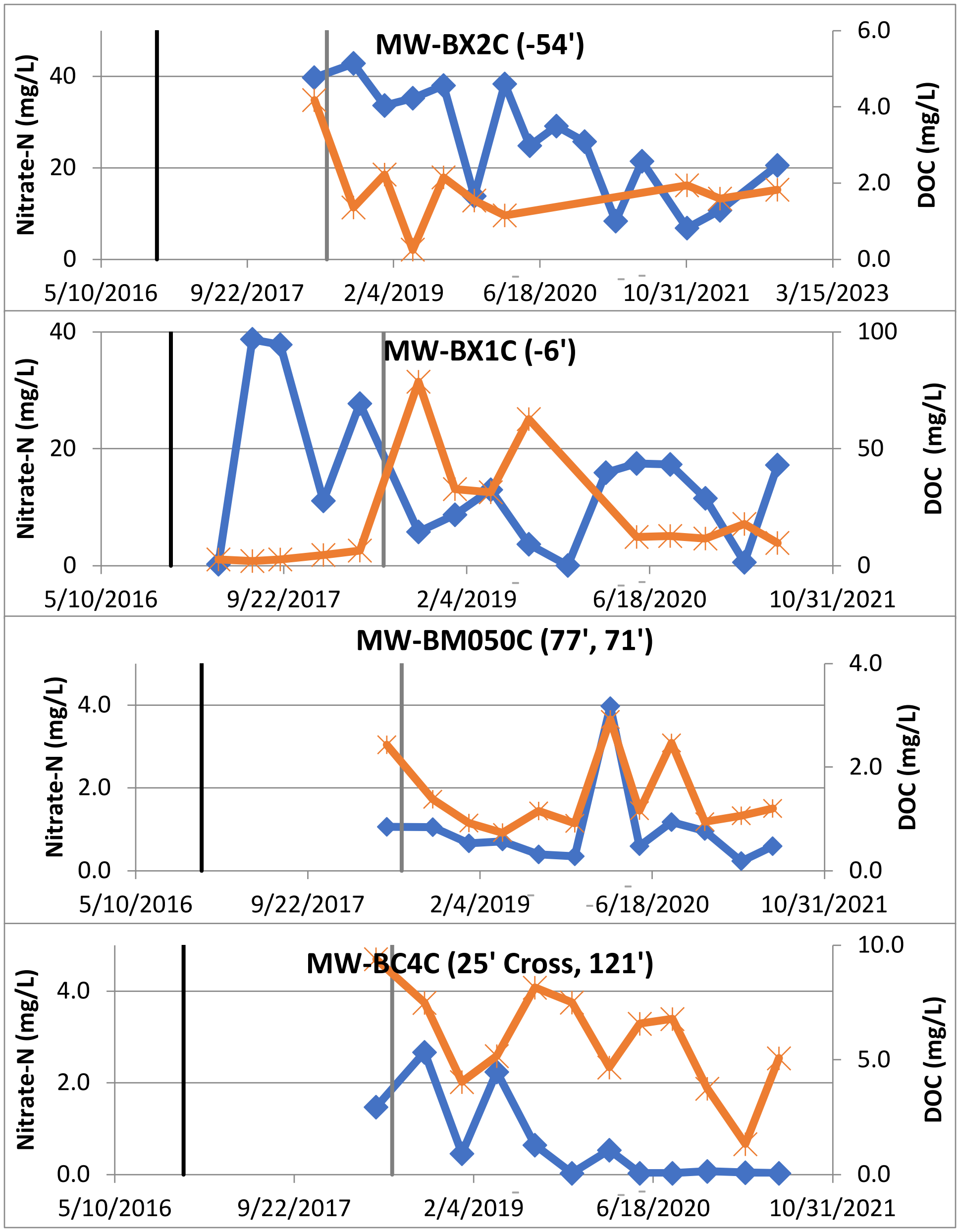


Figure 17. C Zone Wells Transect C

C.c. Conclusions

The first in-situ EVO PRB demonstration test on Cape Cod to remove nitrate from groundwater by denitrifying bacteria was initiated in November 2016 with a second EVO injection to extend the PRB in June 2018 to intercept elevated nitrate concentrations flowing from the west of the demonstration test PRB. The demonstration test site was chosen based on a site screening evaluation with more than 20 scored criteria (AECOM 2016)A modified formulation of EVO was injected based on the results of bench scale column tests performed to assess effectiveness in removing nitrate, persistence of the EVO and denitrifying conditions, and migration of EVO in a sandy aquifer. Negligible impact of EVO was observed, based on turbidity, pH, conductivity, alkalinity, and DOC, from monitoring wells nearest to injection points during the injection event. This lack of observation has been viewed as successfully achieving the design objective of injecting a stickier emulsion, with the oil staying near to the injection points to increase the longevity of the carbon substrate. In the first injection in 2016, there was no obvious difference in the nitrate-N reduction or DOC distribution between the single row of injection points and the double row of injection points. DOC levels have persisted above 4 mg/L for over 4.7 years with good denitrification at distances of up to 50 feet downgradient of the PRBs. DOC levels above 5 mg/L supported denitrification.

Table 2. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, and Total N % Removal for Eldredge Park, Orleans, MA

Well	**Transect**	**Screened Interval MSL ft**	**First Sampling Date**	**Distance (ft) to Injection Points**	**Nitrate-N (mg/L)**	**Max DOC (mg/L)**	**Last Sampling Date**	**Most Recent DOC (mg/L)**	**%Nitrate-N Removal**	**% Total N Removal**
MW-12A	A	-24.4 to -34.4	11/3/2016	18 Up	0.78	2.2	6/2/2022	1.0	-43.0	-43.0
MW-B1050A	A	-26.1 to -36.1	11/4/2016	49, 33	37.0	28	6/2/2021	6.8	99.7	97.5
MW-BN1A	A	-25.5 to -35.5	5/9/2018	34 Cross	10.1	3.7	6/3/2021	2.3	-58.4	-58.4
MW-BU2A	B	-24.9 to -34.9	11/3/2016	12 Up	0.36	1.6	6/3/2021	1.2	-49.3	-152.4
MW-B2050A	B	-25.4 to -35.4	11/3/2016	45, 91	35	9.4	6/2/2021	9.4	86.5	84.9
MW-B2075A	B	-20.4 to 30.4	3/27/2017	84, 139	0.35	2.3	6/2/2021	1.2	-546.6	-542.9
MW-BX2A	C	-23.6 to -33.6	5/9/2018	52 Up	29.0	5.3	6/3/2021	1.5	64.1	64.4
MW-BM050A	C	-25.3to -35.3	5/8/2018	68, 72	2.57	9.5	6/3/2021	2.6	-47.9	-537.7
MW-BC4A	C	-26.6 to -36.5	5/8/2018	54, 147	5.65	14.5	6/3/2021	6.7	95.9	25.3
MW-12B	A	-9.4 to -19.4	11/3/2016	19 Up	6.17	3.7	6/2/2021	0.8	32.9	35.6
MW-B1020B	A	-10.4 to -20.4	11/4/2016	19, 80	28.4	668	9/7/2022	4.1	99.3	97.3
MW-B1050B	A	-11.1 to -21.1	11/6/2016	44, 93	25.7	243	9/7/2022	7.8	99.2	96.3
MW-B1075B	A	-11.5 to -21.5	11/4/2016	65, 41	1.93	11	6/3/2021	5.6	-64.2	-31.6
MW-BN1B	A	-10.6 to -20.6	5/9/2018	31 Cross	8.85	6.2	6/3/2021	1.6	15.8	-4.8
MW-BU2B	B	-9.9 to -19.9	11/3/2016	13 Up	1.06	2.9	6/3/2021	1.5	-40.6	-69.8
MW-B2020B	B	-10.1 to -20.1	11/3/2016	13, 82	16.9	30	6/3/2021	6.0	72.9	68.9
MW-B2050B	B	-10.4 to -20.4	11/3/2016	39, 34	4.75	7.4	6/2/2021	6.8	86.9	73.2
MW-BM050B	B	-10.2 to -20.2	5/8/2018	71, 73	4.9	3.2	6/3/2021	2.7	32.7	-2737.8
MW-BX2B	C	-8.6 to -18.6	5/9/2018	52 Up	27.9	27.7	6/3/2021	1.0	46.6	46.6
MW-BX1B	C	-9.4 to -19.4	3/27/2017	6 Up	11.4	112	6/7/2022	9.3	84.3	78.3
MW-BC3B	C	-10.8 to -220.	3/27/2017	56 Cross	2.2	5.0	6/3/2021	1.9	-122.7	-89.2
MW-BC4B	C	-11.5 to -21.5	5/8/2018	53, 145	1.25	14.1	6/3/2021	6.4	-189.6	-592.2
MW-12C	A		10/4/2016	17, 8 Up	6.74	4.0	6/7/2022	2.5	81.2	78.3
MW-B1010C	A	-0.1 to -10.1	11/3/2016	9, 16	13.6	321	6/2/2021	25.3	98.5	91.8
MW-B1020C	A	4.5 to -5.5	11/4/2016	21, 26	10.6	46	6/2/2021	46	98.0	92.1
MW-B1050C	A	4.9 to -5.1	11/4/2016	44, 94	3.83	29	6/2/2021	5.0	99.2	90.3
MW-BN1C	A	4.4 to -5.6	9/20/2018	30 Cross	9.66	4.2	6/3/2021	1.3	61.8	52.3
MW-BU2C	B	5.1 to -4.9	11/3/2016	13 Up	5.39	3.4	6/3/2021	1.4	26.9	-29.7
MW-BC2C	B	-1.5 to -11.5	11/4/2016	24 Cross, 118	4.16	11	6/3/2021	1.8	57.2	47.9
MW-B2010C	B	0 to -10.0	11/3/2016	22, 24	15.7	94	6/3/2021	9.7	97.1	87.3
MW-B2020C	B	4.8 to -5.2	11/3/2016	14, 82	8.71	57	6/3/2021	10.4	99.7	93.0
MW-B2050C	B	4.5 to 5.4	11/3/2016	43, 93	3.01	5.3	6/2/2021	5.3	63.5	42.1
MW-B2100C	B	9.6 to 0.4	10/4/2016	82, 141	1.29	2.3	6/3/2021	1.9	-34.9	-2.0
MW-BX2C	C	6.5 to -3.5	5/9/2018	54 Up	39.7	4.2	9/7/2022	1.8	48.4	47.9
MW-BX1C	C	5.4 to -4.6	3/27/2017	6 Up	0.25	79	6/2/2021	9.7	-6780.0	-113.8
MW-BM050C	C	4.8 to -5.2	5/9/2018	77, 71	1.06	2.9	6/3/2021	1.2	44.0	37.0
MW-BC4C	C	3.5 to -6.5	5/8/2018	25 Cross, 121	1.47	9.4	6/3/2021	5.1	98.0	8.3

Table 3. % Dissolved Oxygen Removal, % Sulfate Consumed, Maximum Dissolved Iron, Maximum Dissolved Manganese, Maximum Methane, and Maximum Dissolved Arsenic

Well	**Transect**	**pH Change**	**% DO Consumed**	**% Sulfate Consumed**	**Max Dis Fe (mg/L)**	**Max Dis Mn (mg/L)**	**Max CH4 (mg/L)**	**Max Dis As (mg/L)**
MW-12A	A	1.3	-581.4	-18.0	0.7	0.3	NA	NA
MW-B1050A	A	0.4	-646.3	>18.0	50.8	3.1	NA	NA
MW-BN1A	A	-1.0	0.0	>76.7	0.4	0.3	NA	NA
MW-BU2A	B	0.9	-416.1	1.4	1.1	0.2	NA	NA
MW-B2050A	B	1.6	86.7	-521.4	3.2	0.4	NA	NA
MW-B2075A	B	-0.3	72.3	-54.4	0.4	0.5	NA	NA
MW-BX2A	C	-0.4	94.9	-161.4	0.6	0.6	NA	NA
MW-BM050A	C	0.2	83.1	-10.4	1.8	0.2	NA	NA
MW-BC4A	C	-0.5	-23.1	-168.9	0.2	3.7	NA	<0.025
MW-12B	A	1.6	92.4	-12.2	0.4	0.2	NA	NA
MW-B1020B	A	0.2	99.0	0	58.4	5.3	NA	NA
MW-B1050B	A	0.5	99.1	0	151.0	5.9	12.4	NA
MW-B1075B	A	1.3	-23.9	10.5	0.9	0.4	NA	NA
MW-BN1B	A	-0.2	75.0	72.9	0.3	0.1	NA	NA
MW-BU2B	B	1.3	-364.6	0.0	0.7	0.1	<0.002	NA
MW-B2020B	B	1.6	68.7	-542.9	17.6	3.5	<0.002	NA
MW-B2050B	B	1.4	90.7	-237.4	1.9	1.3	NA	NA
MW-BM050B	B	-0.7	0.0	19.5	0.5	0.6	NA	NA
MW-BX2B	C	-0.7	-37.5	-31.3	0.7	0.6	NA	NA
MW-BX1B	C	-1.5	99.4	100.0	152.0	5.0	16.6	NA
MW-BC3B	C	0.1	-60.8	-27.7	1.6	1.3	<0.002	<0.001
MW-BC4B	C	-0.5	16.7	-59.7	0.5	0.8	5.9	<0.001
MW-12C	A	-0.6	98.8	100.0	3.7	0.7	NA	NA
MW-B1010C	A	0.1	97.7	<73	139.0	5.8	16.7	NA
MW-B1020C	A	0.4	87.5	-546.4	140.0	4.6	6.3	0.0360
MW-B1050C	A	1.1	82.1	58.7	60.7	4.9	NA	NA
MW-BN1C	A	-0.8	79.1	>82.2	0.1	3.5	NA	NA
MW-BU2C	B	1.9	-416.8	0.0	0.8	0.3	<0.002	NA
MW-BC2C	B	1.6	-69.7	-75.0	0.7	0.2	NA	NA
MW-B2010C	B	0.5	88.1	-167.3	157.0	7.9	10.4	0.0430
MW-B2020C	B	0.3	95.4	>56.9	103.0	11.5	11.8	NA
MW-B2050C	B	1.7	88.1	-197.5	0.3	0.3	NA	NA
MW-B2100C	B	-0.2	25.6	22.0	0.2	0.2	NA	NA
MW-BX2C	C	-0.3	-13.5	100.0	0.2	0.8	NA	NA
MW-BX1C	C	-1.5	95.2	>-154	85.7	2.4	13.8	NA
MW-BM050C	C	-0.5	-25.4	0.0	0.3	0.1	NA	NA
MW-BC4C	C	-0.6	44.4	31.3	3.7	6.7	0.7	<0.005

D. SALT POND, EASTHAM, MA PRB

A 200-feet long PRB was installed near the Salt Pond within Nauset Estuary watershed near the Town of Eastham in the northern portion of the Cape Cod National Seashore Salt Pond Visitor's Center (Verdantas and MT Environmental Restoration, 2023). The pilot PRB is located downgradient of a neighborhood with mainly single-family homes using septic systems for wastewater disposal (GHD, 2018). The groundwater discharges into the Salt Pond. Injections were performed by ES&M and the project has been sampled and evaluated by ES&M, GHD, and MT Environmental Restoration. The pilot was installed in the shallow groundwater south of the Salt Pond Visitor Center with the water table at 20 feet bgs with a total depth of injection of 70 feet. The groundwater flow rate at this location is estimated to be 0.5 feet/day. A nitrogen flux of 440 kg/yr was estimated for this area. The PRB was installed approximately 600 feet from Salt Pond.

The PRB included 21 direct push injection points on 10-feet intervals with a barrier width of 12 feet parallel to groundwater flow based upon a 6 feet radius of influence (**Figure 18**). The injections points 1-10 on the western side of the PRB were from 21 to 64 feet bgs and the injection points 11-21 were installed from 19 to 62 feet bgs. Substrate was injected in 5-foot thick lifts. A total of 6,600 gallons of SRS®-NR, 264 gallons of 60% sodium lactate, 550 pounds of sodium bicarbonate, and 550 pounds of calcium carbonate were diluted with 24,400 gallons of tap water. Each injection point received about 1,500 gallons of the diluted EVO. The injections were performed from March 31 to April 8, 2020.

D.a Results and Discussion

A monitoring well network was established to evaluate performance of the PRB Demonstration Test, which includes monitoring wells upgradient and downgradient of the PRB to evaluate changes to nitrate and groundwater quality. Monitoring wells downgradient of the PRB are located at various distances away from the PRB between 25 to 355 feet to assess extent of reducing conditions for denitrification away from the PRB, potential for metals mobilization, and groundwater flow velocity. Monitoring wells were installed at two depths; the shallow zone was from 25 to 38 feet bgs (10 feet screens) and the intermediate zone from 40 to 55 ft bgs (10 feet screens).

Routine groundwater sampling by Verdantas continued quarterly for a period of two years after the SRS®-NR injection. Quarterly sampling analyses include nitrate-N, nitrite-N, ammonia-N, Total Kjeldahl Nitrogen (TKN), Total Nitrogen, chloride, sulfate, dissolved iron, dissolved manganese, dissolved arsenic, boron, DOC, methane, and alkalinity and field parameters including dissolved oxygen, redox potential, temperature, specific conductivity, and pH. The primary objectives of the post-injection sampling were to assess reduction in nitrate concentrations, removal of nitrate flux from groundwater as it flows through the PRB, identify distance traveled by EVO emulsion and DOC, evaluate persistence of EVO emulsion and conditions favorable for denitrifying bacteria, and assess changes to other groundwater quality parameters including metals mobilization.

The groundwater flow near the PRB is estimated to be 0.5 ft/day (J. Begley personal communication). The initial nitrate-N in the 17 monitoring wells near the PRB (excluding MW-105S) ranged from 0.42 to 37.6 mg/L with an average of 4.6 mg/L. The initial dissolved oxygen ranged from 1.0 to 10.2 mg/L with an average of 7.2. The initial pH ranged from 5.4 to 6.3 SU with an average of 5.9 SU.

In the shallow zone shown in **Figures 18** and **19** and **Table 4**, the upgradient wells ESM-312S and ESM-313S showed variable transformation of nitrate-N (88.9% to 92.9%) and total N (84.5% and 92.9%). DOC levels were not collected. Shallow well ESM-11S (25 feet downgradient) had 339 mg/L maximum DOC and had >94.7%% removal of the nitrate-N and 28.6% removal of Total N through September 2022. Shallow well ESM-12SR (25 feet downgradient) had 24 mg/L maximum DOC and had 94.3% removal of the nitrate-N but Total N increased by 14.3%. Wells ESM-310S and ESM-308S were about 25 to 50 feet from the nearest injection point and had maximum DOCs of 19 to 15 mg/L and 2.6 mg/L or less DOC in September 2022. Well ESM-310S didn't show removal of nitrate-N or Total N. Well MW-308S showed >86.7% removal of nitrate-N and >63.9% removal of Total N. Well ESM-309S, about 100 feet from the injection point line, had a maximum of 5.1 mg/L DOC and modest 64.8% reduction in nitrate-N and 65.4% in total N. Note that surface water infiltration was suspected at this location. Well ESM-311S was 175 feet downgradient and DOC was not monitored; it showed an increase in nitrate-N of 78.3% and an increase in total N of 18.3%. Well ESM-105S was about 355 feet away from the injection line and crossgradient to the expected groundwater flow direction. DOC was not monitored in this well, but nitrate-N decreased by 96.8% and total N by 96.8%. While reducing conditions with low dissolved oxygen, negative ORPs, or substantial sulfate removal, iron-reduction, or manganese reduction were never maintained in well ESM-105S, treatment of nitrate-N in the upgradient zone may have impacted this well.

DOC persisted above 100 mg/L in well ESM-11S (25 feet downgradient) for 2.4 years. The only other shallow well with detectable DOC in September 2022 was 2.6 mg/L in well ESM-310S (25 feet downgradient). The pH decreased by 0.1 to 0.6 SU in shallow wells ESM-312SR (25 feet downgradient), ESM-308S (50 feet downgradient), ESM-309S (100 feet downgradient), and ESM-311S (175 feet downgradient) from the first monitoring period to the last sampling event but increased by 0.6 to 1.3 SU in wells ESM-313S (upgradient well not impacted by substrate or buffer), ESM-11S (25 feet downgradient), ESM-12SR (25 feet downgradient), ESM-310S (25 feet downgradient), and ESM-105S (355 feet crossgradient). Total alkalinity increased in well ESM-11S (25 feet downgradient) by 3,637%, by 50.9% in well ESM-12SR (25 feet downgradient), by 432.5% in well ESM-310S (25 feet downgradient), and by 15.6% in well ESM-308S (50 feet downgradient) as result of the buffer addition but decreased by 68.4% in ESM-309S (100 feet downgradient). Dissolved oxygen consumption by 50% or more through September 2022 was observed in wells ESM-11S (25 feet downgradient), ESM-12SR (25 feet downgradient), and ESM-308S (50 feet downgradient). Sulfate removal was variable with sulfate persisting in wells ESM-312S (25 feet downgradient), ESM-313S (117 feet upgradient), ESM-12SR (25 feet downgradient), ESM-310S (25 feet downgradient), ESM-308S (50 feet downgradient), ESM-309S (100 feet downgradient), and ESM-311S (175 feet downgradient), with well ESM-11S (25 feet downgradient) having <2 mg/L sulfate in September 2022. The maximum dissolved iron was 263 mg/L in well ESM-11S (25 feet downgradient) with wells ESM-313S (117 feet upgradient), ESM-12SR (25 feet downgradient), ESM-308S (50 feet downgradient), ESM-309S (100 feet downgradient), and ESM-311S (175 feet downgradient) having more than 1 mg/L dissolved iron. Maximum dissolved manganese was above 1 mg/L only in shallow wells ESM-11S (25 feet downgradient), ESM-310S (25 feet downgradient), ESM-308S (50 feet downgradient), ESM-309S (100 feet downgradient), and ESM-311S (175 feet downgradient). Maximum Methane was detected above 18 mg/L in the shallow-zone well ESM-11S (25 feet downgradient) and >1 mg/L in well ESM-12SR (25 feet downgradient) and 0.14 mg/L in ESM-310S; none of the other well were monitored for methane. Dissolved arsenic reached a maximum of 0.0362 mg/L with wells

ESM-12SR (25 feet downgradient), and ESM-310S having more than 0.010 mg/L dissolved arsenic.

In the intermediate zone shown in **Figures 20** and **21** and **Table 5**, the upgradient wells ESM-312I (117 feet upgradient)and ESM-313I (121 feet upgradient) showed variable removal nitrate-N (-30.1% to 48.2%) and total N (-966.7 and 48.4%) with DOC levels not collected. Shallow well ESM-11I (25 feet downgradient) had 220 mg/L maximum DOC and had >96.7%% removal of the nitrate-N and 78.5% removal of Total N. Shallow well ESM-12S (25 feet downgradient) had 39 mg/L maximum DOC and had >98.1%% removal of the nitrate-N and 49.1% removal of Total N. Well ESM-310I was about 25 feet from the nearest injection point and had maximum DOCs of 46.1 mg/L. Well ESM-310I showed >92.4% removal of nitrate-N and >78.6% removal of Total N. Well ESM-308I, 50 feet downgradient from the injection line, showed a maximum DOC of 3.7 mg/L and increases in nitrate-N and Total N. Well ESM-309I, about 100 feet from the injection point line, had a maximum of 2.7 mg/L DOC and >93.2% reduction in nitrate-N and >80.0% in total N. Well ESM-315I was 75 feet downgradient with 13.6 mg/L maximum DOC (in September 2022); it showed a decrease in nitrate-N of 94.7% and >88.9% total N. Well ESM-311I was 175 feet downgradient with 2.6 mg/L DOC; it showed a decrease in nitrate-N of 86.1% and a decrease in total N of >81.3%.

DOC persisted above 10 mg/L through September 2022 in well ESM-12S(I) (25’ downgradient), and ESM-315I (75 feet downgradient) and above 4.0 mg/L in wells ESM-11I (25 feet downgradient), 2.4 years after the SRS®-NR injections. The pH remained stable in intermediate wells ESM-312I and ESM-308I from the first monitoring period to the last sampling event but increased by 0.2 to 1.9 SU in wells ESM-313I (121 feet upgradient), ESM-11I (25 feet downgradient), ESM-12S(I) (25 feet downgradient), ESM-310I (25 feet downgradient), ESM-309I (100 feet downgradient), ESM-315I (75 feet downgradient), and ESM-311I (175 feet downgradient). Total alkalinity increased in wells ESM-11I (25 feet downgradient)by 143.3%, well ESM-12S(I) (25 feet downgradient) by 317.3%, ESM-310I (25 feet downgradient) by 392.8%, ESM-309I (100 feet downgradient) by -122.9%, and ESM-311I (175 feet downgradient) by 23.9% as result of the buffer addition. Decreases in total alkalinity of 24.8% in ESM-308I (50 feet downgradient) and 52.3% in well ESM-315I (75 feet downgradient) from September 2020 to September 2022. Dissolved oxygen consumption by 50% or more was observed in wells ESM-11I (175 feet downgradient), ESM-12S(I) (25 feet downgradient), ESM-310I (25 feet downgradient), ESM-309I (100 feet downgradient), and ESM-315I (75 feet downgradient) through September 2022. Sulfate removal was variable with sulfate persisting in September 2022 in all wells except ESM-12S(I) (25 feet downgradient) and ESM-310I (25 feet downgradient). The maximum dissolved iron was 75.9 mg/L in well ESM-310I (25 feet downgradient) with wells ESM-312I (117 feet upgradient), ESM-313I (121 feet upgradient), ESM-11I (25 feet downgradient), ESM-12S(I) (25 feet downgradient), ESM-308I (50 feet downgradient), ESM-309I (100 feet downgradient), ESM-315I (75 feet downgradient), and ESM-311I (175 feet downgradient) having more than 1 mg/L dissolved iron. Dissolved manganese was above 1 mg/L only in intermediate wells ESM-11I (25 feet downgradient), ESM-12S(I) (25 feet downgradient), ESM-310I (25 feet downgradient), ESM-308I (50 feet downgradient), ESM-309I (100 feet downgradient), and ESM-315I (75 feet downgradient). Methane was detected above 1 mg/L in the intermediate-zone wells ESM-11I (25 feet downgradient) and ESM-12S(I) (25 feet downgradient) with no methane found in ESM-310I (25 feet downgradient); none of the other wells were monitored for methane. Dissolved arsenic reached a maximum of 0.0497 mg/L with wells ESM-11I (25 feet downgradient), ESM-12S(I) (25 feet downgradient), ESM-310I (25 feet downgradient), ESM-308I

(50 feet downgradient), and ESM-315I (75 feet downgradient)having more than 0.010 mg/L dissolved arsenic.

D.b Salt Pond, Eastham, MA Conclusions

DOC levels have persisted above 5 mg/L for over 2.4 years for wells up to 25 feet in the shallow and intermediate zones. Good denitrification (>50%) was observed at distances of up to 175 feet downgradient in the shallow and intermediate zones. The buffer increased the pH up to 25 feet downgradient in the shallow zone and 100 feet in the intermediate zone.

Table 6. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, Total N % Removal, pH Change, % Alkalinity Removal, %DO Consumed, % Sulfate Consumed, Maximum Dissolved Iron and Manganese, Maximum Methane, and Maximum Arsenic for Salt Pond Eastham, MA PRB

Shallow Wells	**Screened Interval (ft bgs)**	**Distance (ft) to Injection Points**	**Initial Nitrate-N (mg/L)**	**Max DOC (mg/L)**	**Most Recent DOC (mg/L)**	**%Nitrate-N Removal**	**% Total N Removal**	**pH Change**	**% Alkalinity Removal**	**% DO Consumed**	**% Sulfate Consumed**	**Max Dis Fe (mg/L)**	**Max Dis Mn (mg/L)**	**Max CH4 (mg/L)**	**Max As (mg/L)**
ESM-312S	20-30	117 Up	7.9	NA	NA	92.9	92.9	0.6	NA	-15.6	15.8	0.571	0.0606	NA	NA
ESM-313S	25-35	121 Up	6.21	NA	NA	88.9	84.5	-0.6	NA	-25.5	>-9.0	1.44	0.017	NA	NA
ESM-11S	28-38	25	2.09	339	140	>94.7	28.6	-1.33	-3636.8	99.6		263	18.1	18.7	0.0362
ESM-12SR	25-35	25	2.11	24	<1	94.3	-14.3	-0.9	-50.9	96.8	-19.0	34.1	0.976	1.05	0.0303
ESM-310S	20-30	25	0.422	18.8	2.6	-42.2	-48.6	-0.9	-432.5	1.0	<54.0	39	1.54	0.136	0.019
ESM-308S	22-32	50	0.827	15	<1	>86.7	>63.9	0.1	-15.6	95.9	<4.0	3.74	7.23	NA	0.003
ESM-309S	21-31	100	2.56	5.1	<1	64.8	65.4	0.4	68.4	31.7	<64.0	2.84	2.51	NA	0.0033
ESM-311S	20-30	175	0.617	NA	NA	-78.3	-18.3	0.1	NA	-106.3	<63.0	7.99	1.93	NA	<0.003
ESM-105S		355 Cross	37.6	NA	NA	96.8	96.8	-1.6	NA	54.8	12.0	0.121	0.505	NA	NA
Intermediate Wells															
ESM-312I	40-50	117 Up	3.09	NA	NA	48.2	48.4	0.0	NA	8.2	<1.0	2.44	0.0734	NA	NA
ESM-313I	45-55	121 Up	1.23	NA	NA	-30.1	-966.7	-0.6	NA	-50.7	>-10.0	1.18	0.114	NA	NA
ESM-11I	45-55	25	3.38	220	4.2	>96.7	78.5	-0.95	-143.3	98.4	76.4	23.2	2.5	5.39	0.0221
ESM-12S	45-55	25	5.52	39	15	>98.1	49.1	-1.16	-317.3	98.7		49.5	4.6	11.1	0.0497
ESM-310I	42-52	25	1.45	82.85	82.5	>92.4	>78.6	-1.9	-392.8	99.7	81.8	75.9	4.33	0	0.0425
ESM-308I	42-52	50	2.34	3.7	<1	-19.7	-21.7	0.0	24.8	73.3	11.7	8.36	5.13	NA	0.0142
ESM-309I	41-51	100	1.48	2.7	<1	>93.2	>80.0	-0.2	-122.9	98.3	16.7	9.49	2.39	NA	0.0045
ESM-315I	45-55	75	2.66	13.6	13.6	94.7	>88.9	-0.4	52.3	97.3	77.1	19.6	9.05	NA	0.0229
ESM-311I	40-50	175	1.65	2.6	<1	86.1	>81.3	-0.4	-23.9	35.6	20.0	8.22	0.391	NA	<0.003

94.7	Nitrate or total N reduced to below detection limits
59.2	Alkalinity measurements started in 9/2020

Figure 18. Eastham Site Shallow Zone Map

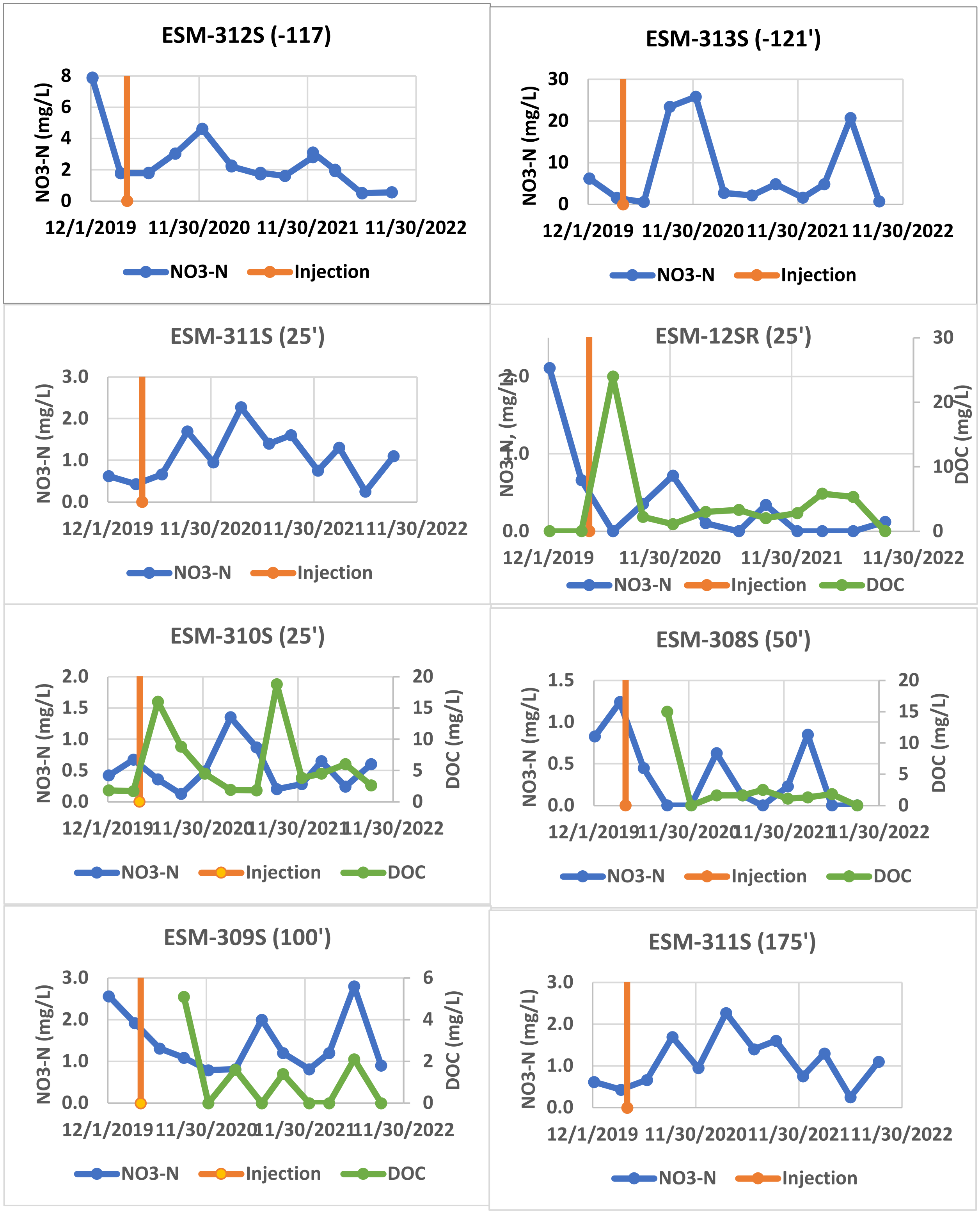


Figure 19. Nitrate and DOC Concentrations in Salt Pond, Eastham, MA Shallow Zone

Figure 20. Eastham Site Intermediate Zone Map

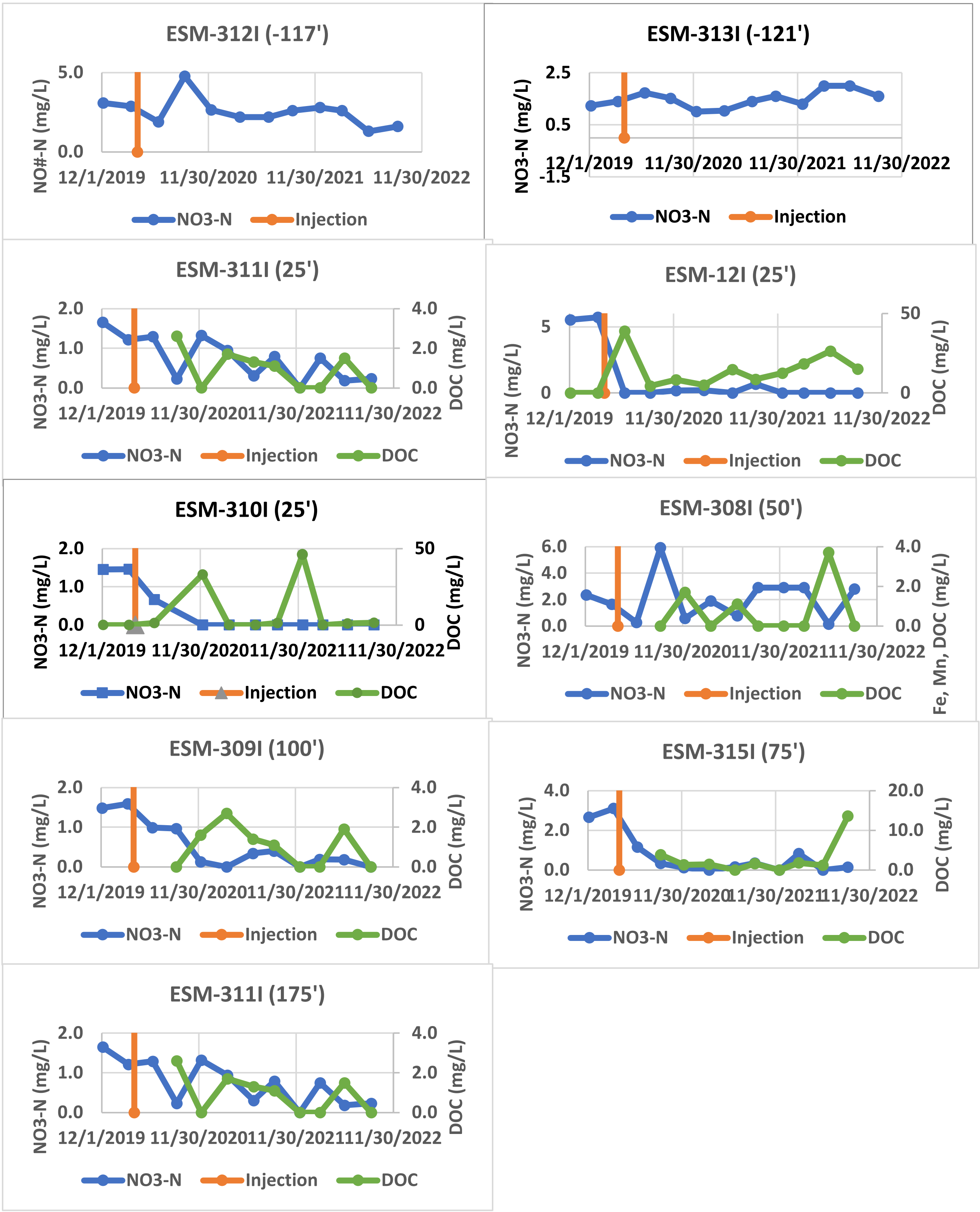


Figure 21. Nitrate and DOC Concentrations in Salt Pond, Eastham, MA Intermediate Zone

E, SHOREWOOD DRIVE, FALMOUTH, MA

Woods Hole Oceanographic Institute (WHOI) received a Southeast New England Project (SNEP) Watershed Grant to evaluate a denitrification PRB within the Great Pond watershed in Falmouth, MA with the Town of Falmouth, the Cape Cod Commission. Key In-Situ Oxidative Technologies, Inc. (ISOTEC), Terra Systems, Inc., and Science Wares, Inc. as Partner Organizations. The groundwater flow rate was estimated to be 0.13 ft/day. The pilot layout is shown in **Figure 28**. ISOTEC performed the injections using 3,100 gallons of SRS®-NR and 1,450 pounds of calcium carbonate into 12 injection points. Two loadings were injected with 10% SRS®-NR (1 year demand) and 20% SRS®-NR (2 years demand) injected into 6 injection points each, with the dosage aligning with the anticipated duration of the . The same volume of total injectate (6,300 gallons) was used for both halves of the demonstration test PRB. Injection was by direct push with three intervals between -5 to -29 feet msl; injection depth was adjusted to grade elevation with terminal injection depth ranging from 41 to 46 feet bgs. Injection rates ranged from 0 to 6.25 gallons per minute with an average of 4.1 gallons per minute at injection pressures of 3 to 80 psi and an average of 36.3 psi. Average injection rates ranged from 4.2 to 5.0 gallons per minute across the three injection intervals, but the average injection pressure was highest in the deepest interval (49 psi) compared to 5-9 psi in the shallower intervals).

Ten multi-level wells were used to monitor the PRB demonstration with screens at depths of between 0 to 50 feet below mean sea level (**Figure 28**). Two sets of three monitoring wells with multi-level sampling porters approximately 12-14 feet upgradient of the PRB, in line with the PRB, and approximately 16-17 feet downgradient of the PRB. Wells WHOI-1 was located 14 feet upgradient and WHOI-5 15 feet downgradient, respectively, of the 1-year dosage side of the PRB, with WHOI-3 within the PRB between IP-3 and IP-4. Multi-level well MTER-6 was about 125 feet downgradient. Wells WHOI-2 and WHOI-6 were located 12 feet upgradient and 17 feet downgradient, respectively, of the 2-year dosage side of the PRB, with WHOI-4 within the PRB between IP-9 and IP-10. An additional monitoring well with a 10-foot screen (WHOI-7) was installed along the line of PRB injection points between IP-6 and IP-7. Multi-level wells WHOI-8 was 64 feet downgradient of the 2-year PRB, and well MTER-9 is 25 crossgradient of the PRB. The well network collected approximately 22 samples from each event from multi-level ports or monitoring well screens to evaluate the PRB vertically and spatially for field parameters (temperature, dissolved oxygen, pH, specific conductivity, turbidity, nitrate-N, nitrite-N, ammonium-N, phosphate, arsenic, iron, manganese, sodium, chloride, sulfate, total alkalinity, and TOC.

E.a One Year PRB

In the 1 Year PRB shown in **Figures 29** and **30** and **Table 5**, well WHOI-1 (14 feet upgradient) had nitrate-N concentrations in June 2020 between 0.5 to 14.6 mg/L with the highest concentrations between -20.5 (14.6 mg/L) and -28.5 feet (11.1 mg/L). Over the course of the pilot, nitrate-N decreased by 9.1 to 98.9% at depths of -8.5 (34.1%), -12.5 (42.6%), -16.5 (9.1%), -20.5 (35.3%), -28.5 (34.9%), and -43.5 (98.9%) feet with increased nitrate-N at depths of -0.5 (-124.5%), -4.5 (-11.9%), -24.5 (-28.8%), and -33.5 feet (-1,165.0%). Total N followed a similar pattern. The maximum TOC or DOC was 1.6 mg/L at -12.5 ft. TOC or DOC was not monitored at most depths. Phosphate was below the detection limit at most depths in May 2022. Dissolved oxygen increased at most depths. The pH was not impacted with -43.5 feet depth showing an increase of 0.5 SU. Only a few depths on WHOI-1 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. Only low levels of manganese and arsenic were detected. This well was not impacted by the substrate injections.

Well WHOI-3 between IP-3 and IP-4 was only screened at -14.4 ft. It had nitrate-N concentrations in June 2020 of 8.6 mg/L. Over the course of the pilot, nitrate-N and total N decreased by 25.1 to 25.2%. The maximum TOC or DOC was 1.1 mg/L in November 2021, but TOC was not monitored at most sampling intervals. Little change in the phosphate was observed. Dissolved oxygen increased. The pH was not impacted. Only a few sampling intervals for WHOI-3 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. Maximum levels of 0.01 mg/L iron, 0.065 mg/L manganese, and 0.002 mg/L arsenic were detected. The substrate never reached this well.

Well WHOI-5 about 16 feet downgradient of the injection line had nitrate-N concentrations in June 2020 between 0.7 to 6.1 mg/L with the highest concentrations between -20 (6.1 mg/L) and -24 feet (4.8 mg/L). Over the course of the pilot, nitrate-N decreased by 4.0 to 99.7% at depths of 0 (4.0%), -8 (48.6%), -20 (22.6%), -24 (19.8%), and -43 (99.7%) feet with increased nitrate-N at depths of 4 (-5.8%), -12 (21.9%), -16 (-48.4%), -28 (-136.1%) and -33 (-19.2%) feet. Only in November 2021 did there appear to be any impact on the nitrate-N from the concentrations in the upgradient well WHOI-1. Total N followed a similar pattern. The maximum TOC or DOC was 1.3 mg/L at -4 ft. Phosphate was below the detection limit at most depths in May 2022. Dissolved oxygen increased at most depths. The pH was not impacted by the buffer. Only a few depths on WHOI-5 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. The maximum dissolved iron was 0.237 mg/L at -8 feet, maximum manganese was 1.14 mg/L also at -8 ft, and maximum arsenic was 0.003 mg/L.

Well MTER-6 about 125 feet downgradient of the injection line had nitrate-N concentrations in June 2020 between 0.6 to 6.6 mg/L with the highest concentrations between –14.8 (6.6 mg/L) and -24.9 feet (4.6 mg/L). Over the course of the pilot, nitrate-N decreased by 54.7 to 98.3% at depths of -14.8 (98.3%), -24.9 (54.7%), -35 (95.7%), and -45.1 (94.3%) feet with increased nitrate-N at depths of -1.8 (-102.6%) and -55.2 (-205.7%) feet. Total N followed a similar pattern. The maximum TOC or DOC was 5.2 mg/L at -14.8 ft, but DOC or TOC were not routinely monitored. Phosphate was reduced at all depths except -35.0 feet. Dissolved oxygen decreased at most depths except for the shallowest (-1.8) and deepest (-55.2) feet intervals. The pH was impacted by the buffer with increases of between 0.4 and 0.9 SU at depths of -14.8 (-0.8 SU), -24.9 (0.9 SU), -45.1 (0.4 SU), and -55.2 (-0.4 SU). Only a few depths on MTER-6 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. The maximum dissolved iron was 1.13 mg/L at -14.8 feet, maximum manganese was 8.18 mg/L also at -14.8 ft, and no arsenic was detected. From August 2020 to February 2022 nitrate-N was generally lower in MTER-6 than the upgradient wells WHOI-1 and WHOI-5. In May 2022, nitrate-N was non-detected in MTER-6 from -4.7 to -12.7 feet.

While limited denitrification was observed in the well WHOI-3 between the two injection points and the closest downgradient monitoring well WHOI-5, there does seem to have been an impact in well MTER-6 about 125 feet downgradient for over 18 months and in shallow zone from -4.7 to -12.7 for 22 months.

E.b Two Year PRB

In the 2 Year PRB shown in **Figure 31** and **32** and **Table 6**, the upgradient well WHOI-2 (-12')had nitrate-N concentrations in June 2020 between 0.7 to 21.9 mg/L with the highest concentrations between -1.2 (9.5 mg/L) and -5.2 feet (21.9 mg/L). Over the course of the pilot, nitrate-N decreased by 1.9 to 72.2% at depths of -1.2 (19.9%), -5.2 (72.2%), -13.2 (15.2%), and -21.2 (1.9%) feet with increased nitrate-N at depths of 2.8 (-51.9%), -9.2 (-8.6%), -17.2 (-58.8%), -25.2 (-289.8%), and -30.2 feet (-1,698.9%). Total N followed a similar pattern. The maximum TOC or DOC was 1.7 mg/L at -13.2 ft, but TOC was not monitored at most depths. Phosphate was below the detection limit at 2.8, -17.2, -25.2, and -30.2 feet in May 2022. Dissolved oxygen increased at most depths. The pH was not impacted with -5.2 feet depth showing an increase of 0.3 SU. Only a few depths on WHOI-2 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. A maximum of 0.02 mg/L dissolved iron, 29.7 mg/L dissolved manganese and no arsenic were detected. This well was not impacted by the substrate injections.

Wells WHOI-4 between IP-9 and IP-10 andWHOI-7 between IP-6 and IP-7 were screened at -15 and -15.3 ft. They had nitrate-N concentrations in June 2020 of 2.2 to 3.0 mg/L. Over the course of the pilot, nitrate-N and total N increased by -183.3 to -279.7%. The maximum TOC or DOC was 1.3 mg/L in WHOI-4 in November 2020 with TOC concentrations between <0.5 to 1.2 mg/L through May 2022. Little change in the phosphate was observed. Dissolved oxygen increased. The pH increased by 0.5 SU in WHOI-7 and decreased by 0.5 SU in WHOI-4. Only a few sampling intervals for WHOI-4 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. Maximum levels of 0.033 mg/L iron, 0.108 mg/L manganese, and 0.02 mg/L arsenic were detected. The substrate never reached these wells.

Well WHOI-6 about 17 feet downgradient of the injection line had nitrate-N concentrations in June 2020 between 0.4 to 28.2 mg/L with the highest concentrations between -4.7 (28.2 mg/L) and -8.7 feet (10.6 mg/L). Over the course of the pilot, nitrate-N decreased by 25.6 to 99.99% at depths of -0.7 (29.8%), -4.7 (99.99%), -8.7 (99.99%), -12.7 (99.99%), -16.7 (25.6%) and -43.7 (72.4%) feet with increased nitrate-N at depths of -20.7 (-71.3%), -24.7 (-362.6%), -28.7 (-241.9%), and -33.7 (-1,785.9%) feet. Nitrate-N was reduced from -4.7 to -12.7 feet (and sometimes at -16.7 feet) from the concentrations in the upgradient well WHOI-2 from August 2020 through May 2022. Total N followed a similar pattern. The maximum TOC or DOC was 99 mg/L at -4.7 ft with between 1.1 to 59 mg/L maximum TOC at depths of -8.7 to -28.7 feet. TOC remained elevated above 20 mg/L through August 20202 at depts of -4.7 to -12.7 feet. Little DOC was found at -20.7 to -43.7 feet msl. The injection target zone for the 2-year PRB was -1.2 to -33.5 feet msl so the bottom 13 feet of treatment zone received little substrate, or it was washed away. Phosphate decreased by 82.5% at -4.7 feet and 53.7% at -12.7 feet. Phosphate increased at the other depths. Dissolved oxygen was depleted at depts of -8.7 and -16.7 feet msl with less impact at the other depths. The pH was impacted by the buffer with increases of between 0.4 to 1.6 SU at depths of -4.7 to -16.7 feet through May 2022. Only a few depths on WHOI-6 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. The maximum dissolved iron was 23.9 mg/L at -8.7 feet, maximum manganese was 3.26 mg/L also at -8.7 ft, and maximum arsenic was 0.013 mg/L.

Well WHOI-8 about 64 feet downgradient of the injection line had nitrate-N concentrations in June 2020 between 0.3 to 13.3 mg/L with the highest concentrations between -4.5 (13.3 mg/L) and -20.5 feet (10.5 mg/L). Over the course of the pilot, nitrate-N decreased by 38.3 to 99.99% at depths of -4.5 (99.3%), -8.5 (99.99%), -12.5 (99.99%), -16.5 (81.1%), and -43.5 (61.3%) feet with increased nitrate-N at depths of -0.5 (-16.9%), -24.5 (-781.7%), -28.5 (-343.6%), and -33.5 (-853.6%) feet. Nitrate-N was reduced from -4.5 to -12.5 feet (and sometimes -20.5 feet) from the concentrations in the upgradient well WHOI-2 from November 2020 through May 2022. Total N followed a similar pattern. The maximum TOC or DOC was 68 mg/L at -8.5 ft with 8.7 mg/L maximum TOC at a depth of -20.5 feet. TOC remained elevated above 15 mg/L through May

20202 at a depth of -48.5 feet. TOC or DOC was not monitored in the deeper zones. The injection target zone for the 2-year PRB was -1.2 to -33.5 feet msl so the bottom 13 feet of treatment zone received little substrate, or it was washed away. Phosphate decreased by >23 to >89.7% at -0.5, -4.5, -28.5, -33.5, and -58.5 feet. Phosphate was unchanged or increased at the other depths. Dissolved oxygen was depleted at depths of -8.5, -12.5, and -16.5 feet msl with less impact at the other depths. The pH was impacted by the buffer with increases of between 0.9 to 2.2 SU at depths of -4.5 to -20.5 feet through May 2022. Only a few depths on WHOI-8 were ever monitored for sulfate and dissolved iron, manganese, and arsenic. The maximum dissolved iron was 71 mg/L at -8.5 feet, maximum manganese was 6.72 mg/L at -20.5 ft, and maximum arsenic was 0.009 mg/L.

Well MTER-9 about 25 feet crossgradient from the injection line was screened at -20.5 to -50.4 ft. It had nitrate-N concentrations in June 2020 of 1.2 to 9.4 mg/L. Over the course of the pilot, nitrate-N and total N at the -20.5 feet interval decreased by 90.5%. The maximum TOC or DOC was 0.65 mg/L at -40.4 feet, but TOC was not monitored at most sampling intervals. Phosphate decreased below the detection limit at MTER-9A (unknown depth), -40.4 ft, and -50.4 feet but increased at the -20.5 feet interval. Dissolved oxygen decreased by 80% at the -20.5 feet interval. The pH also increased by 0.8 SU at this interval. Maximum levels of 0 mg/L iron, 0.024 mg/L manganese, and 0 mg/L arsenic were detected. The substrate appeared to have impacted the 20.5 feet interval.

E.c Shorewood Drive, Falmouth PRB Conclusions.

Extensive denitrification was observed in the wells WHOI-6 in 1 Yr PRB (125’ downgradient) and WHOI-8 (64 feet downgradient) between -4.5 to -12.5 feet msl for 22 months.

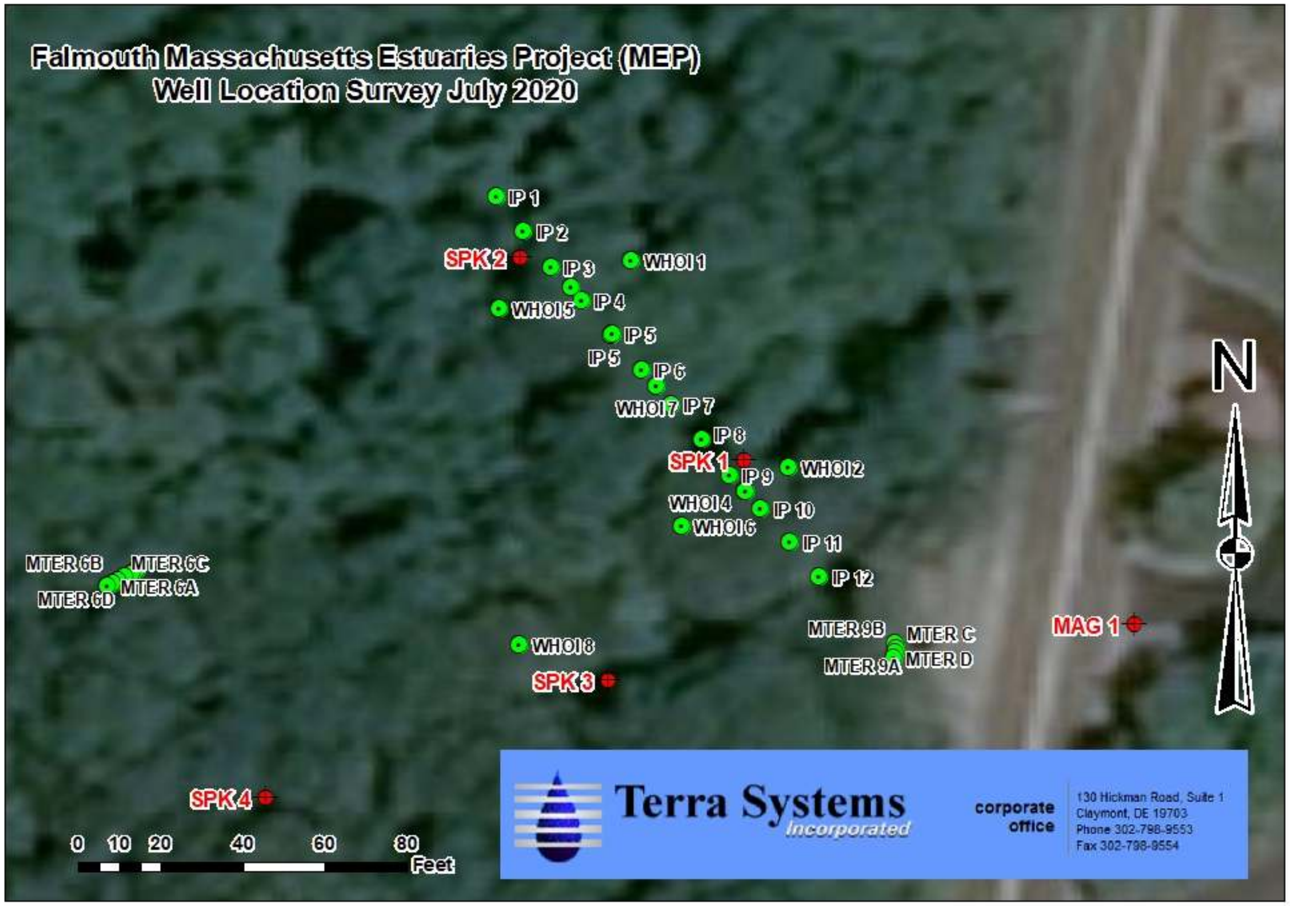


Figure 28. WHOI Falmouth MA PRB

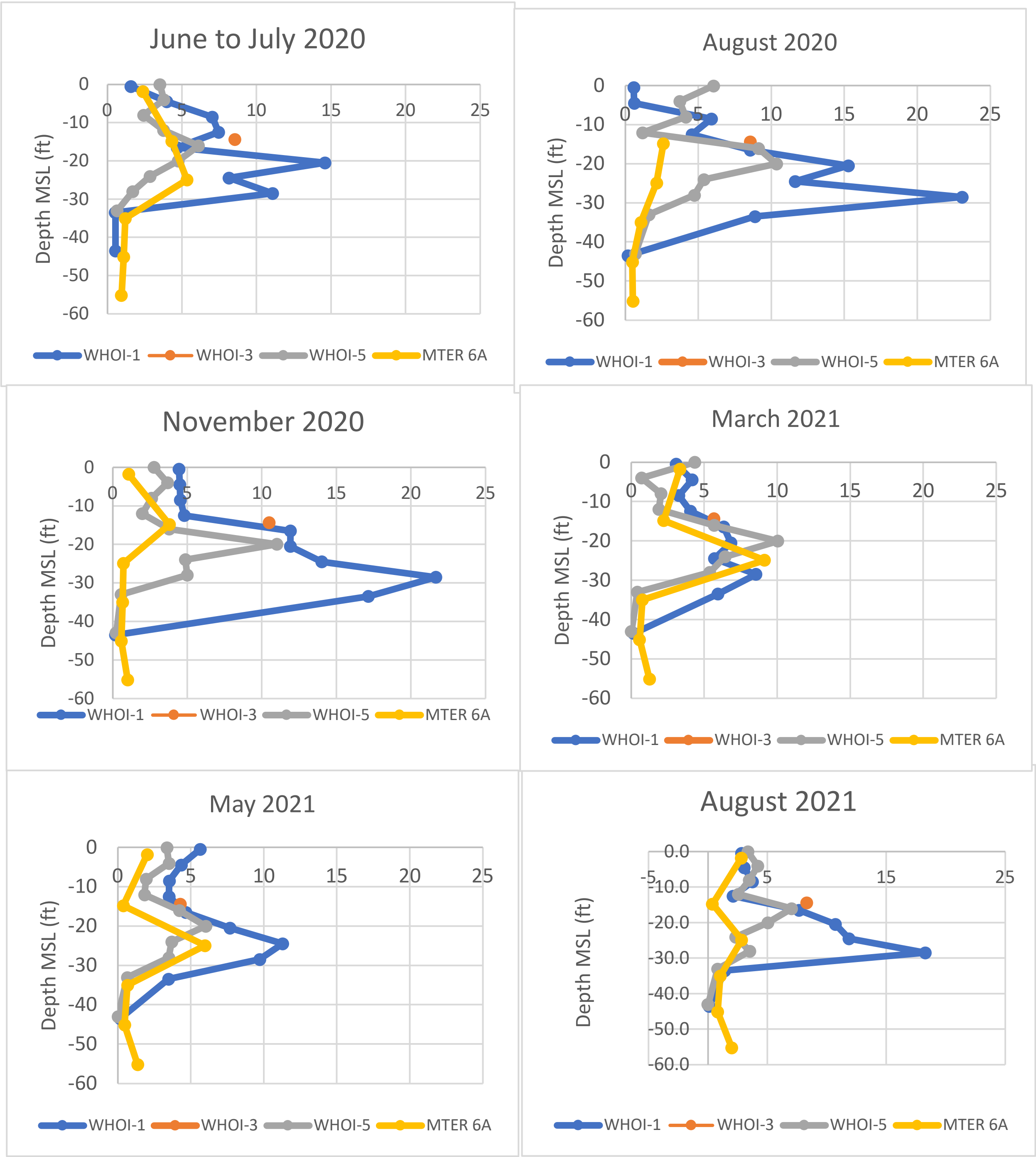


Figure 29. Nitrate-N by Depth Over Time for Falmouth 1 Year PRB June 2020 to August 2021

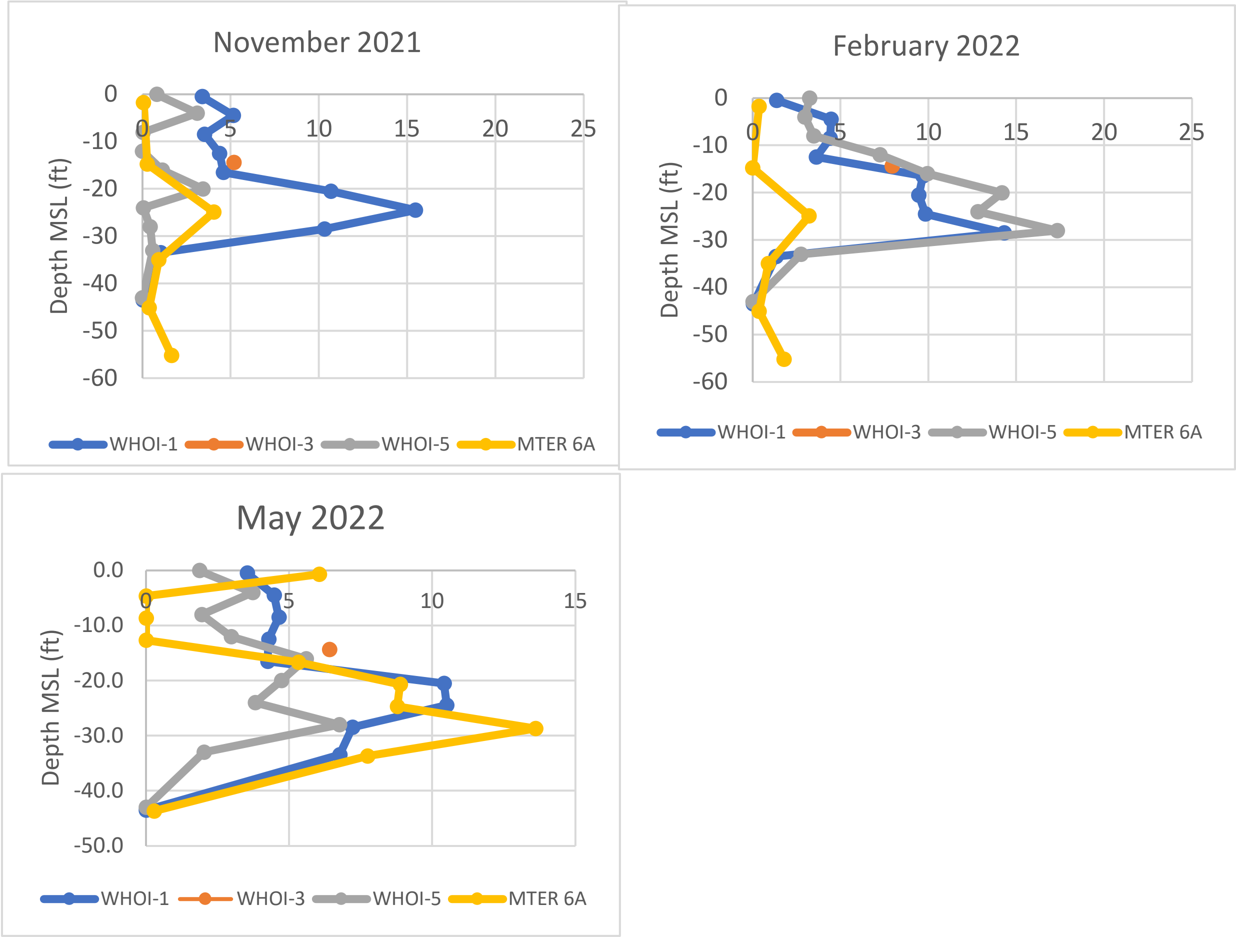


Figure 30. Nitrate-N by Depth Over Time for Falmouth 1 Year PRB November 2021 to May 2022

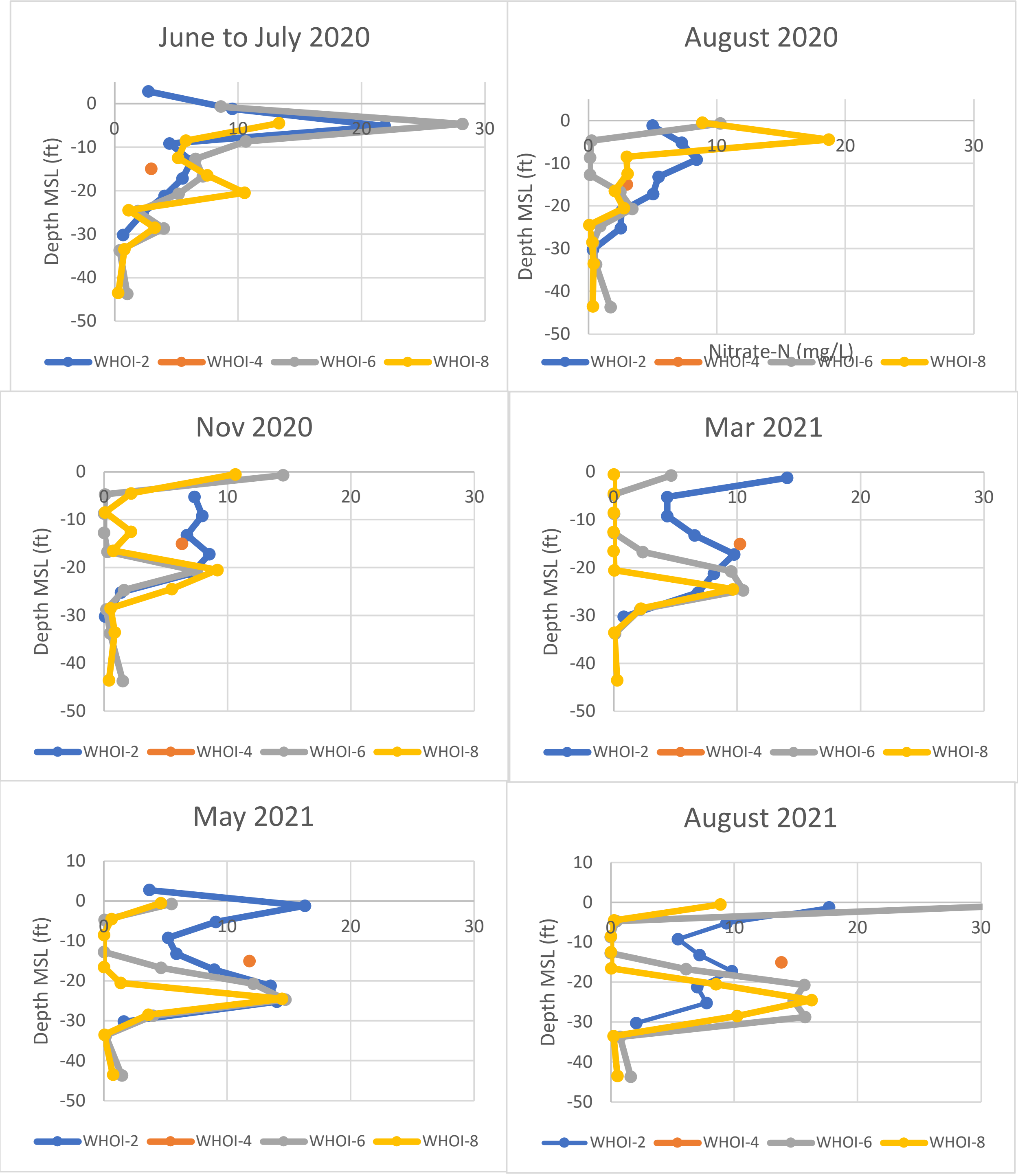


Figure 31. Nitrate-N by Depth Over Time for Falmouth 2 Year PRB from June 2020 to August 2021

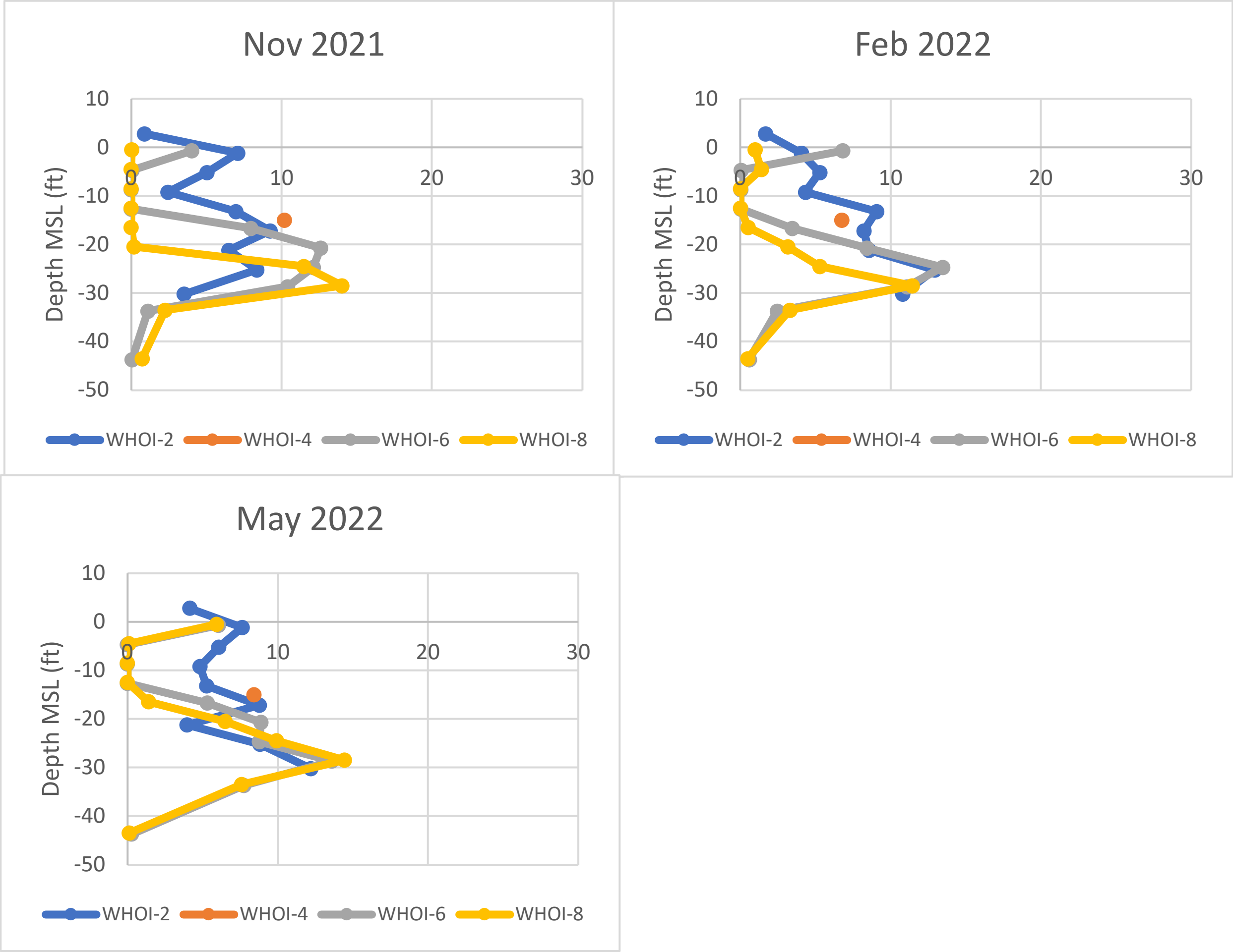


Figure 32. Nitrate-N by Depth Over Time for Falmouth 2 Year PRB from November 2021 to May 2022

Table 4. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, Total N % Removal, % Phosphate Removal, pH Change, % Alkalinity Removal, %DO Consumed, % Sulfate Consumed, Maximum Dissolved Iron and Manganese, and Maximum Arsenic for Falmouth 1 Year PRB

Well	**Depth ft bgs**	**Distance (ft) to Injection Points**	**Initial Nitrate -N (mg/L)**	**Max TOC or DOC (mg/L)**	**Latest TOC or DOC Sampling**	**Most Recent TOC or DOC (mg/L)**	**%Nitrate -N Removal**	**% Total N Removal**	**%Phosphate Removal**	**pH Change**	**% Alkalinity Removal**	**% DO Consumed**	**% Sulfate Consumed**	**Max Dis Fe (mg/L)**	**Max Dis Mn (mg/L)**	**Max As (mg/L)**
WHOI-1	-0.5	14 Up	1.58	NA		NA	-124.5	-121.2	-9.5	1.1	NA	-93.8	NA	NA	NA	NA
WHOI-1	-4.5	14 Up	3.995	NA		NA	-11.9	-8.8	23.4	0.1	NA	-20.3	NA	NA	NA	NA
WHOI-1	-8.5	14 Up	7.037	0.4	3/9/2021	0.4	34.1	34.1	0	1.1	NA	-7.6	NA	NA	NA	NA
WHOI-1	-12.5	14 Up	7.463	1.6	2/9/2022	1.6	42.6	42.7	>49.2	0.2	NA	-43.0	NA	NA	NA	NA
WHOI-1	-16.5	14 Up	4.675	NA		NA	9.1	9.2	>21.1	-0.3	NA	9.1	NA	NA	NA	NA
WHOI-1	-20.5	14 Up	14.597	0.9	5/9/2022	0.9	35.3	35.3	>21.1	-0.1	0	1.1	-7.4	0	0.079	0.002
WHOI-1	-24.5	14 Up	8.156	NA		NA	-28.8	-28.7	>28.6	-0.2	NA	-17.8	NA	NA	NA	NA
WHOI-1	-28.5	14 Up	11.076	0.98	5/11/2021	0.98	34.9	34.9	>21.1	-0.1	NA	-40.2	NA	NA	NA	NA
WHOI-1	-33.5	14 Up	0.534	NA		NA	-1165.0	-1152.8	>69.4	0	NA	-1525	NA	NA	NA	NA
WHOI-1	-43.5	14 Up	0.538	NA		NA	98.9	98.8	12.6	-0.5	NA	-40.0	NA	NA	NA	NA
WHOI-3	-14.4	0	8.556	1.1	11/17/2021	1.1	25.1	25.2	<-7.1	0.1	13.3	-55.9	1.1	0.01	0.065	0.002
WHOI-5	0	16	1.954	NA		NA	4.0	4.7	>51.6	0.3	NA	-855.0	NA	NA	NA	NA
WHOI-5	-4	16	3.517	1.5	11/16/2021	1.3	-5.8	-5.6	>25.0	0.4	NA	-53.7	NA	NA	NA	NA
WHOI-5	-8	16	3.785	1.2	11/16/2021	1.2	48.6	48.8	-19.8	0.1	NA	-35.9	NA	0.237	1.14	0.003
WHOI-5	-12	16	2.454	5.6	11/16/2021	1.1	-21.9	-21.0	>53.8	0.0	NA	41.3	NA	NA	NA	NA
WHOI-5	-16	16	3.768	1.1	2/9/2022	1.1	-48.4	-47.3	>16.7	0.1	NA	0.5	NA	NA	NA	NA
WHOI-5	-20	16	6.116	0.9	2/9/2022	0.9	22.6	22.7	>25.0	0.1	NA	5.1	NA	0.01	0.1	0.003
WHOI-5	-24	16	4.752	0.8	2/9/2022	0.8	19.8	20.0	>33.3	-0.1	NA	-13.5	NA	NA	NA	NA
WHOI-5	-28	16	2.862	0.8	11/16/2021	0.8	-136.1	-135.6	-52.3	0	NA	-159.4	NA	NA	NA	NA
WHOI-5	-33	16	1.699	NA		NA	-19.2	-18.6	9.3	0	NA	-700.0	NA	NA	NA	NA
WHOI-5	-43	16	0.667	NA		NA	99.7	99.7	21.6	-0.1	NA	-300.0	NA	NA	NA	NA
MTER-6F	-1.83	125	0.612	NA		NA	-102.6	-105.7	52.5	0	NA	-4.9	NA	NA	NA	NA
MTER-6E	-14.8	125	6.613	5.2	3/10/2021	5.2	98.3	97.7	>70.0	-0.8	-250.0	99.4	-4.2	1.13	8.18	0
MTER6D	-24.9	125	4.58	NA		NA	54.7	54.3	0	-0.9	NA	56.9	NA	NA	NA	NA
MTER6C	-35.0	125	0.676	NA		NA	95.7	93.4	-87.1	0.1	NA	99.8	NA	NA	NA	NA
MTER6B	-45.1	125	0.935	NA		NA	94.3	94.1	76.5	-0.4	NA	69.3	NA	NA	NA	NA
MTER6A	-55.2	125	0.581				-205.7	-205.6	55.2	-0.4		-31.2	NA	NA	NA	NA

1.1 Change calculated over shorter period.

Table 5. Estimated Distance to Nearest Injection Point, Initial Nitrate-N, Maximum DOC, Most Recent DOC, Nitrate % Removal, Total N % Removal, % Phosphate Removal, pH Change, % Alkalinity Removal, %DO Consumed, % Sulfate Consumed, Maximum Dissolved Iron and Manganese, and Maximum Arsenic for Falmouth 2 Year PRB

Well	Depth ft bgs	Distance (ft) to Injection Points	Initial Nitrate-N (mg/L)	Max TOC or DOC (mg/L)	Latest TOC or DOC Sampling	Most Recent TOC or DOC (mg/L)	%Nitrate-N Removal	% Total N Removal	%Phosphate Removal	pH Change	% Alkalinity Removal	% DO Consumed	% Sulfate Consumed	Max Dis Fe (mg/L)	Max Dis Mn (mg/L)	Max As (mg/L)
WHOI-2	2.8	12 Up	2.741	NA		NA	-51.9	-37.2	>90.9	0.8	NA	-202.9	NA	NA	NA	NA
WHOI-2	-1.2	12 Up	9.543	NA		NA	19.9	21.1	-2159.2	0.9	NA	-32.9	NA	NA	NA	NA
WHOI-2	-5.2	12 Up	21.891	NA		NA	72.2	72.2	-69.0	-0.3	NA	-25.7	NA	NA	NA	NA
WHOI-2	-9.2	12 Up	4.453	NA		NA	-8.6	-0.5	-17.7	-0.1	NA	-47.3	NA	NA	NA	NA
WHOI-2	-13.2	12 Up	6.217	1.7	8/15/2022	0.5	15.2	22.8	47	0.3	NA	-83.0	NA	NA	NA	NA
WHOI-2	-17.2	12 Up	5.509	1.1	2/9/2022	0.96	-58.8	-54.9	>68.2	0.6	NA	-25.1	86.9	0.02	29.7	0
WHOI-2	-21.2	12 Up	4.054	NA		NA	1.9	4.0	31.1	0.5	NA	-30.2	NA	NA	NA	NA
WHOI-2	-25.2	12 Up	2.262	NA		NA	-289.8	-274.1	>80.0	0.7	NA	-45.8	NA	NA	NA	NA
WHOI-2	-30.2	12 Up	0.678	NA		NA	-1698.9	-1510.7	>83.3	0.6	NA	-358.9	NA	NA	NA	NA
WHOI-4	-15	0	2.971	1.3	5/10/2022	0.7	-183.2	-182.3	0	0.5	>-140.0	-34.9	21.4	0.033	0.108	0.020
WHOI-7	-15.3	0	2.215	NA		NA	-279.7	-178.5	-8.3	-0.5	NA	-21	NA	NA	NA	NA
		.														
WHOI-6	-0.7	17	8.615	NA		NA	29.8	29.9	-61.3	0.1	NA	54.5	NA	NA	NA	NA
WHOI-6	-4.7	17	28.183	99	5/10/2022	58	99.99	99.9	82.5	-1.6	NA	-183.3	NA	NA	NA	NA
WHOI-6	-8.7	17	10.639	59	8/15/2022	59	99.99	99.9	0	-0.4	13.4	95.6	>72.2	23.9	3.26	0.013
WHOI-6	-12.7	17	6.567	45	8/15/2022	21	99.99	99.9	53.7	-0.4	NA	98.1	NA	NA	NA	NA
WHOI-6	-16.7	17	7.150	14	8/15/2022	1.4	25.6	22.1	-821.8	-0.8	NA	62.2	NA	0.074	1.5	0.002
WHOI-6	-20.7	17	5.186	1.4	8/15/2022	<0.5	-71.3	-70.9	0.5	-0.1	NA	-12.2	NA	NA	NA	NA
WHOI-6	-24.7	17	1.885	1.1	5/10/2022	0.55	-365.4	-362.6	-356.0	0.0	NA	-37.7	NA	NA	NA	NA
WHOI-6	-28.7	17	3.978	6.1	5/10/2022	0	-241.9	-241.3	-191.5	0.0	NA	-17.1	NA	NA	NA	NA
WHOI-6	-33.7	17	0.410	0	3/10/2021	0	-1785.9	-1771.5	-160.9	-0.1	NA	-248.6	NA	NA	NA	NA
WHOI-6	-43.7	17	1.025	0	3/10/2021	0	72.4	72.5	-42.3	-0.2	NA	91.5	NA	NA	NA	NA
WHOI-8	-0.5	64	5.073	NA			-17.0	-16.9	>75.0	-0.1	NA	48.8	NA	NA	NA	NA
WHOI-8	-4.5	64	13.322	NA			99.3	98.2	>89.7	-2.2	NA	-18.2	NA	NA	NA	NA
WHOI-8	-8.5	64	5.779	68	5/9/2022	17	99.99	99.1	-30.6	-1.5	NA	96.6	>67.7	71	4.63	0.009
WHOI-8	-12.5	64	5.145	NA			99.99	97.7	-546.5	-1.9	NA	95.4	NA	NA	NA	NA
WHOI-8	-16.5	64	7.513	NA			81.1	80.1	-8.2	-1.0	NA	95.7	NA	NA	NA	NA
WHOI-8	-20.5	64	10.537	8.7	11/9/2020	8.7	38.3	38.2	0	-0.9	NA	39.8	NA	0.134	6.72	NA
WHOI-8	-24.5	64	1.124	NA			-781.7	-777.9	0	0.1	NA	-115.7	NA	NA	NA	NA
WHOI-8	-28.5	64	3.25	NA			-344.2	-343.3	>23.1	0.4	NA	-9.9	NA	NA	NA	NA
WHOI-8	-33.5	64	0.788	NA			-863.4	-853.6	>94.6	0.1	NA	-111.2	NA	NA	NA	NA
WHOI-8	-43.5	64	0.297	NA			61.3	58.5	>72.7	-0.2	NA	44.6	NA	NA	NA	NA
MTER-9A		25 Cross	1.23	NA			-16.3	-16.1	>94.1	0.3		-81.1	NA	NA	NA	NA
MTER-9B	-20.5	25 Cross	9.382	NA			90.5	90.5	-301.8	-0.8		83.1	NA	NA	NA	NA
MTER-9C	-40.4	25 Cross	1.096	0.65	5/12/2021	0.47	-312.3	-309.9	>65.1	0.6		-415.2	NA	0	0.024	0
MTER-9D	-50.4	25 Cross	2.681	NA			-84.4	-84.2	>94.3	0.2		-25.8	NA	NA	NA	NA

1.1 Change calculated over shorter period.

F. LAGOON POND, MARTHA'S VINEYARD, MA

A pilot PRB was installed near Lagoon Pond on Martha's Vineyard (SMAST 2023). Martha's Vineyard Commission (MVC) in conjunction with the School of Marine Science and Technology (SMAST), University of Massachusetts Dartmouth, New Bedford, MA designed and operated the pilot PRB. ESM performed the injections in November 2020. The groundwater is approximately 3 to 4 feet bgs and the nitrate plume extends to 18 feet bgs. The site soils are primarily coarse to fine sands with some silt and clay layers near the Lagoon Pond. Groundwater flow is east/northeast towards Lagoon Pond. Nitrate-N were 2 to 15 mg/L range and average of 5 mg/L with the maximum levels between 10 and 16 feet below ground surface. Prior to installation, two natural gradient tracer studies were conducted with potassium bromide to determine groundwater velocity and confirm groundwater flow direction. Samples were collected daily for 40 to 43 days. The groundwater velocity was 0.5 to 0.75 ft/day (average 0.6 ft/day) with a slight deviation from the groundwater flow direction based upon the groundwater elevation contours. **Figure 33** shows the Lagoon Pond PRB and multi-level wells.

A total of 3,432 gallons of SRS®-NR with 13,723 gallons of dilution water (20% SRS®-NR) and 1,600 pounds of calcium carbonate was injected on November 5, 2020, by direct push into the PRB which was 80 feet from the Lagoon Pond and extended 150 feet with 12 injection points spaced 10 feet apart on the northern side of the PRB and 15 feet on the southern side of the PRB. Injection flow rates ranged from 3 to 12 gallons per minute and under a pressure of 3 to 17 pounds per square inch.

Denitrification was noted in well W4, 22 feet downgradient of the PRB, within 14 days after injection. Well PW-4M, 33.5 feet downgradient showed a significant reduction in nitrate within 60 days. **Figure 34** shows the nitrate-N concentrations in upgradient wells PW-3S and PW-3M and the downgradient wells W4 (22 feet from the PRB) and PW-4S and PW-4M (33.5 feet downgradient of the PRB). Nitrate-N concentrations ranged between an estimated 2.5 to 11.6 mg/L in the upgradient wells. As shown in **Figure 34**, Nitrate-N fell from 6.7 to 0.2 mg/L in well W4 within 14 days and to non-detect in 30 days. Well PW-4S had decreases in nitrate-N from 0.9 mg/L to non-detect in about 60 days. Well PW-4M saw decreases in nitrate-N from 6.7 mg/L to non-detect in about 60 days. Deeper wells W14 and PW-4D did not respond as well as the other wells within the treatment area nor did shallow well PW-2S where the spacing of the injection locations was further apart. **Figure 34** shows the nitrate-N concentrations in all the monitored wells. Excess nitrogen gas versus argon was measured by high precision membrane inlet mass spectrometry. Excess nitrogen was present at approximately 8X the background level seen in the upgradient well PW-3D in well W5 located about 22 feet from the PRB. Excess nitrogen was found at 4X background in midlevel well PW-4M and 5X background in deep well PW-4D 33.5 feet downgradient of the PRB (**Figure 35**). SMAST (2023) estimated 91% removal of nitrogen or 1.87 kg/N removed per linear m of PRB per year or 1.3 pounds per foot of PRB per year.

The maximum DOC of about 600 mg/L was 3 feet from the injection point with elevated levels of about 80 mg/L up 22 feet downgradient (**Figure 31**). The pH and alkalinity increased in wells 20 and 35 feet downgradient due to the calcium carbonate injections with impacts on wells 80 feet downgradient. Phosphate increased to as high as 180 mg/L in wells 20 feet downgradient (**Figure 32**). The phosphate was thought to have been released due to the ferrous iron reduction. At 35 feet downgradient, the maximum phosphate was 40 mg/L. There was no change in phosphate in the wells 80 feet downgradient. Elevated manganese up to 50 mg/L was observed at wells 20 feet downgradient of the PRB, maximum of 65 mg/L at 35 feet downgradient, but at 80 feet downgradient, the maximum manganese was about 10 mg/L. Elevated ferrous iron up to 260 mg/L was observed at wells 20 feet downgradient of the PRB, maximum of 250 mg/L at 35 feet downgradient, but at 80 feet downgradient, the maximum ferrous iron was about 40 mg/L. Arsenic was found at 0.002 to 0.095 mg/L but were below level of concern of 0.34 mg/L established by EPA for freshwater systems. Only low levels of 0.01 mg/L arsenic were detected in the wells 80 feet downgradient.

The Martha's Vineyard pilot by SMAST showed that:

1. The PRB was situated as close as 80 feet from the water body.
2. The PRB had minimal impact on wells closest to the water body.
3. The PRB was estimated to remove 91% of the nitrogen or about 1.3 pounds per foot of PRB per year.
4. Phosphate was released as ferric oxide was reduced to ferrous iron, but the elevated phosphate did not reach the wells located 80 feet downgradient of the PRB and closest to the water body.

Figure 33. Lagoon Pond Road Site As Built Map Showing Final Placement of the PRB and Multi-Level Monitoring Wells (SMAST 2023)

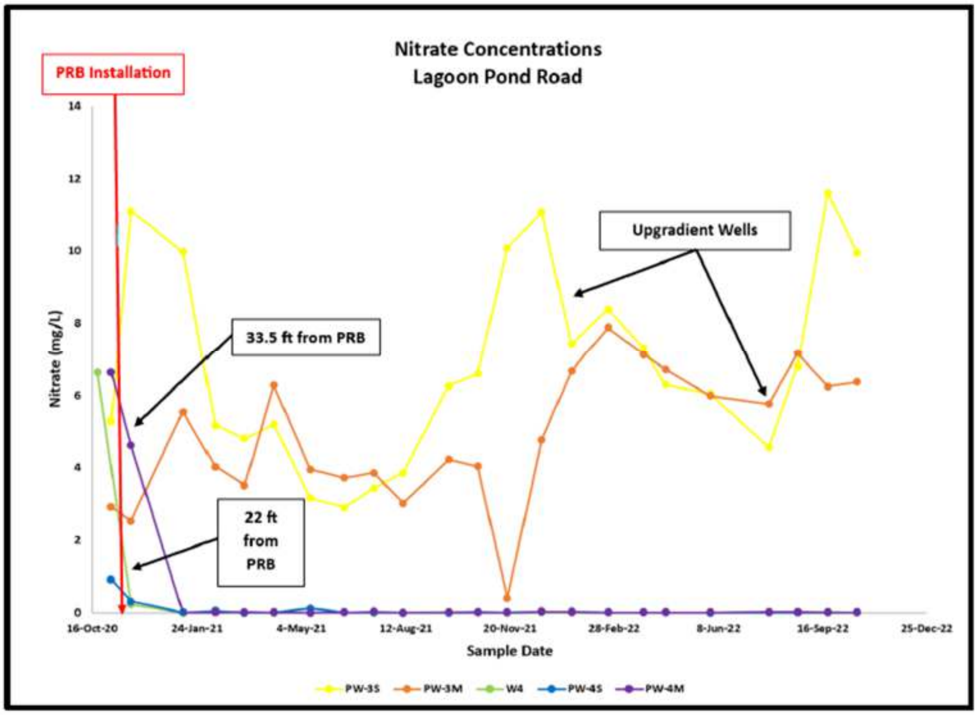


Figure 34. Pre- and Post-Injection Nitrate Sampling of Select Monitoring Wells Located Both Upgradient and Downgradient of the Installed PRB. Downgradient Monitoring Wells W4 and PW-4M are Located 22 and 30.5 Ft Respectively from the 10-Ft Spaced PRB Injection (SMAST 2023)

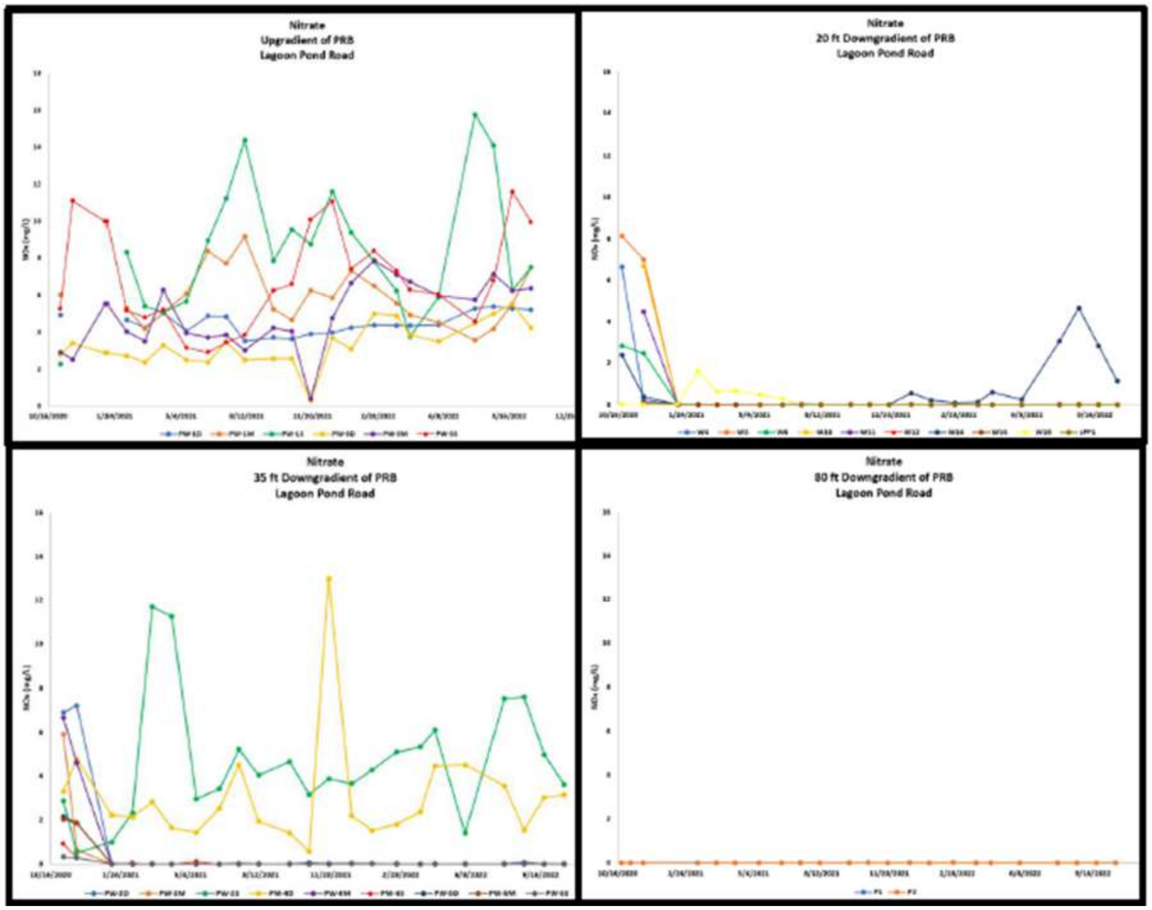


Figure 35: Pre- and Post-injection Nitrate Sampling of Wells Located Upgradient of the PRB (Upper Left), 20 ft Downgradient (Upper Right), 35 ft Downgradient (Lower Left), and 80 ft Downgradient (Lower Right). EVO Injection was November 5, 2020. (SMAST, 2023)

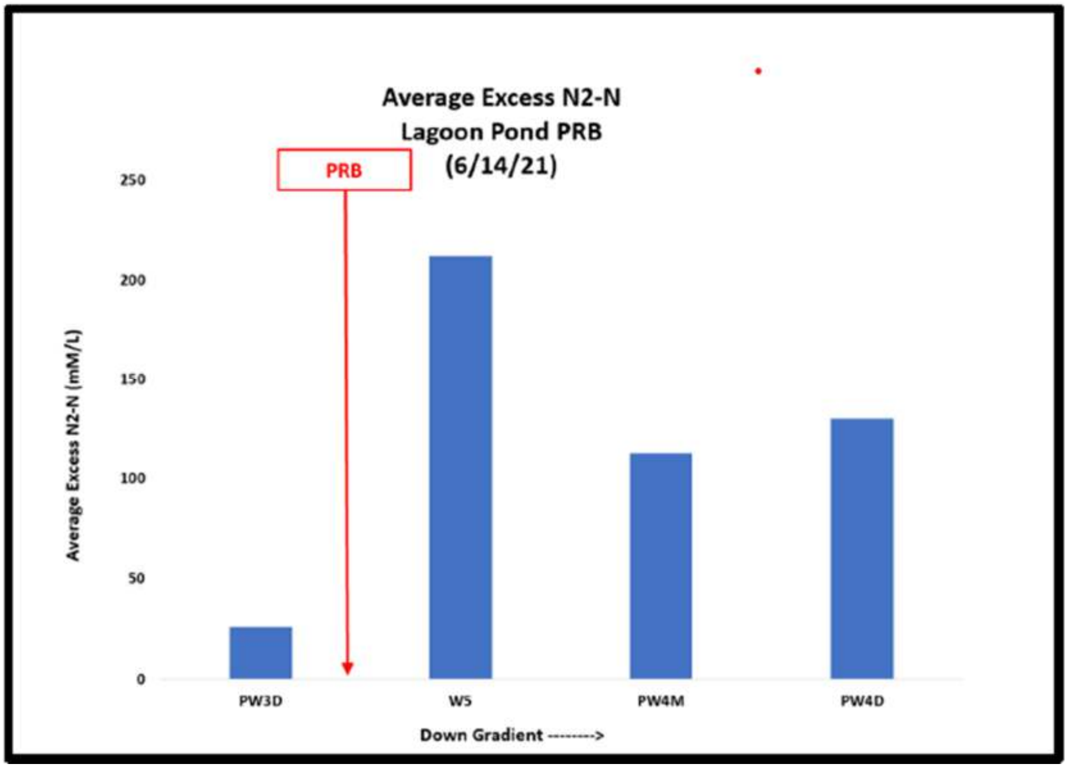


Figure 36: N2/Ar Measurements by High Precision Membrane Inlet Mass Spectrometry, Where N2 Excess was Measured Using Membrane-Inlet Mass Spectrometry (MIMS). PW-3D is Located Upgradient, W5 is Located 22 ft Downgradient, and PW-4M/PW-4D are Located 33.5ft Downgradient of the PRB.

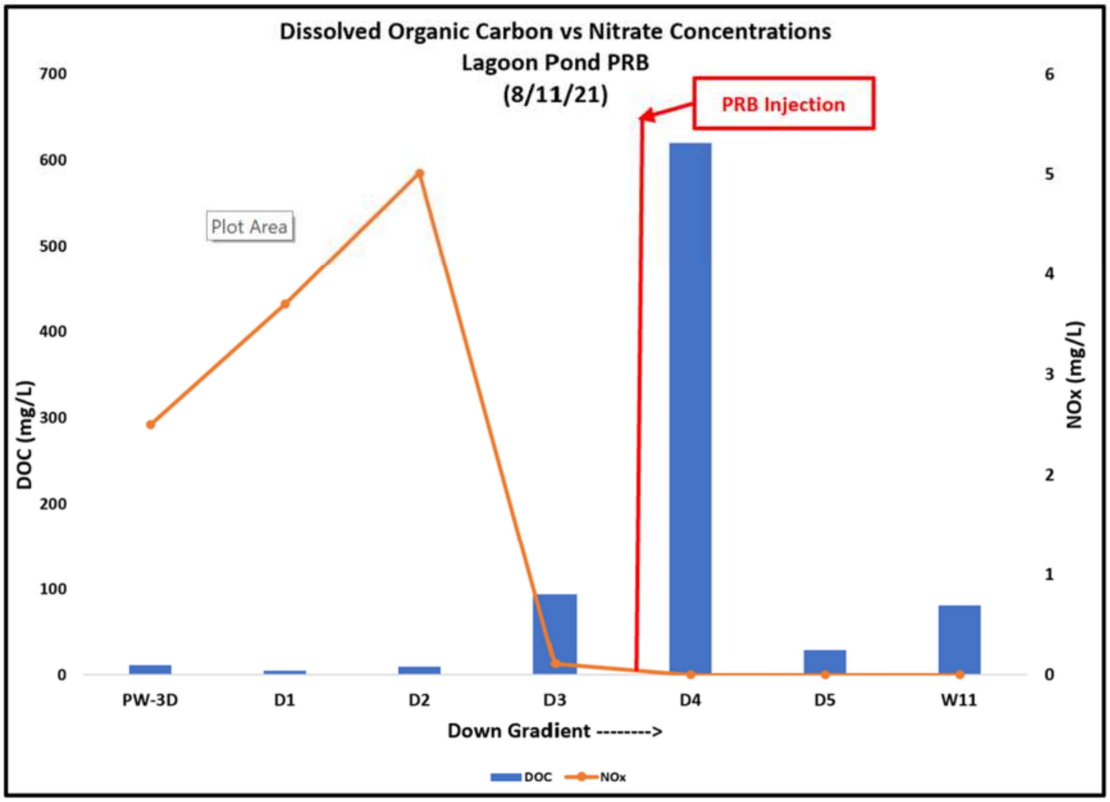


Figure 37. Dissolved Organic Carbon (DOC) and Nitrate Sampling Both Up and Downgradient of the Installed PRB. Downgradient Sampling Location D4 is Located Approximately 3 Ft from the PRB Injection Well (SMAST 2023)

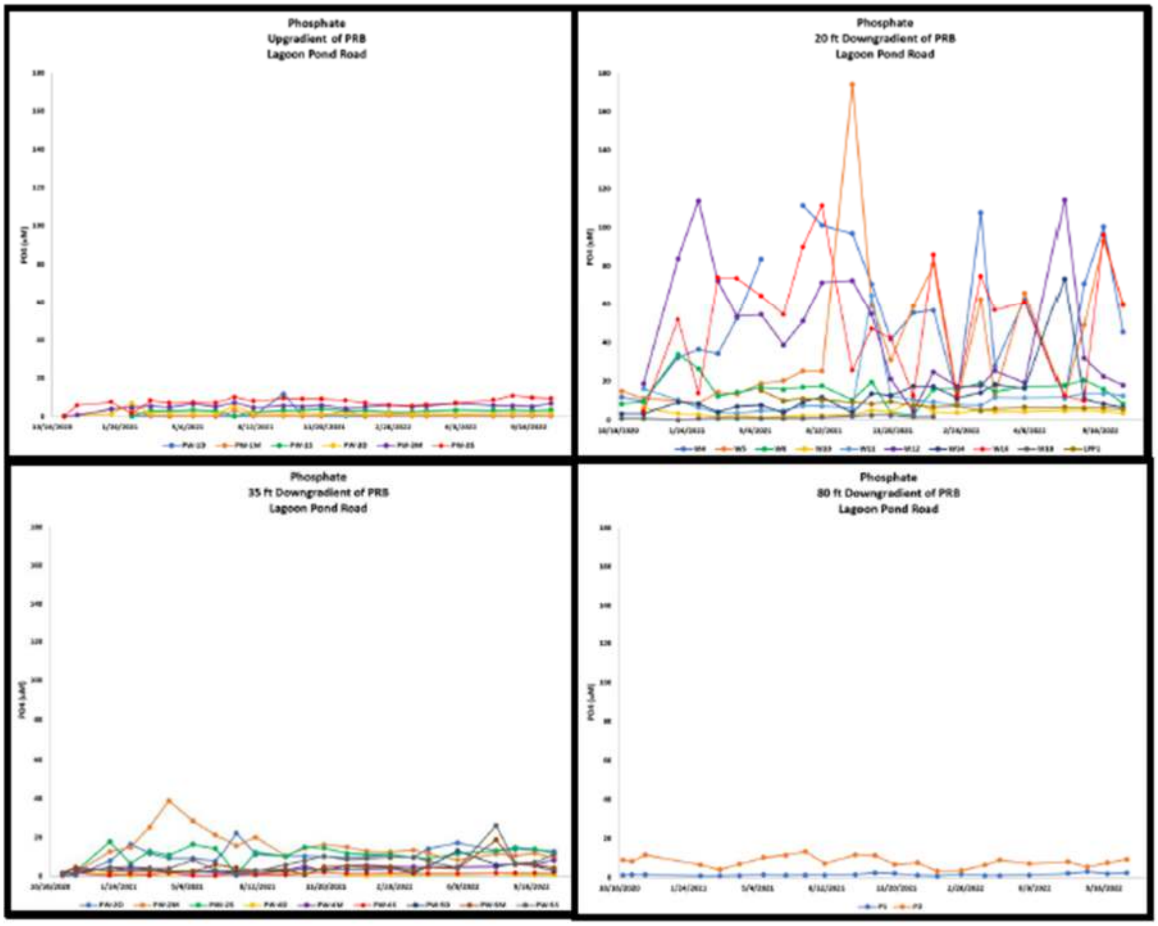


Figure 38: Pre- and Post-Injection Phosphate Sampling of Wells Located Upgradient of the PRB (Upper Left), 20 ft Downgradient (Upper Right), 35 ft Downgradient (Lower Left), and 80 ft Downgradient (Lower Right). EVO Injection was November 5, 2020 (SMAST 2023)

G. EVO LOADING CONCLUSIONS

The following conclusions can be made from these pilots:

- SRS®-NR loadings ranged from 0.040 to 0.102 gallons per cubic foot of aquifer with an average of 0.072 gallons per cubic foot of aquifer.
- Understanding the groundwater flow rate and direction is important for a proper design.
- No impact on surface water bodies were noted with the PRBs installed as close as 80 and 130 feet upgradient of the water bodies.
- The PRBs were effective in promoting denitrification for more than 0.4 and up to 4.7 years.
- Buffer additions of 0.0053 to 0.0492 pounds per cubic foot of the PRB increased the groundwater pH by 0.9 to 1.8 SU for up to 5.8 years. Sodium bicarbonate, sodium bicarbonate and calcium carbonate, and calcium carbonate alone were all effective in increasing the pH of the groundwater up to 100 feet downgradient. The average loading was 0.015 pounds per cubic foot of PRB. Higher loadings may be required for acidic aquifers with a groundwater pH of <5.0 SU. A mixture of 50% sodium bicarbonate and 50% calcium carbonate should provide rapid neutralization with the more soluble sodium bicarbonate and the less soluble calcium carbonate should last longer.
- Iron, manganese, and carbon dioxide reductions to ferrous iron, manganese(II), and methane can be significant electron donor demands.
- Anaerobic conditions can mobilize arsenic with the maximum concentration was 0.050 mg/L.

REFERENCES

AECOM. (2016). Water Quality and Wastewater Planning Task Number 3 – NT Demonstrations Projects. Deliverable 3.c.5 – Draft Technical Memorandum on Site Characterization and Evaluation for Permeable Reactive Barriers (Evaluation Criteria and Ranking). Town of Orleans, MA.

Dombrowski, P.M. Temple, M., Parece, T., Marrion, J., Shreve, B., Begley, J., Lee, M.D. Raymond, R. Jr., & Hostrop, F. (2017). Denitrifying Permeable Reactive Barriers on Cape Cod: Bench Scale Studies and Implementation of the First In-situ EVO PRB. 4th International Symposium on Bioremediation and Sustainable Environmental Technologies.

GHD. (2018). Eastham Salt Pond Groundwater Analysis and Permeable Reactive Barrier Investigation.

Gonsalez, V., Dombrowski, P.M., Lee, M.D., & Ramsburg, C.A. (2023). The Influence of pH on Subsurface Denitrification Stimulated with Emulsified Vegetable Oil. Water 2023:15(5),883. https://doi.org/10.3390/w15050883

Lee, M. D., Hostrop, F., Hauptmann, E., Raymond, R.L. Jr., & Begley, J.F. (2016). Column Studies to Evaluate EVO for Nitrate Removal in Permeable Reactive Barriers on Cape Cod, MA. G-106. 10th International Conference on Remediation of Chlorinated and Recalcitrant Compounds.

Parece, T. (2022). Water Quality and Wastewater Planning, NT Demonstration Projects. Task 15.1.B-Technolical Memorandum for Eldredge Park Permeable Reactive Barrier Demonstration Project, June 2022 Groundwater Monitoring Quarterly Report. Town of Orleans.

Woods Hole Oceanographic Institute. (2022). PRB Working Group. September 2022. Meeting #12. Field Scale Validation of Permeable Reactive Barriers for Non-Point Source Groundwater Nitrogen Remediation.

School for Marine Science and Technology (SMAST). (2023). Final Report (September 1, 2018-December 31, 2022). Siting, Installation and Monitoring of PRB Technology for Nitrogen Mitigation in the Lagoon Pond Watershed, Oak Bluffs and Tisbury, MA. Contract #SNEPWG18-11-MVC.

Verdantas and MT Environmental Restoration (2023). Pilot Permeable Reactive Barrier Project. 3rd Quarter 2022 Status Report. Town of Eastham, Health Department. January 2023.