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Denitrifying Permeable Reactive Barriers on Cape Cod: Bench-Scale Studies and Implementation of the First In Situ EVO PRB

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ABSTRACT: Nitrogen in the form of urea and other organic materials in wastewater is mainly converted into nitrate by on-site septic tank and leach field systems. The partially treated wastewater is infiltrated to groundwater. Nitrate is typically stable under aerobic conditions in groundwater. As a result, nitrate-laden plumes travel without significant attenuation to coastal waters of Cape Cod, Massachusetts (MA). The cost to bring Cape Cod communities in compliance with the Clean Water Act has been estimated to be at least $4 billion. Non-traditional treatment alternatives like permeable reactive barriers (PRBs) to remove nitrate from groundwater via denitrification are being evaluated to meet estuary nitrate Total Maximum Daily Loads (TMDL) and minimize sewering and wastewater treatment costs. Fast groundwater flow (0.3 to 0.6 meters per day; 1 to 2 feet per day) and high fluxes of nitrate and dissolved oxygen (DO) are PRB design challenges for the site. Column studies were performed to evaluate the nitrate treatment capability of emulsified vegetable oil (EVO) in denitrification PRBs. Different EVO formulations and doses were tested at anticipated high groundwater flow rates, including modifications to surfactant properties to make the EVO amendment more adhesive to soil to minimize migration of oil. The first EVO PRB demonstration test on Cape Cod was initiated in November 2016 with a 33.5-meter (110-foot) barrier. Preliminary post-injection monitoring has indicated reductions in nitrate in monitoring wells nearest the PRB.

INTRODUCTION

This section presents an overview of the project background, objectives related to nitrate in groundwaters of Cape Cod, effects on coastal waters, and strategy to mitigate. Cape Cod is a cape extending into the Atlantic Ocean from Massachusetts.

Background and Objectives. Septic systems are used to manage about 85 percent of the wastewater flow on Cape Cod (Cape Cod Commission, 2013). Many of these systems are simple leaching pits and cesspools installed decades ago. Septic systems that process wastewater flows up to 10,000 gallons per day are regulated under Title 5, the state's sanitary code for on-site wastewater systems (310 CMR 15.00). These systems are permitted by local Boards of Health and the MassDEP. Title 5 septic systems were designed to remove pathogens but not nutrients. Dissolved nitrogen from waste material travels through a septic tank and into leach fields down to groundwater. Bacterial reactions transform organic nitrogen to ammonia in the septic tank. Under aerobic conditions, ammonia is converted by bacteria to nitrate below and downgradient of the leach field.

Subsurface geology on Cape Cod consists of relatively permeable sandy formations with high groundwater flow velocities (0.3 to greater than 0.9 meters per day; 1 to greater than 3 feet per day). Groundwater velocity will vary depending on the local groundwater gradient and hydraulic conductivity of the aquifer material. As a result, nitrate-laden groundwater emanating from septic systems travels as a plume without significant attenuation in groundwater to Cape Cod's coastal waters (Cape Cod Commission, 2013), which has enhanced eutrophication. Lawn fertilizer and stormwater infiltration adds to the groundwater nitrogen load. Areas of more dense development will have multiple plumes that may merge to form a large dilute nitrate plume, transporting a significant nitrogen mass or nitrogen load toward downgradient surface waters.

FIGURE 1. Orleans on Cape Cod.

The cost to bring Cape Cod communities in compliance with the Clean Water Act entirely through traditional wastewater treatment and sewering has been estimated to be \$4.6 to \$6.2 billion (Cape Cod Commission, 2017). To reduce the eventual overall cost, the Cape Cod 208 Water Quality Management Plan, prepared by the Cape Cod Commission with AECOM as the lead consultant, would implement sewers with traditional wastewater treatment in combination with non-traditional technologies for reducing nitrate mass flux to coastal waters (PRBs, aquaculture, coastal habitat restoration, constructed wetlands). The goal is to minimize the proposed sewered footprint (area of Town and number of properties to be sewered) and cost by maximizing the use of multiple non-traditional technologies. The Cape Cod 208 Water Quality Management Plan has been approved by both the United States Environmental Protection Agency (USEPA) and the Massachusetts Department of Environmental Protection (MassDEP). The work described was performed on behalf of the Town of Orleans, the first community on Cape Cod to implement the "Hybrid" approach. The Hybrid Plan was vetted through the Orleans Water Quality Advisory Panel (OWQAP), a panel consisting of stakeholder representatives (Orleans Selectmen and representatives of engaged citizen constituencies), and liaisons from key town boards and commissions, organizations, neighboring towns, and regional, state, and federal partners.

PRBs for Denitrification. Denitrification is a process by which naturally occurring bacteria utilize nitrate as terminal electron acceptor for respiration and convert nitrate to inert nitrogen gas ($NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_{2\,(g)}$). Under anoxic or anaerobic conditions, maximum energy is gained by microbes using nitrate as an electron acceptor (denitrification reaction). Therefore, nitrate is the preferred electron acceptor to soil microbes after oxygen is consumed. Denitrifying bacteria are ubiquitous in soils. 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. PRBs are typically oriented perpendicular to the direction of groundwater flow and rely on the natural groundwater gradient to carry the contaminant through the PRB (ITRC, 2011). The system is permeable because the amendments added do not interfere with groundwater flow, and nitrate is removed as groundwater passes through. A denitrification PRB is designed to intercept and treat nitrate in groundwater by biological denitrification before groundwater reaches downgradient surface waters. This method typically introduces a carbon food substrate into the groundwater, allowing naturally occurring microbes in the groundwater to consume the carbon substrate while respiring oxygen and creating anoxic conditions (without oxygen) favorable for denitrifying bacteria. A PRB would be most cost effective where groundwater transport of nitrogen is significant, with higher nitrate concentration and a relatively fast groundwater velocity, resulting in a high mass flux of nitrate through the treatment zone.

MATERIALS AND METHODS

Site evaluation for PRBs, field investigation, and bench scale tests were performed to support design and planning for a PRB demonstration test.

Site Evaluation and Selection. The Town's engineering consultant, AECOM, completed an evaluation of 8 potential sites for performing a PRB demonstration test. A site selection matrix included 4 major criteria (Site Suitability, Permitting, Project Evaluation and Other/Overriding Considerations) with 20 sub-criteria. Property ownership and use, upgradient land use, downgradient groundwater use, distance to shoreline, nitrate concentrations and flux, topography, overall ease of monitoring, and potential for full scale PRB implementation were among the criteria evaluated and rationale for selection.

The site suitability evaluation process narrowed the list of potential Demonstration Test sites to four locations. To support further evaluation of these sites and the design for PRB Demonstration Test, a groundwater and soil investigation was completed in Spring 2016. The investigation included the installation of several groundwater monitoring wells, groundwater sampling, and data analysis on these four sites. Key information to obtain for each site included depth to groundwater, groundwater flow direction, predominant soil type with identification of any less permeable lens, groundwater flow velocity, speciation of nitrogen forms present (nitrate, nitrite, ammonia), distribution of vertical nitrogen concentration profile, and general groundwater chemistry. Based on the matrix and further groundwater investigation, a preferred Demonstration Test site was selected at the location of a Town park and school parking lot. This location was selected based on site use as a parking lot, relatively shallow depth to groundwater below ground surface compared to other proposed locations in the Town (10 to 11 meters, 34 to 36 feet), more than five years of groundwater data from nearby wells, and the ability to provide results representative of other areas in the Town. The parking lot area provides sufficient room for both the layout of the PRB and upgradient and downgradient monitoring wells. In addition, the groundwater flows from this area toward Town Cove (Figure 2), a priority surface water receptor for reducing nitrate loading, and a significant mass flux of nitrate in groundwater is expected at the preferred Demonstration Test location (estimated 710 kilograms per year as calculated with WatershedMVP) (AECOM, 2016). The preferred Demonstration Test location is also greater than 30 meters (100 feet) from any surface water body, another site selection criterion.

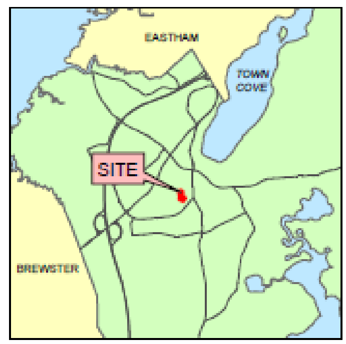

FIGURE 2. Demonstration test site and Town Cove.

Bench Scale Testing. Sand column studies were conducted by TerraSystems, Inc. with soil and groundwater from a site in another Cape Cod community to evaluate emulsified vegetable oil (EVO) to support denitrification. 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 column reactors were tested with each column 3.8 feet (0.9 meters) long and 2 inches (0.78 cm) in diameter (Figure 3). Each reactor was constructed with 5.2 kilograms (kg) soil, and the total pore space was 592 milliliters (mL). Column 1 and Column 2 received 30.8 grams and 61.6 grams, respectively, of a small-droplet EVO (SRS®-SD, manufactured by TerraSystems, Inc., average droplet size of 0.6

and 41.4 grams zero valent iron (ZVI). Water was pumped through each column at 0.37 meters per day (1.2 feet 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 reactors 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, in effluent for the first 2 to 11 pore volumes, and emulsion was not 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 4A. However, when total organic carbon TOC levels fell below 4.0 mg/L, nitrate began to appear in effluent. Based on the three reactors no obvious difference in effectiveness or longevity was measured with increased loading of SRS®-SD or with combination with ZVI.

FIGURE 3. Three columns.

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 TerraSystems, 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).

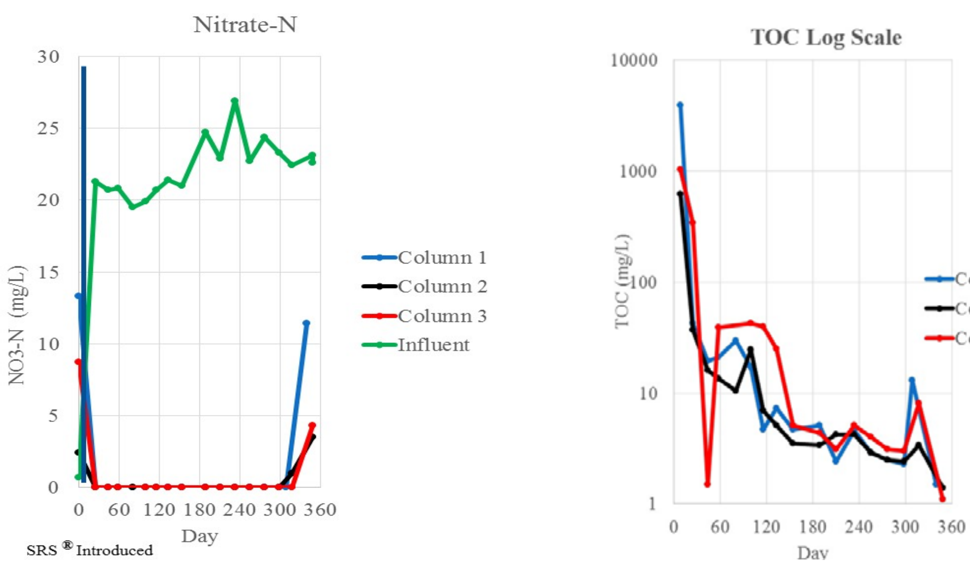

FIGURE 4. Initial bench scale testing results A) Nitrate-N concentrations B) TOC.

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) was applied to the influent of the column. Influent water

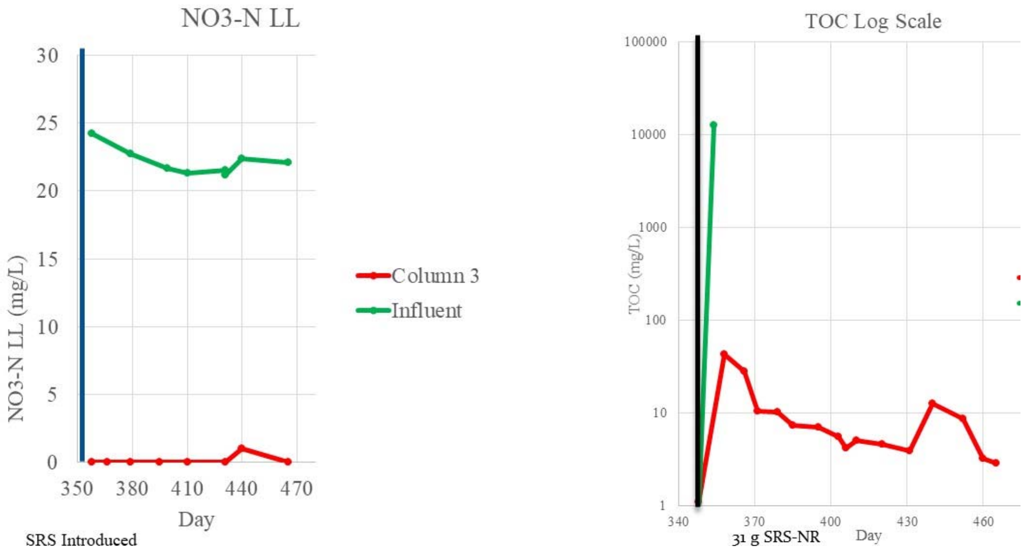

FIGURE 5. Bench scale testing results with SRS®-NR A) Nitrate-N concentrations B) TOC.

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). The column test was operated for an additional 110 days (28 additional pore volumes).

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 5B with Figure 4B). Effective removal of nitrate-nitrogen in the effluent was achieved for the entire period of additional testing (Figure 5A) 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, emulsion was not visually observed or detected through turbidity measurements in the effluent water, suggesting that the modified formulation did not migrate 3.5 meters through the column in 110 days at average flow of 0.58 meters per day water flow rate. This observation suggested that 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.

PRB Design. For the PRB Demonstration Test, EVO is the recommended amendment based on the desire for extended PRB longevity and relative ease of injection. For the demonstration test, it was desired to have the denitrification PRB attain an effective longevity of at least three years. The Substrate Estimating Tool for Enhanced Anaerobic Bioremediation of Chlorinated Solvents developed for the Environmental Security Technology Certification Program (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 2 feet per day.

Using the results of the bench scale testing, the modified, stickier 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. EVO dilution and injection volume were selected to establish residence time and longevity. A thicker EVO solution (diluted 4.3:1, 14% soy bean oil) was chosen to increase carbon loading. Total design injection volume was prescribed to be 14% of 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 5.2 to 7.0. Denitrifying bacteria are most active in circumneutral groundwater (pH 6 to 8). However, denitrification has been observed to occur at conditions less than pH 6, including in the bench scale testing performed by TerraSystems, Inc. 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.

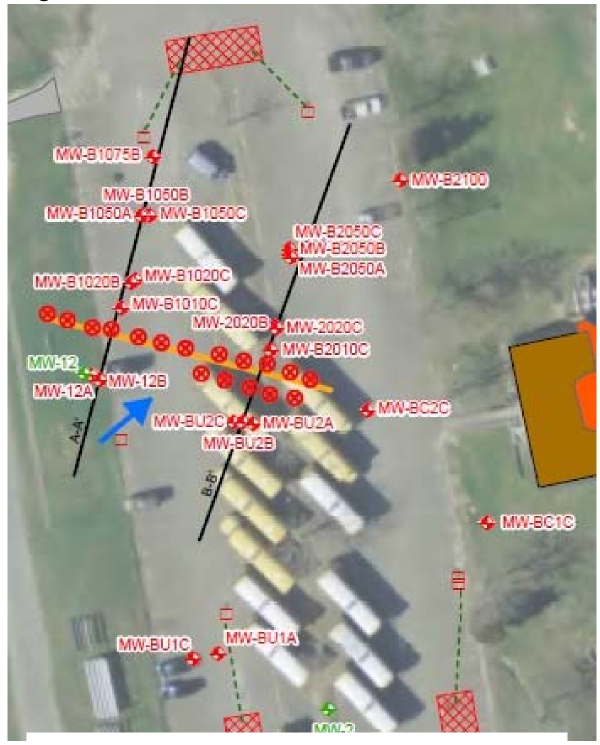

FIGURE 6. Demonstration test PRB injection points and monitoring well transects.

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 33.5 meters (110 feet) with injection points closely spaced on a 3-meter (10-foot) spacing to establish a continuous barrier length to minimize potential for groundwater to flow through gaps in the reactive zone (see Figure 6). On the west side, seven injection points were set up in a single row. On the east side, 10n injection points were laid out in two parallel rows of points to compare nitrate removal, longevity, and groundwater quality. Pre-injection groundwater monitoring indicated that nitrate concentrations were present at depth of 21 meters (70 feet) below ground surface (bgs). For the demonstration test, the vertical treatment interval was established to be 11 to 21 meters (36 to 68 feet) bgs.

Demonstration Test Implementation. ISOTEC performed injection of SRS®-NR to establish the PRB from November 15 through 18, 2016 with oversight by the AECOM PRB Team. Injection of carbon substrate was performed directly through direct-push rods using the custom-designed ISOTEC proprietary 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. The average injection flow rate was approximately 1.7 liters per minute (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,

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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 2.1, 3.0 and 6.1 meters (7, 10, and 20 feet) downgradient of the PRB injection points during the injection event.

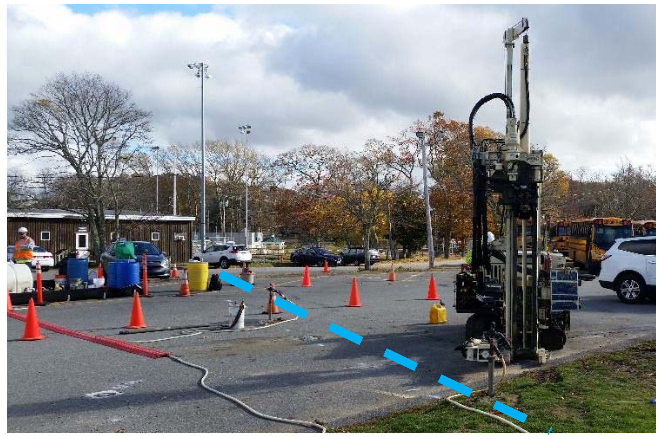

FIGURE 7. Demonstration test PRB implementation (blue line illustrates PRB).

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 (2.1 to 30 meters; 7 to 100 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. Field and laboratory analyses used to evaluate PRB Demonstration Test performance are presented in Table 1.

Groundwater samples were collected in November 2016 prior to EVO injection. During injection activities, select groundwater wells were monitored for field parameters (pH, temperature, dissolved oxygen, oxidation-reduction potential, and conductivity). Additionally, TerraSystems, Inc. monitored the 3 and 6 meter (10 and 20 foot) downgradient monitoring wells using an in-well probe for these same parameters to observe any potential changes during injection. DOC and alkalinity test results did not indicate EVO migration.

The first post-injection sampling event was a stand-alone sampling event approximately 7 weeks after injections with samples collected on January 5 and January 10, 2017. Some wells were not accessible for sampling during January 2017 due to snow piles.

Routine groundwater sampling will continue quarterly for a period of three years after injection. 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, boron, DOC, methane, and alkalinity. The primary objectives of the post-injection sampling will be 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 will be dynamic and continuously evaluated to adjust the selected monitoring parameters and frequency of monitoring based on data collected and observations.

The first quarterly post-injection sampling was completed February 2017, with the most attention given to groundwater sample locations closest to the PRB: monitoring wells MW-B1010C and MW-B2010C, located approximately 3 meters (10 feet) downgradient of the injection zone (Figure 6). DOC increased in both wells from <1 to 14 mg/L in MW-B1010C and 2.2 to 19 mg/L at MW-B2010C. In these two wells nitrate was also observed to decrease compared to baseline samples (Figure 8). Significant increases in DOC were not observed at other monitoring well locations, and corresponding changes in nitrate concentration did not appear in other downgradient monitoring wells. No changes for dissolved iron and manganese were noted comparing baseline and first quarter sample results, and methane was not detected in groundwater. These results indicate no significant impacts with respect to secondary water quality. No migration of EVO material was indicated by sampling observations and test results.

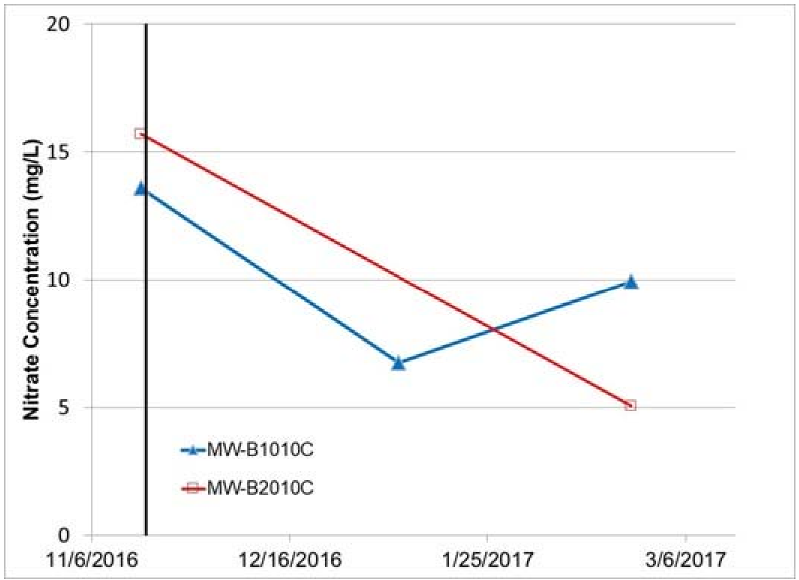

FIGURE 8. Nitrate concentration in two wells approximately 3 meters downgradient of PRB.

The groundwater flow direction is influenced by stormwater recharge 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. More complete estimates of groundwater flow will support calculations for nitrate mass flux removed through the Demonstration Test PRB.

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. The demonstration test site was chosen based on a site screening evaluation with more than 20 scored criteria. 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 fast-flowing, 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. Preliminary results from groundwater samples collected 7 weeks and 3 months after injection indicate decreases in nitrate concentrations and increases in DOC in monitoring wells approximately 3 meters (10 feet) downgradient of the PRB injection points. Performance monitoring will continue quarterly for a period of three years.

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REFERENCES

AECOM. 2016. Final Technical Memorandum on Site Characterization and Evaluation for Permeable Reactive Barriers.

Cape Cod Commission. 2013. Cape Code Regional Wastewater Management Plan Technology Assessment: Conventional Infrastructure.

Cape Cod Commission. 2017. Cape Cod Area Wide Water Quality Management Plan Update. Presentation at Waquoit Bay Coastal Training Program.

Interstate Technology & Regulatory Council (ITRC). 2011. Permeable Reactive Barrier: Technology Update (PRB-5).