Assessment of Nitrate Concentrations in Groundwater Near an Onsite Wastewater System Before and After Installation of a Permeable Reactive Barrier

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Abstract

There are approximately 2 million onsite wastewater systems (OWS) in North Carolina that provide soil-based treatment of wastewater. Wastewater contains elevated concentrations of environmental pollutants including nitrogen. Prior studies have shown that many OWS are efficient at oxidizing nitrogen, but groundwater plumes enriched with nitrate (NO_3^-) may extend to surface waters and/or wells creating various environmental and public health risks. Groundwater monitoring near the OWS drain field of a school in Eastern North Carolina showed NO_3^- concentrations routinely exceeded the 10 mg/L groundwater standard. In 2014, a permeable reactive barrier (PRB) was installed between the OWS and a monitoring well (with elevated NO_3^-) to enhance nitrogen removal via denitrification. The PRB was constructed by excavating a trench with the approximate dimensions of 1.2 m wide x 6 m long x 8 m deep. The bottom of the trench was dug below the water table. Woodchips were used to fill the bottom 2 to 3 m of trench, and the rest of the trench was filled with the excavated soil. The woodchips were used as a carbon source for denitrifying microorganisms. Groundwater samples were collected from the well and analyzed for NO_3^- three times each year (2005- 2023) following the installation of the PRB. Groundwater NO_3^- concentrations were lower post (most < 8 mg/L) relative to pre (mean = 13.7 mg/L) PRB installation. Results show that PRBs may be effective practices for reducing the groundwater transport of NO_3^- for many years with little to no maintenance.

Introduction

Permeable reactive barriers (PRBs) are trenches that are excavated below the water table and filled with reactive material such as woodchips and sawdust (Robertson and Cherry, 1995; Long et al., 2011) or zero valent iron (Fe^0) and charcoal (Wu et al. 2017) to facilitate the interception and removal of mobile pollutants such as nitrate (NO_3^-). The PRBs are installed downgradient from a pollutant source and perpendicular to the direction of groundwater flow thus allowing groundwater to pass through the porous, reactive material and enabling various reactions such as denitrification. Denitrification is the transformation of NO_3^- to N^2 gas and is facilitated by microorganisms in saturated, anaerobic soils with an abundance of labile carbon that serves as an electron donor for the microbes. While N^2 gas is harmless, NO_3^- in excess concentrations can be a public and environmental health threat. For example, while NO_3^- in soils promotes plant and crop growth, in water it may cause an overgrowth of algae, some of which produce toxins that are dangerous to animals and humans. Elevated concentrations of NO_3^- in water supplies may cause methemoglobinemia if consumed by infants (Bednarek et al., 2010). There have also been reported links between drinking well water containing elevated NO_3^- and diabetes along with hypothyroidism and hypotension (Guan et al., 2019; Amoako-Nimako et al., 2021). Groundwater NO_3^- levels have been rising since 1960 as agriculture production increased to meet the demand for food created by a growing human population (Guan et al., 2019). Wastewater treatment via septic systems or onsite wastewater systems has also been documented as a significant source of NO_3^- in groundwater (Robertson and Cherry, 1995; Baker et al., 1998). NO_3^- is an anion and is very mobile in soil and groundwater. Remediation of groundwater enriched with NO_3^- is thus very important (Bednarek et al., 2010; Guan et al., 2019). Some research has shown that PRBs may be an effective method at reducing groundwater NO_3^- concentrations over long periods of time with little maintenance (Shipper and Vojvodic-Vukovic, 2001; Long et al., 2011). The organic carbon present in PRBs is essential to denitrification (Bednarek et al., 2010). Bacteria within the barrier require a carbon source as the electron donor in reduction reactions, reducing conditions, optimal temperature and pH, anaerobic conditions, and a surface matrix for attachment (Amoako-Nimako et al., 2021). Comparison of denitrification rates of barrier materials from the time of installation (1992) and fifteen years after installation showed continued reduction in groundwater NO_3^- concentrations downgradient of a tile bed septic system (Robertson et al., 2008).

Robertson et al (2008) reported that carbon sources in PRBs such as cellulose, alfalfa, and wheat were initially very efficient at removing NO_3^- but experienced a rapid decline in the reduction rate over a 91 day period, while saw dust was not as efficient initially at removing nitrate but the performance was more stable (Robertson et al., 2008). A permeable barrier consisting of a mixture of 30% Fe^0, 10% activated carbon, and 60% sand reduced NO_3^- concentrations from 122 mg/L to 10 mg/L after 5 days (Guan et al., 2019). Research on Fe^0 as the active media in a PRB found a decreased porosity and passivation over time as a result of secondary precipitation of the iron within the barrier (Wu et al., 2017). Fe^0 can be effective at aiding in reduction of nitrogen compounds when added to wheat straw as shown by a study where a field scaled PRB containing Fe^0 modified wheat straw received varying rates of nitrate and was effective at reducing nitrate (Guo et al., 2021). A study by Liu et al. (2013) demonstrated the potential for a two-layer PRB to reduce NO_3^- with the first layer being anaerobic to promote growth of denitrifying bacteria and the second layer serving to biodegrade nitrogen (Liu et al., 2013). Bekanska et al. (2018) concluded that using a woodchip horizontal barrier greatly improved NO_3^- reduction in shallow soils when using a managed aquifer recharge system. Another study on effects of managed aquifer recharge and its effect on denitrification found that woodchip barriers both with and without native soils increased denitrification rates with changes in microbial environment affected more by exclusion of native soils from the mixture (Gorski et al., 2020).

The treatment efficiency of a PRB may be influenced by NO_3^- concentrations in groundwater. A PRB with dimensions of around 1.5 m deep and 1 m wide, filled with sawdust from sylvestris tree species installed downstream of an open pig manure storage area was able to reduce NO_3^- concentrations from 228 mg/m^3 to 10.8 mg/m^3 after 1 year since installation (Bednarek et al., 2010). An 11-month controlled study for NO_3^- concentration in a PRB containing a mixture of mulch and gravel in Europe showed this configuration to be effective at reducing nitrate concentrations of up to 230 mg/L when exposed to nitrate concentrations ranging from 1 to 530 mg/L (Gilbert et al., 2019).

Dissolved carbon concentrations may serve as an indicator of barrier functioning by characterizing the availability for denitrifying activity to occur. Woodchips which were used in the PRB under study are chosen due to their high carbon/nitrogen ratio; however, the high volumes of dissolved carbon generated by decomposition of the organic substrate by bacteria in the denitrifying process results in the media potentially being less effective over time (Amoako-Nimako et al., 2021). Ozkaraova et al. (2022) studied the long term carbon availability of various agriculture residue organic carbon sources which were peanut, walnut, and almond shells as well as Luffa sponge using column experiments and found a correlation between carbon content and denitrification where carbon concentrations exceeding the optimum level reduced denitrification and resulted in ammonium production where concentrations at or slightly below the optimum level reduced undesired end products and facilitated denitrification. It was also noted that there are 2 main processes for generation of organic carbon which are initial sublimation from the solid media and hydrolases by bacteria (Ozkaraova et al., 2022). Monitoring of a field scale PRB over 9 years showed a 13% loss in wood chip capacity at a depth of 155 cm to 170 cm (Baker et al., 2021). This demonstrates that organic matter will decompose over time during normal functioning of the PRB emphasizing the importance of continued monitoring to ensure proper functioning.

The aim of this study was to assess the function of the woodchip PRB at a school in Martin County (Figure 1.) 8 years after installation. Field scale studies provide real-world evaluation of nitrogen reduction via denitrification as the barrier is exposed to variations in temperature, pH, and dissolved oxygen combined which cannot be easily produced in a laboratory setting (Amoako-Nimako et al., 2021). Few studies have been conducted using field-scale PRBs treating groundwater NO_3^- as a function of time. Given that PRBs have been shown to be effective at supporting denitrification following several years after installation it is anticipated that NO_3^- concentrations will remain below the maximum contaminant level of 10 mg/L. Determinations will be made by comparing NO_3^- groundwater concentration data before installation to data after installation and assessing trends in post installation data to determine any changes in overall effectiveness.

Methods

PRB Dimensions

Figure 1. A permeable reactive barrier was installed between the septic drain field (red rectangle) and well 2. Well 2 had groundwater NO_3^- concentrations that routinely exceeded 10 mg/L.

The PRB under study is located at Rodgers Elementary in Martin County North Carolina which serves 250-350 students. The PRB was installed in 2014 downgradient of an onsite wastewater system treating wastewater effluent from the school. The system consists of a large septic tank, multiple pump tanks, a pressure manifold, and 9 drain field trenches, each 64 m long. Three monitoring wells were installed, one upgradient which is well 1 and two downgradient from the drain field trenches which are wells 2 and 3. Elevated NO_3^- concentrations were observed at well 2 a few years after monitoring was initiated. The NO_3^- concentrations steadily increased prior to installation of the barrier. The barrier was installed just upslope of well 2. The barrier was excavated to have dimensions of 1.2 m wide, 8 m deep, and 6 m long with the bottom 3 m filled with wood chips and sawdust from various tree species, including pine. The top 5 m of the trench were backfilled with excavated soil from the site.

Collection of Samples & Testing Protocols

Three samples were collected each year following expansion of the OWS and installation of monitoring wells in 2005. A bailer was lowered into each well and retrieved a few times to purge the wells. Next, groundwater samples were collected and placed in a sealed bottle. The samples were placed into a cooler with ice to be taken to Environmental 1 laboratory in

Greenville NC for testing of NO_3^-. Laboratory determinations of NO_3^- were also performed using a smart chem 200 at East Carolina University for several samples after the PRB was installed.

Concentrations of NO_3^- in groundwater were compared to the maximum contaminant level of 10 mg/L.

Data Analysis

The PRB effectiveness was evaluated by comparing NO_3^- concentrations in groundwater at well 2 before and after installation of the PRB. Groundwater data were provided by the Department of Health and Human Services. Data were plotted and regression analyses were performed using Microsoft Excel. NO_3^- concentrations were also compared between well 2 and wells 1 and 3 to determine if any trends were present in groundwater not influenced by the septic system. (Humphrey et al., 2015).

Results

Prior to installation of the PRB, NO_3^- concentrations in well 2 increased by approximately 2.18 mg/L each year from 2005 to 2014 $r^2 = 0.907$ (Figure 2 and 3). The highest NO_3^- concentration in well 1 was 8.76 mg/L in December of 2012. The highest NO_3^- concentrations in well 2 was 32.8 mg/L in December of 2013. The highest NO_3^- concentration in well 3 was 8.88 mg/L in April of 2013. The highest annual average of NO_3^- concentrations preceding PRB installation for wells 1, 2, and 3 were 8.23 mg/L in 2012 for well 1, 25.92 mg/L in 2014 for well 2, and 7.45 mg/L in 2013 for well 3 (Table 1). Prior to PRB installation, 16 out of 26 samples from well 2 exceeded the 10 mg/L limit for NO_3^- in groundwater. Furthermore, 15 consecutive samples collected between August 2009 and May of 2014 exceeded the NO_3^- concentration standard of 10 mg/L.

From 2015 to 2023 (post PRB installation), NO_3^- concentrations in well 2 decreased by approximately 0.99mg/L each year $r^2 = 0.7746$ (Figure 2 and 4). The lowest NO_3^- values following barrier installation were the September 2020 and September 2021 sampling events with values of 1.33 mg/L and 1.97 mg/L, respectively. In 2014, the year of the PRB installation, the average NO_3^- concentration in well 2 was 25.92 mg/L before the barrier and 13.98 mg/L after the barrier, a decrease of 46.06% (Table 1). There was a 27.9% decrease in NO_3^- average yearly concentrations in well 2 from 12.79 mg/L in 2015 to 9.2 mg/L in 2016. After the September 2015 sampling event which was the first following barrier installation, the groundwater NO_3^- concentrations at well 2 dropped under the 10 mg/L limit in September of 2016. Since then, 2 samples have exceeded 10 mg/L including on January 1st, 2016, when the NO_3^- concentration was 13.67 mg/L and on May 8th, 2018, when the NO_3^- concentration was 10.44 mg/L.

Test parameters measured onsite in December of 2022 were as follows. The oxidation reduction potential was 213. The pH was 4.9. The dissolved oxygen reading was 4.3 mg/L. The groundwater temperature taken from samples from well 2 was 19.2 degrees Celsius. The electrical conductivity was 173 microsiemens /cm.

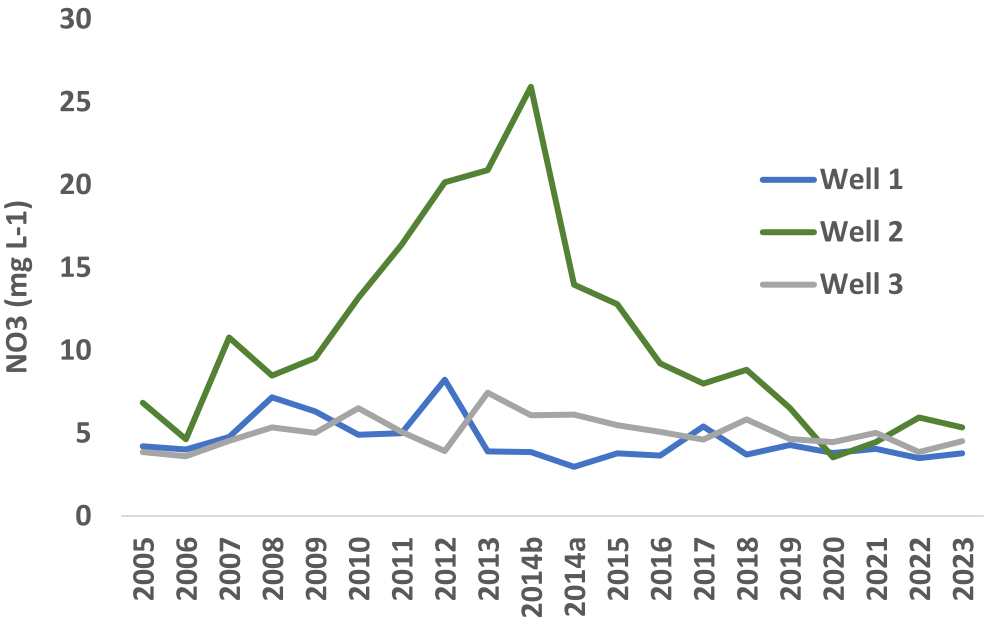

Figure 2. Nitrate concentrations in groundwater sampled from wells 1, 2, and 3 between 2005 and 2023. The PRB was installed in 2014, thus 2014b is before and 2014a is after installation.

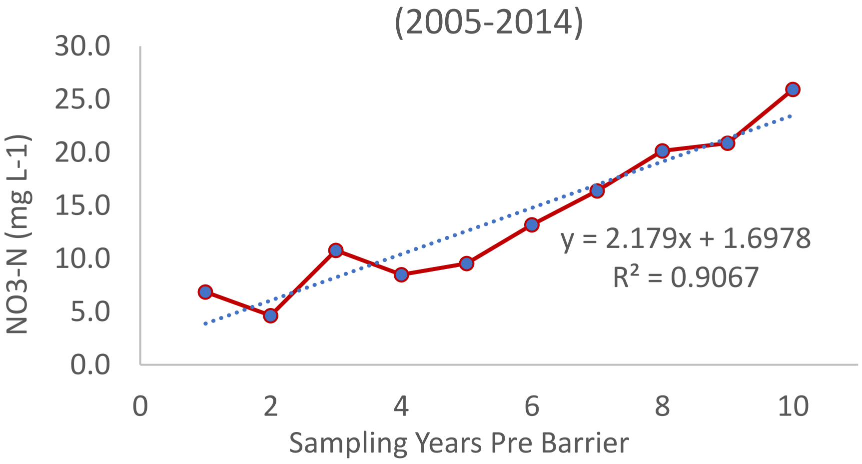

Figure 3. Mean annual groundwater NO_3^- concentrations at well 2 prior to installation of the PRB.

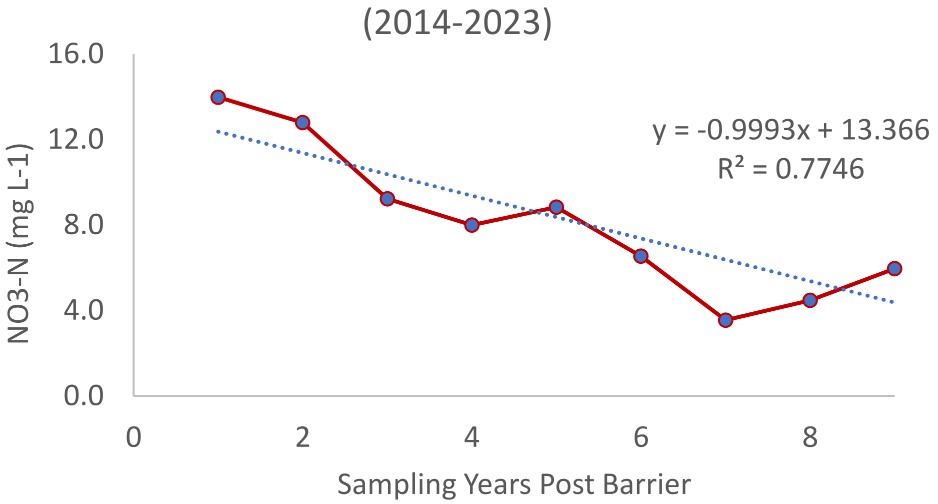

Figure 4. Mean annual groundwater NO_3^- concentrations at well 2 after installation of the PRB.

Table 1. Mean annual NO_3^- concentrations in groundwater sampled from well 2.

Year	Pre barrier NO_3mg/L	Year	Post Barrier NO_3mg/L
2005	6.85	2014a	13.98
2006	4.64	2015	12.79
2007	10.78	2016	9.22
2008	8.49	2017	8.00
2009	9.54	2018	8.84
2010	13.19	2019	6.53
2011	16.39	2020	3.55
2012	20.15	2021	4.47
2013	20.88	2022	5.95
2014b	25.92	2023	5.36

Discussion & Conclusion

Well 2 NO_3^- concentrations decreased by approximately 0.99 mg/L each year following installation of the woodchip PRB downgradient from a large onsite wastewater system in Martin County. Well 2 was experiencing elevated NO_3^- concentrations from septic system effluent prior to installation of the PRB, but concentrations dropped to below 10 mg/L soon after the PRB was installed (Humphrey et al., 2015). The study findings are consistent with the literature stating that PRBs are an effective method for groundwater remediation from excess NO_3^-. The initial reduction of 46.06% is consistent with NO_3^- reductions of 97% observed by Gibert et al. (2019) following exposure of a field scale PRB to 500mg/L of NO_3^-. Bednarek et al. (2010) observed a decrease in NO_3^- concentrations from 228mg/L upgradient of a 1.5 m deep by 1 m wide sawdust barrier to 10.8mg/L after 1 year. This research suggests that woodchip PRBs can function as desired over an 8-year period with no noticeable decline in functioning. This research can be used in the selection of best management practices for remediating groundwater containing excess NO_3^- from OWS.

More research is needed to confirm the PRB effectiveness to reduce NO_3^- concentrations in various geological settings. Additional work is suggested to assess the quality of the media as this may change over time. By extracting barrier material, determinations of the media to support denitrification based on carbon content can be made. It could also be useful to know the hydraulic flow rate of groundwater to determine NO_3^- loadings to groundwater. Future studies could collect dissolved carbon samples for analysis to provide further evidence that the reduction in NO_3^- is a result of denitrification by denitrifying bacteria.

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