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Performance Assessment of a Permeable Reactive Barrier on Reducing Groundwater Transport of Nitrate from an Onsite Wastewater Treatment System

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Abstract: Elevated concentrations of nitrate in potable water supplies have been linked to negative health outcomes such as methemoglobinemia and various cancers. Groundwater can become contaminated with nitrate from sources including onsite wastewater treatment systems (OWTSs). A groundwater well down-gradient from an OWTS serving an elementary school in Eastern North Carolina USA had 15 consecutive water samples collected over a 5-year period that exceeded the maximum contaminant level of 10 mg/L for nitrate. Corrective actions were required. A permeable reactive barrier (PRB) filled with woodchips was installed between the OWTS drainfield and the contaminated well. The concentration of nitrate in groundwater from the well steadily decreased after the PRB was installed, and a significant (p = 0.001) inverse correlation (−0.859) was observed between the mean annual nitrate concentration and years after the PRB. The nitrate concentration in groundwater from the well has been below 10 mg/L for the last 17 consecutive sampling events. The median nitrate concentration in the well was significantly lower (p = 0.007) post (6.93 mg/L) relative to pre (12.66 mg/L) PRB. The PRB has not required any maintenance over the past 10 years. The implemented PRB directly influences the sampling results from a monitoring well, but it is not necessarily confirmed that it intercepts the entire groundwater flow or fully prevents aquifer contamination. To confirm this, additional monitoring wells would need to be installed. This research has shown that PRBs can be an effective, low-maintenance, best-management practice to reduce the groundwater transport of nitrate.

Keywords: groundwater; nitrate; onsite wastewater treatment system; permeable reactive barrier

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1. Introduction

Onsite wastewater treatment systems (OWTSs) are used in rural areas of many countries and regions where a connection to the central sewer is not available or feasible. For example, OWTSs are prevalent in suburban locations of Ireland [1], Canada [2], Australia [3], the USA [4], Scotland [5], and New Zealand [6]. Most OWTSs include a septic tank, drainfield trenches filled with porous media, and soil beneath the trenches [7]. The septic tank provides the primary treatment of wastewater, including the separation of solids and liquid, the anaerobic digestion of organic matter, and a reduction in biochemical oxygen demand and total suspended solids [8]. Septic tanks are typically designed/sized to provide for a few days of detention time of influent wastewater while allowing for the accumulation of solids. Most residential-scale septic tanks have a capacity of approximately 3780 L or more [9]. Septage from the tanks must be pumped periodically to prevent the overaccumulation of solids [8,10], which correlates to a reduction in the hydraulic residence time of wastewater and an increased likelihood of solids exiting the tank and potentially clogging downstream components [9]. Septic tank effluent is piped to a distribution mechanism where effluent is then dispersed to drainfield trenches [11]. Drainfield trenches are excavations typically between 0.6 and 0.9 m wide and approximately 0.6 to 1 m or so below the surface [12,13]. The trenches are backfilled with approximately 0.3 m of porous media surrounding an effluent conveyance pipe, or chambers with open bottoms are placed in the trenches and connected until they occupy the entire length of the trench [12–14]. The porous media is capped with 0.3 m or more top cover. The drainfield trenches store liquid effluent until it infiltrates the soil. The length and number of drainfield trenches are based on the estimated daily volume of wastewater generated from the home/facility and the characteristics of soil beneath the drainfield trenches [12,15]. OWTSs installed in more hydraulically conductive sandy soils typically have fewer or shorter drainfield trenches relative to OWTSs in less hydraulically conductive clayey soils [12]. The aerobic treatment of wastewater occurs in soil beneath the trenches [7]. Local health officials and/or environmental consultants assess the soil and site characteristics of properties to determine if they meet the local regulations for the installation of an OWTS. If the property contains suitable soil and site conditions, the OWTS is designed and permitted by regulatory officials, installed by a septic contractor, and operated by the home/system owner. Once the OWTS is installed, most are not monitored to determine how well they perform regarding the removal of pollutants of environmental concern.

Residential wastewater contains concentrations of nitrogen that may cause negative public and environmental health outcomes if the concentrations are not reduced prior to reaching water resources used for drinking water or recreational activities. For example, multiple studies have shown that excess nitrogen loads in surface waters may stimulate algal blooms, eutrophication, and water use impairment [16–18]. Eutrophic conditions may arise when total nitrogen concentrations in some surface waters exceed 1.5 mg/L [19]. Concentrations of nitrogen in septic tank effluent are typically 50 mg/L or higher [20–23], and thus wastewater contains nitrogen concentrations that are an order of magnitude greater than concentrations of environmental concern. Most of the nitrogen (>75%) in septic tank effluent is in the ammonium form due to the mineralization of organic nitrogen in the septic tank [7]. Septic tank effluent discharged to trenches installed in well-drained soils can be very efficient at lowering ammonium concentrations via nitrification [22,24–26]. Nitrification is the microbially mediated transformation of ammonium to nitrate, and it occurs in oxidizing environments [22,23,26]. Nitrate is an anion that is very mobile in the subsurface due to its negative charge and repulsion from negatively charged soil particles. Research has shown that elevated nitrate concentrations in drinking water can lead to methemoglobinemia in infants [27], increase the risks for non-Hodgkin's lymphoma [28], and have positive associations with bladder cancer in older women [29] and an increased risk of colorectal cancer [30]. The US EPA has set the maximum contaminant level for nitrate-nitrogen in drinking water at 10 mg/L [7]. Prior research has shown that soil water and groundwater near OWTSs may contain nitrate concentrations that exceed the MCL of 10 mg/L due to the oxidation of ammonium in the soil beneath drainfield trenches [22,24,26,31]. While many states require setbacks of 15 m or more from OWTS drainfields to wells or recreational water to allow for additional treatment processes to occur, numerous studies have reported plumes of nitrate with concentrations exceeding 10 mg/L in groundwater extending more than the required 15+ m away from OWTSs [24,31,32]. Therefore, in some settings, OWTS may be significant contributors of nitrate to groundwater tens of meters away from OWTSs.

Furthermore, several studies have reported that streams draining watersheds with high densities (>1 system/ha) of OWTSs may contain elevated concentrations of nitrogen relative to nearby streams in watersheds served by centralized sewer systems [33,34]. These studies have shown that OWTSs can influence water quality at the site and watershed scales.

Nitrate can be removed from soil water and groundwater via processes such as denitrification, which is the transformation of nitrate to dinitrogen gas [22,23]. Denitrification occurs in anoxic environments where there is a source of labile carbon, nitrate, and suitable physicochemical conditions (e.g., pH, temperature) for the denitrifying microorganisms to survive [35,36]. While septic tank effluent is enriched with dissolved organic carbon (DOC), which could serve as an electron donor for denitrification, studies have shown that much of the labile DOC is oxidized in the vadose zone (along with ammonium) and thus denitrification is often limited by DOC availability [35–37]. Denitrification may occur along a groundwater flow path away from an OWTS if the nitrate plume moves through carbon-rich riparian or hyporheic zones. For example, a study [24] in Canada showed that concentrations of nitrate in a groundwater plume emanating from an OWTS were lowered by more than 95% within a few meters of a stream due to the denitrification in the organic matter-laden riparian sediments. Another study [31] in coastal North Carolina, USA, showed an 85% reduction in the mass of nitrate as an OWTS-influenced groundwater plume extended toward a coastal estuary. In these scenarios, there was negligible impact on surface waters regarding nitrate because of the denitrification processes in the surficial aquifer that were stimulated by labile carbon supplies along the fringe of water bodies. While surface waters were not impacted by the OWTS in the previously mentioned studies, the groundwater quality more than 15 m away from the OWTS was negatively influenced. Forested riparian buffers adjacent to downgradient streams can reduce groundwater nitrogen loadings to streams. However, if groundwater flow paths are deeper than the zone of organic-rich riparian sediments or groundwater upwells at seeps or springs that short-circuit the buffer, buffers may not be effective at nitrogen attenuation [38,39]. In other settings, or settings lacking forested riparian buffers, other approaches are called for to reduce the groundwater transport of nitrogen to nutrient-sensitive surface waters or water-supply wells.

OWTSs are used by nearly 50% of residences in North Carolina [4] but most OWTSs are not required to be monitored to determine their effectiveness regarding pollutant treatment. Many studies [2,3,25,26,31,32] have shown that concentrations of nitrate in groundwater near and down-gradient from OWTSs can exceed water quality standards. Other research [33,34] has shown that watersheds served by OWTSs typically export more nitrogen via stream discharge in comparison to watersheds where homes are served by centralized sewers. Excess nitrogen loading has caused the eutrophication and impairment of water resources in North Carolina and other regions [16–19]. It is important that nitrogen loading from sources such as OWTSs is reduced to protect nutrient-sensitive waters [18,19] and environmental health. Best-management practices that are efficient at reducing nitrogen transport while being relatively low-maintenance and cost-effective are needed in many regions that experience the impairment of water resources due to excess nitrogen inputs. Permeable reactive barriers (PRBs) have been used as best-management practices to reduce nitrate loading from non-point sources of pollution [37,40–45]. For nitrogen removal via PRBs, a carbon source like woodchips or sawdust is placed within the groundwater flow path of a nitrate plume emanating from a source (e.g., OWTS, farm) [40–45]. As the nitrate plume enters the PRB, microorganisms use carbon as an electron donor and nitrate as an electron acceptor, thus transforming nitrate to dinitrogen gas, resulting in a loss of nitrate mass in groundwater. PRBs may be an effective retrofit to reduce nitrate transport, but more work has been suggested to determine the long-term efficiency of the passive technology [41,43]. The primary objective of this study was to assess the long-term (10-years) effectiveness of a PRB in maintaining nitrate concentrations below 10 mg/L in groundwater down-gradient from an OWTS serving a school. This is one of the first studies where a PRB was installed downgradient from an OWTS to enable compliance with the groundwater MCL for nitrate.

2. Materials and Methods

2.1. Study Site

The study site was on the property of an elementary school that accommodates over 220 students in Williamston, North Carolina (NC), USA (Figure 1). Williamston is in the Coastal Plain geological region and, on average, receives about 125 cm of annual rainfall with monthly averages ranging from 7.8 cm in November to 15.4 cm in September [46]. The mean daily high temperatures are greatest during July (31.7 °C) and the mean daily low temperatures are coldest during January (−1.1 °C). There is about a 7 °C difference in the average daily high and low temperatures for each month. The soils on the property are mapped as well-drained Norfolk loamy fine sand (Supplementary Materials) and the property is approximately 15 m above sea level. Details regarding the OWTS and preliminary monitoring of the PRB were previously reported [43]. The school is served by an OWTS that includes a septic tank, a pump tank, a pressure manifold, and 576 m of drainfield trenches (each trench is 0.9 m wide and approximately 64 m long). The OWTS has been in operation since 2004. Three wells (Wells 1, 2, and 3) for groundwater monitoring were installed on the perimeter of the septic drainfield (Figure 1), as required by the NC Onsite-Water Protection Branch. The wells were each constructed using a 5 cm diameter PVC casing coupled to a 3 m section of the well screen. The wells extend about 8 m below the surface and are required to be sampled three times each year (typically in January, May, and September) to determine if groundwater quality is in compliance with state regulations. Water samples from the wells are analyzed for nitrate by a private laboratory in Greenville, NC, USA. The results of the analyses are sent to the school and the NC Onsite Water Protection Branch. After approximately 5 years of use, the groundwater nitrate concentrations in Well 2 to the northwest of the OWTS drainfield began to routinely exceed the nitrate maximum contaminant level (MCL) of 10 mg/L and the school received notices of violation regarding the results. Three-point contouring using groundwater elevation data at each of the three wells indicated the groundwater flow direction was northwest and thus the OWTS for the school was the likely source of elevated nitrate concentrations [43]. Remediation was required to allow the school to comply with state water quality regulations. Funding was received from an NC Department of Health and Human Services grant to install a PRB at the school to improve groundwater quality with regard to nitrate concentrations. Researchers from ECU designed the PRB and oversaw the installation [43]. The PRB was installed in early May 2014 between the OWTS drainfield and Well 2 (Figure 1) by excavating a trench with dimensions of approximately 8 m deep, 6 m long, and 1.2 m wide and filling the bottom 2.5 m of the trench with various size woodchips (typically between 2 and 15 cm long) made from mostly *Pinus taeda* (loblolly pine) trees. A diagram of the PRB is shown in Figure 2 and images of the PRB installation are shown in Figures 3 and 4. Groundwater at the site was more than 6 m below the surface. When the bucket of the excavator reached the water table, the sidewalls of the trench near the bottom began to collapse. Several more excavator buckets of soil were removed so the bottom of the PRB would be close to the same depth as the bottom of the well screen at Well 2 (Figure 2). Due to the sluffing of the side wall, some sections of the PRB were wider than 1.2 m. The trench bottom was excavated in segments to reduce the likelihood of major sidewall collapse. When the intended depth of about 8 m was reached, a front-end loader was used to quickly place woodchips in the bottom before excess sluffing could occur. The next segment of the trench was then excavated and filled with woodchips, and the process was repeated until the PRB extended north and south of Well 2 on the upgradient side. A woodchip and native soil mixture was used to fill the rest of the trench to the surface (Figures 2 and 4).

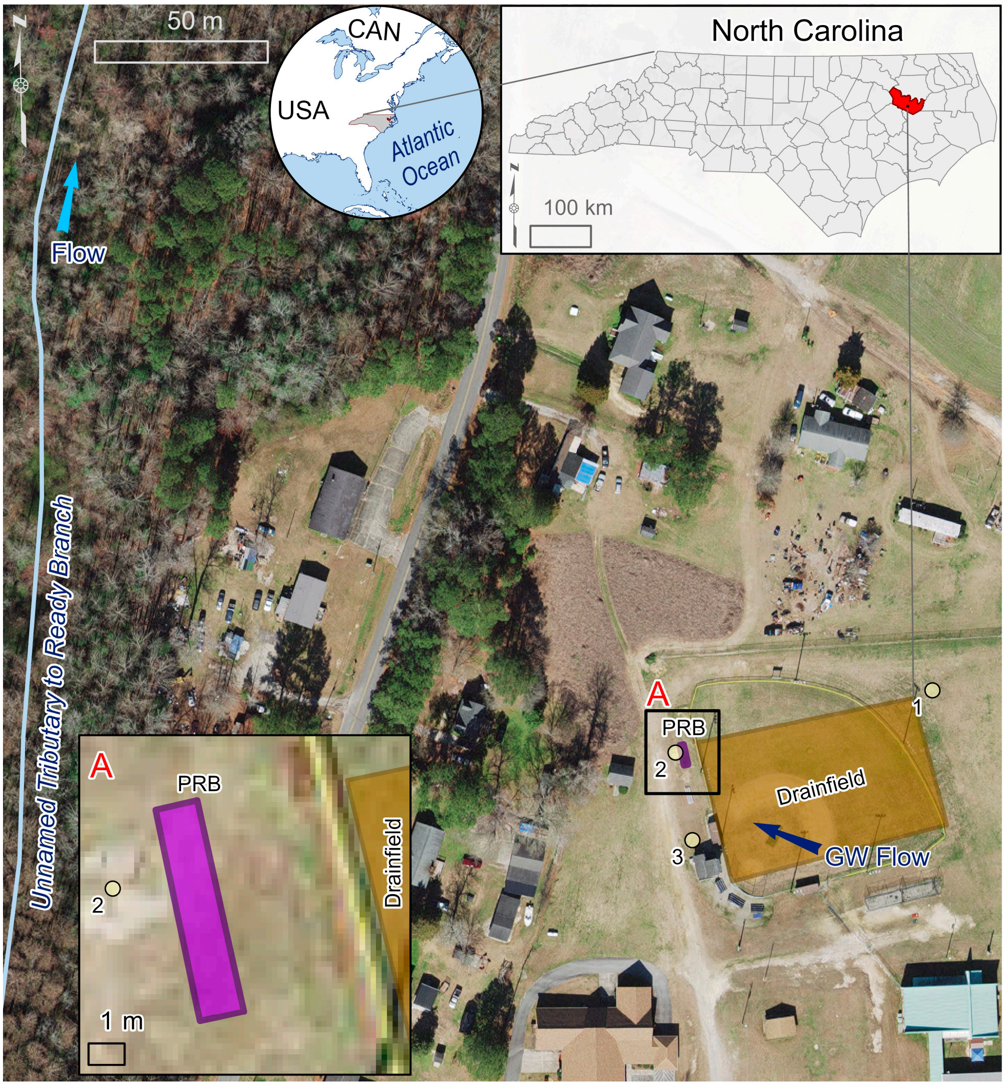

Figure 1. Aerial view of the study site showing locations of the septic drainfield and groundwater monitoring Wells 1–3. The groundwater flow direction (northwest) is shown as a dark blue arrow. A magnified image of the barrier is shown in (A).

2.2. Groundwater Sampling

For a few months after the installation of the PRB (May to September 2014), sampling of groundwater (n = 5) from the wells was performed by researchers at ECU using disposable bailers to determine if there were noticeable changes in the nitrate concentration. First, at each well, a Solinst model 107 temperature, level, and conductivity meter (Solinst Canada Ltd., Georgetown, ON, Canada) was used to determine the depth of the groundwater. Next, a new disposable bailer with a string attached was lowered into the well, filled with groundwater, pulled up to the surface, and emptied. The purging procedure was repeated three times at each well. The wells were allowed to recharge, then a new, well-specific bailer was used to pull a groundwater sample to the surface and the contents were transferred to a 250 mL HDPE bottle for later nutrient analyses and to the calibration cup of a YSI

556 multi-meter (YSI Environmental, Yellow Springs, OH, USA). The physicochemical properties of water including the temperature, pH, specific conductance, and oxidation-reduction potential were determined in the field using the multi-meter, and these data were recorded. Wastewater samples from the septic tank were collected using HDPE bottles, and the physicochemical properties of wastewater were also determined in the field using the multi-meter. Sample bottles were placed in coolers with ice for preservation. Analyses of nitrate, total nitrogen, dissolved organic carbon, and chloride occurred at the East Carolina University Environmental Research Lab after the samples were filtered using Whatman GF/F 0.7 um pore-size filters (MilliporeSigma, Burlington, MA, USA). A SmartChem 200 discrete analyzer (KPM Analytics, Westborough, MA, USA) was used for nitrate and chloride analyses, while a TOC-VCPN/TNm-1 (Shimadzu Scientific Instruments, Inc., Durham, NC, USA) with catalytic thermal decomposition/chemiluminescence was used for total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) analyses. After grant funding ended later that summer of 2014, the school continued to sample the wells 3 times per year using new, disposable bailers, and nitrate analyses were completed by the same private laboratory that was used prior to the installation of the barrier. Some additional groundwater samples were collected periodically by researchers at ECU for nitrate analyses at laboratories on ECU's campus.

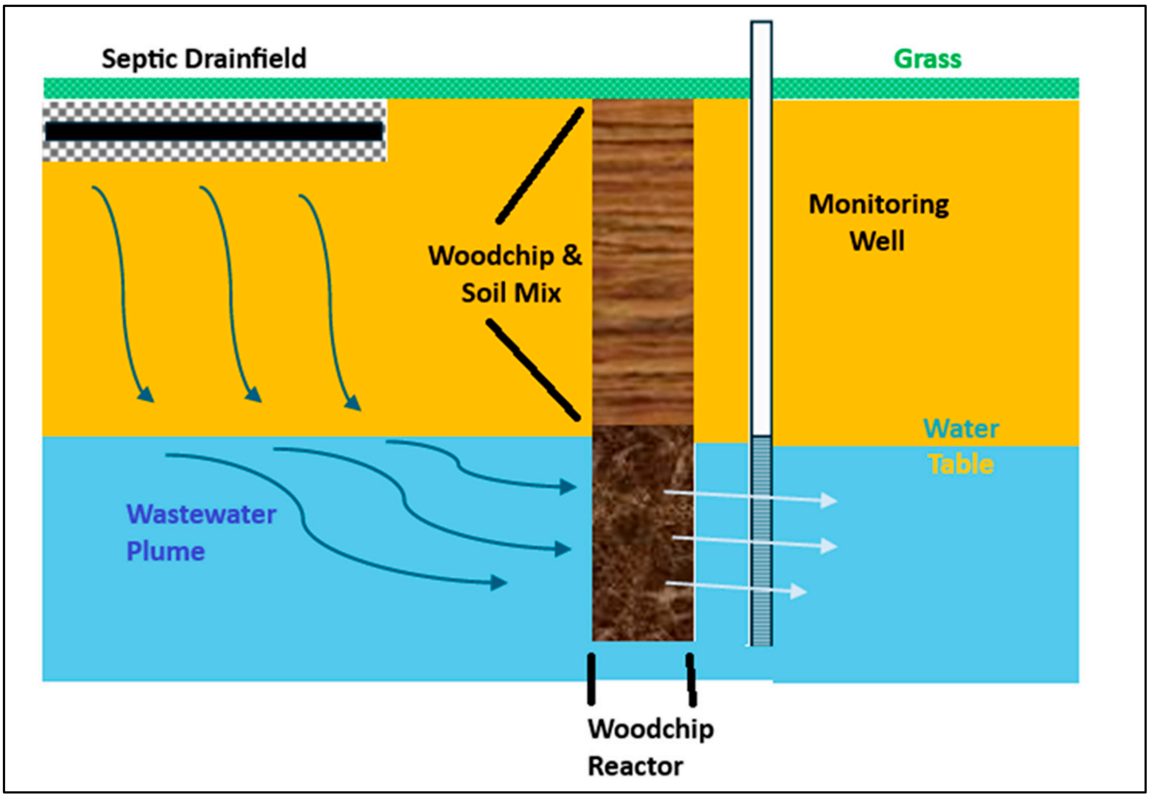

Figure 2. Diagram of the PRB including the placement of woodchips in a trench between the septic drainfield for the school and the monitoring well. The woodchip reactor was installed at the same depth as the well. A woodchip and native soil mix was used to fill the rest of the trench to the surface.

2.3. Statistical Analyses

Scatter plots of nitrate concentrations in groundwater sampled from Wells 1–3 were produced to allow for visual temporal comparisons of concentrations between wells. Nitrate and physicochemical (specific conductance, pH, and oxidation-reduction potential) data were tested for normality using an Anderson–Darling test. Pearson correlations were used to determine if significant ($p < 0.05$) associations between mean annual nitrate concentrations and years since the start-up of the OWTS were observed. Correlations and slopes of the fitted lines were analyzed pre- and post-implementation of the barrier to determine if trends (declines or increases) in nitrate concentrations were statistically significant. Concentrations of nitrate in groundwater sampled from Well 2 before and after the installation of the barrier were compared to the MCL of 10 mg/L using a single sample T-test. The concentrations of nitrate in Well 2 sampled pre- and post-implementation of the barrier were compared to determine if differences in concentrations were statistically significant and if the barrier was effective at lowering nitrate concentrations. T-tests (if the data showed a normal distribution) or Mann–Whitney tests (if the data did not follow a normal distribution) were used for paired data comparisons. Minitab 20 statistical software was used for statistical analyses and the development of figures.

Figure 3. A trench was excavated between the onsite wastewater treatment system and Well 2.

Figure 4. Woodchips were placed at the bottom of the trench and used as a carbon source for the reactive barrier. The trench was covered with native soil.

3. Results

3.1. Nitrate Concentrations

During the first two years of groundwater monitoring (2005–2006) at the school, all groundwater samples from the three wells were below the MCL of 10 mg/L for nitrate (Figure 5). However, the average annual nitrate concentration in Well 2 increased by almost 2 mg/L each year since the OWTS was first put into operation, and by 2014, the mean nitrate annual concentration at Well 2 had increased to 20.53 mg/L (Figure 6). There was a statistically significant correlation ($p < 0.001$; r = 0.952) between the years after the initiation of monitoring and the mean annual nitrate concentration in groundwater sampled from Well 2 (Figure 7). The mean nitrate concentrations at Well 1 and Well 3 also increased between 2005 and 2014, but by less than 2.5 mg/L overall, and all groundwater samples from Wells 1 and 3 were below 10 mg/L (Figure 6). There were 15 consecutive water samples collected from Well 2 over a five-year period (2009–2014) that exceeded the MCL for nitrate (Figure 5). The mean nitrate concentration during that period was 16.87 mg/L at Well 2, 5.53 mg/L at Well 1, and 5.64 mg/L at Well 3. One groundwater sample collected in late 2013 from Well 2 reached a concentration of 32 mg/L nitrate (Figure 5). The concentrations of nitrate in groundwater sampled from Well 2 were significantly ($p < 0.01$) elevated relative to groundwater sampled from Wells 1 and 3. A single-sample T-test revealed that the concentrations of nitrate in water sampled from Well 2 between 2009 and 2014 were also significantly elevated ($p < 0.05$) relative to the MCL for nitrate. These data, along with specific conductance and chloride trends, indicate that Well 2 intercepted portions of the wastewater plume.

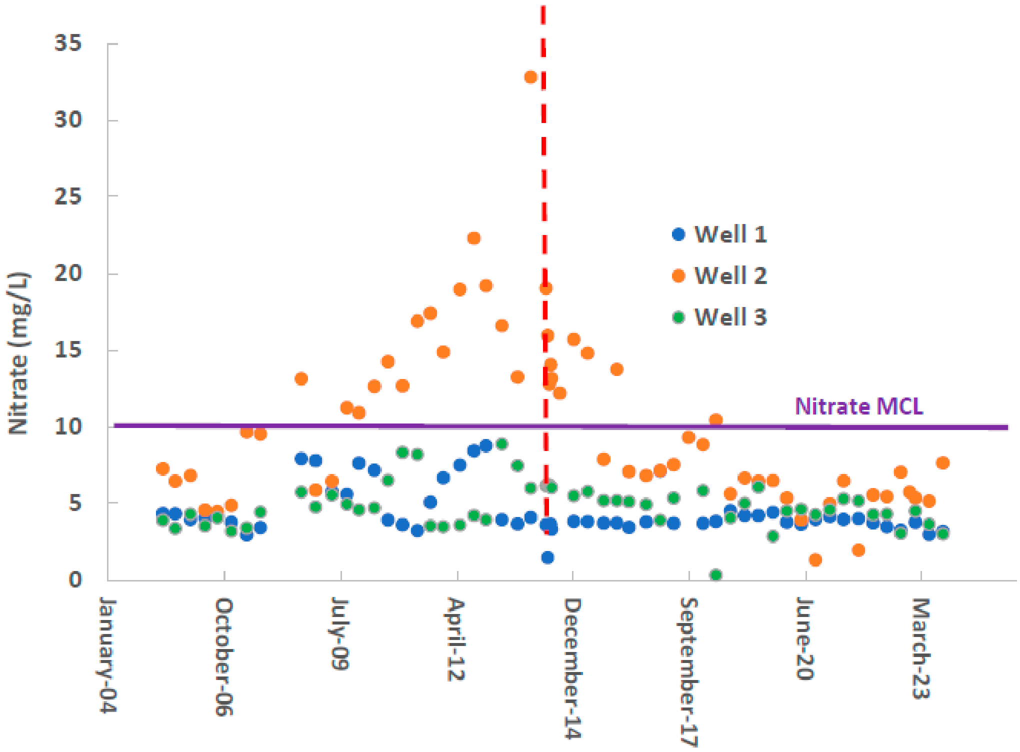

Figure 5. Scatter plot of nitrate concentrations in groundwater sampled from Wells 1, 2, and 3 between 2005 and 2023.

After the installation of the PRB, there was a steady decline of almost 1 mg/L each year in the concentration of nitrate in groundwater sampled from Well 2 (Figure 6). A statistically significant ($p = 0.001$) inverse correlation ($r = -0.859$) between the years after installation of the barrier and the annual mean nitrate concentrations in groundwater collected from Well 2 was observed (Figure 8). By 2016, two years after the installation of the PRB, the mean annual nitrate concentration in groundwater sampled from Well 2 had declined below 10 mg/L (Figure 6). Wastewater discharge records were not available for the school, but the number of students attending (and generating wastewater) was accessible. During the period spanning 2014 to 2017 when a steep decline (16 mg/L) in mean annual nitrate concentrations in groundwater from Well 2 was observed, the number of students at the school was between 262 to 269, similar to the numbers of students (range: 262 to 272) attending a few years prior (2012–2014) to the PRB installation when the nitrate concentrations were the highest. Wastewater volumes discharged by the OWTS during these years prior to and after installation of the PRB would likely have been similar. Thus, the reasons for the quick decline in nitrate concentrations in groundwater sampled from

Well 2 after the PRB was installed were not likely related to changes in the volume of effluent discharged by the OWTS.

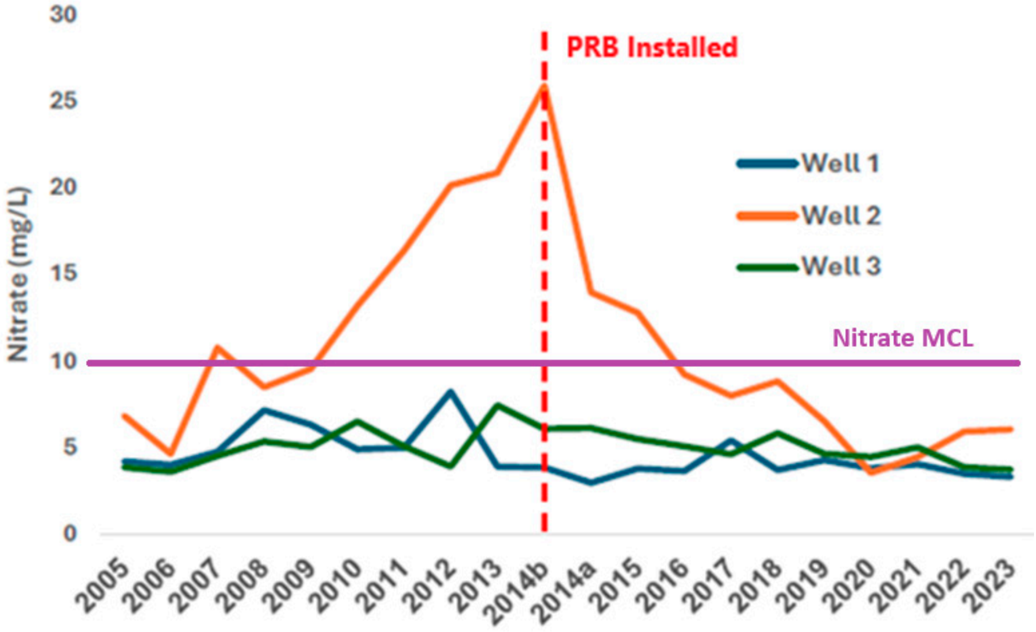

Figure 6. Mean annual nitrate concentrations in groundwater sampled from Wells 1, 2, and 3. Concentrations of nitrate in groundwater sampled from Wells 1 and 3 typically fluctuated between 4 and 6 mg/L before and after the barrier was installed in mid-2014 (red dashed line). Nitrate concentrations in groundwater sampled from Well 2 were increasing prior to installation of the PRB and decreased after installation of the PRB.

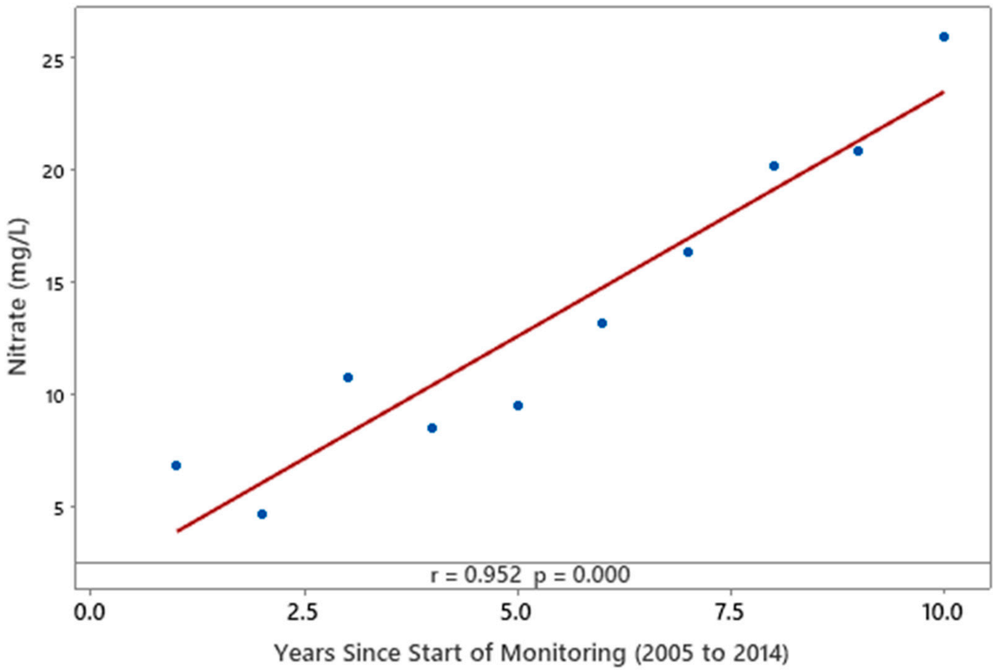

Figure 7. Mean annual nitrate concentration in groundwater sampled from Well 2 prior to installation of the PRB. The blue dots represent the mean nitrate concentrations for individual years. The red line is the “best fit” slope.

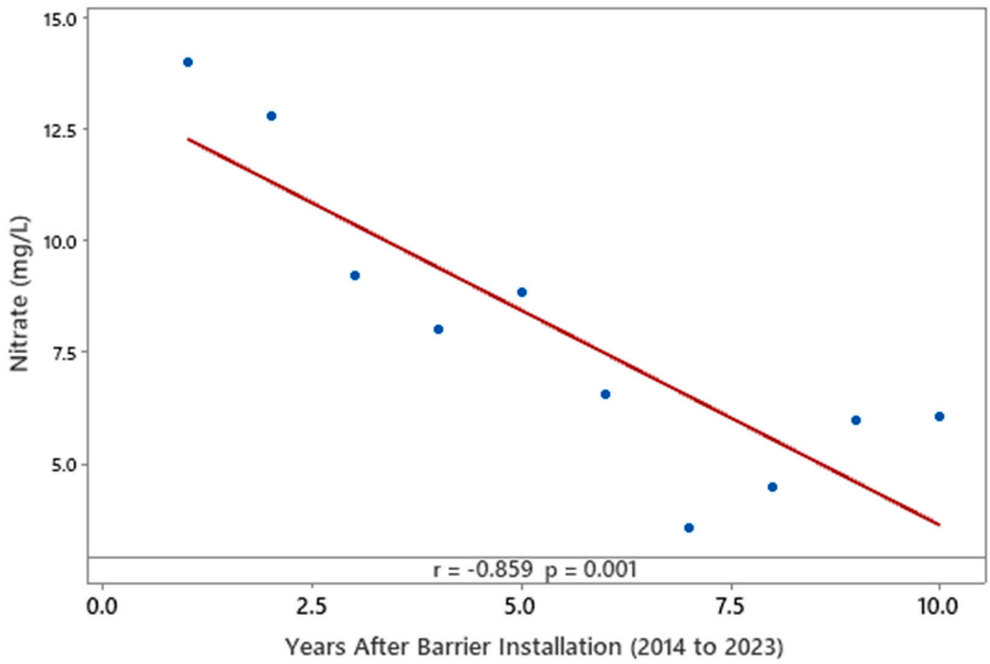

Figure 8. Mean annual nitrate concentration in groundwater sampled from Well 2 after installation of the PRB. The blue dots represent the mean nitrate concentrations for individual years. The red line is the "best fit" slope.

The nitrate concentration in groundwater collected from Well 2 has been below 10 mg/L for 22 of the last 23 sampling events. Furthermore, the last 17 consecutive groundwater samples collected from Well 2 revealed nitrate concentrations below 10 mg/L (Figure 5). Over the past 5 years, the mean annual nitrate concentration has been under 7 mg/L for Well 2, and the differences in concentrations of nitrate in groundwater sampled from Wells 1, 2, and 3 were not significantly different ($p > 0.05$). The median concentrations of nitrate in the groundwater sampled from Well 2 (n = 26) prior to installation of the PRB (12.66 mg/L) were significantly higher ($p = 0.007$) relative to the groundwater sampled from Well 2 after (n = 32) the PRB was installed (6.93 mg/L) (Figure 9). An overall 45% reduction in the median concentration of nitrate in the groundwater sampled from Well 2 was observed after the installation of the PRB.

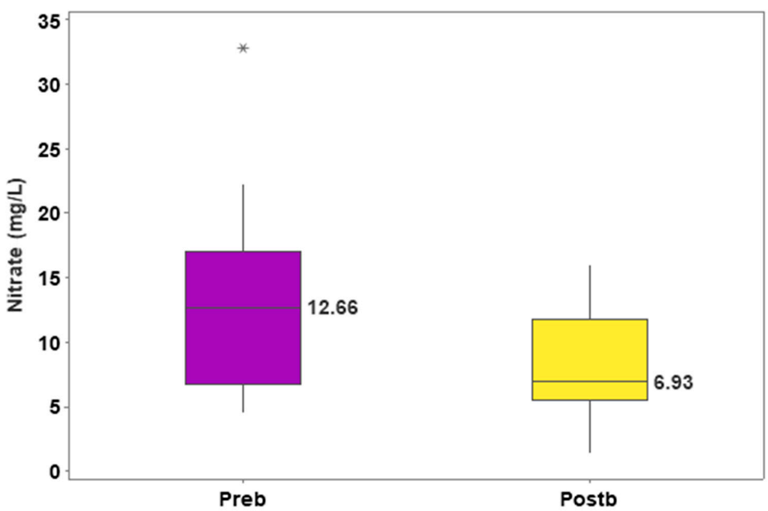

Figure 9. Concentrations of nitrate in groundwater sampled from Well 2 before (Preb) and after (Postb) installation of the PRB in May 2014. A statistical outlier is shown as (*).

3.2. Physicochemical Characteristics of Groundwater

The mean specific conductance of groundwater sampled from Well 2 (259.2 µs/cm) was significantly elevated relative to the groundwater sampled hydrologically upgradient from the drainfield at Well 1 (72.0 µs/cm) (Table 1). The mean oxidation-reduction potential of the groundwater sampled from Well 2 (−40.8 mV) was significantly lower (p = 0.035) relative to the groundwater at Well 1 (52.8 mV). The mean pH of the groundwater sampled from the three wells was similar and ranged from 4.7 to 4.8. The mean concentrations of dissolved organic carbon in the groundwater sampled from Well 2 (16.9 mg/L) were significantly higher ($p < 0.05$) relative to the groundwater sampled from Well 1 (0.8 mg/L) and Well 3 (3.3 mg/L). The mean temperature of the groundwater sampled from the wells ranged from 17.2 to 19.5 °C, and differences in temperatures were not statistically significant ($p > 0.05$).

Table 1. Means (standard deviation) of physicochemical properties of groundwater including pH, temperature, oxidation-reduction potential (ORP), and specific conductance (SC), along with dissolved organic carbon (DOC) and chloride (Cl) concentrations.

Location	pH	Temp (°C)	ORP (mV)	SC (uS/cm)	DOC (mg/L)	Cl (mg/L)
Well 1	4.8 (0.3)	17.5 (5.6)	52.8 (36.7)	72.0 (2.9)	0.8 (0.2)	4.3 (0.1)
Well 2	4.8 (0.2)	17.2 (7.0)	−40.8 (86.9)	259.2 (27.4)	16.9 (9.3)	14.7 (1.0)
Well 3	4.7 (0.2)	19.5 (6.6)	15.2 (28.9)	219.0 (22.0)	3.3 (4.0)	26.2 (1.4)

4. Discussion

The mean concentration of TDN in wastewater at the site (65.7 mg/L) was within the range of concentrations reported by numerous other studies. For example, in a recent project in eastern North Carolina, USA [21], that sampled wastewater from 18 septic tanks for nitrogen analysis, the researchers reported a mean TDN of 66 mg/L with a range of 45 to 167 mg/L. Another project also in eastern NC, USA, where four septic tanks were sampled, showed septic tank effluent with a mean TDN of 77.8 mg/L with a range of 55.4 to 109.5 [26]. In a review of several studies [7], a range of TDN concentrations spanning 26 to 124 mg/L were reported. The wastewater characteristics observed at the current study site were typical for domestic wastewater. Ammonium (>97%) was the most dominant species of nitrogen in wastewater sampled from the septic tank at the school site. This was expected as the anaerobic digestion of organic matter and mineralization are processes in septic tanks that transform organic nitrogen into ammonium [22,47]. Most of the TDN in groundwater at Well 2 was nitrate (95%). Given the thick (>5 m) vadose zone beneath the drainfield, oxidation of the wastewater likely occurred as effluent infiltrated and percolated through the soil. Research has shown that most of the nitrogen in groundwater beneath OWTSs is nitrate when there is greater than 0.45 m separating the water table and drainfield trenches [24,25,36,48]. Groundwater nitrate concentrations in Well 2 reached a high exceeding 30 mg/L and averaged over 16 mg/L for a 5-year period just prior to installation of the PRB.

The concentrations of nitrate in groundwater at this site prior to the PRB installation are also similar to concentrations in groundwater near OWTSs reported in other studies. For example, previous research [24] showed nitrate concentrations of 30 mg/L in the groundwater near two large OWTSs, while another study [25] reported nitrate concentrations in groundwater near 12 different OWTSs in sand and sandy loam soils with mean nitrate concentrations between 9.7 and 18.1 mg/L. Furthermore, groundwater beneath the drainfields of three septic systems in eastern North Carolina averaged 16.7 mg/L with a range of 5.8 to 25.4 mg/L [15]. Therefore, the concentrations of nitrate in groundwater up-gradient from the PRB at the study site were similar to the concentrations in groundwater or soil water beneath onsite wastewater systems reported in several other studies.

The decrease in nitrate concentration in groundwater sampled downgradient from the PRB may be related to denitrification. The DOC concentrations in the groundwater at Well 2 were significantly higher relative to concentrations in Well 1 and Well 3 after the installation of the barrier. The DOC from the woodchips may have provided an electron donor for the microbial conversion of nitrate to nitrogen gas [36,37]. The mean oxidation-reduction potential of groundwater sampled from Well 2 (−40.8 mV) was lower relative to readings from Well 1 (52.8 mV) and Well 3 (15.2 mV) and was within the range expected for denitrification to occur [49]. It is unlikely that the entire nitrate plume emanating from the OWTS hydraulically bypassed the PRB because the chloride concentration in the groundwater at Well 2 remained stable after the PRB was installed with a standard deviation of concentrations of 1.0 mg/L. Wastewater typically has a higher concentration of chloride relative to groundwater [24,36]. Had the PRB restricted groundwater flow, then the plume may have passed around the PRB and resulted in more background groundwater influencing Well 2, thus resulting in a lower Cl concentration. However, the chloride concentration in groundwater sampled from Well 2 (mean 14.7 mg/L) had a standard deviation of 1 mg/L and thus was stable and elevated relative to the chloride concentration in groundwater samples from Well 1 (mean of 4.3 mg/L), which is hydraulically up-gradient from the OWTS. Also, after the PRB was installed, the specific conductance of the groundwater sampled from Well 2 (259.2 µs/cm) was elevated relative to the groundwater sampled at Well 1 (72.0 µs/cm), thus also indicating that dissolved ions from the wastewater plume were passing through the PRB and into Well 2. While these data indicate that portions of the wastewater plume were moving through the PRB, it is also possible the wastewater plume extended beyond the boundaries of the PRB and thus some of the plume was not treated. The only true way to know the full extent and dimensions of the wastewater plume would be to install an intensive network of wells surrounding the OWTS and sample for water quality. Several attempts to secure funding to install additional monitoring wells were unsuccessful. With knowledge of the wastewater plume dimensions and orientation, a PRB could be designed and installed to intercept the full extent of the impacted groundwater.

The purpose of the PRB installation was to reduce the groundwater transport of nitrate from the OWTS serving an elementary school and allow the school to come into compliance with the MCL for nitrate in groundwater. Within a few weeks after the PRB was installed, a noticeable decline in nitrate concentration from Well 2 was observed. The nitrate concentration in groundwater sampled from Well 2 continued to decline to levels below the MCL of 10 mg/L and have remained below the MCL for more than five consecutive years. Other studies [41,50] have reported that PRBs may function effectively for decades. For example, a PRB containing a mixture of approximately 33% sawdust (*Pinus radiata*) and 67% native soil was installed in New Zealand to remediate excess nitrate in groundwater from a dairy farm [41]. Even after 14 years of operation, denitrifying enzyme activity was high, resulting in a 92% reduction in nitrate exports. The authors [41] estimated that the carbon in the PRB may last for more than 60 years. Nitrate removal in a PRB filled with a mixture of 20% sawdust and 80% native sand in Ontario Canada was evaluated 15 years after installation, and column experiments on PRB core samples showed the PRB still lowered nitrate concentrations by approximately 39% [50]. The PRB evaluated in our study has been in use for 10 years with no supplemental additions of carbon since the installation.

While it is unknown how long the carbon in the barrier may continue to serve as an effective electron donor, prior studies have shown that the longevity and performance of the PRBs can be influenced by factors including the type and size of organic matter used and whether the media remains saturated [44,45,51–53]. A study comparing nitrate removal in PRBs using different carbon types reported each PRB was effective, and the greatest nitrate removal was observed when using maize cobs, followed by green waste, wheat straw, and woodchips [51]. Woodchips made from softwood tree species were typically more effective at nitrate removal relative to hardwood woodchips, but the overall differences were not statistically significant [51]. Other research [52] reported that using smaller woodchip sizes resulted in more efficient nitrogen removal relative to larger sizes. The woodchips used for the barrier in this study were of different sizes, but typically the largest pieces were between 2 and 15 cm long and comprised of mostly *Pinus taeda* trees (softwood). In research conducted on the denitrification activity in a 9-year-old woodchip bioreactor [53], it was concluded that the longevity of the carbon supply was influenced by the depth of the media relative to the groundwater. Woodchips in the PRB that remained saturated had a half-life of 36.6 years, while woodchips closer to the surface and periodically unsaturated had a half-life of 4.6 years [53]. The woodchips for the PRB in our study were placed at depths (5–8 m below the surface) coinciding with the screening interval of the well. There are woodchips of varying sizes both above and below the water table and some woodchips remain continuously saturated, which may contribute to their longevity as a carbon supply for several more decades [41,53].

The concentrations of nitrogen observed in groundwater from Well 2 after the installation of the barrier are lower relative to effluent discharged from many package treatment plants and advanced wastewater treatment systems, which would have been alternative options for remediating nitrogen discharges at the school. For example, a study [54] conducted on the barrier islands of NC, USA, reported that three extended aeration plants, two advanced media filtration systems, and two sequencing batch reactors discharged effluent with mean TN concentrations of 12.9 mg/L, 11.6 mg/L, and 11.6 mg/L, respectively. Forty-two advanced treatment wastewater systems in Rhode Island were evaluated [55] and it was reported that the median TN concentration in effluent of the systems was 16.7 mg/L with median effluent concentrations ranging from 11.3 mg/L to 17.1 mg/L, based on the specific technology implemented. Another study [56] of 50 advanced treatment systems showed median TN concentrations in the effluent ranging from 13.2 mg/L to 33.8 mg/L. Advanced treatment technologies are typically much more expensive to install and maintain relative to conventional-style OWTSs [57]. There have been no maintenance activities regarding the barrier since its installation, thus resulting in significant savings relative to an advanced treatment system retrofit.

5. Conclusions

The PRB was installed at the school 10 years ago to help reduce the transport of nitrate from the OWTS to a downgradient monitoring well and allow the school to comply with state water-quality guidelines. After the installation of the PRB, the nitrate concentrations in groundwater steadily declined, and the mean annual nitrate concentration has been below 10 mg/L for the last 5 consecutive years. The PRB was influencing groundwater quality at Well 2 but the full extent of the wastewater plume is unknown, and it is possible that elevated concentrations of nitrate are present in other areas of the surficial aquifer near the OWTS. These findings show that permeable reactive barriers can be effective, relatively low-maintenance practices that reduce the concentrations of nitrate in groundwater to below the MCL of 10 mg/L for many years in some settings. Additional work to investigate the full dimensions of the wastewater plume and determination of the microbiological assemblages and activity within the barrier are suggested. These data would enhance our understanding of the processes at work in the PRB and provide a better estimate of the expected longevity of the best management practice.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/hydrology12010018/s1, Figure S1. Aerial view of study site with soil survey overlays. Norfolk (NoA, NoB) soil series is shown near the onsite wastewater system drainfield (red outline).

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