Tanbark Creek Long-Term PRB Performance Monitoring

Data Report
2/16/24

Submitted to:

Peconic Estuary Partnership
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Submitted by:

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Introduction:

The Tanbark Creek PRB is a pilot project intended to demonstrate the use of carbon emulsion injection for groundwater nitrate reduction. The installation of injection wells and the injection of the carbon emulsion concluded at the end of 2022. Post-installation research to determine the effectiveness of the current design and learn ways to improve upon it began in summer 2023. This project intends to add to the repository of PRB performance data and inform several long-term goals for PRB implementation and specifically the carbon injection installation approach. Long term project goals include relating inland PRB performance to offshore porewater and surface water quality, varying the carbon amendment solution strength to minimize the installation time, quantifying the PRB longevity, characterizing the redox reactions downgradient of the PRB, and maximizing nitrate reduction by potentially including other environmentally approved amendments along with EOS-100 to support the proper conditions and/or microbial community.

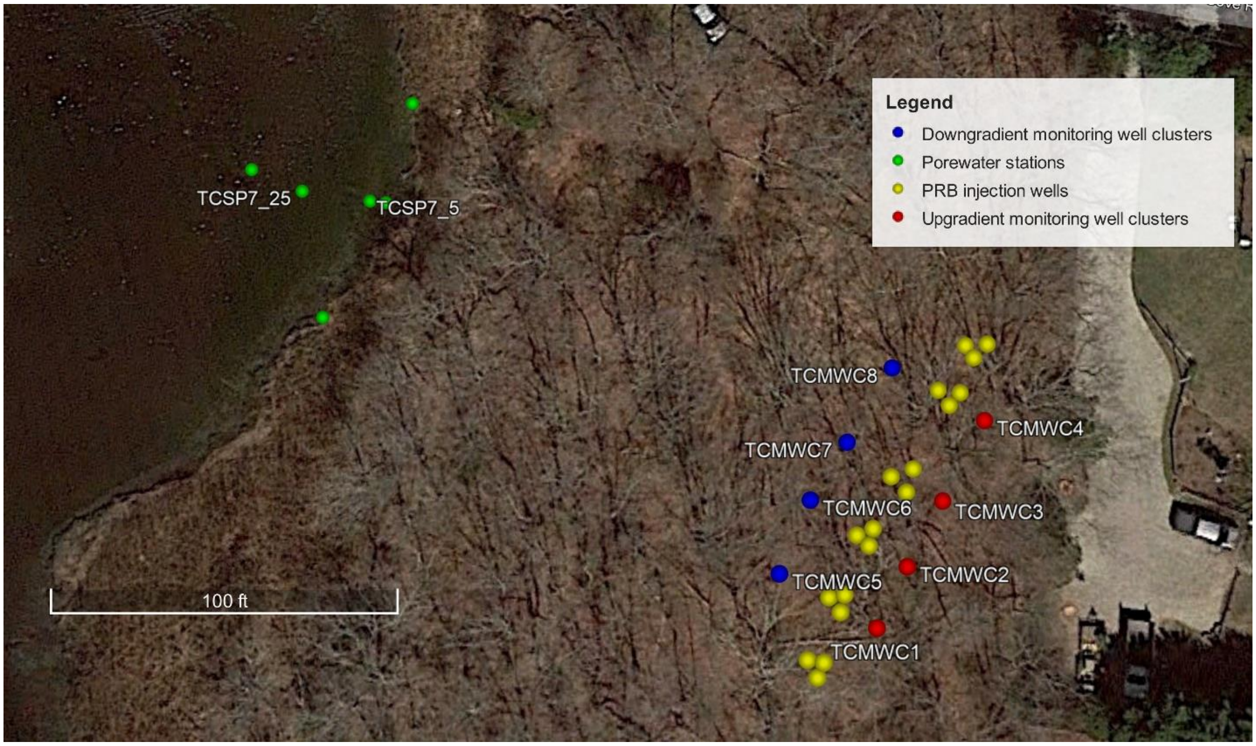

Figure 1: Tanbark Creek site schematic showing location of PRB injection wells, upgradient and downgradient monitoring well clusters (TCMWC1-8). There are six injection clusters starting with TCINJ1 in the south and moving northeast to TCINJ6. The red and blue dots indicate 2 wells within 1 ft of each other screened at 20-25 ft and 15-20 ft below grade.

Methods:

A. PRB performance monitoring

Four upgradient PRB performance monitoring well clusters (TCMWC1-4; untreated groundwater) and 4 downgradient well clusters (TCMWC5-8; treated water) (2 depth intervals per cluster; 16 wells total) were sampled for nitrate, nitrite, ammonium, and TKN (Fig. 1). Summer samples were collected between 8/24/23 and 9/6/23. Fall samples were collected on 11/28/23. Additionally, performance monitoring samples were analyzed for sulfate, hydrogen sulfide, alkalinity, dissolved organic carbon (DOC) and dissolved iron during the summer 2023 sampling event. Hydrogen sulfide is defined as the sum of H_2S and HS^- present in the sample after the laboratory stabilized the pH at 7.

PRB performance monitoring wells were purged of three well volumes prior to sampling using a peristaltic pump running at approximately 500 mL/min. Samples were collected for laboratory analysis when field parameters including conductivity, total dissolved solids (TDS), oxidation reduction potential (ORP), pH, and temperature were stable (±10% relative standard deviation (RSD)). Conductivity, TDS, ORP, pH, and temperature were measured onsite at the time of collection with a Myron Ultrameter. Dissolved oxygen (DO) was measured with a YSI DO meter. Depth to water was measured with a Solinst water level sounder. Performance monitoring of the nitrogen species is anticipated to continue quarterly.

Total Nitrogen (TN) concentration is the sum of TKN and nitrate. Nitrite was not included due to values always below the limit of quantitation (LOQ). For values below the LOQ, half the LOQ was used for calculating average and standard deviation for nitrate, ammonium, and TKN.

B. PRB carbon injection longevity monitoring

Soil borings were collected approximately 2 ft away from the PRB injection wells at 20-25 ft below grade near Tanbark Creek PRB injection well clusters 2, 4, and 5 (TCINJ2, TCINJ4, TCINJ5). Soil borings were also collected approximately 2 ft away from the upgradient PRB monitoring wells at 20-25 ft below grade at TCMWC1, TCMWC 3, and TCMWC4 between 8/21/23 and 8/28/23. Soybean oil analysis was done at Long Island Analytical laboratory using FID instrument and chromatography method. This test could detect presence or absence of soybean oil. Replicates within the PRB zone of influence and outside the expected zone of influence were collected to validate the anticipated presence/absence of soybean oil which is the primary carbon source in the PRB. Soybean oil presence was expected 2 ft away from the injection well. Absence of soybean oil was expected 2 ft away from the upgradient PRB performance monitoring wells. Soil samples were also analyzed for total organic carbon (TOC) as another approach to validate and quantify the presence of organic carbon.

C. Tanbark Creek water quality monitoring

Porewater, surface water, and submarine groundwater discharge (SGD) rates were previously measured in 2021 prior to PRB installation. The recent sample stations are very close to the same locations as the previous 2021 stations. Five porewater samples and 6 surface water samples were collected on 10/24/23 within Tanbark Creek to begin to establish a time series of water quality conditions. Three porewater samples were collected along the shoreline and two additional samples were collected approximately 25 ft and 45 ft west of the shoreline to form an offshore transect. This was accomplished using a patented porewater evaluation instrument called the Trident Probe provided by Coastline Evaluation Inc. (CLEAR). The probe uses a direct-push approach and is deployed by boat. The probe also simultaneously collected in-situ temperature and conductivity readings. Specifically, the Trident Probe measures temperature and bulk conductivity contrast between porewater 1 ft below the sediment-water interface and surface water 1 ft above the sediment-water interface. Areas with high temperature contrast and low porewater conductivity are conditions indicative of groundwater discharge. A seepage meter was deployed at 2 stations (TCSP7_5 and TCSP7_25) to quantify SGD flow rate over a tidal cycle (Fig. 1). The seepage meter is calibrated, and a zero check is done during the deployment at each station by collecting a “zero” reading with the outflow tube closed. Surface water grab samples were collected by hand from the middle of the water column just above the porewater stations and porewater samples were collected using a low-flow peristaltic pump. A minimum of 200 mL was purged prior to collection of a porewater sample.

Results and Discussion:

A. Summer 2023 PRB performance monitoring

Groundwater conductivity at the Tanbark Creek PRB site ranged from 200-600 µS/cm and groundwater temperature was an average of 15.4 °C during the summer sampling event. Groundwater nitrogen consisted of nitrate, ammonium, and organic nitrogen. Nitrite was always below the LOQ in all samples. TKN, or the sum of ammonium and organic nitrogen, was the dominant form of nitrogen in 14 out of 16 samples. There was a strong south-north gradient with highest TKN values measured in the southern wells (TCMWC1 and TCMWC5) at both 10-15 ft and 20-25 ft below grade (Fig. 2). In all upgradient and downgradient monitoring wells except for TCMWC5, higher TN values were observed at the 20-25 ft depth interval compared to the 10-15 ft depth interval (Fig. 2). There was no significant difference between ammonium or TKN values in the upgradient and downgradient monitoring wells (Fig. 3B). This was expected because carbon-based PRBs are not able to treat ammonium or organic nitrogen.

In contrast, there was a significant nitrate reduction between the upgradient and downgradient monitoring wells (Fig. 3A) Nitrate reduction at the 10-15 ft and 20-25 ft depth was 1.0 and 2.0 mg N-NO_3^-/L respectively or an average of 81% nitrate removal (Fig. 3A). Downgradient of the PRB, monitoring well samples had slightly elevated pH (6.4 ±0.2) and significantly higher alkalinity (73 ±17 mg/L) compared to upgradient monitoring well pH (6.1 ±0.2) and alkalinity (44 ±10 mg/L). These results are consistent with the denitrification reaction which produces bicarbonate ions and increases alkalinity. The optimal pH range for denitrification is 7 to 7.5 so the pH levels at this site are below optimal conditions but still within the range that denitrification activity can occur (Saleh-Lakha et al. 2009). Dissolved oxygen concentrations were below 1 mg/L in all but one sample and concentrations were similar across upgradient (0.6 ±0.6 mg/L) and downgradient monitoring wells (0.5 ±0.3 mg/L). However, ORP values were negative in the downgradient wells (-86 ±33 mV) compared to positive in the upgradient wells (108 ±80 mV). Negative ORP values are reflective of anoxic conditions which are required for denitrification to occur.

Dissolved organic carbon was also elevated in the downgradient samples (63 ±65 mg/L) compared to the upgradient samples (1.0 ±0.3 mg/L). The presence of DOC in downgradient samples confirms that soybean oil emulsion which coats the sand grains within the PRB is metabolized by microbes into a dissolved form. On average, the samples collected from 20-25 ft had less DOC (31 mg/L) compared to the 10-15 ft well samples (95 mg/L). Its presence at lower concentration at the 20-25 ft depth where higher nitrate reduction (2 mg N/L reduction) was also measured, suggests that denitrification occurred, and that carbon was not the limiting reactant in the reaction. Some studies have found that anaerobic environments with high ratio of carbon to nitrate favors dissimilatory nitrate reduction to ammonia (DNRA) (Hardison et al. 2015). Summer 2023 results do not indicate the occurrence of DNRA at this site because the presence of organic nitrogen and ammonium in the upgradient monitoring wells is likely from the nearby nitrogen inputs such as the community septic system and there is no significant difference between upgradient and downgradient ammonium and TKN concentrations.

Woodchip-based PRBs are known to initially release a pulse of DOC at similar concentrations measured at Tanbark and then return to steady-state conditions and last for decades (Robertson et al. 2008, Gilbert et al. 2019). Similarly, microbial degradation of vegetable oil emulsion to DOC supports heterotrophic denitrification. While vegetable oil PRBs for chlorinated solvent removal have continued to function for over 2.5 years (Borden and Lieberman 2009), there are less published studies on the lifetime of vegetable oil PRBs for nitrate removal. Together the field parameters, alkalinity, DOC and nitrate data indicate that denitrification occurred within the PRB resulting in an average nitrate reduction of 81%. However microbial metabolism is temperature dependent and the reactions which support PRB function (aerobic respiration, carbon degradation, denitrification) are presumably occurring at a maximum rate during the first summer after PRB installation. The values measured during this sampling effort thus likely represent maximums. Collecting ancillary data in addition to groundwater nitrogen each summer will help evaluate long term performance.

Sulfate, an ion present naturally in the aquifer, was 22 ±14 mg/L in the upgradient performance monitoring wells which is within the normal range of 3 to 30 mg/L for freshwater (EPA 2003). Sulfate concentration in downgradient monitoring wells was 10 ±8 mg/L. Hydrogen sulfide concentration was also higher in upgradient (4 ±2 mg/L) compared to downgradient monitoring wells (2 ±1 mg/L). These results are somewhat contradictory because the difference in average sulfate concentration suggests that sulfate reduction may be occurring within the PRB which would increase the sulfide concentration in downgradient samples. However, the opposite trend in sulfide was observed.

Background levels of dissolved iron in the upgradient monitoring wells were 2 ±5 mg/L. The EPA sets a secondary maximum contaminant level of 0.3 mg/L for iron. There is no EPA maximum contaminant level for iron or ammonium, but the World Health Organization recognizes odor effects and many European nations have set an ammonium drinking water standard of 0.5 mg N/L. Thus, background levels of iron and ammonium present at the site prior to groundwater entering the PRB make the groundwater unfit for human consumption. There are no drinking water wells on the property or downgradient of the PRB, so this is not a concern. Downgradient monitoring wells had elevated iron of 40 ±40 mg/L. It's important to note that downgradient monitoring wells are roughly 20 ft away from the PRB injection wells and that dissolved iron can reprecipitate into iron sulfide and iron oxide minerals when exposed to reduced sulfur compounds (H_2S, HS^-) and to oxygen, respectively. In fact, Borden and Lieberman 2009 found that elevated dissolved iron levels due to a vegetable oil based PRB reprecipitated within 100 ft downgradient of the barrier. In fact, the slightly lower concentration of sulfide in downgradient monitoring wells at Tanbark Creek could be explained by iron sulfide mineral precipitation. The downgradient distance from the PRB where mineral precipitation occurs is influenced by the natural groundwater sulfate concentration, groundwater travel time, rainfall, rate of mixing and other site-specific parameters. Additional wells at multiple distances away from the PRB can further elucidate the redox reactions occurring downgradient of the barrier and the distance to achieve complete reprecipitation. This will be a major focus of next year's monitoring efforts.

B. Fall 2023 PRB Performance monitoring

Groundwater conductivity ranged from 230-519 μS/cm and average groundwater temperature was 12.6 °C during the fall sampling event. Like the summer, groundwater nitrogen consisted of nitrate, ammonium, and organic nitrogen and nitrite was always below the LOQ. In both fall and summer, there was a strong south-north gradient at the 10-15 ft depth with highest TKN values measured in the southern wells (TCMWC1 and TCMWC5) (Fig. 4). However, this trend was not observed at the 20-25 ft depth like it was in the summer. At both depths there was higher average nitrate in upgradient wells in fall. Specifically, at 10-15 ft we measured 2.0 ±1.1

mg N/L and 1.2 ±0.9 mg N/L in the fall and summer, respectively. At 20-25ft we measured 3.6 ±0.8 mg N/L and 2.5 ±1.4 mg N/L in the fall and summer, respectively. Most notably there was significantly higher nitrate at 20-25 ft in TCMWC4 in the fall (4.47 mg N/L) compared to summer (<0.4 mg N/L). Downgradient nitrate values were similar across both seasons, and this resulted in slightly higher average percent nitrate removal in fall (84%) compared to summer (81%). In both seasons was no significant difference between ammonium or TKN values in the upgradient and downgradient monitoring wells (Fig. 5B).

C. Summer 2023 PRB carbon injection longevity monitoring

All soil samples collected 2 ft away from the PRB injection wells at 20-25 ft below grade had 2 peaks between 11 and 13 second elution time which corresponds to soybean oil presence (Fig. 4A). The peak signal response between 11 and 13 seconds was above 10,000 for all samples collected within the anticipated PRB zone of influence. Although signal strength is related to the concentration of soybean oil, the current test could only provide qualitative information on soybean oil presence or absence. This test confirmed that soybean oil was not present in soil samples collected 2 ft away from upgradient performance monitoring wells (Fig. 4B). There were initially concerns that the upgradient monitoring wells were not far enough upgradient from the PRB and that soybean oil could potentially reach those wells. However, these results verify that upgradient performance monitoring wells are outside of the zone of influence of the PRB and nitrate samples from upgradient wells can be compared to downgradient monitoring wells to calculate nitrate reduction. Soil organic carbon was consistent with the results of the soybean oil test with samples 2 ft away from the PRB injection wells and upgradient monitoring wells containing over 2300 mg/kg and <500 mg/kg TOC, respectively. In future monitoring efforts using an EOS-100 laboratory standard and peak integration, we plan to quantify the amount of soybean oil present at the same distance from the injection wells. With multiple measurements over several years, a rate of carbon removal and an estimate of PRB longevity can be calculated.

D. Fall 2023 Tanbark Creek water quality monitoring

Surface water nitrogen downgradient of the PRB at Tanbark Creek consisted of nitrate and organic nitrogen. Nitrite and ammonia were always below LOQ in surface water samples. Surface water nitrate ranged from <0.40 to 1.0 mg N/L and TKN ranged from <1.0 to 1.7 mg

N/L. Porewater nitrogen was primarily in the form of nitrate. One out of the 5 porewater samples contained TKN while nitrite and ammonia were always below the LOQ. Porewater nitrate ranged from 4.0 to 5.5 mg N/L. There were no significant changes to the porewater nitrate values when comparing 2020 pre-installation to current fall 2023 post-installation values (Fig. 5) despite significant removal within the PRB. A possible explanation for this observation is that groundwater direction is not perpendicular to the shoreline as originally anticipated in CDM Smith model predictions (Fig. 8).

The SGD area being monitored is a focal point for groundwater discharge and is a mixture of groundwater that is not only coming through the PRB but from beneath, above, and around the inland PRB treatment area as well. The modeled saltwater interface beneath the injection wells is >100 ft below the top of the water table (Town of East Hampton Basis of Design Report Conceptual (30%) Design; Feb. 23, 2022; Memorandum pg. 4). Essentially, the fresh groundwater treated within the PRB is approximately 20% of the total fresh groundwater column above the saltwater interface.

Recommendations to verify the flow direction and monitor the PRB influence on the groundwater discharge area include collecting additional water level data from existing near shore cluster wells (Fig. 8 TCCW1-3) at the time of sampling. Furthermore, we recommend modifying the porewater sample plan to include additional stations offshore and expand the current survey area to determine if the plume of treated water leaving the PRB is north or south of the area shown in the original model output (Fig. 8). Lastly, we recommend reviewing the groundwater direction with CDM Smith and updating the model with recent groundwater elevation data and seepage rates to verify previous model flow outputs. If necessary, a groundwater tracer test downgradient of the PRB can also help verify the groundwater direction.

The strongest part of the Tanbark Creek SGD zone was within the first 10 ft from the shoreline but could extend offshore up to 50 ft due to bottom variability. The 24-hour average SGD rate at the mid-point of the SGD zone at station TCSP7_5 was 36.69 mL/min. At this station there was also a strong tidal trend with highest seepage rates measured at low tide and minimum seepage rate measured at high tide. Even at high tide the seepage rate was still positive, which is indicative of strong groundwater drive and is one of the reasons this site was identified as suitable for a PRB. The fall 2023 average rate was very similar to the daily average rate of 40.95 mL/min measured at the same location in 2021. Thus, no significant change in SGD rate was observed since installation of the PRB. At 25 ft away from the shoreline at station TCSP7_25 the sediment was ~6 inches of muck which was starkly different than the sediment within the first 10 ft which consisted of sand and some gravel. Muck is much less conductive of groundwater. Consequently, the seepage data at this station did not show a clear tidal trend, was very noisy, and hovered around zero, with a 24-hour average of -2.9 mL/min.

Figures:

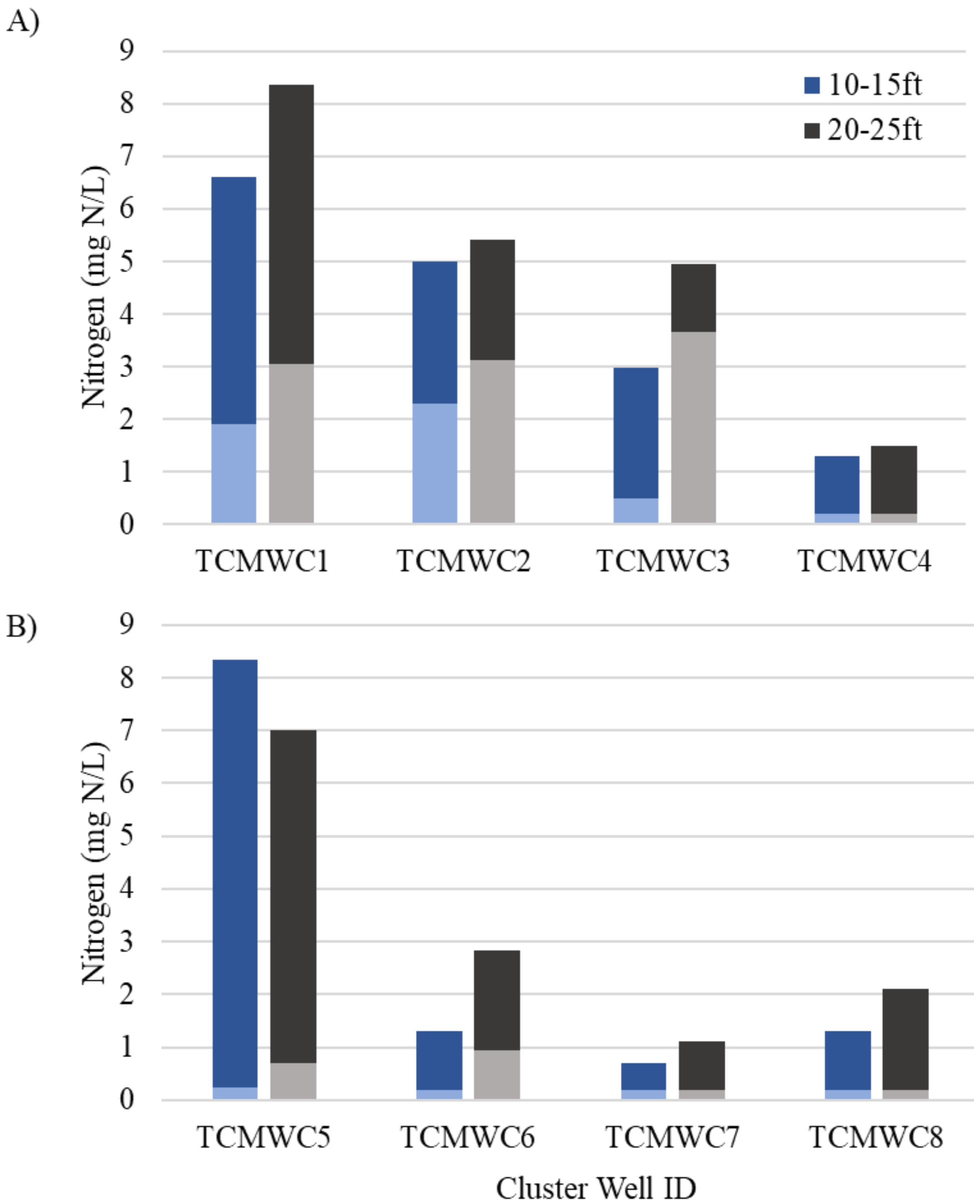

Figure 2: Summer 2023 total nitrogen (TN) in upgradient (A) and downgradient (B) PRB performance monitoring wells with each column showing nitrate (light blue and light gray) and TKN (dark blue and dark gray) for wells 10-15 ft and 20-25 ft depth below grade.

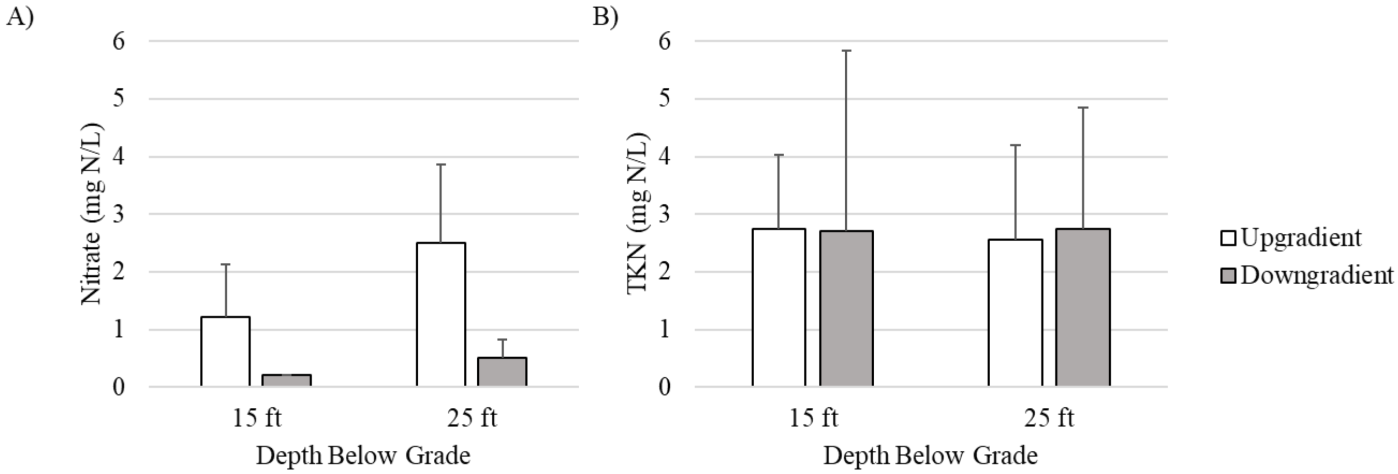

Figure 3: Nitrate (A) and TKN (B) values in upgradient (untreated) and downgradient (treated) PRB performance monitoring wells at 10-15 ft (abbreviated as 15 ft) and 20-25 ft (abbreviated as 25 ft) depth below grade. Each bar represents an average ± standard deviation of 4 samples from summer 2023 sampling event.

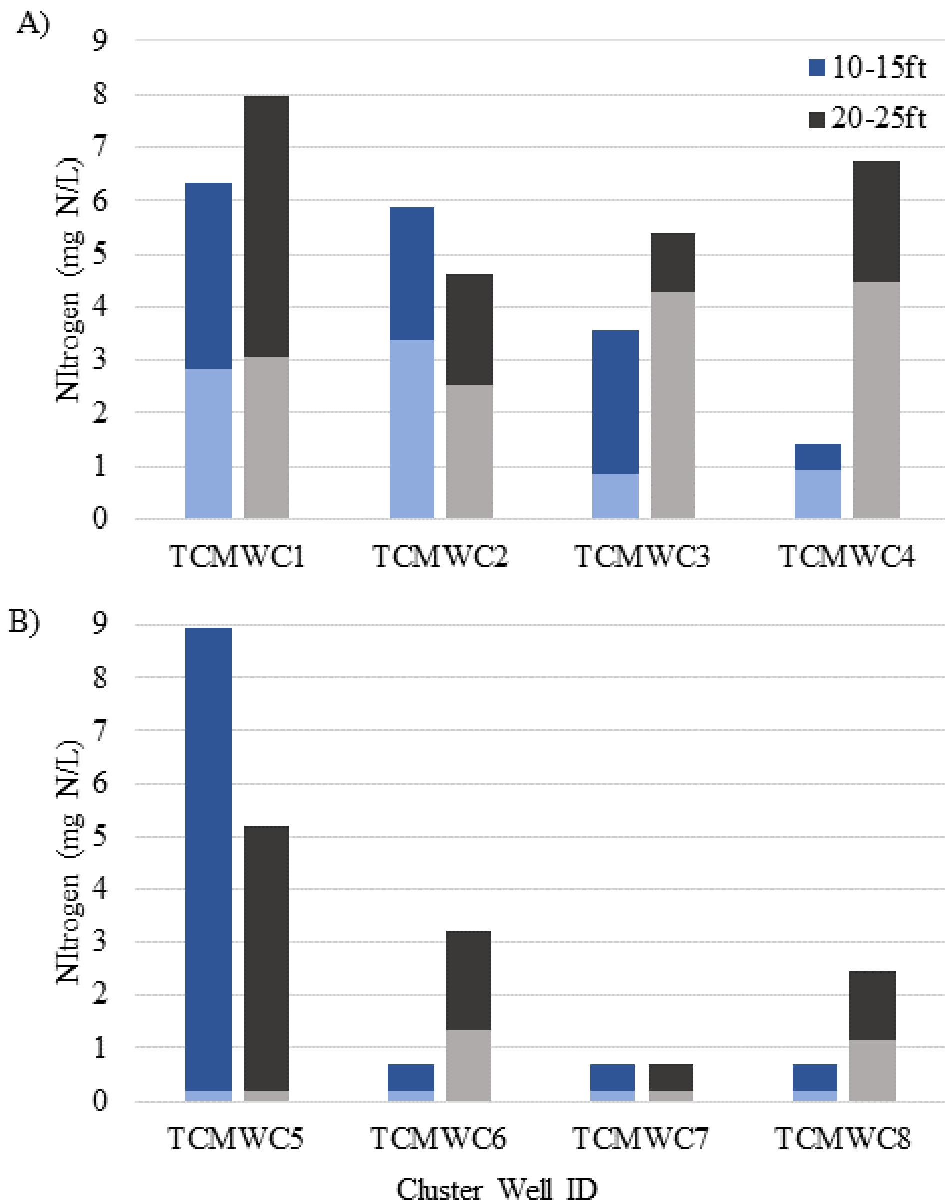

Figure 4: Fall 2023 total nitrogen (TN) in upgradient (A) and downgradient (B) PRB performance monitoring wells with each column showing nitrate (light blue and light gray) and TKN (dark blue and dark gray) for wells 10-15 ft and 20-25 ft depth below grade.

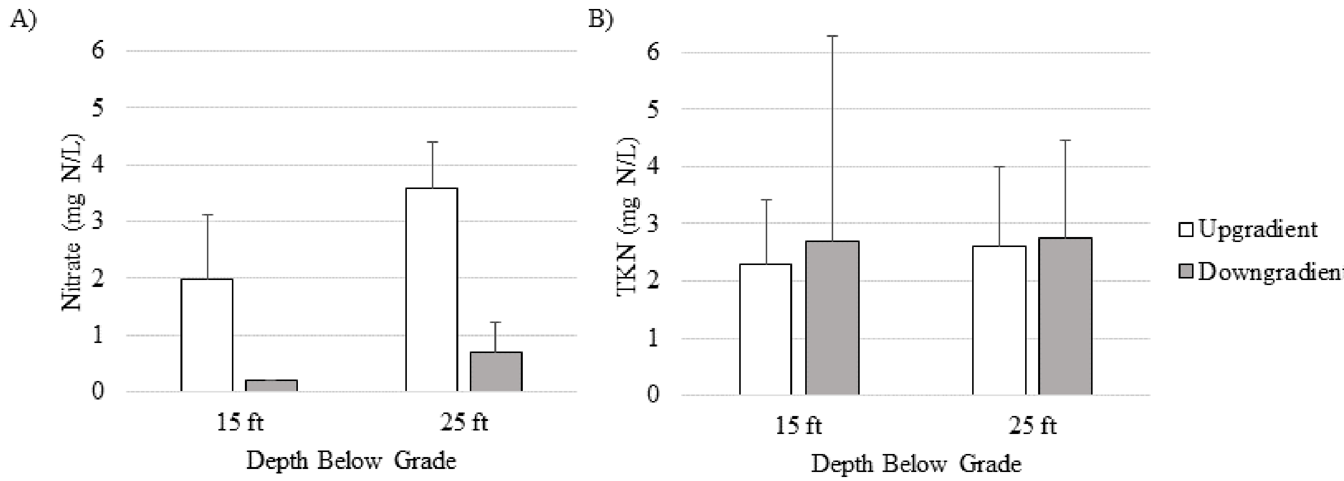

Figure 5: Nitrate (A) and TKN (B) values in upgradient (untreated) and downgradient (treated) PRB performance monitoring wells at 10-15 ft (abbreviated as 15 ft) and 20-25 ft (abbreviated as 25 ft) depth below grade. Each bar represents an average ± standard deviation of 4 samples from fall 2023 sampling event.

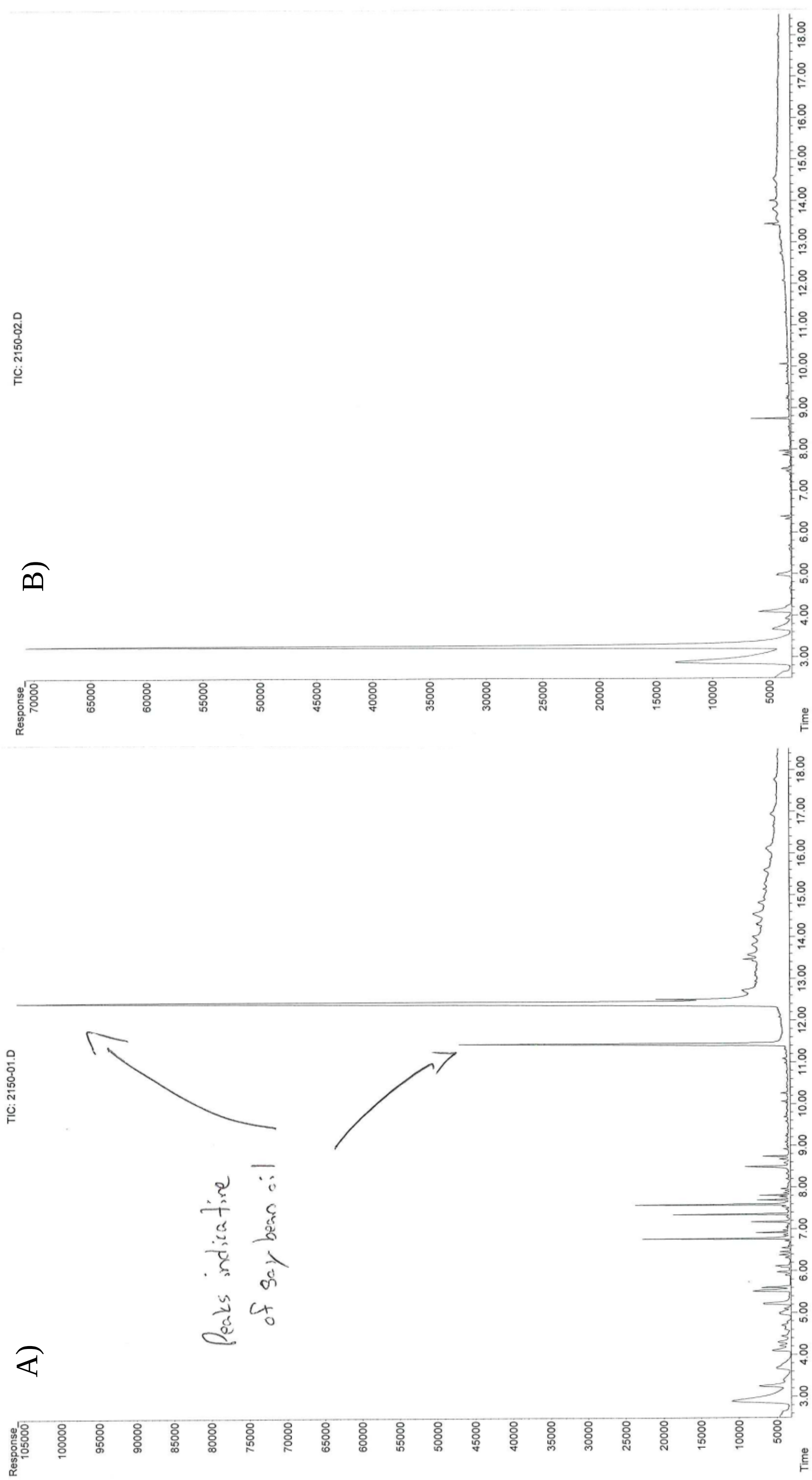

Figure 6: Chromatograms for soil collected 20-25ft below grade and 2 ft horizontally away from (A) TCINJ5 within the PRB and (B) TCMWC4 upgradient performance monitoring well. Y-axes are on different scales.

Figure 7: Porewater nitrate values in mg N/L from 2020 pre-PRB installation survey (red squares/blue text) and current values from fall 2023 monitoring (red circles/red text).

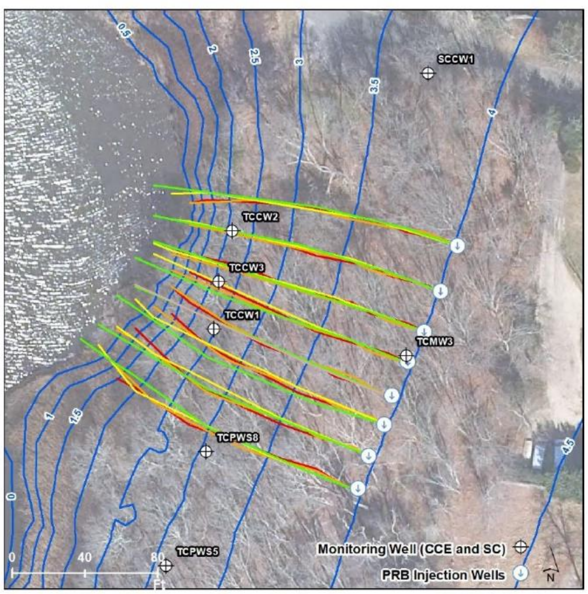

Figure 8: Copied from Town of East Hampton Basis of Design Report Conceptual (30%) Design by CDM Smith. "Simulated particle tracks from the proposed PRB injection wells. Red tracks were released at 0 ft NAVD; orange tracks at -10ft NAVD; yellow tracks at -20ft NAVD and green tracks at -30ft NAVD. Figure created by CDM Smith using a 3D groundwater flow model to aid in the design on the injection PRB. Model was calibrated under transient conditions and reasonably represents the groundwater flow field."

References:

Borden, R.C., Lieberman, M.T. (2009). Passive Bioremediation of Perchlorate Using Emulsified Edible Oils. In: Stroo, H.F., Ward, C.H. (eds) *In Situ* Bioremediation of Perchlorate in Groundwater. SERDP/ESTCP Environmental Remediation Technology. Springer, New York, NY. https://doi-org.proxy.library.cornell.edu/10.1007/978-0-387-84921-8_8

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Gibert, O., Assal, A., Devlin, H., Elliot, T., & Kalin, R. M. (2019). Performance of a field-scale biological permeable reactive barrier for in-situ remediation of nitrate-contaminated groundwater. *Science of the total environment*, *659*, 211-220.

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Saleh-Lakha, S., Shannon, K. E., Henderson, S. L., Goyer, C., Trevors, J. T., Zebarth, B. J., & Burton, D. L. (2009). Effect of pH and temperature on denitrification gene expression and activity in Pseudomonas mandelii. *Applied and environmental microbiology*, *75*(12), 3903-3911.

APPENDIX A

Tanbark PRB Offshore Porewater Sampling and Seepage Measurement Progress Report 1

Report prepared by CLEAR

Coastline Evaluation Corp.

Ron Paulsen P.G.

Patrick Murray

12-26-2023

Overview

In accordance with the monitoring plan established with the Peconic Estuary Program and described in detail in the proposal and summarized below,

CLEAR has completed the Fall offshore porewater and seepage sampling run related to the PRB pilot upgradient. This status report summarizes the work completed by CLEAR as well as observations and recommendations.

The long-term monitoring plan includes the following:

1. Porewater and surface water measurements from approximately 10 stations will be collected bi-annually within Tanbark Creek to establish a time series of water quality conditions.
2. Seepage meter will be deployed bi-annually at 2 stations for 1-2 days to quantify SGD flow rate over a tidal cycle.

Fall 2023 Survey:

During the month of November, planning, equipment preparation, and mobilization of boat and equipment were performed. During a low tidal period in mid-November, 11 samples were collected from Tanbark creek according to the plan presented in figure 1 below. Five porewater and six surface water samples were collected during a period of low tide. Samples were delivered to an ELAP certified laboratory (Long Island Analytical), and results are presented below along with field parameter readings in tables 1-4 and maps (figures 10-18). In addition to porewater sampling, collection of seepage measurements was made at two locations and plots of data are presented in figures 5-7. A plot of 2021 seepage rates is also included in figure 7 for comparison.

Background information:

Tanbark Creek water quality monitoring consisted of porewater and surface water samples collected in the Fall of 2023 (figure 1). These 11 stations were part of the bi-annual monitoring of the Tanbark Creek PRB to establish a time series of water quality conditions. These same locations will be the stations used for every sampling event. Since a similar survey was performed prior to PRB installation in 2021, there is already information about the submarine groundwater discharge (SGD) zone for this area. This data includes porewater and surface water quality and SGD rates. The current locations are very close to the same locations as the previous 2021 survey stations.

Figure 1 Sample stations for porewater (red circles) and surface water (blue circles)

Sampling was accomplished using a patented porewater evaluation instrument called the Trident Probe provided by Coastline Evaluation Inc. (CLEAR). The probe uses a direct-push approach and is deployed from an 18 ft long outboard motorboat. The probe has sensors integrated for temperature and conductivity. The probe also samples porewater and was developed to screen sites for areas where groundwater may be discharging to a surface water body and collect porewater samples from groundwater discharge zones (Chadwick et al., 2003). Specifically, the Trident Probe measures temperature and conductivity contrast between porewater 1 ft below the sediment-water interface and surface water 1 ft above the sediment-water interface. Areas with high temperature contrast and low porewater conductivity values are conditions indicative of groundwater discharge. In addition to temperature and conductance measurement additional porewater parameters are measured and include, conductance, ORP, pH, DO and TDS. Porewater samples were collected from 5 porewater stations in Tanbark Creek for laboratory analysis. In addition to porewater samples surface water grab samples are collected from the middle of the water column at 3 offshore locations and at three shoreline porewater stations.

Porewater samples are collected using a low-flow peristaltic pump. A minimum of 200 mL is purged prior to collection of a porewater sample. Samples are stored on ice and analyzed for nitrogen by a NYS ELAP certified laboratory.

Additionally, at each sampling station the surface water column height, measured by hand-held acoustic sounder or by direct reading from a meter stick, and a qualitative description of the sediment bottom type are recorded. Coordinates for each station are recorded using a Wide Area Augmentation System locked GPS, an instrument capable of sub-meter accuracy.

SGD flow rates were measured in areas previously evaluated in 2021 using a patented ultrasonic seepage meter provided by CLEAR (Paulsen et al. 2001, Paulsen et al. 2004). The ultrasonic seepage meter is calibrated, and a zero check is done during the deployment at each site by collecting a “zero” reading with the outflow tube closed. The meter was deployed at 2 stations, one in an area previously measured in 2021, for 1-2 days to quantify SGD flow rate over a tidal cycle. A yearly nitrogen load to the surface water (lbs N/year) will be extrapolated using the average volume of discharge per day and the porewater nitrogen concentration in the future.

Porewater and surface water parameters and nitrogen results for Fall Survey

Porewater Parameters

Table 1 Porewater parameters

Station ID	Date	Time	Longitude	Latitude	Cond (µS/cm)	TDS	pH	ORP	D.O. (mg/L)	Temp (°C)	Depth (in)	Bottom Type (Muck, Sand, Silt, Gravel)
TCF2023PW6_0	2023-10-24	15:00	-72.184010	40.998059	304	155.0	5.81	156	2.0	15.6	0	M
TC2023PW7_0	2023-10-24	14:10	-72.183946	40.998154	289	150.8	6.76	83	3.1	16.8	0	G, S
TCF2023PW7_25	2023-10-24	13:30	-72.184037	40.998164	461	237.1	5.83	162	2.0	16.2	6	2" M then S
TCF2023PW7_45	2023-10-24	12:20	-72.184093	40.998183	485	250.0	6.12	111	4.9	16.1	12	6" M then S
TCF2023PW8_0	2023-10-24	14:30	-72.183919	40.998237	260	132.3	5.75	175	2.0	15.9	0	M

Porewater Nitrogen Results

Table 2 Porewater Nitrogen results in mg/l (note zero values indicate value below detection levels)

Station ID	Date	Time	Longitude	Latitude	Total N	Total N DL	Ammonia (as N)	Ammonia DL	Nitrate	Nitrate DL	Nitrite	Nitrite DL	TKN Kjeldahl	Kjeldahl DL	Total N calc
TCF2023PW6_0	2023-10-24	15:00	-72.18401003	40.99805919	5.87	1.8	0	1.46	4.37	0.4	0	0.4	1.5	1	5.87
TC2023PW7_0	2023-10-24	14:10	-72.18394599	40.99815421	5.5	1.8	0	1.59	5.5	0.4	0	0.4	0	1	5.5
TCF2023PW7_25	2023-10-24	13:30	-72.18403717	40.99816446	4.9	1.8	0	1.46	4.9	0.4	0	0.4	0	1	4.9
TCF2023PW7_45	2023-10-24	12:20	-72.18409325	40.99818332	5.32	1.8	0	1.75	5.32	0.4	0	0.4	0	1	5.32
TCF2023PW8_0	2023-10-24	14:30	-72.18391911	40.99823742	4.06	1.8	0	1.63	4.06	0.4	0	0.4	0	1	4.06

Surface Water Parameters

Table 3 Surface water parameters

Station ID	Date	Time	Longitude	Latitude	Cond (µS/cm)	TDS	pH	ORP	D.O. (mg/L)	Temp (°C)	Depth (in)	Bottom Type (Muck, Sand, Silt, Gravel)
TCF2023SW1	2023-10-24	11:35	-72.184380	40.997778	22050	13240.0	6.57	108	7.3	17.9	10	M
TCF2023SW2	2023-10-24	11:45	-72.184227	40.982418	37700	23440.0	7.12	112	7.5	17.8	12	M
TCF2023SW3	2023-10-24	11:50	-72.184358	40.998183	39990	24930.0	7.40	126	7.4	16.5	14	M
TCF2023SW6	2023-10-24	14:35	-72.184010	40.998059	35310	21870.0	7.23	51	9.8	19.8	0	M
TCF2023SW7	2023-10-24	14:20	-72.183946	40.998154	32320	19910.0	6.51	118	8.1	19.9	0	G, S
TCF2023SW8	2023-10-24	15:30	-72.183919	40.998237	29870	18270.0	6.72	41	8.8	19.5	0	M

Surface Water Nitrogen

Table 4 Surface water Nitrogen results in mg/l (note zero values indicate value below detection level)

Station ID	Date	Time	Longitude	Latitude	Total N	Total DL	Ammonia (as N)	Ammonia DL	Nitrate	Nitrate DL	Nitrite	Nitrite DL	TKN Kjeldahl	Kjeldahl DL	Total N calc
TCF2023SW1	2023-10-24	11:35	-72.18438044	40.99777808	0	1.8	0	1.32	0	0.4	0	0.4	0	1	0
TCF2023SW2	2023-10-24	11:45	-72.18422748	40.9824177	0	2.36	0	1	0	0.4	0	0.4	1.71	1.56	1.71
TCF2023SW3	2023-10-24	11:50	-72.18435759	40.99818332	0	1.8	0	1.46	0	0.4	0	0.4	1.5	1	1.5
TCF2023SW6	2023-10-24	14:35	-72.18401003	40.99805919	0	1.8	0	2	0.48	0.4	0	0.4	1.3	1	1.78
TCF2023SW7	2023-10-24	14:20	-72.18394599	40.99815421	2.27	1.8	0	1.4	0.97	0.4	0	0.4	1.3	1	2.27
TCF2023SW8	2023-10-24	15:30	-72.18391911	40.99823742	0	1.8	0	1.46	0.68	0.4	0	0.4	1.1	1	1.78

Plots of results including porewater and surface water field and laboratory nitrogen results

Figure 2 Porewater nitrate results mg/l-zero value indicates value below detection level of 0.4mg/l

Porewater Nitrates (mg/l) 2021 and 2023

Figure 3 Porewater nitrate results for 2020 pre prb survey survey (red Square and blue text) and fall 2023 post PRB installation (red circles and red text) results in mg/l

Surface Water Nitrates (mg/l) 2023

Figure 4 Surface water nitrogen results (mg/l)-zero indicates value is below detection level 0.4 mg/l

Submarine Groundwater Discharge (SGD)

Measurements of SGD were made at two locations along the TBSP7 transect (2023TCSP7_5 and 2023TCSP7_25). The advective discharge zone in this area was strongest within the first 10 feet from the shoreline. The advective zone mid-point was measured during the fall 2023 monitoring period at station 2023TCSP7_5 (Figure 5) and during 2021 fall monitoring period at station 2021TBT3_25 (figure 7) . The 24 hr. average SGD rates were similar, 36.69 ml/min and 40.95 ml/min respectively. No apparent change in SGD rates was observed since installation of PRB. The data indicated station 2023TC7_25 was on the fringe of the advective zone in an area with ~6 inches of muck that is less conductive than sand sediment and gravel in advective zone.

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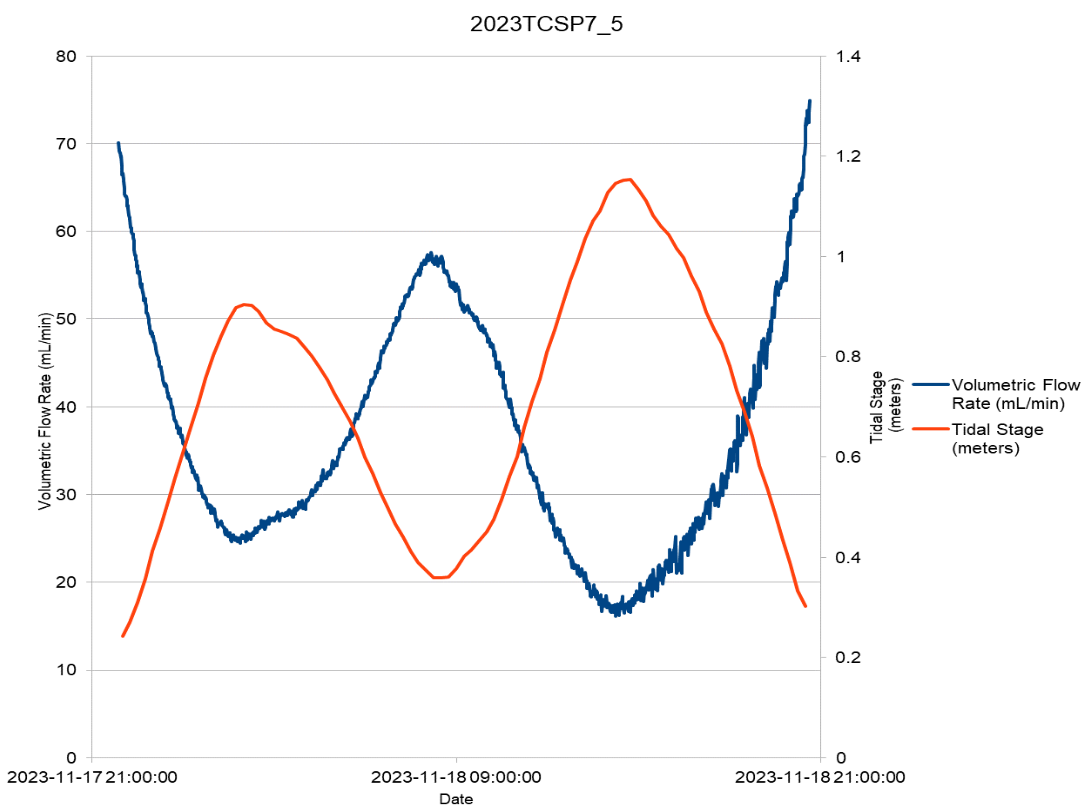

Figure 5 SGD Rate from station TCSP7_5 (volumetric flow rate in ml/minute) -blue line SGD and red line is tidal stage in meters.

24 hr. Average SGD Rate Summary

2023TCSP7_5	
Average Volumetric Flow Rate (ml/min)	36.69
Average Specific Discharge (cm/day)	25.28

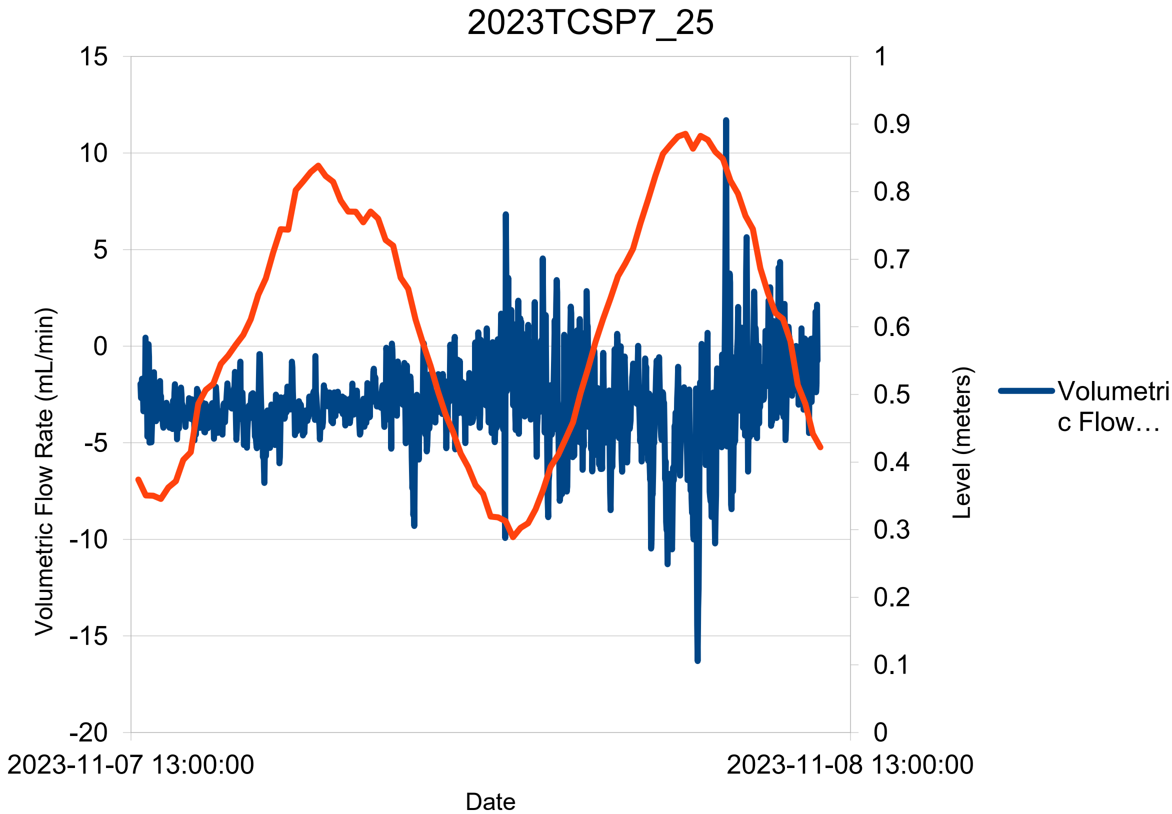

Figure 6 SGD rate from station TCSP7 -25 (volumetric flow rate in ml/min) -blue line SGD rate and red line tidal stage in meters.

24 hr Average SGD Rate Summary

2023TCSP7_25	
Average Volumetric Flow Rate (ml/m	-2.927
Average Specific Discharge (cm/day)	-2.016

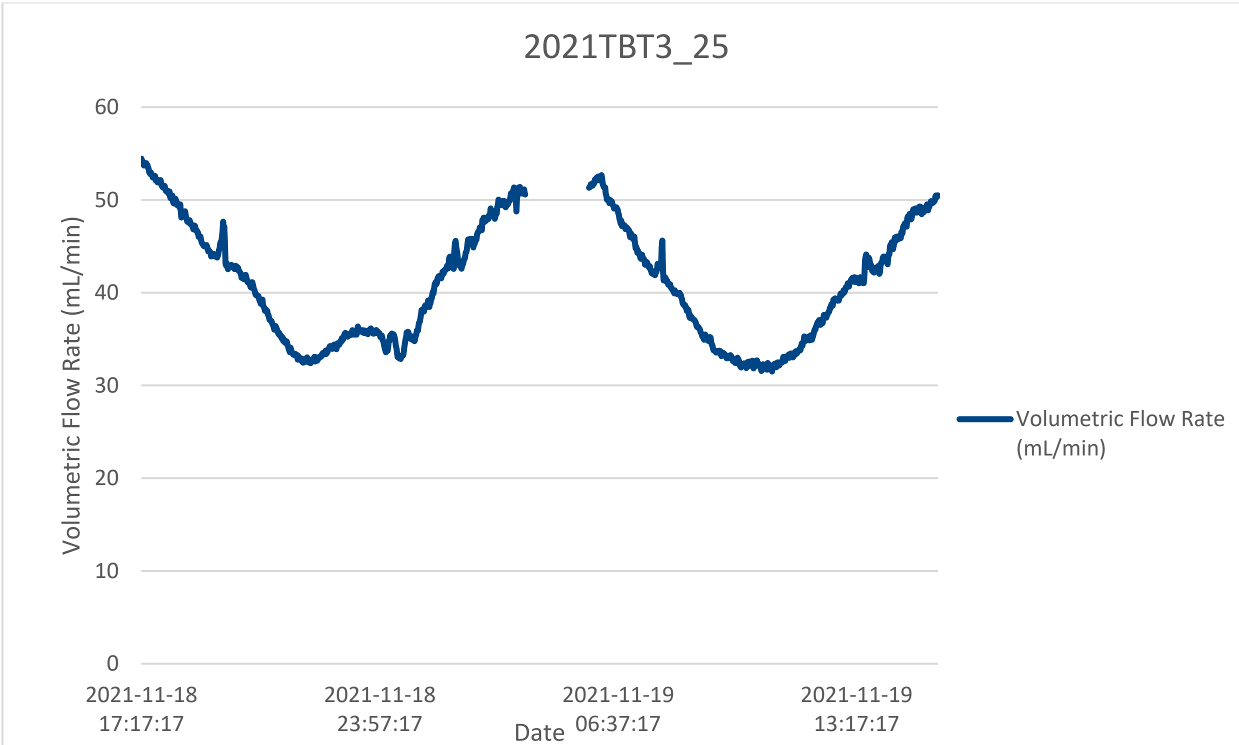

Figure 7 SGD Rate from station 2021 TBT3_25 (near present station TCSP7_5) (Volumetric flow rate in ml/minute) -blue line SGD .

24 hr Average SGD Rate Summary

2021TBT3_25	
Average Volumetric Flow Rate (ml/min)	40.95
Average Specific Discharge (cm/day)	29.1

Observations

Porewater collected during the 2023 survey was similar in concentration to that of the 2020 pre survey. The 2024 survey results for nitrate ranged from 4.0 to 5.5 mg N/L. There were no significant changes to the porewater nitrate values when comparing 2020 pre-installation to current fall 2023 post-installation values (Figure 3) despite the reported significant removal within the PRB. A possible explanation for this observation is that groundwater direction is not "perpendicular" to the shoreline as originally anticipated in figure 8). Additionally, the thickness of the freshwater above the reported saltwater interface is over 100 ft below top of water table according to CDM design report (figure 9. Essentially the PRB treatment area is approximately 20 percent of the total fresh groundwater column below the PRB.

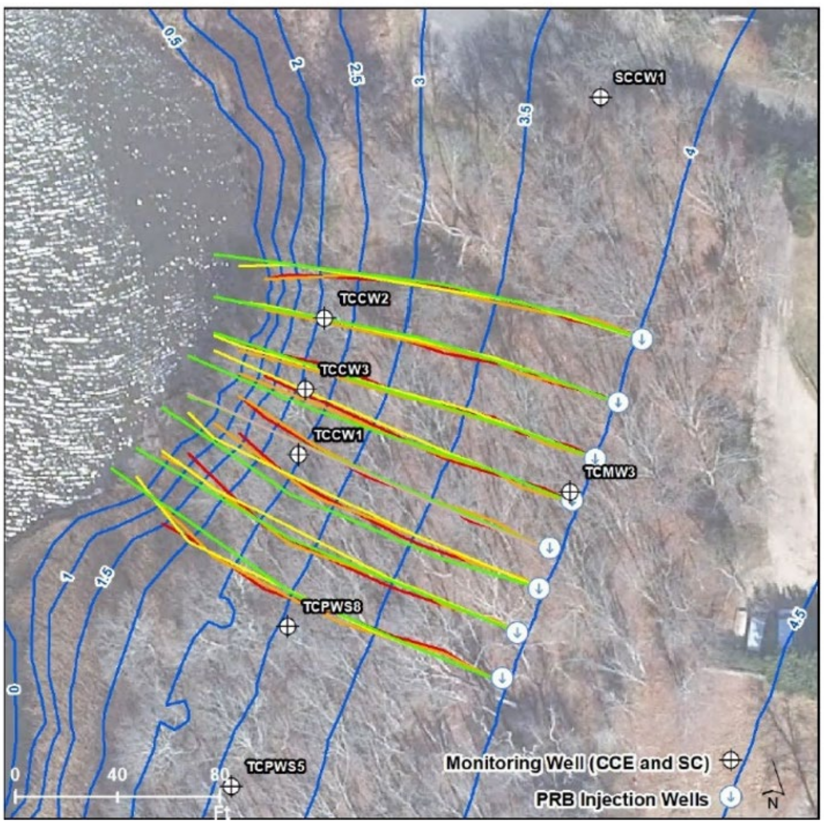

Figure 8: CDM simulated particle tracks from the proposed PRB injection wells. Red tracks were released at 0 ft, NAVD; orange at -10 ft, NAVD; yellow at -20 ft, NAVD; and green tracks at -30 ft, NAVD. Plot acquired from CDM Basic Design Report - Conceptual.

It is also important to keep in mind the area of discharge currently being monitored was found to be focal point for groundwater discharge during the 2021 pre survey. The focused discharge area is a mixture of groundwater that is not only coming through inland PRB groundwater section but from beneath, above and around the inland PRB treatment area. Figure 9 indicates groundwater head contours beneath the PRB area. Groundwater flow paths are typically perpendicular to these head contours and indicate groundwater from depths of as much as 200 ft below sea level are converging and discharging in the near shore discharge area of Tanbark Creek. Typically, deeper flow paths are found to be discharging further offshore and shallow groundwater found closer to shore. This being the case its necessary to have several transects of porewater stations to capture groundwater discharge from shallow, mid and deeper flow paths including the PRB section.

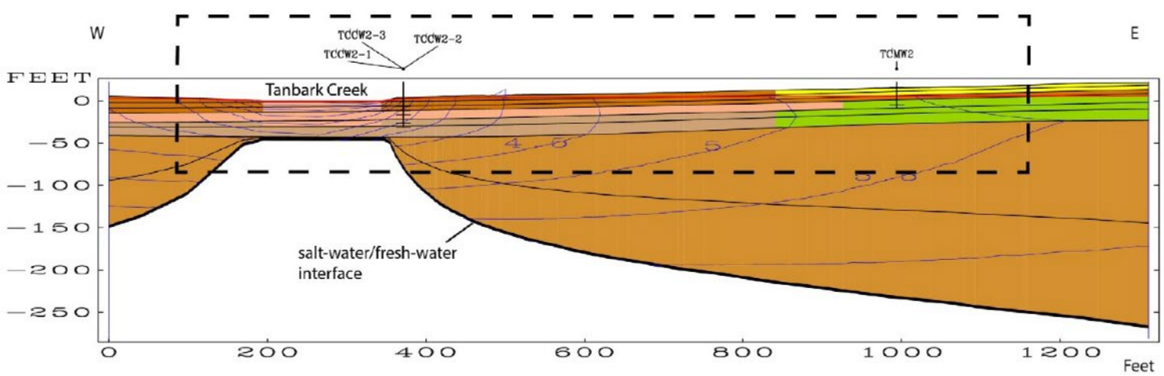

Figure 9: Hydrogeological cross section in vicinity of PRB injection area. Plot acquired from CDM Basic Design Report - Conceptual.

In order to verify the flow pattern and monitor the PRB influenced discharge area, we recommend several actions. Collecting water level data at the time of sampling and sampling near-shore existing cluster wells (TCCW1-3) will help verify direction of flow and add additional nitrogen plume tracking data. Additionally, we recommend modifying the porewater sample plan to include additional stations offshore and adding stations north and south of the current area to capture PRB related groundwater discharge. Lastly, we plan to review the modeled groundwater direction with CDM using recent groundwater elevation data and seepage rates to verify past outputs on flow direction. The expanded grid pattern will enable us to determine what areas of the discharge zone are seeing reduction of nitrogen and are likely related to the PRB treatment inland over time.

Summary and Observations

- No significant reduction of nitrogen observed in porewater stations.
- One station, TBPW6, did have a 1 mg/l reduction, others had similar concentrations or slightly higher .
- No unusual deviations in other parameters including dissolved oxygen, pH and ORP in porewater or surface water.
- Seepage rates are similar to 2021 measurements.
- No significant shoreline changes.
- A small area of iron was noted at Station 7 (iron was also noted in prior survey).

Recommendations

- Verify groundwater time travel and direction of flow with CDM. Refine model with current data.
- Continue to monitor but expand slightly to determine if plume has shifted in direction due to treatment and move to quarterly sampling for 2024.
- Explore natural denitrification in hyporheic zone.

Acknowledgment

Like to thank CLEAR associates Patrick Melfi and Christina Badalamenti, CCE Peconic Estuary Program for supporting this project

Appendix B

Additional Data Plots

Figure 10: Porewater conductance (µS/cm)

Figure 11: Surface water conductance (µS/cm)

Figure 12: Porewater Dissolved Oxygen (mg/L)

Figure 13: Porewater ORP

Figure 14: Porewater pH

Figure 15: Sediment type M-muck, S-sand. Value depth of muck layer in inches

Figure 16: Surface water dissolved oxygen (mg/L)

Figure 17: Surface water conductance (µS/cm)

Figure 18: Surface water ORP

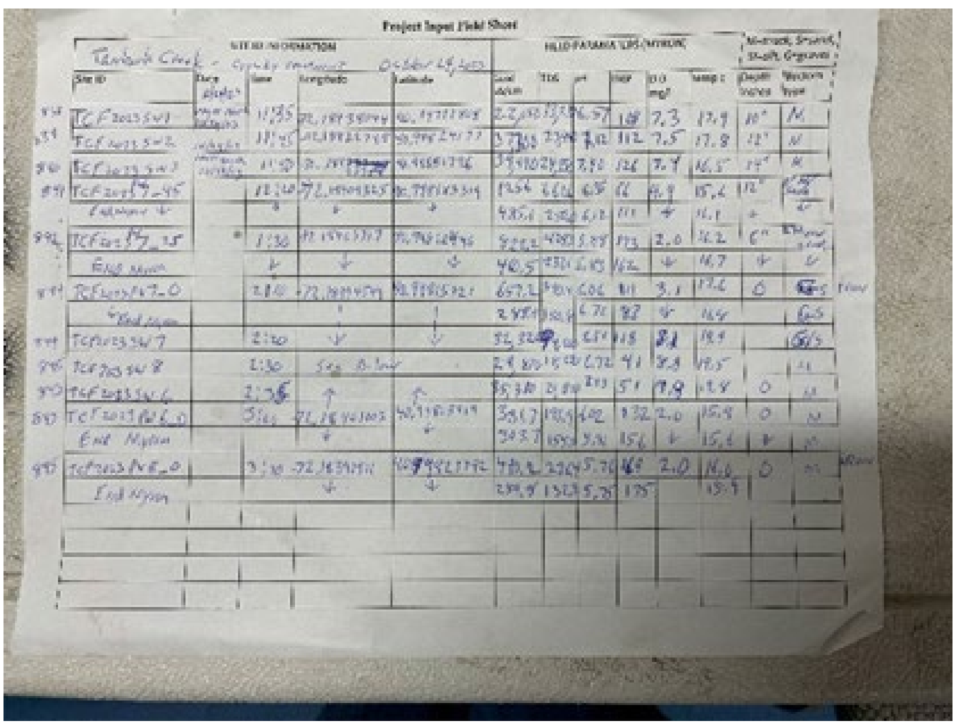

Figure 19: Field notes