Influence of NIRTEX barrier on groundwater flow paths, dissolved organic carbon and nitrate concentrations

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Abstract

Nutrient loading from septic systems to Waquoit Bay Estuary has been an increasing concern as algae blooms continue to blanket large portions of the estuary in the summer. Recently a NIRTREX permeable reactive barrier comprised primarily of wood chips has been installed to act as a filter, removing the high concentrations of nitrate through the process of dentrification. Total nitrate removal was measured at almost 100%. Supporting data of dentrification was also collected such as DOC, DO, pH. Salt water intrusion to the barrier is identified due to the tide and high permeability of the barrier. The flow velocity of the groundwater entering the barrier was identified as 0.35 m day^{-1} with the fluoroscein injection. Patterns were determined after 11 days of sampling and following the flow of Rhodamine that was injected into a well point.
et al.

Keywords: Dentrification, Nitrate, NO_3^-, NITREX, Permeable Reactive Barrier, Groundwater, Rhodamine, Fluoroscein.

Introduction

Increased nutrient inputs to watersheds have been linked to the seemingly exponential growth of densely packed housing and increased septic systems and causes eutrophication to the estuary. Waquoit Bay, located on the south shore of Cape Cod Massachusetts is among these densely packed areas. This bay has a serious eutrophication problem (Schwartzman, 2002). Beth Schwartzman (2002) expresses her concern for the environment as she is noticing a transition from a clear, eel grass dominated estuary with a high species diversity to a smothering filamentous algae dominated estuary with a declining species diversity. Nutrient loading to the estuary is caused by the increased wastewater inputs of septic systems to the area around the bay. A highly concentrated septic plume is always being added to the estuary mainly because the sandy soils on the cape there is little or no attenuation of nutrients between the leech field and water table. Factors making Waquoit Bay more vulnerable to eutrophication include the shallow depth of the estuary of 1.5-3 meters and because of this shallow water the light can penetrate to the bottom maximizing the total area where primary production can take place.

A combination of oxidation reactions that take place in primary septic system treatment change the organic nitrogen mostly from human wastes, most commonly in the form of ammonium (NH_4), into nitrate (NO_3). This nitrate from septic plumes is commonly found in higher concentrations than the drinking water standards for nitrate, 10 mgL^{-1} (Robertson, 2005).

Dr. Vallino (2004) proposed the use of a NITREX reactive barrier to remove nitrate directly from the septic plume. In late July of 2005, two preliminary NITREX Permeable Reactive Barriers (PBR) were installed, one is located at the head of Waquoit Bay estuary on Waquoit Bay Estuarine Research Reserve, WBNERR (Figure 1).The PRB is located 0.5 meters below the surface and it reaches a depth of 2.5 meters. The PRB is 3.25 meter wide and stretches for 16.5 meters along the beach. The PRB is located just above the high tide on the shore.

Initially the barrier was going to be at a 4 meter depth because that is where the highest septic nitrate plume is located in the groundwater. Because of complications during construction of the PRB depth was not able to be as deep as the most concentrated area of the nitrate plume. Successful operation of the barrier filtering this deeper nitrate plume requires the barrier soil conductivity to be higher than the surrounding soil conductivity. The differences in the conductivity will allow the groundwater to be pulled through the barrier fast than the groundwater is flowing through the ground. This pulling motion will allow for the septic plume that is lower than the barrier to be pulled up into the barrier and then treated (Figure 2).

The PRB is comprised of wood chips creating a carbon source allowing a microbial community to create an anoxic environment needed for the nitrate removal. This nitrate removal is known as the dentrification process.

Dentrification: $4NO_3^{-}+5CH_2O\rightarrow 2N_2+5CO_2+3H_2O+4OH^{-}$
Nitrate + Carbon source (wood chips)→ nitrogen gas ↑ +carbon dioxide (DOC)

Gentrification takes place when there is nitrate and an organic carbon source such as the wood chips in the barrier. In the woodchips a microbial community is formed and as they consume the carbon substrate they release the nitrogen as a gas, use up oxygen, produce carbon dioxide and water to create an excess of dissolved organic carbon (DOC) and hydroxide (makes the system more basic).

About three months after the initial construction of the NIREX PRB I have collected samples to measure groundwater dissolved oxygen (DO), salinity, pH, temperature, nitrate, ammonium and dissolved organic carbon (DOC) concentrations. I have also preformed a fluorescent dye tracing study using Rhodamine and Fluoroscein to measure the actual groundwater velocity and flow patterns through the PRB.

Methods

At the PRB site we have installed a series of 11 cluster wells ranging in depths from 0.4 to 5 meters with a total amount of 50 sampling points (Figure 3). We also installed 4 piezometers to measure the depth to the top of the water table over time with a water tape.

Quantum

In the field we collected water samples using a Quantum Hydrolab connected to a peristaltic pump. Dissolved oxygen (DO), salinity, pH, and temperature was measured from the well water after purging the wells 3 times and before the water was introduced to the atmosphere.

Nitrate and Ammonium

I collected 20mL water samples to measure the nitrate and ammonium concentrations at each of the well depths. In the field these samples will need to be filtered with 0.25 um GFF filters. In the lab the nitrate samples were stored in the freezer preserved until analysis by the Lachat Quikchem 8000 Instrument. Ammonium samples were run using standard colorimetric analysis on the Schimadzu 1600 spectrophotometer.

Dissolved Organic Carbon (DOC)

Dissolved Organic Carbon (DOC) samples were also collected to determine the DOC distribution around the barrier. I collected 20ml samples from each of the wells points surrounding the barrier. In the field all samples were are filtered using pre-ashed 0.25um GFF filters and stored in pre-ashed glass DOC scintillation vials. All 20 ml samples were acidified for preservation with 10ul of 50% phosphoric acid and stored in the refrigerator until analysis. DOC samples were run on the HTCO machine designed by Ed Peltzer and manufactured by Woods Hole Oceanographic Institution.

Dye Tracer Injections

After all other samples were collected two florescent tracer dyes, Rhodamine and fluoroscein, were added simultaneously to the groundwater. One liter of $2.5*10^4$ ppm (2.5g/L) of 20% Rhodamine was injected into well 2, 1.25 meters before the edge of the barrier, and at a depth of 3 meters. One liter of 100ppm Fluoroscein was injected into well 2, 4 meters below the surface (Figure 2). After one liter of the dyes was pushed down into the wells 60ml of DI water was pushed down the wells to clear the well tubing.

The dyes do not mix so they can be added simultaneously. Two hours after the dyes were added, the wells were purged with 60ml of well water and 40 ml of sample was taken from well 3 at depths of 2.8, 3.3, and 3.8 meters. Sample times increased to 4 hours increments after 12 hours of 2 hour sampling because there was no breakthrough of either the fluoroscein or rhodamine. Four hours sample increments were then increased to 6 hour sample increments after 28 hours of not seeing any breakthrough of either dye in well 3.

Samples were collected in glass scintillation vials and compared to a series of glass vials with rhodamine and fluoroscein dilutions. The comparator of dilutions was made the day of the injection and stored in a dark refrigerator. Fluoroscein and rhodamine sample concentrations were determined by using the comparator and the rhodamine was further analyzed using a 10-AU Flourometer.

Results

Nitrate

Nitrate concentrations around the PRB decreased as samples were collected through the barrier and they continued to remain low after the barrier. Concentrations peaked at 161 uM in well 2 at a depth of 3 meters (Figure 4). In well 4 the concentrations greatly decreased to less than 60uM. Nitrate concentrations in wells 5, 6, 7 and 8 continued to dramatically decreased to concentrations lower than 5 uM as the groundwater passed through the barrier.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) measurements of each well depth had concentrations ranging form the high of 3388 uM to the low of 200 uM (Figure 5). There was a plume of highly concentrated DOC in well 3 and at a depth of 3.3 meters the concentration was the highest measured at 3388 uM. This plume is also seen in well 3 at 2.8 meters at lower concentrations. Well 4 has low DOC concentrations ranging from 1900 uM at the depth of 1.5 meters to much lower concentrations with an average of 400 uM DOC. The center of a second DOC plume is located in well 6 at a depth of 2 meters. This plume is towards the end of the barrier and the concentration in the center is 3430 uM.

pH

The pH before the PRB is measured at an average of 6 and as it passes through the barrier the pH increases towards being more neutral at an average of 7 (figure 6). After the groundwater passes through the barrier the pH remains around neutral.

Dissolved Oxygen

Dissolved oxygen is highest before the barrier in well 1 at a percent saturation of about 60% and it gradually decreases until it reaches the barrier where is drops to below a 2% saturation (figure 7). There is an area beginning at well 5 towards the top of the barrier and through wells 7 and 8 where there is a 2-5 % saturation.

Salinity

Salinity is highest in well 8 when it reaches 16 o/oo and it decreases as the groundwater and saltwater mix in the PRB (figure 8). The lowest concentration of salinity is before the barrier in wells 1 and 2 when the concentrations are lower than 1 o/oo.

Groundwater elevation

Piezometer readings taken during the dye injection indicate a fluctuation of groundwater elevation with the tidal cycle (Table 1 and figure 9). Figure 9 shows the difference between piezometer readings from the piezometer located below the barrier and the piezometer located in the barrier. This difference is 0.01 foot at low tide to 0.1 foot at high tide.

Rhodamine

The Rhodamine dye was injected at well 2 at a depth of 3 meters, this dye then traveled to well 3b over the course of 11 days (figure 10). The Rhodamine did appear to travel up towards the PRB 0.25 meters however, this information would be more reliable if there were more sample wells installed to gain a better understanding of the vertical and lateral distribution of the dye travel. More time is also necessary to follow the dye dispersal and its travel through the barrier.

Fluoroscein

Groundwater velocity directly in front of the PRB was measured by a breakthrough curve of the fluoroscein dye (figure 11). The fluoroscein was measured by in well 3 at a depth of 3.8 meters. Fluoroscein concentration peaked at 48 hours and the groundwater velocity was calculated with this measurement. The velocity of the fluoroscein traveling between well 2 and well 3 was calculated to be 0.35 md $^{-1}$.

Discussion

Nitrate removal

The combination of the nitrate plume being greatly reduced (figure 4), the total percent saturation of oxygen also being reduced (figure 7) and the small production in DOC (figure 5) and the increase in alkalinity (figure 6) are all indicators that the dentrification process is occurring within the barrier (Robertson *et al.* 2005, Robertson *et al.* 2000, MacQuarrie *et al.* 2001, Schipper *et al.* 2004). Robertson *et al.* (2000) also states that the barrier is able to attenuate 60-100% of all nitrate passing through them within the first year of installation. The new Waquoit Bay barrier is able to attenuate nearly 100% of the nitrate passing through the barrier. Robertson *et al.* (2000) indicates a similar loss of DO and an increase in excess of DOC leaching from the barrier.

Nitrate reduction in the barrier relies in a few limitations that concerned Robertson *et al.* (2000) such as the total availability of a carbon source. Through a 7 year study of a barrier Robertson *et al.* was able to conclude through barrier cores that even over 7 years the small sawdust was still able to perform dentrification at rates greater than 60%.

Salinity

Unfortunately, the barrier constructed on Waquoit Bay does seem to have salt water intrusion. Figure 8 shows that there is salt water from the estuary entering the barrier. Most wells within the barrier have concentrations of salinity over 10 o/oo. This is a concern because the addition of salt could potentially change the microbial composition in the barrier to a sulfate reducing community. This sulfate reducing community would not perform dentrification anymore and the nitrate plume would enter the estuary.

Piezometer readings collected from December 1st through the 4th (figure 9 and table 1) indicate that the water level within the barrier fluctuates dramatically with the tides. This indicates that the barrier may potentially become filled with salt water twice a day. All sampling for this project was taken during receding tides and it can be predicted that the measurements are the lowest salinity concentrations.

Flow Patterns and Velocity

Fluoroscein injected into well 2 at a depth of 4 meters had a breakthrough at 36 hours after the injection. The fluoroscein then continued to increase in concentration until it reached its peak at 48 hours (figure 11). From this peak the velocity of the groundwater was calculated to be 0.35 m day^{-1}. The soil conductivity was as predicted for the Cape Cod soils.

Rhodamine was injected into well 2 in to determine the flow patterns of the groundwater. The rhodamine travel over 11 days indicates that the plume was pulled up 0.25 meters (figure 10). This information alone is not enough to interpret the entire groundwater flow pattern around the barrier. As the tracer experiment continued over the 11 days more information continued to add to the potential complexity of the patterns. The main reason for this is because of the increasing uncertainty that the groundwater was flowing directly through the barrier with no influence from the tides.

Piezometer readings (table 1 and figure 9) indicated that there was a strong tidal influence on the barrier is stronger inside the barrier than it was originally expected because of the increased porosity within the barrier. The barrier was constructed to have a higher porosity than the surrounding soils. If the tide has a stronger force moving into the barrier from the opposite direction than the groundwater, than it would also make sense for the groundwater to be pushed through the barrier in reverse during high tides and as the tide recedes then the groundwater is able to flow through the barrier and treated before it enters the estuary.

Conclusions

Although the barrier is currently performing dentrification it is also being inundated with salt water on a regular basis. The effects of salt water could result in a transition from dentrification to sulfate reduction and the timing of this transition is also unknown. Understanding the tidal influence on the barrier can be done by more frequent replications of the Quantum Hydrolab sampling during different and replicate times in the tidal cycles. This Quantum data could also help describe the flow patterns and distribution of DOC.

The flow pattern analysis can be improved by adding more wells to determine the vertical and horizontal distribution of the dyes and by increasing the total sampling time greater than 11 days.

Acknowledgements

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Figures and Tables:

Figure 1. The Nitrex Permiable Reactive Barrier is located at the head of Waquoit Bay in Falmouth, MA. The Barrier begins 0.5 meters below the surface and continues for 2 meters. The barrier is 3.5 meters wide and stretches along the beach for 16.5 meters. The photograph here was taken from googlemaps.com, October, 2005.

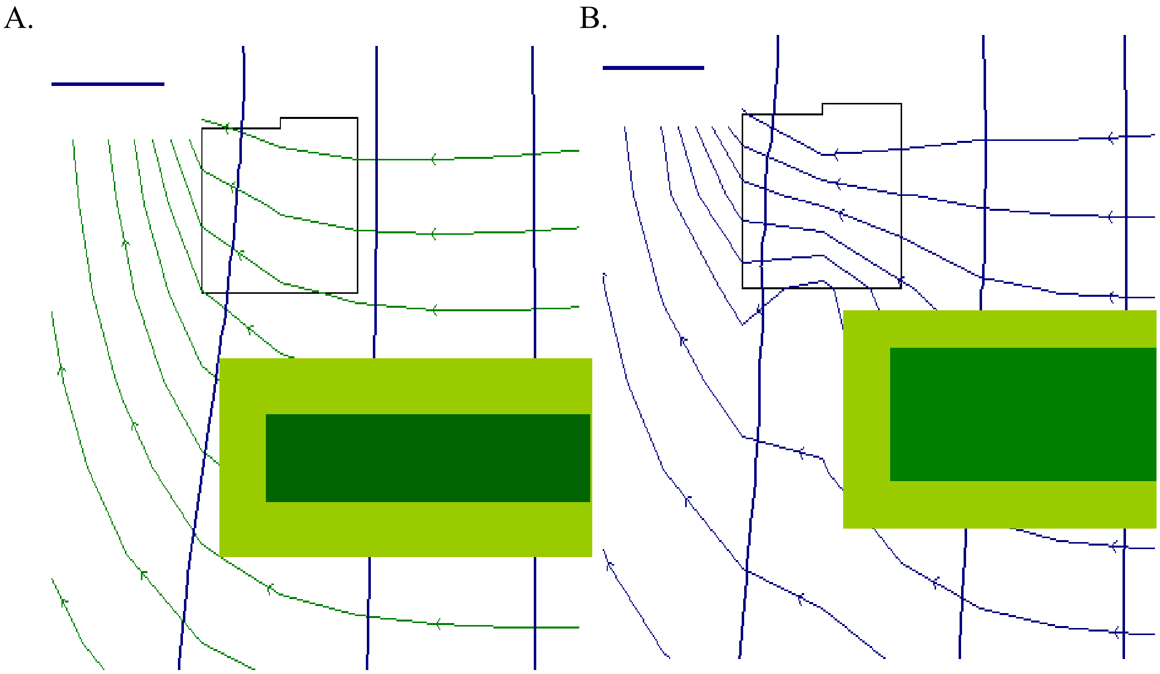

Figure 2. A computer generated model created by Richard McHorney describing the importance of the hydraulic conductivity of the barrier. Image A shows the groundwater flowing through the barrier at an equal hydraulic conductivity as the surrounding soil and what the projected pattern of the nitrate plume in the groundwater will be and image B shows the nitrate plume and groundwater flow changing with an increased hydraulic conductivity of the barrier (Richard McHorney, 2005).

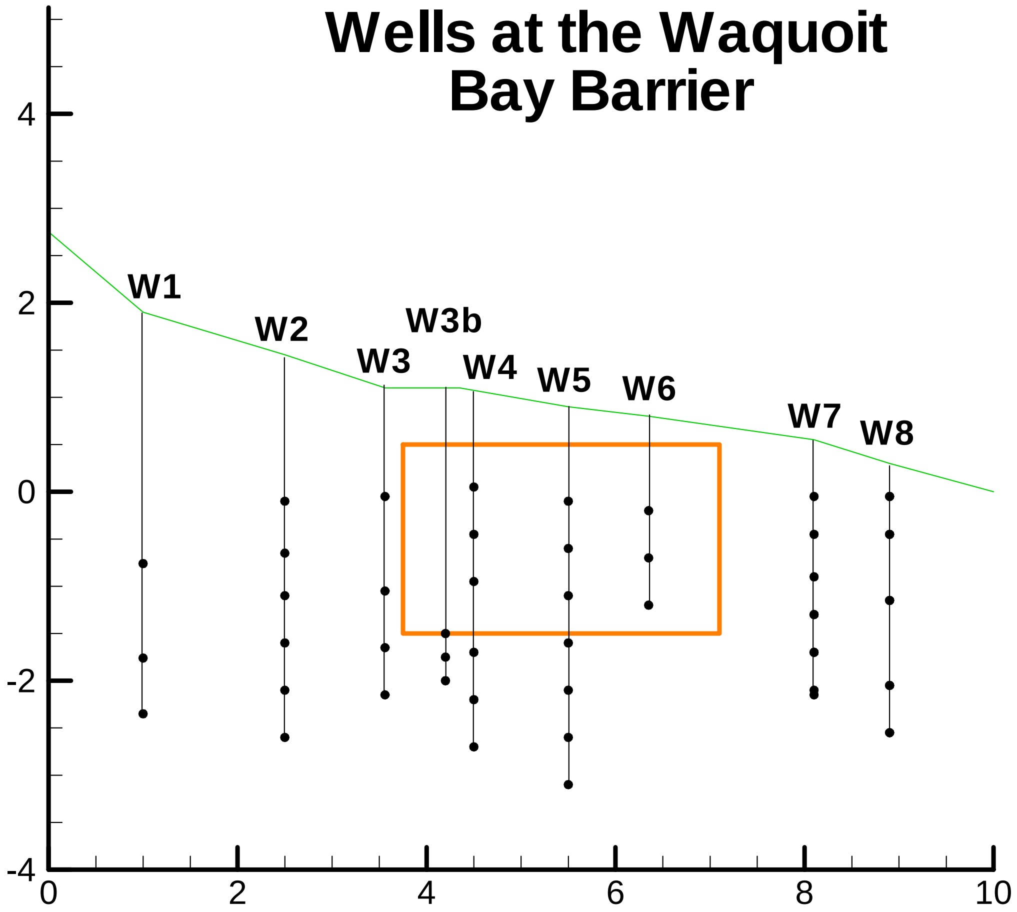

Figure 3. This is a side view drawn to scale of all 9 multi-depth cluster wells along a perpendicular gradient of the barrier. Above well 1 is the bluff and below well 8 is the ocean. The Y-axis on this figure indicates the actual elevation of each well. An elevation of 0 is at sea level. Elevation was determined by surveying using NGVD 1929. Both the X and Y-axis are in units of meters. The green line indicates the surface contour measured from the top of each well. The barrier is shown here by the orange box below the surface.

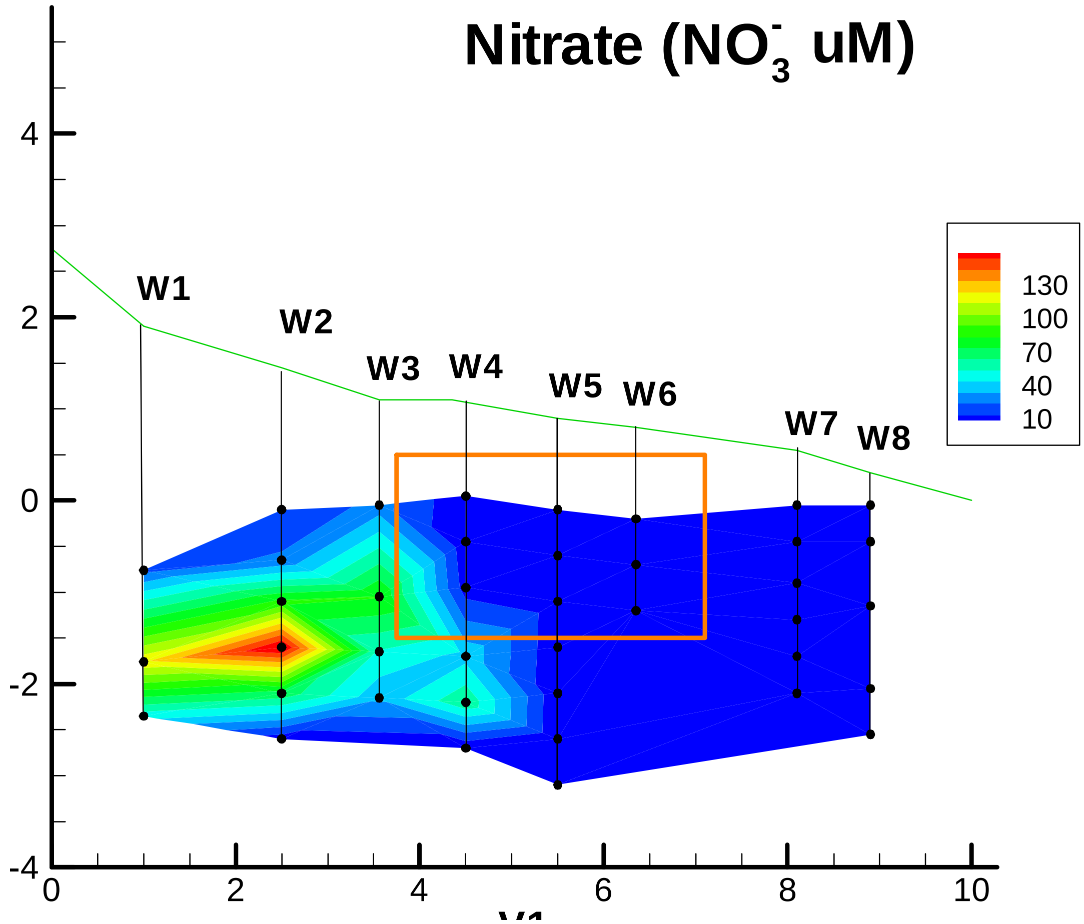

Figure 4. This figure shows the total nitrate distribution around the barrier. Samples were collected at each well point and taken back to the lab for analysis. Nitrate was measured at the highest concentration of 161 uM in well 2 at a depth of 3 meters before the barrier. The lowest concentrations of nitrate are measured at many wells in and after the barrier with concentrations either at or lower than 1 uM.

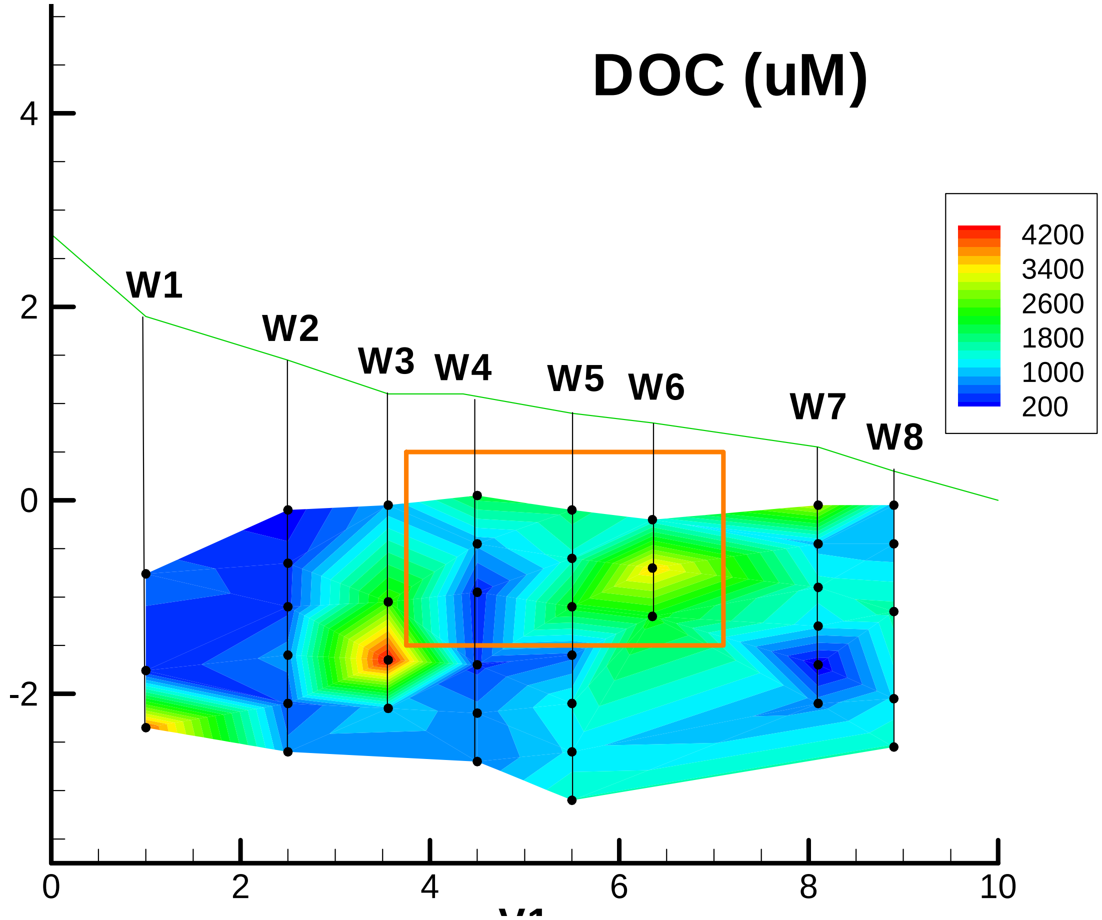

Figure 5. A scale image of the barrier and well points show the distribution of measured dissolved organic carbon (DOC) in the groundwater as it passes through the barrier. There are two concentrated areas of DOC, one with the most concentrated area at well 3 at a depth of 3.3 meters and a second located in the later portions of the barrier with the highest concentrations located at well at the depth of 1.5 meters. The highest concentrations are measured before the barrier at concentrations of ~3,900 uM. And the lowest concentrations were measured are also before the barrier at ~200uM.

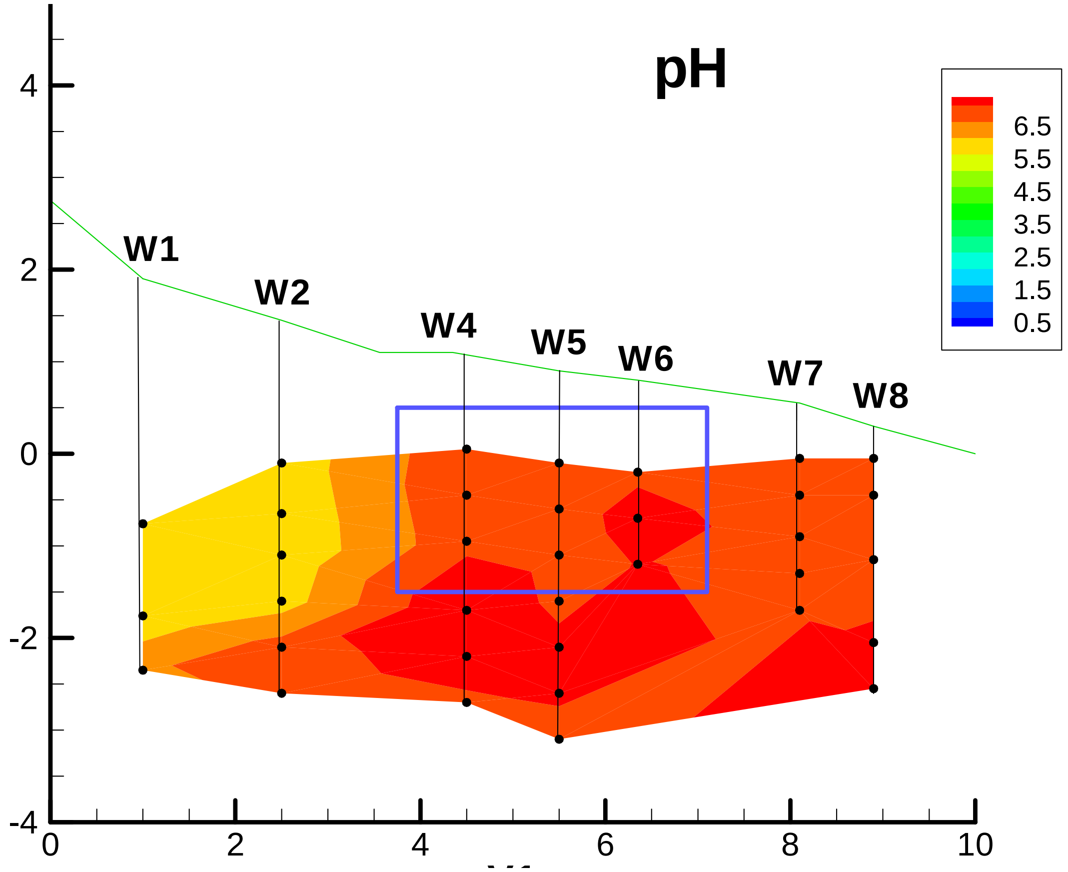

Figure 6. A scale image of the barrier plots the total acidity of the groundwater as it passes through the barrier. The highest acidity is before the barrier measuring at 5.6 and as it passes through the barrier it becomes more neutral with an increase of pH as it continues to flow through the barrier.

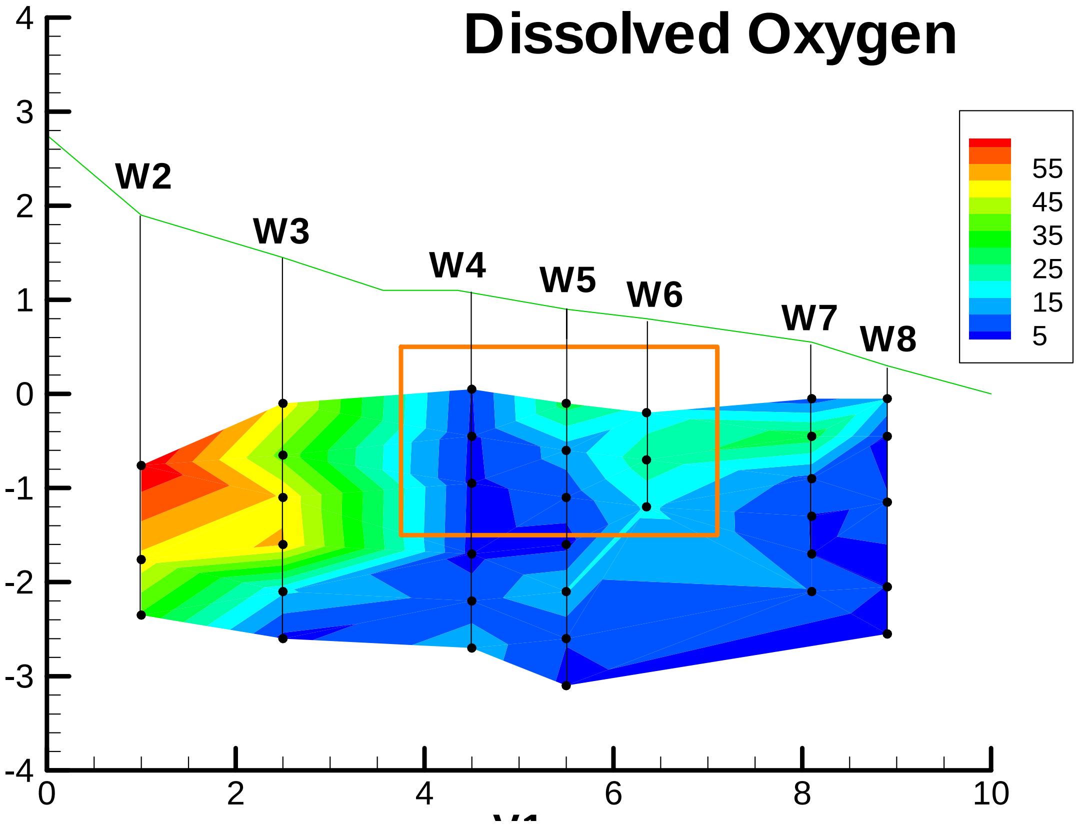

Figure 7. Dissolved oxygen (DO) is plotted on a scale image of the barrier. The DO has the highest concentration before the groundwater reaches the barrier at 60% saturation. As the groundwater begins to flow through the barrier the DO drops to percent saturations lower than 5.

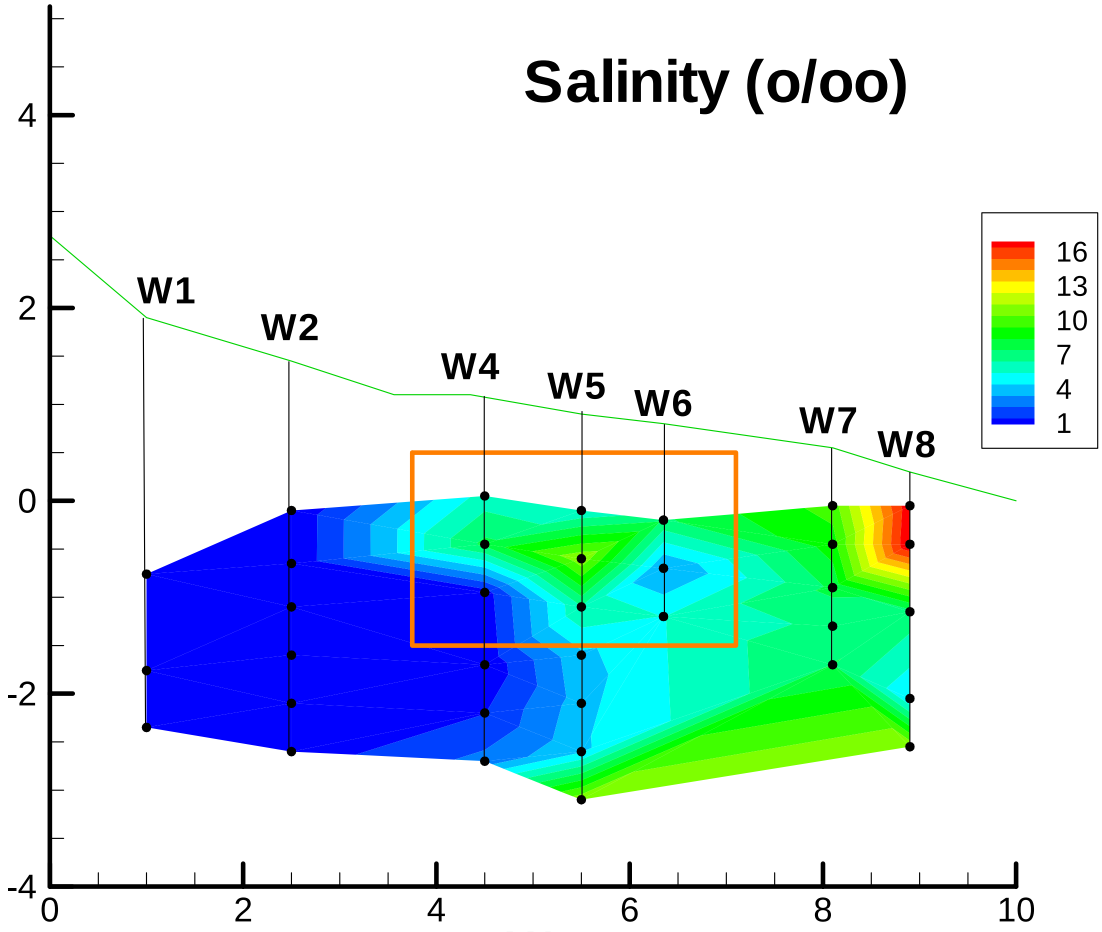

Figure 8. The salinity of all of the well points around the barrier is highest in the 8th well measuring the total of 16 parts per thousand. The lowest salinity is at the wells before the barrier with salinity measuring lower than 1 part per thousand.

Table 1. Measured depth and elevations of piesometers 1, 2, 3, and 3s along an perpendicular gradient of the barrier. Piezometer one is located at well 2. Piezometer 2 id located 0.25 meters before well 3 (outside the barrier). Piezometers 3 and 3s are located at 0.25 meters after the 4th well.

12/1/2005 Barrier Piezometer measurements and sampling times starting 12/01/2005-12/0/2005

	date	1-Dec						
	sample #	1	2	3	4		5	6
Piezo #	TOC	12:12	14:12	16:12	18:07	19:11	20:03	21:50
	time from initial (hr)	0	2	4	6	7	8	10
	elev							
P1	4.57	2.58	2.93	3.3	3.58	3.61	3.52	3.31
		1.99	1.64	1.27	0.99	0.96	1.05	1.26
P2	3.24	1.21	1.62	2.02	2.31	2.32	2.21	1.97
		2.03	1.62	1.22	0.93	0.92	1.03	1.27
P3	4.41	2.4	1.78	3.2	3.49	3.49	3.4	3.14
		2.01	2.63	1.21	0.92	0.92	1.01	1.27
P3s	4.41	-	-	-	-	-	-	-
		-	-	-	-	-	-	-

	date	2-Dec						
	sample #	7	8				9	
Piezo #	TOC	0:29	4:05	5:06	6:06	7:00	8:06	9:31
	time from initial (hr)	12	16	17	18	19	20	21
	elev							
P1	4.57	3.11	3.3	3.37	3.36	3.23	2.97	2.56
		1.46	1.27	1.2	1.21	1.34	1.6	2.01
P2	3.24	1.77	2	2.07	2.04	1.91	1.61	1.16
		1.47	1.24	1.17	1.2	1.33	1.63	2.08
P3	4.41	2.94	3.16	3.23	3.22	3.07	2.78	2.35
		1.47	1.25	1.18	1.19	1.34	1.63	2.06
P3s	4.41	-	-	-	-	Piezo #	P3s	2.32
		-	-	-	-			2.09

	date							
	sample #		10					
Piezo #	TOC	10:17	11:07	12:10	13:17	14:18	15:15	16:08
	time from initial (hr)	22	23	24	25	26	27	28
	elev							
P1	4.57	2.45	2.43	2.27	2.38	2.61	2.85	3.04
		2.12	2.14	2.3	2.19	1.96	1.72	1.53
P2	3.24	1.07	1.05	0.88	1.03	1.29	1.55	1.75
		2.17	2.19	2.36	2.21	1.95	1.69	1.49
P3	4.41	2.23	2.22	2.06	2.17	2.43	2.7	2.91
		2.18	2.19	2.35	2.24	1.98	1.71	1.5
P3s	4.41	2.22	2.21	2.04	2.19	2.46	2.73	2.93

		2.19	2.2	2.37	2.22	1.95	1.68	1.48

	date			3-Dec			
	sample #			11	12	13	14
Piezo #	TOC	17:55	19:05	0:04	7:00	12:17	18:17
	time from initial (hr)	29	31	36	43	48	54
	elev						
P1	4.57	3.38	3.55	3.65	3.98	3.23	3.7
		1.19	1.02	0.92	0.59	1.34	0.87
P2	3.24	2.1	2.27	2.34	2.69	1.86	2.4
		1.14	0.97	0.9	0.55	1.38	0.84
P3	4.41	3.28	3.46	3.53	3.88	3.02	3.64
		1.13	0.95	0.88	0.53	1.39	0.77
P3s	4.41	3.3	3.47	3.52	TD(3.66)	3.05	TD(3.66)
		1.11	0.94	0.89	NA	1.36	NA

	date	4-Dec					5-Dec
	sample #	15	16	17	18	19	20
Piezo #	TOC	1:06	6:30	12:59	18:28	24:22:00	7:05
	time from initial (hr)	60	65	71	76	82	89
	elev						
P1	4.57	3.82	3.91	2.73	3.24	3.66	3.82
		0.75	0.66	1.84	1.33	0.91	0.75
P2	3.24	2.49	2.61	2.29	1.95	2.34	2.53
		0.75	0.63	0.95	1.29	0.9	0.71
P3	4.41	3.68	3.8	2.49	3.14	3.57	3.72
		0.73	0.61	1.92	1.27	0.84	0.69
P3s	4.41	TD(3.66)	TD(3.66)	2.45	3.08	3.56	TD(3.66)
		NA	NA	1.96	1.33	0.85	NA

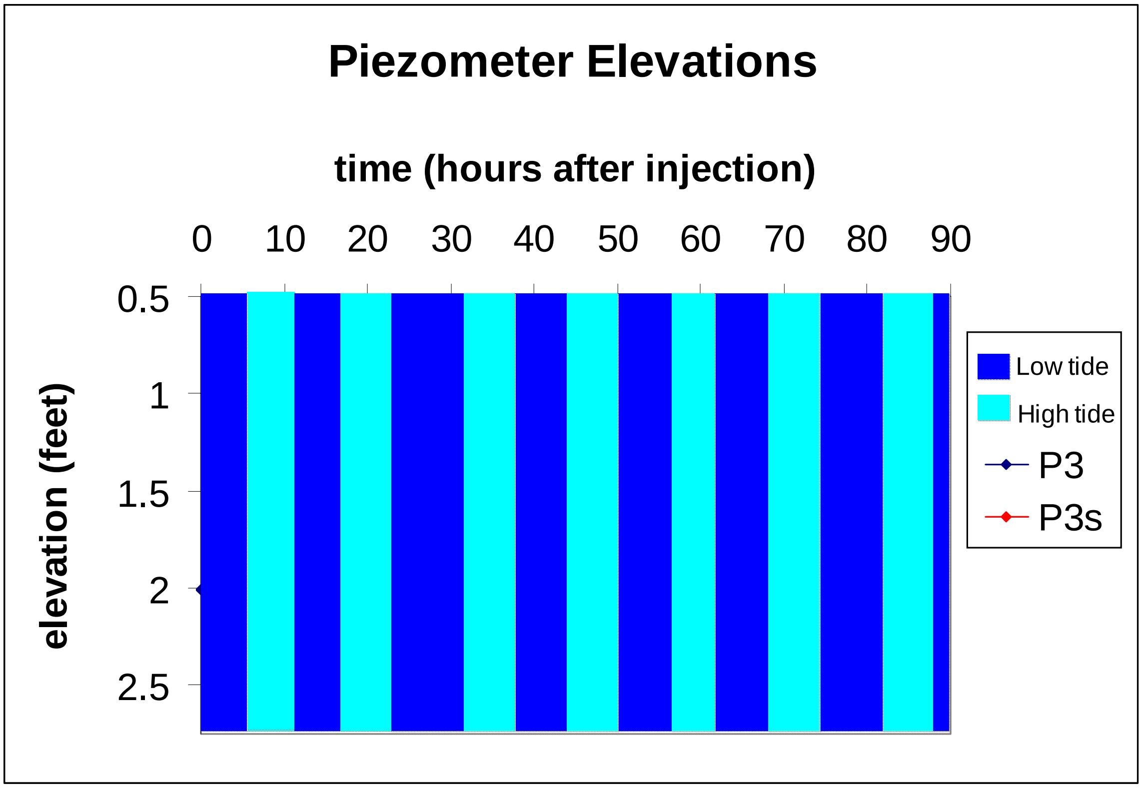

Figure 9. Piezometer 3 is located in the barrier and it reaches a depth below the barrier. Piezometer 3s is in the same location of piezometer 3 except it only reaches to a depth of 3.66 feet, which is located within the barrier. The difference between the two (0.1-0.2 feet) indicate that the tide is influencing the water table within the barrier.

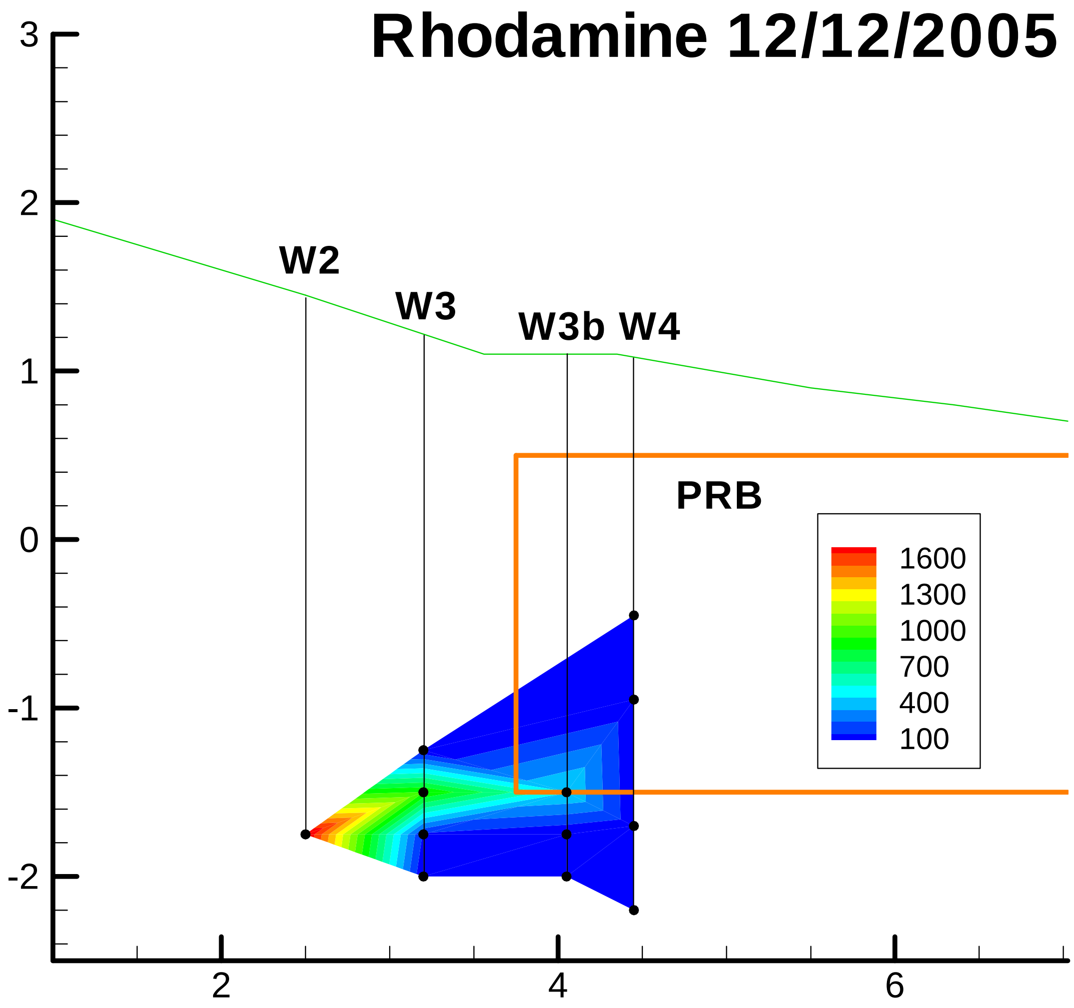

Figure 10. Rhodamine was injected into well 2 at a depth of 3 meters at a concentration of 2500 ug/L to measure the flow patterns of groundwater through the barrier. Eleven days later the Rhodamine concentration in the injection well decreased to a concentration of 1725 ug/L. On December 12, 11 days post injection, the Rhodamine concentration was still highest at the injection depth in well 2. Over time the Rhodamine did travel up through the barrier to a depth of 2.5 meters in wells 3 and 3b.

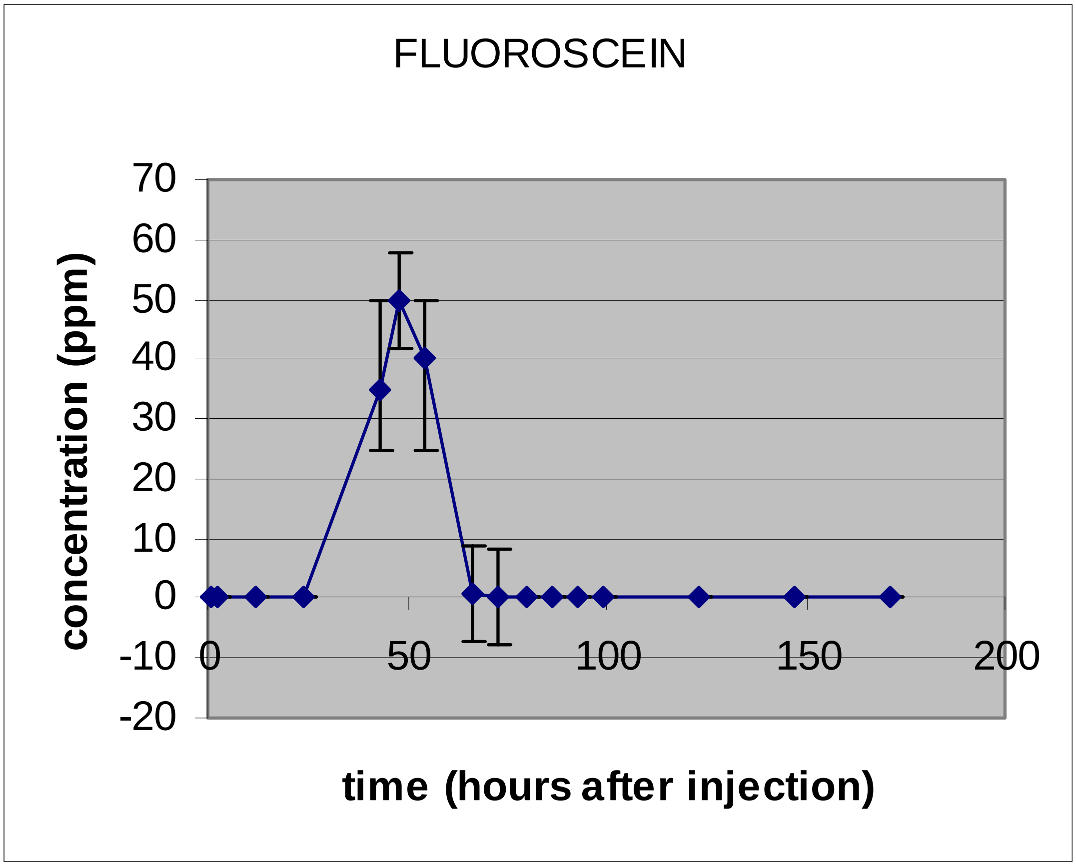

Figure 11. Fluoroscien was injected into well 2 at 4 meters deep at a total concentration of 100 ppm. 36 hours after injection fluoroscein started to show in well 3 at a depth of 3.8 meters. The concentration of the fluoroscein peaked at 48 hours with a concentration of about 50ppm. Concentrations were determined by comparing the color of the sample to a series of known dilutions. The error bar indicates the possible range of concentration between each of the dilutions.