

**Nitrate Removal in NITREXTM Permeable Reactive Barriers:
Investigating Denitrification Using a ¹⁵NO₃ Tracer.**

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ABSTRACT

Eutrophication from anthropogenic nutrient loading (particularly of nitrate) to aquatic systems is a growing problem. The NITREX™ Permeable Reactive Barrier (PRB) is a system for removing nitrate in groundwater. We investigated the nitrate removal processes and hydrology of a PRB in Waquoit Bay. Denitrification is assumed to be the primary removal process in NITREX™ medium barriers, but there are several other possible processes such as dissimilatory nitrate reduction to ammonium (DNRA) that could be removing nitrate. We attempted to quantify the importance of denitrification to overall nitrate removal using a $^{15}\text{NO}_3^-$ tracer experiment. An injection solution containing $500\mu\text{M } ^{15}\text{KNO}_3$, 100ppm fluorescein and 40mM KBr (as a conservative tracer) was injected into the barrier and a nearby section of beach as a control. Groundwater samples were collected and analyzed for nutrients and N_2 . Bromide and nitrate concentrations were used to investigate the differences in flow patterns between the beach and the barrier. Bromide was also used to calculate dilution of the injection. N_2/Ar analysis was done using membrane inlet mass spectrophotometry. Signals of $^{30}\text{N}_2$ in the barrier were higher than the beach, indicating denitrification occurred. Percent denitrification was very low, ranging from 1-14%, averaging 5%. This was inconsistent with some previous findings from similar studies. However, this data, combined with downgradient groundwater samples, implies that one of more of the other possible nitrate removal processes is at work.

KEYWORDS: *nitrate removal, denitrification, permeable reactive barrier, dissimilatory nitrate reduction to ammonium (DNRA), ^{15}N tracer method*

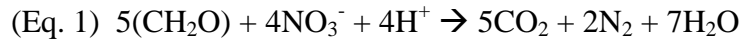
INTRODUCTION

In Cape Cod and around the world, coastal ecosystems have become heavily impacted by human activities on land. One of the major problems humans have caused is eutrophication by increasing the nutrient loads to these areas. Eutrophication can cause macro-algae and phytoplankton blooms, as well as increased epiphytes that grow on seagrasses (Valiela, 1995). Phytoplankton, macro-algae, and epiphytes reduce the amount of light reaching seagrasses, eventually killing them. Over the past 50 years in Waquoit Bay (Cape Cod, Massachusetts), there has been a replacement of native eelgrass (*Zostera marina*) by macro-algae (Valiela et al., 1992). Eutrophication in the bay has not only altered the natural habitat for benthic organisms, but also increased the number of anoxic events and corresponding fish kills (Valiela et al., 1992).

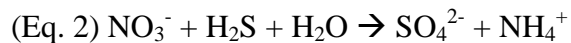
Much of the eutrophication is due to the huge increase in the number of people coming to visit or live on Cape Cod. High population density areas, like those near Waquoit Bay, add large

amounts of wastewater and lawn fertilizer to the nutrient load through groundwater entering the bay. Most people on Cape Cod just have a standard septic tank which removes pathogens and break down organic matter from human waste, but does not remove nitrate. Nitrate is a key nutrient for photosynthetic organisms and in marine aquatic systems, nitrogen tends to be the limiting nutrient (Howarth, 1988). Plumes from septic tanks put extremely high levels of nitrate into groundwater that seeps into coastal waters, contributing to eutrophication. In Waquoit Bay, groundwater that has intercepted these plumes enters the bay with nitrate concentrations estimated to be 1-3 orders of magnitude higher than the concentrations within the bay (Charette et al., 2001).

As the Cape Cod population continues to grow and the effects of eutrophication worsen, people have begun to think about how to decrease the nutrients in the groundwater. Through funding from the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET), an alternative system for reducing the high nitrate concentrations in the groundwater entering the bay is being tested. The CICEET project has installed NITREXTM Permeable Reactive Barrier (PRB) in two locations: one in the Childs River and one at the head of the bay. In a freshwater study in Ontario, NITREXTM barriers were able to reduce nitrate concentrations by 96% (Robertson et al. 2005). The barrier is essentially a trench filled with wood chips about one meter under the surface of the beach that allows groundwater to pass through it. The wood chips are both a substrate for growth and carbon source for a microbial community. As nitrate rich groundwater flows into the barrier, microbial processes remove the nitrate. So far, studies on these types of barriers have assumed that the main nitrate removal process is denitrification. Denitrification is a microbial process that takes place in anoxic environments (such as the barrier) and reduces nitrate (NO_3^-) to nitrogen gas (N_2).



One study in New Zealand has shown that denitrification can be the main removal process, but it did not rule out that there are other possible nitrate removal processes at work in these barriers (Schipper and Vojvodic'-Vukovic', 2000). One possible process is N-immobilization in microbial biomass. Microbes in the barrier could be immobilizing nitrate and assimilating the nitrogen into their biomass. Another possible process is dissimilatory nitrate reduction to ammonium (DNRA).



This is very possible in Waquoit Bay because, unlike the Ontario barrier, the Waquoit Bay PRB is exposed to salt water infiltration. This salt water brings sulfates into the barrier. DNRA microbes need the sulfides produced from sulfate reduction, so this would be an ideal environment for DNRA microbes. Sulfides also inhibit denitrification, improving the chances that DNRA plays a more important role in nitrate removal (Burgin and Hamilton 2007). DNRA nitrate removal is less effective than denitrification because the ammonium produced from DNRA is more bio-available to organisms in the bay. It can then be continued to be recycled in the ecosystem. In contrast, denitrification “permanently” removes the nitrogen from the ecosystem by reducing it into a gas.

In my study, I first needed to establish that nitrate removal was still occurring in the Waquoit Bay barrier. After that, I wanted to investigate the fate of nitrate in the barrier because it

appears that there are several possibilities. Specifically, I was interested in the effectiveness of the barriers in terms of amount of nitrate removed by denitrification. How important was denitrification to nitrate removal? By injecting isotopically labeled nitrate, I was able to track the nitrate and estimate how much of the labeled nitrate ended up as nitrogen gas using membrane inlet mass spectrometry. This provided me with an estimate of how much nitrate was removed by denitrification. Any nitrate that was unaccounted for by the gas analysis suggests that DNRA or biomass immobilization may be playing a more significant role in nitrate removal than expected and this system may need to be reevaluated if it is to become a viable method of reducing eutrophication.

METHODS

Site Description

I studied the NITREXTM Permeable Reactive Barrier located in the Waquoit Bay National Estuarine Research Reserve (WBNERR) in East Falmouth, Massachusetts (figure 1). This 825 acre bay is fairly shallow bay with an average depth of less than 3m (WBNERR Website). The bay water is brackish: freshwater enters the north end of the bay and saltwater enters from the southern end.

The NITREXTM PRB consists of a mixture of wood chips and limestone. It is approximately 1m underneath the beach surface on the bay's northern shore. The barrier is roughly 3m wide by 2m deep and runs under a 20m length of the beach. Groundwater flow runs downhill from a bluff, through the barrier and into the bay.

Sampling Well Installation

We installed two grids of sampling wells using a slide hammer to drive steel pipe through which 0.25 inch ID nylon tubing was threaded to the desired depths along the beach. Attached to the tubing at the end of each drive pipe was a releasable stainless steel drive point that was perforated and screened to allow sampling of groundwater. One grid was installed within the barrier and one grid was installed in the beach next to the barrier as a control. The grids were approximately the same distance from the low tide line. Each grid was made of five different wells, spaced 0.25m from each other (figures 2, 3). Four of the wells had three sampling depths at 1.5m, 1.75m, and 2m below a reference point at the surface. The fifth well (also called well “U” for “upgradient well”) had one sampling depth at 1.75m. This well was originally the injection site for our tracer solution, but instead it became our lone up-gradient well.

Fluorescein Tracer Study

I performed an exploratory qualitative study of the flow patterns in the two grids to better understand their hydrodynamics. Using fluorescein as a tracer, I injected one liter of 20ppm fluorescein solution into the U well of each grid around high tide. Samples were collected using a 60ml syringe, purging the first 60 ml to clear the well point tubing. Wells were checked for fluorescein breakthrough every two hours over five time points. Only colored samples were kept for analysis and a full suite (every depth, every well) of samples from each grid was collected after 24 hours. The kept samples were compared to a comparator of eight different fluorescein concentrations.

At the same time, we monitored the water table height in both the barrier and control using piezometers and a water tape. These measurements were taken roughly every half hour to hour during the sampling period.

Rhodamine and Fluorescein Absorption Test

To ensure that the fluorescein was an appropriate visual tracer and was not being absorbed by the wood chips in the barrier, we set up a simple test. Four beakers were filled with 500ml of wood chips (from a barrier microcosm) and soaked in tracer solutions. Two were soaked in 20ppm and 1 ppm rhodamine solution and two were soaked in 20ppm and 1ppm fluorescein solution. Samples were taken every hour. Rhodamine samples were analyzed using a fluorometer, but fluorescein samples were analyzed visually for qualitative analysis.

Downgradient Groundwater Sampling

Before the injection experiment, we collected some data on the initial conditions down-gradient of the two sampling grids. At low tide, we sampled groundwater every 2m along a 20m transect using a drive point well. 5 of the samples were below the barrier and 5 samples were below the control beach (figure 4). Each sample was filtered through a glass fiber filter (GF/F) and analyzed for nitrate, ammonium, and sulfide content. Sulfide samples were analyzed using a method adapted from Gilboa-Garber (1971). Nitrate and ammonium samples were analyzed using the same method as other groundwater samples (see below).

¹⁵N Injection Experiment

For the injection experiment, we prepared an injection solution with various quantitative and qualitative tracers. The solution contained 500 μ M ¹⁵N-labeled potassium nitrate (ISOTEC, minimum 98% ¹⁵N) as well as 40mM potassium bromide. Bromide was used as a conservative tracer to estimate the dilution of the injection solution. We also added 100ppm fluorescein to the

solution to visually track the injection's location and approximate dilution while we were in the field.

At approximately an hour before high tide, two liters of the tracer solution were slowly pumped into well 1 at 1.75m depth in each grid. Samples were collected at three different time points: 3-4 hours after injection (low-mid tide), ~18 hrs after injection (mid-high tide) and ~48 hours (low tide) after injection. At every time point, samples were collected from all wells and at all depths. The sampling suite at each well and depth included nitrate, ammonium, bromide, and N₂/Ar samples. Water was pulled up from the well point using a GeoPump at a low rate so that we did not induce a head pressure. 60-100 ml of water was pumped out to purge the tubing of residue from the last sample or other contaminants before analytical samples were taken.

We also collected data on tide height and water table height during the injection sampling. For most time points, we recorded the tide height using a meter stick and the water table height using piezometers and a water tape.

N₂/Ar Sampling and Analysis

Nitrogen and argon gas samples were stored in exetainers to reduce the chance of introducing air from the atmosphere. Samples were also treated with 25μL of concentrated mercuric chloride. This killed microbes in the sample, halting any microbial processes that would alter the gas or nutrient content of the samples. Exetainers were stored in a 9°C water bath until they were analyzed using a membrane inlet mass spectrometer (MIMS).

Nitrate, Ammonium and Bromide Sampling and Analysis

All samples used for nitrate, ammonium and bromide analysis were filtered through glass fiber filters (GF/F) into scintillation vials. Nitrate samples were frozen until analyzed on a

Lachat Flow Injection Analyzer using a method adapted from Wood et al. (1967). Ammonium and bromide samples were refrigerated until analysis. Bromide was analyzed on a Dionex™ DX-120 Ion Chromatograph. Ammonium was analyzed using a colorimetric analysis method adapted from Strickland and Parsons (1972).

Dilution Calculations

We used the following equations to calculate dilution factors based on bromide concentrations:

$$(Eq. 3) \underbrace{\frac{Br_I}{(Br_S - Br_B)}}_{\text{dilution factor}} * (NO_{3S} - NO_{3B}) = NO_{3R}$$

$$(Eq. 4) NO_{3I} - NO_{3R} = NO_3 \text{ removed by processes in barrier}$$

Br_I = bromide in injection

Br_S = bromide in sample

Br_B = background concentration of bromide

NO_{3S} = nitrate in sample

NO_{3B} = background concentration of nitrate

NO_{3I} = nitrate in injection

NO_{3R} = NO_{3I} remaining in sample

The background bromide and nitrate concentrations were estimated from samples taken from the injection well right before the solution was injected.

We then used signal data from the N₂/Ar analysis with MIMS to calculate the concentration of ³⁰N₂ and the corresponding amount of ¹⁵NO₃ needed to create that gas. We used a solubility table to find the equilibrium concentration of gas, accounting for salinity and temperature. The equilibrium concentration represented the concentration of all masses of N₂. We calculated an average response factor (concentration of gas corresponding to amount of signal) from the ²⁸ and ²⁹N₂ data to convert from signal to concentration. Knowing the natural

abundances of $^{14}\text{N} = 99.64\%$ and $^{15}\text{N} = 0.36\%$, we used a Hardy-Weinberg equilibrium type equation to predict the formation probability of 28 , 29 , or $^{30}\text{N}_2$. We used the following equations:

$$\text{Probability of } ^{28}\text{N}_2 = ^{14}\text{N} * ^{14}\text{N} = (0.9964)^2$$

$$\text{Probability of } ^{29}\text{N}_2 = ^{14}\text{N} * ^{15}\text{N} = (0.9964 * 0.0036)*2$$

$$\text{(Eq. 5) } \frac{[N_2]@ \textit{equilibrium} * (0.9964)^2}{^{28}N_2 \textit{signal}} = ^{28}\text{N}_2 \text{ response factor}$$

$$\text{(Eq. 6) } \frac{[N_2]@ \textit{equilibrium} * (0.9964 * 0.0036) * 2}{^{29}N_2 \textit{signal}} = ^{29}\text{N}_2 \text{ response factor}$$

We then calculated the nitrate needed to produce the gas. Using this information, the dilution factors and nitrate removal, we calculated the percent of nitrate removal attributed to denitrification.

RESULTS

Tidal Flow

Overall, the difference in water table height (difference between the water table height in an upgradient piezometer and a downgradient piezometer) was larger and more varied in the control site than in the barrier site (figure 5). The positive numbers mean that the water table is slanted downward towards the bay. The height difference reached its maximum in the control site shortly after low tide, but the barrier site stayed relatively constant throughout the entire sampling period. When looking at the tides, high and low tide heights were very extreme during

the injection experiment (November 28-30, 2007) which was a spring tide (figure 6). Tide height at our site ranged from 50cm (on a tide stick) to -10cm (figure 7).

Visual Tracers

The absorption test for rhodamine showed that the concentration of the solution decreased by half after the first hour of soaking (table 1). Based on qualitative visual analysis, there appeared to be no change in the concentration of the fluorescein solution over the sampling period.

Groundwater Nutrients and Bromide Tracer

Nitrate concentrations in groundwater were much lower downgradient of the barrier than the control beach (figure 8). However, ammonium and sulfide concentrations were lower downgradient of the control beach than the barrier (figures 9, 10). In the grids, nitrate concentrations were also generally much lower in the barrier than in the control beach. For wells U, 1, and 3, nitrate stayed below $7\mu\text{M}$ in the barrier, but reached concentrations over $200\mu\text{M}$ in the control (figures 11, 12).

In these same wells (U, 1, 3), there were spikes (over the background) in both nitrate and bromide concentrations across the sampling time points. At time 1 (T1) in both the control and the barrier, the injection site (well 1, depth 1.75m) showed a peak in nitrate and bromide concentration (figures 11, 12). In the control, this peak disappeared from the injection well at T2 but reappeared in well 3 at the same depth (figure 11). The bromide peak in the barrier repeated itself at T2 in the same well as the first peak, but at a lower depth (figure 12). The nitrate peak,

however, does not appear at this lower depth at T2. There is also a nitrate and bromide peak in the upgradient well at T1 in the control (figure 11).

Nitrogen Gas Signals

$^{30}\text{N}_2$ signals from control samples remained close to the baseline concentrations ($R^2 = 0.999$, figure 13). The baseline concentration represents what the MIMS reads when at rest. In contrast, many samples from the barrier had $^{30}\text{N}_2$ signals that were higher than the baseline ($R^2 = 0.998$, figure 13). 29 and $^{28}\text{N}_2$ signals also showed a pattern between the control and barrier samples. With both molecular weights, barrier samples had higher signals than control samples (figures 14, 15). Generally, 29 and $^{28}\text{N}_2$ also had higher signals than any $^{30}\text{N}_2$ signals.

Nitrate Removal and Denitrification

Only six of the samples from the barrier were used to estimate denitrification due to complications calculating dilution factors. Percent of nitrate removal attributed to denitrification was very low, ranging from 1-14% with an average of 5% (table 2). Concentrations of nitrate removed by denitrification were also low, averaging $11\mu\text{M}$ among the six samples.

DISCUSSION

The control and barrier sites showed striking differences in their responses to tide changes over time. It is obvious from piezometer data that the barrier significantly changes the permeability of the beach for groundwater flow and seawater infiltration. The very stable water table height difference in the barrier shows that the barrier is probably retaining water, while the normal beach area in the control is much more responsive to the tide changes (figure 5). This

water retention, along with the spring tide cycle and the associated extreme high/low tide heights (figures 6, 7), mean that the barrier may be more susceptible to seawater infiltration and retention, especially during my sampling period. This idea will become more important later in the discussion of results from denitrification estimates.

The downgradient groundwater sampling indicates that there is still nitrate removal happening in the barrier (figure 8). The fact that the data had to be presented on a logarithmic scale to accommodate such high nitrate concentrations in the control groundwater demonstrates that the barrier is continuing to be effective in reducing these high concentrations. However, there is evidence that some of this removal may not be from denitrification as has been assumed. The higher ammonium and sulfide concentrations, as products of DNRA and sulfate reduction respectively, suggest that nitrogen may be still entering the bay but as ammonium from DNRA (figures 9, 10). Even though they are higher than the control, the concentrations are still very low in the barrier groundwater, so the contribution of DNRA is probably minimal. This is consistent with similar downgradient groundwater ammonium data from this summer found in the CICEET Project Progress Report (Vallino and Foreman, unpublished data September 2007).

From the $^{15}\text{NO}_3^-$ and bromide tracer experiment we were able to gain more knowledge on the hydrology of the system as well as nitrate removal. In data from the central axis (well U, 1, 3), it was very easy to identify the “pulse” of the injection based on high concentrations of nitrate and bromide (when compared to the nitrate background concentration). In the control grid, the pulse appears in the injection well and in the upgradient well at time 1 (T1) showing that water was actually flowing backwards into the beach at the time (figure 11). We then saw that the flow direction shifted between T1 and T2 (about a 16hr span) and the pulse moved into well 3, downgradient from the others but at the same depth. The control grid water seems to resist

vertical movement but moves back and forth horizontally. In contrast, water in the barrier grid seems to resist horizontal movement and instead moves vertically. Just like the control, the injection pulse is in the injection well at T1 and there may even be a small emergence of the pulse in the upper depth of that same well (figure 12). However at T2, only the bromide pulse has moved down in the same well but to a different depth. If the pulse has simply moved to this point, we would have expected to see the same relative dilution for both nitrate and bromide. The lack of a corresponding nitrate pulse at the same sampling point indicates that there was nitrate removal. At T3, the pulse has disappeared from both the barrier and control, either from dilution or it moved on past the sampling grid (figures 11, 12). The quick disappearance of the injection may be related to the spring tide conditions that would have created strong gradients.

N₂ gas analysis from the MIMS provided additional insight into the nitrate removal processes in the barrier. ³⁰N₂ signals indicate that there is denitrification occurring in the barrier. Because of the rarity of ¹⁵N in the natural environment, the large ³⁰N₂ signals seen over the barrier sample baseline could only come from denitrification of the ¹⁵NO₃⁻ tracer (figure 13). The ²⁹ and ²⁸N₂ signals also have higher signals in the barrier than the control (figure 14, 15). This could also be indicative of denitrification in the barrier, but it is difficult to tell solely from the signal data because it does not represent the actual quantitative concentration of the gases. In any case, it does show an interesting pattern of higher signals in barrier samples, consistent with the ³⁰N₂ data.

The denitrification estimates calculated from the MIMS signals and bromide dilutions were very different from what we expected. I expected the percentages to be low, but not as low as we found them to be. Even the highest percentage we found (14%) was only approximately half of the lowest percentages from a microcosm experiment that also measured N₂ gas using

MIMS (table 2). The CICEET Project conducted experiments using “mini” barrier systems in microcosms in the lab (Vallino and Foreman, unpublished data March 2007). There were three different treatments for the microcosms: 30psu sea water inflow, fresh ground water inflow, or 10psu tidal inflow. The lowest percentages of the amount of inflow nitrate denitrified were in the tidal inflow at 23.4-26.5% (Vallino and Foreman, unpublished data March 2007).

There are several reasons why my estimates might be so different from previous studies. It was very difficult to accurately calculate dilutions based on the bromide, particularly in the barrier. The barrier ground water was very high in chloride (salty), so samples had to be extremely diluted when analyzed on the DionexTM ion chromatograph or else it would overload the machine. With such small bromide readings, very small errors were magnified when back calculated to account for the analytical dilution. Another reason the estimates differ may have to do with how we calculated the amount of nitrate removed by denitrification. We took gas solubilities into account, but we did not correct for excess air injection and assumed that no outside air was introduced with our injection procedure. However, there were probably some gases present in the injection solution.

Finally, tidal cycle and barrier permeability characteristics may have also had an effect on the estimates. The intrusion of salt water (and the associated sulfates) from the spring tide cycle may have induced sulfate reduction. The sulfides produced from the reaction would have inhibited the final steps of the denitrification process and could have also stimulated dissimilatory nitrate reduction to ammonium (DNRA) (Burgin and Hamilton, 2007). DNRA has been shown to be coupled to sulfide oxidation processes, and sulfate reduction could have encouraged nitrate removal by DNRA instead of denitrification (Brunet and Garcia-Gil, 1996). Another final alternative to denitrification could be N-immobilization into microbial biomass,

but other studies have found that this would be very difficult to measure and little is known about it at this time (Schipper and Vojvodic'-Vukovic', 2000).

CONCLUSIONS

Studying the potential nitrate removal processes involved in permeable reactive barriers is important if they are to continue to develop and become a more viable means of stemming nutrient loading to aquatic ecosystems. Particularly for its application to coastal areas, tidal infiltration and permeability characteristics can be important to understanding the hydrology and potential chemistry in the barrier.

Previous studies suggest that denitrification is the key process in nitrate removal (Schipper and Vojvodic'-Vukovic', 2000), but from this study (and others) we can see that there is also evidence that there are other processes such as DNRA at work (Vallino and Foreman, September 2007). Maximizing the potential for denitrification in these barriers will help ensure that less of the bio-available products of other nitrate removal processes (such as ammonium) do not end up contributing to eutrophication and the destruction of natural coastal habitats.

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FIGURES

1. Aerial photograph of Waquoit Bay with locations of NitrexTM permeable reactive barriers (PRB). Red star is Child's River PRB. Blue star is WBNERR PRB on Waquoit Bay. Photograph courtesy of Ken Foreman.
2. Bird's eye view of sampling well grid.
3. Cross-sectional view of sampling well grid. Green triangle represents injection well and depth.
4. Diagram of downgradient groundwater well point locations. Red points are downgradient of barrier. Green points are downgradient of control beach.
5. Difference in water table height (in cm - downgradient piezometer height subtracted from upgradient piezometer height) across the sampling grid on November 19, 2007. Low tide was at approximately 12:00hr.
6. Water level (m) in Woods Hole, MA for November 12 - December 10, 2007. A spring tide cycle occurs during injection sampling period (November 28 – 30, 2007). From NOAA Tides and Currents Online.
7. Tide height (cm) from a reference meter stick on November 28 to 30, 2007. This was during a spring tide cycle.
8. Nitrate concentration (μM) in groundwater along a transect downgradient of the barrier and the control beach.
9. Ammonium concentration (μM) in groundwater along a transect downgradient of the barrier and the control beach.

10. Sulfide concentration (μM) in groundwater along a transect downgradient of the barrier and the control beach.
11. Nitrate and bromide concentration in groundwater samples from control grid. All axes have the same scale. Black line represents background nitrate concentration of $46.3 \mu\text{M}$.
12. Nitrate and bromide concentration in groundwater samples from barrier grid. All axes have the same scale. Black line represents background nitrate concentration of $2.7 \mu\text{M}$.
13. $^{30}\text{N}_2$ signal (volts) from membrane inlet mass spectrometry. Time represents when the sample was run and a reading was taken. Regressions and equations represent baseline signals for control and barrier samples.
14. $^{29}\text{N}_2$ signal (volts) from membrane inlet mass spectrometry. Time represents when the sample was run and a reading was taken. Regressions and equations represent baseline signals for control and barrier samples.
15. $^{28}\text{N}_2$ signal (volts) from membrane inlet mass spectrometry. Time represents when the sample was run and a reading was taken. Regressions and equations represent baseline signals for control and barrier samples.

TABLES

1. Concentration of rhodamine solution over a four and half hour sampling period.
2. Estimates of nitrate removal (μM), % denitrification, and other associated calculations for six samples from the barrier. Bold numbers at the bottom are averages of all six samples.

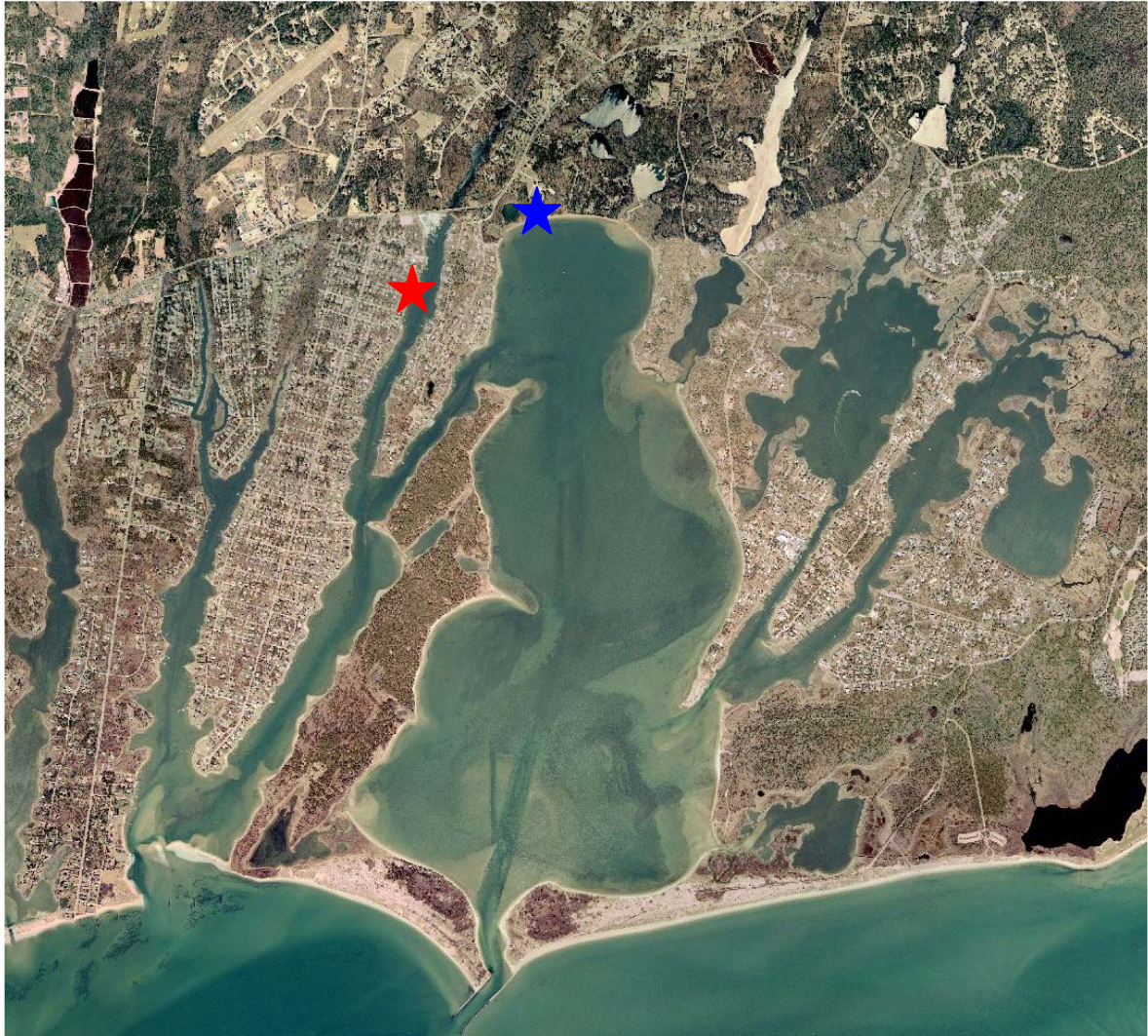


Figure 1.

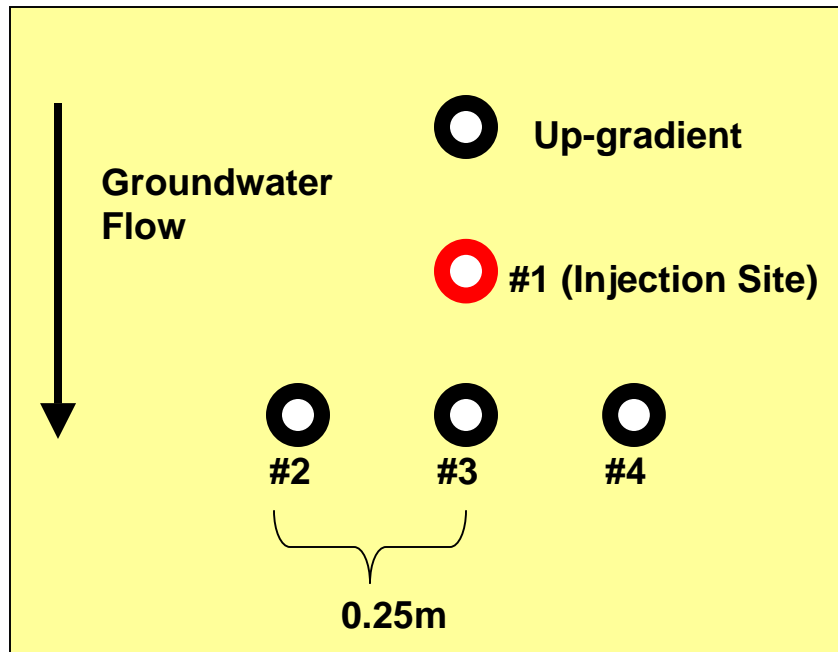


Figure 2.

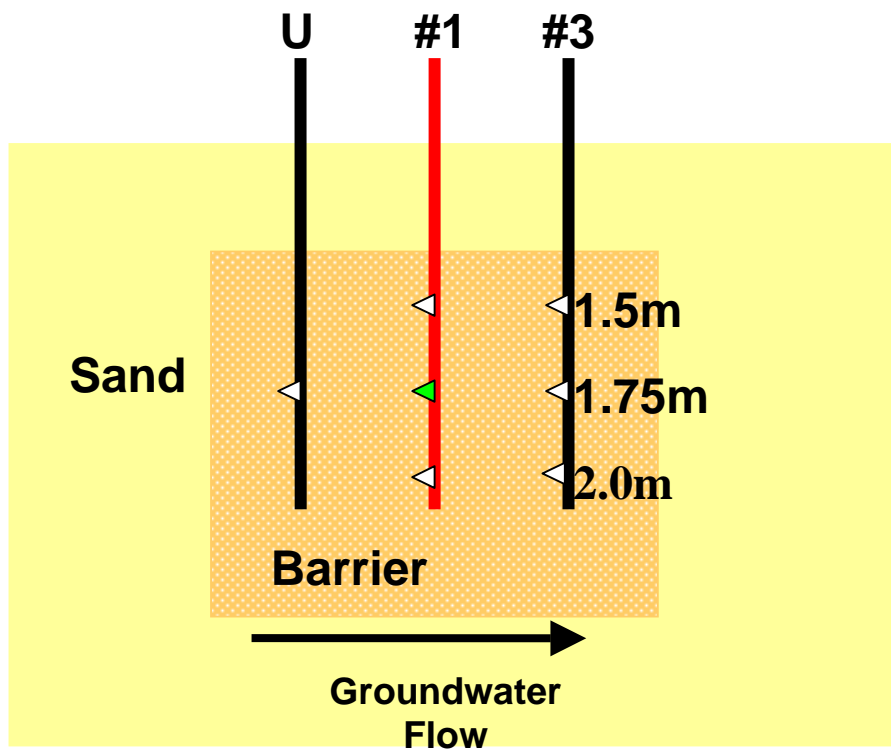


Figure 3.

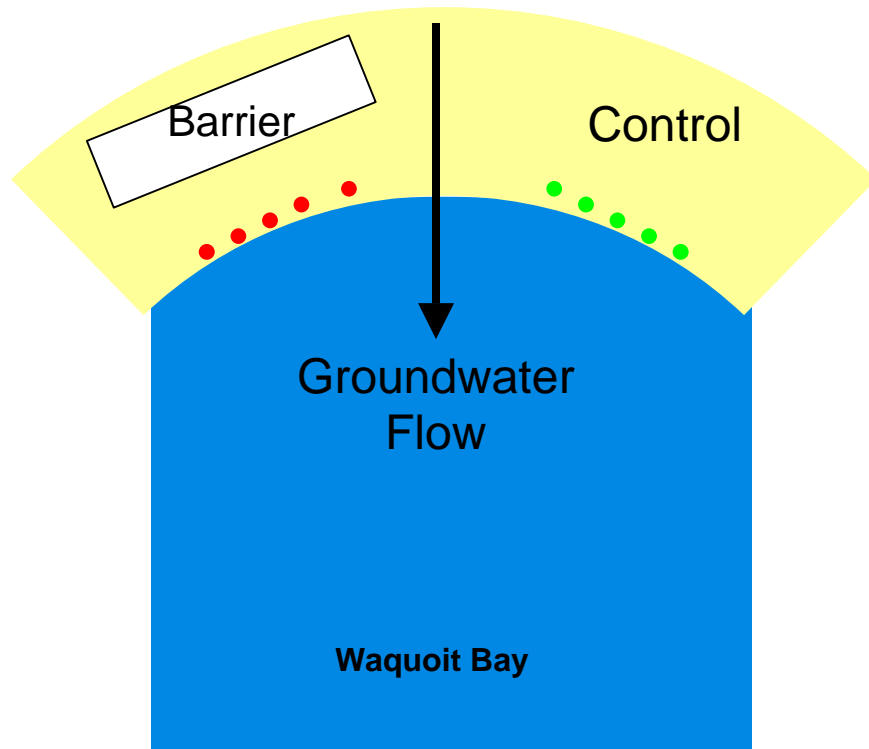


Figure 4.

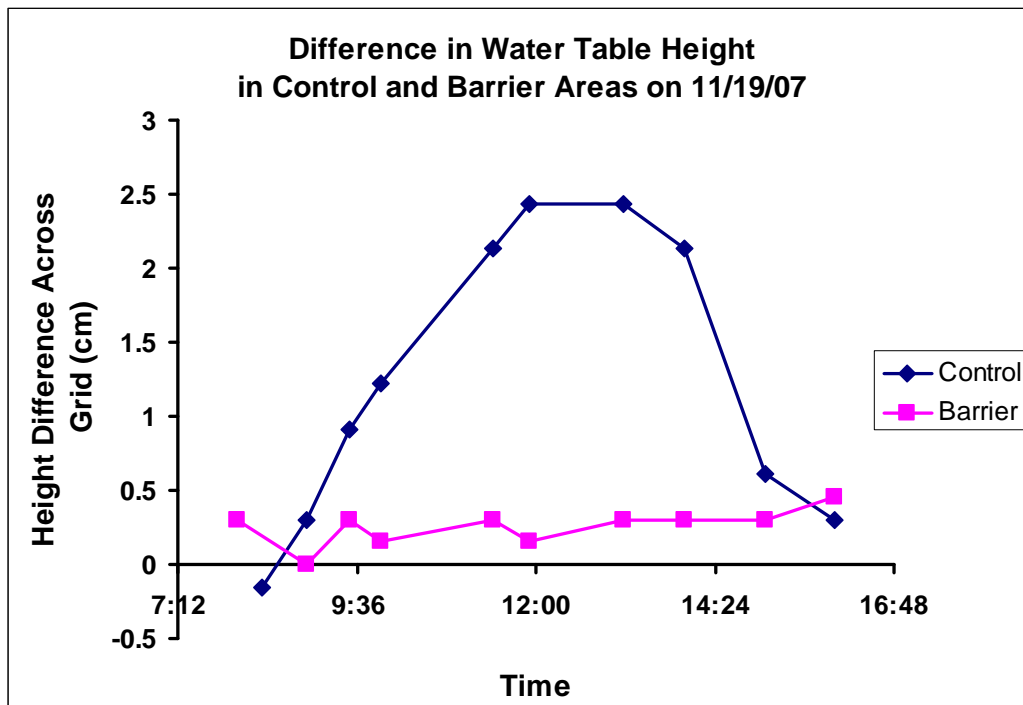


Figure 5.

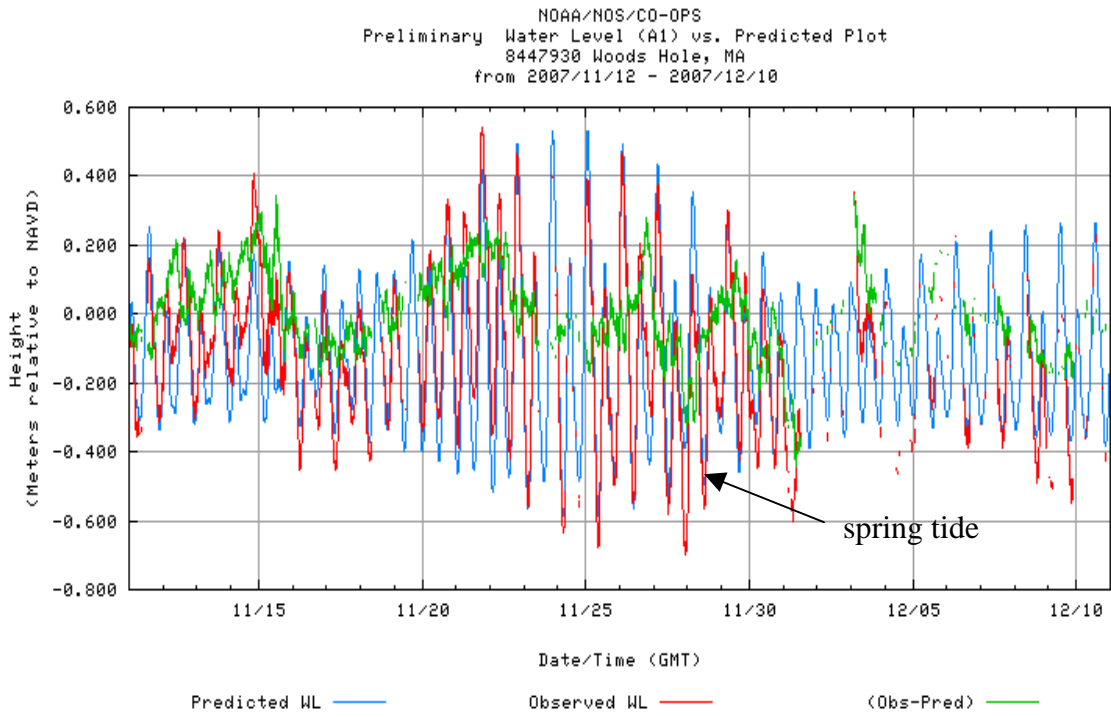


Figure 6.

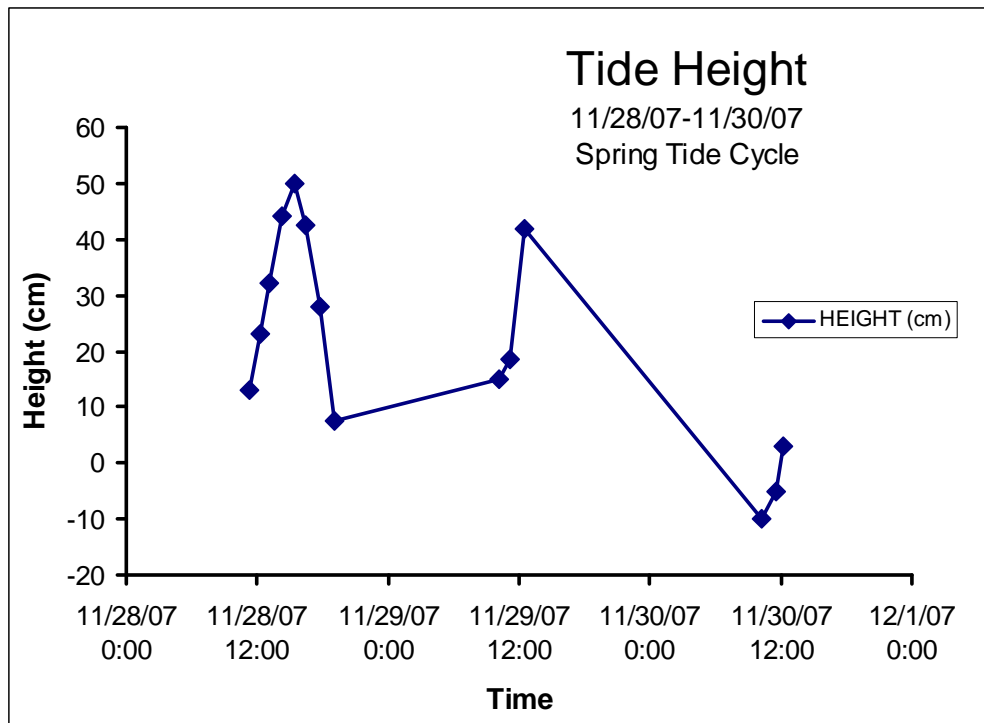


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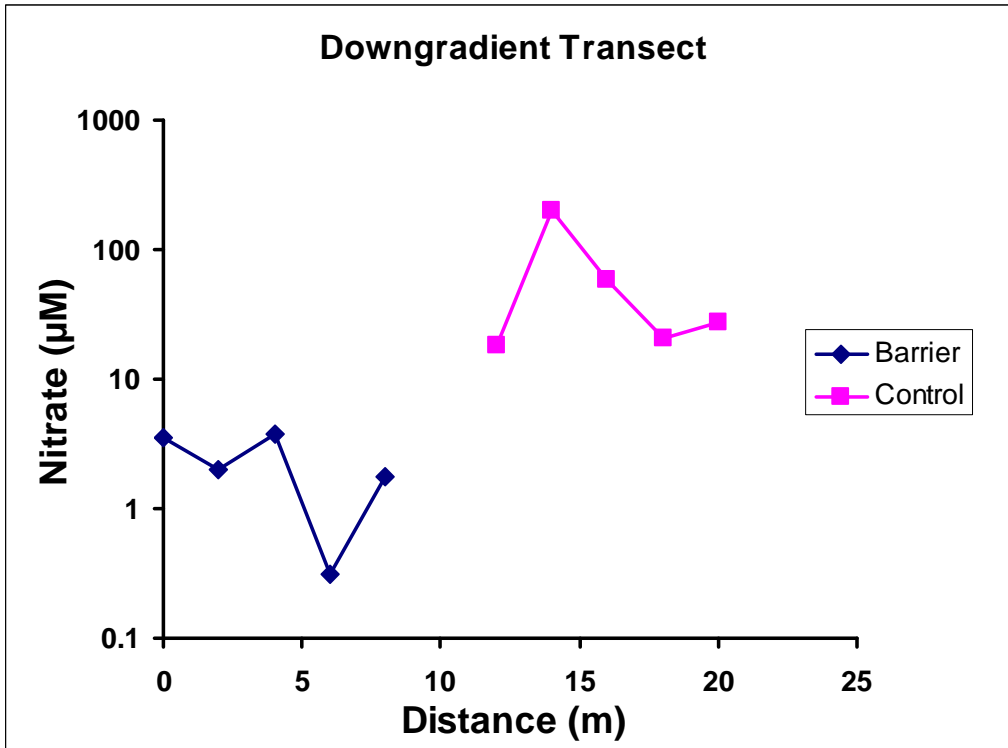


Figure 8.

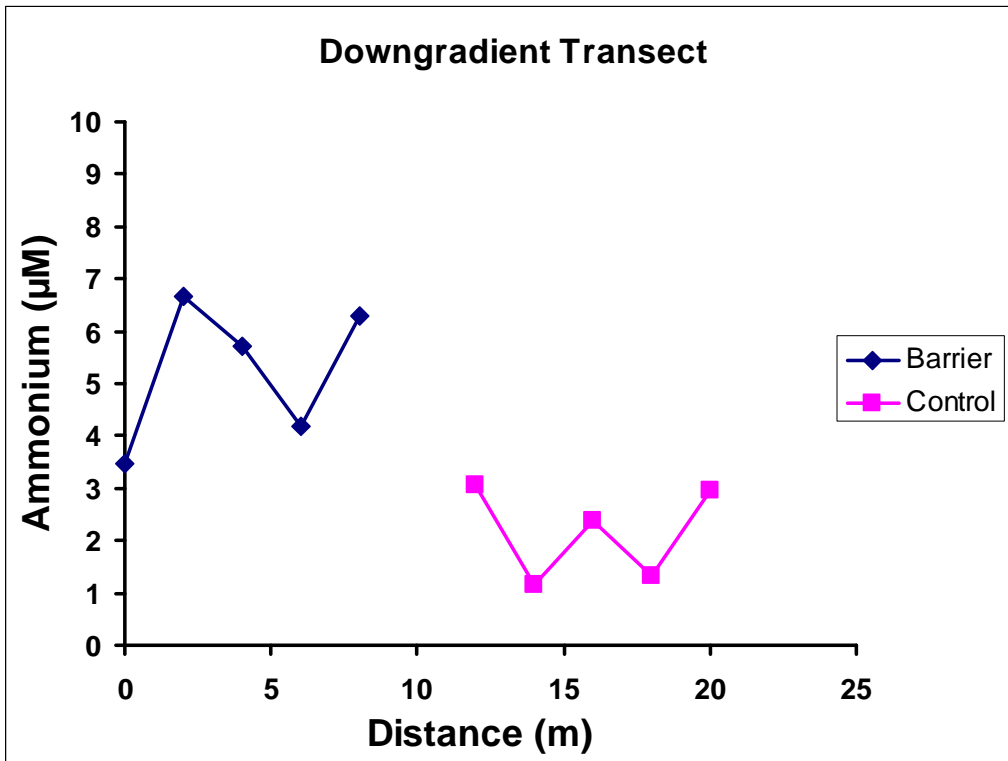


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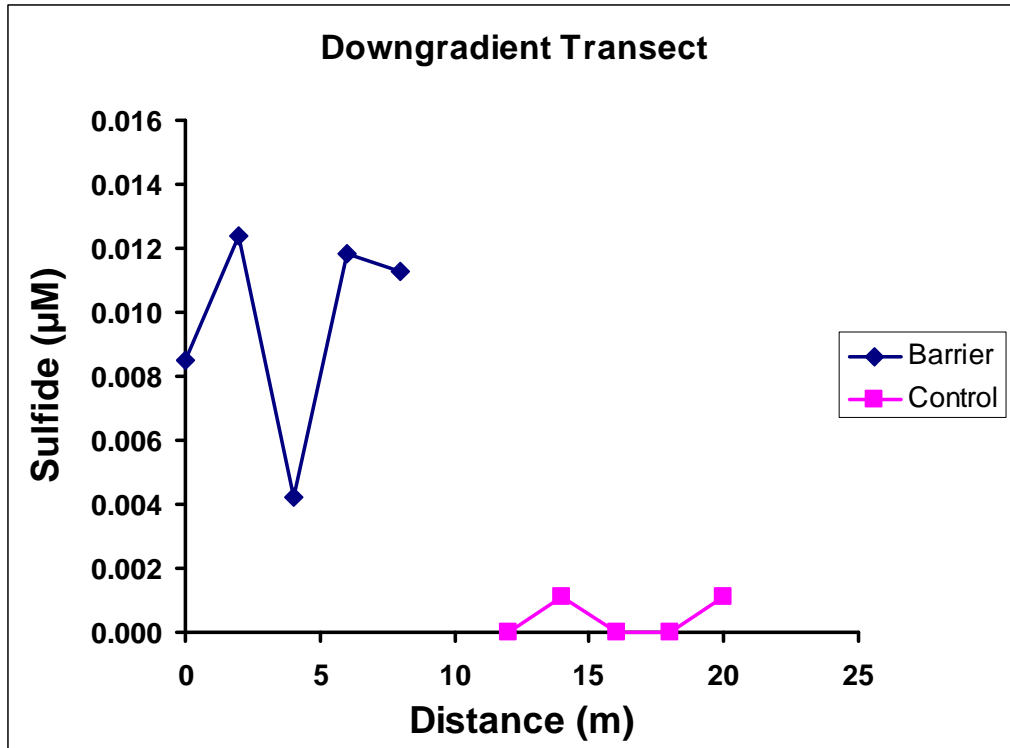


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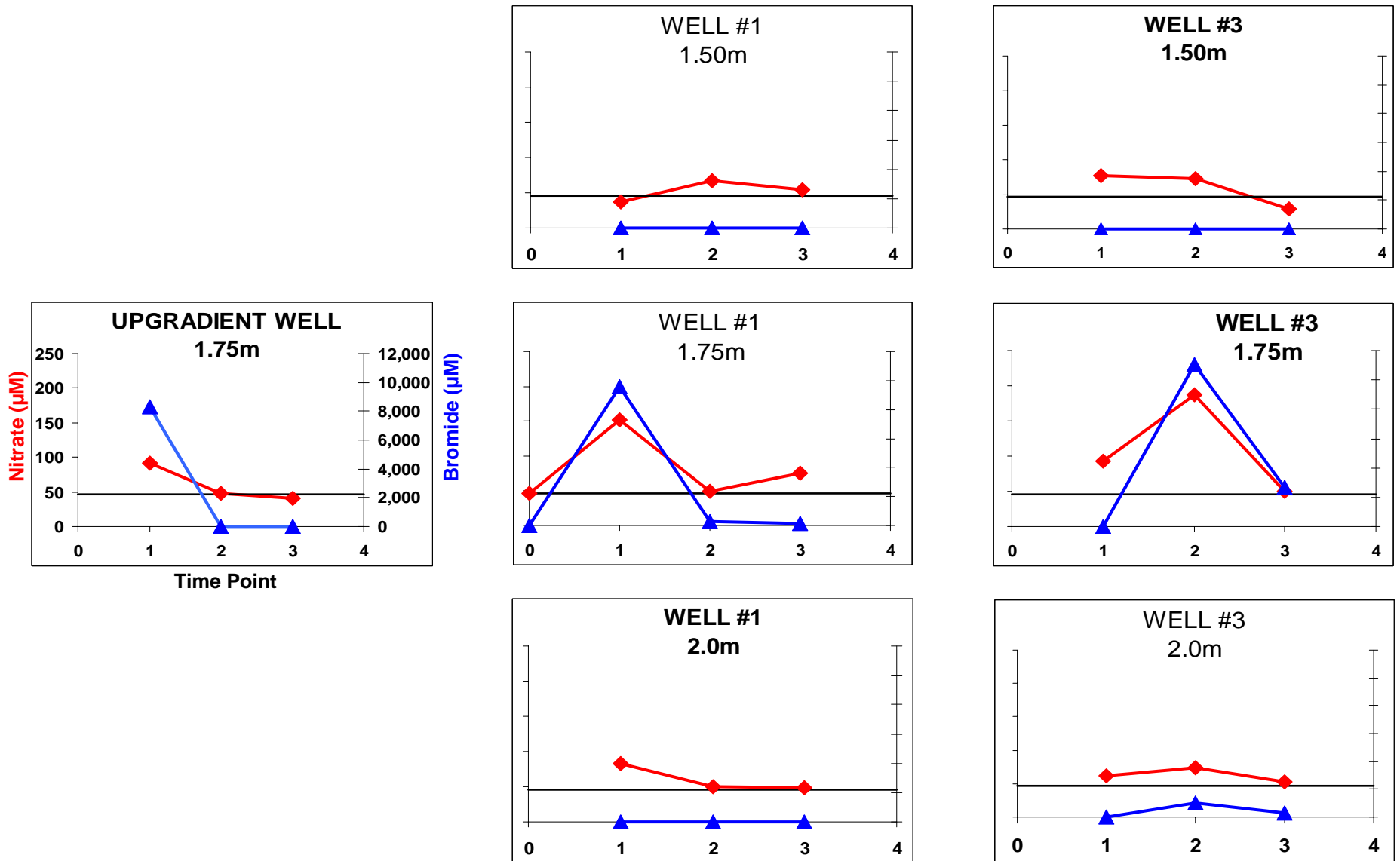


Figure 11.

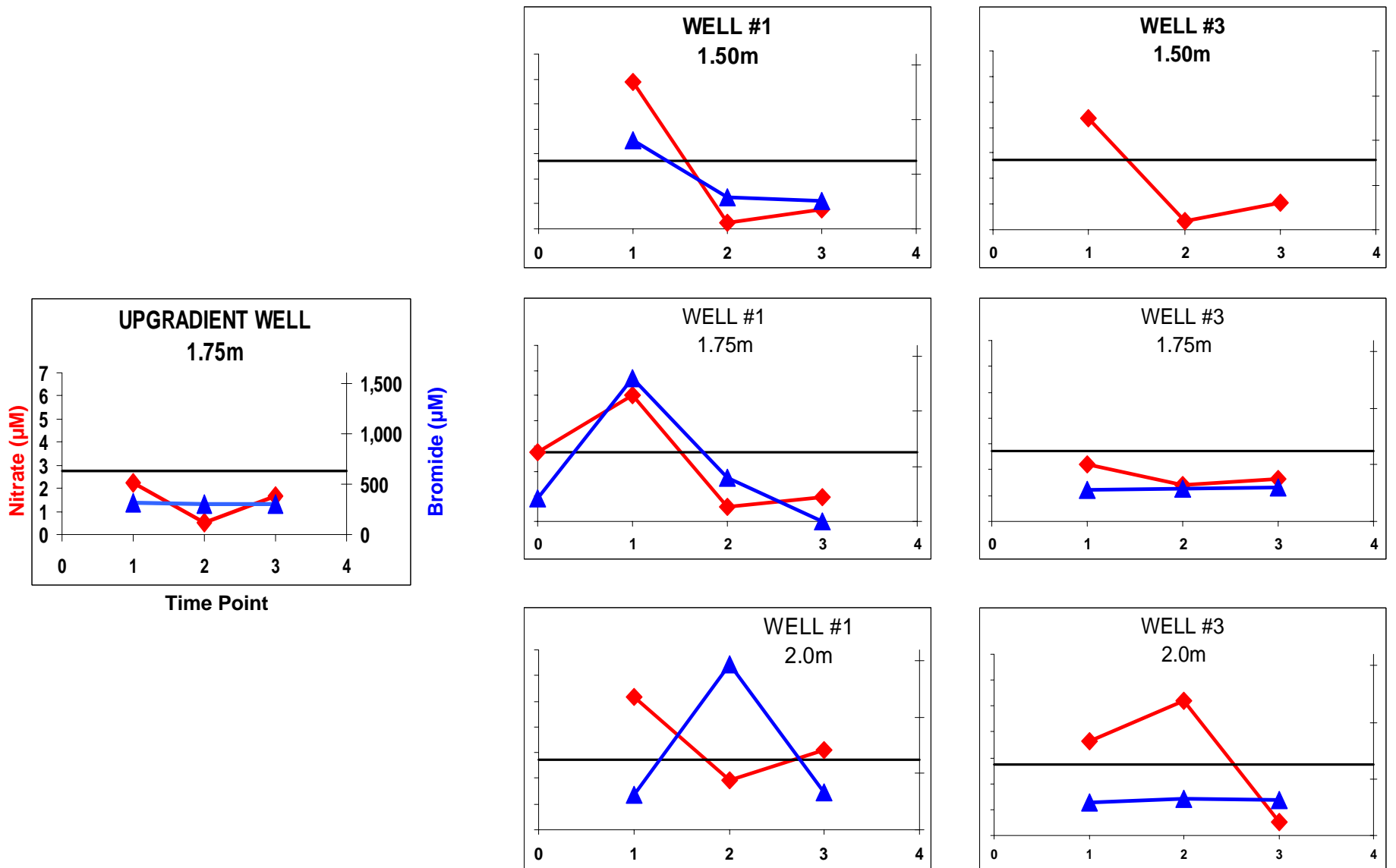


Figure 12.

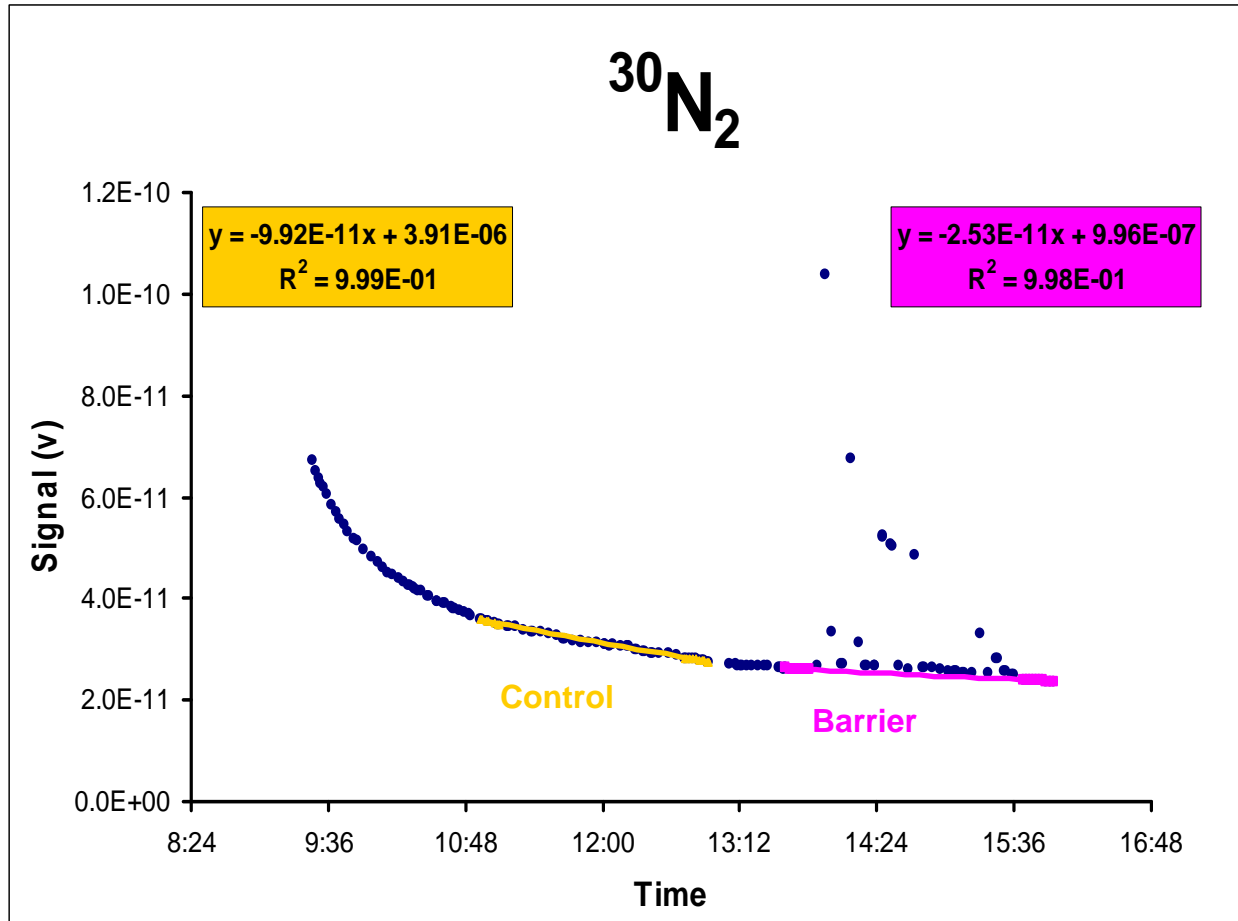


Figure 13.

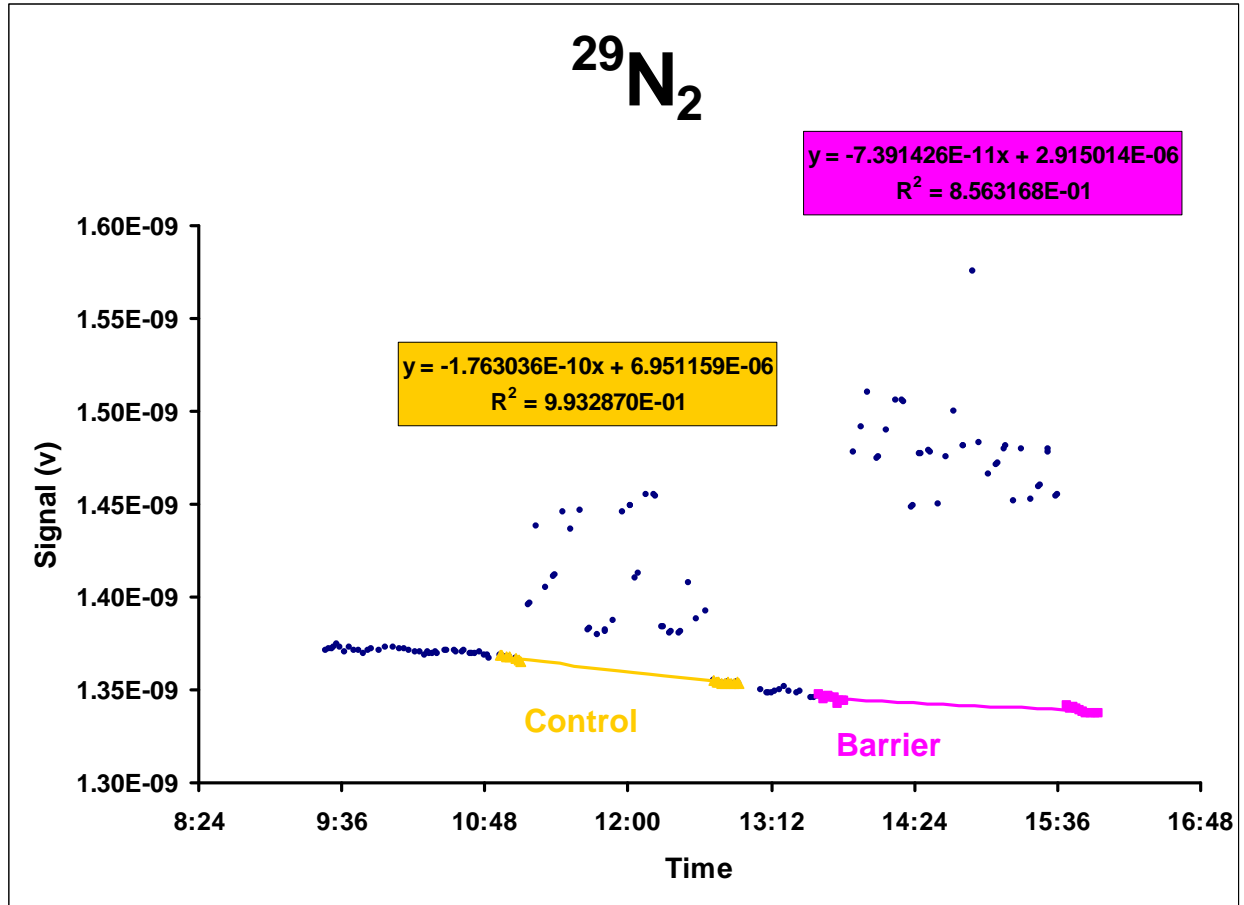


Figure 14.

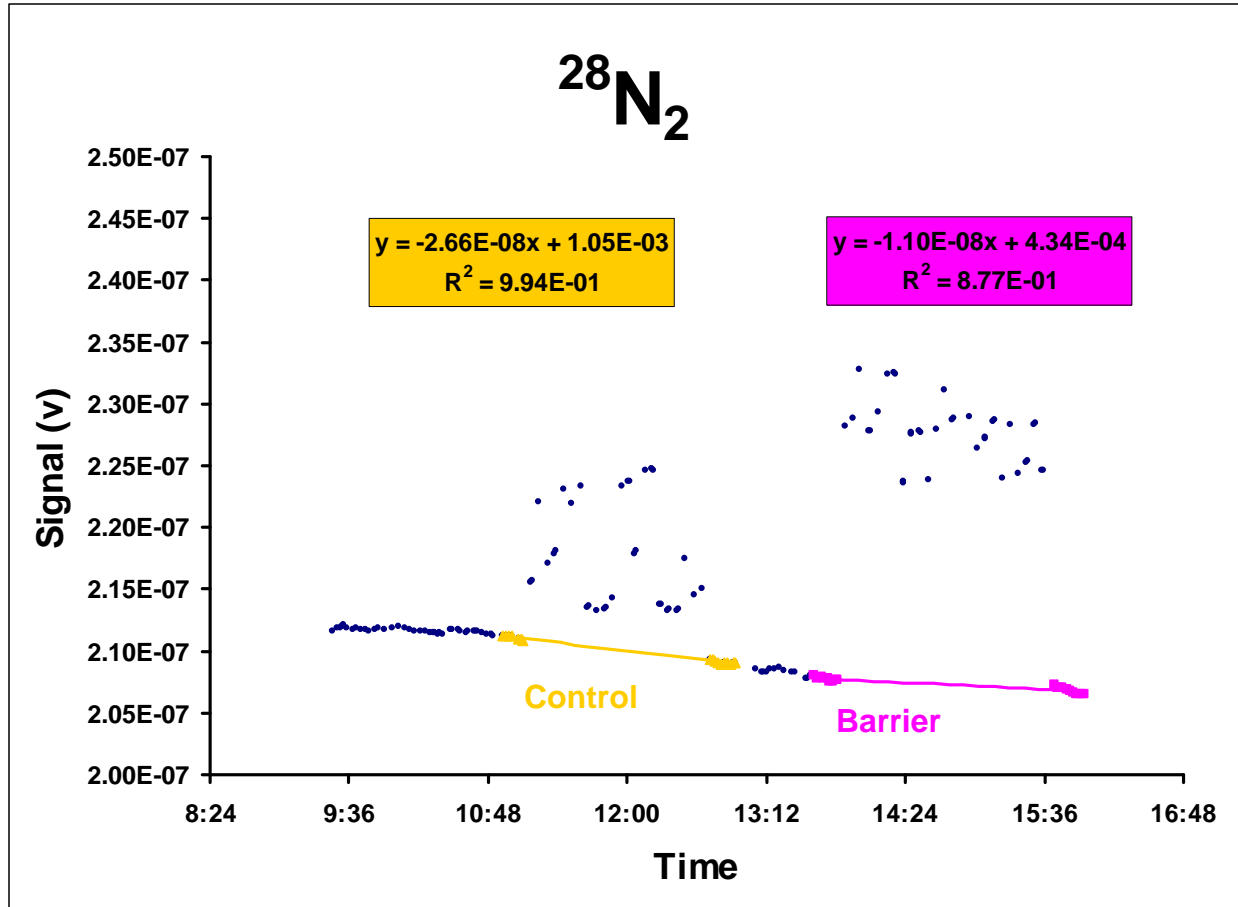


Figure 15.

Table 1.

Hour	Fluorometer Reading (ppm)	
	1ppm Rhodamine	20ppm Rhodamine
0	1.070	22.60
1	0.437	11.34
2	0.359	9.04
4.5	0.385	11.36

Table 2.

Measured Nitrate (μM)	Dilution Factor	Total Nitrate Remaining (μM)	Total Nitrate Removed (μM)	Nitrate Removed to N_2 (μM)	Percent (%) Denitrification
5.9	61	193	307	17	6%
5.0	30	69	431	16	4%
1.0	293	282	218	3	1%
1.9	27	0	500	5	1%
3.1	915	350	150	10	7%
6.2	107	377	123	17	14%
3.9	239	212	288	11	5%