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## **Nitrogen Cycling in Pore Water and Sediment at the Base of a Standing Recharge Basin**

### **INTRODUCTION**

#### **Purpose**

The artificial recharge basin located to the northwest of the Stony Brook University campus; north of North Loop Road and south of Rte 25A; is the subject of much interest primarily due to its status as a “standing water” recharge basin. The primary source of this standing water is precipitation, which when falling on impervious surfaces is collected as runoff in storm drains, and finally enters the basin by way of a stream. In addition to this, the basin also collects cooling water from the Van de Graff Accelerator, as well as hot and chilled leaking water from the Stony Brook University campus (Pizzulli 1999).

The water in this basin has a relatively long residence time of approximately 4-20 days (Pizzulli 1999), possibly attributed to the clogging of the base with decomposing organic matter and fall out from the atmosphere. When compared to “dry” basins where inputs and outputs of water are fairly high, it becomes obvious that in such artificial lakes, the geochemistry of the water is likely to be significantly altered from the time it enters the basin until it continues its path into the ground water system. Investigation into the nature of these geochemical changes may offer important natural mechanisms for the reduction of undesirable species in recycled wastewaters. Of specific interest in this study is the cycling of nitrogen bearing species in water as it leaves the atmosphere in the form of precipitation, until it eventually enters the ground water via this basin.

Water leaving the recharge basin enters the ground water system and its quality is assessed via a strategically located well. It has been observed that water entering the recharge basin has a significantly higher nitrate ( $\text{NO}_3\text{-N}$ ) concentration (0.88 mg/L), than that leaving the system (0.55 mg/L in the well). This implies that there is some process within the system that promotes the removal of this nutrient. Previous studies have suggested that such a process is likely to be occurring at the sediment-water interface, as the nitrate concentration throughout the water column seems to be consistent. In addition to this, there seems to be no seasonal constraint on this mechanism, in that the loss of nitrate from the system occurs throughout the year. Such a trend indicates that biological activity might not play a significant role in the elimination of nitrates, as one would expect a significant decrease in flora and fauna within the basin throughout the colder seasons.

In light of these factors, this study aims to assess the geochemical processes which govern the cycling of nitrogen bearing species in the accumulated sediments on the basin floor. The interactions of particular interest, being those which are coupled with the reduction of nitrate concentration within the system. Thus, results of this study should give some insight into the activities which take place in standing water recharge basins,

and hence generate useful applications for increasing the efficiency of nitrate removal in other applicable systems

## **Regional Hydrology**

Hydrogeological issues on Long Island are of utmost importance as the sole source of potable water in the region is ground water. Thus, it is essential to continuously evaluate and document the pathways that water takes from the time it leaves the atmosphere in the form of precipitation until it is used for domestic, industrial and agricultural purposes several hundreds of years later. This water is primarily retrieved from the Glacial and Magothy aquifers, the latter being the older and larger of the two, and storing water up to hundreds of years old. Of utmost importance is the assessment of how water is returned to this system via recharge, defined by the amount of precipitation excluding losses from evapotranspiration and runoff. As evapotranspiration is a process which cannot be easily curtailed, the most efficient way to increase recharge is to reduce runoff. The use of artificial means in the form of storm drains and recharge basins to serve this purpose has led to a 12% increase in annual recharge on the Island (Ku, et al 1992).

The main source of fresh water on Long Island is from precipitation averaging 45 in/yr, of which an average of 21.5 in/yr is lost as evapotranspiration, and approximately 50% or 1.1 billion gallons/day enters the ground water system via an extensive network of recharge basins (Ku, et al 1992). Recharge tends to be highest during the late fall, winter, and early spring months when there are large amounts of precipitation, whereas during the drier summer period, precipitation contributes very little to the annual average recharge of 22.5 in/yr (Ku, et al 1992).

Of particular concern is the treatment of wastewater, that is water reentering the system from industrial and domestic effluent. Suffolk county is one of the four regions in the United States where septic tanks are the primary means of recovering domestic waste, serving more than 100,000 housing units (Ku, et al 1992). These gradually release sewage into the underlying sediment, where it is oxidized and decomposed via microorganisms, until it eventually infiltrates the water table. When compared to sewer systems, the primary benefit of septic tanks is the return of wastewater to the ground water system, however pollution of this self-same system by nitrogen oxides is a major issue in areas of high septic tank density.

## **Previous Work**

Pizzulli 1998 investigated nitrogen concentrations in rainwater, stream water entering the basin, the recharge basin, and the monitory well. This documented the pathway of nitrogen compounds in precipitation and runoff until finally infiltrating the ground water. Water from all sources was collected during storm events, whilst during drier periods the basin was sampled at varying depths. All samples were collected between June and November 1998. Nitrate, nitrite, ammonia and organic nitrogen concentrations in all samples were determined using colorimetry. In addition, pH, temperature and oxygen concentrations were also noted. Nitrate was found to be the dominant nitrogen bearing species, the highest concentrations of which were detected in

the rain (2.90 mg/L) and stream water (1.8 mg/L) with a significant decrease observed from the basin (0.92 mg/L) to the well (0.77 mg/L). Pizzulli deduced that some denitrifying process must be occurring within the basin despite seemingly high oxygen concentrations within the water column. Hanley-Lanberg 1999 collected additional data between January and May of 1999. During these warmer months a gradual decrease in nitrate concentration from rainwater (0.87 mg/L) to the stream (0.75 mg/L), the basin (0.76 mg/L), and finally the well (0.39 mg/L), was also evident. Analysis of this data not only supports Pizzulli's denitrification hypothesis, but also indicates that this process is not limited by seasonal constraints.

## METHODOLOGY

### Sediment Collection and Preparation

Sediment was sampled from the deepest section of the basin on October 10<sup>th</sup> 1999 using clear plastic cores 6.35 cm (2.5”) in diameter and 25.4 cm (10”) in length. Two cores were collected manually by divers at a depth of 6.7 m (22ft) and temperature of 16.7°C. Upon collection they were placed securely in a crate and brought to the surface carefully in an attempt to keep the samples unagitated. The core thickness represents the maximum depth to which the divers could insert the core borers at any particular location. Core A was 3.81 cm (1.5”) in thickness and fairly undisturbed, whilst Core B was 10.16 cm (4”) thick and slightly agitated during transportation to the surface. Divers noted that the sediment consisted primarily of mud and organics to a maximum depth of 10.2 cm, below which is an impenetrable clay like material. A high percentage of biological activity was also observed, including a large number of oligochaetes - long segmented worms - forming burrows in the sediment.

Cores were taken to the Analytical Geochemistry lab at Marine Sciences where they were aerated, and oxygen gradients determined immediately. Keeping the cores unagitated and aerated was necessary to preclude the loss of oxygen in the overlying and interstitial waters to respiring fauna. These precautions functioned by keeping oxygen concentrations in the water equilibrated with that of the air. Though slightly agitated during collection, on examination of the oxygen profiles, there was no apparent evidence of deoxygenation of Core B. With this in mind, and being the thicker of the two cores, this sample was used for further analysis.

Excess water was siphoned off of Core B, and the core placed on an extruder to extract the sediment from the plastic liner. Core A was not extruded primarily due to its smaller size and sloping of the surface of the sediment, which would have made it difficult to extrude in equal sections. Core B was extruded in 1 cm intervals producing 6 samples representative of the sediment profile up to a depth of 6cm. These samples were labeled ARS1 through ARS6. A small portion of wet sample from each layer was weighed and placed in an oven at 75°C for a period of 7 days after which the samples were re-weighed and weight percent water determined.

Sample	% Water
ARS1 (0-1cm)	74.201
ARS2 (1-2cm)	69.879
ARS3 (2-3cm)	54.766
ARS4 (3-4cm)	57.542
ARS5 (4-5cm)	56.352
ARS6 (5-6cm)	50.635

Table 1. Weight percent water of Core B sediment profile

The extruded samples were placed in centrifuge tubes, and centrifuged for 10 minutes to separate the pore water from the sediment. The separated pore water was

retrieved using a 10 cc syringe, and filtered with a 0.2  $\mu\text{m}$  membrane which was attached to the tip of the syringe subsequent to collection of the water. Approximately 6-10 mL of interstitial water was obtained from each successive section, and these samples were named ARP1 through ARP6. 2 mL of each sample was collected and refrigerated for alkalinity analysis. Remaining pore water and sediment samples were frozen for future geochemical analysis: pore water was analyzed for ammonium, nitrate/nitrite concentrations and alkalinity, whilst sediment was analyzed for total nitrogen and carbon content.

### **Water Collection**

Water samples were collected from the stream on October 21<sup>st</sup> 1999, the day following a storm. Water from the basin was collected on November 6<sup>th</sup> 1999 at 5 ft intervals up to 25 ft in depth for a total of six samples ARW1 through ARW6. All samples were analyzed for nitrate, nitrite and ammonia concentrations immediately after collection. Oxygen concentrations, pH and temperatures were also noted. These data were combined with those of Pizzulli and Hanley-Lanberg to give a general overview of existing hydrological conditions within the system (Table 5).

## **GEOCHEMISTRY**

### **Sediment Analysis**

#### Total Carbon and Nitrogen

Samples ARS1 to ARS6 were analyzed for total carbon and nitrogen content at the Marine Sciences Research Center, SUNY Stony Brook by David Hirschberg. Samples were weighed and heated overnight in an oven at 75°C. Dried samples were re-weighed and approximately 2 g ground to a fine powder using a mortar and pestle. Samples were combusted at 2000°C in a CHN Elemental Analyzer and the percentage carbon and nitrogen obtained from resultant chromatograms. Results show a decrease in total carbon and nitrogen down the sediment profile (Table 2), carbon being the more abundant of the two (Figure 1). The relative standard deviation of obtained values is +/- 1.8% for C, and +/- 8.3% for N.

#### Pore Water Analysis

##### Oxygen Gradient

Oxygen gradient in the aerated cores was measured in millivolts (mV) using a platinum microelectrode with Ag/AgCl electrodes and a gold plated tip. The electrode was kept in sea-water saturated with nitrogen gas prior to running the experiment to give an approximation of the zero oxygen voltage. The oxygen concentration in the overlying water of the core was taken, and then the electrode placed at the sediment-water interface. Voltage readings were recorded at 200 µm intervals to a depth of 2 cm, after which there appeared to be no change in the oxygen gradient in the sediment, and voltage of the overlying water was re-recorded. The values over which the voltage appeared to stabilize were averaged and taken as zero oxygen concentration, which was subtracted from all other values. 100% oxygen saturation was measured as the average of the voltage of the overlying water before and after the experiment.

The collected data were graphed and are represented in Figure 2. The oxygen gradients of both core A and B show no penetration of oxygen beyond 1.5 cm, indicative of the predominance of anaerobic conditions within the remainder of the sediment profile.

##### Ammonium (NH<sub>4</sub>-N)

Ammonium NH<sub>4</sub><sup>+</sup> concentrations were measured using colorimetry methods. Standard solutions of varying concentrations, 25, 50, 100, 150 µM, were prepared by dissolving 1.337 g ammonium chloride in 500 mL distilled water to make a 50 mM solution, and then diluted accordingly. Reagents used were also prepared: phenol (4 g phenol/500 mL), nitroprusside (0.375 g sodium nitroprusside/500 mL), citrate (7.5 g trisodium citrate and 0.4 g sodium hydroxide/500 mL), mixed reagent (100 mL citrate and 4 mL chlorox).

ARP1 through ARP6 were diluted by adding 750 µL of distilled water to 250 µL sample to give a 4:1 water to sample ratio. Standards, blanks (plain distilled water), and pore water samples were prepared by adding 1 mL of distilled water to 1 mL of sample, to dilute to 2 mL total volume. 1 mL of phenol was added to each using an automatic

Sample	Total Mass (g)	%N	Mass N (mg)	%C	Mass C (mg)
ARS1	2.31	0.44	10.05	8.74	201.342
ARS2	2.56	0.34	8.64	7.33	187.941
ARS3	2.43	0.34	8.36	7.44	180.939
ARS4	2.76	0.28	7.63	6.29	173.773
ARS5	2.62	0.27	6.97	6.38	167.014
ARS6	2.68	0.25	6.67	5.99	160.352

Table 2. CHN analysis results for total carbon and nitrogen

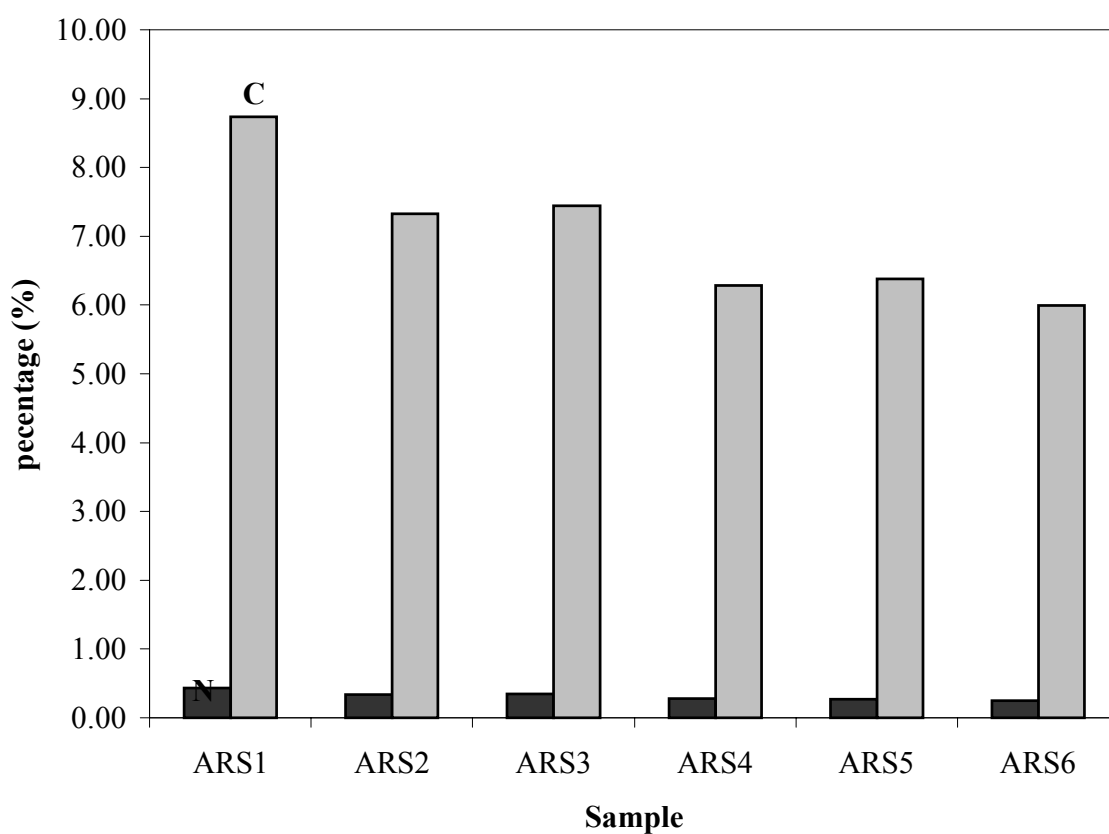


Figure 1. Comparison of total carbon and nitrogen in samples ARS1 to ARS6

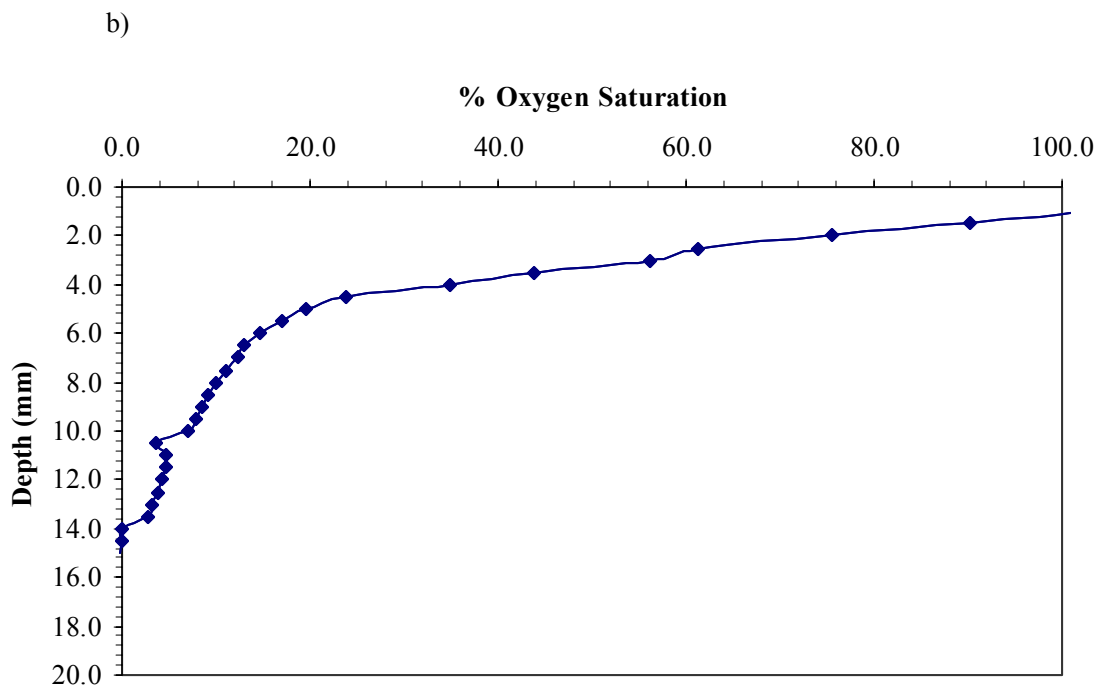
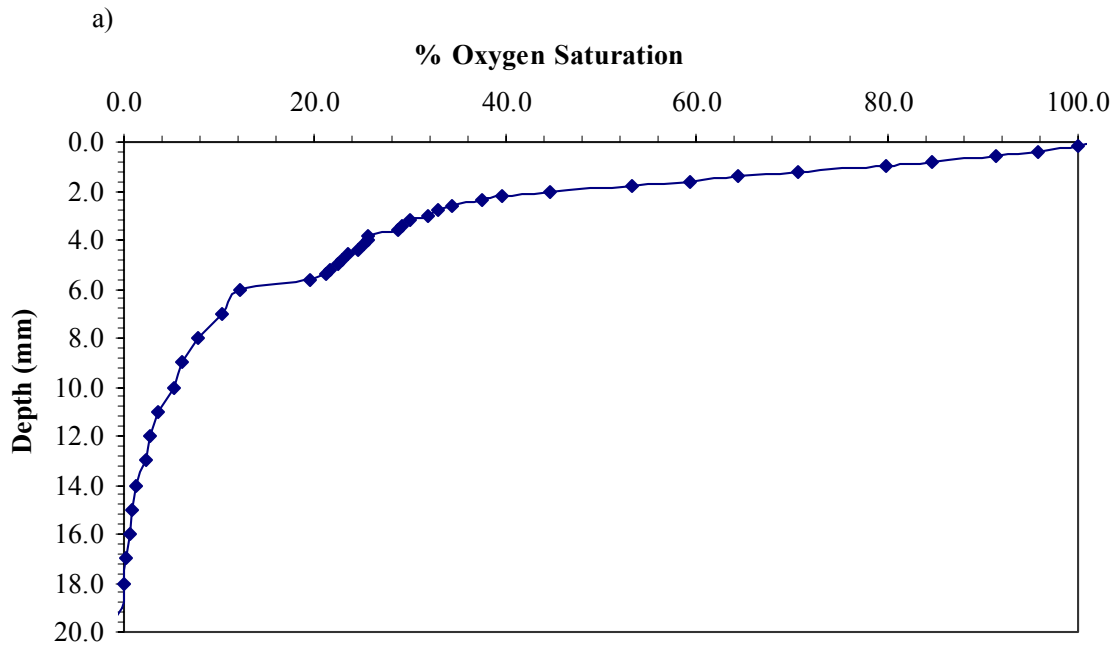


Figure 2. Oxygen profiles of a) core A, b) core and B



pipette. 1 mL nitroprusside was then added, immediately followed by 2 mL of the mixed reagent. The samples were stored in the dark for approximately 2 hrs to allow color to develop, and the absorbencies read at 630 nm wavelength on a spectrophotometer.

Blanks were run first, followed by standards in order to establish the absorbance curves (Figure 3). Finally samples ARP1 through ARP6 were analyzed.  $\text{NH}_4^+$  concentrations were determined by reading the corresponding concentrations off of the standard curve, and these were in turn converted to  $\text{NH}_4\text{-N}$  (Table 3). Figure 4 shows the general increase in concentration of ammonium ions with depth of sample, from 0.33 mg/L in the first centimeter, to 4.04 mg/L in the sixth.

### Alkalinity

A microcombination pH electrode was calibrated using pH 4 and pH 7 standards, and placed in the sample along with a magnetic stir bar, and the tip of a 2 mL microburette containing 0.01M HCl. The magnetic stirrer was then turned on, the pH of the sample allowed to stabilize, and this value recorded as the initial pH. Titrant was added in 0.01 mL increments up to 0.2 mL, the pH recorded and the change in pH calculated. A sample of overlying water (ARW5) was titrated initially, to establish an approximation for the reaction endpoints, followed by ARP1 to ARP6.

During the titration protons from the acid are added to carbonate ions ( $\text{CO}_3^{2-}$ ) to form bicarbonate ions ( $\text{HCO}_3^-$ ), and bicarbonate is subsequently converted to carbonic acid ( $\text{H}_2\text{CO}_3$ ) with the addition of more protons. The reaction is completed when there are no more species available for protonation, and hydronium ions accumulate in the sample. Alkalinity or acid neutralizing capacity (ANC) is thus a measure of the anionic content of the sample.

Data from each titration was used to construct Gran function plots, as opposed to a simple titration curve, to determine the two endpoints of the reaction accurately. In these plots straight lines on the curves are extrapolated to volumes on the x axis to give reaction endpoints (Figure 5). This is more accurate than estimating inflection points on titration curves. Both bicarbonate and carbonate endpoints were determined, and these values converted to alkalinity in milliequivalents per liter. Alkalinity and initial pH values were used to estimate the dissolved inorganic carbon (DIC) content of the samples. These values are represented in Table 4, which shows a general increase in total alkalinity, as well as DIC with depth of sample.

### Nitrate/Nitrite

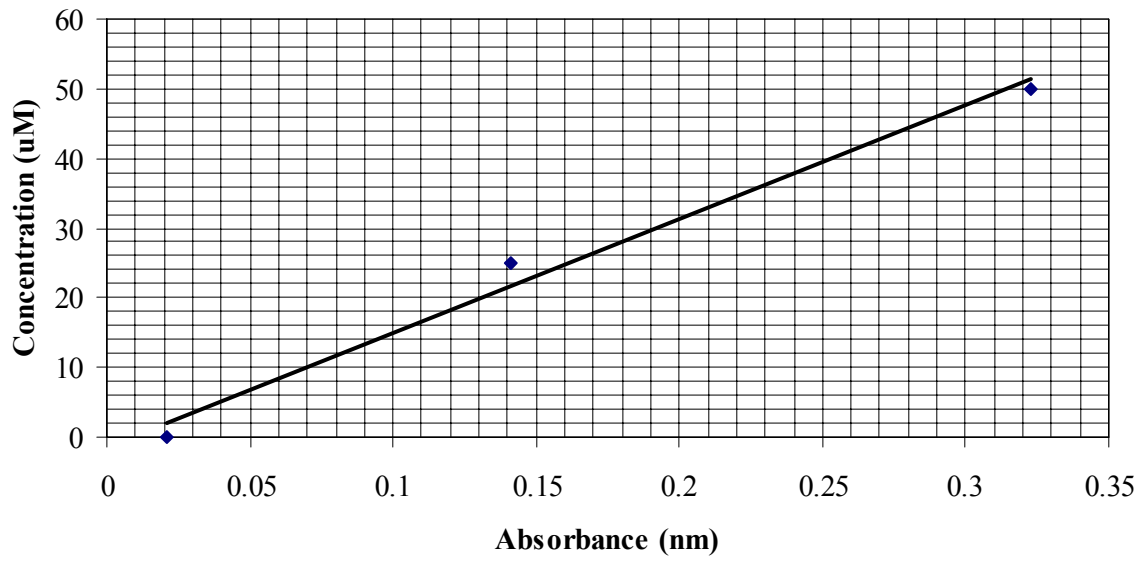
An attempt was made to measure the nitrate/nitrite concentration of samples via anion chromatography. However, resulting chromatographs showed no detectable nitrate concentrations, but high concentrations of other anions such as chloride and sulfate.

### **Water Analysis**

All water samples analysis was performed via colorimetric methods, using the Hach Spectrophotometer. Results obtained were combined with those of Pizzulli 1998 and Hanley-Lanberg 1999 to give a wholistic perspective of the ongoing processes in the basin (Table 5).

a)

$$y = 163.27x - 1.3952$$



b)

$$y = 121.36x + 13.35$$

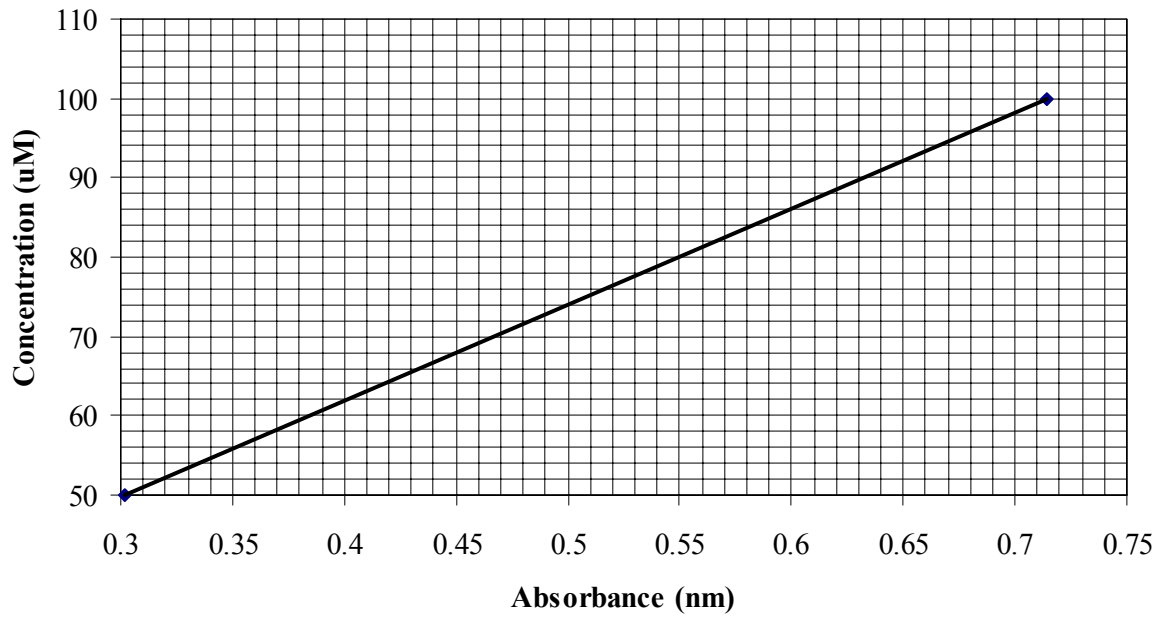


Figure 3. Concentration curves for ammonium standards a) 25 to 50mm, and b) 50 to 100mm

sample	absorb(nm)	1/4 conc(uM)	conc(uM)	conc(mg/L)
ARP1	0.045	5.95	23.81	0.33
ARP2	0.061	8.56	34.26	0.48
ARP3	0.074	10.69	42.75	0.60
ARP4	0.091	13.46	53.85	0.75
ARP5	0.104	15.58	62.34	0.87
ARP6	0.485	72.21	288.84	4.04

Table 3. Ammonium concentrations ARP1 to ARP6

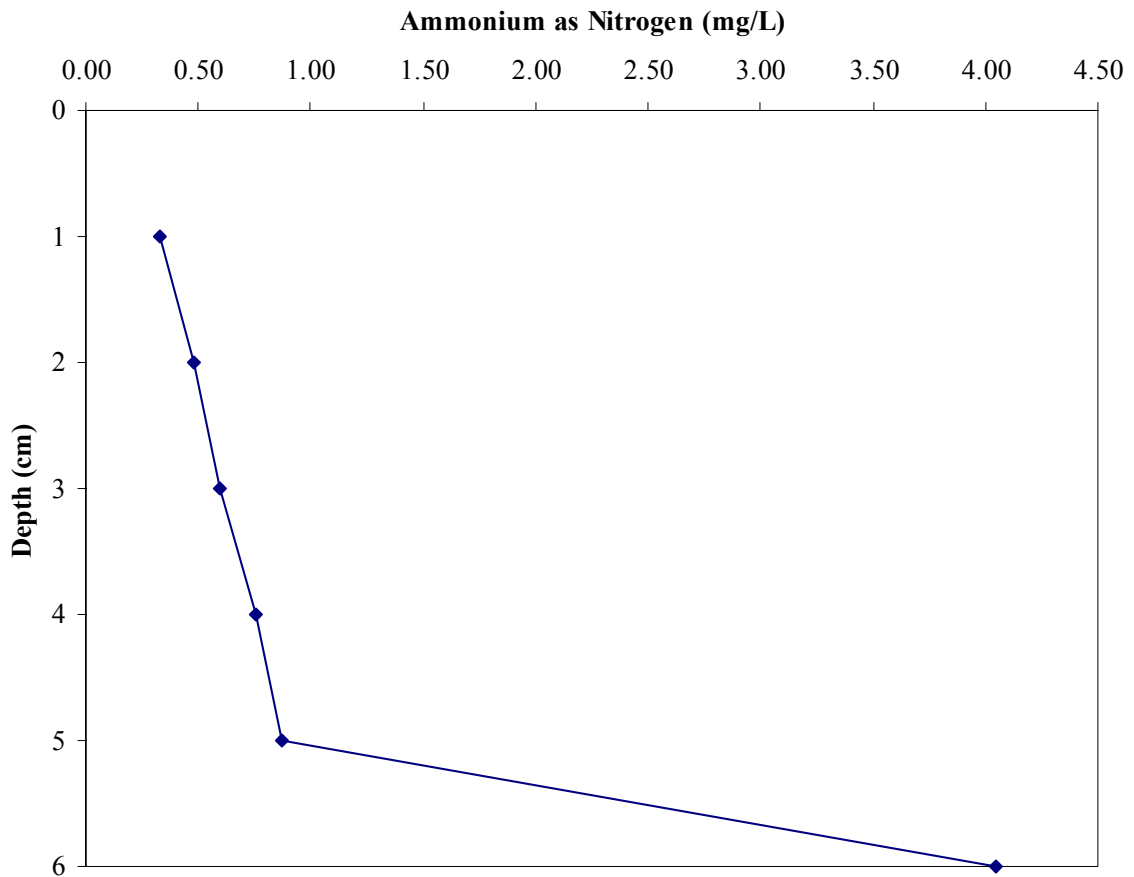
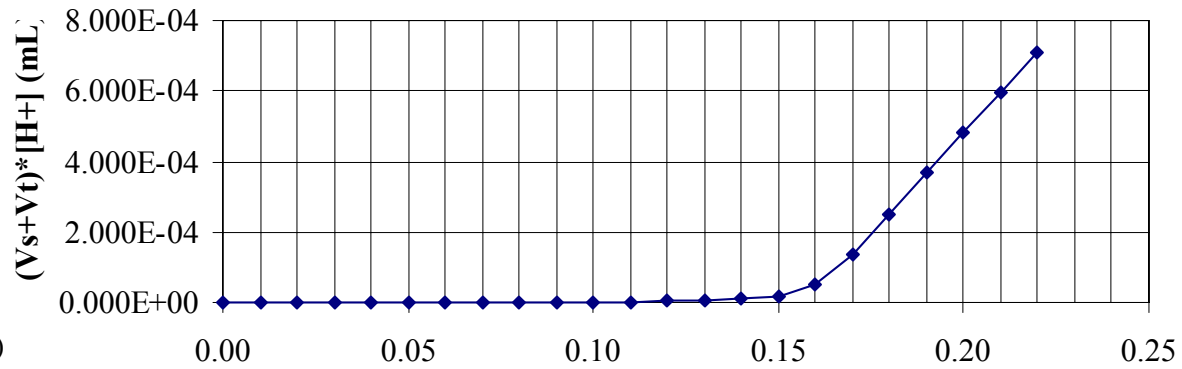


Figure 4. Ammonium ion concentrations of pore water

a)



b)

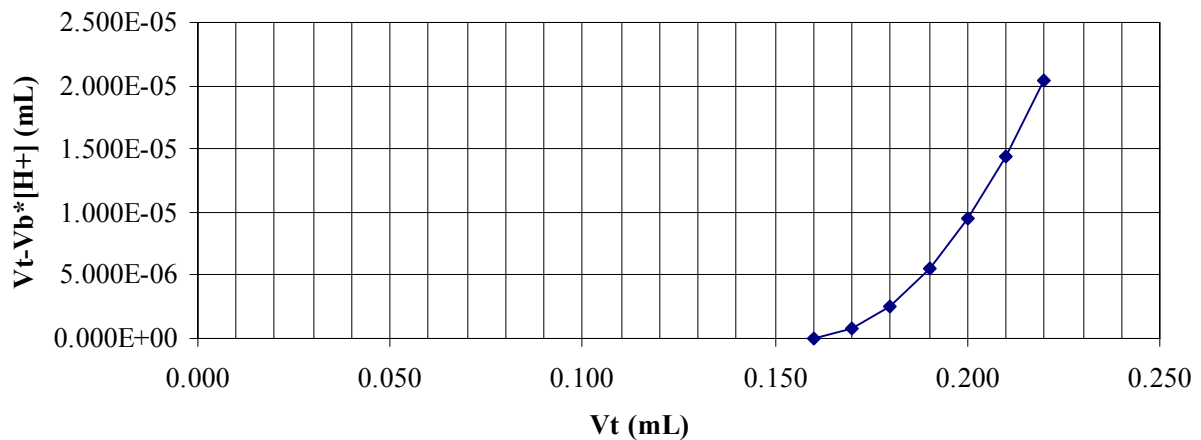


Figure 5. Example of Gran function plot for ARP1 a) bicarbonate, b) carbonate equivalence  $V_t$  titrant volume,  $V_s$  sample volume,  $V_b$  volume of titrant needed to reach the bicarbonate equivalence point.

sample	Total(mL)	HCO <sub>3</sub> (mL)	CO <sub>3</sub> (mL)	HCO <sub>3</sub> (meq)	CO <sub>3</sub> (meq)	Total Alkalinity	DIC mg/L
ARW5	0.156	0.127	0.029	0.635	0.145	0.925	0.278
ARP1	0.186	0.158	0.028	0.814	0.144	1.103	0.331
ARP2	0.186	0.165	0.021	0.859	0.109	1.078	0.323
ARP3	0.190	0.171	0.019	0.891	0.099	1.089	0.327
ARP4	0.179	0.155	0.024	0.833	0.129	1.091	0.327
ARP5	0.170	0.146	0.024	0.768	0.126	1.021	0.306
ARP6	0.183	0.160	0.023	0.842	0.121	1.084	0.325

Table 4. Bicarbonate and carbonate alkalinity expressed as total alkalinity in meq/L and dissolved inorganic carbon (DIC).

a)

Date	Sample	pH	Temp	Oxygen	Nitrate (ppm)	Ammonia (ppm)	Nitrite (ppm)	Organic (ppm)	Total (ppm)
6/22/98	Basin(1ft)				0.40	0.01	0.15		
	Basin(10ft)				0.80	0.02	0.15		
	Basin(16ft)				1.00	0.11	0.20		
	Basin(26ft)				4.50	1.09	0.33		
7/7/98	Basin(1ft)				0.40	0.02	0.03	0.04	0.49
7/23/98	Rain	4.4		8					
	Stream	6.4	24	6	1.50	0.17	0.01	0.86	2.54
	Basin(1ft)	9.5	27	12	0.00	0.01	0.01	0.65	0.67
	Well	6.3	18	8	0.70	0.00	0.01	0.38	1.09
7/30/98	Stream	6.7	29	7	0.80	0.00	0.01	0.38	1.19
7/31/98	Rain	4.8	19	7	2.90	0.70	0.02	0.05	3.67
	Stream	6.3	28	6	2.10	0.92	0.05	0.77	3.84
	Catch Basin	6.6	24	7	0.60	0.93	0.03	0.48	2.04
	Basin(1ft)	9.1	24	8	0.20	0.01	0.01	0.46	0.68
	Well	6.3	19	7	0.40	0.00	0.00	0.28	0.68
9/3/98	Culvert	8.6	21	9	0.90	0.01	0.03	0.74	1.68
	Basin(1ft)	6.9	29	8	1.30	0.00	0.00	0.28	1.58
9/30/98	Basin(1ft)	8.4	21		0.70	0.00	0.01	0.75	1.46
	Basin(7ft)	8.3	20		0.70	0.00	0.02	0.38	1.10
	Basin(13ft)	7.3	19		0.80	0.00	0.01	0.28	1.09
	Basin(19ft)	7.1	19		0.80	0.01	0.01	0.46	1.28
	Basin(25ft)	6.9	19		0.70	0.04	0.01	1.37	2.12
11/12/98	Basin(1ft)	6.6	12		1.30	0.04	0.01	0.24	1.59
	Basin(7ft)	6.8	12		1.30	0.03	0.01	0.06	1.40
	Basin(13ft)	6.8	11		1.20	0.01	0.01	0.08	1.30
	Basin(19ft)	7.0	11		1.30	0.01	0.01	0.08	1.40
	Basin(25ft)	7.0	11		1.40	0.01	0.02	0.08	1.51
	Well	6.2	10.5		1.20	0.00	0.00	0.09	1.29

Table 5. Water analysis data a) Pizzulli

b)

Date	Sample	pH	Temp.	Dissoved Oxygen	Nitrate (ppm)	Ammonia (ppm)	TKN (ppm)	Total (ppm)
1/22/99	Standard				0.9	1.01		
	Rain	5.3	12	10	0.6	0.12		<b>0.72</b>
	Culvert	6.9	15	6	0.45	0.3		<b>0.75</b>
	Stream	6.88	15	6	0.3	0.94		<b>1.24</b>
	Catch Basin	6	6	5	0.2	1.01		<b>1.21</b>
	Recharge Basin	6.98	10	9	0.5	0.1		<b>0.6</b>
2/28/99	Standard				0.9	1.02	26	
	Rain	5.3	11	11	0.5	0.49	0.5	<b>1</b>
	Culvert	6.58	11	9	0.7	0.4	0.18	<b>0.88</b>
	Stream	6.33	9	8	0.6	0.52	0.85	<b>1.45</b>
	Catch Basin	6.4	7	8	0.4	0.65	0.43	<b>0.83</b>
	Recharge Basin	7	8	8	0.9	0.27	0.4	<b>1.3</b>
	Well	6.06	10	9	0.04	0.06	0.2	<b>0.24</b>
3/13/99	Standard				0.9	1.02	26	
	culvert	6.82	10	10	1.2	0.01	0.38	<b>1.58</b>
	Recharge Basin	6.76	14	10	0.9	0.04	0.84	<b>1.74</b>
	Well	6.24	14	10	0.4	0.02	0.47	<b>0.87</b>
2/1/99	Standard				0.9	0.98	26	
	Rain	5.3	19	10	0.8	0.32	0.5	<b>1.3</b>
4/10/99	Standard				0.9	0.98	26	
	Rain	4.9	14	11	0.6	0.3	1.2	<b>1.8</b>
4/12/99	Standard				0.9	0.98	26	
	Rain	5.4	17	11	1.5	0.42	0.84	<b>2.34</b>
4/16/99	Standard				0.9	1.01	26	
	Rain	5.8	18	11	0.6	0.21	1.03	<b>1.63</b>
4/26/99	Standard				1	1.01	26	
	culvert	6.6	14	>10	0.8	0.01	0.4	<b>1.2</b>
	Recharge Basin	6.8	18	>10	0.8	0.03	0.8	<b>1.6</b>
	Well	6.3	14	>10	0.6	<.01	0.3	<b>0.9</b>
5/19/99	Standard				0.9	0.99	26	
	Rain	5.5	20	>10	1.5	1.38	2.15	<b>3.65</b>
	Culvert	6.47	18	>10	1.1	0.03	1.03	<b>2.13</b>
	Stream	6.9	19	>10	0.9	0.02	0.93	<b>1.83</b>
	Catch Basin							
	Recharge Basin	7.57	20	>10	0.7	0.04	0.56	<b>1.26</b>
	Well	6.9	16	>10	0.5	0.01	0.2	<b>0.7</b>

Table 5. Water analysis data b) Hanley-Lanberg

c)

Date	Sample	pH	Temp	Oxygen (ppm)	Nitrate (ppm)	Ammonia (ppm)	Nitrite (ppm)
11/6/99	ARW1 (0ft)	6.8	23		0.80	0.18	0.01
	ARW2 (5ft)	6.8	16.2	4.30	0.80	0.15	0.01
	ARW3 (10ft)	6.9	15.9	3.40	0.80	0.15	0.01
	ARW4 (15ft)	7.0	15.5	3.40	0.80	0.14	0.01
	ARW5 (20ft)	7.3	15.3	2.20	0.85	0.13	0.01
	ARW6 (25ft)	7.4	15.3	2.20	0.80	0.13	0.01

Table 5. Water analysis data c) Rouff

#### Nitrate NO<sub>3</sub>-N

40 mL of sample was placed in a beaker, and used to fill a NitraVer 5 Nitrate AccuVac ampul. The ampul was shaken for one minute then allowed to sit for a five minute reaction period. The spectrophotometer was set to a wavelength of 400 nm, and the intensity of color of the sample measured. In addition to ARW1 to ARW6, a 1 mg/L NO<sub>3</sub>-N standard, as well as an Ampul of deionized water were run for calibration purposes. The precision for this method is  $\pm 0.03$  mg/L.

#### Nitrite NO<sub>2</sub>-N

40 mL of sample was placed in a beaker, and used to fill a NitraVer 3 Nitrite AccuVac ampul. The ampul was inverted to mix the contents, then allowed to sit for a fifteen minute reaction period. The spectrophotometer was set to a wavelength of 507 nm, and the intensity of color of the sample measured. In addition to ARW1 to ARW6, a 0.1 mg/L NO<sub>2</sub>-N standard, as well as an Ampul of deionized water were run for calibration purposes. The precision for this method is  $\pm 0.00007$  mg/L.

#### Ammonium NH<sub>3</sub>-N

25 mL of sample was placed in a graduated cylinder, followed by three drops of Polyvinyl Dispersing Agent, three drops of Mineral Stabilizer and 1 mL Nessler Reagent. The mixture was shaken, then allowed to sit for a one minute reaction period. The sample was transferred to a cuvette, and placed in the spectrophotometer, which was set to a wavelength of 630 nm. In addition to ARW1 to ARW6, a 1 mg/L NH<sub>3</sub>-N standard, as well deionized water were run for calibration purposes. The precision for this method is  $\pm 0.015$  mg/L.

#### Oxygen

As samples were collected, 25 mL was placed in a beaker and used to fill a High Range Dissolved Oxygen AccuVac ampul. Without inverting the ampul, an ampul cap filled with sample was immediately placed over the tip. The ampul was shaken for approximately thirty seconds and allowed for approximately one hour. On returning to the lab the spectrophotometer was set to a wavelength of 535 nm, the ampul shaken for another thirty seconds, and the intensity of color measured. The precision for this method is  $\pm 0.2$  mg/L.

## DISCUSSION

### Chemistry of Sediment and Pore Water

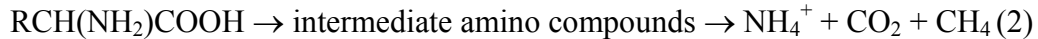
The general trends noted in the pore water are an increase in  $\text{NH}_4^+$  and alkalinity, with no detectable nitrate/nitrite concentrations, and general decreases in the total carbon and nitrogen of the sediments. These trends can generally be described in terms of a variety of chemical reactions.

The decrease in nitrate concentration from 0.8 mg/L in the overlying water, to zero concentration in the oxygenated pore water implies some type of oxic denitrification process, where nitrate is possibly converted to nitrogen gas, and is subsequently lost from the system. Alternatively, the disappearance of nitrate may be due to its conversion to organic nitrogen, via a photosynthetic process:



Also, conditions in the burrows of oligochaetes are likely to be anoxic, leading to localized denitrification in these regions of the sediment.

Ammonium concentration increases at a relatively constant rate of 0.14 mg/L per cm in the first five centimeters. However, in the last centimeter, the rate increases drastically to 3.17 mg/L per cm. The general increase in  $\text{NH}_4^+$  concentration down profile is suggestive of an ammonification reaction, where organic nitrogen is decomposed by bacteria, and  $\text{NH}_4^+$  released into solution:



As this reaction proceeds, organic carbon and nitrogen constituents of total N and C will also decrease. As conditions become more anoxic, the ammonium accumulates, as there is a decreased probability of conversion of  $\text{NH}_4^+$  to more oxidized forms due to the lack of oxygen.

Down profile, the percentage of total nitrogen and carbon decreases. However, a constant N to C ratio of 1:22 is maintained. This ratio in algal material is 1:7, this suggests that most of the total nitrogen is present as organic nitrogen.

Increases in alkalinity result from the formation of organic material by basic photosynthetic processes as in equation (1). Changes in concentrations of ions such as  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}^+$  result in an increase in alkalinity as this is necessary for charge balance. Alkalinity also increases when the rate of decomposition, as in equation (2), is greater than the rate of production of organic matter. The continued increase in alkalinity down profile can be attributed to other redox reactions, such as sulfate reduction, ions of which are known to be present from chromatographic results.

Dissolved inorganic carbon, which is derived from alkalinity in this experiment, also increases in concentration with depth, and can be coupled with the decrease in total carbon of the sediment.

### Mass Balance



<b>Nitrogen (ppm)</b>	<b>Rain</b>	<b>Stream</b>	<b>Basin</b>	<b>Sediment</b>	<b>Well</b>
<b>Nitrate</b>	1.13	1.06	0.88	0.00	0.55
<b>Ammonium</b>	0.49	0.51	0.09	0.33	0.03
<b>Organic</b>	0.45	0.75	0.39		0.25

Table 6. Average concentrations of nitrogen bearing species along the pathway of water from rain to the well

Table 6 shows the average concentrations of all nitrogen bearing species using data from Pizzulli, Hanley-Lanberg, and Rouff in Table 5. Nitrite was omitted due to its relatively low concentration at all locations. Focusing on the pathway of nitrate, there is a net decrease in the concentration of this nutrient from the stream (1.06 mg/L) to the lake (0.88 mg/L) and finally to the well (0.55 mg/L). The balance of nitrate in the recharge basin was calculated using the following equation (Berner 1996):

$$\Delta M/\Delta t = [C_i F_i + C_r F_p] - C F_o - R_s$$

$C_i F_i + C_r F_p$  is the total mass of nitrate entering the basin and  $C F_o$  is the mass of nitrate leaving the basin on an annual basis.  $R_s$  should thus represent the mass of nitrate removed from the water per year, assuming a steady state with regards to nitrate. Thus, the change in mass with time should be equal to zero, and the rate of inflow minus the rate of outflow should be equal to the rate of sedimentation:

$$\begin{aligned} \Delta M/\Delta t &= 0 \\ R_s &= [C_i F_i + C_r F_p] - C F_o \end{aligned}$$

Using data in Table 5 to obtain average annual values for nitrate concentrations, and assuming that the inflow rate at 700 million liters per year (Pizzulli 1998), is equal to the outflow rate (see appendix for calculations):

$$\begin{aligned} R_s &= [C_i F_i + C_r F_p] - C F_o \\ 1.6 \times 10^7 \text{ mg/yr} &= 7.5 \times 10^8 \text{ mg/yr} - 6.2 \times 10^8 \text{ mg/yr} \\ 1.6 \times 10^7 \text{ mg/yr} &\neq 1.3 \times 10^8 \text{ mg/yr} \end{aligned}$$

The equation shows that sedimentation cannot be the sole mechanism for loss of nitrate in the water, as there is an excess of this nutrient, approximately 90%, which remains unaccounted for by this mass balance equation.

In addition to changes in nitrate concentrations, ammonium and organic nitrogen concentrations also vary along the pathway of water. Ammonium concentration decreases from 0.5 mg/L in rain and stream water to 0.09 mg/L in the water column of the basin. This value however, increases to 0.33 mg/L in the sediment pore water, and is once again reduced to 0.03 mg/L in the well. Organic nitrogen values increase from 0.45 mg/L in rainwater, to 0.75 mg/L in the stream. This value decreases to 0.39 mg/L in the basin

water, and finally 0.25 mg/L in the well. Unfortunately the concentration of organic nitrogen in the pore water was not obtained.

## **Interpretation**

Nitrogen constituents in water entering the recharge basin from the stream, remain fairly unaffected when compared to concentrations in rainwater, with the exception of organic nitrogen. This slight increase in concentration from rain to stream water can be attributed to water picking up organic matter as it flows to the catchment area.

Within the basin, concentrations of nitrate and ammonium drop significantly, with a smaller decrease in the concentration of organic nitrogen, which may simply be due to filtering out of this material as it enters the basin. It is likely that nitrate is used during photosynthesis for the production of algae (equation 1). This is evident by increased nitrate removal after a dry spell followed by a period of heavy rain; 0.4 mg/L on 7/7/98 to 0.0 mg/L on 7/23/98 (Pizzulli 1998); indicative of increased production of algal material under wet conditions. With the possibility of nitrate concentrations acting as a limiting factor during photosynthesis, loss of ammonium from the system may be accounted for via nitrification, where these ions are oxidized to form nitrate, which is utilized during photosynthesis. Alternately, the ammonium ions may be used directly in this process without prior formation of nitrate. In order to determine exactly which of these two processes may be taking place, it would be necessary to compare the rates of these reactions under the given conditions in the basin. Under very limiting conditions of nitrate, the use of ammonium directly in the photosynthetic reaction is likely to be the more favorable pathway when compared to an intermediate nitrification reaction.

In the pore waters of the basin, nitrate concentrations are undetectable, with a steady increase in the concentration of ammonium ions. The increase in ammonium concentration is reflective of an ammonification reaction (equation 2) where decomposing algal material releases ammonium ions, methane gas and carbon dioxide. Elevated N:C ratios of 1:22 in the sediment indicates that most of the nitrogen in the sediment may in fact be organic, and is thus the source of this decomposing material.

Nitrate deficiencies in the pore water, can be attributed to a denitrification process whereby nitrate is converted to nitrogen gas which escapes into the atmosphere. As the sediment is highly bioturbated and oxygen in the overlying water penetrates the first 1.5 centimeters, it is evident that such a process may be occurring under oxic conditions. It is also possible that at the bottom of the basin, oxygen is consumed in other processes such as methane oxidation, hydrogen sulfide oxidation (noted by the presence of sulfates in the pore water), and aerobic mineralization due to high organic matter contents. The consumption of oxygen by these processes would perpetuate the reduction of nitrate, due to the inavailability of this gas, and hence release of nitrogen from the system. It would thus be of value to measure concentrations of gases such as hydrogen sulfide, methane, carbon dioxide and nitrogen gas at the sediment-water interface. Alternately, localized denitrification can take place under anoxic conditions in the burrows of oligochaetes, or by bacteria in the digestive tracts of these worms, releasing nitrogen and nitrous oxide gases. This theory can be further explored by the collection and examination of these worms, and analysis of conditions in their burrows.

Nitrate concentrations decrease significantly from the basin to the well, with only slight decreases in ammonium and organic nitrogen. Water infiltrating the bottom of the basin will lose any nitrate to denitrification under anaerobic conditions, and ammonium, via cation exchange with the sediment. In general, most of the water exiting the basin would do so via the sides. It is possible that at this locale, denitrification might occur as a result of anoxic conditions within existing sediment. It is likely that this sediment is less thick, and finer grained than that of the base, with very little biological activity, except that of anaerobic bacteria. These sediments will thus be less oxygenated and provide an ideal location for denitrification and loss of nitrogen from the system. Loss of organic nitrogen from the basin to the well may be due to filtration, where particles are caught in the sediment at the sides of the basin during outflow.

Mass balance calculations infer that loss of nitrogen from the system cannot be simply accounted for via sedimentation. This suggests that the major process perpetuating this loss is denitrification, which as previously stated occurs at the bottom of the basin, and which also appears to occur at the sides. Overall this study has proven that conditions at the bottom of the recharge basin are effective in decreasing nitrate concentration, however within the scope of the study, the exact mechanism cannot be determined. The only definite inference that can be made is that this mechanism is not merely a sedimentation process.

Determination of the processes occurring within the basin can be attempted by observing variations in the ratios of  $^{14}\text{N}$  and  $^{15}\text{N}$  isotopes within the system. If nitrogen gas is generated, the proportion of  $^{15}\text{N}$  in the well should be greater than that in the water entering the basin, as  $^{14}\text{N}$  is the primary constituent of nitrogen gas, and is thus lost from the system. To give a better overview of nutrient transformation within the basin, carbon and phosphorous cycling should be examined in conjunction with that of nitrogen, as these biogeochemical cycles are often interdependent and interrelated. Of utmost importance is a better understanding of the nature of activity on the sides of the basin, and detailed mapping of the distribution of sediment at these locations, and on the base might help to answer many of the questions which have surfaced.

Deduction of a mechanism which would naturally extract nitrate from recycled waters, is an application which may be important for reducing ground water pollution on Long Island. Though nitrate concentrations in the well, and on the Island in general, are far below the drinking water standard of 10 mg/L, the regulation of this nutrient is vital due to the high septic tank density of the Island, and thus the continual threat of contamination of potable water.

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## CALCULATION APPENDIX

### Mass Balance Calculation

$$\Delta M/\Delta t = [C_i F_i + C_r F_p] - C F_o - R_s$$

$\Delta M/\Delta t$  = change in mass of nitrate over change in time

$C_i$  = concentration of dissolved nitrate in the stream

$C_r$  = concentration of dissolved nitrate in rainwater

$C$  = concentration of nitrate in lake water

$F_i$  = rate of water inflow from the stream

$F_o$  = rate of water outflow

$F_p$  = rate of precipitation x SA of lake

$R_s$  = rate of sedimentation

$$C_i = 1.06 \text{ mg/L}$$

$$C_r = 1.13 \text{ mg/L}$$

$$C = 0.88 \text{ mg/L}$$

$$F_i = 7 \times 10^8 \text{ L/yr}$$

$$F_o = 7 \times 10^8 \text{ L/yr}$$

$$F_p = (1.14 \text{ m/yr} \times 4097 \text{ m}^2) = 4.7 \times 10^6 \text{ L/yr}$$

$R_s$  was determined by using the surface area of the core and the Total Nitrogen deposited in ARS1 (Table 2) to determine the rate of deposition per year per square meter (the basin was last drained about 8 years ago, and the maximum depth of sediment is 10cm). The surface area of the basin was then used to approximate the total sedimentation:

$$\text{SA of core} = 3.17 \times 10^{-3} \text{ m}^2$$

$$\text{Rate of deposition} = 1.25 \text{ cm/yr} = 12.5 \text{ mg/yr}$$

$$\text{Deposition per square meter} = 3943 \text{ mg/m}^2 \text{ yr}$$

$$\text{SA of basin} = 4097.43 \text{ m}^2$$

$$R_s = 3943 \text{ mg/m}^2 \text{ yr} \times 4097.43 \text{ m}^2 = 1.6 \times 10^7 \text{ mg/yr}$$

$$\begin{aligned} \Delta M/\Delta t &= [C_i F_i + C_r F_p] - C F_o - R_s \\ \Delta M/\Delta t &= 7.4 \times 10^8 \text{ mg/yr} - 6.2 \times 10^8 \text{ mg/yr} - 1.6 \times 10^7 \text{ mg/yr} \end{aligned}$$