

ABSTRACT

REYES, MANUEL MIGUEL. River Nitrate Gains from Groundwater Discharge at Waste Application Fields. Neuse River, North Carolina. (Under the direction of Dr. William Showers.)

Nitrate is a common pollutant in rivers worldwide. Samples of groundwater discharging into the Neuse River adjacent the Neuse River Wastewater Treatment Plant (NRWWTP) waste application fields (WAFs) have been measured as high as 86 mg NO₃/L. The NC surface water standard is 10 mg NO₃/L (N.C. Division of Water Quality, 2007).

Geophysical surveys of the WAFs revealed diabase dikes intruded into the granitic bedrock. Groundwater flow is occluded across the dikes; however, fractures around the contact metamorphic zone along the dikes are likely areas of high groundwater flow.

At the NRWWTP, four seasonal sampling periods were conducted at a dike/river crossing in the NW, and one sampling period at another crossing in the E. Samples were analyzed for NO₃, NH₄, Si, and Cl concentrations. At each sample point, parameters of hydraulic conductivity (K), hydraulic gradient (j) were measured yielding specific discharge (v) and nitrate flux. A 'hot spot' of nitrate flux discharging into the river was found downstream of the dike at the NW reach. Using sampling data from each period, a multiquadric radial basis function with anisotropy interpolation was computed and prediction maps for NO₃, Si, Cl conc., j, K, v, riverbed elevation, and nitrate flux were made. Assuming an accurate interpolation, the nitrate flux at this 'hot spot' was measured in some hydrologic conditions to discharge amounts of nitrate as high as 27 kg NO₃/d over an area of 1181.25 m³. This nitrate has an isotopic signature of bio-solid nitrate with denitrification in some areas.

River Nitrate Gains from Groundwater Discharge at Waste Application Fields
Neuse River, North Carolina

by
Manuel Miguel Reyes

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Marine, Earth, and Atmospheric Sciences

Raleigh, North Carolina

2009

APPROVED BY:

Dr. William Showers
Chair of Advisory Committee

Dr. David Genereux

Dr. DeWayne Bohnenstiehl

BIOGRAPHY

The author was born in Manila, Philippines and currently resides in Chapel Hill, North Carolina. He graduated high school from Grimsley High School in Greensboro, NC in 2002, received his B.S. in Environmental Engineering at North Carolina State University in 2006 and is receiving his M.S. in Marine, Earth, and Atmospheric Science with a concentration in Hydrology from North Carolina State University in 2009. He became interested in environmental work because he likes playing outside and is passionate about helping underprivileged people get clean water and opportunity through entrepreneurship. Post-graduation, he is moving to the Philippines to manage and operate Kingfisher Park, his family's private biodiversity park and social eco-tourism business.

ACKNOWLEDGEMENTS

Thanks to my advisory committee: Dr. William Showers, Dr. David Genereux, and Dr. DelWayne Bohnenstiehl, and also Bernard Genna, Miranda Stamper, Ted Dodson, Jeffrey Siceloff, Jonathan Harris, Justin Maslack, Walt Gurley, Maggie Coon, Kristen McSwain, Dr. Casey Kennedy, Dr. Tom Wolcott, Dr. Helena Mitsova, Dr. Christopher Osburn, Dr. Lonnie Leithold, Katherine Almquist, Kimberly Null, God, friends, and family for helping and supporting me through graduate school.

Thanks to The Red Bicycle coffee shop in Chapel Hill and the tunes of Jack Johnson, Ben Harper, Bob Marley, Mat Kearney, and Brandon Heath for helping me write this thesis.

This work was funded by the North Carolina RiverNet program.

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I. INTRODUCTION

Nitrate is a common pollutant in rivers worldwide (Mayer, et al., 2002). Environmentally it is a contributor to algal blooms and eutrophication in aquatic ecosystems and high concentrations of nitrate in drinking water have been linked to cancer incidence and reproductive complications in human health (Ward, et al., 2005). These adverse effects of nitrate to aquatic ecosystems and human health have resulted in environmental legislation regulating nitrate in surface water. The North Carolina Department of Environment and Natural Resources (NC DENR) Division of Water Quality nitrate surface water standard is 10 mg/L (N.C. Division of Water Quality, 2007). This matches the national drinking water standard set by the World Health Organization and United States Environmental Protection Agency (U.S. Environmental Protection Agency, 2008). In comparison, pore water samples from the riverbed adjacent the Neuse River Wastewater Treatment Plant (NRWWTP) waste application fields (WAFs) have been measured to be as high as 86 mg/L.

Bio-solid disposal on WAFs is a common practice for nutrients generated by wastewater treatment. The fields are designed to dispose of the nutrients by crop uptake. Land application of bio-solids however has been proven to leach nutrients, specifically nitrates, into groundwater and surface water (Spalding et al., 1993; Joshua et al., 1998). This groundwater contamination results in a nitrate plume down-gradient of WAFs. Worldwide, many activated sludge wastewater treatment plants are located adjacent to rivers, lakes or other bodies of water for the discharge of treated water. If possible, these plants are surrounded by WAFs to minimize costs of transporting bio-solids off site.

II. RESEARCH LOCATION AND OBJECTIVES

A. Neuse River Wastewater Treatment Plant

The NRWTP is an activated sludge plant located on a reach of the Neuse River near Clayton, NC (Figure 1). The west side of a 6.7 km reach is adjacent to the WAFs used by the NRWTP and separated only by a riparian buffer (Figure 2). Previous research showed nitrate gains in the river (Showers et al., 2005) as well as nitrogen flux from streams within the WAFs (Harris, 2008). Further research is needed to determine the NPS nitrate gains to the river from deep groundwater. Previous research has also shown that increases in river nitrate flux along this reach have been associated with rain events. Groundwater recharge and discharge during a rain event has not been mapped.

The hydrogeology of the Piedmont area of North Carolina is characterized by a soil zone with an underlying saprolite regolith underlain by a transition zone into fractured granitic bedrock (Figure 3). Most of the water storage is contained in the unconfined aquifer located in the saprolite regolith. The transition zone between the regolith and the fractured bedrock is the zone of the fastest groundwater flow and contaminant transport (Daniel & Dahlen, 2002). Geophysical studies have proven this model to be accurate at the NRWTP (Akah, 2008; McSwain et al., 2009). Diabase dikes buried in the WAFs were mapped using electromagnetic and magnetic techniques.

The geology of this area of North Carolina is also characterized by intruding diabase dikes. These dikes hinder horizontal groundwater flow perpendicular to the dikes but they also act as preferential flow paths for groundwater flow parallel to the dikes as they occur in

fracture zones in the granitic bedrock (Daniel & Dahlen, 2002). These preferential flow paths of groundwater within the nutrient plume could be non-point sources of nitrate gains in the river.

B. Research Hypothesis and Objectives

Hypothesis

Diabase dikes intruded into the granitic bedrock occur in fracture zones in the bedrock causing preferential flow paths for groundwater. These flow paths may act as discrete point sources of nitrate-contaminated groundwater into the Neuse River at the NRWWTP.

Objectives

1. Map the spatial and temporal variability of groundwater discharge and nitrate concentration and quantify groundwater discharge and nitrate flux in a reach of the Neuse River crossing a diabase dike in the northwest fields of the NRWWTP in four sampling periods (September 2008, January 2009, April 2009, and July 2009). These four sampling periods had differing river stage, groundwater conditions, and season.
2. Map the spatial variability of groundwater discharge in a reach of the Neuse River crossing a different diabase dike in the eastern fields of the NRWWTP and compare it to the results of the northwest dike crossing.
3. Develop a riverbed differential head pressure transducer for use to make time-series measurements of the spatial and temporal effects of a rain event on groundwater flow on hydraulic gradient at the dike.

III.BACKGROUND

A. Bio-solid Nitrate

Bio-solid disposal on WAFs is a common practice for nutrients generated by wastewater treatment. The fields are designed to dispose of the nutrients by crop uptake. Land application of bio-solids however has been proven to leach nutrients, specifically nitrates, into groundwater (Spalding et al., 1993, Joshua et al., 1998). Spalding analyzed over 100 groundwater well samples in and down-gradient of WAFs in Nebraska for nitrate. He found that nitrate was leaching into the groundwater and also found decreasing nitrate concentrations at depth. Down-gradient of the WAFs, he found evidence of denitrification by increasing $\delta^{15}\text{N}$ values and decreasing nitrate concentration. Joshua identified pathways for sheep bio-solid nitrate via runoff and infiltration in surface water and groundwater. Evidence of nitrate leaching into groundwater at the NRWWTP has been proven in the USGS monitoring wells (Showers et al., 2005). Total applied bio-solids at the NRWWTP vary in each field and from the amount and duration of application (Figure 2).

Nitrate as a tracer

Excess nitrate in groundwater can be used as a tracer for groundwater movement (Bohlke, 2002). In agricultural watersheds on the Delmarva Peninsula, Bohlke has used groundwater nitrate concentration stratigraphy, environmental age-dating tracers, and isotopic tracers to resolve the history and fate of nitrate (Bohlke & Denver, 1995; Bohlke, 2002). He also used these measures to quantify denitrification processes in a stream (Bohlke et al., 2004). For this project, bio-solid nitrate can be used as a tracer in the riverbed to find

areas of groundwater discharge from the WAFs as well as to determine denitrification in this nitrate discharging into the river. Using nitrate as a tracer, a larger plume of nitrate evident at the diabase dike may be an indication that the area around the dike is an area of higher groundwater flux into the river.

$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ Isotopes

$\delta^{15}\text{N}$ isotope analysis can be used to trace the source of nitrate. Kendall showed that comparing the relationship between groundwater $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopes can effectively trace the source of nitrate. Nitrate from manure and septic waste exhibited $\delta^{15}\text{N}$ values of 8 to +40 ‰ with $\delta^{18}\text{O}$ values from -5 to +15 ‰. Denitrification drives the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values higher (Figure 4) as the microbes responsible for denitrification prefer the lighter isotopes driving groundwater nitrate values heavier (Kendall & Aravena, 2000). Samples from the NRWWTP wells and streams have $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values that are consistent with bio-solids (Showers et al., 2005; Harris, 2008). In the NRWWTP monitoring wells using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ tracers, Showers found that bio-solid $\delta^{15}\text{N}$ in groundwater ranges from 10 to 15‰, 15 to 35‰ with denitrification. 57% of the wells were affected by bio-solid nitrate and 22% showed denitrification.

B. Denitrification and Dissolved Organic Carbon

Nutrient flux from groundwater to surface water is affected by denitrification in the riverbed hyporheic zone. Three conditions are needed for denitrification: presence of nitrate, anoxic conditions, and electron donors such as organic carbon (Seitzinger et al., 2006). One of these conditions controls denitrification in every system. Triska found that Little Lost

Man Creek had high concentrations of dissolved organic carbon (DOC), therefore denitrification was controlled by nitrate concentrations in low dissolved oxygen (DO) areas, and by DO in high nitrate areas (Triska et al., 1993). In contrast, Hedin found that DOC controlled denitrification as glucose additions increased denitrification in Smith Creek (Hedin et al., 1998). Denitrification rate is controlled by temperature. Stanford found that in soil cores, denitrification rates decrease as temperature decreases (Stanford et al., 1975).

The NRWWTP has a sandy streambed with silty areas near the banks. Chesnutt found a relationship between hydraulic conductivity (K) and DOC and NH_4 concentrations in the hyporheic zone (Chesnutt & McDowell, 2000). Sandy high K areas showed low DOC and low NH_4 ; silty low K areas showed increased DOC and NH_4 . NH_4 is an indicator for microbial activity and DOC is needed for denitrification suggesting a high likelihood for denitrification in these silty areas near the banks of the NRWWTP. Supporting this, Hedin found stream banks are the most significant location for denitrification (Hedin et al., 1998).

$\delta^{13}\text{C}$ isotopes

$\delta^{13}\text{C}$ isotope tracers can be used to trace the origin of the carbon in the environment. Organic carbon, of interest in this study, is depleted in $\delta^{13}\text{C}$ from biological isotope fractionation from photosynthesis (Boutton, 1991). In the terrestrial environment, there are two major pathways for carbon in photosynthesis: C_3 and C_4 . C_3 plants are generally larger vegetation and exhibit a $\delta^{13}\text{C}$ of -27‰. C_4 plants are smaller shrubs and exhibit a $\delta^{13}\text{C}$ of -13‰. In the aquatic environment, shoreline vegetation takes the C_3 pathway with $\delta^{13}\text{C}$ of -27‰, and is generally the source of peat, with similar isotopic composition. Aquatic

plankton, however, differs from the plants with a range of $\delta^{13}\text{C}$ of -30 to -25‰ (Figure 5). Kendall found that in sediment, C:N ratios are indicative of the source of the carbon; with C:N < 8 dominated by plankton, and C:N > 15 dominated by terrestrial plants (Kendall et al., 2001).

C. Magnetic Surveying and Diabase Dikes

Diabase contains magnetite and iron, making diabase dikes display magnetic anomalies in magnetic and electromagnetic surveys. Two different geophysical methods were used to map dikes: magnetic surveying and electromagnetic induction. These methods were used according to instrument availability.

Magnetic surveying is conducted using a magnetometer which measures the Earth's total magnetic field at any location. A secondary magnetic field generated by the remnant magnetization in a magnetic rock such as diabase as well as induced magnetization by the Earth's magnetic field creates an anomaly in the total magnetic field in a location. A magnetic survey can be used to model the size, strike, and dip of a diabase dike or simply to show magnetic anomalies from diabase dikes (Burger et al., 2006).

Electromagnetic (EM) induction method uses an electric coil to generate an EM field. Lower frequencies of EM waves penetrate deeper in the ground (Burger et al., 2006). These EM fields are measured by electrical conductivity using a receiver coil. The source generates an induced magnetic field in rocks such as diabase creating an EM anomaly. The GEM-2 by Geophex contains the source and receiver coil in a short ski. It can simultaneously generate multiple EM frequencies giving it the ability to survey at various depths (Won, 2003).

Dikes affect groundwater hydrology in that they influence flow in fracture zones in bedrock spanning different layers. Dikes in Hanford, MA are proven areas of high aquifer vertical leakage and contaminant transport (Murray et al. 2007). Diabase dikes in Minnesota have been shown to occlude shallow groundwater flow and strongly influence fracture flow of water (Winterstein, 2002).

D. Groundwater Discharge

There are many methods used to study groundwater contribution to stream flow. Cey compared four different methods 3 base flow and 1 event flow: velocity-area methods, Darcy's equation methods (hydraulic conductivity K and gradient j), direct sampling methods (seepage meters) and for event flow hydrograph separations (Cey et al., 1998). Cey found that during base flow the velocity-area method and Darcy's equation methods did not yield similar results, and the seepage meters were ineffective. For a small reach of river across a diabase dike, velocity-area and hydrograph separation methods cannot be used. Also, with the temporally variable nature of riverbed K , a direct sampling with seepage meters will be ineffective as seepage meters disallow sediment changes affecting K . For this project, Darcy's equation methods are the best way to measure groundwater discharge. Darcy's equation methods relate specific discharge (v) to hydraulic conductivity (K) and hydraulic gradient (j). Volumetric discharge is calculated using specific discharge and cross sectional area (Fetter, 2001).

$$v = Kj$$

Other conditions affect groundwater/surface water interaction. Harvey proved the effect of streambed topography on groundwater exchange. He found that recharge zones generally occur at steeper stream slopes, and discharge zones at flatter slopes. The topography affected both the j and K (Harvey & Bencala, 1993). Secondary porosity in the topography in rocky stream beds such as fracture zones in bedrock or karst areas have been proven to act as discrete point sources for groundwater exchange (Oxtobee & Novakowski, 2002; Chanton et al., 2003). Denitrification in the hyporheic zone produces nitrogen bubbles that can get trapped in silty sediment and reduce K in those areas (Song et al., 2007). These areas are limited to near the bank on the Neuse River. The Neuse River has a sandy riverbed; however, the fractures in bedrock around contact metamorphic zones adjacent to the diabase dikes may act as discrete point sources of groundwater (Winterstein, 2002).

Previous isotope research by Bohlke has shown that nitrate-affected deep groundwater flow-paths bypass riparian buffers and discharge into streams (Bohlke & Denver, 1995), and that seasonal variability of groundwater head changes the flow-paths of water discharging into streams (Bohlke et al. 2007). Well logs and river stage logs show seasonal changes in the groundwater head and river levels in the Neuse River at the NRWTP as well (Showers et al., 2005). These seasonal changes could also affect the groundwater discharging into the Neuse at the NRWTP necessitating seasonal sampling.

Hydraulic Conductivity (K)

Riverbed hydraulic conductivity can be measured using various techniques. Landon compared constant and falling head permeameter methods solved using Darcy and Hvorslev

solutions, piezo-seep meter, Hazen grain-size, Bouwer and Rice slug test, and Alyamani and Sen grain size methods for the most robust method of determining riverbed hydraulic conductivity (Landon et al., 2001). He concluded the most robust method for determining riverbed hydraulic conductivity in the upper 0.25 m of the riverbed is an in situ falling head permeameter test solved with the Hvorslev solution (Hvorslev, 1951). Hvorslev conducted permeameter tests on saturated soil cores in a laboratory; however Chen tested a method for conducting in situ falling head permeameter tests in the field. He applied straight and L-shaped standpipes directly into streambeds to measure vertical and horizontal hydraulic conductivity using falling head tests (Chen, 2000). For the purposes of this project, a standpipe falling head permeameter (as per specifications by Genereux, modified to 1.84m length) pushed into the riverbed was used to measure vertical hydraulic conductivity (Genereux et al., 2008; Leahy, 2007).

Vertical hydraulic conductivity varies with depth. Cardenas conducted multilevel constant head injection (CHIT) and slug tests to three-dimensionally model hydraulic conductivity in riverbeds (Cardenas & Zlotnik, 2003). Given the temporal variability of hydraulic conductivity in the upper layers of the riverbed, three dimensional modeling is not needed. Spatial variability in vertical hydraulic conductivity in the riverbed was measured.

The water level at the Neuse River at the NRWWTP is largely controlled by nearby Falls Dam. Springer conducted a study on the Colorado River in the Grand Canyon in a reach of river controlled by the Glen Canyon Dam and found that a dam release deposited new sediment and compacted old sediment affecting riverbed hydraulic conductivity over the

course of a year (Springer et al., 1999). The Neuse River at the NRWWTP is subject to dam releases from Falls Dam as well as exhibiting a flashy rain event hydrograph as it is affected by urban areas in Raleigh, NC. Rain events and dam releases can affect the sediment and riverbed hydraulic conductivity at the NRWWTP.

Hydraulic Gradient (j)

Hydraulic gradient measurements are usually made by piezometers comparing surface water head to groundwater head at a measured depth in the riverbed. Preliminary piezometer designs were used by Lee and Woessner to simply measure groundwater head at depth for use in conjunction with seepage meters (Lee & Cherry, 1978; Woessner & Sullivan, 1984). Winter improved on this design creating a piezometer with an air manometer board to measure differential head and capable of taking groundwater samples using a syringe (Winter et al., 1988). Kennedy and Genereux developed a piezo-manometer similar to the Winter piezometer operating with oil rather than air contacting both the surface water and groundwater to amplify the head difference to accurately measure miniscule head gradients between groundwater and surface water (Kennedy et al., 2007). Piezo-manometers of the same design were used in this project.

The head gradient between surface water and groundwater varies temporally even affecting the direction of groundwater exchange. Chanton used seepage meters, wells, and tracers to show varying surface water head by Atlantic Ocean tides controlled groundwater levels and discharge in the Florida Bay in the karst terrain of the Florida Keys (Chanton et al., 2003). Rain event flow has been shown to control groundwater exchange over the course

of an rain event. An electrical conductivity experiment by Oxtobee over a rain event showed temporally variable recharge and discharge in a fractured bedrock stream (Oxtobee & Novakowski, 2002). Electrical conductivity data can only yield direction of flow, not flux. Dam release and rain events may cause similar effects on the Neuse River.

Event flow can create hazardous situations from high flow velocities and debris in rivers therefore in-stream measurements cannot be accomplished during an event. In order to get hydraulic head measurements during a rain event, an inexpensive differential head pressure transducer must be designed. The device must have low profile to minimize damage during a rain event and must be connected to a data logger for temporal readings of multiple devices. An electronic differential head piezometer has never been designed in previous research and can be used in future research involving temporal variability of hydraulic gradient in surface water/groundwater interaction.

E. Groundwater and Sediment Sampling

Groundwater Sampling

In conjunction with groundwater discharge measurements, ion concentrations found in groundwater samples can be used to calculate fluxes of that ion into the river. This technique can be used to identify areas in bodies of water where specific ions are entering the surface water via groundwater, and quantify the flux of the ion entering the surface water (Fetter, 2001, Kennedy et al. 2009). For example for nitrate:

$$NO_3 \text{ flux} = v(NO_3 \text{ concentration})$$

Nitrate is the ion of most interest in this study; however, concentrations of other ions such as ammonium, silicate, and chloride are of interest as well. Ammonium is a natural microbial pathway for nitrate in the environment (Tiedje, 1988). Ammonium ions, however, are known to readily sorb to sediment particles and high concentrations (above 1 mg/L) are not often found in solution. Silicate, which from our sampling is known to have a concentration of 6-8 mg/L in the river, has a high concentration in groundwater (40+ mg/L), and thus can be used as a tracer for areas of groundwater discharge. Chloride is a tracer for bio-solids (Showers et al., 2005). At the NRWWTP, high concentrations of silicate and chloride are sometimes found in conjunction with high concentrations of nitrate.

These samples also can be used for stable isotope analyses. As stated (section A), $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope analysis can be used to trace the source of nitrate (Kendall & Aravena, 2000). Using a method devised by Chang and modified by Showers, nitrate can be taken from samples and analyzed for these isotopes (Chang et al., 1999; Showers et al. 2005).

For this project, groundwater sampled at 30 cm depth is assumed to have the same chemical composition as discharging groundwater in flux calculations. This is a good assumption for most areas with a sandy streambed. Silty areas of the riverbed may have geochemistry affecting chemical concentrations in that 30 cm. As nitrate is of most interest in this study, denitrification is a factor that can change the nitrate concentration in that final 30 cm of riverbed from the measured DOC is a primary electron donor for denitrification in the hyporheic zone (Seitzinger et al. 2006). The presence of high concentrations of DOC in

groundwater, along with nitrate and anoxic conditions may indicate areas of denitrification. DOC concentration and $\delta^{13}\text{C}$ in groundwater samples were analyzed.

Sediment Sampling and Grain Size Analysis

Sediment grain size affects hydraulic conductivity (K), as well as geochemistry in the hyporheic zone (Chestnutt & McDowell, 2000; Fetter, 2001). For descriptive purposes, grain size ranges fall into classifications such as gravel, sand, silt, and clay. For this project, we will use American Association for State Highway and Transportation Officials (AASHTO) grain size ranges of: 0.001-0.075 mm for silt and clay, 0.075-0.425 mm for fine sand, and 0.075-2 mm for coarse sand (Holtz & Kovacs, 1981). Sediment samples were taken at key locations in the riverbed and analyzed for grain size.

As discussed previously (section B), sediment $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio can be used to trace the origin of the carbon and nitrogen in the sediment. The sediment samples will also be analyzed for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio in sediment using a method outlined by Kendall et al. (2001).

IV. MATERIALS AND METHODS

A. Geophysical Methods

Geophysical methods were used to locate diabase dikes in the NRWTP WAFs and on the Neuse River. These surveys were accomplished using a Scintrex NAVMAG CS-5 cesium magnetometer and a Geophex GEM-2 electromagnetic (EM) surveyor. Both instruments are synchronized to GPS units in order to spatially georeference their measurements. These instruments were used according to their availability.

Electromagnetic surveying was conducted first on the NRWTP WAFs. The EM was mounted on a PVC sled and pulled behind a Polaris all-terrain vehicle in order to minimize the amount of extraneous magnetically susceptible material close to the EM. The EM surveyed the fields at four different frequencies: 2130, 9990, 20130, and 47790 Hz. As lower frequencies of EM waves penetrate further into the ground; magnetic susceptibility anomalies for diabase dikes show the most at the 2130 and 9990 Hz frequencies.

Magnetic surveying was conducted on the river and riparian buffer. On the river, the magnetometer was mounted on a small Hobie Float Cat boat with minimal aluminum (non-magnetic) metal parts and was pulled by a larger boat upstream from the Mial Plantation Road bridge in Clayton, NC past the NRWTP up to the Auburn Knightdale Road bridge to conduct a single transect survey of the whole river reach (Figure 6). A multiple transect survey of the northwest diabase dikes was conducted by mounting the magnetometer on a tandem fiberglass kayak without metal parts and paddling upstream and downstream across the dikes. The riparian buffer south of the northwest dikes was surveyed by walking the

buffer with the magnetometer mounted on a backpack. Magnetic anomalies from these surveys mark the spatial locations of these diabase dikes.

B. River Nitrate Concentration Surveying

A survey of river nitrate concentration was completed from the stretch of river from Auburn Knightdale Road to Mial Plantation road with the purpose of finding spatial locations of high river nitrate concentrations and the overall rise in river nitrate concentration across the reach. The survey was conducted two days after a small rain event in September 2007 in base flow conditions. A Satlantic ISUS nitrate analyzer fed by a flow-through cell taking repeating measurements was time-synchronized with a Trimble GPS unit in order to georeference measurements. Water samples were taken every five minutes to verify nitrate concentrations and correct for instrument drift.

C. Sampling Periods

a. Seasonal Sampling Periods

As the Northwest dike showed this as an area of high nitrate concentration, four sampling periods were completed in September 2008, January 2009, April 2009, and July 2009. This dike is located adjacent to four continuously monitored wells with two other well clusters in hydrologically up-gradient fields. The initial sampling strategy was designed to best estimate the extent of the affected area. Sampling strategies changed over time though April and July 2009 were similar due to conditions such as river safety and the desire to optimize the sampling strategy to most accurately map the effect of the dike on the nitrate plume. Kennedy found diminishing returns for sampling densities above 0.06 points/m²

(Kennedy et al., 2008). The sampling strategies used in this project varied in sampling density from 0.02 to 0.052 points/m². At each sample location, a groundwater sample was taken 30 cm below the streambed, a falling head test was performed, and a differential head gradient between groundwater and surface water was measured.

September 2008

Nine lines of samples were taken with seven samples per line spanning from the center of the dike downstream with 12.5 meters between each line. Samples were spaced 3 meters apart on the line with the first sample 3 meters from the south bank with the seventh sample being in the middle of the river. The total river reach for this sampling period was 100 m long and 21 m wide (to mid-river), for an area of 2100 m². 63 samples were taken over 2100 m² resulting in a sampling density of 0.03 points/m². A grid was formed with each sample location having its own id. The lines were signified by letters: 'A' being farthest downstream and 'I' being the farthest upstream on the dike. Along each line, samples were numbered 1-7 with 1 being closest to the south bank and 7 in the middle of the river (Figure 12). Surface water samples were taken at three random measurement points.

January 2009

Three lines of seven samples were taken in the same locations as the most upstream lines (lines G – I) in the September 2008 sampling period (Figure 12). The total river reach for this sampling period was 24.5 m long and 21 m wide (to mid-river), for an area of 514.5 m². 27 samples were taken over 514.5 m² resulting in a sampling density of 0.052 points/m². This sampling period was truncated due to unsafe river conditions.

April 2009/July 2009

Five lines of seven samples were taken (lines F-J) including an additional line designated line J added 12.5 m upstream of line I at the location of the USGS staff plate for river stage. The total river reach for this sampling period was 56.25 m long and 21 m wide (to mid-river), for an area of 1181.25 m². Three additional samples were taken halfway between each line and downstream of line F. These samples were spaced in a line 6m apart with the first sample 6m from the south bank and designated using letter of the closest line downstream followed by an 'M' and the sample number. For example, between lines I and J is line IM (Figure 12). 50 samples were taken over 1181.25 m² resulting in a sampling density of 0.042 points/m².

b. Eastern Dike Sampling Period (October 2008)

An additional sampling period was completed on another diabase dike crossing the fields and river to the east of the WWTP. The sampling area spanned 100 m of river, 21 m wide (to mid-river), with sampling lines spaced 10 m apart for an area of 2100 m² on the southern half of the river. Three lines were downstream of the dike, one line was on the dike, and six lines were upstream of the dike. Four equally spaced samples per line were taken on the southern half of the river with the fourth sample being in the middle of the river. A fifth sample was taken on the northern half of every line. A total of 44 samples were taken on the southern half of the river for a sampling density of 0.02 points/m². This is a wider dike than the northeast dikes and is also separated by a wider riparian buffer.

D. Groundwater Discharge and Nutrient Flux

Groundwater discharge was calculated using Darcy's Equation. This requires measuring two parameters, hydraulic conductivity (K) and hydraulic gradient (j) to determine specific discharge (v), $v = Kj$. Multiplying specific discharge and nitrate concentration (from groundwater sampling) yields nitrate flux.

Hydraulic Conductivity: Falling Head Test with Hvorslev Solution

Hydraulic conductivity was measured at each sample location using field falling-head permeameters. The field permeameter is a 7 cm diameter, 184 cm tall clear pipe with graduated measurements pushed 30 cm into the sediment at each piezometer location as in Genereux et al. (2008). The permeameter was pushed into the streambed to the flange set at 30cm and filled with water. The water level drop to several intervals will be timed and computed with the Hvorslev falling head permeameter solution (shown below) to calculate the hydraulic conductivity (Hvorslev, 1951).

$$K_v = \frac{\frac{\pi D}{11m} + L_v}{t_2 - t_1} \ln\left(\frac{H_1}{H_2}\right)$$

D is the permeameter diameter (7 cm), m is the square root of the ratio of horizontal to vertical K assumed to equal 1 ($m = \sqrt{K_H / K_V}$), L_v is the depth of penetration into the riverbed (30 cm), H is the water level inside the permeameter relative to the initial (pre-test) water level, and t is the time. Letting $t_1 = 0$, when $H_1 = H_0$, or the beginning of the test and transforming the Hvorslev equation to a linear equation yields:

$$\ln H = -\frac{K_v}{\frac{\pi D}{11m} + L_v} t + \ln H_0$$

There are three sources of uncertainty in this measurement: uncertainty in the value of m , uncertainty in the measurands, and model error (Genereux et al., 2008; Leahy, 2007). In this study, uncertainty in m ($\pm 5\%$) and model error ($\pm 12\%$) were approximated as in Genereux et al. (2008), with the uncertainty in the measurands calculated and reported for each sample point. The total uncertainty in K is calculated as the root of the sum of uncertainties from these three sources squared. Every K value in this study is in-situ K , without temperature correction.

Hydraulic Gradient and Sampling: Piezo-manometer

Riverbed groundwater to surface water head gradient and groundwater samples were measured using light-oil piezo-manometers similar to those designed by Kennedy (Kennedy et al., 2007). The piezo-manometers will yield the head difference between the groundwater 30 cm at depth and the surface water. The head gradient is this head difference divided by the distance between the groundwater and surface water (30 cm).

$$j = (h_{gw} - h_{sw}) / d$$

150 mL samples were taken at every location at 30cm depth for nutrient analysis and any sample greater than 5 mg/L nitrate also went through $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope analysis. Assuming the porous medium has a porosity of 0.35, the radius of influence for a 150 mL sample is estimated to be 4.5 cm. With a radius of influence of 4.5 cm and samples taken at 30 cm depth, it is assumed no surface water was taken with the groundwater samples.

During our sampling, the uncertainty in j (as per Kennedy's equation for uncertainty in Δhw , divided by our sampling depth of 30 cm yielding uncertainty in j) for each specific sample was at least one order of magnitude lower than the measured j for the sample with a mean of approximately 5% uncertainty at 95% confidence (Kennedy et al., 2007).

Riverbed Elevation

Measured in addition to the K data was the water level outside the falling head permeameter, or the depth of the river. A USGS staff plate from research by McSwain is at the northwest dike and has a surveyed elevation of 142.65 ft projected in NAVD88 (McSwain et al., 2009). By subtracting the river depth from a staff plate reading during the time of sampling and adding the total to the surveyed staff plate elevation riverbed elevation can be calculated.

$$\text{staff plate reading} - \text{river depth} + 142.65 = \text{riverbed elevation}$$

E. Laboratory Techniques

Ion concentration analysis

Samples were filtered and nitrate, chloride, silicate, phosphate and ammonium concentrations were measured with a La Chat Quick-Chem 8000 Ion Chromatograph. The following methods were used for each ion: nitrate EPA Method 353.2, chloride EPA Method 300.0, silicate EPA Method 370.1, phosphate EPA Method 365.1, ammonium EPA Method 350.1. Check standards and QC standards of known concentration were used for control as well as blanks and spiked samples to check for matrix effects. Instrument tolerance for uncertainty in sample concentrations from these methods is $\pm 10\%$.

$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic analysis

Sample analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopes was accomplished through methods outlined in Chang et al., 1999 and Silva et al. 2000, modified by Showers et al. 2005. The filtered water samples were passed through a column of anion exchange resin (Biorad AG 2-X8) to remove the nitrate. 15 mL of hydrochloric acid (HCl) was then passed through the anion exchange resin column to elute the nitrate from the resin and into solution. This elutant is neutralized using silver oxide (Ag_2O), filtered leaving only silver nitrate (AgNO_3) in solution, and freeze dried into a powder removing all water. The silver nitrate was then analyzed for $\delta^{15}\text{N}$ isotopes by a Finnigan Mat Delta+ XL CF-IRMS with results calibrated against internal standards as well as NIST 8550, 8548, and 8547. ^{18}O samples were pyrolyzed in a thermal conversion elemental analyzer (TCEA) and then analyzed by the Finnigan Mat Delta+ XL CF-IRMS with results calibrated against internal standards as well as NIST 8542, 8549, and USGS 34, 35. A standard deviation of $\pm 0.2\text{‰}$ was reported for standards run for $\delta^{18}\text{O}$ and $\pm 0.15\text{‰}$ was reported for $\delta^{15}\text{N}$.

Sediment grain size analysis

Sediment samples from transects G-I, at locations 1, 3, 5, and 7 were analyzed for grain size in Dr. Elana Leithold's lab using a Beckman Coulter LS 13 320 Laser Diffraction Particle Size Analyzer (Beckman Coulter, 2009). The samples were pre-wetted using 15mL DI water, homogenized and suspended using a magnetic stir plate, and added to the PSA using a large pipette until obscuration of the beams reached between 40-50%. This reported

obscuration is the percentage of light scattered out of the beam by the particles, using a PIDS (Polarization Intensity Differential Scattering) assembly.

Groundwater DOC concentration and $\delta^{13}\text{C}$ isotope analysis

DOC concentration and $\delta^{13}\text{C}$ in groundwater samples from transects G-I, at locations 1, 3, 5, and 7 were analyzed in Dr. Christopher Osburn's lab using a wet chemical oxidation (WCO) TOC analyzer (Osburn & St-Jean, 2007). These samples were pre-filtered and drops of phosphoric acid were added to drop the pH below 4 to stop microbial activity during sample storage. The instrument tolerance for uncertainty is <5% relative standard deviation for DOC. A standard deviation of $\pm 0.23\%$ was reported for standards run for $\delta^{13}\text{C}$.

Sediment $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ isotopic and C:N ratio analysis

Sediment samples from transects G-I, at locations 1, 3, 5, and 7 were analyzed for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio using a method by Kendall (Kendall et al. 2001). Samples were freeze dried, ground, and loaded it into silver capsules. These capsules were placed in a dessicator above 3M HCl for 24 hours and then analyzed using a Finnigan Mat Delta+ XL CF-IRMS with results calibrated against internal standards. A standard deviation of $\pm 0.1\%$ was reported for standards run for $\delta^{13}\text{C}$ and $\pm 0.15\%$ was reported for $\delta^{15}\text{N}$.

V. RESULTS AND DISCUSSION

A. Geophysical Surveying

Using EM surveying, diabase dikes were identified in two areas at the NRWWTP: Fields 4, 5 and 6 in the northwest, and fields 17-24 in the east (figures 7, 9). Using the Geophex GEM-2 EM Surveyor, the diabase dikes were mapped on the fields. The lower frequencies of 2130 and 9990 Hz were found to be more effective at detecting the magnetic susceptibility anomalies created by the diabase dikes. These lower frequencies penetrate deeper into the ground (Burger et al., 2006), and are more affected by the buried dike.

A Scintrex CS-5 magnetometer was pulled on a Hobie Float Cat boat upriver the length of the reach adjacent the NRWWTP behind a larger boat to measure total magnetic field on the river and find where the diabase dikes cross the river (Figure 6). This magnetic survey discovered a previously unknown diabase dike running adjacent the stream emptying most of the watershed of the NRWWTP or the “pipe” stream (Harris, 2008). It also proved that the two diabase dikes in the northwest WAFs come together in the riparian buffer, and then splay again when they enter the river. This affects the hydrogeology of the area, as the dikes impede any contaminated groundwater from flowing into the area between the dikes. Groundwater discharging between the two dikes into the river should therefore have low nitrate concentrations. This survey also identified the two river crossings of the eastern dike at the NRWWTP and a third crossing of the same dike to the southeast.

Two more in-depth magnetic surveys were completed on the northwest dikes. The total magnetic field was measured in the riparian buffer between the WAFs by walking the

buffer with the magnetometer stowed on a backpack. In the river, the magnetometer was mounted on a tandem fiberglass kayak and high resolution transects of the three dikes from the pipe stream to 100 yards past the downstream dike were measured (Figure 8).

B. River Nitrate Concentration Surveying

Using an ISUS nitrate analyzer fed by a flow-through cell and synced with a GPS unit, the surface water nitrate concentration was surveyed to find changes in surface water nitrate concentration from the reach of the Neuse River adjacent the NRWWTP. These changes are caused by point and non-point inputs of nitrate into the river, such as streams, groundwater, and the WWTP discharge pipe. Of interest were the non-point sources (Figure 10). The overall river nitrate jumped 0.2 mg/L at the discharge pipe masking any further non-point nitrate sources. The overall river nitrate from upriver of the WAFs to the discharge pipe increased from 0.25 mg/L to 0.37 mg/L indicating non-point source nitrate increased the overall river nitrate concentration approximately 0.12 mg/L over this 3.5 km reach.

Momentary non-point increases in nitrate concentration were measured and explanations for these increases explained as follows (Figure 10): Streams draining into the river from the WWTP and from land on the opposite bank of the WWTP increased the river nitrate. Some increases also may be linked to farm ponds on the north side of the river. Of the most interest in this study though are the river nitrate concentration increases associated with the diabase dikes, specifically the northwest dikes, where the river nitrate concentration increased from 0.28 mg/L to 0.34 mg/L while crossing the dike. This suggests a nitrate

contaminated groundwater hotspot (McClain, et al., 2003) from the dike caused the surface water concentration to increase at that location, and gives reason to sample and study the hydrogeology of the system where the diabase dike and the river intersect. Subsequently, a sampling strategy was devised to map the effect of the dike on the groundwater discharge and contamination in the river.

C. Sampling Periods

Five sampling periods were completed on two different reaches at the NRWWTP. Four sampling periods, one each season, at the northwest diabase dike, and one sampling period on the eastern diabase dike. The purpose of the seasonal sampling periods was to identify seasonal cycles specifically from changes in water table and temperature conditions. The water table elevation at the NRWWTP at well cluster 2, well 2-1 is plotted in Figure 11. Sampling periods from September and January were in low water table conditions, and April and July were in high water table conditions. The eastern dike was sampled as a comparison to the northwest diabase dike but was only sampled once as overall there were orders of magnitude less nitrate discharging into the river at that reach than the northwest reach. Well sampling at the NRWWTP has yielded groundwater concentrations at the NW dike hydro-observatory of 44.0 mg/L and at monitoring wells at the edge of the fields at the E dike of 106.7 and 22.0 mg/L (Showers et al. 2005).

An interpolation technique was used to create prediction contour maps for the sampled reach of river from the sample points. It was determined by Kennedy that the multiquadric radial basis function (mRBF) interpolation technique with anisotropy is the

most effective technique for this project (Kennedy et. al., 2009). Anisotropy is useful as riverbed parameters are more variable perpendicular to flow than parallel to flow and minimize bulls-eye effects on sample points. The anisotropy factor used was 0.25 (major axis 0.00005 decimal degrees, minor axis 0.0002 decimal degrees) with an anisotropy angle of 353° for the northwest dike crossing and 14° for the eastern dike crossing. As river nitrate concentration abruptly changed in the river, a smaller minor axis was used than by Kennedy.

a. Sampling Period Observations

September 2008

This sampling period was the first sampling period in a period of low water table and low surface water. (Figures 14-21 show spatial NO₃, Si, and Cl concentrations, j, K, and v riverbed parameters, riverbed elevation, and NO₃ flux; Appendix B contains the data plotted.)

The two upriver lines, I and H were anomalous, with line I on the dike and line H adjacent the dike. These two lines had significant concentration differences as line I was found to have no nitrate, and line H had four samples with nitrate above 70 mg/L. This indicates that adjacent the diabase dike may be a ‘hot spot’ for nitrate flux into the river (McClain, et al., 2003; Loague & Abrams, 1999). These two lines are significantly different from the rest of the lines downstream each of which only had one or two samples with nitrate concentration above 10 mg/L (Figure 14). These high nitrate concentrations found downstream of the dike in areas unaffected by the dike suggest a thin long plume of contaminated groundwater running the reach of the river adjacent the NRWTP.

Ammonium, silicate, and chloride ion concentrations were also measured. The highest ammonium concentrations were found in silty areas near shore. High ammonium concentrations (>1 mg/L) were found however in the mid-river sandy areas. These concentrations were not found mid-river during the January and April sampling periods (Appendix B-E). High silicate concentrations were found near land and adjacent the dike (Figure 15). Chloride seemed to appear in the same locations as nitrate (Figure 16).

Riverbed parameters such as hydraulic gradient and conductivity were measured; and other parameters such as depth (converted to riverbed elevation) and sediment type in the river were observed. For this sampling period, an uncharacteristically large amount of negative hydraulic gradient measurements were made compared to the other sampling periods (Figure 17). This may have occurred because the two days of sampling occurred between two rain events and in a time with a low water table (Figure 11), and the river may not have returned to base flow. One high j measurement was made in an area of low K , consistent with the findings of Kennedy that low K can cause high j values (Kennedy et al., 2009). The sediment changes from silt to coarse sand to fine sand from the bank to mid-river (Figure 13). That was reflected in the hydraulic conductivities, as they were low in the silty areas and increased in the sand (Figure 18). At the riverbed level, there is no measurable difference in specific discharge from areas on the dike and not on the dike (Figure 19). Uncharacteristic to normal river morphology, the Neuse in this reach is deepest nearest to the land in the silty areas. Approximately 6 meters from the bank, the sediment changes from silt to sand and the riverbed slopes up to a sandy plateau mid-river (Figure 13, 20).

Combining discharge and concentration data, the highest nitrate flux was found in a ‘hot spot’ in the sandy areas adjacent the dike (Figure 21).

January 2009

Due to near freezing weather and dangerously high conditions in the river, this sampling period was shortened to three lines spanning 25 m of the riverbed. This sampling occurred as the groundwater in the observation wells began recharging and rising (Figure 11). At locations G1 and H1, in the silty areas of the river, hydraulic gradient measurements could not be made due to gas bubbles in the silt disallowing the piezo-manometers to equilibrate without gas developing in the tubing and the sample at H3 was lost. (Figures 14-21 show spatial NO₃, Si, and Cl concentrations, j, K, and v riverbed parameters, riverbed elevation, and NO₃ flux; Appendix C contains the data plotted.)

Compared to the previous sampling period, the nitrate contaminated area seemed to spatially increase. Similar to the September sampling period, there was a ‘hot spot’ of high nitrate flux adjacent to the dike. Although, the nitrate concentrations were overall lower in the ‘hot spot’ (Figure 14) in this month. Consistent with previous ammonium measurements, one high ammonia concentration was measured at location G1 in the silt near shore.

Hydraulic gradient measurements in this sampling period were consistently positive unlike the September sampling (Figure 17). The change in gradient did not change the observation that at the riverbed level, there is no measurable difference in specific discharge from areas on the dike and not on the dike. River parameters of hydraulic conductivity and riverbed elevation were consistent with the previous sampling period (Figure 18, 20).

April 2009

This sampling period was conducted in a period of high water table (Figure 11) and high surface water conditions. At location F1, in a silty area of the river, a hydraulic gradient measurement could not be made due to gas bubbles in the silt. In order to achieve higher resolution and better interpolation, a sampling line of three samples was added halfway between sampling lines for this sampling period. To more accurately measure the effect of the dike, the sampling reach was truncated downriver beginning with line EM, and extended upriver adding line J 12.5 m upstream of line I, at the same location as the USGS staff plate. This resulted in a sampling reach of 56 m. (Figures 14-21 show spatial NO₃, Si, and Cl concentrations, j, K, and v riverbed parameters, riverbed elevation, and NO₃ flux; Appendix D contains the data plotted.)

High concentrations of nitrate, silicate, and chloride were found in the same location adjacent the dike, and with the finer resolution of measurements, the effect of the dike on the transport of those three ions into the river can be clearly seen as the border of the groundwater discharge plume is the dike (Figures 14-16). Compared to previous sampling, the contaminant plume seems to be growing; however the highest concentrations were consistent with the January sampling period (50-60 mg/L) rather than the September period (70-80 mg/L). Consistent with previous sampling, high ammonia concentrations were found in the near-shore silty areas.

Hydraulic gradient values in this sampling period were consistently positive, with one high j measurement in an area of low K near shore (Figures 17, 18). Summary statistics for

this sampling period showed higher average K than the other 3 sampling periods (Figure 18, Table 1). This may be because of spring rainfall destabilizing sediment in the riverbed (Figure 11). Riverbed elevation was consistent with previous sampling periods (Figure 20). This was the only sampling period though that when plotted and interpolated, showed higher specific discharge values on the dike (Figure 19). With the increase in size of the nitrate concentration plume, an increase in the size of the nitrate flux 'hot spot' was measured. This increase was only noticed mid-river where the plume grew in sandy sediment; whereas in the silty areas near shore, the 'hot spot' did not grow due to lesser groundwater flow (Figure 21).

July 2009

This sampling period was conducted in a period of high water table (Figure 11) and low surface water conditions. The sampling strategy was the same of that of the April sampling. (Figures 12-19 show spatial NO₃, Si, and Cl concentrations, j, K, and v riverbed parameters, riverbed elevation, and NO₃ flux; Appendix E contains the data plotted.)

The plume of nitrate, silicate, and chloride is spatially the same size and shape as in April (Figures 14-16). The nitrate concentrations in the plume however rose to levels above those in September with concentrations over 80 mg/L. Also consistent with September, some high ammonia concentrations (>1 mg/L) were found mid-river. At location F1, an ammonia concentration of 30.4 mg/L was measured suggesting high microbial action there.

Contrary to the expectation of high j in low K areas and conclusions from Kennedy et al. (2009), the gradient in the low K areas was negative for this sampling period (Figures 17, 18; Appendix E). This phenomenon is consistent on several sampling lines. One possible

explanation for this is increased summer vegetation in the riparian buffer drawing water from the shallowest flow lines in the river. Complicating the situation, the sampled water in these negative head gradient locations had ion concentrations consistent with groundwater. If these are truly recharge areas, then these nitrate concentrations would be consistent with surface water, suggesting that this negative head gradient is a temporary occurrence. Also the areas near the river banks are silty, low K areas, therefore recharged river water may not have broken through to the sampling depth of 30 cm in the recharge area. The sampled water may be groundwater that did not discharge before the area became a recharge area.

River parameters of hydraulic conductivity and riverbed elevation were consistent with the previous sampling periods (Figures 18, 20). Specific discharge was not consistent with previous sampling however, as the near shore silty areas were recharge areas.

Quantitatively comparing the nitrate flux of the April and July sampling periods of similar size, both reaches discharged roughly 27 kg NO₃/d (Table 2).

Eastern Dike Sampling Period (October 2008)

The north river crossing of the eastern dike was sampled in October 2008. This sampling was during a period of low water table and this reach is on a slight bend. The south side of the river adjacent the treatment plant is a shallow sandbar with most of the river flow to the north side of the river, which is also deeper. In comparison with the northwest dike, this dike crossing has a thicker riparian buffer, 150 yards compared to 50 yards. Entering that buffer the topography slopes down into a perennial stream that was dry at the time of sampling due to water table conditions, then back up a hill before going into the river. Due

to this larger buffer and topography within the buffer, there is a lesser elevation gradient between the fields and the river at this dike compared to the northwest dike. (Figures 22-27 show spatial NO_3 , Si, and Cl concentrations, j, K, and v riverbed parameters; Appendix F contains the data plotted.)

There was little to no nitrate discharging into the river from this reach (Figure 22). This may be because the contaminated groundwater may be up-taken by plants within the larger riparian buffer. It also may be discharging into the perennial stream in the buffer rather than in the river. In the river, higher silicate concentrations were measured around the dike suggesting groundwater inputs around the dike; however those silicate concentrations were not accompanied with high nitrate and chloride concentrations as in the other dike (Figure 23). The silicate seemed to come from the north side of the river.

As the south side of this reach is a shallow sandbar, hydraulic conductivity values were uniform for the entire reach and consistent with those of sand (Figure 26). Hydraulic gradient on this reach seemed to be different upstream and downstream of the dike. Upstream, the reach was characterized by extremely uniform hydraulic gradient measurements resulting in uniform specific discharge. Downstream, more variability in the hydraulic gradient was evident, with some recharge areas mapped resulting in variability in the specific discharge (Figures 25, 27). There is not enough data however to make any conclusions regarding the effect of the dike on the discharge.

b. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ Isotope Data

$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope data shows that the nitrate from the samples is likely from bio-solid waste from the WAFs of the NRWWTP (Figure 28). Showers found that bio-solids at the NRWWTP exhibited $\delta^{15}\text{N}$ values of 12-15‰ (Showers et al., 2005). All but two samples plotted above 12‰ with many showing heavier $\delta^{15}\text{N}$ due to denitrification. Denitrification is exhibited in some samples, especially samples taken in silty areas of the river due to the natural attenuation of nitrate in groundwater in fine particles (Kendall & Aravena, 2000). A plot of $\delta^{15}\text{N}$ and NO_3 concentration also shows that as the $\delta^{15}\text{N}$ gets heavier, nitrate concentrations get lower from denitrification with little denitrification evident in samples with $\delta^{15}\text{N}$ of 15-25 ‰ (Figure 28). This value is greater than the measured value of 10-15‰ in wells at the same site by Showers (Showers et al., 2005). Seasonally, there was no denitrification exhibited in the winter sampling period. As microbial action lessens in the cold weather, denitrification diminished as well. Samples taken from the eastern diabase dike reach however did seem to exhibit higher $\delta^{18}\text{O}$ values, and did not show any denitrification. That reach is almost completely uniform coarse sand (as evidenced by hydraulic conductivity values) and not a conducive habitat for denitrifying microorganisms (Appendix G).

c. Grain Size Analysis

Sediment and pore water samples were taken from transects G-I, at locations 1, 3, 5, and 7 at the northwest reach for carbon and grain size analyses. The river exhibited a deep section near the bank, with a shallow sandbar mid-river, getting deeper in the main channel

(Figure 13). Grain size analyses showed that the deeper sediments near the bank had higher percent silt and clay than the rest of the river. The shallow sandbar was coarse sand, yielding to finer sand in the channel near the middle of the river.

d. Groundwater DOC and $\delta^{13}\text{C}$ analysis

Pore water samples at near-shore silty locations I1 and G1 had high DOC concentrations of 43.46 mg/L and 9.54 mg/L respectively (compared to the surface water concentration of 4.94 mg/L). In contrast, the sample at H1 had a low DOC concentration; an aberration from the other two samples taken from near-shore silt (Figure 13, Appendix H). Comparing these DOC concentrations with $\delta^{15}\text{N}$ isotope data from previous sampling periods shows little denitrification from samples at H1 (Jan, Apr, Jul), while high denitrification at samples taken from G1 (Jul), and IM1 (Apr); as well as high denitrification from another near-shore sample F2 (Sept 08). Evidence of denitrification at high DOC G1 and IM2, without similar evidence low DOC H1 suggests that DOC concentration in pore water limit controls the denitrification at this site.

Pore water $\delta^{13}\text{C}$ suggests that the origin of the DOC is C_4 plants or shoreline vegetation (Figure 5, Appendix H). Higher $\delta^{13}\text{C}$ values were measured at H1 and H3, suggesting possible algal or plankton growth in that area. $\delta^{13}\text{C}$ in the DOC in pore water was measured higher than sediment $\delta^{13}\text{C}$ collected at the same location. This may be because the pore water was collected at 30cm depth, while sediment samples were taken from the riverbed surface.

e. Sediment $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio analysis

Sediment $\delta^{13}\text{C}$ generally follows the trend of riverbed sediment (-27‰) with unexplained heavier $\delta^{13}\text{C}$ isotopes measured at G5 and G7 (Figure 13, Appendix H). Sediment $\delta^{15}\text{N}$ was in the soil N range, rather than the bio-solid range (Figure 4, Appendix H) with much variability. This variability may be because lack of nitrogen in the samples. The weight percent of nitrogen in most sediment samples was below detection limit. With little to no nitrogen and the presence of carbon, C:N ratios were high; all >15, suggesting a terrestrial source of carbon. This supports the DOC $\delta^{13}\text{C}$ suggesting carbon originating from terrestrial C_4 plants and shoreline vegetation.

f. Overall Observations

High nitrate samples correlated with high chloride and high silicate samples especially in the April and July sampling periods; however, they did not correlate as strongly during the January sampling period (Figure 29). This correlation follows as silicate and chloride are found in discharging groundwater, nitrate contamination in groundwater from the site may be found in areas of groundwater discharge as well. High ammonium concentrations and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ measurements and denitrification indicating microbial activity are mostly found in areas of high nitrate and a silty riverbed. These silty areas also have bubbles trapped in the sediment, possibly N_2 product from denitrification. These measurements and observations are evidence that microbes involved in denitrification are in the near shore silty areas of the river.

Over the course of a year, the hydraulic conductivity and riverbed elevation at the northwest dike reach were consistent. The deepest areas were near shore with slow-moving water exhibiting a sharp slope upward to shallow areas of coarse sand with fast-moving water mid-river. The sloped areas showed the most variability in riverbed elevation.

Higher groundwater discharge and consequently nitrate flux was found in the middle of the river in the sandy areas, with low discharge near shore in the silty areas. A high nitrate flux 'hot spot' was located adjacent the dike in the sandy sediment.

Quantitatively over the sampling reach at the hotspot, daily nitrate flux from the riverbed during some sampling periods (table 2) is comparable in amount and magnitude to the average daily flux over a year in some of the NRWTP streams (Harris, 2008). Harris' two streams (pipe and eastern streams) that transported the most nitrate averaged 37 kg NO₃/d. Comparably, the sampling periods on April 4 and 5, 2009 and July 2, 2009 in an 1181.25 m² reach of river each yielded an average discharge of 27 kg NO₃/d. (Results computed using a mean flux per area.) These sampling periods are snapshots in time of the groundwater discharge at base flow over that day. This is most evident in the September 2008 sampling period. It was conducted after a rain event in the tail of the storm hydrograph in the river and before another rain event (Figure 11) and also during a time when the river elevation and the water table elevation (in well 2I) had the least difference of all the sampling periods (Table 2). Consequently, there were many recharge areas in the river during this sampling period and the nitrate flux into the river was the lowest of all sampling periods, even though the sampling period was conducted over a larger spatial area. This shows that

these sampling periods are snapshots in time; therefore their results cannot be extrapolated over larger periods of time.

g. Statistical Uncertainty

Percent uncertainty in K from the measurands was calculated using methods outlined by Genereux for every falling head test (Appendices B-F) and averaged $\pm 10.2\%$, with most values around 6-8% ranging to a maximum of 192% at 95% confidence (Genereux 1998, Genereux et al., 2008; Leahy, 2007; Zar, 1999). Propagating this uncertainty (as the root of the sum of the squared uncertainties in: m of $\pm 5\%$, and model error of $\pm 12\%$) yields an uncertainty in K of $\pm 16.5\%$. Due to less uncertainty from the measurands in this project, this value is comparably less than Genereux and Leahy's 20% uncertainty in K (Genereux et al. 2008; Leahy, 2007). This difference in average uncertainty can be explained as the K observed in Bear Creek is lower than the K in the Neuse River. In both studies, lower K yielded higher uncertainty.

Uncertainty in j from the piezo-manometers is $\pm 5\%$ (Kennedy et al., 2007). Uncertainty in NO_3 concentration from lab technique is reported $\pm 10\%$. Propagating this uncertainty with the $\pm 16.5\%$ uncertainty in K (as the root of the sum of the squared uncertainties) yields uncertainty in v of $\pm 17.0\%$ in the NO_3 flux as $\pm 19.7\%$.

VI. RIVERBED DIFFERENTIAL HEAD PRESSURE TRANSDUCER

A. Design

A riverbed electronic differential pressure transducer was designed for the purpose of logging head gradient over the course of a rain event. The transducer was designed to measure differential pressure between two ports: a groundwater port set 30cm in the riverbed, and a surface water port set 2 cm off the riverbed and output that differential pressure as a voltage that can be translated into a head gradient. The output voltage is by a Campbell CR-10X data-logger onshore. The CR-10X is powered by 12 volt batteries that also power each unit. Each transducer has its own calibration curve and differential head values are periodically measured at each location using a piezo-manometer to correct for instrument drift.

Circuit Board Design

A Silicon Microstructures SM-5812-005 chip with a pressure range of 5 psi was used to measure differential pressure. Assuming a density of 34 feet of freshwater (ffw) per atm, the chip can accurately measure a differential pressure range of -5.78 to 5.78 ffw for a range of 11.76 ffw. (A pressure of 5 psi is approximately 0.34 atm or 11.75 ffw). The SM-5812 outputs linear differential pressure curves and calibration curves were made using a column of water for each chip (Figure 35) with an average calibration curve of:

$$dh = 0.1789(V) - 0.4459$$

Output voltage is V , and differential head is dh measured in meters.

Output voltage can be measured and logged to the third decimal place. At the third decimal place, the SM-5812 is sensitive to 2×10^{-4} m (Silicon Microstructures, Inc., 2005). The SM-5812 requires an input voltage of 5V. The transducers were powered from 12V power outputs from the CR-10X with a 7805 (5V, 1.0A) voltage regulator ensuring 5V into the SM-5812. A 10 μ F radial electrolytic capacitor and a 1 μ F radial electrolytic capacitor were used as per specifications for the voltage regulator, as well as a 0.1 μ F ceramic disc capacitor bridging the power and ground as per specifications on the SM-5812 datasheet. (Wiring diagram Figure 30, photo of the circuit board Figure 31, Campbell program Appendix J.)

Waterproof Housing

Waterproof housings were made from a 3" PVC end cap glued (using PVC glue) onto a 3" threaded female coupling with a threaded cap used to access the circuit board. This threaded cap was sealed using Teflon tape before installation. Three 0.1" holes were drilled into the housing: two as groundwater and surface water ports and one for a power/communication cable going to the CR-10X. Each port contained a stainless steel type 304 hypodermic tube cut down to 1.5 cm length attached to the SM-5812 chip on the circuit board using 1/16" ID x 1/8" OD x 1/32" W size polyurethane tubing filled with mineral oil to contact the electronics. The elevation of the chip within the housing and each port was equal, making the density effects of mineral oil hydraulically negligible. Each port was secured and the seal waterproofed using marine epoxy (Figure 32, 33).

Power/Communication Cable

The power/communication cable is a 4 solid copper conductor 14 AWG fire alarm cable with three conductors used: red for power, black for ground, and green for communications. The cable was cut to an appropriate length for each transducer to reach the Campbell, threaded into a port and soldered into the circuit board. The cable was secured in the hole and the connection waterproofed using marine epoxy.

Groundwater Screen and Port

A stainless steel 316L seamless annealed tube was used for a groundwater port. The end of the tube was plugged and a 4 cm screen was cut into the tube (Figure 34). Each tube measured 34 cm, with 30 cm in the riverbed, and 4 cm used to secure the tube to the waterproof casing using a hose clamp. At the top of the tube, a 1.5 cm stainless steel type 304 hypodermic tube was inserted into the larger tube to act as a port. Marine epoxy was used to seal and secure the port into the larger tube. This port is connected to the groundwater port on the housing using a short length of 1/16"ID x 1/8"OD x 1/32"W size polyurethane tubing filled with water. During installation, the screened groundwater tube was filled with water and connected to the groundwater port on the housing (Figure 33).

B. Results

Nine differential head pressure transducers were deployed in the nitrate flux 'hot spot' in July 2009, with five of the nine recording data for a sampling period of July 17 to July 26. The biggest problem causing transducers to fail was flooding in the river, as Teflon threaded seals in some transducers leaked. The working pressure transducers were located in T1

(transducer 11), T3 (transducer 3), T4 (transducer 1), T7 (transducer 7), and T8 (transducer 8). (Transducer logs for each location are plotted in Figures 37-42, with an extra log of T7 from July 8 to July 17 in figure 42. Sample data from July 17 and July 23 are in Appendix I.)

a. Measurement Observations

At the peak of the rain event hydrograph, the pressure transducers show that the groundwater discharge decreases. From the data that we have, it seems as if rain events do not drive significantly more groundwater than at base flow; however it is challenging to analyze the transducer data to delineate when effects of a rain event begin and end. At location T3 and T8 (Figures 38, 41), no signal from the rain events were measured. It is unknown whether this is because of transducer error, or actual groundwater conditions. In order to test that, another transducer should be placed adjacent one of those two in the river and the results compared.

A comparison of hydraulic gradient measured by piezo-manometer by differential head pressure transducers during the time period shows a gradient offset of approximately 0.1 at every location except T3. During instrument design, the chips were tested with a data-logger using actual water columns from cups and hoses, signaling that the offset error is being caused by the hose connections and ports to the groundwater and surface water.

During the month of July, four rain events hit the watershed. Previous to the first event on the 14th there was a time of no rainfall. In the data measured from 7/8 to that event on 7/14, a daily cycle was seen in the differential head measurement that could be representative of a daily groundwater discharge cycle caused by evapo-transpiration (Figure

42). As seen in results from T7, this cycle caused as much of a signal in the differential head as an event that caused the river to jump 0.2 m. The cycle was only seen prior to the rain events.

b. Possible Design Improvements

After the instruments were deployed, it became apparent that leaks in the threaded seals were the cause of most of the transducers failing. Of the six transducers that failed, five failed because of flooding. The first transducer made, transducer 11, had deeper, tighter threads in the cap and the coupling as it was from a different manufacturer (Mueller Industries Inc/B&K). Future casings should be made using PVC from Mueller.

Judging from performance, there was an offset in the data collected in the field, however the chips performed perfectly in the lab in water column testing. This suggests that the problem lies in the hoses and connections. Possible sources of error include pressure differences caused by moving water and unseen air bubbles in the stainless steel groundwater tube. Possible design considerations for the future include: The moving water in the river may cause an increase or decrease in pressure at the surface water port. This problem can be remedied by designing a stilling well for the surface water port. During installation, care was taken to eliminate bubbles in all connections; however unseen bubbles may have been seen in the groundwater tube. If larger tubing were used in future designs, a three way stopcock could be installed on the groundwater hoses to allow the user to take a samples and make sure that the groundwater tube was filled with water to complete the connection.

VII. CONCLUSIONS

1. Quantitatively, the nitrate flux at the 'hot spot' of nitrate discharging into the river at the northwest dike can at some hydrologic conditions discharge amounts of nitrate comparable to that of streams draining the NRWWTP (Harris, 2008) assuming sampling density is sufficient (table 2). The higher the elevation difference between the water table measured at well 2I and the river elevation, the more nitrate is discharged.
2. River parameter measurements, especially hydraulic gradient, are snapshots of conditions at a specific time. They cannot and should not be extrapolated to a longer period of time or season. Concentration measurements are more indicative of temporal or seasonal change of a plume.
3. Diabase dikes do not cause significant increases in groundwater flow at the riverbed level; however, they show evidence of being preferential flow-paths for groundwater flow by exhibiting larger spatial plumes of nitrate, chloride, and silicate tracers in the river. At the northwest diabase dike at the NRWWTP there is a non-point source of nitrate into the Neuse River from a nitrate hotspot adjacent the dike.
4. Isotopic composition of nitrate in groundwater discharging into the river at the NRWWTP is that of bio-solid nitrate (Figure 28, 29). Heavier $\delta^{15}\text{N}$ values in some samples are evidence of denitrification due to natural attenuation of nitrate contaminated groundwater in areas of fine sediment.

5. The eastern diabase dike did not show much evidence of nitrate discharging into the river at that site. In comparison with the northwest dike, this dike crossing has thicker riparian buffer including a perennial stream in the buffer as well as lesser elevation gradient between the fields and the river on this point bar. Bio-solid nitrate in groundwater at the eastern dike is likely up-taken by vegetation in the riparian buffer.
6. Comparing DOC concentrations and $\delta^{15}\text{N}$ isotopic compositions in pore water suggests that in areas of high nitrate, DOC is the limiting factor for denitrification. The $\delta^{13}\text{C}$ composition of this DOC, as well as high C:N ratios suggest that this carbon is originating from C_4 plants and shoreline vegetation (Appendix H).

This study raises some questions that may be addressed in future studies and are beyond the scope of this study:

Increases in spatial extent of the nitrate plume and nitrate flux 'hot spot' were measured over the course of a year as well as variability in the concentration in the nitrate plume. These changes are probably not seasonal changes, but are more-likely changes in the source function of the nitrate applied on the fields, as well as dispersion and diffusion of nitrate within the soil. This hypothesis can only be tested however with future sampling past this study.

While sampling, there were some results showing areas with high nitrate concentrations with negative hydraulic gradients. These areas cannot be true recharge areas

if the sampled water has characteristics similar to the groundwater and not surface water. As hydraulic gradient measurements are snapshots of time, these areas are only temporary recharge areas. Also, there were some samples of low nitrate concentrations bordered by high nitrate concentrations with no conceivable explanation of why this is the case.

The electronic differential pressure transducers revealed the influence of daily evapo-transpiration cycles on groundwater discharge in the streambed. As the large sampling periods took one to two days to complete, does this daily evapo-transpiration cycle affect the validity of the hydraulic gradient measurements of the large sampling periods?

Several areas on the river reach were identified as areas with higher nitrate concentrations due to contamination from farm ponds on the north side of the river. Sampling the ponds, streams, and groundwater discharging into the river at these areas may provide more evidence to the source of that contamination.

A goal of the waste application fields is to have sustainable system where the nutrients spread on the fields are used by the crops on the field and the wildlife around the fields without contaminating the river. This end may be accomplished using wetlands on the river to slow down water flow and increase denitrification, having larger riparian buffers, or injecting DOC into the dike fracture zone as it is the limiting factor for denitrification.

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FIGURES

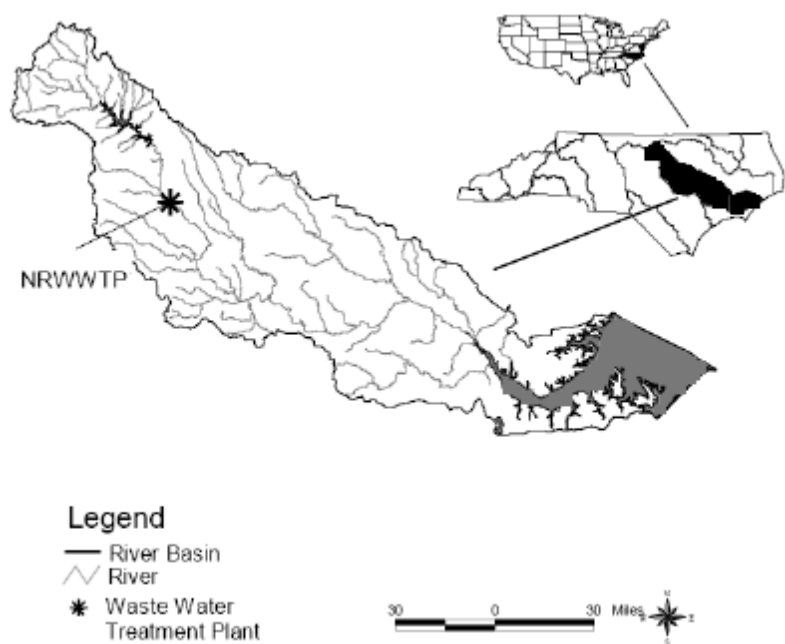


Figure 1: Location of the Neuse River Wastewater Treatment Plant (Showers et al., 2005)

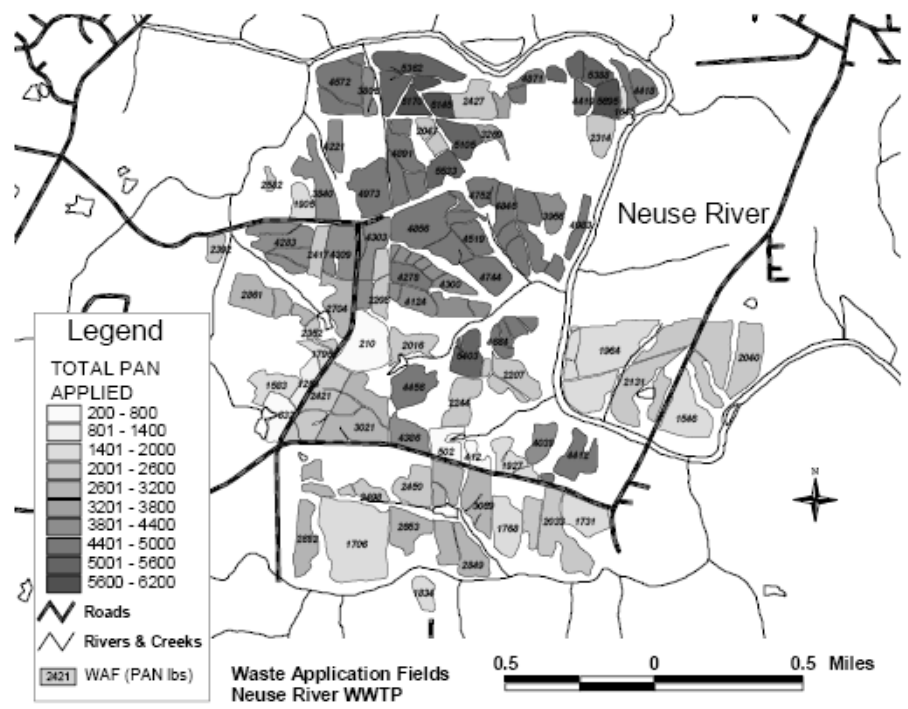


Figure 2: Total amount of Plant Available Nitrogen (PAN) in lbs/ac applied in the NRWWTW Waste Application Fields since biosolid application began in 1980. (Showers et al., 2005)

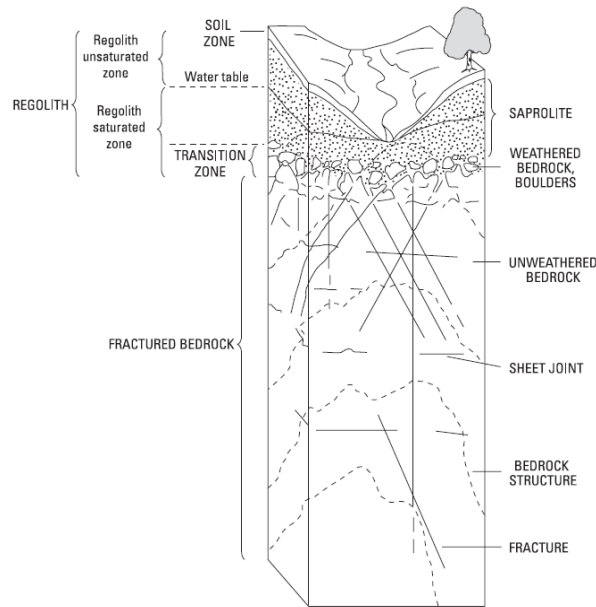


Figure 3: Principle components of the groundwater system in the Blue Ridge and Piedmont provinces of North Carolina (Daniel & Dahlen, 2002)

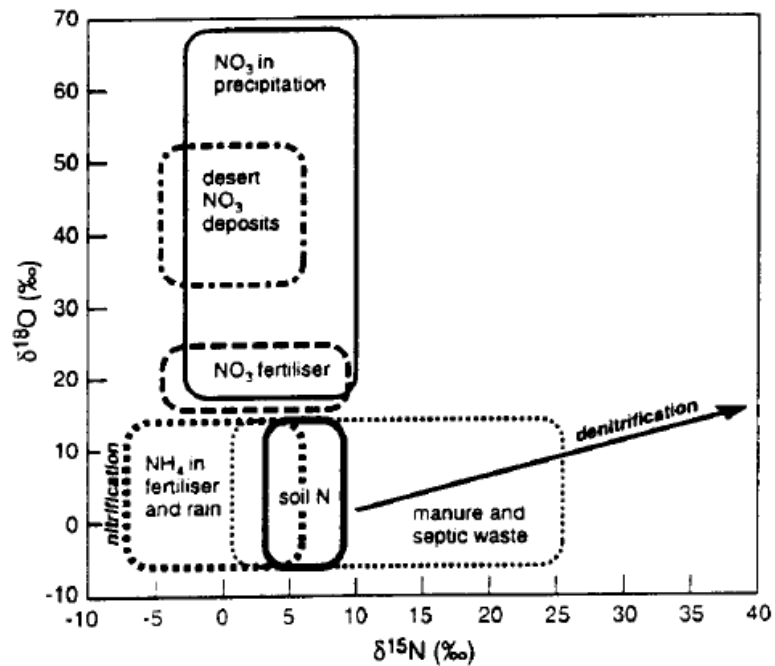
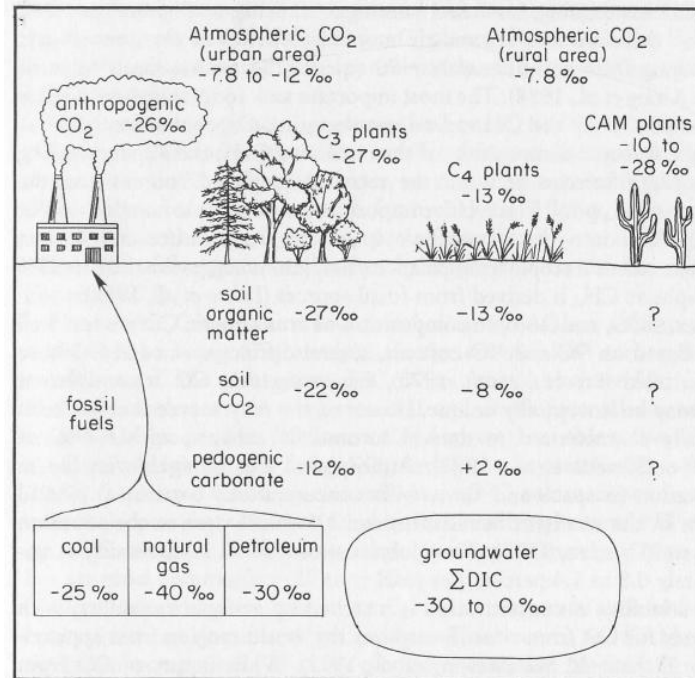
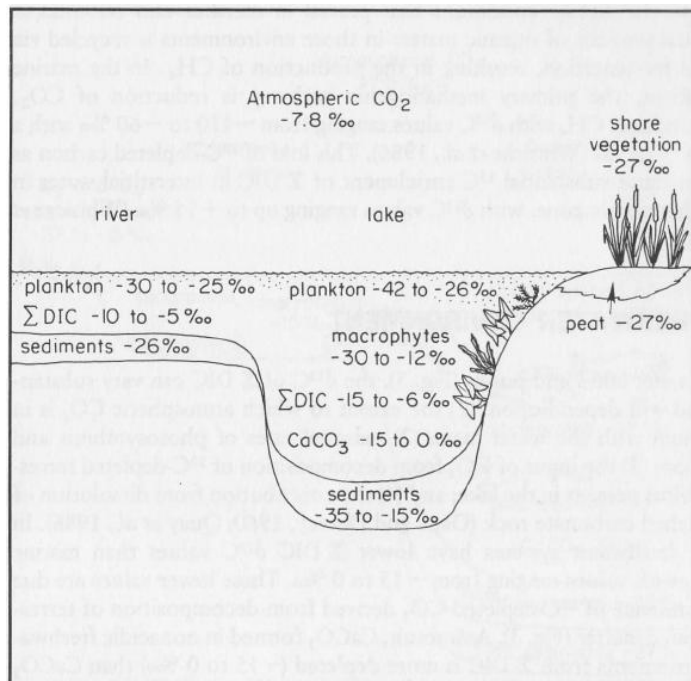


Figure 4: Schematic of typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ isotopic values of nitrate (Kendall & Aravena, 2000)



A.



B.

Figure 5: Stable carbon isotope ratios of major components of terrestrial and freshwater systems (Boutton, 1991). A: terrestrial, B: freshwater

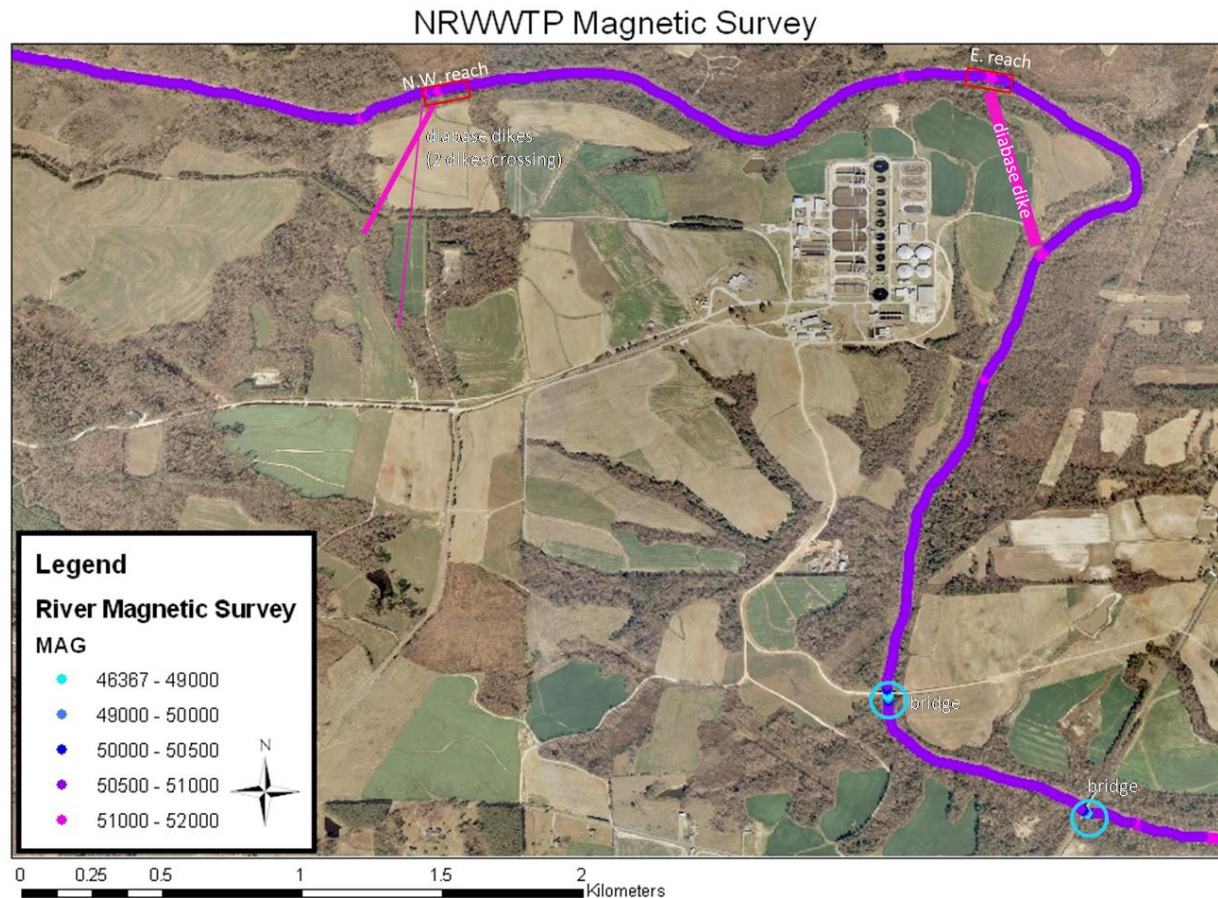


Figure 6: Auburn Knightdale Road to Mial Plantation Road river magnetic survey. Data is reported is the total magnetic field in nT measured by the magnetometer. Marked in red boxes are the sampled reaches, and points of interest are listed. The diabase dikes drawn in the WAFs are from EM survey results shown in Figures 6, 8.

NRWWTP EM Survey Fields 4, 5, 6

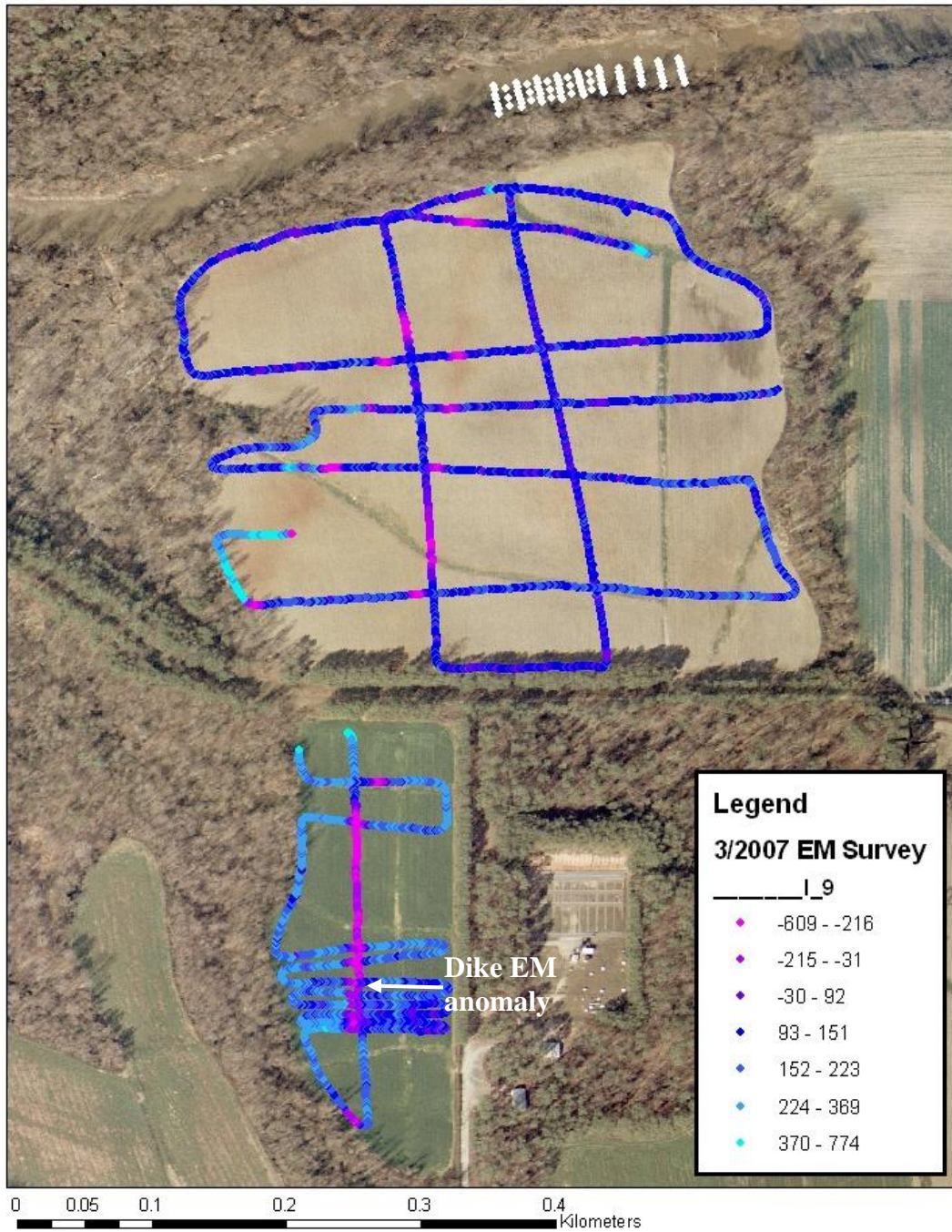


Figure 7: Northwest dikes electromagnetic survey, fields 4-6. Data is reported in magnetic susceptibility to 9990 Hz measured by the GEM-2. EM anomalies are in pink. White dots are the NW dike sample locations. Not all locations were sampled each sampling period.

NRWWTP Northwest Dike River and Buffer Magnetic Survey

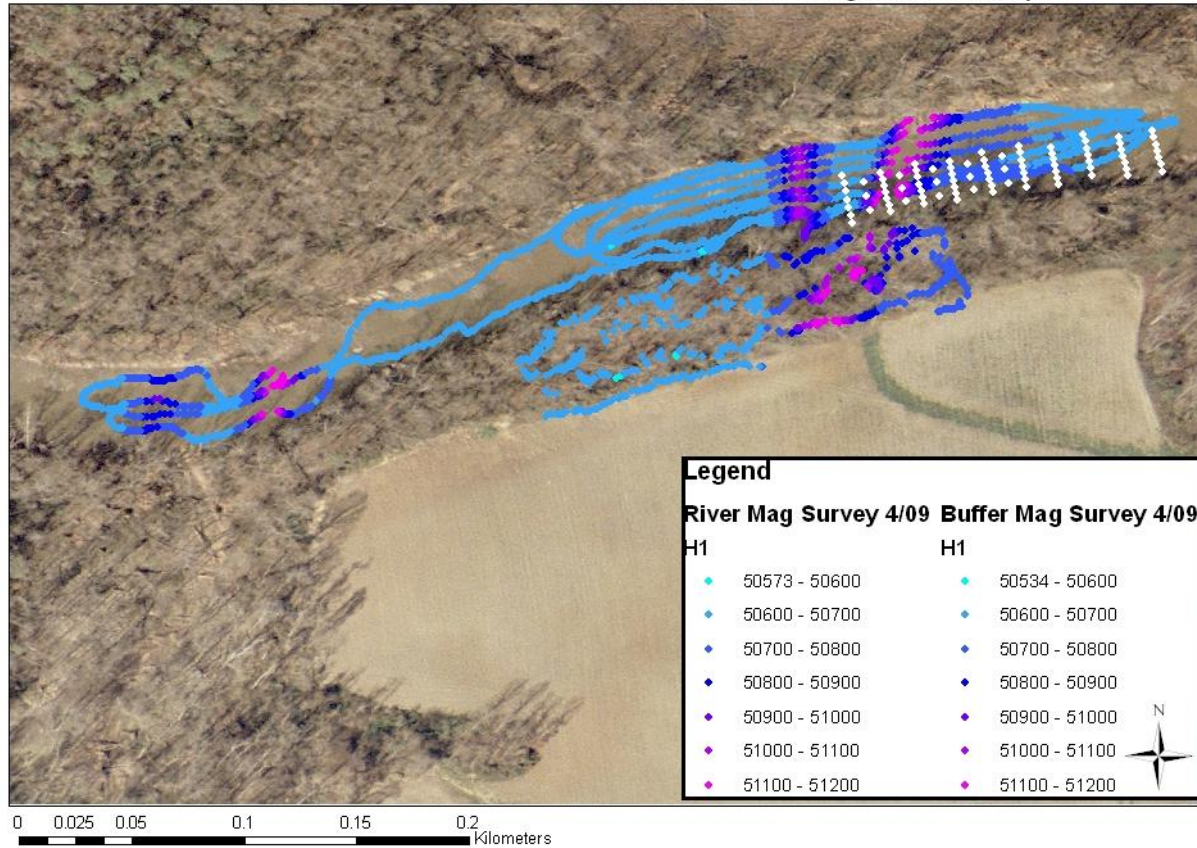


Figure 8: Northwest dikes river and riparian buffer magnetic surveys. Data is reported is the total magnetic field in nT measured by the magnetometer. Magnetic anomalies are in purple and pink. White dots are the NW dike sample locations. Not all locations were sampled each sampling period.

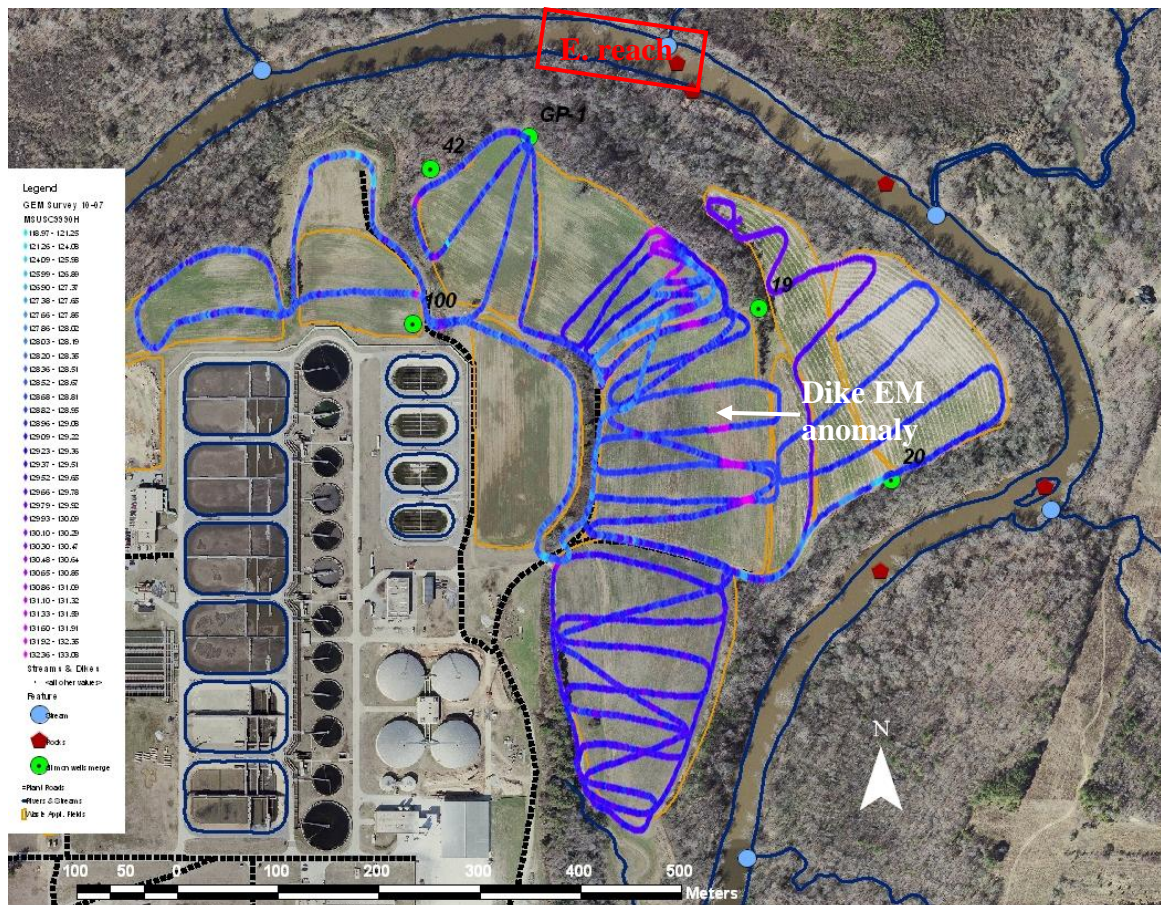


Figure 9: Eastern dike electromagnetic survey, fields 17-24. Data is reported in magnetic susceptibility to 9990 Hz measured by the GEM-2. EM anomalies are in pink. (Map made by Dr. William Showers, 2007)

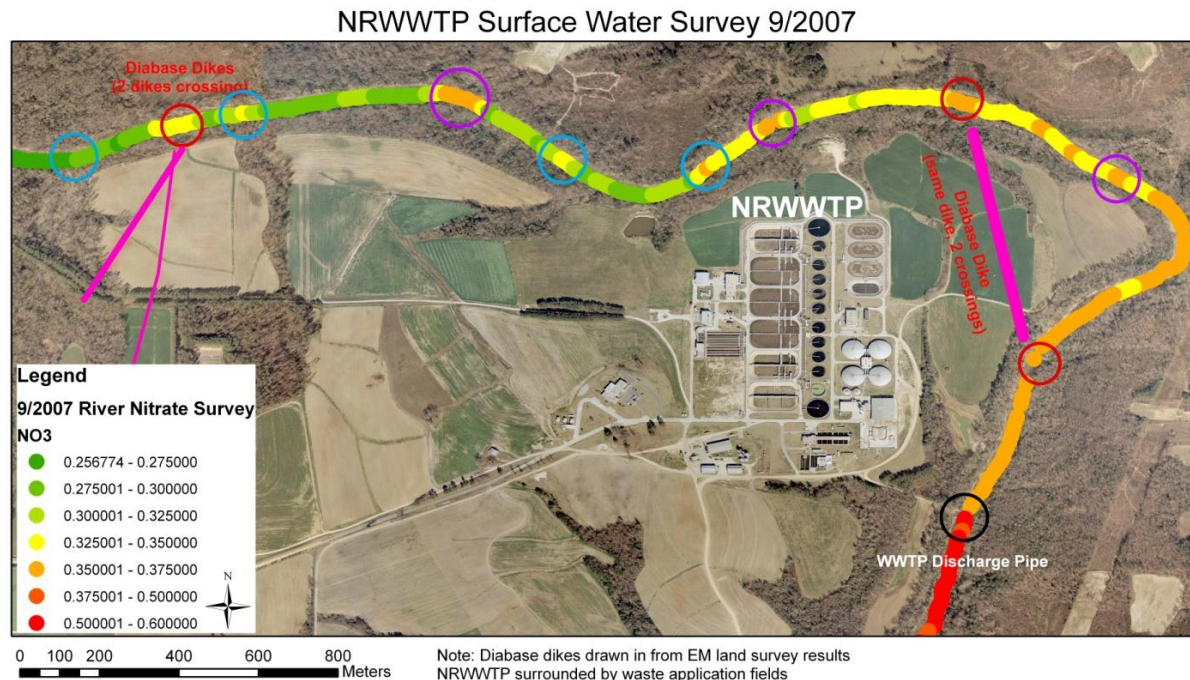


Figure 10: NRWWTP Surface Water River Nitrate Survey 9/2007. **Red** circles represent possible gains from diabase dikes. The downriver (SE) dike crossing is masked by the high nitrate in the river. **Blue** circles represent possible gains from streams from the NRWWTP. The stream furthest upriver (NW) is a larger stream that drains most of the WAFs to the south. **Purple** circles represent possible nitrate gains from non NRWWTP sources. The two upriver purple circles may be caused by farm ponds feeding streams north of the WWTP. The downriver purple circle is caused by Poplar Creek north of the Neuse River. The **Black** circle represents the WWTP discharge pipe. The overall river nitrate jumped 0.2 mg/L at the discharge pipe masking any further non-point nitrate sources. **Note:** The overall river nitrate from upriver of the WAFs to the discharge pipe increased from 0.25 mg/L to 0.37 mg/L indicating non-point source nitrate increasing the overall river nitrate concentration approximately 0.12 mg/L over this 3.5 km reach.

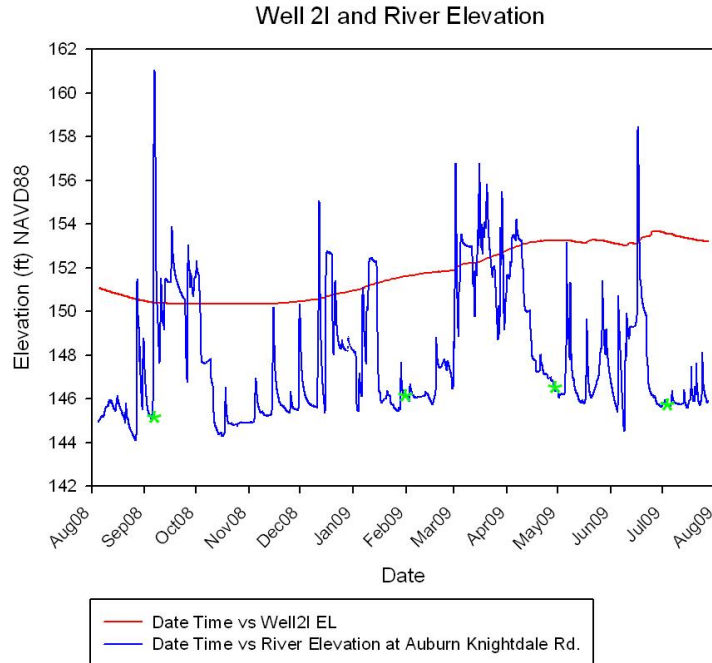


Figure 11: Well 2-I water elevation and river elevation at Auburn Knightdale Rd., 1.4 km upstream of the NW dike (8/08 to 8/09). Green stars indicate NW dike sampling periods. NRWWTP Sampling Locations and IDs

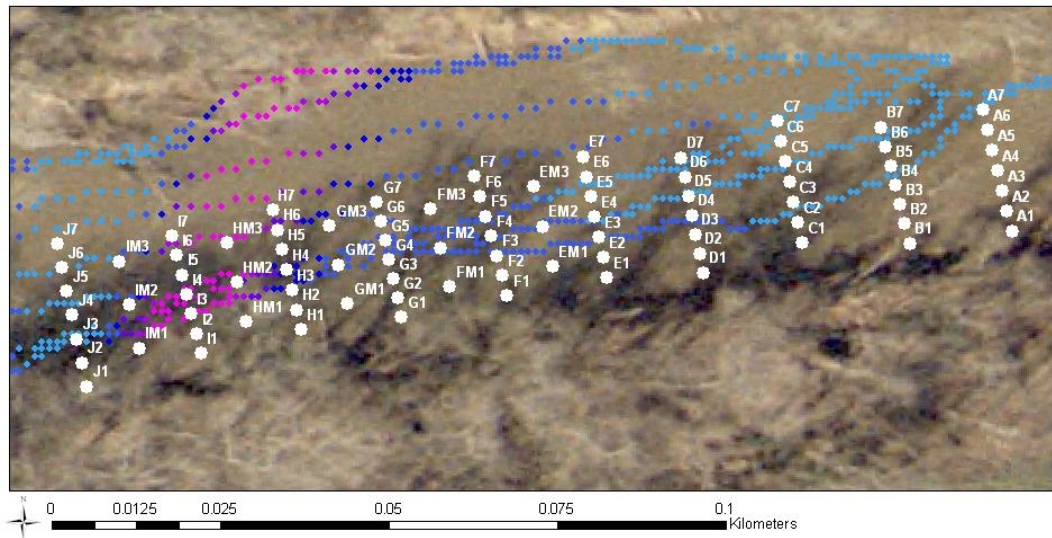


Figure 12: Northwest dike sampling locations and point IDs. Not all locations were sampled each sampling period. Also shown is river magnetic survey data to show the location of the diabase dike going through this reach in relation to the sample points. See Figure 8 for the magnetic survey.

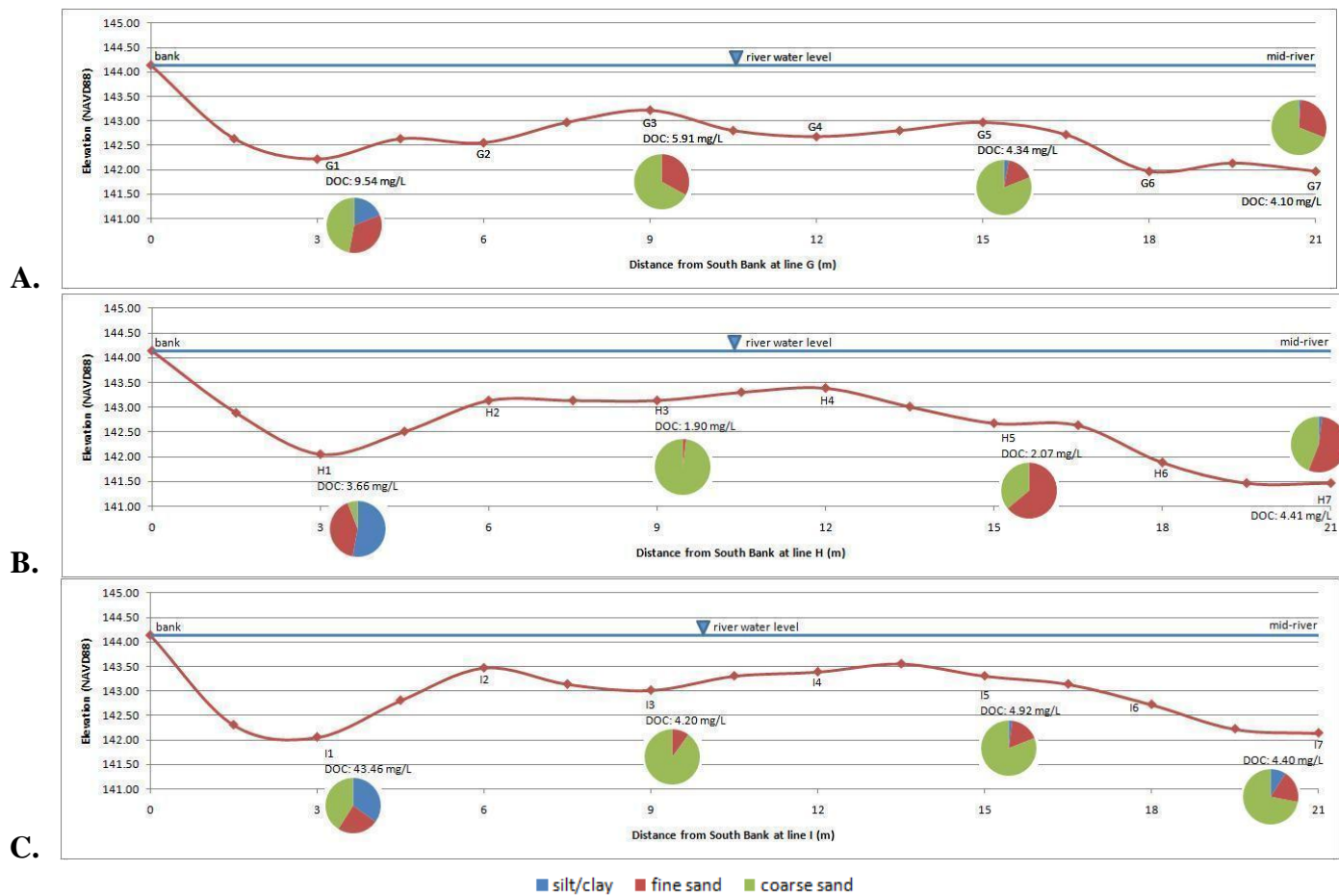


Figure 13: Riverbed elevation, grain size percentages, and DOC concentration for transects G, H, and I in September, 2009; grain size in pie charts; surface water DOC concentration: 4.94 mg/L. A: line G, B: line H, C: line I

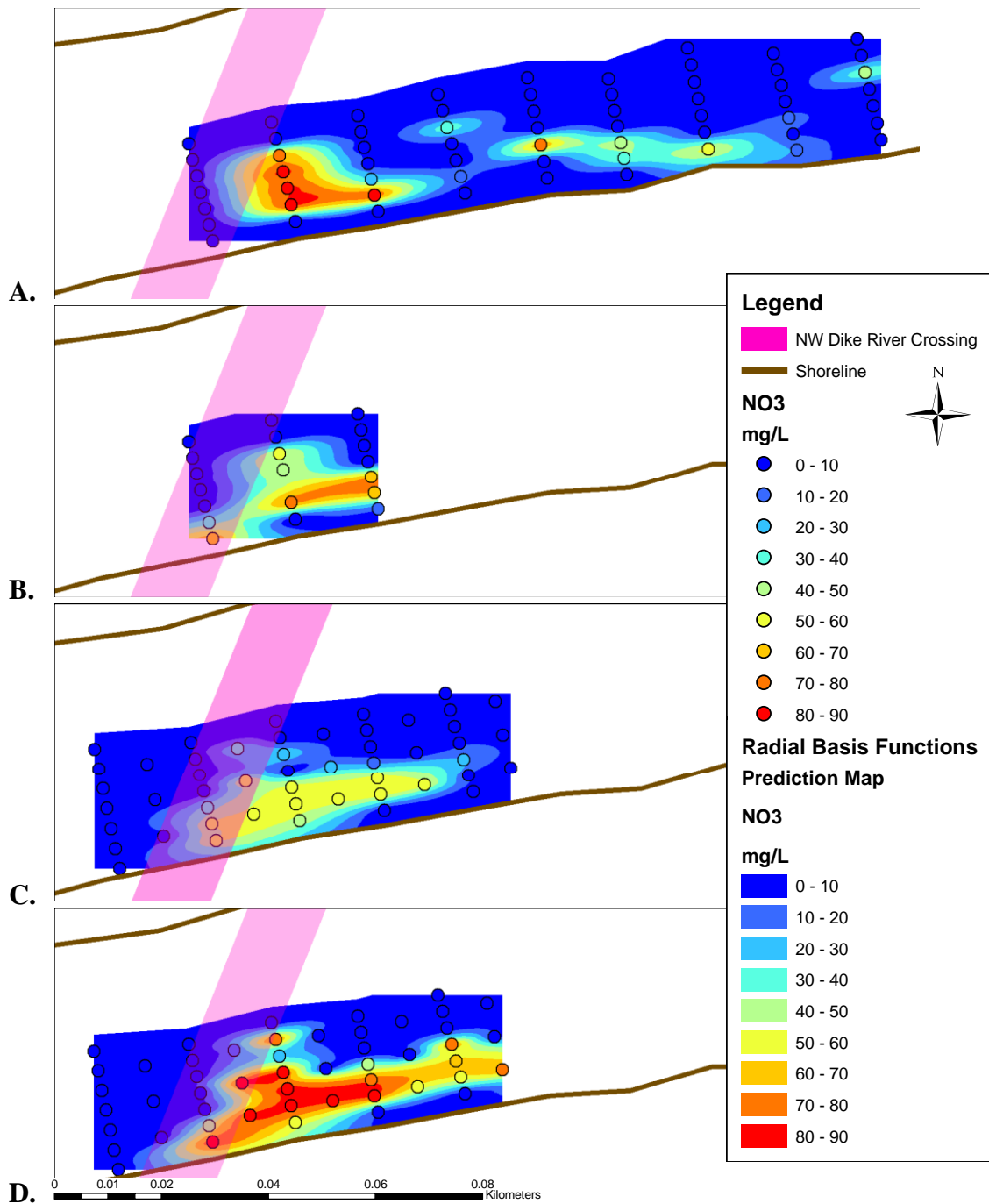


Figure 14: Sampling period nitrate concentrations (mg/L). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

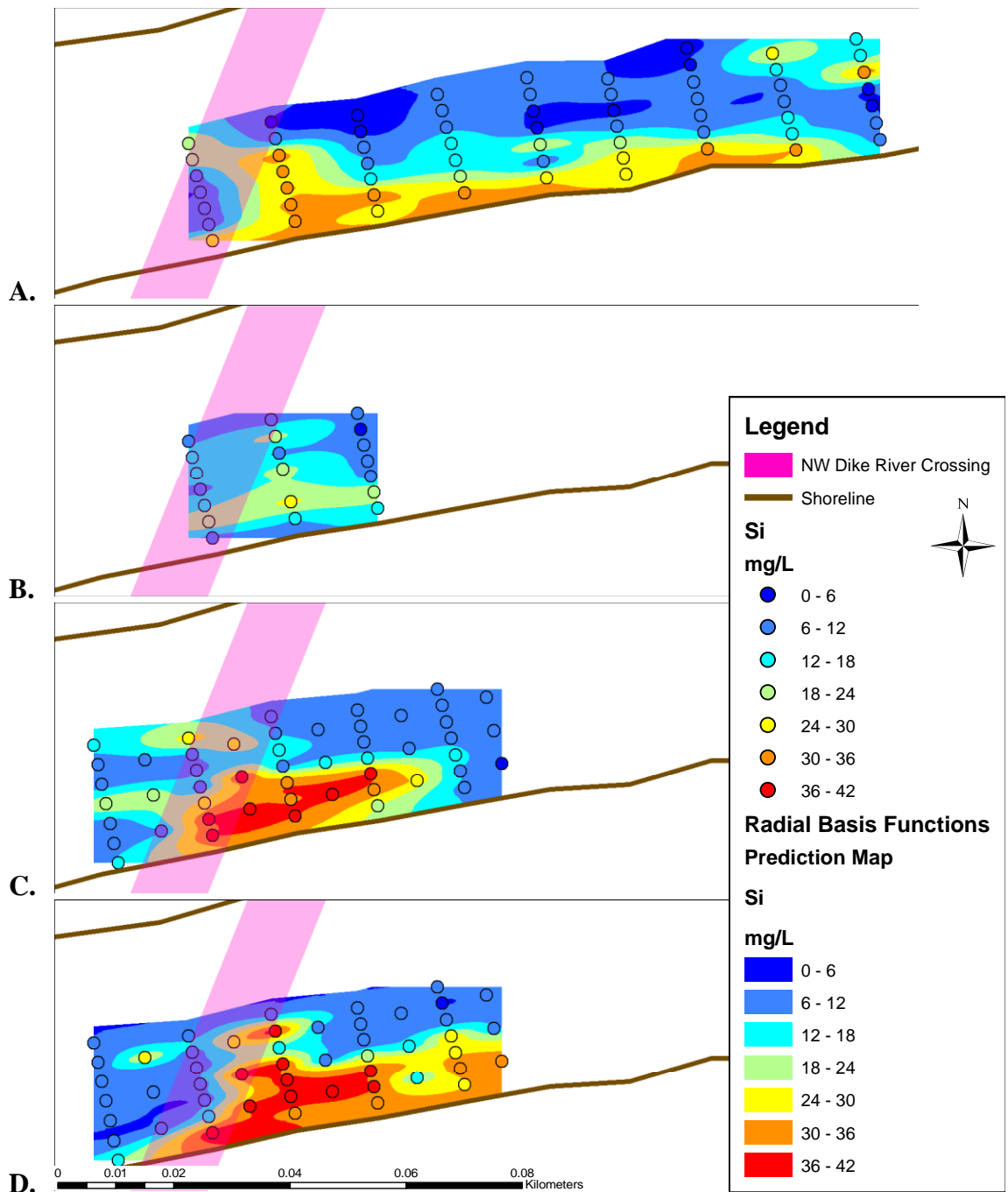


Figure 15: Sampling period silicate concentrations (mg/L). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

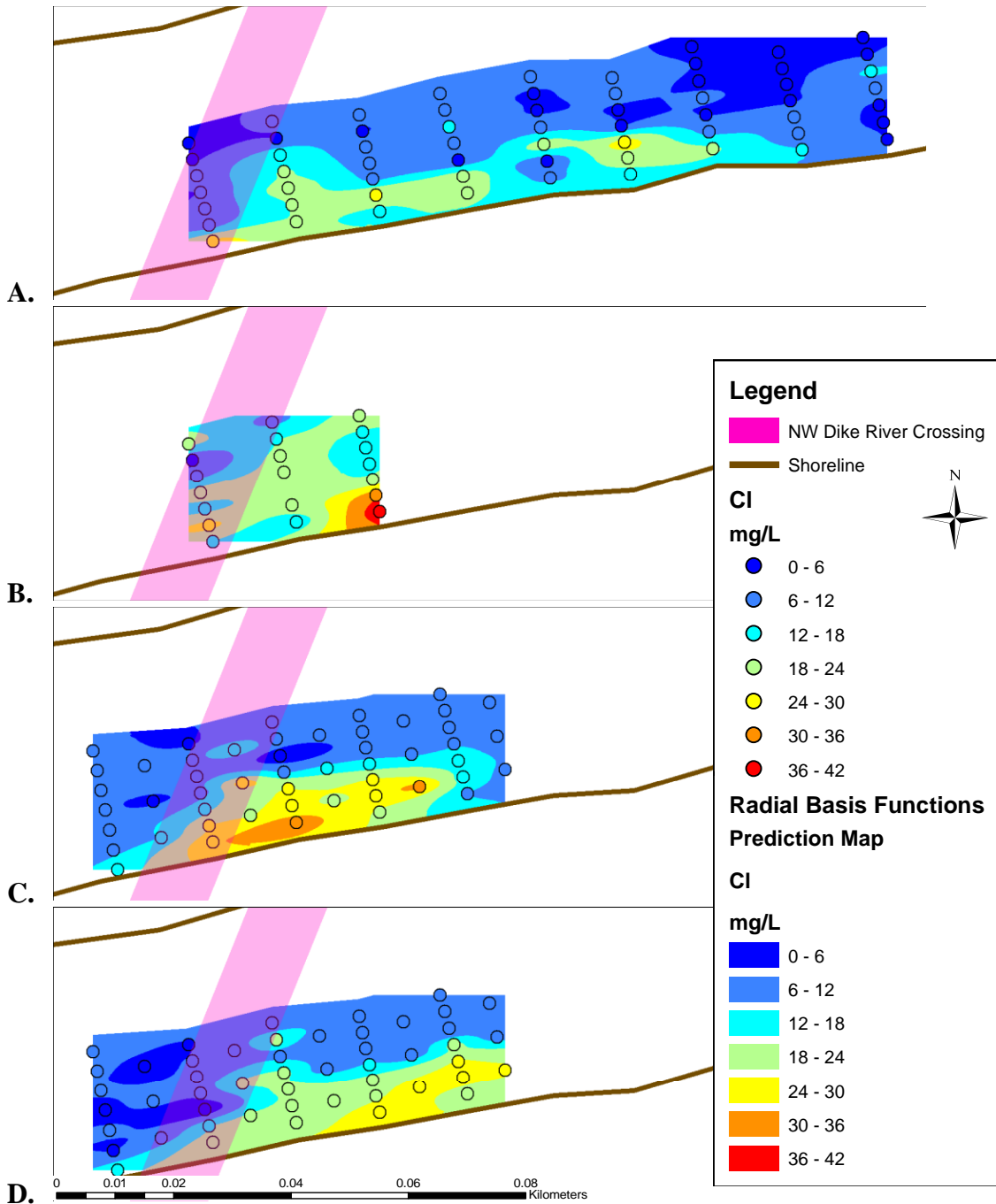


Figure 16: Sampling period chloride concentrations (mg/L). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

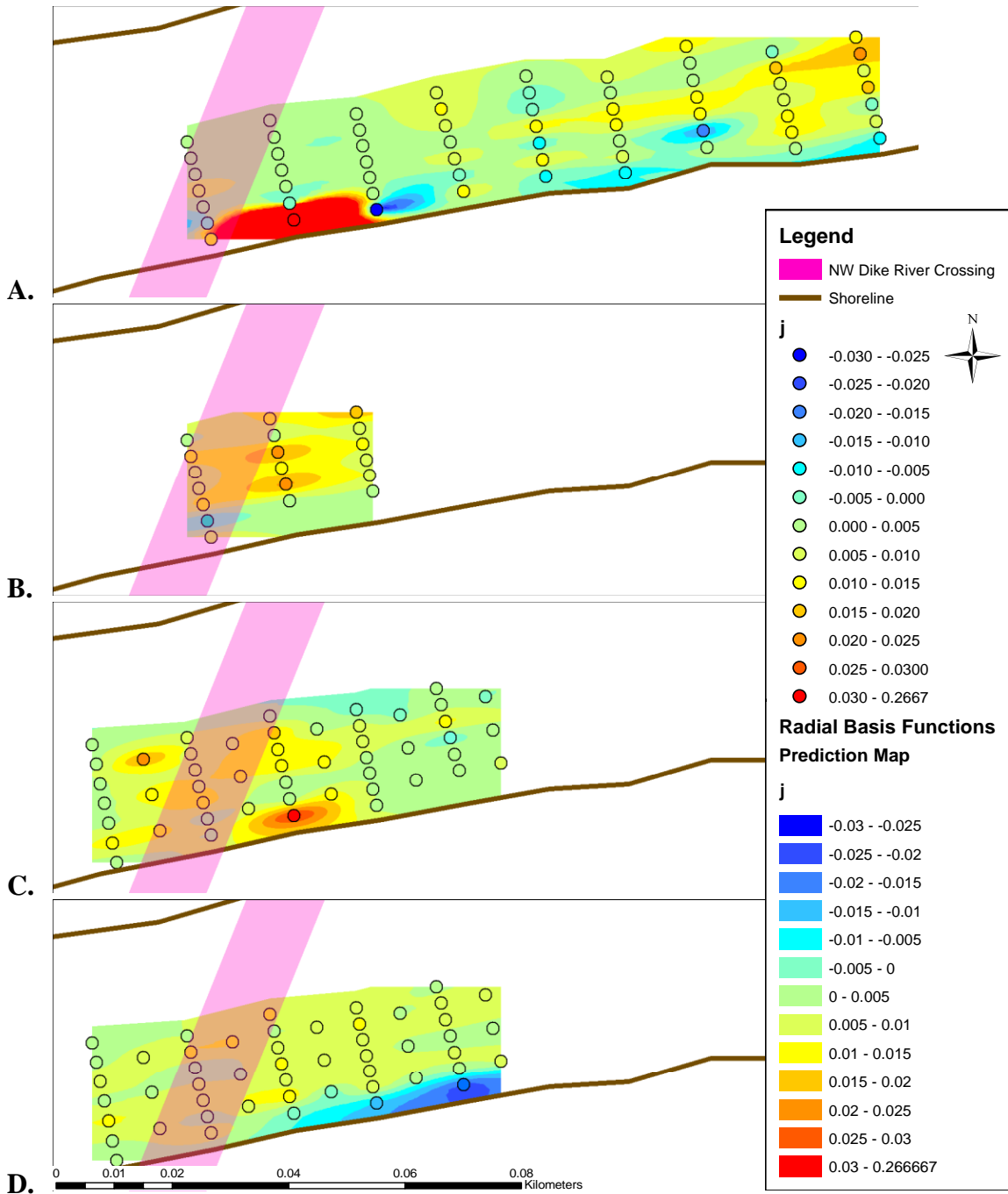


Figure 17: Sampling period hydraulic gradient. A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

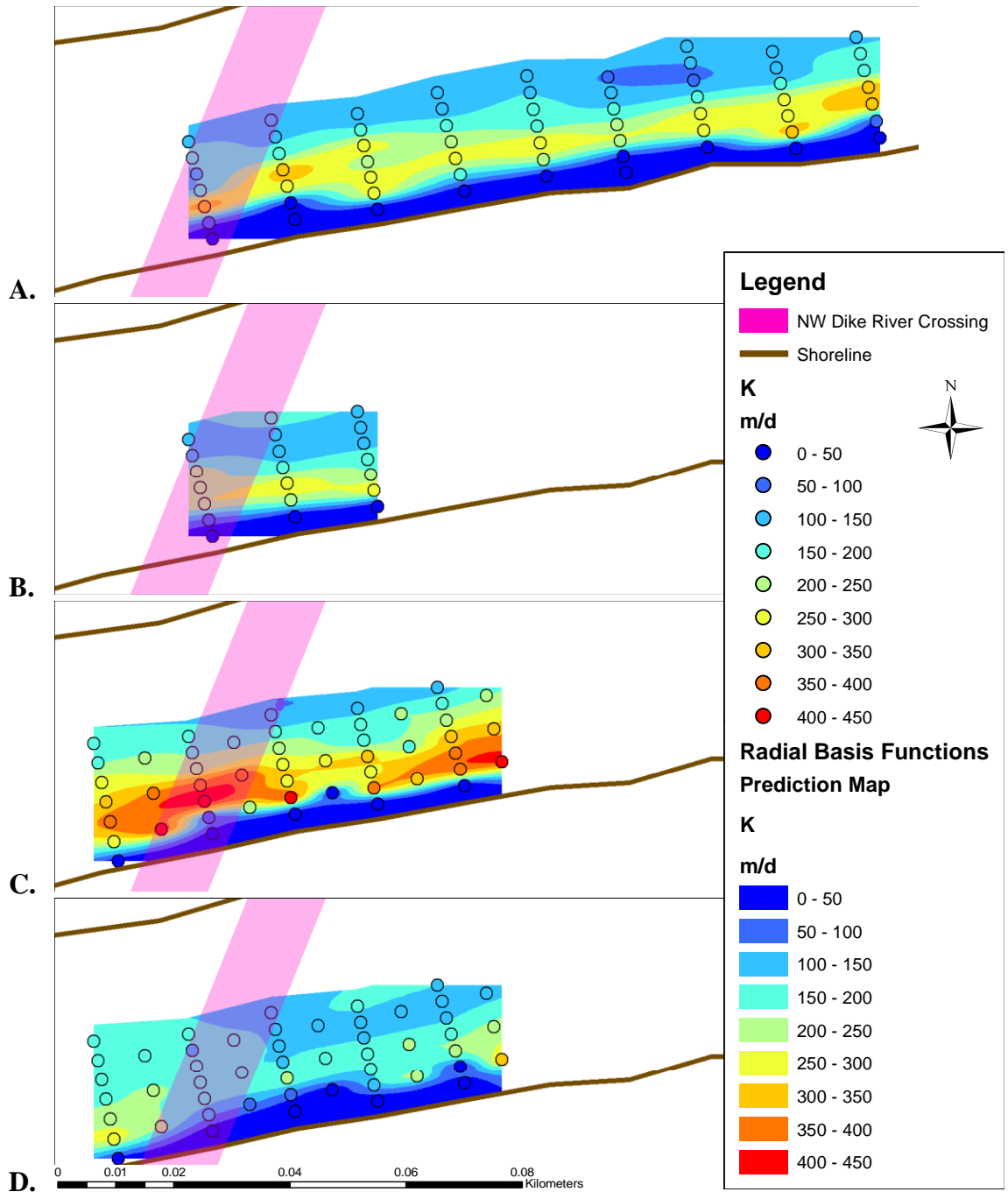


Figure 18: Sampling period in-situ hydraulic conductivity (m/d). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

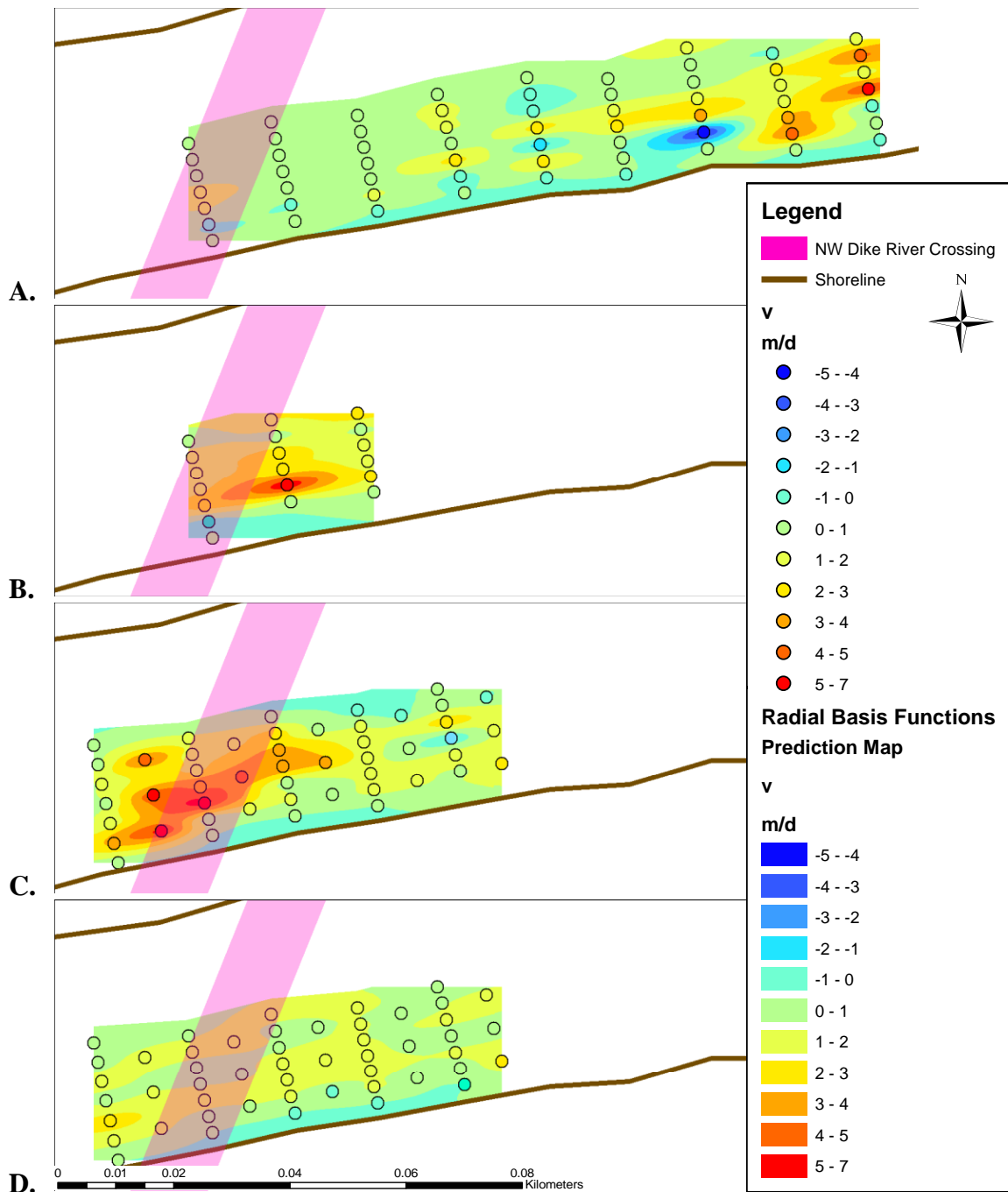


Figure 19: Sampling period specific discharge (m/d). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

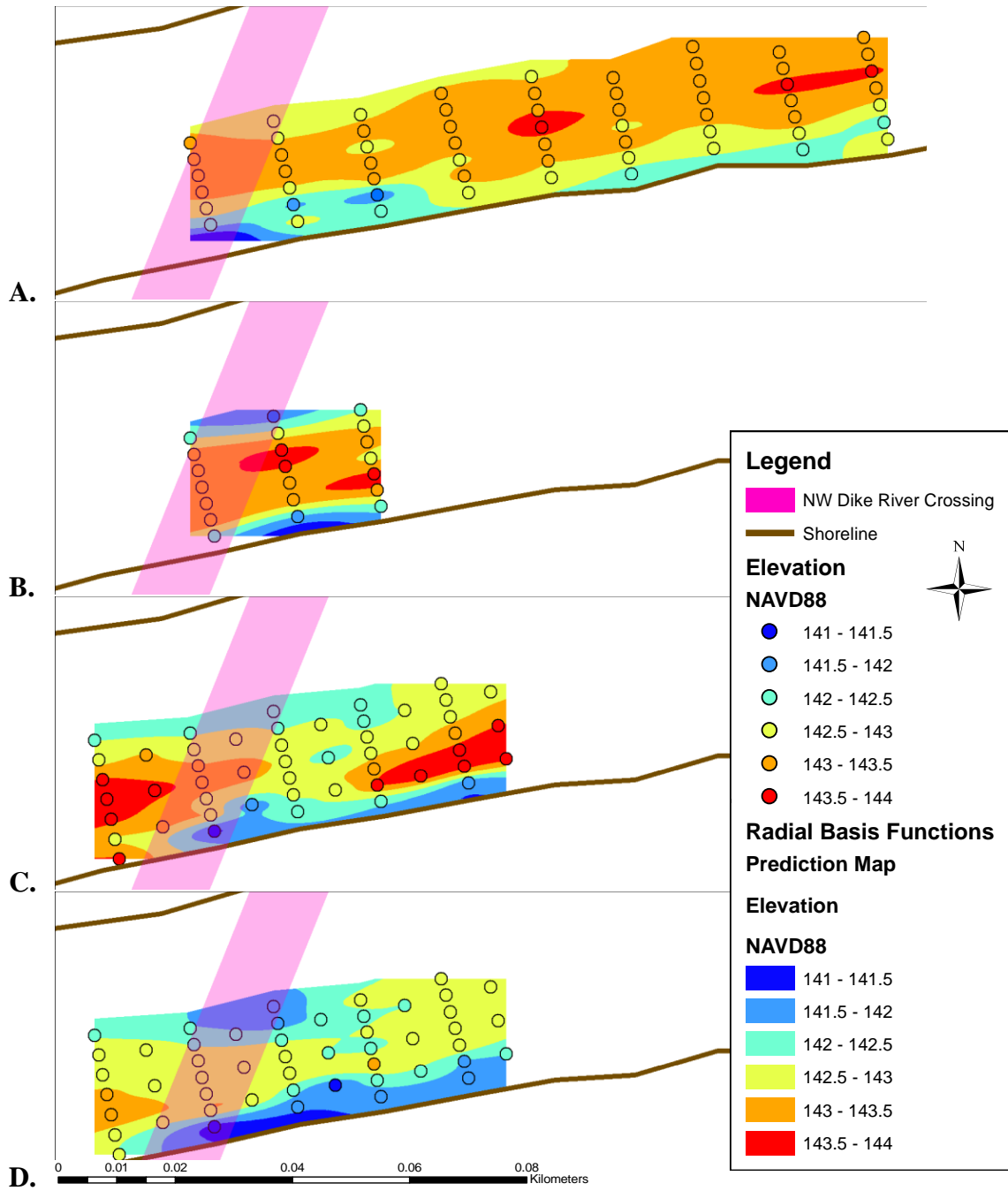


Figure 20: Riverbed elevation (projected in NAVD88). Parameter measured during sampling, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

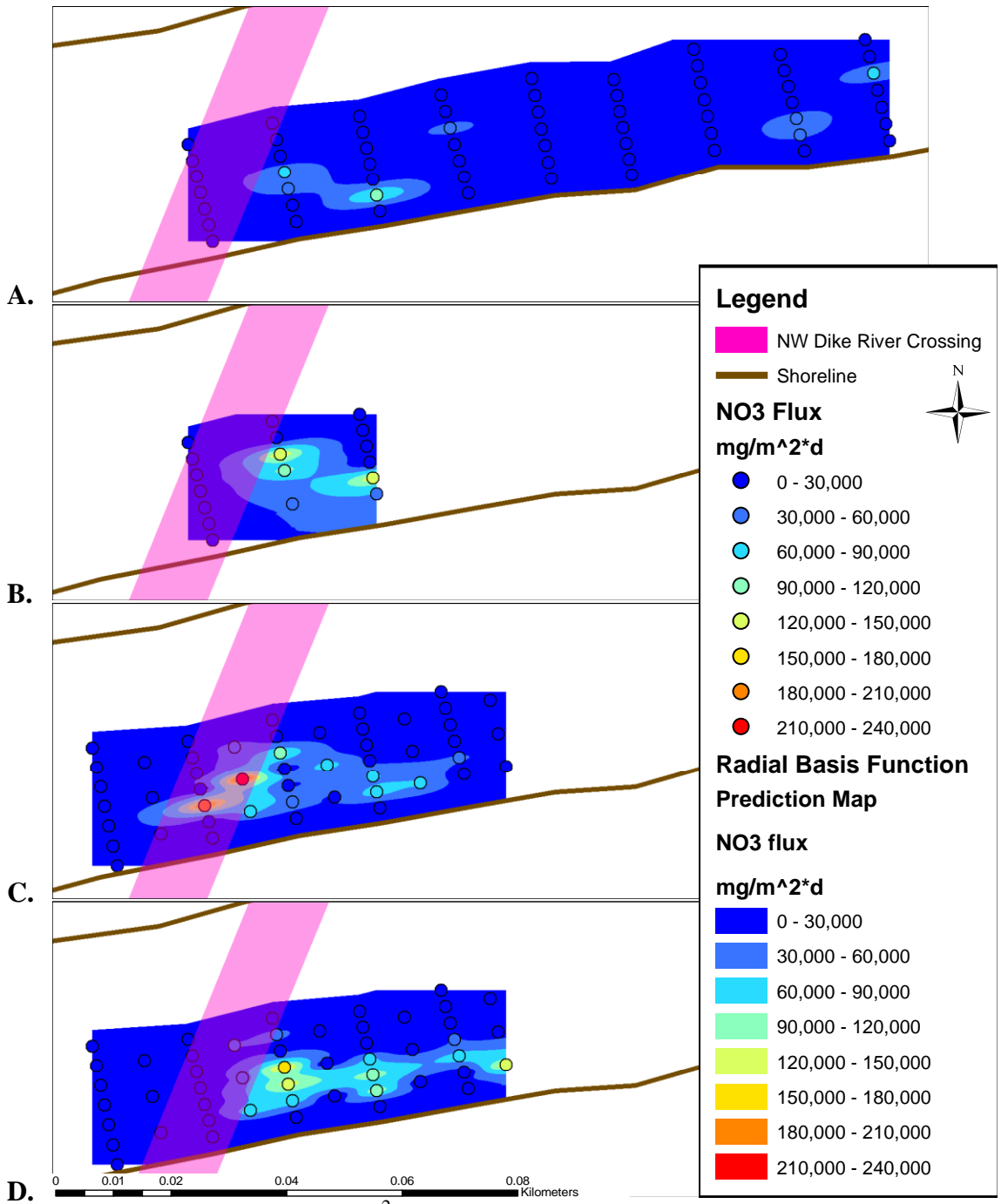


Figure 21: Nitrate flux ($\text{mg}/\text{m}^2\text{d}$). Flux is calculated by multiplying the specific discharge and the nitrate concentration at each point with an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. A. September 2008. B. January 2009. C. April 2009. D. July 2009.

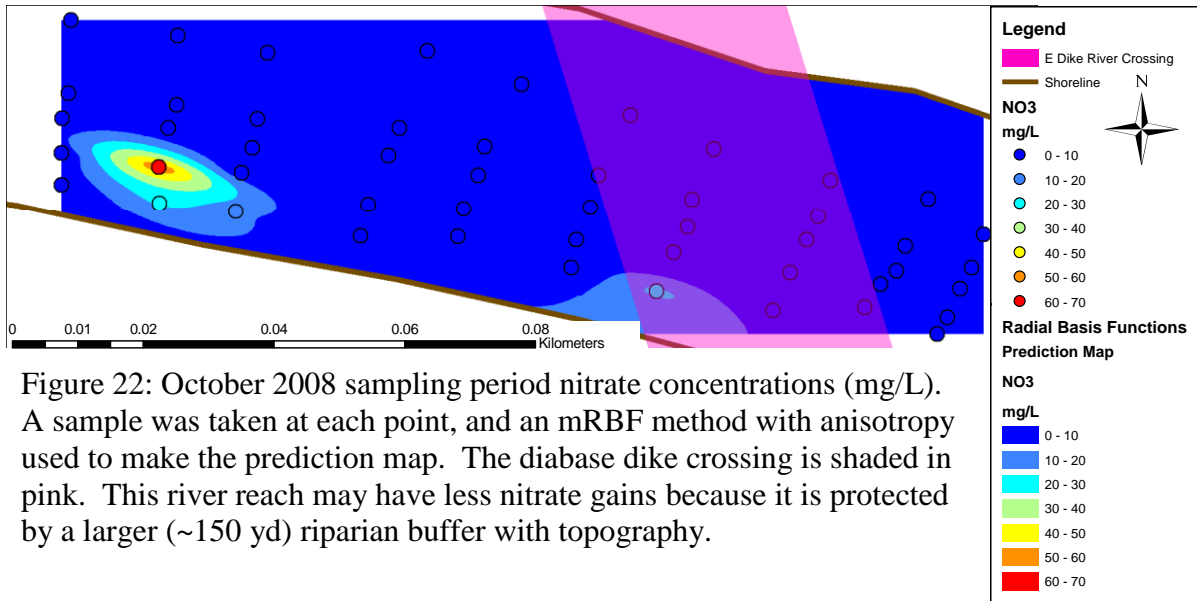


Figure 22: October 2008 sampling period nitrate concentrations (mg/L). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. This river reach may have less nitrate gains because it is protected by a larger (~150 yd) riparian buffer with topography.

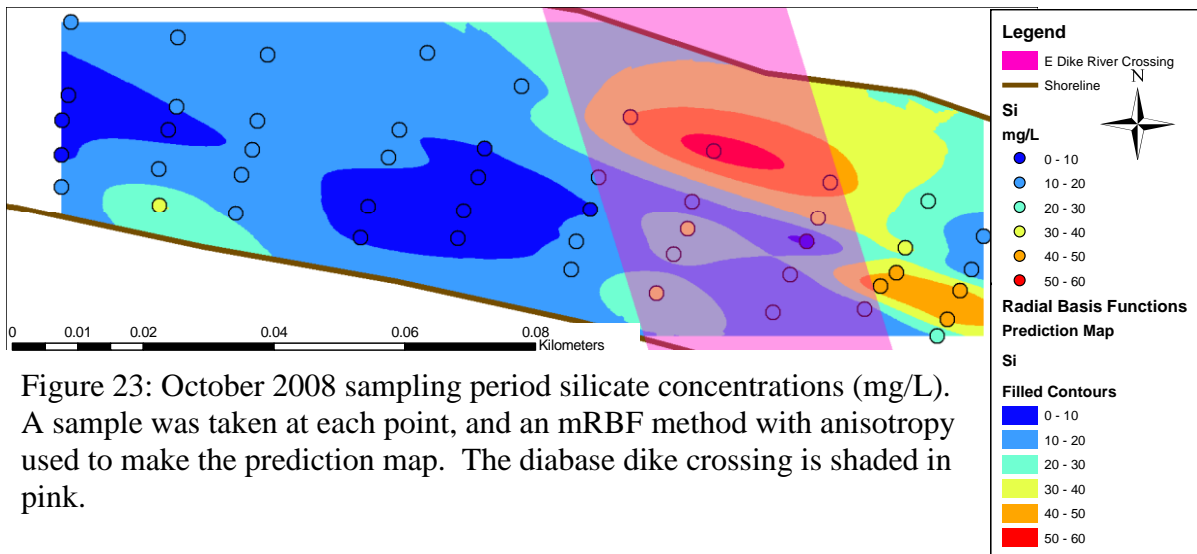


Figure 23: October 2008 sampling period silicate concentrations (mg/L). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink.

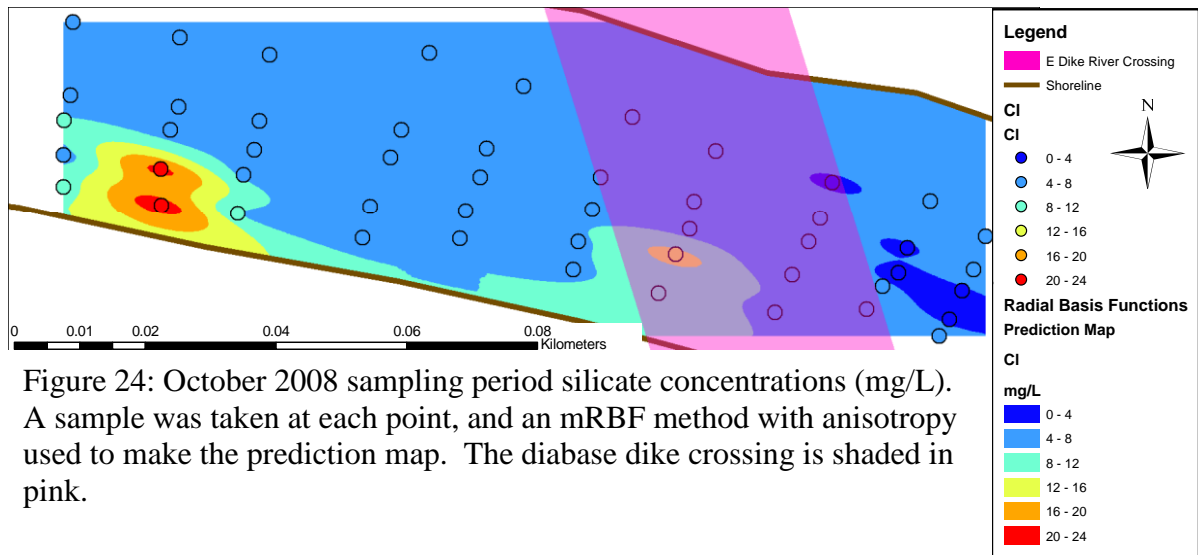


Figure 24: October 2008 sampling period silicate concentrations (mg/L). A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink.

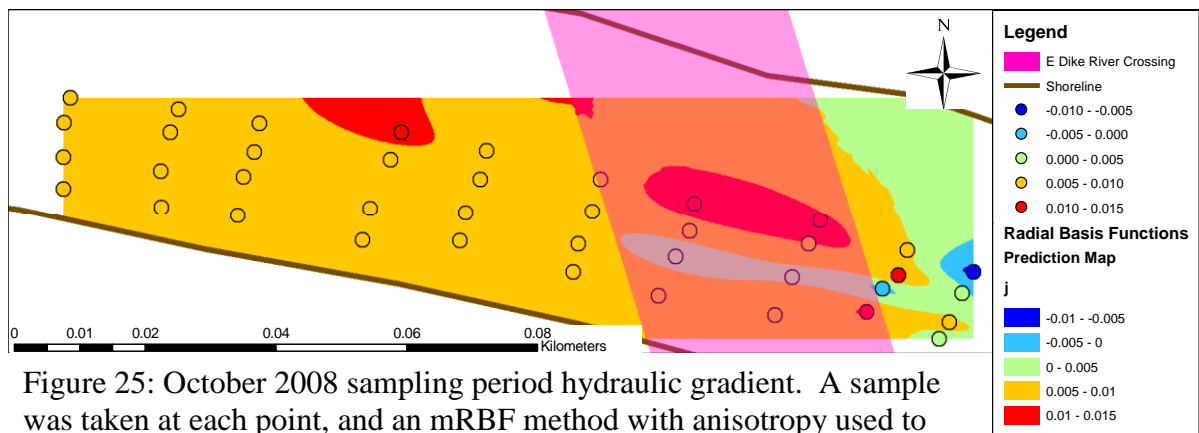


Figure 25: October 2008 sampling period hydraulic gradient. A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink.

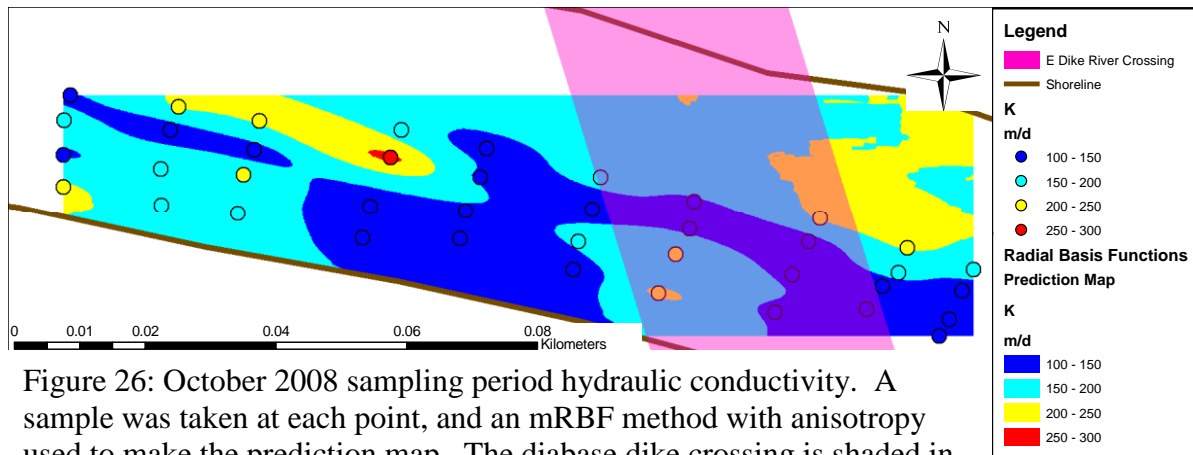


Figure 26: October 2008 sampling period hydraulic conductivity. A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink. The riverbed sediment here is a uniform sand.

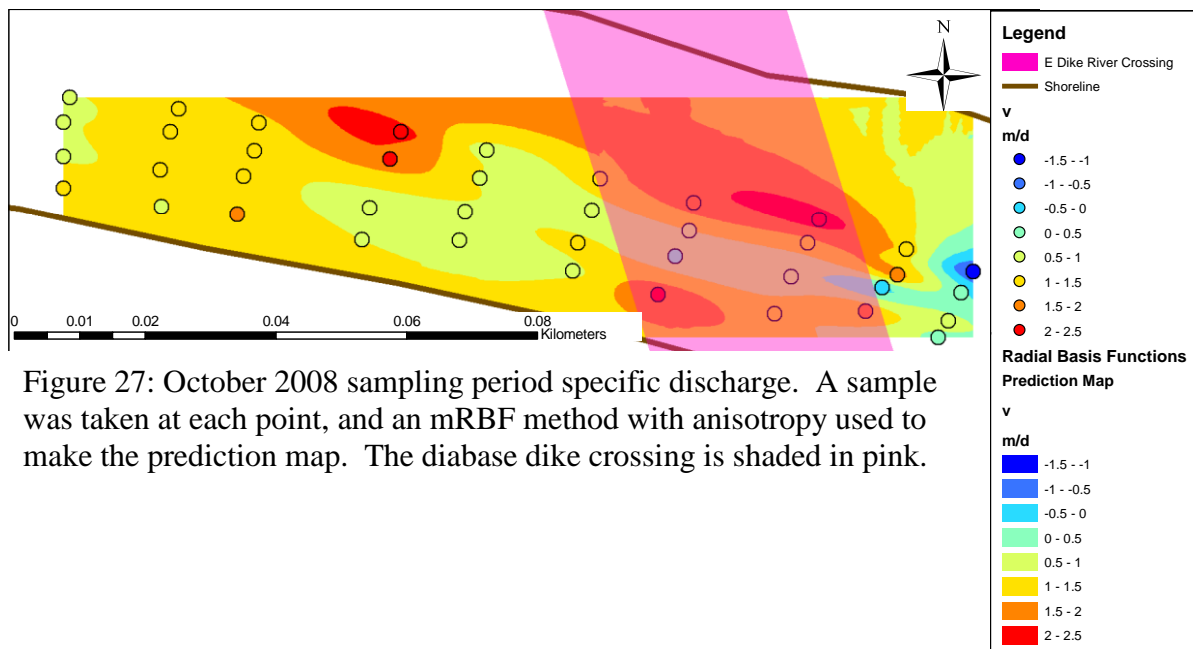
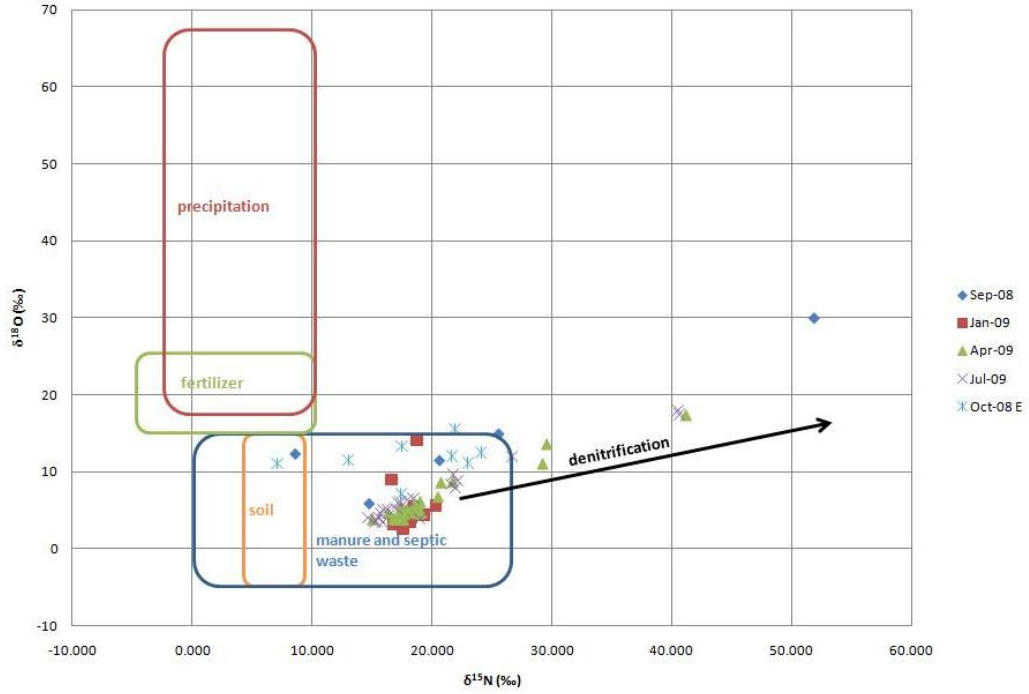
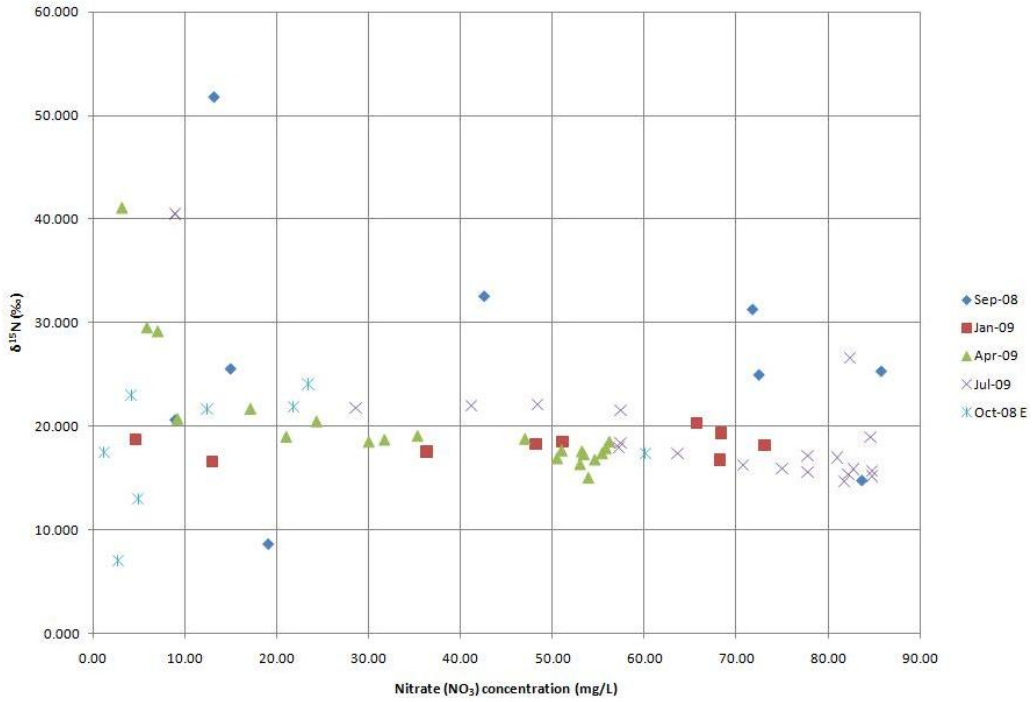


Figure 27: October 2008 sampling period specific discharge. A sample was taken at each point, and an mRBF method with anisotropy used to make the prediction map. The diabase dike crossing is shaded in pink.

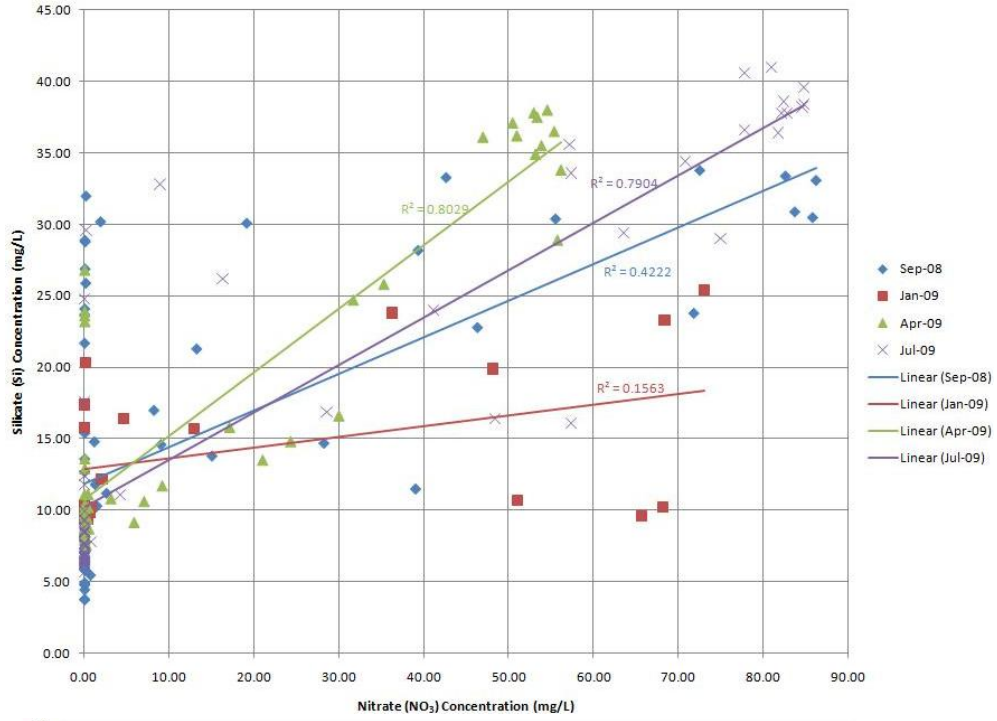


A.

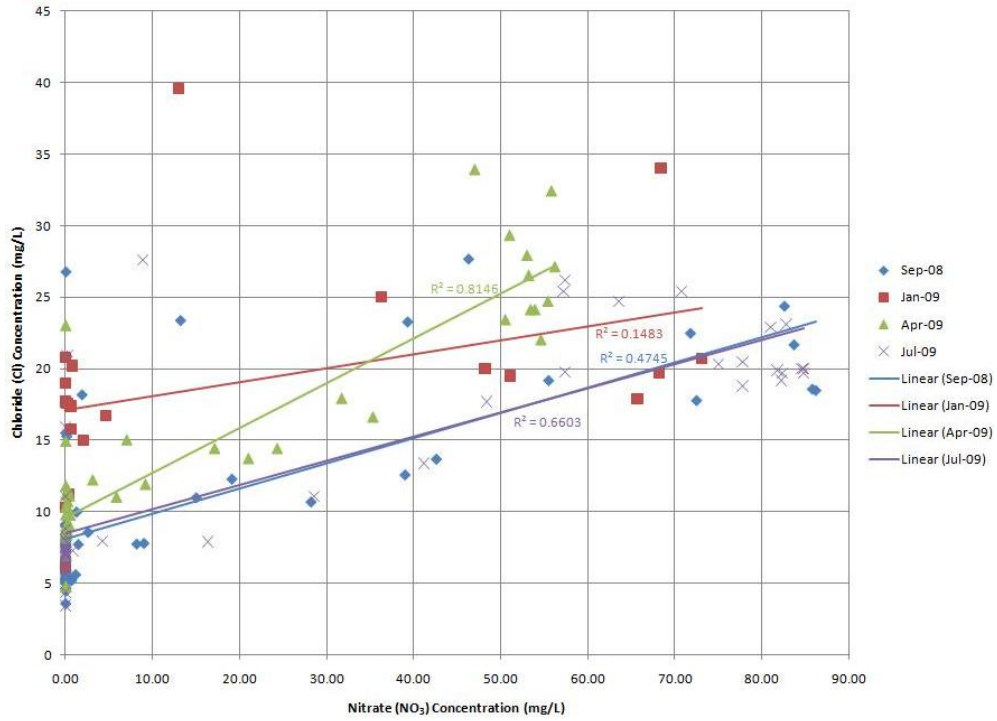


B.

Figure 28: Isotopic composition of nitrate in water sampled from the riverbed of the Neuse River at the NRWTP. A. $\delta^{18}\text{O}$ nitrate vs. $\delta^{15}\text{N}$ nitrate compared to Kendall and Aravena, 2000. B. $\delta^{15}\text{N}$ nitrate vs. NO_3 concentration



A.



B.

Figure 29: Correlation of nitrate concentration with other silicate and chloride concentration for each sampling period. A. Si vs. NO₃. B. Cl vs. NO₃

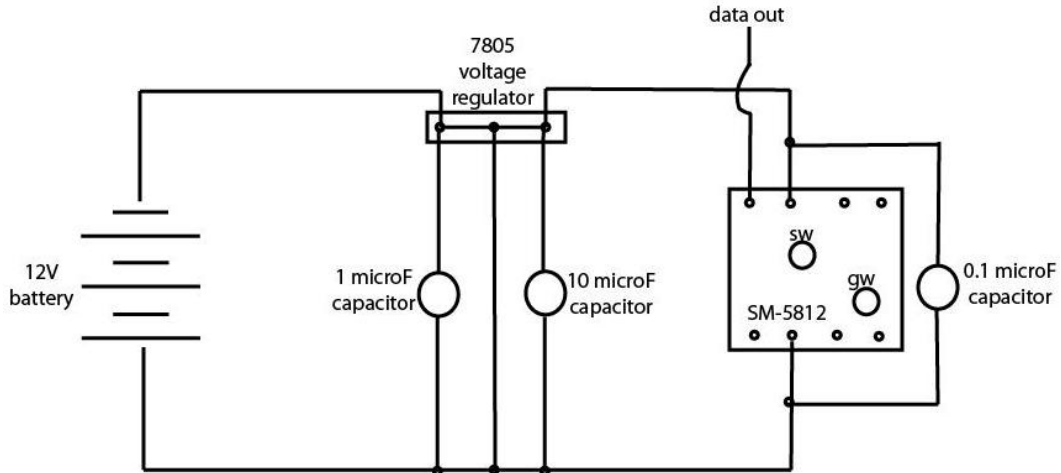


Figure 30: Differential pressure transducer wiring diagram

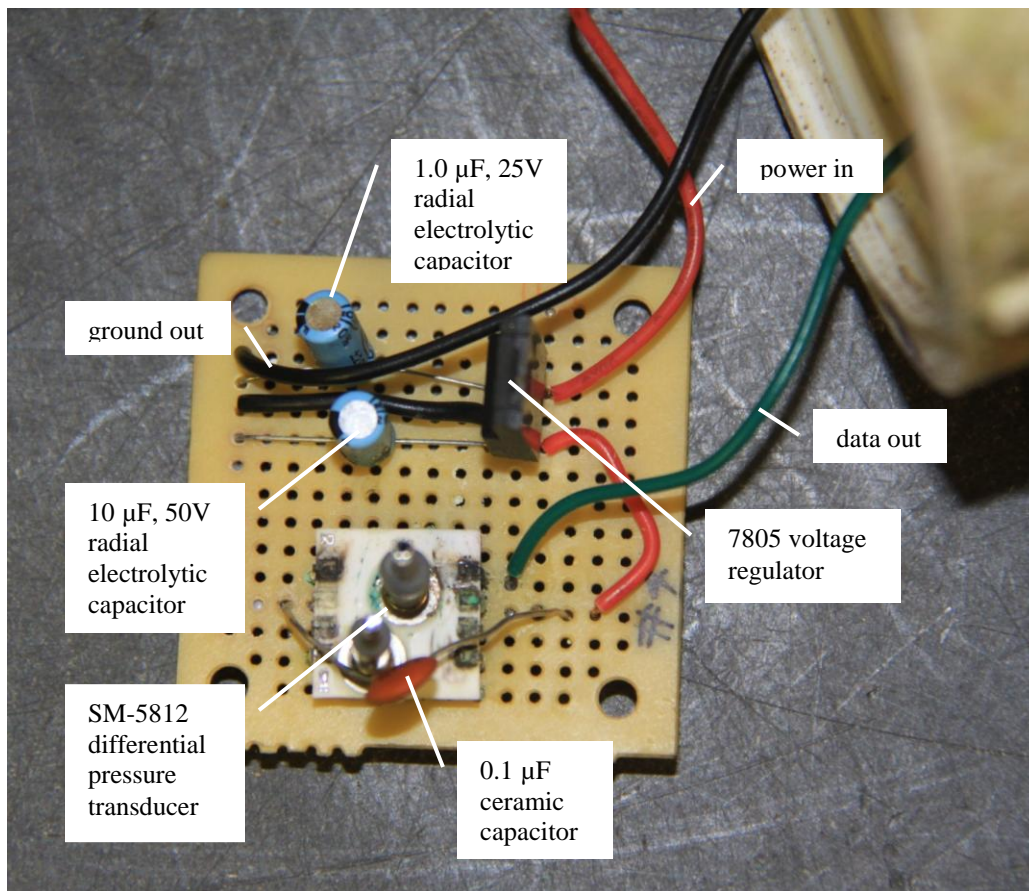


Figure 31: Differential pressure transducer circuit board

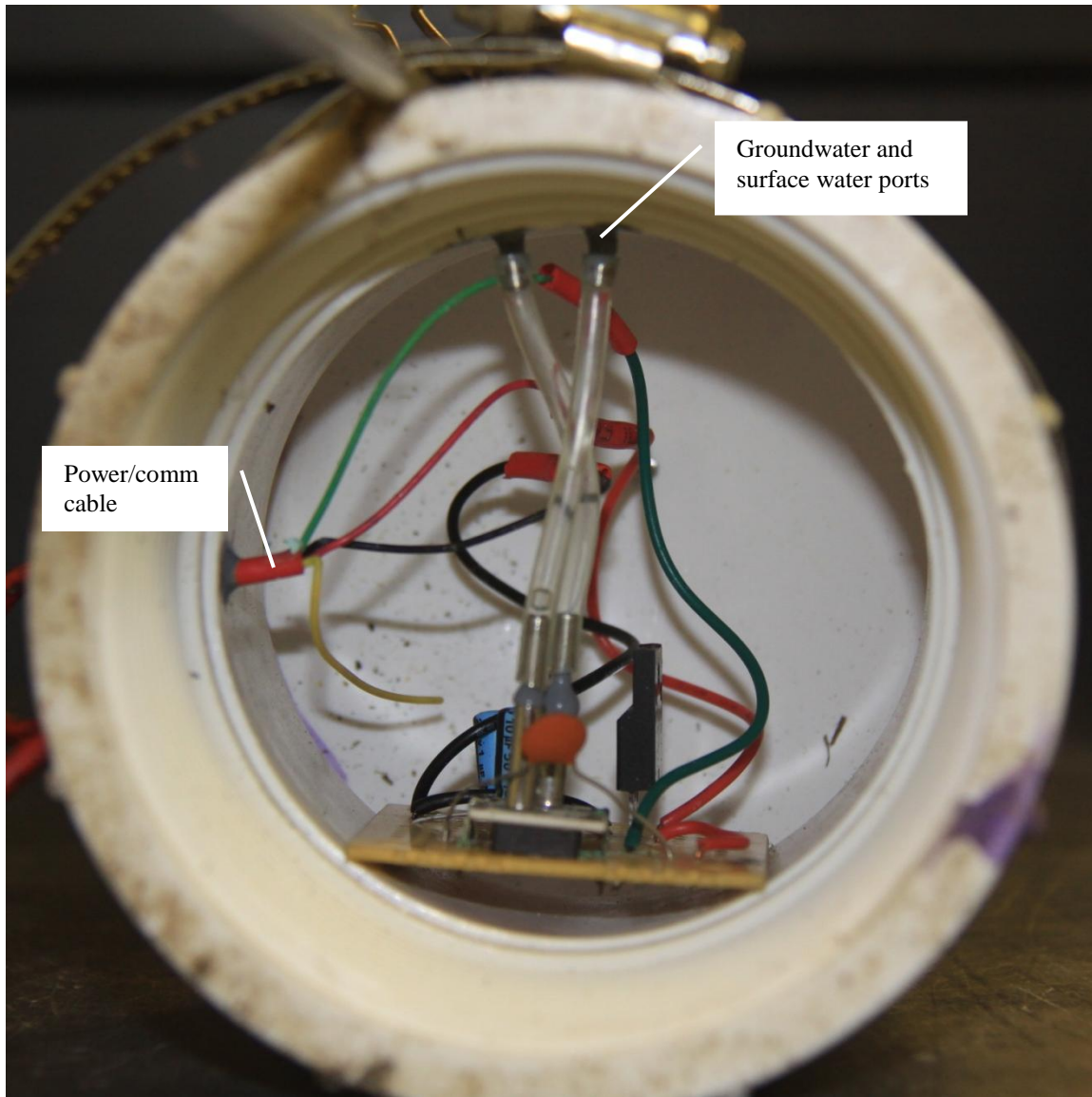


Figure 32: Differential pressure transducer waterproof housing

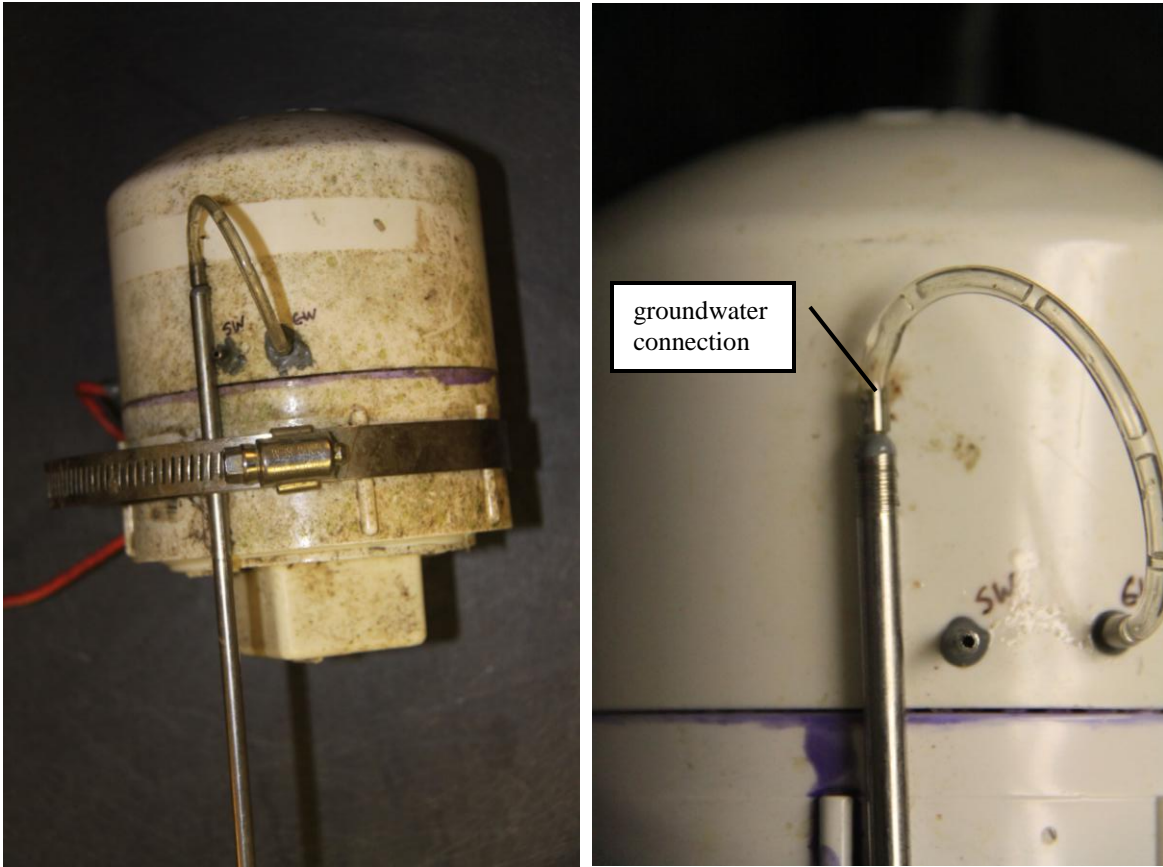


Figure 33: Differential pressure transducer groundwater port



Figure 34: Differential pressure transducer groundwater screen

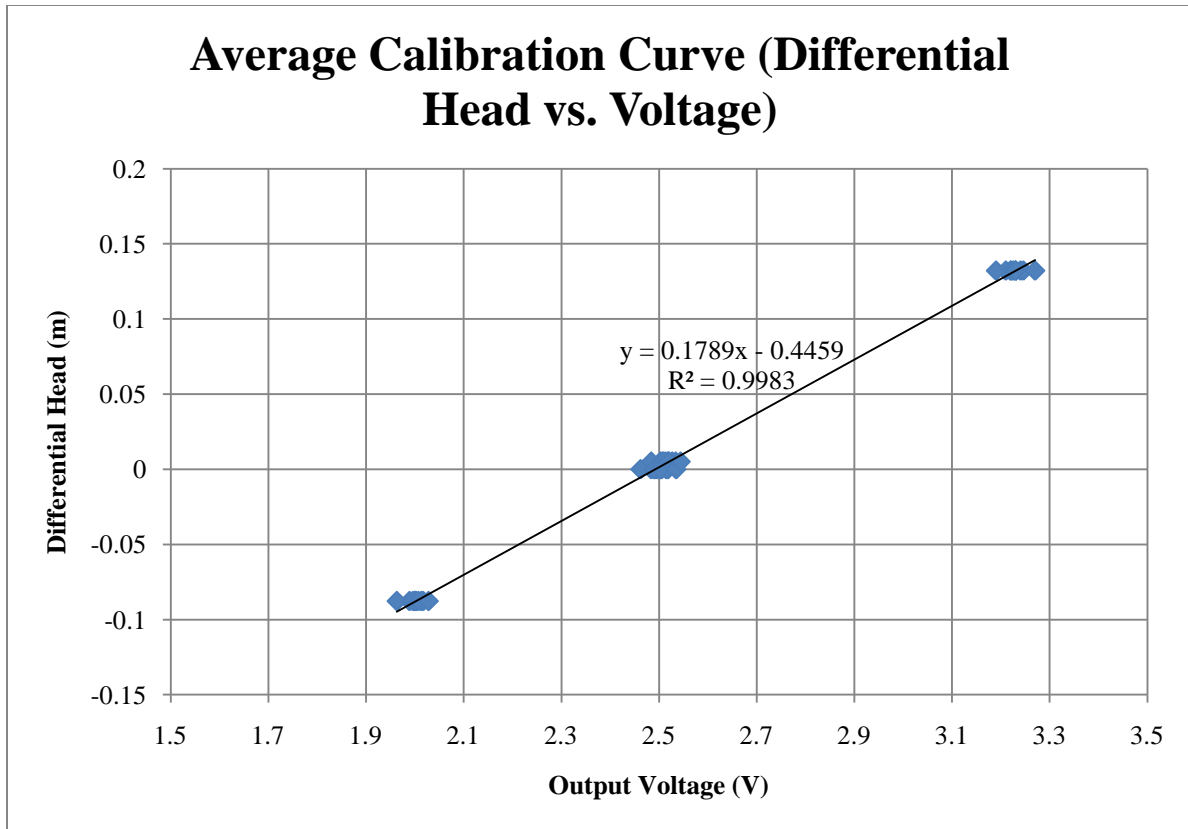


Figure 35: Differential head pressure transducer average calibration curve (Differential Head vs. Voltage)

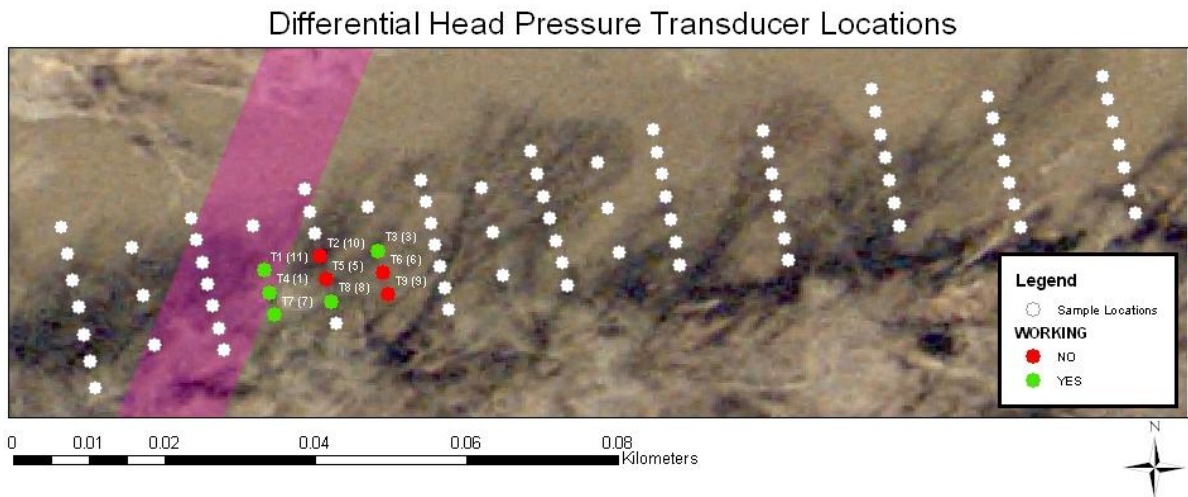


Figure 36: Differential head pressure transducer locations

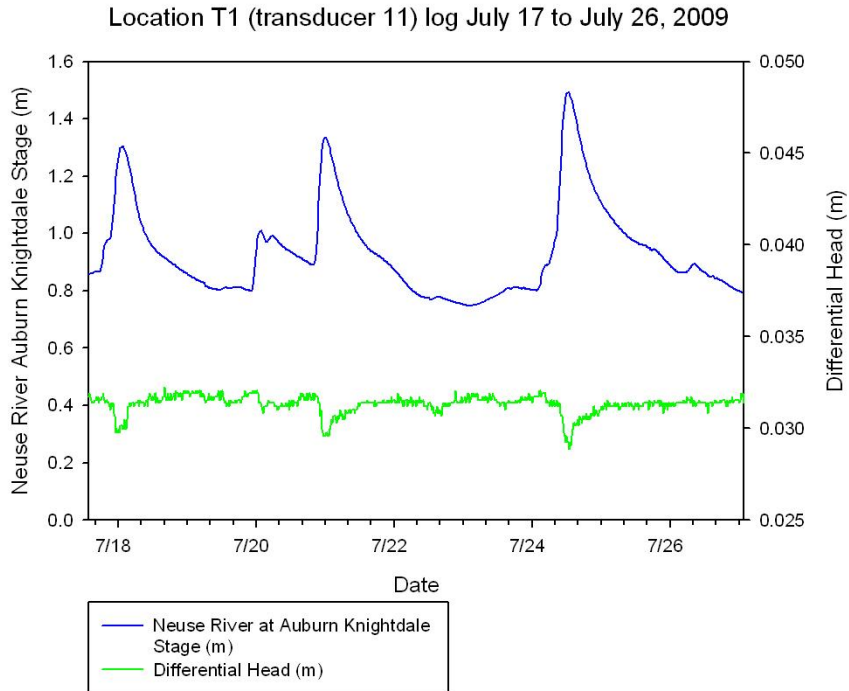


Figure 37: Location T1, transducer 11 log (7/17 – 7/26)

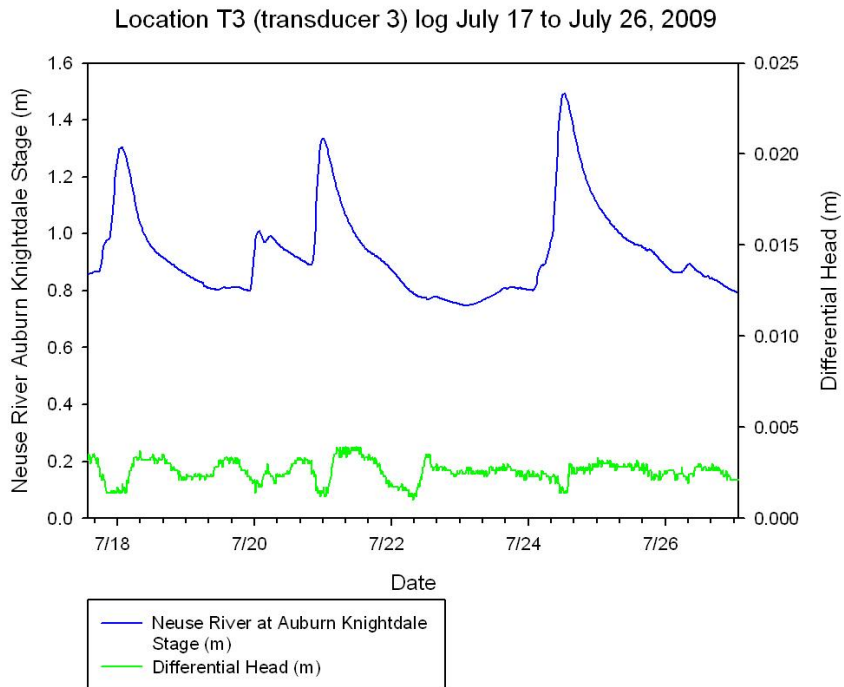


Figure 38: Location T3, transducer 3 log (7/17 – 7/26)

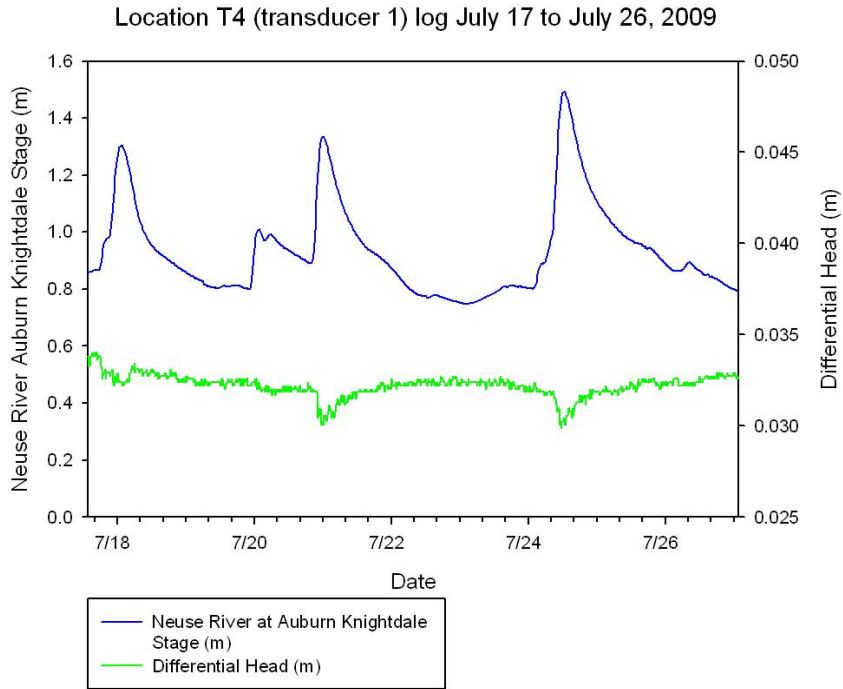


Figure 39: Location T4, transducer 1 log (7/17 – 7/26)

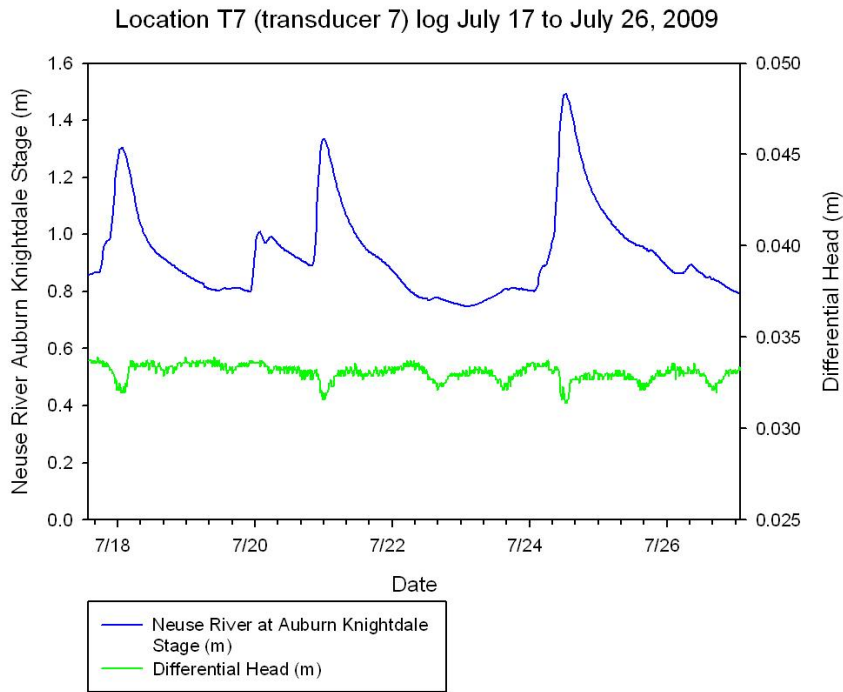


Figure 40: Location T7, transducer 7 log (7/17 – 7/26)

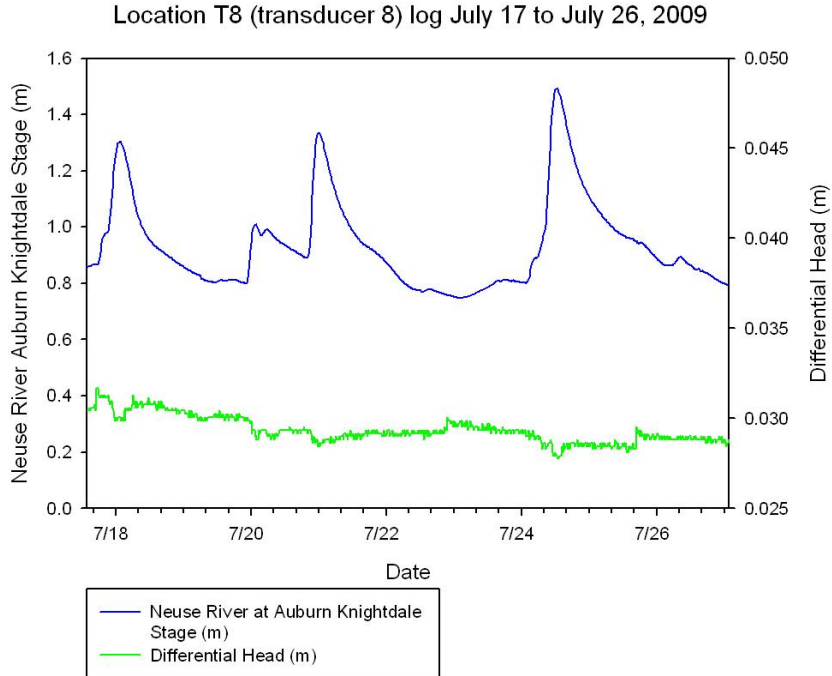


Figure 41: Location T8, transducer 8 log (7/17 – 7/26)

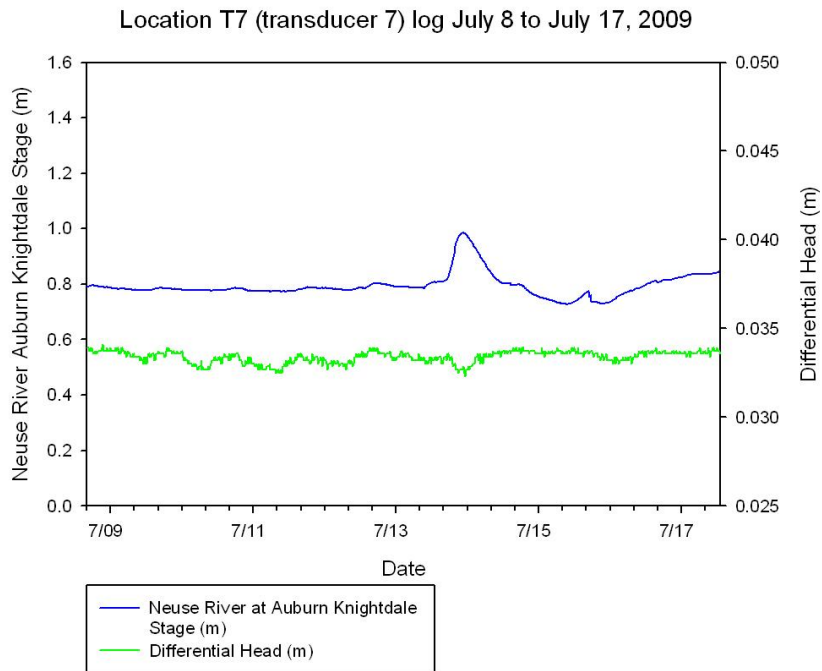


Figure 42: Location T7, transducer 7 log (7/8 – 7/17). Notice the daily ET cycle noted in the groundwater differential head before the storm

TABLES

Table 1: Summary statistics for each sampling period

	Sep 2008	Jan 2009	Apr 2009	Jul 2009
n	63	21	50	50
	j			
MEAN	0.0081	0.0090	0.0066	0.0051
ST DEV	0.0341	0.0069	0.0066	0.0060
CV (%)	420	77	100	118
MIN	-0.030	-0.007	-0.003	-0.023
MAX	0.267	0.022	0.033	0.014
	K (m/d)			
MEAN	159	151	231	145
ST DEV	95	80	123	72
CV (%)	60	53	53	50
MIN	0.11	0.08	0.08	0.04
MAX	330	278	438	329
	v (m/d)			
MEAN	0.78	1.59	1.52	0.91
ST DEV	1.47	1.43	1.61	0.64
CV (%)	189	90	106	70
MIN	-4.78	-0.55	-1.14	-0.01
MAX	5.22	6.08	5.50	2.58
	NO₃⁻ (mg/L)			
MEAN	12.82	21.67	15.43	27.01
ST DEV	25.56	29.06	22.05	35.17
CV (%)	199	134	143	130
MIN	0.00	0.00	0.00	0.00
MAX	86.20	73.10	56.20	84.80
	NO₃⁻ flux (mg/m²d)			
MEAN	7153	27202	22997	23049
ST DEV	19340	48411	46914	42974
CV (%)	270	178	204	186
MIN	-1408	-302	-255	-2
MAX	100328	140928	218334	160151
	Si⁺ (mg/L)			
MEAN	15.12	14.50	17.61	19.19
ST DEV	10.08	5.49	10.96	13.10
CV (%)	67	38	62	68
MIN	3.74	9.36	7.56	5.68
MAX	33.80	25.40	38.00	41.00
	Cl⁻ (mg/L)			
MEAN	10.39	19.21	14.35	13.16
ST DEV	6.52	7.38	7.69	7.32
CV (%)	63	38	54	56
MIN	3.59	6.18	4.72	3.46
MAX	27.70	39.60	33.90	27.60

Table 2: Quantitative nitrate flux for each sampling period

Date	¹ Well 2I EL	¹ River EL	² Elev diff	³ Area	Mean Flux/Area	Flux
	ft	ft	ft	m ²	mg NO ₃ /m ² d	kg NO ₃ /d
Sep 4/5, 2008	150.41	144.25	6.16	2100	7153	15.02
Jan 30, 2009	151.58	144.95	6.63	514.5	27202	14.00
Apr 27/28, 2009	153.24	145.05	8.19	1181.25	22997	27.17
Jul 2, 2009	153.57	143.95	9.62	1181.25	23049	27.23

1: referenced to NAVD88 projection

2: elevation difference between well 2I and river

3: spatial area of sampled reach

APPENDICES

APPENDIX A: Northwest Dike Sample Locations (Lat./Long., WGS84)

ID	LONGITUDE	LATITUDE
A1	-78.49792417	35.72541706
A2	-78.49793066	35.72544396
A3	-78.49793714	35.72547087
A4	-78.49794362	35.72549777
A5	-78.49795011	35.72552467
A6	-78.49795659	35.72555157
A7	-78.49796308	35.72557848
B1	-78.4980607	35.72540079
B2	-78.4980671	35.72542652
B3	-78.49807349	35.72545225
B4	-78.49807988	35.72547799
B5	-78.49808627	35.72550372
B6	-78.49809267	35.72552945
B7	-78.49809906	35.72555518
C1	-78.4982045	35.72540173
C2	-78.49821002	35.72542871
C3	-78.49821554	35.72545568
C4	-78.49822106	35.72548265
C5	-78.49822658	35.72550963
C6	-78.4982321	35.7255366
C7	-78.49823761	35.72556357
D1	-78.49833636	35.72536179
D2	-78.49834127	35.72538726
D3	-78.49834618	35.72541274
D4	-78.49835109	35.72543821
D5	-78.498356	35.72546368
D6	-78.49836091	35.72548915
D7	-78.49836582	35.72551462
E1	-78.49846511	35.72535529
E2	-78.49847046	35.72538213
E3	-78.49847581	35.72540896
E4	-78.49848117	35.7254358
E5	-78.49848652	35.72546263
E6	-78.49849187	35.72548946
E7	-78.49849722	35.7255163
EM1	-78.498538	35.72536998
EM2	-78.49855068	35.72542318
EM3	-78.49856335	35.72547639
F1	-78.49859822	35.72533144
F2	-78.49860554	35.72535782
F3	-78.49861286	35.72538419
F4	-78.49862018	35.72541056
F5	-78.4986275	35.72543694

ID	LONGITUDE	LATITUDE
F6	-78.49863482	35.72546331
F7	-78.49864214	35.72548968
FM1	-78.49867524	35.72534284
FM2	-78.49868807	35.7253948
FM3	-78.49870089	35.72544677
G1	-78.49873943	35.72530226
G2	-78.49874493	35.72532785
G3	-78.49875044	35.72535345
G4	-78.49875595	35.72537904
G5	-78.49876145	35.72540463
G6	-78.49876696	35.72543022
G7	-78.49877247	35.72545581
GM1	-78.49881241	35.72532005
GM2	-78.4988243	35.72537225
GM3	-78.49883619	35.72542445
H1	-78.4988735	35.72528563
H2	-78.49887989	35.72531224
H3	-78.49888627	35.72533885
H4	-78.49889265	35.72536546
H5	-78.49889903	35.72539207
H6	-78.49890542	35.72541868
H7	-78.4989118	35.7254453
HM1	-78.49894669	35.72529631
HM2	-78.49895962	35.72534901
HM3	-78.49897256	35.7254017
I1	-78.49900693	35.72525429
I2	-78.49901349	35.72528037
I3	-78.49902004	35.72530646
I4	-78.49902659	35.72533255
I5	-78.49903315	35.72535863
I6	-78.4990397	35.72538472
I7	-78.49904625	35.7254108
IM1	-78.49909008	35.72526102
IM2	-78.4991033	35.72531878
IM3	-78.49911652	35.72537653
J1	-78.49916	35.72521
J2	-78.49916667	35.72524167
J3	-78.49917333	35.72527333
J4	-78.49918	35.725305
J5	-78.49918667	35.72533667
J6	-78.49919333	35.72536833
J7	-78.4992	35.7254

APPENDIX B: September 2008 Sampling Data

Point	Date/Time	j	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Elev	dh	Temp	AF	W _k	W _k
			m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	NAVD88	m	deg C		m/d	%
A1	9/4/2008 10:55	-0.00717	19.64454	-0.1408	0.00	-41.4891733	1.08	0.07	9.83	5.8	142.9377	-0.026	27.6	12.09178	1.203099	6.12%
A2	9/4/2008 11:12	0.008322	50.86792	0.423338	0.00	0.47413809	0.24	0.03	6.24	5.32	142.2159	0.03	29.2	12.01592	3.133891	6.16%
A3	9/4/2008 11:16	-0.0025	317.8008	-0.79345	0.01	-233.802976	0.24	0.26	5.94	5.22	142.872	-0.009	29.2	12.01592	19.62886	6.18%
A4	9/4/2008 11:23	0.015812	330.259	5.222171	0.00	0	0.87	0.15	5.83	8.08	143.2986	0.057	29.2	12.01592	20.68105	6.26%
A5	9/4/2008 11:28	0.009155	156.6569	1.434118	42.60	61093.4378	0.04	0.01	33.30	13.7	143.561	0.033	29.2	12.01592	9.55385	6.10%
A6	9/4/2008 11:35	0.021915	199.0329	4.361878	1.14	4972.54065	0.03	0.01	14.80	5.62	143.2657	0.079	29.2	12.01592	12.20479	6.13%
A7	9/4/2008 11:40	0.013593	108.4792	1.474566	0.00	0	0.98	0.00	13.60	5	143.1673	0.049	29.2	12.01592	6.615697	6.10%
B1	9/4/2008 12:42	0.000556	1.384516	0.00077	19.10	14.7107648	0.22	0.00	30.10	12.3	142.1503	0.002	29.9	11.98409	0.790469	57.09%
B2	9/4/2008 12:38	0.013629	319.0832	4.348844	8.99	39096.1075	0.05	0.01	14.60	7.81	142.872	0.049	29.9	11.98409	19.67339	6.17%
B3	9/4/2008 12:29	0.013629	254.1146	3.463375	15.00	51950.6219	0.03	0.00	13.80	11	143.3314	0.049	29.9	11.98409	15.58264	6.13%
B4	9/4/2008 12:22	0.006954	257.9781	1.793893	0.00	0	0.26	0.00	6.47	5.39	143.3314	0.025	29.9	11.98409	15.81884	6.13%
B5	9/4/2008 12:14	0.008901	150.2092	1.336966	0.00	0	0.38	0.01	6.37	4.66	143.6594	0.032	29.9	11.98409	9.19283	6.12%
B6	9/4/2008 12:08	0.017245	122.8692	2.11889	0.01	17.7986799	0.10	0.01	15.40	4.47	143.2329	0.062	29.9	11.98409	8.436616	6.87%
B7	9/4/2008 12:00	-0.00139	135.2889	-0.18815	0.01	-55.4417411	0.66	0.00	24.10	5.03	143.2657	-0.005	29.9	11.98409	8.293316	6.13%
C1	9/4/2008 13:30	0.00279	27.93718	0.077937	55.50	4325.47705	0.05	0.01	30.40	19.2	142.6424	0.01	30.7	11.94869	1.813168	6.49%
C2	9/4/2008 13:23	-0.01813	263.5515	-4.779	1.24	-1408.21296	0.06	0.01	11.80	10	142.7736	-0.065	30.7	11.94869	16.37075	6.21%
C3	9/4/2008 13:16	0.011159	275.1001	3.069794	0.02	57.4051498	0.16	0.01	6.74	5.62	143.2329	0.04	30.7	11.94869	16.86903	6.13%
C4	9/4/2008 13:41	0.011717	165.9845	1.944801	0.00	7.00128472	0.78	0.07	7.57	7.24	143.397	0.042	30.7	11.94869	10.35466	6.24%
C5	9/4/2008 13:34	0.000558	96.01135	0.053569	0.00	0.17731238	0.32	0.07	7.28	5.06	143.1673	0.002	30.7	11.94869	5.943508	6.19%
C6	9/4/2008 13:37	0.000837	101.0866	0.084601	0.04	3.31634173	0.30	0.01	5.80	5.87	143.1673	0.003	30.7	11.94869	6.252767	6.19%
C7	9/4/2008 13:39	0.012275	128.6194	1.578766	0.00	0	0.92	0.01	3.78	4.62	143.2329	0.044	30.7	11.94869	8.037244	6.25%
D1	9/4/2008 14:08	-0.00894	0.114265	-0.00102	0.13	-0.3011186	8.78	0.02	25.90	15.3	142.2815	-0.032	31.2	11.92709	0.016772	14.68%
D2	9/4/2008 14:18	0.006707	47.70836	0.32	39.30	12575.9982	0.07	0.01	28.20	23.3	142.7736	0.024	31.2	11.92709	17.19165	36.03%
D3	9/4/2008 14:26	0.000279	243.9352	0.068174	46.30	3156.45571	0.04	0.01	22.80	27.7	143.2657	0.001	31.2	11.92709	15.1007	6.19%
D4	9/4/2008 14:38	0.010061	212.3622	2.136603	0.00	0	0.39	0.02	8.68	5.67	142.872	0.036	31.2	11.92709	13.86968	6.53%
D5	9/4/2008 14:51	0.011179	154.8473	1.731042	0.00	4.76036674	0.40	0.01	4.79	5.47	143.4626	0.04	31.2	11.92709	9.538911	6.16%
D6	9/4/2008 14:52	0.002795	112.497	0.314402	0.01	1.64117743	0.50	0.02	7.83	7.66	143.1345	0.01	31.2	11.92709	6.901054	6.13%
D7	9/4/2008 14:54	0.007825	93.8932	0.734744	0.00	0	1.10	0.01	6.22	9.06	143.0361	0.028	31.2	11.92709	5.842827	6.22%
E1	9/4/2008 15:35	-0.00559	8.453666	-0.04727	0.06	-13.9285468	3.89	0.04	28.80	10.5	142.872	-0.02	31.3	11.92282	4.31587	51.05%
E2	9/4/2008 15:20	0.011183	214.5864	2.399727	0.00	0	0.37	0.01	6.64	5.33	143.0033	0.04	31.3	11.92282	13.463	6.27%
E3	9/4/2008 15:28	-0.00559	297.847	-1.66542	71.80	-490.74283	0.05	0.03	23.80	22.5	143.397	-0.02	31.3	11.92282	18.44243	6.19%
E4	9/4/2008 15:35	0.013979	184.5722	2.580097	0.00	0	1.17	0.09	4.44	9	143.6923	0.05	31.3	11.92282	14.32858	7.76%
E5	9/4/2008 15:40	-0.00335	172.4354	-0.57851	0.68	-170.466221	0.64	0.04	5.46	5.21	143.4954	-0.012	31.3	11.92282	10.99801	6.38%
E6	9/4/2008 15:51	-0.00252	148.7692	-0.37433	0.01	-110.302747	0.44	0.09	7.05	5.21	143.1673	-0.009	31.3	11.92282	9.166905	6.16%
E7	9/4/2008 15:53	0.000839	125.7202	0.105445	0.00	0	1.54	0.01	9.90	7.77	142.9705	0.003	31.3	11.92282	7.869	6.26%
F1	9/4/2008 16:26	0.011195	0.47088	0.005271	0.16	0.83289593	8.96	0.04	32.00	20.9	142.8392	0.04	31.6	11.9101	0.050246	10.67%
F2	9/4/2008 16:15	-0.00364	152.0863	-0.55335	13.20	-163.052552	0.22	0.01	21.30	23.4	143.1673	-0.013	31.6	11.9101	9.329587	6.13%
F3	9/4/2008 16:25	0.009796	261.9637	2.566093	0.00	0	0.11	0.01	12.70	5.73	142.9049	0.035	31.6	11.9101	16.30414	6.22%
F4	9/4/2008 16:33	0.00028	233.6016	0.065379	8.16	533.493537	0.42	0.01	17.00	7.76	143.1673	0.001	31.6	11.9101	14.68171	6.28%
F5	9/4/2008 16:42	0.006997	172.3197	1.205697	39.00	47022.1693	0.12	0.00	11.50	12.6	143.2329	0.025	31.6	11.9101	10.69262	6.21%
F6	9/4/2008 16:50	0.010635	125.6366	1.336174	0.00	0	1.28	0.01	8.18	7.69	143.2329	0.038	31.6	11.9101	7.752833	6.17%
F7	9/4/2008 16:55	0.008956	108.8232	0.974618	0.00	2.35857589	0.78	0.01	6.62	9.16	143.0689	0.032	31.6	11.9101	6.791841	6.24%
G1	9/5/2008 9:53	-0.02995	0.162735	-0.00487	0.04	-1.43641143	6.28	0.00	26.90	15.5	142.2815	-0.11	24.7	12.24065	0.020417	12.55%
G2	9/5/2008 9:46	0.004629	262.3719	1.214621	82.60	100327.658	0.04	0.00	33.40	24.4	141.6581	0.017	24.7	12.24065	19.02366	7.25%
G3	9/5/2008 10:00	0.002197	268.5946	0.590169	28.20	16642.7774	0.09	0.01	14.70	10.7	143.1345	0.008	26.7	12.13638	17.13063	6.38%

Point	Date/Time	j	K m/d	v m/d	NO3 mg/L	NO3 flux mg/(m ² *d)	NH4 mg/L	PO4 mg/L	Si mg/L	Cl mg/L	Elev NAVD88	dh m	Temp deg C	AF	W _k m/d	W _k %
G4	9/5/2008 10:14	0.002747	223.689	0.614376	2.57	1578.94577	0.64	0.04	11.20	8.58	143.1345	0.01	26.7	12.13638	13.80389	6.17%
G5	9/5/2008 10:07	0.000549	273.297	0.150125	0.04	6.39534312	0.16	0.01	7.31	6.6	142.872	0.002	26.7	12.13638	16.86159	6.17%
G6	9/5/2008 10:16	0.000275	156.7822	0.043061	0.00	0	2.20	0.04	3.74	5.71	143.1345	0.001	26.7	12.13638	9.616962	6.13%
G7	9/5/2008 10:22	0.001648	143.3951	0.236306	0.00	0	0.79	0.08	4.82	6.46	142.9049	0.006	26.7	12.13638	9.104342	6.35%
H1	9/5/2008 10:47	0.266667	0.919261	0.245136	1.87	458.404847	1.09	0.00	30.20	18.2	142.7736	0.08	26.7	1	0.391906	42.63%
H2	9/5/2008 10:40	-0.00275	46.32626	-0.12724	86.20	-37.4927839	0.09	0.01	33.10	18.5	141.8878	-0.01	26.7	12.13638	2.876825	6.21%
H3	9/5/2008 10:55	0.001923	280.6639	0.539603	83.70	45164.7402	0.06	0.01	30.90	21.7	142.9705	0.007	26.7	12.13638	18.2145	6.49%
H4	9/5/2008 11:00	0.002206	318.3054	0.702259	85.80	60253.8275	0.06	0.01	30.50	18.6	143.2001	0.008	27.7	12.08691	19.54423	6.14%
H5	9/5/2008 11:10	0.000276	166.7623	0.04599	72.50	3334.25866	0.13	0.01	33.80	17.8	143.3314	0.001	27.7	12.08691	10.2295	6.13%
H6	9/5/2008 11:15	0.001379	147.0753	0.202802	0.00	0	0.95	0.01	8.13	5.93	142.9705	0.005	27.7	12.08691	9.076735	6.17%
H7	9/5/2008 11:19	0.003309	142.2701	0.470824	0.01	2.76373497	0.35	0.00	4.92	7.35	142.6096	0.012	27.7	12.08691	8.780968	6.17%
I1	9/5/2008 12:05	0.013727	4.288064	0.058863	0.03	1.69524602	1.14	0.00	28.90	26.8	142.7408	0.05	26.6	12.14143	0.271999	6.34%
I2	9/5/2008 11:55	-0.00083	73.57624	-0.06087	0.00	-17.9371414	0.09	0.01	6.57	8.22	142.9049	-0.003	27.7	12.08691	4.554024	6.19%
I3	9/5/2008 11:51	0.003309	327.5269	1.083906	0.00	0	0.12	0.01	7.86	6.77	142.872	0.012	27.7	12.08691	20.58657	6.29%
I4	9/5/2008 11:45	0.008549	158.37	1.353936	0.00	0	0.11	0.07	6.43	6.21	143.1017	0.031	27.7	12.08691	9.745535	6.15%
I5	9/5/2008 11:42	0.003585	146.5	0.525224	1.45	761.574419	0.23	0.01	10.30	7.73	143.3642	0.013	27.7	12.08691	8.986251	6.13%
I6	9/5/2008 11:38	0.002758	159.4404	0.439705	0.00	0	0.45	0.04	21.70	5.11	143.3314	0.01	27.7	12.08691	9.998347	6.27%
I7	9/5/2008 11:34	0.003034	148.5539	0.450651	0.00	0	0.32	0.05	23.70	3.59	143.1673	0.011	27.7	12.08691	9.218757	6.21%
SURF.					0.29		0.10	0.02	6.44	7.22						

APPENDIX C: January 2009 Sampling Data

Point	Date/Time	j	K m/d	v m/d	NO3 mg/L	NO3 flux mg/(m ² *d)	NH4 mg/L	PO4 mg/L	Si mg/L	Cl mg/L	Elev NAVD88	dh m	Temp deg C	AF	W _k m/d	W _k %
G1	1/30/2009 14:42	#VALUE!	1.995563	#VALUE!	13.00	#VALUE!	2.840	0.021	15.700	39.6	142.3581	-	8.7	13.37572	-	-
G2	1/30/2009 14:36	0.00324	267.7203	0.867334	68.40	59325.6271	0.156	0.026	23.300	34	143.3752	0.013	8.7	13.37572	16.71959	6.25%
G3	1/30/2009 14:27	0.009719	205.9852	2.001991	68.20	136535.796	0.099	0.018	10.200	19.7	143.6049	0.039	8.7	13.37572	12.93427	6.28%
G4	1/30/2009 14:20	0.005981	178.8702	1.06982	0.60	645.101574	0.105	0.028	10.000	17.4	142.9487	0.024	8.7	13.37572	10.97319	6.13%
G5	1/30/2009 14:15	0.010467	137.5902	1.440119	0.67	963.439792	0.066	0.016	9.850	15.8	143.1783	0.042	8.7	13.37572	8.441376	6.14%
G6	1/30/2009 14:08	0.005483	138.6284	0.76004	0.01	9.12048144	0.066	0.014	9.360	17.7	142.9487	0.022	8.7	13.37572	8.556006	6.17%
G7	1/30/2009 14:02	0.019937	144.4204	2.879255	0.04	123.807961	0.053	0.016	10.100	20.8	142.4566	0.08	8.7	13.37572	8.861665	6.14%
H1	1/30/2009 13:56	#VALUE!	0.081898	#VALUE!	2.06	#VALUE!	0.055	0.018	12.200	15	141.9972	-	8.4	13.40306	0.1572	191.95%
H2	1/30/2009 13:30	0.002487	217.0838	0.539886	73.10	39465.6846	0.053	0.028	25.400	20.7	143.2768	0.01	8.4	13.40306	13.61822	6.27%
H3	1/30/2009 13:25	0.021886	277.8579	6.081073	-	#VALUE!	-	-	-	-	143.1783	0.088	8.4	13.40306	17.76177	6.39%
H4	1/30/2009 13:20	0.012186	165.2677	2.013997	48.20	97074.6729	0.106	0.027	19.900	20	143.5064	0.049	8.4	13.40306	10.37796	6.28%
H5	1/30/2009 13:18	0.021139	130.4611	2.757877	51.10	140927.522	0.112	0.125	10.700	19.5	143.5392	0.085	8.4	13.40306	8.096706	6.21%
H6	1/30/2009 13:10	0.004477	129.2719	0.578697	0.21	118.632934	0.049	0.032	20.300	17.6	142.6862	0.018	8.4	13.40306	7.931613	6.14%
H7	1/30/2009 13:05	0.011191	173.6664	1.943583	0.37	724.956568	0.066	0.014	9.400	11.2	141.8004	0.045	8.4	13.40306	10.79612	6.22%
I1	1/30/2009 11:25	0.008614	0.481809	0.00415	65.70	272.676682	0.098	0.022	9.620	17.9	142.3581	0.035	6.9	13.54374	0.074161	15.39%
I2	1/30/2009 11:30	-0.00665	82.45386	-0.54792	36.30	-301.628381	0.048	0.026	23.800	25	143.3096	-0.027	6.9	13.54374	5.05873	6.14%
I3	1/30/2009 11:35	0.011075	242.1256	2.681597	4.64	12442.6079	0.072	0.028	16.400	16.7	143.1127	0.045	6.9	13.54374	15.12105	6.25%
I4	1/30/2009 11:45	0.007876	211.5233	1.665897	0.79	1316.05887	0.095	0.018	10.200	20.2	143.244	0.032	6.9	13.54374	15.19033	7.18%
I5	1/30/2009 11:50	0.006153	215.8271	1.327963	0.00	0	0.073	0.020	15.800	10.3	143.244	0.025	6.9	13.54374	13.3916	6.20%
I6	1/30/2009 11:55	0.012306	137.1467	1.687701	0.00	0	0.083	0.024	17.400	6.18	143.1783	0.05	6.9	13.54374	8.413847	6.13%
I7	1/30/2009 12:00	0.00371	121.9917	0.452584	0.00	0	0.054	0.016	10.400	19	142.4894	0.015	7.6	13.47725	7.485397	6.14%
G3 S					0.64		0.064	0.026	24.300	17.1						
H5 S					0.46		0.049	0.016	10.600	19.5						

APPENDIX D: April 2009 Sampling Data

Point	Date/Time	j	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Elev	dh	Temp	AF	W _k	W _k
			m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	NAVD88	m	deg C		m/d	%
EM1	4/28/2009 14:43	0.005252	408.7176	2.146734	0.12	261.901584	0.09	0.02	7.56	11.20	143.6392	0.019	28.3	12.05806	26.11109	6.39%
EM2	4/28/2009 14:47	0.004147	317.9936	1.318594	5.83	7687.40137	0.21	0.03	9.13	11.00	143.508	0.015	28.3	12.05806	19.84826	6.24%
EM3	4/28/2009 14:49	-0.00028	200.0132	-0.05529	0.01	-12.4129888	0.18	0.03	9.77	11.80	142.819	-0.001	28.3	12.05806	12.3458	6.17%
F1	#VALUE!	#VALUE!	0.079166	#VALUE!	0.27	#VALUE!	3.52	0.03	9.44	11.50	141.5395	-	#VALUE!	#VALUE!	0.022629	28.58%
F2	4/28/2009 14:37	0.001935	371.3365	0.718567	7.01	5037.15142	0.51	0.02	10.60	15.00	143.672	0.007	28.3	12.05806	25.56588	6.88%
F3	4/28/2009 14:32	0.004699	372.9114	1.752492	21.00	36802.3246	0.18	0.03	13.50	13.70	143.6392	0.017	28.3	12.05806	23.95553	6.42%
F4	4/28/2009 14:25	-0.00332	342.9229	-1.13757	9.15	-255.385056	0.03	0.03	11.70	11.90	143.3112	-0.012	28.3	12.05806	21.45527	6.26%
F5	4/28/2009 14:23	0.011887	243.0674	2.889326	0.00	0	0.02	0.04	8.69	8.14	142.8518	0.043	28.3	12.05806	15.09434	6.21%
F6	4/28/2009 14:16	0.004423	169.8544	0.751273	0.02	18.2559456	0.44	0.02	8.62	11.20	142.9175	0.016	28.3	12.05806	10.42092	6.14%
F7	4/28/2009 14:14	0.001382	127.2662	0.175908	0.06	9.69250704	0.03	0.05	8.47	8.32	142.7862	0.005	28.3	12.05806	7.808574	6.14%
FM1	4/28/2009 13:07	0.003582	341.9265	1.224868	55.80	68347.6151	0.34	0.03	28.90	32.40	143.9673	0.013	27.5	12.09667	21.59537	6.32%
FM2	4/28/2009 13:06	0.001378	197.1301	0.271604	0.24	64.9133136	0.05	0.03	9.35	10.70	142.9175	0.005	27.5	12.09667	12.16859	6.17%
FM3	4/28/2009 13:01	-0.00138	202.7517	-0.27935	0.50	-62.7139077	0.05	0.04	8.68	9.75	142.5238	-0.005	27.5	12.09667	12.81921	6.32%
G1	4/28/2009 12:57	0.002192	0.234283	0.000513	0.01	0.00275229	5.08	0.04	23.90	23.00	142.1629	0.008	26.1	12.16691	0.235654	100.59%
G2	4/28/2009 12:54	0.00411	366.6116	1.506593	56.20	84670.531	0.24	0.03	33.80	27.10	143.5408	0.015	26.1	12.16691	22.87288	6.24%
G3	4/28/2009 12:51	0.00411	278.414	1.144144	55.40	63385.5911	0.03	0.04	36.50	24.70	143.2455	0.015	26.1	12.16691	17.38572	6.24%
G4	4/28/2009 12:47	0.004383	319.2793	1.399553	17.10	23932.3507	0.02	0.04	15.80	14.40	142.9175	0.016	26.1	12.16691	19.70589	6.17%
G5	4/28/2009 12:44	0.008493	150.2092	1.275724	0.13	162.016937	0.03	0.04	9.40	8.40	142.5566	0.031	26.1	12.16691	9.216997	6.14%
G6	4/28/2009 12:38	0.006849	151.6716	1.038826	0.02	23.4774736	0.06	0.03	9.58	8.76	142.3597	0.025	26.1	12.16691	9.307489	6.14%
G7	4/28/2009 12:30	-0.00192	132.7497	-0.25458	0.03	-57.1539557	0.03	0.04	10.40	8.28	142.3269	-0.007	26.1	12.16691	8.095848	6.10%
GM1	4/28/2009 12:19	0.012329	34.73907	0.428281	54.60	23384.1632	0.04	0.04	38.00	22.00	142.5566	0.045	26.1	12.16691	2.18778	6.30%
GM2	4/28/2009 12:17	0.010959	297.4227	3.259363	24.30	79202.5095	0.01	0.03	14.80	14.40	142.1629	0.04	26.1	12.16691	18.36246	6.17%
GM3	4/28/2009 12:18	0.00274	182.1423	0.49901	0.22	109.283184	0.03	0.04	8.84	8.58	142.6878	0.01	26.1	12.16691	11.17527	6.14%
H1	4/28/2009 12:00	0.033424	0.112336	0.003755	47.00	176.472164	0.02	0.03	36.10	33.90	142.4253	0.122	26.1	12.16691	0.012418	11.05%
H2	4/28/2009 11:56	0.00245	417.0424	1.021658	53.20	54352.191	0.02	0.04	34.90	26.50	142.6878	0.009	24.6	12.24605	26.37355	6.32%
H3	4/28/2009 11:54	0.001089	298.9559	0.325499	53.90	17544.4039	0.04	0.05	35.50	24.10	142.9175	0.004	24.6	12.24605	18.67464	6.25%
H4	4/28/2009 11:46	0.014154	265.8947	3.763532	0.43	1599.5013	0.02	0.05	10.20	11.10	142.9175	0.052	24.6	12.24605	17.45543	6.56%
H5	4/28/2009 11:21	0.013882	244.7999	3.398318	30.00	101949.551	0.06	0.05	16.60		142.8846	0.051	24.6	12.24605	15.01954	6.14%
H6	4/28/2009 11:26	0.01606	160.6393	2.579802	0.40	1031.92094	0.03	0.04	11.10	9.06	142.4253	0.059	24.6	12.24605	9.856478	6.14%
H7	4/28/2009 11:30	0.002178	100.5209	0.218892	0.04	7.8144278	0.22	0.03	8.07	8.70	142.1957	0.008	24.6	12.24605	6.205989	6.17%
HM1	4/27/2009 15:12	0.006133	222.4644	1.364343	50.50	68899.339	0.04	0.05	37.10	23.40	141.6379	0.022	30.5	11.95744	13.65928	6.14%
HM2	4/27/2009 15:14	0.010314	399.3964	4.119518	53.00	218334.449	0.03	0.03	37.80	27.90	143.1799	0.037	30.5	11.95744	24.78778	6.21%
HM3	4/27/2009 15:16	0.009199	183.4697	1.687792	31.70	53502.9955	0.05	0.05	24.70	17.90	142.9503	0.033	30.5	11.95744	11.18905	6.10%
I1	4/27/2009 14:58	0.00446	9.822915	0.043813	51.00	2234.45206	0.02	0.04	36.20	29.30	141.4083	0.016	30.5	11.95744	0.727795	7.41%
I2	4/27/2009 14:57	0.000836	73.28375	0.061287	53.40	3272.7338	0.02	0.04	37.50	24.10	142.9831	0.003	30.5	11.95744	4.512032	6.16%
I3	4/27/2009 14:50	0.012544	438.0632	5.49528	35.30	193983.385	0.14	0.04	25.80	16.60	142.819	0.045	30.5	11.95744	28.14476	6.42%
I4	4/27/2009 14:45	0.009757	374.1328	3.650349	0.00	0	0.22	0.02	9.85	8.37	143.344	0.035	30.5	11.95744	27.20502	7.27%
I5	4/27/2009 14:41	0.008363	208.5855	1.744399	0.10	166.415659	0.08	0.03	9.35	9.06	143.0159	0.03	30.5	11.95744	12.94779	6.21%
I6	4/27/2009 14:38	0.006412	197.8276	1.268397	0.00	0	0.04	0.04	11.10	9.77	142.655	0.023	30.5	11.95744	12.28294	6.21%
I7	4/27/2009 14:30	0.006133	189.8049	1.164047	0.01	6.94936216	0.22	0.04	26.80	4.77	142.4253	0.022	30.5	11.95744	11.64593	6.14%
IM1	4/27/2009 13:52	0.013083	414.7924	5.426588	3.10	16822.4225	0.02	0.03	10.80	12.20	143.0815	0.047	30.1	11.97514	25.75218	6.21%
IM2	4/27/2009 13:54	0.013918	363.6867	5.06169	0.02	114.900362	0.21	0.03	23.20	4.72	143.672	0.05	30.1	11.97514	23.5116	6.46%
IM3	4/27/2009 13:56	0.022825	205.8598	4.698764	0.00	0	0.07	0.03	10.10	8.74	143.0815	0.082	30.1	11.97514	13.23646	6.43%
J1	4/28/2009 15:30	0.001656	11.83597	0.0196	0.01	0.19345669	0.79	0.03	12.90	14.90	143.6064	0.006	27.9	12.07723	0.952171	8.04%
J2	4/28/2009 15:26	0.013248	255.5385	3.385393	0.01	17.8071689	0.13	0.04	8.16	10.30	142.9175	0.048	27.9	12.07723	15.86462	6.21%

Point	Date/Time	j	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Elev	dh	Temp	AF	W _k	W _k
			m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	NAVD88	m	deg C		m/d	%
J3	4/28/2009 15:22	0.003312	368.958	1.221996	0.01	14.9083477	0.31	0.03	8.03	8.48	143.6392	0.012	27.9	12.07723	24.55828	6.66%
J4	4/28/2009 15:21	0.002208	301.4887	0.665691	0.01	3.74118246	0.21	0.04	23.60	6.90	143.7705	0.008	27.9	12.07723	19.04388	6.32%
J5	4/28/2009 15:17	0.003864	285.2409	1.102177	0.00	0.47724272	0.20	0.03	8.68	8.62	143.5408	0.014	27.9	12.07723	18.43831	6.46%
J6	4/28/2009 15:15	0.00276	197.5543	0.545253	0.18	100.326568	0.02	0.03	7.57	10.30	142.7534	0.01	27.9	12.07723	12.12088	6.14%
J7	4/28/2009 15:07	0.001656	169.4687	0.280642	0.03	7.97022457	0.20	0.03	13.60	7.05	142.4909	0.006	27.9	12.07723	10.46131	6.17%
EM3 S					0.23		0.11	0.02	6.78	9.35						
H5 S					0.21		0.06	0.01	7.62	16.60						
IM1 S					0.23		0.07	0.02	7.10	9.89						
J4 S					0.23		0.08	0.02	7.44	19.70						

APPENDIX E: July 2009 Sampling Data

Point	Date/Time	j	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Elev	dh	Temp	AF	W _k	W _k
			m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	NAVD88	m	deg C		m/d	%
EM1	7/2/2009 14:47	0.006148	329.0376	2.023077	70.8	143233.838	0.064	0.149	34.4	25.40	142.0143	0.022	31.2	11.92709	20.30415	6.17%
EM2	7/2/2009 14:48	0.002236	221.2398	0.494649	4.240	2097.31287	0.251	0.014	11.100	7.93	142.6705	0.008	31.2	11.92709	14.13497	6.39%
EM3	7/2/2009 14:49	0.008664	132.9457	1.151808	0.000	0	1.290	0.010	6.990	7.43	142.9657	0.031	31.2	11.92709	8.107806	6.10%
F1	7/2/2009 14:42	-0.02264	0.626351	-0.01418	0.227	-2.19066251	30.4	0.021	29.600	20.90	141.8503	-0.081	31.2	11.92709	0.079045	12.62%
F2	7/2/2009 14:37	0.001677	0.224962	0.000377	57.2	21.5774571	0.030	0.027	35.6	25.40	141.9487	0.006	31.2	11.92709	0.030589	13.60%
F3	7/2/2009 14:12	0.005869	200.6496	1.177611	63.6	74896.0488	0.513	0.026	29.4	24.70	142.8673	0.021	31.2	11.92709	12.30879	6.13%
F4	7/2/2009 14:12	0.002236	181.1426	0.405	75	30374.9873	0.018	0.022	29	20.30	142.7689	0.008	31.2	11.92709	11.24009	6.21%
F5	7/2/2009 14:12	0.009502	142.6526	1.35551	0.188	254.835909	0.343	0.000	7.490	7.85	142.9001	0.034	31.2	11.92709	8.751271	6.13%
F6	7/2/2009 14:02	0.006428	149.7528	0.962602	0.000	0	0.738	0.000	5.680	6.89	142.8017	0.023	31.2	11.92709	9.29457	6.21%
F7	7/2/2009 14:00	0.003913	149.8428	0.586284	0.000	0	0.592	0.004	6.710	7.52	142.6705	0.014	31.2	11.92709	9.246325	6.17%
FM1	7/2/2009 13:49	0.000835	237.9311	0.198688	57.400	11404.6652	0.005	0.009	16.100	26.20	142.408	0.003	30.1	11.97514	14.84981	6.24%
FM2	7/2/2009 13:48	0.003062	204.7702	0.626986	0.003	1.58627381	0.035	0.012	12.400	6.32	142.6377	0.011	30.1	11.97514	12.78298	6.24%
FM3	7/2/2009 13:46	0.003897	104.8504	0.408598	0.022	9.15259615	0.497	0.006	9.240	7.08	142.4736	0.014	30.1	11.97514	6.394389	6.10%
G1	7/2/2009 13:21	-0.0103	0.04352	-0.00045	8.930	-0.06925001	0.040	0.024	32.800	27.60	141.7846	-0.037	30.1	11.97514	0.019644	45.14%
G2	7/2/2009 13:21	0.009742	135.1603	1.316786	82.800	109029.918	0.039	0.033	37.800	23.10	142.3424	0.035	30.1	11.97514	8.438283	6.24%
G3	7/2/2009 13:16	0.009186	150.1128	1.37889	77.800	107277.66	0.029	0.050	36.600	20.50	143.0642	0.033	30.1	11.97514	9.207731	6.13%
G4	7/2/2009 13:11	0.008351	187.5807	1.566417	41.200	64536.3991	0.019	0.035	24.000	13.40	142.3752	0.03	30.1	11.97514	11.64407	6.21%
G5	7/2/2009 13:10	0.006959	146.6061	1.020211	0.000	0	1.360	0.001	6.630	6.69	142.5392	0.025	30.1	11.97514	9.102101	6.21%
G6	7/2/2009 13:05	0.010299	109.9674	1.132567	0.000	0	1.090	0.000	6.740	7.29	142.4408	0.037	30.1	11.97514	6.74649	6.13%
G7	7/2/2009 13:01	0.007516	168.138	1.263653	0.032	40.4368894	0.595	0.006	8.520	11.10	142.7689	0.027	30.1	11.97514	10.5512	6.28%
GM1	7/2/2009 12:58	-0.00305	1.131045	-0.00345	82.200	-0.53344385	0.017	0.042	37.800	19.20	141.4894	-0.011	29.3	12.01133	0.451362	39.91%
GM2	7/2/2009 12:52	0.008325	176.2442	1.467317	0.871	1278.03292	0.652	0.000	7.820	7.28	142.4736	0.03	29.3	12.01133	10.87276	6.17%
GM3	7/2/2009 12:52	0.006938	124.4281	0.863269	0.002	1.45029223	0.082	0.017	11.800	7.42	142.1127	0.025	29.3	12.01133	7.723738	6.21%
H1	7/2/2009 12:43	-0.00361	0.125257	-0.00045	57.400	-0.06981727	0.027	0.035	33.600	19.80	141.5878	-0.013	29.3	12.01133	0.122728	97.98%
H2	7/2/2009 12:37	0.013876	72.88519	1.01134	81.800	82727.591	0.018	0.032	36.400	19.90	142.2112	0.05	29.3	12.01133	4.477042	6.14%
H3	7/2/2009 12:34	0.007215	219.0959	1.580867	84.800	134057.545	0.040	0.028	38.400	20.00	142.9986	0.026	29.3	12.01133	14.21831	6.49%
H4	7/2/2009 12:33	0.012766	148.2903	1.893034	84.600	160150.668	0.040	0.036	38.200	20.00	142.9657	0.046	29.3	12.01133	9.148196	6.17%
H5	7/2/2009 12:29	0.005828	147.9303	0.862113	28.600	24656.4366	0.114	0.006	16.900	11.10	142.4736	0.021	29.3	12.01133	9.128872	6.17%
H6	7/2/2009 12:28	0.004163	136.086	0.56649	77.800	44072.9453	0.005	0.044	40.600	18.80	141.7846	0.015	29.3	12.01133	8.399778	6.17%
H7	7/2/2009 12:24	0.010268	124.306	1.276384	0.000	0	0.212	0.025	9.370	7.16	141.6534	0.037	29.3	12.01133	7.762881	6.24%
HM1	7/2/2009 12:09	0.009436	99.82982	0.941948	84.800	79877.205	0.007	0.034	39.600	19.70	142.9657	0.034	29.3	12.01133	6.192669	6.20%

Point	Date/Time	j	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Elev	dh	Temp	AF	W _k	W _k
			m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	NAVD88	m	deg C		m/d	%
HM2	7/2/2009 12:12	0.00333	157.5954	0.524823	82.400	43245.3912	0.019	0.026	38.600	19.70	142.8017	0.012	29.3	12.01133	9.782282	6.21%
HM3	7/2/2009 12:14	0.011378	169.594	1.929666	16.320	31492.1524	0.024	0.023	26.200	7.91	142.1127	0.041	29.3	12.01133	10.46437	6.17%
I1	7/2/2009 11:53	0.008596	0.623265	0.005358	81.000	433.98486	0.005	0.049	41.000	22.90	141.2597	0.031	29.1	12.02054	0.049671	7.97%
I2	7/2/2009 11:46	0.001387	108.7524	0.150787	48.400	7298.08987	0.052	0.014	16.400	17.70	142.9986	0.005	29.1	12.02054	6.632358	6.10%
I3	7/2/2009 11:43	0.009706	165.2484	1.603837	0.000	0	0.510	0.003	6.970		142.7033	0.035	29.1	12.02054	10.19794	6.17%
I4	7/2/2009 11:38	0.005823	158.3829	0.922322	0.000	0	1.120	0.000	6.440	7.05	142.9657	0.021	29.1	12.02054	9.968717	6.29%
I5	7/2/2009 11:30	0.000277	166.4088	0.046146	0.000	0	0.699	0.000	6.350	7.04	142.8017	0.001	29.1	12.02054	10.26818	6.17%
I6	7/2/2009 11:29	0.01026	146.4679	1.502792	0.000	0	0.778	0.003	8.400	6.94	142.4736	0.037	29.1	12.02054	8.985394	6.13%
I7	7/2/2009 11:23	0.004991	162.8442	0.81283	0.000	0	0.757	0.019	8.590	5.67	142.0471	0.018	29.1	12.02054	9.991305	6.14%
IM1	7/2/2009 15:32	0.006444	201.1028	1.29589	0.000	0	0.488	0.003	7.700	8.04	142.6049	0.023	31.9	11.89753	12.6077	6.27%
IM2	7/2/2009 15:36	0.004763	219.2148	1.044097	0.000	0	0.923	0.004	9.940	8.30	143.2938	0.017	31.9	11.89753	14.08779	6.43%
IM3	7/2/2009 15:45	0.009806	172.0175	1.686797	0.000	0	0.632	0.017	24.800	3.46	142.8345	0.035	31.9	11.89753	10.67539	6.21%
J1	7/2/2009 15:30	0.001121	24.25917	0.027187	0.000	0	0.938	0.012	17.600	15.90	142.5064	0.004	31.9	11.89753	1.479466	6.10%
J2	7/2/2009 15:25	0.004763	277.7229	1.322765	0.000	0	0.556	0.004	6.590	5.71	142.7033	0.017	31.9	11.89753	17.66891	6.36%
J3	7/2/2009 15:25	0.011487	224.9522	2.584021	0.000	0	0.049	0.000	7.660	7.20	143.4579	0.041	31.9	11.89753	14.50967	6.45%
J4	7/2/2009 15:18	0.003642	184.8711	0.67334	0.000	0	0.808	0.008	8.820	4.38	143.2282	0.013	31.9	11.89753	11.59318	6.27%
J5	7/2/2009 15:16	0.009246	158.3508	1.46405	0.000	0	0.825	0.005	6.250	6.53	142.6049	0.033	31.9	11.89753	9.770162	6.17%
J6	7/2/2009 15:20	0.001681	169.083	0.284232	0.000	0	1.000	0.000	6.390	7.51	142.7361	0.006	31.9	11.89753	10.49029	6.20%
J7	7/2/2009 15:13	0.001681	162.3396	0.272896	0.000	0	0.136	0.011	7.520	8.79	142.4736	0.006	31.9	11.89753	10.07573	6.21%
EM2 S					0.152		0.037	0.234	7.240	7.58						
G3 S					0.206		0.051	0.004	8.160	10.60						
I5 S					0.135		0.050	0.006	7.150	7.56						
J4 S					0.125		0.042	0.004	6.680	7.43						

APPENDIX F: October 2008 Sampling Data

Point	Longitude	Latitude	Date/Time	j	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Depth	dh	Temp	AF	W _k	W _k
					m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	cm	m	deg C		m/d	%
A1	-78.481071995	35.725619649	10/16/2008 12:49	0.002195	102.353	0.224708	0.012	2.67402481	0.694	0.026	20.300	5.5	29	0.8	26.5	12.14649	6.674021	6.52%
A2	-78.481058575	35.725641085	10/16/2008 12:47	0.006861	120.8507	0.82912	2.020	1674.82156	0.036	0.040	42.500	3.55	54	2.5	26.5	12.14649	7.498102	6.20%
A3	-78.481041957	35.725678564	10/16/2008 12:35	0.000823	114.9687	0.094652	1.180	111.689136	0.060	0.056	43.000	3.57	47	0.3	26.5	12.14649	7.094845	6.17%
A4	-78.481026301	35.725705966	10/16/2008 12:30	-0.00768	170.0954	-1.30701	0.020	0	0.348	0.014	10.300	6.79	43	-2.8	26.5	12.14649	10.55611	6.21%
A5	-78.481010723	35.725749979				0.070			0.216	0.022	12.800	6.71						
B1	-78.481167059	35.725654281	10/16/2008 12:59	0.010977	139.6473	1.532924	0.013	19.4681362	0.609	0.026	13.100	6.38	19	4	26.5	12.14649	8.565796	6.13%
B2	-78.481145880	35.725684642	10/16/2008 13:05	-0.00193	124.4892	-0.24051	4.900	0	0.024	0.040	49.200	4.34	13	-0.7	27.9	12.07723	7.636191	6.13%
B3	-78.481125618	35.725701852	10/16/2008 13:11	0.010764	172.0175	1.851607	1.350	2499.66972	0.050	0.025	40.300	3.5	34	3.9	27.9	12.07723	10.67539	6.21%
B4	-78.481113909	35.725734842	10/16/2008 13:13	0.006624	205.9723	1.364368	0.018	24.0128853	0.053	0.034	32.800	3.64	49	2.4	27.9	12.07723	12.86635	6.25%
B5	-78.481083163	35.725797572				0.751			0.083	0.025	24.900	6.08						
C1	-78.481287089	35.725650610	10/16/2008 13:43	0.007452	136.0924	1.014166	0.011	10.952998	0.444	0.014	10.300	6.43	13	2.7	27.9	12.07723	8.397526	6.17%
C2	-78.481264936	35.725699580	10/16/2008 13:41	0.00414	135.726	0.561909	0.021	11.9686583	0.567	0.014	14.300	4.66	10	1.5	27.9	12.07723	8.421382	6.20%
C3	-78.481243416	35.725743468	10/16/2008 13:36	0.009936	125.1674	1.24367	0.017	20.5205538	0.787	0.014	6.210	6.61	22	3.6	27.9	12.07723	7.768321	6.21%
C4	-78.481228272	35.725774068	10/16/2008 13:30	0.01104	205.3391	2.266957	4.130	9362.53213	0.047	0.022	32.700	5.73	52	4	27.9	12.07723	12.74629	6.21%
C5	-78.481212059	35.725821882				1.170			0.047	0.032	45.600	3.51						
D1	-78.481439901	35.725675651	10/16/2008 13:51	0.00966	213.5836	2.063229	23.400	48279.5559	0.024	0.016	30.100	11.2	10	3.5	27.9	12.07723	13.64046	6.39%
D2	-78.481417404	35.725726046	10/16/2008 14:00	0.002212	204.5613	0.45257	0.057	25.8870117	0.100	0.017	22.200	13.2	7	0.8	28.4	12.05331	12.68852	6.20%

Point	Longitude	Latitude	Date/Time	J	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Depth	dh	Temp	AF	W _K	W _K
					m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	cm	m	deg C		m/d	%
D3	-78.481399262	35.725759523	10/16/2008 14:05	0.006914	144.0379	0.995839	3.590	3575.0633	0.243	0.019	31.300	6.53	14	2.5	28.4	12.05331	8.885317	6.17%
D4	-78.481393267	35.725796221	10/16/2008 14:10	0.013274	140.0459	1.85902	0.123	228.659441	0.086	0.019	16.300	6.16	35	4.8	28.4	12.05331	9.002933	6.43%
D5	-78.481364597	35.725862916					2.690		0.023	0.041	56.400	7.07						
E1	-78.481551999	35.725706308	10/16/2008 14:40	0.007467	111.4974	0.832532	0.023	18.8984707	0.531	0.022	12.800	6.91	10	2.7	28.4	12.05331	6.87786	6.17%
E2	-78.481545262	35.725743469	10/16/2008 14:35	0.007467	159.1061	1.188018	0.043	51.203573	0.658	0.011	11.000	7.25	13	2.7	28.4	12.05331	9.817258	6.17%
E3	-78.481526702	35.725785865	10/16/2008 14:29	0.006361	126.4852	0.804526	0.016	12.5506005	1.120	0.008	8.480	5.86	19	2.3	28.4	12.05331	7.759457	6.13%
E4	-78.481515830	35.725827987	10/16/2008 14:24	0.00719	175.0453	1.258625	0.029	36.3742534	0.896	0.013	13.000	5.41	24	2.6	28.4	12.05331	10.7382	6.13%
E5	-78.481474239	35.725906768					0.112		0.252	0.028	41.100	4.32						
F1	-78.481700605	35.725747015	10/16/2008 14:50	0.006084	102.8994	0.626048	0.022	13.5852494	1.220	0.013	6.850	7.55	21	2.2	28.4	12.05331	6.621592	6.44%
F2	-78.481693670	35.725784398	10/16/2008 14:55	0.006361	140.1423	0.891394	0.017	14.7971349	0.859	0.010	7.010	6.48	18	2.3	28.4	12.05331	8.697573	6.21%
F3	-78.481674124	35.725828489	10/16/2008 15:00	0.00665	139.1138	0.925126	0.025	23.2206723	0.447	0.013	9.390	7.23	27	2.4	28.9	12.02982	8.533714	6.13%
F4	-78.481665319	35.725865966	10/16/2008 15:03	0.005265	126.3888	0.665398	0.015	10.1140554	0.603	0.021	9.870	5.43	25	1.9	28.9	12.02982	7.797487	6.17%
F5	-78.481617218	35.725946846					0.203		0.112	0.016	13.600	6.82						
G1	-78.481828787	35.725747751	10/16/2008 15:32	0.008313	119.9796	0.997352	0.034	33.7105017	0.467	0.019	8.650	6.41	25	3	28.9	12.02982	7.444898	6.21%
G2	-78.481818684	35.725789827	10/16/2008 15:27	0.005542	102.2501	0.566648	0.038	21.7026258	0.684	0.022	7.430	5.88	22	2	28.9	12.02982	6.343709	6.20%
G3	-78.481791777	35.725854085	10/16/2008 15:18	0.007481	268.5946	2.009466	0.023	46.2177243	0.734	0.025	10.900	6.22	34	2.7	28.9	12.02982	17.13063	6.38%
G4	-78.481777789	35.725889925	10/16/2008 15:15	0.013023	176.3503	2.296644	0.027	61.0907326	0.429	0.018	10.200	6.51	28	4.7	28.9	12.02982	10.8828	6.17%
G5	-78.481740668	35.725990341					0.025		0.081	0.017	13.500	7.47						
H1	-78.481992553	35.725780893	10/17/2008 10:25	0.008158	184.2411	1.503088	12.400	18638.2953	0.521	0.017	16.600	8.37	34	3.1	17.7	12.66609	11.50227	6.24%
H2	-78.481984759	35.725831316	10/17/2008 10:31	0.006316	200.1418	1.264111	0.069	86.7180145	0.048	0.017	14.600	7.26	26	2.4	17.7	12.66609	12.56612	6.28%
H3	-78.481970422	35.725864600	10/17/2008 10:36	0.008685	126.0738	1.094901	0.125	136.862631	0.268	0.012	10.700	6.37	20	3.3	17.7	12.66609	7.915648	6.28%
H4	-78.481964011	35.725901578	10/17/2008 10:37	0.006316	204.5067	1.29168	0.018	23.2502389	0.341	0.015	13.500	6.65	22	2.4	17.7	12.66609	13.13265	6.42%
H5	-78.481950292	35.725988147					0.020		0.190	0.018	11.300	6.44						
I1	-78.482092177	35.725791518	10/17/2008 11:05	0.006023	163.9788	0.987704	21.800	21531.9528	0.071	0.022	31.600	22	40	2.3	16.8	12.72821	10.29167	6.28%
I2	-78.482093643	35.725839454	10/17/2008 11:00	0.006547	168.1894	1.101159	60.100	66179.6537	0.707	0.013	16.500	20.7	28	2.5	16.8	12.72821	10.55992	6.28%
I3	-78.482080799	35.725889848	10/17/2008 10:55	0.008685	128.1823	1.113213	0.015	16.252905	1.160	0.014	7.090	5.74	23	3.3	17.7	12.66609	7.909723	6.17%
I4	-78.482069953	35.725920338	10/17/2008 10:50	0.006053	205.1624	1.241829	0.013	16.0195917	0.871	0.013	10.100	6.97	25	2.3	17.7	12.66609	12.75508	6.22%
I5	-78.482068698	35.726010210					0.020		0.129	0.015	10.900	6.67						
J1	-78.482221325	35.725815836	10/17/2008 11:20	0.006023	214.0528	1.289318	0.127	163.743427	0.951	0.014	11.900	9.99	40	2.3	16.8	12.72821	13.43954	6.28%
J2	-78.482221020	35.725857715	10/17/2008 11:25	0.006547	144.999	0.949328	0.083	79.1739502	0.864	0.012	8.470	6.29	28	2.5	16.8	12.72821	9.050748	6.24%
J3	-78.482220783	35.725902906	10/17/2008 11:30	0.006023	163.667	0.985826	0.012	12.2242462	0.992	0.012	8.210	8.37	23	2.3	16.8	12.72821	10.03963	6.13%
J4	-78.482212242	35.725935129	10/17/2008 11:35	0.006547	144.7868	0.947939	0.012	11.5648564	1.120	0.012	8.310	5.45	25	2.5	16.8	12.72821	9.077348	6.27%
J5	-78.482208734	35.726030561					0.010		0.438	0.013	11.000	7.02						

APPENDIX G: $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ Isotope Data

Sample Name	N15	%N	O18	%O2
A5 9-2008	32.566	8.346		
B1 9-2008	8.623	13.923	12.351	0.480
B2 9-2008	20.626	5.824	11.511	0.420
B3 9-2008	25.555	6.958	14.942	0.395
E3 9-2008	31.294	8.270		
F2 9-2008	51.815	6.832	29.966	0.443
H3 9-2008	14.766	6.972	5.912	0.515
H4 9-2008	25.320	8.556		
H5 9-2008	24.973	8.392		
B2 10-16-08	13.003	6.385	11.534	0.304
C4 10-16-08	22.995	5.401	11.161	0.400
C5 10-16-08	17.479	4.543	13.292	0.352
D1 10-16-08	24.085	7.412	12.520	0.436
D5 10-16-08	7.075	5.284	11.034	0.342
H1 10-17-08	21.651	5.210	12.062	0.348
I1 10-17-08	21.883	5.454	15.561	0.539
I2 10-17-08	17.416	7.034	7.116	0.462
G1 1-30	16.592	7.035	9.026	22.33
G2 1-30	19.360	6.597	4.433	29.39
G3 1-30	16.772	6.230	3.228	26.29
H2 1-30	18.150	7.073	3.420	26.35
H4 1-30	18.278	7.020	4.056	27.48
H5 1-30	18.516	7.171	5.464	26.79
I1 1-30	20.317	7.593	5.590	25.40
I2 1-30	17.563	7.042	2.630	25.16
I3 1-30	18.729	5.796	14.060	25.61
EM2 4-28	29.517	5.605	13.528	24.86
F2 4-28	29.173	6.115	10.982	27.12
F3 4-28	18.958	7.023	6.068	28.92
F4 4-28	20.690	6.822	8.544	27.01
FM1 4-28	17.864	5.618	5.097	30.35
G2 4-28	18.491	8.472	4.715	36.54
G3 4-28	17.364	7.290	5.265	29.04
G4 4-28	21.675	7.527	8.622	27.90
GM1 4-28	16.755	7.732	3.917	27.32
GM2 4-28	20.451	7.267	6.685	27.61
H1 4-28	18.769	6.843	4.543	26.33
H2 4-28	17.558	7.263	3.738	27.98
H3 4-28	15.000	8.175	3.775	36.40
HM1 4-27	16.877	6.924	3.709	27.72
HM2 4-27	16.318	7.759	4.611	30.45
HM3 4-27	18.677	7.673	5.500	30.58
I1 4-27	17.634	7.135	4.453	29.05
I2 4-27	17.266	7.549	4.461	29.99
I3 4-27	19.039	7.045	4.679	29.55
IM1 4-27	41.121	5.331	17.299	25.91

Sample Name	N15	%N	O18	%O2
EM1 7-2	16.240	7.700	5.068	22.93
F2 7-2	17.940	6.866	6.355	25.43
F3 7-2	17.369	7.597	6.069	25.52
F4 7-2	15.935	7.596	5.080	25.57
FM1 7-2	21.574	7.841	8.337	24.75
G1 7-2	40.483	5.882	18.012	22.40
G2 7-2	15.868	7.735	3.411	23.19
G3 7-2	15.614	7.801	3.988	21.74
G4 7-2	21.965	7.288	7.906	22.18
GM1 7-2	15.331	7.552	3.637	23.32
H1 7-2	18.417	7.775	6.578	20.61
H2 7-2	14.653	7.949	3.999	22.31
H3 7-2	15.196	7.944	3.412	22.78
H4 7-2	18.952	6.408	3.848	23.46
H5 7-2	21.739	7.731	9.658	12.67
H6 7-2	17.139	8.126	6.010	22.13
HM2 7-2	15.711	8.121	4.567	24.93
HM3 7-2	26.628	7.972	11.963	25.08
I1 7-2	16.989	7.958	5.240	24.78
J3 7-2	22.141	7.453	8.872	22.25

APPENDIX H: DOC, $\delta^{13}\text{C}$, and Sediment Data

ID	DOC	DOC $\delta^{13}\text{C}$	WT% N*	sed $\delta^{15}\text{N}$	WT% C	sed $\delta^{13}\text{C}$	CN %
	mg/L	‰	%	‰	%	‰	%
G1 9/17	9.54	-26.64	0.018(BDL)	4.41	0.43	-26.77	23.49
G3 9/17	5.91	-28.96	0.008(BDL)	4.65	0.12	-26.99	15.66
G5 9/17	4.34	-27.12	0.068	4.88	4.29	-22.06	63.50
G7 9/17	4.10	-26.15	0.004(BDL)	6.08	0.22	-24.07	54.06
H1 9/17	3.66	-31.77	0.126	4.32	2.23	-26.54	17.75
H3 9/17	1.90	-30.09	0.005(BDL)	0.39	0.22	-24.69	44.77
H5 9/17	2.07	-28.55	0.004(BDL)	3.11	0.07	-25.03	19.66
H7 9/17	4.41	-26.55	0.006(BDL)	5.59	0.24	-26.13	42.26
I1 9/17	43.46	-27.21	0.004(BDL)	4.16	0.08	-25.26	18.76
I3 9/17	4.20	-26.05	0.002(BDL)	8.26	0.04	-25.46	20.16
I5 9/17	4.92	-27.25	0.005(BDL)	5.24	0.11	-25.56	23.56
I7 9/17	4.40	-25.69	0.004(BDL)	1.52	0.11	-25.28	27.80
surf. 9/17	4.94	-26.24	-	-	-	-	-

*BDL: below detection limit of 0.04%

APPENDIX H: Differential Pressure Transducer Sampling Data

Point	Date/Time	j	j (trans)	j error	K	v	NO3	NO3 flux	NH4	PO4	Si	Cl	Elev	dh	Temp	AF	W _K	W _K
					m/d	m/d	mg/L	mg/(m ² *d)	mg/L	mg/L	mg/L	mg/L	NAVD88	m	deg C		m/d	%
T1	7/17/2009 11:57	0.004148	0.105770	0.101622	160.9221	0.667543	59.5	40324.5692	0.054	0.040	30.3	19.5	143.30	0.015	28.4	12.05331	15.43012	9.59%
T2	7/17/2009 12:15	0.003891	-	-	150.3924	0.585196	74.6	43781.7812	0.053	0.048	38.1	20.6	143.30	0.014	29.7	11.9931	9.225582	6.13%
T3	7/17/2009 12:32	0.002779	0.011200	0.008421	172.3518	0.47903	47	22152.2439	0.051	0.051	33	16.6	143.04	0.01	29.7	11.9931	10.63263	6.17%
T4	7/17/2009 12:00	0.003057	0.112751	0.109694	167.958	0.5135	74.8	39284.6041	0.057	0.059	38.1	21.4	143.37	0.011	29.7	11.9931	10.54506	6.28%
T5	7/17/2009 12:17	0.001668	-	-	223.9847	0.373523	75.7	27821.2165	0.049	0.058	36.8	20.3	143.17	0.006	29.7	11.9931	13.81779	6.17%
T6	7/17/2009 12:33	0.002501	-	-	185.4947	0.464003	72	33699.5276	0.050	0.064	36.8	21	142.68	0.009	29.7	11.9931	11.38024	6.14%
T7	7/17/2009 12:02	0.001112	0.113117	0.112005	51.71004	0.057489	75	4278.04376	0.052	0.059	36.8	21.1	143.40	0.004	29.7	11.9931	3.15358	6.10%
T8	7/17/2009 12:20	-0.00445	0.102030	0.106477	90.30293	-0.40158	75.1	-79.5933129	0.048	0.058	36.2	21.2	143.10	-0.016	29.7	11.9931	5.5397	6.13%
T9	7/17/2009 12:38	0.005003	-	-	46.67339	0.233501	76.1	17669.0212	0.049	0.063	37.8	20.7	142.68	0.018	29.7	11.9931	2.863213	6.13%
T5 S							0.197		0.088	0.025	6.44	9.36						
T1	7/23/2009 13:49	0.00139	0.104590	0.103200	132.2482	0.183784	65.3	12256.282	0.103	0.046	23.3	19.4	143.46	0.005	29.7	11.9931	9.852643	7.45%
T2	7/23/2009 14:04	0.000837	-	-	175.6046	0.146966	80.6	11648.4952	0.056	0.063	35.9	21.9	143.30	0.003	30.7	11.94869	10.8324	6.17%
T3	7/23/2009 14:20	0.000279	0.009400	0.009121	160.2214	0.044697	33.7	1552.44508	0.081	0.045	19.7	14.9	143.10	0.001	30.7	11.94869	9.887707	6.17%
T4	7/23/2009 13:46	0.004447	0.107378	0.102931	181.6666	0.807871	79.4	65140.9681	0.117	0.069	35.5	22	143.33	0.016	29.7	11.9931	11.14438	6.13%
T5	7/23/2009 14:04	0.004464	-	-	189.3646	0.845234	78	66644.4246	0.070	0.063	35.9	21.5	143.36	0.016	30.7	11.94869	11.61652	6.13%
T6	7/23/2009 14:22	0.003627	-	-	208.4216	0.755865	73.5	57474.7765	0.077	0.069	36.6	22.4	142.68	0.013	30.7	11.94869	12.93972	6.21%
T7	7/23/2009 13:55	0.004447	0.108912	0.104465	119.6807	0.53222	81.3	43835.6485	0.100	0.066	38.3	22.6	143.46	0.016	29.7	11.9931	7.298829	6.10%
T8	7/23/2009 14:04	0.002232	0.098464	0.096233	130.1944	0.290563	80.1	23238.0107	0.062	0.065	36.3	22.3	142.97	0.008	30.7	11.94869	8.052975	6.19%
T9	7/23/2009 14:27	0.005858	-	-	50.54329	0.296102	81.2	24092.9525	0.055	0.072	38	22.4	143.00	0.021	30.7	11.94869	3.082425	6.10%
T5 S							0.188		0.105	0.037	8.12	8.24						

APPENDIX I: CR-10X Program

};CR10X	MODE 1	6:0.0	2:0	3:28		1:1220	2:14
;multisensorcalc.DLD	SCAN		3:5		41:P35		
;Created by Short Cut (2.5)	RATE	10:P1		30:P30	1:6	53:P70	67:P70
;\$	10.0000	1:1	19:P36	1:0.1802	2:5	1:1	1:1
::Batt_Volt:Prog_Sig :SEVolt1		2:25	1:9	2:0	3:30	2:1	2:30
:_____ :CSI_R	1:P10	3:6	2:5	3:5			
::CSI_1	1:1	4:13	3:6		42:P30	54:P70	68:P70
:_____ :Diff_Head:SEVolt2		5:1.0		31:P36	1:0.1783	1:1	1:1
:SEVolt3	2:P92	6:0.0	20:P30	1:12	2:0	2:3	2:15
::SEVolt4 :SEVolt5 :SEVolt6 :SEVolt7	1:0		1:4511	2:5	3:5		
:SEVolt8	2:1440	11:P1	2:0	3:6		55:P70	69:P70
::SEVolt9	3:30	1:1	3:5		43:P36	1:1	1:1
:_____ :_____ :_____ :		2:25		32:P30	1:15	2:32	2:29
_____	3:P19	3:7	21:P35	1:4484	2:5		
::_____ :_____ :DH6 :DH5	1:2	4:14	1:6	2:0	3:6	56:P70	70:P70
:_____		5:1.0	2:5	3:5		1:1	1:1
::DH2 :DH3 :DH4 :DH8	4:P95	6:0.0	3:26		44:P30	2:9	2:16
:DH7				33:P35	1:4481		
::DH9 :DH1	5:P1	12:P1	22:P30	1:6	2:0	57:P70	71:P70
;\$	1:1	1:1	1:0.18	2:5	3:5	1:1	1:1
	2:25	2:25	2:0	3:24		2:26	2:31
;%	3:1	3:8	3:5		45:P35		
;Final Storage Label File for:	4:3	4:15		34:P30	1:6	58:P70	MODE 2
multisensorcalc.SCW	5:1.0	5:1.0	23:P36	1:0.1788	2:5	1:1	SCAN RATE
;Date: 6/5/2009	6:0.0	6:0.0	1:10	2:0	3:29	2:10	10.0000
;Time: 10:29:47			2:5	3:5			1:P96
;	6:P1	13:P1	3:6		46:P30	59:P70	1:71
;101 Output_Table 15.00 Min	1:1	1:1		35:P36	1:0.1788	1:1	
;1 101 L	2:25	2:25	24:P30	1:13	2:0	2:27	
;2 Year_RTM L	3:2	3:9	1:4461	2:5	3:5		MODE 3
;3 Day_RTM L	4:9	4:16	2:0	3:6		60:P70	
;4 Hour_Minute_RTM L	5:1.0	5:1.0	3:5		47:P36	1:1	MODE 10
;5 Batt_Volt L	6:0.0	6:0.0		36:P30	1:16	2:11	1:32
;6 SEVolt1 L			25:P35	1:446	2:5		2:102
;7 DH1 L	7:P1	14:P30	1:6	2:0	3:6	61:P70	3:0
;8 SEVolt2 L	1:1	1:0.1791	2:5	3:5		1:1	
;9 DH2 L	2:25	2:0	3:27		48:P30	2:28	MODE 12
;10 SEVolt3 L	3:3	3:5		37:P35	1:4444		1:0000
;11 DH3 L	4:10		26:P30	1:6	2:0	62:P70	2:0000
;12 SEVolt4 L	5:1.0	15:P36	1:0.1792	2:5	3:5	1:1	3:0000
;13 DH4 L	6:0.0	1:3	2:0	3:23		2:12	
;14 SEVolt5 L		2:5	3:5		49:P35		
;15 DH5 L	8:P1	3:6		38:P30	1:6	63:P70	
;16 SEVolt6 L	1:1		27:P36	1:0.1802	2:5	1:1	
;17 DH6 L	2:25	16:P30	1:11	2:0	3:31	2:24	
;18 SEVolt7 L	3:4	1:0.4467	2:5	3:5			
;19 DH7 L	4:11	2:0	3:6		50:P92	64:P70	
;20 SEVolt8 L	5:1.0	3:5		39:P36	1:0	1:1	
;21 DH8 L	6:0.0		28:P30	1:14	2:15	2:13	
;22 SEVolt9 L		17:P35	1:4401	2:5	3:10		
;23 DH9 L	9:P1	1:6	2:0	3:6		65:P70	
;	1:1	2:5	3:5		51:P80	1:1	
;Estimated final storage locations used	2:25	3:32		40:P30	1:1	2:23	
per day: 2208	3:5		29:P35	1:4481	2:101		
;%	4:12	18:P30	1:6	2:0		66:P70	
	5:1.0	1:0.1798	2:5	3:5	52:P77	1:1	