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Using high frequency data collection to study nitrate on clear creek during high flow events

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USING HIGH FREQUENCY DATA COLLECTION TO STUDY NITRATE ON CLEAR CREEK DURING HIGH FLOW EVENTS

by

Maclaine Kenneth Putney

A thesis submitted in partial fulfillment
of the requirements for the Master of
Science degree in Civil and Environmental Engineering
in the Graduate College of
The University of Iowa

May 2010

Thesis Supervisor: Professor Jerald L. Schnoor

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CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

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has been approved by the Examining Committee for the
thesis requirement for the Master of Science degree in
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TABLE OF CONTENTS

LIST OF TABLES ... iii

LIST OF FIGURES ... iv

CHAPTER I: INTRODUCTION ... 1

- Sources and Impacts of Nitrate ... 2
- Nitrate Measuring and Monitoring ... 7
- Hypothesis and Objectives ... 11

CHAPTER II: MATERIALS AND METHODS ... 13

- Deployment Sites ... 13
- The Nitratax Sensor ... 17
- Data Collection and Storage ... 21
- Powering the Sensors ... 22

CHAPTER III: RESULTS AND DISCUSSION ... 24

- Data Analysis ... 26
- Comparison of High Frequency Samples to Hourly/Daily Samples ... 33
- Interpolation of Data Gaps ... 39
- Percent Error ... 54

CHAPTER IV: CONCLUSIONS ... 56

REFERENCES ... 59

APPENDIX ... 61

LIST OF TABLES

Table

3.1. Calculated total seasonal flux in metric tons for all three deployment sites for 104 day time frame 49

3.2. Calculated total seasonal flux in metric tons for all three deployment sites for 101 day time frame 51

3.3. Percent error calculated using high frequency samples as the theoretical total flux and hourly/daily samples as the measured values 55

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LIST OF FIGURES

Figure

1.1. A typical liquid-N toolbar used in Iowa to side dress corn during early summer 5

2.1. Map showing the location of Clear Creek watershed in the State of Iowa 14

2.2. Orientation of the two pipes at the SAC site 15

2.3. Picture of what the assembled sensor stations look like at Oxford and Coralville 17

2.4. Picture of the Nitratax sensor and the sc-100 controller 19

2.5. Close-up of the Nitratax sensor showing the measuring path and the wiper blade 20

2.6. Picture of the "white box” contents 22

3.1. Plot of nitrate-N concentrations at the SAC site for the entire 2009 deployment season 28

3.2. Hydrograph for the entire 2009 deployment season at the SAC 28

3.3. Plot of the flux for each 15 minute collection interval during the entire 2009 deployment season at the SAC 29

3.4. Plot of nitrate-N concentrations at the Oxford site for the entire 2009 deployment season 29

3.5. Hydrograph for the entire 2009 deployment season at the Oxford site...... 30

3.6. Plot of the flux for each 15 minute collection interval during the entire 2009 deployment season at the Oxford site........ 30

3.7. Plot of nitrate-N concentrations at the Coralville site for the entire 2009 deployment season 31

3.8. Hydrograph for the entire 2009 deployment season at the Coralville site……………………………………………………………...

3.9. Plot of the flux for each 15 minute collection interval during the entire 2009 deployment season at the Coralville site 32

3.10. Plot of hourly nitrate-N flux at the SAC 34

3.11. Plot of hourly nitrate-N flux at the Oxford site 35

3.12. Plot of hourly nitrate-N flux at the Coralville site..................................... 35

3.13. Plot of daily nitrate-N flux at the SAC.. 36

3.14. Plot of daily nitrate-N flux at the Oxford site 37

3.15. Plot of daily nitrate-N flux at the Coralville site 37

3.16. Plot of the base 10 logarithm of nitrate-N concentration vs. base 10 logarithms of flow in cfs for the SAC 41

3.17. Plot of the base 10 logarithm of nitrate-N concentration vs. base 10 logarithm of flow in cfs for the Oxford site 42

3.18. Plot of the base 10 logarithm of nitrate-N concentration vs. base 10 logarithm of flow in cfs for the Coralville site 43

3.19. Plot of the flux calculated using high frequency samples and all holes interpolated with data using log (C) vs. log (Q) at the SAC 43

3.20. Plot of the flux calculated using high frequency samples and all holes interpolated with data using log (C) vs. log (Q) at the Oxford site............44

3.21. Plot of the flux calculated using high frequency samples and all holes interpolated with data using log (C) vs. log (Q) at the SAC 44

3.22. Plot of hourly flux with all holes interpolated with data using log (C) vs. log (Q) at the SAC 45

3.23. Plot of hourly flux with all holes interpolated with data using log (C) vs. log (Q) at the Oxford site... 45

3.24. Plot of hourly flux with all holes interpolated with data using log (C) vs. log (Q) at the Coralville site 46

3.25. Plot of daily flux with all holes interpolated with data using log (C) vs. log (Q) at the SAC 46

3.26. Plot of daily flux with all holes interpolated with data using log (C) vs. log (Q) at the Oxford site 47

3.27. Plot of daily flux with all holes interpolated with data using log (C) vs. log (Q) at the Coralville site 47

3.28. Plot of nitrate-N load calculated using high frequency data vs. drainage area for 104 day time period 50

3.29. Plot of nitrate-N load calculated using high frequency data vs. drainage area for 101 day time period 52

CHAPTER 1

INTRODUCTION

Agriculture is a huge part of Iowa's heritage and economy; the grain grown by Iowa farmers provides food not only for Americans but also people all over the world. Iowa's prehistoric landscape of native prairies has undergone a large transformation over the last 150 years (McCorvie and Lant, 1993). Mechanized agriculture has transformed the prairies into open fertile land which has provided the backbone for this state's rich agriculture success. Over this 150 year time span watersheds in the Midwest have had their subsurface hydrology altered due to the installation and use of subsurface tile lines (McCorvie and Lant, 1993). These tile lines allow drainage of the soil which helps establish better growing conditions for farming. The downside to row crop production of corn and the use of subsurface drain tile is the possible water quality impacts that arise due to nutrient inputs required for high yield corn production. The row crop production of grain requires a number of macro/micronutrients for proper growth. These nutrients are available naturally in some soils, but to insure healthy high yielding growth farmers must input additional forms of these key nutrients to their fields.

This project will focus on the nutrient nitrogen which is the most important limiting macronutrient essential to high yielding corn production and is also a major contributor to negative water quality issues. It has been known since the mid 1980's that high levels of nitrate being exported from the Midwest is responsible for the seasonal hypoxic zone that forms in the Gulf of Mexico every summer (Schilling and Zhang, 2004). Nitrate is also a key contributor to increased levels of primary production in fresh water lakes, a process called eutrophication. What is not well understood about nitrate is where exactly it comes from. Most nitrate studies conducted in Iowa focus on the nitrate concentrations in large rivers such as the Iowa, Des Moines, or the Raccoon. However not much focus has been placed in the tributaries that feed these rivers. Also previous nitrate concentration studies such as the one conducted by Schilling and Zhang (2004) and Tomer *et al.* (2004) only look at nitrate on a weekly or monthly time scale. This lack of frequency in water sample collection creates time gaps in the dataset that makes understanding the nitrate dynamic in Iowa streams difficult. Also by only sampling once a week there are large errors in estimating the nitrate load directly in Iowa streams during large flow events.

Sources and Impacts of Nitrate

Nitrogen makes up 78 percent of the earth's atmosphere in the form of inert nitrogen gas which is not directly available for plant biosynthesis. In watersheds dominated by mono-crop agriculture some plants such as soybeans (a legume) can convert this atmospheric nitrogen into usable nitrogen forms due to a symbiotic relationship they have with nitrogen fixing bacteria in their roots. The nitrogen fixing bacteria takes the inert atmospheric nitrogen gas and combines it with hydrogen ions to form the ammonium ion (Brennan, 2005). The ammonium ion by itself is biologically available for uptake by plants such as corn; however this ion will be converted to other forms of nitrogen relatively quickly in the soil by another form of soil bacteria known as the nitrifying bacteria. There are two main species of nitrifying bacteria *Nitrosomonas* and *Nitorbacter*. *Nitrosomonas* is the bacteria species that is responsible for the conversion of ammonium into nitrite. Nitrite by itself is not biologically available for plant uptake but *Nitrobacter* converts nitrite into the biologically available ion nitrate (Brennan and Withgott, 2005). The nitrate that is formed by the legume plants relationship with nitrogen fixing bacteria and the other soil microbes will be used by the plant during the growing season; however any nitrate that is left over is quite mobile and available to be leached out before the next growing season. The corn plant on the other hand cannot convert atmospheric nitrogen to usable nitrogen (like legumes) so they require the input of synthetic nitrogen fertilizers. Nitrogen can be applied to agricultural fields in many forms including anhydrous ammonia, liquid-N, and organic fertilizers such as animal manure or compost. The anhydrous ammonia and animal manure must undergo nitrification in order for the ammonia to be converted to the usable nitrogen form nitrate. Liquid-N is a combination of urea and ammonium nitrate dissolved in water, this solution is typically called UAN in the fertilizer industry (Allen, 2002). In order for the urea in UAN to become biologically available it must be hydrolyzed into ammonium carbonate by an enzyme called urease (Efficient Fertilizer Use Manual). The ammonium carbonate brakes down quickly in soil to form ammonium which must undergo nitrification (Efficient Fertilizer Use Manual). The ammonium nitrate part of UAN brakes down into ammonium and nitrate, the nitrate is directly available for plant up take but again the ammonium must undergo nitrification (Efficient Fertilizer Use Manual).

The problem with the nitrate ion as a pollutant lies in its charge. Nitrate has a negative charge which means it will not bind to soil particles; which are also predominantly negative in charge. Since nitrate cannot bind to soil it can become mobilized during high rainfall events and washed out of the soil column through field tile if it is not taken up by the corn plant immediately. It is a reasonable estimate that 40-60% of the nitrogen applied to fields for corn production is actually taken up by the plant and used for cell production. The remaining nitrogen that is not used in plant growth will either be stored in the field for later use or is washed out into the surrounding surface water (Matson et al, 1997). The nitrate that gets washed out of Iowa farm soil and into surrounding surface water is then carried from the Midwest to the Gulf of Mexico by means of the Mississippi River. According to Spalding and Exner (1993) the nitrate concentrations in Midwest streams has increased over the last 50 years. In fact the average export of nitrate from Iowa surface waters is estimated in the range of 204,000 to 222,000 metric tons annually, this is 25% of the nitrate delivered to the Gulf of Mexico by the Mississippi River (Schilling and Libra, 2000).

Once the nitrate reaches the Gulf of Mexico it triggers a certain set of circumstances that eventually leads to the Gulf's dissolved oxygen content becoming extremely low; a condition that is known as hypoxia. The hypoxic zone in the Gulf begins in the late spring when the nitrate concentration in the Mississippi River begins to rise because nitrate is being leached out of farm fields due to snow melt and spring ammonia application. The nitrate concentration in Iowa streams and the Mississippi River continues to be high through the early summer because this is the time that Midwest farmers are applying liquid-N to their corn fields through an application process known as side dressing. Side dressing is accomplished with the use of a tool bar that injects liquid-N directly next to the corn plants roots, side dressing rates in Iowa are typically in the range of 50-100 pounds of nitrogen per acre (but can vary significantly due to individual farmers' nitrogen plan). A typical side dressing tool bar is shown in Figure 1.1 If side dressing is followed by large rainfall events the possibility of nitrate loading to streams increases since there may not have been enough time for the corn plant to take up the nitrate before it is leached out.

Figure 1.1. A typical liquid-N toolbar used in Iowa to side dress corn in early summer. http://www.yetterco.com

In the Gulf of Mexico, just like in a farm field, the amount of nitrogen present controls the amount of plant growth. With the increased amount of nitrate flowing into the Gulf from the Mississippi River the growth of aquatic photosynthetic algae is stimulated which creates large algal blooms in the warm/upper part of the Gulf's water column. With an increase in algae comes an increase of detritus as the old photosynthetic organisms die and get replaced by new organisms. This detritus sinks down through the upper water column then through what is known as the pycnocline, a layer in the ocean that separates two water layers based on density (Wood, 1975). In this lower water column, of colder denser water, the detritus provides food to decomposer bacteria which consume oxygen as they break down the dead algae cells (Brennan and Withgott, 2005). It is the decomposer bacteria which create the “dead zone” in the Gulf by using up the available dissolved oxygen leaving a region that cannot support higher aquatic life such as fish. Fish need a dissolved oxygen (DO) content of 6-7 mg/l to support normal gill function (Brennan and Withgott, 2005). According to Rabalais *et. al* (2002) the Gulf of Mexico has surface water DO levels greater than 8 mg/l at summer time temperatures and salinities, however, lower water levels below the pycnocline can dip down below 2 mg/l DO during these same summer months. The “dead zone” will last through the entire summer until seasonal storms in the Gulf can break up the pycnocline by mixing the upper less dense oxygenated layer with the lower denser hypoxic zone (Brennan and Withgott, 2005).

The “dead zone” in the Gulf of Mexico has been studied in great detail since 1985 when Nancy Rabalais started to map the area of low DO levels. Her research began when the fishing industry wanted to know why they had to travel further offshore to find significant numbers of fish to catch (Brennan and Withgott, 2005). From the 1980’s to 2000 the hypoxic zone in the Gulf of Mexico has doubled in size and the largest total area to date ever recorded occurred in the summer of 2002 and 2007 when the hypoxic zone reached 22,000 square kilometers (Brennan and Withgott, 2005). The Gulf of Mexico hypoxic zone is currently the second largest in the world behind the hypoxic zone in the

Baltic basin (with an approximate area of 70,000 square kilometers) (Rabalais *et al.*, 2002). With the growth of the hypoxic zone in the Gulf of Mexico not showing any signs of shrinking scientists need to figure out with better accuracy exactly where the nitrate is coming from so mitigation can be implemented in watersheds with the most nitrate loading. This can only be accomplished with better nitrate monitoring within watersheds in the Upper Mississippi drainage basin.

Nitrate Measuring and Monitoring

In the past, water quality data was collected using a grab sample or some kind of automated sampler. The grab sample method involves a person physically retrieving the water sample and taking it back to the lab and analyzing it for nitrate concentrations. The automated sampler on the other hand is a machine that can be set to collect a water sample on a given time interval or it can be linked to a stream gauge and programmed to take a sample whenever the stage of a stream changes. All samples collected by an automated sampler still must be analyzed in a lab to generate a value for the nitrate concentration. Both of these methods are time consuming because they require a person to retrieve a sample from the field and a person to analyze it in the lab. These methods can become expensive for two reasons 1) the cost of the person retrieving and analyzing the sample can add up with large sample size 2) the cost of reagents can become an expense with large sample size, also the data analysis machines used in the lab can be expensive as well.

These two methods of water sampling have been used with large success on two water quality monitoring projects in Iowa. The first project was conducted by the Des

Moines River Water Quality Network operated by Iowa State University (Zhang and Schilling, 2005). This project is one of the longest running water quality monitoring programs alive in the Midwest (Zhang and Schilling, 2005). From 1972 to 2000 the Network collected a total of 981 grab samples from the Raccoon River on a weekly or bimonthly schedule (Zhang and Schilling, 2005). All collected samples were analyzed at the Analytical Services Laboratory at Iowa State University. This large collection of nitrate concentration data from a Midwest stream is rare but does provide a great dataset for anyone looking to study nitrate loading or nitrate flux relationships on the Raccoon River. Schilling and Zhang (2004) used this data to show that 81% of the total nitrogen exported from the Raccoon River is in the form of nitrate. Also the Raccoon River is responsible for more than 10% of Iowa's nitrate contribution to the Gulf of Mexico (Schilling and Zhang, 2004). These results are not surprising because the Raccoon River watershed has a total area of 16,861 square kilometers and agriculture accounts for 76.2% of the total land use within the watershed.

The second nitrate monitoring project conducted in Iowa occurred in a small watershed (51.34 square kilometers) for a stream in Central Iowa named Walnut Creek. Walnut Creek is a small tributary that is within the Upper Mississippi River Drainage Basin. The project used grab samples that were collected on a weekly interval and an automated sampler that collected a water sample every three days or when the stage changed (Tomer *et al.*, 2003). Once the samples were collected they were analyzed in a laboratory using an auto analyzer method described by Hatfield et al. (1999). The Walnut Creek project had a time span of approximately 8.5 years and concluded that over this time period the watershed exported 168 kilograms per hectare of nitrate-N (Tomer *et al.*, 2003). The nitrate concentration data collected in both projects is valuable and was used to quantify the amount of nitrate-N leaving watersheds in Iowa. However, there are two large disadvantages with the sampling techniques used by the two projects above.

The first disadvantage in collecting nitrate concentration data using the grab sample method and automated sampling is the time it takes to get a result. The literature made no mention to the amount of time it took to get nitrate concentration result after the samples were taken. Most likely there was a span of at least one day before the results were recorded. This does not provide any kind of “real time” monitoring. The second major disadvantage to these two water quality sampling strategies is the infrequency of samples. A weekly grab sampling schedule, like the one used on Walnut Creek, will generate only 52 samples a year and these samples can only be compared to average daily flow to generate load estimates. Also one grab sample a day does not give much insight to the nitrate dynamic during high flow events. The Isco automated sampler by Teledyne Technologies has the capacity to take samples at a frequency of one an hour for 24 hours. Hourly samples are better than weekly samples because they can show better trends related to nitrate transport and time of day but still hourly water sample data is not frequent enough to capture the nitrate dynamic during high flow events in flashy streams where the peak discharge may only occur in a brief five or ten minute window. Also using the automated sampler to gather 24 samples a day may become too overwhelming for the researcher since the collection bottles would need to be replaced every day and the collected samples would need to be analyzed every day.

Up until now, the two nitrate sampling methods mentioned above provided the most common way to sample Iowa streams for nitrate concentration. However, as technology becomes more advanced the ability to monitor nitrate concentrations in streams can move from a weekly schedule to a more daily real time schedule. The Nitratax nitrate sensor by Hach Environmental can provide this real time nitrate concentration monitoring. The Nitratax is a remote sensor that can be deployed virtually anywhere in a stream and programmed to collect nitrate concentration values on a range of time intervals. This sensor eliminates the problem of infrequent data samples due to its ability to collect nitrate concentration values with high frequency. High frequency means samples collected more often than once an hour. This sensor also eliminates multiple trips to the field because once it is calibrated it can run for months without losing the calibration. This sensor does not totally replace the need for grab samples since any remote sensing of the environment should be double checked with ground truth data such as laboratory analyzed grab samples. The Nitratax also provides a new tool that can be used to study nitrate behavior during high flow events because it can be deployed in streams when conditions are not ideal for grab sample collection or when flow can be life threatening. This sensor can collect data around the clock (with some limitations to be discussed latter) even during storm events. The Nitratax sensor coupled with occasional grab samples may provide a powerful new research tool that will help study the nitrate dynamic in Iowa streams. This sensor may also provide data that can be used to calculate better load estimations especially during high flow events because high frequency data can capture concentrations over an entire day.

Hypothesis and Objectives

The goal of this study was to test the feasibility of using high frequency nitrate concentration data collected by the Nitratax sensor to make better estimations of mass loading in Clear Creek with particular interest in high flow events. The data collected in this study will also be analyzed for trends that will help understand the mechanisms and overall dynamics of nitrate delivery and transport in Clear Creek. To test this hypothesis the Nitratax (Hach Environmental) nitrate sensor, the DTS-12 turbidity meter (FTS), and the Hydrolab DS-5X (Hach Environmental) were deployed at three locations in Clear Creek these sites include: 1) the South Amana Catchment, 2) Oxford, and 3) Coralville. These sensors were equipped to collect water quality measurements including: 1) nitrate concentration 2) pH, 3) turbidity, 4) specific conductivity, 5) temperature and 6) dissolved oxygen on an interval of one measurement each every fifteen minutes. The nitrate concentration data will be the focus of this study; however the rest of the water quality data has been plotted for the deployment season and placed in the appendix. The plots in the appendix complement this study by better characterizing the events. These plots are also included to show other water quality parameters that can be measured by high frequency remote sensing.

The reason for setting the measurement interval at fifteen minutes was so that we would have a nitrate concentration value captured at the same time the United States Geological Survey (USGS) stream gauge stations (located at the Oxford and Coralville sites) collect a discharge measurements. The Amana site does not have a USGS stream gauge station at its location, but it does have a network of pressure transducers deployed at the site which are used to measure flow every fifteen minutes as well. With our sensors synchronized with the stream gauge and pressure transducers nitrate concentrations can be captured at base flow conditions in the stream as well as high flow events. By collecting high frequency nitrate data to match the high frequency flow data the nitrate flux (metric tons/day of nitrate-N) can be calculated and this will provide insight to Clear Creek contribute to the total nitrate export to the Gulf of Mexico.

CHAPTER II

MATERIALS AND METHODS

All nitrate data collected for this project came from a small Iowa stream named Clear Creek. This stream stretches approximately 47 km between two western Iowa counties (Iowa County and Johnson County) (Loperfido, 2009). The location of the Clear Creek watershed within the state of Iowa is shown in Figure 2.1. The Clear Creek watershed covers a total area of 267 square kilometers (Loperfido, 2009). Agriculture is the primary land use in this watershed at approximately 85% of the total land use followed by forest cover at 8%, roads or urban cover 6%, and what remains is either water or barren (Loperfido, 2009). A study conducted by Iowa State University found that the overall sinuosity of Clear Creak's main channel has declined from 1940-1963 (Iowa State University (ISU, 2006). This study was able to conclude that many of the stream segments are straighter than they were in 1940 but offered no insight to whether or not this straightening occurred naturally or if it was the result of channelization (ISU, 2006). This decrease in sinuosity provides a faster path for nitrate to be exported out of the Clear Creek watershed and into the Iowa River.

Deployment Sites

The deployment site furthest away from the confluence of Clear Creek with the Iowa River was located at the following GPS coordinates N41˚43.834' W091˚54.428'. This site called the South Amana Catchment (SAC) is right near the head waters of Clear Creek and approximately 6 miles from the Amana Colonies and has a total drainage area of 26.1 square kilometers (Loperfido, 2009).

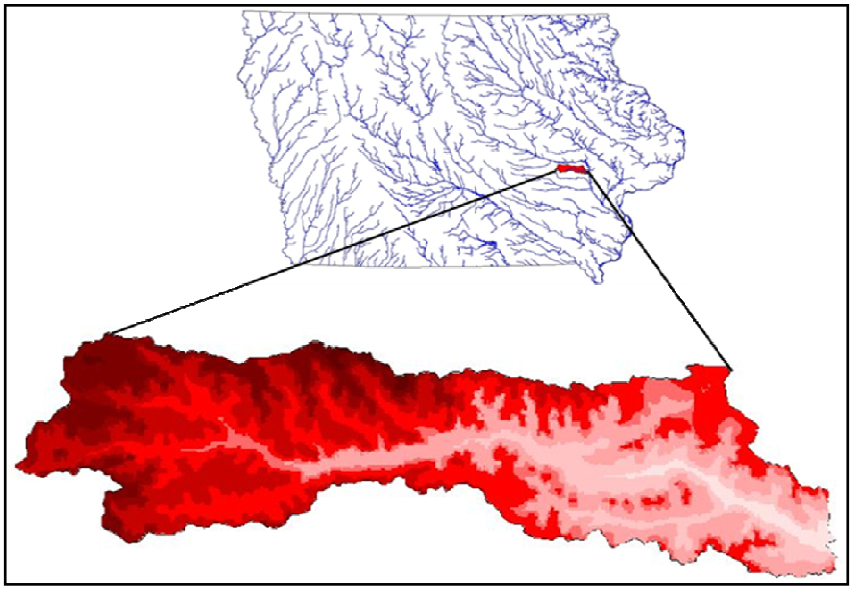

Figure 2.1: Map showing the location of the Clear Creek watershed in the state of Iowa. The areas of darker red in the watershed map show steep topography where the white areas are generally more flat (Loperfido, 2010).

The stream channel at this location is highly unstable and significant erosion occurred while the sensors were deployed. Because high velocity flows that carry large amounts of debris were expected at this site the sensors were deployed in such a way to minimize the likelihood of this debris making contact with them. The three sensors were hung from a 3-inch pipe that was pounded into the stream bed using a post pounder. The sensors were hung on the post using chains and locking “D” rings and all three sensors were zip-tied into a triangle formation. This formation cut down on the total area taken up by the sensor station which would hopefully decrease the amount of grass and tree limbs that could attach to it. Also for added security another 2-inch steel pipe was pounded in directly upstream from the sensors as a barricade that blocked most of the large debris from hitting the sensors during high flow events. The orientation of these two pipes can be seen in Figure 2.2.

Figure 2.2: Orientation of the two pipes at the SAC site. This picture was taken looking up stream, the closest pipe has the sensors attached and the one farthest away was added as a barricade to protect the sensors. Note the sunken large wooded pole that was stopped by the first pipe.

The next deployment site downstream from the SAC was located at Oxford Iowa, GPS coordinates N41˚43.106’ W091˚54.428’. This deployment site shared a location with a USGS stream gauge and lies 13.5 miles upstream from the confluence of Clear Creek with the Iowa River and has a drainage area of 151.3 square kilometers (USGS, 2009). This site has a wider channel than the site at the SAC so high velocity flows were not a huge concern like they were previously. Also the Oxford site was the deepest out of all three sites. Water quality sensors were deployed at this location the year before so we used the same installation apparatus. At this site two 3 inch pipes were pounded into the stream bed and provided the support for the sensor mounting. Since this site had a larger channel width the sensors were mounted differently than they were at the SAC since debris was not as big of a concern here. This site was equipped with a PVC housing for the Hydrolab on one of the pipes which also housed the turbidity sensor, and the Nitratax was deployed on its own apparatus which mounted directly to the second steel pipe, shown in Figure 2.3. Flow statistics from the Oxford site for the 2009 water year were available from the USGS since this site was shared with a USGS stream gauge station. These flow statistics were used to define what a high flow event was. For this project high flow events were the 10% frequency flows that exceeded 173 cubic feet per second (4.9 cubic meter per second); this statistic was developed by the USGS and reported in the 2009 water-data report for Oxford stream gauge.

The last deployment site downstream from Oxford was located at Coralville Iowa, GPS coordinates N41˚40.604’ W091˚54.428’. This deployment site also shared a location with a USGS stream gauge station and is 2.8 miles upstream from the confluence of Clear Creek with the Iowa River; the drainage area equaled 254.2 square kilometers (USGS, 2009). This deployment site also is characterized by a wide channel width and was the shallowest of all three sites. The water quality sensors were deployed using the same methods as the Oxford site. The statistics provided by the USGS 2009 water-data report for the Coralville stream gauge were again used to define

Figure 2.3. Photo of the assembled sensor station at Oxford and similar to Camp Cardinal Road. The Nitratax sensor is located on the farthest pipe.

high flow events at this site. High flow events were the 10% frequency of flows that exceeded 278 cubic feet per minute (7.8 cubic meters per second).

The Nitratax Sensor

The Nitratax sensor by Hach Environmental was designed for use in water treatment facilities to measure the nitrate concentration in activated sludge tanks, treated drinking water, or as a means to measure the nitrate concentration in the water plant discharge. The sensor is designed to be fully submerged which adds to its versatility in environmental applications. This sensor can be programmed to collect nitrate concentrations on a variety of time intervals that range from one sample every fifteen seconds to one sample every half hour. The nitrate concentration measurements recorded by the Nitratax are reported as milligrams per liter (mg/l) or parts per million (ppm) the concentrations can also be reported as nitrate or as nitrate-N. This sensor can detect concentrations from 0.1 mg/l up to 100 mg/l.

The sensor measures nitrate concentration photometrically without the use of reagents by utilizing a two beam absorption photometer. The sensor operates on the principle that nitrate dissolved in water will absorb ultra violet (UV) light at wavelengths below 250 nm. When it is time to take a reading the sensor emits a beam of UV light with a wavelength of 250 nm, the beam passes through the water medium and hits the measuring window on the opposite side of measuring path from the light source. The measuring window records the wavelength of the light beam minus what was absorbed by the water. The amount of light absorbed in the water corresponds to a known concentration of nitrate. The second beam of light emitted from the sensor’s two beam photometer is a turbidity compensator; which measures the turbidity of the water and corrects nitrate concentration for possible interference due to UV light absorption by entrained particles.

The Nitratax sensor is a two piece apparatus as shown in Figure 2.4. The actual sensor that is deployed in the water can only operate in conjunction with the sc-100 control module, also shown in Figure 2.4. The sc-100 provides the link between the sensor and the data logger by storing the recorded nitrate concentration data internally then sending it to the data logger at the time of data transfer. The sc-100 also controls all

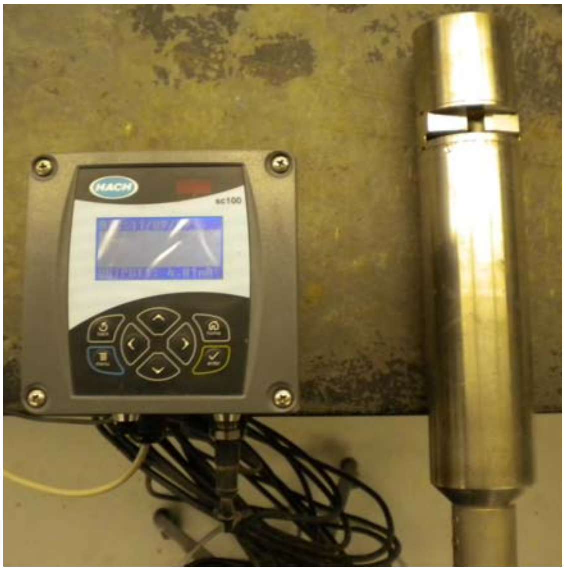

Figure 2.4. Photo of the Nitratax sensor (object on the right) and the sc-100 controller (object on the left).

the sensor's settings, in other words the sc-100 is used to set the time intervals and what units the concentration data will be reported in. The maintenance on this sensor is minimal since it requires calibration only before deployment then again after the deployment season. It should be noted here that this project had a deployment time of six months and in that time frame the data showed no evidence of drift or a loss of calibration. Also after all the sensors were retrieved from the stream their calibrations were cheeked using a standard nitrate solution of 11.3 mg/l nitrate-N. The result of this calibration test showed no significant loss of calibration through deployment since all three sensors reported concentrations close to or exactly 11.3 mg/l. However, longer deployments may need some kind of calibration schedule to validate the accuracy of the sensors. Calibrating the sensor occurred before deployment in the lab. To calibrate the Nitratax sensor a solution of known nitrate concentration (11.3 mg/l nitrate-nitrogen) supplied by Hach Environmental is poured into the measuring path (Figure 2.5).

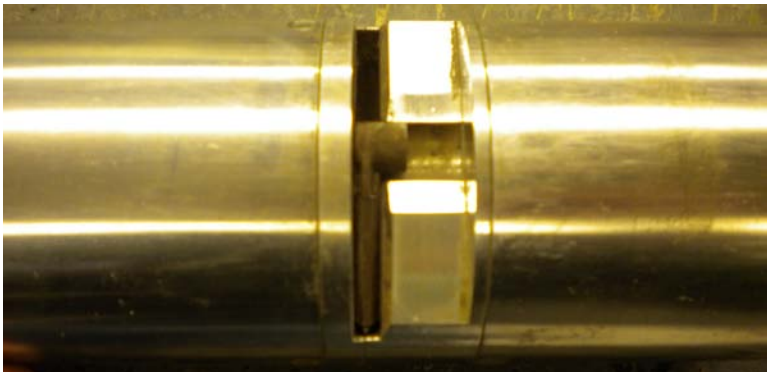

Figure 2.5. Close-up of the Nitratax sensor showing the measuring path and the wiper blade.

The solution is kept in the measuring path until the nitrate reading on the sc-100 stabilizes. Once the reading stabilizes the standard value is stored as a reference and the instrument is calibrated and ready for deployment. The step-by-step instructions for sensor calibration can be found in the Nitratax operation manual on page 34 (Hach company, 2004). To help keep debris from fowling the measurement window the Nitratax comes equipped with a wiper blade, shown in Figure 2.5, that sweeps the window clean before each measurement. This wiper blade does wear out over time and must be replaced in order to keep the sensor working at peak performance.

Data Collection and Storage

The Nitratax sensor deployed in the creek is connected to the sc-100 control module by a specially designed deployment cable. The nitrate concentration data collected by the Nitratax is stored internally in the sc-100 which is then hardwired to a remote data collection platform, the CR-1000 data logger by Campbell Scientific. This data logger collects and stores all measurements taken by the sensors in the stream. The data logger was programmed using software supplied by Campbell Scientific called PC200w. The data logger is connected to a Raven CDMA model C3211 wireless cellular modem (AirLink Communications, Inc) which transmits the collected data remotely back to a computer in the lab. This wireless telemetry is achieved using a small antenna that is mounted in a high location at each deployment site. The cellular modem is the key to this whole project because without it we would have needed to take multiple trips to the field to retrieve the data off the data logger. Each wireless modem was activated with a data plan that allowed 5 megabytes of data transfer a month through the Verizon Cellular Network. Once the data is received back in the lab the files are archived and can be accessed through the Iowa Institute of Hydraulic Research's (IIHR) ftp site (www.ftp.iihr.uiowa.edu). The nitrate concentration in the creek can also be monitored in real time using software provided with the data logger called Loggernet remote. This program allows the viewer to access an individual data logger out in the field by connecting to it through the cellular modem and looking at the data as it gets collected. The data logger and cellular modem are placed in a water proof box out in the field to protect them from the elements. This water proof bow known as the “white box” is shown in Figure 2.3.

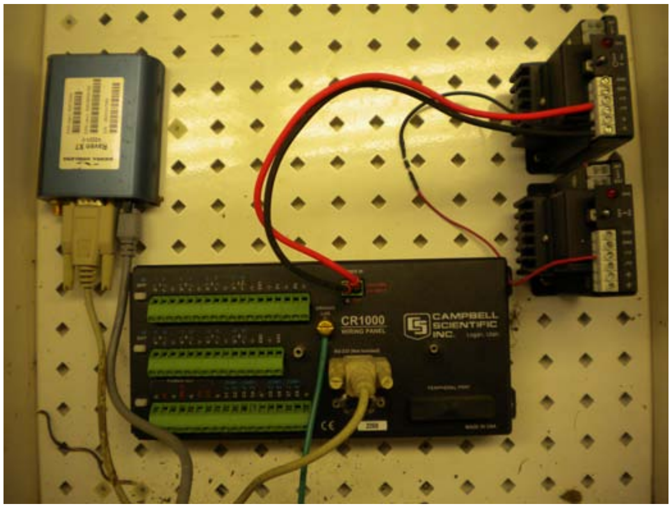

Figure 2.5. Photo of the “white box” contents. The object in the upper left is the cellular modem, the object in the middle is the data logger, and the two objects in the upper right are charge controllers.

Powering the Sensors

The deployment sites(which contain cellular modems, data loggers, and complex sensing equipment equipped with UV lamps and moving parts) must be provided at least 11 volts of electricity in order to operate successfully. Solar panels and deep cycle marine batteries were used to fill the electricity needs at all three sites. At the SAC site solar panels that had a maximum power output of 20 watts were used to provide power during the day and charge the batteries; then the batteries would keep the sensors going through the night. At the Oxford and Coralville sites solar panels with a power output of

10 watt maximum were used to power the stations during the day and charge the batteries, and again the batteries provided the power during the night. The batteries would stay charged above 11 volts as long as the solar panels were provided with at least six hours of direct sunlight. The battery voltage could be monitored using the Loggernet Remote software and the batteries were replaced whenever voltage dropped below 11 volts.

CHAPTER III

RESULTS AND DISSCUSSION

All sensors were deployed within a two week time span in mid April however due to technical difficulties at the SAC and the Coralville sites samples did not start recording until June. Originally the sensors at the SAC were not hung on a steel pipe but instead they were placed directly on the stream bed. This proved to be an ineffective deployment setup since at low flow the SAC had large sedimentation rates and the sensors were buried under approximately 2 inches of sediment within two weeks of being deployed. The sediment blocked the sensors from actually recording any water quality data from the stream so the deployment site was moved further up stream where the water was swifter and the sensors were then hung on the steel pipe as was described in the materials and methods section. The data logger at the SAC also was not equipped with the most updated operating system when it was deployed which inhibited its ability to communicate with the cellular modem. The trouble-shooting of this problem also added gaps where the sensors were not collecting data.

The issue with the Coralville site which inhibited its data collection for the first month of deployment was a product of being underpowered. The Coralville site is located along the bridge on Camp Cardinal Road in Coralville Iowa. This location is surrounded by tall tree canopies that support large leaf cover during the summer months. These trees interfered with the solar panels ability to collect enough solar radiation to power the sensors and keep the batteries charged; the result was large gaps in the data for the first month of deployment. Moving the solar panels closer to the road and as far away from the trees as possible was the best solution and did allow the sensors to operate longer between battery exchanges. However this solution still did not fix the problem of being under powered entirely. During rain events when the sun was veiled by cloud cover the trees still could block a portion of the solar radiation. The solar panels could not store enough energy to keep the sensors operation during the entire rain event which caused "blackouts" where no data was collected. These "blackouts" occurred at the Oxford site as well but not as frequently since this site was not located in an area of intense tree cover. The "black out" episodes where voltage dropped below 11 can be seen on the battery voltage plots for both Oxford and Coralville located in the appendix. The SAC never had a problem of being underpowered; in fact the batteries were only exchanged twice during the entire deployment. The plot of battery voltage for the SAC site located in the appendix shows only two times where the voltage dropped below 11. I credit this with the larger solar panels that were deployed at the SAC, the 20 watt maximum power output produced by each of these panels were double the maximum power of the panels deployed at Oxford and Coralville (10 watts each). This larger power output provided enough electricity to power the sensors, and keep the batteries charged, even during storm conditions when the sun was blocked by cloud cover. Once these technical issues were resolved the three sites collected nitrate data until they were retrieved at the beginning of October.

Data Analysis

At the end of the deployment season all data collected by the sensors was stored on the IIHR ftp site. From the ftp site all raw Nitratax data was downloaded as comma delimited files, then opened in Microsoft Excel. One spread sheet for each deployment site was developed and all flux calculations were performed in the spread sheets. Each spread sheet contained a column for the date and time and one for the concentration of nitrate-N (mg/l). The data was then manipulated by manually inserting all missing dates and times and the missing concentration data was left blank. A plot of the nitrate concentration over the entire deployment season for each site was then created and is shown in Figure 3.1, 3.4, and 3.7 for the SAC, Oxford, and Coralville respectively. Next a column for the flow data was created and the flow data for the Oxford and Coralville site was inserted into the spread sheets from the USGS Instantaneous Data Archive (IDA). Any missing flow measurements were filled by averaging the two flows surrounding the blank. The flow data for the SAC was imported in the proper spread sheet from the discharge data provided by Thanos Papanicolaou's pressure transducers deployed at the SAC. All discharge data collected by the USGS is reported in cubic feet per second but to calculate flux in metric tons per day the flow needed to be converted to cubic meters per second which was done in the next column on the Oxford and Coralville spread sheets. The discharge data for the SAC was recorded in cubic meters per second so no converting was needed. The deployment season hydrograph for each site (using flow in cubic meters per second) was plotted and is shown in Figures 3.2, 3.5, and 3.8 for the SAC, Oxford, and Coralville respectively. The final column in the three spread sheets was set up to calculate the nitrate flux (metric tons per day) using the same equation as Goolsby *et al.* (1999). The equation is defined as follows:

Flux (metric tons/day) = concentration (mg/l) x flow (cubic meters/second) x .0864

The 0.0864 term in the above equation is a conversion factor that will convert the product of concentration and flow into metric tons/day. This conversion factor is found by the following calculation:

0.0864 metric tons/day = (mg/l) x (cubic meter/sec) x (86400 sec/day) x (1000 L/cubic meter) x (1 kg/1,000,000 mg) x (1 ton/1000 kg)

In order to accurately represent the flux that occurred using 15 minute time intervals, or quarter hours, the right side of the equation needed to be multiplied by 1/96 since there are 96 quarter hours in a day. The new resulting conversion factor for 15 minute data is 0.0009. The resulting flux values were plotted for the entire season and are shown in Figures 3.3, 3.6, and 3.9 for the SAC, Oxford, and Coralville respectively.

The three plots depicting the nitrate-nitrogen concentrations (Figure 3.1, 3.4, and 3.7) show some interesting dynamics that occurred during the deployment season. First the highest nitrate concentrations occurred from mid-June to the end of July at all three sites. This elevated level of nitrate occurs at the same time of year that nitrogen fertilizer is being applied by side dressing. Side dressing corn with nitrogen must be completed before the plant grows too tall; the period of high nitrate concentrations on the three plots is typically the time frame when farmers are in their fields applying nitrogen by side dressing. Also since the 2009 growing season was extremely wet it is likely that a lot of the applied nitrogen may have been washed out before it could be taken up by the corn plants. The second interesting dynamic is the

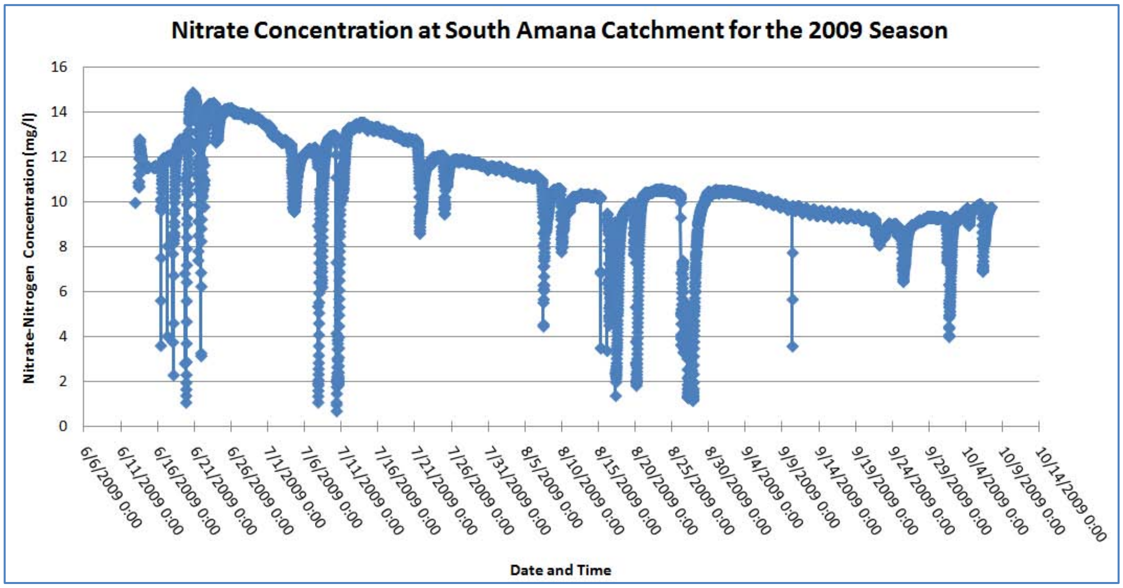

Figure 3.1: Plot of Nitrate-nitrogen concentrations (mg/l) at the SAC for the entire 2009 deployment season

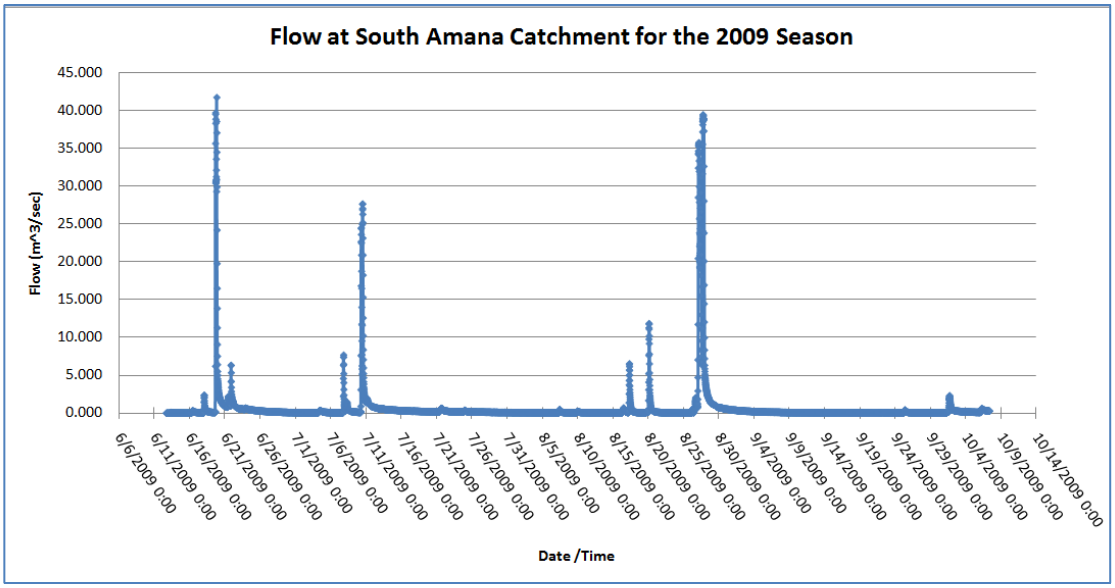

Figure 3.2: Hydrograph for the entire 2009 deployment season at the SAC

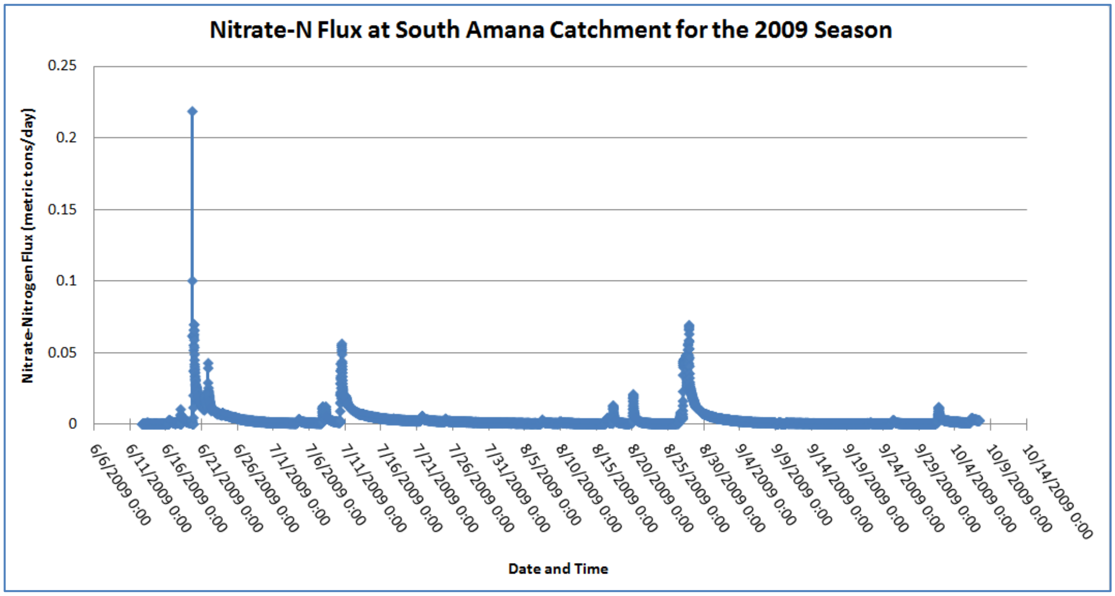

Figure 3.3: Plot of the flux for each 15 minute collection interval during the entire2009 deployment season at SAC.

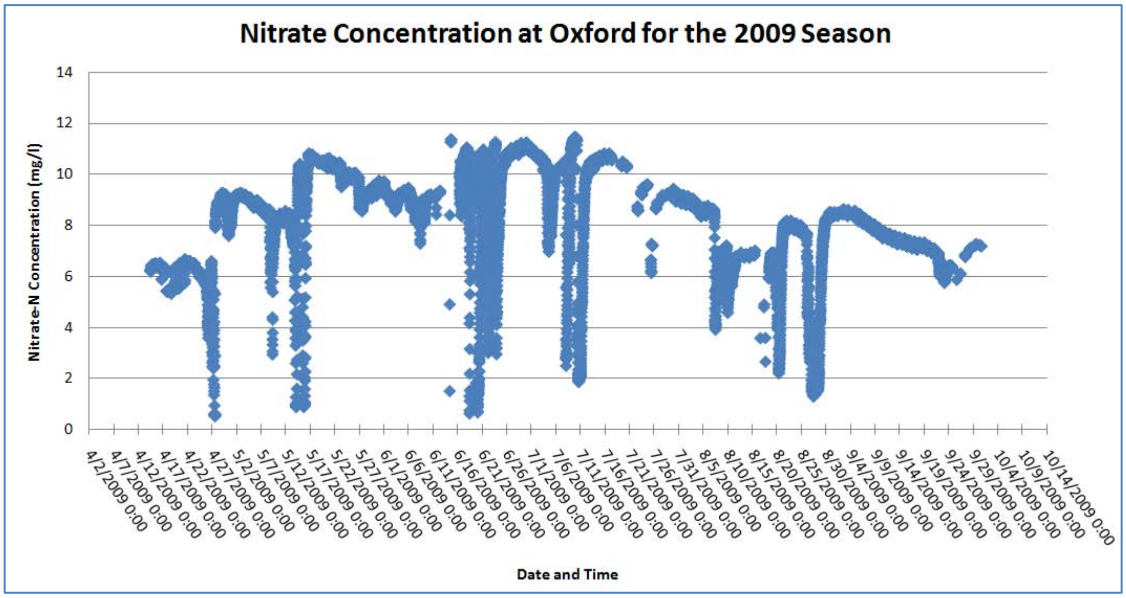

Figure 3.4: Plot of Nitrate-nitrogen concentrations (mg/l) at Oxford for the entire 2009 deployment season

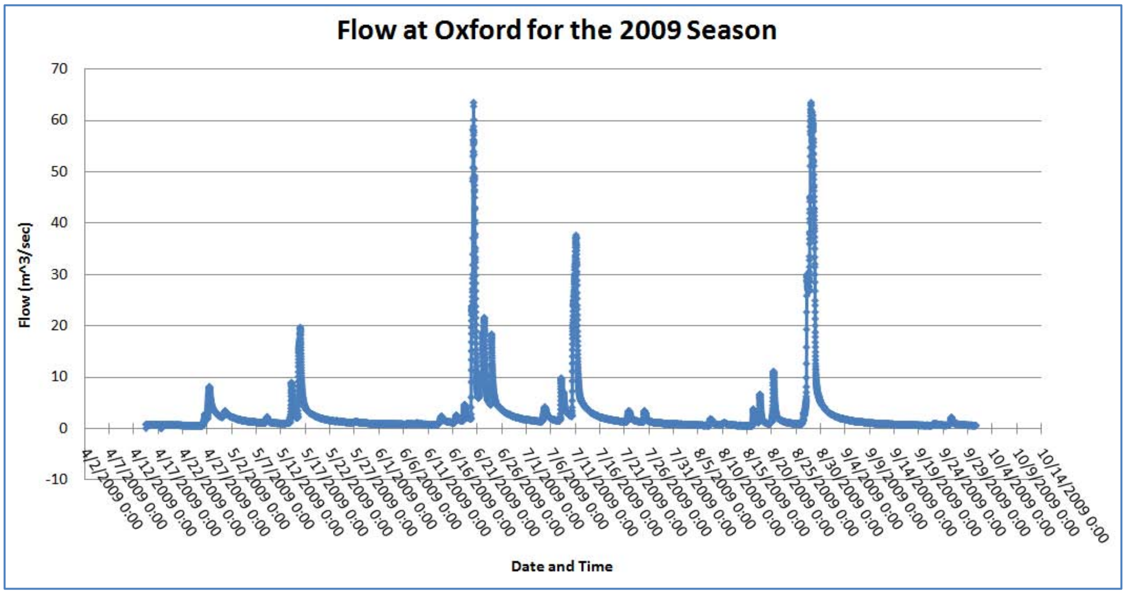

Figure 3.5: Hydrograph for the entire 2009 deployment season at Oxford

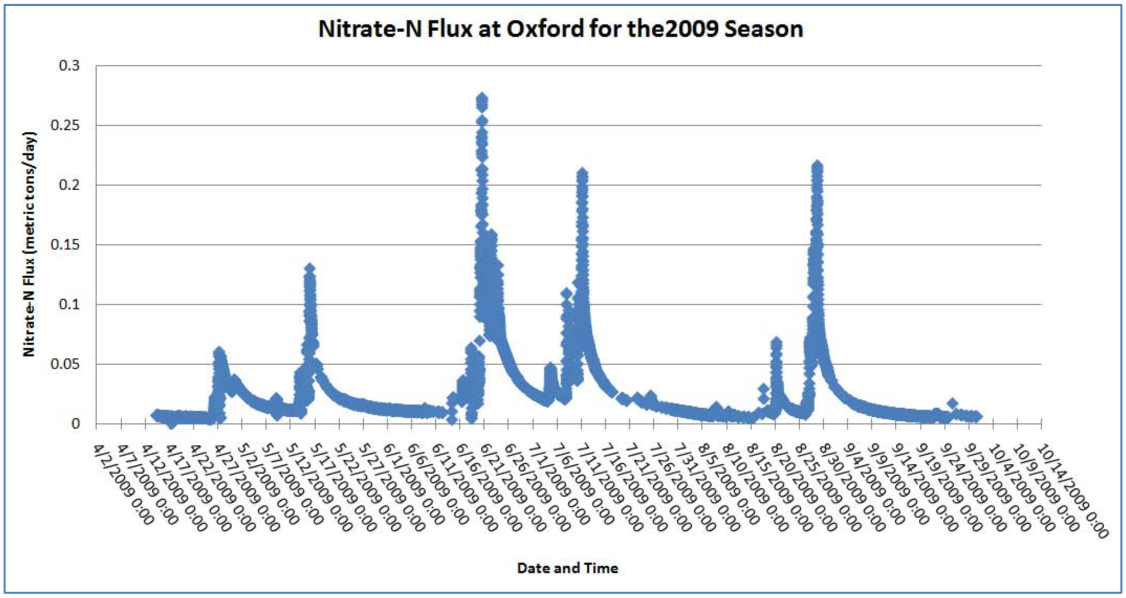

Figure3.6: Plot of the flux for each 15 minute collection interval during the entire 2009 deployment season at Oxford

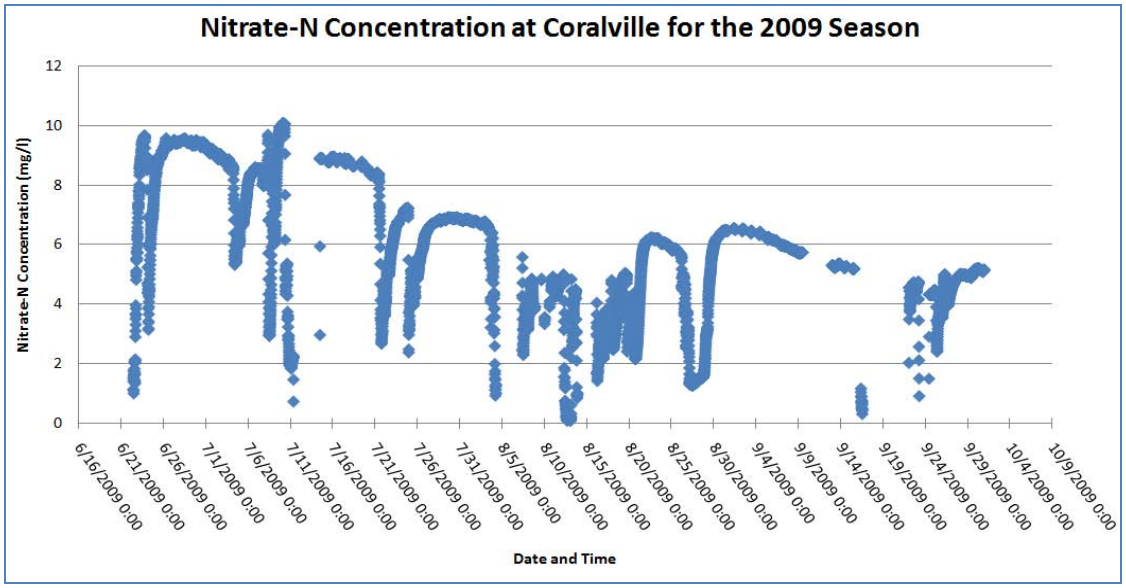

Figure 3.7: Plot of Nitrate-nitrogen concentrations (mg/l) at Coralville for the entire 2009 deployment season

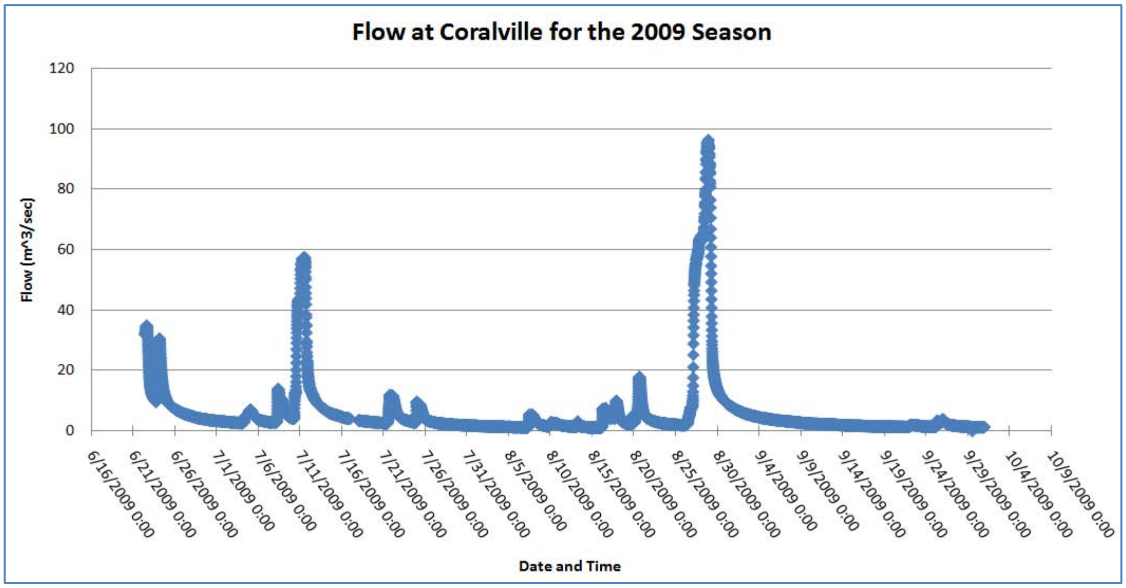

Figure 3.8: Hydrograph for the entire 2009 deployment season at Coralville

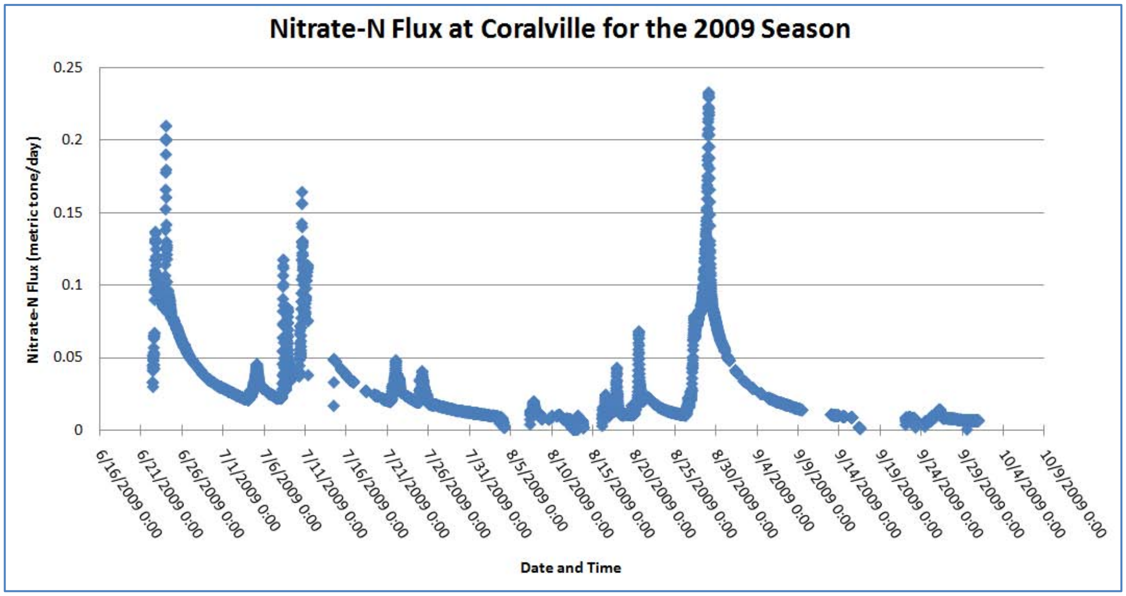

Figure 3.9: Plot of the flux for each 15 minute collection interval during the entire 2009 deployment season at Coralville

sudden dip in nitrate concentration that can be seen on Figure 3.1, 3.4, and 3.7. These dips occur at the same date and time as the peaks on the hydrographs (Figures 3.2, 3.5, and 3.8). The reason for the sudden decrease in nitrate concentration is because during a storm event the volume of water passing through the site increases which results in a dilution of the total nitrate concentration. The final dynamic to note from the plots pictured above is that the episodes of high flow also have the highest mass loading of nitrate. This is evident for the date of June 19, 2009 on Figure 3.3 and 3.6 which happens to be the day with the highest flow of the season that was recorded for the SAC and Oxford. The Nitratax sensor was not functioning properly at the Coralville site on this day so, unfortunately, no comparison can be made between the Coralville site and the other two on June 19. The data presented in Figures 3.1, 3.4, and 3.7 also show that the

SAC and Oxford both had extended time frames where the nitrate-N concentration exceeded the 10 mg/l drinking water standard.

The nitrate dynamics mentioned above are not new phenomenon; in fact these trends were expected. The reason that it is important to mention these dynamics is because it proves that the Nitratax sensor is capable of monitoring nitrate in Clear Creek and record nitrate-N dynamics that are expected to occur during peak events.

Comparison of High Frequency Samples to Hourly/Daily Samples

The purpose of this project was not only to gather nitrate concentration data for the calculation of mass loading on Clear Creek; but also to see if high frequency data samples are the best at estimating total mass flux for the season and during storm events. To answer the second question the high frequency data was compared to data samples collected every hour and samples collected once a day.

To generate the hourly nitrate-N samples for this comparison the original dataset, from each deployment site, containing high frequency nitrate-N concentration were artificially sampled to pull out the values at the top of each hour. These samples were placed into a new spread sheet that was set up similar to the original spread sheets described on pages 24-25. By gathering only the samples collected at the top of each hour this new dataset can be thought of as either grab samples taken every hour or samples that may have been collected by an automated sampler with a collection interval of one per hour. Next, the flow measurement that occurred at the corresponding hours were used to calculate the mass flux using the equation defined on the top of page 27. However now the right hand side of the equation must me multiplied by 1/24 to produce a new conversion factor of 0.0036, this will correct for the proper time since there are 24 hours in one day. The calculation for the new conversion factor is shown below:

0.0036 metric tons/hour = (mg/l) x (cubic meter/sec) x (86400 sec/day) x (1000 L/cubic meter) x (1 kg/1,000,000 mg) x (1 ton/1000 kg) x (1day/24hours)

The results were plotted in Figures 3.10, 3.11, and 3.12 for the SAC, Oxford, and Coralville sites respectively.

To generate the daily nitrate-N samples for this comparison the original dataset from all three sites was again used, this time the sample taken at 11:00 a.m. was extracted.

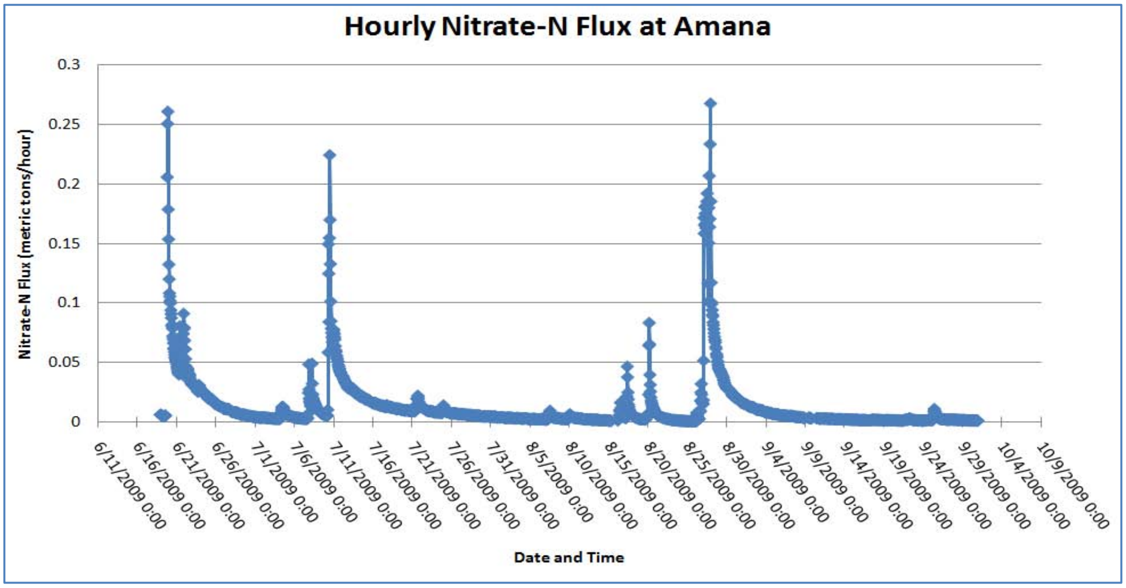

Figure 3.10: Plot of hourly nitrate-N flux at the SAC

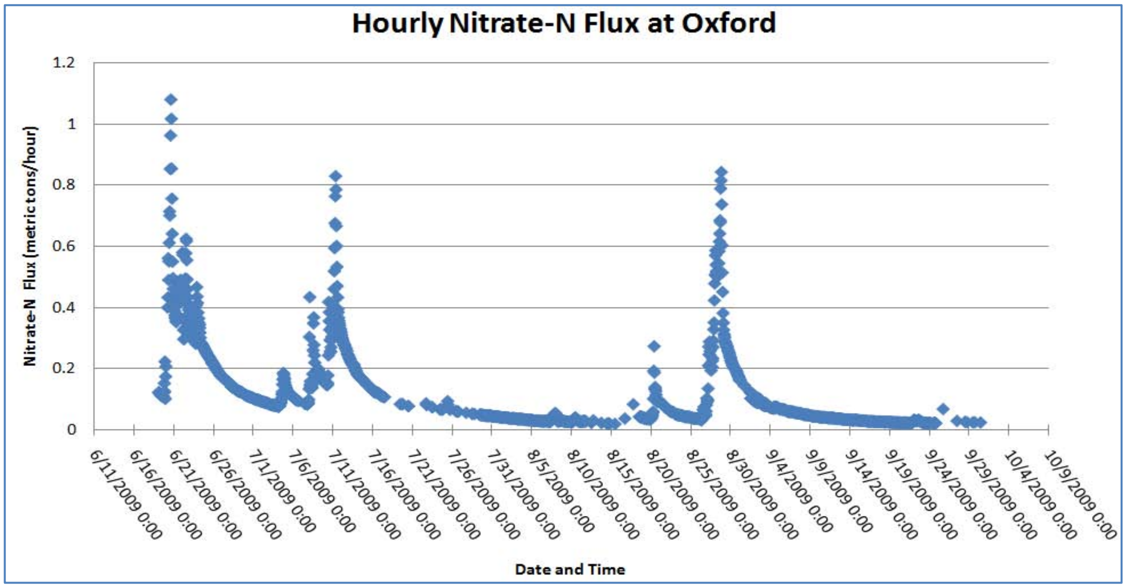

Figure 3.11: Plot of hourly nitrate-N flux at Oxford

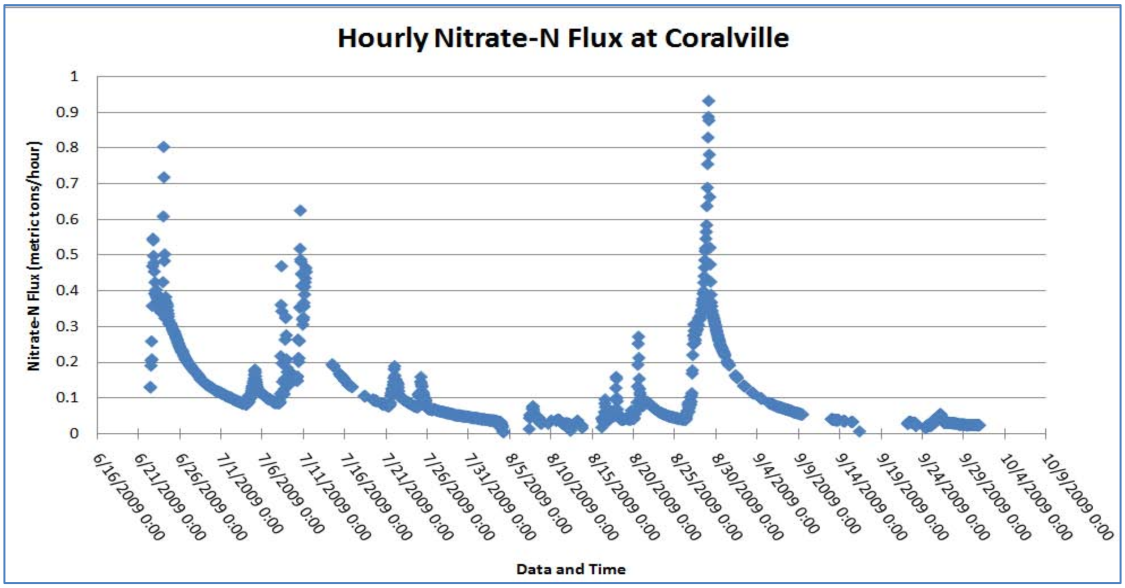

Figure 3.12: Plot of hourly nitrate-N flux at Coralville

This artificially sampled data was again placed into a new spread sheet where the daily flux values were calculated using the equation at the top of page 27 and using daily flow averages reported by the USGS (for Oxford and Coralville) and the pressure transducers (at the SAC). By pulling out only one sample a day this new dataset represents one that would be generated if daily grab samples were collected on a set time schedule. The resulting flux values were plotted and are shown in Figures 3.13, 3.14, and 3.15 for the SAC, Oxford, and Coralville sites respectively.

For a fair comparison of high frequency samples to hourly and daily samples to be most accurate the time span plotted in the following figures for hourly and daily flux calculations needed to be equal. The time span in the figures for the SAC and Oxford sites has a total of 104 day starting on June 19 and ending on September 30.

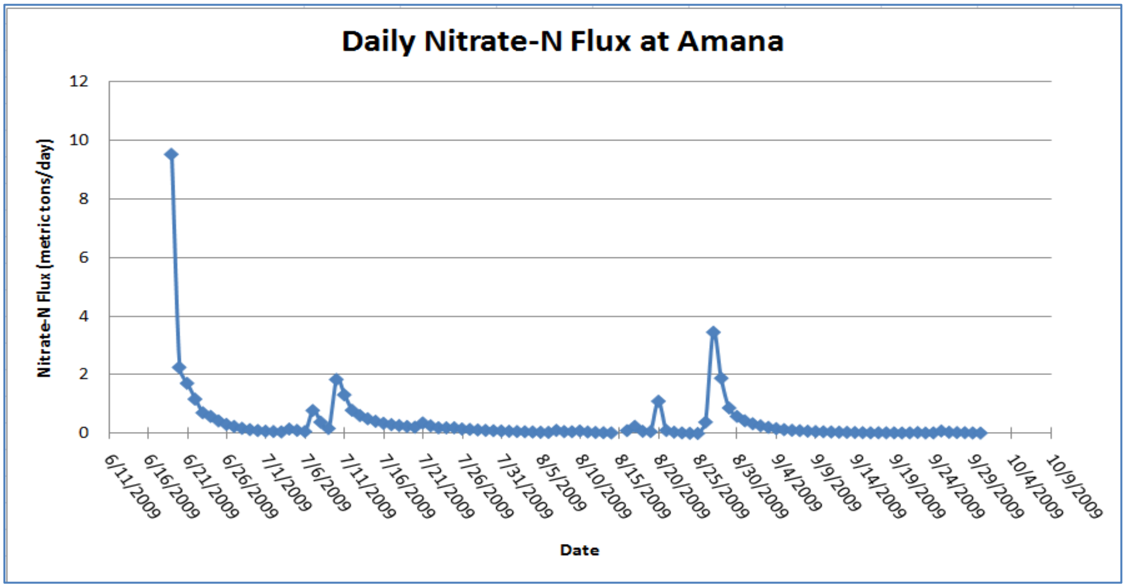

Figure 3.13: Plot of daily nitrate-N flux at the SAC

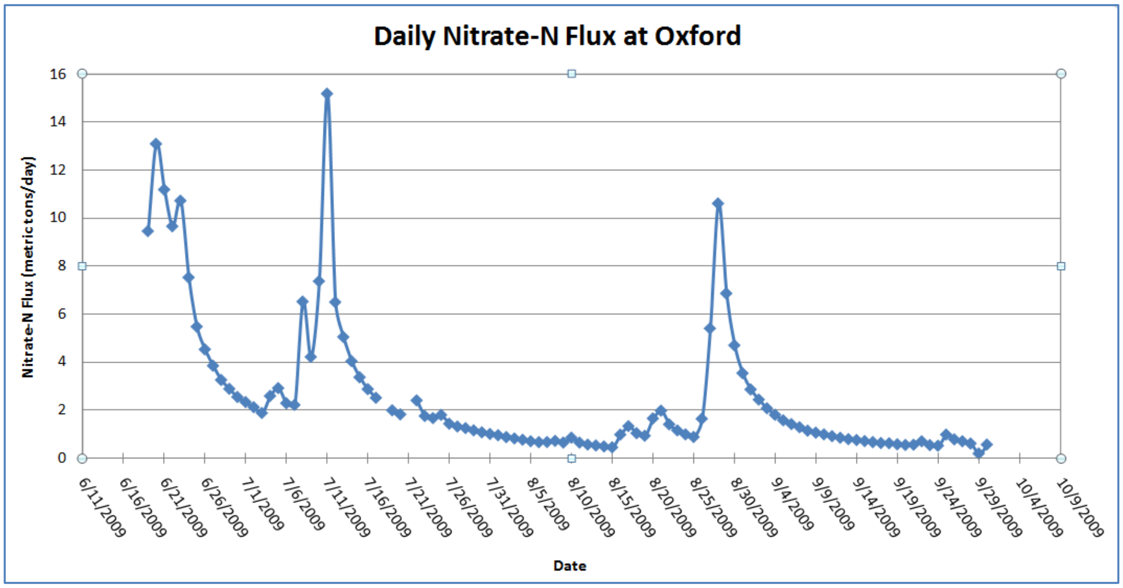

Figure 3.14: Plot of daily nitrate-N flux at Oxford

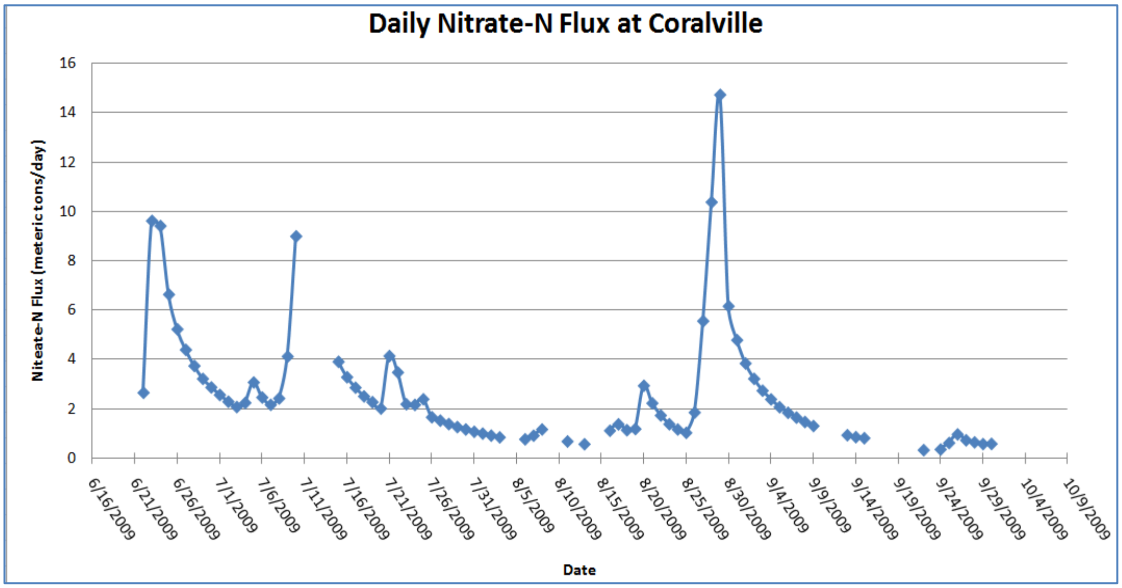

Figure 3.15: Plot of daily nitrate-N flux at Coralville

This time span was chosen because June 19 was the storm event that produced the highest flows for the season and the USGS only had fifteen minute flow data up to September 30 published for research use. Due to a sensor malfunctions the flux plots for the Coralville site has a time span of only 100 days because no nitrate data was collected on the 19, 20, and 21 of June also there was no flow data recorded by the USGS on July 17.

The problem of sensor malfunctions was common at all three sites and the main cause was inadequate voltage to power the Nitratax sensor. When the voltage in the batteries dropped below 11 volts the sensor would not have enough power to make a sample, the result is a gap in the dataset. These gaps are present in the high frequency flux pots, Figures 3.3, 3.6, and 3.9, however are difficult to see since there are a lot of data points represented on these three figures. The missing data can be recognized with greater ease in the hourly and daily flux plots. This missing data poses are a huge problem because they make calculating the nitrate-N flux for the total season and high flow events impossible since lines with missing values cannot be integrated directly. To overcome the problem of missing data a technique for estimating the missing nitrate-N concentration values using flow data needed to be developed. The method that was used will be discussed in the next section.

Interpolation of Data Gaps

As previously mentioned the sensors that were deployed in Clear Creek did not work flawlessly throughout the entire deployment and as a result the dataset from all three sites contained gaps. These gaps needed to be filled in order to integrate the flux curves for high frequency, hourly, and daily data samples so that the total seasonal flux for the given time period could be calculated. The gaps that existed in the dataset were mainly due to the fact that the Nitratax sensor did not capture nitrate-N concentrations at certain times. However the flow data for all three sites were not tied to the sensor sites in anyway; so even though a nitrate-N concentration may not have been recorded there was still a time stamped flow measurement taken either by the USGS or the pressure transducer network. According to Haggard *et. al* (2002) logarithmic transformation of concentration and flow coupled with a regression methods can be a technique to estimate missing concentration values over time periods if there is a dataset containing a large amount of samples (like the data set from this project). Haggard *et. al* (2002) used this method of regression modeling to fill missing data needed to estimate total phosphorus loads on the Illinois River in Arkansas with success.

A similar method as mentioned above was used in this project to fill in the gaps of missing nitrate-N concentrations. A plot of the base 10 logarithm nitrate-N concentration vs. the base 10 logarithm flow was developed for each site. The resulting log (C) vs. log (Q) plots are shown in Figures 3.16, 3.17, and 3.18 for the SAC, Oxford, and Coralville sites respectively. A linear regression was fit through each plot to generate a corresponding line equation which was used to calculate the missing concentration values using the known flow values where a hole occurred in the data set. The regression equations were rearranged to solve for concentration in mg/l and are reported below with the R squared values.

South Amana Catchment

[Nitrate-N] (mg/l) = 10^(-0.0727 x flow (cfs) + 1.0667)

R squared value= 0.0996

Oxford

[Nitrate-N] (mg/l) = 10^(-0.1646 x flow (cfs) + 1.2084)

R squared value = 0.2238

Coralville

[Nitrate-N] (mg/l) = 10^(/0.187 x flow (cfs) + 1.15)

R squared value = 0.187

This method of interpolating missing data is not perfect which can be inferred from the low R squared values for each plot. This suggests that nitrate concentration and flow are not log-linearly related. The regression lines in all three cases will over estimate the concentrations that were missing during the highest flow and will underestimate the concentrations that were missing at base flow conditions. However these estimated concentrations were used to calculate the missing flux data and the resulting plots for the high frequency samples that contain interpolated data are shown in Figures 3.19, 3.20, and 3.21 for the SAC, Oxford, and Coralville sites respectively. Figures 3.22, 3.23, and 3.24 show plots of the flux using hourly samples with the interpolated data for the SAC, Oxford, and Coralville sites respectively. Finally Figures 3.25, 3.26, and 3.27 show plots of the daily flux with interpolated data.

The high frequency, hourly, and daily nitrate-N flux plots from all three sites follow the trend that was expected when the regression equations were used to

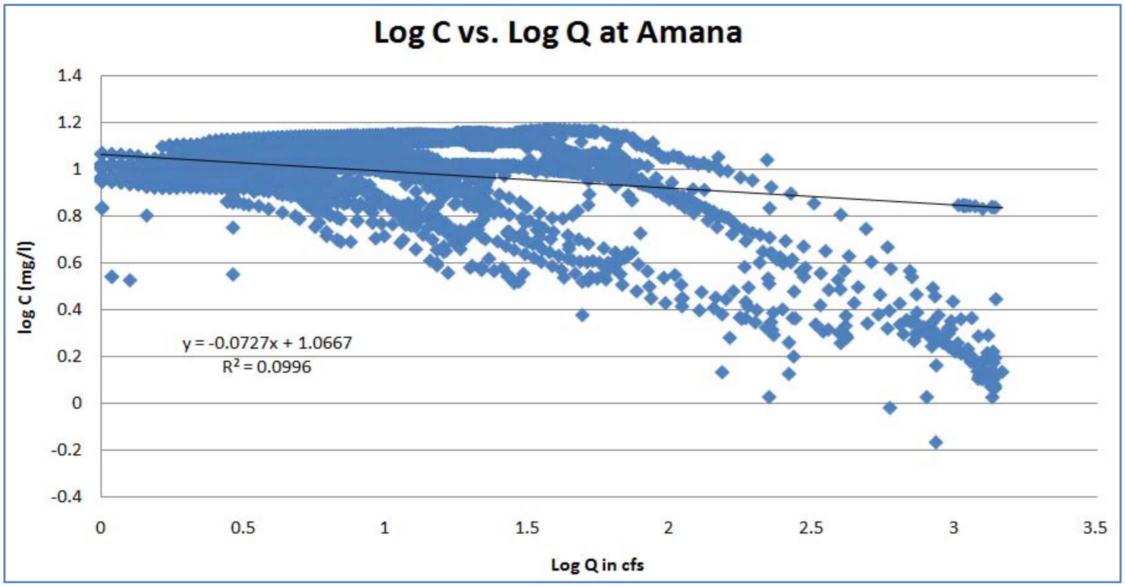

Figure 3.16: Plot of the base 10 logarithm of nitrate-N vs. the base 10 logarithm of flow in cfs second for the SAC site

estimate the missing concentration data. The overestimation during high flow events can be seen on the day of June 19 on Figure 3.19 for the SAC site. The peak value of 0.245 metric tons/day of nitrate-N is 0.027 metric tons/day higher than the highest peak on figure 3.3 (plot of flux with the gaps in the data). This over estimation at high flow cascades down to the hourly and daily flux plots since they all originated from the same dataset. The plot for the high frequency samples with interpolated data (Figure 3.20) showed a maximum peak that was 0.41 metric tons per day higher. Again this over estimation cascades down to the hourly and daily flux plots with interpolated data because all plots come from the same original dataset. It is important to note that even though there is an overestimation at the highest flow the overall shape of the interpolated graph is very similar to the overall shape of the plot with the gaps. In other words the plot of nitrate-N flux without interpolation has the same overall shape as the plot of nitrate-N flux with interpolated data or Figure 3.3 and Figure 3.19 are similar, Figure 3.6 and Figure 3.20 are similar, and Figure 3.9 and Figure3.21 are similar for the SAC, Oxford and Coralville respectively.

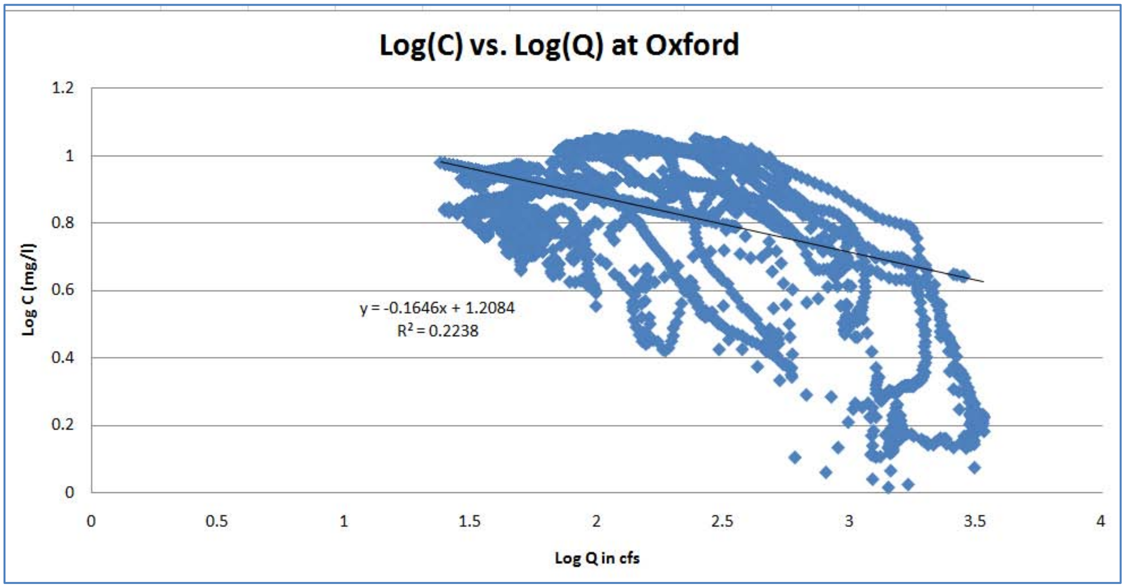

Figure 3.17: Plot of the base 10 logarithm of nitrate-N vs. the base 10 logarithm of flow in cfs for the Oxford site

The method of estimating the missing concentration data using log transformed concentration and flow measurements was compared to estimating the missing data by closing the gap with a connecting line between the point before and after the gap. This method was done only on the storm event that occurred on June 19 at the Amana site.

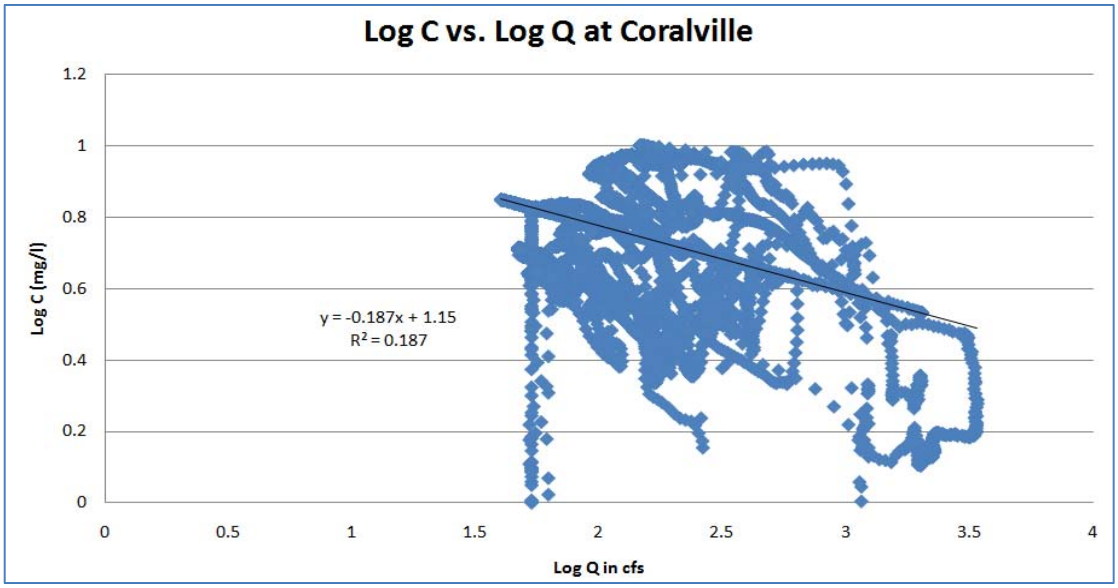

Figure 3.18: Plot of the base 10 logarithm of nitrate-N vs. the base 10 logarithm of flow in cfs for the Coralville site

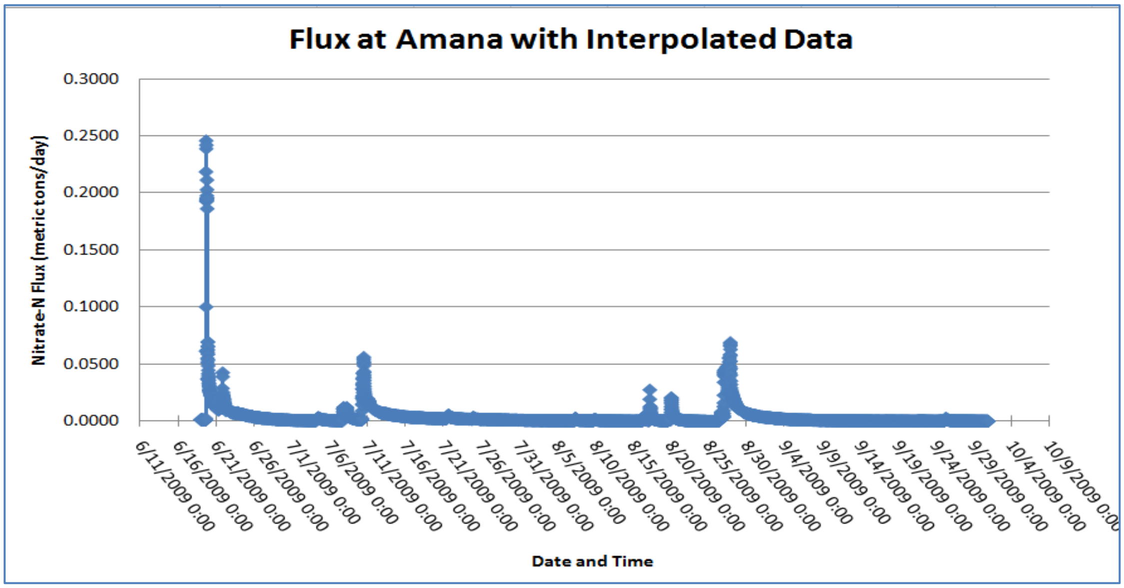

Figure 3.19: Plot of Flux calculated using high frequency samples and all holes interpolated with data using log (C) vs. log (Q) at the SAC site

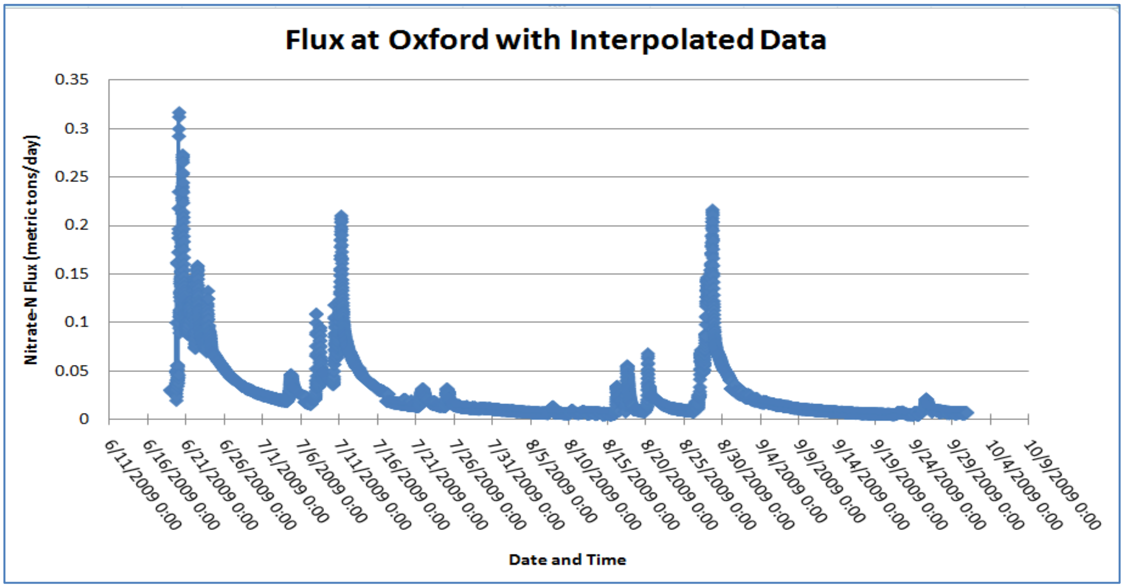

Figure 3.20: Plot of Flux calculated using high frequency samples and all holes interpolated with data using log (C) vs. log (Q) at the Oxford site

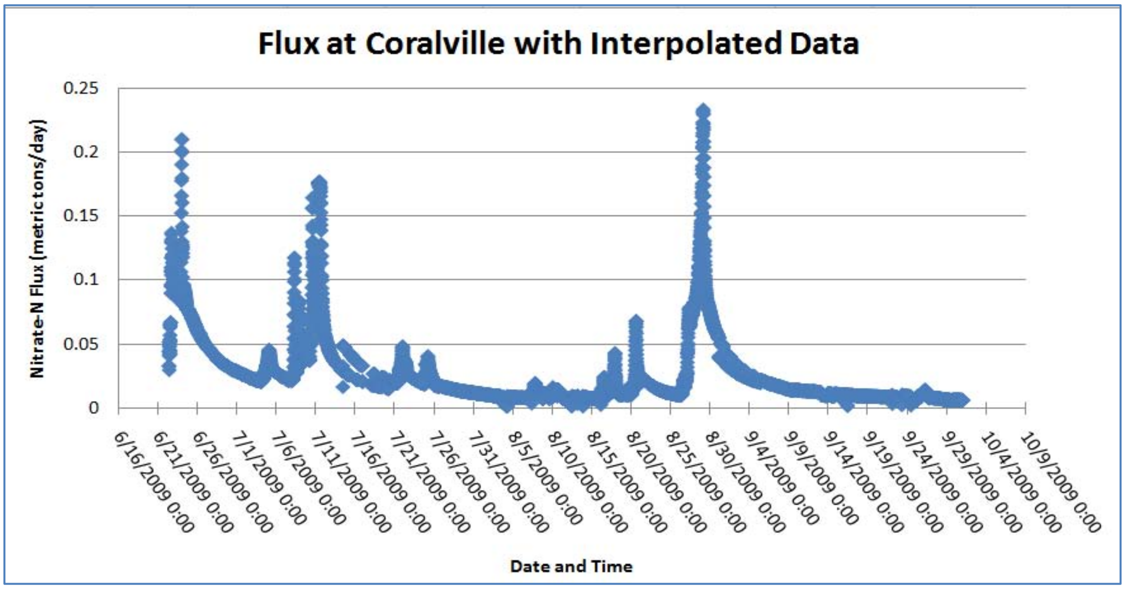

Figure 3.21: Plot of Flux calculated using high frequency samples and all holes interpolated with data using log (C) vs. log (Q) at the Coralville site

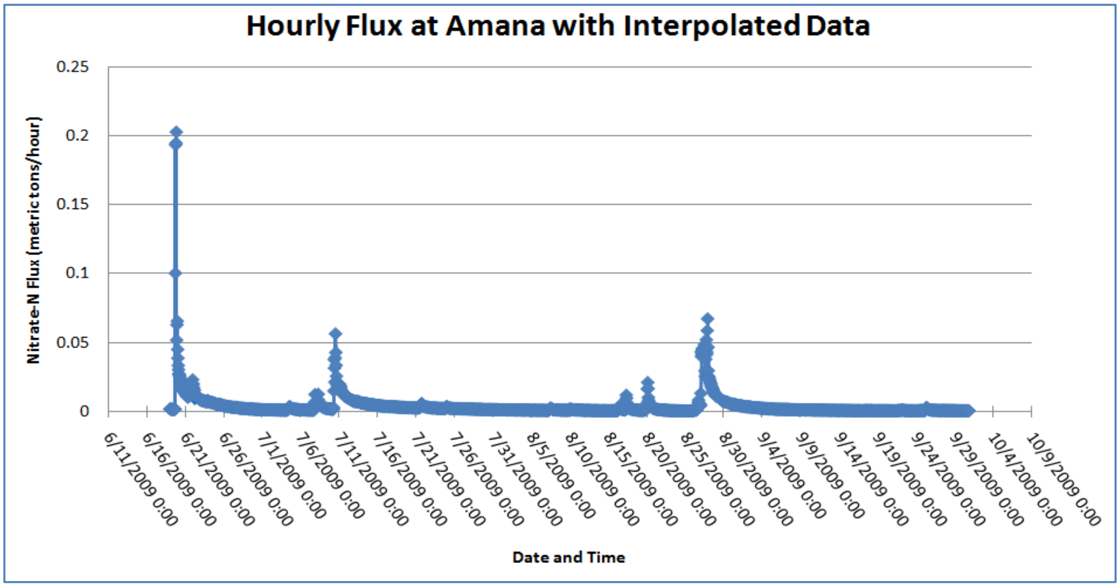

Figure 3.22: Plot of hourly flux with all holes interpolated with data using log (C) vs. log (Q) at the SAC site

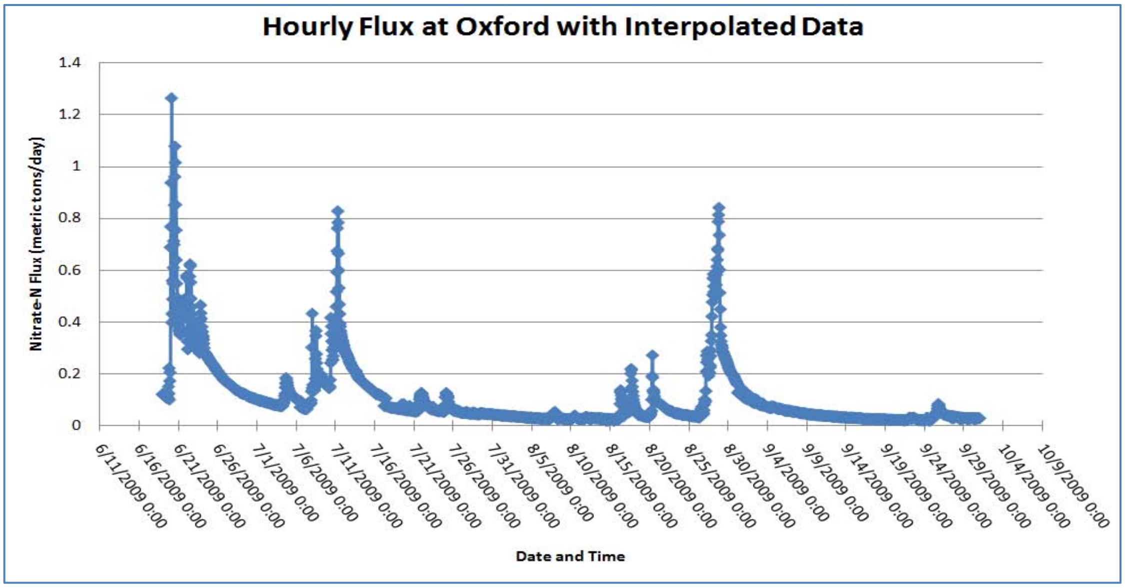

Figure 3.23: Plot of hourly flux with all holes interpolated with data using log (C) vs. log (Q) at the Oxford site

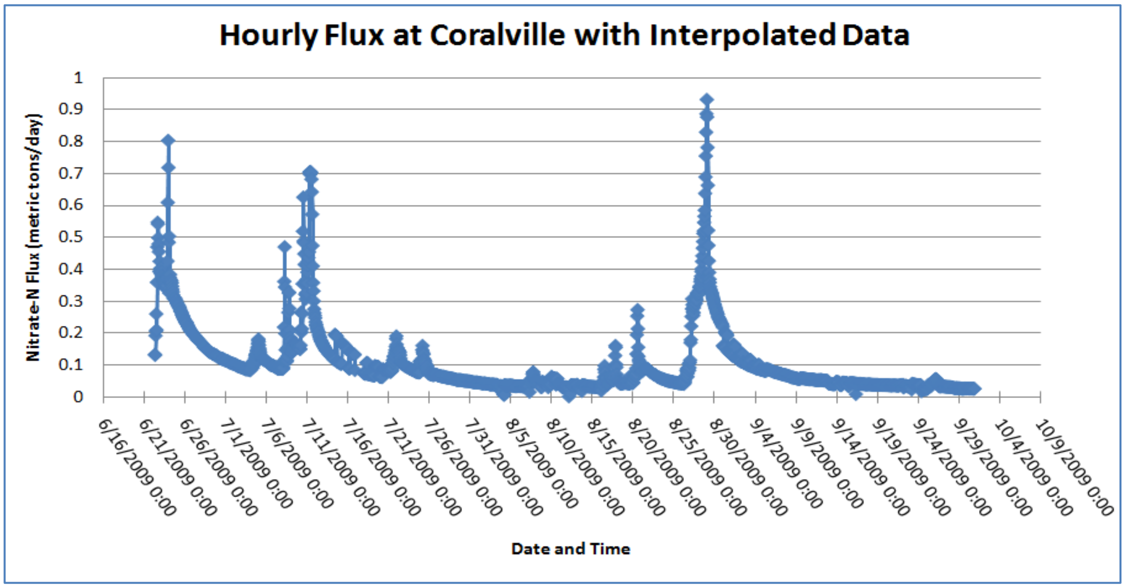

Figure 3.24: Plot of hourly flux with all holes interpolated with data using log (C) vs. log (Q) at the Coralville site

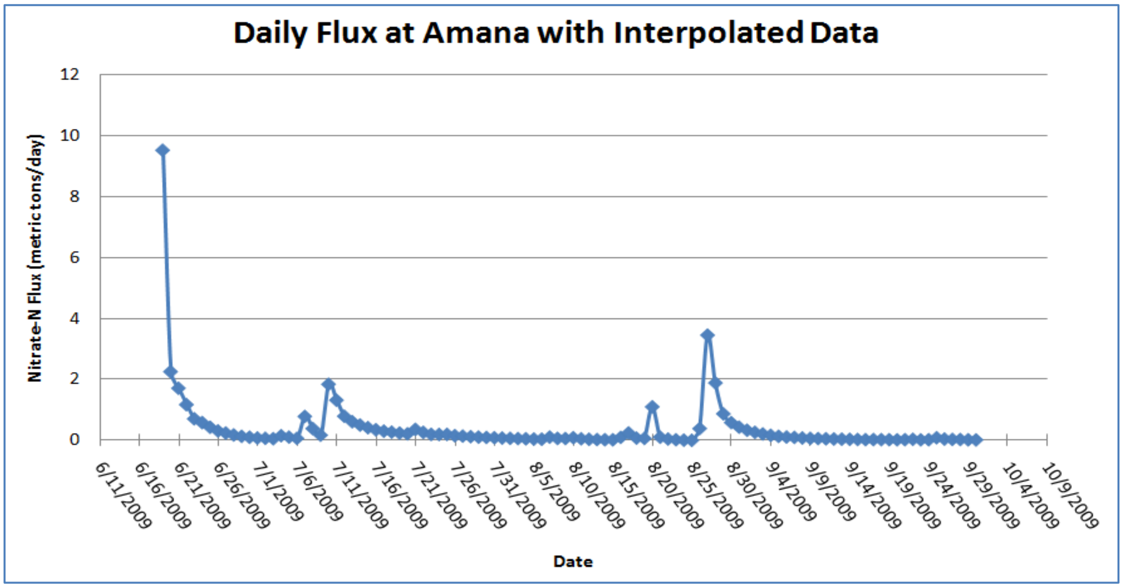

Figure 3.25: Plot of daily flux with all holes interpolated with data using log (C) vs. log (Q) at the SAC site

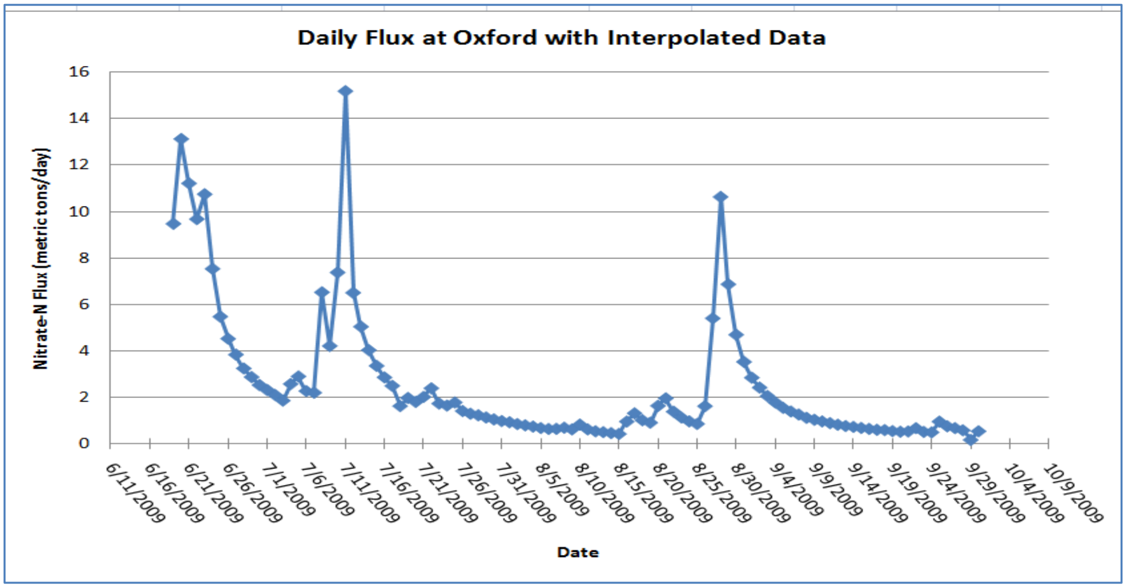

Figure 3.26: Plot of daily flux with all holes interpolated with data using log (C) vs. log (Q) at the Oxford site

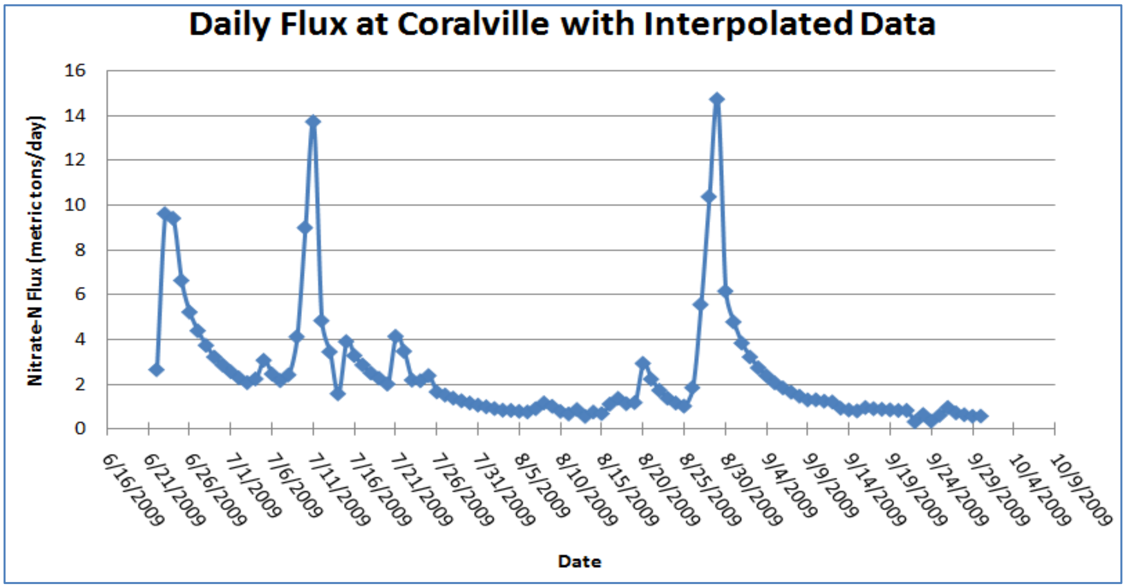

Figure 3.27: Plot of daily flux with all holes interpolated with data using log (C) vs. log (Q) at the Coralville site

By integrating under the continuous curve for the entire event on the 19th the total nitrate-N flux for the storm was found to be 1.82 metric tons for that day. The total nitrate flux calculated by integrating the curve generated with the regression equation from the log transformed plots was found to be 3.35 metric tons for the same event at Amana. The percent error between the two methods was calculated to be 45.6% which is quite large suggesting that the log transformation method may not bee the best way to fill in the gaps and future projects should try to develop a better way of filling in the data gaps. However this does not affect the results of this project to much since all three sites will be compared using the regression method and any error associated with this method will be accounted for in each sites flux calculations.

With the gaps in the flux plots filled using estimated flux data from the regression equations the total seasonal flux for each site was calculated for the 104 days from June 19, 2009 through September 30, 2009 at the SAC and Oxford. Since the Coralville site had 4 days of missing data (3 days of no nitrate-N data for June 19-21 and one day with out recorded flow for July 17) these gaps were filled in so that the time span would equal 104 days to match the Oxford and SAC sites. Using flow data collected at the Oxford site to fill in the missing flow on June 19-21 and July 17, because the Oxford flow record had less missing data than the Coralville site, and the log transformation plot generated for the Coralville site to estimate the missing nitrate-N concentrations. The total season flux for the selected time period for the SAC, Oxford, and Coralville sites using high frequency, hourly, and daily samples are reported in Table 3.1. A plot of nitrate-N loads (calculated using 15 high frequency data) vs. drainage area of each site is shown in

Figure 3.28. This plot shows that the calculated load increases as drainage area increases from the SAC to Oxford but then raises only slightly and levels off from Oxford to Coralville site. This means that the nitrate load on Clear Creek is not linearly related through the entire watershed.

Table 3.1: Calculated total seasonal flux in metric tons for all three deployment sites.

	Nitrate-N flux (metric tons)		
Station	Sample Interval		
	High Frequency	Hourly	Daily
SAC	34.11	33.54	41.87
Oxford	257.99	258.01	264.76
Coralville	273.84	252.55	283.69

This leveling off of the nitrate flux at Coralville may be due to fact that the bottom part the Clear Creek watershed being more urbanized than the upper portion. This would explain why the overall nitrate-N concentrations collected at Coralville (Figure 3.7) is less than the overall nitrate-N concentration collected at the SAC (Figure 3.1).

This decrease in overall nitrate concentration from the upper part of the watershed to the lower portion of the watershed may also be a product of the flatter topography which could support higher rates of denitrification if the soils are poorly drained.

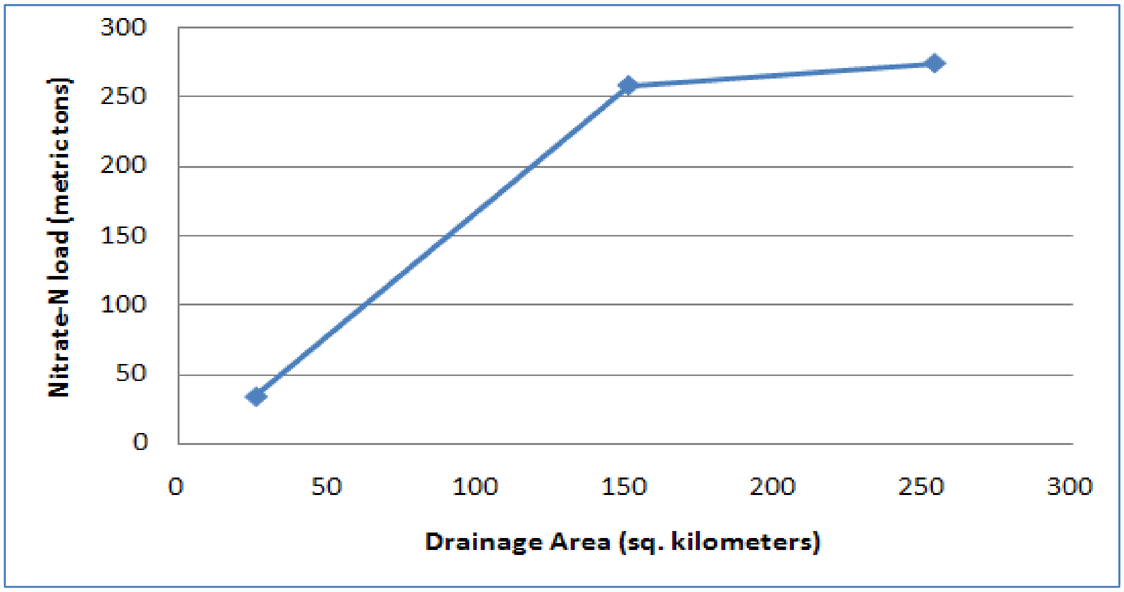

Figure 3.28: Plot of nitrate load calculated using high frequency data vs. drainage area

For comparison the total nitrate flux from each site was calculated again only the time frame was shortened to 101 days (June 22-September 30). This shortened length of time removes the portion of data from June 19-21 which contained all estimated data using flow from Oxford; however the filled in flow for July 17 using Oxford data was left in to make the 101 days a complete record. By removing the 3 days of June 19-21 the highest flow event was left out of this flux calculation to see if the relationship of nitrate-N load to drainage area shows the same non linear relationship between Oxford and Coralville as was mentioned above. Table 3.2 shows the calculated flux for this 101 day period.

Table 3.2: Calculated total seasonal flux in metric tons for all three deployment sites for the 101 days from June 22 through September-30.

	Nitrate-N flux (metric tons)		
Station	Sample Interval		
	High Frequency	Hourly	Daily
SAC	26	26	28
Oxford	224	224	230
Coralville	246	246	253

The flux for 15 minute data vs. drainage area was plotted again to see how the 101 day period compares to the 104 day period, the plot is shown in figure 3.29. This plot shows the same leveling off of nitrate-N load at the site with the highest drainage area, Coralville. By comparing the mass flux calculated for the 104 day time frame to the 101 day at the Coralville site the data shows that the plateau in Figure 2.28 is not caused by error using Oxford data to fill in missing Coralville data. This is due to the same plateau being present when the estimated flux at high flow using Oxford data is removed as sown in Figure 3.29.

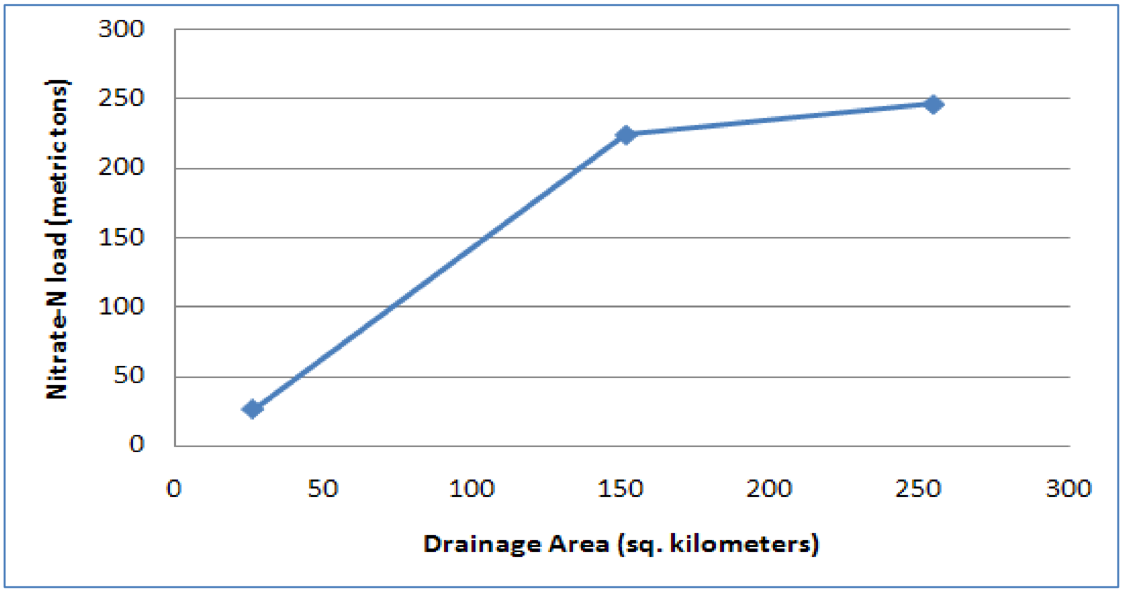

Figure 3.29: Plot of nitrate-N load calculated using high frequency data vs. drainage area for 101 days from June 22 through September 30

Looking at Table 3.1 at first glance it appears that there is a very small difference between the seasonal flux calculated using high frequency samples and the seasonal flux calculated using hourly samples. At the SAC flux calculated using high frequency samples is only 0.57 metric tons higher than the flux calculated using hourly samples. At Oxford the difference between high frequency and hourly samples is only 0.02 metric tons. All seasonal flux values for the Coralville site are lower than expected due to the four day deficit in the season. The total flux should be higher at the Coralville site because it is downstream of the other two sites and there is still drainage at the Coralville site that has not been accounted for at the other two sites. Even though the total flux is smaller than expected the results are still important because they follow the same trend as the SAC and Oxford sites. The difference between the flux calculated at Coralville using high frequency and hourly samples is 0.39 metric tons. The results from all three sites suggest that hourly sampling of nitrate-N is as effective as high frequency sampling of nitrate-N since the differences between flux calculated by the two methods never exceeded 1.0 metric ton.

The total seasonal flux calculated using samples taken only daily had larger total flux values compared to high frequency sampling. The difference between high frequency and hourly samples at the SAC was 7.76 metric tons. The difference between the two sample methods at Oxford and Coralville was 6.77 metric tons and 8.62 metric tons respectively. These results show that calculating the seasonal flux using grab samples collected once a day and average daily flow will produce total flux estimates that will be over 5 metric tons higher than the flux calculated using high frequency samples.

This over prediction of total flux is due to sample bias because one grab sample taken per day does not show the overall nitrate trend for an entire day because it will only represent one snapshot in time. However the average daily flow is representative of the flow from the entire day because it integrates all measured flow during the day. To make the daily flux plots more accurate multiple grab samples should be taken in a day and the results averaged just like the flow data. The data in table 3.1 also shows that flux and sample frequency are negatively correlated since the total flux for high frequency data is lower than the total flux for daily data samples.

Percent Error Comparisons

By looking only at the difference between the flux calculated using the three sampling regimes, as was discussed above, one does not get the best comparison since the difference only shows how far away one value was from another. A better way to compare high frequency sampling to hourly and daily samples is to look at the percent error between the total seasonal fluxes calculated by each method. The percent error is calculated using the following equation:

$$\%\ \text{Error} = [(\text{measured value} - \text{theoretical value}) / \text{theoretical value}]*100$$

The theoretical values in this case were defined as the total seasonal flux calculated using high frequency data, and the measured values were the total seasonal flux calculated using hourly and daily samples. The percent error results are shown in Table 3.2. Table 3.2 shows that the percent error between high frequency data and hourly data is quite low, in fact all sites have errors below 3%. The SAC has the highest percent error between hourly samples and high frequency samples at 2%, then Coralville at 0.2%, followed by Oxford at 0.1%. The percent errors were higher between high frequency samples and daily samples. Again the SAC had the highest percent error at 22.6%, next came Coralville at 3.53%, followed by Oxford at 2.62%. The results in table 3.2 show that the SAC has the highest percent error between high frequency samples and both hourly and daily samples. This higher error is most likely a product of the SAC being the flashiest of all three sites. This flashiness means that during storm events hourly samples are not frequent enough to capture the nitrate-N concentrations that occur at the peaks of the flow because this stream section can have large flows that only last for fifteen

Table 3.3: Percent error calculated using high frequency samples as the theoretical total seasonal flux and hourly/daily samples as the measured values

	Sample Interval	
	Hourly	Daily
SAC	2.0 %	22.6 %
Oxford	0.1 %	2.62 %
Coralville	0.2 %	3.53 %

minutes of less. A percent error of 22.6% for the comparison of high frequency sampling and daily sampling proves that the SAC is not a good location to use daily grab samples to gather nitrate-N concentration data for mass flux calculations if greater accuracy is needed. The low percent errors between hourly sampling and high frequency sampling at the Oxford and Coralville sites are a product of these two sites being less flashy than the SAC. These two sites will have high flows that last for intervals longer that fifteen minutes so the nitrate concentrations during high flow can be captured accurately using samples taken every hour. The percent error between daily samples and high frequency samples for the Oxford and Coralville sites are also relatively low, both below 5%, which also shows that daily grab samples could be an effective way of collecting nitrate-N concentration values for use in calculating nitrate-N flux through these two sites on Clear Creek.

CHAPTER IV

CONCLUSIONS

The land use in Iowa watersheds has drastically changed over the past 150 years. The native prairies that once dominated the landscape have been incorporated into the rich fertile soil used by Iowa farmers to grow this state to what it is today. The large scale effects of this land use change come at the cost of environmental quality. One of the most significant environmental impacts from watersheds dominated by row crop grain production is the degradation of water quality due to nutrient inputs.

It has been documented for almost 25 years now the effect of nitrogen inputs from the Midwest on the hypoxic “dead zone” that forms in the Gulf of Mexico every summer. This hypoxic zone has doubled in size since it was first identified in the mid-80s and continues to be a major topic of research because of the environmental and economic problems that it causes. The study of nitrate nitrogen fluxes and overall nitrogen contributions from large Midwest watersheds such as the Raccoon River have been conducted in the past. One such project by Schilling and Zhang (2004) found that the Raccoon River exports about 10% of the total nitrogen from Iowa. Nitrate data collected as weakly grab samples by the Des Moines River Water Quality Network was used as the inputs for Schilling and Zhang’s modeling project. Projects like this are great steps towards understanding where the nitrogen leaving Iowa is coming from but large rivers like the Raccoon are only part of Iowa’s surface hydrology. To understand where the nitrogen in surface water is coming from better water quality of the small creeks and tributaries that feed the larger rivers should be monitored.

Water quality monitoring of the small feeder streams in a watershed can help isolate the areas that are more prone to nitrate contamination. By identifying problematic areas within a watershed conservation organizations can design mitigation plans that are better suited for the topography, hydrology and soil type of that problematic area instead of trying to make a one size fits all mitigation plan for the entire watershed.

This study examined the feasibility of using high frequency remote sampling as a viable way to monitor nitrate concentrations for the purpose of calculating nitrate mass loading on Clear Creek, a tributary of the Iowa River. The Nitratax nitrate sensor by Hach Environmental was deployed at three sites on Clear Creek to collect nitrate-N concentration from late spring to early fall in 2009. These sites included one located near the Amana Colonies called the SAC, one near Kent Park in Oxford, and one in Coralville on Camp Cardinal Road.

The nitrate-N dataset for the 2009 did contain gaps where there was no nitrate-N concentration data. These gaps were filled using a linear regression between the base 10 log of the nitrate-n concentration and the base 10 log of the flow (cfs). The mass flux for nitrate-N was calculated using the dataset from high frequency samples with all gaps filed by the linear regression method. The resulting mass flux of nitrate-N for the 2009 sampling record was calculated to be 34.11, 357.99, and 244.38 metric tons for the SAC, Oxford, and Coralville sites respectively.

The collected data was then resampled artificially on the top of each hour and again once a day and the mass flux was calculated again. The results show that remotely sensed high frequency samples can be successfully collected on Clear Creek and can be used to calculate the total mass flux for a given season full of large flow events. The most significant finding however is that high frequency sampling on Clear Creek is the most beneficial at the South Amana Catchment near the Amana Colonies because this site is the most flashy. The percent difference between mass flux calculated using high frequency sampling and hourly sampling was 2%. When compared to the Oxford and Coralville site the percent difference between high frequency sampling and hourly sampling is 0.1% and 0.2% respectively. The study also found that there was no significant difference between mass flux calculated using hourly concentration values compared to high frequency samples at Oxford or Coralville since the percent error was less than 4% for the two sites respectively. This result suggests that hourly nitrate concentration data is acceptable to use in nitrate-N mass flux calculations for Iowa streams with a drainage area of approximately 270 square kilometers. There was however a large variation between calculating the total seasonal flux using daily samples compared to high frequency samples at the South Amana Catchment. The percent error between the two methods was 22% which is substantially higher than the comparison between high frequency and daily sampling at the other two sites. This large error at the South Amana Catchment shows that 15 minute high frequency data is necessary to keep the error in mass loading calculations under 20%. This large error was a product of the South Amana Catchment sites being flashier than the other two sites due to its narrow channel width and high velocities during high flow events.

For future work on Clear Creek with the Nitratax sensors investment in two sets of 20 watt solar panels like the ones used at the South Amana Catchment would be beneficial. These larger solar panels are the reason this site did not have as many days of missing data since the larger power output provided optimum charging even in cloudy conditions. By decreasing the amount of days with missing the total flux calculations for the deployment season will be more accurate since there will be less gaps filled by interpolation.

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APPENDIX

Figure

1-A. Plot of turbidity data collected for entire deployment at the SAC A-1

2-A. Plot of pH data collected for entire deployment at the SAC A-2

3-A. Plot of specific conductivity data collected for entire deployment at the SAC A-3

4-A. Plot of temperature data collected for entire deployment at the SAC........ A-4

5-A. Plot of battery voltage data collected for entire deployment at the SAC ... A-5

6-A. Plot of turbidity data collected for entire deployment at Oxford A-6

7-A. Plot of pH data collected for entire deployment at Oxford A-7

8-A. Plot of specific conductivity data collected for entire deployment at Oxford A-8

9-A. Plot of temperature data collected for entire deployment at Oxford.......... A-9

10-A. Plot of battery voltage data collected for entire deployment at Oxford A-10

11-A. Plot of turbidity data collected for entire deployment at Coralville.......... A-11

12-A. Plot of pH data collected for entire deployment at Coralville................... A-12

13-A. Plot of specific conductivity data collected for entire deployment at Coralville A-13

14-A. Plot of temperature data collected for entire deployment at Coralville A-14

15-A. Plot of battery voltage data collected for entire deployment at Coralville. A-15