AN ABSTRACT OF THE THESIS OF

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Title: _	Monitoring Water Quality to	Demonstrate the	Impact of Agricultural Best		
Management Practices along a Defined Segment of Eagle Creek					
	<u>,</u>	<u> </u>			
Abstract Approved:					

Several parameters related to water quality were monitored systematically during two years to assess the impact of recently implemented agricultural Best Management Practices (BMPs) along a defined segment of Eagle Creek in southern Lyon County (KS). Earlier studies, conducted by Kansas Department of Health and Environment (KDHE), identified several impairments to water-quality in Eagle Creek. Previously cited impairments included nutrient concentrations (nitrogen and phosphate containing compounds) exceeding Environmental Protection Agency (EPA) recommendations and dissolved oxygen concentration chronically below the EPA's threshold (5-mg/L) for the survival of most aquatic organisms.

Measurements in the current study included *in situ* and others were made on samples returned to the laboratory. Seasonal monitoring at base-flow conditions was done in fall, spring and summer. Three additional sets of data were collected during storm-event conditions. Storm-event sampling included additional sampling points to identify and/or isolate sources of nutrients carried into the stream as run-off from the surrounding agricultural operations. First-flush buckets were used to identify contributions from the cropland conservation buffer, before the runoff entered the Creek.

Most of the parameters exhibited a normal seasonal variation for base-flow measurements. During storm-events, turbidity, conductivity, nitrite, and nitrate

concentrations were higher in the first-flush buckets than in water entering the Creek as runoff. The trend for dissolved oxygen concentration shows sufficient increase so that the concentration is above EPA's 5-mg/L threshold for aquatic life.

The agricultural BMPs now utilized are improving the quality of the water by allowing sedimentation to occur before runoff. This not only reduces the amount of sediment entering the Creek, but it helps reduce nutrient flux into the stream since some nutrients tend to adsorb to the sediments. Monitoring of parameters should continue to provide confirmation that the agricultural BMPs have improved the water quality of Eagle Creek.

Monitoring Water Quality to Demonstrate the Impact of Agricultural Best Management Practices along a Defined Segment of Eagle Creek

A Thesis

Presented to

the Departments of Physical Sciences

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In Partial Fulfillment
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Master of Science

by Brenna M. Zimmer May 2011

	Approved by the Department Chair
	Committee Member
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Background

Introduction

Water is a necessary resource for environmental and societal processes. The best available data on global water supply estimates that 96.5% of all Earth's water is in the oceans and seas, leaving less than 4% as fresh (non-salt) water. Additionally, approximately 69% of the fresh water is held in ice caps, glaciers and permanent snow cover. This leaves less than 30% of all fresh water available for human use, and this supply is not equally distributed around the globe¹. According to the United Nations, the world is currently appropriating 54% of all available fresh water. They also report that water withdrawals are estimated to increase by 50% by 2025 in developed countries and by 18% in developing countries. If these trends continue, by 2025 800 million people will be living in a region with absolute water scarcity and two-thirds of the world's population could be under stress conditions². Actions that impact the quantity and quality of water should be of concern to everyone.

The concerns related to use, protection and adequacy of water resources are complex including the scientific, technological and social/political perspectives. The quality of water for human use and consumption is one of these concerns. The degree of quality required depends, of course, on the intended use with drinking water commanding the highest quality standards. Nash, in "Water in Crisis", writes that impairments of water quality may be categorized as toxic metals (such as lead, arsenic and mercury); herbicides/pesticides and other synthetic organic compounds; and nitrogen compounds³.

Nitrogen-containing compounds in water are of special concern. Nitrogen can occur in both organic and inorganic with both forms causing harm to humans, especially the inorganic nitrate anion. According to the EPA, nitrate and nitrite in the water supply beyond the maximum contaminant level can cause death in infants if ingested⁴. In surface waters, such as lakes and rivers, where the environment is aerobic, nitrogen principally exists as the fully oxidized nitrate. In anaerobic conditions, nitrogen is in the fully reduced form of ammonia or the ammonium ion. In specialized cases, the nitrite ion will occur in anaerobic environments; usually due to waterlogged soils where the nitrogen does not get converted to ammonia fully because the environment is not fully reducing. Importantly, most plants only absorb nitrogen as the nitrate ion⁵. Thus, any ammonia addition to the water supply via surface runoff must be oxidized to nitrate before it can act as a nutrient to plant life⁵.

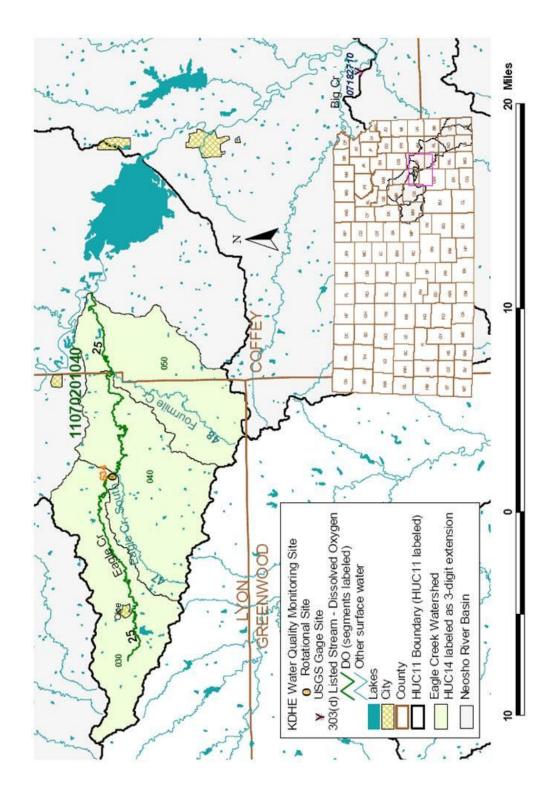
To achieve water quality standards to support various uses, maximum pollutant loads, or Total Maximum Daily Loads (TMDLs), are established. The EPA defines a TMDL as the calculated maximum amount of a pollutant that a water body can receive and still meet water quality standards⁶. Additionally, the Safe Drinking Water Act (SDWA) ensures the quality of Americans' drinking water. This law requires many actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs and ground water wells⁷. The EPA has issued a set of legally enforceable standards for most contaminants to evaluate water quality and ensure clean drinking water⁴.

Agricultural best management practices (BMPs) are put in place to improve and protect water quality⁸. Examples for crop land include no-till systems and the placement of grassed waterways to prevent soil erosion and concurrently retard fertilizer/pesticide

runoff into streams⁹. For grazing pastures, fencing to prevent cattle from entering the stream prevents fecal waste from directly entering a stream. Water-entry control (conservation buffer or grassed waterway), runoff management, and use of waste storage/treatment facility are BMPs for barnyard and feedlots that help protect water-quality¹⁰. A conservation buffer is a grassed waterway which acts as a barrier between land and water by capturing and eliminating pollutants from entering surface waters⁸.

To address water quality concerns, many states, including Kansas, have developed Watershed Restoration and Protection Strategy (WRAPS) plans. There are four phases to the WRAPS process; they include development, assessment, planning and implementation. Development is where interested stakeholders are recruited to determine interest and documentation of stakeholder information. During the second phase, assessment, watershed conditions and trends are reviewed, and expectations for the watershed and management measures in use are identified. In the next phase, planning by establishing realistic goals, identifying actions to achieve goals and estimations of costs and implementation of a strategy are performed. Finally, implementation includes securing resources to execute the plan as well as monitoring and documenting the progress of the plan¹¹.

The Eagle Creek watershed (HUC 11070201040), in Lyon and Coffey counties of Kansas, is predominantly a farming/ranching community. Figure 1 shows that Eagle creek is a part of the headwaters of the Neosho River watershed (HUC 11070201) which in turn feeds into the Missouri River. Designated uses of the stream include the support of expected aquatic life, secondary contact recreation, and food procurement for downstream users.



Inset: Map of Kansas, highlighting the Eagle Creek Watershed and the study area within the Neosho watershed. Figure 1: The position of Eagle Creek within Eagle Creek Watershed, located in the Neosho River Basin.

In a study conducted by the Kansas Department of Health and Environment (KDHE) between 1993 and 2001, water quality impairments to designated uses of Eagle Creek were identified¹². For Eagle Creek, these are low dissolved oxygen and excessive copper. The water quality standard for dissolved oxygen (DO) is 5 mg/L to support aquatic life. KDHE found that between 1997 and 2001 the DO levels were chronically below the standard. Thus, Eagle Creek does not have adequate capacity to support aquatic life¹². Influences from non-point sources, including extensive livestock and crop production land uses, have been identified as likely causes of the impairments.

To address the impairments, a watershed restoration and protection strategy (WRAPS), was created. The Eagle Creek WRAPS (ECWRAPS) is a stakeholder-driven effort. The stakeholders identified BMPs that landowners and producers in the watershed would most likely accept and implement to address water-quality impairments.

Information and education, conservation buffers, and grazing management were ranked the three most important strategies for implementation. Progress has been made in implementing the designated BMPs. Grazing management and livestock management have been completed within a portion of the Eagle Creek watershed.

Study Site Description

BMPs have been put in place on both sides of a segment of Eagle Creek approximately a half-mile in length out of approximately 22 mile total length of Eagle Creek, as shown in Figure 2. On the north bank a grassed waterway (conservation buffer) has been placed in the cropland. Also, a diversion pipe was positioned on the north bank to control water entry. Fencing along the south bank prevents cattle from entering the streambed from the pasture.

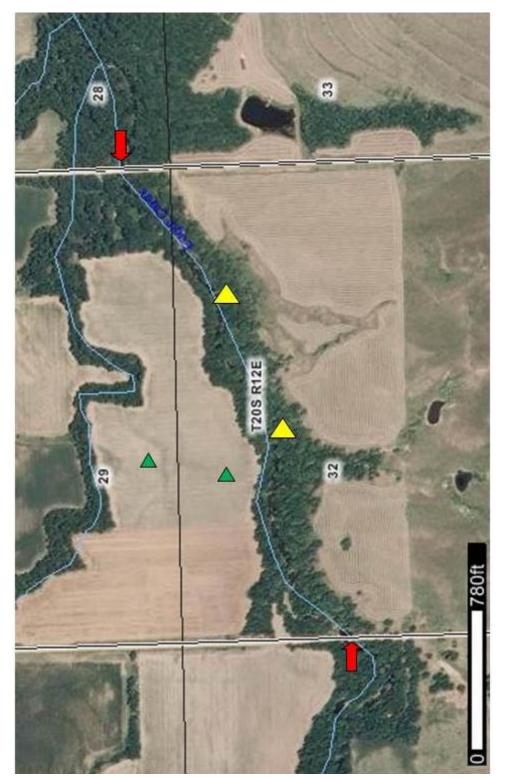


Figure 2: Aerial view of study site, Eagle Creek, south Lyon Co., KS.

- Represent the upper and lower limits of the study site (Primary sites, S1 (west limit) & S6 (east limit)). Represent the first flush storm event sampling sites (S2 (north bucket) & S3 (south bucket)).
- Represent storm event sampling sites, post diversion pipe and pasture contribution (S4 (post-diversion pipe) & S5 (pasture contribution)).

Flow is from west to east. The west boundary is a low-water crossing, giving easy access to the stream. On the east, the county road bridge gives access to the stream. Landowner agreement allows sampling at other points along the stream and in the grassed waterway in the cropland.

Study Goals and Design

To evaluate overall effectiveness of BMPs, two primary sample collection sites were selected for base-flow and four additional secondary sites for storm event contributions. Base-flow exists when the stream is not receiving runoff. For this study, a storm event was defined as precipitation of at least 0.5 inch. The primary sampling sites were the west (upstream) and east (downstream) ends of the study segment. Two of the secondary sites were located in the cropland grassed waterway, allowing measurement of parameters in runoff water before it entered the stream. Another secondary site was located just downstream from where the diversion pipe flow joined the stream. The final secondary site was immediately downstream from a major entry point of runoff from the pasture.

EXPERIMENTAL

Materials

Chemicals

Ascorbic acid was obtained through Acros Organics (Thermo Fisher Scientific, Fair Lawn NJ) and N-(1-Naphthyl)-ethylenediamine HCl were obtained from Fisher Scientific (Pittsburg, PA). Sulfanilamide was acquired from Matheson Coleman and Bell (Cincinnati, OH). Purified water for reagent and standard solutions came from a Millipore Synergy ASTM Type 1 system (Billerica, MA). The filters used for determination of total suspended solids (TSS) were Hach 47 mm Glass-Microfibre Discs (Loveland, CO). Standards for calibration of probes, sensors and ion selective electrodes came from Vernier (Beaverton, OR). All other chemicals were of reagent grade or better and used as received.

Equipment

In situ data was obtained using Vernier Labquest® hand-held data loggers, in conjunction with Vernier ion selective electrodes, sensors and probes (Vernier Software and Technology, Beaverton, OR). The hand-held data loggers could accept data from up to four different sensors at one time. The sensors used included temperature, conductivity, pH, flow rate, turbidity, dissolved oxygen, ammonium and nitrate ions (also from Vernier). Sensor response time was less than 30 s for all sensors except flow rate, which required 30-60 s to produce a stable read-out.

Ex situ colorimetric measurements were carried out using a ThermoScientific Genesys 20 Spectrophotometer (Waltham, MA). A three-manifold vacuum filtration

apparatus was used to filter samples for determination of total suspended solids (Fisher Scientific, Pittsburg, PA). First flush buckets were assembled according to the instructions obtained from Nye County Nuclear Waste Repository Project Office ¹³. The sand used in the buckets was collected between Tyler Equivalent 16 Mesh and 32 Mesh U.S.A. Standard Testing Sieves.

Procedures

Sample collection

The primary sampling sites for base-flow collections were the upstream and downstream limits of the designated segment. Four secondary sampling sites between the upstream and downstream limits were selected to separate the contributions of various influx points during storm events. Base-flow sample collections were made twice each in fall 2009 and 2010, once in spring 2010 and once in 2011, and twice in summer 2010. One base-flow sample collection was made in the winter (2010-2011). Storm event sample collections were made three times in fall 2010.

In situ analyses

In situ analyses were performed and recorded in the field. Each parameter was performed in duplicate or triplicate.

Conductivity, Temperature and Flow Rate

Determination of conductivity, temperature and flow rate was carried out using the corresponding probe. Conductivity and temperature were measured by placing the probe in the stream at a depth of approximately 5 cm and the reading recorded. Flow rate

was performed in a similar manner, except the probe was placed at a depth of approximately 30 cm from the surface of the water.

Dissolved Oxygen

Measurement of dissolved oxygen (DO) was carried out using a DO sensor. The probe was calibrated before each sample collection according to the manufacturer's specifications. Briefly, the membrane was soaked in DO Electrode Filling Solution for 30 min prior to use and left to soak in reverse osmosis, RO, water. To calibrate, the electrode was placed into the Sodium Sulfite Calibration Solution and a value of 0 mg/L was recorded. Then, the probe was placed in the calibration bottle. After the voltage read-out stabilized, a value of saturated dissolved oxygen was entered according to the table based on barometric pressure and temperature ¹⁴. Samples were measured by placing the probe in a sample of water and gently swirling until there was a stable digital read-out. The probe was stored in a bottle of RO water when not in use.

рН

pH was measured using a pH probe. pH was quantified by placing the probe in stream for approximately 5-10 s until a stable reading could be recorded. The probe was calibrated every 3-4 months. It was calibrated by placing the probe in pH=7.00 standard and entering the value, followed by placing the probe in pH=4.00 entering the value. The probe was stored in a 1 M KCl solution between use.

Turbidity

Determination of turbidity was carried out using the turbidity sensor. The sensor was calibrated before each sample collection according to the manufacturer's

specifications. Briefly, the 100 NTU (Nephelometric Turbidity Units) standard gently shook multiple times and then inserted into the sensor. Then, a cuvette containing RO water was placed in the sensor, representing 0 NTU and completing the calibration. Samples were measured by filling a glass cuvette with a representative water sample, placing it in the sensor and recording the digital readout. No special directions for storage of the sensor.

Ion Selective Electrodes

Ion selective electrodes (ISEs) were used to determine ammonium and nitrate levels. Before use, each electrode was calibrated. Briefly, the NH₄⁺ and NO₃⁻ electrodes were soaked for 30 minutes in the high concentration standard (100 mg/L NH₄⁺ and 100 mg/L NO₃⁻ as N solutions). Then, the electrodes were removed from the solution, rinsed with RO water and placed in the low concentration standard (1 mg/L NH₄⁺ and 1 mg/L NO₃⁻ as N solutions) to complete calibration. To use the ISEs, the electrode was placed in a sample of water and swirled until there was a stable digital read-out.

Ex situ analyses

All sample bottles were 300-mL glass biological oxygen demand (BOD) bottles and 1-L Nalgene bottles and were rinsed with a 1:1 HNO₃ solution and then triple rinsed with RO water. Samples for phosphate, nitrite and biological oxygen demand were collected in 300-mL glass BOD bottles. Samples for total suspended solids were collected in 1-L Nalgene bottles. All samples collected were returned to the lab in closed bottles and kept at 4°C until analyzed, a period not exceeding one week.

Phosphate

Determination of phosphate was carried out by the "Ascorbic Acid Method" in Standard Methods for the Examination of Water and Wastewater (4500-P E., pgs 4-146-147)¹⁵. Samples were analyzed within 72 hrs of collection. Combined reagent for phosphate analysis, included 5N sulfuric acid, potassium antimonyl tartrate solution and ammonium molybdenate solutions and were prepared and stored individually in glass-stoppered bottles at room temperature until used. Ascorbic acid solution (0.1 M) was prepared weekly and refrigerated until used. Immediately prior to sample analysis the combined reagent was prepared by mixing 50 mL of sulfuric acid, 5 mL of potassium antimonyl tartrate solution, 15 mL of ammonium molybdenate solution and 30 mL of ascorbic acid solution. To analyze the sample, 8 mL of combined reagent was added to each 50 mL sample. After at least 10 minutes, but no more than 30 minutes elapsing, the sample was read at 880 nm on a Genesys 20 spectrophotometer.

Nitrite

Determination of nitrite was carried out using the colorimetric method described by the *Standard Methods for the Examination of Water and Wastewater* (4500-NO₂⁻, pgs 4-112-114)¹⁵. Samples brought back to the lab for analysis were kept at 4°C for 24 h, but not exceeding 72 h. The color reagent was prepared by adding 100 mL of 85% phosphoric acid and 10 g sulfanilamide to 800 mL of RO water in a 1 L volumetric flask. Then, 1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride was added and diluted to the mark. To analyze the sample, 2 mL of color reagent was added to each 50 mL sample. Between a 10-120 minute period the sample was read at 543 nm on a Genesys 20 spectrophotometer.

Biological oxygen demand

Determination of biological oxygen demand (BOD) was carried out using the Vernier dissolved oxygen probe. Water samples were collected in 300-mL glass BOD bottles, wrapped in foil and kept in a dark cupboard for five days. On the fifth day the dissolved oxygen was measured. To calculate the BOD, the final dissolved oxygen value was subtracted from the initial dissolved oxygen value.

$$BOD = DO_{initial} - DO_{final}$$

Total suspended solids

Determination of total suspended solids was carried out by the gravimetric method described in the *Standard Methods for the Examination of Water and Wastewater* (2540 D, pgs 2-57-58)¹⁵. Briefly, a filter was dried to constant mass at 105°C. A manifold vacuum filtration apparatus was used to filter 450 mL of each sample. The filters with residue were weighed to constant mass. Calculation for TSS was performed according to the following equation:

$$\frac{mg}{L}$$
 total suspended solids = $\frac{(A-B) \times 1000}{\text{sample volume, mL}}$

Where A is the mass of the filter and residue and B is the mass of the dry filter.

Results/Discussion

Flow rate

The base-flow conditions varied widely depending on the season and location. The upstream sampling site generally gave a higher flow rate than the downstream limit, see Table I. The water pools at both limits; however, the pool at the downstream limit is much shallower and almost stagnant; however, the creek flow increases further east of the study segment. The pool at the upstream limit is deeper and exhibits greater movement. In April 2010, it was observed that a very large tree had fallen across the creek in between sites S4 and S5. This separated the two ends of the creek resulting in no measureable flow downstream. About a year later, March 17, 2011, the same general trend was still observed.

Temperature

Base-flow temperature was recorded seven times over a two year period for the upstream and downstream limits. Figure 3 shows temperature following a normal seasonal variation. Figures 4 and 5 present the temperature range measured during storm events for the creek and first flush buckets, respectively. Again, recorded values show the expected seasonal variation.

pН

Figure 6 shows the measured pH during base-flow conditions for the creek. There was not a value recorded for October 17, 2009 because the sensor had not been obtained at that time. Additionally, the average value for November 4, 2009, shown in Table I, of 6.94 ± 0.02 is lower than the other recorded values. The most likely reason is that the

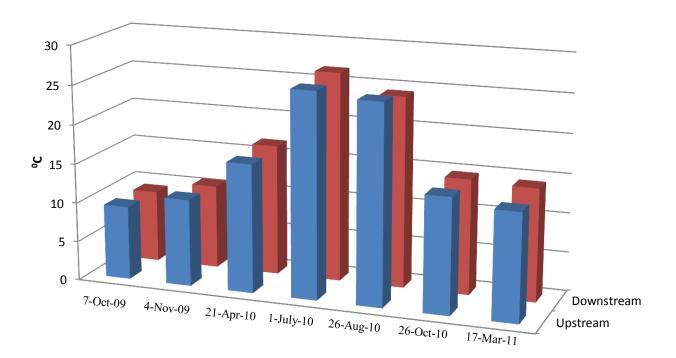


Figure 3: Water temperature at upstream and downstream sites during base-flow sampling.

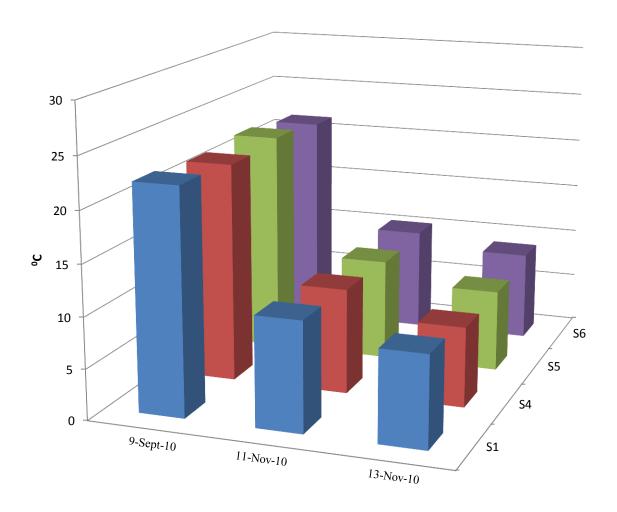


Figure 4: Water temperature for creek sites, S1, S4, S5, & S6 during storm event sampling.

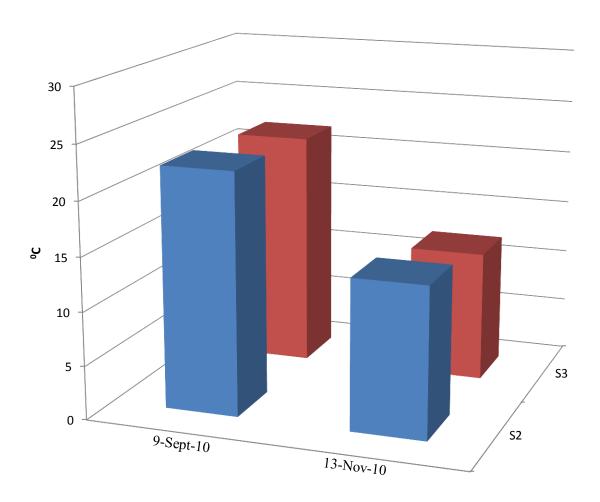


Figure 5: Water temperature for first flush buckets, S2 & S3 during storm event sampling.

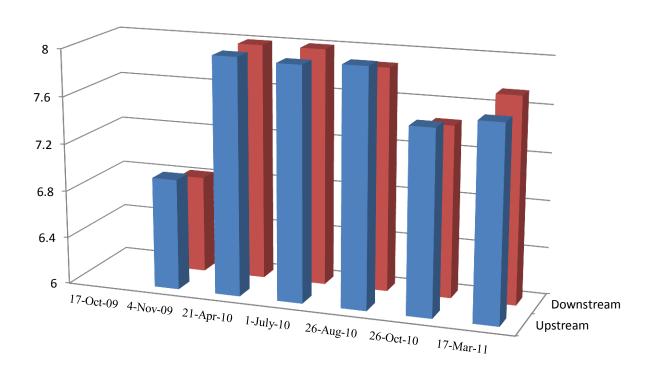


Figure 6: pH at upstream and downstream sites during base-flow sampling

sensor was a different one than had been previously used and through subsequent employment of the sensor have found it to take longer to equilibrate. Figures 7 and 8 show the pH values during storm events for the creek and first flush buckets. These values are close to the expected pH values of 7-8 for creeks and ground waters⁵.

Turbidity

Turbidity, a measurement of the cloudiness of water, was recorded in units of Nephelometric Turbidity Units⁴. The base flow turbidity varied, depending on the season (Figure 9). During the warmer, drier months the turbidity is lower. On October 17, 2009, November 4, 2009 and March 17, 2011 the turbidity values were much higher. This could be due to residual soil erosion caused by storm events happening during those seasons. Prior to the base flow measurement taken in March 2011, a series of snow storms left a lot of snow on the ground. After melting, there would be a higher influx of water causing more soil to be brought into the water; hence, the higher turbidity recorded. Turbidity recorded during storm events is given in Figures 10 and 11. As with the seasonal variation observed, there should be higher levels of turbidity detected during a storm event due to the increased soil runoff caused by the rain flow. On September 9, 2010 and November 13, 2010 this was observed. On November 11, 2010 the recorded values are much lower. The storm event for this date does not qualify as base-flow conditions or storm event conditions; rather, a "pre-storm event" condition. There was a slight drizzle, but not enough to disturb the soil to the point of carrying soil or sediment in the runoff. Additionally, the turbidity levels of the buckets are elevated; especially so during the November 13, 2010 storm. As the buckets are situated in the conservation buffer, elevated readings were expected here.

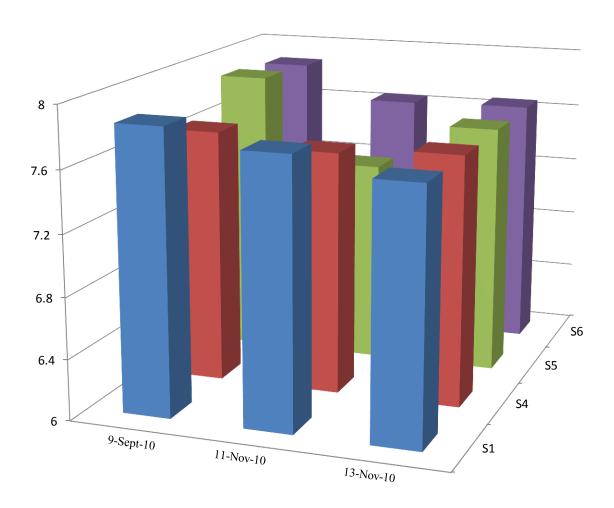


Figure 7: pH for creek sites, S1, S4, S5, & S6 during storm event sampling.

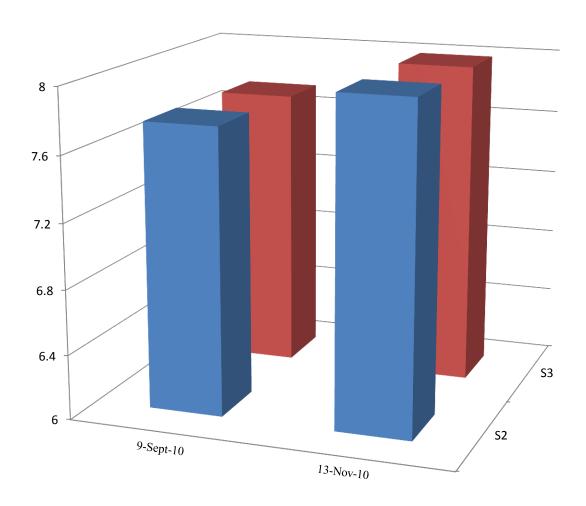


Figure 8: pH for first flush buckets, S2 & S3 during storm event sampling.

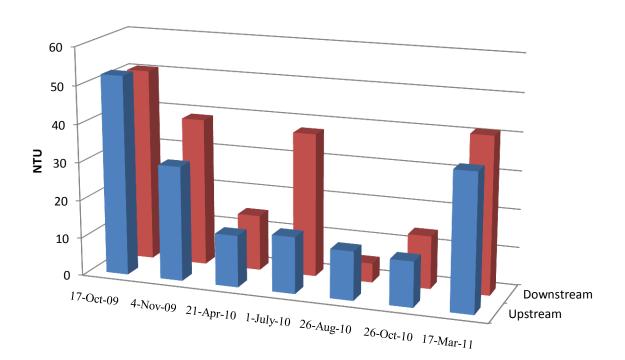


Figure 9: Turbidity at upstream and downstream sites during base-flow sampling.

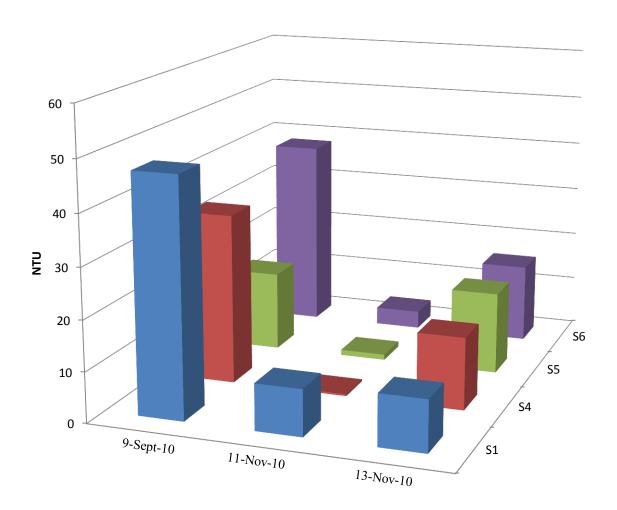


Figure 10: Turbidity for creek sites, S1, S4, S5, & S6 during storm event sampling.

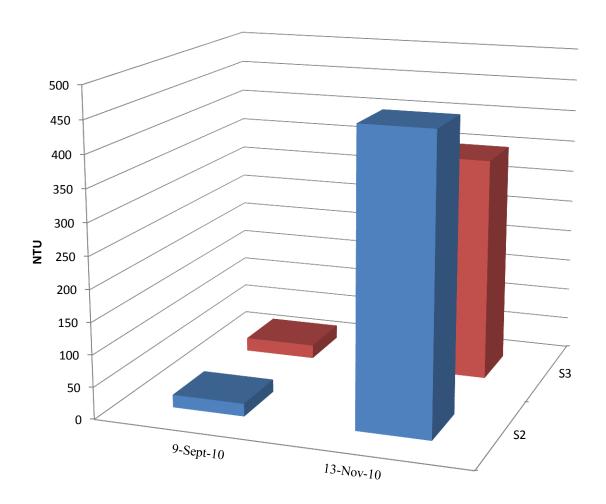


Figure 11: Turbidity for first flush buckets, S2 & S3 during storm event sampling. Note that the vertical axis scale is different than in Figures 0 and 10 to accommodate the approximately ten-fold higher values measured on 13 November 2010.

Conductivity

According to the EPA, conductivity is a measure of water to pass an electrical current ¹⁶. Furthermore, the conductivity is affected by inorganic materials dissolved in water. Thus, nitrate and phosphate anions (along with additional ions not measured in this study) affect the water's conductivity. Conductivity is also affected by temperature and is generally higher in warmer weather. This general trend was observed for baseflow conditions as shown in Figure 12. Levels were elevated during storm events, as was expected, see Figure 13. However, the values recorded on November 13, 2010 for both first flush buckets was much lower, 102 and 104 µS/cm, for S2 and S3, as shown by Table II and Figure 14. As conductivity increases with more dissolved inorganics present, elevated levels should have been observed with the elevated turbidity levels.

Total suspended solids

Base-flow conditions were measured three times over the two-year study and no storm event measurements were made. Figure 15 gives the measured base-flow values. The November 4, 2009 and July 1, 2010 measurements are close in value; however, these measurements to not correlate to either conductivity or turbidity recordings.

Ammonium

Ammonium, at concentrations usually found in drinking waters, is not directly harmful to humans¹⁷. However, if the water with higher than expected concentrations of ammonium ions is to be chlorinated, then ammonium present in the water supply may pose a threat through the production of various chloroamines.¹⁸. Ammonium interferes with chlorine, reducing its disinfecting abilities; thus, it is important to keep ammonium concentration low. The recorded values for ammonium did not exhibit an obvious trend

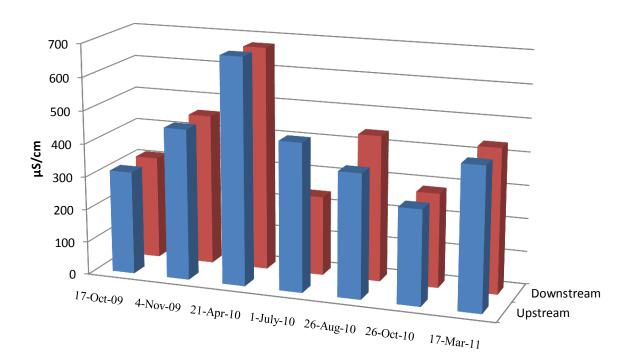


Figure 12: Conductivity at upstream and downstream sites during base-flow sampling.

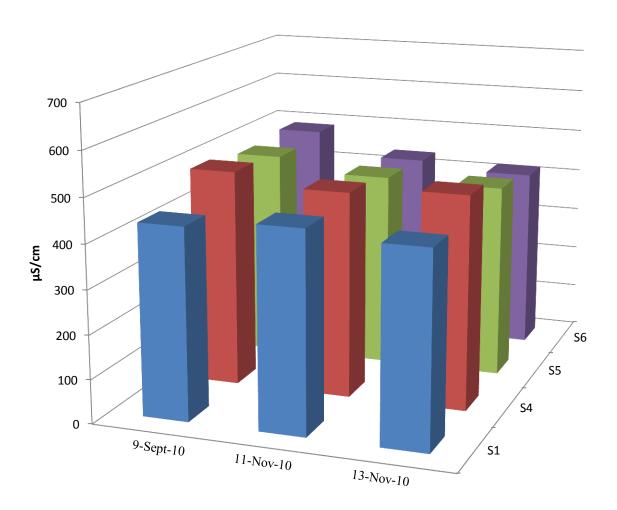


Figure 13: Conductivity for creek sites, S1, S4, S5, & S6 during storm event sampling.

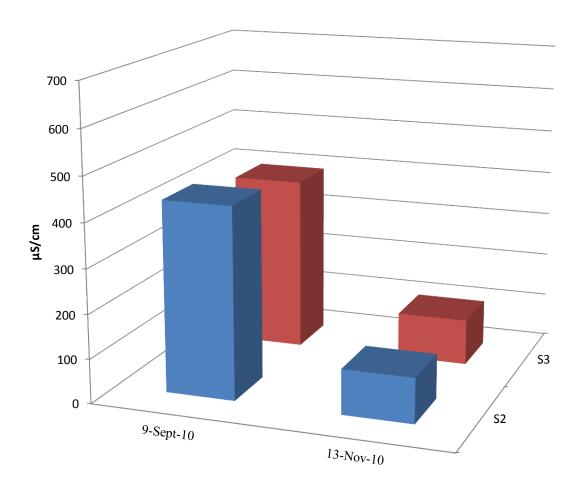


Figure 14: Conductivity for first flush buckets, S2 & S3 during storm event sampling.

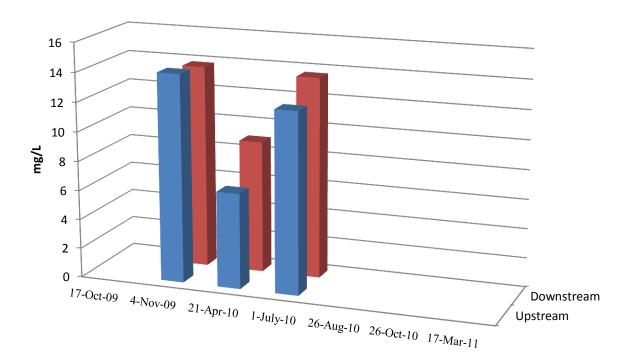


Figure 15: Total suspended solids at upstream and downstream sites during base-flow sampling.

for base-flow conditions. Values were never higher than 2 parts per million, (mg/L), as shown in Figures 16, 17 and 18. In some cases, values were undetectable by the sensor (registered as a zero). Also, concentrations were neither higher nor lower during storm events than during base-flow conditions. This could indicate that fertilizer runoff is at a minimum or that the ammonium has been oxidized to nitrate or partially oxidized to nitrite.

Nitrate

Base-flow concentrations for nitrate exhibit the same low-concentration conditions as ammonium, (see Figure 19). Additionally, the contributions into the creek during a storm event remained low, as can be seen in Figure 20. However, during the September 9, 2010 storm event first flush buckets showed a huge spike in nitrate concentration, illustrated in Figure 21. This could be caused by the ammonium from fertilizers becoming oxidized. Again, it is important to note that the spike was only observed in the conservation buffer and not in the creek during this storm event or any storm event. The readings for the buckets during the November 13, 2010 storm event were slightly elevated, but not the same spike as observed in September. Never in this study did nitrate levels exceed the maximum contaminant level (MCL) of 10-ppm designated by the EPA⁴.

Nitrite

The base-flow values for nitrite are shown in Figure 22. There is not a reading for October 17, 2009 because the colorimetric method had not yet been fully implemented. The recorded values are much lower than that for either ammonium or nitrate. As nitrite occurs from either incomplete oxidation or reduction, a low value was expected. During

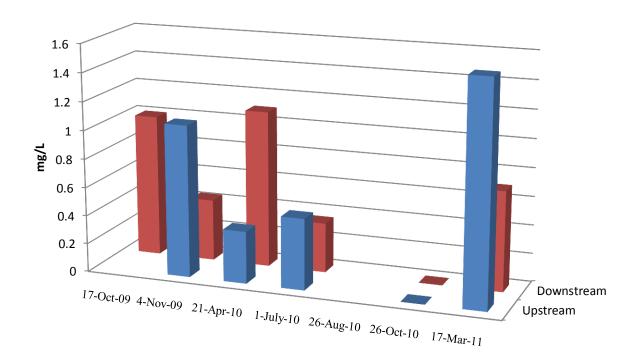


Figure 16: Ammonium at upstream and downstream sites during base-flow sampling.

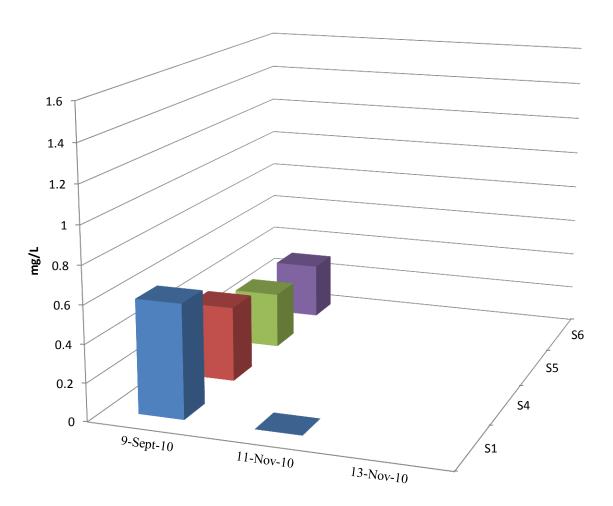


Figure 17: Ammonium for creek sites, S1, S4, S5, & S6 during storm event sampling.

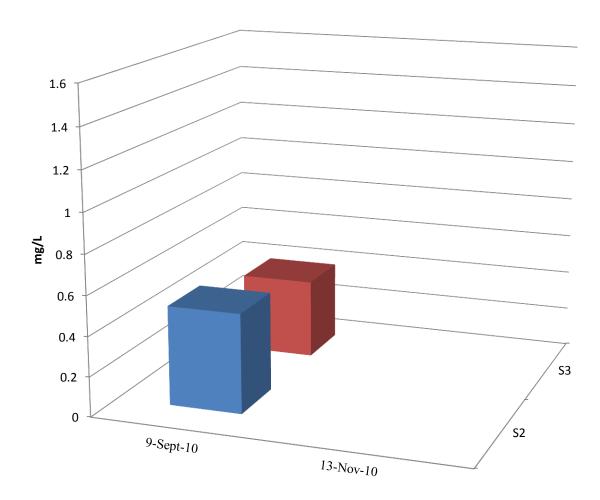


Figure 18: Ammonium for first flush buckets, S2 & S3 during storm event sampling.

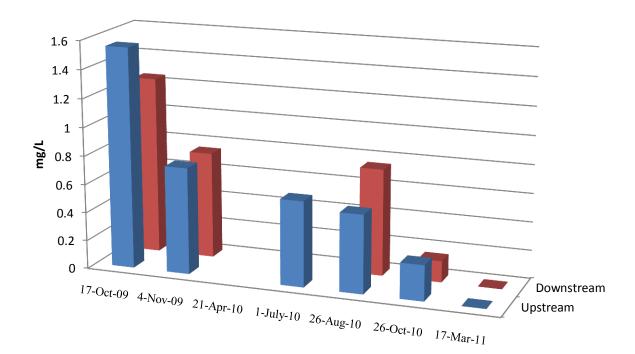


Figure 19: Nitrate at upstream and downstream sites during base-flow sampling.

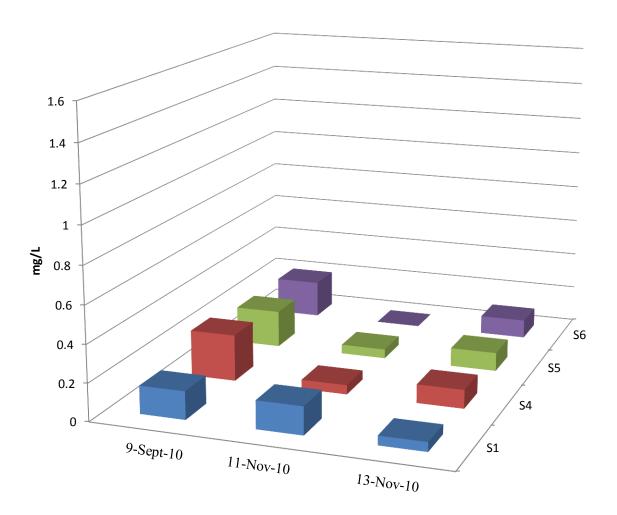


Figure 20: Nitrate for creek sites, S1, S4, S5, & S6 during storm event sampling.

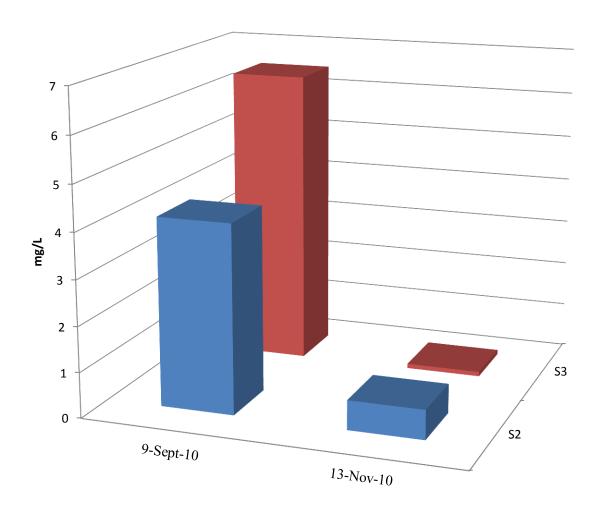


Figure 21: Nitrate for first flush buckets, S2 & S3 during storm event sampling. Note that the vertical axis scale is different than in Figures 19 and 20 to accommodate the higher values measured on 9 September 2010.

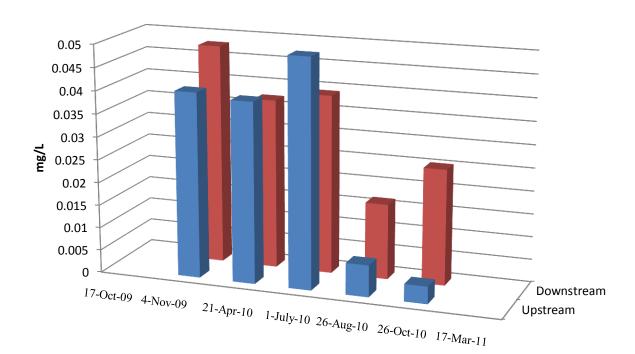


Figure 22: Nitrite at upstream and downstream sites during base-flow sampling.

storm events, the observed concentrations in the creek were close to base flow conditions, just slightly elevated (Figure 23). As observed with nitrate, the bucket readings were again higher than every other location (see Figure 24). In fact, there was almost a 10-fold increase in nitrite levels on November 13, 2010 in the first flush buckets. As previously discussed, nitrite ion tends to occur in waterlogged soils which is exactly the type of environment found in the buckets during a storm event. Thus, elevated concentrations were expected and observed.

Phosphate

As with nitrate, a reading was not available for the October 17, 2009 base-flow measurement. Figure 25 shows the recorded phosphate concentrations for base-flow conditions. Phosphorus is a necessary element for plant and aquatic life. It does not become harmful to animals or humans until concentrations exceed 0.1 mg/L. The only values approaching that maximum were from the November 4, 2009 base-flow reading. Every other recorded value was much lower, including storm events (Figures 26 and 27). In fact, the measurements are a little below the healthy range of 0.01-0.03 mg/L, for surface waters to support plant and aquatic life¹⁹. The values recorded during storm events were much lower than those recorded during base-flow. Phosphates normally enter surface waters through fertilizer and soil runoff; however, this study shows a lack of phosphates entering the water during runoff.. There are large quantities of limestone visible along the creek bed throughout the segment of Eagle Creek. Calcium phosphate is insoluble. It is possible that the incoming phosphate reacts with the limestone to form insoluble calcium phosphate, accounting for the low concentrations observed.

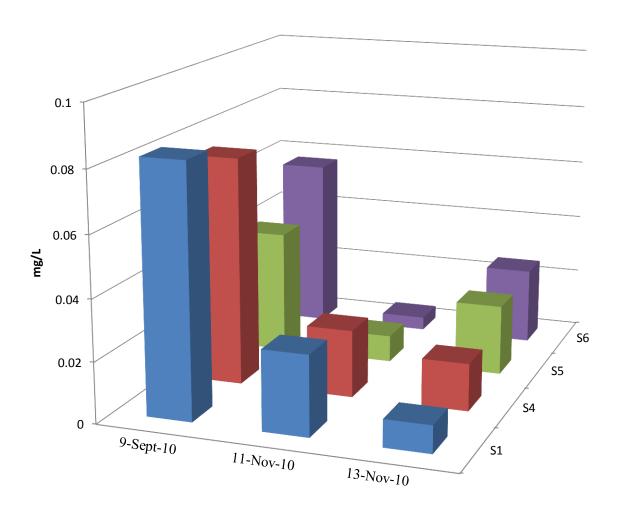


Figure 23: Nitrite for creek sites, S1, S4, S5, & S6 during storm event sampling.

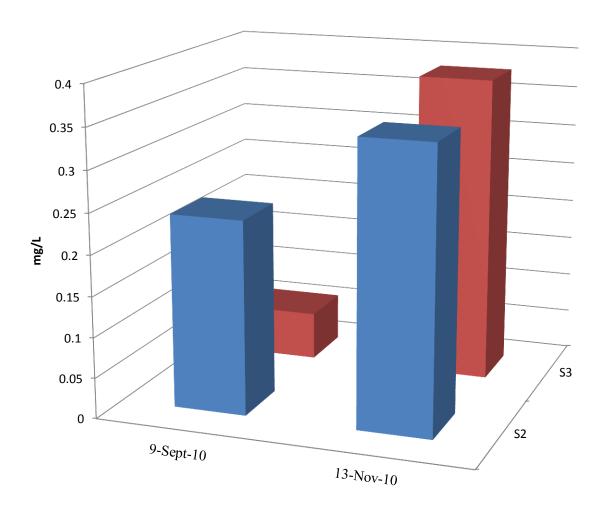


Figure 24: Nitrite for first flush buckets, S2 & S3 during storm event sampling. Note that the vertical axis scale is different than in Figures 22 and 23 to accommodate the higher values measured on 9 September and 13 November 2010.

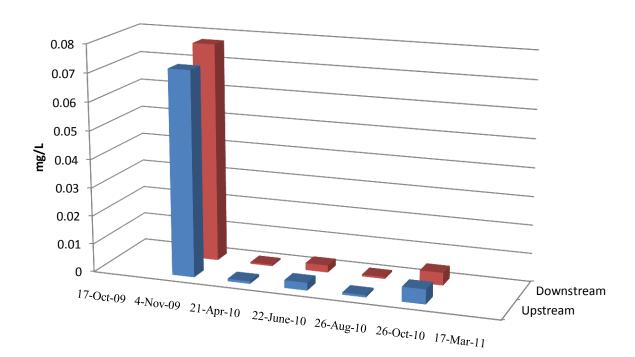


Figure 25: Phosphate at upstream and downstream sites during base-flow sampling.

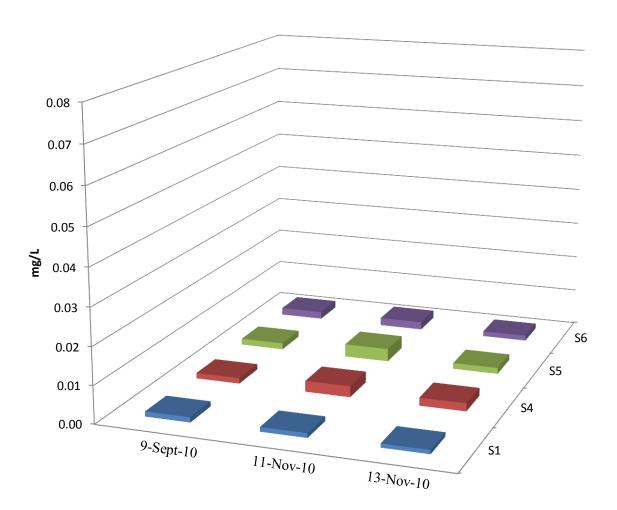


Figure 26: Phosphate for creek sites, S1, S4, S5, & S6 during storm event sampling.

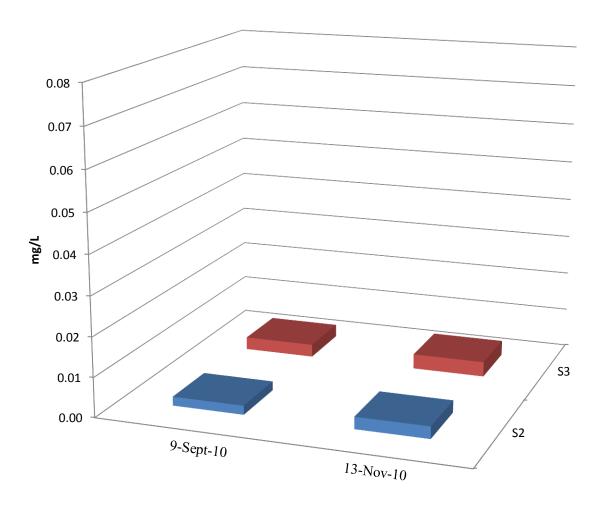


Figure 27: Phosphate for first flush buckets, S2 & S3 during storm event sampling.

Dissolved oxygen

The barometric pressure was not recorded for each DO reading recorded. However, based on the elevation of Kansas, the standard air pressure is around 730-740 mm Hg, discounting variations in weather conditions. Saturated dissolved oxygen levels then become a function of temperature for a given air pressure¹⁴. A total of eight base-flow measurements were made for dissolved oxygen. For all readings except the first two, the values recorded for the upstream and downstream limits were similar. On October 17, 2009 and November 4, 2009 the upstream limit exhibited much lower dissolved oxygen than the downstream, see Figure 28. For the temperatures recorded for those dates, the saturated DO concentrations would have been between 10.65-11.3 mg/L. The actual observed DO concentrations were 1.5 ± 0.2 and 7.5 ± 0.5 and 1.5 ± 0.1 and 8.1 ± 0.1 , respectively. Thus, even the downstream limit was well below the saturated level. However, directly east of the upstream sampling location, the creek has a natural dam. This forces the water over a bed of limestone and riffles the water. This could cause increased aeration in the water and account for the higher DO concentration observed downstream. Table I shows the April, June and July 2010 and the March 2011 readings to be much closer to the saturated levels for those temperatures. August and October 2010 were again well below saturation. All of these dates correlate to a low or non-existent flow rate. Without a high flow rate, proper aeration does not occur. This limits the amount of DO in the water. During storm events, the concentration of DO remained about the same as during base-flow conditions, as shown by Figures 29 and 30. When KDHE performed their study (1993-2001), DO concentrations were chronically below the water standard for support of aquatic life of 5 mg/L¹².

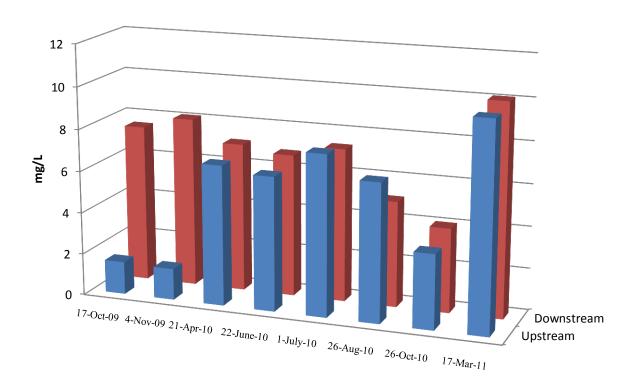


Figure 28: Dissolved oxygen at upstream and downstream sites during base-flow sampling.

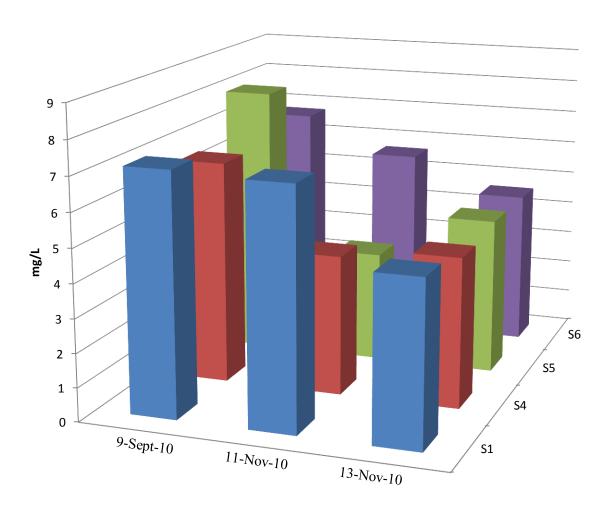


Figure 29: Dissolved oxygen for creek sites, S1, S4, S5, & S6 during storm event sampling.

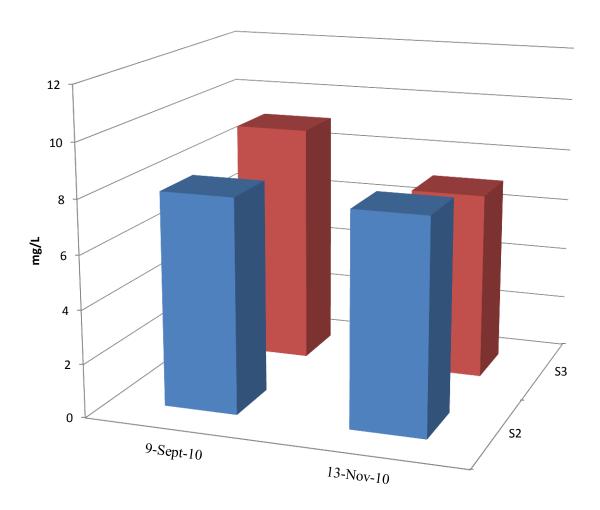


Figure 30: Dissolved oxygen for first flush buckets, S2 & S3 during storm event sampling.

Biological oxygen demand

The biological oxygen demand can correlate to dissolved oxygen. However, BOD should not exceed 5 mg/L for pristine waters²⁰. As observed by Figure 31, the base-flow conditions for the creek vary widely. Though, the base-flow conditions were only slightly elevated compared to the 2 mg/L standard. A higher BOD could mean more organic material dissolved in the water. This could account for the increased BOD observed on Mar. 17, 2010. During storm events, as shown by Figure 32, the conditions of the creek increased greatly. As previously discussed, the turbidity increased during storm events. The BOD would have to increase in order to breakdown the increased level of organics in the water. On the September 9, 2010 recordings the BOD was almost as high as the DO itself. Values were not reported for the first flush buckets.

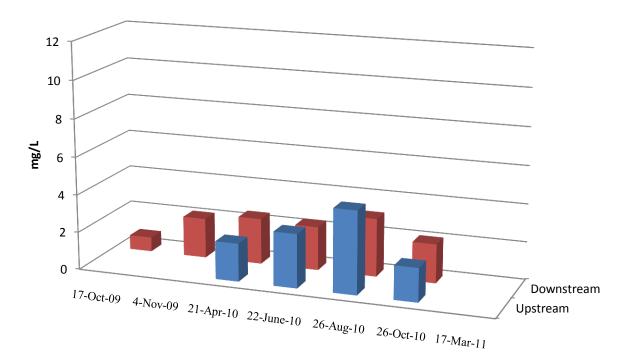


Figure 31: Biological oxygen demand at upstream and downstream sites during base-flow sampling.

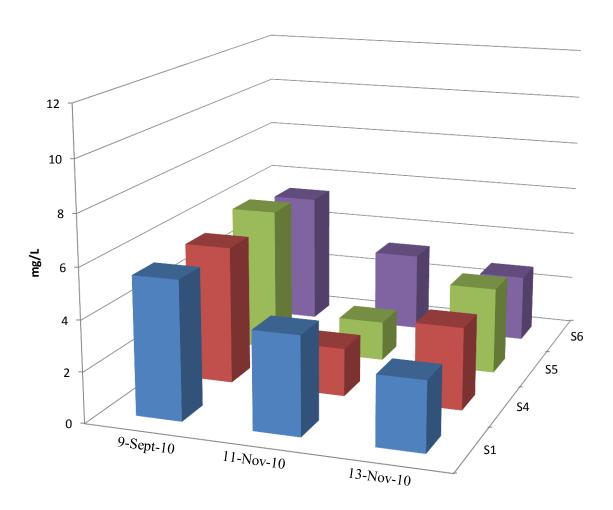


Figure 32: Biological oxygen demand for creek sites, S1, S4, S5, & S6 during storm event sampling.

Table I Base-flow Measurements Reported as Average \pm Standard Deviation

Date:	10/1	7/2009	11/4/2009	
	Upstream	Downstream	Upstream	Downstream
Flow Rate (m/s)	0.25 ± 0.01	0	0.151 ± 0.006	0.013
T (°C)	9.4	9.2	11.1	10.7
pН			6.94 ± 0.02	6.8 ± 0.2
Turbidity (NTU) Conductivity	52.4 ± 1.3	50.7 ± 1.5	30.167 ± 0.05	38.8 ± 0.4
(µS/cm)	312 ± 1	313 ± 1	457 ± 1	457.3 ± 2
TSS (mg/L)			14.15 ± 0.2	13.84 ± 1.6
$\mathrm{NH_4}^+ (\mathrm{mg/L})$		0.5 ± 0.7		0 ± 0
NO_3^- (mg/L)	1.55 ± 0.07	1.25 ± 0.07	0.75 ± 0.07	0.75 ± 0.07
NO_2^- (mg/L)			0.0626 ± 0.0009	0.074 ± 0.002
$PO_4^{3-}(mg/L)$			$0.0036 \pm 3x10^{-5}$	0.03 ± 0.02
DO (mg/L)	1.6 ± 0.2	7.5 ± 0.5	1.5 ± 0.1	8.1 ± 0.1
BOD (mg/L)		1.5 ± 0.5		2.1 ± 0.2

Table I (continued) Base-flow Measurements

Buse 1 (continued) Buse 110 w Wedstrements						
Date:	4/21	/2010	2010			
	Upstream	Downstream	Upstream	Downstream		
Flow Rate (m/s)	0.012 ± 0	0.012 ± 0	0.015 ± 0			
T (°C)	16.43 ± 0.05	16.7 ± 0	26.1	26.65 ± 0.07		
pН	8.143 0.006	8.18 ± 0.01	7.97 ± 0.04	8.08 ± 0.01		
Turbidity (NTU)	13 ± 2	14.6 ± 0.2	14.9 ± 0.2	37.6 ± 0.3		
Conductivity						
$(\mu S/cm)$	683.7 ± 0.6	677 ± 1	448 ± 1	240.1 ± 0.2		
TSS (mg/L)			12.3 ± 0.5	13.7 ± 0.2		
NH_4^+ (mg/L)	0.33 ± 0.06	1.1 ± 0.1	0.5	0.35 ± 0.07		
NO_3^- (mg/L)			0.6			
NO_2^- (mg/L)	0.037 ± 0	0.039 ± 0	0.050 ± 0.002	0.039 ± 0.002		
$PO_4^{3-}(mg/L)$	$9.16 \times 10^{-4} \pm 0$	$5.58 \times 10^{-4} \pm 0$	0.0030 ± 0.0001	$0.003 \pm 2x10^{-5}$		
DO (mg/L)	6.7 ± 0	7.1 ± 0	7.7 ± 0.4	7.3 ± 0.4		
BOD (mg/L)	2.03 ± 0.08	2.4 ± 0.1	3.9 ± 0.5	2.8 ± 0.7		

Table I (continued) Base-flow Measurements

Date:	8/26	/2010	10/26/2010		
	Upstream	Downstream	Upstream	Downstream	
Flow Rate (m/s)	0	0			
T (°C)	25.4	24.3	14.7	14.7	
pН	8.09 ± 0.02	7.885 ± 0.007	7.555 ± 0.007	$7.4 \pm .01$	
Turbidity (NTU)	12.8 ± 0.1	5.0 ± 0.2	11.9 ± 0.1	13.9 ± 0.2	
Conductivity	2745 07		207.0	205.05	
$(\mu S/cm)$	374.5 ± 0.7		287.0 ± 0.2	285.05 ± 0.07	
TSS (mg/L)					
NH_4^+ (mg/L)			0	0	
NO_3^- (mg/L)	0.55 ± 0.07	0.75 ± 0.07	0.25 ± 0.07	0.15 ± 0.07	
NO_2^- (mg/L)	0.0069 ± 0.0009	0.017 ± 0.004	0.0253 ± 0.0009	0.0038 ± 0	
$PO_4^{3-}(mg/L)$	$7.8x10^{-4} \pm 8x10^{-5}$	0.00067 ± 0.0002	$5.21x10^{-3}\pm 8x10^{-5}$	0.0045 ± 0	
DO (mg/L)	6.6 ± 0.1	5.05 ± 0.07	3.6 ± 0.2	4.0 ± 0.2	
BOD (mg/L)	4.4 ± 0.3	3.1 ± 0.2	1.6 ± 0.1	2.3 ± 0.2	

Date:	3/17/	/2011
	Upstream	Downstream
Flow Rate (m/s)	0.026 ± 0	
T (°C)	13.7 ± 0	14.35 ± 0.07
pН	7.64 ± 0.01	7.74 ± 0.02
Turbidity (NTU)	35.8 ± 0.2	41.1 ± 0.3
Conductivity		
$(\mu S/cm)$	428 ± 2	436 ± 1
TSS (mg/L)		

 1.55 ± 0.07

0

 9.9 ± 0.2

 6.6 ± 0.4

 0.7 ± 0

 10.1 ± 0.1

 8.2 ± 0.5

 NH_4^+ (mg/L)

 NO_3^- (mg/L)

NO₂⁻ (mg/L) PO₄³⁻ (mg/L) DO (mg/L)

BOD (mg/L)

Table I (continued) Base-flow Measurements

Table II: Storm Event Values Reported as Averages ± Standard Deviation: S1 (upstream), S2 (north bucket), S3 (south bucket), S4 (post-diversion pipe), S5 (grazing land contribution) and S6 (downstream).

-		diversion pipe), 33	(grazing land contribut	ion) and 50 (downs	ircain).	
Date:	Sept. 9, 2010					
	S 1	S2	S 3	S 4	S5	S 6
T (oC)	22.2	22.5	22	21.7	22.1	21.4
pH Turbidity	7.86 ± 0.01	7.75 ± 0.01	7.74 ± 0.01	7.67 ± 0.01	7.9 ± 0.01	7.87 ± 0.01
(NTU) Conductivity	47 ± 0.2	20 ± 0.1	21.6 ± 0.1	33.9 ± 0.1	16.1 ± 0.2	38.1 ± 0.2
(μS/cm) TSS (mg/L)	435± 1	432 ± 1	395 ± 1	496 ± 1	478 ± 1	489 ± 2
NH_4^+ (mg/L)	0.6 ± 0	0.5	0.4	0.4	0.3	0.3
NO_3^- (mg/L)	0.15 ± 0.07	4.15 ± 0.07	6.5 ± 0.1	0.25 ± 0.07	0.2 ± 0	0.2 ± 0
NO_2^- (mg/L)	0.08249 ± 9E-04 1.35E-03 ±	0.2397 ± 0.0009	0.0595 ± 0.0008	0.07534 ± 0	0.0411 ± 0.0009	0.056 ± 0.001
$PO_4^{3-}(mg/L)$	2E-05	$2.29E-03 \pm 3E-05$	$3.24E-03 \pm 2.5E-05$	$1.47E-03 \pm 0$	$1.71E-03 \pm 0$	$1.99E-03 \pm 0$
DO (mg/L)	7.15 ± 0.07	8	9.05 ± 0.07	6.6 ± 0.1	8.05 ± 0.07	6.75 ± 0.07
BOD (mg/L)	5.48 ± 0.07			5.5 ± 0.2	5.85 ± 0.07	5.35 ± 0.07

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4	

Table II (continued) Storm Event Values							
Date:		Nov. 11, 2010					
	S 1	S4	S5	S 6			
T (oC)	10.8	10.4	10.1	10.3			
pН	7.75	7.595 ± 0.007	7.34 ± 0.01	4.645 ± 0.007			
Turbidity (NTU) Conductivity	9.25 ± 0.07	0.3 ± 0.2	1.1 ± 0.2	3.6 ± 0.2			
(μS/cm) TSS (mg/L)	454 ± 1	470.5 ± 0.7	447.5 ± 0.7	435			
NH4+ (mg/L)	0	0	0	0			
NO3- (mg/L)	0.15 ± 0.07	0.05 ± 0.07	0.05 ± 0.07	0			
NO2- (mg/L)	0.026 ± 0.004	0.0222 ± 0.0009	0.008 ± 0.001	0.0043 ± 0.0009			
PO43-(mg/L)	$0.00123 \pm 7E-05$	$0.00295 \pm 3E-05$	0.00348 ± 9.5 E-05	$0.00212 \pm 5E-05$			
DO (mg/L)	7.05 ± 0.07	4.15 ± 0.07	3.3 ± 0.1	5.65 ± 0.07			
BOD (mg/L)	4.33 ± 0.05	1.9 ± 0.4	1.6 ± 0.2	3.2 ± 0.1			

Table	II	(continu	ned)	Storm	Event	Values
I aine	11	COMMI	ucui	SWIIII	EVEIL	values

			rable if (continued)	Dioini Event values			
Date:	Nov. 13, 2010						
	S 1	S2	S 3	S 4	S 5	S 6	
T (oC)	9	14	12.2	7.9	8.1	8.9	
pН	7.64	8.01	7.99	7.64	7.65	7.66	
Turbidity (NTU)	10.2 ± 0.1	454	351	14.4	16.4 ± 0.1	15.8 ± 0.2	
Conductivity (µS/cm)	439	102	104	487.5	443 ± 1	418 ± 1	
TSS (mg/L)							
NH4+ (mg/L)	0	0	0	0	0	0	
NO3- (mg/L)	0.05 ± 0.07	0.65 ± 0.07	0.1	0.1	0.1	0.1	
NO2- (mg/L)	$0.01 \pm 9E-04$	0.346 ± 0.003	0.379 ± 0.007	0.015 ± 0.001	0.023 ± 0.001	0.0253 ± 0.0008	
PO43-(mg/L)	$0.00107 \pm 7E-05$	0.0030 ± 1 E-04	0.0038 ± 9.8 E-05	$0.0021 \pm 1E-04$	0.00162 ± 0	0.00139 ± 2.9 E-05	
DO (mg/L)	4.85 ± 0.07	7.95 ± 0.07	7.05 ± 0.07	4.45 ± 0.07	4.65 ± 0.07	4.6 ± 0.1	
BOD (mg/L)	2.7 ± 0.1			3.2 ± 0.1	3.4 ± 0.1	2.7 ± 0.6	

Conclusions

Stream Quality

The data from this study show that the water quality of Eagle Creek has improved in comparison to the 1993 and 2001 KDHE studies. In particular, dissolved oxygen (DO) concentrations have increased. The previous studies cited DO as an impairment because the concentration were consistently below the EPA's established minimum of 5 mg/L necessary to sustain aquatic life. In the current study, most of the recorded values show DO concentrations above that minimum threshold.

Additionally, data from stream sampling sites during storm events and first-flush buckets indicate that the conservation buffer in the cropland is inhibiting nutrient flow into the creek. Since the concentration of nitrogen-containing nutrients in the buckets, which sample cropland runoff prior to entering the stream, are higher than nutrient concentrations in the stream at the point where cropland runoff enters (via the diversion pipe), it is reasonable to say that the conservation buffer regions are having the desired effect. The conservation buffer BMP not only reduces sediment and nutrient influx to the stream, it retains topsoil on the cropland.

Nutrient concentrations upstream and downstream from where pasture runoff entered the stream were found to be the same during storm events. Thus, the installation of fencing to exclude cattle from direct access to the stream also appears to be effective with respect to nutrient load. Turbidity was sometimes higher downstream from the pasture runoff entry than upstream. This suggests that sediment is eroding from the gully

leading into the stream during heavy and rapid rainfall. Although the sediment does not appear to be adding nutrient, it would be desirable to provide erosion control in this area.

Future Work

This study has provided initial evidence that agricultural BMPs implemented along Eagle Creek are improving the water quality. It also established a set of parameters for monitoring the stream water quality. Additionally, this study provided some base-line values for those parameters beginning soon after the BMPs were in place along the defined segment.

Water-quality impairments, especially those from non-point sources, usually develop over time. Consequently, reversing the impairment does not happen suddenly. Additional benefits can be realized from this study if the monitoring is continued. Future monitoring could confirm that the chosen parameters improve over time, thus ensuring that the water quality improves. Since BMPs have not been installed along the entire length of the Creek, future monitoring could potentially alert stakeholders to declines in quality occurring upstream from the study segment, allowing for correction in a timely fashion.

References

- [1] Shiklomanov, I. A., World Fresh Water Resources. In *Water in Crisis*; Gleick, P.H. Ed.; New York, 1993; p 13-24.
- [2] United Nations water, statistics page, http://www.unwater.org/statistics-use.html, accessed 23 March 2011.
- [3] Nash, L., Water Quality and Health. In *Water in Crisis*; Gleick, P.H. Ed.; New York, 1993; p25-39.
- [4] United States Environmental Protection Agency, Drinking Water Contaminants page, http://water.epa.gov/drink/contaminants/index.cfm, access 24 March 2011.
- [5] Baird, C., Cann, M., The Chemistry of Natural Waters. In *Environmental Chemistry*; 4th Ed. W.H. Freeman and Company: New York, 2008; p 558-600.
- [6] United States Environmental Protection Agency, Impaired Waters page, http://water.epa.gov/lawsregs/lawsguidance/cwa/tmdl/index.cfm, accessed 20 March 2011.
- [7] United States Environmental Protection Agency, Safe Drinking Water Act page, http://water.epa.gov/lawsregs/rulesregs/sdwa/index.cfm, accessed 24 March 2011.
- [8] United States Environmental Protection Agency, Agricultural Management Practices page, http://www.epa.gov/owow/watershed/wacademy/acad2000/agmodule/, accessed 12 March 2011.
- [9] Surface Water Nutrient Reduction Plan, Technical Report, Kansas Department of Health and Environment: Bureau of Water, Topeka, KS, December 2004.
- [10] Wright, P., Barnyard/Feedlot Runoff Management. Information Bulletin, United States Department of Agriculture, Washington, DC, no date given.
- [11] Kansas Watershed Restoration and Protection Strategy, process page, http://kswraps.org/the-wraps-process, accessed 23 March 2011.
- [12] Kansas Department of Health and Environment, Eagle Creek Study page, http://www.kdheks.gov/tmdl/ne/EagleCr_DO.pdf, accessed 16 March 2011.
- [13] Runoff Sampler Construction, Field Sample Collection, and Handling of Surface Runoff Water Samples; TP-11.1; Nye County Nuclear Waste Repository Project Office: Pahrump, NV, 2008; 1-14.

- [14] Vernier, Dissolved Oxygen Sensor, User Guide page, http://www2.vernier.com/booklets/do-bta.pdf, accessed 12 April 2011.
- [15] Standard Methods for the Examination of Wastewater; Clesceri, Lenore, S., Greenberg, Arnold, E., Eaton, Andrew D., Eds.; Baltimore: American Public Health Association, American Works Association, and Water Environment Federation, 1998.
- [16] United State Environmental Protection Agency, Conductivity page, http://water.epa.gov/type/rsl/monitoring/vms59.cfm, accessed 12 April 2011.
- [17] Iowa State University, University Extension, Crop Management page, http://www.extension.iastate.edu/CropNews/2008/0502JohnSawyer.htm, accessed 12 April 2011.
- [18] Bunce, N.J. Sewage and Waste Disposal. In *Environmental Chemistry*; Wuerz Publishing Ltd: Canada, 1990; p 206-251.
- [19] United State Environmental Protection Agency, Phosphorus page, http://water.epa.gov/type/rsl/monitoring/vms56.cfm, accessed 12 April 2011.
- [20] Missouri Department of Natural Resources, Water Quality Parameters page, http://www.dnr.mo.gov/env/esp/waterquality-parameters.htm, accessed 12 April 2011.

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