Diurnal Variations in Nitrate Concentrations in the Cobb Mill Creek, VA

Wendy Marie Robertson
Charlottesville, VA

Bachelors of Science, Jackson School of Geological Sciences, The University of Texas at Austin, 2006

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Abstract

Nitrate is the most pervasive and ubiquitous global contaminant of ground and surface waters. Ninety percent of the anthropogenic input of nitrate in to the environment comes from fertilizer application, with the United States alone applying 12.5 million tons of fertilizer between 2003 and 2006. High nitrate concentrations in ground and surface waters can have a deleterious effect on both human health and on the ecological systems of impacted areas.

One mircobially driven process by which nitrate is removed from the environment is denitrification; organic carbon oxidation coupled to nitrate as a terminal electron acceptor, a process which can occur in organic-rich streambed sediments. In low relief coastal watersheds, groundwater with high concentrations of nitrate (~20 mg/L nitrate as N) discharge to streams through the zone of denitrification in these streambed sediments. The resulting concentration of nitrate in the streamwater can vary dependent upon many factors including the residence time of the discharging groundwater in the zone of denitrification. Evapotranspiration (ET) in the forested riparian zone surrounding the stream can potentially alter the water table gradient, which, in turn, causes the residence time of groundwater in the zone of denitrification to vary by 1 to 14 hours diurnally.

In the Cobb Mill Creek watershed, VA, multiple 72-hour field events were undertaken to monitor weather conditions, streamwater levels, and streamwater chemistry in order to quantify the effects of ET in the riparian zone on the streamwater flow and chemistry. Estimates of potential evapotranspiration (PET) for the riparian zone of Cobb Mill Creek have been calculated to be as much as 0.5-0.9 mm per hour between 11:00

and 15:00. During the June 2008 monitoring event, stream stage at the creek varied diurnally by an average of 6 cm, and nitrate concentrations varied diurnally by 2.7 mg/L nitrate as N, with a minimum nitrate concentration of 2.9 mg/L nitrate as N at 12:00 on the 26th of June, and a peak nitrate concentration of 6.5 mg/L nitrate as N at 00:00 on the 28th of June.

The pattern and timing of the diurnal variations in both stream discharge and nitrate concentrations observed in Cobb Mill Creek are unique among currently published observations. Within the Cobb Mill Creek watershed during periods of evapotranspiration there exists a diurnal variation in stream discharge which peaks daily near the time of peak calculated evapotranspiration. The patterns of nitrate concentrations of the streamwater are sinusoidal in shape with a greater magnitude of variation than had been previously modeled or recorded and do not coincide with any expected pattern in potential evapotranspiration or stream discharge. These revelations raise significant questions about the validity of current grab sample practices for the monitoring of reactive contaminants within watersheds.

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Chapter 1: Introduction

Overview

The study of nitrate contamination in ground and surface waters around the globe is a topic of great importance. Nitrate is the world's most pervasive groundwater contaminant (Korom, 1992; Spalding and Exner, 1993) and affects 40% of the rivers and 57% of the estuarine systems in the United States alone (EPA and USDA, 1998). Nitrate is introduced into the environment is by three primary sources: nitrogen fixation during lightning strikes, the burning of fossil fuels, and the use of nitrogen based fertilizers. Fertilization practices associated with agriculture accounts for 90% of the anthropogenic input of nitrate into the environment (Galloway and Cowling, 2002) and between 52 and 61% of the total input of nitrate into the environment (Galloway et al., 1995).

The most widespread and persistent problem associated with nitrate is the contamination of both ground and surface waters of agricultural areas as a result of fertilization practices. In 1931 the Haber-Bosch process, which allows for the large scale production of synthetic ammonia, was introduced. This process allowed for the inexpensive production of ammonium nitrate fertilizers as an alternative to organic fertilization processes. The use of these inorganic nitrogen-based fertilizers has become the primary choice of the majority of farming communities, especially since the end of World War II (Smil, 1997). Ammonium nitrate fertilizer allows for intensive high-yield agriculture practices that enable farmers to greatly increase the crop volume per unit area of land farmed (Evans, 1996). As a result, there has been a world-wide increase in the volume of fertilizers used (Galloway and Cowling, 2002). During the time period between 2003 and 2006, the United States alone used 12.5 million tons of nitrogen-based fertilizers (Wiebe and Gollehon, 2006). Due to these types of fertilization practices, the concentrations of nitrate in the groundwaters of many of these agricultural areas exceed the US EPA drinking water limit of 10 mg NO_3^- -N L^{-1}, some by as much as double or more (Denver et al., 2003). The excessive amount of nitrate in water resources can potentially have deleterious effects on both human health and on the ecological systems of impacted areas.

Effects of Excessive Nitrate on Human Health and Ecological Systems

Studies of human health effects of nitrate in drinking water have suggested that exposure can have both acute and long-term health effects (Ward et al., 2005). The foremost concern for acute high-level nitrate exposure is methemoglobinemia, a disorder caused by the binding of nitrite to hemoglobin. After ingestion, nitrate is reduced to nitrite in the digestive system. The nitrite binds to hemoglobin which prevents oxygenation of the blood and tissue and can be fatal. In recent years, concerns have been raised about the health effects of long-term low-level exposure to nitrate (Ward et al., 2005). Preliminary studies have linked habitual consumption of water containing nitrate to colon and other cancers (DeRoos et al., 2003; Gulis et al., 2002; Sandor et al., 2001; Weyer et al., 2001) and potentially to issues with reproductive health (Croen et al., 2001).

Excessive nitrate can also cause serious problems in ecological systems such as eutrophication of surface waters. Nitrate serves as a nutrient for plant growth in agricultural systems, but it also serves the same purpose in water bodies. Under normal conditions in fresh water systems, nitrate is a nutrient of limited availability, which can, in part, limit the growth of plants and algae. When excess nitrate is introduced to the surface water, algal blooms can occur. These bursts of algal growth are accompanied by the eventual death of the algae. As the algae die, bacteria that respire organic carbon using oxygen as an electron acceptor experience an exponential growth as a result of the large increase in availability of an energy source. The bacteria rapidly use up all of the available oxygen in the environment, creating “dead zones,” areas of hypoxic or anoxic conditions where oxygen-based life cannot be sustained (Hill, 1997).

Pathways of Removal of Nitrate from the Aquatic Environment

Nitrate can be removed from groundwater through two main pathways: assimilation into biomass and microbially driven denitrification processes. Nitrate is taken up by vegetation and assimilated into the cells of all types of plant life (Imsande and Touraine, 1994). This assimilated nitrate is sequestered for as long as the plant is alive, eventually being returned to the environment upon the death or consumption and subsequent elimination of the plant material.

During denitrification, denitrifying bacteria use organic carbon as an energy source and nitrate as an electron acceptor in systems with low levels of oxygen (Freeze and Cherry, 1979).

$$5\ CH_2O + 4NO_3^- + 4H^+ \dashrightarrow 2N_2 + 5CO_2 + 2H_2O \qquad (1.1)$$

The bacteria responsible for the denitrification process are ubiquitous in the environment (Knowles, 1982) but only denitrify under specific conditions. Most denitrifiers are facultative anaerobes, meaning they preferentially use oxygen as an electron acceptor and only switch to NO_3^- when oxygen is no longer available. In order for the denitrification process to occur, an aqueous system must contain an available energy source, low dissolved oxygen concentration, and ample nitrate.

Denitrification is a process observed occurring in many different natural settings. Chen et al. (1972) estimated that up to 63% of the nitrate input into anaerobic lake bottom sediments was removed via denitrification. Bacteria capable of denitrification have been found in aquifer systems around the globe (Korom, 1992), and have been demonstrated by Korom et al. (1991a) and Trudell et al. (1986) to actively denitrify *in situ* in the presence of organic carbon as an energy source in oxygen-depleted groundwaters. Laboratory experiments in water-logged soils have demonstrated that rates of denitrification are dependent upon dissolved oxygen concentrations (Patrick and Reddy, 1976). Denitrification can also occur within the water column of oceanic waters in regions with low levels of dissolved oxygen (Knowles, 1982) and in the water column of lakes (Seitzinger, 1988), but the efficiency of denitrification in the water column is often dwarfed by the capacity for denitrification within anoxic sediments (Seitzinger, 1988).

Forested riparian zones especially have a heightened capacity to remove nitrate from the environment, both via uptake and assimilation by vegetation (Lowrance et al., 1984) and via denitrification processes in riparian soils in comparison to riparian zones with crops or grassland cover. Cooper (1990) estimated that between 56-100% of the nitrate loss in the headwaters of a small agricultural watershed was the result of denitrification in organic rich riparian soils. The capacity of riparian zones to remove nitrate can be altered dependent upon different conditions. Hill et al. (2000) examined the spatial variability of denitrification in the groundwater beneath the riparian zone, concluding that the variability in the presence of organic matter within the sediments could enhance or decrease the removal of nitrate in the groundwater along the flow path.

Seasonal variability of *in situ* denitrification rates has also been observed, ranging from 3 to 78 mg/L nitrate per square meter of soil from the summer to the winter seasons in the forested riparian zone (Pinay et al., 1993).

Studies examining the role of streambed sediments in the denitrification process have observed that streambed sediments can potentially remove 40% of the initial nitrate from discharging groundwater (Hill, 1983) dependent upon the initial groundwater nitrate concentration. Observations by Mulholland et al. (2008) have demonstrated that the capacity of streambed sediments to denitrify is related to the initial nitrate concentration so that higher initial concentrations of nitrate cause the total amount of nitrate remove to be higher. However, the effectiveness of the streambed sediments to denitrify is reduced when the initial groundwater nitrate concentration is increased so that more nitrate is left unaltered when the initial concentration is elevated.

For a gaining stream, groundwater with high nitrate concentration discharges to the stream through streambed sediments typically containing mats of organic matter such as decaying leaves (figure 1.1). Colonies of denitrifying bacteria residing in these organic matter rich streambed sediments utilize the NO_3^- from the discharging groundwater, converting it to N_2 gas, removing the nitrate from the discharging groundwater (Knowles, 1982). The area, or “zone of denitrification,” in which the denitrification process occurs in sediments tends to be distributed heterogeneously (in both thickness and presence) throughout the lateral extent of the stream channel dependent upon the presence of organic matter in the streambed sediments.

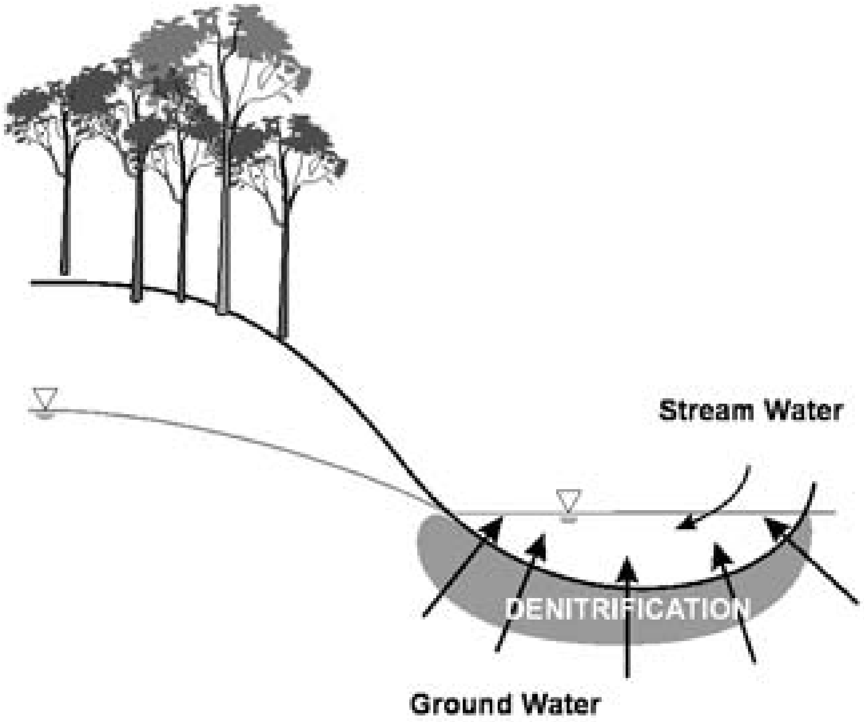

Figure 1.1: Conceptual model of the discharge of high-nitrate groundwater through the zone of denitrification. Adapted from Robertson et al. (2008).

Environmental Factors Which Can Affect Denitrification

Spatial Distribution of Organic Matter

The effectiveness of the denitrifying bacteria in the zone of denitrification within streambed sediments in denitrifying discharging groundwater depends upon factors such as the distribution of organic matter and the rate of groundwater discharge. Cook and White (1987) demonstrated that the variability in the spatial distribution of organic matter in the streambed sediments can alter the amount of nitrate removed from discharging groundwater in small agricultural catchments. Not all streambed sediments in studied watersheds have demonstrated the capacity to denitrify discharging groundwater. Some studies have observed that some groundwaters discharging through streambed sediments remain chemically unaltered (Bohlke and Denver, 1995; Denver et al., 2003).

Studies of “hotspots” of denitrification in streambed sediments have documented the spatial variability in denitrification due to changes in the organic matter content, permeability, and discharge rates of groundwater through the zone of denitrification (Cooke and White, 1987; Hill et al., 2000; McClain et al., 2003). Laboratory and *in situ* experiments measuring denitrification rates in streambed sediments have revealed a complex relationship between these three factors: decreased discharge rates through streambed sediments do not directly translate to increased denitrification, however organic matter in the sediment column both provides an energy source for denitrification and tends to decrease permeability (Hill et al., 2000) which decreases discharge rates. The spatial variation of these factors combines to create heterogeneous denitrification rates which can complicate the study of nitrate variability in surface waters.

Variability in Groundwater Discharge

Residence time of groundwater in the zone of denitrification is altered by discharge rates and has been observed to have a significant effect on nitrate removal (Hill, 1988). Typically, in systems with readily available organic carbon sources the denitrification process is modeled as a 1st order reaction (Boyer et al., 2006):

$$[NO_3^-]_t = [NO_3^-]_0 * e^{-kt} \tag{1.2}$$

where $[NO_3^-]_t$ is the nitrate concentration at a time t after the reaction starts, $[NO_3^-]_0$ is the initial concentration of nitrate in the system, k is a rate coefficient, and t is time. The amount of nitrate removed from a volume of water in the denitrification process is dependent upon that volume of water's residence time in the zone of denitrification. This residence time is a function of the rate of discharge of the groundwater to the stream:

$$t_r = V_r / Q \tag{1.3}$$

where t_r is the residence time, V_r is the volume of saturated sediment through which the water is traveling (length^3), and Q is the discharge (length^3/time).

In the environmental setting of an unconfined aquifer and where physical properties such as the permeability of the sediments are constant, the rate of groundwater discharge can be changed by altering the head gradient. Discharge through such a system can be calculated using Darcy's Law (Freeze and Cherry, 1979):

$$Q = KA\ dh/dL \tag{1.4}$$

where K is the hydraulic conductivity (length/time), A is the cross sectional area of the flow tube (length^2), dh is the finite change in total head (length), and dL is the finite change in length of the flow path (length). When the hydraulic conductivity remains unchanged and the flow path length and cross sectional area are held constant, change in discharge results from change in the total head. In an unconfined aquifer system, total head at a location in the system can be approximated by the elevation head, or height of the water table above the elevation of the discharge location.

The head gradient in a watershed can be altered in both transient and prolonged ways that can affect the discharge rate of groundwater and, by extension, the effectiveness of the zone of denitrification to remove nitrate from the environment. Discharge to streams is altered by transient storm events (Gu et al., 2008a) and limited research has examined the relationship of changing discharge rate to the extent of denitrification in small intact cores of streambed sediments rich with organic matter (Gu et al., 2007; Hill, 1988).

Effects of Evapotranspiration in the Riparian Zone on Denitrification

Evapotranspiration (ET) is the process by which vegetation uses water through a combination of evaporative loss to the atmosphere and photosynthesis. The amount of water the vegetation uses is known as evapotranspirative demand and is measured in units of length. Most vegetation has both seasonal and diurnal periods of growth and dormancy or death dependant upon the availability of water and sunlight. During seasons when vegetation is actively evapotranspiring water (most dominantly the summer), a diurnal variation in demand arises from the change in availability of sunlight from day to nighttime. In systems with shallow water tables (Butler et al., 2007), evapotranspirative demand of water translates to a drawdown of the water table beneath vegetation because as the vegetation draws water from the soil and sediments in the unsaturated zone, capillary action forces water to be pulled upward from the water table into the unsaturated zone to replace the water taken up by the vegetation (Loheide et al., 2005) thereby lowering the water table.

Seasonal patterns and diurnal variations in head gradient and discharge as a result of evapotranspiration (ET) by vegetation in the riparian zones of streams have been linked to the seasonal activity of ET in watersheds (Czikowsky and Fitzjarrald, 2004). In 1932, White (1932) observed the relationship between ET and variation in depth to water table and Loheide et al. (2005) used diurnal variations in water table depth to estimate the use of groundwater by plants. During baseflow conditions, diurnal variations in river discharge have been attributed to the effects of ET in a California watershed (Troxell, 1936).

Because vegetation is dormant during the fall and winter seasons, the water table is not drawn down by evapotranspirative water demand. This dormancy causes an overall higher water table during baseflow conditions than is seen during seasons with active evapotranspirative demand (Czikowsky and Fitzjarrald, 2004). In seasons when vegetation is active, it uses water during the daylight hours and becomes dormant during the night hours, so the drawdown of the water table is based upon a demand that varies diurnally (Loheide et al., 2005; White, 1932). This diurnal change in water demand changes the head gradient of the water table in a cyclical pattern, which alters discharge cyclically.

Diurnal variations in stream stage and discharge attributed to evapotranspiration within a watershed had been documented for river systems of multiple sizes. Lundquist and Cayan (2002) observed a diurnal variation in discharge on the order of 10-40% in 100 watersheds of varying size in the western United States which they hypothesized to be a result of evapotranspiration. In two studies performed in a small (<10 km^2) watershed in Japan, Kobayashi et al (1995; 1990) measured a diurnal variation in discharge on the order of 50 to 100% (from an average discharge of ~0.015 m^3/s) and Burt (1979) noted a diurnal variation in stream discharge of between 50 and 100% (from an average discharge of ~0.002 m^3/s) during baseflow conditions in a small (<1 km^2) watershed, which he attributed to the effects of evapotranspiration on the water table gradient.

Lundquist and Cayan (2002) reported that the shape of the diurnal variations attributed to evapotranspiration had characteristically slow rising limbs and sharp declines in a saw-tooth pattern. In two studies, Kobayashi et al. (1990; 1995) reported the shape of their observed diurnal variation in discharge was sinusoidal. Burt (1979) reported very spiked diurnal variations with v-shaped peaks and troughs. The timing of the diurnal variations in stream discharge was examined by Wondzell et al. (2007) in order to quantify the presence of a lag between peak evapotranspiration and minimum in stream discharge. The amount of lag between peak ET and the minimum stream discharge was observed to vary between as little as 1-2 hours to as much as over 24 hours dependent upon the rate of stream discharge. Wondzell et al. (2007) made field observations as well as constructed a simulation model that predicted that low discharge rates, either during periods of very low flow or due to small catchment size, resulted in increased lag time between maximum evapotranspirative demand and minimum stream discharge.

Seasonal variations in nitrate fluxes have been observed in small agriculturally dominated catchments, and variations have been hypothesized to occur on diurnal cycles as well. In a first order stream on the Atlantic Coastal Plain, nitrate loads during baseflow periods in the winter were much greater than those observed during the summer seasons (Angier and McCarty, 2008). The diurnal control of ET in the riparian zone on the effectiveness of streambed denitrification has been hypothesized in small agriculturally dominated catchments (Denver et al., 2003), but to date very few experimental data are available to support this hypothesis. In a small agricultural watershed with a forested riparian zone such as investigated by Flewelling (2009), the conceptual model for how ET in the riparian zone affects the concentration of nitrate in groundwater discharging to the stream operates is illustrated in figure 1.2. Based upon the observed conditions in the small agriculturally dominated coastal watersheds of Denver et al. (2003), Flewelling (2009) developed a one dimensional model for denitrification in the Cobb Mill Creek watershed, a small agricultural watershed, in which he modeled a diurnal variation in nitrate concentrations of discharging groundwater ranging from 0.4 to 0.6 mg/L. The model considered ET driven changes in discharge and residence time of groundwater as factors affecting the extent of denitrification. Scholefield et al. (2005) measured diurnal variations in nitrate concentrations of streamwater whose daily excursions from the mean nitrate concentration was on the order of 30% from a mean concentration of ~1 mg/L.

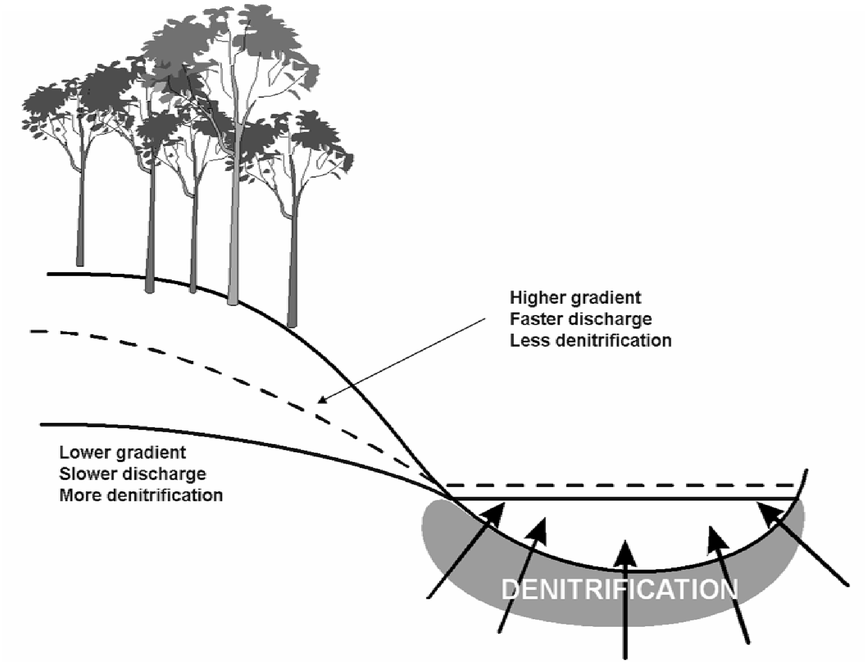

Figure 1.2: Conceptual model of how evapotranspiration in the riparian zone alters the effectiveness of denitrifying bacteria removing nitrate from discharging groundwater. Not to scale. From Robertson et al. (2008).

The extent of denitrification is expected to be influenced by evapotranspiration. During time periods of evapotranspiration, the water table is drawn down, lowering the head gradient of the water table. A smaller gradient reduces the rate of discharge of the groundwater to the stream, increasing residence time in the zone of denitrification and increasing the opportunity for denitrifying bacteria to remove nitrate from the discharging groundwater. When evapotranspiration is not occurring, the water table rebounds (Gribovski et al., 2008), increasing the head gradient of the water table. With the increase in gradient, the rate of discharge increases, decreasing the residence tine in the zone of denitrification and decreasing the opportunity for denitrifying bacteria to remove nitrate from the discharging groundwater.

Research Questions and Goals

In light of the speculation over the presence and magnitude of hypothesized diurnal variations in nitrate concentrations of groundwater discharging to streams in small agricultural catchments, the question this research addresses is:

Is there a measurable diurnal variation in nitrate concentrations in the streamwater of Cobb Mill Creek, VA, a low order stream in a small agricultural watershed?

The goals of this research are to determine and quantify the presence and magnitude of any diurnal variation in nitrate concentration in the streamwater of Cobb Mill Creek, VA**.** I hypothesize that evapotranspiration by vegetation in the riparian zone of the stream in this small agricultural watershed is causing diurnal variation in nitrate concentrations of the discharging groundwater and thus the stream itself. To test this end, three 72 hour field excursions were undertaken; one during a time period when no evapotranspiration was expected to be occurring in the riparian zone, and two during time periods of expected evapotranspiration.

Chapter 2: Site Description and Methods

Site Description

The Cobb Mill Creek watershed is located on the southern end of the Delmarva Peninsula, near the town of Oyster, Virginia (figure 2.1). The watershed is approximately 4.96 km^2 in area. The creek drains east into Oyster Harbor and towards the seaside lagoons. Overall, the Cobb Mill Creek watershed is typified by low topographic relief. At two locations in the watershed the creek is impounded for agricultural use, creating two ponds. Both ponds are near the headwaters of the main stream, and one pond flows directly downstream into the other. The outlet of the second pond forms the main channel of Cobb Mill Creek downstream from both impoundments. Cobb Mill Creek is a gaining stream with the majority of its flow downstream of the pond outlets resulting from the discharge of groundwater into the stream channel. Average rainfall in the catchment is ~1000 mm/year (Krovetz et al., April 1989 to 2008) with the 2007/08 water year having 837.4 mm.

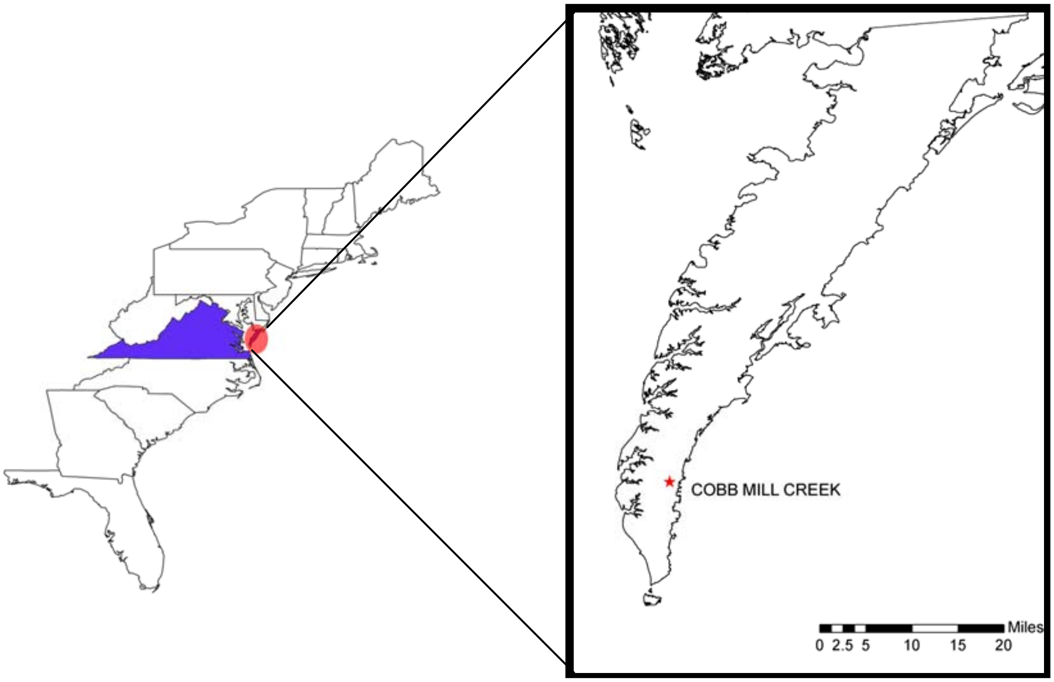

Figure 2.1: Location of the Cobb Mill Creek Watershed on the Eastern Shore of Virginia.

The near-surface sedimentary layers underlying the Cobb Mill Creek watershed are largely composed of unconfined sands, silts, and clays (Trapp and Meisler, 1992) with interbedded organic matter prominent in low-lying areas and stream channels and are part of the shallow unconfined Columbia aquifer system. The soils in the Cobb Mill Creek watershed are largely sandy loams in the upland areas and loamy sands along the creek itself (Gu, 2007). Beneath these soils lies the unconfined Columbia aquifer system, with a thickness of ~8-20 m in the region of the Cobb Mill Creek watershed (Trapp and Meisler, 1992). The aquifer consists mainly of unconsolidated sands and gravel, and has a measured hydraulic conductivity ranging from 5.5×10^{-4} to 1.5×10^{-7} m/s (Gu, 2007).

The main channel of Cobb Mill Creek at the upper reaches of the watershed is a man-made channel draining agricultural fields with some surface water input from a forested wetland. Above the first pond, the tributaries to the stream are primarily a series of tile drains from agricultural fields. The upper pond is approximately 130 m long by 15 m wide and drains to the lower pond through culverts beneath a sand berm dam. The lower pond is approximately 180 m long by 20 m wide and drains to the stream channel through an outlet in the sand and shell dam located at the southern end of the pond. Between the second pond and the culvert at Route 600, the Cobb Mill Creek riparian zone is typically a low-relief wooded wetland, 5-40 m wide from the center of the channel on either side of the stream. Downstream of the culvert at Route 600, the north bank of the stream increases in relief, with the 10-80 m wide riparian zone occupying a hillslope of 1-4% gradient. The riparian zone along the south bank of the stream continues as a low-relief wooded wetland of 10-80 m in width. The trees in the forested riparian zones abutting the stream are approximately 60% deciduous and 40% coniferous.

Roughly 64% of the land in the catchment is being used for agricultural purposes (*i.e.*, fertilized land) based upon the 2001 National Land Cover Data set (appendix A). Crops commonly grown in the watershed include corn, wheat, soy beans, cotton, and green beans. Land use abutting the stream banks is approximately 25% agricultural, 21% non-forested wetland (grassy wetland and marsh), and 54% forested land as determined by categorizing the land use in a zone reaching out 10 m on both sides of the stream channel using the 2008 Virginia Base Mapping Program ortho-imagery aerial photographs (2 foot resolution) (Glendon, 2008, appendix A). For details on how these estimates were determined, refer to appendix A.

Concentrations of nitrate in the groundwater of the Cobb Mill Creek watershed have been recorded in the range of 10-20 mg NO_3^--N L^{-1}, resulting from a combination of contamination of the groundwater by fertilizer from the agricultural areas of the watershed and the oxic conditions in the groundwater as it moved through the watershed (Galavotti, 2004). Streamwater concentrations of nitrate in Cobb Mill Creek vary widely (1-8 mg NO_3^--N L^{-1}) dependent upon seasonal, diurnal, and stream stage variations in the watershed.

Monitoring of Hydrological Conditions

Water table levels, stream stage, discharge, and weather conditions were monitored throughout the Cobb Mill Creek watershed using both temporary and permanent installations. Flow from the outlet of the pond has been monitored on a sporadic basis since 1999 to develop an estimate of the volume of water contributed to the stream as surface water from the pond. Periodic measurements by Flewelling (2009) used flow velocity at the surface and an estimate of the channel geometry to calculate flow. In August 2008, a temporary flume was installed in the pond outlet channel to measure flow (location A, figure 2.2). A Levelogger™ pressure transducer was placed in the stilling well of the Parshall flume to continuously monitor water depth in the flume. Hand measurements of water depth were also made four times per day to calibrate the transducer results.

Stream stage has been monitored at the culvert beneath Route 600 since 2000 using a stilling well installation ~3 m downstream of the double barreled culvert (location B, figure 2.2). A Levelogger™ pressure transducer has been deployed in the stilling well at the culvert to record stream stage and temperature every ten minutes. A rating curve has been established at this point and was used to calculate the stream discharge.

The hillslope location is a 20 meter long stretch of Cobb Mill Creek downstream of Route 600 in the forested riparian zone on the north bank (location C, figure 2.2). The hillslope is ~80 m wide with a topographic gradient of 3-4%. It has been outfitted with several permanent installations to monitor water table levels and stream stage. A stilling well installed at the upstream end of the hillslope has Barologger™ and Levelogger™ pressure transducers deployed to monitor barometric pressure in the watershed and stream stage at the hillslope. Both take measurements every ten minutes of pressure (stage) and temperature.

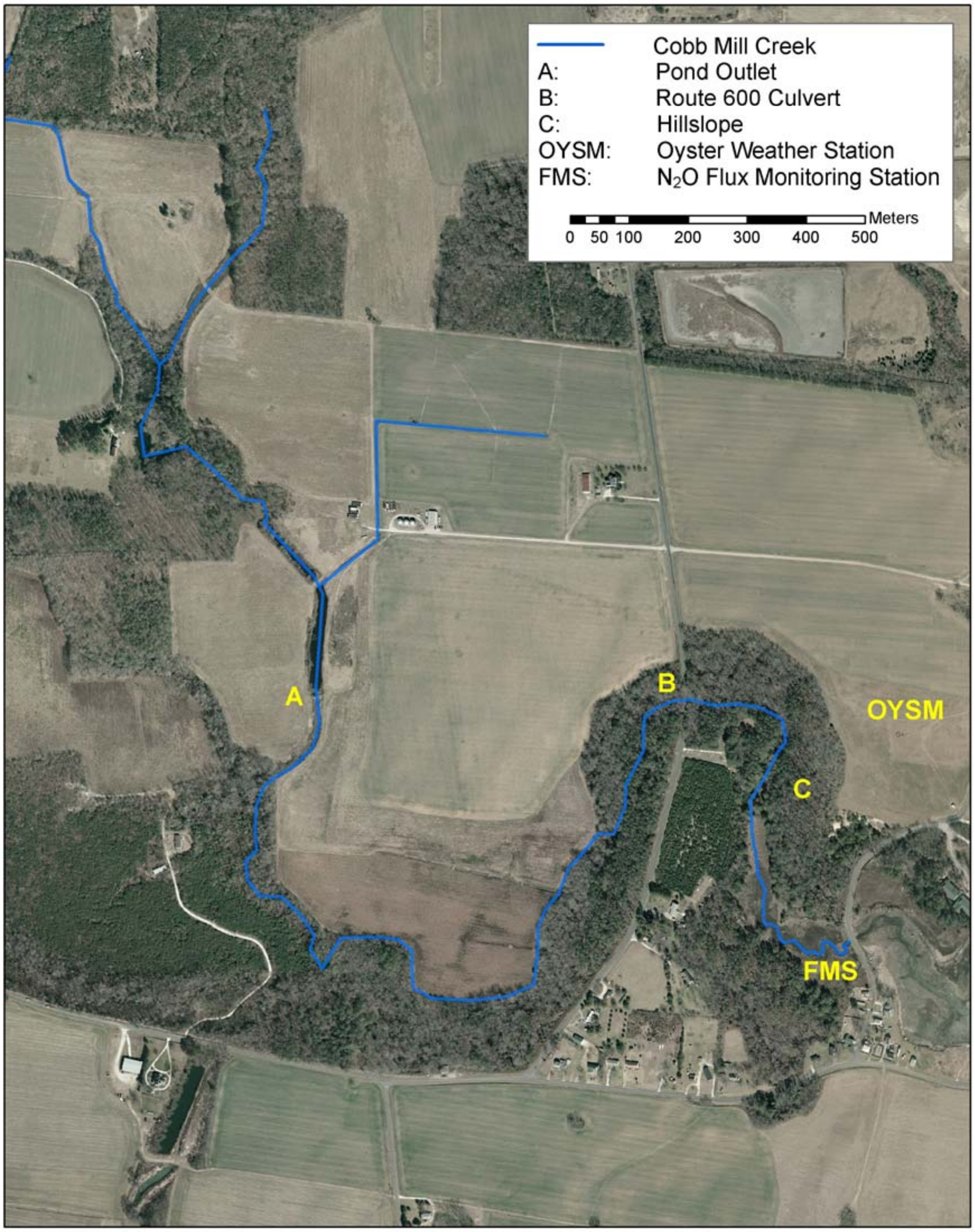

Figure 2.2: Aerial overview of Cobb Mill Creek. Ortho-imagery taken from the 2008 Virginia Base Mapping Program.

Depth to the groundwater table has also been monitored at the hillslope location using pressure transducers located in a series of piezometer installations extending up to the top of the hillslope (figure 2.3) (Gu, 2007). N13 is a piezometer approximately 3 m from the stream bank and driven to a depth of 2.98 m. A Levelogger™ pressure transducer monitors temperature and depth to the water table every ten minutes from August 2008 to present. Further up the hillslope, N11 is a monitoring well driven to a depth of 4.58 m with a Levelogger™ pressure transducer monitoring water table depth and temperature every ten minutes from August 2008 to present. At the top of the hillslope, the hilltop monitoring well (Hilltop) is driven to a depth of 5.95 m with a Levelogger™ pressure transducer monitoring water table depth and temperature every hour from June 2008 to present. Results from the monitoring of the hillslope piezometers are reported in Appendix F.

Weather conditions in the Cobb Mill Creek watershed have been monitored at a series of weather stations in the area (figure 2.2). Air temperature, precipitation, and wind speed were monitored at the Oyster Weather station (OYSM). Solar radiation data were taken from two monitoring stations: the N_2O flux monitoring station (FMS) and the Hog Island weather station (HOGI) located approximately 30 km from the Cobb Mill Creek watershed.

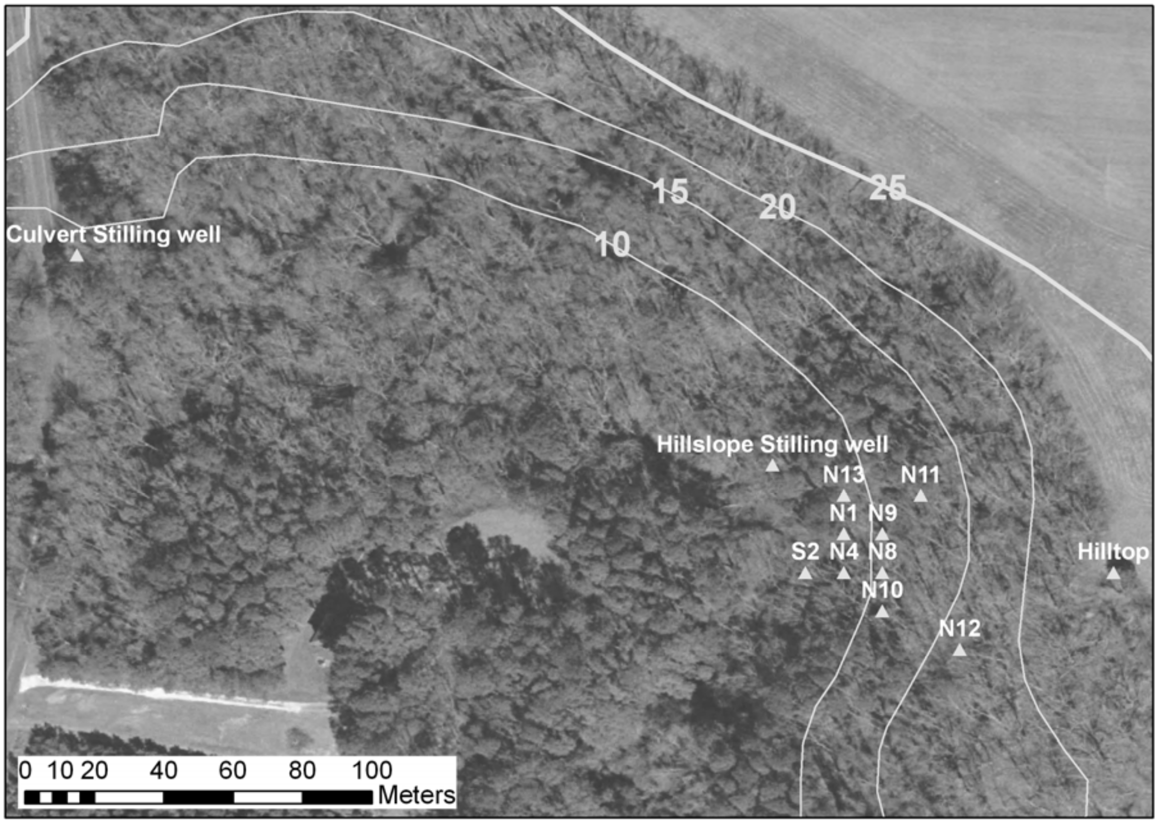

Figure 2.3: Locations of piezometer and stilling well installations at the hillslope location of Cobb Mill Creek, VA. Ortho-imagery taken from the 2008 Virginia Base Mapping Program. Contours are labeled in feet above sea level.

Sampling Campaigns and Locations

Three 72 hour sampling campaigns were undertaken during the spring and summer seasons of the year 2008 in order to determine the presence and magnitude of diurnal changes in stream stage and water chemistry. During the sampling campaigns a range of data was collected at the pond, culvert, and hillslope sampling locations including stream stage, water table levels, as well as streamwater samples analyzed for major anions, DOC, and DON concentrations. All sampling campaigns occurred at baseflow conditions, when no rainfall had been recorded at the OYSM weather station for at least 48 hours prior to the start of the sampling campaign. The March event was undertaken during a period with no leaves on the trees in order to establish baseline conditions within the stream and the watershed in the absence of evapotranspiration by the riparian zone vegetation. The subsequent sampling campaigns were conducted during periods of time with leaves on the trees and expected active evapotranspiration in order to quantify the effects which evapotranspiration might have on the physical and chemical properties of the streamwater. Water samples were taken at three locations within the watershed: at the outlet of the second (down-gradient) pond, immediately upstream of where the creek crosses beneath Route 600, and at the hillslope (figure 2.2). The Cobb Mill Creek hillslope location is a ~20 m stretch of the stream in the non-tidally influenced stretch of the stream ~200 m east (downstream) of Route 600 (figure 2.2). Water samples were collected from the stream channel approximately half way through this 20-m stretch.

The sampling campaign used to establish baseline conditions within Cobb Mill Creek (CMC) and the CMC watershed occurred from 00:00 March 27, 2008, to 23:00 March 29, 2008. The most recent rainfall event recorded prior to the sampling campaign was 9.91 mm on March 16, leaving 11 days to allow the system to return to baseflow conditions before sampling began. A small rainfall event of 0.76 mm in the watershed was recorded from 02:00 to 04:00 on March 29th, however, the event was small enough that it did not impact the baseflow conditions in the watershed. During this sampling campaign, stream stage was monitored at the culvert location, an ISCO automatic sampler was deployed to collect hourly streamwater samples at the hillslope location, and grab samples were taken every four to eight hours at both the pond outlet and hillslope locations.

The first summer sampling campaign with riparian-zone vegetation fully leafed out occurred from 17:00 June 25, 2008, to 16:00 June 28, 2008. Prior to the June sampling campaign, a 1.02 mm rainfall event was recorded on June 22. A larger (10.16 mm) rainfall event occurred on June 17th, which allowed 7 days for the system to return to baseflow conditions from the previous rainfall event of notable magnitude to the start of the sampling campaign. No rainfall was recorded between June 25 and June 29. During the June sampling campaign, stream stage was monitored at the culvert location, ISCO automatic samplers were deployed to collect hourly streamwater samples at the culvert and at the hillslope, and grab samples were taken every four hours at both the culvert and hillslope locations.

The final summer sampling campaign occurred from 10:00 August 20, 2008, to 09:00 August 23, 2008. Prior to the August sampling campaign, a 5.33 mm rainfall event was recorded on August 15th, which allowed 5 days for the system to return to baseflow conditions. No rainfall was recorded between August 20 and August 23. During the August sampling campaign, stream stage was monitored at the culvert location and ISCO automatic sampler were deployed to collect hourly streamwater samples at the pond outlet and at the hillslope.

Sample Collection and Processing

Grab samples were collected every six hours (except at midnight) during the March 2008 sampling campaign and were collected every six hours (including midnight) during the June 2008 sampling campaign. Samples were collected in the center of the channel within 2 m of the ISCO automatic sampler's intake. Clear Whirl-Pak™ bags (1.4 L) were used to collect the samples. Bags were filled with 800-1000 mL of streamwater, leaving ~400-600 mL headspace of air. The bagged samples were placed in coolers and immediately taken to the field lab for processing.

Two ISCO automatic samplers were deployed during our field sampling campaigns. The ISCO automatic samplers were programmed to draw a 500 mL sample of streamwater hourly for a 24 hour period three times during each of the 72 hour sampling campaigns. In order to collect a sample representative of the water column of interest, the intake hose of the ISCO was placed as close to the center of the stream channel (or in the case of the pond, the outlet) as possible. The 24 ISCO sample bottles were lined with clear 1.4 L Whirl-Pak™ bags which were replaced with new bags daily during the reset time in order to eliminate the need to acid wash the sample bottles. After daily sample collection, the bagged samples were placed in coolers and immediately taken to the field lab for processing.

Samples analyzed for anion concentrations using ion chromatography (IC) were pulled from both the grab and ISCO sample sets. An aliquot of 45 mL was pulled from the sample using a syringe which had been rinsed 3-5 times with water purified by reverse osmosis (RO) and three times with sample. The aliquot was filtered through a 0.45 μm sample-rinsed filter into three 2 mL glass autosampler vials for IC analysis and one 25 mL plastic scintillation vial for backup storage. Additional samples were collected from some of the ISCO samples for analysis of Cl^- concentrations using an ion specific electrode (ISE). These samples were kept in Whirl-Pak ™ bags and were left unfiltered.

Samples analyzed for dissolved organic carbon (DOC) concentrations were pulled from the grab samples only in order to limit the gap in time between collection and processing. Two aliquots of 40 mL were pulled from the sample using a single syringe which had been rinsed five times with RO water and three times with sample. The aliquots were filtered through a 0.45-μm sample-rinsed filter into two 40 mL amber vials. Each sample was acidified to a pH of ~2-3 with 0.78 mL of 85% H_3PO_4.

After processing in the field lab, the IC and DOC samples were refrigerated at 5 °C until transport back to the analytical lab. The samples were transported on ice and refrigerated at 5 °C until analysis. The IC samples were analyzed within two months of collection and processing. The samples analyzed for DOC were analyzed within one week of collection and processing. The samples analyzed for Cl^- using the ISE were kept un-refrigerated in coolers at ~23 °C and analyzed 10-14 days after collection.

Samples analyzed for dissolved organic nitrogen (DON), NH_4^+, and NO_2^- were taken from some of the ISCO samples. An aliquot of 30-40 mL was pulled from the sample using a syringe which had been rinsed 3-5 times with RO water and three times with sample. The aliquot was filtered through a 0.45 μm sample-rinsed filter into two 25 mL clear Whirl-Pak™ bags. The samples were frozen to a temperature of -80 °C at the field lab, transported back to the analysis lab on ice and stored in a freezer until analysis. The samples were analyzed within 3 months of collection.

Chemical Analysis

Anion analysis was performed using two different methods; ion chromatography (IC) for major anions and the use of an ISE for Cl^- concentrations. All IC samples were analyzed with standards for Cl^-, NO_3^-, and SO_4^{2-} in concentrations of 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, and 40.0 mg/L. Blanks of the RO water from both the field and analytical labs were also analyzed. Samples were run in triplicate, with the three 2 mL IC vials being randomly assigned a value of A, B, and C for each sample. The 25 mL vial of additional sample was kept in reserve to be used in case of a need for a re-run. The samples from the March 2008 sampling campaign were analyzed using a Dionex IC consisting of a Gilson 234 auto-sampler, Dionex™ IC and guard columns, and a Kipp and Zonen BD41 paper strip chart recorder. All standard curves and sample concentrations were measured by hand. Standard curves for Cl^-, NO_3^-, and SO_4^{2-} had r^2 values greater than 0.967, using linear regression (figures B.1 – B.3, appendix B). The samples from the June 2008 and August 2008 sampling campaigns were analyzed using a Dionex ICS 3000 IC consisting of a Gilson™ 231 auto-sampler with a 401 dilutor, Dionex™ IC and guard columns, and a computer software program called Chromeleon™ v. 6.80, which calculated standard curves and sample concentrations. Standard curves for Cl^-, NO_3^-, and SO_4^{2-} had r^2 values greater than 0.993 using a quadratic fit regression (figures B.4 – B.6, appendix B).

Measurements of Cl^- concentration in the August 2008 pond samples were performed using an Orion™ ISE for Cl^- anion. Calibration standards of 1, 2, 5, 10, 20, 25, 40, 50, and 100 parts per million (mg/L) were analyzed with the samples. The standard curve was calculated using the 5-100 mg/L standards because a) the replicate measurements of Cl^- concentrations beneath 5 mg/L are unreliable and cannot be fit to a semi-log calibration curve (Cole-Parmer) and b) none of the samples analyzed contained concentrations of Cl^- less than 15 mg/L. The standard curve had an R^2 value of 0.880, using a linear regression (figure B.7, appendix B).

Analysis of DOC concentrations was performed using a Teledyne-Tekmar™ Phoenix 8000 TOC Analyzer. Standards with concentrations of 1, 2, 5, 10, and 20 mg/L were analyzed in order to calculate the standard curve. The software program TOC Talk for Phoenix 8000 (version 3.6.385.2) performed the standard curve calculations and reported sample concentration values based upon the standard curves. The r^2 value for the DOC standard curve equals 0.9995 (figure B.8, appendix B). Samples were run in triplicate by pulling three separate aliquots of 10 mL each from a single 40 mL amber vial. The second vial was kept in reserve to be used in case of a re-run. In order to assess the risk of contamination from rinsing the syringes at the field site, sample vials of RO water from the field lab were also processed and analyzed using the same procedure outlined above in order to quantify the amount of DOC present. The DOC concentration data are presented in Appendix C.

Analysis for DON, NH_4^+, and NO_2^- was performed by a third party lab using methodology developed by the Virginia Institute of Marine Science (VIMS). Five mL of 1:20 diluted DON sample was combined with 5 mL of a 0.185 molar solution of potassium persulfate in a baked glass ampule to oxidize the DON to nitrate. The samples were autoclaved for 40 minutes and then refrigerated until analysis approximately 2-3 days later. The anion analysis was performed using a Quikchem 8000 (Lachat Instruments) and following the analysis protocol outlined in the method documentation 31-107-04-1-E (Smith and Bogren, 2003). The concentrations of NO_2^- and NH_4^+ for all samples were below detection limits (lower detection limit of this method is 0.36 μM), and the concentration of DON was also negligible (<530 μg/L), therefore, other than the reporting of the data in Appendix C, no further discussion of DON will be presented.

Chapter 3: Results

Stream Stage and Discharge

The stage at Cobb Mill Creek has been monitored using stilling well installations at both the hillslope and culvert locations since 2000. Periodic stream gaging during a range of stage levels has resulted in a rating curve for Cobb Mill Creek at the culvert location (figure 3.1) which was used to calculate the discharge measurements for this research.

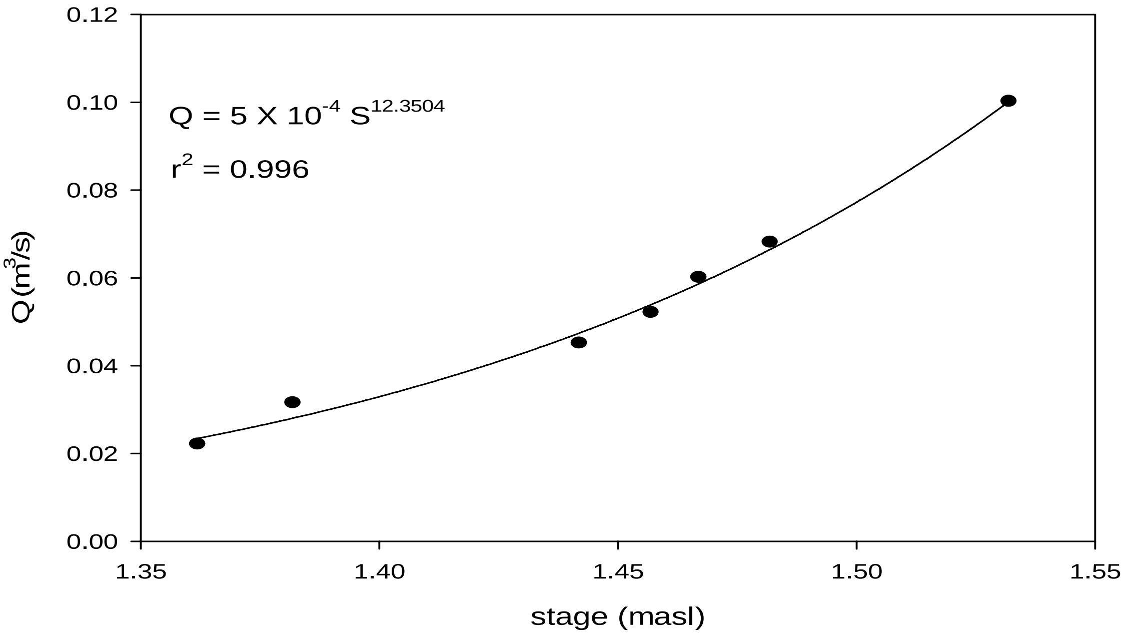

Figure 3.1: Rating curve for the culvert location of Cobb Mill Creek

For the period of time between January 2008 and September 2008, the stilling well at the hillslope location was having continual clogging issues, which led to erratic and inaccurate stage measurements. Because the stage record from the hillslope stilling well was so erratic, all of the stage measurements used for calculations in this research were taken from the culvert stilling well. A comparison of the stage measured at the culvert and the hillslope stilling wells from July 2005 to December 2005 demonstrated that while the magnitude of variation was different in each location, the timing of variation was identical (figure 3.2), justifying the use of the culvert stage record as an analog for the hillslope location during the period in 2008 when the field studies discussed in this research occurred and when the hillslope transducer data were clearly compromised.

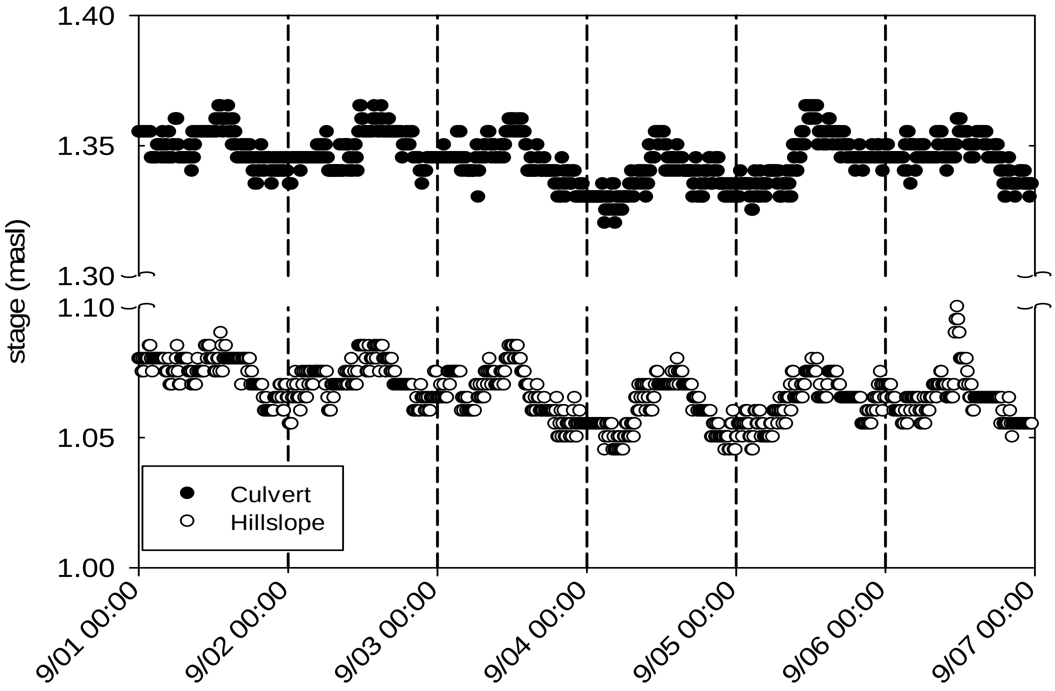

Figure 3.2: Comparison of the stilling well stage records from the culvert (top) and hillslope (bottom) at Cobb Mill Creek, VA from September 1, 2005, to September 7, 2005.

Throughout gathering the baseline data for Cobb Mill Creek during the March 2008 sampling campaign, the stream stage at the culvert location averaged 1.48 masl, with a standard deviation of 0.9 cm (figure 3.3). Average discharge calculated at the culvert of 0.064 m^3/s, with a standard deviation of 0.004 m^3/s (figure 3.4).

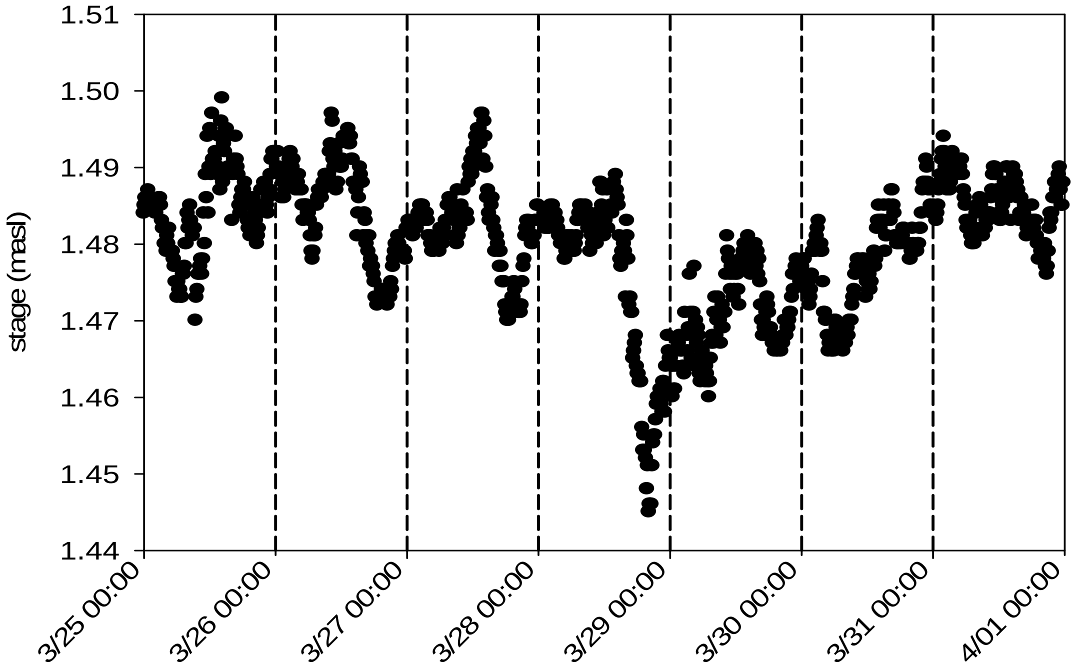

Figure 3.3: Stream stage measured every 10 minutes at the culvert location of Cobb Mill Creek – March 25-31, 2008.

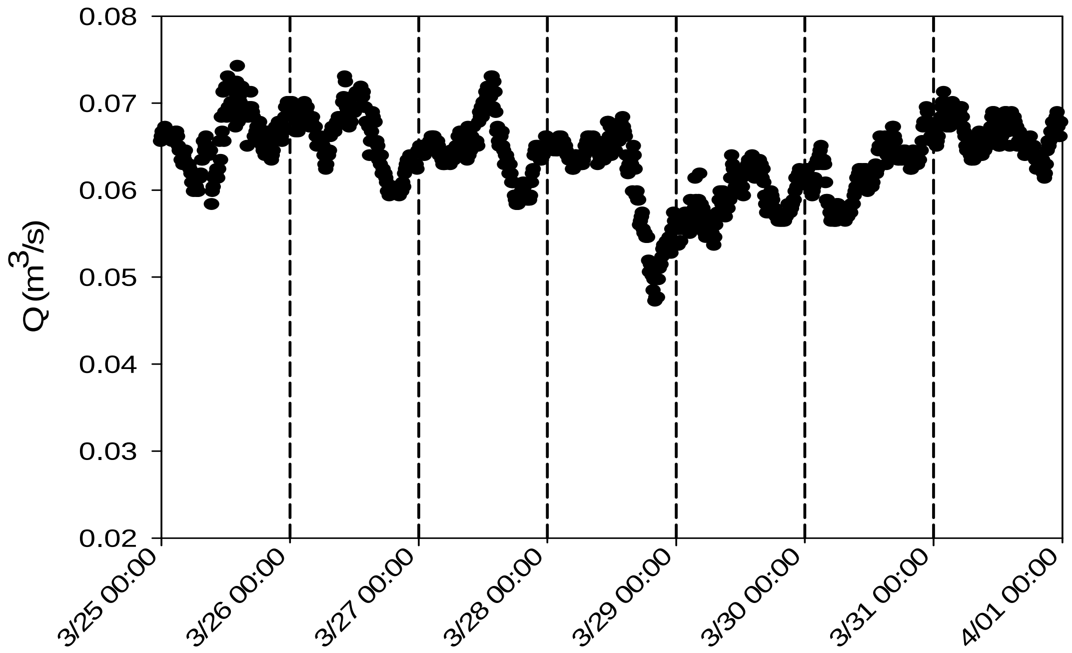

Figure 3.4: Stream discharge calculated every 10 minutes at the culvert location of Cobb Mill Creek – March 25-31, 2008.

During the June 2008 sampling period, the stream stage at the culvert location of Cobb Mill Creek ranged from a minimum of 1.38 masl to a maximum of 1.45 masl (figure 3.5). A sinusoidal variation in stage with one maximum and one minimum in each 24-hour time period was observed throughout the sampling period, with an average variation of 5 cm. This periodic behavior in stage variation is taken to be diurnal. The observed minimum stage occurred between 22:00 and 01:00 daily and the observed maximum occurred between 10:00 and 13:00. Stream discharge at the culvert location varied from a minimum of approximately 0.03 m^3/s to a maximum of approximately 0.05 m^3/s. The average variation was ~ 0.02 m^3/s (figure 3.6).

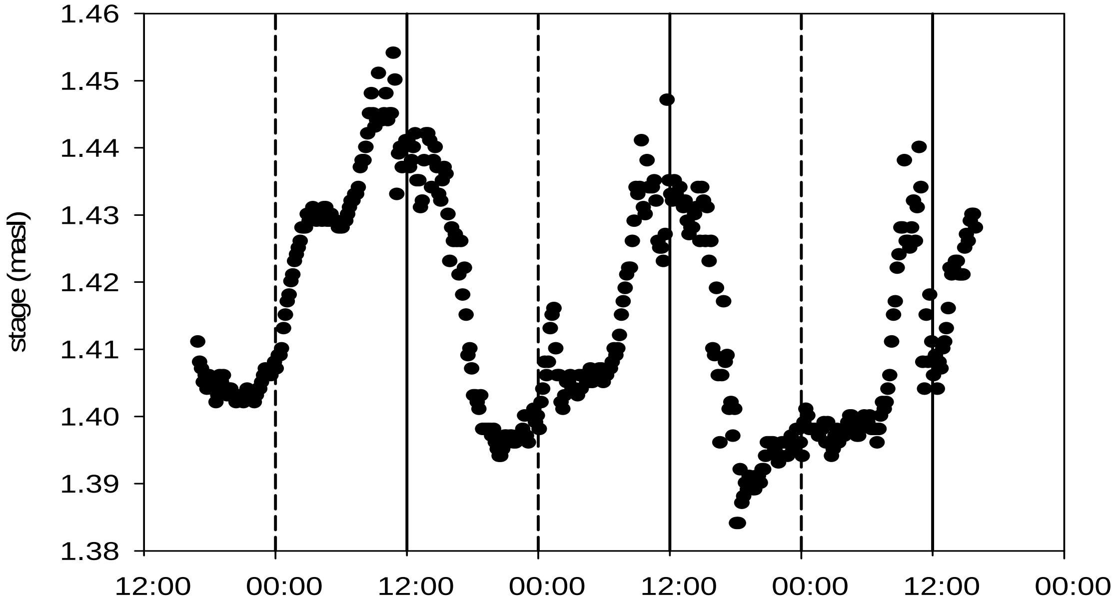

Figure 3.5: Stream stage measured every 10 minutes at the culvert location of Cobb Mill Creek – June 25-28, 2008.

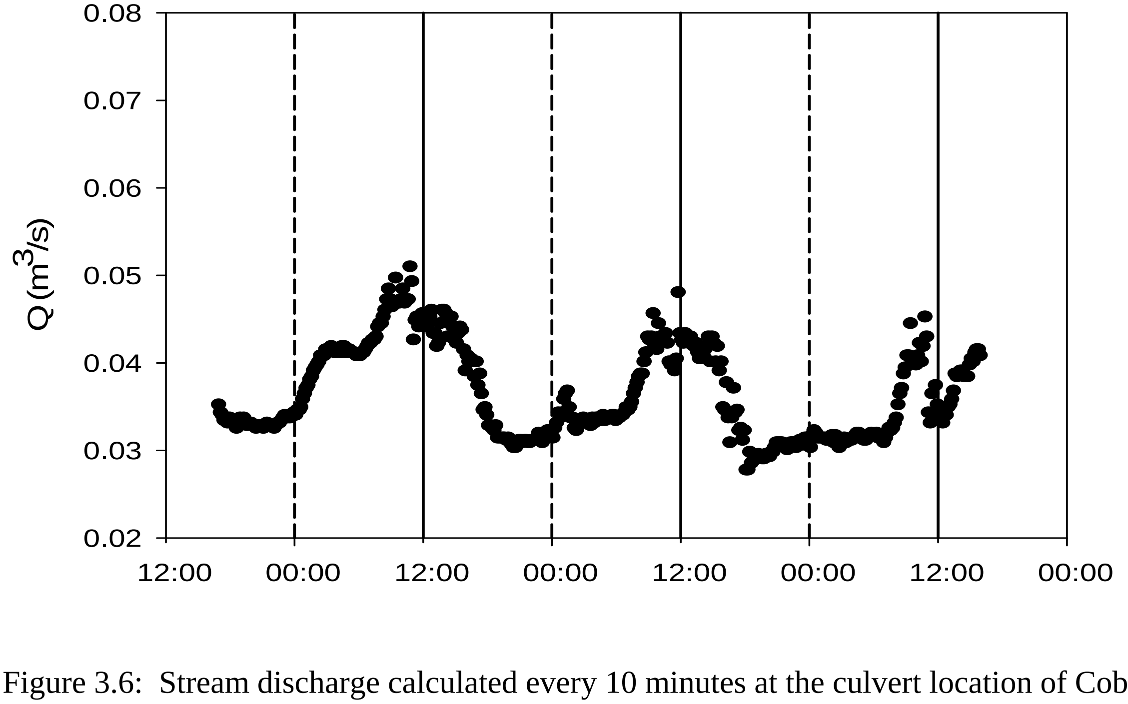

Figure 3.6: Stream discharge calculated every 10 minutes at the culvert location of Cobb Mill Creek – June 25-28, 2008.

During the August 2008 sampling period, the stream stage at the culvert location of Cobb Mill Creek ranged from a minimum of approximately 1.37 masl to a maximum of approximately 1.47 masl (disregarding the errant spikes thought to be electrical noise occurring around noon each day) (figure 3.7). A sinusoidal variation in stage with daily maxima and minima was observed throughout the sampling period, with an average variation of 9 cm. The observed minimum stage occurred between 22:00 and 02:00 daily and the observed maximum occurred between 10:00 and 13:00. Stream discharge at the culvert location varied from a minimum of approximately 0.025 m^3/s to a maximum of approximately 0.055 m^3/s. The average variation was ~ 0.02 m^3/s (figure 3.8).

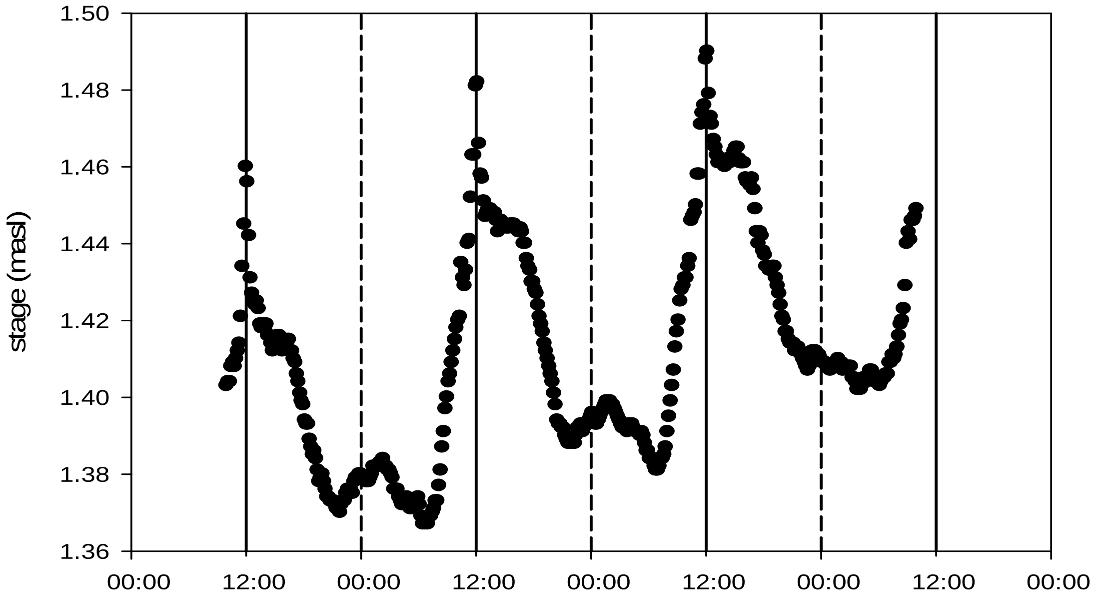

Figure 3.7: Stream stage measured every 10 minutes at the culvert location of Cobb Mill Creek – August 20-23, 2008.

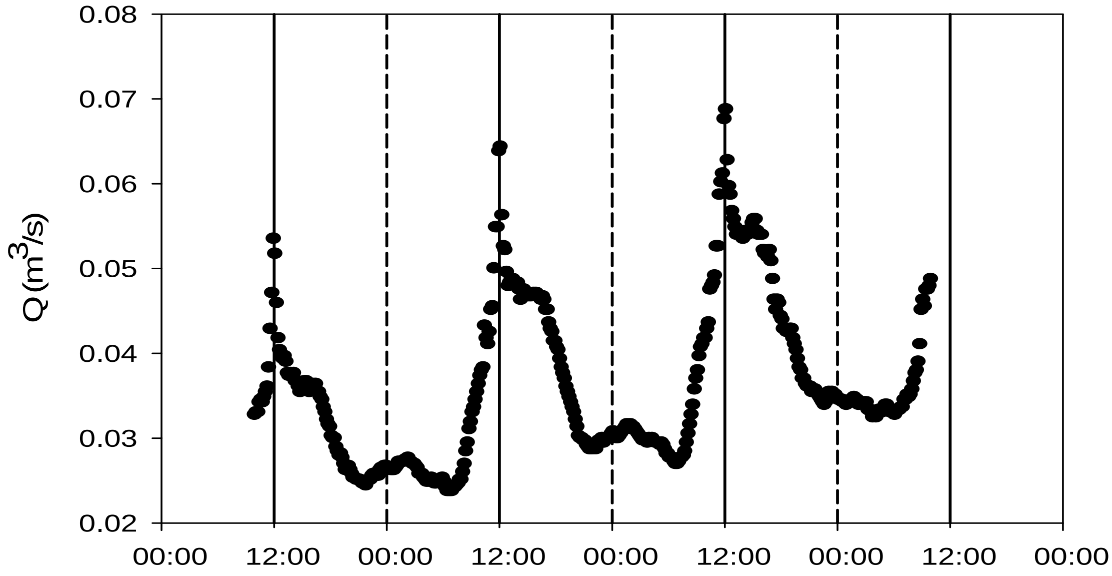

Figure 3.8: Stream discharge calculated every 10 minutes at the culvert location of Cobb Mill Creek – August 20-23, 2008.

Streamwater Chemical Composition

Background Conditions

During the March 27-29, 2008, sampling campaign, nitrate concentrations at the hillslope averaged 1.8 mg NO_3^- -N L^{-1}, with a standard deviation of 0.2 mg/L (figure 3.6). The average chloride concentration was 27.25 mg/L, with a standard deviation of 3.97 (figure 3.6). No diurnal variation was observed in either NO_3^- or Cl^- concentrations. The grab samples collected from the pond averaged 0.81 mg NO_3^- -N L^{-1} +/- 0.06 and 21.92 mg/L Cl^- +/-0.72 (figures C.7, appendix C).

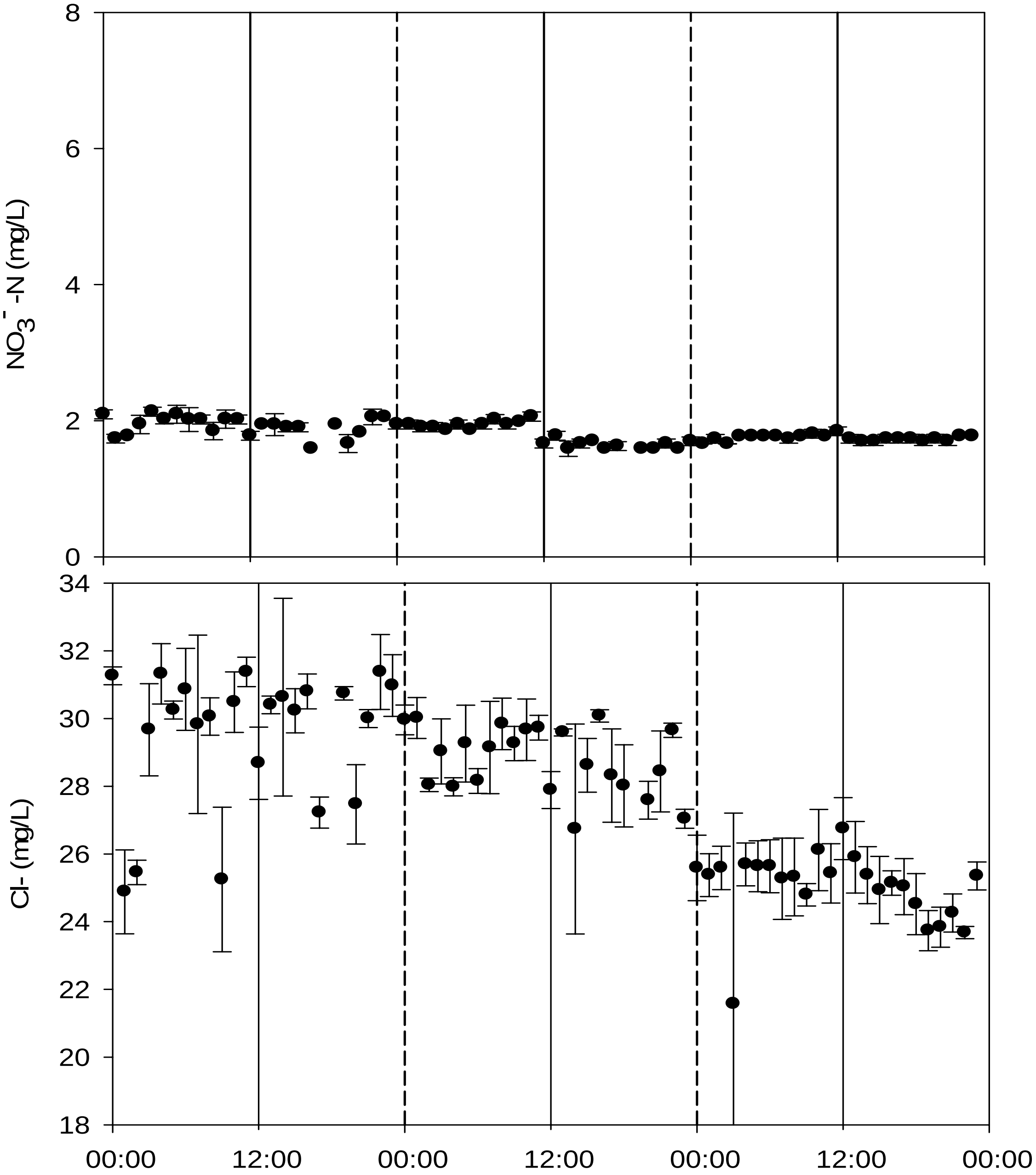

Figure 3.9: Hourly NO_3^- (top) and Cl^- (bottom) concentrations in the streamwater at the hillslope location of Cobb Mill Creek – March 27-29, 2008.

Conditions During Diurnal Variation

The first 72-hour field sampling campaign was undertaken during a period when appreciable evapotranspiration occurred from June 25-28, 2008. At the culvert, nitrate concentrations ranged from a minimum of 2.9 mg NO_3^- -N L^{-1} to a maximum of 7.5 mg NO_3^- -N L^{-1}, with an observed diurnal variation of an average of 2.7 mg NO_3^- -N L^{-1} (figure 3.7). At the hillslope location, observed nitrate concentrations ranged from a minimum of 3.1 mg NO_3^- -N L^{-1} to a maximum of 5.6 mg NO_3^- -N L^{-1}, with an observed diurnal variation of an average of 1.7 mg NO_3^- -N L^{-1} (figure 3.7).

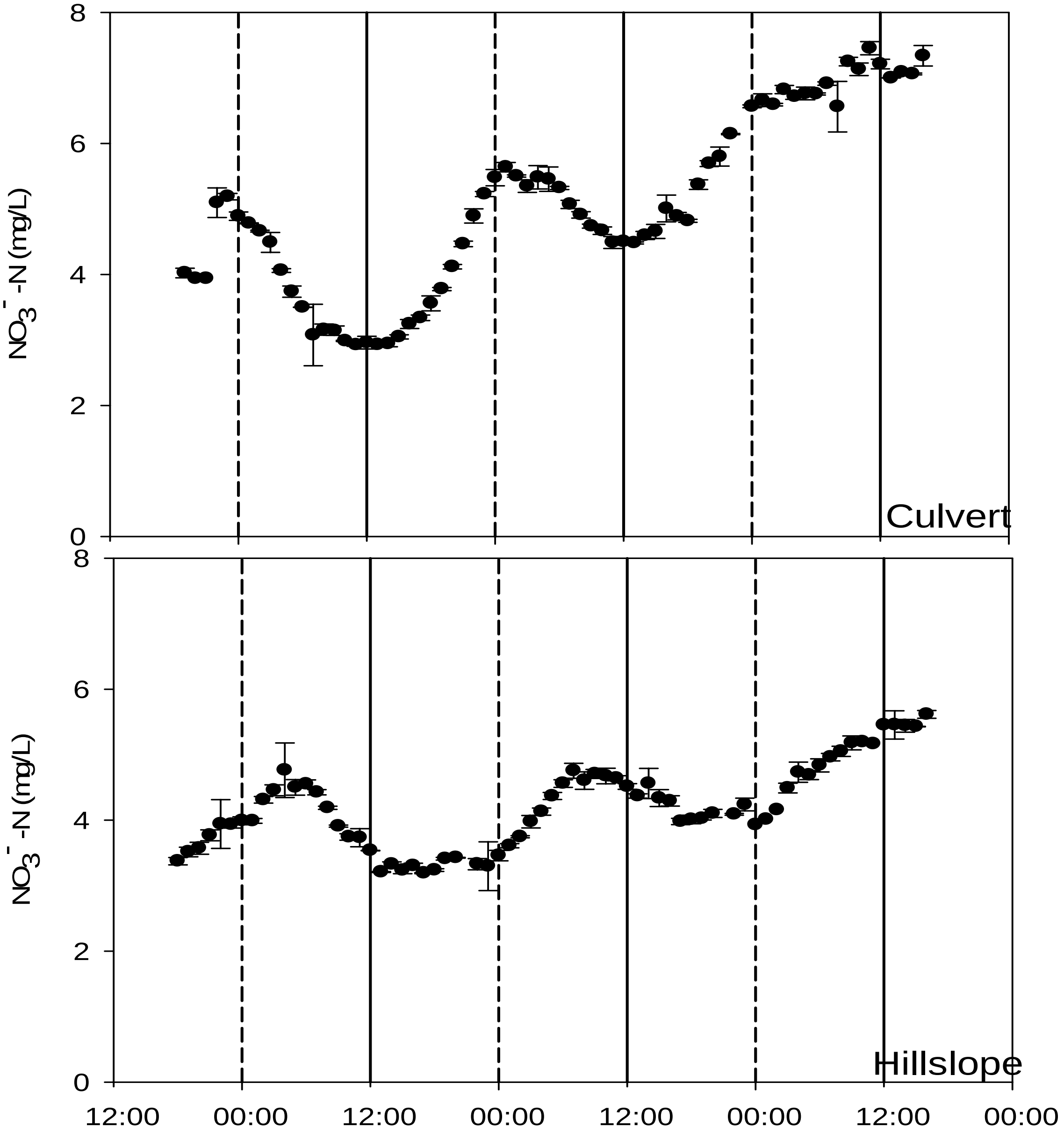

Figure 3.10: Hourly NO_3^- concentrations in the streamwater at the Culvert (top) and Hillslope (bottom) locations of Cobb Mill Creek – June 25-28, 2008.

The Cl^- concentrations in the streamwater at the culvert ranged from a minimum of 21.1 mg/L to a maximum of 27.6 mg/L, with an observed diurnal variation of an average of 2.8 mg/L (figure 3.8). The Cl^- concentrations in the streamwater at the hillslope ranged from a minimum of 21.1 mg/L to a maximum of 29.1 mg/L, with no distinctly observed diurnal variation during the sampling period (figure 3.8). The overall trend of the Cl^- concentration was to decrease during the 72 hour sampling campaign, with occasional peaks.

Dissolved organic carbon (DOC) concentrations in the streamwater at the culvert and hillslope locations ranged from 2.3 mg/L to 4.6 mg/L, with no distinct diurnal variability at either location. Complete details of the DOC concentrations are located in appendix C, figures C.4 and C.5.

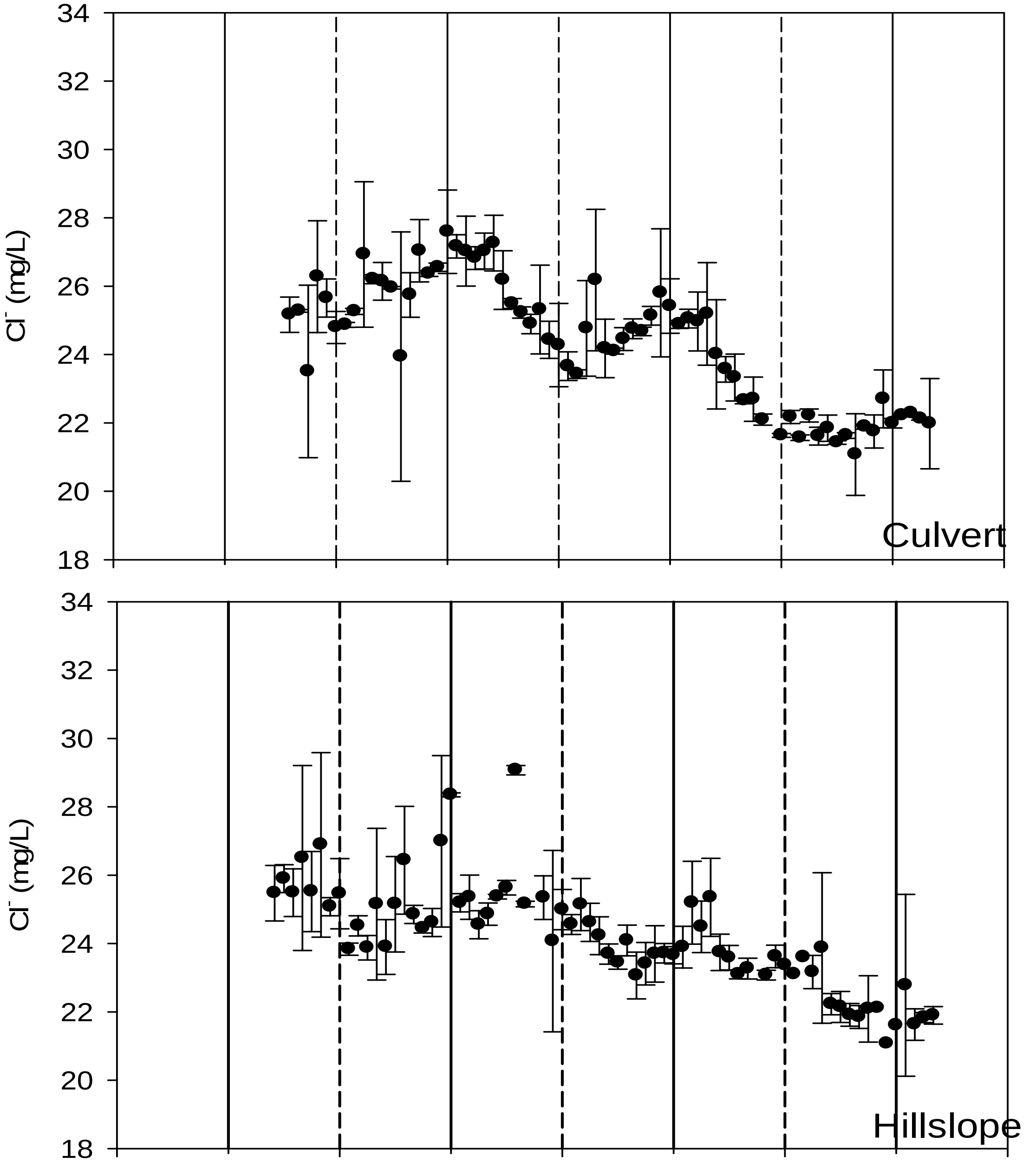

Figure 3.11: Hourly Cl$^-$ concentrations in the streamwater at the Culvert (top) and Hillslope (bottom) locations of Cobb Mill Creek – June 25-28, 2008.

The second 72 hour field sampling campaign undertaken during a period of expected evapo-transpiration occurred from August 20-23, 2008. During this time period, the overall nitrate concentration in the streamwater at the hillslope location was higher, with an average of approximately 5.5 mg NO_3^- -N L^{-1} (see figure 3.9), than the average concentrations during the previous two sampling campaigns. The observed variation in nitrate concentration in the streamwater at the hillslope was an average of 0.4 mg NO_3^- -N L^{-1}, which is a smaller magnitude diurnal variation than was observed during the June sampling campaign (figure 3.7). While the diurnal variation in nitrate concentration was smaller, it was nonetheless distinct and regular. The Cl^- concentration in the streamwater at the hillslope location was on average 21.9 mg/ L +/- 0.4 mg/L and did not display any diurnal variability (appendix C, figure C.8).

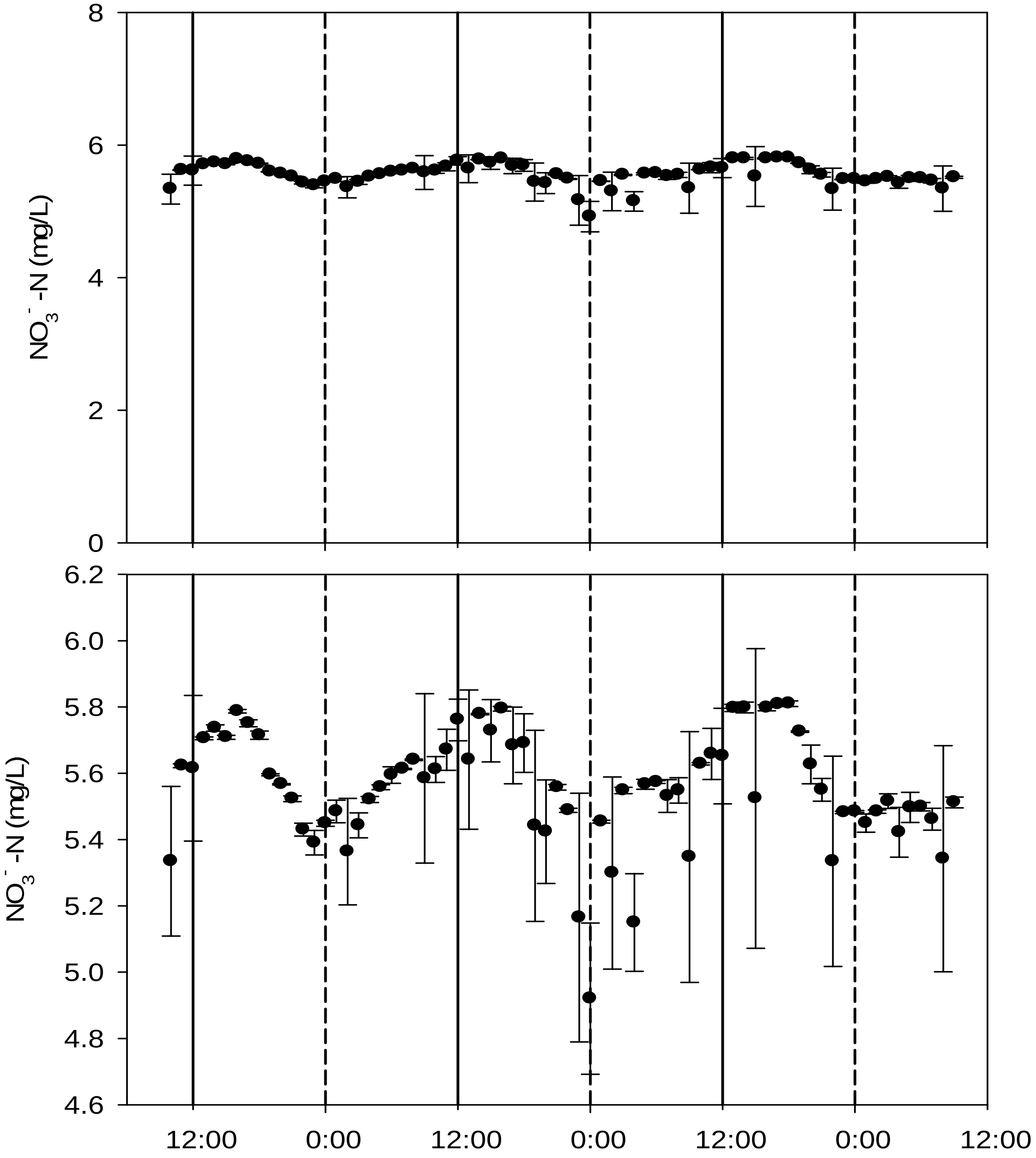

Figure 3.12: Hourly NO_3^- concentrations in the streamwater at the Hillslope location of Cobb Mill Creek (top is scaled 0-8 mg NO_3^- -N L^{-1}, bottom is scaled 4.6-6.2 mg NO_3^- -N L^{-1} to display the diurnal variation in concentration) – August 20-23, 2008.

The NO_3^- concentration in the streamwater coming from the pond was 0 mg/L +/- 0.02 mg NO_3^--N L^{-1} (appendix C, figure C.7). The concentration of Cl^- in the streamwater coming from the pond was on average 25.3 mg/L +/- 0.15 mg/L as measured using IC, and 40.8 mg/L +/- 1.9 mg/L as measured using a Cl^- ISE. Neither displayed a diurnal variability in concentration. Detailed results for both the IC and ISE measured Cl^- concentrations are located in appendix C, figures C.6 and C.7.

The concentrations of dissolved organic nitrogen (DON) and NH_4^+ measured from the grab samples taken at the pond and hillslope locations were both negligible. Detailed results for both DON and NH_4^+ concentrations are located in appendix C figure C.10.

Chapter 4: Discussion

Magnitude and Timing of Diurnal Variations in Stage and NO_3^- Concentrations

Magnitude and Shape of Diurnal Variations

Diurnal variations in both discharge and NO_3^- concentrations are occurring in the streamwater at Cobb Mill Creek. The diurnal variation in discharge observed at the culvert location of Cobb Mill Creek is as large or larger than the observed diurnal variation in discharge attributed to evapotranspiration in the literature and displays a sinusoidal pattern rather than the more spiked, saw-toothed, and abrupt pattern observed in much of the literature (Burt, 1979; Kobayashi et al., 1995; Kobayashi et al., 1990; Lundquist and Cayan, 2002). In the historical record at Cobb Mill Creek, diurnal variations in stage and discharge have been observed on the order of 20 to 100% from the average during the seasons of active evapotranspiration. During the June 23-25, 2008, sampling campaign the diurnal variations in discharge were measured as 50-100% from the average discharge (approximately 0.04 m^3/s) at the culvert and during the August 20-23, 2008, sampling campaign the diurnal variations in discharge were measured as 100% from the average discharge (approximately 0.045 m^3/s) at the culvert. The shape of the diurnal variation in stage/discharge at Cobb Mill Creek (both in the historical record and during the sampling periods) is largely sinusoidal with a slightly sharper rising limb and a more gradual receding limb.

Within the body of literature, a few studies have observed diurnal variations in discharge. Burt (1979) observed a spiky variation with v-shaped peaks and troughs whose variation was on order of 50-100% around the average discharge of ~0.0002 m^3/s. The watershed studied by Burt (1979) was very small (<1 km^2), with both forested and agricultural land use, and was prone to flashy responses to change in water table depth. The studies with conditions and responses most like those observed at Cobb Mill Creek were the two performed by Kobayashi et al. (1995; 1990) within the Moshiri basin, a small forested watershed (<10 km^2) with typically high relief. Kobayashi et al. (1995; 1990) measured a diurnal variation in discharge on the order of 50 to 100% around the average discharge of ~0.015 m^3/s. The magnitude of diurnal variation and the sinusoidal shape of the discharge record observed by the authors were similar to the discharge conditions observed in Cobb Mill Creek.

Timing of Diurnal Variations

Spectral analysis of the stage record at the culvert location of Cobb Mill Creek during the time periods surrounding the three sampling campaigns revealed regular periodicity of signal in the changes in stage. The stage record was examined from March 25-31, 2008, June 20-30, 2008, and August 18-22, 2008, and was analyzed for periodicity and strength of signal using the spectral analysis routine contained in the software package SAS v. 9.1.3. During the June and August 2008 records, a regular pattern in signal was observed every 144 measurements with a spectral density of 1.4 in June and 4.7 in August, orders of magnitude larger than the second strongest signals during either record (figures 4.2-4.3). Stage record at the culvert location was measured every ten minutes, which translates to 144 measurements per 24 hour time period. No major signal was observed at the 144th period during the March 2008 stage record (figure 4.1). There was a signal present at the 72nd period in all three stage records, but its magnitude was much smaller (1-1.5 orders of magnitude smaller) than the spectral densities of the signals observed daily during the June and August 2008 records. Because of its timing (approximately every 12 hours) this signal could possibly be a result of tidal influences, but considering the magnitude is much smaller than that of the daily signal, and because 72 is a harmonic of 144, this signal may also be a result of either noise or a residual effect from the spectral analysis procedure. Regardless, there is a clear strong daily signal observed in the stage record of Cobb Mill Creek during baseflow conditions in the season of highest expected evapotranspiration.

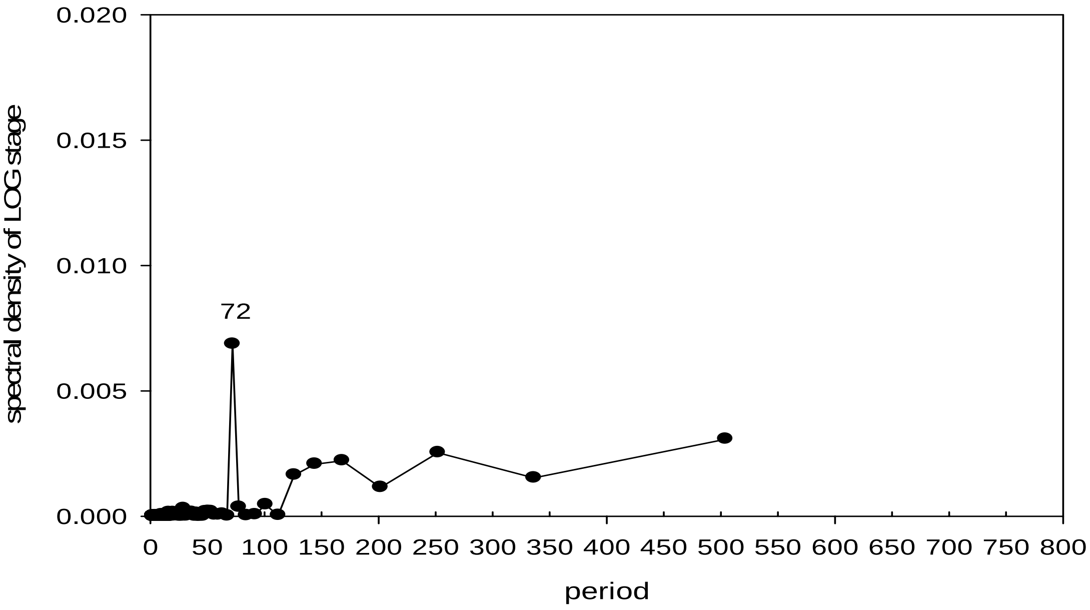

Figure 4.1: Spectral Density analysis of the March 25-31, 2008, stage record from the culvert location of Cobb Mill Creek, VA.

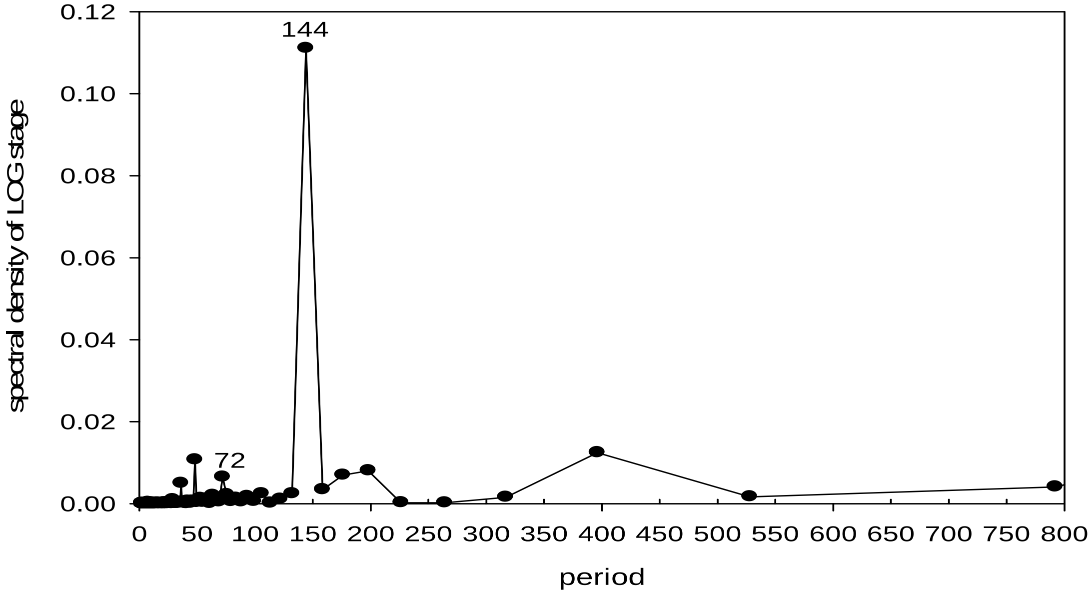

Figure 4.2: Spectral Density analysis of the June 20-30, 2008, stage record from the culvert location of Cobb Mill Creek, VA.

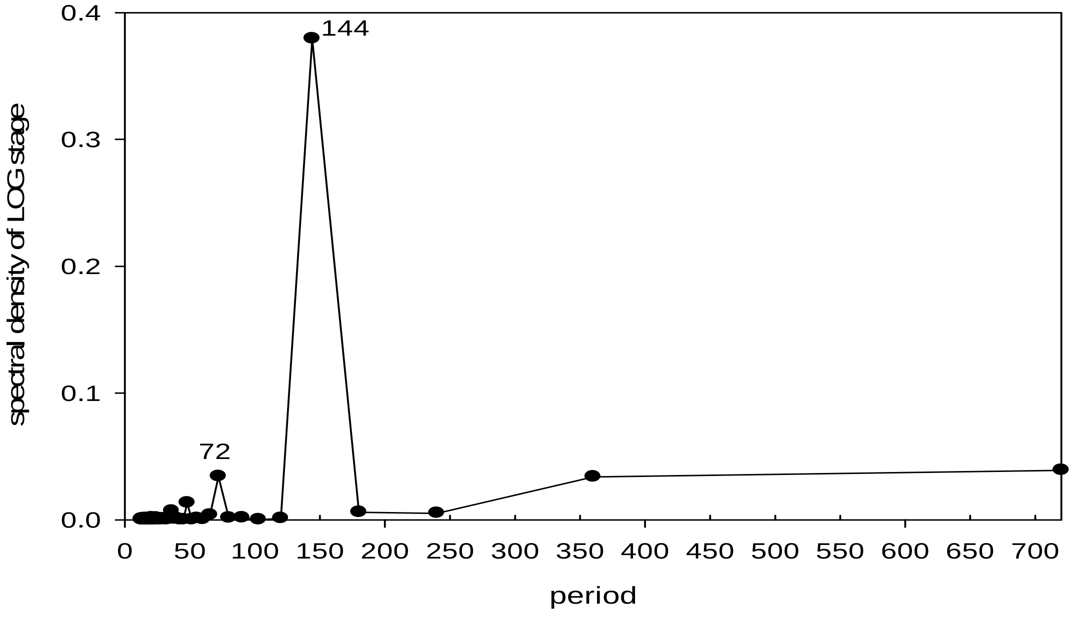

Figure 4.3: Spectral Density analysis of the August 18-22, 2008, stage record from the culvert location of Cobb Mill Creek, VA.

Using the ARIMA (auto-regressive integrated moving average) procedure contained within the SAS software v. 9.t1.3, an ARIMA model was also developed for the stage records from March, June, and August 2008. The stage record during both June and August was stationary, as evidenced by the rapid decay of the autocorrelation function, while the results from the autocorrelation function performed on the March 2008 stage record indicated that theses data may be non-stationary. Additionally, an autocorrelation check for white noise revealed that the overall patterns in stage record during all three time periods were not random.

An ARIMA model was fit to all three stage records (figure 4.4-4.6), and observing that the residuals for all three records were sufficiently random, it was determined that no drift was occurring within the modeled results for any of the stage records. The modeled results for the March time period were less accurate overall than that of the modeled results for either the June or August time periods, likely because of the non-stationary nature of the data during that time frame. For both the June and August stage records, the model was more accurate in predicting the up and down slopes in stage than it was at predicting the peaks and valleys of the record, indicating that there may be noise issues associated with the record at these times. The model does successfully depict the stationary nature of the data during these time periods, reflecting that the daily timing of maxima and minima of stage during the ET season remains fairly constant.

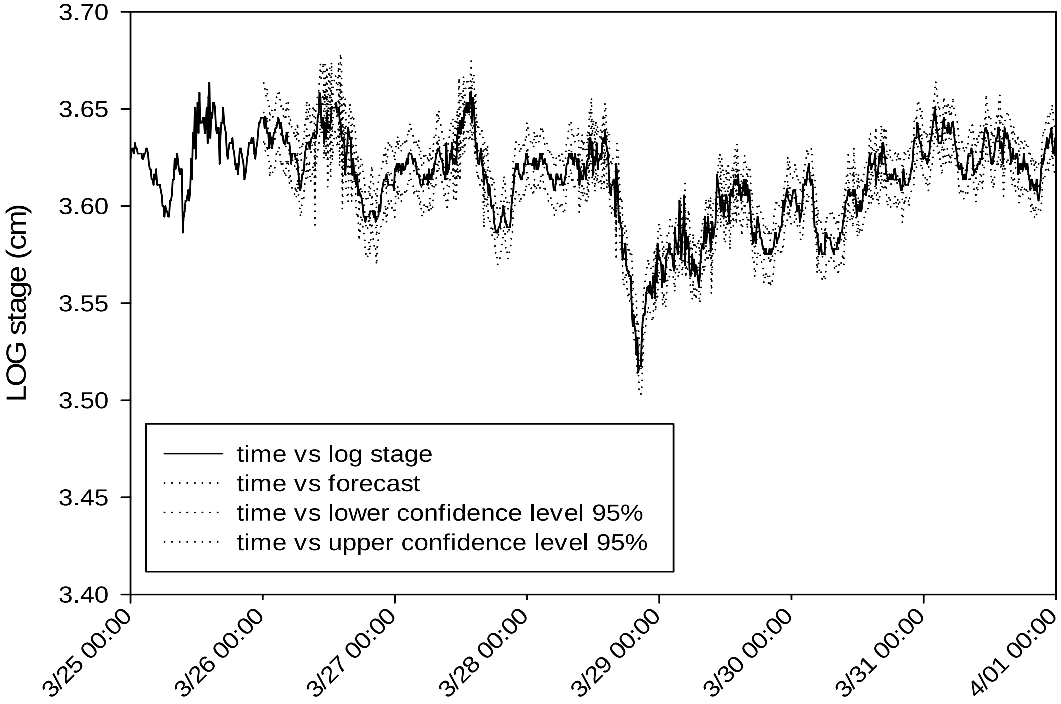

Figure 4.4: Graph of the $\log_{10}$ of actual and forecasted stage values plotted with 95% confidence intervals for the culvert location of Cobb Mill Creek, VA – March 25-31, 2008.

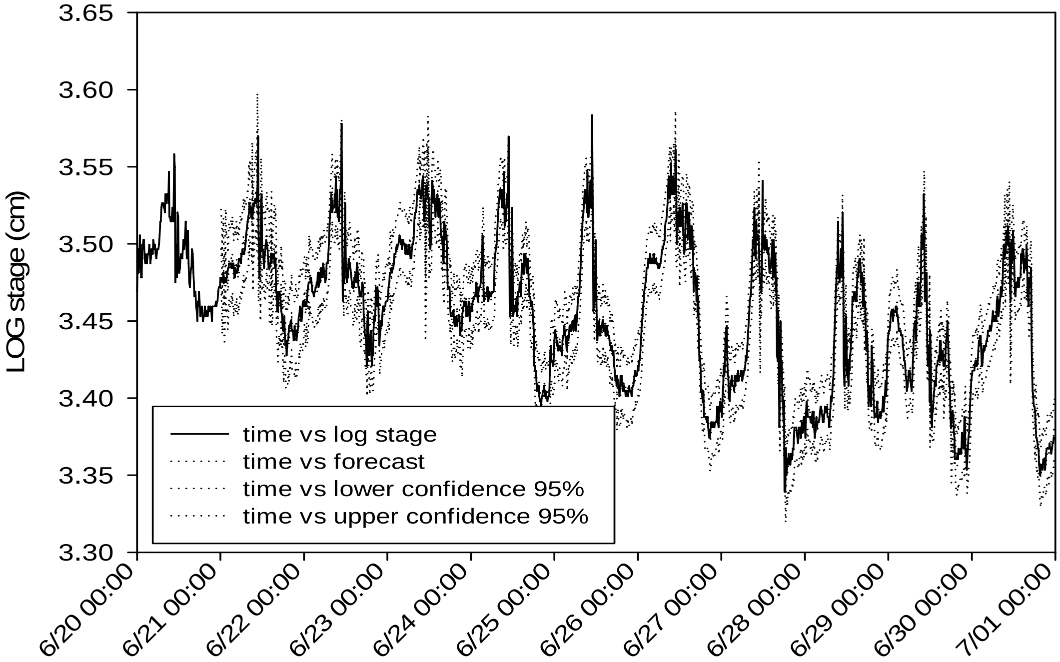

Figure 4.5: Graph of the $\log_{10}$ of actual and forecasted stage values plotted with 95% confidence intervals for the culvert location of Cobb Mill Creek, VA – June 20-30, 2008.

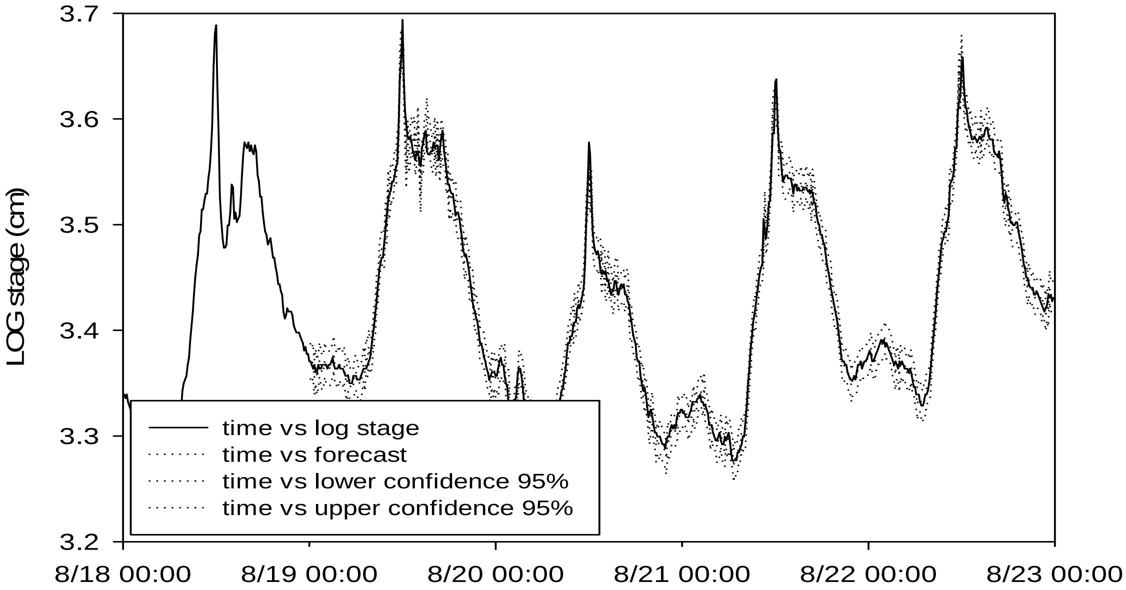

Figure 4.6: Graph of the $\log_{10}$ of actual and forecasted stage values plotted with 95% confidence intervals for the culvert location of Cobb Mill Creek, VA – August 18-22, 2008.

To reconfirm the constancy of daily timing of stage maxima and minima and in order to characterize the range in timing of stage maxima and minima throughout the ET season in 2008, three time periods were selected from the record during which little to no precipitation fell in the watershed (to ensure baseflow conditions). Throughout the months of June, July, and August a total of 28 days and 27 nights were selected as a representative for the whole ET season (Table 4.1). The timing of the daily maxima and minima was then recorded and plotted on a 24-hour clock with the percentages of minima and maxima that fell into each hour-long time period (figure 4.1).

Table 4.1: The time periods sampled for stream stage maxima and minima and the amount of precipitation in the Cobb Mill Creek, VA, watershed during the sampled dates – Summer, 2008

Time Period	*Day Count*	*Night Count*	*Precipitation (days)*	*Precipitation (mm)*
June 20-30, 2008	10	10	June 22nd, 2008 June 29th, 2008	1.02 1.78
July 12-22, 2008	10	10	July 14th, 2008	4.83
August 18-23, 2008	8	7	n/a	0

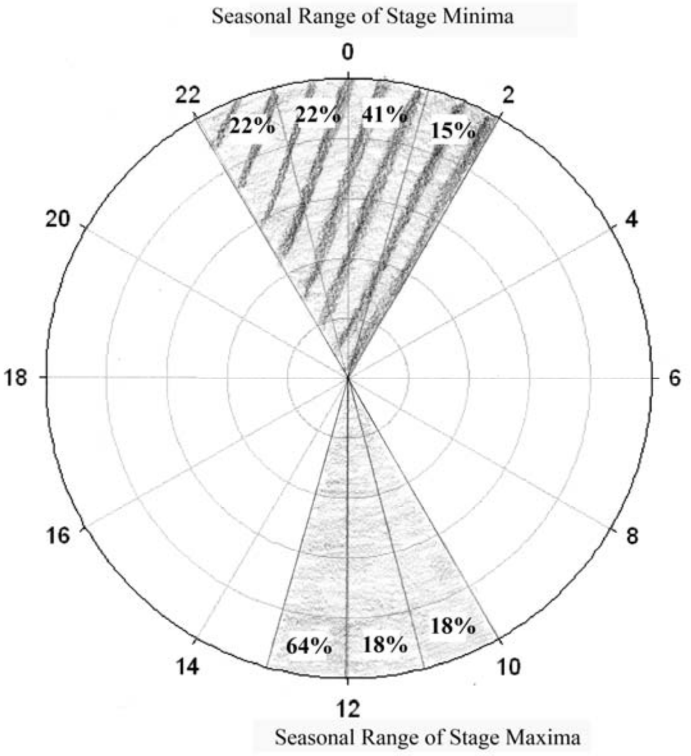

Figure 4.7: Twenty-four hour clock plotting the timing of daily maxima and minima in stream stage height in the Cobb Mill Creek VA, (0 = midnight) for 28 days during June-August, 2008. The percentage of readings falling within each hour-long interval is written directly on the plot.

While there is some variation (+/- 1.5-2 hours) around a central time, the daily maxima and minima do occur consistently in the same time periods throughout the ET season: 11:00-13:00 for the maxima and 23:00-01:00 for the minima. The timing of the maxima and minima is offset by approximately 12 hours, again indicating a diurnal pattern in stage during baseflow conditions. In contrast, other authors have reported the timing of maxima occurring anywhere between 10:00 – 13:00 (Burt, 1979) and 16:00 – 19:00 (Kobayashi et al., 1990, 1995) and timing of minima occurring anywhere between 18:00 – 22:00 (Burt, 1979) and 04:00 – 08:00 (Kobayashi et al., 1990, 1995). The diurnal patterns observed by Burt (1979) were not regularly offset by 12 hours, likely because of the flashy response of the studied stream to changes in head gradient. However, the maxima and minima observed by Kobayashi et al., (1995; 1990) in a similarly sized watershed to that of the present study were regularly offset by 12 hours as was observed in Cobb Mill Creek, even though the timing of the maxima and minima does not coincide with the timing observed in Cobb Mill Creek.

To quantify the magnitude and timing of maximum evapotranspirative demand that the forested riparian zone of Cobb Mill Creek could produce, the Priestly-Taylor equation (1972) was used to calculate PET for the time periods during which the sampling campaigns occurred (figure 4.3; see appendix D for the details of the calculations). Based upon the weather data gathered at Cobb Mill Creek (OYSM and HOGI weather stations; figure 2.2) during the sampling campaigns, the daily maxima in PET occurred between 12:00 and 13:00 for both the June and August 2008 time periods.

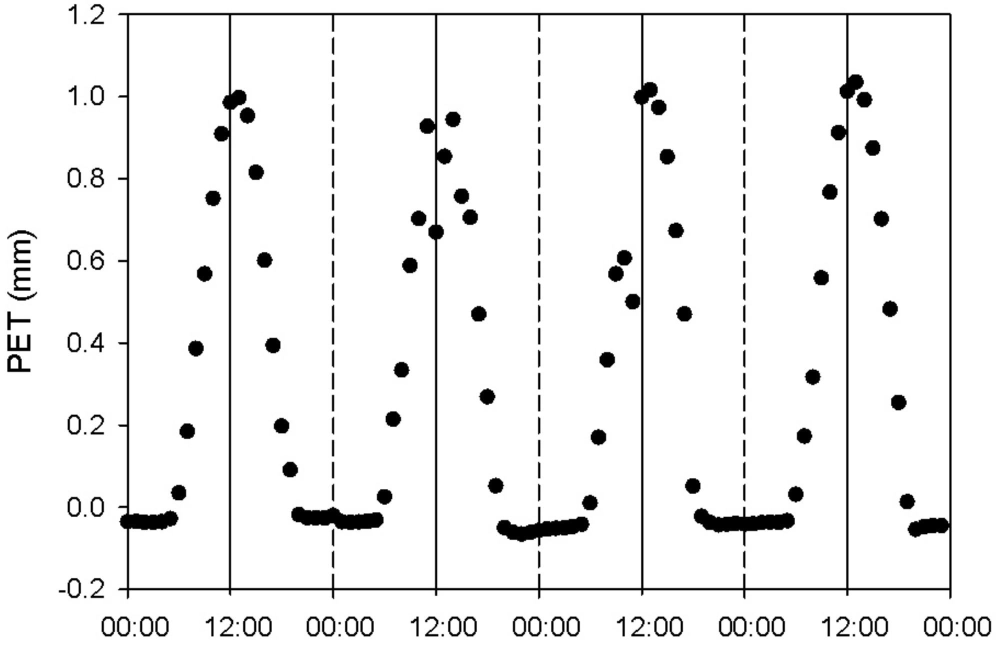

Figure 4.8: Graph of calculated hourly PET (mm) for the forested riparian zone of Cobb Mill Creek, VA – June 25-28, 2008. PET unites are in millimeters of water demand by the forest vegetation.

The stream stage/discharge recorded at the culvert (figure 4.7) also peaks during the time of maximum PET (figure 4.8). This concurrence is confounding, because, at first glance, the expectation would be that peak ET would coincide with the minimum discharge because evapotranspiration draws down the water table which would result in a lower head gradient, decreasing the rate of groundwater discharge to the stream. Observations of long lag times between evapotranspirative demand and stream response have been recorded in other systems as well. Wondzell et al. (2007) observed lag times in response of 1 to greater than 24 hours in a small (~1 km^2) watershed during baseflow conditions. The authors determined that this variation in lag time was attributable to the variation in discharge of the stream. As stream discharge decreased, lag times were observed to increase (Wondzell et al., 2007). This lag time effect is less observable in the discharge records of larger watersheds with comparable rainfall records due to the increased overall stream flow (Czikowsky and Fitzjarrald, 2004; Lundquist and Cayan, 2002; Troxell, 1936). During the year in which Wondzell et al. performed their study, the observed stream discharge in their watershed ranged from 0.002 – 0.12 m^3/s. During baseflow conditions in the seasons of active evapotranspiration discharge measured in Cobb Mill Creek at the culvert remains (for the most part) consistently between 0.02 – 0.05 m^3/s, so it seems to make sense that the timing of the stream discharge in Cobb Mill Creek lags the evapotranspirative demand by about twelve hours because the discharge at Cobb Mill Creek is on the order of that of Wondzell et al. where the authors observed lag times in stream response to water demand of ~12-16 hours. Additionally, the magnitude of stream discharge in Cobb Mill Creek is small, so lag times would be greater consistently than those observed in watersheds with greater stream discharge. Also, greater consistency of stream discharge in Cobb Mill Creek would lead to more consistent lag times in the Cobb Mill Creek record than the lag times observed by Wondzell et al. due to the vastly varying baseflow discharge of their stream.

The streamwater chemistry record collected during June and August 2008 was not long enough to attempt either a spectral analysis or an ARIMA model upon, as neither the June nor August sampling campaigns captured three clear maxima and minima. The pattern of variation within the NO_3^- concentrations observed during the June and August sampling campaigns was similar to that of the established diurnal pattern observed in the stage record for the same time periods. While the timing of maxima and minima in NO_3^- concentrations appeared to lag from day to day and sampling campaign to sampling campaign, there was still a single maximum and a single minimum observed within a single 24 hour period, and thus a diurnal pattern was observed in streamwater NO_3^- concentrations during the June and August 2008 sampling campaigns.

Seasonal variation in streamwater nitrate concentrations in Cobb Mill Creek varied greatly from March, when there was no evapotranspiration occurring, to June and August, when evapotranspiration was occurring. The average nitrate concentrations in March 2008 were much lower (~2 mg/L) than either June or August, with a combined average around 5 mg/L. Calculated as nitrate load (taking the stream discharge in L/day and multiplying it by the streamwater nitrate concentrations mg/L converted to kg), this is roughly 10.4 kg of NO_3^- -N per day in March 2008, and roughly 17.3 kg of NO_3^- -N per day during June/August. This observation is the opposite of what Angier and McCarty (2008) observed during baseflow conditions within the small, low-relief, agricultural watershed which the authors studied to examine seasonal and long-term variations in NO_3^- concentrations. The authors of this study found that nitrate load through their catchment was increased during seasons with no effect of evapotranspiration and they hypothesized that this was, in part, due to a) increased discharge resulting from the absence of ET related water table draw down and b) lack of nitrate uptake by vegetation during its dormant season. In Cobb Mill Creek it is possible that due to more intensive fertilization of the agricultural land within the catchment, overall nitrate load is higher within this watershed than in the watershed studied by Angier and Mcarthy (2008).

The diurnal variations in NO_3^- concentrations observed during the June study period at Cobb Mill Creek (1.7 - 2.7 mg/L) are an order of magnitude larger than the diurnal variations in NO_3^- concentrations observed by Scholefield et al. (2005) (0.15 - 0.2

mg/L) and have a vastly different shape in the pattern of the variation -- sinusoidal pattern at Cobb Mill Creek with a single maximum and minimum daily as opposed to saw-toothed with two maxima and minima daily observed by Scholefield et al. So while the Scholefield et al. study demonstrates that diurnal variation in NO_3^- concentrations is an observable phenomenon in streamwater, there is likely to be very little in common between the factors controlling the diurnal variations within the Scholefield et al. study site and those controlling the diurnal variations in Cobb Mill Creek simply because the responses of the two systems are so very different.

In order to highlight the large scale variations in concentrations and smooth out any small scale fluctuations, a five point moving average was performed on the nitrate and chloride data from the June 2008 culvert and hillslope and August 2008 hillslope streamwater results (Figures 4.9-4.10). For instances where a diurnal pattern could be observed, the timing of the maxima and minima was recorded. In cases where the peaks or troughs were plateaued the middle value was taken as the max/min. While there was variation in chloride concentrations during both the June and August 2008 sampling campaigns at the hillslope, the only distinctly diurnal pattern in chloride concentrations was observed at the culvert location during the June 2008 sampling campaign. The average diurnal variation in chloride concentrations was ~12%, smaller than the observed diurnal variations in nitrate concentrations from the same time period (~54% at the culvert and ~41% at the hillslope).

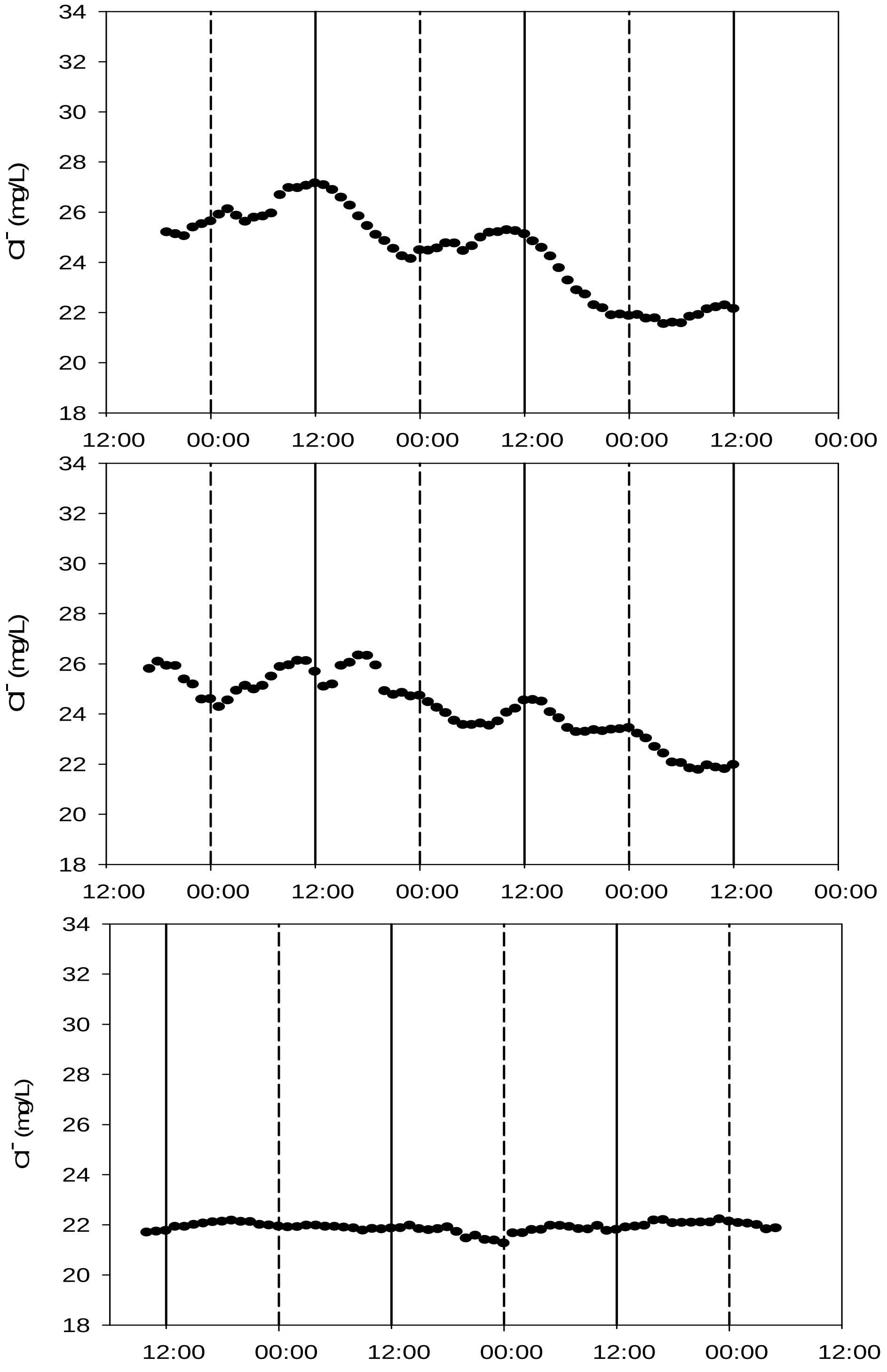

Figure 4.9: Graphs of the 5 point running averages of Cl^- concentrations from the June 2008 culvert (top), June 2008 hillslope (middle), and August 2008 hillslope (bottom) streamwater sampling campaigns.

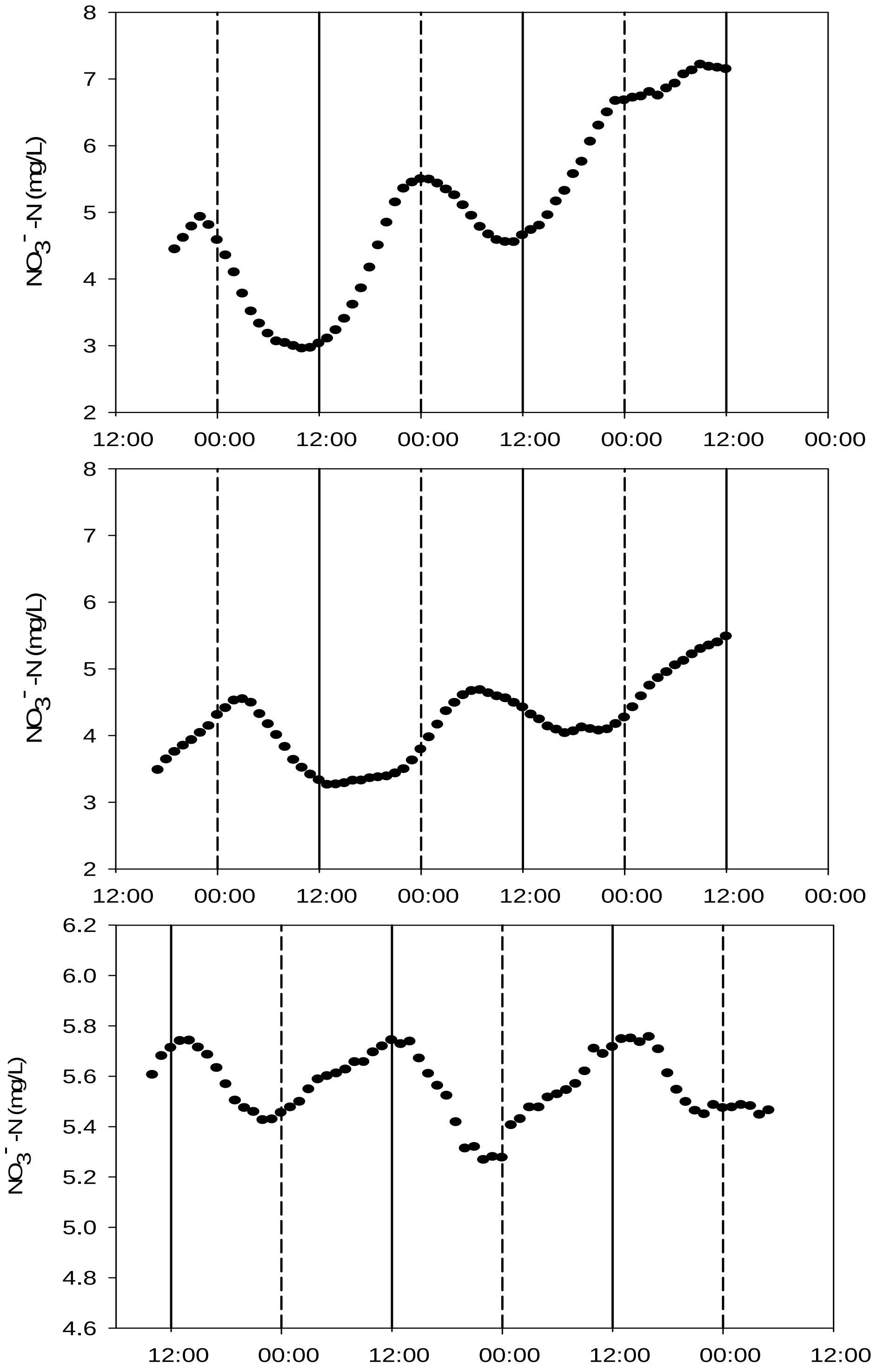

Figure 4.10: Graphs of the 5 point running averages of NO_3^- concentrations from the June 2008 culvert (top), June 2008 hillslope (middle), and August 2008 hillslope (bottom) streamwater sampling campaigns.

The timing of the daily maxima and minima in stream NO_3^- concentrations in Cobb Mill Creek has been plotted on twenty-four hour clocks for the two primary sampling locations: the culvert (June 2008, figure 4.11A) and the hillslope (June and August 2008, figure 4.11B). For each 72-hour sampling campaign, two or three maxima and minima were captured. Examining these three plots and comparing the timing of the daily maxima and minima, interesting patterns begin to arise. There are distinct diurnal patterns at each location and in each time period but, with the exception of the June 25-28, 2008, sampling at the culvert location, the diurnal patterns in NO_3^- concentration maxima and minima do not align with the diurnal patterns in stage. At the culvert, which was only sampled in June 2008, the range of times for NO_3^- maxima align with the range of times for stage minima and the range of times for NO_3^- minima are largely aligned with the range of times for stage maxima. This alignment is the exact opposite of what would be initially expected because low stage is associated with low discharge (Freeze and Cherry, 1979) and low discharge is associated with increased groundwater residence time (equation 1.3) which increases the opportunity for denitrification to occur (equation 1.4) and results in lower concentrations of NO_3^- in the water. The above pattern has been documented on the seasonal time scale in watersheds where denitrification processes are occurring in the streambed sediments (Hill, 1988; Pinay et al., 1993). On shorter time intervals such as are being observed in this study, however, these suppositions may not have as much validity, as the hillslope data demonstrate. No clear relationships exist between the timing of stage maxima and minima with the timing of maxima and minima in NO_3^- concentrations at the hillslope for either the June 2008 or August 2008 sampling campaigns.

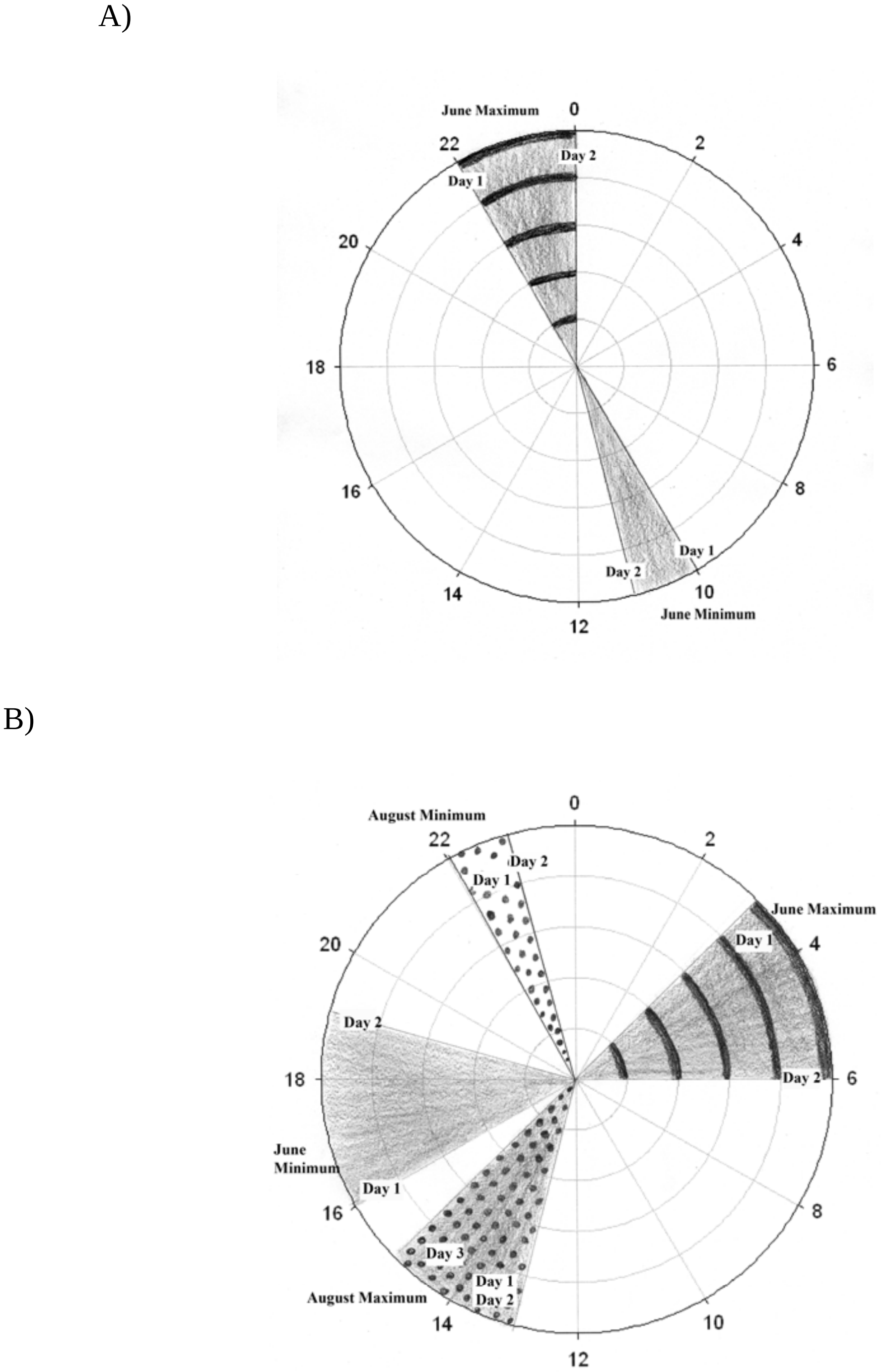

Figure 4.11 A-B: Twenty-four hour clocks plotting the timing of daily maxima and minima in NO_3^- concentrations at the (A) culvert sampling location June 25-28, 2008, and at the (B) hillslope sampling location June 25-28, 2008, and August 20-23, 2008. The day of measured samples with maximum and minimum NO_3^- concentrations for each time period at each location is written directly on the plot in the appropriate one-hour interval in which it was observed.

There is both a lag in the timing of the maxima and minima between the samples collected at the culvert and those collected at the same time at the hillslope as well as a difference in magnitude of the diurnal variation observed between the samples collected at the culvert (average diurnal variation of ~2.7 mg NO_3^--N L^{-1}) and the hillslope location (average diurnal variation of ~1.7 mg NO_3^--N L^{-1}). The diurnal pattern exhibited by the June 2008 hillslope NO_3^- concentrations is offset from that of the culvert NO_3^- concentrations by 3-8 hours (figures 4.11A-B). The distance between the two locations is only ~250 m, and the travel time calculated for the stream stretch is ~0.75-2.5 hours at baseflow conditions (Mills, A.L.; personal communication) so this difference in timing cannot be simply explained by a delay in the 'plug' of streamwater traveling downstream from one location to the other. In addition to the difference in magnitude of diurnal variability of the NO_3^- concentrations, both the concentration and magnitude of diurnal variation in the samples at the culvert location was higher overall (5.1 mg NO_3^--N L^{-1}) than at the hillslope (4.2 mg NO_3^--N L^{-1}). Furthermore, the nitrate concentration of both the culvert and hillslope samples trended higher over the duration of the sampling period, ending with an overall higher NO_3^- concentration in the streamwater than at the beginning.

In-stream processes of nitrate removal have been documented at other experimental sites (Christensen et al., 1990), but the conditions under which those processes can occur are largely absent from Cobb Mill Creek (*i.e.*, presence of algae in the water column). There is also evidence to suggest that while the process of hyporheic exchange can remove nitrate from the water column (Findlay, 1995), this process is not occurring in Cobb Mill Creek because the stream is a predominantly gaining stream throughout the stretch between the culvert and the hillslope locations (Mills, A.L.; personal communication). Denitrification occurs in the sediments along this reach of Cobb Mill Creek (Galavotti, 2004; Gu et al., 2007) with some degree of spatial variability (Flewelling, 2009), so a mixing of groundwaters higher in NO_3^- concentrations with those lower in NO_3^- concentrations is occurring along the stream stretch. Groundwater which has had the majority of its nitrate removed prior to discharge to the stream is mixing into the stream with groundwater which experienced relatively little or no denitrification prior to discharge. This spatial mix of waters with varying nitrate concentrations complicates the understanding of how nitrate concentrations vary temporally in the stream.

The timing of the maxima and minima of NO_3^- concentrations is also not remaining the same temporally. The timing of the maxima and minima in NO_3^- concentrations in June 2008 at the hillslope is offset from those in August 2008 at the same location by 9-11 hours for the maxima (figure 4.11B) and by 4-7 hours for the minima (figure 4.11B). One insight into why this phenomenon is being observed is the way in which the variation in maxima and minima timing is occurring during each sampling period, not just between sampling periods. While the maxima and minima of NO_3^- concentrations is diurnal in pattern (ie: one maximum and one minimum in a 24 hour period) it is not strictly diurnal such as was observed in stage, where over the course of the season, the maxima and minima were separated by 12 hours +/- 2 hours. Rather, in the case of the variation in NO_3^- concentrations, there was a separation of 11-14 hours between the maximum and minimum on a given day, but often a greater than 24 hour difference between the timing of the maximum from one day to the next. The timing of the pattern invariably was equal to or greater than 24 hours, and not less. For example, the timing of the maximum NO_3^- concentrations from the hillslope samples collected during June 25-28, 2008, sampling campaign went as follows: 03:00 on day one, 06:00 on day two (figure 4.10). This pattern also occurred in the maxima of the June 2008 culvert samples and in both the maxima and minima of the August 2008 hillslope samples.

This pattern of “marching” maxima and minima indicates that the variation in timing between August and June moves continually around the clock throughout the ET season rather than remaining in a (relatively) fixed position like the stage variation. One factor which likely controls this effect is the variability in groundwater discharge (and thus residence time in the zone of denitrification) at baseflow conditions, which results from both diurnal and seasonal fluctuations of the water table. A change in water table gradient creates a change in the pressure driving flow along the flow path. Assuming a rigid and incompressible media, this pressure wave is transferred instantaneously along the flow path, but the water itself is not. The result is that the water traveling along a flow path is affected by the pressure wave of each change in head gradient. The cumulative effect of multiple pressure changes alters the residence time of a volume of water along both the flow path and in the zone of denitrification. This relationship is more complex than can be encompassed by examining the system as being affected by a single pressure wave.

There is not a rich enough body of literature on observed diurnal variations in NO_3^- concentrations to go beyond speculation of the processes affecting the temporal variability of diurnal variations of NO_3^- concentrations in Cobb Mill Creek. The timing and magnitude of the maxima and minima in NO_3^- concentrations does not directly relate to the timing or magnitude of either PET or stream discharge. Additionally, the timing of the NO_3^- variation is not displaying a consistent offset between daily maximum and daily minimum. Because there is not exactly a 12 hour separation between the daily maximum and the daily minimum (separation is between 11-14 hours, but it tends to increase from day to day, *i.e*., day 1, the separation is ~12 hours, day two, the separation is ~13 hours, and so on), the timing of the diurnal variation moves around on the clock. These “marching” maxima and minima appear to continually move around the clock throughout the ET season. For example, if we see a timing difference due to “marching” maxima of 1.5 hours per day, then between June 2008 and August 2008 the maxima and minima would have moved around the clock by ~35 hours, so there would be an 11 hour temporal lag from one sampling campaign to the next. The timing of the observed lag is between 7-11 hours (figure 4.11B), lining up strikingly well with the estimated effect of the “marching” temporal lag.

Chapter 5: Ideas for Future Research

Due to the degree of complexity associated with the denitrification process in the Cobb Mill Creek watershed, it seems very unlikely that a one dimensional model could be legitimately developed to model the diurnal variation of nitrate concentrations in the streamwater of Cobb Mill Creek. The spatial variability of organic matter in and hydraulic conductivity of the sediments leads to varying extents of denitrification of discharging groundwater. The effect of multiple pressure waves (resulting from the continual variation of the head gradient) upon the groundwater along the flow path causes a continual variation of discharge rate, meaning that it would be difficult to quantify a residence time of any significant volume of water within the zone of denitrification. Compounding with both of these factors is the effect of the travel time and mixing of water in the stream channel with discharging groundwater. In fact, the 1-D model of this system by Flewelling (2009) was unable to match the shape, timing, or magnitude of the diurnal variation in nitrate concentrations observed in Cobb Mill Creek.

In light of the facts stated above, the ideal way to model the diurnal variation of both stream discharge and streamwater chemistry in Cobb Mill Creek would be to develop a three dimensional model. A 3-D model could be made to account for the spatial variability of organic matter and hydraulic conductivity of the sediments. It could model the variation of travel time of groundwater along the flow path and it could be made to account for the travel time and mixing along the stream channel itself. Currently, not enough information is known about the Cobb Mill Creek watershed to legitimately parameterize a 3-D model. To that end, I propose several steps of further research in order to be able to effectively model the processes occurring in Cobb Mill Creek:

Monitoring of local conditions to better quantify evapotranspiration in the riparian zone of Cobb Mill Creek

A station which monitors local net radiation and surface emissivity along with both air and surface temperatures, precipitation, and cloud cover needs to be installed within the Cobb Mill Creek watershed. For the purposes of the research outlined in this document, some of these parameters (solar radiation) had to be taken from a station 17 miles away, and some of these parameters (surface emissivity, surface temperatures, and cloud cover) had to be estimated based upon previous values reported in the literature. Additionally, measurements of leaf area index for the riparian zone of Cobb Mill Creek watershed need to be taken. This value was also estimated from literatures values. Having this type of data for the Cobb Mill Creek watershed could refine the estimates of both seasonal and diurnal water demand of the vegetation within the riparian zone of Cobb Mill Creek, allowing for more accurate estimates of water table drawdown as a result of evapotranspiration.

One to two high intensity 5-6 day sampling campaigns monitoring both rates and streamwater chemistry of groundwater seepage along the stream channel of Cobb Mill Creek

Neither the spatial nor the temporal variability of groundwater seepage rates and chemistry have been extensively quantified for Cobb Mill Creek. Flewelling (2009) deployed some seepage meters in multiple locations along the stream channel between the culvert and hillslope at Cobb Mill Creek to monitor rates of groundwater discharge, but no chemistry was done for these samples and during the sampling, the meters were relocated multiple times in order to gain a greater understanding of spatial variability at the cost of temporal variability. Cox and others (appendix E) measured water chemistry and seepage rates for a small stretch near the hillslope location, but the samples were only collected in 4, 8, or 12 hour intervals which limits their usefulness for quantifying diurnal variability in chemistry and discharge because the resolution simply isn't available. There currently is no water chemistry data available during periods without evapotranspiration occurring in the riparian zone and only limited seepage data.

What needs to occur are two high-intensity field sampling campaigns; one during the dormant season and one during the season of active evapotranspiration, each being five to six days in length in order to attempt to catch the minimum peaks and troughs necessary for completing spectral analysis and ARIMA modeling of the results. Five to ten seepage meters should be deployed within a 5 m stretch of stream channel every 15-20 m from above the culvert all the way to the hillslope. These meters should be monitored for seepage rate and samples should be collected for water chemistry every one to two hours. In addition, streamwater chemistry at both the culvert and the hillslope locations should be monitored hourly using the same ISCO based sampling process outlined in this study.

This high-intensity sampling protocol will be able to account for both the spatial variability of the zone of denitrification and the hydraulic conductivity of the streambed sediments as well as being able to quantify the diurnal and seasonal variability of groundwater discharge rates and water chemistry. These samples would be a major step forward towards the parameterization of the factors affecting diurnal stream discharge and streamwater chemistry, allowing for a 3-D model which more accurately depicts the processes occurring in Cobb Mill Creek.

Having an accurate 3-D model of the diurnal variation of stream discharge and water chemistry for Cobb Mill Creek would be a worthwhile research endeavor because the presence of any diurnal variability in streamwater chemistry calls to question the current watershed monitoring practices for reactive contaminants. Current practices most commonly involve the use of grab sampling techniques to monitor streamwater chemistry. Grab samples are taken on the frequency of months or weeks and used as a representative sample of the conditions within the watershed. Depending upon the season and time day in which these samples are taken, the concentrations of reactive contaminants can vary greatly, as has been demonstrated by this research. Being able to quantify the timing and magnitude of the diurnal variation in streamwater chemistry is a luxury which most watershed monitoring studies do not have the time or resources to complete. If a model can be developed which predicts the timing and magnitude of diurnal variations in stream discharge and water chemistry for watersheds of comparable size and land use, then perhaps the monitoring process for reactive contaminants can be improved with little additional cost of time and resources.

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Appendix A: Land Use in the Cobb Mill Creek Watershed

This appendix contains the processes and results from two different studies of land use within the Cobb Mill Creek watershed. The first study examined the different land use types within the limits of the Cobb Mill Creek watershed using the 2001 National Land Cover Dataset and watershed boundaries created by myself, based upon work performed by John Porter as a part of the delineation of the 17 watersheds of interest in the synoptic survey of the Eastern Shore of VA (Olson et al., 2006). Land use reported took the 15+ available land covers and agglomerated them into “forested”, “agricultural”, and “other” categories. The “other” category included open water, urban area, and non forested wetland (figure A.1). The study results were that the land cover within the Cobb Mill Creek watershed is ~58% agricultural, 28% forested, 12% urban, and 1% open water.

The second study examined the land use immediately adjacent within a 10 m distance of the stream itself performed by Sarah Glendon (undergraduate research assistant, UVA). She used the 2008 Virginia Base Mapping Program ortho-imagery aerial photography (2 ft resolution) to delineate the stream channel. She created a 10 m buffer around the digitized channel and classified land use within that buffer based upon the aerial photos. The classifications she used were “forested”, “agricultural”, and “non forested wetland” categories (figure A.2). The 10 m stream buffer drawn contained no urban land use. The study results were that the land cover within the 10 m buffer adjacent to Cobb Mill Creek is ~54% forested, 21% non-forested wetland, and 25% agricultural.

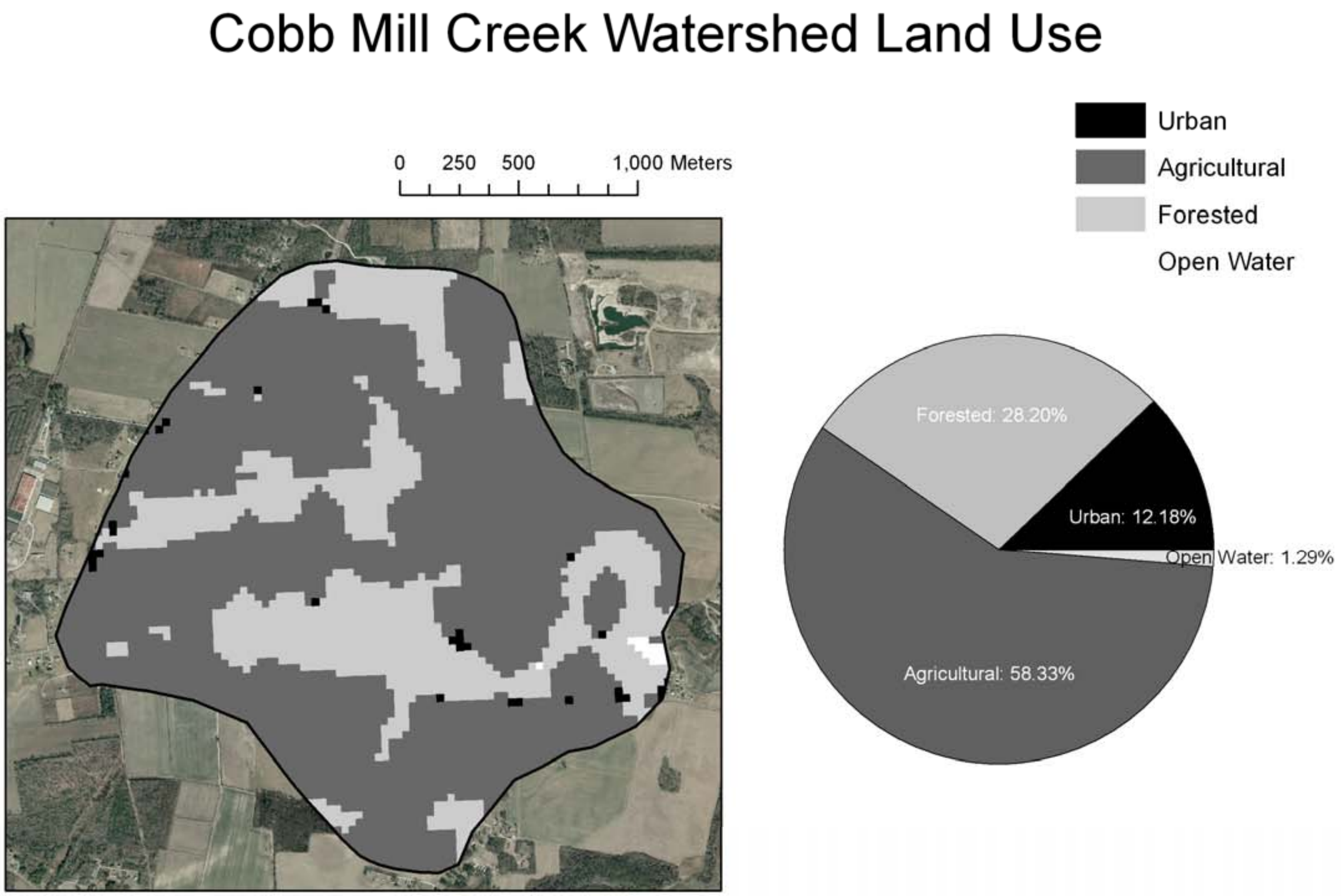

Figure A.1: Land use within the Cobb Mill Creek watershed

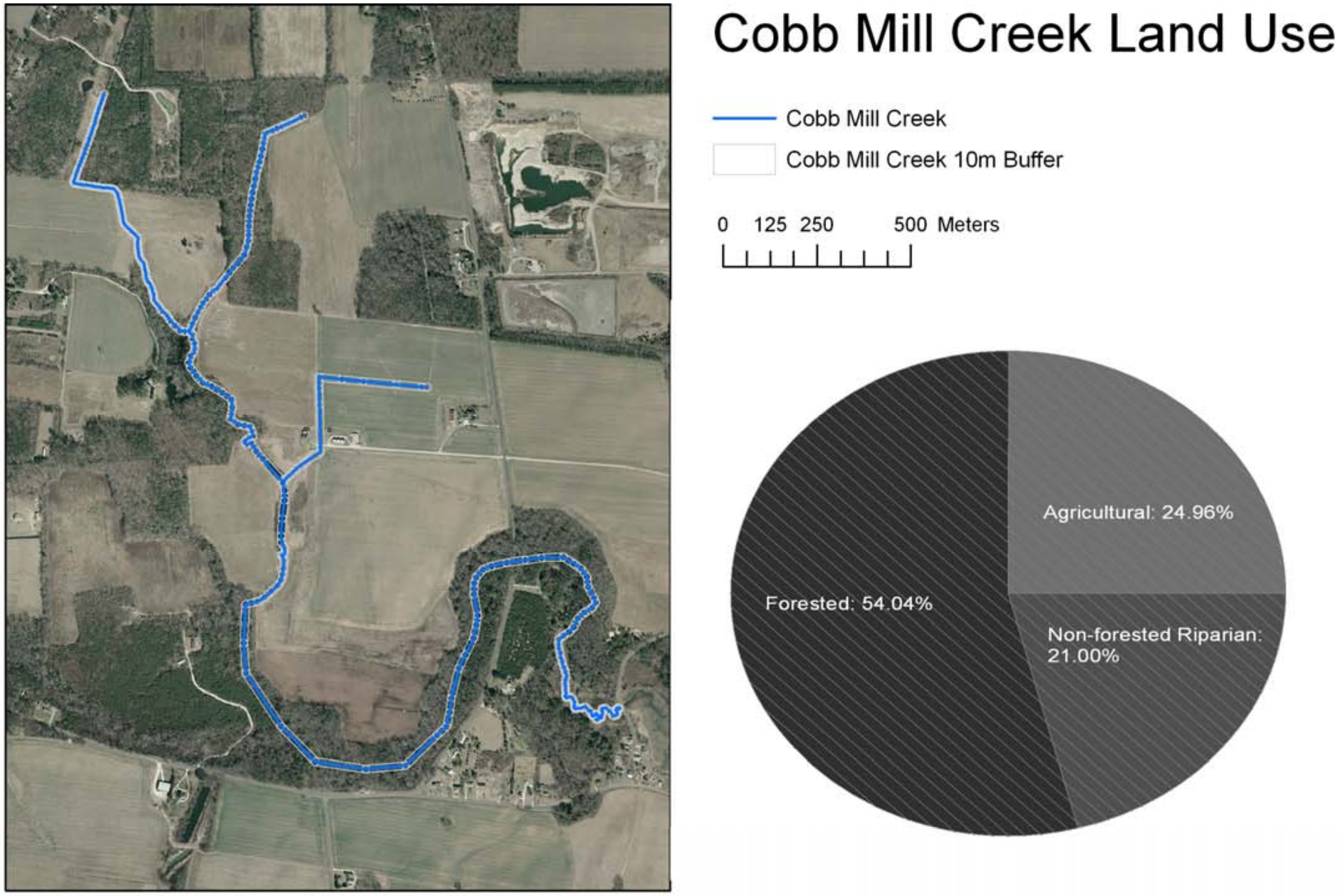

Figure A.2: Land use adjacent to Cobb Mill Creek in a 10 m zone around the stream channel.

Appendix B: Standard Curves for Streamwater Chemistry Analysis

March Ion Chromatography

The standard curve used to calculated the anion concentrations for NO_3^-, Cl^-, and SO_4^{2-} was based upon a sample blank (0 mg/L), 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 20 mg/L, and 40 mg/L standards. Each standard was run in triplicate. All three anion standard curves had r^2 values greater than 0.967 with linear fit lines on all three graphs (figures B.1-B.3).

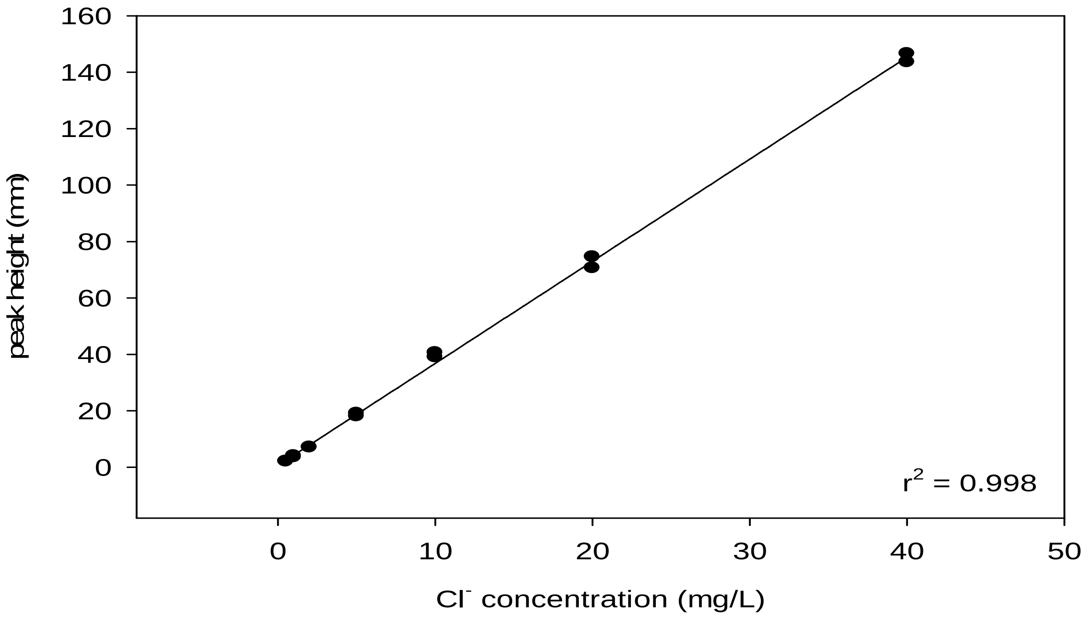

Figure B.1: Standard curve for March Cl^- concentrations; linear fit

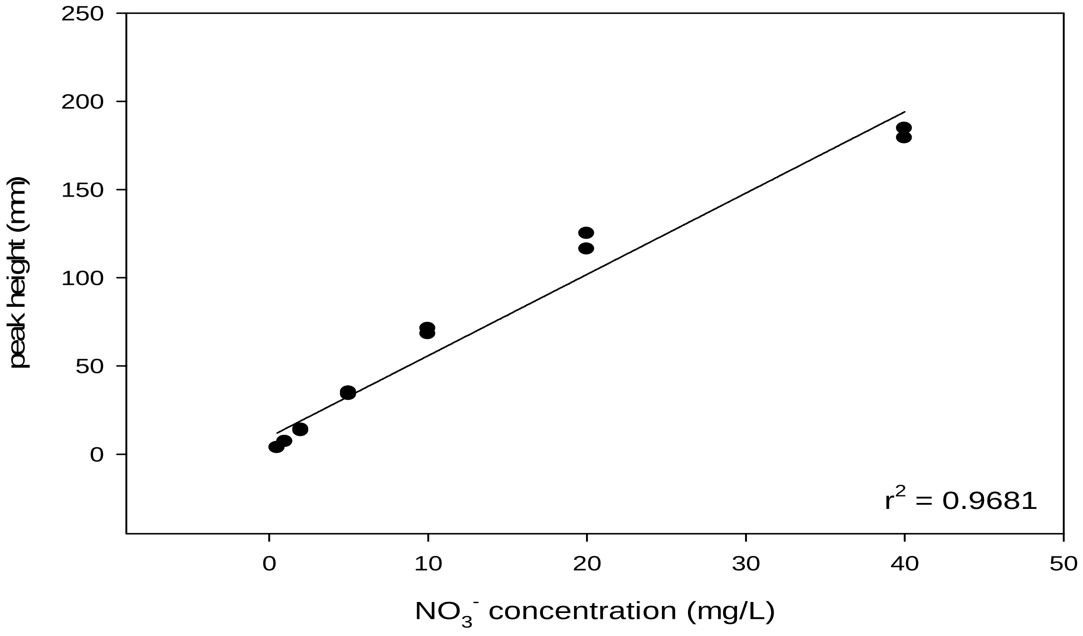

Figure B.2: Standard curve for March NO_3^- concentrations; linear fit

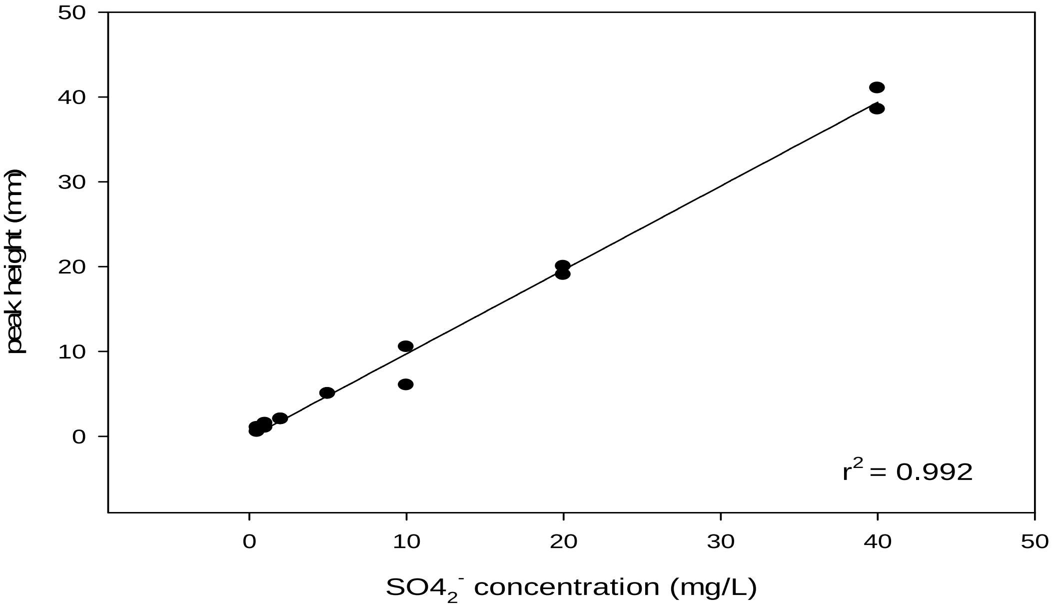

Figure B.3: Standard curve for March SO_4^{2-} concentrations; linear fit

May Ion Chromatography

The standard curve used to calculated the anion concentrations for NO_3^-, Cl^-, and SO_4^{2-} was based upon a sample blank (0 mg/L), 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 20 mg/L, and 40 mg/L standards. Each standard was run in triplicate. All three anion standard curves had r^2 values greater than 0.975 with linear fit lines on all three graphs (figures B.4-B.6).

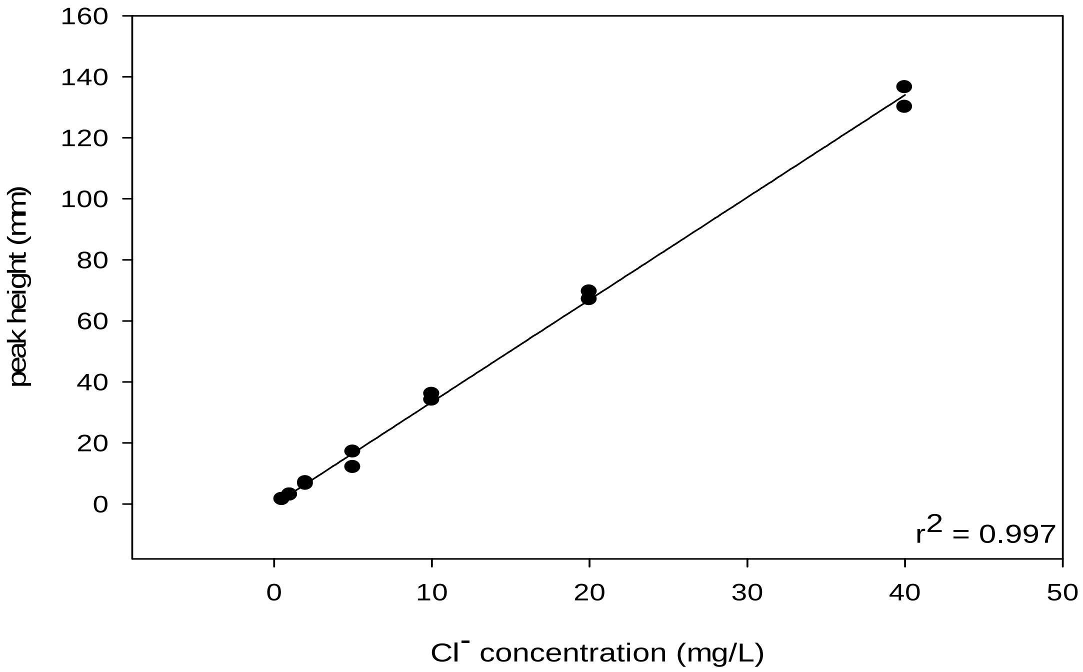

Figure B.4: Standard curve for May Cl^- concentrations; linear fit

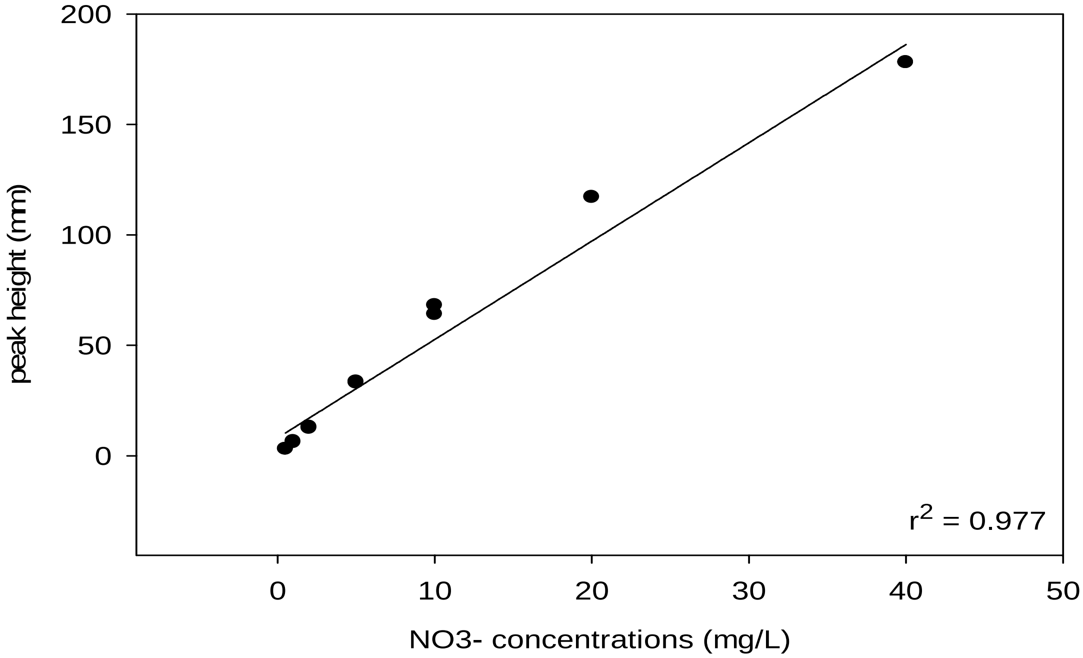

Figure B.5: Standard curve for May NO_3^- concentrations; linear fit

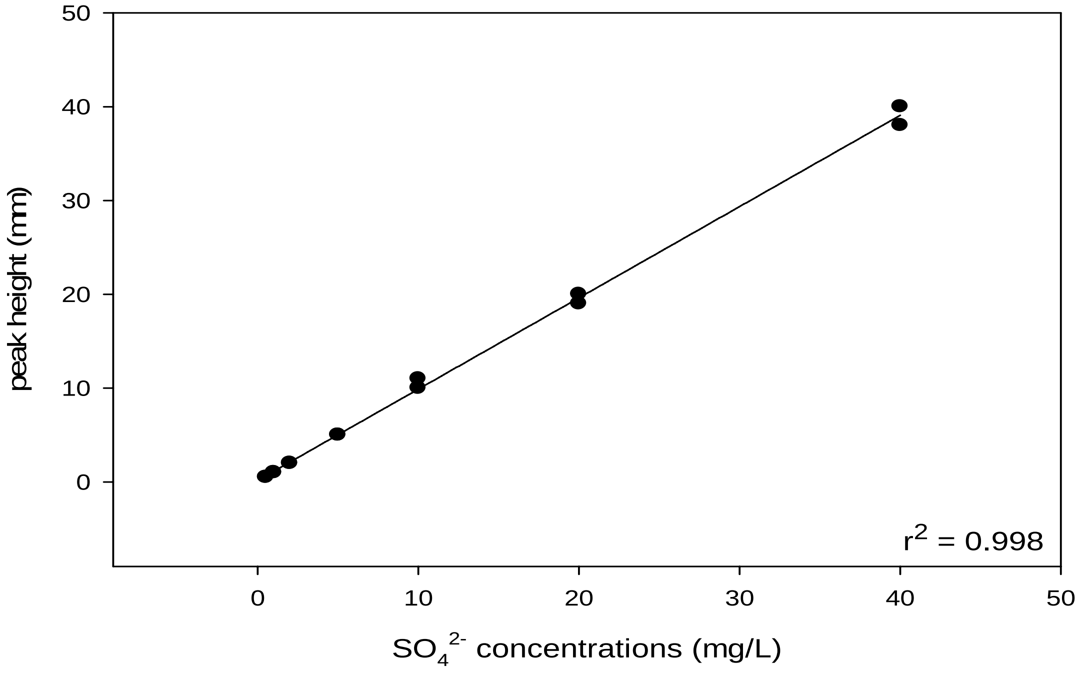

Figure B.6: Standard curve for May SO_4^{2-} concentrations; linear fit

June and August Ion Chromatography

The standard curve used to calculated the anion concentrations for NO_3^-, Cl^-, and SO_4^{2-} was based upon a sample blank (0 mg/L), 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 20 mg/L, and 40 mg/L standards. Each standard was run in triplicate. All three anion standard curves had r^2 values greater than 0.993 with quadratic fit lines on all three graphs (figures B.7-B.9).

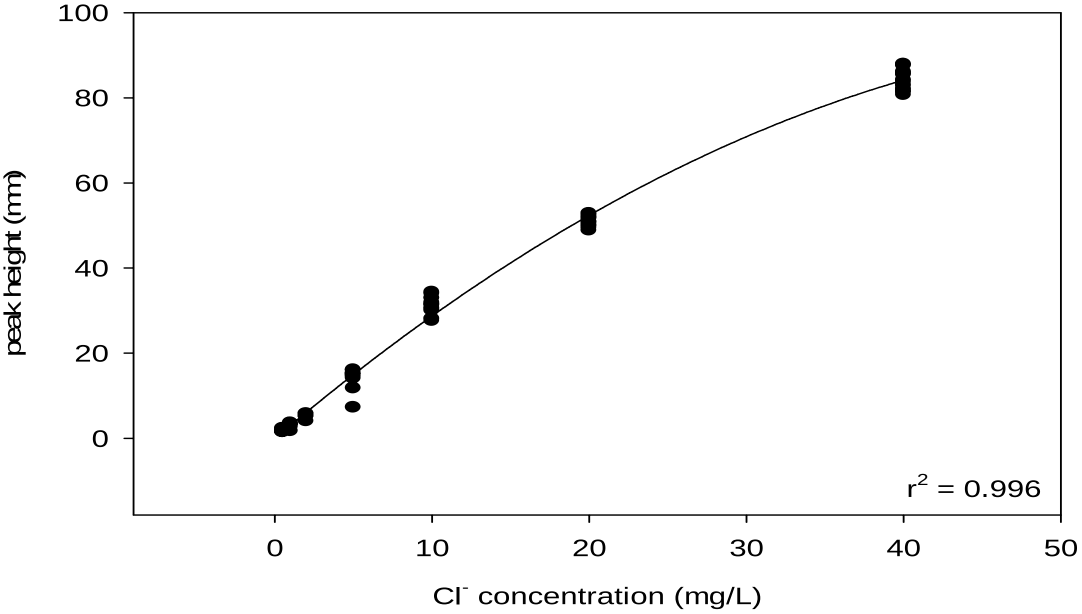

Figure B.7: Standard curve for June and August Cl^- concentrations; quadratic fit

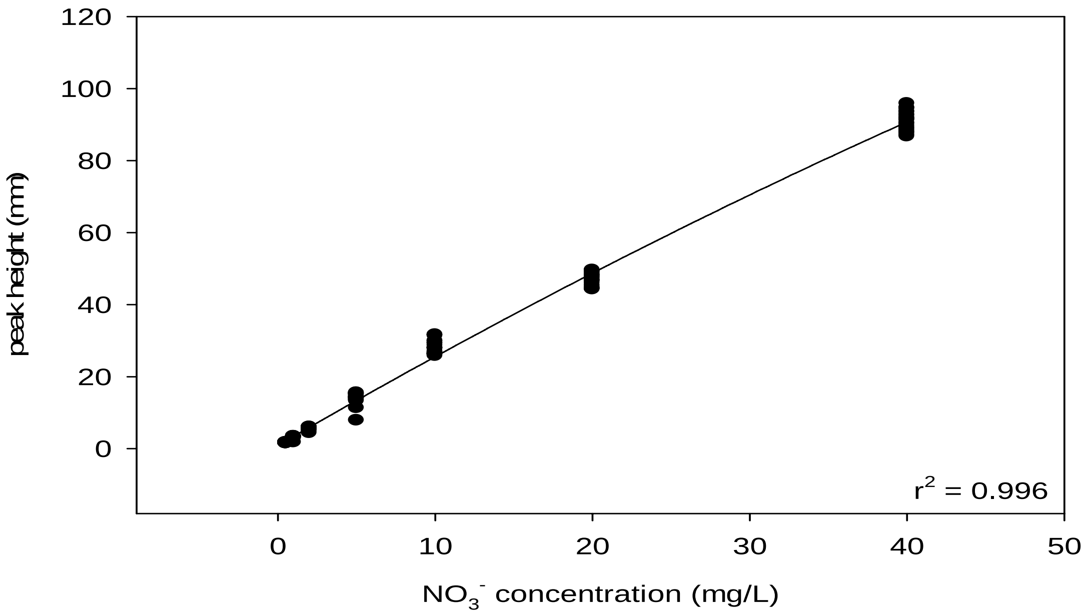

Figure B.8: Standard curve for June and August NO_3^- concentrations; quadratic fit

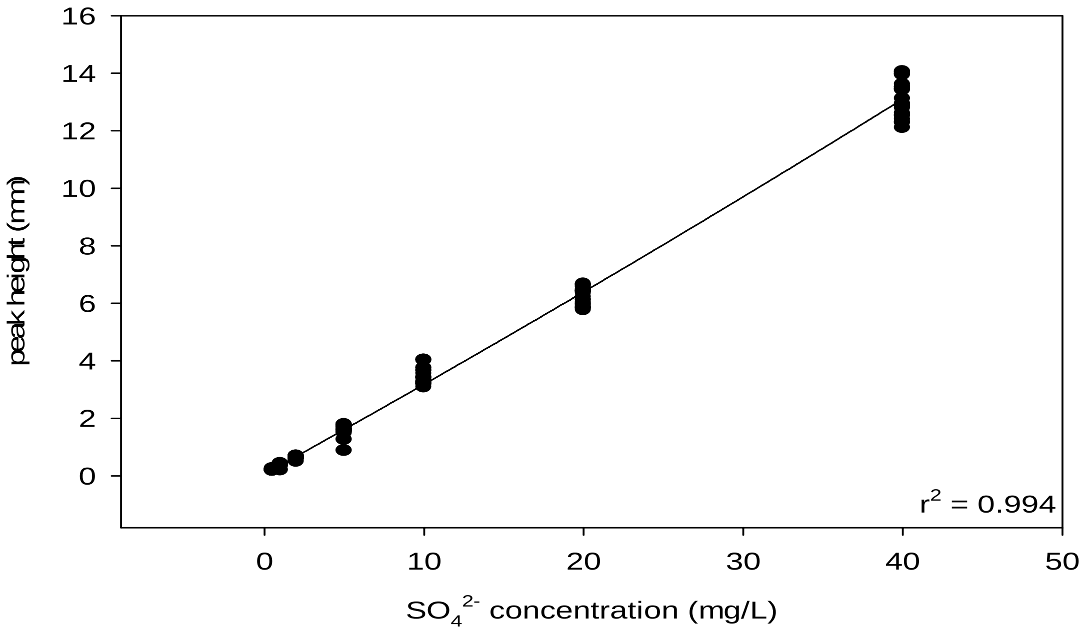

Figure B.9: Standard curve for June and August SO_4^{2-} concentrations; quadratic fit

August Pond Cl^- using ISE

The standard curve used to calculated the Cl- concentrations for the August pond samples using the ion specific electrode (ISE) was based upon 5 mg/L, 10 mg/L, 20 mg/L, 25 mg/L, 40 mg/L, 50 mg/L, and 100 mg/L standards. The fit curve displayed on the graph below is a linear fit with an r^2 value of 0.880 (figure B.10).

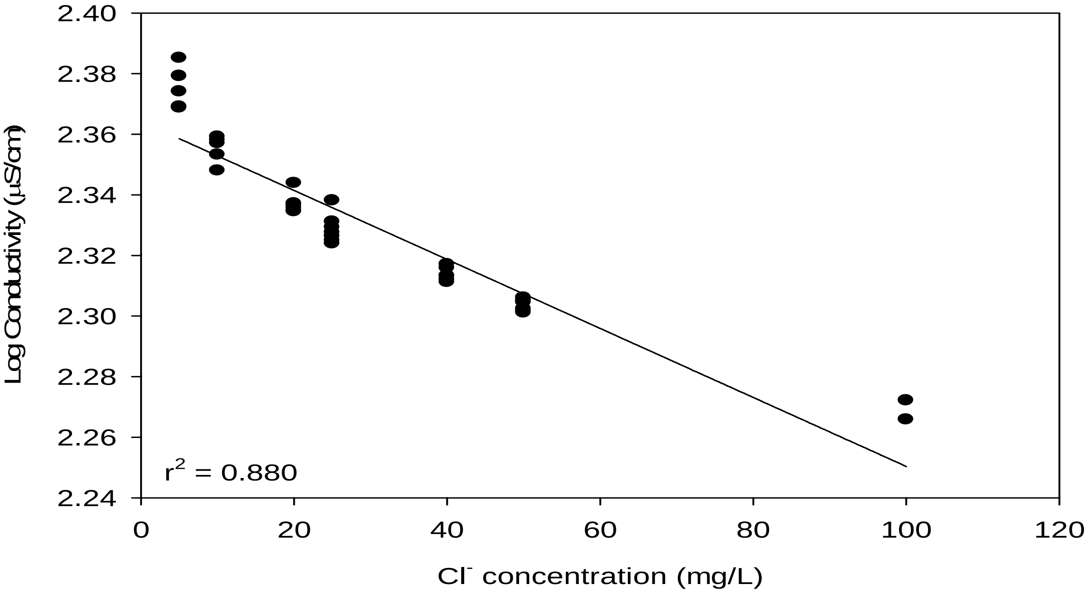

Figure B.10: Standard curve for August Pond Cl- concentrations using ISE, linear fit

Dissolved Organic Carbon

The standard curve used to calculate the dissolved organic carbon (DOC) concentrations was based upon a sample blank (0 mg/L), 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L, and 20 mg/L standards. Each standard was run in triplicate. The fit curve displayed on the graph below is a linear fit with an r^2 value of 0.995 (figure B.11).

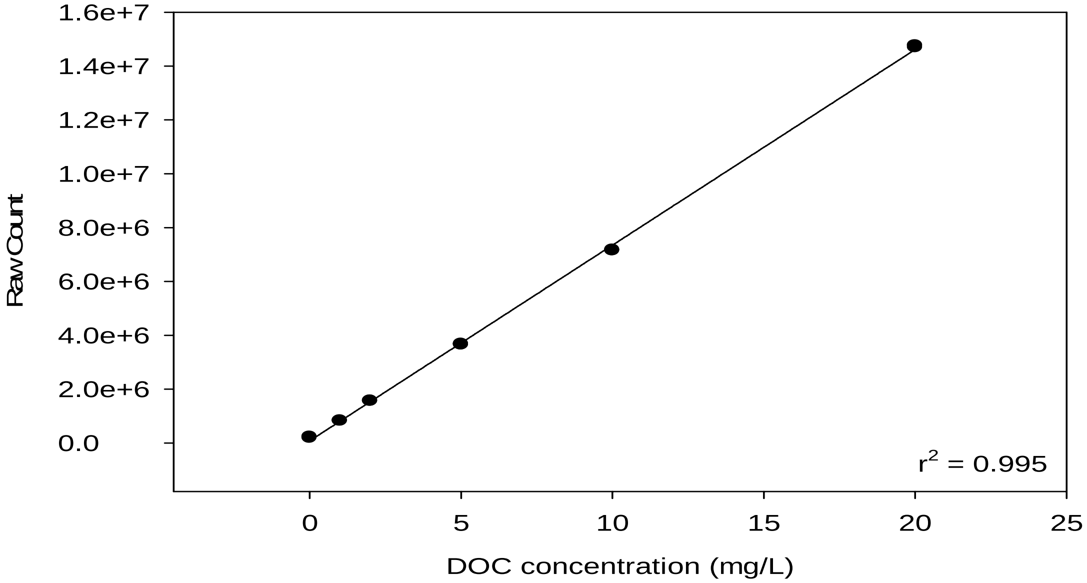

Figure B.11: Standard curve for DOC concentrations; linear fit

Appendix C: Streamwater Chemistry Results

One factor to keep in mind when examining the SO_4^{2-} anion concentrations in the streamwater at Cobb Mill Creek, is that the highest anion standard for SO_4^{2-} ran for these samples was at a concentration of 40 mg/L. Because of this, many of the streamwater chemistry results for SO_4^{2-} anion concentration are estimated values based upon a linear interpolation of the standard curve extended to the sample concentration.

March 2008 Streamwater Chemistry

During the March 27-29, 2008 sampling campaign, streamwater samples were collected at the hillslope and pond locations at Cobb Mill Creek, VA, using an ISCO automatic sampler at the hillslope location and grab samples at the pond outlet. The grab samples taken at the pond outlet were taken at 06:00, 12:00, and 18:00 daily. Anion concentrations of Cl^-, NO_3^-, and SO_4^{2-} in the pond grab samples are displayed below (figure C.1). The average Cl^- concentration in the pond was 21.9 mg/L +/- 0.7 mg/L, the average NO_3^- concentration was 0.8 mg/L +/- 0.06 mg/L, and the average SO_4^{2-} concentration was 40.8 mg/L +/- 3.4 mg/L. At the pond, the streamwater chemistry did not display diurnal variation during this time of expected baseline conditions.

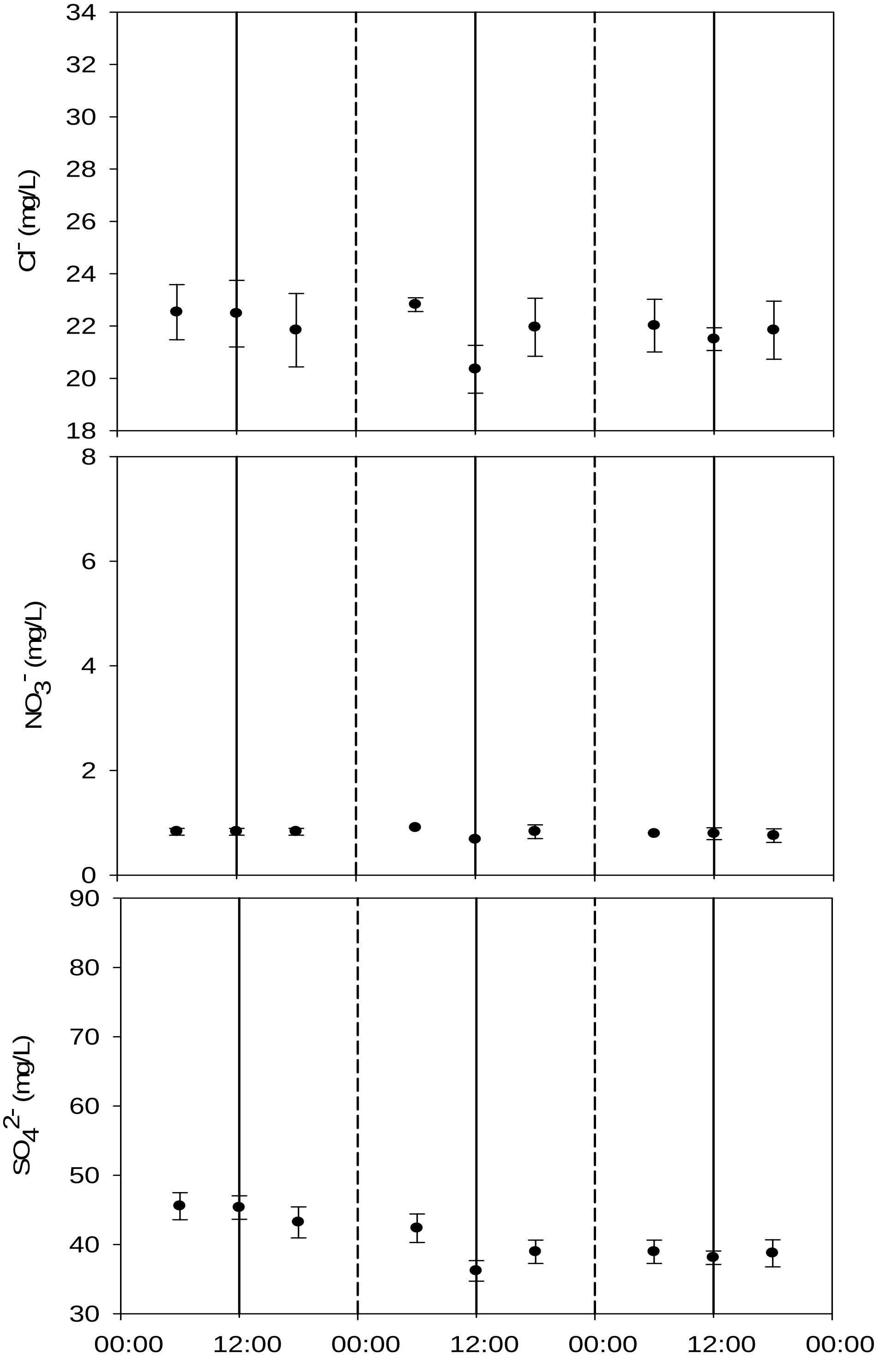

Figure C.1: Grab sample anion concentrations for the pond outlet location at Cobb Mill Creek, VA – March 27-29, 2008

Streamwater concentrations of SO_4^{2-} were also measured during the anion analysis of the hourly ISCO samples from the hillslope location of Cobb Mill Creek. The SO_4^{2-} concentrations ranged from ~38.5 to 74.4 mg/L, with an average concentration of 60.1 mg/L (figure C.2).

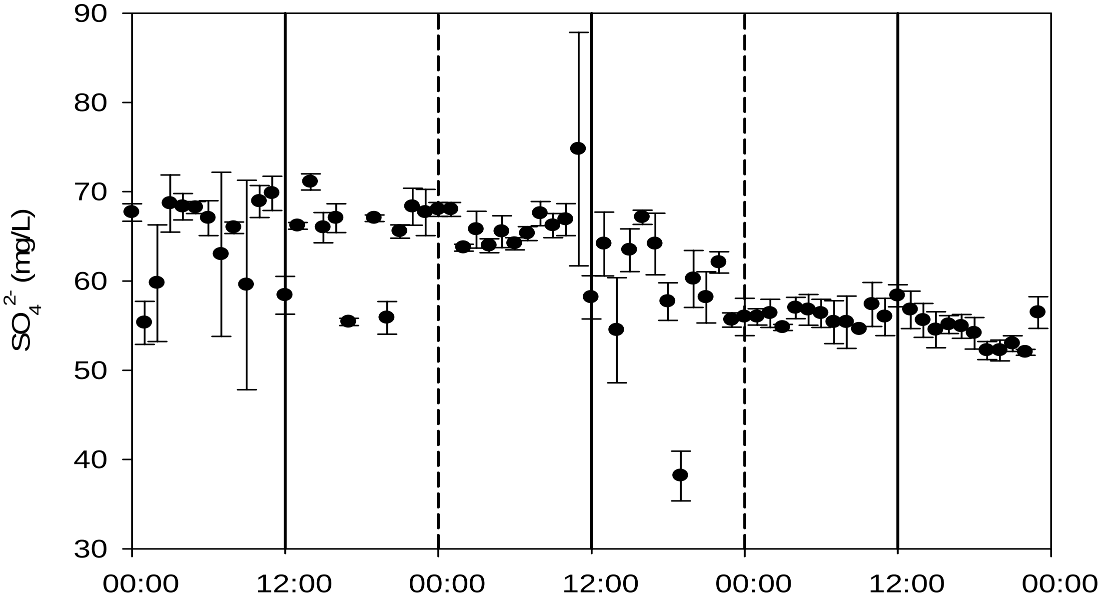

Figure C.2: Hourly SO_4^{2-} concentrations in the streamwater from the hillslope location at Cobb Mill Creek, VA – March 27-29, 2008

May 2008 Streamwater Chemistry

During the May 28-31, 2008 sampling campaign, streamwater samples were collected at the hillslope and pond locations at Cobb Mill Creek, VA, using an ISCO automatic sampler at the hillslope location and grab samples at the pond outlet. The grab samples taken at the pond outlet were taken at 06:00, 12:00, and 18:00 daily. Anion concentrations of Cl^-, NO_3^-, and SO_4^{2-} in the hillslope hourly samples and pond grab samples are displayed below (figures C.3- C.4). The average Cl^- concentration in the pond was 21.9 mg/L +/- 0.7 mg/L, the average NO_3^- concentration was 0.8 mg/L +/- 0.06 mg/L, and the average SO_4^{2-} concentration was 40.8 mg/L +/- 3.4 mg/L. The average Cl^- concentration in the hillslope was 21.9 mg/L +/- 0.7 mg/L, the average NO_3^- concentration was 0.8 mg/L +/- 0.06 mg/L, and the average SO_4^{2-} concentration was 40.8 mg/L +/- 3.4 mg/L. Just prior to this sampling campaign on the morning of May 28th, 2008, there was a significant (~18.5 mm) rainfall event recorded in the Cobb Mill Creek watershed. As a result of this rainfall, the stream and the watershed could not be considered to be under baseflow conditions, therefore the samples which were taken between May 28-31, 2008, were not used within the context of this research.

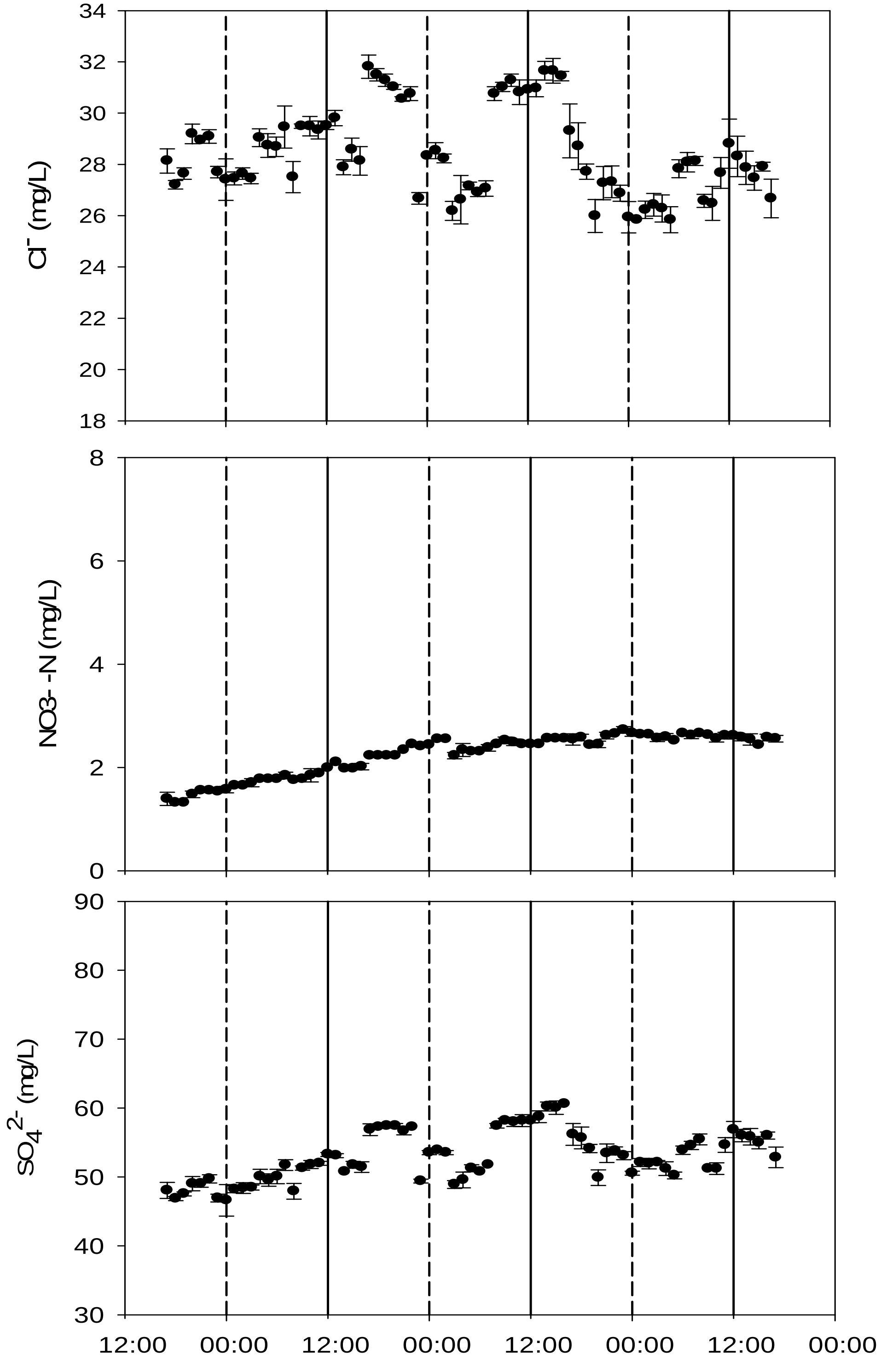

Figure C.3: Hourly Cl^-, NO_3^-, and SO_4^{2-} concentrations in the streamwater from the hillslope location at Cobb Mill Creek, VA – May 28-31, 2008

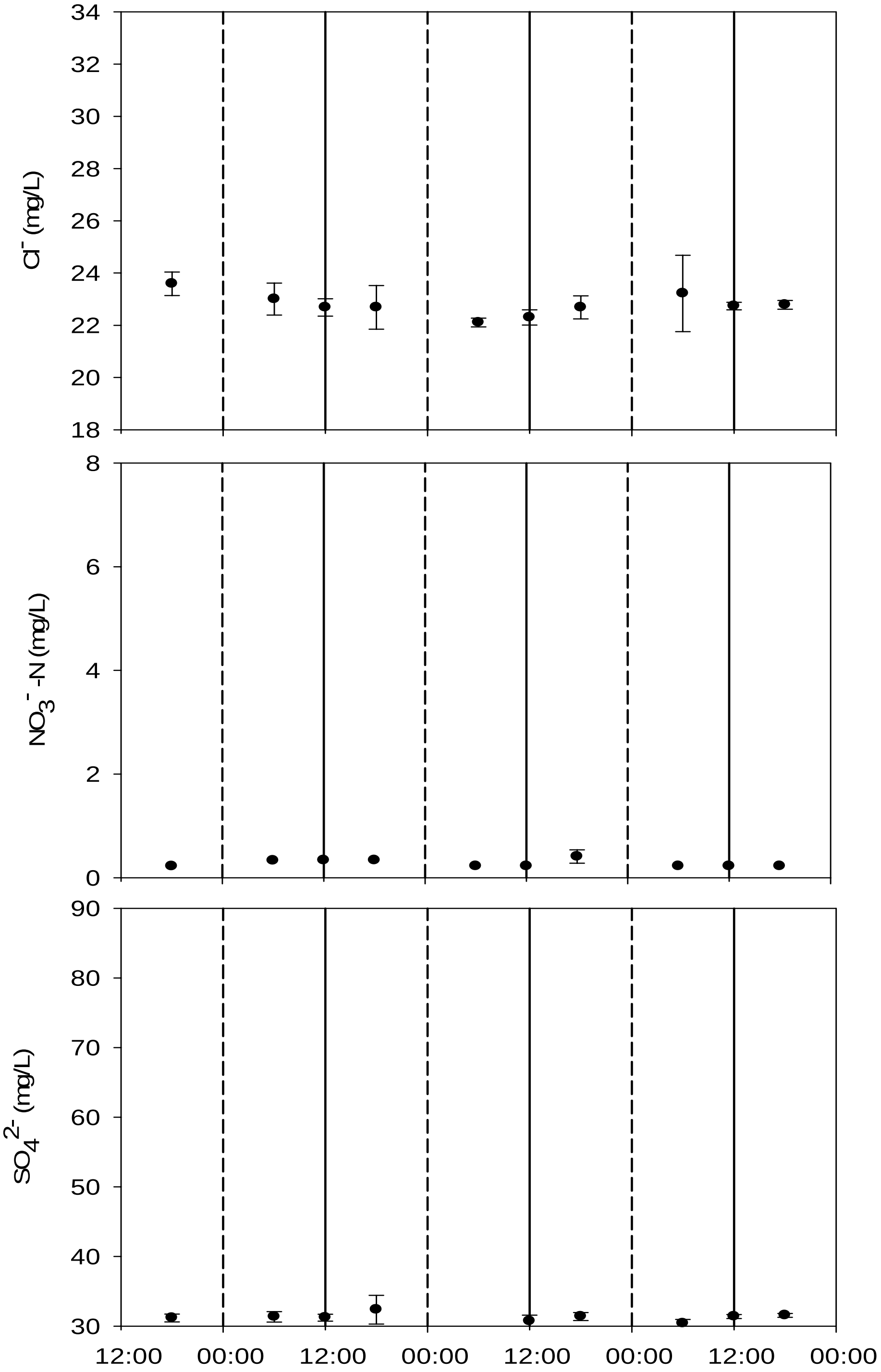

Figure C.4: Grab sample Cl^-, NO_3^-, and SO_4^{2-} concentrations in the streamwater from the pond location at Cobb Mill Creek, VA – May 28-31, 2008

June 2008 Streamwater Chemistry

During the June 25-28, 2008 sampling campaign, streamwater samples were collected at the hillslope and culvert locations at Cobb Mill Creek, VA, using an ISCO automatic sampler and grab samples at both locations. The hourly ISCO samples were analyzed for SO_4^{2-} anion concentrations at both locations (figure C.5). At the culvert location, the SO_4^{2-} concentration ranged from 30.5 mg/L to 74.4 mg/L, with an average concentration of 60.1 mg/L. A diurnal variation of ~15 mg/L is visible with the maximum occurring between 14:00 and 16:00 daily and the minimum occurring between 02:00 and 04:00 daily. At the hillslope location, the SO_4^{2-} concentration ranged from 30.4 mg/L to 71.8 mg/L, with an average concentration of 52.8 mg/L. Because of the wide range in standard deviation for the SO_4^{2-} concentrations at the hillslope, no clear diurnal pattern can be distinctly identified in these data.

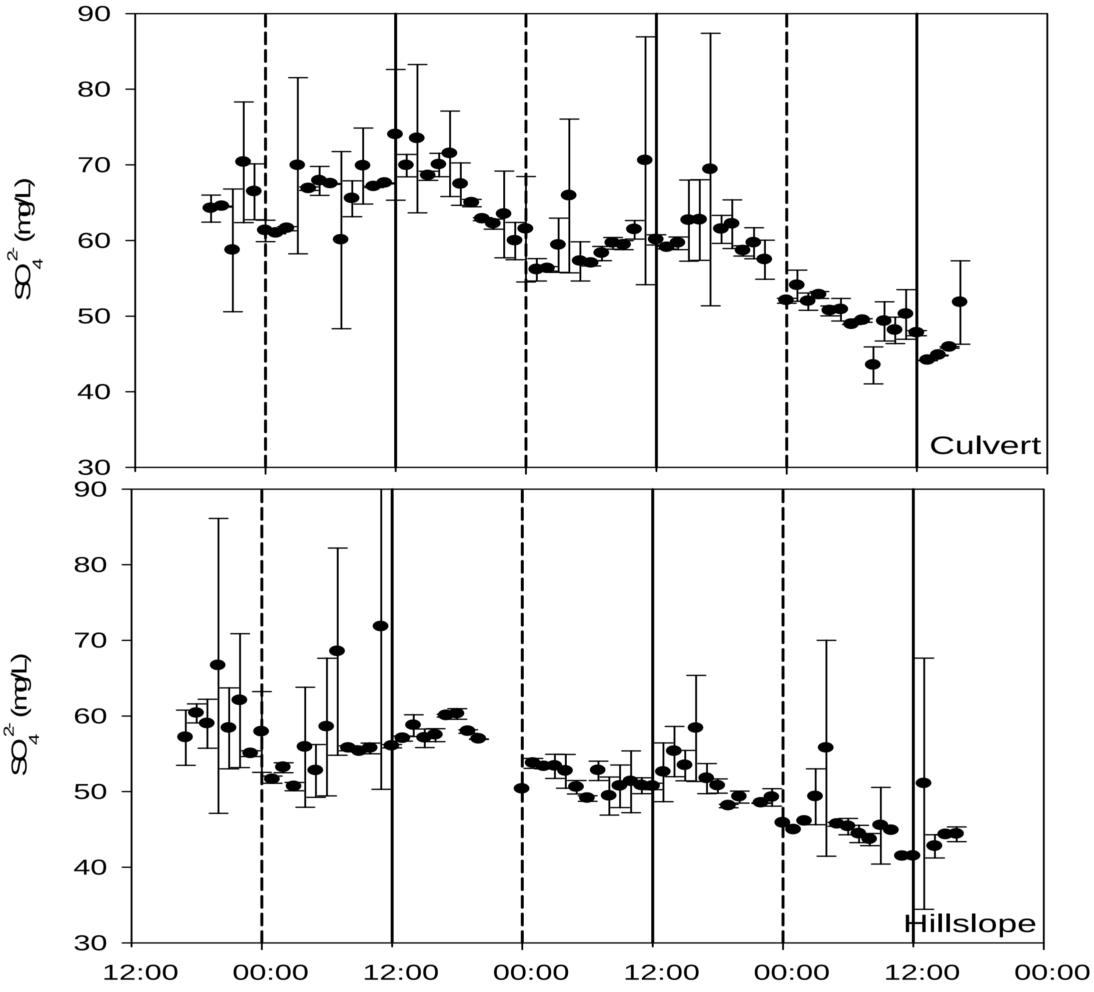

Figure C.5: Hourly SO_4^{2-} concentrations in the streamwater from the culvert (top) and hillslope (bottom) locations of Cobb Mill Creek, VA – June 25-28, 2008

Streamwater grab samples were taken from both the culvert and hillslope locations at Cobb Mill Creek and analyzed for DOC concentration. The grab samples were taken at 06:00, 12:00, 18:00, and 00:00. Results for both locations are displayed below (figures C.6-C.7).

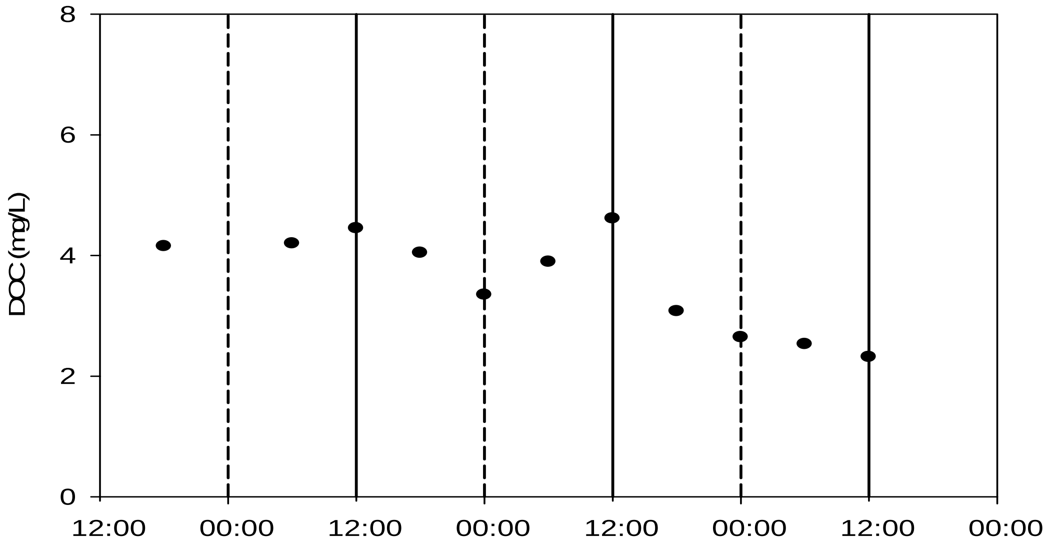

Figure C.6: Grab sample DOC concentrations for the culvert location of Cobb Mill Creek, VA – June 25-28, 2008

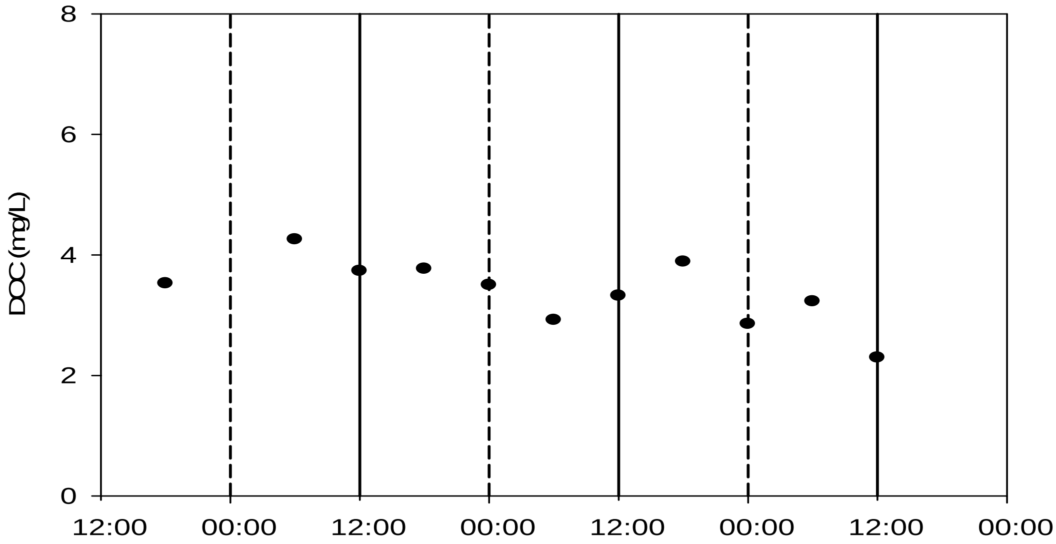

Figure C.7: Grab sample DOC concentrations for the hillslope location at Cobb Mill Creek, VA – June 25-28, 2008

August 2008 Streamwater Chemistry

During the August 20-23, 2008 sampling campaign, streamwater samples were collected at the pond and hillslope locations at Cobb Mill Creek, VA, using ISCO automatic samplers at both locations. Hourly Cl^- concentrations at the pond were measured using an ISE (figure C.8) and anion concentrations for Cl^-, NO_3^-, and SO_4^{2-} were measured using IC (figure C.9). The Cl^- concentration as measured by ISE averaged 40.8 mg/L +/- 1.8 mg/L, Cl^- concentration measured by IC averaged 25.3 mg/L +/- 0.2 mg/L, the NO_3^- concentration averaged 0.07 mg/L +/- 0.0 mg/L, and the SO_4^{2-} concentration averaged 40.3 mg/L +/- 0.8 mg/L.

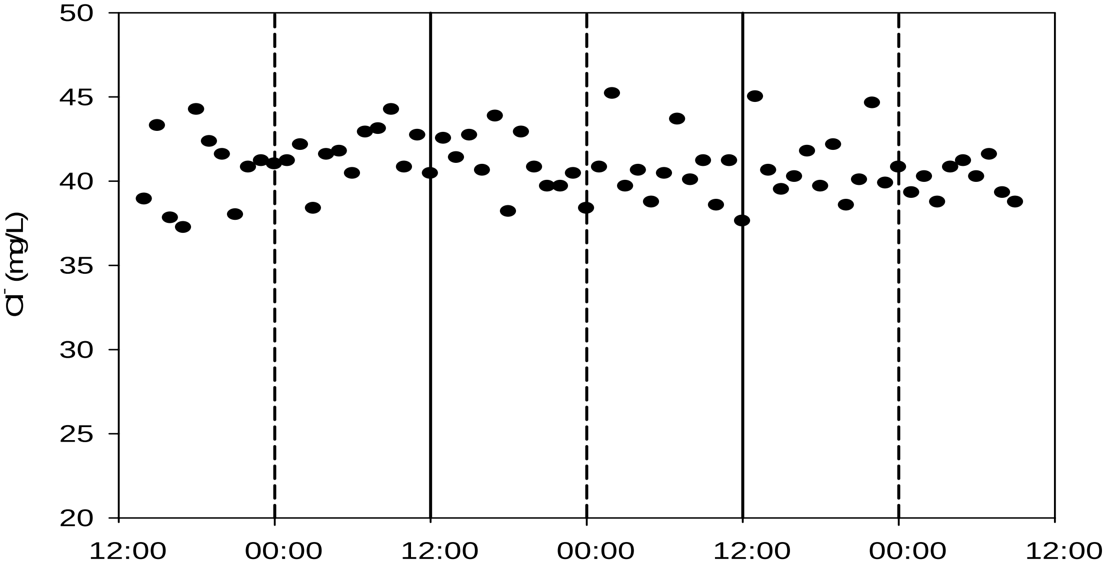

Figure C.8: ISE measured hourly Cl- concentration in the streamwater at the pond outlet location of Cobb Mill Creek, Va – August 23-25, 2008

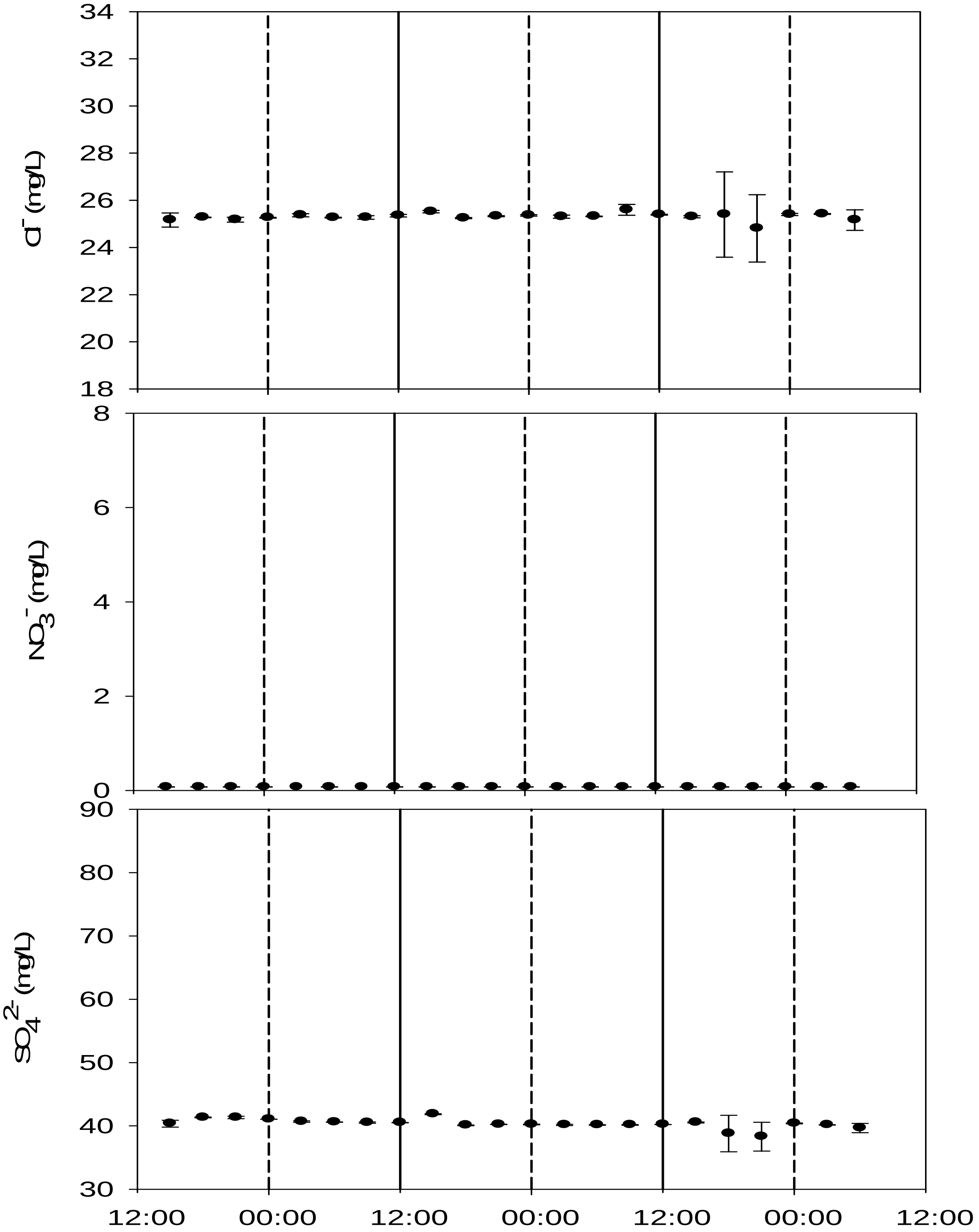

Figure C.9: IC measured anion concentrations for the streamwater at the pond outlet location of Cobb Mill Creek, VA – August 23-25, 2008

Streamwater concentrations of Cl^- and SO_4^{2-} were also measured during the anion analysis of the hourly ISCO samples from the hillslope location of Cobb Mill Creek. The Cl^- concentrations ranged from ~20.1 to 22.5 mg/L, with an average concentration of 21.8 mg/L +/- 0.4 mg/L (figure C.10). The SO_4^{2-} concentrations ranged from ~36.9 to 41.9 mg/L, with an average concentration of 40.8 mg/L +/- 0.96 mg/L (figure C.11).

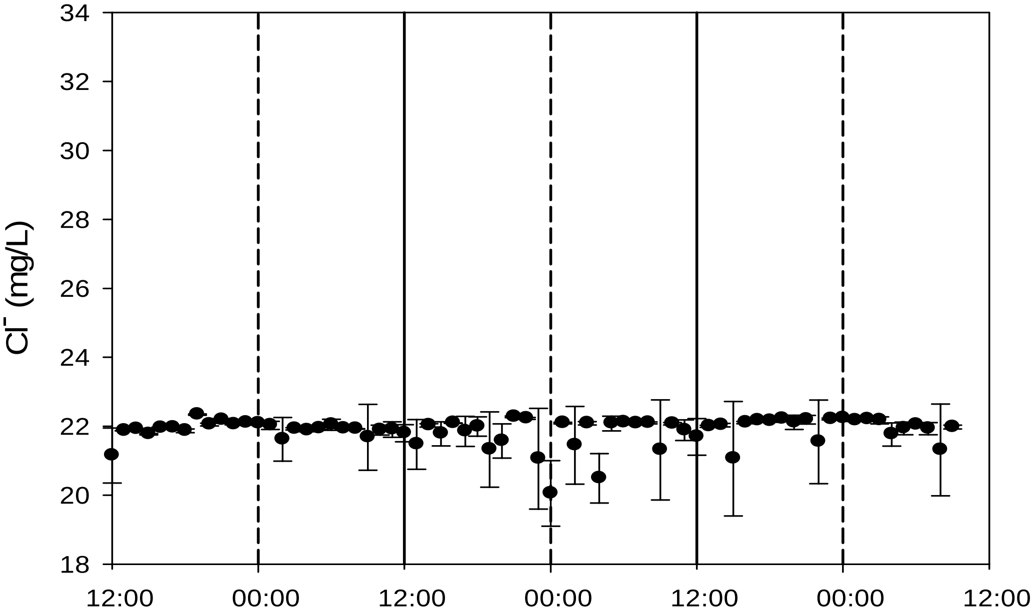

Figure C.10: Hourly Cl^- concentrations in the streamwater from the hillslope location at Cobb Mill Creek, VA – August 20-23, 2008

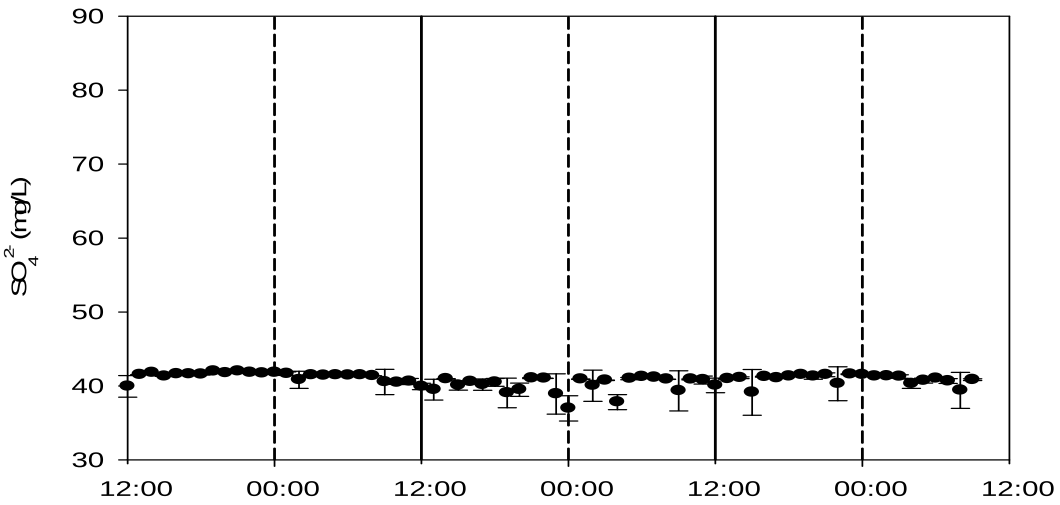

Figure C.11: Hourly SO_4^{2-} concentrations in the streamwater from the hillslope location at Cobb Mill Creek, VA – August 20-23, 2008

In addition to the anion chemistry performed during the August 20-23 2008 sampling campaign, both DON and NH_4^+ concentrations were measured at the pond and hillslope locations. All concentrations were negligible (Table C.1).

Table C.1: Table of average DON and NH_4^+ concentrations for samples taken at the pond and hillslope locations at Cobb Mill Creek, VA – August 20-23, 2008

Location	**DON (mg/L)**	**Standard Dev**	**NH_4^+ (µM)**	**Standard Dev**
Pond	0.0076	.00056	0.0	n/a
Hillslope	0.0078	0.00071	0.5	n/a

Appendix D: Equations used in PET Calculations

Potential Evapotranspiration (PET) - Priestly-Taylor equation (1972)

$$ET_0 = l/\lambda * [s(R_{net} - G)/(s + \gamma)] * a \qquad \text{(D.1)}$$

where λ is the latent heat of vaporization (2.45 MJ/kg), R_{net} is the net radiation (equation D.3, MJ/m^2 h), G is the soil heat flux (equation D.12, MJ/m^2 h), s is the slope of the saturation vapor pressure-temperature relationship (equation D.2, kPa/ °C), γ is the psychrometric constant (equation D.13, kPa/ °C), and a is the Priestly-Taylor coefficient (1.26, unit-less).

Slope of the saturation vapor pressure-temperature relationship (s) – Stanghellini equation (Stanghellini, 1987)

$$s = 0.04145 * e^{0.06088*T} \qquad \text{(D.2)}$$

where T is temperature (measured, °C).

Net radiation (R_{net}) – for Priestly-Taylor equation (1972)

$$R_{net} = R_{ns} + R_{nl} \qquad \text{(D.3)}$$

where R_{ns} is the net shortwave radiation (equation D.4, MJ/m^2 h) and R_{nl} is the net long wave radiation (equation D.5, MJ/m^2 h).

Net shortwave radiation (R_{ns}) – for Priestly-Taylor equation (1972)

$$R_{ns} = (1 - \alpha) * R_{solar} \qquad \text{(D.4)}$$

where α is the albedo (0.15, unit-less), which was estimated using combined albedo calculations from (Campbell and Norman, 2000) for coniferous and deciduous temperate forest, and R_{solar} is the solar radiation (measured, MJ/m^2 h).

Net long wave radiation (R_{nl}) – for the Priestly-Taylor equation (1972)

$$R_{nl} = R_{lin} - R_{lou} \qquad \text{(D.5)}$$

where R_{lin} is the incoming long wave radiation (equation D.6, MJ/m^2 h) and R_{lout} is the outgoing long wave radiation (equation D.7, MJ/m^2 h).

Incoming long wave radiation (R_{lin}) – for the Priestly-Taylor equation

$$R_{lin} = \varepsilon_s * \sigma * T_k^4 * \varepsilon_{at} \tag{D.6}$$

where ε_s is the surface emissivity of the forest canopy (0.96 (Campbell and Norman, 2000), unit-less), σ is the Stefan-Boltzmann constant (2.043 * 10-10 MJ/m^2 K^4 h), T_k is the absolute temperature (measured, °K), and ε_{at} is the atmospheric emissivity (equation D.8, unit-less).

Outgoing long wave radiation (R_{lout}) – for the Priestly-Taylor equation

$$R_{lout} = \varepsilon_s * \sigma * T_k^4 \tag{D.7}$$

where ε_s is the surface emissivity of the forest canopy (0.96 (Campbell and Norman, 2000), unit-less), σ is the Stefan-Boltzmann constant (2.043 * 10-10 MJ/m^2 K^4 h), and T_k is the absolute temperature.

Atmospheric emissivity (ε_{at}) – (Campbell and Norman, 2000)

$$\varepsilon_{at} = (1-F) * 1.72 * (e_a / (T + 237.2))^{1/7} * (1 + 0.22 + C^2) + F \tag{D.8}$$

where e_a is the actual vapor pressure (equation D.9, kPa), F is the forest cover correction (0.5 (estimated), unit-less), and C is the cloud cover (0.1(estimated), unit-less).

Actual vapor pressure (e_a) – for Priestly-Taylor equation (1972)

$$e_a = Rh * e_s \tag{D.9}$$

where e_s is the saturated vapor pressure (equation D.10, kPa) and Rh is the relative humidity (measured, unit-less).

Saturated Vapor Pressure (e_s) – to calculate actual vapor pressure

$$e_s = 0.6108 * e^{[(17.27 * T_d)/(T_d + 237.3)]} \qquad (D.10)$$

where T_d is the dew point temperature (equation D.11, °C).

Dew point temperature (T_d) – for Priestly-Taylor equation (1972)

$$T_d = T - (100 - Rh)/5 \qquad (D.11)$$

where T is the air temperature (measured, °C) and Rh is the relative humidity (measured, unit-less).

The soil heat flux (G) – for Priestly-Taylor equation (1972)

$$G = KG * R_{net} * e^{-0.5LAI} \qquad (D.12)$$

where KG is the soil heat flux coefficient (0.4 for night, 1.8 for day, unit-less), R_{net} is net radiation (equation D.3, MJ/m^2 h), and LAI is the leaf area index (6.00, unit-less), which was taken from (Scurlock et al., 2001) for a mixed temperate forest.

The psychrometric constant (γ) – Campbell (Campbell and Norman, 2000)

$$\gamma = (C_p * P)/(\varepsilon * \lambda) \qquad (D.13)$$

where C_p is the specific heat of moist air at a constant pressure (0.001013 MJ/kg °C), P is the barometric pressure (measured, kPa), ε is the ratio of molecular weight of water to dry air (0.622, unit-less), and λ is the latent heat of vaporization (2.45 MJ/kg).

Appendix E: Groundwater Seepage Meter Results

From June 26-29, 2008, a sampling campaign conducted by Arden Spencer Cox (undergraduate research assistant), Kate Abshire (undergraduate research assistant), Janet Herman, and Wendy Robertson was undertaken to collect groundwater discharge samples from seepage meters placed into the streambed sediments at the hillslope location of Cobb Mill Creek. The seepage meters were 10 cm in diameter with a single outlet ~0.5 cm wide (figure E.1). Latex bladders were attached to the outlet of each meter to collect groundwater discharge. Discharge was monitored every four hours at 18:00, 22:00, 02:00, 06:00, and 10:00, and collected once it reached greater than ~40 mL (*i.e.*, if within four hours, a meter discharged at least 40 mL, the sample was collected for processing. If the meter had not discharged at least 40 mL, the bladder was left on the meter until it did reach the minimum volume necessary). Estimates of discharge volume were recorded from samples collected after 18:00 June 27, 2008. All samples collected were filtered into two 2 mL clear glass IC vials and refrigerated until analysis per the protocol outlined in chapter 2 of this document.

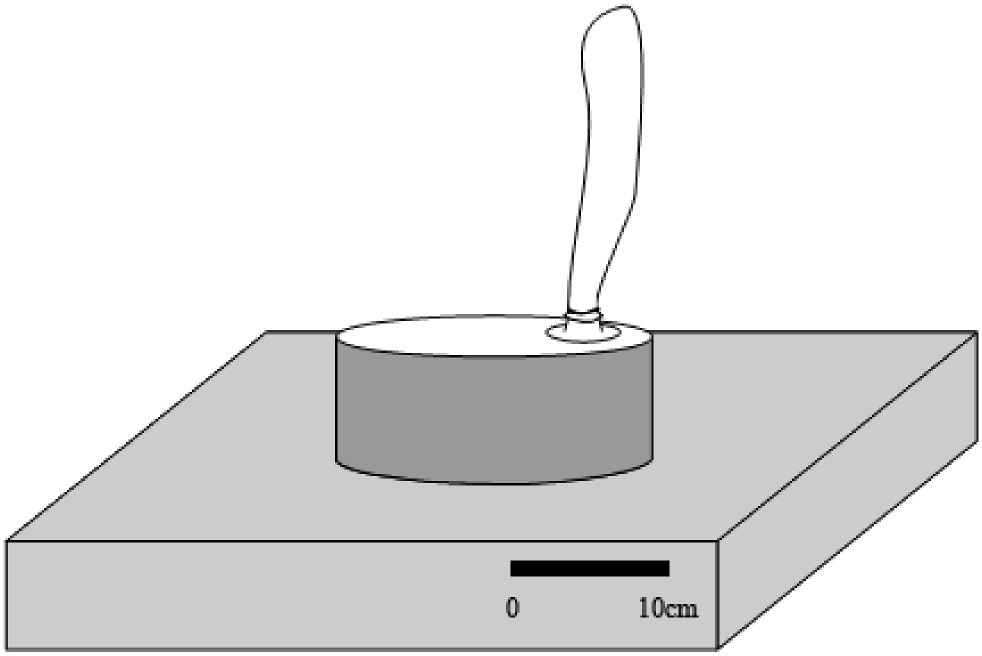

Figure E.1: Depiction of a seepage meter placed into the streambed sediments and collecting groundwater discharge. Modified from Flewelling (2009).

There appeared to be some diurnal variability in the volume of groundwater discharged from the seepage meters during the June 2008 sampling campaign (figure E.2). The daily time when the fewest samples were collected was consistently at 22:00. The daily time when the most samples were collected was between 10:00 and 14:00, but the specific time varied from day to day during the sampling period. This variation in discharge is similar to the diurnal variation in stream discharge recorded at the culvert location in Cobb Mill Creek during the same time period (10:00-14:00 for the maximum discharge, 22:00-02:00 for the minimum discharge).

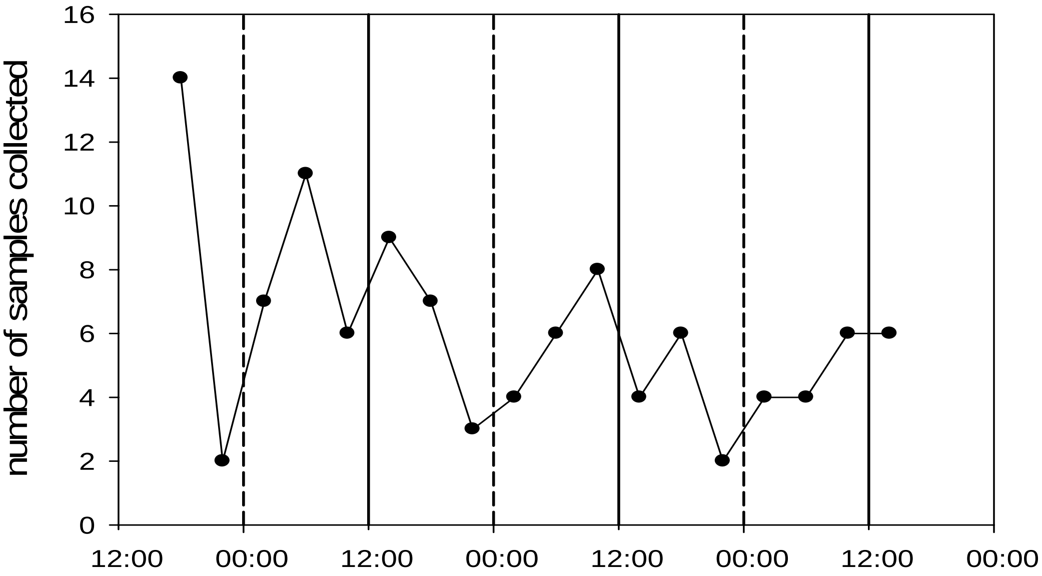

Figure E.2: Graph of the number of samples collected from the groundwater seepage meters deployed at the hillslope location of Cobb Mill Creek – June 26-29, 2008.

Of the twenty three seepage meters deployed during the June 2008 sampling campaign, six meters yielded 8 or more samples and only two meters yielded more than ten samples. The nitrate concentrations of the discharging groundwater collected from these meters ranged from 0 to ~9.5 mg NO_3^--N L^{-1}. A single meter continually discharged groundwater with no detectable nitrate (6 of 8 samples were below detection, the other two were 0.5 mg/L and 1.9 mg/L). Only one meter displayed any diurnal variability in nitrate concentrations (figure E.3) and it was the meter which yielded the greatest number of samples. Because many of the seepage meters failed to yield a sample large enough for collection within four hours, the nitrate concentrations from these samples are integrated values over 8-16 or more hours and cannot be examined in the context of diurnal variation.

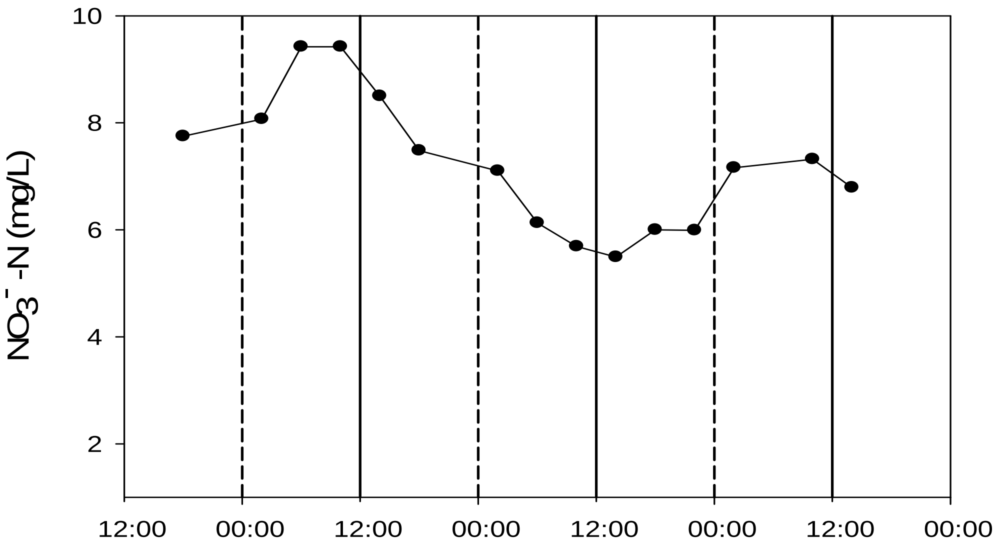

Figure E.3: Graph of the nitrate concentrations from seepage meter #40 deployed at the hillslope location in Cobb Mill Creek, VA – June 26-29, 2008.

Appendix F: May 2008 Stream Stage and Discharge and Hillslope Water Table Monitoring Results

Stream stage was monitored at the culvert location of Cobb Mill Creek during the May 28-31, 2008, sampling campaign. Discharge was calculated using the rating curve provided in chapter 3. A rainfall event of ~18.5 mm was recorded in the watershed between the afternoon of May 27th to the morning of May 28th. Figures F.1-F.2 are the stream stage and discharge values from the culvert location of Cobb Mill Creek for the time period between May 28-31, 2008.

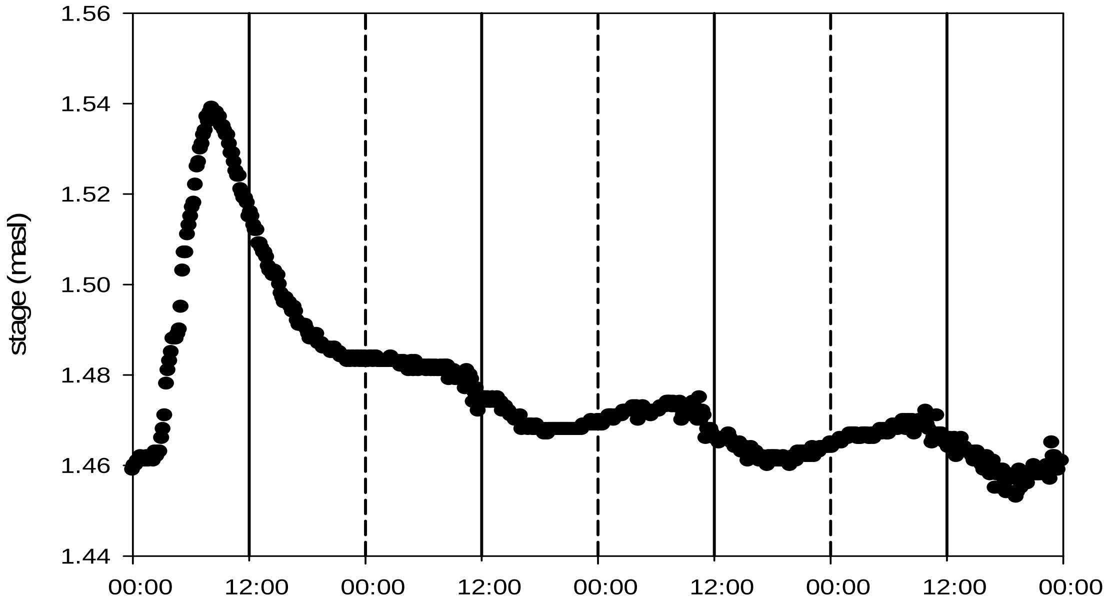

Figure F.1: Stream stage measured every 10 minutes at the culvert location of Cobb Mill Creek – May 28-31, 2008.

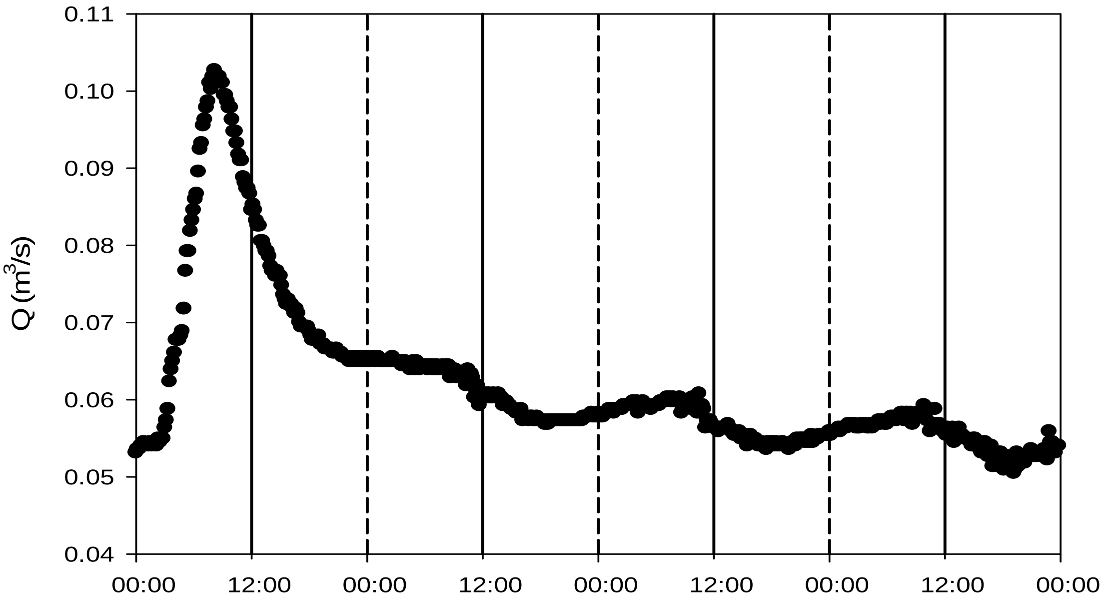

Figure F.2: Stream discharge calculated every 10 minutes at the culvert location of Cobb Mill Creek – May 28-31, 2008.

Three Solinst™ levelogger pressure transducers were deployed in monitoring wells/piezometers along the hillslope to monitor changes in depth to water table from August 23-November 8, 2008(see chapter two for details). The transducers were deployed in the hilltop monitoring well, N11, and N13 (figure 2.3). The pressure transducer in the hilltop monitoring well measured the water level hourly and the transducers in piezometers N11 and N13 measured the water level very ten minutes. The entirety of the log for each location is presented here (figures F.3, F.5, F.7) as well as a selection of days during the month of September 2008 (September 15-20) when no rainfall was recorded in the watershed (figures F.4, F.6, F.8). These water level logs were corrected for barometric pressure changes but were not set on the absolute scale of meters above sea level because the exact elevations of the wells is not currently known.

No distinct pattern is visible in the water levels from either of the upslope installations (hilltop monitoring well, N11), but a diurnal pattern was observed between September 15-20, 2008, in the water level of the N13 installation.

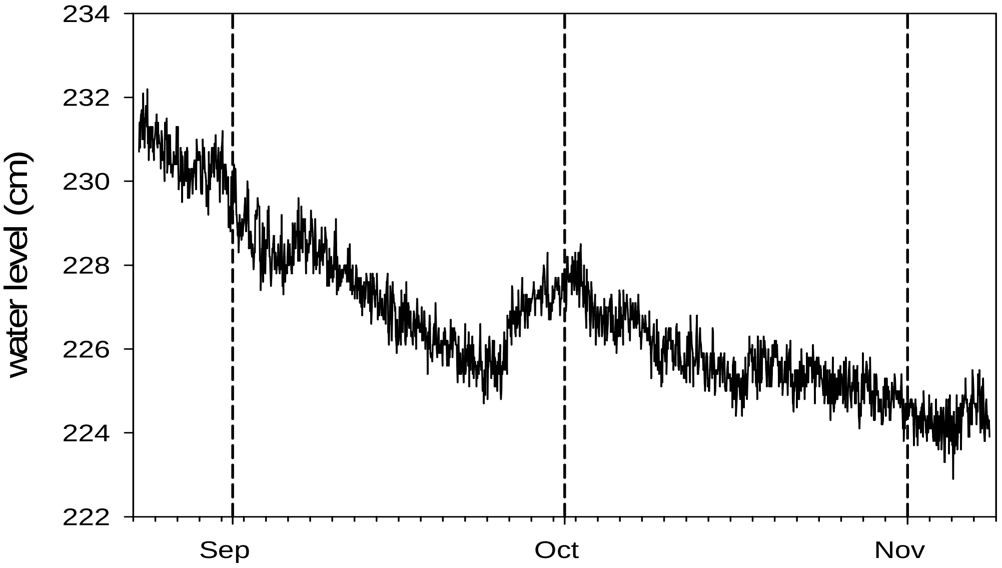

Figure F.3: Graph of water level (cm) recorded in the hilltop monitoring well at the hillslope location of Cobb Mill Creek – August 23-November 8, 2008.

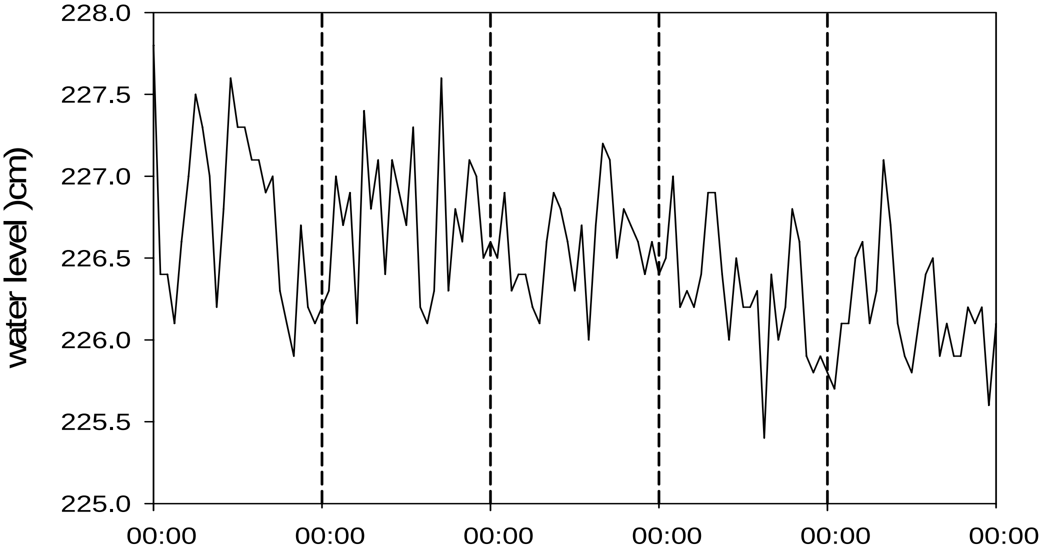

Figure F.4: Graph of water level (cm) recorded in the hilltop monitoring well at the hillslope location of Cobb Mill Creek – September 15-20, 2008.

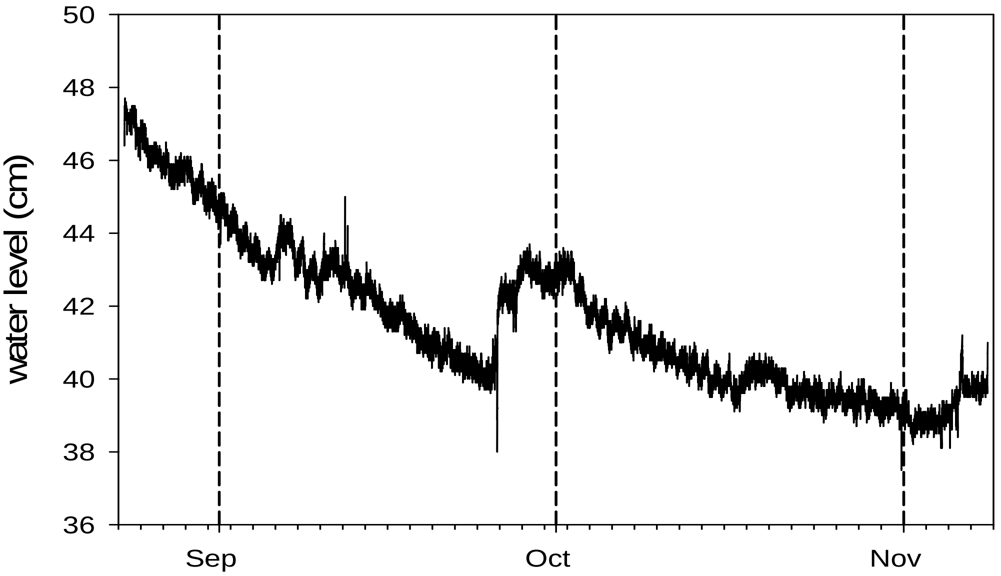

Figure F.5: Graph of water level (cm) recorded in the N11 piezometer at the hillslope location of Cobb Mill Creek – August 23-November 8, 2008.

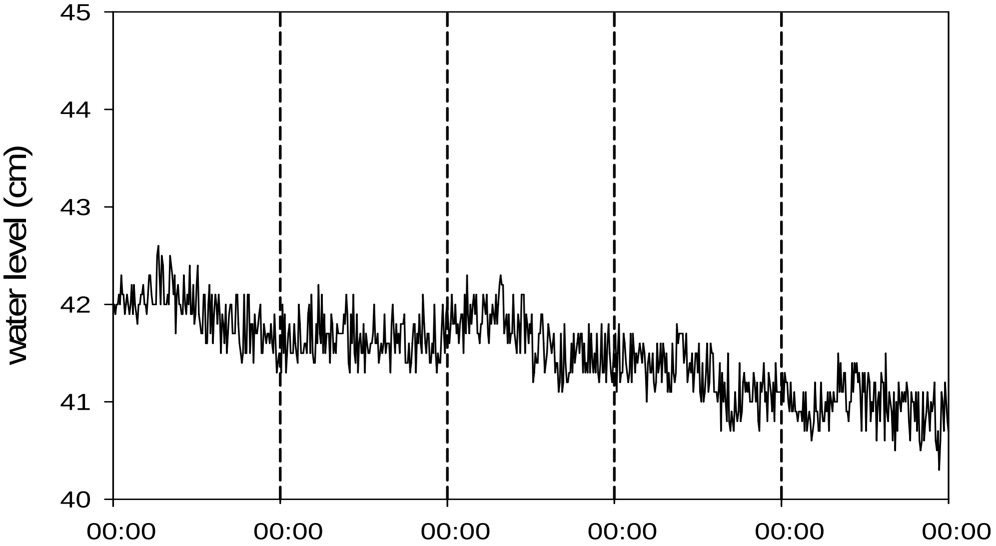

Figure F.6: Graph of water level (cm) recorded in the N11 piezometer at the hillslope location of Cobb Mill Creek – September 15-20, 2008.

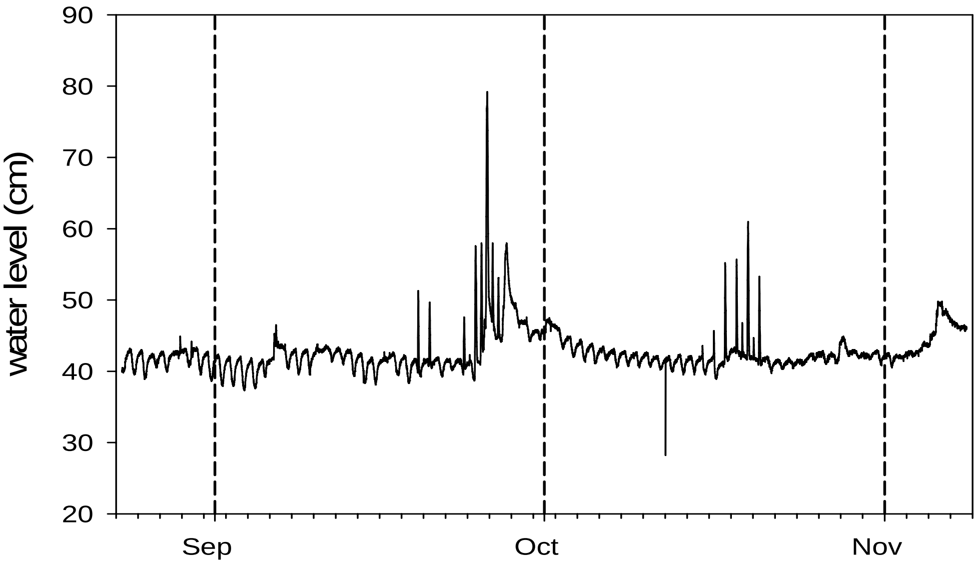

Figure F.7: Graph of water level (cm) recorded in the N13 piezometer at the hillslope location of Cobb Mill Creek – August 23-November 8, 2008.

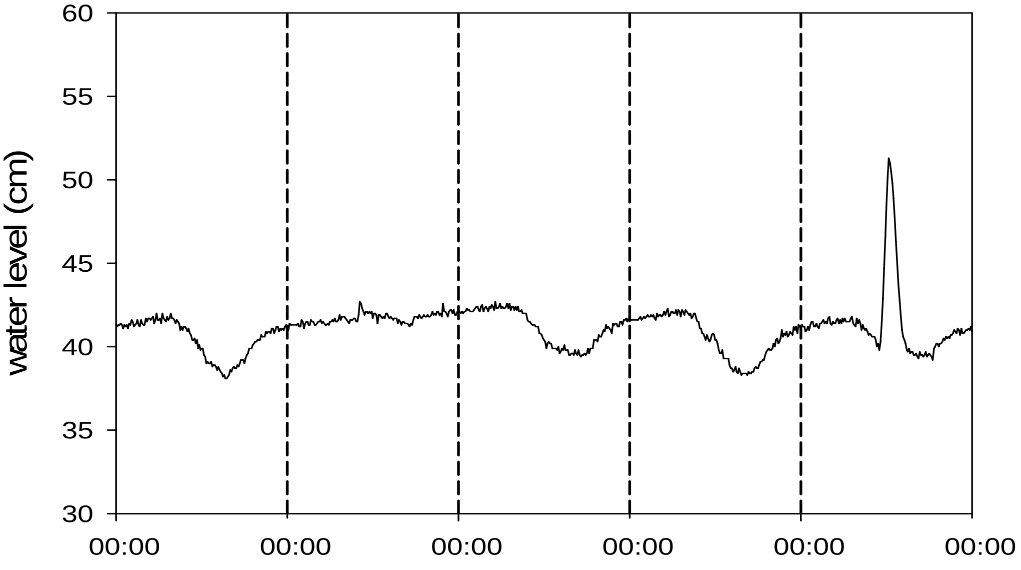

Figure F.8: Graph of water level (cm) recorded in the N13 piezometer at the hillslope location of Cobb Mill Creek – September 15-20, 2008.