WATER QUALITY MONITORING

TO ASSESS THE EFFECT OF NON-POINT

SOURCE NUTRIENT AND OTHER POLLUTANT

LOADS ON ESTUARINE WATERS

SOUTHERN NEW CASTLE COUNTY, DELAWARE

TRIBUTARIES OF THE DELAWARE BAY

by

Anne Mundel

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Geology

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This manuscript is dedicated to:

My daughter Rachel for her support and encouragement.

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ABSTRACT

This study established water quality monitoring baseline values for the discharge of nutrient and non-pollutant loads from two drainage basins prior to suburban housing with golf course development. The drainage basins studied were the Beaver Branch and Hangman's Run in southern New Castle County, Delaware. Beaver Branch drains directly into the upper portion of the Blackbird Creek, the principal waterway within one component of Delaware's National Estuarine Research Reserve. Water quality monitoring included the collection of field measurements and samples for laboratory analyses at two-week intervals for the duration of this two-year project. In addition, a series (~2-3 per season) of storm-event, field, and biweekly laboratory measurements were collected at the sampling sites. Field measurements included specific conductivity, temperature, pH, depth, turbidity, salinity, and dissolved oxygen. Laboratory measurements of total dissolved and suspended solids, chlorophyll a, b, and c, pheophytin a, silicate, and dissolved and particulate constituents of ammonium-nitrogen, nitrate-nitrogen, total Kjeldahl nitrogen, orthophosphate, total phosphates, total dissolved phosphorus, and chemical oxygen demand. These data were collected to analyze the loading rates of nitrate species, phosphorus species, silicate, and total solids on streams at the three sites. Stream flow data from the USGS gauge station on Blackbird Creek was used to model flow in the creeks without gauges. This study examined the data on various time scales: annual, seasonal, and storm events.

Annual data showed loading rates attributable to local meteorological events on a large temporal scale. The stream flow data (observed and modeled) shows higher loading rates associated with high rates of precipitation. Annual loading rates of nitrogen species vary with rates of precipitation, plant production and decay of plant material. Phosphate species loading rates are associated with amounts of total

suspended and dissolved solids. Silicate loading rates are linked to groundwater discharge to streams and precipitation.

Similar to annual results, seasonal loading data for nitrogen species reflects the nitrogen cycle (oxidation / reduction). Phosphates are associated with suspended and dissolved solids and silicates follow groundwater discharge. The seasonal data follows climate.

Storm events show signals that were not observed in the longer time-scale seasonal and annual data. For example, silicate loads were higher during the July 2003 storm than the October 2002 storm event. The storm data also showed an increased load for nitrogen species during periods of intense rain and after a prolonged steady rain. Storm events also show increased phosphate loads.

This study has shown that variability in loading rates of small systems occur on a scale of hours to days. A signal that could not be detected if longer temporal measuring scales were used. This result has implications for the timing intervals of measurements in future studies aimed at measuring changes in loading rates within smaller tidal systems.

Chapter 1

INTRODUCTION

Scope and Purpose

This research project established a water quality-monitoring program in the vicinity of Avon Bridge / Odessa National, a 250-hectare site of residential/golf course development, adjoining a portion of the Upper Blackbird Creek component of Delaware's National Estuarine Research Reserve (Figure 1.1). This research was based in part upon conversations with Dr. Robert Scarborough, Research Coordinator, of Delaware's National Estuarine Research Reserve and in answer to regional, state, county, and general public concern about the impact of a major suburban residential development on the local watershed (e.g., Brown, 2000; Hale, 2000; White, 2001). Given that the estuarine setting of the study area is comparable to numerous locations in the Mid-Atlantic region, the results of this study are directly applicable to, and can be used in developing models for the assessment of development impact on estuarine watersheds. This will aid the establishment of best management practices for development in this type of environment.

Anthropogenic influence on water quality needs to be quantified and modeled in greater detail to be better able to assess non-point nutrient and other pollutant loading pressures to estuaries and the watersheds that discharge to them. As nutrients and pollutants flow through watersheds that discharge into coastal bays, inland bays, and/or the open ocean, they have a significant impact on estuarine systems. For example, in a recent survey of 138 estuaries, encompassing over 90% of the estuarine surface of the continental United States, moderate to high degrees of eutrophication were found in 84 estuaries (Bricker et al., 1999). This represents nearly 65% of the total estuarine surface area involved in the survey. In the Mid-Atlantic region, of the 22 rivers, bays, and inland bays surveyed, 15 (68%) exhibited moderate to high eutrophication (Bricker et al., 1999).

The impact of reduced water quality and increased eutrophication is profound. For example, in response to increased levels of nutrients (primarily nitrogen and phosphorous), accelerated production of pelagic algae occurs with concomitant decrease in light availability and increase in chlorophyll-a concentration. These factors in turn may lead to the presence of nuisance algae blooms, with the possibility of toxic blooms, loss of submerged aquatic vegetation, and low dissolved oxygen levels. In the Bricker et al. (1999) survey, 69 of the 84 (in the Mid-Atlantic 15 of the 22) problem estuaries were identified as having human-use (e.g., commercial or recreational fishing, shellfisheries, swimming, boating, and general tourism) impairments related to eutrophication (Bricker et al., 1999).

Site Selection

This research established a monitoring program to begin assessing the impact of the Avon Bridge / Odessa National developments on water quality in Beaver Branch and Hangman's Run, two waterways adjacent to the site (Figures 1.1 and 1.2). Beaver Branch drains directly into the upper portion of Blackbird Creek, the principal waterway within one component of Delaware's National Estuarine Research Reserve (Figure 1.1). In consultation with representatives from Delaware's National

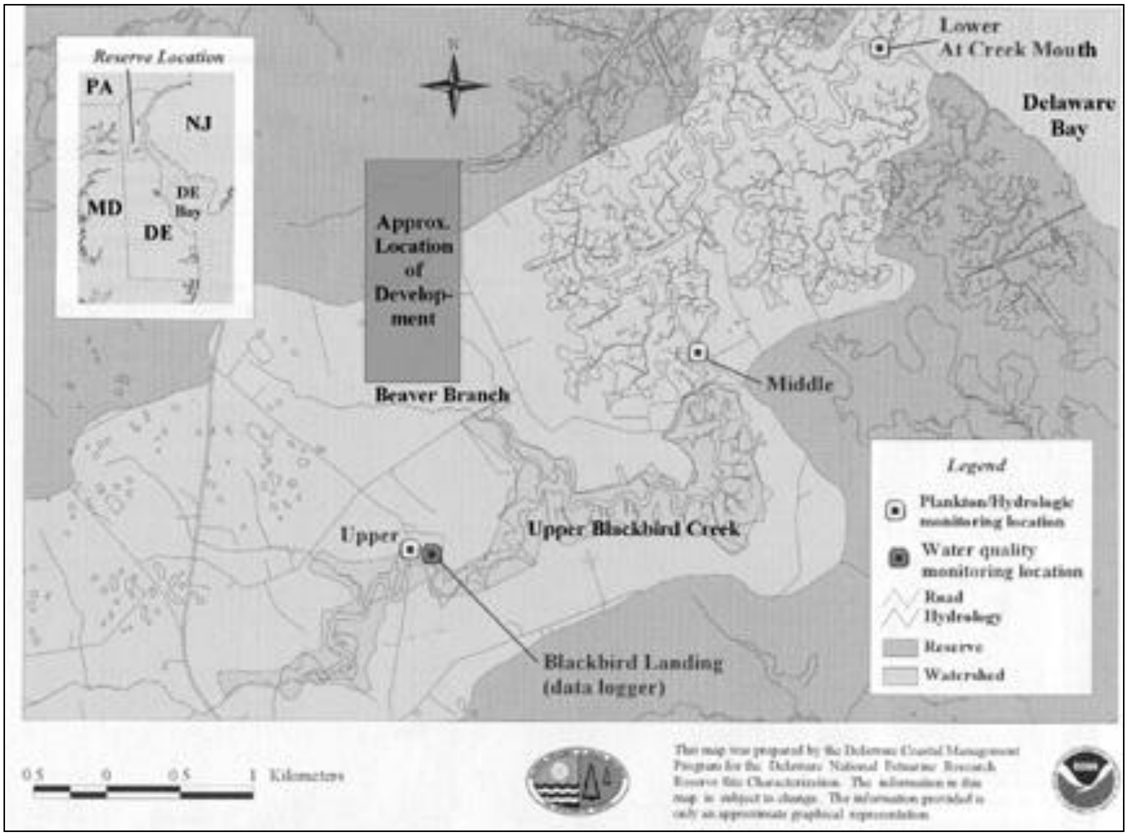


Figure 1.1. Location of the Upper Blackbird Creek Component of the Delaware National Estuarine Research Reserve (DNERR). Figure is modified from DNERR (1999).

Estuarine Research Reserve, three sites were chosen for the installation of water quality measuring equipment. As shown in Figure 1.2, two of these sites are located near the northern and southern ends of the proposed residential/golf course development along Hangman's Run and Beaver Branch. A third site was selected on Blackbird Creek (Figure 1.2).

The area of Beaver Branch drainage basin upstream from the sampling site is approximately 455 hectares (Figure 1.2). Approximately one quarter of the drainage area drains the southern extent of the development. Nearly one-half of Hangman's Run drainage basin's 383 hectares lie within the proposed development. The area of the proposed development was fallow during the study period. Hangman's Run is impounded downstream from the sampling site (Figure 1.2). The Run's impoundment is privately owned and maintained under the auspices of Ducks Unlimited. Unlike Beaver Branch and Blackbird Creek, Hangman's Run is freshwater and not tidally influenced.

Geology and Hydrogeology of Site

Hydrological maps shows the Columbia Formation and Holocene sediments dominating the surface area of the study site (Woodruff, 1990 & Ramsey, 2005). Ramsey (1997) identified two distinct formations, the Lynch Heights and Scotts Corner that overlie the Columbia Formation along the margin of the Delaware Bay. The Columbia Formation consists of fluvial sands and gravels that serve as a shallow unconfined aquifer (Columbia aquifer) with areas where the sands thicken to more than forty feet capable of supporting high yielding wells (Woodruff, 1990). Though residences in the area utilize this groundwater aquifer for domestic use (Delaware Geological Survey, 2002), the practice is discouraged because the high hydraulic conductivity of the formation contributes to its susceptibility to contamination from agricultural and residential sources (Woodruff, 1990).

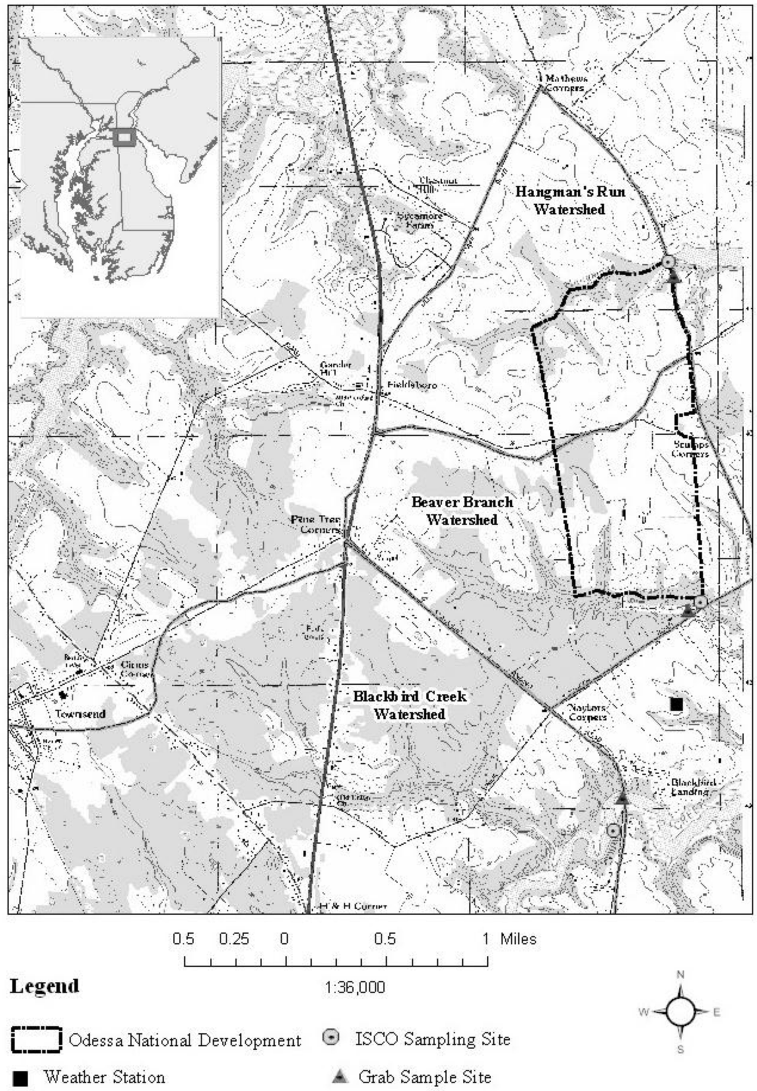


Figure 1.2. Location of Avon Bridge/Odessa National housing/golf course development. Also shown are Hangman's Run and Beaver Branch drainage basins. The triangles are the sites of YSI data loggers, and ISCO samplers.

For much of the 20 Century there existed a disagreement amongst geologists working the margin of the Delaware Bay as to the spatial aspect of the Columbia Formation as it converged with the Delaware Bay (Ramsey, 1997). Miller (1906) and Bascom and Miller (1920) identified the distinct Talbot Formation running parallel on the margin of the Bay overlying the Columbia Formation (Ramsey, 1997).

The term was rejected by other authors (Jordan, 1962, 1974) until Ramsey and Schenk (1990) affirmed the existence of these unique deposits running parallel along the Delaware Bay margin and mapped them as Delaware Bay deposits (Ramsey, 1997). In reviewing the historical literature and well logs, Ramsey (1997) indisputably recognized the distinct deposits, grouping them as the Delaware Bay Group consisting of the Scott's Corners Formation overlying the Lynch Heights Formation.

The formation of the Delaware Bay Group is a result of the erosion and deposition associated with fluctuations in sea level occurring during several glacial and interglacial cycles within the Quaternary Period (Ramsey, 1997). The Delaware Bay Group runs along the entire Delaware Bay margin south from Wilmington to west of Cape Henlopen. The Lynch Heights and Scotts Corners formations are wedge-shaped deposits pinching out toward the inland and thickening towards the Delaware Bay. Their stratigraphic position is one of cut-and-fill bodies positioned unconformably on older deposits (Ramsey, 1997). The contact between the formations is defined by changes in sediment attributes and sorting or a stratum of iron-cemented sandstone (Ramsey, 1997).

Fragments of iron-cemented sandstone ranging in thickness from one-half to two centimeters and up to 11 by 8.5 cm long were found in the talus at the base of the scarp at the Blackbird Creek storm-sampling site. Fragments in the scarp face at approximately 3 to 4 meters above the low slack tidewater were traced with some linearity easterly across the scarp for approximately 6 meters. Many of the samples found over the study period were caked in fine yellow silt. Ramsey (1997) describes sediment colors of the Columbia Formation as ranging from, "light to dark reddish brown to white" and the Lynch Heights colors ranging from "light red (almost pink) to yellow or gray" (Ramsey 1997). These fragments indicate the contact between the

Lynch Heights and Columbia Aquifer (Ramsey, 1997).The ground water in the Columbia Aquifer is the source of recharge for the deeper aquifers and for stream flow. The Columbia Formation is approximately 6 meters thick in the study area (Woodruff, 1990). It overlies the Calvert Formation that is composed of silt and acts as a semi-confining unit (Woodruff, 1990; Bachman and Ferrari, 1995). The Calvert formation is less than 6 meters thick in the study area. Below the Calvert Formation lies the Nanjemoy Formation that overlies the Rancocas Group. These units consist of sands differentiated by microfossils. Together these two units act as a single aquifer designated as the Rancocas aquifer (Woodruff, 1990; Bachman and Ferrari, 1995). The Rancocas aquifer near the Appoquinimink River is approximately 8 to 16 meters thick. Truncation of the Rancocas aquifer occurred from erosion before the deposition of the Columbia Formation (Bachman and Ferrari, 1995). Most domestic wells in the area draw water from this aquifer (Delaware Department of Natural Resources and Environmental Control, 2002; Delaware Geological Survey, 2002). These groups overlie the Mount Laurel Formation that consists of varying amounts of silt and fine to medium, glauconitic and quartz sand (Woodruff, 1990).

The Mount Laurel Formation overlies the Matawan Group underlain by the Magothy Formation and Potomac Formation. Portions of the Matawan Group can provide enough water for domestic use at approximately 75 gallons per minute but the Group in general probably acts as a leaky aquifer (Woodruff, 1990). The Englishtown-Mount Laurel Aquifer System includes the Mount Laurel Formation and the productive portions of the Matawan Group (Bachman and Ferrari, 1995). The Magothy and Potomac aquifer system are the last in downward sequence and is approximately 600 meters thick at the Appoquinimink River (Bachman and Ferrari, 1995). Test drilling and ground water exploration of the Potomac Formation in this area increased in 1994 in anticipation of increased public need by large residential developments (Bachman and Ferrari, 1995). Well records show that a major commercial water provider has sunk wells into the Potomac Formation in the study region (Delaware Geological Survey, 2002).

Sampling Protocol

Water quality monitoring included the collection of field measurements and samples for laboratory analyses at two-week intervals for the duration of this two-year project. In addition, a series (~2-3 per season) of storm-events, Sonde, and biweekly laboratory measurements were collected at the sampling sites. The water measurements involve standard techniques (Ritter, 1986a, 1986b; Hem, 1985; Cierco et al., 1994). Water quality measurements included field measurements of samples collected from the three sampling sites in the study area included specific conductivity, temperature, pH, depth, turbidity, salinity, and dissolved oxygen. Laboratory measurements of samples collected from the three sampling sites in the study area included, total dissolved and suspended solids, chlorophyll a, b, c, pheophytin a, silicate and dissolved and particulate constituents of ammonium-nitrogen, nitrate-nitrogen, total Kjeldahl nitrogen, orthophosphate, total phosphates, total dissolved phosphorus, and chemical oxygen demand.

Load

This research examined the contribution of non-point source nutrient and other pollutant loads (including suspended sediments) from the land to water bodies.

Water quality studies, by convention, use the concept of load (Chapra, 1997). The units of loading rates for this study are mass/time. The assumption is that the concentration of a constituent found in the water column is directly related to the amount of that constituent found in the landscape. What is applied to the surface of the landscape in the form of anthropogenic applications or natural processes is transported through the soil profile into the groundwater and then expresses itself in the creek. Constituents are discussed as particulate and dissolved fractions (Chapra, 1997). All biweekly base flow data are discussed. Two sets of storm data were selected for discussion here because of their completeness of data and the attributes of the precipitation event. Monthly and seasonal variability of nutrient movement were determined for Beaver Branch, Hangman's Run, and Blackbird Creek by surface water sampling.

Significance

This research directly addressed one of the critical problems in watersheds that discharge to estuaries, that is, it assessed the effect of non-point source nutrient and other pollutant loads (including suspended sediments) on water quality. Non-point source pollution has been identified as the most serious environmental stressor to water quality in the watersheds of Delaware's National Estuarine Research Reserve (DNERR) (Delaware National Estuarine Research Reserve, 1999). Of particular local concern are the addition of dissolved and particulate nutrients and suspended sediments from agricultural runoff and from developed areas with impervious surfaces or residential landscapes, the leaching of nutrients and bacteria from septic fields, and the atmospheric deposition of nutrients and toxic chemicals to surface waters. Other likely contributors to non-point source pollution problems and water quality degradation in DNERR are increased sediment runoff and other contaminants associated with land-use (i.e., development) changes in the region surrounding the reserve. The non-point pollution sources described above are not unique to DNERR, but are of concern to the vast majority of estuarine watersheds along the Mid-Atlantic, if not the entire coastal United States.

This research project directly begins to assess the impact of a major golf course/housing development on the local estuarine watershed. The study is timely in that the opportunity existed for pre-construction determination of the baseline setting of water quality, and then as construction proceeds and new land use commences, any resulting changes may be monitored. This thesis project was part of a larger research effort devoted to studying the impact of suburban development on the local watersheds and their surrounding wetlands near DNERR. These combined research efforts will provide managers with useful information regarding how suburban development impacts nutrient loading and water quality. This type of information can be used to develop improved best management practices to minimize these impacts on wetlands and estuarine environments.

Coordination with Other Research in Progress or Proposed

This thesis project was closely aligned with on-going and proposed research efforts in DNERR. Funding for this project came from several sources. A Graduate Research Fellowship in the National Estuarine Research Reserve System covered two years worth of a graduate student stipend and limited supplies and travel monies. The water quality monitoring and weather station equipment (i.e., YSI data loggers, ISCO samplers, Campbell Scientific station) in this project were supplied at no cost by DNERR. The cost of the water quality laboratory analyses for the first year of this project were covered from a grant to Drs. Madsen and Ritter from the Delaware Coastal Program which is in the Division of Soil and Water Conservation within the State of Delaware's Department of Natural Resources and Environmental Control (DNREC). The second year of laboratory sampling costs, and an expanded water quality monitoring program, was funded by DNREC in conjunction with the Wetland Program Development Grants section of the United States Environmental Protection Agency.

Chapter 2

DATA COLLECTION AND ANALYSIS

Summary

Field data measurements were taken by instruments that are permanently installed on the sides of bridges that span the creeks in this study. DNERR owns, maintains, and operates the instruments. A complete data set for field parameters is available in digital format from the DNEER St. Jones Research Center. Laboratory data were analyzed at the University of Delaware's Bioresources Laboratory. Stream flow data was modeled using available USGS data and a reference basin. Laboratory data were factored by stream flow to determine loads.

Field Data

Data Collection

Field measurements of temperature, specific conductance, salinity, dissolved oxygen, depth, pH, and turbidity were taken at each of the three monitoring sites with YSI Model 6600 Sondes at fifteen minute intervals. Sondes reside in 10 cm diameter PVC tubes that are permanently bolted to the bridges at each sampling site. The probes are attached to the sondes bulkhead, each probe contain sensors specific for each measurement. The bulkhead is lowered by cable through a steel tube to a depth of approximately 30 cm from the creek bottom. The sondes bulkheads have an internal battery and data logger. The YSI system is owned, maintained, and monitored by DNERR.

Deployment of the instruments on Blackbird Creek occurred on July 14, 1995. The instruments on Beaver Branch and Hangman's Run were deployed on July 1, 2002 and July 31, 2002, respectively. The instruments are offline on a biweekly schedule for routine maintenance and data retrieval. The sondes were removed in mid-winter due to icy conditions and redeployed in early spring.

The collection of field parameters with a brief discussion is presented in this paper. The initial proposal of this study included analysis of Biological Oxygen Demand (BOD). BOD analysis would have used the field parameters in modeling nitrogen species. Because the BOD analysis was unavailable, only depth data was used in this study. Complete sonde data is available through the Delaware National Estuarine Research Reserve System.

Data Quality Control and Validation

Data retrieved from the YSI data logger was downloaded into a spreadsheet format. The data were then uploaded into YSI's EcoWatch software. The program displays the data in tabular and graphical displays. Graphs and data are scrutinized for possible anomalies (Delaware National Estuarine Research Reserve, 2004a). A committee at the National Estuarine Research Reserve performs the final validation of data.

Parameters

Temperature. Temperature sondes utilize a resistor made of thermistor semiconductors. Changes in resistance result from temperature changes. Sondes have an internal software program with an algorithm that calculates the conversion of resistance to temperature (YSI Inc, 2003). This method has a range of –5 to 45 °C with an accuracy of ±0.15 °C with a resolution of 0.01 °C (Table 2.1).

Specific Conductance. The specific conductance sondes consist of a cell with four electrodes. Two of the electrodes emit a current and two measure the drop in voltage. An internal software program converts the measured drop in voltage to a conductance value in milli-Siemens per cm (mS/cm). The software takes into consideration the effect of temperature on specific conductance and factors in the appropriate correction (YSI Inc, 2003). This method has a range of 0 to 100 mS/cm and an accuracy of ±0.5% of reading +0.001 mS/cm with a resolution of 0.001 mS/cm to 0.1 mS/cm (Table 2.1).

Salinity. Software contained within the system utilizes values from temperature and specific conductance sondes in correspondence with algorithms found in the Standard Methods for the Examination of Water and Wastewater (APHA, 1989). The calculated value is reported in units of parts per thousand (ppt). It should be noted that actual calculations are performed without the use of units. Values generated however, correspond well to ppt (YSI Inc, 2003). This method has a range of 0 to 70 ppt with an accuracy of ±1.0% of reading or 0.1 ppt, (whichever is greater) with a resolution of 0.01 ppt (Table 2.1).

Dissolved Oxygen. The dissolved oxygen sonde utilizes a teflon membrane covered probe. This patented system consists of three electrodes that measure the charge associated with oxygen reduction. Internal software calculates the values correcting for the effect of temperature (YSI Inc., 2003). Dissolved oxygen content in the water column is dependent on temperature and salinity. The software calculates the percent of dissolved oxygen using the temperature and salinity values. Readings of dissolved oxygen in mg/L have a range of 0 to 50 mg/L with an accuracy of 0 to 20mg ±2% of Table 2.1 Range, accuracy, and resolution of field data parameters reading or 0.2 mg/L (whichever is greater) and 20 to 50 mg/L ±6% of the reading, with a resolution of 0.01 mg/L.

Table 2.1. Range, accuracy, and resolution of field parameters

Parameter	Range	Accuracy	Resolution
Temperature	-5 to 45 °C	± 0.15 °C	0.01 °C
Specific Conductance	0 to 100 mS/cm	± 0.5% of reading or 0.1mS/cm	0.001 to 0.1 mS/cm
Salinity	0 to 70 ppt	± 1.0% or 0.1 ppt (whichever is greater)	0.01 ppt
Dissolved Oxygen	0 to 50 mg/L	0 to 20 mg/L: ± 2% of reading or 0.2 mg/L (which ever is greater) 20 to 50 mg/L: ± 6%	0.01 mg/L
Dissolved Oxygen %	0 to 500% air saturation	0-200% air saturation: ± 2% of reading or 2% air saturation 200 to 500 % air saturation: ± 6% of reading	0.1 % air saturation
Depth	0 to 9.1 m	± 0.018 m	0.001 m
pH	0 to 14 units	± 0.2 units	0.001 units
Turbidity	0 to 1000 NTU	± 5% of reading or 2 NTU (whichever is greater)	0.1 NTU

Reading for percent dissolved oxygen have a range of 0 to 500% air saturation with an accuracy of 0-200 % air saturation, ± 2% of the reading or 2% air saturation (whichever is greater) and for 200-500 % air saturation, ±6% of reading with a resolution of 0.1% air saturation (Table 2.1).

Depth. The depth sondes utilize a differential strain gauge transducer to measure pressure. One side of the transducer is exposed to a vacuum and the other to the water. Depth measurements are based on water column pressure and atmospheric pressure at the atmosphere water interface. The software allows for corrections due to the effect of temperature (YSI Inc., 2003). This method has a range of 0-9.1 m with an accuracy of ±0.018 m and a resolution of 0.001 m (Table 2.1).

pH. The pH sonde consists of two electrodes separated by a glass slide. One electrode is in an invariant buffer solution and the other is in a gelled electrolyte. A potential gradient is generated across the glass slide. The difference in the potential, relative to the reference electrode is proportional to the pH. Software corrects for the effect of temperature by using the established linear relationship between pH and the millivolt value (YSI Inc., 2003). This method has a range of 0 to 14 units and an accuracy of ±0.2 units with a resolution of 0.01 units (Table 2.1).

Turbidity. Turbidity sondes utilize a light emitting diode (LED) set at a wavelength of 830 - 890 nm to measure the content of suspended solids in the water column. Internal software compensates for the effect of temperature (YSI Inc., 2003). This method has a range of 0 to 1000 NTU and an accuracy of ±5% of the reading or two NTU (whichever is greater) with a resolution of 0.1 NTU (Table 2.1).

Precipitation Data

Precipitation data was obtained from a variety of sources. DNERR installed a Campbell Scientific weather station with a CR10X data-logger in the Blackbird Creek Estuarine Research Reserve in October of 2002 (Fig 1.2). The station was set up in support of the project and is maintained by DNERR. The Delaware Environmental Observing System has incorporated the station into its databases.

Additional data came from NOAA and The Office of the Delaware State Climatologist.

Laboratory Data

Sample Collection

One-liter biweekly grab samples from each of three sites were retrieved with a Beta-type Horizontal Sampler. Sampling occurred at a depth of approximately 15 cm above the creek bed, center channel, within a three-hour window of the incoming low slack tide. Samples were transported on ice to the laboratory.

Storm samples were taken using an ISCO Model 6700 sampler at each of the three sites. The equipment was deployed in the field based upon reports of imminent rain. Sampler's siphon tubes were secured to set 15 cm off the creek bottom. The ISCO's computers were triggered to begin sampling by standard tipping bucket rain gauges when precipitation reached 5.08 mm in a 2-hour period. The ISCO sampler siphons a one-liter aliquot per hour for a period of 24 hours. The cores of the samplers were filled with ice at deployment. The ice was replenished during the sampling period. Samples were transported to the laboratory in ice.

Quality Assurance

Analysis of samples was performed at the Bioresources Laboratory at the University of Delaware, with the exception of silicate measurements, which were performed at the Soil Science Laboratory at the University of Delaware. The laboratories are analytical in that capacity: single samples are analyzed without repetition. Quality assurance is maintained using Shewhart's control chart method (Taylor, 1987).

In this method, seven control samples are analyzed: two repeats, one spike and four standards of different concentrations. The resulting values are plotted to determine the standard deviation. The method detection limit is determined to be three times the standard deviation. The method detection limit is the lowest value that can be reported with 95% confidence (Taylor, 1987).

Validation

Laboratory data were sorted and examined for range and anomalies. Particulate (unfiltered) and dissolved (filtered) constituents were evaluated in concord. Values less than one standard deviation (std dev.) below the method detection limit (MDL) were assumed zero where unfiltered and filtered values were in concordance. Values less than or equal to one standard dev. of the MDL were included. Anomalies were identified as values that were out of concordance with other constituents. Values where the unfiltered sample was less than one standard dev. of the MDL and the filtered sample was significantly above the MDL were assumed to be equal to the lesser value. This assumption is based on the test method and is determined by colorimetric methods, which is a subjective analysis. The filtered values were assumed equal to the unfiltered value when the unfiltered and filtered samples were greater than the MDL but the filtered value was significantly greater than the unfiltered value.

Laboratory Analysis

Sample Preparation. Bi-weekly samples were processed from one-liter field collection bottles. Storm samples were composited as follows: samples one and two constitute composite A, three through thirteen, B, and, fourteen through twenty-four, C. One liter of each composite was retained for analysis

The one-liter composited samples were mixed well and 50 ml aliquots were transferred using calibrated cylinders for immediate analysis of total suspended and dissolved solids. Samples were remixed and 250 ml aliquots were filtered through 9-H glass filters. Filter papers with collected sediments were placed in labeled petri dishes for analysis of chlorophyll a, b, c, and pheophytin a. An additional 200 ml of sample was filtered and combined with the filtered 250 ml aliquots. The combined 450 ml aliquot was then tested for filtered values of ammonia-nitrogen, nitrate-nitrogen, total Kjeldahl nitrogen, orthophosphates, total phosphates, and chemical oxygen demand. The remaining 500 ml of each original sample was analyzed for unfiltered values of all the constituents.

Ammonia-nitrogen (NH4N). Ammonia-nitrogen (NH_4-N) analyses were determined in accordance with Standard Methods for the Examination of Water and Wastewater (SMWW) 4500-NH_3 B (Preliminary Distillation Step) and 4500-NH_3-E (Titrimetric Method) (APHA, 1989).

Samples were distilled after the addition of a buffering solution. The steam was condensed and collected in a solution of boric acid, an indicator solution. Ammonia ions combine with boric acid to form ammonium and borate.

Samples were titrated with sulfuric acid to return them to original pH. Titration with acid measures the amount of borate ion present in solution (Sawyer and McCarty, 1978). The amount of ammonium nitrate can then be inferred by calculation (APHA, 1989). This method has a detection limit of 0.199 mg/L with a standard deviation of ±0.066 mg/L (Table 2.2).

Nitrate-nitrogen (NO3N). Nitrate-nitrogen values were determined using Devarda's alloy reduction method. This method uses SMWW 4500-NH_3 B (Preliminary Distillation Step) and SMWW 4500-NH_3-E (Titrimetric Method). Devarda's alloy reduction method reduces nitrate to ammonia by adding Devarda's alloy and magnesium oxide to the sample under hot alkaline conditions before distillation (Sawyer and McCarty, 1978). Samples were then distilled and titrated using the ammonia-nitrogen procedure described above (Sawyer and McCarty, 1978).

Table 2.2. Detection limits and standard deviation of laboratory analyses.

Parameter	Method	MDL* mg/L	Std. Dev. mg/L
Ammonia-N	Preliminary Distillation Step Acid Titrimetric Method	0.199	± 0.066
Nitrate-N	Devarda's Alloy Reduction Acid Titrimetric Method	0.320	± 0.107
Total Kjeldahl-N	Micro-Kjeldahl Method Acid Titrimetric Method	0.460	± 0.153
Orthophosphate	Colorimetric: Ascorbic Acid Method	0.012	± 0.004
Total Phosphate	Sulfuric-Nitric Acid Digestion Colorimetric: Ascorbic Acid Method	0.029	± 0.097
Silica	ICP – Mass Spectrometer	0.020	± 0.007
Total Suspended Solids	TSS Dried at 103 –105 °C	0.330	± 0.110
Total Dissolved Solids	TDS Dried at 103–105 °C	0.330	± 0.110
Chemical Oxygen Demand	Closed Reflux, Colorimetric Method	7.00	± 2.50
Chlorophyll a	Acetone Extraction / Colorimetric	1.50	± 0.50
Chlorophyll b	Acetone Extraction / Colorimetric	1.50	± 0.50
Chlorophyll c	Acetone Extraction / Colorimetric	1.50	± 0.50
Pheophytin a	Acetone Extraction / Colorimetric	1.50	± 0.50

*MDL = Method Detection Limit

This method has a detection limit of 0.320 mg/L with a standard deviation of ±0.107 mg/L (Table 2.2).

Total Kjeldahl Nitrogen (TKN). Total Kjeldahl nitrogen measures the amount of organic-nitrogen and ammonia-nitrogen combined. Since nitrogen levels cannot be measured directly, nitrogen is reduced to ammonia-nitrogen for quantification by distillation. The procedures used are in accordance with SMWW 4500-Norg C (Semi-Micro-Kjeldahl Method) and 4500-NH_3-E (Titrimetric Method).

Samples are set up in Kjeldahl flasks with Kjeldahl catalyst and concentrated sulfuric acid. Flasks are placed on a micro-Kjeldahl digestion unit and heated for 1.5 to 2 hours. Heating removes excess water and allows the acid to digest the organic matter. Organic-nitrogen is released as ammonia-nitrogen. Samples are then distilled and titrated in the same manner as ammonia-nitrogen described above (Sawyer and McCarty, 1978). This method has a detection limit of 0.46 mg/L with a standard deviation of ±0.153 mg/L (Table 2.2).

Orthophosphates (OP). Orthophosphate determinations were made in accordance with the SMWW 4500-P E (Ascorbic Acid Method). This method is based on the principle that phosphate ions, under acid conditions, combine with ammonium molybdate to form ammonium phosphomolybdate. Ascorbic acid is then introduced to form molybdenum blue. This precipitate is then quantified using a spectrophotometer (Sawyer and McCarty, 1978).

The spectrophotometer was calibrated to 100% transmittance using the distilled water blank. If sample values are below 90% transmittance, a blank containing the non-reactive reagent was used to calibrate the instrument to 100% transmittance, thereby eliminating interference from colored or turbid water (APHA, 1989). The method has a detection limit of 0.011 mg/L with a standard deviation of ±0.004 mg/L (Table 2.2).

Total Phosphates (TP). Total phosphates cannot be measured directly; they must be converted to orthophosphate by digestion (Sawyer and McCarty, 1978). Following standard procedures, samples were digested with sulfuric acid and nitric acid to oxidize the organic matter and release phosphorous as orthophosphate for quantification. The digested sample is then neutralized and titrated with sodium hydroxide. Neutralized samples were then titrated with a sulfuric acid until the sample turned clear. These solutions were transferred to a test tube and analyzed in the same manner as explained above in orthophosphates. This method has a detection limit of 0.029 mg/L with a standard deviation of ±0.010 mg/L (Table 2.2).

Silicates. Silicate determinations were made using the Inductively Coupled Plasma Method (ICP) in accordance with SMWW 3120B (APHA, 1989). The ICP apparatus utilizes radio frequencies to ionize argon gas. Argon gas is injected into a torch chamber with an aerosol of sample. This aerosol is then subjected to temperatures of 6000 to 8000 EK. The aerosol ionizes at these temperatures. The ICP is equipped with a spectrometer to read wavelengths emitted by the ionized mixture. Signature wavelengths were then analyzed (APHA, 1989). This method has a detection limit of 0.020 mg/L with a standard deviation of ±0.007 mg/L (Table 2.2).

Total Suspended and Dissolved Solids. Analyses of suspended and dissolved solids were performed in accordance with SMWW 2540D and 2540B, respectively (APHA, 1989). Following standard procedures, an aliquot of sample is suctioned through a pre-wetted, pre-dried, and pre-weighed glass fiber filter (9 H). The filtered portion of the sample is transferred to a crucible. The filters with attached solids and crucibles are placed in a 105EC oven and dried overnight. Determinations of TSS are calculated by subtracting the dry weight of the filter paper from the weight of dried filter with residue. Determinations of TDS are calculated by subtracting the weight of the crucible from the weight of crucible with residue. These methods have a detection limit of 0.33 mg/L with a standard deviation of ±0.11mg/L (Table 2.2).

Chemical Oxygen Demand (COD). Determinations for COD were made using SMWW 5220 D. Closed Reflux and Colorimetric Method (APHA, 1989). The method is based on the principle that organic matter is prone to oxidation by a strong chemical oxidant; hence, COD values are the measure of oxygen equivalent of the organic matter contained in the sample (APHA, 1989). COD differs from Biological Oxygen Demand (BOD) in that COD measures all oxidizable material whereas BOD measures biologically oxidizable material (Sawyer and McCarty, 1978).

An aliquot of sample is added to a commercially prepared digestion ampule. Blanks, standards, and samples are heated at 150 EC for two hours. The reaction with reagents forms a precipitate. The precipitate is allowed to settle and cool before the ampule is read using a spectrophotometer.

A linear regression equation is calculated by plotting the absorbance of the standards against their known concentrations. The linear regression graph serves as a calibration curve. COD values are determined by comparing the sample's absorbance to the calibration curve values (Bioscience-Inc., 1999). The method has a detection limit of ±2.5 mgO2/L with a standard deviation of ±0.833 (Table 2.2).

Chlorophyll a, b, c, and Pheophytin a. Following standard procedures, 250 ml aliquots of sample were filtered through 9-H glass filters (APHA, 1989). Filter papers with collected sediment were ground using a tissue grinder and brought up to a volume of 5 ml with an aqueous acetone solution (90% acetone and 10% of MgCo3).

The resulting solutes were centrifuged and refrigerated overnight. Before analysis, solutes were centrifuged for 20 minutes and decanted into cuvettes.

Spectrophotometer readings were recorded at optical densities (OD): 664 nm, 647 nm, 630 nm, and 750 nm. Samples were then acidified with 0.02 ml of 1N HCL per ml of extract and reread at 665 mm OD. Calibration of the instrument was performed with a blank of aqueous acetone solution. Chlorophyll a, b, and c are detected at 664 nm, 647 nm, and 630 nm OD readings, respectively. Pheophytin a values were calculated from the acidified solution. Interference from turbidity was corrected by subtracting the OD 750 nm readings from sample readings. Extract concentrations of chlorophyll a, b, and c were calculated using the corrected OD readings (APHA, 1989). The method has a detection limit of 01.5 mg/L with a standard deviation of 0.5 mg/L (Table 2.2).

Stream Flow

The United States Geological Survey (USGS) has operated and maintained a stream gauge on Blackbird Creek since its installation in 1956. A complete record of stream flow data was not available for the study period due to the quality control and validation process practiced by the USGS. This necessitated the development of a model to predict estimated stream flow for a portion of the study period.

Morgan Creek stream flow data were successfully used as a reference basin in studies conducted in the 1970's to estimate stream flow for Appoquinimink River (Dr. W. Ritter, personal communication, 2004). Morgan Creek is in the Chesapeake Estuary watershed, approximately fourteen miles to the west of the study site (Figure 2.1). The Appoquinimink drainage basin is directly north of the study site (Figure 2.1).

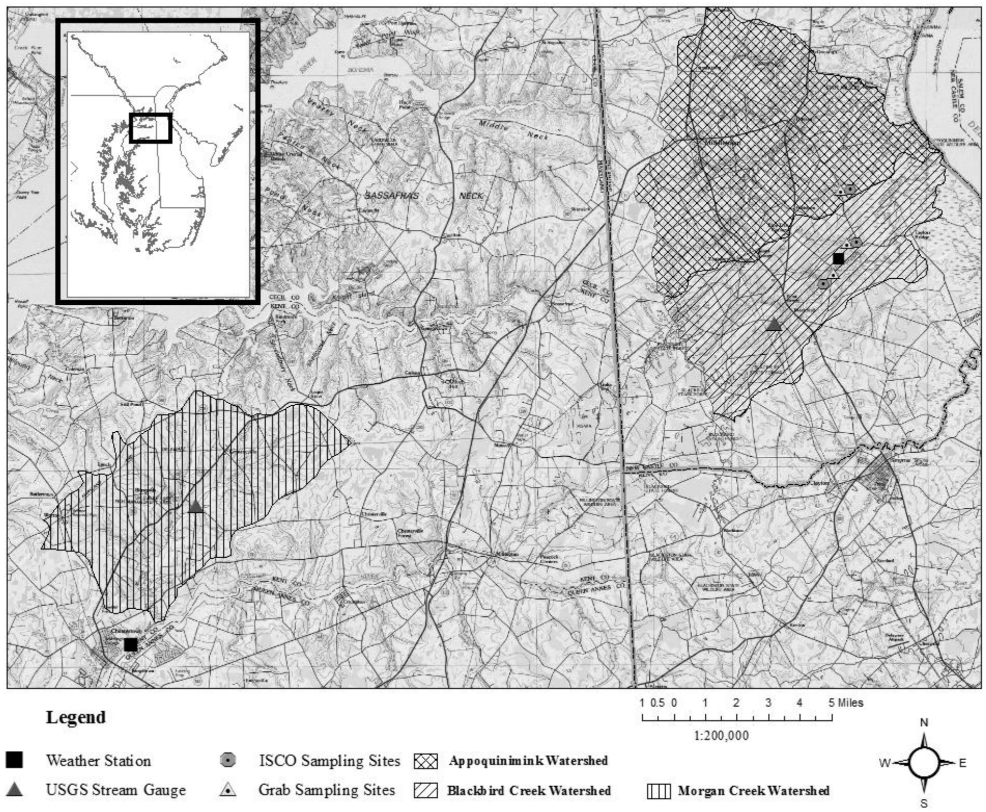


Figure 2.1. Study Area in Relationship to Morgan Creek and the Appoquinimink River

USGS stream flow data for a five year period from September 1996 to September 2002 for Morgan and Blackbird Creeks were converted to unit area units by dividing the gauged flow (m^3/s) by the drainage basin area (m^2), (Ritter and Harris, 1984). This yields $m^3/m^2/s$. The resulting graph over time demonstrated the acceptability of Morgan Creek as a reference basin (Figure 2.2). Determination of unit area values were calculated from data using an ESRI GIS spatial analysis (Table 2.3).

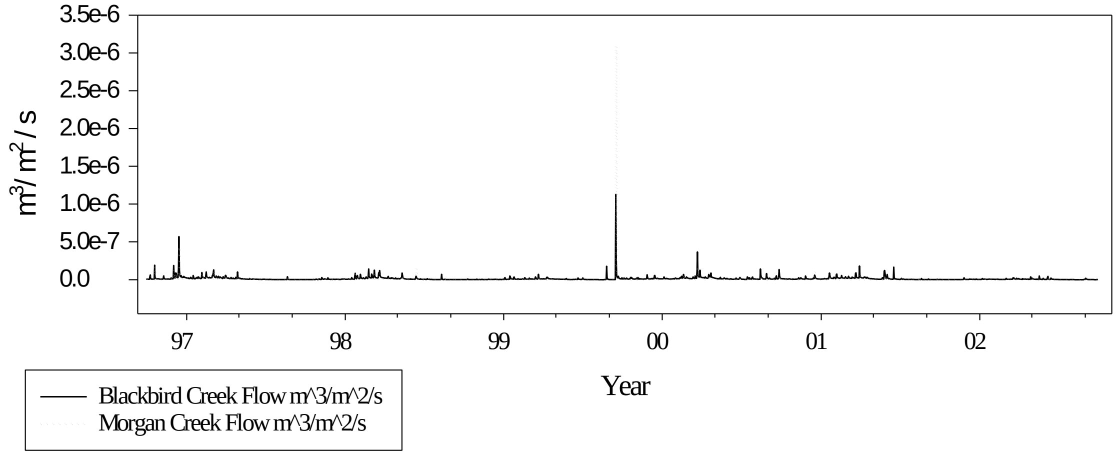


Figure 2.2. USGS Flow data from 1996 – 2002 for Blackbird and Morgan Creeks (USGS, 2004a, b).

Unit area values for Blackbird Creek and Morgan Creek were analyzed using regression equations (Table 2.4). A linear regression analysis showed an R^2 of 0.69. Based on this observation, the data were analyzed using several investigative non-linear regression equations (Table 2.4). The hyperbola regression equation B demonstrated the best correlation: R^2 = 0.87 (Table 2.4 and Figure 2.3).

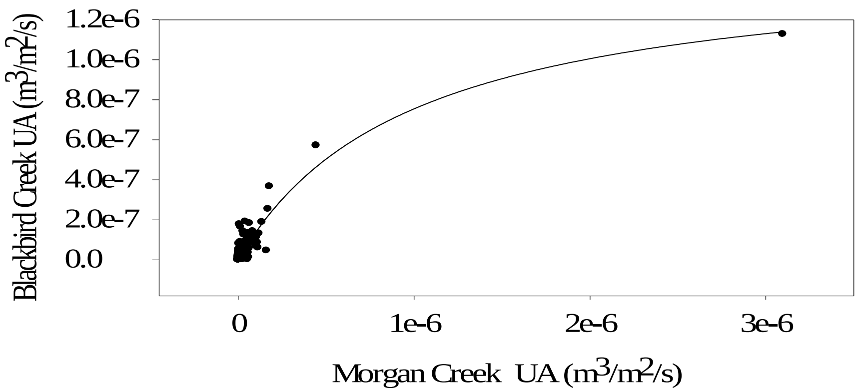


Figure 2.3. Correlation of Morgan Creek and Blackbird Creek using the regression equation: $y = (ax)/(a+b)$.

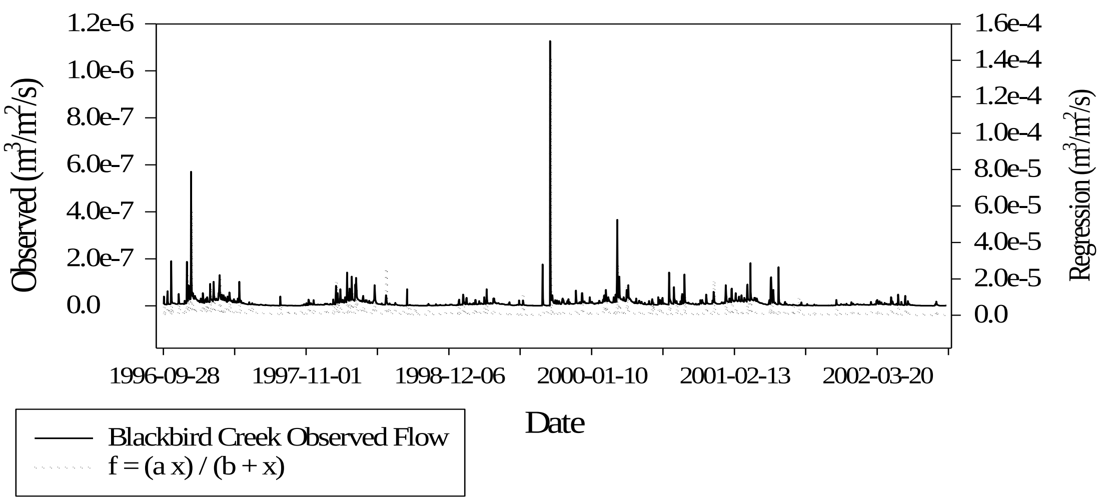


Figure 2.4. Blackbird Creek observed flow (USGS, 2004a) and regression equation: $f = (ax)/(b+x)$. This equation is B in Table 2.3 and demonstrated the best correlation for Blackbird and Morgan Creeks.

Table 2.3 Watershed Areas

Watershed	$mile^2$	m^2	hectares
Blackbird Creek			
Area Above Gauge	3.85	9,971,500.00	997.15
Area Above Site	18.80	48,698,387.74	4,869.84
Hangman's Run			
Area Above Site	1.48	3,829,421.83	382.94
Beaver Creek			
Area Above Site	1.76	4,551,925.75	455.19
Morgan Creek			
Area Above Gauge	12.70	32,893,000.00	3,289.30

Table 2.4. Investigation of regression equations for flow correlation of Blackbird and Morgan Creeks

EQ.	Regression Equation	R	R^2
A	$f = y(0)+ax$	0.831	0.690
B	$f = (ax)/(b+x)$	0.930	0.870
C	$f =(1+ax)/(b+cx)$	0.930	0.869
D	$f = x/(a+bx)$	0.919	0.843
E	$f = ax/(1+bx)$	0.885	0.793
F	$f = a(1-b^x)$	0.783	0.613

Efforts to improve the correlation included quartile analysis that identified three outliers in the data set for possible elimination. These points coincided with Hurricane Floyd and two other major storms. Regression analysis of the data with outliers removed also generated unacceptable R^2 values. Therefore, the data points were retained.

The hyperbola Regression B over-predicted stream flow compared to observed data by two orders of magnitude with R^2 of 0.86 (Table 2.5). Addition of a coefficient to the Regression B more accurately estimated stream flow bringing the predicted value in the same magnitude of the observed value. The addition of three terms to Model I accounted for precipitation and the response time of the basin to the event (Model P, Table 2.6). The resulting Model P showed a R^2 of 0.92. A complete record of precipitation was available from NOAA for Morgan Creek. Data for Blackbird State Forest from the Delaware State Cooperative Observation System record was incomplete. Available data presented 256 points with precipitation records for both sites. Applying Model P to the available precipitation data set returned an R^2 of 0.92 with an overall R^2 of 0.86. Model P tracked the observed data well (Figures 2.5 and 2.6). Model P was accepted to estimate stream flow for the unavailable data. Recent publication of USGS 2003 stream flow data for Blackbird Creek demonstrated an R^2 of 0.76 when compared to modeled flow for the same period (USGS, 2004a).

Table 2.5. R^2 values for Regression B, Model I, and Model P

Equation		$m^3/m^2/s$		
		Max	Min	R^2
Observed Flow		5.7e-7	4.5e-09	--
Regression B	$f = (ax)/(b+x)$	5.8e-05	8.0e-07	0.86
Model I	$f = (ax/(b+x))C$	3.5e-07	4.9e-09	0.86
Model P	See Table 2.6	4.5e-07	5.1e-09	0.92

The model predicted stream flow for Blackbird Creek based on the unit area of $m^3/m^2/s$. To determine the stream flow for Beaver Creek and Hangman's Run, the resulting unit area for Blackbird Creek stream flow was multiplied by area of the each basin in m^2 to calculate stream flow. Hangman's Run and Beaver Branch are approximately 455.19 and 382.94 hectare respectively (Figure 2.3).

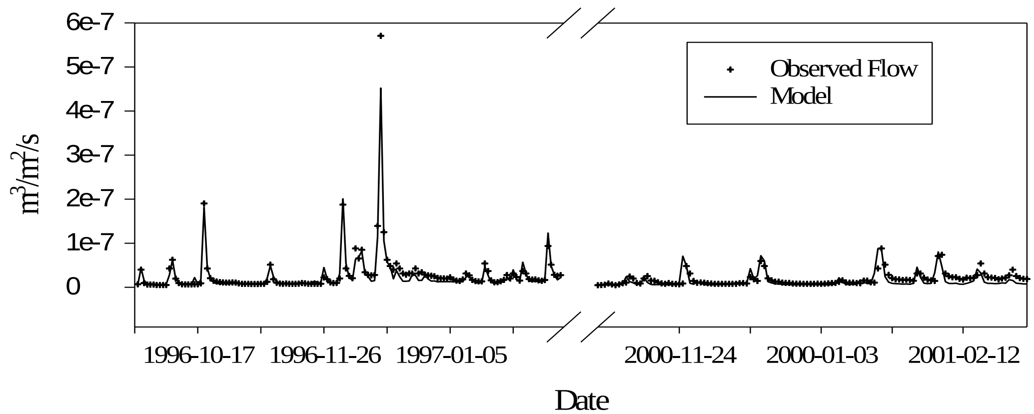


Figure 2.5. Blackbird Creek observed flow data 1999 to 2002 (USGS, 2004a) and predicted flow from Model P.

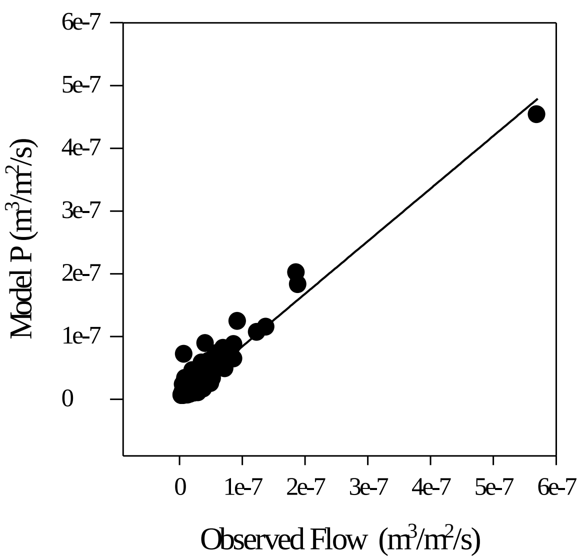


Figure 2.6. Blackbird Creek observed flow 1999 to 2002 data (USGS, 2004a) vs. Model P with an R^2 = 0.923.

Table 2.6. Model P, equation, coefficients, and parameters.

Model P: $Q = [((ax) / (b+x))\ c] + (P_i k_1) + (P_{i-1} k_2) + (P_{i-2} k_3)$		
Symbol	Value	Units
x =	Morgan Creek Flow	$m^3/m^2/s$
a =	0.000188633	
b =	1.0116E-06	
c =	6.10E03	
P =	Blackbird Precipitation – Chestertown Precipitation	m
	If less than 0: Then P = 0	
k_1 =	1.3273E-07	
k_2 =	1.6801E-06	
k_3 =	4.8440E-07	

Calculated Values

Particulate and Dissolved Species

Filtered values were subtracted from the unfiltered values to yield particulate (P) and dissolved species (D).

Organic-Nitrogen

Total Kjeldahl nitrogen is the measure of the organic-nitrogen and ammonia combined (APHA, 1989). Dissolved organic-nitrogen (Norg-N) was calculated by subtracting the filtered ammonia-nitrogen value from the filtered total Kjeldahl value. Particulate organic-nitrogen (Norg P) was derived by subtracting the unfiltered ammonia-nitrogen value from the unfiltered total Kjeldahl value. The dissolved organic-nitrogen value was derived in the same way using the filtered ammonia-nitrogen.

Load

Concentrations for each constituent were converted to kilograms per meter cubed (kg/m^3), multiplied by the stream flow (m^3/s) and the time interval to yield kg/year, kg/season, kg/aliquot. Laboratory data for biweekly and storm samples were averaged by month, multiplied by daily stream flow, and summed to yield seasonal loads. Seasonal loads were summed to yield annual loads.

Storm loads were calculated in terms of composite aliquots multiplied by stream flow. Calculations of monthly average base-flow loads were based solely on the biweekly samples.

Chapter 3

RESULTS

Seasonal Data

Precipitation

Precipitation data from the year 2002 shows that Delaware met the criteria for a one- hundred year drought (DNREC, 2003). Within the Blackbird Creek basin the precipitation, decreased 66% from the mean average (Table 3.1.) based on Blackbird State Forest data (Leathers, 2001). Drought conditions began recovery with above average precipitation in the fall of 2002 (F02); precipitation remained above seasonal averages until the winter of 2004 (W04). The winter of 2004 had 27% less precipitation than the seasonal average. Precipitation for spring 2004 (SPR04) was comparable to the seasonal average with a 29% decline in the summer of 2004 (S04) (Figure 3.1, Table 3.1.).

Hangman's Run

The largest loads for the particulate fraction for ammonia-nitrogen (NH4-N P) occurred in W03, SPR03, and S04 (Figure 3.2, Table 3.2). These loads 91.81, 84.86, 86.60 kg/season respectively, were at least twice the mean value of 38.6 kg/season (Table 3.3). The lowest loads occurred in S02, F02, and W0: 8.52, 3.08, and 0 kg/season respectively. These values were less than 25% of the mean value. The largest load for the dissolved fraction for ammonia-nitrogen (NH4-N D) occurred in SPR03: 143.61 kg/season (Figure 3.2, Table 3.2). The lowest loads occurred in S02, F02, W03, and S03: 3.23, 2.46, 0, and 0 kg/season respectively. These values were significantly lower than the mean value of 62.19 kg/season (Table 3.2, Table 3.3).

Table 3.1 Seasonal Precipitation Data

Season	Study Period (DNERR)	Blackbird State Forest, DE (Average 11 year period)	Chestertown, MD (NOAA)	Difference: Blackbird State Forest Ave. vs. Study Period
	Precipitation (mm)			
S02	*100.6	299.9	118.9	-66%
F02	324.0	269.3	418.8	+20%
W03	291.0	232.0	356.6	+25%
SPR03	317.0	305.5	371.1	+4%
S03	394.2	299.9	487.7	+31%
F03	324.0	269.3	417.3	+21%
W04	169.4	232.0	214.4	-27%
SPR04	306.0	305.5	290.7	0
S04	212.8	299.9	237.7	-29%

*Calculated value: Chestertown minus average difference between Chestertown and study period observed data

The largest load for the particulate fraction for nitrate-nitrogen (NO3-N P) occurred at Hangman's Run in SPR03: 1,308.11 kg/season (Figure 3.2, Table 3.2). This load was approximately than four times the mean value of 304.7 kg/season (Table 3.3). The lowest loads occurred in S02 and F02: 7.70 and 0 kg/season respectively. These values were a fraction of the mean value. The largest loads for the dissolved fraction for nitrate-nitrogen (NO3-N D) occurred in SPR03 and W04:

1,655.95 and 1,499.39 kg/season respectively (Figure 3.2, Table 3.2). The lowest load occurred in S02: 3.37 kg/season.

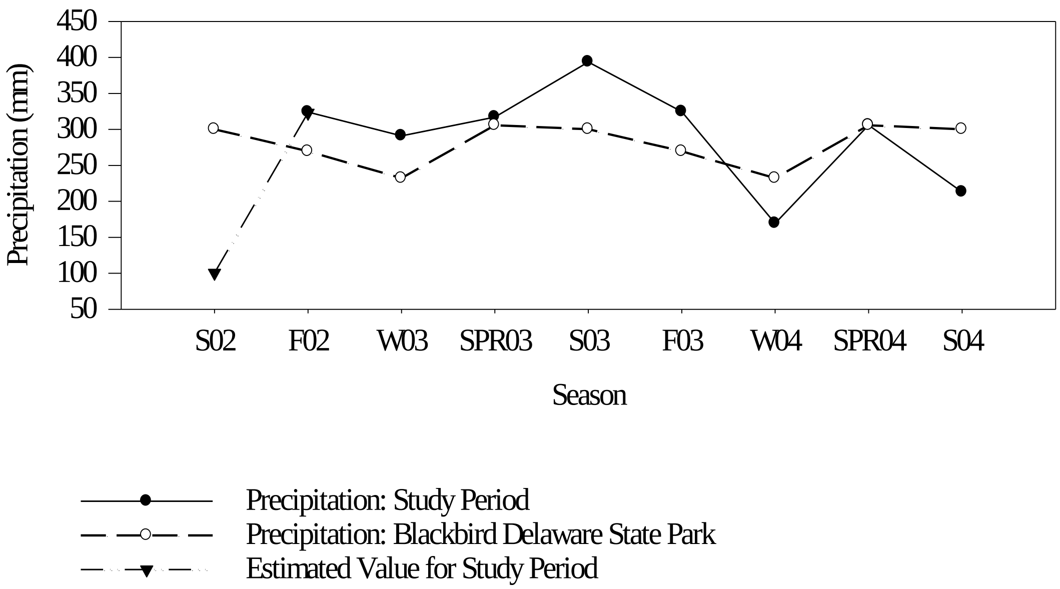


Figure 3.1. Seasonal mean average precipitation based on data from Blackbird State Forest data (Leathers, 2001) and composited precipitation for study period (Delaware National Estuarine Research Reserve, 2002, 2003, 2004b).

The largest load for the particulate fraction for organic nitrogen (Norg P) occurred in F02 369.77 kg/season (Figure 3.2, Table 3.2). This load was four times the mean 91.01 kg/season (Table 3.3). The lowest loads occurred in S02, W03, and W04: 22.27, 0, and 0 kg/season respectively. These values were a fraction of the mean value. The largest loads for the dissolved fraction for organic nitrogen (Norg D) occurred in SPR04 and S04: 222.27 and 200.38 kg/season respectively (Figure 3.2, Table 3.2). The lowest loads occurred in S02 and W03: 22.27 and 0 kg/season respectively.

At Hangman's Run, the largest loads for the particulate fraction for orthophosphate (OP P) occurred in SPR03, S03, and F03: 40.30, 58.06, and 39.07 kg/season respectively (Figure 3.3, Table 3.4). These loads were approximately twice the mean value of 23.16 kg/season (Table 3.5). The lowest loads occurred in S02 and W03. These values, 1.89 and 5.64 kg/season respectively, were a fraction of the mean value. The largest load of the dissolved fraction of orthophosphate (OP D) occurred in S03: 30.09 kg/season (Figure 3.3, Table 3.4). The lowest loads occurred in S02: 0.192 kg/season. This value was a fraction of the mean value of 9.7 kg/season (Table 3.5).

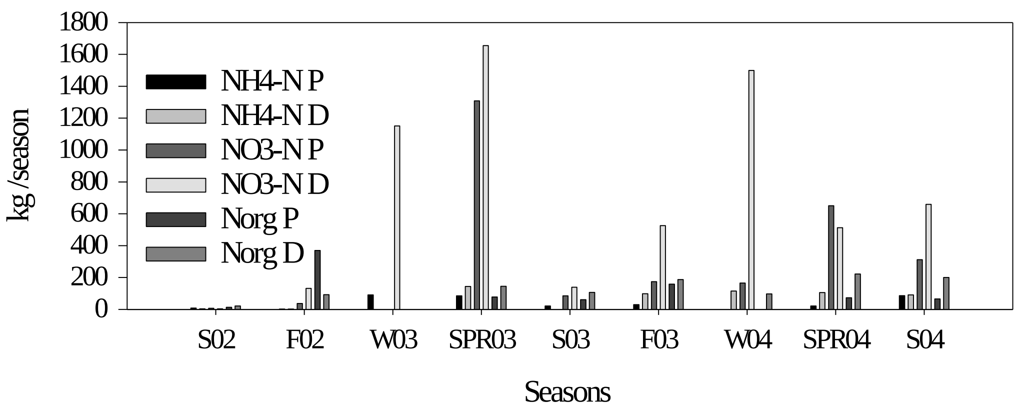


Figure 3.2. Hangman's Run Seasonal Data for Nitrogen Species

Table 3.2. Hangman's Run Seasonal Load Data for Nitrogen Species

Season	Ave Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/season					
S02	0.003	8.52	3.23	7.70	3.37	13.52	22.27
F02	0.031	3.08	2.46	37.33	132.06	369.77	92.22
W03	0.098	91.81	0.00	0.00	1151.61	0.00	0.00
SPR03	0.143	84.86	143.61	1308.41	1655.95	77.79	145.44
S03	0.092	21.82	0.00	85.87	139.90	60.76	107.47
F03	0.066	29.57	98.41	173.86	526.07	158.05	187.20
W04	0.139	0.00	115.24	165.38	1499.39	0.00	96.77
SPR04	0.065	21.11	105.62	651.27	512.82	73.49	222.27
S04	0.044	86.60	91.15	312.46	658.73	65.71	200.38

Table 3.3. Statistics of Hangman's Run Seasonal Load Data for Nitrogen Species

	Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/season					
Total	0.682	347.4	559.7	2742.3	6279.9	819.1	1074.0
Mean	0.076	38.6	62.2	304.7	697.8	91.0	119.3
Min	0.003	0	0	0	3.4	0	0
Max	0.143	91.8	143.6	1308.4	1655.9	369.8	222.3

The largest loads for the particulate fraction for total phosphate (TP P) occurred in SPR03, SPR04, and S04: 91.23, 101.32, and 113.22 kg/season respectively (Figure 3.3, Table 3.4). These loads were approximately twice the mean value of 57.82 kg/season (Table 3.5). The lowest loads occurred in S02, W03, and W04: 3.77, 1.71, and 6.11 kg/season respectively. These values were well below the mean value 47.62 kg/season. The largest loads of the dissolved fraction of total phosphate (TP D) occurred in S03 (Figure 3.3, Table 3.4). The lowest loads occurred in S02, W03, and S04: 0, 0, and 1.52 kg/season respectively. These values were significantly less than the mean value of 13.26 kg/season (Table 3.5).

The largest loads for the silicate occurred in S03: 3,938.9 kg/season (Figure 3.4, Table 3.4). This load was approximately twice the mean value of 1,807.50 kg/season (Table 3.5). The lowest load occurred in S02:134.8 kg/season and was significantly less than the mean value.

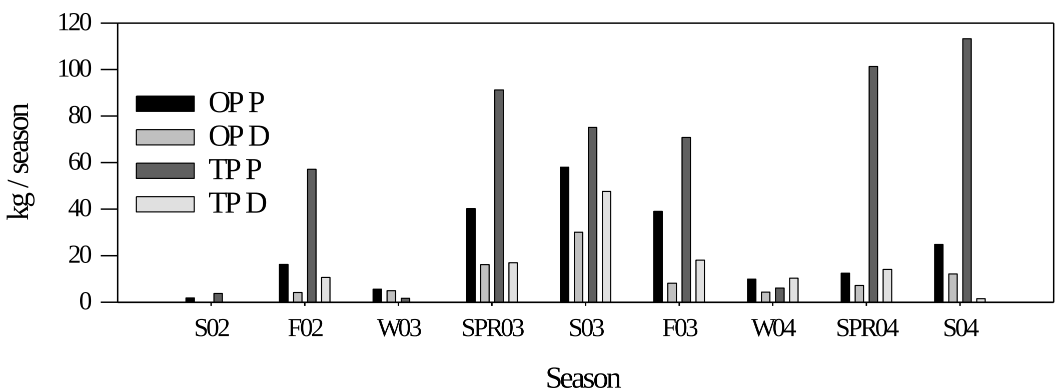


Figure 3.3. Hangman's Run Seasonal Data for Phosphate Species

Table 3.4. Hangman's Run Seasonal Load Data for Phosphates, Silicate, and Solids

Season	Ave Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg/season						
S02	0.003	1.89	0.192	3.77	0	134.8	1174.7	1613.9
F02	0.03	16.23	4.18	57.11	10.68	1062.4	65834.1	35066.2
W03	0.10	5.64	4.98	1.71	0	1163.0	19359.3	50268.1
SPR03	0.14	40.30	16.21	91.23	16.98	2303.9	22924.4	115424.5
S03	0.09	58.06	30.09	75.12	47.62	3938.9	10855.1	87970.1
F03	0.07	39.07	8.18	70.82	18.13	2903.1	14000.6	52486.0
W04	0.14	9.97	4.37	6.11	10.38	2055.7	3245.9	46663.2
SPR04	0.06	12.50	7.22	101.32	14.07	1616.4	8042.9	76589.9
S04	0.04	24.78	12.21	113.22	1.52	1089.3	4925.2	41068.3

Table 3.5. Statistics of Hangman's Run Seasonal Load Data for Phosphates, Silicate, and Solids

	Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg/season						
Total	0.682	208.44	87.63	520.41	119.38	16267.48	150362.17	507150.12
Mean	0.076	23.16	9.74	57.82	13.26	1807.50	16706.91	56350.01
Min	0.003	1.89	0.19	1.71	0.00	134.81	1174.72	1613.87
Max	0.143	58.06	30.09	113.22	47.62	3938.90	65834.07	115424.55
Min Pos	0.003	1.89	0.19	1.71	1.52	134.81	1174.72	1613.87

The largest loads for total suspended solids occurred in F02: 65,834.1 kg/season (Figure 3.3, Table 3.4). This load was approximately four times the mean (Table 3.5). The lowest loads occurred in S02: 1,174.7. This value was significantly less than the mean value: 16,706.91 kg/season. The largest load of total dissolved solids occurred in SPR03: 115,424.5 kg/season (Figure 3.3, Table 3.4). The lowest loads occurred in S02: 1613.9 kg/season. This value was significantly less than the mean value of 56,350.01 kg/season (Table 3.5).

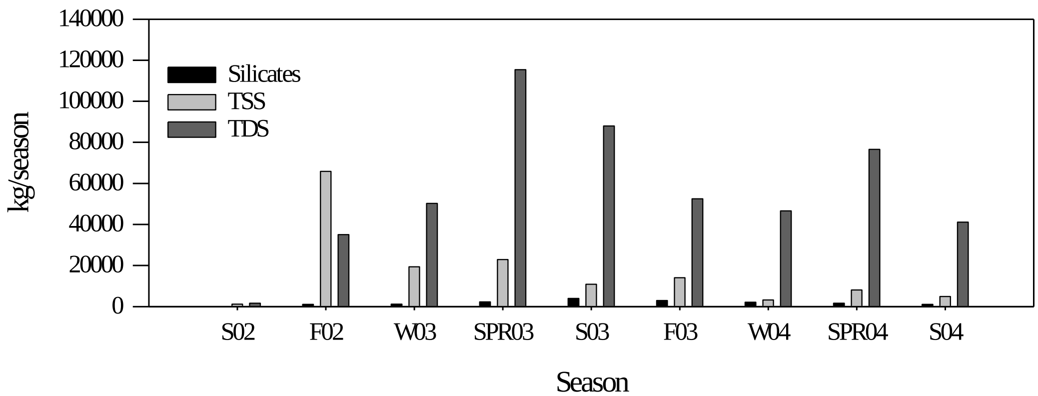


Figure 3.4. Hangman' Run Seasonal Date for Silicate, Total Suspended and Dissolved Solids.

Beaver Branch

The largest loads for the particulate fraction for ammonia-nitrogen (NH4-N P) occurred in S03 760.09 kg/season (Figure 3.5, Table 3.6). This load was four and a half times larger than the mean value of 166.4 kg/season (Table 3.7). The lowest loads occurred in S02, F02, and W03: 0.74, 2.93, and 0 kg/season respectively. These values were significantly less than the mean value. The largest load for the dissolved fraction for ammonia-nitrogen (NH4-N D) occurred in SPR04: 208.63 kg/season (Figure 3.5, Table 3.6). The lowest loads occurred in S02, F02, and W03:

0, 13.27, and 0 kg/season respectively. These values were significantly lower than the mean value of 88.1 kg/season (Table 3.6, Table 3.7).

The largest load for the particulate fraction for nitrate-nitrogen (NO3-N P) occurred in S03: 4,900.25 kg/season (Figure 3.5, Table 3.6). This load was greater than five and one-half times the mean (Table 3.7). The lowest loads occurred in S02 and F02: 1.38 and 15.73 kg/season respectively. These values were a fraction of the mean value 883.56 kg/season. The largest loads for the dissolved fraction for nitrate-nitrogen (NO3-N D) occurred in SPR03 and W04: 1,336.18 and 1,502.41 kg/season respectively (Figure 3.5, Table 3.6). The lowest loads occurred in S02 and F02: 0.82 and 0 kg/season respectively.

The largest load for the particulate fraction for organic nitrogen (Norg P) occurred in S04: 433.51 kg/season (Figure 3.5, Table 3.6). This load was approximately two times the mean of 193.64 kg/season (Table 3.7). The lowest loads occurred in S02 and S03: 18.57 and 38.99 kg/season respectively. These values were a fraction of the mean value. The largest loads for the dissolved fraction for organic nitrogen (Norg D) occurred in W03, F03, and S04: 398.94, 329.39, and 394.72 kg/season respectively (Figure 3.5, Table 3.6). The lowest load occurred in S02: 16.06 kg/season.

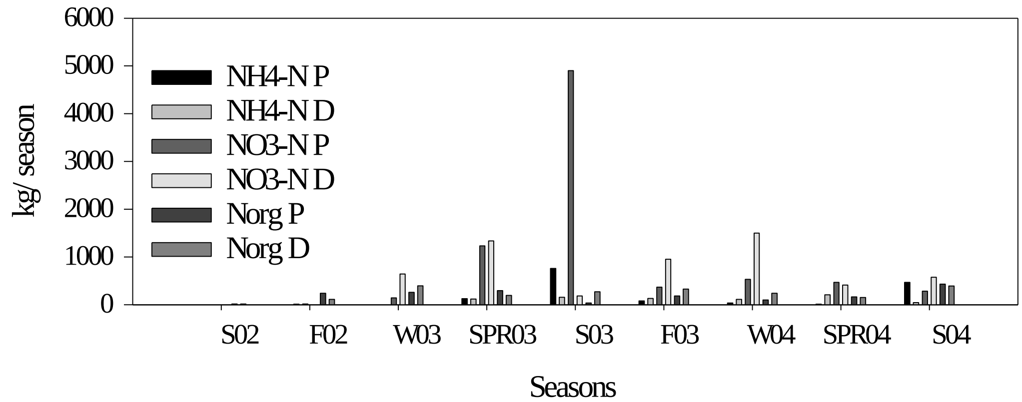


Figure 3.5. Beaver Branch Seasonal Data for Nitrogen Species

Table 3.6. Beaver Branch Seasonal Load Data for Nitrogen Species

Season	Ave Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/season					
S02	0.004	0.737	0.000	1.388	0.818	18.573	16.058
F02	0.037	2.929	13.270	15.723	0.000	240.367	112.025
W03	0.117	0.000	0.000	143.855	644.558	261.711	398.938
SPR03	0.170	129.646	121.680	1231.665	1336.183	296.598	198.966
S03	0.110	760.093	156.707	4900.247	187.189	38.994	274.063
F03	0.079	82.485	133.673	368.522	951.610	184.920	329.389
W04	0.110	39.114	114.701	534.336	1502.410	101.360	242.788
SPR04	0.077	14.298	208.627	470.031	413.852	166.707	153.929
S04	0.052	468.055	43.885	286.287	575.817	433.510	394.716

Table 3.7 Beaver Branch Distribution Statistics for Nitrogen species

	Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/season					
Total	0.755	1497.356	792.542	7952.053	5612.437	1742.739	2120.873
Mean	0.084	166.373	88.060	883.561	623.604	193.638	235.653
Min	0.004	0	0	1.388	0	18.573	16.058
Max	0.170	760.093	208.627	4900.247	1502.410	433.510	398.938
Min Pos	0.004	0.737	13.270	1.388	0.818	18.573	16.058

The largest loads at Beaver Branch for the particulate fraction for orthophosphate (OP P) occurred in F03: 84.71 kg/season (Figure 3.6, Table 3.8). This load was approximately two and one-half the mean value of 31.88 kg/season (Table 3.9). The lowest load occurred in S02 and W04: 2.46 and 8.62 kg/season respectively. These values were significantly lower than the mean value. The largest load of the dissolved fraction of orthophosphate (OP D) occurred in S03: 81.48 kg/season (Figure 3.6, Table 3.8). The lowest loads occurred in S02, W04, and SPR04: 1.63, 3.73, and 2.8 kg/season respectively. These values were less than a third of mean value of 17.71 kg/season (Table 3.9).

The largest load for the particulate fraction for total phosphate (TP P) occurred in F03: 161.66 kg/season (Figure 3.6, Table 3.8). This load was approximately two and one-half greater than the mean value of 64.07 kg/season (Table 3.9). The lowest loads occurred in S02: 3.08 kg/season. This value was significantly lower than the mean. The largest loads of the dissolved fraction of total phosphate (TP D) occurred in S03 and SPR04: 80.95 and 77.38 kg/season respectively (Figure 3.6, Table 3.8). The lowest loads occurred in S02 and W04: 0.26 and 4.22 kg/season respectively. These values were significantly less than the mean value of 32.10 kg/season (Table 3.9).

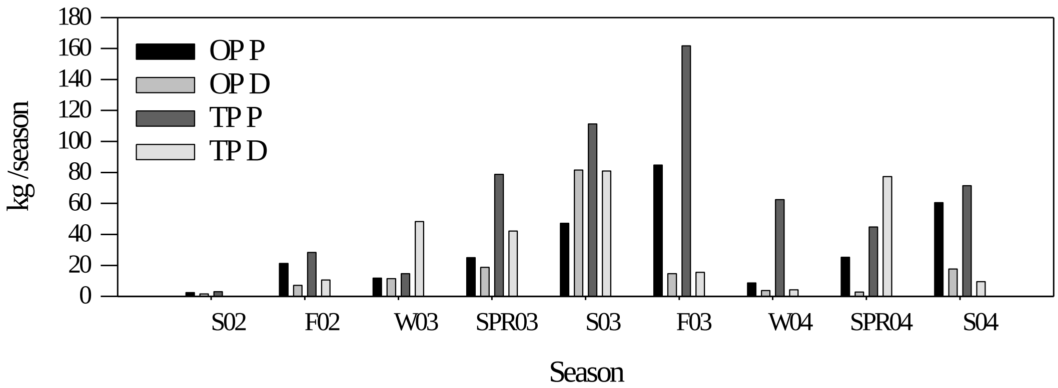


Figure 3.6. Beaver Branch Seasonal Data for Phosphate Species

The largest loads for the silicate occurred in SPR03, S03, and W04: 4,732.5, 4,648.9, and 4,561.6 kg/season respectfully (Figure 3.6, Table 3.8). These loads were approximately one and one-half greater than the mean value of 2,934.97 kg/season (Table 3.9). The lowest load occurred in S02: 2,637.4 kg/season.

The largest loads for total suspended solids occurred in W03 and F03: 32,723.4 and 32,085.2 kg/season respectfully (Figure 3.6, Table 3.8). This load was approximately one and one-half times the mean: 20,339.13 kg/season (Table 3.9). The lowest load occurred in S02: 2,637.4 kg/season. This value was significantly less than the mean value. The largest load of total dissolved solids occurred in F02: 542,270.1 kg/season (Figure 3.6, Table 3.8). The lowest loads occurred in S02: 50,727.3 kg/season. This value was less than 25% the mean value of 189,917 kg/season (Table 3.9).

Table 3.8. Beaver Branch Seasonal Load for Phosphates, Silicate, and Solids

Season	Ave Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg/season						
S02	0.004	2.46	1.63	3.08	0.26	70.6	2637.4	50727.3
F02	0.037	21.30	7.13	28.32	10.62	1223.9	25570.6	542270.1
W03	0.117	11.77	11.50	14.64	48.31	3230.4	32723.0	181977.0
SPR03	0.170	25.05	18.79	78.80	42.16	4732.5	18976.2	120428.8
S03	0.110	47.24	81.48	111.32	80.95	4648.9	20465.0	206827.6
F03	0.079	84.71	14.72	161.66	15.50	3585.3	32085.2	200362.2
W04	0.110	8.62	3.73	62.47	4.22	4561.6	7683.5	80568.7
SPR04	0.077	25.28	2.80	44.84	77.38	2669.7	23941.9	170602.5
S04	0.052	60.49	17.66	71.50	9.53	1691.9	18969.5	155488.7

Table 3.9. Beaver Branch Distribution Statistics for Phosphates, Silicate, and Solids

	Flow	OP P	OP D	TP P	TP D	Silicates	TSS	TDS
	m^3/s	kg/season						
Total	0.755	286.92	159.43	576.64	288.92	26414.77	183052.20	1709253.01
Mean	0.084	31.9	17.7	64.1	32.1	2934.97	20339.13	189917.00
Min	0.004	2.5	1.6	3.1	0.265	70.62	2637.40	50727.32
Max	0.170	84.7	81.5	161.7	80.9	4732.48	32722.99	542270.10
Min Pos	0.004	2.5	1.6	3.1	0.265	70.62	2637.40	50727.32

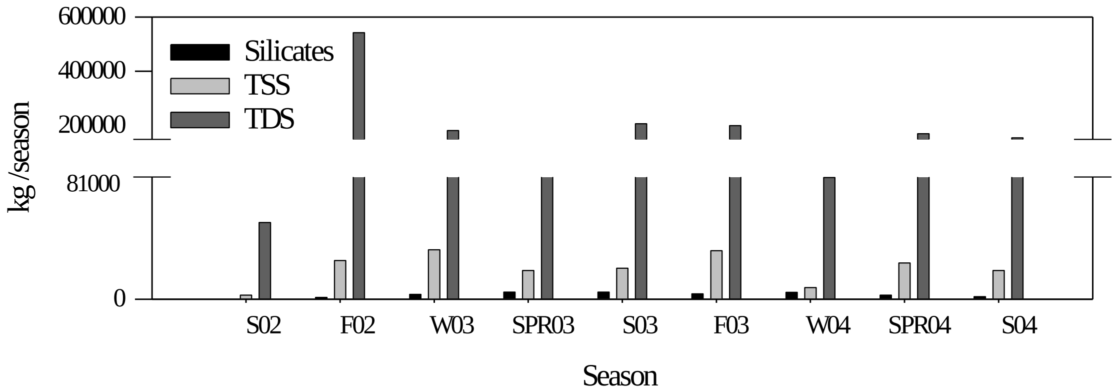


Figure 3.7. Beaver Branch Seasonal Data for Silicates, Total Suspended and Dissolved Solids

Blackbird Creek

The largest loads for the particulate fraction for ammonia-nitrogen (NH4-N P) occurred in SPR03 and S03: 1,417.18 and 1,394.75 kg/season respectfully (Figure 3.8, Table 3.10). The lowest loads occurred in S02, F02, and SPR04: 0, 0, and 12.79 kg/season respectfully. These values were significantly less than the mean value 487.39 kg/season. The largest load for the dissolved fraction for ammonia-nitrogen (NH4-N D) occurred in SPR03: 2,901.64 kg/season (Figure 3.8., Table 3.10.). The lowest loads occurred in S02, F02, and W03: 0, 23.53, and 0 kg/season respectfully. These values were significantly lower than the mean value of 643.29 kg/season (Table 3.11).

The largest load for the particulate fraction for nitrate-nitrogen (NO3-N P) occurred in SPR03: 22,645.67 kg/season (Figure 3.8, Table 3.10). This load was greater than five times the mean of 4,353.45 kg/season (Table 3.11). The lowest loads occurred in S02: 19.82 kg/season. This value was a fraction of the mean value. The largest loads for the dissolved fraction for nitrate-nitrogen (NO3-N D) occurred in W04: 16,203.71 kg/season (Figure 3.8, Table 3.10). The lowest loads occurred in S02 and F02: 14.29 and 54.87 kg/season respectfully.

The largest load for the particulate fraction for organic nitrogen (Norg P) occurred in SPR04: 4305.01 kg/season (Figure 3.8, Table 3.10). This load was approximately two times the mean 2,195.18 kg/season (Table 3.11). The lowest loads occurred in S02: 28.88 kg/season. This value was a fraction of the mean value. The largest loads for the dissolved fraction for organic nitrogen (Norg D) occurred in W04: 6,264.98 kg/season (Figure 3.8, Table 3.10). The lowest load occurred in S02 and W03: 38.03 and 0 kg/season respectively.

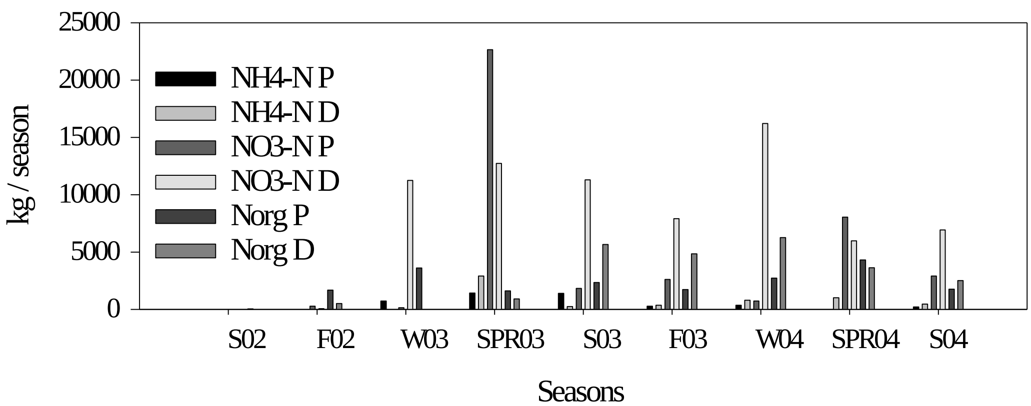


Figure 3.8. Blackbird Creek Seasonal Data for Nitrogen Species.

The largest loads at Blackbird Creek for the particulate fraction for orthophosphate (OP P) occurred in W03: 549.5 kg/season (Figure 3.9, Table 3.12). This load was approximately two times the mean value of 266.78 kg/season (Table 3.13). The lowest load occurred in S02 and F02: 10.76 and 75.28 kg/season respectfully. These values were significantly lower than the mean value. The largest load of the dissolved fraction of orthophosphate (OP D) occurred in S03: 586.42 kg/season (Figure 3.9, Table 3.12). The lowest load occurred in S02: 3.18 kg/season. This value was less than the mean value of 184.16 kg/season (Table 3.13).

Table 3.10. Blackbird Creek Seasonal Load Data for Nitrogen Species

Season	Ave Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Org –N P	Org-N D
	m^3/s	kg/season					
S02	0.040	0	0	19.82	14.29	28.88	38.03
F02	0.400	0	23.53	273.44	54.87	1676.03	506.39
W03	1.249	723.06	0	147.76	11243.75	3600.43	0
SPR03	1.814	1417.18	2901.64	22645.67	12731.91	1605.16	903.01
S03	1.175	1394.75	233.67	1818.44	11291.51	2337.97	5664.82
F03	0.841	270.72	361.89	2611.01	7903.08	1721.02	4834.49
W04	1.178	359.42	788.23	718.61	16203.71	2730.64	6264.98
SPR04	0.824	12.79	1016.56	8040.01	5971.89	4305.01	3621.96
S04	0.559	208.63	464.12	2906.32	6925.94	1751.49	2513.89

Table 3.11. Blackbird Creek Distribution Statistics for Nitrogen species

	Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/season					
Total	8.081	4386.555	5789.645	39181.072	72340.947	19756.632	24347.573
Mean	0.898	487.395	643.294	4353.452	8037.883	2195.181	2705.286
Min	0.040	0.000	0.000	19.818	14.287	28.878	0.000
Max	1.814	1417.179	2901.642	22645.670	16203.705	4305.012	6264.980
Min Pos	0.040	12.793	23.533	19.818	14.287	28.878	38.025

The largest load for the particulate fraction for total phosphate (TP P) occurred in SPR03: 16,762.20 kg/season (Figure 3.9, Table 3.12). This load was approximately two times greater than the mean value of 814.84 kg/season (Table 3.13). The lowest load occurred in S02: 12.46 kg/season. This value was significantly lower than the mean. The largest loads of the dissolved fraction of total phosphate (TP D) occurred in S03: 1,248.49 kg/season (Figure 3.9, Table 3.12). The lowest loads occurred in S02 and W04: 0 and 70.84 kg/season. These values were significantly less than the mean value of 345.56 kg/season (Table 3.13).

At Blackbird Creek, the largest loads for the silicate occurred in SPR03: 39,276.37 kg/season (Figure 3.10, Table 3.12). The lowest load occurred in S02: 267.44 kg/season and was significantly less than the mean value of 29,823.80 (Table 3.13).

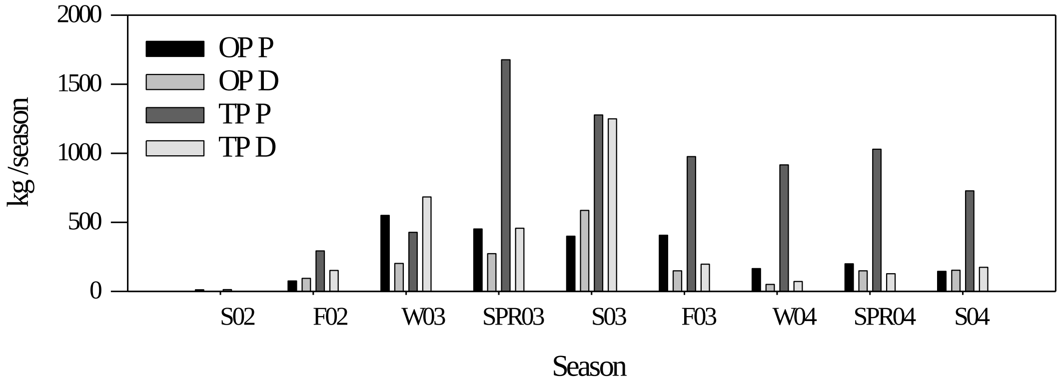


Figure 3.9. Blackbird Creek Seasonal Data for Phosphate Species.

Table 3.12. Blackbird Creek Seasonal Load Data for Phosphates, Silicate, and Total Suspended Solids and Total Dissolved Solids

Season	Ave Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg/season						
S02	0.040	10.76	3.18	12.46	0.00	267.44	9756.8	535839.0
F02	0.400	75.28	94.41	292.52	151.64	14406.22	267878.9	6273401.4
W03	1.249	549.50	202.14	427.54	683.77	51837.08	551370.3	1997161.4
SPR03	1.814	451.57	272.11	1676.20	457.00	39276.37	613347.2	1733051.8
S03	1.175	399.01	586.42	1277.12	1248.49	36022.08	475316.5	2281119.6
F02	0.841	405.85	148.47	975.44	196.18	39282.05	320647.5	1980344.5
W04	1.178	164.06	49.36	915.91	70.84	42613.22	150959.3	3285533.3
SPR04	0.824	199.78	148.82	1028.53	127.98	20519.29	291861.5	1434577.1
S04	0.559	145.24	152.54	727.82	174.13	24190.46	161658.8	1008548.5

Table 3.13. Blackbird Creek Distribution Statistics for Phosphates, Silicate, and Solids

	Flow	OP P	OP D	TP P	TP D	Silicates	TSS	TDS
	m^3/s	kg/season						
Total	8.081	2401.04	1657.46	7333.55	3110.02	268414.20	2842796.9	20529576.5
Mean	0.898	266.782	184.16	814.84	345.56	29823.80	315866.33	2281064.05
Min	0.040	10.759	3.180	12.457	0.000	267.44	9756.78	535839.02
Max	1.814	549.503	586.419	1676.20	1248.49	51837.08	613347.22	6273401.43
Min Pos	0.040	10.759	3.180	12.457	70.836	267.44	9756.78	535839.02

The largest loads for total suspended solids occurred in SPR03: 613,347.2 kg/season (Figure 3.10, Table 3.12). This load was approximately two times the mean of 315,866 kg/season (Table 3.13). The lowest load occurred in S02: 9,756.8 kg/season. This value was significantly less than the mean value. The largest load of total dissolved solids occurred in F02: 6,273,401.4 kg/season (Figure 3.10, Table 3.12). The lowest loads occurred in S02: 535,839.0 kg/season. This value was significantly less than the mean value of 2,281,064 kg/season (Table 3.13).

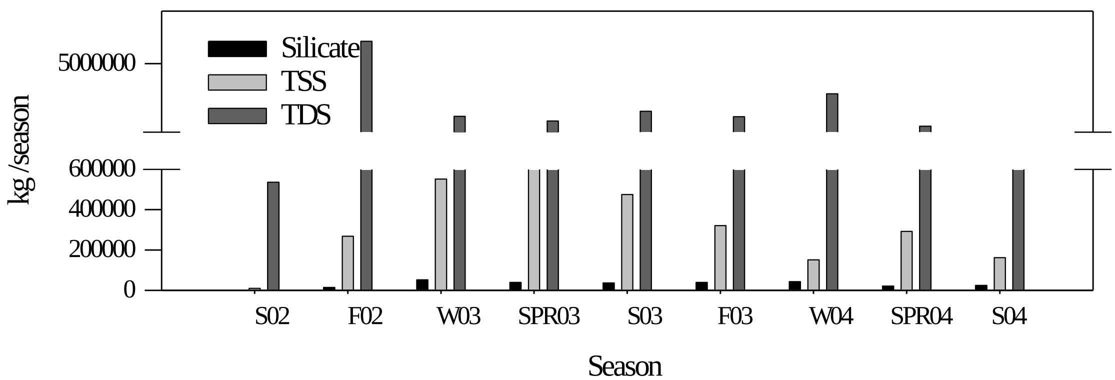


Figure 3.10. Blackbird Creek Seasonal Data for Silicates, Total Suspended and Dissolved Solids.

Annual

Analysis of data is in two periods: Year 1 and Year 2. Year 1 is the period from the summer of 2002 through the winter 2003. Year 2 covers the summer of 2003 through the winter of 2004. The data for the summer of 2004 was omitted.

Precipitation

Year 1 includes data from a one hundred year drought. Year 2 includes the winter of 2004 that showed record low precipitation. Data for year 1 shows an annual average precipitation rate of 2.83 mm/day. In comparison, Year 2 had an annual average of 3.26 mm/day (Table 3.14). This shows an approximate 13 % increase in precipitation in the second year.

Table 3.14. Annual Precipitation Rate

	Precipitation	Difference
	mm/day	%
Year 1	2.83	
Year 2	3.26	+13%

Hangman's Run

The load for the particulate fraction of ammonia nitrogen (NH4-N P) in Year 2 was 72.51 kg/yr; this was 38% of the load in Year 1 (Figure 3.11., Table 3.15). The load for the dissolved fraction of ammonia nitrogen (NH4-N D) in Year 1 was 46% of the 319.27 kg load in Year 2 (Figure 3.11., Table 3.15).

The 1076.37 kg/yr load for the particulate fraction of nitrate nitrogen (NO3-N P) in Year 2 was approximately 79% of the 1353.45 kg load in Year 1. The loads for the dissolved fraction of nitrate nitrogen (NO3-N D) 2942.99 kg/yr in year 1 and the 2678.18 kg/yr in year two were comparable. The load for the particulate fraction of organic nitrogen (Norg N P) in Year 2 was approximately 63% of the Year 1load. The dissolved fraction of organic-nitrogen (Norg-N D) in Year 1 was approximately 42% of the 613.71 kg/yr in Year 1.

The loads for Year 1 for both fractions of orthophosphate (OP P & OP D) were approximately 53% and 51% respectively of the Year 2 load (Figure 3.12., Table 3.16). The particulate fraction of total phosphates (TP P) in Year 1 was approximately 60% of the load in Year 2. The 27.66 kg/y load of the dissolved fraction of total phosphate (TP D) was 31% of the Year 2 load of 90.19 kg/yr (Figure 3.12, Table 3.16).

Table 3.15. Hangman's Run Annual Average Load for Nitrogen Species

Year	Ave Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/yr					
Year 1	0.325	188.27	149.31	1353.45	2942.99	461.08	259.93
Year 2	0.362	72.51	319.27	1076.37	2678.18	292.30	613.71

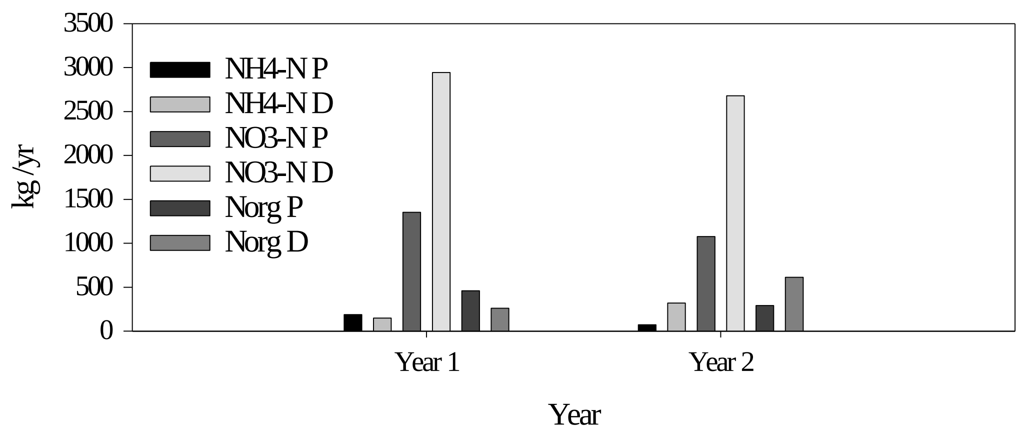


Figure 3.11. Hangman's Run Annual Data for Nitrogen Species.

The load for silicate in Year 1 was 44% of the load in Year 2 (Figure 3.13., Table 3.16). Total suspended solids (TSS) in Year 2 were approximately 33% of the load shown in Year 1. The load for total dissolved solids (TDS) in Year 2 was approximately 25% higher than the load in Year 1.

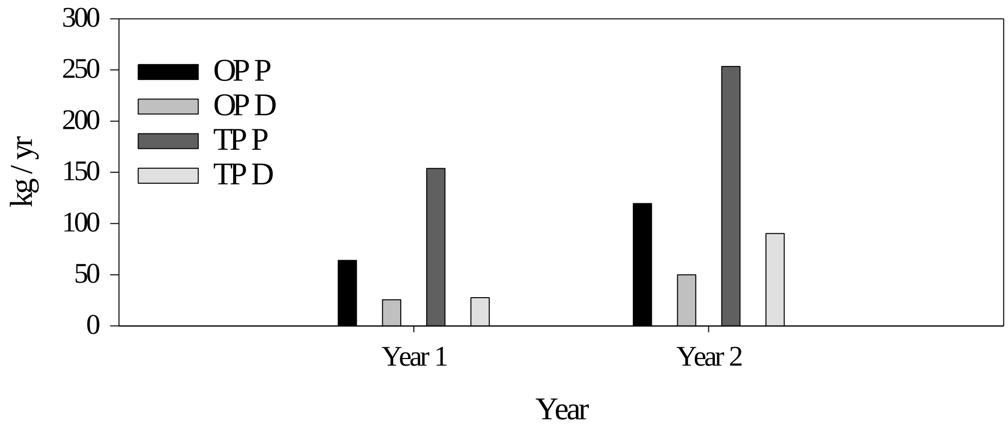


Figure 3.12. Hangman's Run Annual Data for Phosphate Species.

Table 3.16. Hangman's Run Annual Average Load for Phosphates, Silicate, and Solids

Year	Ave Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg/yr						
Year 1	0.325	64.05	25.56	153.82	27.66	4664.08	109292.42	202372.77
Year 2	0.362	119.60	49.86	253.37	90.19	10514.07	36144.53	263709.08

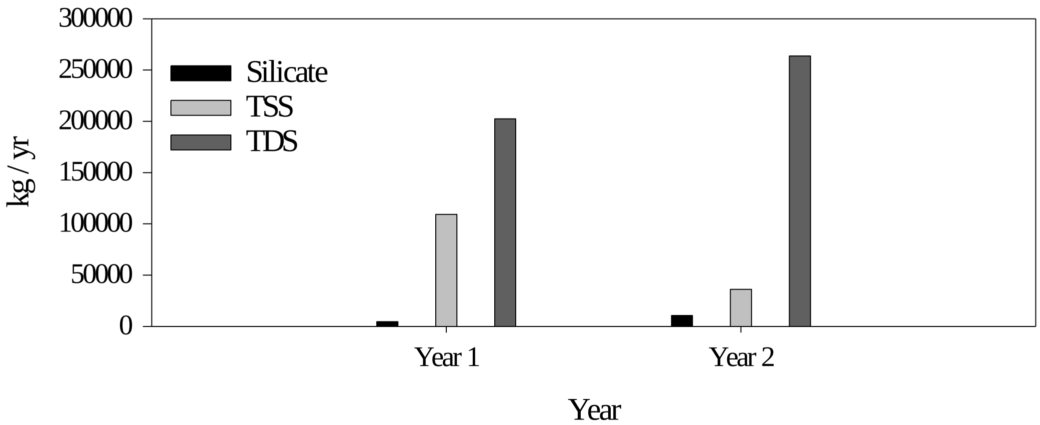


Figure 3.13. Hangman's Run Annual Data for Silicate, Total Suspended, and Dissolved Solids.

Beaver Branch

The load for the particulate fraction of ammonia nitrogen (NH4-N P) in Year 1 was 133.31 kg/yr; this was 15% of the load in Year 2 (Figure 3.14., Table 3.17). The load for the dissolved fraction of ammonia nitrogen (NH4-N D) in Year 1 was 22% of the 613.71 kg/yr load in Year 2 (Figure 3.14., Table 3.17).

The 1392.63 kg/yr load for the particulate fraction of nitrate nitrogen (NO3-N P) in Year 1 was approximately 22% of the 6273.14 kg load in Year 2. The load for the dissolved fraction of nitrate nitrogen (NO3-N D) 1981.56 kg/yr in Year 1 was 64% of the load in Year 2. The load for the particulate fraction of organic nitrogen (Norg N P) in Year 2 was approximately 60% of the Year 1 load. The dissolved fraction of organic-nitrogen (Norg-N D) in Year 1 was approximately 72% of the load in Year 2.

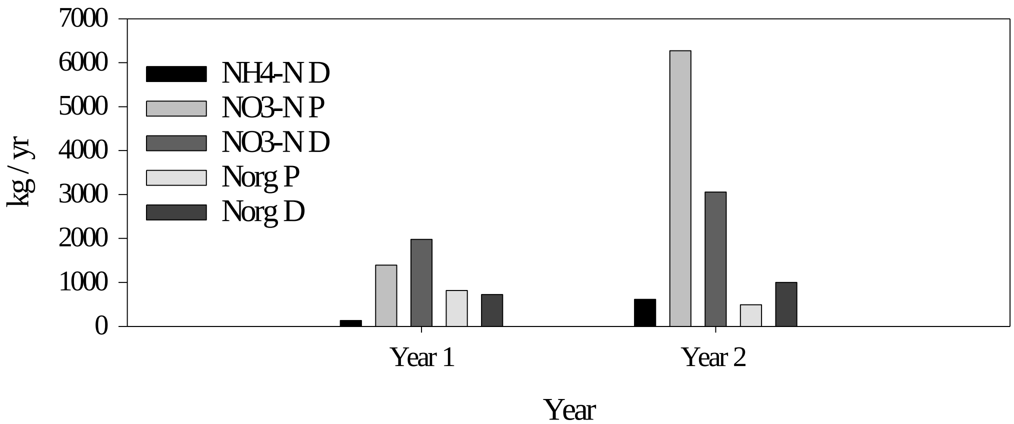


Figure 3.14. Beaver Branch Annual Data for Nitrogen Species.

Table 3.17. Beaver Branch Annual Average Load for Nitrogen Species

Year	Ave Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/yr					
Year 1	0.082	133.31	134.95	1392.63	1981.56	817.25	725.99
Year 2	0.094	895.99	613.71	6273.14	3055.06	491.98	1000.17

The load at Beaver Branch for Year 1 for particulate fraction of orthophosphate (OP P) was approximately 36% of the 165.9 kg/yr load of Year 2. The dissolved fraction of orthophosphate load of 39.00 kg/yr was approximately 38% of the Year 2 load (Figure 3.15., Table 3.18). The particulate fraction of total phosphates (TP P) in Year 1 was approximately 32% of the load in Year 2. The 101.4 kg/yr load in Year 1 for the dissolved fraction of total phosphate (TP D) was 56% of the Year 2 load of 178.0 kg/yr in Year 2 (Figure 3.15, Table 3.18).

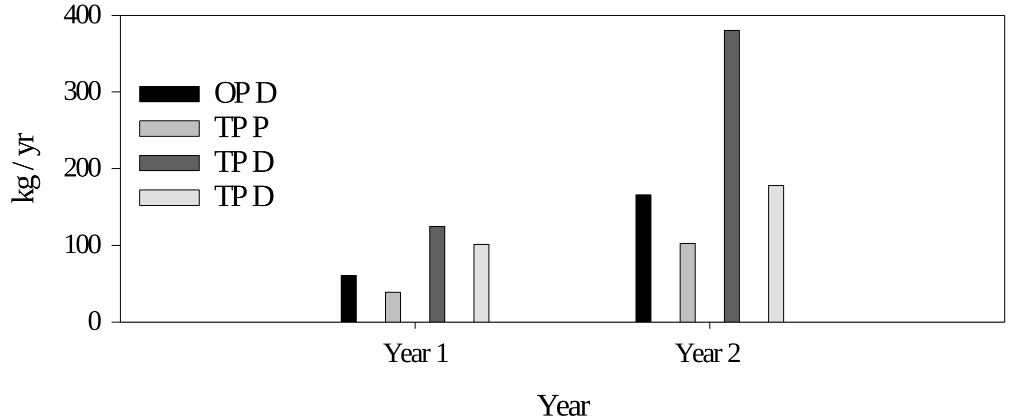


Figure 3.15. Beaver Branch Annual Data for Phosphate Species.

Table 3.18. Beaver Branch Annual Average Load for Phosphates, Silicate, and Solids

Year	Ave Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg / yr						
Year 1	0.082	60.6	39.0	124.8	101.4	9257.4	79907.1	895403.2
Year 2	0.094	165.9	102.7	380.3	178.0	15465.5	84175.5	658361.1

The load for silicate in Year 1 was approximately 60% of the load in Year 2 (Figure 3.16., Table 3.18). Total suspended solids (TSS) in Year 1were comparable to the load shown in Year 2. The load for total dissolved solids (TDS) in Year 1 was approximately 72% of the load in Year 2 (Figure 3.16., Table 3.18).

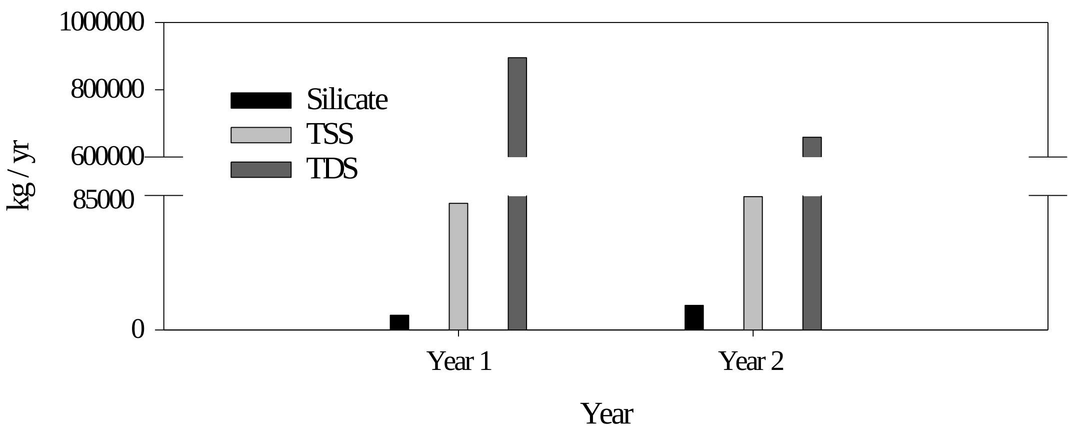


Figure 3.16. Beaver Branch Annual Data for Silicate, Total Suspended and Dissolved Solids.

Blackbird Creek

The load for the particulate fraction of ammonia nitrogen (NH4-N P) in Year 1 and Year 2 were comparable (Figure 3.16., Table 3.19). The load for the dissolved fraction of ammonia nitrogen (NH4-N D) in Year 2 was 82% of the 2400.35 kg/yr load in Year 2 (Figure 3.16., Table 3.19).

The 13,188.07 kg/yr load for the particulate fraction of nitrate nitrogen (NO3-N P) in Year 2 was approximately 57% of the load in Year 1 (Figure 3.16., Table 3.19). The load for the dissolved fraction of nitrate nitrogen (NO3-N D) of 24,044.82 kg/yr in Year 1 was 58% of the load in Year 2. The load for the particulate fraction of organic nitrogen (Norg N P) in Year 1 was approximately 62% of the Year 2 load. The dissolved fraction of organic-nitrogen (Norg-N D) load of 1447.43 kg/yr in Year 1 was approximately 7% of the load shown in Year 2.

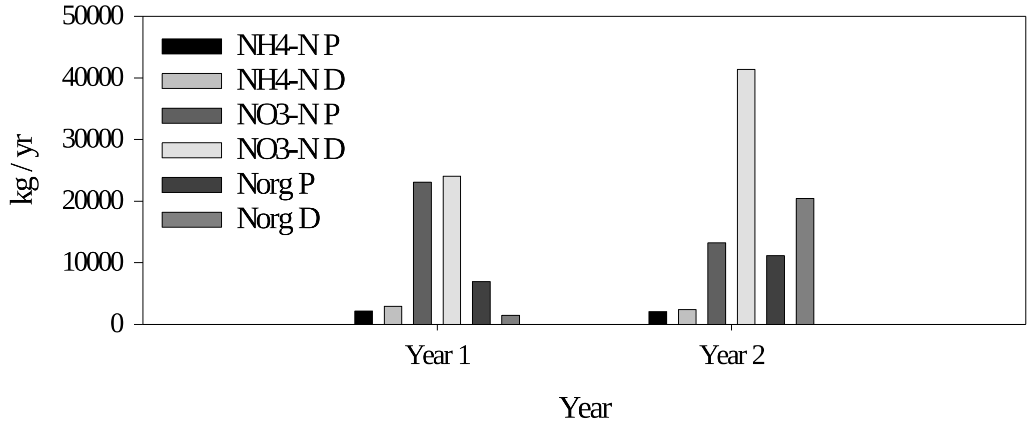


Figure 3.17. Blackbird Creek Annual Data for Nitrogen Species.

Table 3.19. Blackbird Creek Average Annual Load for Nitrogen Species

Year	Ave Flow	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Norg P	Norg D
	m^3/s	kg/yr					
Year 1	0.876	2140.24	2925.17	23086.68	24044.82	6910.50	1447.43
Year 2	1.005	2037.69	2400.35	13188.07	41370.19	11094.64	20386.25

The annual loads at Blackbird Creek for Years 1 and 2 for the particulate fraction of orthophosphate (OP P) were comparable (Figure 3.18., Table 3.20). The Year 1 load of the dissolved fraction of orthophosphate of 571.84 kg/yr was approximately 61% of the Year 2 load (Figure 3.18., Table 3.20). The particulate fraction of total phosphates

(TP P) in Year 1 was approximately 57% of the load in Year 2. The 1292.41 kg/yr load in Year 1 for the dissolved fraction of total phosphate (TP D) was approximately 78% of the Year 2 load of 1643.48 kg/yr in Year 2 (Figure 3.18, Table 3.20).

The load for silicate in Year 1 was approximately 76% of the load in Year 2 (Figure 3.19., Table 3.20). Total suspended solids (TSS) and total dissolved solids in Year 2 were approximately 85% of the load shown in Year 2 (Figure 3.19., Table 3.20)

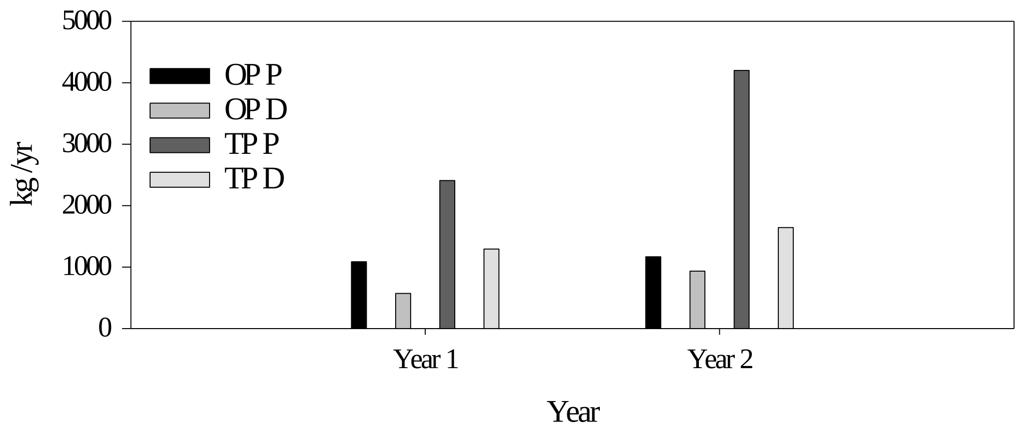


Figure 3.18. Blackbird Creek Annual Data for Phosphate Species.

Table 3.20. Blackbird Creek Average Annual Load for Phosphates, Silicate, and Solids

Year	Ave Flow	OP P	OP D	TP P	TP D	Silicate	TSS	TDS
	m^3/s	kg/yr						
Year 1	0.876	1087.11	571.84	2408.7	1292.4	105787.11	1442353.3	10539453.6
Year 2	1.005	1168.70	933.08	4197.0	1643.5	138436.63	1238784.9	8981574.4

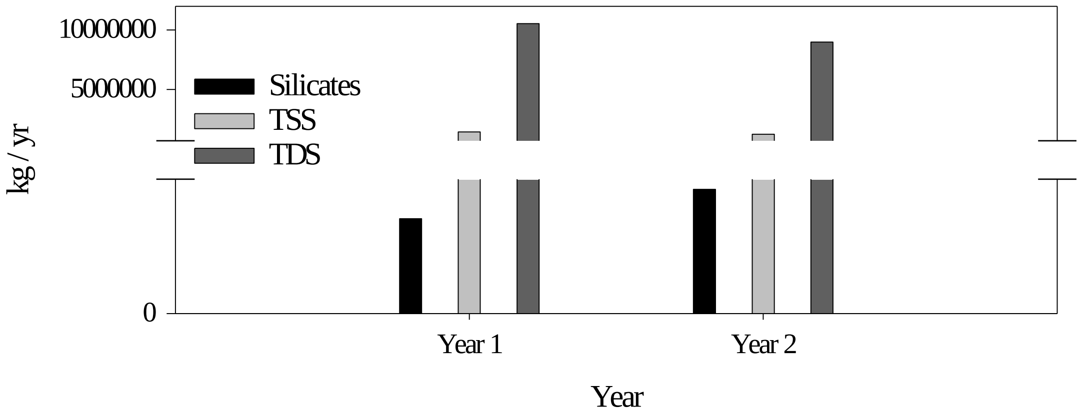


Figure 3.19. Blackbird Creek Annual Data for Silicate, Total Suspended and Dissolved Solids

Storms

During the study period, the ISCO samplers were deployed in the field twenty times. Seven deployments yielded no samples. In four of the failed deployments, either the storm missed the study site or the storm lacked the intensity to trip the samplers. Three events failed to retrieve samples due to equipment failure. Two deployments yielded samples from only one site and three deployments yielded samples from only two sites. Failure to retrieve samples for these deployments was attributed to equipment failure or vandalism. Two representative storms were selected here for discussion because of the completeness of data and the attributes of the precipitation event.

October 10, 2002 Storm

The storm on October 10, 2002 affected the entire Atlantic Seaboard. It resulted from a slow moving warm front that caused heavy rain starting at 18:00 hours

(NOAA, 2002). The storm reached the study site at approximately 21:45 hours and produced approximately 55 mm of precipitation before ending at approximately 13:30 hours on October 11, 2002. The samplers all tripped at approximately 22:15 hours; two and one half hours after the initial onset of rain and coincided with the low slack water before the flood tide (Figures 3.20, 3.21, and 3.22).

Hangman's Run is not under tidal influence. The highest volume of water in Hangman's Run occurred during the sampling of Composite C (Figure 3.20). Both Beaver Branch and Blackbird Creek sampling for Composites B and C occurred during a tidal cycle (Figures 3.21, and 3.22).

Hangman's Run. The particulate fraction of ammonia-nitrogen was absent in all Composites. The dissolved fraction of ammonia-nitrogen showed only in Composite A and was approximately four times the load found in the seasonal average (Figure 23, Table 21). The particulate fraction of nitrate-nitrogen was absent in Composite A. The load in Composite B was approximately 36% of the seasonal average and the load in Composite C was greater than double the seasonal load. The particulate and dissolved fractions of organic nitrogen in Composites B and C exceeded the seasonal averages. The particulate and dissolved fractions of orthophosphate showed loads in all three composites. The particulate fraction of total phosphate was shown in all three Composites and the dissolved fraction was not detected. The storm totals for silicate and total dissolved solids exceeded the seasonal average (Figure 3.23, Table 3.21).

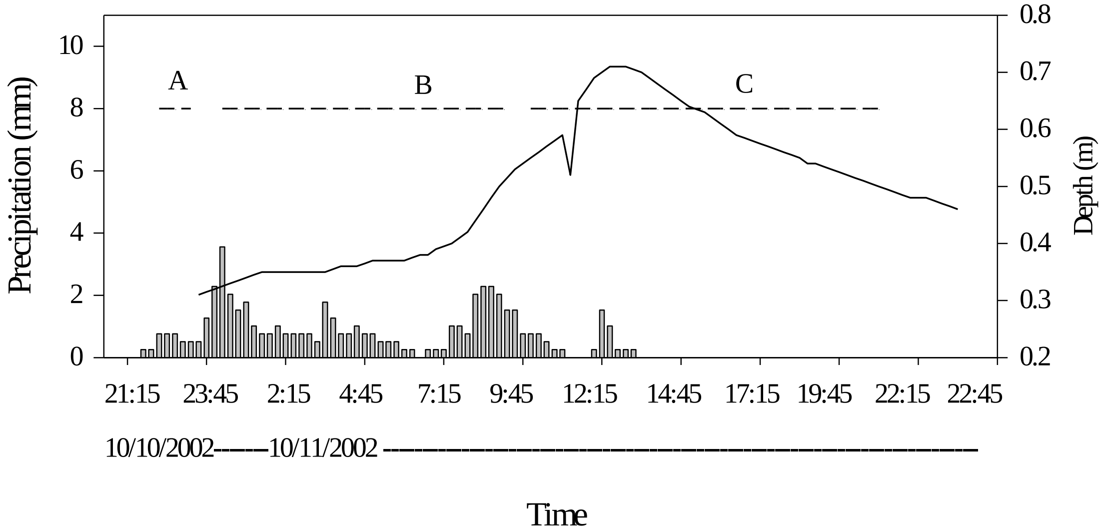


Figure 3.20. Hangman's Run for the storm beginning on October 10, 2002 at approximately 22:15 hours and ending on October 11, 2002 at 22:15 hours. The histogram represents precipitation. The solid line shows channel depth. The dashed line represents each composite time interval.

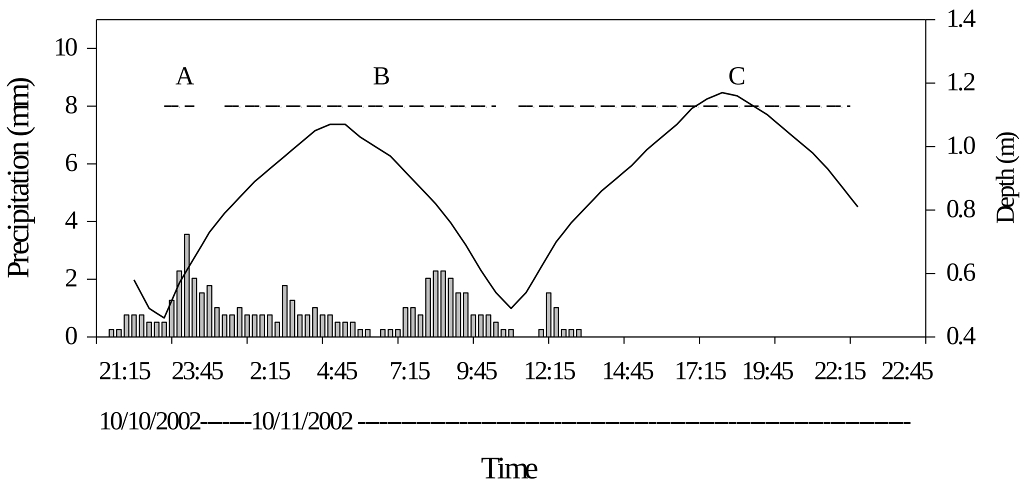


Figure 3.21. Beaver Branch for the storm beginning on October 10, 2002 at approximately 22:15 hours and ending on October 11, 2002 at 22:15 hours. The histogram represents precipitation. The solid line shows channel depth. The dashed line represents each composite time interval.

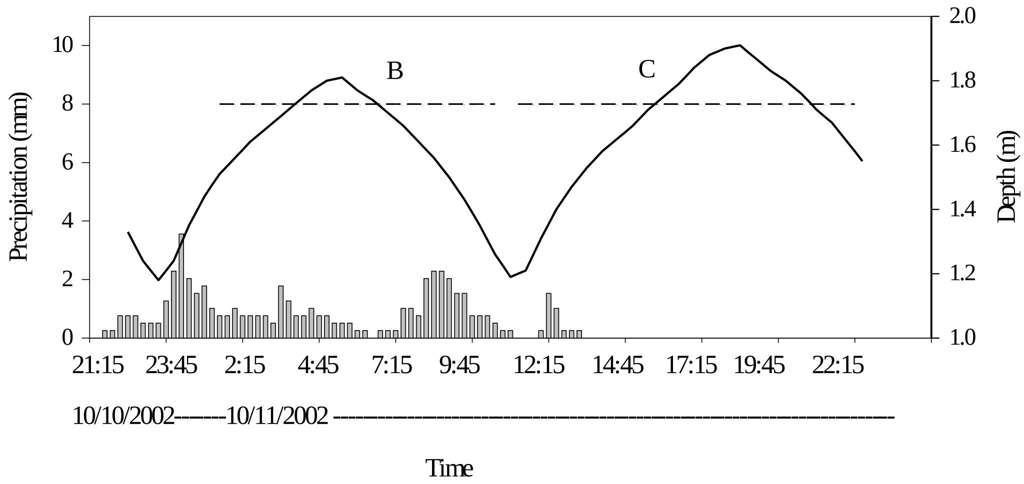
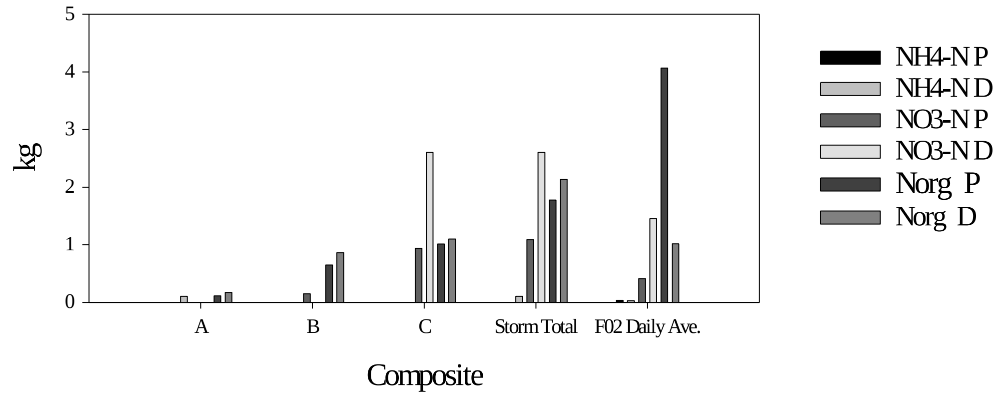
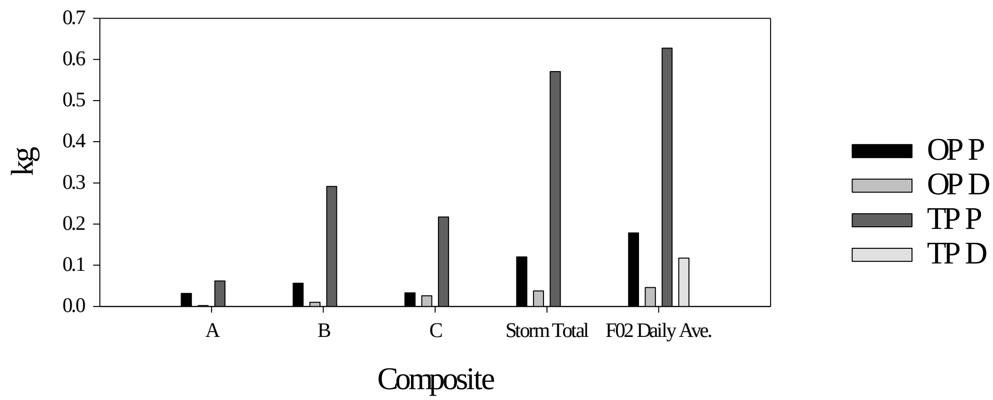


Figure 3.22. Blackbird Creek for the storm beginning on October 10, 2002 at approximately 22:15 hours and ending on October 11, 2002 at 22:15 hours. The histogram represents precipitation. The solid line shows channel depth. The dashed line represents each composite time interval.





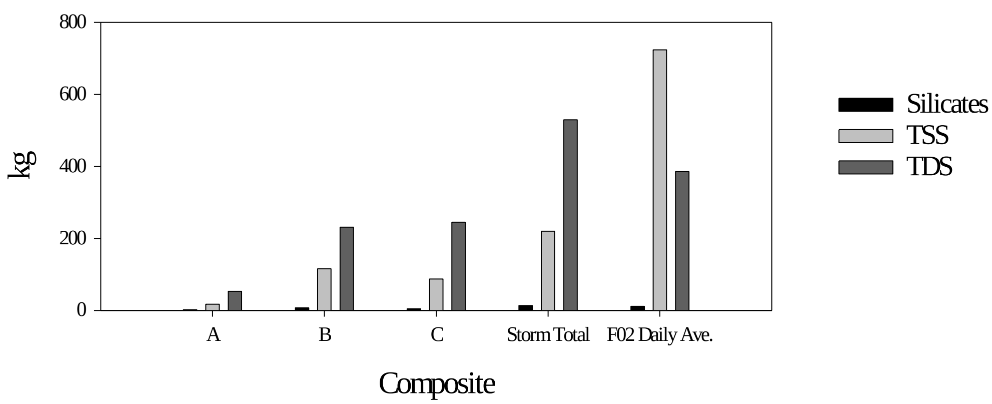


Figure 3.23. Hangman's Run data for October 10-11, 2002 and seasonal daily average load for fall 2002 (F02).

Table 3.21. Hangman's Run Storm Data for October 10-11, 2002 and seasonal daily average load for the fall of 2002 (F02)

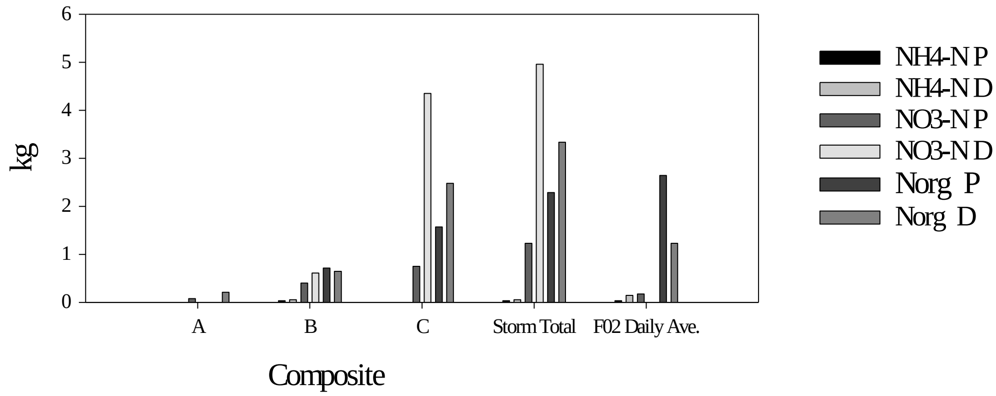
Load					
	kg / composite			kg / storm	kg / day
	A	Composite B	C	Storm Total	Seasonal Average
NH4-N P	0	0	0	0	0.034
NH4-N D	0.104	0	0	0.104	0.027
NO3-N P	0	0.150	0.937	1.087	0.410
NO3-N D	0	0	2.602	2.602	1.451
Norg P	0.112	0.649	1.013	1.774	0.178
Norg D	0.171	0.863	1.100	2.134	0.046
OP P	0.031	0.056	0.033	0.120	0.628
OP D	0.002	0.010	0.026	0.038	0.117
TP P	0.062	0.291	0.217	0.570	4.063
TP D	0	0	0	0	1.013
Silicate	2.07	7.29	4.28	13.64	11.67
TSS	17.43	115.38	87.16	219.96	723.45
TDS	53.12	231.17	244.86	529.16	385.34

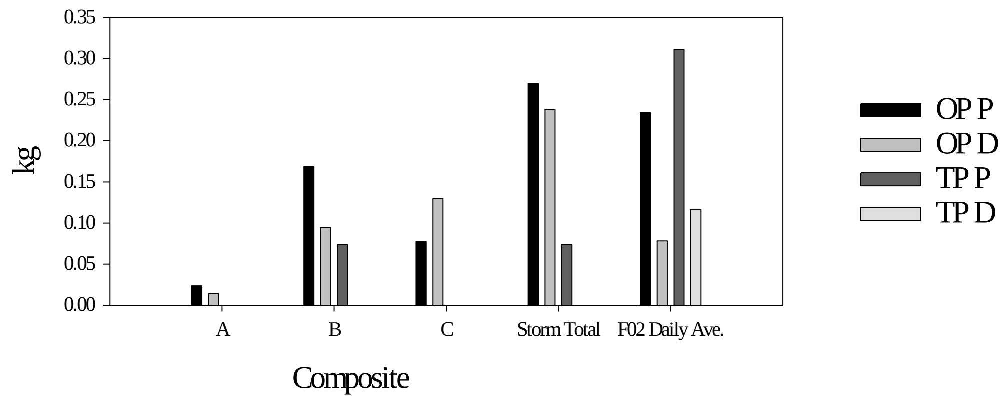
Beaver Branch. Composites A and C did not detect the particulate fraction of ammonia-nitrogen. Composite B showed a load comparable to the seasonal average. The particulate and dissolved fraction for nitrate-nitrogen exceeded the seasonal average in Composites B and C (Figure 3.24, Table 3.22). The storm total for the particulate fraction of organic nitrogen was comparable to the seasonal average. The dissolved fraction exceeded the seasonal average in Composite C (Figure 3.24, Table 3.22).

The storm total for the particulate fraction of orthophosphate exceeded the seasonal daily average. The dissolved fraction of orthophosphate exceeded the seasonal daily average in Composites B and C (Figure 3.24, Table 3.22). The storm total for suspended solids exceeded the seasonal daily average. Total dissolved solids exceeded the seasonal daily average in Composites B and C (Figure 3.24, Table 3.22).

Table 3.22. Beaver Branch Storm Data for October 10-11, 2002 and seasonal daily average load for the fall of 2002 (F02)

Load					
	kg/composite			kg/storm	kg/day
	A	Composite B	C	Storm Total	Seasonal Average
NH4-N P	0.000	0.034	0.000	0.034	0.032
NH4-N D	0.000	0.055	0.000	0.055	0.146
NO3-N P	0.079	0.401	0.749	1.229	0.173
NO3-N D	0.000	0.609	4.351	4.960	0.000
Norg P	0.000	0.716	1.569	2.285	2.641
Norg D	0.208	0.647	2.479	3.333	1.231
OP P	0.024	0.168	0.078	0.270	0.234
OP D	0.014	0.095	0.130	0.238	0.078
TP P	0.000	0.074	0.000	0.074	0.311
TP D	0.000	0.000	0.000	0.000	0.117
Silicate	1.26	6.23	3.03	10.53	13.45
TSS	17.27	158.36	255.74	431.37	281.00
TDS	2789.28	14303.08	1941.74	19034.10	5959.01





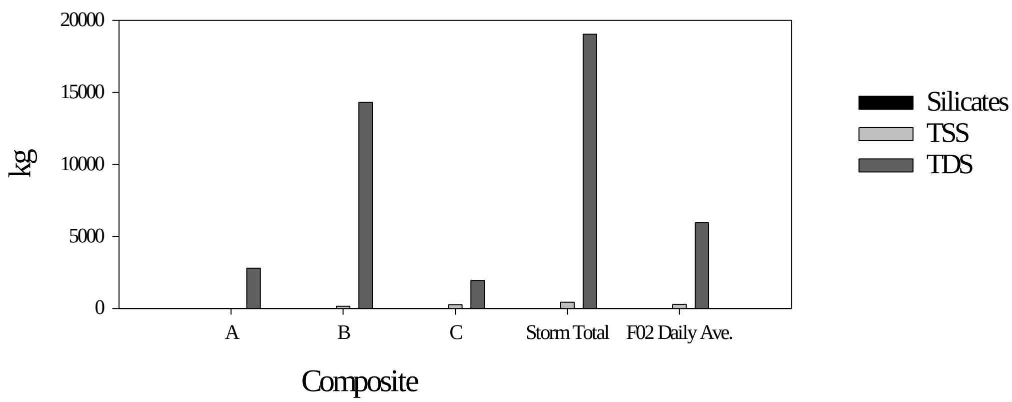
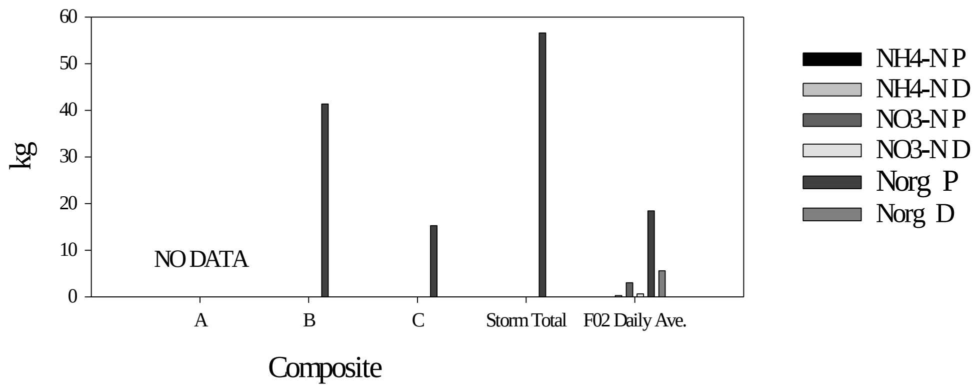
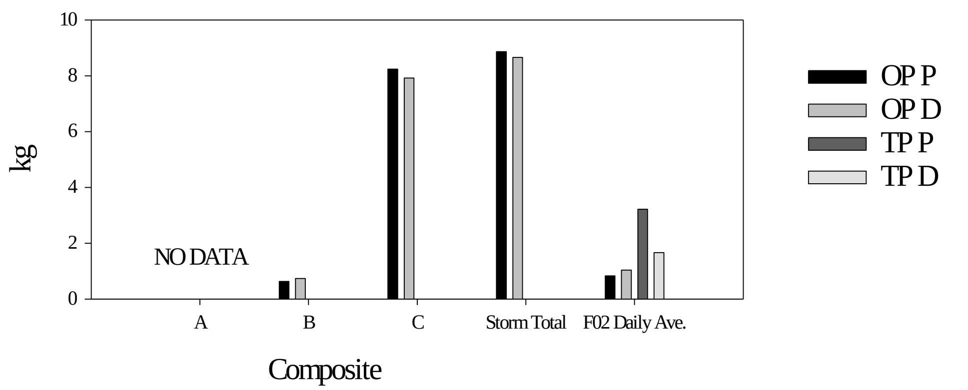


Figure 3.24. Beaver Branch data for October 10-11, 2002 and seasonal average daily load for fall 2002 (F02).

Blackbird Creek. No data is available for Composite A. Composites B and C did not detect loads for the particulate or dissolved fractions of ammonia-nitrogen, nitrate-nitrogen, and total phosphates (Figure 3.25, Table 3.23). The particulate fraction of organic nitrogen exceeded the seasonal daily average in Composites B and C. The dissolved fraction was non-detect. The particulate and dissolved fractions of orthophosphate exceeded the seasonal daily average in Composite C. The storm total exceeded the seasonal daily average for total suspended solids (Figure 3.25, Table 3.23)





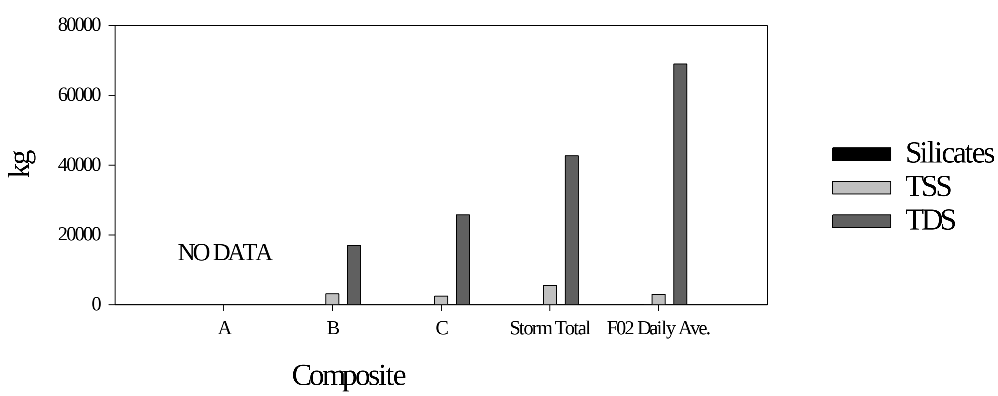


Figure 3.25. Blackbird Creek data for October 10-11, 2002 and seasonal average daily load for the fall of 2002 (F02).

Table 3.23. Blackbird Creek Storm Data for October 10-11, 2002 and seasonal daily average for F02

Load					
	kg/composite			kg/storm	kg/day
	A	Composite B	C	Storm Total	Seasonal Average
NH4-N P	No Data	0	0	0	0.000
NH4-N D	--	0	0	0	0.259
NO3-N P	--	0	0	0	3.005
NO3-N D	--	0	0	0	0.603
Norg P	--	41.325	15.263	56.589	18.418
Norg D	--	0	0	0	5.565
OP P	--	0.633	8.233	8.866	0.827
OP D	--	0.739	7.917	8.656	1.037
TP P	--	0	0	0	3.215
TP D	--	0	0	0	1.666
Silicate	--	46.37	54.47	100.83	158.31
TSS	--	3113.92	2470.03	5583.95	2943.72
TDS	--	16941.85	25713.61	42655.45	68938.48

July 9, 2003 Storm

A westerly high-pressure system moved across the study site at approximately 18:30 hours on the night of July 9, 2003 (NOAA/NWS/NCEP/HPC, 2003). The first hour of the event yielded approximately 0.5 mm of precipitation. Precipitation increased between 19:00 and 19:15 hours to 7.1 mm and an additional 8.4 mm from 19:15 to 19:30 hours. An average of 1.4 mm fell within each fifteen-minute interval until 20:45 hours. The amount of precipitation decreased to an average of 0.4 mm and the storm event ended at 21:45 hours (Figures 3.26, 3.27, and 3.28). Total precipitation from the event was 25 mm. The National Weather Service characterized the storm as a thunderstorm with high winds (NOAA, 2002). Sampling began approximately 2.5 hours after low slack tide on the incoming tide and one half hour after the onset of rain (Figures 3.26, 3.27, and 3.28).

Hangman's Run. The load in Composite A for particulate and dissolved fractions of ammonia-nitrogen and nitrate-nitrogen were non-detect (Figure 3.29, Table 3.24). Composites B and C for dissolved fraction of ammonia-nitrogen exceeded the seasonal daily average. The particulate fraction for nitrate-nitrogen was approximately double the seasonal daily average. The dissolved fraction was comparable to the seasonal daily average (Figure 3.29, Table 3.24). The dissolved and particulate fractions of organic nitrogen exceeded the seasonal daily average in Composites B and C. Composite C for the dissolved fraction of orthophosphate exceeded the seasonal daily average. The load for silicate in Composites B and C exceeded the seasonal daily average (Figure 3.29, Table 3.24).

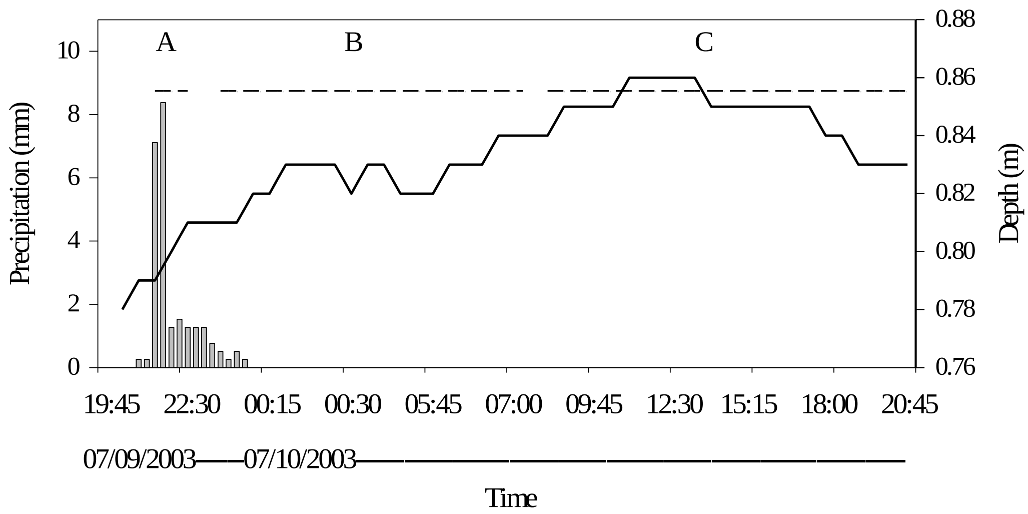


Figure 3.26. Hangman's Run storm beginning on July 9, 2003 at approximately 19:45 hours and ended on July 10, 2003. The histograms represent precipitation. The solid line shows channel depth. The dashed lines represent composite time interval.

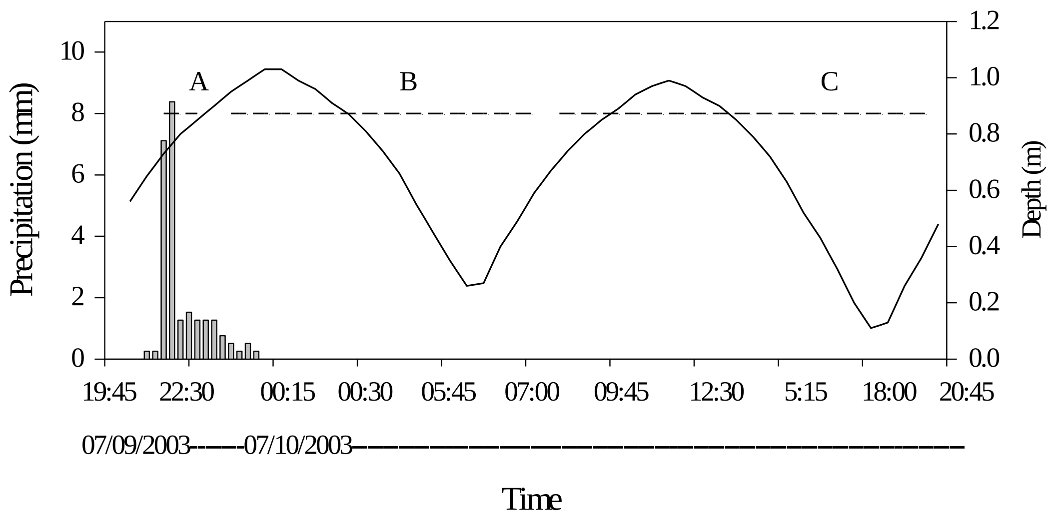


Figure 3.27. Beaver Branch storm beginning on July 9, 2003 at approximately 19:45 hours and ended on July 10, 2003. The histograms represent precipitation. The solid line shows channel depth. The dashed lines represent composite time interval.

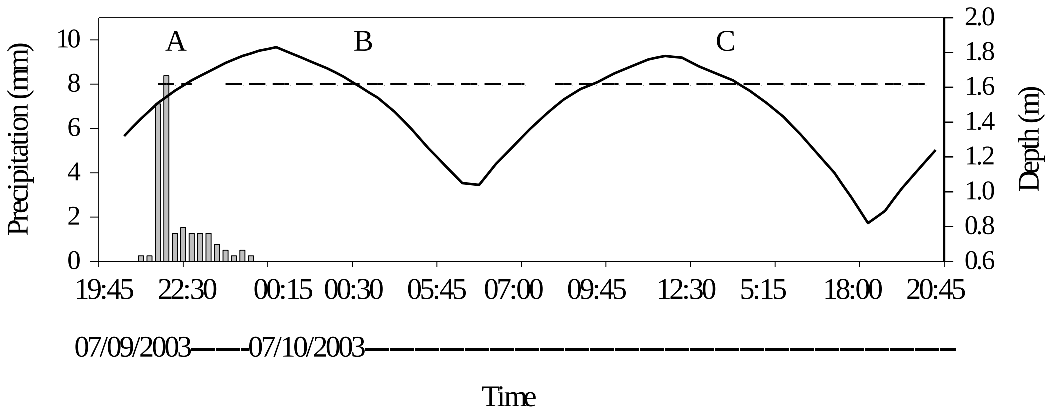


Figure 3.28. Blackbird Creek storm beginning on July 9, 2003 at approximately 19:45 hours and ended on July 10, 2003. The histograms represent precipitation. The solid line shows channel depth. The dashed lines represent composite time interval.

Table 3.24. Hangman's Run Storm Data for July 9-10, 2003 and seasonal daily average load for summer 2003 (S03)

Load					
	kg / composite			kg / storm	kg / day
	A	Composite B	C	Storm Total	Seasonal Average
NH4-N P	0	0.005	0.004	0.009	0.237
NH4-N D	0	1.096	1.316	2.412	0.000
NO3-N P	00	1.875	0.796	2.671	0.933
NO3-N D	0	0	1.848	1.848	1.521
Norg P	0.081	2.642	1.980	4.703	0.660
Norg D	0.132	2.478	2.578	5.188	1.168
OP P	0.018	0.340	0.197	0.555	0.631
OP D	0.021	0.334	0.408	0.763	0.327
TP P	0.047	0.197	0.342	0.587	0.817
TP D	0.013	0.110	0.309	0.432	0.518
Silicate	3.27	46.08	54.32	103.66	42.81
TSS	4.71	10.96	0	15.68	117.99
TDS	42.43	723.55	0	765.98	956.20

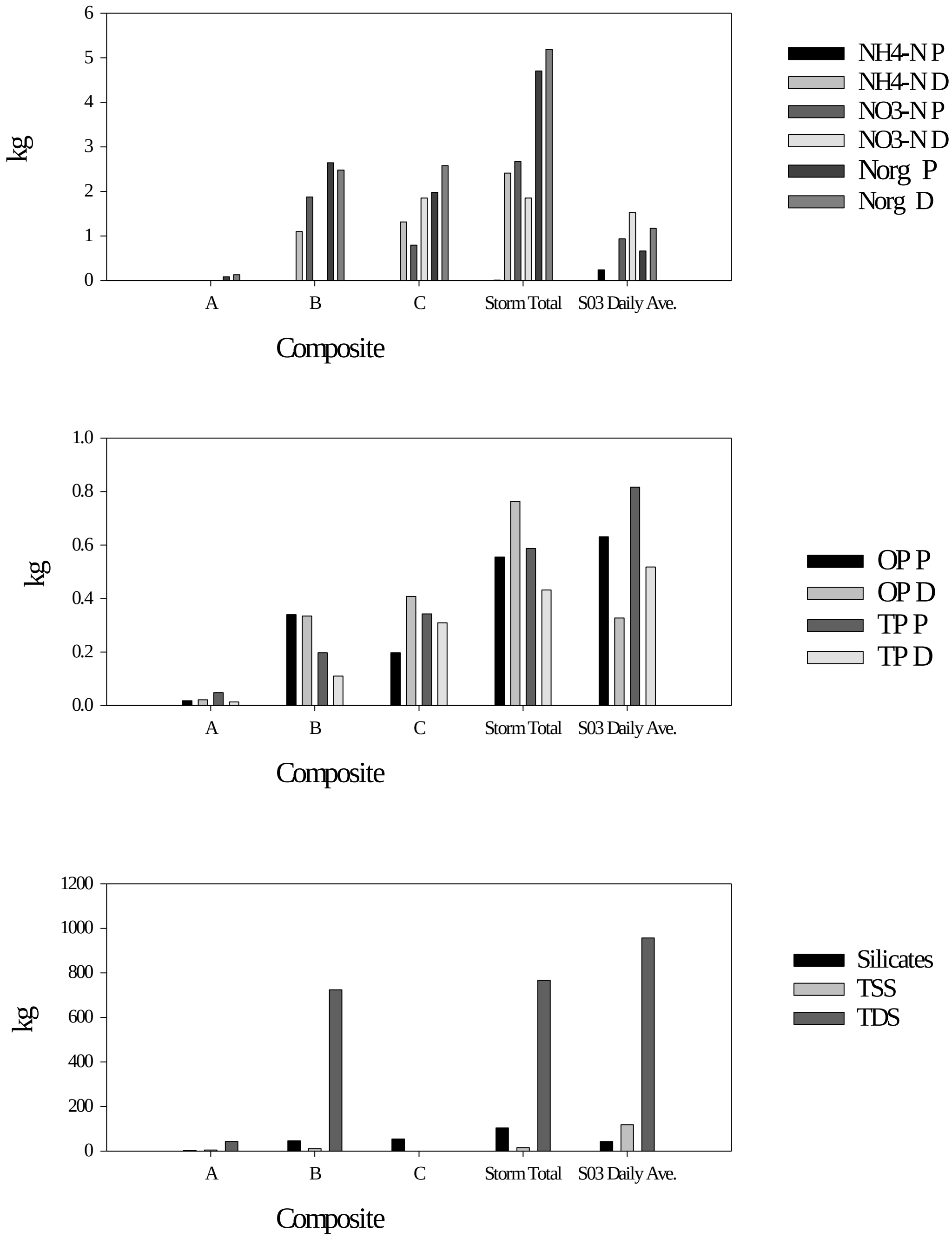


Figure 3.29. Hangman's Run Data for July 9-10, 2003 and seasonal daily average load for summer 2003 (S03).

Beaver Branch. Composites B and A for the load for the dissolved fraction of ammonia-nitrogen was approximately double the seasonal daily average (Figure 3.30, Table 3.19). The dissolved fraction for nitrate-nitrogen exceeded the seasonal daily average in all three Composites. Composite B for the particulate fraction of organic nitrogen exceeded the seasonal daily average. The dissolved fraction of organic nitrogen exceeded the daily seasonal average in Composites B and C (Figure 3.30, Table 3.19). The total storm load exceeded the seasonal daily average for the dissolved fraction of orthophosphate. Composite B for total suspended solids (TSS) and dissolved solids (TDS) exceeded the seasonal daily average (Figure 3.30, Table 3.19).

Blackbird Creek. All three Composites for the dissolved fraction of ammonia-nitrogen and the particulate fraction of nitrate-nitrogen exceeded the seasonal daily average with Composite C showing the highest load (Figure 3.31, Table 3.20). The total storm load for the dissolved fraction of nitrate-nitrogen and the particulate fraction of organic nitrogen exceeded the seasonal daily average. The storm total load for the dissolved fraction of orthophosphate and silicate was comparable to the seasonal daily average. Composite C for total suspended solids (TSS) was greater than the seasonal daily average. The storm total load for total dissolved solids was greater than the seasonal daily average (Figure 3.31, Table 3.20).

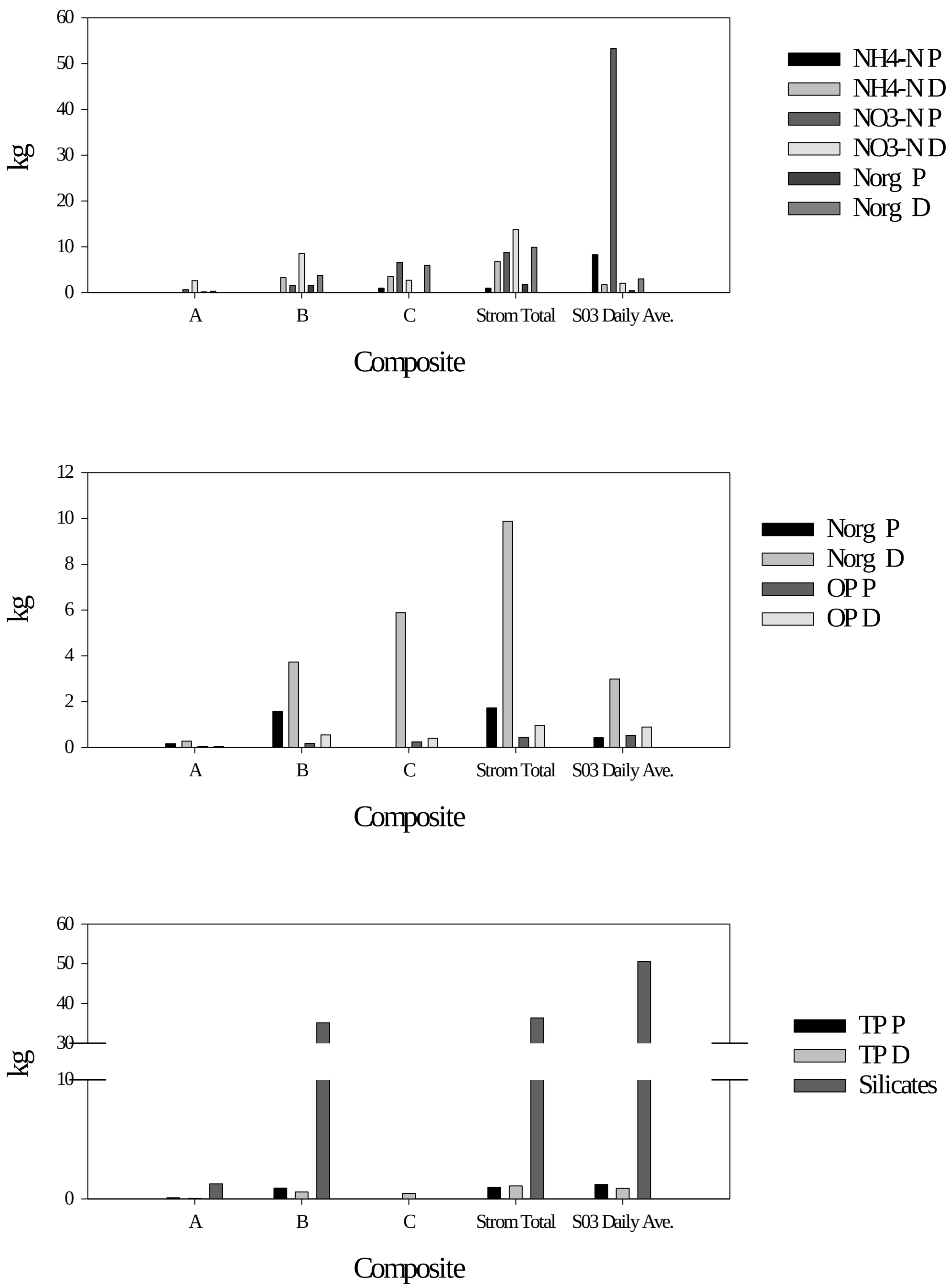


Figure 3.30. Beaver Branch Data for July 9-10, 2003 and seasonal daily average load for summer 2003 (S03).

Table 3.25. Beaver Branch storm data for July 9-10, 2003 and seasonal daily average load for summer 2003 (S03)

Load					
	kg / composite			kg / storm	kg / day
	A	Composite B	C	Storm Total	Seasonal Average
NH4-N P	0.000	0.000	0.941	0.941	8.262
NH4-N D	0.000	3.270	3.453	6.722	1.703
NO3-N P	0.603	1.570	6.591	8.764	53.264
NO3-N D	2.572	8.503	2.674	13.749	2.035
Norg P	0.156	1.570	0.000	1.727	0.424
Norg D	0.265	3.727	5.888	9.880	2.979
OP P	0.025	0.169	0.235	0.429	0.513
OP D	0.035	0.541	0.391	0.967	0.886
TP P	0.077	0.893	0.000	0.970	1.210
TP D	0.037	0.580	0.461	1.078	0.880
Silicate	1.25	35.09	0.00	36.34	50.53
TSS	22.41	234.56	156.38	413.35	222.45
TDS	192.92	2332.61	1501.21	4026.73	2248.13

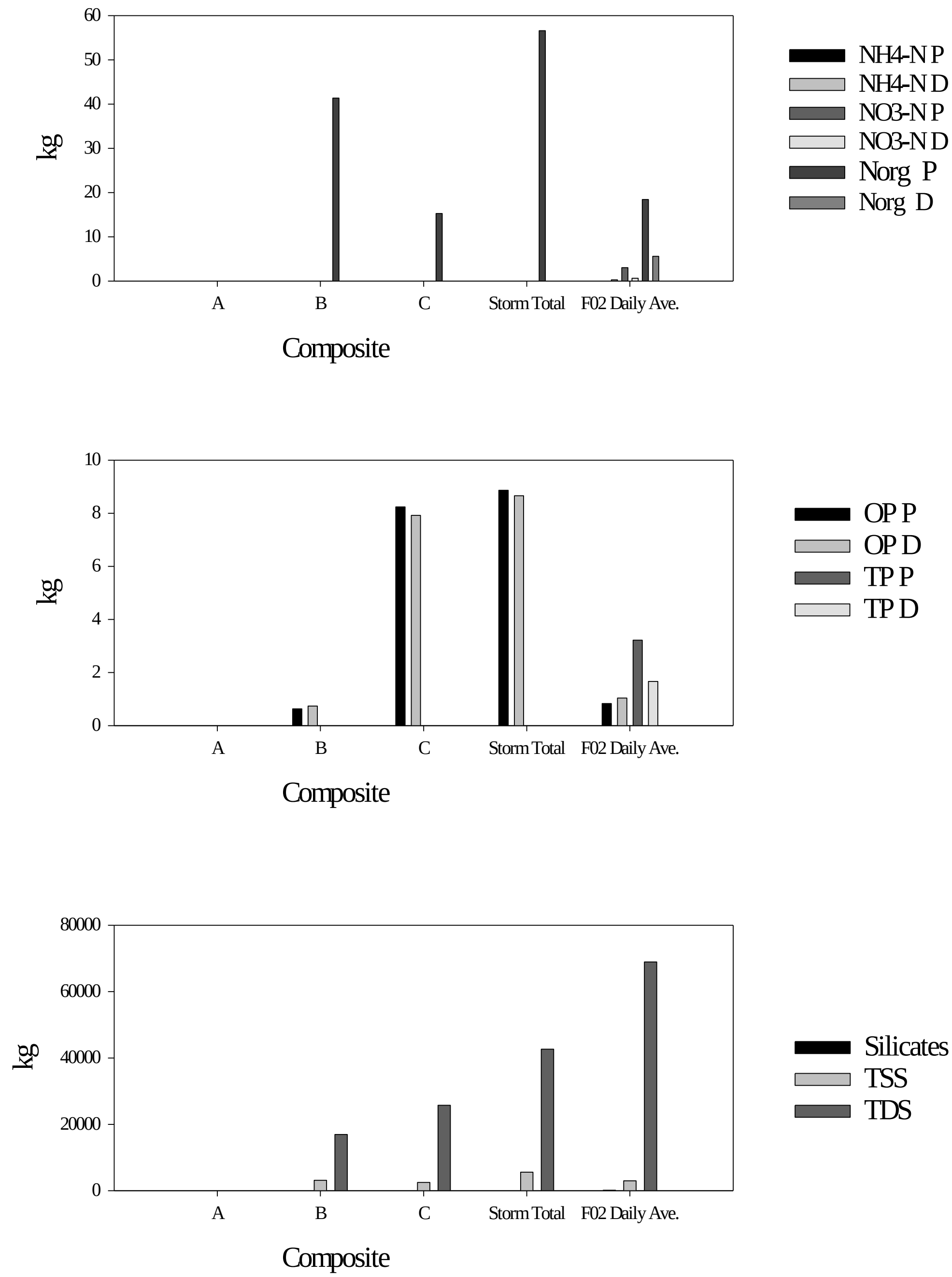


Figure 3.31. Blackbird Creek Storm Data for July 9-10, 2003 and seasonal daily average load for the summer 2003 (S03).

Table 3.26. Blackbird Creek Storm Data for July 9-10, 2003 and seasonal daily average load for summer 2003 (S03)

Load					
	kg / composite			kg/storm	kg / day
	A	Composite B	C	Storm Total	Seasonal Average
NH4-N P	0.839	0.000	5.036	5.875	15.160
NH4-N D	6.157	14.011	36.939	57.107	2.540
NO3-N P	31.075	20.982	211.631	263.689	19.766
NO3-N D	19.044	37.724	179.242	236.011	122.734
Norg P	6.717	23.118	13.885	43.720	25.413
Norg D	2.668	5.195	5.999	13.863	61.574
OP P	0.697	0.115	0.874	1.686	4.337
OP D	1.087	3.259	2.622	6.969	6.374
TP P	3.569	0.805	1.656	6.030	13.882
TP D	0.404	2.032	1.279	3.715	13.571
Silicate	47.82	117.51	209.61	374.94	391.54
TSS	864.37	3603.86	5244.7	9713.0	5166.4
TDS	4795.86	12388.22	9753.4	26937.5	24794.7

Chapter 4

DISCUSSION

Eutrophication is a result of nutrient enhancement of natural waters that often leads to detrimental alga blooms that compromise water quality (Hem, 1985; Chapra, 1997; Bricker et al., 1999; Rabalasis, 2002). The processes involved in the eutrophication of natural waters are complex. Nitrification is dependent on temperature and dissolved oxygen. Nitrate and phosphorus availability to algae for growth in abundant concentrations can stimulate detrimental blooms. Plant production directly influences oxygen and carbon dioxide levels. Bottom waters can become void of oxygen from decaying plants and lead to fish kills (Chapra, 1997).

Anthropogenic activities in agriculture, recreation, and development enhance the landscape with non-point source pollutants (nutrients). These changes in the landscape can also increase the potential for erosion. Transport of nutrients, minerals, and sediments from terrigenous sources to surface waters are by groundwater, runoff, and erosion. The fate of these constituents in surface water is governed by the particular characteristics inherent to each constituent.

The primary nutrients of concern are nitrogen and phosphorus (Hem, 1985; Chapra, 1997; Bricker et al., 1999). Unlike freshwater systems, nitrogen is the limiting nutrient in alga production in estuaries and tidal streams (Hem, 1985; Maidment, 1992; Rabalasis, 2002). Sediments influence the biological, chemical, and physical processes that occur in natural waters (DiToro, 2001), and are important in the evaluation of water quality (APHA, 1989; Maidment, 1992; Viessman and

Hammer, 1998). Silicate is an essential mineral in the metabolism of phytoplankton (Chapra, 1997; Rabalasis, 2002) and is an indicator of groundwater fluxes in tidal channels (Burton and Liss, 1976; Hubertz and Cahoon, 1999).

Precipitation and Stream Flow

The data shows higher daily average precipitation and stream flow rates in Year 2 than Year 1 (Table 3.8). This temporal scale would suggest a direct correlation between precipitation and stream flow. However, an analysis of seasonal data contradicts this inference.

Direct correlation of stream flow and precipitation on a seasonal scale is difficult because the relationship is complex. Stream flow is the rate of flowing water in the stream. Sources of water entering the stream are overland flow, return flow, interflow, and baseflow.

Baseflow is directly related to the streams interface with the surficial aquifer. The potential for precipitation to infiltrate the landscape and reach the aquifer (return flow) is a function of soil saturation, evapotranspiration, and the intensity and duration of storm events (Fetter, 2001; Hubertz, 1999; Hughes, 1998). If the precipitation rate exceeds the infiltration rate and the aquifer is at storage capacity, overland flow will flow directly into the stream. Infiltrated water also moves through the vadose zone as interflow, flowing directly into the stream before entering the aquifer. The potential for increased groundwater flow to the stream is dependent on the volume of water reaching the aquifer, the storage capacity of the water table aquifer and the volume of water diverted from the aquifer by anthropogenic use (wells, ditches, and reservoirs).

Baseflow is a function of the water table (Fetter, 2001). However, rapid fluctuations of local water table levels have been shown near tidal streams. This fluctuation is a result of intrusion of tidal waters into the aquifer (Hughes et al., 1998; Fetter, 2001; Montlucon and Sanudo-Wilhelmy, 2001). On a seasonal scale, the relationship between precipitation and stream flow is complicated and does not directly correlate (Figure 4.1).

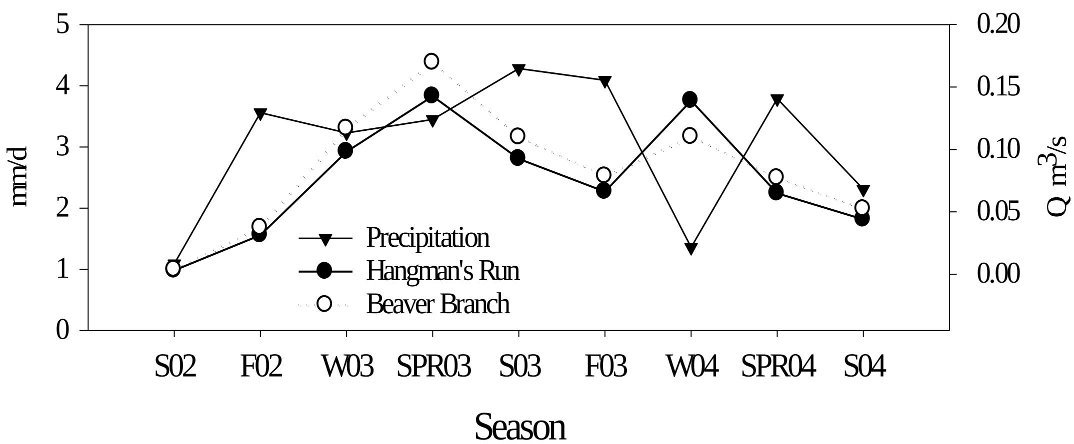


Figure 4.1. Averaged Daily Precipitation and Stream Flow for Hangman's Run and Beaver Branch on a Seasonal Time Scale. Calculation of stream flow data is discussed in Chapter 2.

Drought conditions still prevailed in Delaware during September 2002 with precipitation at normal levels. F02 showed high levels of precipitation with a small increase in stream flow from S02. This is attributable to recharge of the surficial water table aquifer. Stream flow reached its highest level in SPR03 with less precipitation than F02. This reflects aquifer recovery near storage capacity. Stream flow decreased from the SPR03 until F03 even with high levels of precipitation. W04 showed high stream flows with unseasonably low precipitation rates. This is attributable to the lag in temporal response of the basins and aquifer storage. SPR04 showed a high rate of precipitation with stream flow rates comparable to S04 with considerably less precipitation. These patterns strongly show the complexity of the factors involved in stream flow rates.

Storm Characteristics

The storm of October 2002 produced approximately 55 mm of precipitation over a nineteen-hour period (Figures 3.20, 3.21, and 3.22), in comparison, the July 2003 storm had a duration of approximately two and one quarter hours producing approximately 25 mm of precipitation (Figures 3.26, 3.27, and 3.28). Sampling for the October storm began at approximately low slack tide before the incoming tide and two hours after the onset of rain. The July storm began approximately two and one half hours after low slack tide also on the incoming tide and one half hour after the onset of rain. The available data for the October storm showed similarities in loads for all three basins. The July storm data showed more variability in loads between the basins. The October 2002 storm occurred five days after a storm event (Figures 4.2, 4.3, and 4.4). The July 2003 storm occurred three days after a storm event (Figures 4.5, 4.6, and 4.7). Unlike Figures 3.26, 3.27, and 3.28 that show depth, Figures 4.2, 4.3, and 4.4 show stream flow. The less intense storm of October with a longer duration and higher volume increased the stream flow for approximately four days. Stream recovery to after the more intense storm in July was approximately two days. Surface water supplies in the study area had shown improvement during September, and beginning on October 10, 2002, soil conditions were wetter than normal (NOAA, 2002). A commonality of the events is that baseflow had normalized. This suggests that the hydraulic conditions of the basins were comparable. The discussion of the data uses the seasonal averaged load as a reference to accommodate for seasonal differences.

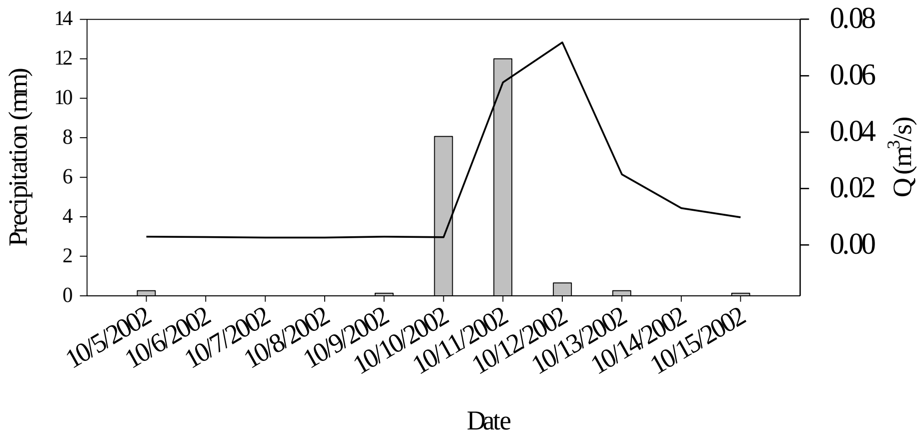


Figure 4.2. October 10-11, 2002 Storm Data Showing Precipitation in histogram and Stream Flow at Hangman's Run as a line.

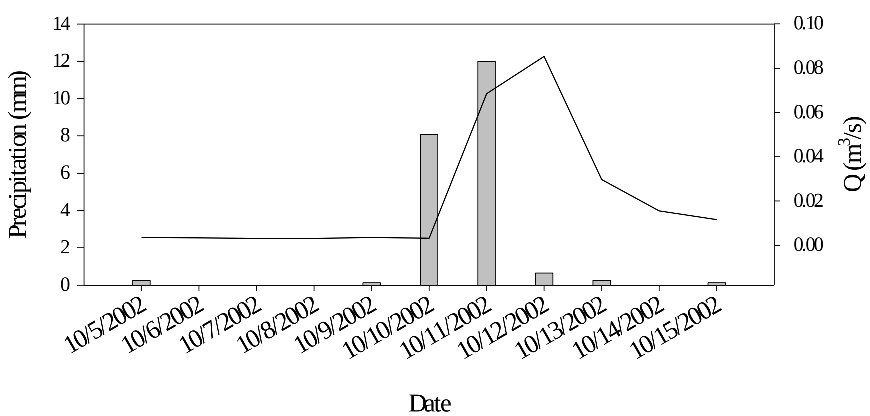


Figure 4.3. October 10-11, 2002 Storm Data Showing Precipitation in histogram and Stream Flow at Beaver Branch as a line.

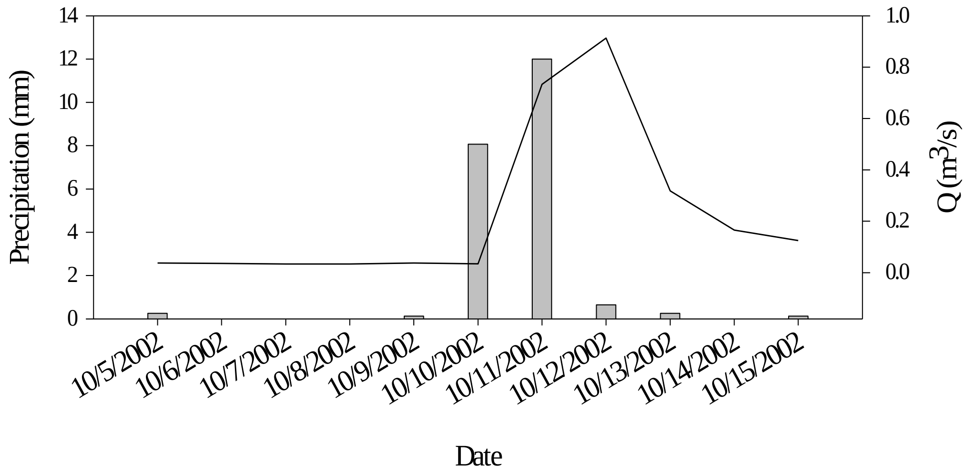


Figure 4.4. October 10-11, 2002 Storm Data Showing Precipitation in histogram and Stream Flow at Blackbird Creek as a line.

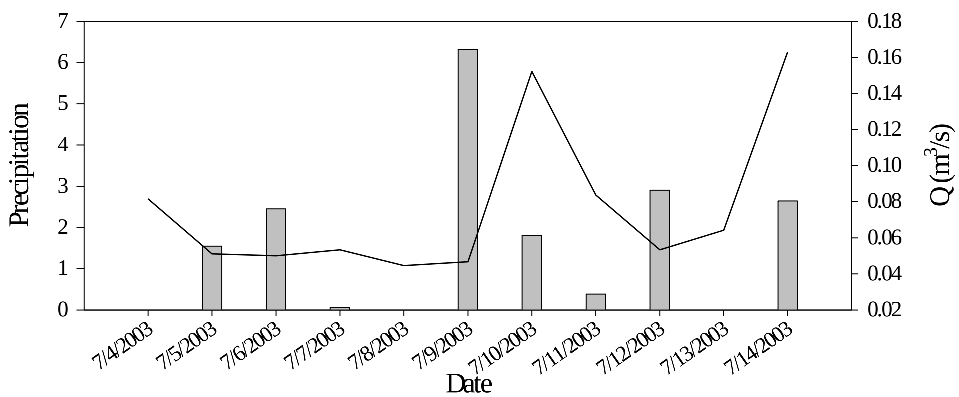


Figure 4.5. July 9-10, 2002 Storm Data Showing Precipitation in histogram and Stream Flow at Hangman's Run as a line.

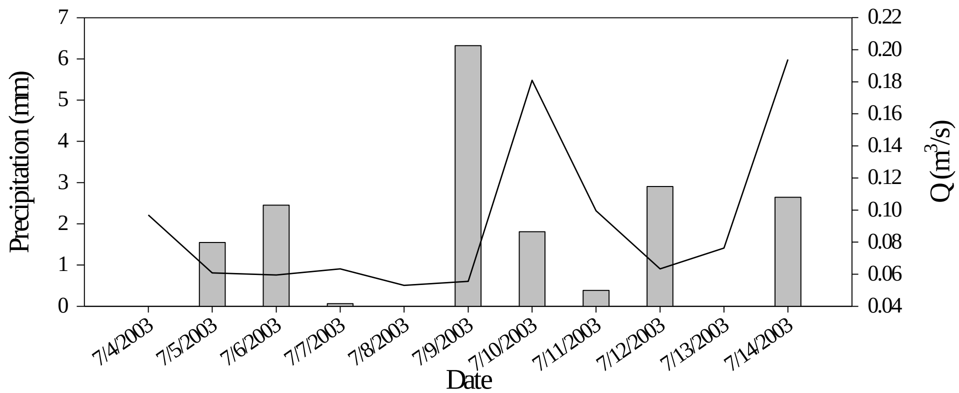


Figure 4.6. July 9-10, 2002 Storm Data Showing Precipitation in histogram and Stream Flow at Beaver Branch as a line.

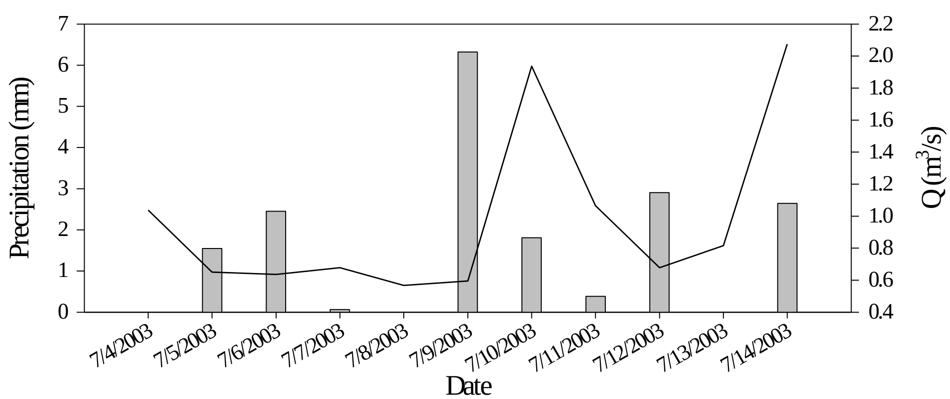


Figure 4.7. July 9-10, 2002 Storm Data Showing Precipitation in histogram and Stream Flow at Blackbird Creek as a line.

Silicate

The primary source of silicate in natural waters is the result of the weathering of silica-containing rocks (APHA, 1989; Hem, 1985). In marine environments, silicate is essential in phytoplankton metabolism for example, diatoms use silicate in the production of their shells (Chapra, 1997; Rabalasis, 2002). These processes tend to deplete the surface waters of silicate (Hem, 1985). Early studies of estuaries accepted rivers and streams as the source of silicate (Burton and Liss, 1976). The source of silicate in rivers is groundwater (Hem, 1985; Hubertz and Cahoon, 1999).

Groundwater is in constant movement. Precipitation infiltrates pervious soil moving downward and down slope until it reaches the water table or seeps from stream banks into the stream by interflow. When sufficient amounts of precipitation reach the water table, the response will cause an increase in groundwater flow into nearby streams (Fetter, 2001). Groundwater responses to precipitation events are correlative to the intensity of the storm event (Hughes et al., 1998; Nagorski et al., 2003). The study area consists of a layer of soil underlain by the fluvial sands and gravels of the unconfined Columbia Aquifer. The Columbia Aquifer is the source of base-flow water for Hangman's Run, Beaver Branch, and Blackbird Creek. It is composed of fluvial silicate sands and gravels of quartz composition (Bachman and Ferrari, 1995). Since the primary source of silicate is the matrix of aquifers, variations in silicate loads, signal changes in groundwater flow (Hubertz and Cahoon, 1999; Montlucon and Sanudo-Wilhelmy, 2001; Nagorski et al., 2003).

Storms. The available data for the October 10-11, 2002 storm data showed an increase in silicate load in the second sampling cycle at Hangman's Run. The total storm load was higher than the seasonal average for F02 (Figure 3.23; Table 3.21). Beaver Branch and Blackbird Creek showed no significant changes (Figures 3.24 3.25; Tables 3.22 – 3.23).

The July 2003 data showed a significant increase in the load of silicate in the second and third sampling cycle at Hangman's Run (Figure 3.29; Table 3.24). Beaver Branch Composite B accounted for 97% of the storm load (Figure 3.30; Table 3.25). Blackbird Creek had the highest loads in the second and third sampling cycles showing a load comparable to the seasonal average for S03 (Figure 3.31; Table 3.26).

Basin response time to precipitation events is dependent on the intensity and duration of the storm (Hubertz and Cahoon, 1999). The October 2002 storm induced a significantly lower or no response in the silicate signal. The July 2003 storm produced a strong groundwater signal at Beaver Branch and Hangman's Run after the storm ended. Large groundwater signals were observed in significant storm events with a lag in response (Hughes et al., 1998). The difference in the signal at Blackbird Creek is attributable the larger basin size and tidal influence.

Annual. The annual data shows a higher load for silicate in year 2 (Figures 3.13, 3.16, & 3.19; Tables 3.16, 3.18, & 3.20). These higher loads are attributed to a higher volume of precipitation and increased stream flow. Increases in precipitation will raise the water table and increase the hydraulic gradient directly increasing stream flow on and annual scale.

Seasonal. The data shows increases in silicate loads in all basins and increases in precipitation except in W04 (Figure 4.8). W04 shows low precipitation with a high silicate load. S03 and F03 precipitation rates were above average with low stream flow. The increased silicate loads correlate to an increased stream flow in W04. A small portion of the increased silicate load in winter is attributable to a decrease in production of silicate dependent organisms. Increases in silicate loads area associated with an influx of groundwater (Hughes, 1998; Montlucon, 2001)

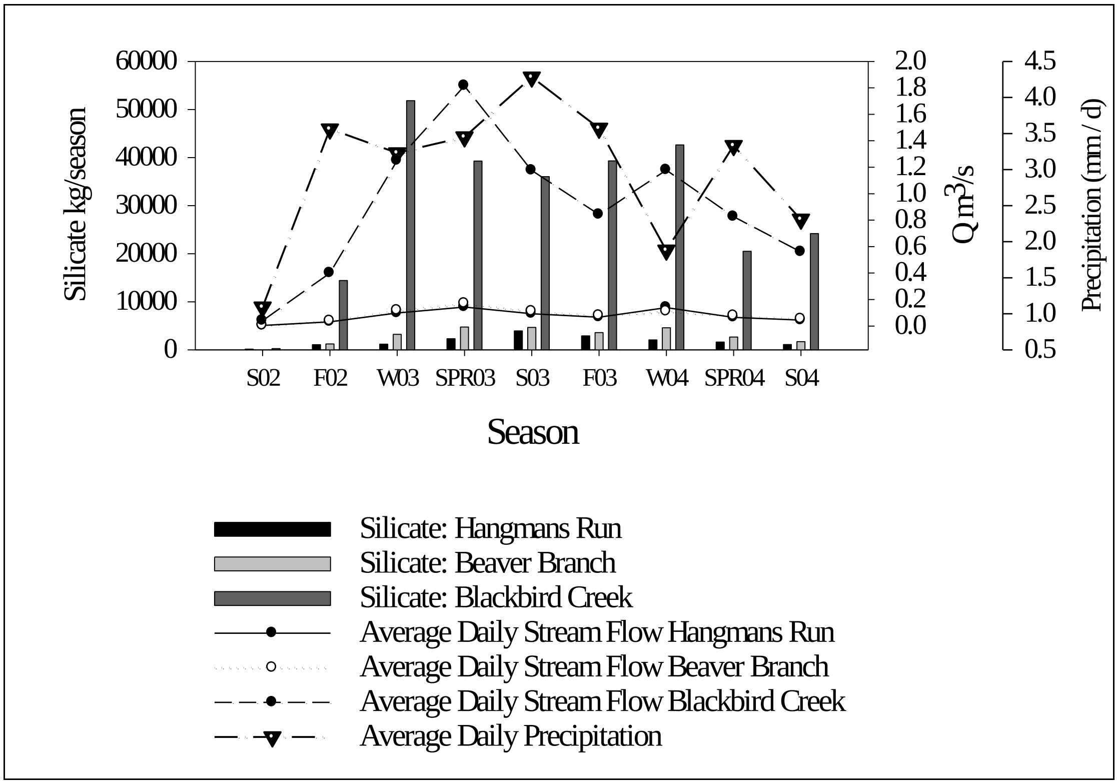


Figure 4.8. Precipitation, Stream Flow, and Silicate loads for Hangman's Run, Beaver Branch, and Blackbird Creek.

Total Suspended and Dissolved Solids

Sediments (total suspended and dissolved solids) play an integral role in water quality (Robinson, 1970; APHA, 1989; Maidment, 1992). Solids are composed of dissolved and particulate fractions of rocks, minerals, nutrients, and plant detritus

The differentiation of solids is important because different particle sizes present different problems (Robinson, 1970). This study defines dissolved solids as particles that are less than 1μm in size. The chemically active surfaces of suspended particles have an enormous potential to sorb nutrients and minerals to their surfaces (Robinson, 1970; Chapra, 1997; DiToro, 2001; Rabalasis, 2002), transport of these sorbed constituents increase the pollutant load in the channel sediment (Robinson, 1970). The deposition occurs when the stream's competency declines after base-flow normalizes. The primary source of solids in natural waters is from the erosion of stream banks and run off over disturbed landscapes due to natural processes and anthropogenic activities (Robinson, 1970). Precipitation events increase stream flow augmenting erosion of the stream banks. The process of erosion is selective, finer grain particles transport more readily than the coarser grains (Robinson, 1970). Coarse grains mitigate the streams potential to erode and finer sediments alter the composition of the dissolved and particulate loads (Robinson, 1970). Storm direction, velocity, and duration show overland flow patterns unique to each storm affecting erosion (de Lima and Singh, 2002; de Lima et al., 2003). An increase in solids is an expected result given that an increase in stream flow and runoff caused by a rain event with the capability of setting in motion the selective process of erosion.

Storms. The October 2002 storm was less intense and had a longer duration than the July 2003 storm (Figures 3.20 3.21, 3.22, 3.26, 3.27, & 3.28). Hangman's Run data for total suspended solids shows loads less than the seasonal average for both storms (Figure 3.23; Table 3.21). This data indicates that Hangman's Run is less susceptible to bank erosion and channel scouring because it has a lower gradient over its length and ends in an impoundment. As an impoundment, it tends to fill with water and sediment rather than have water run through it with higher velocities during precipitation events and tidal cycles. The data for total dissolved solids shows a higher load in Hangman's Run compared to the seasonal average during the October 2002 storm (Figure 3.23, Table 3.21). The bulk of the load for the

July 2003 storm occurred in Composite B (Figure 3.29, Table 3.24) after the storm ended (Figure 3.26). This is consistent with the selective process of erosion and the silicate data that shows an influx of groundwater.

The October 2002 storm data for Beaver Branch shows higher loads for total suspended solids compared to the seasonal average and total dissolved solids were significantly higher (Figure 3.24; Table 3.22). This result is consistent with the influx of groundwater movement from the longer duration of the storm. The data for the more intense July 2003 storm showed a load higher than the seasonal average for total suspended and dissolved solids (Figure 3.30; Table 3.25). This is consistent with the pulsed influx of groundwater in the intense storm.

Available data for Blackbird Creek shows loads for total suspended solids were higher than the seasonal average for the October 2002 storm and the July storm (Figures 3.25, 3.31; Tables 3.23, 3.26). Loads for total dissolved solids for the October 2002 storm were below the seasonal average. The data for the more intense July 2003 storm showed a slightly higher load than the seasonal average at Blackbird Creek.

Annual. Unlike the small temporal and spatial scale of the storms, small changes are lost in the annual data. The annual data shows higher loads of total suspended solids for Hangman's Run and Blackbird Creek in Year 1 than Year 2 (Figures 3.13, 3.19; Tables 3.15, 3.20). Beaver Branch loads were comparable (Figure3.15, Table 3.18). This is likely a function of drought conditions causing a lower water table and a deeper vadose zone with less soil moisture. These dryer conditions would result in more eolian input and the stronger influence of erosion by the tides. In Year 2, the loads for total dissolved solids were higher for Beaver Branch and Blackbird Creek (Figures 3.16, 3.19; Tables 3.18, 3.20). This is attributable to a higher rate of precipitation. Hangman's Run showed a higher rate for dissolved solids in Year 1 compared to Year 2 (Figure 3.13, Table 3.12). Hangman's Run is an impoundment and the increase in dissolved solids is attributable to an increase in concentrations due to evaporation that decreases water volume. The lack of tidal influence restricts dilution from increased water volume.

Seasonal. S02 shows similar patterns for total solids in all three basins: loads for total dissolved solids were higher than the suspended solids (Figures 3.4, 3.7, 3.10; Tables 3.4, 3.8, 3.12) and both values were lower than any other season (Tables 3.5, 3.9, 3.13). This is attributable to the drought. The above average rainfall following the drought had a dramatic effect on the basins. As precipitation increased to above average rates in F02 total suspended and dissolved solids increased significantly in all three basins. Beaver Branch and Blackbird Creek had higher loads for total dissolved solids. These loads were the highest observed in the study period (Table 3.9, 3.13). Hangman's Run showed a higher rate of total suspended solids. This was the highest rate observed in the study period (Table 3.5).

The data shows a similar pattern in loads for all three basins in for all other seasons in that the dissolved fraction was higher (Figure 4.9). Blackbird Creek showed loads an order of magnitude over Hangman's Run and Beaver Branch. The differences in the suspended and dissolved loads at Hangman's Run were less than those at Beaver Branch and Blackbird Creek (Figure 4.9).

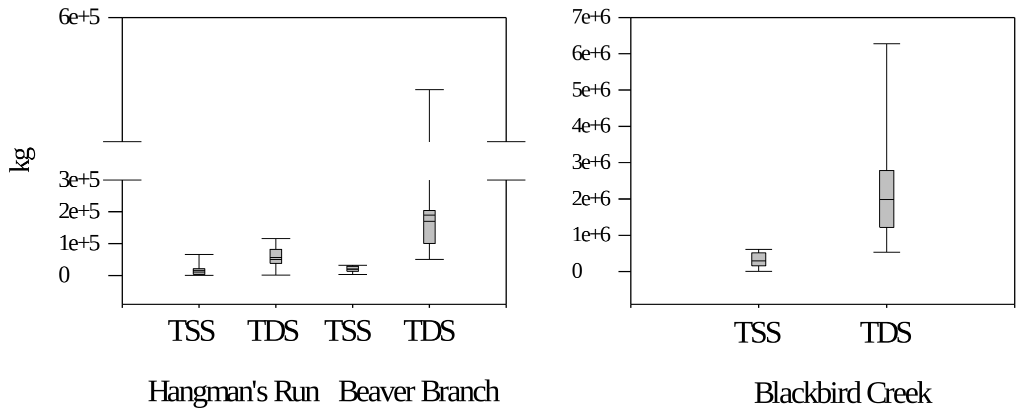


Figure 4.9. Distribution Seasonal Data for Total Suspended and Dissolved Solids for all Basins

Seasonal variations in loads are attributable to climatic variations in temperature, rainfall, and tidal force (erosion). Variations in temperature influence production rates in flora and fauna and the resulting wastes. Changes in loads for total suspended solids vary greatly over time (Meybeck et al., 2003). As basin size increases, temporal variability decreases (Meybeck et al., 2003). “Multiple factors are shown to regulate the variability of suspended solids transport at the dynamic (daily) level, including runoff, relief, lithology, rainfall pattern, vegetation protection, and basin size” (Meybeck et al., 2003). Analysis of data on a seasonal scale allows for only a broad interpretation.

Total dissolved solids increase as waters move over land surfaces, through soils, and aquifers (Maidment, 1992). Total dissolved solids are an indicator of the water quality as it is composed of the ionic form of constituents. It affects the saturation concentrations of dissolved oxygen (Maidment, 1992).

Phosphates

Solids play a major role in the transport and fate of phosphates because phosphates tend to sorb to their surfaces by a strong ionic bond (Hem, 1985; Chapra, 1997). While phosphates are not very mobile in soils or sediments, soil erosion may add considerable amounts of suspended phosphate to streams (Hem, 1985). Settling of sediments sequesters phosphates in the channel that tend to re-suspend and reintegrate into the water column, providing a reservoir of the nutrient (Robinson, 1970; Maidment, 1992; Chapra, 1997; DiToro, 2001).

Phosphates are a product of rock weathering and a constituent of fertilizer (Hem, 1985; Maidment, 1992). Plants and algae metabolize orthophosphate and incorporate it into their structure; it exists in the water column as complex dissolved organic molecules and detritus from the decay of plant matter (Maidment, 1992; Chapra, 1997). Two species of phosphate found in natural waters are orthophosphates and polyphosphates (Maidment, 1992).

Orthophosphates are generally referred to as “reactive phosphorous” and is the form found in fertilizers and is used in plant metabolism (APHA, 1989; Maidment, 1992). Total phosphate, is a measure of polyphosphates and orthophosphates combined (APHA, 1989). Conversion of polyphosphates to orthophosphate by hydrolysis is slow (Maidment, 1992). Hydrolysis is accelerated in wastewater (Sawyer and McCarty, 1978). Orthophosphate is highly soluble in water (Maidment, 1992).

In studies involved in the analysis of urban storm water and combined sewer flows: the “first flush phenomenon” was observed (Gupta and Saul, 1996;

Bertrand-Krajewski et al., 1998; Deletic, 1998; Deletic and Maksumovic, 1998; Lee et al., 2002). These studies have shown that there exists a period in a storm event where the concentrations of pollutants is significantly higher than other sampling periods within the storm. This period is referred to as the "first flush". First flush phenomenon is not limited to combined sewer flow systems; it is also applied to systems without storage that discharge into water ways (Gupta and Saul, 1996). A study of 197 catchments (Saget et al., 1995) found that the first flush effect is not always observed (Deletic and Maksumovic, 1998). "The concentration peak may vary for different pollutants during the same storm event or the same watershed during different storm events (Gupta and Saul, 1996)" (Lee et al., 2002). The first flush effect was observed in some of the storms studied in a five-year study of six watersheds in southern Delaware. The first flush observed in the study was attributed to highly permeable soils and the slope of the small watersheds found in southern Delaware (Ritter, 1986b).

Storms. Hangman's Run data for the July 2003 storm shows the first flush for the particulate and dissolved fractions of orthophosphate in Composite B. Total dissolved solids were highest in composite C. The load of dissolved fraction of orthophosphate in Composites B and C exceeded the total seasonal daily average (Figure 3.29, Table 3.24). Though the storm patterns were different the storm data for July 2003 show patterns in loading resembling the first flush phenomenon in Composites B (Figure 3.29, Table 3.24).

The October 2002 storm data for Beaver Branch shows an increase for the dissolved fraction of orthophosphate in Composite B from Composite A and is higher than the seasonal daily average (Figure 3.24, Table 3.22). The load for the dissolved fraction of orthophosphate was highest in Composite C. Both Composite B and C were higher than the seasonal daily average load. The particulate fraction of orthophosphate is highest in Composite B at a load greater than half the seasonal daily averaged load. This coincides with an increase in total dissolved solids (figure 3.24, Table 3.22). Similarly, data at Beaver Branch the July 2003 storm showed the highest load for dissolved orthophosphate in Composite B. The particulate and dissolved fractions of total phosphate were also elevated.

The distinction between dissolved and particulate phosphate is arbitrary; dissolved phosphate is operationally defined as that “fraction which passes through a 0.45-micron cellulose membrane filter (Broberg and Persson, 1988)” (Heathwaite and Dils, 2000). The laboratory used to process the samples for this study used a 1μm glass filter; this resulted in a bias towards the dissolved fraction. In this study, total suspended and dissolved solids were differentiated with the same 1μm glass filter size.

Blackbird Creek data for the October 2002 storm showed a significant increase in Composites C for the particulate and dissolved fractions of orthophosphate based available data. These increases coincide with an increase in total dissolved solids.

Heathwaite and Dils (2000) unexpectedly found high concentrations of dissolved phosphate in storm runoff. The study only concerned total phosphate.

Conventional theory holds that run off is the primary pathway for particulate fractions of phosphate and the dissolved fraction is transported in groundwater flow. These findings proved to be transient and dependent on the duration and intensity of the storm. The bulk of phosphate transport to streams is via phosphate absorbed to solids (Heathwaite and Dils, 2000; Drexler and Bedford, 2002).

This relationship between rain induced erosion and increases in the particulate fractions is shown at Hangman's Run and Beaver Branch. The October 2002 storm data shows a corresponding increase in total suspended solids when the particulate fractions of orthophosphate and phosphates are elevated (Figures 3.23, 3.24, Tables 3.21, 3.22). Blackbird Creek data shows an increase in the particulate and dissolved fractions of orthophosphate Composites B and C. This also corresponded to an elevated rate of total suspended and dissolved solids. Total phosphates were not detected (Figure 3.25, Table 3.23).

Blackbird Creek October 2002 storm data shows a load of the dissolved fraction of orthophosphate significantly higher than the seasonal daily average (Figure 3.25, Table 3.23). There are two likely causes. The first being the discrepancy in differentiating fractions or the settling of solids with sorbed particulate fractions and their diffusion into the water column. Phosphates in general, tend to sorb to sediment and settle into the channel bed (Maidment, 1992; Chapra, 1997; DiToro, 2001). Secondly, dissolved orthophosphate has been shown to be independent of groundwater flow (Montlucon and Sanudo-Wilhelmy, 2001). The higher level of dissolved orthophosphate may be a result of flux through the sediment-stream water interface (Mallin et al., 2004).

A framework to examine the flux of phosphorous at the sediment-stream water interface was established by the work of Mortimer (1941, 1942) (DiToro, 2001). Mortimer showed that a thin layer of precipitate formed from the oxidation of ferrous iron, trapped phosphates within the aerobic layer of sediment. This iron precipitate oxyhydroxide, formed by oxidation because of the depletion of the dissolved oxygen concentration of the overlying water. The reaction is reversible and as the dissolved oxygen concentration of the water column increases, the precipitate undergoes reduction. The reduction to the soluble ferrous iron form breaks the bond with phosphate and allows the phosphate to diffuse into the water column (DiToro, 2001). Iron concentrations that exceed the Secondary Maximum Contaminant Levels (SMCLs) established by the United States Environmental Protection Agency are found in all Delaware aquifers (Bachman and Ferrari, 1995). The large load of orthophosphate found in Blackbird Creek during the October 2002 storm may be a function of resuspension of the constituent from the Creek bed sediments.

Blackbird Creek data for the July 2003 storm shows a response to the storm in Composite A with increases in the particulate fraction of total phosphate and the particulate and dissolved fractions of orthophosphate. This data does not correlate with the total suspended or dissolved solids.

Annual. Annual data for Hangman's Run, Beaver Branch, and Blackbird Creek shows orthophosphate and total phosphate loads highest in Year 2. Analysis of data on an annual scale has long been accepted to be of more importance than shorter scales. It has been shown that increased temporal scale analysis misses small-scale variations in precipitation and tidal inundation (Hubertz and Cahoon, 1999). The difference in loads on an annual scale for phosphate species is simply attributed to the increase in precipitation and basin size. This scale disallows interpretation with attributes that are only quantifiable on a smaller temporal scale.

Seasonal. Patterns in orthophosphate and total phosphate loads were similar per season for all three basins with some exceptions. S02 showed the lowest rates of phosphate species for all seasons in the study. White et al. (2004) found a strong annual cycle in orthophosphate related to temperature. Higher concentrations were found in summer months with rates decreasing through fall and winter. However, this study found high loads in the all the fractions of orthophosphate and total phosphates in F03 for all basins (Figures 3.12, 3.15, 3.18; Tables 3.4, 3.8, 3.12)

Blackbird Creek showed loads higher than Hangman's Run and Beaver Branch by an order of magnitude (Figure 4.10). This is attributable to the larger size of the Blackbird Creek basin. As this larger basin recovered from the long-term effects of drought conditions the response to increased precipitation mobilized more dissolved constituent from sediments. White et al. 2004 found that concentrations of are a function of internal processing, inputs, and biological uptake. As an example of internal processes, Mortimer 1940 and 1941 discuss the flux of phosphates between the sediments and water column with fluctuations in dissolved oxygen concentrations.

Overall, Beaver Branch showed higher loads with mean values of 31.9 and 64.1 for the particulate fraction of orthophosphates and total phosphates respectively compared to Hangman's Run with loads of 23.16 kg and 57.82 kg (Tables 3.5 & 3.9). At Beaver Branch the mean value of the dissolved fraction orthophosphates and total phosphates were 17.7 and 32.1 kg respectively, compared to Hangman's Run with loads of 9.74 and 13.6 kg. However, in some seasons (SPR03, SPR04, and S04) the particulate fractions were significantly higher in Hangman's Run (Tables 3.4 & 3.8).

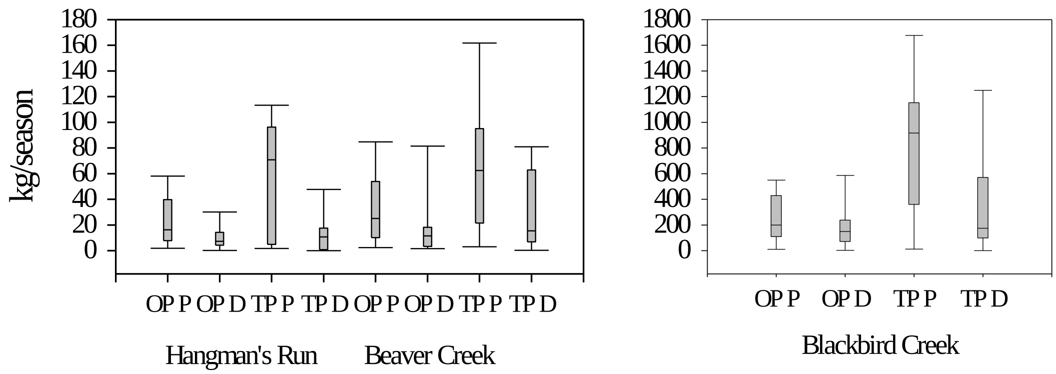


Figure 4.10. Distribution of Orthophosphate and Total Phosphate Fractions for Seasonal Data

Nitrogen

The chemical expression of nitrogen phases is governed by the nitrogen cycle (Figure 4.11.). The phase nitrate-nitrogen is caloric and is an essential nutrient in plant growth (Hem, 1985). Animals ingest plant material, incorporating organic-nitrogen into their protein structure and expelling organic-nitrogen as waste. The decay process of animal and plant matter composed of organic nitrogen produces ammonia-nitrogen that undergoes nitrification by reduction. The reduction of ammonia-nitrogen to nitrite in soils is by bacteria of the genus *Nitrosomonas* (Chapra, 1997). Nitrite is an unstable phase of nitrogen and rapidly reduces to nitrate in soil by bacteria of the genus *Nitrobactor* (Chapra, 1997) and in water by the aquatic bacteria of the genus *Cyanobacteria* (Horton et al., 1996). The decay process is dependent on temperature, pH, and available oxygen (Chapra, 1997).

In the evaluation of water quality, the primary focus of nitrogen is on nitrate-nitrogen and ammonia-nitrogen (Maidment, 1992). Ammonia-nitrogen in high concentrations causes ammonia toxicity to fish and other aquatic life (Maidment, 1992). Nitrate in conjunction with phosphorous leads to excessive algae blooms (Bricker et al., 1999). Nitrogen is the limiting nutrient in alga production in coastal waters (Maidment, 1992; Chapra, 1997; Bricker et al., 1999; Edwards et al., 2003). Nitrate in high concentrations poses a human health hazard by causing the condition Methemoglobinemia in infants (Maidment, 1992; Chapra, 1997).

The practical application of the nitrogen cycle in water quality entails considering the processes involved in the production and maintenance of agricultural crops and turf grasses. Fertilizers in the form of ammonia-nitrogen are applied with the assumption that nitrification will happen over time to provide a slow production

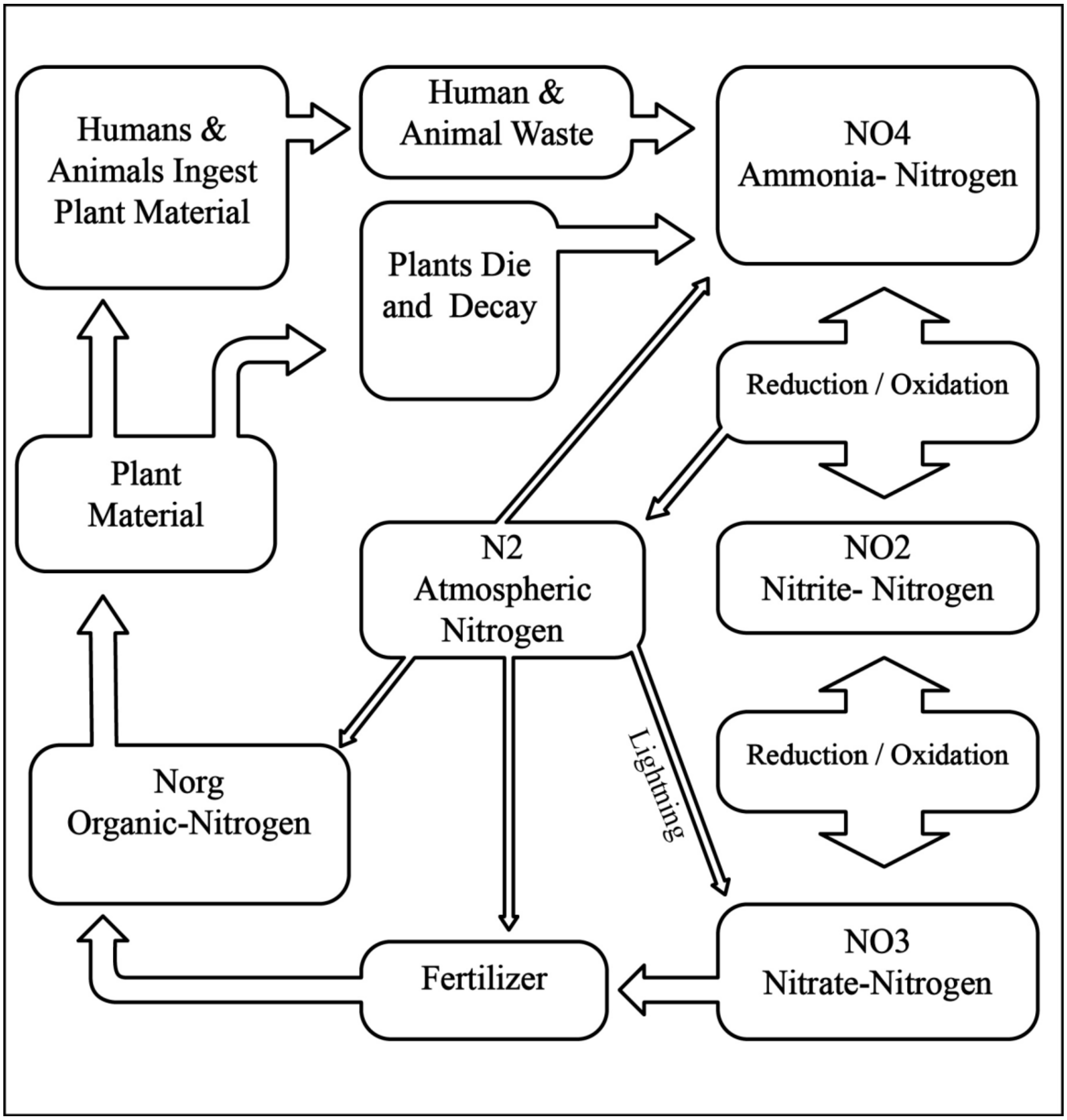


Figure 4.11. The Nitrogen Cycle

and release of caloric nitrate to the crop. It is common practice in the turf grass management to use nitrate in a soluble form for immediate availability (Horsley, 1996). Nitrate is the most soluble of the nitrogen phases and is moves readily through the soil profile by leaching and into streams via groundwater and surface runoff (Maidment, 1992). The presence of nitrogen in tidal creeks is not only from anthropogenic inputs but also from natural sources within the marsh and landscaper. Nitrogen is transported by tidal flows, rainfall, stream flow, and groundwater (Page et al., 1995).

Storms. Hangman's Run and Beaver Branch data show a significant increase in the load for the particulate and dissolved fractions of nitrate-nitrogen in Composite C during the October 2002 storm. The data also showed significantly higher loads for the dissolved fractions of organic-nitrogen in Composite C. The silicate response was in Composite B. As noted previously, concentration peaks for different constituents may occur during the same storm (Lee et al., 2002). Increased nutrient loads are associated with rainfall and the degree of change is dependent on the duration and intensity of the event (Hughes et al., 1998; Hubertz and Cahoon, 1999).

Additionally, Hangman's Run had a significant rate of the dissolved fraction of ammonia-nitrogen. Ammonia-nitrogen tends to sorb to soil particles reducing the concentration in groundwater (Maidment, 1992). It has been shown that ammonia-nitrogen is a product of a marsh environment (Page et al., 1995). Particulate ammonia-nitrogen and nitrate-nitrogen tend to sorb to solids and thus are transported by solids in runoff. The bond formed with the solids is not as strong as the bond that phosphates form. This weak bond allows ammonia-nitrogen and nitrate-nitrogen to move into the water column after settling occurs (Chapra, 1997).

Available data for Blackbird Creek for the October 2002 storm show only an increase in the particulate fraction of organic-nitrogen in Composite B during the event. Lack of data limits a reasonable comparison.

Hangman's Run and Beaver Branch data for the July 2003 storm show a significant increase in the dissolved fraction of ammonia-nitrogen and total dissolved solids in Composite B. This is attributable to ammonia-nitrogen's tendency to sorb to solids. Though this phenomenon has been observed in the particulate fractions, it can be considered here because of the bias to the dissolved fraction.

The particulate fractions of organic-nitrogen and nitrate-nitrogen at Hangman's Run are highest in Composite B for the July 2003 storm. These rates are congruent with the groundwater pulse as indicated by the silicate load and an increase in total dissolved solids in Composite B at Hangman's Run (Figure 3.29, Table 3.24). Organic nitrogen is comprised of humus, macromolecules, and other organic molecule fragments that originate from nekton and vegetation (Maidment, 1992). The contribution of these constituents to the stream flow is attributable to runoff. The variation in temporal response of the basin to the July storm is attributable to the increased volume of precipitation and the increased intensity of the storm compared to results of the October 2002 storm.

Beaver Branch data for the July 2003 storm shows the significant load of the dissolved fraction of nitrate-nitrogen in Composite B. The dissolved fraction of organic-nitrogen is highest in Composite C. Silicate rate that is highest in Composite B (Figure 3.30 & Table 3.25). Nitrate-nitrogen is highly soluble in water it is quite mobile in groundwater (Maidment, 1992). Nitrate-nitrogen is easily carried in runoff and leaches rapidly into shallow groundwater (Maidment, 1992). Basins draining fertilized areas under irrigation are susceptible to high levels of nitrate-nitrogen (Maidment, 1992).

Blackbird Creek data for the July 2003 storm indicates little similarities with the other basins. The particulate and dissolved fractions of ammonia-nitrogen and nitrate-nitrogen appear to show pulsed contributions in Composites A and C. These rates coincide with increased rates in silicate and total suspended solids in the same composites (Figure 3.31 & Table 3.26). The Blackbird Creek basin is approximately an order of magnitude bigger than both Hangman's Run and Beaver Branch. The size of the basin may account for the pattern in loads. An initial increase in runoff at the onset of the event introduced an increase of constituent on the outgoing tide. Composite C sampling occurred after the rain event had past and included more headwater than Composite B.

Annual. Annual data for Hangman's Run shows the highest loads for the particulate fractions of ammonia-nitrogen, nitrate-nitrogen, and organic-nitrogen in Year 1. Loads for the dissolved fractions of ammonia-nitrogen, and organic-nitrogen were highest in Year 2. The dissolved loads of nitrate-nitrogen were comparable (Figure 3.11 & Table 3.15). This finding is attributable to drought conditions resulting in the retardation of the decay process that requires an influx of oxygen bearing water.

It has been suggested, that freshwater has an influence on ammonia-nitrogen (White et al., 2004). Beaver Branch data show all nitrogen species and their fractions to be highest in Year 2 with the exception of the particulate fraction of organic-nitrogen (Figure 3.14 & Table 3.17). Blackbird Creek Year 1 and 2 data show comparable rates for the particulate and dissolved fractions of ammonia-nitrogen. The particulate fraction of nitrate-nitrogen was highest in Year 1 (Figure 3.17 & Table 3.19). The dissolved fraction of nitrate-nitrogen and the particulate and dissolved fraction of organic-nitrogen were higher in Year 2. The higher loads are attributable to an increase in precipitation.

Seasonal. Seasonal data shows some similarities in patterns of loads for specific seasons. Some data correlates well between basins and between seasons.

All the nitrogen species showed significantly low loads during S02 compared to S03 and S04 (Figures 3.2, 3.5, 3.8 & Tables 3.2, 3.6, & 3.10). S02 extreme drought conditions resulted in a lack of production of terrestrial and aquatic plant growth. The lack of precipitation resulted in conditions of low baseflow in the streams. The source of baseflow was the water table. The low loads are attributable to low precipitation and the utilization of available nutrients by producers. S04 showed similar patterns for nitrogen species at Hangman's Run and Blackbird Creek (Figures 3.2, 3.8 & 3.2, 3.10). Beaver Branch showed a higher rate for the particulate fraction of ammonia-nitrogen. Ammonia-nitrate was the dominant nitrogen species in an undeveloped tidal creek in North Carolina. The study sample 12 stations for 6-7

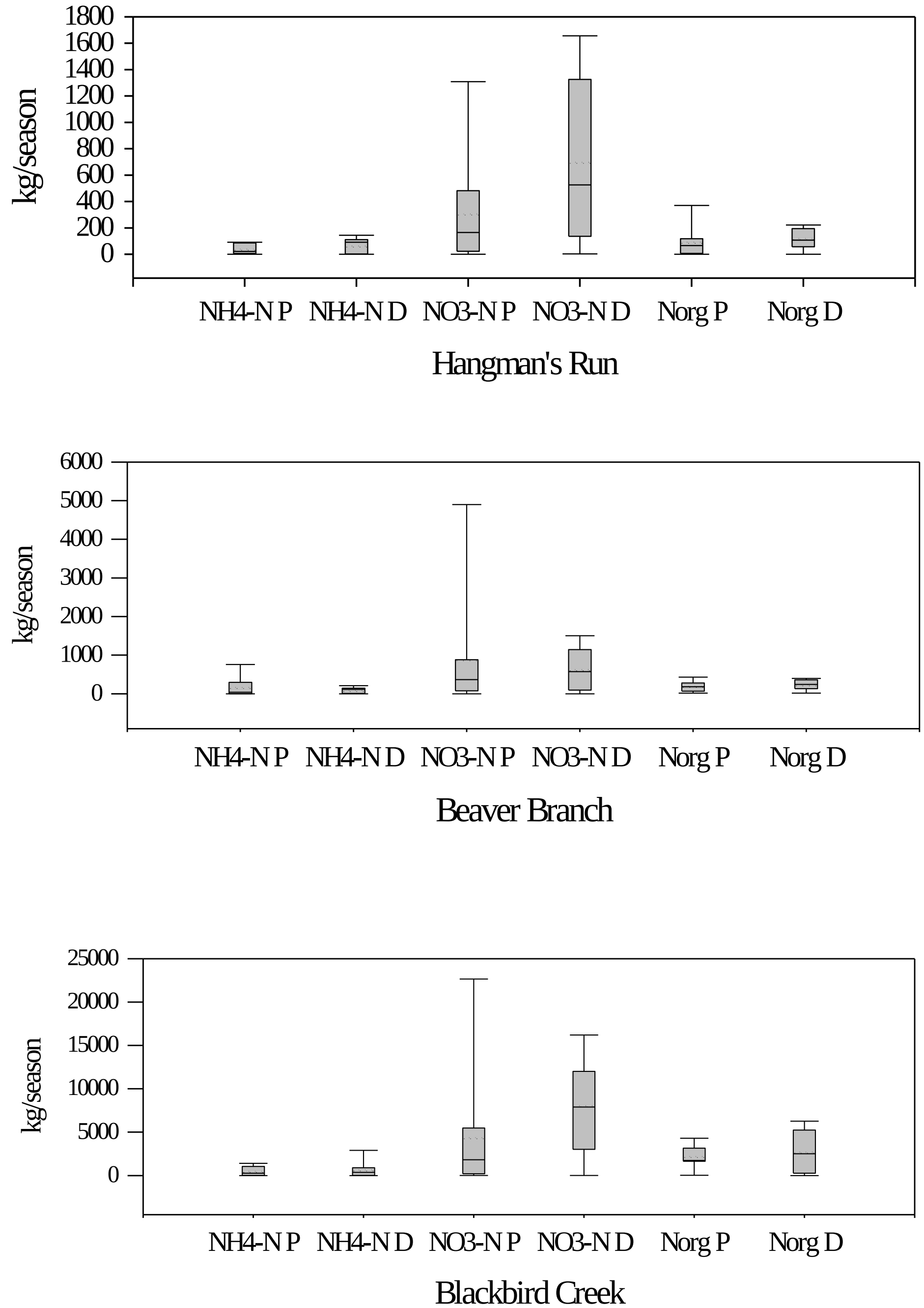


Figure 4.12 Nitrogen Species Distribution for Seasonal Data

years focused on three tidal creeks. Two creeks showed a seasonal pattern of an increase in ammonia-nitrogen in summer (Mallin et al., 2004).

The characteristics of the basins may attribute to the differences in the findings. Production of ammonia-nitrogen is within the tidal creek environment. Blackbird Creek is a larger creek and by water volume, dilution and flushing have a large effect on concentration and transport. Hangman's Run is an impoundment and not subject to the turbulence, Beaver Branch and Blackbird Creek undergo.

F02 showed a dominance of the particulate fraction of organic-nitrogen in all three basins. The seasonal variability in pattern of high loads of particulate organic-nitrogen was found to be related to patterns in stream flow (Page et al., 1995; White et al., 2004). As organic-nitrogen is the first constituent in the decay process of organic matter, its dominance in a wet period following a season of drought is attributable to an excess of material decaying in the environment. In contrast, the F03 shows a dominance of nitrate-nitrogen. F03 was a wet season following a more normal period of production. Unlike F02, higher precipitation rates in F03 flushed nitrate-nitrogen from the landscape.

W03 and W04 showed a dominance of the dissolved fraction of nitrate-nitrogen for all three basins. Winter is a season of low production of plants and organisms that utilize nitrate-nitrogen in their metabolism. The lack of producers reflects the higher rates of nitrate-nitrogen moving through the system. In contrast to W04 data, the other constituents in the W03 data do not correlate well between basins.

SPR03 and SPR04 data shows correlation between basins and seasons with one exception. All basins in SPR03 show significantly higher loads for nitrate-nitrogen. Increased nitrate-nitrogen discharge in spring is associated with increases in spring stream flow (Page et al., 1995). By comparison, the drought conditions of 2002 left a large reserve of nutrient in the landscape affecting SPR03 data. SPR04 data reflects conditions occurring after normalization of the environment after a long recovery period.

Chapter 5

CONCLUSION

As coastal development increases, the anthropogenic influence on water quality can become apparent by the increased incidence of nuisance algae blooms (Bricker et al., 1999). Nuisance alga blooms are the result of eutrophication of estuarine systems due to an influx of excessive nutrients. This study established baseline values for the discharge of nutrient and non-pollutant loads from drainage basins prior to development. The fields around the proposed development were fallow for several years. The development of a residential-golf course community within the basins may lead to changes in water quality.

This study analyzed the loads of nitrate species, phosphorus species, silicate, and total solids on streams from three basins. The research examined the data on various time scales: annual, seasonal, and storm events.

Annual data showed loads attributable to climate on a large temporal scale. Annual stream flow data shows higher rates associated with high rates of precipitation. Loads of nitrogen species vary with rates of precipitation, plant production, and decay of plant material. Phosphate species loads are associated with rates of total suspended and dissolved solids. Resuspension of solids is a function of stream flow. Input of solids is a function of erosion of stream banks and run off. Silicate loads are linked to groundwater discharge rates and precipitation. Annual data may be useful in evaluating long-term (decades) basin studies on a watershed scale. Studies of this kind miss the smaller signal found in seasonal data.

Seasonal data for nitrogen species reflects the nitrogen cycle itself. Fall brings to end the growing season. Dead plant material expresses itself in the landscape and streams as organic-nitrogen. In fall, this material decays to ammonia-nitrogen and is reduced to nitrate-nitrogen. The lack of production in winter creates a reservoir of ammonia-nitrogen in the landscape. An increased spring temperature stimulates the reduction of ammonia-nitrogen to nitrate-nitrogen that is available to spring and summer production. Precipitation transports nitrogen species via infiltration, runoff, and groundwater discharge.

Loads for total dissolved and suspended solids follow precipitation patterns. Phosphates follow solids and silicates follow groundwater discharge. Seasonal data closely follows climate where storm data shows the nuances of the relationship of nutrient transport from the landscape to streams.

Storm events showed signals that were lost in larger time scales. The storm data showed the differences in the effect of storm intensity on groundwater flow as indicated by silicate loads. Silicate loads demonstrated “first flush” phenomena during the intense storm of July 2003 and not during the less intense storm of October 2002. This phenomenon is linked directly to groundwater discharge.

Storm data showed pulsed loads of nitrogen species during periods of intense rain and after a prolonged steady rain. Ammonia-nitrogen and organic nitrogen are more closely linked to run off than groundwater flow. This is supported by the correlation with load of solids and not silicate rates. Increased nitrogen loading in a tidal creek is a result of the combined runoff from the terrestrial landscape and the marsh environment.

Phosphates are transported by solids in runoff and are resuspended in turbulent flow. This dynamic was supported by the data of both storms.

This study has shown that variability in loads of small systems occurs on a scale of hours to days. A signal lost on larger temporal scales. The implication of this finding is important. Large tidal systems do not respond as rapidly and as distinctly as small tidal systems. Further studies that focus on storm events are needed to investigate this variability. Coastal development impacts small systems especially hard when a golf course is involved. Golf courses introduce turf grass that requires intense maintenance. This maintenance includes the addition of nutrients and irrigation. Irrigation by design, mimics low intensity precipitation events. This study has shown that low intensity precipitation events are capable of moving significant amounts of nutrients.

Further studies would benefit by inclusion of a sample taken at the time the Samplers are deployed in the field. This would establish a distinct value to use in calculating any changes. Direct calculation of stream flow would further isolate signals during storm events. In addition, analysis of Biological Oxygen Demand (BOD) would allow for the modeling of nitrogen species based on the biweekly samples and the continuous readings of dissolved oxygen from the sondes. The use of these methods would allow for a quantitative evaluation of any changes caused by the development.

APPENDIX

Table A.1. Hangman's Run Corrected October 10, 2002 and July 9, 2003 Storm Data Calculated for Particulate and Dissolved Fractions for Nitrogen Species.

DATE	Aliquot	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Org-N P	Org-N D
		mg/L					
10/10/02	A	0	0.5	0	0	0.542	0.825
10/10/02	B	0	0	1.802	0	3.488	4.82
10/10/02	C	0	0	3.436	12.539	4.52	4.637
07/09/03	A	0	0	0	0	0.241	0.392
07/09/03	B	0.001	0.2	0.342	0	0.482	0.452
07/09/03	C	0.001	0.2	0.121	0.281	0.301	0.392

Table A.2. Hangman's Run Corrected October 10, 2002 and July 9, 2003 Storm Data Calculated for Particulate and Dissolved Fractions for Phosphate Species, Silicate, and Solids.

DATE	Aliquot	OP Unfiltered	OP Filtered	TP Unfiltered	TP Filtered	Silicate	TSS	TDS
		Std. Dev. ±0.004 mg/L MDL= 0.012 mg/L		Std. Dev. ±0.097 MDL= 0.029		Std. Dev. ± 0.007 MDL= 0.020	Std. Dev. ±0.110 MDL= 0.330	
		mg/L						
10/10/02	A	0.151	0.009	0.299	0	9.962	84	256
10/10/02	B	0.291	0.062	1.576	0	37.759	590	1238
10/10/02	C	0.138	0.111	0.874	0	17.996	386	1056
07/09/03	A	0.052	0.063	0.141	0.038	9.698	14	126
07/09/03	B	0.062	0.061	0.036	0.02	8.406	2	132
07/09/03	C	0.03	0.062	0.052	0.047	8.258	0	0

Table A.3. Hangman's Run Corrected Data Calculated for Particulate and Dissolve Fractions for Nitrogen Species

DATE	Slack Tide	Sample	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Org-N P	Org-N D
					mg/L			
07_23_02	11:30:00	14:30:00	0.783	0	0	0		1.235
08_05_02	16:30:00	15:30:00	0.181	0.221	0.783	0.984	0.542	2.219
08_20_02	17:38:00	17:00:00	0	0.723	0.482	0	0.06	
09_04_02	17:02:00	04:25:00	0.301	0.241	0	0		
09_16_02	15:35:00	14:35:00	0	0	0.060	0.482	1.325	0
10_02_02	15:36:00	16:40:00	0	0	0	0	0	
10_29_02	11:54:00	11:30:00	0	0	0.241	0.221	1.024	0.482
11_13_02	13:36:00	15:30:00	0	0	0.181	0.763	2.048	0.482
12_18_02	17:58:00	15:55:00	0	0	0	2.530	0	0
01_09_03	11:15:00	12:30:00	0.482	0	0	2.711		
01_28_03	15:32:00	16:10:00	-	-	NO DATA	FROZEN	-	-
02_14_03	17:05:00	16:30:00	-	-	NO DATA	FROZEN	-	-
03_03_03	19:15:00	17:20:00	0	0	1.928	1.235	0	0
03_17_03	18:08:00	17:20:00	0.140	0	0.783	2.349	0.252	0
03_27_03	18:05:00	17:30:00	0.080	0	1.566	2.289	0	0.301
04_16_03	19:23:00	17:10:00	0	0.261	0.538	1.57	0.221	0
04_28_03	17:40:00	17:15:00	0.060	0.342	3.132	0.944	0	0
05_12_03	16:18:00	16:45:00	0	0	0	0.583	0	0.482
05_29_03	18:29:00	19:10:00	0.241	0.361	0	0.944	0	0.121
06_17_03	10:01:00	10:45:00	0	0	0	0	0	0
07-01-03	08:56:00	10:30:00	0.181	0	0	0	0	0.392
07-15-03	08:50:00	09:50:00	0	0	0	0	0.572	0
07_28_03	18:56:00	18:35:00	0.140	0	1.687	0.964	0	0.422
08_11_03	18:50:00	20:00:00	0.080	0	0	0.422	0.281	0.422
08_25_03	17:40:00	16:55:00	0	0	0	0.904	0.181	0.542
09_08_03	17:41:00	18:15:00	0.030	0.422	0.572	0.693	0	0.361
10_03_03	13:24:00	15:15:00	0.121	0.09	0.121	0.301	0.994	0
10_15_03	10:11:00	12:45:00	0	0	1.085	0.301	0	0.663
10_30_03	10:06:00	11:20:00	0.181	0.241	0.964	1.446	0.241	0.602
11_17_03	12:03:00	12:35:00	0	0.181	0	1.867	0	0.512
12_16_03	13:15:00	12:30:00	0	0.422	0.180	3.434	0	0
12_30_03	12:11:00	12:40:00	0.241	0.241	0.121	2.771	0	0.271
01_12_04	09:25:00	11:00:00	-	-	NO DATA	FROZEN	-	-
01_30_04	13:26:00	14:10:00	-	-	NO DATA	FROZEN	-	-
02_11_04	10:05:00	11:05:00	0	0	0	2.53	0	0
02_27_04	11:59:00	11:55:00	0	0	0.723	0.964	0	0.602
03_15_04	14:12:00	14:35:00	0	0	0	1.06	0	0.392
03_30_04	13:58:00	14:10:00	0	0.181	1.084	1.185	0.060	0.331
04_12_04	13:52:00	15:05:00	0.181	0.221	0	1.06	0	0.652
04_27_04	13:18:00	13:30:00	0	0.342	0	0.884	0.240	0.02
05_25_04	13:18:00	13:30:00	0	0.221	5	0.873	0.361	0.743
06_21_04	10:05:00	10:55:00	0.602	0.482	1.988	4.759	0	0.542
07_09_04	11:40:00	12:30:00	0	0	0.241	0.361	0	1.030
07_22_04	10:46:00	11:15:00	0	0.422	0.663	0.241	0.846	0.452
08_04_04	10:22:00	11:05:00	0.261	0	0	0.361	0.040	0.572
08_20_04	10:15:00	10:55:00	0.080	0	0	0.422	0	0

Table A.4. Hangman's Run Calculated Dissolved and Particulate Fractions for Phosphate Species, Silicate, and Solids.

DATE	Slack	Sample	OP P	OP D	TP P	TP D	Silicates	TSS	TDS
			mg/L						
07_23_02		14:30:00	0.029	0.019	0.285	0	7.57	94	286
08_05_02	16:30:00	15:30:00	0.284	0	0.231	0	8.051	40	248
08_20_02	17:38:00	17:00:00	0.182	0	0.029	0	9.002	26	196
09_04_02	17:02:00	04:25:00	0.113	0.032	0.154	0.048	6.25	30	154
09_16_02	15:35:00	14:35:00	0.406	0.016	0.121	0	7.403	94	180
10_02_02	15:36:00	16:40:00	0.283	0.017	0.34	0.044	6.243	150	154
10_29_02	11:54:00	11:30:00	0.004	0.017	0.051	0.105	3.627	32	414
11_13_02	13:36:00	15:30:00	0.006	0.016	0.26	0.032	3.702	372	76
12_18_02	17:58:00	15:55:00	0.005	0.013	0	0	4.632	68	138
01_09_03	11:15:00	12:30:00	0.023	0.009	0.009	0	-	12	82
01_28_03	15:32:00	16:10:00	-	-	-	-	-	-	-
02_14_03	17:05:00	16:30:00	-	-	-	-	-	-	-
03_03_03	19:15:00	17:20:00	0.033	0.022	0.166	0	1.627	62	26
03_17_03	18:08:00	17:20:00	0.033	0.022	0	0	1.838	2	14
03_27_03	18:05:00	17:30:00	0.01	0.013	0.047	0	2.136	4	120
04_16_03	19:23:00	17:10:00	0.049	0.01	0.111	0	1.171	44	104
04_28_03	17:40:00	17:15:00	0.028	0.01	0.083	0	1.152	2	114
05_12_03	16:18:00	16:45:00	0.051	0.007	0.114	0.032	2.905	18	94
05_29_03	18:29:00	19:10:00	0.05	0.013	0.047	0.08	3.403	8	266
06_17_03	10:01:00	10:45:00	0.068	0.063	0.091	0.105	3.534	10	116
07-01-03	08:56:00	10:30:00	0.095	0.007	0.144	0.032	6.859	4	116
07-15-03	08:50:00	09:50:00	0.108	0.021	0.13	0	7.062	38	118
07_28_03	18:56:00	18:35:00	0.109	0.009	0.124	0	8.215	26	122
08_11_03	18:50:00	20:00:00	0.069	0.009	0.108	0	9.021	18	130
08_25_03	17:40:00	16:55:00	0.112	0	0.111	0	9.436	26	148
09_08_03	17:41:00	18:15:00	0.042	0.026	0.042	0.026	5.932	32	134
10_03_03	13:24:00	15:15:00	0.189	0.017	0.354	0	6.75	66	104
10_15_03	10:11:00	12:45:00	0.052	0.013	0.068	0	5.634	8	118
10_30_03	10:06:00	11:20:00	0	0.051	0	0.15	1.869	8	136
11_17_03	12:03:00	12:35:00	0.026	0	0.064	0.047	5.455	2	66
12_16_03	13:15:00	12:30:00	0	0.016	0	0.038	3.728	6	92
12_30_03	12:11:00	12:40:00	0.012	0	0.026	0	3.27	2	78
01_12_04	09:25:00	11:00:00	-	-	-	-	-	-	-
01_30_04	13:26:00	14:10:00	-	-	-	-	-	-	-
02_11_04	10:05:00	11:05:00	0.043	0	0.038	0	4.107	6	74
02_27_04	11:59:00	11:55:00	0.019	0	0	0	2.348	4	60
03_15_04	14:12:00	14:35:00	0	0	0.062	0	1.602	14	92
03_30_04	13:58:00	14:10:00	0.023	0	0.868	0	1.765	8	94
04_12_04	13:52:00	15:05:00	0.017	0	0.032	0	2.167	20	266
04_27_04	13:18:00	13:30:00	0.041	0.035	0.076	0.038	2.822	12	132
05_25_04	13:18:00	13:30:00	0.034	0.028	0.096	0.086	6.711	22	130
06_21_04	10:05:00	10:55:00	0.125	0.028	0.47	0	5.264	34	180
07_09_04	11:40:00	12:30:00	0.085	0.057	0.051	0.02	5.845	4	92
07_22_04	10:46:00	11:15:00	0.005	0.035	0.62	0	-	2	-
08_04_04	10:22:00	11:05:00	0.016	0.027	0.08	0	-	4	118
08_20_04	10:15:00	10:55:00	0.054	0.021	0.044	0	-	4	16.2

Table A.5. Beaver Branch Corrected Data Calculated for Particulate and Dissolve Fractions for Nitrogen Species

DATE	Slack	Sample	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Org-N P	Org-N D
			mg/L					
07_23_02	11:20:00	14:10:00	-	-	-	-	-	-
08_05_02	16:30:00	03:10:00	0	0	0.100	0.201	0.481	1.657
08_20_02	17:38:00	17:10:00	0.181	0	0.241	0	0	0.422
09_04_02	17:02:00	16:15:00	0.241	0	0	0	0	0
09_16_02	15:35:00	14:20:00	0	0	0.542	0	0	0
10_02_02	15:36:00	16:15:00	0	0.321	0	0	0	0
10_29_02	11:54:00	11:00:00	0	0	0.221	0	1.205	0
11_13_02	13:38:00	15:20:00	0	0	0	0	1.024	0.602
12_18_02	17:58:00	16:00:00	0	0	0.482	0.602	0.723	0
01_09_03	11:15:00	12:20:00	0	0	0	0.663	0	0.723
01_28_03	15:32:00	16:00:00	-	-	-	-	-	-
02_14_03	17:05:00	16:40:00	0	0	0	0.843	0.123	0.63
03_03_03	19:15:00	17:30:00	0	0	0.422	0.09	0	0
03_17_03	18:00:00	18:35:00	0	0	0.723	0.723	0	0
03_27_03	18:05:00	17:40:00	0	0	2.892	2.771	0.783	0
04_16_03	19:23:00	17:05:00	0.137	0	0.06	0.663		0
04_28_03	17:40:00	16:05:00	0.603	0.281	1.084	0.944	0	0
05_12_03	16:18:00	16:25:00	0	0.402	0.944	0	0.603	0.2
05_29_03	18:29:00	19:00:00	0.000	0	0	1.61	0.116	0.904
06_17_03	10:01:00	10:35:00	1.325	0.301	9.036	0.161	0	
07-01-03	08:56:00	10:15:00	0	0	0.181	0.221	0.362	0.572
07-15-03	08:56:00	09:40:00	0	0	0	0.663	0.121	0.512
07_28_03	18:56:00	18:25:00	0	0	0.301	0.663	0	0.602
08_11_03	18:50:00	18:25:00	0	0	1.084	0	0.12	0.663
08_25_03	17:40:00	16:45:00	0.863	0	0.964	0.120	0	1.45
09_08_03	17:41:00	18:30:00	0.181	0.211	0.843	0.964	0.18	0.693
10_03_03	13:24:00	15:00:00	0.422	0.151	1.687	1.506	1.265	0.391
10-14-03	10:11:00	13:00:00	0.151	0	0	0.904	0.452	1.084
10_30_03	10:06:00	10:55:00	0.12	0	1.27	1.862	-0.12	1.084
11_17_03	12:03:00	12:40:00	0	0.361	0	2.289	0.241	0.091
12_16_03	11:37:00	12:45:00	0	0.361	2.048	1.386	0.085	0.212
12_30_03	12:11:00	12:51:00	0.241	0.12	0.422	3.132	0	0.392
01_12_04	09:25:00	11:00:00	0	0.241	0.12	2.41	0.121	0.271
01_30_04	13:26:00		-	-	-	-	-	-
02_11_04	10:05:00	10:50:00	0	0	0.482	1.506	0	0
02_27_04	11:59:00	11:45:00	0	0	0.121	0.602	0.362	0.542
03_15_04	14:12:00	14:30:00	0	0	0.121	0.823	0.181	0.331
03_30_04	13:58:00	14:00:00	0.06	0.301	0	0.703	0	0.151
04_12_04	13:52:00	15:05:00	0.06	0.402	0.422	1.185	0	0.471
04_27_04	13:18:00	13:25:00	0	0.452	0.181	0.703	0.783	0.09
05_25_04	13:18:00	13:25:00	0	0.452	2.81	0	0.301	0.211
06_21_04	10:05:00	10:50:00	0.241	0.301	0.482	3.614		1.205
07_09_04	11:40:00	12:10:00	2.289	0	0.663	0	2.229	0.783
07_22_04	10:46:00	11:05:00	2.41	0	1.018	0.542	-	-
08_04_04	10:22:00	10:55:00	0.201	0	1.446	0	0.642	1.235
08_20_04	10:15:00	10:45:00	0	0	0	0	0.061	0.512

Table A.6. Beaver Branch Calculated Particulate and Dissolved Fractions for Phosphate Species, Silicate, and Solids.

DATE	slack	sample	OP P	OP D	TP P	TP D	Silicates	TSS	TDS
			mg/L						
07_23_02	11:30:00	14:10:00	0.08	0.048	0.192	0	3.331	116	4330
08_05_02	16:30:00	03:10:00	0.203	0	0.177	0.021	3.876	96	5252
08_20_02	17:38:00	17:10:00	0.165	0.260	0.015	0.044	3.655	210	6796
09_04_02	17:02:00	16:15:00	0.095	0.013	0.031	0.04	4.396	72	4428
09_16_02	15:35:00	14:20:00	0.312	0	0.326	0	5.043	212	7646
10_02_02	15:36:00	16:15:00	0.292	0.047	0.179	0.047	4	272	7492
10_29_02	11:54:00	11:00:00	0.009	0.009	0.14	0	4.633	56	1572
11_13_02	13:38:00	15:20:00	0.021	0.025	0.058	0.044	4.043	46	112
12_18_02	17:58:00	16:00:00	0.001	0.021	0.015	0.038	5.056	58	280
01_09_03	11:15:00	12:20:00	0.021	0	0.035	0	no data	12	118
01_28_03	15:32:00	16:00:00							
02_14_03	17:05:00	16:40:00	0.018	0.014	0.006	0.099	4.61	34	192
03_03_03	19:15:00	17:30:00	0.008	0.009	0	0	2.39	6	64
03_17_03	18:00:00	18:35:00	0.008	0.009	0.137	0	2.768	12	58
03_27_03	18:05:00	17:40:00	0.009	0.009	0.078	0.059	5.711	16	90
04_16_03	19:23:00	17:05:00	0.042	0	0.044	0	2.916	18	116
04_28_03	17:40:00	16:05:00	0.015	0.025	0.036	0.032	3.075	16	124
05_12_03	16:18:00	16:25:00	0.031	0.017	0.086	0.044	3.841	28	106
05_29_03	18:29:00	19:00:00	0.023	0.031	0.019	0.089	3.73	4	78
06_17_03	10:01:00	10:35:00	0.052	0.102	0.07	0.102	3.988	8	150
07-01-03	08:56:00	10:15:00	0.008	0.120	0.141	0.068	7.884	6	154
07-15-03	08:56:00	09:40:00	0.045	0.054	0.089	0.077	7.114	8	132
07_28_03	18:56:00	18:25:00	0.034	0.046	0.184	0.038	8.215	32	434
08_11_03	18:50:00	18:25:00	0.053	0.013	0.475	0	7.617	112	384
08_25_03	17:40:00	16:45:00	0.13	0.172	0.137	0.206	6.73	54	662
09_08_03	17:41:00	18:30:00	0.27	0.012	0.35	0	5.733	72	612
10_03_03	13:24:00	15:00:00	0.137	0.153	0.62	0.186	5.71	124	372
10-14-03	10:11:00	13:00:00	0.095	0.019	0.213	0.023	4.383	42	184
10_30_03	10:06:00	10:55:00	0.023	0.034	0.255	0.059	4.63	32	154
11_17_03	12:03:00	12:40:00	0.032	no data	0.08	0	6.649	18	76
12_16_03	11:37:00	12:45:00	0	0	0.029	0	5.374	14	1.02
12_30_03	12:11:00	12:51:00	0	0.023	0	0.026	5.947	0	188
01_12_04	09:25:00	11:00:00	0.014	0	0.38	0	6.212	18	112
01_30_04	13:26:00	14:20:00							
02_11_04	10:05:00	10:50:00	0	0	0	0	4.26	4	88
02_27_04	11:59:00	11:45:00	0.034	0	0	0	5.055	10	84
03_15_04	14:12:00	14:30:00	0	0	0.077	0	4.848	4	92
03_30_04	13:58:00	14:00:00	0	0	0	0	4.782	8	750
04_12_04	13:52:00	15:05:00	0	0	0.065	0	4.804	6	230
04_27_04	13:18:00	13:25:00	0.043	0	0.057	0.02	3.629	12	132
05_25_04	13:18:00	13:25:00	0.145	0.021	0.152	0.56	4.059	152	274
06_21_04	10:05:00	10:50:00	0.104	0.09	0.071	0.053	5.645	60	174
07_09_04	11:40:00	12:10:00	0.176	0.016	0.443	0.02	4.815	42	810
07_22_04	10:46:00	11:05:00	no data	0.016	0	0	no data	20	138
08_04_04	10:22:00	10:55:00	0.228	0.016	0.396	0	no data	78	546
08_20_04	10:15:00	10:45:00	0.077	0.021	0.08	0	no data	26	456

Table A.7. Beaver Branch Corrected October 10, 2002 and July 9, 2003 Storm Data Calculated for Particulate and Dissolved Fractions for Nitrogen Species.

DATE	Aliquot	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Org-N P	Org-N D
		mg/L					
10/10/02	A	0	0	0.321	0	0	0.844
10/10/02	B	0.138	0.223	1.867	4.036	3.715	3.555
10/10/02	C	0	0	0.783	3.855	1.837	2.62
07/09/03	A	0	0	1.506	6.426	0.391	0.663
07/09/03	B	0	0.502	0.241	1.305	0.241	0.572
07/09/03	C	0.120	0.442	0.843	0.342	0	0.753

Table A.8. Beaver Branch Corrected October 10, 2002 and July 9, 2003 Storm Data Calculated for Particulate and Dissolved Fractions for Phosphate Species, Silicate, and Solids.

DATE	Aliquot	OP Unfiltered	OP Filtered	TP Unfiltered	TP Filtered	Silicate	TSS	TDS
		Std. Dev. ±0.004 mg/L MDL= 0.012 mg/L		Std. Dev. ±0.097 MDL= 0.029		Std. Dev. ± 0.007 MDL= 0.020	Std. Dev. ±0.110 MDL= 0.330	
		mg/L						
10/10/02	A	0.096	0.057	0	0	5.112	70	11308
10/10/02	B	0.698	0.426	0.299	0	26.225	766	58222
10/10/02	C	0.084	0.156	0	0	2.858	222	2536
07/09/03	A	0.063	0.088	0.193	0.092	3.12	56	482
07/09/03	B	0.026	0.083	0.137	0.089	5.386	36	358
07/09/03	C	0.03	0.05	0.091	0.059	7.531	20	192

Table A.9. Blackbird Creek Biweekly Data Calculated for Particulate and Dissolved Fractions for Nitrogen Species.

DATE	Slack	Sample	NH4-N	NH4-N	NO3-N	NO3-N	Org –N	Org-N
			mg/L					
07/23/02	11:30:00	14:00:00	0	0	0	0	0.964	0.813
08/05/02	16:30:00	15:00:00	0	0	0	0	0.663	0.873
08/20/02	17:38:00	17:40:00	0	0	0.455	0.328	0	0
09/04/02	17:02:00	16:00:00	0	0.181	0	0	0	0
09/16/02	15:35:00	14:00:00	0	0	0.120	0.422	0	0
10/02/02	15:36:00	16:00:00	0	0	0	0	0	0
10/29/02	11:54:00	10:55:00	0	0	0.583	0	0.265	1.145
11/13/02	13:38:00	15:10:00	0	0	0	0	0.783	0
12/18/02	17:58:00	16:20:00	0	0	0	0.663	0.663	0
01/09/03	11:15:00	12:05:00	0	0	0.061	1.084	0	0
01/28/03	15:32:00	15:50:00	0	0	0.061	1.867	0.331	0
02/14/03	17:05:00	16:45:00	0.181	0	0	1.390	0.271	0
03/03/03	19:15:00	17:45:00	0.090	0	0.783	0.633	0.302	0
03/17/03	18:08:00	18:50:00	0.080	0	5.000	1.930	0	0
03/27/03	18:05:00	17:50:00	0	0.321	1.325	0.783	0	0
04/16/03	19:23:00	16:55:00	0.239	0	0.723	0	0.303	0
04/28/03	17:40:00	16:55:00	0	0	0.663	0.281	0	0
05/12/03	16:18:00	16:15:00	0.241	0.944	0.241	0.944	0	0
05/29/03	18:29:00	18:50:00	0	0.181	0	1.426	0.241	0.421
06/17/03	10:01:00	10:25:00	0.241	0	0	1.486	0.120	0.663
07/01/03	08:56:00	10:05:00	0.081	0.361	0.141	0.381	0.762	0.272
07/15/03	08:56:00	09:30:00	0	0	2.344	1.446	0.602	0.633
07/28/03	18:56:00	18:15:00	0	0	0	0.723	0.241	0.602
08/11/03	18:50:00	19:35:00	0	0	0	0.843	0.181	0.542
08/25/03	17:40:00	16:55:00	0	0	0.241	0.723	0.543	0.602
09/08/03	17:41:00	18:35:00	0	0	0.301	0.422	0.362	0.843
10/03/03	13:24:00	14:55:00	0	0.151	0.542	0.542	0.181	0.873
10/15/03	10:11:00	13:15:00	0	0	0.844	0.361	0.362	1.024
10/30/03	10:06:00	10:15:00	0	0	0.964	1.446	0.121	1.084
11/17/03	12:03:00	13:00:00	0.121	0.120	0.180	2.410	0.180	0.392
12/16/03	11:37:00	13:15:00	0	0.313	0.241	2.470	0	0.380
12/30/03	12:11:00	13:00:00	0	0	0.060	2.229	0	0.994
01/12/04	09:25:00	11:20:00	0.181	0.301	0.241	2.289	0	0.693
01/30/04	13:26:00	14:45:00	0.261	0	0	1.988	0.462	0
02/11/04	10:05:00	10:45:00	0	0	0	0.964	0.790	1.080
02/27/04	11:59:00	11:40:00	0	0	0	1.270	0.362	0.542
03/15/04	14:12:00	14:20:00	0.012	0.121	0	1.470	0	0.451
03/30/04	13:58:00	13:50:00	0	0.301	0.181	1.064	0.060	0.693
04/12/04	13:52:00	14:50:00	0	0.161	0.301	1.245	0	0.712
04/27/04	13:18:00	13:20:00	0	0.221	0.301	0.583	0.602	0.502
05/25/04	11:51:00	12:45:00	0	0	4.879	0.392	2.349	0.422
06/21/04	10:05:00	10:45:00	0	0	0	3.370	0.361	0.723
07/09/04	11:40:00	12:00:00	0	0	0	0	0.180	0.663
07/22/04	10:46:00	10:50:00	0	0.301	0.241	0	0	0.939
08/04/04	10:22:00	10:45:00	0	0	0.181	0.241	0	0.573
08/20/04	10:15:00	10:45:00	0	0	0.600	0	0.301	0.392

Table A.10. Blackbird Creek Biweekly Data Calculated for Particulate and Dissolved Fractions for Phosphate Species, Silicate, and Solids.

DATE	Slack	Sample	OP	OP	TP	TP	Silicate	TSS	TDS
			mg/L						
07/23/0	11:30:0	14:00:0	0	0	0.000	0	0.000	0	0
08/05/0	16:30:0	15:00:0	0.147	0.027	0.218	0	2.892	88	5276
08/20/0	17:38:0	17:40:0	0.100	0.046	0.068	0	3.248	136	7026
09/04/0	17:02:0	16:00:0	0.070	0.012	0.063	0.000	4.109	6	3644
09/16/0	15:35:0	14:00:0	0.014	0.066	0.105	0.052	3.883	98	7300
10/02/0	15:36:0	16:00:0	0.081	0.053	0.531	0.089	3.387	136	7724
10/29/0	11:54:0	10:55:0	0.015	0.016	0.000	0.000	4.204	52	1632
11/13/0	13:38:0	15:10:0	0.011	0.027	0.018	0.053	5.028	86	358
12/18/0	17:58:0	16:20:0	0.013	0.023	0.041	0.000	4.8	54	346
01/09/0	11:15:0	12:05:0	0.049	0.016	0.000	0.000	No Data	40	134
01/28/0	15:32:0	15:50:0	0.034	0.021	0.080	0.083	6.357	42	240
02/14/0	17:05:0	16:45:0	0.102	0.021	0.050	0.146	5.285	70	110
03/03/0	19:15:0	17:45:0	0.014	0.012	0.140	0.000	2.142	82	54
03/17/0	18:08:0	18:50:0	0.014	0.012	0.096	0.000	2.889	50	60
03/27/0	18:05:0	17:50:0	0.016	0.012	0.030	0.038	3.557	26	86
04/16/0	19:23:0	16:55:0	0.029	0.034	0.105	0.041	2.241	6	144
04/28/0	17:40:0	16:55:0	0.074	0.019	0.163	0.029	2.273	26	210
05/12/0	16:18:0	16:15:0	0.035	0.026	0.163	0.056	2.599	66	220
05/29/0	18:29:0	18:50:0	0.047	0.021	0.131	0.068	3.219	34	98
06/17/0	10:01:0	10:25:0	0.048	0.054	0.099	0.172	3.367	44	212
07/01/0	08:56:0	10:05:0	0.024	0.111	0.317	0.118	6.46	12	148
07/15/0	08:56:0	09:30:0	0.032	0.076	0.187	0.102	6.348	6	162
07/28/0	18:56:0	18:15:0	0.033	0.078	0.169	0.074	0.474	82	324
08/11/0	18:50:0	19:35:0	0.018	0.061	0.150	0.062	4.896	98	436
08/25/0	17:40:0	16:55:0	0.067	0.070	0.183	0.053	5.058	92	356
09/08/0	17:41:0	18:35:0	0.100	0.017	0.147	0.032	5.83	66	434
10/03/0	13:24:0	14:55:0	0.075	0.043	0.200	0.050	5.833	48	474
10/15/0	10:11:0	13:15:0	0.066	0.000	0.192	0.000	4.138	68	466
10/30/0	10:06:0	10:15:0	0.023	0.016	0.137	0.000	4.853	48	148
11/17/0	12:03:0	13:00:0	0.024	0.031	0.125	0.038	6.926	24	98
12/16/0	11:37:0	13:15:0	0.007	0.010	0.380	0.000	4.414	16	100
12/30/0	12:11:0	13:00:0	0.012	0.010	0.051	0.023	5.869	6	246
01/12/0	09:25:0	11:20:0	0.016	0.018	0.015	0.038	6.801	10	184
01/30/0	13:26:0	14:45:0	0.022	0.000	0.000	0.000	6.182	8	116
02/11/0	10:05:0	10:45:0	0.026	0.000	0.032	0.000	2.784	12	100
02/27/0	11:59:0	11:40:0	0.023	0.000	0.044	0.000	4.163	36	1094
03/15/0	14:12:0	14:20:0	0.018	0.000	0.176	0.000	3.822	32	180
03/30/0	13:58:0	13:50:0	0.007	0.019	0.124	0.000	3.023	14	274
04/12/0	13:52:0	14:50:0	0.009	0.018	0.108	0.000	3.526	20	132
04/27/0	13:18:0	13:20:0	0.027	0.036	0.192	0.044	3.305	38	136
05/25/0	11:51:0	12:45:0	0.084	0.034	0.185	0.044	2.167	110	388
06/21/0	10:05:0	10:45:0	0.059	0.089	0.199	0.068	4.04	108	222
07/09/0	11:40:0	12:00:0	0.059	0.013	0.114	0.000	1.781	120	1174
07/22/0	10:46:0	10:50:0	0.036	0.047	0.099	0.047	No Data	38	136
08/04/0	10:22:0	10:45:0	0.595	0.025	0.176	0.000	No Data	58	790
08/20/0	10:15:0	10:45:0	0.120	0.017	0.127	0.000	No Data	14	568

Table A.11. Blackbird Creek Corrected October 10, 2002 and July 9, 2003 Storm Data Calculated for Particulate and Dissolved Fractions for Nitrogen Species.

DATE	Aliquot	NH4-N P	NH4-N D	NO3-N P	NO3-N D	Org-N P	Org-N D
		mg/L					
10/10/02	A	No Sample	No Sample	No Sample	No Sample	No Sample	No Sample
10/10/02	B	0	0	0	0	1.566	0
10/10/02	C	0	0	0	0	0.482	0
07/09/03	A	0.060	0.442	2.229	1.366	0.482	0.191
07/09/03	B	0	0.201	0.301	0.944	0.603	0.13
07/09/03	C	0.060	0.442	2.530	3.896	0.302	0.130

Table A.12. Blackbird Creek Corrected October 10, 2002 and July 9, 2003 Storm Data Calculated for Particulate and Dissolved Fractions for Phosphate Species, Silicate, and Solids.

DATE	Aliquot	OP Unfiltered	OP Filtered	TP Unfiltered	TP Filtered	Silicate	TSS	TDS
		Std. Dev. ±0.004 mg/L MDL= 0.012 mg/L		Std. Dev. ±0.097 MDL= 0.029		Std. Dev. ± 0.007 MDL= 0.020	Std. Dev. ±0.110 MDL= 0.330	
		mg/L						
10/10/02	A	-	-	-	-	-	-	-
10/10/02	B	0.026	0.025	0	0	1.757	118	642
10/10/02	C	0.260	0.250	0	0	1.720	78	812
07/09/03	A	0.050	0.078	0.256	0.029	3.430	62	344
07/09/03	B	0.003	0.085	0.021	0.053	3.065	94	310
07/09/03	C	0.019	0.057	0.036	0.032	4.556	114	212

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