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The Effectiveness of the Chemical Perturbation Index for Monitoring Water Quality in Three Mixed-use Urban Watersheds, Knoxville, Tennessee

Brooks A. Jolly
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To the Graduate Council:

I am submitting herewith a thesis written by Brooks A. Jolly entitled "The Effectiveness of the Chemical Perturbation Index for Monitoring Water Quality in Three Mixed-use Urban Watersheds, Knoxville, Tennessee." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geography.

Carol P. Harden, Major Professor

We have read this thesis and recommend its acceptance:

Shih Shaw

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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The Effectiveness of the Chemical Perturbation Index for Monitoring Water Quality in Three Mixed-use Urban Watersheds, Knoxville Tennessee

A Thesis
Presented for the
Master of Science
Degree
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ABSTRACT

Landscape change within the United States has resulted in significant physical and chemical alteration of our nation's surface waters. Many research projects have demonstrated that landscape features moderate or cause observed water quality conditions. Urbanization is a rapidly growing form of landscape change in the United States and ranks second to agriculture as a major cause of stream degradation. Understanding the effect of urbanization on surface waters is only one component of the larger issue of restoring and maintaining the integrity of urban stream water quality. Effective watershed management is a social process that requires the inclusion of local citizens and community alliances. To this end, communities need the tools to gather useful and interpretable data about water quality. The Chemical Perturbation Index (CPI) may potentially be an inexpensive and easily interpretable index of water quality parameters that may be able to characterize both spatial and temporal changes in stream chemistry due to urbanization. The primary purpose of this study is to test the usefulness of the Chemical Perturbation Index as a tool for urban water quality assessment. To gain insight into this question, I explored the ability of the CPI to describe differences in the water quality of three mixed-use urban watersheds: Third Creek, Second Creek, and Goose Creek in Knox County, Tennessee.

To explore the usefulness of the CPI for urban water quality monitoring, I compared the CPI to other methods of describing and determining water quality found in the literature. My research into the CPI's effectiveness as a water quality monitoring tool yielded mixed results. Statistical measures of the individual components of the CPI

correlated with changes in landscape and land use characteristics throughout the research subbasins. The CPI itself did not show a relationship with the landscape or land use characteristics within the subbasins, but did show a general relationship with geologic characteristics. Pollution indicators modeled using the Hydrologic Simulation Program Fortran (HSPF) also failed to correlate significantly with the CPI or to demonstrate clear relationships between simulated pollution indicators and the individual components of the CPI. The lack of expected correlations between landscape and land use factors and many of my chemical measures raises several questions about water quality in urban watersheds.

While previous research has demonstrated a connection between water chemistry and land use, previous studies have generally been done in larger watersheds than those in my research. In smaller watersheds that are urbanized to a high degree, the relationship between the degree of urbanization and water quality may not be as strong. This suggests that the relationship between water chemistry and landscape alteration does not necessarily extend across threshold levels for watershed scale and amount of urbanization. The CPI reflected to geologic characteristics, suggesting that, in extensively urbanized watersheds, factors other than land use account for the observed differences in water quality.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Context of Research

Section 101 of the Clean Water Act calls for the restoration and maintenance of the physical, chemical, and biological integrity of the nation's waters (U.S. Congress, 2002). Scientifically sound methods for determining stream water quality are necessary to accomplish the mission laid out by the Clean Water Act. Current studies suggest that the effects of watershed disturbance (including urbanization) are controlled by many factors, including rainfall intensity, antecedent hydrologic/climatic conditions, local anthropogenic activities, underlying geology, and numerous surface characteristics (Pitt *et al*., 1995). The unpredictable nature of urban landscapes and the pollution associated with them cause the chemical effects of urbanization to be far more variable than hydrologic and geomorphic effects (Paul and Meyer, 2001).

Despite the varying chemical characteristics of wastewater, inputs from non-point sources, like surface runoff, and point sources, such as industrial discharges, are generally ion-rich in comparison to water in the receiving stream (Stewart, 2001). Current research indicates urbanization consistently results in increased specific conductance and generally results in elevated levels of calcium, sodium, potassium, and magnesium (Paul and Meyer, 2001). Consequently, many studies dealing with the degradation of surface waters track the effects of urbanization using combinations of these chemical parameters. For urban water quality monitoring, it is important that monitoring programs encompass as many of the potential pollution effects associated with urbanization as possible.

Understanding the effect of urbanization on surface waters is only one component of the larger issue of restoring and maintaining the physical and ecological integrity of urban streams. Water quality monitoring tools are only useful if they are used by the groups (in this case, community groups) for which they are designed. Over the last several decades, the philosophy of environmental management has changed from a top-down strategy, with policy determined by centralized governmental agencies, to a bottom-up strategy that includes local communities — especially community organizations — in the decision making process (Rhoads *et al.*, 1999). Rhoads and his co-authors point out that watershed management, while dependent on science and engineering, is a social process that requires the inclusion of local citizens and community alliances. Lasting change in stream quality, which is directly linked to effective local management, can only be achieved through a shift in a community's ethic toward its water resources, and such a change can only be accomplished socially.

When a community is involved in the monitoring of streams and in watershed management decisions, citizens are more likely to understand the water issues associated with urbanizing and more likely to comply with good management practices (Rhoads *et al.*, 1999). Bringing local citizens into the decision making process and equipping them with the tools to quantify water quality provides an additional advantage to government beyond water quality compliance problems. The existing condition of many low-order streams is unknown, and the manpower costs required to develop data on baseline conditions would be financially prohibitive. Equipping community organizations to monitor local surface waters would reduce the cost of compiling a database of baseline conditions and extending the spatial coverage of existing datasets.

Many studies have shown that chemical analysis can determine the export of specific ions and nutrients from catchments; however, testing for specific ions, cations, and nutrients can be costly and time-consuming, tending to discourage long-term chemical-based monitoring that involves frequent sampling (Stewart, 2001). Providing community organizations with the tools for monitoring a stream requires the consideration of two issues: 1) The cost of the test cannot be prohibitively expensive for local government to provide testing equipment to community organizations, and 2) The test must produce scientifically meaningful results without overcomplicated or time-consuming procedures. Community volunteers should not be required to have a scientific or engineering background to achieve accurate and interpretable results. My interest in water quality and my belief in the need for volunteer monitoring are driving forces behind my investigation into the CPI as a potentially inexpensive and easily interpretable index of water quality parameters that may be able to characterize both spatial and temporal changes in stream chemistry due to urbanization.

Research Objectives

The primary purpose of this study was to investigate the effectiveness of the Chemical Perturbation Index (CPI) developed by Dr. Arthur J. Stewart of the Oak Ridge National Laboratory (ORNL) as a water quality monitoring technique in urban environments. To gain insight into this larger question, I explored the ability of the CPI to describe changes in the water quality of three mixed-use urban watersheds: Third Creek, Second Creek, and Goose Creek in Knox County, Tennessee. A consequence and secondary goal of my investigation into the CPI was the development of a Geographical Information Systems (GIS) database to provide future researchers and organizations concerned about urban water quality in Knoxville, Tennessee with baseline data on water quality and land use/landscape characteristics. Documentation of current and historical surface water conditions is necessary for any future exploration of changes in water quality associated with anthropogenic forcings.

To explore the usefulness of the CPI for urban water quality monitoring, I compared the CPI to other methods of describing and determining water quality found in the literature. My analysis was designed to answer four broad questions:

1) How do the results of CPI calculations performed on samples in a non-point source, mixed land use, urban environment compare with the results published by Dr. Stewart for streams receiving primarily point source pollution discharges?
2) How does the CPI method compare to water quality assessments made using other commonly used statistical techniques?
3) Do the between-site water quality relationships indicated by the CPI follow the 'expected' relationship between landscape variables and water quality seen in the literature?
4) Do water quality rankings established using the CPI agree with water quality rankings established using watershed models?

To answer these questions I looked for linkages, if any, between the CPI and the individual components of the index with land surface conditions. Using descriptive statistics and accepted statistical methods for water resources, I attempted to characterize the individual components of the CPI and their relationships to water quality, and to compare those relationships with the relationships illuminated by the CPI method. I also ranked the water quality at sites using the Hydrologic Simulation Program Fortran (HSPF) to simulated flow volume and in-stream constituent loadings as indicators of water quality, and compared CPI index values with simulated water quality conditions. By applying the CPI to urban stream waters, I expected to gain insight into its utility as a tool for urban water quality assessment and to determine whether I would recommend it to watershed alliances in this region.

Understanding what environmental factors influence water chemistry in the receiving streams is important for correct interpretation of test results. I collected and statistically analyzed water chemistry and land surface data to determine linkages between them. This analysis also provides insight regarding which surface characteristics (land use type, impervious cover prevalence, slope, surficial geology) have the greatest influence on both individual water quality parameters and the CPI in these three streams. Increased landscape disturbance may be expected to change the amount of influence natural controls such as geology and climate have on water chemistry, resulting in a change in the CPI. Preliminary sampling and statistical analyses using the components of the CPI in the Third Creek watershed provided encouraging results, with seven test sites exhibiting spatial groupings that may be related to Total Impervious Area (TIA) and/or land use (Jolly, 2003). Based on these results, I expanded the number of sample sites to 15 throughout the three watersheds and began a more comprehensive exploration into the usefulness of the CPI as a tool for urban water quality monitoring.

Layout of Thesis

This thesis is divided into eight chapters. I discuss the current state of water quality in my study streams in Chapter 2. This chapter also includes a detailed discussion of the development of the CPI, what the components of the CPI measure, water quality studies related to landscape water quality linkages, and previous water quality research done in the Knoxville urban area. Chapter 3 discusses the climate, landscape and geology of the study area and individual water characteristics. My methods and sources for obtaining landscape and geologic basin characteristics are included in this chapter. Chapter 4 details my water sampling and testing methods and compares the water quality data I collected to the data reported by Stewart (2001). This chapter also discusses the different methods of interpreting the CPI to characterize water quality. Chapter 5 applies statistical methods for characterizing water quality data and compares the results of these analyses to the results obtained using the CPI method. Chapter 6 uses statistical techniques to relate both the CPI and its constituents to landscape characteristics to explore whether they reflect relationships seen in the literature. Chapter 7 describes the development of the HSPF simulation and compares the results of this model with site characterizations generated with the CPI. My conclusions about the usefulness of the CPI as a watershed monitoring technique for community monitoring groups and the effectiveness of the different water quality characterization methods I used during this research are presented in Chapter 8.

CHAPTER 2

METHODS OF STREAM WATER QUALITY ANALYSIS

Development of the Index

Arthur J. Stewart developed the Chemical Perturbation Index (CPI) in response to a perceived need for a mechanism that integrates science into community-based decision-making in the realm of watershed management. His paper, "A Simple Stream Monitoring Technique Based on Measurements of Semiconservative Properties of Water," offered many policy-based arguments detailing how the CPI would be a useful tool for watershed management at the local level (Stewart, 2001). Because this thesis applies and tests the CPI, it is informative to first review the circumstances under which the CPI was developed and how the CPI is computed, used, and interpreted.

The development of the Chemical Perturbation Index was one result of broad-based stream biological monitoring programs undertaken by the Department of Energy facilities located in and around Oak Ridge, Tennessee (Stewart, 2001). These studies spanned a 13-year period and involved more than 55 individual monitoring sites on 16 streams. Much of the research done during these studies focused special attention on the relationship between stream water chemistry and stream ecologic condition. Stewart used data collected during these stream-monitoring programs to compute the CPI for multiple sample sites located on five streams (East Fork Poplar Creek, Melton Branch, White Oak Creek, First Creek, and Fifth Creek). Grab samples were collected from each site daily for a period of seven days either on a once per month or once per quarter basis, depending on the needs of the specific research projects.

Computed from a time series of chemical observations obtained from a specific site, the CPI is the sum of the three pairwise Spearman's rank correlation coefficients between alkalinity, hardness, and specific conductance. Spearman's rank correlation coefficient varies between –1 and 1, with positive 1 indicating a perfect positive linear relationship between two variables and –1 indicating an inverse relationship. Neither of these 'perfect' relationships is likely to be found in nature. Computing the CPI involves summing the three correlation coefficients and subtracting them from 3.0, resulting in an index that varies from 0 to 6. The bicarbonate-rich natural waters generally found throughout the United States tend to exhibit a near unity relationship between alkalinity and hardness and almost always have a positive relationship between hardness or alkalinity and specific conductance (Stewart, 2001). Non-perturbed systems would thus be expected to exhibit a high degree of correlation between the parameters, usually no less than 0.4 or 0.5, resulting in low CPI values (approaching zero). Larger index values indicate a greater the amount of perturbation (disturbance) in the natural system.

Stewart (2001) provided three examples that demonstrated how spatial and temporal changes in water quality can be described by the CPI. The first example used both annual and seasonally-matched data to depict stream conditions in White Oak Creek, First Creek, and Fifth Creek. Data from 80 to 84 samples, collected March 1986 to March 1987, showed that sites in the headwaters of these streams had low index values (0.14, 0.21, and 0.35), and that CPI values increased with distance downstream (59.9%/km, 14.6%/km, and 39.4%/km) as the streams received wastewater inputs from

Oak Ridge National Laboratory facilities. Comparing index values computed from two seasonally-matched time periods from the years 1986-1989 and 1991-1992 shows how the CPI can indicate both spatial and temporal changes in water quality. Once again, the sites exhibited an increase in CPI values with distance downstream. Additionally, a large difference in CPI values between the two time periods was evident (Figure 2.1). Lower values for the CPI during the 1991-1992 time period demonstrate the results of a number of pollution abatement programs instituted by ORNL facilities in response to National Pollutant Discharge Elimination System (NPDES) permit requirements. Significant improvements in fish and invertebrate communities over the same time period provide corroborative evidence of the improvement in water quality shown by the CPI (Stewart, 2001).

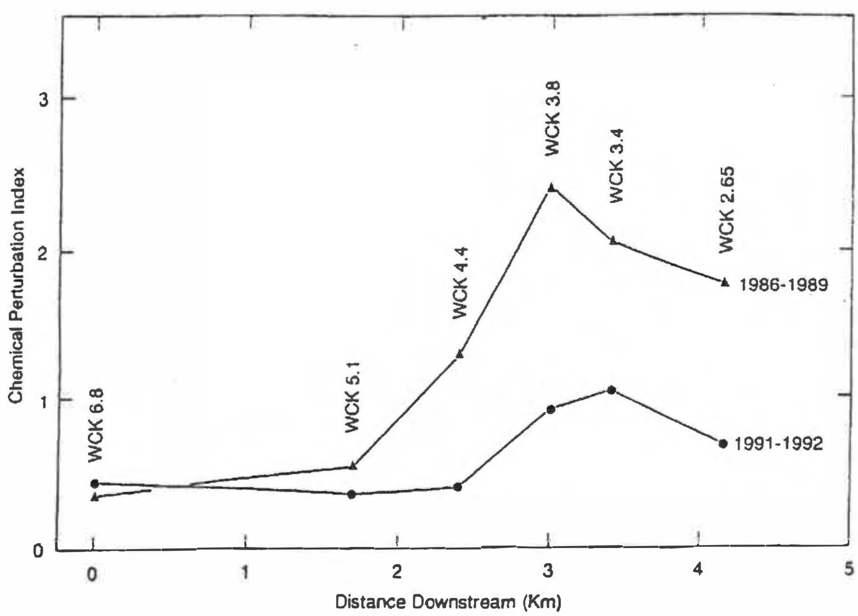

Figure 2.1: CPI Values for White Oak Creek (Source: Stewart, 2001)

Melton Branch, a 1.9 km long tributary of White Oak Creek, provides another good example of the CPI's ability to indicate both spatial and temporal changes in water quality. Three sites were sampled on this tributary, two above and one below a DOE High Flux Isotope Reactor that contributes from 23.3% to 43.9% of the stream's average annual flow (Stewart, 2001). The site above the reactor discharge point exhibited low index values (0.70, 0.53, 0.29, 0.14, and 0.47) over five time periods between 1986 and 1992. In contrast, the two sites below the point source discharge had significantly higher index values over four of the time periods (3.52-3.67, 3.43-3.02, 2.41-1.83, and 3.61-3.70). During the second sampling period, from 2/19/87-12/20/89, all three sites had similar CPI values (0.53, 0.56, and 0.61). This can be directly attributed to the fact that reactor operations stopped during this time period and no wastewater was discharged. Sites on the East Fork Poplar Creek showed the same response (lowering of the CPI) in index values to changes in wastewater inflows as sites in White Oak Creek and Melton Branch. Several new wastewater treatment facilities were brought on line in October 1988 at the Y-12 Plant, and CPI values for those sites in the East Fork Poplar Creek below the High Flux Isotope Reactor were significantly reduced.

The simplest way to interpret the Chemical Perturbation Index is to compare the index values between sites; however, due to site-specific differences, no universal value for the index can be used as a threshold value when characterizing water quality. Calculating Spearman's rank correlation coefficients for the high number of observations needed to compute the CPI requires use of a statistical software package, but some community groups or individuals may lack the resources or training to do the calculations. In part because of these factors, Stewart explored a method of graphically illustrating deviations in the natural covariance between alkalinity, hardness, and specific conductance by plotting the ratio of alkalinity to hardness (A:H) versus specific conductance. Two assumptions were made, first that there is a near-unity relationship between alkalinity and hardness in most surface waters, and second that runoff from developed areas and point source contributions tend to be ion-rich in comparison to the receiving stream. The physical basis for these assumptions will be discussed in greater detail later in this chapter. Stewart used data from 15 sites, each sampled 84 times over a 12-month period, on streams near the Oak Ridge National Laboratory in the White Oak Creek watershed to create a plot of the relationship between the CPI's components (Figure 2.2). Observations from the three headwater sites, those above known point sources, clustered together and are defined on the graph with a square bounded by A:H ratios from 0.74 to 1.08 and specific conductance readings between 80µS and 380µS. Most of the observations with conductivities greater than 500µS and low A:H ratios were from sites below the High Flux Isotope Reactor on the Melton Branch. Establishing bounding limits for the reference sites allows for easy recognition of observations that may be indicating pollution inputs.

In the course of developing and testing the Chemical Perturbation Index, Stewart came to several conclusions. CPI values are most easily used to compare sites or detect long-term change in water quality conditions at a given site over time. The CPI method intrinsically incorporates temporal variation in water quality conditions by requiring the collection of samples over time but compares how those variables relate to each other without any specific association with time. Researchers can gain more detailed information about stream water quality and steam ecology using more time-consuming

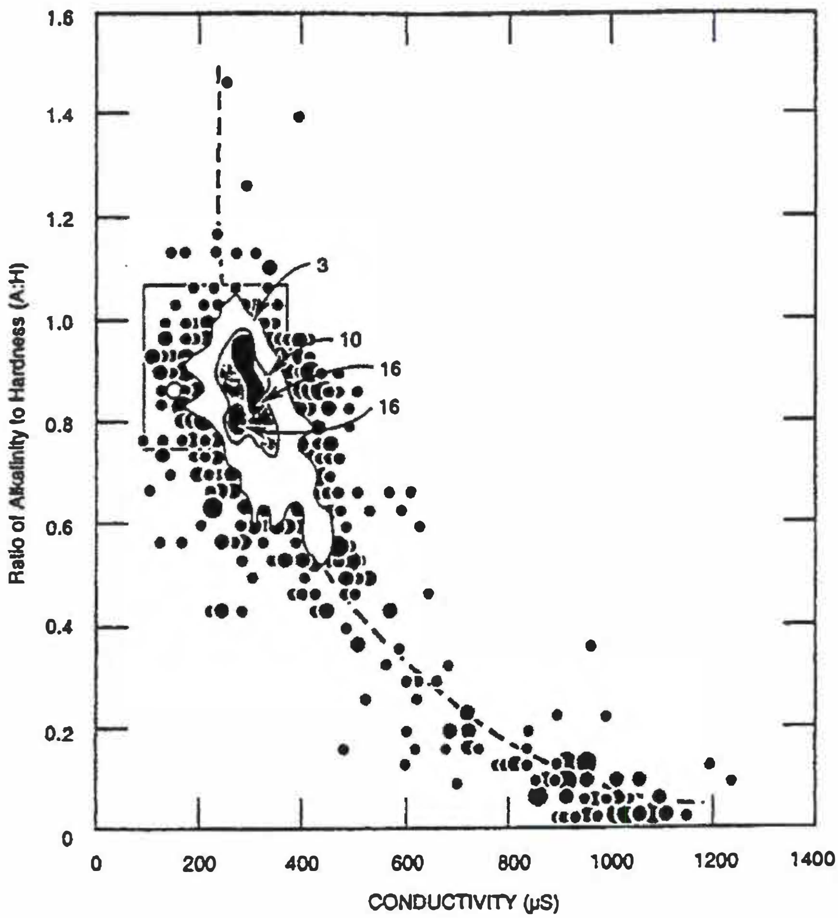

Figure 2.2: Plot of A:H ratio vs. Specific Conductance (Source: Stewart, 1997)

and expensive sampling protocols, but these methods are difficult to incorporate into community water monitoring programs. The CPI method uses easily measured and inexpensive water-quality parameters but provides only non-specific indications of water quality. Some of the limitations of biological and specific-constituent monitoring as part of stream monitoring programs may be overcome by using techniques such as the Chemical Perturbation Index (Stewart, 2001). Stewart's analysis offered strong evidence that the CPI does provide a useful indication of the temporal and spatial changes in water quality for streams with specific point source inputs.

Alkalinity, Hardness, and Specific Conductance

Understanding the water quality constituents measured by the parameters derived from water samples to calculate the Chemical Perturbation Index, and how those constituents relate to each other, is necessary for accurate and complete interpretation of CPI results. The underpinning assumption of this method is that the three parameters — alkalinity, hardness, and specific conductance — will tend to vary in unison in natural waters. This assumption is justified for most regions of the United States, but may not be true under certain geologic and environmental conditions. Here, I will briefly discuss alkalinity, hardness, and specific conductance, and the similarities and differences in the constituents they measure.

Alkalinity

Alkalinity, a measure of the ability of a body of water to accept protons, is commonly referred to as the water's buffer capacity (Lind, 1985). Buffers are solutions that resist changes in hydrogen ion concentration (pH) when either basic or acidic solutions are added. A weak acid may become a buffer when alkaline constituents are added, and conversely, a weak base may become a buffer when a weak acid is added. Total alkalinity is a measure of a stream's buffering capacity or its ability to turn acidic solutions entering the stream into buffer materials. Total alkalinity is the sum of three constituents: hydroxide (OH^-), normal carbonate (CO_3^{-2}), and bicarbonate (HCO_3^-) ions; however, by convention it is generally reported as mg/L of calcium carbonate ($CaCO_3$). Five conditions of alkalinity can exist in a stream sample: carbonate, bicarbonate, or hydroxide alone; a combination of carbonate and hydroxide, or a combination of carbonate and bicarbonate — bicarbonate and hydroxide ions are not found together (Lind, 1985). When a strong base is added to water, it reacts with carbonic acid (found in abundance in most natural waters) to form bicarbonate and eventually carbonate, using up the base in the process. When acid is added to a stream, it is used in the conversion of carbonate to bicarbonate and bicarbonate to undissociated H_2CO_3 (carbonic acid)(Cole, 1988). Bicarbonate and carbonate are generally responsible for measured total alkalinity in natural waters except in waters with a high pH (Hem, 1985). Hydroxides are rare in nature; the presence of hydroxides in water samples can generally be attributed to anthropogenic sources. Alkalinity is ordinarily a function of the geology of a drainage basin and the amount of chemical weathering that is taking place (Cole, 1988).

Hardness

Hardness refers to cations that form insoluble compounds with soap. Hardness, for water quality applications, refers to the concentration of calcium and magnesium ions in a sample; however, for convention it is reported as mg/L of calcium carbonate ($CaCO_3$). When no other ions are present in significant amounts, hardness will be equal to the sum of the carbonate and bicarbonate alkalinities; this is known as carbonate hardness. Hardness can exceed the sum of these alkalinities due to the presence of sulfates and chlorides that are not revealed by alkalinity measurements. Conversely, sodium and potassium compounds can contribute to alkalinity but not be revealed by hardness titration. For example, samples taken from soda lakes (salt lakes) may have alkalinity readings up to 6000 mg/L but practically no hardness (Cole, 1988). Organic ligands, phosphate alkalinity, silicates, arsenates, borate, and aluminates may also contribute to alkalinity without corresponding increases in hardness values.

Specific Conductance

Specific conductance is the measure of a water body's capacity to conduct electricity. Specific conductance values for natural waters are generally reported in microsiemens (μS), that is, equivalent to the water's electrical resistance in micromhos (*mho*) measured over a distance of 1 cm. The value of specific conductance is that it is a simple way to analyze the total dissolved solids (TDS) of a sample. As a water body's ion concentration increases, its specific conductance will also increase. In fact, using the formula $Kc = T$ where K is specific conductance and c is an empirically determined coefficient, T, or total dissolved solids can be calculated (Cole, 1988). The concentration of ions (measured by TDS and specific conductance) in a water body gives an indication of its productivity and can be used as a way to check for alterations in total water quality by the addition of many types of pollutants (Lind,1985). Carbonate, most commonly occurring as the bicarbonate ion, is the principal anion found in dilute fresh waters in humid regions throughout the world (Cole, 1988). Hem (1985) found that specific conductance commonly is strongly associated with carbonate ions.

Association Between Alkalinity, Hardness, and Specific Conductance and Pollution

Typical inland water systems can be described as calcium bicarbonate solutions. Carbonate and bicarbonate in surface waters are produced primarily through the chemical weathering of carbonate rocks (e.g., limestone and dolomite). Precipitation is naturally acidic due to its exposure to atmospheric carbon dioxide (CO_2), and ground water is also saturated with CO_2, and therefore acidic, because of bacterial processes. As ground water or meteoric water flows over and percolates through soils and rock formations, the acidity produced by the CO_2 dissolves limestone to form bicarbonate salts (Wurts and Durborow, 1992):

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \quad \text{(Eq. 1)}$$

or

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 = Ca^{2+} + Mg^{2+} + 2HCO_3^- \quad \text{(Eq. 2)}$$

This increases the receiving stream's alkalinity and carbonate hardness while also increasing the concentration of ions, thus increasing specific conductance. This process defines the chemical makeup of most inland waters, and it produces the primary constituents measured by alkalinity, hardness, and specific conductance, leading to a strong natural covariance between these parameters. Samples taken from Knox Spring, near Jefferson City, Tennessee illustrate the strong relationship between lithology and water chemistry found in East Tennessee (Hem, 1985, Figure 2.3). The Knox Spring sample site is located in a dolomite formation from the same geologic complex (Knox) as my research area. The left bar of the graph, which represents hardness as the sum of magnesium and calcium ion concentrations, is nearly equal to the bar representing bicarbonate, the primary contributor to alkalinity.

Constituent	1 Feb. 27, 1952 mg/L	meq/L
Silica (SiO_2)	8.4	
Aluminum (Al)	1.4	
Iron (Fe)	.24	
Calcium (Ca)	40	1.996
Magnesium (Mg)	22	1.809
Sodium (Na)	.4	.017
Potassium (K)	1.2	.031
Carbonate (CO_3)	0	
Bicarbonate (HCO_3)	213	3.491
Sulfate (SO_4)	4.9	.102
Chloride (Cl)	2.0	.056
Fluoride (F)	.0	.000
Nitrate (NO_3)	4.8	.077
Dissolved solids:		
Calculated	190	
Residue on evaporation	180	
Hardness as $CaCO_3$	190	
Noncarbonate	16	
Specific conductance (micromhos at 25°C).	326	
pH	7.4	
Color	5	

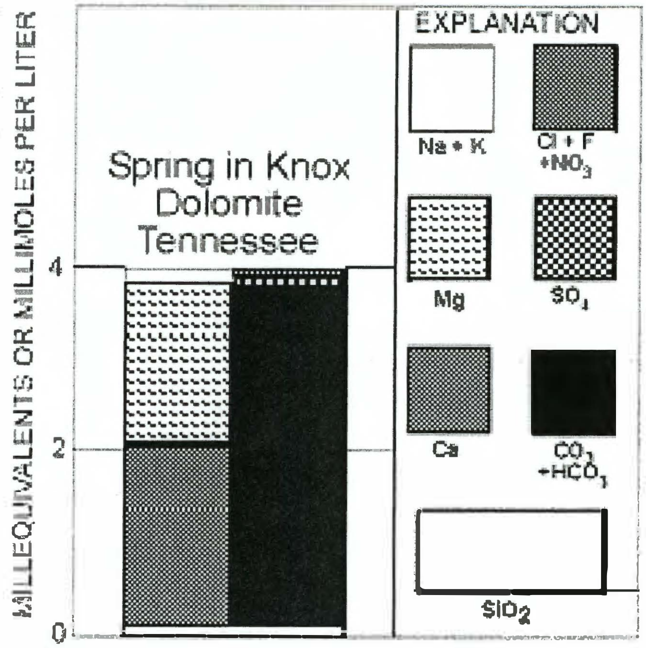

Figure 2.3: Knox Spring Constituent Loadings (Source: Hem, 1985)

Accepting that the relationship between alkalinity, hardness, and specific conductance is strong in natural waters, the second assumption central to the Chemical Perturbation Index concept is that deviations in the relationship between these measures are due to anthropogenic forcing. Chemical interactions allow some pollutants to be measured by one or more of the parameters used to calculate the CPI in some chemical forms while not in other forms. For example, orthophosphates (PO_4^{-3}) enter the stream from many sources, including soil and rocks, wastewater treatment plants, runoff from fertilized lawns and crop land, failing septic systems, runoff from manure storage areas, disturbed land areas, drained wetlands, road salt (which incorporates phosphorus compounds as anti-caking agents), and commercial cleaning preparations (Dates, 1994). This and other forms of the phosphate ion (PO_4^{-3}, HPO_4^{-3} and $H_2PO_4^{-2}$) may combine with H^+ and increase alkalinity measurements. Anthropogenic activities can affect CPI values in many ways. Industrial discharges into streams may change the specific conductance and alkalinity depending on their composition. A failing sewage system would raise the specific conductance and possibly alkalinity because of the presence of chloride, phosphate, and nitrate in sewage discharges; conversely, an oil spill would lower the specific conductance (USEPA, 1997). Certain forms of chloride and sulfur, both of which may be the result of a variety of anthropogenic forcings, would increase hardness values (Cole, 1985). Many of the constituents that may change the value of one or more of the parameters used to calculate the CPI are the result of pollutants entering the stream. These pollutants in many cases will change alkalinity, hardness, or specific conductance but not all three, thus the correlation between the parameters measured by Spearman's rank correlation coefficient will be reduced. The chemical reactions that determine the values of the individual parameters and relationships between the parameters are complex; however, they are predictable and can therefore provide some inferences about the causes of any chemical perturbations observed at a sample location.

Human activities may modify the chemical composition of natural waters through direct pollution, from both point and non-point sources, and by the indirect results of development, such as the modification of flow paths water takes before entering the receiving body (Hem, 1985). Many studies have used a variety of chemometric (the statistical treatment of chemical data) approaches to characterize water quality and relate it to anthropogenic controls (Dow and Zampella, 2000; Silva and Williams, 2001). Several of the water quality parameters used in these studies have provided consistent results. Water quality parameters have been used to describe the disturbance regime in watersheds, and a number of these research projects, discussed in the next section, indicate that specific conductance, alkalinity, and hardness are sensitive to watershed disturbance regimes.

Related Water Quality Research

CPI Water Quality Parameters as Indicators of Watershed Disturbance

To obtain additional information on the association of the parameters used to calculate the CPI and characterize the landscape, I looked at a series of research projects in the New Jersey pinelands that compared the water chemistry of watersheds draining a broad range of land uses and were able to relate water quality to landscape characteristics (Zampella, 1994; Dow and Zampella, 2000). In the southern New Jersey study area, located on the Atlantic Coastal Plain, ground water discharge accounted for 89% of the annual flow of the streams sampled. Ground water discharge also accounts for a large percentage of the annual flows in Knoxville's Third, Second and Goose Creeks (Kung, 1980).

In the initial New Jersey study, data for chemical water parameters were collected and summarized from 14 sample sites (Zampella, 1994). A water quality gradient of increasing pH, specific conductance, calcium, magnesium, nitrate nitrogen, ammonia nitrogen, and total phosphorous was found to correspond to a watershed disturbance gradient of increasing land use intensity. The intensity of the associations between these variables was investigated by calculating Spearman rank correlation coefficients for median values (Zampella, 1994). Strong positive correlations existed between all seven water quality variables with each other. Spearman's r-values of 0.92 and 0.98 were found between specific conductance and the main constituents of hardness, calcium and magnesium, supporting the assertion that specific conductance is often strongly associated with carbonate ions. The lowest correlation coefficient between specific conductance and the other variables was 0.79 for ammonia nitrogen. Substantial changes associated with increased land use intensity and domestic wastewater flows were observed for all the water quality variables (Zampella, 1994).

Based upon the results of Zampella's 1994 research, Dow and Zampella (2000) looked at pH and specific conductance as potential indictors of watershed disturbance. It is important to note that their research involved naturally acidic streams and thus allowed for more dramatic increases in pH due to pollutant inputs than would be observed in more alkaline streams. Using sample values collected at 45 sites over a period of two years, Dow and Zampella showed pH and specific conductance to relate to altered land use (a surrogate for watershed disturbance) consistently across sub-regions. They established a correlation between pH and specific conductance (independent variables) and percentage altered land use within the sub-watersheds (dependent variables) with a predictive linear regression model. No statistical difference was found between the intercept and slope coefficients of single-sample and median-defined models. Including both parameters in a single-sample model explained 79% of the variation in altered land use. By using a variety of regression models, Dow and Zampella demonstrated a consistent water-quality versus altered-land relationship across a range of conditions. The increased amount of variance explained by models using both variables indicates that each variable reflects different disturbance effects than the other. Their general conclusion was that these indicators could be used for a quick assessment of watershed disturbance, to indicate general water quality conditions, and as a 'red flag' to indicate the need for more comprehensive sampling. Their conclusion supports Stewart's (2001) assertion that specific conductance, as a measure of TDS, is an indicator of pollution associated with increased urbanization.

Silva and Williams (2001) investigated the benefits and limitations of using existing USGS databases to determine the effects of both human and natural landscapes on water quality and to compare the influence of catchment-wide landscape variables to that of 100 m buffer zone landscape characteristics. They analyzed data from 12 Ontario Ministry of Environment water quality monitoring sites in three watersheds, located on the east side of the Greater Toronto Area, for 11 variables, including alkalinity and total solids (Silva and Williams, 2001). Using GIS, they defined the landscape characteristics for each sub-catchment and buffer zone based on four land use and four surficial geologic categories. Six independent variables (percent agricultural, forested, urban, and pasture land use, standard deviation of slope, and percent silt and clay deposition) were used to determine the nature and strength of the relationship between individual water quality parameters and landscape characteristics. They used redundancy analysis (RDA) and multiple regression to explore the interactions between landscape variables when explaining the variation in water quality parameters.

Silva and Williams (2001) used multiple regression to determine whether landscape variables had a positive or negative effect on separate water quality variables and how strong the influence was using the six predictor (independent) variables. Using RDA, Silva and Williams gained insights into which landscape factors had the greatest influence on the ordination of axes (variates) and the portion of each predicted variable explained. The most significant results of the Silva and Williams (2001) research pertaining to the CPI were that urban land use exerted the greatest influence on water quality, and alkalinity was not strongly correlated with any landscape parameters. The lack of association between alkalinity and landscape factors suggests that urban areas may produce deviations in the strength of the natural correlation between specific conductance, which is related to landscape, and alkalinity. This would suggest that rank correlation coefficients between specific conductance and alkalinity would be lower in watersheds with urban areas than in undisturbed watersheds. Urban and forest were the dominant variables explaining the variance for all the water quality parameters. Slope was the dominant variable in the second axis explaining variation during the fall and spring months. Urban land appeared to exert a stronger influence on water quality within the buffer zone, and forest appeared to exert the strongest influence at the catchment scale. Both the multiple regression and RDA showed water quality to be slightly more correlated with catchment scale landscape than buffer scale landscape.

Johnson and others (1997), in a midwestern stream study, also researched the relationship between landscape factors and surface water chemistry. They developed landscape structures based both on land use and surficial geology using multiple regression and redundancy analysis to explore the relationships between landscape and water chemistry. Urban land use was the most important explanatory factor with regard to total dissolved and suspended solids. This agrees with previous studies that showed specific conductance, an indicator of total dissolved solids, to be correlated with urban land use. Temporal analysis showed autumn samples had a weak relationship between agricultural land use and alkalinity, probably due to a reduction in the amount of fertilizer applied. A positive relationship between nitrate, alkalinity, and specific conductance was observed in all catchments, and the constituents measured by alkalinity as a percentage of the total dissolved solids were nearly constant throughout the sample data. As with previous studies, mixed results were obtained when comparing buffer landscape influences to whole catchment landscape influences. Individual water quality parameters varied in the direction and intensity of their associations at the different landscape scales. The reported connections between land use and chemical parameters are corroborated by these and other research studies involving alkalinity, hardness, and specific conductance.

Urbanization and Water Quality

A defining feature of urbanization is a decrease in perviousness and a corresponding increase in surface runoff (Dunne and Leopold, 1978). Urban runoff is a major contributor to the degradation of urban streams. Impervious source areas are likely to contribute most of the surface runoff to a stream during small storm events when the infiltration capacity of pervious areas is not exceeded (Pitt *et al.*, 1995). Impervious surfaces collect, accumulate, and convey a variety of pollutants to surface waters. Watershed studies have consistently indicated that urban pollutant loads are directly related to the proportion of a catchment's total impervious area (Schueler, 1994). Due to the consistently strong relationship found between impervious cover and water degradation, Schueler (1994) called impervious surfaces "a very useful indicator with which to measure the impacts of land development on aquatic systems."

Urban streams exhibit increased levels of many constituents. Two consistently higher constituents are total suspended solids and oxygen demand (Paul and Meyer, 2001). These increases can be attributed to the effects of non-point-source runoff. Sufficient dissolved oxygen (DO) levels are critical for maintaining healthy aquatic life in surface waters. Biological oxygen demand (BOD), a biological indicator of water quality, measures the amount of oxidizable substances in the water that can reduce DO by determining the amount of oxygen consumed by bacteria from the decomposition of organic matter (Delzer and McKenzie, 2003). BOD is used as an indicator of the amount of organic waste in surface waters and is commonly used to indicate the effects of sewage in a stream. Suspended solids include all organic and inorganic material held in suspension by the water. Suspended solids transport nutrients, pesticides, trace elements, or any other constituent that may be adsorbed by soil particles (Veenhuis and Slade, 1990). Both suspended solids and BOD are strong indicators of water quality because of their association with pollutants.

Research indicates not only that urbanization increases constituent loadings during storm flow, but that the loadings increase at base flow levels as well. Veenhuis and Slade (1990) analyzed water quality constituents during storm flow and base flow at 18 sites in the Austin, Texas area. With the exception of dissolved solids, they found that, in general, median concentrations of samples taken at sites draining more urbanized areas were significantly larger during the rising and falling stage of storm flow as well as at base flow. The mean concentration and variability of BOD also increased with increasing impervious cover. During base flow, suspended solid concentrations from samples taken at sites classified as urban or partly urban were slightly larger than those taken from sites classified as rural or mostly rural.

Significantly for this thesis, research also shows that major ion concentrations are elevated during base flow in urban catchments. A study of major ion geochemistry in the Atlanta metropolitan region found that concentrations of total dissolved solids, calcium, magnesium, sodium, sulfate, and chloride and alkalinity values were elevated in the urbanized basin when compared with values from a less urbanized basin (Rose, 2002). Urbanization in this case seems to have reversed the expected ion level concentrations. Differences in major ion concentration are usually attributed to lithologic differences. The non-urbanized basin in the Atlanta study is characterized by more soluble geologic formations that should have resulted in higher levels of alkalinity and base ions due to more rapid weathering; however, the opposite situation was observed. These findings support Stewart's (2001) assertion that urbanized areas will disrupt the natural relationship between stream geochemistry and geology.

Previous Studies in Knoxville, an Urban Area

Several studies assessing water quality have been conducted within my study watersheds in Knoxville, Tennessee. In the early 1970s, Betson undertook a study of the hydrology of urban areas in Knoxville with an emphasis on water quality, using mathematical models (Betson, 1976). Four sub-watersheds were sampled, one each from Fourth Creek, Third Creek, First Creek, and Plantation Hills. Betson's findings in Third Creek are especially relevant to this thesis. Integrated single storm samples were taken from the East Fork of Third Creek at Proctor Avenue by an automatic sampler from May 1972 until December 1974. The contributing area for this site was characterized as industrial/commercial, but also included several high-density housing developments and residential areas; the population density in 1970 was estimated to be 18.8 persons per hectare. In addition to the automatic sampler, a rain gage, stream gage, and bulk precipitation sampler were installed in the watershed to provide model inputs. Several mathematical models were used to determine the impact of urbanization on the stream.

In Betson's (1976) analysis, observed sample values and model results separated Third Creek from the other study sites in several ways. Stream flow models showed transmission loss in Third Creek to be negligible due to the less soluble geologic formations characterizing the drainage area. Betson theorized that observed flows in the other study areas were less than predicted flows because underground drainage allowed significant portions of the stream flow to bypass the gage. Observed constituent loadings were higher in Third Creek than the other creeks, perhaps due, in part, to a higher percentage of ground water contribution to stream flow. Betson's (1976) Third Creek models had elevated sulfate and chloride levels when compared to models based on rural land use.

Another significant finding of Betson's (1976) study was that, unlike all the other study catchments, atmospheric loading from bulk precipitation in Third Creek could not account for observed pollution loading. This led Betson to conclude that urbanization did impact pollution loading in Third Creek to a greater extent than in the other watersheds. This is potentially the result of the relatively insoluble geologic formations and impermeable soils in Third Creek. Urban runoff from regions not directly connected to the stream in the other catchments entered the stream through subsurface flows, allowing them to be filtered by the soils and rock formations. For example, in the Betson study, the Plantation Hills drainage had a total impervious surface value only slightly lower than that of Third Creek, yet the runoff yield was about one-tenth that of Third Creek. This difference was attributed to the soluble carbonate rocks underlying the Plantation Hills drainage. Median values for hardness, alkalinity, and specific conductance as well as the bulk precipitation constituent loadings reported in Table 2.1 are also of interest for comparison with my sample and model data.

Expanding on Betson's initial results, and as part of the Nationwide Urban Runoff Program (NURP), Milligan and Betson conducted projects in Second Creek and First Creek, which were known to be highly degraded (Milligan, 1984). Urban runoff was the suspected cause of degradation in these two urban drainages. Four subbasins, three within Second Creek and one within First Creek, were chosen for water quality analysis, and two additional subbasins in Second Creek were added to investigate the effect of carbonate geology on the hydrologic transport of storm runoff (Milligan, 1984). The predominant land uses of the six subbasins were low density residential (3), medium density residential (1), strip commercial (1), and high density commercial (1). Rainfall; atmospheric deposition, both dry and wet fall; stream flow; and runoff water quality data for four of the sites were collected during 27 storm events.

Milligan calculated Event Mean Concentrations (EMC) for each of the sample sites using discrete sample data (Milligan, 1984). EMC's can be represented in simple form by the equation:

$$EMC = Total\ load\ /\ Total\ runoff \qquad (Eq.\ 3)$$

Table 2.1: Median Values of Storm Flow and Bulk Precipitation Samples, Third Creek (Betson, 1976)

Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (μS)	Nitrite-nitrate-nitrogen (kg/ha/yr)	Total Phosphorus (kg/ha/yr)	Total Suspended Solids (kg/ha/yr)	Biological Oxygen Demand (kg/ha/yr)
130	110	290	5.6	13	1100	95

Runoff loads were calculated by subtracting baseflow load from the total storm load, and baseflow load generally accounted for a large percentage of total storm load (Milligan, 1984). Predicted annual stormwater runoff loads for Second Creek exceeded the summed average annual loads of four wastewater treatment facilities in the Knoxville vicinity discharging into the Fort Loudoun reservoir, indicating urban runoff may be contributing a significant amount of pollution to the reservoir. Modeling also showed an inverse relationship between percentage of impervious area and runoff losses to the carbonate rock solution channel; that is, areas with the least imperviousness retained more pollutant inputs than regions with a greater amount of imperviousness.

Data collected during Milligan's (1984) study were analyzed to explore two questions about urban runoff quality and quantity: 1) the effect of land use on urban runoff quantity and 2) the effect of carbonate geology on urban runoff quality and quantity. The data in this study indicated that in areas underlain by carbonate rock, the amount of imperviousness and runoff pollutant load have a positive relationship; that is, as imperiousness increases, so does pollutant load. Alkalinity showed a moderate loading response to urbanization, while total dissolved solids had a high loading response. Milligan came to the conclusion that, in Second Creek, the soluble carbonate geology is the main controlling factor of the area's hydrology. Significant quantities of runoff originating in pervious areas do not leave the drainage via surface flow but through sub-surface drainage paths. This could lead to an underestimation of pollutant export from Second Creek by models that are based on observed surface water characteristics alone. The models being developed and tested by Milligan and Betson were based on regression equations developed to estimate pollutant export from catchments based on land use and meteorological data. Milligan's findings suggest that geology is an important factor controlling the amount of surface runoff and should be considered in surface runoff models. Additionally, regions of karst geology can affect pollutant loadings by introducing more complicated subsurface flow patterns. Subsurface flow through karst formations may be filtered by soil and rock formations or pass relatively quickly through voids in the geologic formations that act as subsurface stream channels.

Summary of Research Applicable to the Testing of the Chemical Perturbation Index

There is strong evidence to suggest that, over relatively large scales, water quality parameters, particularly specific conductance, show strong correlations to broad land use types (urban, agricultural, forest, etc.). Most current research has been conducted over extended periods of time (> 1 year) and in geographically large drainage basins. The research presented in this thesis was designed to discover whether the parameters that comprise the CPI will also differ significantly over smaller spatial scales. The CPI has been shown to be an effective indicator of water quality degradation downstream of pollution point sources. Research has shown that some of the parameters that comprise the CPI are strongly related to land use; however, the CPI had not previously been tested for its ability to distinguish water quality differences primarily caused by pollutants from non-point sources. Finally, while other researchers have related stream water quality to landscape characteristics, the type and strength of these associations vary between watersheds. Therefore, specific water quality parameters that accurately describe one watershed may not be appropriate descriptors of others.

CHAPTER 3

STUDY AREAS

Introduction

To test the CPI's ability to give a quantitative assessment of water quality conditions in urban watersheds, I selected three small urban catchments, Third Creek, Second Creek, and Goose Creek, in the Knoxville urban area. These streams represent a variety of landscape and geologic conditions. This chapter describes the sources of data and techniques I used to derive landscape and geologic characteristics for each of the watersheds and the subbasins associated with my sample sites.

One primary foundation of the theory behind the Chemical Perturbation Index (CPI) is that the parameters used to calculate it are controlled by environmental variables such as geology and weather/climate. Therefore, I acquired detailed information on these variables for my study watersheds. The chemical makeup of surface waters is strongly related to the path or paths precipitation takes before entering the receiving water body. Understanding the differences in soils and geology between individual sites and watersheds aids in the interpretation of water chemistry data and allows for an examination of the effects environmental variables may have on CPI values. The timing and duration of storm events are also important factors for the interpretation of water quality data. Landscape modification associated with urbanization, such as increased total impervious area (TIA), has been linked to water quality (Pitt *et al.* 1995, Johnson *et al.* 1997, Paul and Meyer, 2001). Differences in the landscape and geologic characteristics of the subwatersheds may provide indirect evidence of the surface water quality conditions at sites within them.

Location and Climate

Second, Third, and Goose Creeks are located within the Knoxville, Tennessee urban area. The mouth of Goose Creek is located at 35°56'N latitude and 83°55'W longitude. All three of these creeks are part of the Tennessee River watershed, designated with the Hydrologic Unit Code 0601020102 by the Environmental Protection Agency (Figure 3.1), and lie within the Ridge and Valley ecoregion. The Second and Third Creek watersheds are completely within the Level IV Southern Limestone/Dolomite Valleys and Low Rolling Hills subecoregion (67f) (Borders and Wang, 1998). Most of the Goose Creek watershed lies within the Southern Shale Valleys subecoregion (67g).

Knoxville, on average, received 119.86 cm (47.2 in) of rainfall annually during the period from 1948 to 1999 (NCDC 2003a). The highest average monthly rainfall occurred during March (12.94 cm) and the lowest rainfall average during October (6.79 cm). During this 52 year period, an average of 73.44 storm events occurred annually, with 'storm events' defined as events with total precipitation accumulations more than 2.5 mm and hourly accumulation rates of 0.25 mm or greater. The highest mean precipitation intensities (3.1 mm/hr) were observed during the summer months (June-August); the annual mean storm event intensity was 2.0 mm/hr.

Despite the higher storm intensities observed during the summer months, a large proportion (71%) of the annual floods in Eastern Tennessee occur during late winter and early spring. This reflects Knoxville's propensity to receive rainfall associated with

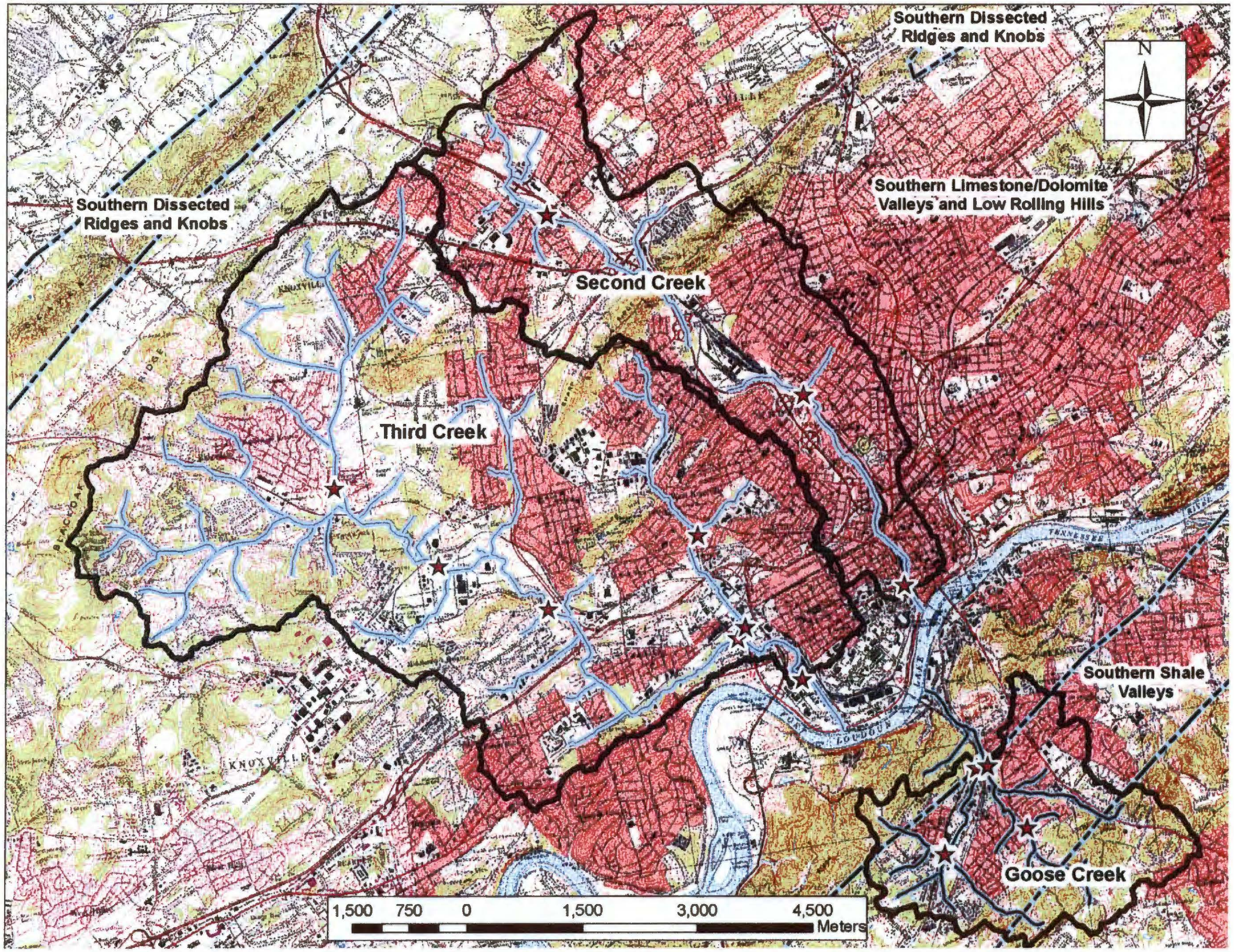

Figure 3.1: Watershed Location Map (Source: Griffith, 1995)

frontal boundaries during the winter and spring months, and the fact that during the warmer months evapotranspiration rates are higher and soil moisture is typically low, increasing the soil's potential water holding capacity (Lecce, 2000). Summer storm events, often the result of convective activity, are generally of shorter duration than winter storms. Ninety-five percent of 61 storms that produced over 7.62 cm of precipitation in Rogersville, Tennessee (approximately 129 km northeast of Knoxville) were identified as frontal events (Keim, 1996), suggesting that frontal events are the primary producers of precipitation in Eastern Tennessee. Frontal events typically have higher rainfall intensities, which potentially lead to more pollutant export in surface runoff from the land surface.

Methods for Deriving Surface Characteristics

To derive the surface characteristics of the study catchments and their subbasins, I used two geographical information system platforms developed by the Environmental Systems Research Institute (ESRI): ArcView and ArcGIS. I began the process of defining watersheds by digitizing the stream networks from digital raster graphics (DRG), which are scanned 7.5' topographic quads. Then I imposed this stream feature class on a 1/3-arc-second digital elevation model (10 meter DEM) and, using the Arc Hydro Tools application for ArcGIS, defined the watershed catchments and subbasins (Maidment, 2002). I calculated land use percentages, detailed soil distribution, slope, impervious surface, and geologic metrics for the sub-watersheds using environmental datasets obtained from the government sources and standard spatial analysis techniques with tools available with ArcMap8.3 (Greene and Wolfe, 2000; Minami, 2000; USGS, 1999, 2003a, 2003b). Subbasin soil characteristics including permeability, mean depth to bedrock, percent silt and clay, and soil erodibility were computed using the Better Assessment Science Integrating point and Nonpoint Sources (BASINS), a set of tools designed for the EPA that integrate into ArcView GIS (USEPA, 2001b). The State Soil Geographic Database (STATSGO) was used in the BASINS analysis. The STATSGO database was developed by the Natural Resource Conservation service (NRCS) from 1:250,000 scale topographic quadrangles (USDA, 1994). The minimum soil unit area mapped is about 625 hectares (1,544 acres). The percent slit and clay variable refers to the percentage of soil material by weight that is less than 7.6 cm (3 in) in size and passes through a number 200 sieve. Following geoprocessing and spatial analysis, I incorporated all the resulting layers into a single geodatabase.

Geology

The Third and Second Creek watersheds have complex lithologies consisting of formations from three different geologic groups (Hardeman, 1966). Formations of the Knox Group cover 47% of the Second Creek watershed and 62% of Third Creek watershed. The Knox Group is composed of siliceous, well-bedded dolomite and magnesian limestone (contains magnesium carbonate). Two of the main Knox Group formations present in Second Creek watershed are the Copper Ridge Dolomite, a coarse, medium-grained, well-bedded dolomite with abundant chert, and the Newala Formation, a fine-grained thickly-bedded dolomite formation (Hardeman, 1966). Longview Dolomite, Chepultepec Dolomite, and Jonesboro Limestone formations are also present in the Second Creek watershed but cover a larger area of the Third Creek watershed. The Jonesboro formation is a ribboned (silt and dolomite) limestone with numerous interbeds of dolomite and quartz sandstone base. Both the Longview and Chepultepec Dolomite formations are interbedded with limestone in the upper parts, and the Chepultepec formation has quartz sandstone beds at its base (Hardeman, 1966). The Copper Ridge Dolomite is the most soluble of these formations (Kung, 1980). Formations of the Conasauga Group cover 13% of the Third Creek and 22% of the Second Creek watersheds (Figure 3.2). Other than Maryville Limestone, generally the formations that comprise the Conasauga group are shale formations and are among the least soluble of the geologic formations present in these watersheds. Formations from the middle and lower parts of the Chickamauga Group cover 26% and 23% of the Third and Second Creek watersheds, respectively, and the entirety of the Goose Creek watershed. The predominant four formations of the Chickamauga Group are the Bays Formation, predominantly siltstone; the Ottosee Shale, a relatively insoluble calcareous shale with marble lenses; the Holston Formation, a crystalline limestone cross-bedded with shale that is the most soluble of all the geologic formations present in the study areas; and Lenoir Limestone, an argillaceous silty limestone (Hardeman, 1966). The earlier studies of Milligan (1984) and Betson (1976) underscore the possible effects of geology on flow and pollutant loads in watersheds within the Knoxville region.

Soil Characteristics

Kung (1980) found a significant correlation between soil depth, soil permeability, and underlying geology in urban watersheds in the Knoxville, Tennessee area. Soils greater than 1.2 m in depth with permeabilities more than 1.5 cm/hr are associated with carbonate geology. Shallow soils (less than 1.2 m in depth) and less permeable soils (less than 1.5 cm/hr) are generally associated with shale formations, specifically the Ottosee and Pumpkin Valley shales. This suggests that areas underlain by shale formations

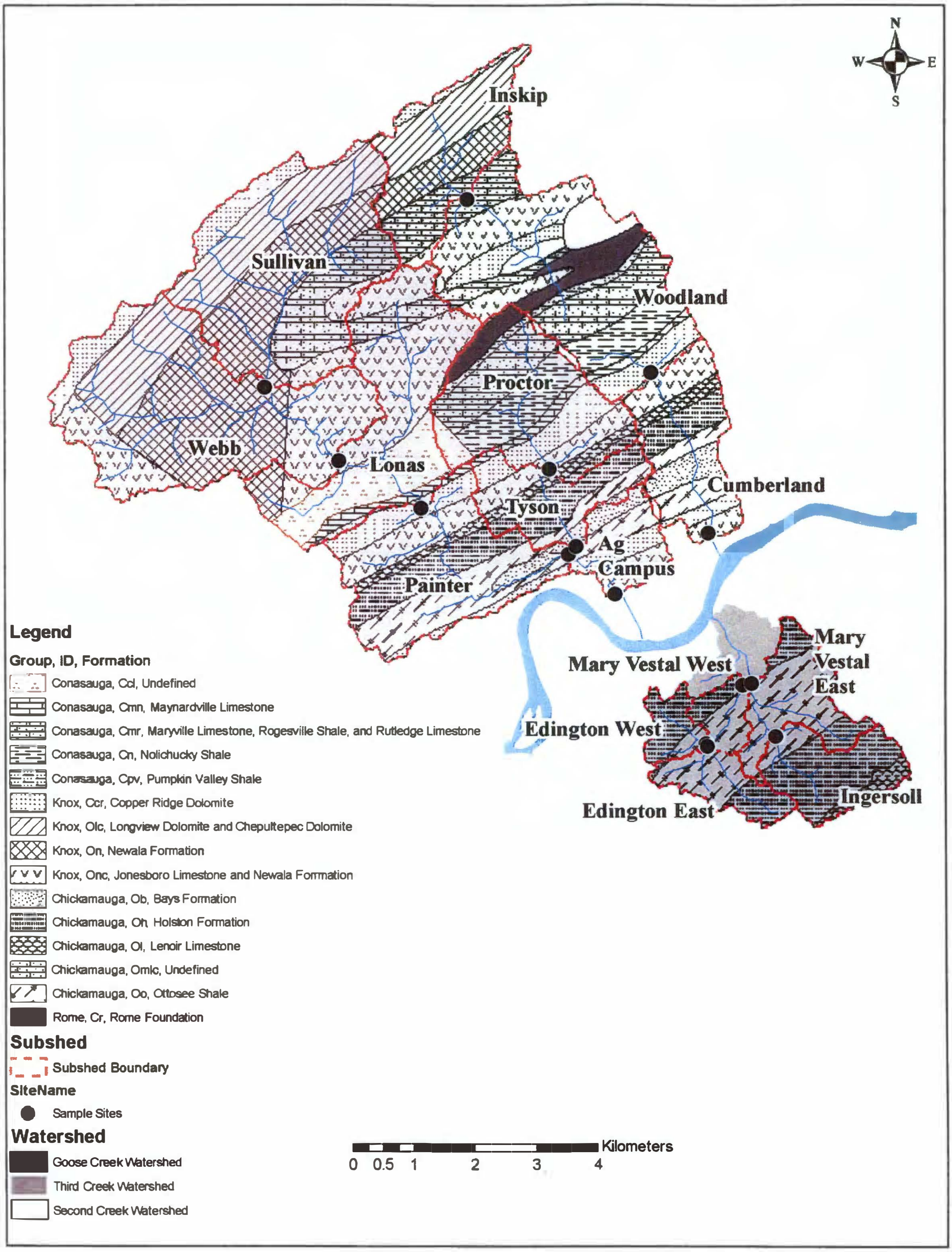

Figure 3.2: Watershed Geology (Source: Hardeman, 1966)

will produce a greater amount of surface runoff during precipitation events, potentially transporting more pollutants to the receiving surface waters.

Twenty-one soil complexes are prominent throughout either Goose, Second, or Third Creeks, each covering 4% or more of the land area within the individual watersheds (Hartgrove, 2003, Table 3.1, Figure 3.3, Figure 3.4). The most prevalent soil series in Third and Second Creeks are Urban Land, Udorthents, and Dewey. The Dewey series consists of very deep, well-drained, moderately permeable soils on uplands formed from limestone parent material. Found on gently sloping to steep uplands, these soils have depths greater than 1.5 m to the limestone bedrock (Soil Survey Staff, 2004). Medium to rapid surface runoff is associated with this soil series. The Udorthents series is a component of many of the soil complexes found throughout all three watersheds and is a significant individual complex by percentage land area in the Second and Third Creeks watersheds. Udorthents are a site-specific soil classification. Soils classified in this way have been subject to anthropogenic modification generally through cut and/or fill (Newton, 2004). Hydrological characteristics of Udorthents differ due to differences in the source material; however, in the Knoxville urban area, this series is generally associated with construction and is shallow with low permeability resulting in moderate to high potential runoff. The Urban Land Use series refers to those soils that have been extensively modified due to urban construction. Regions designated as Urban Land Use would be expected to have high runoff potentials. These two soil series classifications cover significant areas of both the Second and Third Creek watersheds.

The predominant soil series in Goose Creek are the Corryton and Coghill series (Figure 3.5). Coghill soils are formed from limestone, shale, and sandstone parent

Table 3.1: Major Soil Complexes and Percent of Watershed Coverage (symbols and names compiled from Hartgrove, 2003)

Map Unit Symbol	Map Unit Name	Third Creek	Second Creek	Goose Creek
AmF	APISON-MONTEVALLO COMPLEX, 35 TO 75 PERCENT SLOPES, ROCKY	*	5	*
CcC	COGHILL-CORRYTON COMPLEX, 5 TO 12 PERCENT SLOPES	*	*	5
CcD	COGHILL-CORRYTON COMPLEX, 12 TO 25 PERCENT SLOPES	*	*	7
CcE	COGHILL-CORRYTON COMPLEX, 25 TO 65 PERCENT SLOPES, ROCKY	*	*	21
CtC	CORRYTON-TOWNLEY COMPLEX, 5 TO 12 PERCENT SLOPES	*	*	4
CzC	CORRYTON-UDORTHENTS-URBAN LAND COMPLEX, 2 TO 12 PERCENT SLOPES	4	9	14
CzD	CORRYTON-UDORTHENTS-URBAN LAND COMPLEX, 12 TO 25 PERCENT SLOPES	*	*	13
DeC2	DEWEY LOAM, 5 TO 12 PERCENT SLOPES, ERODED	4	4	*
DyC	DEWEY-UDORTHENTS-URBAN LAND COMPLEX, 2 TO 12 PERCENT SLOPES	14	14	*
DyD	DEWEY-UDORTHENTS-URBAN LAND COMPLEX, 12 TO 25 PERCENT SLOPES	6	9	*
EvB	ETOWAH-MINVALE COMPLEX, 2 TO 5 PERCENT SLOPES	4	*	*
FvC	FULLERTON-MINVALE COMPLEX, 5 TO 12 PERCENT SLOPES	5	*	*
FzD	FULLERTON-UDORTHENTS-URBAN LAND COMPLEX, 12 TO 25 PERCENT SLOPES	6	4	*
HeB	HEISKELL SILT LOAM, 2 TO 5 PERCENT SLOPES	*	*	4
LtC	LOYSTON-TALBOTT-ROCK OUTCROP COMPLEX, 2 TO 15 PERCENT SLOPES	*	*	5
LtD	LOYSTON-TALBOTT-ROCK OUTCROP COMPLEX, 15 TO 50 PERCENT SLOPES	*	*	4
MfD	MINVALE-FULLERTON COMPLEX, 12 TO 25 PERCENT SLOPES, STONY	5	*	*
MfE	MINVALE-BODINE-FULLERTON COMPLEX, 25 TO 50 PERCENT SLOPES, STONY	6	*	*
Ur	URBAN LAND	7	18	*
Uu	URBAN LAND-UDORTHENTS COMPLEX	13	21	7

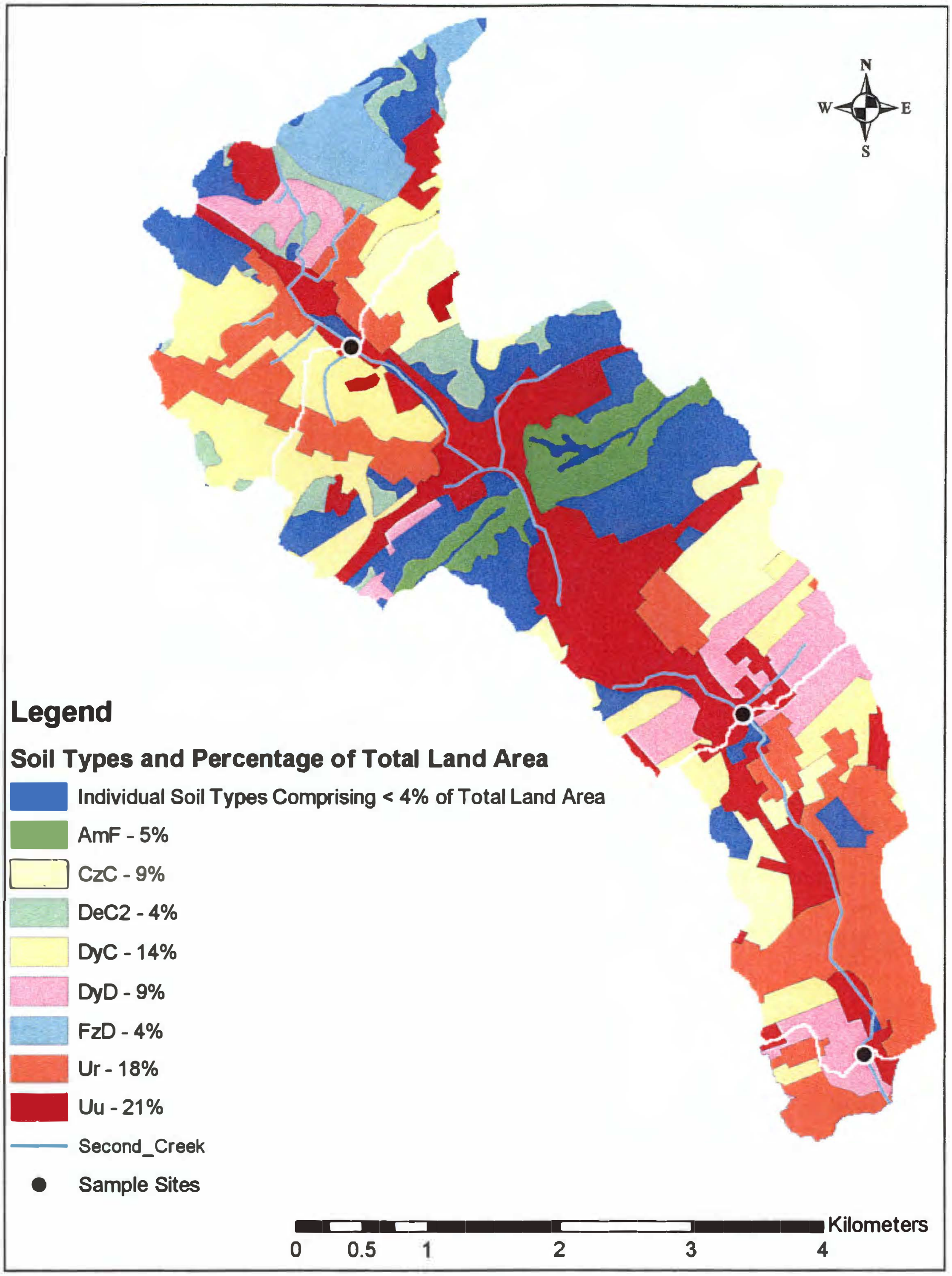

Figure 3.3: Second Creek Soils[1] (Source: Hartgrove, 2003)

[1] Soil series names listed in Table 3.1.

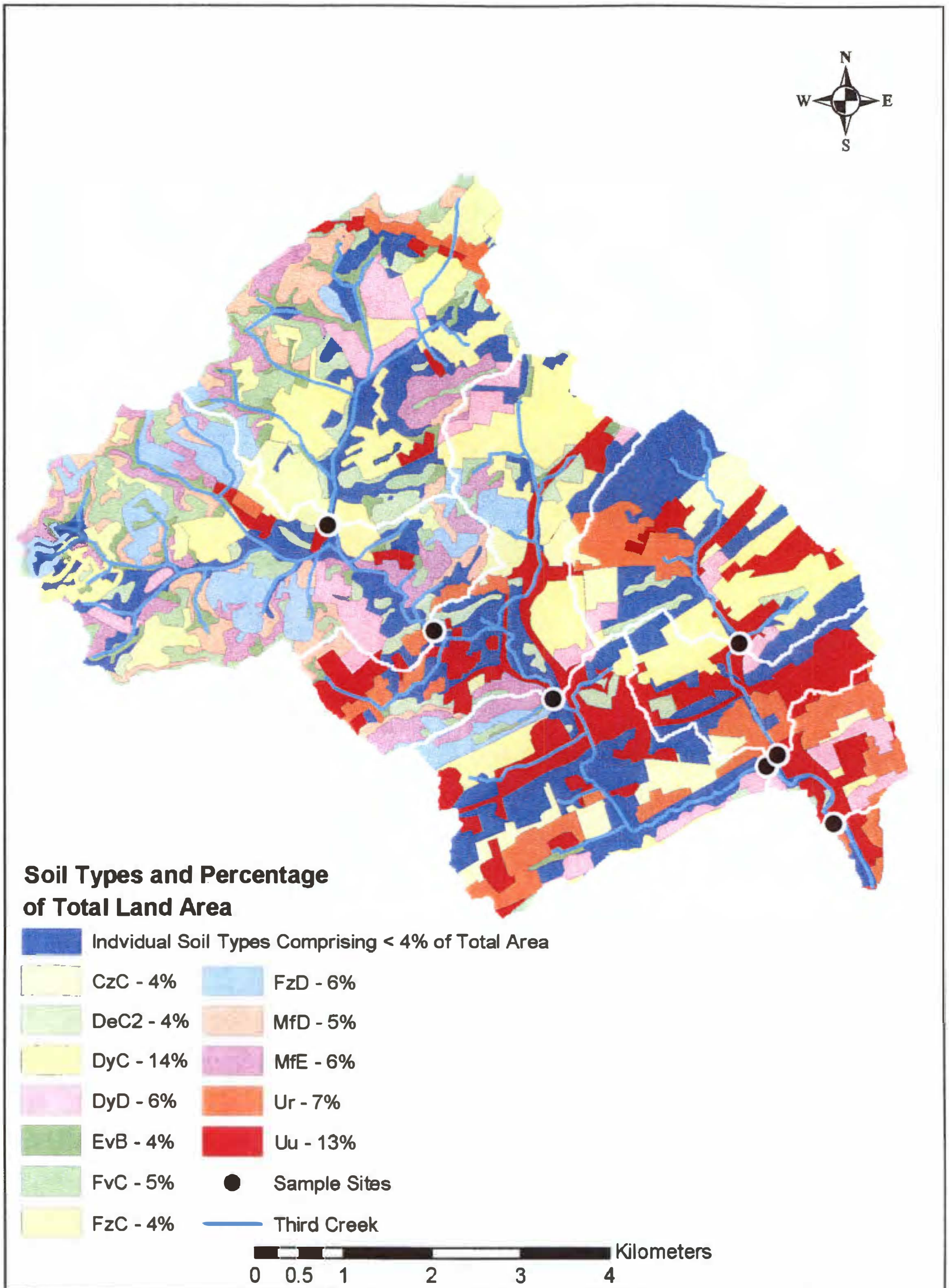

Figure 3.4: Third Creek Soils[1] (Source: Hartgrove, 2003)

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[1] Soil series names are listed in Table 3.1.

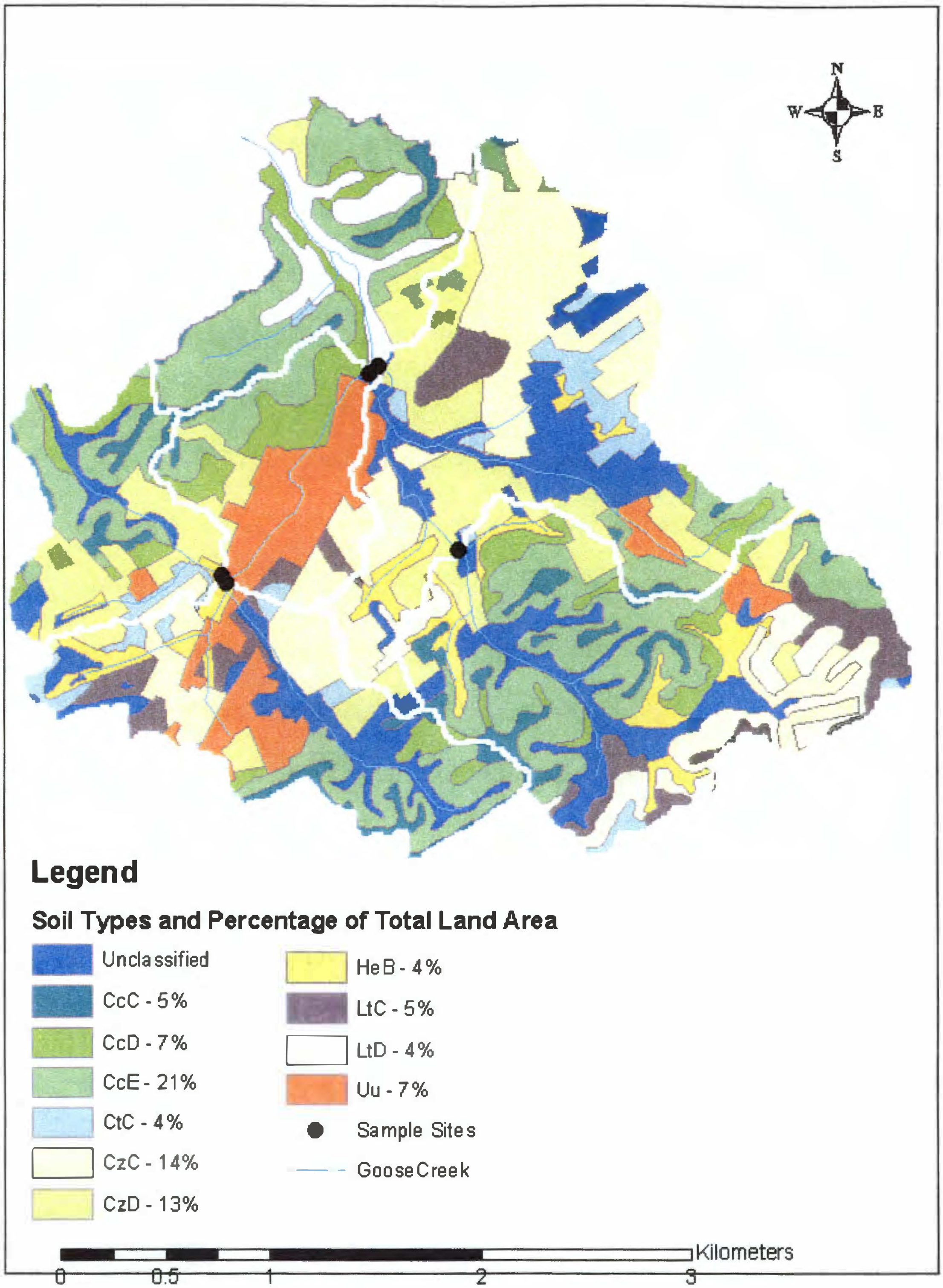

Figure 3.5: Goose Creek Soils[1] (Source: Hartgrove, 2003)

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[1] Soil series names are listed in Table 3.1.

material. Holston limestone and Ottosee shale are the two prominent geologic formations in Goose Creek. The Coghill series consists of very deep (>1.5 m), well-drained soils, with moderately slow permeability resulting in medium surface runoff. The Corryton series consists of very deep (>1.5 m to shale bedrock), well-drained soils, with moderately slow permeability resulting in medium surface runoff. Ottosee and Conasauga Shale formations are associated with this soil series. Significant areas of Corryton soils are associated with urban land types around Knoxville.

Drainage Basin Characteristics

Second Creek Drainage Basin

Second Creek is an elongated watershed that shares its western border with Third Creek. Second Creek is the most urbanized of the three study watersheds. It drains an area of 16.24 km^2 (6.27 mi^2) and, unlike the other streams in this study, which exhibit the more classical dendritic drainage pattern, has no major tributaries. Approximately halfway along its length, Second Creek passes through a culvert, resulting in a 1.29 km^2 (0.5 mi^2) area with no surface channel (Kung, 1980). Slopes generally less than 12% characterize this drainage basin, but slopes greater than 25% can be found along Sharp Ridge in the upper portion of the watershed and in valley banks near the stream's mouth. Local relief is 180 m (590 ft), with a maximum elevation of 427 m (1,400 ft) and minimum of 247 m (810 ft) at the mouth.

I monitored water quality at three sites along the main stem of Second Creek, dividing the watershed into three subbasins: Cumberland, Inskip, and Woodland (Figure 3.6). The defining soil complexes of the Cumberland subbasin are Ur (42%) and Uu (18%), both of which are the result of anthropogenic soil modification. Cumberland has

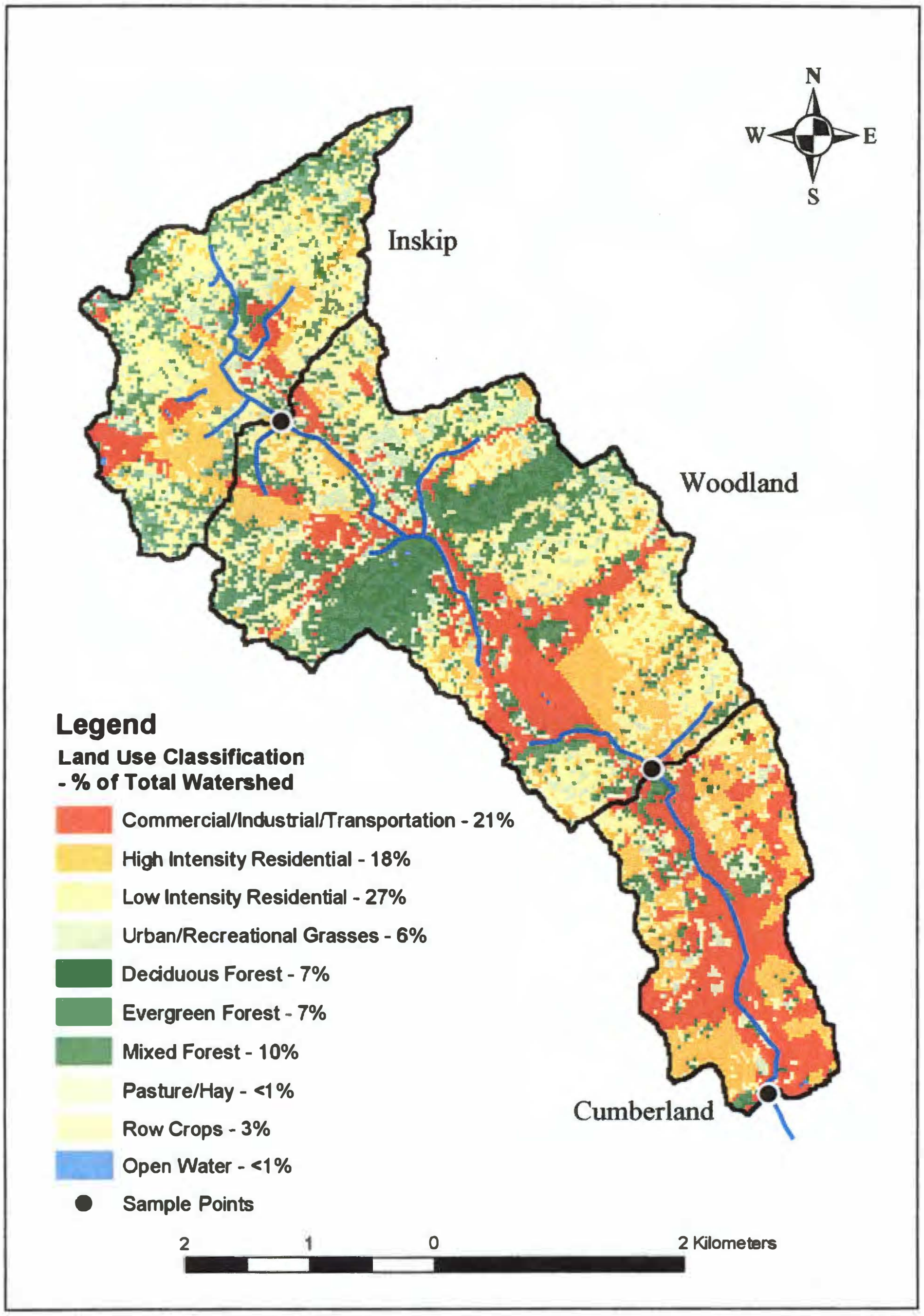

Figure 3.6: Land Use and Subbasins - Second Creek

the highest total impervious area (64%) and the highest percentage of land use classified as either Commercial/Industrial/Transportation (44%) or High Intensity Residential (28%) of all subbasins in this study. Four major soil complexes of the Inskip subwatershed in terms of total area are DyC (23%), Ur (17%), FzD (15%) and Uu (11%) (Table 3.2). The Fullerton series, which like the Dewey series is deep and well drained, is classified as medium in regard to potential surface runoff (Hartgrove, 2003). The Inskip subbasin has the lowest amount of impervious area, the highest percentage of low intensity land use, and lowest percentage of high intensity land use of the three test basins in Second Creek. Woodland, the largest of the Second Creek subbasins, has the only occurrence of the Apison-Montevallo complex within the study basins. The Apison-Montevallo complex is found on steep slopes and is characterized as moderately deep well-drained soils with moderate to rapid surface runoff. Woodland has the most evenly distributed land use of the Second Creek subbasins, with High Intensity and Low Intensity Residential and Commercial/Industrial/Transportation land uses accounting for 60% of the total coverage. Woodland has the most different soil complexes of the Second Creek subbasins and the highest weighted average soil permeability (59.9 mm/hr).

Third Creek Drainage Basin

Third Creek, the second largest drainage basin in the Knoxville urban area, is a mixed-use watershed encompassing land uses from forest to industrial/manufacturing. Several industrial and manufacturing facilities are permitted to discharge pollutants into Third Creek, including a significant number of petroleum storage facilities whose

Table 3.2: Second Creek Subbasin Surface Characteristics by Percentage Area (compiled from Hartgrove, 2003, EPA 2001b, and NLCD 1992)

	Cumberland	Inskip	Woodland
Land Use Percent Land Area			
Commercial/Industrial/Transportation	44	8	16
High Intensity Residential	28	16	15
Low Intensity Residential	10	39	29
Urban/Recreational Grasses	3	7	7
Deciduous Forest	4	7	9
Evergreen Forest	1	7	10
Mixed Forest	4	14	11
Pasture/Hay	0	< 1	1
Row Crops	4	1	3
Open Water	0	0	0
Soils Percent Land Area			
AmF	0	0	9
CzC	11	4	11
DeC2	0	8	4
DyC	12	23	11
DyD	11	7	8
FzC	0	5	0
FzD	0	15	0
Ur	42	17	6
Uu	18	11	28
Miscellaneous Surface Characteristics			
Percent Impervious Surface	64	36	45
Permeability (mm/hr)*	41.4	47.5	59.9
Mean Depth to Bedrock (meters)	1.12	1.45	1.15
Percent Silt/Clay*	57.6	59.2	57.9
Soil Erodibility (kfact)*	.26	.30	.28

* Type of Estimate: Mean; Components: Area-weighted; Layers: Surface Layer.

discharges increase both Total Suspended Solids (TSS) and Biological Oxygen Demand (BOD) (USEPA, 2004; Figure 3.7). Neither of the other study watersheds has a significant number of facilities permitted to discharge into the creeks. Third Creek drains an area of 48.17 km^2 (18.6 mi^2) and is a geologically tight catchment, confining most of the surface and groundwater to the basin (Kung, 1980). The watershed has a high drainage density as a result of its rolling topography and permeable surficial geology. Topographically, the catchment is characterized by moderate slopes (<12%), although slopes of greater than 25% are found along ridges. Local relief is 161.5 m (530 ft), with elevations ranging from a minimum of 247 m (810 ft) to a maximum over 396 m (1300 ft). Except in areas with high elevation or steep slope, soil depth is greater than 1.83 m (6 ft). These soils are generally permeable with infiltration rates greater than 1.5 cm (0.6 in) per hour. Permeable soils underlain by impermeable shale result in Third Creek receiving sustained groundwater contributions throughout the year.

I sampled at seven sites within the Third Creek watershed that represent its seven interconnected subbasins (Figure 3.8). The Tyson and Proctor subbasins encompass the East Fork of Third Creek and are the two of the three subbasins with the highest amount of impervious surface in Third Creek (USGS, 2003b). Third Creek, like all the study watersheds, exhibits a general increase in the cumulative proportion of land use classified as Commercial/Industrial/Transportation and High Intensity Residential within the subbasins moving in a downstream direction (Table 3.3). Eighty-two percent of the Agricultural Campus (site location on University of Tennessee Agricultural Campus) catchment, the subbasin furthest downstream in Third Creek, is classified as either commercial or residential. The Sullivan and Webb basins have a relatively large number

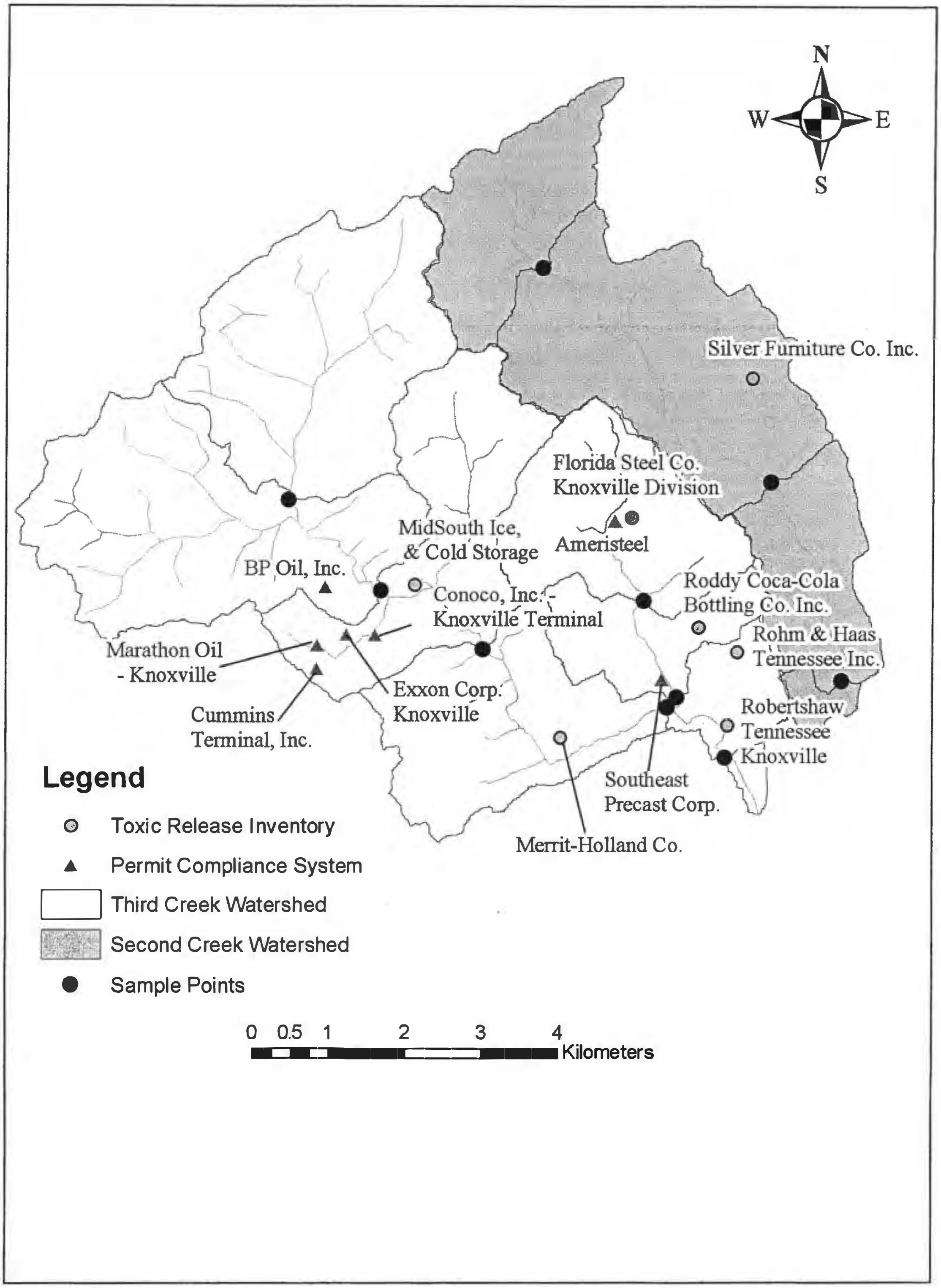

Figure 3.7: Location of Permit Compliance System and Toxic Release Inventory Sites (Date source – EPA 2001b core data)

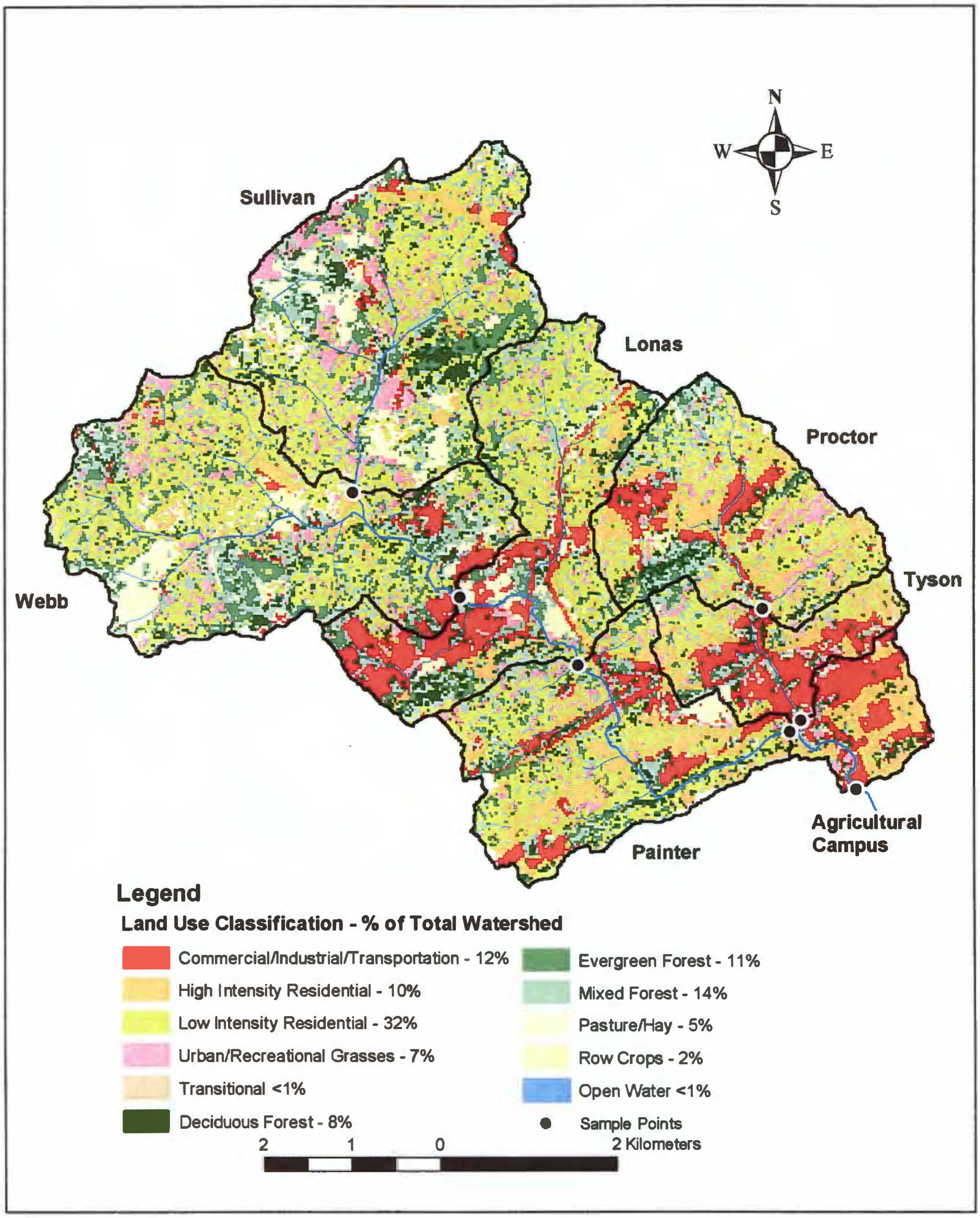

Figure 3.8: Land Use and Subbasins – Third Creek

Table 3.3: Third Creek Subbasin Surface Characteristics by Percent Area (Data from Hartgrove soils data, 2003, EPA 2001b, and NLCD 1992)

Land Use Percent Area	Main Stem Third Creek					East Fork	
	Sullivan	Webb	Lonas	Ag Campus	Painter	Proctor	Tyson
Commercial/Industrial /Transportation	3	5	19	43	12	12	33
High Intensity Residential	5	5	6	31	16	15	15
Low Intensity Residential	31	34	32	8	35	35	22
Urban/Recreational Grasses	11	6	5	3	6	8	5
Deciduous Forest	9	7	7	6	7	8	7
Evergreen Forest	12	15	11	2	10	8	5
Mixed Forest	16	17	14	4	11	11	9
Pasture/Hay	9	8	6	0	2	1	1
Row Crops	2	3	0	4	1	2	3
Soils Percent Land Area							
CzC	0	0	2	3	10	6	13
CzD	0	0	0	0	6	4	5
DeC2	6	3	5	2	2	3	3
DeE2	1	3	2	0	6	5	6
DyC	20	7	25	4	8	14	19
DyD	7	5	6	21	4	1	4
EvB	8	7	2	0	1	0	0
FvC	8	10	2	0	1	0	0
FzC	10	8	3	0	0	0	0
FzD	3	16	4	0	5	0	0
MfD	9	12	3	0	0	0	0
MfE	8	12	6	0	3	0	0
Ur	3	2	5	34	11	13	11
Uu	2	3	20	32	23	38	14
Miscellaneous Surface Characteristics							
% Impervious Surface	27	27	38	67	39	42	56
Permeability (mm/hr)*	48.4	57.8	45.9	53.1	40.5	57.5	35.7
Mean Depth to Bedrock (meters)	1.47	1.52	1.22	1.30	1.11	1.09	1.08
Percent Silt/Clay*	58.7	50.9	58.0	52.4	58.0	56.5	59.9
Soil Erodibility (kfact)*	.30	.29	.28	.27	.26	.25	.26

* Type of Estimate: Mean; Components: Area-weighted; Layers: Surface Layer.

of consequential soil complexes that distinguish them from the other Third Creek basins. Notably the Urban Land and Udorthent soil complexes are significantly less prevalent in these sub-watersheds. Surface characteristics of the Tyson basin — low permeability, high impervious area, and shallow depth to bedrock — suggest that this basin would generate the most rapid surface runoff.

Goose Creek Drainage Basin

Goose Creek, the smallest of the watersheds included in this study, drains an area of 8.29 km^2 (3.2 mi^2). Of the three watersheds, this catchment has the lowest percentage of urban land use and the highest percentage of woodland cover (Table 3.4). This watershed has the steepest topography of the research regions — slopes over 30% cover more than 9% of three of Goose Creek's five subbasins (Table 3.5). Much of the landscape disturbance (i.e., urban land use) within the watershed is confined to a region of moderate slope (<12%) that runs from the southwest to northeast through the middle of the catchment (Figure 3.9). Local relief is 179 m (587 ft), with a maximum elevation of 363 m (1191 ft) and a minimum elevation of 184 m (604 ft).

Unlike the Second and Third Creek watersheds, where Urban Land and Udorthents soil complexes cover 25% or more of the individual subbasins, these soils only exceed 25% coverage in Goose Creek's Mary Vestal West subbasin. Goose Creek's subbasins are less permeable, with shallower soils (lower depth to bedrock), and higher slit/clay content than its companion study watersheds across the Tennesee River. These characteristics, coupled with its steeper slopes, suggest that Goose Creek would naturally have a greater amount of surface runoff per acre than the other watersheds. However, the lower amount of impervious cover and higher amount of forest cover observed in all

Table 3.4: Goose Creek Subbasin Surface Characteristics by Percentage Area (Data from Hartgrove soils data, 2003, EPA 2001b, and NLCD 1992)

Land Use Percent Area	**Ingersoll**	**Edington West**	**Edington East**	**Mary Vestal West**	**Mary Vestal East**
Commercial/Industrial /Transportation	2	2	4	16	9
High Intensity Residential	2	4	6	10	16
Low Intensity Residential	17	32	29	26	34
Urban/Recreational Grasses	2	5	3	4	3
Deciduous Forest	25	12	14	14	9
Evergreen Forest	22	16	21	7	11
Mixed Forest	29	28	22	19	16
Pasture/Hay	2	0	1	0	1
Row Crops	0	0	0	3	1
Soils Percent Land Area					
CcC	7	9	7	3	2
CcD	6	12	4	19	2
CcE	27	25	16	16	7
CtC	1	4	5	1	7
CzC	4	2	17	11	33
CzD	9	30	6	8	19
EmB	5	0	0	0	0
HeB	7	3	6	0	3
LtC	9	0	7	4	4
LtD	13	0	0	0	1
Ph	3	8	6	0	0
Ur	0	0	0	0	8
Uu	2	2	13	37	3
Miscellaneous Surface Characteristics					
% Impervious Surface[2]	29	29	30	34	35
Permeability (mm/hr)*	32.7	33.0	33.0	33.0	33.0
Mean Depth to Bedrock (meters)	1.14	0.86	0.80	1.00	0.82
Percent Silt/Clay*	62.7	61.9	62.1	61.3	62.0
Soil Erodibility (kfact)*	.26	.24	.24	.25	.24

[2] Estimated by overlaying Third Creek land use with impervious surface raster, whose extent does not cover Goose Creek, then mean impervious values for land use were applied to Goose Creek land use.
* Type of Estimate: Mean; Components: Area-weighted; Layers: Surface Layer.

Table 3.5 Percent of Land Area ≥ 30% Slope (Data source: USGS, 2003a)

Third Creek		Second Creek		Goose Creek	
Sullivan	3.30	Inskip	0.50	Ingersoll	17.81
Webb	1.83	Woodland	8.49	Edington West	12.90
Lonas	1.28	Cumberland	0.63	Edington East	9.33
Painter	2.28			Mary Vestal West	1.38
Ag Campus	1.56			Mary Vestal East	4.48
Proctor	3.54				
Tyson	1.98				

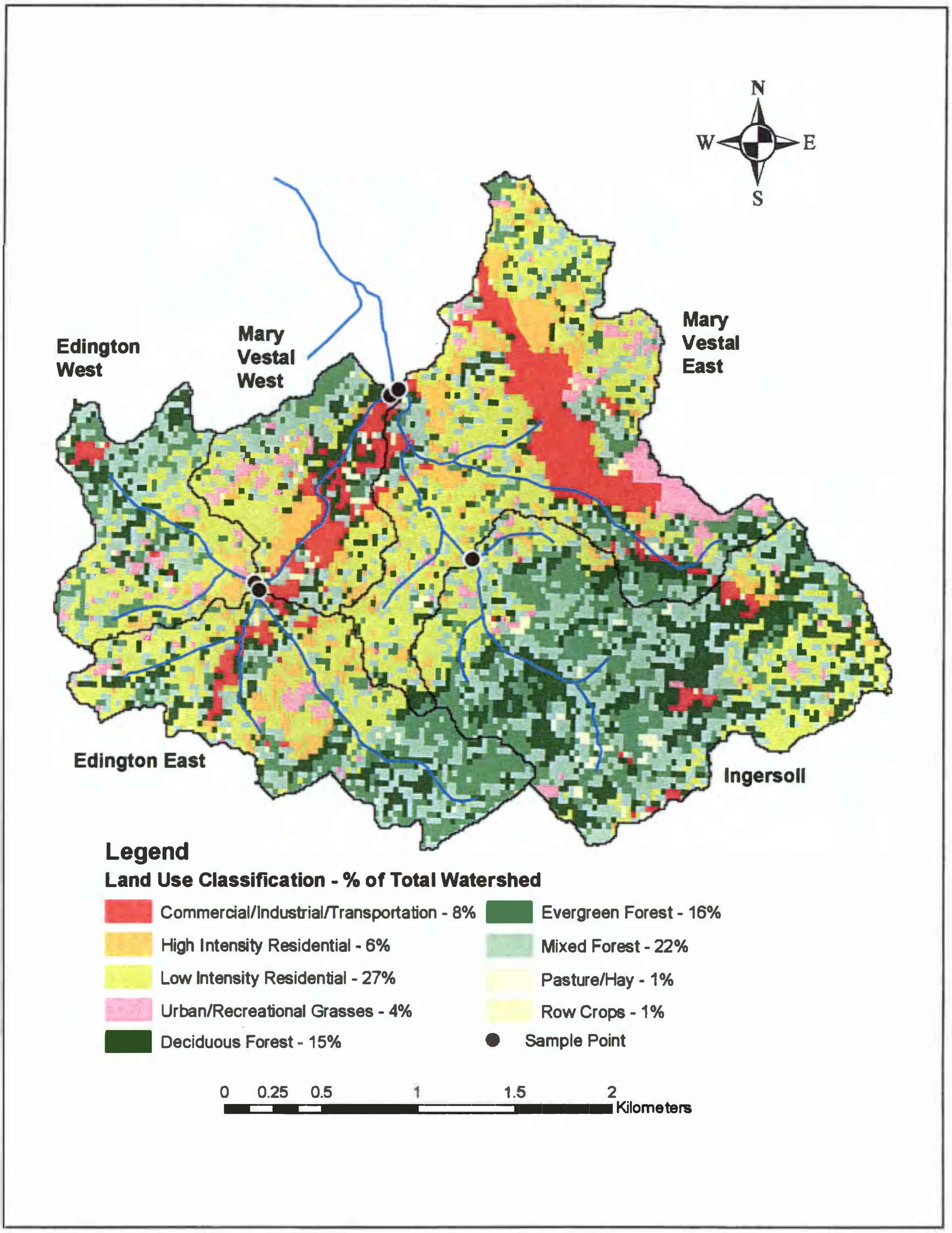

Figure 3.9: Land Use and Subbasins – Goose Creek (Data source: USGS, 2003a)

Goose Creek's subbasins should reduce the amount of surface runoff relative to the more urbanized subbasins in Third and Second Creeks.

Current State of Water Quality in Goose, Second, and Third Creeks

All 33.3 km of Third Creek, 20.6 km of Second Creek, and 7.9 km of Goose Creek have been assessed by the Tennessee Department of Environment and Conservation and listed on its 303(d) list of "water quality limited" streams as not supporting the streams' designated uses (TDEC, 2004). Designated uses for all three creeks include fish and aquatic life, recreation, irrigation, and livestock watering and wildlife. Additionally, Second Creek is designated for industrial water supply and Third Creek is designated as both a domestic and industrial water supply. Streams classified as not supporting are severely impacted by pollution and frequently exceed water quality standards. Tennessee's statewide assessment of streams was based on water quality data collected during 2001 and early 2002.

The types of water quality impairment listed by the state include pathogens, nutrients, siltation, and habitat alteration for all three creeks. Metals from the Southern Rail/Coster Shop and PCB's from the Witherspoon Landfill, both Superfund sites, are also listed as pollutants for Second Creek and Goose Creek, respectively. The state determined collection system failure and urban runoff/storm sewers to be major sources of water quality impairment for all three watersheds (TDEC, 2004). Other pollutant sources affecting these water bodies are hydromodification (defined by TDEC as channelization, dams, and dredging) in Second and Third Creeks, hazardous waste in Goose Creek, and land development in Third Creek. Water contact advisories have been issued for all three streams due to pathogens.

CHAPTER 4

THE CHEMICAL PERTURBATION INDEX

Framework of Analysis

Stewart's (2001) results provided strong evidence that the Chemical Perturbation Index (CPI) is an effective indicator of water perturbation in less developed areas with known point source pollution inputs. This thesis compares the results of CPI calculations performed on samples in a non-point source, mixed land use, urban environment with the results published by Stewart for streams impacted primarily by point source discharges. To achieve this comparison, I investigated three specific questions: 1) Do the urban stream data (non-point source) show a similar graphical pattern to the bounded plot produced by Stewart? 2) Do sites graphically cluster in the bounded plot by CPI range? 3) Are the CPI values similar between watersheds, and are the range of CPI values seen in the non-point source streams similar to the range seen in the streams around Oak Ridge? I ask these three questions to gain insight into the interoperability of CPI results in urban streams and the effectiveness of the CPI in waters not dominated by point source pollution.

Collection and Analysis of Samples

I collected water samples at 15 sites throughout the Goose (five sites), Second (three sites) and Third Creek (seven sites) watersheds (see Figure 3.2). Five of the sites in Third Creek were the locations of previous water quality sampling by various University of Tennessee classes taught by Dr. Carol Harden and were included to extend the temporal extent of water quality analysis at these sites. The Proctor site on the East

Fork of Third Creek was also the site of Betson's (1976) water quality research in Third Creek. The three sites in Second Creek were chosen based on accessibility and their ability to capture different landscape characteristics of the watershed. The Inskip and Cumberland sites also had been part of a comprehensive geomorphic analysis of Second Creek (Grable, 2003). The Goose Creek sites were chosen based on their ability to reflect different landscape characteristics in the watershed, their accessibility, and, in the case of the Mary Vestal and Edington sites, their close geographic proximity. Testing sites located close to each other that have contributing areas with different landscape characteristics may highlight the link between water chemistry and basin landscape rather than geographic location.

I took between 20 and 24 grab samples from each test site and analyzed them in lab facilities at the University of Tennessee-Knoxville Burchfiel Geography Building for specific conductance, total alkalinity, total hardness, and pH. The samples were collected on the same day and stored packed in a cooler until they could be returned to the lab. The samples were refrigerated after being returned to the lab, and analyses were performed within 36 hours of the sample's collection. I tested for total alkalinity using the LaMotte Company's WAT-DR model Total Alkalinity Direct Reading Titrator system. This kit uses titration (4 mg/L minor divisions) with a standard acid to the total alkalinity endpoint (Campbell and Wildberger, 1992). I used LaMotte's PHT-DR-LT model test system to calculate total hardness. This system uses EDTA titration (titrator scale equals 4 mg/L) with inhibitors to eliminate metal interferences to determine hardness with a red to blue endpoint. EDTA is a chelating agent that attracts the cations that contribute to hardness. All results for total alkalinity and total hardness are expressed as the $CaCO_3$ equivalent. Specific conductance and pH were measured in the lab with the 330i Cond (WTW) conductance meter and the Oakton Instruments pHtest 3+ pH meter. Measures for water temperature and water depth at the sample point (approximately the center of the stream flow) were taken in the field at the time of sample collection.

Descriptive Statistics of Alkalinity, Hardness and Specific Conductance

Tables 4.1 and 4.2 report some measures of central tendency and dispersion for each sample site; a complete list of discrete sample results is available in Appendix A. Sites in Goose Creek generally have higher mean hardness values and more variation within sites than the other watersheds with the exception of the Tyson and Cumberland sites. The Tyson site has the greatest amount of variation for all of the water quality variables among the entire set of sample sites. Sites on the East Fork of Third Creek (Tyson and Proctor) are also separated from the main branch sites by higher mean values for alkalinity, hardness, and specific conductance. Generally, there is only a small difference between the mean and median values at each sample site for all three parameters, indicating that the samples are symmetrically distributed and outliers do not have a significant impact on the data distribution.

Calculation of Chemical Perturbation Index

Using the procedures outlined by Stewart (2001), I calculated the CPI for my research sites. Calculation of the CPI sums the Spearman's rank correlation coefficients of the specific conductance, alkalinity, and hardness and subtracts them from 3.0. Higher values of the CPI indicate a greater amount of perturbation of water quality. Spearman's

Table 4.1: Minimum, Maximum, and Mean Sample Values

Location	Hardness (mg/L)			Alkalinity (mg/L)			Specific Conductance			pH			Depth (cm)			Water Temp (°C)		
	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean
Goose Creek																		
Edington East	120	200	155	156	240	207	309	481	418	7.18	7.93	7.68	14	38	31	10	19	14
Edington West	108	164	129	148	200	179	286	361	343	7.64	8.32	7.92	7	34	11	9	19	14
Ingersoll	152	236	175	188	272	238	417	488	450	7.09	7.95	7.77	11	18	15	11	17	14
Mary Vestal East	148	200	176	188	288	240	368	496	464	7.81	8.34	8.05	28	41	35	10	18	14
Mary Vestal West	120	176	154	160	248	218	341	481	436	7.76	8.34	8.08	29	49	39	8	19	13
Second Creek																		
Inskip	96	148	125	184	240	205	352	468	398	7.35	7.91	7.63	27	38	33	12	19	15
Woodland	108	148	129	188	252	221	366	535	439	7.86	8.40	8.20	27	49	40	10	20	15
Cumberland	60	152	127	108	260	221	227	556	461	7.84	8.43	8.16	27	52	41	9	20	14
Third Creek																		
Sullivan	84	124	107	164	224	194	298	392	355	7.34	8.35	7.69	33	49	42	11	18	14
Webb	76	116	96	146	212	184	272	374	341	7.42	8.05	7.76	35	69	51	11	18	14
Lonas	88	132	104	136	236	192	279	393	363	7.74	8.32	8.07	28	55	43	10	19	14
Painter	88	140	112	128	232	201	252	421	384	7.77	8.51	8.12	46	84	65	9	19	13
Proctor	108	168	136	200	276	236	409	543	491	7.89	8.35	8.13	8	26	14	9	20	14
Tyson	128	216	181	120	280	238	433	883	630	7.79	8.09	7.96	2	29	14	8	20	14
Ag Campus[1]	80	140	116	112	236	202	236	461	408	7.72	8.38	8.16	18	62	36	9	20	13

[1] Only eight depth measurements were taken at the Ag Campus site due to back water conditions as the result of Fort Loudon Lake reservoir levels.

Table 4:2 Measures of Dispersion

Location	Hardness				Alkalinity				Specific Conductance				CPI Site Ranking[1]
	Median (mg/L)	Standard Deviation	Skewness	Kurtosis	Median (mg/L)	Standard Deviation	Skewness	Kurtosis	Median (µS)	Standard Deviation	Skewness	Kurtosis	
Goose Creek													
Edington East	156	21.51	0.43	-0.29	212	24.26	-0.54	-0.50	425	48.33	-0.84	0.02	14
Edington West	130	12.06	0.97	2.82	182	13.63	-0.90	0.32	349	16.47	-2.62	8.02	1
Ingersoll	174	17.41	2.11	7.47	242	21.27	0.16	0.14	452	18.85	0.51	0.99	3
Mary Vestal East	176	15.55	-0.28	-0.65	241	23.33	-2.35	7.12	474	27.87	0.51	0.99	4
Mary Vestal West	157	16.21	-0.60	-0.40	224	24.16	-1.44	1.36	450	37.30	0.51	0.99	9
Second Creek													
Inskip	125	11.30	-0.35	1.81	206	15.76	1.29	3.56	394	23.98	0.51	0.99	10
Woodland	132	10.39	-0.36	-0.34	218	14.58	1.19	5.33	436	31.70	0.51	0.99	2
Cumberland	132	20.95	-2.04	5.40	224	33.76	-2.21	6.74	468	62.72	-2.74	11.04	7
Third Creek													
Sullivan	104	11.56	-0.07	-1.15	192	17.89	0.09	-1.02	356	25.89	-0.40	-0.35	13
Webb	96	9.74	-0.16	0.01	186	14.71	-0.99	1.77	342	23.49	0.47	0.92	15
Lonas	100	9.92	0.89	1.38	196	18.99	-1.39	3.61	362	25.83	0.47	0.92	12
Painter	113	12.21	-0.09	0.42	200	22.86	-2.59	9.73	388	34.07	0.47	0.92	11
Proctor	136	13.73	-0.02	0.74	238	17.63	-1.10	5.01	492	24.93	0.47	0.92	6
Tyson	188	23.58	-0.79	0.38	248	35.49	0.83	4.67	630	79.50	0.47	0.92	5
Ag Campus	116	14.81	-1.10	1.66	212	23.89	-2.45	8.68	413	42.68	-2.94	11.89	8

[1] CPI rankings from 1 (most perturbed) to 15 (least perturbed)

rank correlation coefficient is a nonparametric test calculated using the squared difference between the ranks of pair observations (Rogerson, 2001). A set of ranks, a rank of one being assigned to the lowest value, is developed for each variable. The assumption of normality is not required for this test; however, it is most robust for large sample sizes (n>20). Spearman's rho incorporates the magnitude of the difference between ranks and measures their monotonic association (Helsel and Hirsch, 1992). Monotonic associations measure whether one variable generally either increases or decreases in relation to a second variable; however, this does not need to be a linear association. After collecting at least 20 individual samples of specific conductance, alkalinity, and hardness from each site, I calculated the CPI for my research sites to rank their water quality.

Results of CPI Calculations

Generally, CPI values in Third Creek increase from the headwaters to successive downstream sites along its two forks, though the Agricultural Campus site had a lower CPI value than sites on the East Fork of Third Creek that join the main channel above the Agricultural Campus site (Figure 4.1). This spatial trend was not evident in Goose Creek, where two of three headwater sites had higher CPI values than the next downstream site. The Edington West and East sites, though spatially near each other, have the maximum and minimum CPI values in Goose Creek. Of the three sites in Second Creek, the middle site (Woodland) had the highest CPI value. Assuming that higher CPI values represent more surface water perturbation, Goose Creek had three of the four most perturbed sites and Third Creek had four of the five least perturbed sites.

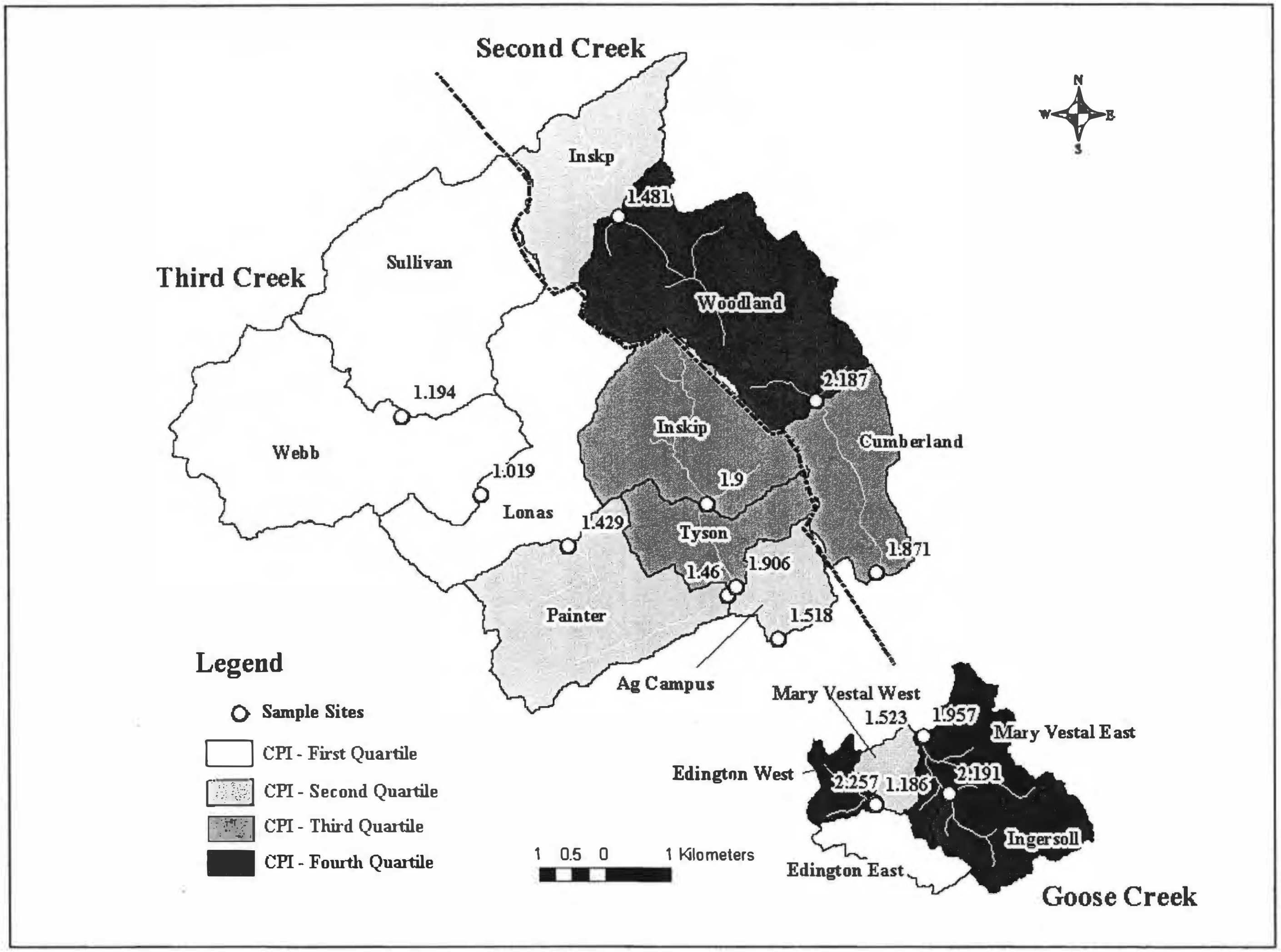

Figure 4.1 – Sample Site CPI Values for Goose, Second, and Third Creeks

Individual parameter correlation coefficients, values for the Chemical Perturbation Index, and the CPI rankings are reported in Table 4.3. The strongest correlations for all sites are generally between hardness and specific conductance. The Ingersoll site (Goose Creek), which had no significant correlations between any of the three parameters, was the only site not to have a significant correlation between those two parameters. The Webb site (Third Creek) was the only site to have significant correlations for all three variations of the correlation coefficients, and the only site to have a significant correlation between alkalinity and hardness. All sites in Third Creek, with the exception of Tyson, had significant correlations between alkalinity and specific conductance, something not found in the majority of the other sample sites located in Second and Goose Creeks. The expected near-unity relationship between alkalinity and hardness was not observed at any of the sample sites; in fact, the correlation between alkalinity and hardness was lower at all but one site than either individual component's correlation with specific conductance.

Comparison of CPI Values with Previous Research

Comparison of the CPI values calculated from my research samples with the CPI values reported by Dr. Stewart shows the differences in my CPI values, measuring non-point source or unidentified point source pollution, to be much smaller in magnitude than the differences in index values Stewart computed upstream and downstream of known point sources. The largest index value of my study sites was 2.26 at the Edington West site on Goose Creek, and the smallest index value was 1.02 at Webb Lane in Third Creek. Stewart's results have differences in CPI values greater than 3.0 between sites upstream and downstream of point source pollution inputs, with a maximum value of 3.70 and a minimum value of 0.14 (Stewart, 2001).

Table 4.3: Spearman's Rank Correlation Coefficients and CPI Value

Location	Alkalinity and Hardness	Specific Conductance and Hardness	Specific Conductance and Alkalinity	CPI Value	CPI[1] Ranking
Goose Creek					
Edington East	.357	.854(**)	.603(**)	1.19	14
Edington West	.111	.477(*)	.155	2.26	1
Ingersoll	.093	.329	.387	2.19	3
Mary Vestal East	.199	.571(**)	.273	1.96	4
Mary Vestal West	.334	.610(**)	.533(*)	1.52	9
Second Creek					
Inskip	.401	.589(**)	.529(*)	1.48	10
Woodland	.046	.633(**)	.134	2.19	2
Cumberland	.250	.464(*)	.415	1.87	7
Third Creek					
Sullivan	.375	.747(**)	.684(**)	1.19	13
Webb	.537(**)	.709(**)	.735(**)	1.02	15
Lonas	.391	.589(**)	.591(**)	1.43	12
Painter	.331	.738(**)	.471(*)	1.46	11
Proctor	.254	.425(*)	.421(*)	1.90	6
Tyson	.165	.814(**)	.115	1.91	5
Ag Campus	.205	.749(**)	.528(**)	1.52	8

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

[1] CPI rankings from 1 (most perturbed) to 15 (least perturbed)

A plot of the ratio of alkalinity to hardness and specific conductance, using z-scores to compensate for the different scale ranges of the variables and with points categorized by CPI quartile, illustrates several differences between the individual sample data from sites within the different quartiles (Figure 4.2). Samples from the first quartile, representing the lowest CPI values, which come from of the Edington East, Sullivan, Webb, and Lonas sites, cluster at the lower end of the specific conductance values and have greater dispersion along the axis representing the ratio of alkalinity to hardness. The samples from the second and fourth quartiles are dispersed equally along the two axes. The center of the second quartile group is slightly above the overall mean of the y-axis (ratio A:H) and slightly below the overall mean of the x-axis. The fourth quartile is broken into two distinct clusters with their centers to either side of the overall mean of specific conductance and slightly below the overall mean of the ratio of alkalinity to hardness. The third quartile, based on CPI values, contains the sample sites with the highest specific conductance values and has the greatest amount of dispersion along the x-axis representing specific conductance. Much of the dispersion along the x-axis is the result of samples taken from the Tyson Park site; many of the individual samples taken at this site are clearly distinct from the main cluster of sample points.

A plot of the ratio of alkalinity to hardness and specific conductance with markers set by watershed shows distinct groupings between Second and Goose Creeks (Figure 4.3). Alkalinity to hardness ratios and specific conductance values for the Third Creek watershed are much more dispersed than those from either of the other watersheds. Tyson Park is again responsible for much of the dispersion of Third Creek data points

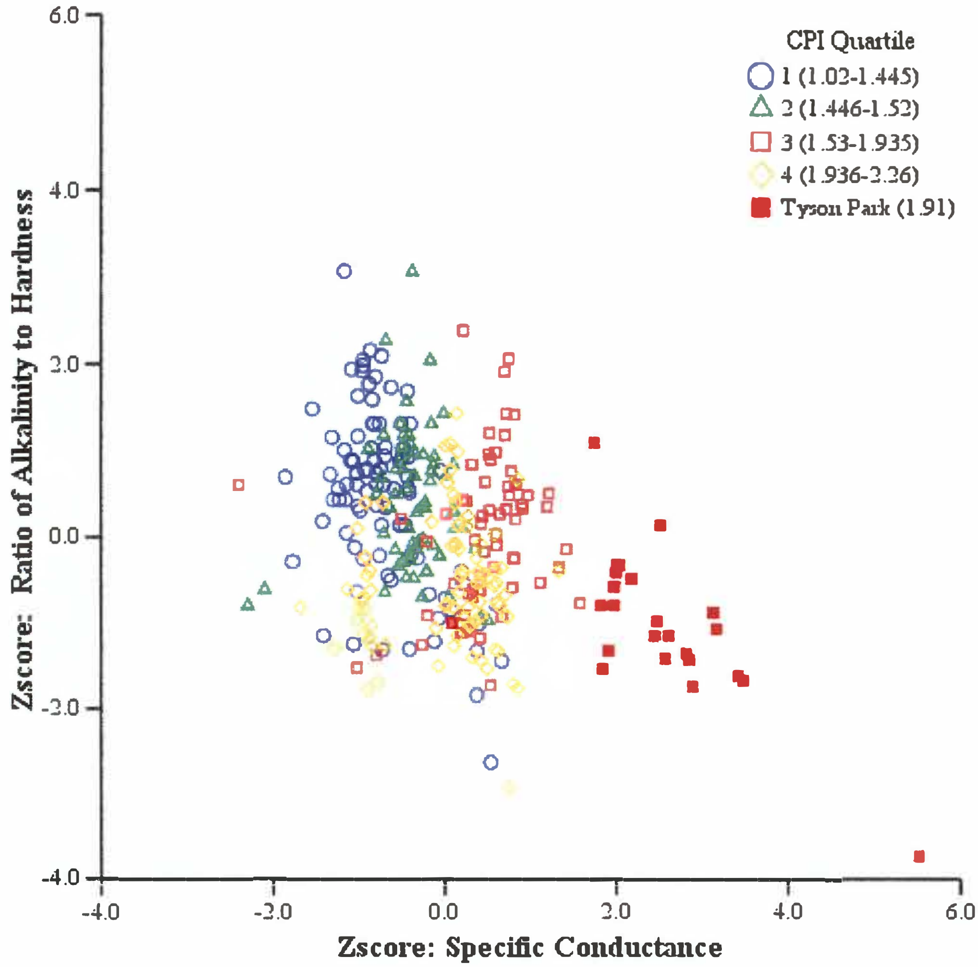

Figure 4.2 Z-Score Plot of Sample Sites by CPI Quartile

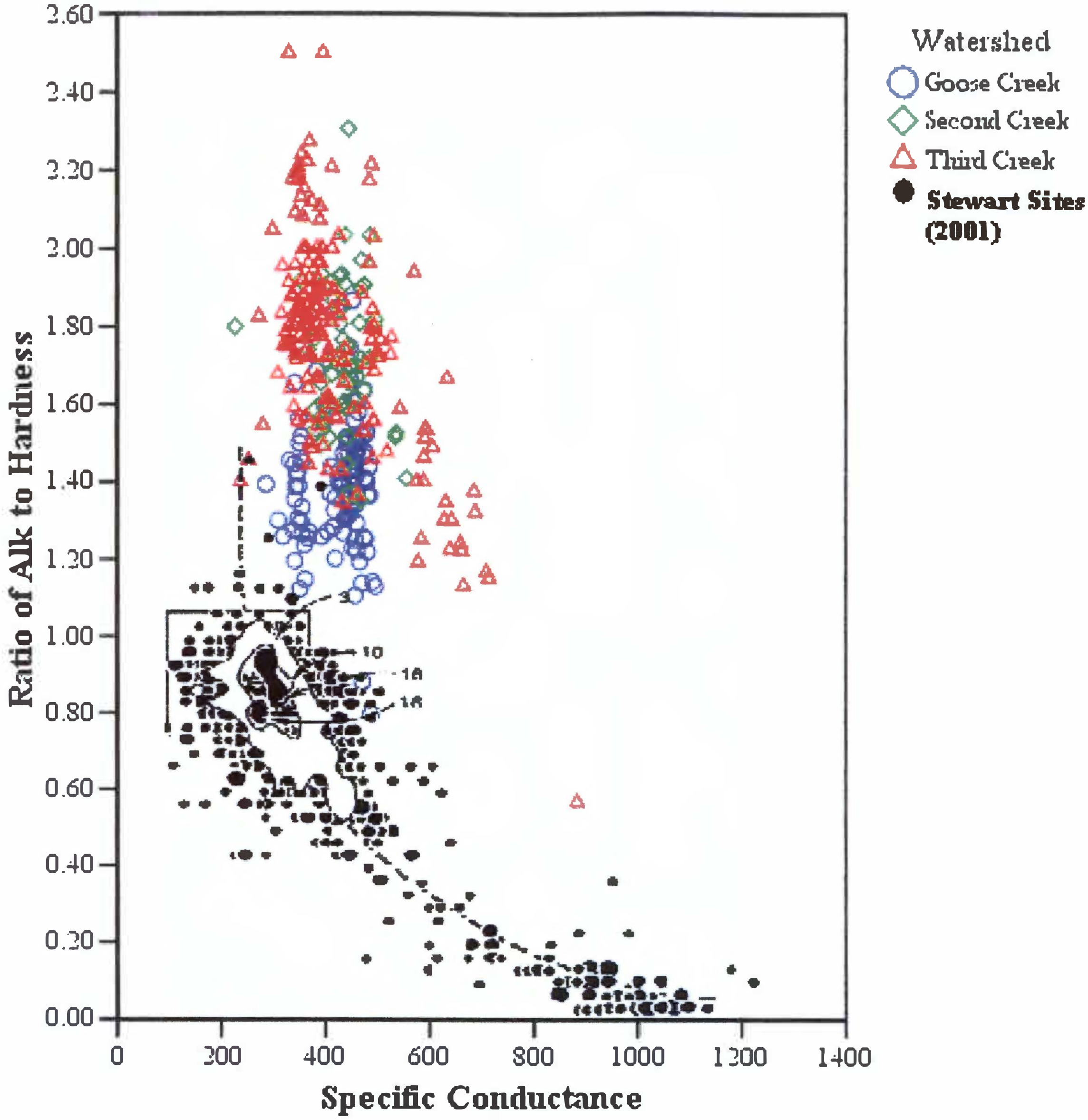

Figure 4.3: Plot of Sample Sites by Watershed

along the x-axis (specific conductance). The ratio of alkalinity to hardness is generally lower for sites in Goose Creek than either Second or Third Creeks. All the samples from the research watersheds fall outside the bounded plot area that defines the majority of the samples taken from headwater (reference) sites in Stewart's study (2001). Stewart's plot shows that the overwhelming majority of samples taken from streams around Oak Ridge National Laboratory have higher hardness values than alkalinities. Conversely, with few exceptions, my urban stream samples have alkalinity values that exceed hardness, in some cases by over 100%. The range of specific conductance values for my samples is much smaller than the range of values observed by Stewart. Taken together, the greatest difference among the samples I collected from urban Knoxville streams is in the ratio of alkalinity to hardness. Overlaying Stewart's plot with my data shows there are almost no overlapping points, despite the relatively close geographic proximity between the Oak Ridge sites reported on in Stewart's paper and the Knoxville urban area sites I sampled.

Interpretation of CPI in urban streams

As one method to evaluate the CPI as an effective tool for volunteer watershed monitoring groups, I explored how the results of CPI calculations performed on my samples from a non-point source mixed land use environment compared with the results published by Dr. Stewart for streams impacted primarily by point source discharges. The larger range of CPI values between sites reported in Stewart's (2001) paper might be due to the amount of wastewater that point sources around Oak Ridge National Laboratory contributed to the overall stream flow. Point sources increased total annual flow in one of Stewart's example streams by 23.3% during a wet year and 43.9% during a dry year. Samples taken during my research were collected during base flow conditions when non-point sources are unlikely to be contributing a large percentage of the flow. Perhaps during storm flows, when surface runoff accounts for a large percentage of the total stream flow, greater differences between CPI values would be seen in urban areas; however, sampling during storm events in urban streams can be dangerous and is not likely to be attempted by volunteer monitors.

Plots of my sample data show some evidence of clustering by CPI quartile value and by watershed. This suggests that graphical methods may be used to identify sites falling outside the bounds of an accepted bounding box. When a plot of my data points is overlaid with Stewart's plot and set to the same scale, all of my data points fall outside the bounded area containing the samples from his reference streams. This may be due to a difference in the natural ratio of alkalinity to hardness or may indicate that anthropogenic activities have disrupted the relationship between the parameters used to calculate the CPI at all my research sites. Interestingly, most of my sample points plot above the samples reported by Stewart. When no other ions are present in significant amounts, hardness will be equal to the sum of the carbonate and bicarbonate alkalinities. Organic ligands, phosphate alkalinity, silicates, arsenates, borate, and aluminates may contribute to alkalinity without contributing to hardness. Total alkalinities much greater than hardness may indicate that inputs of potassium cations (K^+) and chlorides (Cl^-) may be widespread throughout the research watersheds.

While there is clustering by both quartile value and watershed due to the lack of distinct graphical separation between samples, no one group of points stands out as an area from which a bounding plot of 'healthy' water quality could be drawn. The clustering by watershed seems to dominate. While points from the first quartile exhibit generally lower specific conductance, samples from the Edington East site in Goose Creek separate themselves from the other first quartile samples, all of which were from the upper part of Third Creek's main branch (Figure 4.4). Scatter plots of individual watersheds (not shown) showed that quartile clustering is only evident in Third Creek where the two East Fork sites (Proctor and Tyson), both in quartile three, are clearly separated from a cluster containing samples from sites in the first two quartiles. Furthermore, plots on the individual quartiles show that samples taken in Goose Creek generally separate themselves from samples collected in Second and Third Creeks. This suggests that graphic analysis should only be performed on sites within the same watershed due to the differing base constituent concentrations. Numerous samples must be plotted and assumptions on which sites represent 'healthy' waters need to be made in order to define a bounding area representing non-perturbed hydrologic conditions. The plot of sample values (see Figure 4.3) shows one Third Creek sample clearly separated from other sample values, with a specific conductance of over 800μS. This sample was taken on 02/26/03, several days after deicing agents, which include chlorides, were applied to the roads around Knoxville. This sample also deviates from the usual association between alkalinity and hardness seen in my samples. The alkalinity value of this sample is smaller than expected, indicating salt in the deicing compounds may have caused dealkalization, a process by which NaCl (usually in conjunction with a small amount of caustic substance) added to water replaces the bicarbonate and carbonate ions with chloride ions. This would also account for a high specific conductance value. The presence of outliers in graphic plots of the sample data seems to indicate abnormal conditions and could be used to flag sites for further investigation.

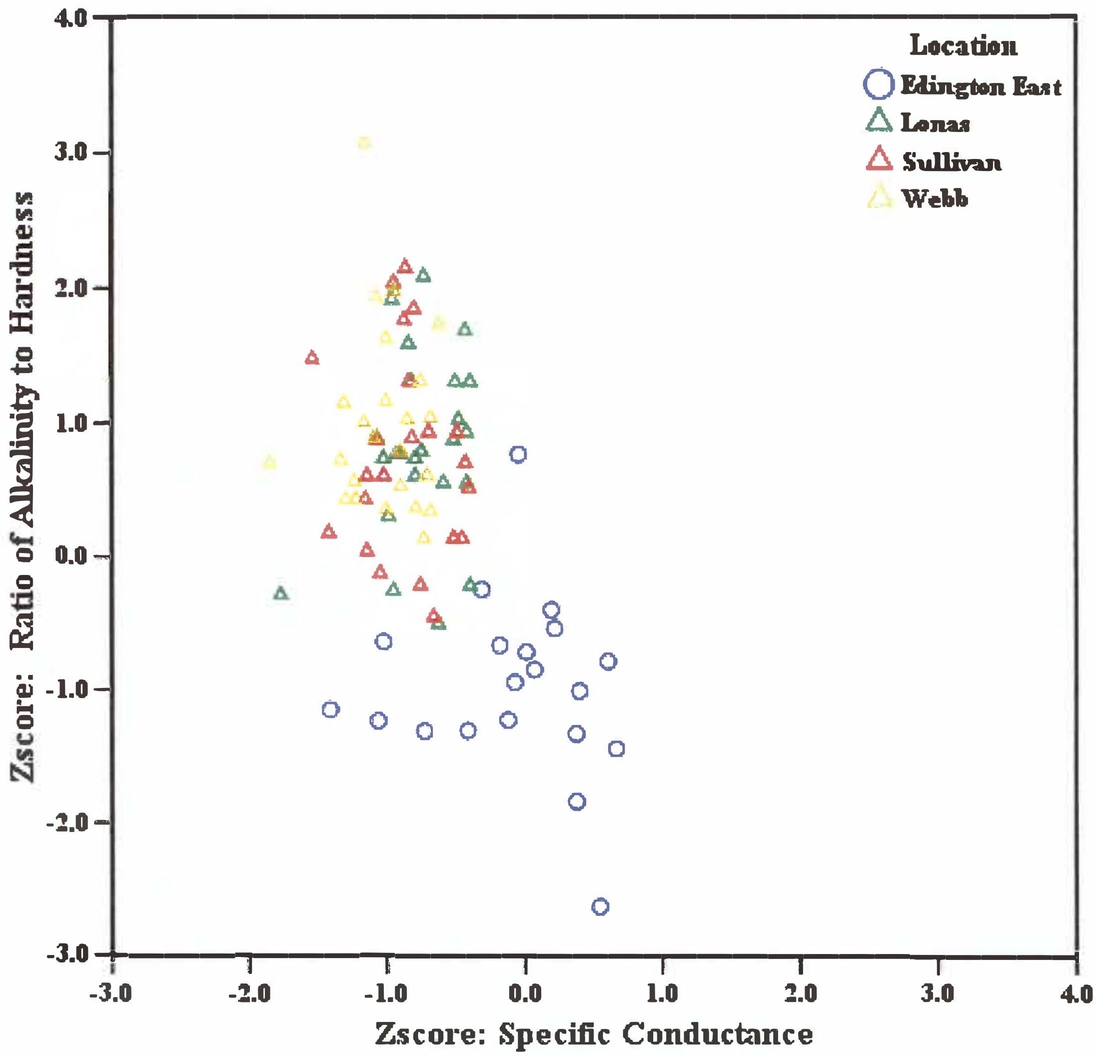

Figure 4.4: Scatter plot of CPI Quartile

CHAPTER 5

STATISTICAL ASSESSMENT OF SAMPLE DATA

Basis for Statistical Analysis

Samples with similar chemical constituent values often have similar source areas, flow paths to the receiving water body, climate, and geology. Statistical techniques are often used to classify water chemistry samples into homogenous groups in an attempt to characterize the contributing hydrologic systems. Using analysis of variance, the median polish procedure, and graphic methods presented by Helsel and Hirsch (1992), I summarized the sample data in order to compare water quality assessments using these statistical methods to the assessment made with the Chemical Perturbation Index.

I used SPSS Version 12 to describe, summarize, and statistically explore my water chemistry data (SPSS, 2003). Many statistical operations assume normality of the sample distribution. To test for normality I used the Kolmogorov-Smirnov goodness of fit test, which tests the difference between a cumulative probability distribution function and the sample cumulative distribution function (Burt and Barber, 1996). Water quality data (alkalinity, hardness, and specific conductance) for each individual site were tested, and, in all cases, the hypothesis that the cumulative probability distribution differed from the sample cumulative distribution was rejected at the 0.05 significance level. This showed that the data are normally distributed.

Box Plots for Water Quality Parameters

To explore the water quality data, I used box plots to assist in the visualization of measures of central tendency. One purpose of describing the data is to answer the questions: (1) What do individual parameter descriptive statistics say about the differences and similarities between sites? and (2) Do measures of central tendency and dispersion relate more information about water quality than the CPI? Box plots of alkalinity, hardness, and specific conductance by location aid in the display and summarization of the descriptive statistics. A box plot of sample values by sample date provides information on the possible effects of sample timing on water parameter values.

Box plots of parameters by location graphically illustrate several patterns in the sample data. The Edington West site is chemically different from the other sites within the Goose Creek watershed, which have some of the highest values for parameters of all the research sites (Figure 5.1). For all three parameters, the sites in Second Creek exhibit increasing values from upstream sites to downstream sites. Alkalinity varies less than either hardness or specific conductance throughout the entire dataset, but the amount of variation within the individual sites appears larger (Figure 5.2). There are substantially more outliers and extreme values for specific conductance than either of the other parameters (Figure 5.3). There is also a greater variation in the interquartile range between sites for specific conductance. The East Fork sites in Third Creek are clearly separated from the other sites in Third Creek, particularly with respect to alkalinity concentrations and specific conductance values. Box plots for specific conductance, hardness and alkalinity have a similar shape with respect to relationship between sites.

A box plot of sample values by date with values standardized by using z-scores gives a visual indication of how sample values for the entire dataset vary over time. Direct comparison of the measures of central tendency is difficult because all three measures have different scales, which influence numbers like standard deviation. To

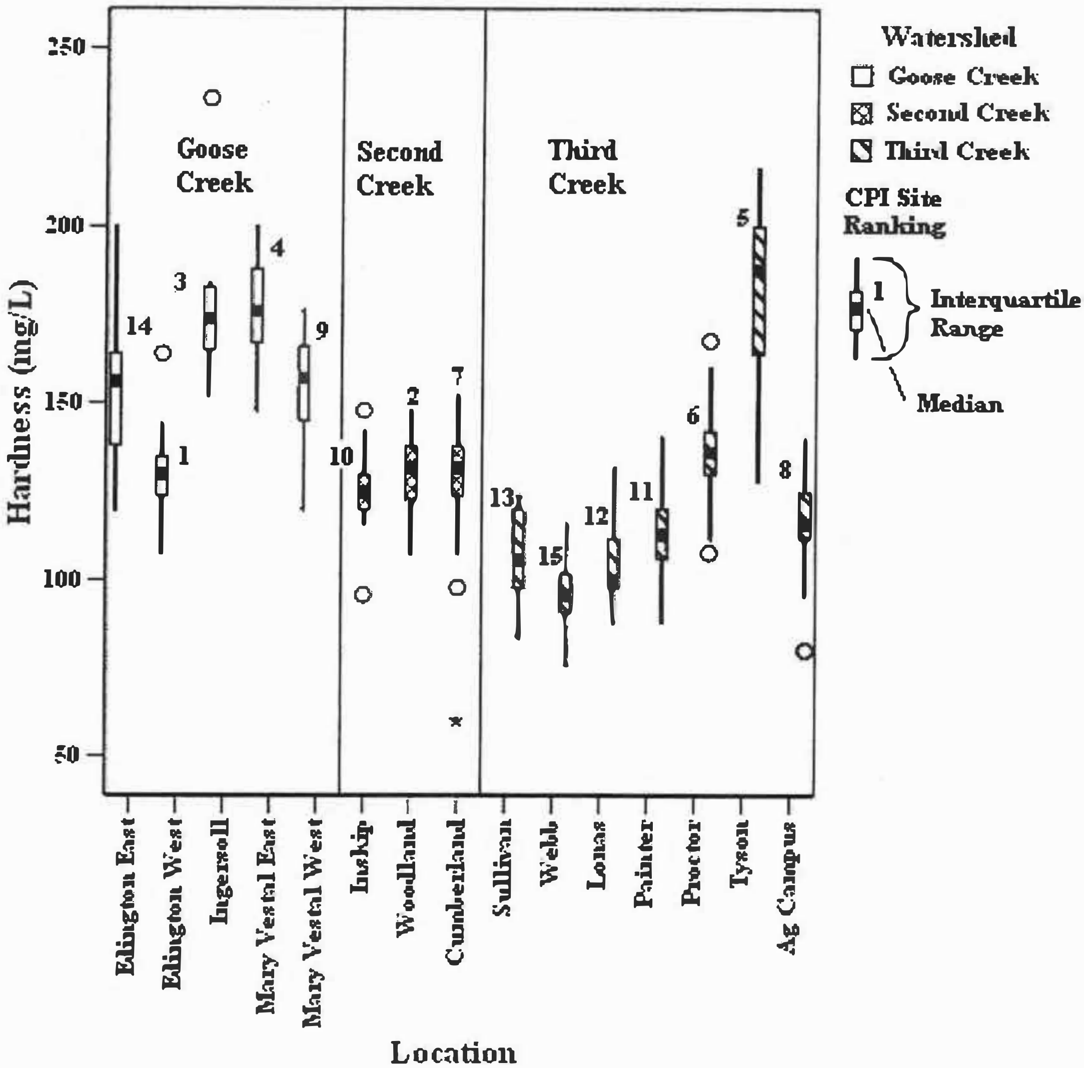

Figure 5.1: Box Plot – Hardness by Location in the Three Study Streams

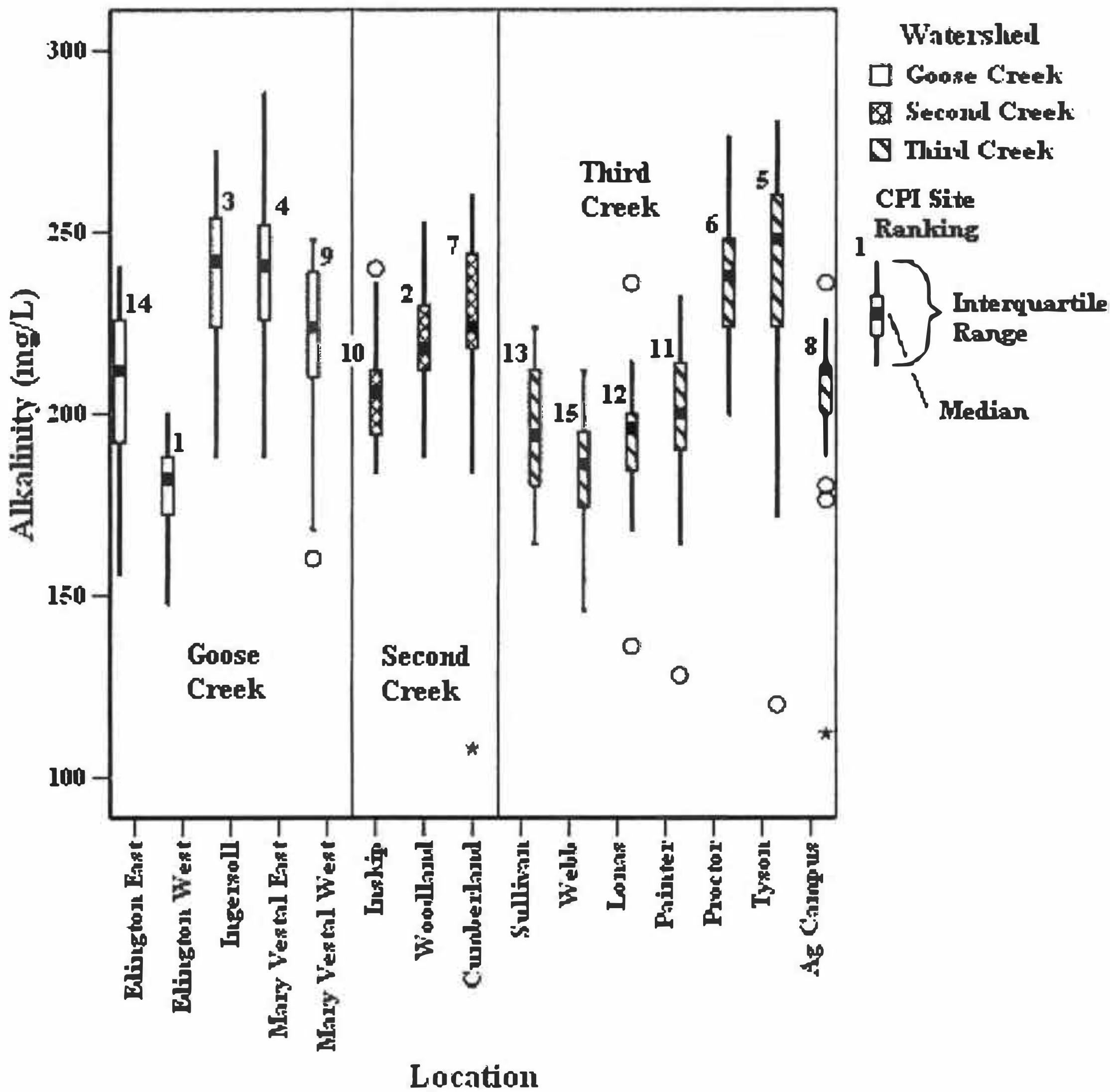

Figure 5.2: Box Plot – Alkalinity by Location in the Three Study Streams

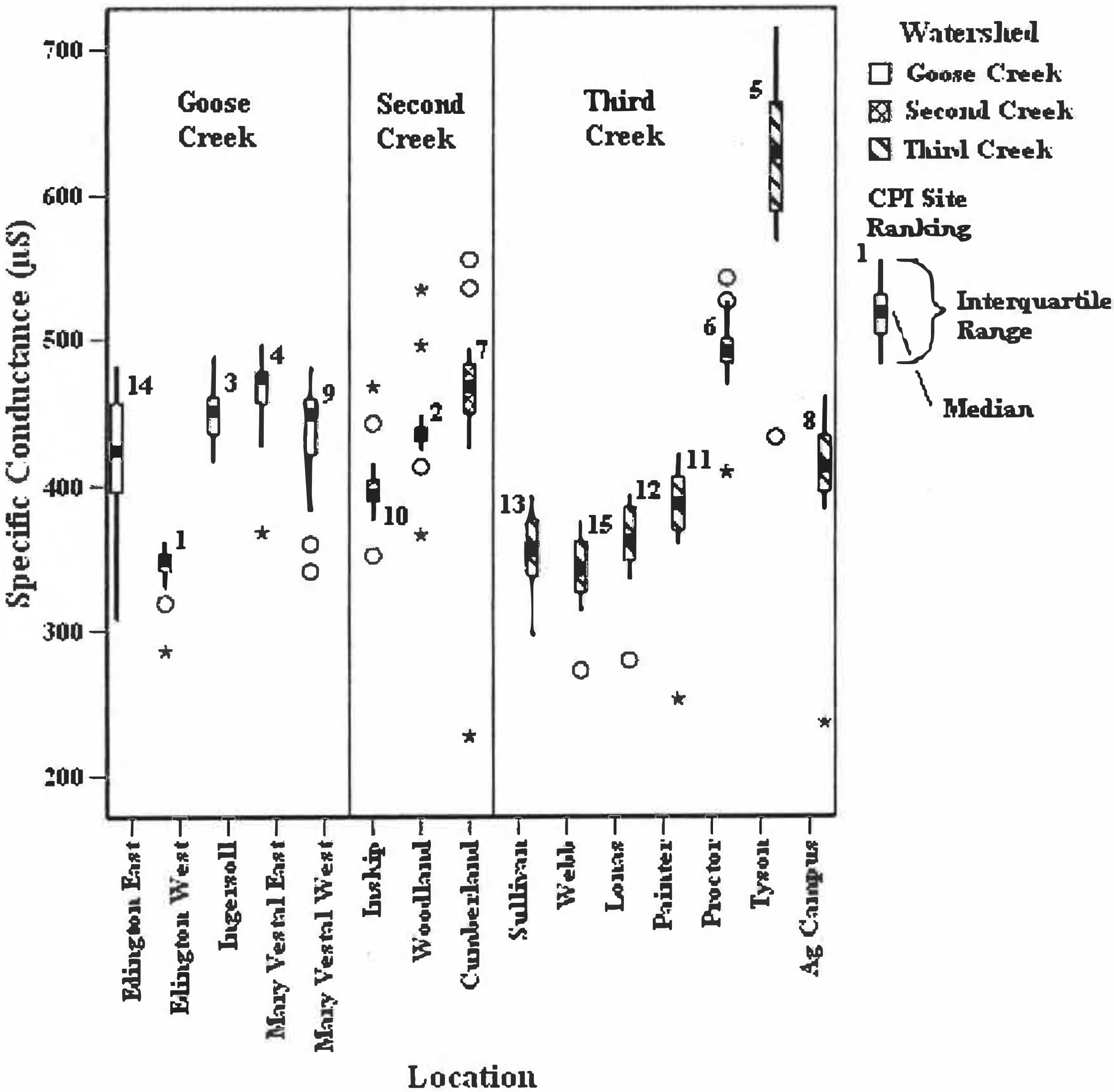

Figure 5.3: Box Plot - Specific Conductance (µS) by Location in the Three Study Streams

account for the different scales I used z-scores to plot the data grouped by date — this plot shows that the overall variance in specific conductance is generally less than that of either hardness or alkalinity when adjusted for scale range (Figure 5.4). Samples taken on 2/26/03, when the Tyson site had an extreme specific conductance value, had low overall specific conductance and hardness values when compared with other dates. The lowest values for hardness, alkalinity, and specific conductance occurred on 5/11/03; however, when plotting values by date but splitting the data by watershed, the 5/11/03 date stands out only in Second and Third Creeks. During the last part of May, hardness values increased without a subsequent increase in either alkalinity or specific conductance. Generally, all three parameters move in the same direction on the plot, though the magnitude of change in the individual parameters differs.

Boxplots provide a concise visualization of essential data characteristics. The groupings observed in boxplots of individual parameters do not reflect groupings observed with the CPI. Those sites that make up the third quartile of the CPI rankings (Proctor, Tyson, and Cumberland) plot in a similar range for alkalinity and specific conductance, but several sites from Goose Creek that are not in the third quartile also plot in similar positions. Mary Vestal West, which has a low CPI value ranking (9^{th}) consistently plots near the third and fourth ranked CPI sites. The site with the highest CPI value, Edington West, plots lowest for all parameters and also generally has a smaller interquartile range than most other sites. Only in the Third Creek watershed does the ranking CPI pattern follow generally the boxplot pattern from lowest to highest.

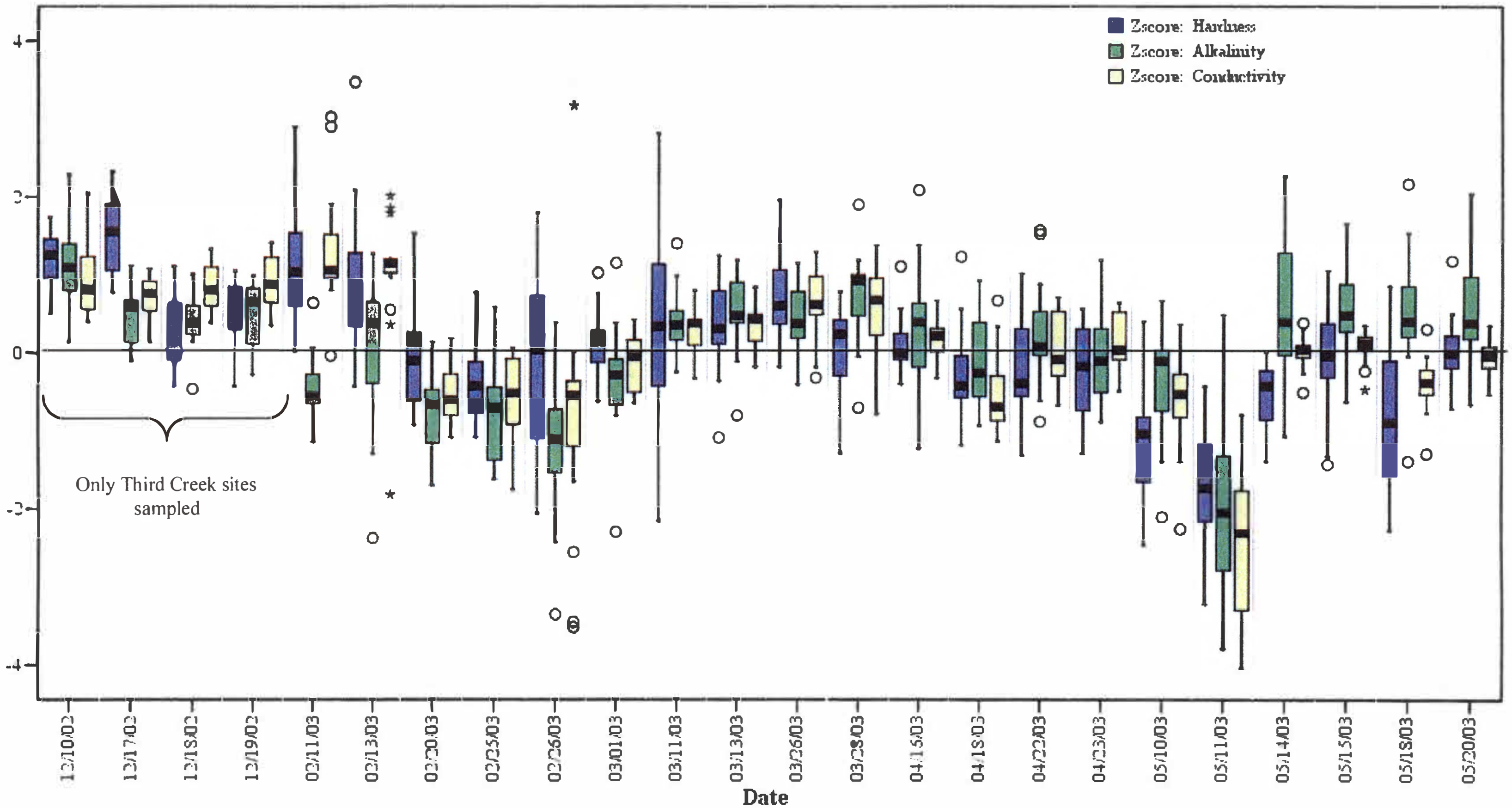

Figure 5.4: Box Plot - Specific Conductance (_S), Alkalinity, and Hardness for Samples by Date

Boxplots of individual parameters do show the similarities and dissimilarities between sample sites; however, they do not provide direct information about water quality. The boxplot of sample parameters by sample date clearly shows that timing as well as location has an effect on sample values. To further explore the effect that location has on sample values, I performed an ANOVA and a median polish procedure to explore the effects of date in relation to location.

Analysis of Variance

To determine the similarity or dissimilarity of water quality data at the study sites, I performed a one-factor analysis of variance (ANOVA) on the observed water quality parameters grouped by site. This test determines whether differences between group means (signal) is greater than the variation within groups (noise) (Helsel and Hirsch, 1992). To meet the assumption of ANOVA that population differences are equal, I log-transformed hardness and alkalinity and used a reciprocal root transformation for the specific conductance. Originally, I had log-transformed specific conductance; however, after transformation the data still did not meet the requirements of Levene's test for the equality of variance. After testing several transformations, the reciprocal root transformation of specific conductance met the test requirements. The reciprocal root transformation lowered Levene's statistic for hardness and alkalinity, so I used the original log-transformed data for those parameters.

To provide further insight into how mean parameter values by location differed in relation to one another, I used the Tukey post hoc multiple comparison test. This test compares the mean data value at one location to all possible combinations of means from all locations to indicate whether the data from an individual location are similar or different from the others. Tukey's method uses an overall error rate and is the most powerful comparison test available for unequal sample sizes (Helsel and Hirsch, 1992).

Analysis of Variance Results

The ANOVA showed clearly that the difference between water-quality parameter means at different locations exceeds the variation of the data within the locations. The sums of squares show that hardness and specific conductance have greater between-group (grouping by sample site) variation than within-group variation (Table 5.1). Alkalinity data have more within-group variation than between-group variation. Table 5.2 displays the homogenous groups defined by Tukey's method for the log-transformed hardness variable. The groups are aligned from the smallest group (grouping of sample sites) mean to the largest. Groups 6 and 7 are the two most distinctive groups (1.00 significance level), and the sites comprising these groups are not members of any other group. Groups 1 and 2 are only populated by sites along the main branch of Third Creek, though the Painter and Ag Campus sites are not exclusively in these groups. Groups 3, 4, and 5 are populated by sites from all three watersheds, and sites within these groups generally have membership in at least two groups. Membership of sites in Second Creek is confined to groups 3, 4, and 5.

Applied to the alkalinity data, Tukey's test divided locations into five groups that were less distinct and generally had lower significance values than either the groups defined for hardness or specific conductance (Table 5.3). The significance value indicates the chance of a Type I error — declaring a false difference between groups. The significance value does not reflect the overall mean error rate of approximately 40% that

Table 5.1: ANOVA Results

		Sum of Squares	df	Mean Square	F	Sig.
Log Hardness	Between Groups	2.357	14	0.168	65.641	0.000
	Within Groups	0.800	312	0.003		
	Total	3.157	326			
Log Alkalinity	Between Groups	0.533	14	0.038	15.037	0.000
	Within Groups	0.790	312	0.003		
	Total	1.322	326			
Reciprocal Root Specific Conductance	Between Groups	0.005	14	0.000	56.408	0.000
	Within Groups	0.002	312	0.000		
	Total	0.006	326			

Table 5.2: Tukey's Homogeneous Groups - Log-Hardness

			Groups						
Location	CPI Quartile	CPI Rank	1	2	3	4	5	6	7
Goose Creek									
Edington East	1	14						2.187	
Edington West	4	1				2.109	2.109		
Ingersoll	4	3							2.243
Mary Vestal East	4	4							2.244
Mary Vestal West	2	9						2.187	
Second Creek									
Inskip	2	10			2.098	2.098	2.098		
Woodland	4	2				2.110	2.110		
Cumberland	3	7			2.098	2.098	2.098		
Third Creek									
Webb	1	13	1.984						
Lonas	1	15	2.016	2.016					
Sullivan	1	12	2.028	2.028					
Painter	2	11		2.050	2.050				
Proctor	3	6					2.132		
Tyson	3	5							2.255
Ag Campus	2	8		2.063	2.063	2.063			
Sig.			0.240	0.149	0.106	0.125	0.643	1.000	1.000

Table 5.3: Tukey's Homogeneous Groups - Log-Alkalinity

Location	CPI Quartile	CPI Rank	Groups 1	2	3	4	5
Goose Creek							
Edington East	1	14		2.313	2.313	2.313	
Edington West	4	1	2.252				
Ingersoll	4	3					2.376
Mary Vestal East	4	4					2.379
Mary Vestal West	2	9			2.337	2.337	2.337
Second Creek							
Inskip	2	10		2.312	2.312	2.312	
Woodland	4	2				2.344	2.344
Cumberland	3	7			2.339	2.339	2.339
Third Creek							
Sullivan	1	13	2.287	2.287	2.287		
Webb	1	15	2.263	2.263			
Lonas	1	12	2.283	2.283			
Painter	2	11	2.3	2.3	2.3	2.3	
Proctor	3	6					2.372
Tyson	3	5					2.372
Ag Campus	2	8	2.303	2.303	2.303	2.303	
Sig.			0.07	0.08	0.05	0.2	0.28

at least one error was made in the comparison of means for the five groups. Lack of clearly defined groups using alkalinity was probably the result of the high amount of within-group variance that ANOVA reported. None of the groups identified by SPSS for alkalinity had fewer than five members, and no group had membership exclusive to any one watershed. The two East Fork sites (Proctor and Tyson) were exclusively members of group 5, and no other sites within Third Creek are members of that group.

Nine groups were formed above the 0.05 significance level for specific conductance. Groups 1 and 2 were almost exclusively from main branch sites in Third Creek, similar to the first two groups defined by hardness (Table 5.4). The one difference between groups 1 and 2 for specific conductance and hardness is Goose Creek's Edington West site. This site consistently groups with sites other than those in Goose Creek for all parameters. Both the East Fork sites in Third Creek have significantly higher means than the main branch Third Creek sites. The Tyson site had a mean so much larger than the rest of the sites in this study that it formed its own group. As with hardness and alkalinity, specific conductance at all three Second Creek sites had membership in multiple groups. The ANOVA test and Tukey comparisons showed that location can be used as an explanatory variable to describe at least some of the variation in the water chemistry data.

Discussion of Analysis of Variance (ANOVA)

ANOVA and Tukey's test for homogeneous groups provided some insight into the ability of the CPI's components to describe the difference between sample sites. The Sullivan, Webb, Lonas, and Painter sites grouped together for all three parameters. The

Table 5.4: Tukey's Homogeneous Subgroups - Reciprocal Root Specific Conductance

Location	CPI Quartile	CPI Rank	Groups 1	2	3	4	5	6	7	8	9
Goose Creek											
Edington East	1	14				-0.0492	-0.0492	-0.0492			
Edington West	4	1	-0.0540								
Ingersoll	4	3						-0.0472	-0.0472	-0.0472	
Mary Vestal East	4	4							-0.0465	-0.0465	
Mary Vestal West	2	9					-0.0480	-0.0480	-0.0480		
Second Creek											
Inskip	2	10			-0.0502	-0.0502	-0.0502				
Woodland	4	2					-0.0478	-0.0478	-0.0478		
Cumberland	3	7						-0.0470	-0.0470	-0.0470	
Third Creek											
Webb	1	13	-0.0542								
Sullivan	1	15	-0.0532	-0.0532							
Lonas	1	12	-0.0526	-0.0526	-0.0526						
Painter	2	11		-0.0512	-0.0512	-0.0512					
Proctor	3	6								-0.0451	
Tyson	3	5									-0.0400
Ag Campus	2	8				-0.0498	-0.0498				
Sig.			0.64	0.31	0.07	0.28	0.09	0.21	0.74	0.27	1.00

Edington West site that had the highest CPI values of all the sites grouped with the above sites for both alkalinity and specific conductance; despite the fact the Sullivan, Webb, Lonas, and Painter sites had high CPI rankings (they are less perturbed). The high within-site sums of squares for alkalinity indicate that it would not be a good measure for differentiating between sites. Both hardness and specific conductance had large F ratios, indicating they are potentially good indicators of the difference between sample locations. Several of the groups, but not all, formed by Tukey's test, formed among sites with similar CPI rankings. Many of the sample sites had membership in two or more of the groups created by Tukey's test for hardness and specific conductance. This made it difficult to assess whether these groups represented the variation in a specific landscape parameter. While ANOVA and Tukey's test did show that hardness and specific conductance can be used to separate the sites, they did not provide a clear indication of the difference in landscape factors between sample sites. Grouping sites by one factor only (location) provided only limited information about associations between location factors (landscape variable, geology, etc.) and parameter values. Perhaps the influence of sample timing partially accounts for the inability of the ANOVA procedure, which only uses one factor in the analysis to form interpretable groupings of sites.

Median Polish Procedure

One-factor ANOVA analysis uses only one explanatory variable (location) when testing the difference between means. However, water quality samples were taken on different dates, so differences in the parameter values may be the result of the sampling date rather than location, or more likely a combination of these two general factors. The median polish procedure fits an additive model that employs a randomized complete block design by operating on a data table. The median polish procedure blocks out and provides an indication of the amount of noise in the data set caused by sampling on different dates. This is a nonparametric statistical technique that uncovers the effect that each row and column has on the model and provides a residual in each cell of the table that tells how far apart that particular cell is from the value predicted by the model. Median polish is an iterative process that is resistant to outliers and provides an estimate of the overall mean, group effects, and block effects (Helsel and Hirsch, 1992).

To perform the median polish, I aligned the data into a table of rows (date) and columns (location). First, the procedure calculates the median of each row and subtracts it from that row's data. Then, the median of the column of the row medians is computed, as the first estimate of the overall median, and subtracted from each row median. Next, the median of each column of residuals is computed and subtracted from that column's data. Finally, the median of the column medians is subtracted from the column medians and added to the overall median. This is the first 'polish'. In principle, the process continues until all the rows have zero median; however, generally only two polishes are needed to provide stable estimates of the overall median and the row and column effects (Helsel and Hirsch, 1992). Using the PROPHET 5.0 (BBN Systems and Technology, 1996) software package, I performed two polishes each for hardness, alkalinity, and specific conductance on both the entire dataset and data broken down by watershed.

Median Polish Results

The median polish table for hardness shows that location (column effects) generally has greater effect (larger in absolute magnitude) on hardness concentrations at the Edington West, Proctor, and Tyson sites than the date (row effect) (Table 5.5). The

Table 5.5: Median Polish Hardness by Individual Watersheds

	Goose Creek						Second Creek				Third Creek							
Date	Edingtion East	Edingtion West	Ingersoll	Mary Vestal East	Mary Vestal West	Row Effects	Inskip	Woodland	Cumberland	Row Effects	Sullivan	Webb	Lonas	Painter	Proctor	Tyson	Ag Campus	Row Effects
2/11/2003	-10.0	18.0	2.0	-14.0	10.0	14.0	8.0	0.0	-1.0	12.0	4.0	-1.0	0.0	-4.0	0.0	-4.0	0.0	16.0
2/13/2003	26.0	-26.0	-2.0	42.0	-6.0	18.0	-4.0	0.0	17.0	4.0	-4.0	-1.0	-16.0	8.0	0.0	4.0	8.0	12.0
2/20/2003	-14.0	0.0	-8.0	4.0	24.0	0.0	-8.0	0.0	7.0	8.0	0.0	7.0	-2.0	-2.0	12.0	-12.0	2.0	-4.0
2/25/2003	-16.0	0.0	-4.0	4.0	20.0	-8.0	-4.0	0.0	7.0	-4.0	-2.0	1.0	0.0	-2.0	10.0	30.0	2.0	-6.0
2/26/2003	20.0	0.0	-6.0	24.0	-8.0	-20.0	0.0	6.0	-37.0	14.0	0.0	-1.0	0.0	14.0	-28.0	32.0	-4.0	4.0
3/1/2003	0.0	0.0	0.0	-4.0	12.0	0.0	0.0	8.0	-3.0	4.0	-4.0	-1.0	0.0	8.0	8.0	-8.0	0.0	0.0
3/11/2003	44.0	0.0	-32.0	0.0	8.0	-8.0	0.0	0.0	-16.0	12.0	0.0	7.0	20.0	0.0	-24.0	12.0	-8.0	8.0
3/13/2003	12.0	-24.0	0.0	0.0	-4.0	8.0	8.0	0.0	-15.0	4.0	8.0	-1.0	0.0	0.0	-4.0	6.0	-8.0	8.0
3/26/2003	20.0	-4.0	-16.0	0.0	8.0	8.0	-4.0	0.0	5.0	4.0	4.0	11.0	-4.0	0.0	-8.0	24.0	0.0	12.0
3/28/2003	12.0	0.0	4.0	-14.0	-8.0	0.0	0.0	-4.0	5.0	-8.0	0.0	-1.0	0.0	-4.0	0.0	8.0	-4.0	8.0
4/16/2003	0.0	0.0	-10.0	-8.0	0.0	4.0	0.0	6.0	-1.0	-2.0	12.0	-1.0	0.0	-4.0	0.0	0.0	-8.0	4.0
4/18/2003	-12.0	10.0	2.0	6.0	-6.0	2.0	-4.0	0.0	1.0	-4.0	0.0	7.0	0.0	0.0	-8.0	-12.0	0.0	-4.0
4/22/2003	-14.0	-6.0	2.0	10.0	18.0	-2.0	-8.0	0.0	5.0	-4.0	-12.0	7.0	-4.0	0.0	-4.0	12.0	10.0	0.0
4/23/2003	2.0	2.0	2.0	-16.0	-22.0	2.0	0.0	-4.0	9.0	-4.0	0.0	7.0	-2.0	0.0	16.0	-8.0	4.0	-4.0
5/10/2003	-20.0	4.0	-16.0	0.0	0.0	-16.0	0.0	-4.0	17.0	-12.0	4.0	13.0	0.0	-8.0	-8.0	0.0	-24.0	-12.0
5/11/2003	-2.0	16.0	0.0	0.0	16.0	-24.0	0.0	12.0	-39.0	-32.0	0.0	7.0	4.0	0.0	12.0	-28.0	-16.0	-20.0
5/14/2003	-22.0	0.0	-14.0	4.0	4.0	-4.0	0.0	0.0	-5.0	-6.0	0.0	3.0	4.0	8.0	12.0	-4.0	-12.0	-8.0
5/15/2003	0.0	-2.0	8.0	2.0	-14.0	4.0	-18.0	0.0	5.0	12.0	0.0	-9.0	-14.0	2.0	8.0	0.0	0.0	0.0
5/18/2003	2.0	-2.0	14.0	0.0	-6.0	-22.0	0.0	6.0	-31.0	-2.0	0.0	-9.0	8.0	8.0	24.0	-40.0	0.0	-8.0
5/20/2003	0.0	0.0	14.0	-4.0	0.0	0.0	-6.0	2.0	-1.0	2.0	-8.0	-7.0	-10.0	2.0	0.0	0.0	4.0	4.0
Column Effects	-4.0	-28.0	0.0	16.0	16.0	160.0	0.0	0.0	3.0	128.0	-4.0	-15.0	-4.0	0.0	24.0	68.0	8.0	108.0

magnitude of row or date effects was approximately equal to that of location effects for Goose and Third Creeks, while date effects were much greater in magnitude than location effects for Second Creek. Goose Creek has an estimated hardness median much higher than either the Second or Third Creek watersheds.

The location and column effects for alkalinity have similar trends to those of hardness (Table 5.6). Once again, date effects have a greater impact on alkalinity concentrations than location effects in Second Creek. East Fork sites in Third Creek had much higher location-related residuals for alkalinity than any of the other sites in Third Creek. Unlike the pattern for hardness, the Edington West site (Goose Creek), while still exhibiting a large effect from location, had a negative instead of positive value. There were large negative residuals in the row effects for sample dates in late February and on 5/11/03. Meteorological records at McGee Tyson Airport show sporadic light rain events with precipitation totaling 1.37 cm during the late February period, and a rainfall amount of 0.89 cm in the early morning of 5/11/03. Many, but not all, of the negative values present in the date effects column are associated with precipitation events of varying intensity (Figure 5.5). The estimated median for alkalinity is much closer for the three watersheds than was median hardness.

The median polish for specific conductance has many of the same large negative residual values in the row effects column as alkalinity (Table 5.7). Location exerts a larger influence on specific conductance than on either of the other parameters, particularly at East Fork sites. Tyson and Proctor have the two highest location effects for specific conductance of any of the sites in this study. A general progression from

Table 5.6: Median Polish Alkalinity by Individual Watersheds

Date	Goose Creek						Second Creek				Third Creek							
	Edingtion East	Edingtion West	Ingersoll	Mary Vestal East	Mary Vestal West	Row Effects	Inskip	Woodland	Cumberland	Row Effects	Sullivan	Webb	Lonas	Painter	Proctor	Tyson	Ag Campus	Row Effects
2/11/2003	0.0	20.0	12.0	-4.0	-8.0	-16.0	2.0	8.0	-4.0	-14.0	20.5	4.0	9.0	0.0	-8.0	-12.0	-8.0	-12.0
2/13/2003	-4.0	40.0	-20.0	0.0	52.0	-36.0	-14.0	8.0	0.0	14.0	-12.5	3.0	0.0	-9.0	3.0	-25.0	7.0	9.0
2/20/2003	-22.0	4.0	0.0	12.0	0.0	-16.0	2.0	12.0	-4.0	-14.0	-4.5	3.0	0.0	9.0	1.0	-17.0	-1.0	-23.0
2/25/2003	-24.0	12.0	8.0	0.0	-12.0	-24.0	-26.0	0.0	8.0	-2.0	-7.5	0.0	5.0	-20.0	-8.0	36.0	16.0	-16.0
2/26/2003	8.0	0.0	0.0	-32.0	-36.0	-28.0	4.0	0.0	-30.0	-4.0	0.5	0.0	-3.0	2.0	-4.0	-100.0	8.0	-20.0
3/1/2003	0.0	-20.0	-4.0	4.0	4.0	-16.0	2.0	-4.0	0.0	-2.0	-11.5	-12.0	1.0	0.0	-12.0	40.0	0.0	0.0
3/11/2003	-4.0	-8.0	4.0	0.0	0.0	0.0	-3.0	3.0	0.0	3.0	8.5	-8.0	-7.0	0.0	4.0	-12.0	24.0	12.0
3/13/2003	4.0	-8.0	0.0	0.0	0.0	16.0	-2.0	0.0	24.0	2.0	-20.5	-5.0	0.0	3.0	-5.0	7.0	3.0	9.0
3/26/2003	0.0	-8.0	0.0	-16.0	8.0	8.0	-18.0	0.0	28.0	6.0	-0.5	3.0	0.0	-17.0	-5.0	31.0	3.0	9.0
3/28/2003	12.0	0.0	-8.0	-32.0	6.0	8.0	2.0	8.0	-8.0	10.0	-3.5	0.0	-3.0	0.0	-24.0	0.0	0.0	24.0
4/16/2003	2.0	-16.0	20.0	0.0	-4.0	4.0	-38.0	8.0	0.0	26.0	-12.5	-31.0	0.0	3.0	-9.0	19.0	3.0	9.0
4/18/2003	-12.0	2.0	0.0	-22.0	6.0	6.0	2.0	-8.0	8.0	-2.0	0.5	0.0	9.0	-4.0	2.0	-4.0	24.0	-12.0
4/22/2003	-20.0	-20.0	12.0	12.0	0.0	16.0	-26.0	0.0	0.0	6.0	4.5	0.0	17.0	0.0	0.0	-16.0	-12.0	0.0
4/23/2003	28.0	0.0	24.0	-2.0	-4.0	-8.0	-14.0	0.0	34.0	-6.0	-3.5	0.0	-11.0	0.0	-12.0	12.0	0.0	0.0
5/10/2003	-52.0	4.0	-12.0	2.0	0.0	-8.0	-26.0	0.0	4.0	-2.0	-11.5	-20.0	9.0	0.0	12.0	0.0	0.0	0.0
5/11/2003	0.0	0.0	-4.0	32.0	-28.0	-28.0	2.0	0.0	-80.0	-30.0	35.5	13.0	0.0	-17.0	19.0	-13.0	-33.0	-55.0
5/14/2003	8.0	0.0	-44.0	-4.0	8.0	16.0	6.0	0.0	-8.0	18.0	0.5	-4.0	-11.0	0.0	40.0	8.0	12.0	0.0
5/15/2003	10.0	0.0	-2.0	2.0	0.0	2.0	-22.0	0.0	30.0	6.0	17.5	-19.0	-6.0	13.0	1.0	15.0	-1.0	15.0
5/18/2003	-4.0	4.0	12.0	-40.0	0.0	0.0	2.0	0.0	-18.0	26.0	8.5	-10.0	-11.0	0.0	4.0	-4.0	0.0	12.0
5/20/2003	-8.0	0.0	-8.0	36.0	0.0	4.0	2.0	-4.0	44.0	-2.0	24.5	0.0	-3.0	20.0	0.0	4.0	-8.0	8.0
Column Effects	-8.0	-40.0	20.0	24.0	0.0	224.0	-6.0	0.0	0.0	218.0	-8.5	-12.0	-9.0	0.0	36.0	40.0	0.0	200.0

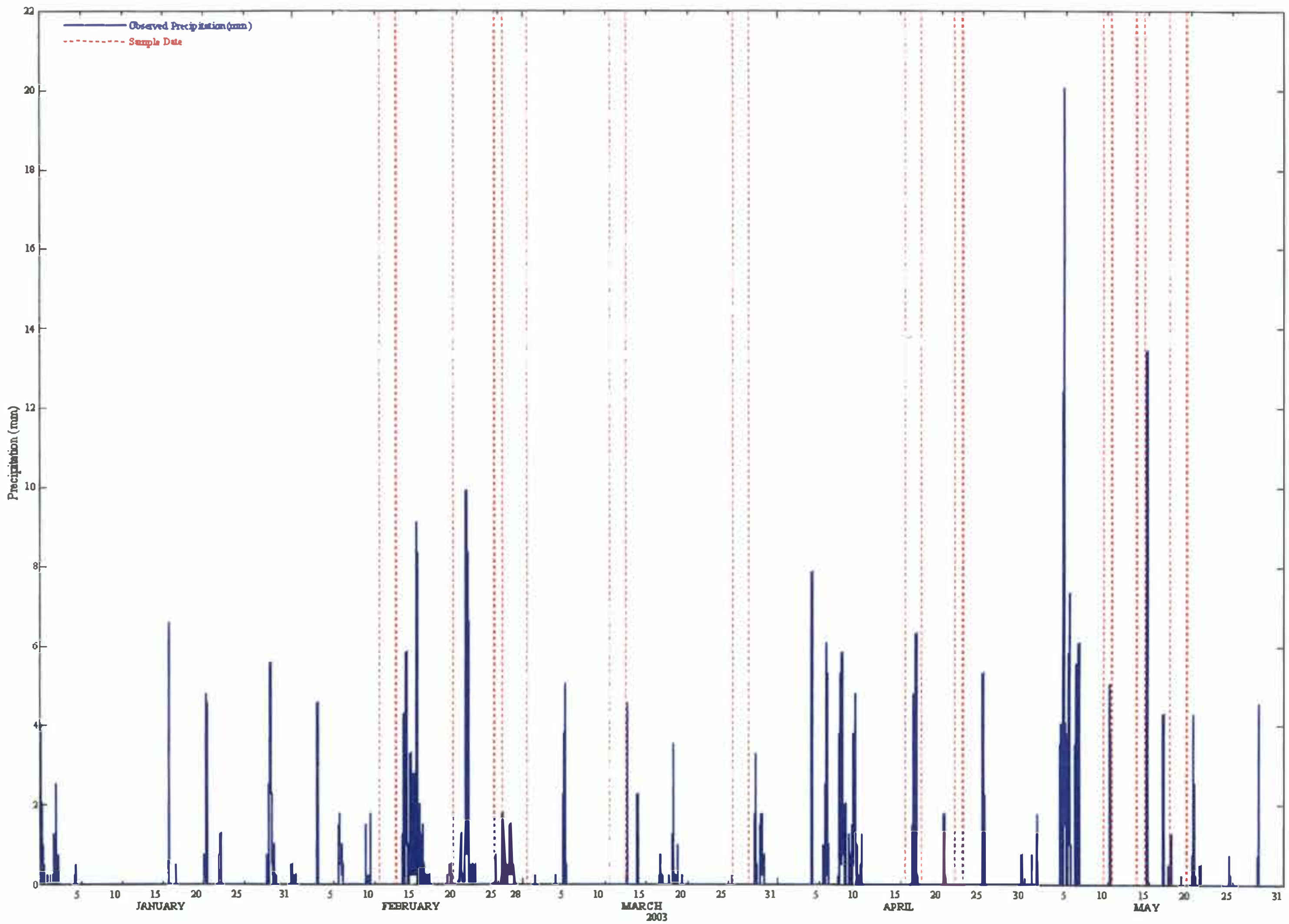

Figure 5.5: Precipitation Plot with Sample Dates

Table 5.7: Median Polish Specific Conductance by Individual Watersheds

	Goose Creek						Second Creek				Third Creek							
Date	Edingtion East	Edingtion West	Ingersoll	Mary Vestal East	Mary Vestal West	Row Effects	Inskip	Woodland	Cumberland	Row Effects	Sullivan	Webb	Lonas	Painter	Proctor	Tyson	Ag Campus	Row Effects
2/11/2003	7.5	-11.0	11.5	-2.8	0.0	22.0	-17.5	11.5	0.0	90.8	-39.0	-6.3	0.0	5.0	-32.5	78.0	20.5	33.3
2/13/2003	10.5	-30.0	2.5	-8.8	0.0	33.0	-15.0	0.0	7.5	63.3	-79.0	-2.3	0.0	5.0	-22.5	73.0	14.5	33.3
2/20/2003	-43.0	15.5	0.0	6.8	-20.5	-18.5	0.0	9.0	-17.5	-2.8	-4.0	-1.3	3.0	0.0	1.5	0.0	-3.5	-18.8
2/25/2003	-54.0	27.5	0.0	29.8	-8.5	-35.5	-9.5	7.5	0.0	-4.3	-6.0	-3.3	-1.0	2.0	19.5	43.0	-0.5	-17.8
2/26/2003	28.5	0.0	30.5	-39.8	-43.0	-64.0	0.0	13.0	-32.5	-5.8	-2.0	-1.3	0.0	-2.0	6.5	293.0	10.5	-12.8
3/1/2003	-12.5	0.0	-15.5	1.3	1.0	1.0	-4.5	0.5	0.0	9.8	-3.5	0.3	0.5	-0.5	-5.0	40.5	5.0	-9.3
3/11/2003	25.0	-10.5	0.0	-0.3	-0.5	4.5	0.0	-10.0	3.5	13.3	0.0	-1.3	0.0	-1.0	-20.5	22.0	3.5	14.3
3/13/2003	26.5	-14.0	1.5	-3.8	0.0	5.0	0.0	-8.0	5.5	14.3	0.0	-0.3	0.0	-3.0	-19.5	11.0	2.5	17.3
3/26/2003	45.0	-17.5	0.0	-3.3	7.5	8.5	-19.0	0.0	13.5	15.3	-1.5	0.3	0.5	1.5	-15.0	54.5	-3.0	30.8
3/28/2003	38.0	-29.5	0.0	-32.3	1.5	10.5	0.5	-15.5	0.0	19.8	0.0	4.8	0.0	-1.0	-27.5	51.0	-4.5	31.3
4/16/2003	-0.5	0.0	-1.5	2.3	0.0	5.0	-1.0	0.0	4.5	5.3	1.0	-4.3	-4.0	0.0	1.5	-5.0	0.5	8.3
4/18/2003	-8.0	13.5	0.0	-7.3	9.5	-8.5	3.0	0.0	-2.5	-19.8	0.0	-0.3	0.0	0.0	2.5	-4.0	-0.5	-22.8
4/22/2003	2.5	-8.0	-3.5	0.3	0.0	12.0	0.0	-1.0	0.5	-3.8	3.0	0.8	0.0	0.0	3.5	-21.0	-7.5	-3.8
4/23/2003	7.0	-6.5	-2.0	-1.3	2.5	9.5	-2.5	1.5	0.0	-0.3	2.0	1.8	-2.0	0.0	0.5	-13.0	-2.5	2.3
5/10/2003	-92.0	26.5	0.0	12.8	-37.5	-26.5	-6.5	3.5	0.0	-10.3	-3.0	-1.3	0.0	0.0	11.5	0.0	1.5	-13.8
5/11/2003	-55.5	0.0	12.5	1.3	-57.0	-31.0	24.0	0.0	-171.5	-66.8	25.5	15.3	0.5	-49.5	0.0	-88.5	-90.0	-81.3
5/14/2003	-4.5	0.0	0.5	4.3	0.0	-1.0	0.0	0.0	4.5	-1.8	-0.5	1.3	-2.5	0.5	0.0	-14.5	2.0	2.8
5/15/2003	0.5	0.0	-0.5	3.3	0.0	-1.0	0.0	-1.0	3.5	0.3	0.0	3.8	0.0	1.0	-1.5	-14.0	0.5	5.3
5/18/2003	-14.5	12.0	7.5	-30.8	0.0	-13.0	4.0	0.0	-19.5	-1.8	4.5	2.3	0.5	-4.5	0.0	-21.5	-10.0	-11.3
5/20/2003	-3.0	1.5	0.0	6.8	-1.5	-4.5	0.5	-0.5	0.0	3.8	2.5	0.3	0.5	2.5	-1.0	-11.5	-4.0	-2.3
Column Effects	-20.5	-98.0	4.5	23.8	0.0	448.0	-38.0	0.0	32.5	432.8	-29.0	-44.8	-23.0	0.0	107.5	220.0	24.5	382.8

smaller to larger location-effect residuals for specific conductance can be seen going downstream for all the watersheds. The Tyson site had an extremely large positive residual for specific conductance on 2/26/03. On that same date, Tyson had an extremely large negative residual for alkalinity and a positive residual for hardness of much smaller magnitude. This date was a few days after deicing agents were applied to the streets around Knoxville. The large difference in residuals for alkalinity, hardness, and specific conductance demonstrates that values do vary independently at certain times.

Specific conductance, an easy measure of total dissolved solids, is often used as an indicator of water quality. Hardness and alkalinity, though also commonly included in watershed monitoring programs, are not commonly used individually as water quality indicators. Despite this, I ranked alkalinity and hardness as well as specific conductance by location (column) effect values and compared those rankings with the site ranking within individual watersheds (Table 5.8). A rank of one indicates the site has highest location effect for the specific parameter in a particular watershed. A rank of one for the CPI means the site has the highest CPI value (most perturbed) within the individual watershed. The rankings for all three parameters do not compare well between sample sites in Goose or Second Creeks, though the Inskip site is at least tied for the least perturbed rank for all three constituent location effects and has the lowest CPI in Second Creek. Rankings of site location effects by parameter and CPI values in Third Creek track very closely for all constituents and match exactly between specific conductance and CPI value.

Table 5.8: Comparison of Specific Conductance Rank and CPI Rank

Location	Hardness Ranking	Alkalinity Ranking	Specific Conductance Ranking	CPI Ranking
Goose Creek				
Edington East	4	4	4	5
Edington West	5	5	5	1
Ingersoll	3	2	2	2
Mary Vestal East	1.5	1	1	3
Mary Vestal West	1.5	3	3	4
Second Creek				
Inskip	2.5	3	3	3
Woodland	2.5	1.5	2	1
Cumberland	1	1.5	1	2
Third Creek				
Sullivan	5.5	5	6	6
Webb	7	7	7	7
Lonas	5.5	6	5	5
Painter	4	3.5	4	4
Proctor	2	2	2	2
Tyson	1	1	1	1
Ag Campus	3	3.5	3	3

Note: Rank of 1 given to highest CPI value and highest specific conductance value.

Discussion of Median Polish Procedure

The median polish tables for Second Creek show that location has very little effect on values of hardness and alkalinity. The magnitude of timing effects with respect to alkalinity and hardness is equal to or higher than the magnitude of the location effects on many occasions for my research sites. The Tyson, Proctor, and Edington West sites have consistently strong location effects for all the parameters. Interestingly, these sites did not group together in the ANOVA Tukey's test despite the fact that they all have high CPI values. This may be an indication that geology overpowers grouping strategies based on mean constituent values alone. The large difference in the overall watershed median values computed using the median polish procedure indicates that any characterization of water quality parameters based solely on absolute constituent values may miss pollution effects. For example, one of the sites on the main branch of Third Creek may receive pollutants that boost the specific conductance significantly but still fall below the median specific conductance for a site on Goose Creek that had no pollutant inputs.

The column effects (location) as a ranking of water quality within the individual watersheds correlated very well with site rankings derived from CPI computations. Parameter rankings for Third Creek generally agreed with the CPI ranking, and the specific conductance ranking matched exactly. Specific conductance, the most accepted measure of water quality of the three parameters, indicates that the CPI is tracking water quality within Third Creek effectively. The rankings by specific conductance do not equate as well to CPI ranks in Second and Goose Creeks. Second Creek had only three sites, and therefore a difference reversing two sites is not necessarily an indication that the CPI is invalid in this watershed. The specific conductance ranking for Goose Creek follows an upstream (highest ranks, lowest conductance) to downstream (lowest rank) pattern that would generally be expected as the creek flows through increasingly urbanized area towards its mouth. The CPI ranking does not follow this ranking, perhaps due to influences not directly attributable to increased urbanization.

CHAPTER 6

LANDSCAPE AND WATER QUALITY

The ionic composition of surface waters is a result of the hydrologic processes occurring within the contributing watersheds. Water chemistry reflects the many paths and interactions that take place during the journey taken by waters that make up a surface stream. Many studies of water chemistry have demonstrated the relationship between landscape variables, such as geology, lithology, and land use, and the resulting water chemistry. In this chapter, I explore the relationships between landscape variables and CPI values using statistical techniques. I also attempt to determine whether through correlation analysis and qualitative assessments the associations between landscape and the values of the parameters used to compute the CPI follow patterns reported in the literature.

Methods for Comparison of Landscape Variables and CPI

To determine if the landscape associated with each test site differed significantly between sites, I employed two tests, the median method and the Kruskal-Wallis test. With only 15 test sites, I had a limited number of observations for the basin data so I used the Kruskal-Wallis test, a nonparametric version of ANOVA to compare the similarity of my basin variables between CPI quartiles. I also used the median method, which makes no assumptions about the distribution of the test variables, and which tests the null hypothesis that two or more independent samples have the same median. The median method computes a variable's median without respect to group membership, and then creates a frequency table separated by group with the number of members of a specific group either above or below the overall median. A chi-square statistic is then calculated on the resulting frequency table to test the null hypothesis that the group medians are the same. This test can only determine whether the median of the landscape characteristic for one of the quartiles differs significantly from the others. The Kruskal-Wallis test ranks the original data and performs an analysis of variance on the ranks, measuring how group ranks differ from the average rank of all the data. Due to the small sample size and small number of group members (15 sites/4 quartiles), I computed the exact p-value during both tests as required when comparing four or more groups with membership of less than five (Helsel and Hirsch, 1992).

Total impervious surface has been linked to water quality degradation and elevated ion levels by numerous research projects. To determine if water chemistry relationships in my research study agree with the relationships between water chemistry and impervious surface found in the literature, I also performed the median methods test for my water quality parameters grouped by impervious surface percentage. I divided the sites into three equal impervious surface groupings, with cut points at 31% and 41% total impervious surface, using impervious surface values derived from the USGS impervious surface raster dataset.

Associations Between Landscape and Water Chemistry in Knoxville, Tennessee

I performed both tests on 22 landscape variables grouped by CPI quartile. The Kruskal-Wallis test found six variables (percent slope > 30, mean slope, USGS total impervious surface, percent evergreen forest, percent total forest, and percent Urban Land/Udorthent soil complex) to be significantly different at the 0.05 level. Using the median method, the null hypothesis of equal medians was rejected for only three of the six landscape variables (percent slope > 30, percent evergreen forest, and percent Urban Land/Udorthent soil complex) identified by the Kruskal-Wallis test. Inspection of the frequency table generated by the median method provides some indications of how landscape variables relate to the different site groupings (Table 6.1).

The sites with CPI values in the fourth quartile, those sites with the highest CPI values and the most perturbed water chemistry, have lower K-factor values, permeability, and depth to water table. K-factor is a soil erodibility factor that is part of the Revised Universal Soil Loss Equation (RUSLE), which represents both susceptibility of soil to erosion and the rate of runoff. Soils that are easily detached have high K factors and soils that are not easily detached, like those high in clay content, have low K factors. The fourth quartile sites also have above-median values for percent of slope > 30% and mean slope. Interestingly, both the first and fourth quartiles have values above the median for forest-related variables, while the second and third quartiles have values below the median. This is also true for the Urban Land and Udorthent soil complexes: both the first and fourth quartiles have values below the median and the second and third quartiles have values above the overall median. When I originally designed the sampling strategy, I was operating under the assumption that sites draining heavily forested subbasins would be less perturbed and therefore have lower CPI values. After collecting the water samples, calculation of the CPI proved this to be a false assumption, as several sites in the Goose Creek watershed have high CPI values despite the large amount of forested land throughout the watershed.

The median methods test on sample values for alkalinity, hardness, and specific conductance grouped by impervious surface, indicating that sample values are following

Table 6.1: Median Test for Landscape Variables

		CPI Quartile			
		1	2	3	4
Percent Silt & Clay	> Median	1	2	1	3
	<= Median	3	2	2	1
KFACT	> Median	3	2	1	1
	<= Median	1	2	2	3
Urban Land and Udorthent soil complexes %[1]	> Median	0	4	2	1
	<= Median	4	0	1	3
Permeability	> Median	3	2	1	1
	<= Median	1	2	2	3
Depth to Bedrock	> Median	3	2	0	2
	<= Median	1	2	3	2
Depth to Water Table	> Median	3	2	1	1
	<= Median	1	2	2	3
Percent Slope > 30[1]	> Median	2	0	1	4
	<= Median	2	4	2	0
Mean Slope	> Median	2	1	0	4
	<= Median	2	3	3	0
Low Intensity Residential %	> Median	2	2	1	2
	<= Median	2	2	2	2
High Intensity Residential %	> Median	0	3	2	2
	<= Median	4	1	1	2
Evergreen Forest %[1]	> Median	4	0	0	3
	<= Median	0	4	3	1
Mixed Forest %	> Median	3	1	0	3
	<= Median	1	3	3	1
Deciduous Forest %	> Median	2	1	0	4
	<= Median	2	3	3	0
Commercial/Industrial %	> Median	1	3	2	1
	<= Median	3	1	1	3
Urban Recreational Grasses %	> Median	2	2	2	1
	<= Median	2	2	1	3
Total Forest %	> Median	3	1	0	3
	<= Median	1	3	3	1
Total Population	> Median	3	2	1	1
	<= Median	1	2	2	3
Population Density	> Median	1	2	2	2
	<= Median	3	2	1	2
USGS - Impervious Area (raster coverage)	> Median	1	2	3	1
	<= Median	3	2	0	3

[1] Landscape variables identified by the median method as having significantly different medians when grouped by CPI quartile.

the expected patterns found in the literature. A table of the median method procedure results also indicates some differences between Goose Creek and Second and Third Creeks (Table 6.2). Second and Third Creeks show a clear difference between sample values from sites with greater than 41% impervious cover and from sites with less than 41% impervious cover. The majority of the sample values for all three parameters fall above the overall median value (calculated separately for individual watersheds) at sites with greater than 41% impervious surface in both Third and Second Creeks. Goose Creek also shows a trend towards higher sample values for sites with more impervious surface; however, the difference in the number of samples above and below the watershed median is not as great as in the other watersheds for both the <31% and 31-41% impervious surface groups.

Correlating Water Quality Parameters with Landscape Variables

To examine any links between the CPI or its parameters and landscape characteristics, I correlated the CPI and different descriptive statistics derived from my water quality data with variables representing basin characteristics. The basin variables only included landscape data unique to the sample site and excluded landscape data contributing to any upstream sample sites. When more than one site was located along the same stream reach, I assumed that any change in water quality between the upstream and downstream sites was the result of processes within the land area unique to the downstream site. Due to the small size of the dataset, only 15 cases, I used Kendall's Tau, a non-parametric procedure, to measure the strength of the relationship between my variables. Kendall's Tau is a ranked-based correlation procedure that is resistant to small

Table 6.2 : Median Method for Water Chemistry Parameters Grouped by Total Impervious Surface (Source: USGS, 2003b)

	Water Chemistry Parameter		Total Impervious Surface		
			< 31%	31%-41%	> 41%
Third Creek	Hardness	> Median	5	10	51
		<= Median	35	30	9
	Alkalinity	> Median	6	9	46
		<= Median	34	31	14
	Specific Conductance	> Median	0	12	56
		<= Median	39	28	4
Second Creek	Hardness	> Median	0	5	23
		<= Median	0	15	16
	Alkalinity	> Median	0	3	24
		<= Median	0	17	15
	Specific Conductance	> Median	0	2	27
		<= Median	0	18	13
Goose Creek	Hardness	> Median	23	24	0
		<= Median	37	16	0
	Alkalinity	> Median	19	24	0
		<= Median	41	16	0
	Specific Conductance	> Median	19	30	0
		<= Median	41	10	0

sample sizes; however, it does not account for the magnitude of difference between ranked data (Helsel and Hirsch, 1992). I used the correlations between the CPI and its components to landscape to explore whether the between-site water quality relationships indicated by the CPI follow 'expected' relationships between landscape variables and water quality seen in the literature.

Table 6.3 reports the results of the correlation analysis for all 15 sample sites. Correlation coefficients in bold font were significant at the 0.05 level. The landscape variable names in bold font show the parameters that the Kruskal-Wallis test found to have significantly different means for at least one of the CPI quartiles. Parameter values in italics indicate parameters that the median method test found to have significantly different medians for at least one quartile. Only the descriptive statistics for water quality with a meaningful number of significant correlations to landscape are presented in the table.

Most noteworthy is the lack of any significant correlation between the CPI and any of the explanatory parameters. The skewness value for hardness has the most and strongest correlations with the landscape variables. Skewed distributions are not symmetric around the mean, and the skewness value is heavily influenced by outliers. Hardness data for the majority of my sites are negatively skewed (the tail extends to the left) to varying degrees (See Table 4.2). Negatively skewed hardness distributions indicate the presence of abnormally low hardness values. The amount of skewness negative and/or positive in the hardness concentrations is positively correlated with slope and forest factors, which in the Ridge and Valley region are certainly related, and negatively correlated with several land use variables indicating urbanization. The

Table 6.3: Correlation Analysis - Kendall's Tau All Sample Sites

Landscape Metrics	CPI	Hardness Median	Hardness Mean	Standard Deviation Hardness	Skewness Hardness	Standard Deviation Specific Conductance	Coefficient of Variation Alkalinity
Percent Silt & Clay	0.238	**0.402**	**0.448**	0.314	0.314	-0.048	-0.010
KFACT	-0.295	**-0.478**	**-0.505**	**-0.486**	-0.029	-0.238	-0.238
Permeability	-0.245	**-0.414**	**-0.422**	**-0.441**	-0.245	-0.069	-0.226
Depth to Bedrock	-0.352	**-0.536**	**-0.562**	**-0.467**	-0.086	-0.219	-0.143
Percent Slope > 30	0.333	0.230	0.276	0.105	**0.486**	-0.181	-0.257
Depth to Water Table	-0.257	**-0.383**	**-0.429**	-0.295	-0.105	-0.162	-0.086
Mean Slope	0.143	0.077	0.124	-0.048	**0.486**	-0.295	-0.333
Standard Deviation of Slope	0.238	0.172	0.219	0.010	**0.505**	-0.238	**-0.390**
USGS TIA	0.144	0.116	0.067	0.163	**-0.490**	**0.413**	0.260
Low Intensity Res. %	-0.105	-0.211	-0.162	-0.333	0.276	**-0.390**	**-0.390**
High Intensity Res. %	0.067	0.019	-0.029	0.105	**-0.543**	0.352	0.276
Evergreen Forest %	-0.067	-0.057	-0.010	-0.181	**0.695**	**-0.467**	-0.352
Mixed Forest %	-0.048	0.038	0.086	-0.010	**0.562**	**-0.410**	-0.219
Deciduous Forest %	0.181	0.268	0.276	0.143	**0.448**	-0.181	-0.257
Commercial/Industrial %	0.010	0.000	-0.048	0.086	**-0.638**	**0.562**	0.371
Urban & Rec. Grasses %	-0.162	-0.306	-0.295	**-0.390**	-0.010	-0.143	-0.333
Row Crops %	0.067	0.057	0.010	0.105	**-0.695**	**0.390**	0.162
Total Forest	-0.048	0.038	0.086	-0.086	**0.524**	-0.371	-0.257
Total Population	-0.352	**-0.498**	**-0.486**	**-0.505**	-0.124	-0.067	-0.181
Ur_UU Soils	0.038	0.087	0.038	0.211	**-0.708**	**0.612**	**0.421**

standard deviation of specific conductance is positively correlated with urban land use factors and negatively correlated with forest parameters. The mean, median, and standard deviation of hardness are correlated with soil, lithologic factors, and total population. Hardness seems to be the water quality parameter most connected to landscape factors describing my research sites.

Discussion of Landscape Analysis

The CPI failed to correlate significantly with any of the landscape factors derived from available DEM, land use, and soil coverages when correlations included data from all the sample sites. Several measures of central tendency and dispersion for hardness and specific conductance did correlate with aspects of the landscape. The median, mean, and standard deviation of hardness correlated with landscape metrics associated with lithology. The strength of these associations varied, but the direction remained the same. These measures have a negative association with permeability and soil depth, both of which affect the amount of potential surface runoff. Greater permeability and soil depth will reduce surface runoff, which may result in lower sample values and less variation. Soil characteristics reflect the composition of the parent material and therefore may be indicating differences in geologic characteristics between the sites. These measures are also positively correlated with percent silt and clay. Clay soils tend to be less permeable than soils composed of larger regolith and therefore would be expected to produce a greater amount of surface runoff. Soils with high silt content are easily detached, creating potentially high surface runoff.

The standard deviation of specific conductance has positive correlations with factors indicative of urban land use and negative correlations with factors associated with percent forest. The association between specific conductance and landscape factors indicating urbanization agrees with findings published in the literature. Unpredictable timing of point source discharges from a variety of sources associated with increased urbanization may be a factor contributing to the positive correlation between the standard deviation of specific conductance and urban land uses. The median method tables show that alkalinity, hardness, and specific conductance increase with the amount of impervious cover, a landscape factor commonly used to measure urbanization.

Non-parametric correlation analysis comparing the CPI and landscape factors did not produce any significant correlations. This lack of response may be associated with lithologic factors rather than land use, suggesting that varying percentages of urban land use are less important than other landscape and timing factors at some sites. The Knoxville region is a highly developed area, so perhaps there is not always a great amount of differentiation in the polluting effects of land uses within these highly urbanized watersheds.

Further Possible Contributing Factors Related to Landscape

The first and second CPI value quartiles contain sites along the main branch of Third Creek, the headwaters of Second Creek, and the Edington East and Mary Vestal West Sites in Goose Creek. The Edington West and Ingersoll sites, in the CPI's fourth quartile (most perturbed), and the Tyson and Proctor sites in Third Creek, in the CPI's third quartile, have the lowest base discharge volumes and the highest CPI values of the sites within their respective watersheds. This certainly suggests that flow volume affects the relationship between the parameters used to calculate the CPI. Similar amounts of pollutant inputs would have a larger relative effect on streams with less flow and therefore less dilution potential. The Edington West, Ingersoll, Proctor, and Tyson sites have the greatest amount of variation in their flow volumes. This suggests that those sites with the smallest fraction of groundwater input are the most perturbed. Knowing that surface runoff carries the majority of non-point source pollutants to receiving streams, it follows that streams whose volume is most dependent on surface runoff would have higher CPI values.

CPI values seem to be related to the relative solubility of the geology and the density of drainage within their drainage areas. Kung (1980), in his geographic analysis of hydrology in Knoxville ranked the geologic formations by solubility and drainage density. Kung assigned a rank of one to the geologic formation that is most soluble or has the highest drainage density. The Holston, Maryville Limestone, Copper Ridge Dolomite, and Maynardville Limestone are the four most soluble geologic formations within my research area. They also have the highest drainage densities among the 11 formations ranked in Kung's study. The East Fork sites of Third Creek, Woodland site in Second Creek, and Ingersoll and Edington West sites in Goose Creek all have significant portions of their drainage basins in these relatively soluble geologic formations with high drainage density. These sites also have the highest CPI values within their respective watersheds. The Nolichucky Shale formation, which is also significant in both the Woodland and Proctor sites, ranks ninth in solubility but fifth in drainage density (Kung, 1980). The Inskip, Sullivan, Webb, and Edington East sites are characterized by a combination of the Chepultepic, Longview, Newala, and Ottosee formations, which rank sixth or higher in drainage density and have the lowest within-watershed CPI values. With the exception of Inskip they have the lowest overall CPI values.

Low drainage density reduces the amount of surface runoff entering the streams, thus reducing the pollutant load entering the stream (Golladay and Battle, 2002). The fact that those sites whose drainage areas are characterized by the highest drainage densities also have the highest CPI values, both between and within watersheds, lends credence to the idea that the CPI gives an indication of water quality. Sites at the mouth of Goose, Second, and Third Creeks may not be characterized by highly soluble geologic formations with high drainage density; however, they have higher percentages of total impervious area, which, like high drainage density, increases the amount water entering the stream through surface runoff. They are also undoubtedly affected by the water chemistry and water quality conditions from upstream sites.

CHAPTER 7

WATER QUALITY MODELING

Hydrologic Simulation Program FORTRAN Simulation

The purpose of using the HSPF model to simulate water quality for this project was to provide an independent check of the ranking of impaired reaches determined with empirical and statistical methods for comparison with the rankings derived from the CPI. I chose HSPF for this work because it is a well-accepted model in common use by public and private agencies (Donigan and Huber, 1991). My work with HSPF also afforded me the opportunity to become familiar with the model.

The HSPF model comes packaged with the EPA's BASINS, a multipurpose environmental analysis system (USEPA, 2001b). Developed for the EPA in the early 1970s from predecessor models like the Agricultural Runoff Model (ARM) and Non-point Source Model (NPS), HSPF is still in use, and a streamlined version of HSPF called the Loading Simulation Program in C^{++} is currently being developed (Bicknell *et al.*, 2001). HSPF uses a basin-scale analysis framework that simulates fate and transport in one-dimensional stream channels. It is a comprehensive model of watershed hydrology and water quality that simulates both land and soil contaminant runoff processes and in-stream hydraulic process (Donigan and Huber, 1991). Generally considered a physically-based, lumped model, HSPF represents a watershed in terms of land segments defined as areas with similar hydrologic properties and reaches/reservoirs. Flows move 'down' the system, passing through a series of storages. Water moves through pervious land segments along three paths: overland flow, interflow and groundwater flow. A variety of storage zones are used to simulate storage on the surface and in the soil horizons. Impervious surfaces move water by overland flow only, although evaporation can also occur. A variety of empirical and unitless (meaningless in a physical sense) parameters are used to control the movement of water through the system. HSPF is considered to be one of the most accurate and appropriate tools available for continuous simulation of watershed hydrology and water quality (Bicknell *et al*., 2001). HSPF and the earlier models from which it was developed have been extensively applied in a wide variety of hydrologic and water quality studies, including the development of TMDL's (Total Maximum Daily Loads) for Third, Second, and Goose Creeks by Tennessee Department of Environment and Conservation (TDEC) (Donigan and Huber, 1991; Borders and Wang, 1998).

Methodology of Model Development

Using HSPF, I chose to model Total Suspended Solids (TSS) and five-day Biological Oxygen Demand (BOD) because of their ability to indicate water quality, the fact they are 'built-in' to the WinHSPF interface, and the availability of model parameter values for these constituents in the HSPFParm database (Donigan *et al*., 1999). WinHSPF is an interactive Windows interface to HSPF, which is integrated into the BASINS system (Duda *et al*., 2001). HSPFParm contains parameter values from completed HSPF models throughout the United States. BOD and TSS are constituents commonly found within these models. Because detailed input data are seldom available and HSPF parameters do not always reflect observable values, one common practice is to use a "paired watershed" approach that applies parameter values developed for other watersheds with similar characteristics (USEPA, 2001b). This strategy assumes that minimal adjustments need to be made between comparable streams and watersheds.

Using the automatic delineation feature available within the BASINS application, I generated values for the initial watershed and reach (streams) files necessary for creation of an HSPF project. Land segments were classified based on 1992 NLCD land use categories. I used the closest available meteorological dataset, McGhee Tyson Airport (TN004950), available from the EPA BASINS website (USEPA, 1998). I obtained initial parameter values for my model from a variety of sources. I transferred most of the hydrologic parameters from the HSPF model developed by TDEC for the Total Maximum Daily Load (TMDL) for fecal coliform in the Fort Loudoun Lake watershed (Borders and Wang, 1998). I adjusted some of these initial hydrologic parameters using values from the HSPFParm database. Following procedures outlined by Donigan and Love (2003), I generated calibration targets for the sediment loading rates of different land segments using both the TMDL USLE (Hummel *et al.,* 2000) program and loading rates reported in studies by Betson (1976) and Milligan (1984). Next, I calibrated the sediment production parameters to reflect these target values and to fall with the range of expect erosion rates reported by Donigan and Love (2003). I obtained initial parameter values from the HSPFParm database for modeling BOD and TSS from a model of the Upper James River located in west-central Virginia's Appalachian Ridge and Valley terrain.

I simulated water quality conditions during my sample period using hourly rainfall data for McGhee Tyson Airport, obtained from the National Climatic Data Center's Local Climatological Data publications (NCDC, 2003b). Because HSPF requires a large of amount of meteorological data not easily obtainable for simulations, I used meteorological data from 1978 (available from the EPA meteorological dataset) to supplement the 2003 precipitation data. Potential Evapotranspiration is the most significant meteorological variable other than rainfall affecting flow in HSPF. I chose 1978 because regression and visual analysis of the available meteorological data showed maximum daily temperatures (used in the estimation of potential evapotranspiration) for 1978 to be most closely aligned with those of 2003. I also copied the 2003 data into the 2002 year and ran a two-year simulation that allows one year for the model hydrologic and surface storages to reach a steady state before the period of simulation (2003).

I located minimal data for flow and in-stream constituent concentrations, to calibrate and check the validity of the model, from a TVA report on Second Creek (Milligan, 1984) and from a City of Knoxville NPDES annual report (City of Knoxville, 2001). I added three additional catchments to Second Creek to allow for model validation against observed data from Milligan's report (Figure 7.1). After minimal adjustment of parameter values to better represent the annual flow and constituent loadings, I transferred applicable parameter values to the Goose and Third Creek watershed models. Then I compared the model with storm event summaries reported by Milligan (1984) and estimated total annual flow volume and annual BOD and TSS loads reported in the City of Knoxville's NPDES annual report (2001).

HSPF Model Validation

The model of Second Creek matches closely the annual flow volumes and pollutant loads estimated by the City of Knoxville in its 2001 NPDES annual report. I did not compare the model with total estimated annual loads for Goose and Third Creeks

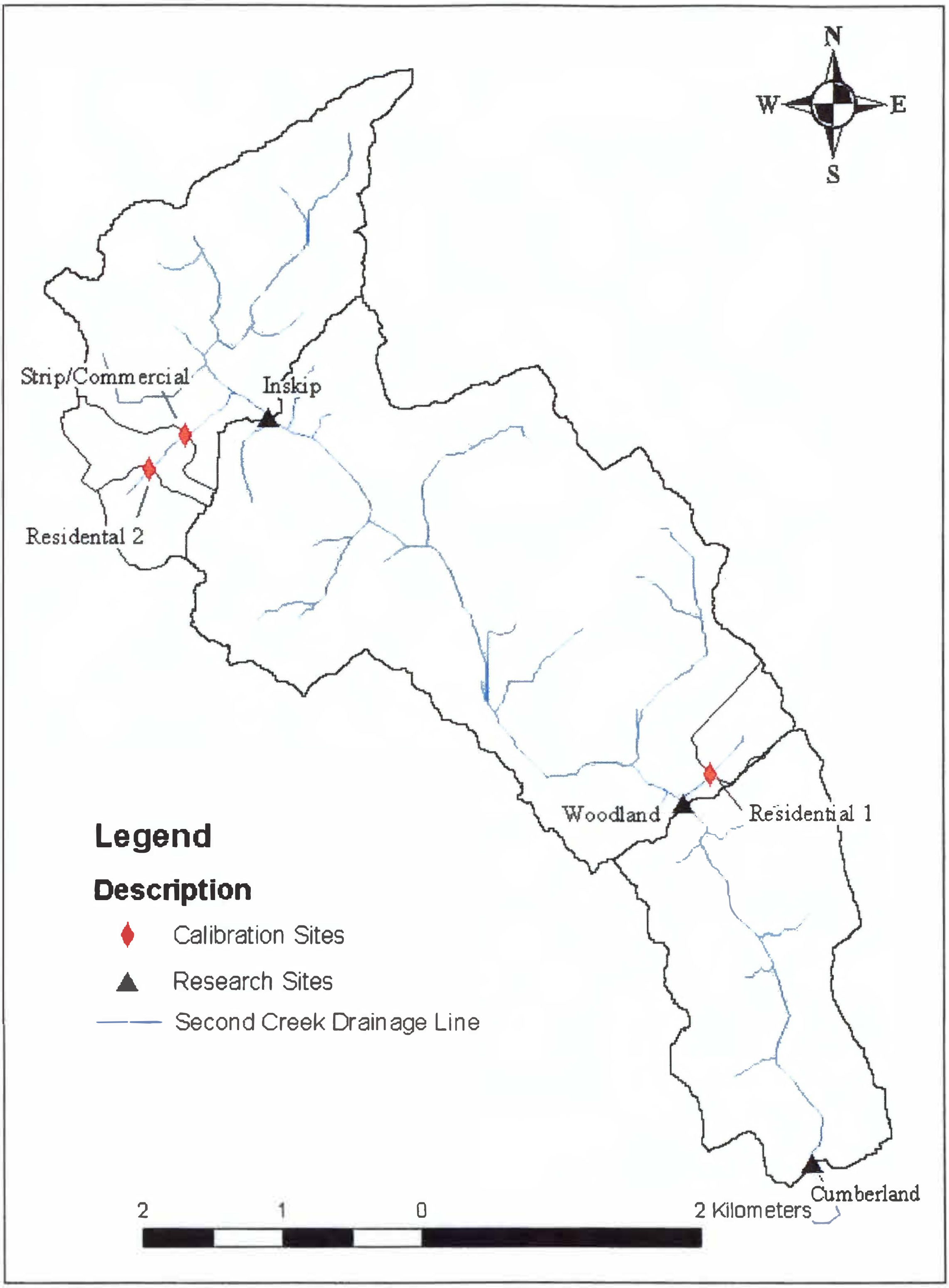

Figure 7.1: Research and Calibration Sites - Second Creek

because significant portions of these watersheds lie outside the city limits and were not included in the NPDES estimates (Table 7.1). The highlighted years 1975 and 1993 are the closest in precipitation amount to the average annual rainfall amount used for the NPDES estimations. Despite the fact I only made minimal adjustments to initial parameter values gained from a variety of sources, the model does seem to perform well in estimating total annual loads and flows. Over the 22-year period from 1972-1995, the model predicts reasonable fluctuations in annual volume and annual loads in relation to the amount of precipitation.

When compared to the observed storm flow and EMC (Event Mean Concentration) data reported by Milligan (1984) in his study of urban runoff in Second Creek, the model does not perform well, suggesting that further calibration needs to be done to accurately simulate short-term fluxes in stream conditions. The model over-predicts storm flow by 4959 m^3 (203%) for nine storm events at Residential Site 1 that have similar rainfall inputs (Table 7.2). Simulated EMC's are also much lower than observed EMC's for TSS and BOD. The model also predicts a constant base flow at both this and the Residential 2 site; however, Milligan (1984) and my field observations confirm these as dry creek beds (there is no flow though there is water storage) except during storm events. I removed the base flow component from storm flow by multiplying the simulated flow volume the hour before the storm event, by the length of the storm event but achieved only marginally better results.

The model performance was no better for Residential Site 2 as it was for Residential Site 1. Using eight storms for comparison, simulated storm flow volumes were over-predicted by 140% (Table 7.3). Unlike Residential Site 1, where simulated

Table 7.1: Annual Volumes and Pollution Loadings

		Second Creek			Goose Creek			Third Creek		
NPDES estimates based on 115.49 centimeters of Rainfall		11,492,096	147,095	4,298,480						
Year	Rainfall cm/yr	Flow (cubic meters	BOD (kg)	TSS (kg)	Flow (cubic meters)	BOD (kg)	TSS (kg)	Flow (cubic meters)	BOD (kg)	TSS (kg)
1974	150.62	16,405,309	263,000	7,360,000	7,746,266	62,200	1,768,000	39,594,768	597,000	22,000,000
1975	115.06	11,249,355	150,000	4,320,000	5,143,619	32,700	926,000	27,013,253	216,000	8,000,000
1976	107.70	9,140,101	133,000	3,480,000	3,860,798	31,400	882,000	21,092,540	150,000	5,660,000
1977	129.29	12,458,167	168,000	4,740,000	5,538,334	41,700	1,080,000	29,233,520	305,000	10,480,000
1978	108.20	9,781,511	151,000	3,900,000	4,366,526	35,000	998,000	23,189,459	214,000	7,120,000
1979	136.91	13,321,604	196,000	4,880,000	6,007,057	47,400	1,160,000	31,577,135	449,000	12,640,000
1980	102.87	9,485,475	125,000	3,420,000	4,243,178	25,400	752,000	22,572,718	149,000	5,860,000
1981	111.25	8,523,360	118,000	2,960,000	3,392,075	24,900	648,000	19,118,969	127,000	4,840,000
1982	138.94	13,814,997	244,000	6,400,000	6,216,749	60,700	1,802,000	32,563,921	467,000	13,660,000
1983	107.95	9,411,467	127,000	3,240,000	4,095,160	27,500	756,000	22,079,325	138,000	3,960,000
1984	123.19	12,458,167	226,000	5,400,000	5,809,700	54,400	1,320,000	30,096,957	516,000	12,060,000
1985	92.46	6,919,833	94,800	2,260,000	2,824,673	17,900	478,000	15,911,916	106,000	2,980,000
1986	82.55	5,982,387	80,900	1,884,000	2,368,285	15,200	384,000	13,568,300	93,400	2,360,000
1987	88.14	7,376,221	101,000	2,540,000	3,219,388	22,600	674,000	17,392,094	130,000	3,600,000
1988	88.14	6,167,409	89,200	2,220,000	2,343,616	16,200	484,000	13,691,649	96,300	2,920,000
1989	142.75	13,938,345	161,000	4,100,000	6,216,749	44,000	1,066,000	32,687,269	187,000	4,720,000
1990	140.21	14,185,041	203,000	5,980,000	6,512,784	50,300	1,570,000	33,797,403	372,000	10,640,000
1991	148.08	15,048,479	216,000	6,360,000	6,858,159	57,600	1,746,000	35,770,974	377,000	11,500,000
1992	112.27	10,102,216	128,000	3,380,000	4,489,874	29,200	852,000	23,929,548	148,000	4,060,000
1993	114.55	10,521,600	148,000	4,180,000	4,637,892	34,800	1,178,000	24,792,985	197,000	5,920,000
1994	160.78	18,502,228	231,000	6,840,000	8,868,735	59,300	1,510,000	44,898,740	515,000	14,500,000
1995	108.71	9,497,810	158,000	3,860,000	4,119,829	33,400	934,000	22,202,673	295,000	7,620,000

Table 7.2: Storm Event Summaries - Residential 1 Site, Second Creek[1]

OBSERVED						SIMULATED				OBSERVED vs SIMULATED EMC's			
Date	Time	Runoff	Base	Runoff + Base (m^3)	Total Rainfall (cm)	Simulated Storm Volume (m^3)	Total Rainfall (cm)	Difference in Rainfall Totals (cm)	Storm Volume - Baseflow (m^3)	Observed EMC BOD (mg/L)	Simulated EMC BOD (mg/L)	Observed EMC TSS (mg/L)	Simulated EMC TSS (mg/L)
05/19/81	1817	74	0	74	0.38	33	0.30	-0.08	10	nd	1.7	nd	1.5
07/01/81	2053	227	0	227	3.81	233	1.52	-2.29	-	12.9	1.5	93.54	93.5
08/06/81	1011	54	0	54	0.94	247	1.09	0.15	228	16	4.4	250	146.1
08/20/81	2247	407	0	407	3.30	921	3.53	0.23	902	4.8	1.5	470	110.9
09/15/81	202	407	0	407	2.41	2042	3.91	1.50	-	12	0.2	560	12.1
09/15/81	1746	457	0	457	2.18	1014	2.08	-0.10	961	9	0.8	1100	37.4
10/01/81	2216	101	0	101	1.02	458	1.14	0.13	424	nd	4.4	nd	80.2
10/23/81	412	268	0	268	2.49	1955	3.38	0.89	-	33	0.5	170	30.1
10/25/81	1852	442	0	442	2.51	1540	2.36	-0.15	1365	nd	0.3	nd	12.7
10/26/81	1931	549	0	549	2.06	974	1.57	-0.48	-	nd	0.6	730	29.0
11/19/81	2259	75	0	75	0.56	328	1.12	0.56	-	63.2	3.4	1089	152.6
11/23/81	2314	141	0	141	1.17	453	0.91	-0.25	-	6.6	2.0	180	29.6
12/01/81	439	385	0	385	1.73	1287	1.60	-0.13	1206	nd	0.6	nd	28.0
02/09/82	408	703	0	703	2.54	2580	2.26	-0.28	-	nd	0.6	1000	19.4
03/21/82	528	510	0	510	2.31	1422	1.93	-0.38	-	9	0.9	305	29.7
03/25/82	1743	89	0	89	0.56	17	0.10	-0.46	-	nd	2.6	nd	0.0
03/31/82	623	157	0	157	1.04	671	1.04	0.00	628	nd	3.4	nd	54.3
04/17/82	835	362	0	362	1.93	1226	2.06	0.13	-721	nd	2.1	919	68.6
Total				2438		7397			5003				

[1] Highlighted rows show storm events where the model's meteorological dataset is within .254 cm of observed precipitation measured using rain gages within the individual sub-watershed.

Table 7.3: Storm Event Summaries - Residential 2 Site, Second Creek[1]

OBSERVED						SIMULATED				OBSERVED vs SIMULATED EMC's			
Date	Time	Runoff	Base	Runoff + Base (m^3)	Total Rainfall (cm)	Simulated Storm Volume (m^3)	Total Rainfall (cm)	Difference in Rainfall Totals (cm)	Storm Volume - Baseflow (m^3)	Observed EMC BOD (mg/L)	Simulated EMC BOD (mg/L)	Observed EMC TSS (mg/L)	Simulated EMC TSS (mg/L)
07/01/81	2049	467	0	467	2.26	357	1.52	-0.74	-	9.9	1.7	800	72.9
08/06/81	950	75	0	75	0.97	146	1.09	0.13	-264	16	4.1	23	113.6
08/20/81	2220	573	0	573	3.56	1199	3.53	-0.03	1114	8	0.6	18	36.4
09/15/81	145	576	0	576	3.05	915	2.95	-0.10	334	6.2	0.4	47	19.8
09/15/81	1726	440	0	440	2.13	439	2.62	0.48	-	3.2	3.1	75	138.1
10/18/81	433	82	0	82	1.04	148	1.04	0.00	121	0	3.3	nd	46.6
10/23/81	303	434	0	434	2.36	1618	3.38	1.02	-	6.4	0.7	28.8	28.4
10/26/81	1910	383	0	383	1.35	1135	1.57	0.23	1066	0	0.3	46	11.4
11/23/81	2223	159	0	159	1.02	277	0.91	-0.10	250	0	1.8	nd	17.7
01/22/82	635	857	0	857	2.49	3239	1.60	-0.89	-	3.3	0.1	71	2.5
02/09/82	348	820	0	820	2.46	3185	2.26	-0.20	3000	0	0.3	nd	8.6
03/21/82	457	924	0	924	2.54	1516	1.93	-0.61	-	5.7	0.4	68	9.7
03/31/82	542	474	0	474	1.27	565	1.04	-0.23	526	15	1.6	62	25.5
04/17/82	829	506	0	506	1.80	1216	2.18	-0.38	-	0	0.7	45.1	21.9
Total				3143		7570			6147				

[1] Highlighted rows show storm events where the model's meteorological dataset is within .254 cm of observed precipitation measured using rain gages within the individual sub-watershed.

EMC's are consistently lower than observed values, EMC's at Residential Site 2 were both higher and lower than reported values. The Strip/Commercial Site is located downstream of the Residential 2 Site (see Figure 7.1) and, unlike the two residential sites, has a continuous base flow component. The model more accurately simulated flow for this site, only over-predicting storm flow volumes by 36% for 13 comparable storm events (Table 7.4). After subtracting the simulated base flow component, the model under-predicts storm flow, demonstrating the model's tendency to over-predict the volume of base flow in these small headwater catchments. Simulated EMC's are consistently lower than reported values for this catchment. In general, the model performed poorly in simulations of individual storm events; however, total volumes for flow, BOD and TSS in Second Creek compared favorably with estimated annual values for these parameters listed in the City of Knoxville's 2001 NPDES report. Using flow data collected for TDEC by members of the University of Tennessee's Geography Department from locations near the mouths of my study creeks, I was able to compare simulated flow values to observed data (Table 7.5). Visual inspection of simulated flow graphs plotted with the discrete observations (Appendix B) indicates that the model under-predicts base flow and that extreme variations in flow values evident in Table 7.5 (example 11/22/03) are likely the result of the timing of the flow hydrograph.

HSPF Modeling Results

The purpose of using the HSPF model was to provide insight into the expected in-stream water quality conditions at my individual sample sites. While the validation procedure shows that the model does not accurately reflect individual events, there is

Table 7.4: Storm Event Summaries - Strip/Commercial Site, Second Creek[1]

OBSERVED						SIMULATED				OBSERVED vs SIMULATED EMC's			
Date	Time	Runoff	Base	Runoff + Base (m^3)	Total Rainfall (cm)	Simulated Storm Volume (m^3)	Total Rainfall (cm)	Difference in Rainfall Totals (cm)	Storm Volume - Baseflow (m^3)	Observed EMC BOD (mg/L)	Simulated EMC BOD (mg/L)	Observed EMC TSS (mg/L)	Simulated EMC TSS (mg/L)
04/18/81	649	363	9	372	0.51	338	0.30	-0.20	255	nd	1.12	nd	0.93
05/10/81	1856	450	24	475	0.66	831	0.74	0.08	656	nd	1.45	nd	12.80
06/04/81	342	1475	51	1526	1.22	1422	0.99	-0.23	1090	nd	0.26	nd	4.42
08/06/81	932	910	20	930	0.89	1168	1.09	0.20	1022	nd	2.39	83.50	41.98
08/06/81	1824	364	10	374	0.33	215	0.46	0.13	127	nd	2.09	nd	22.59
08/20/81	2158	4097	54	4151	3.58	5490	3.53	-0.05	5161	nd	0.73	51.80	20.20
09/03/81	1739	1928	28	1956	2.03	2582	1.93	-0.10	2415	nd	1.65	nd	52.60
09/15/81	1714	2229	35	2263	nd	4402	2.08	nd	-	nd	0.60	27.40	13.07
10/05/81	1152	445	20	465	0.61	366	0.53	-0.08	250	nd	2.77	nd	12.85
10/18/81	401	1034	62	1096	1.14	1370	1.12	-0.03	1009	nd	1.09	nd	8.26
10/22/81	2204	3139	121	3261	2.31	5825	3.38	1.07	-	nd	0.28	29.90	8.98
10/25/81	911	202	27	229	0.28	230	0.25	-0.03	46	nd	0.58	nd	2.57
10/26/81	1853	2192	96	2289	1.47	4122	1.57	0.10	3462	nd	0.12	36.80	1.97
12/01/81	313	3002	72	3074	1.78	4034	1.60	-0.18	3528	nd	0.22	nd	6.00
01/22/82	635	3810	170	3979	2.49	6968	1.60	-0.89	-	nd	0.12	111.90	2.44
03/21/82	447	3461	43	3504	2.54	3604	1.93	-0.61	-	nd	0.55	107.40	13.19
03/25/82	1730	1346	54	1400	0.84	525	0.18	-0.66	-	nd	0.16	805.30	0.16
03/31/82	542	1815	42	1856	1.47	3659	1.04	-0.43	-	nd	0.52	111.80	7.14
04/17/82	828	2986	78	3064	2.03	5000	2.18	0.15	-1384	nd	0.26	48.80	5.78
Total		19,449	551	20,000		27,166			17,638				

[1] Highlighted rows show storm events where the model's meteorological dataset is within .254 cm of observed precipitation measured using rain gages within the individual sub-watershed.

Table 7.5: Comparison of Discrete Flow Samples and Simulated Flow

	Second Creek		*Goose Creek*		*Third Creek*	
Date	Observed Flow (m^3/s)	Simulated Flow (m^3/s)	Observed Flow (m^3/s)	Simulated Flow (m^3/s)	Observed Flow (m^3/s)	Simulated Flow (m^3/s)
8/25/03	0.05	0.08	0.06	0.06	0.31	0.11
9/2/03	0.14	0.11	0.04	0.05	0.37	0.26
9/15/03	0.25	0.19	0.04	0.05	0.37	0.71
9/22/03	0.54	1.22	0.08	9.25	1.71	0.26
9/29/03	0.08	0.18	0.02	0.09	0.54	0.31
10/6/03	0.08	0.10	0.02	0.06	0.30	0.16
10/14/03	0.10	0.09	0.04	0.05	0.29	0.25
10/21/03	0.05	0.08	0.02	0.04	0.26	0.11
11/3/03	0.10	0.07	0.01	0.04	0.25	0.13
11/10/03	nd	-	0.04	0.05	0.29	0.45
11/13/03	nd	-	0.08	0.06	nd	-
11/17/03	0.12	0.11	0.04	0.05	0.33	0.30
12/14/03	0.20	0.18	0.08	0.09	0.52	0.45

evidence that the simulation may provide an indication of annual hydrologic conditions. The purpose of this simulation was not to provide simulations of future water quality due to changing conditions within the watershed, but to rank the general water quality conditions at each individual site. I feel that the model does reflect the 'expected' water quality conditions at each site based on the use of parameters values gleaned from the literature and accepted model development practices.

To rank the water quality of individual sites, I chose only to look at annual loadings for BOD and TSS. Table 7.6 provides the annual simulated flow volume, BOD load, and TSS load at each of the sample sites. I also included columns for CPI ranking and the ranking of area- and flow-weighted BOD and TSS loads. Both the overall dataset ranking and within-watershed rankings (within-watershed rankings are in parenthesis) are

Table 7.6: Simulated Annual Loadings[1]

Location	CPI Ranking	Volume (m^3)	BOD (kg)	Area BOD (kg/ha)	Area BOD Ranking	Flow BOD (kg/m^3)	Flow BOD Ranking	TSS (kg)	Area TSS (kg/ha)	Area TSS Ranking	Flow TSS (kg/m^3)	Flow TSS Ranking
Goose Creek												
Edington East	*14 (5)*	980,722	3,229	22.2	*14 (4)*	0.00329	*14 (4)*	182,592	1,255	*3 (3)*	0.1862	*3 (3)*
Edington West	*1 (1)*	600,414	2,167	25.1	*13 (3)*	0.00361	*13 (3)*	60,950	707	*7 (5)*	0.1015	*5 (5)*
Ingersoll	*3 (2)*	1,632,646	4,320	17.4	*15 (5)*	0.00265	*15 (5)*	315,574	1,274	*2 (2)*	0.1933	*2 (2)*
Mary Vestal East	*4 (3)*	3,465,356	12,647	25.7	*11 (1)*	0.00365	*11 (1)*	597,028	1,214	*4 (4)*	0.1723	*4 (4)*
Mary Vestal West	*9 (4)*	2,248,526	8,195	25.6	*12 (2)*	0.00364	*12 (2)*	593,938	1,859	*1 (1)*	0.2641	*1 (1)*
Second Creek												
Inskip	*10 (3)*	3,284,549	17,955	41.1	*9 (3)*	0.00547	*7 (3)*	210,344	481	*13 (3)*	0.0640	*13 (3)*
Woodland	*2 (1)*	10,892,661	68,603	49.9	*2 (2)*	0.00630	*1 (1)*	704,611	513	*12 (2)*	0.0647	*12 (2)*
Cumberland	*7 (2)*	14,344,902	88,963	50.9	*1 (1)*	0.00620	*2 (2)*	991,905	567	*10 (1)*	0.0691	*11 (1)*
Third Creek												
Sullivan	*13 (6)*	7,024,958	38,286	40.6	*10 (7)*	0.00545	*8 (5)*	340,133	360	*15 (7)*	0.0484	*15 (7)*
Webb	*15 (7)*	14,598,303	82,917	41.8	*7 (5)*	0.00568	*5 (3)*	1,036,314	522	*11 (5)*	0.0710	*10 (5)*
Lonas	*12 (5)*	20,817,338	113,943	42.3	*6 (4)*	0.00547	*6 (4)*	1,574,524	584	*9 (4)*	0.0756	*9 (4)*
Painter	*11 (4)*	25,496,806	138,138	41.4	*8 (6)*	0.00542	*10 (7)*	2,427,416	727	*5 (1)*	0.0952	*6 (1)*
Proctor	*6 (2)*	4,579,108	26,564	46.4	*4 (2)*	0.00580	*4 (2)*	232,803	407	*14 (6)*	0.0508	*14 (6)*
Tyson	*5 (1)*	7,019,528	40,943	48.0	*3 (1)*	0.00583	*3 (1)*	564,625	662	*8 (3)*	0.0804	*8 (3)*
Ag Campus	*8 (3)*	34,141,461	185,246	42.4	*5 (3)*	0.00543	*9 (6)*	3,119,962	714	*6 (2)*	0.0914	*7 (2)*

[1] Site rankings assign the highest site parameter or index value as 1 and lowest as 15

given for each site. Using annual flow volume and total contributing area for each site, I weighted the annual loadings of BOD and TSS. Flow- and area-weighted values for TSS in Goose Creek are significantly higher than those in either Second or Third Creek, despite the generally smaller annual total load. Although BOD was modeled as sediment-associated (i.e., a function of sediment), weighted values for BOD in Goose Creek are lower than those simulated for Third and Second Creeks, suggesting that BOD contributions from interflow and ground water, parameters included in the model by inputting mg/L concentrations, are greater in these creeks. Generally, the area-weighted values for TSS increase moving from headwater sites to successive downstream sites. Two exceptions to this trend are the Ingersoll site in Goose Creek and the Ag Campus Site in Third Creek. Area- and flow-weighted values for BOD in Goose and Second Creeks follow the headwaters-to-mouth increasing trend, but Third Creek does not exhibit this increasing trend as strongly. Variations in flow- and area-weighted TSS and BOD loads indicate that HSPF may provide insight into water quality conditions at the sample sites other than just the simple relationship that downstream points are more polluted.

Discussion of HSPF Model Results

I developed an HSPF model to explore modeling as a method of predicting water quality and to test whether water quality rankings based on the CPI agree with water quality rankings established using watershed models such as HSPF and PLOAD (Pollution Loading Application). The complexity of the HSPF model and my difficultly validating the model reduced its ability to provide the desired information. These issues alone make model simulations undesirable tools for use by watershed groups, who may not have the technical skills or hydrology background needed to understand complex models like HSPF. Despite adhering to guidelines outlined in several papers on the subject of hydrologic and sediment calibration, my HSPF model of Second Creek performed poorly when compared with observed data. The most important factor limiting calibration of the model was lack of long-term flow records. When modeling any hydrologic region, it is important that flow be simulated as accurately as possible. Highlighting the need for accurate flow simulations is the fact that water quality data gathered in the field are most often reported in volume-dependent units. Without an extended continuous time series of flow data, identifying the source of errors is difficult.

An important design difference between my model of Second Creek and the TMDL model that supplied the most of the hydrologic parameters for my model is that the TMDL model, primarily concerned with total outflow of fecal coliform from Second Creek, treated the watershed as a single unit and used a single reach to model flow. The hydrograph of a small watershed, like those with available calibration data in Second Creek, is influenced more strongly by surface detention and near-surface moisture storages than those over 200 hectares (500 acres) (Donigan, 2002). This requires a finer calibration of surface and near surface parameters for accurate simulation of flow in small watersheds than would be necessary in larger watersheds. Another likely contributing factor to the difference in modeled and observed storm volumes is bypass loss along these small reaches that may join the main channel at some point below the gage station. Milligan's modeled-versus-observed flows indicated lower than expected annual runoff; my initial model results also indicated lower than expected observed runoff as it over-predicted total flow during observed storm events for two of the three calibration watersheds. Once again, this would not be an issue for watershed calibrations based on a single reach.

Contributing to the difficulty in calibrating with observed storm events is that Milligan (1984) only reported total flow for selected storm events sampled between October 1981 and September 1982 and did not provide depth or stage, making it difficult to now use those data to calibrate the timing of surface runoff and interflow. Another possible factor compounding the lack of agreement between observed and modeled storm flows is the model's FTABLE. The FTABLE is an approximation of a reach's stage-discharge-volume relationship that, for relatively long reaches, generally doesn't require calibration (Donigan, 2002). However, for short reaches like those present in my model, the FTABLE may require calibration. The BASINS program will generate the required input for computation of the FTABLE, but the values are based on an assumed channel/floodplain geometry that is of suspect accuracy especially in urban watersheds where anthropogenic channel modifications are common. Stage-discharge-volume relationships have been developed for many sites where USGS gages are present, however, there is a lack of gage data available to establish these relationships for small urban tributaries. Developing typical stage-discharge-volume relationships for urban streams would undoubtedly improve model accuracy in highly urbanized watersheds. Even though the model does not accurately predict flow and concentration levels well at my calibration sites, the calibration watersheds are much smaller than the subbasins I sampled during my research. Given the known problems simulating small catchments and lack of long-term continuous calibration data, poor model performance is not unexpected. However, my research sites are much larger than the calibration catchments and therefore some of the flow volume problems theoretically would produce much smaller error for them than was observed at the calibration sites. This is illustrated by the improved agreement between the Strip/Commercial site observed and simulated flow characteristics as opposed to a lack of agreement with the two residential sites. Also, I chose to develop this model only to give a relative indication of water quality at my sample sites, so, while matching observed data would preferable, it is not absolutely necessary for the purposes of this research.

To reduce the effect of basin size on pollution loads, I divided the total load of BOD and TSS passing through each research site by the total contributing area and total annual volume at that site. Originally, I had expected Goose Creek to have the least water quality problems because it is the most forested watershed. This did not prove to be the case when looking at the empirical data or the CPI. My HSPF model supported those results, as Goose Creek had the highest weighted loads for TSS. Correlation of the CPI and its constituents against the flow and loadings generated by the model did not find many significant results. Analysis of the empirical data and the poor performance of the model on small scales suggest that a way to distinguish soil and/or geologic characteristics between subbasins needs to be included when defining the land segments in the HSPF model. This may also suggest that point sources are an important source of pollution to urban streams that are not accounted for in the model. For example, recent research in the Nashville metropolitan area using thermal imaging and a subsequent ground investigation of 42 stream miles found nine sewer leaks and illicit discharges (Hunt and Bryant, 2004).

Comparing the within-watershed and overall site rankings with CPI values does not indicate a strong relationship between BOD, TSS, and the CPI as indicators of water quality. I modeled BOD as sediment-associated and therefore expected to find a strong relationship between the weighted BOD and TSS parameters. A ranking of these parameters among the entire dataset provides a nearly inverse relationship between the weighted BOD and TSS parameters. This may indicate that I have over-estimated the contribution of BOD from ground water and interflow in relation to the amount of sediment that washes off the land segments. The HSPF modeling experience was valuable in that it forced me to consider how a myriad of hydrologic processes and variables interact to produce the modeled constituent loadings; however, this particular simulation is unsuited as a test of the CPI's ability to indicate changes in water quality within a watershed. The results of the HSPF modeling demonstrate that there is a large amount of variability in the effect of parameters, such as land use, on water quality, and that while a common range of values for input variables may be defined, accurate results depend on calibration to local conditions.

CHAPTER 8

DISCUSSION AND CONCLUSIONS

Alkalinity, Hardness, Specific Conductance, the Chemical Perturbation Index and Landscape Variables as Indicators of Variations in Water Quality

To investigate the CPI's effectiveness as a tool for monitoring water quality in mix-use urban watersheds I posed four broad questions. Answering these questions raised more questions, especially when I compared the CPI to the 'expected' water quality and land use relationship. My first research objective compared the results of the CPI calculations for my study sites with those published by Stewart (2001). All CPI index values for my study sites are significantly higher than those Stewart reported for sites upstream of point source discharges in White Oak Creek (CPI < 0.70). In fact, all the CPI values seen in this study are higher than any CPI values for White Oak Creek, both up and downstream of point source discharges after pollution abatement programs were instituted by ORNL. Stewart's CPI values downstream from point sources, before pollutant abatement programs were instituted, are higher than CPI values I found. A significant portion of the flow for Stewart's sample creeks is from wastewater input. Non-point sources are less likely to create such dramatic changes in the water chemistry relationships over short spatiotemporal periods within the sample creeks. Using the CPI to assess non-point source pollution, as opposed to point-source pollution, will likely not produce as large a difference in CPI values, making the distinctions between sites less clear. With no reference sites with which CPI values or graphical plots of its constituents can be compared, it is difficult to assess the accuracy of the CPI in ranking sites along urban streams.

Water quality relationships between different sample locations are commonly described using statistical techniques that compare the values of individual water quality parameters for each sample site. To further assess the usefulness of the CPI as a tool for water quality monitoring, I compared inferences about water quality made using accepted statistical methods in water resources with the results of the CPI calculations. Boxplots and Analysis of Variance are two statistical methods commonly used to provide insight into water quality relationships between different locations. While differences in the values of the components of the CPI can be indicators of water quality degradation and have been linked to urban land uses, their discrete values can vary dramatically based on local geology. When using these values, natural reference levels for these parameters must be estimated. Since the CPI is not based on discrete values of its component parameters but compares them with each other, it should theoretically provide a stronger indication of water quality.

Descriptive statistics, such as measures of central tendency that represent a group of sample data with a single value, do not separate the effects of timing from the effects of location, though measures of dispersion of the data may indirectly be a function of time. Therefore, correlations between measures of central tendency that represent water quality and landscape metrics do not incorporate the effects of the timing of sample collection. The lack of any significant correlations between CPI, its components, and landscape variables may therefore be the result of the difference in the relative impact of location versus timing on the samples.

The median polish tables for the individual watersheds clearly show that sample timing has a significant effect on the CPI's constituent values. The magnitude of sample timing on parameter concentrations higher than the effect of site location for alkalinity and hardness in Third Creek, when the East Fork sites (Proctor and Tyson) are excluded. The effect of site location is equal to the effect of sample timing in Goose Creek, suggesting that location is more important to water chemistry in Goose Creek than in Third Creek. Median polish tables for Second Creek show that location along the creek channel has very little effect on hardness or alkalinity and that changes in parameter concentrations are primarily related to when the sample was taken. Changes in water chemistry related to sample timing reflect any deviations from the watershed median that cannot be attributed to the sample site location like different flow and meteorological conditions.

The median polish exposes a limitation in watershed analysis that uses only values derived from a single factor. Single factors only yield information about how the values from one site vary in relation to values from another site. Some sites may be more resistant to pollutant inputs due to the paths water takes before entering the receiving stream. Some sites may receive more direct surface runoff, while others receive a greater percentage of stormwater inputs through subsurface flow. The user must decide how these differences may or may not affect water quality. This is where the CPI improves on the statistical techniques I compared it to in this thesis. The importance of temporal effects on water quality was demonstrated by the median polish procedure results. The CPI incorporates time as a factor by measuring the relationship between alkalinity, hardness, and specific conductance over time. Potentially, then it is a more complete tool for water quality characterization than landscape metrics.

The third question I investigated produced the most unexpected results. I found little relationship between CPI values and the individual landscape variables used to infer water quality. Many studies have found a direct relationship between urban land use and water quality, but I found only a few correlations between water quality parameters and landscape factors, with some descriptive statistics for hardness being related to geologic factors and some descriptive statistics for specific conductance related to land use factors. Thus, neither parameter completely represents landscape differences between sample sites. The fact that these two parameters respond to sets of separate hydrologic signals in the contributing basin indicates that they vary differently in response to changes in the water history of the stream, disrupting the strong natural association between the parameters. One insight the correlation analysis provides is that urban water quality is not a linear function of any single drainage basin characteristic. The ranking of 'water quality' at the sites sampled in this study depends largely on which factor or factors are used to characterize the watershed. The median polish analysis showed that different sites within the individual watersheds respond differently to landscape factors, and thus no single landscape metric or group of metrics will produce a correct, all-encompassing ranking of water quality.

The watersheds sampled for this study may be so degraded that some threshold value has been crossed, which limits the ability of the CPI or any of its constituents to reflect differences in the amount water quality degradation between sample sites. The high percentage of urbanization in all the study watersheds may provide a nearly constant input of pollutant loads, decreasing the variations in the relationship between alkalinity, hardness, and specific conductance that the CPI measures. Differences between 'expected' water quality-landscape relationships and CPI values suggest that different processes are at work at different sites. Streams fed by areas with highly soluble geologic formations will naturally have high ion levels. Betson's calculated event mean concentrations at Third Creek's Proctor site (see Table 2.1) are lower the mean concentrations I observed for alkalinity, hardness, and specific conductance at the same site during base flow conditions (see Table 4.1) suggesting that surface runoff, while no doubt very polluted, may reduce the ionic load of the receiving stream given certain geologic conditions. Surface waters with naturally high ionic loads would be less likely to have dramatic increases in their chemical composition due to pollutant input. This may reduce the amount of deviation among alkalinity, hardness, and specific conductance, reducing the effectiveness of the CPI. To reduce the effect of the natural variation in the strength of the relationships between the variables used to calculate the CPI, the CPI will probably be most effective as a tool for ranking water quality between multiple sites if it is used to rank water quality between sites within a single watershed.

Most researchers who have found strong indications of landscape effects on water quality have used data from individual sites on different streams or along a stream, but in much larger watersheds with greater distances between sample locations than was the case in this thesis. This study applied similar sample and analysis techniques on a much smaller scale with more detailed landscape variables. Instead of urban, agricultural, and forest land use classes, I subdivided land use into more specific classes, potentially changing the homogeneity of the land use patterns found at larger scales by previous researchers.

Two issues associated with the effect of data aggregation on the landscape analysis have been defined as the Modifiable Areal Unit Problem (MAUP) (Jelinski and Wu, 1996). The first issue associated with MAUP could very well explain the lack of consistency between my results and the associations between land use and water chemistry variables found in the literature. The 'scale problem' occurs when a set of areal data is aggregated into several sets of areal data at different scales and each set of combined data leads to different data values and inferences. Understanding the effects of landscape on surface water requires integrating units representing land use, watersheds, soils, elevation, population, and geology that differ in size, shape, and scale. Research has shown that statistical relationships between data change based on zonal and scale decisions. Changing the location of or size of zonal units, like watersheds, could produce entirely different results for the same statistical test using the same land use data set. For example, research using random computer-generated maps and USGS land use data showed the existence of thresholds in spatial patterns across different scales (Turner *et al*., 1989). The MAUP is a consequence of the complexity of natural processes and it demonstrates that researchers should not assume the homogeneity of landscape structures and should recognize the effects of spatiotemporal heterogeneity and scale on hydrologic systems.

Schueler (1994) developed an impervious cover model with 25% total impervious area (TIA) as the upper bound for watershed vulnerability. Impervious area in all sub-catchments in this thesis exceeded this percentage. Perhaps once this threshold value is surpassed, the relative ranking of impervious cover is not as accurate an indicator of water quality as with watersheds below 25% TIA. In heavily urbanized areas, such as the three research watersheds in this study, water quality along the stream may not be as directly related to landscape factors as has been seen in other studies operating on larger scales and across a wider range of landscape characteristics. Geomorphic channel alteration by direct anthropogenic modification, such as adding artificial drainages or channelizing specific reaches of the stream, may cause alterations in water quality not directly associated with landscape factors. Local effects, like a leaking sewer pipe, the presence or lack of a retention pond, or construction sites, may be small when compared to the general effect of changing land use on a broad scale. When working at fine scales, relationships between land use and water quality are not as strong, and individual events, like failure to properly implement best management practices, can have a large effect on water quality.

The CPI rankings also did not correlate well with water quality as ranked using output from the HSPF model. Again, the lack of agreement between the two methods for ranking water quality raises questions not only about the CPI but about the HSPF model as well. Without sufficient calibration and verification data — data generally not available for streams without continuous samplers installed — these models can only be thought of as a 'best guess' based on the modelers' understanding of the hydrologic processes at work in the simulated watershed. The MAUP also applies in this case. Most watersheds that are monitored only have continuous data for one point within the hydrologic system. Data collected from aquatic systems at a fine scale can often not be summed to produce accurate regional estimates (Turner *et al.*, 1989). Weighted averages used to define the hydrologic characteristics of the modeled land segments do not always produce reasonable results because the heterogeneity of landscapes may influence hydrologic process in nonlinear ways. Model variables calibrated to data from a small sub-catchment may not be extendible to an entire watershed and visa versa. This may be the case with my HSPF model, which matches well with estimated total watershed flow rates and pollutant export but does not match the calibration data for the small sub-catchements monitored by Betson and Milligan (1981).

CPI as a Tool for Water Quality Monitoring Groups

From my modeling and empirical research of water quality in the Knoxville urban area, I believe the CPI would be a useful tool for assessing water quality. Community groups are generally organized at local levels. Therefore, they need techniques that operate effectively at local scales. Water quality models that require technical knowledge and access to long-term flow and chemistry data for correct calibration are unsuitable for community water monitoring groups. While knowledge of the contributing landscape is necessary to identify pollution source areas, it is not always an accurate way to characterize water quality. Chemical assessments of water quality parameters provide valuable information and insight into the hydrologic process within the watershed. The CPI provides a way to interpret chemical data without complicated statistical analysis or a complete understanding of the complicated chemical interactions that generate the measured variables.

Some combinations of alkalinity, hardness and specific conductance are already required parameters for many water quality-testing protocols, including the USGS National Water-Quality Assessment (Shelton, 1994, USEPA, 1997). Adding any one of these parameters to a sampling program would only negligibly increase the cost and the amount of time required for water quality analysis. Larger watersheds, with greater variations in land use and less impervious cover, may provide a clearer indication of the relationships between water quality, the CPI, and landscape metrics. Implementation of the CPI would be most useful if reference sites known to have good water quality were established within the targeted watersheds. Further testing of the CPI with a research design that isolates the factors affecting water quality could provide stronger evidence of the CPI usefulness as a water quality monitoring tool. One method of testing the CPI would be to obtain long-term water quality data that include the components of the CPI for a watershed that has undergone urbanization during the period of record, and compare CPI values from different time periods at the site. Despite the lack of conclusive evidence supporting use of the CPI, this thesis demonstrates that it can be a helpful tool for understanding differences in water quality within a watershed.

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APPENDICES

APPENDIX A

Discrete Water Quality Sampling Results

Table A.1: Discrete Samples

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Ag Campus	12/10/2002	11:01:00	124	216	438	8.34	.	10	no rain previous 72hrs
Third	Lonas	12/10/2002	9:41:50	112	236	390	8.23	.	12	no rain previous 72hrs
Third	Painter	12/10/2002	10:28:00	128	232	412	8.25	.	11	no rain previous 72hrs
Third	Proctor	12/10/2002	10:03:00	160	254	543	8.19	.	11	no rain previous 72hrs
Third	Sullivan	12/10/2002	8:50:00	124	220	392	8.35	.	13	no rain previous 72hrs
Third	Tyson	12/10/2002	10:15:00	216	244	665	7.94	.	.	no rain previous 72hrs
Third	Webb	12/10/2002	9:12:00	108	200	351	7.94	.	.	no rain previous 72hrs
Third	Ag Campus	12/17/2002	14:45:00	140	200	430	8.35	.	13	no rain previous 72hrs
Third	Lonas	12/17/2002	13:45:00	114	214	383	8.16	.	14	no rain previous 72hrs
Third	Painter	12/17/2002	14:35:00	140	200	404	8.31	.	13	no rain previous 72hrs
Third	Proctor	12/17/2002	14:00:00	168	248	518	8.22	.	14	no rain previous 72hrs
Third	Sullivan	12/17/2002	13:15:00	120	200	383	7.59	.	14	no rain previous 72hrs
Third	Tyson	12/17/2002	14:10:00	200	260	642	8.01	.	13	no rain previous 72hrs
Third	Webb	12/17/2002	13:10:00	112	194	360	7.75	.	.	no rain previous 72hrs
Third	Ag Campus	12/18/2002	12:30:00	124	212	434	8.35	.	12	no rain previous 72hrs
Third	Lonas	12/18/2002	13:40:00	100	200	384	8.23	.	13	no rain previous 72hrs
Third	Painter	12/18/2002	12:45:00	118	224	405	8.34	.	12	no rain previous 72hrs
Third	Proctor	12/18/2002	13:20:00	132	228	525	8.31	.	13	no rain previous 72hrs
Third	Sullivan	12/18/2002	14:10:00	120	200	388	7.67	.	14	no rain previous 72hrs
Third	Tyson	12/18/2002	13:10:00	200	244	662	8.05	.	12	no rain previous 72hrs
Third	Webb	12/18/2002	14:00:00	98	196	363	7.82	.	13	no rain previous 72hrs
Third	Ag Campus	12/19/2002	14:55:00	132	226	435	8.35	.	12	no rain previous 72hrs
Third	Lonas	12/19/2002	14:00:00	100	192	386	8.18	.	13	no rain previous 72hrs
Third	Painter	12/19/2002	14:45:00	124	216	407	8.3	.	12	no rain previous 72hrs
Third	Proctor	12/19/2002	14:15:00	140	248	527	8.24	.	14	no rain previous 72hrs

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Sullivan	12/19/2002	13:30:00	116	212	390	7.64	.	14	no rain previous 72hrs
Third	Tyson	12/19/2002	14:30:00	200	248	659	7.97	.	13	no rain previous 72hrs
Third	Webb	12/19/2002	13:45:00	100	180	367	7.85	.	14	no rain previous 72hrs
Goose	Edington East	2/11/2003	15:35:00	160	200	457	7.69	30	10	rain past 24 hrs
Goose	Edington West	2/11/2003	15:50:00	164	188	361	8.02	7	10	rain past 24 hrs
Goose	Ingersoll	2/11/2003	15:28:00	176	240	486	7.82	11	12	rain past 24 hrs
Goose	Mary Vestal East	2/11/2003	16:00:00	200	228	491	7.97	38	10	rain past 24 hrs
Goose	Mary Vestal West	2/11/2003	16:00:00	176	200	470	8.17	36	10	rain past 24 hrs
Second	Cumberland	2/11/2003	15:05:00	142	200	556	8.27	27	10	rain past 24 hrs
Second	Inskip	2/11/2003	13:09:00	148	200	468	7.64	30	13	rain past 24 hrs
Second	Woodland	2/11/2003	13:24:00	140	212	535	8.34	27	10	rain past 24 hrs
Third	Ag Campus	2/11/2003	11:20:00	132	180	461	8.24	18	9	rain past 24 hrs
Third	Lonas	2/11/2003	12:08:00	120	188	393	8.15	28	10	rain past 24 hrs
Third	Painter	2/11/2003	11:35:00	120	188	421	8.21	51	9	rain past 24 hrs
Third	Proctor	2/11/2003	11:57:00	148	216	491	8.26	10	10	rain past 24 hrs
Third	Sullivan	2/11/2003	12:38:00	124	200	.	7.87	33	12	rain past 24 hrs
Third	Tyson	2/11/2003	11:47:00	188	216	714	7.85	9	9	rain past 24 hrs
Third	Webb	2/11/2003	12:25:00	108	180	365	7.98	52	11	rain past 24 hrs
Goose	Edington East	2/13/2003	12:30:00	200	176	471	7.93	32	10	Sunny, no rain past 24hrs
Goose	Edington West	2/13/2003	12:35:00	124	188	353	8.32	8	9	Sunny, no rain past 24hrs
Goose	Ingersoll	2/13/2003	12:20:00	236	188	488	7.93	13	11	Sunny, no rain past 24hrs
Goose	Mary Vestal East	2/13/2003	12:42:00	188	212	496	8.34	38	10	Sunny, no rain past 24hrs
Goose	Mary Vestal West	2/13/2003	12:45:00	176	240	481	8.19	35	8	Sunny, no rain past 24hrs
Second	Cumberland	2/13/2003	9:50:00	152	232	536	8.27	27	9	Sunny, no rain past 24hrs
Second	Inskip	2/13/2003	11:46:00	128	212	443	7.91	31	13	Sunny, no rain past 24hrs
Second	Woodland	2/13/2003	12:05:00	132	240	496	8.3	28	10	Sunny, no rain past 24hrs

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Ag Campus	2/13/2003	10:02:00	136	216	455	8.25	18	9	Sunny, no rain past 24hrs
Third	Lonas	2/13/2003	10:55:00	100	200	393	8.32	48	11	Sunny, no rain past 24hrs
Third	Painter	2/13/2003	10:30:00	128	200	421	7.92	52	9	Sunny, no rain past 24hrs
Third	Proctor	2/13/2003	10:40:00	144	248	501	8.29	9	9	Sunny, no rain past 24hrs
Third	Sullivan	2/13/2003	11:20:00	112	188	308	8.1	43	11	Sunny, no rain past 24hrs
Third	Tyson	2/13/2003	10:20:00	192	224	709	8.09	9	8	Sunny, no rain past 24hrs
Third	Webb	2/13/2003	11:10:00	104	200	369	8.05	49	11	Sunny, no rain past 24hrs
Goose	Edington East	2/20/2003	12:54:00	142	178	366	7.71	35	10	rain previous evening
Goose	Edington West	2/20/2003	13:00:00	132	172	347	7.78	11	11	rain previous evening
Goose	Ingersoll	2/20/2003	12:45:00	180	228	434	7.76	14	12	rain previous evening
Goose	Mary Vestal East	2/20/2003	13:10:00	200	244	460	7.95	39	12	rain previous evening
Goose	Mary Vestal West	2/20/2003	13:25:00	152	208	409	7.95	49	10	rain previous evening
Second	Cumberland	2/20/2003	10:20:00	146	200	445	7.98	34	12	rain previous evening
Second	Inskip	2/20/2003	12:16:00	128	200	392	7.72	34	13	rain previous evening
Second	Woodland	2/20/2003	12:30:00	136	216	439	8.12	35	13	rain previous evening
Third	Ag Campus	2/20/2003	10:30:00	114	176	385	8.03	54	11	rain previous evening
Third	Lonas	2/20/2003	11:30:00	98	168	344	7.92	46	12	rain previous evening
Third	Painter	2/20/2003	10:58:00	102	186	364	7.96	55	12	rain previous evening
Third	Proctor	2/20/2003	11:16:00	140	214	473	8.03	12	12	rain previous evening
Third	Sullivan	2/20/2003	11:50:00	100	164	331	7.54	44	12	rain previous evening
Third	Tyson	2/20/2003	10:45:00	160	200	584	7.79	18	11	rain previous evening
Third	Webb	2/20/2003	11:45:00	96	168	318	7.87	69	12	rain previous evening
Goose	Edington East	2/25/2003	12:23:00	132	168	338	7.71	38	10	flooding rain lasting previous 3-4 days
Goose	Edington West	2/25/2003	12:30:00	124	172	342	7.94	9	9	flooding rain lasting previous 3-4 days
Goose	Ingersoll	2/25/2003	12:15:00	172	228	417	7.72	17	11	flooding rain lasting previous 3-4 days
Goose	Mary Vestal East	2/25/2003	12:40:00	188	224	466	8.06	40	11	flooding rain lasting previous 3-4 days

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Goose	Mary Vestal West	2/25/2003	12:45:00	148	188	404	7.99	39	9	flooding rain lasting previous 3-4 days
Second	Cumberland	2/25/2003	9:55:00	134	224	461	8.13	39	11	flooding rain lasting previous 3-4 days
Second	Inskip	2/25/2003	11:50:00	120	184	381	7.73	38	12	flooding rain lasting previous 3-4 days
Second	Woodland	2/25/2003	12:01:00	124	216	436	8.13	37	.	flooding rain lasting previous 3-4 days
Third	Ag Campus	2/25/2003	10:10:00	112	200	389	8.09	.	11	flooding rain lasting previous 3-4 days
Third	Lonas	2/25/2003	11:00:00	98	180	341	8	55	11	flooding rain lasting previous 3-4 days
Third	Painter	2/25/2003	10:35:00	100	164	367	8.05	81	11	flooding rain lasting previous 3-4 days
Third	Proctor	2/25/2003	10:50:00	136	212	492	7.89	13	11	flooding rain lasting previous 3-4 days
Third	Sullivan	2/25/2003	11:25:00	96	168	330	7.64	46	12	flooding rain lasting previous 3-4 days
Third	Tyson	2/25/2003	10:28:00	200	260	628	8.01	27	10	flooding rain lasting previous 3-4 days
Third	Webb	2/25/2003	11:15:00	88	172	317	7.73	67	11	flooding rain lasting previous 3-4 days
Goose	Edington East	2/26/2003	12:35:00	156	196	392	7.67	.	11	light snow previous day - light rain
Goose	Edington West	2/26/2003	12:40:00	112	156	286	7.85	.	10	light snow previous day - light rain
Goose	Ingersoll	2/26/2003	12:30:00	180	216	419	7.63	.	12	light snow previous day - light rain
Goose	Mary Vestal East	2/26/2003	12:50:00	148	188	368	7.91	.	11	light snow previous day - light rain
Goose	Mary Vestal West	2/26/2003	12:52:00	134	160	341	7.88	.	12	light snow previous day - light rain
Second	Cumberland	2/26/2003	12:15:00	108	184	427	8.06	52	12	light snow previous day - light rain
Second	Inskip	2/26/2003	10:04:00	142	212	389	7.59	38	14	light snow previous day - drizzle
Second	Woodland	2/26/2003	9:45:00	148	214	440	7.88	37	13	light snow previous day - rain
Third	Ag Campus	2/26/2003	11:45:00	116	188	405	7.72	.	12	light snow previous day - light rain
Third	Lonas	2/26/2003	10:57:00	108	168	347	7.86	54	.	light snow previous day - drizzle
Third	Painter	2/26/2003	11:15:00	126	182	368	7.91	78	12	light snow previous day - drizzle
Third	Proctor	2/26/2003	10:23:00	108	212	484	7.9	12	12	light snow previous day - drizzle
Third	Sullivan	2/26/2003	10:42:00	108	172	339	7.66	49	13	light snow previous day - drizzle
Third	Tyson	2/26/2003	11:25:00	212	120	883	7.86	27	12	light snow previous day - drizzle
Third	Webb	2/26/2003	10:35:00	96	168	324	7.89	60	13	light snow previous day - drizzle
Goose	Edington East	3/1/2003	14:20:00	156	200	416	7.62	29	.	overcast no rain previous 24hrs

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (μS)	pH	Depth (cm)	Water Temp (°C)	Comments
Goose	Edington West	3/1/2003	14:30:00	132	148	351	7.78	14	.	overcast no rain previous 24hrs
Goose	Ingersoll	3/1/2003	14:10:00	172	224	438	7.8	18	15	overcast no rain previous 24hrs
Goose	Mary Vestal East	3/1/2003	14:50:00	188	236	474	7.97	41	.	overcast no rain previous 24hrs
Goose	Mary Vestal West	3/1/2003	14:45:00	160	212	450	8.04	38	.	overcast no rain previous 24hrs
Second	Cumberland	3/1/2003	14:00:00	132	216	475	8.17	44	14	overcast no rain previous 24hrs
Second	Inskip	3/1/2003	12:15:00	132	212	400	7.61	34	15	overcast no rain previous 24hrs
Second	Woodland	3/1/2003	12:00:00	140	212	443	8.13	37	14	overcast no rain previous 24hrs
Third	Ag Campus	3/1/2003	13:45:00	116	200	403	8.13	62	14	overcast no rain previous 24hrs
Third	Lonas	3/1/2003	12:45:00	104	192	351	7.99	49	14	overcast no rain previous 24hrs
Third	Painter	3/1/2003	13:20:00	116	200	373	8.11	75	14	overcast no rain previous 24hrs
Third	Proctor	3/1/2003	12:35:00	140	224	476	7.96	10	14	overcast no rain previous 24hrs
Third	Sullivan	3/1/2003	13:08:00	100	180	341	7.54	44	14	overcast no rain previous 24hrs
Third	Tyson	3/1/2003	13:35:00	168	280	634	7.92	20	13	overcast no rain previous 24hrs
Third	Webb	3/1/2003	12:58:00	92	176	329	7.7	59	15	overcast no rain previous 24hrs
Goose	Edington East	3/11/2003	13:50:00	192	212	457	7.69	33	14	Sunny
Goose	Edington West	3/11/2003	13:55:00	124	176	344	8.16	12	14	Sunny
Goose	Ingersoll	3/11/2003	13:45:00	168	248	457	7.09	17	14	Sunny
Goose	Mary Vestal East	3/11/2003	14:10:00	176	248	476	8.05	34	15	Sunny
Goose	Mary Vestal West	3/11/2003	14:05:00	120	224	452	8.25	37	12	Sunny
Second	Cumberland	3/11/2003	11:15:00	.	.	482	8.26	37	12	Sunny
Second	Inskip	3/11/2003	13:15:00	140	212	408	7.65	38	16	Sunny
Second	Woodland	3/11/2003	13:05:00	140	224	436	8.34	42	14	Sunny
Third	Ag Campus	3/11/2003	22:30:00	116	236	425	8.22	44	12	Sunny
Third	Lonas	3/11/2003	12:20:00	132	196	374	8.22	42	14	Sunny
Third	Painter	3/11/2003	12:00:00	116	212	396	8.25	66	13	Sunny
Third	Proctor	3/11/2003	12:15:00	116	252	484	8.25	9	15	Sunny
Third	Sullivan	3/11/2003	12:50:00	112	212	368	7.82	44	15	Sunny

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Tyson	3/11/2003	11:45:00	196	240	639	8.04	8	12	Sunny
Third	Webb	3/11/2003	12:40:00	108	192	351	7.82	53	14	Sunny
Goose	Edington East	3/13/2003	12:10:00	176	236	459	7.75	34	16	partly cloudy
Goose	Edington West	3/13/2003	12:20:00	116	192	341	8.25	7	15	partly cloudy
Goose	Ingersoll	3/13/2003	12:00:00	184	260	459	7.83	16	16	partly cloudy
Goose	Mary Vestal East	3/13/2003	12:30:00	180	264	473	8.23	35	15	partly cloudy
Goose	Mary Vestal West	3/13/2003	12:25:00	168	240	453	8.34	37	13	partly cloudy
Second	Cumberland	3/13/2003	10:05:00	120	244	485	8.26	46	14	partly cloudy
Second	Inskip	3/13/2003	11:45:00	140	212	409	7.75	31	17	partly cloudy
Second	Woodland	3/13/2003	11:35:00	132	220	439	8.4	35	15	partly cloudy
Third	Ag Campus	3/13/2003	10:20:00	116	212	427	8.35	34	.	partly cloudy
Third	Lonas	3/13/2003	10:55:00	112	200	377	8.28	42	15	partly cloudy
Third	Painter	3/13/2003	12:50:00	116	212	397	8.51	65	15	partly cloudy
Third	Proctor	3/13/2003	10:40:00	136	240	488	8.35	9	15	partly cloudy
Third	Sullivan	3/13/2003	11:15:00	120	180	371	7.79	45	15	partly cloudy
Third	Tyson	3/13/2003	12:40:00	190	256	631	8.09	7	16	partly cloudy
Third	Webb	3/13/2003	11:05:00	100	192	355	7.87	55	15	partly cloudy
Goose	Edington East	3/26/2003	14:40:00	184	224	481	7.75	30	14	water tanic look
Goose	Edington West	3/26/2003	14:45:00	136	184	341	8.27	8	14	sandy bottom
Goose	Ingersoll	3/26/2003	14:30:00	184	252	461	7.94	15	15	overcast - air temp drop
Goose	Mary Vestal East	3/26/2003	14:55:00	192	240	477	8.18	34	.	overcast
Goose	Mary Vestal West	3/26/2003	14:50:00	152	240	464	8.19	29	.	overcast
Second	Cumberland	3/26/2003	11:20:00	140	252	494	8.24	41	16	overcast -showers last 12hrs
Second	Inskip	3/26/2003	14:15:00	128	200	391	7.66	35	16	overcast -cloudy water
Second	Woodland	3/26/2003	13:30:00	132	224	448	8.29	43	15	light rain
Third	Ag Campus	3/26/2003	11:35:00	128	212	435	8.29	22	15	water level back down
Third	Lonas	3/26/2003	12:35:00	112	200	391	8.22	35	15	light rain

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Painter	3/26/2003	12:00:00	120	192	415	8.19	62	15	overcast
Third	Proctor	3/26/2003	12:20:00	136	240	506	8.27	8	15	overcast
Third	Sullivan	3/26/2003	13:05:00	120	200	383	7.85	39	15	light rain
Third	Tyson	3/26/2003	11:48:00	212	280	688	7.94	2	15	misting showers
Third	Webb	3/26/2003	12:50:00	116	200	369	7.8	41	15	light rain
Goose	Edington East	3/28/2003	13:45:00	168	236	476	7.91	29	18	sunny/party cloudy
Goose	Edington West	3/28/2003	13:55:00	132	192	331	8.32	8	18	sunny/party cloudy
Goose	Ingersoll	3/28/2003	13:35:00	162	244	463	7.76	15	17	sunny/party cloudy
Goose	Mary Vestal East	3/28/2003	14:05:00	168	224	450	8.29	34	18	sunny/party cloudy
Goose	Mary Vestal West	3/28/2003	14:00:00	164	238	460	8.24	36	16	sunny/party cloudy
Second	Cumberland	3/28/2003	11:40:00	128	220	485	8.43	41	16	sunny/party cloudy
Second	Inskip	3/28/2003	13:20:00	120	224	415	7.7	27	18	sunny/party cloudy
Second	Woodland	3/28/2003	13:05:00	116	236	437	8.31	39	17	sunny/party cloudy
Third	Ag Campus	3/28/2003	11:50:00	120	224	434	8.38	36	16	sunny/party cloudy
Third	Lonas	3/28/2003	12:30:00	112	212	391	8.28	31	16	sunny/party cloudy
Third	Painter	3/28/2003	12:10:00	112	224	413	8.3	60	16	sunny/party cloudy
Third	Proctor	3/28/2003	12:20:00	140	236	494	8.35	8	18	sunny/party cloudy
Third	Sullivan	3/28/2003	12:45:00	112	212	385	8.07	41	17	sunny/party cloudy
Third	Tyson	3/28/2003	12:00:00	192	264	685	8.05	10	17	sunny/party cloudy
Third	Webb	3/28/2003	12:40:00	100	212	374	7.88	35	16	sunny/party cloudy
Goose	Edington East	4/16/2003	12:50:00	160	222	432	7.58	33	16	
Goose	Edington West	4/16/2003	12:55:00	136	172	355	7.75	11	16	
Goose	Ingersoll	4/16/2003	12:40:00	172	268	456	7.68	16	16	
Goose	Mary Vestal East	4/16/2003	13:10:00	180	252	479	8.02	32	16	
Goose	Mary Vestal West	4/16/2003	13:05:00	154	224	453	8.05	48	15	
Second	Cumberland	4/16/2003	10:16:00	128	244	475	8.05	43	16	
Second	Inskip	4/16/2003	12:15:00	126	200	399	7.52	32	17	

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Second	Woodland	4/16/2003	11:57:00	132	252	438	8.17	47	16	
Third	Ag Campus	4/16/2003	10:30:00	112	212	416	8.06	.	15	
Third	Lonas	4/16/2003	11:20:00	108	200	364	7.94	41	15	
Third	Painter	4/16/2003	10:55:00	108	212	391	8.06	59	15	
Third	Proctor	4/16/2003	11:05:00	136	236	500	8.07	11	17	
Third	Sullivan	4/16/2003	11:40:00	120	188	363	7.45	41	16	
Third	Tyson	4/16/2003	10:45:00	180	268	606	7.94	17	16	
Third	Webb	4/16/2003	11:35:00	96	166	342	7.55	51	15	
Goose	Edington East	4/18/2003	13:35:00	146	210	411	7.6	35	16	sunny > 1"rain 4/10/03
Goose	Edington West	4/18/2003	13:40:00	144	192	355	7.76	10	17	sunny > 1"rain 4/10/03
Goose	Ingersoll	4/18/2003	13:25:00	184	250	444	7.78	17	17	sunny > 1"rain 4/10/03
Goose	Mary Vestal East	4/18/2003	13:50:00	172	232	456	8.01	34	.	sunny > 1"rain 4/10/03
Goose	Mary Vestal West	4/18/2003	13:45:00	164	236	449	8.03	46	.	sunny > 1"rain 4/10/03
Second	Cumberland	4/18/2003	11:30:00	128	224	443	8.15	49	16	sunny > 1"rain 4/10/03
Second	Inskip	4/18/2003	13:10:00	120	212	378	7.56	36	19	sunny > 1"rain 4/10/03
Second	Woodland	4/18/2003	13:00:00	124	208	413	8.2	48	17	sunny > 1"rain 4/10/03
Third	Ag Campus	4/18/2003	11:40:00	112	212	384	8.11	.	16	sunny > 1"rain 4/10/03
Third	Lonas	4/18/2003	12:20:00	100	188	337	7.92	49	16	sunny > 1"rain 4/10/03
Third	Painter	4/18/2003	12:05:00	104	184	360	7.94	59	16	sunny > 1"rain 4/10/03
Third	Proctor	4/18/2003	12:10:00	120	226	470	8.04	14	18	sunny > 1"rain 4/10/03
Third	Sullivan	4/18/2003	12:45:00	100	180	331	7.45	44	16	sunny > 1"rain 4/10/03
Third	Tyson	4/18/2003	11:50:00	160	224	576	7.97	17	16	sunny > 1"rain 4/10/03
Third	Webb	4/18/2003	12:30:00	96	176	315	7.57	57	16	sunny > 1"rain 4/10/03
Goose	Edington East	4/22/2003	14:25:00	140	212	442	7.66	31	15	partly cloudy
Goose	Edington West	4/22/2003	14:30:00	124	180	354	7.71	9	15	partly cloudy
Goose	Ingersoll	4/22/2003	14:15:00	184	272	461	7.88	15	15	partly cloudy
Goose	Mary Vestal East	4/22/2003	14:40:00	192	276	484	8.08	32	15	partly cloudy

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Goose	Mary Vestal West	4/22/2003	14:35:00	160	240	460	8.12	41	15	partly cloudy
Second	Cumberland	4/22/2003	12:30:00	132	224	462	8.19	43	15	overcast and windy
Second	Inskip	4/22/2003	14:00:00	116	192	391	7.62	34	16	partly cloudy
Second	Woodland	4/22/2003	13:45:00	124	224	428	8.25	47	15	partly cloudy
Third	Ag Campus	4/22/2003	12:35:00	126	188	396	8.2	.	.	overcast and windy
Third	Lonas	4/22/2003	13:15:00	100	208	356	8.04	46	15	partly cloudy
Third	Painter	4/22/2003	12:55:00	108	200	379	8.15	46	15	overcast and windy
Third	Proctor	4/22/2003	13:05:00	128	236	490	8.06	20	16	partly cloudy
Third	Sullivan	4/22/2003	13:30:00	92	196	353	7.57	43	15	partly cloudy
Third	Tyson	4/22/2003	12:45:00	188	224	578	8	13	15	overcast and windy
Third	Webb	4/22/2003	13:25:00	100	188	335	7.67	49	15	partly cloudy
Goose	Edington East	4/23/2003	14:30:00	160	236	444	7.71	31	.	sunny
Goose	Edington West	4/23/2003	14:40:00	136	176	353	7.91	8	.	sunny
Goose	Ingersoll	4/23/2003	14:25:00	162	260	460	7.89	15	.	sunny
Goose	Mary Vestal East	4/23/2003	14:50:00	156	238	480	8.13	32	.	sunny
Goose	Mary Vestal West	4/23/2003	14:45:00	164	212	460	8.15	38	.	sunny
Second	Cumberland	4/23/2003	12:30:00	136	246	465	8.25	39	15	sunny
Second	Inskip	4/23/2003	14:05:00	124	192	392	7.58	32	.	sunny
Second	Woodland	4/23/2003	13:55:00	120	212	434	8.32	47	.	sunny
Third	Ag Campus	4/23/2003	12:40:00	116	200	407	8.2	.	14	sunny
Third	Lonas	4/23/2003	13:25:00	98	180	360	8.05	37	.	sunny
Third	Painter	4/23/2003	13:00:00	104	200	385	8.21	53	15	sunny
Third	Proctor	4/23/2003	13:10:00	144	224	493	8.18	18	.	sunny
Third	Sullivan	4/23/2003	13:40:00	100	188	358	7.59	41	.	sunny
Third	Tyson	4/23/2003	12:50:00	164	252	592	8.04	12	15	sunny
Third	Webb	4/23/2003	13:30:00	96	188	342	7.74	52	.	sunny
Goose	Edington East	5/10/2003	10:50:00	120	156	309	7.18	37	17	

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Goose	Edington West	5/10/2003	11:00:00	120	180	350	7.64	13	17	
Goose	Ingersoll	5/10/2003	10:45:00	160	224	426	7.76	18	15	
Goose	Mary Vestal East	5/10/2003	11:15:00	160	242	458	7.87	36	17	
Goose	Mary Vestal West	5/10/2003	11:10:00	128	216	384	7.76	49	17	
Second	Cumberland	5/10/2003	11:25:00	136	220	455	8.08	46	18	
Second	Inskip	5/10/2003	9:05:00	116	184	378	7.35	38	17	
Second	Woodland	5/10/2003	8:50:00	112	216	426	7.86	49	17	
Third	Ag Campus	5/10/2003	11:35:00	80	200	395	7.81			
Third	Lonas	5/10/2003	9:50:00	92	200	346	7.78	46	16	
Third	Painter	5/10/2003	10:15:00	88	200	369	7.77	72	16	
Third	Proctor	5/10/2003	10:05:00	112	248	488	7.93	23	18	
Third	Sullivan	5/10/2003	9:25:00	96	180	337	7.34	41	16	
Third	Tyson	5/10/2003	10:25:00	164	240	589	7.91	17	18	
Third	Webb	5/10/2003	9:39:59	94	168	323	7.42	50	16	
Goose	Edington East	5/11/2003	14:51:00	130	188	341	7.78	14	19	
Goose	Edington West	5/11/2003	15:05:00	124	156	319	7.64	34	19	
Goose	Ingersoll	5/11/2003	13:42:00	152	212	434	7.84	16	16	water clear
Goose	Mary Vestal East	5/11/2003	15:17:00	168	252	442	8.03	31	18	
Goose	Mary Vestal West	5/11/2003	15:15:00	136	168	360	7.97	42	19	
Second	Cumberland	5/11/2003	13:00:00	60	108	227	7.84	46	20	cloudy - very turbid
Second	Inskip	5/11/2003	17:04:00	96	184	352	7.59	38	19	
Second	Woodland	5/11/2003	16:51:00	108	188	366	8.08	45	20	
Third	Ag Campus	5/11/2003	15:37:00	80	112	236	7.81		20	
Third	Lonas	5/11/2003	16:15:00	88	136	279	7.9	52	19	
Third	Painter	5/11/2003	15:52:00	88	128	252	7.89	84	19	
Third	Proctor	5/11/2003	16:05:00	124	200	409	7.97	26	20	
Third	Sullivan	5/11/2003	16:35:00	84	172	298	7.56	45	18	

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Tyson	5/11/2003	15:45:00	128	172	433	7.85	29	20	
Third	Webb	5/11/2003	16:25:00	80	146	272	7.66	61	18	
Goose	Edington East	5/14/2003	15:40:00	130	240	422	7.5	31	16	
Goose	Edington West	5/14/2003	15:45:00	128	200	349	7.73	11	16	
Goose	Ingersoll	5/14/2003	15:35:00	176	216	452	7.65	14	16	
Goose	Mary Vestal East	5/14/2003	15:55:00	176	260	475	7.81	28	16	
Goose	Mary Vestal West	5/14/2003	15:50:00	142	248	447	7.94	36	16	
Second	Cumberland	5/14/2003	13:30:00	120	228	468	8.06	44	17	overcast
Second	Inskip	5/14/2003	15:20:00	122	236	393	7.45	35	17	
Second	Woodland	5/14/2003	15:00:00	122	236	431	8.07	43	17	
Third	Ag Campus	5/14/2003	13:40:00	96	212	412	7.93	.	16	
Third	Lonas	5/14/2003	14:25:00	100	180	360	7.74	44	16	
Third	Painter	5/14/2003	14:05:00	108	200	386	7.89	71	16	
Third	Proctor	5/14/2003	14:15:00	136	276	493	7.92	22	17	
Third	Sullivan	5/14/2003	14:45:00	96	192	356	7.45	36	15	
Third	Tyson	5/14/2003	14:00:00	164	248	591	7.82	13	17	smell gas
Third	Webb	5/14/2003	14:35:00	88	184	342	7.53	45	16	
Goose	Edington East	5/15/2003	16:05:00	160	228	427	7.62	30	17	partly cloudy
Goose	Edington West	5/15/2003	16:10:00	134	186	349	7.68	14	17	partly cloudy
Goose	Ingersoll	5/15/2003	16:00:00	182	244	451	7.79	15	16	partly cloudy
Goose	Mary Vestal East	5/15/2003	16:20:00	166	252	474	8.04	30	17	partly cloudy
Goose	Mary Vestal West	5/15/2003	16:15:00	172	226	447	8.07	35	17	partly cloudy
Second	Cumberland	5/15/2003	14:10:00	148	254	469	8.18	42	18	partly cloudy
Second	Inskip	5/15/2003	15:40:00	122	196	395	7.61	35	18	partly cloudy
Second	Woodland	5/15/2003	15:25:00	140	224	432	8.24	41	18	partly cloudy
Third	Ag Campus	5/15/2003	14:15:00	116	214	413	8.16	.	17	partly cloudy
Third	Lonas	5/15/2003	14:55:00	90	200	365	8.07	38	17	partly cloudy

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Third	Painter	5/15/2003	14:30:00	110	228	389	8.13	67	17	partly cloudy
Third	Proctor	5/15/2003	14:40:00	140	252	494	8.15	21	19	partly cloudy
Third	Sullivan	5/15/2003	15:10:00	104	224	359	7.6	45	16	partly cloudy
Third	Tyson	5/15/2003	14:25:00	176	270	594	7.98	9	18	partly cloudy
Third	Webb	5/15/2003	15:00:00	84	184	347	7.71	39	16	partly cloudy
Goose	Edington East	5/18/2003	12:30:00	136	212	400	7.69	32	16	sunny-partly cloudy
Goose	Edington West	5/18/2003	12:35:00	108	188	349	7.88	9	17	sunny-partly cloudy
Goose	Ingersoll	5/18/2003	12:20:00	154	256	447	7.83	14	16	sunny-partly cloudy
Goose	Mary Vestal East	5/18/2003	12:45:00	148	208	428	7.93	38	17	sunny-partly cloudy
Goose	Mary Vestal West	5/18/2003	12:40:00	152	224	435	8.01	35	17	sunny-partly cloudy
Second	Cumberland	5/18/2003	10:30:00	98	226	444	8.07	43	17	overcast - drizzle
Second	Inskip	5/18/2003	12:05:00	126	240	397	7.63	32	17	sunny-partly cloudy
Second	Woodland	5/18/2003	11:50:00	132	244	431	8.24	43	17	sunny-partly cloudy
Third	Ag Campus	5/18/2003	10:45:00	108	212	386	8.06	.	16	overcast - drizzle
Third	Lonas	5/18/2003	11:20:00	104	192	349	7.97	48	16	overcast - drizzle
Third	Painter	5/18/2003	10:55:00	108	212	367	8.05	77	16	overcast - drizzle
Third	Proctor	5/18/2003	11:05:00	148	252	479	8.08	19	17	overcast - drizzle
Third	Sullivan	5/18/2003	11:35:00	96	212	347	7.59	48	16	sunny-partly cloudy
Third	Tyson	5/18/2003	10:50:00	128	248	570	7.93	15	17	overcast - drizzle
Third	Webb	5/18/2003	11:28:00	76	190	329	7.67	46	16	sunny-partly cloudy
Goose	Edington East	5/20/2003	15:08:00	156	212	420	7.82	31	16	
Goose	Edington West	5/20/2003	15:12:00	132	188	347	8.08	11	17	
Goose	Ingersoll	5/20/2003	15:00:00	172	240	448	7.95	14	16	
Goose	Mary Vestal East	5/20/2003	15:25:00	176	288	474	8.17	41	17	
Goose	Mary Vestal West	5/20/2003	15:20:00	174	228	442	8.17	36	17	
Second	Cumberland	5/20/2003	14:50:00	132	260	469	8.35	42	18	
Second	Inskip	5/20/2003	13:10:00	124	212	399	7.81	32	17	

Table A.1: Continued

Watershed	Sample Site	Date	Time	Hardness (mg/L)	Alkalinity (mg/L)	Specific Conductance (µS)	pH	Depth (cm)	Water Temp (°C)	Comments
Second	Woodland	5/20/2003	12:55:00	132	212	436	8.4	40	17	
Third	Ag Campus	5/20/2003	14:40:00	124	200	401	8.33	.	17	
Third	Lonas	5/20/2003	13:40:00	98	196	358	8.2	35	16	
Third	Painter	5/20/2003	14:15:00	114	228	383	8.22	67	16	
Third	Proctor	5/20/2003	13:25:00	136	244	487	8.25	18	18	
Third	Sullivan	5/20/2003	13:58:00	100	224	354	7.85	46	16	
Third	Tyson	5/20/2003	14:30:00	180	252	589	8.08	6	18	
Third	Webb	5/20/2003	13:50:00	90	196	336	7.78	45	16	

APPENDIX B

Simulated and Observed Flow Plots

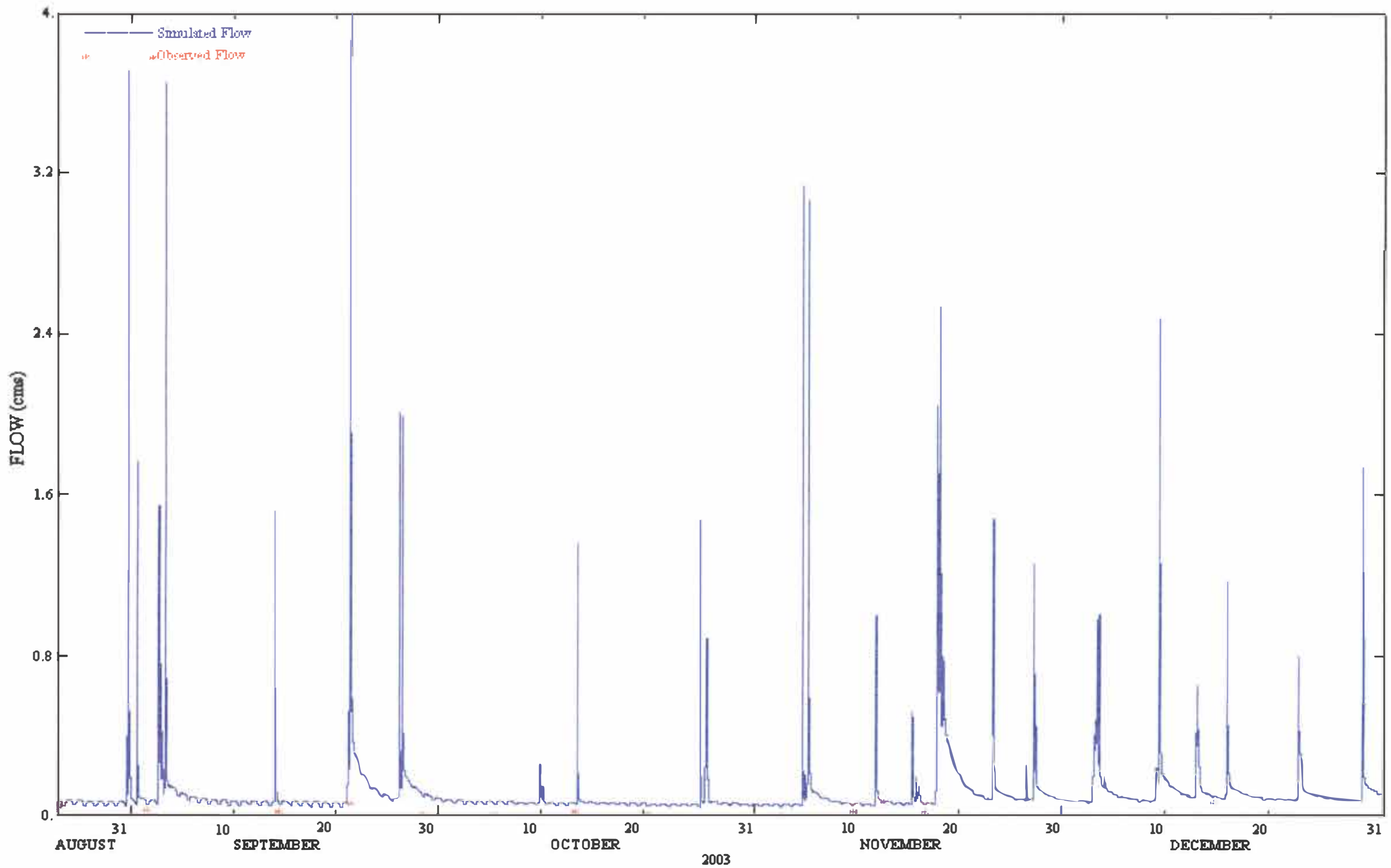

Figure B.1: Flow Plot - Goose Creek

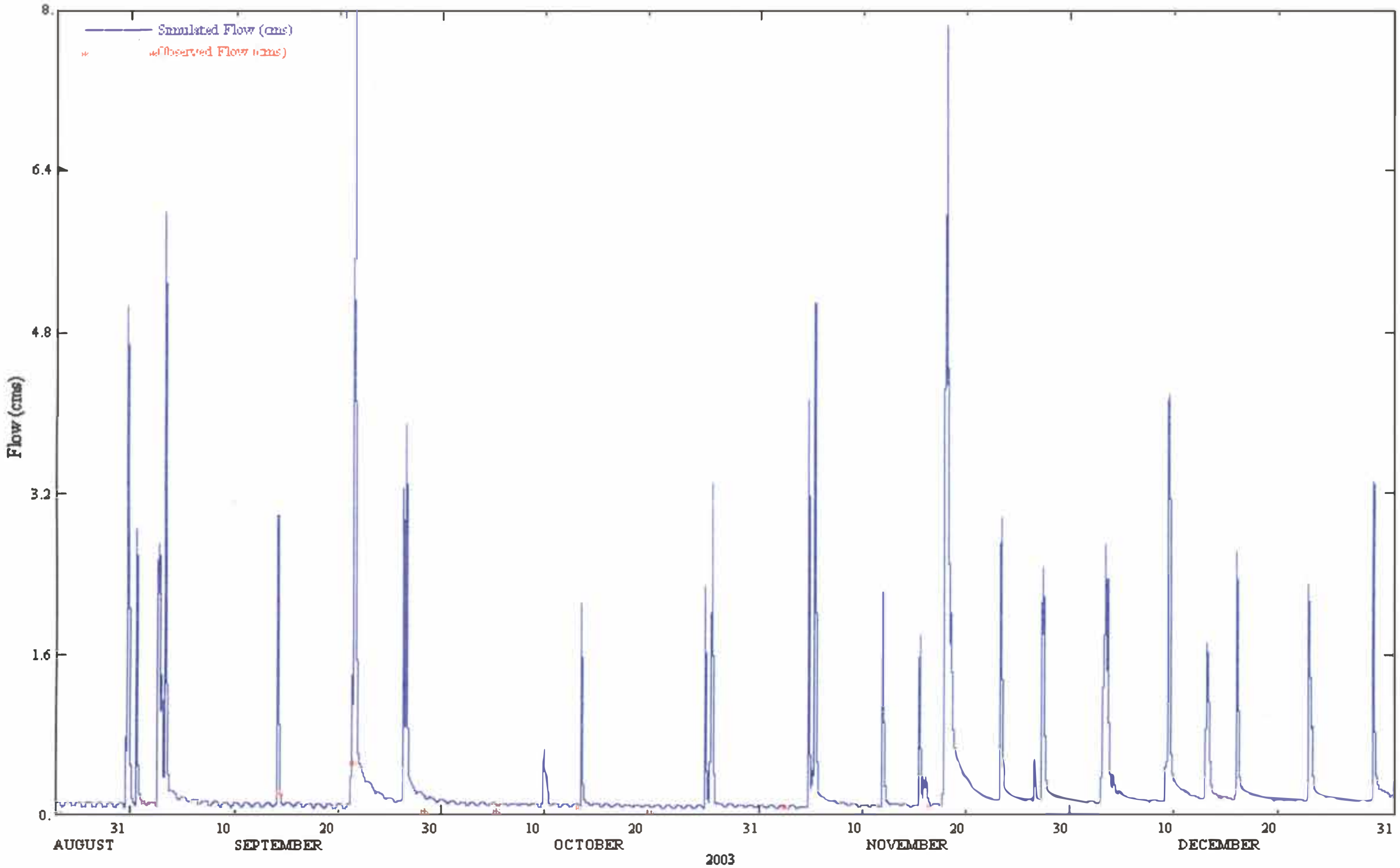

Figure B.2: Flow Plot - Second Creek

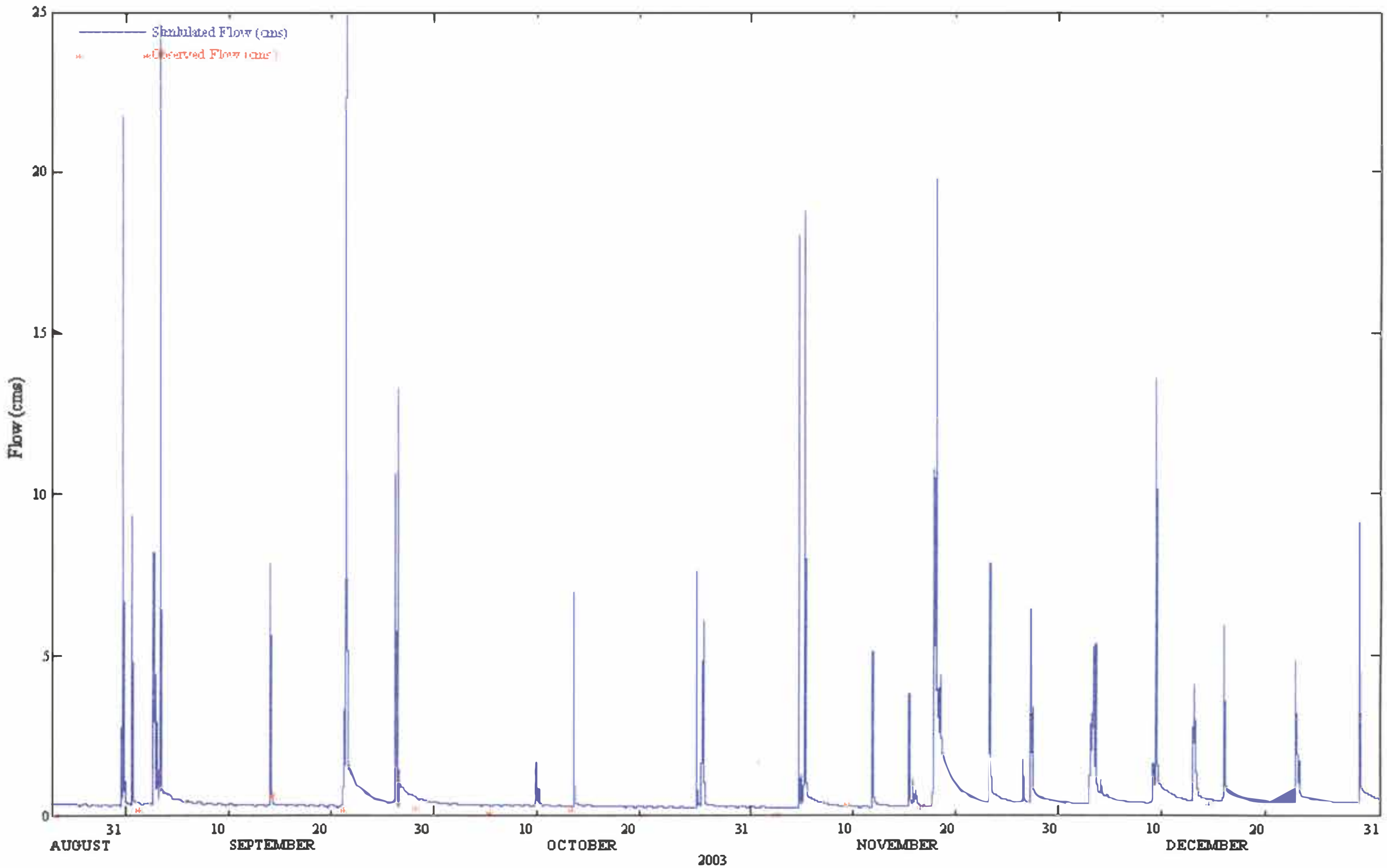

Figure B.3: Flow Plot - Third Creek

VITA

Brooks Alan Jolly was born in Mobile, Alabama on February 6, 1970. Raised in Mobile, he graduated from W.P. Davidson high school in 1988. Jolly received an associate's degree in drafting sciences from Southeast College of Technology in 1995 and went on to work in the field of power generation and distribution for six years, attaining the status of electrical designer. While working fulltime, Jolly attended the University of South Alabama, graduating *cum laude* in 2000 with a Bachelor of Science, major in Geography and a minor in Geology. After receiving his Bachelor's degree Alan continued his academic pursuits at the University of Tennessee – Knoxville and obtained a Master of Science degree in Geography with a focus on environmental modeling and watershed processes.

During his time at the University of Tennessee – Knoxville, Alan worked as a consultant for the Tennessee Valley Authority's Environmental Stewardship Division where he developed watershed models. Currently Alan is working as an extension specialist for Tennessee's Extension Service.