EVALUATING THE ROLE OF SINUOSITY IN THE REMOVAL OF NITRATE FROM A THIRD ORDER AGRICULTURAL STREAM IN CENTRAL ILLINOIS

Carol Jean Glennon

91 Pages December 2008

This study assesses the role of sinuosity in the removal of nitrate from a third order agricultural stream in central Illinois

APPROVED:

Date Eric W. Peterson, Chair

Date Stephen J. Van der Hoven

Date John C. Kostelnick

EVALUATING THE ROLE OF SINUOSITY IN THE REMOVAL OF NITRATE FROM A THIRD ORDER AGRICULTURAL STREAM IN CENTRAL ILLINOIS

Carol Jean Glennon

91 Pages December 2008

The hyporheic zone is an important ecotone found in rivers and streams with a natural ability to remove nitrate. In areas supporting heavy agricultural practices nitrate is a non-point source pollution problem. Groundwater in agricultural areas is at high risk of nitrate contamination. This study aims to assess what role sinuosity plays in nitrate removal from a low gradient stream in central Illinois.

To accomplish this, 13.3 km of Little Kickapoo Creek (LKC) was divided into six segments of varying lengths and sinuosity indices. Chloride, nitrate and sulfate data were collected at seven sampling locations along LKC. Mass flux calculations were performed using stream gauging data and depth to water measurements. A Geographic Information System (GIS) was used to calculate land use in the sub basins for each segment. An ANOVA ($\alpha = 0.05$) was performed to determine if concentrations among locations and mass fluxes between sampling locations were different. If the ANOVA results indicated a statistical difference ($p < 0.05$), then individual paired t-tests ($\alpha = 0.05$) between each location were conducted.

Statistically, the results show no net change in the fluxes of chloride, nitrate or sulfate along LKC but there is variation in fluxes between segments. The greatest loss in fluxes for all constituents correlates to the most sinuous segment. Long hyporheic flow paths beneath meanders result in a loss of chloride and sulfate flux. Chloride flux loss is related to hyporheic storage beneath meanders while sulfate flux loss is related to highly reducing conditions beneath meanders of LKC. Nitrate is lost to denitrification in short hyporheic flow paths found in the streambed, along longer flow paths beneath meanders and to vegetative uptake.

Excess anthropogenic nitrate additions are effectively remediated through natural stream function in LKC. Nitrate removal from LKC appears related to sinuosity; however, whether hyporheic interaction beneath meanders in the streambed or a combination of both is responsible for denitrification along LKC remains unanswered.

APPROVED:

Date Eric W. Peterson, Chair

Date Stephen J. Van der Hoven

Date John C. Kostelnick

EVALUATING THE ROLE OF SINUOSITY IN THE REMOVAL OF NITRATE FROM A THIRD ORDER AGRICULTURAL STREAM IN CENTRAL ILLINOIS

CAROL JEAN GLENNON

A Thesis Submitted in Partial
Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Geography-Geology

ILLINOIS STATE UNIVERSITY

2008

THESIS APPROVED:

Date Eric W. Peterson, Chair

Date Stephen J. Van der Hoven

Date John C. Kostelnick

ACKNOWLEDGEMENTS

From the beginning stages to the final draft I would like to thank my committee chair Dr. Eric Peterson. I would also like to thank my other committee members Dr. Stephen Van der Hoven and Dr. John Kostelnick for their willingness to help me through this process.

For funding part of this project I would like to thank the Illinois Groundwater Association.

I would also like to extend my gratitude to the Geography-Geology Department and the Biology Department.

This thesis is dedicated to my mother, Dorothy J. Benning, my father the late Edward W. Benning and my husband Michael W. Glennon.

C.J.G.

CONTENTS

TABLES

Table Page

FIGURES

CHAPTER I

GENERAL INTRODUCTION AND OVERVIEW

Introduction

Hyporheic Zone

Researchers have traditionally treated streams and groundwater as two distinct entities (Brunke and Gonser, 1997). Although hydrologists and ecologists noted a connection in flowpaths between streams and the stream bed (Brunke and Gonser, 1997) the significance was not well understood.

Faunal exploration in the mixing zone of surface and groundwater called the hyporheic zone (HZ) began in the 30's with Karaman (1935). HZ faunal work continued in the 40's and 50's with Chappuis (1942) and Angelier (1953). Modern ecological research in the HZ began in the 60's with Schwoerbel (1961a, b, 1964, 1967). The ecological significance of the HZ was only recently established in the early 1980's (Bencala, 1993).

Streams are an integral part of the watershed and are influenced by geologic, ecologic, and biotic factors. Stream water continually passes back and forth between the channel and subsurface hyporheic flow paths mixing stream water and discharging groundwater giving the HZ a unique chemical character (Schwartz and Zhang, 2003). The HZ of a river or stream can extend away from the immediate surrounding area for tens to hundreds of meters (Triska et al., 1993). Orghidan (1959) was the first to notice the transition between streams and groundwater as a distinct zone calling it the 'hyporheic biotope'. In the 1960's the general view of streams began to broaden with

Schwoerbel (1961a, b, 1964, 1967) describing the hydrology and faunal community of the HZ as a fundamental part of the stream ecosystem.

Since these initial observations further research has been conducted in an effort to delineate the HZ. A study by Hynes (1974) indentified the HZ through observations of unexpectedly high levels of dissolved oxygen (DO) in the shallow groundwater beneath the streambed. Temperature was used by White et al. (1987) as a tracer attempting to specify the extent of the HZ. Triska et al. (1989) defined two zones within the HZ through the use of solute tracers. Using mixing ratios Triska (1989) found a surface HZ containing 98% surface water directly beneath the channel and a deeper HZ containing 10% or greater surface water. Harvey and Bencala (1993) along with Wroblicky et al. (1998) used flow paths originating in the stream and returning to the channel within a given study area to define the HZ. Wondzell and Swanson (1996) along with Angradi and Hood (1998) found that the extent of the HZ can vary seasonally and in response to groundwater levels, stream stage and stream velocity. Harvey et al. (1991) found that varying rates of evapotranspiration cause diurnal fluctuations of groundwater, which also affect the HZ’s extent. Defining and putting a physical constraint on the HZ is difficult; the most practical HZ definition is simply of surface and groundwater exchange (Gibert et al., 1990, Veriver et al., 1992). This study will use the deeper HZ definition from Triska et al. (1989): the subsurface zone surrounding a stream that has 10% or greater surface water.

Hyporheic function is an important part of natural stream processes (Ostrom et al., 2002). Stream water entering the HZ comes into close contact with sediments that are both microbially and geochemically active in governing stream water chemistry (Findlay, 1995) and remediating excess anthropogenic nitrogen inputs (Ostrom et al., 2002).

Individual hyporheic flowpaths along streams can range from tens of centimeters to meters; beginning where surface water enters the subsurface and ending when it re-enters the stream. Hyporheic flowpaths enter and leave the channel many times while groundwater flowpaths enter and leave only once. Hydrologic exchange is greatest along shorter hyporheic flowpaths (Harvey and Wagner, 2000). Interaction that occurs along these short hyporheic flowpaths has a powerful influence on stream chemistry affecting dissolved concentrations and composition of nitrogen in surface waters (Duff and Triska, 2000).

Nitrogen Species

Nitrogen in fluvial environments can be found as dinitrogen (N_2), nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+) and as dissolved organic nitrogen (DON). Redox potential depends upon the valence state of nitrogen. A maximum shift of eight-electrons (reduced valence state of -3 to oxidized valence state of +5) exists between ammonium and nitrate, which creates a large redox potential (Duff and Triska, 2000). The energy produced during nitrogen transformations is what makes nitrogen an essential nutrient for all living things.

Elemental N_2 is readily available in the atmosphere in gaseous form. However, there are few organisms that can use nitrogen directly. Nitrogen fixing bacteria have developed a symbiotic relationship with legumes, clover, and alfalfa, residing in their root nodules (Krebs, 2001). Microbial processes drive nearly all nitrogen transformations. The release of nitrogen from plant litter and animal residue is reliant upon the activity of microfauna and microflora in soils (Follett and Delgado, 2002).

Ammonia (NH_3) and the ammonium ion (NH_4^+) can enter the nitrogen cycle through the decomposition of organic materials, nitrogen fertilizer application in row crop agriculture, animal waste or through a small number of organisms that can fix nitrogen directly from the atmosphere. Once nitrogen has been fixed as NH_3 or NH_4^+ nitrification takes place through bacterial processes. Nitrification converts NH_3 and NH_4^+ to NO_2^- or NO_3^- where NO_3^- is either taken up by plants or lost to denitrification.

Nitrogen Sources

Natural (litterfall and biotic nitrogen fixation) and anthropogenic (sewage discharge and fertilizer runoff) sources are both responsible for nitrogen inputs to the natural system. Nitrogen is a necessary nutrient for all living things; the availability of nitrogen is a limiting factor in crop yield (Ritter and Bergstrom, 2001). In the interest of increased crop yields, the intensive farming practices of North American farmers involve application of nitrogen fertilizers (Ritter and Bergstrom, 2001). Over the course of the 1960's and 1970's the use of nitrogen fertilizers in agricultural practices increased by six fold (Cirmo and McDonnell, 1997). Human activities contribute approximately 140 Tg of nitrogen per year above and beyond contributions from natural processes (Galloway et al., 1995).

In many areas of the world agriculture has been acknowledged as the single largest source of nitrogen input to aquatic environments (Turlan et al., 2007). Thus, in agricultural areas a major non-point source pollutant problem for streams and rivers is the use of nitrogen fertilizers (Dick et al., 2000). As of 2001, the Illinois Department of Agriculture estimated the number of farms in the state of Illinois at 76,000, covering 28 million acres, almost 80% of the state's total land area. Surface runoff from Illinois farms contributes nineteen percent of the NO_3^- load in the Mississippi River (Keeney and Hatfield 2001).

DON enters an ecosystem through precipitation and is produced when water comes into contact with soils and vegetation (Neff et al., 2003). Nearly every aquatic and terrestrial ecosystem contains DON, a complex mixture of materials, ranging from things that are difficult to metabolize to simple compounds that are readily utilized by plants (Neff et al., 2003). DON can become mineralized through microbial action and available to plants as soluble amino acid forms of nitrogen.

Impact of Excess Nitrogen

The excess nitrogen in surface waters has a negative effect on aquatic ecosystems and creates human health hazards. In aquatic ecosystems, eutrophication occurs in lakes (NRC, 1978) and far downstream (Davis et al., 2000) from agricultural areas where surface runoff and leaching (Ritter and Bergstrom, 2001) contribute to waters becoming over enriched with nutrients. The surge of nutrients stimulates an algal bloom. When the plant growth dies bacteria begin the process of decomposition. Oxygen is required by bacteria to break down or decompose the dead plant matter leading to a decrease in dissolved oxygen levels as bacteria consume larger amounts of dead plant matter. Any aquatic life that cannot leave the area will suffocate. The zone of hypoxia or “dead zone” at the mouth of the Mississippi in the Gulf of Mexico is a result of eutrophication.

In a nitrogen rich stream with excessive anthropogenic nitrogen input, much of the excess nitrogen is retained and stored in deep groundwater (Cirmo and McDonnell, 1997), leaving areas that support intensive agriculture at the highest risk of having groundwater contaminated with nitrate. The widespread occurrence of nitrate in groundwater is a result of nitrate’s high solubility, mobility, and easy displacement by water (Follett and Delgado, 2002).

Humans experience ill health effects when nitrate consumption is above the maximum contaminant level (MCL) of 10 mg/L for nitrate as nitrogen (NO_3^--N) or 45 mg/L NO_3^-. In adults NO_3^- is reduced to NO_2^- in the stomach, which then forms carcinogenic nitrosamines. When the MCL is exceeded in infants the oxygen carrying capacity of the blood is reduced resulting in a condition called methemoglobinemia or “blue baby syndrome”. The associated human health risks of nitrate consumption above the MCL have led the scientific community to look to stream function as a possible means of remediation.

Nitrogen Cycling in the Hyporheic Zone

The HZ is an area of intense nitrogen cycling, most notably between nitrification and denitrification. Factors controlling nitrogen cycling processes and rates differ among streams. Differences are due to nutrient availability and quality, amount of dissolved organic carbon (DOC) available (Storey et al., 2004), and the supply of DO (Triska et al., 1993). Hydrologic exchange delivers surface water containing oxygen and organic carbon to oxygen depleted hyporheic flowpaths (Triska et al., 1993; Grimm and Fisher, 1984; Findlay et al., 1993) enhancing microbial activity, which leads to nitrification (Triska et al., 1993) and the uptake of dissolved carbon (Findlay et al., 1993). Because nitrogen can exist in many redox states, concentrations of DO in the HZ play an especially important role in nitrogen transformations. The supply of DO is governed by respiration (Findlay, 1995) and hydrologic residence time (Duff and Triska, 2000).

Nitrification

Nitrogen transformations provide energy to the system. Two energy-producing processes are nitrification and denitrification. Nitrification is defined as the oxidation of ammonia into nitrate. In the HZ, rate of nitrification is controlled by an upward diffusion of NH_4^+ from deeper hyporheic water and a downward diffusion of oxygen from the land surface (Hinkle et al., 2001; Fischer et al., 2005). This mixing of surface and groundwater allows oxygen, which is readily available from the atmosphere, to mix with nitrogen that is upwelling from deeper hyporheic waters. Bacteria in the HZ nitrify available NH_4^+ to NO_2^-, which then further nitrifies to NO_3^-. Deeper water containing NH_4^+ may indicate NO_3^- that has been transported from the regional aquifer to the HZ and reduced under the prevailing redox conditions (Hinkle et al., 2001).

Denitrification

The most commonly observed nitrate reduction process in the HZ is denitrification (Hinkle et al., 2001). In the HZ denitrification is dependent upon organic carbon (Fischer et al., 2005), oxygen, and NO_3^- concentrations (Triska et al., 1993). The rate of denitrification in a nitrogen rich agricultural stream is limited by the supply of NO_3^- (Christensen and Sorensen, 1988) and the concentration of DOC in down welling surface water (Storey et al., 2004). The rate of denitrification is usually negatively correlated with concentration of oxygen (Storey et al., 2004). Streams have the ability to retain nitrogen through denitrification. The dissolved oxygen in stream water is rapidly consumed upon entry into the HZ. In this low-oxygen environment, NO_3^- is readily reduced to nitrogen gas (N_2) when there is sufficient dissolved organic carbon for microorganisms to oxidize. In streams that have not been significantly impacted by anthropogenic nitrogen inputs, the rates of nitrification and denitrification may be linked (Kemp and Dodds, 2002).

Proper functioning of the sediment-stream interface in NO_3^- removal also depends on the available supply of DOC to support denitrification (Ostrom et al., 2002). The land surface provides a ready supply of the organic carbon from organic rich soils, subsurface deposits (Ostrom et al, 2002), flood events or by advection of DOC in river or stream water that flows into the HZ (Hinkle et al., 2001).

The process of denitrification generally occurs in oxygen-depleted, organic carbon rich areas. The removal of nitrogen from streams through microbial denitrification limits nitrogen content (Ventullo and Rowe, 1982) and improves stream water quality (Swanke and Caskey, 1982).

Nitrate Retention in the Hyporheic Zone

Increased nitrate retention has been correlated with longer water residence times in extensive HZs (Hill et al., 1998). The retention of nitrate in nitrogen rich streams is influenced by the size of surface water storage zones. The size of these storage zones can increase residence time of channel water in contact with sites of rapid nitrate depletion rather than being influenced by the dimensions of the HZ (Hill et al., 1998). In low gradient streams hyporheic interaction has resulted in a reduction of nitrate (Buyck, 2005; Van der Hoven et al., 2008). More specifically, hyporheic interaction beneath meander lobes has been found to increase the size of the HZ (Peterson and Sickbert, 2006) and result in a net loss of nitrogen (Fromm, 2005).

Research has definitively shown that the dynamic HZ ecotone is commonly associated with high levels of nitrate uptake (Hinkle et al., 2001) and exhibits a natural capacity for nitrogen removal (Storey et. al. 2004, Hill et. al. 1998, Follett and Delgado, 2002). The removal of nitrate from groundwater entering a stream is an essential attribute of natural ecosystem function in sediment-stream interfaces (Ostrom et al., 2002). Previous studies have examined nitrogen removal through HZ processes in streams that flow through areas dominated by agriculture (Storey et. al. 2004, Hill et. al. 1998, Follett and Delgado, 2002). However, available research has not examined how the sinuosity of a stream affects the removal of nitrogen from the system. Maguffin and Peterson (2005) proposed that stream segments with higher sinuosities remove more nitrogen than segments with lower sinuosities. The increased removal is hypothesized to be a result of increased denitrification processes associated with increased hyporheic pathways beneath meanders (Van der Hoven et al., 2008; Peterson and Sickbert, 2006).

Hypothesis

This study focuses on assessing the role of stream sinuosity in the removal of nitrate from surface water with the hope of furthering existing knowledge of HZ processes in small streams. Specifically, the research examines the following: stream segments possessing higher sinuosity indices will experience greater nitrate reduction.

CHAPTER II

SITE DESCRIPTION

The study focuses on Little Kickapoo Creek (LKC) a low gradient, low order, perennial stream that occupies a glacial outwash valley. LKC's headwaters are in an urban area near the Bloomington-Normal airport; however, the stream begins flowing through agricultural areas after 1.52 km (Figure 1). Field data were collected along 13.1 km of LKC, which was broken into six segments (Figure 1). Stream segment varies in length from 0.9 km to 3.7 km (Table 1). The overall sinuosity value for the stretch of LKC in this study is 1.6 with sinuosity values for individual segments ranging from 1.3 to 2.4 (Table 1).

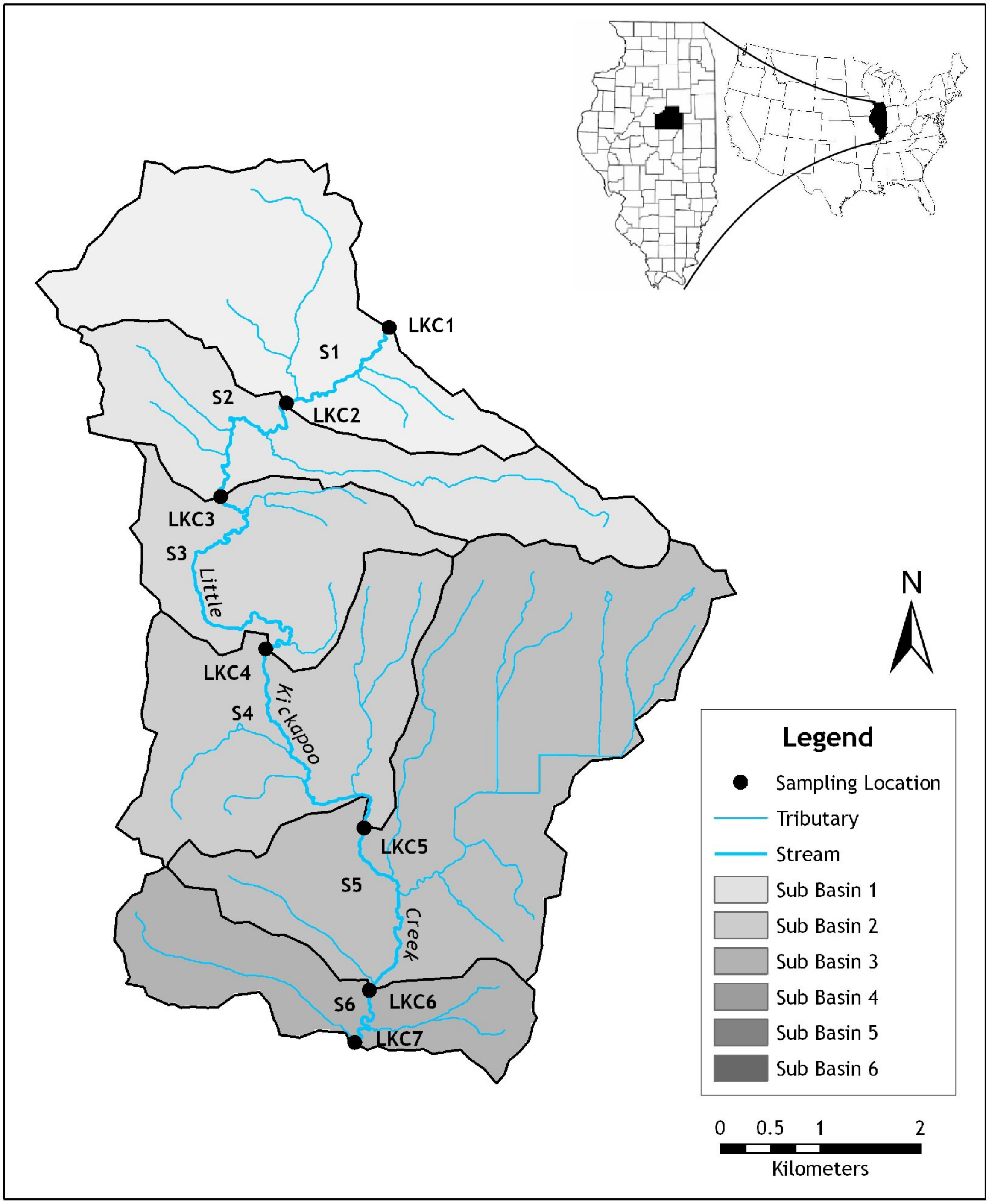

Figure 1. Site map showing segments, sampling locations and sub basins of Little Kickapoo Creek.

Tile drains and tributaries discharge into all five segments (Figure 2,3 and Table 1). Debris or beaver dams were found in five of the six segments, there were none found in S5 (Figure 4 and Table 1). The debris dams found in S1-S3 were large vertically and horizontally. Composition of the dams consisted of small woody debris along with trees 0.5 meter to greater than 1 meter in diameter that washed down during storm events. There was no observable head drop across the dams; however, there were large pools greater than 1 meter in depth on either side of the debris dams. Beaver dams were found in S4 and S6 composed solely of small woody material less than 0.5 meter in diameter and all had head drops from 0.5 meter to 1 meter. Deep pools were present behind each debris dam from the resulting dammed conditions.

Table 1. Physical characteristics of each study segment. GPS stream data was collected on 09/05/08, 09/22/08 and 09/23/08. Stream data used for S6 was not collected using the GPS.

		Segment					
		S1	S2	S3	S4	S5	S6
Stream (km)		1.62	2.02	3.73	2.88	2.13	0.95
Straight-Line (km)		1.29	1.12	1.58	2.02	1.65	0.56
Sinuosity Index		1.25	1.80	2.37	1.43	1.29	1.71
Tile Drains	Wet	0	1	1	6	5	1
	Dry	1	2	6	4	2	1
	Total	1	3	7	10	7	2
Tributaries	Wet	2	0	2	2	2	1
	Dry	3	2	1	0	0	0
	Total	5	2	3	2	2	1
Debris/Beaver Dams		3	13	9	3	0	1

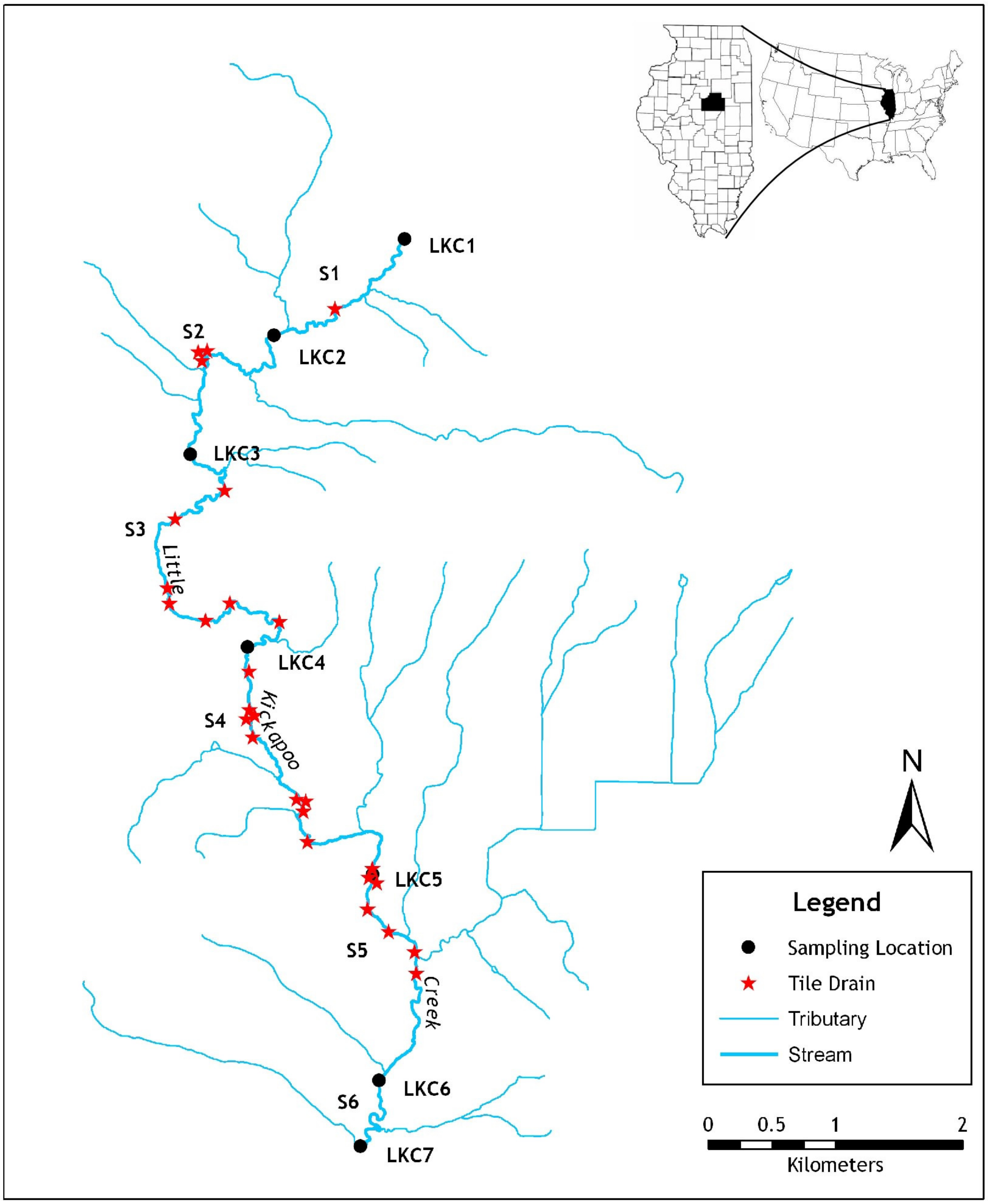

Figure 2. Site map showing distribution of tile drains mapped with GPS along Little Kickapoo Creek.

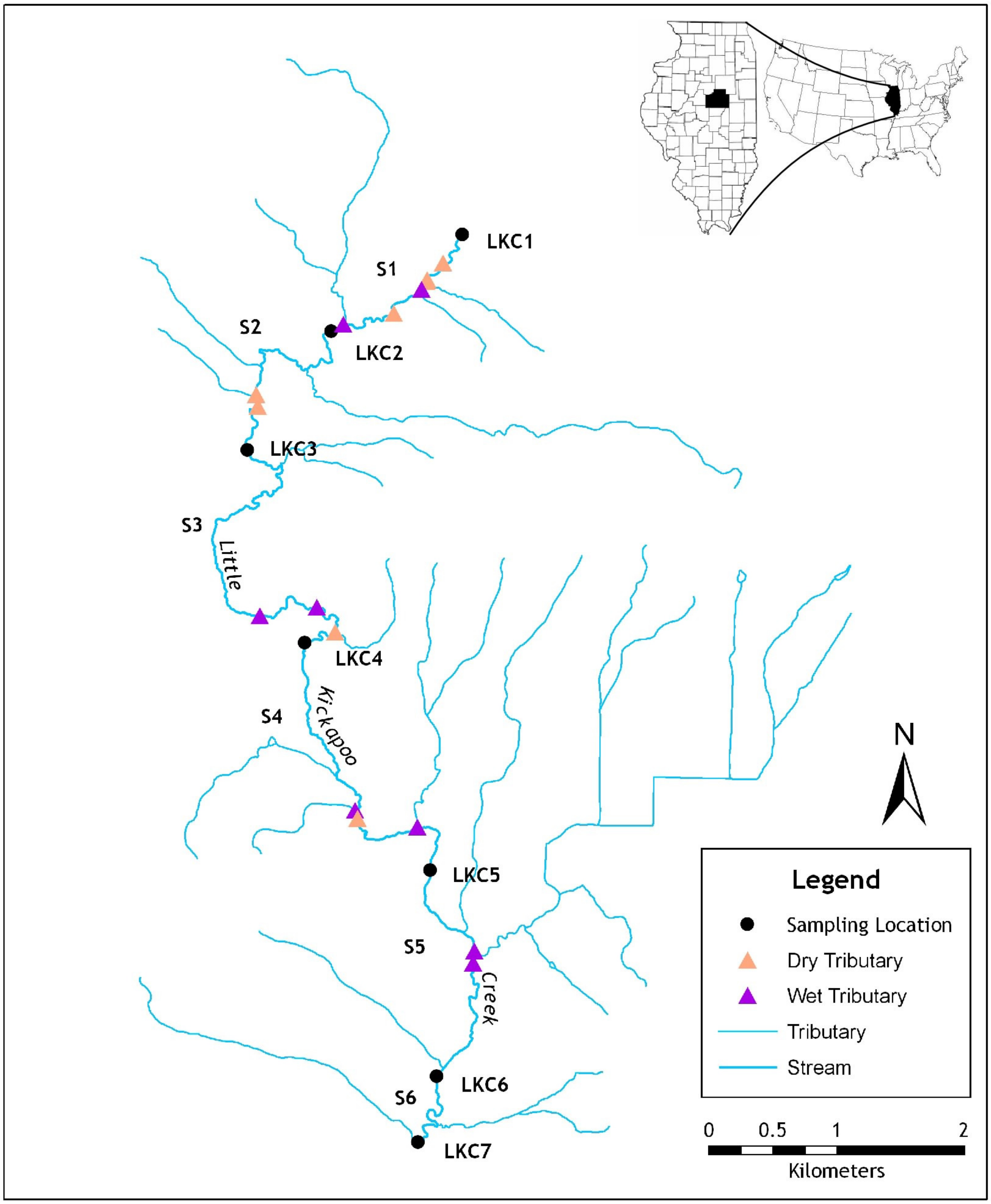

Figure 3. Site map showing distribution of tributaries mapped with GPS unit along Little Kickapoo Creek.

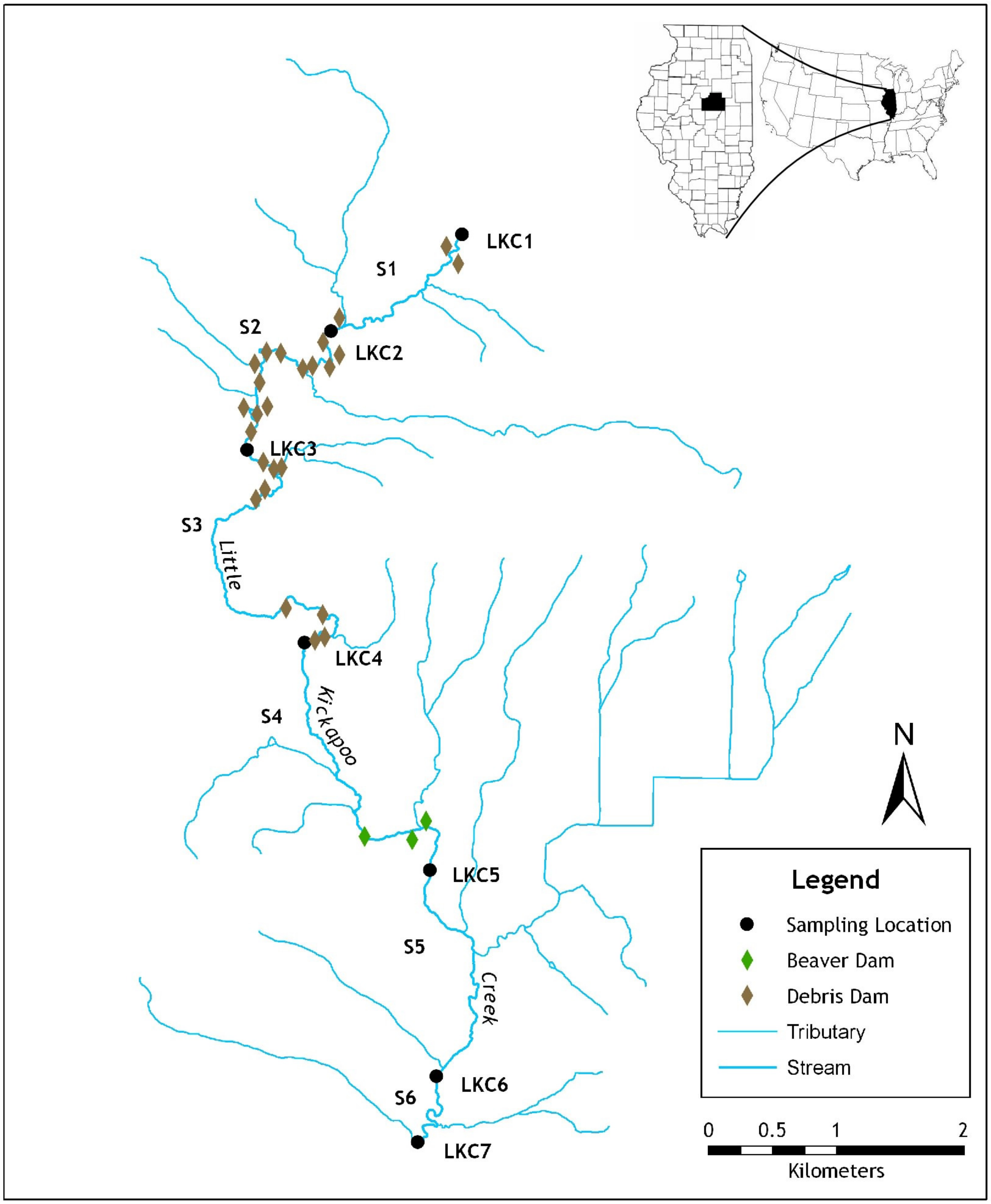

Figure 4. Site map showing distribution of debris and beaver dams mapped with GPS unit along Little Kickapoo Creek.

Under base flow conditions LKC is generally a gaining stream with a gradient of 0.002. LKC becomes a third order stream approximately 0.8 km upstream from where this study begins at LKC1.

As LKC meanders south, land use varies along the six segments. The land use consists mostly of either agricultural production or urban developments. In all six segments ≥ 50% of land use is in agricultural production, which varies between corn and soybeans. One land use of note in the urban development of segment 4 (S4) is the Crestwicke Country Club golf course.

Three major geologic formations are found in the outwash valley LKC occupies. They are, from oldest to youngest, the Wedron Formation (WF), the Henry Formation (HF) and the Cahokia Alluvium (CA).

Retreating glaciers deposited the WF at the end of the Wisconsinan Period in the late Pleistocene, which ended 10,000 to 12,000 years ago. Glacial deposits in the upper two thirds of the Lower Sangamon River Area where LKC is found are generally 30 meters thick or more (Piskin and Bergstrom, 1975). The WF, composed of clay-rich lodgement till, end moraines, and debris flow deposits, overlies the Pennsylvanian age bedrock of the area and underlies the hills along the valley. Reducing conditions in the WF have given the formation a grey color. Debris flow deposits may extend out into the valley and can be either interbedded with or overlie the outwash. In the valley center, glacial melt water eroded the till of the WF. The cohesive, fine-grained, clay-rich, low permeability till of the WF acts as a lower confining unit for the coarse-grained sand and gravel aquifer that rests above.

When glacial ice retreated and stood still to form the Bloomington Moraine, glacial outwash eroded the valley that LKC now meanders through. Outwash sediments consisting of coarse-grained sand, gravel, and cobbles partially backfilled the valley, these poorly sorted sediments make up the HF that overlies the WF. This buried glacial outwash valley is the local aquifer.

LKC has occupied the outwash valley since the end of the Pleistocene. During the Holocene the valley floor has aggraded through deposition of alluvial floodplain sediments to form the CA. The cohesive clays and silts that are predominant in the CA are intermixed with some thin sand lenses. Within the CA, varying degrees of soil development are observed which have been influenced by episodes of erosion and deposition. Macroporosity within the CA is the result of plant roots and burrowing insects or small mammals. LKC is inset into Holocene alluvium and flows on top of the HF.

CHAPTER II

METHODOLOGY

Thirty-two separate sampling events took place at seven locations (LKC1-7) along LKC (Figure 1). During each sampling event field water quality parameters were measured and water samples were collected. Temperature, specific conductance, and dissolved oxygen in mg/L and percent were collected in the field using a YSI 85 Dissolved Oxygen & Conductivity Meter (Appendix A). Water samples were taken at each location with one duplicate collected during each sampling event. Each 60 mL plastic Nalgene sample bottle was triple rinsed with stream water prior to collection of each water sample. Water samples being examined for anions were refrigerated and analyzed within 48 hours of collection. Analysis for major anions (NO_3^-, Cl^-, and SO_4^{2-}) was performed in the Illinois State University (ISU) Department of Geography-Geology with a Dionex DX 120 ion chromatograph. Quality assurance (QA) and quality control (QC) were maintained during analysis of each sampling event by running blank, duplicate and replicate samples. In addition, after approximately every ten samples a known solution was run as an unknown.

To gain a better understanding of complexities between each sampling location, the 13.3 km of LKC involved in the study was walked, in the stream bed, using a handheld Trimble GeoXH Global Positioning System (GPS). The locations of tile drains, debris dams and tributaries were recorded using the GPS. Distance and sinuosity values were calculated using GPS data and supplemented with data from the 1:24:000 USGS Bloomington East Quadrangle.

This study focuses on nitrate as the dominant nitrogen species in LKC. Basu (2007) and Van der Hoven et al. (2008) analyzed LKC for NH_4^+, DON, NO_2^- and NO_3^-, concluding that the dominant N species is nitrate. Van der Hoven et al. (2008) found ammonium concentrations in LKC ranging from non-detectable to 0.16 mg/L and non-detectable or very low concentrations of nitrite. Ammonia at base flow in LKC ranges from 0.10 mg/L to non-detectable. A limited number of samples were analyzed for DON; the highest concentration was 0.56 mg/L. Unpublished data from three different sampling events in LKC show non-detectable levels of DON. In support of the conclusion that NO_3^- is the dominant N species, Van der Hoven et al. (2008) found nitrate levels in LKC that exceed 5 mg/L for extended periods of time.

Although NO_3^- is the dominant N species, two rounds of samples, during the fall of 2008, were analyzed for the presence of DON and ammonia. DON sample containers preserved with sulfuric acid (H_2SO_4) were provided by Microbac Laboratories. Approximately one liter of stream water was filtered with 0.45 micron filter paper into the provided DON sample containers. Analysis of the DON samples was performed at Microbac Laboratories, Inc. (Merrillville, Indiana). Ammonia samples were filtered in the ISU Department of Geography-Geology laboratory, with gloved hands, using 0.45 micron filter paper into 60 mL plastic Nalgene bottles, and immediately frozen. Ammonia analysis was performed by the ISU Department of Biology.

The primary focus of this study is on NO_3^-; however, Cl^- and SO_4^{2-} concentrations were also measured. Chloride is a non-conservative tracer and will be used in flux calculations to determine if dilution is occurring from upstream to downstream. Concentrations of sulfate in surface waters will be used as a proxy to nitrate in determining whether hyporheic processes are responsible for nitrate reduction or if nitrate is being lost to denitrification.

Stream gauging was performed ten times at each sampling location. An electromagnetic flowmeter was employed using the velocity-area method (Mosely and McKerchar, 1993), where velocity in a vertical section (v_i) was measured at the 0.6 depth with an electromagnetic velocity meter. Calculated discharge was used in conjunction with concentration data to generate mass flux calculations for NO_3^-, Cl^-, and SO_4^{2-} (Appendix B). Twenty-four depth-to-water (DTW) measurements were made from an established point at each location. By using events when both DTW and calculated discharge data were available a stage-discharge rating curve was created. From the created stage-discharge rating curve, discharge was interpolated for days when stream gauging was not performed.

Both sampling and stream gauging were performed during base flow conditions with no less than one day between sampling events in an effort to eliminate additional complexities such as surface or vadose zone flushing and variable hyporheic interaction.

Using a one-way analysis of variance (ANOVA) ($\alpha = 0.05$), a statistical analysis was performed to determine if concentrations among locations and mass fluxes between locations were different. If the ANOVA results indicated a statistical difference ($p < 0.05$), then individual paired t-tests ($\alpha = 0.05$) between each location were conducted. Statistics were compiled using SPSS version 16.0 (SPSS Inc., 2007).

To help delineate land use in the area and also determine possible sources and explanations for nitrate input outside of the area immediately surrounding LKC a Geographic Information System (GIS) was constructed using ESRI ArcGIS version 9.2. Land cover/land use data for the GIS came from the two best data sets available to the public: the USGS 2001 National Land Cover Database (NLCD 2001) and the 1999-2000 Illinois Gap Analysis Project (ILGAP 1999-2000) which both have 30-meter spatial resolution. Landsat satellite imagery was used in the construction of both the NLCD 2001 and ILGAP 1999-2000 datasets. Satellite imagery was acquired between April 30, 1999 and October 10, 2000 for ILGAP 1999-2000 and between April 30, 1999 and August 24, 2003 for the NLCD 2001. Overall accuracy for ILGAP 1999-2000 was assessed at an intermediate level and found to be generally greater than 80% accurate. The overall accuracy for NLCD 2001 is 78.2%.

Location information for LKC came primarily from the GPS data. Supplemental location information for LKC and tributary location was digitized from the United States Geological Survey (USGS) 1981 Bloomington East, IL

Quadrangle downloaded from the USGS seamless website. Sub basins were created for each segment using the National Elevation Dataset (NED) digital elevation model (DEM) available for the study area (Figure 1). Land cover/land use percentages were then calculated for each of the sub basins.

CHAPTER IV

RESULTS AND DISCUSSION

Results

Chemistry

Chloride

Chloride concentrations between sampling locations are statistically different (F(6, 203) = 10.881; p = < 0.001). There is a statistically significant net decrease of 81.62 mg/L in average chloride concentration from LKC1 to LKC7 (t(58) = 5.261; p = < 0.001) (Table 2). Box and whisker plots along with average concentration confirm the decreasing trend in chloride concentration from upstream to downstream (Figure 5 and Table 7).

Although average chloride concentrations from LKC1 to LKC2 decreases 4.32 mg/L and 27.9 mg/L from LKC1 to LKC3, statistically from LKC1 to LKC2 and LKC1 to LKC3 chloride concentrations are similar (Table 2).

Chloride concentration is statistically different when LKC1 is compared to LKC4 (t(58) = 2.717; p = 0.009) through LKC7 (t(58) = 5.261; p = < 0.001) (Table 2). Average concentration decreases 44.26 mg/L from LKC1 to LKC4 and 63.26 mg/L from LKC1 to LKC5 (Table 7). From LKC1 to LKC6 average concentration decreases 76.21 mg/L and 81.62 mg/L from LKC1 to LKC7 (Table 7).

When sampling locations are compared side by side in the downstream direction, chloride concentrations are statistically equivalent (Table 2).

Table 2. Calculated p-values from paired t-test for chloride concentration by sampling location.

	LKC2	LKC3	LKC4	LKC5	LKC6	LKC7
LKC1	0.835	0.110	0.009	<0.001	< 0.001	< 0.001
LKC2		0.152	0.012	< 0.001	< 0.001	< 0.001
LKC3			0.229	0.008	< 0.001	< 0.001
LKC4				0.114	0.007	0.003
LKC5					0.250	0.161
LKC6						0.823

Although there is an overall net increase of 3157.10 mg/s in mean mass flux from LKC1 to LKC7 (Table 7), statistically the mass fluxes between sampling locations are similar (F(6,132) = 0.740; p = 0.618). Box and whisker plots support the statistical results (Figure 5). Mean fluxes increase 2683.30 mg/s from LKC1 to LKC2 and 3742.34 mg/s from LKC1 to LKC3 (Table 7). There is an increase of 84.99 mg/s in mean flux from LKC1 to LKC4 (Table 7). From LKC1 to LKC5 mean flux increases 6783.00 mg/s and 3017.03 mg/s from LKC1 to LKC6 (Table 7).

The variation in mean mass fluxes between segments, from a loss of -5066.52 mg/s to a gain of 9243.84 mg/s (Table 8) is statistically different (F(5,101) = 6.763; p = < 0.001). Box and whisker plots support the results (Figure 5). The overall decrease of 3041.69 mg/S in chloride mass flux from S1 to S6 is statistically different (t(36) = 2.217; p = 0.033) (Table 3). Chloride mass fluxes are increasing at S1 (2830.97 mg/s), S2 (911.37 mg/s) and S4

(9243.84 mg/s), while chloride mass fluxes are decreasing at S3 (-5066.52 mg/s), S5 (-3186.02 mg/s) and S6 (-165.40 mg/s) (Table 8).

Table 3. Calculated p-values from paired t-test for chloride flux differences by segment.

	S2	S3	S4	S5	S6
S1	0.215	0.002	0.084	0.021	0.033
S2		0.015	0.028	0.112	0.382
S3			0.001	0.463	0.043
S4				0.005	0.013
S5					0.266

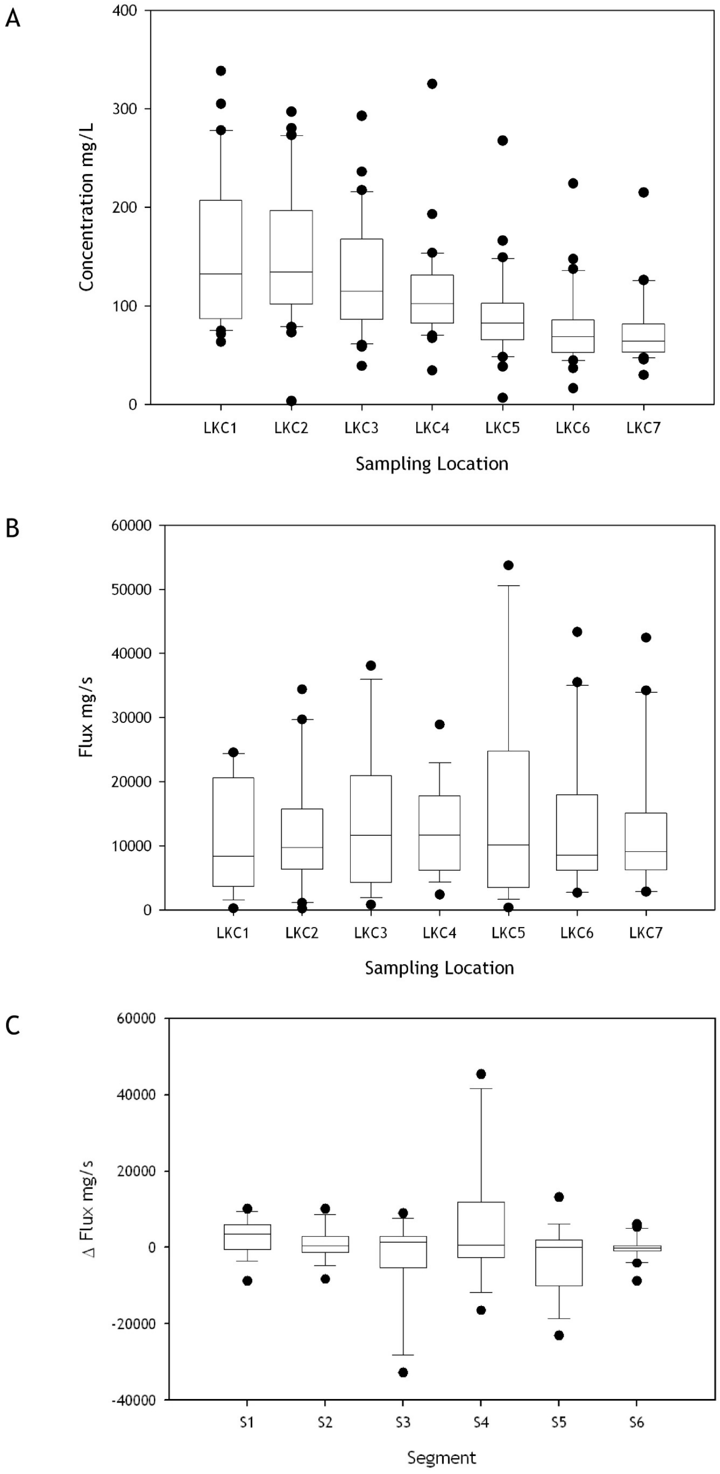

Figure 5. Box and whisker plot of chloride concentration by sampling location (A), chloride flux by sampling location (B) and change in chloride flux by segment (C). The ends of the boxes represent the 25th and 75th percentiles with the line at the median; the error bars depict the 10th and 90th percentiles.

Nitrate

Statistically, mean nitrate concentrations (F(6,203) = 1.424; p = 0.207) and mean mass fluxes (F(6,132) = 1.193; p = 0.314) among sampling locations are the same. Box and whisker plots corroborate the statistical data (Figure 6). While it is not statistically significant, mean nitrate concentrations show a subtle decreasing trend similar to chloride, from 3.39 mg/L at LKC1 to 2.91 mg/L at LKC5 (Table 7). Nitrate concentration increases at LKC6 to 4.02 mg/L and makes a slight decrease to 4.01 mg/L at LKC7 (Table 7).

The mean mass flux of nitrate from LKC1 through LKC7 exhibits a similar trend to chloride mean mass flux. From LKC1 to LKC2 mean mass flux of nitrate increases 84.38 mg/s and 298.38 mg/s LKC1 to LKC3 (Table 7). Mean mass flux of nitrate increases 38.69 mg/s from LKC1 to LKC4, and 526.24 mg/s from LKC1 to LKC5 (Table 7). Nitrate mean mass flux continues to increase by 609.42 mg/s from LKC1 to LKC6 and 674.75 mg/s from LKC1 to LKC7 (Table 7).

Nitrate fluxes between segments are statistically dissimilar (F(5,101) = 4.777; p = 0.001), varying from a loss of -352.48 mg/L to a gain of 618.25 mg/L (Table 8). Box and whisker plots support the statistical results (Figure 6). Although nitrate mass flux decreases 119.86 mg/s from S1 to S6 statistically the decrease is not significant (t(36) = 1.417; p = 0.171) (Table 4). The same trend seen in chloride mass fluxes between segments is seen in nitrate with S5 deviating from chloride’s trend. An increase in mean mass flux of nitrate is seen at S1 (109.11 mg/s), S2 (189.27 mg/s), S4 (618.25 mg/s) and S5 (168.94

mg/s) (Table 8). There is a decrease in nitrate mean mass flux at S3 (-352.48 mg/s) and S6 (-10.75 mg/s) (Table 8).

Table 4. Calculated p-values from paired t-test for nitrate flux differences by segment.

	S2	S3	S4	S5	S6
S1	0.313	0.003	0.086	0.542	0.171
S2		0.001	0.152	0.952	0.076
S3			0.004	0.007	0.061
S4				0.168	0.038
S5					0.185

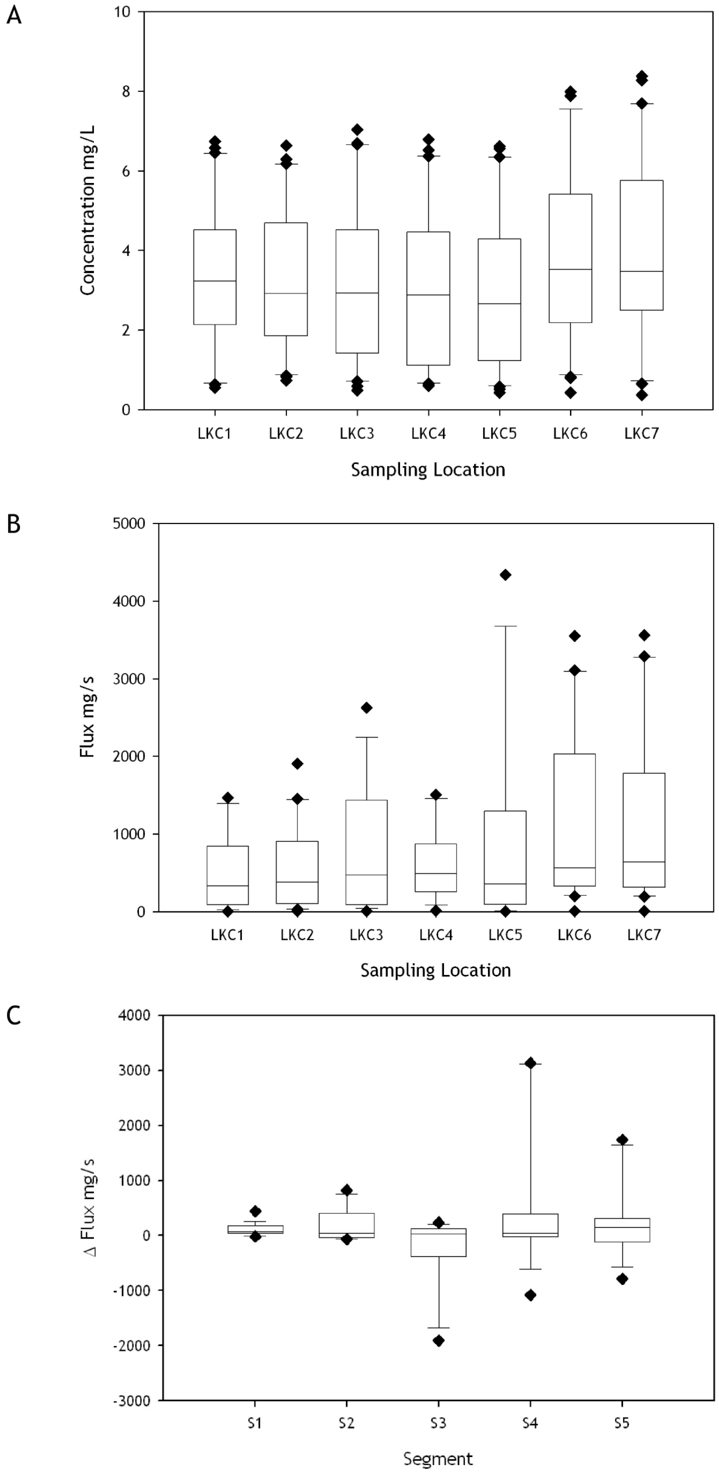

Figure 6. Box and whisker plot of nitrate concentration by sampling location (A), nitrate flux by sampling location (B) and change in nitrate flux by segment (C). The ends of the boxes represent the 25th and 75th percentiles with the line at the median; the error bars depict the 10th and 90th percentiles.

Sulfate

Mean sulfate concentration among the sampling locations is statistically different (F(6,203) = 2.676; p = 0.016). Box and whisker plots support the statistical results (Figure 7). Sulfate concentration decreases by 3.24 mg/L from LKC1 to LKC7, however, the change is not statistically different (t(58) =1.693; p = 0.097) (Table 5). There is an increase of 3.31 mg/L in mean sulfate concentration from LKC1 to LKC2 (Table 7). From LKC1 to LKC3 mean sulfate concentration decreases 1.10 mg/L before increasing 1.94 mg/L from LKC1 to LKC4 (Table 7). There is a subtle decrease from LKC1 to LKC5 of 0.38 mg/L and decreases of 2.32 mg/L from LKC1 to LKC6 and 3.24 mg/L from LKC1 to LKC7 (Table 7).

Although the mean mass fluxes vary among the sampling locations, ranging from 2778.10 to 6270.80 mg/s (Table 7), statistically, the mass fluxes are similar (F(6,132) = 2.113; p = 0.054). Box and whisker plots reinforce the statistical results (Figure 7). The mass fluxes show similar trends to the chloride and nitrate, increasing from LKC1 to LKC2 by 900.99 mg/s and 1591.73 mg/s from LKC1 to LKC3 (Table 7). Mean mass fluxes continue to increase through LKC7, 889.68 mg/s from LKC1 to LKC4, 3492.70 mg/s from LKC1 to LKC5, 3082.68 mg/s from LKC1 to LKC6 and finally 2947.99 from LKC1 to LKC7 (Table 7).

Table 5. Calculated p-values from paired t-test for sulfate concentration by sampling location.

	LKC2	LKC3	LKC4	LKC5	LKC6	LKC7
LKC1	0.153	0.608	0.348	0.856	0.252	0.097
LKC2		0.051	0.522	0.092	0.009	0.002
LKC3			0.128	0.719	0.529	0.246
LKC4				0.228	0.023	0.004
LKC5					0.300	0.109
LKC6						0.581

Sulfate fluxes between segments are statistically dissimilar varying from a loss of -1150.16 mg/s to a gain of 3492.32 mg/s (F(5,101) = 5.504; p = <0.001) (Table 8). The overall decrease of 1274.85 mg/s in sulfate flux from S1 to S6 is statistically different (t(36) = 2.554; p = 0.017) (Table 6). The same trend seen in chloride fluxes between segments is seen in sulfate fluxes. An increase in sulfate mass fluxes is seen at S1 (1094.47 mg/s), S2 (497.26 mg/s) and S4 (3492.32 mg/s) (Table 8). There is a decrease in sulfate fluxes at S3 (-1150.16 mg/s), S5 (-255.48 mg/s) and S6 (-229.86 mg/s) (Table 8).

Table 6. Calculated p-values from paired t-test for sulfate flux differences by segment.

	S2	S3	S4	S5	S6
S1	0.122	0.003	0.069	0.111	0.017
S2		0.030	0.028	0.380	0.229
S3			0.003	0.386	0.226
S4				0.011	0.010
S5					0.930

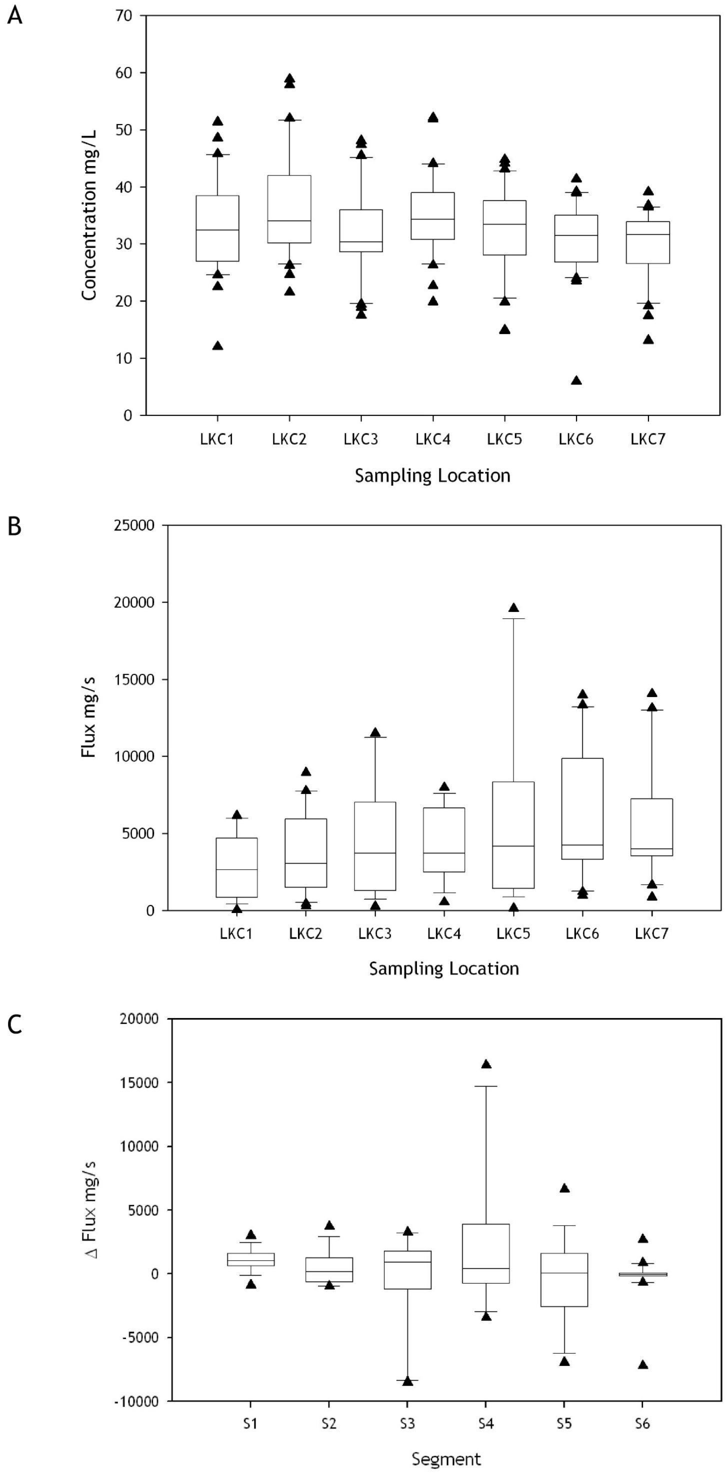

Figure 7. Box and whisker plot of sulfate concentration by sampling location (A), sulfate flux by sampling location (B) and change in sulfate flux by segment (C). The ends of the boxes represent the 25th and 75th percentiles with the line at the median; the error bars depict the 10th and 90th percentiles.

Table 7. Average values for concentration and flux by sampling location for chloride, nitrate and sulfate.

	Chloride		Nitrate		Sulfate	
Sampling Location	Conc. (mg/L)	Flux (mg/s)	Conc. (mg/L)	Flux (mg/s)	Conc. (mg/L)	Flux (mg/s)
LKC1	156.47	10567.33	3.39	492.92	33.08	2778.10
LKC2	152.43	13250.63	3.28	577.30	36.39	3679.09
LKC3	127.75	14309.67	3.24	791.30	31.98	4369.83
LKC4	110.43	10652.32	2.97	531.61	35.02	3667.78
LKC5	90.01	17350.33	2.91	1019.16	32.70	6270.80
LKC6	76.89	13584.36	4.02	1102.34	30.76	5860.78
LKC7	74.67	13724.43	4.01	1167.67	29.84	5726.09

Table 8. Change in mean mass fluxes of chloride, nitrate and sulfate at each segment.

	Chloride	Nitrate	Sulfate
Segment	Δ Mass Flux (mg/s)	Δ Mass Flux (mg/s)	Δ Mass Flux (mg/s)
S1	2830.97	109.11	1094.47
S2	911.37	189.27	497.26
S3	-5066.52	-352.48	-1150.16
S4	9243.84	618.25	3492.32
S5	-3186.02	168.94	-255.48
S6	-165.40	-10.75	-229.86

Ammonia and Dissolved Organic Nitrogen

The two rounds of sampling on 10/02/08 and 10/19/08 found ammonia concentrations ranging from 0.026 mg/L to 0.114 mg/L. DON samples collected on 10/02/08 at locations LKC1 through LKC6 are all higher than samples collected on 10/19/08. LKC7 remained the same on both occasions. The range of DON is from 0.71 mg/L to 8.80 mg/L.

Table 9. Ammonia and dissolved organic nitrogen concentrations on two dates, 10/02/08 and 10/19/08.

Sampling Location	Date	NH_4^+-N	DON
LKC1	10/02/08	0.114	5.6
LKC2	10/02/08	0.040	2.3
LKC3	10/02/08	0.040	8.8
LKC4	10/02/08	0.044	1.9
LKC5	10/02/08	0.066	1.5
LKC6	10/02/08	0.040	1.8
LKC7	10/02/08	0.038	1.1
LKC1	10/19/08	0.045	1.1
LKC2	10/19/08	0.026	0.8
LKC3	10/19/08	0.046	0.71
LKC4	10/19/08	0.048	0.72
LKC5	10/19/08	0.085	1.2
LKC6	10/19/08	0.027	1.7
LKC7	10/19/08	0.038	1.1

Discharge

Where both discharge and depth-to-water data were available, stage rating curves were created (Figure 8). Using the stage rating curves, discharge was calculated for sampling events when stream gauging was not performed. Both measured and calculated discharges were used in mass flux calculations. Because the stream distance from LKC6 to LKC7 is short, discharge data from LKC6 was used in calculating mass fluxes for LKC7. In total, each location had 20 discharge measurements that were used in mass flux calculations (Appendix B).

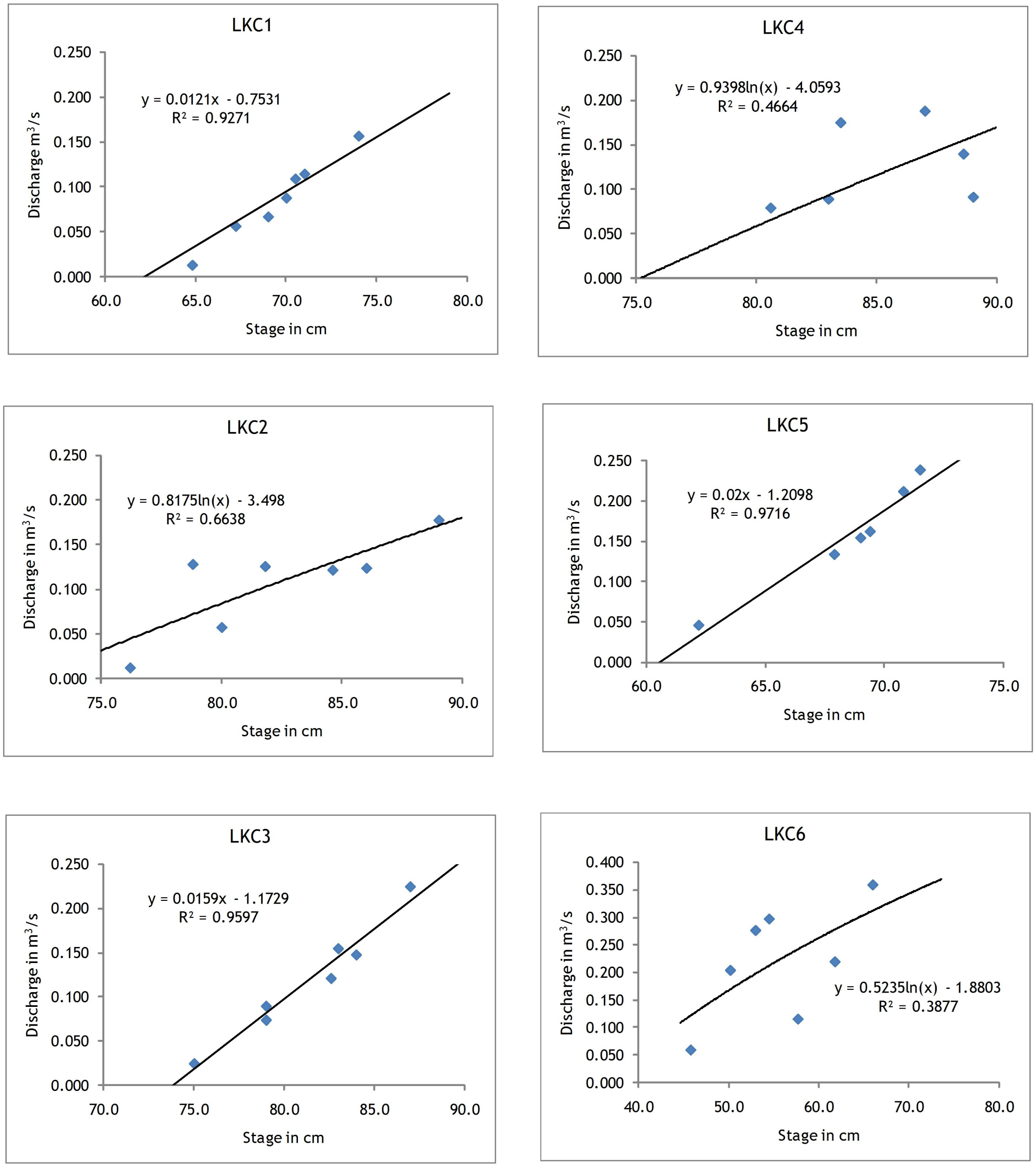

Figure 8. Stage rating curves calculated from stream gauging and depth-to-water measurements for LKC1 to LKC6.

Land Cover/Land Use

To compare between ILGAP 1999-2000 and NLCD 2001, land cover/land use classes in the sub basins of LKC were divided into five general categories: agriculture, urban, forest, wetland, and surface water (Table 10). Comparison between the ILGAP 1999-2000 and NLCD 2001 found two major differences in land cover representations.

First, the representation of urban development differs between the two datasets most notably at locations A, B, and C on Figures 9 and 10. The NLCD 2001 at location A (Figure 9) shows more urban development compared to ILGAP 1999-2000 location A (Figure 10). At locations B and C the NLCD 2001 (Figure 9) shows large areas of urban development, the Windgate and Crestwicke North subdivisions respectively. The ILGAP 1999-2000 data at locations B and C (Figure 10) does not show either subdivision, both of which were present prior to 1999.

Second, the NLCD 2001 does not classify wetlands outside of Alaska and coastal areas. What the ILGAP 1999-2000 classifies as wetlands the NLCD 2001 classifies as forested land (Figures 9 and 10).

Because the ILGAP 1999-2000 under represents two urban areas, the NLCD 2001 will be used for calculating all land cover/land use data in this study. The resulting classes are as follows: agriculture, forest and urban. Surface water accounts for less than 1% of the total land cover/land use in any sub basin and was eliminated from the final results. Because the NLCD 2001 does not classify wetlands, the classification will not be used here.

Table 10. Table explaining the classification of NLCD 2001 land cover/land use codes used to calculate land cover percentages for the six sub basins in the Little Kickapoo Creek study area.

NLCD Land Cover Code	NLCD Category	NLCD Description	Category used in this study
11	Water	Open Water	Surface Water
21	Developed	Open Space	Urban
22	Developed	Low Intensity	Urban
23	Developed	Medium Intensity	Urban
24	Developed	High Intensity	Urban
41	Forested Upland	Deciduous Forest	Forest
71	Herbaceous Upland	Grasslands/Herbaceous	Agriculture
81	Planted/Cultivated	Pasture/Hay	Agriculture
82	Planted/Cultivated	Cultivated Crops	Agriculture

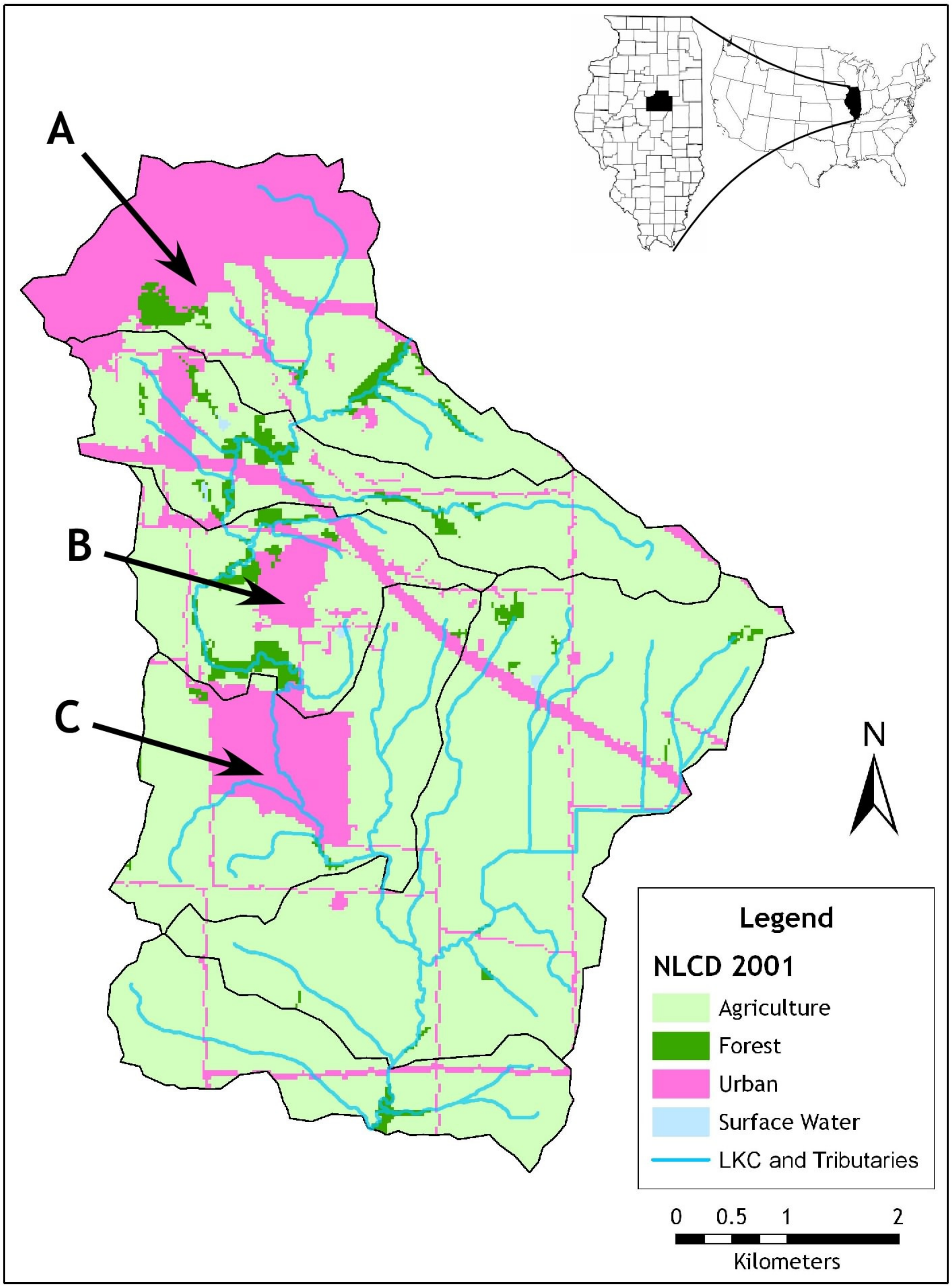

Figure 9. NLCD 2001 land cover/land use broken into four categories: agriculture, forest, urban and surface water. Area A represents the southern edge of Bloomington, IL. Area B is the Windgate subdivision, and Area C is the Crestwicke North subdivision and Crestwicke Country Club golf course.

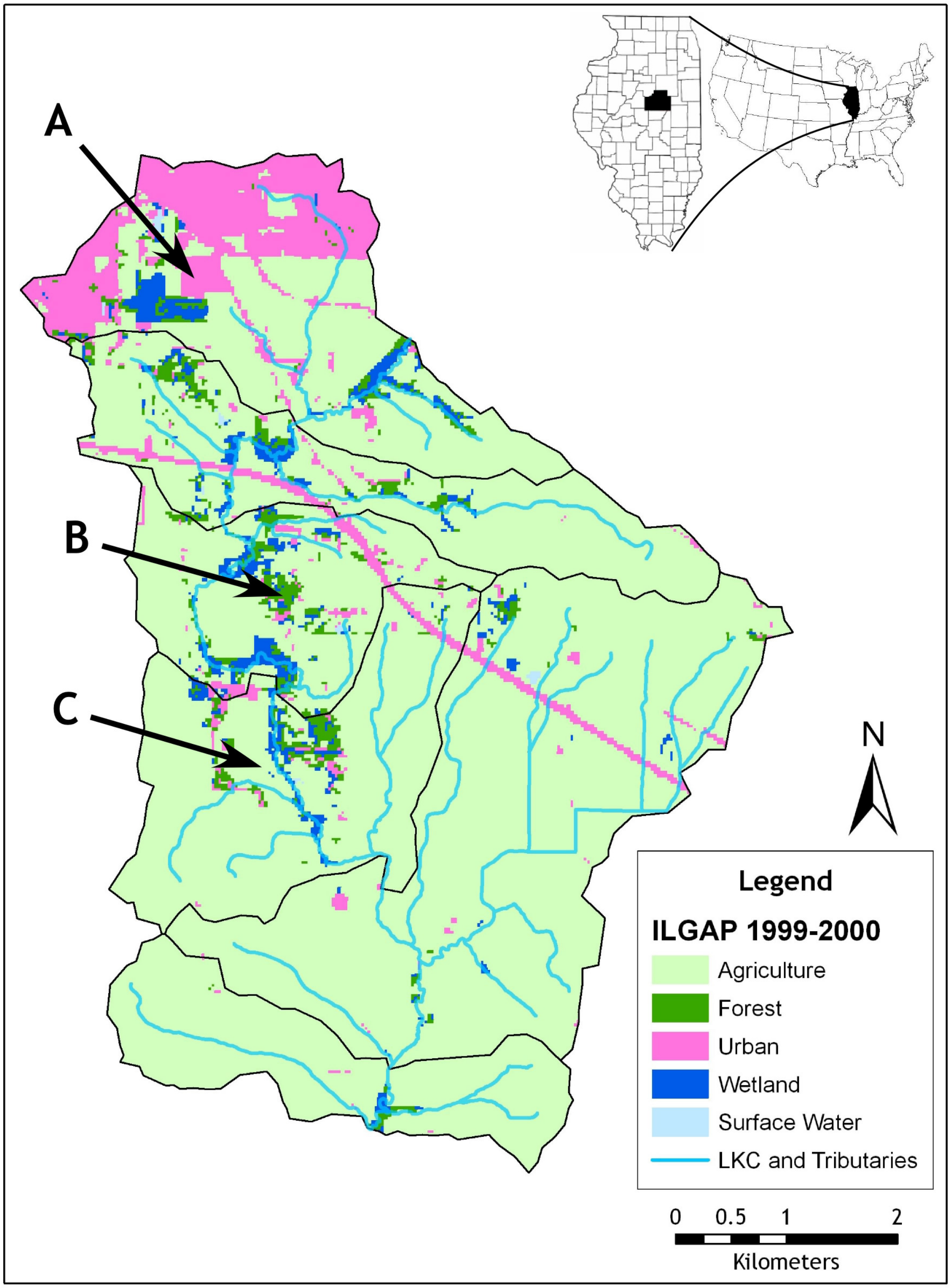

Figure 10. ILGAP 1999-2000 land cover/land use broken into five categories: agriculture, forest, urban, wetland and surface water. Area A represents the southern edge of Bloomington, IL. Area B is the Windgate subdivision, and Area C is the Crestwicke North subdivision and Crestwicke Country Club golf course.

S1 is split almost equally between agricultural and urban land cover/land use, 50% and 49% respectively. Forested land in S1 accounts for 1% of total land cover/land use (Table 11). Agricultural land cover/land use increases by 23% in S2 and urban development decreases by 29%. Forested land cover/land use in S2 increases by 6% (Table 11). In S3 agricultural land cover/land use decreases by 6% while urban land cover/land use increases by 4% and forested land increases by 2% (Table 11). Agricultural and urban land cover/land use both increase in S4 by 4%. In S4 forested land cover/land use decreases by 8% (Table 11). Both S5 and S6 have greater than 90% agricultural land cover/land use. S5 has 92% agricultural land cover/land use, 6% urban and 1% forested land (Table 11). S6 is similar to S5 with 91% agricultural, 7% urban and 2% forested land cover/land use (Table 11).

Table 11. NLCD 2001 land use percentages and areas by sub basin.

Sub Basin	Total	Agriculture		Forest		Urban	
	Area (km^2)	%	Area (km^2)	%	Area (km^2)	%	Area (km^2)
1	6.5	50%	2.9	1%	0.3	49%	3.3
2	4.9	73%	3.6	7%	0.3	20%	1.0
3	3.8	67%	2.6	9%	0.3	24%	0.9
4	5.7	71%	4.1	1%	0.1	28%	1.6
5	11.2	92%	10.3	1%	0.1	6%	0.7
6	3.5	91%	3.2	2%	0.1	7%	0.2

Sinuosity

The average ratio of chloride to nitrate (Cl^-/NO_3^-) concentration at each sampling location (Figure 11) appears to decrease as the sinuosity index increases. However, error bars representing one standard deviation show that the trend may not be real.

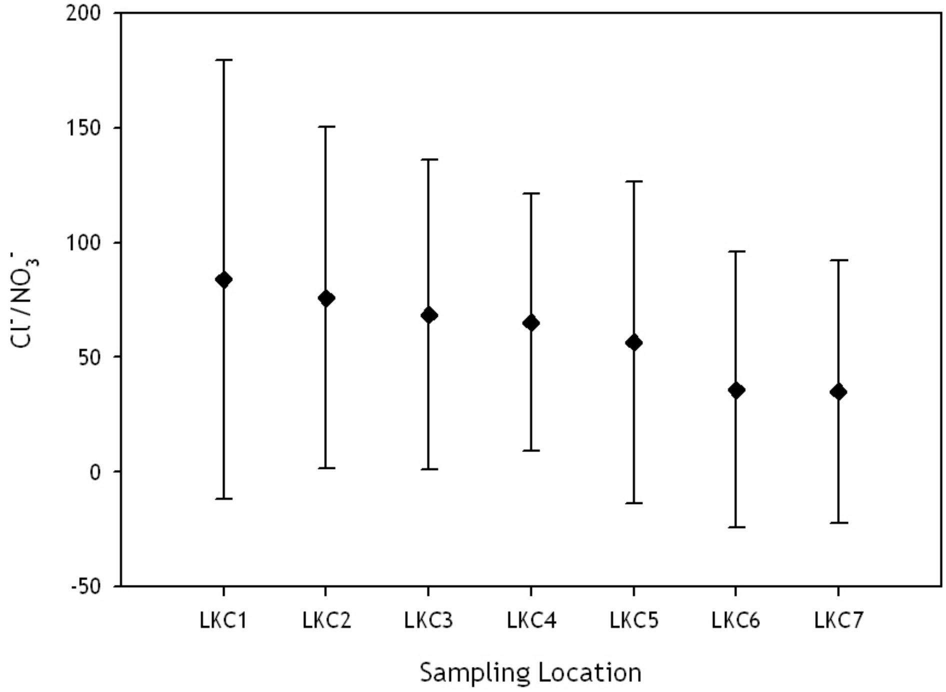

Figure 11. Plot of mean Cl^-/NO_3^- ratio at each sampling location. Error bars represent one standard deviation.

The average change in flux of chloride, nitrate and sulfate plotted against the sinuosity index does not show an overall trend (Figure 12). Average change in chloride flux decreases as sinuosity increases from 1.25 to 1.29, increases as sinuosity increases to 1.43, decreases as sinuosity increases to 1.71, increases when sinuosity increases to 1.80 then decreases when sinuosity reaches 2.37. Average change in nitrate flux increases as sinuosity increases from 1.25 to 1.43 then decreases as sinuosity increases to 1.71, then increases as sinuosity increases to 1.80 before a final decrease as sinuosity reaches 2.37. Sulfate flux shows the same trend as chloride flux. As sinuosity increases from 1.25 to 1.29, sulfate flux decreases. When sinuosity increases to 1.43 the flux of sulfate increases then decreases when sinuosity increases to 1.71 before a slight increase when sinuosity increases to 1.80 and a final decrease when sinuosity reaches 2.37.

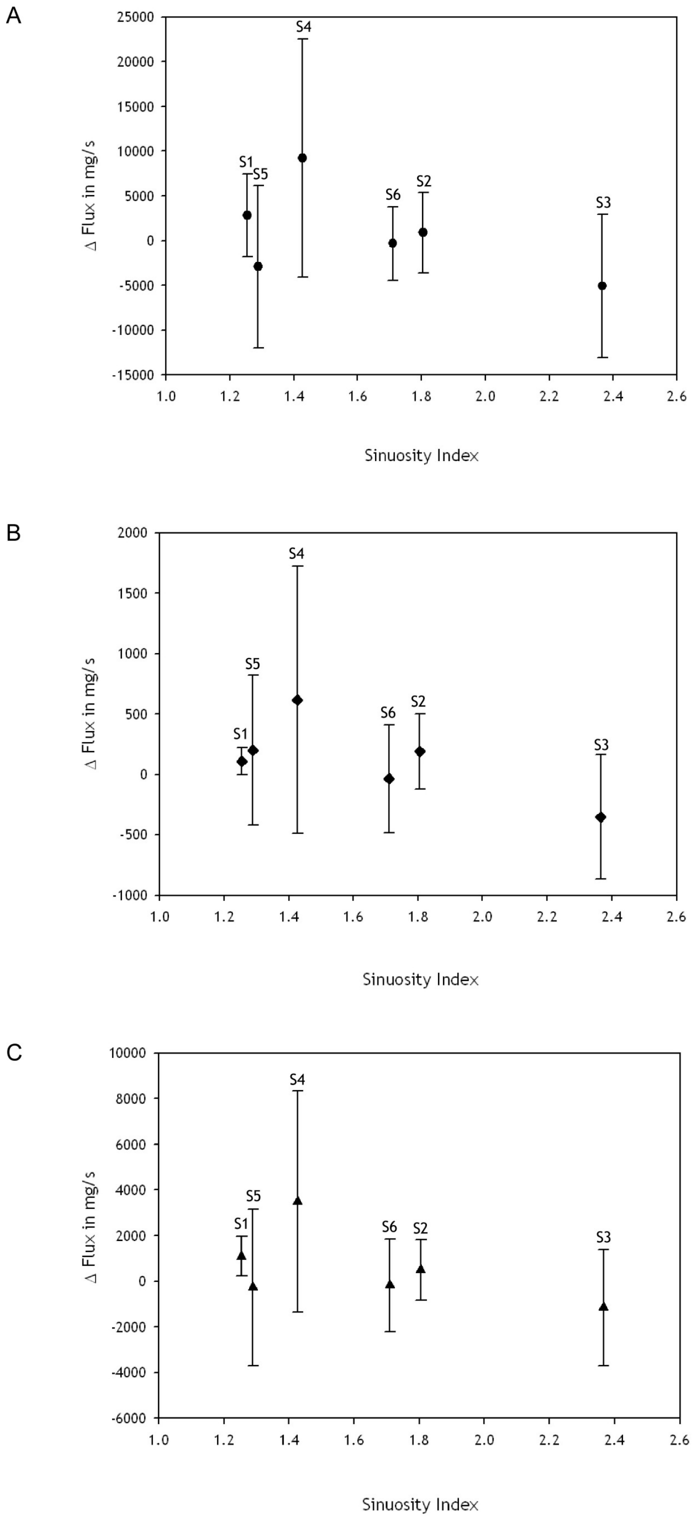

Figure 12. Sinuosity index plotted versus mean change in flux at each segment for (A) chloride, (B) nitrate, and (C) sulfate. Errors bars represent one standard deviation.

Discussion

Chloride unlike nitrate is conservative and will not react with the surrounding sediments. The data show that chloride concentration decreases along the profile of LKC; however, the mass flux of chloride remains statistically the same. With no chloride leaving the system and a decrease in concentration, dilution of chloride by low-chloride water entering LKC explains the observed decrease in chloride concentrations. The presence of dilution validates that LKC is a gaining stream. Dilution affects concentration values but does not affect flux values; therefore, future discussion will focus solely on mass flux values for all constituents.

Generally, there is a decreasing trend from upstream to downstream in mass fluxes for all constituents. Small increases in fluxes were observed within S1 and S2, a greater increase in fluxes was seen in S4.

Increases in chloride flux in S1 and S2 can be explained as runoff and leaching associated with road salts. Although the percent of urban development in S2 is 29% lower than S1 both segments show an increase in chloride flux. There is a tributary in S1 with headwaters in South Bloomington. Snow melt containing sodium chloride trickles into the tributary supplying chloride to LKC. The input of chloride in S2 is more direct than in S1, coming from Interstate 74 that passes over LKC. During the winter months road salting occurs on Interstate 74, runoff containing sodium chloride is input to LKC below. Excess road salts are stored within the unsaturated zone. The chloride is slowly transported to the groundwater, which provides a constant source of chloride to the surface water (Lax and Peterson, 2008).

The increase in nitrate and sulfate fluxes in S1 may be related to fertilizer application. Fertilizers stored in the unsaturated zone are transported to tile drains during precipitation events and discharged into LKC or reach LKC as runoff from agricultural fields.

S2 has a high sinuosity index (SI = 1.80), however nitrate and sulfate fluxes increase, which may correlate with the presence of debris dams. Although debris and beaver dams are believed to be areas of intense denitrification, chloride can limit the process (Hale and Groffman, 2006). Hale and Groffman (2006) found high chloride levels inhibited denitrification processes, leading debris dams to become sources of nitrogen in streams rather than sinks. Strezo (2008) did not study the effects of chloride but did find that the presence of beaver dams increased the flux of nitrogen in LKC.

The most extreme departure from the generally decreasing trend in all fluxes is seen at S4 (SI = 1.43). At S4 the influence of anthropogenic activities is the most direct. Crestwicke North Subdivision, Crestwicke Country Club golf course or both are on either side of LKC for most of S4. The increases in fluxes are a direct result of the surrounding land uses.

Potential sources of chloride additions in S4 include water softener discharge from leaking septic tanks and excess salt, primarily sodium chloride, associated with road deicing. Excess road salt and septic leachate is slowly transported from the unsaturated zone to the groundwater (Lax and Peterson, 2008) or is intercepted by tile drains. In whatever way water discharges to LKC, additional chloride enters into the system.

Sampling took place during the spring and summer growing season. During this time frame, the utilization of nitrate by plants alone should result in an overall net loss of nitrate. Contrary to the expected results, nitrate flux statistically, remains unchanged which implies addition. There are no known point sources of nitrate and the rate of supply to LKC is unknown. However, the influence of anthropogenic activities does affect the flux of nitrate in LKC. In S4, nitrate enters LKC through fertilizer application, tile drain discharge, and septic tank leachate. Sampling was not conducted immediately following storm events; however tile drains will continue to run after the stream has returned to base flow conditions. Sampling events days after a storm event may contain a component of tile drain discharge.

The increase of sulfate flux in S4 may be related to septic field management. Mature landscaping surrounds homes in Crestwicke North subdivision, and many large older trees are found along the banks of LKC. The growth of tree or shrub roots can clog septic field lines. To discourage tree root growth copper sulfate, a water-soluble salt, is used.

The second largest source of groundwater nitrate contamination is from leaking septic tanks (Zhang and Shan, 1999). Given the proximity of urban development to LKC in S4, there is potential for septic tank leachate to impact both nitrate and sulfate levels in LKC.

Fluxes in S3, S5 and S6 are generally decreasing. Land cover/land use in S5 and S6 is greater than 90% agricultural. There is little opportunity for chloride input in S5 and S6 and nitrate input is generally the result of fertilizer application.

In contrast to S4 (SI = 1.43) with the largest gain in mass fluxes, S3 (SI = 2.37) has the largest loss of mass fluxes for all constituents and the highest sinuosity index. The land use in S3 and S4 is similar, with the exception of more forested land in S3, and three fewer tile drains in S3 (7) than S4 (10). Rather than increases in fluxes as seen in S3, fluxes for all constituents decrease. The decrease in fluxes may be the result of hyporheic interaction in the streambed through short flow paths, interaction in longer flow paths beneath meanders, a combination of both or hyporheic storage beneath meanders.

Short hyporheic flow paths within the streambed are known to have the greatest hydrologic exchange (Harvey and Wagner, 2000) to regulate stream chemistry (Duff and Triska, 2000) and to induce denitrification (Ostrom et al. 2002). Buyck (2005) and Van der Hoven et al. (2008) both observed the reduction of nitrate along short hyporheic flows paths within a section of LKC.

Large volumes of water cycling through short hyporheic flow paths experience less contact time with hyporheic sediments leaving an untapped potential for denitrification. Hill et al. (1998) and Storey et al. (2004) noted that in most streams there appears to be a greater capacity for denitrification than the rate at which denitrification occurs.

The high sinuosity of S3 suggests that there is a potential for longer hyporheic flow paths beneath meander lobes. Flow beneath meanders increases the size of the HZ (Peterson and Sickbert, 2006) and results in longer hyporheic flow paths, which leads to increased hyporheic residence time. The increased contact time with microbially active hyporheic sediments results in greater nitrate retention (Hill et al. 1998). Fromm (2005) noted a net decrease in nitrate on the down gradient side of a meander in LKC. The same hyporheic processes responsible for the loss of nitrate noted by Fromm (2005), denitrification and vegetative uptake of nitrate, are taking place beneath the meanders in S3.

The loss of sulfate in S3 is related to availability of nitrate. Denitrification exhausts the supply of available oxygen. As oxygen becomes depleted along a flow path, the redox sequence progresses through manganese and iron reducing conditions, until sulfate reduction begins. Beneath a meander of LKC, Fromm (2005) observed sulfate reducing conditions approximately halfway across. The loss of nitrate flux in S3 coupled with Fromm’s observations suggests sulfate is lost to reducing conditions in long hyporheic flow paths beneath the meanders of S3 (SI = 2.37). Sulfate reducing conditions are not achieved along short hyporheic flow paths. The constant replenishment of hyporheic sediments with oxygenated stream water coupled with the short residence time does not allow the redox sequence in short hyporheic flow paths to progress beyond nitrogen reducing conditions.

Chloride is conservative, which unlike nitrate and sulfate is not being lost to vegetative uptake or redox reactions during time spent in the HZ. The increased residence time associated with longer flow paths beneath meanders acts as a storage mechanism for chloride. Using MODPATH simulations, Fromm (2005) found chloride lag times beneath a meander 71.6 m across ranging from 200 to 250 days. The flux of chloride in LKC varies, which is linked to the lag time seen by Fromm (2005).

The decrease in chloride flux in S3 (SI = 2.37) is related to the increase in sinuosity. Longer flow paths associated with the HZ beneath meanders act as storage mechanisms for chloride. Eventually these longer hyporheic flow paths will reenter LKC at some point downstream. In some cases flow paths may reenter in another segment entirely.

The decrease in chloride flux seen in S3 (SI = 2.37) is directly related sinuosity and the longer hyporheic flow paths found beneath meanders. The decrease in sulfate flux seen in S3 (SI = 2.37) suggests meanders reach sulfate reducing conditions after the supply of nitrate has been exhausted, implying nitrate is lost both beneath meanders as well as to hyporheic processes in the streambed. In segments with lower sinuosity indices interaction in the streambed may be solely responsible for the remediation of excess nitrate additions, which may explain why some segments show a gain in flux.

CHAPTER V

CONCLUSIONS

Excess anthropogenic nitrate additions are effectively remediated through natural stream function in LKC. Given the high risk of groundwater nitrate contamination in agricultural areas, remediation of excess anthropogenic nitrate additions has become an important topic in the scientific community. Natural stream function in small agricultural streams may play an important role in the remediation of excess nitrate additions.

The removal of nitrate from LKC appears related to sinuosity. High sinuosity indices mean greater stream distance leading to increased interaction in the shorter flow paths of the streambed. In these more sinuous segments there is also greater opportunity for interaction beneath meander lobes. Whether hyporheic interaction beneath meanders in the streambed or a combination of both is responsible for the denitrification occurring along LKC remains unanswered.

REFERENCES

Angelier, E., 1953, Recherches ecologiques et biogeographiques sur la faune des sables subergees, Archives de Zoologie Experimentales et Generale, vol. 90, pg. 37-161.

Angradi, T., Hood, R., 1998, An application of the plaster dissolution method for quantifying water velocity in the shallow hyporheic zone of an Appalachian stream system, Freshwater Biology, vol. 39, pg. 301-315.

Basu, A., 2007, Quantifying N cycling between groundwater and surface water using numerical modeling and mass flux [M.S. thesis], Illinois State University, 48 pgs.

Bencala, K.E., 1993, A perspective on stream-catchment connections, Journal of the North American Benthological Society, no.12, pg. 44-47.

Brunke, M, Gonser, T, 1997, The ecological significance of exchange processes between rivers and groundwater, Freshwater Biology, vol. 37, no. 1, pg. 31-33. DOI: 10.1046/j.1365-2427.1997.00143.x.

Buyck, M. S., 2005, Tracking nitrate loss and modeling flow through the hyporheic zone of a low gradient stream through the use of conservative tracers [M.S. thesis], Illinois State University, 80 pgs.

Chappuis, P.A., 1942, Eine neue Methodo zur Untersuchung der Grundwasserfauna. Acta sc. Math. Nat. University of Francico-Josephina, vol. 6, pg. 1-7.

Christian, P.B., Sorensen, J., 1988, Denitrification in sediment of lowland streams: Regional and seasonal variation in Gelbeck and Rabis Back Denmark, FEMS: Microbiology and Ecology, vol. 53, pg. 335-344.

Cirmo, C.P., McDonnell, J.J., 1997, Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of a temperate-forested catchments: a review, Journal of Hydrology, vol. 199, pg. 88-120.

Davis, D.M., Gowda, P.H., Mulla, D.J., and Randall, G.W., 2000, Modeling nitrate nitrogen leaching in response to nitrogen fertilizer rate and tile drain depth or spacing for southern Minnesota, USA: Journal of Environmental Quality, vol. 29, pg. 1568-1581.

Dick, R.P., Christ, R.A., Istok, J.D., Iyamuremye, F., 2000, Nitrogen fractions and transformations of vadose zone sediments under intensive agriculture in Oregon, Soil Science, vol. 165, no. 6, pg. 505-515.

Duff, J.H., Triska, F.J., 2000, Nitrogen biogeochemistry and surface-subsurface exchange in streams, In: Jones J.B. Mulholland, P.J. (eds.) Streams and Ground Waters, Academic Press, Boston, pp. 197-220.

Environmental Systems Research Institute (ESRI). ArcMap, version 9.2, 1999-2006, ESRI Inc.

Findlay, S., 1995, Importance of surface-subsurface exchange in stream ecosystems, the hyporheic zone, Limnology and Oceanography, vol. 40, pg. 159-164.

Findlay, S., Strayer, D., Goumbala, C., 1993, Metabolism of stream water dissolved organic carbon in the shallow hyporheic zone, Limnology and Oceanography, vol. 38, pg. 1493-1499.

Fischer, H., Kloep, F., Wilzcek, S., Pusch, M. T., 2005, A river's liver – microbial processes within the hyporheic zone of a large lowland river, Biogeochemistry, vol. 76, pg. 349-371.

Follett, R.F., Delgado, J.A., 2002, Nitrogen fate and transport in agricultural systems, Journal of Soil and Water Conservation, vol. 57, pg. 402-408.

Fromm, N. J., 2005, Quantifying the flux of water and loss of nitrate as stream water flows beneath a meander of a central Illinois stream [M.S. thesis], Illinois State University, 83 pgs.

Galloway, J.N., Schlesinger, W.H., Levy II, H., Michaels, A. and Schnoor, J.L., 1995, Nitrogen fixation: anthropogenic enhancement – environmental response, Global Biogeochem. Cycles, vol. 9, pg. 235-252.

Gibert, J., Bole-Olivier, M.J., Marmonier, P., Vervier, P., 1990, Surface water-groundwater ecotones, The ecology and management of aquatic-terrestrial ecotones (eds. R.J. Naiman and H. Decamps), pp. 199-216. UNESCO MAB and the Parthenon Publishing Group, Paris and Carnforth.

Grimm N.B., Fisher, S.G., 1984, Exchange between interstitial and surface water: Implications for stream metabolism and nutrient cycling, Hydrobiologia, vol. 111, pg. 219-228.

Harvey, J.W., Bencala, K.E., Zellweger, G.W., 1991, Preliminary investigation of the effect of hillslope hydrology on the mechanics of solute exchange between streams and subsurface gravel zones, Water-Resources Investigation, (U.S. Geological Survey), Report 91-4034, pg. 413-418.

Harvey, J.W., Bencala, K.E., 1993, The effect of streambed topography on surface-subsurface water exchange in mountain catchments, Water Resources Research, vol. 29, pg. 89-98.

Harvey, J.W., Wagner, B., 2000, Quantifying hydrologic interactions between streams and their subsurface hyporheic zones, In: Jones J.B. Mulholland, P.J. (eds.) Streams and Ground Waters, Academic Press, Boston, pg. 3-43.

Hill, A.R., Labadia, C.F., Sanmugadas, K., 1998, Hyporheic zone hydrology and nitrogen dynamics in relation to the streambed topography of a N-rich stream, Biogeochemistry, vol. 45, pg. 285-310.

Hinkle, S.R., Duff, J.H., Triska, F.J., Laenen, A., Gates, E.B., Bencala, K.E., Wentz, D.A., and Silva, S.R., 2001, Linking hyporheic flow and nitrogen cycling near the Willamette River; a large river in Oregon, USA, Journal of Hydrology, vol. 244, pg. 157-180.

Homer, C., Huang, C., Yang, L., Wylie, B., Coan, M., 2004, Development of a 2001 national land cover database for the United States. Photogrammetric Engineering and Remote Sensing, vol. 70, no.7, pg. 829-840.

Hynes, H.B.N., 1974, Further studies on the distribution of stream animals within the substratum, Limnology and Oceanography, vol. 19, pg. 92-99.

Illinois Natural History Survey's 1999-2000 1:100,000 Scale Illinois Gap Analysis Land Cover Classification, Raster Digital Data, Version 2.0, September 2003.

Karaman, S.L., 1935, Die Fauna unterirdischer Gewasser Jugoslawiens, Verhandlungen der Internationalen Vereinigung fur Theoretische und Angewandte Limnologie, vol. 7, pg. 46-53.

Keeney, D.R. and Hatfield, J.L., 2001, The nitrogen cycle, historical perspective, and current and potential future concerns, In: Nitrogen in the Environment: Sources, Problems, and Management, Follett, R. F. and Hatfield J.L. (eds.), Elsevier Science, pg. 3-16.

Kemp, M.J., Dodds, W.K., 2002, The influence of ammonium, nitrate, and dissolved oxygen concentrations on uptake, nitrification, and denitrification rates associated with prairie stream substrata, Limnology and Oceanography, vol. 47, no. 5, pg. 1380-1393.

Krebs, C.J., 2001, Ecosystem Metabolism III: Nutrient Cycles, Ecology -The Experimental Analysis of Distribution and Abundance, 5th ed, San Francisco, Benjamin Cummings, pg. 576-580.

Lax, S. and Peterson, E.W., 2008, Characterization of chloride transport in the unsaturated zone near salted road, Environmental Geology, DOI 10.1007/s00254-008-1584-6.

Maguffin, S.C. and Peterson, E.W., 2005, The hydrogeological effects of altering land use along Wolf Creek, Geological Society of America Abstract with Programs, vol. 37, no 7, pg. 510.

Mosley, M.P., McKerchar, A.I., 1993, Handbook of Hydrology, McGraw-Hill, Inc.

Neff, J. C., Chapin III, F. S., Vitousek, P. M., 2003, Breaks in the cycle: dissolved organic nitrogen in terrestrial ecosystems, Frontiers in Ecology and the Environment, vol. 1, no. 4, pg. 205-211.

NRC, 1978, Nitrates: An Environmental Assessment, A Report, Washington, DC, National Research Council.

Orghidan, T, 1959, Ein neuer Lebenraum des unterrirdischen Wassers: Der hyporheische Biotop, Archiv fur Hydrobiologie, vol. 55, pg. 392-414.

Ostrom, N.E., Hedin, L.O., von Fischer, J.C., Robertson, G.P., 2002, Nitrogen transformations and NO_3^- removal at a soil-stream interface: a stable isotope approach, Ecological Applications, vol.12, pg. 1027-1043.

Peterson, E.W. and Sickbert, T.B., 2006, Stream water bypass through a meander neck, laterally extending the hyporheic zone, Hydrogeology Journal, vol. 14, no. 8, pg. 1443-1451. DOI: 10.1007/s10040-006-0050-3

Piskin, K., Bergstrom, R.R., 1975, Glacial drift in Illinois – thickness and character, Illinois State Geological Survey circular 490, 35 pgs.

Ritter, W.F., Bergstrom, L., 2001, Nitrogen and water quality, In: Agricultural Nonpoint Source Pollution Watershed Management and Hydrology, New York, Lewis Publishers, pg. 59-89.

Schwoerbel, J., 1961a, Uber die Lebensbedingungen und die Besiedlung des hyporheischen Lebensraumes. Archiv fur Hydrobiologie, Supplementband, vol. 25, pg. 182-184.

Schwoerbel, J., 1961b, Subterrane Wassermilben (Acari, Hydrachnellae, Porohalacaridae und Stygothrombidae), ihre Okologie, und Bedeutung fur die Abgrenzung eines aquatischen Lebensraumes zwischen Oberflache und Grundwasser, Archiv fur Hydrobiologie, Supplementband, vol. 25, pg. 242-306.

Schwoerbel, J., 1964, Die Bedeutung des Hyporheals fur die benthischen Lebensgemeinschaften des Fliessgewassers, Verhandlungen der Internationalen Vereinigung fur theoretische und Angewandte Limnologie, vol. 15, pg. 215-226.

Schwoerbel, J. 1967, Das hyporheische Interstitial als Grenzbiotop zwischen oberirdischem – und subterranem okosystem und seine Bedeutung fur die Primar-Evolution von Kleinsthohlenbewohnern, Archiv fur Hydrobiologie, Supplementband, vol. 33, pg. 1-62.

Schwartz, F.W., Zhang, H., 2003, Fundamentals of Groundwater, 1st ed, John Wiley & Sons, 583 pgs.

SPSS for Windows, Rel. 16.0.1, 2007, Chicago: SPSS Inc.

Storey, R.G., Williams, D.D., Fulthorpe, R.R., 2004, Nitrogen processing in a hyporheic zone of a pastoral stream, Biogeochemistry, vol. 69, pg. 285-313.

Swank, W.T., Caskey, W.H., 1982, Nitrate depletion in a second-order mountain stream, Journal of Environmental Quality, vol. 11, pg. 581-584.

Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G., Bencala, K.E., 1989, Retention and transport of nutrients in a third order stream: hyporheic processes, Ecology, vol. 70, pg. 1893-1905.

Triska, F.J., Duff, J.H., Avanzino, R.J., 1993, The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial-aquatic interface, Hydrobiologia, vol. 251, pg. 167-184.

Turlan, T., Birgand, F., Marmonier, P., 2007, Comparative use of field and laboratory mesocosms for in-stream nitrate uptake measurement, Annales de Limnologie, vol 43, no. 1 pg. 41-51.

Ventullo, R.M., Rowe J.J., 1982, Denitrification potential of epilithic communities in a lotic environment, Current Microbiology, vol 7., no. 1, pg. 29-33.

White, D.S., Elzinga, C.H., Hendricks, S.P., 1987, Temperature patterns within the hyporheic zone of a northern Michigan river, Journal of the North American Benthological Society, vol. 6, pg. 85-91.

Wondzell, S.M. and Swanson, F.J., 1996, Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream, Hydrologic processes, Journal of the North American Benthological Society, vol. 15, pg. 3-19.

Wroblicky, G.J., Campana, M.E., Valett, H.M. Dahm, C.N., 1998, Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of tow stream-aquifer systems, Water Resources Research, vol. 34, pg. 317-328.

Van der Hoven, S., Fromm, N. and Peterson, E., 2008, Quantifying nitrogen cycling beneath a meander of a low gradient, N-impacted, agricultural stream using tracers and numerical modeling, Hydrological Processes, vol. 22, no, 8, pg. 1206-1215. DOI: 10.1002/hyp.6691.

Veriver P., Gibert, J., Marmonier, P., Dole-Olivier, M-J., 1992, A perspective on the permeability of the surface freshwater-groundwater ecotone. Journal of the North American Benthological Society, vol. 11, no. 1, pg. 93-102.

Zhang, T.C., Shan, J, 1999, In situ septic tank effluent denitrification using a sulfur-limestone process, Water Environment Research, vol. 71, no. 7, pg. 1283-1291.

APPENDIX A

FIELD PARAMETERS AND CHEMISTRY DATA

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC1	09/21/06	0.00	0.00	0.00	0.00	108.20	3.22	34.10	33.59
LKC1	10/05/06	66.40	6.55	694.00	16.50	82.08	2.75	31.27	29.88
LKC1	11/10/06	78.10	8.70	747.00	10.50	85.13	4.34	35.65	19.62
LKC1	03/11/07	42.10	5.39	804.00	4.40	157.67	4.51	31.11	34.96
LKC1	07/12/07	70.50	6.44	1306.00	20.00	304.90	3.29	45.80	92.54
LKC1	07/24/07	50.20	4.19	564.00	23.70	178.46	1.07	38.51	166.95
LKC1	10/25/07	119.40	13.65	598.00	9.10	90.84	0.55	26.92	164.74
LKC1	02/19/08	189.50	no data	0.00	0.60	187.42	3.39	26.51	63.59
LKC1	02/25/08	202.70	no data	1129.00	3.20	231.64	3.97	29.54	68.01
LKC1	04/07/08	162.10	16.42	1077.00	14.60	154.79	3.70	31.76	49.30
LKC1	05/25/08	97.50	10.11	879.00	13.50	113.84	6.74	33.07	19.28
LKC1	06/01/08	110.70	9.69	845.00	21.80	116.95	6.58	27.06	20.36
LKC1	07/09/08	152.10	12.07	1253.00	26.00	273.66	4.55	42.24	71.05
LKC1	07/13/08	129.70	10.91	740.00	23.90	87.66	6.28	25.49	16.30
LKC1	07/15/08	107.00	9.52	691.00	21.10	71.58	6.45	26.97	12.68
LKC1	07/17/08	118.80	10.08	685.00	23.30	76.33	5.45	26.94	15.91
LKC1	07/20/08	116.50	9.65	700.00	24.50	63.33	4.15	24.56	20.99
LKC1	07/26/08	114.60	9.88	812.00	22.40	124.89	6.16	34.86	24.10
LKC1	07/28/08	109.00	9.36	760.00	22.60	155.09	3.12	22.51	33.08
LKC1	08/01/08	88.70	7.62	834.00	22.60	125.77	1.71	12.01	32.15
LKC1	08/04/08	80.70	7.01	671.00	22.20	75.00	3.24	27.18	27.27
LKC1	08/06/08	90.30	7.21	632.00	26.90	74.86	2.39	24.90	31.30
LKC1	08/08/08	75.30	6.65	944.00	22.10	129.75	2.84	35.93	53.61
LKC1	08/10/08	152.60	12.83	1194.00	23.80	241.55	2.81	42.24	93.64
LKC1	08/12/08	89.30	8.13	1244.00	19.30	244.95	2.27	44.38	128.92
LKC1	08/14/08	71.30	6.57	962.00	19.00	134.92	2.79	38.40	52.08
LKC1	08/18/08	92.60	8.11	1356.00	21.40	278.17	1.30	48.55	254.92
LKC1	08/20/08	79.40	7.12	1477.00	20.60	338.34	0.94	51.36	413.70
LKC1	08/25/08	80.70	6.98	984.00	22.00	187.46	0.64	37.68	328.36
LKC1	08/27/08	111.00	9.44	908.00	22.50	199.03	0.63	34.87	361.61

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC2	09/21/06	104.00	10.60	766.00	14.40	107.02	2.98	35.54	35.95
LKC2	10/05/06	80.60	7.80	742.00	16.70	104.60	2.30	35.03	45.58
LKC2	11/10/06	96.80	10.55	816.00	10.70	90.96	4.09	36.38	22.22
LKC2	03/11/07	41.60	5.28	891.00	4.60	160.09	4.76	32.67	33.61
LKC2	07/12/07	59.00	5.22	938.00	21.50	203.06	1.45	42.76	140.52
LKC2	07/24/07	57.00	4.63	923.00	26.30	168.77	0.83	39.67	202.79
LKC2	10/25/07	132.40	15.28	513.00	9.00	78.58	0.73	21.58	107.39
LKC2	02/19/08	214.00	no data	0.00	0.10	194.73	3.38	30.17	64.56
LKC2	02/25/08	181.30	no data	1324.00	2.90	280.16	4.02	32.83	82.45
LKC2	04/07/08	124.30	12.96	1100.00	14.00	193.88	4.66	41.79	47.78
LKC2	05/25/08	88.80	9.13	916.00	13.30	117.89	6.18	36.44	22.04
LKC2	06/01/08	95.50	8.33	912.00	20.70	134.84	6.63	32.07	23.41
LKC2	07/09/08	100.40	8.22	805.00	24.70	104.27	4.15	33.01	29.40
LKC2	07/13/08	117.70	10.01	772.00	23.40	94.78	6.09	28.57	18.00
LKC2	07/15/08	96.60	8.47	728.00	21.70	72.86	6.29	29.99	14.35
LKC2	07/17/08	106.70	9.29	726.00	23.90	83.09	5.72	30.38	16.54
LKC2	07/20/08	99.40	8.17	742.00	24.90	92.01	4.54	29.00	23.14
LKC2	07/26/08	105.30	8.76	887.00	23.60	133.88	5.04	33.02	27.35
LKC2	07/28/08	103.70	8.56	908.00	23.80	169.37	4.15	30.20	34.47
LKC2	08/01/08	96.20	8.05	882.00	23.80	105.85	2.86	24.67	39.23
LKC2	08/04/08	81.80	6.86	749.00	23.90	114.83	2.16	29.49	60.27
LKC2	08/06/08	83.10	6.55	679.00	26.80	3.35	2.07	26.27	47.21
LKC2	08/08/08	95.30	8.32	816.00	23.40	113.59	2.49	36.19	53.30
LKC2	08/10/08	112.50	9.15	1032.00	25.60	179.62	2.38	42.51	81.38
LKC2	08/12/08	115.30	10.32	1302.00	19.80	273.15	1.99	48.29	159.98
LKC2	08/14/08	66.80	6.24	1330.00	18.40	267.19	2.07	51.98	154.90
LKC2	08/18/08	148.60	12.63	1378.00	23.30	263.70	1.46	57.88	214.89
LKC2	08/20/08	113.50	10.36	1471.00	19.80	296.99	1.05	58.87	327.53
LKC2	08/25/08	77.80	6.89	919.00	21.10	153.69	1.14	38.29	158.64
LKC2	08/27/08	166.70	14.51	1147.00	27.30	216.02	0.86	46.32	289.90

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC3	09/21/06	46.30	4.70	792.00	13.40	111.37	3.17	35.91	35.16
LKC3	10/05/06	72.50	7.11	758.00	16.50	92.08	2.27	34.69	40.62
LKC3	11/10/06	106.20	11.44	774.00	12.50	92.23	3.74	40.39	24.67
LKC3	03/11/07	43.00	5.34	869.00	4.50	155.81	4.58	33.74	34.05
LKC3	07/12/07	38.40	3.43	967.00	20.30	167.93	2.14	35.99	78.50
LKC3	07/24/07	55.00	4.91	829.00	22.80	131.52	0.93	35.50	141.67
LKC3	10/25/07	119.80	13.43	443.10	9.90	58.48	0.73	20.18	80.46
LKC3	02/19/08	215.00	no data	0.00	0.20	192.78	3.57	29.96	61.45
LKC3	02/25/08	161.40	no data	1355.00	2.50	292.61	4.23	33.03	81.75
LKC3	04/07/08	148.50	15.31	1006.00	14.10	116.06	3.98	30.12	39.36
LKC3	05/25/08	94.00	9.78	887.00	13.60	109.53	6.66	35.74	18.70
LKC3	06/01/08	94.80	8.61	893.00	20.30	115.53	6.69	30.02	20.01
LKC3	07/09/08	100.20	8.32	757.00	24.70	88.50	4.10	29.22	24.27
LKC3	07/13/08	94.90	8.27	761.00	22.60	89.76	6.60	28.08	15.74
LKC3	07/15/08	95.10	8.48	734.00	21.20	71.91	7.03	29.37	12.46
LKC3	07/17/08	102.20	8.12	729.00	23.80	78.53	6.30	29.85	14.01
LKC3	07/20/08	1070.00	8.77	695.00	24.60	78.93	4.49	26.61	20.68
LKC3	07/26/08	84.20	7.28	819.00	22.60	113.87	5.46	30.63	21.43
LKC3	07/28/08	100.60	8.51	799.00	22.70	123.15	4.18	28.85	27.61
LKC3	08/01/08	79.90	6.88	827.00	22.90	102.08	2.69	18.90	27.99
LKC3	08/04/08	79.10	6.67	866.00	23.30	167.77	1.94	29.63	89.13
LKC3	08/06/08	80.50	6.76	587.00	25.80	38.97	1.38	17.53	42.32
LKC3	08/08/08	82.30	7.06	762.00	22.80	126.46	2.14	31.58	49.41
LKC3	08/10/08	94.50	8.16	960.00	23.40	148.13	2.25	39.72	73.69
LKC3	08/12/08	103.10	9.35	1052.00	20.00	180.92	1.77	41.57	122.39
LKC3	08/14/08	65.30	6.01	1210.00	19.00	236.04	1.44	45.47	197.51
LKC3	08/18/08	101.00	8.90	1163.00	21.60	202.89	0.97	47.43	255.38
LKC3	08/20/08	95.70	8.55	1179.00	20.70	217.45	0.71	48.09	346.23
LKC3	08/25/08	105.00	8.75	487.30	22.30	60.18	0.59	19.47	112.78
LKC3	08/27/08	101.00	8.87	552.00	21.50	71.01	0.49	22.07	162.27

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC4	09/21/06	76.30	8.00	806.00	13.40	106.11	2.93	36.40	36.17
LKC4	10/05/06	79.50	7.78	794.00	16.40	102.31	1.81	37.85	56.56
LKC4	11/10/06	120.40	12.62	821.00	10.80	89.33	3.25	37.53	27.46
LKC4	03/11/07	59.20	7.56	860.00	5.40	145.02	4.42	33.65	32.81
LKC4	07/12/07	39.40	3.56	911.00	20.20	131.01	1.53	39.73	85.52
LKC4	07/24/07	53.30	4.58	753.00	23.00	86.53	0.79	35.32	109.16
LKC4	10/25/07	76.40	8.43	787.00	10.80	147.31	0.80	33.95	183.90
LKC4	02/19/08	215.00	no data	0.00	0.10	193.04	3.89	31.28	50.63
LKC4	02/25/08	178.20	no data	0.00	1.90	325.10	4.17	36.17	90.42
LKC4	04/07/08	154.30	15.40	975.00	15.20	153.81	4.58	42.52	39.87
LKC4	05/25/08	102.90	10.55	872.00	14.00	101.81	6.35	36.09	18.29
LKC4	06/01/08	102.10	9.11	885.00	20.50	115.14	6.52	30.84	19.29
LKC4	07/09/08	106.90	8.62	741.00	25.50	83.74	3.41	31.33	29.25
LKC4	07/13/08	111.30	9.41	762.00	22.50	86.24	6.37	28.39	15.83
LKC4	07/15/08	104.30	7.07	749.00	21.90	71.63	6.79	30.58	12.79
LKC4	07/17/08	115.10	9.68	749.00	24.10	77.56	5.92	31.41	15.28
LKC4	07/20/08	95.20	7.76	591.00	25.70	34.31	2.83	19.87	20.42
LKC4	07/26/08	103.10	8.75	832.00	23.30	88.75	4.78	31.57	21.04
LKC4	07/28/08	115.50	9.78	828.00	23.40	102.78	3.39	26.30	25.13
LKC4	08/01/08	88.40	7.58	791.00	23.00	73.42	3.20	28.75	29.74
LKC4	08/04/08	97.10	8.02	801.00	23.40	91.73	2.47	34.59	43.60
LKC4	08/06/08	107.00	8.31	669.00	27.10	67.28	1.17	22.71	71.16
LKC4	08/08/08	118.50	9.95	726.00	23.90	75.51	1.39	33.82	63.10
LKC4	08/10/08	115.80	9.70	820.00	24.50	105.54	1.56	38.70	69.96
LKC4	08/12/08	95.40	8.44	904.00	20.40	110.66	1.24	42.16	109.07
LKC4	08/14/08	60.10	5.50	924.00	19.50	116.28	0.97	44.10	144.61
LKC4	08/18/08	90.00	7.78	1037.00	21.80	136.70	0.74	51.90	222.05
LKC4	08/20/08	89.70	7.90	1033.00	21.20	132.15	0.66	52.12	233.49
LKC4	08/25/08	98.90	8.44	731.00	22.80	69.89	0.62	29.36	127.67
LKC4	08/27/08	103.90	8.87	839.00	22.90	92.18	0.60	41.64	173.74

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC5	09/21/06	113.00	11.56	794.00	14.50	94.58	2.68	36.26	35.24
LKC5	10/05/06	94.80	9.16	791.00	16.60	95.46	1.40	37.40	68.12
LKC5	11/10/06	95.40	10.12	802.00	12.30	81.07	2.99	36.64	27.08
LKC5	03/11/07	48.50	5.96	841.00	6.10	136.81	4.47	34.24	30.59
LKC5	07/12/07	55.10	4.75	864.00	22.70	102.46	1.88	39.25	54.42
LKC5	07/24/07	67.80	5.36	676.00	27.50	63.35	0.88	32.55	71.64
LKC5	10/25/07	181.70	18.83	937.00	11.10	166.20	0.43	43.11	386.99
LKC5	02/19/08	189.50	no data	0.00	0.20	149.11	3.94	30.93	43.38
LKC5	02/25/08	170.10	no data	1281.00	2.20	267.49	4.23	35.76	70.57
LKC5	04/07/08	117.20	12.08	808.00	14.80	133.44	4.17	39.74	37.50
LKC5	05/25/08	95.10	9.78	836.00	14.20	87.60	6.56	34.94	15.30
LKC5	06/01/08	96.10	8.61	859.00	20.60	91.86	6.23	28.05	17.20
LKC5	07/09/08	108.50	8.73	660.00	26.10	71.42	2.76	27.83	29.01
LKC5	07/13/08	124.90	105.10	705.00	22.40	78.75	6.35	27.73	14.28
LKC5	07/15/08	106.00	9.18	744.00	21.90	66.14	6.62	30.17	12.14
LKC5	07/17/08	107.70	8.88	748.00	24.10	6.72	5.84	31.54	14.46
LKC5	07/20/08	106.30	8.62	529.00	26.00	68.38	2.64	19.88	20.11
LKC5	07/26/08	114.60	9.69	792.00	23.60	77.39	5.16	32.52	16.83
LKC5	07/28/08	111.00	9.30	778.00	23.90	81.41	3.61	29.98	22.56
LKC5	08/01/08	93.90	8.09	740.00	23.00	38.37	1.89	14.88	19.74
LKC5	08/04/08	112.30	9.44	764.00	23.80	86.93	3.21	35.78	31.67
LKC5	08/06/08	123.10	9.73	714.00	27.10	51.20	1.06	14.98	55.46
LKC5	08/08/08	110.00	9.16	669.00	24.90	58.00	1.40	31.75	48.19
LKC5	08/10/08	116.00	9.66	753.00	24.50	67.42	1.43	36.79	54.60
LKC5	08/12/08	97.00	8.57	819.00	21.20	87.44	1.29	37.92	80.13
LKC5	08/14/08	55.50	5.10	851.00	19.20	83.41	1.32	39.93	75.30
LKC5	08/18/08	108.50	8.68	946.00	27.10	105.46	0.81	44.12	156.00
LKC5	08/20/08	91.80	7.99	908.00	21.60	102.69	0.87	44.77	134.45
LKC5	08/25/08	98.40	8.23	571.00	24.30	48.16	0.58	25.87	92.13
LKC5	08/27/08	111.10	9.26	606.00	24.20	51.50	0.51	25.69	105.88

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC6	09/21/06	94.30	9.69	797.00	14.00	83.04	3.56	34.18	23.30
LKC6	10/05/06	43.50	4.26	817.00	16.30	84.76	2.57	35.90	32.97
LKC6	11/10/06	127.80	13.20	773.00	14.30	70.40	3.48	34.27	20.24
LKC6	03/11/07	44.50	5.42	816.00	6.50	117.04	4.87	31.62	24.01
LKC6	07/12/07	47.40	4.12	832.00	22.30	78.42	2.97	35.61	26.44
LKC6	07/24/07	23.90	1.74	657.00	25.40	52.50	1.48	29.69	35.47
LKC6	10/25/07	117.40	13.15	899.00	10.40	147.51	0.43	41.37	339.69
LKC6	02/19/08	221.90	no data	0.00	0.30	137.34	4.36	31.03	35.92
LKC6	02/25/08	170.90	no data	1169.00	2.40	224.20	4.94	33.95	50.29
LKC6	04/07/08	150.80	15.09	894.00	15.00	120.63	5.14	38.89	27.19
LKC6	05/25/08	91.10	9.20	780.00	13.80	73.96	7.55	32.42	11.17
LKC6	06/01/08	85.90	7.83	840.00	20.00	89.31	7.47	26.83	12.48
LKC6	07/09/08	80.50	6.51	639.00	26.60	58.13	4.43	26.61	14.63
LKC6	07/13/08	92.20	8.04	715.00	22.10	65.18	7.55	25.43	9.51
LKC6	07/15/08	97.70	8.57	726.00	21.80	55.14	7.88	28.24	8.48
LKC6	07/17/08	99.00	7.86	724.00	23.80	36.69	7.22	29.35	9.26
LKC6	07/20/08	97.90	7.71	544.00	26.80	46.20	7.99	39.14	12.06
LKC6	07/26/08	83.70	7.02	753.00	23.20	16.36	6.24	26.76	9.44
LKC6	07/28/08	108.60	8.97	757.00	22.90	76.12	4.67	24.01	11.69
LKC6	08/01/08	96.70	8.60	715.00	22.40	93.32	1.29	5.95	8.44
LKC6	08/04/08	89.30	7.52	749.00	23.10	67.00	4.65	31.32	17.15
LKC6	08/06/08	164.20	12.73	688.00	28.50	52.65	3.27	24.33	20.08
LKC6	08/08/08	156.70	12.66	679.00	22.60	44.46	3.37	27.99	15.51
LKC6	08/10/08	115.00	9.56	703.00	24.70	52.71	3.06	32.35	19.22
LKC6	08/12/08	92.10	8.32	763.00	20.10	58.32	3.07	32.78	21.66
LKC6	08/14/08	47.50	4.33	795.00	19.60	64.20	2.33	34.82	32.24
LKC6	08/18/08	91.30	7.83	839.00	22.90	70.66	1.74	38.94	46.84
LKC6	08/20/08	74.50	6.45	867.00	21.40	77.13	1.45	38.64	60.44
LKC6	08/25/08	94.50	8.28	579.00	21.90	48.46	0.80	23.50	66.91
LKC6	08/27/08	67.60	5.84	629.00	22.20	44.82	0.83	27.00	57.10

Sampling Location	Date	DO %	DO mg/L	SpC µS/cm	Temp °C	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Cl^-/NO_3^-
LKC7	09/21/06	77.30	7.90	760.00	14.30	80.87	3.46	33.81	23.39
LKC7	10/05/06	93.50	8.95	676.00	17.40	83.20	2.49	35.40	33.45
LKC7	11/10/06	102.10	10.83	773.00	13.10	71.16	3.47	33.87	20.49
LKC7	03/11/07	43.30	5.26	816.00	6.70	126.07	5.11	32.96	24.65
LKC7	07/12/07	44.30	3.89	832.00	21.80	78.05	2.72	35.10	28.66
LKC7	07/24/07	60.90	5.02	693.00	25.30	50.34	1.29	26.94	39.03
LKC7	10/25/07	109.80	11.70	782.00	12.20	117.55	0.37	36.33	318.80
LKC7	02/19/08	181.00	no data	0.00	0.30	126.09	5.58	32.67	24.92
LKC7	02/25/08	167.00	no data	1185.00	2.50	215.05	4.92	33.94	51.45
LKC7	04/07/08	140.50	14.18	832.00	14.70	118.10	5.27	39.12	26.52
LKC7	05/25/08	95.10	9.74	775.00	14.00	73.12	7.69	31.93	10.69
LKC7	06/01/08	120.70	9.95	809.00	20.20	86.08	8.27	28.46	12.09
LKC7	07/09/08	113.00	8.91	649.00	26.30	57.55	4.11	24.27	14.62
LKC7	07/13/08	105.30	9.03	710.00	22.20	65.85	7.58	25.13	9.30
LKC7	07/15/08	89.20	8.13	724.00	21.40	56.49	8.38	29.06	8.11
LKC7	07/17/08	99.60	8.39	589.00	23.40	63.13	7.34	29.59	8.90
LKC7	07/20/08	114.70	9.20	545.00	26.90	54.72	2.62	13.14	10.70
LKC7	07/26/08	98.70	7.94	749.00	22.70	53.54	6.30	26.63	9.17
LKC7	07/28/08	112.40	9.43	723.00	23.00	45.57	6.29	30.35	11.43
LKC7	08/01/08	78.00	6.73	714.00	22.30	49.95	4.51	19.16	11.66
LKC7	08/04/08	103.70	8.78	802.00	22.70	78.80	4.38	31.34	20.11
LKC7	08/06/08	126.70	9.94	691.00	27.20	29.81	2.62	17.43	19.47
LKC7	08/08/08	105.20	8.93	693.00	23.70	47.23	3.24	27.67	16.53
LKC7	08/10/08	114.20	9.70	678.00	24.10	47.13	3.00	32.15	19.41
LKC7	08/12/08	97.50	8.70	751.00	21.10	58.66	2.73	32.44	24.50
LKC7	08/14/08	64.80	5.93	778.00	19.70	58.58	2.50	33.03	27.53
LKC7	08/18/08	179.10	14.27	796.00	25.30	65.26	1.61	36.45	46.33
LKC7	08/20/08	137.80	11.24	840.00	22.20	73.43	1.27	36.75	65.01
LKC7	08/25/08	116.40	9.82	613.00	24.10	57.96	0.65	23.70	93.44
LKC7	08/27/08	112.80	9.54	660.00	23.70	50.65	0.66	26.43	83.08

APPENDIX B

DISCHARGE AND FLUX DATA

Sampling Location	Date	DTW (cm)	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- (mg/s)	NO_3^- (mg/s)	SO_4^{2-} (mg/s)
LKC1	10/05/06	-	0.068	-	5575.36	186.59	2124.24
LKC1	11/10/06	-	0.073	-	6204.36	316.20	2598.46
LKC1	10/25/07	-	0.045	-	4054.05	24.61	1201.22
LKC1	04/07/08	26.0	0.157	-	24316.64	581.43	4988.81
LKC1	05/25/08	24.0	-	0.186	21208.29	1255.84	6160.30
LKC1	06/01/08	22.5	-	0.210	24542.19	1380.00	5679.42
LKC1	07/09/08	31.0	-	0.076	20907.50	347.90	3227.41
LKC1	07/13/08	21.0	-	0.233	20460.83	1466.36	5950.37
LKC1	07/15/08	25.0	-	0.171	12211.12	1099.93	4600.57
LKC1	07/17/08	27.0	-	0.139	10625.14	758.63	3749.74
LKC1	07/20/08	29.0	0.115	-	7269.92	475.87	2819.85
LKC1	07/26/08	31.0	-	0.076	9541.42	470.60	2663.36
LKC1	07/28/08	32.0	-	0.061	9413.81	189.58	1366.48
LKC1	08/01/08	32.8	0.056	-	7088.67	96.55	677.09
LKC1	08/04/08	33.8	-	0.032	2433.09	105.14	881.71
LKC1	08/06/08	33.8	-	0.032	2428.37	77.58	807.61
LKC1	08/08/08	35.2	0.013	-	1680.00	36.82	465.23
LKC1	08/10/08	35.8	-	0.001	251.21	2.92	43.93

Sampling Location	Date	DTW cm	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- mg/s	NO_3^- mg/s	SO_4^{2-} mg/s
LKC2	10/05/06	-	0.078	-	8155.98	178.94	2731.65
LKC2	11/10/06	-	0.090	-	8195.83	368.78	3277.76
LKC2	10/25/07	-	0.014	-	1109.63	10.33	304.72
LKC2	04/07/08	11.0	0.177	-	34380.18	826.17	7410.94
LKC2	05/25/08	7.1	-	0.207	25158.94	1319.94	7776.08
LKC2	06/01/08	6.5	-	0.212	29577.50	1455.05	7033.51
LKC2	07/09/08	17.0	-	0.114	12032.57	478.89	3808.96
LKC2	07/13/08	-3.0	-	0.291	29703.13	1907.59	8953.79
LKC2	07/15/08	7.6	-	0.202	15189.04	1310.21	6251.30
LKC2	07/17/08	12.2	-	0.160	13536.83	932.28	4949.57
LKC2	07/20/08	15.4	0.122	-	11190.21	551.86	3527.50
LKC2	07/26/08	18.1	-	0.103	13992.20	527.18	3451.18
LKC2	07/28/08	19.2	-	0.092	15856.26	388.57	2826.86
LKC2	08/01/08	20.0	0.058	-	6097.86	164.57	1421.27
LKC2	08/04/08	21.5	-	0.069	8135.74	153.10	2089.41
LKC2	08/06/08	22.0	-	0.064	220.63	136.35	1731.34
LKC2	08/08/08	23.8	0.013	-	1423.16	31.19	453.37
LKC2	08/10/08	24.6	-	0.036	7213.73	95.53	1707.08
LKC2	08/12/08	25.8	-	0.023	7724.77	56.36	1365.61
LKC2	08/14/08	26.4	-	0.016	5968.97	46.23	1161.18

Sampling Location	Date	DTW cm	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- mg/s	NO_3^- mg/s	SO_4^{2-} mg/s
LKC3	10/05/06	-	0.050	-	4645.51	114.36	1749.93
LKC3	11/10/06	-	0.090	-	8264.63	334.96	3618.95
LKC3	10/25/07	-	0.014	-	822.39	10.22	283.86
LKC3	04/07/08	13.0	0.224	-	26035.03	892.24	6755.55
LKC3	05/25/08	6.0	-	0.322	35236.82	2143.69	11497.88
LKC3	06/01/08	5.5	-	0.330	38083.60	2203.94	9895.57
LKC3	07/09/08	18.0	-	0.131	11585.25	536.30	3825.25
LKC3	07/13/08	1.2	-	0.398	35728.18	2627.58	11176.44
LKC3	07/15/08	9.4	-	0.268	19247.17	1881.79	7860.92
LKC3	07/17/08	13.4	-	0.204	16023.79	1286.23	6090.48
LKC3	07/20/08	16.0	0.148	-	11646.58	663.02	3925.71
LKC3	07/26/08	18.4	-	0.125	14180.80	680.36	3815.04
LKC3	07/28/08	20.2	-	0.096	11812.18	401.13	2767.22
LKC3	08/01/08	21.0	0.074	-	7563.21	199.25	1399.99
LKC3	08/04/08	23.0	-	0.051	8623.24	99.76	1523.06
LKC3	08/06/08	23.0	-	0.051	2003.13	70.68	901.17
LKC3	08/08/08	25.0	0.025	-	3169.23	53.75	791.37
LKC3	08/10/08	25.0	-	0.020	2903.42	44.15	778.48

Sampling Location	Date	DTW cm	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- mg/s	NO_3^- mg/s	SO_4^{2-} mg/s
LKC4	10/05/06	-	0.132	-	13507.26	238.83	4996.44
LKC4	11/10/06	-	0.087	-	7786.05	283.54	3271.16
LKC4	10/25/07	-	0.016	-	2392.65	13.01	551.42
LKC4	04/07/08	13.0	0.188	-	28888.23	860.90	7986.10
LKC4	05/25/08	7.0	-	0.200	20406.77	1272.78	7232.87
LKC4	06/01/08	6.0	-	0.210	24236.28	1371.94	6490.69
LKC4	07/09/08	16.0	-	0.105	8774.15	356.91	3282.98
LKC4	07/13/08	14.1	-	0.126	10849.42	801.23	3570.90
LKC4	07/15/08	11.2	-	0.157	11245.97	1065.59	4802.00
LKC4	07/17/08	14.2	-	0.125	9672.30	738.40	3917.54
LKC4	07/20/08	16.5	0.175	-	5997.21	494.53	3473.34
LKC4	07/26/08	18.4	-	0.078	6881.44	370.69	2447.58
LKC4	07/28/08	19.8	-	0.061	6297.58	207.57	1611.23
LKC4	08/01/08	19.4	0.079	-	5793.48	252.17	2268.86
LKC4	08/04/08	20.8	-	0.049	4538.91	122.42	1711.48
LKC4	08/06/08	21.0	-	0.047	3169.42	55.34	1069.83

Sampling Location	Date	DTW cm	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- mg/s	NO_3^- mg/s	SO_4^{2-} mg/s
LKC5	10/05/06	-	0.112	-	10665.21	156.58	4178.52
LKC5	11/10/06	-	0.101	-	8155.08	301.18	3685.22
LKC5	10/25/07	-	0.021	-	3499.90	9.04	907.81
LKC5	04/07/08	24.0	0.310	-	41421.84	1292.88	12335.29
LKC5	05/25/08	11.5	-	0.560	49073.78	3672.18	19572.19
LKC5	06/01/08	12.0	-	0.550	50543.87	3427.38	15433.70
LKC5	07/09/08	33.0	-	0.130	9298.57	359.90	3623.76
LKC5	07/13/08	5.4	-	0.682	53724.67	4334.40	18914.83
LKC5	07/15/08	20.8	-	0.374	24750.20	352.63	3733.46
LKC5	07/17/08	26.3	-	0.264	1774.49	1542.37	8332.67
LKC5	07/20/08	29.2	0.212	-	14495.03	559.35	4214.30
LKC5	07/26/08	31.2	-	0.166	12862.13	857.61	5404.83
LKC5	07/28/08	28.8	-	0.214	17437.03	772.48	6421.25
LKC5	08/01/08	31.0	0.154	-	5916.60	291.02	2294.66
LKC5	08/04/08	33.7	-	0.116	10101.79	372.88	4157.84
LKC5	08/06/08	35.0	-	0.090	4618.29	96.02	1351.28
LKC5	08/08/08	37.8	0.045	-	2633.98	63.53	1441.71
LKC5	08/10/08	38.3	-	0.024	1631.46	34.66	890.39
LKC5	08/12/08	39.3	-	0.004	367.26	5.41	159.25

Sampling Location	Date	DTW cm	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- mg/s	NO_3^- mg/s	SO_4^{2-} mg/s
LKC6	10/05/06	-	0.145	-	12268.88	372.13	5196.25
LKC6	11/10/06	-	0.131	-	9197.39	454.33	4476.82
LKC6	10/25/07	-	0.024	-	3539.43	10.42	992.52
LKC6	04/07/08	34.0	0.359	-	43353.19	1847.46	13978.53
LKC6	05/25/08	29.5	-	0.348	25701.61	2624.07	11265.17
LKC6	06/01/08	30.3	-	0.342	30537.73	2553.01	9172.17
LKC6	07/09/08	50.2	-	0.166	9622.71	732.61	4405.09
LKC6	07/13/08	26.5	-	0.369	24074.62	2789.07	9391.88
LKC6	07/15/08	38.5	-	0.276	15220.64	2175.21	7793.63
LKC6	07/17/08	44.0	-	0.227	8327.71	1639.64	6660.85
LKC6	07/20/08	47.0	0.277	-	12789.87	2212.45	10834.25
LKC6	07/26/08	47.2	-	0.196	3208.73	1223.14	5248.97
LKC6	07/28/08	50.2	-	0.166	12601.20	773.14	3974.04
LKC6	08/01/08	49.8	0.205	-	19093.68	263.17	1217.28
LKC6	08/04/08	53.0	-	0.135	9062.11	628.31	4236.33
LKC6	08/06/08	54.8	-	0.115	6044.34	374.92	2793.30
LKC6	08/08/08	54.2	0.060	-	2672.16	202.80	1682.52
LKC6	08/10/08	52.6	-	0.140	7362.97	426.76	4518.29
LKC6	08/12/08	53.2	-	0.133	7757.82	408.82	4361.01
LKC6	08/14/08	52.2	-	0.144	9250.32	335.30	5016.68

Sampling Location	Date	DTW cm	Measured Discharge (m^3/s)	Calculated Discharge (m^3/s)	Mass Flux		
					Cl^- mg/s	NO_3^- mg/s	SO_4^{2-} mg/s
LKC7	10/05/06	-	0.145	-	12042.20	359.96	5123.39
LKC7	11/10/06	-	0.131	-	9297.15	453.71	4425.46
LKC7	10/25/07	-	0.024	-	2820.53	8.85	871.63
LKC7	04/07/08	-	0.359	-	42444.65	1894.51	14059.87
LKC7	05/25/08	-	-	0.348	25411.49	2673.27	11096.45
LKC7	06/01/08	-	-	0.342	29431.96	2827.41	9732.20
LKC7	07/09/08	-	-	0.166	9527.46	679.94	4017.64
LKC7	07/13/08	-	-	0.369	24319.69	2798.21	9280.37
LKC7	07/15/08	-	-	0.276	15591.54	2314.21	8020.59
LKC7	07/17/08	-	-	0.227	14328.81	1666.45	6716.22
LKC7	07/20/08	-	0.277	-	15149.22	724.32	3638.13
LKC7	07/26/08	-	-	0.196	10503.35	1236.81	5223.25
LKC7	07/28/08	-	-	0.166	7544.30	1041.08	5024.77
LKC7	08/01/08	-	0.205	-	10220.36	922.07	3920.14
LKC7	08/04/08	-	-	0.135	10658.16	592.99	4238.31
LKC7	08/06/08	-	-	0.115	3422.15	300.66	2001.57
LKC7	08/08/08	-	0.060	-	2838.79	194.85	1663.33
LKC7	08/10/08	-	-	0.140	6583.65	419.11	4490.56
LKC7	08/12/08	-	-	0.133	7803.09	362.76	4315.69
LKC7	08/14/08	-	-	0.144	8440.57	360.65	4758.87

APPENDIX C

T-TEST VALUES

Sampling Location		Chloride			Nitrate			Sulfate		
		df	T-Value	P-Value	df	T-Value	P-Value	df	T-Value	P-Value
LKC1	LKC2	58	0.210	0.835	58	0.231	0.818	58	-1.450	0.153
	LKC3	58	1.623	0.110	58	0.302	0.763	58	0.515	0.608
	LKC4	58	2.717	0.009	58	0.840	0.404	58	-0.946	0.348
	LKC5	58	4.030	<0.001	58	0.970	0.336	58	0.182	0.856
	LKC6	58	5.009	< 0.001	58	-1.157	0.252	58	1.157	0.252
	LKC7	58	5.261	< 0.001	58	-1.127	0.264	58	1.693	0.097
LKC2	LKC3	58	1.451	0.152	58	0.086	0.932	58	1.997	0.051
	LKC4	58	2.588	0.012	58	0.627	0.533	58	0.645	0.522
	LKC5	58	3.962	< 0.001	58	0.757	0.452	58	1.713	0.092
	LKC6	58	4.996	< 0.001	58	-1.371	0.176	58	2.705	0.009
	LKC7	58	5.266	< 0.001	58	-1.338	0.186	58	3.282	0.002
LKC3	LKC4	58	1.215	0.229	58	0.510	0.612	58	-1.546	0.128
	LKC5	58	2.751	0.008	58	0.633	0.529	58	-0.362	0.719
	LKC6	58	3.917	< 0.001	58	-1.381	0.173	58	0.634	0.529
	LKC7	58	4.223	< 0.001	58	-1.351	0.182	58	1.173	0.246
LKC4	LKC5	58	1.603	0.114	58	0.124	0.902	58	1.217	0.228
	LKC6	58	2.808	0.007	58	-1.871	0.066	58	2.338	0.023
	LKC7	58	3.112	0.003	58	-1.835	0.072	58	3.007	0.004
LKC5	LKC6	58	1.162	0.250	58	-1.988	0.052	58	1.045	0.300
	LKC7	58	1.419	0.161	58	-1.950	0.056	58	1.629	0.109
LKC6	LKC7	58	0.225	0.823	58	0.013	0.990	58	0.555	0.581

Segment		Chloride			Nitrate			Sulfate		
		df	T-Value	P-Value	df	T-Value	P-Value	df	T-Value	P-Value
S1	S2	34	1.263	0.215	34	-1.034	0.313	34	1.593	0.122
	S3	32	3.471	0.002	32	3.511	0.003	32	3.356	0.003
	S4	32	-1.920	0.084	32	-1.834	0.086	32	-1.953	0.069
	S5	35	2.449	0.021	35	-0.620	0.542	35	1.666	0.111
	S6	36	2.217	0.033	36	1.417	0.171	36	2.554	0.017
S2	S3	32	2.643	0.015	32	3.767	0.001	32	2.320	0.030
	S4	32	-2.384	0.028	32	-1.501	0.152	32	-2.395	0.028
	S5	35	1.641	0.112	35	-0.061	0.952	35	0.894	0.380
	S6	36	0.885	0.382	36	1.833	0.076	36	1.225	0.229
S3	S4	30	-3.685	0.001	30	-3.184	0.004	30	-3.394	0.003
	S5	33	-0.743	0.463	33	-2.870	0.007	33	-0.878	0.386
	S6	34	-2.150	0.043	34	-1.944	0.061	34	-1.239	0.226
S4	S5	33	3.098	0.005	33	1.411	0.168	33	2.676	0.011
	S6	34	2.771	0.013	34	2.230	0.038	34	2.840	0.010
S5	S6	37	-1.137	0.266	37	1.355	0.185	37	-0.088	0.930