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Spatio-temporal variability of stream nitrate in a small agricultural catchment in East-Central Pennsylvania

Christopher W. Shade
Lehigh University

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Spatio-Temporal
Variability of
Stream Nitrate in
a Small
Agricultural
Catchment in...

January 2001

***SPATIO-TEMPORAL VARIABILITY OF STREAM
NITRATE IN A SMALL AGRICULTURAL CATCHMENT
IN EAST-CENTRAL PENNSYLVANIA***

by
Christopher W. Shade

A Thesis

Presented to the Graduate and Research Committee

of Lehigh University

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Master of Science

in

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This thesis is accepted and approved in partial fulfillment of the requirements for the degree of *Master of Science*.

Date

Thesis Advisor:

Carl O. Moses

Committee:

Donald P. Morris

Edward B. Evenson

Department Chair:

Peter Zeitler

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Abstract

This paper reports on water chemistry data gathered at several sites across a small, medium-relief agricultural catchment in East-central Pennsylvania and their analysis using semi-empirical models that link these observations to spatial data generated using GIS. The chemistry data set includes measurements of nitrate, phosphate, and other solute concentrations at the mouths of the branches of the main stream and 10 tributaries over a 14-month period. These data were modeled using a modified rating curve approach, a log-linearized regression method that separates the dependence of concentrations on the temporal variables flow and season from the dependence on spatial variables. The model showed a statistically significant dependence of nitrate concentrations on farm extent, extent of non-riparian forest, extent of near-stream saturated sediments, and length of tributary at different gradient ranges. The effect of length and gradient suggested that catchments with different morphological characteristics have differing capacities to attenuate nitrate loads from the land. Specifically, catchments with more of their stream length at a low gradient have a greater potential to develop biogeochemical sinks for nitrate in the near-stream and in-stream environment than do catchments dominated by high gradient streams. The change in ratios of different catchment concentrations with temporal variables (fixed space) showed a pattern consistent with the inferred catchment-dependence of processing. The results also suggest that the width of riparian vegetated buffer alone was not a good proxy for the nitrate attenuation potential of a subcatchment, due to the varying presence or absence of near-stream saturated sediments in subcatchments.

1. Introduction:

1.1 Non-Point Source Pollution Concerns

Stream length and gradient are good indexes of a catchment's potential for attenuating nitrate inputs in low-order headwater catchments. The development of seasonally- or permanently-saturated flood-plain soils creates areas of high redox gradient that are conducive to denitrification of waters passing through from land to stream. In the medium-relief, hill-lands of east-central Pennsylvania these sediment accumulations form in low gradient stretches of first-order streams and in second or higher-order catchments, where energy has subsided enough for the stream to deposit some of its load. Lower gradient streams also provide a longer transit time, either through lower velocity alone, or, more importantly, through mechanisms of retention, such as woody debris dams or pool and riffle sequences, which allow sediment to accumulate and water to increase its residence time in the system. The longer transit time and sediment accumulations provide an environment more conducive to in-stream denitrification than do high-gradient, high velocity, bedrock-strath streams.

Landscape properties must be examined as directly as possible to understand the effect of spatial variability on the biogeochemical transformation processes of catchments. The method we present here involves the use of a solute-rating curve to separate flow and time from space. One rating curve, with regression-determined varying amplitude, is used for all of the subcatchments in a third-order basin, and GIS generated spatial data are used as continuous variables to account for variations in catchment sources and sinks-processes contributing to differences in stream nitrate concentration.

The separation of space and time is necessary to clearly understand spatio-temporal

variability of catchment processes in a view toward gauging the total impact of specific land-uses in various settings.

Even though water quality is clearly correlated with land-use (Hynes, 1969; Worrall and Burt, 1999; Correl, 1982), few tools have been developed for land use planning to simply but effectively monitor and evaluate changes in water quality and to predict impacts on water quality stemming from future changes. It is relatively simple to gauge impacts from point-source discharges into surface waters, but non-point source loadings, which build their effect cumulatively along the length of a stream and which characterize agricultural activities, are complex and difficult to predict. Not only are the flow paths from land to water difficult to predict, but there are often extensive biogeochemical transformations involved during transport as well. This complexity, combined with the limited monetary resources of farmers for infrastructure changes, makes it essential to have a realistic but pragmatic approach to controlling agricultural discharges into surface waters; one which can only be drawn from in-depth, interdisciplinary understanding of the biogeochemical cycles of impacting chemical elements and the effects on those cycles of the various environments encountered by the elements while in-transport.

Antropogenic eutrophication of surface waters in modern times, due to excessive loading of nutrient species, primarily nitrogen and phosphorus, has led to public concern and government legislation (*e.g.* Public Law 92-500 and section 319 of the Clean Water and Air act) requiring local and regional planning authorities to develop and implement plans to manage surface water quality (Karr and Schlosser, 1978). The recent movement from the EPA to impose total maximum daily load (TMDL) allocations to non-point

pollutant sources, including agriculture, silviculture, and forestry, has increased pressure to regulate or control non-point source pollution (Slaughter, 1999).

Non-point source pollution from agricultural activity takes of the form of surface and sub-surface runoff from agricultural land (Hynes, 1969; Pionke *et al.*, 1999; Collins *et al.* 1996), and includes pesticide, herbicide, and sediments, in addition to dissolved and particulate nutrient species. Many "conservation" farming techniques, such as conservation tillage, contour plowing, and grassed waterways, have been proposed and implemented to the ends of reducing inputs to surface waters. However, these techniques, lumped together under the term "Best Management Practices" (BMPs), have had relatively little scientific testing of their effectiveness on a watershed scale. Some models have been created to predict effect of individual techniques, mostly sediment transport models, but again, not in the context of the whole watershed (Hjelmfelt and Wang, 1999).

Many of the chemical solutes draining into surface waters from agricultural areas are nutrient elements (mostly nitrogen and phosphorus) and are thus highly biologically reactive. This aspect of agricultural pollution dynamics makes it imperative to understand the biogeochemical cycles that characterize the land-water interface, known as the riparian zone, and also to understand how geomorphic controls on both the riparian zone and stream channel will determine the type of biogeochemical processing that will take place. These processes include uptake and conversion to biomass by both higher plants and microbes, denitrification by bacteria, anion and cation exchange on clay and humic colloids, and sedimentation and burial (Gregory, *et al.*, 1991, Lowrance *et al.*, 1984; Peterjohn and Correll, 1983, Osbourne and Kovacic, 1993).

The complex nature of the multiple landscape and environmental interaction involved, and the pressing need to find practical solutions to non-point source loading problems will require a combination of field data collection, spatial data generation, and model development to test different scenarios of land management for their potential benefits. This study is intended to add to a growing body of works that serve to elucidate the nature of landscape and environmental interactions and their effect on solute transport to surface waters. We combine field and laboratory analyses from a one year study of a small group of low-order nested catchments with GIS spatial analysis and a combination of statistical and mechanistic modeling techniques to examine the interaction of the spheres of time and space in their effects on nitrate concentrations in streams. We also introduce the idea of using a single rating curve, generated from flow data at a USGS stream-gauge and then adjusted in amplitude to fit individual subcatchment tributaries, thus enabling a more detailed study of small-scale spatial variations. Finally, we will examine relationships in the raw data of different sites that will serve validate conclusions drawn from our statistical analysis, and hopefully illuminate the nature of the processes occurring throughout the subcatchments. These methods may also serve as a useful framework for studying other chemical species, or to look at a set of specific spatial questions, such as the effectiveness of various BMPs at reducing agricultural input to streams.

1.2 Previous Work

Previous field studies of nutrient inputs to surface water from agricultural land have tended to be either spatially or temporally based, relying on either synoptic ("snapshot") sampling (Grayson et al., 1997) or time series from a gauged weir or USGS gauging station (Bilby, 1981). Studies have also tended to be done on large catchments, which integrate many different processes and microenvironments into one sample (Johnson et al., 1997; Smith et al., 2000). Few studies have looked at spatial variability in the landscape and its correlation with stream chemistry in a small area of nested catchments.

More recently attempts have been made to link spatial and temporal variables together utilizing a log-linearized rating curve approach. Smith et al. (1997) used the a rating curve approach that included seasonality and spatial variables as the basis for their SPARROW model, though this was done at a very large scale (hydrologic cataloging units over the conterminous United States), making it difficult to delineate subtle differences in behavior of varying hydrogeomorphic environments and in the effects of various different combinations of landscape factors. Potentially illuminating effects of unique biogeochemical microenvironments may become obscured by larger regional geologic, anthropogenic, or biotic signals at this large scale.

In this paper we will provide a simple descriptive rating curve model, using a flow dependence coupled to a seasonal signal (Cohn et al., 1994) to separate the components of time and space and thus analyze landscape effects on nitrate concentrations in detail. One key innovation in our rating curve approach is our use of one archetypal rating curve, generated from flow values at a USGS gauge downstream of

the mother catchment, for all of the tributaries in the catchment. This one curve is then adjusted in amplitude with regression-determined coefficients to fit the different sites. This aspect allows greater flexibility to investigate more closely the spatial variability among the subcatchments. Because we do not directly gauge each site, we are modeling concentration instead of load, the variable commonly addressed in rating curve analyses (Cohn et al., 1994). We will apply this modeling approach to a data set collected from a small agricultural medium-relief watershed to explore the effectiveness of catchments with different spatial characteristics at ameliorating nitrate inputs from the land to the stream.

In addition to the fine-scale spatial resolution, the study area, located in the transition zone between montaine headwaters and lowland meandering streams and comprised of 1st, 2nd, and 3rd order streams, presents a unique opportunity to study how the geomorphic evolution of a fluvial valley (i.e. change from a straight and steep to a shallow gradient, meandering stream) affects the potential for biogeochemical transformations of solutes in that catchment. Lastly, we will examine the assumption of singular rating curve shape by looking at time dependence of ratios between sites (fixed space), and, using insights gained from our empirical model into the processes involved, with a view toward mathematically characterizing the mechanistic relationships between landscape and stream water chemistry, suggest a semi-mechanistic process-based model to apply more universally.

1.3 Temporal Effects on Stream Nitrate Concentration

1.3.1 Flow

A positive correlation between nitrate concentration and stream flow in northern temperate, agriculturally-influenced systems has been well-documented in past studies (Pionke, 1999; Cirimo and McDonnell, 1997) as streamflow contributions shift from predominantly baseflow at low discharge to an increasing fraction of interflow (soil water component) with high discharge. However there is also a dilution effect at peak storm flow, presumably caused by a move from interflow to surface runoff resulting in dilution of stream nitrate level during peak flows. Though there is an obvious spatial dependence of weather systems on regional scales, this can be regarded as a largely temporal effect as flow varies over time according to weather patterns that generally encompass the whole study area, an assumption especially valid in our small study area.

1.3.2 Seasonality

One of the strongest determinants of biological activity, in addition to moisture levels, is temperature. Temperate climates exhibit a considerable seasonal cyclicality. This cyclicality affects nitrate transfer from land to water in two ways. During the growing season (spring, summer, fall), plants in both the fields and riparian zones are actively metabolizing and taking up nutrients, including nitrate, leaving less in the soil pore waters. The process of microbial denitrification is an enzymatic one, making it extremely sensitive to changes in temperature, the warm summers providing an environment for more rapid denitrification in near-stream saturated zones, the stream water column, and stream sediments than during cooler times of the year. These two effects generally reinforce each other to yield lower nitrate levels during the summer and

higher nitrate levels during the winter. Opposite seasonal patterns have been found in unimpacted, low-nitrate sites (Mulholland, 1992). In these areas, temperature may be regulating nitrate release through organic matter mineralization processes, which are amplified at higher temperature. These systems are defined as nitrogen-limited, so atmospherically deposited nitrogen will be rapidly assimilated into biomass, only to be released later during decomposition.

There are also more complex seasonal patterns, including senescence of crops and litter decomposition, which will not be addressed in this study. Seasonality will be treated as a sinusoidal variation above and below a mean, the amplitude and zero-points of which will be determined through regression analysis.

1.3.3 Yearly Variation in Nitrogen Pool

Outflow of nitrate from a catchment is not dependent solely on recent inputs of nitrogen to the fields. Fertilizer applications are gauged by estimates of yearly losses of soil nitrogen to crops and to the environment. However variations in weather patterns from year to year cause fluctuations in the amount of nitrogen taken up into the crops and the amount leached from the fields. Drought years often lead to lower crop uptake, due to stunted growth, and low leaching potential, due to lack of water throughput. These factors will combine to result in a larger pool of nitrogen in the soil the following year, giving higher potential for mobilization of nitrate to the stream (Wente et al., in prep)

1.3.4 Long-Term Trends

Surface water solute concentrations may exhibit long-term trends of aggradation or degradation as pools of soil nitrogen change, due to changes in mass

balance of inputs and outputs. These changes are usually slow and difficult to analyze without a sufficiently long data set.

1.4 Two-Dimensional Spatial Variables Affecting Nitrogen Transfer -Land Surface Cover

1.4.1 Areal Extent of Farming

The major source of excess nitrate coming from the land in any agricultural area is from the farmland soil, be it pasture, feedlot, hayfield, or row-cropped field. To enable a simpler analysis of spatial variability of sinks, we have limited our analysis to tributary catchments that are row-crop and hay field dominated (>90% of farm area) and are predominantly in agricultural land use (>56% of land area). Tributaries are either first or second order, by system of Strahler, (1950), so as to reduce complication of mixing of tributaries. We then assume even distribution of fertilizer on crop lands, so that differences between nitrate levels in each catchment are due to differing extents of agricultural use (source) and differing environments for biogeochemical transformation (sinks), presumed to be primarily denitrification and biomass uptake in the riparian zone and within the water column and sediments of the stream. This is a simplification of sources and, owing to our more thorough treatment of spatial influences on sink-environments, may bias the model's accuracy towards times when sinks become a more dominant force in controlling the chemistry of the stream water.

1.4.2 Riparian Buffering:

Regardless of non-point source loading type, one of the main biogeochemical influences shown to moderate land use effects is the extent of the riparian zone buffering the stream from the land use in question. Previous studies in agricultural areas have

shown a reduction of concentration of nutrient species (*i.e.* both total and dissolved nitrogen and phosphorus) in surface and subsurface flow moving through the riparian zone towards the stream (Karr and Schlosser, 1978; Schlosser and Karr, 1981; Peterjohn and Correll, 1984; Lowrance, *et al.*, 1984; Gregory, *et al.*, 1991; Osborne and Kovacic, 1993). These reductions encompassed a wide range of environment types and nutrient-scouring effectiveness (see review in Osborne and Kovacic, 1993). The effect seemed to be spread between N and P uptake and conversion to biomass by microbial life and vegetation and denitrification in riparian soils. Different vegetation types, presumably due to litter quality, root-microbe interactions, physical characteristics, and successional stage, create different potentials for buffer effectiveness, as do different buffer morphologies and slopes (*e.g.* seasonally waterlogged floodplain soils provide better conditions for denitrification than do drier toeslope and hillslope soils - Gregory *et al.*, 1991; Cirimo and McDonnell, 1997). In an unimpacted watershed with low nitrogen concentrations, however, Mulholland (1992) showed riparian zone can be either a source or a sink depending on redox conditions. Cirimo and McDonnell (1997) review studies which have shown that near-stream saturated sediment zones and riparian wetlands are active sites for nitrogen transformation, including removal by redox change of reactive aqueous nitrate to unreactive evolved nitrogen gas (denitrification), uptake into and sequestration in biomass, and other redox changes, including ammonification and nitrification, and point out that "N transformation and retention should occur where hydraulic residence time is increased and where saturated conditions prevail." This leads to an inference that geomorphic characteristics (*i.e.* the shape of the valley and the gradient of the stream) in a watershed may exert a control over the catchment's ability to

attenuate N inputs by regulating sediment accumulation and hydrology. There may also be a significant difference in the attenuation potential of high-gradient hillslope forested riparian buffer versus a low-gradient wetland/saturated sediment or combination forested-wetland riparian buffers, a distinction that has not been expressly addressed in previous studies (Peterjohn and Corell, 1984; Lowrance *et al.*, 1984; Osbourne and Kovacic, 1993), presumably because they were done on relatively flat landscapes (e.g. Illinois, and the Maryland and Georgia coastal plains) compared to those addressed in this study.

1.4.3 Non-riparian Forest

Forests are areas where there is presumably no added nitrogen, save for atmospheric deposition. In agricultural areas atmospheric deposition should be inconsequential compared to fertilizer inputs. Depending on whether the forest areas are aggrading or at steady state growth, they may act as a sink for nutrients or be neutral. Though there are small seasonal pulses of discharge from winter and spring decomposition periods, the overall nitrate contribution of a forest is much smaller than that of agricultural fields (Correll, 1981). Also, certain combinations of vegetation and soils may encourage denitrifying bacterial communities, creating another potential sink for nitrate moving from land to stream (Gregory et al, 1991), depending on the hydrologic proximity of the farm land to the forest or soils in question (Wente, 2000).

1.4.4 Residential Areas

The effect of residential land use on nitrate export depends strongly on whether there is a sewage system in place or whether the houses are using septic drain fields. Though little data is available as to the effect of residential non-point source additions, presumably nitrate export will be lower than from agricultural fields due to

denitrification and ammonification in the reducing conditions of the septic drainfield, however this may vary according to the efficacy of the drainfield. A spot sample we gathered at the emergence of a stream draining a housing development gave a nitrate value about 50% lower than purely cropped + riparian forest catchments on that same date (unpublished data). Residential areas also frequently use significant amounts of lawn and garden fertilizers, but nitrate levels are expected to be between those of forested and agricultural area.

1.5 Three-Dimension Spatial Variables affecting Nitrate Transfer- Geomorphology

1.5.1 Geomorphology and In-Stream Processing:

Lotic systems are, by their nature, dynamic, both physically and chemically. In addition to differential treatment of loads from the land along the length of the stream, there are also many chemical transformations within the water column and channel sediments. These include transitions between solid and aqueous phases, aqueous and gaseous phases, and between organic and inorganic species. Many of these processes are, in a variety of ways, enhanced, regulated, catalyzed, or modified by the near-stream habitat and the character of the streambed and surrounding sediments. Though the effect of riparian buffers on nutrient loads flowing through them is well documented, little information is available as to the influence of near-stream habitat on the processing of waters already in the stream. Possibilities for effect center around biogeochemical transformations within the hyporheal zone and include anion and cation exchange with humic and clay colloids, denitrification in sediments and in the water column, bacterial uptake and utilization of nutrients, and DOC export to stream waters from riparian soils (Grimm et al., 1984; Cirimo and McDonnell, 1997).

Flow regimes along the length of a stream, dictated primarily by streambed morphology and stream gradient, play a major role in processing of in-stream nutrients by dictating the degree of oxidation or reduction in and accumulation of sediments in any reach of stream and also the ability of algae and aquatic plants to establish themselves on or along the streambed. It is only when bacteria in sediments have exhausted the supply of dissolved oxygen that they will use nitrate as an electron acceptor in their energy-generating metabolism. Thus mechanisms of flow retention, which provide slow-moving, potentially reducing conditions, are critical to in-stream processing. We will use stream gradient as a proxy for the tendency for a stream section to have mechanisms for retention (the lower the gradient the more likely the build up of woody debris and formation of pools), and thus more possible zones with the reducing environment necessary for efficient denitrification. Though this is a simplistic measure of in-stream processes, it is one that can be acquired relatively easily for any area without a field survey, and that is constant over a span of several years. A more detailed treatment of in-stream processes and the effect of near-stream habitat on those processes is beyond the scope of this study.

1.5.2 Geomorphology and Near-Stream Saturated Sediments - "the floodplain"

The strong biogeochemical effect of near-stream saturated sediments and riparian wetlands on the chemistry of water passing through from the land to the stream has been extensively observed, but the chemical complexity of these redox reactors defies most modeling attempts (see review in Cirimo and McDonnell, 1997). The fate of agricultural-level nitrate in these zones is, however, qualitatively certain. The near-stream saturated zone, with its high carbon soils from litter accumulation and low oxygen

levels, provides an ideal environment for bacterial denitrification. The saturated region expands and contracts with changes in both seasonal and episodic hydrologic conditions. However, the areal extent of this saturated zone depends on the slope of the land adjacent to the stream. In the high relief streams, there is no floodplain sediment build up at all. Since sediments do not readily find places to deposit and are washed out easily in the fast moving waters. The near- stream zone here will likely be an oxidizing zone with a shallow, mineral soil.

Once a stream has cut down enough to slow down, lose energy, and start depositing its load, there can be build up of a floodplain with its saturated sediments and high carbon content, conditions favoring denitrification. Typically, these areas will act as a source for carbon and a sink for nitrate en route to the stream (David et al., 1997; Peterjohn and Correll, 1984), depending on their lateral extent, vegetation, and the valley width profile. The wider and more gently sloping this area is, the longer the residence time of water transiting through this environment and the greater the chances for retention and/or biogeochemical transformation.

Again here, stream gradient is intertwined with a key issue in solute transport and transformation. In the case of the riparian soils, nitrogen transformation processes work strongly on water in transit to the stream from its non-point source, though the near-stream environment expectedly has also been shown to influence in-stream chemical environment and processes through diffusion and exchange with surrounding pore waters (Grimm et al., 1984).

1.6 Model Theory

The combined influences of the above processes on the chemical composition of stream water can be summarized in the form of a simple end-member mixing model (Fig. 1). Thus, streamwater nitrate levels reflect what remains after stream system sinks act on the mixture of flows entering it. In equation form, this can be written as:

$$C(Q_i) = \left[\sum_j C_{fp} \cdot X_{fp}(Q_i) \right] \cdot (1 - loss_{transport}) \quad (\text{eq. 1})$$

The terms in equation 1 depend on temporal variables, particularly season and discharge, in different ways. Among the three end member concentrations, the most significant seasonal variations occur in the interflow end member since a) groundwater temperatures are more stable and less influenced by surface processes and b) runoff likely has variable and low concentrations. The partitioning of flows among the three pathways is clearly a function of stream discharge, although not a monotonic function due to the different flowpaths employed on the rising and receding stages of high flow events. Finally, the extent to which stream-system sinks remove nitrate will depend on the residence time of water within the system, which in turn will depend inversely on discharge, and on season.

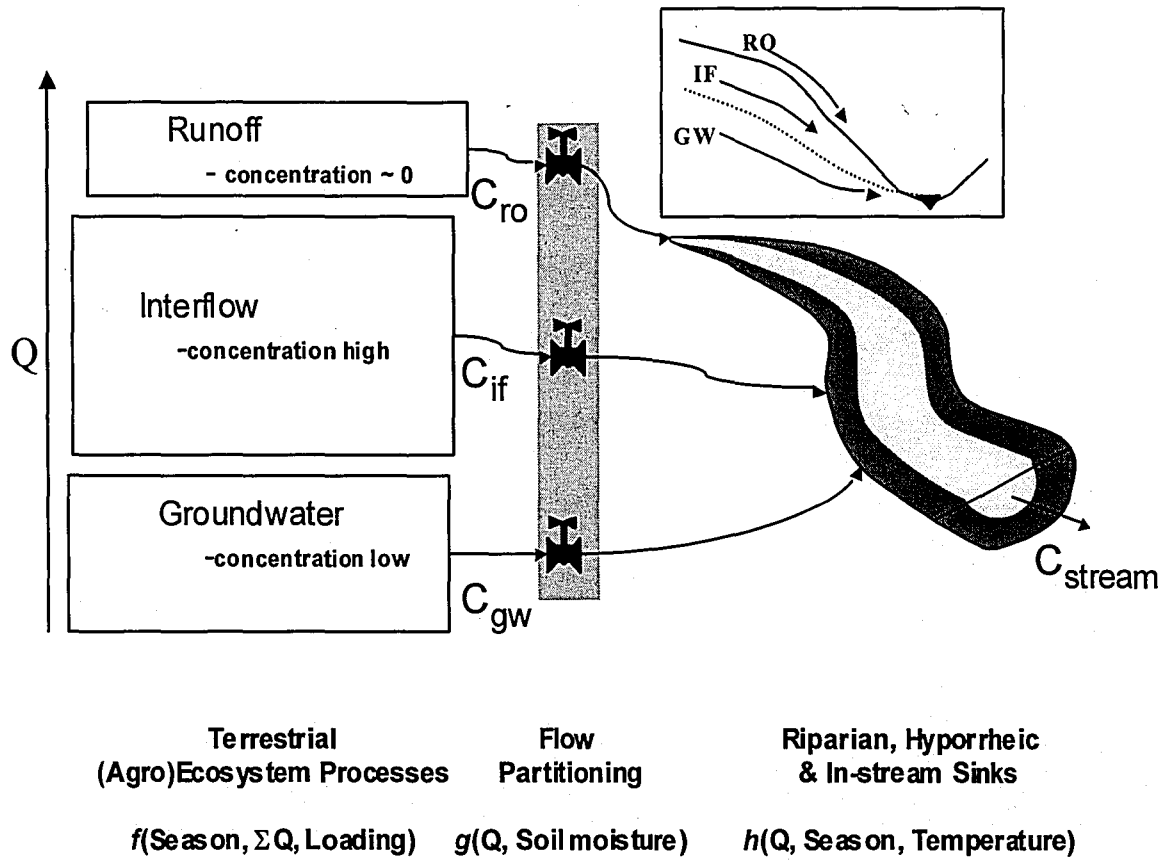


Figure 1. Schematic of variables affecting in-stream concentration of nitrate.

2. Materials and Methods

2.1 Site Characterization

The Lyon Creek is a fourth order tributary, by the classification scheme of Strahler (1950), to the Jordan Creek in the Lehigh River Basin of East-Central Pennsylvania (fig 2). Its basin covers 19.4 km² and has 31,558 linear meters of stream, which is divided into two fault-bound branches separated by a ridge (fig. 3); see also geologic map, fig. 20). The bedrock in the basin consists of Ordovician Martinsburg and Hamburg sequence shales, and soils are developed from the shale parent material. The dominant land use in the catchment is agriculture (68% of the land surface), but there are some houses and residential developments (5%) and a few commercial lots (<1%). The remainder consists of riparian vegetation (14%), riparian wetlands (2.6%), and non-riparian forest (9.9%) and roads (<1%), (fig. 3; Appendix 1).

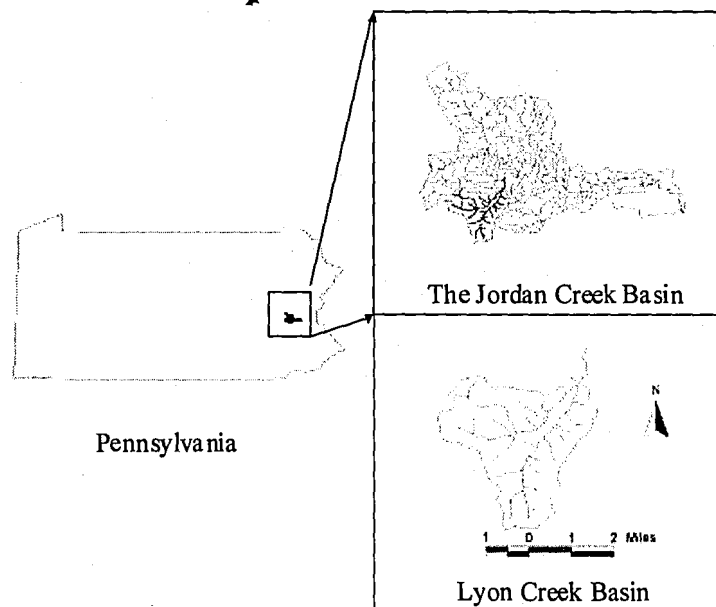


Figure 2. The study area.

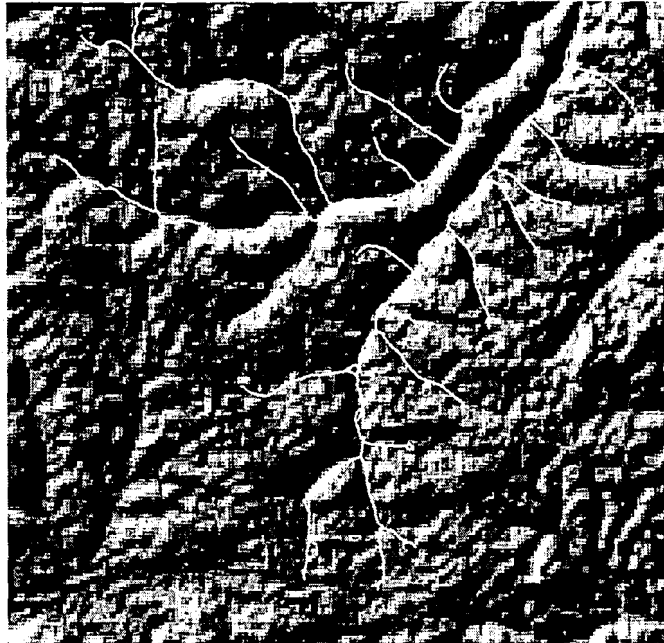


Figure 3. Shaded-relief image of Lyon basin (from USGS digital orthophoto quarter-quad - Slatedale NW).

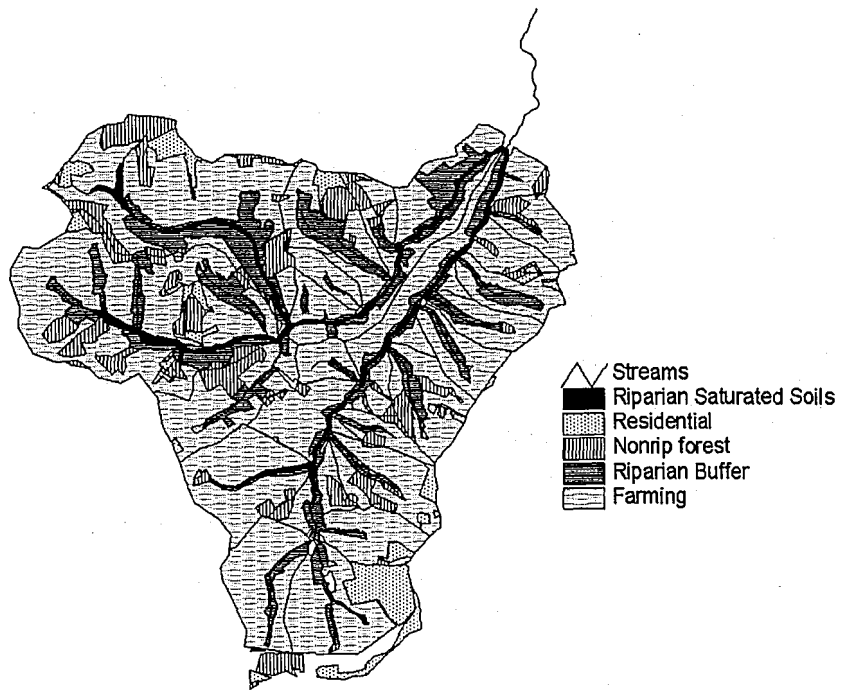


Figure 4. Land use in the Lyon Valley

2.2 Sample Handling and Processing

Streamwater samples were collected in a 1-L HCl acid-washed high-density polyethylene bottle (HDPE - Nalgene) using a method similar to an integrated depth sampler, use of which was prohibited by shallow depth. The bottles were moved up and down and side to side through the water column while filling to get a sample of the stream water. No air was allowed in the bottle and the samples were immediately placed on ice in a cooler and transported to the lab within 8h of collection for filtration and treatment of subsamples. Two subsamples were vacuum filtered through 0.45 μm pre-rinsed nylon membrane filters. One 125ml subsample was acidified to below pH 2 with 200 μL of concentrated sulfuric acid for analysis of metallic cations, ammonia, and dissolved organic carbon (DOC). A second filtered subsample was left unacidified for nitrate and phosphate automated nutrient analysis, chloride and sulfate anion chromatography, and colorimetric silica analysis. An unfiltered subsample was used for Gran-alkalinity titration. Titrations were performed the day of sampling, nutrient analysis was performed within 24 hours, and other analyses were performed within 30 days of the sampling, as time permitted.

For some samples where only nutrient analyses were performed, samples were taken in the same manner as the 1-litre samples but using 125-ml HCl acid-washed HDPE Nalgene bottles. The samples were kept on ice during transport and then filtered through pre-rinsed GFF filters and kept at 4° C until analyzed (within 24h).

2.3. Sample Analysis

Nutrient ion analyses for nitrate-N, ortho-phosphate (SRP), and ammonia-N were performed on a Lachat/Zellwegger auto-analyzer. Chloride and sulfate anions were analyzed by ion chromatography using a Dionex AS4 analytical column. Metallic cations were analyzed using ICP atomic emission spectroscopy. Dissolved silica, as H_4SiO_4 was measured by molybdosilicate colorimetry. DOC was measured on a Shimadzu TOC analyzer. All analyses were performed as described in Standard Methods (APHA, 1998). Gran-Alkalinity is calculated by titrating with 0.1N HCl and plotting on Gran curves (Gran, 1952).

Site measurements of pH, conductivity, DO, and temperature were made with a Hydrolab Datasonde II datalogger, outfitted with a Scout field display. During a repair period, a YSI O₂ meter, Orion pH meter, and Denver Instruments conductivity meter were used.

2.4 Spatial Data Acquisition

GIS coverages were acquired or created for the study area. Sources included the National Resource Conservation Service, the Lehigh Valley Planning Commission (LVPC), the Lehigh Earth Observatory, and the USGS. All coverages were "groundtruthed" with spatially referenced USGS digital orthophoto quarter-quads, which were ortho-corrected by the LVPC. Riparian buffer zones were delineated from aerial photos and checked in the field for current accuracy. Land use was modified from a LVPC land use map, using aerial photos and field observations. Subcatchments were manually delineated using DEM-generated topo maps and USGS paper quads and their boundaries digitized. The low-resolution of currently available DEMs precluded

computer-generated watershed delineation and necessitated the use of paper maps for reference. Saturated floodplain soils were digitized from county soil maps from the DCNR. All spatial data used in the regressions were calculated from a combination of ArcView and Arc/INFO GIS softwares, with the exception of the stream profiles, which were generated using SigmaScan software. USGS 7.5 minute quad maps were digitally scanned as TIFFs and put into SigmaScan along with markers on the map for distance. The software allows calculation of area or distance by triangulating from three known points. Profiles are generated by measuring the distance along the length of the stream between each topographic contour (fixed rise).

2.5 Model Development

2.5.1 Descriptive Empirical Model

2.5.1.1 Approach

The mathematical model for data analysis was based on the log-linearized rating curve approach (Cohn et al., 1992). This approach is based on a solute's load being proportional, either directly or inversely, to stream discharge. The rating curve can also incorporate a seasonal signal into the curves of species that are temperature dependent, like nitrate is.

The typical usage of the rating curve is to employ one curve for each site, with concentration and instantaneous discharge being measure at each site for each sampling date. In some cases, flow at a gauge downstream from the sampling site was used to develop the rating curve (Smith et al. 1997).

Our approach represents a departure from the one site - one curve approach. We use one daily average flow value, downstream from the basin, to be a proxy for flow

in all of the subcatchments in the basin. We consider this approach reasonable due to the small scale of our study area. We are exploring the hypothesis that within a limited area, parameters of the rating curve are constant, with the exception of the (site-specific) intercept. If that hypothesis were correct, then we could substitute in spatial variables for the intercept parameter to find the causes of the differences in nitrate concentrations of streams draining different catchments. A reduced precision of flow dependent fit is expected, but the tradeoff is for an increased coverage of spatial variability.

To test whether our hypothesis of rating curve parameter constancy we utilize an extended form of covariance analysis where a class variable for each site, j , is fitted with a coefficient, λ_j , to adjust the amplitude of our one rating curve to fit each sites data (eq 2). The class variable approach gives us the best possible fit of a single, amplitude-adjusted rating curve to the data set, and thus tests the suitability of the data set for this approach of separating the dependence of concentration on space and time in order to execute a spatial analysis.

$$\ln(NO_3) = \lambda_j + \ln f(Q) + \ln f(season) \quad (\text{eq.2})$$

If the fit of the class variable approach is deemed acceptable, the next step is to substitute in individual continuous spatial variables for the class variable, using multiple linear regressions to gauge to contribution of that variable towards explaining the variability in the data set above that from the temporal variables of flow and season. The final step is to select a combination of variables that best represents or proxies the sum of controls on the concentration of dissolved nitrogen in the stream waters of the subcatchments.

The greatest advantage of the rating curve approach is that it removes much of the seasonal and flow- dependent bias on nitrate concentration and can thus be preferable to the straight use of averages, which can be easily biased by environmental conditions when the samples are collected, especially if every site is not represented each time. This accounting for temporal variation may allow a deeper exploration the spatial variability in a study area without needing to sample every site on every sampling date.

The rating curve model is commonly applied with log-transformed data in order to use a linear regression approach. However, there are issues of transformation bias involved in this approach (Draper and Smith, 1981). Cohn et al. (1992) have shown that, despite the statistical complications involved in log-linearized models of stream transport, they still provide satisfactory estimates, even when the models have shown significant lack of fit. In order to avoid overestimation of fit, we report the R^2 of a $y=x$ fit to a scatter plot of the observed data vs. re-transformed model prediction data using SigmaPlot graphing software with coefficients generated from a SAS general linear model (GLM).

2.5.1.2 Terms

Different chemical elements have different flow dependences and thus differently shaped rating curves, usually due to the relative concentrations of stream water contributors. In the case of nitrogen in areas without point-source discharges, the contribution end-members are ground water (baseflow), soil water (interflow), and, at very high discharge, surface runoff (overland flow). The soil water concentration, due to fertilization, is usually higher than the groundwater concentration in agricultural areas. Consequently, there is a rise in concentration as discharge increases, bringing with it an

increasing fraction of the interflow in the stream water. However, there is also need for a decay term that will kick in at higher flows and represents a dilution of interflow by an increase in overland flow. Though the runoff concentration is probably not zero, we will assume the runoff concentration to be negligible, compared to interflow. The common approach to flow dependence is to use a power series of flow (Cohn et al., 1992). Smith et al. (1997) use $(\ln Q)$ and $(\ln Q)^2$, but others have been used.

Nitrate, being a biologically reactive species, exhibits a seasonal pattern, which is based on temperature and growing season, as well as its flow dependent pattern. However, since flow is a weather driven phenomenon, it is also coupled to seasonality. Thus the seasonality term acts like an amplifier of the general flow trends (fig. 5). We have adopted the common approach of creating a sinusoidal function (first-order Fourier) composed of both sine and cosine of the fraction of time (td) elapsed since an arbitrary starting point (in our case January 1, 1999) for season (eq. 3) (Cohn, et al., 1992).

$$f(\text{time}) = \lambda_1 2\pi \sin(td) + \lambda_2 2\pi \cos(td) \quad (\text{eq. 3})$$

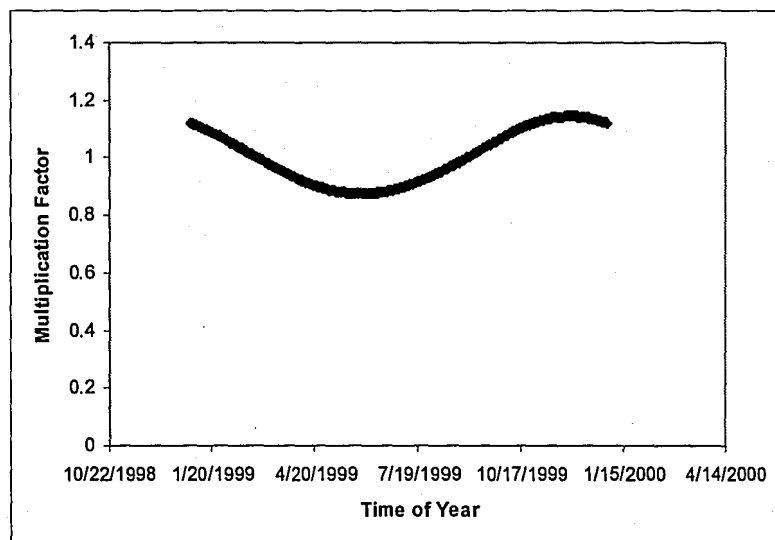


Figure 5. Multiplicative effect of seasonality term

A rating curve was also constructed for dissolved calcium concentration in order to examine the relationship of the nitrate rating curves to the mixing of different end-members. Calcium, being less biologically reactive than nitrogen, should yield information about the mixing of different end-members, especially the mixing of groundwater and surface water. The rating curve will include the previously explained terms of USGS gauge flow, seasonality, and class variables for the sample sites (eq. 4).

$$Ca(obs) = Q \cdot \exp\{\lambda_1 \cdot \sin(2\pi td) + \lambda_2 \cdot \cos(2\pi td) + \lambda_5(site)\} \quad (eq. 4)$$

Selected temporal and spatial variables will be included in a spatial multiple regression, in order to determine significant variables affecting Ca concentration.

2.6 Ratio Analysis

Ratios between sites (fixed space) will be examined as functions of time and the temporally-dependent variables, flow, and temperature. By fixing space and looking at the change in relationships between sites with time, we hope to gain insights about processes and verify the inferences about concentration-controlling variables and in-transport processes that we draw from our fixed-temporal spatial analysis.

An index of temperature is used to approximate relative soil temperature. The index for a given day, d_i , is a weighted average of the high (T_h) and low (T_l) temperatures recorded at a local NOAA weather station over a three day period (eq. 5). The ratio of concentration between the branches, site L9:L1, varied from 1.36 to 2.27, and the ratio between the average concentrations was 1.56. The ratio of farming extent, site L9:L1, is 1.25. The ratio of saturated floodplain sediments, L9:L1, is 0.51.

$$Temp. Index(d_i) = \frac{\{[3 \cdot T_h(d_i) + 2 \cdot T_h(d_{i-1}) + T_h(d_{i-2})]/6 + [3 \cdot T_l(d_i) + 2 \cdot T_l(d_{i-1}) + T_l(d_{i-2})]/6\}}{2} \quad (eq. 5)$$

3. Results

3.1 Spatial Variability (GIS)

Fewer, larger tributaries feed the northern branch of the Lyon creek, designated L1, than feed the southern branch, designated L9 (fig. 11). Eight streams feed the northern branch (though we have only divided it into 6 subcatchments for sampling logistics), while 12 streams feed the southern branch, though the total drainage area of each branch is similar (the south branch is 2% larger). Land use properties for the whole catchment are described above in the materials and methods section. The southern branch had more farm area (76% of land use) than the northern branch (62%). The northern branch was covered by more riparian buffer (21% vs. 13%) and non-riparian forest (13% vs. 7%), and less residential area (4% vs. 6%) than the southern branch. Individual tributaries varied in their properties. See Appendix 1 for complete spatial data.

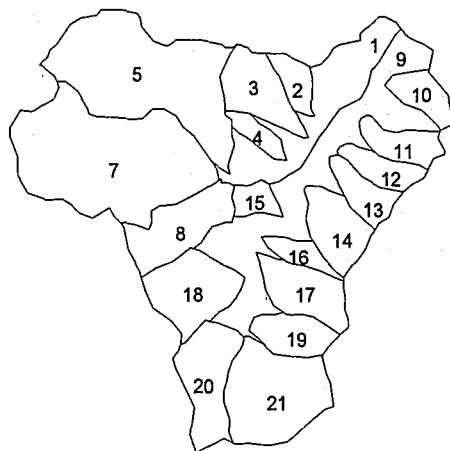


Figure 6. Tributary numbering scheme

3.2 Chemical Data

3.2.1 Nitrate Data

The Lyon basin was ranked as a "low threat" by the Pennsylvania-DEP for nitrogen loading relative to other basins within the Jordan Creek catchment (fig. 7), based on fertilizer sales and livestock holdings. This is mainly due to the low number of livestock, relative to other basins in the area.

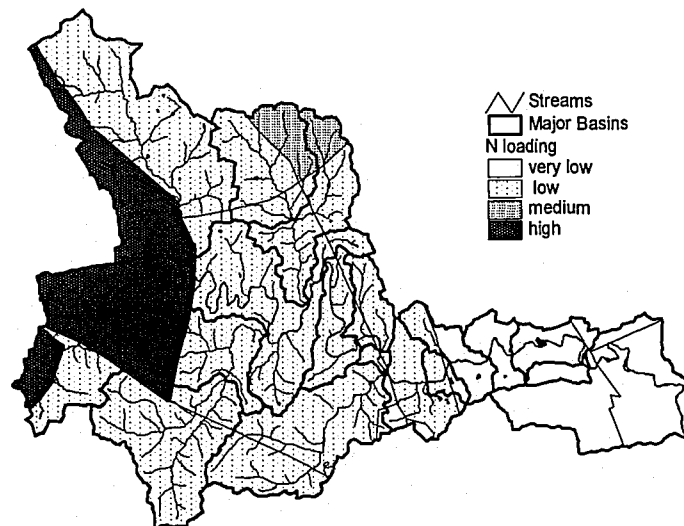


Figure 7. Relative Nitrogen loading in the Jordan Creek Catchment.

Throughout the study, measured stream nitrate levels never exceeded the 10ppm $\text{NO}_3^- - \text{N}$ (all concentration levels subsequently referred to will be in these units) level set by the EPA as a limit for a safe drinking water level. Confluence stations ranged in concentration from 0.29 to 5.37. The concentration in the southern branch of the Lyon Creek ranged from 0.5 to 5.37 with an average of 3.50 and was always higher than that of

the northern branch, which ranged between 0.22 and 3.66, with an average of 2.25. Concentrations in the tributaries ranged from 0.18 to 7.8 and demonstrated strong variation between sites. All sites exhibited strong variation with the temporal variables of date and flow (fig. 8). Data also showed trends with spatial variables, especially fraction farm, fraction non-riparian forest, stream length, and stream gradient (fig. 9).

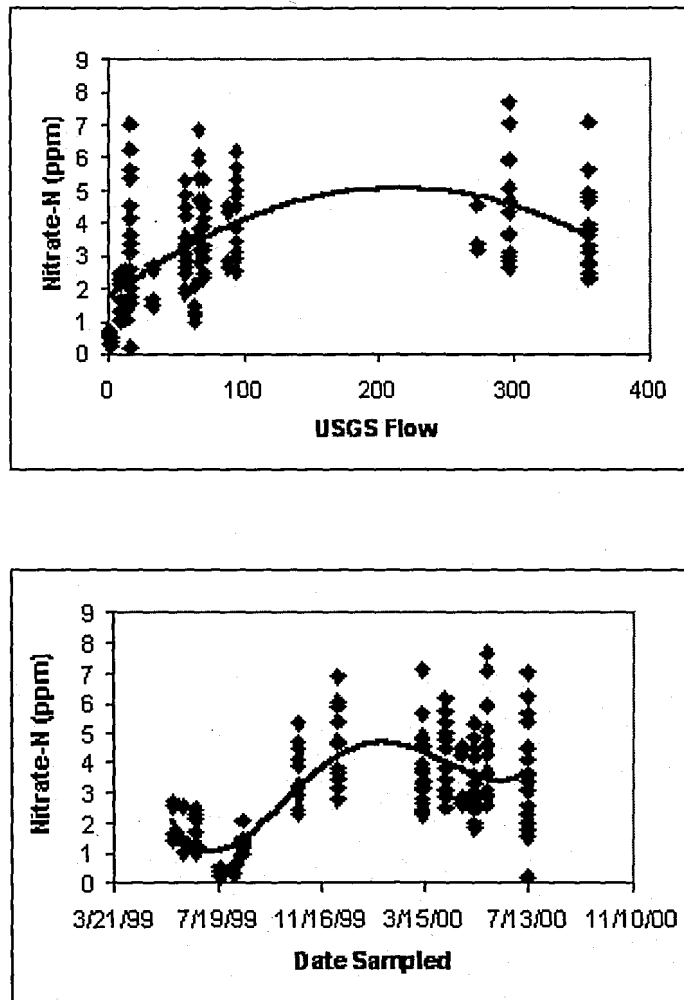


Figure 8. Dependence of $\text{NO}_3\text{-N}$ concentration on temporal variables.

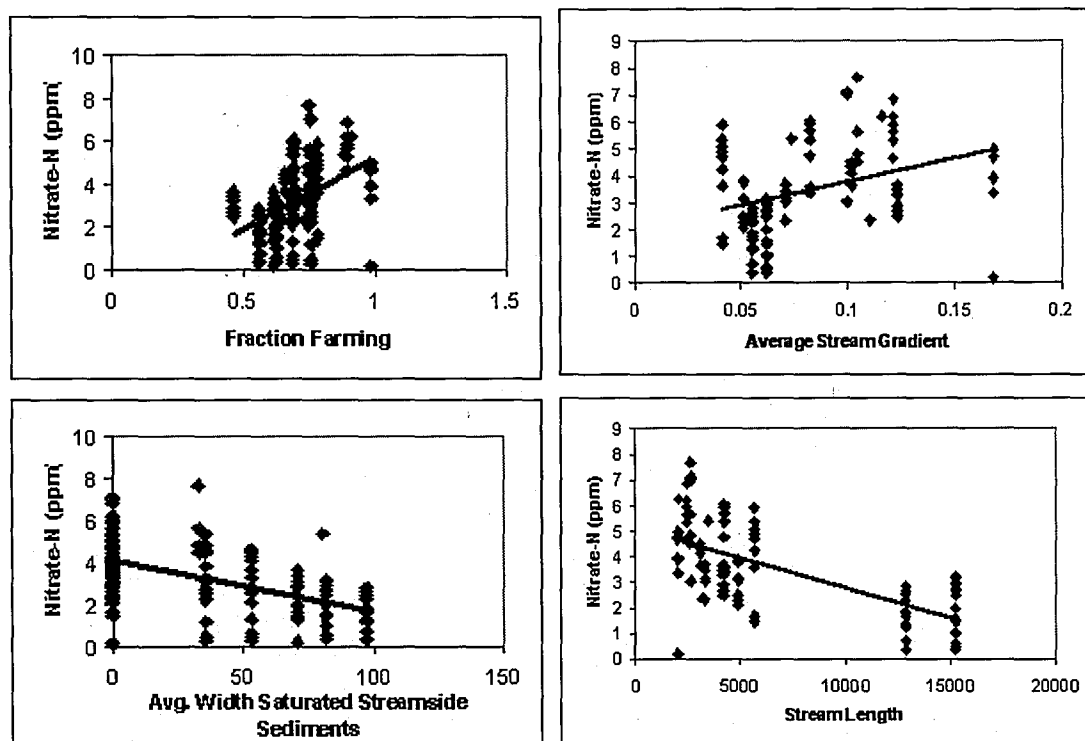


Figure 9. Dependence of $\text{NO}_3\text{-N}$ concentration with selected spatial variables. Landscape properties, fraction farming and saturated floodplain sediments, are for all sites; stream characteristics, length and gradient, are for tributary sites only.

Ratios can be calculated between the two main branches and the change in that ratio with time (fig. 10) and the temporally-dependent parameters of flow and temperature (figs. 11). The ratio shows a negative trend with flow and a positive trend with temperature.

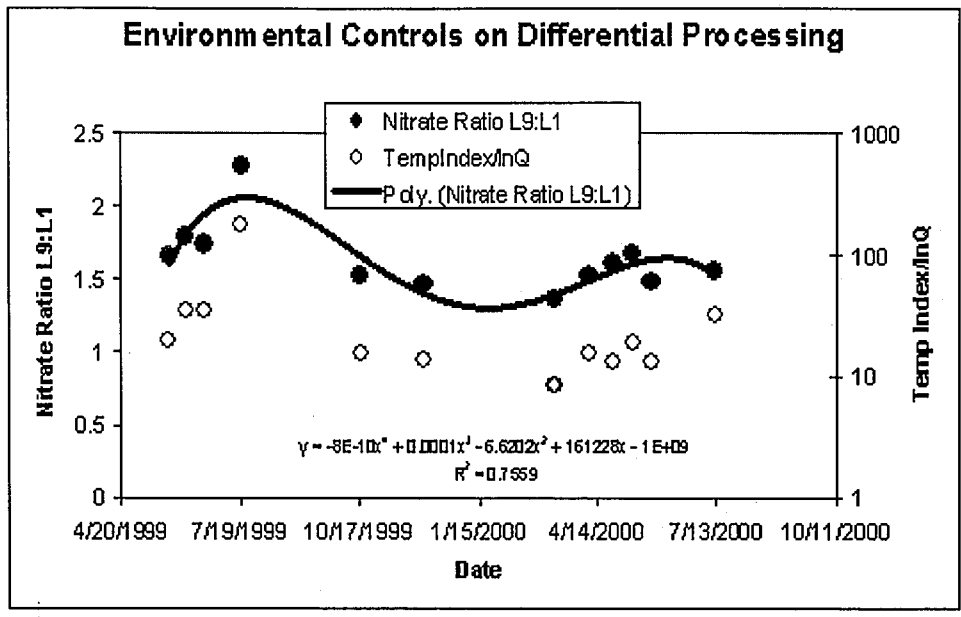


Figure 10. Change in ratio of South branch (L9) to North branch (L1) nitrate concentrations over the the sampling period.

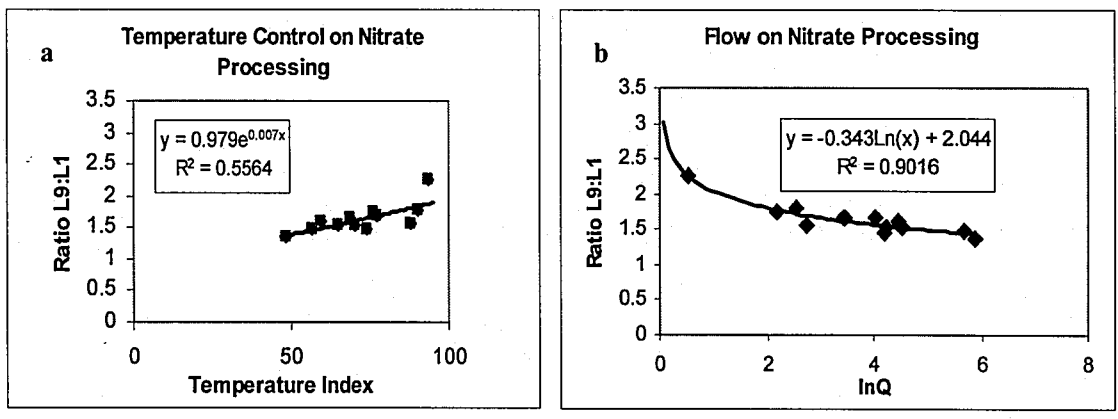


Figure 11. Changes in nitrate ratio L9:L1 with variation in temperature (a) and flow (b).

3.2.2 Ca Data

Calcium concentrations ranges from 9.53 to 23.91 ppm dissolved Ca. The northern branch, L1 was consistently lower in concentration than the southern branch, L9. Branch L1 ranged from 11.39 to 20.63, with an average of 16.18, while branch L9 ranged from 13.14 to 21.51, with an average of 18.29. The data showed apparent temporal trends with *date* and *flow* (fig. 12), and showed an apparent positive trend with the spatial variables *farm fraction* and negative trend with *average gradient* (fig. 13). There were no apparent trends with the spatial variables *stream length* and *average width saturated streamside sediments* (fig. 13). The ratio between the two branches showed no trend with the temporal variables of *flow* and *temperature* (fig. 14).

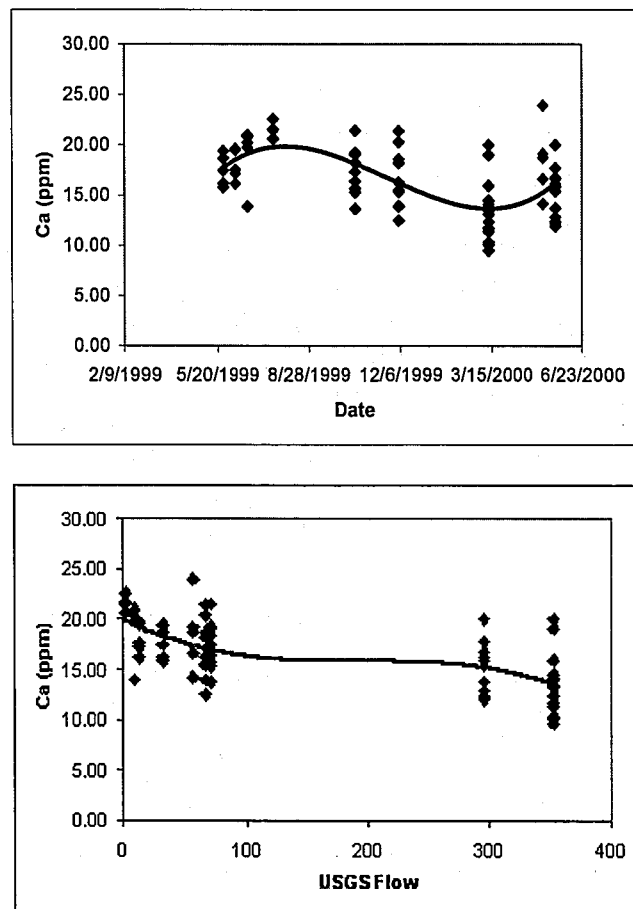


Figure 12. Dependence of Ca concentration on temporal variables.

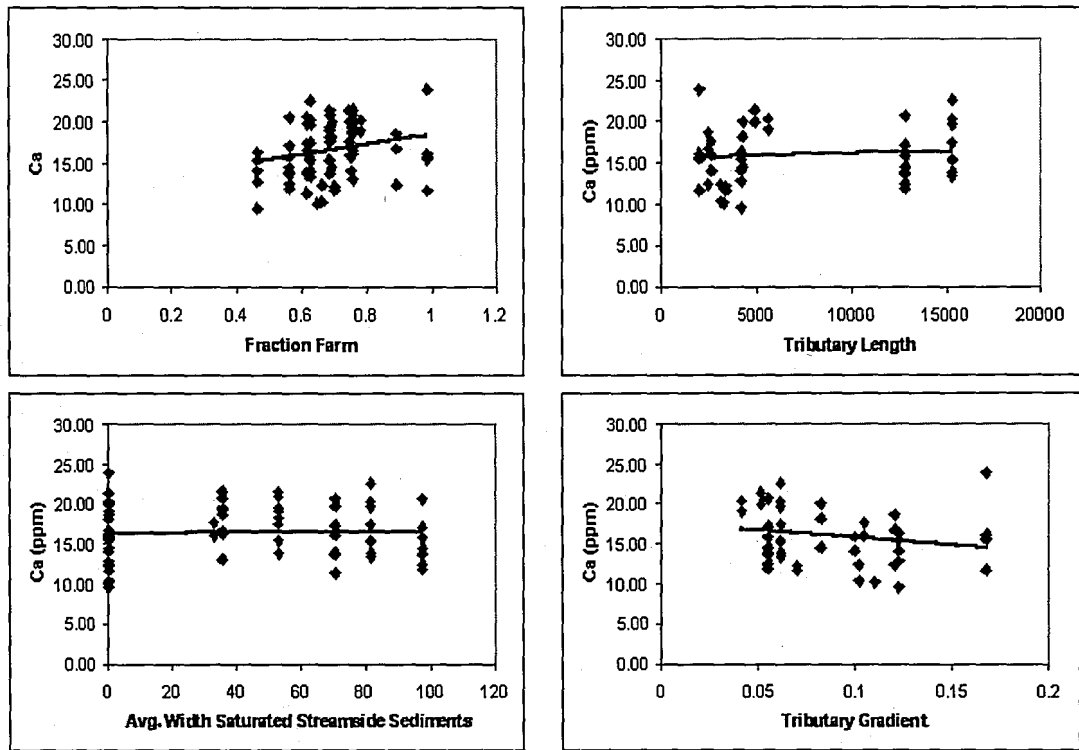


Figure 13. Dependence of Ca concentration on selected spatial variables.

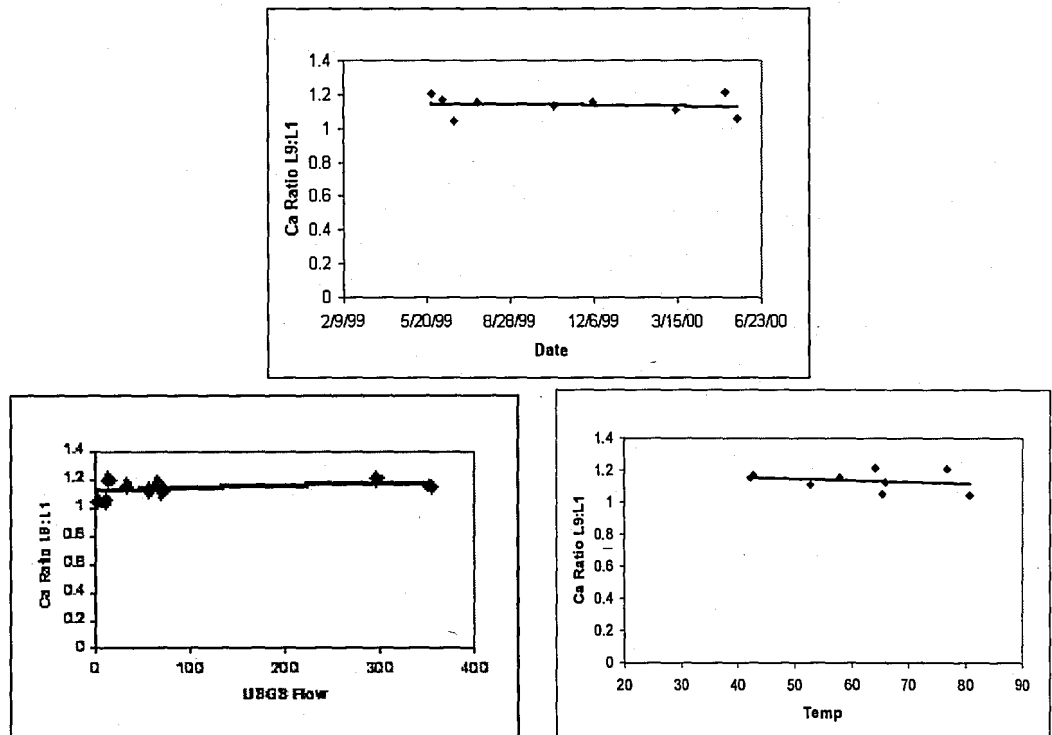


Figure 14. Changes in Ca ratio L9:L1 over the sampling period (a) and with variation in temperature (b) and flow (c).

3.2 Model Results

3.3.1 Nitrate Rating Curve (Empirical) Model

We first used the power series of flow terms $\ln Q$ and $(\ln Q)^2$ and found this to be satisfactory for the confluence stations, but the tributaries needed a higher peak and a stronger decay at high flow. We use an increase with $\ln Q$ and a decrease with Q^2 for the tributaries (fig. 15). Parameter coefficients are calculated from regressions of the data.

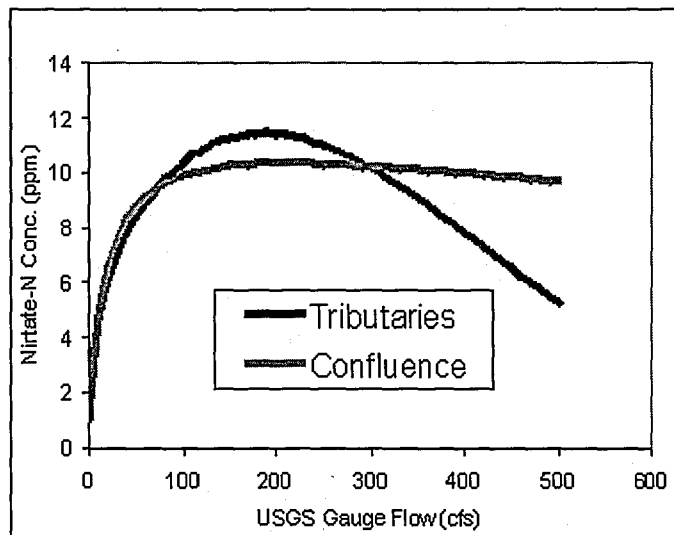


Figure 15.. Flow dependence of nitrate concentration

The temporal part of the rating curve is then a combination of flow and seasonal terms (eqs. 6 and 7, and fig. 16).

Confluence:

$$C(\text{solute}) = \exp \{ \lambda_1 \ln Q + \lambda_2 (\ln Q)^2 + \lambda_3 \sin(2\pi t d) + \lambda_4 \cos(2\pi t d) \} \quad (\text{eq. 6})$$

Tributaries:

$$C(\text{solute}) = \exp \{ \lambda_1 \ln Q + \lambda_2 (Q)^2 + \lambda_3 \sin(2\pi t d) + \lambda_4 \cos(2\pi t d) \} \quad (\text{eq. 7})$$

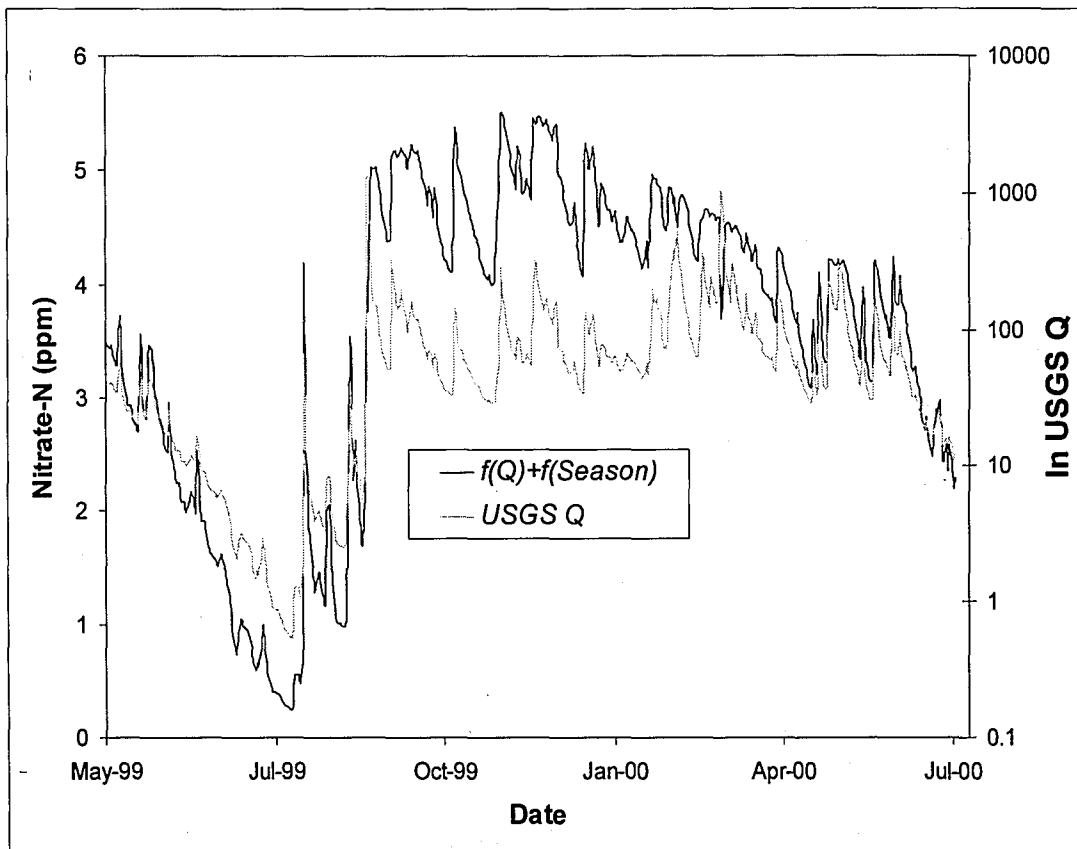


Figure 16. Flow and season terms of rating curve model combined for confluence stations.

The summer of 1999 was marked by an extreme drought, which resulted in the cessation of flow in the northern branch of the Lyon creek during part of July and August. Crop growth was stunted, and, according to local farmers, yields were low that year. Presumably, this reduced growth and uptake in the fields will leave an excess of nitrogen in the fields compared to average years. The excess nitrogen can be exported through the following year, resulting in higher nitrate concentrations than would be normally predicted. We added a class variable to sample points taken after October to adjust the shape of the rating curve to accommodate this effect.

The rating curve model was first tested with class variables representing each tributary instead of the spatial variables from the tributaries in order to test the suitability of the data set for modeling with our single adjusted-amplitude rating curve approach (eqs. 8 and 9). Data from tributaries L4 and L21 were not used in the models due to the animal intensive agriculture in these catchments. Tributary L4 consisted of a group of rotational grazing paddocks for sheep around a small stream, which is dry most of the summer, even without the drought. Tributary L21 had a cattle feed lot along the stream close to its confluence with the main stem and a high degree of residential area. We could not estimate the difference in loading of these sites compared with the predominantly cropped and hayed fields of other catchments, so these sites would skew the estimates of sinks in their catchments.

The rating curves with class variables yielded R^2 fits of .90 for the confluence and .93 for the tributaries (figs. 17), and we then proceeded to remove the class variables and add individual spatial variables to test their addition to the predictive power of the rating curve terms alone (tables 1 and 2).

Confluence equation:

$$NO_3 = \exp \{ \lambda_1 \ln Q + \lambda_2 (\ln Q)^2 + \lambda_3 \sin(2\pi t d) + \lambda_4 \cos(2\pi t d) + \lambda_5 * (\text{site class variable or continuous spatial variable}) \} \quad (\text{eq. 8})$$

Tributary equation:

$$NO_3 = \exp \{ \lambda_1 \ln Q + \lambda_2 (Q)^2 + \lambda_3 \sin(2\pi t d) + \lambda_4 \cos(2\pi t d) + \lambda_5 * (\text{site class variable or continuous spatial variable}) \} \quad (\text{eq. 9})$$

The most significant individual spatial variables added to the rating curve were fraction of the basin in *farming*, extent of *saturated floodplain sediments*, *stream length*, *basin size* (highly correlated with *stream length*), and fraction of stream with

gradient less than 4%. The only non-significant factors were fraction of basin in *riparian vegetated buffer*, and fraction of stream length with *gradient between 4% and 8%*.

Due to the co-variance of many of the variables, only a limited number of terms could be used in the model. This limitation led us to combine the terms of length and gradient into length at different classes of gradient.

Based on the results of the individual spatial variable regressions, we constructed a log-linearized model that combined length at *the low ($L_G < 4\%$) medium ($4\% < L_G < 8\%$) and high ($L_G > 8\%$) gradient classes*, fraction of basin in farming (Farm), fraction of basin with *non-riparian forest (NRFor)*, and a *drought class variable*, all with fitted coefficients (eq. 10). The coefficients generated by the model (table 3) were used to predict concentrations for a plot of modeled vs. observed data fitted to a $y=x$ line (fig. 18).

$$NO_3 = \exp\{\lambda_1 \ln Q + \lambda_2 (Q)^2 + \lambda_3 \sin(2\pi td) + \lambda_4 \cos(2\pi td) + \lambda_5 \text{Farm} + \lambda_6 \text{NRFor} + \lambda_7 L_G < 4\% + \lambda_8 L_G > 8\% + \lambda_9 \text{DroughtCV}\} \quad (\text{eq.10})$$

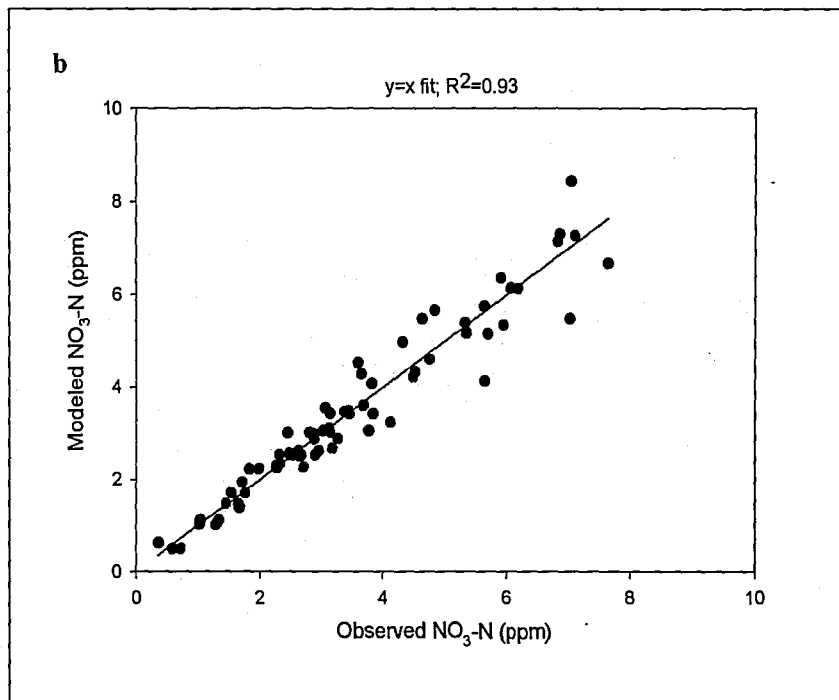
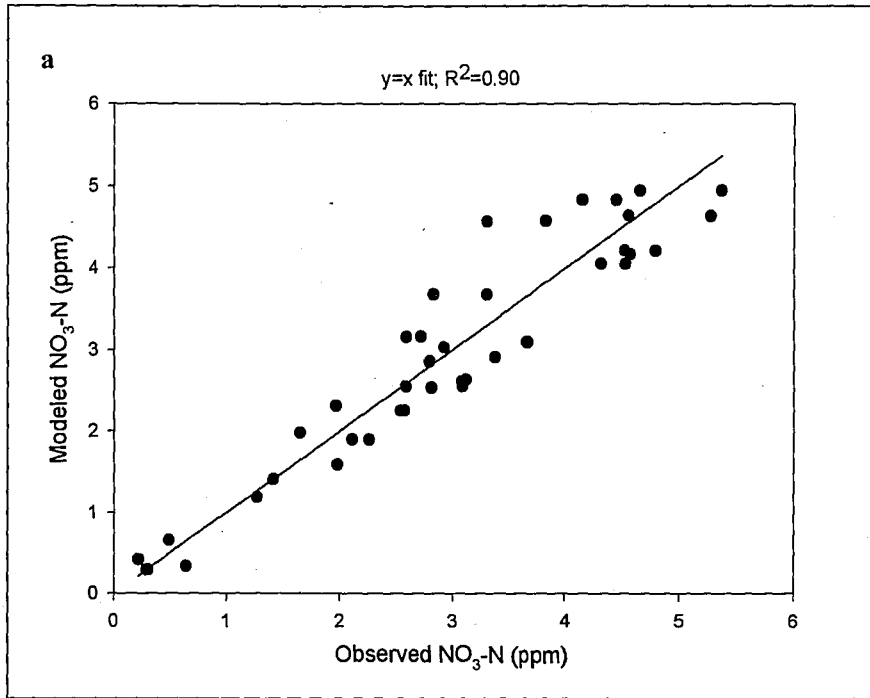


Figure 17. Rating Curve models with class variables for confluence sites (a) and tributary sites (b).

Table 1. Parameter coefficients and significance for flow and seasonal terms (temporal terms).
Adj. R²= 0.537

<i>Variables</i>	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	-0.7073	0.2510	-2.818	0.0064
lnQ	0.4832	0.0654	7.384	<0.0001
Q ²	-5.502E-06	1.680E-06	-3.274	0.0017
sin(2 π td)	-0.1635	0.1141	-1.434	0.1564
cos(2 π td)	-0.0873	0.1090	-0.801	0.4260

Table 2. Parameter coefficients, significance and effect on R² of individual spatial variables added to rating curve equation.

<i>Added Variable</i>	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>R²</i>
Drought CV	-0.6089	0.146	-4.175	<0.0001	0.629
Fraction Farm	2.5676	0.376	6.837	<0.0001	0.727
Fraction Non-Rip Forest	-4.7874	0.922	-5.192	<0.0001	0.668
Fraction Residential	-8.7984	1.665	-5.286	<0.0001	0.671
Fraction Riparian Buffer	0.0557	0.240	0.232	0.8170	0.530
Area Floodplain Seds	-5.074E-07	0.000	-7.015	<0.0001	0.733
Frac. Stream w/ FP Seds	-0.8126	0.146	-5.550	<0.0001	0.681
Stream Length	-6.369E-05	0.000	-8.259	<0.0001	0.771
Basin Area	-2.659E-08	0.000	-8.338	<0.0001	0.773
Avg. Stream Gradient	9.2081	1.794	5.133	<0.0001	0.666
Frac. Stream w/ Grad<4%	-1.0478	0.107	-9.807	<0.0001	0.774
4%<Grad<8%	0.4105	0.344	1.194	0.2368	0.477
8%<Grad<12%	2.0559	0.342	6.014	<0.0001	0.650
Grad>12%	2.4589	0.323	7.622	<0.0001	0.709

Table 3. Coefficients and significance of the empirical log-linearized spatio-temporal model.

<i>Variable</i>	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	-1.92485	0.322654	-5.97	<.0001
lnQ	0.339419	0.028677	11.84	<.0001
Q ₂	-5 E-06	6.9E-07	-7.29	<.0001
sin2 π td	-0.16278	0.048191	-3.38	0.0013
cos2 π td	0.030429	0.044418	0.69	0.4959
Farm	2.658204	0.304502	8.73	<.0001
NRFor	-3.47448	0.561598	-6.19	<.0001
L_G<4%	-0.00011	1.41E-05	-7.87	<.0001
4%L_G<8%	0.000177	4.52E-05	3.91	0.0002
L_G>8%	0.000246	3.72E-05	6.62	<.0001
Drought CV	-0.25809	0.069789	-3.7	0.0005

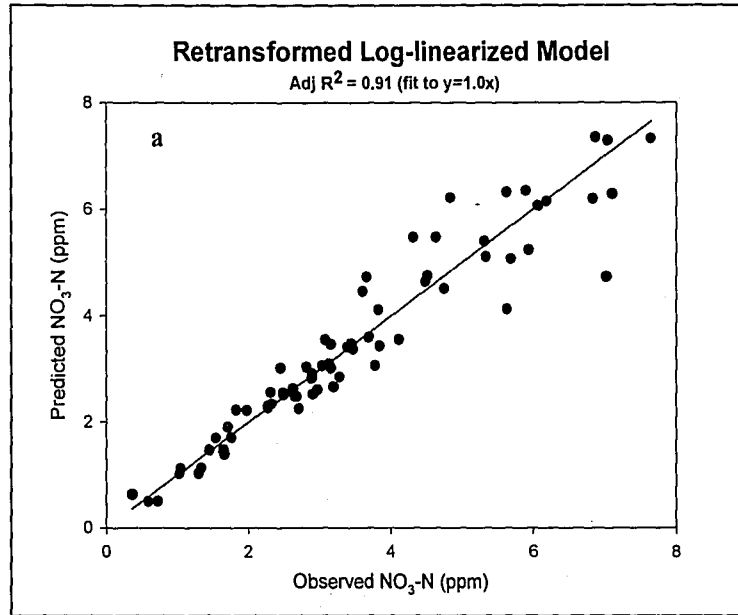


Figure 18. Fit of observed vs. predicted nitrate concentrations for the empirical log-linear model.

3.3.2 Calcium Rating Curve

The flow dependence of Ca shows a negative correlation, the opposite of nitrate's, indicating a higher concentration in groundwater than in surface water. Though there appears to be a dilution from runoff at high flow (fig 12), this effect could not be modeled with our log-linearized rating curve. The significant spatial variables affecting Ca concentration were *fraction farming* (positive correlation) and *average stream gradient* (negative correlation) (table 4). *Stream length* and *average width of saturated streamside sediments* were not significant.

Table 4. Coefficients and significance of spatial multiple regression.

	Coefficients	Standard Error	t Stat	P-value
Intercept	2.898107039	0.225640427	12.84392	1.37E-15
lnQ	-0.085746248	0.025659509	-3.34169	0.001845
sintd	-0.046961865	0.047431903	-0.99009	0.328233
costd	-0.074806699	0.04250425	-1.75998	0.086253
Gradient	-2.485662854	0.836391336	-2.97189	0.005049
Farm	0.723804669	0.184874547	3.915113	0.000353
AvgWidthFPS	-0.002692219	0.001585251	-1.69829	0.097419
StmLength	8.30799E-06	1.47282E-05	0.564089	0.575923

Table 5. Regression coefficients and significance for covariance test with class variables.

	Adjusted R Square 0.794315			
	Coefficients	Standard Error	t Stat	P-value
Intercept	2.7918	0.0883	31.6041	<.001
lnQ	-0.0580	0.0116	-5.0147	<.001
sin 2 π td	-0.0642	0.0247	-2.5989	0.0123
cos 2 π td	-0.0897	0.0236	-3.8046	<.001
L0	0.2772	0.0752	3.6846	<.001
L1	0.1655	0.0738	2.2433	0.0293
L3	0.0970	0.0774	1.2520	0.2164
L5	0.0862	0.0747	1.1538	0.2540
L7	0.2241	0.0747	2.9991	0.0042
L8	0.4048	0.0840	4.8173	<.001
L9	0.2932	0.0738	3.9746	<.001
L10	0.3019	0.0840	3.5932	<.001
L12	0.3938	0.0914	4.3105	<.001
L13	0.2773	0.0914	3.0350	0.0038
L17	0.0566	0.0914	0.6197	0.5383
L20	0.5599	0.0859	6.5195	<.001
L21	0.4864	0.0859	5.6637	<.001

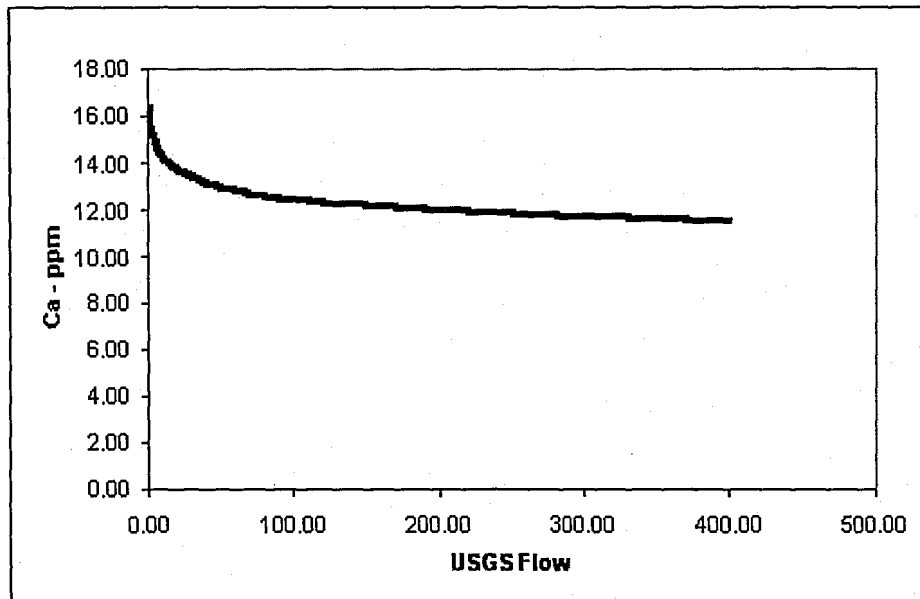


Figure 19. Modeled dependence of Ca concentration on flow.

4. Discussion

4.1 Biogeochemical Controls on Potential Nitrate Sinks

4.1.1 Geologic Controls of Sinks

Geomorphic variables of *length* and *gradient* clearly account for much of the potential for these first- or second-order catchments to attenuate nitrate inputs from agriculture. It is not as clear, however, exactly what the cause of geomorphic variation is within the Lyon Valley, and while a complete geologic investigation is beyond the scope of this work, there are many clues that can be briefly addressed.

It is tempting to infer a control of morphology by lithology, as the majority of the length of the longest streams, L5 and L7, reside within the Hamburg sequence greywacke and shales and the shorter, high-gradient streams reside almost entirely within the Martinsburg shales (fig 20). It would seem that the different properties of the Hamburg sequence rocks allowed the streams to downcut more rapidly and attain a longer, more mature character than did the streams within the Martinsburg shales. However, the fault-controlled main branches of the Lyon trend NE-SW, while the regional gradient trends from the NW to the SE, perpendicular to the long-axis of the Lyon Valley. This means that some of the tributaries run with the local gradient and some run against it, creating differences in elevation drop from headwaters to mouth between the northern-branch tributaries and the southern-branch tributaries and a consequent variability in potential energy for physical weathering processes within the catchments.

Regardless of the cause, the result is that the northern branch of the Lyon is drained by fewer, longer, lower average gradient streams than is the southern branch (fig.

20). We propose that this results in an increased capacity for the northern branch to attenuate excess nitrate levels coming from agricultural areas, and that high gradient tributaries are more at risk of contributing higher loads of nitrate to surface water bodies.

Figure 21 shows representative stream profiles of different gradient classes.

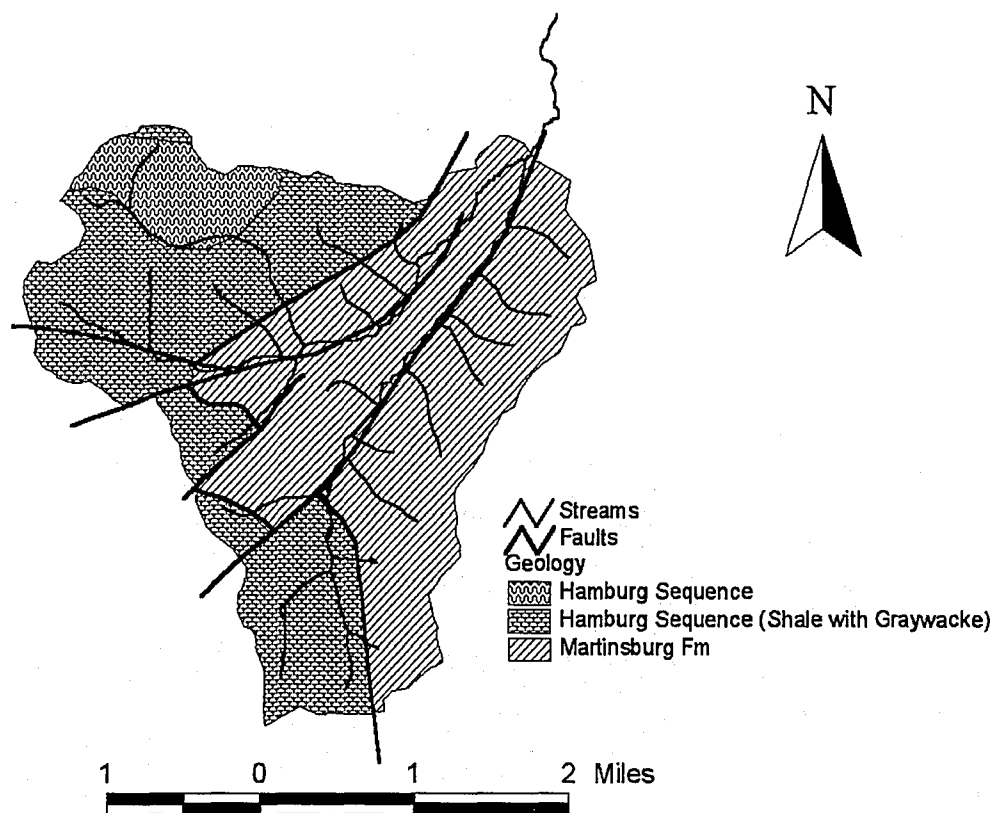


Figure 20. The geology of the Lyon Basin (from Wood and MacLachlan, 1978)

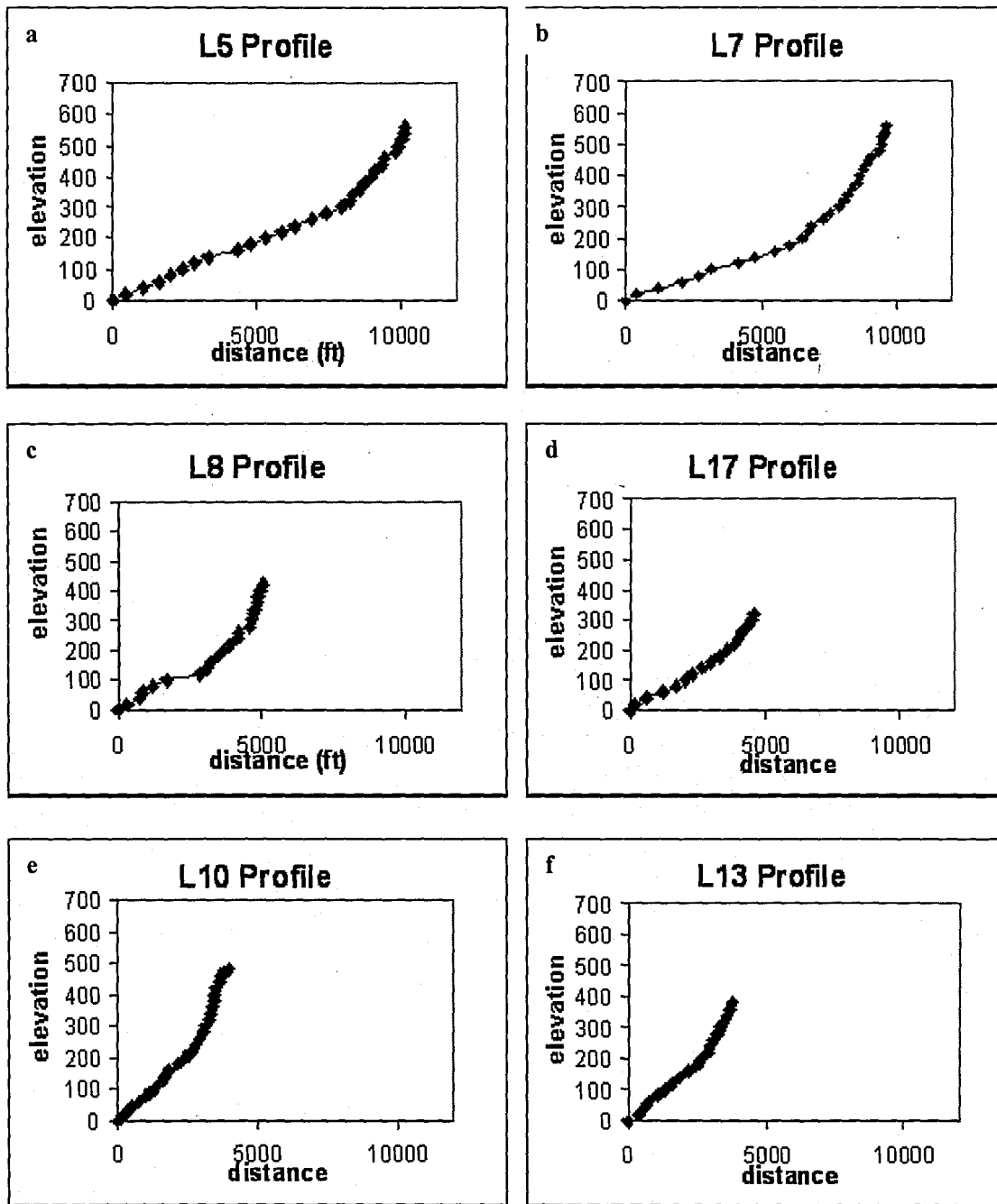


Figure 21. Representative profiles of low (a, b), medium (c, d), and high-gradient (e, f) streams.

4.1.2 Geochemically Active Zones

Since the geomorphic characteristics of the catchment control the hydraulic connections between land and water and many of the characteristics of transport to and within the stream, the morphology provides a control of contact time between the water and basin sediments, and thus exerts a control on chemical reactions in the sediments throughout the catchment. Recent work in The Rocky Mountains by Clow and Sueker (2000) shows similar controls. The basin morphology, particularly the length and gradient of the low-order streams, also strongly defines the presence or absence of streamside-saturated sediments and the soil development there. These seasonally, and often perennially saturated areas create reducing conditions that are perfect for the incomplete oxidation and subsequent build-up of soil-carbon. The high carbon content and high redox gradients in these zones strongly influences the chemistry of the water flowing through them. Numerous studies have shown these zones to be actively influencing the chemistry of water flowing through to the stream and even water within the stream channel, via hydraulic communication with the pore waters in the hyporrhea and in the banks of the stream (see review in Cirimo and McDonnell, 1997; Grimm et al., 1984) In particular, these zones, with high carbon and low oxygen concentrations, can act as large permanent sinks for nitrate through microbiological respiration, as well as a temporary sink from conversion to biomass. Similar conditions are created within the accumulated streambed sediments of pools and both natural debris dams and man-made ponds.

Despite the theoretical agreement with the data interpretation, the argument could be made that the decrease that we see at low flow is not from biogeochemical

processing within the catchment or within the stream, but is from the shifting dominance of streamwater sourcing from interflow to groundwater. However, the evidence from the Ca data analysis does not show any trend that could be misinterpreted as a biogeochemical sink affecting its transport. Ca is much less biologically reactive than NO_3^- is (it is used in lower amounts for biologic anabolism and does not serve in biologic catabolism as a terminal electron acceptor in microbial respiration processes as nitrate does), and thus its behavior with both spatial and temporal variables should reflect the process of groundwater - surface water mixing, rather than that of a species that can be extensively transformed while in transport. We can further examine this by using an endmember-mixing analysis to determine the endmember dominance at various discharge scenarios and comparing the characteristics of a line representing the mixing of groundwater and interflow for a non-reactive species to the shape of our nitrate rating curve over the same range of flow.

We will assume the same baseflow, interflow, and runoff endmembers that were used for nitrate. Since the nature of the rating curve is asymptotic with very low flow, we will estimate end members from both raw data and the rating curve. Again, we will assume the concentration of runoff to be negligible. We will use the rating curve's prediction of concentration vs. flow and an end-member mixing equation to represent the concentration at a given flow, $C(Q_i)$, as a product of a flow-dependent mixture of endmembers (eq. 11) at flow values ranging from all groundwater to predominantly interflow in order to back out an approximation the fraction of streamwater represented by interflow, $X_{\text{gw}}(Q_i)$, (eq. 12). $X_{\text{gw}}(Q_i)$ is the fraction of groundwater in the stream at Q_i , C_{gw} is the concentration of the groundwater, $X_{\text{int}}(Q_i)$ is the fraction of interflow in the

stream, $X_{ro}(Q_i)$ is the fraction of surface runoff in the stream, and C_{ro} is the concentration of the surface runoff, which will be dropped from the equation.

$$C(Q_i) = X_{gw}(Q_i) * C_{gw} + X_{int}(Q_i) * C_{int} + X_{ro}(Q_i) * C_{ro} \quad (\text{eq. 11})$$

$$X_{int}(Q_i) = \{C(Q_i) - X_{gw}(Q_i) * C_{gw}\} \div C_{int} \quad (\text{eq. 12})$$

Figure 22 shows the relationship of a line representing the mixing of a non-reactive species with a much higher concentration in the soilwater than in the groundwater to rating curves generated by our class variable approach for three classes of streams, the confluence stations, the tributaries, and a subset of high-gradient tributaries. If there were no processing of nitrate in the stream and near-stream environment, we would expect the mixing line to be straight. The high-gradient class line shows a nearly straight line, while the tributary line shows more inflection, and the confluence line shows the most inflection. The degree of inflection represents the degree of processing of processing of nitrate, which increases with length of contact time, a variable affected by flow and length. This is consistent with sinks for nitrate that are more active at high flow than at low flow.

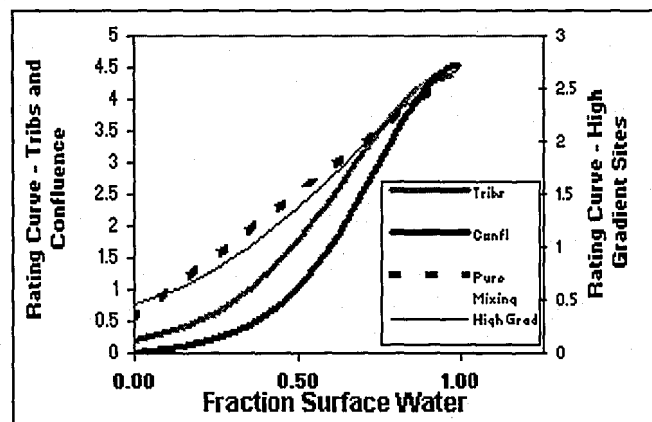


Figure 22. Rating curve predicted concentrations vs. fraction surface water

4.1.3 The Biological Reactor

With the use of rating curves, we attempt to eliminate the temporal variables of flow and season so that we can directly examine the effect of spatial variability on solute concentrations. Arguably, the most intriguing aspect of the spatial variability is the varying potential of each catchment to attenuate inputs from nitrate sources. This finding is consistent with recent work in the Rocky Mountains by Clow and Sueker (2000), showing basin characteristics affecting solute concentrations through control of contact times and degree of soil development. We can also examine landscape control aspect of each site directly without removing time, and in fact by looking at variable change with time. The ratio of concentration between different tributaries, or even between sections of a tributary, at any one time shows the composite effect of sources and sinks within that catchment or reach, but the variation in that ratio with time tells us something about the biogeochemical sink potentials of that tributary or reach.

The varying ratio of nitrate concentrations between different catchments indicates that the spatial attributes of each catchment are exerting a degree of control on element cycling; a control that is dependent on environmental conditions, particularly those of flow and temperature. Figure 24 shows this relationship for the two main branches, for representative high and low denitrification potential streams, and for a high- and low-gradient section of one longer tributary. When plotted over a yearly cycle, the variation in the ratio shows an oppositely phased cyclicality to the seasonality term and the general pattern of flow used in our model (fig. 10).

The sink mechanisms, whether they are due to in-stream or near-stream processes appear to act much like a flow-through biological wastewater reactor. At the right

conditions nitrate flows in off of the land, and is consumed in large part in the sediments before the water reaches the stream. If, however, the flow is increased, the nitrate can only be partially consumed before the water reaches the stream. Temperature has a similar control on the situation by increasing the biochemical reactions at higher temperature and damping them at low temperature. We observe this biochemical signature in the change of the ratio of concentration between catchments of with time. As environmental conditions potentiate the biochemical processes, the difference between sites of high and low sink-potential grows, finding maximums with high temperature and low flow (fig. 10). Thus, though the summer creates lower nitrate levels for all sites, it also accentuates the differences in the nitrate attenuation potentials of the each catchment's stream system.

Importantly, we can see that not only do the confluence stations as well as different tributary stations show this effect, but also sections of tributaries show this effect (fig. 24). In tributary L7, a sample site at the end of the high gradient section (fig. 23) of the stream acted like a high-gradient tributary in relation to the mouth station. This property of similar function at increasing range of scales suggests a fractal dimension to the biogeochemical properties of this nested series of catchments.

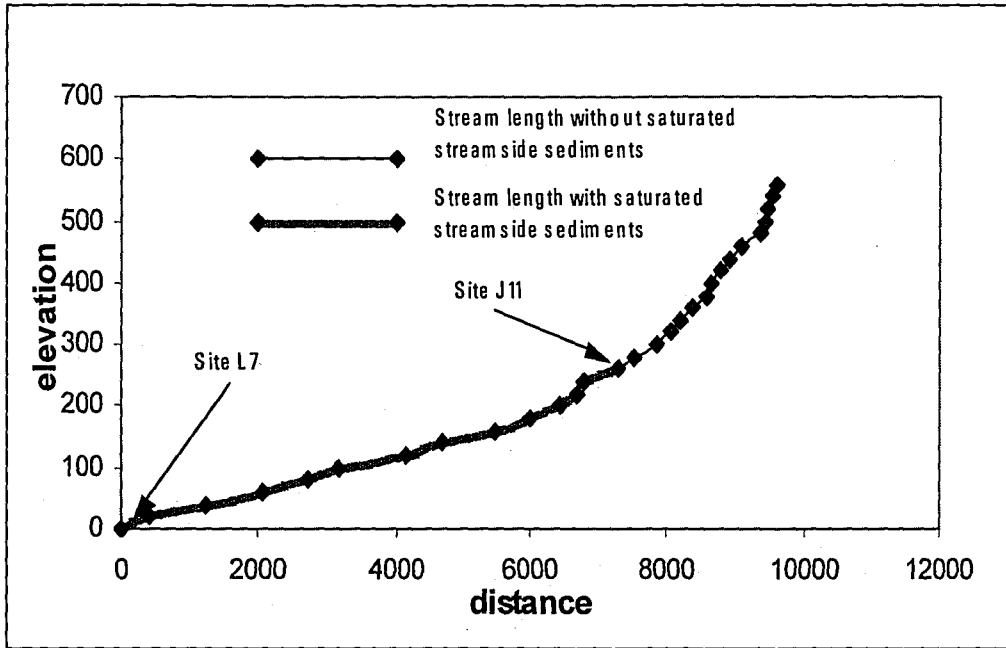


Figure 23. High- and low-gradient sample sites in catchment L7.

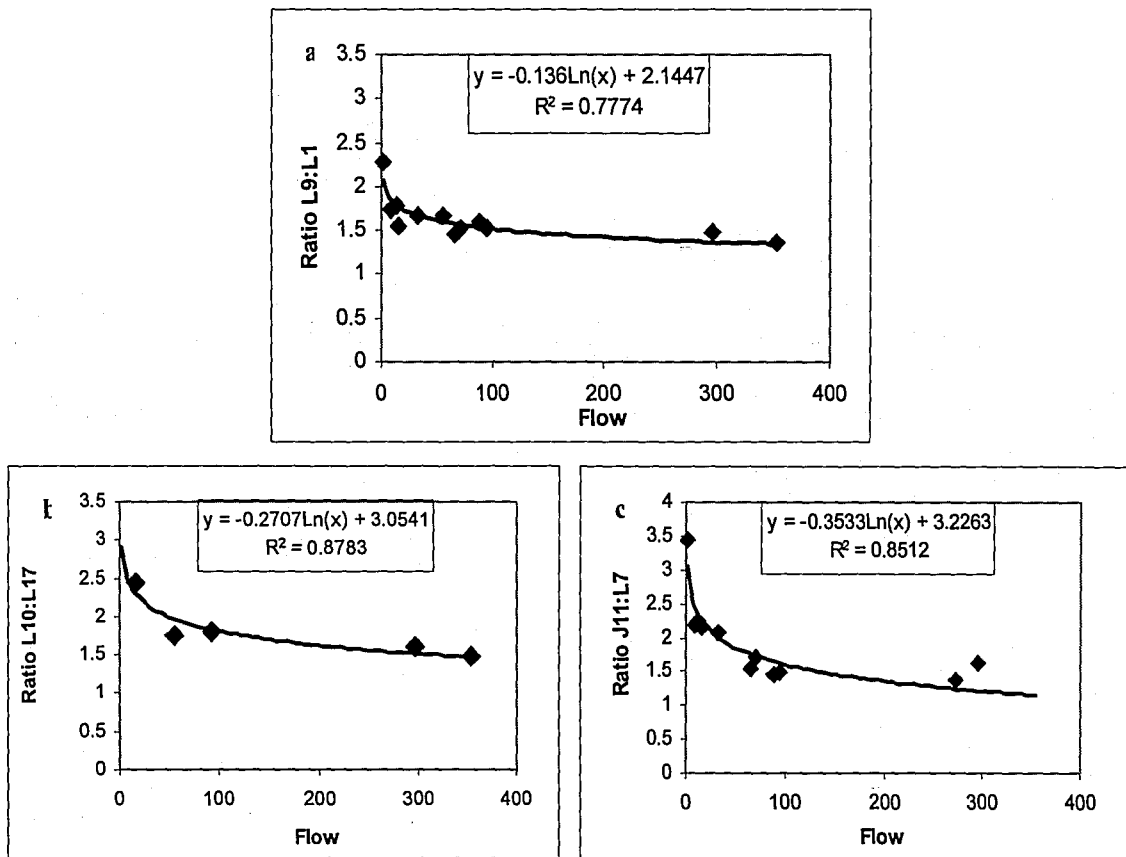


Figure 24. Change in nitrate ratios with flow between branches (a), high and low-gradient tribs (b), and between high- and low-gradient sections of one longer tributary, L7.

4.2 Model Refinement

The empirical single, adjusted-amplitude rating curve approach provided a satisfactory method of separating time from space to allow for a spatial analysis of controls on stream nitrate concentration. However, the evidence of the ratios and the comparison of rating curves generated from different subsets of sites indicate that the shape of the curve does matter, and that for a more universal, mechanistic approach to modeling nested catchment data, there needs to be freedom for each catchment to express its characteristics in the shape of its rating curve, while still using one flow data source.

Our conceptual model suggests that differences in flow partitioning and stream-system sinks are likely factors contributing to differences in rating curve shapes. In rating curve equations, these interactions can be incorporated by allowing for interactions of flow and length-gradient terms. One approach to doing this would be to base a rating curve on semi-mechanistic equations, such as the equation for the concentration of non-conservative non-point source pollutants (eq. 13), where k is a decay constant, and t is travel time.

$$C_{sol} = kt \cdot \{1 - \exp(-kt)\} \quad (\text{eq. 13})$$

From empirical studies of stream travel times (SPARROW nature), a reasonable expectation is that kt is proportional to stream length and inversely proportional to gradient and/or discharge. These spatial and temporal terms can be incorporated into to allow an interaction of flow and stream characteristics. A hypothetical series of stream length-gradient classes is shown in figure 25, representing the differing potential for transport sinks in each class. The different stream classes can now exhibit differing shapes, based on their characteristics and their effect on transport

processing of loads. The ratio of high to low sink-potential sites now shows the same dependence of flow that the raw data show. The current limited data set does not warrant the need to provide freedom of slope in the rating curve, primarily due to the sparseness of points at low flow in the short, high-gradient tributaries. However, if this single flow-source rating curve method is to be applied to other series of nested catchments, this freedom of curve shape must be an available option.

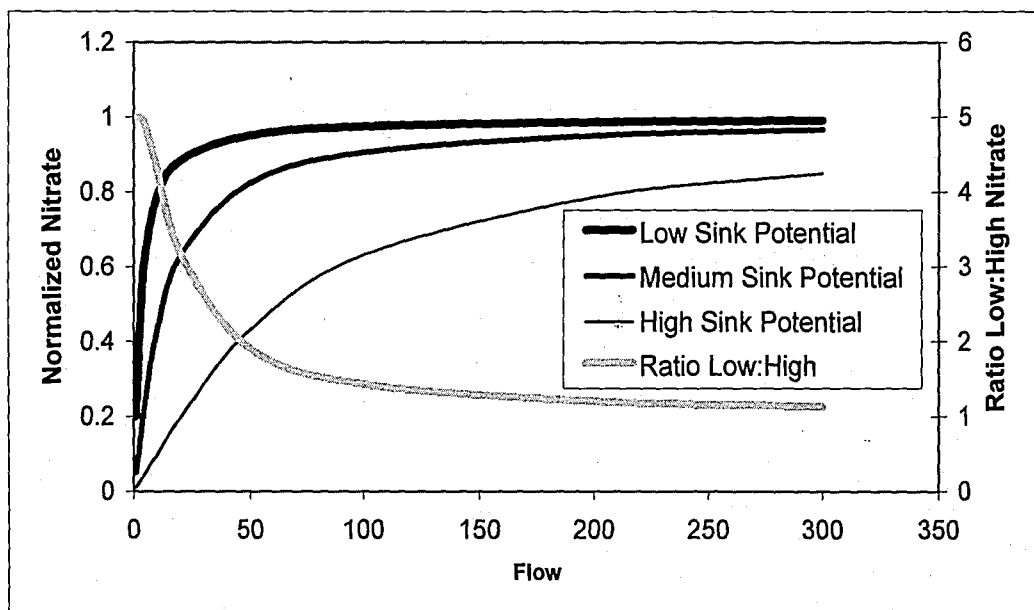


Figure 25. Hypothetic semi-mechanistic rating curves of high and low sink-potential streams and the ratio of high:low vs. flow.

4.3 Implications

The adoption of The Clean Water and Air Act in 1972 and more recent legislation, section 303(d) of The Clean Water Act, requiring establishment of TMDLs, has increased the pressure on science and the agricultural industry to regulate non-point source agricultural pollution. The recent concern over hypoxia in the Gulf of Mexico has increased the pressure to decrease agricultural inputs of nutrients, particularly nitrate, into surface waters. Central to the issue of nutrient discharge from agriculture is the issue of attenuation, whether in transport from land to stream or while in transport within the stream. Our study suggests that low-order catchments in high-gradient areas are more at risk of high loading rates than higher order, lower-gradient streams, which tend to have more mechanisms in place to attenuate nitrate inputs.

A variety of conservation agricultural practices have been proposed over time under the umbrella term, "best management practices". In theory, these practices, such as reduced tillage, riparian buffer strips, and grassed waterways, should reduce sediment and chemical inputs to surface waters from agricultural lands. However, few of these practices, save for physical removal of sediment by grassed waterways and riparian buffer strips, have found scientific proof of effectiveness. One finding in this study was that not all riparian buffers work the same. In fact, the regressions showed no correlation of riparian buffer extent with nitrate concentration. Buffers in high gradient valleys, with no accumulation of floodplain sediments, seemed to have little or no effect on nitrate in waters coming off of the fields. Presumably, previous studies that have shown nitrate reductions of surface and groundwaters through riparian buffers have been done on relatively low-gradient areas with valley floor sediments and appropriate denitrifying

conditions. In riparian wetlands of a low-gradient section of our study area, during a high flow event, we measured a 50% reduction of nitrate through a series of seeps in a 12m and a 20m transect from the edge of a field to stream. However, there was little evidence that these processes were active in the smaller catchments with no valley floor sediments.

We propose that similar methods of spatio-temporal analysis, using GIS techniques and rating curve models based on one gauge in small nested catchments, could be used to investigate the effect of BMP's on water quality, and to further analyze landscape properties and their ties to water quality.

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Appendix 1. Complete GIS spatial data.

Basin Characteristics - Land Use

ID	Basin Area	Land Use Area				Land Use %			
		Farm	Riparian Buffer	Residential	Non-Riparian Forest	Farm	Riparian Buffer	Non-Riparian Forest	Residential
0	19432556	13381623	3250451	985436	1935846	68.9	16.7	10.0	5.1
1	9620388	5939976	2017561	381881	1251236	61.7	21.0	13.0	4.0
9	9812168	7441647	1232890	603555	684610	75.8	12.6	7.0	6.2
3	737584	342070	234293	57578	111703	46.4	31.8	15.1	7.8
4	221758	217891	11274	0	0	98.3	5.1	0.0	0.0
5	2779948	1563304	542193	168198	471789	56.2	19.5	17.0	6.1
7	3227428	2029430	701469	124000	458141	62.9	21.7	14.2	3.8
8	914900	634365	115232	14957	136131	69.3	12.6	14.9	1.6
10	381012	339885	27763	0	59522	89.2	7.3	15.6	0.0
11	433619	287376	105269	26145	16973	66.3	24.3	3.9	6.0
12	376480	281979	73630	0	13033	74.9	19.6	3.5	0.0
13	413188	311443	77267	9063	0	75.4	18.7	0.0	2.2
14	654942	425701	96446	16082	118174	65.0	14.7	18.0	2.5
15	234417	213270	23120	0	534	91.0	9.9	0.2	0.0
16	247808	178222	26345	0	46780	71.9	10.6	18.9	0.0
17	719156	503306	53800	58999	95143	70.0	7.5	13.2	8.2
18	954462	841680	56055	3090	47993	88.2	5.9	5.0	0.3
19	505351	437212	21991	38819	4550	86.5	4.4	0.9	7.7
20	945979	705617	89287	15171	77870	74.6	9.4	8.2	1.6
21	1496802	1169059	90747	430246	23589	78.1	6.1	1.6	28.7

Basin Characteristics - Riparian Zone

<i>ID</i>	<i>Basin Area</i>	<i>Area</i>	<i>Avg. Width</i>	<i>Avg. Width</i>
		<i>Floodplain Seds</i>	<i>Floodplain Seds</i>	<i>Riparian Buffer</i>
0	19432556	510737	16	103.00
1	9620388	337378	22	128.86
9	9812168	173359	11	77.53
3	737584	0	0	183.79
4	221758	0	0	18.59
5	2779948	116112	30	138.38
7	3227428	115592	25	150.78
8	914900	0	0	88.70
10	381012	0	0	37.49
11	433619	0	0	111.86
12	376480	7966	10	92.96
13	413188	0	0	96.01
14	654942	0	0	97.84
15	234417	0	0	36.27
16	247808	0	0	55.17
17	719156	0	0	52.74
18	954462	26039	24	52.73
19	505351	0	0	37.49
20	945979	0	0	60.05
21	1496802	0	0	53.04

Stream Characteristics

ID	Stream length	Avg. Grad.	Slope	G<0.04	0.041<G<0.08	0.081<G<0.12	G>0.121	L w/ G<4%	4.1%<G<8.0%	8.1%<G<12.0%	G>12.1%
0	31558	0.015		0.464	0.261	0.131	0.145	15269	8585	4306	4782
1	15657	0.015		0.466	0.250	0.117	0.167	7938	4258	2000	2843
9	15901	0.015		0.461	0.272	0.145	0.122	7331	4327	2305	1938
3	1275	0.123	3.200	0.000	0.399	0.274	0.327	0	509	350	416
4	606	0.168	2.600	0.000	0.223	0.138	0.639	0	135	84	387
5	3918	0.055	3.200	0.486	0.366	0.084	0.065	1903	1434	329	253
7	4652	0.062	3.200	0.586	0.204	0.127	0.082	2727	950	591	383
8	1299	0.082	2.600	0.000	0.310	0.305	0.386	0	402	396	501
10	741	0.121	2.850	0.000	0.287	0.385	0.328	0	212	285	243
11	941	0.102	2.850	0.000	0.506	0.210	0.284	0	476	197	267
12	792	0.104	2.200	0.000	0.307	0.423	0.270	0	243	335	214
13	805	0.100	2.200	0.000	0.508	0.219	0.273	0	409	176	219
14	986	0.110	2.600	0.000	0.443	0.275	0.282	0	437	271	278
15	637	0.116	1.800	0.000	0.000	0.595	0.405	0	0	379	258
16	478	0.116	2.600	0.000	0.285	0.370	0.344	0	136	177	164
17	1020	0.070	1.800	0.241	0.562	0.091	0.106	246	574	93	108
18	1063	0.073	1.800	0.543	0.253	0.148	0.056	577	269	157	60
19	587	0.089	1.800	0.000	0.493	0.401	0.106	0	289	235	62
20	1487	0.051	2.600	0.504	0.453	0.000	0.043	750	673	0	64
21	1711	0.041	2.200	0.645	0.355	0.000	0.000	1104	607	0	0

09

Appendix 2. Complete Analysis for Lyon Creek streamwater chemistry major elements. June 8, 1999 sampling.

	J1	J2	J3	J4	J5	J6	J7	J8	J9	J11	J12	SITE
H2O TEMP	16.59	16.54	16.91	20.13	21.16	16.96	20.31			18.01	20.4	H2O TEMP
DO %SAT	102.6	103.5	104.1	103.5	108.4	92.4	92.4			90.4	93.3	DO %SAT
DO mgL ⁻¹	9.7	9.76	9.74	9.03	9.32	8.63	8.63			8.28	8.15	DO mg/L
Cond. (µScm ⁻¹)	212	181	213	187	181	190	190	164	157	266*	250*	Cond.
pH	7.75	7.33	7.79	7.82	8.03	7.44	7.44	7.01	7.10	7.4*	7.45*	pH
TDS	136	116	136	120	116	121	121			170	156	TDS
Redox	146	158	160	152	131	116	116			117	90	Redox
Alkalinity(ppm)	54.60	55.39	53.78	57.38	56.91	58.61	57.44	42.84	40.69	57.87	49.60	Alkalinity
NO ₃ ⁻ -N (ppm)	2.572	1.412	2.543	1.250	1.218	1.045	1.332	2.129	1.906	2.337	2.960	NO3-Nppm
PO ₄ ⁻³ -P (ppm)	0.009	0.012	0.010	0.001	0.010	0.009	0.009	0.005	0.007	0.011	0.027	PO4-Pppm
NH ₄ ⁺ -N (ppm)	0.028	0.030	0.022	0.044	0.029	0.017	0.018	0.012	0.011	0.013	0.039	NH4-Nppm
	J1	J2	J3	J4	J5	J6	J7	J8	J9	J11	J12	
Ca (ppm)	17.55	16.14	19.47	19.83	17.98	19.64	17.16	14.27	13.59	22.58	23.15	Ca
Na (ppm)	6.59	4.60	6.29	5.19	4.73	4.99	4.39	3.77	3.55	9.64	9.10	Na
Mg (ppm)	6.08	4.41	6.17	5.64	5.14	5.53	4.97	5.45	5.21	8.51	7.33	Mg
K (ppm)	0.81	0.51	0.19	0.39	0.26	0.35	0.24	0.17	0.39	1.25	1.39	K
Fe (ppm)	0.04	0.04	0.05	0.06	0.06	0.08	0.09	0.03	0.04	0.07	0.24	Fe
Al (ppm)	0.10	0.25	0.27	0.21	0.15	0.09	0.17	0.12	0.14	0.08	0.14	Al
Sr (ppm)	0.60	0.75	0.77	0.71	0.65	0.59	0.67	0.62	0.64	0.58	0.64	Sr
NH4 ⁺ (ppm)	0.04	0.04	0.03	0.06	0.04	0.02	0.02	0.01	0.01	0.02	0.05	NH4+
Cl ⁻ (ppm)	15.05	9.91	15.07	10.16	8.51	9.44	7.03	8.97	8.16	19.33	25.07	Cl
SO ₄ ⁻² (ppm)	9.18	6.04	9.19	6.20	16.89	15.78	17.76	9.89	10.55	15.52	20.80	SO4
NO ₃ ⁻ (ppm)	11.39	6.25	11.26	5.53	5.40	4.63	5.90	9.43	8.44	10.35	13.11	NO3
PO ₄ ⁻³ (ppm)	0.01	0.02	0.01	0.00	0.02	0.01	0.01	0.01	0.01	0.02	0.04	PO4
HCO ₃ ⁻ (ppm)	54.60	55.39	53.78	57.38	56.91	58.61	57.44	42.84	40.69	57.87	49.60	HCO3-
SiO ₂ (ppm)	10.26	9.64	9.73	9.44	9.60	10.91	10.09	10.06	10.27	10.70	9.99	SiO2

Appendix 3. Complete nutrient data

In-stream code	Trib code	date	NO3	PO4	NH4
J1	L0	5/26/99	2.59		
J2	L1	5/26/99	1.64		
J3	L9	5/26/99	2.72		
J4		5/26/99	1.57		
J5		5/26/99	1.63		
J6	L7	5/26/99	1.45		
J7	L5	5/26/99	1.65		
J8		5/26/99	2.24		
J9		5/26/99	2.00		
J11		5/26/99	3.00		
J12		5/26/99	2.93		
J1	L0	6/8/99	2.57	0.009	0.028
J2	L1	6/8/99	1.41	0.012	0.030
J3	L9	6/8/99	2.53	0.010	0.022
J4		6/8/99	1.25	0.001	0.044
J5		6/8/99	1.22	0.010	0.029
J6	L7	6/8/99	1.05	0.009	0.017
J7	L5	6/8/99	1.33	0.009	0.018
J8		6/8/99	2.13	0.005	0.012
J9		6/8/99	1.91	0.005	0.011
J11		6/8/99	2.34	0.011	0.013
J12		6/8/99	2.96	0.027	0.039
J1	L0	6/22/99	2.12	0.007	
J2	L1	6/22/99	1.29	0.009	
J3	L9	6/22/99	2.26	0.008	
J4		6/22/99	1.09	0.010	
J5		6/22/99	1.13	0.010	
J6	L7	6/22/99	1.03	0.010	
J7	L5	6/22/99	1.29	0.009	
J8		6/22/99	2.10	0.006	
J9		6/22/99	2.03	0.008	
J11		6/22/99	2.25	0.011	
J12		6/22/99	2.42	0.016	
J12A	L20	6/22/99	2.49	0.013	
J12B	L21	6/22/99	1.67	0.003	
J1	L0	7/20/99	0.49	0.006	0.013
J2	L1	7/20/99	0.22	0.005	0.011
J3	L9	7/20/99	0.50	0.006	0.010
J4		7/20/99	0.16	0.004	0.008
J5		7/20/99	0.17	0.006	0.027
J6	L7	7/20/99	0.37	0.012	0.006
J7	L5	7/20/99	0.35	0.013	0.013

In-stream code	Trib code	date	NO3	PO4	NH4
J8		7/20/99	1.28	0.004	0.005
J9		7/20/99	1.09	0.007	0.006
J11		7/20/99	1.27	0.011	0.005
J12		7/20/99	0.74	0.045	0.031
J12A	L20	7/20/99			
J12B	L21	7/20/99			
J1	L0	8/4/99	0.29	0.000	
J3	L9	8/4/99	0.31	0.000	
J6	L7	8/4/99	0.53	0.008	
J1	L0	8/8/99	0.65	0.012	
J4		8/8/99	0.39	0.011	
J5		8/8/99	0.35	0.000	
J6	L7	8/8/99	0.60	0.037	
J7	L5	8/8/99	0.73	0.022	
J1	L0	8/14/99	1.31	0.006	
J2	L1	8/14/99	1.44	0.008	
J3	L9	8/14/99	1.19		
J5		8/14/99	1.07	0.003	
J6	L7	8/14/99	0.99	0.000	
J7	L5	8/14/99	1.24	0.003	
J12A	L20	8/14/99	2.10		
J12B	L21	8/14/99	1.46		
J1	L0	8/26/99		0.003	
J2	L1	8/26/99		0.002	
J3	L9	8/26/99		0.004	
J4		8/26/99		0.001	
J5		8/26/99		0.003	
J6	L7	8/26/99		0.003	
J7	L5	8/26/99		0.003	
J8		8/26/99		0.001	
J9		8/26/99		0.002	
J1	L0	10/18/99	4.15	0.004	
J2	L1	10/18/99	2.93	0.004	
J3	L9	10/18/99	4.48	0.003	
J4		10/18/99	2.73	0.003	
J5		10/18/99	2.83	0.004	
J6	L7	10/18/99	2.48	0.012	
J7	L5	10/18/99	2.31	0.004	
J8		10/18/99	2.87	0.003	
J9		10/18/99	2.43	0.003	
J10		10/18/99	2.71		
J11		10/18/99	4.23		
J12		10/18/99	4.34	0.008	
J12A	L20	10/18/99	3.15	0.004	

In-stream code	Trib code	date	NO3	PO4	NH4
J12B	L21	10/18/99	4.69	0.010	
J4A	L3	10/18/99	3.27		
J4C	L4	10/18/99	3.89		
J6A	L8	10/18/99	5.36		
J1	L0	12/4/99	4.66		
J2	L1	12/4/99	3.66		
J3	L9	12/4/99	5.37		
J4		12/4/99	3.50		
J5		12/4/99	3.48		
J6	L7	12/4/99	3.15		
J7	L5	12/4/99	2.81		
J8		12/4/99	2.85		
J11		12/4/99	4.88		
J12a	L20	12/4/99	3.82		
J12b	L21	12/4/99	5.90		
J2a		12/4/99	3.62		
J4a	L3	12/4/99	3.46		
J4c	L4	12/4/99	4.72		
J6a	L8	12/4/99	6.07		
J10		12/4/99	3.09		
D/L10	L10	12/4/99	6.87		
J1	L0	3/12/00	3.30	0.011	0.015
J2	L1	3/12/00	2.80	0.011	0.016
J3	L9	3/12/00	3.83	0.011	0.018
J4		3/12/00	2.86	0.013	0.012
J5		3/12/00	2.80	0.009	0.013
J6	L7	3/12/00	2.71	0.007	0.033
J7	L5	3/12/00	2.28	0.009	0.006
J12a	L20	3/12/00	3.78	0.005	0.038
J12b	L21	3/12/00	4.88	0.061	0.103
J4a	L3	3/12/00	2.48	0.015	0.012
J4c	L4	3/12/00	3.93	0.010	0.011
J6a	L8	3/12/00	4.76	0.011	0.022
	L10	3/12/00	4.64	0.005	0.315
	L11	3/12/00	3.65	0.004	0.015
	L12	3/12/00	5.63	0.006	0.012
	L13	3/12/00	7.11	0.004	0.011
	L14	3/12/00	2.35		0.012
	L17	3/12/00	3.13	0.007	0.015
J1	L0	3/13/00	4.55	0.007	
J2	L1	3/13/00	3.37	0.010	
J6	L7	3/13/00	3.18	0.005	
J11		3/13/00	4.39	0.009	
J11a		3/13/00	3.54	0.009	

In-stream code	Trib code	date	NO3	PO4	NH4
J1	L0	4/8/00	4.52	0.005	0.009
J2	L1	4/8/00	3.12	0.006	0.009
J3	L9	4/8/00	4.79		0.010
J4a	L3	4/8/00	2.88		0.018
J4c	L4	4/8/00	4.98	0.008	0.016
J5		4/8/00	3.06	0.006	-99
J6	L7	4/8/00	2.90	0.004	-99
J6a	L8	4/8/00	5.69	0.009	-99
J6b		4/8/00	3.24	0.003	-99
J7	L5	4/8/00	2.51	0.007	-99
J7Pa		4/8/00	2.61	0.007	-99
J11		4/8/00	4.29	0.007	-99
J11a		4/8/00	2.72	0.003	-99
J12a	L20	4/8/00	3.84	0.004	0.020
J12b	L21	4/8/00	5.35	0.012	0.063
J12		4/8/00			
J12aP		4/8/00	3.99	0.002	0.024
	L10	4/8/00	6.18	0.006	
	L17	4/8/00	3.44	0.006	0.018
J1	L0	4/26/00	4.32		0.003
J2	L1	4/26/00	2.82		0.006
J3	L9	4/26/00	4.53		0.003
J6	L7	4/26/00	2.65		0.010
J11		4/26/00	3.85		0.009
J11a		4/26/00	2.50		0.008
L12		4/26/00	7.50		0.007
J1seep		4/26/00	10.34		0.003
J1	L0	5/11/00	2.83	0.004	-99
J2	L1	5/11/00	1.97	0.007	-99
J3	L9	5/11/00	3.30	0.004	-99
J4a	L3	5/11/00	2.67	0.007	-99
J4c	L4	5/11/00	3.35	0.009	0.019
J6	L7	5/11/00	1.98	0.005	0.008
J6a	L8	5/11/00	3.60	0.010	0.010
J7	L5	5/11/00	1.83	0.009	0.020
	L10	5/11/00	5.32	0.007	-99
	L11	5/11/00	4.49	0.007	0.014
	L12	5/11/00	4.84	0.019	0.007
	L13	5/11/00	3.02	0.008	
	L17	5/11/00	3.02	0.008	0.008
J12a	L20	5/11/00	2.45	0.006	0.015
J12b	L21	5/11/00	4.23	0.016	0.112
J4		5/17/00	1.94	0.009	
J11		5/17/00	3.16	0.009	

In-stream code	Trib.code	date	NO3	PO4	NH4
J11a		5/17/00	1.49	0.005	
J1	L0	5/25/00	3.63	0.014	
J2	L1	5/25/00	3.09	0.011	
J3	L9	5/25/00	4.57	0.012	
J4a	L3	5/25/00	2.88	0.025	
J4c	L4	5/25/00	4.67	0.008	
J6	L7	5/25/00	2.95	0.007	
J6a	L8	5/25/00	5.95	0.014	
J7	L5	5/25/00	2.62	0.009	
J11		5/25/00	4.79	0.018	
J11a		5/25/00	3.49	0.006	
J12a	L20	5/25/00	3.07	0.004	
J12b	L21	5/25/00	5.10	0.026	
	L10	5/25/00	5.90	0.006	
	L11	5/25/00	4.32	0.007	
	L12	5/25/00	7.69	0.028	
	L13	5/25/00	7.05	0.016	
	L17	5/25/00	3.69	0.007	
J1	L0	7/12/00	2.59	0.010	
J2	L1	7/12/00	1.98	0.010	
J3	L9	7/12/00	3.08	0.009	
J4		7/12/00	1.71	0.011	
J4a	L3	7/12/00	3.66	0.010	
J4c	L4	7/12/00	0.18	0.024	
J5		7/12/00	1.76	0.011	
J6	L7	7/12/00	1.54	0.007	
J6a	L8	7/12/00	3.38	0.019	
J6b		7/12/00	1.87	0.005	
J7	L5	7/12/00	1.76	0.007	
J8		7/12/00	2.41	0.003	
J11		7/12/00	3.31	0.011	
J11a		7/12/00	1.02	0.002	
J12a	L20	7/12/00	2.27	0.008	
J12b	L21	7/12/00	3.61	0.022	
	L10	7/12/00	5.64	0.010	
	L11	7/12/00	4.12	0.006	
	L12	7/12/00	4.52	0.037	
	L13	7/12/00	7.03	0.016	
	L15	7/12/00	6.23	0.029	
	L17	7/12/00	2.32	0.010	
	L18	7/12/00	5.38	0.008	

Appendix 4. Complete Cation Data

date	In-stream code	Trib code	Ca	Mg	Na	Sr
5/26/99	J1	L0	19.40	6.20	6.31	0.150
5/26/99	J2	L1	16.19	4.70	4.70	0.130
5/26/99	J3	L9	18.71	6.31	6.20	0.150
5/26/99	J4		16.55	5.00	5.00	0.130
5/26/99	J5		17.00	5.19	5.19	0.140
5/26/99	J6	L7	17.46	5.33	5.33	0.140
5/26/99	J7	L5	15.82	4.93	4.93	0.140
5/26/99	J8		13.63	5.37	5.37	0.140
5/26/99	J9		12.89	5.18	5.18	0.130
5/26/99	J11		20.63	8.25	8.25	0.170
5/26/99	J12		23.66	7.79	7.79	0.220
6/8/99	J1	L0	17.55	6.08	6.59	0.187
6/8/99	J2	L1	16.14	4.41	4.60	0.144
6/8/99	J3	L9	19.47	6.18	6.30	0.154
6/8/99	J4		19.83	5.64	5.19	0.140
6/8/99	J5		17.98	5.14	4.73	0.120
12/4/99	J1	L0	15.36	4.74	5.45	0.009
12/4/99	J2	L1	13.89	3.99	3.63	0.009
12/4/99	J3	L9	16.27	5.42	6.78	0.012
12/4/99	J4		14.48	4.45	4.02	0.010
12/4/99	J5		14.48	4.66	4.47	0.010
12/4/99	J6	L7	13.96	4.62	4.81	0.011
12/4/99	J7	L5	12.51	4.32	3.86	0.010
12/4/99	J8		9.60	4.42	3.32	0.008
12/4/99	J11		15.13	6.62	8.25	0.011
12/4/99	J12a	L20	21.38	7.58	19.30	0.016
12/4/99	J12b	L21	20.31	7.15	10.45	0.017
12/4/99	J2a		14.80	4.32	5.48	0.010
12/4/99	J4a	L3	15.38	3.49	3.20	0.011
12/4/99	J4c	L4	15.50	4.28	4.18	0.011
12/4/99	J6a	L8	18.20	5.73	6.14	0.013
12/4/99	J10		11.99	4.54	4.51	0.009
12/4/99	D/L10	L10	18.61	4.88	3.10	0.014
3/12/00	J1	L0	13.82			
3/12/00	J2	L1	11.39			
3/12/00	J3	L9	13.14			
3/12/00	J4		11.34			
10/18/99	J1	L0	18.26	5.97		
10/18/99	J3	L9	19.24	6.14		
10/18/99	J4		19.88	6.56		
10/18/99	J2	L1	17.34	4.99		
10/18/99	J5		15.61	4.84		

date	In-stream code	Trib code	Ca	Mg	Na	Sr
10/18/99	J6	L7	15.34	4.79		
10/18/99	J7	L5	13.67	4.43		
10/18/99	J8		11.97	4.77		
10/18/99	J9		10.57	4.36		
10/18/99	J11		16.66	6.85		
10/18/99	J12		20.73	6.71		
10/18/99	J12A	L20	21.42	6.95		
10/18/99	J12B	L21	19.00	6.19		
10/18/99	J4A	L3	16.39	3.70		
10/18/99	J4C	L4	15.69	4.02		
3/12/00	J5		13.68			
3/12/00	J6	L7	13.43			
3/12/00	J7	L5	14.49			
3/12/00	J12a	L20	19.98			
3/12/00	J12b	L21	19.02			
3/12/00	J4a	L3	9.53			
3/12/00	J4c	L4	11.72			
3/12/00	J6a	L8	14.47			
3/12/00		L10	12.39			
3/12/00		L11	10.34			
3/12/00		L12	15.94			
3/12/00		L13	14.09			
3/12/00		L14	10.12			
3/12/00		L17	11.75			
5/11/00	J1	L0	19.12			
5/11/00	J2	L1	16.62			
5/11/00	J4a	L3	14.15			
5/11/00	J4c	L4	23.91			
5/11/00	J3	L9	18.76			
5/25/00	J2	L1	13.72			
5/25/00	J3	L9	16.65			
5/25/00	J4a	L3	12.85			
5/25/00	J4c	L4	16.15			
5/25/00	J6	L7	15.40			
5/25/00	J6a	L8	19.99			
5/25/00	J7	L5	11.93			
5/25/00	J11		13.80			
5/25/00	J11a		12.43			
5/25/00		L10	16.77			
5/25/00		L11	12.42			
5/25/00		L12	17.71			
5/25/00		L13	15.87			
5/25/00		L17	12.24			
6/8/99	J6	L7	19.64	5.53	4.99	0.109

date	In-stream code	Trib code	Ca	Mg	Na	Sr
6/8/99	J7	L5	17.16	4.97	4.39	0.109
6/8/99	J8		14.27	5.45	3.77	0.080
6/8/99	J9		13.59	5.21	3.55	0.065
6/8/99	J11		22.58	8.51	9.64	0.098
6/8/99	J12		23.15	7.33	9.10	0.120
6/22/99	J1	L0	20.98			
6/22/99	J2	L1	19.74			
6/22/99	J3	L9	20.81			
6/22/99	J4		19.73			
6/22/99	J5		19.04			
6/22/99	J6	L7	20.24			
6/22/99	J7	L5	13.91			
6/22/99	J8		13.59			
6/22/99	J9		23.70			
6/22/99	J11		17.51			
6/22/99	J12		22.78			
7/20/99	J1	L0	21.48			
7/20/99	J2	L1	20.63			
7/20/99	J3	L9	21.57			
7/20/99	J4		24.63			
7/20/99	J5		21.39			
7/20/99	J6	L7	22.56			
7/20/99	J7	L5	20.59			
7/20/99	J8		15.63			
7/20/99	J9		15.19			
7/20/99	J11		28.55			
7/20/99	J12		24.49			

Appendix 5. Complete anion data plus silica

date	In-stream code	Trib code	Cl	SO4	ALK (HCO3)	SiO2
5/26/99	J1	L0	15.121	22.08	43.40	
5/26/99	J2	L1	9.525	18.66	43.50	
5/26/99	J3	L9	15.917	22.93	47.00	
5/26/99	J4		9.525	18.05	50.80	
5/26/99	J5		8.832	17.07	49.90	
5/26/99	J6	L7	9.911	16.71	51.20	
5/26/99	J7	L5	6.799	15.79	45.20	
5/26/99	J8		8.078	10.49	39.10	
5/26/99	J9		7.294	11.28	38.80	
5/26/99	J11		29.183	18.29	52.00	
5/26/99	J12		34.007	23.29	62.50	
6/8/99	J1	L0	15.048	22.07	54.60	10.255
6/8/99	J2	L1	9.911	18.60	55.39	9.637
6/8/99	J3	L9	15.073	22.07	53.78	9.734
6/8/99	J4		10.164	17.55	57.38	9.441
6/8/99	J5		8.513	16.89	56.91	9.604
6/8/99	J6	L7	9.435	15.78	58.61	10.907
6/8/99	J7	L5	7.026	17.76	57.44	10.093
6/8/99	J8		8.974	9.89	42.84	10.060
6/8/99	J9		8.164	10.55	40.69	10.272
6/8/99	J11		19.326	15.52	57.87	10.695
6/8/99	J12		25.066	20.80	49.60	9.995
6/22/99	J1	L0	13.86	21.88	54.52	7.950
6/22/99	J2	L1	9.71	18.76	55.63	7.416
6/22/99	J3	L9	14.54	17.38	54.74	8.235
6/22/99	J4		10.32	18.02	62.57	7.627
6/22/99	J5		9.46	17.38	59.56	8.049
6/22/99	J6	L7	10.83	16.73	65.78	8.607
6/22/99	J7	L5	7.41	16.09	54.08	8.136
6/22/99	J8		9.69	7.72	45.31	9.289
6/22/99	J9		8.89	11.26	42.80	9.016
6/22/99	J11		32.78	16.73	68.25	8.892
6/22/99	J12		25.37	21.72	56.02	7.727
7/20/99	J1	L0	16.188	20.92	69.96	6.831
7/20/99	J2	L1	10.488	19.31	66.38	5.243
7/20/99	J3	L9	15.618	21.24	69.15	7.207
7/20/99	J4		12.825	17.06	86.18	5.340
7/20/99	J5		8.379	14.80	78.57	7.096
7/20/99	J6	L7	5.814	18.34	81.55	10.745
7/20/99	J7	L5	8.037	11.58	76.37	10.104
7/20/99	J8		11.799	8.37	56.83	10.508
7/20/99	J9		12.027	8.69	54.19	9.617

date	In-stream code	Trib code	Cl	SO4	ALK(HCO3)	SiO2
7/20/99	J11		32.3475	16.09	89.18	10.230
7/20/99	J12		23.37	18.02	74.77	10.132
8/4/99	J1	L0	15.7102	19.07	84.54	6.114
8/4/99	J3	L9	15.9254	19.66	84.69	5.965
8/4/99	J6	L7	7.2098	14.34	88.65	9.450
8/8/99	J1	L0			80.79	6.536
8/8/99	J4		20.88	21.43	90.23	6.561
8/8/99	J5		9.36	14.25	101.72	9.302
8/8/99	J6	L7	4.41	19.23	81.78	9.698
8/8/99	J7	L5	8.45	15.29	81.11	10.542
8/14/99	J1	L0	17.27	41.50	58.51	8.756
8/14/99	J2	L1	16.61	61.30	42.00	8.520
8/14/99	J3	L9	17.64	27.44	68.75	9.078
8/14/99	J5		15.4	69.30		9.351
8/14/99	J6	L7	19.39	101.47		10.443
8/14/99	J7	L5	11.43	40.14		8.706
8/14/99	J12A	L20	34.46	20.42		
8/14/99	J12B	L21	22.82	20.79		
8/26/99	J1	L0			67.91	
8/26/99	J2	L1			66.59	
8/26/99	J3	L9			68.01	
8/26/99	J4				68.05	
8/26/99	J5				71.43	
8/26/99	J6	L7			63.16	
8/26/99	J7	L5			74.69	
8/26/99	J8				56.90	
8/26/99	J9				55.54	
10/18/99	J1	L0			36.37	
10/18/99	J2	L1			35.03	
10/18/99	J3	L9			36.54	
10/18/99	J4				34.56	
10/18/99	J5				33.90	
10/18/99	J6	L7			40.12	
10/18/99	J7	L5			39.62	
10/18/99	J8				33.79	
10/18/99	J9				37.85	
10/18/99	J11				36.35	
10/18/99	J12				48.50	
12/4/99	J2	L1	8.32	21.87		
12/4/99	J3	L9	6.63	23.96		
12/4/99	J4		8.62	22.10		
12/4/99	J5		8.18	21.40		
12/4/99	J6	L7	9.47	23.26		
12/4/99	J7	L5	5.83	18.97		

date	In-stream code	Trib code	Cl	SO4	ALK (HCO3)	SiO2
12/4/99	J8		6.28	15.37		
12/4/99	J11		21.57	19.55		
12/4/99	J12a	L20	32.93	29.64		
12/4/99	J12b	L21	24.07	23.84		
12/4/99	J4a	L3	4.93	22.10		
12/4/99	J6a	L8	10.77	20.71		
12/4/99	D/L10	L10	3.38	24.19		
4/8/00	J1	L0			28.27	
4/8/00	J2	L1			22.95	
4/8/00	J3	L9			29.15	

Appendix 6. On site measurements.

date	In-stream code	Trib code	pH	Cond (μScm^{-1})	DO (mgL^{-1})	Temp ($^{\circ}\text{C}$)
5/26/99	J1	L0	7.89	200	10.38	16
5/26/99	J2	L1	7.88	165	10.44	15.11
5/26/99	J3	L9	7.92	201	10.36	16.33
5/26/99	J4		8.16	167	10.13	19.27
5/26/99	J5		8.04	163	10.18	17.95
5/26/99	J6	L7	7.62	187	9.44	16.14
5/26/99	J7	L5	7.76	146.9	9.72	16.78
5/26/99	J8		7.55	135.7	9.49	14.78
5/26/99	J11		7.66	231	9.76	13.93
5/26/99	J12		7.6	269	8.82	15.47
6/22/99	J1	L0	7.75	212	9.7	16.59
6/22/99	J2	L1	7.33	181	9.76	16.54
6/22/99	J3	L9	7.79	213	9.74	16.91
6/22/99	J4		7.82	187	9.03	20.13
6/22/99	J5		8.03	181	9.32	21.16
6/22/99	J6	L7	7.44	190	8.63	16.96
6/22/99	J7	L5	7.68	164	8.81	20.13
6/22/99	J8		7.27	153		
6/22/99	J9		7.36	147		
6/22/99	J11		7.4	266	8.28	18.01
6/22/99	J12		7.45	250	8.15	20.4
6/22/99	J12A	L20	7.85	300		
6/22/99	J12B	L21	7.37	247		
7/20/99	J1	L0		220	9.9	24.9
7/20/99	J2	L1		193	11.1	23.7
7/20/99	J3	L9		223	10	25.1
7/20/99	J4			234	12.05	25.4
7/20/99	J5			208	11.75	26.3
7/20/99	J6	L7		212	8.25	20.3
7/20/99	J7	L5		200	9.4	25
7/20/99	J8			178	9.1	21.8
7/20/99	J9			179	10	20
7/20/99	J11			328	8.8	20.7
7/20/99	J12			285	7.6	22
7/20/99	J12A	L20		345	11.8	
7/20/99	J12B	L21		270	8.4	
8/4/99	J1	L0	21.14	242	9.97	21.14
8/4/99	J3	L9	21.14	241	10.47	21.24
8/4/99	J6	L7	23.69	211	8.38	23.69
8/8/99	J1	L0	7.07	229	7.05	20.83
8/8/99	J4		7.16	275	7.24	22.15

date	In-stream code	Trib code	pH	Cond	DO	Temp
8/8/99	J5		7.08	237	5.76	22.04
8/8/99	J7	L5	7.12	206	7.36	21.12
8/26/99	J1	L0	8.27	218	9.3	21.7
8/26/99	J2	L1	8.26	216	9.55	21.7
8/26/99	J3	L9	8.265	227	9.45	22
8/26/99	J4		8.665	228	9.25	23.5
8/26/99	J5		8.75	233	10.2	23.8
8/26/99	J6	L7	7.63	273	7.6	20.1
8/26/99	J7	L5	7.05	203	7.6	22.3
8/26/99	J8		7.64	183	7.85	18.9
8/26/99	J9		7.79	185	7.6	20.3
10/18/99	J1	L0	7.74	203		13.7
10/18/99	J2	L1	7.71	172		13
10/18/99	J3	L9	7.8	212		14.2
10/18/99	J4		8.08	178		14.1
10/18/99	J5		8.02	166		13.6
10/18/99	J6	L7	7.52	163		13.6
10/18/99	J7	L5	7.62	150		13.8
10/18/99	J8		7.25	141		13.5
10/18/99	J9		7.37	160		13.7
10/18/99	J10		7.48	144		13.7
10/18/99	J11		7.38	228		12.5
10/18/99	J12		7.53	274		12.7
10/18/99	J4A	L3	7.44	158		12.2
12/4/99	J1	L0	7.11	206	11.1	8.81
12/4/99	J2	L1	7.13	168	11.45	8.13
12/4/99	J3	L9	7.11	211	11.1	8.94
12/4/99	J4		7.12	170	10.8	9.08
12/4/99	J5		7.04	165	11.05	8.93
12/4/99	J6	L7	6.97	167	10.92	8.73
12/4/99	J7	L5	7.02	146	11.02	8.57
12/4/99	J4a	L3	6.86	153	10.82	9.05
12/4/99	J4c	L4	6.73	170	10.05	9.78
12/4/99	J6a	L8	6.9	204	10.97	8.54
4/8/00	J1	L0	7.48	202	9	16.4
4/8/00	J2	L1	7.22	157	9.4	16.6
4/8/00	J3	L9	7.5	204	9.6	16.2
4/8/00	J4a	L3	7.06	136	10	14.6
4/8/00	J4c	L4		164		14.3
4/8/00	J5		16.6			156
4/8/00	J6	L7	7.19	160	9.3	17.7
4/8/00	J6b		7.21	166	9.3	17.7
4/8/00	J7	L5	7.27	136	9.3	16.8
4/8/00	J7Pa		7.2	139	9.2	15.9

date	In-stream code	Trib code	pH	Cond	DO	Temp
4/8/00	J11		7.08	207	9.2	14.3
4/8/00	J11a		6.58	168	7.6	16.6
4/8/00	J12a	L20	7.47	344	9.6	16.3
4/8/00	J12b	L21	7.92	269	10.8	15.4
4/8/00	J12		7.73	295	10.5	15.7
4/8/00		L17	7.14	156	9.4	15.6
4/26/00	J1	L0	8.45	194		10.5
4/26/00	J2	L1	7.85	156		9.6
4/26/00	J3	L9	8.64	201		11
4/26/00	J6	L7		158		12.8
4/26/00	L12		7.73	214		13.4
4/26/00	J1seep		5.8	179		9
5/11/00	J1	L0		197		20.7
5/11/00	J2	L1		172		20
5/11/00	J3	L9		213		20.3
5/11/00	J4a	L3		152		15.6
5/11/00	J4c	L4		189		18.2
5/11/00	J6	L7		173		17.3
5/11/00	J6a	L8		212		16.2
5/11/00	J7	L5		159		17.9
5/11/00		L10		190		17.1
5/11/00		L11		201		18.6
5/11/00		L12		228		17.5
5/11/00		L13		209		17.3
5/11/00		L17		159		18
5/11/00	J12a	L20		305		17.8
5/11/00	J12b	L21		264		18.6
5/17/00	J4		7.75	168	9.55	20.4
5/17/00	J11		7.21	220	9.2	15.6
5/17/00	J11a		6.88	180	7.7	15.4
5/25/00	J1	L0	7.1	167.9	9.88	14.9
5/25/00	J2	L1	7.15	141.6	9.72	15.19
5/25/00	J3	L9	7.21	181.6	9.69	15.56
5/25/00	J4a	L3	6.92	112.2	10.24	11.93
5/25/00	J6	L7	7.14	147.5	9.53	14.27
5/25/00	J6a	L8	7.03	176.7	9.55	13.78
5/25/00	J7	L5	7.19	128.9	9.94	13.59
5/25/00	J11		6.57	315.7	8.29	14.37
5/25/00	J12a	L20	7.38	330.1	9.05	16.16
5/25/00	J12b	L21	7.24	257.6	9.06	15.18
5/25/00		L10	7.05	151.2	10.05	13.5
5/25/00		L11	6.93	146.9	9.87	13.56
5/25/00		L12	7.26	189.1	9.67	14.56
5/25/00		L13	7.14	173.6	9.93	13.79

date	In-stream code	Trib code	pH	Cond	DO	Temp
5/25/00		L17	7	153.6	9.91	13.15
7/12/00	J1	L0		201		20.3
7/12/00	J2	L1		181		19.7
7/12/00	J3	L9		213		20.4
7/12/00	J4			188		25.4
7/12/00	J4a	L3		163		18.2
7/12/00	J4c	L4		267		21
7/12/00	J5			183		24.8
7/12/00	J6	L7		190		19.9
7/12/00	J6a	L8		214		26
7/12/00	J6b			202		25.1
7/12/00	J7	L5		162		22.1
7/12/00	J8			153		21.1
7/12/00	J11			254		18.6
7/12/00	J11a			206		18
7/12/00	J12a	L20		303		18.8
7/12/00	J12b	L21		245		21.5
7/12/00		L10		182		16.5
7/12/00		L11		204		18.6
7/12/00		L12		234		18
7/12/00		L13		222		18.2
7/12/00		L15		238		18.6
7/12/00		L17		161		17.6
7/12/00		L18		231		18

Appendix 6. USGS average Discharge from Schnecksville, PA gauge

Date	Flow (cfs)
5/26/1999	32
6/8/1999	13
6/22/1999	9
7/20/1999	2
8/4/1999	1
8/14/1999	63
10/18/1999	70
12/4/1999	66
3/12/2000	354
3/13/2000	273
4/8/2000	94
4/26/2000	88
5/11/2000	56
5/25/2000	296
7/12/2000	16

Vitae

Christopher W. Shade

Date of Birth: March 1, 1969

Place of Birth: Allentown, PA

Parents: Professor William G. and Mary Louisa Shade

Education:

High School: Liberty High School (1987)
Bethlehem, PA

Undergraduate: B.S. Environmental Science and Resource Management (1993)
Department of Geology
Lehigh University
Bethlehem, PA

Graduate: M.S. Earth and Environmental Science (2000)
Department of Earth and Environmental Sciences
Lehigh University
Bethlehem, PA

Doctorate: Ph.D. Trace Metals Biogeochemistry (in progress)
Dept. of Natural Resources and Environmental Science
University of Illinois, Urbana-Champaign
Champaign, IL

END OF

TITLE