This is to certify that the
dissertation entitled

INFERRING DISSOLVED PHOSPHORUS CYCLING IN A TMDL
WATERSHED USING BIOGEOCHEMISTRY AND MIXED LINEAR
MODELS

presented by

DEAN G. BAAS

has been accepted towards fulfillment
of the requirements for the

Doctoral degree in Geological Sciences and
Biosystems and Agricultural Engineering

Major Professor's Signature

15 MAY 09

Date

MSU is an Affirmative Action/Equal Opportunity Employer

INFERRING DISSOLVED PHOSPHORUS CYCLING IN A TMDL WATERSHED USING BIOGEOCHEMISTRY AND MIXED LINEAR MODELS

By

Dean G. Baas

A DISSERTATION

Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Geological Sciences and
Biosystems and Agricultural Engineering

2009

ABSTRACT

INFERRING DISSOLVED PHOSPHORUS CYCLING IN A TMDL WATERSHED USING BIOGEOCHEMISTRY AND MIXED LINEAR MODELS

By

Dean G. Baas

Eutrophication is a persistent condition of surface waters and a widespread environmental problem. The current state of aquatic ecosystems reflects the anthropogenic impact on processes, chemistry and hydrology; thus understanding relationships between land use and stream biogeochemistry is essential to mitigating eutrophication.

In a two-year study of the Kalamazoo River/Lake Allegan Watershed (KRLAW), a phosphorus (P) total maximum daily load (TMDL) watershed located in southwest Michigan, USA, patterns are identified in suites of chemicals and their relationship to land use to understand the cycling (sources, pathways, fate) of chemicals in the watershed. Although this has been done for P, patterns have not been easily identified with few and weak relationships. Two reasons are proposed for these poor relationships. First, multiple and competing effects on P from temporal (climate, hydrology), catchment (land use, fertilizer application, soil type) and biological (algal productivity, macro-invertebrate grazing) influences. Second, structural restrictions (parameter variance, covariance and correlation) not easily addressed by common statistical methods. Overcoming these deficiencies produces numerous and stronger relationships providing insight into dissolved P (DP) cycling.

The overall hypothesis is DP, stream biogeochemistry and land use have unique relationships and patterns that can be quantified and that DP cycles have characteristic biogeochemical/land use signatures. If true, biogeochemical/land use signatures can be used to identify processes that control DP cycling and outcomes predicted for P mitigation. To test this hypothesis, data is segregated by influence based on biological indicators. Mixed linear models, statistical methods that address parameter covariance and correlation, are used to quantify catchment and biological temporal trends and site effects. Removing these effects, general linear models and principal factor analyses produce improved relationships between DP, stream chemistry and land use.

The catchment influence relationships identify DP source and process correlations with land use. An approach for evaluating DP exports based on readily available land use data is presented. The biological influence analysis identifies impoundment serial discontinuity processes that disconnect the stream system from the landscape, control P cycling and regulate downstream P forms.

Temporal, catchment and biological inferred DP cycling are used to develop an empirical total P (TP) model, based on historical data, to predict Lake Allegan inlet concentrations. The TP model predicts a 63% probability of attaining the 2012 TMDL goal of 72 $\mu g\ L^{-1}$ and mean discharge adjusted 2012 concentration of 65.7 $\mu g\ L^{-1}$.

Results from this study provide insight into the P cycling in a mixed land use watershed and have implications for watershed assessment, P reduction strategies and regulatory TMDL policies.

DEDICATION

This dissertation is dedicated to my parents, Garry and Verna Baas; my brother, Duane Baas; my sisters-in-law, nieces, nephew, great-niece; and in memory of my brother Douglas Baas.

ACKNOWLEDGEMENTS

Thank you to the USDA CSREES and National Water Program for funding this research; the MSU Aqueous and Environmental Geochemistry Laboratory and the W.K. Kellogg Biological Station for laboratory support; and the MSUE Southwest Region and MSUE Land & Water Program for providing resources and funding.

Special thanks to Nora Bello for assistance with statistical analyses and David Week for laboratory analyses and analytical support.

Thank you to my committee of Dr. David T. Long, Dr. Steven I. Safferman, Dr. Theodore L. Loudon and Dr. Phanikumar S. Mantha for their patience and guidance.

I am especially thankful for the support from my many friends and co-workers, especially Dale Mutch, Colleen Mclean, Merideth Fitzpatrick, Neville and Dawn Millar, Danielle Heger, Mike and Cathy McMinn and Drew and Mimi Corbin.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Eutrophication (the over-enrichment of aquatic ecosystems with nutrients) is a persistent condition of surface waters and a widespread environmental problem (Carpenter, 2005; Smith et al., 2006). Carpenter (2005) states, “Eutrophication has become a global problem that is likely to intensify in coming decades because of increases in human population, demand for food, land conversion, fertilizer use and nitrogen deposition.” These increasing human demands on the environment are changing ecosystems in unprecedented ways with long lasting consequences (Vitousek, 1997). Consequences of eutrophication include disproportionate plant production, blooms of harmful algae, increased frequency of anoxic events, deterioration of fisheries and reductions in the aesthetic and economic quality of water bodies (Edmondson et al., 1956; Likens et al., 1971). Human demands, associated with land use and contributing to eutrophication, are reflected in stream biogeochemistry. Understanding land use and stream biogeochemistry relationships is essential to mitigating the causes of eutrophication.

Excessive phosphorus (P) and nitrogen (N) inputs lead to eutrophication (Carpenter et al., 1998; Dodd et al., 2003). Of the two, P is the limiting nutrient and its control is seen as the best means of managing eutrophication (Grobbelaar and House, 1995). Dissolved P (DP) is readily available for biological uptake associated with eutrophication (Sharpley, 1999). Relationships between DP, stream biogeochemistry and land use provide insights into the cycling (sources, transport and fate) of P within a watershed.

Many studies have demonstrated relationships and patterns between land use, human disturbance and stream chemistry (Arntson and Tornes, 1985; Boutt et al., 2001; Fitzpatrick et al., 2007; Wayland et al., 2003; Williams et al., 2005). Although such work has included P, patterns have been difficult to recognize between P, stream chemistry and land use (Liu et al., 2000; Momen et al., 1996; Tsegaye et al., 2006; Zampella et al., 2007). The lack and/or weakness of these patterns is counter-intuitive in light of the many studies that have identified agriculture and urban regions as sources and exporters of P and other chemical solutes (Coulter et al., 2004; Feyereisen et al., 2007; Lewis et al., 2007; Sharpley et al., 2001; Steuer et al., 1997; Waschbusch et al., 1999; Withers and Haygarth, 2007). Two reasons are identified for the lack and/or weakness of the P, stream chemistry and land use patterns and relationships: (1) variable temporal catchment and biological influences, and (2) structural restrictions that complicate data analysis.

First, catchment influence changes the DP, stream chemistry and land use relationships over time with variations in transport pathway (overland, subsurface or groundwater). Within some stream environments, biological influence further varies the catchment influence relationships over time from high rates of biotic DP uptake (Mulholland and Hill, 1997). These two influences introduce different variable temporal trends in the DP data. The catchment and biological influences are addressed by segregating the data by influence.

Second, there are several common structural restrictions associated with analyzing land use and chemical indicators in streams. These include collinearity of land use percentages and spatial autocorrelation of land use and stream data from nesting of sampling sites and serial dependence of time-series data (King et al., 2005). These structural restrictions are not easily accounted for with common multivariate statistical techniques. The structural restrictions are addressed using the mixed linear model (MLM) that permits the data to exhibit correlation (Taskinen et al., 2008). The MLM is a generalization of the standard linear model, making it possible to model not only the means of data but their variances and covariances as well.

Data separation and MLMs are used to quantify the temporal trends and site effects from catchment and biological influences and to improve the DP, stream chemistry and land use relationships. Removing the temporal trends and site effects from the DP allows further evaluation of the stream chemistry and land use patterns and relationships using common multivariate statistical techniques (Pearson's correlations, general linear models (GLM) and principal factor analyses (PFA)). Catchment and biological DP cycling are inferred using these techniques. DP cycling provides insight for watershed P management. These inferences are the basis for developing a P model using contemporary trends in historical P data to predict future P levels.

The overall approach for this research is detailed in Figure 1.1. The objectives of this research are to:

- Identify patterns in suites of chemicals and their relationship to land use.
- Infer DP cycling from the chemical and land use relationships.
- Improve watershed P management using DP cycling insights.
- Predict future P concentrations based on inferred DP cycling.

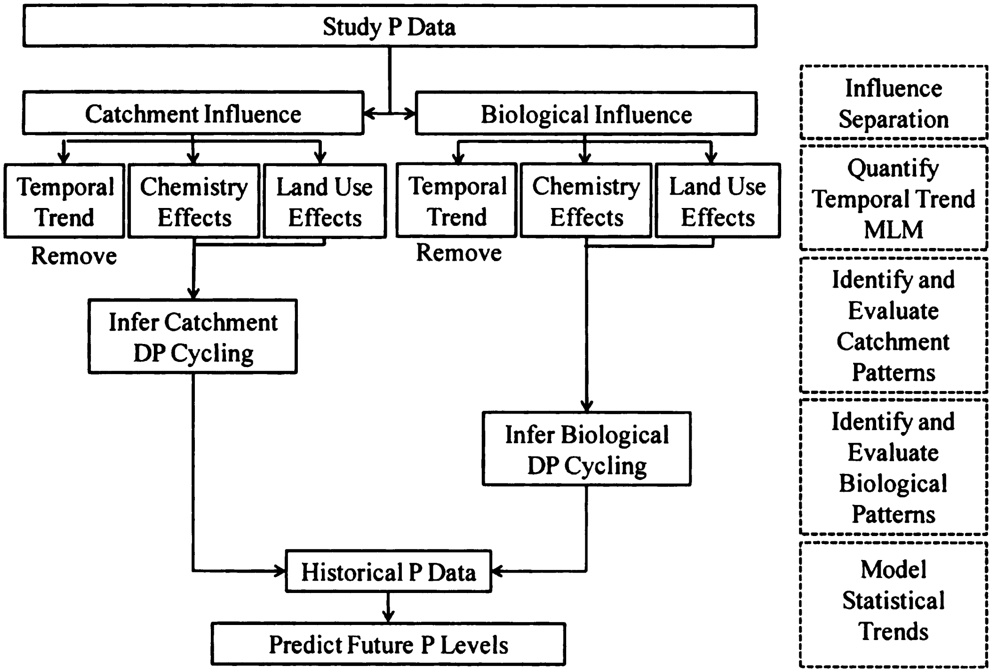


Figure 1.1: Overall research approach.

This study describes a research approach using data separation by influence (catchment or biological), MLMs, GLMs, Pearson's correlations and PFAs to explore the factors controlling DP cycling in the Kalamazoo River/Lake Allegan Watershed (KRLAW). The KRLAW (Figure 1.2) is a mixed land use watershed in southwest Michigan under a P total maximum daily load (TMDL) for Lake Allegan (Figure 1.3), a P impaired waterbody.

This research is predicated on the hypothesis that unique and significant relationships and patterns between DP, stream biogeochemistry and land use can be identified, quantified and used to provide insight into P sourcing, transport and fate that lead to eutrophication. If DP cycling is related to stream biogeochemistry and land use in a predictable manner, the results of this research will facilitate watershed managers and stakeholders in developing reduction programs to mitigate the environmental impacts of P. The approach used in this research can be adapted to other watersheds to improve TMDL development and assessment processes. Furthermore, results from this research have implications for the effectiveness of certain P reduction strategies and TMDL policy development.

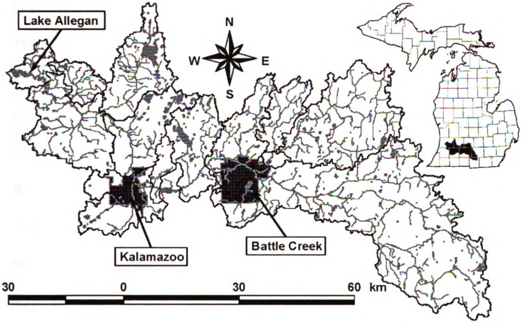


Figure 1.2: Location and extent of the Kalamazoo River/Lake Allegan Watershed, major municipalities (Kalamazoo and Battle Creek) and Lake Allegan.

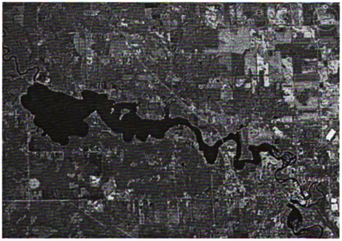


Figure 1.3: Aerial view of Lake Allegan, the P impaired waterbody.

Literature Review

Eutrophication and its effects

Surface water eutrophication resulting from nonpoint source P and N inputs is the most common water quality problem in the United States (USEPA, 1996). The trophic state of surface waters ranges from unproductive (oligitrophic) through intermediate productivity (mesotrophic) to highly productive (eutrophic). Developed most extensively for lakes, factors relating to primary plant production include algal biomass, water column nutrients and water transparency (Dodds, 2007). Consequences of eutrophication include disproportionate plant production, blooms of harmful algae, increased frequency of anoxic events, deterioration of fisheries and reductions in the aesthetic and economic quality of water bodies (Edmondson et al., 1956; Likens et al., 1971). Carpenter (2005) states, "Economic losses attributed to eutrophication include costs of water purification for human use, losses of fish and wildlife production, and loss of recreational amenities."

The adverse effects of eutrophication result from anthropogenic activities in urban and agricultural environments that are major sources of excessive nutrients P and N to aquatic ecosystems (Carpenter et al., 1998; Dodd et al., 2003). P is the limiting nutrient and controlling P concentrations in aquatic systems is a means of controlling aquatic productivity and hence eutrophication (Grobbelaar and House, 1995). Point sources of pollution, including P, from industrial discharges and municipal waste water treatment plants are easily identified and quantified. Point source P loading to surface waters has been greatly reduced since the implementation of the 1972 Federal Clean Water Act (Brett et al., 2005b). However, control of diffuse nonpoint source pollution has been less successful and is considered the main cause of eutrophication in lakes, streams and coastal areas in the United States (National Research Council, 1992; USEPA, 1996).

Sources of eutrophication

Agricultural and urban land uses as sources of P to the environment have been extensively studied. Agriculture has evolved from a net sink of P (e.g., deficits of P limit crop production) to net sources of P (e.g., P inputs in feed and mineral fertilizer can exceed outputs in farm produce) (Sharpley et al., 2001). Continued application of manures and fertilizers in many areas has led to the buildup of soil P concentrations above those required for optimum plant growth (Beauchemin and Simard, 2000; Carpenter et al., 1998; Inamdar et al., 2001; Kleinman et al., 2000; McDowell et al., 2001; McDowell and Sharpley, 2001; Nelson, 1999; Withers and Haygarth, 2007). In-stream concentrations and catchment export of N and P tend to increase with increasing agricultural land use (Bernot et al., 2006; Coulter et al., 2004; Dodds and Oakes, 2006; McDowell et al., 2003).

Compared to rural streams, urban streams often have elevated concentrations of solutes, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^- and base cations (Lewis et al., 2007). The expansion of urban land areas alters land use, which increases impervious surfaces, decreases infiltration, produces higher peak discharge and increases point source inputs from industry and wastewater treatment (Brett et al., 2005a; Brezonik and Stadelmann, 2002; Coulter et al., 2004; Hatt et al., 2004; Lewis et al., 2007; Steuer et al., 1997; Waschbusch et al., 1999). Urban development factors (increases in storm drains, dry wells, impermeable surfaces, etc.) may be responsible for higher P inputs to the stream in urbanizing areas of the Johnson Creek watershed in northern Oregon (Sonoda et al., 2001).

Regulatory requirements

Section 303d of the Federal Clean Water Act requires all states to submit a list of water bodies that do not meet water quality standards to the United States Environmental Protection Agency (USEPA). In addition, the states must identify the impairment, specify the impairment cause and develop and prioritize TMDLs or other watershed restoration approaches for the impaired water bodies (Haggard et al., 2003). As of 2008 in the United States, 5707 water bodies are listed with nutrient impairment and 5084 of those include P (USEPA, 2008b). The proliferation of TMDLs has lead to extensive studies of the relationships between land use change, human disturbance and surface water chemistry, including P.

Land use and surface water chemistry studies

The influence of development, urbanization, agriculture and industrialization, manifested through land use, on surface and groundwater quality is well documented in the literature (Arntson and Tornes, 1985; Boutt et al., 2001; Fitzpatrick et al., 2007; Wayland et al., 2003; Williams et al., 2005). In a study of the Twin Cities metropolitan area (MN), Arnston and Tornes (1985) found the highest concentration of metals, Cl^-, dissolved solids and suspended sediment for the most urbanized site. Rural sites had low concentrations of metals but the highest concentrations of many nutrients. Solute concentrations of Cl^-, SO_4^{2-}, NO_3^- and base cations had significant, positive relationships with the percentage of urban plus agricultural land use in 43 first-order catchments in the Ipswich sub-basins in northeastern Massachusetts

(Williams et al., 2005). Wayland et al. (2003) found elevated levels of Ca^{2+}, Mg^{2+} and alkalinity and frequently K^+, SO_4^{2-} and NO_3^- were associated with agricultural activity while higher concentrations of Na^+, K^+ and Cl^- were associated with urban areas.

Land use changes are known to influence the biogeochemistry of watersheds (Boutt et al., 2001; Fitzpatrick et al., 2007; Tsegaye et al., 2006; Wayland et al., 2003; Williams et al., 2005; Zampella et al., 2007). Fitzpatrick et al. (2007), in a study of the Muskegon River Watershed in Michigan, found all major cations (Na^+, Mg^{2+}, K^+ and Ca^{2+}), anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_x and F^-) and most trace elements (V, Co, Cu, Se, Rb, Sr, Mo, Cd, Ba and U) are higher in both agricultural and urban streams than reference forested streams. Cr and Pb were elevated in urban as compared to agricultural and forested sites. Regression analysis of first-order catchment data indicated a positive and exponential relationship between NO_3^-, acid neutralizing capacity, Cl^-, SO_4^{2-} and base cations and the increasing extent of urban plus agricultural area (Williams et al., 2005).

Land use patterns and their contribution to P exports and loads is also well documented (Glandon et al., 1980; Lehrter, 2006; Lewis et al., 2007; Ontkean et al., 2005; Sonoda and Yeakley, 2007; Tsegaye et al., 2006; Winter and Duthie, 2000). Glandon et al. (1980), in a study of P and N loading from urban, agricultural and wetland sources, found annual P loadings of 0.595 kg ha^{-1}, 0.180 kg ha^{-1} and 0.023 kg ha^{-1} for agricultural, urban and wetland land use, respectively. Fewer studies quantify DP exports and their relationship to land use. One such study by Coulter et al. (2004) documented annual orthophosphate fluxes of 0.28 kg ha^{-1}, 0.12 kg ha^{-1} and 0.07 kg ha^{-1} for agricultural, mixed and urban land uses, respectively, in eastern Kentucky.

Researchers have found large variations in subwatershed stream DP concentrations within the same watershed and attribute this variability to various factors, including seasonal influences, landscape characteristics, hydrology and wetland processes (Novak et al., 2004; Novak et al., 2003; Ontkean et al., 2005).

Lack/weakness of phosphorus relationships

Many studies have demonstrated relationships between land use, human disturbance and surface water chemistry (Liu et al., 2000; Momen et al., 1996; Tsegaye et al., 2006; Zampella et al., 2007). Although such work has included P, patterns have been difficult to recognize between P, stream chemistry and land use by commonly used multivariate statistical techniques (e.g., factor analysis, analysis of variance (ANOVA), multiple regression and cluster analysis). Liu etal. (2000) used factor analysis on 14 subwatersheds throughout the Chesapeake drainage basin to identify the related chemistry variables and their relationship with land cover and physiography. They found DP and PO_4^{3-} had high loadings on a single factor unrelated to other variables which they termed the P factor. Further, for the P factor, regression analyses suggested no significant influence of land cover on P. In a study of the Wheeler Lake Basin of northern Alabama and southern Tennessee, Tsegaye et al. (2006) used ANOVA to identify differences in stream water quality properties in response to seasonal variation, land use practices and location. No significant relationships were found for DP land use, season or the interaction between land use and season. Zampella et al. (2007) used ANOVA and multiple regression in a study of the Mullica River Basin, a major New Jersey Pinelands watershed, to describe the relationship between water quality and land use patterns. In this study, total P (TP) did not appear to vary in relation to land use intensity. Momen et al. (1996) applied multivariate statistics in detecting temporal and spatial patterns in water chemistry from Lake George, New York. Their cluster analysis identified a linear component, which included organic P, which explained a small percentage (10 – 23%) of the total TP variation.

Contributors to phosphorus relationships

Defining the relationship between land use and solute concentrations in large urban and agricultural watersheds is confounded by landscape complexity combining a large variety of human activities, land cover types, topography, geology, soils and vegetation (Herlihy et al., 1998; Norton and Fisher, 2000; Williams et al., 2005). Despite the general trend of higher nutrient exports from disturbed watersheds, it remains difficult to predict flux rates even if land use patterns are well-characterized (Puckett, 1995; Vanni et al., 2001). Several factors can potentially account for variation in nutrient flux rates from watersheds of similar land use, including watershed area, spatial patterns within a landscape, areas which are sources or sinks for nutrients, soil characteristics and the distribution and extent of riparian buffers (Dillon and Kirchner, 1975; Gburek and Sharpley, 1998; Puckett, 1995; Sharpley, 1995; Soranno et al., 1996; Vanni et al., 2001).

In addition to the spatial and physical complexities of large mixed use watersheds, numerous studies have identified temporal effects associated with season hydrological and biological processes. In the Wheeler Lake Basin of northern Alabama, total N (TN), particulate P (PP) and TP concentrations peaked during the summer, TN concentration was lowest in the fall and PP and TP were low in the spring (Tsegaye et al., 2006). Yuan et al. (2007) studied chemical species as indicators for the tracking and apportionment of P within the Table Rock Lake Watershed, Missouri. They found no chemical species had consistent concentration ratios to P due to high seasonal variation of P concentrations. In sub-basins of three different watersheds emptying into an estuary in Mobile Bay, Alabama, P concentrations were strongly regulated by land use/land cover, discharge and seasonality (Lehrter, 2006). A seasonal trend in the daily P dataset was more evident with lower concentrations during intermediate flows than during base flow in the River Kennet, England (Evans and Johnes, 2004). Dorioz et al. (1998) state, "Within the hydrological context of a watershed many physical, biological and chemical processes function to determine the patterns of storage and transport of P." Nonpoint inputs of nutrients are derived from activities dispersed over wide areas of land and are variable in time due to effects of weather (Carpenter et al., 1998).

Mulholland and Hill (1997) found two general modes of control of stream nutrient concentrations: (1) catchment influence via seasonal variation in the dominant hydrologic pathway, and (2) in-stream biological influence via high rates of biotic nutrient uptake during the spring and autumn.

Catchment influence

For catchment control, studies by Mulholland (1993) and Mulholland and Hill (1997) indicate variation in the relative importance of different flow paths. In particular, deep flow permits geochemical interaction with bedrock and shallow lateral flow through the upper soils results in substantial temporal variation in stream water nutrient concentrations. Such hydrological processes helped explain the temporal variation within, and spatial variation between, two streams in southeastern Minnesota with regard to NO_3^-:TP ratios (Green et al., 2007).

Biological influence

For biological influence, surveys and experiments have shown increases in P concentrations lead to increases in algal biomass as chlorophyll *a* in lakes (Edmondson and Lehman, 1981; Smith, 1982), reservoirs (Havel and Pattinson, 2004) and streams (Morgan et al., 2006). Morgan et al. (2006) observed that in high-nutrient agricultural streams, timing and density of algal mats can vary significantly among years and between streams. Biological effects are more prevalent in lakes and reservoirs because they often provide gradients in light and nutrients and retention time for primary production (Kimmel et al., 1990; Knoll et al., 2003).

Restrictions for data analysis

In addition to spatial, physical and temporal complexities, several structural problems have been identified in relating land use to ecological indicators in streams. These include collinearity of land use percentages and spatial autocorrelation of land use and stream data from nesting of sites and serial dependence of time-series data (King et al., 2005; Momen et al., 1996; Zampella et al., 2007). The unidirectional flow of a stream system is such that data from some sampling locations may not be independent observations from other sampling locations. The values at a downstream location are related and correlated to values at the upstream locations. Also, repeated measures over time are not independent from previous sampling dates. Watershed characteristics such as land use have overlapping regions when sampling sites are nested.

Mixed linear model

The MLM provides a method that overcomes these restrictions by permitting the data to exhibit correlation and heteroscedasticity (Taskinen et al., 2008). A MLM is a generalization of the standard linear model, making it possible to model not only the means of data but their variances and covariances as well. Covariance parameters are required when the experimental units can be grouped and the data within a group is correlated and repeated measurements are taken on the same experimental unit and are correlated or exhibit variability that changes (Taskinen et al., 2008).

MLM studies in the biogeochemical sciences are rare but have been used in some environmental applications. Taskinen et al. (2008) used the MLM to study the effects of spatial variation in the saturated hydraulic conductivity on the variation of overland flow in southern Finland. Lehrter (2006) determined station differences in observed constituent concentrations using a MLM with station as a fixed variable and time as a random variable in a study in the Dog River watershed in Alabama. MLMs were used to identify land cover classes that exhibited significant relationships with in-stream nutrient concentrations in a prairie stream in the Mill Creek Watershed in Kansas (Dodds and Oakes, 2006). In that study, spatial autocorrelation was accounted for using MLM for nested sampling locations. Incorporating temporal variables in the MLM analyses with appropriate covariance parameters can identify and quantify the seasonal effects attributable to catchment and biological influences. The remaining significant fixed effects can be evaluated using various statistical methods to develop P land use, stream chemistry and trace element relationships.

Catchment influenced DP cycling

Researchers have found large variations in subwatershed stream DP concentrations within the same watershed and attribute this variability to various factors (Novak et al., 2004; Novak et al., 2003; Ontkean et al., 2005). Some of these include seasonal influences, landscape characteristics, hydrology and wetland processes. In the Herrings Marsh Run Watersheds (Duplin County, North Carolina), Novak et al. (2003) conclude higher DP mass loads were exported during base flow than during storm conditions. They found that mean stream DP concentrations varied throughout the watershed. The percentage of TP as DP was affected by land cover in all sub-basins in the Crowfoot Creek Watershed (Wheatland County, Alberta, Canada) (Ontkean et al., 2005). In that study, the percentage of TP as DP decreased with increased cropped land and increased where grassland acted as a buffer.

Catchment influenced stream segments are connected to the landscape through a system of hydrologically active fields linked to an outlet through a hydrologic network (Jordan-Meille et al., 1998). P is retained and transformed at the watershed-scale through this network. P and N availability vary with seasonal fertilizer application. Their supply, modification and transport through different flow paths produces the greatest variability in nutrient delivery to the stream system (Mulholland and Hill, 1997).

Biological influenced DP cycling

Biological influenced stream segments have been associated with increased nutrient availability for biological activity. TN, TP and benthic and total chlorophyll concentrations were positively correlated to the percentage of upstream land covered by impervious surfaces in the Malibu Creek Watershed, California (Busse et al., 2006). In a study of six streams in Indiana and Michigan, Bernot et al. (2006) demonstrated that biological activity in agriculturally influenced streams is high relative to more pristine streams. This increase likely influences nutrient retention and transport to downstream ecosystems.

The biological activity in streams (Figueroa-Nieves et al., 2006; Morgan et al., 2006; Mulholland, 2004; Stevenson et al., 2006), lakes (French and Petticrew, 2007; Grover and Chrzanowski, 2004; Håkanson, 2005; Reed-Andersen et al., 2000; Yuan et al., 2007) and reservoirs (Havel and Pattinson, 2004; Reed-Andersen et al., 2000; Schreiber and Rausch, 1979) has been shown to regulate many variables, including concentrations of P, suspended solids, many water quality variables and water clarity. Stevenson et al. (2006) state that many measures of algal biomass and nutrient availability were positively correlated in a study of Michigan and Kentucky streams.

Lakes are the most extensively studied biologically influence waterbodies. Researchers have identified relationships between chlorophyll *a*, TP and DP (French and Petticrew, 2007; Håkanson, 2005; Momen et al., 1996) in lake systems. Described as "river-lake hybrids," reservoirs or impoundments represent a transition zone from lotic to lentic ecosystems. They encompass intermediate characteristics that define both lakes and rivers (Kimmel et al., 1990; Wall et al., 2005). Kelly (2001), in a study in the Rio Grande and Colorado basins, found that the connectivity of the aquatic system with the landscape is apparently disrupted by processes within reservoir systems. This concept of process disruption by reservoirs has been termed serial discontinuity (SDC) and results in large changes in solutes (Ward and Stanford, 1995). These changes persist downstream in the absence of significant additional solute inputs. Reservoir processes may be linked for upstream/downstream reservoirs that are located relatively close in a series (Kelly, 2001; Stanford and Ward, 2001).

Predicting future P concentrations

It has long been recognized that P transports in and from catchments are controlled by climate, geology, topography and anthropogenic influences (Dillon and Kirchner, 1975). Models of P transfers range from simple conceptual models to more complex process-based models. Scientists use both theoretical and empirical approaches to prediction. Theoretical predictions are based on a theory of a process or mechanism. However, because of the complexity of catchment systems, the spatial variation of characteristics that control P loss hampers the performance of these models (van der Perk et al., 2007). Empirical predictions are based on curve fitting or pattern recognition without an attempt to represent underlying mechanisms. These models are frequently developed by predicting the contemporary value of a variable from simultaneous values of other variables. Then, by assuming contemporary relationships hold across time, scientist use contemporary models to make future predictions (Carpenter, 2002).

Research Hypothesis

The goal of this research is to use stream biogeochemistry to enhance the understanding of P dynamics (e.g. sourcing, fate and transformation) in a mixed land use watershed under regulatory pressure from a P TMDL. ***The working hypothesis is***

that DP, stream biogeochemistry and land use have unique relationships and patterns that can be quantified, and that certain DP processes have characteristic biogeochemical/land use signatures. If true, these biogeochemical/land use signatures can be used to identify processes that control DP cycling at various locations within the watershed, and the outcome of P mitigation efforts can be predicted.

A crucial assumption of this research is that temporal trends in DP change DP, biogeochemical and land use patterns over time. By quantifying and removing the underlying DP temporal trends, more and stronger correlations are anticipated between DP, stream biogeochemistry and watershed land use.

Quantifying DP temporal trend from catchment influences should result in strong correlations between DP and stream chemistry parameters derived from the same sources as P. NO_3^- and K^+ are applied with P as fertilizers for agricultural production and are also susceptible to loss to surface and groundwaters. Changes in pH, alkalinity and specific conductance associated with urban inputs should relate to DP exported from these environments. Urban and agricultural land uses, as sources of P, are expected to relate to DP. Other land uses contributing to transformations in P form may also be identified.

For biological influenced regions of the watershed, quantifying the DP temporal trends should produce strong correlations between DP, stream solutes and stream chemistry that are modified by biological nutrient uptake and release. DP and NO_3^- concentrations should be highly correlated as essential nutrients for biological activity. Exchanges are expected between PP and DP fractions as DP is removed from the water column and assimilated into biotic biomass. Biomass PP should be released as DP through macroinvertebrate consumption. Photosynthetic effects on pH, alkalinity and Ca^{2+} precipitation from primary productivity may also be evident.

Inferences about the P cycling in the KRLAW should be possible from the relationships and patterns between DP, stream biogeochemistry and land use. DP cycling inferences and historical KRLAW P data can be used to develop an empirical model for predicting future growing season mean P concentration at the inlet of Lake Allegan, the impaired waterbody. This model and the inferred P cycling should provide insight into the effectiveness and outcome of various P reduction strategies.

Study Site

The Kalamazoo River/Lake Allegan Watershed (KRLAW) is a 4200 km^2 watershed located in the southwestern portion of Michigan's Lower Peninsula (Figure 1.2) beginning at the headwaters of the Kalamazoo River and ending at the outlet of Lake Allegan. The Kalamazoo River drains into Lake Michigan approximately 35 km downstream from the outlet of the study area. The geology of the KRLAW is dominated by superficial glacial deposits overlying a bedrock stratigraphy that progresses from Saginaw Formation in the upper northeast through Bayport Limestone and Michigan and Marshall Formations in the central portion. The southeast, northwest and central portions progress from Marshall Formation to Coldwater Shale. Coldwater Shale dominates the southwest and west regions of the KRLAW (Westjohn and Weaver, 1997). Characteristic of Michigan's Lower Peninsula, the Kalamazoo River is predominantly composed of $Ca\text{-}HCO_3$ waters (Wahrer et al., 1996).

The Kalamazoo River has a legacy of serious industrial and nutrient pollution (Heaton, 1999). Largely rural, the watershed is dominated by agriculture and forests. Land use consists of agriculture (46%), upland forest (21%), urban (9%), upland open (9%), non-forested wetlands (8%), lowland forest (5%) and open water (2%). Morrow Lake and Lake Allegan are two large flow-through reservoirs created for electrical generation within the KRLAW.

Lake Allegan is a 6.4 km^2 impoundment formed in 1936 by the building of the Caulkins hydroelectric dam. TheUSEPA conducted a National Eutrophication Study of Lake Allegan in 1972 and classified it as hypereutrophic (USEPA, 1975). The limiting nutrient contributing to eutrophication is P. Additional Michigan Department of Natural Resources (MDNR) studies in 1988, 1994, 1996 and 1997 indicated that Lake Allegan had improved since the 1970s. However, it was still hypereutrophic, with high nutrient and chlorophyll *a* levels, excessive turbidity, periodic nuisance algal blooms, low dissolved oxygen levels and an unbalanced fish community (Heaton, 1999). Lake Allegan was listed in the 1996 and 1998 reports required by section 305(b) of the Clean Water Act as a waterbody not attaining water quality standards (Kosek, 1997; Wycheck, 1998) and was included on Michigan's 303(d) list of impaired surface waters requiring development of a TMDL for P. The USEPA approved the Lake Allegan/Kalamazoo River P TMDL in 2001, setting a TP goal in Lake Allegan of 60 $\mu g\ L^{-1}$ and an inlet goal of 72 $\mu g\ L^{-1}$ (Heaton, 2001). Morrow Lake was used as the reference impoundment to determine Lake Allegan TMDL goals.

Formed in 1939 for the Bryce E. Morrow Power Plant, Morrow Lake is a 4.0 km^2 impoundment. Lake Allegan and Morrow Lake share similar land use characteristics, size and average depth. Morrow Lake has desirable water quality characteristics, including no reported algae blooms, low chlorophyll *a* concentrations, transparency over three feet and a balanced fish community (Bohr and Liston, 1987; Heaton, 2001). These attributes are the basis for the Lake Allegan/Kalamazoo River TMDL goals.

From its inception in 1998, the Lake Allegan/Kalamazoo River TMDL effort has been community based, including landowners, industries, government, community organizations and citizens. These stakeholders collaborated to develop the TMDL goals and P reduction implementation plan. The KRLAW was chosen for this study because of its diverse landscape for examining patterns in P, stream chemistry and land use; regional P reduction challenges; and the TMDL stakeholder interest in P cycling. Furthermore, some biogeochemical data are available from past Michigan Department of Environmental Quality (MDEQ) and MDNR studies for selected locations in the watershed.

Methods

Sample collection and in-stream measurements

Weekly samples were taken from the thalwag portion of the streams in the KRLAW (Figure 1.4). Thirteen and 15 locations (Table 1.1) were sampled during the 2005 and 2006 growing seasons (April through September), respectively. Water samples were collected using a Van Dorn-style horizontal sampler. Filtered samples were filtered through a 0.45 µm Millipore disposable filter. Unfiltered and unpreserved 50 mL samples were retained for TP. Filtered and unpreserved 50 mL samples were retained for DP. Filtered and preserved by acidification with HNO_3 to $pH < 2$, 50 mL samples were collected for cation and anion analysis. Samples were kept on ice in the field and stored at 4 °C until analysis. TP and DP analyses were performed typically within three to seven days of collection. Filtered, unpreserved and unrefrigerated 30 mL samples were collected for alkalinity and analyzed the day of collection. One liter samples were collected at seven locations (BR, WC, KM, KC, KS, KA and KD) in 2006 for chlorophyll *a* and refrigerated and maintained in a dark environment until analysis, typically less than two weeks.

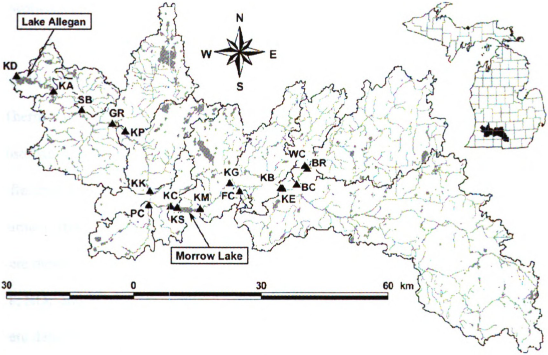


Figure 1.4: Sampling locations ▲ in the Kalamazoo River/Lake Allegan Watershed, and the positions of Morrow Lake and Lake Allegan.

In-stream measurements were taken for temperature, pH, specific conductance, dissolved oxygen and percent dissolved oxygen using a Hydrolab Surveyor 4*a* and Minisonde 4*a* sonde.

The KRLAW was synoptically sampled for trace metals on four dates (June 9, 2005, September 13, 2005, August 8, 2006 and September 12, 2006) corresponding to weekly sampling and in-stream measurement dates. Synoptic sampling was performed at or near stream baseflow conditions. Clean sampling techniques detailed by Fitzpatrick et al. (2007) and Wayland et al. (2003) were used to minimize possible trace element contamination. Trace element samples were filtered through a 0.45 μm Aquaprep disposable filter and acidified with Optima grade HNO_3 to $pH < 2$ and were stored at 4 °C.

Chemical analysis

TP and DP samples were digested using persulfate digestion (Langner and Hendrix, 1982; Valderrama, 1981) and were analyzed by UV/VIS spectrometer (Thermo) using an ammonium molybdate/ascorbic acid method to measure absorbance at 885 nm (Wetzel and Likens, 2000). PP was calculated from the difference between TP and DP. Chlorophyll *a* was analyzed by fluorometer (Sequoia-Turner) after filtering and ethanol extraction (Welschmeyer, 1994). Ca^{2+} and Mg^{2+} were measured using flame atomic adsorption spectroscopy (Perkin-Elmer). Na^+, K^+, Cl^-, NO_3^- and SO_4^{2-} were analyzed using ion chromatography (Dionex). Alkalinities were determined by Gran titration with H_2SO_4. Analytical accuracy was checked using the charge balance method (Freeze and Cherry, 1979). For charge balance errors greater than 10% the source of the error was identified (e.g., recording errors or analysis errors) and corrected, including reanalysis if required. For the final dataset, all sample charge balance errors were less than 8%. The weekly sampled stream chemistry dataset is given in Appendix I.

Trace elements (B, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Ba, Pb, U and Mo) were quantified using a Micromass Platform Hexapole inductively coupled plasma-mass spectrometer. Results below the detection limits for each element were eliminated from the data. This eliminated all results for Cu and some of the results for Co, Ni, Cd, Sn and Pb. The trace element dataset is given in Appendix II.

Land use identification

Land use was quantified for the catchment draining to each sampling location from geographic information system (GIS) data obtained from the Michigan Geographic Data Library (MiGDL). The 2001 Lower Peninsula Land Cover/Use Theme (MiGDL, 2007), derived from classification of Landsat Thematic Mapper imagery was clipped by the sample watersheds delineated from the Kalamazoo River Watershed Theme (MiGDL, 2007) using ArcView GIS (Environmental Systems Research Institute, Inc., 1992 – 1999).

Land use percentages were summarized for each sample catchment at the class levels of (I) urban, (II) agricultural, (III) upland openland, (IV) upland forest, (V) water, (VI) lowland forest, (VII) non-forested wetlands and (VIII) bare/sparsely vegetated (Table 1.1).

Soil group identification

Soil groups were quantified for the catchment draining to each sampling location from GIS data obtained from the MiGDL (MiGDL, 2007). The 1994 State Soil Geographic (STATSGO) database for Michigan Theme was clipped by the sample watersheds delineated from the Kalamazoo River Watershed Theme using ArcView GIS (Environmental Systems Research Institute, Inc., 1992 – 1999).

Twenty soil groups identified by map unit ID (MUID) were represented in the KRLAW. The 13 MUIDs and their corresponding soil group common to all sampled catchments that reflect at least 90% of individual catchment soil groups is given in Table 1.2.

Historical data sources

In addition to P concentration data from this KRLAW study, historical data from other sources were obtained (Table 1.3, Appendices III and IV). P concentration data collected by the MDEQ for the Kalamazoo River was acquired from MDEQ reports (Heaton, 1999; Heaton, 2003), STORET, the EPA's Computerized Environmental Data System (USEPA, 2008a) and through personal communications. Point source loading data were obtained from the Kalamazoo River TMDL Point Source Tracking System (Kieser & Associates, 2008) and an MDEQ report (Heaton, 1999). Discharge information for gaging stations 04106000, Kalamazoo River at Comstock, MI, and 04108670, Kalamazoo River at New Richmond, MI, were obtained from the USGS Annual Water Data Reports (USGS, 2008a; USGS, 2008b).

Table 1.1: Site id, name, longitude, latitude, years sampled and % land use by class level for sampling locations in the Kalamazoo River/Lake Allegan Watershed.

Site ID	Site Name	Longitude	Latitude	Yrs Sampled		Percent land use by class level							
				2005	2006	I	II	III	IV	V	VI	VII	VIII
BC	Battle Creek River @ Emmett St. Dam	-85.1525	42.3303	X	X	5.3	51	6.9	18	1.0	7.5	9.7	0.4
BR	Battle Creek River	-85.1224	42.3642	X	X	5.3	54	6.5	16	1.2	7.6	9.7	0.4
FC	Fort Custer Eagle Lake Tributary	-85.3169	42.3172	X		3.0	0	9.3	72	0.2	6.6	8.6	0.1
GR	Gun River	-85.6789	42.4624	X	X	5.8	47	7.5	23	5.1	3.9	7.0	0.6
KA	Kalamazoo River @ Allegan	-85.8482	42.5312	X	X	8.5	46	8.6	21	1.8	5.4	8.1	0.3
KB	Kalamazoo River @ Battle Creek	-85.1978	42.3241	X	X	6.3	53	7.4	17	0.8	6.0	9.1	0.3
KC	Kalamazoo River @ Comstock	-85.5137	42.2860	X	X	6.8	49	8.1	20	1.4	5.9	8.9	0.3
KD	Kalamazoo River @ Caulkins Dam	-85.9541	42.5639	X	X	8.5	46	8.7	21	2.0	5.4	8.0	0.3
KE	Kalamazoo River East of Battle Creek	-85.1935	42.3226	X	X	6.1	55	7.7	16	0.7	5.3	8.8	0.2
KG	Kalamazoo River @ Augusta	-85.3447	42.3344		X	6.8	50	8.1	19	0.8	6.1	9.2	0.3
KK	Kalamazoo River @ Kalamazoo	-85.5730	42.3180		X	9.1	46	8.4	21	1.4	5.7	8.4	0.3
KM	Kalamazoo River @ Galesburg	-85.4289	42.2802	X	X	6.7	49	8.1	20	1.2	6.0	9.1	0.3
KP	Kalamazoo River @ Plainwell	-85.6420	42.4457	X	X	9.0	46	8.6	21	1.5	5.5	8.3	0.3
KS	Kalamazoo River @ Morrow Dam	-85.4947	42.2828		X	6.7	49	8.1	20	1.3	6.0	9.0	0.3
PC	Portage Creek	-85.5758	42.2877	X	X	31	17	11	32	2.1	3.4	3.8	0.4
SB	Schnable Brook	-85.7676	42.4918	X		5.1	58	7.7	16	1.7	4.0	7.4	0.3
WC	Wanadoga Creek	-85.1289	42.3700		X	3.9	47	7.7	22	0.3	7.4	11	0.2

Class levels: I - Urban, II - Agricultural, III - Upland openland, IV - Upland forest, V - Water, VI - Lowland forest,
VII - Non-forested wetlands and VIII - Barely/sparsely vegetated

Table 1.2: STATSGO soil group distributions representing greater than 90 % of the soils within each sampling site catchment in the Kalamazoo River/Lake Allegan Watershed.

Site ID	Michigan Soil Map Unit Id (MUID)												
	MI011 (%)	MI014 (%)	MI022 (%)	MI024 (%)	MI034 (%)	MI035 (%)	MI036 (%)	MI043 (%)	MI045 (%)	MI047 (%)	MI048 (%)	MI083 (%)	MI091 (%)
BC			15	14	2	27	16	2	18				
BR				17		17	10		32				24
FC									88	12			
GR	47						7				4	16	18
KA	9	4	3	2	15	5	5	3	28	6	4	3	6
KB		8	5	5	28	9	6	7	24	1			2
KC		6	4	4	22	7	5	5	31	4			5
KD	9	4	3	2	14	5	5	3	27	6	4	3	6
KE		12	1		41			9	27	1			
KG		7	5	4	25	8	5	6	25	1			5
KK	1	5	4	3	20	6	4	5	31	8			4
KM		6	4	4	22	7	5	5	30	2			5
KP	3	5	3	3	18	6	4	4	32	8			6
KS		6	4	4	22	7	5	5	31	3			5
PC	23								37	41			
SB	28						17				54		
WC			19	12	3	31	19	2	13				

MUID	Soil Group	MUID	Soil Group
MI011	Coloma-Spinks-Oshtemo	MI043	Matherton-Sebewa-Fox
MI014	Spinks-Houghton-Boyer	MI045	Oshtemo-Kalamazoo-Houghton
MI022	Houghton-Carlisle-Adrian	MI047	Schoolcraft-Kalamazoo-Elston
MI024	Boyer-Oakville-Cohoctah	MI048	Capac-Riddles-Selfridge
MI034	Riddles-Hillsdale-Gilford	MI083	Granby-Gilford-Thetford
MI035	Marlette-Capac-Parkhill	MI091	Oshtemo-Spinks-Marlette
MI036	Marlette-Capac-Spinks		

Research Approach

The working hypothesis is that DP, stream biogeochemistry and land use have unique relationships and patterns that can be quantified and that certain DP processes have characteristic biogeochemical/land use signatures. This hypothesis will be explored for the KRLAW through intensive sampling, various statistical analyses, geographic information system land use/land cover databases and historical data. While other research has linked a limited number of stream chemistry and land use parameters to DP, this research is the first to separate temporal trends in DP to increase the number and strength of correlated stream chemistry and land use parameters. The approach in this proposal is unique in the use of MLMs to overcome structure restrictions in longitudinal, time-series data. The analysis presented provides an approach for inferring P cycling using stream biogeochemistry and land use information that leads to a better understanding of the interaction between competing processes and their potential effect on the outcome of P mitigation strategies.

Chapter 2 develops methods to quantify the temporal trends in DP to increase and strengthen the relationships between DP, stream chemistry and land use. An approach is presented for separating data by catchment or biological influence and uses MLMs to quantify DP temporal trends. The results of these analyses are used to remove temporal trends and site effects from the DP data, allowing the investigation of DP cycling using other common statistical methods.

Chapter 3 explores DP cycling in the catchment influenced MLM results and analyzes the temporal and site adjusted DP and land use relationships. A DP source component associated with agricultural and urban land use and a catchment DP

Table 1.3: Historical data sources by year for P concentrations, point source loading, discharge at Comstock, MI and discharge at New Richmond, MI.

Year	Phosphorus Concentrations	Point Source Loading	Discharge at Comstock, MI	Discharge at New Richmond, MI
2007 - 2008	NA	KR TMDL Point Souce Tracking Program[1]	NA	NA
2005-2006	KRLAW study	KR TMDL Point Souce Tracking Program[1]	USGS Report[2]	USGS Report[3]
2003 - 2004	MDEQ - Personal communication with S. Heaton	KR TMDL Point Souce Tracking Program[1]	USGS Report[2]	USGS Report[3]
2001 - 2002	2003 MDEQ Report[4]	KR TMDL Point Souce Tracking Program[1]	USGS Report[2]	NA
1999 - 2001	2003 MDEQ Report[4]	NA	USGS Report[2]	NA
1998	1999 MDEQ Report[5]	1999 MDEQ Report[5]	USGS Report[2]	NA
1996 - 1997	NA	NA	USGS Report[2]	NA
1995	NA	NA	USGS Report[2]	USGS Report[3]
1994	MDEQ - Personal communication with G. Danneffel	NA	USGS Report[2]	USGS Report[3]
1985 - 1993	MDEQ - STORET[6]	NA	USGS Report[2]	NA
1980 - 1984	MDEQ - STORET[6]	NA	USGS Report[2]	NA
1975 - 1979	MDEQ - STORET[6]	NA	NA	NA
1973 - 1974	NA	NA	USGS Report[2]	NA
1971 - 1972	MDEQ - STORET[6]	NA	USGS Report[2]	NA
1933 - 1970	NA	NA	USGS Report[2]	NA

NA – Not Available

[1] Kalamazoo River TMDL Point Source Tracking Program (Kieser & Associates, 2008).

[2] USGS Annual Water Data Report for USGS Station #04106000, Kalamazoo River at Comstock, MI (USGS, 2008a)

[3] USGS Annual Water Data Report for USGS Station #04108670, Kalamazoo River at New Richmond, MI (USGS, 2008b)

[4] MDEQ Staff Report (Heaton, 2003)

[5] MDEQ Staff Report (Heaton, 1999)

[6] STORET – EPA's Computerized Environmental Data System (USEPA, 2008a)

process represented by lowland forest land use are identified. An approach for evaluating the susceptibility of KRLAW subwatersheds to low, medium and high DP exports based on readily available land use data is presented. To explore the existence and interaction of P source and P process dynamics, Pearson's correlation coefficients and principal factor analyses are used to identify patterns in temporal and site adjusted DP, land use, stream chemistry, trace elements and soil groups. The implications of P management practices on DP are considered in light of the inferred P cycling.

Chapter 4 evaluates DP cycling in the biological influenced MLM results and analyzes the temporal and site adjusted DP and stream chemistry relationships. Large serial flow-through impoundments are identified as environments for biological influence including algal productivity. Impoundment processes are explored that disconnect the stream system from the landscape, control P cycling and regulate downstream P forms. The compensatory nature of these processes to offset P reduction efforts and delay the downstream response is discussed.

Chapter 5 uses inferences into DP cycling developed in Chapters 2 through 4 to develop an empirical TP model for the KRLAW based on contemporary trends in historical TP and discharge data. The model is used to predict the future growing season mean TP concentration to Lake Allegan. Dependencies between TP concentration and various discharge parameters are identified through this model. Probabilities are predicted for attaining the 72 $\mu g\ L^{-1}$ TMDL P goal in 2012 without discharge adjustments. Discharge adjusted inlet concentration to Lake Allegan is forecasted for 2012. The effectiveness and outcome of various point and nonpoint P reduction strategies in the KRLAW are presented.

Literature Cited

Arntson, A.D. and Tornes, L.H., 1985. Rainfall-runoff relationships and water-quality assessment of Coon Creek watershed, Anoka County, Minnesota. US Geological Survey of Water Resources Investigation Report 84-4013.

Beauchemin, S. and Simard, R.R., 2000. Phosphorus status of intensively cropped soils of the St. Lawrence lowlands. Soil Science Society of America Journal, 64(2): 659-670.

Bernot, M.J., Tank, J.L., Royer, T.V. and David, M.B., 2006. Nutrient uptake in streams draining agricultural catchments of the midwestern United States. Freshwater Biology, 51(3): 499-509.

Bohr, J. and Liston, C., 1987. A survey of the fish and benthic communities of Morrow Lake on the Kalamazoo River, Michigan, 1985 and 1986, Report to STS Consultants Ltd.

Boutt, D.F., Hyndman, D.W., Pijanowski, B.C. and Long, D.T., 2001. Identifying potential land use-derived solute sources to stream baseflow using ground water models and GIS. Ground Water, 39(1): 24-34.

Brett, M.T., Arhonditsis, G.B., Mueller, S.E., Hartley, D.M., Frodge, J.D. and Funke, D.E., 2005a. Non-point-source impacts on stream nutrient concentrations along a forest to urban gradient. Environmental Management, 35(3): 330-342.

Brett, M.T., Mueller, S.E. and Arhonditsis, G.B., 2005b. A daily time series analysis of stream water phosphorus concentrations along an urban to forest gradient. Environmental Management, 35(1): 56-71.

Brezonik, P.L. and Stadelmann, T.H., 2002. Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. Water Research, 36(7): 1743-1757.

Busse, L.B., Simpson, J.C. and Cooper, S.D., 2006. Relationships among nutrients, algae, and land use in urbanized southern California streams. Canadian Journal of Fisheries and Aquatic Sciences, 63(12): 2621-2638.

Carpenter, S.R., 2002. Ecological Futures: Building an Ecology of the Long Now. Ecology, 83(8): 2069-2083.

Carpenter, S.R., 2005. Eutrophication of Aquatic Ecosystems: Bistability and Soil Phosphorus. Proceedings of the National Academy of Sciences of the United States of America, 102(29): 10002-10005.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H., 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. Ecological Applications, 8(3): 559-568.

Coulter, C.B., Kolka, R.K. and Thompson, J.A., 2004. Water quality in agricultural, urban, and mixed land use watersheds. Journal of the American Water Resources Association, 40(6): 1593-1601.

Dillon, P.J. and Kirchner, W.B., 1975. Effects of geology and land-use on export of phosphorus from watersheds. Water Research, 9(2): 135-148.

Dodd, J., Large, D.J., Fortey, N.J., Kemp, S., Styles, M., Wetton, P. and Milodowski, A., 2003. Geochemistry and petrography of phosphorus in urban canal bed sediment. Applied Geochemistry, 18(2): 259-267.

Dodds, W.K., 2007. Trophic state, eutrophication and nutrient criteria in streams. Trends Ecol Evol, 22(12): 669-76.

Dodds, W.K. and Oakes, R.M., 2006. Controls on nutrients across a prairie stream watershed: Land use and riparian cover effects. Environmental Management, 37(5): 634-646.

Dorioz, J.M., Cassell, E.A., Orand, A. and Eisenman, K.G., 1998. Phosphorus storage, transport and export dynamics in the Foron river watershed. Hydrological Processes, 12(2): 285-309.

Edmondson, W.T., Anderson, G.C. and Peterson, D.R., 1956. Artificial Eutrophication of Lake Washington. Limnology and Oceanography, 1(1): 47-53.

Edmondson, W.T. and Lehman, J.T., 1981. The effect of changes in the nutrient income on the condition of Lake Washington. Limnology and Oceanography, 26(1): 1-29.

Evans, D.J. and Johnes, P., 2004. Physico-chemical controls on phosphorus cycling in two lowland streams. Part 1 - the water column. Science of the Total Environment, 329(1-3): 145-163.

Feyereisen, G.W., Lowrance, R., Strickland, T.C., Sheridan, J.M., Hubbard, R.K. and Bosch, D.D., 2007. Long-term water chemistry database, Little River Experimental Watershed, southeast Coastal Plain, United States. Water Resources Research, 43(9).

Figueroa-Nieves, D., Royer, T.V. and David, M.B., 2006. Controls on chlorophyll-a in nutrient-rich agricultural streams in Illinois, USA. Hydrobiologia, 568: 287-298.

Fitzpatrick, M.L., Long, D.T. and Pijanowski, B.C., 2007. Exploring the effects of urban and agricultural land use on surface water chemistry, across a regional watershed, using multivariate statistics. Applied Geochemistry, 22(8): 1825-1840.

Freeze, R.A. and Cherry, J.A., 1979. Groundwater. Prentice Hall, Englewood Cliffs, NJ.

French, T.D. and Petticrew, E.L., 2007. Chlorophyll a seasonality in four shallow eutrophic lakes (northern British Columbia, Canada) and the critical roles of internal phosphorus loading and temperature. Hydrobiologia, 575: 285-299.

Gburek, W.J. and Sharpley, A.N., 1998. Hydrologic controls on phosphorus loss from upland agricultural watersheds. Journal of Environmental Quality, 27(2): 267-277.

Glandon, R.P., Payne, F.C., McNabb, C.D. and Batterson, T.R., 1980. A comparison of rain-related phosphorus and nitrogen loading from urban, wetland, and agricultural sources. Water Research, 15: 881-887.

Green, M.B., Nieber, J.L., Johnson, G., Magner, J. and Schaefer, B., 2007. Flow path influence on an N : P ratio in two headwater streams: A paired watershed study. Journal of Geophysical Research-Biogeosciences, 112(G3).

Grobbelaar, J.U. and House, W.A., 1995. Phosphorus as a limiting resource in inland waters; interaction with nitorgen. In: H. Tiessen (Editor), Phosphorus in the global environment. John Wiley & Sons, New York, pp. 255-273.

Grover, J.P. and Chrzanowski, T.H., 2004. Limiting resources, disturbance, and diversity in phytoplankton communities. Ecological Monographs, 74(3): 533-551.

Haggard, B.E., Soerens, T.S., Green, W.R. and Richards, R.P., 2003. Using regression methods to estimate stream phosphorus loads at the Illinois River, Arkansas. Applied Engineering in Agriculture, 19(2): 187-194.

Håkanson, L., 2005. The Importance of Lake Morphometry for the Structure and Function of Lakes. International Review of Hydrobiology, 90(4): 433-461.

Hatt, B.E., Fletcher, T.D., Walsh, C.J. and Taylor, S.L., 2004. The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environmental Management, 34(1): 112-124.

Havel, J.E. and Pattinson, K.R., 2004. Spatial distribution and seasonal dynamics of plankton in a terminal multiple-series reservoir. Lake and Reservoir Management, 20(1): 14-26.

Heaton, S., 1999. Loading assessments of phosphorus inputs to Lake Allegan, 1998. Report No. MI/DEQ/SWQ-99-125, MDEQ, Surface Water Quality Division.

Heaton, S., 2001. Total maximum daily load (TMDL) for total phosphorus in Lake Allegan. http://www.deq.state.mi.us/documents/deq-swq-gleas-tmdlallegan.pdf, MDEQ, Surface Water Quality Division.

Heaton, S., 2003. Water quality monitoring of Lake Allegan and select stations on the Kalamazoo River, 2003. Report No. MI/DEQ/SWQ-03-1.3, MDEQ, Surface Water Quality Division.

Herlihy, A.T., Stoddard, J.L. and Johnson, C.B., 1998. The relationship between stream chemistry and watershed land cover data in the mid-Atlantic region, US, pp. 377-386.

Inamdar, S.P., Mostaghimi, S., McClellan, P.W. and Brannan, K.M., 2001. BMP impacts on sediment and nutrient yields from an agricultural watershed in the coastal plain region. Transactions of the Asae, 44(5): 1191-1200.

Jordan-Meille, L., Dorioz, J.M. and Wang, D., 1998. Analysis of the export of diffuse phosphorus from a small rural watershed. Agronomie, 18(1): 5-26.

Kelly, V.J., 2001. Influence of reservoirs on solute transport: a regional-scale approach. Hydrological Processes, 15(7): 1227-1249.

Kieser & Associates, 2008. Kalamazoo River TMDL Point Source Tracking Program, http://www.kalamazooriver.net/cgi/ps_v2/intro.cgi.

Kimmel, B.L., Lind, O.T. and Paulson, L.J., 1990. Reservoir Primary Production. In: K.W. Thornton, B.L. Kimmel and F.E. Payne (Editors), Reservoir Limnology: Ecological Perspectives. John Wiley & Sons, Inc., New York, NY.

King, R.S., Baker, M.E., Whigham, D.F., Weller, D.E., Jordan, T.E., Kazyak, P.F. and Hurd, M.K., 2005. Spatial considerations for linking watershed land cover to ecological indicators in streams. Ecological Applications, 15(1): 137-153.

Kleinman, P.J.A., Bryant, R.B., Reid, W.S., Sharpley, A.N. and Pimentel, D., 2000. Using soil phosphorus behavior to identify environmental thresholds. Soil Science, 165(12): 943-950.

Knoll, L.B., Vanni, M.J. and Renwick, W.H., 2003. Phytoplankton primary production and photosynthetic parameters in reservoirs along a gradient of watershed land use. Limnology and Oceanography, 48(2): 608-617.

Kosek, S., 1997. Water quality and pollution control in Michigan, 1996 Report. Michigan 305(b) Report: Volume 14. Report No. MI/DEQ/SWQ-97-040, MDEQ, Surface Water Quality Division.

Langner, C.L. and Hendrix, P.F., 1982. Evaluation of a persulfate digestion method for particulate nitrogen and phosphorus. Water Research, 16(10): 1451-1454.

Lehrter, J.C., 2006. Effects of land use and land cover, stream discharge, and interannual climate on the magnitude and timing of nitrogen, phosphorus, and organic carbon concentrations in three coastal plain watersheds. Water Environment Research, 78(12): 2356-2368.

Lewis, G.P., Mitchell, J.D., Andersen, C.B., Haney, D.C., Liao, M.K. and Sargent, K.A., 2007. Urban influences on stream chemistry and biology in the Big Brushy Creek watershed, South Carolina. Water Air and Soil Pollution, 182(1-4): 303-323.

Likens, G.E., Bartsch, A.F., Lauff, G.H. and Hobbie, J.E., 1971. Nutrients and eutrophication. Science, 172(3985): 873-&.

Liu, Z.J., Weller, D.E., Correll, D.L. and Jordan, T.E., 2000. Effects of land cover and geology on stream chemistry in watersheds of Chesapeake Bay. Journal of the American Water Resources Association, 36(6): 1349-1365.

McDowell, R., Sharpley, A. and Folmar, G., 2001. Phosphorus export from an agricultural watershed: Linking source and transport mechanisms. Journal of Environmental Quality, 30(5): 1587-1595.

McDowell, R.W. and Sharpley, A.N., 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. Journal of Environmental Quality, 30(2): 508-520.

McDowell, R.W., Sharpley, A.N. and Folmar, G., 2003. Modification of phosphorus export from an eastern USA catchment by fluvial sediment and phosphorus inputs. Agriculture Ecosystems & Environment, 99(1-3): 187-199.

MiGDL, 2007. Michigan Geographic Data Library Center for Geographic Information. Department of Information Technology, http://www.mcgi.state.mi.us/mgdl/.

Momen, B., Eichler, L.W., Boylen, C.W. and Zehr, J.P., 1996. Application of multivariate statistics in detecting temporal and spatial patterns of water chemistry in Lake George, New York. Ecological Modelling, 91(1-3): 183-192.

Morgan, A.M., Royer, T.V., David, M.B. and Gentry, L.E., 2006. Relationships among nutrients, chlorophyll-alpha, and dissolved oxygen in agericultural streams in Illinois. Journal of Environmental Quality, 35(4): 1110-1117.

Mulholland, P.J., 1993. Hydrometric and steam chemistry evidence of 3 storm flowpaths in Walker-Branch Watershed. Journal of Hydrology, 151(2-4): 291-316.

Mulholland, P.J., 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. Biogeochemistry, 70(3): 403-426.

Mulholland, P.J. and Hill, W.R., 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. Water Resources Research, 33(6): 1297-1306.

National Research Council, 1992. Restoration of aquatic ecosystems: science, technology, and public policy. National Academy Press, Washington, D.C.

Nelson, C.J., 1999. Managing nutrients across regions of the United States. Journal of Animal Science, 77: 90-100.

Norton, M.M. and Fisher, T.R., 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay, pp. 337-362.

Novak, J.M., Stone, K.C., Szogi, A.A., Watts, D.W. and Johnson, M.H., 2004. Dissolved phosphorus retention and release from a coastal plain in-stream wetland. Journal of Environmental Quality, 33(1): 394-401.

Novak, J.M., Stone, K.C., Watts, D.W. and Johnson, M.H., 2003. Dissolved phosphorus transport during storm and base flow conditions from an agriculturally intensive southeastern coastal plain watershed. Transactions of the Asae, 46(5): 1355-1363.

Ontkean, G.R., Chanasyk, D.S. and Bennett, D.R., 2005. Snowmelt and growing season phosphorus flux in an agricultural watershed in south-central Alberta, Canada. Water Quality Research Journal of Canada, 40(4): 402-417.

Puckett, L.J., 1995. Identifying the major sources of nutrient water-pollution. Environmental Science & Technology, 29(9): A408-A414.

Reed-Andersen, T., Carpenter, S.R. and Lathrop, R.C., 2000. Phosphorus Flow in a Watershed-Lake Ecosystem. Ecosystems, 3(6): 561-573.

Schreiber, J.D. and Rausch, D.L., 1979. Suspended Sediment-Phosphorus Relationships for the Inflow and Outflow of a Flood Detention Reservoir. J Environ Qual, 8(4): 510-514.

Sharpley, A., 1995. Identifying sites vulnerable to phosphorus loss in agricultrual runoff. Journal of Environmental Quality, 24(5): 947-951.

Sharpley, A., 1999. Agricultural phosphorus, water quality, and poultry production: are they compatible? Poult Sci, 78(5): 660-673.

Sharpley, A.N., McDowell, R.W. and Kleinman, P.J.A., 2001. Phosphorus loss from land to water: integrating agricultural and environmental management. Plant and Soil, 237(2): 287-307.

Smith, V.H., 1982. The nitrogen and phosphorus dependence of algal biomass in lakes - an empirical and theoretical-analysis. Limnology and Oceanography, 27(6): 1101-1112.

Smith, V.H., Joye, S.B. and Howarth, R.W., 2006. Eutrophication of freshwater and marine ecosystems. Limnology and Oceanography, 51(1): 351-355.

Sonoda, K. and Yeakley, J.A., 2007. Relative effects of land use and near-stream chemistry on phosphorus in an urban stream. Journal of Environmental Quality, 36(1): 144-154.

Sonoda, K., Yeakley, J.A. and Walker, C.E., 2001. Near-stream landuse effects on streamwater nutrient distribution in an urbanizing watershed. Journal of the American Water Resources Association, 37(6): 1517-1532.

Soranno, P.A., Hubler, S.L., Carpenter, S.R. and Lathrop, R.C., 1996. Phosphorus loads to surface waters: A simple model to account for spatial pattern of land use. Ecological Applications, 6(3): 865-878.

Stanford, J.A. and Ward, J.V., 2001. Revisiting the serial discontinuity concept, pp. 303-310.

Steuer, J., Selbig, W., Hornewer, J. and Prey, J., 1997. Sources of contamination in an urban basin in Marquette, Michigan and an analysis of concentrations, loads, and data quality, U.S. Geological Survey Water-Resources Investigations Report 97-4242.

Stevenson, R.J., Rier, S.T., Riseng, C.M., Schultz, R.E. and Wiley, M.J., 2006. Comparing effects of nutrients on algal biomass in streams in two regions with different disturbance regimes and with applications for developing nutrient criteria. Hydrobiologia, 561: 149-165.

Taskinen, A., Sirvio, H. and Bruen, M., 2008. Modelling effects of spatial variability of saturated hydraulic conductivity on autocorrelated overland flow data: linear mixed model approach. Stochastic Environmental Research and Risk Assessment, 22(1): 67-82.

Tsegaye, T., Sheppard, D., Islam, K.R., Johnson, A., Tadesse, W., Atalay, A. and Marzen, L., 2006. Development of chemical index as a measure of in-stream water quality in response to land-use and land cover changes. Water Air and Soil Pollution, 174(1-4): 161-179.

USEPA, 1975. Report on Lake Allegan, Allegan County Michigan. EPA Region V, Working Paper Series No. 182. EPA National Eutropication Studies. 1975, USEPA, Washington, D.C.

USEPA, 1996. Environmental indicators of water quality in the United States. EPA 841-R-96-002. EPA 841-R-96-002, USEPA, Office of Water (4503F), U.S. Government Printing Office, Washington, D.C.

USEPA, 2008a. STORET, EPA's computerized environmental data system, http://www.epa.gov/storet/.

USEPA, 2008b. Total Maximum Daily Loads: National Section 303(d) List Fact Sheet, http://iaspub.epa.gov/waters/national_rept.control.

USGS, 2008a. Annual water data reports, USGS 04106000 Kalamazoo River at Comstock, MI, http://waterdata.usgs.gov/mi/nwis/uv/?site_no=04106000&PARAmeter_cd=00065,00060.

USGS, 2008b. Annual water data reports, USGS 04108670 Kalamazoo River at New Richmond, MI, http://waterdata.usgs.gov/mi/nwis/uv/?site_no=04108670&PARAmeter_cd=00065,00060.

Valderrama, J.C., 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural-waters. Marine Chemistry, 10(2): 109-122.

van der Perk, M., Owens, P.N., Deeks, L.K., Rawlins, B.G., Haygarth, P.M. and Beven, K.J., 2007. Controls on catchment-scale patterns of phosphorus in soil, streambed sediment, and stream water. Journal of Environmental Quality, 36(3): 694-708.

Vanni, M.J., Renwick, W.H., Headworth, J.L., Auch, J.D. and Schaus, M.H., 2001. Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. Biogeochemistry, 54(1): 85-114.

Vitousek, P.M., 1997. Human domination of Earth's ecosystems (vol 277, pg 494, 1997). Science, 278(5335): 21-21.

Wahrer, M.A., Long, D.T. and Lee, R.W., 1996. Selected geochemical characteristics of ground water from the glaciofluvial aquifer in the central lower peninsula of Michigan. . U.S. Geological Survey Water-Resource Investigative Report 944017.

Wall, L.G., Tank, J.L., Royer, T.V. and Bernot, M.J., 2005. Spatial and temporal variability in sediment denitrification within an agriculturally influenced reservoir. Biogeochemistry, 76(1): 85-111.

Ward, J.V. and Stanford, J.A., 1995. The serial discontinuity concept - extending the model to floodplain rivers. John Wiley & Sons Ltd, pp. 159-168.

Waschbusch, R.J., Selbig, W.R. and Bannerman, R.T., 1999. Sources of phosphorus in stormwater and street dirt from two urban residential basins in Madison, Wisconsin, 1994-85, U.S. Geological Survey Water-Resources Investigations Report 99-4021.

Wayland, K.G., Long, D.T., Hyndman, D.W., Pijanowski, B.C., Woodhams, S.M. and Haack, S.K., 2003. Identifying relationships between baseflow geochemistry and land use with synoptic sampling and R-mode factor analysis. Journal of Environmental Quality, 32(1): 180-190.

Welschmeyer, N.A., 1994. Fluorometric analysis of chlorophyll-A in the presence of chlorophyll-B and pheopigments. Limnology and Oceanography, 39(8): 1985-1992.

Westjohn, D.B. and Weaver, T.L., 1997. Hydrogeologic framework of the Michigan Basin aquifer system. U.S. Geological Survey Professional Paper 1418. U.S. Geological Survey Information Services.

Wetzel, R.G. and Likens, G.E., 2000. Limnological Analyses, third ed. Springer-Verlag, New York, NY.

Williams, M., Hopkinson, C., Rastetter, E., Vallino, J. and Claessens, L., 2005. Relationships of land use and stream solute concentrations in the Ipswich River basin, northeastern Massachusetts. Water Air and Soil Pollution, 161(1-4): 55-74.

Winter, J.G. and Duthie, H.C., 2000. Export coefficient modeling to assess phosphorus loading in an urban watershed. Journal of the American Water Resources Association, 36(5): 1053-1061.

Withers, P.J.A. and Haygarth, P.M., 2007. Agriculture, phosphorus and eutrophication: a European perspective. Soil Use and Management, 23: 1-4.

Wycheck, J., 1998. Water quality and pollution control in Michigan, 1996 Report. Michigan 305(b) Report. Report No. MI/DEQ/SWQ-98-030, MDEQ, Surface Water Quality Division.

Yuan, Z., Ramaswami, B., Casaletto, D., Falke, S., Angenent, L.T. and Giammar, D.E., 2007. Evaluation of chemical indicators for tracking and apportionment of phosphorus sources to Table Rock Lake in Southwest Missouri, USA. Water Research, 41(7): 1525-1533.

Zampella, R.A., Procopio, N.A., Lathrop, R.G. and Dow, C.L., 2007. Relationship of land-use/land-cover patterns and surface-water quality in the Mullica River basin. Journal of the American Water Resources Association, 43(3): 594-604.

CHAPTER 2

IDENTIFYING TEMPORAL TRENDS IN WATERSHED DISSOLVED PHOSPHORUS USING A MIXED LINEAR MODEL APPROACH

Abstract

Patterns in suites of chemicals and their relationship with land use can provide insight into the processes influencing eutrophication. In a two-year study of the KRLAW, these patterns are used to understand the cycling (sources, pathways, fate) of chemicals in the watershed. Although such work is being done for P, patterns and relationships of P to stream chemistry and land use are not easily identified because of temporal effects and structural restrictions in the data. Two temporal effects are identified: a catchment influence and a biological influence. Structural restrictions are produced by autocorrelation of the test series, correlation between factors and nesting of sample locations. To address these issues, mixed linear models (MLM) are applied to watershed data segregated by influence.

The catchment MLM identified a temporal trend by year and week-within-year and correlations between DP and Mg^{2+}, K^+, NO_3^-, Na^+, pH, alkalinity, specific conductance and lowland forest, agricultural and urban land uses. The biological MLM identified a temporal trend by year and correlations between DP, PP, NO_3^-, SO_4^{2-}, Cl^-, pH and urban land use.

Results conclude temporal trends in DP are identifiable, differ by influence, vary and change patterns over time. Quantifying temporal trends improves the number and strength of correlated chemistry and land use parameters. Further studies of these correlations advances the understanding of DP cycling within the watershed.

Introduction

Cultural eutrophication (anthropogenic nutrient loading to aquatic ecosystems) is a persistent condition of surface waters and a widespread environmental problem (Carpenter, 2005). Stream chemistry reflects the cumulative effects of biogeochemical and hydrological processes occurring throughout the watershed (Mulholland, 2004). However, nonpoint inputs of nutrients are derived from activities dispersed over wide areas of land and are variable in time due to effects of weather (Carpenter et al., 1998). Many studies have demonstrated relationships between land use/land cover, human disturbance and surface water chemistry (Liu et al., 2000; Momen et al., 1996; Tsegaye et al., 2006; Zampella et al., 2007). Although such work has included P, patterns have been difficult to recognize between P, stream chemistry and land use by commonly used multivariate statistical techniques. Previous studies have used factor analysis (Liu et al., 2000), analysis of variance (Tsegaye et al., 2006), multiple regression (Zampella et al., 2007) and multivariate statistics (Momen et al., 1996), finding few and/or weak correlations between P and watershed parameters.

The lack and/or weakness of statistical relationships between P, stream chemistry and land use is counter-intuitive in light of the many studies that have identified agriculture and urban regions as sources and exporters of P and other chemical solutes (Coulter et al., 2004; Lewis et al., 2007). This inconsistency has led us to propose two potential sources that obscure the existing P, stream chemistry and land use relationships: (1) two distinct and variable temporal effects, and (2) structural restrictions in the data not easily addressed with common multivariate statistical techniques.

First, Mulholland and Hill (Mulholland, 1993; 1997) found two general modes of control of stream nutrient concentrations: catchment control via seasonal variation in the dominant hydrologic pathway, and in-stream control via high rates of biological nutrient uptake during the spring and autumn. They found that variation in the relative importance of different flow paths and in-stream biological modification of catchment delivered nutrients can result in substantial temporal variation in stream water nutrient concentrations. In the context of this study, catchment influence is exhibited through landscape control of stream chemistry and biological influence is an observable modification of catchment controlled stream chemistry resulting from biomass production or consumption.

Second, several common structural problems have been identified in relating land use to ecological indicators in streams. These include collinearity of land use percentages and spatial autocorrelation of land use and stream data from nesting of sites and serial dependence of time-series data (King et al., 2005; Momen et al., 1996; Zampella et al., 2007). The mixed linear model (MLM) provides a statistical method that overcomes these problems by permitting the data to exhibit correlation and heteroscedasticity. A MLM is a generalization of the standard linear model that makes it possible to model not only the means of data but their variances and covariances as well. Covariance parameters are required when the experimental units can be grouped, the data within a group is correlated and repeated measurements are taken on the same experimental unit and are correlated or exhibit variability that changes (Taskinen et al., 2008).

Mixed linear model studies in the biogeochemical sciences are rare, but they have been used in some environmental applications (Dodds and Oakes, 2006; Lehrter, 2006; Taskinen et al., 2008). For example, Taskinen et al. (2008) used the mixed linear model to study the effects of spatial variation in the saturated hydraulic conductivity on the variation of the overland flow in southern Finland. The MLM has been identified as a statistical method that addresses the various structural restrictions within the data. Using the MLM, variable temporal trends are quantified that previously obscured the relationships and patterns between P, stream chemistry and land use.

The hypothesis is that DP concentrations are correlated to land use and stream chemistry, but the specific patterns change over time. To test the hypothesis, stream chemistry and land use data are separated by catchment or biological influence and MLMs are used to identify temporal trends and the relationships between DP, stream chemistry and land use.

For this study, the segregation of catchment and biological influenced data and their separate analysis using MLMs that include temporal variables in the fixed effects provides a unique approach for identifying temporal trends in watershed DP. The approach develops a method to characterize the catchment and biological influenced temporal trends in DP. Quantifying temporal trends improves the number and strength of DP correlations between stream chemistry and land use variables. Results indicate temporal trends are responsible for changing the relationships over time between DP, stream chemistry and land use. This supports the hypothesis that DP concentrations are correlated to land use and stream chemistry, but the specific patterns change over time. Accounting for temporal DP trends allows further evaluation of the remaining fixed and random effects to improve our understanding of anthropogenic impacts on DP cycling.

Methods

Temporal trends in DP were investigated using the KRLAW stream chemistry dataset (Appendix I) and land use description (Table 1.1.). The study site, sampling locations, sampling methods and chemical analyses are described in Chapter 1.

Catchment and biological influence separation

Temporal trends in DP are derived from catchment influences (climate, land use inputs and hydrology) and biological influences (algal production and macro-invertebrate grazing). Catchment influences are assumed to drive temporal trends unless biological influence is identified. PP, chlorophyll *a*, alkalinity and Ca^{2+} concentrations are used to indicate sampling dates and locations under biological influence.

Biological indicators are most evident at reservoirs because reservoirs often provide gradients in light and nutrients and retention time for primary production (Kimmel et al., 1990; Knoll et al., 2003). Nutrient uptake, primarily P and N, occurs from inflow to outflow during productivity (Kennedy and Walker, 1990). Since N is not the limiting nutrient, surplus NO_3^- is available early in the growing season and does not provide a clear pattern for biological influence. In a study of 12 Ohio reservoirs, a high correlation was found between primary productivity, TP and chlorophyll *a* (Knoll et al., 2003). Chlorophyll *a* was used as an indicator of biological activity in 2006 when measurements were taken. There is a strong link between algae and PP, but the relationship between algae and DP forms is weak (Neal et al., 2006). The comparison of PP from inlet to outlet provided a clearer signal of algal activity than TP or DP and was used as another biological indicator.

While chlorophyll *a* and PP provide indication of biological productivity, they are associated with the particulate, not dissolved fraction and are not sufficient to determine the transition between the stream chemistry produced by catchment influence and biological influence. The alkalinity of most fresh waters is imparted by the presence of bicarbonates and carbonates, and the CO_2–HCO_3–CO_3^{2-} equilibrium system is the major buffering mechanism in those waters (Wetzel, 2001). The CO_2 in water can be substantially influenced by photosynthesis and respiration by aquatic organisms, leading to a decrease in alkalinity (Wetzel and Likens, 2000). In a solution where calcium bicarbonate is in equilibrium with CO_2, H_2CO_3 and CO_3^{2-}, CO_2 assimilated by photosynthetic organisms will precipitate calcite to reestablish equilibrium (House, 2003; Wetzel, 2001). Precipitation of calcite is indicated by a decrease in dissolved Ca^{2+} concentration. Decreases in alkalinity and Ca^{2+} from reservoir inflow to outflow are also used as biological indicators. The biological indicators are evaluated for the first large reservoir (Morrow Lake) in the Kalamazoo River system with a retention time greater than seven days.

Reservoirs with retention times greater than seven days provide an environment for phytoplankton production, and upstream reservoirs have been demonstrated to influence downstream systems (Kimmel et al., 1990; Straskrabova et al., 1973). TP concentrations at locations upstream and downstream are compared to

Morrow Lake concentrations to determine if they are also under biological influence on the same sampling dates. TP was used for this evaluation because two biological processes, algal productivity and macro-invertebrate grazing, have opposite effects on PP, chlorophyll *a*, alkalinity and Ca^{2+} concentrations. Locations that maintained the trend in TP seen at the outlet of Morrow Lake were included as biological influenced locations for the same dates as the outlet of Morrow Lake.

Statistical analysis

The catchment and biological datasets present some unique challenges that cannot be addressed with commonly used statistical analyses such as ANOVA, general linear models and factor and cluster analyses. The physical locations sampled in the stream system result in collinearity of land-cover percentages and spatial autocorrelation of land cover and stream data from nesting of sites and serial dependence of time-series data. This scenario occurs in longitudinal studies where repeated measurements are taken over time and the repeated measures could be spatial or multivariate in nature (SAS, 1999). The MLM, a generalization of the standard linear model, makes it possible to model not only the means of data, but also the variances and covariances that exist due to nesting and serial dependence (Taskinen et al., 2008). The separation of the data by dates and locations yields unbalanced designs. The MLM also accommodates unbalanced designs (Milliken and Johnson, 1984; University of Oregon, 2007). A detailed description of mixed linear model theory and its application can be found in the literature (Littel et al., 2006; Milliken and Johnson, 1984; SAS, 1999; Searle, 1971) and is summarized in Appendix V.

In general, the standard GLM can be written as

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon} \tag{2.1}$$

In contrast, the MLM takes into account correlations and heterogeneities between the terms of $\boldsymbol{\varepsilon}$ and is written as (Searle, 1971)

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \mathbf{Z}\boldsymbol{\gamma} + \boldsymbol{\varepsilon} \tag{2.2}$$

where **y** is a vector of observations, $\boldsymbol{\beta}$ is a vector of unknown fixed effects, **X** and **Z** are known design matrices that relate observations to fixed effects and random effects, $\boldsymbol{\gamma}$ is a vector of unkown random effect predictors and $\boldsymbol{\varepsilon}$ is a vector of residuals. $\boldsymbol{\gamma}$ and $\boldsymbol{\varepsilon}$ are assumed to be normally distributed with a zero mean and variance-covariance matrices **G** and **R** respectively.

The matrix **G** can be conceptualized as a between-location variance-covariance matrix and **R** as a within-location variance-covariance matrix (University of Oregon, 2007). Since $\boldsymbol{\gamma}$ and $\boldsymbol{\varepsilon}$ are assumed to be independent, the variance-covariance matrix of the vector of observations **y** (denoted by **V**) from each location has the form (SAS, 1999):

$$\mathbf{V} = \mathbf{Z}\mathbf{G}\mathbf{Z}' + \mathbf{R} \tag{2.3}$$

Unlike the GLM, where only $\boldsymbol{\beta}$ requires estimation through the least squares method, the MLM has $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, **V**, **G** and **R** as unknowns. An estimate for **V** using equation 2.3 is obtained by the generalized least squares method minimization. **G** and **R** are estimated using the maximum likelihood method (ML) incorporating a ridge-stabilized Newton-Raphson algorithm (SAS, 1999) that can handle multi-collinearity problems. Finally, to obtain estimates for $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ the mixed model equations are solved:

$$\begin{bmatrix} \mathbf{X}'\widehat{\mathbf{R}}^{-1}\mathbf{X} & \mathbf{X}'\widehat{\mathbf{R}}^{-1}\mathbf{XZ} \\ \mathbf{Z}'\widehat{\mathbf{R}}^{-1}\mathbf{X} & \mathbf{Z}'\widehat{\mathbf{R}}^{-1}\mathbf{Z}+\widehat{\mathbf{G}}^{-1} \end{bmatrix} \begin{bmatrix} \widehat{\boldsymbol{\beta}} \\ \widehat{\gamma} \end{bmatrix} = \begin{bmatrix} \mathbf{X}'\widehat{\mathbf{R}}^{-1}\mathbf{y} \\ \mathbf{Z}'\widehat{\mathbf{R}}^{-1}\mathbf{y} \end{bmatrix} \tag{2.4}$$

where the symbols$\widehat{\mathbf{G}}$, $\widehat{\mathbf{R}}$, $\widehat{\mathbf{B}}$ and $\widehat{\gamma}$ denote estimates.

The statistical methods for this study were implemented using SAS 9.1.3 (SAS, 2007). The SAS PROC MIXED procedure uses the methods briefly described above and detailed in Appendix V to solve the MLM and to provide estimates for the fixed ($\boldsymbol{\beta}$) and random effects (γ). When the number of fixed effects is greater than one, a general *F*-statistic is constructed, allowing inferences about the fixed effects which account for the variance-covariance model (SAS, 1999).

The model is specified with repeated measures by week-within-year (Week) because the 2005 and 2006 datasets were not contiguous. The first week of both the 2005 and 2006 growing seasons (first week in April) is designated as Week = 1 and weeks are sequentially numbered through the end of the growing season, Week = 26. The structure of the **R** matrix specified in the repeated statement is a direct product of unstructured (SAS designation UN) by year and first order autoregressive (SAS designation AR(1)) by Week input as UN@AR(1). UN is used because no defined structure is expected to exist between years. However, the nature of a stream system in which the current value of a parameter is not independent of but related to the previous values led to the choice of the AR(1) for the week to week structure. The general definition of an AR(1) process indicates that the current value of the process (t_k) can be expressed as a finite linear aggregate of previous values of the process plus a residual (ε_k) (Wade and Quaas, 1993).

In addition to the repeated measures, the model is specified with a random effect by site. This accounts for unknown random effects between sample locations. The structure of the **G** matrix is specified as variance components (SAS designation of VC). VC specifies standard variance components and a distinct variance component is assigned to each random effect (SAS, 1999).

Separate catchment and biological MLMs model the log of DP (log(DP)) as the dependent variable. Stream chemistry, in-stream measurements, land use and temporal variables for Year, Week, Week^2 and Week^3 are the independent variables. Log transforming DP provides a normal distribution for the dependent variable. The forward substitution method is used where each fixed effect is analyzed independently and the most significant effect is retained and added to the model. This iterative process continues, evaluating the individual remaining fixed effects with the significant effects retained from the previous iterations until none of the remaining effects are significant as tested through the F-statistic ($p < 0.05$).

Normality was tested using the Shapiro-Wilk statistic. This statistic, W, tests the null hypothesis of normality, ranging from greater than zero to less than or equal to one ($0 < W \leq 1$). Small values of W lead to rejecting the null hypothesis. The Shapiro-Wilk test was performed using SAS software (SAS, 2007).

Results

Catchment and biological influence separation

The onset of the biologically influenced periods were indicated on June 7, 2005, and July 11, 2006, by the coincidence of a decrease in alkalinity and calcium concentrations and an increase in PP from the Morrow Lake inflow (site KM) to the outflow (site KC) (Figures 2.1 and 2.2). In 2006, chlorophyll *a* concentrations confirmed increasing algal activity as early as May 30, 2006 however, catchment influences continued to dominate until July 11, 2006 as shown by the similarity in inlet and outlet alkalinity, calcium and PP concentrations (Figure 2.2). The biological influenced period, ended on September 27, 2005, and September 19, 2006 as some of the biological indicators were no longer separated (Figures 2.1 and 2.2). On three dates –June 14, 2005, July 19, 2005, and August 29, 2006— Morrow Lake reverted to catchment influence due to runoff events on or near those dates (Figures 2.1 and 2.2). This was most evident in the loss of the decrease in alkalinity from the inlet to the outlet site. The outflow stream chemistry of Morrow Lake (site KC) provides the reference for identifying the temporal distribution (sampling dates) of biological and catchment influences.

The outflow TP of Morrow Lake (site KC) is the reference location for the spatial distribution (sampling sites) under biological influence. Catchment influence is referenced to the Morrow Lake inflow (site KM). TP concentrations at the upstream and downstream sites are compared to sites KM and KC. The TP for sites upstream (WC, BR, BC, KE, KG and FC) and downstream tributary sites (PC, GR and SB) have patterns similar to site KM and are under catchment influence throughout the study periods. The TP for sites downstream on the Kalamazoo River (KS, KK, KP, KA and KD) have similar patterns to site KC and are under biological or catchment influence on the same dates as site KC. The TP means of the catchment influenced sites (CISM) and the biologically influenced sites (BISM) are compared to sites KM and KC in Figures 2.3 and 2.4.

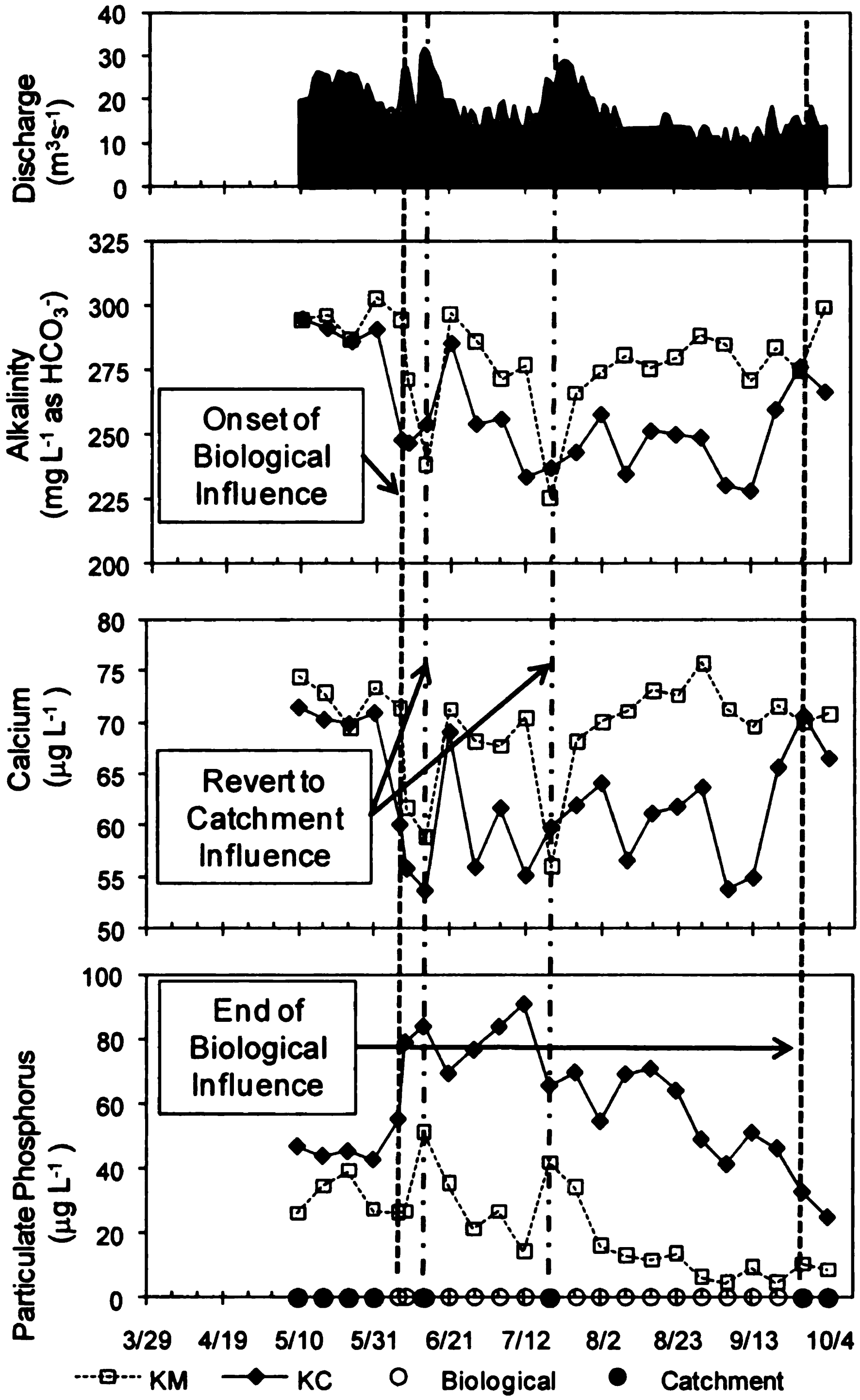


Figure 2.1: Comparison of Morrow Lake inflow (KM) and outflow (KC) concentrations for alkalinity, calcium and PP, outflow discharge and biological and catchment influenced dates, 2005.

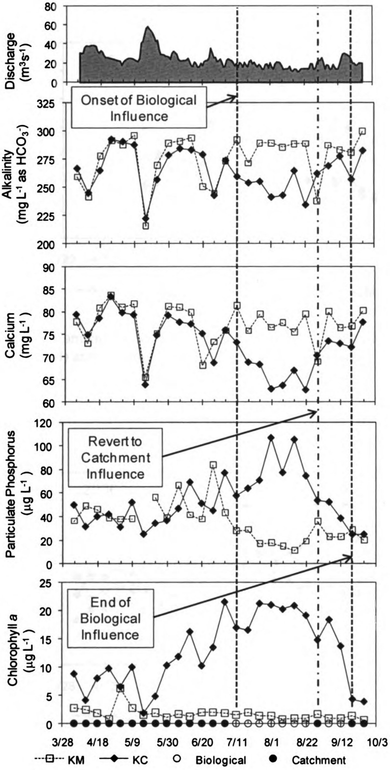


Figure 2.2: Comparison of Morrow Lake inflow (KM) and outflow (KC) concentrations for alkalinity, calcium, PP and chlorophyll *a*, outflow discharge and biological and catchment influenced dates, 2006.

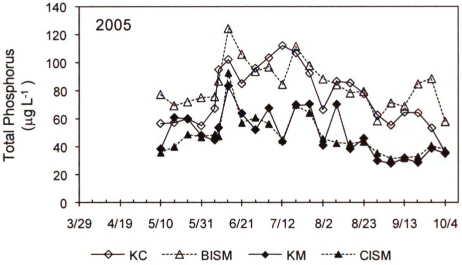


Figure 2.3: Comparison of Morrow Lake outflow (KC) and biological influenced site means (BISM) and Morrow Lake inflow (KM) and catchment influence site means (CISM), 2005.

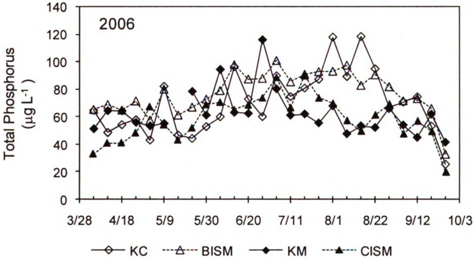


Figure 2.4: Comparison of Morrow Lake outflow (KC) and biological influenced site means (BISM) and Morrow Lake inflow (KM) and catchment influence site means (CISM), 2006.

The stream chemistry, in-stream measurements and land use data were separated into catchment and biological datasets by the dates and sites determined from the influence analysis. Figure 2.5 shows the sites and sampling dates in each dataset.

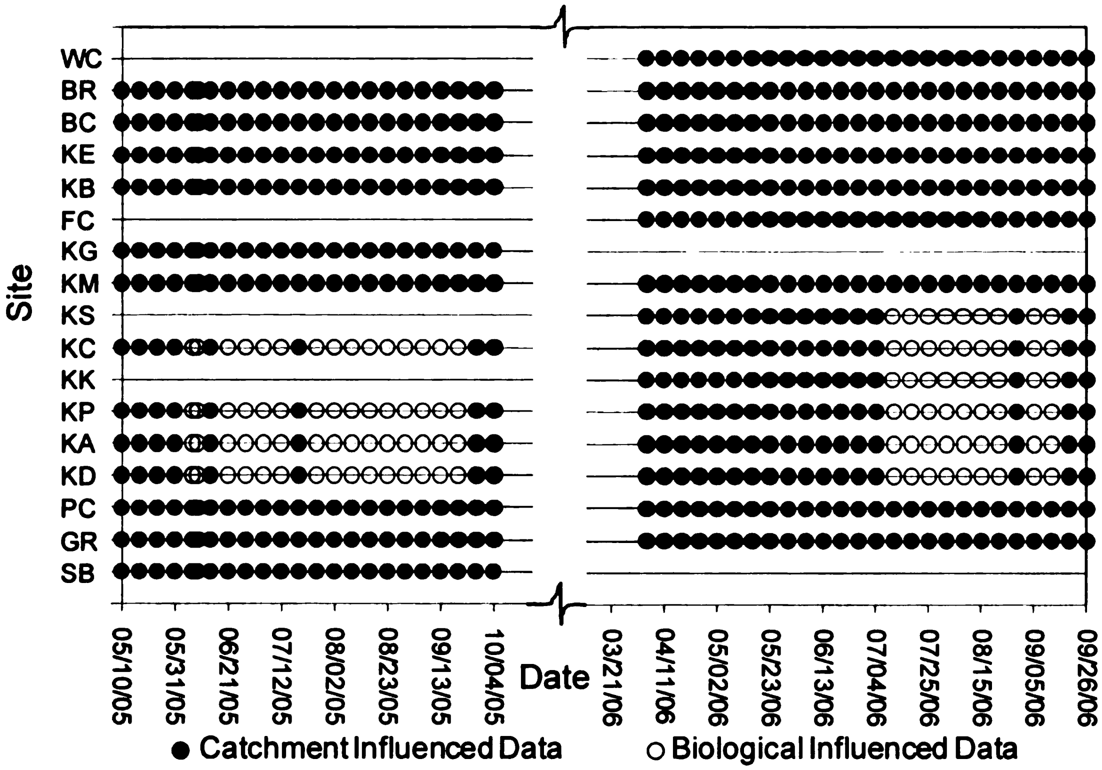


Figure 2.5: Data separation into catchment and biological influenced datasets by date and site.

Catchment influence model

The catchment influenced MLM yielded significant relationships between log(DP) and Mg^{2+}, K^+, NO_3^-, Na^+, pH, alkalinity (Alk), specific conductance (SPC), lowland forest land use, agricultural land use, urban land use, Year, Week, $Week^2$ and $Week^3$ (Table 2.1). Significance is tested using the *F*-statistic with the criteria of $p < 0.05$ (Table 2.1). The estimates (coefficients) for the fixed effects and variable groupings by category are given Table 2.1. The results, including the estimates, for the random effects by site are given in Table 2.2. The general form of the model is:

$$\log(DP) = int + SC + LU + TT + SE + \varepsilon \qquad (2.5)$$

where: int = intercept, SC = stream chemistry, LU = land use, TT = temporal trend, SE = site effect and ε = residual error.

Table 2.1: Fixed effects results from the catchment influenced MLM.

Fixed Effect	**Year**	**Estimate**	***F*-statistic p value**	**Effect Category**
Intercept		2.4932		Intercept (int)
Mg^{2+}		-0.01365	0.0145	Stream Chemistry (SC)
K^+		0.05108	0.0003	
NO_3^-		0.04687	<.0001	
Na^+		0.006301	0.0046	
pH		-0.3136	<.0001	
Alk		0.002215	<.0001	
SPC		-0.0011	0.0001	
Lowland Forest		13.4145	<.0001	Land Use (LU)
Agricultural		0.6828	0.0001	
Urban		1.9947	0.0003	
Year	2005	-1.2438	<.0001	Temporal Trend (TT)
	2006	0		
Week	2005	0.27	<.0001	
	2006	0.01034		
$Week^2$	2005	-0.01467	<.0001	
	2006	0.002318		
$Week^3$	2005	0.000245	<.0001	
	2006	-0.00009		

Table 2.2: Random effects results from the catchment influenced MLM.

Random Effect	**Estimate**	**Effect Category**
BC	-0.04909	Site Effect (SE)
BR	0.1077	
FC	0.01627	
GR	-0.07224	
KA	0.1394	
KB	-0.06732	
KC	-0.06304	
KD	-0.09911	
KE	-0.07914	
KG	-0.00616	
KK	0.06564	
KM	0.01322	
KP	0.171	
KS	-0.08243	
PC	-0.02585	
SB	0.09083	
WC	-0.05962	

The temporal variables Year, Week, Week^2 and Week^3 estimate the temporal trend in the log(DP). Including these variables, equation 2.5 for the 2005 sampling period is:

$$\log(DP) = \text{int} + SC + LU + [\,-1.2348 + 0.27(\text{Week}) - 0.01467(\text{Week})^2 + 0.000245(\text{Week})^3] + SE + \varepsilon \tag{2.6}$$

and for the 2006 sampling period is:

$$\log(DP) = \text{int} + SC + LU + [\,0.01034(\text{Week}) + 0.002318(\text{Week})^2 - 0.00009(\text{Week})^3] + SE + \varepsilon \tag{2.7}$$

Transforming equation 2.4 back to DP yields

$$DP = (10^{\text{int}})(10^{SC})(10^{LU})(10^{TT})(10^{SE})(10^{\varepsilon}) \qquad (2.8)$$

Equation 2.7 shows that the estimate for DP is derived from the product of the exponential terms for the fixed and random effects. Therefore, temporal trends will amplify or diminish the combination of the random and other fixed effects. Using the equation 2.8 and the temporal trend variables in equations 2.6 and 2.7, the catchment temporal trend factors (CTTF) for 2005 and 2006 can be represented as follows:

$$CTTF_{2005} = 10^{[-1.2348 + 0.27(\text{Week}) - 0.01467(\text{Week})^2 + 0.000245(\text{Week})^3]} \qquad (2.9)$$

$$CTTF_{2006} = 10^{[0.01034(\text{Week}) + 0.002318(\text{Week})^2 - 0.00009(\text{Week})^3]} \qquad (2.10)$$

The plot of the CTTFs by week of the growing season is given in Figure 2.6.

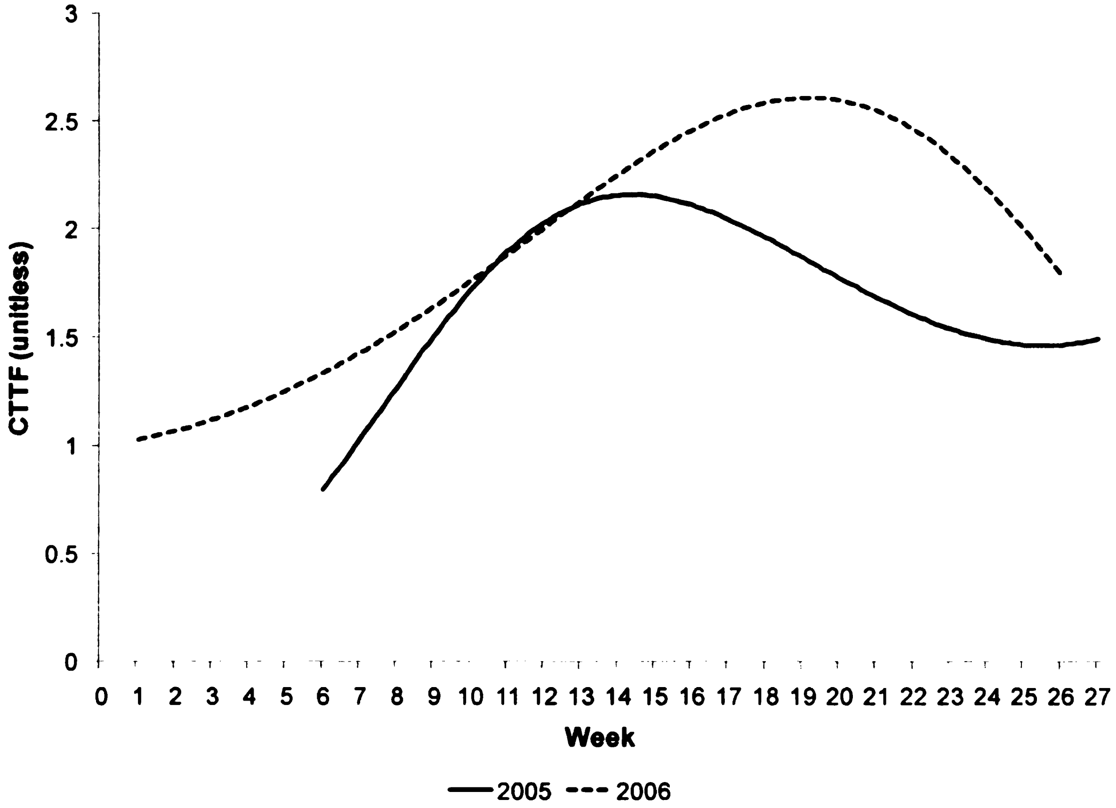


Figure 2.6: Plot of the estimated catchment temporal trend factors (CTTF) by week from the catchment influenced MLM. Note: Week 1 = first week of April.

The CTTFs are watershed-wide factors that apply equally to all sites. However, the other fixed and random effects vary by site and are amplified or diminished by the temporal effect. This is demonstrated by the 2006 MLM estimated contributions to total DP from the temporal effect DP and other fixed effects for the Battle Creek River location (site BR) (Figure 2.7).

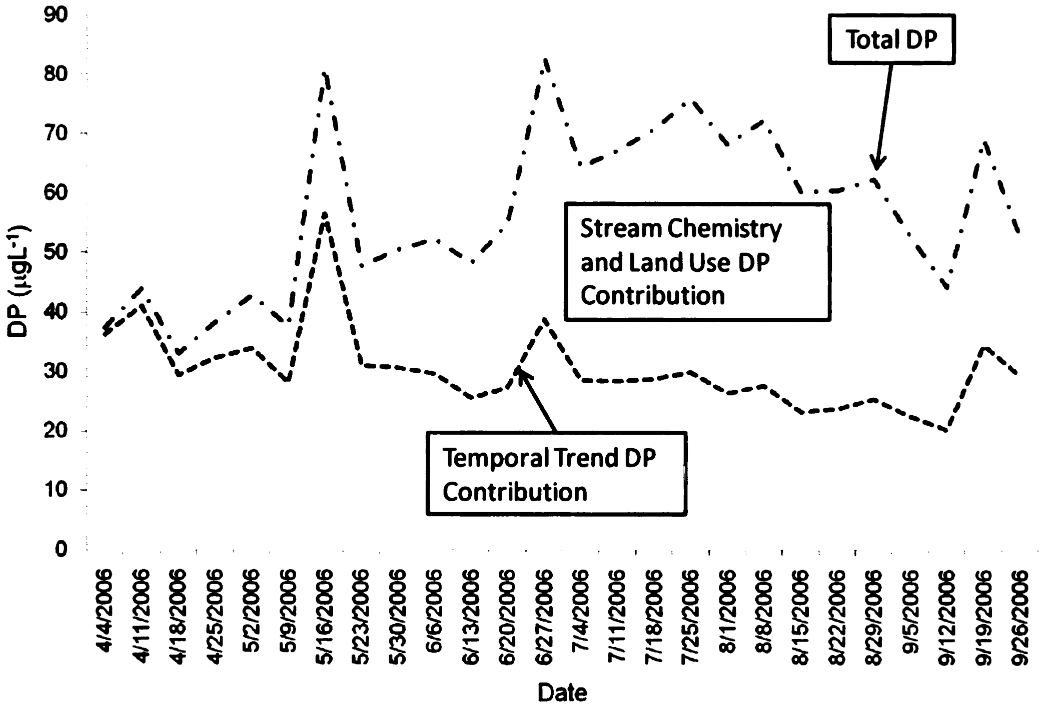


Figure 2.7: The catchment influenced MLM estimates for the 2006 contributions to total DP from the temporal trend DP and the stream chemistry and land use DP for the Battle Creek River (site BR).

Biological influenced model

The biological influenced MLM yielded significant (*F*-statistic, p<0.05) relationships between log(DP) and PP, NO_3^-, SO_4^{2-}, Cl^-, pH, urban land use and Year (Table 2.3). No Week variables were significant. The estimates (coefficients) for the fixed effects and variable groupings by category are given Table 2.3. The results, including the estimates, for the random effects by site are given in Table 2.4.

Table 2.3: Solution for the fixed effects for the biology influenced MLM.

Fixed Effect	**Year**	**Estimate**	***F*-statistic p value**	**Effect Category**
Intercept		3.4486		Intercept (int)
PP		-0.00138	0.0054	Stream Chemistry (SC)
NO_3^-		0.1426	0.0004	
SO_4^{2-}		-0.01444	<.0001	
Cl^-		0.003959	0.0060	
pH		-0.2856	<.0001	
Urban		7.4666	0.0452	Land Use (LU)
Year	2005	-0.1041	0.0020	Temporal Trend (TT)
	2006	0		

Table 2.4: Solution for the random effects for the biology influenced MLM.

Random Effect	**Estimate**	**Effect Category**
KA	0.08775	Site Effect (SE)
KC	0.0185	
KD	-0.1334	
KK	0.007106	
KP	0.02753	
KS	-0.00752	

Following the form of equation 2.8, for the 2005 sampling period:

$$DP = (10^{int})(10^{SC})(10^{LU})(10^{-0.1041})(10^{SE})(10^{\varepsilon}) =$$

$$(10^{int})(10^{SC})(10^{LU})(0.787)(10^{SE})(10^{\varepsilon}) \tag{2.11}$$

and for the 2006 sampling period:

$$DP = (10^{int})(10^{SC})(10^{LU})(10^{0})(10^{SE})(10^{\varepsilon}) =$$

$$(10^{int})(10^{SC})(10^{LU})(1.000)(10^{SE})(10^{\varepsilon}) \tag{2.12}$$

From equations 2.11 and 2.12, the biological temporal trend factor (BTTF) for 2005 is $BTTF_{2005} = 0.787$ and for 2006 is $BTTF_{2006} = 1.000$. The intercept and land use terms are equal in equations 2.10 and 2.11 on a given date for a given site. The plot of the BTTFs for 2005 and 2006 by week of the growing season are given in Figure 2.8. The biological influence is zero prior to establishing the level of productivity required to control the stream chemistry –week 10 in 2005 and week 15 in 2006. The biological influence reverts to zero during runoff events that return stream chemistry control to the catchment influence. The variability in DP is a combination of variations in stream chemistry and season (year to year).

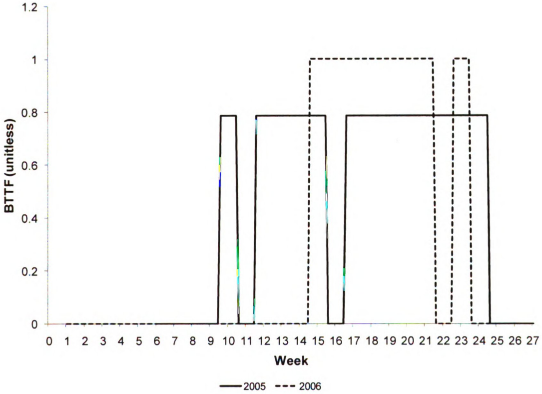


Figure 2.8: Plot of the estimated biological temporal trend factors (BTTF) by week from the biological influenced MLM. Note: Week 1 = first week of April.

Catchment and biological model assessment

To assess the suitability of the catchment and biological MLMs for identifying relationships between DP and watershed variables, the normality of the residuals and the correlation between actual and predicted log(DP) were evaluated. Both the MLM and the GLM have the key assumption that the residuals are zero-mean and normally distributed (SAS, 1999). Normality was evaluated using the Shapiro-Wilk statistic, W. For the catchment MLM residuals, $W = 0.9837$ ($p < 0.0001$) and for the biological model residuals, $W = 0.9729$ ($p < 0.0194$). The Shapiro-Wilk statistics for both indicate a high probability that the residuals are normally distributed.

The actual log(DP) and the catchment and biological model predicted log(DP) were correlated from the model outputs using linear regression. The catchment and biological MLMs estimate the log(DP) based on the stream chemistry, land use, temporal trend and site effect using equation 2.5 and the estimates from Tables 2.1 and 2.2 for the catchment model and Tables 2.3 and 2.4 for the biological model.

The plots of actual log(DP) versus the predicted log(DP) from the catchment and biological MLMs and the linear regression analysis are shown in Figure 2.9. The square of the correlation coefficient, R^2, represents the fraction of the variation in the actual log(DP) explained by the MLM predicted log(DP). The catchment model ($R^2 = 0.8658$) explained 87 percent of the variation and the biological model ($R^2 = 0.8455$) explained 85 percent of the variation in actual log(DP). In environmental studies, an $R^2 > 0.75$ is considered highly correlated.

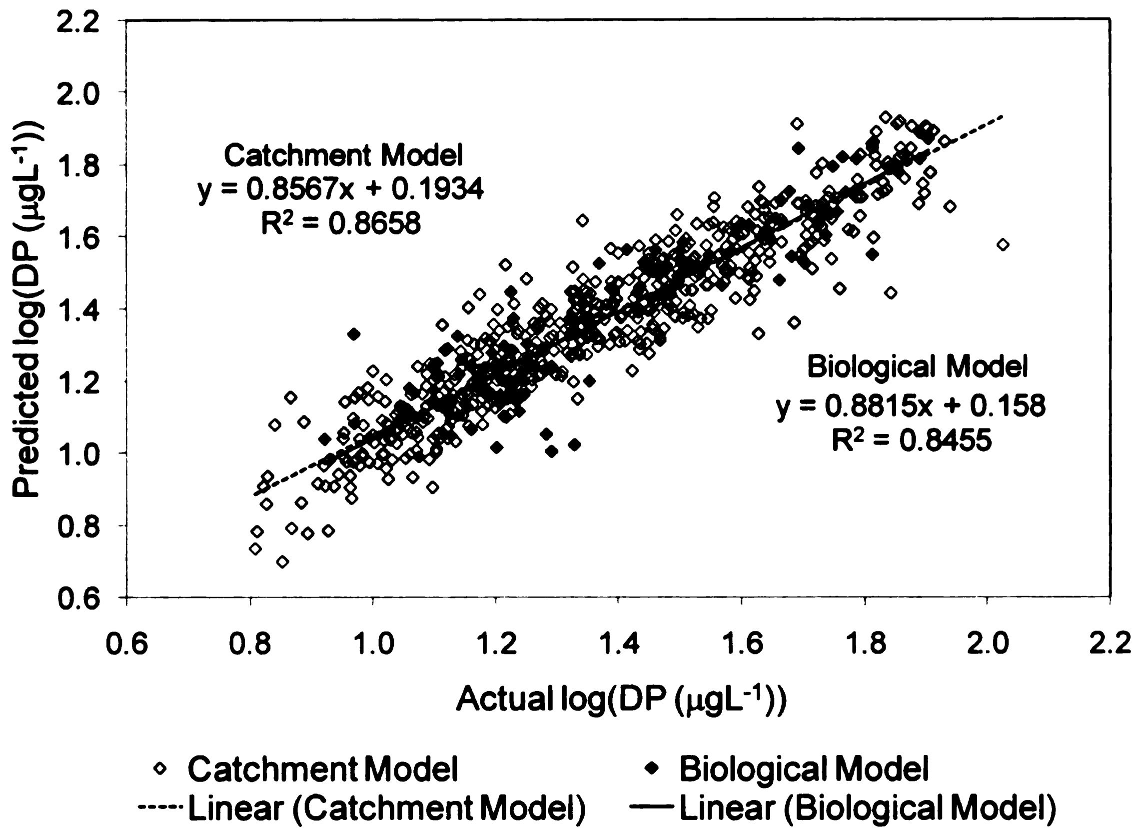


Figure 2.9: Actual log(DP) versus predicted log(DP) and linear regressions for the catchment and biological models on the KRLAW datasets.

Discussion

MLMs provide estimates for the significant relationships between DP and temporal trends, stream chemistry and land use for catchment and biological influenced datasets from the KRLAW. The data are segregated by date and location using PP, alkalinity, Ca^{2+} and chlorophyll *a*, and are separted into catchment and biological influenced datasets. While chlorophyll *a* and PP may be reliable indicators of primary productivity, they were not sufficient for determining when the biological processes are the dominant influences on stream chemistry. In 2006, as the chlorophyll *a* and PP concentrations elevated, alkalinity and calcium were similar from the inlet to the outlet of Morrow Lake, indicating continued catchment influence for an additional six weeks. Also, the influence of the primary producers on stream chemistry could not overcome the catchment influence during runoff events. Particular attention should be given to multiple indicators when separating data by dominant influence. The catchment and biological models produced different temporal variations and different stream chemistry and land use relationships.

The catchment model estimated a cubic expression for the temporal trend on log(DP) as a function of Year, Week, Week^2 and Week^3. While both the 2005 and 2006 temporal trends were modeled by a cubic expression, the coefficients varied between years. Therefore, the CTTFs varied week to week within year and also varied for the same week in different years. The $CTTF_{2005}$ varied from 0.76 to 2.16 and peaked week 14 (the first week in July). The $CTTF_{2006}$ varied from 1.03 to 2.61 and peaked week 19 (the first week in August).

The catchment MLM showed a significant relationship between the log(DP) and Mg^{2+}, K^+, NO_3^-, Na^+, pH, alkalinity, specific conductance and lowland forest, agricultural and urban land uses. These relationships will be further explored to provide insight into DP cycling within the watershed.

The biological model estimated a year to year temporal effect, but no week to week effect on the log(DP). The $BTTF_{2005}$ was 0.80 compared to a $BTTF_{2006}$ of 1.00. The lack of week to week effect may result from the level of primary productivity, near the maximum, required to alter the catchment influenced stream chemistry. The 2006 chlorophyll *a* data indicate that once the maximum productivity is reached, that level is maintained until the end of the growing season unless disturbed. This is consistent with the concept of biological thresholds put forth by Grover and

Chrzanowski (2004) where minimum nutrient and maximum light thresholds at varying times limit phytoplankton productivity to a maximum threshold unless disturbed. The disturbances of runoff events did not impact the biological model because they were included in the catchment dataset as the system reverted to catchment influence. The limitation in 2005 of the temporal trend to 79 percent of the 2006 value is probably due to a lower nutrient threshold, particularly P, in 2005 and will be investigated in a separate study. Similar to the catchment model, identifying the year to year temporal trend resulted in the identification of significant relationships between log(DP) and stream chemistry and land use parameters.

The biological MLM showed significant relationships between log(DP) and PP, NO_3^-, SO_4^{2-}, Cl^-, pH and urban land use. These relationships will be further evaluated to provide insight into biological processes affecting the sources, fate and transport of DP within the watershed.

The temporal trends apply equally to all locations, but produce greater effects in high DP watersheds than in low DP watersheds. Although this study is inconclusive as to the source of the catchment temporal and biological influences, Mulholland and Hill's (1997) catchment and biological control, warrant further investigation. As a first step, the identification of temporal trends, regardless of the source, generates more significant relationships with stream chemistry and land use variables than statistical methods where a temporal component is not included.

We propose data separation by influence and statistical analysis using the MLM as a method to identify temporal trends and the relationships between DP and stream chemistry and land use in the KRLAW to test our hypothesis. Temporal trends in DP are identified from both catchment and biological influences and from establishing relationships among DP, stream chemistry and land use variables. These results support the hypothesis that DP concentrations are related to land use and stream chemistry, but that the specific patterns change over time. These MLMs show that the changes in land use and stream chemistry patterns over time are the result of temporal trends from the dominant influence, year-to-year and week-within-year for catchment influence and year to year for biological influence. The variability associated with these temporal trends changes the patterns and relationships among DP, land use and stream chemistry.

Conclusions

The approach described in this study develops a method using data separation by influence and MLMs to characterize the temporal effects on DP by catchment and biological influences. Stream biological indicators –alkalinity, Ca^{2+} concentration, PP and chlorophyll *a*– allow us to segregate the KRLAW data into catchment and biological datasets by locations and dates. From separate MLMs used to evaluate the catchment and biological data, we conclude for the KRLAW that: 1) temporal trends in DP are identifiable, 2) temporal trends for catchment and biological influences are different, 3) temporal trends exhibit variation over time, 4) DP, land use and stream chemistry are correlated, and (5) specific land use and stream chemistry patterns change over time due to temporal trends.

Results from this study support our hypothesis that DP concentrations are correlated to land use and stream chemistry, but that the specific patterns change over time. Data separation and including temporal variables in MLMs improve the number and strength of the significant fixed effect relationships for stream chemistry and land use to DP compared to studies using traditional statistical techniques. These significant land use and stream chemistry fixed effects and the random effects by site provide a basis for additional studies to provide inferences into watershed DP cycling.

Literature Cited

Carpenter, S.R., 2005. Eutrophication of Aquatic Ecosystems: Bistability and Soil Phosphorus. Proceedings of the National Academy of Sciences of the United States of America, 102(29): 10002-10005.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H., 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. Ecological Applications, 8(3): 559-568.

Coulter, C.B., Kolka, R.K. and Thompson, J.A., 2004. Water quality in agricultural, urban, and mixed land use watersheds. Journal of the American Water Resources Association, 40(6): 1593-1601.

Dodds, W.K. and Oakes, R.M., 2006. Controls on nutrients across a prairie stream watershed: Land use and riparian cover effects. Environmental Management, 37(5): 634-646.

Grover, J.P. and Chrzanowski, T.H., 2004. Limiting resources, disturbance, and diversity in phytoplankton communities. Ecological Monographs, 74(3): 533-551.

House, W.A., 2003. Geochemical cycling of phosphorus in rivers. Applied Geochemistry, 18(5): 739-748.

Kennedy, R.H. and Walker, W.W., 1990. Reservoir Nutrient Dynamics. In: K.W. Thornton, B.L. Kimmel and F.E. Payne (Editors), Reservoir Limnology: Ecological Perspectives. John Wiley & Sons, Inc., New York, NY.

Kimmel, B.L., Lind, O.T. and Paulson, L.J., 1990. Reservoir Primary Production. In: K.W. Thornton, B.L. Kimmel and F.E. Payne (Editors), Reservoir Limnology: Ecological Perspectives. John Wiley & Sons, Inc., New York, NY.

King, R.S., Baker, M.E., Whigham, D.F., Weller, D.E., Jordan, T.E., Kazyak, P.F. and Hurd, M.K., 2005. Spatial considerations for linking watershed land cover to ecological indicators in streams. Ecological Applications, 15(1): 137-153.

Knoll, L.B., Vanni, M.J. and Renwick, W.H., 2003. Phytoplankton primary production and photosynthetic parameters in reservoirs along a gradient of watershed land use. Limnology and Oceanography, 48(2): 608-617.

Lehrter, J.C., 2006. Effects of land use and land cover, stream discharge, and interannual climate on the magnitude and timing of nitrogen, phosphorus, and organic carbon concentrations in three coastal plain watersheds. Water Environment Research, 78(12): 2356-2368.

Lewis, G.P., Mitchell, J.D., Andersen, C.B., Haney, D.C., Liao, M.K. and Sargent, K.A., 2007. Urban influences on stream chemistry and biology in the Big

Brushy Creek watershed, South Carolina. Water Air and Soil Pollution, 182(1-4): 303-323.

Littel, R.C., Milliken, G.A., Strup, W.W. and Wolfinger, R.D., 2006. SAS system for mixed models. SAS Institute, Cary, NC.

Liu, Z.J., Weller, D.E., Correll, D.L. and Jordan, T.E., 2000. Effects of land cover and geology on stream chemistry in watersheds of Chesapeake Bay. Journal of the American Water Resources Association, 36(6): 1349-1365.

Milliken, G.A. and Johnson, D.E., 1984. Analysis of Messy Data, Volume 1: Designed Experiments. Van Norstrand Reinhold Company, New York, NY.

Momen, B., Eichler, L.W., Boylen, C.W. and Zehr, J.P., 1996. Application of multivariate statistics in detecting temporal and spatial patterns of water chemistry in Lake George, New York. Ecological Modelling, 91(1-3): 183-192.

Mulholland, P.J., 1993. Hydrometric and steam chemistry evidence of 3 storm flowpaths in Walker-Branch Watershed. Journal of Hydrology, 151(2-4): 291-316.

Mulholland, P.J., 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. Biogeochemistry, 70(3): 403-426.

Mulholland, P.J. and Hill, W.R., 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. Water Resources Research, 33(6): 1297-1306.

Neal, C., Hilton, J., Wade, A.J., Neal, M. and Wickham, H., 2006. Chlorophyll-a in the rivers of eastern England. Science of the Total Environment, 365(1-3): 84-104.

SAS, 1999. SAS/STAT User's Guide: The Mixed Procedure. SAS Institute, Cary, NC.

SAS, 2007. SAS 9.3.1 for Microsoft Windows. SAS Institute Inc., Cary, NC.

Searle, S.R., 1971. Linear Models. John Wiley & Sons, New York, NY.

Straskrabova, V., Prochazkova, L. and Popovsky, J., 1973. Influence of reservoirs on chemical and bacteriological properties. In: J. Hrbacek and M. Straskraba (Editors), Hydrobiological Studies 2. Czechoslovak Academy of Sciences, Prague, pp. 348.

Taskinen, A., Sirvio, H. and Bruen, M., 2008. Modelling effects of spatial variability of saturated hydraulic conductivity on autocorrelated overland flow data: linear mixed model approach. Stochastic Environmental Research and Risk Assessment, 22(1): 67-82.

Tsegaye, T., Sheppard, D., Islam, K.R., Johnson, A., Tadesse, W., Atalay, A. and Marzen, L., 2006. Development of chemical index as a measure of in-stream water quality in response to land-use and land cover changes. Water Air and Soil Pollution, 174(1-4): 161-179.

University of Oregon, 2007. An Introduction to the features of the MIXED procedure, http://rfd.uoregon.edu/StatisticalResources/glm02_mixed.txt.

Wade, K.M. and Quaas, R.L., 1993. Solution to a system of equations involving a first-order autoregressive process. J Dairy Sci, 76: 3026-3032.

Wetzel, R.G., 2001. Limnology: Lake and river ecosystems. 3rd ed. Academic Press, New York, 1006 pp.

Wetzel, R.G. and Likens, G.E., 2000. Limnological Analyses, third ed. Springer-Verlag, New York, NY.

Zampella, R.A., Procopio, N.A., Lathrop, R.G. and Dow, C.L., 2007. Relationship of land-use/land-cover patterns and surface-water quality in the Mullica River basin. Journal of the American Water Resources Association, 43(3): 594-604.

CHAPTER 3

INFERRING CATCHMENT INFLUENCED DISSOLVED PHOSPHORUS DYNAMICS USING LAND USE AND STREAM BIOGEOCHEMISTRY

Abstract

Patterns in suites of chemicals and their relationships to land use can provide insight into catchment processes influencing eutrophication. In a two-year study of the KRLAW, these patterns are used to understand the catchment cycling (sources, pathways, fate) of chemicals. These types of studies are being done for DP, but temporal trends are obsuring the catchment patterns. To address this issue, a MLM is used to quantify the temporal trend, improving the relationships between DP, stream chemistry and land use. The MLM results are used to remove the temporal trend, and patterns are explored using common multivariate statistical techniques.

MLM and PFA land use and stream chemistry relationships provide evidence that agricultural and urban land uses represent P sources, but lowland forest does not. Lowland forest land use indicates watershed characteristics that provide DP processes that dissolve and/or release P supplied from other sources. From these results an approach is developed to estimate subwatershed DP contributions using readily available land use information. The implications for some common P management practices are considered in light of the inferred DP cycling.

The approaches developed in this paper advance the knowledge of the stream DP response to catchment anthropogenic P inputs, land use and management practices. These insights have implications for watershed P assessment and bring into question the long term effectiveness of some common management practices for P remediation.

Introduction

The use of the world's water resources has intensified in the last 100 years, hastened by the subtle and direct consequences of unprecedented human population growth (Turner et al., 2003). A consequence of increased anthropogenic influence is excessive inputs of N and P, often resulting in eutrophication, impairing the physical and biologic integrity of surface waters (Carpenter et al., 1998; Dodds et al., 2002). Among the important constituents of aquatic ecosystems leading to eutrophication is DP. How human activity affects changes in water quality and chemistry, including DP, deserves increasing attention as water quality management becomes more complex, if not more uncertain (Turner et al., 2003).

This study attempts to identify patterns and relationships between DP, land use, stream chemistry, trace elements and soil groups to infer the influence of catchment DP cycling on eutrophication. In Chapter 2, a MLM was used to identify a temporal trend that changes the catchment DP, stream chemistry and land use relationships. By removing these effects, temporal trend and site adjusted DP (DP_{TSA}) increases and strengthens the stream chemistry and land use relationships. Patterns and relationships between DP_{TSA}, biogeochemistry and land use are analyzed using MLM results and common univariate and multivariate statistical techniques.

Land use changes derived from human activity are known to influence the biogeochemistry of watersheds ((Boutt et al., 2001; Fitzpatrick et al., 2007; Tsegaye et al., 2006; Wayland et al., 2003; Williams et al., 2005; Zampella et al., 2007). Fitzpatrick et al. (2007), in a study of the Muskegon River Watershed in Michigan, found all major cations (Na^+, Mg^{2+}, K^+ and Ca^{2+}), anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_x and

F^-) and most trace elements (V, Co, Cu, Se, Rb, Sr, Mo, Cd, Ba and U) are higher in both agricultural and urban streams than reference forested streams. Cr and Pb were elevated in urban as compared to agricultural and forested sites.

Land use patterns and their contribution to P exports and loads is also well documented (Glandon et al., 1980; Lehrter, 2006; Lewis et al., 2007; Ontkean et al., 2005; Sonoda and Yeakley, 2007; Tsegaye et al., 2006; Winter and Duthie, 2000). Glandon et al. (1980), in a study of P and N loading from urban, agricultural and wetland sources, found annual P loadings of 0.595 kg ha^{-1}, 0.180 kg ha^{-1} and 0.023 kg ha^{-1}, respectively. Few studies quantify DP exports and their relationship to land use. One such study, by Coulter et al. (2004), documented annual orthophosphate fluxes of 0.28 kg ha^{-1}, 0.12 kg ha^{-1} and 0.07 kg ha^{-1} for agricultural, mixed and urban land uses, respectively, in eastern Kentucky.

Researchers have found large variations in subwatershed stream DP concentrations within the same watershed, and attribute this variability to various effects (Novak et al., 2004; Novak et al., 2003; Ontkean et al., 2005). Including seasonal influences, landscape characteristics, hydrology and wetland processes. This study explores the variability in DP cycling through stream biogeochemistry and land use patterns and relationships.

The hypothesis is that catchment influenced DP, land use and stream chemistry patterns identify sources and processes that affect DP cycling. To test this hypothesis MLM quantified fixed temporal trend and random site effects are removed from the DP. DP_{TSA}, stream chemistry, trace element, soil type and land use pattern and relationship results from MLM, PFA, GLM and Pearson correlation coefficient analyses provide inferences about catchment DP cycling.

Results show land use coefficient ratios are consistent with published P export ratios for urban to agricultural (approximately 3:1) land use (Glandon et al., 1980). However, lowland forest to agricultural (19.5:1) land use and lowland forest to urban (6.8:1) land use coefficient ratios are considerably higher than published export ratios (0.13:1 and 0.04:1, respectively) (Glandon et al., 1980). The high degree of influence and relatively low percentage of lowland forest land use suggests that lowland forest does not represent a P source. Instead, lowland forest is a proxy for watershed characteristics (% wetlands and soil types) that provide processes that dissolve and/or release P from other sources. Additional evidence for the P source, DP process and land use relationships is presented from the stream biogeochemical fingerprints identified for agricultural, urban and mixed agricultural/urban land uses.

From these results, a method is developed to estimate the DP_{TSA} contribution using only readily available agricultural, urban and lowland forest land use information. Insights into the contributions to mean DP_{TSA} from different land use effects provided by this approach are described. Finally, the implications of P management practices on DP in light of the inferred P cycling are considered.

The approaches developed in this paper advance the knowledge of the stream DP response to catchment anthropogenic P inputs, land use and management practices. These insights have implications for watershed P assessment and bring into question the long term effectiveness of some common management practices for P remediation.

Methods

Catchment influenced DP cycling was investigated using the KRLAW stream chemistry dataset (Appendix I), KRLAW trace element dataset (Appendix II), land use descriptions (Table 1.1.) and STATSGO soil group distribution (Table 1.2). The study site, sampling locations, sampling methods and chemical analyses are described in Chapter 1. The catchment influenced MLM fixed stream chemistry, land use and temporal trend effects (Tables 2.1) and random effects (Table 2.2) detailed in Chapter 2 were used for this study. The sites and dates that constitute the catchment influenced datasets are shown in Figure 2.5

Temporal trend and site adjusted DP

Temporal trends and site effects from the catchment MLM were removed from the catchment influenced DP to improve the number and strength of the DP, stream chemistry and land use relationships. DP_{TSA} is determined by rearranging equation 2.5 as follows:

$$\log(DP)_{TSA} = \log(DP) - TT - SE = int + SC + LU \qquad (3.1)$$

Equation 3.1 and the estimates from Table 2.1 were used to calculate $\log(DP)_{TSA}$. DP_{TSA} was calculated by back transforming $\log(DP)_{TSA}$.

Statistical Analysis

MLM, Pearson correlation coefficients, GLM and PFA are the statistical methods used to identify patterns among $DP_{TSA,}$ suites of chemicals and land use to infer catchment influenced DP cycling. MLMs are described in Chapter 2 and Appendix V. Pearson correlation coefficients are nonparametric measures and probabilities of association between two variables (SAS, 1999). GLM uses the least squares method to fit a general linear model relating continuous dependent variables to independent variables (SAS, 1999). PFA detects structure in variables identifying a common factor that explains the variability between variables. The common factor is an unobservable, hypothetical variable that contributes to the variance of at least two observed variables (SAS, 1999). The statistical methods for this study were implemented using SAS 9.1.3 (SAS, 2007), including PROC MIXED, PROC CORR, PROC GLM and PROC FACTOR procedures.

Results

The MLM temporal trend and random site effects (Tables 2.1 and 2.1) were removed from the DP, using eq. 3.1, providing a dependent variable, DP_{TSA}, related to stream chemistry and land use that can be analyzed using common univariate and multivariate statistical techniques. The significant ($p<0.05$) fixed effects for stream chemistry (Mg^{2+}, K^+, Na^+, NO_3^-, pH, alkalinity and specific conductance, Table 2.1) and land use (lowland forest, agricultural and urban, Table 2.1) from the catchment influenced MLM were evaluated with respect to DP_{TSA}. The mean and standard deviation by site for DP, DP_{TSA}, and the significant stream chemistry, and the percent by site for each significant land use are given in Table 3.1.

Land use relationships

The relationship, between the land use variables and mean DP_{TSA} was analyzed by plotting the result of the MLM land use fixed effects (Table 2.1) equation (13.4145lowland forest + 0.6828agricultural + 1.9947urban) against the mean DP_{TSA} by site (Figure 3.1).

Table 3.1: The mean and standard deviation (mean ± standard deviation) by site for dissolved phosphorus (DP), temporal trend and site adjusted dissolved phosphorus (DP_{TSA}) and the significant ($p<0.05$) stream chemistry fixed effects (Mg^{2+}, K^+, NO_3^- ,Na^+, pH, alkalinity (Alk) and specific conductance (SPC)) and land use percentages for the significant ($p<0.05$) land use fixed effects (lowland forest, agricultural and urban) from the catchment influence MLM.

SITE	DP	DP_{TSA}	MG^{2+}	K^+	NO_3^-	NA^+	pH	Alk	SPC	Lowland Forest	Agri-cultural	Urban
	(μgL^{-1})	(μgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(pH)	(mgL^{-1} as HCO_3^-)	(μgL^{-1})	%	%	%
BC	37.02 ± 10.10	23.20 ± 5.34	23.00 ± 2.07	2.09 ± 0.34	0.59 ± 0.49	19.00 ± 3.47	7.73 ± 0.09	288.3 ± 27.5	696 ± 65	7.5	51.4	5.3
BR	61.86 ± 16.07	26.82 ± 5.37	23.43 ± 2.23	2.32 ± 0.39	0.81 ± 0.51	22.65 ± 5.19	7.71 ± 0.09	293.0 ± 28.7	727 ± 82	7.6	53.8	5.3
FC	12.12 ± 3.43	6.96 ± 1.09	19.72 ± 1.07	0.67 ± 0.24	0.04 ± 0.01	6.15 ± 0.53	7.71 ± 0.13	236.4 ± 13.1	463 ± 21	6.6	0.0	3.0
GR	10.32 ± 2.56	6.96 ± 1.68	23.92 ± 1.69	1.87 ± 0.40	1.33 ± 0.48	8.95 ± 0.81	7.69 ± 0.08	257.9 ± 15.4	611 ± 39	3.9	46.7	5.8
KA	30.65 ± 13.75	13.87 ± 3.64	22.23 ± 2.08	2.40 ± 0.42	1.32 ± 0.22	27.42 ± 4.72	7.97 ± 0.13	263.1 ± 23.3	676 ± 57	5.4	46.2	8.5
KB	22.11 ± 6.23	14.51 ± 3.33	22.47 ± 1.52	1.64 ± 0.29	1.18 ± 0.18	17.34 ± 2.33	7.87 ± 0.09	278.0 ± 15.9	670 ± 43	6.0	53.3	6.3
KC	18.30 ± 8.20	13.57 ± 4.56	21.64 ± 1.73	1.73 ± 0.37	0.81 ± 0.21	19.43 ± 2.86	7.99 ± 0.14	270.7 ± 19.5	645 ± 44	5.9	48.8	6.8
KD	13.09 ± 3.14	10.70 ± 2.10	22.28 ± 1.12	2.46 ± 0.38	0.84 ± 0.32	28.85 ± 5.22	8.12 ± 0.19	246.4 ± 17.8	655 ± 38	5.4	45.9	8.5
KE	17.91 ± 5.90	11.94 ± 2.74	22.34 ± 1.59	1.45 ± 0.24	1.36 ± 0.13	15.91 ± 1.56	7.87 ± 0.09	276.5 ± 11.7	657 ± 36	5.3	54.9	6.1
KG	28.82 ± 10.51	15.00 ± 2.73	22.46 ± 1.76	1.82 ± 0.31	1.08 ± 0.18	22.01 ± 3.73	7.84 ± 0.09	275.9 ± 20.5	703 ± 66	6.1	50.0	6.8
KK	33.67 ± 12.73	18.86 ± 10.63	22.20 ± 1.94	2.45 ± 0.48	1.17 ± 0.22	30.68 ± 5.84	7.74 ± 0.19	271.0 ± 20.3	714 ± 61	5.7	46.2	9.1
KM	27.22 ± 8.64	14.98 ± 3.64	21.91 ± 1.70	1.75 ± 0.26	1.00 ± 0.17	21.44 ± 3.10	7.85 ± 0.09	277.4 ± 19.9	673 ± 53	6.0	48.8	6.7
KP	41.61 ± 20.77	17.42 ± 6.46	21.83 ± 2.12	2.64 ± 0.53	1.43 ± 0.28	31.10 ± 5.46	7.79 ± 0.17	266.8 ± 26.0	706 ± 65	5.5	45.7	9.0
KS	18.42 ± 7.09	14.00 ± 4.90	22.04 ± 1.98	1.77 ± 0.37	0.87 ± 0.21	18.70 ± 2.85	7.88 ± 0.18	267.7 ± 18.3	648 ± 51	6.0	48.7	6.7
PC	21.94 ± 14.32	12.69 ± 6.85	22.65 ± 3.00	1.68 ± 0.35	0.46 ± 0.15	41.24 ± 5.15	7.75 ± 0.13	282.2 ± 35.4	787 ± 92	3.4	17.0	30.6
SB	18.48 ± 5.05	9.01 ± 2.01	22.36 ± 1.22	1.61 ± 0.49	0.87 ± 1.39	10.77 ± 1.66	7.83 ± 0.11	264.1 ± 21.5	551 ± 22	4.0	58.3	5.1
WC	40.58 ± 13.78	23.74 ± 3.67	21.67 ± 2.31	1.55 ± 0.34	0.33 ± 0.12	8.76 ± 0.96	7.56 ± 0.14	287.2 ± 33.4	593 ± 63	7.4	47.2	3.9

A linear regression of these data shows a good fit with $R^2 = 0.84$. This relationship exhibits three clusters that have been assigned the categories low, medium and high mean DP_{TSA}. Further inspection of the individual land use fixed effect contribution to DP_{TSA} category (Table 3.2) indicates that no individual land use contribution directly relates to DP_{TSA}.

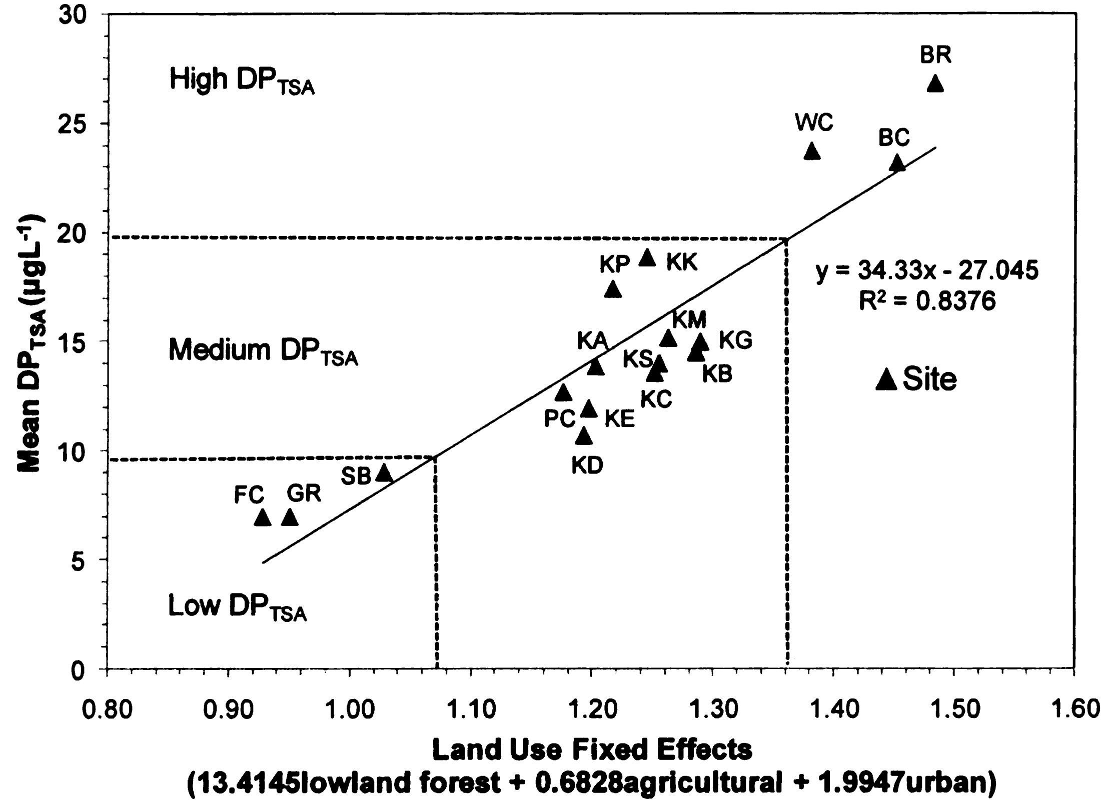


Figure 3.1: A plot and linear regression of the catchment MLM land use fixed effects equation versus the mean DP_{TSA} by site.

High lowland forest contribution exists in all three DP_{TSA} categories (indicated by the dark highlight) while low lowland forest contribution exists in the medium and low DP_{TSA} categories (indicated by the light highlight). The high DP_{TSA} category does not include a low lowland forest contribution. The agricultural and urban contributions are similar among DP_{TSA} categories with the exception of sites FC and PC.

The fixed effect coefficients provide insight into the relative contributions of each land use. Urban has a 2.9:1 ratio of impact compared to agricultural land use. This is consistent with the ratio between published P loading values for urban and agricultural land use. Glandon et al. (1980), in a study of P and N loading from urban, wetland and agricultural sources, found P loading from urban sources at 0.595 kg ha^{-1} and from agricultural at 0.180 kg ha^{-1}, a ratio of 3.3:1 urban to agricultural land use. The fixed effect coefficients for urban and agricultural land use reflect their contributions as sources of P. However, lowland forest land use and its coefficient are inconsistent with this explanation.

Table 3.2: A comparison of DP_{TSA} category, site, mean DP_{TSA} and the catchment influenced MLM lowland forest, agriculture, urban and total land use effects. Dark highlight compares high lowland forest effect sites. Light highlight compares low lowland forest effect sites.

			Land Use Effect			
DP_{TSA} Category	Site	Mean DP_{TSA} (μgL^{-1})	Lowland Forest (13.285 x %)	Agricultural (0.6824 x %)	Urban (1.9588 x %)	Total
Low	FC	6.96	0.87	0.00	0.06	0.93
	GR	6.96	0.52	0.32	0.11	0.95
	SB	9.01	0.53	0.40	0.10	1.03
Medium	KD	10.70	0.71	0.31	0.17	1.19
	KE	11.94	0.70	0.37	0.12	1.20
	PC	12.69	0.45	0.12	0.60	1.17
	KC	13.57	0.79	0.33	0.13	1.25
	KA	13.87	0.72	0.32	0.17	1.20
	KS	14.00	0.79	0.33	0.13	1.26
	KB	14.51	0.80	0.36	0.12	1.29
	KM	14.98	0.80	0.33	0.13	1.26
	KG	15.00	0.81	0.34	0.13	1.29
	KP	17.42	0.73	0.31	0.18	1.22
	KK	18.86	0.75	0.32	0.18	1.25
High	BC	23.20	1.00	0.35	0.10	1.45
	WC	23.74	0.98	0.32	0.08	1.38
	BR	26.82	1.01	0.37	0.10	1.48

Lowland forest is one of the wetland land use categories. The Glandon et al. (1980) study found a wetland loading of 0.023 kg ha^{-1}, resulting in ratios for wetland to agricultural land use of 0.13:1 and wetland to urban land use of 0.04:1. The fixed effects coefficients indicate ratios for wetland (lowland forest) to agricultural land use of 19.5:1 and wetland (lowland forest) to urban land use of 6.8:1. This large inconsistency suggests that lowland forest land use represents something other than a P source. Lowland forest land use is low, ranging from 3.4 to 7.6% for the study area, yet it exerts a large influence in the land use component of the MLM. It does not seem reasonable that this influence is solely from the small percentage of lowland forest.

Instead, lowland forest land use percentage indicates watersheds that have processes that promote the dissolution and release of P. While urban and agricultural land use indicates the level of P sources, lowland forest land use indicates the level of P dissolution/release processes. If other watershed characteristics also promote the dissolution/release of P they should be related lowland forest land use.

The Pearson correlation coefficients for land use and soil group were calculated to identify these relationships (Table 3.3). Non-forested wetland has a high positive correlation (0.87) with lowland forest land use. Both are lowland systems, defined as areas that have hydric soils and are permanently or temporarily inundated, with high water tables (Pacific Meridian Resources, 2001). These lowland systems are buffers to the stream system, retarding the movement of water and collecting PP transported via surface runoff from upland portions of the catchment. These areas provide an environment and time for the processes that dissolve, adsorb and desorb P (Novak et al., 2004). In addition to a correlation with similar environments, lowland forest land use is correlated with three soil groups.

Table 3.3: Pearson's correlation coefficients for land use and soil groups for the Kalamazoo River/Lake Allegan Watershed. See Tables 1.1 and 1.2 for abbreviations. High correlations (>0.75) with lowland forest (land use class VI) are highlighted.

Pearson Correlation Coefficients, N = 573

	Land use class (Table 1.1)								STATSGO soil group (Table 1.2)														
	I	II	III	IV	V	VI	VII	VIII	MI011	MI014	MI022	MI024	MI034	MI035	MI036	MI043	MI045	MI047	MI048	MI083	MI091
I	1	-0.58	0.82	0.18	0.17	-0.59	-0.87	0.03	0.30	-0.19	-0.27	-0.32	-0.21	-0.33	-0.42	-0.26	0.16	0.96	-0.11	-0.11	-0.22
II		1.00	-0.79	-0.90	-0.04	0.31	0.59	0.31	-0.18	0.38	0.23	0.35	0.39	0.32	0.45	0.43	-0.69	-0.77	0.20	0.03	0.24
III			1.00	0.53	0.07	-0.62	-0.78	-0.33	0.21	-0.06	-0.29	-0.62	-0.08	-0.52	-0.59	-0.13	0.44	0.90	-0.07	-0.13	-0.44
IV				1.00	-0.03	-0.12	-0.29	-0.41	0.09	-0.32	-0.19	-0.32	-0.34	-0.28	-0.35	-0.37	0.74	0.43	-0.12	0.03	-0.20
V					1.00	-0.64	-0.52	0.81	0.92	-0.36	-0.38	-0.36	-0.39	-0.41	-0.04	-0.45	-0.50	0.10	0.13	0.93	0.49
VI						1.00	0.87	-0.22	-0.76	-0.02	0.59	0.84	0.02	0.81	0.47	0.12	0.22	-0.55	-0.33	-0.45	0.13
VII							1.00	-0.21	-0.67	0.26	0.54	0.61	0.30	0.64	0.46	0.39	-0.03	-0.85	-0.16	-0.27	0.10
VII								1.00	0.67	-0.41	-0.12	0.18	-0.42	0.05	0.28	-0.44	-0.67	-0.13	0.01	0.75	0.68
MI011									1.00	-0.46	-0.39	-0.46	-0.49	-0.47	0.01	-0.55	-0.49	0.25	0.37	0.83	0.29
MI014										1.00	-0.14	-0.35	1.00	-0.31	-0.52	0.97	0.08	-0.26	-0.22	-0.29	-0.32
MI022											1.00	0.55	-0.07	0.86	0.68	0.09	-0.23	-0.29	-0.19	-0.25	-0.38
MI024												1.00	-0.32	0.90	0.65	-0.23	-0.08	-0.36	-0.22	-0.29	0.36
MI034													1.00	-0.26	-0.48	0.99	0.06	-0.28	-0.23	-0.30	-0.34
MI035														1.00	0.77	-0.11	-0.17	-0.36	-0.23	-0.30	0.03
MI036															1.00	-0.36	-0.55	-0.48	0.38	0.03	0.09
MI043																1.00	0.02	-0.33	-0.27	-0.35	-0.41
MI045																	1.00	0.37	-0.38	-0.49	-0.19
MI047																		1.00	-0.12	-0.15	-0.28
MI048																			1.00	0.03	-0.11
MI083																				1.00	0.49
MI091																					1.00

Lowland forest is highly, positively correlated with MI024, Boyer-Oakville-Cohoctah (0.84) and MI035, Marlette-Capac-Parkhill (0.81) soil groups and highly, negatively correlated with MI011, Coloma-Spinks-Oshtemo (-0.76). The positively correlated soil groups increase in percentage with lowland forest land use. The Boyer-Oakville-Cohoctah and Marlette-Capac-Parkhill groups consist of two types of soils: 1) rapidly-permeable sandy or loamy, gravelly soils, and 2) slowly-permeable loamy soils (USDA, 1990; USDA, 1997). Soil P adsorption capacity has been shown to increase with increasing surface area and clay content (Penn et al., 2005). The first soil type has coarse particles, low surface area and a low capacity for P retention (high release), and drains water and DP rapidly into hydrologic pathways. The second has less coarse particles and a higher P retention, but drains slower, providing additional time for P desorption to occur. The negatively correlated soil group increases with decreasing lowland forest land use. The Coloma-Spinks-Oshtemo group consists of moderately-slow permeable loamy to loamy silt soils (USDA, 1990; USDA, 1997). These finer soils, more prevalent in watersheds low in lowland forest, have a higher capacity to retain P, resulting in the inverse relationship.

These soil groups and non-forested wetland correlations to lowland forest are examples of watershed characteristics that contribute to P dissolution and release that are identifiable from this data. It is anticipated that other characteristics (e.g. depth to water table, runoff lag time, hydrology) potentially correlated to lowland forest land use but not measured in this study are also contributing to the strength of the lowland forest relationship to DP.

Using the land use MLM coefficients and lowland forest as an indicator of P processes and urban/agricultural as an indicator of P sources, it is evident from Table 3.4 that both source and process are required to produce high mean DP_{TSA}. Site FC has a high lowland forest effect (high process) and low urban and agricultural effects (low source), resulting in low mean DP_{TSA}. Site BR has high lowland forest effect (high process) and high agricultural effect (high source), producing high mean DP_{TSA}. Site GR has low lowland forest effect (low process) and high agricultural effect (high source), resulting in low mean DP_{TSA}. Additional insights into these dynamics between land use, P sources and P processes are inferred from the stream chemistry and trace element relationships.

Stream chemistry relationships

An un-rotated PFA was performed on the catchment influenced stream chemistry, land use and DP_{TSA} data. The results are given in Table 3.4 and explain 79.6% of the variance in the data with four factors. Factor 1, unrelated to $DP_{TSA,}$ is the urban influence on stream chemistry, reflecting strong and moderate loadings of urban land use, alkalinity, Mg^{2+}, specific conductance and Na^{+}, most likely from the high level of road salt loss to streams in urban environments. Factor 2 has strong positive lowland forest and agricultural loadings, a moderate negative urban and moderate positive DP_{TSA}, K^{+} and alkalinity loadings. This factor is interpreted as reflecting the source effect of agricultural nutrients in the DP_{TSA} and K^{+} and the lowland forest process effect in DP_{TSA} and alkalinity. Urban land use is inversely correlated to both agricultural and lowland forest land use (Table 3.3), leading to the inverse relationship in this factor. Factor 3 is the inverse relationship between agricultural and lowland forest with DP_{TSA} loading directionally, with lowland forest indicating that DP_{TSA} levels relate to process when source is present. The strong loading of NO_3^- directly to agricultural land use but inversely to DP_{TSA} and lowland forest indicates a short flow path and lack of process for N conversion in low lowland forest watersheds. The opposing situation of factor 2, the direct relationship between agricultural and lowland forest land use, has low loading for NO_3^- as the environment and processes indicated by lowland forest convert NO_3^- to other N forms.

Table 3.4: Un-rotated factor loading matrix from principal factor analysis for the stream chemistry dataset from the Kalamazoo River/Lake Allegan Watershed.

	Factor 1	Factor 2	Factor 3	Factor 4
DP_{TSA}		*0.6448*	-0.5504	
Lowland Forest		**0.7343**	*-0.4453*	
Agricultural		**0.7620**	*0.4473*	
Urban	*0.6717*	*-0.6121*		
Mg^{2+}	*0.6162*			*-0.4524*
K^+		*0.4466*		*0.6494*
NO_3^-			**0.7044**	*0.4307*
Na^+	**0.8615**			
pH			*0.5750*	
Alk	*0.6313*	*0.4497*		*-0.5096*
SPC	**0.9248**			
Percent of total variance explained				
	0.2808	0.2306	0.1520	0.1325
Total percentage of variance explained: 79.6%				

Strong loadings (≥ 0.70) are indicated by bold type.

Moderate loadings (>0.40 and <0.70) are indicated by italics.

Factor 4 is unrelated to DP_{TSA} and relates Mg^{2+}, K^+, NO_3^- and alkalinity. The catchment stream chemistry PFA demonstrates patterns and relationships in land use and stream chemistry that supports the P source and P process dynamics discussed ea

dy

Ir

po

ie

Sn

Lo

e.a

(F

inc

mo

str

lo

tha

me

an

urb

ins

Tra

N.

earlier. The catchment trace element PFA provides further evidence of these dynamics.

Trace element relationships

The catchment trace element PFA (Table 3.5) has four factors explaining 99.6 % of the variance in the data. Factor 1 is the DP factor with strong and moderate loadings on DP_{TSA}, lowland forest, agricultural, many trace metals (Mn, As, Cd Ni, Sn, Sr, Co, Pb, V, Se, Ti, Ba, Cr, Sc, Zn and Mo) and inverse loading on urban. Lowland forest and undeveloped land uses are not known to be a source of trace elements, and their strong positive loadings are contrary to previous studies (Fitzpatrick et al., 2007; Williams et al., 2005). This factor suggests that the processes indicated by lowland forest that dissolve P also result in the dissolution of many trace metals if a source of those, agricultural land use in this case, is present. As in the stream chemistry PFA, urban land use is inversely correlated to both agricultural and lowland forest land use, leading to the inverse relationship in this factor. Factor 4 is the lowland forest only factor and the lack of or inverse loading on DP_{TSA} and trace metals reinforces the need for source along with process. Factor 2 is urban land use and associated trace element loadings. Factor 3 is direct and inverse agricultural, urban and trace element loading.

Further inspection of the patterns across factors 1, 2 and 3 in the PFA provides insight into stream biogeochemical fingerprints of agricultural and urban land use. Trace elements that load only with agricultural land use and DP_{TSA} are Mn, As, Cd, Ni, Sn, Sr, and Co (dark highlight in Table 3.5). Boron loads only with urban land use and is

agricultu

Table 3.
catchme
Watersh
DP_{734}
commer

Lowla
Urban
Agric
DP
Mn
As
Cd
Ni
Sn
Sr
Co
Ti
Ba
Sc
Pb
V
Se
Cr
U
Zn
Mo
B
Fe
Rb
Al
Perce
Total

Strong
Moder

use and is not related to DP_{TSA} (medium highlight in Table 3.5). Iron loads only with agricultural land use and is not related to DP_{TSA} (light highlight in Table 3.5).

Table 3.5: Un-rotated factor loading matrix from principal factor analysis for the catchment synoptic trace element dataset from the Kalamazoo River/Lake Allegan Watershed. Stream biogeochemical fingerprints: dark highlight = agricultural and DP_{TSA}; medium highlight = urban only; light highlight =agricultural only; and box = common agricultural and urban.

	Factor 1	Factor 2	Factor 3	Factor 4
Lowland Forest	**0.7721**			*0.4678*
Urban	*-0.4387*	*0.5201*	*0.6398*	
Agricultural	*0.4727*		**-0.7173**	
[illegible]	**0.91[illegible]**			
[illegible]	**0.94[illegible]**			
[illegible]	**0.91[illegible]**			
[illegible]	**0.91[illegible]**			
[illegible]	**0.89[illegible]**			
[illegible]	**0.89[illegible]**			*-0.4126*
[illegible]	**0.87[illegible]**			
[illegible]	**0.8[illegible]**			
Ti	*0.6714*	**-0.7075**		
Ba	*0.6168*	*-0.5233*		
Sc	*0.5607*	**-0.7853**		
Pb	**0.7467**		*0.4950*	*-0.4048*
V	**0.7343**	*0.4384*	*0.4049*	
Se	**0.6880**	*0.5885*		
Cr	*0.6031*		*0.4931*	
U		*0.4685*	*-0.6486*	
Zn	*0.4652*	*0.6525*		
Mo	*0.4378*	**0.8521**		
B		**0.8559**		
Fe			*-0.5080*	*-0.6969*
Rb		**-0.7822**	*0.5040*	
Al				
Percent of total variance explained				
	0.5158	0.2520	0.1381	0.0896
Total percentage of variance explained: 99.6%				

Strong loadings (≥ 0.70) are indicated by bold type.

Moderate loadings (>0.40 and <0.70) are indicated by italics.

Common trace element loadings to agricultural and urban land uses with some relationships to agricultural and DP_{TSA} are Ti, Ba, Sc, Pb, V, Se, Cr, U, Zn and Mo (box in Table 3.5). Rubidium inconsistently loads with urban, inversely in Factor 2 and directly in Factor 3. Aluminum does not load with any land use, DP_{TSA} or other trace elements. These biogeochemical fingerprints show promise for relating DP_{TSA} to agricultural inputs and the anthropogenic influence on stream chemistry of urban and agricultural land uses. The catchment trace element PFA demonstrates patterns and relationships in biogeochemical fingerprints, supporting agricultural and urban land use as P sources and high loadings with lowland forest land use indicating P process dynamics.

The DP_{TSA}, land use and stream chemistry patterns and relationships examined through stream chemistry and trace element PFAs lead to the identification of a P source and P process dynamic that is quantifiable through MLM land use coefficients and lowland forest, agricultural and urban land use percentages, providing a method to assess watershed DP.

Watershed DP assessment

Stream chemistry and trace metal patterns support the DP_{TSA} and land use dynamics and provide additional insights into sources and processes. However, stream chemistry and trace element sampling and analysis is time consuming and expensive for a large number of subwatersheds. Identifying agricultural and urban land uses as measures for P sources and lowland forest as a proxy for P processes provides a method for assessing the land use contribution to DP_{TSA} throughout the watershed using readily available land use data. The relationship developed in Figure 3.1 using the M

subw

or hig

susce

adjac

reduc

is tha

contr

River

samp

From

$\mu g L^{-1}$

DP in

estim

grea

dyna

high

indic

the MLM land use coefficients and land use percentages was applied to 78 subwatersheds in the KRLAW to estimate their mean DP_{TSA} category as low, medium or high (Figure 3.2 and Appendix VI).

The estimated categories depicted in Figure 3.2 identify subwatershed susceptibility to DP, a consideration when developing P reduction strategies. The adjacency of low, medium and high DP_{TSA} subwatersheds indicates that a single P reduction strategy within a region may not be appropriate. A benefit of this approach is that individual land use effects identify the P source and DP process dynamics contributing to these differences, demonstrated by the following examples.

The Pine Creek Watershed (sub 73), with high mean DP_{TSA}, is near the Gun River Watershed (sub 70), with low mean DP_{TSA}. Pine Creek and Gun River were sampled by the Michigan Department of Environmental Quality (MDEQ) in 1998. From unpublished MDEQ results, the mean DP concentrations were 34 μgL^{-1} and 9 μgL^{-1} for Pine Creek and Gun River, respectively. With nearly four times the level of DP in Pine Creek as compared to Gun River, these results are consistent with the estimates made here. Comparing the land use effects in Appendix II, Gun River has a greater P source dynamic (0.510) than Pine Creek (0.443), but a much less DP process dynamic (0.379 versus 1.383). The difference in mean DP_{TSA} is due to Pine Creek's higher level of watershed characteristics that promote the dissolution and release of P, indicated by the higher lowland forest land use effect.

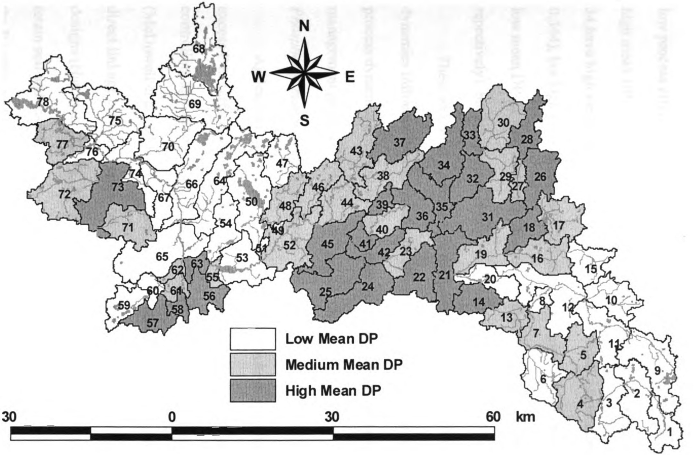


Figure 3.2: Categories for mean DP_{TSA} for the Kalamazoo River/Lake Allegan Watershed, HUC 4050003, basin 17, by sub number estimated using the catchment MLM land use equation and mean DP_{TSA} relationship (Appendix VI).

The high
Battle C
low pro
high m
34 hav
0.344
low m
repect

dynan
proces
manag
Phosp

excess
contro
(McDo
direct
design
retain
the P s
consequ
process

The high mean DP_{TSA} levels in sub 63, the city of Kalamazoo, and sub 41, the city of Battle Creek, are due to high urban source effects (1.078 and 1.154, respectively) with low process effects (0.579 and 0.479). Agricultural subwatersheds exhibit from low to high mean DP_{TSA} with similar agricultural land use effect contributions. Subs 32 and 34 have high mean DP_{TSA} with medium high agricultural source effects (0.333 and 0.344), but high process effects (1.234 and 1.024, respectively). Subs 69 and 70 have low mean DP_{TSA} with medium high agricultural source effects (0.350 and 0.390, repectively), but low process effects (0.559 and 0.379).

These examples illustrate how the combination of P source and DP process dynamics influence the estimated subwatershed mean DP_{TSA}. The P source and DP process dynamics inferred by these results have implications for watershed P management practices.

Phosphorus management implications

Agricultural and urban environments have long been recognized as sources of excess P to surface waters (Lewis et al., 2007; Sharpley, 1999). Common practices for controlling agricultural inputs are filter strips, buffer strips and minimum tillage (McDowell et al., 2003). Common urban P control practices are aimed at breaking the direct linkage between impervious areas and receiving waters through low impact designs (Hatt et al., 2004). All of these practices are "at source measures" intended to retain soil and associated P at the source location and out of surface waters. In light of the P source and DP process dynamics inferred from this research, an unintended consequence of these practices is to increase P source potential while increasing DP process potential. These practices, while reducing sediment delivery, also retard

runof
the ti

may
highe
Inam
manag
manag
reduct
increa
reduct
ortho

200
que
in

we
ML
relation
were rep

runoff delivery to surface waters (Hatt et al., 2004; Sharpley et al., 2000), producing the time and environment for DP dissolution and release processes.

These measures may have the short term effect of reducing total P (TP), but may result in a long term return to near previous TP concentrations consisting of higher DP and lower particulate P (PP) fractions when a new steady state is reached. Inamdar et al. (2001) studied the Nomini Creek Watershed after seven years of best management practice (BMP) implementation including no-till, filter strips and nutrient management. At one location, they found the TP load was reduced by 4 % with a PP reduction of 30% offset by dissolved orthophosphate and dissolved organic P increases of 92 and 83%, respectively. A second location exhibited a TP load reduction of 24% with 41% PP reduction offset by increases of 123% in dissolved orthophosphate and 55% in dissolved organic P.

The Inamdar et al. study, others (Hickey and Doran, 2004; Schippers et al., 2006; Sharpley et al., 2000; Uusi-Kamppa et al., 2000) and this research bring into question the long term effectiveness of P management practices that alter P dynamics in lieu of reducing P inputs.

Discussion

In a previous study of the KRLAW examining temporal trends in DP, data were separated by catchment and biological influence and were analyzed using MLMs. This study focuses on the land use, stream chemistry and trace element relationships in the catchment influenced data. The temporal trend and site effects were removed from the DP data –referred to as DP_{TSA} – using the relationships dev

and

vari

by s

repr

coef

agric

and l

fores

lowla

agric

indi

pro

ar

F

i

in

m

proc

lowlan

developed in the previous study. Patterns among DP_{TSA}, land use, stream chemistry and trace elements are used to infer catchment influenced DP dynamics.

A plot and linear regression of the equation for the significant land use variables (lowland forest, agricultural and urban) from the MLM and the mean DP_{TSA} by site exhibited a strong relationship, and three clusters were divided into categories representing low, medium and high mean DP_{TSA}. The ratios of the land use coefficients from this relationship were consistent with published P export ratios for agricultural to urban land uses, but were much higher for lowland forest to agricultural and lowland forest to urban land uses. The large influence contributed by lowland forest land use in the equation is inconsistent with other studies that have found lowland forest to be a low source of P. From these results it is proposed that agricultural and urban land uses represent P sources and that lowland forest is an indicator of watershed characteristics that promote DP dissolution and release processes.

Further evidence for these P source and DP process dynamics was gained by analyzing patterns in land use, stream chemistry, trace elements and soil groups using Pearson's correlation coefficients and PFA. Pearson's correlation coefficients identified another wetland land use –non-forested wetlands– and three soil groups that impact the dissolution time for and the release of P. The PFA of stream chemistry and trace element data that supports lowland forest as an indicator of watershed DP process dynamics. Direct lowland forest, DP_{TSA} and trace elements are unrelated, but lowland forest in combination with a P source land use has numerous strong and mod

indi

urb

the

land

Mn.

urba

Mo.

asso

The

thos

re

w

(

I

three

to estim

moderate loadings. These results support that lowland forest land use does not indicate a P source dynamic, but a DP process dynamic when P sources are present.

The PFAs also provide insight into the P source dynamics of agricultural and urban land uses. The strong and moderate loading patterns for DP_{TSA}, stream chemistry and trace elements provide biogeochemical fingerprints related to P source land uses. The biogeochemical fingerprint of agricultural sources includes DP_{TSA}, Mn, As, Cd, Ni, Sn, Sr and Co. Not related to DP_{TSA}, a combine agricultural and urban source biogeochemical fingerprint includes Ti, Ba, Sc, Pb, V, Se, Cr, U, Zn and Mo. The agricultural land use fingerprint may include DP_{TSA} because trace elements associated with agrichemicals are applied proportionately to P for crop production. The lack of DP_{TSA} in the urban and mixed agricultural/urban fingerprint indicates that those trace elements have variable sources not linked P application or use.

The PFAs, mean DP_{TSA} and land use relationships and Pearson's correlations reinforce the association of the combination of the P source and DP process dynamics with DP_{TSA} levels. A low P source (indicated by low agricultural and/or urban land use) and a high DP process (indicated by high lowland forest land use) result in low DP_{TSA}. A high P source (high agricultural and/or urban land use) and a low process (low lowland forest land use) produce low DP_{TSA}. A high P source (high agricultural and/or urban land use) and a high process (high lowland forest land use) provide high DP_{TSA}. Both P source and DP processes are required for increased DP_{TSA} levels.

The inferences into the P source and DP process dynamics indicated by the three land use relationships allows development of a watershed DP assessment method to estimate and categorize subwatershed mean DP_{TSA} using only readily available land

use inform
evaluated t
described.
watershed

Th
dynamics
managem
practices
that pro
should
reduced
confirm
evaluat
that the
researc
commo

group d
removal
between
process

use information for the KRLAW. Underlying individual land use effects that can be evaluated to understand the P source and DP process contributions to DP_{TSA} levels are described. This approach has the potential improve P reduction strategies at both the watershed and subwatershed levels.

The watershed DP assessment and inferences about P source and DP process dynamics have implications for P management. Common P agricultural and urban management practices are aimed at preventing PP from entering surface waters. These practices are believed to have the potential to increase the watershed characteristics that promote the dissolution and release of P. While a short-term improvement in TP should result, long-term TP levels may increase as a new steady state is achieved and reduced PP is replaced by increased DP. Agricultural watershed studies have confirmed this phenomenon (Inamdar et al., 2001). Studies have not been found that evaluate urban P management practices and associate DP increases, but speculation is that the P source and DP process dynamics apply to urban environments as well. This research along with that of others raises questions about the long term effectiveness of common P management practices in lieu of P input reductions.

Conclusions

This study uses patterns in land use, stream chemistry, trace element and soil group data to infer catchment influenced DP dynamics in the KRLAW after the removal of seasonal trend and site effects. The combination of and interaction between a P source dynamic –related to agricultural and urban land use– and a DP process dynamic –indicated by lowland forest land use as a proxy for watershed characteris

that catchn

sources ar

P

and land

biogeoch

uses in t

conclud

be used

this app

sources

consid

manag

result i

cycling

assessn

characteristics, were inferred from this research. These results support the hypothesis that catchment influenced DP, land use and stream chemistry patterns identify P sources and processes that affect DP cycling.

PFAs and Pearson's correlations provide evidence of P sources, DP processes and land use relationships. The PFA results show potential for identifying stream biogeochemical fingerprints for agricultural, urban and mixed agricultural/urban land uses in the KRLAW.

From the evidence of P dynamics, mean DP_{TSA} and land use relationships it is concluded that three land use relationships (agricultural, urban and lowland forest) can be used to estimate and categorize subwatershed mean DP_{TSA} concentrations. From this approach, individual land use effects show promise for additional insight into P sources and DP processes contributing to elevated mean DP_{TSA} concentrations.

The interaction between P sources and DP processes described here leads to consideration of the unintended consequences toward DP levels of some common P management practices. These practices, while reducing PP to surface waters, may result in long term increases in DP. The inferences into catchment influenced DP cycling identified here provide insights that can be use to improve watershed P assessment and management strategy development.

Bourn, D.F.
pot
wa

Carpenter
Sn
N

Coulter, C
ur
R

Dodds, V
r
c

Fitzpatri
t
v

Glandor

Hart, B

Hickey,
r
-

Inamdar
i
c

Lehrter, .
in
or
E

Lewis, G.
K.
Br
4)

Literature Cited

Boutt, D.F., Hyndman, D.W., Pijanowski, B.C. and Long, D.T., 2001. Identifying potential land use-derived solute sources to stream baseflow using ground water models and GIS. Ground Water, 39(1): 24-34.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H., 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. Ecological Applications, 8(3): 559-568.

Coulter, C.B., Kolka, R.K. and Thompson, J.A., 2004. Water quality in agricultural, urban, and mixed land use watersheds. Journal of the American Water Resources Association, 40(6): 1593-1601.

Dodds, W.K., Smith, V.H. and Lohman, K., 2002. Nitrogen and phosphorus relationships to benthic algal biomass in temperate streams. Canadian Journal of Fisheries and Aquatic Sciences, 59(5): 865-874.

Fitzpatrick, M.L., Long, D.T. and Pijanowski, B.C., 2007. Exploring the effects of urban and agricultural land use on surface water chemistry, across a regional watershed, using multivariate statistics. Applied Geochemistry, 22(8): 1825-1840.

Glandon, R.P., Payne, F.C., McNabb, C.D. and Batterson, T.R., 1980. A comparison of rain-related phosphorus and nitrogen loading from urban, wetland, and agricultural sources. Water Research, 15: 881-887.

Hatt, B.E., Fletcher, T.D., Walsh, C.J. and Taylor, S.L., 2004. The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environmental Management, 34(1): 112-124.

Hickey, M.B.C. and Doran, B., 2004. A review of the efficiency of buffer strips for the maintenance and enhancement of riparian ecosystems. Water Quality Research Journal of Canada, 39(3): 311-317.

Inamdar, S.P., Mostaghimi, S., McClellan, P.W. and Brannan, K.M., 2001. BMP impacts on sediment and nutrient yields from an agricultural watershed in the coastal plain region. Transactions of the Asae, 44(5): 1191-1200.

Lehrter, J.C., 2006. Effects of land use and land cover, stream discharge, and interannual climate on the magnitude and timing of nitrogen, phosphorus, and organic carbon concentrations in three coastal plain watersheds. Water Environment Research, 78(12): 2356-2368.

Lewis, G.P., Mitchell, J.D., Andersen, C.B., Haney, D.C., Liao, M.K. and Sargent, K.A., 2007. Urban influences on stream chemistry and biology in the Big Brushy Creek watershed, South Carolina. Water Air and Soil Pollution, 182(1-4): 303-323.

McDowe
e
i

Novak.
I

Novak.

Ontke

Pacifi

Penn.

SAS.

SAS.

Schip

Sharpl

Sharpl

Sonoda.
(
(

McDowell, R.W., Sharpley, A.N. and Folmar, G., 2003. Modification of phosphorus export from an eastern USA catchment by fluvial sediment and phosphorus inputs. Agriculture Ecosystems & Environment, 99(1-3): 187-199.

Novak, J.M., Stone, K.C., Szogi, A.A., Watts, D.W. and Johnson, M.H., 2004. Dissolved phosphorus retention and release from a coastal plain in-stream wetland. Journal of Environmental Quality, 33(1): 394-401.

Novak, J.M., Stone, K.C., Watts, D.W. and Johnson, M.H., 2003. Dissolved phosphorus transport during storm and base flow conditions from an agriculturally intensive southeastern coastal plain watershed. Transactions of the Asae, 46(5): 1355-1363.

Ontkean, G.R., Chanasyk, D.S. and Bennett, D.R., 2005. Snowmelt and growing season phosphorus flux in an agricultural watershed in south-central Alberta, Canada. Water Quality Research Journal of Canada, 40(4): 402-417.

Pacific Meridian Resources, 2001. Integrated forest monitoring assessment and prescription IFMAP, Review of remote sensing technologies for the IFMAP project, 2nd Revision. Report for the Michigan DNR. On the web at http://www.mcgi.state.mi.us/mgdl/?rel=thext&action=thmname&cid=5&cat=Land+Cover+2001.

Penn, C.J., Mullins, G.L. and Zelazny, L.W., 2005. Mineralogy in relation to phosphorus sorption and dissolved phosphorus losses in runoff. Soil Science Society of America Journal, 69(5): 1532-1540.

SAS, 1999. SAS/STAT User's Guide: The Mixed Procedure. SAS Institute, Cary, NC.

SAS, 2007. SAS 9.3.1 for Microsoft Windows. SAS Institute Inc., Cary, NC.

Schippers, P., van de Weerd, H., de Klein, J., de Jong, B. and Scheffer, M., 2006. Impacts of agricultural phosphorus use in catchments on shallow lake water quality: About buffers, time delays and equilibria. Science of the Total Environment, 369(1-3): 280-294.

Sharpley, A., 1999. Agricultural phosphorus, water quality, and poultry production: are they compatible? Poult Sci, 78(5): 660-673.

Sharpley, A., Foy, B. and Withers, P., 2000. Practical and innovative measures for the control of agricultural phosphorus losses to water: An overview. Journal of Environmental Quality, 29(1): 1-9.

Sonoda, K. and Yeakley, J.A., 2007. Relative effects of land use and near-stream chemistry on phosphorus in an urban stream. Journal of Environmental Quality, 36(1): 144-154.

Tsegaye,
M
wa
Sc

Turner, F
d

USDA.
A

USDA.

Uusi-K

Waylar

Willia

Winte

Zamp

Tsegaye, T., Sheppard, D., Islam, K.R., Johnson, A., Tadesse, W., Atalay, A. and Marzen, L., 2006. Development of chemical index as a measure of in-stream water quality in response to land-use and land cover changes. Water Air and Soil Pollution, 174(1-4): 161-179.

Turner, R.E., Rabalais, N.N., Justic, D. and Dortch, Q., 2003. Global patterns of dissolved N, P and Si in large rivers. Biogeochemistry, 64(3): 297-317.

USDA, 1990. Soil survey of Barry County, Michigan. United States Department of Agriculture, Soil Conservation Service.

USDA, 1997. Soil survey of Calhoun County, Michigan. United States Department of Agriculture, Soil Conservation Service.

Uusi-Kamppa, J., Braskerud, B., Jansson, H., Syversen, N. and Uusitalo, R., 2000. Buffer zones and constructed wetlands as filters for agricultural phosphorus. Journal of Environmental Quality, 29(1): 151-158.

Wayland, K.G., Long, D.T., Hyndman, D.W., Pijanowski, B.C., Woodhams, S.M. and Haack, S.K., 2003. Identifying relationships between baseflow geochemistry and land use with synoptic sampling and R-mode factor analysis. Journal of Environmental Quality, 32(1): 180-190.

Williams, M., Hopkinson, C., Rastetter, E., Vallino, J. and Claessens, L., 2005. Relationships of land use and stream solute concentrations in the Ipswich River basin, northeastern Massachusetts. Water Air and Soil Pollution, 161(1-4): 55-74.

Winter, J.G. and Duthie, H.C., 2000. Export coefficient modeling to assess phosphorus loading in an urban watershed. Journal of the American Water Resources Association, 36(5): 1053-1061.

Zampella, R.A., Procopio, N.A., Lathrop, R.G. and Dow, C.L., 2007. Relationship of land-use/land-cover patterns and surface-water quality in the Mullica River basin. Journal of the American Water Resources Association, 43(3): 594-604.

INFERR
FROM S

P

biologic

Biologi

many al

and cla

pathwa

watersl

quanti

chemi

pattern

aquati

theimp

impour

watersh

impaire

impoun

CHAPTER 4

INFERRING DISSOLVED PHOSPHORUS CYCLING ON A RIVER SYSTEM FROM SERIAL IMPOUNDMENTS USING STREAM BIOGEOCHEMISTRY

Abstract

Patterns in suites of chemicals can be used to provide insight into the biological cycling (sources, pathways, fate) of P resulting from serial impoundments. Biological activity in streams, lakes and impoundments has been shown to regulate many abiotic variables (P concentrations, suspended solids, water quality variables and clarity). The role of serial impoundments in the biological cycling (sources, pathways, fate) of P in stream systems has been difficult to discern from other watershed influences (temporal trends and catchment influence).

To address this issue, in a two-year study of the KRLAW, a MLM is used to quantify the temporal trend, improving the relationships between DP, stream chemistry and land use. The MLM results are used to remove the temporal trend, and patterns are explored using common multivariate statistical techniques.

Results show that for stream systems containing serial impoundments the aquatic system connectivity with the landscape is disrupted by processes within theimpoundment systems that control P and delay eutrophic recovery. Additionally, impoundment processes are linked for upstream/downstream impoundments.

The inferences into biological impoundment DP cycling have implications for watershed P assessment and management. The inlet P status to Lake Allegan, the impaired waterbody, is largely determined by the downstream effect of Morrow Lake impoundment processes.

Th
ubiquitou
2003). E
of recov
persister

2006. N
Grover
al., 20
Schrei
with e
quality
of alg
Michi
chloro
Håkan

ecosys
both lai
1990; V
basins,
apparen

Introduction

The USEPA (1996) identified accelerated eutrophication as the most ubiquitous water quality problem in the United States (McDowell and Sharpley, 2003). Eutrophication can be reversed by decreasing input rates of P and N, but rates of recovery are highly variable among waterbodies and often the eutrophic state is persistent and recovery is slow (Carpenter et al., 1998).

The biological activity in streams (Figueroa-Nieves et al., 2006; Morgan et al., 2006; Mulholland, 2004; Stevenson et al., 2006), lakes (French and Petticrew, 2007; Grover and Chrzanowski, 2004; Håkanson, 2005; Reed-Andersen et al., 2000; Yuan et al., 2007) and reservoirs (Havel and Pattinson, 2004; Reed-Andersen et al., 2000; Schreiber and Rausch, 1979) has been shown to regulate many variables associated with eutrophication. These include concentrations of P, suspended solids, many water quality variables and water clarity. Stevenson et al. (2006) state that many measures of algal biomass and nutrient availability were positively correlated in a study of Michigan and Kentucky streams. Researchers have identified relationships between chlorophyll *a*, total P (TP) and DP in lake systems (French and Petticrew, 2007; Håkanson, 2005; Momen et al., 1996).

Reservoirs or impoundments represent a transition zone from lotic to lentic ecosystems, and given that they encompass intermediate characteristics that define both lakes and rivers, they have been described as 'river-lake hybrids' (Kimmel et al., 1990; Wall et al., 2005). Kelly (2001), in a study of the Rio Grande and Colorado basins, found that the connectivity of the aquatic system with the landscape is apparently disrupted by processes within reservoir systems and that these processes result in la

the absenc

upstream

concept

also bee

systems

trends a

influen

proces

catchm

and ra

and si

use re

relati

impou

correla

chloro

betwee

regulat

downst

result in large changes in characteristics for solute transport that persist downstream in the absence of significant inputs. Additionally, reservoir processes may be linked for upstream/downstream reservoirs that are located relatively close in a series. This concept of process disruption by reservoirs –termed serial discontinuity (SDC)– has also been explored by Ward and Stanford (2001; 1995).

The role of serial impoundments in the biological cycling of P in stream systems has been difficult to discern from other watershed influences such as temporal trends and catchment influence. The hypothesis is that patterns in biological influenced DP, land use and stream chemistry correlate to impoundment SDC processes. To test this hypothesis, biological influenced data are separated from catchment influenced data and the MLM, used to quantify the fixed temporal trend and random site effects (see Chapter 2). By removing these effects, temporal trend and site adjusted DP (DP_{TSA}) increase and strengthen the stream chemistry and land use relationships. DP_{TSA}, stream chemistry, trace element and land use patterns and relationships are analyzed using MLM, PFA and GLM to provide inferences about impoundment DP cycling and stream system response to impoundment SDC.

Patterns and relationships in DP_{TSA}, PP and chlorophyll *a* are shown to correlate to biological influenced impoundment DP cycling. Changes in P forms and chlorophyll *a* are identified for two impoundments and for the stream segment flowing between them. This study provides evidence for biological influence and the regulation of P from the impoundment SDC of the first impoundment on the downstream river and impoundment. Impoundment P sourcing and sinking processes are identified as contributors to DP cycling. Historical P data is explored to evaluate impoundment regulation of P outlet concentrations.

The approaches developed in this study advance the knowledge of the stream DP response to the biological influence of impoundment SDC. These insights have implications for P management strategies and expectations. Results indicate that current P reduction strategies of TP and PP management should be refocused on DP for serial impoundment systems. DP reductions at impoundment inlets should accelerate the rate of decline in outlet P concentrations. The expectations for watershed recovery should be based on this rate of decline in outlet concentrations as opposed to reductions in catchment TP inputs.

Methods

Impoundment biological influenced DP cycling was investigated using the KRLAW stream chemistry dataset (Appendix I), KRLAW trace element dataset (Appendix II), land use descriptions (Table 1.1.), historical mean growing season data (Appendix III) and historical mean monthly discharge data (Appendix IV). The study site, sampling locations, sampling methods and chemical analyses are described in Chapter 1. The biological influenced MLM fixed stream chemistry, land use and temporal trend effects (Tables 2.3) and random effects (Table 2.4) detailed in Chapter 2 were used for this study. The sites and dates that constitute the biological influence datasets are shown in Figure 2.5.

Temporal trend and site adjusted DP

The temporal trend and site effects were removed from the biological influenced DP to improve the number and strength of the DP, stream chemistry and land use relationships. DP_{TSA} is determined by rearranging equation 2.5 as follows:

$$\log(DP)_{TSA} = \log(DP) - TT - SE = int + SC + LU \qquad (4.1)$$

Equation 4.1 and the estimates from Table 2.3 were used to calculate $\log(DP)_{TSA}$. DP_{TSA} was calculated by back transforming $\log(DP)_{TSA}$.

Load estimation

Constituent loads were estimated by multiplying the period mean daily discharge by the period mean weekly constituent concentrations by the period of interest. Mean daily discharge for the outlet of Morrow Lake was calculated from USGS gaging station data for the Kalamazoo River at Comstock, Michigan, station number 04106000. Morrow Lake inlet mean daily discharge was calculated by adjusting the outlet mean daily discharge by the ratio of the catchment area at the inlet, divided by the catchment area at the outlet (0.96). Lake Allegan inlet and outlet daily mean discharge was calculated from USGS gaging station data for the Kalamazoo River near New Richmond, Michigan, station number 04108670. Lake Allegan outlet mean daily discharge was calculated by adjusting the New Richmond gaging station daily mean discharge by the ratio of the catchment area at the outlet, divided by the catchment area at New Richmond (0.81). Lake Allegan inlet mean daily discharge was calculated by adjusting the New Richmond gaging station daily mean discharge by the ratio of the catchment area at the inlet, divided by the catchment area at New Richmond (0.78).

Statistical analysis

MLM, GLM and PFA are the statistical methods used to identify patterns among the $DP_{TSA,}$ suites of chemicals and land use to infer impoundment influenced DP cycling. MLMs are described in Chapter 2 and Appendix V. GLM uses the least squares method to fit a general linear model relating continuous dependent variables to independent variables (SAS, 1999). PFA detects structure in variables identifying a common factor that explains the variability between variables. The common factor is an unobservable, hypothetical variable that contributes to the variance of at least two observed variables (SAS, 1999). Rotations are used with PFA analyses to achieve a simple structure having a few high loadings and many zero or near-zero loadings (Reyment and Joreskog, 1993). The statistical methods for this study were implemented using SAS 9.1.3 (SAS, 2007), including PROC MIXED, PROC GLM and PROC FACTOR procedures.

Results

The MLM temporal trend and random site effects (Tables 2.3 and 2.4) were removed from the DP using equation 4.1, providing a dependent variable –DP_{TSA}– related to stream chemistry and land use that can be analyzed using common univariate and multivariate statistical techniques. The significant ($p<0.05$) fixed effects for stream chemistry (PP, NO_3^-, SO_4^{2-}, Cl^- and pH; Table 2.3) and land use (urban; Table 2.3) from the catchment influenced MLM were evaluated with respect DP_{TSA}. The mean and standard deviation by site for DP, DP_{TSA}, and significant stream chemistry, and the percent by site for each significant land use are given in Table 4.1.

Table 4.1: The mean and standard deviation (mean ± standard deviation) by site for dissolved phosphorus (DP), temporal trend and site adjusted dissolved phosphorus (DP_{TSA}) and the significant ($p<0.05$) stream chemistry fixed effects (PP, NO_3^-, SO_4^{2-}, Cl^- and pH) and land use percentages for the significant ($p<0.05$) land use fixed effect (urban) from the biological influenced MLM.

SITE	DP (μgL^{-1})	DP_{TSA} (μgL^{-1})	PP (μgL^{-1})	Cl^- (mgL^{-1})
KS	14.15 ± 2.23	14.39 ± 2.26	72.87 ± 20.64	53.33 ± 4.81
KC	15.37 ± 3.17	17.33 ± 4.57	67.38 ± 17.85	54.45 ± 6.82
KK	35.60 ± 12.49	35.02 ± 12.29	80.78 ± 20.44	84.42 ± 11.82
KP	46.74 ± 19.90	49.45 ± 17.47	51.00 ± 25.69	87.34 ± 19.61
KA	33.94 ± 16.47	30.65 ± 11.98	47.81 ± 27.07	74.16 ± 8.64
KD	14.81 ± 2.38	23.52 ± 4.64	52.80 ± 10.82	71.60 ± 9.28

SITE	SO_4^{2-} (mgL^{-1})	NO_3^- (mgL^{-1})	pH (pH)	Urban %
KS	45.30 ± 2.27	0.40 ± 0.18	8.08 ± 0.17	6.7
KC	45.43 ± 2.84	0.32 ± 0.19	8.06 ± 0.16	6.8
KK	49.89 ± 3.02	1.00 ± 0.24	7.90 ± 0.16	9.1
KP	48.49 ± 6.46	1.36 ± 0.40	7.72 ± 0.19	9.0
KA	49.12 ± 2.89	1.12 ± 0.31	8.06 ± 0.15	8.5
KD	48.33 ± 2.62	0.45 ± 0.20	7.98 ± 0.20	8.5

A block diagram of the system with KM, the site upstream, and biological influenced sites (KS, KC, KK, KP, KA and KD), is shown in Figure 4.1. The mean growing season (April through September) and mean biological influenced (data from dates under biological influence) TP, DP and PP concentrations for 2005 and 2006 are plotted in Figure 4.1.

General trends in mean TP concentrations through this region for both 2005 and 2006 are typified by an increase from in TP the inlet to the outlet of Morrow Lake; an increase in TP from the Kalamazoo Water Reclamation Plant (KWRP); a decrease in TP at sites (KP in 2005, KK in 2006) following the KWRP to the inlet of Lake Allegan; and a decrease in TP from the inlet to the outlet of Lake Allegan. For both

200

the

grov

infl

grov

con

Fig
20
ma
PP
per

Ka

2005 and 2006, trends in DP and PP are the same from the Morrow Lake inlet to after the KWRP, but these fractions differ for the remainder of the system. The mean growing season TP concentrations follow the mean TP concentrations of the biological influenced dates. Although under biological influence for a only portion of the growing season, this biological influence provides the greatest control on mean TP concentrations.

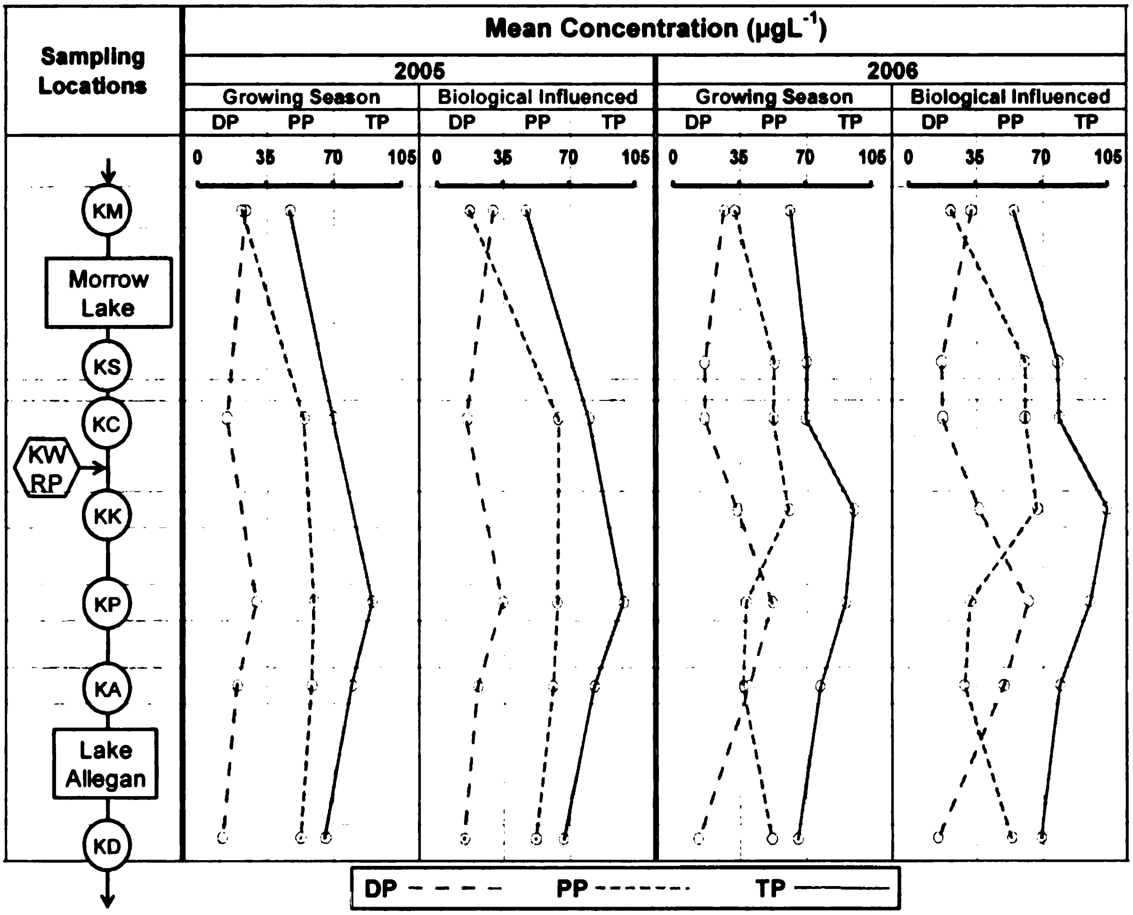


Figure 4.1: Diagram of the biological influenced region of the KRLAW depicting 2005 and 2006 sampling sites○, 2006 sampling sites ○, impoundments ▭, the major point source ⬡ (Kalamazoo Water Reclamation Plant) and mean TP, DP and PP concentrations for the 2005 and 2006 growing seasons and biological influenced periods.

A closer inspection of growing season mean TP, DP and PP for the six Kalamazoo River main stem locations (Figure 4.2) shows similar concentrations at the outlets of the impoundments (KC and KD) in 2005 and 2006. Prior to the Morrow Lake outlet (KE and KM), differences exist between 2005 and 2006 in all three P forms that are associated with variable catchment influences (sources and flow paths). Impoundment processes within Morrow Lake compensate for these differences, producing similar concentrations for all three P forms at the outlet. Therefore, Morrow Lake processes disrupt the connection of the downstream system from the upstream catchment influence. Similar mean TP concentrations after the outlet of Morrow Lake show the persistence of the impoundment biological influence downstream and the linkage with the downstream impoundment (Lake Allegan). While the mean TP concentrations are comparable year to year downstream of Morrow Lake, the DP and PP forms vary for the sites (KP and KA) between the impoundment outlets. This indicates impoundment processes control TP, PP and DP, but additional processes downstream change the DP and PP fractions without changing the TP relationship year to year.

For the impoundment processes to produce similar outlet P forms, Morrow Lake sourced an additional 8000 kg P (2005) and 3900 kg P (2006) and Lake Allegan sinked 6100 kg P (2005) and 5900 kg P (2006) between the inlet and outlet (Table 4.2). Similar mean outlet P concentrations are attained with yearly variable mean inlet P concentrations and under differing yearly climatic conditions evident in the discharge hydrographs (Figure 4.3). The consistent increase in TP concentration from KC to KP is the result of the similar loading in 2005 and 2006 by the point source input of the KWRP (Table 4.2).

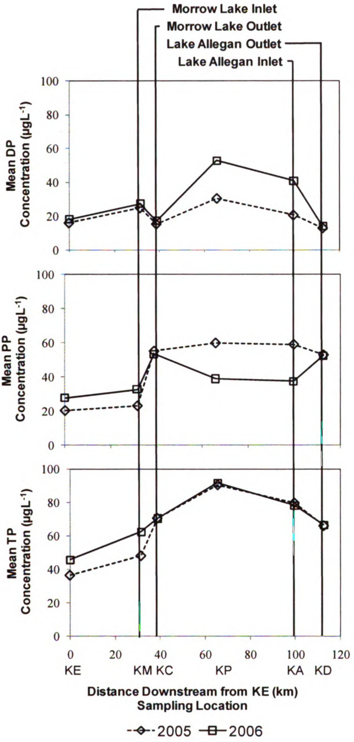


Figure 4.2: Comparison of 2005 and 2006 growing season mean TP, PP and DP for six Kalamazoo River main stem sites sampled both years versus distance downstream from the site KE, with Morrow Lake and Lake Allegan inlets and outlets identified by vertical lines.

Table 4.2: Morrow Lake and Lake Allegan 2005 and 2006 growing season mean TP, discharge and estimated TP load and Kalamazoo Water Reclamation Plant TP load.

	2005			2006		
	Mean TP (μgL^{-1})	Mean Discharge (m^3s^{-1})	TP Load (kg)	Mean TP (μgL^{-1})	Mean Discharge (m^3s^{-1})	TP Load (kg)
Morrow Lake Inlet	48.3	19.4	14,794	62.4	22.9	22,611
Morrow Lake Outlet	71.6	20.1	22,758	70.4	23.8	26,485
Difference (Outlet-Inlet)			7,964			3,875
Lake Allegan Inlet	79.5	33.1	41,666	78.1	38.3	47,283
Lake Allegan Outlet	65.9	34.1	35,527	66.4	39.4	41,407
Difference (Outlet-Inlet)			-6,139			-5,876
Kalamazoo Water Reclamation Plant*			8,209			8,341

*Source: (Kieser & Associates, 2008)

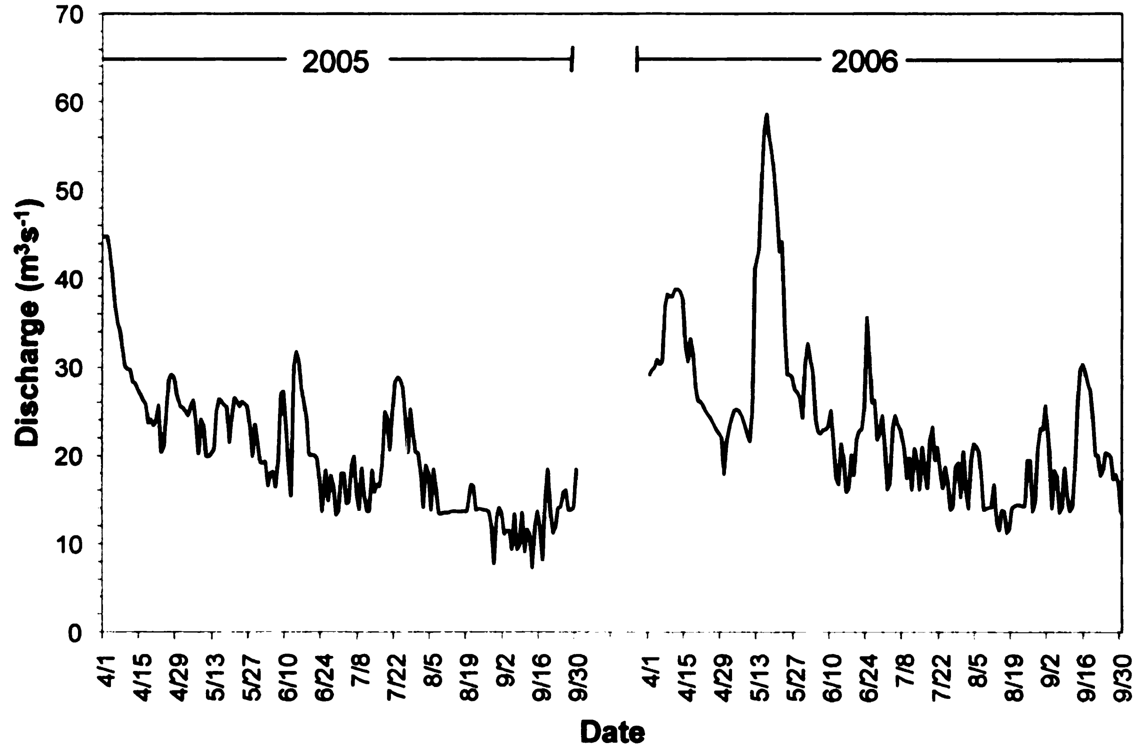


Figure 4.3: Discharge hydrographs for the 2005 and 2006 growing seasons at the outlet of Morrow Lake (site KC).

Prior to discussing the P cycling of these individual systems, the overall system will be considered. Patterns and relationships among DP_{TSA} and stream chemistry, land use and trace elements are investigated using the MLM results (Table 2.3) and PFA to provide insight into DP cycling due to impoundment biological influences.

Stream chemistry and land use relationships

A varimax-rotated PFA was performed on the biological influenced stream chemistry, land use and DP_{TSA} data (Table 4.1). The results are given in Table 4.3 and explain 90.4% of the variance in the data with three factors. Factor 1 is interpreted as the urban influence indicated by a strong DP_{TSA} loading directly with moderate urban land use, NO_3^- and Cl^- and inversely with moderate pH. Factor 2, unrelated to $DP_{TSA,}$ is another urban factor with the stream chemistry reflecting strong and moderate loadings of urban land use to DP_{TSA}, NO_3^-, SO_4^{2-} and Cl^-. Inspection of the mean NO_3^-, SO_4^{2-}, Cl^- and pH (Table 4.1) reveals the greatest change in these parameters occur after the KWRP (site KK). Urban relationships of Factors 1 and 2 reflect the point source input of the KWRP as a source for DP, NO_3^-, SO_4^{2-} and Cl^- and as a modifier of pH. Factor 3 is interpreted as the biological influence with moderate inverse loading between DP_{TSA} and PP and moderate direct loading between DP_{TSA} and NO_3^-.

Factor 3 relationships are consistent with changes in DP, PP and NO_3^- with an increase associated with algal productivity and macro-invertebrate grazing. NO_3^- is confounded with Factor 1, and changes could be from the KWRP, biological influence or a combination of both. PP is unique in loading with DP_{TSA} in Factor 3, indicating PP is the best parameter to use when inferring DP cycling associated with biological influence. Patterns in the biological trace element PFA were investigated for relationships between DP_{TSA}, urban land use and trace elements.

Table 4.3: Varimax-rotated factor loading matrix from principal factor analysis for the biological influenced stream chemistry dataset and urban land use from the Kalamazoo River/Lake Allegan Watershed.

	Factor 1	Factor 2	Factor 3
DP_{TSA}	**0.7708**		*0.5339*
PP			*-0.5253*
NO_3^-	*0.4877*	*0.4190*	*0.5490*
SO_4^{2-}		**0.8472**	
Cl^-	*0.4763*	**0.8011**	
pH	*-0.6664*		
Urban	*0.5691*	*0.4801*	
Percent of total variance explained			
	0.3613	0.3461	0.1963
Total percentage of variance explained: 90.4%			

Strong loadings (≥ 0.70) are indicated by bold type.

Moderate loadings (>0.40 and <0.70) are indicated by italics.

Trace element relationships

The varimax-rotated biological trace element PFA (Table 4.4) has four factors explaining 82.3% of the variance in the data. Factor 2 is the only DP factor with strong loadings on DP_{TSA}, urban land use, B, V, Mo and Cr. The inclusion of urban land use in this factor suggests that the DP_{TSA}, B, V, Mo and Cr relationship results from the KWRP and does not relate DP to biological influence. Factors 1, 3 and 4 are unrelated to DP_{TSA} with strong and moderate loadings between suites of trace elements. Due to the lack of relationships with DP_{TSA} in Factors 1, 3 and 4, as well as the interaction with urban land use in Factor 2, the trace element PFA does not provide additional information for inferring biological influenced DP cycling.

Phosphorus forms

The biological MLM and stream chemistry PFA provide an association between DP and PP. Changes in PP concentrations are the result of biological PP and DP exchanges and sediment PP settling and resuspension. The analysis for PP in the study does not discriminate between biological and sediment PP forms. When exploring DP exchanges, these forms will be described as DP, sediment PP and algae bound PP. Morrow Lake, Lake Allegan and the connecting stream segment will be evaluated to infer DP cycling from biological and impoundment influences.

Table 4.4: Varimax-rotated factor loading matrix from principal component analysis for the biological influenced DP_{TSA}, urban land use and trace element dataset from the Kalamazoo River/Lake Allegan Watershed.

	Factor 1	Factor 2	Factor 3	Factor 4
DP_{TSA}		**0.8389**		
Urban		**0.7506**		
B		**0.9633**		
V		**0.8713**		
Mo		**0.8033**		
Cr		**0.7197**		*0.4356*
Se				**0.7128**
Rb				**-0.7612**
Mn	**0.8694**			
Fe	**0.9030**			
As	**0.8844**			
Ba	**0.9383**			
U	**-0.9489**			
Sr	**-0.7811**		*0.4218*	
Al			*0.6922*	
Sc			**0.8872**	
Ti			**0.9205**	
Percent of total variance explained				
	0.3052	0.2543	0.1706	0.0927
Total percentage of variance explained: 82.3%				

Strong loadings (≥ 0.70) are indicated by bold type.

Moderate loadings (>0.40 and <0.70) are indicated by italics.

Morrow Lake – A phosphorus sourcing impoundment

The Morrow Lake impoundment is the first impoundment in the Kalamazoo River system with a residence time greater than seven days. Reservoirs with retention times greater than seven days provide an environment for primary productivity (Kimmel et al., 1990; Straskrabova et al., 1973). TP concentrations increase from the inlet (KM) to the outlet (KS and KC) of Morrow Lake during the biological influenced sampling dates (Figure 4.4). TP loads were increased by 8000 and 3900 kg per growing season from inlet to outlet in 2005 and 2006, respectively (Table 4.2). These TP load increases reflect growing season exports of 0.76 and 0.31 kg ha^{-1}, which are much greater than the growing season exports ranging from 0.03 to 0.17 ha^{-1} estimated during this study for other catchments in the KRLAW.

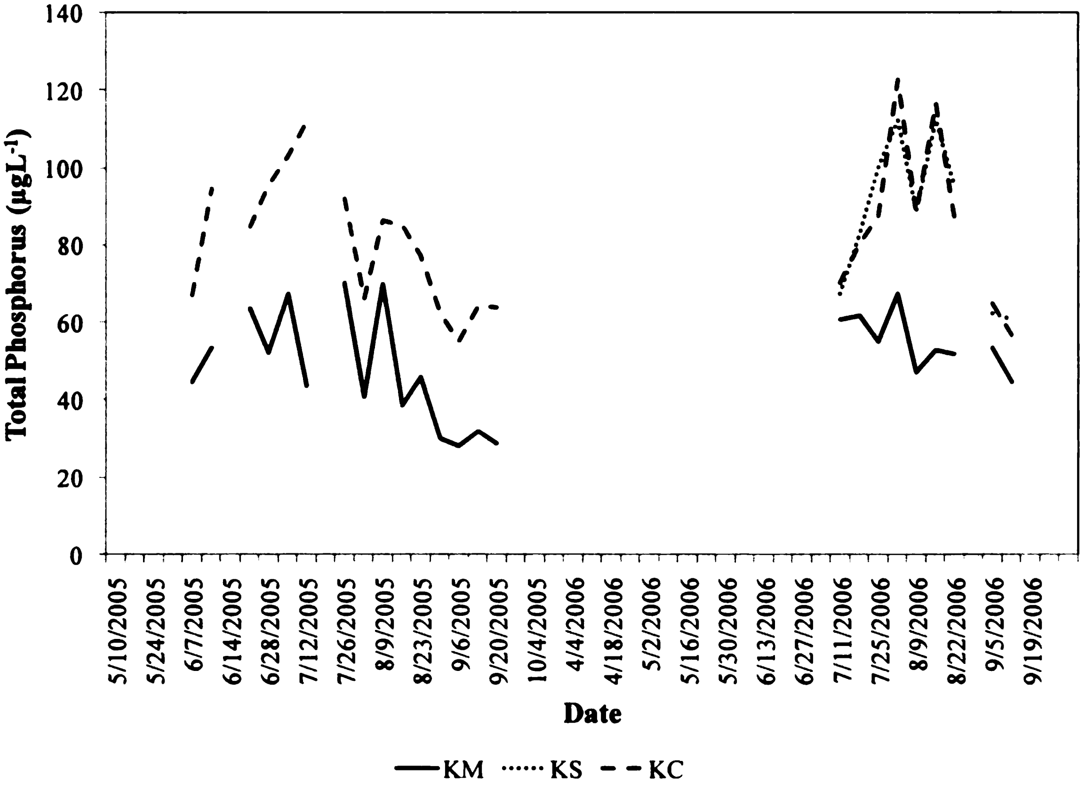


Figure 4.4: TP changes from Morrow Lake inlet (KM) to outlet (KS and KC) for the biological influenced sampling dates. Note: Site KS sampled in 2006 only.

The increase in TP concentrations and P loads are believed to be sourced from within Morrow Lake. Impoundment biological influences are proposed as part of the P release process. Before examining the Morrow Lake influence, the catchment surrounding and draining into Morrow Lake was considered as a potential source for these increases.

An industrial P input the size of the KWRP located in the Morrow Lake catchment would be required to supply the 2005 P load increase, yet there are no industries located in the Morrow Lake catchment, thus eliminating industry as the source. The DP concentration decreases while the PP concentration increases from the Morrow Lake inlet (KM) to the outlet (KC) (Figure 4.5). The discharge hydrograph in Figure 4.5 shows that the PP increase occurs during lower flows and therefore is not associated with runoff transporting catchment PP. Chlorophyll *a* was sampled in 2006 to determine if algal productivity contributed to TP loading, mean DP decreases and mean PP increases. Increases in chlorophyll *a* correspond to increases in PP, decreases in DP and decreases in dissolved NO_3^- from the inlet (KM) to the outlet (KC) of Morrow Lake (Figure 4.6). TP, chlorophyll *a*, NO_3^- and primary productivity have been shown to be highly correlated (Knoll et al., 2003). From these chemistry associations with primary productivity and the lack of industry present, it is assumed that the increases in TP and PP at the outlet of Morrow Lake are sourced from within the impoundment, not from catchment influences.

Mass balances of inlet to outlet P fractions and the accounting for exchanges between DP and algae bound PP are used to provide insight into DP cycling from biological and impoundment processes within Morrow Lake. Mass balances of the P fractions show that the increase in PP is 8000 kg greater than the decrease in DP for the 2005 growing season and 3900 kg greater for 2006. This additional P comes from within Morrow Lake –most likely from P stores in the bottom sediments– to support algal productivity. More DP was available from the inlet in 2006 compared to 2005 (mean DP concentrations of 27.4 μgL^{-1} and 23.0 μgL^{-1}, respectively), resulting in less P required from the Morrow Lake bottom sediments to support similar algal productivity.

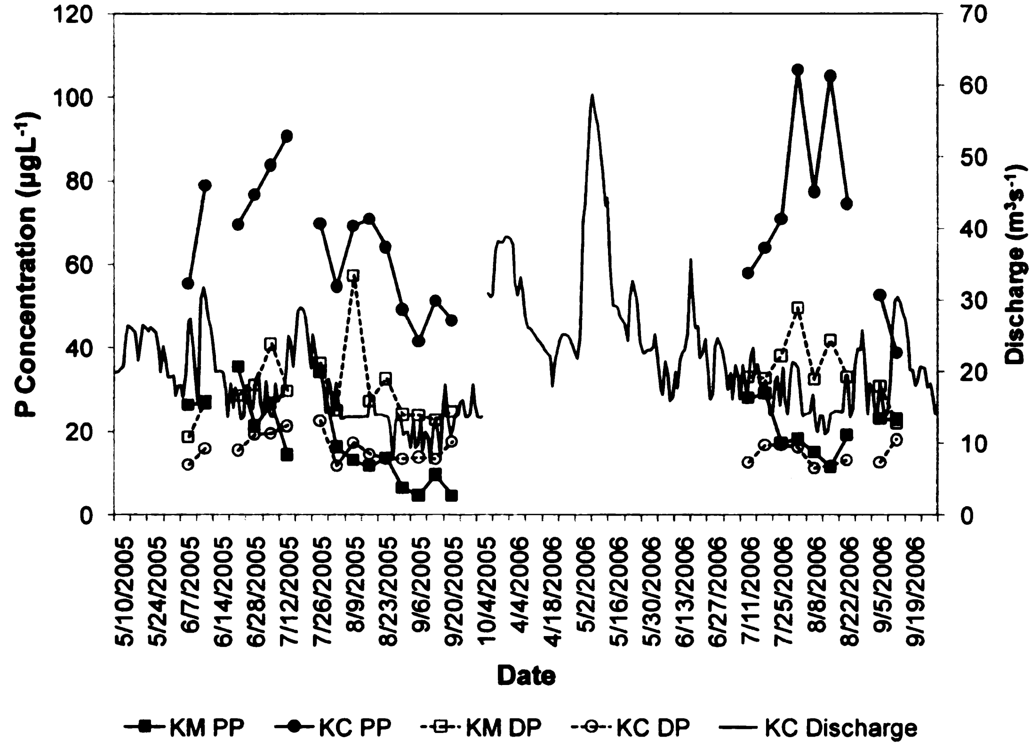


Figure 4.5: Inlet PP (KM PP), outlet PP (KC PP), inlet DP (KM DP) and outlet DP (KC DP) concentrations for the biological influenced dates and the outlet discharge (KC Discharge) for the 2005 and 2006 growing seasons.

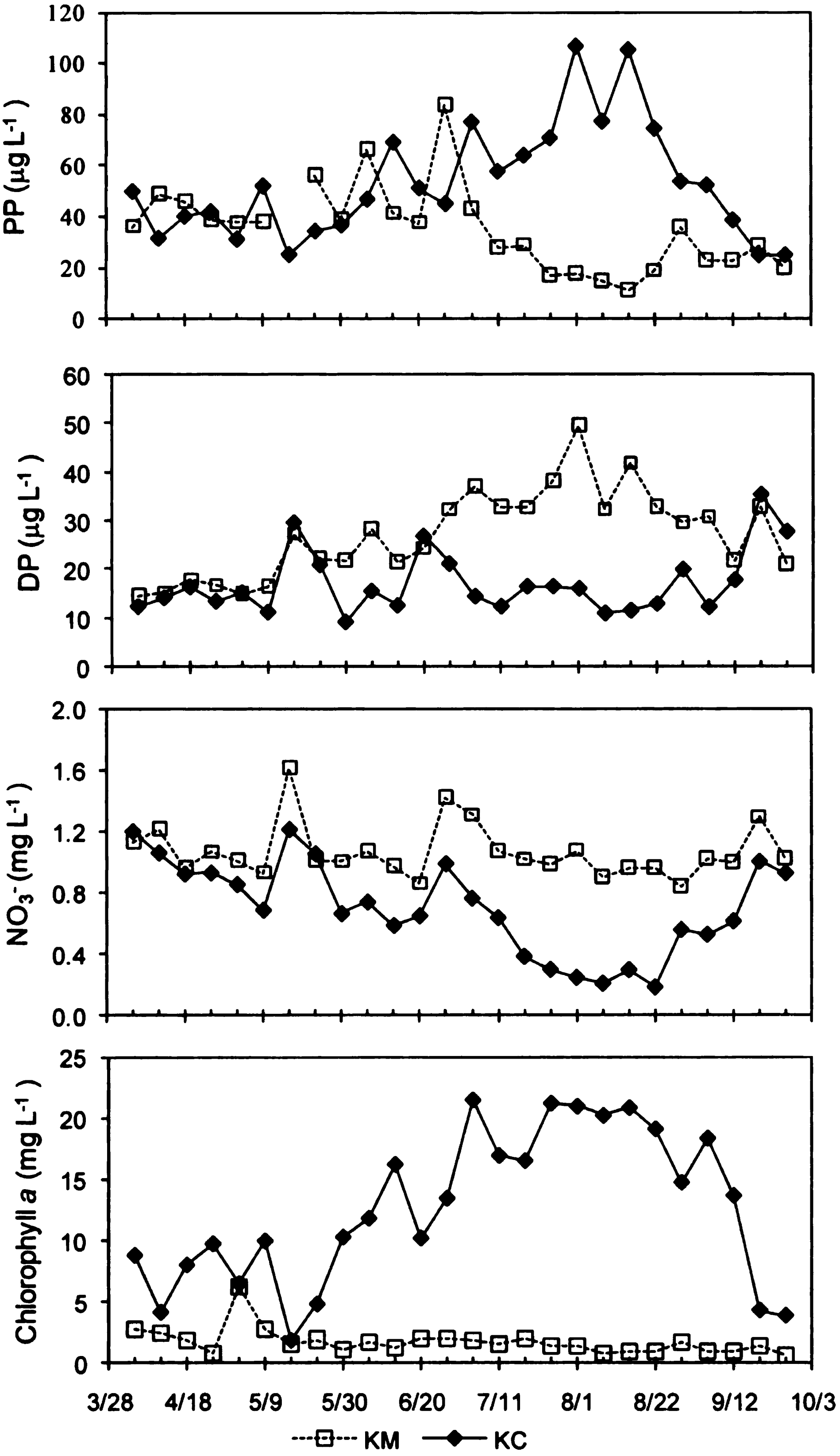


Figure 4.6: Morrow Lake inlet (KM) and outlet (KC) PP, DP, NO_3^- and chlorophyll *a* concentrations for the 2006 growing season.

imp

def

Mo

sea

cor

20

wi

19

Ju

un

La

fr

le

In

co

sc

co

se

M

The similarity in mean outlet TP concentrations between 2005 and 2006 implies a comparable annual algal productivity that controls outlet TP levels. The deficit between inlet P and the P required for algal productivity is supplied from Morrow Lake bottom sediments. Historical P data (Appendix III) of mean growing season outlet TP concentrations indicate impoundment biological processes have controlled mean growing season outlet TP since 1981 (Figure 4.7). From 1981 to 2006 the outlet TP concentrations and variability have reduced from pre-1981 levels with the exception of 2003 (Figure 4.7). Data were not available to assess 1973, 1995, 1996 or1997. Late season discharge in 2003 was at consecutively low levels from July through September. Increased water residence time and decreased algae flushing under these conditions probably led to higher than normal productivity within Morrow Lake and to higher TP concentrations. The 2003 growing season data was excluded from the analyses. Outlet TP levels and variability prior to 1981 suggest that inlet P levels were in excess of biological needs and that the impoundment was sinking P. Industrial control of P due to regulations in the 1970s may have reduced P concentrations at the inlet below biological requirements, leading to a switch to P sourcing to maintain productivity.

The trend line indicates a decrease in mean growing season outlet TP concentrations since 1981. This suggests that the release rate of P stored in the bottom sediments of the lake may be declining. The biological influenced DP cycling Morrow Lake processes decreases DP and converts DP and stored P to algae bound

PP. These processes control outlet mean TP, DP and PP concentrations, compensating for inlet differences across both years of the study.

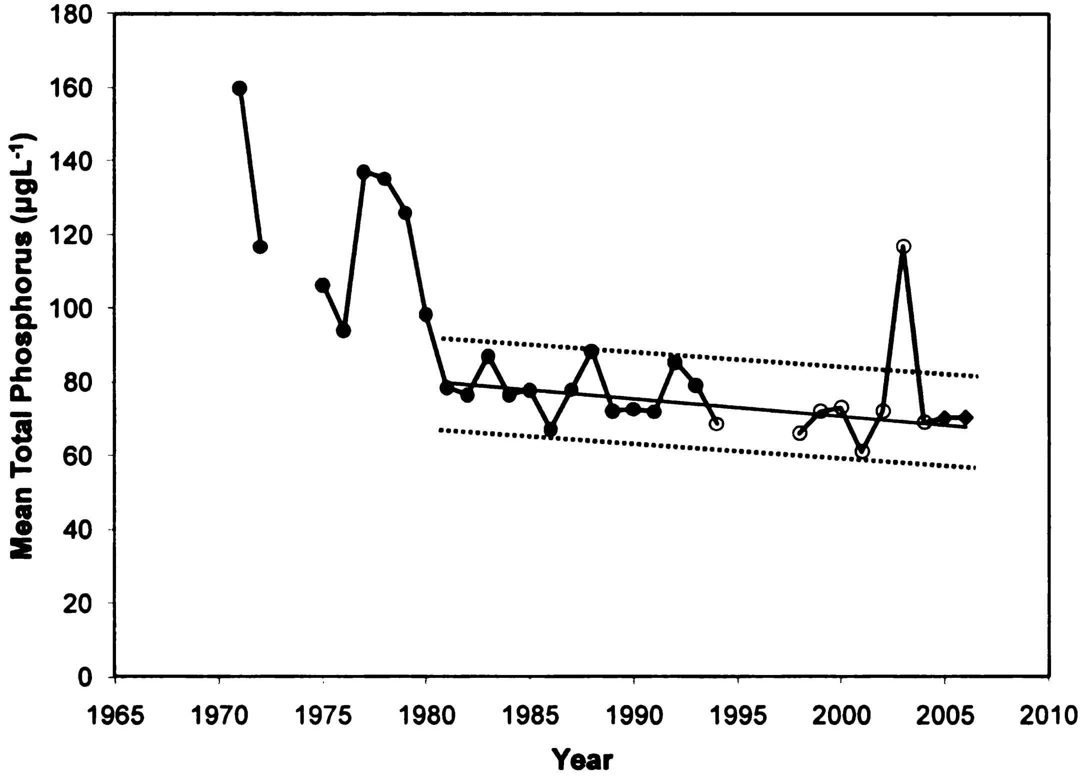


Figure 4.7: Historic Morrow Lake outlet mean growing season TP concentrations. Trend — and range ∷∷ from 1981to 2006 excluding 2003. Data Sources: ● USEPA STORET Database; ○ MDEQ; and ♦ KRLAW study.

Morrow Lake outlet to Lake Allegan inlet

The changes in mean TP, DP and PP for the 2005 and 2006 growing seasons are given in Figure 4.1 for the sampling sites from the Morrow Lake outlet to the Lake Allegan inlet (KC, KK, KP and KA). The KWRP is located between sampling sites KC and KP. Mean TP concentrations were similar at sites KC, KP and KA in 2005 and 2006. Growing season TP loadings reported for the KWRP were comparable at 8209 kg in 2005 and 8341 in 2006 (Kieser & Associates, 2008).

In 2006, sampling site KK, downstream of the KWRP, was added to better understand the impact of the KWRP. The 2006 mean TP data show that the KWRP load increases the Morrow Lake outlet mean TP concentration by 25.4 μgL^{-1} by site KK. Lower TP concentrations from catchment inputs, typically 36 to 60 μgL^{-1}, mix with higher stream concentrations, reducing concentrations at sites KP and KA. The 2006 growing season mean DP and PP increases at site KK are attributed to the KWRP point source input. After the KWRP, changes occur in the DP and PP fractions. Chlorophyll *a*, PP and DP relationships at sites KC and KA (Figure 4.8) indicate a conversion of PP to DP associated with algal consumption. The stream segment from KK to KP contains substrates to support macroinvertebrate populations (Cooper, 2005) that graze on algae and convert DP to PP.

Without chlorophyll *a* data and sampling site KK, only DP and PP data are available to assess the macroinvertebrate conversion of algae bound PP to DP in 2005 (Figure 4.8). The DP and PP patterns seen in 2006 are not present in 2005. The KWRP increase between sites KC and KP is evident. However, the conversion between DP and PP does not appear to occur until later in the season and in much lower levels. Cooper (2005) noted in the 2004 bioassessment that macroinvertebrate densities were low due to an unusually wet spring that created multiple high water events. Discharge conditions were similar in 2005, with multiple high water events that may have reduced macroinvertebrate communities, grazing populations and the conversion of algal PP to DP. Speculation is that in 2005 higher levels of PP –consisting partially of algae that were not consumed after exiting Morrow Lake– reached the Lake Allegan inlet.

Figure 4.8: PP, DP and chlorophyll *a* concentrations for the 2005 and 2006 biological influenced dates for locations from the outlet of Morrow Lake [illegible] Site KK sampled

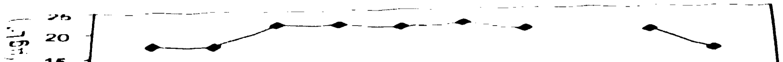
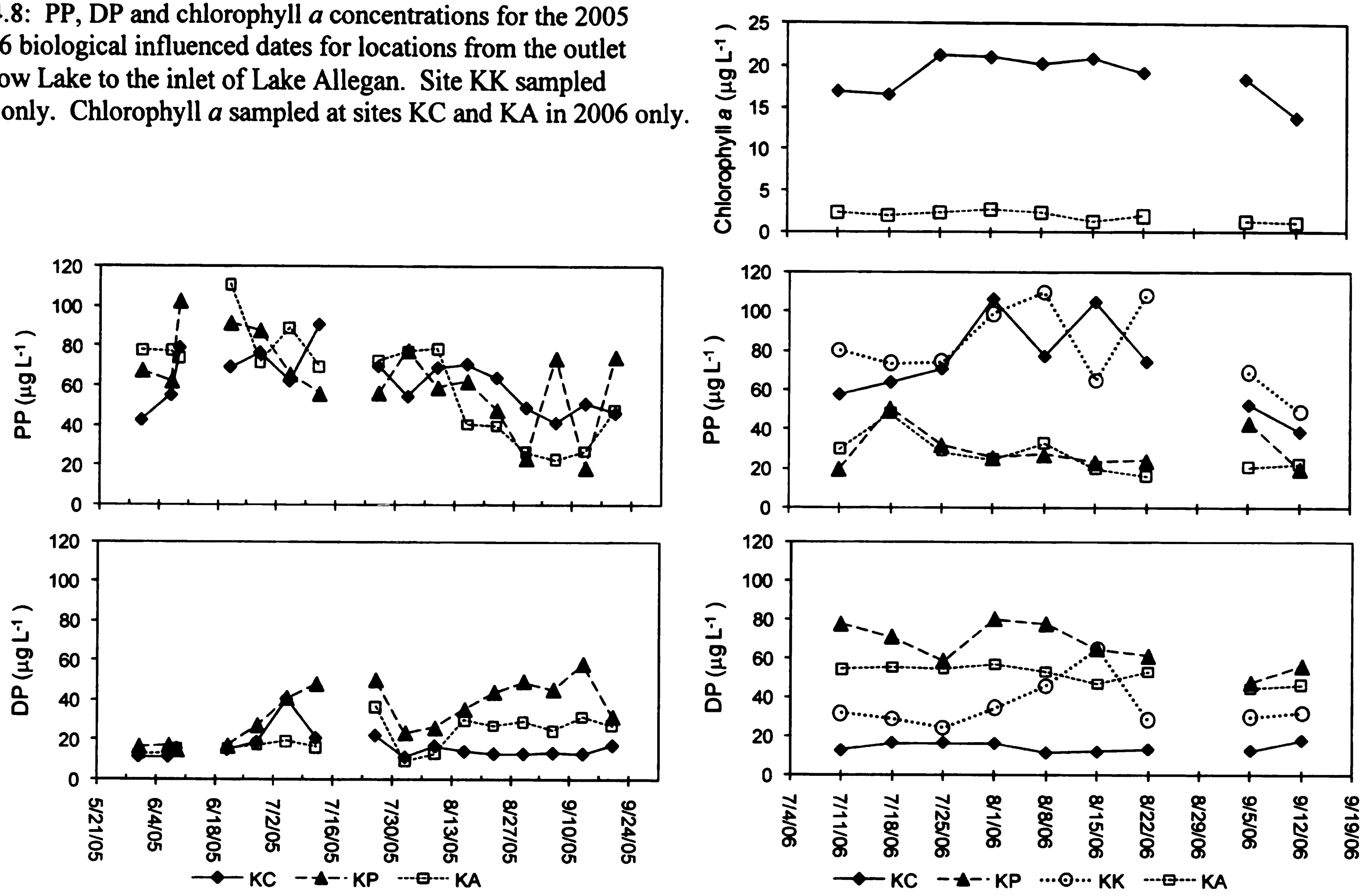


Figure 4.8: PP, DP and chlorophyll *a* concentrations for the 2005 and 2006 biological influenced dates for locations from the outlet of Morrow Lake to the inlet of Lake Allegan. Site KK sampled in 2006 only. Chlorophyll *a* sampled at sites KC and KA in 2006 only.



The DP cycling from the Morrow Lake outlet to the Lake Allegan inlet is variable between years. DP concentrations decreased after the KWRP in 2005 and increased in 2006. Variation in DP and PP forms appears to be caused by climatic effects on the integrity of the macroinvertebrate community. TP concentrations were comparable from 2005 to 2006 through this stream segment supporting the minimal effect of catchment inputs and the dominance of biological influences on P. Morrow Lake control of DP and PP mean concentrations is disrupted by variable downstream biological influences that determine the concentrations reaching Lake Allegan.

Lake Allegan – A phosphorus sinking impoundment

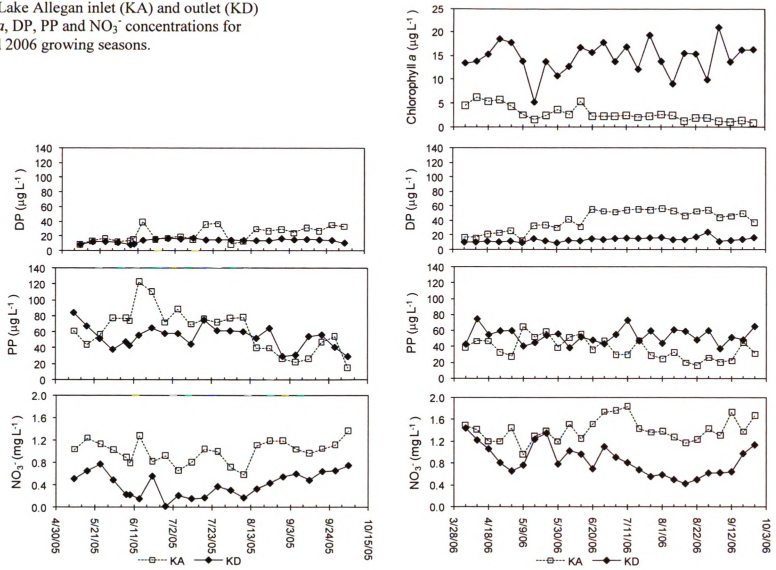
The Lake Allegan mean inlet TP concentrations were similar for the growing seasons in 2005 and in 2006 (Figure 4.1). The P cycling within Lake Allegan produced similar, but lower mean outlet TP concentrations (Figure 4.1). The TP load estimations show sinking of TP within Lake Allegan of 6100 kg in 2005 and 5900 kg in 2006 (Table 4.2).

The TP load retention and outlet mean TP, DP and PP concentrations were comparable in 2005 to 2006, with differences in mean inlet DP and PP concentrations (Figure 4.1). As with Morrow Lake, the year to year consistency of the P forms exiting Lake Allegan suggests that productivity limits the biological processes. In 2006, when chlorophyll *a* data are available, the biological influence in Lake Allegan is evident through the increase in chlorophyll *a* corresponding to a decrease in DP, an increase in PP and a decrease in NO_3^- from the inlet (KA) to the outlet (KD) (Figure 4.9). Compared to Morrow Lake, Lake Allegan PP changes are smaller for similar chlorophyll *a* changes. Since Lake Allegan is sinking P, the exchange of sediment PP for algae PP in the water column may account for this difference.

Without chlorophyll *a* data in 2005, the DP, PP and NO_3^- patterns are used to provide insight into DP cycling (Figure 4.9). The inlet PP concentrations are higher and the DP and NO_3^- concentrations lower in 2005 than 2006, which supports the previous speculation that algae survived transport to Lake Allegan as multiple high water events reduced macroinvertebrate communities in 2005. This algal load produced in Morrow Lake contributes to the total algae populations in Lake Allegan but reduces the algae produced within the impoundment. The reduction in NO_3^- within Lake Allegan should result in a larger than observed increase in PP and a decrease in DP, would suggest that a portion of the algae produced in Lake Allegan may die and remain there. As in 2006, the P fractions are rebalanced as a portion of the inlet PP as sediment P settles out and is replaced algal PP.

Comparing the 2005 and 2006, the Lake Allegan outlet mean DP and PP concentrations are similar indicating similar productivity. However, because of the differences between 2005 and 2006 in inlet mean DP and PP, this productivity was achieved by different pathways. Productivity is limited by the combination of incoming algae as PP and DP. In 2005, algae PP was high and DP low. The low DP was reduced from a mean concentration of 21 μgL^{-1} to 13 μgL^{-1} by additional algal uptake. In 2006, algae PP was low and DP high. The high DP was reduced from a mean concentration of 41 μgL^{-1} to 14 μgL^{-1} by algal uptake.

Figure 4.9: Lake Allegan inlet (KA) and outlet (KD) chlorophyll *a*, DP, PP and NO_3^- concentrations for the 2005 and 2006 growing seasons.



In both years, approximately 6000 kg of TP were retained in Lake Allegan. The settling of sediment PP was probably responsible for a large portion of this TP, but algae –produced in either Morrow Lake or Lake Allegan– dying, settling and burying in Lake Allegan may also contribute to this load.

Available historic mean TP data (Figure 4.10) show that Lake Allegan P dynamics have produced a relatively stable range of outlet concentrations with large fluctuations in inlet concentrations since 1998. 2005 and 2006 produced similar inlet TP concentrations, leading to the retention of similar TP loads. The large differences in inlet to outlet TP in previous years would require the amount of P retained within Lake Allegan to vary substantially year-to-year to produce this outlet TP stability.

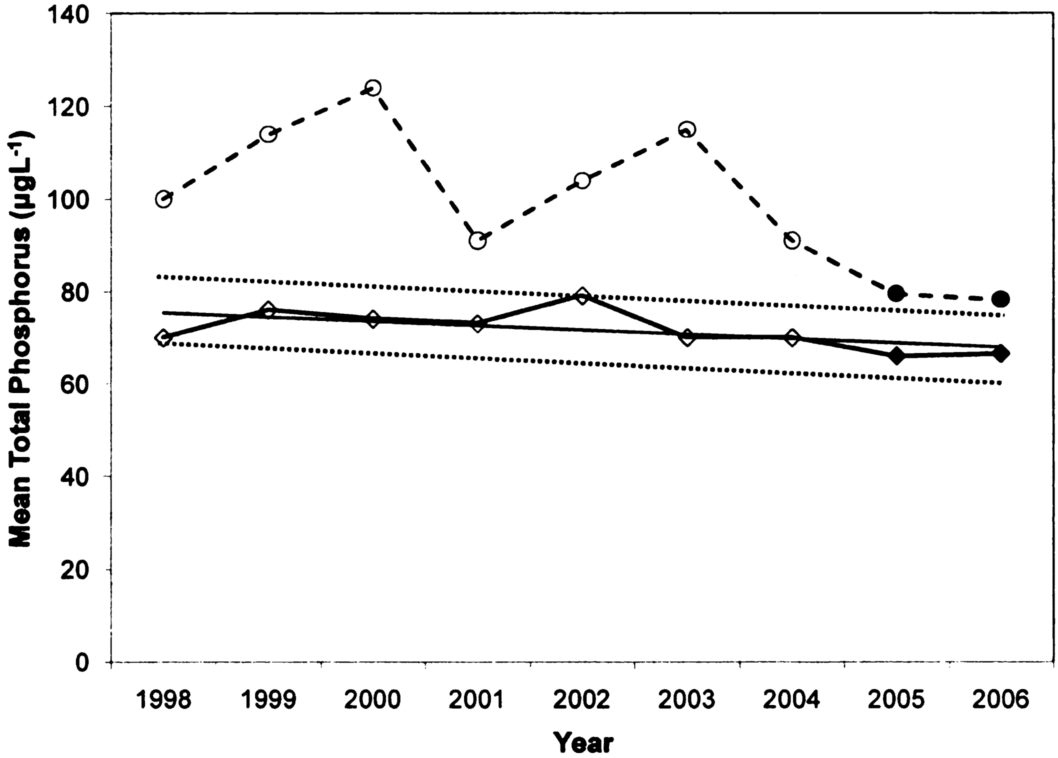


Figure 4.10: Historic Lake Allegan inlet (circles) and outlet (diamonds) mean growing season TP concentrations from 1998-2006. Outlet trend — and range ⁚⁚⁚⁚
Data Sources: ○ ◇ MDEQ and ● ◆ KRLAW study.

Since1998, a downward trend in outlet TP is observed. This decline corresponds to the downward trend previously discussed in the outlet TP concentrations exiting Morrow Lake, one major source of DP and algal PP depending on the condition of the downstream macroinvertebrate community.

The DP cycling from processes in Lake Allegan modifies DP and PP concentrations and controls TP outlet concentrations. Available DP is taken up by algae growth down to minimum levels of 9 to10 μgL^{-1}. The distribution of DP and PP is a function of Morrow Lake impoundment processes, upstream/downstream linkage of serial impoundments and macroinvertebrate grazing upstream of the Lake Allegan inlet. Lake Allegan is a P sink retaining approximately 6000 kg of TP for both years of the study. The P cycling produces similar outlet mean TP, DP and PP concentrations, regardless of inlet concentrations across both years of the study.

Impoundment phosphorus sourcing and sinking dynamics

This study has inferred biological influenced P dynamics occurring within large flow-through impoundments that produce major modifications to the P forms between the inlet and the outlet. Within the same watershed, one impoundment (Morrow Lake) is sourcing P and one (Lake Allegan) is sinking P. While evaluating inlet and outlet stream chemistry supports the existence of P sourcing and sinking, the exact nature of the processes that produce these results cannot be determined without extensive in-lake water and sediment sampling. Regardless, the impoundment processes have a controlling effect on the P status of the downstream system that has not been previously identified and was not anticipated at the beginning of the study. Knowledge of the release and accumulation of P is important to watershed P recovery.

The ability to compesate for variable incoming P conditions to produce a similar narrow range of outlet conditions year to year has significant implications for P management strategy.

Phosphorus management implications

The control exerted on P forms by flow-through impoundments such as Morrow Lake and Lake Allegan compensates for changes in P delivered by the upstream system. In a P stressed watershed like the KRLAW, P reduction efforts upstream of these impoundments will be compensated for by this natural process. It is encouraging that recent historical evidence shows a decline in mean yearly TP concentrations being produced by these processes. Intervention to modify these impoundment processes is limited to accelerating the rate of this decline. Reductions in DP at the inlet should accelerate the decline in mean yearly TP at the outlet of these impoundments. In the meantime, upstream P reductions will be will be compensated for with remaining stored P by impoundment processes. The overall watershed response to P reductions will be delayed by those processes.

Discussion

By removing the temporal trend and site effects from biological influenced DP data, patterns between DP_{TSA} and land use, stream chemistry and trace elements are used to provide insight into DP cycling associated with flow-through impoundment processes. MLM results and PFAs develop DP and PP relationships associated with biological processes. Other DP, stream chemistry and trace element relationships relate to urban land use, including industrial inputs. The urban influence prevents their use as indicators for biological influence.

Biological influences are identified through the changes in and exchanges between DP and PP for Morrow Lake, Lake Allegan and the stream segment flowing between them. Impoundment SDC processes and biological influences are shown to regulate P concentrations and forms on a watershed scale. Morrow Lake compensates for deficits in incoming DP by internally sourcing additional DP to support biological productivity. This process releases previously stored P from within the impoundment, reduces inlet P variability and regulates outlet mean P forms from growing season to growing season. Morrow Lake is a natural control on the P delivered from the upstream landscape and from industrial inputs (approximately 64% of the KRLAW catchment area). Exchanges between the pools of DP and PP are shown to be variable depending on climatic conditions and the integrity of the macroinvertebrate community. The total DP represented by these two forms –largely determined by Morrow Lake and the point source input of the KWRP– establish the inlet conditions for processes within Lake Allegan. Lake Allegan processes provide a regulating effect similar to Morrow Lake but as a P sink. The apparent productivity in the Lake Allegan system is similar from year to year. The actual productivity differs depending on the amount of algae that survives the transport from Morrow Lake and the amount produced internally. Data from 2005 and 2006 exhibit similar outlet P forms from growing season to growing season. The total productivity in Lake Allegan is controlled by Morrow Lake and the industrial inputs after Morrow Lake, while the actual productivity is controlled by the macroinvertebrate community exchanges between DP and PP.

Impoundments processes exert the greatest control and regulation within this system. Sourcing or sinking P, the impoundments produced comparable mean TP, DP and PP concentrations for both years of the study. The first impoundment (Morrow Lake) in the KRLAW study system is the primary control. The sinking of P in Lake Allegan accounts for excess P delivered to the inlet beyond the needs for biological productivity. Until inlet TP is reduced below productivity needs, Lake Allegan responds to Morrow Lake and industrial inputs by accumulating P. Reducing inlet DP and algae PP concentrations below the levels required for productivity will force Lake Allegan to switch to sourcing P to meet productivity requirements.

The biological influence and inferences about P sourcing, P sinking and DP cycling have implications for P management. Common P agricultural and urban management practices are aimed at preventing catchment PP from entering surface waters. However, biological influenced systems are governed by DP, not catchment supplied sediment PP. Moreover, the P compensation and regulation imposed by impoundment processes overrides the inlet conditions to produce similar outlet conditions from growing season to growing season. Managing impoundment DP cycling is limited to reducing inlet concentration to accelerate the depletion of P stored in lake-bottom sediments. Reducing the catchment inputs of DP to the inlet of a P sourcing impoundment will have minimal immediate impact, but should accelerate the of decline outlet P concentrations over time. Reducing DP inputs to P sinking impoundments will accelerate the decline in the rate of P accumulation. The ultimate goal of these reductions should be to transition the P sinking impoundment to P sourcing conditions. Once P is being removed from the system, recovery from anthropogenic P degradation and the long-term reversal of eutrophication will begin.

Results from this study support the hypothesis that patterns among biological influenced DP, stream chemistry and land use correlate to impoundment SDC processes. Prior to this study the extent of the control imparted by flow-through impoundments in the KRLAW on P levels was not understood. Fortunately, historical data indicate a downward trend in mean TP concentrations exiting these impoundments, suggesting progress towards recovery. In light of these findings, watershed managers should recognize impoundment P dynamics, target reductions in DP and gauge the watershed response by the rate of decline in impoundment mean TP concentrations.

Conclusions

This study uses patterns among land use, stream chemistry and trace element data to infer biological influenced DP cycling in the KRLAW. These results support the hypothesis that patterns among biological influence DP, stream chemistry and land use correlate to impoundment SDC processes.

MLM results and stream chemistry PFA provide evidence of the biological influence on DP cycling through DP and PP relationships. The trace element PFA identified the association of DP, Cl^-, SO_4^{2-}, NO_3^-, pH and trace elements urban land use, not biological influence.

From the DP dynamics inferred for the biological influenced segments of the KRLAW, it is concluded that: 1) impoundment processes disrupt the connection between the landscape and the stream system; 2) processes in Morrow Lake –the first large impoundment– are sourcing P and are regulating P forms delivered downstream; 3) the KWRP P input is additive to the Morrow Lake P outputs; 4) DP and PP –but not TP– are altered by biological processes and diluted by catchment inputs after the KWRP; and 5) the processes in Lake Allegan –the second large impoundment– are linked to the processes in Morrow Lake, sinking P and regulating P forms downstream.

The inferences into biological influenced DP dynamics identified here have implications for watershed P assessment and management strategy development. The regulatory processes resulting from impoundment SDC are a natural control on outlet P concentrations. The compensatory nature of impoundment processes will offset P reduction efforts and delay the downstream response. Current P reduction strategies that promote conservation practices such as reducing PP inputs should be reconsidered and redirected towards DP reductions. The downstream effects of Morrow Lake impoundment processes and the point source inputs of the KWRP are largely responsible for the inlet P concentrations to Lake Allegan, the impaired waterbody. Two control points exist in the KRLAW which affect and assess P concentrations at the inlet to Lake Allegan: the Morrow Lake outlet TP concentrations and the industrial point source loading after Morrow Lake.

Literature Cited

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H., 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. Ecological Applications, 8(3): 559-568.

Cooper, J., 2005. A biological survey of the Kalamazoo River and selected tributaries from the City of Battle Creek to Lake Michigan July-September 2004. Report No. MI/DEQ/WB-05/064, MDEQ, Water Bureau.

Figueroa-Nieves, D., Royer, T.V. and David, M.B., 2006. Controls on chlorophyll-a in nutrient-rich agricultural streams in Illinois, USA. Hydrobiologia, 568: 287-298.

French, T.D. and Petticrew, E.L., 2007. Chlorophyll a seasonality in four shallow eutrophic lakes (northern British Columbia, Canada) and the critical roles of internal phosphorus loading and temperature. Hydrobiologia, 575: 285-299.

Grover, J.P. and Chrzanowski, T.H., 2004. Limiting resources, disturbance, and diversity in phytoplankton communities. Ecological Monographs, 74(3): 533-551.

Håkanson, L., 2005. The Importance of Lake Morphometry for the Structure and Function of Lakes. International Review of Hydrobiology, 90(4): 433-461.

Havel, J.E. and Pattinson, K.R., 2004. Spatial distribution and seasonal dynamics of plankton in a terminal multiple-series reservoir. Lake and Reservoir Management, 20(1): 14-26.

Kelly, V.J., 2001. Influence of reservoirs on solute transport: a regional-scale approach. Hydrological Processes, 15(7): 1227-1249.

Kieser & Associates, 2008. Kalamazoo River TMDL Point Source Tracking Program, http://www.kalamazooriver.net/cgi/ps_v2/intro.cgi.

Kimmel, B.L., Lind, O.T. and Paulson, L.J., 1990. Reservoir Primary Production. In: K.W. Thornton, B.L. Kimmel and F.E. Payne (Editors), Reservoir Limnology: Ecological Perspectives. John Wiley & Sons, Inc., New York, NY.

Knoll, L.B., Vanni, M.J. and Renwick, W.H., 2003. Phytoplankton primary production and photosynthetic parameters in reservoirs along a gradient of watershed land use. Limnology and Oceanography, 48(2): 608-617.

McDowell, R.W. and Sharpley, A.N., 2003. Uptake and release of phosphorus from overland flow in a stream environment. Journal of Environmental Quality, 32(3): 937-948.

Momen, B., Eichler, L.W., Boylen, C.W. and Zehr, J.P., 1996. Application of multivariate statistics in detecting temporal and spatial patterns of water chemistry in Lake George, New York. Ecological Modelling, 91(1-3): 183-192.

Morgan, A.M., Royer, T.V., David, M.B. and Gentry, L.E., 2006. Relationships among nutrients, chlorophyll-alpha, and dissolved oxygen in agericultural streams in Illinois. Journal of Environmental Quality, 35(4): 1110-1117.

Mulholland, P.J., 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. Biogeochemistry, 70(3): 403-426.

Reed-Andersen, T., Carpenter, S.R. and Lathrop, R.C., 2000. Phosphorus Flow in a Watershed-Lake Ecosystem. Ecosystems, 3(6): 561-573.

Reyment, R.A. and Joreskog, K.G., 1993. Applied factor analysis in the natural sciences. Cambrigde University Press, New York, NY, 371 pp.

SAS, 1999. SAS/STAT User's Guide: The Mixed Procedure. SAS Institute, Cary, NC.

SAS, 2007. SAS 9.3.1 for Microsoft Windows. SAS Institute Inc., Cary, NC.

Schreiber, J.D. and Rausch, D.L., 1979. Suspended Sediment-Phosphorus Relationships for the Inflow and Outflow of a Flood Detention Reservoir. J Environ Qual, 8(4): 510-514.

Stanford, J.A. and Ward, J.V., 2001. Revisiting the serial discontinuity concept, pp. 303-310.

Stevenson, R.J., Rier, S.T., Riseng, C.M., Schultz, R.E. and Wiley, M.J., 2006. Comparing effects of nutrients on algal biomass in streams in two regions with different disturbance regimes and with applications for developing nutrient criteria. Hydrobiologia, 561: 149-165.

Straskrabova, V., Prochazkova, L. and Popovsky, J., 1973. Influence of reservoirs on chemical and bacteriological properties. In: J. Hrbacek and M. Straskraba (Editors), Hydrobiological Studies 2. Czechoslovak Academy of Sciences, Prague, pp. 348.

USEPA, 1996. Environmental indicators of water quality in the United States. EPA 841-R-96-002. EPA 841-R-96-002, USEPA, Office of Water (4503F), U.S. Government Printing Office, Washington, D.C.

Wall, L.G., Tank, J.L., Royer, T.V. and Bernot, M.J., 2005. Spatial and temporal variability in sediment denitrification within an agriculturally influenced reservoir. Biogeochemistry, 76(1): 85-111.

Ward, J.V. and Stanford, J.A., 1995. The serial discontinuity concept - extending the model to floodplain rivers. John Wiley & Sons Ltd, pp. 159-168.

Yuan, Z., Ramaswami, B., Casaletto, D., Falke, S., Angenent, L.T. and Giammar, D.E., 2007. Evaluation of chemical indicators for tracking and apportionment of phosphorus sources to Table Rock Lake in Southwest Missouri, USA. Water Research, 41(7): 1525-1533.

CHAPTER 5

A MODEL FOR PREDICTING THE PHOSPHORUS REDUCTIONS TO A FLOW THROUGH RIVER IMPOUNDMENT

Abstract

The Federal Clean Water Act Section 303(d) requires all states to identify water quality impaired waterbodies and develop Total Maximum Daily Loads (TMDLs) or other watershed restoration approaches to correct impairments. Models using historical data can be used to predict TMDL recovery and guide P reduction strategies. Historical data is often limited and difficult to use in a modeling framework. To address this, intensive sampling is used to provide insight into the cycling (sources, pathways and fate) of chemicals and to simplify model development.

A two-year study of stream chemistry in the KRLAW identified DP cycling within impoundments that regulate P concentrations downstream. Using this knowledge, an empirical model developed for Lake Allegan's (the KRLAW impaired waterbody) inlet TP concentration is reduced to three terms. The model is used to predict progress toward TMDL goals and to understand the effects of reduction efforts.

The model predicts with 95% confidence that the Lake Allegan inlet TP goal will be achieved when adjusted to mean discharge. TP and discharge relationships are identified that influence Lake Allegan inlet TP. P recovery and timing for various management and reduction strategies are estimated using the model. This research has broader implications for P TMDL development and assessment.

Introduction

The Federal Clean Water Act Section 303(d) requires all states to identify streams and rivers that do not attain water quality standards and to submit a list of these streams to the U.S. Environmental Protection Agency (USEPA) (USEPA, 2008b). For listed streams, the Act requires that states must develop Total Maximum Daily Loads (TMDLs) or other watershed restoration approaches. TMDLs are an estimation of the amount of a constituent that streams can receive and still meet water quality standards (Haggard et al., 2003). Models using historical data can be used to predict TMDL recovery and guide P reduction strategies. In general, developing these models involves using historical data amassed by federal, state and local monitoring programs. These data are collected on a fairly regular schedule (often at monthly or bimonthly intervals) but with varying periods of record by location. While such limited data can form the basis for water quality characterization, they are often difficult to use in a modeling framework. Model studies often require intensive sampling for a reliable assessment (Litwack et al., 2006).

Intensive sampling can provide insight into processes that control constituent sourcing, fate and transformation. These insights simplify modeling and trend analysis by reducing the model to fewer terms that describe constituent loading at a point of interest. By individually analyzing model terms, the maximum historical data available from associated locations can be used to improve the reliability of that term's prediction. Improving the reliability of individual terms should improve the capability of the final model combining those terms.

Scientists use both theoretical and empirical approaches to prediction. Theoretical predictions are based on a theory of a process or mechanism, while empirical predictions are based on curve fitting or pattern recognition without an attempt to represent underlying mechanisms (Carpenter, 2002). Empirical models are developed by predicting the contemporary value of a variable from simultaneous values of other variables. Then, assuming that contemporary relationships hold across time, scientist use empirical models to make future predictions (Carpenter, 2002).

An empirical model is developed that uses statistical trends and relationships as the basis for predicting TP from the KRLAW at the inlet to Lake Allegan. An empirical model was chosen because KRLAW historical data –although limited to TP, discharge and a few locations– could provide trends that could be used for model predictions. To address data limitations, intensive sampling over two growing seasons provided insight into temporal (Chapter 2), catchment (Chapter 3) and biological (Chapter 4) influences on DP cycling in the KRLAW. Impoundment processes were identified that control DP cycling in Morrow Lake (Chapter 2). These processes reduce the model to three terms: 1) the Morrow Lake outlet; 2) point source inputs after Morrow Lake; and 3) catchment and in-stream influences after Morrow Lake. Historical TP and discharge data are available to model these three terms.

The model is developed for the mean growing season (April to September). TP concentration is predicted for the inlet to Lake Allegan in 2012, the year for achieving the TMDL P goal of 72 $\mu g\ L^{-1}$. Sixty-nine years of discharge data are used to assess the probability of attaining the TMDL P goal under various discharge conditions. The TP concentration is forecast below the 2012 TMDL goal at the mean discharge parameters from the 69 year period of record. The short- and long-term effectiveness of reduction strategies targeted at catchment and point source P inputs based on the model terms are discussed.

The results of this study have implications for evaluating the progress toward TMDL goals in the KRLAW relevant to stakeholders and the regulatory agency. Implications for current and future P reduction strategies with respect to maximizing short-term P reduction potential in the KRLAW are presented. Finally, the broader implications for P TMDL development and assessment are considered.

Methods

The empirical KRLAW TP model was developed using the KRLAW stream chemistry dataset (Appendix I), historical mean growing season data (Appendix III) and historical mean monthly discharge data (Appendix IV). The study site, sampling locations, sampling methods, chemical analyses and historical data sources are described in Chapter 1. Insights and inferences into catchment and biological influenced DP cycling developed in Chapters 3 and 4 were used to develop the model system.

Statistical analysis

The general linear model (GLM) was the method used to identify trends in TP. GLM uses the least squares method to fit a general linear model relating continuous dependent variables to independent variables (SAS, 1999). A 95% confidence/prediction interval for individual predictions is used for the statistical analysis to account for the variability within the data. The 95% individual prediction interval is given by the equation (Ott and Longnecker, 2001):

$$y_{n+1} \pm t_{\alpha/2}\, s_{\varepsilon}\sqrt{1+\frac{1}{n}+\frac{(x_{n+1}-\bar{x})^2}{S_{XX}}} \tag{5.1}$$

where $t_{\alpha/2}$ is the Student's t for $\alpha/2 = 0.05/2 = 0.025$ and $n - 2$ degrees of freedom. Prediction equations and confidence/prediction intervals were developed from the GLM output. Standard statistical methods were used to develop frequency distributions and probability plots. Normality was tested using the Shapiro-Wilk statistic. This statistic –*W*–, tests the null hypothesis of normality, ranging from greater than zero to less than or equal to one ($0 < W \leq 1$). Small values of *W* lead to rejecting the null hypothesis. The statistical methods for this study were implemented using SAS 9.1.3 (SAS, 2007), including PROC GLM and PROC UNIVARIATE procedures.

Model Development

Impoundment processes that control DP cycling were identified in Chapter 2 which disconnects the upstream landscape from the Kalamazoo River at the Morrow Lake outlet. Variations in Morrow Lake inlet TP concentration are compensated for by interaction between biological activity and the storage and release of sediment phosphorus regulating outlet TP concentration. These processes simplify modeling the TP concentrations at the inlet to Lake Allegan by eliminating approximately two-thirds of the catchment (the area upstream of the Morrow Lake outlet) from the model.

Available historical P data from the KRLAW project, the MDEQ and the KRLAW TMDL point source tracking system is separated into three model terms to predict the Lake Allegan inlet concentration: 1) the Morrow Lake outlet; 2) point source inputs after Morrow Lake; and 3) the combined catchment and in-stream influences after Morrow Lake. KRLAW sampling cannot discriminate between catchment (sources, climate, hydrology, etc.) and in-stream influences (settling, resuspension, adsorption, desorption, etc.). The combined effects of catchment and in-stream influences are modeled in term 3. A block diagram of the system showing the model terms is given in Figure 5.1.

Concentration, load and discharge considerations

Available historical P data have been reported as TP concentrations (μg L^{-1}) from stream sampling locations, and TP load (kg $month^{-1}$) has been reported for point source inputs. The model is developed based on growing season TP loading.

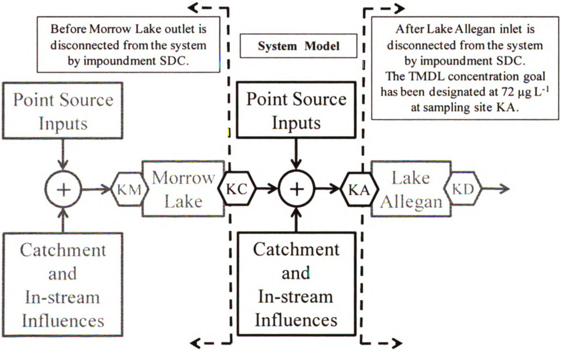


Figure 5.1: Block diagram for the TP model development for KRLAW Lake Allegan inlet concentration (KA) identifying inputs and influences ▭ and sampling locations ⬡.

TP loading is calculated by multiplying mean TP concentration by total discharge volume as follows:

L_{SITE} (kg gs^{-1}) = TP_{SITE} (μg L^{-1}) D_{SITE} (m^{3}s^{-1})(0.0864 kg L s m^{-3} d^{-1})(183 d gs^{-1}) (5.2)

or

$$L_{SITE} = 15.811 TP_{SITE} D_{SITE} \quad (5.3)$$

where: L_{SITE} = growing season TP load, TP_{SITE} = growing season mean TP concentration, D_{SITE} = growing season mean daily discharge and SITE is the location designation.

Load calculation using 5.3 requires discharge. The USGS gaging station for the Kalamazoo River at Comstock, Michigan –station number 04106000 at sampling site KC– has discharge records dating back to 1931. The discharge at KC (D_{KC}) was used as the reference discharge for the model because of this extensive record. Discharge is required site KA (D_{KA}). The relationship between D_{KA} and D_{KC} is developed using data from the USGS gaging station for the Kalamazoo River near New Richmond, Michigan –station number 04108670– downstream from KA. D_{KA} is estimated by adjusting the discharge at New Richmond by the ratio of the catchment area at site KA to the catchment area at New Richmond (0.81). The correlation between the growing season monthly means for D_{KA} and D_{KC} for the period of record for New Richmond (1994, 1995 and 2003 to 2007) is shown in Figure 5.2. D_{KA} and D_{KC} are highly correlated ($R^2 = 0.97$) and their relationship is represented by the equation:

$$D_{KA} = 1.7765 D_{KC} + 1.5568 \quad (5.4)$$

Growing season mean monthly discharge (MD_{KC}) at site KC is available from USGS gaging data. In addition, MD_{KC} was separated into mean monthly direct discharge (MDD_{KC}) and mean monthly base flow discharge (MBD_{KC}). The recursive digital filter method was used for base flow separation. The digital filter method is used in signal analysis and processing to separate high frequency signal from low frequency signal and has been used in base flow separation because high frequency waves can be associated with direct runoff and low frequency waves with base flow (Eckhardt, 2005; Lim et al., 2005). The Web-based Hydrograph Analysis Tool (WHAT) (Lim et al., 2004) was used to generate mean monthly direct and base flow separated data directly from the USGS data for the period of record at KC.

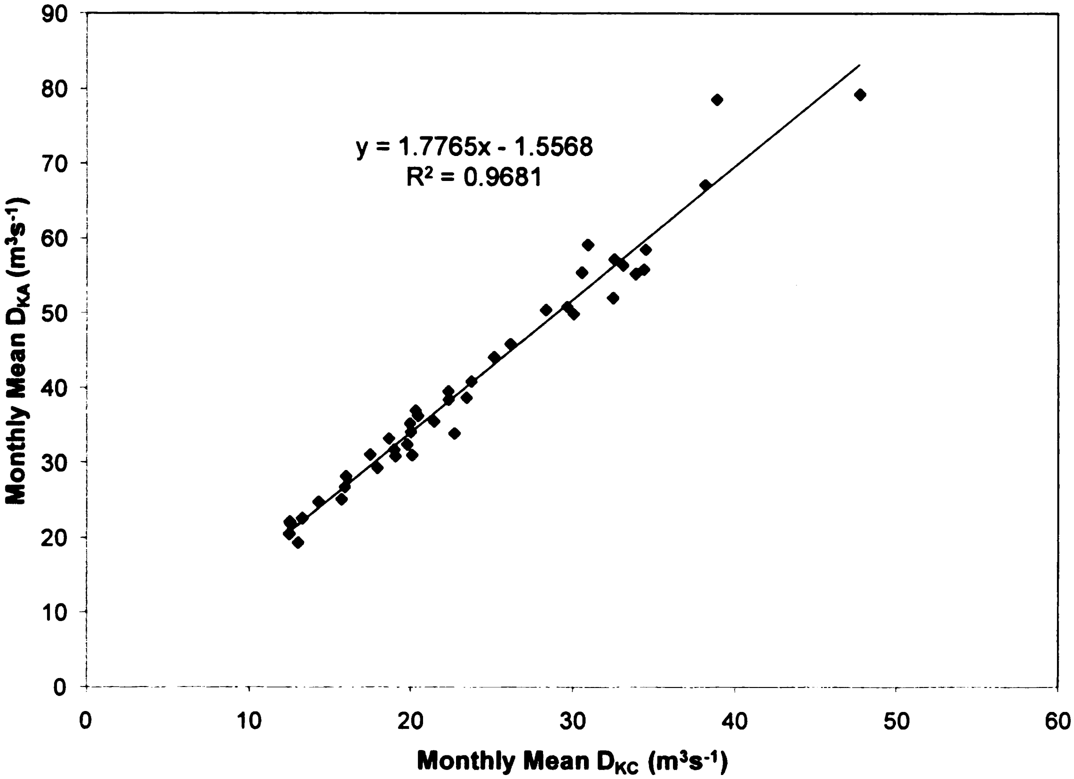


Figure 5.2: The relationship between monthly mean discharge at the outlet of Morrow Lake (D_{KC}) and the inlet of Lake Allegan (D_{KA}).

All of the discharge data are summarized in Appendix IV. TP concentration, TP loading and various discharge parameters were used to create a TP load model for the inlet to Lake Allegan.

The goal is to produce a model that can be used to predict the inlet concentration to Lake Allegan with 95% confidence and thus predict the future potential to attain the TMDL goal.

TP load model

The TP load model is the summation of the growing season TP loads to the inlet of Lake Allegan shown in Figure 5.1 and is represented by the equation:

$$L_{KA} = L_{KC} + L_{CAM} + L_{PAM} \tag{5.5}$$

where L_{KA} = TP load at the inlet to Lake Allegan (KA), L_{KC} = TP load at the outlet of Morrow Lake (KC), L_{CAM} = TP load from catchment inputs and in-stream influences after Morrow Lake, and L_{PAM} = TP load from the point sources after Morrow Lake. Each term is considered individually and recombined to create the final model.

TP load from Morrow Lake (L_{KC})

The available historical Morrow Lake outlet mean growing season TP concentration data by year is given in Figure 5.3. Visual inspection of this plot shows a shift after 1981 –with the exception of 2003– where the growing season mean TP concentrations appear to be regulated by the processes within the Morrow Lake system to a narrower range of values. Late season discharges in 2003 were at consecutively low levels compared the period of record from July through September. Increased residence time and lack of flushing under these conditions probably allowed for higher than normal productivity and outlet TP concentrations. As an outlier for the period, the 2003 growing season was excluded from the analyses.

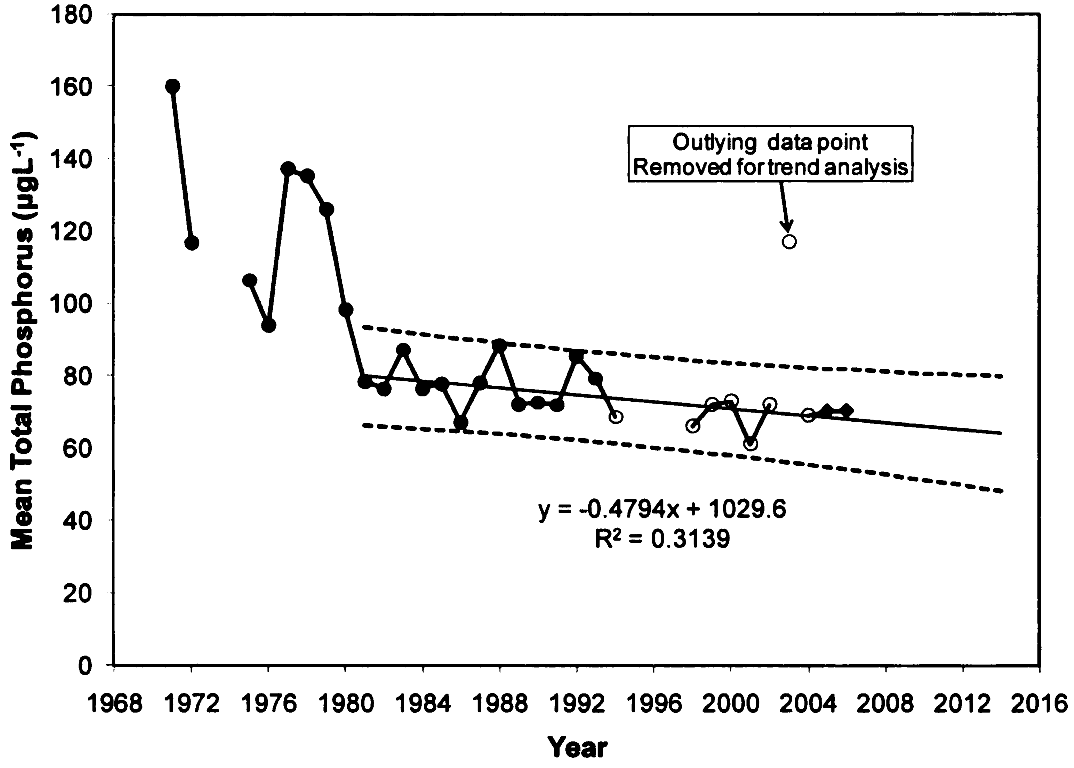


Figure 5.3: Historic Morrow Lake outlet mean growing season TP concentrations. Trend — and 95% prediction interval :::: from 1981 to 2006, excluding 2003. Data Sources: ● USEPA STORET Database, ○ MDEQ and ♦ KRLAW study.

The data from 1981 to 2006 –excluding 2003– was analyzed using a GLM (Table 5.1). Year was the only significant variable ($p = 0.0067$). All discharge parameters including D_{KC}, MD_{KC}, MDD_{KC} and mean MBD_{KC} were evaluated and none were significant for explaining the remaining variability. The equation for the trend line shown in Figure 5.4 from the GLM model output is:

$$TP_{KC} = -0.4794\text{Year} + 1029.6 \qquad (5.6)$$

Table 5.1: GLM output for TP_{KC} = Year for the outlet of Morrow Lake.

Source	df	SS	MS	F Value	Pr > F
Model	1	307.6146	307.615	9.15	0.0067
Error	20	672.5105	33.6255		
Total	21	980.1251			

Parameter	Estimate	S.E	t Value	Pr > |t|
Intercept	1029.6	315.863	3.26	0.0039
Year	-0.4794	0.1585	-3.02	0.0067

$n = 22$
$\bar{x} = 1993.73$
$\bar{y} = 74.259$
$s_{\varepsilon} = 5.7987$
$S_{XX} = 672.5105$

The upper and lower 95% prediction limits from equation 5.1 are shown in Figure 5.4 using $t_{0.05/2} = 2.086$ and the model output from Table 5.1. The range of the 95% predicted mean growing season TP values is approximately ± 12.5 to 15.8 $\mu g\ L^{-1}$, the result of a low R^2 (0.31) and the unexplained variability remaining in the data. Combining equations 5.4 and 5.6 –substituting TP_{KC} for y_{n+1}, Year for x_{n+1}, and using the values for the GLM output– the equation for predicting growing season mean TP_{KC} with a 95% prediction interval is:

$$TP_{KC} = (-0.4796Year + 1029.6) \pm (152.96 + (0.4664Year - 929.48)^2)^{0.5} \qquad (5.7)$$

Incorporating the growing season discharge volume to produce the equation for predicting the TP load at the outlet of Morrow Lake using equation 5.3 yields:

$$L_{KC} = TD_{KC}((-7.583Year + 16,279.0) \pm (38,238.1 + (7.374Year - 14,696.0)^2)^{0.5} \qquad (5.8)$$

Equation 5.8 provides the 95% confidence statistical prediction for L_{KC} for the final model.

TP load from catchment and in-stream influences after Morrow Lake (L_{CAM})

The TP load from the catchment and in-stream influence (L_{CAM}) after Morrow Lake and before the inlet to Lake Allegan was not measured directly. Growing season L_{CAM} was calculate as the remaining load after the subtracting the Morrow Lake outlet load (L_{KA}) and the point source load after Morrow Lake (L_{PAM}) from the load at the inlet to Lake Allegan (L_{KA}), or $L_{CAM} = L_{KA} - L_{KC} - L_{PAM}$. Historical data were available for 1998 and 2001 to 2006 to calculated L_{CAM}. The calculated values for L_{CAM} are given in Appendix III.

Year and the distribution of discharge for the growing season are used to account for the variability in L_{CAM}. Green et al. (2007) found that TP concentrations were more variable in a watershed with a higher contribution from overland flow. Moog and Whiting (2002) concluded that stream flow tended to dominate the other explanatory variables in explaining load variation, including TP load. A GLM was used to evaluate Year and various discharge parameters to estimate L_{CAM}. Year, monthly direct discharge in May (MDD_5), monthly base discharge in July (MDB_7) and monthly total discharge in August (MD_8) were significantly ($p < 0.05$) related to L_{CAM} (Table 5.2). The equation for the prediction from the GLM output in Table 5.2 and shown in Figure 5.4 is:

$$L_{CAM} = -1761.7Year + 316.9MDD_5 - 1113.4MBD_7 + 2753.6MTD_8 + 3{,}518{,}413.0 \qquad (5.9)$$

The upper and lower 95% prediction limits from equation 5.4 are given in Figure 5.4 using $t_{0.05/2} = 2.571$ and the model output from Table 5.2.

Table 5.2: GLM output for L_{CAM} = Year + MDD_5 + MBD_7 +MD_8 for the growing season catchment input and in-stream influence TP load after Morrow Lake.

Source	df	SS	MS	F Value	Pr > F
Model	4	790,048,419.3	197,512,104.8	7184.4	0.0001
Error	2	54,983.4	27,491.7		
Total	6	790,103,402.7			

Parameter	Estimate	S.E	t Value	Pr > |t|
Intercept	3,518,413.011	65,455.87555	53.75	0.0003
Year	-1761.69	32.55766	-54.11	0.0003
MDD_5	316.939	15.97918	19.83	0.0025
MBD_7	-1113.41	33.80229	-32.94	0.0009
MD_8	2753.553	33.53644	82.11	0.0001

$n = 7$
$\bar{x} = 25{,}206.07$
$\bar{y} = 25{,}206.07$
$s_\varepsilon = 165.8062$
$S_{XX} = 790{,}048{,}419.3$

Combining equations 5.4 and 5.9 –substituting for y_{n+1} and x_{n+1}, and including the values from the GLM output– the equation for predicting growing season mean L_{CAM} with a 95% prediction interval is:

$$L_{CAM} = -1761.7\text{Year} + 316.9\text{MDD}_5 - 1113.4\text{MBD}_7 + 2753.6\ \text{MD}_8 + 3{,}518{,}413.0 \pm ((207{,}613.5 + (-26.7\text{Year} + 4.8\text{MDD}_5 - 16.9\text{MBD}_7 + 41.8\text{MD}_8 + 52{,}969.9)^2)^{0.5} \quad (5.10)$$

Equation 5.10 provides a strong correlation ($R^2 = 0.99$) between L_{CAM} and Year, MDD_5, MBD_7 and MD_8. This is a statistical relationship where in addition to Year, a combination of mean growing season monthly direct, base flow and total monthly discharges in May, July and August, respectively, estimate L_{CAM}. The association of TP loading with the amount and timing of discharge parameters is consistent with the results of other research (Green et al., 2007; Moog and Whiting, 2002). Equation 5.10 provides the 95% confidence statistical prediction for L_{CAM} for the final model.

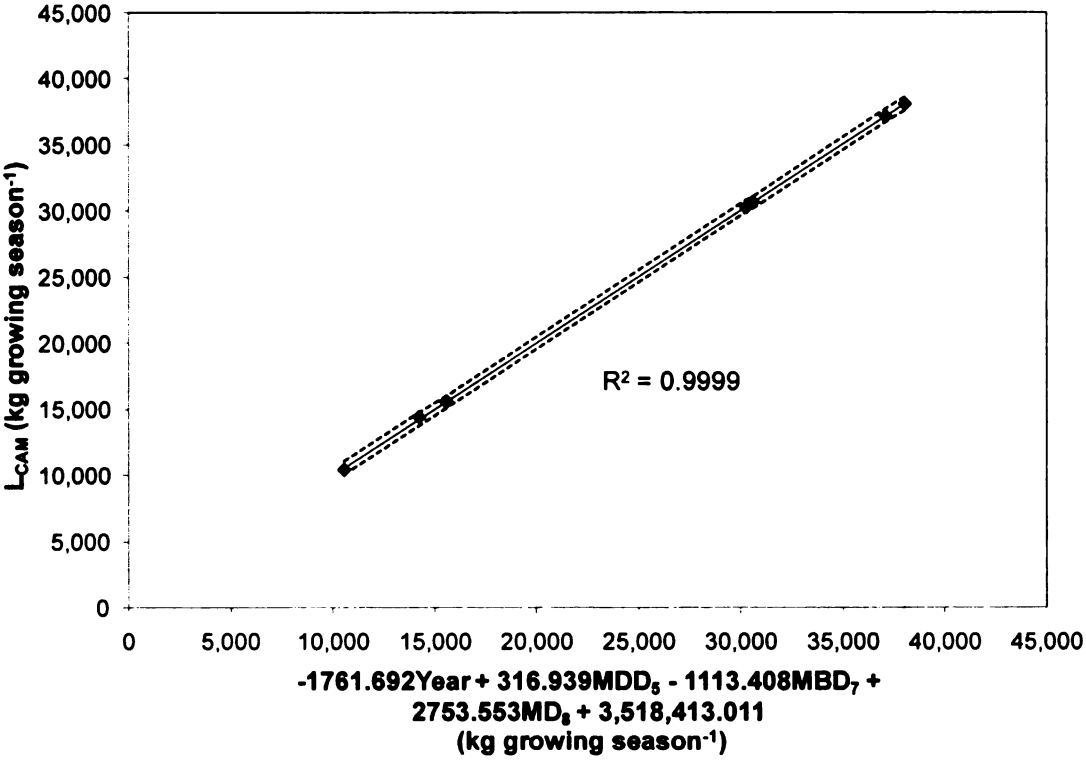


Figure 5.4: GLM relationship for growing season catchment input and in-stream influence load. Prediction — and 95% prediction interval ⁞⁞⁞ for 1998 and 2001-2006. Data Sources: MDEQ and KRLAW study and KRLAW TMDL point source tracking system.

TP load from point sources after Morrow Lake (L_{PAM})

Thirty-seven industrial and municipal point sources that discharge into the KRLAW system were signatories of the Kalamazoo River/Lake Allegan Watershed Cooperative Agreement for the Reduction of Phosphorus Loading (known as the“Cooperative Agreement”) (Molloy et al., 2002). As part of the Cooperative Agreement, their monthly loading is reported and tracked on the Web-based Kalamazoo River/Lake Allegan TMDL Point Source Tracking System (Kieser &

Associates, 2008). The growing season point source loading before Morrow Lake, after Morrow Lake and the total are shown in Figure 5.5. Under the Cooperative Agreement, the point sources have committed to maintaining 1998 loading levels for April through June and to reducing 1998 loading levels by 23 % for July through September. This amounts to an overall reduction goal of 11.5 % for the growing season by 2012 (Figure 5.5). As of 2008, total point source loading has been reduced by over 40%, aided by the closure of manufacturing facilities between 1998 and 2001.

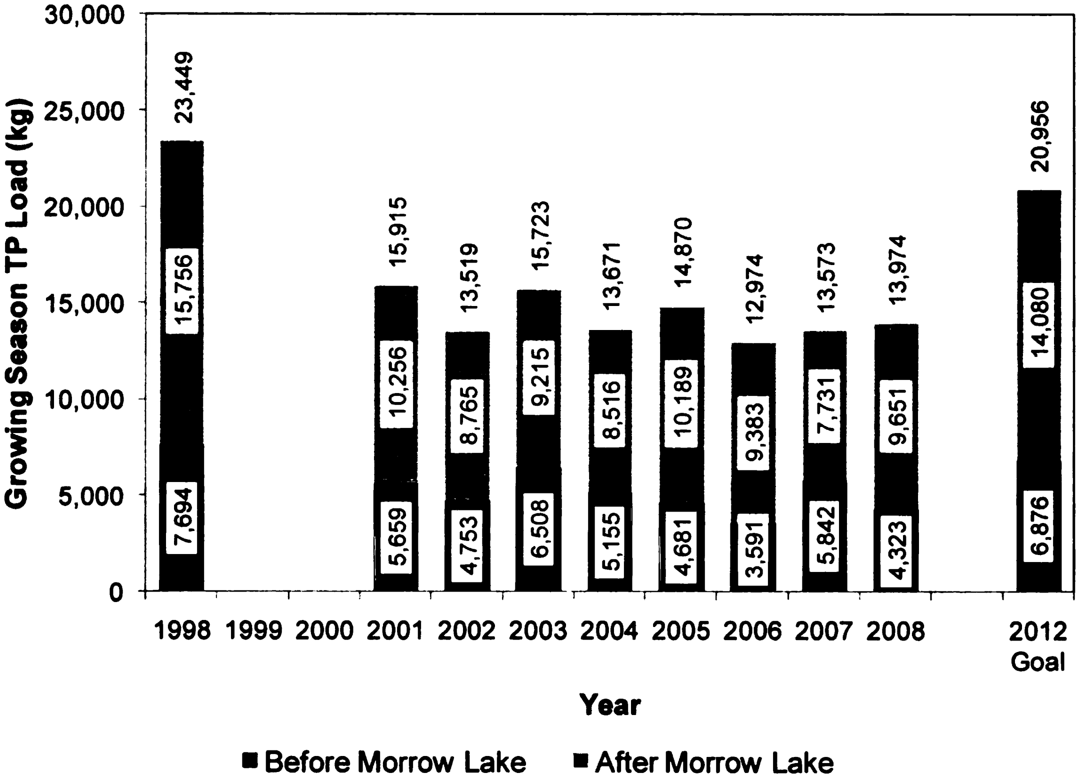


Figure 5.5: Growing season documented point source TP loads before the Morrow Lake inlet (L_{PBM}), after the Morrow Lake outlet (L_{PAM}), total point source load and the KRLAW TMDL point source goal in 2012. Sources: 1998: (Heaton, 1999) 2001 – 2008: (Kieser & Associates, 2008).

Morrow Lake impoundment processes disconnect the point source loads from the model system before the impoundment. However, the point source loads after

Morrow Lake (L_{PAM}) contribute to the loading at the Lake Allegan inlet. Since the decline before 2001, the L_{PAM} has ranged from 8,516 kg to 10,256 kg. Industrial and municipal TP loading is demand driven and does not lend itself to statistical prediction using watershed parameters. For the final model, L_{PAM} will be retained and estimates assumed for this loading will be used for prediction purposes.

Final model for TP loading at the Lake Allegan inlet (L_{KA})

Statistical inferences with 95 % prediction intervals for the trends in L_{KC} (equation 5.7) and L_{CAM} (equation 5.9) have been developed. L_{PAM} remains to be estimated based on assumptions for future point source loading after Morrow Lake. Combining these terms into the load model (equation 5.5) produces the final model equation:

$$\begin{aligned}
L_{KA} = {} & \overbrace{[D_{KC}(-7.583\text{Year} + 16{,}279.0)]}^{L_{KC}\ \text{estimate}} \\
& + \overbrace{[-1761.7\text{Year} + 316.9\text{MDD}_5 - 1113.4\text{MBD}_7 + 2753.6\ \text{MD}_8 + 3{,}518{,}413.0]}^{L_{CAM}\ \text{estimate}} \\
& + \overbrace{L_{PAM}}^{L_{PAM}\ \text{estimate}} \\
& \pm \overbrace{[D_{KC}(38{,}238.1 + (7.374\text{Year} - 14{,}696.0)^2)^{0.5}]}^{L_{KC}\ 95\%\ \text{prediction interval}} \\
& \pm \overbrace{[(207{,}613.5 + (-26.7\text{Year} + 4.8\text{MDD}_5 - 16.9\text{MBD}_7 + 41.8\text{MD}_8 + 52{,}969.9)^2)^{0.5}]}^{L_{CAM}\ 95\%\ \text{prediction interval}}
\end{aligned} \tag{5.11}$$

Equation 5.11 represents a model for the 95% confidence prediction of the TP load at the inlet to Lake Allegan (L_{KA}) based on statistical inferences of the trends in the

Morrow Lake outlet TP load (L_{KC}) and the catchment input and in-stream influenced load after Morrow Lake (L_{CAM}) and an estimate for the point source inputs after Morrow Lake (L_{PAM}).

Results

The goal in producing the loading model for the inlet to Lake Allegan is to estimate the short-term TP recovery prospects for Lake Allegan and the implications to TP reduction strategies based on recent trends in watershed characteristics. The use of any model to forecast future values comes with assumptions. The assumptions made in forecasting L_{KA} and thereby TP_{KA} are: 1) the statistical trends inferred for L_{KC} and L_{CAM} will continue, and 2) the estimate for L_{PAM} is reasonable for the prediction year. The year 2012 was chosen for the prediction year because it is the year designated for attaining the TMDL goal.

Recovery prospects by 2012

The KRLAW TMDL produced an implementation plan (Molloy et al., 2002) for P reductions to attain a Lake Allegan inlet growing season mean TP concentration of less than or equal to 72 $\mu g\ L^{-1}$ by 2012. Given a value for TP_{KA} for a target year, an estimate for L_{PAM} is required to evaluate the model equation. As previously discussed, the point source load is demand driven. The highest recorded loading (10,256 kg) since 2001 was increased by 10% to estimate L_{PAM} (11,282 kg) in 2012.

The load model (equation 5.11) is used to evaluate $TP_{KA} \leq 72\ \mu g\ L^{-1}$ –attainment of the TMDL goal. Using equation 5.3, TP_{KA} is represented by:

$$L_{KA} = 15.811 TP_{KA} D_{KA} \qquad (5.12)$$

D_{KC} is the reference discharge location. Substituting equation 5.4 for D_{KA} and rearranging equation 5.12 yields:

$$TP_{KA} = (L_{KA}/15.8112)(1.7765D_{KC} + 1.5568) \qquad (5.13)$$

To ensure 95% confidence in the prediction, L_{KC} and L_{CAM} must be less than their upper prediction limits, so these are used from equation 5.11 when substituting for L_{KA}. Substituting equation 5.11 for L_{KA}, Year = 2012, and L_{PAM} = 11,282 kg in equation 5.13 creates the following model equation predicting TP_{KA} (PTP_{KA}) $\leq 72\ \mu g\ L^{-1}$ in 2012:

$$PTP_{KA} \leq 72\ \mu g\ L^{-1} \leq [1262.43D_{KC} - 11{,}282 + 316.9MDD_5 - 1113.4MBD_7 + 2753.6\ MD_8 + ((207{,}613.5 + (-750.5 + 4.8MDD_5 - 16.9MBD_7 + 41.8MD_8)^2)^{0.5})] / [(28.088D_{KC} + 24.6149)] \qquad (5.14)$$

Equation 5.14 describes the combination of discharge conditions for D_{KC}, MDD_5, MBD_7 and MD_8 that predict PTP_{KA} in 2012. Discharge conditions in 2012 were estimated based on the probability of the discharge conditions from the period of record for D_{KC}. Equation 5.14 was evaluated for each of the 69 years of growing season discharge data (1933 to 1979 and 1985 to 2006) to generate the frequency distribution for PTP_{KA} based on historical discharge at KC (Figure 5.6).

For the distribution of PTP_{KA}, the Shapiro-Wilk statistics ($W = 0.9535$, $p < 0.0119$) indicate that the distribution of PTP_{KA} is normal and can be used to estimate the probability of discharge conditions that may occur in 2012. The probability plot for PTP_{KA} and the theoretical diagonal distribution line based on a normal distribution are given in Figure 5.7.

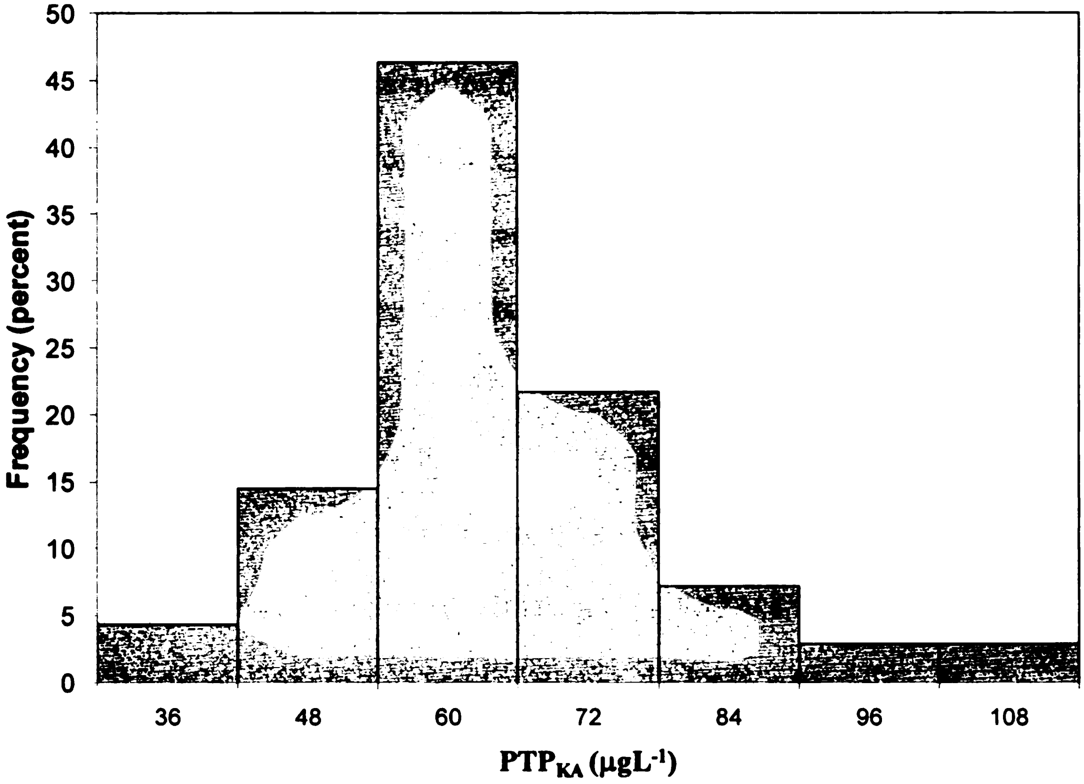


Figure 5.6: Histogram of PTP_{KA} in 2012 based on equation 5.14, using 69 years of discharge data at site KC.

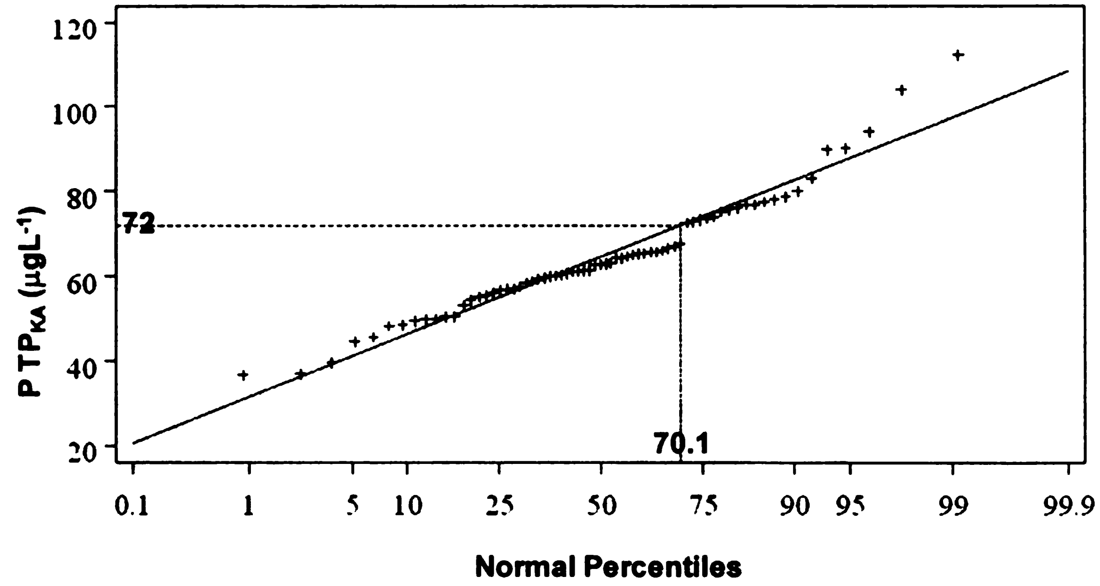


Figure 5.7: Normal probability plot for PTP_{KA} and the theoretical diagonal distribution line based on a normal distribution.

Based on the 69 years of discharge recorded at KC, the probability that the combination of discharge conditions for D_{KC}, MDD_5, MBD_7 and MD_8 will satisfy $PTP_{KA} \leq 72$ µg L^{-1} is 70.1%. However, L_{KC} and L_{CAM} are predicted at 95% prediction intervals. The probability of multiple events occurring is the product of the probability of those events. Therefore, the probability of meeting the TMDL goal in 2012 is:

$$\begin{aligned} \text{Prob}(TP_{KA} \leq 72 \ \mu g \ L^{-1}) &= \text{Prob}(PTP_{KA}) \ \text{Prob}(L_{KC})\text{Prob}(L_{CAM}) \\ &= (0.701)(0.950)(0.950) = 0.633 \text{ or } 63.3\% \end{aligned}$$

The probability of meeting the TMDL goal in 2012 is 63.3% assuming the Morrow Lake outlet concentration trend continues, the loading trend from the catchment and in-stream processes after Morrow Lake continues and the point source loading is not greater than 11,282 kg.

Discharge dependencies

The load model (equation 5.11) shows the dependency of the outcome of L_{KA} and therefore TP_{KA} on discharge and discharge distribution during the growing season. In developing the TMDL goal, the MDEQ recognized this dependency and "normalized" the 1998 nonpoint source monthly load data to monthly mean discharge for the period of record (1931 to 1997) (Heaton, 1999). The mean values for the current period of record through 2006 are 24.3, 6.6, 15.4 and 16.4 m^3s^{-1} for D_{KC}, MDD_5, MBD_7 and MD_8, respectively. Using these mean values in equation 5.14, the predicted value for the growing season mean TP concentration at the inlet to Lake Allegan –PTP_{KA}– in 2012 is 65.7 µgL^{-1}, below the 72 µgL^{-1} goal.

Implications for reduction strategies

Since the inception of the KRLAW P TMDL in 2000, various P reduction strategies have been implemented in the watershed. This research and the load model provide insight into the potential effectiveness of these efforts in different parts of the watershed. P reductions upstream of the outlet of Morrow Lake, by point sources after Morrow Lake and from the catchment after Morrow Lake will be considered.

Reductions upstream of the Morrow Lake outlet

Morrow Lake processes disconnect the outlet TP concentrations from the catchment and point source inputs upstream of the inlet. While these processes regulate the outlet TP concentrations, they are not totally unrelated to the inlet concentration. The declining trend in the outlet concentrations are speculated to result from the finite availability of P stored in the Morrow Lake bottom sediments. As this stored P is removed, subsequent removal becomes more difficult. Between 1999 and 2006, it is estimated that 46,340 kg of P were removed from Morrow Lake during the growing seasons. Over the same period, the trend in outlet TP concentration declined by 3.4 $\mu g\ L^{-1}$, or 0.000073 $\mu g\ L^{-1}\ kg^{-1}$ of P removed. Further P reductions, in particular DP at the inlet to Morrow Lake from reductions in point source and catchment inputs, may increase the release of P from the bottom sediments and accelerate the decline in outlet concentration. For example, increasing mean P removal by 20% between 2007 and 2012 could result in an additional 0.5 $\mu g\ L^{-1}$ reduction in the outlet concentration by 2012. This example illustrates that reductions upstream of the Morrow Lake outlet will have a long term effect on the outlet TP concentration. However, substantial reductions will not be realized short-term.

Point source reductions after Morrow Lake

All of the point sources within the KRLAW have exceeded their goal of a combined 11.5% growing season load reduction as of 2008. Given the other trends remain the same –and if the point sources after Morrow Lake could produce an additional 10% reduction over 2001 to a load of 9230 kg– the model predicts PTP_{KA} in 2012 at the mean discharge parameters of 62.8 $\mu g\ L^{-1}$. This is an additional 2.9 $\mu g\ L^{-1}$ reduction.

Catchment input reductions after Morrow Lake

To understand the sensitivity of TP_{KA} to L_{CAM} reductions the model is evaluated with a reduction in combined catchment and in-stream loading of 20% by 2012. The model predicts at mean discharge parameters a PTP_{KA} concentration of 64.7 $\mu g\ L^{-1}$ –an additional reduction of 1.0 $\mu g\ L^{-1}$.

Watershed-wide reduction implications

The load model provides insight into the contribution reductions in various watershed inputs may have on the mean growing season TP concentration at the inlet to Lake Allegan. Discharge parameters influence the contributions of L_{PAM} and L_{CAM}, but not L_{KC} to PTP_{KA}. The contributions to PTP_{KA} and the percentage of PTP_{KA} for the minimum (1934), mean and maximum (1994) discharge parameters for the period of record are shown in Figure 5.8.

The Morrow Lake outlet concentration and its contribution to the Lake Allegan inlet concentration (43.4 $\mu g\ L^{-1}$) are not related to discharge parameters. The point sources after Morrow Lake are a fixed load and their contribution increases with low discharge (26.3 $\mu g\ L^{-1}$ at the minimum) and decreases with high discharge (14.1 $\mu g\ L^{-1}$

at the maximum). The catchment inputs and in-stream processes are opposite of the point source inputs. At low discharge they retain P prior to the inlet of Lake Allegan because of low landscape loading and settling to the stream bed (-32 µg L^{-1} at the minimum). At high discharge they provide the greatest loading because of large landscape inputs and the transport of resuspended bed load (54.6 µg L^{-1} at the maximum).

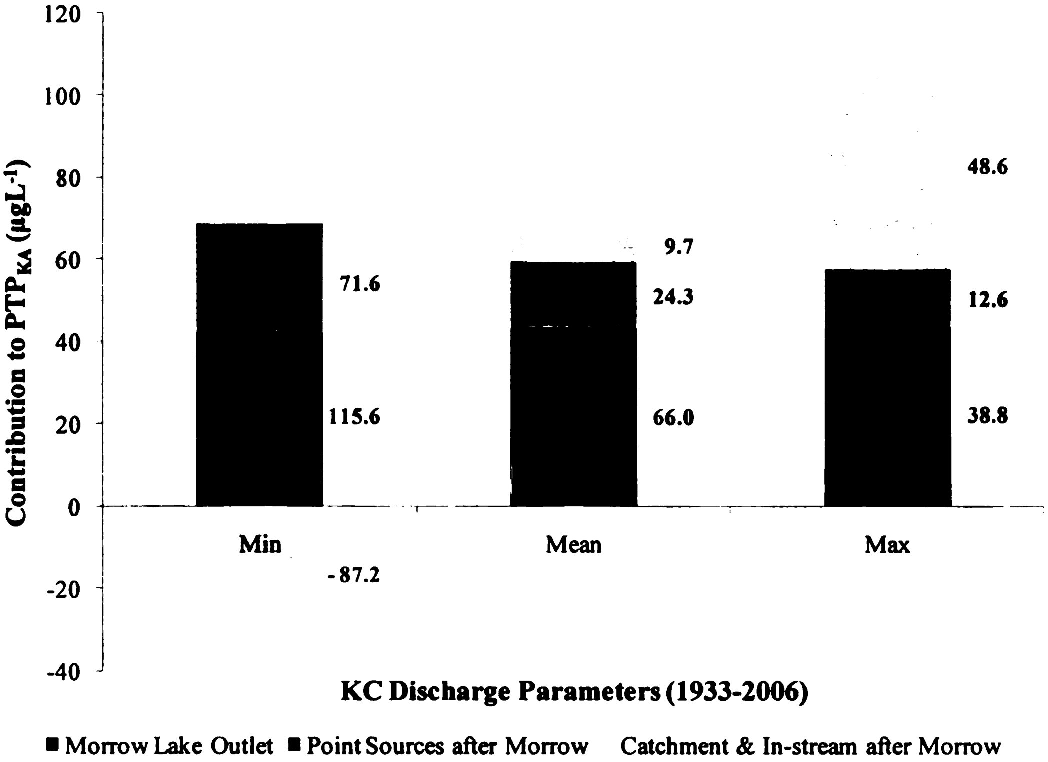


Figure 5.8: Predicted 2012 contributions to PTP$_{KA}$ of the modeled P sources at the minimum, mean and maximum discharge parameters for the period of record at KC. Percentage contribution to the total listed in bold next to the bars.

TP$_{KC}$ can only be minimally affected by reductions upstream of Morrow Lake and represents 66% of the concentration at the inlet to Lake Allegan when adjusted to mean discharge parameters. Stakeholder reduction efforts can only target the remaining 34% of the concentration at the inlet to Lake Allegan. Of that 34%, point source load reductions will have a greater impact than catchment input reductions.

Discussion

The inlet to Lake Allegan is the site identified by the MDEQ for assessing attainment of the KRLAW TMDL P goal. An empirical model was developed to predict TP concentration to Lake Allegan. Central to this model development is the identification of the control imparted by processes in Morrow Lake on outlet TP concentrations. The TP control imparted by Morrow Lake disconnects the downstream Kalamazoo River from the upstream catchment inputs and exhibits recent trends in mean growing season TP outlet concentrations. In the KRLAW system, Morrow Lake's location minimizes the effect of approximately two-thirds of the watershed. This reduces the model to three terms: 1) the Morrow Lake outlet; 2) point source inputs after Morrow Lake; and 3) catchment and in-stream influences after Morrow Lake.

A load model was developed identifying statistical trends in recent historical mean growing season TP loads for these three terms. Future point source loading after Morrow Lake was estimated. The load model was used to predict the TP concentration at the inlet to Lake Allegan in 2012, the TMDL goal deadline. The load model shows the dependency of the predicted TP concentration at the inlet to Lake Allegan on growing season mean discharge and mean monthly direct, base flow and total discharge distribution. To account for these discharge dependencies, the probability of 2012 discharge parameters occurring that satisfy the TMDL goal of less than or equal to 72 μg L^{-1} was calculated based on 69 years of discharge data. The load model for 2012 was also evaluated at mean discharge parameters for the period of record.

Results from the load model indicate a 63% probability that mean growing season TP concentration –unadjusted for discharge– will meet the 2012 goal assuming the recent TP trends continue and the point sources after Morrow Lake maintain their total loading below 11,282 kg. At mean discharge parameters, the model predicts a 2012 mean growing season TP concentration of 65.7 μg L^{-1} –6.3 μg L^{-1} below the TMDL goal.

Evaluating the 2012 load model for the period of record discharge parameters with the lowest and highest result for Lake Allegan inlet concentration yields a range of 37 to 112 μg L^{-1}. The probability that either of these discharge extremes will occur is very low. However, the range reinforces the importance of including discharge criteria in the specification of a TMDL P goal for both the TMDL stakeholder and the regulatory agency. Discharge conditions could occur by random chance and lead to success or failure in meeting the TMDL goal when concentration is not adjusted for discharge.

Results from the model predict progress towards reducing TP concentrations at the inlet to Lake Allegan. The model provides insight into the impact, interaction and implications of different P inputs for continued reduction efforts. While catchment and point source reductions upstream of the Morrow Lake inlet have minimal short-term effects, these efforts should have long-term effects accelerating the trend in declining Morrow Lake outlet concentrations. At mean discharge conditions, the catchment and in-stream loads represent less than 10% of the load to Lake Allegan. Their contribution becomes much greater –as high as 48%– at high discharge and continued reductions should provide greater protection from P exports during high discharge conditions. The point sources in general and after Morrow Lake have exceeded their TMDL load goal, which has contributed to the progress to date. Further reductions by the point sources after Morrow Lake should have the greatest short-term impact on Lake Allegan.

In light of these findings, watershed managers should continue P reduction efforts throughout the KRLAW, but increase catchment and point source P reduction efforts after Morrow Lake to maximize the short-term recovery prospects of Lake Allegan. Morrow Lake impoundment P dynamics should be recognized as a supplier of P from within the impoundment. Reduction efforts upstream of Morrow Lake should be evaluated and acknowledged at the inlet to Morrow Lake. Stakeholders upstream of Morrow Lake should not be discouraged by the lack of short-term progress reflected by the Morrow Lake outlet concentration. Their efforts are required to accelerate the depletion of P stores in Morrow Lake and will contribute to the long-term recovery of Lake Allegan.

Conclusions

This study develops an empirical load model for predicting the inlet TP concentration to Lake Allegan based on statistical trends in limited historical data for the KRLAW. Insights into DP cycling developed from two years of intensive sampling reduced the model to three terms that are combined to predict Lake Allegan inlet concentrations from the available historical data. The model predicts TP concentrations (65.7 μg L^{-1}) below the TMDL goal (72 μg L^{-1} by 2012) at the inlet to Lake Allegan. A 63% probability is predicted that TP concentrations will be below the goal without adjustments for discharge. Dependencies between TP concentration and various discharge parameters are identified through this model. These dependencies reinforce the importance of including discharge criteria in evaluating progress towards the KRLAW P TMDL goal.

Results from this study have implications for point and nonpoint P reduction strategies in the KRLAW. Reduction efforts upstream of Morrow Lake will have minimal short-term impact, but will have a long-term effect by accelerating the declining trend in outlet concentration. Reduction efforts should be focused on point source and catchment loads after Morrow Lake to maximize the short-term P reduction to Lake Allegan.

This research has broader implications for P TMDL development and assessment. The P TMDL development process must include identifying P cycles that have potential interaction and which compensate for reduction strategies. Accounting for these processes will lead to improved P goals and reduction timelines. Assessing progress toward P reduction goals should include monitoring locations before compensation occurs to acknowledge progress and to maintain motivation for continued reduction efforts.

Literature Cited

Bohr, J. and Liston, C., 1987. A survey of the fish and benthic communities of Morrow Lake on the Kalamazoo River, Michigan, 1985 and 1986, Report to STS Consultants Ltd.

Carpenter, S.R., 2002. Ecological Futures: Building an Ecology of the Long Now. Ecology, 83(8): 2069-2083.

Eckhardt, K., 2005. How to construct recursive digital filters for baseflow separation. Hydrological Processes, 19(2): 507-515.

Green, M.B., Nieber, J.L., Johnson, G., Magner, J. and Schaefer, B., 2007. Flow path influence on an N : P ratio in two headwater streams: A paired watershed study. Journal of Geophysical Research-Biogeosciences, 112(G3).

Haggard, B.E., Soerens, T.S., Green, W.R. and Richards, R.P., 2003. Using regression methods to estimate stream phosphorus loads at the Illinois River, Arkansas. Applied Engineering in Agriculture, 19(2): 187-194.

Heaton, S., 1999. Loading assessments of phosphorus inputs to Lake Allegan, 1998. Report No. MI/DEQ/SWQ-99-125, MDEQ, Surface Water Quality Division.

Heaton, S., 2001. Total maximum daily load (TMDL) for total phosphorus in Lake Allegan, MDEQ, Surface Water Quality Division.

Heaton, S., 2003. Water quality monitoring of Lake Allegan and sellect station on the Kalamazoo River, 2003. Report No. MI/DEQ/SWQ-03-1.3, MDEQ, Surface Water Quality Division.

Kieser & Associates, 2008. Kalamazoo River TMDL Point Source Tracking Program, http://www.kalamazooriver.net/cgi/ps_v2/intro.cgi.

Kosek, S., 1997. Water quality and pollution control in Michigan, 1996 Report. Michigan 305(b) Report: Volume 14. Report No. MI/DEQ/SWQ-97-040, MDEQ, Surface Water Quality Division.

Langner, C.L. and Hendrix, P.F., 1982. Evaluatin of a persulfate disgestion method for particulate nitrogen and phosphorus. Water Research, 16(10): 1451-1454.

Lim, K.J., Engel, B.A., Tang, Z.X., Choi, J., Kim, K.S., Muthukrishnan, S. and Tripathy, D., 2005. Automated Web Gis based hydrograph analysis tool, what. Journal of the American Water Resources Association, 41(6): 1407-1416.

Lim, K.J., Engel, B.A., Tang, Z.X., Theller, L. and Muthukrishnan, S., 2004. WHAT: Web-based hydrograph analysis tool, http://cobweb.ecn.purdue.edu/~what/.

Litwack, H.S., DiLorenz, J.L., Huang, P. and Najarian, T.O., 2006. Development of a simple phosphorus model for a large urban watershed: A case study. Journal of Environmental Engineering-Asce, 132(4): 538-546.

Molloy, J., Heaton, S., Carter, D. and Kieser, M., 2002. Water Quality Improvement (Implementation) Plan for the Kalamazoo River Watershed and Lake Allegan through a Phosphorus Total Maximum Daily Load (TMDL) Process, Kalamazoo River/Lake Allegan TMDL Implementation Committee

Moog, D.B. and Whiting, P.J., 2002. Climatic and agricultural factors in nutrient exports from two watersheds in Ohio. Journal of Environmental Quality, 31(1): 72-83.

Ott, R.L. and Longnecker, M., 2001. An introduction to statistical methods and data analysis. Wadsworth Group, Pacific Grove, CA, 1152 pp.

SAS, 2007. SAS 9.3.1 for Microsoft Windows. SAS Institute Inc., Cary, NC.

USEPA, 1975. Report on Lake Allegan, Allegan County Michigan. EPA Region V, Working Paper Series No. 182. EPA National Eutropication Studies. 1975, USEPA, Washington, D.C.

USEPA, 2008a. STORET, EPA's computerized environmental data system, http://www.epa.gov/storet/.

USEPA, 2008b. Total Maximum Daily Loads: National Section 303(d) List Fact Sheet, http://iaspub.epa.gov/waters/national_rept.control.

USGS, 2008a. Annual water data reports, USGS 04106000 Kalamazoo River at Comstock, MI, http://waterdata.usgs.gov/mi/nwis/uv/?site_no=04106000&PARAmeter_cd=00065,00060.

USGS, 2008b. Annual water data reports, USGS 04108670 Kalamazoo River at New Richmond, MI, http://waterdata.usgs.gov/mi/nwis/uv/?site_no=04108670&PARAmeter_cd=00065,00060.

Valderrama, J.C., 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural-waters. Marine Chemistry, 10(2): 109-122.

Wahrer, M.A., Long, D.T. and Lee, R.W., 1996. Selected geochemical characteristics of ground water from the glaciofluvial aquifer in the central lower penninsula of Michigan. U.S. Geological Survey Water-Resource Investigative Report 944017.

Westjohn, D.B. and Weaver, T.L., 1997. Hydrogeologic framework of the Michigan Basin aquifer system. U.S. Geological Survey Professional Paper 1418. U.S. Geological Survey Information Services.

Wetzel, R.G. and Likens, G.E., 2000. Limnological Analyses, third ed. Springer-Verlag, New York, NY.

Wycheck, J., 1998. Water quaity and pollution control in Michigan, 1996 Report. Michigan 305(b) Report. Report No. MI/DEQ/SWQ-98-030, MDEQ, Surface Water Quality Division.

APPENDICES

APPENDIX I

KALAMAZOO RIVER/LAKE ALLEGAN WATERSHED STREAM CHEMISTRY DATASET

2005 and 2006 growing season stream chemistry results for the Kalamazoo River/Lake Allegan Watershed, Michigan, USA sampling locations: BC – Battle Creek River at Emmet Street Dam, Battle Creek, MI; BR – Battle Creek River at McAllister Rd, Pennfield, MI; FC – Eagle Lake Tributary at Fort Custer, MI; GR – Gun River at 106th Street, Otsego, MI; KA – Kalamazoo River inlet to Lake Allegan at M222, Allegan, MI; KB – Kalamazoo River at Battle Creek, MI; KC – Kalamazoo River outlet of Morrow Lake at Comstock, MI; KD – Kalamazoo River outlet of Lake Allegan at Caulkins Dam, Allegan, MI; KE – Kalamazoo River east of Battle Creek at Battle Creek, MI; KG – Kalamazoo River at Augusta, MI; KK – Kalamazoo River at Mosel Street, Kalamazoo, MI; KP – Kalamazoo River at Plainwell, MI; PC – Portage Creek at Kalamazoo, MI; SB – Schnable Brook at M-89, Otsego, MI and WC – Wanadoga Creek at Pennfield Road, Pennfield, MI.

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
BC	4/5/2005	22.06	11.93	10.13	-	-	-	-	-	-	-	-	-	-	-
BC	4/12/2005	55.07	16.83	38.24	-	-	-	-	-	-	-	-	-	-	-
BC	4/19/2005	46.06	9.38	36.69	-	-	-	-	-	-	-	-	-	-	-
BC	4/26/2005	35.38	12.60	22.78	-	-	-	-	-	-	-	-	-	-	-
BC	5/3/2005	39.30	11.93	27.36	-	-	-	-	-	-	-	-	-	-	-
BC	5/10/2005	33.76	11.82	21.94	665	7.72	303	38.32	0.261	71.70	18.13	1.887	22.81	75.04	-
BC	5/17/2005	47.26	28.51	18.75	620	7.85	295	32.29	0.511	44.59	15.23	1.795	20.92	70.92	-
BC	5/24/2005	56.50	34.75	21.76	642	7.80	307	33.17	0.475	58.46	16.35	1.740	21.13	73.98	-
BC	5/31/2005	55.96	27.61	28.35	682	7.91	315	40.89	0.451	62.13	19.36	1.780	22.08	78.37	-
BC	6/7/2005	55.16	31.37	23.79	692	7.90	315	40.37	0.472	67.37	17.87	1.756	23.28	78.77	-
BC	6/9/2005	63.37	43.38	20.00	701	7.84	334	43.04	0.478	72.55	19.06	1.867	22.92	77.84	-
BC	6/14/2005	86.80	60.40	26.40	652	7.79	288	38.99	0.542	59.89	17.36	1.891	20.71	72.78	-
BC	6/21/2005	74.62	46.11	28.51	670	7.84	304	35.59	0.877	66.17	16.35	2.047	21.71	77.31	-
BC	6/28/2005	59.28	38.54	20.75	706	7.86	305	42.23	0.396	75.30	18.91	1.894	22.81	78.37	-
BC	7/5/2005	62.78	43.43	19.36	658	7.86	271	39.66	0.563	67.98	18.25	2.128	21.29	71.05	-
BC	7/12/2005	53.14	37.96	15.18	662	7.74	281	41.07	0.422	64.64	18.20	1.440	21.50	74.38	-
BC	7/19/2005	57.79	42.20	15.59	691	7.66	290	45.80	0.348	66.48	19.70	1.337	22.50	76.37	-
BC	7/26/2005	65.13	51.13	14.00	659	7.70	296	37.09	0.381	53.75	16.78	2.407	21.87	74.11	-

Site	Date	TP (µgL^{-1})	DP (µgL^{-1})	PP (µgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (µgL^{-1})
BC	7/25/2006	64.39	46.49	17.90	730	7.71	287	44.65	0.432	66.67	21.93	2.368	23.49	83.31	1.588
BC	8/1/2006	66.97	51.81	15.16	767	7.73	302	47.94	0.391	69.39	21.30	1.996	25.12	82.50	2.062
BC	8/8/2006	67.53	50.62	16.91	755	7.77	305	46.25	0.429	62.92	20.46	2.040	24.43	82.70	1.075
BC	8/15/2006	51.76	35.78	15.98	780	7.75	300	48.96	0.268	74.74	21.20	1.919	25.08	83.71	1.915
BC	8/22/2006	53.08	39.01	14.08	779	7.78	293	49.83	0.306	76.64	22.42	1.986	25.33	86.68	1.886
BC	8/29/2006	60.35	39.00	21.35	781	7.76	298	48.71	0.334	77.75	22.63	2.122	24.93	82.20	2.171
BC	9/5/2006	55.66	39.39	16.27	748	7.82	287	44.77	0.416	70.58	19.46	2.159	23.34	83.01	0.701
BC	9/12/2006	55.34	37.65	17.69	816	7.79	304	50.48	0.381	82.78	22.34	2.043	26.15	88.32	0.584
BC	9/19/2006	79.13	56.89	22.25	708	7.56	246	34.38	1.335	90.96	15.67	2.885	20.46	81.30	0.622
BC	9/26/2006	71.84	54.12	17.72	774	7.70	295	40.07	0.785	84.71	20.16	2.245	23.39	86.12	0.643
BR	4/5/2005	26.63	16.83	9.80	-	-	-	-	-	-	-	-	-	-	-
BR	4/12/2005	68.14	27.78	40.36	-	-	-	-	-	-	-	-	-	-	-
BR	4/19/2005	42.28	20.56	21.72	-	-	-	-	-	-	-	-	-	-	-
BR	4/26/2005	39.97	17.35	22.62	-	-	-	-	-	-	-	-	-	-	-
BR	5/3/2005	59.50	22.43	37.07	-	-	-	-	-	-	-	-	-	-	-
BR	5/10/2005	47.14	22.03	25.11	705	7.63	305	43.67	0.460	80.55	21.67	2.147	23.65	79.04	-
BR	5/17/2005	61.16	42.73	18.43	500	7.78	304	30.21	0.532	43.87	14.27	1.718	21.76	75.71	-
BR	5/24/2005	69.02	49.30	19.72	662	7.70	310	38.10	0.591	63.24	18.58	1.834	21.34	75.58	-
BR	5/31/2005	74.85	43.20	31.65	709	7.87	323	43.53	0.571	70.25	20.90	2.002	22.71	81.17	-
BR	6/7/2005	78.80	61.30	17.50	716	7.79	316	44.82	0.635	74.40	21.54	2.041	23.13	78.37	-
BR	6/9/2005	84.77	71.81	12.97	723	7.82	342	48.88	0.598	72.44	21.65	2.076	22.50	79.04	-
BR	6/14/2005	126.48	79.62	46.86	671	7.72	290	43.71	2.087	59.23	19.56	2.091	21.18	72.65	-
BR	6/21/2005	89.98	61.97	28.01	706	7.89	315	40.26	0.921	78.64	19.77	2.177	22.34	79.44	-
BR	6/28/2005	98.58	68.73	29.85	713	7.81	292	46.05	0.598	85.03	22.31	1.996	22.13	76.24	-
BR	7/5/2005	102.50	71.87	30.63	644	7.82	281	42.92	0.760	67.32	20.29	2.577	19.77	68.13	-
BR	7/12/2005	87.01	65.82	21.19	733	7.75	308	54.59	0.621	41.14	22.43	1.323	23.23	79.57	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
BR	7/19/2005	103.72	74.91	28.81	733	7.64	304	53.53	0.557	71.11	24.76	1.609	22.97	76.64	-
BR	7/26/2005	98.05	75.15	22.90	674	7.62	282	45.94	0.544	61.22	22.41	2.310	20.61	72.12	-
BR	8/2/2005	86.22	65.09	21.13	719	7.65	311	45.49	0.531	75.36	22.76	2.062	22.13	78.10	-
BR	8/9/2005	75.89	68.96	6.92	763	7.69	308	56.19	0.483	86.34	27.03	2.481	24.02	80.23	-
BR	8/16/2005	87.75	78.29	9.46	777	7.79	317	62.85	0.628	79.70	29.90	2.505	25.59	79.97	-
BR	8/23/2005	99.51	77.10	22.41	759	7.79	307	50.43	0.341	73.70	26.75	2.536	25.48	80.90	-
BR	8/30/2005	89.24	78.78	10.46	758	7.69	309	60.22	0.470	86.32	27.33	2.347	24.49	82.50	-
BR	9/6/2005	83.67	67.45	16.22	773	7.73	314	68.13	0.498	84.13	31.68	2.607	24.61	79.53	-
BR	9/13/2005	83.06	68.39	14.68	761	7.66	309	65.72	0.423	81.98	29.49	2.871	24.67	78.91	-
BR	9/20/2005	91.55	73.16	18.39	786	7.64	320	70.64	0.560	85.04	33.17	2.985	24.61	81.39	-
BR	9/27/2005	83.40	66.14	17.26	768	7.72	304	62.77	0.620	97.63	30.63	3.015	23.99	82.26	-
BR	10/4/2005	86.87	55.15	31.71	736	7.63	287	57.98	0.586	91.49	27.25	2.660	22.90	78.67	-
BR	4/4/2006	39.69	27.11	12.58	586	7.65	228	32.92	1.232	88.62	15.05	2.634	20.92	75.68	2.323
BR	4/11/2006	41.06	21.93	19.13	520	7.69	196	28.26	1.984	76.24	11.98	2.587	17.23	68.51	1.680
BR	4/18/2006	45.80	27.79	18.01	631	7.79	250	38.04	0.702	87.00	15.66	2.517	22.19	82.41	2.008
BR	4/25/2006	67.16	46.17	20.99	704	7.72	294	42.70	0.728	91.87	20.99	2.661	25.22	91.05	2.184
BR	5/2/2006	65.33	44.30	21.03	692	7.64	298	41.20	0.644	91.76	19.34	2.474	25.29	91.19	0.773
BR	5/9/2006	74.48	51.16	23.32	731	7.75	301	44.28	0.799	91.95	21.11	1.818	25.10	89.63	0.609
BR	5/16/2006	63.66	48.95	14.70	503	7.41	191	24.03	2.961	53.16	10.52	2.500	16.30	64.64	1.113
BR	5/23/2006	48.07	35.81	12.26	626	7.72	250	33.38	1.050	68.49	14.42	1.927	20.87	78.23	0.924
BR	5/30/2006	90.44	61.89	28.55	723	7.63	301	41.10	0.847	72.94	17.72	1.800	24.21	87.16	2.129
BR	6/6/2006	96.10	60.67	35.43	753	7.65	313	44.87	0.922	80.25	20.98	1.745	25.92	90.20	0.819
BR	6/13/2006	74.85	49.00	25.84	764	7.75	307	46.89	0.691	81.98	21.86	2.184	27.65	90.20	0.626
BR	6/20/2006	85.00	67.52	17.48	764	7.72	303	48.76	0.667	84.20	23.21	1.937	25.28	87.07	0.718
BR	6/27/2006	89.41	68.15	21.25	715	7.60	270	37.28	2.291	85.29	16.85	3.154	22.78	84.77	1.029
BR	7/4/2006	90.75	65.48	25.27	760	7.69	297	46.04	0.812	84.01	21.94	2.174	24.75	85.15	0.962

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chloro-phyll *a* (μgL^{-1})
BR	7/11/2006	76.17	64.86	11.31	777	7.65	295	48.81	0.677	80.78	21.93	2.331	24.28	86.78	0.953
BR	7/18/2006	92.44	79.89	12.55	757	7.61	274	50.41	0.675	73.11	24.02	2.452	24.39	84.30	1.147
BR	7/25/2006	95.42	79.22	16.20	735	7.70	288	45.26	0.431	66.64	21.74	2.385	22.99	83.19	0.916
BR	8/1/2006	99.50	85.02	14.48	800	7.72	296	55.75	0.597	73.80	25.73	2.332	24.87	85.88	0.697
BR	8/8/2006	95.55	81.46	14.09	771	7.78	293	53.26	0.635	66.75	24.63	2.429	23.64	80.94	0.743
BR	8/15/2006	83.73	74.14	9.59	848	7.81	309	63.21	0.583	90.15	28.32	2.244	25.88	88.51	0.668
BR	8/22/2006	84.46	72.92	11.53	828	7.80	303	58.14	0.638	81.55	27.33	2.344	26.12	89.55	0.878
BR	8/29/2006	86.16	72.10	14.07	798	7.75	288	55.46	0.587	84.60	26.60	2.322	24.60	82.06	0.865
BR	9/5/2006	90.34	71.44	18.90	863	7.85	310	59.62	0.663	96.99	27.06	2.688	26.35	93.97	0.365
BR	9/12/2006	84.71	62.35	22.36	916	7.80	295	70.21	0.815	115.95	32.44	2.491	26.42	93.69	1.264
BR	9/19/2006	106.85	71.16	35.69	754	7.48	263	39.55	1.318	98.76	18.33	2.970	21.57	85.28	1.331
BR	9/26/2006	82.24	53.78	28.45	815	7.60	293	49.23	0.991	93.17	24.18	2.460	23.58	88.17	0.546
FC	4/5/2005	10.62	3.43	7.19	-	-	-	-	-	-	-	-	-	-	-
FC	4/12/2005	16.01	5.07	10.95	-	-	-	-	-	-	-	-	-	-	-
FC	4/19/2005	19.91	7.07	12.83	-	-	-	-	-	-	-	-	-	-	-
FC	4/26/2005	11.97	3.90	8.07	-	-	-	-	-	-	-	-	-	-	-
FC	5/3/2005	20.52	11.77	8.75	-	-	-	-	-	-	-	-	-	-	-
FC	5/10/2005	29.62	6.44	23.18	486	7.69	243	15.99	0.053	25.43	6.08	0.517	20.08	52.29	-
FC	5/17/2005	18.97	7.65	11.32	451	7.84	245	14.38	0.040	23.93	5.86	0.745	19.30	50.56	-
FC	5/24/2005	19.09	8.14	10.96	458	7.91	246	13.90	0.040	22.47	5.69	0.460	18.88	52.42	-
FC	5/31/2005	26.82	9.34	17.48	481	7.90	256	15.26	0.043	23.90	6.01	0.479	20.08	53.76	-
FC	6/7/2005	33.05	10.64	22.41	481	7.90	253	16.37	0.071	22.60	6.28	0.954	19.56	52.69	-
FC	6/9/2005	21.51	13.23	8.28	429	7.90	233	15.06	0.049	20.33	5.62	0.710	21.81	45.51	-
FC	6/14/2005	29.16	13.38	15.78	433	7.82	218	15.35	0.043	19.09	5.23	0.188	17.36	46.44	-
FC	6/21/2005	34.30	21.51	12.80	458	7.78	244	14.45	0.046	22.46	5.74	0.305	18.83	49.76	-
FC	6/28/2005	41.91	16.11	25.80	466	7.73	236	16.23	0.049	22.07	6.54	0.551	19.72	48.57	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
FC	7/5/2005	39.05	15.15	23.90	451	7.65	217	15.00	0.077	22.57	5.77	0.436	18.30	42.45	-
FC	7/12/2005	31.62	16.77	14.85	425	7.75	220	16.82	0.036	22.73	6.06	0.566	19.42	50.46	-
FC	7/19/2005	25.25	12.54	12.71	428	7.59	209	15.17	0.026	20.41	4.98	0.620	18.14	44.18	-
FC	7/26/2005	34.12	14.55	19.56	448	7.59	224	14.78	0.039	19.43	5.66	0.618	18.46	46.70	-
FC	8/2/2005	50.55	9.81	40.74	457	7.55	225	16.74	0.039	22.07	6.54	0.681	19.40	47.77	-
FC	8/9/2005	23.53	14.24	9.29	461	7.51	225	17.87	0.037	22.79	6.76	0.838	19.66	48.83	-
FC	8/16/2005	23.06	13.26	9.80	487	7.69	248	17.26	0.039	23.19	6.43	0.420	21.18	53.22	-
FC	8/23/2005	21.66	10.53	11.12	471	7.66	237	20.62	0.048	23.55	6.50	0.894	20.87	51.63	-
FC	8/30/2005	22.60	14.00	8.60	467	7.56	239	18.04	0.049	23.95	6.66	0.854	20.45	52.82	-
FC	9/6/2005	16.78	11.76	5.02	470	7.60	236	19.20	0.044	25.30	6.77	0.776	20.71	50.92	-
FC	9/13/2005	17.10	10.35	6.75	478	7.76	236	18.87	0.033	24.04	7.17	0.977	20.66	51.29	-
FC	9/20/2005	16.59	9.99	6.60	486	7.59	245	17.08	0.028	23.93	6.52	0.923	20.40	54.63	-
FC	9/27/2005	15.23	8.95	6.28	493	7.64	253	17.76	0.031	23.96	6.31	0.858	20.30	57.48	-
FC	10/4/2005	15.17	10.51	4.65	492	7.66	252	17.94	0.026	24.88	6.38	1.135	19.98	58.10	-
GR	4/5/2005	13.40	3.43	9.97	-	-	-	-	-	-	-	-	-	-	-
GR	4/12/2005	19.45	5.07	14.38	-	-	-	-	-	-	-	-	-	-	-
GR	4/19/2005	18.92	4.77	14.15	-	-	-	-	-	-	-	-	-	-	-
GR	4/26/2005	16.56	5.48	11.07	-	-	-	-	-	-	-	-	-	-	-
GR	5/3/2005	13.20	4.30	8.91	-	-	-	-	-	-	-	-	-	-	-
GR	5/10/2005	29.34	7.13	22.21	593	7.64	267	17.54	1.383	85.49	8.31	1.412	23.23	69.06	-
GR	5/17/2005	25.27	8.46	16.81	560	7.74	258	16.51	1.301	75.59	7.60	1.142	22.29	63.87	-
GR	5/24/2005	46.33	9.23	37.09	554	7.78	251	20.15	1.213	69.25	9.01	1.231	21.45	61.74	-
GR	5/31/2005	41.78	9.19	32.60	574	7.79	255	16.95	1.203	77.73	7.78	1.125	22.44	65.86	-
GR	6/7/2005	55.01	9.88	45.13	594	7.76	259	17.73	1.199	83.82	8.39	1.485	22.92	67.73	-
GR	6/9/2005	49.47	12.29	37.18	560	7.75	263	18.45	1.366	73.34	7.86	1.484	18.93	62.67	-
GR	6/14/2005	131.01	17.91	113.10	561	7.61	216	18.77	3.640	82.22	7.63	2.676	20.50	62.54	-

Site	Date	TP	DP	PP	Specific	pH	Alkalinity	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Chloro-
					Cond.		as HCO_3^-								phyll *a*
		(μgL^{-1})	(μgL^{-1})	(μgL^{-1})	(mScm^{-2})	(pH)	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(μgL^{-1})
GR	6/21/2005	55.90	11.19	44.71	551	7.79	242	16.69	1.120	72.73	8.42	1.180	21.18	61.87	-
GR	6/28/2005	37.02	10.88	26.14	586	7.84	256	18.45	1.106	78.73	9.28	1.484	21.66	61.61	-
GR	7/5/2005	28.28	10.44	17.84	619	7.85	263	20.47	1.096	88.01	10.07	1.574	23.07	70.12	-
GR	7/12/2005	19.77	10.93	8.84	629	7.77	263	20.77	0.957	87.86	10.66	1.324	23.49	72.38	-
GR	7/19/2005	53.04	11.02	42.03	594	7.61	240	22.02	1.297	88.09	8.95	1.987	21.97	68.39	-
GR	7/26/2005	52.41	10.89	41.51	562	7.65	242	17.04	0.940	70.27	8.05	1.953	21.81	63.73	-
GR	8/2/2005	23.84	6.93	16.91	594	7.63	257	19.76	0.980	75.43	9.41	1.669	22.50	67.73	-
GR	8/9/2005	21.67	9.85	11.82	614	7.70	268	20.54	0.946	79.80	9.98	1.880	23.18	70.79	-
GR	8/16/2005	31.00	10.05	20.95	604	7.72	269	20.28	1.077	80.59	9.77	2.084	24.02	70.39	-
GR	8/23/2005	20.14	8.51	11.63	607	7.73	268	21.60	1.054	82.53	9.67	1.867	24.17	71.45	-
GR	8/30/2005	17.37	11.30	6.07	619	7.69	279	20.94	0.998	84.35	9.45	1.802	23.49	75.98	-
GR	9/6/2005	15.94	9.42	6.52	616	7.72	281	21.73	0.964	82.07	10.43	1.935	23.05	73.22	-
GR	9/13/2005	19.29	8.32	10.97	619	7.64	276	20.05	0.837	80.78	10.05	1.866	23.31	73.96	-
GR	9/20/2005	18.39	8.79	9.59	615	7.62	271	19.26	0.989	79.50	9.80	1.508	23.47	73.46	-
GR	9/27/2005	24.99	10.17	14.82	615	7.66	272	20.68	1.152	86.77	9.64	2.178	23.42	72.72	-
GR	10/4/2005	20.51	9.31	11.20	618	7.64	267	20.07	1.073	87.25	9.50	2.244	23.16	73.96	-
GR	4/4/2006	19.90	6.48	13.42	556	7.84	240	17.63	1.631	80.59	8.47	2.152	22.85	72.15	-
GR	4/11/2006	28.42	7.83	20.58	568	7.79	248	17.87	1.816	84.28	7.90	1.682	24.65	73.77	-
GR	4/18/2006	24.19	7.38	16.81	563	7.70	241	18.64	1.458	78.97	8.54	2.303	27.68	70.93	-
GR	4/25/2006	25.69	6.72	18.97	587	7.75	262	17.77	1.424	85.63	8.90	2.352	25.16	73.91	-
GR	5/2/2006	41.67	11.61	30.06	567	7.62	251	17.59	1.344	83.17	8.69	2.574	24.78	74.18	-
GR	5/9/2006	28.52	6.75	21.78	612	7.69	299	18.22	1.373	91.47	8.25	1.828	26.46	76.36	-
GR	5/16/2006	41.94	9.52	32.41	601	7.56	234	17.68	2.640	94.31	7.39	2.011	24.35	73.54	-
GR	5/23/2006	28.83	6.65	22.19	589	7.67	237	17.99	1.512	81.94	7.95	1.635	24.65	71.94	-
GR	5/30/2006	45.67	9.18	36.49	603	7.65	250	17.66	1.233	82.18	8.12	1.550	25.10	72.89	-
GR	6/6/2006	76.04	12.78	63.26	602	7.51	244	18.25	1.985	87.03	7.95	1.942	25.03	72.21	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
GR	6/13/2006	50.54	10.67	39.88	610	7.56	243	18.40	1.837	86.03	8.34	1.851	25.63	72.49	-
GR	6/20/2006	48.00	15.08	32.93	621	7.64	258	18.87	1.659	85.04	8.80	1.897	24.56	72.72	-
GR	6/27/2006	40.21	11.25	28.95	631	7.64	255	19.36	1.589	85.46	9.11	1.998	24.95	73.18	-
GR	7/4/2006	41.88	12.09	29.79	648	7.64	263	19.17	1.584	88.78	8.86	1.924	25.41	76.69	-
GR	7/11/2006	22.50	10.35	12.15	686	7.63	277	21.65	1.269	92.30	10.05	1.772	26.15	81.82	-
GR	7/18/2006	46.31	11.53	34.77	654	7.55	260	19.30	1.175	88.25	8.94	2.315	25.42	77.63	-
GR	7/25/2006	28.76	11.20	17.56	652	7.71	268	20.06	1.108	80.33	9.81	1.912	25.55	75.91	-
GR	8/1/2006	52.49	16.55	35.94	592	7.72	237	19.51	0.954	70.23	9.18	1.881	23.47	65.32	-
GR	8/9/2006	47.64	7.35	40.29	590	7.72	238	18.79	0.908	67.50	9.06	1.746	23.36	64.26	-
GR	8/15/2006	22.32	11.38	10.94	665	7.76	275	21.23	0.980	83.61	9.69	1.586	25.08	74.80	-
GR	8/22/2006	21.37	11.53	9.84	676	7.77	273	20.88	0.956	79.80	9.85	1.617	25.59	80.15	-
GR	8/29/2006	89.97	16.99	72.98	683	7.64	238	22.66	1.599	110.85	9.17	3.132	24.87	80.17	-
GR	9/5/2006	27.39	9.64	17.75	670	7.81	268	20.05	1.129	86.50	9.34	1.966	25.40	75.75	-
GR	9/12/2006	33.82	9.29	24.53	677	7.71	265	20.63	1.329	84.35	9.34	2.199	25.20	76.15	-
GR	9/19/2006	25.34	12.89	12.45	674	7.77	272	19.81	1.133	86.77	9.05	2.028	25.43	75.51	-
GR	9/26/2006	34.02	10.68	23.34	689	7.59	257	20.54	1.556	95.30	8.30	2.481	26.38	76.83	-
KA	4/5/2005	24.84	9.97	14.87	-	-	-	-	-	-	-	-	-	-	-
KA	4/12/2005	58.50	9.31	49.18	-	-	-	-	-	-	-	-	-	-	-
KA	4/19/2005	63.50	11.02	52.48	-	-	-	-	-	-	-	-	-	-	-
KA	4/26/2005	61.32	8.81	52.52	-	-	-	-	-	-	-	-	-	-	-
KA	5/3/2005	50.91	8.11	42.80	-	-	-	-	-	-	-	-	-	-	-
KA	5/10/2005	71.14	9.47	61.67	593	7.64	267	17.54	1.383	85.49	8.31	1.412	23.23	69.06	-
KA	5/17/2005	58.74	14.28	44.46	673	8.10	287	60.46	1.244	50.56	29.30	1.965	21.60	69.99	-
KA	5/24/2005	74.19	16.90	57.28	664	8.12	287	57.42	1.128	47.32	29.00	1.945	20.98	68.26	-
KA	5/31/2005	90.91	12.97	77.95	688	8.28	286	61.32	1.036	49.87	31.48	2.095	22.23	70.52	-
KA	6/7/2005	91.39	13.71	77.67	640	8.19	242	62.58	0.895	46.49	32.91	2.561	20.24	58.94	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KA	6/9/2005	89.93	15.88	74.04	623	8.33	246	64.64	0.797	48.90	31.71	2.406	20.24	47.50	-
KA	6/14/2005	163.03	39.78	123.25	504	7.84	183	46.54	1.283	35.39	22.95	2.404	15.36	46.57	-
KA	6/21/2005	126.92	15.91	111.01	671	8.33	284	62.26	0.830	46.50	31.02	1.942	20.82	66.26	-
KA	6/28/2005	89.81	17.79	72.02	696	8.17	261	72.66	0.927	52.00	35.85	2.900	21.39	56.95	-
KA	7/5/2005	108.73	19.52	89.21	713	8.31	257	80.74	0.659	51.46	41.46	2.861	22.39	62.27	-
KA	7/12/2005	86.18	16.43	69.74	701	8.21	253	76.27	0.810	51.93	37.62	3.023	21.87	62.94	-
KA	7/19/2005	113.38	36.44	76.94	671	7.93	247	70.64	1.043	48.37	33.49	2.535	20.50	62.40	-
KA	7/26/2005	109.66	36.98	72.69	628	7.93	242	56.23	0.997	41.70	26.04	2.348	21.55	51.23	-
KA	8/2/2005	86.72	9.30	77.43	678	8.17	254	72.47	0.725	47.55	32.99	3.175	20.71	63.60	-
KA	8/9/2005	91.93	13.23	78.70	667	8.21	242	74.42	0.588	48.63	33.74	3.067	21.55	58.01	-
KA	8/16/2005	70.69	29.98	40.71	715	8.04	261	80.76	1.112	51.88	36.36	3.387	23.07	63.87	-
KA	8/23/2005	67.16	27.22	39.94	704	8.05	263	81.57	1.188	51.44	32.88	2.964	22.13	67.99	-
KA	8/30/2005	56.17	29.18	26.99	710	7.90	260	80.85	1.195	52.02	35.36	3.025	22.29	66.79	-
KA	9/6/2005	47.55	24.64	22.91	723	8.04	267	83.30	1.038	53.36	35.93	2.609	22.95	65.66	-
KA	9/13/2005	58.94	31.77	27.16	713	7.91	252	88.37	0.972	50.76	39.00	3.175	22.79	61.08	-
KA	9/20/2005	75.56	27.58	47.97	744	7.86	257	92.47	1.051	51.45	41.77	3.267	22.69	63.92	-
KA	9/27/2005	90.37	35.80	54.57	720	7.89	258	88.71	1.123	52.37	37.61	3.354	21.54	64.30	-
KA	10/4/2005	48.95	33.44	15.51	727	7.87	266	82.40	1.370	53.46	36.39	3.189	22.48	66.65	-
KA	4/4/2006	56.62	17.22	39.41	646	8.10	261	52.35	1.493	60.11	24.78	2.485	21.88	76.22	4.536
KA	4/11/2006	63.75	16.75	47.00	617	8.07	253	48.06	1.413	57.72	21.50	1.908	21.13	73.37	6.300
KA	4/18/2006	68.61	21.78	46.83	648	7.96	267	49.11	1.198	60.20	22.96	2.678	22.50	77.04	5.460
KA	4/25/2006	56.41	23.34	33.08	694	8.04	288	58.26	1.200	60.52	27.92	2.825	24.33	81.16	5.720
KA	5/2/2006	54.49	26.56	27.93	698	7.74	280	65.81	1.445	58.25	29.05	2.944	25.16	78.41	4.431
KA	5/9/2006	77.91	12.58	65.34	684	8.22	272	61.03	0.963	56.30	27.07	2.259	24.35	74.95	2.520
KA	5/16/2006	85.04	32.91	52.13	573	7.79	235	39.46	1.293	45.56	18.30	1.810	19.64	66.71	1.487
KA	5/23/2006	93.03	34.11	58.92	598	8.08	239	43.45	1.389	51.11	19.55	1.993	21.18	73.71	2.365

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KA	5/30/2006	68.65	30.09	38.55	704	7.95	279	55.35	1.197	54.16	24.32	1.919	23.77	78.36	3.587
KA	6/6/2006	93.83	42.06	51.77	695	7.86	279	55.09	1.516	53.30	24.89	1.978	23.77	75.49	2.646
KA	6/13/2006	87.34	31.38	55.96	713	7.91	263	63.30	1.249	54.04	28.04	2.578	24.66	73.03	5.376
KA	6/20/2006	91.62	55.64	35.98	715	7.87	262	66.11	1.515	52.77	29.57	2.456	24.05	69.29	2.184
KA	6/27/2006	100.29	52.76	47.53	681	7.88	249	58.03	1.737	47.81	26.90	2.513	21.55	68.05	2.289
KA	7/4/2006	81.21	51.75	29.45	718	7.91	253	65.96	1.762	51.00	28.75	2.497	22.65	70.05	2.268
KA	7/11/2006	84.10	54.40	29.70	761	7.89	264	73.95	1.839	52.57	32.78	2.857	23.10	74.31	2.352
KA	7/18/2006	103.47	55.47	48.00	684	7.88	231	64.78	1.434	45.21	28.69	2.543	21.54	64.05	1.995
KA	7/25/2006	82.97	54.50	28.47	754	8.02	265	72.32	1.365	49.74	33.12	3.025	24.00	70.52	2.226
KA	8/1/2006	81.28	56.92	24.36	728	7.95	237	79.20	1.386	49.20	34.41	3.213	22.40	61.90	2.646
KA	8/9/2006	85.61	53.11	32.50	700	7.99	245	65.05	1.281	44.17	28.78	2.477	22.86	63.28	2.352
KA	8/15/2006	66.23	46.55	19.68	712	8.00	238	73.46	1.173	47.22	31.49	2.708	24.07	59.10	1.197
KA	8/22/2006	68.85	52.91	15.94	753	8.05	244	78.62	1.237	49.03	33.60	2.631	24.02	64.69	1.848
KA	8/29/2006	80.87	54.88	25.98	727	7.93	243	71.48	1.428	47.48	31.14	2.724	22.82	63.63	1.974
KA	9/5/2006	64.87	44.49	20.38	752	8.11	268	67.57	1.308	47.96	29.86	2.566	23.60	70.44	1.260
KA	9/12/2006	68.19	46.16	22.02	794	8.01	270	78.05	1.735	49.24	33.21	2.596	24.13	74.69	1.050
KA	9/19/2006	95.40	50.08	45.32	713	7.99	256	57.89	1.377	48.65	25.66	2.609	21.32	70.68	1.411
KA	9/26/2006	68.78	37.43	31.35	779	7.92	279	63.41	1.668	55.88	27.59	2.499	24.41	77.32	0.840
KB	4/5/2005	19.45	8.01	11.44	-	-	-	-	-	-	-	-	-	-	-
KB	4/12/2005	52.78	9.31	43.47	-	-	-	-	-	-	-	-	-	-	-
KB	4/19/2005	29.78	7.57	22.21	-	-	-	-	-	-	-	-	-	-	-
KB	4/26/2005	27.00	7.22	19.77	-	-	-	-	-	-	-	-	-	-	-
KB	5/3/2005	22.27	6.52	15.75	-	-	-	-	-	-	-	-	-	-	-
KB	5/10/2005	44.24	10.99	33.25	657	7.72	297	43.69	1.114	56.29	17.46	1.456	22.71	75.04	-
KB	5/17/2005	39.82	17.19	22.63	630	7.91	293	40.43	1.182	49.93	16.45	1.467	21.71	73.58	-
KB	5/24/2005	54.15	19.56	34.59	639	7.93	297	39.93	1.145	48.35	16.42	1.387	21.13	72.78	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. $(mScm^{-2})$	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KB	5/31/2005	48.40	18.16	30.23	666	7.98	272	43.10	1.255	52.09	16.87	1.524	22.60	74.51	-
KB	6/7/2005	43.49	17.70	25.79	692	7.95	296	53.26	1.120	53.18	21.72	1.658	22.60	72.92	-
KB	6/9/2005	31.97	21.35	10.62	668	7.94	288	46.41	1.141	50.76	17.92	1.441	21.71	71.45	-
KB	6/14/2005	88.83	32.75	56.08	604	7.87	261	39.30	1.118	42.46	14.99	1.536	19.30	67.59	-
KB	6/21/2005	46.11	31.97	14.14	668	8.00	289	43.04	1.407	52.67	17.43	1.545	21.50	73.31	-
KB	6/28/2005	43.94	23.02	20.91	673	7.94	283	48.28	0.948	56.03	19.25	1.592	22.13	71.45	-
KB	7/5/2005	48.64	26.43	22.22	648	7.95	262	43.76	1.091	52.09	17.53	1.641	21.18	74.65	-
KB	7/12/2005	41.13	26.95	14.18	663	7.86	275	46.94	1.062	52.67	18.91	1.213	21.92	69.99	-
KB	7/19/2005	69.14	29.66	39.49	652	7.73	267	50.71	0.942	51.63	19.73	1.182	20.92	69.46	-
KB	7/26/2005	68.31	35.07	33.24	630	7.77	269	38.62	1.042	46.15	15.21	1.871	19.98	70.12	-
KB	8/2/2005	50.72	28.57	22.15	663	7.78	285	44.55	0.966	50.17	16.76	1.731	21.71	74.51	-
KB	8/9/2005	39.75	22.01	17.73	683	7.82	285	51.63	0.919	54.67	20.01	1.741	22.44	73.58	-
KB	8/16/2005	40.46	27.28	13.18	692	7.90	293	53.97	1.007	56.27	21.30	1.984	23.91	74.78	-
KB	8/23/2005	38.51	25.19	13.31	674	7.89	285	52.36	1.059	55.62	18.83	1.846	23.18	73.85	-
KB	8/30/2005	29.69	20.41	9.28	686	7.79	281	57.75	0.913	57.38	21.53	1.723	22.86	75.04	-
KB	9/6/2005	21.29	15.77	5.52	670	7.80	282	54.75	1.000	53.93	20.35	1.482	22.95	71.36	-
KB	9/13/2005	21.82	12.54	9.28	671	7.84	268	56.65	0.934	52.71	21.39	1.583	22.95	69.00	-
KB	9/20/2005	21.99	14.99	7.00	688	7.74	282	51.29	1.190	51.83	20.05	1.910	22.22	74.21	-
KB	9/27/2005	28.30	16.27	12.03	684	7.83	281	53.81	1.128	55.14	20.34	2.025	22.38	75.69	-
KB	10/4/2005	24.82	15.51	9.31	673	7.80	287	51.11	1.182	54.14	19.18	1.828	22.12	74.46	-
KB	4/4/2006	35.66	16.71	18.95	611	7.97	260	37.97	1.495	65.10	14.25	2.103	21.94	79.92	-
KB	4/11/2006	43.65	15.61	28.04	568	7.88	229	34.27	1.524	63.16	13.24	2.244	19.84	74.32	-
KB	4/18/2006	36.19	14.75	21.44	638	7.87	272	39.14	1.197	65.53	16.43	2.435	22.50	82.82	-
KB	4/25/2006	35.76	13.10	22.67	674	7.88	295	43.84	1.207	63.64	17.08	2.067	24.52	86.43	-
KB	5/2/2006	51.69	15.22	36.47	648	7.83	279	44.06	1.170	61.37	18.59	1.955	24.20	83.37	-
KB	5/9/2006	41.39	14.29	27.10	675	7.88	286	44.27	1.180	59.76	16.59	1.245	24.41	80.18	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KB	5/16/2006	61.15	30.24	30.91	524	7.60	218	26.03	1.847	46.94	10.78	1.799	17.40	65.61	-
KB	5/23/2006	44.33	18.13	26.20	639	7.84	271	35.04	1.175	56.82	13.69	1.380	22.41	80.28	-
KB	5/30/2006	54.96	17.80	37.17	683	7.86	283	41.13	1.121	55.50	15.46	1.213	23.96	81.11	-
KB	6/6/2006	65.68	25.72	39.96	693	7.78	291	42.68	1.338	55.19	15.99	1.276	24.46	82.62	-
KB	6/13/2006	44.73	17.17	27.55	694	7.81	291	44.49	1.245	55.16	16.43	1.392	24.85	81.52	-
KB	6/20/2006	56.66	23.90	32.76	651	7.79	271	40.22	1.130	48.97	15.22	1.422	22.14	74.73	-
KB	6/27/2006	75.52	31.34	44.18	640	7.73	263	35.28	1.496	51.66	13.60	2.082	21.04	76.06	-
KB	7/4/2006	100.79	27.15	73.63	629	7.80	253	38.20	1.284	45.66	14.42	1.427	20.04	71.55	-
KB	7/11/2006	37.18	22.33	14.85	714	7.83	291	43.70	1.309	52.94	16.03	1.309	22.97	83.19	-
KB	7/18/2006	71.24	29.01	42.24	639	7.76	257	42.32	1.079	44.99	16.07	1.632	21.91	73.95	-
KB	7/25/2006	36.94	24.83	12.10	716	7.91	284	46.44	1.150	51.57	18.00	1.673	24.32	80.34	-
KB	8/1/2006	48.91	32.22	16.69	708	7.91	284	45.19	1.205	49.43	16.64	1.639	23.91	77.89	-
KB	8/8/2006	37.19	24.92	12.27	720	8.01	291	47.62	1.141	48.57	17.34	1.570	23.93	78.93	-
KB	8/15/2006	34.10	21.98	12.11	729	8.00	286	50.30	1.166	51.83	18.58	1.378	23.71	76.92	-
KB	8/22/2006	32.22	23.40	8.82	723	7.99	276	49.24	1.160	51.59	18.79	1.572	23.89	78.88	-
KB	8/29/2006	65.97	26.09	39.88	695	7.87	277	44.43	1.160	46.40	16.67	1.633	22.42	75.22	-
KB	9/5/2006	32.98	19.34	13.64	730	8.09	284	46.50	1.244	50.54	16.95	1.483	22.95	78.96	-
KB	9/12/2006	31.65	18.63	13.01	741	7.98	288	49.11	1.282	50.62	18.44	1.374	24.33	79.23	-
KB	9/19/2006	47.26	30.99	16.27	728	7.94	277	44.34	1.384	61.81	17.07	1.948	22.70	80.45	-
KB	9/26/2006	34.19	19.37	14.82	747	7.93	291	45.56	1.352	54.56	17.50	1.661	24.18	82.74	-
KC	4/5/2005	26.31	9.31	16.99	-	-	-	-	-	-	-	-	-	-	-
KC	4/12/2005	63.56	14.22	49.35	-	-	-	-	-	-	-	-	-	-	-
KC	4/19/2005	44.09	11.02	33.07	-	-	-	-	-	-	-	-	-	-	-
KC	4/26/2005	58.95	6.59	52.36	-	-	-	-	-	-	-	-	-	-	-
KC	5/3/2005	40.09	7.16	32.93	-	-	-	-	-	-	-	-	-	-	-
KC	5/10/2005	56.52	9.61	46.91	655	7.90	295	49.49	0.742	51.41	20.92	1.499	21.66	71.45	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KC	5/17/2005	57.12	13.15	43.97	638	8.13	291	48.10	0.866	47.77	20.70	1.616	20.92	70.25	-
KC	5/24/2005	59.63	14.24	45.39	631	8.07	286	44.68	0.848	44.80	19.49	1.443	20.45	69.86	-
KC	5/31/2005	54.85	12.02	42.83	647	8.23	291	46.64	0.716	46.42	20.01	1.491	21.50	70.92	-
KC	6/7/2005	67.13	11.87	55.26	611	8.25	248	50.73	0.326	48.23	21.92	1.570	22.08	60.14	-
KC	6/9/2005	94.77	15.88	78.89	574	8.32	247	49.30	0.301	42.16	20.70	1.588	19.82	55.88	-
KC	6/14/2005	101.95	18.22	83.73	602	8.25	254	47.84	0.386	39.29	19.53	1.584	19.35	53.76	-
KC	6/21/2005	84.75	15.41	69.34	635	7.98	286	43.50	0.770	42.08	19.47	1.647	20.29	69.06	-
KC	6/28/2005	95.71	19.14	76.57	622	7.94	254	51.94	0.147	46.53	21.96	1.625	21.39	56.02	-
KC	7/5/2005	103.18	19.52	83.65	637	8.17	256	54.35	0.242	46.20	23.37	1.697	20.92	61.74	-
KC	7/12/2005	111.87	21.27	90.60	600	7.95	234	52.10	0.142	47.03	23.60	1.357	21.24	55.22	-
KC	7/19/2005	106.60	41.01	65.58	604	7.76	237	52.62	0.603	39.11	21.29	1.586	19.24	59.88	-
KC	7/26/2005	92.17	22.51	69.66	580	7.91	243	40.86	0.515	38.14	17.63	1.565	18.20	62.00	-
KC	8/2/2005	66.27	11.66	54.60	616	7.91	258	46.27	0.405	42.24	19.87	1.511	20.45	64.13	-
KC	8/9/2005	86.36	17.28	69.08	609	7.87	235	54.76	0.118	44.69	23.12	1.727	21.29	56.68	-
KC	8/16/2005	85.22	14.44	70.78	639	8.05	251	59.82	0.173	46.44	25.45	1.799	22.50	61.21	-
KC	8/23/2005	77.44	13.40	64.04	635	8.12	250	61.20	0.265	48.18	23.48	1.624	22.65	61.87	-
KC	8/30/2005	62.41	13.33	49.09	633	7.94	249	61.77	0.241	49.01	24.87	1.828	21.92	63.73	-
KC	9/6/2005	55.24	13.77	41.47	613	7.91	230	65.31	0.054	49.64	26.36	1.787	22.33	53.89	-
KC	9/13/2005	64.50	13.38	51.12	625	7.84	228	65.62	0.081	48.05	27.58	1.794	22.38	55.01	-
KC	9/20/2005	63.96	17.59	46.37	658	7.93	260	62.02	0.482	45.29	26.15	1.609	22.01	65.66	-
KC	9/27/2005	53.24	20.28	32.95	679	7.98	276	62.03	0.675	48.23	25.42	2.018	21.86	70.61	-
KC	10/4/2005	35.68	10.51	25.16	643	8.03	267	57.79	0.546	47.27	23.65	1.872	21.54	66.53	-
KC	4/4/2006	62.49	12.52	49.97	621	8.11	267	42.38	1.194	61.19	18.08	2.025	22.31	79.37	8.778
KC	4/11/2006	46.08	14.32	31.77	587	7.94	245	37.57	1.056	56.45	15.78	1.422	20.33	74.86	4.133
KC	4/18/2006	56.78	16.47	40.31	622	7.93	265	41.96	0.919	59.40	16.74	1.750	21.86	78.55	8.001
KC	4/25/2006	55.74	13.60	42.14	668	7.96	292	47.46	0.925	58.95	22.24	3.126	23.70	83.37	9.723

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chloro-phyll *a* (μgL^{-1})
KC	5/2/2006	46.76	15.39	31.38	656	7.95	290	48.82	0.851	57.40	20.64	2.153	24.71	79.79	6.468
KC	5/9/2006	63.51	11.38	52.13	663	8.07	288	46.29	0.684	53.71	19.27	1.479	23.66	79.33	9.954
KC	5/16/2006	55.14	29.74	25.40	519	7.67	223	28.49	1.207	40.11	12.45	1.684	17.75	63.81	1.848
KC	5/23/2006	55.57	21.00	34.56	608	7.84	257	34.66	1.049	49.31	14.83	1.635	20.57	74.81	4.809
KC	5/30/2006	46.18	9.35	36.83	671	8.08	279	43.68	0.662	51.95	18.32	1.330	23.27	79.19	10.269
KC	6/6/2006	62.61	15.69	46.92	658	8.00	284	44.06	0.737	45.81	18.11	1.498	22.96	77.68	11.802
KC	6/13/2006	81.86	12.72	69.14	677	8.01	283	47.69	0.585	48.54	19.81	1.476	23.64	77.27	16.191
KC	7/4/2006	91.58	14.60	76.98	676	8.16	274	46.63	0.761	48.30	18.94	1.569	21.55	75.94	21.441
KC	7/11/2006	70.26	12.54	57.72	664	8.09	260	46.88	0.635	47.51	19.16	1.602	21.75	73.21	16.905
KC	7/18/2006	80.57	16.62	63.95	667	7.96	254	50.82	0.386	47.17	20.82	1.752	22.99	68.81	16.485
KC	7/25/2006	87.40	16.65	70.75	663	8.08	255	60.20	0.302	44.87	21.21	1.752	23.30	68.32	21.168
KC	8/1/2006	122.67	16.21	106.46	658	7.85	242	53.33	0.250	43.70	21.92	1.710	22.65	62.87	20.916
KC	8/8/2006	88.42	11.16	77.26	638	8.40	243	50.20	0.211	40.08	20.59	1.626	21.82	63.65	20.160
KC	8/15/2006	116.70	11.72	104.98	696	8.22	265	59.30	0.299	45.75	24.12	1.458	22.93	66.98	20.790
KC	8/22/2006	87.51	13.06	74.45	680	8.14	235	61.76	0.188	46.73	25.08	1.518	23.82	62.67	19.068
KC	8/29/2006	73.92	20.13	53.78	695	8.08	262	53.61	0.557	42.90	22.08	1.575	21.97	70.31	14.726
KC	9/5/2006	64.87	12.44	52.43	693	8.32	269	50.16	0.526	45.63	20.64	1.606	22.82	73.49	18.312
KC	9/12/2006	56.67	17.96	38.71	730	8.17	278	54.71	0.614	45.07	23.17	1.399	23.74	72.96	13.650
KC	9/19/2006	60.54	35.47	25.07	671	7.91	257	42.84	0.999	48.72	18.16	1.890	20.33	72.13	4.309
KC	9/26/2006	53.10	27.89	25.22	735	7.93	283	50.02	0.925	49.19	21.13	1.703	23.17	77.68	3.881
KD	4/5/2005	30.23	8.99	21.24	-	-	-	-	-	-	-	-	-	-	-
KD	4/12/2005	70.59	9.15	61.44	-	-	-	-	-	-	-	-	-	-	-
KD	4/19/2005	40.47	9.87	30.60	-	-	-	-	-	-	-	-	-	-	-
KD	4/26/2005	68.44	6.91	61.53	-	-	-	-	-	-	-	-	-	-	-
KD	5/3/2005	79.71	7.16	72.55	-	-	-	-	-	-	-	-	-	-	-
KD	5/10/2005	93.22	8.65	84.57	629	8.00	257	62.55	0.517	53.03	31.88	2.197	22.02	58.01	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KD	5/17/2005	80.08	12.50	67.58	658	8.36	264	64.14	0.655	53.07	32.40	2.293	21.81	63.34	-
KD	5/24/2005	64.64	12.68	51.96	650	8.22	264	62.47	0.777	51.38	31.45	2.098	21.03	62.67	-
KD	5/31/2005	49.81	11.55	38.27	623	8.36	244	62.54	0.494	49.83	31.96	2.285	21.60	56.95	-
KD	6/7/2005	56.23	8.34	47.89	606	8.11	218	64.17	0.233	49.35	32.18	2.204	21.81	49.50	-
KD	6/9/2005	52.44	9.32	43.11	605	8.04	239	68.36	0.226	49.31	33.43	2.251	22.23	55.35	-
KD	6/14/2005	70.56	14.48	56.08	596	8.12	211	66.74	0.157	47.49	32.56	2.305	20.77	45.77	-
KD	6/21/2005	81.37	16.08	65.29	604	8.01	245	55.73	0.563	43.83	28.10	2.024	19.66	55.62	-
KD	6/28/2005	75.48	17.12	58.36	578	7.73	203	62.03	0.022	45.89	32.23	2.155	20.56	42.18	-
KD	7/5/2005	74.56	16.33	58.24	645	7.99	226	71.99	0.215	48.33	33.39	2.362	21.55	52.29	-
KD	7/12/2005	62.65	17.60	45.05	630	7.83	211	74.39	0.160	48.71	37.02	2.817	21.45	46.57	-
KD	7/19/2005	89.99	14.91	75.08	632	7.49	208	78.24	0.175	47.98	37.51	2.921	21.50	50.69	-
KD	7/26/2005	76.90	15.03	61.87	604	7.92	214	64.50	0.375	43.13	29.84	2.713	19.24	61.47	-
KD	8/2/2005	76.41	14.88	61.54	596	7.75	210	60.75	0.309	44.35	29.26	2.910	19.72	50.16	-
KD	8/23/2005	78.95	14.24	64.71	676	8.03	223	82.70	0.437	50.20	36.12	3.186	22.23	58.15	-
KD	8/30/2005	46.56	16.87	29.69	677	7.92	232	84.55	0.550	52.84	36.51	3.208	22.08	57.61	-
KD	9/6/2005	46.54	15.27	31.27	686	8.00	229	87.88	0.603	53.59	38.60	3.375	22.48	54.88	-
KD	9/13/2005	70.58	15.92	54.66	686	7.80	230	88.14	0.489	51.46	39.68	3.166	22.64	53.64	-
KD	9/20/2005	71.76	15.19	56.57	704	7.86	235	89.06	0.645	50.56	41.07	3.304	22.48	56.62	-
KD	9/27/2005	55.50	14.53	40.97	691	8.09	240	90.59	0.660	53.24	38.95	3.234	22.12	57.11	-
KD	10/4/2005	40.50	11.03	29.47	681	7.99	203	83.47	0.754	51.69	36.57	3.164	21.86	58.23	-
KD	4/4/2006	52.93	10.51	42.43	659	8.26	267	54.99	1.440	64.06	26.55	2.773	22.56	78.82	13.461
KD	4/11/2006	84.82	10.59	74.23	618	8.24	251	48.97	1.223	58.60	22.21	2.079	21.69	74.05	13.839
KD	4/18/2006	65.85	11.49	54.36	623	8.24	256	49.15	1.063	59.15	23.52	2.911	21.69	74.59	15.288
KD	4/25/2006	69.84	10.75	59.10	649	8.34	265	54.43	0.811	61.45	27.63	3.014	23.07	74.73	18.522
KD	5/2/2006	71.08	11.77	59.30	645	8.27	260	59.05	0.661	60.43	29.66	2.777	23.76	72.83	17.766
KD	5/9/2006	49.96	9.83	40.13	663	8.24	256	60.99	0.766	57.74	27.95	2.215	24.10	69.77	13.839

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KD	5/16/2006	59.65	15.20	44.44	598	7.86	240	46.10	1.239	48.11	20.80	1.951	20.73	66.99	5.208
KD	5/23/2006	65.78	12.22	53.56	598	8.08	239	40.11	1.349	48.60	18.28	2.038	20.27	70.58	13.755
KD	5/30/2006	64.93	9.52	55.41	634	8.27	242	51.33	0.787	53.48	23.44	1.942	22.65	67.85	10.752
KD	6/6/2006	50.96	12.94	38.02	649	8.20	254	51.30	1.026	52.86	23.87	2.143	22.53	69.76	12.726
KD	6/13/2006	63.72	12.21	51.51	672	8.06	259	56.42	0.966	52.31	26.11	2.199	23.73	69.21	16.716
KD	6/20/2006	62.60	15.08	47.52	675	8.04	245	62.33	0.700	52.55	28.50	2.534	23.86	64.47	15.666
KD	6/27/2006	56.77	13.93	42.84	693	8.13	253	66.35	1.103	51.81	30.31	2.515	23.56	64.94	17.766
KD	7/4/2006	70.00	15.44	54.56	678	7.95	246	60.31	0.908	49.40	27.64	2.331	21.43	64.45	13.734
KD	7/11/2006	88.49	16.09	72.40	672	8.21	235	63.58	0.812	49.52	28.59	2.384	22.07	63.33	16.842
KD	7/18/2006	62.25	15.61	46.65	690	7.85	237	65.19	0.681	49.93	29.43	2.525	22.99	62.84	12.138
KD	7/25/2006	75.64	16.48	59.16	673	8.27	238	63.95	0.559	47.53	29.55	2.609	22.54	61.75	19.278
KD	8/1/2006	60.50	16.89	43.60	701	7.91	232	72.98	0.589	49.77	32.39	2.779	22.72	59.47	13.776
KD	8/9/2006	74.33	13.82	60.52	659	8.16	211	69.33	0.503	45.95	30.50	2.674	22.72	52.40	9.072
KD	8/15/2006	72.45	13.91	58.55	663	8.00	214	69.77	0.429	45.87	30.72	2.567	22.30	51.79	15.456
KD	8/22/2006	65.46	17.64	47.82	700	8.20	220	76.93	0.501	47.51	33.92	2.765	23.37	54.96	15.330
KD	8/29/2006	83.68	24.27	59.41	722	7.98	226	78.86	0.622	48.96	35.13	2.785	24.33	56.41	9.933
KD	9/5/2006	48.27	11.45	36.82	674	8.36	224	67.27	0.629	47.64	29.80	2.457	21.97	55.39	20.916
KD	9/12/2006	63.68	12.79	50.89	705	8.19	237	67.65	0.647	47.71	29.93	2.251	22.82	60.14	13.650
KD	9/19/2006	62.20	14.39	47.81	730	8.05	255	66.40	0.978	47.30	29.16	2.345	21.88	67.06	16.170
KD	9/26/2006	81.55	16.81	64.74	717	8.21	256	60.36	1.137	48.55	27.20	2.529	22.49	68.39	16.254
KE	4/5/2005	15.85	6.86	8.99	-	-	-	-	-	-	-	-	-	-	-
KE	4/12/2005	29.09	8.50	20.59	-	-	-	-	-	-	-	-	-	-	-
KE	4/19/2005	26.49	6.75	19.74	-	-	-	-	-	-	-	-	-	-	-
KE	4/26/2005	23.83	6.59	17.24	-	-	-	-	-	-	-	-	-	-	-
KE	5/3/2005	17.18	5.09	12.09	-	-	-	-	-	-	-	-	-	-	-
KE	5/10/2005	33.76	9.06	24.70	640	7.71	290	43.38	1.407	50.94	16.12	1.360	22.44	73.58	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KE	5/17/2005	40.31	13.63	26.68	630	7.93	290	40.29	1.493	47.57	15.41	1.335	21.97	73.31	-
KE	5/24/2005	49.30	15.65	33.65	624	7.94	293	39.82	1.381	44.67	15.59	1.291	20.61	71.19	-
KE	5/31/2005	46.82	15.33	31.49	647	8.00	289	41.25	1.508	48.96	15.80	1.308	21.71	73.85	-
KE	6/7/2005	40.27	13.10	27.17	656	7.93	280	44.58	1.374	48.89	16.76	1.487	22.13	71.32	-
KE	6/9/2005	35.41	15.73	19.68	661	7.90	294	48.27	1.260	47.41	17.66	1.449	17.62	69.99	-
KE	6/14/2005	92.58	29.32	63.27	588	7.86	260	36.93	1.226	38.87	13.92	1.404	19.14	64.80	-
KE	6/21/2005	40.71	18.28	22.44	652	8.03	292	42.63	1.556	49.27	16.49	1.353	21.87	72.25	-
KE	6/28/2005	31.96	18.97	12.99	644	7.95	270	46.32	1.198	49.07	17.97	1.472	21.81	67.19	-
KE	7/5/2005	42.08	23.23	18.85	636	7.97	267	42.87	1.269	48.35	16.22	1.540	21.39	68.13	-
KE	7/12/2005	38.29	22.27	16.02	654	7.88	271	46.14	1.240	50.27	17.48	0.889	22.29	69.99	-
KE	7/19/2005	68.30	24.91	43.38	620	7.74	257	44.88	1.273	45.25	15.46	1.042	20.56	66.40	-
KE	7/26/2005	67.04	31.89	35.15	609	7.75	258	36.72	1.189	44.75	14.33	1.835	19.56	68.66	-
KE	8/2/2005	42.60	21.81	20.79	646	7.80	279	41.88	1.168	47.39	15.45	1.612	21.34	72.78	-
KE	8/9/2005	34.17	18.97	15.20	654	7.84	274	46.55	1.144	48.98	17.21	1.955	21.87	71.45	-
KE	8/16/2005	30.15	19.85	10.30	655	7.90	275	47.10	1.356	48.23	16.74	1.615	23.07	71.05	-
KE	8/23/2005	34.97	18.79	16.18	635	7.89	267	49.56	1.363	47.63	16.41	1.765	22.13	70.52	-
KE	8/30/2005	24.63	18.56	6.07	649	7.78	270	51.74	1.218	50.30	18.15	1.498	22.18	70.92	-
KE	9/6/2005	18.95	13.27	5.69	644	7.80	270	52.40	1.184	50.29	18.74	1.412	22.59	68.63	-
KE	9/13/2005	14.73	9.84	4.89	644	7.80	261	53.59	1.073	48.56	19.65	1.269	22.53	66.77	-
KE	9/20/2005	17.79	9.99	7.80	657	7.72	282	49.29	1.409	47.37	18.25	1.540	21.80	72.97	-
KE	9/27/2005	21.16	15.92	5.23	654	7.82	278	48.90	1.434	47.87	17.26	1.922	21.96	73.22	-
KE	10/4/2005	22.92	12.24	10.69	651	7.78	285	48.33	1.381	48.12	17.21	1.502	21.80	72.47	-
KE	4/4/2006	37.51	12.69	24.82	620	7.97	275	39.47	1.698	57.26	14.59	1.709	22.81	81.85	-
KE	4/11/2006	35.06	10.43	24.64	627	7.97	272	40.48	1.719	59.40	14.62	1.305	22.56	83.79	-
KE	4/18/2006	37.05	11.84	25.22	649	7.85	279	40.46	1.450	57.03	13.15	1.807	23.00	83.10	-
KE	4/25/2006	33.08	7.72	25.35	661	7.88	295	42.66	1.445	56.18	16.16	1.863	24.14	84.76	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KE	5/2/2006	58.10	11.77	46.33	639	7.85	283	43.96	1.410	54.35	15.03	1.622	24.01	82.41	-
KE	5/9/2006	35.56	8.97	26.58	670	7.86	279	45.57	1.370	54.62	16.21	1.220	24.72	79.61	-
KE	5/16/2006	70.34	17.21	53.13	560	7.73	244	31.45	1.256	46.64	11.85	1.138	19.64	72.28	-
KE	5/23/2006	42.46	15.04	27.41	655	7.89	278	37.69	1.411	53.12	13.43	1.016	23.34	81.79	-
KE	5/30/2006	59.02	12.73	46.29	673	7.86	281	40.87	1.293	51.52	14.49	1.092	24.46	80.01	-
KE	6/6/2006	55.33	21.19	34.14	682	7.78	282	42.39	1.482	51.90	14.97	1.169	24.34	82.48	-
KE	6/13/2006	37.02	13.58	23.45	685	7.80	282	43.80	1.436	52.38	15.32	1.235	24.77	80.97	-
KE	6/20/2006	60.22	23.05	37.17	629	7.76	260	38.71	1.276	44.84	14.23	1.432	21.07	72.00	-
KE	6/27/2006	71.50	27.99	43.51	621	7.73	266	34.01	1.262	45.12	12.90	1.782	20.48	75.44	-
KE	7/4/2006	96.10	25.31	70.79	625	7.82	256	38.49	1.431	42.27	14.15	1.425	19.54	71.43	-
KE	7/11/2006	38.03	22.33	15.70	700	7.83	281	41.85	1.464	50.29	14.78	1.310	23.10	82.57	-
KE	7/18/2006	69.38	25.95	43.42	649	7.77	260	41.92	1.225	42.19	15.39	1.699	21.85	74.31	-
KE	7/25/2006	32.34	21.08	11.25	706	7.93	290	44.76	1.360	47.98	16.47	1.501	24.39	80.34	-
KE	8/1/2006	43.12	28.47	14.65	691	7.92	276	43.12	1.363	46.11	15.58	1.472	23.53	75.90	-
KE	8/8/2006	33.88	20.95	12.93	704	8.00	281	45.04	1.311	45.74	15.99	1.465	23.29	77.42	-
KE	8/15/2006	32.08	19.63	12.45	709	7.98	281	47.77	1.390	48.51	16.79	1.352	23.93	75.80	-
KE	8/22/2006	32.22	20.18	12.04	701	7.98	271	46.41	1.371	46.67	16.69	1.443	23.04	76.92	-
KE	8/29/2006	67.63	25.43	42.20	685	7.86	272	43.19	1.322	42.64	15.81	1.629	22.36	74.29	-
KE	9/5/2006	28.71	17.20	11.50	724	8.08	288	45.81	1.393	47.64	16.31	1.404	23.87	81.25	-
KE	9/12/2006	25.97	14.79	11.18	725	7.99	287	47.74	1.446	45.97	17.20	1.355	24.07	76.82	-
KE	9/19/2006	33.31	18.87	14.44	729	8.03	291	47.04	1.410	47.57	16.82	1.452	23.58	79.85	-
KE	9/26/2006	23.80	12.72	11.07	731	7.95	287	45.59	1.561	46.24	16.61	1.406	24.46	80.21	-
KG	4/4/2006	47.06	14.70	32.36	621	7.92	263	43.82	1.203	63.70	18.14	1.850	21.63	79.10	-
KG	4/11/2006	66.51	16.59	49.92	578	7.91	235	37.93	1.301	60.76	15.81	1.797	19.84	74.45	-
KG	4/18/2006	59.86	16.47	43.40	646	7.84	270	45.21	0.976	63.21	17.12	2.052	21.75	80.06	-
KG	4/25/2006	59.60	17.63	41.97	695	7.90	289	53.85	1.042	62.75	23.24	2.577	23.82	84.21	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KG	5/2/2006	56.79	16.04	40.74	680	7.84	289	54.61	1.008	61.04	26.22	2.541	23.70	81.85	-
KG	5/9/2006	47.22	16.69	30.52	704	7.86	290	54.89	0.936	58.89	23.06	1.542	24.35	81.31	-
KG	5/16/2006	55.80	29.07	26.73	527	7.61	216	28.80	1.676	44.39	12.53	1.763	17.52	65.61	-
KG	5/23/2006	75.32	22.70	52.61	645	7.82	265	40.38	1.020	54.59	17.17	1.510	21.48	77.82	-
KG	5/30/2006	70.00	21.00	48.99	709	7.78	288	49.79	0.976	55.12	20.79	1.429	23.84	80.83	-
KG	6/6/2006	98.20	28.96	69.24	716	7.72	293	53.85	1.047	52.63	22.43	1.400	23.59	82.62	-
KG	6/13/2006	62.35	22.13	40.22	725	7.83	292	56.62	0.983	54.16	23.29	1.556	24.48	81.52	-
KG	6/20/2006	71.42	25.09	46.33	676	7.75	261	52.00	0.918	48.51	21.68	1.715	21.70	73.58	-
KG	6/27/2006	96.94	34.85	62.09	656	7.72	263	42.61	1.391	50.71	18.05	2.190	20.73	74.93	-
KG	7/4/2006	91.42	41.38	50.04	706	7.82	271	52.36	1.378	51.27	20.80	1.529	21.87	78.08	-
KG	7/11/2006	68.57	32.63	35.95	744	7.79	291	57.58	1.030	51.36	23.16	1.501	22.71	82.07	-
KG	7/18/2006	82.61	32.74	49.87	718	7.79	276	57.43	1.028	48.41	22.98	2.285	22.29	76.52	-
KG	7/25/2006	67.11	41.03	26.08	761	7.91	292	60.71	1.029	50.19	25.00	1.894	24.32	80.96	-
KG	8/1/2006	85.19	50.28	34.92	752	7.90	283	59.80	1.046	48.75	24.29	1.884	23.53	79.38	-
KG	8/8/2006	59.41	33.05	26.36	759	7.91	289	62.10	0.947	47.01	24.58	1.782	23.36	79.56	-
KG	8/15/2006	71.28	51.76	19.52	785	7.95	290	70.25	1.014	52.80	28.50	1.660	23.85	77.68	-
KG	8/22/2006	64.78	37.48	27.30	783	7.93	292	66.56	0.981	52.30	26.74	1.724	23.76	80.71	-
KG	8/29/2006	74.08	31.06	43.03	638	7.74	237	48.33	0.805	38.65	20.15	1.617	18.66	64.29	-
KG	9/5/2006	63.71	37.25	26.46	782	8.02	294	63.42	1.053	50.58	25.41	1.811	23.08	80.71	-
KG	9/12/2006	44.49	21.13	23.36	746	7.82	276	60.11	1.029	47.62	24.77	1.770	22.55	75.62	-
KG	9/19/2006	72.49	35.14	37.35	742	7.84	273	52.83	1.282	59.08	21.95	2.084	21.76	79.25	-
KG	9/26/2006	44.24	22.43	21.81	781	7.84	295	58.10	1.062	53.17	24.41	1.797	23.73	80.93	-
KK	4/4/2006	57.96	22.58	35.38	691	7.39	275	63.59	1.403	63.79	29.25	2.759	22.63	80.61	-
KK	4/11/2006	108.48	69.42	39.06	643	7.27	254	52.57	1.084	57.85	23.88	2.032	20.76	75.41	-
KK	4/18/2006	70.67	26.93	43.74	678	7.79	276	59.19	1.258	62.42	28.31	2.933	22.06	81.16	-
KK	4/25/2006	73.20	21.32	51.88	746	7.88	292	73.92	1.116	61.50	34.01	3.075	24.46	84.35	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KK	5/2/2006	99.66	41.67	57.99	700	7.76	273	74.22	1.285	54.66	35.55	3.216	23.13	78.14	-
KK	5/9/2006	71.05	16.35	54.70	734	8.02	292	70.19	0.841	56.43	31.39	2.400	24.28	80.04	-
KK	5/16/2006	62.15	33.58	28.57	561	7.61	222	40.76	1.301	41.49	18.97	2.027	17.81	64.92	-
KK	5/23/2006	69.53	30.30	39.23	665	7.73	263	50.86	1.246	52.20	23.36	1.936	21.18	75.90	-
KK	5/30/2006	57.83	15.94	41.90	738	7.88	287	65.16	1.109	53.79	28.83	1.948	23.59	80.56	-
KK	6/6/2006	98.04	33.97	64.07	746	7.77	287	68.76	1.271	50.31	31.44	2.207	23.40	79.05	-
KK	6/13/2006	108.56	31.21	77.36	784	7.83	296	82.35	1.281	52.73	35.92	3.073	24.54	81.11	-
KK	6/20/2006	108.59	37.82	70.77	771	7.84	283	77.40	0.990	53.89	34.38	2.325	24.11	75.30	-
KK	6/27/2006	95.43	43.22	52.21	670	7.71	254	56.64	1.433	45.12	26.19	2.490	19.85	70.05	-
KK	7/4/2006	120.54	31.67	88.86	708	7.93	258	63.20	1.187	46.66	27.64	2.140	20.98	71.68	-
KK	7/11/2006	111.78	31.62	80.16	794	7.80	279	78.60	1.209	54.12	35.64	2.477	22.65	78.37	-
KK	7/18/2006	102.28	28.84	73.45	685	7.64	233	69.17	0.673	45.43	31.46	2.598	21.04	64.42	-
KK	7/25/2006	98.65	24.32	74.33	758	7.92	254	75.72	0.752	49.75	34.27	2.810	23.37	69.90	-
KK	8/1/2006	133.06	34.61	98.45	743	7.71	250	78.05	0.736	47.44	33.78	2.663	23.41	65.93	-
KK	8/8/2006	155.07	45.81	109.26	859	8.16	275	105.11	1.176	52.29	45.44	3.153	22.44	70.57	-
KK	8/15/2006	129.99	64.88	65.11	788	7.93	258	89.77	0.827	48.56	37.61	2.771	23.85	66.61	-
KK	8/22/2006	136.35	28.32	108.03	818	7.92	257	97.74	1.124	51.83	41.83	2.986	24.47	68.63	-
KK	8/29/2006	111.31	43.30	68.01	720	7.83	245	76.37	1.074	42.76	34.04	2.631	20.30	66.50	-
KK	9/5/2006	99.05	30.02	69.03	780	8.08	274	75.86	1.174	46.81	32.37	2.465	23.27	75.08	-
KK	9/12/2006	81.20	31.98	49.22	845	7.91	289	89.76	1.302	52.79	39.92	2.836	24.07	77.76	-
KK	9/19/2006	74.15	42.77	31.38	755	7.75	260	106.99	0.578	44.58	43.27	1.558	20.70	72.37	-
KK	9/26/2006	57.19	30.27	26.92	827	7.66	290	78.89	1.374	54.91	35.20	2.823	23.70	79.12	-
KM	4/5/2005	32.52	9.97	22.55	-	-	-	-	-	-	-	-	-	-	-
KM	4/12/2005	56.86	14.38	42.49	-	-	-	-	-	-	-	-	-	-	-
KM	4/19/2005	47.71	9.38	38.33	-	-	-	-	-	-	-	-	-	-	-
KM	4/26/2005	30.48	8.49	21.99	-	-	-	-	-	-	-	-	-	-	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KM	5/3/2005	26.25	7.80	18.45	-	-	-	-	-	-	-	-	-	-	-
KM	5/10/2005	38.58	12.65	25.94	675	7.70	294	51.97	0.955	51.87	22.53	1.634	22.60	74.51	-
KM	5/17/2005	60.84	26.41	34.44	642	7.89	297	44.56	1.076	47.27	19.04	1.598	21.45	72.92	-
KM	5/24/2005	60.10	20.97	39.13	631	7.88	287	43.55	1.000	45.04	19.02	1.757	20.40	69.59	-
KM	5/31/2005	48.24	21.15	27.09	672	7.95	303	47.70	1.102	48.39	20.38	1.733	21.71	73.45	-
KM	6/7/2005	44.87	18.63	26.25	672	7.97	294	50.30	0.959	47.90	21.60	1.804	21.92	71.45	-
KM	6/9/2005	53.69	27.13	26.56	602	7.83	271	46.88	0.667	38.90	20.31	1.593	21.92	61.74	-
KM	6/14/2005	83.21	32.13	51.08	554	7.76	238	40.93	0.719	32.84	16.87	1.550	17.30	58.94	-
KM	6/21/2005	63.83	28.57	35.26	666	7.97	297	48.63	1.131	46.82	21.16	1.719	20.87	71.32	-
KM	6/28/2005	52.20	31.12	21.08	672	8.00	286	53.99	0.837	48.22	23.30	1.691	21.39	68.26	-
KM	7/5/2005	67.49	40.90	26.59	656	7.99	272	50.86	0.974	49.09	21.84	1.901	21.08	67.73	-
KM	7/12/2005	43.80	29.62	14.18	678	7.87	277	55.93	0.836	48.08	24.27	1.290	21.34	70.52	-
KM	7/19/2005	69.82	28.13	41.69	571	7.66	225	48.35	0.749	37.31	20.96	1.109	17.78	56.02	-
KM	7/26/2005	70.38	36.34	34.04	635	7.74	266	45.28	0.868	42.82	19.74	1.981	20.03	68.26	-
KM	8/2/2005	41.08	25.02	16.06	663	7.81	274	50.16	0.747	44.56	21.42	1.701	21.18	70.12	-
KM	8/9/2005	70.15	57.31	12.84	698	7.88	281	62.24	1.253	48.54	26.34	1.851	21.76	71.19	-
KM	8/16/2005	38.60	27.11	11.49	700	7.86	276	59.89	0.931	48.46	25.20	2.094	22.92	73.18	-
KM	8/23/2005	46.09	32.61	13.48	686	7.87	280	63.21	1.095	50.31	23.74	1.809	22.97	72.65	-
KM	8/30/2005	30.20	23.95	6.24	698	7.77	288	64.52	0.957	50.63	25.99	1.820	22.55	75.84	-
KM	9/6/2005	28.32	23.80	4.52	689	7.81	285	61.84	0.920	51.05	24.43	1.789	22.53	71.36	-
KM	9/13/2005	32.11	22.66	9.45	701	7.78	271	69.24	0.791	49.96	28.69	1.576	22.74	69.62	-
KM	9/20/2005	28.98	24.59	4.40	688	7.72	284	60.86	0.953	46.22	26.19	2.060	21.91	71.61	-
KM	9/27/2005	38.94	28.65	10.29	661	7.79	275	57.66	0.939	45.30	23.66	1.936	20.66	70.00	-
KM	10/4/2005	35.33	26.89	8.45	667	7.76	299	57.66	0.882	47.68	23.86	1.814	20.92	70.86	-
KM	4/4/2006	50.92	14.70	36.22	612	7.95	259	41.32	1.128	59.55	17.96	2.001	21.63	77.73	2.801
KM	4/11/2006	64.07	15.29	48.79	574	7.93	241	36.88	1.212	59.28	15.47	1.666	19.47	72.96	2.482

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chloro-phyll *a* (μgL^{-1})
KM	4/18/2006	63.98	18.01	45.97	637	7.84	278	41.57	0.960	60.55	16.80	2.173	22.06	80.75	1.865
KM	4/25/2006	55.57	16.79	38.78	680	7.88	292	49.54	1.063	59.08	23.05	2.698	24.01	83.65	0.795
KM	5/2/2006	53.01	15.22	37.78	660	7.81	288	49.63	1.006	56.25	21.17	2.301	23.57	81.03	6.237
KM	5/9/2006	54.76	16.69	38.07	688	7.88	296	49.52	0.926	55.34	21.20	1.590	24.22	81.74	2.764
KM	5/16/2006	-	27.40	-	524	7.63	216	28.01	1.612	42.73	12.38	1.743	17.69	65.47	1.642
KM	5/23/2006	78.21	22.19	56.02	632	7.81	270	37.82	1.004	51.36	16.14	1.490	20.51	75.08	1.970
KM	5/30/2006	60.88	21.85	39.03	692	7.84	289	45.47	1.001	52.04	19.28	1.397	22.41	81.11	1.180
KM	6/6/2006	94.32	28.31	66.01	696	7.77	291	48.07	1.063	50.05	20.15	1.452	23.84	80.97	1.806
KM	6/13/2006	62.87	21.45	41.42	708	7.83	294	52.09	0.970	50.77	21.42	1.472	24.58	79.87	1.235
KM	6/20/2006	62.09	24.41	37.68	634	7.78	251	45.72	0.857	43.82	19.52	1.652	20.57	68.15	2.092
KM	6/27/2006	116.02	32.34	83.68	599	7.78	245	40.54	1.420	48.12	17.12	2.094	20.04	73.30	1.987
KM	7/4/2006	80.04	37.03	43.01	687	7.79	273	47.55	1.303	47.37	19.31	1.508	21.62	75.81	1.936
KM	7/11/2006	60.81	32.97	27.85	725	7.85	292	51.49	1.064	50.62	21.22	1.651	23.10	81.33	1.630
KM	7/18/2006	61.74	32.74	29.01	705	7.80	271	51.59	1.012	45.30	21.18	1.746	23.37	75.79	2.033
KM	7/25/2006	55.18	38.13	17.05	736	7.90	289	55.13	0.985	47.26	23.36	1.871	24.26	79.48	1.508
KM	8/1/2006	67.65	49.59	18.06	730	7.88	289	54.17	1.071	45.41	21.92	1.807	23.34	76.52	1.436
KM	8/8/2006	47.31	32.39	14.92	734	7.96	285	55.46	0.897	43.65	22.95	1.693	23.71	77.55	0.819
KM	8/15/2006	53.11	41.83	11.27	750	7.90	288	61.23	0.956	48.63	24.71	1.583	23.22	75.55	0.987
KM	8/22/2006	51.89	32.90	18.99	757	7.93	289	59.89	0.962	49.80	24.29	1.675	23.69	79.44	0.991
KM	8/29/2006	65.64	29.73	35.91	681	7.78	238	50.48	0.836	42.27	21.42	1.723	20.49	69.00	1.785
KM	9/5/2006	53.69	30.84	22.85	740	8.00	287	53.63	1.021	46.51	21.70	1.701	23.93	80.04	0.953
KM	9/12/2006	44.66	21.97	22.69	747	7.89	283	57.29	0.996	45.57	24.25	1.654	23.08	76.42	1.063
KM	9/19/2006	61.53	32.81	28.72	720	7.87	281	47.37	1.291	55.46	19.57	2.068	21.51	76.83	1.386
KM	9/26/2006	41.17	21.24	19.93	757	7.89	300	52.29	1.018	49.58	22.23	1.768	23.79	80.21	0.706
KP	4/5/2005	22.22	8.99	13.24	-	-	-	-	-	-	-	-	-	-	-
KP	4/12/2005	59.81	14.38	45.43	-	-	-	-	-	-	-	-	-	-	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chloro-phyll *a* (μgL^{-1})
KP	4/19/2005	62.19	13.65	48.53	-	-	-	-	-	-	-	-	-	-	-
KP	4/26/2005	78.72	9.12	69.60	-	-	-	-	-	-	-	-	-	-	-
KP	5/3/2005	45.98	11.61	34.36	-	-	-	-	-	-	-	-	-	-	-
KP	5/10/2005	67.42	13.89	53.53	747	7.84	296	77.09	1.299	55.31	35.64	2.579	22.34	73.05	-
KP	5/17/2005	69.09	21.23	47.85	712	7.97	289	70.61	1.445	50.54	31.96	2.496	21.87	71.58	-
KP	5/24/2005	77.01	23.01	54.00	705	7.95	292	68.51	1.321	48.45	31.81	2.399	20.92	70.25	-
KP	5/31/2005	84.30	16.43	67.87	738	8.07	292	76.57	1.313	50.29	33.76	3.408	22.08	72.25	-
KP	6/7/2005	79.41	16.94	62.48	729	8.04	272	80.38	1.027	52.05	36.83	2.960	22.44	65.73	-
KP	6/9/2005	117.58	14.79	102.79	638	8.29	251	67.66	0.591	47.35	30.04	2.505	22.08	56.68	-
KP	6/14/2005	138.04	32.28	105.76	620	7.97	240	60.71	0.754	38.43	26.73	2.394	18.56	58.68	-
KP	6/21/2005	108.53	16.76	91.78	722	8.01	290	71.02	1.314	45.04	35.61	2.226	20.66	70.39	-
KP	6/28/2005	115.11	27.07	88.04	704	7.85	251	77.48	0.767	48.85	37.89	2.960	21.81	59.88	-
KP	7/5/2005	106.71	40.90	65.81	624	7.77	206	73.01	1.164	38.50	36.31	3.036	18.14	51.49	-
KP	7/12/2005	104.03	47.97	56.06	753	7.74	247	92.25	1.266	52.40	43.82	3.912	22.13	63.47	-
KP	7/19/2005	129.98	35.93	94.06	628	7.66	223	68.92	0.928	42.67	31.07	2.059	18.72	56.68	-
KP	7/26/2005	106.48	50.02	56.46	658	7.74	247	63.29	1.113	43.60	30.09	3.039	19.09	63.47	-
KP	8/2/2005	101.26	23.33	77.93	733	7.74	268	79.58	1.178	47.30	36.11	3.386	20.98	68.39	-
KP	8/9/2005	85.18	25.90	59.28	759	7.72	260	95.73	1.206	51.53	42.52	3.783	22.55	63.60	-
KP	8/16/2005	97.55	35.22	62.33	763	7.78	250	101.95	1.144	52.21	44.61	4.236	23.23	62.14	-
KP	8/23/2005	91.76	43.90	47.86	778	7.81	264	104.09	1.602	53.36	42.56	4.071	23.33	67.33	-
KP	8/30/2005	72.70	49.26	23.45	858	7.62	276	127.56	2.295	57.05	53.33	4.494	23.18	72.38	-
KP	9/6/2005	119.29	45.21	74.08	833	7.63	264	122.74	1.829	59.46	53.39	4.092	23.11	66.40	-
KP	9/13/2005	76.82	58.09	18.73	850	7.51	275	123.96	1.890	56.35	54.95	4.552	23.57	67.52	-
KP	9/20/2005	106.34	31.58	74.76	742	7.68	252	95.93	1.120	50.22	42.74	2.758	22.69	61.57	-
KP	9/27/2005	119.14	65.09	54.05	765	7.78	270	100.75	1.434	53.00	42.63	3.810	22.33	68.14	-
KP	10/4/2005	84.46	59.29	25.16	765	7.73	277	95.89	1.526	52.12	42.13	3.397	22.12	69.50	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KP	4/4/2006	42.37	16.55	25.82	675	8.11	270	60.13	1.575	59.96	26.84	2.016	22.69	80.06	-
KP	4/11/2006	88.55	42.36	46.19	637	7.95	257	54.97	1.322	58.38	24.62	2.069	21.32	75.41	-
KP	4/18/2006	73.76	33.11	40.65	681	7.85	272	59.03	1.471	59.96	29.70	3.178	22.12	79.92	-
KP	4/25/2006	76.22	28.37	47.85	734	7.86	293	69.25	1.283	59.57	30.80	3.158	24.14	83.65	-
KP	5/2/2006	83.73	40.69	43.04	723	7.80	284	72.59	1.475	56.90	32.46	3.104	23.70	81.99	-
KP	5/9/2006	75.86	14.29	61.56	722	7.99	281	70.76	0.983	54.93	31.38	2.908	24.28	76.92	-
KP	5/16/2006	73.35	36.59	36.76	564	7.68	231	40.48	1.335	41.24	18.69	1.761	18.58	65.33	-
KP	5/23/2006	86.22	30.63	55.58	631	7.91	251	48.92	1.433	50.30	22.55	2.021	20.75	74.67	-
KP	5/30/2006	62.56	29.28	33.28	739	7.81	281	67.00	1.342	53.04	28.72	2.003	23.71	79.19	-
KP	6/6/2006	94.32	50.64	43.68	729	7.65	275	66.91	1.523	48.00	30.32	2.162	23.59	76.31	-
KP	6/13/2006	91.96	50.72	41.25	788	7.65	282	82.44	1.697	51.15	36.92	3.175	24.91	76.86	-
KP	6/20/2006	121.15	86.70	34.45	795	7.63	277	85.87	1.767	52.92	38.22	2.709	24.24	74.44	-
KP	6/27/2006	119.70	70.00	49.70	683	7.55	251	62.28	1.908	44.41	28.49	2.614	20.41	68.30	-
KP	7/4/2006	149.82	80.54	69.28	722	7.56	249	71.34	1.952	46.91	31.98	2.498	21.11	68.55	-
KP	7/11/2006	96.93	77.52	19.41	776	7.54	272	78.42	1.924	51.11	35.03	2.795	22.78	74.31	-
KP	7/18/2006	121.45	71.07	50.38	691	7.42	227	69.56	1.239	43.53	30.87	2.666	20.54	62.48	-
KP	7/25/2006	90.47	58.76	31.71	768	7.65	261	80.02	1.346	48.84	34.58	3.001	23.75	70.03	-
KP	8/1/2006	105.29	80.08	25.21	757	7.55	248	48.10	0.907	27.62	18.78	1.126	23.41	64.95	-
KP	8/9/2006	104.34	77.65	26.69	807	7.51	253	96.30	1.688	48.57	42.30	3.097	23.00	65.25	-
KP	8/15/2006	87.76	64.88	22.88	775	7.56	235	94.68	1.463	47.45	40.47	3.426	23.85	59.10	-
KP	8/22/2006	84.79	61.22	23.57	795	7.62	246	93.56	1.510	49.18	39.30	2.989	23.89	64.15	-
KP	8/29/2006	126.70	65.81	60.90	589	7.49	187	59.93	1.254	32.51	27.62	2.602	16.56	50.07	-
KP	9/5/2006	90.50	47.61	42.90	740	7.70	250	75.05	1.241	44.22	31.69	2.472	22.23	65.46	-
KP	9/12/2006	75.53	56.01	19.52	797	7.75	257	83.75	1.742	48.05	37.10	2.871	22.55	70.05	-
KP	9/19/2006	89.09	55.06	34.03	740	7.73	260	66.18	1.581	48.24	28.91	2.592	20.77	71.04	-
KP	9/26/2006	66.90	41.86	25.05	823	7.66	287	75.79	1.719	53.84	33.54	2.767	23.95	78.64	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
KS	4/4/2006	59.98	13.53	46.45	620	7.69	270	42.32	1.191	61.25	17.91	1.996	22.31	78.55	10.290
KS	4/11/2006	46.89	14.64	32.25	583	7.44	249	37.86	1.052	56.76	15.92	1.480	20.33	73.64	3.486
KS	4/18/2006	60.21	15.44	44.77	621	7.93	261	40.83	0.915	59.66	18.31	2.598	21.50	79.10	9.093
KS	4/25/2006	57.59	13.94	43.65	668	7.95	289	47.10	0.820	59.12	23.17	2.477	23.63	83.37	6.573
KS	5/2/2006	49.23	15.06	34.17	659	7.93	285	48.88	0.995	57.68	20.80	2.284	24.84	82.54	7.371
KS	5/9/2006	64.02	12.06	51.96	663	8.08	285	46.31	0.659	53.76	19.56	1.557	23.54	79.33	9.828
KS	5/16/2006	56.31	29.24	27.07	519	7.65	221	28.13	1.233	40.11	12.50	1.481	17.34	62.71	2.373
KS	5/23/2006	49.10	21.68	27.42	610	7.71	255	34.59	1.040	49.35	14.79	1.609	21.24	76.72	4.221
KS	5/30/2006	45.16	9.01	36.15	671	8.08	281	43.74	0.659	52.13	18.35	1.427	23.71	76.72	10.815
KS	6/6/2006	62.45	14.56	47.89	658	7.99	281	43.05	0.719	45.91	18.02	1.502	22.78	77.00	12.369
KS	6/13/2006	86.66	12.38	74.28	680	7.95	281	47.52	0.594	48.46	19.84	1.514	23.61	77.41	16.296
KS	6/20/2006	80.08	27.13	52.95	695	7.88	273	53.21	0.649	50.53	22.14	1.620	23.60	75.30	10.752
KS	6/27/2006	61.79	22.30	39.50	599	7.78	245	36.84	0.965	41.94	15.69	1.905	18.67	68.55	13.398
KS	7/4/2006	102.13	13.10	89.03	677	8.16	277	46.65	0.758	48.42	19.13	1.524	22.00	75.81	21.294
KS	7/11/2006	67.39	12.54	54.85	662	8.08	256	47.52	0.615	47.53	19.21	1.617	21.75	72.23	15.813
KS	7/18/2006	83.11	16.79	66.32	670	7.95	253	51.34	0.384	47.26	20.82	1.768	22.92	69.78	17.094
KS	7/25/2006	100.19	16.14	84.05	663	8.08	259	49.98	0.579	45.24	21.34	2.579	23.49	68.32	21.147
KS	8/1/2006	112.45	15.02	97.43	662	7.74	247	53.38	0.228	43.59	21.84	1.633	22.78	63.24	20.454
KS	8/8/2006	88.59	11.50	77.10	637	8.32	244	50.47	0.195	40.16	20.73	1.630	22.37	63.03	19.824
KS	8/15/2006	112.33	11.55	100.77	705	8.10	263	59.92	0.345	46.18	24.01	1.457	23.43	68.34	21.798
KS	8/22/2006	95.82	13.23	82.59	684	8.06	241	61.77	0.171	46.77	25.22	1.533	23.69	62.80	20.076
KS	8/29/2006	68.62	18.64	49.98	695	8.05	263	53.84	0.552	42.93	22.32	1.551	22.16	70.18	12.831
KS	9/5/2006	62.40	13.26	49.14	693	8.24	276	50.27	0.519	45.79	20.89	1.652	23.08	72.96	18.207
KS	9/12/2006	60.85	17.30	43.55	731	8.13	281	55.32	0.604	45.18	22.55	1.571	23.80	74.95	13.902
KS	9/19/2006	58.05	33.31	24.74	671	7.89	253	42.85	0.998	48.72	18.28	1.972	20.21	72.01	5.292
KS	9/26/2006	54.12	27.20	26.92	735	7.88	282	49.95	0.912	49.07	21.13	1.678	23.11	75.99	3.826

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
PC	5/17/2005	31.26	12.66	18.59	796	7.93	289	103.33	0.440	52.98	43.64	1.473	22.97	73.05	-
PC	5/24/2005	39.13	12.99	26.14	779	7.93	298	95.55	0.384	56.64	41.17	1.551	22.18	72.92	-
PC	5/31/2005	44.46	13.91	30.55	801	7.92	296	100.44	0.389	52.77	41.88	1.626	23.65	74.65	-
PC	6/7/2005	42.72	16.48	26.25	777	7.88	294	93.78	0.400	51.82	40.51	1.696	22.86	72.65	-
PC	6/9/2005	45.41	29.32	16.09	735	7.92	284	91.04	0.363	46.80	39.28	1.670	20.29	70.92	-
PC	6/14/2005	83.52	38.84	44.68	520	7.66	186	57.94	0.365	31.54	25.44	1.523	14.16	47.90	-
PC	6/21/2005	54.72	18.11	36.61	784	7.90	294	97.76	0.432	50.75	41.77	1.668	22.08	71.85	-
PC	6/28/2005	48.15	22.52	25.64	781	7.83	285	93.56	0.411	54.18	40.56	1.733	22.13	70.65	-
PC	7/5/2005	56.39	22.55	33.83	747	7.84	267	88.71	0.417	49.51	38.30	1.799	21.87	68.39	-
PC	7/12/2005	47.30	22.44	24.86	807	7.79	290	97.74	0.383	57.30	46.88	1.382	23.02	72.78	-
PC	7/19/2005	86.43	28.81	57.62	538	7.47	183	62.69	0.459	33.75	29.09	1.423	14.74	48.17	-
PC	7/26/2005	54.00	23.14	30.86	782	7.71	281	92.55	0.410	52.30	40.25	1.825	22.13	73.05	-
PC	8/2/2005	33.64	16.57	17.07	814	7.70	298	96.59	0.359	59.63	41.88	1.752	23.02	74.78	-
PC	8/9/2005	38.06	21.17	16.89	812	7.71	295	100.58	0.369	56.44	43.60	1.920	23.23	76.91	-
PC	8/16/2005	39.78	19.68	20.10	809	7.78	302	97.00	0.381	57.54	41.22	1.869	24.12	76.64	-
PC	9/6/2005	32.83	17.61	15.22	801	7.72	301	99.58	0.378	56.75	40.67	1.660	23.21	74.46	-
PC	9/13/2005	35.65	18.11	17.55	802	7.85	298	98.60	0.308	55.68	42.37	1.550	23.21	76.81	-
PC	9/20/2005	34.78	17.59	17.19	797	7.68	297	94.83	0.419	54.00	40.13	1.449	22.69	77.06	-
PC	9/27/2005	42.08	16.10	25.98	770	7.72	284	92.15	0.449	47.62	40.32	1.502	21.70	73.59	-
PC	10/4/2005	42.23	18.61	23.61	806	7.70	296	98.24	0.412	62.12	40.10	1.614	23.26	79.04	-
PC	4/4/2006	23.25	9.00	14.25	766	8.07	285	100.41	0.469	47.08	43.57	1.936	24.39	78.14	-
PC	4/11/2006	26.15	9.62	16.53	800	8.01	297	109.05	0.376	47.61	46.22	1.365	24.84	79.79	-
PC	4/18/2006	27.27	10.46	16.81	805	7.82	304	101.81	0.355	47.83	48.54	2.359	24.90	80.61	-
PC	4/25/2006	36.60	12.76	23.84	836	7.73	311	108.61	0.682	51.57	50.50	3.043	26.19	83.93	-
PC	5/2/2006	203.81	48.41	155.41	561	7.55	203	69.95	0.479	32.49	36.25	2.392	16.76	55.16	-
PC	5/9/2006	40.70	13.60	27.10	849	7.79	307	112.76	0.458	50.37	46.07	1.455	26.28	80.89	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. (mScm^{-2})	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
PC	5/16/2006	39.10	15.71	23.39	698	7.64	246	85.19	0.456	40.82	38.40	1.224	20.66	67.82	-
PC	5/23/2006	34.62	10.19	24.43	826	7.79	295	106.88	0.444	47.87	44.01	1.273	25.67	79.74	-
PC	5/30/2006	54.46	17.12	37.34	841	7.76	301	105.35	0.403	44.72	43.87	1.187	25.73	80.42	-
PC	6/6/2006	80.73	21.68	59.05	829	7.67	295	103.64	0.444	47.23	45.23	1.299	24.91	79.05	-
PC	6/13/2006	49.00	18.54	30.46	849	7.70	299	108.25	0.436	47.29	45.60	1.481	25.43	80.01	-
PC	6/20/2006	56.83	25.94	30.89	843	7.68	301	105.25	0.445	45.75	44.67	1.677	25.15	81.38	-
PC	6/27/2006	41.88	18.28	23.60	872	7.67	306	111.49	0.493	46.59	46.45	1.637	25.21	79.21	-
PC	7/4/2006	85.89	26.99	58.91	694	7.51	236	83.79	0.547	33.53	37.28	1.435	18.86	61.96	-
PC	7/11/2006	40.73	22.33	18.40	884	7.68	309	108.42	0.432	48.52	46.94	1.494	24.61	79.85	-
PC	7/18/2006	111.44	28.84	82.61	566	7.47	189	59.73	0.407	30.45	29.32	1.604	15.49	51.13	-
PC	7/25/2006	57.91	23.13	34.78	880	7.73	303	104.30	0.453	48.49	46.35	1.662	25.16	79.85	-
PC	8/1/2006	74.46	30.52	43.95	868	7.71	299	103.89	0.464	45.02	43.54	1.692	23.91	78.01	-
PC	8/8/2006	41.34	20.95	20.39	855	7.93	296	101.62	0.474	44.07	41.86	1.502	23.22	77.05	-
PC	8/15/2006	42.51	21.14	21.37	878	7.82	301	105.23	0.456	46.47	43.35	1.532	24.36	78.55	-
PC	8/22/2006	46.98	25.95	21.03	874	7.82	301	101.79	0.423	44.38	43.63	1.470	24.02	80.57	-
PC	8/29/2006	154.01	105.69	48.32	611	7.61	181	71.53	0.650	31.62	30.96	2.306	14.87	53.23	-
PC	9/5/2006	61.91	19.50	42.40	860	7.76	295	100.37	0.476	40.05	41.92	1.603	23.47	78.29	-
PC	9/12/2006	45.66	16.96	28.70	811	7.69	269	93.03	0.521	39.48	40.35	1.572	21.45	71.50	-
PC	9/19/2006	39.62	18.54	21.08	900	7.73	307	68.17	1.401	49.76	30.57	2.493	24.34	81.66	-
PC	9/26/2006	33.68	14.26	19.42	911	7.67	311	106.27	0.536	44.50	44.85	1.528	25.03	81.30	-
SB	4/5/2005	13.40	4.41	8.99	-	-	-	-	-	-	-	-	-	-	-
SB	4/26/2005	15.77	4.53	11.23	-	-	-	-	-	-	-	-	-	-	-
SB	5/3/2005	14.00	6.05	7.95	-	-	-	-	-	-	-	-	-	-	-
SB	5/10/2005	30.44	8.37	22.07	573	7.80	286	21.13	0.618	46.58	9.54	1.050	23.07	63.34	-
SB	5/17/2005	35.30	12.34	22.96	556	7.96	273	24.05	0.640	39.67	11.60	1.074	22.34	61.07	-
SB	5/24/2005	45.39	15.81	29.58	561	7.99	290	31.26	0.584	36.10	14.61	1.227	22.02	62.44	-

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
SB	5/31/2005	33.91	11.08	22.83	567	7.95	283	20.88	0.661	44.94	10.12	0.916	23.39	63.07	-
SB	6/7/2005	46.56	18.78	27.78	563	7.89	271	25.60	0.562	39.20	11.78	1.290	22.81	59.48	-
SB	6/9/2005	41.34	21.51	19.84	554	7.89	286	22.56	0.653	39.57	9.61	1.072	20.82	59.88	-
SB	6/14/2005	109.92	28.07	81.86	589	7.90	240	32.64	7.224	39.52	11.77	2.295	21.97	62.14	-
SB	6/21/2005	52.69	18.11	34.58	564	7.98	277	20.02	0.698	46.07	9.31	0.880	22.81	61.21	-
SB	6/28/2005	133.49	24.71	108.79	553	7.85	260	25.72	0.697	36.26	11.70	1.454	22.23	65.60	-
SB	7/5/2005	58.91	20.70	38.21	552	7.96	261	21.96	0.636	42.46	10.77	1.233	22.71	59.08	-
SB	7/12/2005	41.13	18.44	22.69	578	7.93	277	24.45	0.718	48.20	11.45	1.338	22.86	61.47	-
SB	7/19/2005	94.23	24.57	69.65	487	7.70	192	36.39	0.887	31.66	15.68	2.184	18.51	46.04	-
SB	7/26/2005	67.20	22.98	44.22	502	7.84	224	22.39	0.406	39.22	8.66	2.132	19.56	51.49	-
SB	8/2/2005	31.11	17.24	13.86	544	7.74	258	22.51	0.521	38.07	10.91	1.851	22.29	57.21	-
SB	8/9/2005	36.37	18.13	18.24	553	7.78	260	21.44	0.530	36.91	9.98	1.620	22.29	58.41	-
SB	8/16/2005	38.26	19.17	19.09	548	7.88	264	21.85	0.527	37.51	10.52	1.691	23.70	58.28	-
SB	8/23/2005	31.94	15.59	16.35	534	7.93	266	20.71	0.531	39.78	9.53	1.778	23.07	60.81	-
SB	8/30/2005	31.04	17.71	13.33	540	7.73	266	21.24	0.539	39.68	10.10	1.602	22.81	61.87	-
SB	9/6/2005	24.47	14.44	10.03	547	7.75	271	21.03	0.569	41.65	9.79	1.847	22.90	64.05	-
SB	9/13/2005	29.75	14.90	14.85	548	7.74	266	20.94	0.494	39.61	10.56	2.019	22.79	59.34	-
SB	9/20/2005	34.38	13.99	20.39	542	7.62	259	18.09	0.409	36.28	8.71	2.060	22.48	59.34	-
SB	9/27/2005	60.56	28.13	32.43	558	7.67	270	24.38	0.486	40.68	10.64	2.781	23.31	60.46	-
SB	10/4/2005	40.50	20.34	20.17	559	7.68	276	22.61	0.348	40.82	10.40	1.691	23.52	62.44	-
WC	4/4/2006	25.43	15.71	9.73	502	7.51	240	15.17	0.250	57.54	7.72	1.861	19.17	69.45	1.361
WC	4/11/2006	33.60	18.86	14.75	438	7.49	198	14.27	0.201	49.66	6.62	2.219	15.69	61.06	1.441
WC	4/18/2006	35.68	21.61	14.07	549	7.53	280	17.63	0.120	53.49	9.24	2.188	20.64	74.86	4.473
WC	4/25/2006	33.92	19.14	14.77	581	7.66	301	17.47	0.162	51.41	9.99	1.905	23.00	79.92	1.722
WC	5/2/2006	39.70	21.47	18.23	562	7.61	295	16.37	0.274	48.76	8.76	1.724	22.25	76.91	3.184
WC	5/9/2006	53.90	31.10	22.81	599	7.56	302	17.26	0.258	47.37	8.75	1.329	22.67	77.91	1.159

Site	Date	TP (μgL^{-1})	DP (μgL^{-1})	PP (μgL^{-1})	Specific Cond. ($mScm^{-2}$)	pH (pH)	Alkalinity as HCO_3^- (mgL^{-1})	Cl^- (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Chlorophyll *a* (μgL^{-1})
WC	5/16/2006	40.43	31.24	9.19	427	7.21	197	12.67	0.658	35.27	6.15	2.036	14.85	57.24	0.685
WC	5/23/2006	38.03	25.06	12.97	527	7.39	257	14.76	0.098	38.63	7.53	1.499	19.18	69.35	0.916
WC	5/30/2006	88.58	44.15	44.43	606	7.47	314	16.64	0.294	38.21	8.12	1.245	22.59	77.41	2.486
WC	6/6/2006	77.49	42.55	34.95	615	7.48	310	17.09	0.390	40.35	9.08	1.156	23.21	78.78	1.445
WC	6/13/2006	71.94	39.08	32.86	615	7.50	307	17.23	0.333	39.95	9.00	1.069	23.53	77.41	1.033
WC	6/20/2006	107.74	53.60	54.14	603	7.49	296	16.55	0.381	40.01	9.07	1.446	22.14	75.59	1.546
WC	6/27/2006	104.64	44.22	60.41	625	7.48	309	17.53	0.388	39.80	9.74	1.392	23.23	75.31	1.378
WC	7/4/2006	173.92	40.71	133.21	566	7.49	276	15.26	0.396	35.50	8.29	1.061	20.16	67.56	1.953
WC	7/11/2006	160.21	45.12	115.10	636	7.47	310	18.07	0.324	38.59	9.96	1.172	22.39	75.66	1.735
WC	7/18/2006	207.96	50.55	157.41	570	7.45	251	15.61	0.373	34.26	8.88	1.612	20.91	68.93	1.890
WC	7/25/2006	161.74	54.50	107.24	633	7.59	307	17.60	0.289	35.96	9.64	1.659	23.18	77.02	1.168
WC	8/1/2006	159.97	61.01	98.96	617	7.64	299	17.15	0.387	31.80	8.93	1.550	21.84	72.44	0.790
WC	8/8/2006	111.47	61.90	49.57	644	7.75	310	18.30	0.362	32.20	9.39	1.508	23.43	76.42	0.529
WC	8/15/2006	72.62	50.92	21.70	640	7.79	310	18.18	0.332	37.26	9.56	1.206	23.57	76.92	0.643
WC	8/22/2006	81.23	55.63	25.61	643	7.73	307	18.23	0.312	36.36	9.47	1.282	23.11	76.78	0.504
WC	8/29/2006	82.02	53.73	28.30	591	7.64	276	15.55	0.368	36.12	8.19	1.427	20.81	68.34	0.710
WC	9/5/2006	61.25	43.99	17.26	661	7.83	316	18.08	0.409	40.15	9.56	1.470	23.74	79.10	0.584
WC	9/12/2006	60.01	39.32	20.69	648	7.77	307	17.45	0.471	38.77	9.25	1.470	22.88	76.02	0.848
WC	9/19/2006	72.99	52.40	20.59	644	7.37	286	17.48	0.375	55.74	8.74	1.850	21.63	76.11	0.470
WC	9/26/2006	62.64	37.60	25.05	680	7.58	309	17.72	0.462	55.40	8.04	2.042	23.74	81.42	0.349

APPENDIX II

KALAMAZOO RIVER/LAKE ALLEGAN WATERSHED STREAM TRACE ELEMENT DATASET

2005 and 2006 growing season trace element results for the Kalamazoo River/Lake Allegan Watershed, Michigan, USA sampling locations: BC – Battle Creek River at Emmet Street Dam, Battle Creek, MI; BR – Battle Creek River at McAllister Rd, Pennfield, MI; FC – Eagle Lake Tributary at Fort Custer, MI; GR – Gun River at 106th Street, Otsego, MI; KA – Kalamazoo River inlet to Lake Allegan at M222, Allegan, MI; KB – Kalamazoo River at Battle Creek, MI; KC – Kalamazoo River outlet of Morrow Lake at Comstock, MI; KD – Kalamazoo River outlet of Lake Allegan at Caulkins Dam, Allegan, MI; KE – Kalamazoo River east of Battle Creek at Battle Creek, MI; KG – Kalamazoo River at Augusta, MI; KK – Kalamazoo River at Mosel Street, Kalamazoo, MI; KP – Kalamazoo River at Plainwell, MI; PC – Portage Creek at Kalamazoo, MI; SB – Schnable Brook at M-89, Otsego, MI and WC – Wanadoga Creek at Pennfield Road, Pennfield, MI. Shaded values were below lower calibration limit and eliminated for data analysis.

Site	Date	B (μgL^{-1})	Al (μgL^{-1})	Sc (μgL^{-1})	Ti (μgL^{-1})	V (μgL^{-1})	Cr (μgL^{-1})	Mn (μgL^{-1})	Fe (μgL^{-1})	Co (μgL^{-1})	Ni (μgL^{-1})	Cu (μgL^{-1})
BC	6/9/2005	39.50	5.44	40.21	28.32	0.77	0.24	84.11	44.03	0.84	1.45	0.00
BC	9/13/2005	46.73	5.71	37.61	26.48	0.85	0.38	53.54	20.00	0.95	1.30	0.00
BC	8/8/2006	38.74	5.11	51.45	36.23	0.94	0.20	47.41	28.39	0.84	1.40	0.00
BC	9/12/2006	42.02	4.69	45.17	32.17	0.89	0.25	49.61	25.83	1.12	1.23	0.00
BR	6/9/2005	46.32	4.94	38.39	29.20	1.04	0.39	118.91	70.08	0.93	2.23	0.00
BR	9/13/2005	54.36	5.16	37.34	29.04	1.22	0.44	152.31	41.34	1.00	2.24	0.03
BR	8/8/2006	47.08	4.53	50.88	38.70	1.17	0.33	43.71	32.99	0.88	2.11	0.00
BR	9/12/2006	62.32	4.19	42.15	31.56	1.05	0.30	100.76	29.85	1.16	1.69	0.00
FC	6/9/2005	17.44	4.69	47.08	30.69	0.53	0.14	45.10	163.25	0.20	0.32	0.00
FC	9/13/2005	16.45	4.26	49.30	32.96	0.60	0.15	22.74	89.03	0.26	0.34	0.00
GR	6/9/2005	28.25	6.08	33.77	23.33	0.60	0.25	21.43	89.72	0.59	1.11	0.00
GR	9/13/2005	31.91	4.57	42.03	28.79	0.61	0.18	28.99	37.05	0.75	0.91	0.00
GR	8/8/2006	29.86	6.21	40.97	28.08	0.59	0.16	23.79	69.25	0.53	0.84	0.00
GR	9/12/2006	32.48	4.56	38.84	30.05	0.63	0.22	37.86	74.79	0.89	1.18	0.31

Site	Date	B (μgL^{-1})	Al (μgL^{-1})	Sc (μgL^{-1})	Ti (μgL^{-1})	V (μgL^{-1})	Cr (μgL^{-1})	Mn (μgL^{-1})	Fe (μgL^{-1})	Co (μgL^{-1})	Ni (μgL^{-1})	Cu (μgL^{-1})
KA	6/9/2005	51.94	7.41	23.96	16.58	0.88	0.30	8.15	23.22	0.51	1.23	0.00
KA	9/13/2005	59.91	7.32	17.95	13.27	1.04	0.47	14.50	36.65	0.60	1.37	0.08
KA	8/8/2006	50.04	8.62	30.48	22.14	1.03	0.28	28.67	27.54	0.57	1.34	0.06
KA	9/12/2006	51.85	5.71	33.60	26.56	0.99	0.26	23.79	32.35	0.8	1.18	0.48
KB	6/9/2005	31.35	3.87	34.58	23.93	0.77	0.32	34.40	54.86	0.70	1.03	0.00
KB	9/13/2005	34.15	3.93	34.24	23.87	0.85	0.31	24.64	31.07	0.62	0.93	0.00
KB	8/8/2006	28.59	6.27	43.05	30.03	0.79	0.21	27.45	23.97	0.72	0.95	0.00
KB	9/12/2006	31.18	4.30	37.89	26.76	0.74	0.24	23.67	21.45	0.88	1.09	0.00
KC	6/9/2005	38.12	3.10	27.13	18.41	0.75	0.26	9.96	12.38	0.46	0.99	0.00
KC	9/13/2005	46.45	5.45	8.49	5.96	0.83	0.29	19.14	23.29	0.40	1.04	0.00
KC	8/8/2006	37.67	3.73	15.21	10.05	0.78	0.15	3.33	10.10	0.43	0.80	0.00
KC	9/12/2006	39.22	3.73	28.93	22.71	0.86	0.22	8.07	11.51	0.82	1.09	0.27
KD	6/9/2005	54.65	3.22	5.63	3.79	0.73	0.27	12.96	13.20	0.28	1.23	0.05
KD	9/13/2005	62.32	4.16	10.15	7.61	0.93	0.29	2.06	24.22	0.40	1.46	0.00
KD	8/8/2006	54.05	3.97	17.79	12.16	1.02	0.18	4.97	13.52	0.31	1.05	0.00
KD	9/12/2006	48.77	6.27	23.58	18.65	1.05	0.21	1.59	14.02	0.55	1.21	0.40
KE	6/9/2005	28.45	3.90	33.28	22.60	0.66	0.25	30.64	54.08	0.59	0.81	0.00
KE	9/13/2005	31.73	4.13	34.60	23.57	0.81	0.29	24.83	30.94	0.58	0.77	0.00
KE	8/8/2006	26.01	3.76	42.20	29.33	0.74	0.21	27.08	25.34	0.69	0.89	0.00
KE	9/12/2006	28.21	3.23	36.85	25.06	0.69	0.20	22.36	26.68	0.78	0.62	0.00
KG	8/8/2006	43.63	6.96	43.00	30.15	0.88	0.24	22.22	26.06	0.73	0.99	0.00
KG	9/12/2006	46.34	8.81	35.67	25.14	0.83	0.34	22.52	38.81	0.81	1.02	0.00
KK	8/8/2006	63.32	9.08	26.63	19.54	1.10	0.27	12.16	27.00	0.70	1.63	0.14
KK	9/12/2006	59.39	18.72	30.69	24.50	1.00	0.26	13.24	16.16	0.85	1.36	0.63

Site	Date	B (μgL^{-1})	Al (μgL^{-1})	Sc (μgL^{-1})	Ti (μgL^{-1})	V (μgL^{-1})	Cr (μgL^{-1})	Mn (μgL^{-1})	Fe (μgL^{-1})	Co (μgL^{-1})	Ni (μgL^{-1})	Cu (μgL^{-1})
KM	6/9/2005	36.65	6.07	35.10	24.08	0.78	0.28	33.32	48.58	0.55	0.91	0.00
KM	9/13/2005	47.23	11.24	30.78	23.00	0.93	0.32	29.52	26.30	0.67	1.04	0.00
KM	8/8/2006	44.41	5.22	42.97	30.47	0.90	0.27	21.70	21.18	0.71	1.07	0.79
KM	9/12/2006	46.22	8.18	34.25	26.15	0.79	0.25	22.25	43.27	0.82	0.98	0.43
KP	6/9/2005	30.85	6.16	40.18	27.81	0.84	0.22	66.99	83.56	0.54	0.78	0.00
KP	9/13/2005	82.67	4.43	23.94	19.04	1.25	0.41	14.04	42.87	0.72	2.01	0.42
KP	8/8/2006	62.83	7.34	28.31	21.37	1.18	0.29	16.27	39.47	0.61	1.60	0.21
KP	9/12/2006	65.15	5.09	29.09	23.57	1.06	0.40	10.73	21.45	0.73	1.33	0.71
KS	8/8/2006	38.75	4.09	14.20	9.82	0.79	0.18	3.24	11.98	0.44	0.97	0.00
KS	9/12/2006	39.57	14.24	29.15	23.07	0.87	0.27	8.52	16.21	0.83	1.19	0.28
PC	6/9/2005	48.07	5.33	27.26	18.85	0.94	0.38	4.46	16.62	0.49	1.26	0.00
PC	9/13/2005	32.15	5.25	42.27	29.84	0.91	0.35	36.00	41.82	0.75	0.89	0.00
PC	8/8/2006	33.95	20.64	41.08	29.57	0.97	0.28	53.44	151.00	0.76	0.92	0.00
PC	9/12/2006	31.18	5.86	37.32	28.34	0.90	0.22	52.04	35.43	0.74	0.66	0.53
SB	6/9/2005	32.94	4.23	37.72	25.87	0.77	0.34	37.55	46.19	0.56	0.96	0.00
SB	9/13/2005	36.89	5.29	34.41	23.44	0.75	0.24	29.22	35.54	0.50	0.63	0.00
WC	8/8/2006	24.39	6.45	61.23	44.22	0.94	0.38	72.72	36.61	0.96	1.42	0.00
WC	9/12/2006	22.37	12.74	49.79	35.99	0.66	0.28	40.09	57.53	0.85	1.44	0.00

Site	Date	Zn (μgL^{-1})	As (μgL^{-1})	Se (μgL^{-1})	Rb (μgL^{-1})	Sr (μgL^{-1})	Cd (μgL^{-1})	Sn (μgL^{-1})	Ba (μgL^{-1})	Pb (μgL^{-1})	U (μgL^{-1})	Mo (μgL^{-1})
BC	6/9/2005	335.70	2.16	2.20	1.02	331.86	0.24	0.12	104.38	0.09	0.92	2.15
BC	9/13/2005	399.53	1.55	1.75	0.85	285.73	0.20	0.06	116.94	0.06	0.80	2.27
BC	8/8/2006	29.83	2.51	2.25	0.95	334.20	0.16	0.06	111.09	0.06	0.78	1.71
BC	9/12/2006	118.36	1.77	1.91	0.84	387.76	0.12	0.04	111.29	0.04	0.85	1.69
BR	6/9/2005	453.55	3.66	6.13	1.21	329.86	0.57	0.26	95.13	0.21	1.13	2.92
BR	9/13/2005	400.52	3.53	6.58	1.12	352.21	0.61	0.28	111.08	0.23	1.01	3.27
BR	8/8/2006	12.71	3.95	6.05	1.24	364.06	0.48	0.24	96.13	0.18	0.87	2.48
BR	9/12/2006	39.42	2.40	3.70	1.11	524.38	0.29	0.13	103.11	0.10	0.91	1.97
FC	6/9/2005	103.85	2.31	1.06	1.01	66.77	0.13	0.10	52.24	0.07	0.23	0.54
FC	9/13/2005	177.85	2.00	1.62	1.16	74.63	0.17	0.06	56.98	0.06	0.25	0.51
GR	6/9/2005	14.96	1.81	2.85	1.12	146.56	0.28	0.14	99.78	0.11	0.96	1.16
GR	9/13/2005	156.16	1.26	1.52	0.91	163.33	0.16	0.04	116.22	0.07	0.75	1.21
GR	8/8/2006	34.48	1.61	1.58	1.44	152.78	0.10	0.03	94.77	0.04	0.76	1.24
GR	9/12/2006	43.35	1.70	2.87	1.42	162.37	0.19	0.19	108.98	0.07	0.87	1.23
KA	6/9/2005	145.04	1.92	2.02	1.43	122.20	0.22	0.07	64.46	0.20	0.62	2.83
KA	9/13/2005	275.15	2.09	2.10	1.60	129.13	0.21	0.06	71.99	0.35	0.57	2.77
KA	8/8/2006	90.01	2.64	2.41	1.49	129.83	0.16	0.07	72.27	0.31	0.62	1.97
KA	9/12/2006	98.71	1.84	1.35	1.44	134.90	0.06	0.01	68.84	0.21	0.62	1.61
KB	6/9/2005	227.23	2.12	2.41	1.20	137.29	0.24	0.11	63.10	0.12	0.76	1.61
KB	9/13/2005	166.50	1.92	2.47	0.64	125.49	0.24	0.08	60.84	0.09	0.70	1.35
KB	8/8/2006	29.45	2.13	1.72	1.23	146.86	0.10	0.04	64.27	0.05	0.76	1.46
KB	9/12/2006	133.07	1.86	2.54	1.18	143.37	0.16	0.07	59.29	0.07	0.72	1.15

Site	Date	Zn (µgL^{-1})	As (µgL^{-1})	Se (µgL^{-1})	Rb (µgL^{-1})	Sr (µgL^{-1})	Cd (µgL^{-1})	Sn (µgL^{-1})	Ba (µgL^{-1})	Pb (µgL^{-1})	U (µgL^{-1})	Mo (µgL^{-1})
KC	6/9/2005	4.72	2.08	2.42	1.34	126.61	0.23	0.08	59.20	0.09	0.66	1.51
KC	9/13/2005	257.65	2.04	2.08	0.86	122.61	0.22	0.07	60.23	0.11	0.62	1.75
KC	8/8/2006	35.36	2.15	1.02	1.14	127.51	0.04	0.01	60.56	0.02	0.61	1.47
KC	9/12/2006	500.56	1.98	2.30	1.09	134.72	0.14	0.06	57.85	0.06	0.65	1.34
KD	6/9/2005	134.97	2.04	1.88	0.00	123.35	0.20	0.09	55.20	0.13	0.66	2.71
KD	9/13/2005	162.14	2.16	1.94	0.00	123.46	0.20	0.08	67.99	0.16	0.59	2.77
KD	8/8/2006	15.47	2.53	1.30	0.00	120.66	0.06	0.06	64.25	0.07	0.58	1.93
KD	9/12/2006	69.34	1.93	1.59	24.52	123.68	0.08	0.03	64.41	0.11	0.62	1.60
KE	6/9/2005	72.78	1.81	1.49	1.04	107.18	0.17	0.05	56.33	0.08	0.74	1.46
KE	9/13/2005	125.91	1.74	1.69	0.91	104.94	0.18	0.13	54.47	0.07	0.69	1.19
KE	8/8/2006	19.19	2.17	1.69	0.99	111.52	0.09	0.03	55.76	0.04	0.79	1.47
KE	9/12/2006	49.66	1.45	0.91	0.92	106.54	0.02	0.05	51.31	0.02	0.69	0.96
KG	8/8/2006	161.28	2.09	1.83	1.20	147.82	0.11	0.08	70.21	0.07	0.70	1.63
KG	9/12/2006	40.02	1.66	2.31	1.13	141.32	0.14	0.06	63.25	0.19	0.62	1.29
KK	8/8/2006	29.26	2.43	2.04	1.73	133.23	0.11	0.05	64.37	0.08	0.61	2.42
KK	9/12/2006	88.96	1.90	2.01	1.55	135.22	0.11	0.13	58.58	0.07	0.62	1.65
KM	6/9/2005	88.75	1.82	1.87	1.20	124.76	0.20	0.06	64.31	0.12	0.57	1.60
KM	9/13/2005	38.06	1.81	2.53	1.14	128.86	0.25	0.09	67.59	0.12	0.62	1.54
KM	8/8/2006	67.43	2.26	2.42	1.20	138.46	0.16	0.07	68.22	0.09	0.66	1.46
KM	9/12/2006	128.02	1.57	1.68	1.04	136.38	0.09	0.03	63.61	0.10	0.61	1.17
KP	6/9/2005	228.72	3.76	2.18	1.08	105.43	0.21	0.07	98.83	0.15	0.32	0.87
KP	9/13/2005	91.36	2.32	2.77	1.03	128.40	0.27	0.10	69.72	0.26	0.56	4.54
KP	8/8/2006	98.93	2.53	2.11	0.96	130.20	0.12	0.05	68.56	0.23	0.60	2.36
KP	9/12/2006	115.23	1.82	1.94	1.16	123.40	0.10	0.04	57.08	0.12	0.56	1.65

Site	Date	Zn (µgL^{-1})	As (µgL^{-1})	Se (µgL^{-1})	Rb (µgL^{-1})	Sr (µgL^{-1})	Cd (µgL^{-1})	Sn (µgL^{-1})	Ba (µgL^{-1})	Pb (µgL^{-1})	U (µgL^{-1})	Mo (µgL^{-1})
KS	8/8/2006	46.77	2.41	1.78	0.94	128.80	0.10	0.04	61.36	0.05	0.63	1.56
KS	9/12/2006	173.18	2.01	2.39	1.05	136.00	0.15	0.06	57.85	0.08	0.65	1.36
PC	6/9/2005	257.00	2.00	2.09	0.62	125.16	0.22	0.07	59.66	0.15	0.64	2.87
PC	9/13/2005	355.11	3.91	3.01	2.06	112.83	0.28	0.10	106.74	0.14	0.36	0.97
PC	8/8/2006	31.32	3.88	2.87	1.66	114.13	0.17	0.08	96.42	0.42	0.44	0.91
PC	9/12/2006	111.38	2.68	1.73	1.42	105.41	0.08	0.03	85.17	0.07	0.39	0.88
SB	6/9/2005	221.97	2.41	2.25	1.46	166.55	0.23	0.08	87.83	0.09	0.61	0.72
SB	9/13/2005	186.37	2.04	1.77	1.53	182.37	0.20	0.06	91.88	0.07	0.65	0.74
WC	8/8/2006	14.65	3.20	5.93	25.95	382.58	0.56	0.26	134.39	0.23	0.43	1.06
WC	9/12/2006	173.84	2.44	5.49	1.39	369.36	0.44	0.28	125.06	0.17	0.53	1.20

APPENDIX III

HISTORICAL MEAN GROWING SEASON DATA

Historical mean growing season data by year for total phosphorus (TP_{SITE}), discharge (D_{SITE}) and P load (L_{SOURCE}).

Year	TP_{KM} (μgL^{-1})	TP_{KC} (μgL^{-1})	TP_{KA} (μgL^{-1})	D_{KM} (m^{3}s^{-1})	D_{KC} (m^{3}s^{-1})
2008					
2007					
2006	62.4	70.4	78.1	22.8	23.8
2005	47.9	70.3	79.5	19.3	20.1
2004	63.0	69.0	91.0	26.9	28.0
2003	58.0	117.0	115.0	19.2	20.0
2002	49.0	72.0	104.0	26.1	27.2
2001	61.0	61.0	91.0	30.5	31.8
2000	86.0	73.0	-	23.8	24.8
1999	65.0	72.0	-	20.7	21.5
1998	-	66.0	100.0	26.6	27.7
1997	-	-	-	-	26.7
1996	-	-	-	-	21.3
1995	-	-	-	-	24.3
1994	-	68.5	-	-	27.6
1993	-	79.2	-	-	35.7
1992	-	85.4	-	-	25.8
1991	-	72.0	-	-	27.2
1990	-	72.7	-	-	28.6
1989	-	72.2	-	-	32.8
1988	-	88.4	-	-	21.1
1987	-	78.0	-	-	19.3
1986	-	67.1	-	-	29.9
1985	-	77.9	-	-	30.0
1984	-	76.5	-	-	-
1983	-	87.1	-	-	-
1982	-	76.5	-	-	-
1981	-	78.5	-	-	-
1980	-	98.3	-	-	-
1979	-	126.0	-	-	24.8
1978	-	135.3	-	-	27.2
1977	-	137.1	-	-	18.3
1976	-	93.9	-	-	29.9
1975	-	106.3	-	-	34.9
1974	-	-	-	-	34.1
1973	-	-	-	-	36.1

Year	TP_{KM} (μgL^{-1})	TP_{KC} (μgL^{-1})	TP_{KA} (μgL^{-1})	D_{KM} (m^3s^{-1})	D_{KC} (m^3s^{-1})
1972	-	116.7	-	-	25.7
1971	-	160.0	-	-	16.7
1970	-	-	-	-	27.9
1969	-	-	-	-	32.0
1968	-	-	-	-	25.8
1967	-	-	-	-	22.2
1966	-	-	-	-	18.8
1965	-	-	-	-	16.2
1964	-	-	-	-	11.0
1963	-	-	-	-	12.8
1962	-	-	-	-	17.4
1961	-	-	-	-	19.3
1960	-	-	-	-	28.1
1959	-	-	-	-	17.9
1958	-	-	-	-	13.6
1957	-	-	-	-	18.7
1956	-	-	-	-	26.3
1955	-	-	-	-	16.5
1954	-	-	-	-	20.5
1953	-	-	-	-	17.2
1952	-	-	-	-	27.3
1951	-	-	-	-	26.7
1950	-	-	-	-	39.2
1949	-	-	-	-	21.1
1948	-	-	-	-	27.6
1947	-	-	-	-	41.8
1946	-	-	-	-	14.7
1945	-	-	-	-	25.1
1944	-	-	-	-	24.1
1943	-	-	-	-	42.3
1942	-	-	-	-	27.5
1941	-	-	-	-	16.4
1940	-	-	-	-	21.0
1939	-	-	-	-	19.8
1938	-	-	-	-	22.5
1937	-	-	-	-	28.8
1936	-	-	-	-	13.1
1935	-	-	-	-	16.6
1934	-	-	-	-	14.4
1933	-	-	-	-	22.4

Year	D_{KA} (m^3s^{-1})	L_{PBM} (kg)	L_{PAM} (kg)	L_{CBM} (kg)	L_{CAM} (kg)
2008		4,323	9,651		
2007		5,842	7,731		
2006	40.7	3,591	9,383	18,941	14,402
2005	34.2	4,681	10,189	9,939	10,405
2004	48.1	5,155	8,516	21,595	30,226
2003	34.0	6,508	9,215	11,121	15,593
2002	46.7	4,753	8,765	15,458	37,122
2001	54.9	5,659	10,256	23,753	38,061
2000	42.4	-	-	-	-
1999	36.7	-	-	-	-
1998	47.6	7,694	15,756	-	30,633
1997	-	-	-	-	-
1996	-	-	-	-	-
1995	-	-	-	-	-
1994	-	-	-	-	-
1993	-	-	-	-	-
1992	-	-	-	-	-
1991	-	-	-	-	-
1990	-	-	-	-	-
1989	-	-	-	-	-
1988	-	-	-	-	-
1987	-	-	-	-	-
1986	-	-	-	-	-
1985	-	-	-	-	-
1984	-	-	-	-	-
1983	-	-	-	-	-
1982	-	-	-	-	-
1981	-	-	-	-	-
1980	-	-	-	-	-
1979	-	-	-	-	-
1978	-	-	-	-	-
1977	-	-	-	-	-
1976	-	-	-	-	-
1975	-	-	-	-	-
1974	-	-	-	-	-
1973	-	-	-	-	-

Year	D_{KA} (m^3s^{-1})	L_{PBM} (kg)	L_{PAM} (kg)	L_{CBM} (kg)	L_{CAM} (kg)
1972	-	-	-	-	-
1971	-	-	-	-	-
1970	-	-	-	-	-
1969	-	-	-	-	-
1968	-	-	-	-	-
1967	-	-	-	-	-
1966	-	-	-	-	-
1965	-	-	-	-	-
1964	-	-	-	-	-
1963	-	-	-	-	-
1962	-	-	-	-	-
1961	-	-	-	-	-
1960	-	-	-	-	-
1959	-	-	-	-	-
1958	-	-	-	-	-
1957	-	-	-	-	-
1956	-	-	-	-	-
1955	-	-	-	-	-
1954	-	-	-	-	-
1953	-	-	-	-	-
1952	-	-	-	-	-
1951	-	-	-	-	-
1950	-	-	-	-	-
1949	-	-	-	-	-
1948	-	-	-	-	-
1947	-	-	-	-	-
1946	-	-	-	-	-
1945	-	-	-	-	-
1944	-	-	-	-	-
1943	-	-	-	-	-
1942	-	-	-	-	-
1941	-	-	-	-	-
1940	-	-	-	-	-
1939	-	-	-	-	-
1938	-	-	-	-	-
1937	-	-	-	-	-
1936	-	-	-	-	-
1935	-	-	-	-	-
1934	-	-	-	-	-
1933	-	-	-	-	-

APPENDIX IV

HISTORICAL MEAN MONTHLY DISCHARGE DATASET

Historical data by year for monthly mean total discharge (MD_{month}), direct discharge (MDD_{month}) and base flow discharge (MBD_{month}) for USGS gaging station number 04106000, the Kalamazoo River at Comstock, MI.

Year	MD_4 (m^3s^{-1})	MD_5 (m^3s^{-1})	MD_6 (m^3s^{-1})	MD_7 (m^3s^{-1})	MD_8 (m^3s^{-1})	MD_9 (m^3s^{-1})
2008	-	-	-	-	-	-
2007	-	-	-	-	-	-
2006	30.0	34.3	23.4	19.0	16.0	20.0
2005	29.6	23.7	20.4	20.1	14.3	12.6
2004	22.3	47.7	38.1	22.3	19.9	17.5
2003	32.5	30.9	17.9	13.3	12.5	13.0
2002	40.2	41.9	25.3	18.4	21.4	15.8
2001	36.0	49.2	38.6	21.1	21.6	24.1
2000	25.0	35.6	30.3	20.1	18.9	18.6
1999	41.7	25.8	17.8	20.6	12.7	10.7
1998	50.0	35.8	22.8	23.5	18.6	15.4
1997	37.7	32.0	29.3	18.8	17.1	25.3
1996	27.8	30.7	29.6	14.9	12.8	12.1
1995	33.8	32.5	21.4	19.8	22.7	15.7
1994	33.1	26.1	25.1	28.3	34.5	18.6
1993	58.3	34.4	38.2	29.4	21.7	32.0
1992	37.7	27.3	20.5	20.9	23.7	24.7
1991	52.1	34.5	22.7	18.4	19.4	16.2
1990	41.4	41.5	24.5	24.1	20.3	19.8
1989	38.9	27.2	58.4	24.1	21.0	27.3
1988	42.5	23.1	13.8	12.0	13.3	21.7
1987	27.9	19.8	15.3	14.6	17.2	20.9
1986	34.9	31.4	36.4	30.6	19.9	26.4
1985	65.1	31.0	24.5	21.0	18.3	20.0
1984	-	-	-	-	-	-
1983	-	-	-	-	-	-
1982	-	-	-	-	-	-
1981	-	-	-	-	-	-
1980	-	-	-	-	-	-
1979	43.1	32.5	20.1	20.2	19.9	12.8
1978	44.6	27.7	28.1	28.7	14.5	19.7
1977	36.1	19.5	13.9	11.8	12.4	16.2
1976	44.6	50.0	28.5	26.0	15.7	14.3
1975	57.7	42.7	34.2	18.5	23.0	33.1
1974	59.1	51.8	35.9	20.5	18.9	18.2
1973	49.2	44.9	44.9	31.4	27.5	18.5

Year	MD_4 (m^3s^{-1})	MD_5 (m^3s^{-1})	MD_6 (m^3s^{-1})	MD_7 (m^3s^{-1})	MD_8 (m^3s^{-1})	MD_9 (m^3s^{-1})
1972	38.4	30.9	22.7	18.6	19.6	23.8
1971	26.5	18.5	14.8	14.1	11.8	14.3
1970	47.0	36.3	21.8	25.4	20.5	16.6
1969	49.1	41.8	38.5	27.9	19.5	15.1
1968	30.5	21.2	26.4	36.5	21.8	18.5
1967	43.8	25.0	22.3	17.1	12.4	12.5
1966	26.9	34.6	17.0	12.1	12.3	9.8
1965	35.9	15.4	14.0	9.3	10.4	12.2
1964	17.5	14.5	9.6	8.0	7.3	8.9
1963	19.4	19.5	11.0	9.6	9.2	7.9
1962	28.1	24.4	14.2	13.4	13.2	10.9
1961	32.0	25.7	16.6	11.9	13.3	16.5
1960	48.4	29.0	36.5	24.8	15.8	13.9
1959	35.6	22.1	15.1	12.8	11.9	10.0
1958	19.2	13.0	13.1	14.4	11.4	10.2
1957	28.3	29.8	16.6	15.3	10.3	11.7
1956	32.3	58.4	20.5	19.0	15.6	12.0
1955	26.2	17.0	18.2	15.8	11.3	10.2
1954	35.4	19.9	28.1	16.5	12.1	11.3
1953	25.3	22.0	19.7	14.3	12.7	9.5
1952	48.8	38.0	26.6	19.8	15.4	14.9
1951	37.3	33.9	26.3	24.6	20.9	17.0
1950	85.5	41.1	34.5	27.3	18.3	28.2
1949	40.8	23.1	21.6	13.9	13.2	14.3
1948	43.5	53.2	21.9	19.0	14.0	13.6
1947	83.8	50.4	45.9	24.3	19.3	26.9
1946	18.5	19.2	18.7	11.7	9.8	10.1
1945	25.9	44.8	33.6	17.0	13.2	16.0
1944	48.6	32.4	23.2	13.4	13.1	14.0
1943	30.3	70.3	57.9	41.0	22.6	31.5
1942	33.9	25.8	33.0	23.4	29.7	18.9
1941	30.5	17.9	18.4	13.9	8.8	8.8
1940	27.7	19.5	23.3	14.7	16.7	24.1
1939	40.9	21.8	17.3	14.3	14.4	10.2
1938	30.0	25.0	30.9	16.3	17.5	15.4
1937	39.6	26.8	41.0	30.7	20.4	14.0
1936	22.4	17.7	10.0	7.8	7.8	13.2
1935	18.0	23.1	21.0	10.2	16.8	10.6
1934	38.5	14.6	8.6	7.6	6.6	10.6
1933	37.5	35.9	16.4	21.9	12.0	10.9

Year	MDD_4 (m^3s^{-1})	MDD_5 (m^3s^{-1})	MDD_6 (m^3s^{-1})	MDD_7 (m^3s^{-1})	MDD_8 (m^3s^{-1})	MDD_9 (m^3s^{-1})
2008	-	-	-	-	-	-
2007	-	-	-	-	-	-
2006	3.8	10.1	4.4	3.4	3.5	4.8
2005	2.7	4.1	4.1	5.4	2.0	3.7
2004	2.4	20.8	5.4	5.1	4.6	3.0
2003	7.4	8.5	2.6	3.2	2.9	3.7
2002	7.1	9.3	2.3	3.7	4.6	2.1
2001	7.6	14.9	3.2	3.8	5.4	6.1
2000	8.3	11.3	6.1	2.5	4.7	4.6
1999	16.3	2.0	3.6	4.9	2.7	2.3
1998	9.2	5.6	4.5	4.7	3.7	2.5
1997	5.1	6.5	6.8	2.2	4.3	7.6
1996	8.0	5.8	7.2	1.5	2.4	3.0
1995	7.2	6.3	3.4	4.6	6.4	2.4
1994	4.7	3.5	9.3	4.3	10.7	2.3
1993	11.8	2.6	11.0	3.9	4.3	9.7
1992	7.9	2.4	3.9	5.8	5.2	6.5
1991	12.1	2.4	2.5	3.3	4.4	4.4
1990	7.3	9.8	2.6	5.6	4.2	5.5
1989	5.1	5.1	18.4	2.7	3.3	6.7
1988	10.3	2.0	1.8	2.4	3.1	8.0
1987	5.2	2.9	2.4	2.8	5.1	5.1
1986	3.3	6.6	8.2	7.3	3.3	9.4
1985	14.8	4.4	3.1	4.0	3.2	4.1
1984	-	-	-	-	-	-
1983	-	-	-	-	-	-
1982	-	-	-	-	-	-
1981	-	-	-	-	-	-
1980	-	-	-	-	-	-
1979	9.6	4.9	3.5	4.3	5.1	1.9
1978	7.7	6.2	10.8	4.5	2.1	5.8
1977	7.6	1.6	2.8	2.1	3.2	4.7
1976	9.3	8.6	4.8	5.8	2.0	3.4
1975	18.4	4.1	5.5	2.2	9.1	8.6
1974	11.8	12.8	3.6	2.1	3.5	3.7
1973	9.4	10.8	8.1	5.6	5.6	4.6

Year	MDD_4 (m^3s^{-1})	MDD_5 (m^3s^{-1})	MDD_6 (m^3s^{-1})	MDD_7 (m^3s^{-1})	MDD_8 (m^3s^{-1})	MDD_9 (m^3s^{-1})
1972	8.5	5.2	4.0	3.4	5.3	6.5
1971	2.5	2.7	1.9	3.1	2.0	4.3
1970	14.5	7.7	3.1	7.1	3.0	3.6
1969	13.1	6.7	9.1	7.8	2.1	2.7
1968	5.5	4.5	9.1	10.2	3.0	5.1
1967	8.0	1.6	5.4	2.4	2.2	2.5
1966	6.7	8.0	2.0	1.9	3.0	1.6
1965	9.8	1.1	3.0	1.5	3.1	2.7
1964	4.2	2.6	1.7	1.4	1.3	2.3
1963	1.6	4.3	1.8	2.2	1.8	1.3
1962	2.0	6.1	3.0	3.2	2.2	2.3
1961	10.5	2.3	2.3	2.0	3.3	4.1
1960	14.8	5.9	12.6	5.5	2.5	2.7
1959	6.1	3.9	3.4	2.9	1.9	1.4
1958	3.6	3.2	3.8	3.3	1.9	1.9
1957	9.1	8.4	3.4	3.8	2.1	2.5
1956	9.3	18.5	4.6	3.8	2.5	2.1
1955	4.1	2.2	4.5	3.4	2.0	1.6
1954	5.2	1.1	9.8	2.7	3.1	2.5
1953	4.3	2.9	5.4	2.5	2.5	1.6
1952	10.6	11.0	2.3	3.9	2.1	3.0
1951	9.0	6.2	5.7	6.2	3.1	3.0
1950	25.8	4.0	6.9	6.8	2.1	8.7
1949	11.3	4.2	5.7	1.5	2.4	3.3
1948	4.8	16.4	5.6	2.5	2.4	3.0
1947	28.4	13.4	8.0	3.6	4.4	6.6
1946	1.5	4.8	3.7	1.2	1.7	2.3
1945	6.2	16.7	4.6	2.6	2.0	4.7
1944	10.3	9.4	4.1	1.7	3.3	2.5
1943	3.7	27.4	10.0	8.9	2.4	8.2
1942	2.6	5.3	8.2	4.4	6.6	2.2
1941	7.4	1.0	4.4	2.1	1.2	2.2
1940	5.1	3.2	7.1	2.3	6.7	6.0
1939	13.1	3.3	3.3	2.0	4.4	2.0
1938	5.5	9.7	7.4	3.3	4.4	3.6
1937	14.8	3.7	20.4	5.3	6.0	3.8
1936	4.4	3.8	2.1	1.4	1.8	4.5
1935	1.3	7.2	5.8	2.2	4.8	1.7
1934	12.4	1.0	1.4	1.4	1.3	3.3
1933	8.6	8.3	1.6	5.5	1.5	3.4

Year	MBD$_4$ (m^3s^{-1})	MBD$_5$ (m^3s^{-1})	MBD$_6$ (m^3s^{-1})	MBD$_7$ (m^3s^{-1})	MBD$_8$ (m^3s^{-1})	MBD$_9$ (m^3s^{-1})
2008	-	-	-	-	-	-
2007	-	-	-	-	-	-
2006	26.2	24.2	19.0	15.6	12.5	15.2
2005	26.9	19.6	16.3	14.6	12.3	8.8
2004	19.9	26.9	32.8	17.2	15.3	14.5
2003	25.1	22.4	15.3	10.1	9.6	9.3
2002	33.1	32.6	23.0	14.7	16.8	13.6
2001	28.4	34.3	35.4	17.3	16.1	18.1
2000	16.7	24.3	24.2	17.6	14.3	14.0
1999	25.4	23.7	14.2	15.7	10.0	8.4
1998	40.7	30.2	18.3	18.8	14.9	12.9
1997	32.7	25.5	22.5	16.6	12.8	17.6
1996	19.8	24.9	22.4	13.4	10.4	9.1
1995	26.7	26.1	18.0	15.1	16.2	13.3
1994	28.4	22.6	15.8	24.0	23.8	16.3
1993	46.5	31.8	27.2	25.5	17.4	22.3
1992	29.9	24.9	16.6	15.1	18.5	18.3
1991	40.1	32.1	20.2	15.1	15.0	11.9
1990	34.1	31.7	22.0	18.4	16.1	14.3
1989	33.7	22.1	40.0	21.4	17.7	20.6
1988	32.2	21.1	12.0	9.6	10.3	13.7
1987	22.7	16.9	12.9	11.7	12.1	15.8
1986	31.5	24.8	28.1	23.4	16.6	17.0
1985	50.3	26.7	21.4	17.0	15.2	15.9
1984	-	-	-	-	-	-
1983	-	-	-	-	-	-
1982	-	-	-	-	-	-
1981	-	-	-	-	-	-
1980	-	-	-	-	-	-
1979	33.6	27.5	16.6	15.9	14.7	11.0
1978	36.9	21.5	17.4	24.2	12.4	13.8
1977	28.5	17.9	11.1	9.8	9.2	11.4
1976	35.3	41.4	23.7	20.2	13.7	11.0
1975	39.3	38.5	28.7	16.3	13.9	24.5
1974	47.3	39.0	32.3	18.4	15.3	14.5
1973	39.8	34.0	36.8	25.8	22.0	13.9

Year	MDD$_9$ (m^3s^{-1})	MBD$_4$ (m^3s^{-1})	MBD$_5$ (m^3s^{-1})	MBD$_6$ (m^3s^{-1})	MBD$_7$ (m^3s^{-1})	MBD$_8$ (m^3s^{-1})	MBD$_9$ (m^3s^{-1})
1972	6.5	29.9	25.7	18.7	15.3	14.3	17.3
1971	4.3	24.1	15.8	12.9	11.0	9.8	10.1
1970	3.6	32.5	28.6	18.8	18.3	17.5	13.0
1969	2.7	36.1	35.2	29.4	20.2	17.4	12.4
1968	5.1	25.0	16.8	17.4	26.3	18.8	13.3
1967	2.5	35.8	23.4	16.9	14.6	10.3	10.1
1966	1.6	20.2	26.6	15.0	10.2	9.3	8.2
1965	2.7	26.1	14.3	11.0	7.8	7.3	9.5
1964	2.3	13.3	11.9	7.9	6.6	5.9	6.5
1963	1.3	17.8	15.2	9.2	7.4	7.4	6.6
1962	2.3	26.0	18.2	11.2	10.3	11.0	8.6
1961	4.1	21.5	23.4	14.2	9.9	10.0	12.4
1960	2.7	33.6	23.1	23.9	19.3	13.3	11.2
1959	1.4	29.5	18.2	11.7	9.9	10.0	8.5
1958	1.9	15.5	9.8	9.3	11.1	9.5	8.3
1957	2.5	19.2	21.4	13.2	11.5	8.2	9.2
1956	2.1	23.0	39.9	15.9	15.2	13.1	10.0
1955	1.6	22.1	14.8	13.8	12.4	9.3	8.6
1954	2.5	30.2	18.8	18.3	13.8	9.0	8.8
1953	1.6	21.0	19.1	14.3	11.8	10.2	7.8
1952	3.0	38.2	27.1	24.3	15.9	13.3	12.0
1951	3.0	28.3	27.7	20.6	18.4	17.8	14.0
1950	8.7	59.6	37.1	27.6	20.5	16.3	19.6
1949	3.3	29.5	18.9	15.9	12.5	10.8	10.9
1948	3.0	38.7	36.8	16.4	16.6	11.7	10.7
1947	6.6	55.3	37.1	37.9	20.7	14.9	20.3
1946	2.3	17.0	14.3	15.0	10.5	8.2	7.8
1945	4.7	19.7	28.2	29.1	14.4	11.2	11.3
1944	2.5	38.3	23.1	19.1	11.7	9.8	11.5
1943	8.2	26.7	42.9	47.9	32.0	20.2	23.3
1942	2.2	31.3	20.5	24.8	18.9	23.1	16.7
1941	2.2	23.1	16.9	14.0	11.8	7.6	6.6
1940	6.0	22.6	16.3	16.2	12.4	10.0	18.1
1939	2.0	27.8	18.5	14.0	12.3	10.0	8.2
1938	3.6	24.5	15.3	23.5	13.0	13.1	11.8
1937	3.8	24.9	23.1	20.7	25.4	14.4	10.2
1936	4.5	18.0	13.9	7.8	6.5	6.0	8.8
1935	1.7	16.7	15.9	15.2	8.0	12.0	9.0
1934	3.3	26.1	13.5	7.2	6.2	5.4	7.4
1933	3.4	28.9	27.7	14.8	16.4	10.6	7.6

APPENDIX V

MIXED LINEAR MODEL THEORY

Mixed Linear Model Theory

An overview of a likelihood-based approach to the mixed linear models (MLM) used for this research is presented here. This approach simplifies and unifies many common statistical analyses, including those involving repeated measures, random effects and random coefficients. The basic assumption is that the data are linearly related to unobserved multivariate normal random variables. Only the model options used for this analysis are included in this discussion. Many options are available for the construction of MLMs and additional theory with examples is provided in Littell et al. (2006). This information has been consolidated from numerous references (Littel et al., 2006; Milliken and Johnson, 1984; SAS, 1999; Searle, 1971; Taskinen et al., 2008; University of Oregon, 2007).

Formulation of the mixed model

The classical general linear model can be written as

$$\mathbf{y} = \mathbf{X\beta} + \boldsymbol{\varepsilon} \tag{1}$$

where **y** is a vector of observations, **X** is a known matrix of explanatory variables, $\boldsymbol{\beta}$ is an unknown fixed effects parameter vector and $\boldsymbol{\varepsilon}$ is an unobserved vector of residuals. The residuals are often assumed to be independent and identically distributed. In many cases this is unrealistic. Correlations and heterogeneities between the terms of $\boldsymbol{\varepsilon}$ can be taken into account in a MLM, written as

$$\mathbf{y} = \mathbf{X\beta} + \mathbf{Z}\gamma + \boldsymbol{\varepsilon} \tag{2}$$

with the addition of a known design matrix **Z** and a vector γ of unknown random terms added to the classical linear model. Equation 2 is called a mixed model because it contains both deterministic, $\boldsymbol{\beta}$, and random, $\boldsymbol{\gamma}$, components. A key assumption is that $\boldsymbol{\gamma}$ and $\boldsymbol{\varepsilon}$ are zero-mean, normally distributed with

$$\mathbf{E}\begin{bmatrix}\boldsymbol{\gamma}\\ \boldsymbol{\varepsilon}\end{bmatrix} = \begin{bmatrix}\mathbf{0}\\ \mathbf{0}\end{bmatrix} \text{ and } \mathbf{Var}\begin{bmatrix}\boldsymbol{\gamma}\\ \boldsymbol{\varepsilon}\end{bmatrix} = \begin{bmatrix}\mathbf{G} & \mathbf{0}\\ \mathbf{0} & \mathbf{R}\end{bmatrix} \qquad (3)$$

V denotes the variance of **y** and is determined by the matrix **Z** and by the covariance matrices, **G** and **R** through the formula $\mathbf{V} = \mathbf{ZGZ}' + \mathbf{R}$.

Parameter estimation for the mixed model

The general linear model requires only an estimate of $\boldsymbol{\beta}$, where in the MLM $\boldsymbol{\gamma}$, **G** and **R** are unknown and must be estimated along with $\boldsymbol{\beta}$. Instead of the least squares method (LS) the generalized least squares (GLS) method is more appropriate. The GLS minimizes

$$(\mathbf{y} - \mathbf{X}\boldsymbol{\beta})'\mathbf{V}^{-1}(\mathbf{y} - \mathbf{X}\boldsymbol{\beta}) \qquad (4)$$

Since **G** and **R** and therefore **V** are unknown, the GLS solution can be estimated in which some reasonable estimate for **V** is inserted into the minimization problem. To find a reasonable estimate of **G** and **R**, the method of maximum likelihood (ML) was implemented in the PROC MIXED procedure of SAS 9.1.3 (SAS, 2007). Based on the assumption that $\boldsymbol{\gamma}$ and $\boldsymbol{\varepsilon}$ are normally distributed, the solution minimizes the following for **G** and **R**:

$$l(\mathbf{G},\mathbf{R}) = -\frac{1}{2}\log|\mathbf{V}| - \frac{1}{2}\mathbf{r}'\mathbf{V}^{-1}\mathbf{r} - \frac{n}{2}\log(2\pi) \qquad (5)$$

where $\mathbf{r} = \mathbf{y} - \mathbf{X}(\mathbf{X}'\mathbf{V}^{-1}\mathbf{X})^{-}\mathbf{X}'\mathbf{V}^{-1}\mathbf{X}\mathbf{y}$ and $^{-}$ denotes a generalized inverse (Searle, 1971).

PROC MIXED actual minimizes -2 times the function in equation 5 using a ridge-stabilized Newton-Raphson algorithm.

The **G** and **R** estimates are denoted $\widehat{\mathbf{G}}$ and $\widehat{\mathbf{R}}$, respectively. To obtain estimates of $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$, the standard method is to solve the mixed model equations (Henderson, 1984):

$$\begin{bmatrix} \mathbf{X}'\widehat{\mathbf{R}}^{-1}\mathbf{X} & \mathbf{X}'\widehat{\mathbf{R}}^{-1}\mathbf{XZ} \\ \mathbf{Z}'\widehat{\mathbf{R}}^{-1}\mathbf{X} & \mathbf{Z}'\widehat{\mathbf{R}}^{-1}\mathbf{Z}+\widehat{\mathbf{G}}^{-1} \end{bmatrix} \begin{bmatrix} \widehat{\boldsymbol{\beta}} \\ \widehat{\boldsymbol{\gamma}} \end{bmatrix} = \begin{bmatrix} \mathbf{X}'\widehat{\mathbf{R}}^{-1}\mathbf{y} \\ \mathbf{Z}'\widehat{\mathbf{R}}^{-1}\mathbf{y} \end{bmatrix} \tag{6}$$

The solution can also be expressed as

$$\widehat{\boldsymbol{\beta}} = (\mathbf{X}'\widehat{\mathbf{V}}^{-1}\mathbf{X})^{-}\,\mathbf{X}'\widehat{\mathbf{V}}^{-1}\mathbf{y} \tag{7}$$

$$\widehat{\boldsymbol{\gamma}} = \widehat{\mathbf{G}}\mathbf{Z}'\widehat{\mathbf{V}}^{-1}(\mathbf{y}-\mathbf{X}\widehat{\boldsymbol{\beta}}) \tag{8}$$

If **G** and **R** are known, $\widehat{\boldsymbol{\beta}}$ is the best linear unbiased estimator (BLUE) of $\boldsymbol{\beta}$ and $\widehat{\boldsymbol{\gamma}}$ is the best linear unbiased predictor (BLUP) of $\boldsymbol{\gamma}$, where "best" means minimum mean square error. In this study, **G** and **R** are unknown and estimated using the ML method. BLUE and BLUP are no longer appropriate and the word empirical is added to indicate the approximation, leading to the acronyms EBLUE and EBLUP.

Statistical inferences and test statistics

For inferences concerning the fixed and random effects parameters in the MLM, estimable linear combinations of the form

$$L\begin{bmatrix} \boldsymbol{\beta} \\ \boldsymbol{\gamma} \end{bmatrix} \tag{9}$$

are considered. Statistical inferences are made by testing the hypothesis

$$H : L\begin{bmatrix}\beta \\ \gamma\end{bmatrix} = 0$$

or by constructing point and interval estimates.

When the rank of L (number of fixed effects) is greater than one, a general F-statistic can be constructed as follows:

$$F = \frac{\begin{bmatrix}\beta \\ \gamma\end{bmatrix} L'(L'\hat{C}\,L)^{-1}L\begin{bmatrix}\beta \\ \gamma\end{bmatrix}}{\text{rank}(L)} \qquad (10)$$

where $\hat{C}$ is the left hand side matrix of equation 6. The F-statistic enables making inferences about the fixed effects which account for the selected variance-covariance model.

APPENDIX VI

KALMAZOO RIVER/LAKE ALLEGAN SUBWATERSHED LAND USE AND LAND USE EFFECT DATA

Kalamazoo River/Lake Allegan Watershed, HUC 4050003, basin 17: sub numbers; watercourse name; urban, agricultural and lowland forest land use percentages and land use effect estimated using Total = 13.285*lowland forest + 0.6824*agricultural + 1.9588*urban, DP_{TSA} from the catchment influenced MLM. DP_{TSA} categories: low; Total '< 1.090, med; 1.090 ≤ Total ≤ 1.365 and high; Total > 1.365.

		Land Use			Land Use Effect				
Sub	Watercourse Name	Urban (%)	Agricultural (%)	Lowland Forest (%)	Urban	Agricultural	Lowland Forest	Total	DP_{TSA} Category
1	S Br Kalamazoo River	3.7	56.8	3.8	0.073	0.388	0.511	0.971	low
2	S Br Kalamazoo River	4.1	57.0	2.3	0.080	0.389	0.302	0.770	low
3	S Br Kalamazoo River	3.9	54.8	3.8	0.077	0.374	0.508	0.959	low
4	S Br Kalamazoo River	4.0	65.9	5.0	0.078	0.450	0.659	1.187	med
5	S Br Kalamazoo River	3.4	53.3	6.1	0.066	0.363	0.816	1.245	med
6	Lampson Run Drain	3.6	75.2	2.5	0.071	0.513	0.334	0.919	low
7	S Br Kalamazoo River	5.1	63.7	5.8	0.100	0.435	0.772	1.307	med
8	S Br Kalamazoo River	10.2	42.1	4.0	0.199	0.287	0.533	1.020	low
9	North Kalamazoo River	4.9	47.6	3.3	0.097	0.325	0.435	0.857	low
10	Spring Arbor and Concord	5.0	58.1	3.7	0.098	0.397	0.497	0.992	low
11	N Br Kalamazoo River	5.1	54.8	2.3	0.100	0.374	0.308	0.782	low
12	Kalamazoo River	8.7	58.8	2.8	0.171	0.401	0.376	0.947	low
13	Wilder Creek	2.9	65.4	5.1	0.058	0.446	0.684	1.188	med
14	Wilder Creek	4.0	59.0	7.7	0.077	0.402	1.020	1.500	high
15	S Br Rice Creek	4.4	55.0	4.1	0.086	0.375	0.548	1.010	low
16	S Br Rice Creek	4.6	47.3	6.8	0.089	0.323	0.907	1.319	med
17	N Br Rice Creek	3.6	65.2	5.0	0.070	0.445	0.663	1.178	med
18	N Br Rice Creek	3.5	43.7	11.3	0.068	0.299	1.505	1.872	high

		Land Use			Land Use Effect				
Sub	Watercourse Name	Urban (%)	Agricultural (%)	Lowland Forest (%)	Urban	Agricultural	Lowland Forest	Total	DP_{TSA} Category
19	Rice Creek	7.8	58.4	5.2	0.152	0.399	0.697	1.248	med
20	Kalamazoo River	4.0	69.9	2.3	0.079	0.477	0.310	0.866	low
21	Kalamazoo River	9.2	46.7	9.7	0.181	0.319	1.287	1.787	high
22	Kalamazoo River	4.1	65.5	8.1	0.080	0.447	1.079	1.606	high
23	Kalamazoo River	5.9	51.2	5.2	0.117	0.350	0.685	1.151	med
24	Harper Creek	6.4	38.1	10.5	0.125	0.260	1.392	1.777	high
25	Minges Brook	14.9	42.5	6.9	0.292	0.290	0.918	1.499	high
26	Battle Creek	3.8	58.8	7.0	0.075	0.401	0.931	1.407	high
27	Hogle and Miller Drain	3.1	66.2	6.1	0.061	0.452	0.804	1.317	med
28	Battle Creek	3.7	66.3	7.2	0.073	0.453	0.959	1.485	high
29	Big Creek	3.5	68.4	5.1	0.069	0.467	0.681	1.217	med
30	Battle Creek	9.5	61.5	4.6	0.187	0.420	0.608	1.215	med
31	Indian Creek	4.0	56.2	8.9	0.078	0.384	1.188	1.650	high
32	Indian Creek	7.2	48.7	9.3	0.141	0.333	1.234	1.708	high
33	Battle Creek	5.2	64.3	6.6	0.103	0.439	0.882	1.424	high
34	Battle Creek	5.9	50.4	7.7	0.116	0.344	1.024	1.484	high
35	Battle Creek	5.0	31.0	10.7	0.098	0.212	1.418	1.727	high
36	Battle Creek	4.1	34.9	9.2	0.080	0.238	1.227	1.546	high
37	Wanadoga Creek	3.7	60.1	7.0	0.072	0.410	0.933	1.415	high
38	Wanadoga Creek	3.8	37.8	7.3	0.075	0.258	0.963	1.295	med
39	Wanadoga Creek	5.4	26.1	9.6	0.106	0.178	1.273	1.557	high

		Land Use			Land Use Effect				
Sub	Watercourse Name	Urban (%)	Agricultural (%)	Lowland Forest (%)	Urban	Agricultural	Lowland Forest	Total	DP_{TSA} Category
40	Battle Creek	12.9	18.9	6.8	0.252	0.129	0.904	1.284	med
41	Battle Creek	58.9	1.1	3.6	1.154	0.007	0.479	1.640	high
42	Kalamazoo River	25.0	16.6	6.5	0.491	0.113	0.861	1.465	high
43	Wabascon Creek	3.6	41.6	6.8	0.070	0.284	0.909	1.263	med
44	Wabascon Creek	8.8	19.8	6.9	0.172	0.135	0.922	1.230	med
45	Kalamazoo River	27.0	8.3	6.6	0.529	0.057	0.881	1.467	high
46	Sevenmile Creek	4.6	38.9	5.8	0.090	0.266	0.767	1.122	med
47	Augusta Creek	4.3	49.5	4.4	0.084	0.338	0.582	1.004	low
48	Augusta Creek	3.7	30.2	7.0	0.072	0.206	0.933	1.211	med
49	Augusta Creek	7.7	14.2	5.9	0.151	0.097	0.778	1.027	low
50	Gull Creek	5.5	44.3	3.1	0.109	0.302	0.407	0.817	low
51	Gull Creek	4.4	55.5	1.7	0.086	0.379	0.225	0.689	low
52	Kalamazoo River	7.9	10.1	8.5	0.154	0.069	1.126	1.349	med
53	Kalamazoo River	7.7	43.4	3.5	0.151	0.296	0.461	0.908	low
54	Comstock Creek	9.3	53.2	3.7	0.183	0.363	0.492	1.038	low
55	Kalamazoo River	19.8	38.8	4.7	0.389	0.265	0.629	1.282	med
56	Davis Creek	27.5	38.5	5.5	0.539	0.262	0.728	1.529	high
57	Portage Creek	27.6	23.0	5.3	0.541	0.157	0.704	1.402	high
58	Portage Creek	47.9	8.3	6.6	0.938	0.057	0.873	1.868	high
59	W Fork Portage Creek	10.4	21.4	2.5	0.204	0.146	0.327	0.678	low
60	W Fork Portage Creek	28.3	26.6	1.9	0.554	0.181	0.251	0.987	low

		Land Use			Land Use Effect				
Sub	Watercourse Name	Urban (%)	Agricultural (%)	Lowland Forest (%)	Urban	Agricultural	Lowland Forest	Total	DP_{TSA} Category
61	Portage Creek	54.8	0.5	1.4	1.073	0.003	0.184	1.260	med
62	Portage Creek	58.4	0.0	1.2	1.144	0.000	0.158	1.303	med
63	Kalamazoo River	55.1	0.2	4.4	1.078	0.002	0.579	1.659	high
64	Spring Brook	5.4	44.8	2.5	0.105	0.305	0.337	0.747	low
65	Kalamazoo River	31.8	17.7	1.7	0.622	0.121	0.223	0.966	low
66	Kalamazoo River	5.1	41.1	4.3	0.099	0.280	0.575	0.955	low
67	Kalamazoo River	10.6	44.6	3.8	0.208	0.304	0.503	1.016	low
68	Gun River	6.6	30.1	4.5	0.129	0.205	0.601	0.936	low
69	Gun River	5.0	51.3	4.2	0.099	0.350	0.559	1.008	low
70	Gun River	6.1	57.1	2.9	0.120	0.390	0.379	0.889	low
71	Sand Creek	6.7	41.6	5.9	0.130	0.284	0.783	1.198	med
72	Base Line Creek	5.4	51.5	6.1	0.105	0.352	0.816	1.273	med
73	Pine Creek	4.8	49.8	10.4	0.094	0.340	1.383	1.816	high
74	Kalamazoo River	12.6	45.1	3.0	0.247	0.308	0.399	0.955	low
75	Schnable Brook	5.1	58.3	4.0	0.099	0.398	0.531	1.029	low
76	Kalamazoo River	5.5	44.7	4.7	0.107	0.305	0.630	1.042	low
77	Kalamazoo River	8.5	38.2	6.2	0.167	0.261	0.830	1.258	med
78	Kalamazoo River	9.0	37.7	3.1	0.177	0.257	0.416	0.850	low

Bibliography

Bibliography

Arntson, A.D. and Tornes, L.H., 1985. Rainfall-runoff relationships and water-quality assessment of Coon Creek watershed, Anoka County, Minnesota. US Geological Survey of Water Resources Investigation Report 84-4013.

Beauchemin, S. and Simard, R.R., 2000. Phosphorus status of intensively cropped soils of the St. Lawrence lowlands. Soil Science Society of America Journal, 64(2): 659-670.

Bernot, M.J., Tank, J.L., Royer, T.V. and David, M.B., 2006. Nutrient uptake in streams draining agricultural catchments of the midwestern United States. Freshwater Biology, 51(3): 499-509.

Bohr, J. and Liston, C., 1987. A survey of the fish and benthic communities of Morrow Lake on the Kalamazoo River, Michigan, 1985 and 1986, Report to STS Consultants Ltd.

Boutt, D.F., Hyndman, D.W., Pijanowski, B.C. and Long, D.T., 2001. Identifying potential land use-derived solute sources to stream baseflow using ground water models and GIS. Ground Water, 39(1): 24-34.

Brett, M.T., Arhonditsis, G.B., Mueller, S.E., Hartley, D.M., Frodge, J.D. and Funke, D.E., 2005a. Non-point-source impacts on stream nutrient concentrations along a forest to urban gradient. Environmental Management, 35(3): 330-342.

Brett, M.T., Mueller, S.E. and Arhonditsis, G.B., 2005b. A daily time series analysis of stream water phosphorus concentrations along an urban to forest gradient. Environmental Management, 35(1): 56-71.

Brezonik, P.L. and Stadelmann, T.H., 2002. Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. Water Research, 36(7): 1743-1757.

Busse, L.B., Simpson, J.C. and Cooper, S.D., 2006. Relationships among nutrients, algae, and land use in urbanized southern California streams. Canadian Journal of Fisheries and Aquatic Sciences, 63(12): 2621-2638.

Carpenter, S.R., 2002. Ecological Futures: Building an Ecology of the Long Now. Ecology, 83(8): 2069-2083.

Carpenter, S.R., 2005. Eutrophication of Aquatic Ecosystems: Bistability and Soil Phosphorus. Proceedings of the National Academy of Sciences of the United States of America, 102(29): 10002-10005.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H., 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. Ecological Applications, 8(3): 559-568.

Cooper, J., 2005. A biological survey of the Kalamazoo River and selected tributaries from the City of Battle Creek to Lake Michigan July-September 2004. Report No. MI/DEQ/WB-05/064, MDEQ, Water Bureau.

Coulter, C.B., Kolka, R.K. and Thompson, J.A., 2004. Water quality in agricultural, urban, and mixed land use watersheds. Journal of the American Water Resources Association, 40(6): 1593-1601.

Dillon, P.J. and Kirchner, W.B., 1975. Effects of geology and land-use on export of phosphorus from watersheds. Water Research, 9(2): 135-148.

Dodd, J., Large, D.J., Fortey, N.J., Kemp, S., Styles, M., Wetton, P. and Milodowski, A., 2003. Geochemistry and petrography of phosphorus in urban canal bed sediment. Applied Geochemistry, 18(2): 259-267.

Dodds, W.K., 2007. Trophic state, eutrophication and nutrient criteria in streams. Trends Ecol Evol, 22(12): 669-76.

Dodds, W.K. and Oakes, R.M., 2006. Controls on nutrients across a prairie stream watershed: Land use and riparian cover effects. Environmental Management, 37(5): 634-646.

Dodds, W.K., Smith, V.H. and Lohman, K., 2002. Nitrogen and phosphorus relationships to benthic algal biomass in temperate streams. Canadian Journal of Fisheries and Aquatic Sciences, 59(5): 865-874.

Dorioz, J.M., Cassell, E.A., Orand, A. and Eisenman, K.G., 1998. Phosphorus storage, transport and export dynamics in the Foron river watershed. Hydrological Processes, 12(2): 285-309.

Eckhardt, K., 2005. How to construct recursive digital filters for baseflow separation. Hydrological Processes, 19(2): 507-515.

Edmondson, W.T., Anderson, G.C. and Peterson, D.R., 1956. Artificial Eutrophication of Lake Washington. Limnology and Oceanography, 1(1): 47-53.

Edmondson, W.T. and Lehman, J.T., 1981. The effect of changes in the nutrient income on the condition of Lake Washington. Limnology and Oceanography, 26(1): 1-29.

Evans, D.J. and Johnes, P., 2004. Physico-chemical controls on phosphorus cycling in two lowland streams. Part 1 - the water column. Science of the Total Environment, 329(1-3): 145-163.

Feyereisen, G.W., Lowrance, R., Strickland, T.C., Sheridan, J.M., Hubbard, R.K. and Bosch, D.D., 2007. Long-term water chemistry database, Little River Experimental Watershed, southeast Coastal Plain, United States. Water Resources Research, 43(9).

Figueroa-Nieves, D., Royer, T.V. and David, M.B., 2006. Controls on chlorophyll-a in nutrient-rich agricultural streams in Illinois, USA. Hydrobiologia, 568: 287-298.

Fitzpatrick, M.L., Long, D.T. and Pijanowski, B.C., 2007. Exploring the effects of urban and agricultural land use on surface water chemistry, across a regional watershed, using multivariate statistics. Applied Geochemistry, 22(8): 1825-1840.

Freeze, R.A. and Cherry, J.A., 1979. Groundwater. Prentice Hall, Englewood Cliffs, NJ.

French, T.D. and Petticrew, E.L., 2007. Chlorophyll a seasonality in four shallow eutrophic lakes (northern British Columbia, Canada) and the critical roles of internal phosphorus loading and temperature. Hydrobiologia, 575: 285-299.

Gburek, W.J. and Sharpley, A.N., 1998. Hydrologic controls on phosphorus loss from upland agricultural watersheds. Journal of Environmental Quality, 27(2): 267-277.

Glandon, R.P., Payne, F.C., McNabb, C.D. and Batterson, T.R., 1980. A comparison of rain-related phosphorus and nitrogen loading from urban, wetland, and agricultural sources. Water Research, 15: 881-887.

Green, M.B., Nieber, J.L., Johnson, G., Magner, J. and Schaefer, B., 2007. Flow path influence on an N : P ratio in two headwater streams: A paired watershed study. Journal of Geophysical Research-Biogeosciences, 112(G3).

Grobbelaar, J.U. and House, W.A., 1995. Phosphorus as a limiting resource in inland waters; interaction with nitorgen. In: H. Tiessen (Editor), Phosphorus in the global environment. John Wiley & Sons, New York, pp. 255-273.

Grover, J.P. and Chrzanowski, T.H., 2004. Limiting resources, disturbance, and diversity in phytoplankton communities. Ecological Monographs, 74(3): 533-551.

Haggard, B.E., Soerens, T.S., Green, W.R. and Richards, R.P., 2003. Using regression methods to estimate stream phosphorus loads at the Illinois River, Arkansas. Applied Engineering in Agriculture, 19(2): 187-194.

Håkanson, L., 2005. The Importance of Lake Morphometry for the Structure and Function of Lakes. International Review of Hydrobiology, 90(4): 433-461.

Hatt, B.E., Fletcher, T.D., Walsh, C.J. and Taylor, S.L., 2004. The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environmental Management, 34(1): 112-124.

Havel, J.E. and Pattinson, K.R., 2004. Spatial distribution and seasonal dynamics of plankton in a terminal multiple-series reservoir. Lake and Reservoir Management, 20(1): 14-26.

Heaton, S., 1999. Loading assessments of phosphorus inputs to Lake Allegan, 1998. Report No. MI/DEQ/SWQ-99-125, MDEQ, Surface Water Quality Division.

Heaton, S., 2001. Total maximum daily load (TMDL) for total phosphorus in Lake Allegan. http://www.deq.state.mi.us/documents/deq-swq-gleas-tmdlallegan.pdf, MDEQ, Surface Water Quality Division.

Heaton, S., 2003. Water quality monitoring of Lake Allegan and select stations on the Kalamazoo River, 2003. Report No. MI/DEQ/SWQ-03-1.3, MDEQ, Surface Water Quality Division.

Herlihy, A.T., Stoddard, J.L. and Johnson, C.B., 1998. The relationship between stream chemistry and watershed land cover data in the mid-Atlantic region, US, pp. 377-386.

Hickey, M.B.C. and Doran, B., 2004. A review of the efficiency of buffer strips for the maintenance and enhancement of riparian ecosystems. Water Quality Research Journal of Canada, 39(3): 311-317.

House, W.A., 2003. Geochemical cycling of phosphorus in rivers. Applied Geochemistry, 18(5): 739-748.

Inamdar, S.P., Mostaghimi, S., McClellan, P.W. and Brannan, K.M., 2001. BMP impacts on sediment and nutrient yields from an agricultural watershed in the coastal plain region. Transactions of the Asae, 44(5): 1191-1200.

Jordan-Meille, L., Dorioz, J.M. and Wang, D., 1998. Analysis of the export of diffuse phosphorus from a small rural watershed. Agronomie, 18(1): 5-26.

Kelly, V.J., 2001. Influence of reservoirs on solute transport: a regional-scale approach. Hydrological Processes, 15(7): 1227-1249.

Kennedy, R.H. and Walker, W.W., 1990. Reservoir Nutrient Dynamics. In: K.W. Thornton, B.L. Kimmel and F.E. Payne (Editors), Reservoir Limnology: Ecological Perspectives. John Wiley & Sons, Inc., New York, NY.

Kieser & Associates, 2008. Kalamazoo River TMDL Point Source Tracking Program, http://www.kalamazooriver.net/cgi/ps_v2/intro.cgi.

Kimmel, B.L., Lind, O.T. and Paulson, L.J., 1990. Reservoir Primary Production. In: K.W. Thornton, B.L. Kimmel and F.E. Payne (Editors), Reservoir Limnology: Ecological Perspectives. John Wiley & Sons, Inc., New York, NY.

King, R.S., Baker, M.E., Whigham, D.F., Weller, D.E., Jordan, T.E., Kazyak, P.F. and Hurd, M.K., 2005. Spatial considerations for linking watershed land cover to ecological indicators in streams. Ecological Applications, 15(1): 137-153.

Kleinman, P.J.A., Bryant, R.B., Reid, W.S., Sharpley, A.N. and Pimentel, D., 2000. Using soil phosphorus behavior to identify environmental thresholds. Soil Science, 165(12): 943-950.

Knoll, L.B., Vanni, M.J. and Renwick, W.H., 2003. Phytoplankton primary production and photosynthetic parameters in reservoirs along a gradient of watershed land use. Limnology and Oceanography, 48(2): 608-617.

Kosek, S., 1997. Water quality and pollution control in Michigan, 1996 Report. Michigan 305(b) Report: Volume 14. Report No. MI/DEQ/SWQ-97-040, MDEQ, Surface Water Quality Division.

Langner, C.L. and Hendrix, P.F., 1982. Evaluation of a persulfate digestion method for particulate nitrogen and phosphorus. Water Research, 16(10): 1451-1454.

Lehrter, J.C., 2006. Effects of land use and land cover, stream discharge, and interannual climate on the magnitude and timing of nitrogen, phosphorus, and organic carbon concentrations in three coastal plain watersheds. Water Environment Research, 78(12): 2356-2368.

Lewis, G.P., Mitchell, J.D., Andersen, C.B., Haney, D.C., Liao, M.K. and Sargent, K.A., 2007. Urban influences on stream chemistry and biology in the Big Brushy Creek watershed, South Carolina. Water Air and Soil Pollution, 182(1-4): 303-323.

Likens, G.E., Bartsch, A.F., Lauff, G.H. and Hobbie, J.E., 1971. Nutrients and eutrophication. Science, 172(3985): 873-&.

Lim, K.J., Engel, B.A., Tang, Z.X., Choi, J., Kim, K.S., Muthukrishnan, S. and Tripathy, D., 2005. Automated Web Gis based hydrograph analysis tool, what. Journal of the American Water Resources Association, 41(6): 1407-1416.

Lim, K.J., Engel, B.A., Tang, Z.X., Theller, L. and Muthukrishnan, S., 2004. WHAT: Web-based hydrograph analysis tool, http://cobweb.ecn.purdue.edu/~what/.

Littel, R.C., Milliken, G.A., Strup, W.W. and Wolfinger, R.D., 2006. SAS system for mixed models. SAS Institute, Cary, NC.

Litwack, H.S., DiLorenz, J.L., Huang, P. and Najarian, T.O., 2006. Development of a simple phosphorus model for a large urban watershed: A case study. Journal of Environmental Engineering-Asce, 132(4): 538-546.

Liu, Z.J., Weller, D.E., Correll, D.L. and Jordan, T.E., 2000. Effects of land cover and geology on stream chemistry in watersheds of Chesapeake Bay. Journal of the American Water Resources Association, 36(6): 1349-1365.

McDowell, R., Sharpley, A. and Folmar, G., 2001. Phosphorus export from an agricultural watershed: Linking source and transport mechanisms. Journal of Environmental Quality, 30(5): 1587-1595.

McDowell, R.W. and Sharpley, A.N., 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. Journal of Environmental Quality, 30(2): 508-520.

McDowell, R.W. and Sharpley, A.N., 2003. Uptake and release of phosphorus from overland flow in a stream environment. Journal of Environmental Quality, 32(3): 937-948.

McDowell, R.W., Sharpley, A.N. and Folmar, G., 2003. Modification of phosphorus export from an eastern USA catchment by fluvial sediment and phosphorus inputs. Agriculture Ecosystems & Environment, 99(1-3): 187-199.

MiGDL, 2007. Michigan Geographic Data Library Center for Geographic Information. Department of Information Technology, http://www.mcgi.state.mi.us/mgdl/.

Milliken, G.A. and Johnson, D.E., 1984. Analysis of Messy Data, Volume 1: Designed Experiments. Van Norstrand Reinhold Company, New York, NY.

Molloy, J., Heaton, S., Carter, D. and Kieser, M., 2002. Water Quality Improvement (Implementation) Plan for the Kalamazoo River Watershed and Lake Allegan through a Phosphorus Total Maximum Daily Load (TMDL) Process, Kalamazoo River/Lake Allegan TMDL Implementation Committee

Momen, B., Eichler, L.W., Boylen, C.W. and Zehr, J.P., 1996. Application of multivariate statistics in detecting temporal and spatial patterns of water chemistry in Lake George, New York. Ecological Modelling, 91(1-3): 183-192.

Moog, D.B. and Whiting, P.J., 2002. Climatic and agricultural factors in nutrient exports from two watersheds in Ohio. Journal of Environmental Quality, 31(1): 72-83.

Morgan, A.M., Royer, T.V., David, M.B. and Gentry, L.E., 2006. Relationships among nutrients, chlorophyll-alpha, and dissolved oxygen in agericultural streams in Illinois. Journal of Environmental Quality, 35(4): 1110-1117.

Mulholland, P.J., 1993. Hydrometric and steam chemistry evidence of 3 storm flowpaths in Walker-Branch Watershed. Journal of Hydrology, 151(2-4): 291-316.

Mulholland, P.J., 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. Biogeochemistry, 70(3): 403-426.

Mulholland, P.J. and Hill, W.R., 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. Water Resources Research, 33(6): 1297-1306.

National Research Council, 1992. Restoration of aquatic ecosystems: science, technology, and public policy. National Academy Press, Washington, D.C.

Neal, C., Hilton, J., Wade, A.J., Neal, M. and Wickham, H., 2006. Chlorophyll-a in the rivers of eastern England. Science of the Total Environment, 365(1-3): 84-104.

Nelson, C.J., 1999. Managing nutrients across regions of the United States. Journal of Animal Science, 77: 90-100.

Norton, M.M. and Fisher, T.R., 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay, pp. 337-362.

Novak, J.M., Stone, K.C., Szogi, A.A., Watts, D.W. and Johnson, M.H., 2004. Dissolved phosphorus retention and release from a coastal plain in-stream wetland. Journal of Environmental Quality, 33(1): 394-401.

Novak, J.M., Stone, K.C., Watts, D.W. and Johnson, M.H., 2003. Dissolved phosphorus transport during storm and base flow conditions from an agriculturally intensive southeastern coastal plain watershed. Transactions of the Asae, 46(5): 1355-1363.

Ontkean, G.R., Chanasyk, D.S. and Bennett, D.R., 2005. Snowmelt and growing season phosphorus flux in an agricultural watershed in south-central Alberta, Canada. Water Quality Research Journal of Canada, 40(4): 402-417.

Ott, R.L. and Longnecker, M., 2001. An introduction to statistical methods and data analysis. Wadsworth Group, Pacific Grove, CA, 1152 pp.

Pacific Meridian Resources, 2001. Integrated forest monitoring assessment and prescription IFMAP, Review of remote sensing technologies for the IFMAP project, 2nd Revision. Report for the Michigan DNR. On the web at http://www.mcgi.state.mi.us/mgdl/?rel=thext&action=thmname&cid=5&cat=Land+Cover+2001.

Penn, C.J., Mullins, G.L. and Zelazny, L.W., 2005. Mineralogy in relation to phosphorus sorption and dissolved phosphorus losses in runoff. Soil Science Society of America Journal, 69(5): 1532-1540.

Puckett, L.J., 1995. Identifying the major sources of nutrient water-pollution. Environmental Science & Technology, 29(9): A408-A414.

Reed-Andersen, T., Carpenter, S.R. and Lathrop, R.C., 2000. Phosphorus Flow in a Watershed-Lake Ecosystem. Ecosystems, 3(6): 561-573.

Reyment, R.A. and Joreskog, K.G., 1993. Applied factor analysis in the natural sciences. Cambrigde University Press, New York, NY, 371 pp.

SAS, 1999. SAS/STAT User's Guide: The Mixed Procedure. SAS Institute, Cary, NC.

SAS, 2007. SAS 9.3.1 for Microsoft Windows. SAS Institute Inc., Cary, NC.

Schippers, P., van de Weerd, H., de Klein, J., de Jong, B. and Scheffer, M., 2006. Impacts of agricultural phosphorus use in catchments on shallow lake water quality: About buffers, time delays and equilibria. Science of the Total Environment, 369(1-3): 280-294.

Schreiber, J.D. and Rausch, D.L., 1979. Suspended Sediment-Phosphorus Relationships for the Inflow and Outflow of a Flood Detention Reservoir. J Environ Qual, 8(4): 510-514.

Searle, S.R., 1971. Linear Models. John Wiley & Sons, New York, NY.

Sharpley, A., 1995. Identifying sites vulnerable to phosphorus loss in agricultrual runoff. Journal of Environmental Quality, 24(5): 947-951.

Sharpley, A., 1999. Agricultural phosphorus, water quality, and poultry production: are they compatible? Poult Sci, 78(5): 660-673.

Sharpley, A., Foy, B. and Withers, P., 2000. Practical and innovative measures for the control of agricultural phosphorus losses to water: An overview. Journal of Environmental Quality, 29(1): 1-9.

Sharpley, A.N., McDowell, R.W. and Kleinman, P.J.A., 2001. Phosphorus loss from land to water: integrating agricultural and environmental management. Plant and Soil, 237(2): 287-307.

Smith, V.H., 1982. The nitrogen and phosphorus dependence of algal biomass in lakes - an empirical and theoretical-analysis. Limnology and Oceanography, 27(6): 1101-1112.

Smith, V.H., Joye, S.B. and Howarth, R.W., 2006. Eutrophication of freshwater and marine ecosystems. Limnology and Oceanography, 51(1): 351-355.

Sonoda, K. and Yeakley, J.A., 2007. Relative effects of land use and near-stream chemistry on phosphorus in an urban stream. Journal of Environmental Quality, 36(1): 144-154.

Sonoda, K., Yeakley, J.A. and Walker, C.E., 2001. Near-stream landuse effects on streamwater nutrient distribution in an urbanizing watershed. Journal of the American Water Resources Association, 37(6): 1517-1532.

Soranno, P.A., Hubler, S.L., Carpenter, S.R. and Lathrop, R.C., 1996. Phosphorus loads to surface waters: A simple model to account for spatial pattern of land use. Ecological Applications, 6(3): 865-878.

Stanford, J.A. and Ward, J.V., 2001. Revisiting the serial discontinuity concept, pp. 303-310.

Steuer, J., Selbig, W., Hornewer, J. and Prey, J., 1997. Sources of contamination in an urban basin in Marquette, Michigan and an analysis of concentrations, loads, and data quality, U.S. Geological Survey Water-Resources Investigations Report 97-4242.

Stevenson, R.J., Rier, S.T., Riseng, C.M., Schultz, R.E. and Wiley, M.J., 2006. Comparing effects of nutrients on algal biomass in streams in two regions with different disturbance regimes and with applications for developing nutrient criteria. Hydrobiologia, 561: 149-165.

Straskrabova, V., Prochazkova, L. and Popovsky, J., 1973. Influence of reservoirs on chemical and bacteriological properties. In: J. Hrbacek and M. Straskraba (Editors), Hydrobiological Studies 2. Czechoslovak Academy of Sciences, Prague, pp. 348.

Taskinen, A., Sirvio, H. and Bruen, M., 2008. Modelling effects of spatial variability of saturated hydraulic conductivity on autocorrelated overland flow data: linear mixed model approach. Stochastic Environmental Research and Risk Assessment, 22(1): 67-82.

Tsegaye, T., Sheppard, D., Islam, K.R., Johnson, A., Tadesse, W., Atalay, A. and Marzen, L., 2006. Development of chemical index as a measure of in-stream water quality in response to land-use and land cover changes. Water Air and Soil Pollution, 174(1-4): 161-179.

Turner, R.E., Rabalais, N.N., Justic, D. and Dortch, Q., 2003. Global patterns of dissolved N, P and Si in large rivers. Biogeochemistry, 64(3): 297-317.

University of Oregon, 2007. An Introduction to the features of the MIXED procedure, http://rfd.uoregon.edu/StatisticalResources/glm02_mixed.txt.

USDA, 1990. Soil survey of Barry County, Michigan. United States Department of Agriculture, Soil Conservation Service.

USDA, 1997. Soil survey of Calhoun County, Michigan. United States Department of Agriculture, Soil Conservation Service.

USEPA, 1975. Report on Lake Allegan, Allegan County Michigan. EPA Region V, Working Paper Series No. 182. EPA National Eutropication Studies. 1975, USEPA, Washington, D.C.

USEPA, 1996. Environmental indicators of water quality in the United States. EPA 841-R-96-002. EPA 841-R-96-002, USEPA, Office of Water (4503F), U.S. Government Printing Office, Washington, D.C.

USEPA, 2008a. STORET, EPA's computerized environmental data system, http://www.epa.gov/storet/.

USEPA, 2008b. Total Maximum Daily Loads: National Section 303(d) List Fact Sheet, http://iaspub.epa.gov/waters/national_rept.control.

USGS, 2008a. Annual water data reports, USGS 04106000 Kalamazoo River at Comstock, MI, http://waterdata.usgs.gov/mi/nwis/uv/?site_no=04106000&PARAmeter_cd=00065,00060.

USGS, 2008b. Annual water data reports, USGS 04108670 Kalamazoo River at New Richmond, MI, http://waterdata.usgs.gov/mi/nwis/uv/?site_no=04108670&PARAmeter_cd=00065,00060.

Uusi-Kamppa, J., Braskerud, B., Jansson, H., Syversen, N. and Uusitalo, R., 2000. Buffer zones and constructed wetlands as filters for agricultural phosphorus. Journal of Environmental Quality, 29(1): 151-158.

Valderrama, J.C., 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural-waters. Marine Chemistry, 10(2): 109-122.

van der Perk, M., Owens, P.N., Deeks, L.K., Rawlins, B.G., Haygarth, P.M. and Beven, K.J., 2007. Controls on catchment-scale patterns of phosphorus in soil, streambed sediment, and stream water. Journal of Environmental Quality, 36(3): 694-708.

Vanni, M.J., Renwick, W.H., Headworth, J.L., Auch, J.D. and Schaus, M.H., 2001. Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. Biogeochemistry, 54(1): 85-114.

Vitousek, P.M., 1997. Human domination of Earth's ecosystems (vol 277, pg 494, 1997). Science, 278(5335): 21-21.

Wade, K.M. and Quaas, R.L., 1993. Solution to a system of equations involving a first-order autoregressive process. J Dairy Sci, 76: 3026-3032.

Wahrer, M.A., Long, D.T. and Lee, R.W., 1996. Selected geochemical characteristics of ground water from the glaciofluvial aquifer in the central lower peninsula of Michigan. . U.S. Geological Survey Water-Resource Investigative Report 944017.

Wall, L.G., Tank, J.L., Royer, T.V. and Bernot, M.J., 2005. Spatial and temporal variability in sediment denitrification within an agriculturally influenced reservoir. Biogeochemistry, 76(1): 85-111.

Ward, J.V. and Stanford, J.A., 1995. The serial discontinuity concept - extending the model to floodplain rivers. John Wiley & Sons Ltd, pp. 159-168.

Waschbusch, R.J., Selbig, W.R. and Bannerman, R.T., 1999. Sources of phosphorus in stormwater and street dirt from two urban residential basins in Madison, Wisconsin, 1994-85, U.S. Geological Survey Water-Resources Investigations Report 99-4021.

Wayland, K.G., Long, D.T., Hyndman, D.W., Pijanowski, B.C., Woodhams, S.M. and Haack, S.K., 2003. Identifying relationships between baseflow geochemistry and land use with synoptic sampling and R-mode factor analysis. Journal of Environmental Quality, 32(1): 180-190.

Welschmeyer, N.A., 1994. Fluorometric analysis of chlorophyll-A in the presence of chlorophyll-B and pheopigments. Limnology and Oceanography, 39(8): 1985-1992.

Westjohn, D.B. and Weaver, T.L., 1997. Hydrogeologic framework of the Michigan Basin aquifer system. U.S. Geological Survey Professional Paper 1418. U.S. Geological Survey Information Services.

Wetzel, R.G., 2001. Limnology: Lake and river ecosystems. 3rd ed. Academic Press, New York, 1006 pp.

Wetzel, R.G. and Likens, G.E., 2000. Limnological Analyses, third ed. Springer-Verlag, New York, NY.

Williams, M., Hopkinson, C., Rastetter, E., Vallino, J. and Claessens, L., 2005. Relationships of land use and stream solute concentrations in the Ipswich River basin, northeastern Massachusetts. Water Air and Soil Pollution, 161(1-4): 55-74.

Winter, J.G. and Duthie, H.C., 2000. Export coefficient modeling to assess phosphorus loading in an urban watershed. Journal of the American Water Resources Association, 36(5): 1053-1061.

Withers, P.J.A. and Haygarth, P.M., 2007. Agriculture, phosphorus and eutrophication: a European perspective. Soil Use and Management, 23: 1-4.

Wycheck, J., 1998. Water quality and pollution control in Michigan, 1996 Report. Michigan 305(b) Report. Report No. MI/DEQ/SWQ-98-030, MDEQ, Surface Water Quality Division.

Yuan, Z., Ramaswami, B., Casaletto, D., Falke, S., Angenent, L.T. and Giammar, D.E., 2007. Evaluation of chemical indicators for tracking and apportionment of phosphorus sources to Table Rock Lake in Southwest Missouri, USA. Water Research, 41(7): 1525-1533.

Zampella, R.A., Procopio, N.A., Lathrop, R.G. and Dow, C.L., 2007. Relationship of land-use/land-cover patterns and surface-water quality in the Mullica River basin. Journal of the American Water Resources Association, 43(3): 594-604.