COMPARISON OF PHOSPHORUS FORMS AT DIFFERENT SPATIAL SCALES AND ASSESSMENT OF AN AREA-WEIGHTED P-INDEX TO MULTI-FIELD WATERSHEDS

by

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ABSTRACT

COMPARISON OF PHOSPHORUS FORMS AT DIFFERENT SPATIAL SCALES AND ASSESSMENT OF AN AREA-WEIGHTED P-INDEX TO MULTI-FIELD WATERSHEDS

Nicholas A. Reckinger

Phosphorus from agricultural runoff is a major concern to the quality of our water resources. Phosphorus in runoff is made up of sediment bound P and soluble P. In many watershed studies, particulate phosphorus (PP) is the dominate form of P. However, past monitoring of rural streams in the Lower Fox River sub-basin in northeastern Wisconsin has found mean concentrations of dissolved phosphorus (DP) representing from 45% to 75% of the total P (TP) concentration. This study was conducted to better understand P forms in tributaries of the Lower Fox River, to determine how the DP fraction changes along a flow path at different scales, and to assess the Wisconsin Phosphorus-Index (WI-PI) on multi-field watersheds in the Apple Creek watershed.

Automated monitoring stations were installed on four Lower Fox River tributaries in September of 2003. Three water years of event and low-flow samples were collected and analyzed for total suspended solids, TP, and DP. In conjunction with the automated monitoring station, event grab samples were collected near peak flow at 11 multi-field (0.25 to 2.5 km^2) and four integrator (12 to 87 km^2) sites in the Apple Creek Watershed.

Across the four sites, the TP concentration during event flows was made up of approximately equal portions of PP and DP (36% to 66% DP fraction). DP loads ranged from 36% to 52% of the TP load in 2004 and from 46% to 61% in the following 2 years. Duck Creek had the consistently lowest concentrations and yields of P and suspended solids among the four tributaries.

For five runoff events in Apple Creek during 2004, median TP was 0.46 mg/L from multi-field sub-watershed sites, 0.48 mg/L from integrator sites, and 0.43 mg/L from the main stem. Median DP percentage was 39% from source areas, 41% from integrator sites, and 44% at the main stem. The median DP percentage for the five events at each source area site, varied greatly (13% to 83%). The portion of DP in a snowmelt and a low intensity event in 2006 were twice the median from earlier events. Area-weighted WI-PI (SnapPlus) values were compared to P concentrations from event monitoring at multi-field sub-watersheds. Field management data, including crop rotation, nutrient applications, and tillage practices were collected from nutrient management plans. The WI-PI was unable to predict the TP and PP losses. However, a strong relationship was found between DP concentration in surface water and soluble P-Index values. It appears that the factors affecting variability in DP export between source areas are reasonably described by the WI-PI.

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LIST OF ACRONYMS

BMP – Best Management Practices
DP –Dissolved Phosphorus
GBMSD – Green Bay Metropolitan Sewage District
LFR – Lower Fox River
LFRSB – Lower Fox River Sub-Basin
LFRWMP – Lower Fox River Watershed Monitoring Program
NMP – Nutrient Management Plan
NRCS – Natural Resource Conservation Service
P – Phosphorus
PP – Particulate Phosphorus
TP – Total Phosphorus
TSS – Total Suspended Solids
USDA – United States Department of Agriculture
USGS – United States Geological Survey
WDNR – Wisconsin Department of Natural Resources
WI-PI – Wisconsin Phosphorus-Index

CHAPTER 1– INTRODUCTION

Project Background

Agricultural land use can have a significant impact on the quality of water in a watershed. The central portion of the Lower Fox River Sub-Basin is dominated by agriculture, with the cities of Neenah/Menasha, Wisconsin located where the Lower Fox River flows out of Lake Winnebago and the City of Green Bay at the mouth of the Fox River. A better understanding of the impacts of agricultural land use can improve the guidance for future land management decisions. The Lower Fox River Watershed Monitoring Program (LFRWMP) is focused on monitoring and predicting the quality of water originating from urban and agricultural land uses within the Lower Fox River Sub-Basin (LFRS-B). As part of the LFRWMP, this project examines the effects of agricultural operations on stream water quality within the LFRS-B and examines the forms of phosphorus (P) at different spatial scales within the Apple Creek Watershed.

The LFRWMP was established in 2003 with a grant form Arjo Wiggins Appleton. It is a multi-year monitoring and assessment program focused on determining the relationship between water quality and land uses. Major program goals are to 1) determine P and suspended solid concentrations and loads for Fox River tributaries and relate them to watershed characteristics and 2) assess the ability of models to estimate stream flows and water quality parameters from different watersheds on an event, monthly, and annual basis. In partnership with the U.S. Geological Survey (USGS) and Green Bay Metropolitan Sewage District (GBMSD), five automatic sampling stations were installed on Lower Fox River (LFR) tributaries. These include Apple Creek, Ashwaubenon Creek, Baird Creek, Duck Creek, and the East River. The University of Wisconsin-Milwaukee also assisted in monitoring the biological integrity of the stream ecosystems.

This study analyzed the forms of P at four of the five tributary gauging stations and compared them to watershed characteristics. The East River was not analyzed in this thesis because of the different sample collection procedures between it and the other four tributaries. To better understand the forms of P that originate in headwater regions of the watershed, this study also investigated the forms of P at various spatial scales within the Apple Creek Watershed.

The Lower Fox River Sub-Basin

The Lower Fox River Sub-Basin (Figure 1.1) drains approximately 1,580 square kilometers of northeastern Wisconsin where the Fox River discharges into the bay of Green Bay. The LFRSB is the lower most sub-basin of the Fox-Wolf River Basin (16,400 km^2) that drains a large portion of northeastern Wisconsin. The Wolf River and the Upper Fox River contribute flow to Lake Winnebago near Oshkosh, Wisconsin. The Lower Fox River flows out of Lake Winnebago near the Cities of Neenah/Menasha, Wisconsin, and flows through twelve dams before it reaches the bay of Green Bay in Green Bay, Wisconsin. The Lower Fox River (LFR) has been severely impacted by a variety of point and non-point source pollutants. The Fox River Valley is one of Wisconsin’s most urbanized and industrialized areas (WDNR, 2006). However, the LFR basin is still dominated by agriculture (52%), primarily dairy farm operations. The climate is temperate and humid: average rainfall is 741 mm yr^{-1} and stream flow is about

250 mm yr^{-1}. Corn, soybeans, hay, and small grains make up the majority of cropped land. The majority of soils are relatively impermeable silty clay loams that result in relatively high runoff rates (Baumgart, 2005a) and high runoff P to soil test P (Andraski and Bundy, 2003). Fertilizer application and manure from dairy cattle are the main P sources.

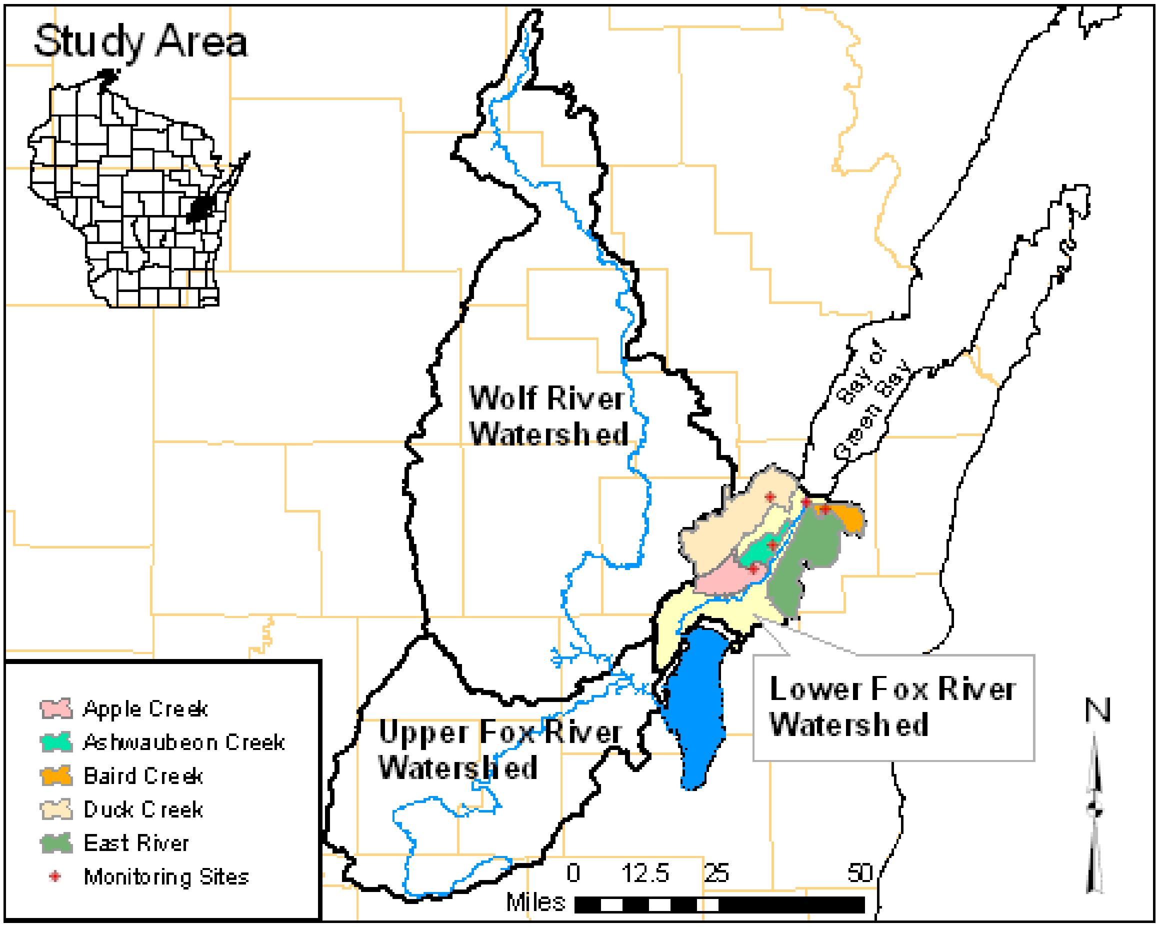

Figure 1.1. Location of Lower Fox River Watershed in northeastern Wisconsin.

The Apple Creek Watershed

The Apple Creek Watershed encompasses approximately 117 km^2 of southeastern Outagamie County and a small portion of Brown County, Wisconsin. Apple Creek flows east into the Fox River as shown in Figure 1.2. The Apple Creek Watershed is located to the north of Appleton, Wisconsin, and its headwaters are beginning to receive pressure from increasing urbanization. However, the watershed is still dominated by agricultural operations, comprising approximately 63% of the area in 2000. Soils of the watershed are classified as Winneconne (Mollic Hapludalfs), Manawa (Aquollic Hapludalfs), Kewaunee (Typic Hapludalfs), and Hortonville (Glossoboric Hapludalfs) silty clay loams. Slopes in the watershed range from 2 to 6 %.

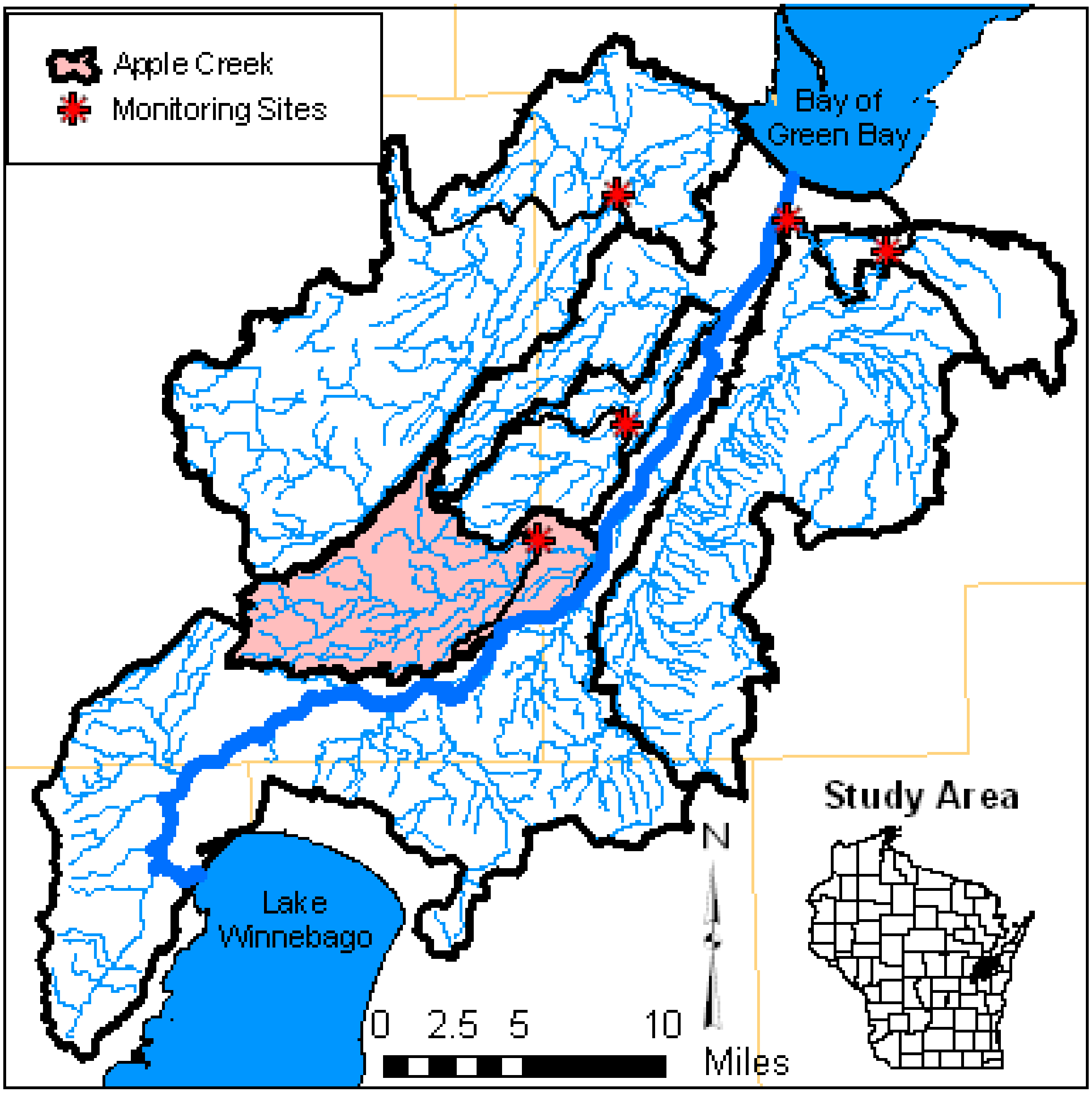

Figure 1.2. Location of Apple Creek Watershed and Lower Fox River Watershed Monitoring Program (LFRWMP) monitoring stations in Lower Fox River Sub-Basin.

Literature Review

Phosphorus Associated with Agriculture

Phosphorus (P) is an essential macronutrient to crop and animal production. An adequate supply of P is necessary to meet global food requirements and make crop and livestock operations profitable (Hedley and Sharpley, 1998). Therefore, it is imperative that agricultural operations effectively manage nutrients on the farm.

Norfleet (1998) explains the importance of P to crop production. The primary function of P is the storage and transfer of energy through the plant. Adenosine diphosphate and adenosine triphosphate are high-energy phosphate compounds that control plant functions such as photosynthesis, respiration, protein and nucleic acid synthesis, and nutrient transport through plant cells. Phosphorus increases seed production, root growth, and grain, fiber and forage yield, enhances early plant maturity and stalk strength, and promotes resistance to root rot disease and winter kill.

Phosphorus has an important physiological role in animal production as well. It is the element with the most known biological functions in animals, mostly found in bones and teeth (80%). Phosphorus is found in cell walls and cell contents as phospholipids, phosphoproteins, and nucleic acids. P is located in every cell of the body and is involved in almost all energy transactions as part of adenosine triphosphate. Acid-base buffer systems of blood and other bodily fluids are dependent on P as well as cell differentiation (Beede and Davidson, 1999).

Phosphorus in excess of crop needs leads to a build up of soil P levels. The excess P can be transported to streams through runoff and erosion processes which contribute to water quality degradation. The amount of P in feed and the amount applied to fields must be managed to improve water quality in nearby streams and lakes.

Agricultural Non-Point Source Pollution

Improper management of manure and fertilizer applications in excess of crop needs leads to a build up in soil P levels. Excess P can be transported to streams through runoff and erosion processes which contribute to water quality degradation. The United States Environmental Protection Agency's (U.S. EPA) 2000 National Water Quality Inventory (U.S. EPA, 2000) states the number one impairment to freshwaters lakes of the United States is eutrophication due to excessive nutrients.

Eutrophication is the natural aging process by which a lake evolves into a bog or a marsh and ultimately assumes a completely terrestrial state and disappears (Carpenter et al., 1998). Individual states estimate that 22% of the assessed lake acres and 50 % of the impaired lake acres receive excessive nutrient contributions (U.S. EPA, 2000), with agriculture being the leading source.

The amount of P transferred from agricultural lands in runoff is small compared to crop and animal production (Haygarth et al., 2005). Total P losses from soil are on the order of 1 kg ha^{-1} $year^{-1}$ (Haygarth and Jarvis, 1999), whereas annual fertilizer and manure inputs are typically between 20 and 50 kg P ha^{-1} $year^{-1}$ (Cameron et al., 2002; Haygarth et al., 1998a). The major source of P imported into dairy farms is from purchased feed, which ranges from 45 to 80% of the total P inputs. Between 62 and 86% of the imported P remains on the farm, and the rest is exported as animal products (Beede and Davidson, 1999).

Phosphorus and nitrogen are the primary nutrients that cause eutrophication (Daniel et al., 1998; Correll, 1998). Phosphorus is typically known to be the limiting nutrient in freshwater systems while nitrogen limits algae growth in most saline systems. Mean total phosphorus (TP) concentration has a strong correlation to chlorophyll *a*, a good estimator of algal abundance (Canfield, 1983; McCauley et al., 1989; Prairie et al., 1989; Pridmore et al., 1985; Seip et al., 2000).

Accelerated eutrophication associated with increased P in runoff has damaging effects to the usability and biological integrity of water resources. Increased primary production increases production at higher trophic levels. This leads to an increase in zooplankton and fish biomass, each of which has been correlated with lake concentrations of P (Peters, 1986). An increase in fish biomass may seem advantageous, but it generally means a decrease in biodiversity (Foy, 2005). Jeppesen et al. (2000) saw proportionately larger increases in planktivorous fish species compared to piscivorous species and a tendency for average fish size to decease at all trophic levels.

Accelerated eutrophication with increased TP has also been linked to human health problems. Cyanobacteria, or blue-green algae, is often associated with excessive eutrophication and produces toxins with potential adverse effects to human and animal health (Foy, 2005). These toxins may be tumor promoters; a report in China that links eutrophic drinking water supplies to an elevated incidence of liver cancer in humans (Yu, 1995).

Classification of Phosphorus Forms

The multidisciplinary approach necessary to study the sources and impacts of P has led to varied and vaguely defined terminology, which causes misinterpretations and can impair scientific communication (Haygarth and Sharpley, 2000). Haygarth and Sharpley (2000) attempted to provide a simple classification of terms for P-forms. The classification of P in water has previously been associated with the physical and chemical definitions (i.e. filtration and chemical methodologies) (Haygarth et al., 1998b). Operational definitions are preferred to avoid problems that arise from physical and chemical definitions (Haygarth and Sharpley, 2000).

For P-forms described by filtration methods, it is suggested that samples be defined by the filter size with a suffix of the filter pore size. Dissolved phosphorus (DP) is thus defined as the portion of P that passes through a 0.45 µm filter and particulate P is the portion that does not pass through the filter. For the chemical methods, the new terms for P, based on the Mo-blue reaction method (Murphy and Riley, 1962) are reactive P (RP), unreactive P (UP) and total P (TP). The determination of TP involves an acid digestion prior to the Mo-blue reaction method.

Although Haygarth and Sharpley (2000) proposed the more uniform classification of P-forms, there is still a wide variety of nomenclature used in current literature. Difficulty in effective communication of P-forms still remains. It is essential to clearly state the nomenclature used when referring to P-forms. In the remainder of this paper, when referring to results from this study, DP refers to the P that passes through a 0.45µm filter.

Phosphorus Runoff and Reduction

Phosphorus is relatively stable in soils but can be transported through water runoff and sediment erosion. The modes and pathways of P transport to water can be described by process and pathway terms. It is important to understand the processes and pathways that regulate P transport in order to identify and quantify non-point source P loads to surface water (Johnes and Hodgkinson, 1998). These pathways are important to understand when determining management strategies to reduce P losses from the watershed.

Transport Mechanisms and Pathways

Three terms describe P transport mechanisms: physical, dissolution, and incidental (Haygarth and Jarvis, 1999). Physical transport is the primary mechanism. The simplest examples are detachment and soil erosion. Dissolution, a mechanism determined by chemistry, describes the transport of DP from the soil particle or absorption site to the soil solution. Incidental mechanisms are conceptually different from physical and dissolution mechanisms. Incidental mechanisms are short-term transport of farm amendments of P in fertilizer, manure, or animal feces. This short-term transfer of P is most often a result of effective rainfall, which removes the amendment shortly after application (Haygarth and Sharpley, 2000; Edwards and Daniel, 1993; Sharpley et al., 1998; Westerman and Overcash, 1980).

Identification of the P pathways from soil to surface waters is important to effectively prevent or control P losses (Sharpley et al. 2000). Transport pathways are dependent on the form being displaced (Sharpley and Syers, 1979; Foy and Withers, 1995) and incorporate a range of spatial and temporal scales of flow. The spatial characteristics considered are the plane and scale of water movement. The plane refers to the direction of water flow (vertical or lateral). The spatial scale is divided into: i) the soil profile (vertical plane), ii) the slope/field (lateral plane), and iii) the watershed/catchment scale. The temporal scale is dependent on local conditions and is usually minutes, hours, or days (Zaimes and Schulz, 2002).

Phosphorus Reduction Strategies

In order to control or prevent excessive P losses during event runoff, it is important to understand the risk of loss under different farming systems and realize the large temporal and spatial variation due to the varying hydrological conditions within different landscapes (Withers et al., 2000). There are several management strategies in use today that intend to control or prevent excessive event P losses. These strategies may be divided into three main groups: those that address the transport of P, those that address sources of P, and those that combine the two through risk management techniques.

Transport factors are associated with P runoff pathways and erosion processes. Management strategies to control these factors include: buffer strips, riparian zones, and wetland areas to intercept upland agricultural runoff, appropriate stock management to reduce overgrazing, treading damage, and to exclude animals from waterways, and conservation tillage, contour tillage, crop residue management, and soil drainage (Sharpley et al., 1999, 2001). These methods are generally more effective at reducing PP than DP and may increase the ratio of DP to PP (Sharpley et al., 1994, 2001).

Source factors refer to inputs of P such as the application of fertilizer and organic manure amendments. Recently, much P reduction strategies have switched from focusing on transport factors to source factors (Sharpley et al. 2001). Suggested management strategies for reducing source factors include: manipulation of dietary P intake by animals, increasing efficiency of animal uptake of dietary P thorough enzyme (phytase) amendment, use of amendments such as alum to decrease P solubility in poultry manure, environmental soil P testing, matching P applications with crop requirements, incorporation of fertilizers and manures into soil against broadcasting, and better timing of fertilizer and manure applications to coincide with periods when P runoff is least likely to occur (Sharpley et al., 1993, 1994, 2001; Sims, 1993; Sharpley and Tunney, 2000). One strategy that combines some of these methods is more exact matching of P applications with crop requirements through nutrient management plans (NMP).

Nutrient management planning is becoming the standard for many states to reduce nutrient hot spots within a watershed. NMP account for P inputs and output and, if used correctly, will aid in the decision process of when to apply fertilizer and organic manure. The use of NMP helps control excessive inputs of P to critical source areas in an attempt to prevent soil P build-up. To simplify the NMP process many states are using a phosphorus index system, which ranks a field’s risk of contributing P based on transport of source factors.

Research Overview

Problem Statement

It is important that decision-makers understand P forms when determining best management strategies. Understanding the relationship between water quality and watershed characteristics helps determine the best management strategy for controlling P losses from the landscape. The main objectives of this research are presented below, along with specific research questions to be explored for each objective.

1. Compare P-forms and suspended solids in Lower Fox River Tributaries.
    - What is the variation in P forms and total suspended solids (TSS) among tributaries?
    - How are variable pairs of P forms and TSS concentration related?
    - How are watershed characteristics related to observed water quality?

2. Evaluate P-forms in runoff at different spatial scales within on of the LFR tributaries (Apple Creek).
    - How do P forms change along a flow path?
    - How are variable pairs of P forms and TSS related?
    - How are P forms related to contributing area characteristics?

3. Compare the Wisconsin Phosphorus Index (WI-PI) and runoff P in Eastern Red Soils at the Multi-field scale.
    - How do the various types of P loss predicted by the WI-PI relate to P-forms in surface runoff?
    - What information is necessary to make WI-PI more useful or applicable?

4. Assess the policy implications of the P-forms research and P-Index comparisons.
    - What is the potential effectiveness of BMP strategies to address P-forms in runoff?
    - Will using the WI-PI to predict and regulate P loss be adequate for meeting water quality objectives?

Study Limitations

Research projects that quantify stream flow and water quality parameters are heavily dependent on rainfall. The amount and intensity of rainfall can significantly alter concentrations and loads of water quality parameters. The multi-scale research study in the Apple Creek Watershed began in 2004 by members of the LFRWMP at UW-Green Bay. Runoff producing precipitation occurred many times in 2004. However, very few runoff events of sufficient magnitude occurred in 2005 and 2006. Thus the P forms study in the Apple Creek Watershed is mostly limited to data from one year.

Document Organization

The remainder of this document is divided into four chapters, each pertaining to a separate research topic. In Chapter Two, we examine water quality and P forms in four Lower Fox River Tributaries. Chapter Three focuses on P forms and sub-watershed characteristics at different spatial scales in Apple Creek Watershed. Chapter Four explores an application of the WI-PI to source area watersheds within the Apple Creek Watershed. Chapter Five summarizes research findings, discusses land management policy implications, and suggests future research topics related to understanding P forms in northeastern Wisconsin agricultural fields and streams.

CHAPTER 2 – WATER QUALITY IN LOWER FOX RIVER TRIBUTARIES

Introduction

Phosphorus and sediments are the primary stressors to the bay of Green Bay ecosystem. They impair more beneficial uses than any other stressor, including toxins (Harris et al., 1993). Green Bay is a major contributor of nutrients to Lake Michigan. Lower Green Bay and Lake Winnebago, which are located just downstream and upstream, respectively, of the Lower Fox River (LFR), have characteristically large amounts of algae and suspended solids which reduce water clarity and impair major water uses (Harris, 1993; Millard and Sager, 1994; WDNR, 1993). To reach water clarity and quality goals in Lower Green Bay, the Green Bay Remedial Action Plan (RAP) Science and Technical Advisory Committee recommended external loads of P be reduced by 50% (WDNR, 1993; GBRAP, 2000). Due to impaired surface water quality related to non-point source pollution, nearly all of the Lower Fox River Sub-Basin (LFRS-B) tributaries have been ranked as priority watersheds or 303d listed by the Wisconsin Department of Natural Resources.

Approximately 70% of the annual P load to Green Bay and about 25% of the P load to Lake Michigan is discharged by the Fox River (Klump et al., 1997; Pauer et al., 2005). About half of the P and TSS load originates in LFR watersheds. Lake Winnebago, which receives flow from the much larger Wolf and Lower Fox River Sub-Basins, contributes the remaining load to Green Bay. Based on Soil and Water Assessment Tool (SWAT) modeling of year 2000 baseline conditions by Baumgart (2005a), agriculture contributes about 49% of the annual P and 61% of the annual suspended solids load to the LFR.

The fraction of total phosphorus (TP) in the dissolved form in the LFR tributaries is uncharacteristically high for an agricultural watershed. Dissolved phosphorus (DP) accounts for 45% to 70% of the TP lost from LFR tributary watersheds (Baumgart, 2005a). High DP concentrations have been found in watersheds with a large portion of the land use being pasture and when large portions of the land is tile drained (Hart et al., 2004; Gentry et al., 2007). The reason for the high fractions of DP in the Lower Fox River Sub-Basin (LFRS-B) is uncertain. To meet the RAP goal of 50% P reduction, it will be necessary to identify sources of DP and implement BMP’s to control sources and transport mechanisms.

In this chapter we present LFR tributary monitoring data and compare median values of total suspended solids (TSS), TP, and DP among four tributaries. We present the results of linear regression to show how DP responds to changes in TSS, TP, and flow. Next, we provide results from multiple regression analysis to determine the best model for predicting DP loads at each site. Finally, the available environmental characteristics of each watershed are compared to the water quality results and are used to help explain the differences in DP concentration among sites.

Methods

Water Quality

Four LFRS-B tributaries were monitored from September 2003 to October 2006 at sites established near their confluence with the LFR or bay of Green Bay (see Chapter 1, Figure 1.1). These included Apple, Ashwaubenon, Baird, and Duck Creeks. In cooperation with the United States Geological Survey (USGS), a monitoring station was installed on each tributary to collect automated samples along with continuous flow measurements. Each station included an ISCO 3700R refrigerated automatic sampler (Teledyne Isco, Inc, Lincoln, NE), a gas-bubble water level measuring system, a tipping-bucket rain gage, a YSI 6200 multi-parameter sonde (YSI Inc., Yellow Springs, OH), a data logger, and a modem. Real-time gage height and sonde measurements were available on-line through the Lower Fox River Watershed Monitoring Project (LFRWMP) and USGS websites.

Sample Collection

Sampling was conducted by established USGS methods (Shelton, 1994). Discrete event samples were triggered by changes in stream gage height and structured to be representative of the entire storm hydrograph. Samples were removed from the automated samplers within 24 to 48 hours and stored on ice for transport to the University of Wisconsin-Green Bay watershed laboratory for processing.

Low-flow samples were collected manually at each site on a biweekly basis. The equal width increment method was used to collect low-flow samples (Thornton et al. 1999). This method includes dividing the stream width into six to ten equally spaced segments (Figure 2.1). At the center of each segment, a DH-48 depth integrated wading sampler was lowered and raised at a constant rate to collect a representative sample.

Low-flow samples were collected in 500 mL glass bottles and transferred to a 500 mL and two 250 mL polyethylene bottle for TSS, TP, and DP analysis, respectively. Samples collected with the automatic ISCO sampler were collected in 1L polyethylene ISCO bottles. A Teflon cone splitter was then used to divide these samples for analysis of TSS, TP, and DP (Shelton, 1994).

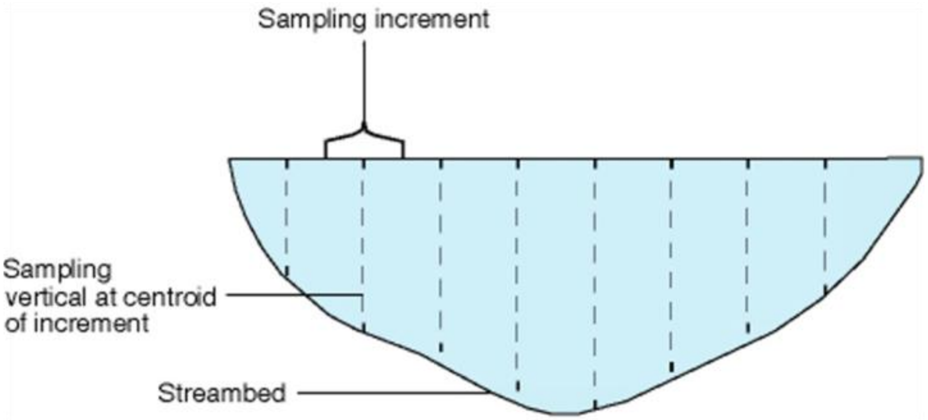

Figure 2.1. Depth-integrated sample collected by use of the equal-width-increment method (figure from Leitz, 1999).

Sample Analysis

Dissolved phosphorus samples were vacuum filtered through a 0.45 µm mixed cellulose ester membrane filter to remove particulate matter. Total P and DP samples were preserved with 3:1 sulfuric acid to a pH less than 2. After processing, samples were immediately refrigerated at 4°C until transported to the Green Bay Metropolitan Sewage District (GBMSD) Laboratory for analysis.

The Green Bay Metropolitan Sewage District's Laboratory analyzed for TSS using Standard Method 2540 D (Clesceri et al, 1998). In this process, an aliquot is pipetted from a well mixed sample and filtered through a weighed glass-fiber filter. The filter and residue are dried to a constant weight at 105°C and the difference in weights is then used to calculate TSS. Total P and DP samples were first digested using the Automated Block

Digester Method 365.4 from the U.S. EPA (U.S. EPA, 1983). In this process, the TP or DP sample is digested in sulfuric acid (H_2SO_4), potassium sulfate (KSO), and mercuric oxide (HgSO) solution for 2.5 hours. The concentration of the resulting orthophosphate sample was quantified using the Murphy Riley procedure and flow injection analysis. The orthophosphate in each sample was reacted with ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_20$) and antimony potassium tartrate ($K_2[Sb_2(C_4H_4O_6)_2]\cdot 4H_2O$). This complex was then reduced with ascorbic acid to form a blue phospho-molybdenum compound. The absorbance of each sample was measured at 880 nm and converted to a PO_4-P concentration using a standard curve. Since our DP samples were fully digested they represent the total dissolved P in the water samples.

Load Calculations

Total suspended solids and TP loads were estimated by the USGS for the four monitored streams using a standard integration method (Porterfield, 1972). The Graphical Constituent Loading Analysis System (GCLAS) (Blanchard and Miller, 2004) software was used to relate continuous stream discharge and instantaneous concentration data from discrete samples. GCLAS computes loads as a function of an equal-interval streamflow time series and an equal or unequal-interval time series of constituent concentrations (Koltun et al., 2006). Total suspended solids and TP loads were output from GCLAS on a five or 15-minute time step, and were added up to get overall seasonal and annual loads. Because DP was measured on fewer samples, we were not able to use GCLAS to estimate 15 minute DP concentrations. Therefore, continuous DP concentrations were determined from a regression model developed from TSS, TP, and

DP concentrations and applied to each five or 15-minute output from GCLAS. The continuous DP concentrations were combined with flow to estimate DP loads.

Environmental Characteristics

Knowledge about environmental characteristics that affect the concentration and loads of water quality parameters can be important for development of reduction strategies. Comparing environmental characteristics among watersheds within close geographic proximity can be difficult when using statewide or larger landuse classification databases. Comparisons at this scale might not generate large differences among sites, and gathering more accurate data was limited by time and resources. In addition, watershed landuse/cover information that closely represents the water quality monitoring period might not be available. The landuse data used in our project was taken from previous work done by other researches from the year 2000 or before. Since 2000, urban development has been rapidly changing the characteristics of these watersheds. Fink (2005) reported the growth of urban development in the South Branch of Baird Creek Watershed as 5.7% with an additional 4.2% under construction between 2000 and 2005.

Landuse/cover characteristics were determined from a GIS coverage created by Baumgart (2005b). The coverage was created by merging the East Central Regional Planning Commission’s (ECRPC) GIS landuse coverage with the 1992 WISCLAND coverage (WDNR, 1998b). The ECRPC’s landuse coverage was based on imagery for the year 2000. Soil characteristics for each tributary watershed were tabulated using the Soil Survey Geographic (SSURGO) Database (USDA NRCS). Basin slopes were calculated using the Wisconsin Department of Natural Resources 30 m DEM (WDNR, 1998a). All Characteristics were obtained for each watershed using ArcGIS 9.

Statistical Analysis

The median concentrations of TSS, TP, and DP and the fraction of TP as DP for discrete samples were calculated for the four streams for various time periods. The data sets were found to be positively skewed and a natural log transformation was used for statistical analysis. No bias correction factor was used because the medians were analyzed. The effects of frozen ground and flow were investigated by separating winter and non-winter periods along with event and low-flows. Winter and non-winter periods were determined from climatological data and observations of when ice-affected conditions ceased in the spring of each year (Table 2.1). Event and low-flow samples were classified based on visual inspection of hydrographs. All statistical analyses were performed using SAS 9.1 computer software (SAS Institute, Inc., 2003).

Concentration and flow data were graphically displayed using boxplots. Concentration differences among sites were determined using the multiple comparison Tukey option for the PROC GLM procedure in SAS. To explain the variance in the DP concentrations (dependent variable), linear regressions were computed using TSS, TP, TP/TSS, and discharge (independent variables). Where sites had significant correlations, the slope and intercept were compared using the dummy variable approach for the PROC REG procedure in SAS (Coady and Smith, 1997). Finally, multiple regressions were performed to find the best model to predict DP concentrations for calculating DP loads.

The multiple regression equation predicted the natural log of the DP concentration and we multiplied the mean square error by 0.5 to correct for the transformation bias.

Table 2.1. Cutoff dates for winter and non-winter conditions for the four Lower Fox River tributaries for water year 2004 – 2006.

Water Year	Winter Period
2004	12/12/2003 - 3/04/2004
2005	1/23/2005 - 3/30/2005
2006	12/3/2005 - 3/11/2006

Results and Discussion

Three years of event and low-flow samples were collected from the four LFR tributaries between October 2003 and September 2006. A total of 975 samples were collected during that period. At Apple Creek, 255 samples were analyzed for TSS and TP, with 103 of those samples analyzed for DP. At Ashwaubenon Creek, 268 samples were analyzed for TSS and TP, with 96 of those samples analyzed for DP. At Baird Creek, 264 samples were analyzed for TSS and TP, with 102 of those samples analyzed for DP. At Duck Creek, 187 samples were analyzed for TSS and TP, with 70 of those samples analyzed for DP.

Precipitation and Flows

The timing and intensities of precipitation events during the study period varied greatly between 2004 and the other two years. The 2004 sampling season was characterized by heavy spring rains followed by a period of summer drought (Table 2.2). According to the National Weather Service office in Green Bay, May 2004 was the second wettest May on record with 211.1 mm of precipitation measured at their Green Bay station. However, the precipitation from July through September was 61% below average (Table 2.2). Precipitation in the 2005 and 2006 water years was more dispersed and followed more closely to the normal seasonal patterns.

Precipitation events during the 2004 water-year caused more runoff compared to the following two years. In 2004, flows were 322 mm, 271 mm, 364 mm, and 344 mm at Apple, Ashwaubenon, Baird and Duck Creeks, respectively. In 2005 and 2006, flows were 136 mm and 103 mm at Apple Creek, 108 mm and 100 mm at Ashwaubenon Creek, 107 mm and 165 mm at Baird Creek, and 139 mm and 100 mm at Duck Creek, respectively. The flows in 2004 were approximately 60% to 70% greater then 2005 and 2006 flows. In water-year 2006, Baird Creek received approximately 160 mm to 180 mm more precipitation than the other three watersheds. This was evident in water-year 2006 flow at Baird Creek being approximately 60 mm more then the other three streams.

Table 2.2. Summary of monthly precipitation for the Lower Fox River Sub-Basin. The precipitation results are an average of Green Bay National Weather Service data and rain gauges at the four tributary stations.

Water Year	Month	Precipitation (mm)	Green Bay 30-year Average	Mean Departure from 30-year Average
2004	Oct.	24.9	55.1	-55%
	Nov.	108.0	57.7	87%
	Dec.	36.6	35.8	2%
	Jan.	29.8	30.6	-3%
	Feb.	40.3	25.6	57%
	Mar.	95.5	52.3	83%
	Apr.	33.2	65.0	-49%
	May	202.9	69.9	190%
	June	116.3	87.1	34%
	July	41.7	87.4	-52%
	Aug.	47.0	95.8	-51%
	Sept.	13.3	79.0	-83%
	Total (mm)	**789.5**	**741.3**	**7%**
2005	Oct.	94.4	55.1	71%
	Nov.	45.4	57.7	-21%
	Dec.	56.8	35.8	59%
	Jan.	38.4	30.6	26%
	Feb.	34.9	25.6	36%
	Mar.	34.2	52.3	-35%
	Apr.	38.4	65.0	-41%
	May	56.5	69.9	-19%
	June	83.4	87.1	-4%
	July	48.0	87.4	-45%
	Aug.	118.2	95.8	23%
	Sept.	79.0	79.0	0%
	Total (mm)	**727.7**	**741.3**	**-2%**
2006	Oct.	36.3	55.1	-34%
	Nov.	77.7	57.7	35%
	Dec.	25.6	35.8	-28%
	Jan.	43.2	30.6	41%
	Feb.	34.9	25.6	36%
	Mar.	33.4	52.3	-36%
	Apr.	51.8	65.0	-20%
	May	133.6	69.9	91%
	June	46.7	87.1	-46%
	July	75.2	87.4	-14%
	Aug.	40.3	95.8	-58%
	Sept.	75.9	79.0	-4%
	Total (mm)	**674.5**	**741.3**	**-9%**

Concentration Comparisons

Total Suspended Solids Comparisons

Total suspended solids concentrations were dependent on flow and climate conditions (Figure 2.2). Combining across sites and years, the median concentration for event-flow/non-winter, event-flow/winter, and low-flow/combined conditions were 124 mg/L, 61 mg/L, and 6.7 mg/L, respectively. All of the sites except Duck Creek had samples with TSS concentrations above 1,000 mg/L, with the maximum of 6,180 mg/L at Ashwaubenon Creek.

Results of among site analyses of TSS concentrations using the Tukey multiple comparison procedure are shown in Table 2.3. For all of the treatments except event-flow/winter, Ashwaubenon Creek had the highest median TSS concentrations; however, the only statistically significant differences among Ashwaubenon Creek and the other streams were found during low-flow conditions. These conditions do not contribute much to the overall load of TSS. Duck Creek had consistently lower TSS concentrations for all flow and weather conditions, with significantly lower concentrations than the other three streams for event-flow/non-winter and low-flow/non-winter conditions. Median TSS concentrations at Apple Creek and Baird Creek were between Ashwaubenon and Duck Creeks for most conditions and were not significantly different from each other for all treatments. Concentrations during low-flow/winter conditions were not significantly different for the four streams.

These comparisons are a starting point to discuss what is affecting the TSS concentrations in the LFR tributaries. Of the four monitored streams, Ashwaubenon Creek seems to have the highest concentrations and Duck Creek the lowest concentrations of TSS, however, this analysis does not consider loads of TSS. If we can distinguish what is affecting these concentration differences, we can begin to understand what is necessary to meet reduction goals.

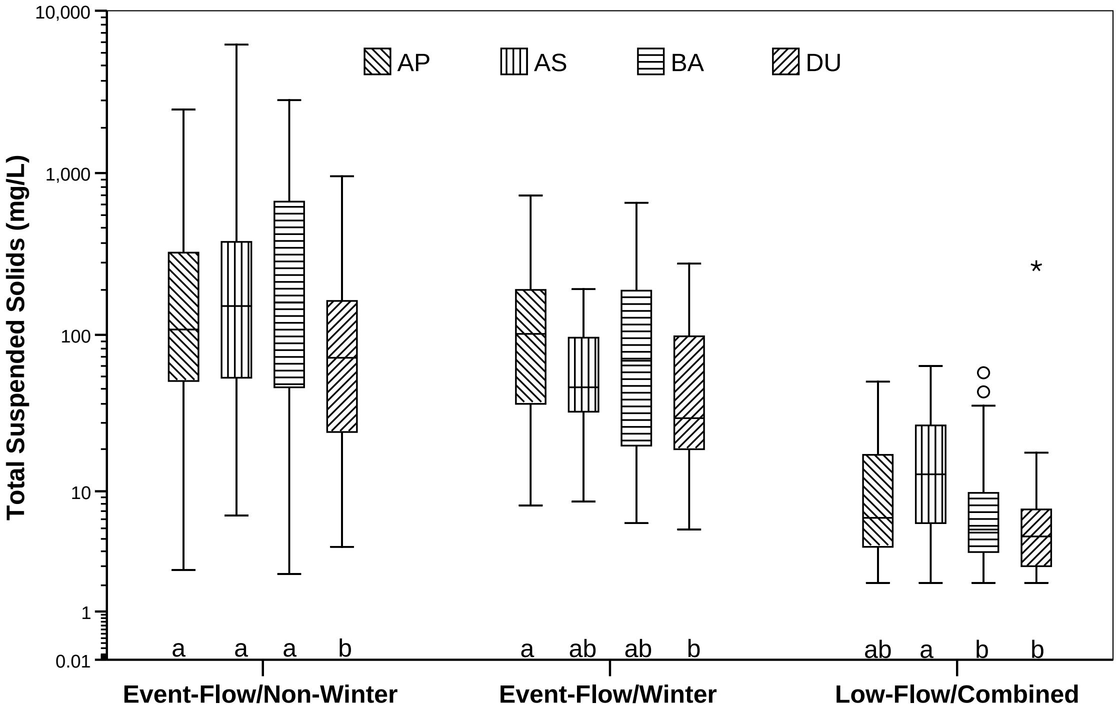

Figure 2.2. Boxplots of total suspended solids concentration for (AP) Apple Creek, (AS) Ashwaubenon Creek, (BA) Baird Creek, and (DU) Duck Creek for WY 04-06. The boxplots represents the median, 25th and 75th percentiles, minimum, and maximum. Outliers (1.5 IQR's from end of box) are represented as circles, and extreme outliers (3 IQR's) are represented as asterisks. Among sites, median values with the same letter are not significantly different using natural log transformation and Tukey multiple comparison procedure in SAS 9.1. Values with two letters are not significantly different then values with either letter.

Table 2.3. Median concentrations and sample count data for Apple Creek (AP), Ashwaubenon Creek (AS), Baird Creek (BA), and Duck Creek (DU) for water years 2004-2006.

	Total Suspended Solids ($mg \cdot L^{-1}$)				**Total Phosphorus ($mg \cdot L^{-1}$)**				**Dissolved Phosphorus ($mg \cdot L^{-1}$)**				**Dissolved Phosphorus Fraction (%)**			
Condition	**AP**	**AS**	**BA**	**DU**	**AP**	**AS**	**BA**	**DU**	**AP**	**AS**	**BA**	**DU**	**AP**	**AS**	**BA**	**DU**
Event-Flow/Non-Winter:																
Median	117^{a}	162^{a}	159^{a}	72^{b}	0.44^{c}	0.70^{a}	0.57^{b}	0.26^{d}	0.19^{b}	0.33^{a}	0.22^{b}	0.14^{c}	48^{a}	47^{a}	36^{a}	51^{a}
Count	148	156	156	99	148	156	156	99	56	46	56	32	56	46	56	32
Event-Flow/Winter:																
Median	106^{a}	48^{ab}	99^{ab}	32^{b}	0.57^{a}	0.60^{a}	0.67^{a}	0.27^{b}	0.22^{bc}	0.45^{a}	0.36^{ab}	0.19^{c}	57^{a}	66^{a}	49^{a}	59^{a}
Count	51	53	58	42	51	53	58	43	17	16	17	12	17	16	17	12
Low-Flow/Non-Winter:																
Median	8.8^{b}	16.0^{a}	6.4^{bc}	5.0^{c}	0.20^{b}	0.36^{a}	0.14^{c}	0.14^{c}	0.15^{b}	0.31^{a}	0.09^{b}	0.11^{b}	71^{a}	80^{a}	66^{a}	78^{a}
Count	47	51	44	37	47	51	44	37	24	29	24	21	24	29	24	21
Low-Flow/Winter:																
Median	3.4^{a}	3.8^{a}	2.5^{a}	2.2^{a}	0.14^{a}	0.16^{a}	0.14^{a}	0.10^{a}	0.11^{a}	0.12^{a}	0.12^{a}	0.07^{a}	82^{a}	82^{a}	82^{a}	91^{a}
Count	9	8	8	8	9	8	8	8	6	5	5	5	6	5	5	5

Total Phosphorus Comparisons

Combining across sites and years, the median concentration for event-flow/non-winter, event-flow/winter, and low-flow/combined conditions were 0.50 mg/L, 0.57 mg/L, and 0.18 mg/L, respectively. All of the sites had some samples with concentrations over 1.0 mg/L TP with a maximum of 9.46 mg/L at Ashwaubenon Creek.

Information about which tributary watersheds have the highest TP concentration can be important for developing management strategies. Table 2.3 shows the results of the Tukey multiple comparison procedure for TP. Ashwaubenon Creek had the highest concentration of TP for all treatments except event-flow/winter conditions. It was also significantly higher than the other streams for event-flow/non-winter and low-flow/non-winter conditions. Differences during event-flow/non-winter conditions are the most important because this is when most of the runoff and loading of non-point source pollutants occur. Duck Creek had the lowest concentration of TP for all treatments and was significantly lower for event-flow/non-winter and event-flow/winter conditions. Apple Creek and Baird Creek median concentrations fell in between the other two streams. For event-flow/non-winter conditions, Baird Creek was significantly higher than Apple Creek and Apple Creek was significantly higher then Baird Creek for low-flow/non-winter conditions. Low-flow/winter conditions were not significantly different among the four streams.

Differences in TP concentrations can help us determine which watersheds are contributing more P and what factors affect it. Differences in watershed characteristics that may be related to the significant differences in TP observed for Ashwaubenon and Duck Creeks are explored in a latter section. Examining the differences in environmental characteristics of these two watersheds could help determine what the best options are for reducing TP loads to Green Bay.

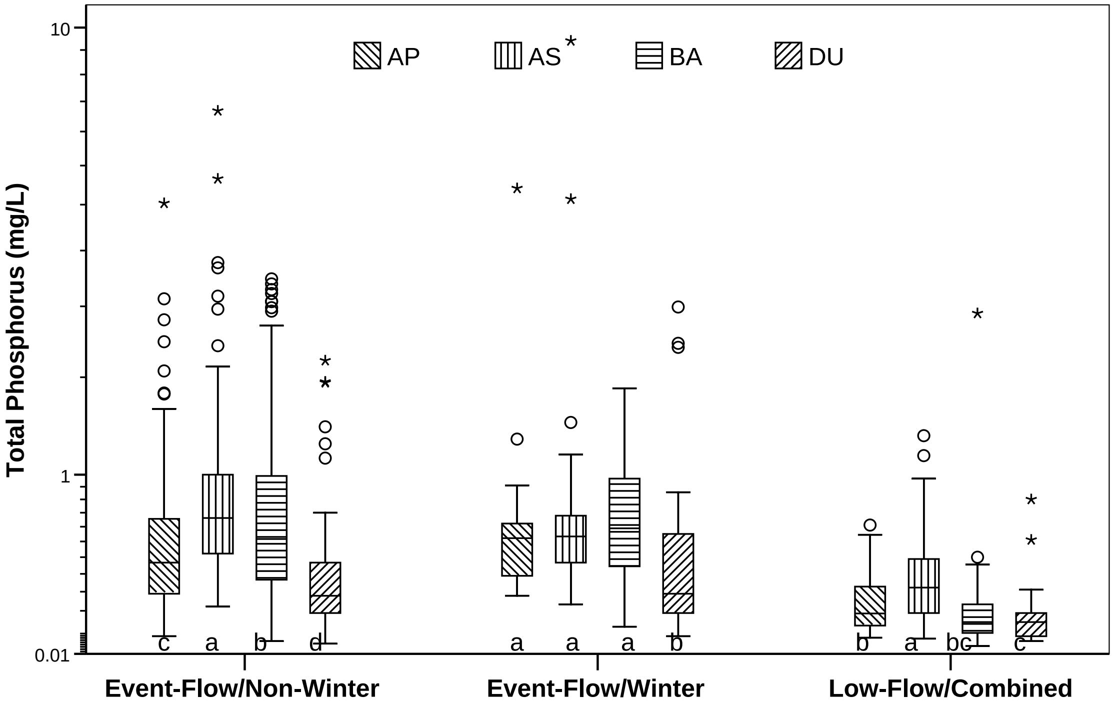

Figure 2.3. Boxplots of total phosphorus concentration for (AP) Apple Creek, (AS) Ashwaubenon Creek, (BA) Baird Creek, and (DU) Duck Creek for WY 04-06. The boxplots represents the median, 25th and 75th percentiles, minimum, and maximum. Outliers (1.5 IQR's from end of box) are represented as circles, and extreme outliers (3 IQR's) are represented as asterisks. Tukey groupings are represented by letters under each boxplot.

Dissolved Phosphorus Comparisons

Dissolved phosphorus usually makes up a small portion of the overall TP in stream flow. However, DP is made up of mostly bioavailable P that can be immediately utilized by aquatic organisms. Seasonal differences in DP were less pronounced with median event-flow/non-winter DP concentration (0.23 mg/L) being about the same as event-flow/winter concentrations (0.29 mg/L) when combining across all sites.

The differences among sites for DP were similar to TSS and TP (Table 2.3 and Figure 2.4). Ashwaubenon Creek generally had the highest median concentrations, with significantly higher values for event-flow/non-winter and low-flow/non-winter conditions. Duck Creek had the lowest median DP concentrations during all treatments except low-flow/non-winter conditions where Baird Creek had slightly lower concentrations. Apple Creek and Baird Creek DP median concentrations were between the other two streams for most conditions.

Lower Fox River tributaries have been monitored over the last decade by the Wisconsin Department of Natural Resource, the USGS, and Fox-Wolf Basin 2000. Their results indicate high fractions of TP in the dissolved form (40-70%). High fractions of DP are unusual in predominantly agricultural watersheds. Therefore, unique conditions might be affecting the concentrations of the various forms of P in the LFRS-B and different management strategies might be needed. The results from our study are consistent with the previous studies. The fraction of DP for the four LFR tributaries ranged from 36% to 51% for event-flow/non-winter conditions and 49% to 66% for event-flow/winter conditions (Table 2.3). The greatest fractions were observed during low-flows as expected, with median DP fractions for low-flow/non-winter conditions ranged from 66% to 80% and from 82% to 91% for low-flow/winter conditions. The fraction of P in the dissolved form was not significantly different among sites for all four treatments.

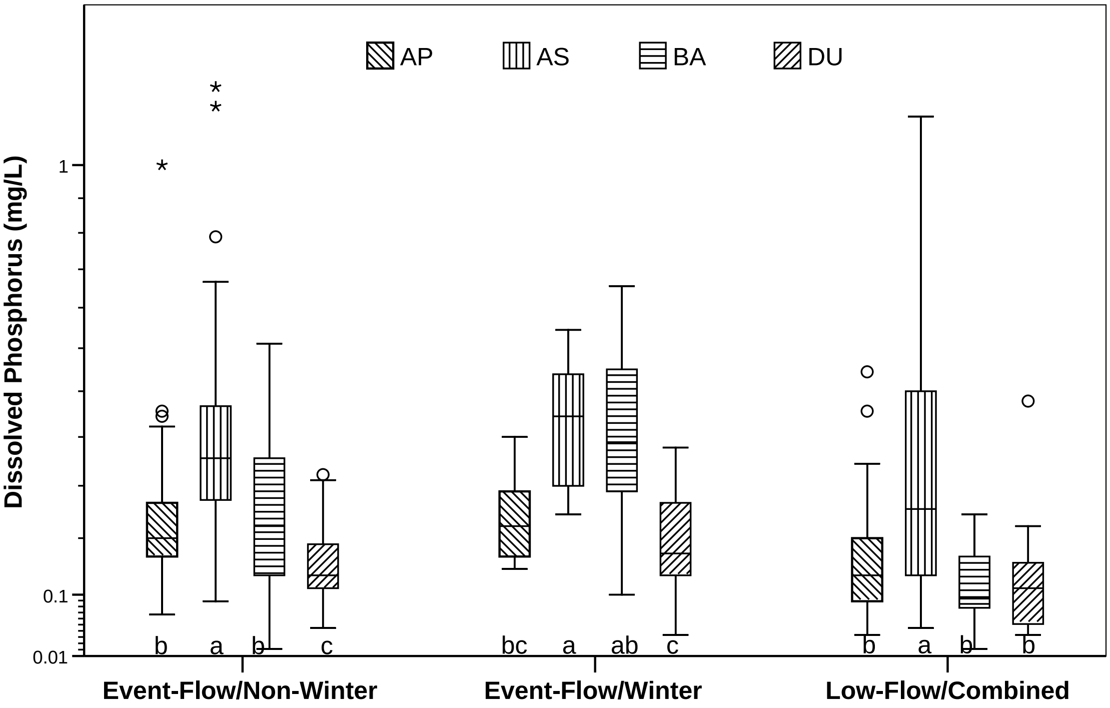

Figure 2.4. Boxplots of dissolved phosphorus concentration for (AP) Apple Creek, (AS) Ashwaubenon Creek, (BA) Baird Creek, and (DU) Duck Creek for WY 04-06. The boxplots represents the median, 25th and 75th percentiles, minimum, and maximum. Outliers (1.5 IQR's from end of box) are represented as circles, and extreme outliers (3 IQR's) are represented as asterisks. Tukey groupings are represented by letters under each boxplot.

Linear Regressions to predict DP Concentrations

Linear regression analysis can be used to determine the correlation between two variables. It helps explain how variables change as other variables increase or decrease. Finding variables that correlate with DP will provide insight into which water quality parameters are important for reducing DP concentrations and loads. The variables we used to compare with DP were TSS, TP, and discharge. Total P and TSS explained some of the variation in the DP concentration and discharge was not a significant determinate of DP concentrations in the streams. We first examined the regressions between these water-quality parameters without separating the data into the four climate and flow conditions. Where significant correlations were found at more then one site, the regression coefficients were compared to determine if streams reacted differently to increases in other water-quality parameters. Finally, for variables that were not significantly correlated with DP, the samples were analyzed for each condition to determine what effects flow or weather conditions might have. Some correlations between DP and TSS and between DP and discharge were found when the data was separated by climate and flow conditions.

Total Phosphorus

Total P was the only variable significantly correlated with DP at all four sites when both flows and weather conditions were combined. The regression between the natural log of DP and the natural log of TP was first determined for each stream. Each stream had a significant regression with R-squared values ranging from 0.49 at Apple and Baird Creek to 0.60 at Duck Creek (Table 2.4). Using the Dummy Variable approach, the regression coefficients were tested to determine if significant differences were present among sites. The null hypothesis that all site-coefficients are equal was not rejected, and we were able to combine sites to show the overall correlation between DP and TP (Figure 2.5).

Table 2.5 displays R-squared values for natural log transformed TP and DP among the different seasonal and flow conditions. Overall, the variation in low-flow samples was explained more than event-flow samples. Also, winter samples explained slightly more than non-winter samples. The combined R-squared of natural log transformed TP and DP was 0.57 when all seasonal and flow conditions were combined and is displayed in Figure 2.5.

Table 2.4. Linear regression results comparing natural log transformed DP to TP and TSS sample data from four Lower Fox River tributaries. Concentration units are mg/L for all samples from water year 2004-2006.

Site	Regression Equation	R-squared	P value
	LnTP		
AP	LnDP = 0.477*LnTP – 1.219	0.49	<0.0001
AS	LnDP = 0.579*LnTP – 0.831	0.52	<0.0001
BA	LnDP = 0.512*LnTP – 1.215	0.49	<0.0001
DU	LnDP = 0.587*LnTP – 1.162	0.60	<0.0001
	LnTSS		
AP	LnDP = 0.118*LnTSS – 2.177	.17	<0.0001
AS	LnDP = .056*LnTSS – 1.406	.03	0.1295
BA	LnDP = 0.147*LnTSS – 2.268	.20	<0.0001
DU	LnDP = 0.093*LnTSS – 2.337	.07	0.0327

Table 2.5. R-squared values for natural log transformed DP and TP samples for water year 2004-2006 combining four Lower Fox River tributaries.

	LnDP vs. LnTP - r^2									
Flow and weather condition	**n**	**AP**	**n**	**AS**	**n**	**BA**	**n**	**DU**	**n**	**All Sites**
Event/non-winter	50	0.33	39	0.01	49	0.08	30	0.25	168	0.26
Event/winter	13	0.04	12	0.68	15	0.72	10	0.76	50	0.59
Low-flow/non-winter	23	0.86	28	0.96	23	0.84	20	0.67	94	0.9
Low-flow/winter	6	0.99	5	0.75	5	0.87	5	0.99	21	0.92
Event	63	0.24	51	0.03	64	0.14	40	0.39	218	0.31
Low-flow	29	0.87	33	0.94	28	0.82	25	0.75	115	0.89
Non-winter	73	0.48	67	0.4	72	0.43	50	0.51	262	0.51
Winter	19	0.49	17	0.89	20	0.87	15	0.85	71	0.79
All	92	0.49	84	0.52	92	0.49	65	0.6	333	0.57

Total Suspended Solids

Total suspended solids were significantly correlated with DP at all sites except Ashwaubenon Creek when samples were combined across the climate and flow conditions (Table 2.4). Although there was a significant relationship at the three sites, the R-squared values ranged from 0.07 at Duck Creek to 0.20 at Baird. Therefore, not much of the variation in the DP concentration can be explained by TSS. Analyzing the regression coefficients between the three sites with significant relationships found no significant differences. By splitting the samples by season and flow, we tested if seasonal or flow conditions affected the relationship between DP to TSS. For the four weather and flow conditions, no more than two sites had significant correlations between DP and TSS. Therefore, the concentration of TSS on its own was not a good determinate of the DP concentrations in our streams (Table 2.4).

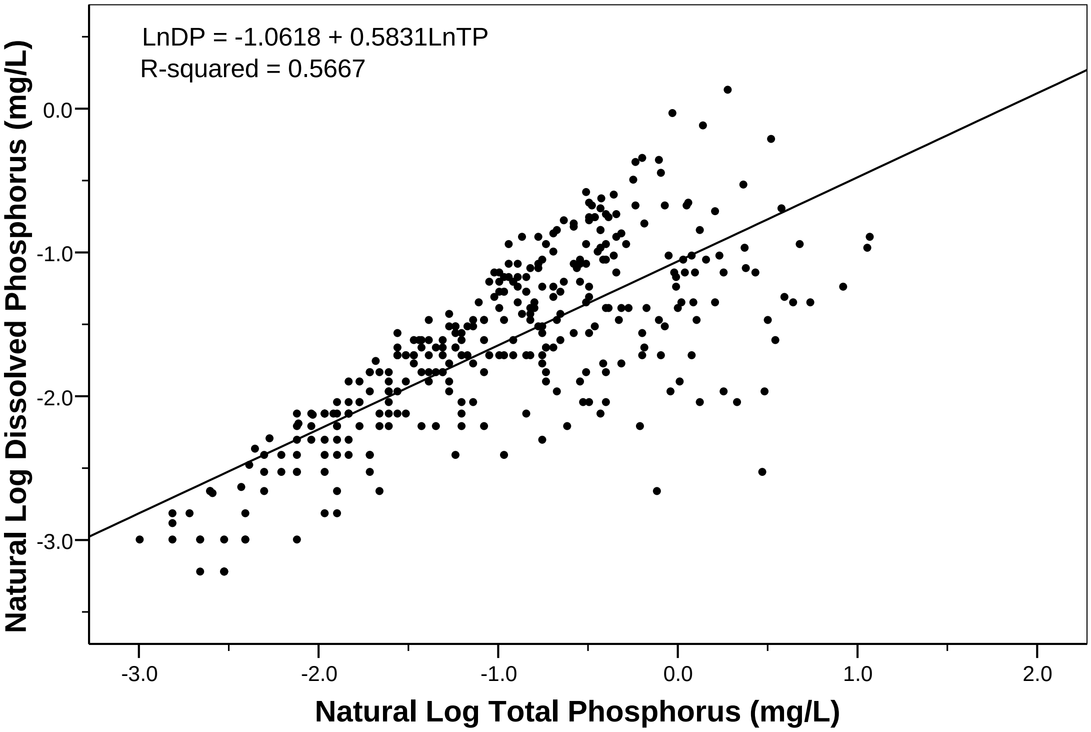

Figure 2.5. Linear Regression between natural log dissolved phosphorus (LnDP, mg/L) and natural log total phosphorus (LnTP, mg/L). The figure combines data from all four monitored streams and both flows and seasons for water years 2004-2006.

Multiple Regression

Dissolved phosphorus was analyzed for approximately 35% of the total samples. To determine DP concentrations for load calculations, multiple regression equations were used to predict unit value concentrations from five or 15-minute concentrations of TSS and TP determined using GCLAS. Along with TSS and TP, discharge and the ratio of TP to TSS were available to construct the best model for predicting DP concentrations. The distribution of DP was positively skewed and was first natural log transformed to meet the normality assumption of multiple regressions. Multiple regression equations were determined for each stream for winter and non-winter conditions. The best fitting models for predicting DP concentration are presented in Table 2.6.

The multiple regression equations explained a large portion of the DP variation at all four streams for non-winter and winter conditions. The models used to predict winter conditions explained between 87% and 95% of the variation in DP. Slightly less of the variation was explained at all sites for the non-winter conditions. Ashwaubenon Creek was explained well with an R-squared value of 0.89. Apple Creek, Baird Creek, and Duck Creek were explained slightly less with R-squared values of 0.65, 0.77, and 0.75, respectively.

The intercepts and coefficients for the independent variables were similar among streams within weather conditions (Table 2.6). The coefficients for the natural log of TP were all positive and had a range of 0.035 among streams for non-winter condition and 0.133 for winter conditions. As expected, DP concentration increases when TP concentrations increase. The coefficients for TSS and Q were also similar among streams (Table 2.6.). These two variables were not used in all of the equations, but when they were used TSS ranged from -0.0002 to -0.004 and Q ranged from -0.0008 to 0.0021. As the TSS concentration increases the DP concentration decreases. Increased particulate matter in the stream may have resulted in adsorption of P and decreased DP concentrations (Sharpley et al., 1981, 2001). Where Q was a significant variable it caused a decrease in the DP concentration at Ashwaubenon and Duck Creeks and an increase at Baird Creek. Baird Creek is characterized by extensive wetlands in the upper portion of the watershed. It may be that as Q increased DP contained in the wetlands was flushed out.

Table 2.6. Multiple Regression equations for predicting dissolved P concentration for Lower Fox River Tributaries (LnDP = natural log of dissolved phosphorus (mg/L), LnTP = natural log of total phosphorus (mg/L), TSS = total suspended solids (mg/L), Q = discharge)

Site	Condition	Regression Equation		R-Squared
AP	Non-winter	LnDP =	-0.554 + 0.883(LnTP) – .0009(TSS) – 0.0004(TSS/TP)	0.65
	Winter	LnDP =	-0.539 + 0.824(LnTP) – 0.0023(TSS)	0.87
AS	Non-winter	LnDP =	-0.264 + 0.918(LnTP) – 0.0002(TSS) – 0.0014(TSS/TP) – 0.0008(Q)	0.89
	Winter	LnDP =	-0.604+0.802*LnTP	0.89
BA	Non-winter	LnDP =	-0.67+.883(LnTP) – 0.001(TSS) – 0.0003(TSS/TP) + 0.0021(Q)	0.77
	Winter	LnDP =	-0.338 + .935(LnTP) – 0.001(TSS) – 0.001(Q)	0.95
DU	Non–winter	LnDP =	-0.592 + 0.854(LnTP) – 0.002(TSS) – 0.0003(Q)	0.75
	Winter	LnDP =	-0.354 + 0.914(LnTP) – 0.004(TSS)	0.93

Load Comparisons

Constituent loads were computed for TSS and TP by the USGS. Loads of DP were calculated from predicted continuous DP concentrations and five or 15-minute discharge. Seasonal flows, loads, and yields for water-year 2004 though 2006 are given in Table 2.7. In water year 2004, loads of TSS, TP, and DP were more than 50% greater than the following 2 water-years. Intense rainfall in March of 2004 contributed to the excessive loading of water year 2004. Across the four sites, DP loads ranged from 36% to 52% of the annual TP load in 2004. In the following 2 years the DP load ranged from 46% to 61% of the TP load. It is evident that the timing (before establishment of crop cover) and intensity of the May and June 2004 events caused disproportionately greater sediment losses when comparing annual rainfall amounts (Table 2.2). It is possible that the large amounts of TSS in the stream channel, from higher intensity precipitation and flows, in

2004 are responsible for the lower fractions of DP (note the negative TSS coefficient in Table 2.6).

In 2006, the greater precipitation at Baird Creek resulted in DP yields during non-winter conditions to be much greater than the other streams (Table 2.7). The Baird Creek watershed DP yield was 0.36 kg/ha compared to 0.22 kg/ha at Ashwaubenon Creek, 0.18 kg/ha at Apple and 0.17 kg/ha at Duck Creek.

For 2004 and 2006 the non-winter period (~ 9 months) contributed most of the annual DP load for all streams. In 2005, however, the winter period (~ 2 months) contributed from 56% to 60% of the annual DP load for all streams. The 2005 water year had the highest winter period flows and the lowest non-winter flows during the three year study. The high winter flows were a result of winter rains and above average precipitation in January and February (Table 2.2). These high flows combined with large event-flow/winter DP concentrations (Table 2.3), presumably caused the unusually high winter season DP loads.

Table 2.7. Seasonal and annual flow and total suspended solids, total phosphorus, and dissolved phosphorus loads and yields for WY 04-06 (some of the values shown below and in the text were modified from the original thesis to reflect updated flows which occurred during ice-affected periods).

Site	Season	Area (km^2)	Flow (mm)	TSS Load (ton)	TSS Yield (t/ha)	TP Load (kg)	TP Yield (kg/ha)	DP Load (kg)	DP Yield (kg/ha)
Apple Creek		117							
2004	Non-Winter		266	10,427	0.89	18,985	1.62	6,124	0.52
	Winter		56	488	0.04	3,205	0.27	1,783	0.15
	Annual		322	10,915	0.93	22,189	1.89	7,901	0.67
2005	Non-Winter		75	914	0.08	3,206	0.27	1,668	0.14
	Winter		69	453	0.04	3,653	0.31	2,122	0.18
	Annual		144	1,367	0.12	6,859	0.59	3,792	0.32
2006	Non-Winter		88	1,755	0.15	5,057	0.43	2,135	0.18
	Winter		33	147	0.01	917	0.08	542	0.05
	Annual		121	1,902	0.16	5,973	0.51	2,719	0.23
Ashwaubenon Creek		48							
2004	Non-Winter		221	3,178	0.66	7,693	1.60	2,929	0.61
	Winter		50	160	0.03	1,874	0.39	1,086	0.23
	Annual		272	3,338	0.69	9,567	1.99	4,014	0.84
2005	Non-Winter		53	819	0.17	1,982	0.41	861	0.18
	Winter		59	147	0.03	1,885	0.39	1,130	0.24
	Annual		112	966	0.20	3,867	0.80	1,991	0.41
2006	Non-Winter		72	280	0.06	1,763	0.37	1,072	0.22
	Winter		29	36	0.01	760	0.16	429	0.09
	Annual		101	316	0.07	2,524	0.52	1,497	0.31

Site		Season	Area (km^2)	Flow (mm)	TSS Load (ton)	TSS Yield (t/ha)	TP Load (kg)	TP Yield (kg/ha)	DP Load (kg)	DP Yield (kg/ha)
Baird Creek			54							
	2004	Non-Winter		323	3,522	0.65	10,608	1.97	5,497	1.02
		Winter		41	425	0.08	1,998	0.37	1,065	0.20
		Annual		364	3,947	0.73	12,606	2.34	6,563	1.22
	2005	Non-Winter		59	225	0.04	1,160	0.22	695	0.13
		Winter		55	296	0.05	1,676	0.31	1,039	0.19
		Annual		114	520	0.10	2,836	0.53	1,734	0.32
	2006	Non-Winter		141	904	0.17	3,353	0.62	1,918	0.36
		Winter		32	51	0.01	556	0.10	395	0.07
		Annual		173	955	0.18	3,909	0.73	2,314	0.43
Duck Creek			276							
	2004	Non-Winter		301	9,255	0.33	30,605	1.11	13,492	0.49
		Winter		43	653	0.02	5,170	0.19	2,997	0.11
		Annual		344	9,908	0.36	35,775	1.29	16,488	0.60
	2005	Non-Winter		85	1,578	0.06	6,712	0.24	3,406	0.12
		Winter		55	1,369	0.05	8,930	0.32	4,380	0.16
		Annual		140	2,947	0.11	15,641	0.57	7,786	0.28
	2006	Non-Winter		89	790	0.03	8,931	0.32	4,664	0.17
		Winter		27	68	0.00	664	0.02	535	0.02
		Annual		116	859	0.03	9,594	0.35	5,289	0.19

Environmental Characteristics

The available environmental characteristics were compared to water-quality results for water-year 2004 through 2006. Table 2.8 shows Spearmen correlation coefficients for the annual and three-year combined mean concentrations (total load/total flow) of TP, PP, and DP compared with some environmental characteristics (Table A.1). Because of the small sample size (n = 4 streams), the only significant correlations were found when the point from each tributary fell on a straight line and the correlation coefficient equaled one. A correlation coefficient equal to 0.8 meant that only one tributary did not line up with the others.

The soil slope and basin slope were both negatively correlated with TP and DP. Both the soil slope and basin slope varied less then one degree among all sites, therefore making conclusions from these results should be done with caution. The soil slope measurement included all areas of the watersheds, including non agriculture landuses. The negative correlation between slope and the concentration of TP and DP may not be found if the soil slope of only the agricultural fields was used.

The soil textural characteristics (silt and clay content) were positively correlated with TP, PP, and DP across the three years (Table 2.8). Silt content was fairly similar among the four watersheds. However, clay content ranged from 25.9% for the Ashwaubenon Creek watershed and 14.3% for the Duck Creek watershed (Table A.1). The significant differences in constituent concentrations in runoff from these watersheds may be partially explained by differences in soil infiltration and water holding capacity caused by the soil textural properties of the watersheds.

The only other marginally significant relationships were found between TP, DP, and the percent of agricultural land in forage crop production. Forage crops, such as hay, have been linked to high concentrations of DP in other studies (Hart et al., 2004), and TP and DP have been found to be significantly correlated with the percentage of agricultural landuse within watersheds in Wisconsin (Robertson et al., 2006). Overall, it is difficult to draw broad conclusions from these comparisons. More data, at a smaller scale and matching the monitoring period, would strengthen the comparisons between watersheds within the same basin.

Table 2.8. Spearman rank correlation coefficients between annual mean (total mass/total flow) and three-year mean concentrations of TP, PP, and DP and specific environmental characteristics for the studied watersheds in the Lower Fox River Sub-Basin.

	Total Phosphorus (total mass/total flow)				**Particulate Phosphorus (total mass/total flow)**				**Dissolved Phosphorus (total mass/total flow)**			
Characteristics†	**2004**	**2005**	**2006**	**04-06**	**2004**	**2005**	**2006**	**04-06**	**2004**	**2005**	**2006**	**04-06**
Urban Development	0	-0.4	0	0	0.8	-0.2	0.6	0.6	0	0	0	0
Row Crops	0.4	0.8	0.4	0.4	-0.4	**1**	0.2	0.2	0.4	0.4	0.4	0.4
Forage Crops	0.8	**1**	0.8	0.8	-0.2	0.8	0.4	0.4	0.8	0.8	0.8	0.8
Agriculture (Total)	0.4	0.8	0.4	0.4	-0.4	**1**	0.2	0.2	0.4	0.4	0.4	0.4
Forest	0	0.4	0	0	-0.8	0.2	-0.6	-0.6	0	0	0	0
Wetlands	-0.4	-0.2	-0.4	-0.4	-0.6	-0.4	-0.8	-0.8	-0.4	-0.4	-0.4	-0.4
Soil Slope	**-1**	-0.8	**-1**	**-1**	-0.4	-0.4	-0.8	-0.8	**-1**	**-1**	**-1**	**-1**
Soil Silt Content	**1**	0.8	**1**	**1**	0.4	0.4	0.8	0.8	**1**	**1**	**1**	**1**
Soil Clay Content	0.8	0.4	0.8	0.8	0.8	0.2	**1**	**1**	0.8	0.8	0.8	0.8
Basin Slope	**-1**	-0.8	**-1**	**-1**	-0.4	-0.4	-0.8	-0.8	**-1**	**-1**	**-1**	**-1**

† See table A.1. in Appendix A for watershed characteristic values used in the correlation analysis.

Conclusions

To reach water-quality objectives for the Lower Fox River and the Bay of Green Bay, losses of TSS and P from the contributing watersheds must be reduced. Determining source area factors that contribute large quantities of TSS and TP and determining the environmental characteristics that account for the differences is necessary. In general, Ashwaubenon Creek had larger concentrations of TSS, TP, and DP compared to the other three monitored streams. However, when comparing yields, Baird Creek contributed as much TSS, TP, and DP, if not more, than Ashwaubenon Creek per unit area. Duck Creek, on the other hand, had concentrations of TSS, TP, and DP significantly less than the other streams and was found to contribute much less per unit area.

Linear regressions were used to compare the concentrations of TSS, TP, and discharge with DP concentrations. Total P was significantly correlated with DP at all 4 streams across all seasonal and flow conditions. Using TP as the independent variable, we were able to combine data for all sites to produce an overall equation for predicting DP concentrations in the LFRS-B. A relationship between TSS and DP was significant at some sites. However, only a small portion of the variation in the DP concentration was explained.

Drawing conclusions about the environmental characteristics that directly affected the concentrations and yields of water quality parameters within this project area was difficult. Usually, only small changes among characteristics could be distinguished among sites. However, as previous research has indicated, the percent of agricultural landuse, particularly in forage crop production, was found to have a strong correlation to the TP and DP concentrations. Watershed soil texture was also correlated with mean annual concentrations. The Duck Creek watershed had soils with the least clay content and had the lowest constituent concentrations. The monitored Lower Fox River Sub-Basin tributaries had significant variations in constituent concentrations among sites. This variation could be used to determine which environmental characteristics, anthropogenic or otherwise, contribute to increased rates of non-point source pollution and could help refine management strategies to meet water-quality goals.

CHAPTER 3 – PHOSPHORUS FORMS AT DIFFERENT SPATIAL SCALES IN APPLE CREEK WATERSHED

Introduction

The determination of phosphorus forms in surface water runoff is important for choosing the most appropriate management strategies for controlling non-point source pollution from tributary watersheds. The literature contains differing assumptions about which form of phosphorus (P), dissolved (DP) or particulate (PP), is predominant in the various P transfer pathways (Hart et al., 2004). Results from most basin studies indicate that PP is the predominate form exported from agricultural runoff (Sharpley et al., 1992). However, the representativeness of in-stream measurements of the proportion of DP to PP may be confounded by adsorption of DP onto sediment particles during overland flow and/or in the stream channel itself (Sharpley et al., 1981, 2000). Dissolved P has been found to be the dominate form in some grassland (pasture) watersheds and dairy farming watersheds (Cooke, 1988; Wilcock et al., 1999; Davies-Colley and Nagels, 2002; Sharpley et al., 1994, 2000; Nash and Murdoch, 1997).

Factors affecting the fraction of DP in runoff are not well understood. Seasonal affects, precipitation intensities, and watershed factors, such as soil permeability, texture, and composition, basin and stream channel slope, and other environmental factors might contribute to differences in the fraction of DP. A strong relationship between soil test P levels and the amount of DP in runoff water has been found by other researchers (Sharpley et al., 1994; Daniel et al., 1994; Pote et al., 1999; Andraski and Bundy, 2003). It may be that reducing soil test phosphorus levels in critical source areas within a watershed will be the most effective management strategy for controlling DP losess.

From previous monitoring, the Lower Fox River Sub-Basin (LFRS-B) tributaries can be characterized by high fractions of DP (Baumgart, 2005a). A rainfall simulation study on small plots in Wisconsin found higher DP concentrations in runoff from soils with slower infiltration rates (Andraski and Bundy, 2003). These soils are similar to the clay loam soils of the LFRS-B. The authors suggest that the slower infiltration rate allowed the interface between runoff and the soil to occur to a greater depth and resulted in more interaction between runoff and near-surface soil water that contained extractable P. However, field scale data are lacking on eastern red-clay soils of Wisconsin, especially within the basin. Knowledge of P forms at the field scale is needed because management strategies to reduce non-point source P pollution are usually implemented at this scale.

Differences in water-quality parameters between source areas might be explained by contributing area characteristics. Some of the more important characteristics may include soil properties, topography, land-use/land-cover, and soil nutrient levels (Andraski and Bundy, 2003). One study on wadeable streams in Wisconsin quantified watershed characteristics and compared them to water quality parameters (Robertson et al., 2006). This chapter aims to determine how the concentration of water-quality parameters and the fraction of DP differ among multi-field source areas and along flow paths from the source area scale to the watershed scale in the Apple Creek Watershed.

Methods

Sampling Sites

In early March 2004, 11 multi-field (source area) monitoring locations were identified through field inspection in the Apple Creek Watershed. Sampling locations were chosen on a quasi-random basis to include predominately agricultural landuse, areas without significant tile drainage, and adequate size for sufficient discharge (Figure 3.1). Four integrator sites where chosen to include runoff from upstream source area sites and other areas in the watershed. The main-stem USGS monitoring station was used as the final integrator site and combined flow from all source areas and integrator sites. Refer to Chapter Two of this document for more details about the automated monitoring station on the main stem. Table 3.1 includes the location, size of contributing areas, and conveyance structure for each site. To determine the contributing land area of the source area sites (Figure 3.1 and Table 3.1), watersheds were delineated using the watershed delineator subroutine of the Soil and Water Assessment Tool (USDA-ARS, 1998), contour maps, infield observations, and digital geoprocessing using ArcGIS 9 (Baumgart, 1998).

All source area and integrator sampling sites were located at road crossings. Fixed reference points were established at each culvert or bridge from which tape-down measurements of relative water height were performed. Continuous flow was measured and computed at the main stem station by the USGS using a gas bubble flow meter and rating curve.

Precipitation

Precipitation in the LFRS-B was measured at 22 rain gauge sites by the National Weather Service, USGS, Lower Fox River Watershed Monitoring Project (LFRWMP), and WBAY Weather Service (Green Bay, WI). Five of these gauges were located within or next to the Apple Creek Watershed (Figure 3.1) and were used to determine the spatial variation of storm events for this study. The rain gauge located next to site 4 and one located to the west of site 5a and 5b were unavailable for the 2004 precipitation events. For these events, the other three rain gauges were used to determine the uniformity of precipitation. The total precipitation for an event was determined by adding up the total rainfall for the day of the event. Because prior rainfall can have an affect on the quantity and rate of runoff, the total precipitation seven days before sample collection was also determined. The 5-minute maximum intensity of each storm and the peak flow at the main stem site were calculated to show relative differences between precipitation events.

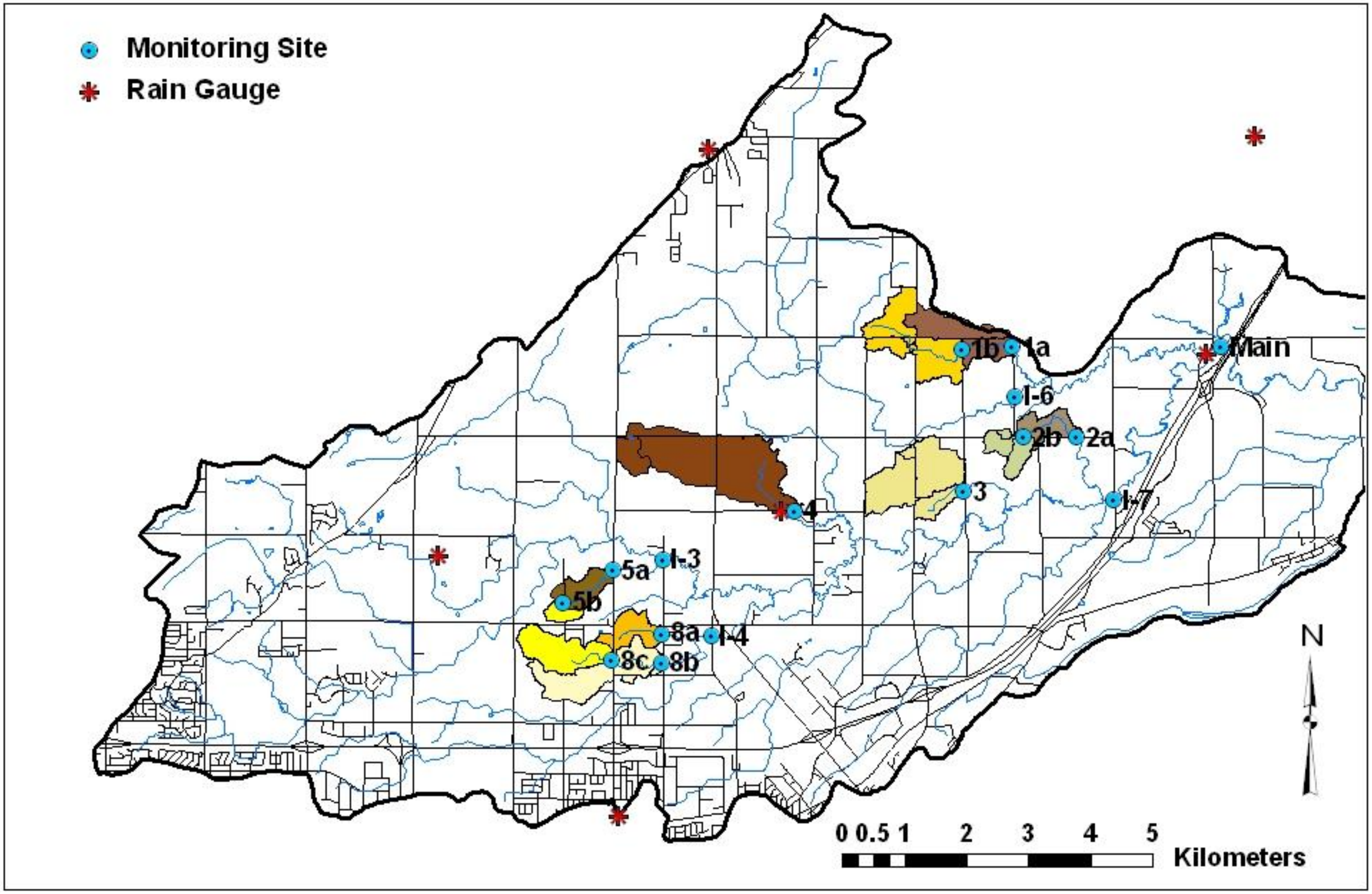

Figure 3.1. Map of the monitoring and rain gauge sites in the Apple Creek Watershed. Source area watersheds are represented by colored polygons.

Table 3.1. Sampling site information for the Apple Creek Watershed phosphorus forms study.

Site ID	Type	Location Description	Area (km^2)	Conveyance Structure
1a	Source	Section Line Road	1.90	Metal pipe arch culvert
1b	Source	Farrell Road	1.13	Pipe arch metal culvert
2a	Source	Greiner Road	0.74	Concrete box culvert
2b	Source	Greiner Road	0.36	Metal pipe arch culvert
3	Source	Farrell Road	1.44	Metal pipe arch culvert
4	Source	Lau Road	2.24	Metal pipe arch culvert
5a	Source	Cty. N	0.53	Metal circular culvert
5b	Source	Vandenbroek Rd.	0.15	Metal circular culvert
8a	Source	Buchanan Road	0.40	Metal circular culvert
8b	Source	Buchanan Road	1.63	Metal circular culvert
8c	Source	Cty. N	0.67	Metal circular culvert
I-3	Integrator	Buchanan Road	37.5	Open stream
I-4	Integrator	Cty. CC	12.4	Open stream
I-6	Integrator	Section Line Road	22.3	Open stream
I-7	Integrator	McCabe Road	87.3	Open stream
USGS	Main Stem	Cty. U - Campground	117.2	Open stream

Water Quality

Sample Collection and Processing

Water quality samples were collected near the peak flow at source area and integrator sites during or immediately following rain events that produced runoff and were relatively uniform. Five events were sampled in 2004, one in 2005, and two in 2006. Sampling in 2005 and 2006 was limited due to the lack of uniform runoff producing rain events. Relative flow was determined by repeated tape-down measurements of water surface height at each culvert or bridge. One liter grab samples were collected in polyethylene bottles and stored on ice for transport to the University of Wisconsin-Green Bay watershed laboratory. At the laboratory, each sample was shaken and then sub-sampled using a Teflon cone splitter. The sample was divided into one 500 mL polyethylene bottle for TSS and two 250 mL polyethylene bottles for TP and DP. Samples analyzed for DP were filtered using a 0.45 μm mixed cellulose ester membrane filter. Total P and DP samples were preserved below pH 2.0 with sulfuric acid. All samples were stored at 4ºC until delivery to the Green Bay Metropolitan Sewage District's laboratory for analysis. Refer to Chapter Two of this document for further details concerning sampling and analysis.

Evaluation of Sampling Protocol

Taking a grab sample near peak flow provides a relatively inexpensive method of sampling many sites in close proximity. However, there is uncertainty as to how representative a grab sample near the peak flow is to an entire event. To determine the validity of this sampling method, we used the Apple Creek main-stem USGS monitoring station to determine if peak flow samples correlated with event mean concentrations. Peak flow concentrations were determined by graphical fit to discrete samples using Graphical Constituent Loading Analysis System (GCLAS) Software (Koltun, 2006). The event mean concentration was determined by dividing the total mass of TSS and TP by the total event flow. The concentration of DP at peak flow was determined from a multiple regression equation based on TSS and TP (see Chapter 2); therefore, it was not necessary to analyze its relationship with the event mean concentration.

Contributing Area Characteristics

Environmental characteristics of the agricultural fields within our source area watersheds were gathered from nutrient management plans, co-ops, and crop consultants. The field data included the dominate soil type, crop rotation, tillage practice, soil test phosphorus levels, fertilizer and manure applications, and distance to a watercourse. Soil sampling dates ranged from October 2002 to October 2006 with the majority of samples in 2004 and 2005. In this chapter, only soil test phosphorus was used to compare with monitored water-quality results from source areas. In the following chapter, all of these characteristics will be combined in a phosphorus index tool to predict losses of P.

Statistical Analysis

Boxplots were used to compare TP and DP concentrations and the DP fraction among source areas, integrator sites, and the main stem site for the 2004 samples. The 2005 and 2006 event samples were not included in the boxplots because the land management changed each year. Because of our small sample size, analysis of variance on the ranks of the data were used in conjunction with the Tukey multiple comparison procedure to determine if differences in median concentrations among sites were significant at the 0.95 probability level (Robertson and Saad, 1996; Fink, 2005). Differences in median concentrations of water-quality parameters between source areas, integrator sites, and the main stem site were tested using this same procedure.

A non-parametric Kruskal-Wallis Test was used to determine the effect of variation in 2004 runoff producing events on the constituent concentrations. Where the source area sites were paired along a flow path (e.g. sites 1a and 1b), a Wilcoxon Signed-Rank Test was used to determine if constituent concentrations changed. All analyses were performed using SAS 9.1 statistical software (SAS Institute Inc., 2003). ArcGIS 9 and Microsoft Excel 2003 were used to calculate an area-weighted soil test phosphorus value for each source area watershed. These values were used in linear regressions to explain the variation in constituent concentrations.

Results and Discussion

Precipitation and Event Hydrology

The 2004 growing season was characterized by above normal precipitation in May and June followed by a summer drought period (Table 3.2). Results from the Lower Fox River tributary analyses presented in Chapter 2 indicated loads of TSS, TP, and DP were more then 50% greater in water year 2004 than the following two water-years. The frequent and large quantity of rain in May 2004 created large flows and high TSS levels. These conditions likely contributed to DP fractions being lower for that water-year compared to the rest. Therefore, it should be noted that our DP fraction results in 2004 from our source area sites might be lower than in years with more normal precipitation.

Table 3.3 presents precipitation data and main-stem peak flow for the eight monitored events from 2004 to 2006. The total precipitation for the day of the event ranged from 6.6 mm to 48.3 mm. Events four and six had one day total precipitation more than twice that of the other events and were the greatest intensity storms. Event four also had the highest peak flow (1073 cfs). These high precipitation events resulted in the greatest median TSS concentrations (event four = 464 mg/L; event six = 508 mg/L) when data are combined across sites by event. The cumulative precipitation for seven days prior to sample collection is also presented to illustrate soil wetness conditions prior to each event. Several of the small sampling events were preceded by significant rain. The maximum 5-minute intensities ranged from 0.25 mm to 12.19 mm. The peak flows at the main stem ranged from 205 to 1073 cfs. The lowest intensity storms (5/14/04 and 5/14/06) had the smallest peak flows.

The concentration of water-quality constituents was significantly affected by the amount and intensity of precipitation events. Results of the Kruskal-Wallis test show that the median concentrations of TSS, TP, and PP were all significantly different ($p < 0.01$) across events. However, both DP concentrations ($p = 0.91$) and the DP fraction ($p = .11$) were both not significantly different. The median concentration of TP for all sites was consistent with precipitation and flow amounts and ranged from 0.35 mg/L for event eight to 1.14 mg/L for event six. The median concentration of DP ranged from 0.04 mg/L for event four to 0.48 mg/L for event seven.

Table 3.2. Monthly precipitation recorded at the USGS rain gauge at the Apple Creek main stem monitoring station for water years 2004 -2006 compared with the 30-year average from the National Weather Service for Green Bay.

Month	Green Bay 30-year Average	WY 2004	Departure from Normal	WY 2005	Departure from Normal	WY 2006	Departure from Normal
Oct.	55.1	26.7	-52%	93.0	69%	35.7	-35%
Nov.	57.7	116.3	102%	38.0	-34%	75.8	31%
Dec.	35.8	29.0	-19%	54.7	53%	25.9	-28%
Jan.	30.6	29.2	-5%	39.1	28%	40.0	31%
Feb.	25.6	39.4	54%	30.1	18%	34.9	36%
Mar.	52.3	91.0	74%	34.0	-35%	37.3	-29%
Apr.	65.0	24.6	-62%	40.3	-38%	52.3	-20%
May	69.9	181.7	160%	55.6	-20%	113.5	62%
June	87.1	108.1	24%	76.6	-12%	35.4	-59%
July	87.4	46.2	-47%	56.8	-35%	71.6	-18%
Aug.	95.8	39.5	-59%	108.6	13%	28.9	-70%
Sept.	79.0	9.3	-88%	69.2	-12%	56.1	-29%
Total (mm)	**741.3**	**741.0**	**0%**	**696.0**	**-6%**	**607.5**	**-18%**

Table 3.3. Precipitation totals and intensities recorded at the Apple Creek USGS rain gauge for eight events in 2004-2006. Precipitation is described by the day of the event total and total seven-day precipitation prior to sample collection.

		------------------------Precipitation----------------------			
Event	Date	Day of Event (mm)	7-day (mm)	Intensity (5 min max.-mm)	Main-stem peak flow (cfs)
1	3/28/2004	14.7	21.3	0.76	587
2	5/14/2004	8.9	63.1	0.25	205
3	5/21/2004	13.2	38.6	0.51	249
4	5/23/2004	45.5	89.9	3.30	1073
5	6/11/2004	17.0	42.2	0.51	520
6	6/13/2005	48.3	58.9	12.19	367
7	1/29/2006	15.5	0.0	-	61†
8	5/14/2006	6.6	79.5	0.25	208

† Average daily flow (ice affected)

Representativeness of Peak Flow Sampling

Peak flow concentrations and event mean concentrations were determined for all events in which source area samples were collected except January 2005 when ice conditions made it difficult to accurately predict flow (Baumgart, 2007; unpublished). Total P and TSS peak flow concentrations were found to have a strong correlation with the event mean concentrations with R-squared values of 0.90 and 0.99, respectively (Figure 3.2 and Figure 3.3). Therefore, the grab sampling technique adequately represented the monitored events, and if it is assumed that the relationship also occurs at the source area sites, the sample concentrations can be used to compare between sites and scales. It should be noted that peak flow at integrator sites likely occurred many hours after peak flow at source areas. Our sampling of integrators occurred approximately one hour after source areas and was likely before peak flow.

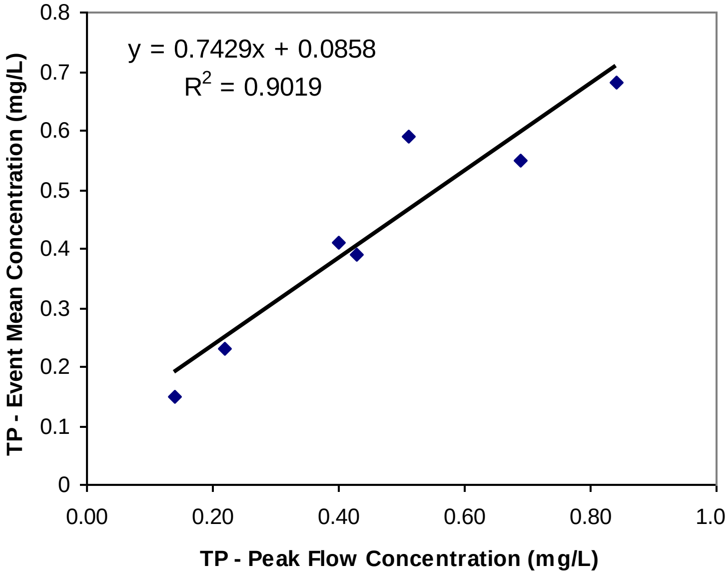

Figure 3.2. Relationship between TP-event mean concentrations and peak flow TP concentrations at the Apple Creek main stem monitoring station for 7 runoff events in 2004-2005.

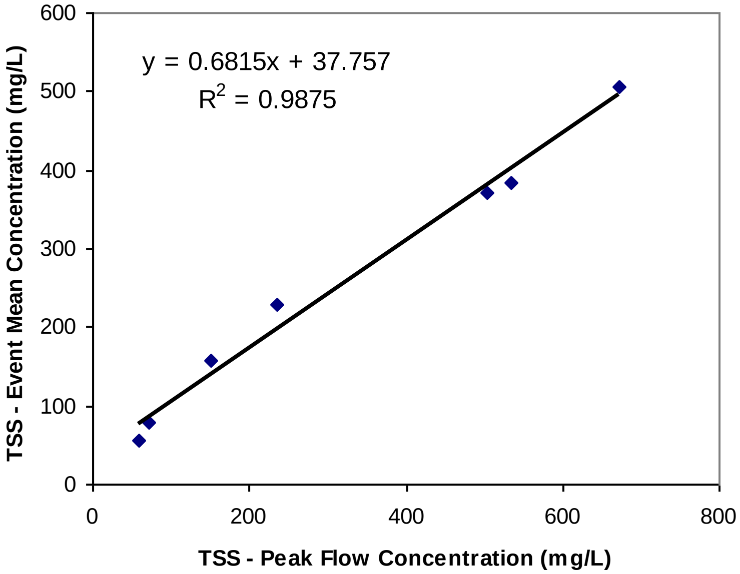

Figure 3.3. Relationship between TSS-event mean concentrations and peak flow TSS concentrations at the Apple Creek main stem monitoring station for six runoff events in 2004-2005.

Scale Comparisons

An objective of this research was to determine if the concentration of water-quality constituents changed at different spatial scales. This experiment allowed us to compare TSS, TP, PP, and DP concentrations and the DP fraction at the source area scale (0.2 – 2.3 km^2), the integrator scale (12 – 85 km^2), and the watershed scale (117 km^2). Median concentrations of TSS, TP, PP, and DP and the DP fraction for five events in 2004 at the three scales are given in Table 3.4. The variability in constituent concentrations for the five 2004 events at each of the 16 monitored sites from the three scales is illustrated by the boxplots in Figure 3.4. Within site and among site variability of source areas tended to be large relative to the integrator and main-stem sites. This is not unexpected given the potential influence of individual site characteristics on water quality at source areas relative to the integrative properties of the larger scales. Comparing median concentrations among source areas, integrators, and main stem scales, all of the water-quality parameters were not significantly different at the 0.05 significance level.

Table 3.4. Median TSS, TP, PP, and DP concentrations and the DP/TP fraction at the source area, integrator and main-stem sites in the Apple Creek Watershed for water-year 2004 samples. Within source area and integrator sites, medians with the same superscript letters are not significantly different at 0.05 significance level.

	Median				
Site	**TSS (mg/L)**	**TP (mg/L)**	**PP (mg/L)**	**DP (mg/L)**	**DP/TP**
1a	168^{a}	0.66^{ab}	0.3^{a}	0.2^{ab}	0.43^{ab}
1b	112^{a}	0.41^{ab}	0.23^{a}	0.17^{ab}	0.42^{ab}
2a	100	0.7^{ab}	0.22^{a}	0.26^{ab}	0.50^{ab}
2b	118^{a}	0.46^{ab}	0.3^{a}	0.16^{bc}	0.35^{ab}
3	704^{a}	1.51^{a}	1.18^{a}	0.31^{ab}	0.22^{ab}
4	58^{a}	0.38^{ab}	0.13^{a}	0.25^{ab}	0.66^{ab}
5a	252^{a}	0.36^{ab}	0.31^{a}	0.04^{c}	0.11^{b}
5b	92^{a}	0.21^{b}	0.13^{a}	0.05^{c}	0.31^{b}
8a	98^{a}	0.66^{ab}	0.13^{a}	0.53^{a}	0.83^{a}
8b	326^{a}	0.62^{ab}	0.39^{a}	0.27^{ab}	0.57^{ab}
8c	320^{a}	0.37^{ab}	0.3^{a}	0.1^{bc}	0.19^{b}
Source Areas	**144**	**0.46**	**0.28**	**0.19**	**0.39**
Int-3	162^{a}	0.33^{a}	0.22^{a}	0.11^{c}	0.38^{a}
Int-4	152^{a}	0.4^{a}	0.23^{a}	0.17^{b}	0.45^{a}
Int-6	130^{a}	0.55^{a}	0.24^{a}	0.25^{a}	0.56^{a}
Int-7	228^{a}	0.42^{a}	0.28^{a}	0.15^{b}	0.33^{a}
Integrators	**165**	**0.48**	**0.26**	**0.16**	**0.41**
Main-Stem	**236**	**0.43**	**0.24**	**0.19**	**0.44**

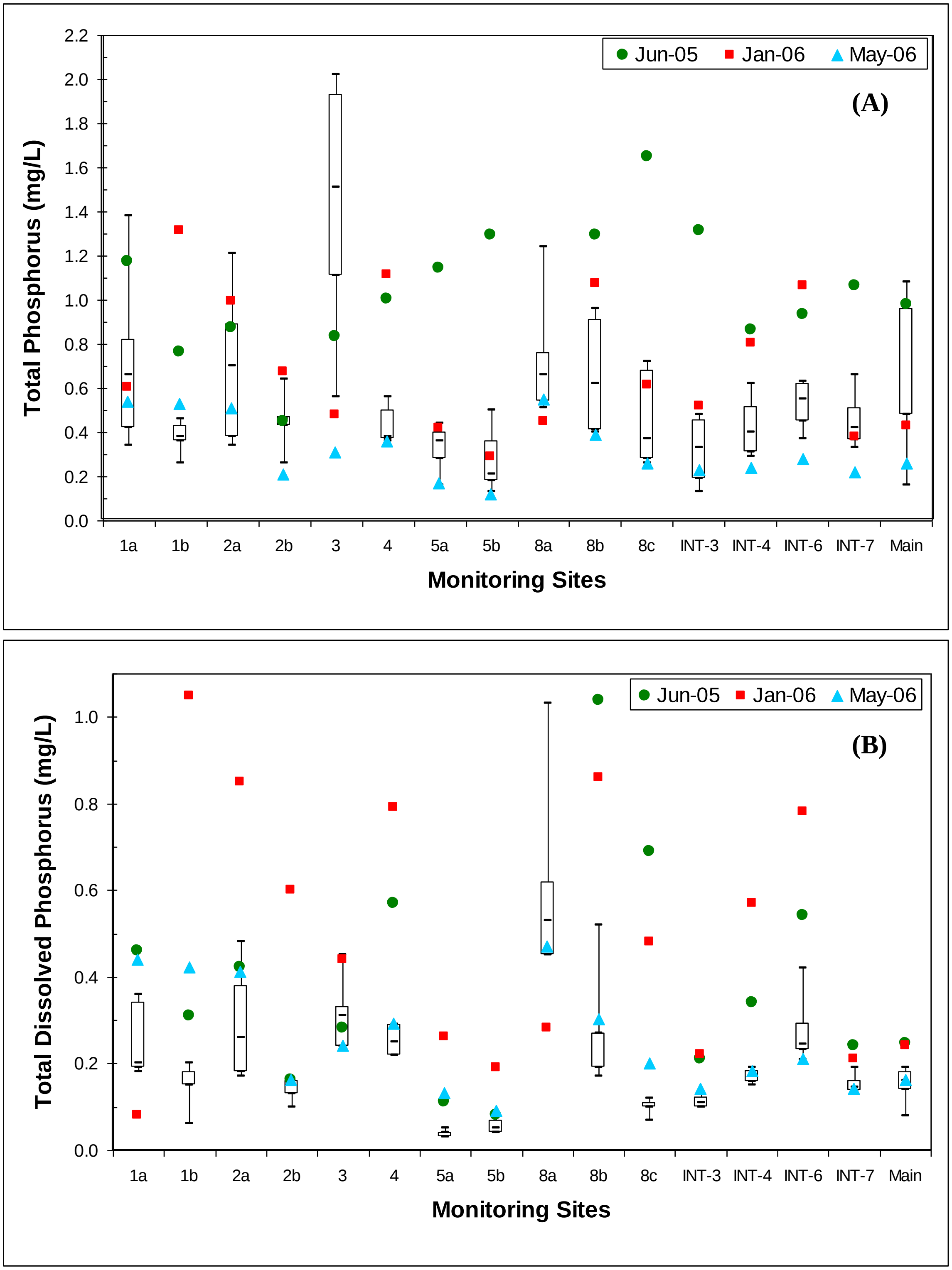

Figure 3.4. Boxplots of (A) TP and (B) DP concentration and (C) DP fraction for source area (1a – 8c), integrator (INT3 – INT-7), and main stem sites in the Apple Creek Watershed in 2004. Boxplots represent the median, 25th and 75th percentiles, minimum, and maximum. Data from the 2005 and two 2006 events are also shown. Note scale change between panels (A) and (B).

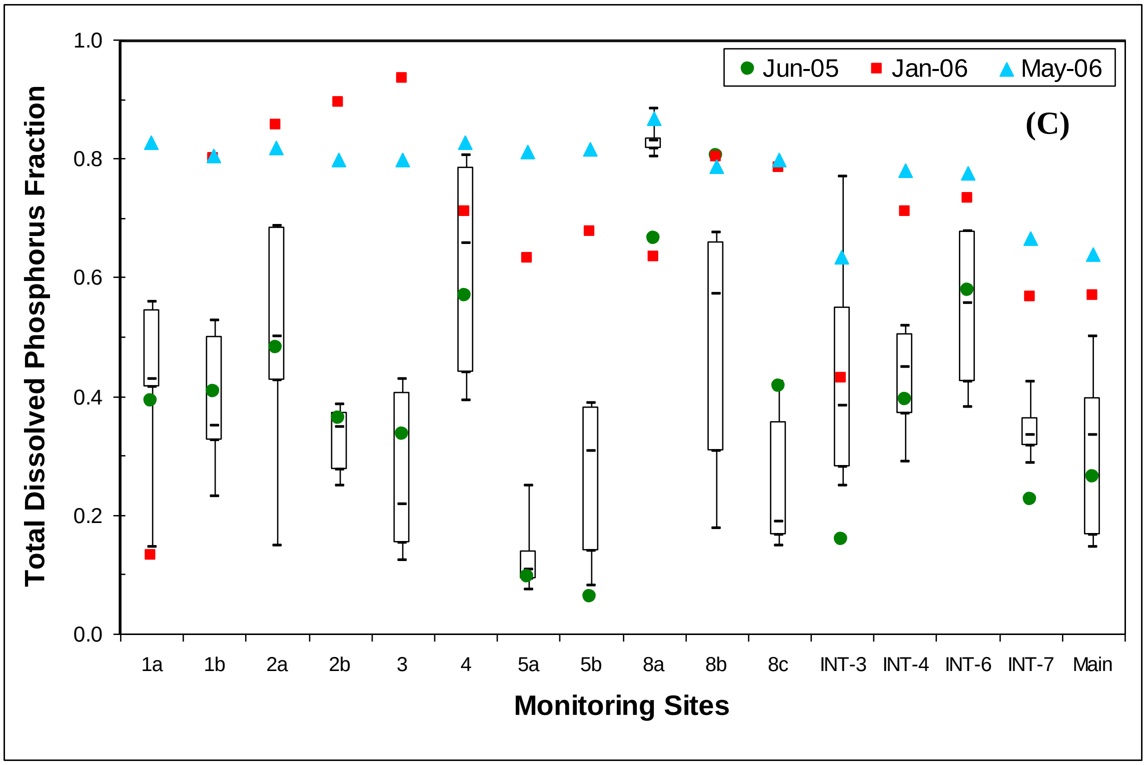

Figure 3.4. Boxplots of (A) TP and (B) DP concentration and (C) DP fraction for source area (1a – 8c), integrator (INT3 – INT-7), and the main stem site in the Apple Creek Watershed in 2004. Boxplots represent the median, 25th and 75th percentiles, minimum, and maximum. Data from the 2005 and two 2006 events are also shown.

Site Comparisons

All Source Areas

There are obvious variations between TP and DP concentrations among the 11 source area sites (Figure 3.4 and Table 3.4). Median TSS, TP, and PP concentrations were two to five times greater at site 3 compared to the other 10 sites. However, the large variation among events (within site) resulted in very few significant differences. Dissolved P at site 3, however, was closer to the average of all sites combined, which reflects high PP.

The concentration of DP was highest at site 8a compared to the other sites and made up approximately 80% of the TP lost.

Nested Source Areas

Eight of the source area watersheds were nested directly upstream and downstream of each other. These sites were 1a and 1b, 2a and 2b, 5a and 5b, and 8b and 8c (Figure 3.1). To determine how water-quality constituents changed along these flow paths we used a Wilcoxon Signed Rank Test. The pooled analysis determined that for all constituents except PP the downstream site had higher concentrations than the upstream site at a 0.05 significance level. This suggests that dilution of water-quality constituent concentrations is not occurring along these flow paths. It is possible that new sources of P become available at downstream sites. This is evident at site 8c, which has a higher area-weighted soil test phosphorus level then the upstream site 8b. The effect of more concentrated flow (e.g. greater erosion potential) on the water-quality constituent concentrations is uncertain and might help explain these results.

Integrator Sites

Determining when peak flow would occur at the integrator sites was much more difficult due to the range of contributing area sizes. Therefore, it should be noted that these samples may not represent peak flow. However, some interesting results were observed from our sample results. Table 3.4 shows that site Int-6 had significantly higher DP concentrations and site Int-3 had significantly lower DP concentrations for the five 2004 events. It has been observed in the field (not quantified) that the North Branch of Apple Creek has a large amount of land that is tile drained. These results are consistent with previous event and low-flow sampling (n = 30) conducted on the North Branch and

South Branch of Apple Creek near the confluence from 1999 to 2002 (P. Baumgart, unpublished data). Median ortho-phosphorus concentrations from the North Branch (0.36 mg/L) were two times greater then the South Branch (0.18 mg/L). The fraction of DP was also greatest in the North Branch (56% vs. 44%). Other researches have found a link between tile-drained fields and DP concentrations in streams (e.g. Gentry et al., 2007).

Integrator site 3 (Int-3) is directly downstream from source area sites 5a and 5b. These sites have two of the three lowest area-weighted soil test phosphorus levels (Figure 3.5) and the lowest median DP concentration (Table 3.4) of all source areas. It should be noted, however, that the contributing area of 5a and 5b make up only a small fraction of the total contributing area for Int-3. The rest of the contributing area consists of mixed landuse with approximately 35% urban, 50% agriculture, and 15% forest and open areas. The contribution of this mixed landuse is unknown.

Area-Weighted Soil Test Phosphorus Analysis

In the previous chapter we attempted to determine environmental factors that control the concentration of PP and DP. It was mentioned that, with watershed in close geographic proximity, it was difficult to distinguish differences among sites and that soil phosphorus content may explain a large portion of the variation in the concentrations. Figure 3.5 represents the relationship between area-weighted soil test phosphorus levels (Bray P1) and DP concentrations for the source area sites. All of the sites, except site 1a, were included in this analysis. Site 1a was taken out of the analysis because we had only a 23% spatial coverage of soil test phosphorus data for this source area. Coverage for the other sites ranged from 40% to 99%.

A strong response of DP to soil test phosphorus levels was detected with a significant relationship ($p < 0.001$) and an R-squared value of 0.83. Site 8a had a unusual influence on the regression, but did not change the significance of the slope. Total P and PP did not show a strong relationship to the soil test phosphorus levels ($r^2 = 0.057$ and 0.002, respectively). Total P and PP concentrations are more closely correlated to TSS concentrations than DP and, therefore, would be dependent on the environmental factors that control erosion processes.

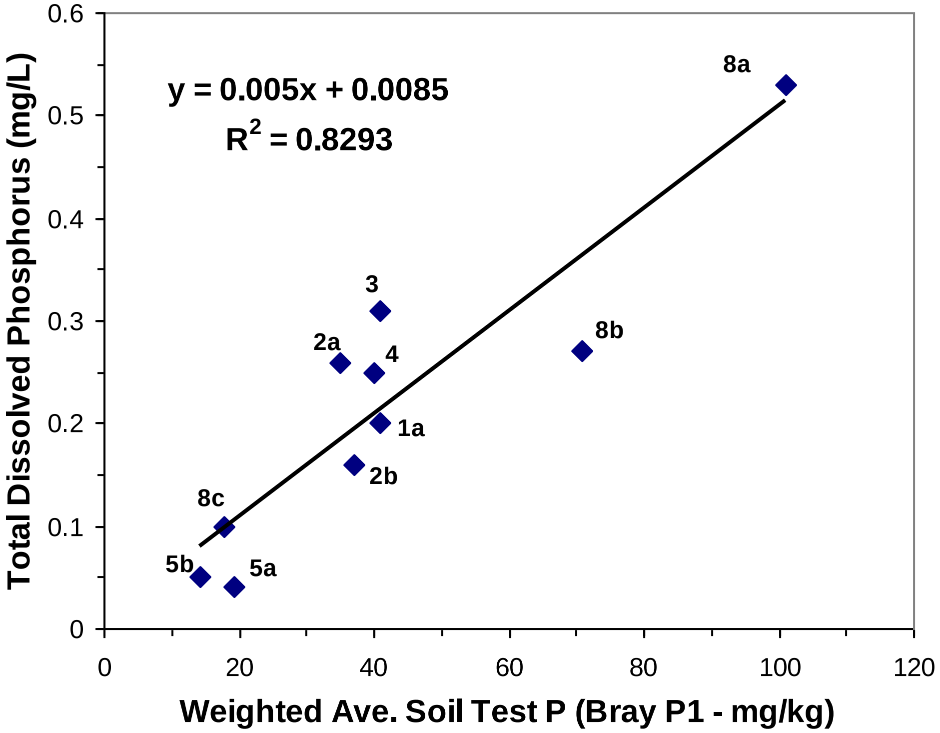

Figure 3.5. Relationship between the area-weighted soil test phosphorus (Bray P1) levels and median DP concentrations from source areas within the Apple Creek Watershed for five events in 2004.

Comparison among Years

Discrete sample concentrations from the 2005 event and the two 2006 events are displayed separately in Figure 3.4. As previously mentioned, the 2005 event was triggered by large, intense precipitation (Table 3.3). As can be seen in Figure 3.4, TP concentrations for nearly all sites exceeded the max values from the 2004 monitoring including a TP measurement at site 8b of 8.26 mg/L and a DP concentration of 2.71 mg/L. Site 3 was the only site with a lower value. In 2005, site 3 was covered nearly 100% by alfalfa, which could explain the lower concentration of TP. Across the various sites, the January 2006 event, which occurred on frozen ground, had TP concentrations both above and below the median. However, DP concentrations were consistently higher at all but two sites than the 2004 event samples. Winter spreading of manure may be responsible for the high levels of DP. The May 2006 event was a small, low-intensity storm. The concentration of TP was below 2004 median concentrations at all sites except for 1b. However, DP concentrations more closely followed the 2004 median concentrations and higher DP fractions at all sites.

Conclusion

Knowledge of P forms at the multi-field scale can help determine the most effective management strategies for reducing non-point P pollution in the LFRS-B. The concentration of DP makes up a large portion of the TP at tributary sites within the LFRS-B and at source areas within the Apple Creek Watershed. Results from source area water-quality monitoring show that the concentrations of TSS, TP, PP, and DP and the fraction of DP did not significantly change from source area watersheds to the main stem.

Observed water-quality measurements were highly variable among source areas in the Apple Creek Watershed. Median TSS and TP concentrations varied by a factor of seven and median DP concentration varied by as much as a factor of 10. Critical source areas exist within the watershed and knowledge about their locations would be beneficial to targeting of improved management practices. The proportion of DP was also highly variable between source areas and sampling events. We observed very high DP proportions during a winter runoff event and during a low intensity storm in 2006.

The concentration of DP in runoff had a strong linear response to the area-weighted soil test P levels that ranged from 14 mg/kg to 101 mg/kg in source area watersheds. These results were consistent with what other researches have found (Sharpley et al., 1994; Daniel et al., 1994; Pote et al., 1999; Andraski and Bundy, 2003). The regression coefficient (0.005) was intermediate to the coefficients (0.012 for clay loam plots and 0.0024 for silt loam plots) reported by Andraski and Bundy (2003) in their simulated rain study on small plots. Therefore, the relationship between the concentration of DP in runoff and soil test P may be different between watersheds. However, these results agree with other studies that indicate that lowering soil test phosphorus levels from critical source-areas within a watershed could significantly reduce non-point source DP losses. Controlling losses of TP through sediment reduction strategies is important for meeting water-quality objectives but might not be enough. A holistic approach to management strategies, which incorporate strategies to reduce DP losses, should be considered. Therefore, it is important to consider the benefits of nutrient management planning to reduce DP losses when considering watershed management strategies for the LFRS-B and other managed watersheds.

CHAPTER 4 – IMPLEMENTATION OF WISCONSIN PHOSPHORUS INDEX TO MULTI-FIELD WATERSHEDS

Introduction

The phosphorus index (P-index) system was developed by the United States Department of Agriculture Natural Resource Conservation Service (USDA NRCS) as part of a joint strategy between the USDA and United States Environmental Protection Agency to use a P-index to limit P applications on fields at greatest risk of P loss (Sharpley et al., 2003). Recently, the NRCS changed their nutrient management standards (590) from N-based to P-based. Under the new NRCS 590 standard, each state's NRCS state conservationists can choose between three P-based approaches to nutrient management planning policy. The three approaches are base on agronomic soil test P recommendations, environmental soil test P thresholds, or a P-index to rank fields according to their vulnerability to P loss (Sharpley et al., 2003). Of the three approaches, the P-index has been the most widely implemented with 47 states adopting some form of the P-index (Torbert et al., 2005).

The P-index is based on a field system in which all land available for manure applications do not have the same potential for nutrient loss (Gburek and Sharpley, 1998; Sharpley and Tunney, 2000). The use of integrated software tools such as the Snap-Plus software program developed by the UW-Extension (2007), that combines conservation planning (RUSLE2), nutrient management (NRCS 590 P based), record keeping (NMP), and manure and feed management into a single program are being widely adopted (Pearson et al., 2004, Good and Bundy 2005). Snap-Plus includes the Wisconsin

Phosphorus Index (WI-PI) tool to rank fields based on their potential to deliver P to surface water bodies (Good and Bundy, 2005).

The Wisconsin Phosphorus-Index (Snap-PLUS)

The WI-PI is modeled after the Iowa P-Index (NRCS IOWA, 2001) and considers both particulate and dissolved P sources, acute losses under frozen and unfrozen conditions, and transport factors. It incorporates a simplified modeling approach to calculate a gross estimate of P losses in lb/acre/year from a particular field (Good, 2004). Snap-Plus calculates P-indices for each of the three major P losses: particulate, soluble, and acute (single event) (Figure 4.1). Therefore, the total risk index for P is calculated by summing up the particulate and soluble P losses for the edge-of-field and the acute P losses from surface application of manure and fertilizer and multiplying by a P delivery ratio. The particulate P-index is calculated by multiplying the annual sediment delivery to edge of field times the P concentration in bulk soil times the sediment P enrichment ratio. The sediment delivery to edge of field is calculated using the latest version of the Universal Soil Loss Equation, RUSLE2 (USDA-ARS, 2004). Sediment P concentration is estimated using routine soil test P and soil organic matter. The soluble P-index equation incorporates an estimate of the annual field runoff volume and soil soluble P concentration multiplied by an extraction efficiency factor. The soil soluble P concentration is based on adjustments to soil test P (Bray-P1) and a P stratification factor for specific sub-soil fertility groups and runoff extraction efficiencies. For calculation of the acute loss P-index a worst-case runoff event approach, instead of the average annual used for calculating particulate and soluble P losses, is used to estimate the potential loss of P from a field from surface P applications. The acute P-index is calculated for losses of fertilizer and manure from non-frozen ground and losses of manure on frozen ground. The three P loss indices are first added together and then the P delivery ratio is factored in. The P delivery ratio is determined by the dominate soil slope and the length of the flowpath from the edge-of-field to the receiving waters. It ranges from 1.0 (< 250 ft. flow path) to 0.45 (>20,000 ft. flowpath; < 2% slope).

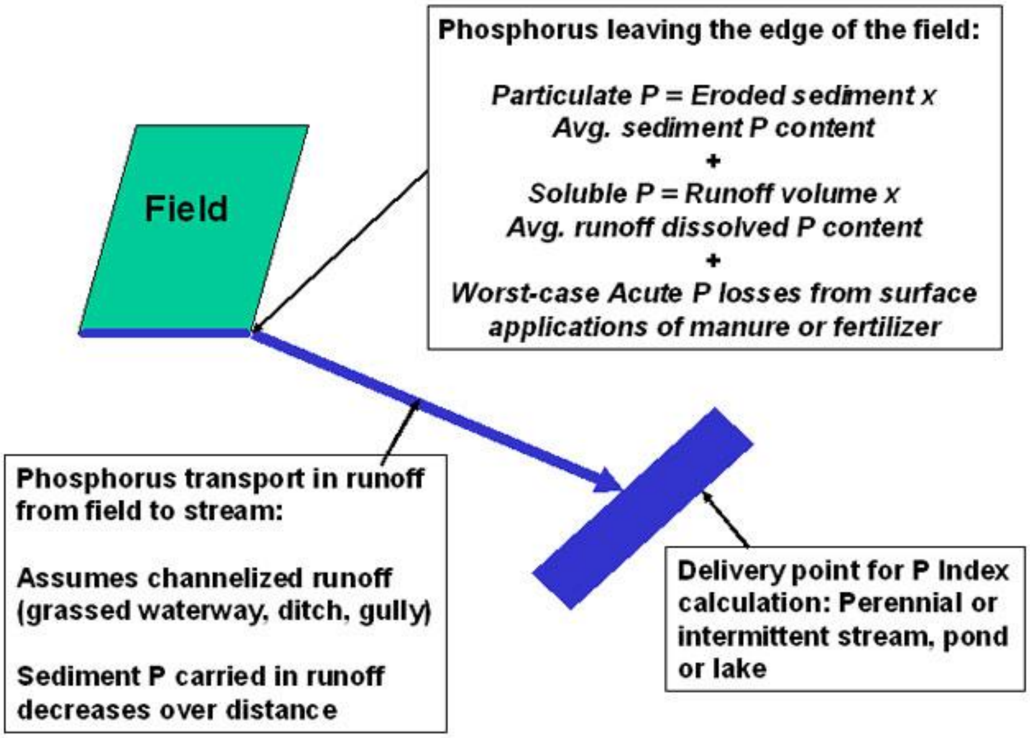

Figure 4.1. Schematic representation of pathways for P movement from field to surface water assumed for P-Index calculations (Bundy and Good, 2007).

At the field scale, Good and Bundy (2005) applied the WI-PI to 18 monitored fields or catchments ranging in size from 0.0002 to 0.16 km^2. They found a strong relationship between the WI-PI edge-of-field P loss estimates and the measured runoff P loss ($r^2 = 0.79$). Other researchers have begun evaluating P indices at the watershed scale (Johansson and Randall, 2003; Schendel et al., 2004; Salvano and Flaten, 2006).

Wisconsin state administrative rules concerning animal feeding operations (permitted farms) regulate on-farm nutrient management. Farm managers are required to manage soil P to levels less than 50 mg/kg soil test P or a 4-year rotational average WI-PI value of six or less (USDA NRCS-WI, 2005; WDNR, 2007). The objective of the WI-PI is to limit P applications to high-risk fields. Meeting the criteria of the WI-PI does not necessarily mean that P-related, water quality -objectives will be met (Figure 4.2). A watershed yield value and corresponding P-index value to meet water-quality objectives might be lower than those from watersheds that meet the WI-NRCS 590 standards (USDA NRCS-WI, 2005). The linkage between the receiving water body and a statewide P-Index model is likely to be specific to an eco-region and perhaps applicable to a limited range of management practices. It is important to better understand this link for effective watershed management and nutrient management planning.

In this chapter we compare the various types of P loss predicted by the WI-PI to P forms measured in surface water from multi-field source areas in the Apple Creek Watershed. We also assess information needs and implementation considerations to application of the WI-PI at the multi-field watershed scale.

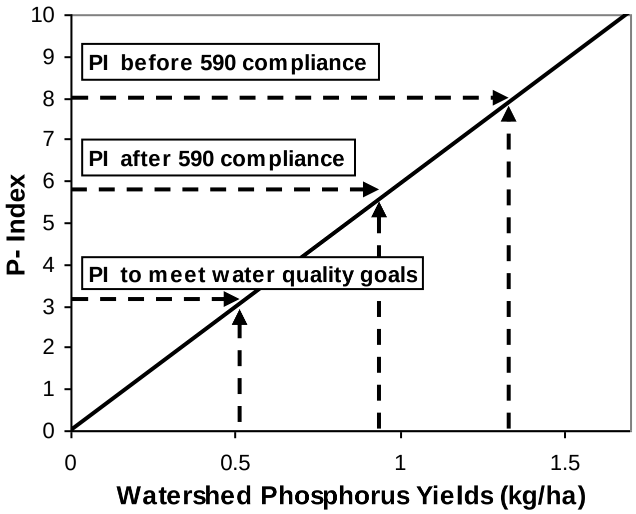

Figure 4.2. Hypothetical P-Index and corresponding average annual watershed phosphorus yield relationship.

Methods

The WI-PI is designed to operate on a farm-field basis. That is, users input geomorphic and agronomic factors about a field for a specified crop rotation and yearly, as well as rotationally average particulate, dissolved, and acute P loss indices are calculated for that particular field. For our study, we combined output from multiple fields within source area watersheds (see Chapter 3) by calculating area-weighted P-index values using Snap-Plus (UW-Extension, 2007, version 1.121.42) and compared them to water-quality results from surface runoff monitoring.

SNAP-Plus Inputs

To fully examine the predictive ability of Snap-Plus on the LFRS-B tributaries, accurate input data are required. Input data for Snap-Plus includes field size, dominate soil type, field slope and length, below field slope to water, distance to water, soil test P, nutrient applications, crop type, yield goals, and tillage practices. To gather the most accurate data, nutrient management plans were obtained from the Wisconsin Department of Natural Resources and the Outagamie Land Conservation Department. Additional information was gathered from crop consultants and co-ops. We were not able to collect this data for all of the fields within each source area watershed. The percent coverage of field information within the source areas ranged from 22% to 85%. Source areas with more than 50% coverage were assumed to have data representative of the entire source area.

Area-Weighted Phosphorus Index Values

For watersheds with representative information, area-weighted P-Index values were calculated and compared to water-quality measurements (see Chapter 3). Snap-Plus generates a total, particulate, soluble, and acute loss (frozen and unfrozen) P-Index for each year of a crop rotation. To calculate the area-weighted P-Index values, the Snap-Plus database was joined to a field layer provided by the Outagamie Land conservation Department in ArcGIS 9 (ESRI, 2005) and the areas of each field were calculated. The areas were used to weight the P-Index values of each field in which management data were available. The fields with missing data were assumed to be represented by the area-weighted average of surrounding fields within the same source area watershed where field management data was available. The area-weighted P-Index values for each source area were compared to TSS, TP, PP, and DP concentrations and the fraction of TP in the dissolved P form measured during five monitored runoff events in 2004.

Statistical Analysis

Regression analysis was performed on the concentration of water-quality constituents to the results of the area-weighted WI-PI values for each source area. The significance of each correlation was determined using the Spearman correlation option for the PROC CORR procedure in SAS 9.1 (SAS Institute Inc., 2003). The Spearman correlation technique was used because of the small sample size and the data being non-normal.

Results and Discussion

Collection of Snap-Plus Input Data

Due to insufficient record keeping and/or lack of soil testing data, we did not obtain complete information for our source area watersheds. The percentage of area in each source area watershed that Snap-Plus was run on is presented in Table 4.1. The percent coverage for source area watersheds ranged from 22% to 85%. Eight out of the 11 source areas had greater than 50% coverage and were used for further analysis with water-quality results.

Table 4.1. Percentage of source area watersheds that field management data was available and Snap-Plus was executed.

Site	Percent Coverage
2b	85%
2a	74%
5b	68%
8a	57%
3	55%
5a	55%
8c	54%
8b	52%
4	38%
1a	27%
1b	22%

Wisconsin Phosphorus Index

We were unable to accurately predict in-stream TP concentrations with the total P-index. Figure 4.3 presents the relationship between the total P-index and the concentration of TP measured in surface runoff. Notice in Figure 4.3 that sites 5a and 5b have among the highest total P-index values. Referring back to Chapter 3, Table 3.4, sites 5a and 5b had the lowest median TP and DP concentrations in 2004. The Nutrient Management Plan obtained for two fields within these watersheds reported that 15,000 and 5,000 gallons of liquid manure per acre were spread in the fall of 2003. Snap-Plus calculated an acute loss P-index of 5.0 for the field that received 15,000 gallons per acre. This was approximately 1/3 of the total P-index. It is possible that monitoring missed these acute losses and that TP concentrations in 2004 did not accurately represent the losses of TP from those sites. It is also possible that manure applications were improperly recorded on those fields or on fields in other source areas. Other then sites 5a and 5b, the median concentration of TP at source areas were represented relatively well by the total P-index.

The relationship between the particulate P-index and the concentration of PP in surface runoff (not shown) was similar to that of the total P-index and TP concentrations. Tillage practices strongly affect the amount of PP predicted by the WI-PI. Tillage practices are not always reported in Nutrient Management Plans. Therefore, it is possible that more accurate tillage practice records could have strengthened this relationship.

There was a significant ($p = 0.015$) relationship (Spearman correlation = 0.81) between the soluble P-index and the concentration of DP in surface runoff for source areas (Figure 4.4). The calculation of the soluble P-index for a field is dependent on soil test P levels and runoff volume. Therefore, these results were not unexpected given the relationship of the area-weighted soil test P levels and the concentration of DP in surface runoff found in Chapter 3.

Figure 4.5 presents the marginally significant ($p = 0.058$, Spearman correlation = 0.69) relationship between the soluble P-index and the total P-index fraction with the DP fraction measured in surface runoff. The fraction of DP in surface runoff ranged from 11% to 83% and the fraction of soluble P-index to total P-index ranged from 4% to 24%. The total P-index includes the contribution of acute P losses. Acute P losses are calculated based on soluble P in fertilizers and manure and an estimate of the fraction of P loss from fall-applied manure. The acute P-index accounted for 10% to 50% of the area-weighted total P-index. It is likely that a substantial portion of the predicted acute P losses were as soluble P. Although the TP concentration was not predicted well by the total P-index, it appears that Snap-Plus is under representing the fraction of TP in the dissolved form lost in surface runoff.

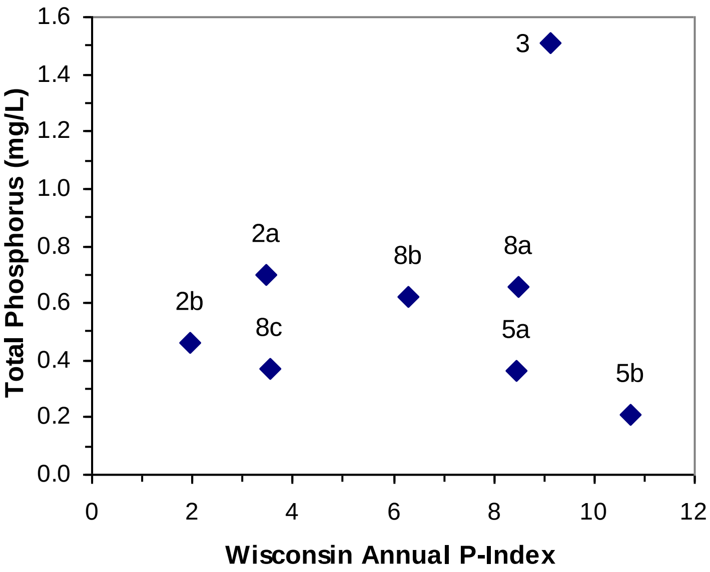

Figure 4.3. The relationship between median TP concentration in runoff and the Wisconsin P-Index for five events in 2004 in the Apple Creek Watershed.

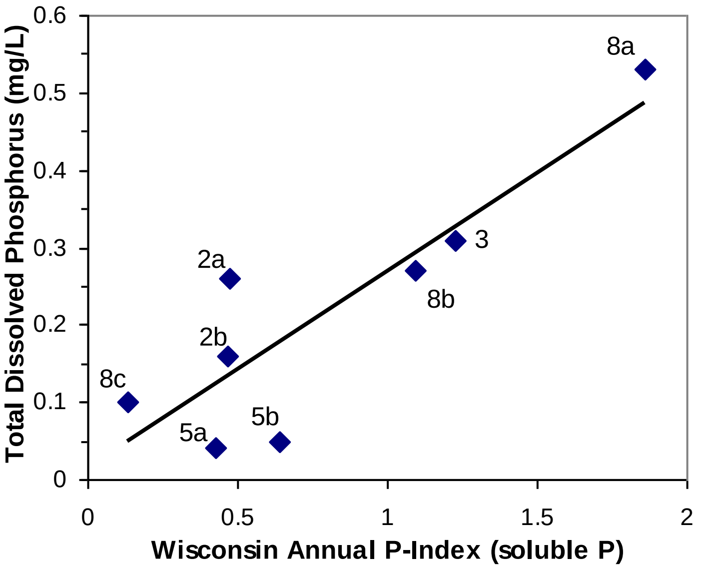

Figure 4.4. The relationship between median DP concentration in runoff and the Wisconsin P-Index (soluble P) for five events in 2004 in the Apple Creek Watershed. Spearman correlation = 0.81.

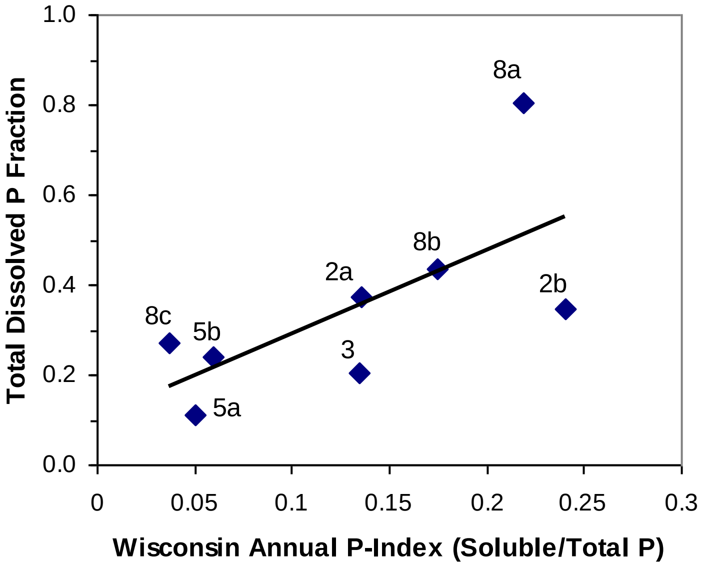

Figure 4.5. The relationship between median DP fraction (DP/TP) in runoff and the ratio of the Wisconsin soluble P-index and total P-Index for five events in 2004 in the Apple Creek Watershed. Spearman correlation = 0.69.

Information Needs and Implementation Considerations

Field operators or crop consultants using Snap-Plus for nutrient management planning will have more accurate field management data than we were able to obtain. It is unknown how comparable nutrient management plans are to actual field management practices. Intentionally, or not, important information (e.g. manure or fertilizer applications) might be missing from nutrient management plans. Inaccurate or missing information could have a significant affect on P-index results. Cabot and Nowak (2005) found that P-index values were more sensitive to discrepancies between planned and actual P management on 210 fields in Wisconsin than soil test P and other field factors. In our study, for example, the field previously mentioned that is located within source areas 5a and 5b had a total P-index value of 14.1. If the manure application is reduced from 15,000 gallons per acre to 5,000 gallons per acre and the tillage practice is changed from fall moldboard plow to fall chisel plow, the total P-index for that field would be reduced to 7.4. It would also reduce the area-weighted P-index values of the source areas from 8.5 to 7.2 at site 5a and from 10.7 to 7.1 at site 5b.

The type of tillage affects the amount of TSS and P lost in surface runoff (Andraski and Bundy, 2003). Information on tillage practices was not always reported in nutrient management plans and was assumed to be moldboard plow. The field slope and below field slope was not determined for each field but was kept as the default of the dominate soil type. It is unsure if more accurate slope information would do much to improve the predictive abilities of the total and particulate P-index. The distance to water may be interpreted in different ways and would have an affect on the transport factors in determining P-index values. The distance to water was determined from stream channels shown on USGS topographic maps and from orthophotographies that show concentrated flow paths. All of our source area sites had intermittent streams that contained flows following a significant precipitation event. Along with intermittent streams, concentrated flow paths within fields will fill up and act like a true stream. Therefore, only fields that were obviously more then 300 feet from an area of concentrated flow were changed from the default of 0 to 300 feet. The most accurate data we obtained was for soil testing results. Most of the nutrient management plans had a copy of the actual soil test report from the laboratory. The accuracy of the soil test results was evident in the relationship found between the concentration of DP in surface runoff and area-weighed soil test P values.

Conclusion

The WI-PI is a useful tool for nutrient management planners and farmers to assess which fields should receive P amendments and which fields should not. It is also important that this tool accurately predicts water-quality impacts of management practices. With information available from mostly nutrient management plans and some from crop consultants, we found a reasonably good relationship between the WI-PI and DP concentrations in runoff from eastern red-clay soils in the Apple Creek Watershed. However, the relationship between WI-PI values and observed runoff TP and PP concentrations and the fraction of TP in the dissolved form was poor. The relationship between water quality and the total and particulate P-index may be strengthened if more complete and accurate field management data could be obtained.

CHAPTER 5 – PROJECT SUMMARY

This project was initiated to further investigate the impacts of agriculture on water quality within the Lower Fox River Sub-Basin (LFRS-B). The Lower Fox River and many of its tributaries have been ranked as priority watersheds or 303d listed by the Wisconsin Department of Natural Resources and the Lower Bay of Green Bay has reduced water clarity from algae and total suspended solids (TSS) (Harris, 1993; Millard and Sager, 1994; WDNR, 1993). More than 40% of the TSS and total phosphorus (TP) lost from the LFRS-B is from agricultural operations (Baumgart, 2005a). The LFRS-B tributaries are also characterized by high dissolved phosphorus (DP) concentrations and fractions of TP.

Through a partnership with the Lower Fox River Watershed Monitoring Program at UW-Green Bay and the United States Geological Survey (USGS) four monitoring stations were installed on Lower Fox River tributaries in 2003. Concentrations and loads of TSS, TP and DP along with continuous flows were measured and analyzed for each of the tributary watersheds. To better understand DP sources and concentrations in LFRS-B tributaries a study of multi-field source areas was performed in the Apple Creek Watershed. The objectives of this study were to determine the variability of contributing source areas and to determining how P forms changed at different spatial scales. Comparisons among small source area sub-watersheds show how land management practices can affect the concentrations of water quality constituents. Land management and environmental characteristics were compared using the Wisconsin Phosphorus Index Tool (Snap-Plus). Area weighted Phosphorus Index values were compared to water quality measurements from event sampling from source area sites.

Summary of Project Results

As part of the Lower Fox River Watershed Monitoring Project water quality and quantity information was gathered at four LFRS-B tributary watersheds for three water years starting in October of 2004. Significant variation in precipitation events occurred among the three water years. The 2004 water year was characterized by heavy spring rains followed by a period of summer drought. Despite heavy rainfalls in May and June, the total annual rainfall amount was only slightly more than the average annual precipitation for Green Bay, WI. The 2005 and 2006 water years received total precipitation amounts only slightly less then the annual average. However, rainfall was more evenly distributed throughout the 2005 and 2006 water years resulting in few runoff events.

Lower Fox River Sub-Basin Tributary Monitoring

Three years of event-flow and low-flow water quality and quantity monitoring on the four LFRS-B tributaries was summarized and analyzed. This research furthered the understanding of suspended solids and P dynamics within the LFRS-B. The above average precipitation in May and June of 2004 resulted in more than double the total loads of TSS and TP compared to the following 2 years. Total annual precipitation was not much different among years, however, the timing (before establishment of crop cover) and intensity of the 2004 events caused significant differences among water quality constituent concentrations and yields. Seasonal effects (non-winter vs. winter) significantly changed the concentrations of TSS, TP, PP, and DP. Analyzing season and flow regimes separately allowed comparisons to be made among tributary watersheds. It was determined that during event flows in the non-winter period, that Ashwaubenon Creek had significantly larger TP and DP concentrations and Duck Creek had significantly lower TP and DP concentrations.

Linear regressions were used to compare the concentrations of TSS, TP, DP and discharge. Total P was significantly correlated to DP at all 4 tributaries across all seasonal and flow conditions. Regression coefficients among sites did not significantly differ, allowing us to combine data for all sites to produce an overall equation for predicting DP concentration in the LFRS-B using only TP as the independent variable. Combining data across climate and flow conditions, significant correlations between TSS and DP were found, however, only a small portion of the variation in the DP concentration was explained. It was determined that TSS by itself was a poor determinate of the DP concentration.

Constituent loads differed significantly between 2004 and the following two years. In 2004, total suspended solids, TP, and DP were more than 50% greater than water years 2005 and 2006. Also, the fraction of DP load was lower at all sites in 2004 compared to 2005 and 2006. This is likely a result of high particulate P losses and adsorption of DP onto suspended solids (Sharpley et al., 1981, 2001).

The last part of the tributary analysis compared watershed characteristics with total annual concentrations (total annual load/total annual flow) of TP, PP, and DP. Because of the close geographic proximity, only small differences among sites were distinguishable. Significant correlations across all years were found between soil and basin slope and the concentration of TP and DP and between the soil silt and clay content and the concentration of TP and DP. On an area-weighted basis, soils in the Duck Creek watershed contained the least amount of clay (14%). The lower clay content corresponded well with the lower median TSS, TP, and DP concentrations in steam water in Duck Creek compared to the other watersheds. Marginally significant correlations were found between the percent of forage crops and the concentrations of TP and DP. However, more precise data for these watersheds is needed to confirm any of these preliminary determinations.

Phosphorus Forms Spatial Scale Analysis

To determine how P forms change along a flow path, a study was conducted in one of the LFR tributaries (Apple Creek). Event grab samples were collected at multi-field source-areas and integrator sites along with automatic event sampling at the main stem site between 2004 and 2006. Water year 2004 produced 5 runoff events that were relatively uniform and produced sufficient runoff at the source area sites. Only 1 event was monitored in water year 2005 and 2 events in 2006. The size of the source area watersheds (0.2 to 2.2 km^2) meant that changes in land management each year could significantly affect in-stream concentrations of water quality constituents. Therefore, much of the analysis in this section was performed on the 5 events from 2004.

It was determined that the median concentration of TSS, TP, PP, and DP and the DP fraction did not significantly change along the flow path from the source-areas to the main stem. Therefore, the perennial stream scale tributary monitoring approach was representative of what was leaving the edge of the fields in surface runoff. However, there was significant differences found among source-areas; indicating that there are critical areas within the watershed contributing more TSS and P than others. We were unable to use the environmental characteristics from Chapter 2 of this thesis to explain the variation among source-areas because of the size and close geographic proximity of the source-areas. However, we were able to obtain finer scale characteristics that did explain some of the differences. In particular for Chapter 3, we were able to gather soil test P results for fields within our source-areas, allowing us to calculate an area-weighted soil test P values for each source-area. Area-weighted soil test P values varied from 14.2 mg/kg to 101 mg/kg within the multi-field source areas. There was a strong positive relationship ($r^2 = 0.83$) between the area-weighted soil test P values and the concentration of DP measured in surface waters leaving source areas.

Assessment of the Wisconsin Phosphorus Index on Multi-Field Watersheds

A simple tool to rank fields based on their risk of contributing P to nearby streams can help managers determine how each of their fields should be managed. The Wisconsin P-Index (WI-PI) can be used by field operators or consultants to understand the risk of their fields for P losses. Simple management decisions can be made that reduce the losses of P from their high risk fields. To improve our understanding of the relationship between field management practices and runoff water quality, the WI-PI was assessed at the multi-field scale on eastern red clay soils in the Apple Creek Watershed. Inputs for the WI-PI (Snap-Plus) were gathered from nutrient management plans and crop consultants. Total, particulate, soluble, and acute P-indices were calculated for each field within the multi-field sub-watersheds. Area-weighted P-indices were calculated using a geographical information system and were used to compare to water quality monitoring of surface runoff.

Given the available input data, we concluded from our study that the WI-PI could be used to obtain a good estimate of DP losses in runoff from eastern red clay soils of northeastern Wisconsin. However, we did not find a good relationship between WI-PI predicted TP and PP losses and stream concentrations. It is important that our results be verified because of the uncertainty of the accuracy of the nutrient management plans obtained and because the non-normal precipitation pattern of the events monitored during the study period. Although the WI-PI predicted DP losses well, it under predicted the fraction of TP lost in the soluble form.

Policy Implications for Land Management

Non-point source losses of suspended solids and P from agricultural operations are regulated by relatively new laws that are continuously changing. The best available information is being incorporated into new regulations as new findings suggest better management techniques. In Wisconsin, non-point source runoff from agricultural operations is regulated by the Wisconsin Runoff Rules written by the Wisconsin Department of Natural Resources and the Wisconsin Department of Agriculture, Trade, and Consumer Protection. The Wisconsin Runoff Rules include four sections that pertain to non-point source runoff from agricultural operations. They are NR 243 (Animal Feeding Operations), NR 151 (Runoff Management), NR 154 (Best Management Practices and Cost-Share Conditions), and ATCP 50. ATCP 50 establishes standards for nutrient management plans and cost-sharing to help implement the programs (WDATCP, 2006).

Under ATCP 50, subsection 2, it states that any landowner engaged in agricultural activities in Wisconsin must implement conservation planning, which includes a nutrient management plan. A nutrient management plan applies to every field to which a farmer mechanically applies nutrients. The plan must be prepared or approved by a qualified planner under ATCP 50.48 and must be based on a soil nutrient test conducted by a certified laboratory. The plan cannot recommend nutrient applications that exceed the amounts required to achieve applicable crop fertility levels recommended by the University of Wisconsin-Extension. The plan must also comply with the NRCS technical guide nutrient management standard 590 (Code 590). The P-based Nutrient Management Standard 590 contains criteria for surface and groundwater protection that manages the amount and timing of all nutrient sources. Annual P and K application are not to exceed the total nutrient recommendation for the rotation except when manure is applied using either the Wisconsin Phosphorus Index (WI-PI), or soil test phosphorus management. Farm managers are required to manage soil P to levels less than 50 mg/kg soil test P or a 4-year rotational average WI-PI value of 6 or less (USDA NRCS-WI, 2005; WDNR, 2007).

Implications of Research

To meet water quality objectives in the Bay of Green Bay, non-point source suspended sediment and P must be reduced from agricultural operations. It has been determined that P in the dissolved form leaving source areas makes up a large portion of the TP losses. Less research on management practices to control DP is available compared to sediment bound P. Controlling sediment bound P is done by implementing physical structures that reduce sediment losses through filtration. However, the effectiveness of these practices on concentrations of DP is not well understood. It is presumed that other than increasing infiltration, physical control measures to reduce suspended sediment and sediment bound P will have little impact on DP losses in surface runoff. Therefore, it is important when considering non-point source P management strategies and policies, to understand the dynamics of P in surface runoff. When DP makes up a large portion of the total P, it may be essential to incorporate strategies to reduce DP losses into management strategies that aim to meet water quality objectives.

Fewer strategies exist for controlling DP losses then sediment bound P. A strong linear response of soil test P levels to DP levels in surface runoff has been determined (see Chapter 3, Figure 3.5; Andraski and Bundy, 2003). Therefore, controlling manure and fertilizer application through nutrient management planning may be the most effective strategy for controlling the DP losses in surface runoff. However, controlling DP alone will most likely not be enough to meet water quality objectives. A combined strategy that reduces suspended sediment losses and lowers P levels in the field will be the most effective strategy for controlling non-point source sediment and P pollution.

Policy will play an important role in increasing water quality in the Bay of Green Bay and the Lower Fox River. At this time, a joint effort is under way by the U.S. Environmental Protection Agency, the Wisconsin Department of Natural Resources, the University of Wisconsin-Green Bay, and others to develop a Total Maximum Daily Load (TMDL) watershed plan which if followed will reduce suspended solids and P loads to the Lower Bay of Green Bay. Monitoring results from this project will help determine the sources of allowable loads of suspended solids and P into the Bay and provide baseline conditions before implementation of the TMDL.

Future Research Opportunities for Phosphorus Forms

Continuing water quality monitoring will be essential to determine the effects of management strategies (e.g. TMDL) within the LFRS-B. The amount of TSS and P lost from contributing watersheds is fairly well understood. However, factors that affect the concentrations and loads of these constituents among tributaries are less well understood. Accurate data about environmental factors and field management within these watersheds could help explain the variability among tributaries and among source areas within the Apple Creek Watershed. Factors affecting concentrations and loads of DP within the LFRS-B are complex and strategies for reducing DP could benefit from further research. The WI-PI can be used to predict DP losses from multi-field watersheds. However, it's usefulness in predicting TP and PP losses are more uncertain. The ability of the WI-PI tool to be used to predict TP losses on the eastern red clay soils could be improved by confirming results from chapter 4 of this study. A sensitivity analysis could be done to determine which Snap-Plus inputs affect the concentration of P forms in surface runoff the most in these types of soils. Snap-Plus is a useful tool for predicting high risk fields with respect to P loss within a watershed, and its predictive abilities need to be confirmed throughout the different regions in the state of Wisconsin.

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APPENDIX A: ENVIRONMENTAL CHARACTERISTICS DETAILS

A.1. Watershed environmental characteristic values used in correlation analysis.

Environmental Characteristic	Apple Creek	Ashwaubenon Creek	Baird Creek	Duck Creek
Urban Development	27.5%	11.2%	7.2%	8.0%
Row Crops	40.7%	48.7%	40.8%	43.0%
Forage Crops	21.2%	28.9%	25.1%	24.1%
Total Agriculture	61.9%	77.6%	65.9%	67.1%
Forest	6.0%	8.7%	12.6%	12.3%
Wetlands	1.4%	0.5%	10.0%	8.4%
Soil Slope	3.5%	2.4%	3.4%	3.5%
Soil Silt Content	46.6%	48.2%	47.6%	46.5%
Soil Clay Content	25.3%	25.9%	19.0%	14.3%
Basin Slope	1.5%	1.0%	1.2%	1.7%
Total P – annual load/annual flow (mg/L)				
2004	0.59	0.73	0.64	0.38
2005	0.40	0.73	0.47	0.40
2006	0.35	0.52	0.42	0.27
2004-2006	0.49	0.69	0.56	0.37
Particulate P – annual load/annual flow (mg/L)				
2004	0.38	0.43	0.31	0.20
2005	0.18	0.35	0.19	0.20
2006	0.18	0.21	0.17	0.12
2004-2006	0.29	0.36	0.25	0.19
Dissolved P – annual load/annual flow (mg/L)				
2004	0.21	0.31	0.33	0.17
2005	0.23	0.37	0.28	0.20
2006	0.17	0.31	0.25	0.15
2004-2006	0.21	0.32	0.30	0.18

APPENDIX B: APPLE CREEK SAMPLING EVENTS

B.1 Details of multi-field, integrator, and main stem sampling in the Apple Creek watershed for 8 precipitation events from 2004 to 2006.

Event 1 – 3/28/2004

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	7:00 PM	32.50	1244	1.38	0.20	1.18
1b	6:51 PM	14.25	-	-	-	-
2a	7:25 PM	56.25	284	0.89	0.38	0.51
2b	7:40 PM	18.50	71	0.26	0.10	0.16
3	7:55 PM	25.50	1544	2.02	0.31	1.71
4	6:13 PM	22.88	58	0.37	0.29	0.08
5a	5:40 PM	26.75	408	0.40	0.03	0.37
5b	5:30 PM	16.63	92	0.21	0.08	0.13
8a	6:02 PM	29.00	116	0.66	0.53	0.13
8b	5:57 PM	21.25	326	0.91	0.52	0.39
8c	5:50 PM	10.13	488	0.37	0.07	0.30
Int-3	-	-	-	-	-	-
Int-4	-	-	-	-	-	-
Int-6	-	-	-	-	-	-
Int-7	-	-	-	-	-	-
Main Stem	-	-	504	0.69	0.21	0.48

Event 2 – 5/14/2004

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	2:40 PM	32.50	62	0.34	0.19	0.15
1b	2:30 PM	32.00	74	0.36	0.18	0.18
2a	2:08 PM	59.75	45	0.38	0.26	0.12
2b	2:00 PM	15.00	74	0.43	0.16	0.27
3	2:25 PM	27.00	318	1.11	0.45	0.66
4	3:20 PM	26.50	20	0.36	0.29	0.07
5a	4:30 PM	20.50	69	0.16	0.04	0.12
5b	3:45 PM	17.75	25	0.13	0.04	0.09
8a	4:15 PM	28.50	17	0.51	0.45	0.06
8b	4:20 PM	24.63	37	0.41	0.27	0.14
8c	4:05 PM	12.00	65	0.26	0.11	0.15
Int-3	4:35 PM	130.50	56	0.21	0.10	0.11
Int-4	4:55 PM	101.50	64	0.29	0.15	0.14
Int-6	5:55 PM	105.00	49	0.37	0.25	0.12
Int-7	5:25 PM	172.00	107	0.33	0.14	0.19
Main Stem	-	-	72	0.14	0.08	0.06

Event 3 – 5/21/2004

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	8:17 PM	31.25	168	0.42	0.18	0.24
1b	8:07 PM	29.00	138	0.43	0.15	0.28
2a	7:56 PM	54.25	66	0.34	0.17	0.17
2b	7:50 PM	14.25	118	0.47	0.13	0.34
3	7:40 PM	24.38	704	1.51	0.33	1.18
4	7:30 PM	24.88	41	0.38	0.25	0.13
5a	7:00 PM	25.75	168	0.28	0.03	0.25
5b	6:50 PM	17.50	36	0.18	0.07	0.11
8a	7:19 PM	28.75	32	0.54	0.45	0.09
8b	7:13 PM	30.00	32	0.40	0.27	0.13
8c	7:05 PM	12.50	93	0.28	0.10	0.18
Int-3	9:25 PM	137.25	91	0.13	0.10	0.03
Int-4	9:42 PM	105.00	61	0.32	0.16	0.16
Int-6	8:42 PM	105.50	96	0.62	0.42	0.20
Int-7	8:58 PM	191.38	166	0.38	0.13	0.25
Main Stem	-		152	0.40	0.20	0.20

Event 4 – 5/23/2004

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	12:00 PM	20.50	352	0.82	0.34	0.48
1b	11:55 AM	26.75	248	0.46	0.15	0.31
2a	11:35 AM	45.00	884	1.21	0.18	1.03
2b	11:30 AM	9.50	340	0.64	0.16	0.48
3	11:45 AM	17.38	1,570	1.93	0.24	1.69
4	11:10 AM	18.00	198	0.50	0.22	0.28
5a	10:45 AM	20.75	464	0.44	0.04	0.40
5b	10:40 AM	11.88	524	0.50	0.04	0.46
8a	11:00 AM	23.75	160	1.24	1.03	0.21
8b	10:55 AM	12.38	740	0.96	0.17	0.79
8c	10:50 AM	0.00	588	0.68	0.10	0.58
Int-3	3:05 PM	69.00	232	0.45	0.13	0.32
Int-4	3:15 PM	81.25	352	0.62	0.18	0.44
Int-6	3:45 PM	79.75	274	0.63	0.24	0.39
Int-7	4:05 PM	133.25	424	0.66	0.19	0.47
Main Stem	-	-	672	0.51	0.11	0.40

Event 5 – 6/11/2004

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	10:15 AM	25.00	150	0.66	0.36	0.30
1b	10:20 AM	26.50	86	0.38	0.20	0.18
2a	10:10 AM	54.00	100	0.70	0.48	0.22
2b	10:05 AM	17.25	132	0.46	0.16	0.30
3	10:30 AM	26.00	200	0.56	0.24	0.32
4	9:55 AM	19.75	136	0.56	0.22	0.34
5a	9:35 AM	23.00	252	0.36	0.05	0.31
5b	9:30 AM	13.00	292	0.36	0.05	0.31
8a	9:50 AM	24.00	98	0.76	0.62	0.14
8b	9:45 AM	10.00	328	0.62	0.19	0.43
8c	9:40 AM	2.50	320	0.72	0.12	0.60
Int-3	11:20 AM	71.00	248	0.48	0.12	0.36
Int-4	10:45 AM	81.00	240	0.48	0.19	0.29
Int-6	11:50 AM	89.50	164	0.48	0.21	0.27
Int-7	12:10 PM	161.00	290	0.46	0.15	0.31
Main Stem	-	-	236	0.43	0.19	0.24

Event 6 – 6/13/2005

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	8:10 PM	13.75	508	1.17	0.46	0.71
1b	8:05 PM	15.00	312	0.76	0.31	0.45
2a	7:50 PM	51.75	252	0.87	0.42	0.45
2b	7:45 PM	20.50	138	0.44	0.16	0.28
3	7:40 PM	29.00	428	0.83	0.28	0.55
4	7:30 PM	27.50	286	1.00	0.57	0.43
5a	7:20 PM	23.25	1,300	1.14	0.11	1.03
5b	6:55 PM	13.75	1,590	1.29	0.08	1.21
8a	7:15 PM	23.50	1,070	8.26	5.51	2.75
8b	7:10 PM	26.00	620	1.29	1.04	0.25
8c	7:00 PM	3.75	1,000	1.65	0.69	0.96
Int-3	8:55 PM	90.50	1,180	1.31	0.21	1.10
Int-4	8:25 PM	93.75	504	0.86	0.34	0.52
Int-6	9:15 PM	104.63	208	0.93	0.54	0.39
Int-7	9:30 PM	171.00	684	1.06	0.24	0.82
Main Stem	-	-	533	0.84	0.25	0.59

Event 7 – 1/29/2006

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	1:05 PM	31.50	84	0.60	0.48	0.12
1b	1:15 PM	30.50	76	1.31	1.05	0.26
2a	1:00 PM	53.50	19	0.99	0.85	0.14
2b	12:50 PM	16.25	7	0.67	0.60	0.07
3	12:45 PM	31.25	3	0.47	0.44	0.03
4	12:40 PM	26.50	59	1.11	0.79	0.32
5a	12:20 PM	28.00	23	0.41	0.26	0.15
5b	12:15 PM	20.50	10	0.28	0.19	0.09
8a	12:25 PM	29.25	73	0.44	0.28	0.16
8b	12:30 PM	23.50	22	1.07	0.86	0.21
8c	12:10 PM	15.00	19	0.61	0.48	0.13
Int-3	1:35 PM	116.00	194	0.51	0.22	0.29
Int-4	1:30 PM	106.00	82	0.80	0.57	0.23
Int-6	-	112.00	49	1.06	0.78	0.28
Int-7	-	185.00	73	0.37	0.21	0.16
Main Stem	-	-	97	0.42	0.26	0.16

Event 8 – 5/14/2006

Site Name	Sample Time (CST)	Tapedown (in.)	TSS (mg/L)	TP (mg/L)	TDP (mg/L)	PP (mg/L)
1a	4:10 PM	38.00	10.0	0.53	0.44	0.09
1b	4:05 PM	29.50	9.2	0.52	0.42	0.10
2a	3:00 PM	57.50	6.8	0.50	0.41	0.09
2b	3:10 PM	25.25	5.0	0.20	0.16	0.04
3	3:15 PM	30.75	5.8	0.30	0.24	0.06
4	3:55 PM	28.25	15.0	0.35	0.29	0.06
5a	3:45 PM	27.00	3.5	0.16	0.13	0.03
5b	3:25 PM	20.75	3.3	0.11	0.09	0.02
8a	3:40 PM	29.25	12.0	0.54	0.47	0.07
8b	4:50 PM	27.50	7.6	0.38	0.30	0.08
8c	3:30 PM	14.00	9.5	0.25	0.20	0.05
Int-3	5:10 PM	104.50	35.0	0.22	0.14	0.08
Int-4	4:35 PM	106.00	21.0	0.23	0.18	0.05
Int-6	5:30 PM	102.50	27.0	0.27	0.21	0.06
Int-7	5:45 PM	173.50	55.0	0.21	0.14	0.07
Main Stem	-	-	67.0	0.25	0.14	0.11