THESIS

EXCESS NUTRIENTS AND CULTURAL EUTROPHICATION OF THE CACHE LA POUDRE RIVER: A STUDY OF THE OCCURRENCE AND TRANSPORT OF PHOSPHORUS

Submitted by

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ABSTRACT

EXCESS NUTRIENTS AND CULTURAL EUTROPHICATION OF THE CACHE LA POUDRE RIVER: A STUDY OF THE OCCURRENCE AND TRANSPORT OF PHOSPHORUS

Excess nutrients resulting in eutrophication of surface waters has become one of the greatest water quality challenges of our time. The development of an effective nutrient management strategy is essential to protecting surface water quality, public health, aquatic ecosystems and economic interests. The complexity of cultural eutrophication and the influence of nutrients, especially in streams and rivers, has delayed the development of an effective regulation and a nationwide management strategy. Variations in hydrologic conditions, geology and both urban and agricultural land use can dramatically influence phosphorus loads to receiving waters. Furthermore, several complex mechanism exist within a river or stream (e.g. the phosphate buffer, light availability, hydraulic retention time, phosphorus spiraling, etc.) that change the concentration and impact of nutrient concentrations and resulting eutrophication. Temporal and spatial variations result in changing and often imprecise threshold between healthy and unhealthy ecosystems.

For this reason, it is important for policy makers to understand how the assimilative nutrient capacity of waterways varies with environmental, seasonal and loading conditions, and that it is not the same for every watershed or even within the same waterway. A one-size-fits all technology solution or a state-wide numeric standard that does not account for these variations is misguided and will result in costly upgrades with minimal improvements to water quality. The most efficient nutrient management method is one that best matches the nutrient load delivered with the maximum assimilative capacity of the receiving water.

This study provides an in-depth analysis of the Cache la Poudre River Watershed in Northern Colorado over the course of a year to examine the influence of different sources, transport pathways and hydrologic regimes on phosphorus concentrations along an urban-agricultural gradient. An extensive and comprehensive design of sampling locations was used to best capture the anthropogenic influence (e.g. wastewater treatment plants, concentrated feeding animal operations, land uses) and transport pathways (e.g. irrigation ditches, overland transport, streams and rivers) of phosphorus within the watershed. Exploratory models were used to better understand the influence of geospatial variables on the occurrence and transport of phosphorus within the watershed.

The influence of phosphorus from wastewater treatment plants (WWTPS) to the Cache la Poudre River was examined in detail. A mass-balance of the phosphorus load in the river and the effluent from WWTPs was used to best estimate the influence of WWTPs. Projections of the influence proposed regulations that reduce WWTP effluent concentrations were made as well as the resulting impact to the river and water quality.

The role of sediment was investigated to better characterize and explain the temporal variations of phosphorus concentrations within this complex system. A brief economic analysis and associated improvements to water quality are discussed as well as effective management strategies in the Cache la Poudre River Watershed.

The objective of the study is to aid in the development of an efficient and effective nutrient management strategy for the Cache la Poudre River Basin and other similar mixed land use watersheds, as well as providing a foundation for creating a decision support system for water quality analysis, monitoring and management.

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“We all live downstream”

-David Suzuki

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1. Introduction

“When the well is dry, we will know the worth of water.”

-Benjamin Franklin

1.1. Origins of the Problem

Since the industrial revolution, rapid global population growth has had increasingly negative effects on surface water quality worldwide. Agricultural intensity [84] and dramatic changes to biogeochemical cycles [12] have had profound impacts on anthropogenic inputs of nutrients on the Earth’s surface. Furthermore, between one-third and one-half of the Earth’s surface has been transformed, typically resulting in more efficient transport pathways for excess nutrients to reach surface waters [136]. A link between excess nutrients and increased aquatic productivity, or eutrophication, has been known since it originated in Europe in the early 1900s [125]. Since that time, extensive eutrophication related research has been done on the subject and it has become unequivocally clear that excessive nutrients have led to eutrophication. However the complexity between nutrients and eutrophication within in a dynamic ecosystem have provided challenges in developing the best cultural eutrophication management strategy.

Eutrophication is a serious public health concern and can have dramatic impacts local and regional economies as well as aquatic and terrestrial ecosystems. The adverse effects of eutrophication include public health concerns, threats to endangered aquatic species, aesthetic issues, algal blooms, etc. These concerns have been growing in recent years as well as the need for a nutrient control plan.

Although eutrophication is the most widespread water quality, no well-defined standard or regulation exists. The complexities of eutrophication and the associated mechanisms and responses have resulted in a changing and often an imprecise threshold between healthy and unhealthy aquatic ecosystems and water quality [30]. Hydrologic conditions [68], geology [48], sediment loading capacity [43], ecosystems [30], and both urban and agricultural land use [118] are examples of factors that influence the nutrient loads and eutrophication of a waterbody. Changes in these factors result in a varying assimilative capacity of the river and a changing numeric threshold limit, even within the same watershed.

For this reason, it has been difficult to develop a nutrient management plan to best protect surface water quality.

1.2. Objectives and Structure of Thesis

An in-depth study of nutrients, specifically phosphorus, in the Cache la Poudre River Watershed was performed to better understand the occurrence and transport and to assist in developing a method to improve water quality and best serve the community. The thesis is naturally divided into four sections: (i) an extensive review of existing literature relating to excess nutrients, (ii) an examination of the sources and transport mechanisms as well as the influence of hydrologic and seasonal variations, (iii) a mass balance of P to determine the influence of WWTPs on the Cache la Poudre River as well as the impact of potential reductions and (iv) a basic cost benefit analysis is performed along with a discussion on best methods for nutrient management within the watershed.

2. Literature Review

2.1. Introduction

Excessive phosphorus and nitrogen in the environment have been linked to several environmental concerns; including eutrophication [98, 17, 26], acidification of freshwater lakes and streams [96], forest decline [35], climate change [136], disturbances to ecosystems and changing decomposition rates. Of all the environmental concerns associated with excessive nutrients, eutrophication consistently ranks as the leading surface water quality impairment and is directly related to public health issues, economic impacts, ecological concerns and aesthetic impairments [131]. In the US almost half of the impaired lake area and 60% of impaired river reaches are a result of eutrophication with similar impairments worldwide [6].

The relationship between nutrient supply and increased growth yields has been known and studied extensively since the work of the German agricultural chemist Justus von Liebig in the mid-1800s. By early 1900, with the work of Weber (1907) and Johnstone (1908), there was evidence of a link between nutrients and aquatic productivity, or eutrophication [125]. During the 1960s and 1970s the need to better manage and understand cultural eutrophication was becoming clear.

Several studies followed to better understand the associated physical, chemical and ecological mechanisms and the profound consequences of cultural eutrophication. Although many important advances have been made in the understanding of eutrophication, the causes and affects remains very complex and the same ecosystems can have high variations in behavior both seasonally and interannually [30]. To date, the complexity and heterogeneity of watersheds has been the largest challenge in developing a well defined numeric nutrient standard.

In 1998 USEPA began working to develop a rational framework for determining acceptable levels of nutrients in the nations surface waters as required as part of the 2001 Clean Water Action Plan. The goal of developing the framework was to allow states and tribal governments to set total maximum daily loads (TMDLs) for nutrients with an implementation date of 2003. Variations in hydrologic conditions [68], geology [48], agriculture [135], [69] and urban [118] land uses as well as sediment adsorption and ecological nutrient uptake all contribute to the complexity of cultural eutrophication and the challenge of developing a management strategy that best protects the nations surface waters.

In 2001, the Colorado Department of Public Health and the Environment established a nutrient criteria work group to began developing a nutrient management plan. However, there is large variations in both nutrient loading and environmental conditions between the largest watershed of Colorado as shown in Figure 2.1. Colorado still faces many of the same challenges and complexities associated with determining maximum anthropogenic nutrient loading rates to reduce cultural eutrophication to an acceptable level.

Colorado policy makers are faced with three fundamental questions when determining nutrient regulations: (1) What is an acceptable level of cultural eutrophication? (2) What is the cause of this level of eutrophication? (3) What is the most effective strategy to reduce cultural eutrophication? A literature review was done relating to these three fundamental questions to better understand the issue and to guide an extensive case study of nutrients within the Cache la Poudre Watershed.

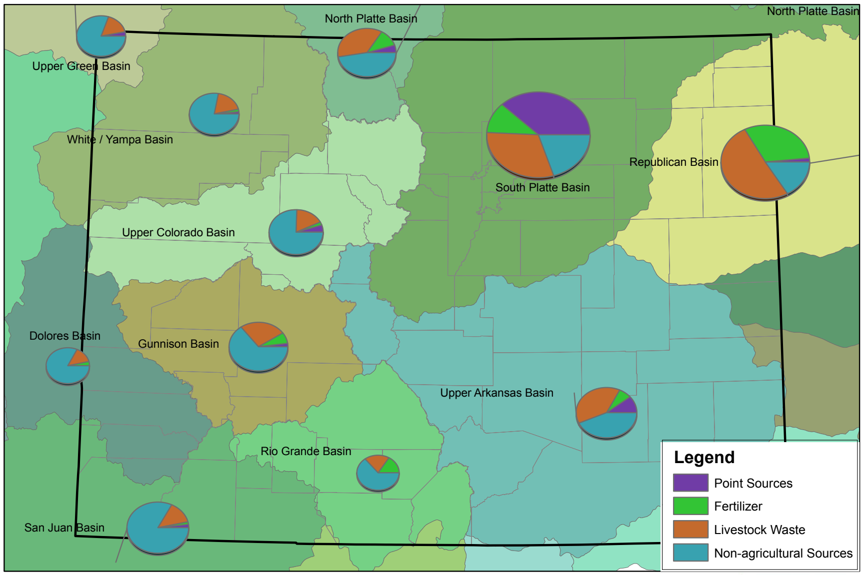

Figure 2.1: Phosphorus Yield in Colorado Watersheds [121]

2.2. Determining an Acceptable Level of Eutrophication

Cultural eutrophication is excessive plant growth caused by nutrient enrichment from human activity and there are several concerns associated with it making it the primary problem facing most surface waters today [125]. It impacts aquatic ecosystems from the Arctic to Antarctica [121]. Table 2.1 shows the most common potential effects of cultural eutrophication as well as economic costs and transnational implications.

There is widespread evidence that nutrient restriction, specifically phosphorus in freshwaters [114, 124], is an effective means for restoring eutrophic water and maintaining desirable water quality and ecosystem integrity [107, 58]. There are several reasons to better manage nutrients and reduce cultural eutrophication: Public health concerns, taste and odor issues, impaired aesthetics.

Table 2.1: Potential effects of cultural eutrophication caused by excessive inputs of phosphorus and nitrogen to lakes, reservoirs, rivers and coastal oceans (Adopted from [124, 6])

Effects of eutrophication
Increased biomass of phytoplankton and macrophyte vegetation
Increase biomass of consumer species
Shifts to bloom-forming algal species that might be toxic or inedible
Increases in blooms of gelatinous zooplankton (marine environments)
Increased biomass of benthic and epiphytic algae
Changes in species composition of macrophyte vegetation
Declines in coral reef health and loss of coral reef communities
Increased incidence of fish kills
Reductions in species diversity
Reductions in harvestable fish and shellfish biomass
Decreases in water transparency
Taste, odor and drinking water treatment problems
Oxygen depletion
Decreases in perceived aesthetic value of water body
Reduced Water Clarity
Blockage of intake screens and filters
Fouling of submerged lines and nets
Disruption of flocculation and chlorination process at water treatment plants
Restrictions of swimming and other water-based recreation

2.2.1. Public Health Concerns

High concentrations of nutrients in water can have direct impacts on public health. For example, a high level of nitrate is the primary cause of metheamoglobemia and has been correlated with stomach cancer [133]. The proliferation of diverse algal species can result in algal blooms that produce many toxins that are harmful to human health [10]. Cyanobacteria (commonly referred to as blue-green algae) is are typically the most dominant algal species [124]. The cyanobacteria can produce extremely hepatoxic, cytotoxic and neurotoxic compounds [10]. It can also form objectionable scum [103], summer fish kills [125] and impair drinking water quality [28]. Eutrophication caused a massive cyanobacteria bloom in the stagnant Murray-Darling River of Australia during a drought, leading to death of livestock [14]. Studies have provided evidence of increasing intensity and frequency of algal blooms, although excess nutrients are likely not the sole contributor [50].

A direct link between eutrophication and disease risk has also been suggested [124]. Increased nutrient availability enhances the replication rate of aquatic viruses [141]. For example, lesions in marine coral grew at a faster rate. Water related diseases are already a major concern of human morbidity and mortality worldwide [139]. The abundance and distribution of hosts is also modified by eutrophication and typically increases the probability of pathogens prospering [130]. Since flowing water is often used as a convenient wastewater disposal system, P loads to rivers and streams are very strongly influenced by human population densities, the population densities of livestock, and land use [102, 110, 121]. Clearly this biological waste disposal will not only provide a larger load of nutrients but also pathogens and bacteria.

2.2.2. Taste and Odor Issues

Taste and odor issues have also been linked to eutrophication [9, 142, 89]. These issues are often linked to the production of odorous metabolites by Cyanobacteria, most commonly geosmin [33]. Although taste and odor issues are not a direct consequence of eutrophication the increased algae growth can lead to taste and odor issues.

2.2.3. Impaired Aesthetics and Recreational Opportunities

Aesthetic impairments are typically the most obvious result of eutrophication and the most difficult to quantify. Several qualitative studies [56, 108] have determined when the chlorophyll a concentration, an indicator of algal growth, is between 100 and 200 mg/m2 is a nuisance. The filamentous green algae Cladophora is exemplifies aesthetic issues related to eutrophication [33]. Common concerns include slowing of water flow in canals and irrigation ditches (decreasing delivery rates and increasing water losses), interference with swimming opportunities and snagging fishing lures [33]. Eutrophication of lakes and reduced aesthetics can have more direct economic impacts and has been shown to reduce property values as well [91].

Figure 2.2 Surface blooms of cyanobacteria in the Baltic Sea [1]

2.2.4. Nutrient Loading and Ecosystem stability

Enriched streams have increased invertebrate biomass and altered invertebrate communities [94]. This disrupts community structure and there is evidence of a direct correlation with phosphorus concentrations [93]. As nutrients increase, organic carbon will build-up in the ecosystem and result in low dissolved oxygen and increased pH, hindering the growth of fish and invertebrates [138]. Streams and rivers with high nutrient concentrations often can have severe and cumulative impacts on downstream waters. The most famous hypoxic or ”dead” zone is likely the Gulf of Mexico and shown in Figure 2.3.

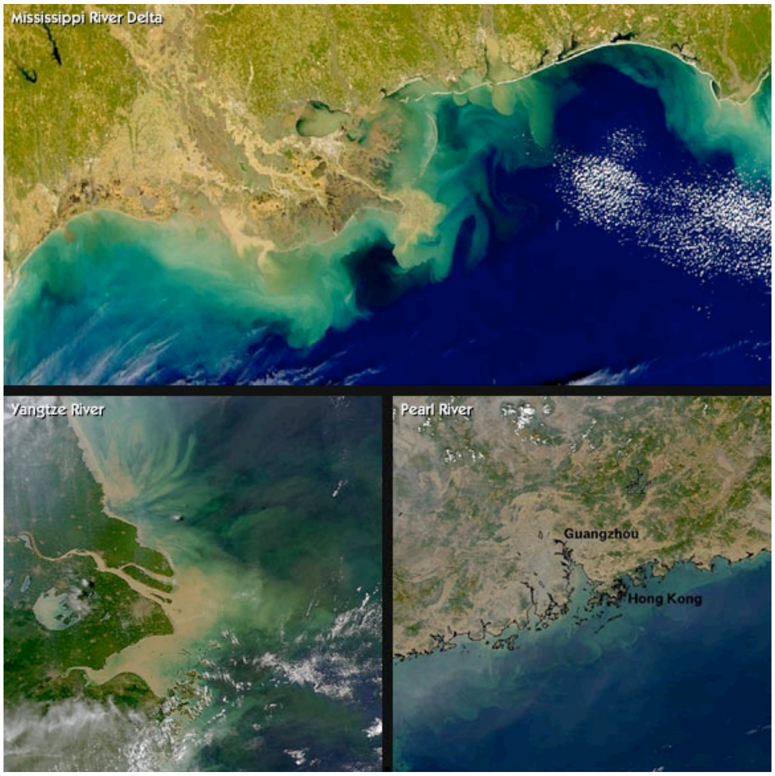

Figure 2.3: Famous anoxic zones of the world [2]

2.2.5. Economic Impacts

Eutrophication-related water quality problems can have very substantial negative economic effects [17, 29]. Eutrophic drinking waters are much more likely to have higher treatment costs; greater difficulties in meeting standards for DBPs; consumer complaints due to objectionable taste and odor; and health hazards due to algal toxins [28].

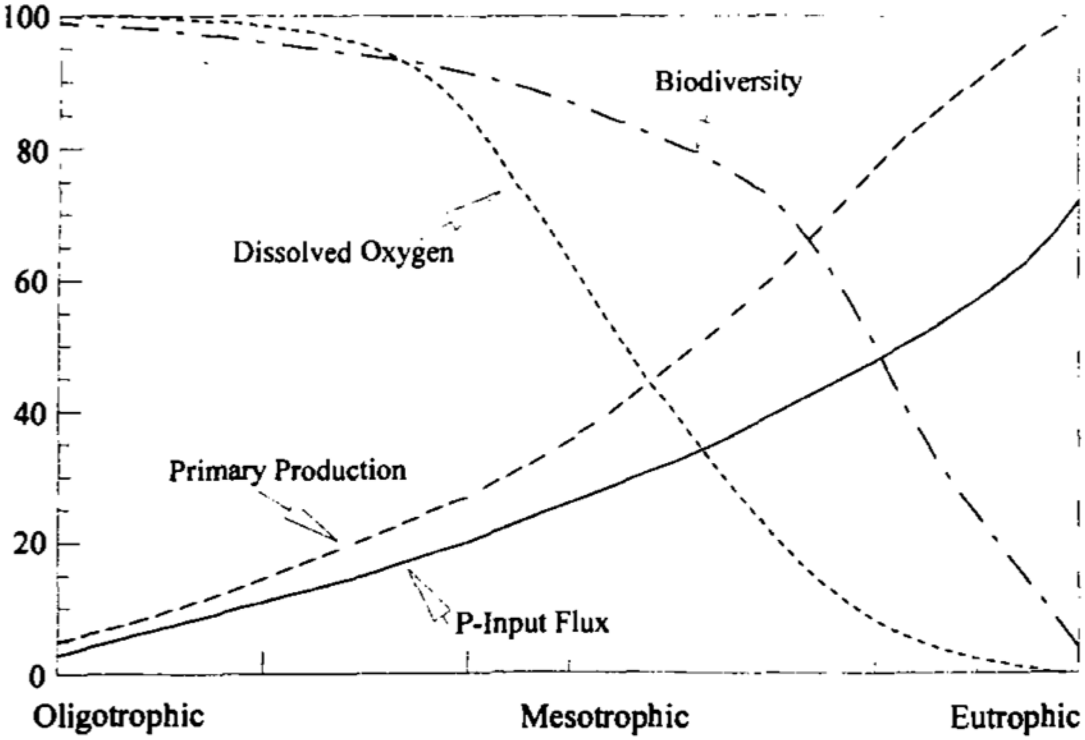

Figure 2.4 Conceptualization of freshwater eutrophication [30]

2.2.6. Nutrient Classification Systems

The challenge with defining a nutrient classification system is determining an objective assessment of the trophic status of a stream or river. Although classification methods exist [88,3], a widely accepted classification system is missing for all streams and rivers [33] due to the dynamic nature and complexity of the system. A number of nutrient-chlorophyll a models for streams and rivers have been developed (e.g. [11, 83, 22]) and often become the basis of nutrient classification systems. However, one study of Lake Washington [122] shows a hysteretic response to reductions in phosphorus concentrations as the lake recovered from eutrophication and further complicates the classification and management [17].

2.3. Factors Determining the Level of Eutrophication

2.3.1. Leibig’s Law of the Minimum

In the mid-1800s, Justin von Liebeg, an agricultural chemist, showed that the yield of plants can be limited by the nutrient that is present in the environment in the least quantity relative to the plant demands for growth; this theory is known as Liebigs Law of the Minimum and has been the principal method of controlling cultural eutrophication. Although N and C are essential to the growth of aquatic biota, P is often the limiting nutrient in freshwater and the nutrient of focus. This is because of the difficulty in controlling the exchange of N and C between the atmosphere and air as well as the fixation of atmospheric N by some cyanobacteria [31]. Typically N becomes the element controlling aquatic productivity in more brackish waters such as estuaries and oceans [30].

2.3.2. Vollenweider Equation

Several studies have provided evidence of phosphorus as the limiting nutrient in lakes and reservoirs (e.g. [105, 115, 38], etc.) As a result of several years of research a simple model was developed to relate total P input to algal biomass, an indication of eutrophication status [137].

$$Cl_a = \frac{L_p}{Q_s} / [1 + (\frac{z}{Q_s})^{0.5}]$$

The strong correlation between data from most of the lakes and reservoirs around the world and the simple model that related algal biomass (Cla) to total P input rate (Lp), mean water depth (z) and outflow per unit of lake surface area (Qs) provided very strong support of importance of phosphorus in lakes and reservoirs.

2.3.3. Algal-Nutrient Relationship

2.3.3.1. Lakes and Reservoirs

At this time, the relationship between P enrichment and primary productivity was unclear. McCauley et al. [85] described a sigmoid relationship between total P and chlorophyll a. A highly phosphorus enriched lake will not be influenced by additional phosphorus loading, because it is no longer the limiting nutrient. A N/P ratio of 22 has been estimated to be the most productive in most lakes [106]. In lakes with high phosphorus loads, N typically becomes the limiting nutrient [40].

2.3.3.2. Estuaries

In estuaries, it is generally accepted that there is a natural shift from P to N limitation [98]; although, a consensus does not exist (e.g. [54]). The efficient recycling of P in estuaries and losses of fixed N to denitrification is an obvious explanation for the shift in limiting nutrients [98]. A correlation between sulfate concentration and productivity of lakes and estuaries has also been observed [17].

2.3.3.3. Rivers and Streams

Rivers and streams are likely the least understood and worst managed in terms of eutrophication. In the US 48% of the 410 water quality monitoring to meet US EPAs standard of 100 mg/m^3 for eutrophication [121]. More recently, 61% of the 2048 cataloging units failed to meet the same standard [121]. Similar reports have documented poor water quality in terms of eutrophication worldwide (e.g. [95], in the UK and [76], 1998 in Germany).

For many years it was believed that streams and rivers are insensitive to nutrient inputs [61] due to factors, such as light availability [47] and a short hydraulic retention time [125], restricting the effects of nutrient enrichment on algal growth in rivers. Several studies have discredited this early belief and it is generally accepted that nutrient limitation of algal growth in flowing waters is common and widespread [30].

The earliest experimental evidence comes from Huntsman (1948), who fertilized an oligotrophic stream in Nova Scotia, Canada, with bags of NPK fertilizer. Downstream sites immediately exhibited an increase in abundances of attached filamentous green algae and fish. Another early experiment by Correll (1958) performed an enrichment of a Michigan stream using continuous additions of ammonium phosphate. TP concentrations increased from 8 mg/m^3 to 70 mg/m^3 resulting in an increase of periphyton growth of three fold.

Similar results were found by several studies in following years (e.g. [56]). However, it was observed in many of the studies that both N and P enrichment produced higher algal yields alone, suggesting N and P being co-limiting in some flowing waters.

2.3.4. Redfield Ratio

These studies are directly related to the concept of the Redfield Ratio, where algae in good growth conditions will have a relatively defined atomic ratio [111]. For N and P, the ratio is about 15 to 16:1. In natural systems this means that the system will be phosphorus limited if the atomic ratio of nitrogen is greater than the Redfield Ratio. However, in practical application the ratio in algae has been shown to vary approximately twofold simply due to light availability [143], ranging from 7 to 30. Temperature has also been shown to vary fourfold by only changes in temperature [62]. For this reason, Redfield Ratios can only provide clues into understanding algal-nutrient interactions and should be used with caution [30].

Streams and rivers typically exhibit more dynamic behavior with more heterogeneity than lakes and reservoirs. However as the hydraulic retention times and the volume of water increase, streams and rivers behave more like lakes and reservoirs [30]. Fundamental differences between the two system include the spiraling of phosphorus

[41], lower algal production per unit of total phosphorus due to washout [30], the phosphate buffer [122], etc. Variations in loading of streams and rivers as well as dynamic mechanisms controlling phosphorus in receiving waters increase the complexity of developing a nutrient management strategy. The most well-known phosphorus regulating mechanisms are highlighted.

2.3.5. Phosphorus Spiraling/Phosphorus Cycle

Spiraling of phosphorus down a river or stream is the result of phosphorus being a very biologically active element. Uptake of phosphorus by attached bacteria, algae and plants as well as the binding of phosphorus in bottom sediment and a release back into the water column [41]. This cycling of phosphorus downstream results in changes in phosphorus concentration and additional complexity in the systems.

Phosphorus spiraling is understood better with an understanding of the phosphorus cycle in an aquatic ecosystem. Phosphorus arrives to receiving water as particulates and may release phosphates to solution in the water column. The phosphorus compounds are hydrolyzed, either chemically or enzymatically, to orthophosphate. This is the only form of phosphorus that can be assimilated by bacteria, algae and plants. Particulates deposited to the bottom sediment may gradually be consumed by microbial communities, releasing phosphorus back into the water column as orthophosphate [125].

2.3.6. Phosphate Buffer

A dynamic equilibria exists between particulate phosphorus and dissolved phosphorus that has become known as the phosphorus buffering mechanism [18, 43]. Several studies have only been able to explain phosphorus concentrations in surface waters when sediment concentrations are considered (e.g. [64, 15]) due to the phosphate buffer. The theory assumes a kinetically rapid and slow population of particulate phosphorus. The rapid population equilibrates due to reactions at the surface within minutes. The slow population equilibrates with solid-state diffusion in a few days. This results in release phosphorus from the sediment in waters with low phosphorus concentrations and vice versa, providing a natural buffer regulating phosphorus concentration.

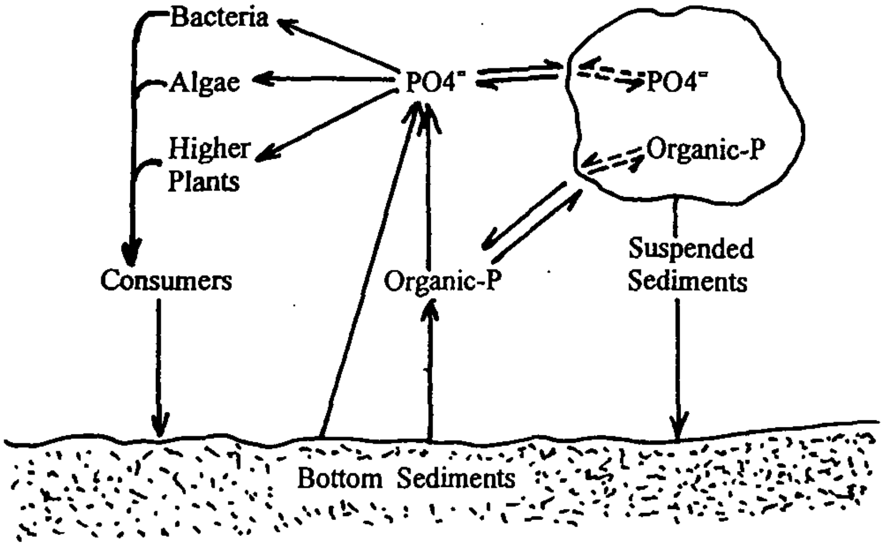

Figure 2.5: Phosphorus Cycle in Aquatic Ecosystems [125]

2.3.7. Sediment Binding and Anoxic Conditions

Furthermore, biological activity occurs once particulates settle to the bottom that can mineralize organic phosphorus gradually and release phosphorus to either diffuse into the water column or bind to nearby sediment again [53]. The binding of phosphorus to the sediment is dependent on the dissolved oxygen content because binding to aluminum and ferric hydroxides are very strong. In anoxic conditions the ferric ions are reduced to ferrous and weakens phosphate binding [60]. This is one component in seasonal changes in phosphorus concentrations.

2.4. What is the most effective nutrient management strategy?

An understanding of hydrologic controls linking spatially variable P sources, sinks, temporary storages, and transport processes are critical to the development of effective nutrient management strategy. The following section discusses the factors influencing nutrient management.

2.4.1. Sources

Phosphorus sources are typically classified as either point or nonpoint sources, as shown in Table 2.2.

Table 2.2: Sources of point and nonpoint chemical inputs recognized by U.S. statutes [125]

Point Sources
Wastewater effluent (municipal and industrial)
Runoff and leachate from waste disposal sites
Runoff and infiltration from animal feedlots
Runoff from mines, oil fields, and unsewered industrial sites
Storm sewer outfalls from cities with populations less than 100,000
Overflows of combined storm and sanitary sewers
Runoff from construction sites with an area less than 2 ha
Nonoint Sources
Runoff from agriculture (including return flows from irrigated agriculture)
Runoff from pastures and rangelands
Urban runoff from unsewered areas and sewered areas with populations less than 100,000
Septic tank leakage and runoff from failed septic systems
Runoff from construction sites with an area less than 2 ha
Runoff from abandoned mines
Atmospheric deposition over a water surface
Activities on land that generate contaminants, such as logging, wetland conversion, construction and development of land or waterways

Since the passage of the the Clean Water Act of 1972, significant progress has been made controlling nutrients from point sources. As additional controls of point sources becomes less cost-effective and water quality problems remain unresolved, more attention is being placed on nonpoint source controls [117]. A lack of attention controlling nonpoint sources has been a result of both easier identification and control of point sources and only a relatively recent realization and concern of the direct health risks associated with eutrophication. As a result, nonpoint source pollution of phosphorus accounts for an increasing majority of water quality problems in the US (Crowder and Young, 1998; Schultz et al., 1992). Agricultural runoff alone has been reported as the cause of impairment of 55% of surveyed river length and 58% of surveyed lake are with water quality problems [100]. Agricultural runoff includes both commercial fertilizer and manure. Phosphorus minerals are mined and processed in large quantities to create commercial fertilizers [125].

2.4.2. Phosphorus Mobility

Although it is generally accepted surface waters receive most of their P in surface flows rather than groundwater, because phosphates bind to most soils and sediment [30], a monitoring study of a phosphorus concentrations in a plume of treated sewage in Cape Cod, Massachusetts has shown evidence of phosphorus migrating in the groundwater [86]. This raises concerns about infiltration basins and septic leaching fields discharges enriching groundwater and releasing to sensitive lakes and streams [132].

2.4.3. Phosphorus Removal Methods

Phosphorus removal is done by the creation of particulate matter that can be separated from the water. Two fundamentally different methods are used to create the particulate matter: physical-chemical precipitation and enhanced biological removal. Physical-chemical precipitation utilizes the solubility of phosphorus-metallic compounds to precipitate the phosphorus down to levels approaching the solubility product of the compounds, and then employs a physical separation process to removed the precipitate from the wastewater. Enhanced biological removal utilizes the uptake of phosphorus by polyphosphate accumulating organisms.

Typically enhanced biological removal has a lower overall operating cost compared to chemical precipitation [113, 49]); although it may not be as reliable and cannot achieve the highest levels of phosphorus removal [65].

Several unit processes for phosphorus removal have been developed and proven as effective removal methods. The most common phosphorus removal methods include biological nutrient removal [78], enhanced biological phosphorus removal [140], the modified Renphosystem [112], crystallization [66], and activated aluminum adsorption [51]. The performance and economic costs of these methods are often difficult to estimate. [65]. Several cost and performance estimation methods have been investigated, including the use of existing data, pilot-scale experiments or computational simulations.

2.5. Objective and Hypothesis

For most of the 20th century eutrophication research has focused on lakes and reservoirs. In the past decade more attention and advances have been made in understanding marine and coastal eutrophication [109]. Although streams are often the most complex systems and are the most visible delivery mechanism of nutrients from a watershed to lakes, reservoirs and estuaries, a disproportionately smaller amount of research has been done on streams and rivers.

As nutrient control regulations are being developed the importance and lack of understanding of the role of rivers and steams eutrophication within a watershed is becoming very clear. Very few large scale watershed studies exist [8] . An in- depth look at nutrients within a watershed that includes the occurrence, transport, influence of known sources, management strategies and economic analysis was to found during this literature review. This study is crucial to the understanding and regulation of nutrients. The objective of this study is to begin to fill a deficiency of integrated watershed studies focusing on all aspects of nutrient management. It is the opinion of the author that several similar studies of Colorado watersheds will be need to truly make an effective and efficient nutrient management regulation. Furthermore, an integrated monitoring system and a dynamic regulation that allows for the maximum assimilation of nutrient loads will provide the best management strategy.

3. Geospatial Analysis of the Occurrence and Transport of Phosphorus in the Cache la Poudre River Basin in Northern Colorado

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Abstract This study examines the effect of different sources, transport pathways, and hydrologic regimes on phosphorus concentrations along an urban-agricultural gradient. A total of 48 sampling locations were monitored to characterize total phosphorus concentrations in the Cache la Poudre River Watershed in Northern Colorado. The comprehensive design of sampling locations aimed to capture the influence of anthropogenic activities, i.e., wastewater treatment plants (WWTPs), concentrated animal feeding operations (CAFOs), and irrigation ditches. Samples were collected at seven points in time with distinct climatic and hydrologic characteristics from April 2010 to February 2011. A geographic information system (GIS) was used to measure the overland, irrigation ditch, and stream/river distances from the sources to sampling locations. Analysis of variance, non-linear regression, and multiple linear regression models were used in combination to explore the co-variation of phosphorus concentrations with capacities of upstream WWTPS and CAFOs, along with other geospatial factors. It was evident, under all hydrologic conditions, that phosphorus concentrations downstream from WWTPs were significantly higher than the concentrations upstream of the facilities. Transport from WWTPs governed phosphorus concentrations in surface water during dry and low flow conditions, whereas contribution of CAFOs was significant during rainfall events. The total flow distance (a function of overland, irrigation ditch, and stream/river distances) from CAFOs to the sample locations was instrumental when determining phosphorus concentrations during precipitation events. The results of this study provide the foundation for creating a decision support system for water quality analysis, monitoring, and management in the Poudre River basin and other similar mixed-land use watersheds.

Keywords: Phosphorus, Cache La Poudre River, Water Quality, WWTPs, CAFOs, Irrigation Canals, Environmental Monitoring

3.1. Introduction

Environmental degradation from nutrient pollution, specifically phosphorus, consistently ranks as one of the top water quality issues in the U.S. [5, 6, 131]. Excess levels of phosphorus in streams and rivers have been shown to pose human health and ecological risks [116, 97]. Hypoxia (low dissolved-oxygen) and eutrophication are also insidious effects of over- enrichment of water bodies with nutrients, which can contribute to the release of toxic substances from bed sediments and fish kills [125, 4]. As the population of the world continues to grow, land use and development will play an increasingly important role in water quality. Contaminant concentrations have been shown to exacerbate with increased anthropogenic activities as water flows through urban and agricultural settings [4, 129, 127, 72]. In mixed-land use watersheds, however, quantifying the relative importance of various nutrient sources and transport mechanisms require carefully designed sampling locations. Understanding how and why nutrient concentrations are changing over time in streams and rivers is essential for effectively managing and protecting water resources.

Two of the largest contributors of phosphorus in the watershed are thought to be wastewater treatment plants (WWTPs) and CAFOs and both are considered a major source of nutrients, contaminants, and environmental degradation in riparian zones and surface water [100, 79, 90, 55]. Establishing a correlation between phosphorus in the watershed and source density (number of animals or wastewater flow) and distance (overland, irrigation ditch and river) will improve the viability and effectiveness of watershed-scale studies when investigating the occurrence, fate, and transport of phosphorus. In this regard, it is not enough to delineate and quantify different land use areas since the source density within each land use must be identified, quantified, and correlated to water quality parameters (e.g. [72]).

Some studies have called for increased regulation of CAFOs and/or downsizing to decrease the environmental impact of this source of pollutants [21]. However, with a continually increasing population, CAFOs remain one of the most economically efficient and productive form for producing meat and other animal products. Since the contaminant transport pathways associated with CAFOs are well understood , it is important to look into transport mechanisms for contaminants, such as irrigation ditches and runoff associated with hydrologic events, especially in semi-arid areas where natural tributaries are not as prevalent.

The abundance of irrigation canals and the absence of small streams in the Cache la Poudre River watershed in Northern Colorado create a unique situation to study this aspect of phosphorus transport. It is thought that irrigation canals and ditches have substantially altered the hydrology and associated phosphorus processes within the Poudre River watershed. Studies elsewhere have shown that irrigation has a significant impact on the processes of recharging alluvial aquifers and transporting contaminants into ground water [13]. Studies have also focused on factors influencing irrigation water quality and quantity [20], but the impacts of irrigation ditch distance and location on phosphorus transport to rivers are still unclear.

Temporal hydrologic variations can have significant impacts on the occurrence and transport of phosphorus to and in surface water. Research has shown significant increases in phosphorus fluxes during rainfall events and phases of retention and mobilization throughout seasonal dry and wet periods, respectively [16]. Other studies have suggested increases in chemical/physical pollutant concentrations in streams as precipitation and runoff inputs increase [24]. However, most previous studies only collected measured data at a few stations within the watershed or at a few points in time mostly during low flow conditions.

In this study, a comprehensive monitoring campaign at forty eight sampling locations was conducted to characterize total phosphorus concentrations in the Cache la Poudre River Watershed. The comprehensive design of sampling locations aimed to capture the influence of anthropogenic activities, i.e., wastewater treatment plants (WWTPs), concentrated animal feeding operations (CAFOs), and irrigation ditches. Samples were collected at five points in time with distinct climatic and hydrologic characteristics. This paper also considers other factors such as irrigation ditch flow rate, river flow rate, precipitation, and snowmelt to characterize how hydrologic regimes impact the fate and transport of phosphorus in a mixed-land use watershed.

The primary objective of this study is to determine the impact of putative anthropogenic sources (i.e., CAFOs and WWTPs) relative to the background phosphorus concentration in the Poudre River under varying hydrologic conditions. Specifically, the capacity and location of the CAFOs and WTTPs will be correlated to the measured phosphorus concentrations in the river along the urban gradient. The secondary objective of the study is to determine which transport mechanism (overland, irrigation, river, etc.) has the greatest impact on phosphorus concentration in the river. In semi-arid regions, such as Colorado, irrigation ditches may be a significant aspect of phosphorus transport due to the lack of regulations and their prevalence in the watershed.

3.2. Materials and Methods

3.2.1. Site Location and Description

The Cache la Poudre River watershed in Northern Colorado is an ideal system to identify urban and agricultural impacts on water quality. The urban gradient in the watershed can be characterized by four regions: pristine region, agricultural tributaries, urban settings, and mixed urban/agricultural influenced region. The dominant phosphorus source in the urban region is thought to be from WWTPs whereas CAFOs are considered to dominate the agricultural tributaries. Although cropland is a source of phosphorus in this region, it was not incorporated in the study because initial sampling showed very little phosphorus influences from irrigated cropland. The watershed is contained in the semi-arid front range of Colorado and has minimal tributaries. Canals and ditches are used extensively for irrigation and inputs to the river are predominantly point sources in the urban landscape and non-point sources in the agricultural areas outside of Fort Collins [74].

Figure 3.1 shows the predominant WWTPs and CAFOs as well as the land uses within the watershed. The river is fed by snowmelt with minimal anthropogenic influences and originates near the Continental Divide in the forested Rocky Mountain National Park. The Cache la Poudre River flows through steep mountainous terrain for approximately 69 km (43 miles) before entering the city of Fort Collins. After traveling through Fort Collins, the river moves through approximately 72 km (45 miles) of a predominately agricultural landscape before joining the South Platte River in Greeley, CO (Yang and Carlson, 2003). Major irrigation diversions on the main stem of the Poudre River begin approximately 100 km (62 river miles) from the source (Kim and Carlson, 2006).

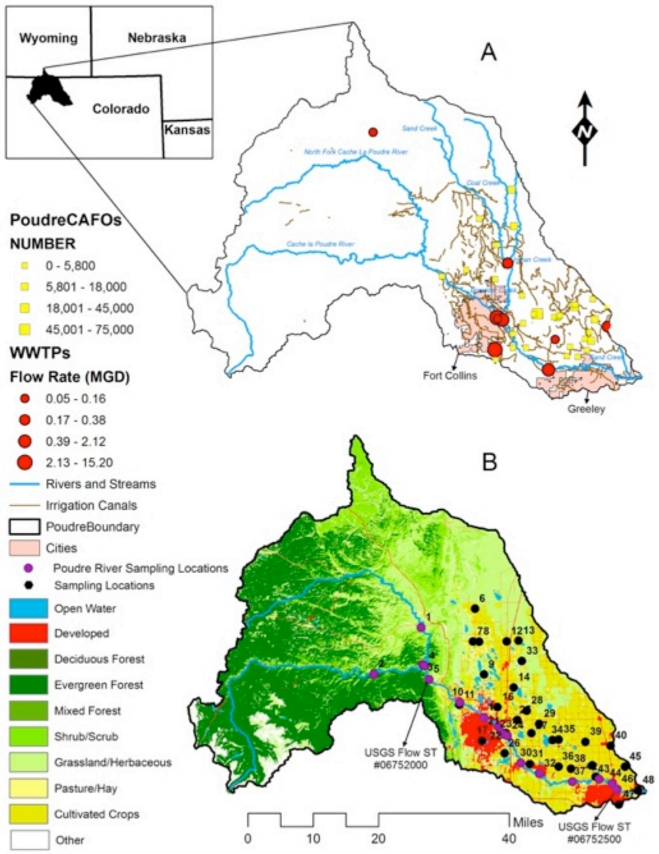

Figure 3.1: (A) Map of the study region showing the Cache La Poudre River, CAFOs, and WWTPs (B) Map of sampling locations with land use indicated

3.2.2. Geospatial Factors

Elevation and hydrography data for the Cache la Poudre River Watershed were obtained from the U.S. Geological Survey data warehouses. The National Elevation Dataset 1/3 Arc-Second (NED 1/3) data for the watershed were used to characterize the terrain. The National Hydrography Dataset (NHD) High Resolution data were used to identify irrigation ditches, canals, rivers, streams, ponds, and dams in the watershed. The location information and capacity values for all WWTPs and CAFOs in the watershed were collected from the U.S. Environmental Protection Agency Facility Registry System (FRS). This dataset was augmented by personal communication with representatives of CAFO and WWTP facilities.

This study presents a new method for explaining river water quality throughout seasonal hydrologic conditions. Several studies have linked land-use type and/or human and animal population variables with water quality parameters, including phosphorus. (Kang et al., 2010; Russell et al., 2008; Schaefer and Alber, 2007) However, some of these methods are rigorous and include multiple input variables. In order to explain the variability of phosphorus concentrations along the Poudre River, a simpler method was constructed. To gain a better understanding of the transport of phosphorus, the Terrain Analysis toolbox in ESRI ArcGIS 9.3 (Redlands, CA, USA) was used to measure overland distance (CAFOs only), irrigation ditch distance (CAFOs only), and river distance from WWTPs and CAFOs to each sample location. To determine overland distance, the cost-surface analysis was used to calculate the distance from each CAFO to the nearest receiving surface water along the flow path. Similarly, irrigation ditch and river distances from WWTPs and CAFOs to each sampling location were calculated. While WWTPs are discharged directly into streams, irrigation ditch and river distances for CAFOs were determined at the points where overland flow entered the bodies of water. For each sampling location situated downstream from a WWTP and/or CAFO, a total flow path was calculated by adding each contributing geospatial factor.

3.2.3. Sample Collection and Analysis

Forty-eight sampling locations were strategically monitored throughout the watershed to capture a range of influences from CAFOs and WWTPs (see 3.1, Panel b). Sample sites were allocated among pristine, agricultural, urban, and mixed urban/ agricultural land use areas. Another important consideration in the placement of sampling sites was based on canal/river distance from anthropogenic sources (WWTPs and CAFOs) and the number of people and animals that impacted each location. The population impacting each sample location was directly correlated to WWTP discharge in million gallons per day (MGD). In order to determine the background load, five sites within the pristine portion of the watersheds were monitored. Three additional sites in cropland areas with no WWTP or CAFO were also included.

Table 3.2 presents the five distinct climatic and hydrologic conditions between April and July 2010 when samples were collected. Since one of the objectives of this study was to determine how different hydrologic conditions impact phosphorus concentrations in rivers, streams, and irrigation ditches, the timing of sampling events was designed to reflect conditions before mountain snowmelt, during snowmelt/runoff, after snowmelt, during a rainfall event, and during the peak irrigation season which typically coincides with low flow conditions. Figure 3.2 illustrates the flow classification of the sampling events based on flow observations at an upstream location at mouth of canyon (USGS 06752000), and a downstream location immediately upstream of the confluence of the Poudre River with the South Platte River (USGS 06752500). The locations of these two sites are depicted in 3.1. Figure 3.2 contains the average snow water equivalent curve based on observed data at two SNOTEL sites located within the study watershed.

The first sampling event occurred on April 23, 2010 while snowpack was still increasing and Poudre River flow rates averaged approximately 5.01 cubic meters per second according to USGS flow monitoring data (U.S. Geological Survey, 2010). Sampling for this date also took place at the end of a 58.4 millimeters rain event (average rainfall recorded for Fort Collins and Greeley, CO on these dates).

Table 3.1: (a) Flow duration curves for the Cache La Poudre River at the mouth of the canyon near Fort Collins, CO (ST 0675000) and near Greeley, CO (ST 06752500) with sampling events indicated, (b) SNOTEL snow water equivalent curve for sites contained in the Cache La Poudre watershed, mean flow rate for the major irrigation ditches in the Cache La Poudre watershed, and the mean rainfall for Fort Collins and Greeley, CO.

Event Number	**Event Date**	**Upstream Flow** (m^3/s)	**Downstream Flow** (m^3/s)	**Average[1] SWE** [2])	**Average[3] Irrigation** (m^3/s)	**Antecedent 3-Day Rainfall[4] (mm)**
1	4/23/10	4.64	13.96	571.5	1.26	58.4
2	5/19/10	26.9	24.15	706.9	0.71	14
3	6/4/10	55.5	24.44	424.2	3.85	0
4	6/18/10	60.32	60.6	0	1.19	0
5	7/16/10	13.54	2.09	0	2.1	0
6	9/17/10	1.16	1.73	0	0.7	0
7	2/22/11	0.33	2.15	494.03	0	0

Table 3.2: Hydrologic Description of Sampling Events

[1] Average of Deadman Hill, Hourglass Lake and Long Draw Reservoir SNOTEL Stations

[2] SWE: Snow Water Equivalent

[3] Average of all monitored irrigation canals

[4] Average of Fort Collins, CO and Greeley, CO

The second set of samples was taken on May 19, 2010 at the height of snowpack prior to peak runoff. Average river flow rates for this date reached nearly 25.5 cubic meters per second and the average cumulative 7-day rainfall for Fort Collins and Greeley was 14.0 millimeters. The third sampling event was on June 4, 2010 in the middle of snowmelt and runoff when average flow rates in the river were near 28.32 cubic meters per second, no rainfall had occurred and water in the major irrigation ditches was flowing at an average rate of 3.85 cubic meters per second. Samples for the fourth event were taken on June 18, 2010 when all snow had melted and runoff was at its peak. River flow rates for this date averaged over 42.48 cubic meters per second. This sampling event also occurred 4 days after 48.3 millimeters of rain fell in Fort Collins, CO and 94.0

millimeters of rain fell in Greeley, CO. The final sampling event took place July 16, 2010. This sampling event was characterized by intense agricultural irrigation, low river flows downstream and no recent precipitation. As shown in Figure 3.2, flows upstream in the Poudre River are classified under moist conditions, while flows downstream near Greeley are near dry conditions. This could be due to the absence of a significant rainfall event for more than a month and/or significant irrigation diversions upstream.

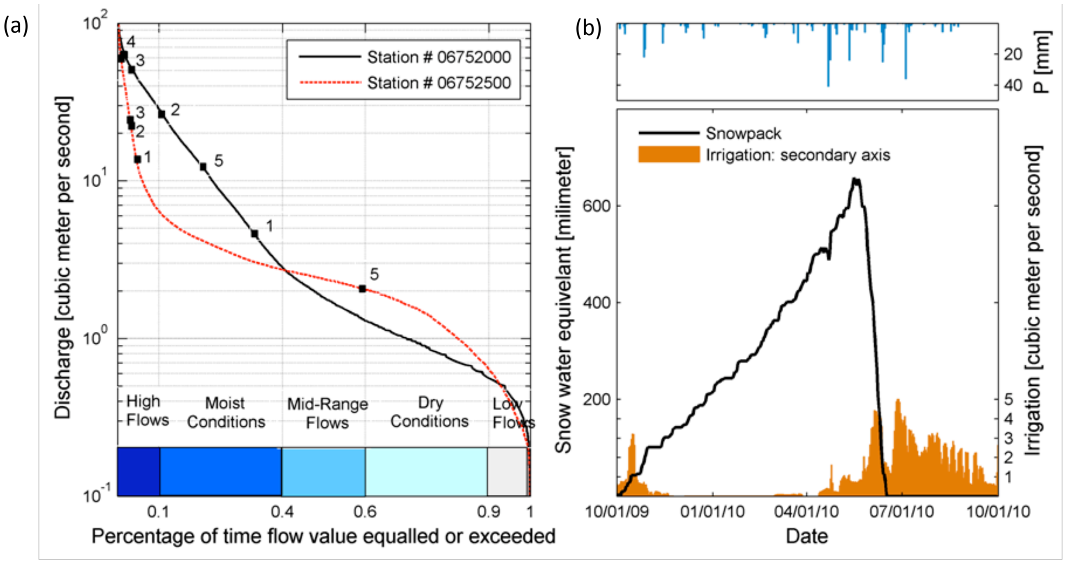

Figure 3.2 (a) Flow duration curves for the Cache la Poudre River at the mouth of the canyon near Fort Collins, CO (ST 0675000) and near Greeley, CO (ST 06752500) with sampling events indicated, (b) SNOTEL snow water equivalent curve for sites contained in the Cache la Poudre watershed, mean flow rate for the major irrigation ditches in the Cache la Poudre watershed, and the mean rainfall for Fort Collins and Greeley, CO.

A minimum of three samples (total volume of 500 milliliters) were taken at each site across the width of the river or canal. The samples were collected in acid washed Nalgene bottles and stored at 4oC. Prior to the total phosphorus analysis, samples were pre-filtered and brought to room temperature. An acid persulfate digestion method (EPA ESS Method 230.1) was used with a 0.06-3.5 mg/L range TP test set (Hach Company, Loveland, CO). TP analyses were completed within a week of the sampling date.

3.2.4. Data Analysis

The aqueous samples were collected and measured for total phosphorus and other water quality characteristics. Variation among hydrologic events was determined with an analysis of variance. A significant change in the phosphorus concentrations occurs 34 miles from the confluence with the South Platte. The data along the Poudre River is separated at this point 34 miles from the confluence into upstream and downstream data sets and a separate analysis of variance was used to measure the variability of these two regions. CAFO and WWTP influences along the river were compared with the phosphorus concentrations.

The variability and complexity of the data required a nonlinear tree regression analysis to determine what anthropogenic sources and transport mechanisms have the greatest impact on phosphorus concentrations in the watershed for each hydrologic condition. The nonlinear tree regression ranked the top variables affecting phosphorus concentrations. A multiple linear regression was used with the entire data set to determine how well the top variables estimated phosphorus concentrations.

3.3. Results and Discussion

A novel approach for determining watershed-scale impacts of point and non- point anthropogenic sources of contamination was developed and used in the Cache la Poudre watershed in Northern Colorado. This method includes WWTP and CAFO capacity and geospatial/location information of sources to obtain occurrence and transport information for phosphorus. In the following sections the impacts of hydrologic events on phosphorus concentrations are discussed. Geospatial factors influencing the transport of phosphorus, including irrigation ditches, are also analyzed and presented. A regression model for determining expected P concentrations based on capacity and location relative to sampling stations is also described.

3.3.1. Variability of TP Concentrations under Varying Hydrologic Regimes

An analysis of variance was performed to determine the differences among samples collected from all of the sampling sites during the five hydrologic sampling periods and the results are shown in Figure 3.3. Phosphorus values for the first samples (taken during a 58.4 millimeters rainfall event) ranged from 0.080 mg/L total phosphorus (TP) to 2.1 mg/L TP. For the second sampling event, phosphorus values ranged from 0.090 mg/L TP to 1.0 mg/L TP. The third sampling event yielded data ranging from 0.12 mg/L TP to 1.0 mg/L TP, fourth sampling results yielded phosphorus values ranging from 0.075 mg/L TP to 0.79 mg/L TP with two outliers (1.3 and 1.7 mg/L TP), and samples taken during the fifth sampling event ranged from 0.11 mg/L TP to 3.1 mg/L TP with one outlier (3.9 mg/L TP). As shown in Figure 3.3, results from the analysis of variance indicated that the first and fifth sampling events were statistically different from the other three sampling events with a p value 1.4E-7, while sampling events 2, 3, and 4 were not statistically different.

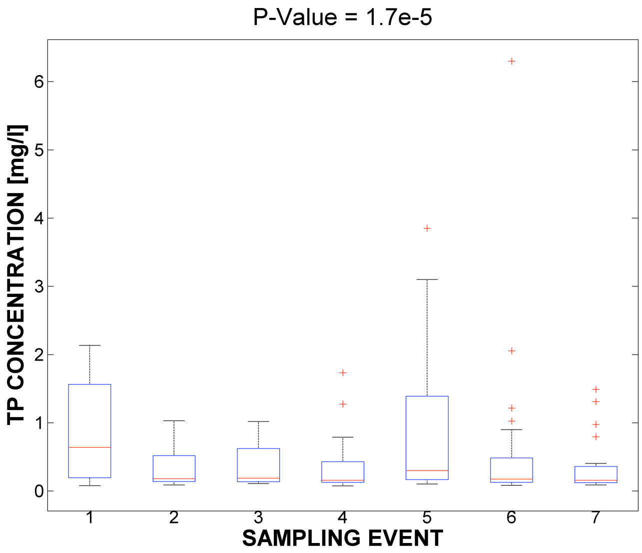

Figure 3.3: Analysis of variance for testing the differences between samples collected during different hydrologic regimes (snow-melt vs. event-driven)

These results show the impacts of different hydrologic regimes on the occurrence and transport of phosphorus concentrations in surface water. The average annual precipitation for the semiarid foothills of Colorado, in which the Cache la Poudre Watershed is contained, is approximately 381 millimeters per year [99]. In this study a 58.4 millimeters rainfall event was captured in the first sampling event. Significantly higher phosphorus concentrations found in the samples taken the day of the rainfall event underline how precipitation, and hence runoff, increases non- point source (in this case, CAFO) phosphorus concentrations in rivers and streams. The fourth sampling event was also taken after a rainfall event but occurred at a different point in the hyetograph (four days after rainfall). As shown in Figure 3.3, samples from this event did not show statistically higher phosphorus concentrations. This suggests that in order to capture nonpoint source impacts on surface water due to excess runoff during precipitation events, samples must be obtained during or immediately after significant precipitation events. This is an important finding with regards to sampling plans because it shows the importance of timing when monitoring surface water quality.

The fifth sampling event also showed elevated phosphorus concentrations. As presented in Table 3.2, the most striking difference between the first and fifth sampling events and the other three sampling events was the average flow in the Poudre River. Average river flows for the first and fifth samples were 5.01 cubic meters per second and 4.08 cubic meters per second, respectively, while the lowest average river flow for the other three events was 25.0 cubic meters per second. Since phosphorus was measured using concentration (in mg/L), low flows and the lack of dilution for point sources helps explain significantly higher P levels during the fifth sampling event.

3.3.2. Phosphorus Concentration along the Poudre River

A statistically significant difference of measured phosphorus concentration occurred upstream and downstream from the point where the effluents from three major WWTPs enter the Poudre River for all hydrologic events, as shown in Figure 3.4. The three WWTPs include Boxelder Sanitation District (2.1 MGD average flow), Drake Water Reclamation Facility (15.2 MGD average flow) and South Fort Collins Sanitation District (2.8 MGD average flow) and combine to be the largest phosphorus point source on the Poudre River. The average monthly flow of the gross effluent from each WWTP was used for the analysis [7]. The gross effluent from each WWTP remained relatively consistent during the sampling period.

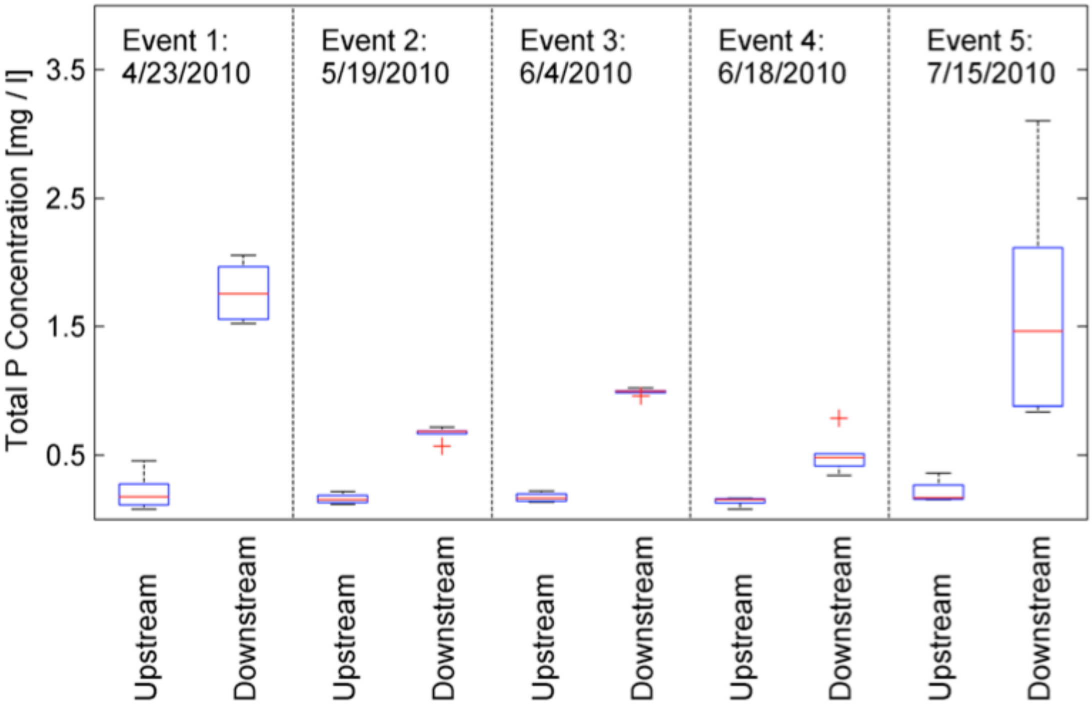

Figure 3.4: Total phosphorus concentration measured along the Poudre River for all five hydrologic events. Each event is divided by samples taken upstream and downstream from significant WWTP influence.

Figure 3.4 illustrates that the variability in the upstream phosphorus concentration is minimal. An average of 0.15 ± 0.065 mg/l was measured for all of the upstream samples and this value is assumed to be the background phosphorus concentration in the Poudre River, which is consistent with the mean total phosphorus concentration of stream water in the continental U.S. of 0.13 mg/l [125]. The upstream region is dominated by pristine region with some urban influence.

While slightly more variation was observed in the downstream data sets corresponding to events two, three and four, events one and five exhibited the highest variation in the downstream phosphorus concentration. The first sampling event was characterized by precipitation, which expedites phosphorus mobilization and inhibits natural attenuation. Event five was characterized by low flows, which minimizes phosphorus mobilization and promotes natural attenuation. These events also captured the highest phosphorus concentrations due to less dilution with low flow conditions.

The natural attenuation, which likely occurred during the fifth sampling events, can be seen in Figure 3.5, as the phosphorus concentration decreases as the distance from sources increases. Furthermore, the influence of CAFOs was greatest during the precipitation event (Event 1), highlighting the temporal importance of capturing nonpoint sources. Event five also showed the impact of CAFOs, where phosphorus concentrations decreased until the location where the river is impacted by a large number of CAFO animals. This may be due to the low flow conditions or an increased return flow from irrigation canals promoting phosphorus transport. The impact of CAFOs on water quality was also seen in the first sampling event, but attenuation was not achieved due to mixing from the rain event and continual inputs from runoff as the water flows downstream. Despite an increased CAFO influence for the first and fifth hydrologic events, the three WWTPs dividing upstream and downstream data sets had the greatest influence on phosphorus concentrations in the Poudre River.

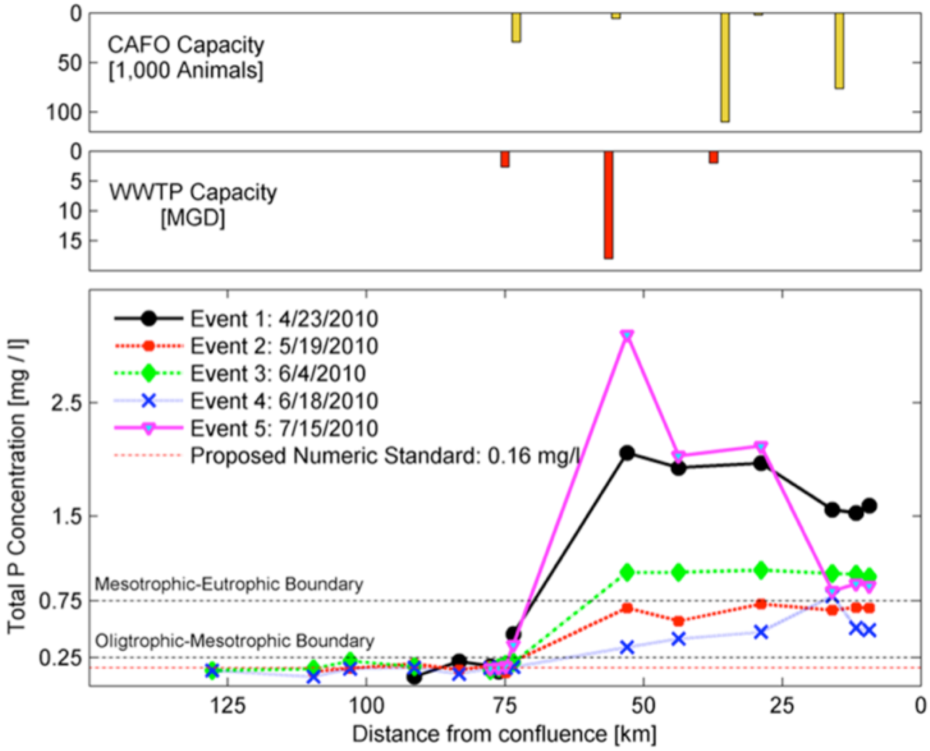

Figure 3.5: The phosphorus concentration along the Poudre River as a function of the distance from the confluence of the river, with WWTP and CAFO influence points shown, for all events. The WWTP and CAFO influence indicates the point where the river is influenced and does not show the cumulative capacity.

In contrast, the high flow events (events 2, 3 and 4) do not appear to be influenced by the distance from the source. For example, event three in Figure 3.5 shows two distinct and consistent phosphorus values upstream and downstream from the WWTPs. For this event the phosphorus concentration in the river substantially increased where major WWTP effluents discharge to the river, and remained relatively unchanged flowing downstream. These events also have a lower phosphorus concentration due to increased dilution. This may suggest low flow conditions have higher background concentrations due to a lack of dilution but natural phosphorus attention reduces the downstream concentration. Furthermore, high flow conditions limit downstream attenuation but dilution reduces the background concentration.

In this study region both CAFOs and WWTPs impact phosphorus concentrations in the Poudre River. For example, the largest increase in phosphorus concentration occurs 53 km from the confluence. This sample location experiences the highest WWTP influence (18 MGD average flow) and the third highest CAFO influence (154,000 animals). Since a significantly smaller increase of phosphorus concentration occurs under the influence of a much higher CAFO influence (76,550) and no WWTP influence, it may indicate WWTP influences dominate the downstream phosphorus concentration of the river.

3.3.3. Key Geospatial Factors

Tree Regression Analysis Due to the complexity of the geospatial setting in the Cache la Poudre watershed, a regression tree analysis was used to determine the most important factors for determining phosphorus concentrations in the watershed. The nonlinear regression method partitions the space into smaller, more manageable regions that make up each branch of the tree. This analysis gives insight into the components that affect phosphorus concentration the most for each hydrologic condition. The results for all of the sampling events are shown in Table 3.3 with the ranking of significance for each component.

Table 3.3: Summary of critical anthropogenic and spatial factors affecting phosphorus concentration along the Cache La Poudre River for each sampling event

Component Significance			
Date	**Primary**	**Secondary**	**Tertiary**
4/23/10	CAFO Capacity	CAFO Canal Distance	WWTP Capacity
5/19/10	WWTP Stream Distance	CAFO Capactiy IDW[1] Overland Distance	WWTP Capacity
6/4/10	WWTP Stream Distance	WWTP Capacity	CAFO Stream Distance
6/18/10	CAFO Capacity IDW Overland Distance	CAFO Canal Distance	CAFO Stream Distance
7/26/10	WWTP Capacity IDW Stream Distance	CAFO Capacity IDW Canal Distance	CAFO Overland Distance

[1] IDW: Inverse Distance Weighted

As shown in Figure 3.6, the most important variable impacting phosphorus concentrations for the first sampling (precipitation event) was CAFO capacity although CAFO canal distance, WWTP capacity and CAFO overland distance were also important. For the fifth sampling event (irrigation dominated), taken during low river flow conditions during irrigation, the most important variables were WWTP capacity and CAFO capacity. It appears that unless there is a precipitation event, WWTP capacity will determine the TP concentration in the system, while CAFO capacity and irrigation canal distance will determine TP during precipitation events. This could also explain the outcome of the fourth sampling events tree regression, which shows all CAFO variables to be most important. Sampling for this event occurred four days after a rain fell throughout the watershed.

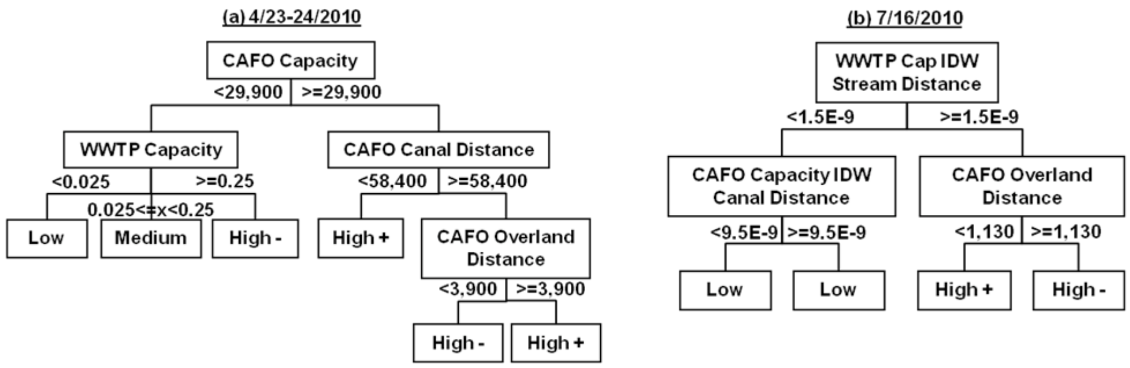

Figure 3.6: Regression tree analysis for the 4/23-24/2010 (precipitation event) and 7/26/2010 (End of runoff and middle of irrigation period) sampling events, where Low is 0 to 0.2 mg/l TP, Medium is 0.2 to 0.4 mg/l TP and High is 0.4 to 1.0 mg/l TP and High+ is greater than 1 mg/l TP.

In the presence of significant rainfall, nonpoint sources have a greater influence on phosphorus concentrations. As the number of animals impacting a location increases, the importance of geospatial factors (e.g. irrigation ditch/canal and overland distance) also increases as shown in Figure 3.6. As the number of animals impacting a location decreases, the importance of point sources (WWTPs) increases. The final sampling event also produced high concentrations of phosphorus, but these results were not due to rainfall. These significantly higher concentrations are likely due to low flow conditions decreasing the WWTP dilution effect. Therefore, it may be inferred that hydrologic events contributing to the occurrence of significantly higher phosphorus levels in surface water include precipitation and low flow conditions.

Multiple Linear Regression The nonlinear tree regression was used to rank critical anthropogenic and spatial factors impacting phosphorus concentrations in the Cache La Poudre River basin. Furthermore, a multiple linear regression was used to determine how well these key factors explain total phosphorus concentrations. Following the tree regression analysis results, spatial distances were used directly or to inverse distance weight anthropogenic factors in the multiple linear regression equations (Equations 1-5 shown in Figure 3.7)

Sampling Event/ Equation Number	Multiple Linear Regression (MLR) Equation	Coefficient of Determination (R^2)
1	$y = a_0 + a_1 \sum_{j=1}^{n} C_{j,CAFO} + a_2 \sum_{j=1}^{n} C_{j,WWTP} + a_3 \sum_{j=1}^{n} d_{j,CAFO_{OL}} + a_4 \sum_{j=1}^{n} d_{j,CAFO_{Canal}} + a_5 \sum_{j=1}^{n} d_{j,CAFO_{Stream}} + a_6 \sum_{j=1}^{n} d_{j,WWTP_{Stream}}$	0.60
2	$y = a_0 + a_1 \sum_{j=1}^{n} C_{j,WWTP} + a_2 \frac{\sum_{j=1}^{n} \frac{C_{j,CAFO}}{d_{j,OL}}}{\sum_{j=1}^{n} \frac{1}{d_{j,OL}}} + a_3 \sum_{j=1}^{n} d_{j,CAFO_{Canal}} + a_4 \sum_{j=1}^{n} d_{j,CAFO_{Stream}} + a_5 \sum_{j=1}^{n} d_{j,WWTP_{Stream}}$	0.72
3	$y = a_0 + a_1 \sum_{j=1}^{n} C_{j,WWTP} + a_2 \frac{\sum_{j=1}^{n} \frac{C_{j,CAFO}}{d_{j,Canal}}}{\sum_{j=1}^{n} \frac{1}{d_{j,Canal}}} + a_3 \sum_{j=1}^{n} d_{j,CAFO_{OL}} + a_4 \sum_{j=1}^{n} d_{j,CAFO_{Stream}} + a_5 \sum_{j=1}^{n} d_{j,WWTP_{Stream}}$	0.84
4	$y = a_0 + a_1 \frac{\sum_{j=1}^{n} \frac{C_{j,WWTP}}{d_{j,Stream}}}{\sum_{j=1}^{n} \frac{1}{d_{j,Stream}}} + a_2 \frac{\sum_{j=1}^{n} \frac{C_{j,CAFO}}{d_{j,OL}}}{\sum_{j=1}^{n} \frac{1}{d_{j,OL}}} + a_3 \sum_{j=1}^{n} d_{j,CAFO_{Canal}} + a_4 \sum_{j=1}^{n} d_{j,CAFO_{Stream}}$	0.59
5	$y = a_0 + a_1 \frac{\sum_{j=1}^{n} \frac{C_{j,WWTP}}{d_{j,Stream}}}{\sum_{j=1}^{n} \frac{1}{d_{j,Stream}}} + a_2 \frac{\sum_{j=1}^{n} \frac{C_{j,CAFO}}{d_{j,Canal}}}{\sum_{j=1}^{n} \frac{1}{d_{j,Canal}}} + a_3 \sum_{j=1}^{n} d_{j,CAFO_{OL}} + a_4 \sum_{j=1}^{n} d_{j,CAFO_{Stream}}$	0.65

Figure 3.7: Multiple linear regression equations for each sampling event using critical anthropogenic and spatial factors obtained from the nonlinear tree regression analysis.

In Equations 1-5, the capacities of animal CAFOs (in number of animals) and WWTPs (in MGD) are represented by C_{CAFO} and C_{WWTP}, respectively. The overland distance, canal distance, and stream distance from each CAFO to the sampling location on the river (in km) are denoted by d_{CAFO_OL}, d_{CAFO_canal} and d_{CAFO_stream} respectively. Similarly, the stream distance from WWTPs to the sampling location (in km) is denoted by d_{WWTP_stream}.

The most important variables for the first sampling event according to the tree regression analysis were CAFO capacity, CAFO canal distance, and WWTP capacity. These three variables along with WWTP stream distance provided the highest R^2 values in the multiple linear regression (MLR) analysis (Equation 1, 3.7). These four values alone with no inverse distance weighting gave a R^2 value of 0.59. When CAFO overland distance and CAFO stream distance were added, the R^2 value increased slightly to 0.60.

Equation 1 shows that all variables were used with no inverse distance weighting, indicating that contribution rather than attenuation was occurring with distance. Table A.2 in the supplementary material shows the relative importance of each variable when added one by one into the MLR equation. The order that each variable was added into the equation was based on the tree regression results. When only CAFO capacity was used, R^2 was 0.34. The next variable added was CAFO canal distance, which produced a R^2 value of 0.41. R^2 value did not increase significantly again until WWTP stream distance was added ($R^2 = 0.59$). According to the tree regression, WWTP capacity was the third most important variable, however the MLR suggests that WWTP stream distance is more important. However, it could just be that the combination of these variables is what produces the higher regression coefficient. As mentioned previously, all variables had to be used separately in the MLR equation with no inverse distance weighting. This could be explained as the distances indicating source areas rather than sink areas due to the confounding nature of stream distance with overland runoff. Attenuation of phosphorus cannot occur due to mixing and continual inputs from runoff as the water flows downstream. This is also supported by Figure 3.5, which shows minimal attenuation downstream.

According to the tree regression analysis, WWTP stream distance, CAFO capacity inverse distance weighted with overland distance, and CAFO stream distance were the three most critical variables for the second sampling event. This was supported by the MLR analysis. The final variables used are shown in Equation 2. Table A.2 in the supplemental information shows that the R^2 value only significantly increased when each of these three variables were added. R^2 values greater or equal to 0.7 were only found when CAFO canal distance and CAFO stream distance were used directly and CAFO capacity was inverse distance weighted with CAFO overland distance in the regression equation. It made no difference whether or not WWTP stream distance was direct or used in inverse distance weighting, but the highest R^2 value was obtained when WWTP stream distance was a separate variable and not used to inverse distance weight WWTP capacity.

WWTP stream distance, WWTP Capacity, and CAFO stream distance were presented as the most critical anthropogenic and spatial variables for the third sampling event by the nonlinear tree regression. This was supported by the MLR analysis (Equation 3). When only WWTP stream distance was used, $R^2 = 0.69$; and when WWTP capacity was included in the regression equation, R^2 values were above 0.75. This sampling event also produced the highest overall regression coefficient ($R^2 = 0.84$).

The most important variables impacting phosphorus concentrations in the fourth sampling event were CAFO capacity inverse distance weighted with overland distance, CAFO canal distance, and CAFO stream distance. These variables did not agree with the multiple linear regression analysis (Equation 4). WWTP capacity needed to be inverse distance weighted with WWTP stream distance (implying attenuation) in order for the R R^2 value to be above 0.50. The top three variables according to the tree regression only produced an R^2 value of 0.31. The highest R^2 values were achieved when CAFO canal distance was input directly into the regression equation and when CAFO capacity was direct or inverse distance weighted by overland distance. However, it was not until the WWTP variable was input into the equation that R^2 increased to 0.59.

WWTP capacity, CAFO capacity, and CAFO canal distance were the most significant variables in the tree regression analysis for the fifth sampling event. The multiple linear regression analysis also seemed to indicate that this event was dominated by WWTP activity. Only when WWTP capacity was inverse distance weighted (implying attenuation with distance) were R^2 values greater or equal to 0.60. The highest coefficient of determination ($R^2 = 0.65$) was obtained when CAFO capacity was inverse distance weighted with CAFO canal distance (Equation 5). Obtaining best possible coefficient of determination ($R^2 = 0.65$) required the inclusion of all variables in the regression equation. This sampling event produced the same three most important variables as the first sampling event. However, inverse distance weighting was used for the regression analysis while it was not used for the data produced from sampling during a precipitation event. It appears that during low flow conditions with no rainfall, attenuation of phosphorus occurs downstream from the source.

3.4. Conclusion

The results of this study suggest that the impacts of CAFOs and WWTPs on phosphorus concentrations throughout a watershed can differ significantly under varying hydrologic conditions. During a precipitation event, CAFO capacity and canal distance appeared to be the most important factors for determining phosphorus concentrations in the Poudre River. The significantly higher phosphorus concentrations during the rainfall event and the importance of canal distance as a geospatial variable substantiate the assumption that irrigation ditches are important transport mechanisms for phosphorus in arid regions where natural tributaries are rare. CAFOs would not have as great an impact on surface water quality without a mechanism for the transport of nutrients and other contaminants. Irrigation ditches provide this mechanism and should be analyzed and managed more closely as regional, state, and local agencies prepare to develop and implement phosphorus regulations and standards.

In the absence of rainfall and during low river flow conditions, WWTPs have a greater impact on phosphorus concentrations. Additionally, as regulations and standards require monitoring programs to be put into place, it is important to beaware of hydrologic conditions when obtaining phosphorus data on a continual basis because precipitation events coupled with irrigation practices and low flows may increase phosphorus concentrations above required levels. This study also shows the importance of location when choosing sampling sites. Geospatial variables such as the intensity of anthropogenic activities (CAFO, WWTP) and surface flow distances are key in representing the fate and transport of hydrophobic compounds. Geospatial analysis presents an opportunity for selecting sampling sites with maximum information content. The methods used could also contribute to more effective placement of pollution control strategies in watersheds.

4. Relative Phosphorus Load Input from Wastewater Treatment Plants to the Cache la Poudre River

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Abstract Excess nutrients are one of the leading sources of water quality impairment and the United States Environmental Protection Agency (USEPA) has been working with states to develop nutrient criteria for wastewater treatment plants. The Colorado Department of Public Health and Environment (CDPHE) is scheduled to establish nutrient regulations in 2012 and a stream standard of 0.16 mg/L of total P (TP) concentration has been proposed for the warm water rivers in the state. The objectives of this study were to monitor TP concentrations and loads along the Cache la Poudre (CLP) River as it flows from the pristine upstream area through urban regions and finally through a mixture of agricultural and urban land uses. The study attempts to evaluate the sources and influences of TP under different hydro- logic conditions. Nine sampling events were conducted from April 2010 to May 2011 to capture the influence of various flow and precipitation conditions on aqueous and riverbed sediment TP concentrations. During mid-range flows and dry conditions, wastewater treatment plants (WWTPs) were the major sources of TP but other sources were observed to be more significant under high flow and rain conditions ac- cording to a load analysis. Reducing the TP load from WWTPs through regulation will only marginally impact the TP load in the river and therefore it appears that other sources (e.g. stormwater and agricultural runoff) will need to be addressed before the aquatic life-based stream standard can be achieved. The study indicates a need for real-time load monitoring in a watershed that could lead to flexibility in WWTP discharge limits based on the overall TP load in the river from other sources.

keywords: Phosphorus, Nutrient Regulations, Wastewater Treatment Plants, Load Analysis, Cache la Poudre River

4.1. Introduction

The Environmental Protection Agency's (EPA) 305(b) reports consistently rank excess nutrients as a leading water quality impairment in assessed rivers, lakes and estuaries [131]. Increases in the concentration of nutrients are the primary cause of eutrophication of water bodies [98, 17, 27, 26]. Excess eutrophication in Colorado's freshwater lakes, reservoirs and streams is chiefly due to phosphorus load- ing [30]. Eutrophication frequently results in algal or cyanobacteria blooms in the summer months leading to anoxia, fish kills, murky water and the depletion of flora and fauna [17, 81, 64]. In drinking water sources, the increased algae growth is a public health concern, requiring additional chlorination creating more disinfection by-products. Taste and odor issues also increase with excess algae and the activity of microbes can potentially lead to additional health concerns.

In 1998 the EPA began to address the need for a national nutrient management program to control eutrophication. In 2001, the EPA placed the responsibility of determining an acceptable nutrient value on the individual states due to the variability of total P discharges that exists throughout the country due to hydrologic conditions [69], geology [48], agricultural [68, 70] and urban land uses [42, 118].

A nutrient criteria work group was established by the Colorado Department of Public Health and Environment (CDPHE) to develop phosphorus and nitrogen limits to best protect Colorado’s waterways and serve the public interest. Studies have shown that an upper limit of 0.16 mg/l TP is required for healthy warm water river ecosystems in

Colorado [80]. The CDPHE has been working to determine a proposed point source limit of total phosphorus necessary to protect uses.

The goal of this study was to examine the role of TP loads from WWTPs on the Poudre River and to determine the impact of temporal, hydrologic and spatial variations. An extensive survey of the Poudre River and WWTPs was done over a more than a year to estimate cumulative loads and contributions from each known source. Finally, projections on the impact of proposed TP reductions at WWTPs on the Poudre River were made using cumulative load calculations.

4.2. Materials and Methods

Study Area The Cache La Poudre (CLP) River is located in the front range of Colorado and is a well-suited watershed to study the occurrence and transport of nutrients within a river. The CLP River originates in the Rocky Mountains, ap- proximately 60 miles west of where the river joins the South Platte River. The value of studying this watershed is the presence of a distinct pristine region upstream of Fort Collins, an urban corridor through Fort Collins that includes four wastewater treatment plants of varying sizes and a downstream section that is dominated by agricultural land uses [144]. A map of the watershed and the associated land uses is shown in Figure 4.1.

The limit of TP concentration in this area has been proposed as 0.16 mg/L for rivers based on ecological and aquatic life concerns. The potential sources of TP in the study area are WWTPs and nonpoint sources, such as storm water from the built environment and agricultural runoff from confined animal feeding operations (CAFOs) and cultivated cropland. 15 sampling sites were selected to study phosphorus load inputs from the relatively pristine area (sample ID 1-3) as a background load, the urbanized area (sample ID 4-10) from the point sources such as WWTPs and storm water, and the agricultural area (sample ID 11-15) from agricultural runoff through irrigation return flows.

The cities in the study area have a total of 5 WWTPs. As shown in Figure 4.2, the most upstream WWTP is the Mulberry Water Reclamation Facility (MWRF) which has a capacity of 6 mgd but it has been offline during the study period due to renovation so the water from MWRF was sent to the Drake Water Reclamation Facility (DWRF) which has the largest capacity (23 mgd) among the 5 WWTPs and highest average annual summer flow (18 mgd). The effluents from DWRF and South Fort Collins Sanitation District (SFCSD), design capacity of 4.5 mgd, are discharged into Fossil Creek Reservoir and the water enters the Poudre River from there. Boxelder Sanitation District (BSD) therefore is the most upstream WWTP since the MWRF has remained closed.

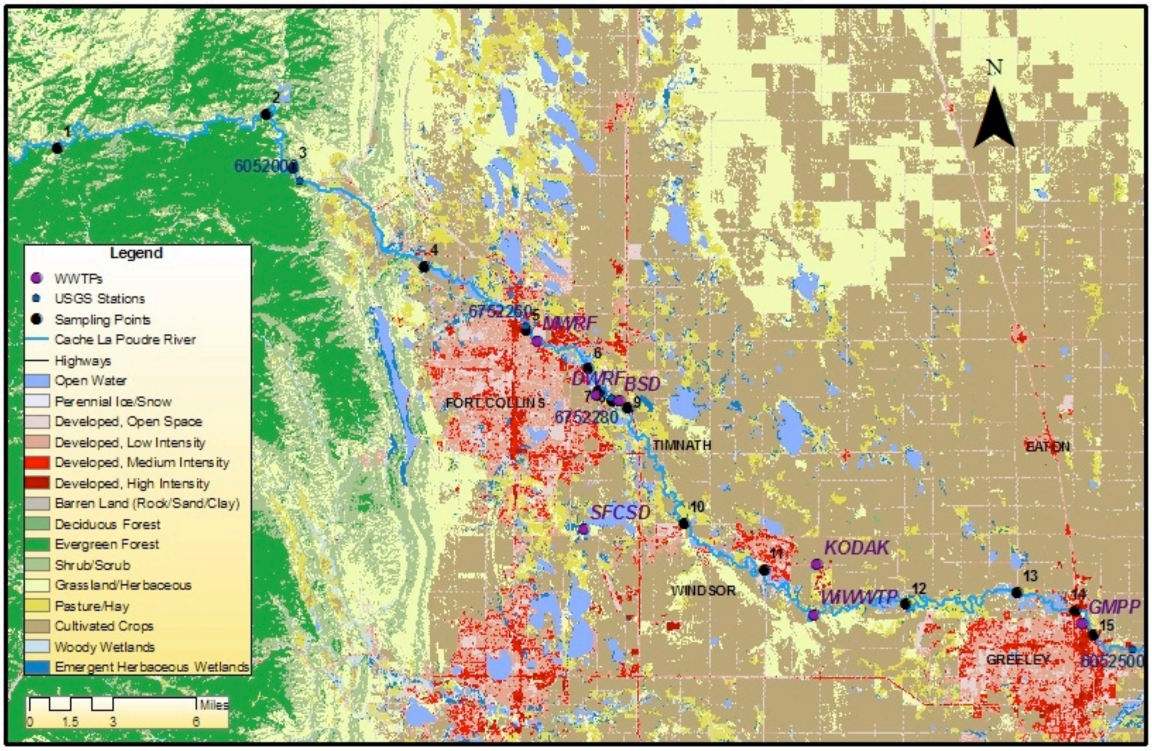
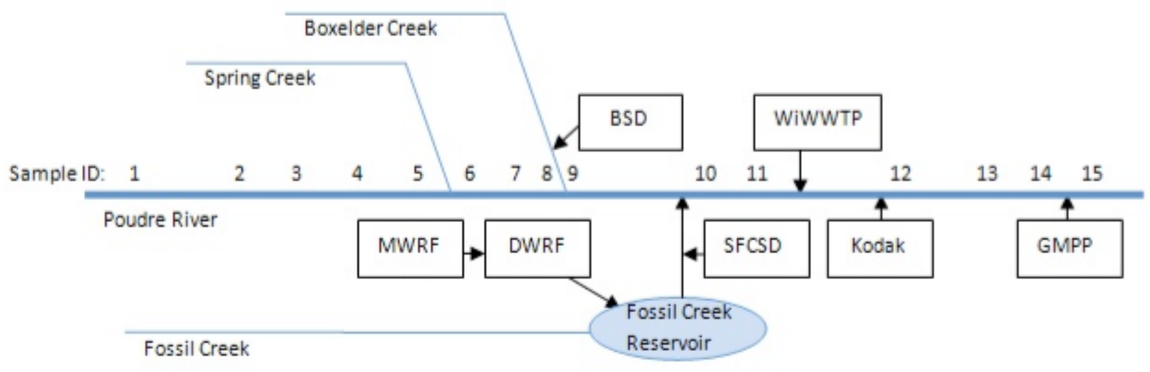


Figure 4.1: Map of study area showing land use, WWTPs, USGS stations and 15 sampling points along the Cache la Poudre River.

Sample sites 1 through 8 are located upstream of all WWTPs and four WWTPs are clustered between sampling sites 9 and 10. The WWTP load analysis is done with results from site 10 and the three upstream WWTPs. The Windsor wastewater treatment plant (WiWWTP) is located between sites 11 and 12 but the capacity is low at 2.8 mgd and the average flow is 1.1 mgd.



MWRF: Mulberry Water Reclamation Facility
DWRF: Drake Water Reclamation Facility
BSD: Boxelder Sanitary District
SFCSD: South Fort Collins Sanitary District
WiWWTP: Windsor Wastewater Treatment Plant
GMPP: Greeley Meat Packing Plant

Figure 4.2: Map of study area showing land use, WWTPs, USGS stations and 15 sampling points along the Cache la Poudre River.

Sampling Events Nine sampling campaigns were conducted between April, 2010 and May 2011 to quantify TP load and concentration variability under different hydrologic conditions. The hydrologic conditions on the event dates are described in Table 4.1. Sampling dates were chosen to represent all 5 classes of hydrologic conditions; high flows, moist conditions, mid-range flows, dry conditions and low flows under various precipitation and irrigation conditions. The flow duration curves in Figure 4.3 were developed from 100-year flow data from 1999 to 2009 collected from USGS station 06052000 for the upstream and 06052500 for the downstream. As shown in the figure, there is a difference between upstream and downstream flow rates of the river, due to irrigation and other water transfers. Therefore the hydrologic conditions can be different on the same day.

The first sampling campaign date (April, 2010) was selected when the snowpack started to melt and there was high precipitation in the study area resulting in moist conditions in the upstream and high flows in downstream sections of the river. The second sampling campaign was conducted under high flows in upstream and downstream and when the snow water equivalent (SWE) was at a peak for the year. SWE is the volume of water equivalent of snowpack that was present in the headwater. SWE is important especially for the study area that is located in a semi-arid region because the major source of the river water is from the snowpack accumulated during winter months. Sampling events 5 and 7 represent the mid- range flow conditions and sampling events 6 and 8 correspond to dry conditions in the downstream section. Figure 4.3 shows the hydrologic conditions and flow rates in upstream and downstream sections of the river on the nine event dates.

It is important to note that downstream flows (USGS 06052500) exceeded the upstream flow (USGS 06052000) during mid-range flow, dry conditions and low flows (Figure 4.3) and the flow decreased through the middle of the stream and increased again in the downstream on most of the sampling event dates (Table 4.1). This phenomenon was clear in event 1 as the flow in the upstream section (USGS 06052000) was 164 ft3/s, decreased to 46 and 88 ft3/s as the stream went through the City of Fort Collins located in the middle of the study area and then increased to 493 ft3/s which is about 3 times that of the upstream flow. From this observation, it is believed that there are irrigation flows taken above the upstream gage and significant return flows in the downstream reach of the CLP River.

Table 4.1: Summary of hydrologic conditions along the Cache La Poudre River for each sampling event

Event	**Date**	**USGS 06052000** [1] **(ft^3/s)**	**USGS 06052260** [2] **(ft^3/s)**	**USGS 06052260** [3] **(ft^3/s)**	**USGS 06052260** [4] **(ft^3/s)**
1	4/23/10	164	46	88	493
2	5/19/10	950	1010	885	853
3	6/4/10	1960	873	716	863
4	6/18/10	2130	1550	1290	2140
5	7/16/10	478	84	72	74
6	9/17/10	40	41	23	60
7	2/22/11	-	19	2.4	75
8	4/26/11	112	35	29	57
9	5/12/11	543	103	141	343

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[1] Cache la Poudre River at canyon mouth near Fort Collins

[2] Cache la Poudre River at Fort Collins

[3] Cache la Poudre River above Boxelder Creek near Timnath

[4] Cache la Poudre River near Greeley

Table 4.2: Summary of hydrologic conditions along the Cache la Poudre River for each sampling event.

Event	**Date**	**Irrigation [1] (ft^3/s)**	**Average SWE (in)**	**Antecedent 3-Day Rainfall (in)**	**Water Temperature [2] (^{o}/C)**
1	4/23/10	118	18.7	1.20	6.8
2	5/19/10	0	24.8	0.4	10.6
3	6/4/10	366	13.7	0	9.4
4	6/18/10	11.6	0	0	11.7
5	7/16/10	108	0	0.02	17.2
6	9/17/10	20.4	0	0.03	14.5
7	2/22/11	0	19.5	0.02	0.5
8	4/26/11	71.7	37.6	0.32	
9	5/12/11	274	39.9	1.21	

[1] Colorado Department of Water Resources measured at 30 ft. Parshall Flume

[2] Measured at the City of Fort Collins Water Treatment Facility Poudre River intake at Gateway Park

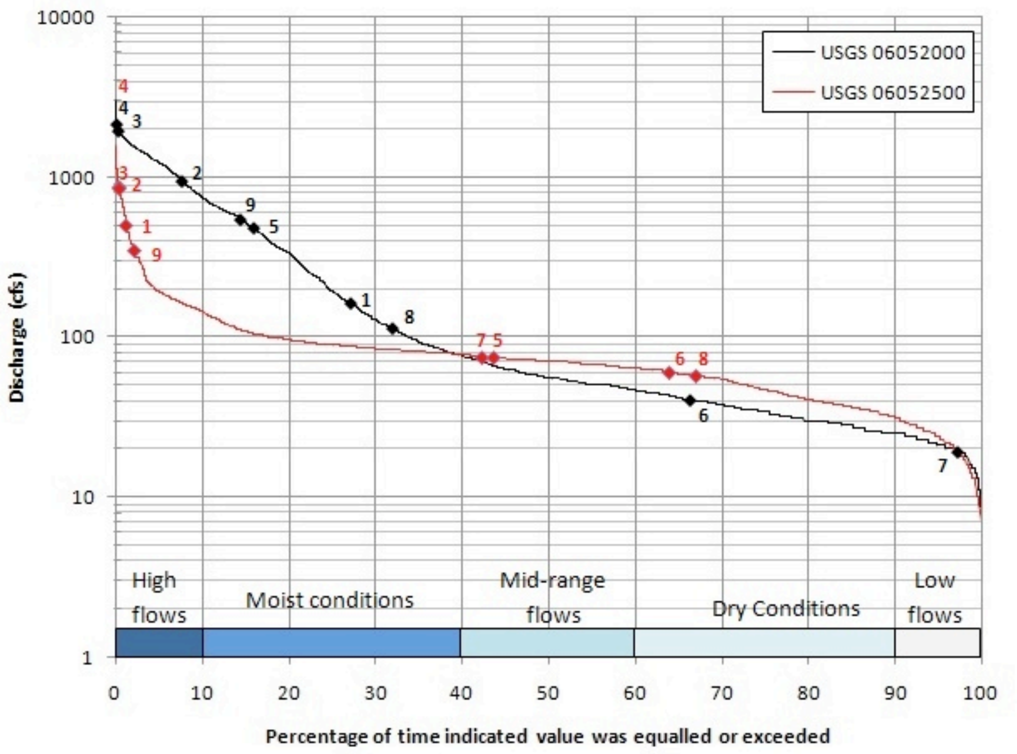

Figure 4.3: Percentage of flow exceedence curve, flow rates and hydrologic conditions on the sampling event dates. Discharge of event 7 at USGS station 06052000 was replaced by a record at USGS station 0672260 due to ice.

Aqueous and Sediment TP Analysis Aqueous and river bed sediment samples were collected from the middle of the stream and transferred to 50ml Nalgene bottles and plastic Ziploc bags, respectively, using a grab sampling method. Collected aqueous samples were then transported to the laboratory and kept at 4oC until measured. Sediment samples were air dried as soon as they were transported to the laboratory, ground and sieved through 2mm sieves and kept at 4oC with aqueous samples until analysis. Aqueous TP was measured using an acid persulfate digestion method (Hach method 8190; USEPA standard method 4500 P-E; Eaton, 2005) with a 0.06- 3.5 mg/L range TP analysis set (Hach Company, Loveland, CO). For the sediment analysis, microwave digestion method (Littau and Engelhart 1990) was used prior to the TP measurement using the colorimetric method (Hach Company, Loveland, CO).

TP Load Duration Curve The load duration curve for the downstream sample site (sample ID 11-15) was created using flow data that were collected from 1999- 2009 at USGS station 06052500 multiplied by the proposed 0.16 mg/L TP stream standard concentration limit in the river in the study area. The background load was estimated using the same flow data used for the load duration curve multiplied by 0.13 mg/L, the background concentration that is the average concentration from sample IDs 1 and 2 for the 9 events. Sample sites 1 and 2 were selected for estimation of the background concentration because these sites are located on the South Fork of the CLP River, upstream of the confluence with the North Fork. These sites are considered pristine since there is no significant source of phosphorus in the area. Since the North Fork is influenced by agricultural areas and septic systems, sample sites downstream of the confluence were excluded from the background estimation.

Annual Cumulative Load Analysis in the Poudre River The cumulative annual phosphorus load was estimated at site 10, located just down stream from the first four WWTPs. Daily Poudre River discharge data from USGS 06752280 and the periodic aqueous total phosphorus concentrations sampled were used to estimate a daily phosphorus load. Although phosphorus concentrations in a river show variability, for this analysis it was assumed the phosphorus concentration at site 10 remained constant between sampling events. The daily total phosphorus load was integrated using a basic trapezoidal integration method to estimate the cumulative annual total phosphorus load in the Poudre River at site 10.

Annual Cumulative Load Analysis from WWTPs WWTP effluent discharge rates and total phosphorus concentrations [7], averaged monthly, were used to estimate a monthly phosphorus load. The cumulative annual phosphorus load was estimated by integrating the monthly phosphorus load using a basic trapezoidal integration method.

4.3. Results and Discussion

The TP concentration profiles in the Poudre River are shown for all nine sampling campaigns in Figure 4.4. Concentrations of TP upstream of WWTPs with only light urban and minimal agricultural influences (sample ID 1-8) were relatively constant in the range of 0.07-0.26 mg/L with 0.036 of standard deviation. However, downstream of the major WWTP inputs (sample ID 9-10) where there are significant urban and agricultural influences (sample ID 9-15), the TP concentrations increase significantly. The first peak was observed at a maximum of 1.49 mg/L downstream of BSD (sample ID 9) except for high flows when dilution is more important. The second peak was at the downstream of Fossil Creek Reservoir (sample ID 10) where MWRF, DWRF and SFCSD discharge their effluents into the river and the TP concentration ranged from 0.34 to 3.1 mg/L.

As seen in events 6 and 7, the TP concentrations in the river are more sensitive to WWTP effluents during dry conditions (no precipitation), low flows and when there is no irrigation. The three peaks were observed at the downstream of WWTPs (sample ID 9, 10 and 12) and the highest peak of event 7 at the downstream of BSD (sample ID 9) was due to the low river flow of 2.4 ft3/s. Attenuation from the peaks was observed during mid-range flows and dry conditions downstream of WWTPs (event 5-8) while downstream TP concentrations were relatively constant or increased from the peak for high flows (event 2-4, 9), most likely due to inputs from agricultural return flows during the irrigation season. However TP concentrations decreased slightly in the downstream fraction of the river during event 1 even though it was during higher flows due to a rainfall event.

In Figure 4.4, the instantaneous TP loads are shown for each sampling event at each sampling location. The instantaneous TP load was estimated by multiply- ing the flow obtained from the closest USGS gauging station by the measured TP concentration data at that point in the river. The calculated TP load depends on the river flow rates and therefore a significant difference of TP load under high flows from other hydrologic conditions were observed even in the upstream of river. The range of TP loads upstream of WWTPs during high flows was 24-1055 kg/d and 98-4136 kg/d in the downstream section. In comparison, the range of TP loads upstream for non-high flow condition was 0.8-52 kg/d in upstream and 5-546 kg/d in the downstream section.

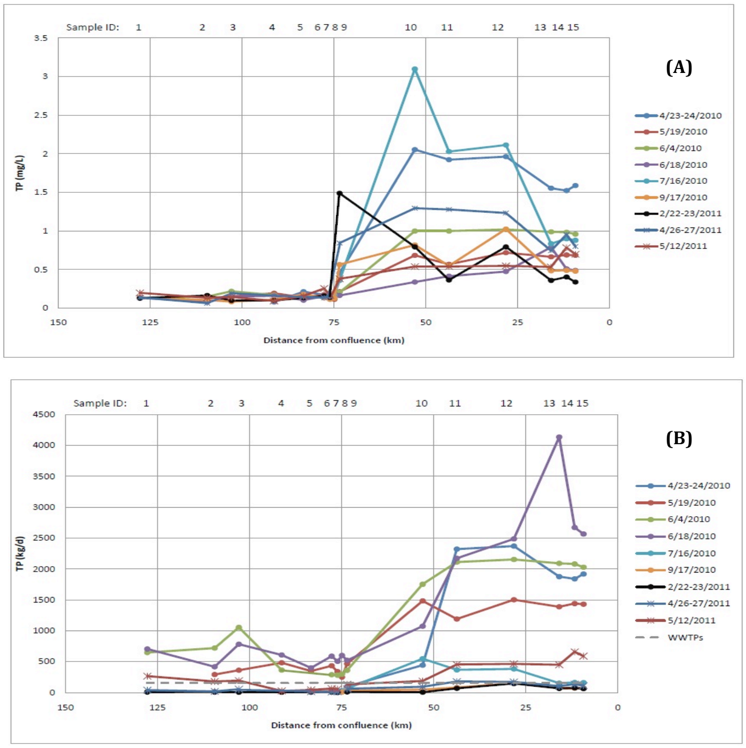

Figure 4.4: (A) TP concentrations and (B) TP loads (kg/d) along Poudre River on different event dates. Discharge data from USGS 06052000 was used for sample ID 1-3, USGS 06752260 for sample ID 4-6, USGS 06752280 for sample ID 7-10, USGS 06052500 for sample ID 11-15.

Although Figure 4.4 shows that a few TP concentrations for high flow events were lower than dry condition concentrations, a significant amount of TP enters the river during high flow periods that corresponds with the the peak irrigation and urban runoff seasons. For high flows, the load inputs were significantly greater than 152 kg/d, the estimated daily load from the five WWTPs. The TP load from WWTPs will vary but it is relatively constant on an annual basis so it is believed that there are other major sources of TP that enters the river during high flow conditions. The peak of TP load in the downstream section was observed on event 4 when the downstream flow peaked at 2140 ft3/s. During mid-range flows and dry conditions, the downstream TP loads were similar to or lower than the loads from WWTPs except event 5 when the influence of irrigation was greater than other events in mid-range flows or dry conditions. Figure 4.5 presents the ranges of TP concentration (mg/L) using box plots in the upstream and the downstream of WWTPs under various hydrologic conditions with different flow rates. For the 9 events, TP concentrations upstream from the municipal wastewater plants (site 10) were relatively constant and ranged from 0.07 to 0.26 mg/L and the median was 0.15 mg/L. However downstream TP concentrations varied from 0.17 to 3.1 mg/L and the median was 0.75 mg/L. The ranges of downstream TP concentrations under high flow conditions were relatively low which indicates a constant input of TP downstream, most like due to irrigation return flows, and less or no attenuation along the river. Compared with Figure 4.4, it was found that there was attenuation in the downstream when ranges of TP concentration were wide (event 1, 5-8).

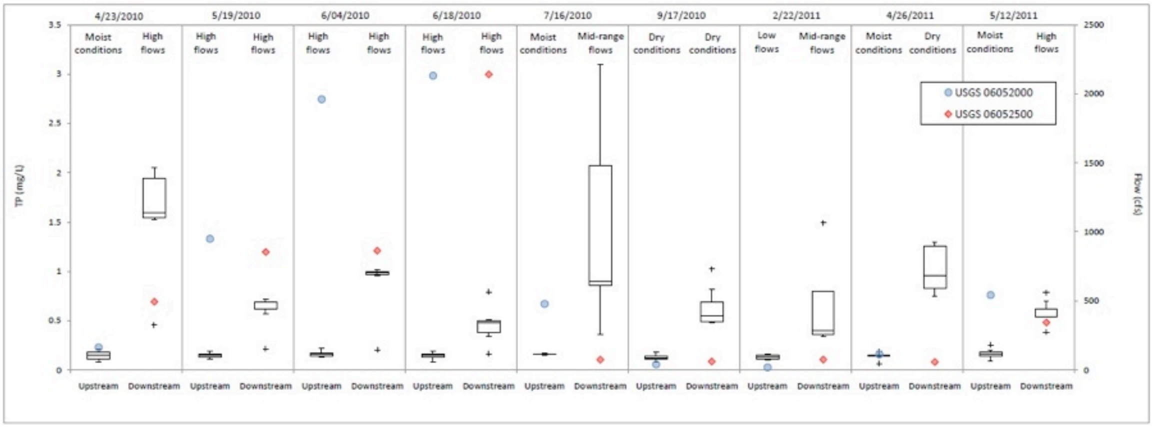

Figure 4.5: Ranges of TP concentrations (mg/L), flow rates (cfs) and hydrologic conditions in upstream (USGS 06052000) and downstream (USGS 06052500) of the CLP River on each event date.

The ranges of TP loads (kg/d) and flow rates for the various hydrologic conditions upstream and downstream are shown in Figure 4.6. The box plots of the upstream section are the loads calculated by multiplying the upstream flow data from USGS station 06052000 by the measured TP concentration from sample IDs 1-3 which correspond to the flow. The downstream load box plots are estimated using the downstream flows collected from USGS station 06052500 and multiplying this by the TP concentration from sample IDs 11-15. The TP concentration data from sample IDs 4-10 were not used for the TP load box plots due to the difference of flow rates from either station. The TP loading limits on the event dates were evaluated by multiplying the flow data in upstream (USGS 06052000) and downstream (USGS 06052500) by the suggested 0.16 mg/l of TP concentration limit in the river.

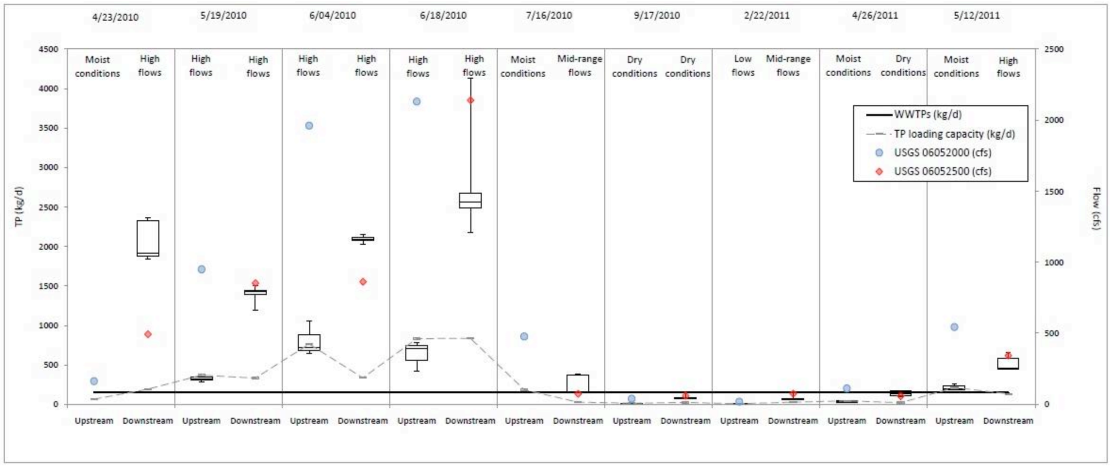

Figure 4.6: TP load box plots, loading capacity based on 0.16 mg/l TP concentration limit and flow rates in upstream and downstream flows durring nine sampling events

During mid-range flows and dry conditions, the TP load from WWTPs was clearly above the estimated TP loading limit; however, is below the limit for high flows. Form this result, it is believed that there is a large input from other sources during high flows and the amount of input is more significant than the load from WWTPs on an annual basis. As seen in Figure 4.6, downstream TP loads were never been below the estimated TP loading limit on 9 event dates and the limits were in the range of upstream TP loads except event 2, 4 and 6 which means that even the upstream TP loads exceeded the limit.

To further analyze overall trends of downstream TP loads for the different hydrologic conditions, the downstream loads calculated for Figure 6 were grouped into 3 hydrologic classes; high flows (event 1-4, 9), mid- range flows (event 5, 7) and dry conditions (event 6, 8). The grouped TP loads are shown in the box plots in Figure 7. The load duration curve and the background load curve were created as in the Materials/ Methods section to study the difference between the observed load data and the estimated loading capacity using the proposed stream standard for TP concentration. The median TP load of the grouped data for mid- range flows was 148kg/d and ranged from 382 to 60kg/d, and the median load for dry conditions was 110kg/d and ranged from 180 to 70kg/d. The median TP load for mid-range flow (2 events) was comparable to the estimated TP loads from WWTPs and the median TP load during dry conditions (2 events) was less than WWTP loads. From this observation, it was assumed that WWTPs are the main source of TP in the river during mid-range flows and dry conditions. Also, it appears that for low flow (dry) conditions, the sediment is acting as a P sink since the load in the river is less than that from WWTPs. For higher flows that correspond with expected urban and agricultural runoff seasons (5 events), TP loads ranged from 4140 to 450 kg/d, and the median was 1920kg/d, greatly exceeding the estimated annual TP load from WWTPs.

As seen in Figure 4.7, the difference between the TP loading limit and the background load is not large enough to receive TP load from other sources. Even with a significant reduction in WWTP TP levels, the load limit cannot be achieved because of the background load and the TP load from other sources such as agricultural and storm water nonpoint sources.

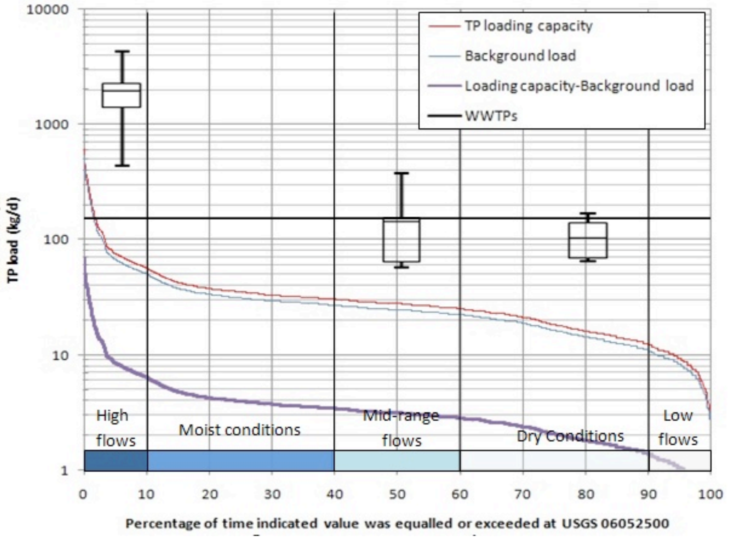

Figure 4.7: TP load duration curve with TP loading capacity based on flow rate at USGS station 06052500, 0.16 mg/l TP stream standard, background load based on 0.13 mg/l measured concentration in pristine area and box plots of TP loads using grouped observed downstream concentration for the three different hydrologic conditions; high flows, mid-range flows and dry conditions for event 1-9

TP loads during dry conditions were clearly lower than the WWTP inputs as shown in Figure 4.7. If it is assumed the only inputs are from WWTPs, there was a 42 kg/day difference between the average annual TP loads from WWTPs and the estimated TP loads from the collected data. House and Denison [57] reported that phosphorus tends to accumulate in bed sediment under low flow conditions due to the comparatively long water-bed contact time which facilitates settling of suspended matter and P adsorption to clays. Based on this study and the observation of aqueous TP load reduction, sediment TP mass concentrations were examined to see how the sediment acts as a sink for TP (Figure 4.8).

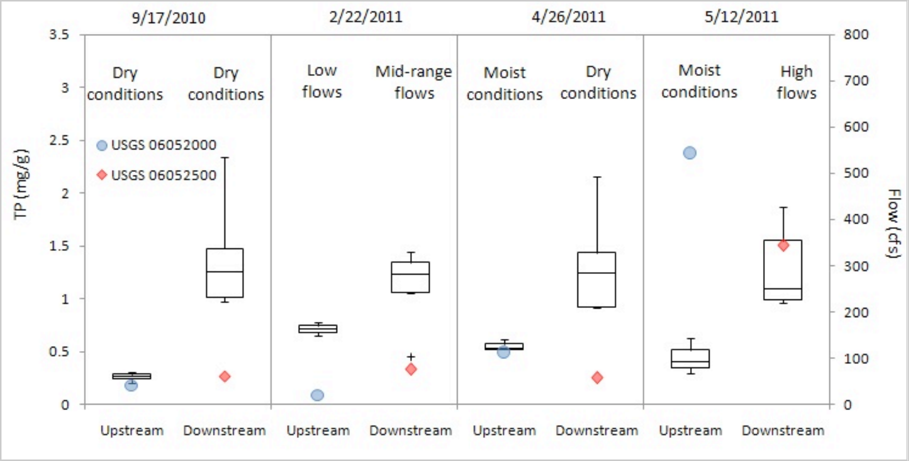

Figure 4.8: Sediment TP concentration (mg/g) and flow rates (cfs) in upstream (sample ID 1-3) and downstream (sample ID 11-15) of the CLP River for the four events.

TP concentration in the river bed sediment increased in the downstream section for the 4 measured events. The medians of upstream (sample ID 1-3) sediment TP concentrations for the observed events were in the range of 0.27-0.71 mg/g and the downstream medians (sample ID 11-15) ranged from 1.09 to 1.25 mg/g. From the data presented in Figure 4.8, it is believed that a significant fraction of TP in the river is adsorbed and stored in the river bed sediment. Previous studies have also shown a similar dynamic equilibria of aqueous and sediment phosphorus concentrations (Hutchinson, 1957; Edmond et al., 1981; Boyton and Kemp, 1985; Jordan et al., 1991). This has been referred to as the phosphate buffer mechanism (Carritt and Goodgal, 1954; Froelich, 1988) and has important implications on phosphorus loading to the river.

When the riverbed sediment itself acts as a sink and a source of TP under different hydrologic conditions, monitoring sediment TP is valuable to understand TP loads in the river. Since many other factors, such as equilibrium P concentration [63, 39], exchangeable Ca, Fe and Al [75], organic matter [125], and sediment particle sizes [87], are important, the effect of sediment P could not be fully explained with this study.

Figure 4.9 shows an estimate of the cumulative annual background and WWTP contributions of total phosphorus to the CLP River at site 10. Although the most dramatic increase in the cumulative annual total phosphorus load (over 300%) occurs at this location, which is downstream of the four WWTPs (averaging 17.6 mgd), only 17% of the annual load can be accounted for with WWTP effluent loads. Furthermore, only 21% can be attributed to background total phosphorus loads, which leaves 62% of cumulative annual total phosphorus load unaccounted for. Possible nonpoint sources contributing to the phosphorus load at site 10 includes two CAFOs (over 100,000 animals) and a city stormwater drainage basin (32 sq mi) that accounted for with WWTP effluent loads.

Furthermore, only 21% can be attributed to background total phosphorus loads, which leaves 62% of cumulative annual total phosphorus unaccounted for in the Poudre River. Possible nonpoint sources contributing to the phosphorus load at site 10 include two CAFOs (over 100,000 animals) and a city stormwater drainage basin that discharges upstream of the sampling location.

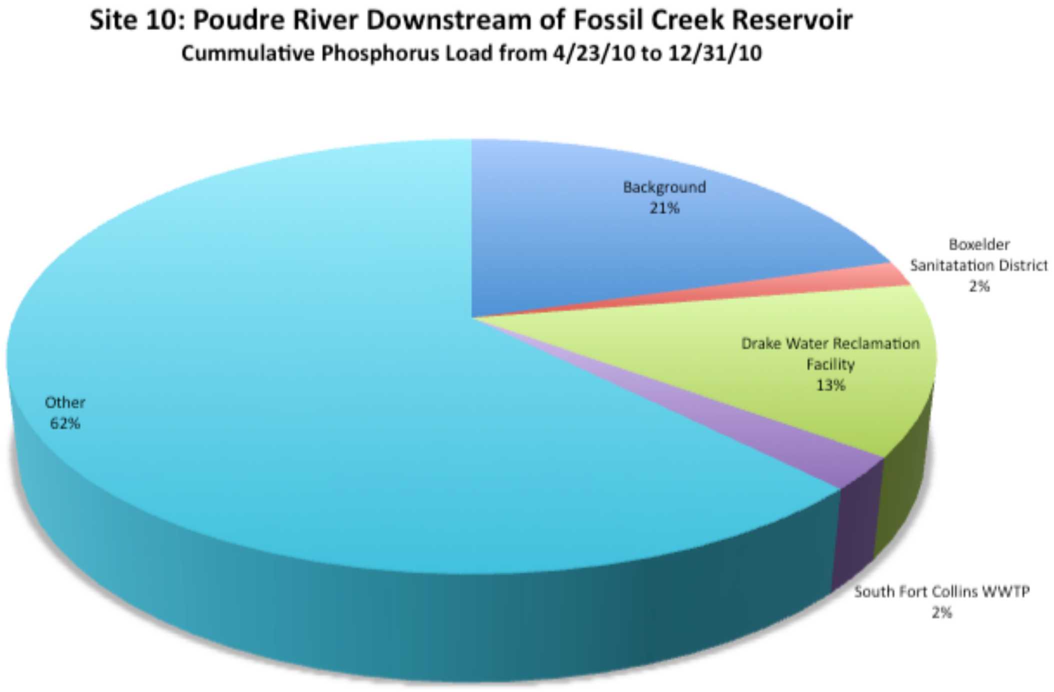

Figure 4.9: Estimated percentages of cumulative annual TP loading contributions by sources at the downstream of Fossil Creek Reservoir (sampling site No. 10)

Although WWTPs may only contribute 17% of the phosphorus on an annual basis, nearly all of the total phosphorus load in the CLP River can be accounted for during low flow periods as shown in Figures 4.10 and 4.11. Figure 4.10 shows the contribution of known phosphorus sources and the total load on a monthly basis. Figure

4.11 classifies each month in terms of flow conditions according to Figure 4.7, using an average of two flow duration curves. The contribution of each source is shown under different hydrologic conditions is shown.

The phosphate buffering mechanism is apparent in both Figures 4.10 and 4.11. In November and December the load from the WWTPs is approximately 850% and 250% of the load in the CLP River, which likely illustrates the sediment storage capacity of phosphorus. Similarly, low flow months, shown in Figure 4.11, show that the load from WWTPs is approximately 250% of the load found in the river.

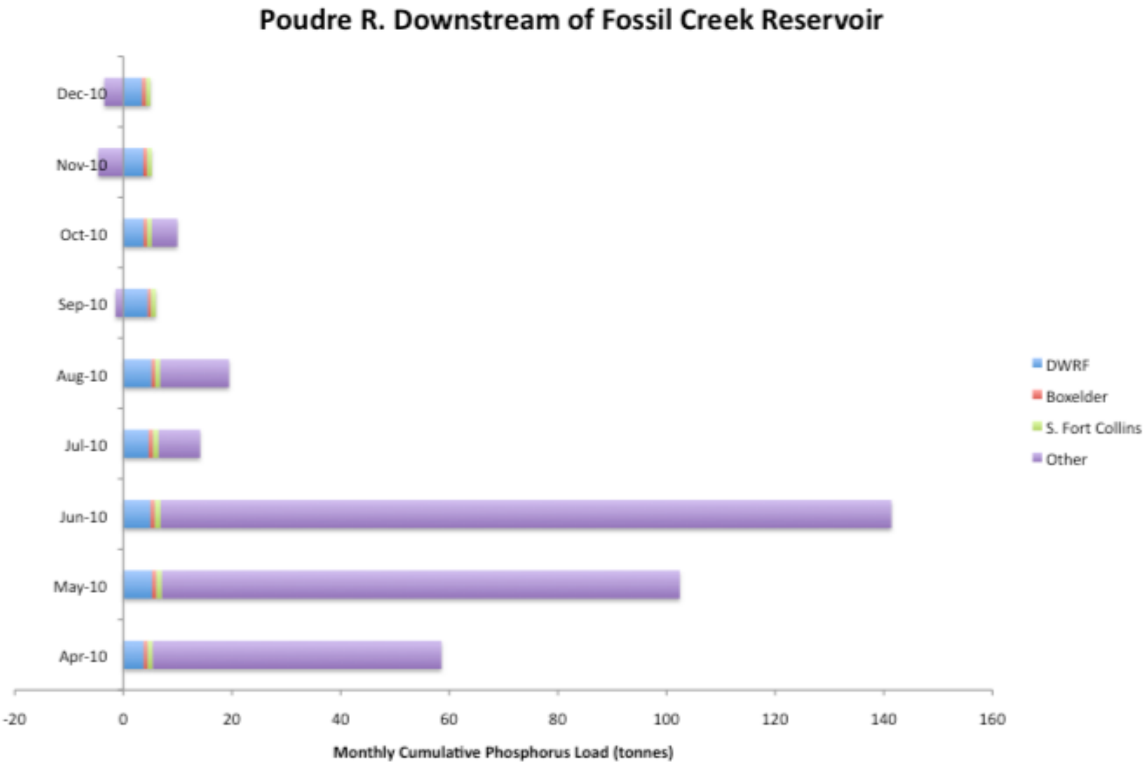

Figure 4.10: Cumulative Monthly Phosphorus Load from Known Sources

Months with high flow, especially after precipitation events, such as May and June deliver the majority of the total phosphorus to the CLP River, which has been found in previous studies [77]. These months also have the highest percentage of unknown total phosphorus sources, possibly indicating a release of bound phosphorus from the sediment and an increase in nonpoint phosphorus sources.

The cumulative total phosphorus inputs (loads) to a whole aquatic ecosystem are best to measure and regulate to protect the ecosystem and public health [30]. However, total phosphorus concentrations provide an easy survey of water quality and can be used to estimate the cumulative load. As regulations on concentrations of total phosphorus in WWTP effluent are proposed, it is important to understand the implications on the water quality of the CLP River. Figure 4.12 shows the percent of total annual phosphorus reduction at the WWTPs with the corresponding annual reductions in the Poudre River as a function of proposed WWTP effluent concentrations.

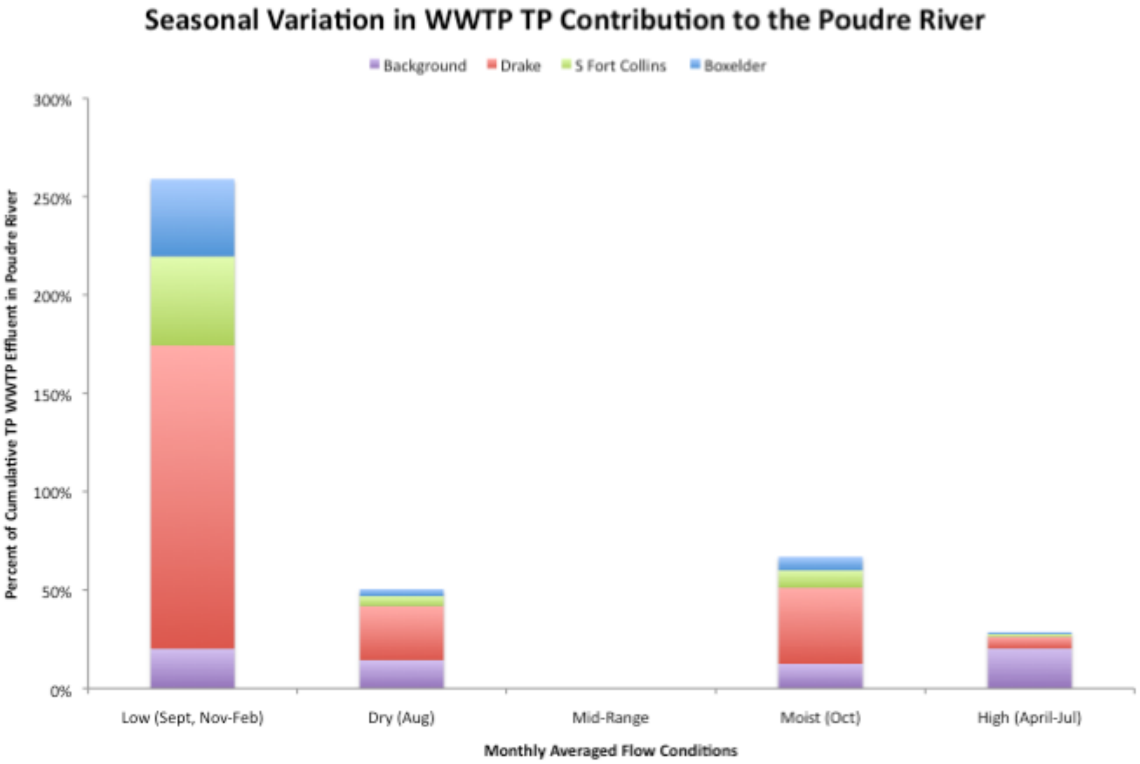

Figure 4.11: Cumulative Monthly Load as a Percentage from Known Sources

As an example, if the CDPHE decides to require WWTPs to treat the effluent to a concentration of 0.7 mg/l, the studied WWTPs would need to reduce their TP effluent load by an average of 78%. Based on the fraction of the total load that this represents, this treatment plant reduction would only result in a 14% annual reduction in total phosphorus in the Poudre River at site 10. Although on a seasonal or flow basis the proposed standards would have a greater effect, it is the higher flow periods that correpond to the lowest relative contributions from WWTPs that deliver the most total phosphorus to the CLP River.

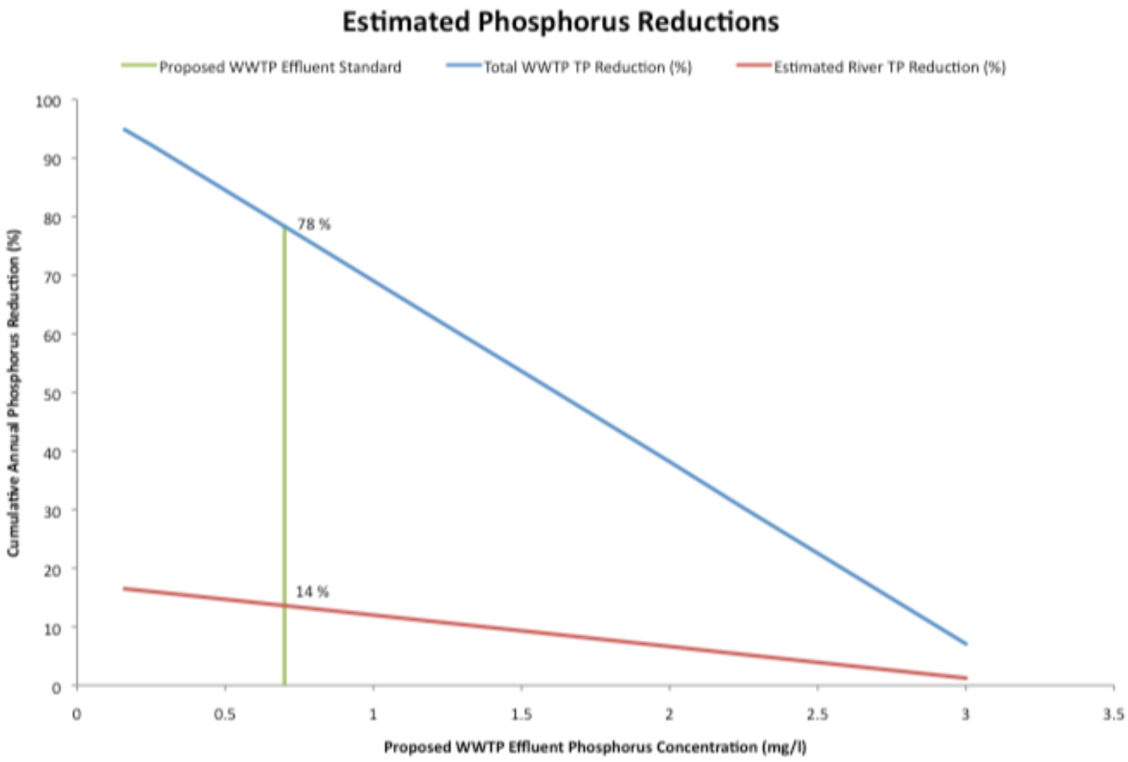

Figure 4.12: The estimated phosphorus reduction in the Poudre R and WWTPs as a function of the proposed WWTP effluent limits.

4.4. Conclusion

It is critical to monitor nutrient concentrations in the river due to ecological and human health issues. However, monitoring nutrient loads is also important since it is directly related to the concentration and helps to explain seasonal variations of the sources under different flow conditions. From this study, it was found that the WWTPs are the major sources of TP during mid-range flows and dry conditions but for the higher flows that correspond to the urban runoff and irrigation return flow season (5/9 events), WWTPs are actually a minor TP load input. It is difficult to quantify other sources of TP loads in the CLP River especially nonpoint sources.

It is important to reduce TP concentrations in WWTP effluents, however it was shown that even if plants are required to significantly reduce TP at relatively high costs, the effect on the total load to the river may be small. The analysis suggests that seasonal flexibility in regulating TP load to the river may be advantageous. In addition, a real-time TP monitoring system in the river could provide valuable guidance as to acceptable loads released from the group of WWTPs in the watershed. Since the TP loading to the river from WWTPs is an aggregate effect, a real-time monitoring system in the watershed could also be used as a basis for water quality trading, thus providing another tool for optimizing the efficiency of individual WWTPs.

Finally, the data collected in this study suggests that aquatic life based stream standards will not be achieved by regulating WWTPs alone. Significant reductions in non-point source loads will also be required.

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5. Conclusion

An in-depth study of phosphorus, in the Cache la Poudre River Watershed was performed to better understand the occurrence and transport and to assist in developing a method to improve water quality and best serve the community. Four sections topics were reviewed: (i) an extensive review of existing literature relating to excess nutrients, (ii) an examination of the sources and transport mechanisms as well as the influence of hydrologic and seasonal variations, (iii) a mass balance of P to determine the influence of WWTPs on the Cache la Poudre River as well as the impact of potential reductions and (iv) a basic cost-benefit analysis is per- formed along with a discussion on best methods for nutrient management within the watershed.

A literature review showed that most eutrophication research has focused on lakes and reservoirs and more recently marine and coastal eutrophication. However, the complexity and importance of streams and rivers is becoming more evident. Streams and rivers are typically the primary delivery mechanism of nutrients from a watershed to receiving waters. Regulations are being developed to better manage and control the delivery of nutrients to surface waters to reduce cultural eutrophication. There are several concerns with cultural eutrophication including public health concerns, economic impacts, aquatic ecosystem and water quality degradation. The goal of nutrient regulations is to best manage the consequences of cultural eutrophication. Integrated studies of watersheds that examine nutrient sources, transport pathways, influence of sources, temporal and spatial variations, economic impacts and management methods are required to develop effective regulations. Although portions of studies are similar, an integrated watershed study like this was not found in the review of literature. The objective of this study was to fill this gap and provide a framework for future studies.

An extensive survey of phosphorus within the watershed attempting to characterize all temporal and geospatial variations was performed within the watershed to better understand the occurrence and transport of phosphorus within the water- shed. Mathematical models were used to provide further insight into the variation of phosphorus concentrations due to sources and geospatial factors. The initial study suggested that WWTPs and CAFOs are the largest sources, but their influence is influenced most dramatically by changing hydrologic conditions. CAFO capacity became the most important factor during precipitation events. Irrigation ditches were also identified as an important transport pathway for delivering nonpoint source phosphorus to the Cache la Poudre River.

A dramatic increase in phosphorus concentration in the Poudre River downstream of WWTPs was noticed in the first study and a mass-balance was done to determine the true influence of WWTPs. The analysis revealed only 17% of the annual phosphorus load was from WWTPs. The majority of phosphorus loading is likely due to nonpoint sources that are more difficult to quantify and control. Tight regulations on WWTP phosphorus effluent concentrations were shown to only result in small reductions in the Cache la Poudre River. Although the influence of WWTPs increases significantly in mid-range flow and dry conditions, the majority of phosphorus is delivered to river during the spring runoff when there are high flows. To best manage phosphorus concentrations in the Cache la Poudre River, nonpoint sources need to be addressed.

Furthermore, a basic cost analysis of phosphorus removal reveals the misguided nature of a regulation focusing solely on WWTPs. The costs of phosphorus removal at WWTPs increases exponentially with decreasing required phosphorus concentration at WWTP effluent. The diminishing returns of WWTP controls on phosphorus as well as the small reductions to the total load in the river make this an inefficient management strategy. However, the cost analysis does provide insight into issues such as nutrient trading and power shaving as more effective approaches. Due to the complexity of the nutrient management problem (e.g. variation in assimilative capacity, power rates, hydrologic conditions, loading, etc.) The most effective management method matches the nutrient loads with the assimilative capacity of the river. This will require an integrated decision support system for water quality analysis, monitoring and management in the watershed to determine both changing assimilative capacities and nutrient loading from sources and adjust the complex system accordingly. A dynamic nutrient regulation would also be required, allow- ing for an integrated approach to best protect water quality, public health, aquatic ecosystems as well as minimizing costs.

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6. Appendix A Supplementary Information

6.1. Cost Estimates

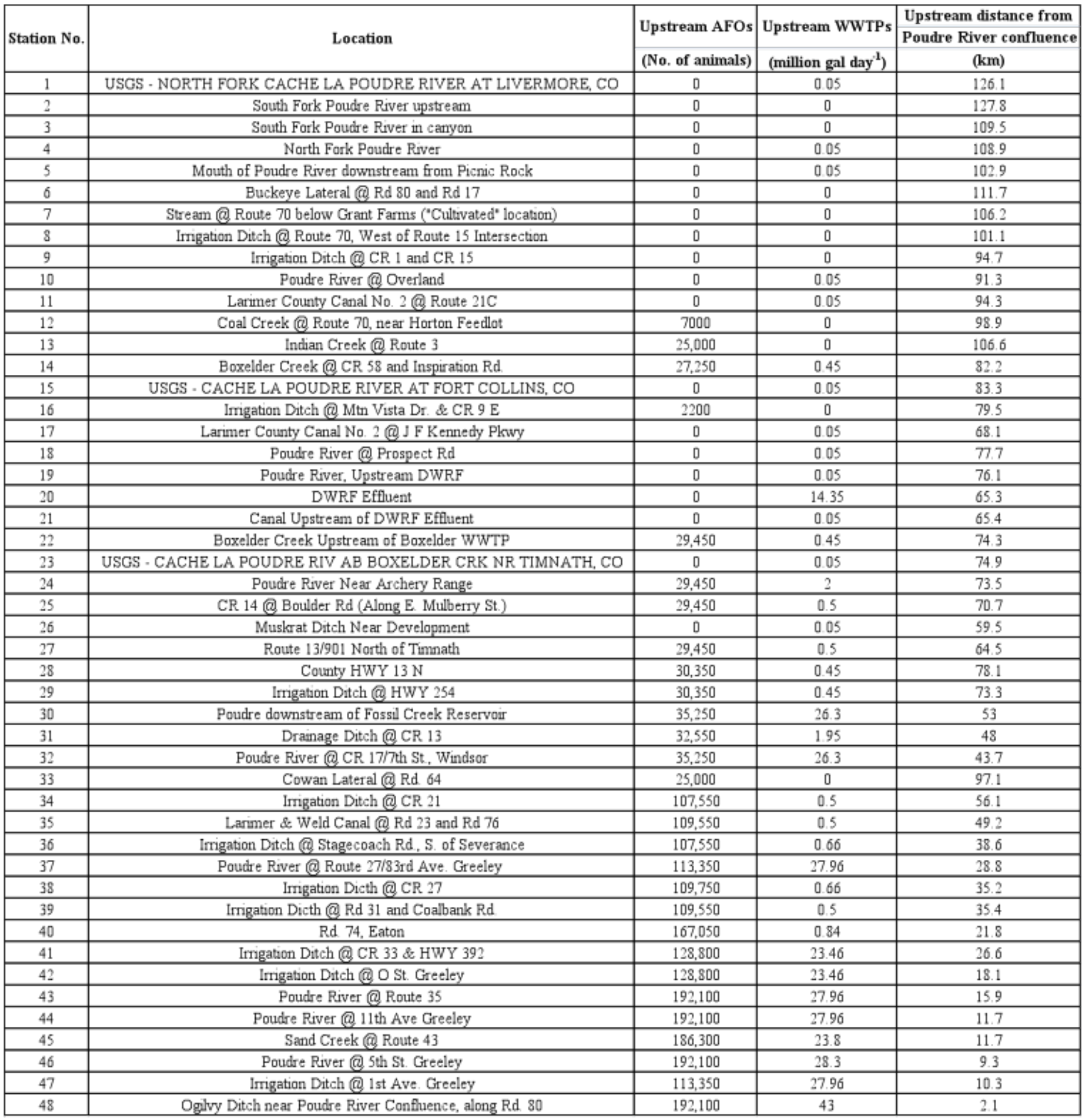
As nutrient regulations are proposed to best protect water quality, aquatic ecosystems and public health, it is also crucial to consider the economic implications of new regulations. Since point sources are often the most recognizable and easiest to control most of the focus has been on point sources, specifically WWTPs. However, the previous chapter shows only 17% of the annual load in the Cache la Poudre River can be traced to WWTPs. Nonpoint sources are also a critical part of controlling cultural eutrophication. USEPA identified agricultural nonpoint-source pollution as the major source preventing attainment of the water quality goals identified in the Clean Water Act [6]. Several studies provide guidance and reviews of nonpoint source controls of phosphorus (e.g. [17]). The complexity and uncertainty associated with nonpoint source controls are beyond the scope of this chapter, but is an important consideration in phosphorus management strategies.

Jiang et al. [65] has provided extensive and detailed cost estimation of phosphorus removal upgrades to WWTPs. Although many phosphorus methods are available Jiang et al. has focused on three of the most common techniques: activated sludge, an anoxic/oxic and an anaerobic/anoxic/oxic arrangement. The foundation of the cost estimation are derived from Construction Costs for Municipal Wastewater Treatment Plants (USEPA, 1980) and Estimating Treatment Costs (USEPA 1979) with updates and modifications. The operations and maintenance costs were estimated using an algorithm developed by the USEPA (1998). The following graphs estimate the costs associated with phosphorus removal in the Poudre River Watershed by interpolating the results from [65] using the WWTP capacity.

6.2. Required Reductions Estimate

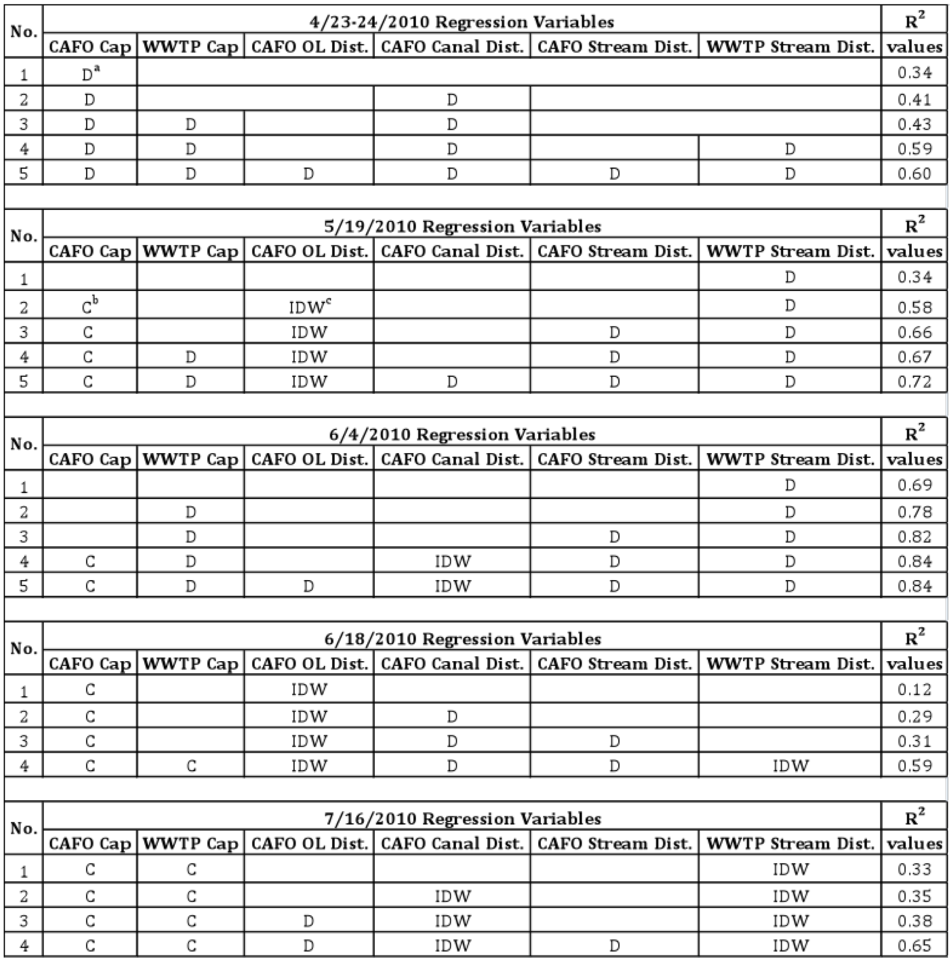
A numeric threshold of 0.16 mg/l for streams and rivers in Colorado's montane region has been estimated for a healthy aquatic ecosystem. Assuming this threshold is required in the CLP Watershed as well, a maximum cumulative annual total phosphorus load was estimated by using a constant concentration of 0.16 mg/l TP for the CLP. The analysis provides a crude approximation of the minimum TP reductions required from WWTPs. By using the average annual loads, the complications of seasonal effects including dilution, the phosphate buffering mechanism or changing hydrologic conditions are assumed to average over the course of a year. To meet the aquatic life standard of 0.16 mg/l, the load in the CLP River would need to be reduced from 320 to 50 tonnes (approximately 85%). The current load results in an average TP concentration in the CLP River of about 1.1 mg/l.

Table A.1: Total number of animals, design flow of WWTPs, and distance upstream from Poudre River confluence for each sampling location.



Station No.	Location	Upstream AFOs	Upstream WWTPs	Upstream distance from Poudre River confluence
		(No. of animals)	(million gal day^{-1})	(km)
1	USGS - NORTH FORK CACHE LA POUDRE RIVER AT LIVERMORE, CO	0	0.05	126.1
2	South Fork Poudre River upstream	0	0	127.8
3	South Fork Poudre River in canyon	0	0	109.5
4	North Fork Poudre River	0	0.05	108.9
5	Mouth of Poudre River downstream from Picnic Rock	0	0.05	102.9
6	Buckeye Lateral @ Rd 80 and Rd 17	0	0	111.7
7	Stream @ Route 70 below Grant Farms ("Cultivated" location)	0	0	106.2
8	Irrigation Ditch @ Route 70, West of Route 15 Intersection	0	0	101.1
9	Irrigation Ditch @ CR 1 and CR 15	0	0	94.7
10	Poudre River @ Overland	0	0.05	91.3
11	Larimer County Canal No. 2 @ Route 21C	0	0.05	94.3
12	Coal Creek @ Route 70, near Horton Feedlot	7000	0	98.9
13	Indian Creek @ Route 3	25,000	0	106.6
14	Boxelder Creek @ CR 58 and Inspiration Rd.	27,250	0.45	82.2
15	USGS - CACHE LA POUDRE RIVER AT FORT COLLINS, CO	0	0.05	83.3
16	Irrigation Ditch @ Mtn Vista Dr. & CR 9 E	2200	0	79.5
17	Larimer County Canal No. 2 @ J F Kennedy Pkwy	0	0.05	68.1
18	Poudre River @ Prospect Rd	0	0.05	77.7
19	Poudre River, Upstream DWRF	0	0.05	76.1
20	DWRF Effluent	0	14.35	65.3
21	Canal Upstream of DWRF Effluent	0	0.05	65.4
22	Boxelder Creek Upstream of Boxelder WWTP	29,450	0.45	74.3
23	USGS - CACHE LA POUDRE RIV AB BOXELDER CRK NR TIMNATH, CO	0	0.05	74.9
24	Poudre River Near Archery Range	29,450	2	73.5
25	CR 14 @ Boulder Rd (Along E. Mulberry St.)	29,450	0.5	70.7
26	Muskrat Ditch Near Development	0	0.05	59.5
27	Route 13/901 North of Timnath	29,450	0.5	64.5
28	County HWY 13 N	30,350	0.45	78.1
29	Irrigation Ditch @ HWY 254	30,350	0.45	73.3
30	Poudre downstream of Fossil Creek Reservoir	35,250	26.3	53
31	Drainage Ditch @ CR 13	32,550	1.95	48
32	Poudre River @ CR 17/7th St., Windsor	35,250	26.3	43.7
33	Cowan Lateral @ Rd. 64	25,000	0	97.1
34	Irrigation Ditch @ CR 21	107,550	0.5	56.1
35	Larimer & Weld Canal @ Rd 23 and Rd 76	109,550	0.5	49.2
36	Irrigation Ditch @ Stagecoach Rd., S. of Severance	107,550	0.66	38.6
37	Poudre River @ Route 27/83rd Ave. Greeley	113,350	27.96	28.8
38	Irrigation Dicth @ CR 27	109,750	0.66	35.2
39	Irrigation Dicth @ Rd 31 and Coalbank Rd.	109,550	0.5	35.4
40	Rd. 74, Eaton	167,050	0.84	21.8
41	Irrigation Ditch @ CR 33 & HWY 392	128,800	23.46	26.6
42	Irrigation Ditch @ O St. Greeley	128,800	23.46	18.1
43	Poudre River @ Route 35	192,100	27.96	15.9
44	Poudre River @ 11th Ave Greeley	192,100	27.96	11.7
45	Sand Creek @ Route 43	186,300	23.8	11.7
46	Poudre River @ 5th St. Greeley	192,100	28.3	9.3
47	Irrigation Ditch @ 1st Ave. Greeley	113,350	27.96	10.3
48	Ogilvy Ditch near Poudre River Confluence, along Rd. 80	192,100	43	2.1

Figure A.2: Multiple linear regression analysis results.



No.	4/23-24/2010 Regression Variables						R^2
	CAFO Cap	WWTP Cap	CAFO OL Dist.	CAFO Canal Dist.	CAFO Stream Dist.	WWTP Stream Dist.	values
1	D[a]						0.34
2	D			D			0.41
3	D	D		D			0.43
4	D	D		D		D	0.59
5	D	D	D	D	D	D	0.60

No.	5/19/2010 Regression Variables						R^2
	CAFO Cap	WWTP Cap	CAFO OL Dist.	CAFO Canal Dist.	CAFO Stream Dist.	WWTP Stream Dist.	values
1						D	0.34
2	C[b]		IDW[c]			D	0.58
3	C		IDW		D	D	0.66
4	C	D	IDW		D	D	0.67
5	C	D	IDW	D	D	D	0.72

No.	6/4/2010 Regression Variables						R^2
	CAFO Cap	WWTP Cap	CAFO OL Dist.	CAFO Canal Dist.	CAFO Stream Dist.	WWTP Stream Dist.	values
1						D	0.69
2		D				D	0.78
3		D			D	D	0.82
4	C	D		IDW	D	D	0.84
5	C	D	D	IDW	D	D	0.84

No.	6/18/2010 Regression Variables						R^2
	CAFO Cap	WWTP Cap	CAFO OL Dist.	CAFO Canal Dist.	CAFO Stream Dist.	WWTP Stream Dist.	values
1	C		IDW				0.12
2	C		IDW	D			0.29
3	C		IDW	D	D		0.31
4	C	C	IDW	D	D	IDW	0.59

No.	7/16/2010 Regression Variables						R^2
	CAFO Cap	WWTP Cap	CAFO OL Dist.	CAFO Canal Dist.	CAFO Stream Dist.	WWTP Stream Dist.	values
1	C	C				IDW	0.33
2	C	C		IDW		IDW	0.35
3	C	C	D	IDW		IDW	0.38
4	C	C	D	IDW	D	IDW	0.65

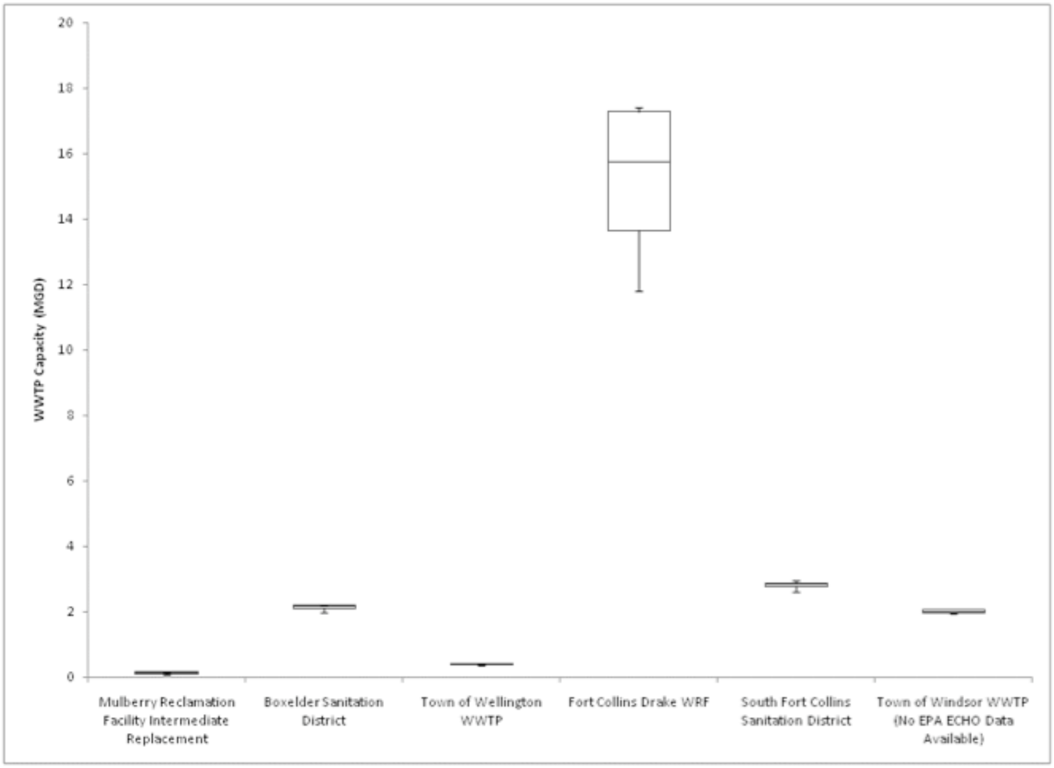


Figure A.3: The variability in the monthly averages of WWTP gross effluent in the study region.

Table A.4: Total phosphorus measurements along the Poudre River

ID Number	Distance	Location	TP (mg/L) - Poudre River							
			4/23-24/2010	5/19/10	6/4/10	6/18/10	7/16/10	9/17/10	2/22-23/2011	4/26-27/2011
1	127.8	South Fork Poudre River upstream			0.135	0.135		0.140	0.130	0.140
2	109.5	South Fork (in canyon)		0.125	0.150	0.080		0.105	0.165	0.065
3	102.9	Mouth of Poudre River		0.155	0.220	0.150		0.085	0.100	0.190
4	91.3	Poudre River @ Overland	0.080	0.195	0.170	0.160		0.110	0.100	
5	83.3	USGS-Cache La Poudre River @ Ft. Collins	0.215	0.140		0.105		0.180	0.135	0.150
6	77.7	Poudre River @ Prospect Rd	0.175	0.175	0.135	0.155	0.155	0.135	0.160	0.135
7	76.1	Poudre River Upstream DWRF	0.125	0.155	0.160	0.160	0.160	0.115	0.140	0.150
8	74.9	USGS-Cache La Poudre Riv Ab Boxelder Crk Nr Timnath		0.115	0.170	0.190	0.170	0.130		
9	73.5	Poudre River Near Archery Range	0.455	0.215	0.205	0.165	0.360	0.565	1.490	0.845
10	53	Poudre Downstream of Fossil Creek Reservoir	2.055	0.685	1.000	0.340	3.100	0.820	0.795	1.295
11	43.7	Poudre River @ CR17 Windsor	1.925	0.570	1.000	0.415	2.03	0.550	0.365	1.280
12	28.2	Poudre River @ Route 27/83rd Ave. Greeley	1.965	0.720	1.020	0.475	2.115	1.025	0.795	1.235
13	15.9	Poudre River @ Route 35	1.555	0.665	0.990	0.790	0.835	0.485	0.360	0.745
14	11.7	Poudre River @ 11th Ave. Greeley	1.525	0.690	0.985	0.510	0.9	0.490	0.405	0.955
15	9.3	Poudre River @ 5th St. Greeley	1.590	0.685	0.960	0.490	0.88	0.480	0.340	0.800

Table A.5: Total nitrogen measurements along the Poudre River

ID Number	Distance	Location	TN (mg/L)		
			9/17/10	2/22-23/2011	4/26-27/2011
1	127.8	South Fork Poudre River upstream	0.034	0.319	0.299
2	109.5	South Fork (in canyon)	0.100	0.259	0.141
3	102.9	Mouth of Poudre River	0.035	0.151	0.180
4	91.3	Poudre River @ Overland	0.010	0.647	
5	83.3	USGS-Cache La Poudre River @ Ft. Collins	0.078	0.616	0.258
6	77.7	Poudre River @ Prospect Rd	0.239	1.600	0.662
7	76.1	Poudre River Upstream DWRF	0.247	0.855	0.557
8	74.9	USGS-Cache La Poudre Riv Ab Boxelder Crk Nr Timnath	1.062		
9	73.5	Poudre River Near Archery Range	2.023	8.144	2.957
10	53	Poudre Downstream of Fossil Creek Reservoir	1.644	3.553	2.646
11	43.7	Poudre River @ CR17 Windsor	1.135	2.252	2.202
12	28.2	Poudre River @ Route 27/83rd Ave. Greeley	1.808	4.104	2.596
13	15.9	Poudre River @ Route 35	2.134	3.986	2.813
14	11.7	Poudre River @ 11th Ave. Greeley	2.702	4.343	2.699
15	9.3	Poudre River @ 5th St. Greeley	5.314	6.149	4.729

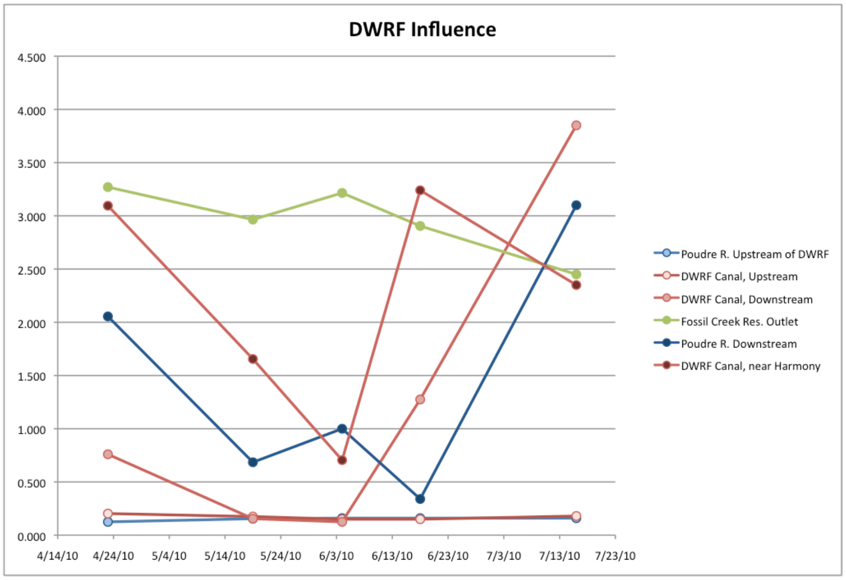


Figure A.6: Influence of Drake Water Reclamation Facility

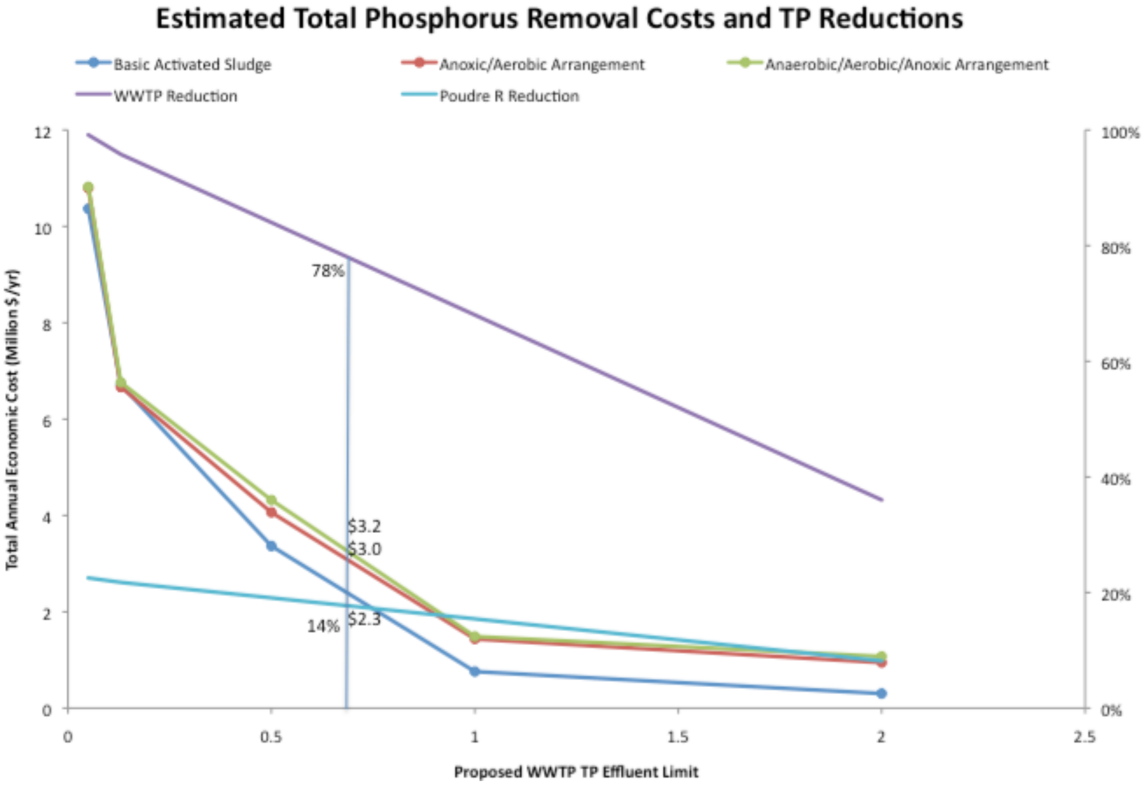


Figure A.7: Estimated reduction costs at DWRF and Poudre River using [65]

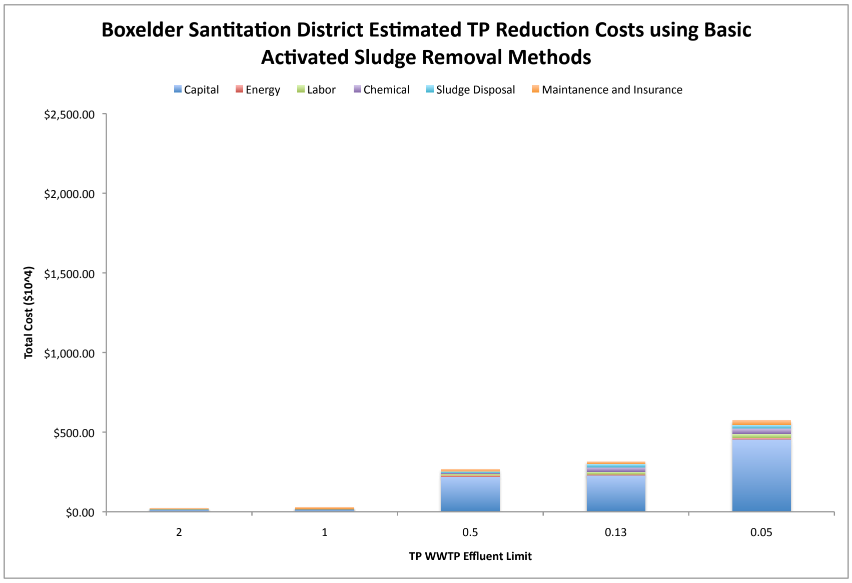


Figure A.8: Estimated reduction costs at Boxelder Sanitation District using basic activated sludge removal [65]

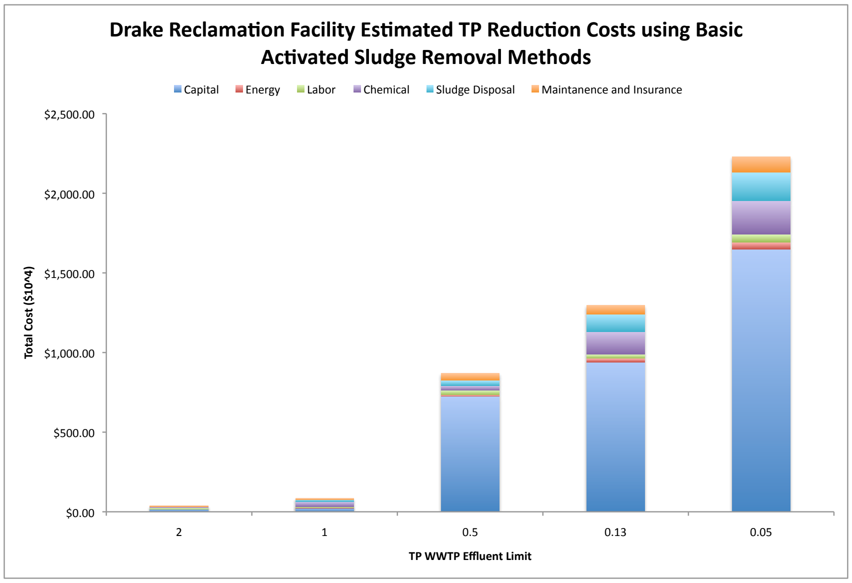


Figure A.9: Estimated reduction costs at Drake Water Reclamation Facility using basic activated sludge methods [65]

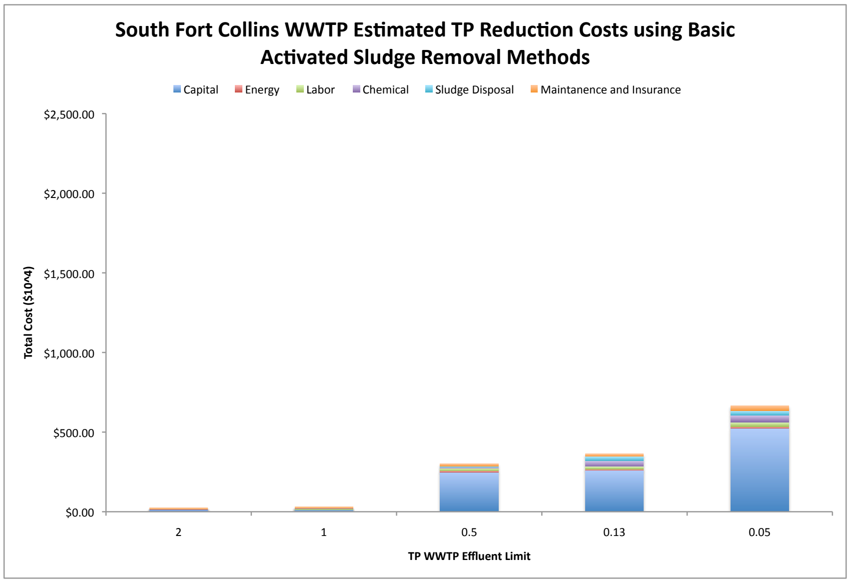


Figure A.10: Estimated reduction costs at South Fort Collins Wastewater Treatment using basic activated sludge methods [65]

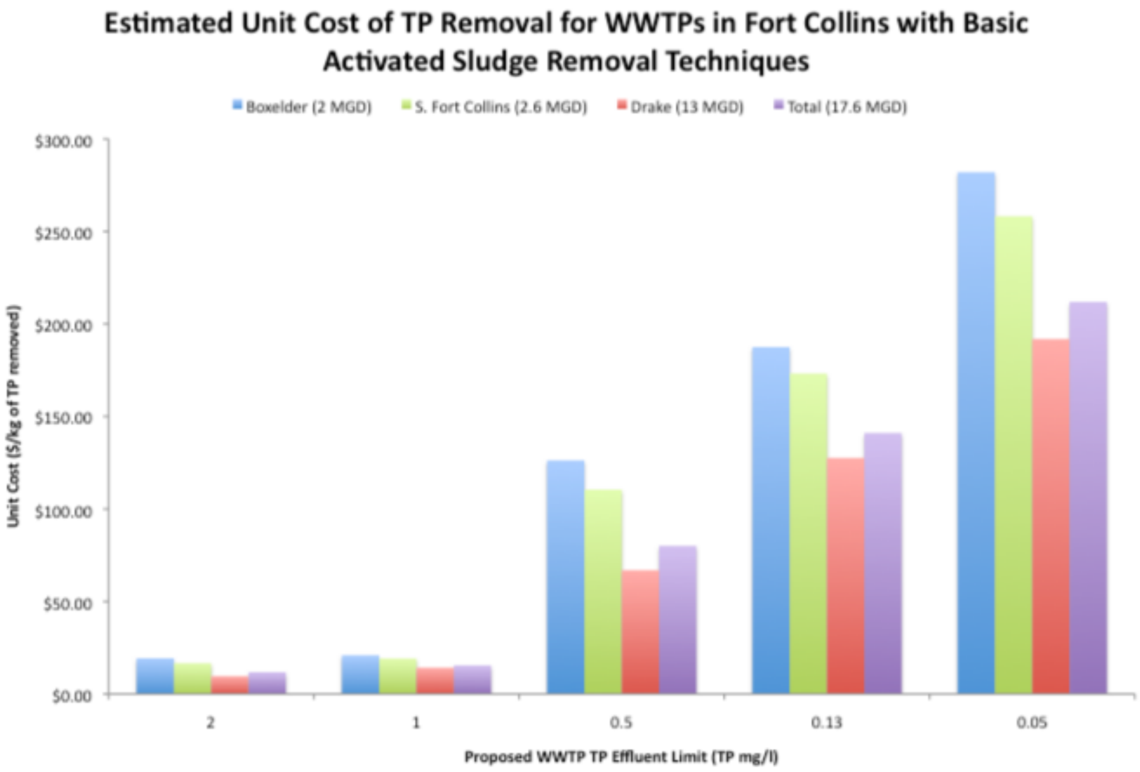


Figure A.11: Estimated unit cost of phosphorus removal using basic activated sludge methods [65]

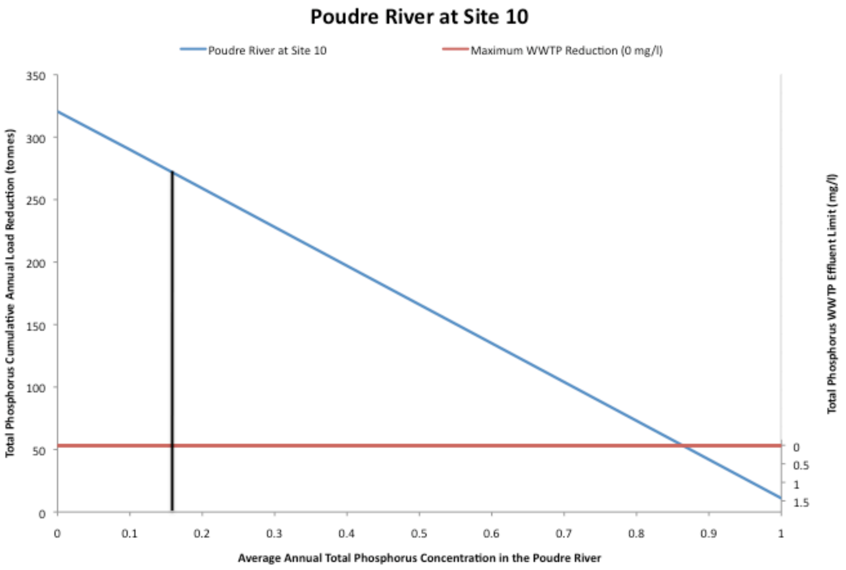


Figure A.11: Estimate of required annual reduction