DISSERTATION

NUTRIENT LOAD INPUTS TO THE CACHE LA POUDRE RIVER WATERSHEDS

Submitted by

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ABSTRACT

NUTRIENT LOAD INPUTS TO THE CACHE LA POUDRE RIVER WATERSHEDS

Nutrient (phosphorus and nitrogen) has been ranked as a leading source of water quality impairment of surface waters in the United States for the past two decades. Based on strong encouragement for developing in-stream nutrient numeric criteria by the Environmental Protection Agency of the U.S., the Colorado Department of Public Health and Environment proposed the in-stream numeric total phosphorus (TP) and total nitrogen (TN) criteria as 2 mg TN L^{-1} and 0.16 mg TP L^{-1} for warm surface waters and 0.40 mg TN L^{-1} and 0.11 mg TP L^{-1} for cold surface waters. As a consequence, nutrient limits for point sources, the municipal wastewater treatment plants, have been proposed as annual averages of 0.7 mg TP L^{-1} and 5.7 mg total inorganic nitrogen (TIN) L^{-1} and quarterly averages of 1.0 mg TP L^{-1} and 9.0 mg TIN L^{-1} to achieve the in-stream standards. Rivers and streams, however, receive nutrient loads from point sources and nonpoint sources in a mixed land-use area and therefore nutrient reduction only at point sources is unlikely to result in improvements to the environment without nonpoint source controls. The objectives of this study were to monitor TP (Chapter 4) and TN (Chapter 5) concentrations and estimate loads along the Cache La Poudre River as it flows from the pristine upstream area through a mixture of agricultural and urban land uses, and compare the loads between point sources and nonpoint sources under various hydrologic conditions. Twelve and seven sampling events were completed between April 2010 and August 2011 for TP and TN, respectively.

Point sources, wastewater treatment plants (WWTPs) in the study area, were the major sources of TP and TN during midrange and dry flow conditions, but nonpoint sources were more substantial under high flow conditions. Loading exceedance of TP from the proposed in-stream TP limit was observed for all hydrologic conditions, but the significance of the exceedance was drastically increased during high flow conditions ($p<0.05$). Contrary to expectations, significant loading exceedance of TN was observed only for lower flow conditions, and other sources dominated during events when exceedance of TN was observed. Nutrient loads increased in areas of greater anthropogenic influence ($p < 0.05$) and nonpoint source loads became significant in the areas with more agricultural activity ($p < 0.05$). We attempted to simulate TP and TN loads in the CLP River to determine whether the loads under different effluent conditions in the WWTPs would comply with the proposed in-stream limits (Chapter 6). The study shows that reducing nutrient load only at WWTPs will merely reduce nutrient load in the river and that the in-stream limits cannot be achieved without substantial reduction of nonpoint source loads (e.g., stormwater and agricultural runoff) and therefore other sources need to be considered in establishing the in-stream standard limits.

An intense wildfire occurred in a forested area of Colorado in June 2012 while a study of the role of riverbed sediment in terms of phosphorus source under various hydrologic conditions was being conducted. River water and sediment samples were collected after the fire, and water quality and sediment properties of the post-fire samples were spatially and temporally compared with the pre-fire samples collected prior to the fire event (Chapter 7). Disturbance of water quality and soil properties by the fire were observed, but the magnitude of significance was relatively small without precipitation; however, in-stream TN and TP concentrations significantly increased in the upstream section after precipitation event. Large amounts of particulate P were introduced to the upstream section and impacts downstream were apparent. After precipitation event, soluble reactive phosphorus (SRP) dominated dissolved P in the river replacing dissolved organic phosphorus (DOP), which was the main dissolved species before the fire event. In the riverbank, TP mass concentration increased significantly after fire with silt-clay and organic matter (OM) concentrations after precipitation. Riverbed TP mass concentrations decreased due to a reduced sorption capacity leading to a considerable P release from the sediments. The results indicate that fire-released P species will impact the downstream area of the watershed for a considerable time period as the bank erosion-sorption-desorption cycles in the watershed adjust to the fire-related loading.

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CHAPTER 1

INTRODUCTION

In 1997, U.S. EPA recognized a need for a national nutrient management program to control nutrient over-enrichment in surface waters. Hence the Clean Water Action Plan (CWAP) was established in 1998. The CWAP mandates the development of water quality-based control programs and adoption of water quality criteria appropriate for the various characteristics of a state's watershed because it is believed that the nation's waters can be protected based on the regulation of states' waters.

In 2001, the U.S. EPA placed the responsibility of developing a nutrient criteria plan on states and authorized tribes. The Colorado Department of Public Health and Environment (CDPHE) Water Quality Control Commission (WQCC) took the lead in establishing nutrient standards for the state. The CDPHE presented its initial proposed nutrient criteria for rivers and streams in February 2010 and scheduled a rulemaking session to adopt the criteria in May 2017. The proposed limits of nutrients are based on the best available science to protect aquatic life use. Studies have shown that upper limits of 0.16 mg TP L^{-1} and 2.0 mg TN L^{-1} for cold surface waters and lower limits of 0.11 mg TP L^{-1} and 0.40 mg TN L^{-1} for warm surface waters are required for a healthy macroinvertebrate community in rivers of Colorado (Lewis and MucCutchan 2010). Accordingly, the CDPHE has been working to determine limits of nutrients (TP and TN) for the public owned treatment works (POTWs) effluent to protect designated uses of receiving waters, and it has proposed annual averages limits of 0.7 mg TP L^{-1} and 5.7 mg TIN L^{-1} and quarterly average limits of 1.0 mg TP L^{-1} and 9.0 mg TIN L^{-1}.

Nutrients enter water bodies not only from point sources but also from nonpoint sources. Point sources such as municipal water treatment plants are easily discovered, and nutrient loading from the sources can be estimated with known nutrient concentrations in their effluent and flow rates. Unlikely, nonpoint sources are hard to indentify and manage because the paths that nutrients from the source deliver to the streams are unknown and scattered, such as runoff from agricultural lands and urban areas. Therefore, the regulations are solely focused on limiting nutrient discharges from point sources. However, a question has been raised: "Can regulating only point sources achieve the proposed in-stream limits?"

Recently, the department newly proposed nutrients limits for in-stream (amended 8/11/12, effective 1/31/13) and POTWs (amended 6/11/12, effective 9/30/12), this research, however, will be based on the proposed limits in 2010 and 2011.

During the study period, an intense fire occurred in June 2012 in upstream area of the Cache la Poudre River. With the distinctive nutrient data from riverbed and bank sediments collected prior to the fire event, a research on effects of wildfire on riverbed and bank sediments and water quality has been also conducted.

In this document, a review of literature with an emphasis on previous researches relating to excess nutrients will be provided in chapter 2 and research hypothesis and objectives will be discussed in chapter 3. Chapters 4-7 will be journal papers that have been submitted, published or in proceeding and results from the studies will be summarized and concluded in chapter 8. At the end of the document, appendices will be provided.

CHAPTER 2

LITERATURE REVIEW

Nutrients such as phosphorus and nitrogen are essential components in freshwater for the growth of aquatic organisms, but when excess amounts of nutrients enter the watershed, growth of algae is accelerated causing many problems in water such as unpleasant odor and taste. In addition, blue-green algae (cyanobacteria) bloom in drinking water sources and may impact the health of both humans and livestock due to its ability to produce toxins (Codd 1995; Chorus and Bartram 1999). The problems become worse because of the oxygen depletion caused by the microorganisms' need to consume large amounts of oxygen in order to decompose the dead cells of algae. This leads to the death of living organisms, fish kills, and deterioration of the aesthetic value of water. This phenomenon is called eutrophication, and it has been a major problem in waters in the United States since it was recognized in the mid 20th century. Nutrients have been ranked as one of the top five leading causes of water quality impairment of rivers and streams in the United States for two decades (USEPA 2009).

2.1. The Problem

The growth of algae involves a number of factors such as nutrients, light, temperature, substrate, etc. When the other factors are not limiting, algae can grow rapidly in response to nutrient levels in water, and the relationship between algae growth and abundance of nutrients has been well researched in several studies (Welch 1992; Van Nieuwenhuyse and Jones 1996;

Dodds et al. 1997; Chetelat et al. 1999). In a series of studies of algae from the 1930's to the 1950's, it was found that phosphorus (P) is the limiting factor for algal growth in freshwater systems (Redfield 1958). The ratio of N to P for algal growth is about 15 to 16:1 and this is also known as the Redfield ratio.

Accelerated algae growth often results in single or multiple species blooms in freshwaters (Fig. 2.1) and causes numerous problems ranging from annoyances to serious health concerns (Dodds and Welch 2000). A nuisance level of algae deteriorates aesthetic and recreational values of water and commonly generates taste and odor problems in drinking water supplies (Silvey and Watt 1971; Dorin 1981; Taylor et al. 1981). It also causes filter clogging problems (Welch 1992) and corrosion of intake pipes of water treatment facilities (Nordin 1985). The water treatment problems associated with this issue include high costs for additional chemicals, backflushing of filters, and further treatments.

Figure 2.1: Algal bloom in the Caloosahatchee River in Florida in June 2008 (Cessani 2008)

One well-known adverse effect of nutrient enrichment is the occurrence of harmful algal blooms. Cyanobacterial species (also known as blue-green algae) produce toxins in water that can poison livestock, waterfowl, and even humans after drinking (Darley 1982; Carmichael 1986, 1994). Algal blooms alter water conditions including level of dissolved oxygen (DO) and pH (Welch 1992; Edmonson 1994; Correll 1998). Depletion of DO caused by algal blooms can create an environment in which toxins are released from sediment and toxic substances such as ammonia and hydrogen sulfide are elevated by the shifting redox potential in waterbodies (Brick and Moore 1996). Stressed riverine freshwater with low DO levels and increased toxins and turbidity may lead to the loss of living organisms and even to fish kills (Nordin 1985; Welch 1992; Smith 1998; Carpenter et al. 1998; Smith et al. 1999). The conceptualized relationship of nutrients (particularly P in freshwaters) and diversity of aquatic biota is described in Fig. 2.2.

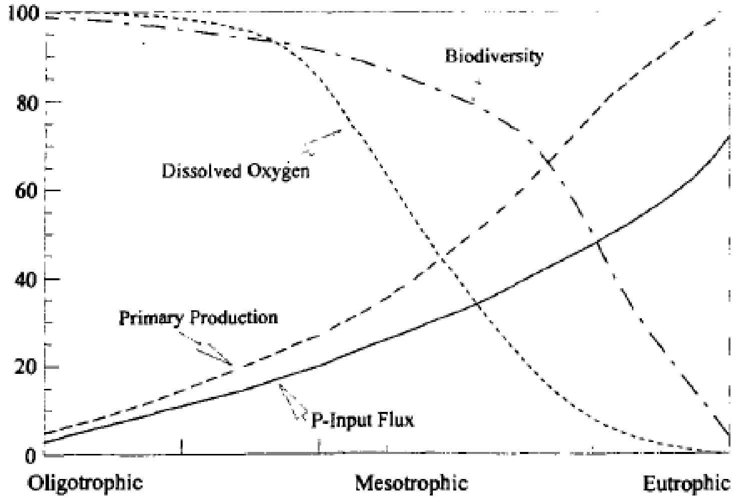


Figure 2.2: Conceptualization of freshwater eutrophication (Correll 1998)

The most important human health problem related with algae is the creation of trihalomethanes (THMs). Trihalomethane is a by-product formed by the reaction of organic matter in influent with bromine and chlorine inserted during the disinfection process of water treatment. An increase in the formation of trihalomethane is correlated with an abundance of organic matter including humic substances, algal metabolites and algal decomposition products in raw water (Oliver and Schindler 1980). This is a serious concern because trihalomethane is a carcinogenic compound that can lead to human deaths.

Nutrients themselves can also cause human health problems. Drinking water contaminated by nitrate generates a fatal blood disorder characterized by a low oxygen level in infants, called blue-baby syndrome. The symptoms of blue-baby syndrome are diarrhea, vomiting, bluish color of skin, and difficulties in breathing. The USEPA set a maximum contaminant level (MCL) at 10 mg NO_3-N/L in 1995 (USEPA 1995).

2.2. Leading Causes of the Problem

The U.S. EPA requires states to monitor the water quality of their waterbodies and provide annual updates for its Report to Congress under Section 305(b) of the CWA. Each state should use the most recent water quality data from all available sources such as state fish and game agencies, health departments, dischargers, and agencies including the U.S. Geological Survey (USGS) and the U.S. Fish and Wildlife Service (USEPA 1997a).

Since 1992, the National Water Quality Inventory Report to Congress (305(b) report) has been published biannually by the U.S. EPA, and it gives information on the nation’s water quality, the level of significance of problems associated with water quality, the leading causes of the problems, and implemented programs which have been implemented for restoration. Nutrients have consistently ranked as one of the leading causes of impaired water listed in

Section 303(d) of the CWA in the 305(b) reports (USEPA 1994, 1995, 1998, 2000a, 2002, 2007a, 2009) and this is documented in Table 2.1.

Table 2.1: River and stream miles impaired by nutrient assessed in the National Water Quality Inventory Report to Congress (305(b) report) and leading sources of impaired rivers and streams (USEPA 1994, 1995, 1998, 2000a, 2002, 2007a, 2009)

	1992	1994	1996	1998	2000	2002	2004
Surveyed river, miles (%)	642,881 (18)	615,806 (17)	693,905 (19)	842,426 (23)	699,946 (19)	695,540 (19)	563,955 (16)
Impaired river, miles (%)	221,877 (35)	224,236 (36)	248,028 (36)	291,263 (35)	269,258 (39)	309,755 (45)	246,002 (44)
Impaired by nutrient, miles (% of impaired water)	82,094 (37)	51,574 (23)	97,147 (40)	84,071 (29)	52,870 (20)	52,228 (17)	38,632 (16)
Leading sources, % of impaired water							
Agriculture	72	60	70	59	48	37	38
Municipal point sources	15	17	14	10	10	–	14
Hydromodification	–	17	14	20	20	26	25
Habitat modification	–		14	6	14	17	17
Resource extraction	11	11	13	9	10	–	9
Urban runoff/storm sewers	11	12	13	11	13	–	9
Unknown	_	_	_	_	_	30	34

Among the distressed surface waters assessed in the nation’s rivers and streams in 1996, the percentage of nutrients was high at 40%. Since then this has begun to decrease. Leading sources of pollutants including siltation, nutrient and pathogens that cause impairment of rivers and streams are agriculture, municipal point sources, hydro and habitat modification including channelization and loss of natural wetlands, resource extraction, urban runoff/storm sewers and unknown.

2.2.1. Point source and nonpoint source

The term “point source” defined in Section 502(14) of the CWA is “any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged.” The term “nonpoint source” refers to sources that cannot be determined by the definition of “point source” such as agricultural storm water discharges and return flows from irrigated agriculture (USEPA 1997b).

The National Water Quality Inventory determined that agricultural nonpoint source pollution is the major source of water quality impacts to surveyed rivers, and that status has not changed since the U.S. EPA assessment of nation’s water was begun although the intensity of the impacts has greatly decreased from 72% in 1992 to 38% in 2004. The percentage of pollutants from municipal point sources such as wastewater treatment plants (WWTPs) ranged from 10% to 17% in the 305(b) reports.

2.2.2. Municipal point source

Municipal water treatment facilities receive waters from municipal areas and discharge treated waters to the surface waters. The raw water usually contains nutrient concentrations of about 5 mg TP L^{-1} and 30 mg TN L^{-1} (USEPA 2008) and effluent concentrations vary depending on the treatment processes, and the minimum concentrations that can be achieved by current technology are 0.01 TP L^{-1} and 1 mg TN L^{-1} (Neethling 2010).

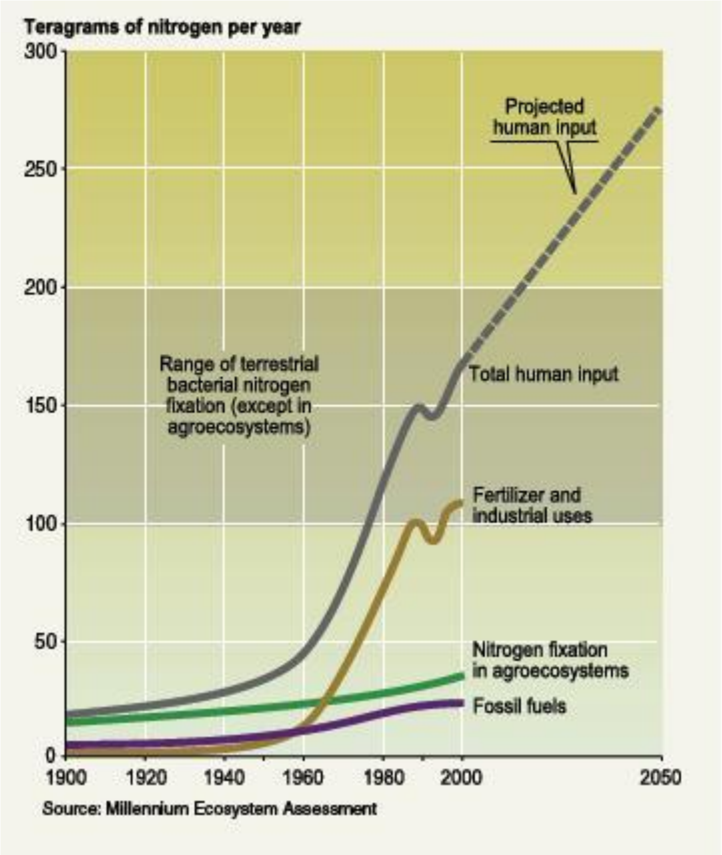
Point source contributions from municipal wastewater treatment plants are largely in a soluble form that is immediately available for biotic assimilation, and they can have significant influences under low flow conditions in the receiving surface waters (Mainstone and Parr 2002).

2.2.3. Agricultural nonpoint source

Agricultural activities and practices including cultivation, application of fertilizer, irrigation, planting, harvesting, and grazing are highly related with nutrient production (USEPA 1997c) and are more influenced by precipitation, while point sources, especially discharges from WWTPs are relatively constant over time (Meyer and Likens 1979).

The use of nitrogen (N) in fertilizer has increased significantly over the past several decades with consequences of N pollution (Bricker et al. 1999; Galloway et al. 2004) (Fig. 2.3). Nitrate (NO_3^-) is hydrophilic, which means it is easily soluble in water and therefore has great mobility in water and may leach into groundwater and enter the waterbodies via surface runoff.

In addition to nitrogen, most fertilizers contain phosphorus as a major component. The excessive use of fertilizer combining P and N leads agriculture to the largest source of nonpoint water pollution in the U.S. Unlike nitrogen, phosphorus is immobile because it is not easily dissolved in water, but it tends to be adsorbed in phosphate form (PO_4^{3-}) to soil particles and transported with sediments (Turner and Haygarth 2000; McDowell et al. 2001). P is frequently accumulated in the top 5cm of the surface sediments and delivered to watersheds along with soil erosion (Addiscott et al. 2000). Studies have observed significant P losses from agricultural fields (Withers and Jarvis 1998; Sharpley et al. 2000) that can have a significant environmental impact (Heckrath et al. 1995) because very small concentrations of P (as low as 10 μ L^{-1}) can cause eutrophication in freshwaters (Powlson 1998; Haygarth et al. 1998; Sharpley et al. 2000).



Source: Millennium Ecosystem Assessment

Figure 2.3: Increase of nitrogen input in the ecosystem (Millennium Ecosystem Assessment 2005)

P inputs to the environment increases with the use of manure in fertilizer, livestock grazing, poor agricultural management practices, and frequent storm events (Sharpley et al. 1994). A number of studies observed a correlation between soil management practices, source soil P concentrations in the landscape, and tributary P load and concentrations from positive linear relationship between soil P and P in runoff (Sharpley 1996; Pote et al. 1996, 1999; Fang et al. 2002; Torbert et al. 2002; Davis et al. 2005). A possible pathway of P transportation is described in Fig. 2.4.

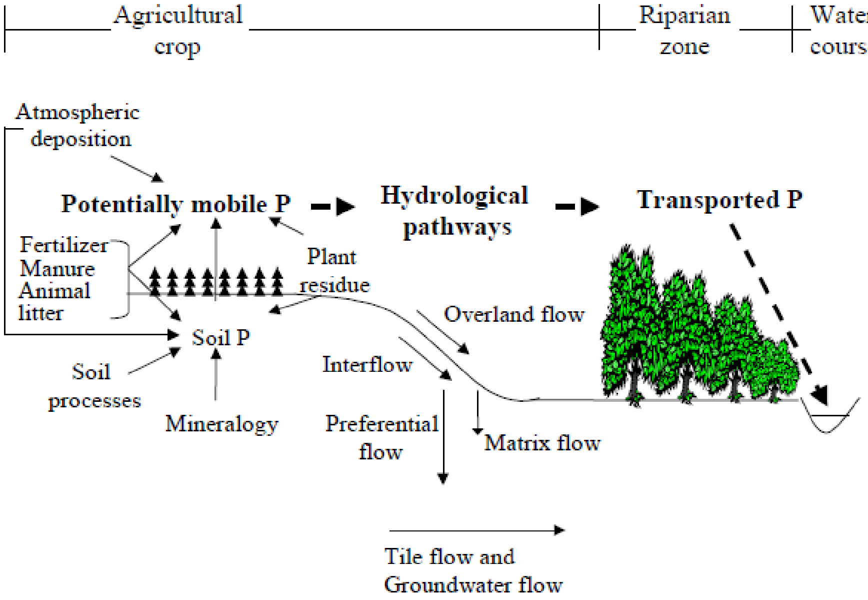


Figure 2.4: Potentially mobile agricultural P inputs and the hydrologic pathways that transport P to reach surface waters (Zaimes and Schultz 2002)

Transport of P can occur in two forms: dissolved form and particulate form. Dissolved P is mainly in a soluble reactive orthophosphate (SRP) form that is bioavailable. In other words, it can be directly assimilated by aquatic plants. Dissolved P moves through surface flows and inter flows via leaching; however, major P travels as particulate P (PP), including mineral P (apatite), non-apatite inorganic P, and organic P with soil through overland flows and land drainage such as ditches, canals, tiles, and moles (Correll 1998; Haygarth and Sharpley 2000). PP has the potential to be used by aquatic organisms once it goes through chemical reactions, thus it is considered as a long-term source of bioavailable P (Sharpley et al. 1994).

2.2.4. Unexpected source: wildfire

Wildfire is sudden and unexpected but can be a long term source of nutrients in the watershed. When a wildfire occurs, a watershed receives fire residues such as ash and wood debris mostly through erosion with drastically increased frequency (Badìa and Martì 2003). The majority of P is transported to streams in a particulate phosphate form, but P is very dynamic and can be released into the water column (Khanna et al. 1994). The released phosphate can be shifted to the orthophosphate form by hydrolization, which may cause eutrophication (Fig. 2.5). Otherwise, the transported particulates can be deposited in riverbed sediments for a time and then gradually released as orthophosphate when PP is in equilibrium with dissolved P (Sharpley et al. 1996) or when bottom waters are in an anoxic condition during the growing season (Correll 1998). These equilibria dynamics of PP and SRP are usually called phosphate buffer mechanisms (Carritt and Goodgal 1953; Froelich 1988).

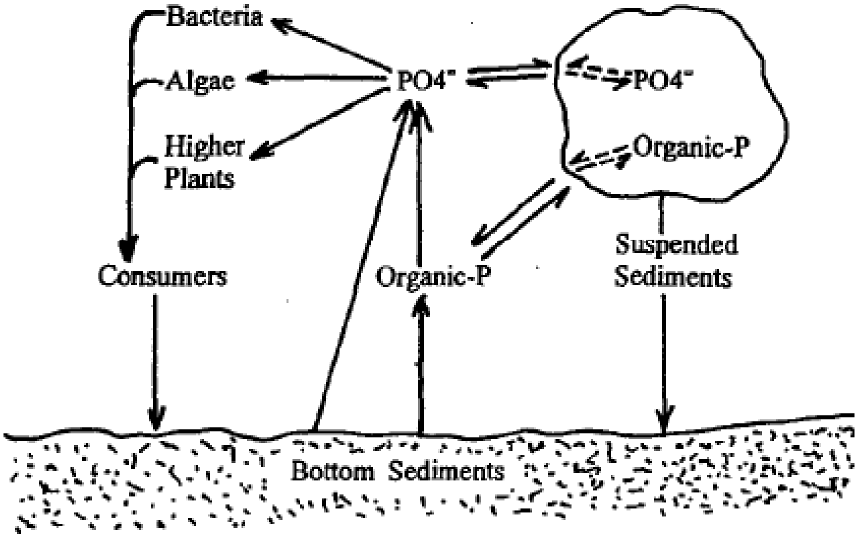


Figure 2.5: Riverbed sediment phosphorus cycle diagram (source: Correll 1998)

P adsorbed in sediments is assumed to be in two forms, organic and inorganic. The inorganic forms are represented by metal-bound-phosphates including iron-bound and calcium-bound phosphates, and these phosphates are easily transformed by the redox condition and pH in water (Gomez et al. 1999). The mechanism of the mobility of organic P is not well known, however. Besides redox potential and pH, exchanges of P in the riverbed sediment-water are affected by several factors such as organic matter (Golterman 1975; Verdouw and Dekkers 1980), mineral content (Fox 1988; Klotz 1998), sediment particle size (Meyer and Likens 1979; McDowell et al. 2002) and the activities of bacteria, fungi, algae, and invertebrates (Haggard et al. 1999; USEPA 2000b).

Benthic sediments can regulate P concentration and productivity in rivers along with biological activities (Taylor and Kunishi 1971; Meyer and Likens 1979; House and Denison 1998, 2000). Under lower flow conditions, hydraulic residence time (HRT) increases due to low flow velocity, and this results in long contact time between the river water and bottom sediments and a higher ratio of sediment surface area to water volume (House and Denison 2002). In such conditions, biological assimilation plays a major role in altering P flux in streams (Van Nieuwenhuyse and Jones 1996; Gosselain et al. 1998; Reynolds and Glaister 1993; Reynolds 2006).

At higher flows, P dynamics are more influenced by the physical and chemical processes occurring at the interface between riverbed and water column. These include scouring of P flux accumulated in riverbed sediments and exchanges of P between riverbed sediments and water column due to lower HRT. The higher velocity also causes washout of plants and increased turbidity (Soballe and Kimmel 1987; Jarvie et al. 2002). These results show that seasonal variation and hydrologic conditions are important factors in P flux mechanisms in large rivers (James 2009).

The equilibrium phosphorus concentration (EPC_0) (Froelich 1988) of riverbed sediments has been considered as an indicator of whether riverbed sediments absorb or liberate SRP into the water column (House and Denison 1998, 2002), and several studies have been conducted to examine how riverbed sediments react in different seasons (Brunet and Astin 1998, 2000; May et al. 2001; Jarvie et al. 2005) and various flow conditions (Casey and Farr 1982; House and Warwick 1998; Jordan-Meille et al. 1998; Banaszuk and Wysocka-Czubazek 2005).

The possibility that the riverbed sediments could be the source of phosphorus in freshwater has gained credence over the past 20 years (Taylor and Kunishi 1971; Meyer and Likens 1979) especially under conditions where sediments transported from agricultural lands accumulate in the riverbed (Ekholm and Krogerus 2003; Jarvie et al. 2005). According to Banaszuk and Wysocka-Czubazek (2005), P-rich particulates are accumulated during high flows in the river floodplain and pools and then transported to the river during runoff events and built up in the riverbed, which can create a great reservoir of P in the river system. Storage and mobilization of P within the river channel has been studied in detail (Jordan-Meille et al. 1998; House and Warwick 1999; Bowes and House 2001). Wildfire, however, can substantially change characteristics of forest and riverbed soils, but there are few studies on the impacts of wildfire on a riverbed and bank sediment characteristics in terms of nutrient dynamics.

2.3. Nutrient Load Analysis

Nutrient load inputs from river basins have been studied using mass balance approaches (e.g. Cooper et al. 2002), and various models have been developed to study nutrient transport from sources to watersheds in several studies (Goolsby et al. 2000; Lepistö et al. 2006; Behrendt et al. 2008; Alexander et al. 2008). Cooper et al. (2002) performed a mass balance on the P budget of a catchment in the U.K. with known point source inputs from WWTPs and estimated diffuse sources gained by the difference between stream discharge and point source inputs. In 2008, Alexander et al. studied nutrient loads from the Mississippi River Basin using the SPARROW water quality model to assess the pollutant sources and transport to the Gulf of Mexico, which suffers from serious seasonal hypoxia. The model estimated nutrients entering the stream in relation to landscape properties using nonlinear methods based on a calibration to the long-term mean annual load of TN and TP collected at 425 stream monitoring stations in the contiguous U.S. The model found agriculture to be the primary source of nutrient (52% of TN and 77-82% of TP) to the Gulf with 9% of TN and 12% of TP coming from urban sources. A study by Behrendt et al. (2008), however, reached a different conclusion using MONERIS to estimate the nutrient inputs by point and diffuse sources via various pathways. They found the predominant source of TP emissions to be from urban sources (61% of TP) with agricultural sources being second at 31%, though agriculture was still the major source of TN (49%). The different results might be due to different populations, land use and characteristics of the catchments.

A number of studies have investigated the spatial influence of different land uses and soils for catchments using developed models without comparing hydrological conditions.

2.4. Nutrient Regulations for Rivers and Streams

One effective way to manage nutrient loading is to develop and insert numeric nutrient criteria into State water quality standards (USEPA 2010). In 2001, the USEPA acknowledged that nutrient control is necessary and began working with states and authorizing tribes to establish numeric criteria in their watersheds using one of three suggested approaches: 1) develop numeric nutrient criteria as their laws or regulations using EPA's Technical Guidance Method, 2) adopt Section 304(a) of the CWA as the criteria, or 3) develop nutrient criteria using other qualified methods.

The CDPHE is responsible for surface water quality of Colorado and for making an effort to establish the State's own nutrient criteria under section 303(c) of the CWA for its unique systems. A work group has been established which includes thirty individuals representing state municipalities, consulting firms, law firms, environmental groups, State and Federal agencies, and the administrator of WQCC. Colorado's waters are divided into two groups for the purpose of developing nutrient criteria: 1) streams/rivers and 2) lakes/reservoirs.

According to ecoregional water quality criteria recommendations published by the USEPA, the Front Range of Colorado falls under Ecoregion II-Western Forested Mountains and Ecoregion IV-Great Plains Grass and Shrublands (USEPA 2000c, 2001). The recommended nutrient criteria based on the 25th percentile in rivers and streams of Ecoregion II and IV include TP limits of 10 $\mu g\ L^{-1}$ and 23 $\mu g\ L^{-1}$ and TN limits of 0.12 $mg\ L^{-1}$ and 0.56 $mg\ L^{-1}$, respectively. However, Colorado has decided not to adopt EPA's recommended nutrient criteria of Section 304(a) but to develop its own criteria using a mixed method of approaches number 1 and 3.

Colorado has made progress in developing numeric nutrient criteria for lakes and reservoirs but has had difficulties in developing nutrient criteria for streams and rivers (CDPHE 2002). In 2004, a study was conducted in 74 sites of montane rivers and streams to investigate ecological response to nutrient enrichment (Lewis and McCutchan 2005) and based on that study water quality criteria for streams and rivers have been developed using the Colorado's Munti-Metric Index (MMI) bioassessment tool.

2.4.1. Regulation 31: in-stream nutrient criteria

In 2010, the CDPHE presented its initial proposed nutrient criteria for rivers and streams to protect aquatic life (stressor/response based) to stakeholders.

Regulation 31 provides in-stream nutrient criteria to protect designated uses of waters (aquatic life use) derived from best available science (macroinvertebrate health) for the least impaired environment (Lewis and McCutchan 2005, 2010). The proposed nutrient limits are listed in Table 2.2.

To implement the proposed limits, sources of nutrients in the watersheds need to be monitored and identified. Nutrient sources can be divided into two categories; point source and nonpoint source as described above. Point sources are well identified sources defined in section 502(14) of the CWA such as effluents from wastewater treatment plants (WWTPs) and industrial plant discharges. Nonpoint sources are difficult-to-identify sources that are not covered under section 502(14) such as atmospheric deposition, stormwater and urban and agricultural overflow and subsurface flow.

Table 2.2: Proposed numeric nutrient standards in rivers/streams (regulation 31) by the CDPHE

		Proposed nutrient standards in rivers/streams (Regulation 31)	
		Cold water	Warm water
Amended 2010	TP, mg L^{-1}	0.11	0.16
	TN, mg L^{-1}	0.40	2.00
Amended 2011	TP, mg L^{-1}	0.11	0.17
	TN, mg L^{-1}	1.25	2.00

Point sources are managed and controlled by the National Pollutant Discharge Elimination System (NPDES) under section 402 of the CWA. The NPDES is a permit program that controls pollutant emissions into navigable waters in the United States. The CDPHE issues permits to facilities that discharge effluents into streams in Colorado. Facilities are required to comply with the state's water quality regulations in order to obtain permits. Unlike point sources, nonpoint sources of pollution are not currently subject to enforceable regulatory requirements.

2.4.2. Regulation 85: POTW effluent nutrient criteria

According to Guidance for Water Quality Based Decisions (USEPA 1991), the entire load reduction must be achieved by point sources if "sufficient assurances" on nonpoint source reduction are not provided. Based upon the difficulties in providing "sufficient assurances" of nonpoint source reduction, nutrient load reduction from point sources is expected to be the only available way to achieve nutrient criteria. Accordingly, the CDPHE has proposed numeric nutrient criteria for the POTWs based on current achievable technology in 2011, and these criteria are summarized in Table 2.3. A concern has been raised about the technology-driven nutrient controls and the fact that majority of costs to meet the standards will be carried by POTWs (Biggs et al. 2011).

Table 2.3: Proposed numeric nutrient standards in POTW effluents (regulation 85) by the CDPHE

			Proposed POTW effluent standards (Regulation 85)	
			Annual average	Quarterly average
Amended 2010		TP, mg L^{-1}	0.70	1.00
		TIN, mg L^{-1}	5.70	9.00
			Annual median	96th percentile
Amended 2011	Existing facilities	TP, mg L^{-1}	1.00	2.50
		TIN, mg L^{-1}	10.00	20.00
	New facilities	TP, mg L^{-1}	0.70	1.75
		TIN, mg L^{-1}	7.00	14.00

To achieve the water quality goals of the watershed, all sources and stressors should be evaluated and implement water quality trading, which is a useful and cost-efficient tool for meeting water quality standards, should be implemented. A water treatment facility can purchase credits from other pollutant reduction activities through the water quality trading at a lower price because costs of pollutant treatment at WWTPs is usually higher than nonpoint source control (USEPA 2008).

2.5. Water Treatment Unit Processes and Technological Limits

The NPDES regulates point source discharges into freshwaters to control pollutant emissions to receiving waters, and pollutant limits for issuing a permit must be developed in consideration of both the technology available for controlling the pollutant, and the water quality standards of the receiving water (USEPA 2008). The technology available water treatment processes and associated costs are well described in USEPA's Municipal Nutrient Removal Technologies Reference Document published in 2008 and WERF 2010 (Neethling 2010)

Nutrient removal processes can be classified into five different levels from Level 1 to Level 5. Based on the assumption that raw water contains typical TP concentrations of 4-8 mg L^{-1} and TN concentrations of 25-35 mg L^{-1}, levels of nutrient removal technologies in water treatment facilities are illustrated in Table 2.4.

Table 2.4: Level of nutrient (TP and TN) treatment technologies in water treatment processes (data source: Neethling 2010)

			Advanced wastewater treatment		
Parameter	Level 1: Typical raw municipal wastewater	Level 2: Secondary treatment	Level 3: Biological nutrient removal (BNR)	Level 4: Enhanced nutrient removal (ENR)	Level 5: Limits of treatment technology
TP, mg L^{-1}	4-8	4-6	1	0.25-0.50	0.05-0.07
Removal, %	0	20	80	90	98
TN, mg L^{-1}	25-35	20-30	10	4-6	3-4
Removal, %	0	20	70	80	90

Level 1 in Table 2.4 indicates raw municipal wastewater with no treatment and Level 2 is secondary treatment that uses activated sludge containing natural bacteria to decompose organic waste under aerobic conditions. A typical secondary treatment process goes through screening, 1° solids separation, aerobic, 2° solids separation, chlorination, and dechlorination, and the expected effluent concentrations of nutrients are 4-6 mg TP L^{-1} and 20-30 mg TN L^{-1} (CDPHE 2010).

The biological nutrient removal (BNR) technology is classified into treatment Level 3. The process includes Ludzack-Ettinger process, modified Ludzack-Ettinger process (MLE), moving-bed biofilm reactor (MBBR), Wuhrman, and Bardenpho (3 or 4 stages) containing stream processes of screening, 1° solids separation, single stages of anaerobic, anoxic and aerobic zones, 2° solids separation, chlorination, and dechlorination with nutrient effluent concentrations of 1 mg TP L^{-1} and 10 mg TN L^{-1}.

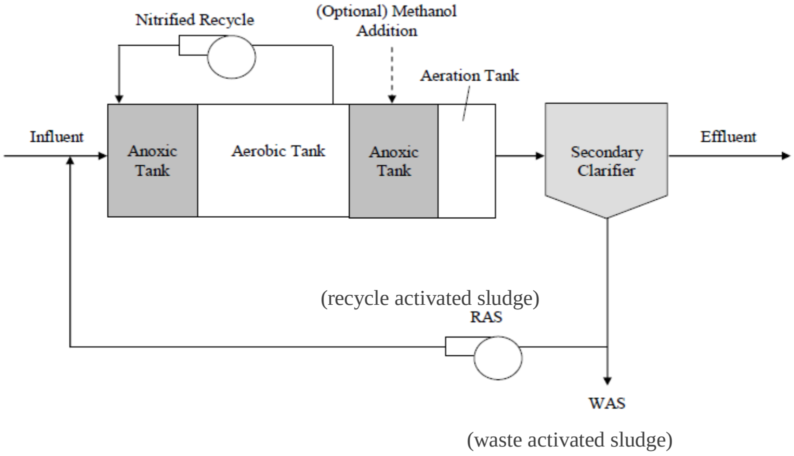


Figure 2.6: Four-stage Bardenpho process (USEPA 2008)

Treatment technology Level 4 implies enhanced nutrient removal (ENR) such as the 5-stage Bardenpho process, University of Cape Town (UCT), Johannesburg, and 3-stage Phoredox. A typical stream being treated flows through screening, 1° solids separation, multiple stages of anaerobic, anoxic and aerobic zones, 2° solids separation, chlorination, and dechlorination processes. The difference between treatment Level 3 and 4 is the number of anaerobic stages that can be seen in Fig. 2.6 and Fig. 2.7. By placing an anaerobic tank before 4-stage system, concentration of TP can be reduced up to 90%. In addition excellent removal of TN with effluent concentration of 0.25-0.5 mg TP L^{-1} and 4-6 mg TN L^{-1} can be achieved through the process (USEPA 2007b).

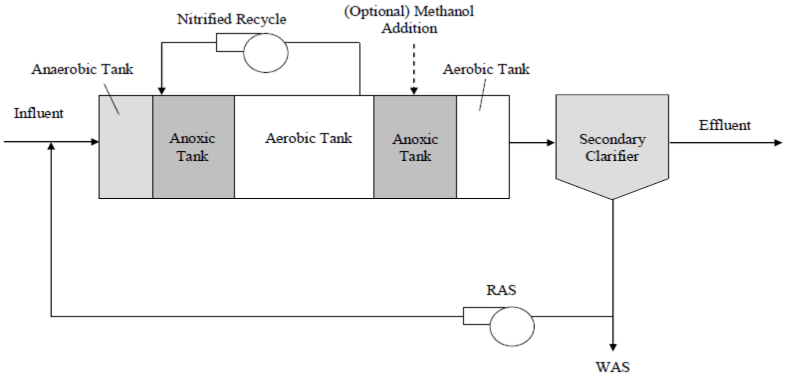


Figure 2.7: Five-stage Bardenpho process (USEPA 2008)

The current limit of technology, Level 5 is a technology that can achieve minimum nutrient effluent concentration throughout the treatment process. This technology typically uses chemicals and 3° filtration with BNR (Level 3) or ENR (Level 4) (USEPA 2010). The addition of chemicals and 3° filtration can reduce nutrient concentrations up to 0.05-0.07 mg TP L^{-1} and 3-4 mg TN L^{-1}, but adding these processes is very expensive. The estimated costs for the five levels of treatment processes to achieve effluent nutrient concentrations are summarized in Fig. 2.8.

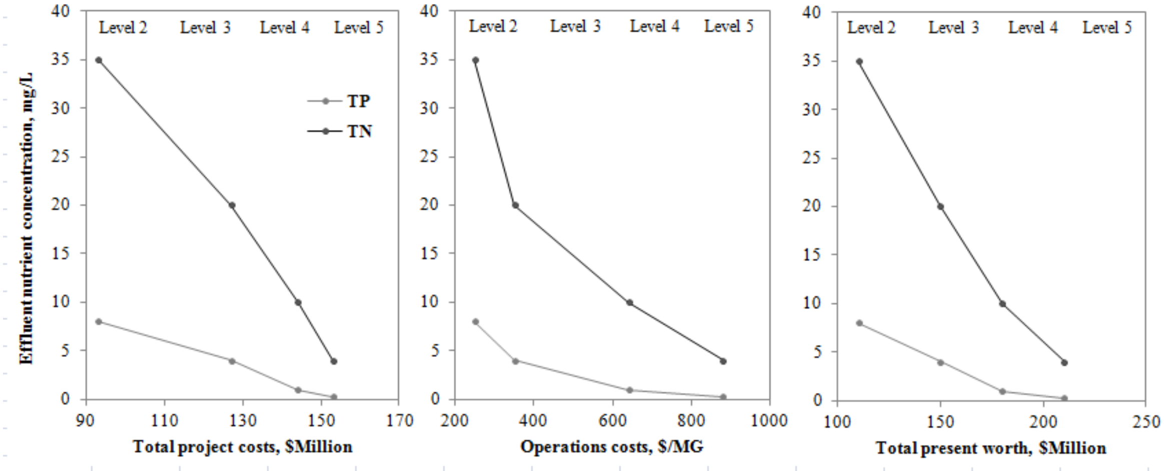


Figure 2.8: Estimated costs and effluent concentrations of five levels of nutrient treatment process (Falk et al. 2011)

Falk et al. (2011) estimated costs of the five levels of treatment based on a water treatment capacity of 10 MGD and 5 percent of discount rate at an escalation rate of 3.5 percent. The total project capital costs include the equipment cost and construction costs, and the operation costs including energy and chemical costs. But labor and maintenance costs were excluded from the estimation.

2.6. Urban Water Management in Fort Collins

Fort Collins is a diverse mixed land-use area and experiencing fast growing communities. The City has challenges related to stormwater management for unique land-use patterns of each land-use type (City of Fort Collins 2011). To manage stomwater efficiently, the City divided the land into 12 drainage basins and 20% of the developed area of the City is being controlled by structural stormwater quality control measures of best management practices (BMPs) and low impact development (LID) such as detention ponds and grass waterways. Stormwater from the urban area ends up in wetlands, ponds, lakes and creeks and the City adopted a regulation for providing onsite water quality treatment of stormwater from new impervious area before the water enters the main corridor of the Cache la Poudre River. For example, the most developed and concentrated area, Old Town, is controlled by parcels and the water from each parcel is treated by the regional water quality treatment facility located in the Udall Natural Area before discharging to the river. There are storm drains and gutters connected to a network of pipes that drains water directly into the river but the City developed a master plan of the integrated stormwater quality management for each drainage basin to minimize urban influences on the river by using 100% BMPs for the area by 2035(City of Fort Collins 2011).

2.7. Summary of Literature Review

Nutrient (nitrogen and phosphorus) is one of leading sources causing water quality impairment in the nation’s waters. Eutrophication is the most well-known problem caused by excess nutrient inputs to waterbodies resulting in fish kills and human health problems. The leading sources of nutrient are agricultural nonpoint source and municipal point source. USEPA encourages states and tribes to develop numeric nutrient criteria for their water, and Colorado has established a workgroup to study nutrient limits in Colorado’s waters. The CDPHE has proposed Colorado’s numeric nutrient criteria based on a study of allowable nutrient concentration for macroinvertebrate health at minimally disturbed sites. Under the CWA, the only federally enforceable controls are point sources through the NPDES permitting process. Implementing stringent nutrient reduction at point sources is associated with high costs which are unlikely to result in improvements to the environment absent nonpoint source controls.

Thorough site-specific analyses of nutrient loading contributions from potential point and nonpoint sources will be necessary to develop appropriate publicly owned treatment works' nutrient effluent limits.

Riverbed sediment might be another potential source of P in the river under diverse flow conditions. Wildfire, however, may alter behavior of riverbed sediments in terms of P sorption reaction, which may have long-term effects.

CHAPTER 3

RESEARCH HYPOTHESIS AND OBJECTIVES

3.1. Research Hypothesis

Nutrients enter the watersheds via point sources and nonpoint sources. WWTPs have been chosen because they represent the major nutrient source in the watershed, particularly in the Front Range of Colorado. The Water Quality Control Division (WQCD) of the Colorado Department of Public Health and Environment (CDPHE) has proposed nutrient limits in warm water rivers and streams as TP of 0.16 mg L^{-1} and TN of 2 mg L^{-1}. To achieve the proposed limits, nutrient load reduction is required, and the reduction work is focused on WWTPs. However, there is seasonal variance of nutrient load contribution of WWTPs to the watersheds under diverse hydrologic conditions, and loads from nonpoint sources might be significant during certain periods of the year. In spite of this, annual nutrient load contributions including point sources and nonpoint sources under various hydrologic condition and retention rates in the whole watershed have been less studied. If the loads from nonpoint sources are significant on an annual basis, they should also be considered for regulation.

A severe wildfire occurred in a forest area of the Cache la Poudre Basin in June 2012 while we were studying impacts of riverbed and bank sediments on nutrient loads in the river as a possible source of phosphorus under different flow conditions. Using the pre-fire water quality and sediment data, wildfire impacts on water quality and riverbed and bank sediment characteristics related to phosphorus were examined.

The research hypotheses are:

I. Nutrient load from nonpoint sources is statistically greater than that from point sources in the Cache la Poudre River Watersheds on an annual basis.

II. The proposed nutrient standards can only be achievable with meaningful reduction of the nonpoint source load. In other words, the standards cannot be met without nonpoint source load reduction in the Cache la Poudre River Basin.

III. Wildfire significantly impacts water quality and riverbed and bank sediment characteristics, and post-fire sediments can be a long-term source of phosphorus in the river.

3.2. Research Objectives

I-A Characterize hydrologic conditions of the CLP River with respect to TP and TN loading limits.

Tasks

- Collect 30-year flow data from available USGS stations to create flow duration curves for each station and define hydrologic conditions.
- Collect antecedent 3-day irrigation flow data in the Cache la Poudre River, antecedent 3-day precipitation data in the study area, snow-water equivalent in the mountain, and river water temperature on each event date.
- Comprehend the proposed nutrient (TP and TN) concentration limits of the CLP River by the CDPHE.

- Calculate nutrient (TP and TN) loading limits using proposed concentration limits and collected flow data.

I-B Estimate total nutrient (TP and TN) load inputs of the CLP River and determine contributions of WWTPs and other sources.

Tasks

- Select event dates representing various hydrologic conditions; high flows, moisture condition, mid-range flows, dry conditions, and low flows of the CLP River.
- Collect aqueous samples from 13 points along the CLP River from upstream of pristine Rocky Mountain National Park as a background through mid-stream of built-environment to downstream surrounded by agricultural areas before its confluence with the South Platte River on the selected event dates.
- Measure TP and TN concentrations in collected aqueous samples.
- Collect flow data on each sampling event date measured in the Cache la Poudre River from available USGS stations.
- Estimate total nutrient (TP and TN) loads in the CLP River using the collected USGS flow data and measured nutrient concentrations.
- Collect discharge flow data and effluent nutrient (TP and TN) concentrations from WWTPs in the study area and calculate average monthly nutrient loads for each WWTP.
- Estimate nutrient loads from other sources with the observed data from collected samples, and calculate loads from WWTPs using the mass balance method.

I-C Compare nutrient loads in the CLP River from WWTPs and other sources.

Tasks

- Conduct statistical analysis using estimated nutrient loads from WWTPs and other sources.

II-A Present exceedance of nutrient loads of the CLP River from the nutrient loading limits and show load reduction needed to comply with the limits.

Tasks

- Create graphs showing the nutrient loads and loading limits of each source and identify level of exceedance.
- Estimate the difference between the observed nutrient loads and the proposed nutrient loading limits.
- Simulate nutrient loads without the presence of WWTP inputs.

III-A Measure and compare parameters of riverbed and bank sediments and water quality before and after fire.

Tasks

- Determine fire boundaries and hydrologic conditions on event dates.
- Sample surface water and riverbed and bank sediments at the 13 points described above on selected event dates.
- Measure in-situ water quality parameters including temperature, turbidity, conductivity, and pH.

- Analyze nutrient and TSS concentrations in water samples including TP, TDP, SRP, and TN and estimate DOP and PP from the analyzed TP, TDP, and SRP concentrations.
- Determine sediment parameters of riverbed and bank: silt-clay contents, OM and TP mass concentrations.
- Measure EPC_0 and estimate sorption constant, sorption state, and percent P saturation in riverbed sediments.
- Test correlation between parameters and spatial trends from upstream to downstream.
- Compare sediment and water quality data before and after fire.

CHAPTER 4

RELATIVE PHOSPHORUS LOAD INPUTS FROM WASTEWATER TREATMENT PLANTS IN A NORTHERN COLORADO WATERSHED

4.1. Introduction

The USEPA's 305(b) reports consistently rank excess nutrients as the leading water quality impairment in assessed rivers, lakes, and estuaries (USEPA, 2009). Increases in the concentrations of nutrients are the primary cause of eutrophication of water bodies (Carpenter et al. 1998; Cloern 2001; Conley 2000; Nixon 1995). Excess eutrophication in Colorado's freshwater lakes, reservoirs, and streams is chiefly due to phosphorus (P) loading (Correll 1998; Lewis and McCutchan 2010). Eutrophication frequently results in algal or cyanobacterial blooms in the summer months, leading to anoxia, fish kills, murky water, and the depletion of flora and fauna (Carpenter et al. 1969; Likens 1972; Jaworski 1981). In drinking water sources, the increased algae growth is a public health concern, requiring additional chlorination and creating more disinfection by-products. Taste and odor issues also increase with excess algae, and the activity of microbes can lead to additional health concerns.

In 1998, the USEPA began to address the need for a national nutrient management program to control eutrophication (USEPA 1998). In 2001, the USEPA placed the responsibility of determining acceptable nutrient values on the individual states due to the variability of total P (TP) discharges that exists throughout the country due to hydrologic conditions (Jordan et al.

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1997a), geology (Grobler and Silberbauer 1985), and agricultural (Jordan et al. 1997b,c) and urban land uses (Frink 1991; Short and Burdick 1996).

A nutrient criteria work group was established by the Water Quality Control Division of the Colorado Department of Public Health and Environment (CDPHE) to develop P and nitrogen limits to best protect Colorado’s waterways and serve the public interest. In February 2011, the division proposed that 0.16 and 0.11 mg L^{-1} of TP concentrations for warm and cold waters, respectively, be required for healthy river ecosystems. In addition, Colorado’s Multimetric Index and annual median concentrations of ambient water should not exceed the limit of TP concentration more than once in 5 years (CDPHE 2012) to avoid being listed in the Section 303(d) list of the Clean Water Act. Cold and warm waters were classified based on sustainable aquatic life, and, for waters that are capable of sustaining cold-water biota, that weekly summer average temperature does not exceed 20°C. The CDPHE has also been working to determine a proposed point source limit of TP “necessary to protect uses,” and a TP concentration of 1 mg L^{-1} has been suggested for effluent limit of municipal wastewater treatment plants (WWTPs). Seasonal and hydrological changes in P concentration and loads in catchments have been studied in previous research (Banaszuk and Wysocka-Czubaszek, 2005; Bowes et al., 2003; Brunet and Astin, 1998; May et al., 2001), but no studies have researched the entire watershed of a river. The goal of this study was to examine the role of TP loads from WWTPs on the Cache La Poudre (CLP) River and to determine the impact of temporal, hydrologic, and spatial variations. An extensive survey of the CLP River and WWTPs was conducted over more than a year to estimate cumulative loads and contributions from each known source. Projections on the impact of proposed TP reductions at WWTPs on the CLP River were made using cumulative load calculations.

4.2. Materials and Methods

4.2.1. Study site description

The CLP River is located in the front range of Colorado and is a watershed (4960 km^2) well suited to study the occurrence and transport of nutrients within a river. The river originates in the Rocky Mountains, approximately 203 km 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 WWTPs of varying sizes, and a downstream section that is dominated by agricultural land uses (Yang and Carlson 2003).

The stream was divided into four segments based on land uses of drainage areas (Table 4.1). 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 including more than 20 irrigation ditches connecting to the river. Thirteen sampling sites were selected to study P load inputs from the relatively pristine area (sampling sites 1 and 2) as a background load, the urbanized area (segments 2 and 3) mainly from the point sources such as WWTPs and storm water, and the agricultural area (segment 4) from agricultural runoff through irrigation return flows.

Table 4.1: Summary of land use of four segments of the Cache La Poudre River Basin.

Segment	Sampling site	Drainage area	Land use		
			Forest/Shrub/Grasslands	Developed	Agriculture
		km^2	%		
1	1-3	105.5	79.6	10.7	8.9
2	4-6	205.7	51.3	21.4	19.2
3	7-9	152.8	16.4	33.8	39.8
4	10-13	674.7	12.6	25.8	55.1

The cities in the study area have a total of five WWTPs. The most upstream WWTP is the Mulberry Water Reclamation Facility (MWRF), which has a capacity of 0.26 $m^3 s^{-1}$ (Fig. 4.1). This treatment plant was offline until the end of June in 2011 for renovation, and during this period the water from MWRF was sent to the Drake Water Reclamation Facility (DWRF), which has the largest capacity (1 $m^3 s^{-1}$) among the five WWTPs and the highest average annual summer flow (0.79 $m^3 s^{-1}$). The effluents from DWRF and South Fort Collins Sanitation District (SFCSD), with a design capacity of 0.2 $m^3 s^{-1}$, are discharged into Fossil Creek Reservoir, and the water enters the CLP River from there. Boxelder Sanitation District (BSD), with a capacity of 0.1 $m^3 s^{-1}$, therefore, was the most upstream WWTP while the MWRF was not in operation.

Sample sites 1 through 5 are located upstream of all WWTPs for all events, and sampling sites 6 and 7 were also upstream from events 1 through 10 while the MWRF was closed. Four WWTPs are clustered in the middle section of the CLP River, and the Windsor wastewater treatment plant (WiWWTP) is located between sites 10 and 11 downstream of the river, but the capacity is low at 0.12 $m^3 s^{-1}$ with an average flow of 0.05 $m^3 s^{-1}$.

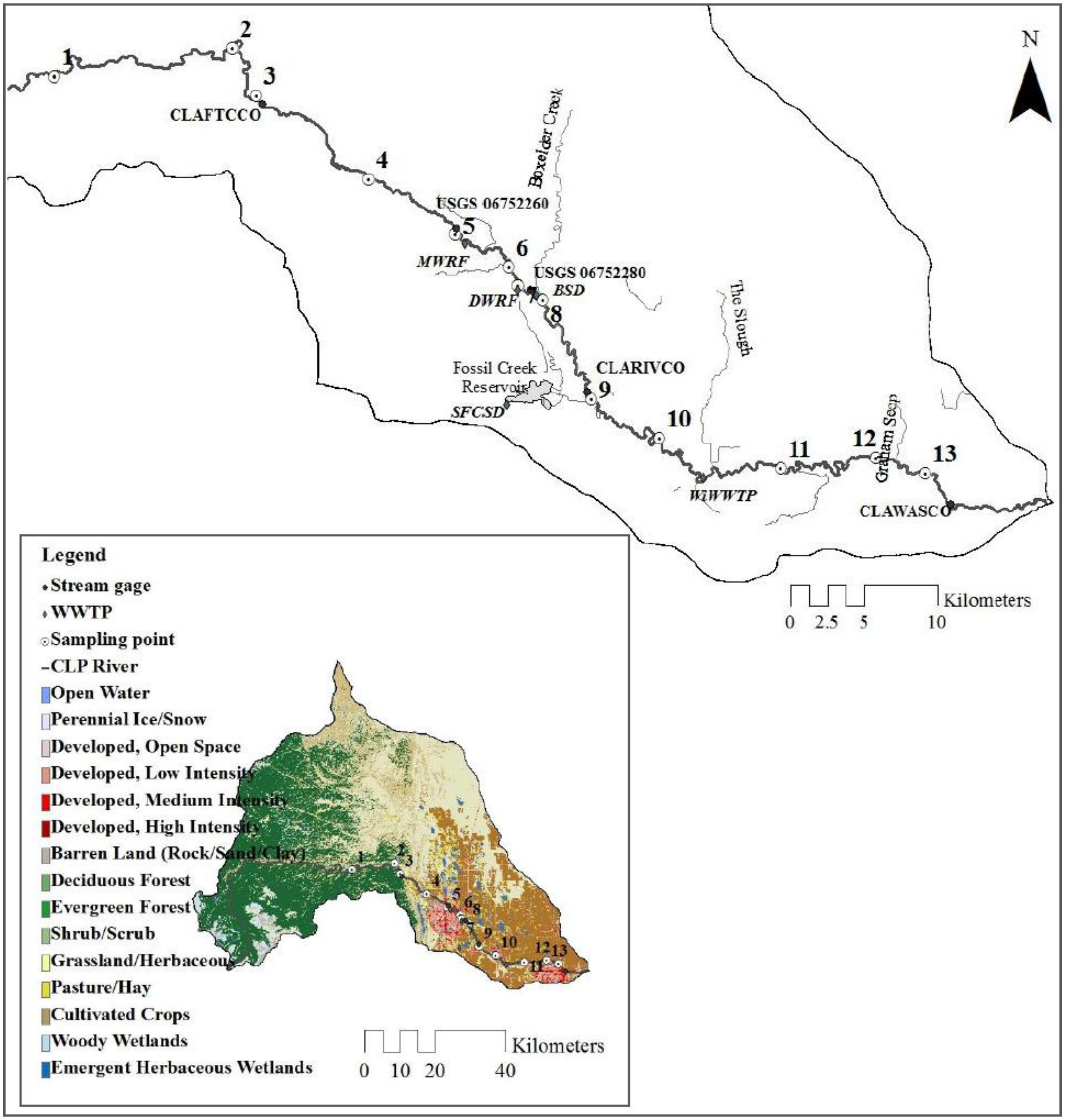

Figure 4.1: Map of the study area showing land use, locations of wastewater treatment plants (WWTPs) (Mulberry Water Reclamation Facility [MWRF], Boxelder Sanitary District [BSD], Drake Water Reclamation Facility [DWRF], South Fort Collins Sanitary District [SFCSD], Windsor Wastewater Treatment Plant [WiWWTP]), flow stations (CLAFTCCO, USGS06752260, USGS06752280, CLARIVCO, CLAWASCO), and 13 sampling points along the Cache La Poudre (CLP) River (data source: City of Fort Collins, USDA).

4.2.2. Sampling events

Twelve sampling campaigns were conducted between April 2010 and August 2011 to quantify TP load and concentration variability under different hydrologic conditions. The hydrologic conditions on the event dates are described in Table 4.2.

Sampling dates were chosen to represent all five classes of hydrologic conditions: high flows, moist conditions, midrange flows, dry conditions, and low flows of the river based on the flow duration curves (Fig. 4.2) under various precipitation and irrigation conditions. The flow duration curves were developed using historical 30-yr flow data from 1981 to 2011 collected from four available flow stations of Colorado Division of Water Resource and USGS located in the study area: CLAFTCCO for the upstream, USGS06752260 for the first midstream, USGS06752280 for the second midstream, and CLAWASCO for the downstream. High flows were identified when the flows were exceeded or equaled less than 10% of the time based on historical data, and moist conditions were identified when the flows had an exceedance between 10 and 40%. Flows between 40 and 60% were midrange flows, and flows between 60 and 90% were classified as dry conditions. The lowest flows that were exceeded or equaled more than 90% of the time were classified as low flows. Flow duration curves of USGS06752280(a) and CLARIVCO were not created due to a lack of historical data. There is a difference between upstream, midstream, and downstream flow rates of the river because of irrigation and other water transfers from upstream to downstream, so flows are lower in this region (Fig. 4.2). Therefore, the hydrologic conditions in the river can be very different on the same day.

Table 4.2: . Hydrologic conditions, flow rates of sites in study area, antecedent 3-d irrigation rates, snow water equivalent, and antecedent 3-d rainfall in the study area between April 2010 and August 2011.

		Flow station (Corresponding sampling site)												
		CLAFTCCO (1-3)		USGS06752260 (4-5)		USGS06752280 (6-7)		USGS06752280(a)† (8)	CLARIVCO (9-10)	CLAWASCO (11-13)				
Event No.	Date	Flow	HC	Flow	HC	Flow	HC	Flow	Flow	Flow	HC	Irrigation‡	Average SWE§	Antecedent 3-Day Rainfall¶
		m^3/s		m^3/s		m^3/s		m^3/s	m^3/s	m^3/s		m^3/s	cm	cm
1	4/23/10	4.64	Moist	1.30	Mid-range	2.49	Moist	3.12	7.33	14.70	High	3.34	47.50	3.06
2	5/19/10	26.90	Moist	28.60	High	25.06	High	25.48	28.12	29.17	High	0	62.87	1.02
3	6/04/10	55.50	High	24.72	High	20.27	High	20.53	19.17	25.40	High	10.36	34.67	0
4	6/18/10	60.32	High	43.89	High	36.53	High	36.78	50.40	59.75	High	0.33	0	0
5	7/16/10	13.54	Moist	2.38	Moist	2.04	Moist	2.29	1.68	2.49	Mid-range	3.06	0	0.06
6	9/17/10	1.14	Dry	1.16	Mid-range	0.65	Moist	0.81	1.49	1.61	Dry	0.58	0	0.08
7	2/22/11	_	Low	0.53	Mid-range	0.07	Low	0.32	0.46	1.47	Dry	0	49.40	0.05
8	4/26/11	3.17	Moist	0.99	Mid-range	0.82	Moist	1.03	1.92	1.82	Dry	2.03	95.50	0.82
9	5/12/11	15.38	Moist	2.92	Moist	3.99	Moist	4.27	4.98	9.77	High	7.76	101.47	3.08
10	6/13/11	73.62	High	59.18	High	56.92	High	57.20	56.35	63.15	High	9.23	76.07	0
11	7/15/11	59.47	High	55.50	High	53.80	High	54.08	55.78	60.31	High	0	_	0.52
12	8/29/11	7.28	Moist	4.79	Moist	3.03	Moist	3.25	1.65	3.26	Moist	5.69	_	0.01

†Sum of flows from USGS06752280, Boxelder Creek, and BSD.

‡ Collected at Larimer and Weld irrigation company; source: Colorado Division of Water Resources.

§ Average of Deadman Hill and Joe Wright; source: NRCS.

¶ Average of antecedent 3-day rainfall of 3 major cities: Fort Collins, Windsor and Greeley.

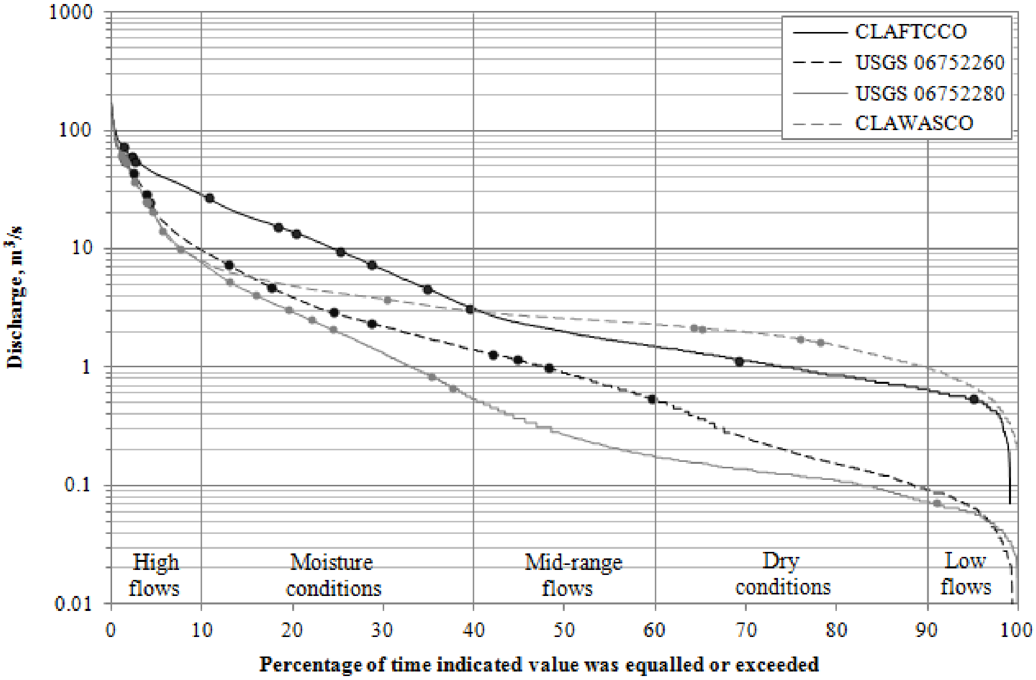

Figure 4.2: Percentage of flow exceedance curves describing flow rates and hydrologic conditions at the flow stations (CLAFTCCO, USGS06752260, USGS6752280, and CLAWASCO) in the study area using a 30-yr record period of flow rates (Oct. 1981–Sept. 2011). The dots on the curves show flow rates and hydrologic conditions at each station on 12 sampling event dates. Discharge of event 7 at USGS station 06052000 was replaced by a record at USGS station 06752260 due to an ice effect.

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 due to snowmelt upstream and downstream and when the snow water equivalent (SWE) was at a peak for the year. The SWE is the volume of water equivalent of snowpack that was present in the headwater. The SWE is important especially for the study area that is located in a semiarid region because the major source of the river water is from the snowpack accumulated during winter months. Sampling during low flows and dry conditions took place in September 2010, February 2011, and April 2011.

4.2.3. Data collection

Water samples were collected in 500-mL Nalgene bottles from three randomly selected points at each of 13 sampling sites using a grab sampling method on 12 sampling dates. Collected samples were transported to the laboratory and kept at 4°C until measured. Concentration of TP was measured using an acid persulfate digestion method (Hach method 8190; USEPA Method 365.2; Standard method 4500 PB and PE) (Eaton 2005) with a detection range of 0.06 to 3.5 mg L^{-1}. All measured TP concentrations in this study were within the detection range.

Monthly TP loads from WWTPs were calculated using 3-yr daily average monthly discharge data (July 2008–June 2011 for BSD, DWRF, SFCSD, and WiWWTP; July 2006–June 2009 for MWRF) from each WWTP gained from the USEPA Enforcement and Compliance History Online and 1-yr monthly TP concentrations in effluents (Apr. 2010–Mar. 2011) provided by the DWRF. Due to a lack of available data from other WWTPs, TP concentration data from the DWRF were used for load estimation for other WWTPs (except for the BSD) based on an assumption that nutrient concentrations in effluents from the WWTPs having the same level of treatment technique are not significantly different. For the BSD, effluent TP concentrations measured at the laboratory were used. The BSD has a secondary treatment process, whereas others use a biological nutrient removal method.

4.2.4. Total phosphorus load analysis

For each site of the river, TP load was estimated by multiplying the flow obtained from the corresponding gauging station (Table 4.2) by the instantaneous TP concentration data for each event:

$$TP_{load\_i} = TP_{concentration\_i} Q_i \quad [1]$$

Loads of TP from each point source (WWTP) were calculated using measured and collected TP concentration and flow data:

$$TP_{load\_j} = TP_{concentration\_j} Q_j \qquad [2]$$

A mass balance method based on load difference between two sampling points was used for estimation of addition and reduction of TP loads along the CLP River:

$$\Delta TP_{load\_i} = TP_{load\_i} - TP_{load\_i\text{-}1} \qquad [3]$$

Positive values of □TP indicate load addition and negative values imply load retention.

Load inputs from other sources considered as mainly nonpoint sources were calculated by subtracting known point source (WWTPs) inputs from added loads between two sites:

$$TP_{load\_i,nonpoint} = \Delta TP_{load\_i,river} - TP_{load\_j,point} \qquad [4]$$

Load inputs in the l^{th} segment are then,

$$(TP_{load})_l = \sum_{i=n}^{m} \Delta TP_{load\_i} \qquad [5]$$

where n and m are the first and last numbers of sampling sites within the l^{th} segment, respectively, and load input from different sources in the l^{th} segment was estimated as:

$$(TP_{load})_{source} \prod_{k=p}^{l} R_{k-1} \qquad [6]$$

where *p* is the segment number where the source entered, and R_k is a load retention rate gained by sum of load retention divided by total added loads for each segment. The background load was estimated using the same flow data for segment 1 multiplied by the background concentration, which is the average concentration from sampling sites 1 and 2 for each event. 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 because there is no significant source of P in the area.

Because the North Fork of the CLP River is influenced by agricultural areas and septic systems, sample sites downstream of the confluence were excluded from the background estimation.

4.3. Results and Discussion

Concentrations of TP in segments 1 and 2 (sampling sites 1–6) with only light urban, minimal agricultural influences and one WWTP that was not functioning from event 1 through event 10 were relatively constant (range, 0.06–0.30 mg L^{-1}; SD, 0.052) (Fig. 4.3). Beginning with segment 3, which starts to receive significant urban and agricultural influences (including WWTPs and irrigation return flows), the TP concentrations increased significantly (range, 0.12–3.1 mg L^{-1}; SD, 0.577). The first peak was observed at a maximum of 2 mg L^{-1} at sampling site 8, where Boxelder Creek joins the river and BSD discharges above the point. The second peak was at the downstream of Fossil Creek Reservoir (sampling site 9), where DWRF and SFCSD discharge their effluents and where TP concentration ranged from 0.34 to 3.1 mg L^{-1}.

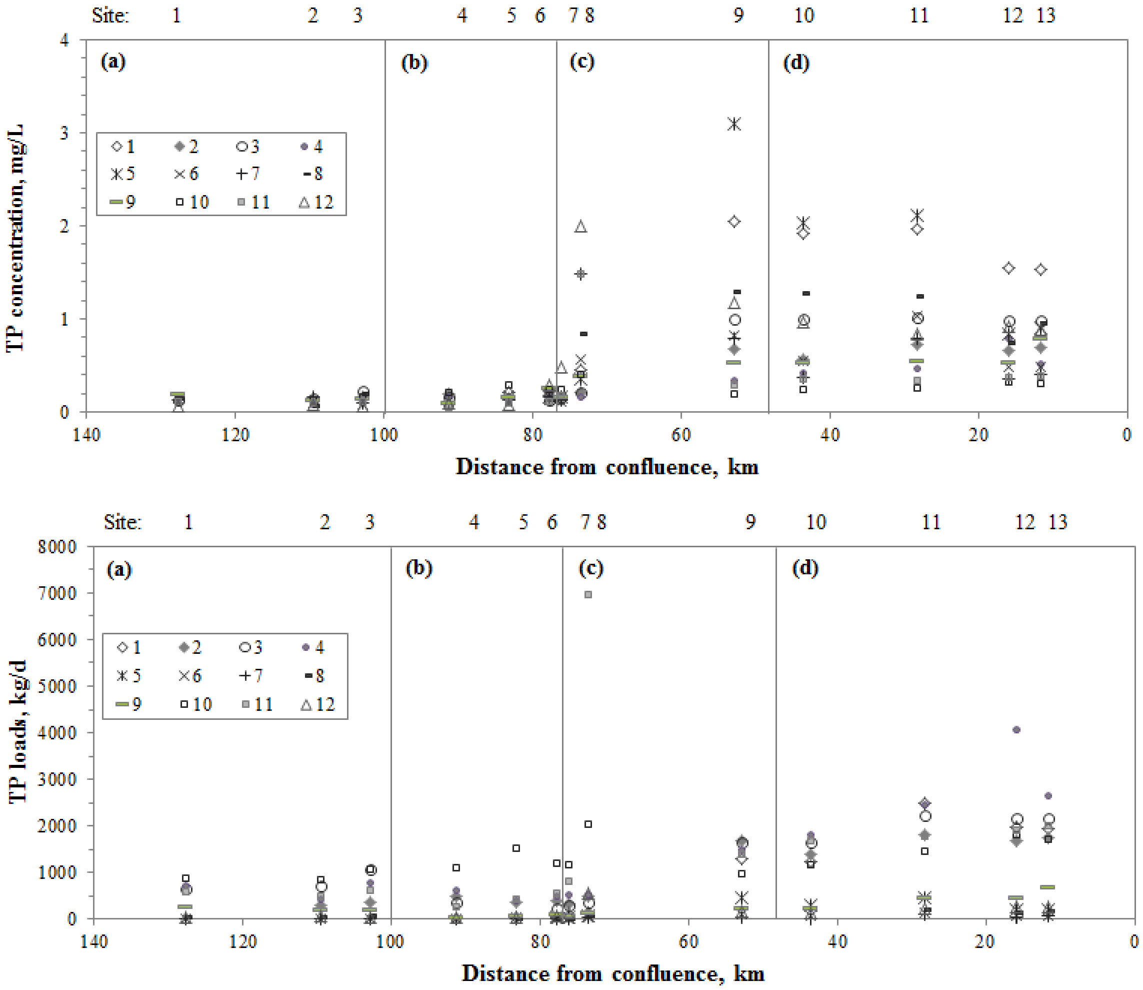

Figure 4.3: Total phosphorus (TP) concentrations (top) and TP loads (bottom) in segment 1 (a), segment 2 (b), segment 3 (c), and segment 4 (d) along the Cache La Poudre River on event dates between April 2010 and August 2011.

As seen in events 6 and 7 in Fig. 4.3, the TP concentrations in the river are more sensitive to WWTP effluents during low flows when there is no irrigation and negligible rainfall. Three peaks were observed at the downstream of WWTPs (sampling sites 8, 9, and 11), and the highest peak of event 7 at the downstream of BSD (sampling site 9) was due to the low river flow of 0.46 $m^3 s^{-1}$. Attenuation from the peaks was observed during moist conditions and dry conditions downstream of WWTPs (events 5–8, 12), whereas downstream TP concentrations were relatively constant or increased from the peak for high flows (events 2–4 and 9–11), most likely due to continuous inputs from agricultural return flows during the irrigation season. However, TP concentrations decreased slightly in the downstream fraction of the river during event 1, although it was during higher flows due to a rainfall event. Similar patterns of low TP concentrations during high flows and high concentrations during low flows can be found in other studies (e.g., Banaszuk and Wysocka-Czubaszek 2005).

The calculated TP load depends on the river flow rates; therefore, a significant difference of TP load under high flows from other hydrologic conditions was observed even in the upstream of the river. The ranges of TP loads were 4.6 to 1517 kg d^{-1} in segments 1 and 2 and 0.8 to 6962 kg d^{-1} in segments 3 and 4. The highest TP loading was recorded at 6962 kg d^{-1} at sampling site 8 on 15 July 2011 (event 11) during high flows.

For the 12 events, TP concentrations in segments 1 and 2 were relatively constant compared with those in other segments (Fig. 4.4). Total P concentrations in segment 1 for all events ranged from 0.06 to 0.22 mg L^{-1} (median, 0.14 mg L^{-1}). The range of TP concentrations in segment 2 for all events was 0.06 to 0.30 mg L^{-1} (median, 0.15 mg L^{-1}). Total P concentrations in samples from segment 1, which has minimal urban and agricultural impacts and no WWTP, already exceeded the proposed TP concentration limit (0.16 mg L^{-1}) in five events (events 3 and 7–10) of various hydrologic conditions from low to high flows out of total 12 observed events. Furthermore, TP concentrations in background (sampling sites 1 and 2) considered as pristine areas exceeded the limit in events 7 and 9 in low-flow and moist conditions, respectively. Segment 2 is a mixed land use area dominated by urban uses that has one WWTP (MWRF) that was not operating during events 1 to 10. Total P concentrations in the area exceeded the proposed limit in eight events (events 1–3, 6–7, 9–10, and 12) in diverse hydrologic conditions, but minimal TP impact was observed in the segment.

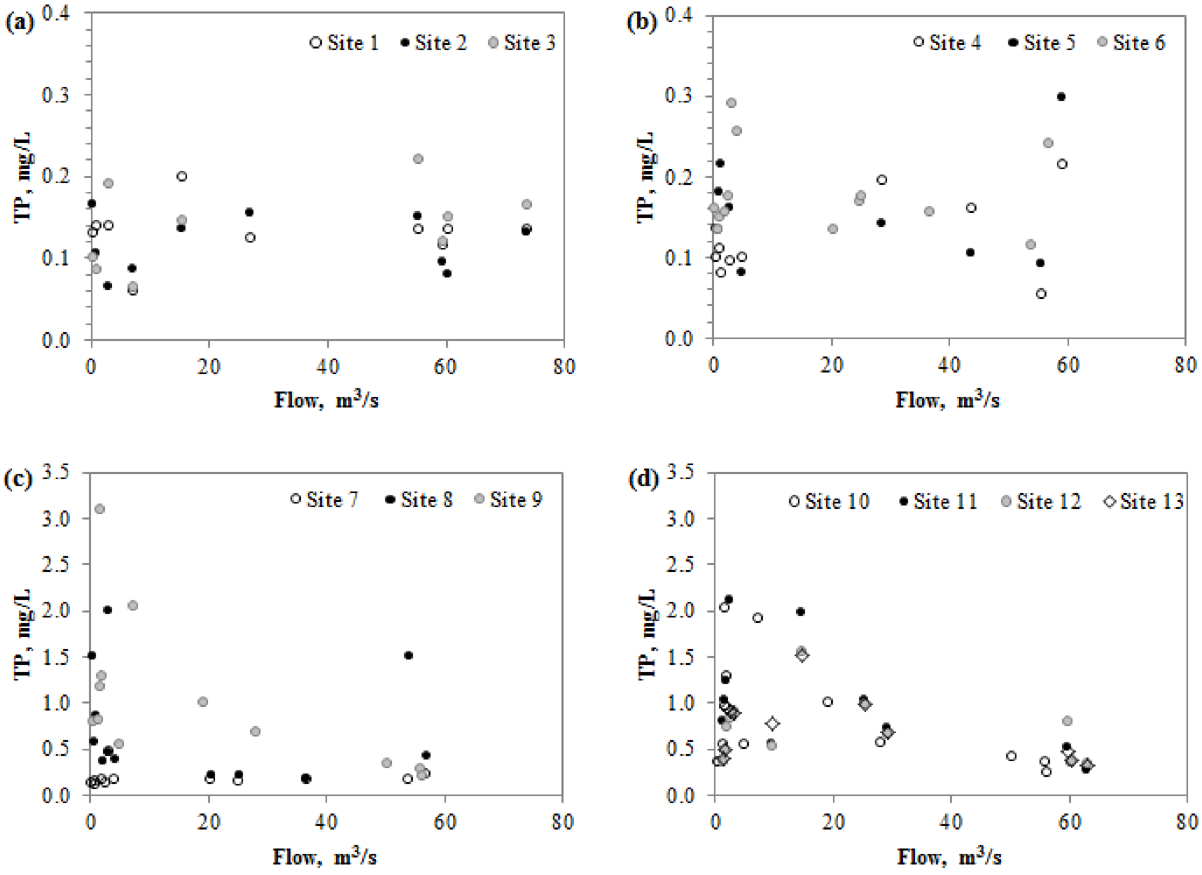

Figure 4.4: Plots of total P (TP) concentrations (mg L^{-1}) and flows (m^3 s^{-1}) of the four segments of the Cache La Poudre River: segment 1 (a), segment 2 (b), segment 3 (c), and segment 4 (d).

Concentrations of TP in the river became much higher from segment 3, with the TP concentrations varying from 0.13 to 3.1 mg L^{-1} (median, 0.37 mg L^{-1}). Total P concentrations in segment 4 were higher and more constant with increased flows (range, 0.24–2.1 mg L^{-1}; median, 0.61 mg L^{-1}). This indicates that there were constant inputs of TP downstream, most likely due to irrigation return flows, and less or no attenuation along the river. Total P concentrations in most, but not all, samples from segment 3 were over the proposed limit in all events, and the concentrations in all samples collected from segment 4 for all events exceeded the limit.

Effluent flows from MWRF and SFCSD were similar (annual average, 0.11 m^3 s^{-1}). Flows from BSD were a little less (annual average, 0.09 m^3 s^{-1}), and the lowest flows were from WiWWTP (annual average, 0.05 m^3 s^{-1}) (Fig. 4.5). Drake Water Reclamation Facility has the largest capacity and highest discharges at an annual average of 0.53 m^3 s^{-1}. The peak flows from WWTPs were in June.

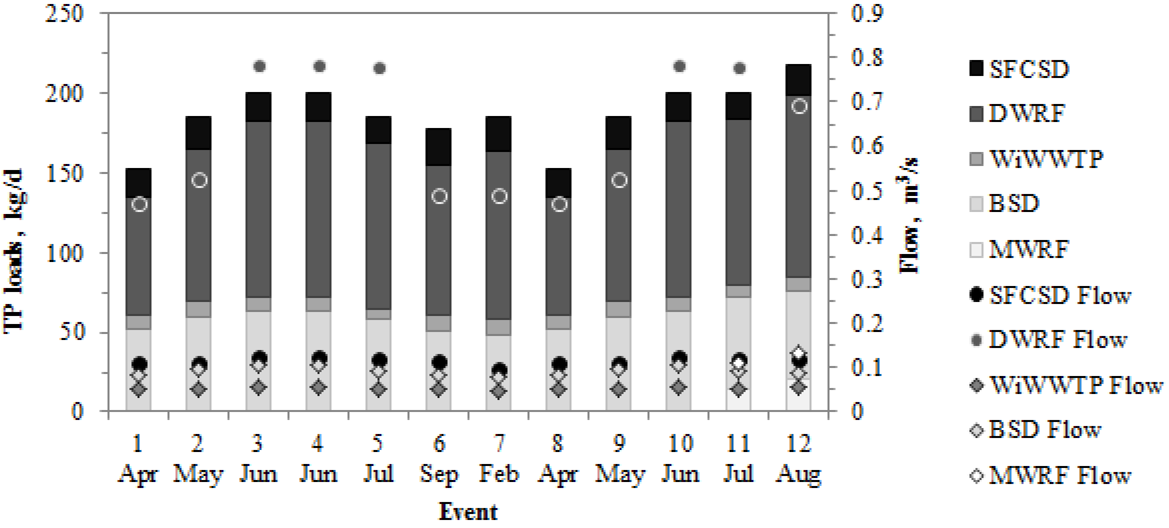

Figure 4.5: Total phosphorus (TP) loads and discharge flows (dots) from five wastewater treatment plants (South Fort Collins Sanitary District [SFCSD], Drake Water Reclamation Facility [DWRF], Windsor Wastewater Treatment Plant [WiWWTP], Boxelder Sanitary District [BSD], and Mulberry Water Reclamation Facility [MWRF]) in the study area in 12 events.

Total effluent flows and TP loads from the WWTPs are highly dependent on effluent of DWRF because of its high discharge rates, but it discharges into the Fossil Creek Reservoir with SFCSD and therefore does not affect the river directly. The indirect impacts of these facilities are not clear and have not been studied. Total P loads from all WWTPs peaked at 217.7 kg d^{-1} in

August with increased outdoor water use, and the lowest was 152.5 kg d^{-1} in April. The highest TP load from WWTPs that discharge into the river directly was 84.9 kg d^{-1} in August, and the lowest was 58.8 kg d^{-1} in July. Total P loads in spring and summer months (Mar.–Aug.) were significantly lower than those of autumn and winter months (Oct.–Feb.) ($p < 0.05$).

Total P loads are dependent on TP concentration and flows, so they showed similar behavior as the TP concentrations described previously (Fig. 4.6). The TP loading limit using the proposed TP concentration limit in the river is already in the range of TP loads in segment 1 of 4.3 to 1055 kg d^{-1}. Segment 2 showed minor influences of TP (range, 0.9–1517 kg d^{-1}; median, 65.5 kg d^{-1}). Total P loads in segment 3, located downstream of the city of Fort Collins, include effluents from three WWTPs both directly and indirectly. Loads in this section increased greatly (range, 0.8–6962 kg d^{-1}; median, 256.4 kg d^{-1}), most likely due to the influence of Boxelder Creek, which flows into the river in this segment. The drainage area of Boxelder Creek is 185.21 km^2 and is dominated by more than 60% of agricultural lands, including crop and grazing land.

Total P loads (daily flux) increased in segment 4 and ranged from 14.6 to 4078 kg d^{-1} (median, 915.5 kg d^{-1}). Segment 4 flows through the city of Windsor to the city of Greeley and has one WWTP with the smallest capacity among the five WWTPs in the study area, but the watershed in this segment is dominated by agricultural lands rather than built areas, including more than seven irrigation ditches. The loads in all observations exceeded the proposed TP loading limit in the river. The exceedance was more significant in high-flow conditions and less significant during other conditions due to relatively low TP loads with low flows, as seen in Fig. 4.6.

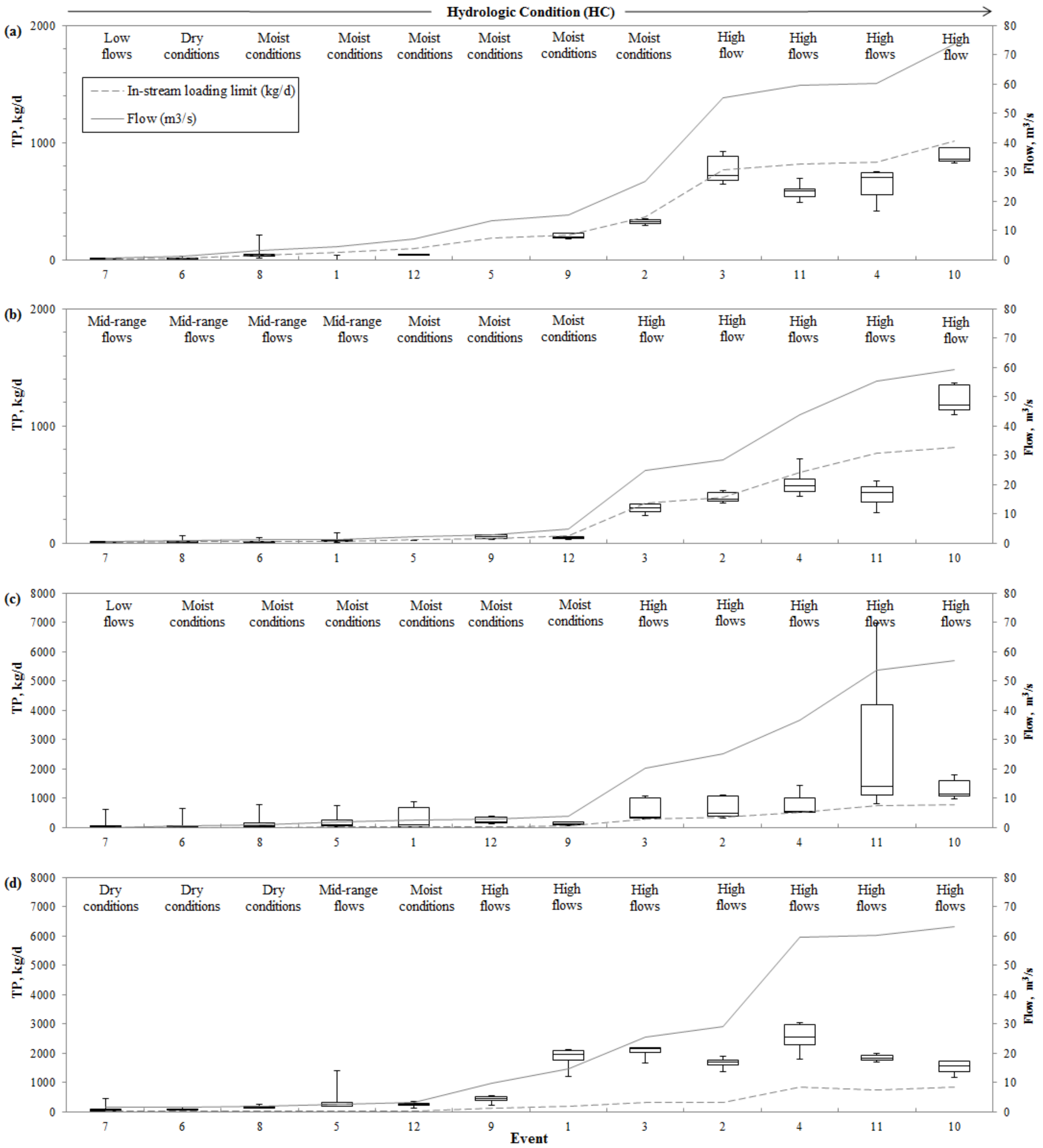

Figure 4.6: Total phosphorus (TP) load box plots and hydrologic conditions of segment 1 (a), segment 2 (b), segment 3 (c), and segment 4 (d) of the Cache La Poudre River on 12 event dates. Dashed lines represent loading capacity of the river based on the proposed TP concentration limit (0.16 mg L^{-1}). Solid lines indicate river flows.

A significant amount of TP enters the river during high-flow periods that correspond with the peak irrigation and urban runoff seasons. Similar results can be found in other studies (Bowes et al. 2003; Brunet and Astin 1998; May et al. 2001). For high flows, the load inputs in segment 3 and 4, which receive strong urban and agricultural influences, ranged from 232.5 to 6962 kg d^{-1}; these values were significantly greater than the estimated load from all WWTPs in the study area, with a maximum of 218 kg d^{-1}. The TP load from WWTPs varies but is relatively constant on an annual basis, so it is believed that there are other major sources of TP that enter the river during high-flow conditions.

The majority of P transported to streams during storm events is in a particulate phosphate form, but P is very dynamic and can be released into the water column in other forms (Correll 1998). Phosphorus in WWTP effluent is mostly in a soluble form, but Bowes et al. (2003) found an increase of particulate P downstream of WWTPs, indicating that P transformation between the P fractions is occurring. Sharpley et al. (1994) suggested that particulate P has the potential to be used by aquatic organisms once it goes through chemical reactions; thus, it is considered as a long-term source of bioavailable P and therefore is regulated as TP.

Total P retained during high flows might be deposited on riverbed and bank sediments, and the stored P can be released with changes of hydrologic and physicochemical conditions of the river (Correll 1998; Sharpley et al. 1996). Total P loads in segment 1 in the mountain area were mainly from the background load, and no other sources were observed during three events of dry conditions, low flow, and moist conditions with negligible precipitation (Fig. 4.7a).

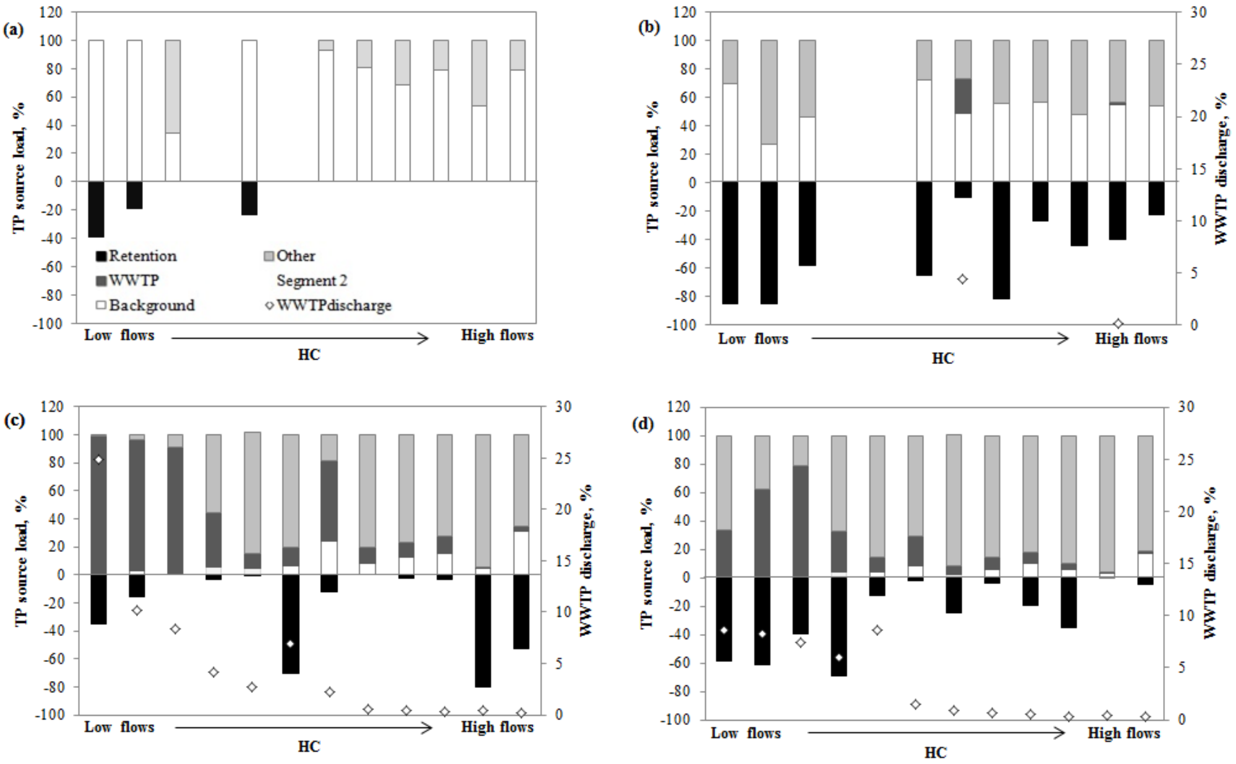

Figure 4.7: Estimated percentages of total phosphorus (TP) loading contributions by sources and percentages of wastewater treatment plant (WWTP) discharges in receiving water (dots) in four segments of the Cache La Poudre River: segment 1 (a), segment 2 (b), segment 3 (c), and segment 4 (d) in diverse hydrologic condition (HC) from low flows to high flows. Negative values indicate percentages of net retention occurred during the event.

Total P loads at segment 2 minus loads at segment 1 provided loads received in segment 2. Total P loads from other sources, such as stormwater from urban and agricultural areas and creeks (Dry Creek and Spring Creek), entered the CLP River in segment 2 and accounted for 27 to 73% of TP flux in the segment with 27 to 72% of background loads (Fig. 4.7b). Influence of TP from MWRF effluent started to be observed from event 11 (high flows) when the facility began operating again. The percent of daily TP flux from MWRF was only 1.7% in event 11 and increased to 25% in event 12 (moist conditions), mainly due to hydrologic conditions in the river. The hydrologic condition of the river in the segment in event 11 was high flow with a flow rate of 53.8 and 55.5 $m^3 s^{-1}$, so dilution had a significant effect on relative importance of TP loads from the facility in the receiving river. The hydrologic condition of the river in event 12 was moist conditions with flow rates of 3 and 4.8 m^3 s^{-1}, which is less than one tenth of the flow rate of event 11. This shows the importance of the hydrologic conditions for the degree of impact of effluents on the river.

Previously it was seen that the CLP River was highly affected by TP from segment 3 especially during high flows; the sources of disturbance were estimated and are shown in Fig. 4.7c. It was expected that the TP loads from WWTPs would dominate the TP loads in the area because three WWTPs are located in the area including DWRF, which has the largest capacity and discharges an annual average TP flux of 95.5 kg d^{-1}. However, TP loads from other sources dominated in the section, except during low flows and moist conditions with lower flow rates. During those conditions, the influence of the BSD elevated to 24 to 98% because dilution in the receiving river was not effective when flow was critically low. When flows were high, the relative contribution of TP loads from the BSD effluent ranged from 0.8 to 4.2%, and TP loads from other WWTPs were also low or not observed, in contrast to the 66 to 95% of TP loads from other sources in segment 3. Total P from other sources took over TP in the CLP River as the river flowed downstream. In segment 4, where the drainage areas are dominated by agricultural lands, 21 to 96% of TP loads were from other sources during all hydrologic conditions (Fig. 4.7d). Although natural retention occurred to varying degrees in all four segments, TP loads in the CLP River exceeded the proposed loading limit (Fig. 4.6).

Additional analysis of retention types of each segments of the river was conducted based on the study of Jarvie et al. (2011). Loads of TP were relatively conservative in segment 1, which has the least biogeochemical, release, and retention processes with minimum TP load inputs from sources other than river itself (Fig. 4.8). The retention pattern in segment 2, having light urban influences, showed increases of P retention at high flows; this finding is related to in-stream retention process and sediment reaction with P. Segment 3, which started to receive significant P loads, has different retention types along the reach. Increases of P retention at high flows were observed at sampling sites 7 and 8, but site 9 showed increases of P retention at lower flow conditions. This pattern was also found in segment 4, which received high agricultural influences. Increases of P retention at lower flows are due to net effects of increased hydraulic residence time, which can enhance P assimilation and deposition and sorption to sediments (Withers and Jarvie 2008).

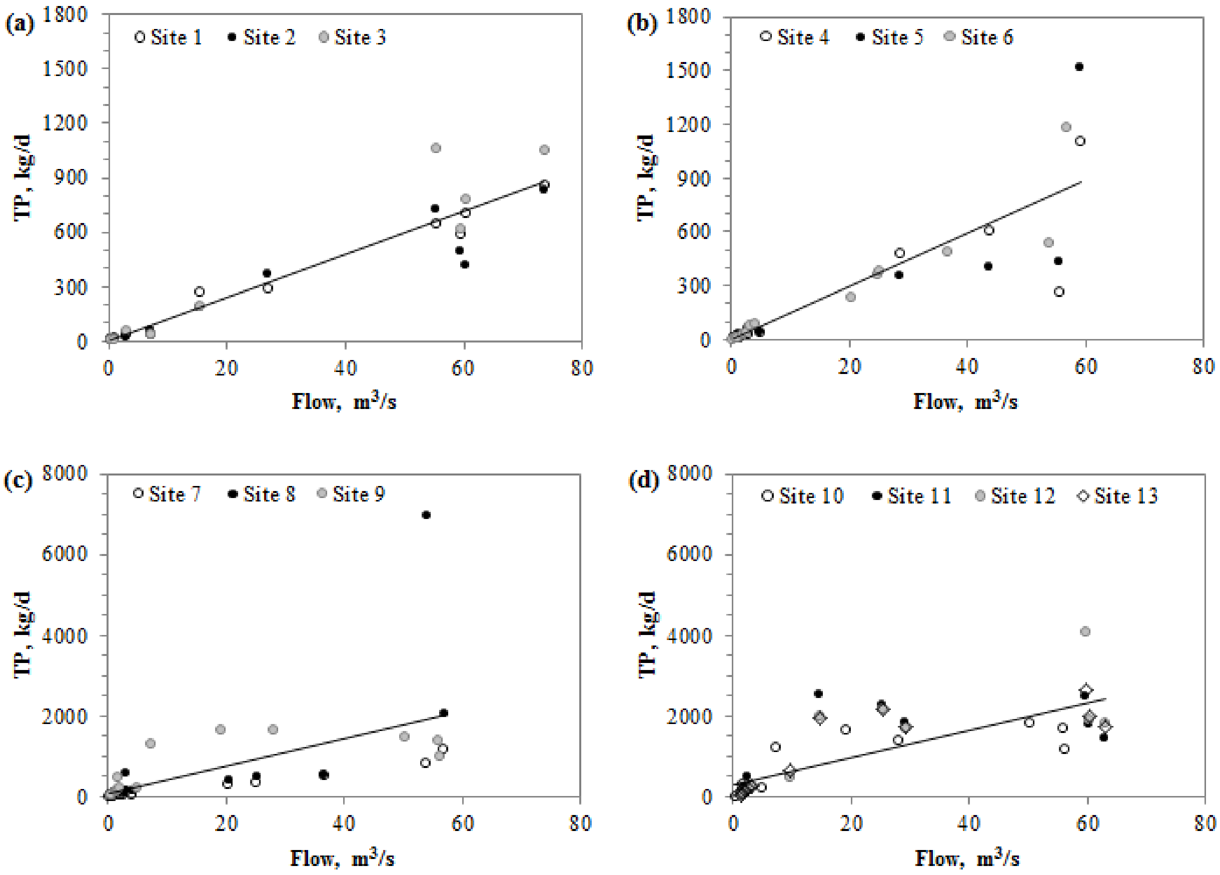

Figure 4.8: Plots of total phosphorus (TP) load and flow for each sampling sites in four segments of the Cache La Poudre River showing retention patterns of TP loads.

Total P loads in all events at segment 3 and 4 exceeded the limit, and it is clear that without control of TP inputs from other sources, the proposed limit cannot be met even if TP loads in effluents of WWTPs are reduced greatly.

4.4. Conclusion

It is critical to monitor nutrient concentrations in rivers due to ecological and human health issues. Monitoring nutrient loads is also important because they are directly related to concentrations, and the data help describe seasonal variation of the sources under different flow conditions. A study was conducted in the CLP River Basin, a suitable location to study occurrence and transport of nutrient loads in the river because it flows through different types of land use areas under diverse hydrologic conditions. From this study, diverse patterns of load retention along the river with different P sources and land use of drainage area have been observed. We determined that the WWTPs are the major sources of TP in a segment of the river that has high urban influences during low flows and dry conditions, but WWTPs are a minor TP load input in a mixed land use watershed for the higher flows that correspond to snow runoff and irrigation return flow. It is important to reduce TP concentrations in WWTP effluent; however, the effect on the total load to the river would likely be small even if WWTPs significantly reduce TP. The analysis suggests that seasonal flexibility in regulating TP load to the river may be advantageous. Finally, the data collected in this study suggest that aquatic life–based stream standards will not be achieved by regulating WWTPs alone. Significant reductions in nonpoint source loads are also required.

CHAPTER 5

WILL STRINGENT TOTAL NITROGEN WASTEWATER TREATMENT PLANT DISCHARGE REGULATIONS ACHIEVE STREAM WATER QUALITY GOAL?

5.1. Introduction

The use of nitrogen (N) in fertilizer has increased significantly over the past several decades with consequences of N causing pollution in waterbodies (Bricker et al. 1999; Galloway et al. 2004). Nitrogen in fertilizer is mainly in nitrate (NO_3^-) form which is hydrophilic and therefore has great mobility in water and may leach into groundwater or enter the waterbodies via surface runoff. Agriculture has continuously ranked as the major source of the pollutants causing water quality impairment of Nation's water, particularly for total nitrogen (TN) in many watersheds (USEPA 1994, 1995, 1998, 2000a, 2002, 2007, 2009). Alexander et al. (2008) estimated that 70 percent of N entering the watersheds of the Gulf of Mexico originated from agricultural lands in the Mississippi River Basin, and only 9 percent of N was from urban areas including wastewater treatment plants (WWTPs), power plants, septic systems and vehicle emissions. Lepistö et al. (2006) proposed that agriculture is the highest single source of N in the rivers in Finland although agricultural land in the area is only 9 percent. The high contribution of agriculture compared to its small area is due to the land management, which has a lack of load reduction in the catchments and nitrogen overapplication, which promotes mobility of nitrogen via leaching (Granlund et al. 2005; Rekolainen et al. 1995; Howarth et al. 1996).

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In 2001, the USEPA acknowledged that nutrient control is necessary and began working with states and authorizing tribes to establish numeric criteria in their watersheds using one of three suggested approaches: 1) develop numeric nutrient criteria as their laws or regulations using EPA's Technical Guidance Method, 2) adopt Section 304(a) of the CWA as the criteria, or 3) develop nutrient criteria using other qualified methods (USEPA 2000b). According to ecoregional water quality criteria recommendations published by the USEPA, the Front Range of Colorado falls under Ecoregion II-Western Forested Mountains and Ecoregion V-South Central Cultivated Great Plains (USEPA 2000c, 2001). The recommended nutrient criteria based on the 25th percentile in rivers and streams of Ecoregion II and V include TP limits of 10 µg L^{-1} and 67 µg L^{-1} and TN limits of 0.12 mg L^{-1} and 0.88 mg L^{-1}, respectively. However, Colorado has decided not to adopt EPA's recommended nutrient criteria of Section 304(a) but to develop its own criteria using a mixed method of approaches number 1 and 3. The Colorado Department of Public Health and Environment (CDPHE) Water Quality Control Commission (WQCC) took the lead in establishing nutrient standards for the state and has been making an effort to develop nutrient criteria. The CDPHE initially proposed in-stream TN and TP limits, Regulation 31, in February 2010 for protecting designated uses of waters (aquatic life use) and modified the limits in February 2011 as 2 mg TN L^{-1} and 0.16 mg TP L^{-1} for warm surface waters and 0.40 mg TN L^{-1} and 0.11 mg TP L^{-1} for cold surface waters. Cold and warm surface waters were classified by sustainable aquatic life for water quality regulations by the CDPHE. Cold waters are waters that weekly summer average temperature does not regularly exceed 20ºC and capable of sustaining cold water biota including trout. The in-stream nutrient standards were derived from best available science (macroinvertebrate health) for the least impaired environment (Lewis and MacCutchan 2005, 2010). Accordingly, the CDPHE has proposed numeric nutrient criteria for municipal wastewater treatment plants (WWTPs, or, the publicly owned treatment works (POTWs)), Regulation 85, as annual averages of 0.7 mg TP L^{-1} and 5.7 mg TIN L^{-1} and quarterly averages of 1.0 mg TP L^{-1} and 9.0 mg TIN L^{-1} based on current achievable technology. To meet the proposed limits of Regulation 85, WWTPs must have at least of an advanced wastewater treatment system such as a biological nutrient removal (BNR) system.

To achieve the in-stream proposed limits, nutrient load reduction is required, and the reduction work is focused on WWTPs because the only federally enforceable source is a point source such as WWTPs through the National Pollutant Elimination System (NPDES). However, there is seasonal variance of TN load contribution of WWTPs to the watersheds under diverse hydrologic conditions, and loads from nonpoint sources might be significant during certain periods of time in a year. If the loads from nonpoint sources are significant on an annual basis, they should be under consideration for regulation. The objective of this study was to examine and compare nitrogen load inputs from known point sources, WWTPs, and other nonpoint sources in different sub-basins under various hydrologic conditions and evaluate effects of load reduction from WWTPs on the river to comply with the proposed nitrogen standards.

5.2. Materials and Methods

5.2.1. Study area and sampling events

The Cache La Poudre (CLP) River basin is located in northern Colorado on the continental divide and drains 4,960 square kilometers of area in Colorado and Wyoming including forests (33%), agricultural areas (18%) and developed areas (5%). The river originates in pristine Rocky Mountain National Park and flows 225 km through the urbanized and rapidly growing city of

Fort Collins and the agriculture dominated area of Greeley before converging into the South Platte River. This unprotected section of the river has more than 20 irrigation and municipal water projects that divert water from the river and substantially reduce its flow.

The study area was divided into six sub-basins according to hydrologic unit (Fig. 5.1), and thirteen sampling locations were selected along the river. Sub-basin 1 (sample ID 1) and 2 (sample ID 2) are located in pristine Rocky Mountain National Park, and these sub-basins are comprised of about 97% forest and shrub/grass lands with less than 2% developed area including roads and no cultivated area (Table 5.1). Therefore, sub-basins 1 and 2 are considered as undisturbed area, and consequently sample ID 1 and 2 were chosen as background. The CLP River flows through a lightly urbanized area in sub-basin 3. Five sampling sites (sample ID 3-7) were selected in sub-basin 3 to study nutrient impacts of light urbanized area on the river. The considerable point sources of nutrients in the study area are WWTPs and a total of five WWTPs are embedded in the region. The most upstream WWTP is the Mulberry Water Reclamation Facility (MWRF), which has an average annual flow of 0.13 $m^3 s^{-1}$, located in sub-basin 3 and discharges water to the river between sampling sites 5 and 6. During event periods from 1 to 5, the MWRF remained closed and sent water to the DWRF due to renovation work, and started operating again during the month of the last sampling event.

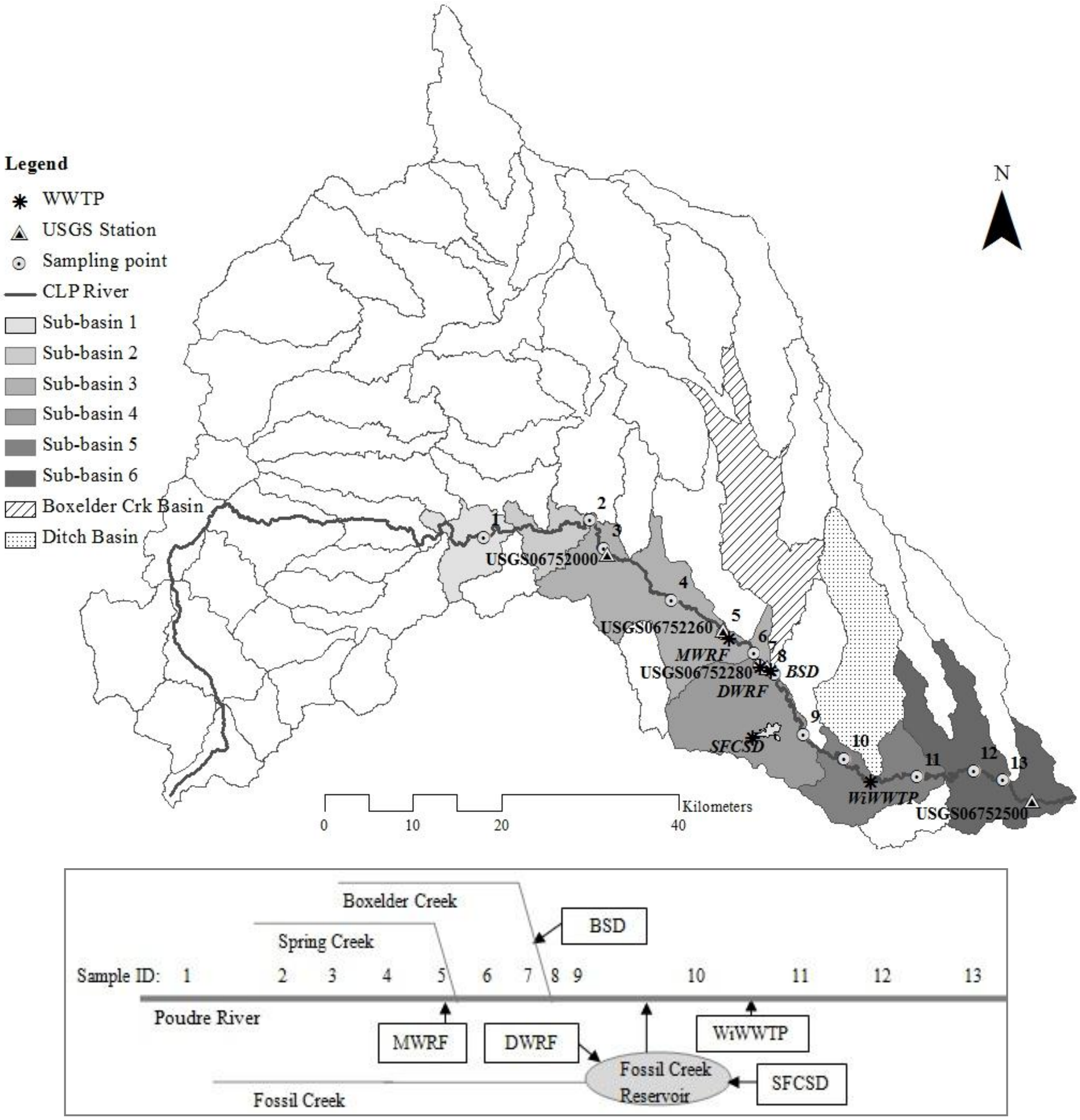

Figure 5.1: Map of Cache La Poudre River Basin showing sub-basins, sampling sites, flow stations and WWTPs in the study area and flow diagram.

Table 5.1: Area (km^2) and percent of land use, number of WWTPs, and range of flow and TN load from WWTPs in the sub-basins.

		Sub-basin															
		1		2		3		4		5		6		Boxelder Crk Basin		Ditch Basin	
		Km^2	%	Km^2	%	Km^2	%	Km^2	%	Km^2	%	Km^2	%	Km^2	%	Km^2	%
Land use	Open water	0.01	0.02	0	0.01	4.24	2.06	9.88	6.47	9.88	3.96	14.23	3.35	11.85	6.4	7.18	4.23
	Developed	0.9	1.49	0.7	1.54	44.09	21.44	51.59	33.77	62.53	25.03	111.38	26.21	13.72	7.41	8.73	5.14
	Barren Land	_	_	_	_	0.5	0.24	0.34	0.22	0.54	0.22	1.06	0.25	0.09	0.05	0.09	0.05
	Forest	36.48	60.52	31.69	70.15	49.95	24.28	1.12	0.73	1.58	0.63	2.01	0.47	0.59	0.32	0.75	0.44
	Shrub/Grassland	22.09	36.64	12.12	26.84	55.63	27.04	23.91	15.65	38.96	15.6	42.57	10.02	40.06	21.63	40.67	23.96
	Pasture	0.02	0.03	0.04	0.08	13.72	6.67	15.17	9.93	21.46	8.59	27.41	6.45	17.36	9.37	8.46	4.99
	Cultivated Crops	_	_	_	_	25.88	12.58	45.62	29.86	107.44	43.01	215.57	50.74	96.42	52.06	100.88	59.44
	Wetlands	0.78	1.3	0.62	1.37	11.63	5.65	5.13	3.36	7.35	2.94	10.53	2.48	5.09	2.75	2.93	1.72
	Other	_	_	0	0.01	0.05	0.03	0.02	0.02	0.04	0.02	0.14	0.03	0.02	0.01	0.04	0.02
	Total	60.28	100	45.17	100	205.69	100	152.78	100	249.8	100	424.88	100	185.21	100	169.71	100
WWTPs	N	_		_		1		3		1		_		_		_	
	Flows (m^3 s^{-1})	_		_		0.09-0.13		0.53-0.96		0.05-0.06		_		_		_	
	TN loads (kg d^{-1})	_		_		62.87-122.80		416.92-829.64		30.47-51.40		_		_		_	

Sub-basin 4 contains three WWTPs: Boxelder Sanitary District (BSD), Drake Water Reclamation Facility (DWRF) and South Fort Collins Sanitary District (SFCSD), which have average annual flows of 0.09, 0.53, and 0.11 $m^3 s^{-1}$, respectively. The BSD discharges effluent between sampling points 7 and 8 where Boxelder Creek flowing through the Boxelder Creek Basin joins the river. The BSD has the highest TN concentration in effluents among all five WWTPs in the study area and the monthly concentrations ranged from 14.95 mg L^{-1} to 26.28 mg L^{-1} while the concentrations from other WWTPs were in the range of 10.13-17.80 mg L^{-1}. The DWRF is the largest municipal plant in the study area and discharges water to the Fossil Creek Reservoir with the SFCSD. The water from the reservoir enters the river between sampling points 8 and 9. Sub-basin 4 is located downstream of the city of Fort Collins, which is considered the most developed area in the study area, and two sampling locations (sample ID 8-9) were chosen downstream of WWTPs, where the receiving water and effluents are well-mixed. Sub-basin 5 flows through the city of Windsor to the city of Greeley and contains two sampling points (sample ID 10-11) and one WWTP, the Windsor Wastewater Treatment Plant (WiWWTP), which has an average annual flow of 0.05 $m^3 s^{-1}$ and discharges water to the river before sampling site 11. The Ditch Basin also converges into the river through irrigation ditches between sampling sites 10 and 11. Surface water drawn from upstream of the CLP River by canals flows through the irrigation area, and the irrigated waters are re-transported to the river by large irrigation ditches in the Ditch Basin. Sub-basin 6 is located in the city of Greeley and also has the largest agricultural area. There are two sampling locations (sample ID 12-13), and no WWTP is located in the sub-basin.

Sampling campaigns were conducted on seven event dates selected based on the hydrologic conditions of the river to represent all five different hydrologic conditions: high flows, moist conditions, mid-range flows, dry conditions and low flows from September, 2010 to August, 2011. Fig. 4.2 in Chapter 4 shows various hydrologic conditions on the event dates using a percentage of flow exceedance curve created by 30-year flow data from four USGS stations located in the study area: the most upstream (USGS 06052000), middle streams (USGS 06752260, USGS 06752280), and the most downstream station (USGS 06052500) in the CLP River.

Flow rates along the river on the event dates were collected from four USGS stations, and hydrologic characteristics are summarized in Table 5.2.

Table 5.2: Hydrologic conditions; flow rates at four USGS gages in study area, antecedent 3-day irrigation rates at Larimer and Weld irrigation company, average of snow water equivalent (SWE) at Deadman Hill and Joe Wright (SNOTEL site no. 438 and 551), and average of antecedent 3-day rainfall of 3 major cities (Fort Collins, Windsor and Greeley) in the study area on event dates from September 2010 through August 2011.

Event	Date	USGS 06052000[a] ($m^3 s^{-1}$)	USGS 06752260[b] ($m^3 s^{-1}$)	USGS 06752280[c] ($m^3 s^{-1}$)	USGS 06052500[d] ($m^3 s^{-1}$)	Antecedent 3-Day Irrigation ($m^3 s^{-1}$)	Average SWE (mm)	Antecedent 3-Day Rainfall (mm)
1	9/17/2010	0.03	0.03	0.02	0.05	0.34	0	548.386
2	2/22/2011	_	0.02	0.00	0.06	0	494.03	0.51
3	4/26/2011	0.09	0.03	0.02	0.05	0.50	955.04	8.21
4	5/12/2011	0.43	0.08	0.11	0.27	1.14	1014.73	30.82
5	6/13/2011	2.08	1.67	1.61	1.74	0.23	760.73	0
6	7/15/2011	1.68	1.57	1.52	1.54	0.54	0	5.16
7	8/29/2011	0.21	0.14	0.09	0.05	0.57	0	0.08

[a] CACHE LA POUDRE AT CANYON MOUTH NEAR FORT COLLINS
[b] CACHE LA POUDRE RIVER AT FORT COLLINS, CO
[c] CACHE LA POUDRE RIV AB BOXELDER CRK NR TIMNATH, CO
[d] CACHE LA POUDRE NEAR GREELEY

The hydrologic condition is affected by various characteristics such as irrigation flows, precipitation and the snow water equivalent (SWE). Water transfers through canals and irrigation ditches from upstream to downstream makes different hydrologic conditions along the river and lowers the mid-stream flow rates. The SWE, defined as the volume of water equivalent to the snowpack existing in the headwater, is imperative for the hydrologic condition in this area since the major source of the river water is melted snowpack accumulated during the cold season.

5.2.2. TN concentrations

River water samples were collected from three points at each site using a grab sampling method and composited, transferred to 50 mL acid washed Nalgene bottles. Collected samples were then transported to the laboratory and kept at 4°C until measured. Measurement was conducted in 48 hours after sampling using a Shimadzu TOC-VCSH analyzer equipped with a TNM-1 (Shimadzu Corporation, Columbia, MD). The detection limit of the analyzer is 5 μg L^{-1}.

5.2.3. TN load analysis

TN loads in the river were calculated using the measured TN concentrations from the collected river water samples multiplied by the flow rates from the nearest USGS station, and load inputs from each sub-basin were determined based on mass balance. Monthly TN load inputs from each WWTP were estimated using 3-year monthly discharge data for five WWTPs (July 2008-June 2011 for BSD, DWRF, SFCSD, and WiWWTP; July 2006-June 2009 for MWRF) collected from EPA-ECHO and 3-year monthly TN concentration (mg L^{-1}) (July 2008-June 2011) in the effluent was provided by the DWRF and the BSD. Due to the lack of TN concentration data from other WWTPs, TN loads from WWTPs were calculated based on the monthly TN concentration from the DWRF with an assumption that TN concentrations in effluents of other WWTPs are not significantly different from those of the DWRF except for the BSD. The assumption was derived from the similarity of monthly ammonia concentrations in effluents of WWTPs.

5.3. Results and Discussion

Concentrations and daily load of TN for the seven events had very similar aspects with different magnitude (Fig. 5.2). Concentration and load of TN were significantly related to the river flow rate. When the flow rates were low, TN concentrations were high, and when the flow rates were high, TN concentrations were low due to the dilution effect (Fig. 4.10a).

The highest concentration among the seven observed events was events 1 and 2 when the flow was low, and the concentration peaked at 8.14 mg L^{-1} at site 8 located downstream of BSD and the confluence with Boxelder Creek when flow was lowest at 0.07 $m^3 s^{-1}$ in event 2 (Table 5.2). The lowest concentration was event 5 when the flow rate was at a peak at 73.58 m^3 s^{-1} in upstream. The high loads appeared in event 5 and 6 and peaked at 32.526 metric-tons per day at site 8 in event 6 during high flow conditions (Fig. 5.2b).

For the all events, it was observed that the TN concentration and load significantly increased at site 8, especially for event 6, when 30.541 metric-tons of TN load entered the river for the day. The potential sources of great amounts of TN loads are BSD, Boxelder Creek and subsurface flow and overflow from the surrounding areas including a corn field and highway. The corn field is located near site 8, and Boxelder Creek flows through the field before it converges into the river. TN concentration in Boxelder Creek was 4.75 mg L^{-1}, which could have significantly affected the CLP river water concentration at site 8, which was 6.70 mg L^{-1}. Retention of TN load was observed in the range of 11-92% during the CLP River flows 11km from site 8 to site 9.

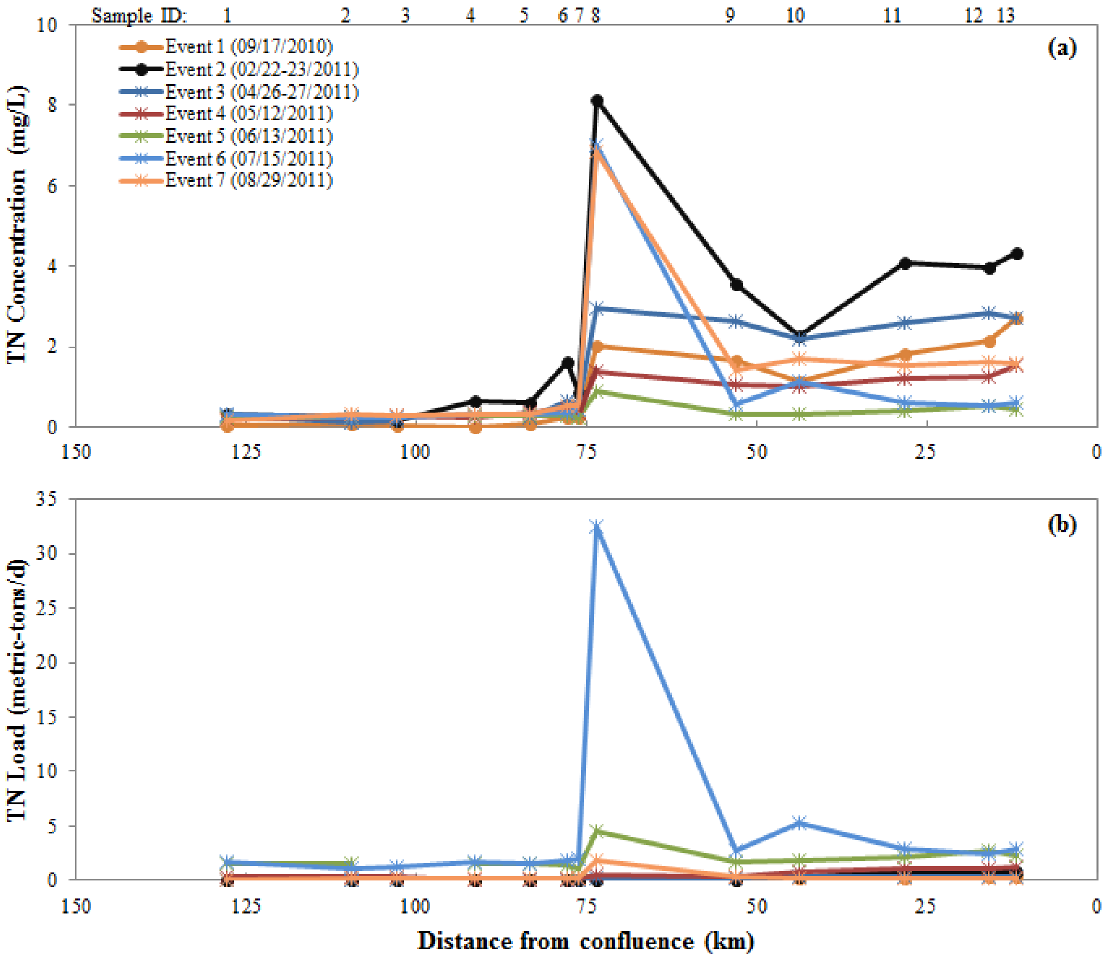

Figure 5.2: (a) TN concentration (mg L^{-1}) and (b) TN load (metric-tons d^{-1}) along the CLP River on different event dates. Discharge data from USGS 06052000 was used for sample ID 1-3 (upstream), USGS 06752260 for sample ID 4-6 (mid-stream 1), USGS 06752280 for sample ID 7-9 (mid-stream 2), USGS 06052500 for sample ID 10-13 (downstream).

High retention of 63% and 92% occurred during high flows (event 5, 6) and 11% and 19% of low retention was observed during dry conditions (event 1, 3). DWRF and SFCDS discharge effluents to the Fossil Creek Reservoir, and the water then flows into the river. Average daily TN loads in the effluents from DWRF and SFCSD are 665.7 kg in the range of 452.1-960.4 kg and 138.2 kg in the range of 121.8-162.6 kg, respectively. A significant influence from DWRF was not observed in the CLP River even though it has the largest capacity among the five WWTPs in the study area. It is believed that the reservoir acts as a buffer for TN (Harrison et al. 2009).

Although the river itself has retention and removal capability (Howarth et al. 1996), TN concentration increased downstream as TN load entered the river via return flows, subsurface flows and overland flows as the river passed through agricultural lands. The most rapid increase was seen in February (event 2) from sampling sites 10 to 13 though the flow rate in the area was not at the lowest point among the seven events. This was because retention processes were limited since the water temperature was near the freezing point (Table 5.2), thus restricting activity of microorganisms.

TN concentration and load in upstream and mid-stream 1 (sample ID 1-6) were significantly lower than mid-stream 2 and downstream (sample ID 7-13) ($p < 0.05$). The lowest concentration from all observed data was 0.01 mg L^{-1} sampled in September (event 1) at site 4, and the highest concentration was 1.6 mg L^{-1} sampled in February (event 2) at site 6, located downstream of the confluence with Spring Creek in a built environment.

Fig. 5.3 shows TN concentration in upstream, mid-streams and downstream of the CLP River under various hydrologic conditions characterized by flow rates collected from the nearest USGS gauges from each sampling location.

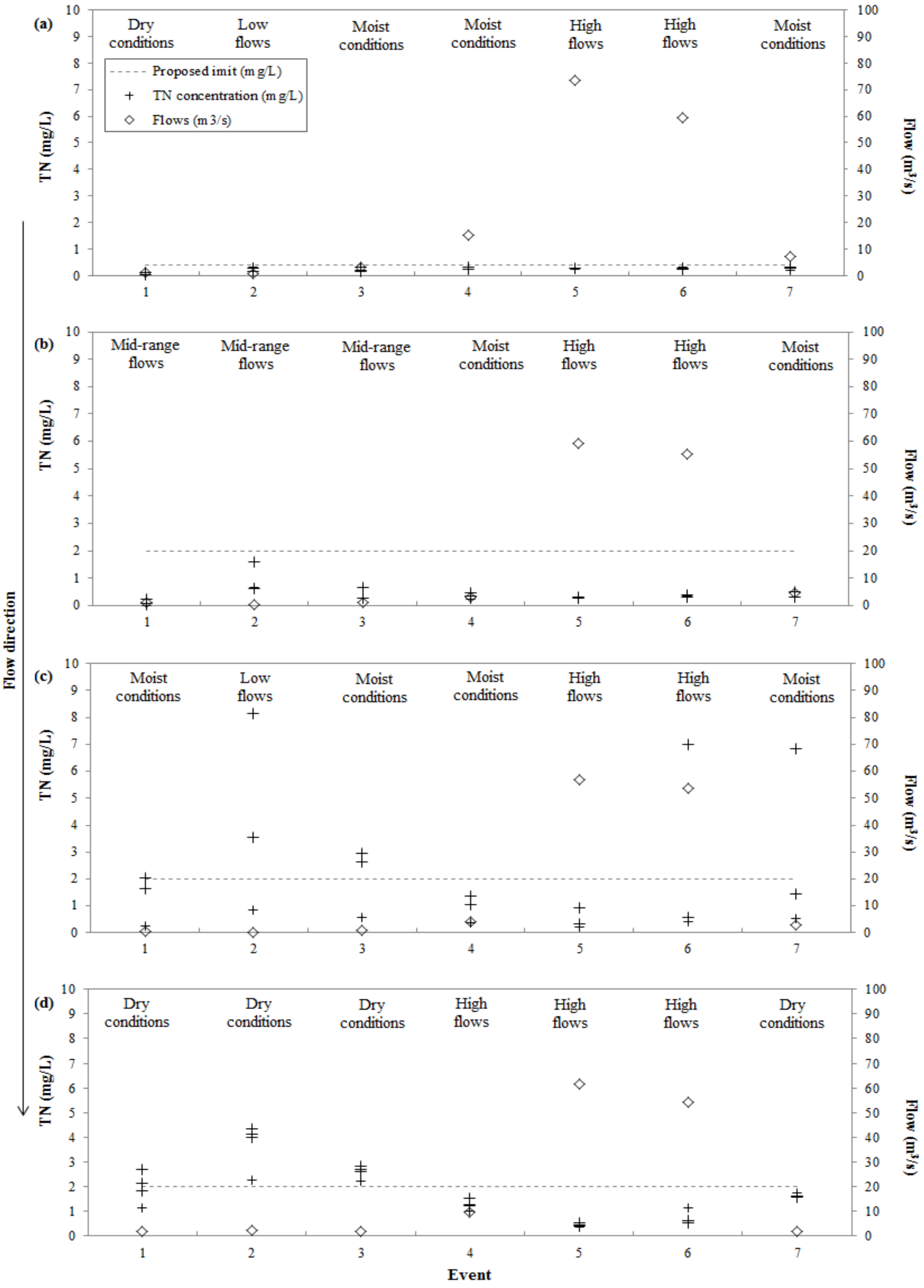

Figure 5.3: TN concentration (mg L^{-1}), proposed limit (mg L^{-1}), flow rate (m^3 s^{-1}) and hydrologic condition in (a) upstream (sample ID 1-3), (b) mid-stream 1 (sample ID 4-6), (c) mid-stream 2 (sample ID 7-9) and (d) downstream (sample ID 10-13) of the CLP River on seven events.

Upstream segment (sample ID 1-3) is only classified as cold surface waters in the study area and TN concentrations in upstream ranged from 0.034 to 0.32 mg L^{-1} with a median of 0.239 mg L^{-1} and a standard deviation of 0.09. All TN concentrations in upstream were under the proposed concentration limits (0.4 mg L^{-1} for cold waters). Concentrations started to increase slightly from mid-stream 1 (sample ID 4-6). Ranges of TN concentrations in mid-stream 1 were 0.01-1.6 mg L^{-1} with a median of 0.32 mg L^{-1} and a standard deviation of 0.33. The flow rate in mid-stream 1 on event 2 was the lowest as 0.54 m^3 s^{-1} and temperature of the river were also at the lowest, near the freezing point. Accordingly, exceedance of TN concentrations on event 2 was greater than on other events. TN concentrations on event 3 when flow and temperature were low also showed exceedance of the limits. The largest range of TN concentrations was found in mid-stream 2 (sample ID 7-9), where the major WWTPs are located. The range of concentrations was 0.23-8.14 mg L^{-1} with a median of 1.04 mg L^{-1} and a standard deviation of 2.39. Events 1, 6, and 7 also exceeded the limit but only at sampling site 8, where effluent of BSD and Boxelder Creek flows into the river.

Downstream (sample ID 10-13) concentrations ranged from 0.34 to 4.34 mg L^{-1} with a median of 1.57 mg L^{-1} and a standard deviation of 1.13. Exceedance was observed during dry conditions except during event 7, and no exceedance was found during high flows.

Frequency of exceedance of TN loads from the estimated loading limits using the proposed limits of concentration was the same as TN concentration but with different magnitude. TN loads in upstream (sample ID 1-3) for all events ranged from 0.003 to 1.644 metric-tons per day and no exceedance was observed (Fig. 5.4).

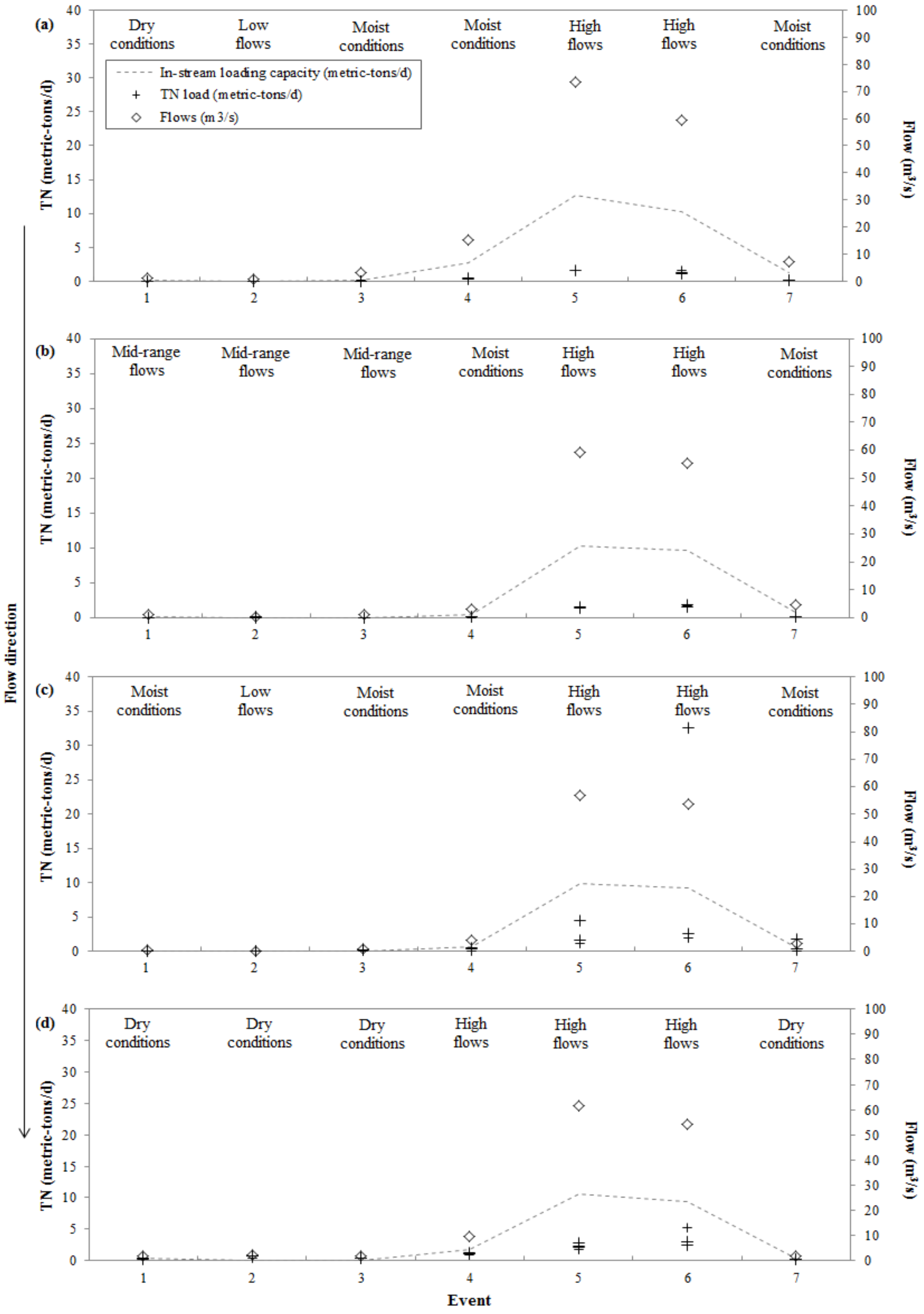

Figure 5.4: Daily TN load (metric-tons d^{-1}), in-stream loading capacity (metric-tons d^{-1}) based on the proposed TN concentration limit, flow rates (m^{3} s^{-1}), and hydrologic conditions in (a) upstream (sample ID 1-3), (b) mid-stream 1 (sample ID 4-6), (c) mid-stream 2 (sample ID 7-9) and (d) downstream (sample ID 10-13) of the CLP River on seven events.

Based on the data observation, cumulative daily TN loads in six sub-basins were analyzed to investigate TN sources in each event (Fig. 5.5).

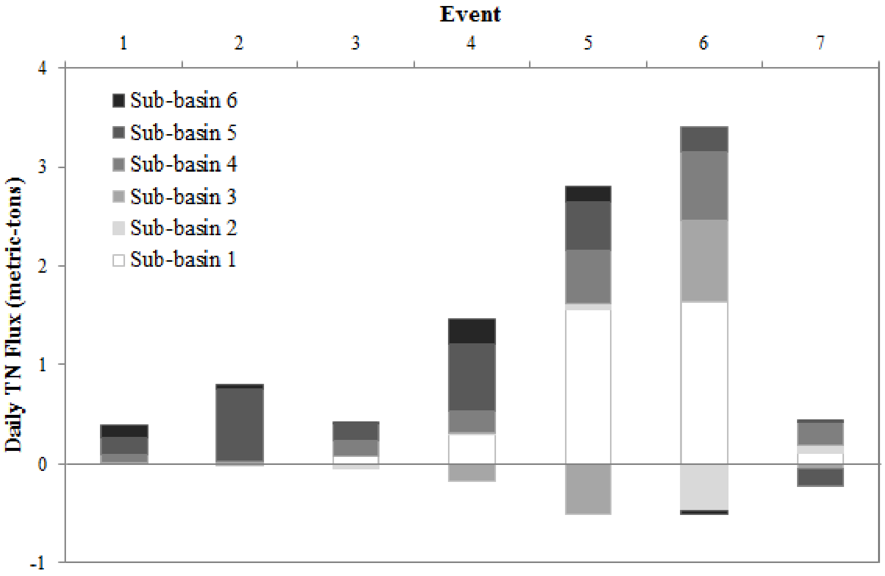

Figure 5.5: Cumulative daily TN load that entered the watershed from sub-basins. Negative load indicates the amount of retention occurring in the sub-basin.

During lower flows, sub-basin 5 was the most significant source of TN load followed by sub-basins 4 and 6. Sub-basins 4-6 are dominated by anthropogenic influences including urban and agricultural areas ranging from 73.6 to 83.4%. Sub-basin 1 comprised mostly of forest and shrub/grass lands, however, became the most significant source during high flows (Fig. 5.6).

Because TN concentration and loads showed exceedance from the proposed limits only during events 1-3 in segments 3 (sample ID 7-9) and 4 (sample ID 10-13) and also in segment 2 (sample ID 4-6) except for event 1, the cumulative TN loads at sub-basins for events 1-3 were analyzed, and contributing source percentages of TN load inputs at each sub-basin were estimated in Fig. 5.6. For these lower flow events, sub-basin 5 showed great influences ranging from 42% to 91%, and sub-basin 4 and 6 also contributed 2-35% and 3-33% of TN loading to the CLP River, respectively.

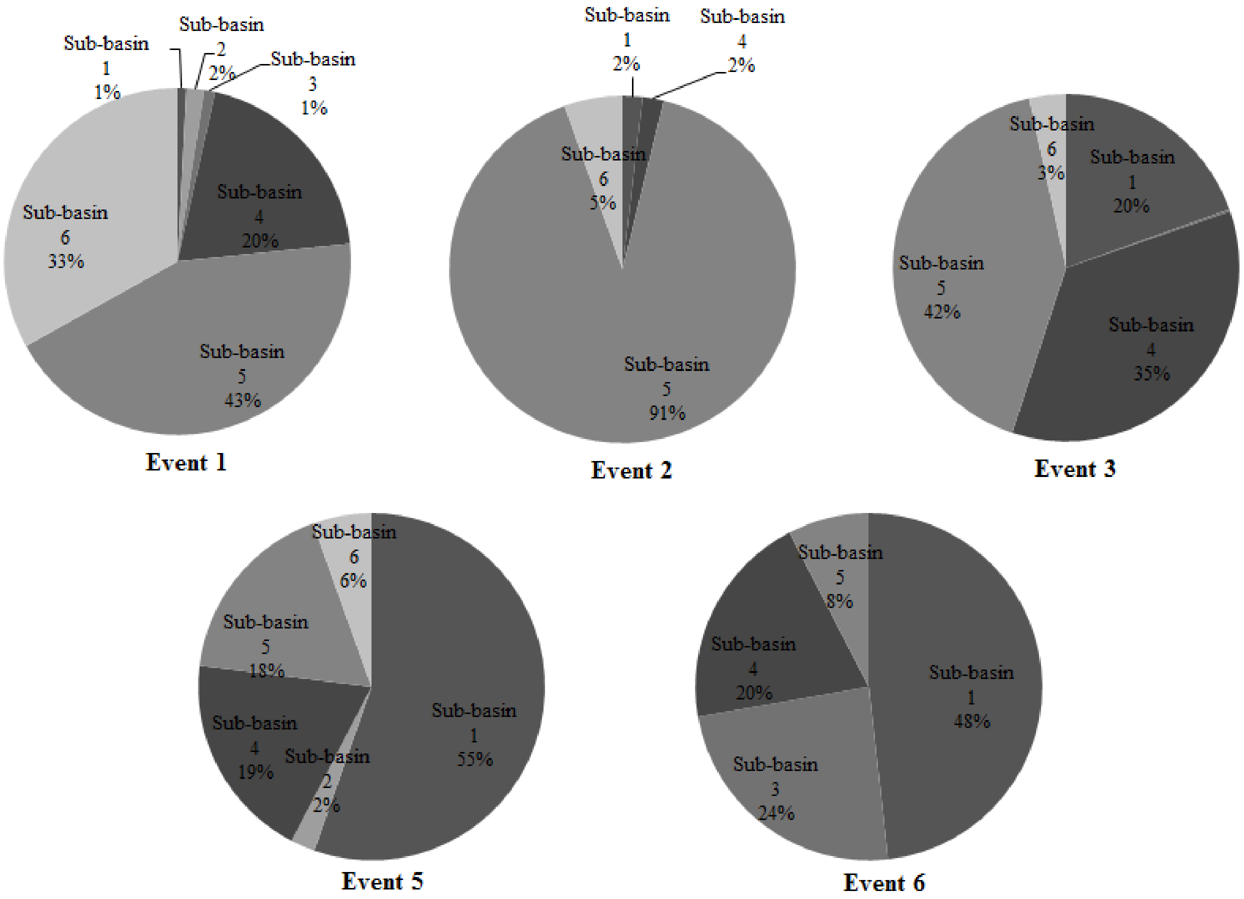

Figure 5.6: Percent of daily TN flux inputs to the watershed from sub-basins during low flow conditions (events 1-3) when the TN flux in the CLP River exceeded the proposed loading limits and during high flows (events 5-6).

TN load inputs from known sources at the three most influencing sub-basins during events 1-3 are illustrated in Fig. 5.7. TN load at sub-basin 4 was dominated by effluent from BSD, which contains 164.6 kg of average daily TN load. TN load inputs from other sources were only observed during event 3 among these three events. This might be due to considerable precipitation (8.21 mm) occurring prior to the sampling event 3, causing runoff from surrounding areas.

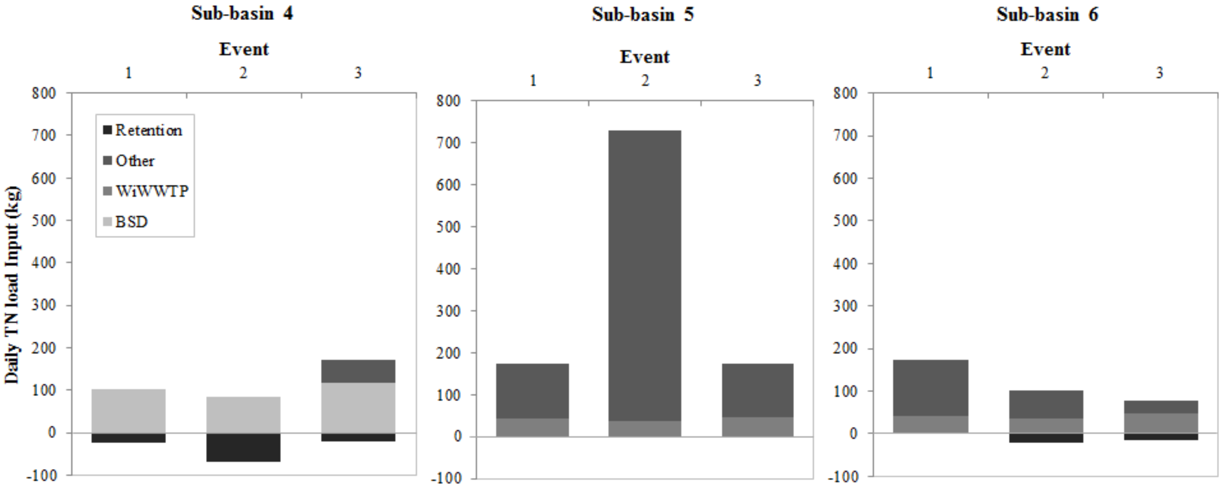

Figure 5.7: Daily TN load inputs (kg) by known sources and other nonpoint sources at sub-basins 4-6 having great TN load contributions on events 1-3 when the TN flux in the CLP River exceeded the proposed loading limits.

Both TN concentrations and loads increased, and no retention occurred while the river passed through sub-basin 5 during events 1-5. For events 1-3, only 5-27% (35.6-46.4 kg d^{-1}) TN loads that entered from sub-basin 5 were from WiWWTP, and 73-95% (127.9-692.5 kg d^{-1}) was from other nonpoint sources, such as irrigation ditches, over flow and sub-surface flow from agricultural lands, and storm water from developed areas. The most significant TN load input from other sources at sub-basin 5 occurred in event 2 although the average of antecedent 3-day rainfall in the study area was low at 0.51 mm, and the antecedent 3-day irrigation rate remained at zero. However, the antecedent 3-day irrigation rate was monitored only at the Larimer and Weld irrigation company, thus there is a possibility that irrigation ditches were running during event 2. TN loads from other sources dominated, ranging from 30.3 kg d^{-1} to 131 kg d^{-1} at sub-basin 6, since no WWTP is located in the sub-basin in the study area.

Control regulation 85 proposed the numeric limitation for the WWTPs effluent as annual averages of 5.7 mg TIN L^{-1} and quarterly averages of 9.0 mg TIN L^{-1}. To meet the proposed limits, WWTPs must have at least level 3 (BNR) of an advanced wastewater treatment system. Based on the observed data, TN loads in the CLP River were simulated in Fig. 5.8.

Observed TN loads from sources at sub-basins 4-6 during events 1-3 are presented at the top of Fig. 5.8, and simulated TN loads using BNR at WWTPs are shown in the middle of the figure. TN loads using BNR were estimated based on assumptions that all five WWTPs have the BNR system, which makes a TN concentration of 10 mg L^{-1} in effluents, and the TN concentration of 10 mg L^{-1} meets the proposed limit of TIN for WWTPs (Regulation 85). From the simulation, it was clear that meeting the proposed limits for rivers and streams (Regulation 31) was still not obtainable even though all five WWTPs met the proposed limits for WWTPs except at sub-basin 4 in event 1.

In another simulation, which is shown at the bottom of Fig. 5.8, the further assumption was made that WWTPs removed 100% of TN from influent. Even if there were no TN loads from WWTPs entering the river, it was still difficult to achieve TN standards in Regulation 31 without reducing TN load inputs from other sources except at sub-basin 6 in event 1.

There was a point (sample ID 8) where the proposed TN loading limit was not met not only during events 1-3 but also during events 6-7. Because the BSD does not have the BNR system and discharges its effluent before the point, the facility was expected to be the largest source of TN at the point. Percentages of sources, which contribute TN loads in the river, were estimated in Fig. 5.9.

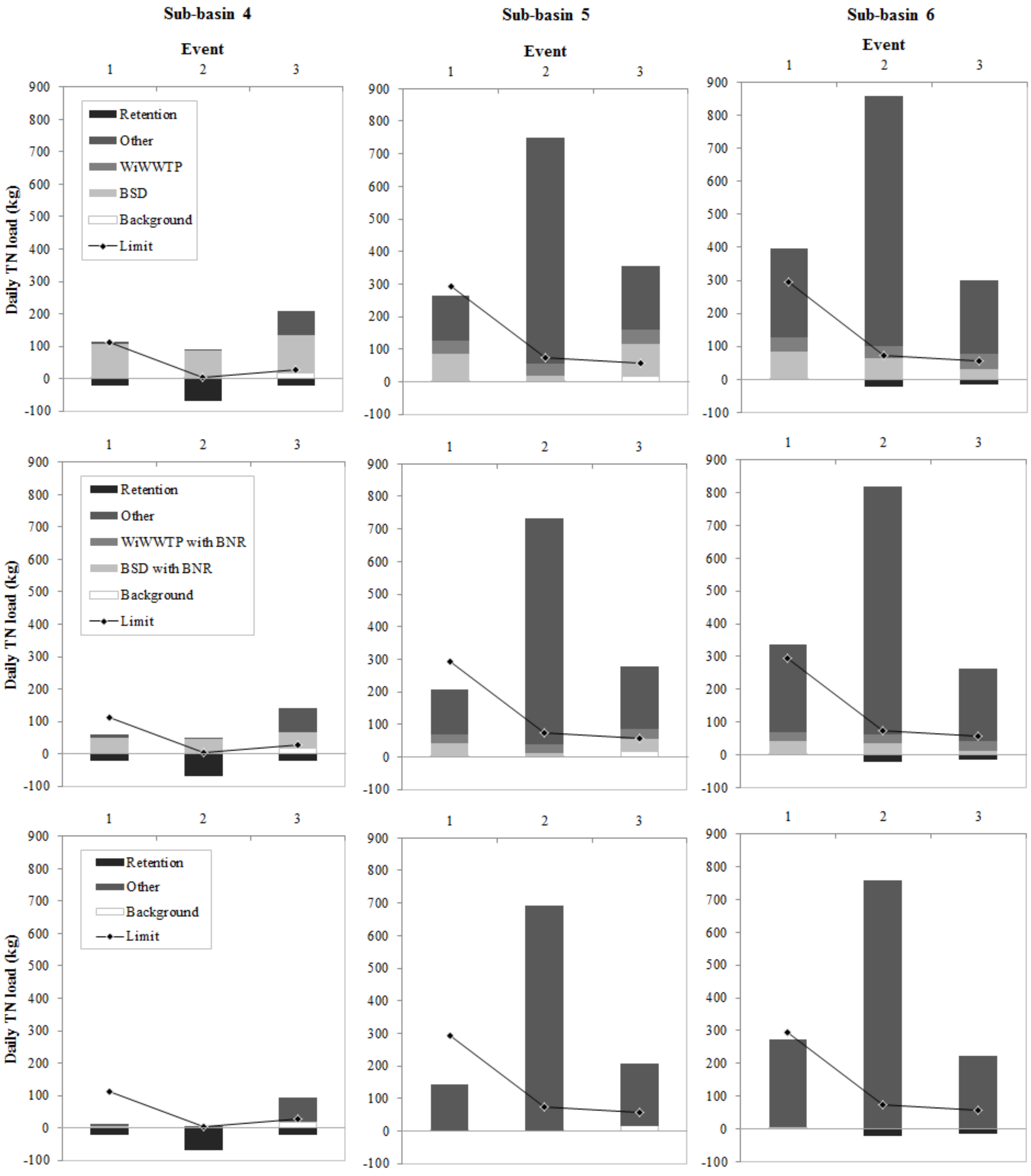

Figure 5.8: Simulated daily TN load (kg) from known sources at sub-basins 4-6 on events 1-3 under three cases with: observed data (top), WWTPs with BNR to meet Regulation 85 (middle), and 100% TN removal from WWTPs (bottom).

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During events 1-3, flow rates collected at the nearest USGS station from sampling point 8 were low, ranging from 0.07 to 0.82 $m^3 s^{-1}$ (Table 5.2). For these low flow conditions, the BSD was identified as the largest source of TN, contributing from 55% to 94% of TN loads at sampling point 8. However, TN contributions of the BSD were insignificant during higher flows in events 6 and 7. Flow rates in events 6 and 7 were 53.77 $m^3 s^{-1}$ and 3.03 $m^3 s^{-1}$, respectively, and TN loads from other sources were significant at 97% and 86%, respectively.

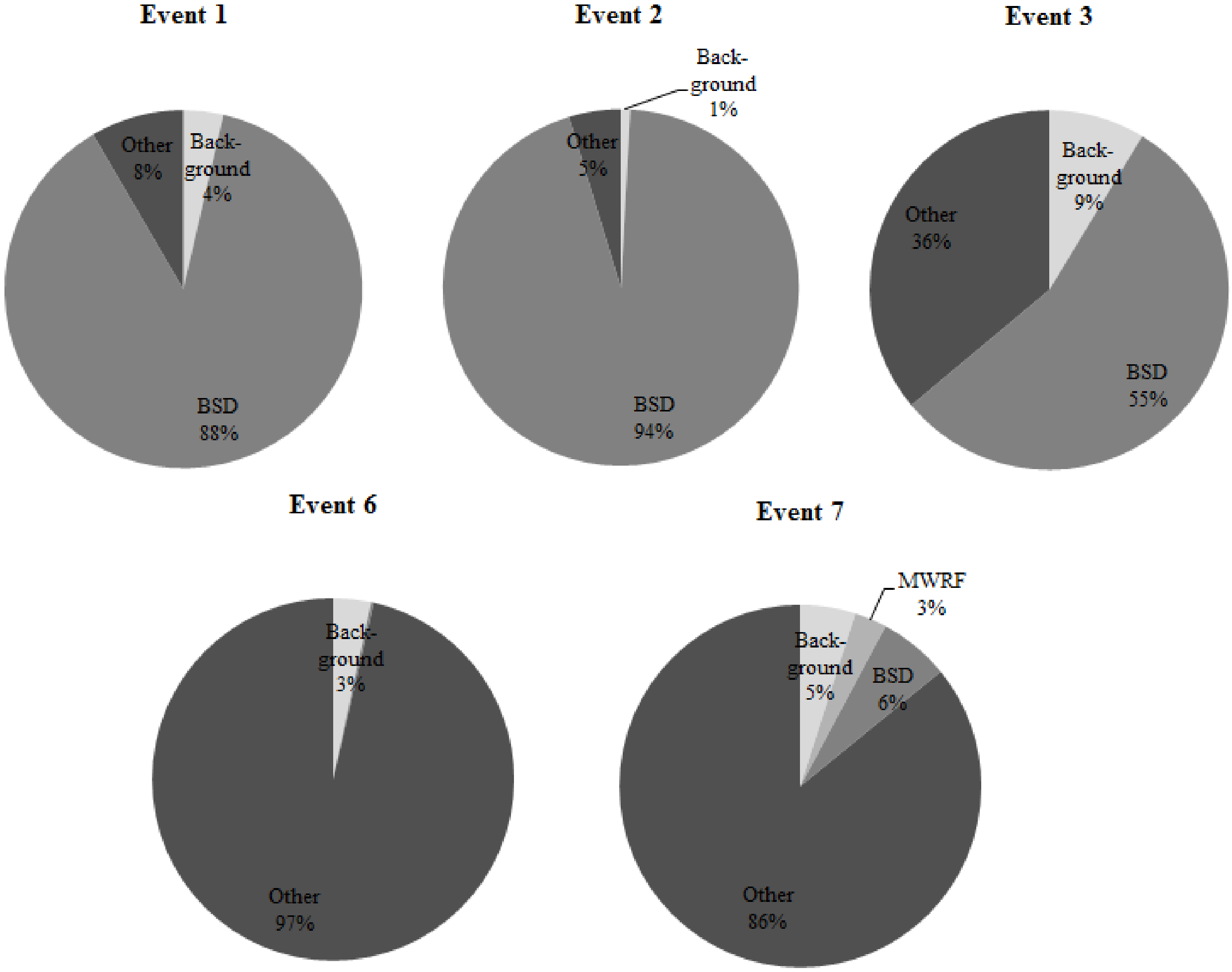

Figure 5.9: Percent of TN flux inputs by known sources at sampling site 8 on the events 1-3 and events 6-7 when the observed TN loads at the site exceeded the proposed TN loading limit.

TN loads at sampling point 8 were also simulated (Fig. 5.10) using the same assumptions made for sub-basins 4-6 in events 1-3 in Fig. 5.8.

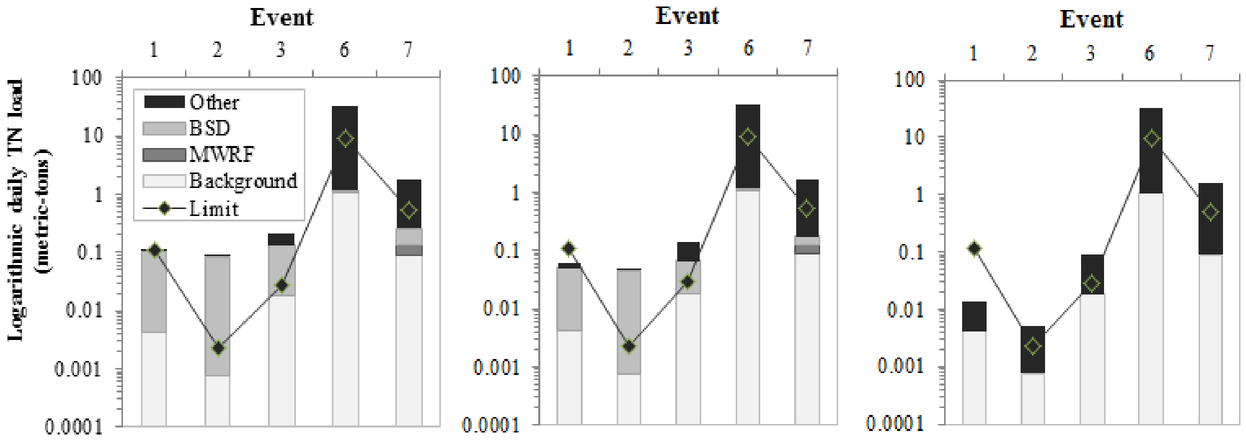

Figure 5.10: Comparison of logarithmic daily TN load at sampling site 8 on events 1-3 and 6-7 when TN loading at the site exceeded the proposed loading limits in three cases with observed data (left), WWTPs with BNR to meet Regulation 85 (middle), 100% TN removal from WWTPs (right).

From the simulation, it was found that meeting the proposed limits of Regulation 31 at sampling point 8 was also impossible while implementing Regulation 85, even with no TN inputs from the MWRF and the BSD without reducing efforts in TN loads from background and other sources.

5.4. Conclusion

The CDPHE has proposed numeric nutrient limits in Colorado for rivers/streams in Regulation 31 and for the WWTPs in Regulation 85. To achieve the nitrogen standard proposed in Regulation 31, significant reduction of TN loading must be conducted through adequate management programs for point sources and nonpoint sources. However, the only enforceable source for reducing TN load inputs has been point sources (WWTPs), thus strict implementation of the numeric nutrient standard is expected as proposed in Regulation 85.

From this study on nitrogen load inputs to the CLP River, it was observed that TN loading exceedance from the proposed limit occurred during low flow conditions, but one point (sampling ID 8) frequently exceeded the limit for five events, including low flows and high flows, out of total seven events. The largest source of TN during the events when exceedance was monitored, was sub-basin 5 followed by sub-basins 4 and 6, and nonpoint sources dominated at sub-basins 5 and 6. At sub-basin 4, where sampling point 8 is located, TN inputs from the BSD were the major source during the low flow events. In high flows, however, TN loads from other nonpoint sources impacted significantly on the TN load exceedance.

Based on the simulations, applying the proposed limits for the WWTPs, and assuming no TN inputs from the WWTPs, it was found that meeting Regulation 31 at sub-basins where exceedance was observed is still not achievable without substantial reduction of TN loading from other nonpoint sources.

To achieve the water quality goals of the watershed, all potential point and nonpoint sources and stressors should be monitored and evaluated.

CHAPTER 6

CONTRIBUTION OF POINT AND NONPOINT SOURCE PHOSPHORUS AND NITROGEN LOADS IN A MIXED LAND-USE WATERSHED

6.1. Introduction

Nutrients (nitrogen and phosphorus) enter water bodies via point sources and nonpoint sources. Point sources are well identified sources defined in section 502(14) of the CWA such as effluents from wastewater treatment plants (WWTPs) and industrial plant discharges, and nutrient loading from these sources can be estimated with known nutrient concentrations in their effluent and flow rates. However, nonpoint sources are hard to indentify and manage because the paths that nutrients from these sources by which they are transported to the streams are unknown and scattered, such as runoff from agricultural lands and urban areas. Therefore, they are often known as diffuse sources. Every two years, the U.S. Environmental Protection Agency (U.S. EPA) conducts a survey of water quality of the nation’s water under Section 305(b) of the Clean Water Act (33 U. S. C., §§ 1288, 1329, passed in 1972 as the Federal Water Pollution Control Act Amendments), and excess nitrogen and phosphorus have continuously ranked as a leading cause of water quality “impairment” of rivers and streams (USEPA 1994, 1995, 1998, 2000a, 2002, 2007, 2009). In 1997, U.S. EPA recognized a need for a national nutrient management program to control nutrient over-enrichment in surface waters. Hence the Clean Water Action Plan (CWAP) was established in 1998. The CWAP mandates the development of water quality-based control programs and adoption of water quality criteria appropriate for the various

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characteristics of a state's watershed because it is believed that the nation's waters can be protected based on the regulation of states' waters.

In 2001, the U.S. EPA placed the responsibility of developing a nutrient criteria plan on states and authorized tribes. The Colorado Department of Public Health and Environment (CDPHE) Water Quality Control Commission (WQCC) took the lead in establishing nutrient standards of total phosphorus (TP) and total nitrogen (TN) for the state. The CDPHE presented its initial proposed nutrient criteria for rivers and streams in February 2010 based on the best available science to protect aquatic life use. Studies have shown that upper limits of 0.16 mg-TP L^{-1} and 2.0 mg-TN L^{-1} for cold surface waters and lower limits of 0.11 mg-TP L^{-1} and 0.4 mg-TN L^{-1} for warm surface waters are required for a healthy macroinvertebrate community in rivers of Colorado (Lewis and MucCutchan 2010). The limits, however, have been revised four times to achieve a more practical level, and the latest proposed limits of nutrients are upper limits of 0.17 mg-TP L^{-1} and 2.0 mg-TN L^{-1} for cold surface waters and lower limits of 0.11 mg-TP L^{-1} and 1.25 mg-TN L^{-1} for warm surface waters. Accordingly, the CDPHE has been working to determine limits of nutrients for the WWTP effluents to protect designated uses of receiving waters, and it has proposed annual medians of 1.0 mg-TP L^{-1} and 10 mg-TIN L^{-1} and 95th percentiles of 2.5 mg-TP L^{-1} and 20 mg-TIN L^{-1} for the existing domestic WWTPs.

Point sources are managed and controlled by the National Pollutant Discharge Elimination System (NPDES) under section 402 of the CWA. Facilities are required to comply with the state's water quality regulations to obtain permits. Unlike point sources, nonpoint sources are not enforceable, and thus the entire nutrient load reduction must be achieved by point sources if "sufficient assurances" on nonpoint source reduction are not provided (USEPA 1991). However, implementing stringent nutrient reductions at point sources is associated with high costs, and it is doubtful that these can bring environmental enhancement without nonpoint source controls. To implement proposed limits, sources of nutrients in the watersheds need to be monitored and identified.

In this study, basin based analyses of nutrient loading contributions from point and nonpoint sources were performed under various hydrologic conditions, and the effects of different levels of nutrient load reduction as compliance with nutrient effluent limits on the river were evaluated.

6.2. Materials and Methods

6.2.1. Study site description

The CLP River Basin (hydrologic unit code: 10190007) is located in the semi-arid region of north-central Colorado. The drainage area of the basin is 4,849 km^2 consisting of 1.1% open water, 6.0% developed area, 32.4% forest, 48.9% grass/shrub lands, and 17.4% agricultural lands (Fig. 4.1). The basin offers a unique opportunity to study pollutant occurrence and transport from its sources because the CLP River originates from a pristine Rocky Mountain region, which generates water from melted snowpack accumulated during the cold season expressed as snow water equivalent (SWE), and flows 225km through the built-environment and downstream of a mixed urban and agricultural land-use area before converging into the South Platte River. In this study, the river was divided into four segments based on the locations of USGS streamflow stations, and thirteen sampling sites were selected from upstream to downstream in the river.

Segment 1 is located upstream of the river and includes three sampling sites (1-3) whose drainage area of 195.07 km^2 is comprised mostly of forest and shrub/grass lands (79.6%) as described in Table 6.1. Sampling sites 1 and 2 were chosen to represent background concentrations because they are embedded in the Rocky Mountain National Park, which has minimal human impact and no notable pollutant sources. Segment 2 also has three sampling sites (4-6) and flows through a transition zone from the minimum impact area to the highly disturbed area. The area includes one WWTP, the Mulberry Water Reclamation Facility (MWRF), out of a total of five WWTPs in the study area and its drainage area is 103 km^2 consisting of 21.4% developed area, 51.3% forest and shrub/grass land, and 19.3% agricultural area including pasture and cultivated lands.

Table 6.1: Summary of drainage areas.

	Drainage area							
	Segment 1		Segment 2		Segment 3		Segment 4	
USGS station	06752000		06752260		06752280		06752500	
Sampling site	1 - 3		4 - 6		7 -9		10 - 13	
No. of WWTPs	_		1		3		1	
Distance from confluence	100-130 km		77-100 km		50-77 km		10-50 km	
Land-use	Km^2	%	Km^2	%	Km^2	%	Km^2	%
Open water	2.14	1.10	2.12	2.06	9.88	6.47	24.11	3.57
Developed	23.64	12.12	22.05	21.44	51.59	33.77	173.91	25.78
Barren Land	_	_	0.25	0.24	0.34	0.22	1.60	0.24
Forest	93.14	47.75	24.97	24.28	1.12	0.73	3.59	0.53
Shrub/Grassland	62.02	31.80	27.81	27.04	23.91	15.65	81.53	12.08
Pasture	6.91	3.54	6.86	6.67	15.17	9.93	48.87	7.24
Cultivated Crops	_	_	12.94	12.58	45.62	29.86	323.01	47.88
Wetlands	7.22	3.70	5.81	5.65	5.13	3.36	17.88	2.65
Other	_	_	0.03	0.03	0.02	0.02	0.18	0.03
Total	195.07	100	102.85	100	152.78	100	674.67	100

The most developed area is the drainage area that drains water to segment 3 and has three sampling sites (7-9). The drainage area of 153 km^2 is composed of 33.8% developed area, 16.4% forest and shrub/grassland, and 39.8% agricultural lands with three WWTPs embedded in the area: the Boxelder Sanitary District (BSD), the Drake Water Reclamation Facility (DWRF), and the South Fort Collins Sanitary District (SFCSD). Unlike other WWTPs in the basin, the DWRF and the SFCSD discharge water into a 0.014 km^3 volume reservoir which might have significant nutrient retention capacity. The reservoir water flows back into the river between sites 8 and 9; therefore, the facilities do not affect the river directly. Segment 4 is located downstream of the basin and includes four sampling sites (10-13). The segment drains the largest and most agricultural area, which comprises 55.1% of the total drainage area of 674.7 km^2. Developed areas account for 25.8% of this drainage area, which has one WWTP, the Windsor Wastewater Treatment Plant (WiWWTP), and forest and shrub/grass land is 12.6%.

6.2.2. Hydrologic conditions and sampling events

Hydrologic conditions of the CLP River were classified into five different conditions: high flows, moisture conditions, mid-range flows, dry conditions, and low flows based on the flow exceedance curve (Fig. 4.2) developed using 30-year flow data from the four USGS flow stations in the study area. Flows which were exceeded or equaled less than 10% of the times were classified as high flows, and the lowest flows which were exceeded or equaled more than 90% of the time were classified as low flows. Flows which had an exceedance between 10 and 40% were called moisture conditions, those between 40 and 60% were mid-range flows, and flows between 60 and 90% were classified as dry conditions.

When the hydrologic conditions of the river are in mid-range flow or drier, downstream flows become greater than upstream flows, and flow rates in mid-stream are substantially reduced. This indicates that there are water transfers from upstream to downstream; in fact, more than 20 irrigation ditches and water diverging canals exist throughout the river. Sampling dates were chosen to capture all five classes of four segments of the CLP River. Thirteen sampling campaigns were conducted over the 2-year period between April 2010 and April 2012 to study phosphorus loadings in the river under various hydrologic conditions, and eight sampling campaigns were performed for a nitrogen loading analysis (Table 6.2).

Table 6.2: Hydrologic conditions of four segments of the CLP River, irrigation rates, average SWE, and antecedent 3-day rainfall on 13 event dates. †Data measured at LAWIRRCO by CODWR. ‡Average of SWE at Deadman Hill and Joe Wright (SNOTEL site No.438 and 551).

Event No.	Date	Hydrologic condition				Irrigation† $(m^3\ s^{-1})$	Average SWE‡ (cm)	Antecedent 3-Day Rainfall (cm)
		Segment 1	Segment 2	Segment 3	Segment 4			
1	4/23/2010	Moist	Mid-range	Moist	High	3.34	47.50	3.06
2	5/19/2010	Moist	High	High	High	0	62.87	1.02
3	6/04/2010	High	High	High	High	10.36	34.67	0
4	6/18/2010	High	High	High	High	0.33	0	0
5	7/16/2010	Moist	Moist	Moist	Moist	3.06	0	0.06
6	9/17/2010	Dry	Mid-range	Moist	Dry	0.58	0	0.08
7	2/22/2011	Low	Mid-range	Low	Dry	0	49.40	0.05
8	4/26/2011	Moist	Mid-range	Moist	Dry	2.03	95.50	0.82
9	5/12/2011	Moist	Moist	Moist	High	7.76	101.47	3.08
10	6/13/2011	High	High	High	High	9.23	76.07	0
11	7/15/2011	High	High	High	High	0	_	0.52
12	8/29/2011	Moist	Moist	Moist	Dry	5.69	_	0.01
13	4/23/2012	Moist	Moist	Moist	Moist	1.04	34.93	0.09

A grab sampling method was used for aqueous samples. At each site, river water samples were collected at three different points of a river cross-section and composited in a 500 mL volume of pre-washed Nalgene bottle at the site. Collected samples were then transported to the laboratory and kept at 4^oC in a refrigerator until measured.

6.2.3. Water quality analysis

TP concentrations were measured using an acid persulfate digestion method followed by an ascorbic acid method (Hach method 8190; USEPA standard method 4500 P-E). A minimum detection limit (MDL) of the method is 0.06 mg L^{-1}. Concentrations of TN were analyzed by a

Shimadzu TOC-VCSH analyzer equipped with a TNM-1 (Shimadzu Corporation, Columbia, MD), which has an MDL of 5 µg L^{-1}.

6.2.4. Nutrient loads analysis

Nutrient loads in the river were estimated by multiplying the measured concentrations by flows collected from the USGS stations representing flows of four segments of the CLP River. A mass balance method was used for estimation of addition and reduction of nutrient loads along the CLP River. Nutrient retention rates were estimated based on the fraction of a total load reduction to a total load addition estimated at each site. Diffuse source loads were gained by the difference between stream discharge and known point source inputs from WWTPs. The monthly TP and TN loadings from each WWTP were estimated as point source contributions because the most considerable point source of nutrients in the study area is a WWTP. Three years of monthly WWTP discharge data were collected from EPA- ECHO and monthly concentration data TP, total kjeldahl nitrogen (TKN), nitrate and nitrite were provided by the DWRF. Monthly TN concentrations were calculated by summing TKN, nitrate and nitrite concentrations. Due to the lack of available nutrient data from other WWTPs, TP and TN concentrations in effluents of the DWRF were applied for estimating nutrient loads from other WWTPs equipped with the biological nutrient removal (BNR) systems, based on an assumption that monthly nutrient concentrations from WWTPs having the same level of treatment area are not significantly different. Monthly nutrient loads from the BSD, however, were estimated using the available TN concentration data and measured TP concentrations in effluents from the BSD because this facility doesn’t contain the BNR system but a secondary treatment.

6.2.5. Estimation of nutrient load reduction at WWTPs

Amounts of nutrient loads needed to be reduced to meet the proposed in-stream limits were calculated by subtracting the limits from the estimated load inputs at each segment. The nutrient limits for WWTPs were classified into three levels: Level 3 (1 mg-TP L^{-1} and 10 mg-TN L^{-1}), Level 4 (0.5 mg-TP L^{-1} and 6 mg-TN L^{-1}), and Level 5 (0.05 mg-TP L^{-1} and 3 mg-TN L^{-1}) and those limits were used for nutrient concentrations in effluents of all WWTPs in the study area to estimate how much nutrient reduction at WWTPs could contribute to the in-stream nutrient limits.

6.3. Results and Discussion

6.3.1. Nutrient concentrations and loads

Concentrations and loads of nutrients (phosphorus and nitrogen) of the CLP River were monitored over 2 years, and a general pattern of increase from upstream to downstream with anthropogenic influences was observed. Nutrient concentrations in segment 1, where distances from confluence with the South Platte River are greater than 100km, were relatively constant and low ranging from 0.06 to 0.31 mg-TP L^{-1} (Fig.6.1) and 0.03 to 0.32 mg-TN L^{-1} (Fig.6.2), respectively, which were not different from ranges of background concentration. Phosphorus concentrations in segment 2, a transition zone receiving light urban influences including effluents from a WWTP, were not statistically different from concentrations in segment 1 using a two-tailed t-test ($p > 0.05$) but nitrogen concentrations increased significantly from the transition zone ($p < 0.05$). Both TP concentration and load and TN concentration were significantly higher from segment 2 to segment 3 ($p < 0.05$) with increased urban and agricultural influences including constant point source inputs from three WWTPs and nonpoint source inputs such as stormwater from urban area and agricultural runoff.

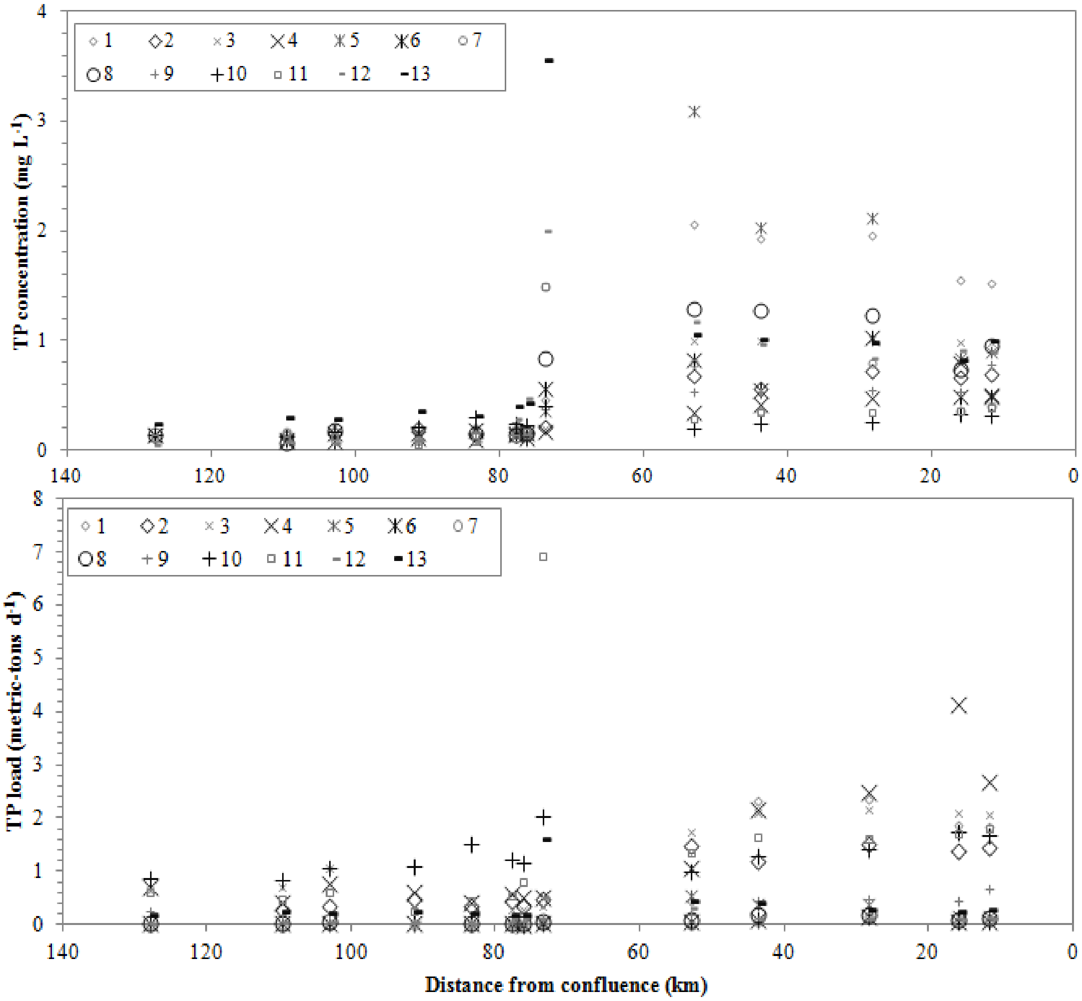

Figure 6.1: Concentrations (mg L^{-1}) and estimated loads (metric-tons d^{-1}) of TP at 13 points of the CLP River in 13 events between April 2010 and April 2012.

Nutrient concentrations and load had a peak at site 8, where the distance from the confluence is 73.5 km. Expected sources of the large amount of nutrient inputs were effluents from the BSD and Boxelder Creek, which joins the river above the site. Boxelder Creek flows approximately 63km from southern Wyoming, and drainage area adjacent to the river is 185.21 km^2 dominated by more than 60% agricultural lands including crop and grazing land. The BSD discharges effluents to Boxelder Creek approximately 0.2 km before the confluence with the CLP River, and this can greatly impact the creek and even the river during lower flow conditions due to the low dilution effect.

Nitrogen retention capabilities of rivers and streams have been studied in the past (Howarth et al. 1996; Lepistö et al. 2006), and significant retention rates of TN concentrations and certain levels of TP retention were monitored in this study as well where the river flows approximately 11km from site 8 to site 9 ($p < 0.05$). Therefore, no significant influences of the DWRF and the SFCSD, discharge water through a reservoir, were found. The magnitude of nitrogen retention rates was strongly correlated with hydrologic conditions and enlarged with the flows; however, there was no statistical difference of either nutrient concentration or load between segment 3 and segment 4 ($p > 0.05$), which indicates continuous nutrient inputs downstream. The downstream drainage area is dominated by agricultural lands and the expected sources of nutrients were irrigation ditches connected to the river and subsurface and overland flows from nearby agricultural area. A correlation between phosphorus retention rates and flows was not found. Phosphorus retention is caused mostly by two mechanisms: microbes' activities and riverbed sediment reactions in the river (Carritt and Goodgal 1953; Froelich 1988; Haggard et al. 1999; USEPA 2000b) and the mechanisms are related to a number of factors such as water temperature, redox potential, pH (Gomez et al. 1999), organic matter (Golterman 1975; Verdouw and Dekkers, 1980), mineral content (Klotz 1998), and sediment particle size (Meyer and Likens 1979; McDowell et al. 2002).

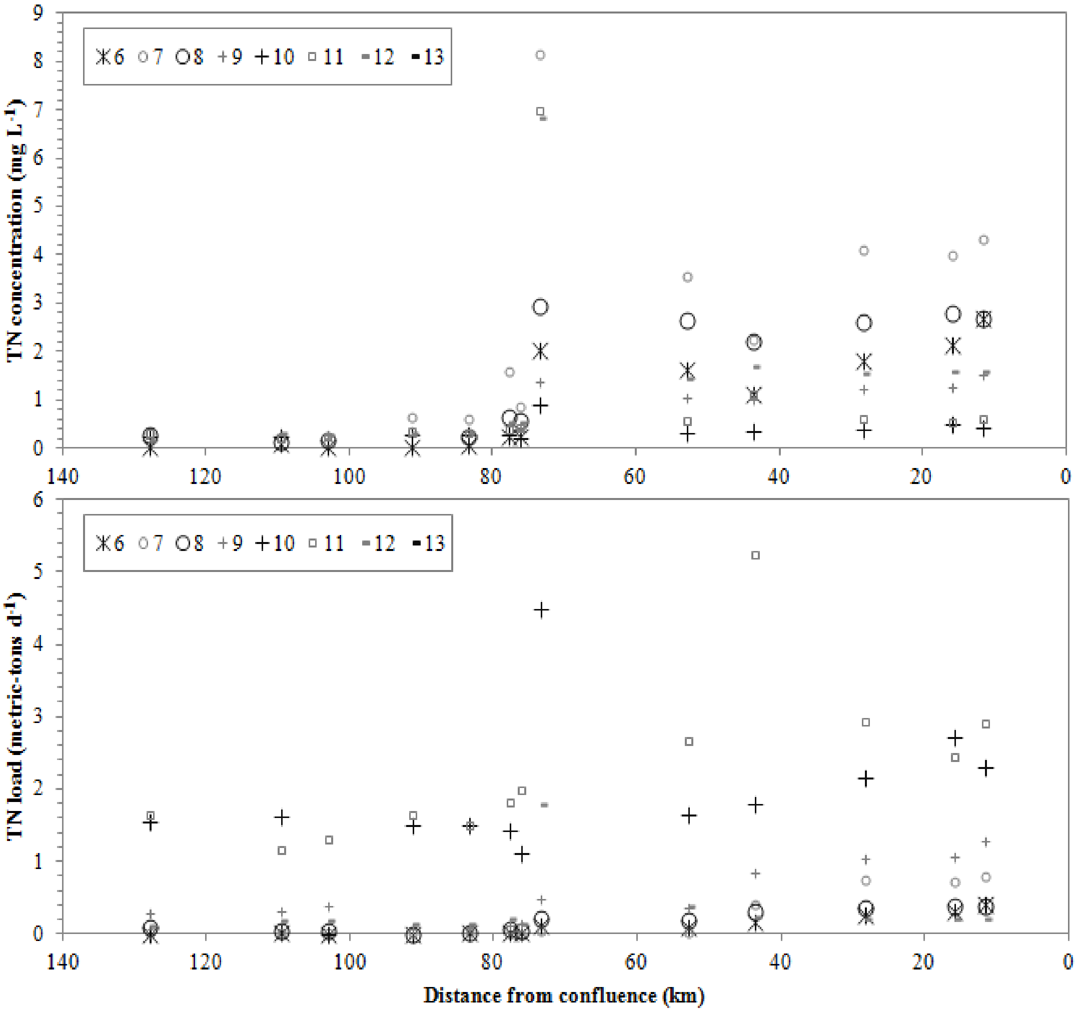

Figure 6.2: Concentrations (mg L^{-1}) and estimated loads (metric-tons d^{-1}) of TN at 13 points of the CLP River in 8 events (event 6-13) between September 2010 and April 2012.

Statistical differences of nutrient concentration and load in the river were tested based on hydrologic conditions along with spatial difference from upstream to downstream as described above. Nutrient concentrations in human influenced areas were sensitive to hydrologic conditions while no significant differences were found in segment 1 and segment 2 ($p > 0.05$). Phosphorus concentrations in moist conditions were greater than those in other hydrological conditions in segment 3 and segment 4 ($p < 0.05$), and nitrogen concentrations highly depended on flow rates only in segment 4 and decreased with the flow rates. Nutrient loads in the river were significantly influenced by hydrological conditions ($p < 0.05$) and rose with the flows. Those loads might be considered as nonpoint source loads because point source loads are relatively constant over time.

6.3.2. Nutrient loading exceedance

Based on the strong correlation between nutrient loads and hydrologic conditions, loading exceedance from proposed nutrient limits in different hydrologic conditions was evaluated. Proposed nutrient loading limits in various hydrologic conditions were estimated by multiplying proposed in-stream nutrient concentration limits by the flow exceedance curves shown in Fig.4.2. As seen in Fig. 6.3, upstream phosphorus loadings already exceeded proposed limits in six events out of thirteen events in all observed hydrologic conditions except for dry conditions. Magnitudes of exceedance amplified from upstream to downstream with intensified agricultural influences, and all observed data greatly exceeded proposed limits in segment 4 in all hydrologic conditions.

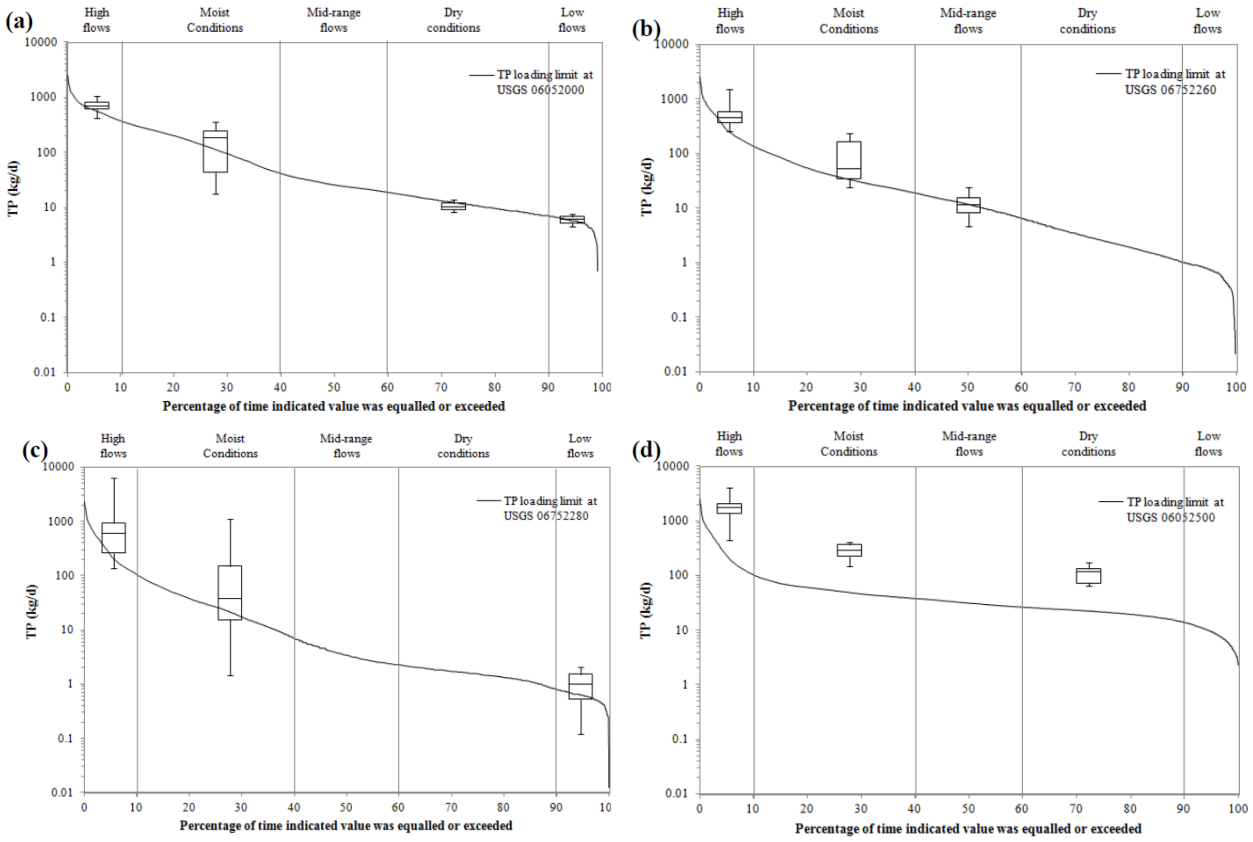

Figure 6.3: Logarithmic loading exceedance of TP from proposed loading limit (solid line) at segment 1 (a), segment 2 (b), segment 3 (c), and segment 4 (d) under five different hydrologic conditions. Box plots indicate TP loads in different hydrologic conditions from the observed 13 events.

Nitrogen loads, however, showed exceedance in segment 4 only in dry conditions, with low retention rates except for site 8 (Fig. 6.4). The low retention rates might be due to low flow rates and limited activities of microbes and aquatic plants resulting in little denitrification and low nutrient consumption levels at low water temperature. Site 8 located in segment 3 consistently exceeded proposed loading limits in all hydrologic conditions.

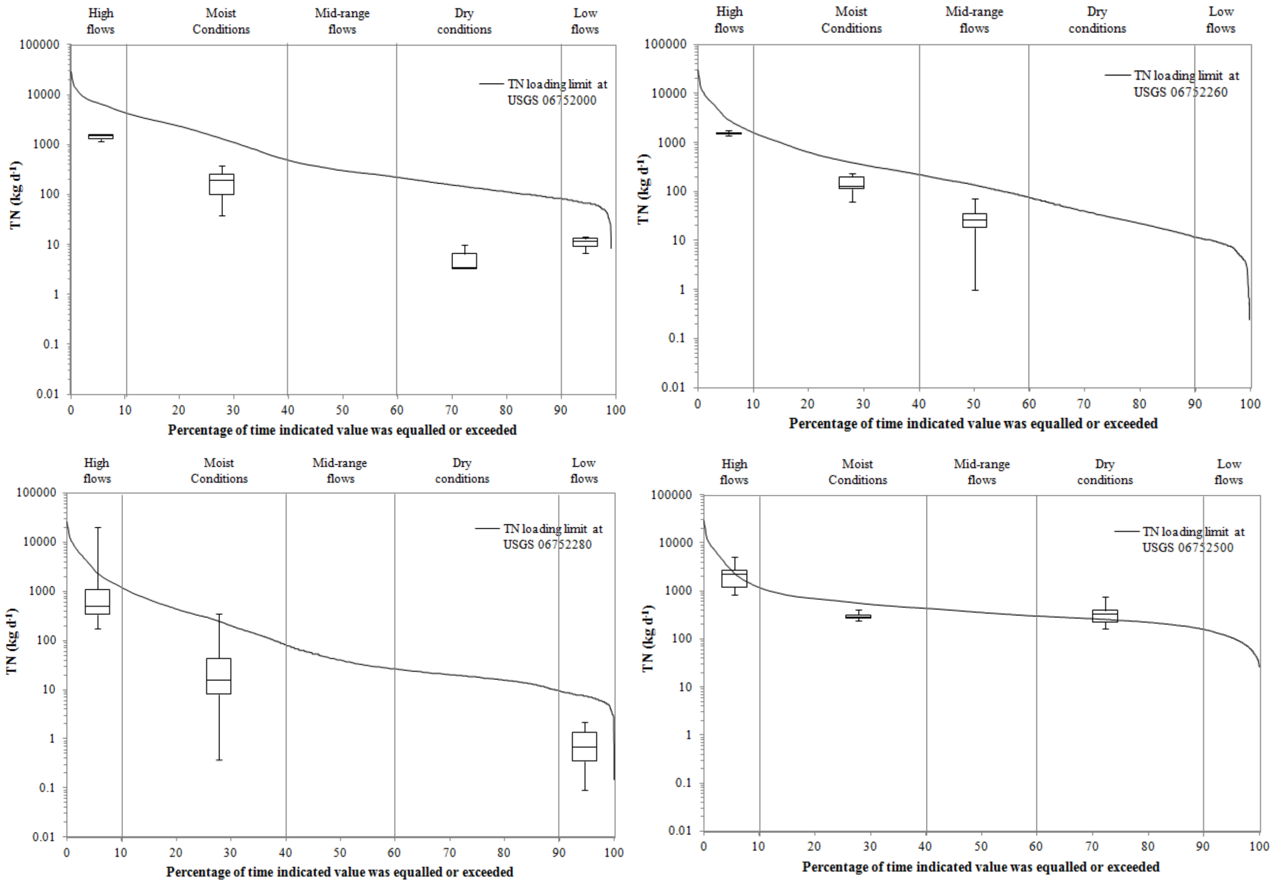

Figure 6.4: Logarithmic loading exceedance of TN from proposed loading limit (solid line) at segment 1 (top-left), segment 2 (top-right), segment 3 (bottom-left), and segment 4 (bottom-left) under five different hydrologic conditions. Box plots indicate TN loads in different hydrologic conditions from the observed 8 events.

Ranges of nutrient loads greatly increased from dry-low flows to moist-high flows, and this might indicate that the degree of impact of nonpoint source loads on the river significantly increased with higher hydrologic conditions of the river.

6.3.3. Nutrient sources

During high flows, discharge rates of WWTPs are marginal (less than 1%) compared with flows of the receiving river, but they become significant when flow rates of the river are low (Fig. 6.5). The influences of effluent flows from the MWRF having a capacity of 0.26 m^3 s^{-1} and located in segment 2 were low at 0.2% in high flows and 1.2-2.8% in moist conditions. The BSD, with a capacity of 0.1 $m^3 s^{-1}$ in segment 3 impacts the receiving river 1.6-12.8% during moist conditions and the impact was critical during low flows. The effluent from BSD dominated the flows of segment 3 for those critical conditions. The WiWWTP located in segment 4 has a capacity of 0.12 $m^3 s^{-1}$ and influents of the effluents on the river ranged from 1.4 to 2.6% in moist conditions and 2.3 to 3.4% under dry conditions.

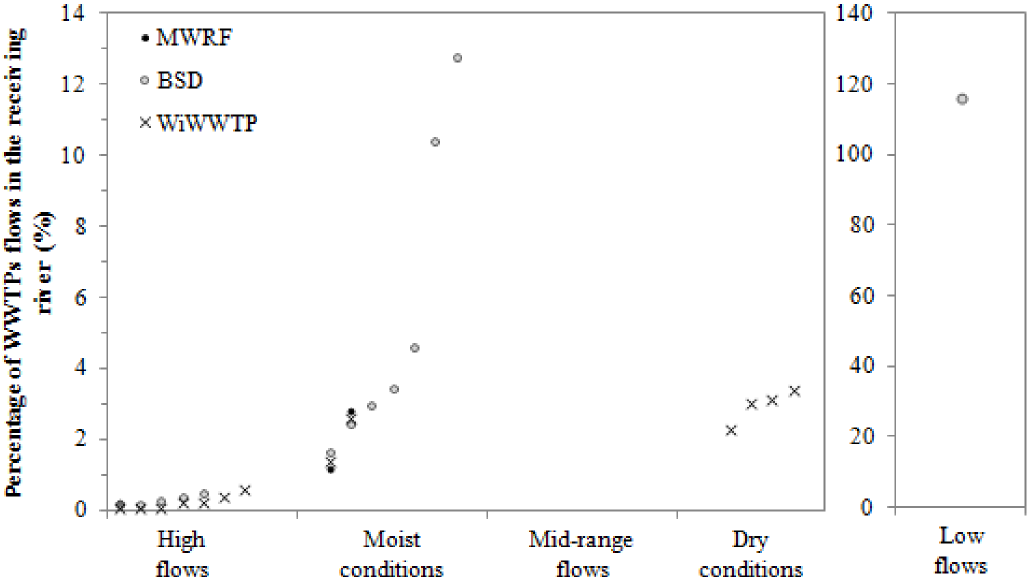

Figure 6.5: Percentages (%) of flows of WWTP effluents that directly discharge to the river in the receiving river under different hydrologic conditions.

As impacts of effluents on the receiving water increased with downgraded hydrologic conditions, percentages of influences of nutrient load inputs from WWTPs were significant with decreased flow conditions ($p < 0.05$) while effluent load inputs were not significantly different under various hydrologic conditions ($p > 0.05$) (Fig. 6.6). Other source inputs mostly from nonpoint sources and influences of those on the river decreased in lower flow conditions but became significant during higher flow conditions in mixed land-use areas, segment 3 and segment 4 ($p < 0.05$). These results show that nutrient loads from point sources such as WWTPs are not significantly different under different hydrologic conditions, but nonpoint source loads are greatly influenced by it.

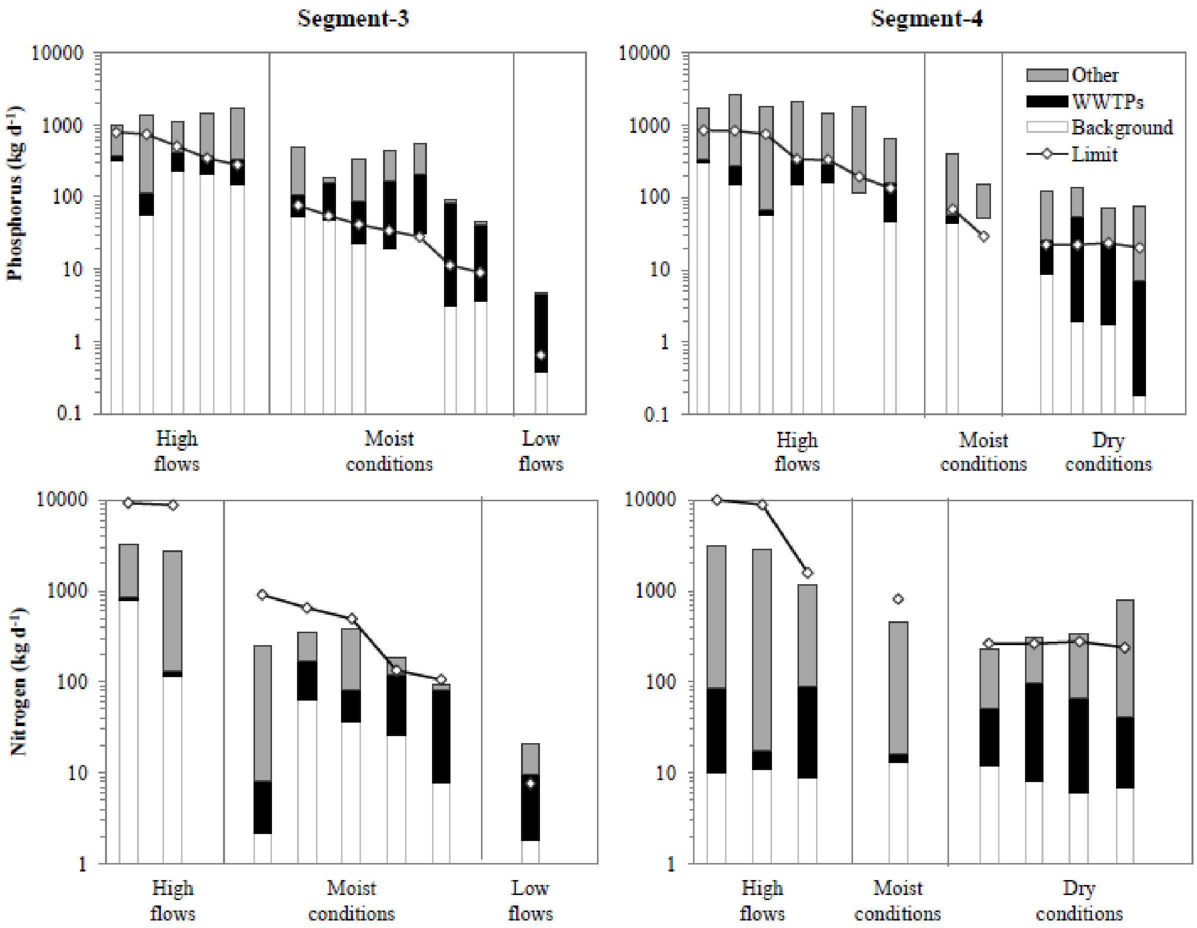

Figure 6.6: Logarithmic scale of nutrient load inputs (kg d^{-1}) from known sources and proposed loading limits in segment 3 and segment 4 under different hydrologic conditions of the river.

The percentage of impacts of nonpoint sources on the river elevated and effluent impacts diminished from segment 3 to segment 4 ($p < 0.05$) with increased agricultural land-use and decreased number of WWTPs in the drainage areas. Background loads significantly increased with higher flow conditions ($p < 0.05$) but percentages of influences in segment 3 and segment 4 were not different from high flows to low flows ($p > 0.05$). This might be due to nutrient retention occurring while the background loads were transported from upstream to downstream.

6.3.4. Nutrient load reduction

Phosphorus loads exceeded the loading limits in all observed events in mixed land-used areas but nitrogen loads exceeded the limits during only one moist condition and all dry-low flows in the areas. Although the currently proposed nutrient limits for WWTP effluents (Level 3) have been adopted, the in-stream phosphorus limits in segment 3 and segment 4 are still not achievable. The in-stream nitrogen limits might be achievable in certain conditions, however.

In a mixed land-used area with urban influence dominated areas (segment 3), 8-25%, 12-89%, and 92% of TP loads from total loads required to be reduced for meeting the proposed in-stream limits could be reduced in high flows, moist conditions, and low flows, respectively, by implementing Level3 limits (Fig. 6.7). The in-stream TN limit could be met in moist conditions by adopting the Level 3 limit, and 53% of nitrogen loads could be reduced in low flows. The in-stream TP limits in all observed events and the in-stream TN limits under low flows were not achieved even though effluent limits of Level 4 were adopted. By applying Level 5 limits, the in-stream TP limits could be met in certain times of moist-conditions and low flows.

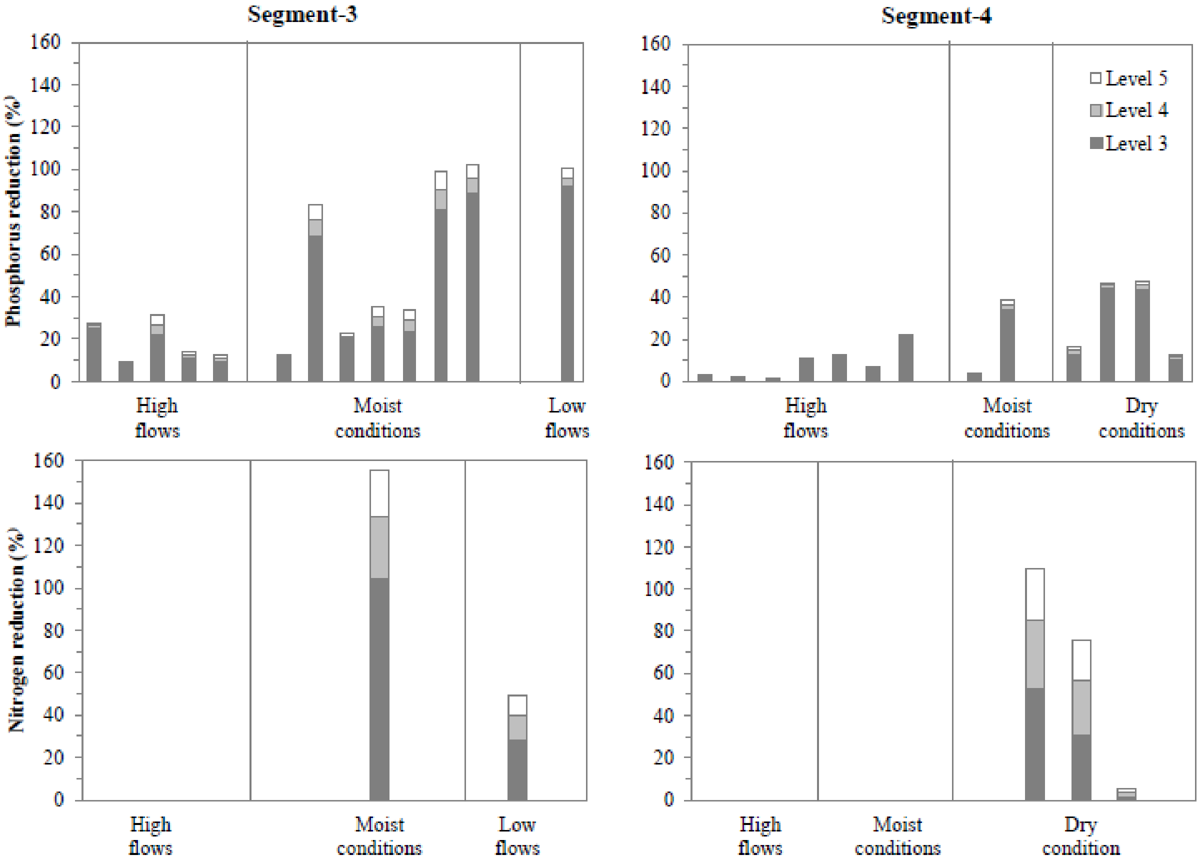

Figure 6.7: Percentages (%) of contributions of nutrient reduction at WWTPs complying with three levels of effluent limits: Level 3 (1 mg-TP L^{-1} and 10 mg-TN L^{-1}), Level 4 (0.5 mg-TP L^{-1} and 6 mg-TN L^{-1}), and Level 5 (0.05 mg-TP L^{-1} and 3 mg-TN L^{-1}) to achieve the proposed in-stream nutrient limits in segment 3 and segment 4 under different hydrologic conditions.

Level 5 limits are considered to be the current technology limits that WWTPs can achieve through a currently available treatment process (Neethling 2010.) However installing the process costs great amount of money and the cost-effectiveness of installing the process is not positive. That is the difference of percentages of TP load reduction between Level 3 and Level 5 were only 0.3-18% although the difference of TN load reduction ranged from 3 to 57%.

Contributions of TP load reduction from WWTPs with different levels of limits were diminished in a mixed land-used area dominated by agricultural lands (segment 4). Even with the most stringent effluent limits, the in-stream TP limits could not be achieved, with the maximum reduction at only 47% of the total reduction required by the laws. The in-stream TN limits could have been met by adopting Level 5 effluent limits in only one case of dry conditions among the three events of dry conditions in which loading exceedances were monitored.

6.4. Conclusion

Nutrient concentrations and loads significantly increased with human influence, and nonpoint source inputs elevated with the increase of agricultural lands in the drainage areas. Significant nitrogen retention occurred under high flows but no correlation was found between phosphorus retention and flow rates. Phosphorus loading exceedances were observed in all observed events even in upstream. Nitrogen, however, exceeded the limits only under dry conditions in an agricultural dominated mixed land-use area except for one point in an urban influence dominated area. The degrees of nutrient loading exceedances amplified as the agricultural land-use of the drainage area increased. Influences of point sources such as WWTPs on the receiving water increased in dry-low flows and became critical during low flows in an urban influence dominated area. Nutrient loads from point sources were not significantly different under different hydrologic conditions but differences of nonpoint source loads between various hydrologic conditions were significant.

Even at the urban influence dominated area, reducing nutrient loads only at WWTPs under stringent limits could not achieve the in-stream nutrient limits, and the impact of nutrient load reduction at WWTPs on the receiving water became much more insignificant in the agriculture dominated area.

CHAPTER 7

EFFECTS OF WILDFIRE ON RIVER WATER QUALITY AND RIVERBED SEDIMENT PHOSPHORUS

7.1. Introduction

When wildfire occurs in a watershed, the surrounding soils undergo physical, chemical and biological disturbances that lead to water quality impacts that can threaten fish populations and their habitat in addition to human life and property (Robichaud et al. 2000). The severity and frequency of fire has increased as a consequence of extended dry periods and increasingly hotter days (Crouch et al. 2006), two factors that control the magnitude of impact on ecosystems (Certini 2005). Fire severity is classified as low, moderate, or high based on fire intensity and duration that can be evaluated using a qualitative measure of fire residue, such as ash color, soil temperature, and consumption of woody debris and litter (DeBano et al. 1998; Hungerford 1996). Fire frequency is related to the climate, the burnable resources, and the source of ignition (Moritz et al. 2012).

The upper 5cm of surface soil receives the greatest impact from wildfire with high temperatures exceeding 150 °C and reaching as high as 850 ºC (DeBano 2000, 1981). In this soil layer, soil structures are distorted and organic matter (OM) and nutrients decrease by volatilization from the site (Cotton and Wilkinson 1988). These compounds can also be mineralized and transported through surface runoff and leaching or deposited in the ash as

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particulates. Organic carbon and nitrogen (N) can be volatilized at relatively low temperatures (> 200 ºC) and consequently substantial amounts of N are combusted at the site while phosphorus (P) and metal cations have high volatilization temperatures: P and potassium (> 774 ºC), calcium (> 1484 ºC), manganese (> 1962 ºC) and therefore are more likely to be mineralized or deposited rather than volatilized during fire. However, much of OM and N can be transformed into carbon dioxide and inorganic N in a low intensity of fire (Weast 1980).

OM can also be mineralized and inorganic ions released from the burnt residue by decreased cation exchange capacity, increased pH and changes of redox potentials caused by fire resulting in an increase in electrical conductivity (Certini 2005) and phosphorus compounds in soils (Pizarro et al. 1995). However, it has also been reported that effects of fire on OM vary from a total loss to 30% increase in OM in the surface layers due to redistribution of organic material during fire (Chandler et al. 1983).

Wildfire also depletes vegetation cover and increases soil water repellency, due to the sealing of mineral soil pores (DeBano et al. 1998) and and clogging of soil pores with ash or the released clay minerals (Durgin and Vogelsang 1984). Along with a loss of organic substances which act as glue between soil particles, infiltration rates and lag-time to flood peaks decrease, and the net effects commonly lead to severe surface runoff and soil erosion (Badìa and Martì 2003; Ice et al. 2004). Eroded soils then enter watersheds accompanied by burnt residues and accumulated ash during precipitation and can either be conveyed downstream as a suspended phase or deposited on riverbeds. Post-fire soil erosion and geomorphic changes have been well-studied since the 1930s and can be found in several studies (e.g. Varela et al. 2010).

Researchers have reported that intense fires could cause irreversible changes to the original properties of soils related to their buffering capacity of nutrient losses (e.g. Alauzis et al. 2004). Furthermore, it has been shown that the erosion risk rose for the first year after a fire event *(*Dìaz-Fierros et al. 1987, 1982; Helvey 1980) and intense fires have long-term impacts on sediment loss, nutrient cycling, vegetation growth, and soil biota lasting for a century or more (Wan et al. 2001).

Numerous researchers have studied the physico-chemical changes of forest soils by different intensity of fires with links to watershed impacts (Arocena and Opio 2003; Badìa and Martì 2003; Fernàndez et al. 1997; Mataix-Solera and Doerr 2004; Romanyà et al. 1993; Saa et al. 1993). Effects of wildfire on riverbed sediments which could have direct impacts on water quality of rivers, however, are rarely studied. The research discussed here considers the impacts on water quality and riverbed and riverbank properties with a particular focus on P sorption and desorption in channel sediment.

7.2. Materials and Methods

7.2.1. Study site and sampling

The study was conducted in the Cache la Poudre River Sub-basin, USA (HUC: 10190007, 4960 km^2) located in the semi-arid region of the northern Front Range of Colorado generating headwater from melted snowpack in the Rocky Mountain National Park area with an average annual precipitation of 305-457 mm (USDA 2009). The basin experienced a serious wildfire in June 2012 and was one of the worst fires in Colorado history burning an area of 353.2 km^2 of the upstream forest area (Fig. 7.1). The river flows 203 km and can be divided into three sections in terms of land-use of drainage areas, fluvial geomorphology and locations from the fire-impacted areas (Table 7.1). The upstream part is located in high mountain ranges with steep gradient mountain valleys and in a transition zone between steep and low gradient areas having boulder, gravel and cobble riverbeds. Vegetation covers vary from shrubs and grasslands to Ponderosa pine and fir with high wind erodiblility, averaging 19278 metric tons per square kilometer yearly (USDA 2009). Mid and downstream areas are located in the Central High Plains and soils are characterized by aeolian and alluvial materials with cobble and sand-beds. The midstream area is the most developed area with mixed lands of grasslands, urban and agricultural area including major wastewater treatment plants (WWTPs). Most of the downstream area is irrigated croplands and rangeland.

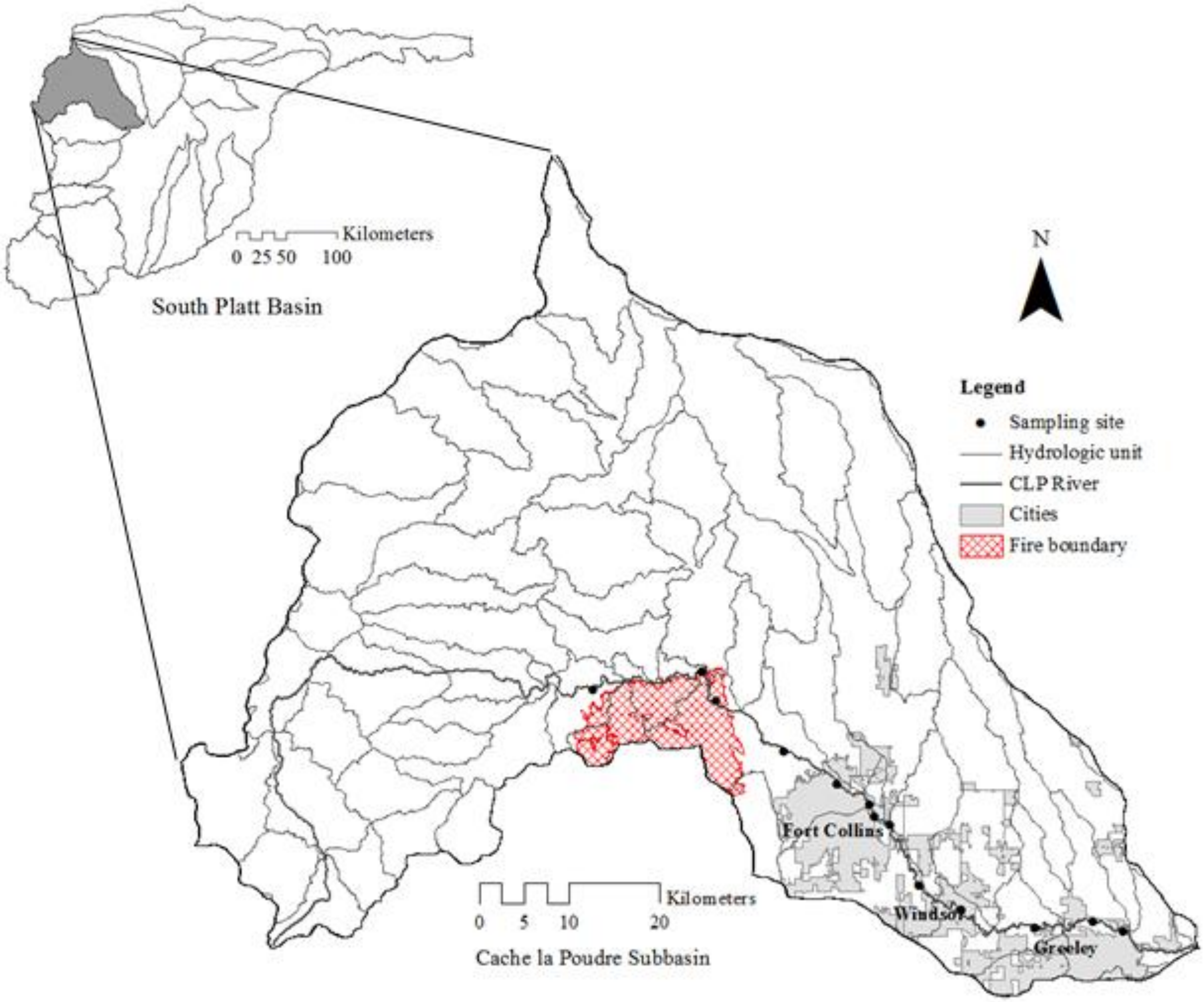

Figure 7.1: Map of the Cache la Poudre River Basin showing the fire boundary and sampling sites.

Sampling campaigns were conducted before and after the fire event. Before the fire, research was being conducted on nutrient sources in the river with sixteen total phosphorus (TP) and eleven total nitrogen (TN) sampling campaigns completed between April 2010 and July 2012 (Table 7.2).

Table 7.1: Location, altitude and distance of sampling site and land use of drainage area.

Sample ID	Coordinates	Altitude (m)	Distance† (km)	HUC	Drainage area (km^2)	Land use
Upstream						
1	40°40'55.7"N 105°23'20.9"W	1865.8	0	101900070303	60	Forest/shrub/grasslands (97.2%)
2	40°42'15.5"N 105°14'50.0"W	1644.2	0	101900070305	45	Forest/shrub/grasslands (97.0%)
3	40°40'15.9"N 105°13'41.7"W	1600.4	0	101900070805	206	Forest/shrub/grasslands (51.3%), developed area (21.4%)
4	40°37'14.0"N 105°8'20.7"W	1537.2	8.6			
Midstream						
5	40°35'14.2"N 105°4'9.0"W	1508.7	16.6			
6	40°34'1.6"N 105°1'36.8"W	1491.5	22.2			
7	40°33'21.5"N 105°1'10.8"W	1487.7	23.8			
8	40°32'48.8"N 105°0'1.1"W	1491.9	26.4	101900071002	153	Agricultural area (39.8%), developed area (33.8%)
9	40°29'11.9"N 104°57'42.4"W	1464.0	46.9			
Downstream						
10	40°27'46.8"N 104°54'26.6"W	1451.8	56.2	101900071005	250	Agricultural area (51.6%), developed area (25.0%)
11	40°26'42.4"N 104°48'40.7"W	1436.5	71.7			
12	40°27'1.3"N 104°44'5.0"W	1424.3	84.0	101900071008	425	Agricultural area (57.2%), developed area (26.2%)
13	40°26'27.8"N 104°41'47.2"W	1416.7	88.2			

† Distance from the burnt area.
HUC, hydrologic unit code

Additionally, two sampling campaigns were conducted in April and May 2012 for further water quality analysis of the river and for sediment analysis of the riverbed and bank to understand P sorption and desorption behavior. After the fire, water quality and sediment sampling campaigns were conducted to quantify the influence of fire on nutrient fluxes in the watershed. Sampling was done post-fire/pre-rainfall and post-fire/post-rainfall to further characterize how hydrological events can impact nutrient transport.

For each of the sediment sampling campaigns pre and post-fire, river water samples were collected from three randomly selected points at each of the 13 sites and transported in 500 ml

Nalgene bottles. Upper 5 cm soil samples were taken from three randomly selected points of approximate 0.10 m × 0.10 m plots of riverbed and bank at each site using a grab sampling method and sieved through a 2 mm sieve (No. 10) at the site. The collected sediment samples were then transported in a plastic bag and brought to the laboratory. Half amounts of sediment samples were air-dried and ground prior to the analysis and the rest of wet sediment and river water samples were stored at 4 ºC until further analysis.

7.2.2. Water quality analysis

Water temperature, turbidity, conductivity, and pH were measured at the site using a multi-parameter Troll 9000 equipped with a rugged reader (In-Situ Inc., Fort Collins, CO). The acid persulfate digestion method was used for measurement of TP and total dissolved P (TDP) with unfiltered and filtered river water samples using a 0.45 µm cellulose filter paper (EMD Millipore Corporation, Billerica, MA), respectively, followed by the ascorbic acid method (USEPA standard method 4500). Soluble reactive P (SRP) concentrations were also measured using the ascorbic acid method (USEPA method 365.2) with filtered river waters within 24 hours. Concentrations of dissolved organic P (DOP) were determined by difference between measured concentrations of TDP and SRP (DOP = TDP - SRP) and concentrations of particulate P (PP) were estimated by subtracting TDP concentrations from TP concentrations (PP = TP - TDP). A Shimadzu TOC-VCSH analyzer equipped with a TNM-1 (Shimadzu Corporation, Columbia, MD) was used to analyze TN concentrations in river water samples with a detection limit of 5 µg L^{-1}.

7.2.3. Soil analysis

OM contents in sediment samples were analyzed as the weight loss on ignition method (USEPA method 160.4). The microwave digestion method was used for analyzing TP concentrations in sediment samples followed by the ascorbic acid method (Littau and Engelhart 1990; Son et al. 2011) and silt-clay content was estimated with a 75 µm sieve (No. 200).

Sediment Equilibrium Phosphorus Concentration (EPC_0) analyses were performed to estimate the sorption capacity of riverbed sediments (Ekka et al. 2006; Haggard et al. 2004; Jarvie et al. 2005). EPC_0 is the P concentration where P is at the equilibrium state between the water column and sediments (Reddy et al. 1995). A mass of 0.5 g wet sediment sample was added into a 500 ml centrifuge tube with 25 ml of standard P solution made with a river matrix of five different concentrations: 0, 0.25, 0.5, 1 and 1.5 mg L^{-1}. The samples were then shaken in an orbital shaker at 150 rpm for 24 hr to react with the overlying standard solutions and immediately centrifuged at 5000 rpm for 15 min. The supernatant was transferred in a glass vial to measure SRP concentration, the major P species released from sediments (Wang et al. 2008), using the same method used for SRP analysis in water samples.

Plots of concentration of standard solution from 0 to 1.5 mg L^{-1} versus P concentration sorbed into sediment sample, calculated by difference between P concentration of added standard solution and that of measured SRP concentration from the supernatant, were created to estimate EPC_0 (x-intercept), where the sediment does not release nor sorb P to/from the overlying water.

The percent of sediment P saturation was estimated as the fraction of the EPC_0 to the river SRP concentration, measured from river water samples collected at the same site where the riverbed sediment samples were taken. From this analysis, the sorption state of the riverbed sediment was defined as over-saturated when the percent saturation equaled or exceeded 120% indicating release of P into the river water. The sediments were considered to be under-saturated when the percent saturation was equal to or less than 80%, a state that assumes net sorption of P to the riverbed. Calculated percent saturation between 80 and 120% was considered at equilibrium with the river water (Jarvie et al. 2005). The sorption constant, K_d was also assessed to evaluate sediment buffer intensity of P sorption (Reddy et al. 1995).

7.2.4. Statistical analysis

The post-fire (post-fire/pre-rainfall and post-fire/post-rainfall) sediment and in-stream water quality data were compared with the pre-fire data from the closest two sampling events (events 13-14) to the post-fire sampling events (Table 7.2). The sign test was applied at 0.05 significance level to test significant differences of data at each site between pre-fire, post-fire/pre-rainfall, and post-fire/post-rainfall events and the Mann-Kendall trend test was performed to examine the trend of concentrations from upstream to downstream of the river. The relationship between variables was evaluated using Pearson's correlation coefficient at 0.05 and 0.01 significant levels.

7.3. Results and Discussion

7.3.1. In-stream water quality

Significant increases of in-stream parameters, such as temperature, turbidity, conductivity, and pH, in post-fire analyses were observed (Fig. 7.2).

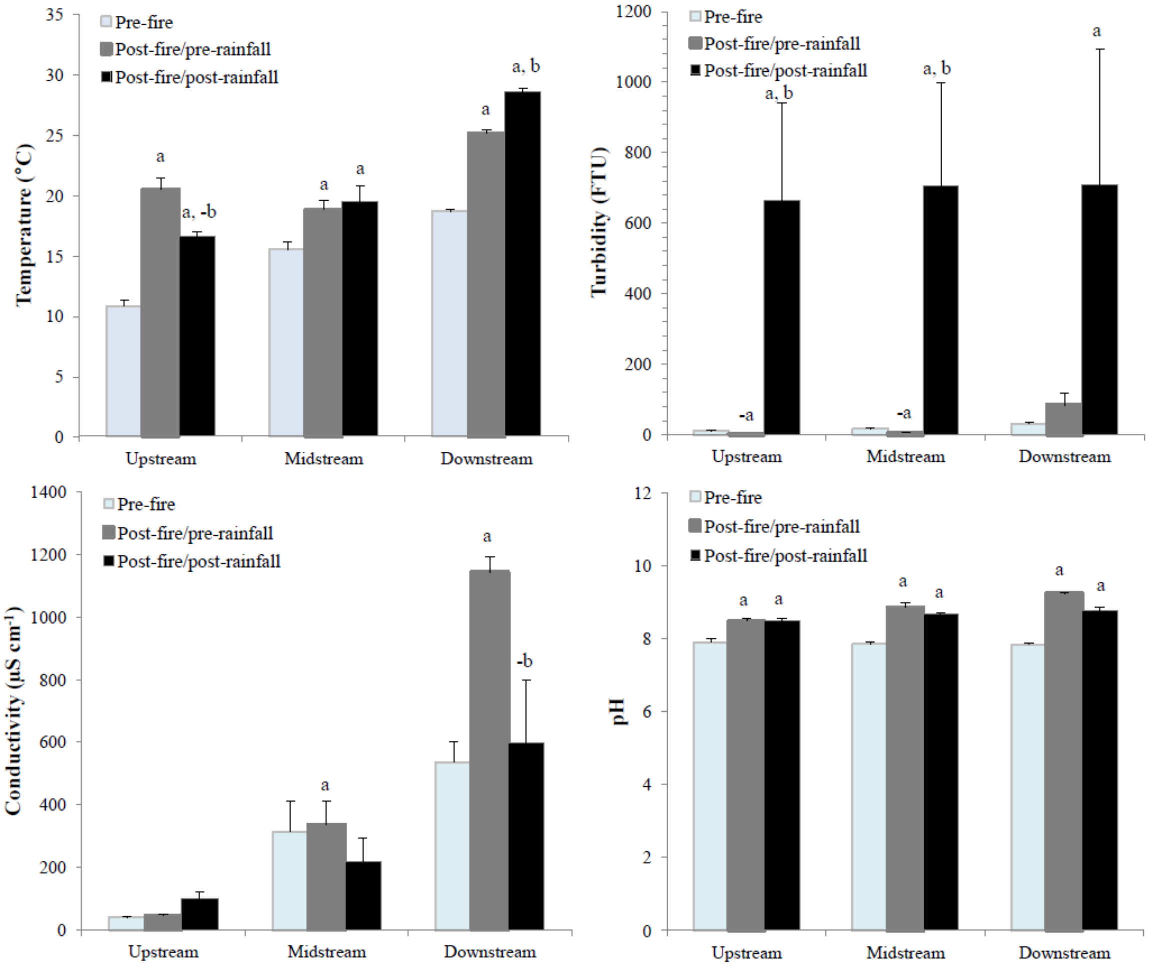

Figure 7.2: Mean riverine water quality parameters (temperature, turbidity, conductivity and pH) of upstream, midstream, and downstream for pre-fire, post-fire/pre-rainfall and post-fire/post-rainfall between April and July 2012. Error bars indicate the standard error. a, b Significant difference tested using the sign test, negative (-) indicates significant decrease. a Significantly different from the pre-fire event at $p = 0.05$. b Significantly different from the post-fire/pre-rainfall event at $p = 0.05$.

Along with the effect of increased air temperature between pre-fire (April-May) and post-fire (July) events, river temperature rose significantly after the fire. Upstream sections in forest area showed the most significant impact on river temperature increasing from 8-15 ºC (pre-fire) to 17-24 °C (post-fire/pre-rainfall), values greater than that in midstream section located in urbanized area, but dropping to the range of 16-18 °C after precipitation (post-fire/post-rainfall).

The pre-fire events, 15 and 16, had precipitation of 0.93 mm and 2.54 mm, respectively, prior to the sampling campaigns (Fig. 7.3).

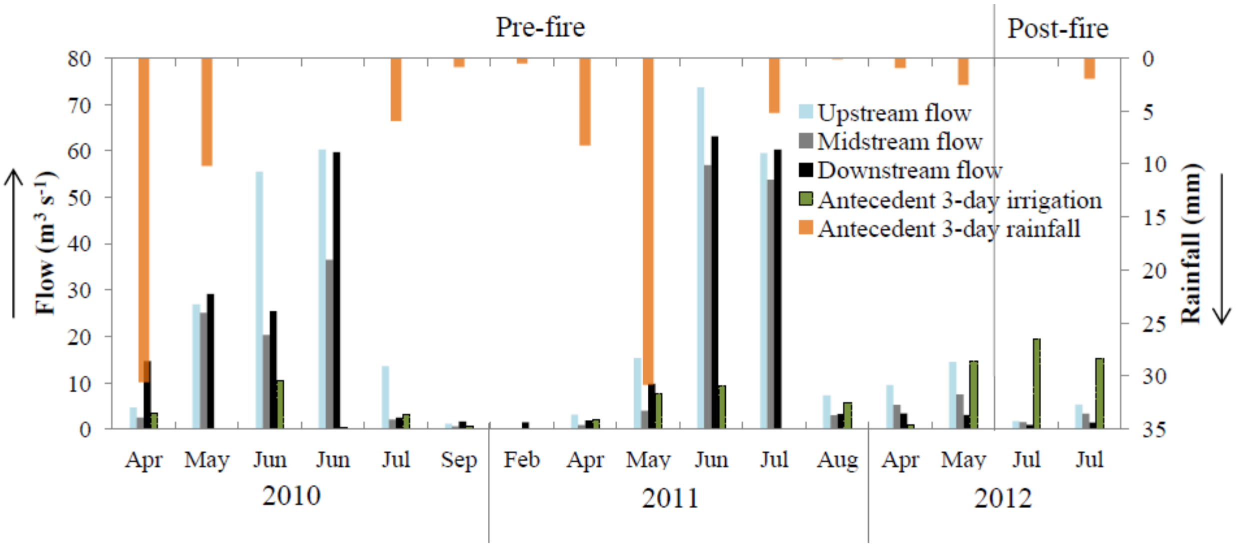

Figure 7.3: Hydrologic conditions: flow rates of upstream, midstream, and downstream of the river, antecedent 3-day irrigation rate and antecedent 3-day rainfall in the study area of sampling campaigns (April 2010-July 2012). Upstream, midstream, downstream flows and irrigation rates were measured at the flow station CLAFTCCO (40°39'52"N, 105°13'26"W), USGS06752280 (40°33'07"N, 105°00'39"W), CLAWASCO (40°25'21"N, 104°40'37"W), and LAWIRRCO (40°37'13"N, 105°06'25"W), respectively.

However, turbidity increased more than other parameters ranging from 30.1 to 2705.6 FTU in the post-fire/post-rainfall event, after 1.95 mm of rainfall prior to the sampling campaign (Fig. 7.3), compared to a range of 1.9-48.9 FTU pre-fire (Fig. 7.2) although flow decreased from 2.4-14.5 m^3s^{-1} pre-fire t o 1.42-5.3 m^3s^{-1} post-fire/post-rainfall (Fig. 7.3). Downstream turbidity also significantly increased after precipitation compared to the post-fire/pre-rainfall event means (> 800%). Likewise, electrical conductivity in the upstream section increased after precipitation (post-fire/post-rainfall event), likely due to the release of inorganic ions from the burnt OM and its transport to the stream by rainfall. Significant difference of electrical conductivity between pre and post-fire, however, was not observed in the upstream section but were observed in mid and downstream which might be due to discharges of WWTP effluents and irrigation return flows.

In-stream pH increased by 0.6-1.4 units after the fire in all sections of the river and slightly decreased after precipitation, a result that was also observed in other studies (e.g. Robichaud et al. 2000). The decrease was limited to mid and downstream sections and no difference between post-fire/pre-rainfall and post-fire/post-rainfall was observed. This might be due to continuous inputs of base cations such as potassium, sodium oxides, hydroxide, and carbonates (Ulery et al. 1993) in the upstream section that increased as a consequence of denaturation of organic acids and the release of bases from soils after the fire (Arocena and Opio 2003; Khanna et al. 1994).

Aqueous TP and TN concentrations were monitored from April 2010 to July 2012 along the length of the river. For all the post-fire events (events 15-16), ranges of TP and TN concentrations were 0.21-123.3 mg L^{-1} and 0.31-4.75 mg L^{-1}, respectively, while ranges of TP and TN concentrations for all the pre-fire event (events 1-14) were 0.06-3.57 mg L^{-1} and 0.01-14.29 mg L^{-1}, respectively (Table 7.2). The flow decrease after the fire but significant changes of riverine TP and TN concentrations were not observed in event 15 (post-fire and pre-rainfall event) compared to the pre-fire events.

Table 7.2: Concentrations of total phosphorus (TP) and total nitrogen (TN) in upstream, midstream, and downstream sections before fire (events 1-14), after fire (event 15), and after fire and rainfall (event 16) (April 2010-July 2012).

Event No.	Event dates	TP (mg L^{-1})			TN (mg L^{-1})		
		Upstream	Midstream	Downstream	Upstream	Midstream	Downstream
Pre-fire							
1	April 2010	_	0.61 ± 0.21 (15)	1.74 ± 0.07 (12)	_	_	_
2	May 2010	0.16 ± 0.01 (9)	0.27 ± 0.06 (15)	0.66 ± 0.02 (12)	_	_	_
3	June 2010	0.17 ± 0.01 (12)	0.38 ± 0.12 (15)	1.00 ± 0.00 (12)	_	_	_
4	June 2010	0.13 ± 0.01 (12)	0.19 ± 0.02 (12)	0.55 ± 0.05 (12)	_	_	_
5	July 2010	_	0.94 ± 0.37 (15)	1.47 ± 0.20 (12)	_	_	_
6	September 2010	0.11 ± 0.01 (12)	0.36 ± 0.08 (15)	0.64 ± 0.08 (12)	0.04 ± 0.01 (12)	0.85 ± 0.24 (15)	1.94 ± 0.19 (12)
7	February 2011	0.12 ± 0.01 (12)	0.54 ± 0.15 (15)	0.48 ± 0.06 (12)	0.34 ± 0.06 (12)	2.95 ± 0.81 (15)	3.67 ± 0.28 (12)
8	April 2011	0.13 ± 0.02 (9)	0.52 ± 0.14 (15)	1.05 ± 0.07 (12)	0.21 ± 0.03 (12)	1.42 ± 0.33 (15)	2.58 ± 0.08 (12)
9	May 2011	0.14 ± 0.01 (12)	0.30 ± 0.04 (15)	0.60 ± 0.04 (12)	0.25 ± 0.01 (12)	0.72 ± 0.12 (15)	1.25 ± 0.06 (12)
10	June 2011	0.16 ± 0.01 (12)	0.28 ± 0.02 (15)	0.29 ± 0.01 (12)	0.26 ± 0.01 (12)	0.41 ± 0.07 (15)	0.42 ± 0.02 (12)
11	July 2011	0.10 ± 0.01 (12)	0.43 ± 0.15 (15)	0.36 ± 0.01 (12)	0.29 ± 0.02 (12)	1.74 ± 0.76 (15)	0.72 ± 0.08 (12)
12	August 2011	0.08 ± 0.01 (12)	0.81 ± 0.20 (15)	0.90 ± 0.02 (12)	0.27 ± 0.02 (12)	1.92 ± 0.72 (15)	1.62 ± 0.02 (12)
13	April 2012	0.30 ± 0.01 (12)	1.16 ± 0.36 (15)	0.96 ± 0.03 (12)	0.22 ± 0.02 (12)	3.09 ± 1.62 (15)	1.35 ± 0.07 (12)
14	May 2012	0.20 ± 0.03 (12)	1.04 ± 0.36 (15)	0.88 ± 0.03 (12)	0.93 ± 0.02 (12)	3.71 ± 1.39 (15)	2.22 ± 0.13 (12)
Post-fire							
15	July 2012	0.23 ± 0.01 (12)	0.38 ± 0.06 (15)	1.20 ± 0.20 (12)	0.47 ± 0.05 (12)	0.72 ± 0.13 (15)	1.85 ± 0.32 (12)
16	July 2012	58.7 ± 18.2 (12)	8.70 ± 3.49 (15)	1.45 ± 0.19 (12)	1.83 ± 0.27 (12)	1.25 ± 0.19 (15)	2.52 ± 0.46 (12)

Entries are mean ± S.E. (n).

Marked increases of the nutrient concentrations, however, were observed after rainfall (event 16) in the upstream section: elevated concentrations of TP (390 times) and TN (6 times) compared to pre-fire averages may be due to the ash that was deposited during fire being transported to the river by rainfall. The increase was significant when compared to other precipitation events (events 1-2, 5-9, 11, 13-14) (Fig. 7.3). The nutrients being transported by the river became insignificant in the midstream for TN and downstream for TP, likely due to attenuation processes such as settling, sorption, microbial assimilation and aquatic plant uptake (Froelich 1988; Haggard et al. 1999; Lepistö et al. 2006).

The increase of in-stream concentration was more significant for TP than TN because N has a lower volatilization temperature (> 200 °C) than TP (> 774 °C) and therefore substantial amounts of TN may have volatilized at the site during the fire. The remaining TN from the fire might have been converted to inorganic forms such as ammonium through combustion (Covington and Sackett 1992) and transported to the river adsorbed onto the negatively charged soil particles (Mroz et al. 1980).

Meaningful decreases in DOP loads were observed in upstream and midstream sections after the fire and increases were observed in upstream and midstream sections post-fire/post-rainfall. Increases in SRP loads were more pronounced in the post-fire/post-rainfall event in the upstream sections compared to both pre and post-fire/pre-rainfall means (Fig. 7.4).

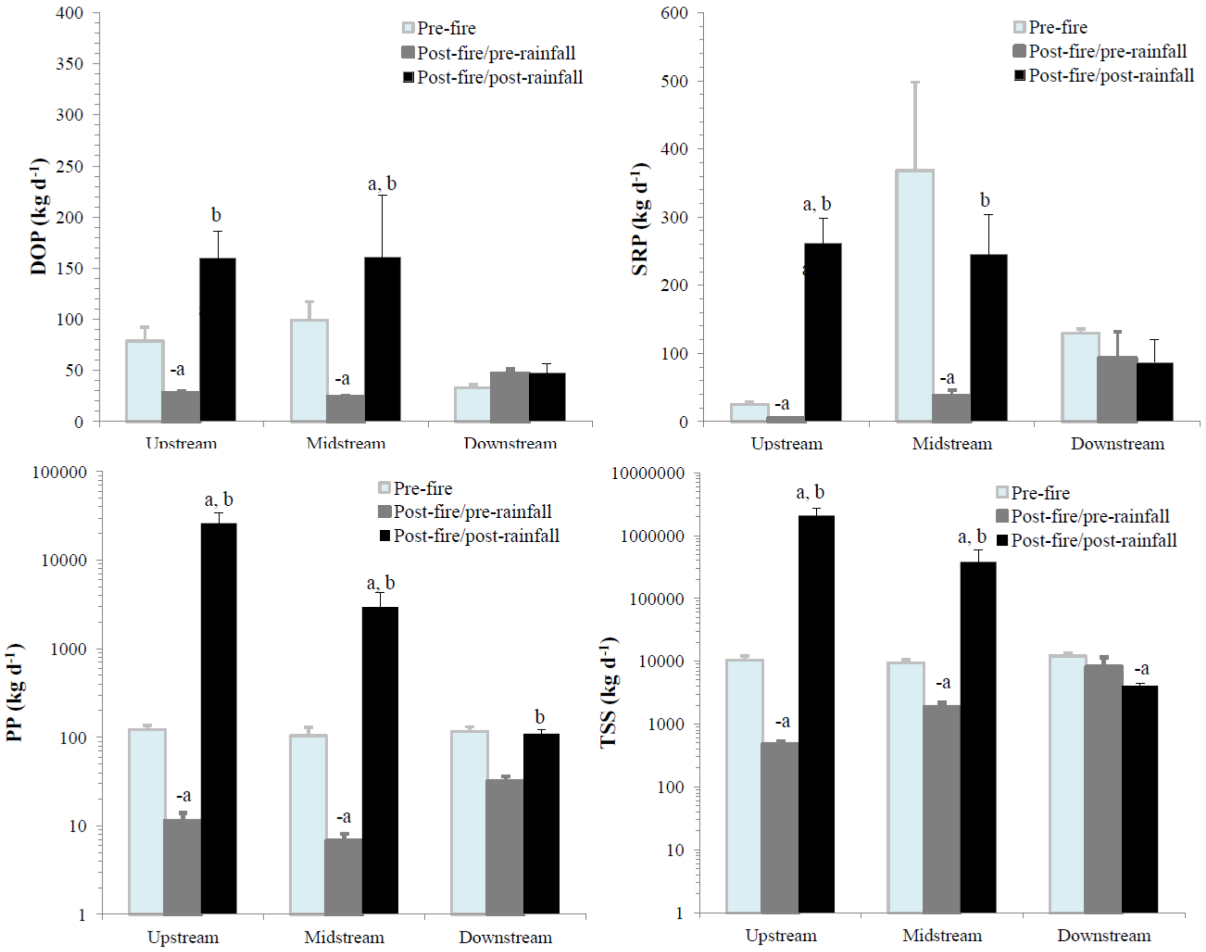

Figure 7.4: Mean riverine loads of dissolved organic phosphorus (DOP), soluble reactive phosphorus (SRP), particulate phosphorus (PP), and total suspended solids (TSS) in upstream, midstream and downstream of pre-fire, post-fire/pre-rainfall and post-fire/post-rainfall events between April and July 2012. Error bars indicate the standard error. [a, b] Significant difference tested using the sign test, negative (-) indicates significant decrease. [a] Significantly different from the pre-fire event at p = 0.05. [b] Significantly different from the post-fire/pre-rainfall event at p = 0.05.

DOP dominated TDP in the upstream section of the river before fire comprising 58-88% of the total. SRP increased significantly after fire and rainfall accounting for 55 to 73% of the TDP, up from 12-42%. The elevated levels of inorganic P may be partially due to the mineralization of surface soil after burning (Ellis and Graley 1983; Ferran et al. 1992; Polglase et al. 1992; Simms 1987; Wilbur and Christensen 1985) resulting in a release of the nutrient to the watershed.

Spatial increase in TDP loads including SRP and decrease in DOP loads from upstream to downstream were observed in the pre-fire events. Spatial increases in all species of TDP (SRP and DOP) and TSS loads were monitored in the post-fire/pre-rainfall events using a trend analysis but not in the post-fire/post-rainfall event (Fig. 7.4). These results might indicate that incoming dissolved P mainly in SRP form to the river increased with anthropogenic influences (e.g. WWTPs) midstream and downstream but upstream the mechanism was related to the fire and subsequent rainfall.

PP and TSS significantly decreased in the upstream and midstream sections post-fire/pre-rainfall when compared to pre-fire but increased markedly after precipitation (post-fire/post-rainfall) in all river sections. PP showed the most significant increase post-fire among the P species rising by 430 and 40 times in the upstream and midstream, respectively (Fig. 7.4). Similar results also have been observed in other studies where PP and TDP loads were significantly higher in burned areas and mainly in particulate form (Burke et al. 2005; Prepas et al. 2003). Since P has a high volatilization temperature, it will mostly accumulate in the surface ash bed soils after fire (Neff et al. 2005) and can be easily transported with rainfall. Supporting this supposition was the strong correlation between PP and TSS in the post-fire/post-rainfall event ($r = 0.98$) in this study.

Spatial increases in the loads of TSS from upstream to downstream were observed in the post-fire/pre-rainfall events but spatial decreases were observed for PP and TSS loads after precipitation which denotes substantial inputs in upstream and retention while the river flows downstream, similar to dissolved P as described above.

7.3.2. Sediment characterization and sorption capacity

The silt-clay fraction in the riverbed and bank increased significantly in all sections of the river post-fire/post-rainfall (Fig. 7.5), likely due to surface runoff. Spatial increase in riverbed silt-clay fraction from upstream to downstream was observed in the pre-fire event but a spatial decrease was found in the post-fire/post-rainfall event. A spatial trend in riverbank silt-clay fraction was not observed with pre-fire data but a decrease was noted in the post-fire/post-rainfall event. These results have also shown that great amount of silt-clay particles entered in the upstream section of the river during the post-fire/post-rainfall event. It appears that increased amounts of silt-clay particles deposited in the riverbanks can easily enter the river and would impact the river for a long period of time since it can be reloaded through precipitation and erosion, a risk that increases after fire (Badìa et al. 2003; Dìaz-Fierros et al. 1987).

OM concentrations in riverbed sediments were not found to have changed significantly pre-fire to post-fire/pre-rainfall except for the midstream section, where a decrease in OM was measured. However, post-fire/post-rainfall analyses showed a large increase in sediment and bank OM concentrations compared to pre and post-fire/pre-rainfall measurements. The surge in OM concentration may be due to significant inputs of the burnt woody residue in the fire area (Fig.7.5). The increase of OM in both the riverbed and riverbank sediments may have a marked impact on P transport by increasing sorption capacity. For example, significant inputs of PP was observed in the post-fire/post-rainfall event in this study (Fig. 7.4) and several studies have also shown that soil-bound P increased after fire due to the increase in soil P sorption capacity by soil-ash interactions and the effect of heat (Romanyà et al. 1994; Polglase et al. 1992; Kwari and Batey 1991).

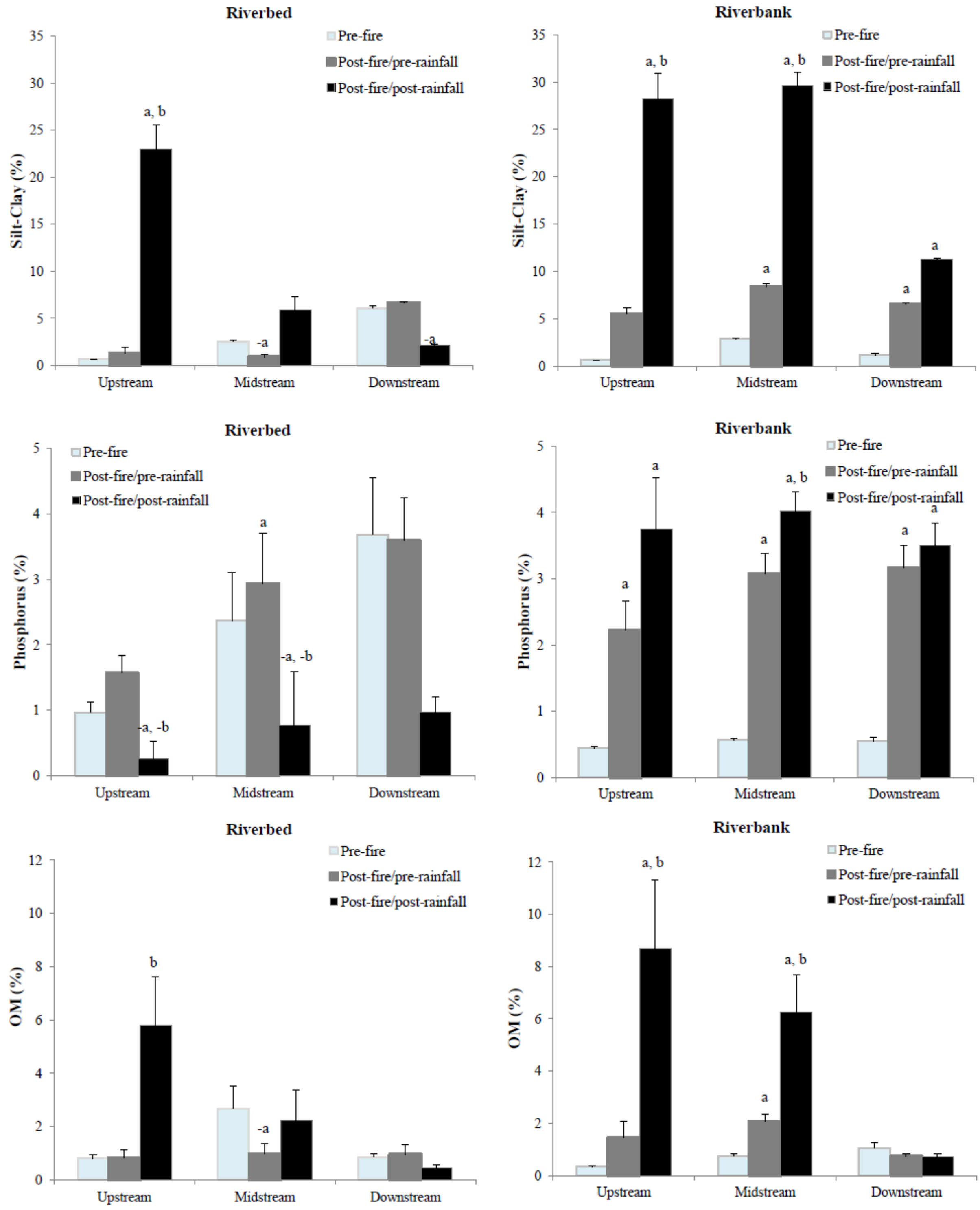

Figure 7.5: Mean silt-clay, TP and OM contents in pre-fire, post-fire/pre-rainfall and post-fire/post-rainfall riverbed (left) and riverbank sediments (right) of upstream, midstream and downstream sections of the river between April and July 2012. Error bars indicate the standard error. $^{a, b}$ Significant difference tested using the sign test, negative (-) indicates significant decrease. ^{a} Significantly different from the pre-fire event at $p = 0.05$. ^{b} Significantly different from the post-fire/pre-rainfall event at $p = 0.05$.

Consequently, the burnt surface soils have considerably greater TP concentrations and P deposited in the ash bed and burnt soils are relatively insoluble in water (Khanna et al. 1994). Therefore, the burnt surface soils that have eroded by precipitation and accumulated in riverbanks after fire contain substantially higher TP concentrations (Fig. 7.5) and potentially pose a risk of entering the aqueous P-cycle in the future. P adsorbed to ash bed soils have been shown to become labile when the adsorbents are neutralized (Khanna et al. 1994) so TP attached to the soils can be lost once the burnt soils are introduced into the river and react with surrounding water.

Indeed, significantly increased EPC_0 with decreases in sorption capacity was observed from upstream riverbed sediments of the post-fire/post-rainfall event using the sorption analysis of riverbed sediments when compared with both pre and post-fire/pre-rainfall events, for example, site 1 went from EPC_0 of 0.16 pre-fire and 0.12 post-fire/pre-rainfall to 1.55 after fire and precipitation (Table 7.3). This was likely due to transport of OM in ash reducing sorption capacity thus increasing EPC_0.

With high aqueous P concentration entering in the upstream section, frequent changes of the sorption status of the riverbed sediments from "release" to "adsorb" were observed in the mid and downstream sections (Table 7.3) and this status can easily change to "release" over again when the aqueous SRP concentration goes down by less than EPC_0 which would make riverbed sediments a significant P source in the river.

Table 7.3: Mean equilibrium phosphorus concentration (EPC_0), percent P saturation, sorption state and sorption constant (K_d) of riverbed sediments from pre-fire and post-fire events.

Sites	EPC_0 (mg L^{-1})	Saturation (%)	State	K_d (mL g^{-1})	EPC_0 (mg L^{-1})	Saturation (%)	State	K_d (mL g^{-1})
				Pre-fire				
	April 2012				May 2012			
Upstream								
1	0.16	620	R	25.3	0.08	770	R	39.1
2	0.03	104	E	14.7	0.07	149	R	20.3
3	0.04	164	R	10.1	0.10	323	R	42.8
4	0.38	1270	R	9.0	0.33	1308	R	7.0
Midstream								
5					0.03	60	A	9.6
6	0.56	1236	R	19.5	0.23	269	R	6.5
7	0.42	492	R	19.5	0.29	420	R	5.9
8	0.70	22	A	46.0	0.96	39	A	23.3
9	0.48	183	R	27.5	0.94	119	R	8.3
Downstream								
10	1.54	571	R	39.5	0.16	31	A	857
11	0.66	140	R	28.4	0.71	134	R	38.0
12	0.31	70	A	29.9	0.46	88	E	27.3
13	0.94	222	R	17.2	1.17	339	R	23.7
				Post-fire				
	July 2012 (post-fire/pre-rainfall)				July 2012 (post-fire/post-rainfall)			
Upstream								
1	0.12	295	R	13.4	1.55	573	R	15.1
2	0.31	1033	R	10.6	1.55	198	R	46.1
3	0.39	965	R	11.2	1.67	203	R	20.1
4	0.05	177	R	7.4	0.98	204	R	11.2
Midstream								
5	0.03	60	A	19.4	0.38	25	A	9.2
6	0.09	66	A[†]	5.7	0.03	11	A[†]	8.2
7	0.77	590	R	3.9	0.32	88	E[†]	6.6
8	0.47	80	A	32.9	0.29	91	E[‡]	30.6
9	0.40	77	A[†]	11.8	0.14	7	A[†]	13.7
Downstream								
10	1.54	90	E	6.7	0.51	32	A	7.1
11	0.10	11	A[†]	10.5	0.08	14	A[†]	18.7
12	0.06	73	A	12.8	0.33	815	R	8.5
13	0.33	206	R	61.2	0.04	29	A[†]	28.2

[†] Sorption status changed after fire from R before fire.

[‡] Sorption status changed after fire from A before fire.

A, adsorb; E, equilibrium; R, release

In the upstream section, where P concentration is naturally sourced and relatively low, flow was the main factor influencing sediment sorption parameters such as EPC_0 (r=0.79), TP mass concentration in the riverbed sediments (r=-0.60), P saturation (Section 2.3, r=-0.48) and K_d (r=0.82) for the pre-fire event (Table 7.4).

Table 7.4: Correlation coefficient (r) between riverbed sediment sorption parameters: TP mass concentration, EPC_0, percent P saturation, sorption strength (K_d) and other parameters: flow, aqueous P concentration and riverbed mass concentration of silt-clay and OM, in the upstream, midstream and downstream sections of pre and post-fire events.

	Pre-fire				Post-fire			
	Riverbed TP	EPC_0	Saturation	K_d	Riverbed TP	EPC_0	Saturation	K_d
Upstream (n=24)								
Flow	0.79**	-0.60**	-0.48*	0.82**	0.58**	0.66**	0.97**	-0.46*
Aqueous concentration								
TP	-0.33	0.26	0.36	-0.17	0.75**	0.75**	0.72**	-0.45*
TDP	0.04	0.22	0.48*	-0.33	0.84**	0.78**	0.84**	-0.54**
DOP	0.07	0.19	0.46*	-0.25	0.95**	0.75**	0.70**	-0.46*
SRP	-0.20	0.04	-0.28	-0.26	0.76**	0.87**	-0.55**	0.72**
PP	-0.40*	0.14	0.06	0.04	0.74**	0.75**	0.72**	-0.45*
Riverbed concentration								
Silt-clay	0.50**	-0.32	-0.06	0.71**	0.98**	0.81**	0.65**	-0.31
OM	-0.21	-0.21	-0.10	0.26	0.97**	0.82**	0.58**	-0.33
Midstream (n=30)								
Flow	0.14	-0.54**	0.21	-0.23	-0.13	-0.10	-0.20	-0.36*
Aqueous concentration								
TP	0.65**	0.71**	-0.47**	0.76**	-0.15	-0.16	0.09	-0.22
TDP	0.04	0.22	0.48**	-0.33	0.84**	0.79**	0.84**	-0.54**
DOP	0.82**	0.62**	-0.38*	0.54**	-0.18	-0.19	-0.41*	-0.30
SRP	0.57**	0.65**	-0.48**	0.74**	0.00	0.11	-0.04	-0.35*
PP	0.38*	0.38*	-0.01	0.26	-0.18	-0.19	0.11	-0.24
Riverbed concentration								
Silt-clay	0.67**	0.68**	-0.42*	0.69**	0.62**	0.70**	0.00	-0.05
OM	0.15	0.49**	-0.33	0.84**	0.76**	0.85**	0.08	-0.06
Downstream (n=24)								
Flow	-0.76**	0.76**	0.81**	-0.58**	-0.47*	0.07	0.69**	0.02
Aqueous concentration								
TP	0.00	0.09	0.13	0.37	-0.40*	-0.05	0.62**	0.52**
TDP	0.39*	-0.80**	-0.81**	0.28	-0.51**	-0.20	0.67**	-0.23
DOP	-0.23	0.04	0.13	-0.22	0.06	0.06	-0.35	0.61**
SRP	0.53**	-0.88**	-0.93**	0.40*	-0.47*	-0.20	0.72**	-0.40*
PP	-0.28	0.63**	0.66**	0.08	0.06	0.19	-0.35	0.05
Riverbed concentration								
Silt-clay	0.83**	-0.27	-0.23	0.63**	0.97**	0.81**	-0.11	0.08
OM	0.82**	-0.68**	-0.60**	0.87**	0.98**	0.82**	-0.14	0.02

*Significantly correlated ($p < 0.05$); **Strongly correlated ($p < 0.01$)

The midstream section has considerable urban influences including WWTP effluents that are dominated by SRP. Accordingly, EPC_0 in this section is influenced by riverine P concentrations (mainly SRP, r = 0.65) while EPC_0 in the downstream section that is largely influenced by agricultural land uses (including irrigation return flows dominated by PP) had strong positive correlation with PP (r = 0.63) and negative correlation with SRP (r = -0.88) in the pre-fire event. In a highly P concentrated condition like downstream, flow became positively correlated with EPC_0 and sorption strength (K_d) decreased as flow increased (Table 4.10) which also indicates that EPC_0 is negatively correlated with sorption strength.

A strong negative correlation (r = -0.60) was observed between EPC_0 and flow in the upstream section before fire but positive correlation (r = 0.66) was observed after fire with excessive P concentrations in the river. This might be because in natural forest area of pre-fire conditions, riverbed sediments are scoured and fresh sediments are introduced to the river, increasing sorption strength of riverbed sediments as flow goes high (r = 0.82) while highly P contaminated soils enter the river after fire and become riverbed with reduced sorption strength as flow increases (r = -0.48) (Table 4.10).

Other factors such as aqueous P concentrations, silt-clay and OM contents also became significantly and strongly correlated with the riverbed sorption parameters in the upstream section after fire, for example, correlation between aqueous TP concentration and riverbed TP mass concentration was not significant (r = -0.33) but it became strong after fire (r = 0.75) (Table 4.10). Likewise, silt-clay and OM contents in the riverbed sediments had strong positive correlation with sorption strength before fire but the strong positive correlation were greatly reduced or shifted to negative in all sections of the river after fire likely due to highly P concentrated silt-clay particles by fire.

7.4. Conclusion

Water quality and soil properties were highly disturbed by wildfire but, in a wide range, the magnitude of disturbance was relatively marginal without precipitation. In the presence of precipitation, data showed that in-stream concentrations of TN significantly increased in the upstream sector located within 10 km distance from the burnt area but increase in TP concentrations was more remarkable. Great amounts of PP with TSS, which had a strong correlation, introduced to the upstream sector and impacted on further downstream of the river. Along with significantly increased loads of SRP and DOP after precipitation, it was found that SRP dominated dissolved P in the river while DOP was the main species of dissolved P before fire in the upstream forest area and this might be due to increased inorganic P during fire, carried by soils, and release of P from the burnt soils in water.

In the riverbank, mass concentrations of TP increased significantly after fire and silt-clay and OM contents also significantly increased after having precipitation, but mass concentrations of TP significantly decreased in the riverbed sediments because sorption capacity of the riverbed sediments significantly decreased and consequently P, mainly in inorganic form, considerably released from the sediments. Long-term increases in the risk of erosion and sediment delivery to streams were observed by numerous studies (e.g. Dìaz-Fierros et al. 1987, 1982) and therefore we propose that the fire-impacted soil highly concentrated by P can be a significant long-term source of P once the soil enters the river through surface runoff and erosion.

CHAPTER 8

CONCLUSION

Excess nutrient inputs into water bodies cause a number of problems, such as health problems, treatment problems, aesthetic and recreational problems as a consequence of algal blooms. Nutrients have been ranked as one of the leading pollutants impairing the nation's waters since the late 20th century. The U.S. EPA strongly encourages states and tribes to establish numeric nutrient criteria for their water bodies, and the WQCD of the CDPHE began to develop nutrient standards for the state's surface waters. The CDPHE proposed nutrient limits for rivers and streams. In addition, nutrient criteria for the WWTPs have also been proposed to reduce nutrient loading to surface waters. Due to the difficulties involved in identifying and controlling nonpoint sources, stringent enforcement on point sources are expected to achieve the proposed nutrient limits in river and streams. To provide a more fundamental understanding of these issues, three hypotheses were proposed for the research described in this dissertation:

I. Nutrient load from nonpoint sources is statistically greater than that from point sources in the Cache la Poudre River Watersheds on an annual basis.

TP loads from nonpoint sources dominated except for downstream sections when stream flows were critically low. Similar to TP loads, nonpoint sources were the major source of TN loads for the events except for sampling point 8. Effluent from the BSD was the largest source of TN at sampling point 8 in lower flow conditions, but TN from nonpoint sources was significant during higher flow conditions. From the study in nutrient load inputs to the CLP River, it was found that nutrient loads in the CLP River are mainly from nonpoint sources on an annual basis.

II. The proposed nutrient standards can only be achievable with meaningful reduction of the nonpoint source load. In other words, the standards cannot be met without nonpoint source load reduction in the Cache la Poudre River Basin.

From the nutrient load analysis for both TP and TN, it was found that meeting the proposed limits for rivers and streams (regulation 31) still cannot be achieved only by reducing nutrient loads at the WWTPs according to the proposed nutrient criteria for the WWTPs (regulation 85).

III. Wildfire significantly impacts water quality and riverbed and bank sediment characteristics, and post-fire sediments can be a long-term source of phosphorus in the river.

In addition, wildfire alters physicochemical water quality and riverbed and bank sediments which might last for a long time. With precipitation, the magnitude of alteration in water quality and sediment characteristics significantly increased. TP mass concentrations in post-fire riverbank sediments increased 5-8 times compared to those in the pre-fire riverbank sediments. However, after post-fire precipitation TP mass concentration in the riverbed sediments decreased compared to its levels in the pre-fire riverbed sediments because of decreased sorption capacity. This might indicate that accumulated P in the riverbank sediment after fire could be eroding and entering the river by precipitation, thus becoming a long-term, significant source of P in the river.

CHAPTER 9

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APPENDICES

Table A.1: Measurement method summary.

Parameter	Abbreviation	Method
Total Phosphorus	TP	Hach 8190; USEPA standard method 4500
Total Dissolved Phosphorus	TDP	Hach 8190; USEPA standard method 4500 (Pre-filtration)
Particulate Phosphorus	PP	PP = TP – TDP
Soluble Reactive Phosphorus	SRP	Hach 8048; USEPA method 365.2
Dissolved Organic Phosphorus	DOP	DOP = TDP – SRP
Total Nitrogen	TN	Shimadzu TOC-VCSH analyzer equipped with TNM-1
Organic Matter	OM	Loss of Ignition; USEPA method 160.4
Sediment Total Phosphorus	Sediment TP	Microwave digestion followed by ascorbic acid method

Table A.2: Example of data sheet of aqueous concentration for one event (Event 13, 4/23-24/12).

Sample ID	Location	Lat (DD)	Long (DD)	Flow (m^3s^{-1})	Aqueous concentration (mgL^{-1}) TN (Shimazdu)	TP (Hach method 4189) 1st	TP (Hach method 4189) 2nd	TP (Hach method 4189) Average	TDP (Hach method 4189) 1st	TDP (Hach method 4189) 2nd	TDP (Hach method 4189) Average
Cache la Poudre River											
1	South Fork Poudre River upstream	40.68214	-105.38915	9.514	0.285	0.24	0.24	0.24	0.12	0.11	0.115
2	South Fork (in canyon)	40.70430	-105.24723	9.514	0.179	0.28	0.33	0.305	0.14	0.1	0.12
3	Mouth of Poudre River	40.67107	-105.22825	9.514	0.128	0.29	0.28	0.285	0.15	0.14	0.145
4	Poudre River @ Overland	40.62055	-105.13910	7.447	0.295	0.38	0.35	0.365	0.08	0.12	0.1
5	USGS-Cache La Poudre River @ Ft. Collins	40.58727	-105.06916	7.447	0.105	0.34	0.29	0.315	0.22	0.34	0.28
6	Poudre River @ Prospect Rd	40.56712	-105.02690	7.447	0.288	0.37	0.44	0.405	0.15	0.15	0.15
7	Poudre River Upstream DWRF	40.55597	-105.01965	5.239	0.148	0.37	0.49	0.43	0.17	0.15	0.16
8	Poudre River Near Archery Range	40.54689	-105.00030	5.239	14.29	3.51	3.62	3.565	3.55	3.56	3.555
9	Poudre Downstream of Fossil Creek Reservoir	40.48663	-104.96177	4.701	0.621	0.99	1.14	1.065	0.39	0.38	0.385
10	Poudre River @ CR17 Windsor	40.46301	-104.90740	4.701	1.123	0.99	1.05	1.02	0.41	0.44	0.425
11	Poudre River @ Route 27/83rd Ave. Greeley	40.44510	-104.81130	3.426	1.192	1.09	0.89	0.99	0.54	0.5	0.52
12	Poudre River @ Route 35	40.45036	-104.73473	3.426	1.597	0.89	0.77	0.83	0.58	0.58	0.58
13	Poudre River @ 11th Ave. Greeley	40.44105	-104.69643	3.426	1.487	1.12	0.87	0.995	0.56	0.52	0.54
Boxelder Creek											
D-1a	Boxelder Creek outlet	40.54987	-105.00403	0.032	12.58	11.2		11.2	3.7	3.6	3.65
Irrigation Ditch											
D-1b	Upstream of BSD effluent	40.55212	-105.00462	0.117	3.444	0.34	0.21	0.275	0.19	0.16	0.175
D-2	Irrigation ditch upstream of Irr-2a	40.44264	-104.88137	0.016	0.693	0.32	0.21	0.265	0.21	0.19	0.2
D-3	Law Ditch outlet	40.44572	-104.86537	2.322	5.439	0.61	0.57	0.59	0.57	0.57	0.57
D-4	Graham Seep Ditch outlet	40.44923	-104.72104	0.008	5.326	0.16	0.45	0.305	0.28	0.27	0.275

Continued

Sample ID	Aqueous concentration (mg L^{-1})					TSS (mg L^{-1}) (EPA method 160.2)	PP/TSS (mg g^{-1})	Partition Coefficient, Kd (L mg^{-1})
	SRP (Hach method 4048; MDL 0.02-2.5 mg L^{-1})			PP (TP-TDP)				
	1st	2nd	Average	mg/L	%			
Cache la Poudre River								
1	0.02	0.03	0.025	0.125	52.08	20	6.250	0.250
2	0.03	0.02	0.025	0.185	60.66	26	7.115	0.285
3	0.02	0.03	0.025	0.140	49.12	21	6.512	0.260
4	0.03	0.03	0.030	0.265	72.60	26	10.192	0.340
5	0.08	0.12	0.100	0.035	11.11	18	1.944	0.019
6	0.03	0.06	0.045	0.255	62.96	20	12.750	0.283
7	0.07	0.10	0.085	0.270	62.79	17	15.882	0.187
8	3.15	3.3	3.225	0.010	0.28	8	1.250	0.000
9	0.25	0.27	0.260	0.680	63.85	49	13.878	0.053
10	0.27	0.27	0.270	0.595	58.33	48	12.396	0.046
11	0.5	0.44	0.470	0.470	47.47	43	10.930	0.023
12	0.43	0.46	0.445	0.250	30.12	38	6.579	0.015
13	0.43	0.42	0.425	0.455	45.73	67	6.791	0.016
Boxelder Creek								
D-1a	3.50		3.500	7.550	67.41	13	580.769	0.166
Irrigation Ditch								
D-1b	0.15	0.13	0.140	0.100	36.36	14	7.143	0.051
D-2	0.11	0.07	0.090	0.065	24.53	6	10.833	0.120
D-3	0.47	0.46	0.465	0.020	3.39	8	2.500	0.005
D-4	0.11	0.15	0.130	0.030	9.84	9	3.333	0.026

Continued

Sample ID	Aqueous load (kg d^{-1})						TP limit (kg d^{-1})	TN limit (kg d^{-1})
	TN	TP	TDP	SRP	DOP	PP		
Cache la Poudre River								
1	234.28	197.29	94.54	20.55	73.98	102.76	139.75	1644.10
2	147.15	250.73	98.65	20.55	78.09	152.08	139.75	1644.10
3	105.22	234.28	119.20	20.55	98.65	115.09	139.75	1644.10
4	189.82	234.86	64.34	19.30	45.04	170.51	109.39	1286.90
5	67.56	202.69	180.17	64.34	115.82	22.52	109.39	1286.90
6	130.35	183.31	67.89	20.37	47.52	115.42	76.94	905.23
7	66.99	194.63	72.42	38.47	33.95	122.21	76.94	905.23
8	6467.89	1613.58	1609.05	1459.69	149.36	4.53	76.94	905.23
9	252.21	432.53	156.36	105.59	50.77	276.17	69.04	812.26
10	456.09	414.25	172.61	109.66	62.95	241.65	69.04	812.26
11	352.87	293.08	153.94	139.14	14.80	139.14	50.33	592.07
12	472.77	245.71	171.70	131.74	39.96	74.01	50.33	592.07
13	440.21	294.56	159.86	125.82	34.04	134.70	50.33	592.07
Boxelder Creek								
D-1a	9.39	0.75	0.48	0.38	0.10	0.27		
Irrigation Ditch								
D-1b	127.15	113.20	36.89	35.37	1.52	76.31		
D-2	0.98	0.38	0.28	0.13	0.16	0.09		
D-3	1091.15	118.36	114.35	93.29	21.06	4.01		
D-4	3.80	0.22	0.20	0.09	0.10	0.02		

Table A.3: Average TP (mg L^{-1}) concentrations (Duplicate measurement).

Sample ID	4/23-24/10	5/19/10	6/4/10	6/18/10	7/16/10	9/17/10	2/22-23/11	4/26-27/11	5/12/11	6/13/11	7/15/11	8/29/11	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12
1			0.14	0.14		0.14	0.13	0.14	0.20	0.14	0.12	0.06	0.24	0.30	0.21	2.52
2		0.13	0.15	0.08		0.11	0.17	0.07	0.14	0.13	0.10	0.09	0.31	0.10	0.21	102.00
3		0.16	0.22	0.15		0.09	0.10	0.19	0.15	0.17	0.12	0.07	0.29	0.20	0.27	123.25
4	0.08	0.20	0.17	0.16		0.11	0.10		0.10	0.22	0.06	0.10	0.37	0.20	0.22	6.95
5	0.22	0.14		0.11		0.18	0.14	0.15	0.16	0.30	0.09	0.08	0.32	0.22	0.22	32.80
6	0.18	0.18	0.14	0.16	0.16	0.14	0.16	0.14	0.26	0.24	0.12	0.29	0.41	0.20	0.27	2.10
7	0.13	0.16	0.16	0.16	0.16	0.12	0.14	0.15	0.17	0.24	0.18	0.48	0.43	0.30	0.31	1.24
8	0.46	0.22	0.21	0.17	0.36	0.57	1.49	0.85	0.38	0.41	1.49	2.00	3.57	3.50	0.76	2.50
9	2.06	0.69	1.00	0.34	3.10	0.82	0.80	1.30	0.54	0.20	0.29	1.18	1.07	1.10	0.34	5.00
10	1.93	0.57	1.00	0.42	2.03	0.55	0.37	1.28	0.54	0.24	0.35	0.97	1.02	1.02	2.08	2.39
11	1.97	0.72	1.02	0.48	2.12	1.03	0.80	1.24	0.55	0.27	0.34	0.84	0.99	0.95	1.35	1.37
12	1.56	0.67	0.99	0.79	0.84	0.49	0.36	0.75	0.54	0.33	0.37	0.92	0.83	0.82	0.49	0.94
13	1.53	0.69	0.99	0.51	0.90	0.49	0.41	0.96	0.79	0.32	0.39	0.90	1.00	0.76	0.90	1.11

Table A.4: Average TDP, SRP and DOP concentrations (Duplicate measurement).

Sample ID	TDP (mg L^{-1})				SRP (mg L^{-1})				DOP (mg L^{-1})			
	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12
1	0.115	0.175	0.210	0.465	0.025	0.010	0.040	0.270	0.090	0.165	0.170	0.195
2	0.120	0.045	0.210	1.435	0.025	0.045	0.030	0.785	0.095	0.000	0.180	0.650
3	0.145	0.040	0.270	1.130	0.025	0.030	0.040	0.825	0.120	0.010	0.230	0.305
4	0.100	0.190	0.215	0.765	0.030	0.025	0.030	0.480	0.070	0.165	0.185	0.285
5	0.280	0.143	0.220	1.770	0.100	0.055	0.050	1.510	0.180	0.088	0.170	0.260
6	0.150	0.160	0.265	1.680	0.045	0.085	0.140	0.255	0.105	0.075	0.125	1.425
7	0.160	0.235	0.310		0.085	0.070	0.130	0.360	0.075	0.165	0.180	
8	3.555	2.960	0.760	0.595	3.225	2.470	0.595	0.315	0.330	0.490	0.165	0.280
9	0.385	0.895	0.520	2.350	0.260	0.790	0.335	2.065	0.125	0.105	0.185	0.285
10	0.425	0.620	2.075	1.750	0.270	0.535	1.710	1.615	0.155	0.085	0.365	0.135
11	0.520	0.635	1.345	1.215	0.470	0.525	0.865	0.605	0.050	0.110	0.480	0.610
12	0.580	0.690	0.485	0.660	0.445	0.520	0.075	0.040	0.135	0.170	0.410	0.620
13	0.540	0.400	0.895	0.275	0.425	0.345	0.160	0.140	0.115	0.055	0.735	0.135

Table A.5: Average PP and TSS concentrations.

Sample ID	PP (mg L^{-1})				TSS (mg L^{-1})			
	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12
1	0.125	0.135	0.000	2.050	20	0	3	396
2	0.185	0.040	0.060	100.430	26	3	2	7916
3	0.140	0.165	0.130	122.120	21	3	5	9463
4	0.265	0.025	0.125	5.970	26	6	3	465
5	0.035	0.078	0.070	31.030	18	6	10	4472
6	0.255	0.000	0.055	1.540	20	15	4	111
7	0.270	0.035	0.100	1.225	17	10	20	49
8	0.010	0.515	0.020	1.890	8	23	10	113
9	0.680	0.185		4.990	49	11	20	189
10	0.595	0.395	0.300	0.555	48	31	17	23
11	0.470	0.310	0.315	1.345	43	35	319	33
12	0.250	0.125	0.240	0.725	38	15	8	22
13	0.455	0.355	0.450	0.820	67	38	60	49

Table A.6: Average TN (mg L^{-1}) concentrations (Duplicate measurement).

Sample ID	9/17/10	2/22-23/11	4/26-27/11	5/12/11	6/13/11	7/15/11	8/29/11	4/23-24/12	5/26/12	7/04-05/12	7/18-19/12
1	0.034	0.319	0.299	0.223	0.244	0.320	0.174	0.29	0.99	0.31	1.023
2	0.100	0.259	0.141	0.233	0.254	0.227	0.310	0.18	0.906	0.61	2.644
3	0.035	0.151	0.180	0.294		0.255	0.288	0.13	0.969	0.35	2.632
4	0.010	0.647		0.246	0.295	0.343	0.317	0.30	0.856	0.62	1.036
5	0.078	0.616	0.258	0.362	0.292	0.314	0.311	0.11	0.94	0.44	2.432
6	0.239	1.600	0.662	0.464	0.279	0.380	0.520	0.29	1.102	0.54	0.671
7	0.247	0.855	0.557	0.378	0.226	0.427	0.532	0.15	1.059	0.47	0.686
8	2.023	8.144	2.957	1.361	0.91	6.997	6.821	14.29	13.33	1.61	0.946
9	1.644	3.553	2.646	1.036	0.336	0.575	1.437	0.62	2.104	0.55	1.521
10	1.135	2.252	2.202	0.998	0.338	1.116	1.716	1.12	1.987	0.86	1.493
11	1.808	4.104	2.596	1.23	0.404	0.624	1.551	1.19	2.032	1.09	1.307
12	2.134	3.986	2.813	1.264	0.512	0.519	1.611	1.60	1.962	2.11	2.535
13	2.702	4.343	2.699	1.523	0.433	0.618	1.588	1.49	2.879	3.32	4.745

Table A.7: Example of data sheet of sediment mass concentration for one event (Event 13, 4/23-24/12).

Sample ID	Riverbed sediment										
	EPC_0	SRP	EPC_0-SRP	Adsorb/Release/Equilibrium	Al (%)	Ca (%)	Fe (%)	TP (%)	OM (%)	Sand (%)	Silt-clay (%)
Cache la Poudre River											
1	0.155	0.025	0.13	R	5.399	1.680	3.374	5.000	2.34	98.31	1.69
2	0.026	0.025	0.001	E	2.892	1.083	5.515	4.842	0.54	99.58	0.42
3	0.041	0.025	0.016	R	3.549	1.154	2.233	2.466	1.18	99.82	0.18
4	0.381	0.030	0.351	R	6.251	1.040	1.82	3.725	0.29	99.94	0.06
5		0.100			3.497	1.654	3.350	14.230	12.13	96.04	3.96
6	0.556	0.045	0.511	R	3.680	0.964	3.189	3.436	1.08	99.13	0.87
7	0.418	0.085	0.333	R	6.626	1.194	2.290	4.081	0.24	99.88	0.12
8	0.702	3.225	-2.523	A	4.521	4.050	3.899	14.700	7.42	91.39	8.62
9	0.475	0.260	0.215	R	6.160	1.367	2.374	5.531	0.57	99.37	0.63
10	1.541	0.270	1.271	R	5.277	1.161	1.393	2.906	0.31	99.65	0.34
11	0.658	0.470	0.188	R	4.877	1.302	3.971	3.407	1.11	98.79	1.21
12	0.312	0.445	-0.133	A	3.076	1.457	2.456	3.453	0.64	97.60	2.40
13	0.944	0.425	0.519	R	3.674	0.972	3.969	2.418	0.37	99.30	0.70
Boxelder Creek											
D-1a	0.409	0.140	0.269	R	5.060	2.261	1.399	2.744	0.46	96.40	3.60
Irrigation Ditch											
D-1b											
D-2	0.079	0.090	-0.011	A	5.615	5.317	3.796	12	4.66	67.63	32.37
D-3	1.742	0.465	1.277	R	3.537	1.266	1.766	4.25	0.34	98.33	1.67
D-4	0.376	0.130	0.246	R	4.533	2.971	3.009	9.226	2.29	85.14	14.86

Continued

Sample ID	Riverbank sediment						
	Al (%)	Ca (%)	Fe (%)	TP (%)	OM (%)	Sand (%)	Silt-clay (%)
Cache la Poudre River							
1	7.033	1.446	2.845	4.969	0.48	97.88	99.52
2	6.187	1.475	4.040	5.279	0.24	99.54	99.76
3	5.892	1.566	3.189	3.933	0.29	98.45	99.71
4	6.608	1.397	1.952	3.550	0.35	99.33	99.65
5	6.213	1.864	4.010	7.757	1.42	94.94	98.58
6	6.149	1.605	4.071	5.597	0.47	96.98	99.53
7	5.999	1.361	3.196	4.580	0.51	97.70	99.49
8	4.838	1.880	3.610	5.420	0.70	96.48	99.30
9	5.420	1.310	2.870	4.794	0.63	96.09	99.37
10	5.932	1.577	2.527	4.060	1.27	95.62	98.73
11	5.664	1.321	2.536	4.384	0.43	96.82	99.57
12	5.118	1.917	3.329	7.987	2.02	97.41	97.98
13	3.910	1.664	2.142	5.461	0.49	90.22	99.51

Table A.8: Example of EPC_0 analysis (Sample 1-4, Event 13, 4/23-24/12).

Sample ID	Solution SRP concentration at T=0 (mg L^{-1})	Solution SRP concentration at T=24hr (mg L^{-1})	Difference of concentration between T=0 and 24hr (mg L^{-1})
1	0.03	0.14	-4.35
	0.23	0.20	0.60
	0.50	0.30	8.19
	1.00	0.62	15.08
	1.74	1.15	23.58
	EPC_0	**0.16**	
2	0.03	0.03	-0.20
	0.23	0.18	2.00
	0.50	0.34	6.48
	1.00	0.77	9.05
	1.74	1.26	18.96
	EPC_0	**0.03**	
3	0.03	0.02	0.20
	0.23	0.15	3.15
	0.50	0.43	2.78
	1.00	0.86	5.48
	1.74	1.35	15.39
	EPC_0	**0.04**	
4	0.03	0.08	-2.17
	0.23	0.23	0.00
	0.50	0.49	0.40
	1.00	0.95	1.97
	1.74	1.44	11.79
	EPC_0	**0.38**	

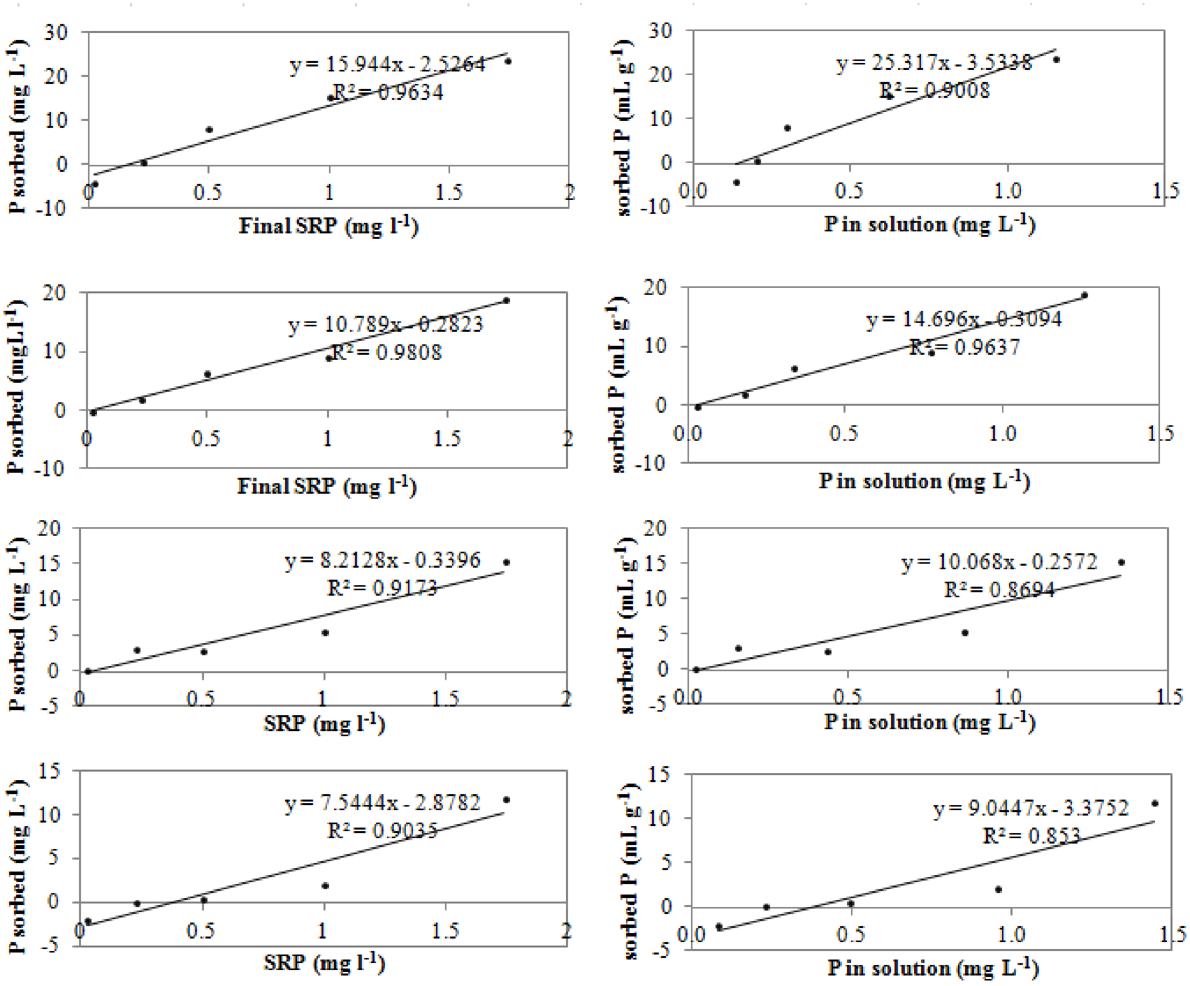

Figure A.1: Example of EPC$_0$ (left) and sorption strength (right) analysis from sample 1 (top) through 4 (bottom) for event 13 (4/23-24/12).