THESIS

MONITORING DESIGN FOR ASSESSING COMPLIANCE WITH NUMERIC NUTRIENT STANDARDS FOR RIVERS AND STREAMS USING GEOSPATIAL VARIABLES

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ABSTRACT

MONITORING DESIGN FOR ASSESSING COMPLIANCE WITH NUMERIC NUTRIENT STANDARDS FOR RIVERS AND STREAMS USING GEOSPATIAL VARIABLES

Elevated levels of nutrients in surface waters are among major human and environmental health concerns. Increases in nutrient concentrations in surface waters have been linked to urban and agricultural development of watersheds across the United States. Recent implementation of numeric nutrient standards in Colorado has prompted a need for greater understanding of human impacts on nutrient levels at different locations within a watershed and for how upstream influences affect the monitoring needs of specific locations. The objectives of this research are (i) to explore the variability of annual nutrient concentration medians under varying levels of upstream anthropogenic influences, (ii) to explore the variability of the standard deviation of nutrient concentrations under varying levels of upstream anthropogenic influences, and (iii) to develop a mathematical expression for approximating the number of samples required for estimating nutrient medians in the context of compliance with numeric standards.

This analysis was performed in the Cache La Poudre (CLP) River watershed, which provides a gradient of anthropogenic influences ideal for studying water quality impacts. Multiple linear regression (MLR) models were used to explain the relationship of the median and lognormal standard deviation of nutrient concentrations in the CLP River, i.e., Total Kjeldahl Nitrogen (TKN), nitrate (NO_3-N), total nitrogen (TN), and total phosphorous (TP) to upstream point and non-point sources of nutrients and general hydrologic descriptors. The number of samples required annually at monitoring locations is predicted based on an equation for determining sample size using relative error of a dataset which accounts for the difference between the median and standard for a lognormal population.

MLR models for annual medians performed better for TN ($R^2 = 0.86$) than TP ($R^2 = 0.90$) despite high coefficients of multiple determination. Anthropogenic predictor variables, which characterize upstream urban and agricultural impacts on nutrient concentrations, were sufficient for describing variation of median concentrations between monitoring sites. A general hydrologic predictor was sufficient for characterizing variability of annual medians between years. The preferred MLR for all of the nutrient parameters uses inverse distance weighted WWTP and AFO capacities with annual mean daily discharge as a hydrologic predictor. The percent land use is equivalent to nutrient point source parameters (i.e., number of WWTPs and AFOs) for predicting median nitrogen concentrations in the watershed, though urban and agricultural land use predictors cannot be employed in the same model due to high multicollinearity. Little value is gained in the MLR models by including capacity of point sources in the predictive variables. For TP, a parameter which describes the variability of medians between years was not found, thus limiting the applicability of the model.

The MLR models were less successful for predicting lognormal standard deviation of nutrients due to limited datasets. However, for robust datasets, high R^2 values were found for TN and TP (0.80 and 0.73, respectively) based on anthropogenic predictors and annual rainfall. Overall, the MLR approach was appropriate for predicting median nutrient concentrations and lognormal standard deviations in the study watershed. Anthropogenic variables and general hydrologic descriptors were sufficient predictive parameters for the MLR models.

Results of the application of an expression derived for predicting annual required samples indicate that sampling requirements to meet a 95% confidence level are lower than the current regulatory monthly sampling requirement. The required number of samples for reporting compliance at a 95% confidence level substantially varied among sampling sites depending on the difference between annual median of the nutrient of concern and its numeric standard. When the median is within 20% of the standard, the required number of samples rapidly increases from several samples per year to hundreds of samples per year. A comprehensive monitoring plan that targets sampling to sites near the standard with limited sampling elsewhere will optimize sampling resources and increase confidence level of the results.

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I would like to acknowledge the City of Fort Collins for their financial support which made this research possible. In addition all the water quality samples were prepared and analyzed in the City of Fort Collins Water Quality Laboratory and Pollution Control Laboratory.

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INTRODUCTION

The human and ecological impacts of nutrients in surface waters, namely nitrogen (N) and phosphorous (P) have been well documented. The presence of high nitrate levels in drinking water has been linked with reproductive problems, methemoglobinemia, and cancer (Townsend et al., 2003; Bryan, 2013). Excessive nutrients, particularly phosphorous, have long been linked to eutrophication processes in surface water (Correll, 1998; Smith, 1999; U.S. Environmental Protection Agency [EPA], 1998; Carpenter et al., 1998). Eutrophication of surface waters results in increased algal biomass and decreased dissolved oxygen concentrations (Carpenter, 1998; Correll, 1998). A substantial production of algal biomass can impact the sediment structure of stream beds (Sand-Jensen, 1998), and may therefore impact the benthic ecosystem. This altered system can cause a decline of ecosystem biodiversity (Carpenter et al., 1998; Smith, 1999).

Agricultural and urban activities have been associated with elevated levels of nutrients in surface waters above natural background levels nationally (Puckett, 1995; U.S. EPA, 1998; Dubrovsky et al., 2010). Non-point sources of nutrients, such as fertilizer and manure used in agriculture and urban areas, are recognized as major sources of excess nutrient inputs in watersheds around the world (Puckett, 1995; Carpenter et al., 1998; Scanlon et al., 2007). Point sources of nutrients including waste water treatment plants (WWTPs) and animal feeding operations (AFOs) also represent significant sources of nutrients in many watersheds and can cause surface water impairment (Welch, 1992; Gollehon et al., 2001; U.S. EPA, 2004). Discerning anthropogenic impacts from background nutrient concentrations in most watersheds can present a challenge when the watershed does not include a portion without major human influences. It can likewise be difficult to distinguish between multiple anthropogenic nutrient sources where both agricultural and urban development influence nutrient levels in the same region.

In the United States, numeric nutrient standards have been increasingly adopted to manage nutrient impairments in surface water bodies for more than a decade (U.S. EPA, 1998). While regional recommendations for nutrient levels have been available from the U.S. EPA since 2001 (U.S. EPA, 2001), the State of Colorado has only recently moved to create enforceable numeric nutrient regulations for its surface waters. In 2012, the Colorado Department of Public Health and Environment (CDPHE) implemented numeric nutrient limits for surface water in order to improve nutrient pollution in surface waters of Colorado (CDPHE, 2012a). These standards are recommended based on designated uses and classification of water bodies. Surface waters are classified by cold or warm water aquatic use. Cold water use supports biota that exist in waters with average weekly summer temperatures that do not typically exceed 20 °C, while warm water use supports biota that exist in waters that frequently exceed this value. For cold water rivers and streams, the annual median total nitrogen concentration is limited to 1.25mg/l, and the annual median total phosphorous concentration is limited to 0.11mg/l (CDPHE, 2012a). For warm water rivers and streams, median concentrations are limited to 2.01 mg/l and 0.17 mg/l for total nitrogen and total phosphorous respectively (CDPHE, 2012a).

The new regulations require wastewater treatment plants (WWTPs) to monitor total nitrogen and total phosphorous levels in their effluent and downstream receiving water bodies (CDPHE, 2012a; CDPHE, 2012b). Currently, sampling requirements are monthly for large WWTPs with effluent discharge greater than 1 million gallons per day (MGD) and every other month for small treatment plants with effluent discharge less than 1 MGD. The sampling requirements do not consider the impacts of nonpoint sources, drainage area characteristics, and other geospatial factors that may play a role in the variability of N and P loads at various locations along streams. As a result, the sampling numbers may be inadequate to describe the annual median nutrient concentrations at various locations along the river system.

In a robust monitoring plan, the sampling frequency should reflect the statistical characteristics of the pollutant of concern, which optimizes the number of samples for available resources and helps assure statistical confidence in the results (Gilbert, 1987; Ward et al., 1990). Because nitrogen and phosphorous populations are a function of upstream influences, the sampling frequency should vary depending on the location of a monitoring site on the river. Many monitoring plans applied on a large scale are simplified to ease implementation and data analysis, and the newly implemented Colorado nutrient regulations are just one such example (CDPHE, 2012a). A statistical evaluation of adequate sampling frequencies may not be feasible state-wide for all individual monitoring sites due to limited historical datasets available for comparison, and the excessive time and cost required to conduct such an analysis. Linking upstream influences to nutrient parameter population characteristics can allow for optimization of sampling resources by minimizing sampling frequencies for a large scale implementation of regulatory requirements.

Two approaches are currently available to model the nutrient levels of a watershed. Process based models compute nutrient levels by simulating the hydrologic and biological processes that control the transport and transformation of nutrient responses for given watershed parameters (Venohr et al., 2005; Lam, 2012; Aguilera, 2012). Multiple linear regression models (MLRs) have been shown to predict water quality levels in surface water (Arheimer and Lide, 2000; Haggard et al., 2003; May et al., 2009; Kang et al., 2010; Spahr, 2010; Aguilera, 2012;). The relatively simple approach of MLR modeling has the advantage of requiring less data for application than physically-based models, and allows for the characterization of sources of variability in water quality data over a region and period of time. Predictor variables for water quality parameters generally used for MLRs include land use, physical watershed properties, hydrologic properties, and soil properties. Presently, point sources of water quality parameters have not been examined in MLR modeling, and they could useful due to potential ease of acquiring the data and a lack of colinearity between these variables as compared to percent land use. Multiple linear regression models used by Haggard (2003) to predict sampling requirements for load estimation on the Illinois River demonstrated the feasibility of predicting sampling requirements based on anthropogenic and watershed characteristics. However, MLR modeling has not been used to direct development of monitoring plans for compliance with nutrient concentration standards.

The overall goal of this study is to develop a procedure for computing minimum sampling frequencies to meet nutrient regulations based on upstream influences on monitoring sites in a northern Colorado watershed. The objectives are (i) to explore the variability of annual nutrient concentration medians under varying levels of upstream anthropogenic influences, (ii) to explore the variability of the standard deviation of nutrient concentrations under varying levels of upstream anthropogenic influences, and (iii) to develop a mathematical expression for approximating the number of samples required for estimating nutrient medians in the context of compliance with numeric standards. This methodology may be a useful tool for regulators and water users to develop optimal monitoring and management plans based watershed properties particularly for western watersheds.

METHODOLOGY

This study was performed in the Cache La Poudre (CLP) River watershed in northern Colorado, where a relatively undeveloped region a joins a developed lower watershed with a gradient of human impacts. Due to the diversity of its land use conditions, the CLP system presents a unique opportunity to study the relationship between human influences and nutrient concentrations, and also to examine the role of sampling frequency in compliance with regulations. Water quality variables including total Kjeldahl nitrogen (TKN), nitrate (NO_3-N) nitrogen, total nitrogen (TN), and total phosphorous (TP) were monitored on a weekly basis over a one year period. These data were augmented with less robust datasets from four previous years to characterize variability of nutrient concentrations throughout the watershed under varying hydrologic conditions through a multiple linear regression approach. ArcGIS was used to delineate subwatershed boundaries for sampling sites on the CLP River, and upstream anthropogenic influences for each site were then defined by these boundaries. Anthropogenic influences are characterized by land use percentage, and the locations and capacities of wastewater treatment plants and animal feeding operations. Assuming a lognormal distribution, the required number of annual samples is calculated for any given location in the watershed based on the median and standard deviation of a nutrient constituent at that location and a known concentration standard. A multiple linear regression approach was used to investigate the correlation between nutrient responses and human influences while taking account of annual hydrologic conditions.

Study Area

The Cache La Poudre Watershed is 4892 km^2 (1887 mi^2) in northeastern Colorado. The river headwaters begin in the pristine Rocky Mountains and the river flows approximately 205 km (127 mi) before its confluence with the South Platte River in the eastern plains of Colorado (Figure 1). The CLP watershed encompasses a largely undeveloped upstream region which allows for characterization of background nutrient conditions. The river enters a mixed land use area 55 miles from the confluence that is characterized by a gradient of human influences including urban development, large and small waste water treatment plants (WWTPs), row crops, grazing land, and confined animal feeding operations (AFOs) (Figure 2). This lower portion of the watershed was the focus of the study due to extent of both urban and agricultural development. The CLP River drains the urban areas of Fort Collins, Windsor, and Greeley, and a total of 16 waste water treatment plants (WWTPs) discharge into the river and its tributaries before its confluence with the South Platte River downstream of Greeley. The lower portion of the watershed is used extensively for irrigated agriculture and confined animal feeding operations. Agriculture accounts for approximately 40% of land use in the lower watershed. With few natural tributaries, irrigation ditches and diversion canals extensively alter the natural hydrology of the lower watershed.

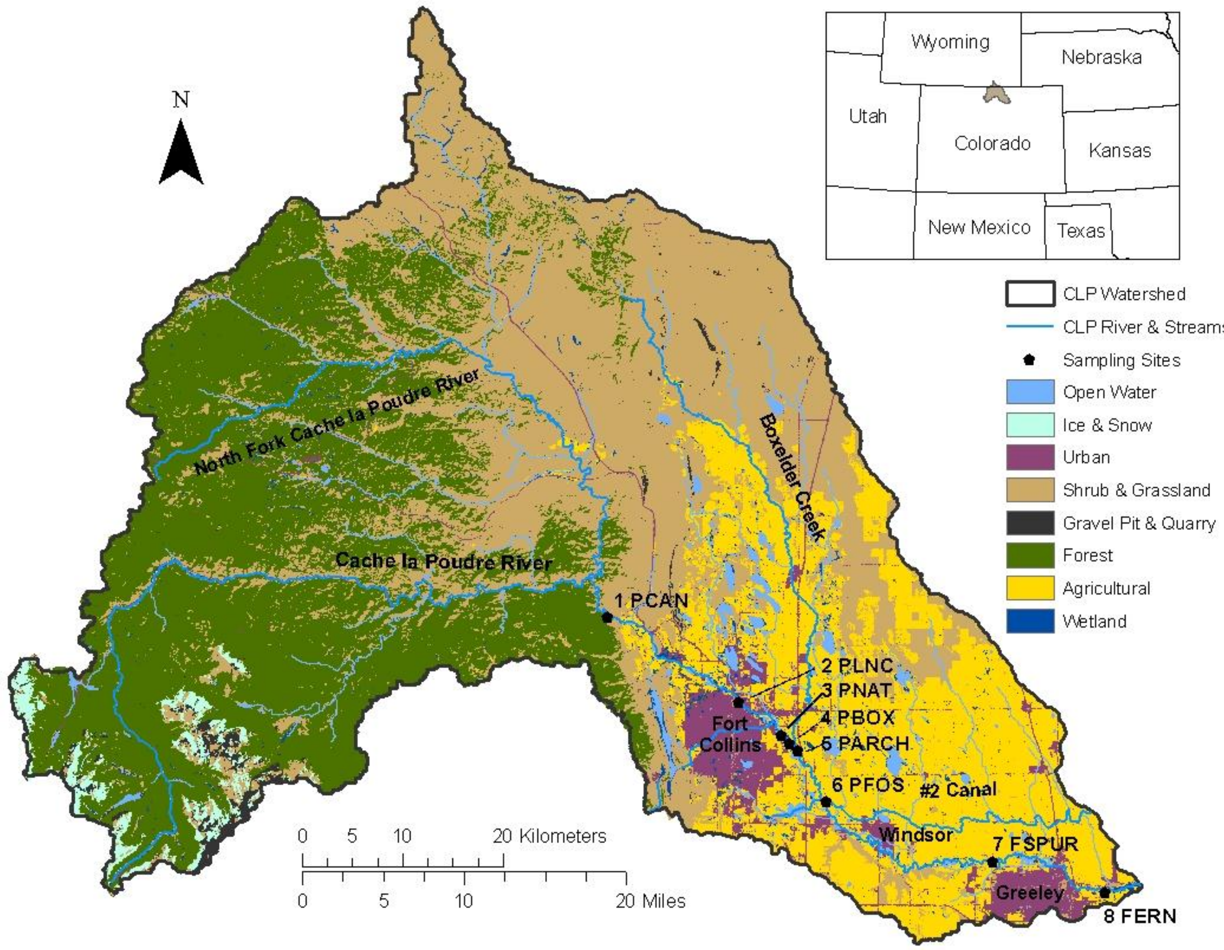

Figure 1: The study area located in northern Colorado: Cache La Poudre Watershed with sampling sites and land use.

Eight sample locations were monitored on the CLP River in the lower watershed. The sites were chosen to target a range of upstream human influences such as urban and agricultural development, WWTPs , and AFOs. All samples were tested for TKN, nitrate-N, TN, and TP. Of those eight locations five had corresponding gage station flow measurements. Site locations and upstream influences are summarized in Table 1. Sampling for this study was performed June 2012 through April 2013 with weekly sampling at each location except for bi-weekly sampling January

2013 through April 2013. A total of 36 sample trips were taken during the complete 2012 to 2013 sampling period. In addition, a less extensive nutrient dataset was available for 2008 through 2012 and was used to supplement sampling for this study. A more detailed description of the sampling sites is provided in Appendix E.

Nutrient Data

Weekly grab samples obtained from the eight monitoring sites for this study were collected according to USGS protocol (Lurry et al., 2004). Laboratory analysis of the samples including preservation and testing was conducted according to U.S. EPA methods and Standard Test Methods (STM) for each nutrient parameter. The respective testing procedures are STM 4500-Norg D for TKN, EPA 300.0 for NO_3-N and NO_2-N, EPA 365.1 Revision 2.0 for TP, and TN is the summation of TKN, NO_3-N and NO_2-N. The test methods are also summarized in Appendix A.

Table 1: Sampling site descriptions for the study area on the Cache La Poudre River. River miles are computed upstream from the confluence of the CLP River with the South Platte River.

Site	River Mile	Name	Flow Data	Description
1	54.6	PCAN	yes	Background site at the Mouth of the Poudre Canyon
2	43.2	PLNC	yes	Upstream in Fort Collins, downstream of some agricultural drainage
3	38.0	PNAT		In Fort Collins, downstream of Mulberry WWTP
4	37.0	PBOX	yes	In Fort Collins, downstream of stormwater drainage, upstream of Drake WWTP
5	36.5	PARCH		In Fort Collins, downstream of Boxelder WWTP and Boxelder Creek tributary
6	32.5	PFOS	yes	Downstream of all Fort Collins stormwater and wastewater treatment
7	14.5	FSPUR		Downstream of agricultural drainage and Windsor WWTP
8	2.2	FERN	yes	Downstream of agricultural drainage, Greeley stormwater, and Greeley WWTP

Geospatial Analysis

Watershed delineation

For each sampling location the boundary of the corresponding drainage area was delineated using the ArcSWAT Watershed Delineator toolbox in ArcGIS version 9.3 (ESRI Inc., Redlands, CA). Watershed delineations were conducted using a 1/3 Arc-Second digital elevation model (DEM) from National Elevation Dataset (NED of the U.S. Geological Survey (USGS), and a high resolution National Hydrography Dataset (NHD) from the USGS which identifies rivers, lakes, streams, canals, and irrigation ditches. The accuracy of the delineation was confirmed by comparison to the NHD Watershed Boundary Dataset.

Further refinement of the subwatershed boundaries was necessary because both the NHD Dataset and watershed delineation assume that water drainage follows the natural topography of the watershed. In the agriculturally dominated lower CLP watershed little natural drainage remains, and irrigation ditches and diversion canals play a dominant role in water drainage. Inaccuracies in the elevation-based watershed delineation were mainly the result of incorrect depiction of irrigation ditches and diversion canals in the NHD. Through comparison with high resolution aerial photographs and field checking, some canals that are connected in the geospatial data layers, were found to not in fact be connected and vice versa. To remedy this situation, the subwatershed boundaries were manually altered assuming that 1) on a local scale and where canal depiction was correct, NHD watershed boundaries are accurate, 2) all irrigation ditches and diversion canals can accept surface water runoff, and 3) drainage of agricultural fields occurs from high elevation to lower elevations according to elevations in the DEM.

The resulting subwatershed boundaries are significantly altered in the agriculturally dominated lower CLP Watershed specifically for sites 6, 7, and 8 (Figure 2) and do in fact appear artificial. The New Cache #2 canal is a primary diversion that provides irrigation water for much of the irrigated agriculture in the lower CLP watershed. The canal runs north of and roughly parallel to the CLP River starting just downstream of the city of Fort Collins and converges again with the river downstream of the city of Greeley and the most downstream sampling site in this study. As a result of the New Cache #2 canal proximity to the CLP River, many AFOs in the lower watershed drain more directly into the canal rather than the river and therefore, did not impact the sampling sites for this study.

WWTP and AFO data

Locations and capacities of WWTPs and AFOs within each subwatershed were obtained from the U.S. EPA Facility Registry System (FRS). Colorado law does not require permitting for all animal feeding operations therefore the locations and areas of cattle feedlots and dairies were confirmed or modified via satellite imagery and manually digitized as polygons (Pruden et al., 2012). The capacities of AFOs in terms of the type and number of cattle were calculated based on the density of known AFOs in the CLP Watershed (Storteboom, 2007). Land use percentage was summarized with 2001 National Land Cover Data Set from the USGS, where urban land use was defined as the combination of low and high intensity residential and commercial/industrial/transportation land use categories. Agricultural land use was defined as row crop and pasture/hay categories.

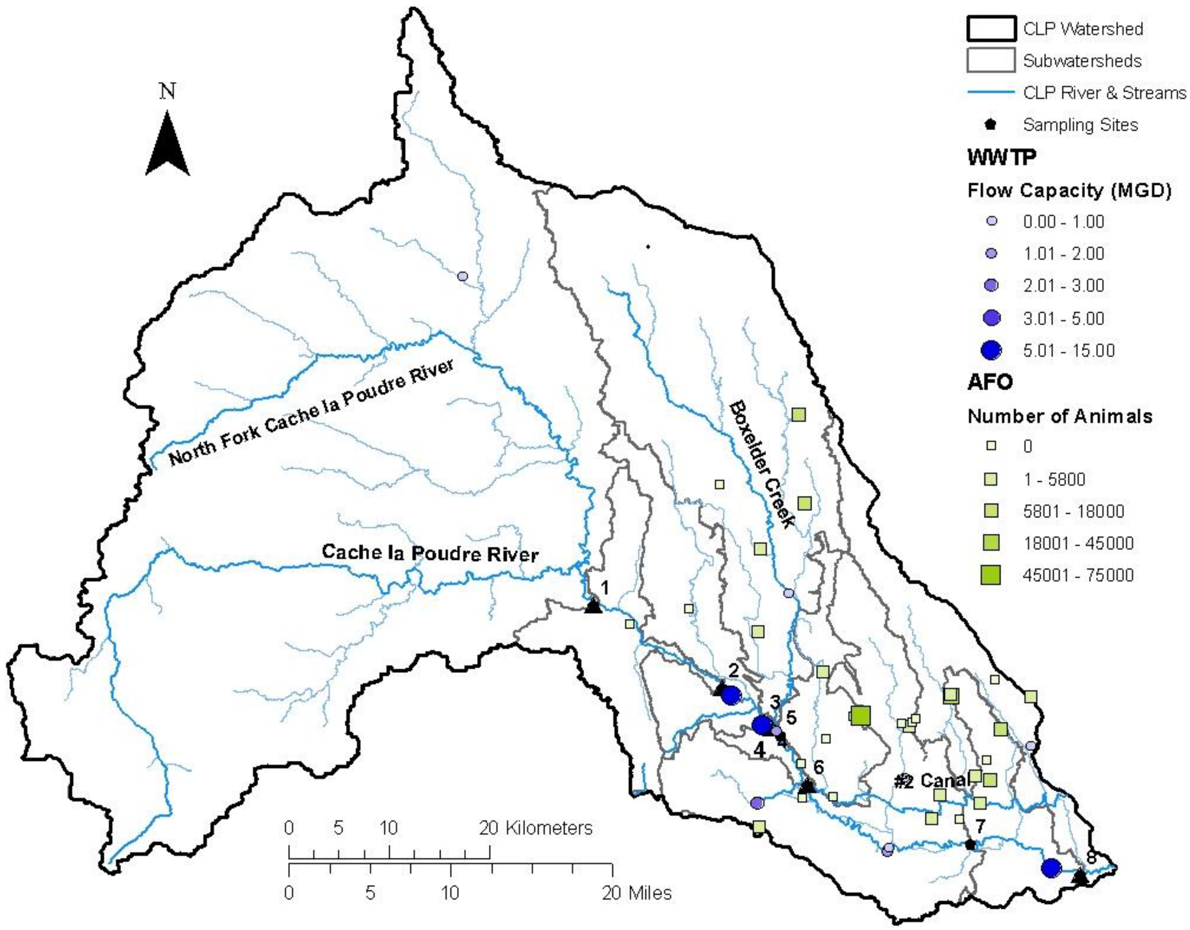

Figure 2: Drainage area boundaries for the eight sampling sites, with WWTP and AFO capacities.

Anthropogenic predictor variables

AFOs, WWTPs, and land use for each subwatershed were summarized with ArcGIS version 9.3 (ESRI, Inc., Redlands, CA) into predictor variables for use in multiple linear regression models. Figure 2 shows the locations of AFOs and WWTPs in CLP subwatersheds. Ten anthropogenic predictor variables were considered in the regression analysis and for the purposes of this study they are described as either non-point source or point sources of nutrients (Table 2). Percent land use is considered non-point sources of nutrients. AFO and WWTP facilities are considered point sources of nutrients and were summarized into the number of facilities, the capacity of the facilities, and the inverse distance (along the elevation contour and stream) weighted number of facilities and capacity of facilities. Including both the number of facilities and capacity of facilities allows evaluation of data significance for characterizing annual nutrient concentration statistics. Weighting the capacities of the point sources using the inverse distance from each facility to the sampling location on the river along the elevation contour and stream path facilitate evaluation of the role of flow pathways in the analysis. Total distances are the sum of the overland distance to the nearest tributary (creek, irrigation ditch, or diversion canal), the distance of the tributary to the CLP River, and the distance in the CLP River to downstream sampling sites. Overland distance and tributary path were determined using terrain analysis in the ArcHydro toolbox in ArcGIS (Pruden et al., 2012).

Hydrologic predictor variables

General hydrologic parameters were included as predictor variables for those five sites with corresponding flow data. Annual mean daily flow and the annual maximum daily flow were collected from USGS and Colorado Division of Water Resources (CDWR) surface water data resources, and annual precipitation for each site was summarized from CDWR precipitation data.

Statistical Data Analysis

Fitting statistical distribution

Identification of a proper statistical distribution to describe nutrient concentrations was a key consideration in deriving the required number of samples for each response variables at each sampling site and also establishing the relation between anthropogenic influences and nutrient responses. Probability plots and the Kolmogorov–Smirnov test for normality were used to analyze the 2012/2013 for fit with normal and lognormal distributions.

Table 2: Summary of predictor variables used in multiple linear regression models.

Variable	Type	Units
# AFOs	Point Sources/Facilities	(#)
# WWTPs	Point Sources/Facilities	(#)
#AFOs IDW	Point Sources/Facilities	(#/km)
#WWTPs IDW	Point Sources/Facilities	(#/km)
# Livestock	Point Sources/Facilities	(# cattle)
Flow Capacity	Point Sources/Facilities	(MGD)
# Livestock IDW	Point Sources/Facilities	(# cattle/km)
Flow Capacity IDW	Point Sources/Facilities	(MGD/m)
% Agriculture Land Use	Land Use	(%)
% Urban Land Use	Land Use	(%)
Annual Mean Daily Flow	Hydrologic	(cfs)
Annual Maximum Daily Flow	Hydrologic	(cfs)
Annual Precipitation	Hydrologic	(in)

Basic Statistics

Sample median and lognormal standard deviation was calculated for each sampling site and nutrient parameter, for each of the five years of data. A limited number of data points are present in some historical datasets (2008-2011) and are concentrated in the April through September timeframe. For this study, it was assumed that the limited sample sets adequately describe the sample median and lognormal standard deviation of the annual concentrations. The regression on order statistics (ROS) technique was employed to estimate median and lognormal standard deviations of datasets with non-detect values (Helsel, 2005a), except for those with >60% non-detect values. Greater than 60% non-detect values occurred for TKN in 2008-2011 at upstream locations, and for this situation non-detect values were estimated as the detection limit included in the dataset for estimation of median and lognormal standard deviation. The ROS approach is a statistical imputation method that employs probability plots to fill in missing data. This technique was performed in the R statistical software environment using the NADA package based on techniques described in Helsel (2005b).

Test for Number of Samples

Appraisal of compliance with ambient nutrient standards in Colorado is based on the annual median nutrient concentration estimated from instantaneous grab samples taken from receiving water bodies downstream of wastewater treatment facilities (CDPHE, 2012a), where for large facilities (effluent discharge greater than 1 MGD) 12 annual samples are required and for small facilities (effluent discharge less than 1 MGD) 6 samples are required (CDPHE, 2012a). However, the number of annual samples required to accurately estimate the true annual median of nutrient populations at a stream location may vary significantly dependent upon the inherent and human-influenced variability of the nutrient of concern and the nearness of the median of the nutrient concentration to the numeric standard. For example, if the median concentration at a location far exceeds the standard and has a large standard deviation that does not encompasses the standard, a minimal number of samples may be required. On the other hand, if the median is close to the standard and the variability is large, more samples are necessary. In fact, as the median concentration approaches the standard, the number of samples required approaches infinity.

To determine the required number of annual samples the nutrient parameter (x) is assumed to be lognormally distributed, such that y = log(x) is normal and y is described by mean (μ_y) and standard deviation (σ_y) parameters. Figure 3 shows the idealized probability density function of y.

$$P[\bar{y} > A] = 1 - F_{\bar{y}}(A) \qquad \text{Eq. 1}$$

where $F_{\bar{y}}(A)$ is the cumulative distribution of A. The probability that mean of y is greater than the log transformed standard (A) should be less than the desired alpha.

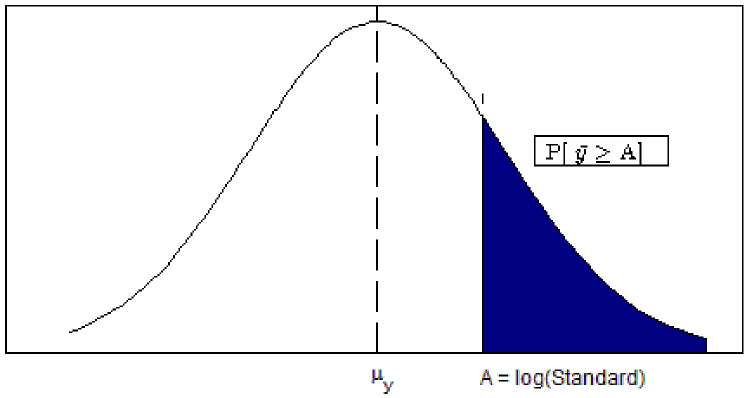

Figure 3: Probability density function for y, log-transformed nutrient concentration data set. The probability that mean of y is greater than the log transformed standard (A) is given in Equation 1.

$$1 - F_{\bar{y}}(A) \leq \alpha \qquad \text{Eq. 2}$$

so,

$$F_{\bar{y}}(A) \geq 1 - \alpha \qquad \text{Eq. 3}$$

Given that the cumulative distribution of A is:

$$F_{\bar{y}}(A) = \Phi\left(\frac{A - \mu_y}{\sigma_y/\sqrt{n}}\right) \qquad \text{Eq. 4}$$

where Φ is the normal cumulative distribution function (CDF). Equation 3 then becomes:

$$\Phi\left(\frac{A - \mu_y}{\sigma_y/\sqrt{n}}\right) \geq 1 - \alpha \qquad \text{Eq. 5}$$

The equation can be rearranged to solve for the annual number of samples, n:

$$\Phi^{-1}\Phi\left(\frac{A-\mu_y}{\sigma_y/\sqrt{n}}\right) \geq \Phi^{-1}(1-\alpha) \qquad \text{Eq. 6}$$

and,

$$\left(\frac{A-\mu_y}{\sigma_y/\sqrt{n}}\right) \geq Z_{1-\alpha} \qquad \text{Eq. 7}$$

where Z is the standard normal deviate calculated as the inverse of standard normal distribution non-exceedance probability.

$$\sqrt{n} \geq \frac{Z_{1-\alpha}\sigma_y}{A-\mu_y} \qquad \text{Eq. 8}$$

Thus the number of annual samples is described by Equation 9.

$$n \geq \left[\frac{Z_{1-\alpha}\sigma_y}{A-\mu_y}\right]^2 \qquad \text{Eq. 9}$$

The term (A - μ_y) can also be written as the log of the ratio between the standard (S) and the median of x (M), assuming that the median of the original data and μ_y are equivalent.

$$n \geq \left[\frac{Z_{1-\alpha}\sigma_y}{\log(S/M)}\right]^2 \qquad \text{Eq. 10}$$

Equation 9 can be rearranged to solve for alpha given that the median concentration is less than the standard. In this case alpha represents the probability of determining that the median nutrient concentration is greater than the standard, when it is actually less. For this analysis the value of 1-α is termed the confidence level.

$$\alpha \geq 1 - \left[\frac{(A-\mu_y)\sqrt{n}}{\sigma_y}\right] \qquad \text{Eq. 11}$$

Multiple Linear Regression

Median and lognormal standard deviations of nutrient parameters were modeled using multiple linear regression models (MLR) based on anthropogenic and hydrologic predictor variables.

$$y = f(WWTP, AFO, Q) \qquad \text{Eq. 12}$$

Regression analysis was performed using the *regress* function in Matlab v7.10 (R2010a) computational environment (MathWorks Inc., 2010). Median nutrient values were transformed by box-cox transformation, which identifies the most appropriate transformation of the response variable (y) to correct skewness of residuals, inequality of residuals, and nonlinearity of the regression (Kutner et al., 2005):

$$y(\lambda) = \begin{cases} \dfrac{c^{\lambda} - 1}{\lambda}; \lambda \neq 0 \\ \log(c); \lambda = 0 \end{cases} \qquad \text{Eq. 13}$$

where c represents measured nutrient concentrations in mg/l and lambda (λ) is the box-cox transformation constant. The box-cox procedure chooses the λ parameter for each nutrient that maximizes the Log-Likelihood Function.

Due to the limited availability of flow data for all sites, regression analysis was performed for two sets of data: (1) five years of data from 2008 – 2013 for the five sites with daily flow data; and (2) one year of data from 2012/2013 for all eight sampling sites without flow as a predictor variable. MLR was performed for Dataset 1 with and without hydrologic predictors, to allow for comparison with Dataset 2. An exhaustive paring of anthropogenic and hydrologic parameters was used to build competing MLR models for each nutrient parameter. The Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) were used to select the best MLR model for each variable (Kutner et al., 2005).

Diagnostic statistical tests were performed to appraise the appropriateness of assumptions in building the MLR models. Overall significance of the regression models was evaluated using the lack of fit F-test based on a 0.05 significance level. Both the coefficient of multiple determination (R^2) and adjusted coefficient of multiple determination (Adj R^2) were employed to compare the strength of different MLR models. The normality of the error terms was examined with the Shapiro-

Wilk test and Lilly test. The Brown-Forythe test was used to evaluate the constancy of the error variance (i.e., homoscedasticity). Randomness in the error terms was tested with the Durbin-Watson test. And the variance inflation factor (VIF) was used to identify multicolinearity in the matrix of predictor variables for each MLR model. Individually, predictor variables should have a VIF value near 1 and collectively the VIF values of all model predictors should be less than 10. Multicolinearity was limited by employing one each agricultural, urban, and hydrologic parameter in the predictor variable matrix.

A summary of the all the median and lognormal standard deviation values as well as the anthropogenic and hydrologic predictor variables used for the regression analysis are presented in Appendix C.

RESULTS & DISCUSSION

Nutrient concentrations were found to generally increase downstream as anthropogenic impacts increase. TN and TP concentrations begin to consistently exceed the numeric standards at Site 5. TKN, NO_3-N, TN, and TP were found to fit a lognormal distribution when non-detect values were accounted for. Calculation of the required number of annual samples for the eight sites revealed that generally sampling needs are lower than the current monthly requirements, however when the median is within 20% of the standard the required number of samples increases rapidly. MLR modeling to predict median and lognormal standard deviations of nutrient parameters based on anthropogenic predictor variables and a hydrologic predictor were significant and strong. Inverse distance weighting of anthropogenic predictor variables limited multicollinearity between anthropogenic predictors. Among valid models, different anthropogenic predictors describing urban and agricultural impacts performed similarly in the models.

Nutrient Concentration along a Gradient of Anthropogenic Impacts

The anthropogenic non-point and point source predictors generally increase from upstream to downstream. Figure 4 shows the cumulative increase of the number of WWTP and AFO facilities along the CLP River moving towards the confluence with the South Platte River. Inverse distance weighting of the number of facilities and capacities of the facilities causes the parameters to not cumulatively increase downstream (Figure 4). This same pattern is shown for AFO and WWTP capacities in Figure 5. Despite that at some locations the urban or agricultural predictor values decreases downstream, there is still a general upward trend of influences downstream. Inverse distance weighting decreases the effect of multicolinearity between anthropogenic factors, which exists due to the cumulative nature of the anthropogenic predictors downstream.

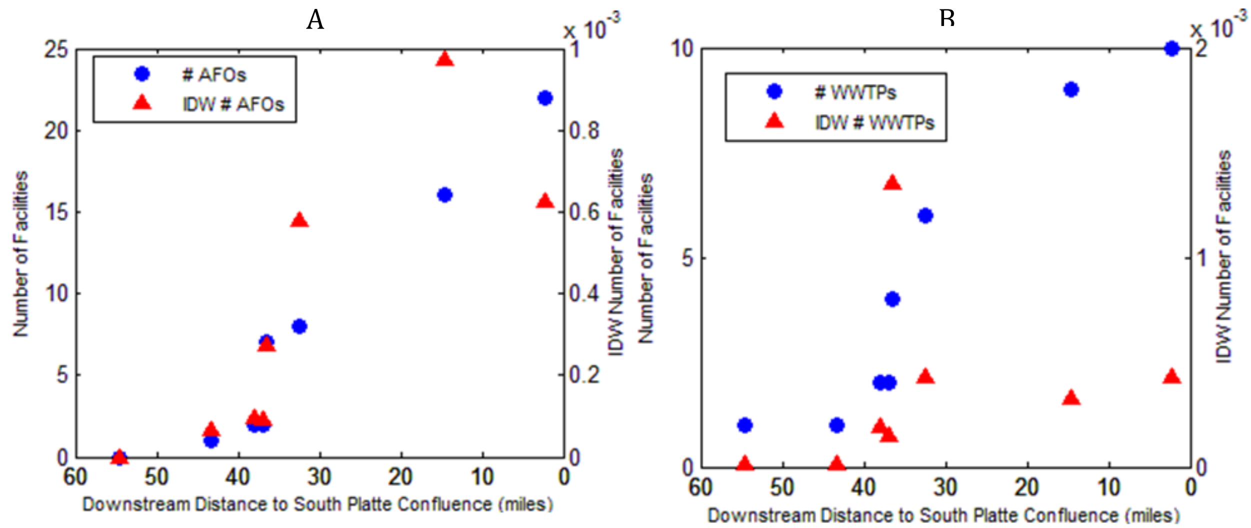

Figure 4: (A) The number of AFOs and corresponding inverse distance weighted (IDW) number of AFO facilities and (B) number of WWTPs and corresponding IDW number of WWTP facilities for each monitoring site.

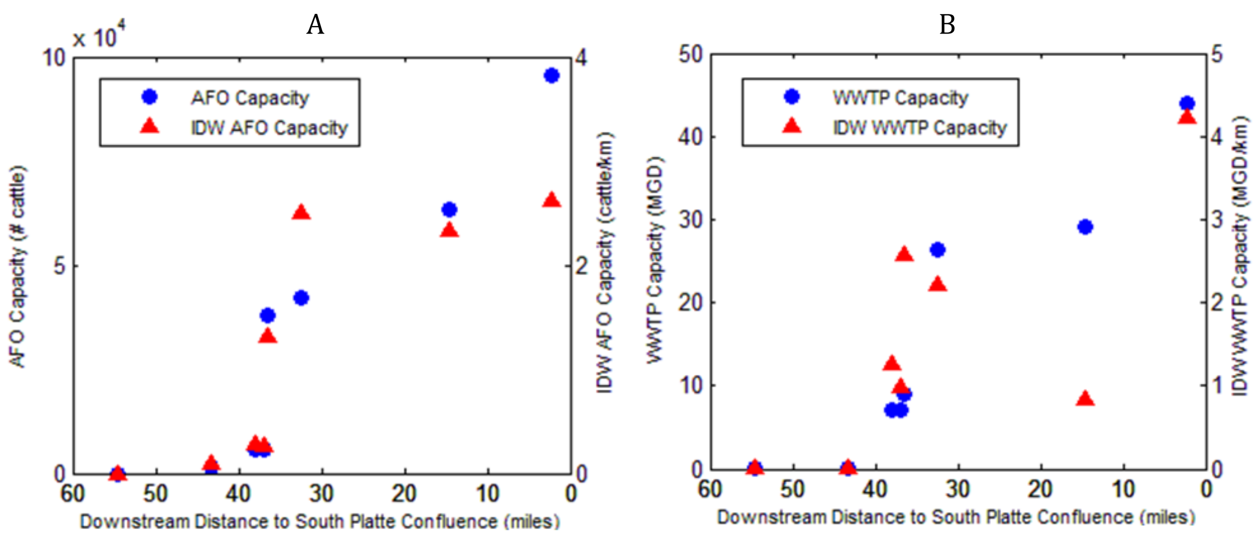

Figure 5: (A) The AFO capacities in number of animals and corresponding inverse distance weighted (IDW) capacities; and (B) WWTP capacities in million gallons per day (MGD) and corresponding IDW capacities for each monitoring site from downstream to upstream.

Manually altering the subwatershed boundaries in the agriculturally dominated lower region of the study watershed has the effect of decreasing the AFOs and the percent agricultural land use that contribute to the most downstream three monitoring sites (6, 7, and 8). There is no alteration of subwatershed boundaries at the upper five sites and the predictors related to WWTPs are not affected at any of the eight monitoring sites. All of the AFOs discluded from subwatersheds have capacities less than 6000 cattle. In comparison the cumulative AFO capacities for subwatersheds 6, 7, and 8 are 42,000, 63,000, and 95,000 cattle respectively. One AFO was discluded from Site 6 due to manual alteration of watershed boundaries. Several AFOs were discluded from subwatersheds of Sites 7 and 8 each. While the cumulative number of AFOs at these sites would be higher assuming natural watershed boundaries, the cumulative AFO capacity and the IDW predictor variables are less impacted by the alteration. The percent agricultural land use at sites 6, 7, and 8 is also decreased. Not only is the overall size of these subwatersheds diminished, the discluded area is primarily agricultural. It is difficult to interpret the exact impacts of the altered watersheds to MLR models without comparing the results of MLR models, but the alterations were made to better reflect the reality of water movement in the agricultural region. By decreasing the values of agricultural predictor variables in the lower watershed, the impact of agriculture on nutrient concentrations at the most downstream three monitoring sites could be underestimated.

Figure 6 provides a box plot of the nutrient parameter dataset for 2012/2013 and characterizes the nutrient concnetrations from upstream to the downstream monitoring site. TKN and NO_3-N concentrations are included in the figure so that the relative contribution of each to TN can be evaluated for different monitoring sites. TKN concentrations increase slightly from upstream to downstream, and the concentrations remain generally below the TN standard. However Site 5, downstream of Boxelder WWTP and Boxelder Creek, has a notable increase in TKN concentration compared to other locations. Samples for Site 5 are taken within 500m of the WWTP discharge, while monitoring directly below all other WWTPs is greater than 3.5km and up to 9km from the discharge points. It is difficult with given data to determine if the large TKN concentrations below

Site 5 are due to an insufficient distance for nutrient attenuation compared to other WWTPs, or a lower capacity of the Boxelder WWTP to reduce nutrient loads.

NO_3-N shows a distinct increase in concentrations from upstream to downstream locations with increasing influence of human activities. Nitrate concentrations remain generally lower than the TN standard until Site 7, and both Sites 7 and 8 are at risk of exceeding the TN standard due to NO_3-N alone. TN is the summation of TKN, NO_3-N, and nitrite (NO_2-N), the last being consistently below detectable levels throughout the CLP River. Background levels of TN are generally below the numeric standard; though some measurements were as much as 2 times greater than the standard. TN concentrations are consistently greater than the TN standard at monitoring sites beginning with and downstream of Site 5 (River Mile 36.5).

The largest concentrations of TP are consistently found at monitoring sites below WWTPs (Sites 5, 6, and 8). Site 3 is also below Mulberry WWTP, however this WWTP has high standards for tertiary treatment of nutrients, and the lower concentrations of TP reflect this. Instances of high TP concentrations are found at every monitoring site including the background location. In fact the background monitoring site is at risk of exceeding the numeric standard. The 2012/2013 year was unusual in that a significant fire affected the upper CLP watershed, which may account for the high background TP concentrations. Looking at median concentrations from the four years of historical data reveals annual median values at Site 1 that exceed the numeric standard in roughly half of the measurements. This suggests that the numeric standard for TP may not be appropriate uniformly to all Colorado watersheds.

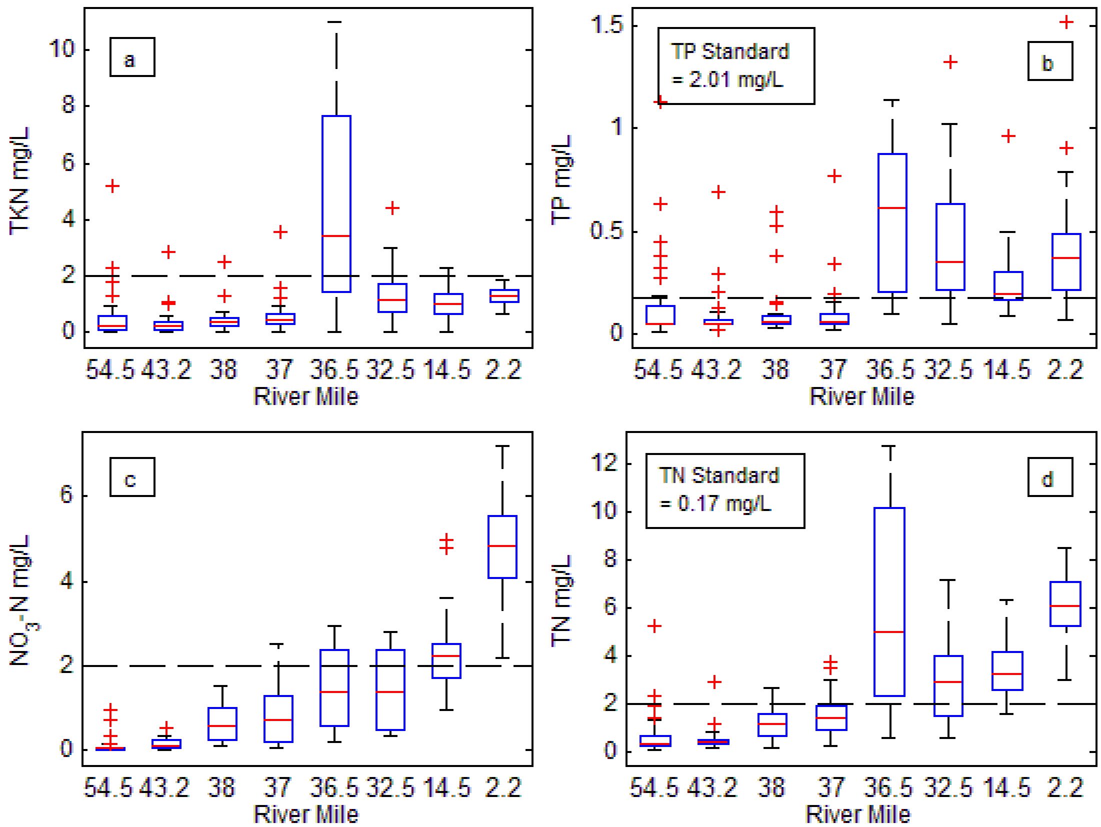

Figure 6: Concentrations of nutrient variables over the 2012-2013 period along the CLP River for (a) TKN; (c) NO_3-N; (d) TN; and (b) TP. Sites are ordered by the river distance to the downstream confluence with the South Platte River. On each box, the central mark is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually.

Nutrient data at sites without non-detect values were adequately described by a lognormal distribution. However, the presence of non-detects caused those upstream sites with lower concentrations of nutrients to lack fit with normal or log-normal distributions at a 95% confidence level. Removing non-detects from these sets of data resulted in better fit with lognormal distributions excepting total phosphorous at Sites 3 and 4 (*P-value* <0.01 and <0.042, respectively) and nitrate-N at Site 3 (*P-value* <0.01). Overall, the log-normal distribution is a good fit for TKN, NO_3-N, TN, and TP datasets from the CLP River, therefore this distribution was assumed to applicable for all further data analysis. A summary of the results for the distribution tests is available in Appendix B.

Annual Sampling Size Requirements

The required number of annual samples was calculated with Equation 10 at a 95% confidence level for each site and water quality parameter based on the median and lognormal standard deviation of the 2012/2013 sample sets (Table 3). A sensitivity was performed to examine the effects of change in the confidence level (1-α), or the water quality numeric standards on the sample size requirements. A summary of sample size requirements is presented in Table 3 for five scenarios:

- S1: Existing standard and a 95% confidence
- S2: Existing standard and a 90% confidence
- S3: Existing standard and a 99% confidence
- S4: A 10% decrease in the standard and a 95% confidence
- S5: A 10% increase in the standard and a 95% confidence

Table 3: Annual sampling size requirements from Eq. 10 for each site and nutrient responses using sample medians and standard deviations computed for the 2012-2013 data where S1-S5 are the sensitivity analysis scenarios.

Site	TN					TP				
#	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
1	2	1	3	2	1	3	2	6	4	3
2	1	1	2	1	1	2	1	3	2	2
3	3	2	5	4	2	2	1	3	2	1
4	7	4	13	10	5	3	2	5	3	2
5	12	8	25	8	20	3	2	6	2	3
6	1259	750	2642	65	289	7	4	13	5	10
7	2	2	4	2	3	68	41	145	14	8e3
8	1	1	1	1	1	3	2	5	2	3

Examination of the required annual sampling sizes in conjunction with the box-plots of nutrient concentrations measured during the 2012/2013 (Figure 6) reveal interesting trends. Generally the required number of annual samples is low (<10) for those sites with median concentrations far from the standard, and high when the median nears the standard. These sampling size requirements are applicable for the 2012/2013 sampling period only and results can vary by year.

For any cases where the median is within 20% of the standard, the required number of samples rapidly increases from several per year to hundreds per year. Figure 7 shows that as the median converges towards the standard (S/M = 1), the number of required annual samples approaches infinity. For sites within 20% of the median, changing the standard by +/- 10% can alter the number of samples by several orders of magnitude. Conversely, for those sites with initially low sampling requirements, changing the standard by +/- 10% changes the required number of samples by less than three samples per year. This is demonstrated in Figure 8 where the sensitivity results of three sites are compared for TP. Sites 1 and 6, which are not within 20% of the TP median, have only small changes in n due to a decrease in the standard of 10%, whereas Site 7 sampling numbers are drastically reduced by decreasing the standard. Overall, of the eight observed sampling sites, no additional sites would be brought within 20% of the standard with a 10% change of the standard.

The response of n to variation in alpha is more gradual, as is observed in Figure 7b. The effects of variation of alpha are not notable until the median concentration is within 20% of the standard. For those sites within 20% of the standard, reducing the confidence level from 95% to 90% reduces the number of required samples by approximately half (Table 3). However this does not make the requirements much more attainable for most of these cases. Outside of the 20% threshold, increasing the confidence level to 99% does not raise the number of samples above a realistic level for most sites and nutrient parameters (Table 3). As with the alpha parameter, standard deviation plays a more significant role in the number of required samples as the median converges towards the standard (Figure 7a).

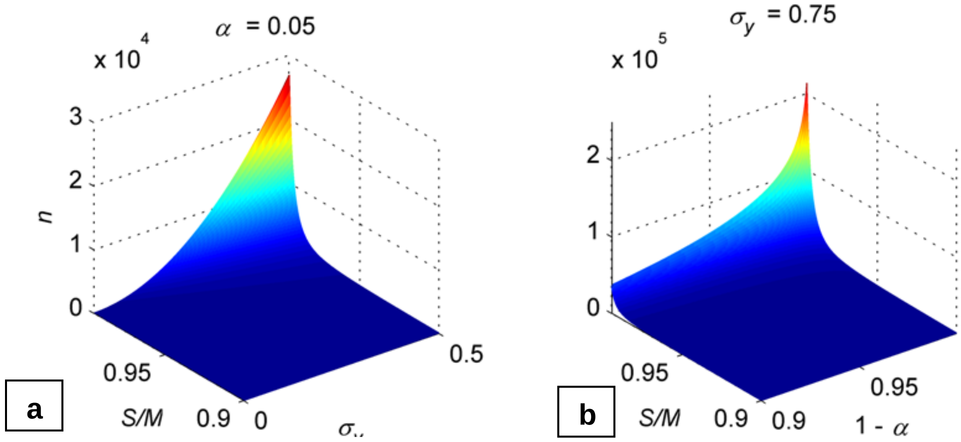

Figure 7: Sensitivity of n to ratio of the standard and median and a) standard deviation and b) alpha

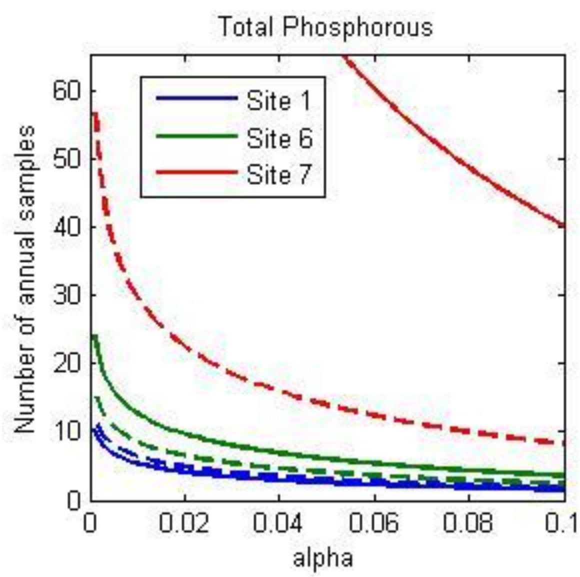

Figure 8: (left) Variation of n for TP with changes in alpha and the standard at Site 8, and (right) Variation in n for TP at three sites (1,6, & 7) for the existing standard (solid) and 10% decrease in the standard (dashed).

The case was also considered when the number of annual samples is fixed at the current monthly requirement (12 per year). In this case, alpha can be calculated for the known number of samples from Equation 11 based on the standard and statistical properties of the nutrient population. Figure 9 demonstrates the increase of alpha (the probability of determining that the median is above the standard when it is not) as the median nears the standard for TN. The increase of alpha at the 20% threshold is notable.

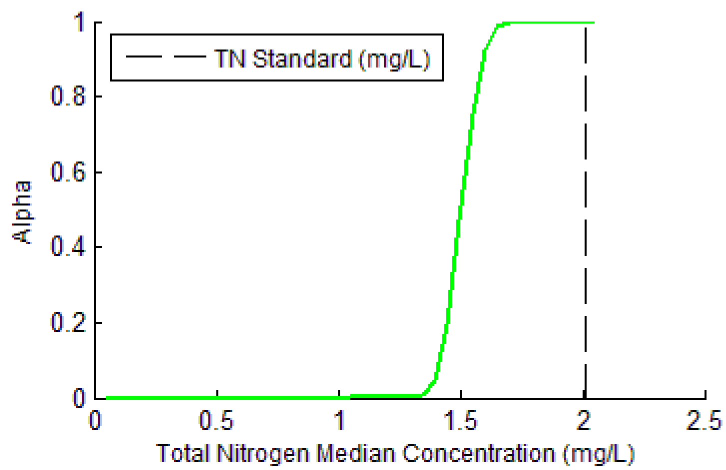

Figure 9: Response of alpha to changes in the median TN concentration for a fixed number of samples (n = 12 annual samples); Assuming a lognormal standard deviation of 0.30 mg/L (1.6 mg/L standard deviation).

MLR Models for Nutrient Concentration Medians

Regression analyses for annual nutrient concentration medians were performed for the two sets of data (1: 5 sites with flow, 2008-2013 years; 2: 8 sites, 2012/2013 year). The performance of different predictor variables in MLR regression for medians was consistent between Datasets 1 and 2, so results are presented just for Dataset 1. Annual nutrient concentration medians were transformed with power functions using a box-cox transformation for the linear regression analysis. Individual lambda values for the power transformations are listed in Table 4. Appendix D summarizes the MLR model results for the medians from all of the predictor variable combinations.

Significant (*p-value* < 0.05) and strong ($R^2 > 0.7$) correlations were found between all of the individual anthropogenic predictor variables and nutrient median concentrations of each response variable. While the hydrologic parameters were not significant on their own, the annual mean daily flow improved the performance of MLR models. The preferred regression models for each nutrient response have three predictor variables: IDW WWTP discharge capacity reflecting the influence of urban areas, IDW AFO capacity representing the influence of food production agricultural, and annual mean daily flow representing hydrologic influence. Using paired anthropogenic predictor variables limits multicolinearity between predictors. Table 4 presents a summary of the preferred regression models for different nutrient parameters along with measures of significance (*F*-statistic and *p-value*) and strength of correlations (R^2).

Table 4: MLR models for Medians with Point source IDW Capacity Predictors; Q_{avg} = annual mean daily flow, P_F = P value for the appropriateness of the model, P_L = P value for Lilly test for normality, P_{BF} = P value for Brown-Forythe test for homoscedasticity, VIF = Variable Inflation Factor, λ = box-cox transformation parameter.

Nutrient	Linear Model	R^2	Adj. R^2	P_F	P	P_L	P_{BF}	λ	VIF
TKN	-0.88 + 0.11 (IDW AFO capacity) + 0.27 (IDW WWTP capacity) - 0.0015 (Q_{avg})	0.79	0.76	3E-7	0.13	0.50	0.07	-0.14	13.33
NO_3-N	-2.24 + 0.07 (IDW AFO capacity) + 0.98 (IDW WWTP capacity) - 0.0031 (Q_{avg})	0.90	0.89	7E-11	0.11	0.03	0.33	-0.02	13.33
TN	-0.54 + 0.06 (IDW AFO capacity) + 0.48 (IDW WWTP capacity) - 0.0017 (Q_{avg})	0.86	0.84	4E-9	-0.06	0.38	0.47	-0.17	13.33
TP	-4.29 + 1.37 (IDW AFO capacity) + 0.13 (IDW WWTP capacity) - 0.0013 (Q_{avg})	0.90	0.88	2E-10	0.23	0.05	0.22	-0.10	13.33

There is strong correlation between WWTP discharge capacity and percent Urban Land Use, as well as between AFO capacity and percent Agricultural Land Use (Figure 10). So alternatively, percent urban land use can be paired with the IDW number of AFOs, or percent agricultural land use can be parried with the IDW number of WWTPs to achieve strong MLR models (Table 5). High multicorrelation exists between percent land use parameters so they should not be used together in a MLR model. Calculating the predictors from the preferred model, IDW WWTP capacity and IDW AFO capacity, can be difficult and time intensive, so MLR models employing percent land use may be more practical and produce comparable results to the preferred models.

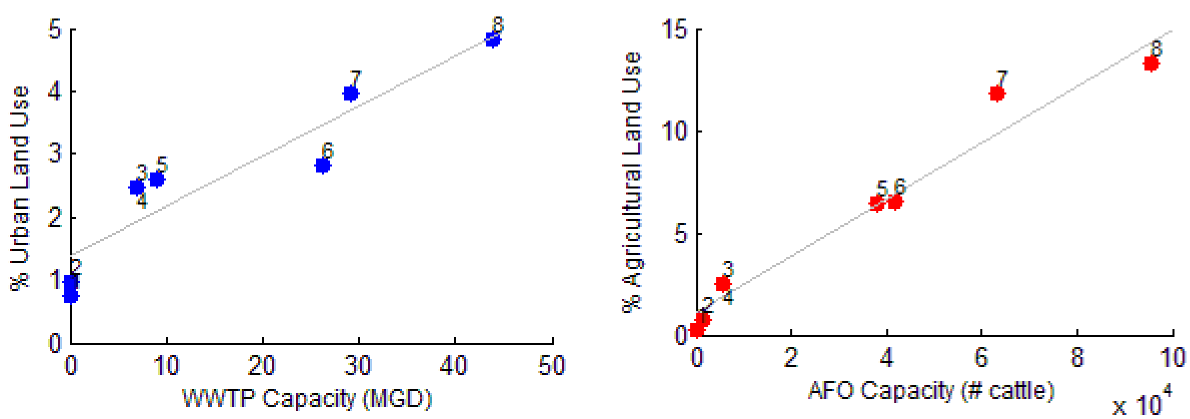

Figure 10: Comparison of Point Source and Non-point source anthropogenic variables. R^2 value for least squares line between (left) WWTP capacity and % Urban land use and (right) AFO capacity and % Agricultural land use are 0.85 and 0.96 respectively.

Nitrogen Variables

Multicolinearity between anthropogenic predictor variables limited the number of valid MLR models for all of the nutrient parameters. Each MLR model that met the criteria for multicolinearity produced strong R^2 values for the three nitrogen species. The highest R^2 values for

TKN, NO_3-N, and TN were 0.81, 0.93, 0.89 respectively, and were produced by MLR models with the predictor.

Table 5: MLR models for Medians with Point Source Facility predictors and Land Use predictors; Q_{avg} = annual mean daily flow, P_F = P value for the appropriateness of the model, P_L = P value for Lilly test for normality, P_{BF} = P value for Brown-Forythe test for homoscedasticity, VIF = Variable Inflation Factor, λ = box-cox transformation parameter.

Nutrient	Linear Model	R^2	Adj. R^2	P_F	P	P_L	P_{BF}	VIF	λ
TKN	-1.20 + 938.47 (#AFO IDW) + 0.22 (% Urban LU) - 0.002 (Q_{avg})	0.81	0.78	9E-8	0.08	0.50	0.06	8.82	-0.14
NO_3-N	-3.41 + 1817.6 (#AFO IDW) + 0.85 (% Urban LU) - 0.0022 (Q_{avg})	0.93	0.92	2E-12	-0.02	0.29	0.42	8.82	-0.02
TN	-1.12 + 984.89 (#AFO IDW) + 0.42 (% Urban LU) - 0.0013 (Q_{avg})	0.89	0.87	4E-10	-0.20	0.50	0.43	8.82	-0.17
TP	-472 + 6056.2 (#AFO IDW) + 0.16 (% Urban LU) - 0.0008 (Q_{avg})	0.90	0.89	1E-10	0.19	0.08	0.22	8.82	-0.10
TKN	-0.93 + 0.08 (% Ag LU) + 821.1 (# WWTP IDW) - 0.0014 (Q_{avg})	0.79	0.77	2E-7	0.14	0.50	0.06	11.4	-0.14
NO_3-N	-2.40 + 0.26 (% Ag LU) + 2151.4 (# WWTP IDW) - 0.0031 (Q_{avg})	0.91	0.89	7E-11	0.10	0.05	0.27	11.4	-0.02
TN	-0.63 + 0.13 (% Ag LU) + 1208.9 (# WWTP IDW) - 0.0017 (Q_{avg})	0.86	0.84	4E-9	-0.07	0.37	0.36	11.4	-0.17
TP	-4.81 + 0.03 (% Ag LU) + 9181.5 (# WWTP IDW) - 0.0005 (Q_{avg})	0.91	0.89	6E-11	0.14	0.50	0.42	11.4	-0.10

variables: 1) IDW number of CAFO facilities, 2) percent urban land use, and 3) annual mean daily flow. Figure 11 compares the MLR predicted versus observed transformed nutrient medians for these MLR models. Among the valid MLR models for nitrogen species, there was only a 0.05 difference between the R^2 value for this model and the lowest performing model. Overall, the MLR models are not very sensitive to the specific anthropogenic predictor variables. Including point source capacities did not greatly improve model performance. The impact of individual point source facilities on nitrogen concentrations in the CLP River may be more a function of management of those facilities than the capacities. For example Mulberry WWTP in Fort Collins has spent considerable time and money on improving nutrient treatment and has low effluent concentrations of TN compared to Boxelder WWTP of similar capacity which has not upgraded. This can also be the case for AFOs that employ management practices to control the runoff from their facilities.

Because the MLR models are not very sensitive to the anthropogenic predictor variables, using percent agricultural land use in place of a point source predictor could be more efficient since in many cases it can be difficult to compile an accurate list of AFOs. The most suitable model to meet this need uses three predictor variables: 1) percent agricultural land use, 2) the IDW number of WWTPs, and 3) annual mean daily flow. The R2 values from these models were 0.79, 0.91, and 0.86 for TKN, NO_3-N, and TN respectively. Figure 11 compares the MLR predicted values for this model versus observed nutrient concentrations.

Inverse distance weighting was important for limiting multicolinearity between anthropogenic predictor variables. This was particularly true for the WWTP predictor variable. There were no valid models without inverse distance weighting of the WWTP predictor. Also, normality and homoskedacity of the MLR model residuals was not satisfied without box-cox transformation of the median nitrogen concentrations. The impact of box-cox transformation of the median concentrations is displayed in Figure 13.

Including a hydrologic predictor was important for the validity of the MLR models. For all nitrogen species the annual mean daily flow was the best predictor for this purpose. When paired with anthropogenic factors, it helps explain the variation in median concentrations between the five years of data. Figure 14 displays the impact of including the hydrologic predictor in the MLR model results for TN. The annual mean daily flow helps distinguish wet hydrologic years from dry hydrologic years, and is linked to the effect of dilution in nitrogen concentrations.

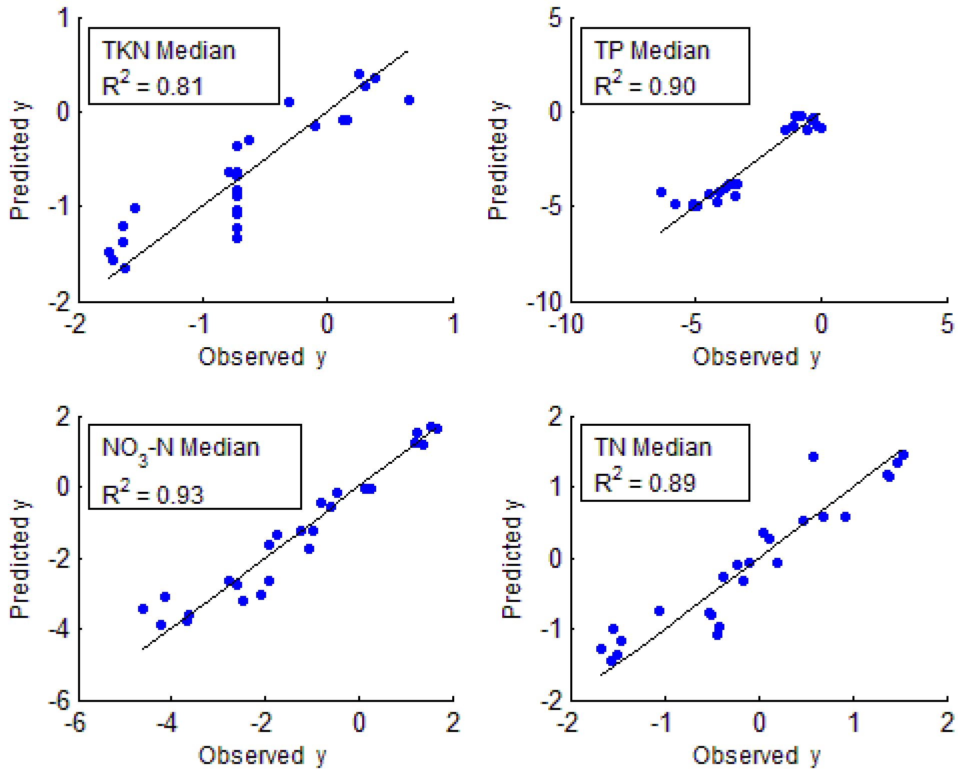

Figure 11: Optimal linear regressions for Medians of each nutrient parameter based on #CAFO IDW, % Urban Land Use, and annual mean daily flow; Y is the box-cox transformed data (mg/l) based on optimal λ.

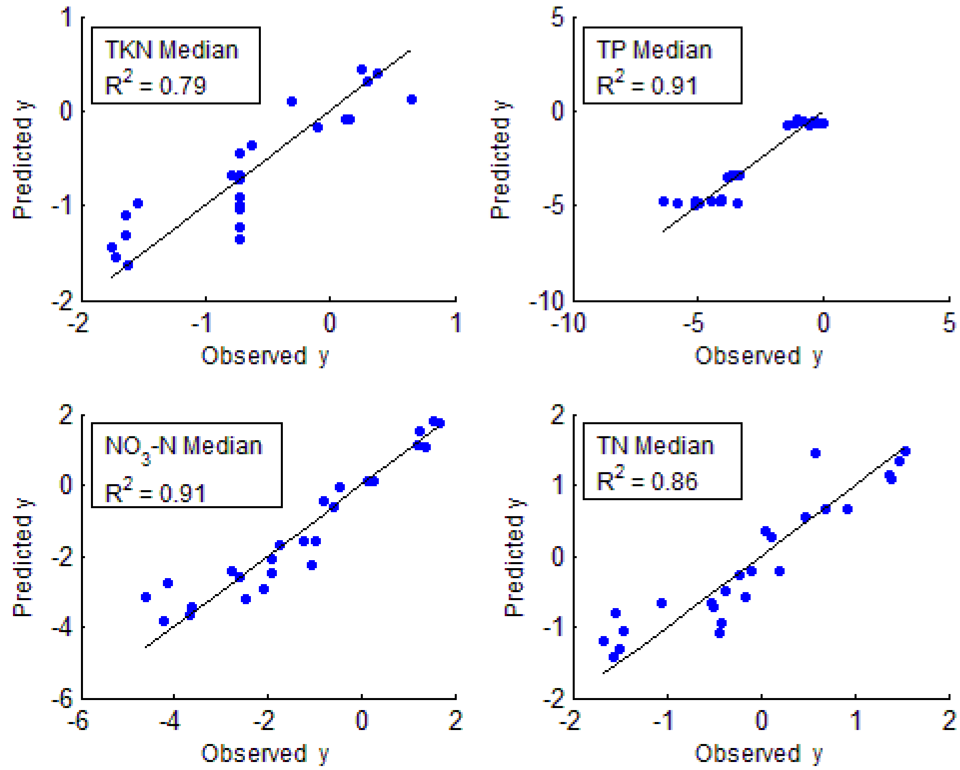

Figure 12: Optimal linear regressions for Medians of each nutrient parameter based on % Agricultural Land Use, #WWTP IDW, and annual mean daily flow; Y is the box-cox transformed annual medians (mg/l) based on optimal λ.

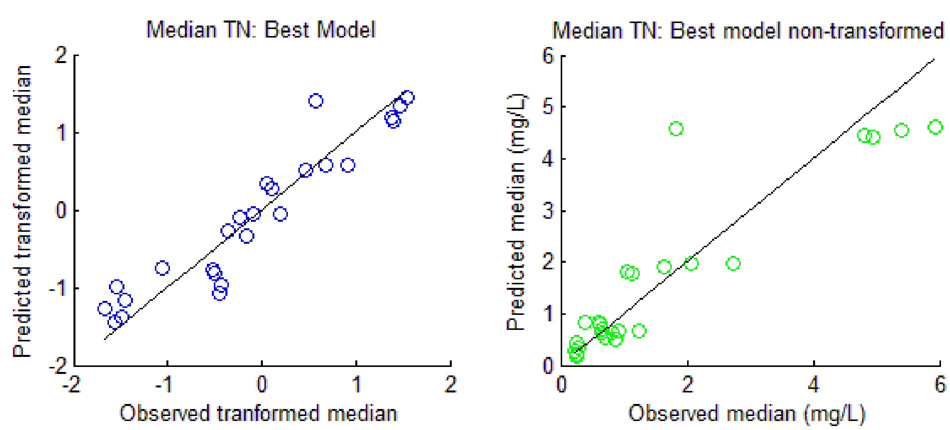

Figure 13: The impact of the box-cox transformation on the MLR model for TN (left) transformed and (right) untransformed.

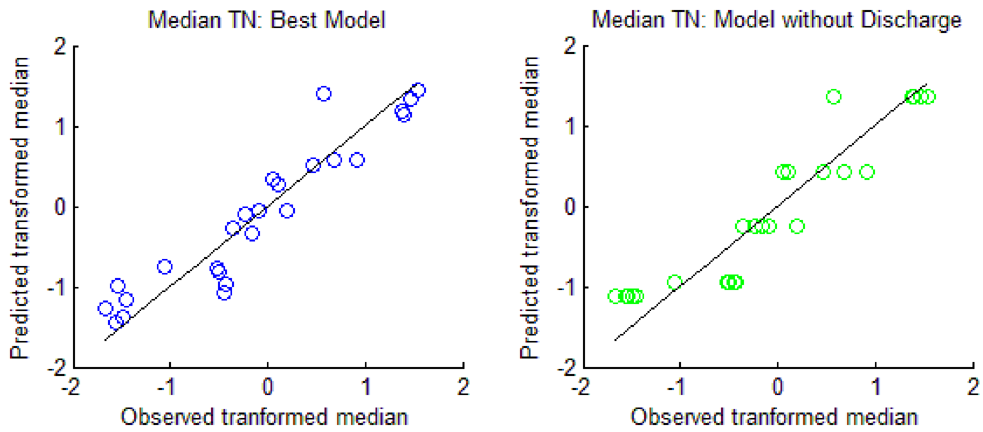

Figure 14: Impact of including the hydrologic predictor variable (annual mean daily flow) on the performance of the MLR model for TN.

The results of linear regressions were compared between datasets using five years of data and just the 2012/2013 data. The 2012/2013 dataset is the most complete; however there would be little confidence in applying results of regression from this one year to subsequent years. This is due to variations in hydrologic conditions and the occurrence of a significant fire in the upper CLP watershed that began just prior to the collection of 2012/2013 samples. Comparison of the regressions for both datasets found that the optimal combination of anthropogenic factors were generally consistent for the single year and multiple years.

Total Phosphorous

MLR models for Total Phosphorous annual medians produced high R^2 values with anthropogenic predictors. However, the hydrologic predictor variable (annual mean daily flow) was not significant in the MLR model and therefore resulted in TP predictions that do not vary by year. None of the hydrologic variables considered describe the variability of TP medians between years, however the anthropogenic predictor variables do describe the variability of TP between sites.

For TP, the highest R^2 value was 0.91 produced by the combination of three hydrologic predictors: 1) percent agricultural land use, 2) the IDW number of WWTPs, and 3) annual mean daily flow. Figure 12 shows the MLR predicted values for this model versus observed nutrient concentrations. As with the MLR models for nitrogen species, the model using the IDW number of CAFO facilities, percent urban land use, and annual mean daily flow also performed well (Figure 11). The MLR models of TP were more sensitive to the specific agricultural predictor variable, but the lowest R^2 value was still 0.75.

The lack of a predictor to describe TP concentration variability between years is concerning and suggests that the model is lacking one or more significant parameters. A comprehensive study of phosphorous constituents in Swedish basins found median concentrations were significantly correlated with soil type, soil temperature, average summer discharge, and atmospheric deposition (Arheimer et al., 2000). None of these parameters were considered in the regression analysis, but could provide better models. In-channel biological and transport processes for TP should be considered when choosing parameters to add to the models. Below WWTPs phosphorous sorbs to stream sediments or is taken up by peryphyton and large scale reductions in TP can be seen within relatively short distances (a few kms) by these processes (Jarvie et al., 2012). This retained phosphorous can then be remobilized during storm events. Therefore, including D_{50} particle diameter, percent fine material in bed, or chlorophyll-a concentrations may be useful as predictors. The bank and bed soil itself can also be a source of phosphorous which was not considered for this study (Bledsoe et al., 2001). Changes in the channel bank erosion and deposition over time could account for variation in annual samples. Changes in WWTP management could also account for the variation of TP concentrations over time, though including a relevant quantitative parameter would be difficult. Further linear regressions should consider predictive variables that represent transport processes and seasonal hydrologic variables (flow or precipitation).

The results of regressions for 5 years of data were compared with the results from regression with data from just 2012/2013. The 2012/2013 dataset is much more robust and includes 8 sites rather than just 5. Regressions from the 2012/2013 dataset confirm the optimal anthropogenic predictor variables found in the 5 year dataset. A closer observation of the MLR model results for 2012/2013 TP suggest that a variable describing the capacity of a WWTP to treat phosphorous would be significant, and may explain more variability in annual TP medians between monitoring sites than WWTP capacity.

Overall, the anthropogenic predictor variables used for this analysis produce linear models with strong R^2 values and can be used to estimate the TP concentrations at a location on the CLP River. However the model lacks any terms that can describe the yearly variability of the median concentration, and thus should be used with caution.

MLR Models for Nutrient Concentration Standard Deviations

Due to the confirmed lognormality of the datasets, multiple linear regressions were performed for the standard deviations of the log transformed data. Results between Datasets 1 and 2 were not consistent. MLR models were insignificant (*p-value* > 0.05) for Dataset 1 (5 sites with flow, 2008-2013 years) for all parameters except NO_3-N. This is likely due to the very low sample sizes for some parameters at some sites as well as the high rate of non-detect values in the sample sets, except for in NO_3-N. As a result, the linear regression summaries for standard deviation focus on Dataset 2, for which significant (*p-value* < 0.05) and strong ($R^2 > 0.7$) models were found. Appendix D summarizes the MLR model results for the lognormal standard deviations from all of the predictor variable combinations.

Significant and strong correlations were found between many individual anthropogenic predictor variables and nutrient lognormal standard deviation concentrations for Dataset 2. Annual precipitation was also considered as a predictor variable since it was available for all eight sample sites. While correlation with annual precipitation was strong for TP, NO_3-N, and TN (R^2 = 0.63, 0.60, 0.77, respectively), combining this predictor with anthropogenic predictors decreased the significance of MLR models and was left out of the final models. The best MLR models for each nutrient response had two predictor variables: one reflects the influence of urban areas and another represents the influence of agricultural food production. For all for nutrient parameters, the percent Urban Land Use is the best predictor for the influence of urban areas. The best predictor for agricultural influences was the IDW number of AFOs for TKN, the AFO capacity for NO_3-N and TN, and the IDW AFO capacity for TP, Using paired anthropogenic predictor variables limits multicolinearity between the predictors. Table 6 presents a summary of the best MLR models for different nutrient parameters along with measures of significance (*F*-statistic and *p-value*) and strength of correlations (R^2).

Table 6: Optimal MLR models for lognormal standard deviations; P_F = P value for the appropriateness of the model, P_L = P value for Lilly test for normality, P_{BF} = P value for Brown-Forythe test for homoscedasticity, VIF = Variable Inflation Factor, λ = box-cox transformation parameter.

Nutrient	Linear Model	R^2	Adj. R^2	P_F	ρ	P_L	P_{BF}	VIF	λ
TKN	0.59 + 281.7 (#AFO IDW) - 0.12 (% Urban Land Use)	0.82	0.74	0.01	-0.10	0.27	0.42	5.71	1.54
NO_3-N	0.49 - 3E-6 (AFO capacity) - 0.015 (% Urban LU)	0.73	0.62	0.04	-0.03	0.50	0.04	11.5	1.06
TN	0.57 + 2E-6 (AFO capacity) - 0.13 (% Urban Land Use)	0.80	0.72	0.02	-0.06	0.50	0.12	11.5	0.57
TP	0.66 - 0.034 (IDW AFO capacity) - 89.7 (% Urban LU)	0.73	0.63	0.04	-0.24	0.50	0.31	2.37	0.015

Fewer valid MLR models for were found for lognormal standard deviation as compared to MLR models for the medians. In fact, only one model passed criteria for TKN, though the R^2 value is strong. For TKN, many of the predictor variables were inadequate for describing the lognormal standard deviations and resulted in high p-values (> 0.05) for the test for overall model appropriateness and invalidation of MLR models. Invalid MLR models for NO_3-N, TN, and TP were mainly due to lack of normality and homoskedacity in the model residuals. Multicolinearity between anthropogenic predictor variables was reduced since values for all eight sites were included in the models.

Nitrogen Variables

Unlike the models of the annual medians, the optimal predictors for lognormal standard deviation at each site were not consistent for the nitrogen species. For TKN the best MLR model had and R^2 value of 0.82 and includes the IDW number of AFOs and percent urban land use. Many more models are valid for NO_3-N and TN. The optimal predictor variables for MLR models of NO_3-N and TN are the AFO capacity and percent urban land use. Figure 15 compares observed versus predicted results from the optimal MLR models. The MLR models for the lognormal standard deviation of nitrogen species were not very sensitive to the specific predictor variables and including capacity in the point source predictors did not substantially improve the models. It should also be noted that the lognormal standard deviations were not transformed for the MLR models.

Total Phosphorous

More MLR models were valid for TP than for the nitrogen species. The percent urban land use produced higher R^2 values than point source predictors of urban influence. Inverse distance weighting of AFO predictors produced more valid models than non-IDW parameters. The optimal predictor variables for TP are percent urban land use and IDW AFO capacity. Overall the TP models are not very sensitive to the specific predictor variables. While the optimal predictors produce an R^2 value of 0.76 the lowest R^2 value produced by the valid models was 0.69.

For all of the nutrient parameters, the valid MLR models for lognormal standard deviation have strong R^2 values that can be used to predict the number of annual samples. A further review of the models is necessary with robust datasets from additional years to have confidence in applying the model to other locations. It appears that annual precipitation will be a strong hydrologic predictor variable for incorporating variability between years.

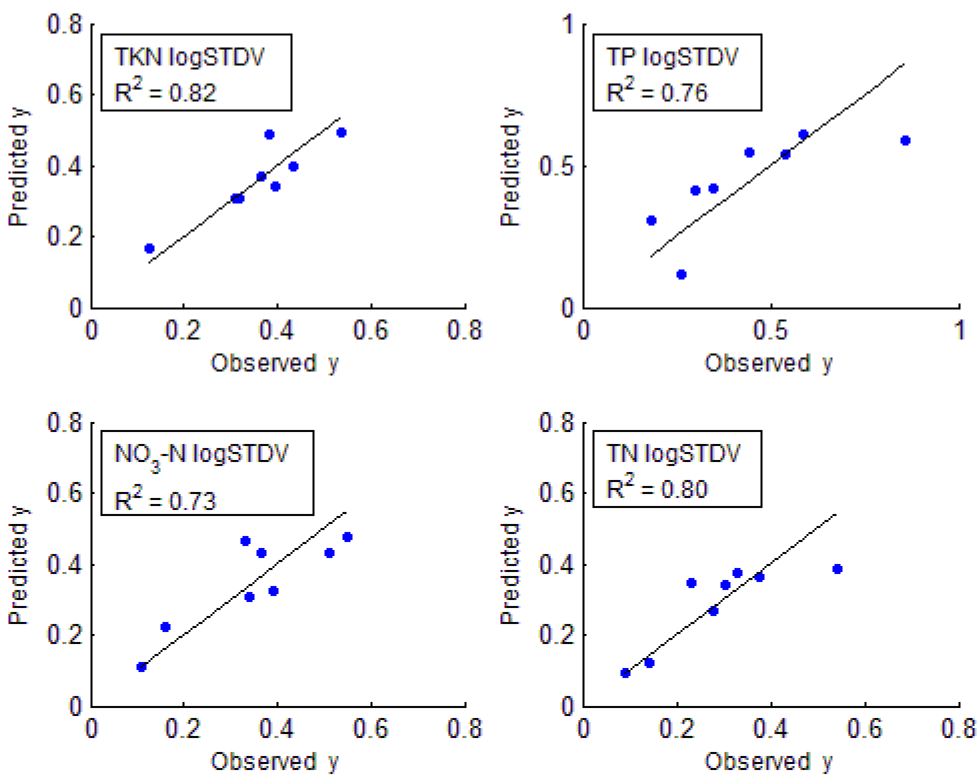

Figure 15: Optimal linear regressions for lognormal standard deviation (y) of each nutrient parameter.

CONCLUSIONS

In the Cache La Poudre River, observation of TN and TP reveals a general increase in median nutrient concentrations from upstream to downstream as anthropogenic influences increase. The NO_3-N component of TN gradually increases downstream and begins to exceed the numeric standard for TN at monitoring Site 5 (river mile 36.5). The TKN component of TN remains generally below the numeric standard for TN except at Site 5 below the Boxelder WWTP, where concentrations often exceed the TN standard. This may be due to limited treatment of nutrients at the WWTP or inadequate time for nutrients to attenuate before sampling compared with other observation sites. Combined, TN begins to exceed numeric standards at Site 6 and consistently exceeds numeric standards at the most downstream monitoring location.

The largest concentrations of TP are consistently found at monitoring sites below WWTPs, although varying capacities of WWTPs to treat incoming nutrient loads can greatly impact the TP concentrations at monitoring sites below WWTPs. Instances of high TP concentrations are found at every monitoring site including the background location. And the background monitoring site is at risk of exceeding the numeric standard, which suggests that the numeric standard for TP may not be appropriate for every river in Colorado.

The first and second objectives of this study to explore the variability annual nutrient concentration medians and lognormal standard deviations under varying levels of upstream anthropogenic influences on the CLP River was achieved through analysis with multiple linear regression modeling. The MLR approach was appropriate for predicting median nutrient concentrations and lognormal standard deviations in the CLP Watershed. Anthropogenic variables and general hydrologic descriptors were sufficient predictive parameters for medians and lognormal standard deviation. MLR models for annual medians performed better for Nitrogen species than TP, however high R^2 values were achieved for both. Regression models for lognormal standard deviation were significant only for the 2012/2013 dataset. This demonstrates that robust datasets with no non-detect values are necessary to model standard deviations.

When considering the regressions for the annual medians, anthropogenic predictor variables representing urban and agricultural influences performed similarly. The preferred MLR for all of the nutrient parameters uses inverse distance weighted WWTP and AFO capacities with annual mean daily discharge as a hydrologic predictor. MLR models that use percent land can perform equivalently to predict median concentrations, though urban and agricultural land use predictors cannot be employed in the same model due to high multicoliearity between them. Little value is gained in the MLR models by including capacity of point sources in the predictive variables. The anthropogenic predictor variables describe the variability of median nutrient concentrations between monitoring sites. Daily mean flow is an important predictor variable for describing variability of medians between years, although it doesn't produce significant correlation on its own.

In regard to TP modeling for annual medians, high R^2 values were obtained from regressions with anthropogenic predictor variables, but a parameter which describes the variability of medians between years was not found. This severely limits the applicability of this model. Accounting for this variability may be possible by including parameters which address capacities of various WWTPs to treat incoming TP loads, or the transport and biological processes associated with TP in surface water. Potential parameters include rank of WWTP treatment capacity, seasonal average flow rates, total suspended sediment concentrations, chlorophyll-a concentration, the percent of fine material, and sediment transport rates.

MLR models were successful for correlating lognormal standard deviation of nutrient parameters with anthropogenic predictor variables for the 2012/2013 dataset. Including capacities of point sources showed little benefit to model performance, however inverse distance weighting predictors does reduce multicoliearily between predictors. Along with anthropogenic variables, annual precipitation was significantly correlated with lognormal standard deviation. Further analysis will likely find hydrologic variables to be significant predictors over many years of data, although the relationships may not be linear. Results for standard deviation regressions should be confirmed with more robust datasets.

To meet the third objective of this study a statistical expression was developed to link annual sampling requirements to meet numeric standards with the median and lognormal standard deviations of the nutrient populations. This expression was used to estimate the required number of annual samples at each monitoring site to evaluate the median concentration to a 95% confidence level. The results suggest that in the case where a comprehensive monitoring plan is being developed for an entire water body, targeted sampling at sites near the standard with limited sampling elsewhere could optimize monitoring resources while possibly increasing the quality of the results. Sampling requirements to meet a 95% confidence level are lower than the current regulation requirements for those sites and nutrient parameters which have annual median values greater or less than 20% of the standard. Sampling for a 99% confidence level is also feasible for these sites. However, if the median concentration is within 20% of the standard, the predicted number of annual samples is often unfeasibly high for grab sampling. Slight variations in the confidence levels do not affect the annual number of samples at any of the observed sites. Small variations in the numeric standard does not greatly affect those sites with initially low samples numbers, but can change the sample number by several orders of magnitudes for sites that are within 20% of the standard.

Overall, this study demonstrates the feasibility of describing the linking the statistical properties of nutrient concentrations on a river based on upstream anthropogenic influences in the watershed. Through the MLR models, anthropogenic influences describing urban and agricultural development were found to describe variation of nutrient concentrations between monitoring sites, and a general hydrologic descriptor was able to describe the variability of concentrations between years. In conjunction with the statistical expression for annual number of samples, the MLR models can be used as a management tool to improve monitoring for water quality parameters. Once the MLR models are developed for a watershed, they can be applied to improve allocation of monitoring resources for a region or predict monitoring requirements for additional sampling locations.

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APPENDIX A: Sample Test Methods

Table 7: Test methods used by the City of Fort Collins laboratories to analyze the nutrient parameters of surface water samples from the CLP River.

Nutrient Parameter	Abbreviation	Test Method	Fort Collins Laboratory
Total Phosphorus as P	TP	EPA365.1 Rev2.0	Pollution Control Lab
Total Kjeldahl Nitrogen	TKN	Standard Methods 4500-Norg D	Pollution Control Lab
Total Nitrogen	TN	Sum of TKN + Nitrate-N + Nitrite-N	Pollution Control Lab
Nitrate-N	NO_3-N	EPA Method 300.0	Water Quality Lab
Nitrite-N:	NO_2-N	EPA Method 300.0	Water Quality Lab
Ortho-Phosphorus as P	OP	EPA 300.0	Water Quality Lab

APPENDIX B: Distribution Analysis Results

Probability plots and the Kolmogorov-Smirnov test for normality were used to evaluate the dataset from 2012/2013 for compliance with the lognormal distribution. The procedures were performed for the full dataset (Figure 16 and 17 and Table 8) and then again with the non-detect values removed (Figure 18 and 19 and Table 9). Removal of the non-detect values found better adherence with the lognormal distribution.

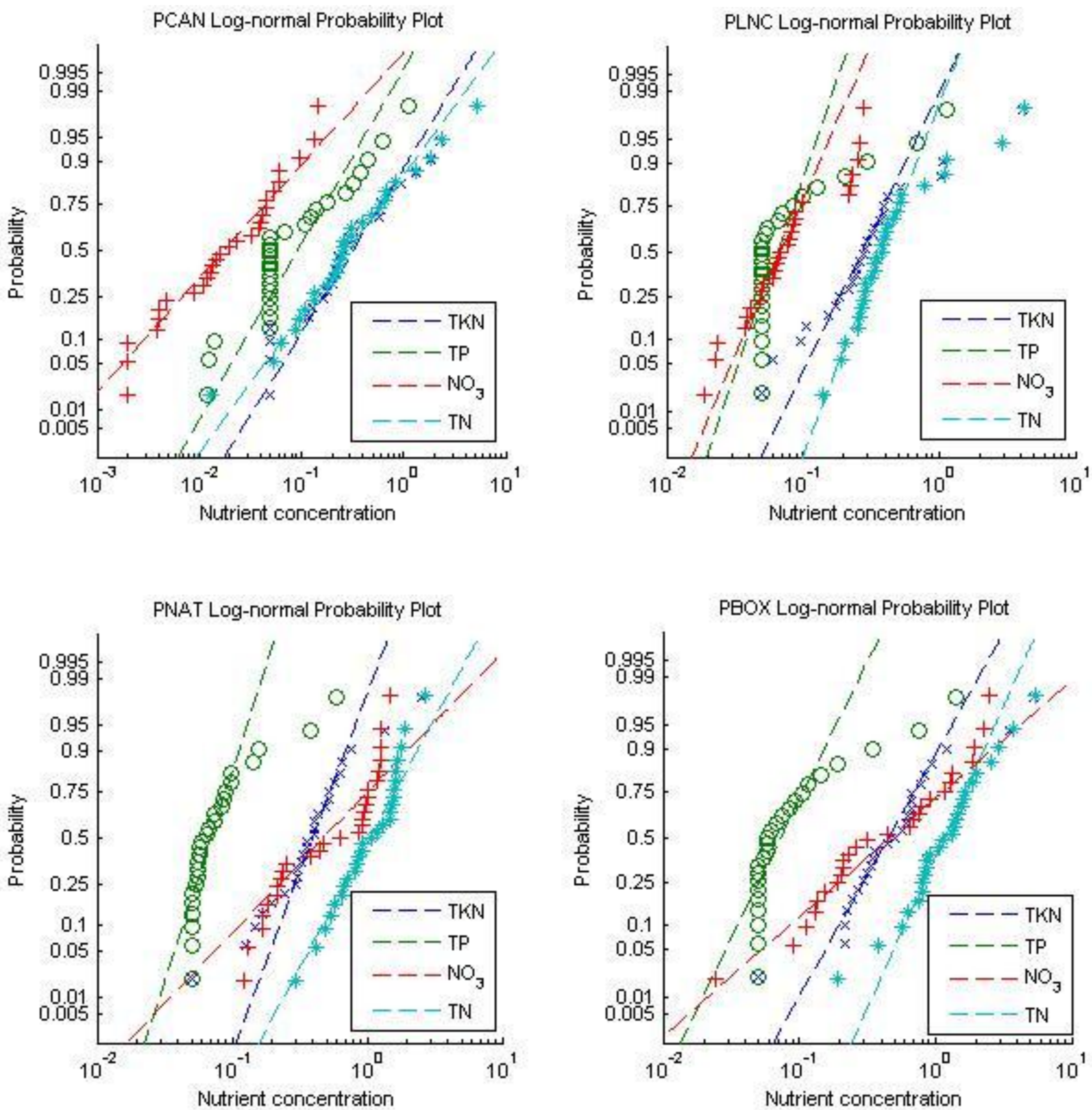

Figure 16: Lognormal probability plots for Sites PCAN, PLNC, PNAT, PBOX for each nutrient parameter with the full 2012/2013 dataset including non-detect values.

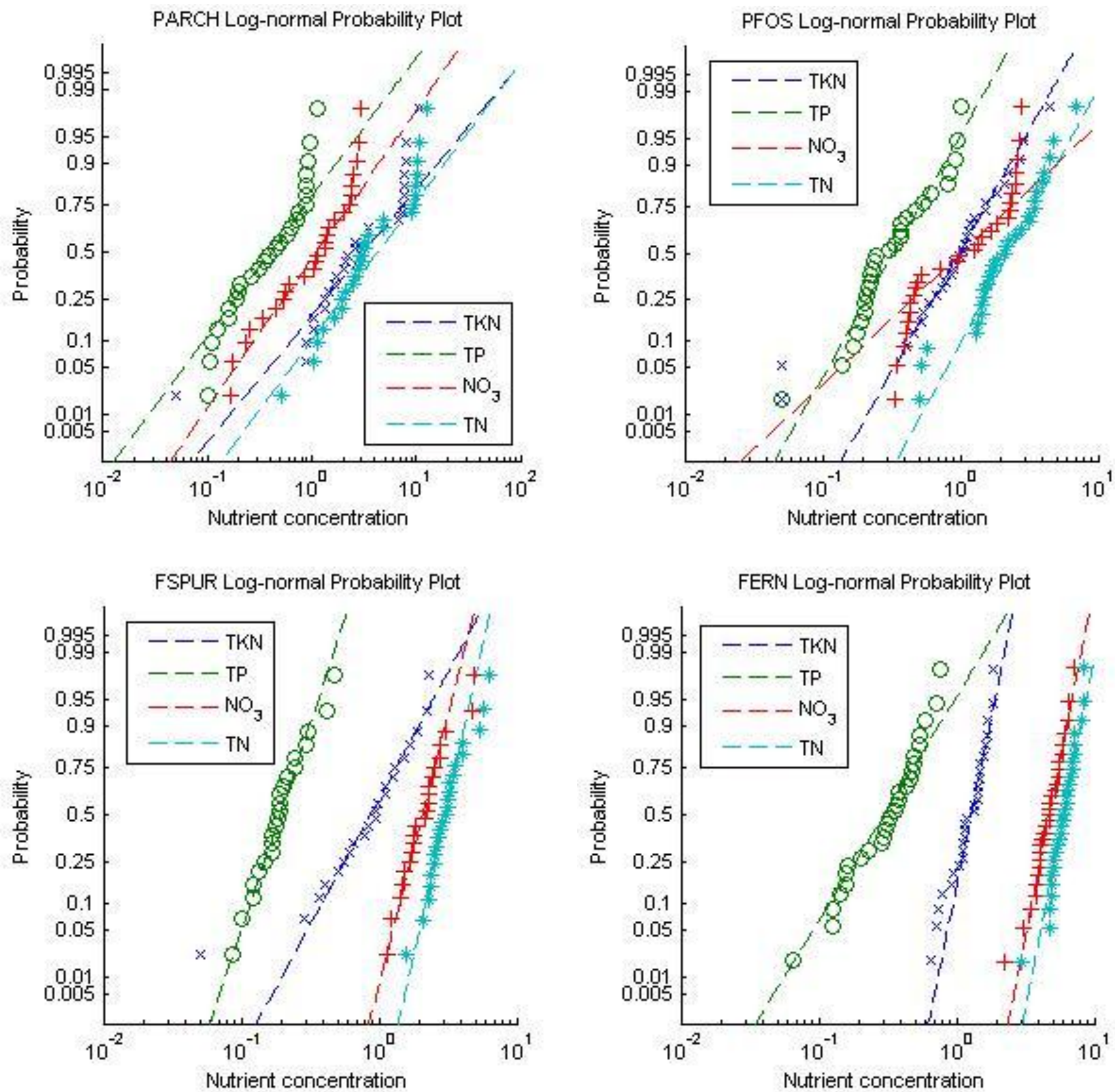

Figure 17: Lognormal probability plots for Sites PARCH, PFOS, FSPUR, and FERN for each nutrient parameter with the full 2012/2013 dataset including non-detect values.

Table 8: The P value reported for the Kolmogorov-Smirnov test for the 2012/2013 dataset that includes non-detect values. Values highlighted in red do not pass lognormality test (α = 0.05 level).

Site	Name	Lognormal (with Non-detects)			
		TKN	TP	NO_3	TN
1	PCAN	>0.15	<0.01	>0.15	>0.15
2	PLNC	0.046	<0.01	0.02	<0.01
3	PNAT	0.107	<0.01	<0.01	0.064
4	PBOX	>0.15	<0.01	>0.15	>0.15
5	PARCH	0.09	0.08	0.082	0.062
6	PFOS	0.047	0.13	0.13	>0.15
7	FSPUR	0.12	0.05	>0.15	>0.15
8	FERN	>0.15	>0.15	<0.01	<0.01

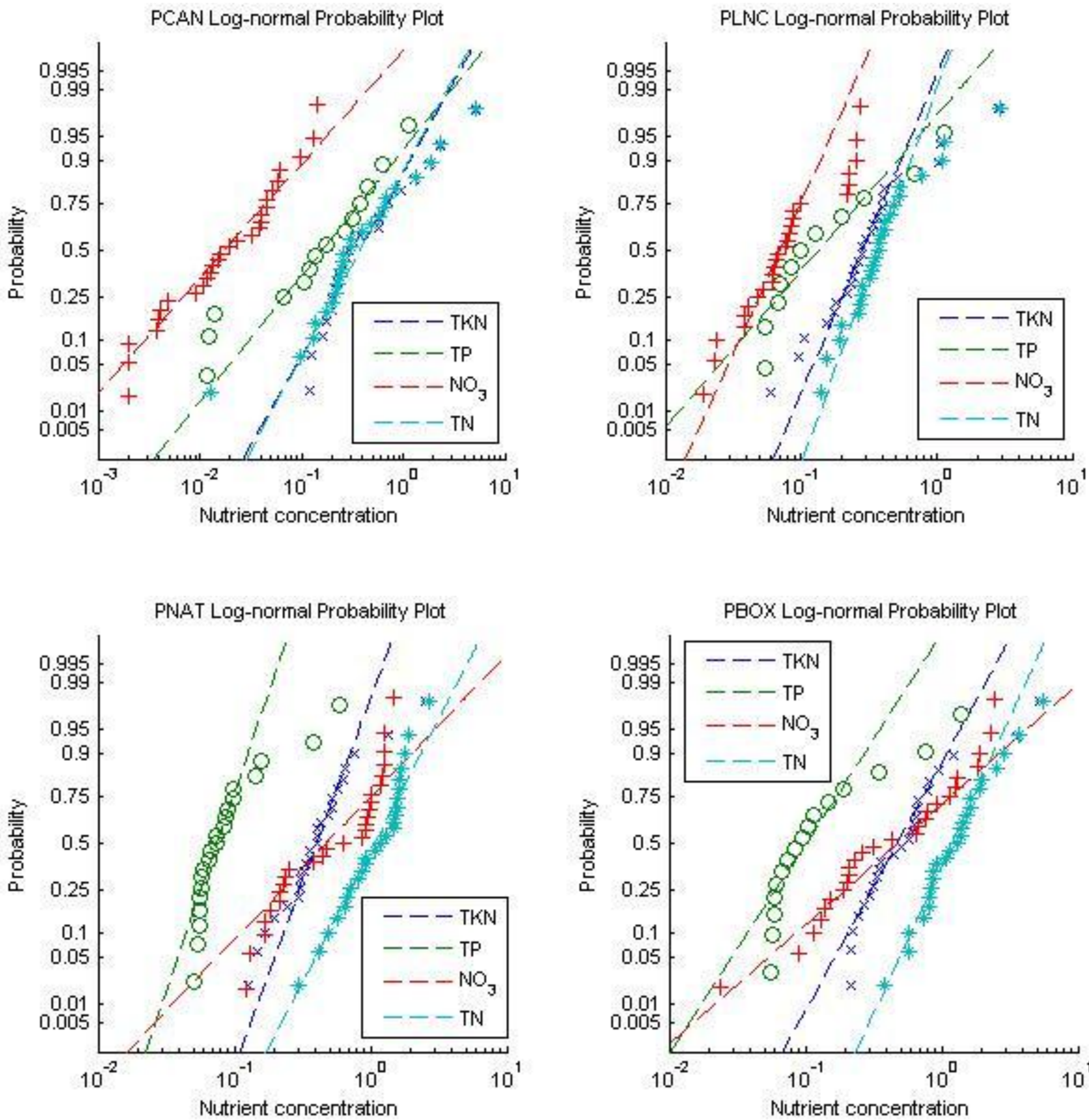

Figure 18: Lognormal probability plots for Sites PCAN, PLNC, PNAT, PBOX and for each nutrient parameter with the full 2012/2013 dataset discluding any non-detect values.

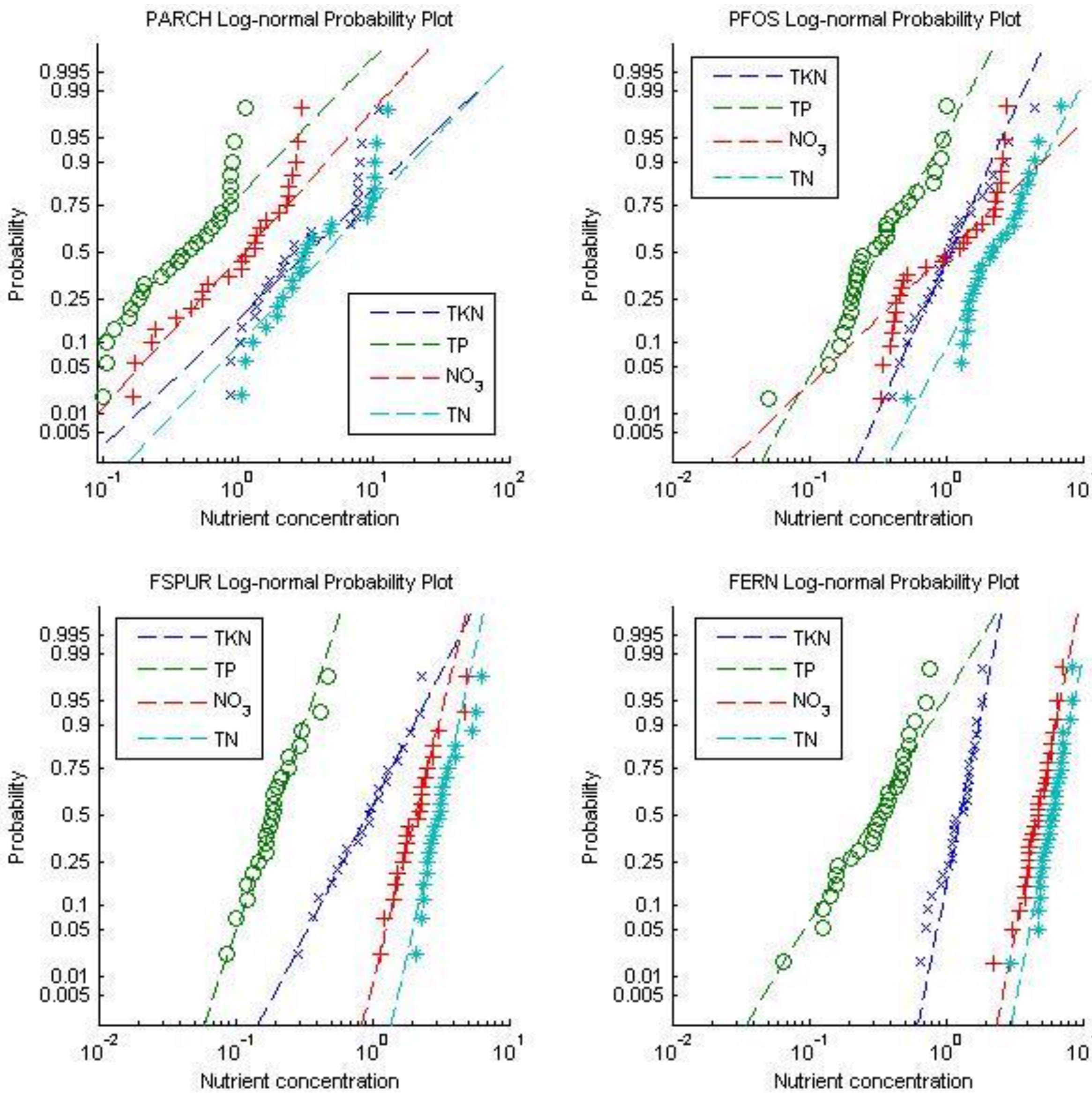

Figure 19: Lognormal probability plots for Sites PARCH, PFOS, FSPUR, and FERN and for each nutrient parameter with the full 2012/2013 dataset discluding any non-detect values.

Table 9: The P value reported for the Kolmogorov-Smirnov test for the 2012/2013 dataset that discludes non-detect values. Values highlighted in red do not pass lognormality test (α = 0.05).

Site	Name	Lognormal (without Non-detect values)			
		TKN	TP	NO_3	TN
1	PCAN	0.144	>0.15	>0.15	0.098
2	PLNC	0.067	>0.15	0.092	0.075
3	PNAT	>0.15	<0.01	<0.01	0.122
4	PBOX	>0.15	0.042	>0.15	>0.15
5	PARCH	0.09	0.08	0.082	0.062
6	PFOS	>0.15	0.13	0.13	>0.15
7	FSPUR	0.12	0.05	>0.15	>0.15
8	FERN	>0.15	>0.15	>0.15	>0.15

APPENDIX C: Data for Linear Regression Models

All of the parameters used for the linear regression models are summarized below including the distribution medians and standard deviations for each water quality parameter, and the anthropogenic and hydrologic predictor variables. Two datasets were used for linear regression models. Dataset 1 includes all five years of data but only for those sites with flow (PCAN, PLNC, PBOX, PFOS, and FERN noted in bold). Dataset 2 includes all 8 sites, but only for the 2012/2013 year.

Table 10: TKN distribution parameters for data sets from 2008 – 2013; N = number of samples in dataset, M = median, SD = lognormal standard deviation; both M and SD are corrected for non-detect values.

TKN		2008			2009			2010			2011			2012/2013		
Site	Name	n	M	SD	n	M	SD	n	M	SD	n	M	SD	n	M	SD
1	**PCAN**	6	0.21	0.24	6	0.23	0.28	7	0.214	0.182	7	0.23	0.21	27	0.23	0.53
2	**PLNC**	8	0.5	0.02	8	0.5	0.03	8	0.5	0.008	8	0.5	0.06	26	0.25	0.38
3	PNAT	8	0.5	0.04	7	0.5	0.09	8	0.5	0.092	7	0.5	0.12	26	0.36	0.31
4	**PBOX**	8	0.5	0.06	7	0.5	0.04	7	0.5	0.025	8	0.5	0.1	25	0.47	0.32
5	PARCH	0	--	--	0	--	--	0	--	--	0	--	--	26	3.44	0.39
6	**PFOS**	4	1.17	0.22	4	0.91	0.22	4	0.551	0.253	4	0.5	0.02	28	1.14	0.43
7	FSPUR	1	0.96	--	4	1.08	0.18	4	0.847	0.191	4	0.5	0.06	22	1.06	0.37
8	**FERN**	9	1.49	0.14	4	1.36	0.18	3	1.995	0.281	4	0.74	0.29	28	1.29	0.12

Table 11: NO_3 distribution parameters for data sets from 2008 – 2013; N = number of samples in dataset, M = median, SD = lognormal standard deviation; both M and SD are corrected for non-detect values.

NO_3		2008			2009			2010			2011			2012/2013		
Site	Name	n	M	SD	n	M	SD	n	M	SD	n	M	SD	n	M	SD
1	**PCAN**	6	0.03	0.67	6	0.01	0.56	7	0.028	0.637	7	0.02	0.3	28	0.02	0.55
2	**PLNC**	48	0.15	0.38	43	0.08	0.27	43	0.13	0.359	47	0.09	0.32	27	0.07	0.33
3	PNAT	44	0.16	0.41	35	0.14	0.33	38	0.155	0.395	42	0.23	0.47	27	0.63	0.37
4	**PBOX**	42	0.29	0.43	35	0.18	0.4	36	0.15	0.409	44	0.35	0.54	26	0.38	0.51
5	PARCH	0	--	--	0	--	--	0	--	--	0	--	--	26	1.22	0.39
6	**PFOS**	4	1.32	0.33	4	0.63	0.29	4	0.455	0.495	4	0.56	0.3	28	1.13	0.34
7	FSPUR	1	1.84	--	4	1.99	0.28	4	1.59	0.468	4	1.04	0.38	22	2.22	0.16
8	**FERN**	4	5.57	0.14	3	3.57	0.1	4	3.35	0.145	4	4.13	0.15	29	4.77	0.11

Table 12: TN distribution parameters for data sets from 2008 – 2013; N = number of samples in dataset, M = median, SD = lognormal standard deviation; both M and SD are corrected for non-detect values.

TN		2008			2009			2010			2011			2012/2013		
Site	Name	n	M	SD	n	M	SD	n	M	SD	n	M	SD	n	M	SD
1	**PCAN**	6	0.23	0.23	6	0.27	0.27	7	0.265	0.15	7	0.25	0.19	28	0.25	0.54
2	**PLNC**	7	0.61	0.07	8	0.62	0.06	8	0.665	0.059	8	0.65	0.08	27	0.38	0.33
3	PNAT	8	0.85	0.09	7	0.77	0.1	8	0.749	0.133	7	0.92	0.15	27	1.09	0.23
4	**PBOX**	8	0.91	0.16	7	0.8	0.1	7	0.7	0.131	7	0.86	0.21	26	1.23	0.31
5	PARCH	0	--	--	0	--	--	0	--	--	0	--	--	26	3.09	0.37
6	**PFOS**	4	2.73	0.26	4	1.63	0.25	4	1.061	0.322	4	1.12	0.16	29	2.07	0.28
7	FSPUR	1	2.92	--	4	3.2	0.2	4	2.477	0.291	4	1.59	0.22	23	3.09	0.14
8	**FERN**	4	1.84	0.13	3	5.4	0.12	4	4.816	0.159	4	4.94	0.17	29	5.94	0.09

Table 13: TP distribution parameters for data sets from 2008 – 2013; N = number of samples in dataset, M = median, SD = lognormal standard deviation; both M and SD are corrected for non-detect values.

TP		2008			2009			2010			2011			2012/2013		
Site	Name	n	M	SD	n	M	SD	n	M	SD	n	M	SD	n	M	SD
1	**PCAN**	6	0.01	0.36	6	0.02	0.26	7	0.018	0.262	7	0.02	0.28	27	0.031	0.54
2	**PLNC**	53	0.01	0.17	50	0.03	0.08	51	0.025	0.179	12	0.05	0.03	26	0.032	0.33
3	PNAT	49	0.06	0.21	42	0.05	0.12	45	0.046	0.04	11	0.05	0.12	26	0.058	0.23
4	**PBOX**	48	0.05	0.17	42	0.05	0.08	43	0.043	0.046	11	0.04	0.06	25	0.056	0.31
5	PARCH	0	--	--	0	--	--	0	--	--	0	--	--	26	0.61	0.37
6	**PFOS**	4	0.83	0.12	4	1.02	0.33	4	0.59	0.455	4	0.26	0.19	28	0.35	0.28
7	FSPUR	1	0.24	--	4	0.36	0.22	4	0.516	0.371	4	0.25	0.07	22	0.19	0.14
8	**FERN**	4	0.48	0.1	3	0.77	0.21	4	0.711	0.118	4	0.69	0.25	28	0.37	0.09

Table 14: Anthropogenic predictors for Point Sources/Facilities.

Point Sources		# AFOs	# WWTPs	#AFOs IDW	#WWTPs IDW	# Livestock	Flow Capacity	# Livestock IDW	Flow Capacity IDW
Site	Name	(#)	(#)	(#/km)	(#/km)	(# cows)	(MGD)	(# cows/km)	(MGD/m)
1	**PCAN**	0	1	0.0E+00	1.5E-05	0	0.05	0.0	0.0
2	**PLNC**	1	1	6.7E-05	1.2E-05	1399	0.05	0.1	0.0
3	PNAT	2	2	9.7E-05	1.9E-04	5638	7.05	0.3	1.3
4	**PBOX**	2	2	9.0E-05	1.5E-04	5638	7.05	0.3	1.0
5	PARCH	7	4	2.7E-04	1.3E-03	38071	9	1.3	2.6
6	**PFOS**	8	6	5.8E-04	4.3E-04	41996	26.3	2.5	2.2
7	FSPUR	16	9	9.7E-04	3.2E-04	63301	29.16	2.3	0.8
8	**FERN**	22	10	6.3E-04	4.3E-04	95404	43.86	2.6	4.2

Table 15: Anthropogenic predictors for Land Use.

Land Use		% Agriculture Land Use	% Urban Land Use
Site	Name	(%)	(%)
1	**PCAN**	0.3	0.7
2	**PLNC**	0.7	1.0
3	PNAT	2.6	2.5
4	**PBOX**	2.6	2.5
5	PARCH	6.4	2.6
6	**PFOS**	6.6	2.8
7	FSPUR	11.9	4.0
8	**FERN**	13.3	4.8

Table 16: Hydrologic predictor, Annual maximum daily flow (cfs), for five sites with flow data.

Site	Name	Annual Maximum Daily Flow (cfs)				
		2008	2009	2010	2011	2012/2013
1	**PCAN**	2200	1740	3910	3430	828
2	**PLNC**	1610	1630	3700	2880	409
4	**PBOX**	1160	1360	3520	2930	344
6	**PFOS**	1020	1390	3830	2980	176
8	**FERN**	1220	1170	3050	2440	197

Table 17: Hydrologic predictor, Annual mean daily flow (cfs) for five sites with flow data.

Site	Name	Annual Mean Daily Flow (cfs)				
		2008	2009	2010	2011	2012/2013
1	**PCAN**	373.7	290.1	446.9	509.1	144.1
2	**PLNC**	91.4	127.9	252.8	344.7	81.3
4	**PBOX**	56.2	95.7	220.1	277.6	58.9
6	**PFOS**	46.3	106.8	236.4	287.3	47.1
8	**FERN**	92.8	157.5	281.2	308.7	65.9

Table 18: Hydrologic predictor, Annual precipitation (inches) for five sites with flow data.

Site	Name	Annual Precipitation (inches)				
		2008	2009	2010	2011	2012/2013
1	**PCAN**	16.7	14.9	15.3	17.8	10.9
2	**PLNC**	15.3	19.3	16.1	16.2	11.1
3	PNAT	15.9	17.6	16.0	15.8	9.2
4	**PBOX**	15.9	17.6	16.0	15.8	9.2
5	PARCH	15.9	17.6	16.0	15.8	9.2
6	**PFOS**	14.6	15.7	16.2	16.5	9.4
7	FSPUR	17.1	15.1	17.0	13.0	8.4
8	**FERN**	16.3	15.9	16.4	13.3	8.6

APPENDIX D: Multiple Linear Regression Model Results

Table 19: R^2 and adjusted R^2 results for regressions of Medians for Dataset 2 (5 sites with flow, 2008-2013 years) with three predictive variables: one WWTP/urban, one AFO/agricultural, and one hydrologic (annual mean daily flow).

Num	Predictive Parameters (with annual mean daily flow)		TKN		NO3		TN		TP	
			R^2	Adj. R^2	R^2	Adj. R^2	R^2	Adj. R^2	R^2	Adj. R^2
1	# CAFO	# WWTP	---	---	---	---	---	---	---	---
6	# CAFO	#WWTP IDW	0.79	0.76	0.90	0.88	0.85	0.83	0.91	0.89
7	# CAFO	WWTP capacity	---	---	---	---	---	---	---	---
8	# CAFO	WWTP capacity IDW	---	---	---	---	---	---	---	---
9	# CAFO	% Urban Land Use	---	---	---	---	---	---	---	---
10	#CAFO IDW	# WWTP	---	---	---	---	---	---	---	---
2	#CAFO IDW	#WWTP IDW	---	---	---	---	---	---	---	---
11	#CAFO IDW	WWTP capacity	---	---	---	---	---	---	---	---
12	#CAFO IDW	WWTP capacity IDW	0.80	0.77	0.91	0.89	0.86	0.84	0.90	0.88
13	#CAFO IDW	% Urban Land Use	**0.81**	**0.78**	**0.93**	**0.92**	**0.89**	**0.87**	0.90	0.89
14	# cattle	# WWTP	---	---	---	---	---	---	---	---
15	# cattle	#WWTP IDW	0.78	0.75	0.88	0.87	0.84	0.82	0.91	0.89
3	# cattle	WWTP capacity	---	---	---	---	---	---	---	---
16	# cattle	WWTP capacity IDW	---	---	---	---	---	---	---	---
17	# cattle	% Urban Land Use	0.79	0.76	0.92	0.91	0.87	0.85	0.75	0.71
18	# cattle IDW	# WWTP	---	---	---	---	---	---	---	---
19	# cattle IDW	#WWTP IDW	---	---	---	---	---	---	---	---
20	# cattle IDW	WWTP capacity	---	---	---	---	---	---	---	---
4	# cattle IDW	WWTP capacity IDW	0.79	0.76	0.90	0.89	0.86	0.84	0.90	0.88
21	# cattle IDW	% Urban Land Use	0.80	0.78	0.93	0.92	0.88	0.87	0.90	0.89
22	% Ag Land Use	# WWTP	---	---	---	---	---	---	---	---
23	% Ag Land Use	#WWTP IDW	0.79	0.77	0.91	0.89	0.86	0.84	**0.91**	**0.89**
24	% Ag Land Use	WWTP capacity	---	---	---	---	---	---	---	---

Table 19 continued.

25	% Ag Land Use	WWTP capacity IDW	---	---	---	---	---	---	---	---
5	% Ag Land Use	% Urban Land Use	---	---	---	---	---	---	---	---

Table 20: R^2 and adjusted R^2 results for regressions of Standard Deviations for Dataset 1 (8 sites, 2012/2013 year) with two predictive variables: one WWTP/urban, one AFO/agricultural.

Num	Predictive Parameters (with annual mean daily flow)		TKN		NO3		TN		TP	
			R^2	Adj. R^2	R^2	Adj. R^2	R^2	Adj. R^2	R^2	Adj. R^2
1	# CAFO	# WWTP	---	---	---	---	---	---	---	---
6	# CAFO	#WWTP IDW	---	---	0.79	0.69	---	---	---	---
7	# CAFO	WWTP capacity	---	---	---	---	---	---	---	---
8	# CAFO	WWTP capacity IDW	---	---	**0.80**	**0.70**	---	---	---	---
9	# CAFO	% Urban Land Use	---	---	0.79	0.69	---	---	---	---
10	#CAFO IDW	# WWTP	---	---	---	---	---	---	---	---
2	#CAFO IDW	#WWTP IDW	---	---	---	---	---	---	---	---
11	#CAFO IDW	WWTP capacity	---	---	---	---	---	---	---	---
12	#CAFO IDW	WWTP capacity IDW	---	---	---	---	---	---	---	---
13	#CAFO IDW	% Urban Land Use	**0.85**	**0.77**	---	---	0.82	0.74	0.79	0.69
14	# cattle	# WWTP	---	---	---	---	---	---	---	---
15	# cattle	#WWTP IDW	---	---	---	---	---	---	---	---
3	# cattle	WWTP capacity	---	---	---	---	---	---	---	---
16	# cattle	WWTP capacity IDW	---	---	---	---	---	---	---	---
17	# cattle	% Urban Land Use	---	---	---	---	**0.84**	**0.76**	---	---
18	# cattle IDW	# WWTP	---	---	---	---	---	---	---	---
19	# cattle IDW	#WWTP IDW	---	---	---	---	0.58	0.36	---	---
20	# cattle IDW	WWTP capacity	---	---	---	---	---	---	---	---
4	# cattle IDW	WWTP capacity IDW	---	---	---	---	---	---	0.70	0.56
21	# cattle IDW	% Urban Land Use	---	---	---	---	---	---	0.78	0.67
22	% Ag Land Use	# WWTP	---	---	---	---	---	---	---	---
23	% Ag Land Use	#WWTP IDW	---	---	0.78	0.68	---	---	**0.79**	**0.68**
24	% Ag Land Use	WWTP capacity	---	---	---	---	---	---	---	---
25	% Ag Land Use	WWTP capacity IDW	---	---	0.77	0.66	---	---	---	---
5	% Ag Land Use	% Urban Land Use	---	---	---	---	---	---	---	---

APPENDIX E: Cache La Poudre River Sampling Site Locations

Site 1: PCAN

PCAN (river mile 54.6) is at the mouth of Poudre Canyon at the site of Colorado Division of Water Resources real-time stage/discharge gage CACHE LA POUDRE AT CANYON MOUTH NEAR FORT COLLINS (Abbreviation: CLAFTCCO). Access is from the first left after entering Poudre Canyon from U.S. highway 287 N (despite private road signs). Samples are taken on the left bank.

Figure 20: PCAN Sample Site; (a) cross-stream (b) downstream views.

Site 2: PLNC

PLNC (river mile 43.2) site is located in the City of Fort Collins near old town at the USGS real-time gage CACHE LA POUDRE RIVER AT FORT COLLINS, CO (#06752260). It is upstream of all WWTPs and most of the Fort Collins stormwater runoff, and little agricultural return flow contributes. It is sampled upstream of the Lincoln Ave. Bridge on the left bank.

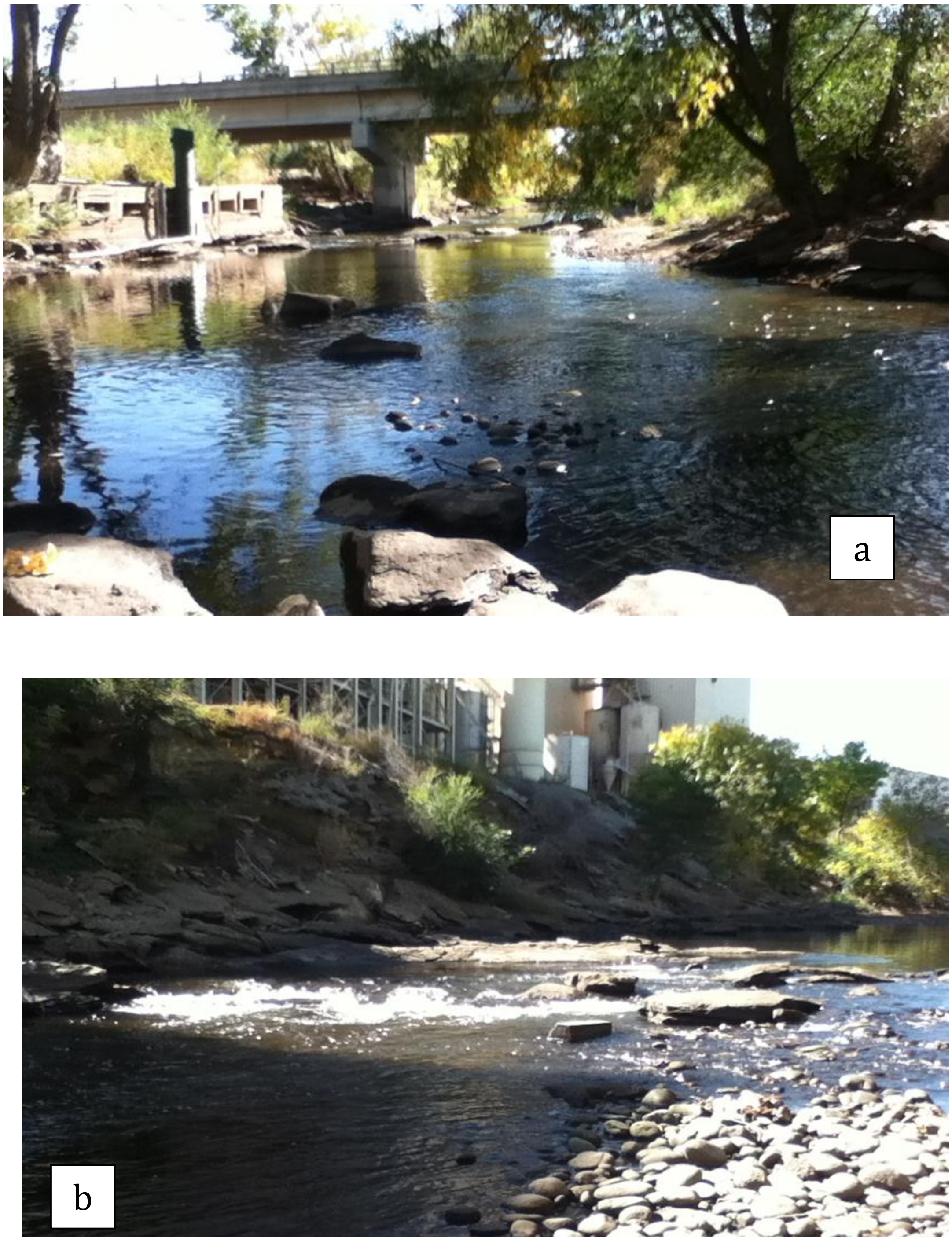

Figure 21: PLNC Sampling Site (a) downstream and (b) upstream views

Site 3: PNAT

PNAT (river mile 38) is at the Nature Center in the Fort Collins. It is downstream of the Mulberry WWTP and Spring Ck. which drains much of Fort Collins stormwater. It has no additional ag. return flows. Access is from a parking lot adjacent to the Drake WWTP at the end of Sharp Point Dr. off of Prospect Rd. Samples are taken from the right bank of the river off of the pedestrian trail.

Figure 22: PNAT Sampling Site (a) cross-stream and (b) upstream views.

Site 4: PBOX

PBOX (river mile 37) is in Fort Collins at the USGS stage/discharge gage CACHE LA POUDRE RIV AB BOXELDER CK NR TIMINATH, CO (#06752280). Drake WWTP does not contribute effluent here. PBOX is just upstream of the Boxelder WWTP. Access is through the Boxelder WWTP, behind a locked gate at the far side of the treatment plant. Samples are taken from the left bank.

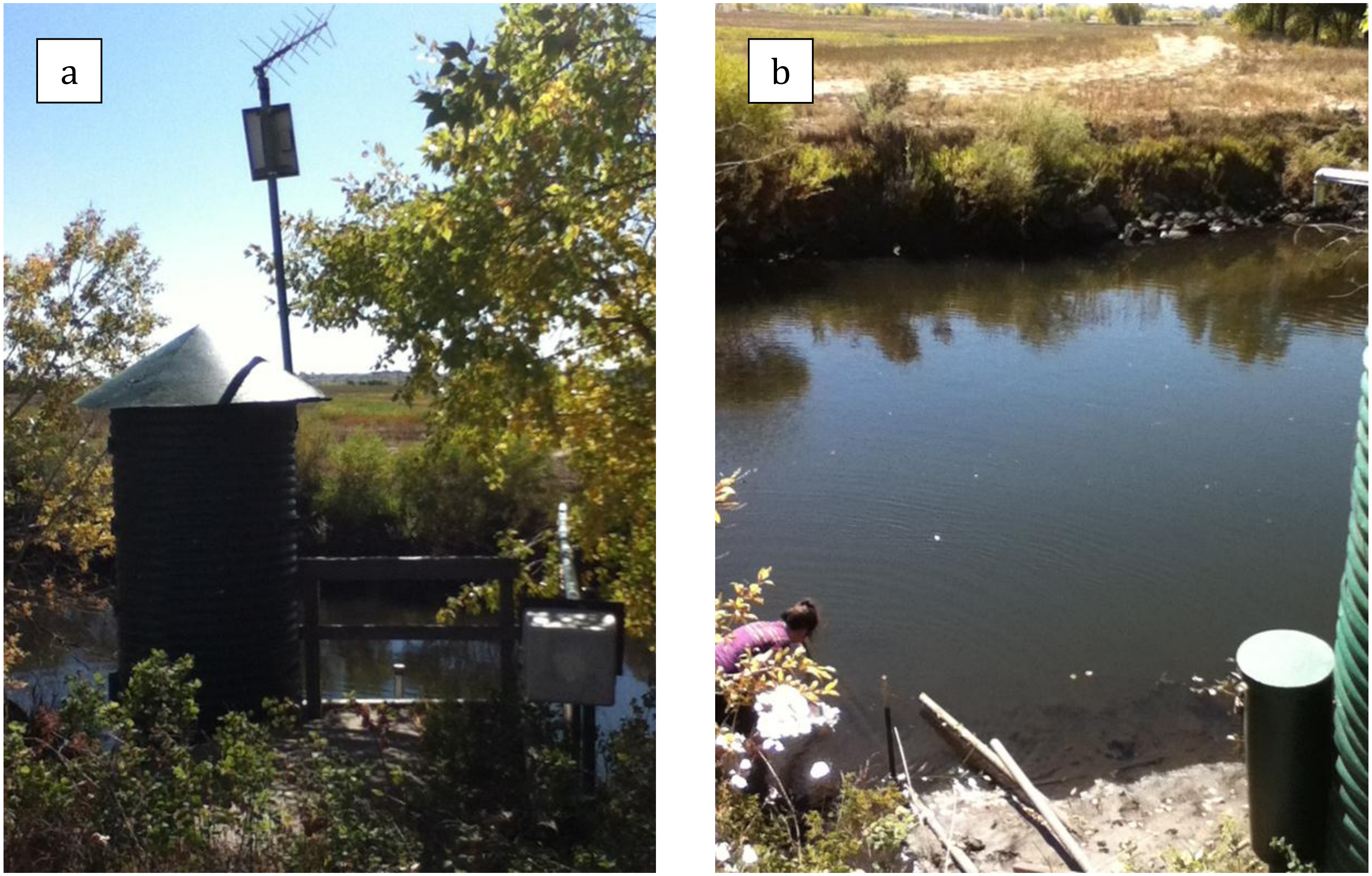

Figure 23: PBOX Sampling Site (a) cross-stream and (b) downstream views

Site 5: PARCH

PARCH (river mile 36.5) is at the Archery Range in Fort Collins downstream of the Boxelder WWTP discharge and Boxelder Creek tributary. The site is across from the Fort Collins Archery Range at the end of the I-25 SW Frontage Rd. south of Prospect Rd. Samples are taken upstream of the abandoned bridge on the left bank.

Figure 24: PARCH Sampling Site (a) downstream and (b) cross-stream views.

Site 6: PFOS

PFOS (river mile 32.5) is at the River Bluffs Natural Area west of Windsor, CO. It is downstream of the Fossil Creek confluence, which includes effluent from the Drake WWTP and S. Fort Collins WWTP. Access is through the parking lot for the River Bluffs Natural Area off of Co-32E (merges with Co-68 ½). Samples are taken downstream of the pedestrian bridge on the left bank.

Figure 25: PFOS Sampling Site (a) cross-stream and (b) downstream views

Site 7: FSPUR

FSPUR (river mile 14.5) is at 59th St. Bridge in west Greeley. It is downstream of the City of Windsor WWTP, Carestream WWTP, AFOs, agricultural return flow, and some stormwater. Assess is at the downstream side of the 59th St. Bridge. Samples are collected from the right bank of the river downstream of the bridge.

Figure 26: FSPUR Sampling Site (a) upstream and (b) downstream views.

Site 8: FERN

FERN (river mile 2.2) is at the eastern side of Greeley at the Fern Ave. Bridge at the Colorado Division of Water Resources stage/discharge gage CACHE LA POUDRE RIVER AT GREELEY WASTEWATER PLANT (Abbreviation: CLAWASCO). It is downstream of the Greeley WWTP, Greeley's stormwater, and agricultural return flows. Access is from the Fern Ave. south of E 8th St. in Greely. Samples are taken from the right bank downstream of Fern Ave. Bridge.

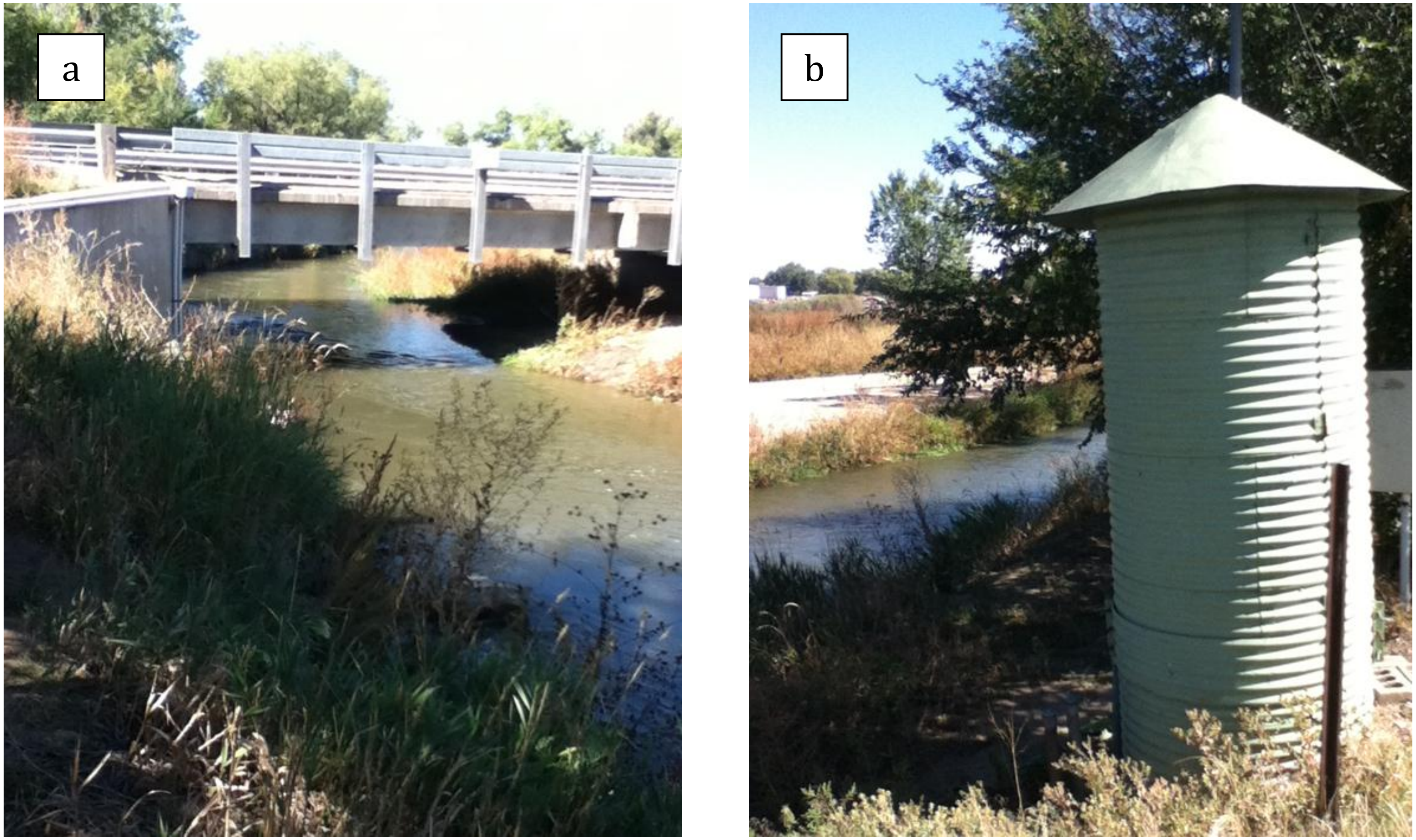

Figure 27: FERN Sampling Sites (a) upstream and (b) downstream views

Table 21: Longitude and latitude coordinates of the 8 sampling sites.

Sample Site	Number	X Decimal Degree	Y Decimal Degree
PCAN	1	-105.22409923700	40.66455286970
PLNC	2	-105.06976645900	40.58895609660
PNAT	3	-105.02159469800	40.55984342310
PBOX	4	-105.01056326500	40.55195514730
PARCH	5	-105.00068722100	40.54702356900
PFOS	6	-104.96168207800	40.48633083960
FSPUR	7	-104.77323424100	40.44572222050
FERN	8	-104.63992201200	40.41763802380

APPENDIX F: Non-parametric Analysis of Sample Size

A non-parametric method for estimating the annual number of samples is necessary when no distributions are appropriate to describe a dataset. This was a concern for the nutrient datasets from the CLP River, which did not consistently fit a distribution when non-detect values were included. The following analysis uses a non-parametric method to predict the required number of samples for TKN, NO_3, TN, and TP at the 8 sampling locations on the CLP River, and compares these results to the lognormal parametric method.

Methodology

The non-parametric method employs bootstrapping of the original dataset and the non-parametric sign test to evaluate whether the median value of the dataset is less than or greater than the given standard. Bootstrapping is performed by randomly selecting a number (n) of samples from the original dataset. This was done for n = 2 to n = N, where N is the total number of samples in the dataset. One thousand repetitions of the bootstrapping were performed for each n and results were averaged in order to reduce noise.

The sign test is a procedure that tests hypotheses for significant differences between the standard and median (Montgomery et al., 2007). By definition, there is 0.5 probability that any given point from a continuous distribution will be above or below the median. To perform the sign test the number of positive differences between the standard and median are calculated for a given dataset. The binomial distribution is then used to find the p value for the number of positive differences compared to a 0.5 probability. For samples where the original median is less than the standard, the sign test was used to determine if the median is significantly less. For samples where the original median is greater than the standard, the sign test was used to determine if the median is significantly greater. The null and alternative hypothesis for these two cases are:

For Median < Standard,

$$H_o\text{: Median = Standard}$$

$$H_1\text{: Median < Standard}$$

For Median > Standard,

$$H_o\text{: Median = Standard}$$

$$H_1\text{: Median > Standard}$$

A P value less than $\alpha = 0.05$ was deemed sufficient to reject the null hypothesis. The required number of samples was defined as the smallest n for which the P value < α. For some sites and parameters the P value was never less than α, and the required number of annual samples was defined as N, though if fact is could be much higher.

Results

The results are summarized in Figure 12 and Table 19. The P values produced for various *n*'s through the bootstrapping procedure are shown in Figure 10 for each nutrient parameter. Table 19 summarizes the required number of annual samples predicted with the non-parametric method and the number of samples calculated with the lognormal method for comparison.

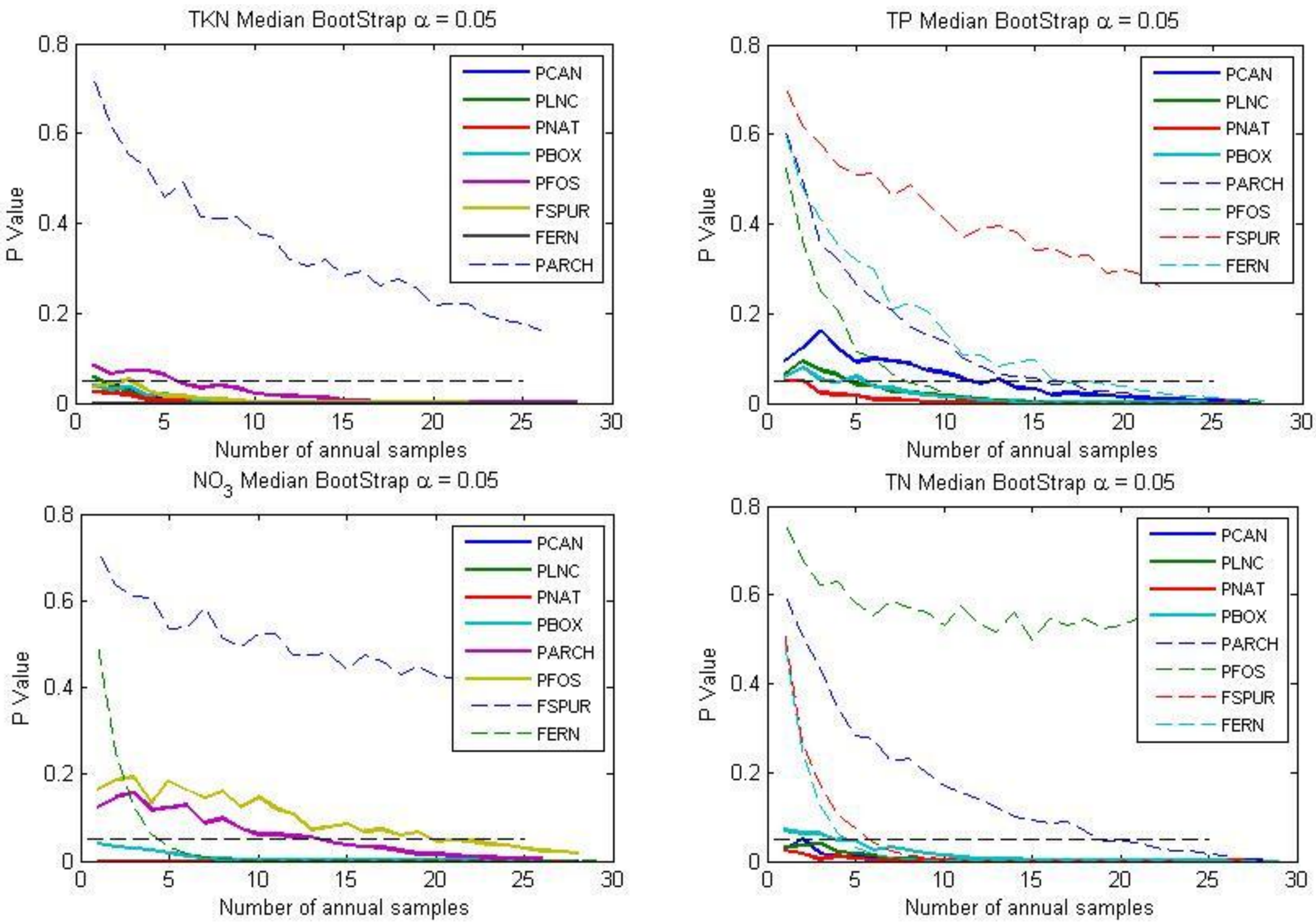

Figure 28: Non-parametric calculation of annual number of samples based on boot-strapping and sign test of the median with a significance level of 0.05. Sites with an original median < standard are shown as a solid line, and those sites with an original median > standard are dashed lines.

Table 22: Required number of annual samples based on Non-parametric method and Lognormal method; for the Non-parametric method, those sites where the predicted number of samples was limited by the maximum number in the dataset are italicized.

#	Site	Non-Parametric (n)				Lognormal (n)			
		TKN	NO_3	TN	TP	TKN	NO_3	TN	TP
1	PCAN	1	2	1	12	1	1	2	3
2	PLNC	2	2	1	4	1	1	1	2
3	PNAT	1	1	1	1	1	2	3	2
4	PBOX	1	3	4	3	2	2	7	3
5	PARCH	26	18	21	15	120	10	12	3
6	PFOS	5	29	26	7	7	6	1259	7
7	FSPUR	1	25	7	22	4	44	2	68
8	FERN	1	3	4	16	2	1	1	3

Discussion

The results from the non-parametric approach to annual sample numbers calculations show some of the strengths and limitations of this method when compared to the same approximations using the lognormal approach. The non-parametric and lognormal methods predict high sampling requirements at the same sties, and with few exceptions the between the two methods the same sites were predicted to require a minimum number of samples (Table 19). The agreement between sample numbers is strongest for TKN and TP. However for TP, the non-parametric method predicts n > 10 for PCAN and FERN, which had just one required sample by the lognormal method. This reflects the emphasis of standard deviation on the required number of samples by the non-parametric method (Figure 13 for reference). Having higher standard deviation causes the non-parametric method to predict a higher ***n*** than the lognormal method. This is also evident in the results of NO_3 and TN. For NO_3-N, the non-parametric method predicts 8 and 23 additional samples for PARCH and PFOS respectively, despite that the median is still relatively low compared to the standard. The larger standard deviation which encompasses the standard accounts for the larger sample number. This also accounts for the larger sample number predicted by the non-parametric method for TN at PARCH.

The non-parametric method can be relied upon to identify sites with high sampling needs, however when using the non-parametric method the exact number of annual samples is limited by the maximum number of samples in the original dataset. There is an example of this for every parameter. Considering TKN, both methods predicted that PARCH would require a high number of annual samples, however the lognormal approach predicted 120 samples, while the non-parametric method arbitrarily recommends 26 since this the total number of samples in the original dataset. An extrapolation method would need to be applied to these situations to get an estimate of the true number of samples required.

The presence of noise in the non-parametric method results is apparent in Figure 12. The bootstrapping method of estimating the median for different numbers of samples produces noise in the results. This is limited by repeating the bootstrap for 1000 iterations as averaging the results; however the noise is still present. As a result, the predicted number of samples for each site and parameter are approximate, and variation of 1 or 2 samples from the predicted n would not be surprising in subsequent repetitions of the analysis.

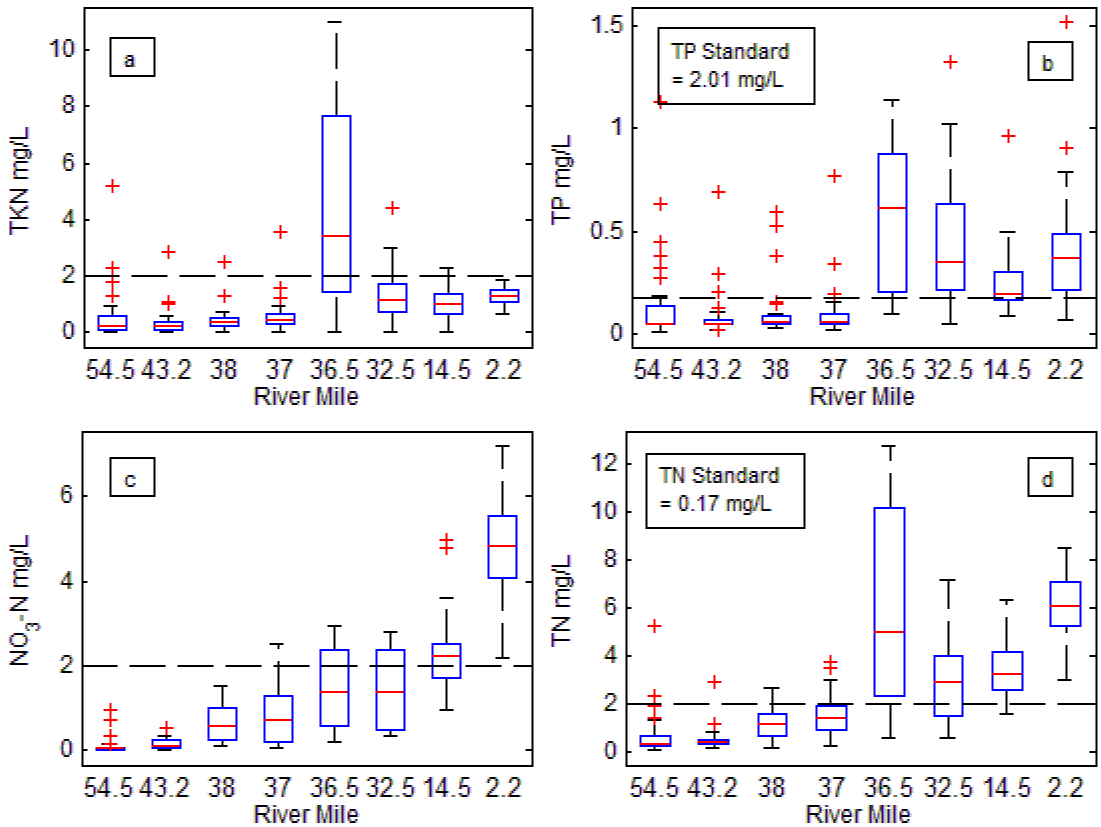

Figure 29: Boxplot of nutrient parameters for the 2012/2013 dataset.