THESIS

CHARACTERIZATION OF THE VULNERABILITY OF URBAN STREAMS TO NUTRIENT POLLUTION UNDER VARYING FLOW REGIMES

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ABSTRACT

CHARACTERIZATION OF THE VULNERABILITY OF URBAN STREAMS TO NUTRIENT POLLUTION UNDER VARYING FLOW REGIMES

Nutrient pollution is a primary cause of water quality impairment in streams in the United States and throughout the world. Regulatory approaches under the Clean Water Act, such as water quality standards and the Total Maximum Daily Load program, aim to improve water quality. In this study, novel probabilistic methods are developed to characterize vulnerability to nutrient pollution along urban streams and to assess risk of water quality impairment under varying hydrologic conditions. Vulnerability is defined as the probability that ambient conditions exceed desired water quality standards. Both EPA ecoregional and state-level targets are included in the analysis. Specifically, the study i) explores relationships between urban influences and risk to nutrient pollution; and ii) expands on the load duration curve framework to quantify vulnerability to nutrient pollution as a function of flow exceedance probability. The study objectives are examined at 20 stream locations in four ecohydrologically different regions across the United States, including Denver, CO; Phoenix, AZ; Portland, OR; and Baltimore, MD. Total phosphorus (TP) and total nitrogen (TN) water quality data collected between 1990 and 2018 with daily discharge measurements are utilized in the analysis. Indicators of urban influence include wastewater treatment capacity, urban land cover, impervious surfaces, and population density. In general, study locations exhibit vulnerability (greater than 5%) to nutrient impairment across urban gradients, including some relatively undisturbed monitoring locations. Nearly 30%

of TP sites and 45% of TN sites are impaired under state level regulation. Results indicate that incorporation of more stringent EPA ecoregional targets lead to higher vulnerability estimates than those corresponding to the state-level targets. Over 70% of TP sites and 55% of TN sites with state level standards are characterized as vulnerable (greater than 5%) when EPA goals are considered. Patterns of impairment through urban gradients are more evident in arid regions with wastewater-dominated river flows, specifically in Denver and Phoenix, than humid regions. Multiple linear regressions between indicators of urban influence and vulnerability provide strong ($R^2 > 0.7$) relationships for most monitoring locations. Inverse distance weighted annual wastewater treatment facility flow capacity and urban land cover are the most significant predictors. However, the most important nonpoint source exploratory variable differ from site to site. More monitoring locations are required to determine model significance. In addition, assessment of nutrient pollution vulnerability using the enhanced load duration approach show that higher vulnerability to impairment tends to occur under consistent hydrologic conditions within each city. For example, high vulnerability to TN and TP impairments are observed under low flow conditions at sites within and around the Denver incorporated area. Conversely, nutrient levels during high flow conditions are more likely to exceed the TN and TP standards in Phoenix, Baltimore, and Portland. Many locations are vulnerable to nutrient pollution (greater than 5%) under all possible flow scenarios, especially at downstream monitoring locations. Approximately 85% of TP sites and 70% of TN sites are vulnerable under all flow conditions assuming EPA water quality goals. The methodology developed in this study can be used to probabilistically quantify the vulnerability to water quality impairments in streams and to identify hydrologic conditions under which higher vulnerabilities prevail.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Water quality is affected when watersheds undergo alterations in land use (Wang et al., 2004; Omernik et al., 2016; Meter and Basu, 2017; Tasdighi et al., 2017). Urbanization, industrialization, and conversion of natural land cover to agriculture have led to cultural eutrophication (anthropogenic inputs of additional nutrients into waterbodies), a primary factor that has resulted in water quality degradation in U.S. surface waters. Though nutrients are important in maintaining health and diversity in water systems, excessive amounts can result in overgrowth of plant life, reduction of biological integrity, and increase human health risks associated with harmful algal blooms (Fuhrer et al., 1999; Boesch et al., 2001; USEPA, 2001). Excess nutrient levels, mainly total phosphorus (TP) and total nitrogen (TN), are the primary cause of impairment in 40% of U.S. rivers (USEPA, 2000).

Impairments are identified when water quality fails to meet designated use criteria for water bodies. In an attempt to mitigate impaired waters, the Clean Water Act (CWA) was created to set a national level goal to achieve water quality, wherever attainable, that protects wildlife and recreation in and on the water through the implementation of water quality criteria and Total Maximum Daily Load (TMDL) development. States were given the responsibility of establishing standards within their boundaries and allocating point source pollutant loads for impaired waters that were achievable and met designated use criteria of the CWA.

While impairments are already being observed across the nation for various pollutants, people and their impact on water quality through land use changes is expected to become even more problematic with population growth. For this reason, predicting risk to nutrient pollution is important. In this research, vulnerability to nutrient pollution is analyzed across four urban gradients and at all probable flow conditions to target conditions and potential sources of pollution leading to impairment. Key outcomes of this research show that, in general, monitoring locations exhibit high vulnerability to impairment across urban gradients and flow regime, especially when the Environmental Protection Agency's (EPA) ecoregional criteria are utilized in the framework. While urban land cover and wastewater treatment facility capacity most often explain vulnerability with strong correlation, predictor variables are not consistent from city to city. In addition, the cities of interest exhibit the same flow condition in which impairment occurs through urban gradients. The methodology developed in this study can be used to probabilistically quantify vulnerability to water quality impairments in streams and to identify hydrologic conditions under which higher vulnerabilities prevail. This work contributes to existing literature in environmental risk analysis to help understand urban influences and flow conditions that lead to impairment to assist watershed managers in meeting the goals of the Clean Water Act.

1.2 UNDERSTANDING WATER QUALITY

Approximately two-thirds of Americans reside within incorporated places (Cohen, 2015). As cities continue to grow, they will increasingly exert stress on nearby water bodies. Extensive efforts have been made to understand the current state of surface waters and anthropogenic influences on water quality degradation across the United States and around the world. Two common methods to link urban influences to vulnerability are expanded to include the characterization of vulnerability. The first method links influences and ambient water quality degradation using multiple linear regression techniques. The second method builds on the conventional load duration curve framework to investigate impairment across all flow conditions by comparing pollutant loads to loading capacity defined by water quality targets.

1.2.1 MULTIPLE LINEAR REGRESSION ANALYSES

Multiple linear regression analyses have been conducted to link anthropogenic activities with water quality degradation. Some studies conclude that strong and significant relationships exist between percentage of urban land use and nutrient concentrations in surface waters (Fuhrer et al., 1999; Wang et al., 2004; Omernik et al., 2016; Tasdighi et al., 2017), though anthropogenic effects may be disproportionately greater than the urban land cover within a watershed (Wickham et al., 2008). Others suggest that waste discharge is the most obvious pollutant in urban settings, where low flows are dominated by effluent (Duda et al., 1982; Williams et al., 2014). However, most studies agree that it is a combination of upstream influences, varying from city to city, that lead to water quality impairment at any given location (Klein, 1979; McMahon and Cuffney, 2000; McMahon, 2012). One study across nine metropolitan regions conducted by the United States Geological Survey demonstrated regional difference in urban effects on streams, suggesting that additional research is needed determine the causes for these differences (Brown et al., 2009). While these analyses are important in identifying primary factors that explain increased pollutant degradation, they do not incorporate risk of impairment into the framework. Rather than relating indicators of urban intensity to ambient water quality, this study related vulnerability to nutrient impairment to urban influences.

1.2.2 LOAD DURATION CURVE FRAMEWORK

Current water quality standards and TMDLs generally focus on a single numeric water quality target in combination with a dominant discharge or design flow (Cleland, 2003). Load duration curves (LDC) are a popular method used by states to assess impairment across all flow conditions and develop TMDLs. In the LDC approach, the frequency and magnitude of numeric target exceedances, allowable loadings, and size of loading reductions can be visually presented. Typically, flow exceedance probabilities are broken into five categories (low flow [90%-100% exceedance], dry [60%-90% exceedance], mid-range [40%-60% exceedance], moist [10%-40% exceedance], and high flows [0%-10% exceedance]), in which impairment is assessed (Cleland, 2002, 2003; USEPA, 2007b; Strickland and Korleski, 2009). Patterns of impairment can be examined to determine potential sources of pollution. For example, exceedances observed under low flow conditions often indicate point source pollution, while impairments under high flow conditions often indicate non-point sources of pollution (Cleland, 2002, 2003; USEPA, 2007b; Strickland and Korleski, 2009). Given a pollutant of interest and potential sources of upstream pollution, this framework is useful to target specific point and non-point sources of pollution leading to impairment and remediation opportunities. Various charts are available through the EPA to link flow conditions in which impairment is occurring to pollution sources and implementation strategies. While this approach considers hydrologic condition, the research presented in this thesis aims to quantify vulnerability to nutrient impairment across all flow exceedances, rather than within flow categories.

1.3 RESEARCH OBJECTIVES

The thesis presented here is composed of four chapters. The first chapter provides literature review of previous methods used for linking water quality to urban influences and risk assessment of waters around the U.S. and around the world. The second chapter's objectives include (i) developing a framework for calculating vulnerability to water quality impairment for TP and TN across four urban gradients, (ii) investigating differences in vulnerability to water quality impairment between EPA ecoregional criteria and state level regulation, and (iii) evaluating factors that influence pollutant concentrations and vulnerability in urban streams. Four properties of water quality standards are incorporated into this frame work: allowable excursion frequency, number of annual samples, and a numeric target that defined quantiles of measured data are compared. Multiple linear regression analyses are conducted to describe ambient nutrient concentrations and vulnerability as a function of urban influences, including cumulative wastewater treatment capacity, population density, urban land use percentage, and impervious percentage.

The third chapter expands on the load duration curve framework to quantify vulnerability to nutrient pollution as a function of flow exceedance probability. Specific objectives of the third chapter include (i) developing a methodology to characterize uncertainty in empirical LDCs, (ii) examining trends in vulnerability to nutrient pollution in four ecohydrologically different regions across the United States, and (iii) exploring hydrologic conditions which urban streams have a greater likelihood of exceeding nutrient standards. In addition to identifying vulnerability to nutrient impairment across all possible flow quantities, the load and concentration reduction required to achieve 95% reliability (5% vulnerability) es also computed as a function of flow exceedance probability. The final chapter summarizes the key results of chapters two and three while providing a general synopsis of this research.

1.4 CHARACTERIZING VULNERABILITY TO NUTRIENT POLLUTION

A statistical approach to the characterization of nutrient impairment was developed in this study to understand risk of surpassing water quality standards across urban gradients at under different flow regimes. In many cases, sufficient water quality data is lacking due to the expensive nature of water quality monitoring. For this reason, the methods developed in this study use available ambient water quality at 20 locations in four U.S. cities to estimate pollutant concentration and loading. Then, a student's t distribution is applied to quanitfy the probability of expected values exceeding water quality targets.

In the first part of the research (Chapter 2), observed nutrient concentrations are fit to a lognormal distribution. Expected values based on the distribution are computed and compared with numeric targets. Typical properties of water quality standards are considered, including frequency of excursion, annual samples collected, a numeric target, and a quantile of ambient water quality that is compared to the numeric target. The likelihood of the quantile value exceeding the numeric target es determined using a student's t distribution, incorporating annual number of samples in the degree of freedom. Then, a binomial distribution is assumed to integrate excursion frequency into the analysis. Vulnerability is compared between EPA ecoregional targets and state level standards to assess the feasibility of meeting water quality goals. In addition, a multiple linear regression (MLR) analyses are applied between vulnerability and point and non-point sources of urban pollution to relate impairment to urban influences.

The second part of this research (Chapter 3) utilizes simple linear regression techniques to estimate nutrient loading and vulnerability across all probable flow conditions. Assuming the errors of the linear regression are normally distributed, confidence or prediction intervals of interest are computed and uncertainty understood. Vulnerability to nutrient pollution is defined as the probability of the standard error for the predicted mean load exceeding the numeric target load using a student's t distribution at any flow exceedance probability. Patterns in vulnerability are then analyzed as a function of flow exceedance probability across urban gradients in the four regions to determine which hydrologic conditions had a greater likelihood of surpassing nutrient standards and load reduction necessary to achieve 95% reliability (5% vulnerability).

CHAPTER 2: A NOVEL AND PROBABILISTIC APPROACH TO CHARACTERIZING VULNERABILITY TO NUTRIENT POLLUTION IN URBAN STREAMS

2.1 BACKGROUND

Changes in land use have led to eutrophication of surface water in the United States and around the word. Addition of excess nutrients, primarily total phosphorus (TP) and total nitrogen (TN), from various anthropogenic activities have resulted in degradation of 40% of U.S. rivers (USEPA, 2000). The Clean Water Act (CWA) was established to improve water quality in U.S. surface waters through the development of Total Maximum Daily Loads (TMDL) and water quality standards. Ultimately, states were given the responsibility of creating, implementing, and maintaining TMDLs and water quality standards.

The U.S. Environmental Protection Agency (EPA) established numeric guidelines for important pollutants, including TP and TN, within relatively homogeneous Level III ecoregions to assist States in developing water quality standards. According to this framework, targets were defined as the 25th percentile of a general population within each ecoregion, which are intended to characterize natural conditions (concentrations that would exist without human influences) regardless of feasible attainability (USEPA, 2001). Research has shown nutrient concentrations, even in relatively undisturbed watersheds, often exceed targets proposed by the EPA (Ice and Binkley, 2003; Herlihy and Sifneos, 2008). For this reason, states establish their own numeric targets to more accurately reflect background conditions and the watershed's ability to feasibly attain standards given current technology and mitigation expenses.

In many cases, four primary characteristics define state level water quality standards: annual sampling frequency, frequency of excursion, numeric target, and a quantile (usually median) of measured concentrations to represent annual conditions that is not to exceed the numeric target. Williams et al. showed that more samples are required as ambient concentrations approach water quality standards to achieve a high levels of significance (Williams et al., 2014), therefore, incorporating annual number of samples in the development of water quality is crucial in impaired locations. The EPA recommends specifying an allowable excursion frequency or using a measure of central tendency to account for extraordinary fluctuations in ambient water quality (USEPA, 2001), however, permissible frequencies should allow for aquatic ecosystems to recover from most exceedances (Stephen et al., 1985). Finally, the numeric target itself is developed to meet designated use criteria for surface waters, in which a given quantile of annual measurements cannot surpass.

Little research has been conducted to quantify risk to nutrient pollution. In an attempt to assess the condition of U.S. waters, previous research defined risk as the probability of equaling or exceeding various quantiles (such as median) of observations (Wickham et al., 2008). However, this procedure only identifies relative risk at each monitoring location without consideration for water quality standards that define impairments.

Multiple linear regression analyses have been utilized to relate various urban influences and water quality to better understand conditions that lead to degradation. Some studies conclude that strong and significant relationships exist between percentage of urban land use and nutrient concentrations in surface waters (Fuhrer et al., 1999; Wang et al., 2004; Omernik et al., 2016; Tasdighi et al., 2017), though anthropogenic effects may be disproportionately greater than the urban land cover within a watershed (Wickham et al., 2008). Others suggest that waste discharge is the most obvious pollutant in urban settings, where low flows are dominated by effluent (Duda et al., 1982; Williams et al., 2014). However, most studies agree that it is a combination of upstream influences, varying from city to city, that lead to water quality impairment at any given location (Klein, 1979; McMahon and Cuffney, 2000; McMahon, 2012). These analyses are important in determining primary factors that can explain increased pollutant concentrations in order to meet the goals of the CWA as cities, and their influences, continue to grow.

In this study, risk to nutrient pollution is characterized as a function of both ambient concentration and likelihood of exceeding water quality targets in various regions across the United States. Specific objectives include (i) developing a framework for calculating vulnerability to water quality impairment for TP and TN across four urban gradients, (ii) investigating differences in vulnerability to water quality impairment between EPA ecoregional criteria and state level regulation, and (iii) evaluating factors that influence pollutant concentrations and vulnerability in urban streams. Understanding the relationship between urban activities and risk of water quality impairment is essential in a time where cities are continuing to grow in order to meet and maintain the goals established by the Clean Water Act.

While many previous studies have focused on relating urban intensity to ambient pollutant concentrations, none have developed a probabilistic model that incorporates ambient water quality and water quality standards to understand risk to impairment, applied in multiple ecohydrological regions around the United States. EPA ecoregional targets have been compared to true background conditions, but not incorporated in a probabilistic framework and compared with implemented state level standards. Ultimately, this framework can be used to determine the likelihood of meeting water quality standards along urban gradients, implications of inappropriate numeric targets, reduction required to meet specific vulnerability goals, and urban influences most related to vulnerability.

2.2 MATERIALS AND METHODS

In this research, vulnerability to nutrient pollution was defined as the probability of ambient water quality exceeding water quality targets in four regions across the United States. Total phosphorus and total nitrogen observations were fit to a lognormal distribution, where the expected quantile of the distribution, defined in water quality standards (EPA ecoregional targets and state level standards), was computed and compared with numeric targets. The likelihood of the quantile value exceeding the numeric target was determined using a student t distribution, incorporating annual number of samples in the degree of freedom. Then, a binomial distribution was assumed to integrate excursion frequency into the analysis. Vulnerability was compared between EPA ecoregional targets and state level standards to assess the feasibility of meeting water quality goals. In addition, a multiple linear regression (MLR) analysis was conducted between vulnerability and point and non-point sources of urban pollution to relate impairment to urban influences.

2.2.1 STUDY AREAS

Four study regions with various ecohydrologic conditions, shown in Figure 1, were selected for analysis. Each city provided unique urban influences, water quality standards, and therefore, vulnerability to nutrient impairment. Figure 1 exhibits the four study regions located in Denver, Colorado; Portland, Oregon; Phoenix, Arizona; and Baltimore, Maryland with land use and wastewater treatment facility (WWTF) locations and capacities.

The South Platte River Basin has a drainage area of approximately 224,300 mi^2, and extends into Colorado, Nebraska, and Wyoming. Headwaters of the South Platte River begin along the Continental Divide in the Rocky Mountains in central Colorado, where the river flows to its confluence with the North Platte River in Nebraska. Approximately three million people reside in the South Platte River basin, where the majority of the population is located in urban corridors along the front range of northern Colorado. This study selected a primarily semi-arid portion of the South Platte River that captures inputs from Denver, Colorado and upstream tributaries. The Colorado Department of Public Health and Environment (CDPHE) has established water quality standards for a variety of parameters, including TP and TN. According to Regulation 31, annual median TP and TN are not to exceed 0.17 mg/L and 2.01 mg/L, respectively, with an allowable exceedance frequency of 1-in-5 years.

The Willamette River Basin is located in Oregon, stretching nearly 300 miles from its headwaters in Eugene to the confluence with the Columbia River near Portland. Approximately 2.5 million people live within the Willamette River Basin's 11, 500 mi^2. Generally, this watershed experiences temperate oceanic climate. The 17 mile portion of the Willamette River that passes through Portland, Oregon focused on in this study serves the most urbanized portion of the watershed and is home to native salmon and steelhead fish that migrate between the ocean and spawning streams. Oregon does not have specific TP and TN water quality regulations in place for the Willamette River and tributaries. However, Oregon's Department of Environmental

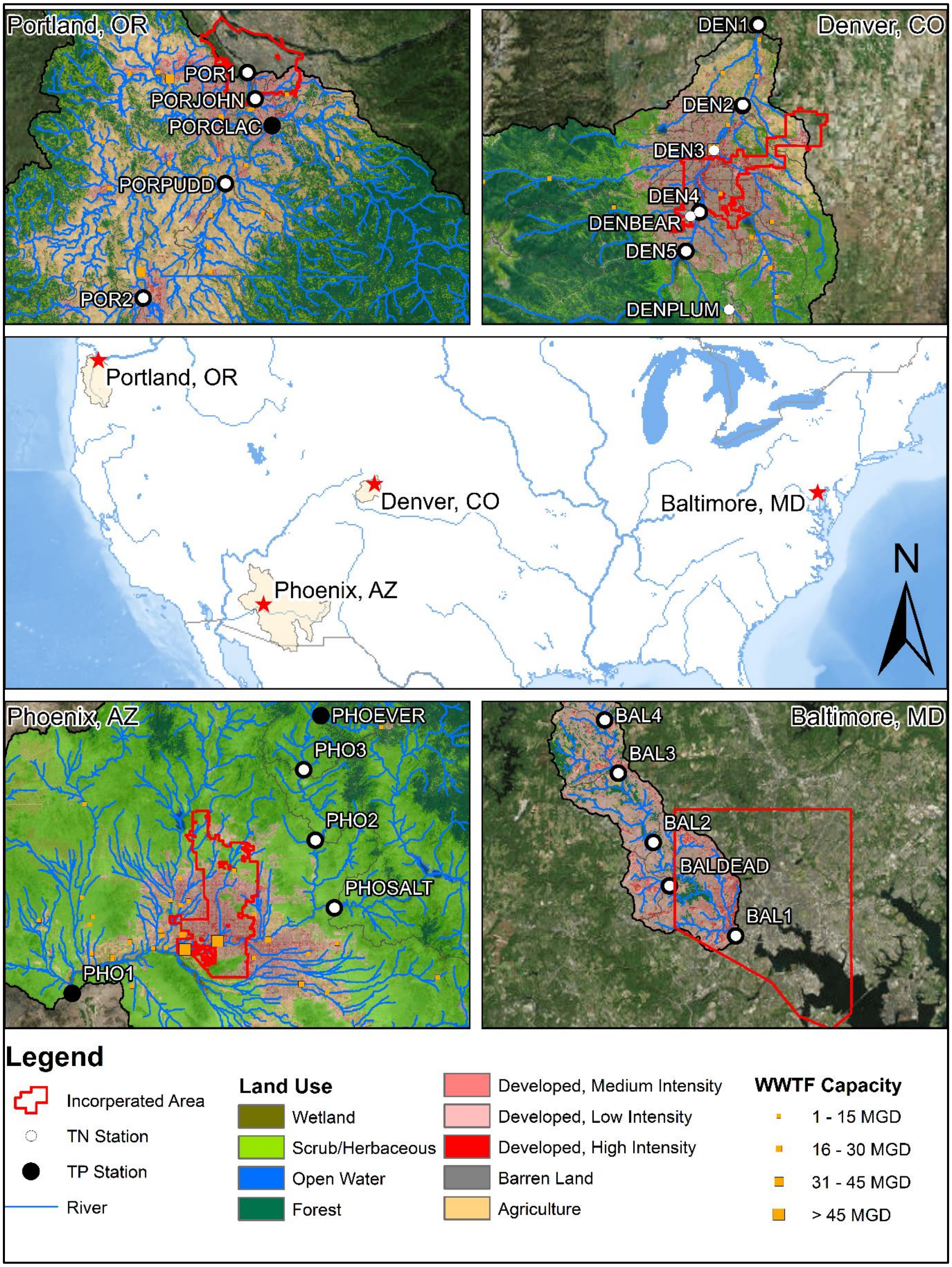

Figure 1. The study areas located in Portland, Oregon; Denver, Colorado; Phoenix, Arizona; and Baltimore, Maryland with sampling sites, land use, and annual wastewater treatment facility (WWTF) capacity.

Quality (DEQ) has numeric standards for chlorophyll-a, pH, and dissolved oxygen, which are intended to prevent eutrophication in rivers and lakes and protect native fishes.

The Salt River Basin stretches 300 miles from mountainous headwaters above 11,000 ft in elevation to the desert just west of Phoenix, Arizona at 1,200 feet, supporting over 4.5 million people along the way. The lower portion of the Salt River is experiencing increasing competition for water resources, leaving little water and hydrologic connectivity for aquatic life. A series of dams and reservoirs regulate and divert flow to provide water and energy for Phoenix and surrounding urban areas. This study focuses on the portion of the Salt River that passes through Phoenix, along with one of its main tributaries, the Verde River. Arizona's DEQ has established water quality standards for particular portions of the Salt and Verde Rivers for a variety of pollutants, including TP and TN. According to Arizona's DEQ Chapter 11 regulation, 90% of annual measurements along the Verde River and upstream tributaries cannot exceed 0.3 and 1.5 mg/L for TP and TN, respectively. In addition, the Salt River below Stewart Mountain Dam to its confluence with the Verde River is to have annual mean TP and TN concentrations less than 0.05 and 0.60 mg/L, respectively.

Gwynns Falls Watershed, located in the southwestern portion of Baltimore County, is much smaller than the other cities included in this study. With an area of 61 mi^2, nearly 350,000 people live in this highly urbanized watershed. Anthropogenic stressors have made Gwynn Falls impaired for nutrients, sediments, and bacteria, impacting biological communities despite not have any wastewater treatment facility contributions. The climate is humid subtropical. While the focus of the study was to investigate Baltimore's influences on Gwynn Falls, upstream urban influences within the watershed were also considered. Maryland does not have specific water quality targets for Gwynn Falls, however, a TMDL was implemented to improve the health of Chesapeake Bay, located downstream of Gwynn Falls. Instead of pollutant concentrations being regulated, Maryland has given load allocation to major point sources to reduce pollution that travels to Chesapeake Bay.

2.2.2 WATER QUALITY DATA

Since the establishment of the CWA and TMDL programs, many cities around the U.S. have implemented extensive monitoring of regulated water quality parameters. Publicly available water quality data collected between 1990 and 2018 were obtained from the United States Geological Survey (USGS), EPA's Storage and Retrieval (STORET) database, and state and regional level water quality monitoring programs, shown in Table 1. Data collected between 1990 and 2018 were selected to incorporate a wide range in climatic variability while reducing the effect of non-stationarity. Grab samples collected for TP and TN were in accordance with approved state or federal methods, allowing comparison between sites with data from different sources. Monitoring locations within HUC 8 watersheds that intersect U.S. Census incorporated areas for each city and with twelve or more samples were selected for analysis. This approach included upstream locations that were intended to indicate relatively undisturbed water quality conditions for each region. Water quality monitoring stations were selected to have corresponding flow data in order to calculate pollutant loading, as discussed in Chapter 2 of this report. A regression of order statistics was conducted for sites that had concentrations below the detection limit using ProUCL 5.1 (USEPA, 2013).

Table 1. Water quality data sources explored for each region of interest. Bolded sources were utilized to characterize vulnerability to nutrient pollution.

City	Water Quality Data Sources
Denver, Colorado	USGS **STORET** **Colorado Department of Health and Environment** Colorado Division of Water Resources
Portland, Oregon	USGS STORET **Ambient Water Quality Monitoring System**
Baltimore, Maryland	USGS STORET **Long Term Ecological Research Program** Chesapeake Bay Program
Phoenix, Arizona	USGS **STORET** **Arizona Department of Environmental Quality** Long Term Ecological Research Program

2.2.3 EPA LEVEL III ECOREGIONAL TARGETS

Under the Clean Water Act, States and Tribes have been given the responsibility of developing and implementing water quality standards. Various levels of progress have been made towards developing criteria around the U.S. Some states have numeric goals established and implemented for multiple parameters; other states remain in the monitoring and development phase (USEPA, 2018).

The EPA has taken steps to guide authorized jurisdictions to establish numeric targets and protect U.S. surface waters. The EPA identified the 25th percentile of the develop distribution of all streams within homogeneous regions, level III ecoregions, to establish numeric nutrient goals that took regional variation and background nutrient conditions into consideration (Omernik and Griffith, 2014). This method for establishing nutrient criteria was selected for the purpose of maintaining consistency between states that lack water quality standards and to allow comparison with established, state level standards in Denver, Colorado and Phoenix, Arizona. It was assumed that the quantile of interest was the median.

The 25th percentile of the general population of sample concentrations is intended to represent naturally occurring conditions. However, additional research has concluded that recommended concentrations do not accurately reflect reference conditions (Ice and Binkley, 2003; Herlihy and Sifneos, 2008). Under an inappropriate assumption that the 25th percentile of all sites represents background conditions, the EPA numeric goals may not be feasibly attainable. Furthermore, the 25th percentile method to represent natural conditions does not incorporate economic feasibility that may hinder regions' ability to meet EPA ecoregional targets.

In addition to the numeric target, it is important for states to identify duration, frequency, and magnitude of allowable exceedance to account for extraordinary conditions in which targets cannot be met (USEPA, 2001). According to the EPA, water quality impairments should not reach levels that harm aquatic species. Studies have shown that recovery from pollutant stress can occur anywhere from six weeks to ten years depending on the magnitude of the stressor. To account for variability in magnitude of exceedance, the EPA recommends an excursion frequency of 1-in-3 years, in which most aquatic systems can recover (Stephen et al., 1985). This excursion frequency was used in combination with EPA ecoregional numeric guidance to characterize vulnerability to nutrient pollution. Little information was available regarding the intended collection and excursion frequencies, therefore the average annual number of samples collected was used as the collection frequency.

2.2.4 CHARACTERIZING VULNERABILITY

A proper statistical distribution to describe nutrient concentrations was important in the characterization of vulnerability and relation of vulnerability to urban influences. Research has shown that nutrient concentrations are lognormally distributed (Kutner et al., 2005; Williams et al., 2014; Tasdighi et al., 2017). Probability plots and the correlation coefficient, R, in ProUCL 5.1 were used to test if observations fit a lognormal distribution with 90% confidence for this analysis. In general, a lognormal distribution described measured TP and TN concentrations for the selected sites when non-detect values were accounted for using a lognormal linear regression of order statistics (R > 0.90 and R > 0.88 for TP and TN, respectively).

Vulnerability to TP and TN was characterized as the probability of exceeding numeric targets (*T*), based on a given quantile (*q*) of measured ambient water quality, excursion frequency (τ), and number of annual samples (*k*) at each monitoring station. Measured pollutant concentrations (*x*) were assumed to be log-normally distributed such that $y = \log(x)$ is normally distributed with sample mean (θ) and variance (ω) computed from a maximum likelihood estimation.

$$x = \{x_1, x_2, \dots, x_n\} \qquad [1]$$

$$y \sim N(\theta, \omega) \qquad [2]$$

In order to determine if a given quantile (*q*) of ambient water quality exceeds numeric targets, the expected value ($\hat{Y}_q$) and standard deviation ($\hat{\sigma}_q$) of the quantile for a normal distribution was calculated as

$$Y_q = \theta + z_q\omega \qquad [3]$$

$$\sigma_{Y_q} = \frac{\omega^2}{n}\left(1 + \frac{1}{2}{z_q}^2\right) \qquad [4]$$

where the standard normal variable (z_q) for a given quantile can be obtained from the standard normal table based on the quantile of interest.

$$z_q = \phi^{-1}(q) \qquad [5]$$

For a given set of *n* log-transformed water quality observations (y), the probability that the expected quantile value (Y_q) exceeds the log-transformed numeric target concentration (T) (either the EPA's ecoregional targets or state level regulation), was computed as

$$P = 1 - F_{Y_q}[\log(T)] \qquad [6]$$

where $F_{Y_q}[\log(T)]$ is the cumulative distribution of Y_q. Applying a student's t distribution, because some monitoring stations have less than 30 observations, with k-1 degrees of freedom, the probability of exceedance in any given year (*P*) was expressed as

$$P = 1 - \phi\left[\frac{\log(T) - Y_q}{\sigma_q}\right] \qquad [7]$$

where ϕ is the non-exceedance probability for the student t distribution, *T* is the target concentration, and *k* is number of annual samples collected. Because the EPA recommends some allowable excursion frequency, and many state level regulations incorporate excursion frequencies into their water quality standards, a binomial distribution was utilized to calculate the probability of exceeding water quality targets 1-in-τ years

$$V = 1 - \sum_{i=0}^{1} \binom{\tau}{i} P^i (1 - P)^{\tau - i} \qquad [8]$$

where *V* is the vulnerability to nutrient pollution. Table 2 shows the values used in the analysis for EPA and state level targets, where available.

Table 2. Properties of water quality standards used to characterize vulnerability, where T is the numeric target (mg/L), q is the quantile which is tested against the target, and τ is the frequency of excursion (1-in-τ years). Annual number of samples collected, k, was assumed to be the average annual number of samples collected for each site.

	City	Total Phosphorus			Total Nitrogen		
		T	q	τ	T	q	τ
EPA	Denver	0.06	0.5	3	1.07	0.5	3
	Baltimore	0.04	0.5	3	2.225	0.5	3
	Portland	0.025	0.5	3	0.607	0.5	3
	Phoenix	0.04	0.5	3	0.32	0.5	3
State	Denver	0.17	0.5	5	2.01	0.5	5
	Phoenix	0.05/0.03	0.5/0.9	1	0.60/1.5	0.5/0.9	1

Because vulnerability was expressed as a probability of impairment, vulnerability was limited to values between zero and one and does not indicate the magnitude of excursion for sites with V = 1. The required concentration reduction to achieve 95% reliability (V = 0.05) was calculated to indicate the magnitude of exceedance at each monitoring site. Assuming a constant coefficient of variation, the concentration associated with V = 0.05 was calculated using Equations 2 through 8. The required reduction was calculated as the difference between median (or other quantile of interest) ambient water quality concentrations and concentration necessary to achieve 95% reliability. Negative difference values were assumed to require zero reduction.

2.2.5 GEOSPATIAL ANALYSIS

In addition to characterizing vulnerability to nutrient pollution, vulnerability was related to various factors of urban intensity within each subbasin. Because all upstream anthropogenic activities impact downstream water quality, where consecutive urban areas have cumulative effects on river quality, watershed delineations were performed to capture all upstream inputs that contribute to each monitoring station (Glińska-Lewczuk et al., 2016). ArcSWAT 2012 (USEPA, 2014) was utilized to delineate drainage areas and estimate flow accumulation locations using the USGS's National Elevation Dataset one-third arc-second (10 m) Digital Elevation Model (DEM) images. Flow accumulations lines developed by ArcSWAT were used in combination with spatial analyst tools in ArcMap to calculate upstream river mile for selected monitoring stations.

2.2.6 CHARACTERIZING URBAN INTENSITY

Various anthropogenic sources of pollution contribute to water quality degradation in urban settings, including wastewater treatment and industrial discharges and urban runoff. Indicators of these influences, such as impervious surfaces, urban land use, population density, and wastewater treatment capacity were used in this analysis to characterize urban intensity. Analyzing one point (WWTF capacity) and one non-point (impervious percentage, urban land use percentage, and population density) predictor variables allowed for a multiple linear regression with the least amount of multicolinearity.

National Pollutant Discharge Elimination data were collected to estimate WWTF contribution using inverse distance weighting (IDW). The total distance used for IDW was calculated as the sum of overland flow distance to the nearest stream segment and the distance from the nearest stream segment to downstream sampling locations along the river. Overland distances and river routing were conducted in ArcMap using spatial analyst tools. Incorporating IDW, which considers both WWTF capacity and distance to the monitoring station, allowed for increased data significance between a major point source of pollution and ambient water quality and vulnerability.

Land use, imperviousness, and population density data that corresponded with mean sampling year for each site was gathered. Impervious surfaces and land use data from the

National Land Cover Database (NLCD) was obtained to calculate impervious percentage and urban land use percentage. Urban areas were defined as low, medium, and high intensity developed land and developed open space under the NLCD classification system. Tract level population data were obtained from the U.S. Census and utilized to calculate population density. ArcMap zonal statistics and geoprocessing tools were used to perform calculations within each drainage area.

2.3 RESULTS

The framework developed to characterize vulnerability to nutrient pollution took the four characteristics of water quality standards into consideration. In general, EPA ecoregional targets were more stringent than state level targets, leading to greater vulnerability. Many sites exhibited 100% vulnerability, suggesting that either standards need to be modified to take current technology into consideration or watershed management practices need to be implemented to reduce the likelihood of impairment. Impairment was especially high at downstream monitoring locations. A threshold existed, causing vulnerability to be equal to either 0% or 100% in most cases. Due to this threshold, the relationship between vulnerability and urban influences was weak and insignificant. Instead, the concentration reduction to achieve 95% reliability was related to urban influences. In general, strong relationships existed, where nonpoint sources of pollution that best correlated with vulnerability differed from region to region.

2.3.1 CHARACTERIZING VULNERABILITY

Vulnerability to nutrient pollution was calculated as function of ambient water quality and four conventional properties of water quality standards. Table 3 shows the results of the vulnerability framework for Denver, CO; Baltimore, MD; Portland, OR; and Phoenix, AZ for each site where data was available. Note that Denver, CO and Phoenix, AZ were the only locations with state level water quality standards implemented.

Table 3. Results of vulnerability analysis for TP and TN in Denver, CO; Baltimore, MD; Portland, OR; and Phoenix, AZ assuming EPA ecoregional criteria and state level regulation, where available.

City	Site	Total Phosphorus		Total Nitrogen	
		EPA Vul	State Vul	EPA Vul	State Vul
Denver	DEN1	1.000	1.000	1.000	1.000
	DEN2	1.000	1.000	1.000	1.000
	DEN3	--	--	1.000	1.000
	DEN4	1.000	0.000	1.000	0.004
	DEN5	0.001	0.000	0.000	0.000
	DENBEAR	--	--	0.003	0.000
	DENPLUM	--	--	1.000	1.000
Baltimore	BAL1	0.000	--	0.000	--
	BAL2	1.000	--	0.000	--
	BAL3	0.717	--	1.000	--
	BAL4	0.000	--	0.000	--
	BAL5	0.000	--	0.000	--
	BALDEAD	0.000	--	1.000	--
Portland	POR1	1.000	--	1.000	--
	POR2	1.000	--	1.000	--
	PORPUDD	1.000	--	1.000	--
	PORCLAC	0.000	--	--	--
	PORJOHN	1.000	--	1.000	--
Phoenix	PHO1	1.000	--	--	--
	PHO2	1.000	--	0.000	--
	PHO3	0.998	0.021	0.000	0.005
	PHOSALT	0.744	0.003	0.000	0.000
	PHOEVER	0.001	0.009	--	--

In arid regions, water quality decreased through urban gradients causing vulnerability to increase with distance downstream. Wastewater often dominated low flow conditions in arid regions, causing water quality impairments with distance downstream. This was true for TP and TN in Denver, CO and TP in Phoenix, AZ. Figure 2 provides a plot of TP and TN concentrations in Denver, CO as a function of river mile for all monitoring locations, where the red line represents Regulation 31 numeric targets. Vulnerability is symbolized by the color of the points. Locations with concentrations below the target are less vulnerable to nutrient pollution than sites with concentrations that exceed the target, validating the framework to characterize vulnerability. In addition, a bar plot of cumulative inverse distance weighted wastewater treatment facility capacity is provided, in which correlations between urban influence and water quality can be visualized. For all median concentrations, except TN and TP in Baltimore and TN in Phoenix, the downstream-most location, usually representing the most urbanized portion of the watershed, exceeded EPA targets and were highly vulnerable to nutrient pollution.

Only two cities, Denver, CO and Phoenix, AZ, had water quality standards implemented, in which vulnerability between EPA ecoregional standards and state level standards could be compared. In Denver, EPA ecoregional targets were 35% less for TP and 53% less for TN than Regulation 31 numeric targets. This resulted in average vulnerability values that were 50% greater for TP and 25% greater for TN. DEN4 had very little risk to surpassing Regulation 31 standards (V = 0.004), however, was highly vulnerable (V = 1.000) under EPA ecoregional criteria. Figure 3 depicts a contour plot of vulnerability at various combinations of numeric targets and median concentrations at DEN4. EPA and Regulation 31 numeric targets and the actual median are displayed as the red polygons. DEN4 was not vulnerable under Regulation 31 and highly vulnerable under EPA recommendation. Similarly, Chapter 11 of the ADEQ had less stringent standards than the numeric goals of the EPA at most monitoring locations, resulting in smaller

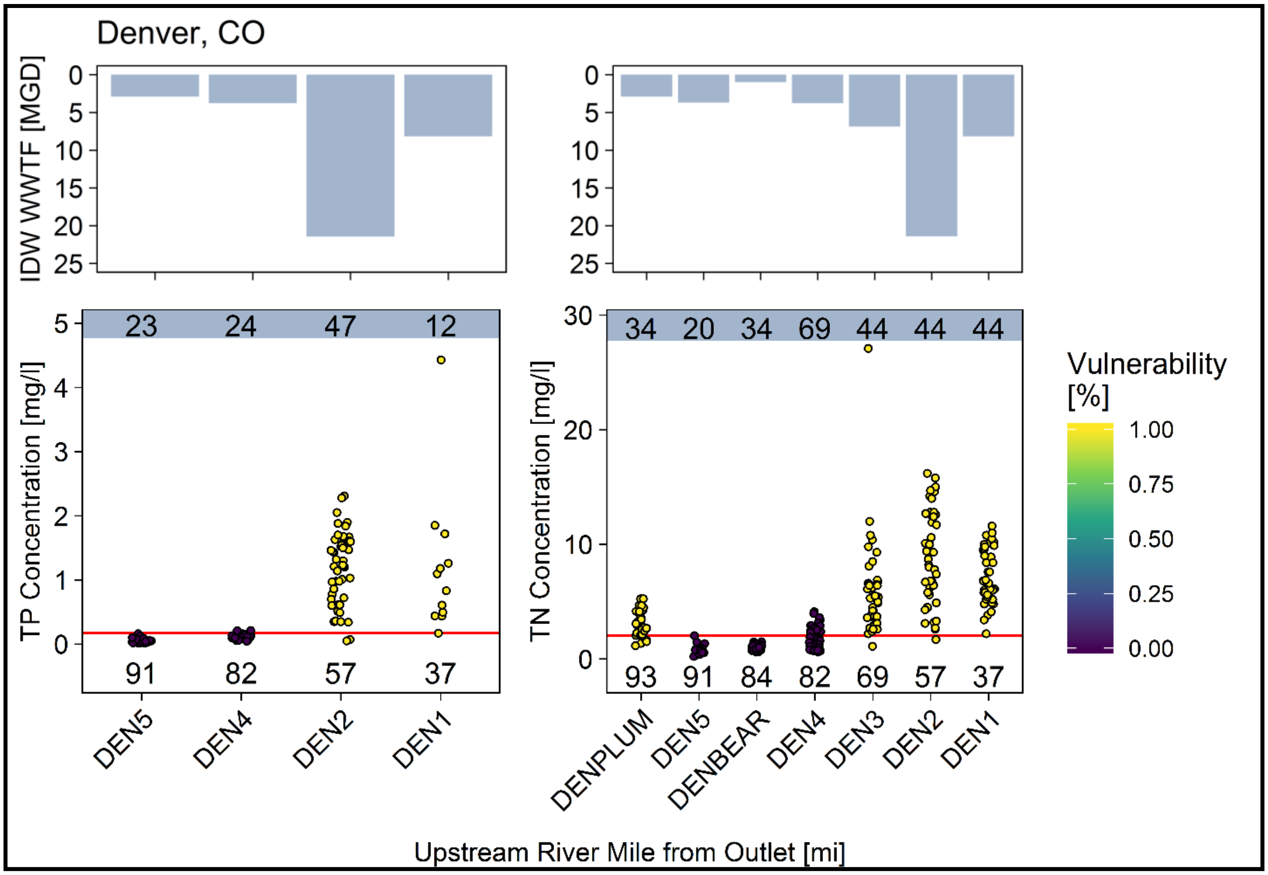

Figure 2. Concentrations of nutrient variables and cumulative inverse distance weighted wastewater treatment capacity (IDW WWTF) as a function of river mile along the South Platte River through Denver, CO for TP and TN. Sites are ordered by river mile to the downstream confluence with the Cache La Poudre River. The color of points symbolized the vulnerability at that site and red line represents the numeric standard established by CDPHE's Regulation 31. In addition, the number of samples collected is shown as the values in the blue shaded region.

vulnerability at all locations except for PHO3 for TP and PHOEVER for TN. Numeric targets between the EPA and ADEQ could not be directly compared due to the fact that ADEQ water quality standards use q = 0.9 at PHO3 and PHOEVER rather than the median, such as in Denver, CO and EPA ecoregional targets.

In most cases, vulnerability was nearly zero or nearly one. BAL3 and PHOSALT were the only two locations that had 0.0 < V < 1.0 when EPA targets were utilized in the calculation of vulnerability. Minimal gradients in vulnerability resulted from insufficient spatial variability in monitoring locations and the existence of a threshold in which a very small window where vulnerabilities less than one and greater than zero exist. Figure 3 shows vulnerability as a function of median TN concentration and target value for station DEN4, assuming the coefficient of variation remains constant and a one-in-five year excursion frequency defined in CDPHE's Regulation 31. Few combinations of median concentration and numeric target values produce vulnerabilities less than one and greater than zero, especially when more stringent targets were assumed, shown by tighter contours in Figure 3. For example, the range in which vulnerabilities are less than one but greater than zero for a target of 2.01 mg/L (as defined by Regulation 31 for the South Platte River in Denver) was greater than a target of 1.07 mg/L (as defined by EPA recommendation). For this reason, more monitoring stations or larger numeric targets were needed to capture the gradients in vulnerability.

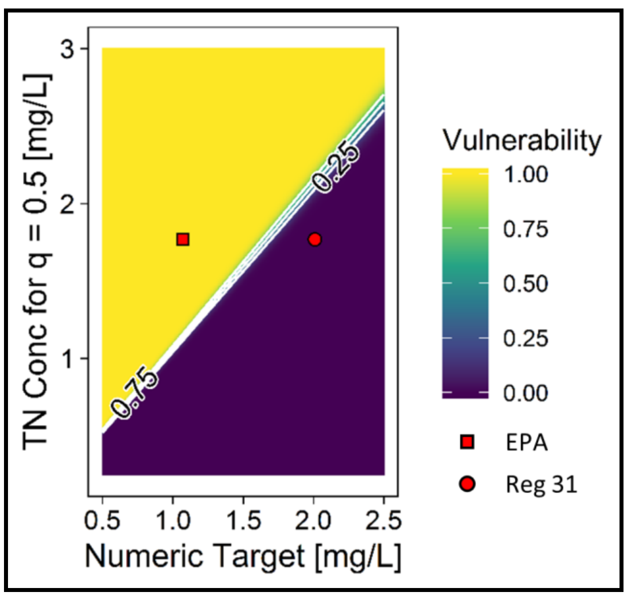

Figure 3. Vulnerability at various combinations of median TN concentrations and numeric targets at DEN4 assuming a constant coefficient of variation and 1-in-5 year excursion frequency. The purple area represents combinations in which the site is not likely to be impaired, while the yellow area represent highly impaired combinations. The red circle and square symbolize the true combination of median TN concentration and the Regulation 31 or EPA ecoregional numeric targets, respectively.

The threshold that exists in the characterization of vulnerability to nutrient pollution makes a multiple linear regression between vulnerability and urban influences invalid. For this reason, the concentration required to achieve V = 0.05 was calculated using the same procedure to calculate vulnerability, except in reverse and assuming the coefficient of variation remained constant. Required reduction reflected the magnitude and gradient of vulnerability, even when vulnerability was 0 and 100%. Figure 4 exhibits required reduction for each site assuming EPA ecoregional criteria where a clear gradient in reduction is shown. More reduction was needed in Denver for TP and TN, Portland for TN, and Phoenix for TP with distance downstream when EPA ecoregional criteria are assumed. This is also true when Regulation 31 TP and TN standards are applied to Denver monitoring sites, where less stringent standards are reflected with less reduction required. See Appendix A for required reduction for each site.

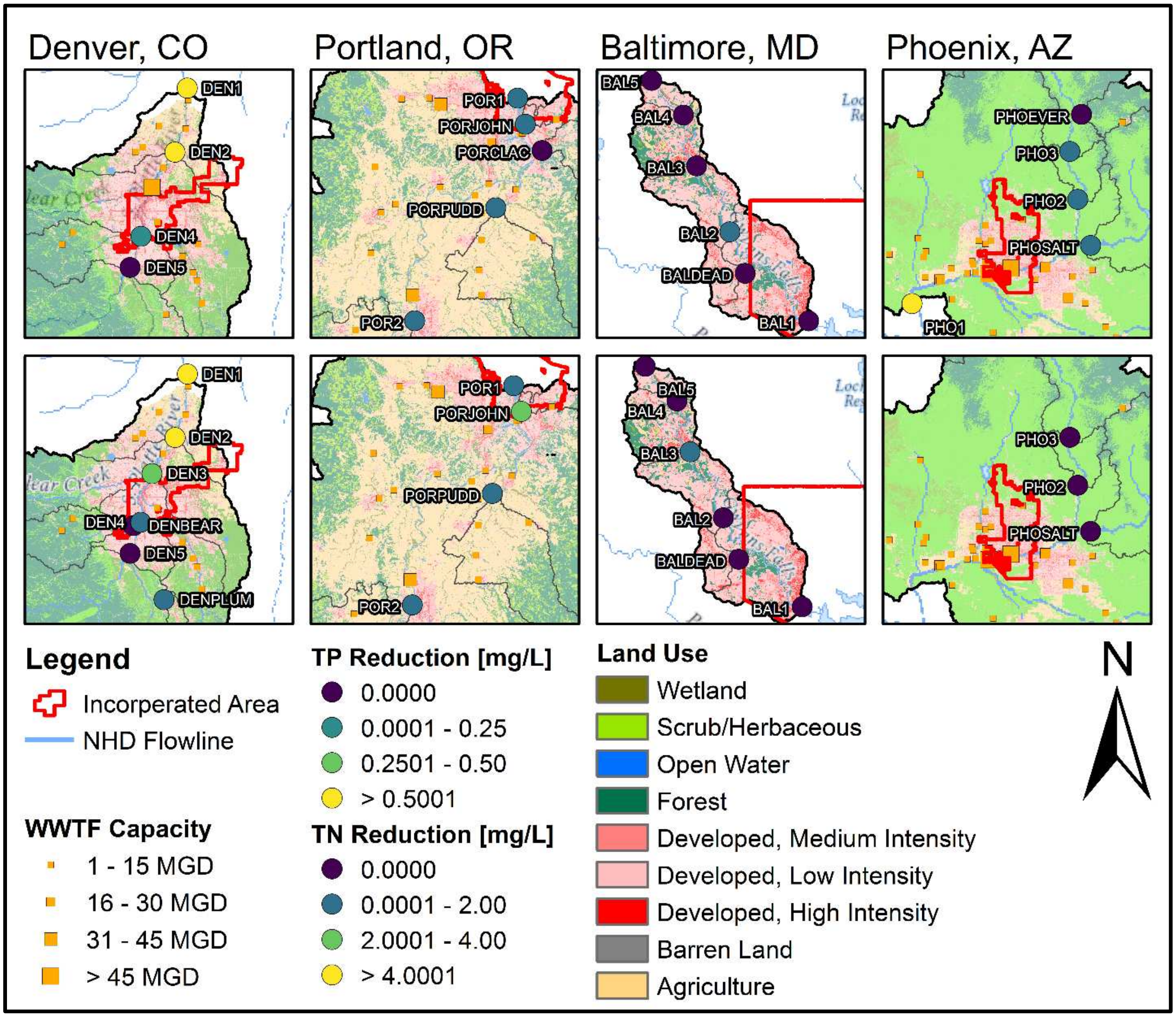

Figure 4. Required reduction at each monitoring site for TP (top) and TN (bottom) in Denver; CO; Portland, OR; Baltimore, MD; and Phoenix, AZ along with incorporated areas, National Hydrography Dataset flowlines, WWTF capacity and locations, and land cover within each watershed of interest.

2.3.2 MULTIPLE LINEAR REGRESSION ANALYSIS

Table 3 shows various urban influences within each drainage area as a result of the geospatial analysis. In general, point and non-point sources of pollution increase with distance downstream through urban gradients, leading to water quality impairment. Some cities, such as Denver for TP and TN and Phoenix for TP experienced obvious reduction in water quality, which may be related to the increased anthropogenic activities occurring with distance downstream. In addition, it is important to note that high vulnerability values resulted even in undisturbed watersheds when using EPA ecoregional criteria, such as at PHO3 and PHOSALT for TP.

Table 4. Urban influences within each subbasin, including cumulative inverse distance weighted wastewater treatment facility capacity (IDW WWTF), urban land cover percentage (ULC), impervious surface percentage (IS), and population density (PD).

City	Site	River Mile (MI)	IDW WWTF (MGD)	ULC (%)	IS (%)	PD (peo/mi^2)
Denver	DEN1	37	8.17	13.35	5.13	502
	DEN2	57	21.42	12.30	4.37	476
	DEN3	69	6.88	9.43	3.44	359
	DEN4	82	3.77	5.45	1.76	170
	DEN5	91	3.69	2.32	0.60	41
	DENBEAR	--	1.00	10.48	3.93	435
	DENPLUM	--	2.91	12.87	3.35	263
Baltimore	BAL1	2	0.00	78.87	27.44	3372
	BAL2	11	0.00	69.75	17.17	2998
	BAL3	17	0.00	64.85	18.97	5048
	BAL4	22	0.00	81.60	20.12	4296
	BAL5	25	0.00	77.80	18.90	2849
	BALDEAD	--	0.00	95.94	40.36	3733
Portland	POR1	13	5.19	7.16	2.47	176
	POR2	91	3.27	4.40	1.31	76
	PORPUDD	--	1.33	5.85	1.79	95
	PORCLAC	--	1.00	3.39	0.91	69
	PORJOHN	--	1.00	67.91	31.18	3367
Phoenix	PHO1	11	10.8	3.61	3.93	93
	PHO2	118	1.48	1.97	0.54	30
	PHO3	149	1.51	2.07	0.57	31
	PHOSALT	--	1.00	0.57	0.19	8
	PHOEVER	--	2.00	1.87	0.54	22

A MLR analysis for vulnerability using IDW WWTF capacity as a point source predictor variable and either urban land use percentage, impervious percentage, or population density as a non-point source predictior variable was performed for both EPA and state level criteria. In general, vulnerability was not strongly correlated with urban influences (R^2 < 0.7) for EPA standards, shown in Table 4. This is likely due to vulnerability being not only a function of ambient water quality concentrations, which are related to urban influences, but also numeric targets. The small window where vulnerability is greater than zero but less than one created a threshold, in which the gradient in vulnerability could not be captured by available data nor explained by a gradient in urban influences. Because thresholds are inherently non-linear, the existence of a threshold in the calculation of vulnerability explains why MLR models relating urban intensity variables to vulnerability are invalid. The probability of exceeding EPA criteria was 100% for over half of TP and TN sites, including some relatively undisturbed sites.

Table 5. Multiple linear regression models for TP and TN vulnerability with point source (IDW wastewater treatment facility [WWTF] annual capacity) and non-point source (urban land cover [ULC], impervious surface percentage [IS]) that produced the best model results assuming EPA ecoregional targets (top) and CDPHE Regulation 31 standards in Denver, CO (bottom), R^2 and Adjusted R^2, P value for the appropriateness of the model, and variable inflation factor (VIF).

City	Nutrient	Linear Model	R^2	Adj R^2	P	VIF
Denver	TP	0.190+0.002(PD)+0.0073(WWTF)	0.61	-0.18	0.628	1.3
	TN	0.128+0.047(ULC)+0.021(WWTF)	0.33	0.00	0.188	1.2
Baltimore	TP	2.714-0.031(ULC)	0.54	0.43	0.094	--
	TN	-0.373+0.030(IS)	0.26	0.07	0.303	--
Portland	TP	0.334+1.55e-04(PD)+0.148(WWTF)	0.38	-0.23	0.615	1.2
	TN	--	--	--	--	--
Phoenix	TP	0.355+0.027(ULC)-0.177(WWTF)	0.34	-0.33	0.664	15.9
	TN	--	--	--	--	--

City	Nutrient	Linear Model	R^2	Adj R^2	P	VIF
Denver	TP	-0.300+0.213(IS)+0.020(WWTF)	0.96	0.89	0.194	1.6
	TN	-0.384+0.084(ULC)+0.024(WWTF)	0.66	0.50	0.113	1.2

Vulnerability was strongly correlated ($R^2 > 0.7$) for Denver when applying Regulation 31 criteria, suggesting that there are situations where, if the standard is not too stringent, a gradient can be formed and related to urban intensity measures, as depicted in Table 5. Because water quality standards for the South Platte River that runs through Denver, Colorado were less stringent than EPA standards, a larger range in which vulnerabilities are not zero or one exist. Therefore, the gradient in vulnerability was calculated and related to urban influences. Though Phoenix had water quality standards in place for three monitoring sites, there was not enough data to conduct a multiple linear regression analysis.

MLR analyses were conducted on the concentration reduction required to achieve 95% confidence that the site will be unimpaired (V = 0.05). Required reduction produced stronger relationships between point and non-point sources of urban pollution than vulnerability alone because the reduction reflected the magnitude and gradient of vulnerability, even when vulnerability was 0 and 100%. Table 6 exhibits MLR required reduction statistics for ecoregional (top) and Regulation 31 (bottom) standards. In general, urban land cover and IDW WWTF capacity were the predominant predictor variables in the regression. However, IDW WWTF and impervious surface percentage for TN in Denver, CO and IDW WWTF and population density for TP in Phoenix, AZ produced the best results, suggesting that different cities, and even sub watersheds, have varying anthropogenic influences that dominate water quality.

The MLR analysis of the concentration reduction required to achieve 95% reliability showed strong correlations to point and non-point source pollution. Predictor variables were strongly correlated ($R^2 > 0.7$) for the Denver, Portland, and Phoenix for TP and Denver for TN. In general, the MLR model for reduction to 95% reliability resulted in stronger correlations as compared to vulnerability alone. However, more monitoring sites are required to validate the significance of the model in all cases except for Phoenix for TP and Denver for TN. Required reduction for TP and TN were strongly correlated and significantly correlated for TN in Denver when assuming Regulation 31 standards, as shown in the bottom portion of Table 6.

Table 6. Multiple linear regression models for TP and TN concentration reduction to achieve V = 0.05 with point source (IDW wastewater treatment facility [WWTF] annual capacity) and non-point source (urban land cover [ULC], impervious surface percentage [IS]) that produced the best model results assuming EPA ecoregional targets (top) and CDPHE Regulation 31 standards in Denver, CO (bottom), R^2 and Adjusted R^2, P value for the appropriateness of the model, and variable inflation factor (VIF).

City	Nutrient	Linear Model	R^2	Adj R^2	P	VIF
Denver	TP	-0.364+0.072(ULC)+0.034(WWT)	0.98	0.95	0.133	1.7
	TN	-1.752+0.757(IS)+0.284(WWTF)	0.90	0.85	0.025	1.2
Baltimore	TP	0.0658-0.001(ULC)	0.37	0.22	0.197	--
	TN	9.642-0.123(ULC)	0.47	0.34	0.133	
Portland	TP	0.018+0.001(ULC)+0.002 (WWTF)	0.15	-0.70	0.851	1.2
	TN	1.171+0.036(ULC)-0.374(WWTF)	0.95	0.86	0.216	1.5
Phoenix	TP	-0.113+0.001(PD)+0.069(WWTF)	0.98	0.96	0.018	15.9
	TN	--	--	--	--	--

City	Nutrient	Linear Model	R^2	Adj R^2	P	VIF
Denver	TP	-0.472+0.072(ULC)+0.033(WWTF)	0.98	0.95	0.132	1.7
	TN	-2.633+0.751(IS)+0.283(WWTF))	0.90	0.85	0.010	1.2

2.4 DISCUSSION

The framework developed to characterize vulnerability to nutrient pollution accounts for the four major components of water quality standards, accommodating most variation in water quality standards established by States. Typical characteristics of water quality standards include frequency of excursion, annual number of sampling events, and a quantile of ambient water quality that is compared with defined numeric targets. The methodology can be applied to other water quality constituents given a numeric target that is compared to a specified quantile, excursion frequency, and number of annual samples collected. One limitation of the approach was that sufficient data is required to fit ambient water quality to a lognormal distribution.

Based on the results of this study, EPA recommendations are too stringent for most urbanized and some relatively undisturbed watersheds. In order to meet the current EPA standards, significant reductions, potentially outside of reasonable ranges given current technology, are necessary. The results of this study highlight the importance of appropriate water quality standards. Given the demands on water bodies in urbanized watersheds, current technology, and data limitations, it does not seem feasible for many locations with urban influence to achieve EPA recommended targets. When targets are too low, vulnerability to pollution becomes extremely high, especially through urban gradients in arid regions. More research utilizing the framework developed in this study is needed to determine if EPA goals are too stringent in other land use scenarios. The goal of the CWA is to restore surface waters to conditions that allow people and aquatic species to thrive, however, standards are intended to be attainable to account for technologic limitations and economic feasibility.

The probabilistic approach for vulnerability was applied to four cities across the United States in an attempt to relate vulnerability to urban influences. Because of a threshold that exists causing minimal gradients in vulnerability, urban intensity factors such as WWTF contribution, urban land use percentage, impervious surface percentage, and population density, did not correlate with vulnerability when stringent targets were specified. However, the same framework for vulnerability can be used to calculate the concentration reduction necessary to achieve a desired level of reliability, which can then be related to urban influences in certain urban settings and under less stringent water quality standard enforcement. In general, strong relationships were seen between urban land cover and cumulative distance weighted wastewater capacity and required concentration reduction values, however, some locations produced better results using impervious surface percentage or population density as a non-point source predictor variable, suggesting that each watershed is unique in its anthropogenic influences on stream quality.

Because the CWA was intended to improve water quality, wherever attainable, it is important for city planners to consider the development of water quality standards from a holistic perspective. While cities may not ever be able to achieve natural conditions given the demands on rivers that exist and will likely continue to grow into the future, steps can be taken to slow or reverse trends in water quality impairment with time, research, and technologic advances. Some states are beginning to regulate non-point sources from agricultural and urban runoff that have been shown to correlate with degradation, which could significantly improve the nation’s waters over time.

As urban development continues to grow, attainment of water quality targets will become more challenging and costly for cities to remediate. In order to achieve the goals of the Clean Water Act, balancing urban development and health of streams is required. This challenge will increasingly require policymakers and watershed managers to adapt innovative solutions.

CHAPTER 3: AN APPROACH TO USING LOAD DURATION CURVES TO UNDERSTAND VULNERABILITY TO NUTRIENT POLLUTION AT VARYING FLOW REGIMES

3.1 BACKGROUND

Changes in land use have led to eutrophication of surface water in the United States and around the word. Addition of excess nutrients, primarily total phosphorus (TP) and total nitrogen (TN), from various anthropogenic activities have resulted in degradation of 40% of U.S. rivers (USEPA, 2000). The Clean Water Act (CWA) was established to improve water quality in U.S. surface waters through the development of Total Maximum Daily Loads (TMDL) and water quality standards.

Conventional approaches for TMDL development focuses on a single numeric water quality target in combination with a dominant discharge or design flow (Cleland, 2002). This approach has been shown to be less effective for impairments resulting from point sources, such as municipal wastewater treatment facilities associated with urban areas (Stiles, 2001; Cleland, 2003), and in conditions where variation in loading is highly weather-dependent (Stow and Borsuk, 2003). Under varying flow regimes, different sources of pollution and transport mechanisms dominate pollutant loading to streams, therefore, TMDLs should consider all ranges in flow conditions to ensure acceptable water quality at all times (Cleland, 2003; USEPA, 2007a; Kim et al., 2012).

An approach supported by the USEPA that considers a full range of hydrologic conditions for TMDL development and maintenance uses load duration curves (LDC). LDCs visually compare instantaneous ambient pollutant loads and the loading capacity required to achieve desired pollutant concentrations as a function of flow exceedance probability. Patterns of impairment across all hydrologic conditions can be depicted using this framework. In addition, the LDC structure can be utilized to quantify median percent load reduction required to meet the TMDL allocations within flow categories. Pollutant delivery mechanisms and contributing source areas that dominate impairments on receiving waters have been linked with duration curve flow categories (low flow [90%-100% exceedance], dry [60%-90% exceedance], mid-range [40%-60% exceedance], moist [10%-40% exceedance], and high flows [0%-10% exceedance]), which can be used for management purposes (Cleland, 2002; PCA, 2006; USEPA, 2007b).

While this approach takes flow regime into consideration, sufficient water quality data is often not available to properly support analyses nor TDML decision making (Morrison and Bonta, 2008). For example, flows and pollutant loads within flow categories can have significant variation, where median percent reduction estimates within each flow category may not reflect actual reduction loads necessary to meet water quality targets and TMDL goals (Morrison and Bonta, 2008). In addition, obtaining water quality grab samples during extreme flows (either high or low) are less likely to be captured, creating data limitations at these flows and potentially erroneous conclusions for average percent reduction required to meet water quality standards (Cassidy and Jordan, 2011).

One problem that cities often face is funding for water quality monitoring to support meaningful analyses to capture water quality at all flows, including extremes (Park and Engel, 2015). According to the Clean Water Act Section 305(b), states are to assess and report water quality within their boundaries. For example, the state of Colorado spent $56 million between 2007 and 2011 on water pollution control efforts (CDPHE, 2012) and the Wisconsin Department of Natural Resources planned to spend over $950,000 on Wisconsin's Water Monitoring Strategy between 2015 and 2019 (Sylvester et al., 2015). One tool to reduce monitoring costs is to estimate loading using linear regression techniques, such as the United State Geological Surveys' LOAD ESTimator (LOADEST), given a time series of discharge, pollutant concentration, and additional user-specified data variables.

While LOADEST can be used to estimate loading at all flow conditions, the model is limited in a few important ways. For example, LOADEST is unable to run under scenarios with minimal ambient water quality, less than approximately 35 observations, and substantial discharge input (Morrison and Bonta, 2008). In this case, long term discharge data is omitted, potentially leaving out important extreme flow values that would affect percent flow exceedances in the load duration curve framework. In addition, proper use of many load estimation techniques requires a lack of multicollinearity between explanatory variables and expertise in statistics, multiple linear regression, and load estimation, making them more challenging to use (Runkel et al., 2004). Accurate estimation of nutrient loading is important despite limited knowledge of uncertainty in various estimation techniques (Rode and Suhr, 2007).

Research has been conducted to assess the accuracy, precision, and bias of various load estimation algorithms and water quality constituents (Moatar and Meybeck, 2005; Stenback et al., 2011; Park and Engel, 2015). Uncertainty using confidence intervals for estimated loading has been applied to the load duration curve framework for the purposes of quantifying changes in water quality between pre and post-best management practice implementation (Morrison and Bonta, 2008). However, confidence intervals have not been used to quantify uncertainty in empirical LDC frameworks and risk analysis.

In this study, we characterize nutrient pollution, specifically TP and TN, at varying flow regimes using the LDC framework in four urban regions across the United States. Specific objectives included (i) developing a methodology to characterize uncertainty in empirical LDCs, (ii) examining trends in vulnerability to nutrient pollution in four ecohydrologically different regions across the United States, and (iii) exploring hydrologic conditions which urban streams have a greater likelihood of exceeding nutrient standards.

This simple method to estimate loading at all flow conditions can be applied in situations where there is limited water quality monitoring, reducing costs to states, and without considerable knowledge of statistics required with LOADEST. In addition, this method can be used in TMDL maintenance to identify flow conditions in which impairment is occurring, which can then be associated with activities that occur during those flow conditions and potential remediation measures implemented. Finally, it can be used to establish or assess the feasibility of numeric water quality targets.

3.2 MATERIALS AND METHODS

Current water quality standards and TMDLs generally focus on a single numeric water quality target in combination with a dominant discharge or design flow (Cleland, 2003). Load duration curves have been shown to be useful in comparing existing conditions with water quality targets at all flow regimes to identify impaired flow categories. This study builds on the LDC framework to compute vulnerability to nutrient pollution (TP and TN) as a function of flow exceedance probability through urban gradients for four ecohydrologically different regions across the United States. Nutrient loading was estimated using a simple linear regression (SLR) for all possible flow exceedance probabilities, in which confidence or prediction intervals were computed and uncertainty understood, even in conditions with limited water quality data and long-term flow data. Vulnerability to nutrient pollution was defined as the probability of the standard error for the predicted mean load exceeding the numeric target load using a student t distribution at any flow exceedance probability. Patterns in vulnerability were then analyzed as a function of flow exceedance probability across urban gradients in the four regions to determine which hydrologic conditions had a greater likelihood of surpassing nutrient standards and load reduction necessary to achieve 95% reliability (vulnerability = 0.05).

3.2.1 STUDY AREAS

Four study regions with various ecohydrologic conditions, shown in Figure 5, were selected for analysis. Each city provided unique urban influences, water quality targets, ecohydrologic conditions, and therefore, vulnerability to nutrient impairment. Figure 5 exhibits the four study regions located in Denver, Colorado; Portland, Oregon; Phoenix, Arizona; and Baltimore, Maryland with land use and wastewater treatment facility (WWTF) locations and capacities.

The South Platte River Basin has a drainage area of approximately 224,300 mi^2, and extends into Colorado, Nebraska, and Wyoming. Headwaters of the South Platte River are located at the Continental Divide in the Rocky Mountains in central Colorado, where the river flows to its confluence with the North Platte River in Nebraska. Approximately three million people reside in the South Platte River basin, where the majority of the population is located in urban corridors along the front range of northern Colorado. This study selected a primarily semi-arid portion of the South Platte River that captures inputs from Denver, Colorado and upstream tributaries. The Colorado Department of Public Health and Environment (CDPHE) has established water quality standards for a variety of parameters, including TP and TN. According to Regulation 31, annual median TP and TN are not to exceed 0.17 mg/L and 2.01 mg/L, respectively, with an allowable exceedance frequency of 1-in-5 years. While these standards are implemented, the South Platte River does not have a TMDL in place for TP and TN.

The Willamette River Basin is located in Oregon, stretching nearly 300 miles from its headwaters in Eugene to the confluence with the Columbia River near Portland, Oregon. Approximately 2.5 million people live within the Willamette River Basin's 11, 500 mi^2. Generally, this watershed experiences temperate oceanic climate. The portion of the Willamette River that passes through Portland, Oregon was focused on in this study. The 17 miles that pass through Portland not only serves the most urbanized portion of the watershed, but is home to native salmon and steelhead fish that migrate between the ocean and spawning streams. Oregon does not have specific TP and TN water quality regulations in place for the Willamette River and tributaries. Instead, Oregon's Department of Environmental Quality (DEQ) has numeric standards for chlorophyll-a, pH, and dissolved oxygen, which are intended to prevent eutrophication in rivers and lakes and protect native fishes. A TMDL has been developed and approved by the EPA for the portions of the Willamette River in this study.

The Salt River Basin stretches 300 miles from mountainous headwaters above 11,000 ft in elevation to the desert just west of Phoenix, Arizona at 1,200 feet, supporting over 4.5 million people along the way. The lower portion of the Salt River is experiencing increasing competition

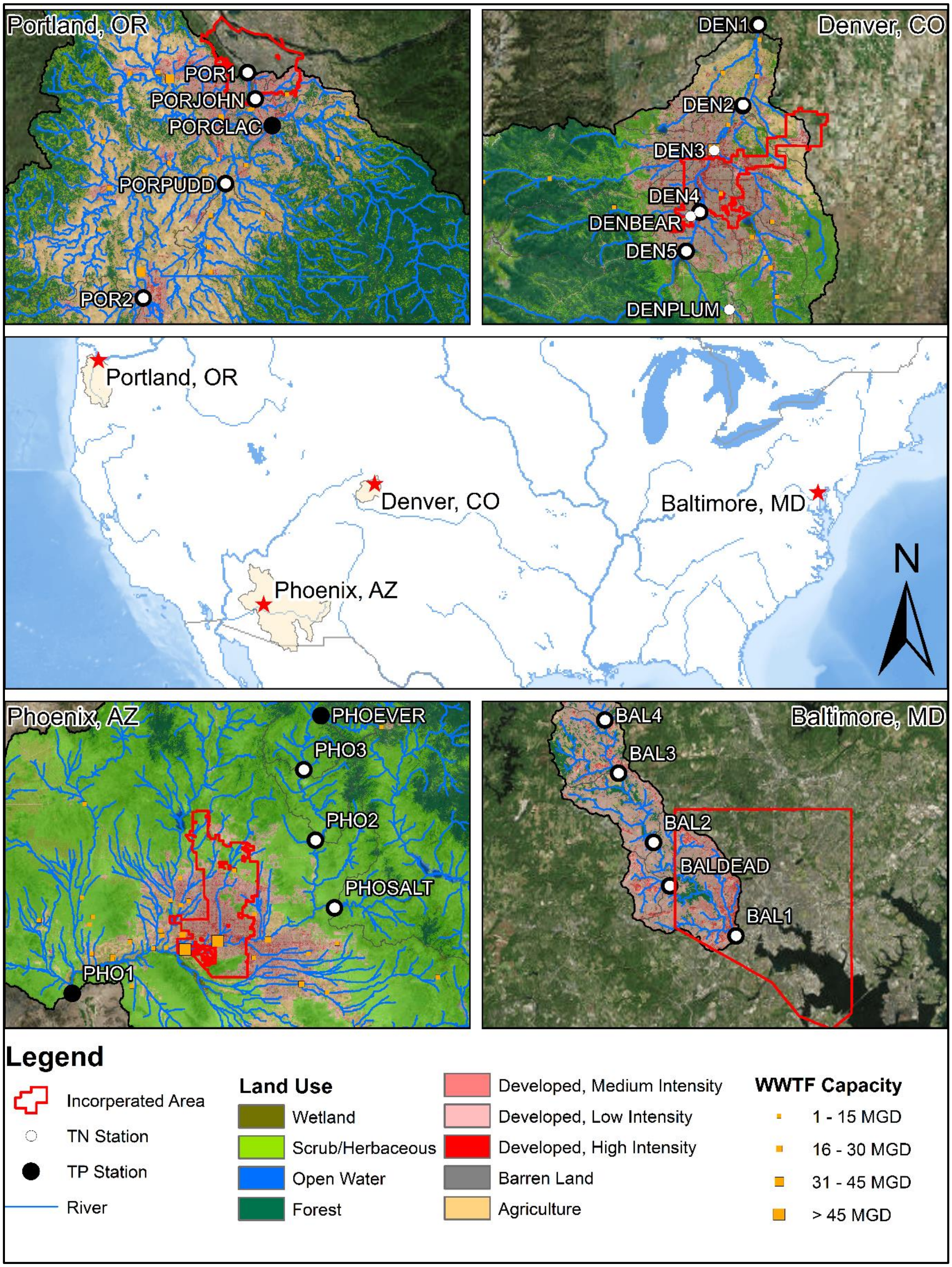

Figure 5. The study areas located in Portland, Oregon; Denver, Colorado; Phoenix, Arizona; and Baltimore, Maryland with sampling sites, land use, and annual wastewater treatment facility (WWTF) capacity

for water resources, leaving little water and hydrologic connectivity for aquatic life. A series of dams and reservoirs regulate and divert flow to provide water and energy for Phoenix and surrounding urban areas. This study focuses on the portion of the Salt River that passes through Phoenix, along with the Verde River, a main tributary of the Salt River. Arizona's DEQ has established water quality standards for some of the Salt and Verde Rivers for a variety of pollutants, including TP and TN. While a TMDL has been developed for the Salt River Basin, the reaches in this study were not concluded to be impaired.

Gwynns Falls Watershed, located in the southwestern portion of Baltimore County, is much smaller than the other three cities included in this study. At 61 mi^2, nearly 350,000 people live in this highly urbanized watershed. Anthropogenic stressors have made Gwynn Falls impaired for nutrients, sediments, and bacteria, influencing biological communities despite not have any wastewater treatment facility contributors. The climate is humid subtropical. While the focus of the study was to investigate Baltimore's influences on Gwynn Falls, upstream urban influences were also considered. Maryland does not have specific water quality targets for Gwynn Falls, however, a TMDL was implemented to improve the health of Chesapeake Bay, located downstream of Gwynn Falls. Instead of pollutant concentrations being regulated, Maryland has given load allocations to major point sources within the watershed to reduce pollution in Chesapeake Bay.

3.2.2 POLLUTANTS

TP and TN were selected for this analysis due to their environmental impact and widespread use as water quality standard constituents. Nutrient loads, especially TP and TN, that exceed the capacity of rivers can cause nuisances levels of algae growth (eutrophication) that can lead to reduced water clarity, cyanotoxins and microcystins, reduced recreation and tourism, impediments on irrigation, and reduced oxygen concentrations accompanied by aquatic species mortality (Kim et al., 2012; McMahon, 2012; Van Meter et al., 2016). Though TP is often a limiting nutrient that controls eutrophication, studies have shown that nitrogen may have greater influence as a limiting nutrient in streams (Smith et al., 1998; USEPA, 2001). For this reason, TP and TN are recommended criteria for the establishment of numeric water quality standards by the U.S. EPA (USEPA, 2001). In addition, current nutrient enrichment necessitates numeric criteria for TP and TN in order to meet the goals of the Clean Water Act.

One underlying assumption of the LDC framework is that there is a relationship between water quality and discharge, where fate and transport mechanisms are not considered (Bonta and Cleland, 2003; USEPA, 2007b; Morrison and Bonta, 2008). Nutrients such as TP and TN have been used in various LDC applications such as in the Ohio EPA TMDL for White Oak Creek Watershed (Strickland and Korleski, 2009) and for the EPA's TMDL for Bear Creek in Missouri (USEPA, 2010). In addition, TP and TN often have consistent numeric targets across all flow conditions, where changes in vulnerability can be seen as a function of changes in discharge.

3.2.3 WATER QUALITY AND FLOW DATA

Since the establishment of the CWA and TMDL program, many cities around the U.S. have implemented extensive monitoring of discharge and regulated water quality parameters. Long term (1950 to present), publicly available daily stream flow data was obtained primarily from the United States Geological Survey (USGS) within HUC 8 watersheds that intersect U.S. Census incorporated areas for each city. This approach included upstream locations with relatively undisturbed water quality conditions for each region. In some instances, such as in Colorado and Arizona, management of flow monitoring stations were transferred to state or local agencies, where measurements from the same station were combined from multiple monitoring agencies. Zero flow, ice conditions, and negative flow values in daily discharge data were omitted.

Publicly available water quality data collected between 1990 and 2018 was obtained from the USGS, EPA's Storage and Retrieval (STORET) database, and state and regional level water quality monitoring programs, as shown in Table 1. Data collected after 1990 were selected to incorporate a wide range in climatic variability while reducing the effect of non-stationarity that can occur rapid land use changes. Grab samples collected for TP and TN were in accordance with approved state or federal methods, allowing comparison between sites with data from different sources. In order to relate flow regime to water quality, water quality monitoring locations within 2000 m of a flow station that were directly connected hydraulically, with negligible inflow or outflow between, and collected within overlapping time periods and twelve or more grab samples were selected for analysis. A linear regression of order statistics was conducted for sites that had concentrations below the detection limit using ProUCL 5.1 (Barnett et al., 2015).

Urban development and land use change also effects flows in surrounding rivers and streams. For example, increased impervious areas can create more intense and flashier peak flows in hydrographs. Therefore, urban development can lead to nonstationarity in average daily flow. Fifteen years of flow data prior to the first water quality parameter reading and fifteen years after the last water quality parameter reading was included to create the flow and load duration curves and to reduce effects of nonstationarity caused by land use changes.

3.2.4 SIMPLE LINEAR REGRESSION

Before the use of modern load estimation techniques, traditional methods required nearly daily measurements over the course of many years, putting financial stress federal, state, and local governments (Porterfield, 1972). In an attempt to reduce sampling costs while providing high quality information to show compliance with water quality related regulations, several methods were developed for estimating nutrient loads in situations with limited data (Cohn et al., 1992; Cohn, 2004; Runkel et al., 2004). In 2004, LOADEST was developed and supported by the USGS. This FORTRAN program included twelve methods for load estimation for various applications and data availability. However, LOADEST requires extensive understanding of statistics, multiple linear regression, and load estimation (Runkel et al., 2004). In addition, LOADEST cannot run under conditions with long-term flow data and limited water quality measurements, therefore flow data must be omitted to allow the model to run, leaving out potentially important information with respect to nutrient loading. LOADEST models utilize simple linear regression techniques, in which a linear model is formed between the log of instantaneous concentration and one more explanatory variables, such as instantaneous discharge (Draper and Smith, 1981; Runkel et al., 2004).

In this study, a simple log-linear regression model was utilized to estimate pollutant loading as a function of exceedance probability under all flow conditions for each water quality monitoring station. Similar to the simplest linear regression model in LOADEST, the log of the instantaneous load, rather than concentration, was related to the log of the daily discharge that occurred on the same day. The natural log of the load ($\hat{Y}$) is computed as a power function from the simple linear regression as

$$\hat{Y} = \ln(L) = \mathrm{a}\ln(\mathrm{Q}) + \mathrm{b} \qquad [1]$$

where L is the instantaneous load, Q is the observed discharge, and a and b are model coefficients. Given this, loading can be estimated at any possible flow exceedance.

3.2.5 VULNERABILITY TO NUTRIENT POLLUTION

Vulnerability to nutrient pollution was defined as the probability of exceeding nutrient standards. Given load as a function of all feasible flow ranges, in which prediction and confidence intervals are determined in order to understand uncertainty, vulnerability to surpassing the target load is computed as the probability of the standard error for the predicted mean exceeding the numeric target loading. This method assumes the residuals of the regression (ε) are normally distributed

$$\varepsilon \sim N(0, \sigma_\varepsilon) \qquad [2]$$

with sample mean equal to zero and variance (${\sigma_\varepsilon}^2$) equal to

$${\sigma_\varepsilon}^2 = \frac{\sum_{i=1}^{n}(Y_i - \hat{Y}_i)^2}{n-2} \qquad [3]$$

where Y_i is the natural log of the observed instantaneous load, $\hat{Y}_i$ is the natural log of the expected instantaneous load from the simple linear regression, and n is the number of observations. The standard error for the predicted mean ($\sigma_{\hat{Y}}$) was computed as

$$\sigma_{\hat{Y}} = \sigma_\varepsilon\sqrt{1 + \frac{1}{n} + \frac{(ln\hat{Q} - ln\bar{Q})^2}{\sum(lnQ_i - ln\bar{Q})^2}} \qquad [4]$$

where $\bar{Q}$ is the average flow, Q_i is the observed instantaneous discharge, and $\hat{Q}$ is any feasible discharge value. Therefore, nutrient loading at each instantaneous flow value is normally distributed as

$$\hat{Y}|_{Q_q} \sim N(\hat{Y}_{|Q_q}, \sigma_{\hat{Y}|Q_q}) \qquad [5]$$

Various levels of progress have been made towards developing water quality regulations around the U.S. While some states have numeric goals established and implemented for multiple parameters, other states are in the monitoring and development phase. The U.S. EPA identified the 25th percentile of the frequency distribution of all streams within a homogeneous region, level III ecoregions (Omernik and Griffith, 2014), to establish numeric nutrient goals that take background nutrient conditions due to regional variation into consideration. This method for establishing nutrient criteria was selected for the purpose of maintaining consistency between states that lack water quality standards (Baltimore, MD; Portland, OR; and Phoenix, AZ). Denver, CO has targets implemented under Regulation 31, in which the actual target was used in the vulnerability analysis. Table 7 shows numeric targets used to calculate target loading.

Table 7. TP and TN targets used for the characterization of vulnerability to nutrient pollution.

City	Total Phosphorus (mg/L)	Total Nitrogen (mg/L)
Denver, CO*	0.060/0.17	1.070/2.01
Portland, OR	0.040	0.320
Baltimore, MD	0.040	2.225
Phoenix, AZ	0.025	0.607

*Regulation 31 numeric targets for TP (0.17 mg/L) and TN (2.01 mg/L) set by the CDPHE were used for the characterization of vulnerability. However, level III ecoregional targets for TP (0.06 mg/L) and TN (1.070 mg/L) were included in contour figures discussed below.

The target load (L_T) can be determined using target concentrations (T) for each city and feasible qth quantile of discharge (Q_q)

$$L_T = T \times \mathrm{Q}_q \times k \qquad [6]$$

where k is a conversion factor.

Similarly, the empirical load duration curve for any discharge quantile can be obtained by $L_q = \exp(b)Q^a$. The 95% prediction interval (P.I.) for the estimated load at qth discharge quantiles can be obtained by

$$95\%\ P.I.\, on\ L_q = \exp\left[Y_q \pm \varepsilon_{d.o.f=\,n-2;\,\alpha=0.05}\ \sigma_{\hat{Y}|Q_q}\right] \qquad [7]$$

Then, a student's t distribution was applied with n-2 degrees of freedom to predict vulnerability to nutrient pollution (V) by computing the probability of $\widehat{Y_q}$ exceeding the natural log of the target load (L_T) assuming a standard deviation of $\sigma_{\hat{Y}}$ at each exceedance probability

$$V = Prob\left[Y_q > \ln(L_T)\right] = 1 - F_{\hat{Y}}[\ln(L_T)] \qquad [8]$$

where $F_{\hat{Y}}(.)$ is the student's t cumulative distribution function. A student's t distribution was selected for the characterization of vulnerability to allow for statistical rigor in situations where limited water quality data is available (n < 30).

The same approach was taken to calculate loading reduction required to achieve sufficient reliability. For this study, acceptable vulnerability was defined as V ≤ 0.05, or a reliability of 95% or more. The threshold defining impairment was selected to be stringent yet reasonable. The reduction required to achieve an acceptable level of vulnerability was calculated as the difference between loading associated with 95% reliability and the target loading across all flow exceedance probabilities.

3.2.6 LOADEST

The SLR method developed in this study was tested against the best performing model of the twelve models available in LOADEST assuming an adjusted maximum likelihood (AMLE) estimation to give an unbiased estimate of instantaneous load. In addition, flow measurements were reduced to years in which sampling occurred to allow the model to function. One drawback of this approach is that extreme discharge values needed to be omitted in order for LOADEST to function, which affects flow exceedance probabilities, especially at low and high flow conditions. LOADEST requires a minimum number of water quality samples per flow data in order to run with sufficient accuracy (Runkel et al., 2004; Morrison and Bonta, 2008). Also, it is important that one or more explanatory variables are not related to one or another for proper use of LOADEST.

3.3 RESULTS

The simple linear regression model to estimate nutrient loading at all possible flow conditions provided strong and significant estimates for TP and TN loading at most monitoring locations. This simple model was validated by the best performing model in LOADEST, which had errors that were not significantly different than the SLR model developed in this study. Using the empirical loading, vulnerability to nutrient pollution was calculated as a function of exceedance probability, of which Denver, CO was more vulnerable under low flow conditions and Baltimore, MD; Portland, OR, and Phoenix, AZ were more vulnerable under high flow conditions. Some sites, especially those downstream of major urban areas, were unacceptably vulnerable under all flow conditions. The load reduction at each flow condition was also calculated to achieve an acceptable level of vulnerability (V = 0.05), in which the greatest magnitude of reduction in nutrient loading was observed at lower flow exceedance conditions (high flow conditions).

3.3.1 SIMPLE LINEAR REGRESSION

The simple linear regression model yielded significant (p-value ≤ 0.05) relationships between the log of the instantaneous discharge and log of measured pollutant load for all monitoring sites and strong ($R^2 > 0.7$) for 50% and 90% of TP and TN sites, respectively. Figure 6 shows the SLR between ln(L) and ln(Q) (left), which was then used to estimate loading and 95% prediction intervals for all flow exceedance probabilities in the LDC (right) for PHO1 in Phoenix, AZ. PHO1 had n = 24 observations, which was sufficient to produce strong ($R^2 > 0.7$) and significant (p-value ≤ 0.05) results. Note that PHO1 has limited observations during extreme flow conditions (flow exceedance probability ≥ 0.95 and ≤ 0.05), which can be estimated with the SLR method with sufficient confidence. In addition, uncertainty can be quantified using confidence or prediction intervals, shown as the grey band in Figure 6.

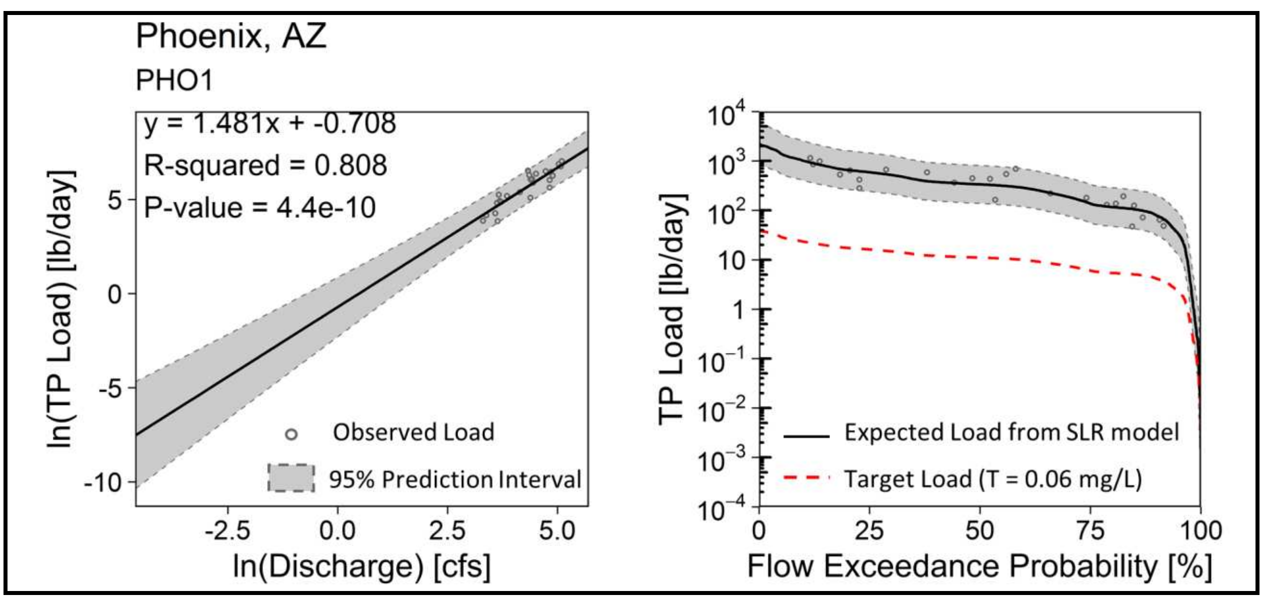

Figure 6. SLR results (left) and fitted LDC (right) with 95% prediction interval for PHO1 in Phoenix, AZ.

Figure 7 shows a boxplot of R^2 values for TP and TN for the simple linear regression model. The method provided stronger results for TN than TP based on the median R^2 value (TN = 0.87, TP = 0.76), however, more significant p-value (TN = 3.0E-36, TP = 2.8E-48) for TP for the four cities of interest. In addition, the variance in R^2 is smaller for TN than TP, shown as smaller boxes in Figure 7. In this research, the log-log relationship between flow and load is more suitable for TN than TP. There was slightly more TP monitoring points than TN monitoring points, explaining great model significance for TP.

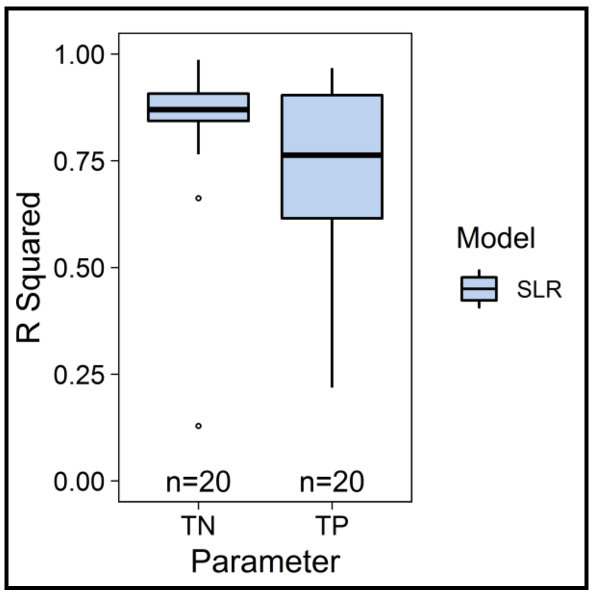

Figure 7. Boxplot of R^2 results from SLR model in Denver, Co; Portland, OR; Phoenix, AZ; and Baltimore, MD. In addition, number of monitoring locations (n) is included for both parameters.

The method developed in this study was tested against the best performing model of the twelve available in LOADEST to further validate the model used in this study. Figure 8 shows the input discharge values (left) and LOADEST results compared to the SLR method (right) at PHO1 in Phoenix, AZ, a site with n = 24 observations. This site had limited data relative to ideal observation quantities used in LOADEST. In order to allow LOADEST to function, flow data between 1983 and 1997 and between 2005 and 2018 were omitted. This omission left out 316 instances of low flow conditions (exceedance ≥ 0.90) and 980 instances of high flow conditions (exceedance ≤ 0.10), impacting flow exceedance probabilities, especially at extreme flow conditions. Figure 8 shows the discharge values used in LOADEST, collected between 1998 and 2004 within the blue shaded region, omitting extreme discharge events defined by the red dashed lines. This omission may explain discrepancies between the SLR models and LOADEST at extreme flow conditions. Consistent reduction in high flow over time may be a result of urban development and construction of water storage systems in the watershed encompassing Phoenix.

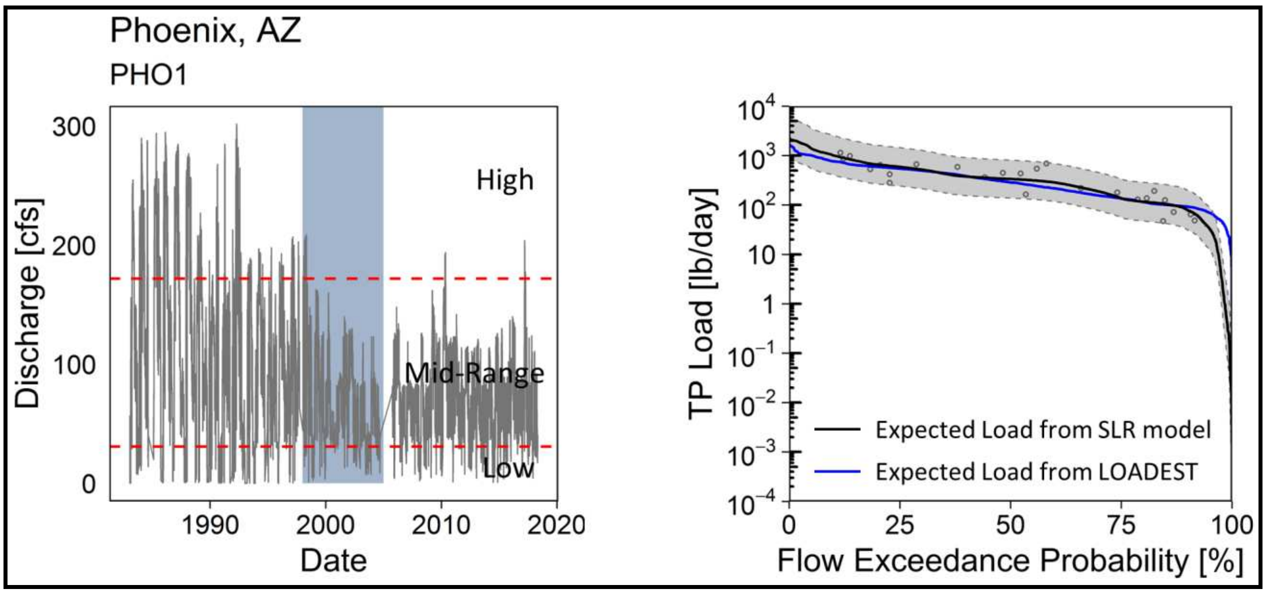

Figure 8. Discharge values used in LOADEST (blue shaded region) (left) and LOADEST and SLR expected load estimation as a function of flow exceedance probability (right) with 95% prediction intervals at PHO1 in Phoenix, AZ.

Figure 9 shows the root mean squared error (RMSE) for the simple linear regression model (SLR) and best performing model in LOADEST, which compares error between model outputs and observed loads. While LOADEST generally produced smaller RMSE values, shown by smaller median RMSE for TP and TN, the error produced in LOADEST was not significantly different than the SLR model, validating the SLR model developed with more advanced modeling procedures.

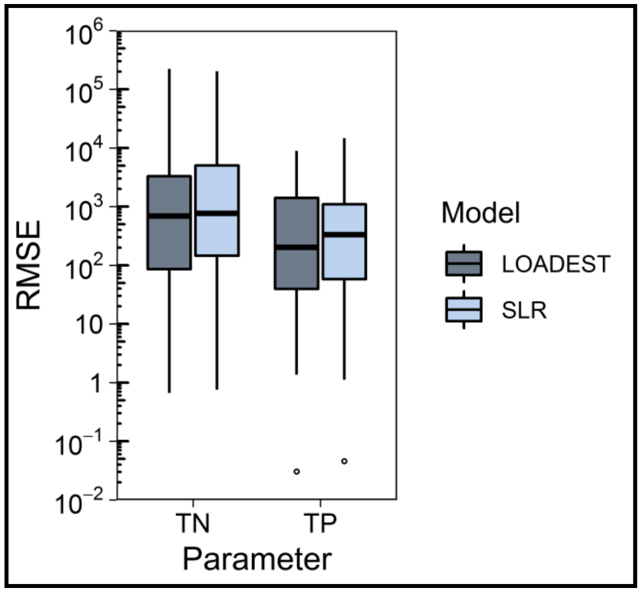

Figure 9. RMSE for TP and TN using LOADEST and the SLR method developed in this study for the four regions of interest.

3.3.2 VULNERABILITY TO NUTRIENT POLLUTION

Vulnerability to TP and TN pollution was calculated as a function of flow exceedance probability for the four study regions. This framework can be used to compare vulnerability at various urban gradients, analyze vulnerability under a range of numeric nutrient targets, identify dominant flow conditions in which impairment is occurring, and determine loading reduction necessary to meet an acceptable level of vulnerability.

Patterns in vulnerability along urban gradients were analyzed across the fours study regions. Upstream sites in Denver, CO were much less vulnerable to nutrient pollution than downstream sites for both TP and TN, shown in Figure 10. Downstream sites, DEN1 and DEN2, were vulnerable under most flow conditions, where upstream site, DEN5 was only vulnerable under low flow conditions for both nutrient constituents. DEN4 laid between, becoming more vulnerable with lower flows. Phoenix experienced a similar pattern in vulnerability along the urban gradient for TN. However, Baltimore, MD; Phoenix, AZ; and Portland, OR for TP and

Baltimore, MD and Portland, OR for TN had high levels of risk to nutrient impairment (V > 0.05) under all flow conditions for nearly all monitoring sites regardless of location along the urban gradient. One explanation for high vulnerabilities for Portland, OR; Phoenix, AZ; and Baltimore, MD is the use of EPA level III ecoregional standards which are often more stringent than state level standards (Ice and Binkley, 2003; Herlihy and Sifneos, 2008) resulting in elevated vulnerability values. See Appendix B for vulnerability as a function of flow exceedance probability for all locations of interest.

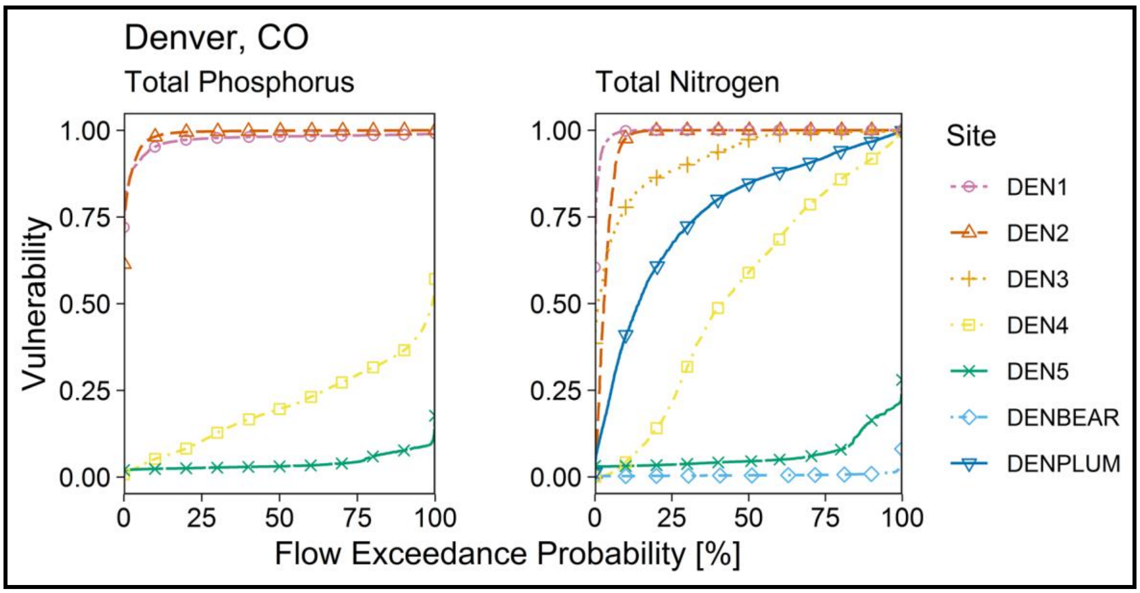

Figure 10. Vulnerability to TP (left) and TN (right) pollution as a function of flow exceedance probability for Denver, CO.

Vulnerability was also accessed as a function of flow exceedance probability at various nutrient target concentrations. While cities exert significant time and effort into establishing feasible water quality standards, this study shows that numeric targets used in this study are either too stringent to feasibly attain or current mitigation practices are not sufficient to meet desired targets under all flow conditions. For example, DEN1 was vulnerable (V > 0.05) under all flow regimes for both TP and TN, as shown in Figure 11. If the target were increased from 0.17

to 0.25 mg/L for TP, this site would remain highly vulnerable to nutrient pollution. Similarly, if the TN target was increased from 2.01 to 3.0 mg/L, DEN1 would remain moderately susceptible to impairment under high flow conditions and highly susceptible under low flow conditions. This suggests that either extreme mitigation efforts at all flow conditions are needed or numeric targets need to increase in order achieve compliance at lower flows for both TP and TN.

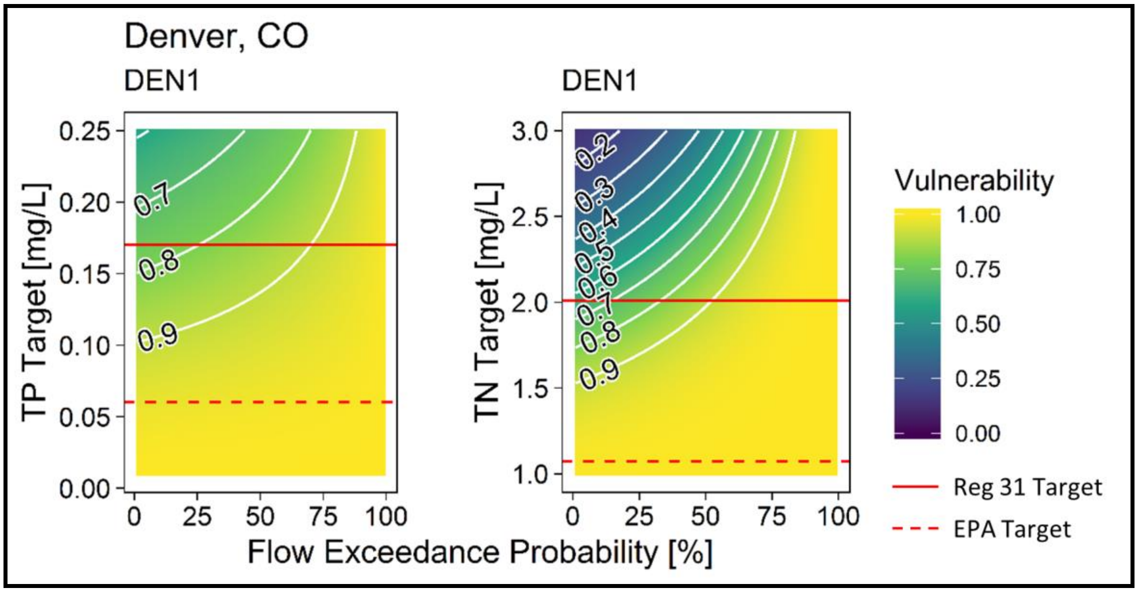

Figure 11. Characterization of vulnerability to TP (left) and TN (right) pollution as a function of flow exceedance probability with varying targets at DEN1 in Denver, CO.

3.3.3 FLOW REGIME AND IMPAIRMENT

The EPA created guidelines for associating impairments occurring in particular flow categories to sources of pollution and potential mitigation efforts, therefore identifying flow ranges in which impairments were likely to occur can provide crucial information for watershed managers. Using the same framework to assess vulnerability to nutrient pollution, flow exceedance probabilities and associated discharge quantities with unacceptable risk to impairment ($V > 0.05$) could be determined. Figure 12 shows the ranges in which vulnerability to nutrient pollution exceeded 0.05 for TP (left) and TN (right). In many cases, sites were highly vulnerable under all flow conditions given current water quality standards implemented by states, such as Regulation 31 in Colorado, and especially the EPA's recommended level III ecoregional targets. Sites that used level III ecoregional targets tended to have higher quantities of vulnerability, likely because these targets are often more stringent than state level targets.

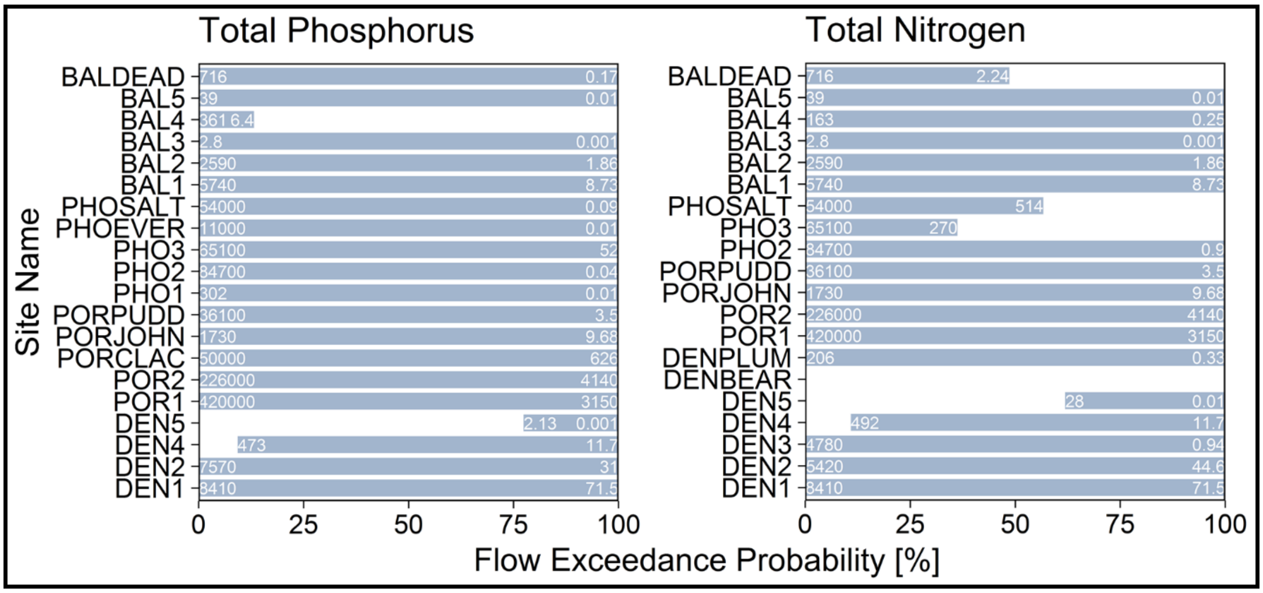

Figure 12. Ranges of flow exceedance probabilities and discharges (cfs) in which V > 0.05 for TP and TN.

One important result of this study was that a given city often exhibits the same dominating flow condition that leads to impairment across urban gradients. Denver, CO had a positive correlation between flow exceedance probability and vulnerability, while Baltimore, MD; Phoenix, AZ; and Portland, OR generally had negative relationships. The South Platte River that runs through Denver is a wastewater dominated system, in which higher flows due to storm runoff dilute river water and improve water quality. However, Portland and Baltimore are in humid regions with naturally high quality baseflows dominating low flow conditions. Though Gwynns Falls watershed in Baltimore does not have wastewater effluent, the Willamette River in

Portland has wastewater contributions that are diluted by high quality baseflow. Gwynns Falls is completely urbanized throughout the entire watershed, where storm events introduce additional nutrient pollution via urban runoff. Phoenix is located is an arid region, however experiences impairment during high flows. One explanation is that Phoenix has superior wastewater treatment procedures due to more stringent state level targets, in which wastewater dominating low flows have better water quality than runoff being introduced during higher flows.

Conventional approaches to quantify load reduction involves calculating the median percent reduction within defined flow categories using observed loads. However, this approach does not reflect variation occurring within the flow category. For this reason, the same framework to calculate vulnerability to nutrient pollution was used to calculate the required load reduction to achieve an acceptable level of risk to surpassing numeric targets ($V = 0.05$) as a function of flow exceedance probability. In general, the magnitude of load reduction was greatest under high flow conditions. This was even true for most sites in Denver, CO which experience greater vulnerability at low flow conditions. Figure 13 shows required reduction for TP and TN in Denver, CO for each site. DEN2 is the only that required more TN reduction at low flow conditions. In addition, no reductions were necessary for downstream sites, DEN4 and DEN5, due to having very low vulnerability values. Significant reductions are necessary at high flow regimes at DEN1 and DEN2. See Appendix B for load reduction as a function of flow exceedance probability for all locations of interest.

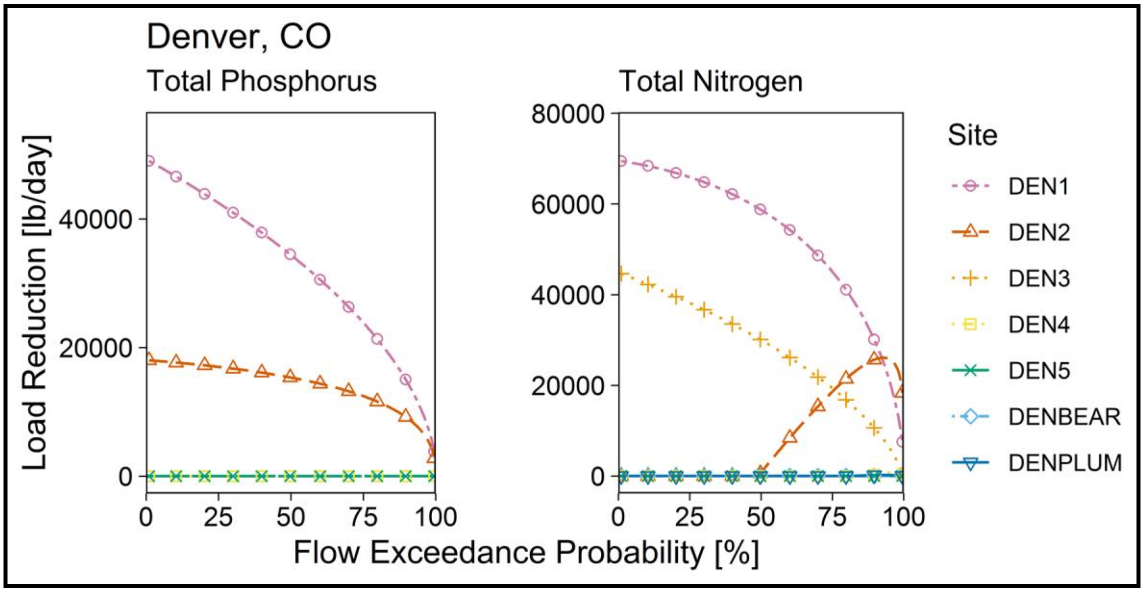

Figure 13. Load reduction required to achieve V ≤ 0.05 for TP (left) and TN (right) in Denver, CO.

The shape of reduction curves appear to be related to the conditions in which vulnerability occurs. For example, Denver, CO experiences greater vulnerability at lower flows, which results in a concave downward curve in Figure 13. However, the other three locations, Portland, OR; Phoenix, AZ; and Baltimore, MD, experience more linear or slightly concave upward trends in reduction as a function of flow exceedance probability, as shown in Figure 14. This is likely due to low flows in Denver, CO needing significant reduction, where low flows in the other three locations are less relative to higher flow conditions.

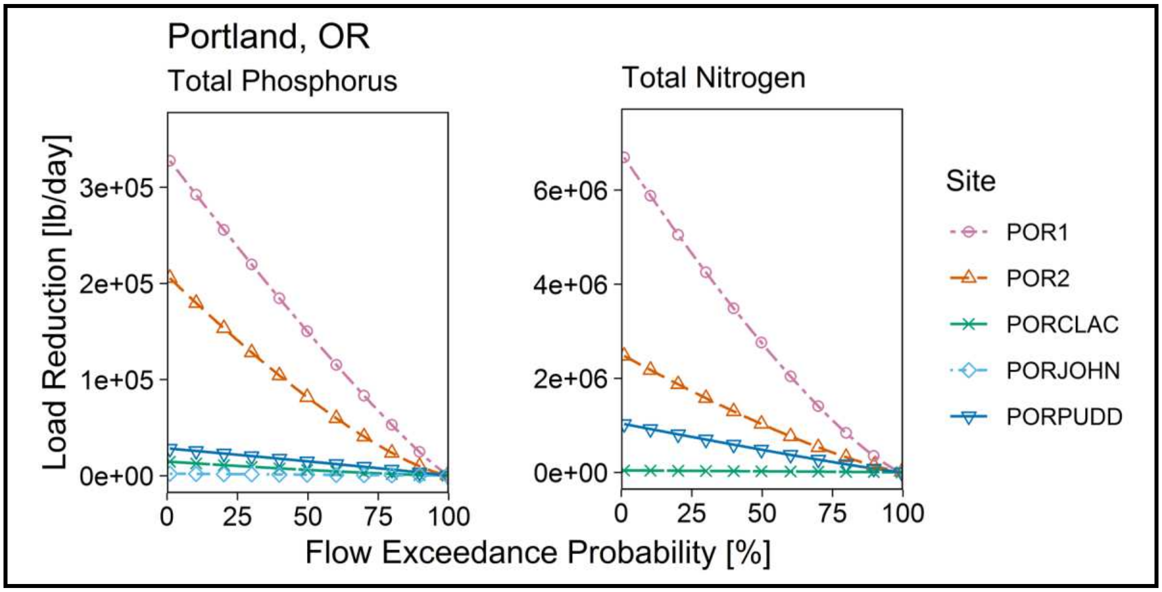

Figure 14. Load reduction required to achieve V ≤ 0.05 for TP (left) and TN (right) in Portland, OR.

In addition to load reduction as a function of flow exceedance probability, the concentration reduction to achieve 95% reliability for each flow condition was also calculated. Similar in nature to the load reduction curves, Denver expressed different behavior than the other three study regions. Figure 15 shows TP and TN concentration reduction increasing with increased flow exceedance, suggesting that the lowest flow conditions require more reduction than mid to high range flows in Denver. One explanation for this trend is that wastewater dominates flow conditions in Denver, resulting in impaired waters at low flow conditions.

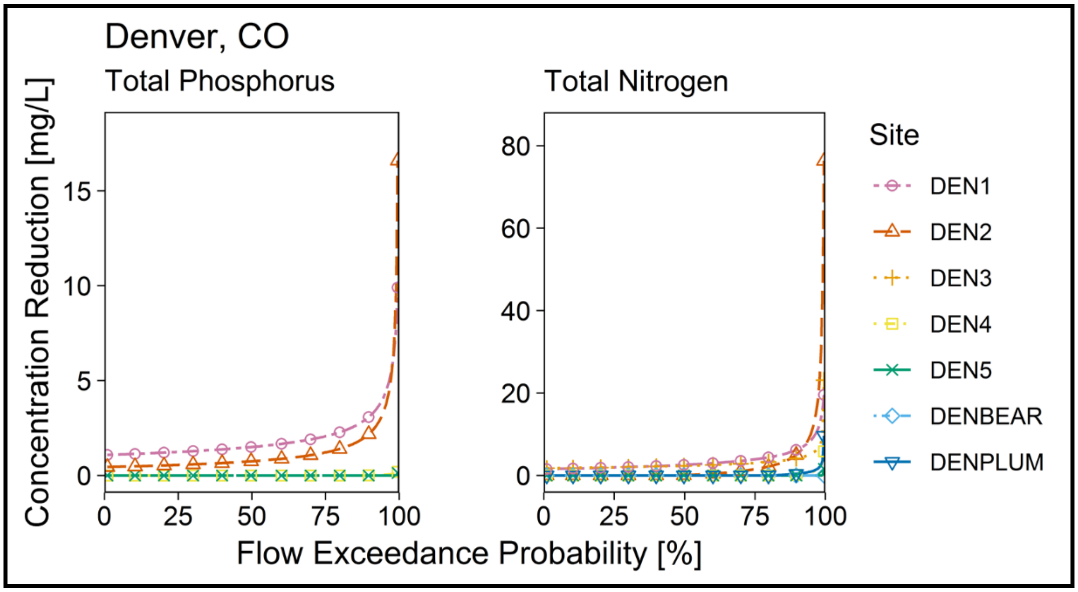

Figure 15. Concentration reduction required to achieve V ≤ 0.05 for TP (left) and TN (right) in Denver, CO.

However, concentration reductions are much more consistent for Phoenix, Portland, and Baltimore. Typically, a slightly downward trend in vulnerability occurred along the urban gradient, where high flow conditions required slightly more concentration reduction. For example, Figure 16 shows TP and TN concentration reduction at each flow condition in Baltimore. Note that the magnitude of concentration reduction is much smaller in Phoenix, Portland, and Baltimore than in Denver. Relatively consistent concentration reductions are seen in these locations as a result of more linear load reduction as a function of flow exceedance probability relative to the curved pattern observed in Denver's load reduction plot. This suggests that Denver receives more pollutants with lower flows, where other cities' pollution is diluted by either high quality baseflows or wastewater treatment effluent. See Appendix B for concentration reduction as a function of flow exceedance probability for each city.

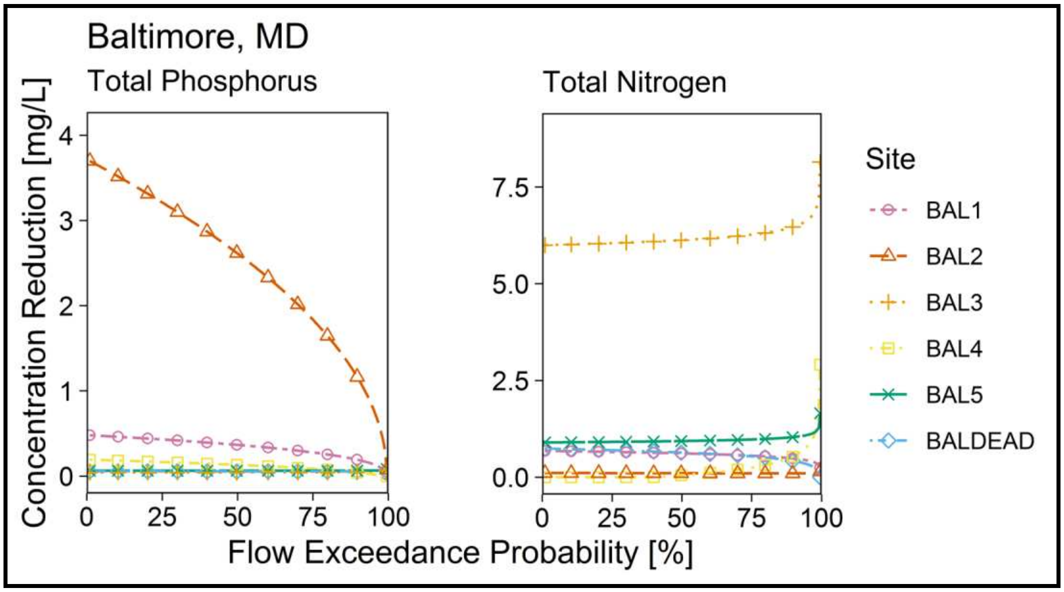

Figure 16. Concentration reduction required to achieve V ≤ 0.05 for TP (left) and TN (right) in Baltimore, MD.

3.4 DISCUSSION

TMDL developers and watershed managers are being confronted with significant challenges when it comes to the condition of the United States water quality. This challenge necessitates methodologies and tools that can be used to quantify risk across all hydrologic conditions, even in scenarios with limited data. Load duration curve based frameworks in combination with simple statistical methods can inform and assist watershed managers in adjusting pollutant load allocations from point sources under variable flow conditions in order to comply with TMDLs and water quality standards. Conventional approaches for the LDC method uses a measure of central tendency to quantify percent reduction in load, leaving out significant variability that may occur and potential error in reduction values. In addition, an adequate number of samples, a minimum of approximately 35 samples, is required to achieve confidence in LOADEST regression analyses to estimate loading as a function of flow exceedance probability.

The method developed in the study can be used to estimate uncertainty using confidence intervals for empirical load duration curves based on a limited number of data points with sufficient precision and accuracy. The load estimation technique provided strong ($R^2 > 0.7$) and significant (p-value ≤ 0.05) results for most monitoring sites, in which confidence bounds could be computed and uncertainty in water quality considered. Applying the expected load, assuming the residuals of the regression are normally distributed, the probability of exceeding a numeric nutrient target, or vulnerability to nutrient pollution, at all possible flow quantities was calculated. Flow conditions with unacceptable levels of risk to surpassing nutrient standards ($V > 0.05$) were then determined, as well as concentration reduction required to achieve acceptable levels of risk at all flow conditions.

Quantifying uncertainty in an inherently variable environment and risk in highly vulnerable regions can provide valuable information for local, state, and federal jurisdictions for the purposes of developing, implementing, and managing TMDLs. The statistical method developed in this study, in combination with load duration curve methods, can be applied to determine flow conditions that lead to impairment, in which these flows can be related to sources of pollution and mitigation efforts. The EPA developed potential sources of pollution and solutions when impairment is observed within certain flow classifications (Cleland, 2002, 2003; USEPA, 2007b). Table 8 shows general relations between flow classifications and potential implementation opportunities.

Table 8. Implementation opportunities based on five flow categories (Cleland, 2002, 2003; USEPA, 2007b).

<table>
<tr><th rowspan="2"></th><th colspan="5">Flow Classification</th></tr>
<tr><th>High</th><th>Moist</th><th>Mid-Range</th><th>Dry</th><th>Low</th></tr>
<tr><td rowspan="5">Implementation Opportunity</td><td>Post Development BMPs</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Streambank Stabilization</td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="3">Erosion Control Programs</td><td></td><td></td></tr>
<tr><td></td><td colspan="3">Riparian Buffer Protection</td><td></td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Municipal WWTF</td></tr>
</table>

For example, unacceptable vulnerability to nutrient pollution is observed only at dry to low flow conditions at upstream locations in Denver, such as at DEN5. This suggests that municipal wastewater treatment facilities may be the source of pollution, where wastewater dominates instream flows during low flow to dry conditions. However, sites that are experiencing high levels of vulnerability at all flow conditions, such as DEN1 and DEN2, multiple sources may be contributing to impairment, such as lack of best management practices and bank erosion during storm events, lack of riparian buffers, and wastewater treatment facilities. The combination of this simple linear regression model, characterization of vulnerability to nutrient pollution as a function of exceedance probability, and charts supported by the EPA relating flow classifications to implementation opportunities can be useful for cities that are experiencing water quality related impairments. Furthermore, using required reduction values at all flow exceedance probabilities can be utilized to achieve acceptable levels of risk to impairment. Greater magnitudes of load reduction is generally needed at high flow conditions in order to achieve an acceptable level of vulnerability to nutrient pollution.

In addition to quantifying vulnerability as a function of flow exceedance probability, the concentration and load reduction required to achieve 95% reliability were quantified using the expanded load duration curve framework. Denver is a wastewater dominated system during low flow conditions, leading to greater concentration reductions at low flows. Conversely, Portland and Baltimore are humid regions, in which naturally high quality baseflows contribute to better quality during low flows. Phoenix is known for excellent wastewater treatment, and therefore baseflow conditions are dominated by high quality effluent due to highly stringent state level standards. Urban runoff may be contributing to impairments at higher flows in these locations. This results in less concentration reduction during low flow conditions and higher concentration reduction during high flow conditions.

The framework is limited in two ways. Water quality standards typically encompass three properties – numeric target of which a given quantile is not to surpass, excursion frequency, and number of samples collected. This framework only takes numeric targets into consideration and assumes the quantile of interest is the expected value, or median. This is the case in Denver. However, the South Platte River's water quality standard also includes a one-in-five year excursion frequency. Thus, this framework is limited in situations where the water quality standard includes more complex characteristics or water quality parameters are not defined. Another limitation of the required reduction is that TMDLs typically focus on annual loading to streams, where this study focuses on daily loading. However, if load reductions are achieved on a daily basis, annual loading should comply with TMDL goals.

The characterization of vulnerability to nutrient pollution developed in this study can provide useful information for TMDL development and maintenance. The methodology builds on widely accepted LDC frameworks, in which risk to impairment can be quantified, dominating flows in which impairments occur identified, and required reduction computed.

CHAPTER 4: CONCLUSION

Probabilistic methods for quantifying vulnerability to water quality impairment are developed in this research. Vulnerability to nutrient impairment is defined as the probability of ambient concentrations exceeding water quality targets. In the second chapter of this paper, four conventional properties of water quality regulation are incorporated into the framework, including frequency of excursion, annual number of samples collected, a numeric target, and a quantile of ambient water quality data that is not to exceed the numeric target. The third chapter of this research explores vulnerability at varying flow regimes by expanding on conventional load duration curve approaches.

The vulnerability analyses developed are applied using both state level regulation and EPA ecoregional goals. In general, EPA targets are more stringent than state level targets, in which sites became more vulnerable to nutrient pollution. In addition, sites become impaired under larger ranges of flow conditions when EPA standards are implemented into the expanded load duration curve approach presented in Chapter 3. This suggests that EPA targets are too stringent to feasibly attain when economic and technologic limitations are considered. While the numeric targets developed for each ecoregion are to represent background conditions, they are often not attainable for urban cities. The method utilized to establish numeric targets assumes the 25th percentile of all data within each ecoregion. Inherently, 75% of locations are impaired under this framework which does not consider attainability. The goal of Clean Water Act, while to improve water around the US, was not intended to financially burden cities.

In arid regions, a gradient in required concentration reduction to achieve 95% reliability is observed. Wastewater often dominates low flow conditions in arid regions, causing water quality impairments with more wastewater contribution and distance downstream. In order to achieve water quality goals in these regions, wastewater effluent should be treated to a high level in order to avoid impairment at downstream locations. Humid regions did not experience a noticeable trend in water quality degradation with distance downstream, likely due to the diluting effects of high baseflows.

A multiple linear regression model between vulnerability and urban influences is conducted. MLR analyses relating indicators of urban intensity and vulnerability values resulted in weak and insignificant results due to a threshold that exists in the calculation of vulnerability. However, when the concentration reduction required to achieve 95% reliability is incorporated into the MLR, rather than vulnerability, strong relationships are formed for most locations. In general, more monitoring locations are needed to determine statistical significance. Urban land cover and wastewater treatment facility capacity generally produce the best results with minimal multicolinearity between exploratory variables, however, non-point predictor variables are shown to vary between cities.

Hydrologic conditions in which impairment occurs is also assessed in the second part of this research. Flow conditions in which impairment occurred is typically the same throughout the urban gradient within each city. Climate and wastewater treatment seemed to play a significant role in dominating flow conditions where exceeding numeric targets is most likely. In Denver, wastewater dominates low flow conditions, leading to impairment under low flow conditions. Phoenix, Portland, and Baltimore all experience impairment during high flows. Portland and

Baltimore are located in humid regions, in which consistent high quality baseflows dominate low flow conditions. Urban runoff and erosion may be causing impairments during storm events at high flows. Phoenix, on the other hand, is in an arid region dominated by wastewater. However, Phoenix has much more stringent water quality standards, in which wastewater is cleaned more rigorously than in other locations.

Average concentration reduction and concentration reduction as a function of flow exceedance probability is determined for each site using the probabilistic methods developed in this research. On average, concentration reduction is greater at downstream locations compared to upstream locations in arid regions. In general, humid regions experience relatively consistent concentration reduction requirements as a function of flow exceedance probability due to diluting effects of high quality baseflows. Slightly more reduction is required during high flow conditions at most monitoring locations, in which urban runoff may be contributing to pollution. Conversely, arid regions requires greater pollutant concentration at lower flows to avoid impairment due to being a wastewater dominated stream. However, the stringency of water quality standards and integrity of wastewater treatment is an important consideration for the analysis. More stringent water quality standards generally motivates wastewater treatment facilities to treat effluent to better water quality, potentially resulting in impairment primarily during high flows rather than low flows. This is the case in Phoenix, where more reduction is necessary at high flow conditions. Quantifying concentration reduction necessary to achieve 95% reliability can be useful in watershed management practices and allocations for TMDL development.

Furthermore, load reduction as a function of flow exceedance probability is quantified. Nearly all locations in this study require greater magnitude of load reduction at high flow conditions. Visually plotting load reduction for every flow possibility can also be used for TMDL development and maintenance to quantify load allocations for point and non-point sources at varying flow regimes to meet water quality standards. While establishing allocations that vary at each flow possibility is not feasible, defining categories of allocations based on flow categories can be used to reduce the likelihood of impairment to nutrient pollution.

Ultimately, these probabilistic models can be utilized to quantify vulnerability for a given location based on four properties of water quality standards or across all flow conditions. As city population in the United States and across the world continues to grow, it will become even more important to understand the condition of surface waters and how urban activities influence them. This research contributes to science by providing novel and probabilistic approaches to characterizing vulnerability to nutrient pollution. More monitoring locations are needed to determine statistical significance between concentration reduction to achieve 95% reliability and urban influences. Building on the load duration curve approach, flow conditions in which impairment is occurring can be identified and linked with pollution that occur during those flows. Load and concentration reductions can be calculated to achieve a desired level of risk to exceeding water quality standards, which can be used for TMDL development and watershed management purposes in order to meet the goals of the Clean Water Act.

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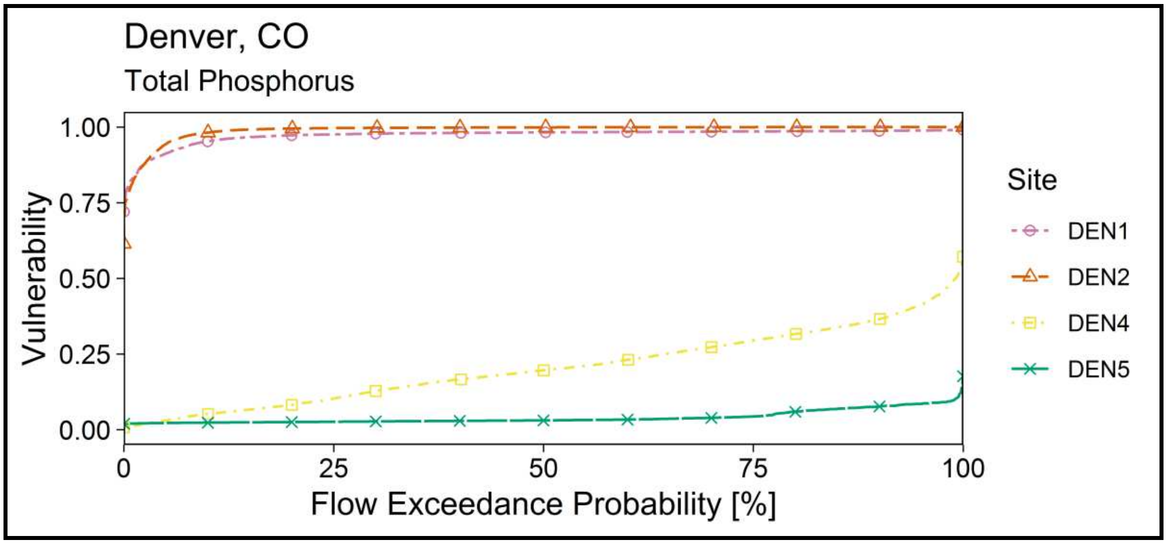
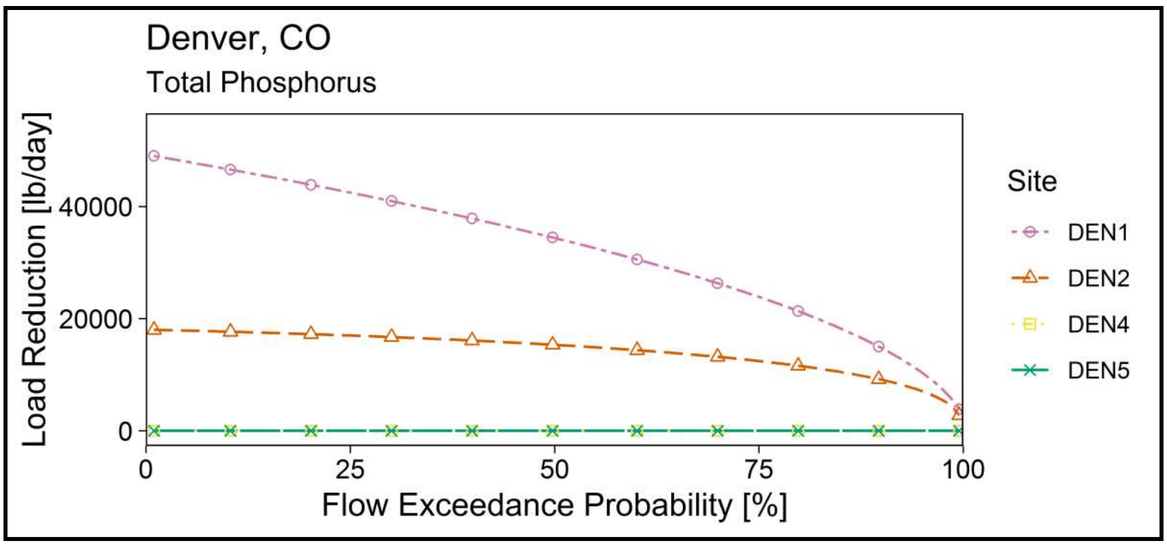
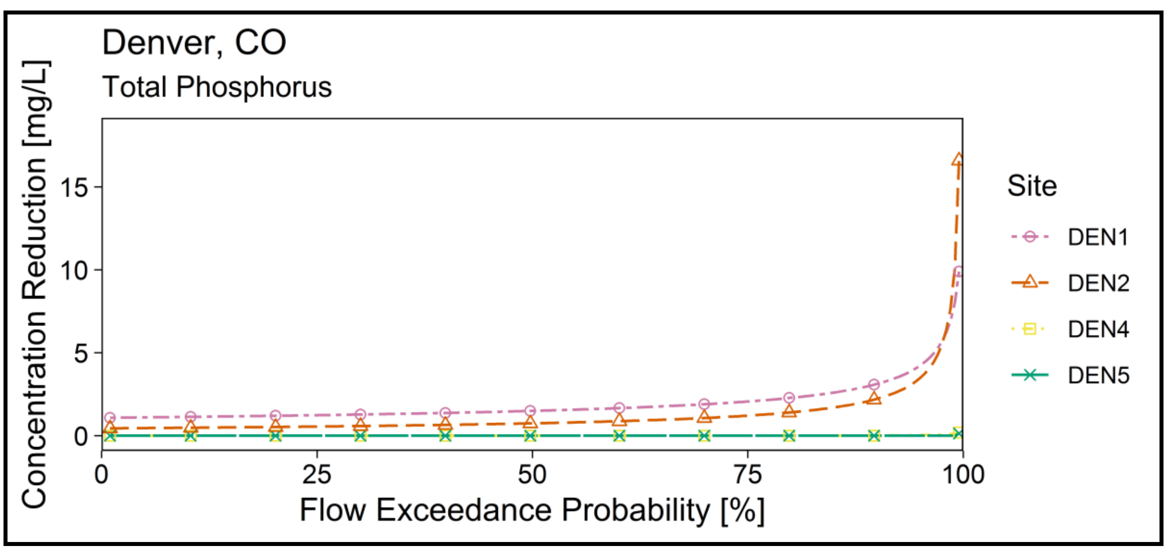
APPENDIX A

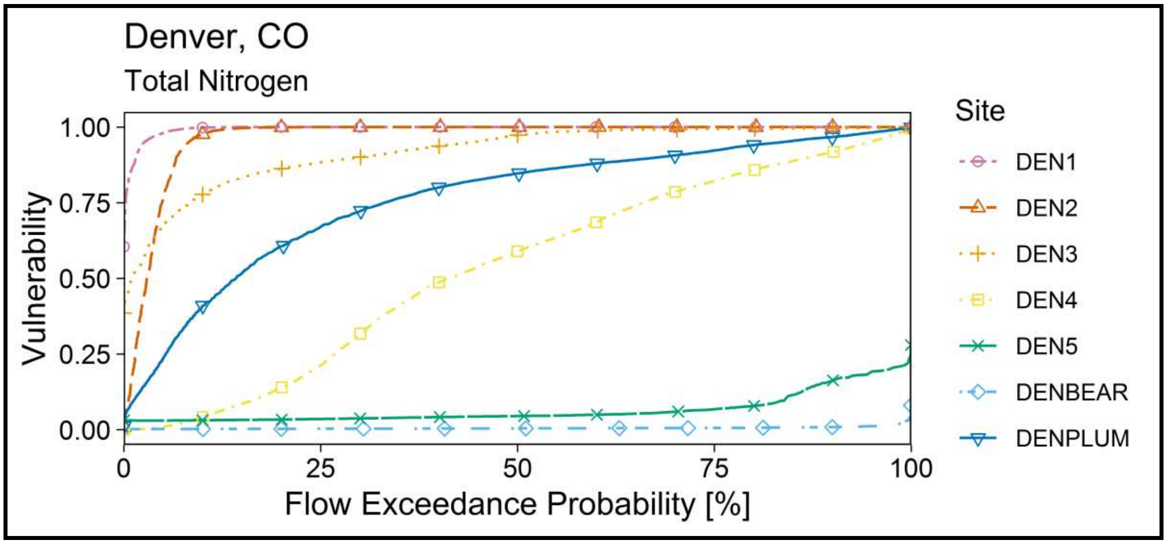
City	Site	Total Phosphorus				Total Nitrogen			
		EPA Vul	EPA Red	State Vul	State Red	EPA Vul	EPA Red	State Vul	State Red
Denver	DEN1	1.000	0.90	1.000	0.79	1.000	5.28	1.000	4.38
	DEN2	1.000	1.15	1.000	1.04	1.000	7.00	1.000	6.09
	DEN3	--	--	--	--	1.000	3.97	1.000	3.01
	DEN4	1.000	0.05	0.000	0.00	1.000	0.90	0.004	0.00
	DEN5	0.001	0.00	0.000	0.00	0.000	0.00	0.000	0.00
	DENBEAR	--	--	--	--	0.003	0.00	0.000	0.00
	DENPLUM	--	--	--	--	1.000	1.66	1.000	0.77
Baltimore	BAL1	0.000	0.00	--	--	0.000	0.00	--	--
	BAL2	1.000	0.01	--	--	0.000	0.00	--	--
	BAL3	0.717	0.00	--	--	1.000	3.89	--	--
	BAL4	0.000	0.00	--	--	0.000	0.00	--	--
	BAL5	0.000	0.00	--	--	0.000	0.00	--	--
	BALDEAD	0.000	0.00	--	--	1.000	0.00	--	--
Portland	POR1	1.000	0.04	--	--	1.000	0.28	--	--
	POR2	1.000	0.01	--	--	1.000	0.13	--	--
	PORPUDD	1.000		--	--	1.000	1.69	--	--
	PORCLAC	0.000	0.00	--	--	--	--	--	--
	PORJOHN	1.000	0.06	--	--	1.000	3.77	--	--
Phoenix	PHO1	1.000	0.70	--	--	--	--	--	--
	PHO2	1.000	0.02	--	--	0.000	0.00	--	--
	PHO3	0.998	0.02	0.021	0.00	0.000	0.00	0.005	0.00
	PHOSALT	0.744	0.00	0.003	0.00	0.000	0.00	0.000	0.00
	PHOEVER	0.001	0.00	0.009	0.00	--	--	--	--

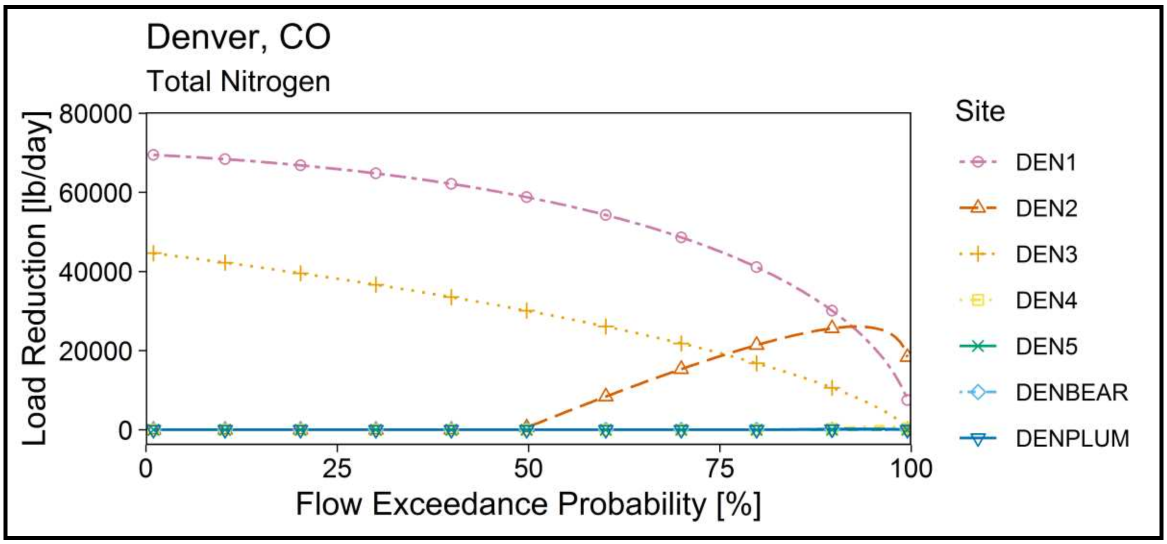
APPENDIX B

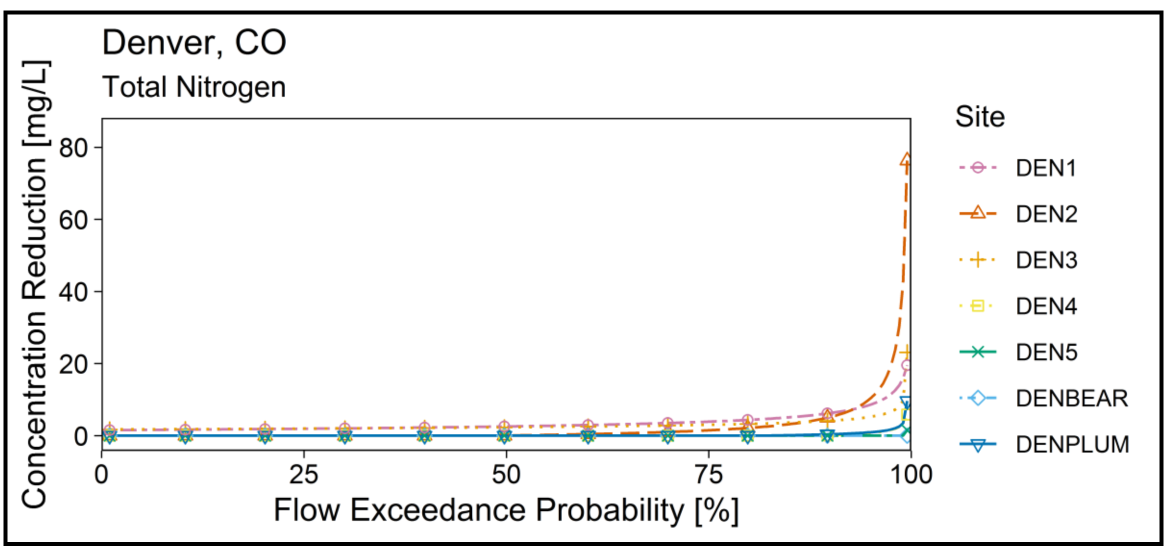

Denver, CO
Total Phosphorus
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
DEN1
DEN2
DEN4
DEN5

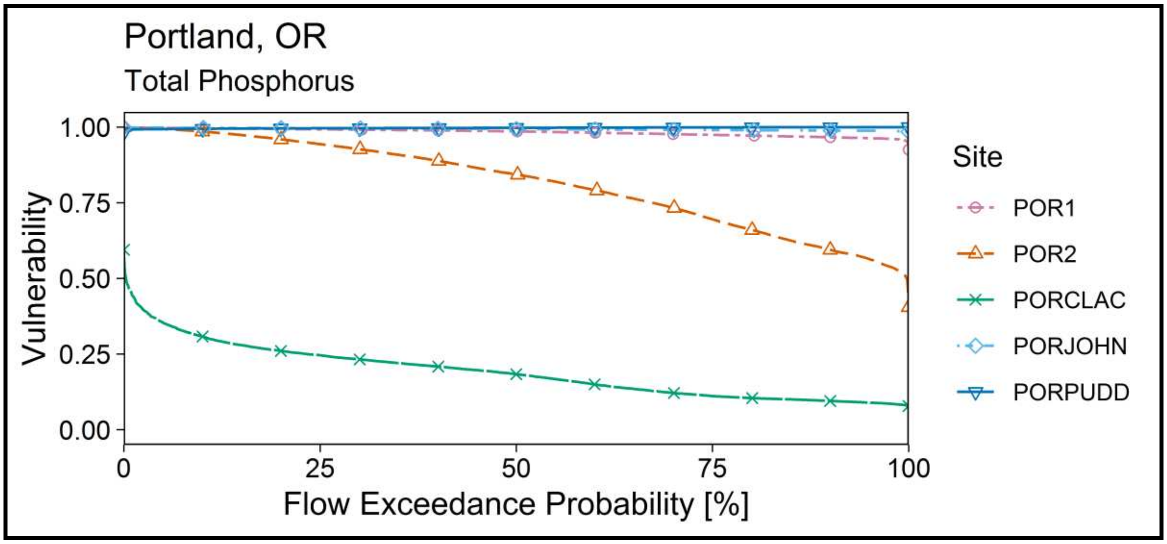

Denver, CO
Total Phosphorus
Load Reduction [lb/day]
40000
20000
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
DEN1
DEN2
DEN4
DEN5


Denver, CO
Total Phosphorus
Concentration Reduction [mg/L]
15
10
5
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
DEN1
DEN2
DEN4
DEN5

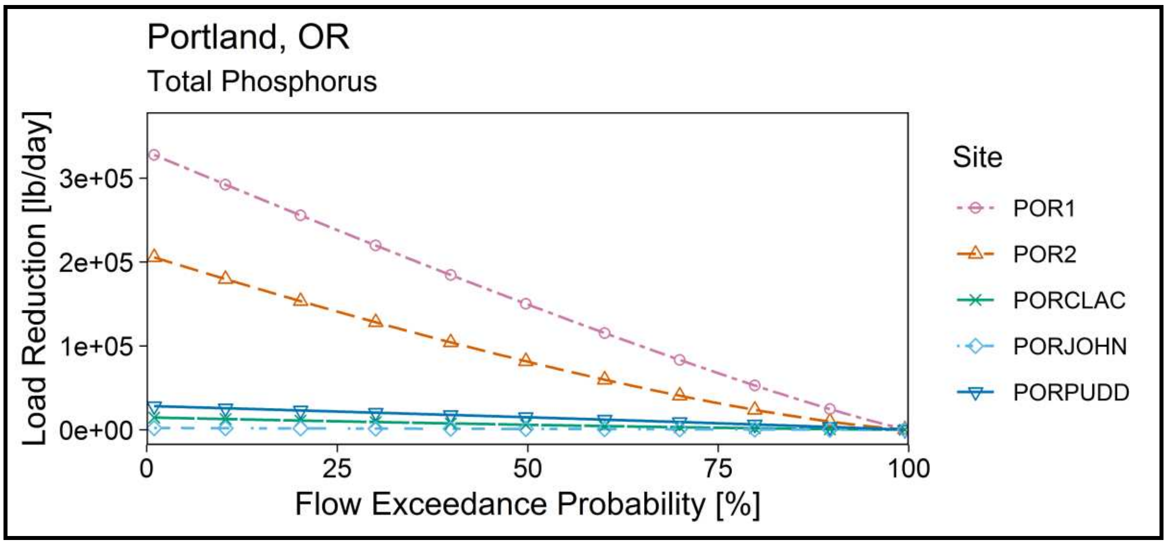

Denver, CO
Total Nitrogen
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
DEN1
DEN2
DEN3
DEN4
DEN5
DENBEAR
DENPLUM


Denver, CO
Total Nitrogen
Load Reduction [lb/day]
80000
60000
40000
20000
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
DEN1
DEN2
DEN3
DEN4
DEN5
DENBEAR
DENPLUM

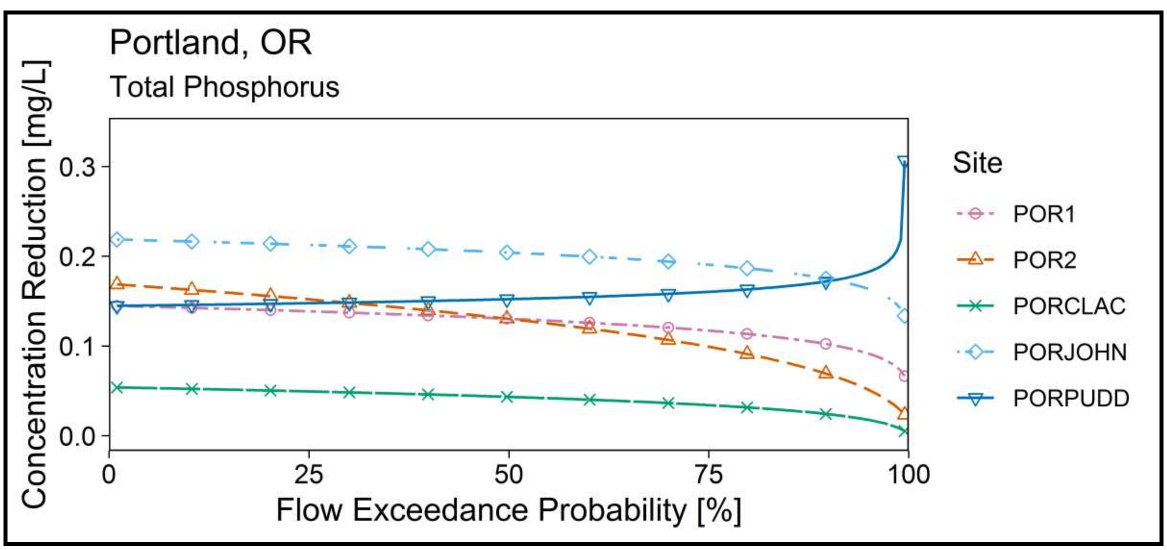

Denver, CO
Total Nitrogen
Concentration Reduction [mg/L]
80
60
40
20
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
DEN1
DEN2
DEN3
DEN4
DEN5
DENBEAR
DENPLUM



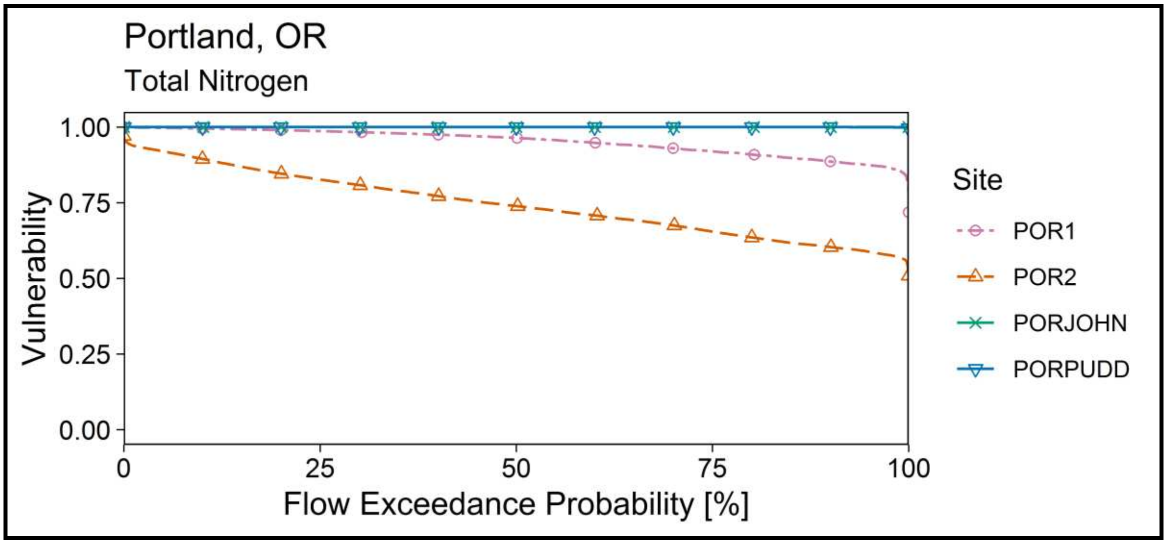
Portland, OR
Total Phosphorus
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
POR1
POR2
PORCLAC
PORJOHN
PORPUDD

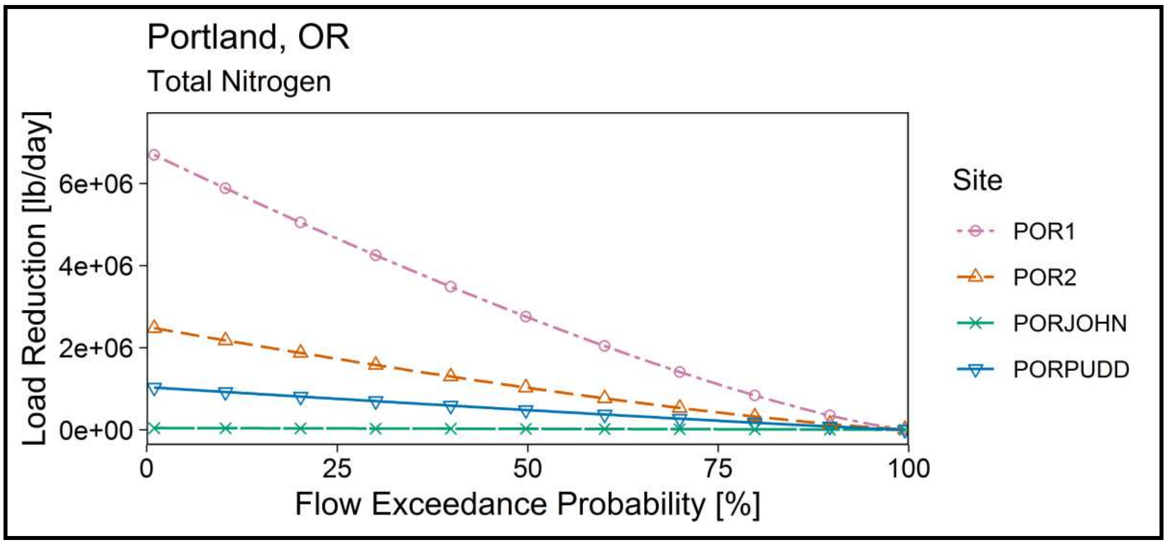


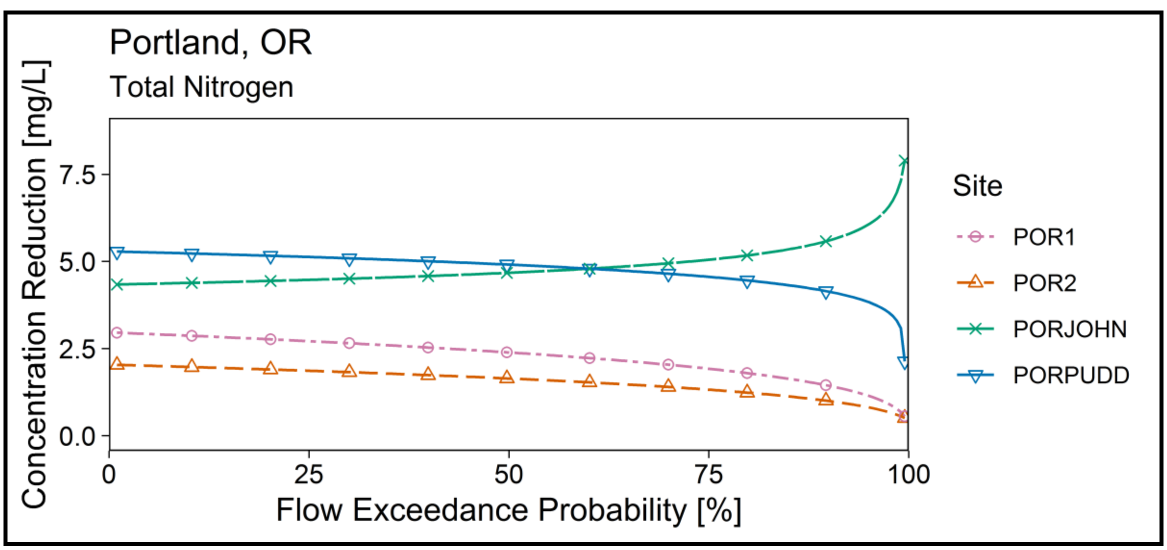
Portland, OR
Total Phosphorus
Load Reduction [lb/day]
3e+05
2e+05
1e+05
0e+00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
POR1
POR2
PORCLAC
PORJOHN
PORPUDD

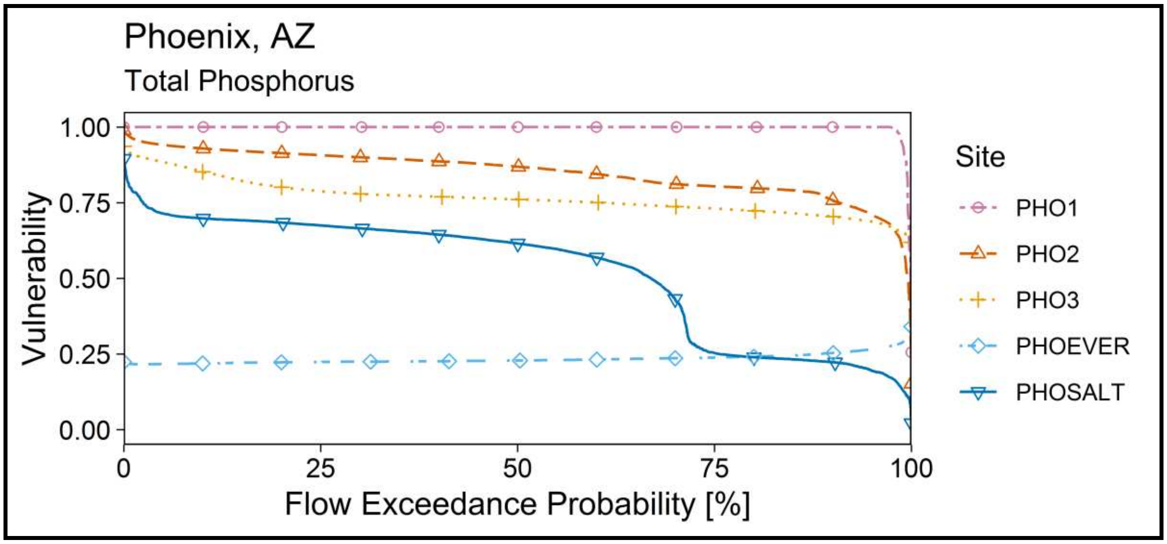


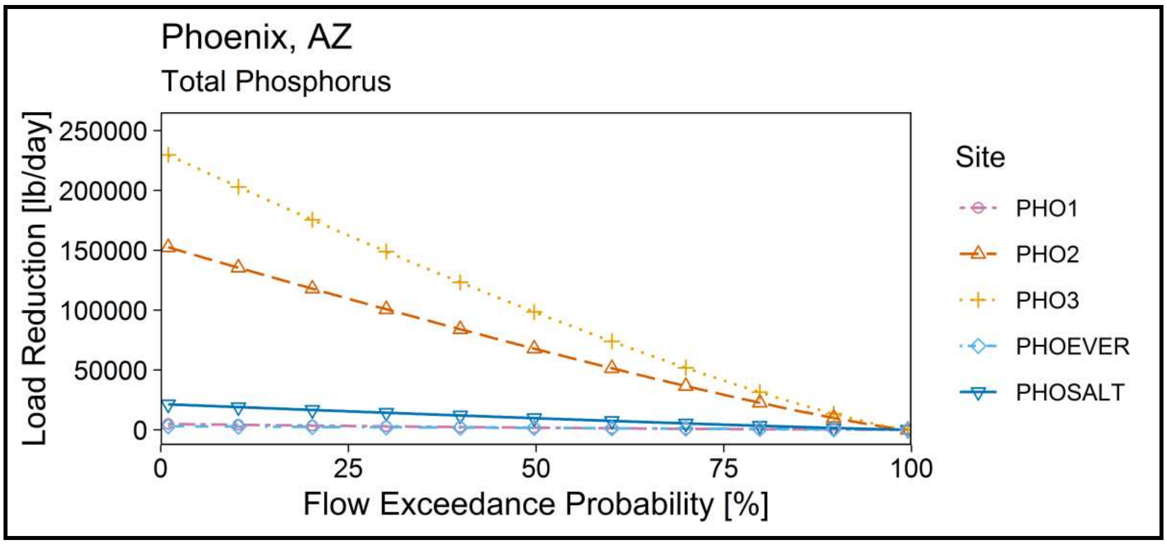
Portland, OR
Total Phosphorus
Concentration Reduction [mg/L]
0.3
0.2
0.1
0.0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
POR1
POR2
PORCLAC
PORJOHN
PORPUDD

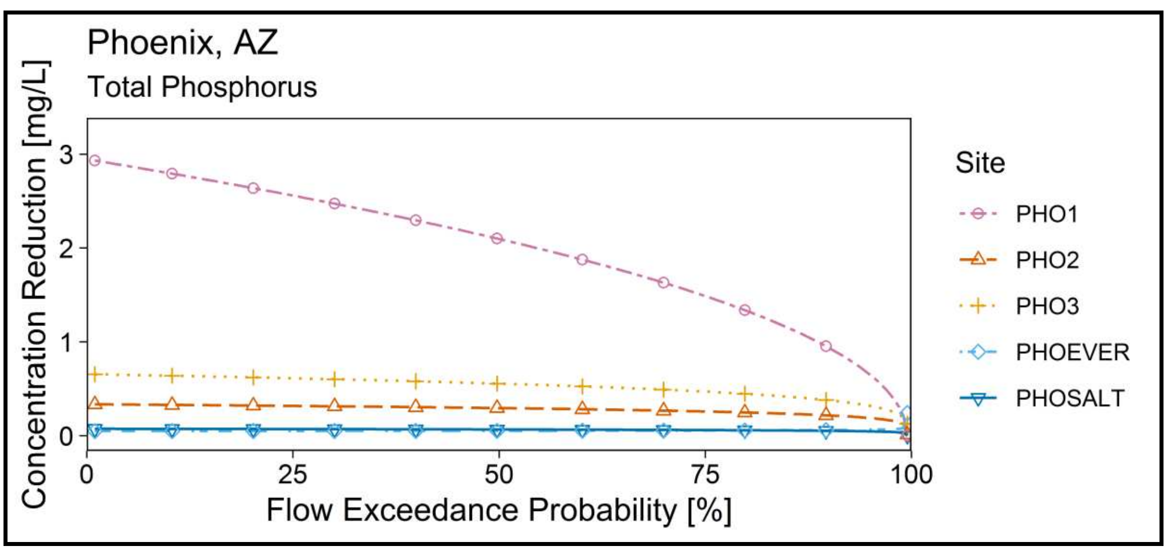

Portland, OR
Total Nitrogen
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
POR1
POR2
PORJOHN
PORPUDD

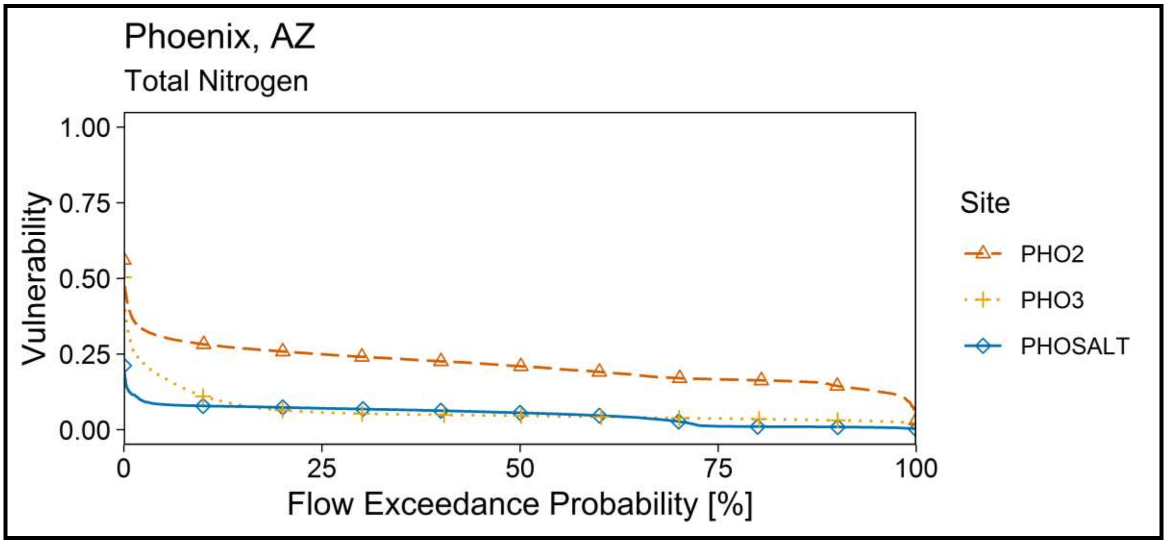

Portland, OR
Total Nitrogen
Load Reduction [lb/day]
6e+06
4e+06
2e+06
0e+00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
POR1
POR2
PORJOHN
PORPUDD

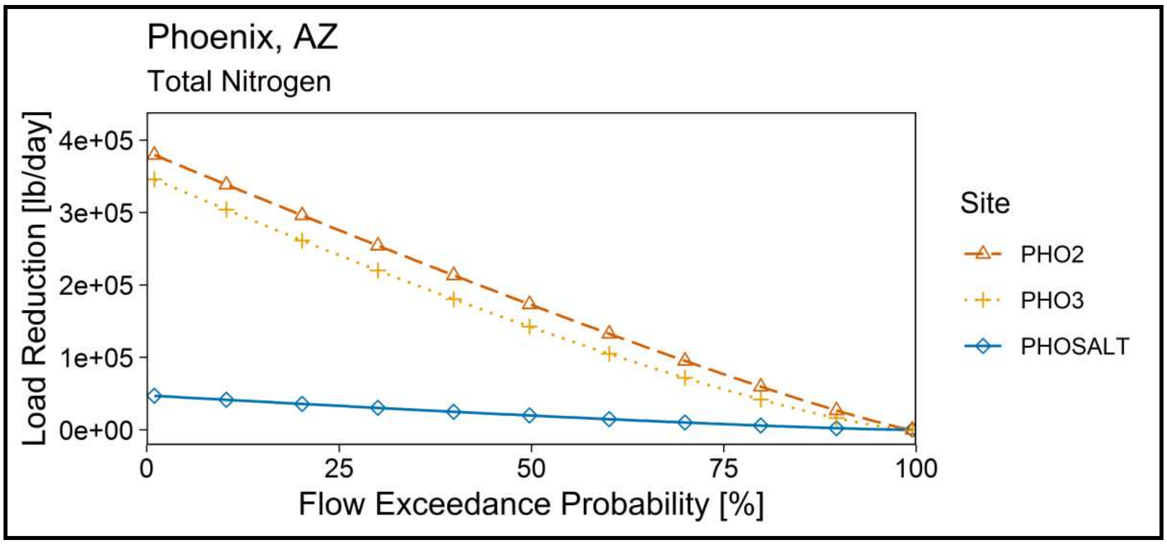

Portland, OR
Total Nitrogen
Concentration Reduction [mg/L]
7.5
5.0
2.5
0.0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
POR1
POR2
PORJOHN
PORPUDD

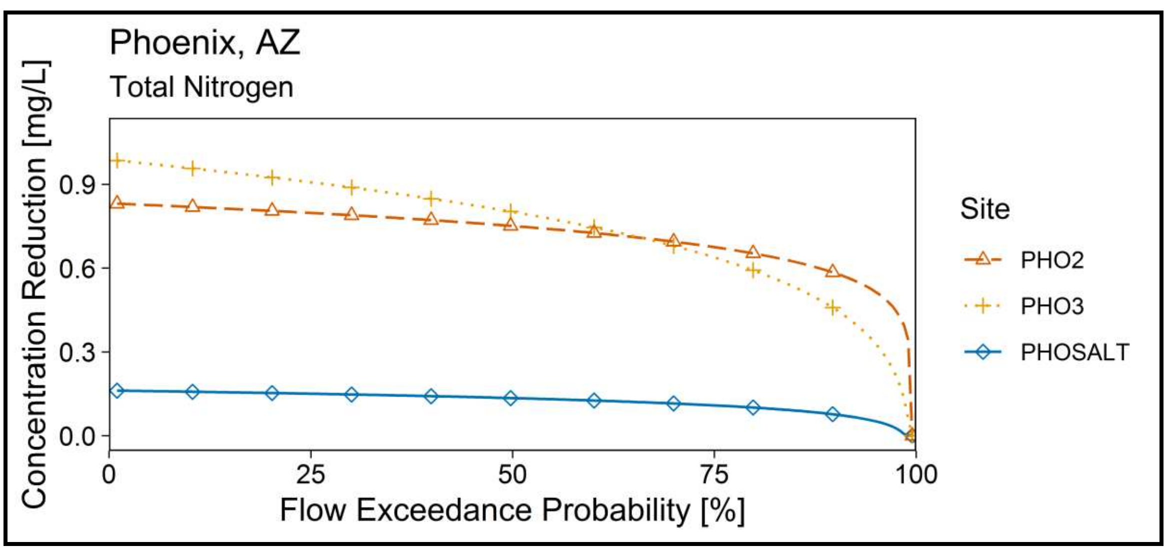

Phoenix, AZ
Total Phosphorus
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
PHO1
PHO2
PHO3
PHOEVER
PHOSALT

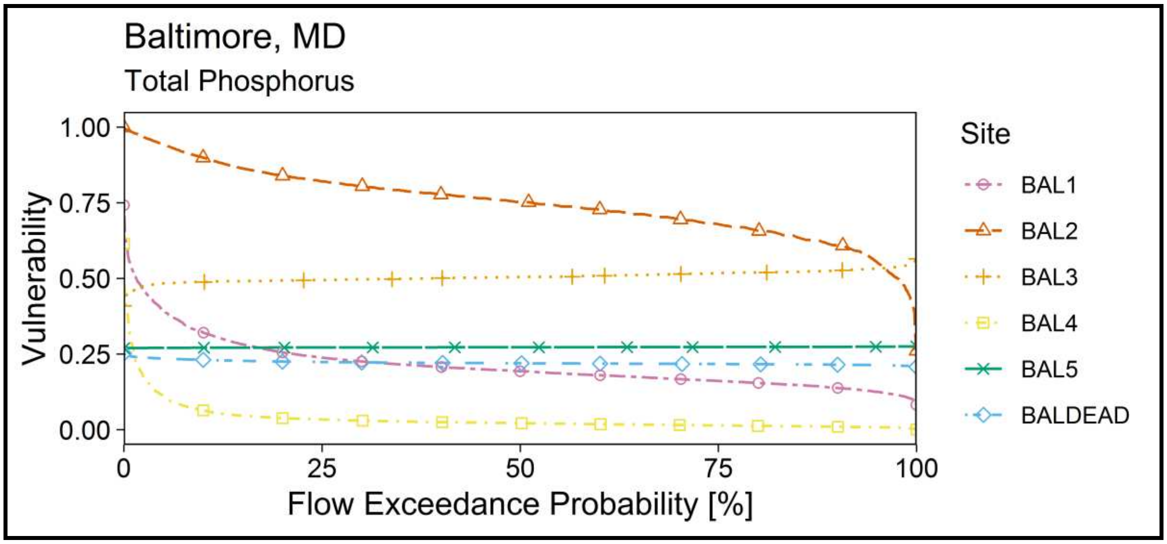

Phoenix, AZ
Total Phosphorus
Load Reduction [lb/day]
250000
200000
150000
100000
50000
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
PHO1
PHO2
PHO3
PHOEVER
PHOSALT

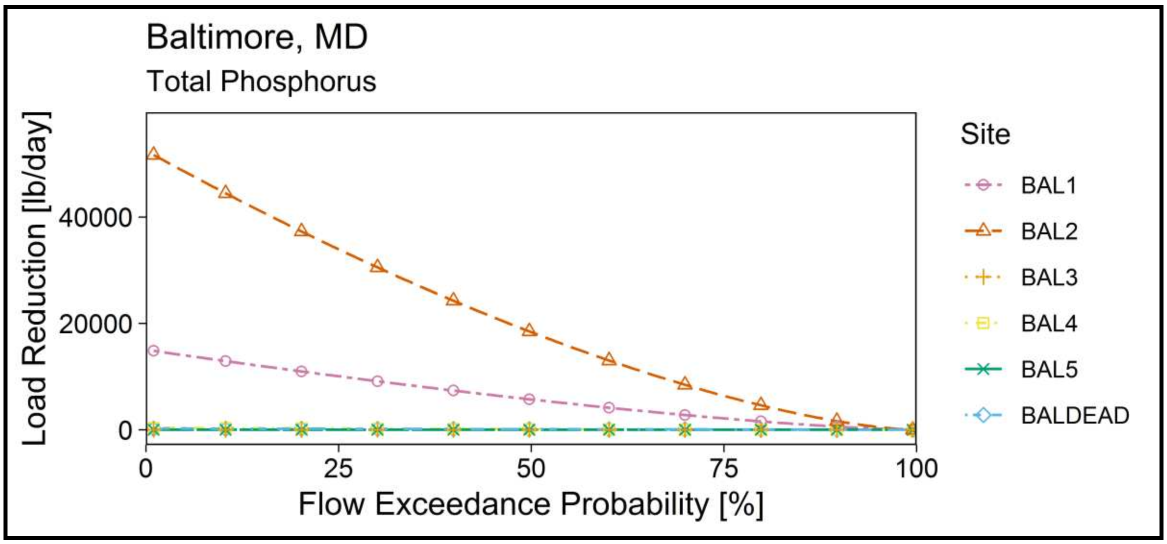

Phoenix, AZ
Total Phosphorus
Concentration Reduction [mg/L]
3
2
1
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
PHO1
PHO2
PHO3
PHOEVER
PHOSALT

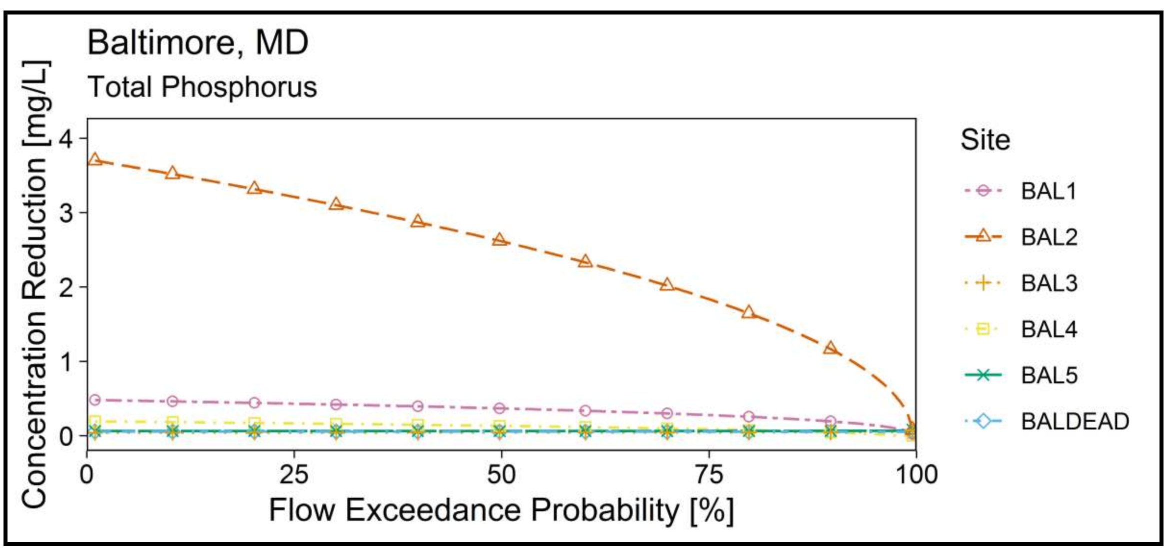

Phoenix, AZ
Total Nitrogen
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
PHO2
PHO3
PHOSALT

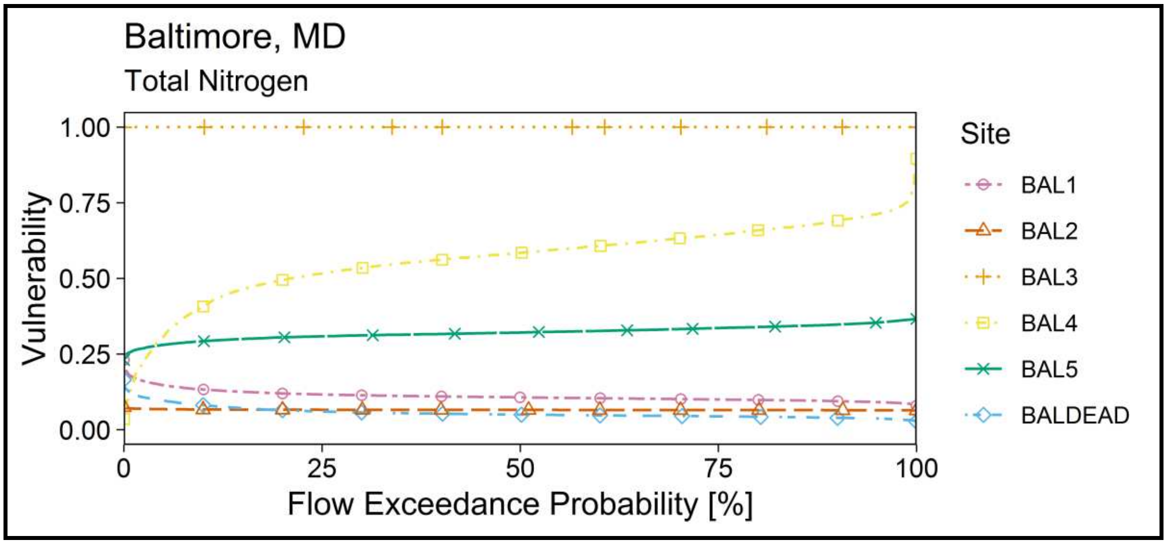

Phoenix, AZ
Total Nitrogen
Load Reduction [lb/day]
4e+05
3e+05
2e+05
1e+05
0e+00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
PHO2
PHO3
PHOSALT

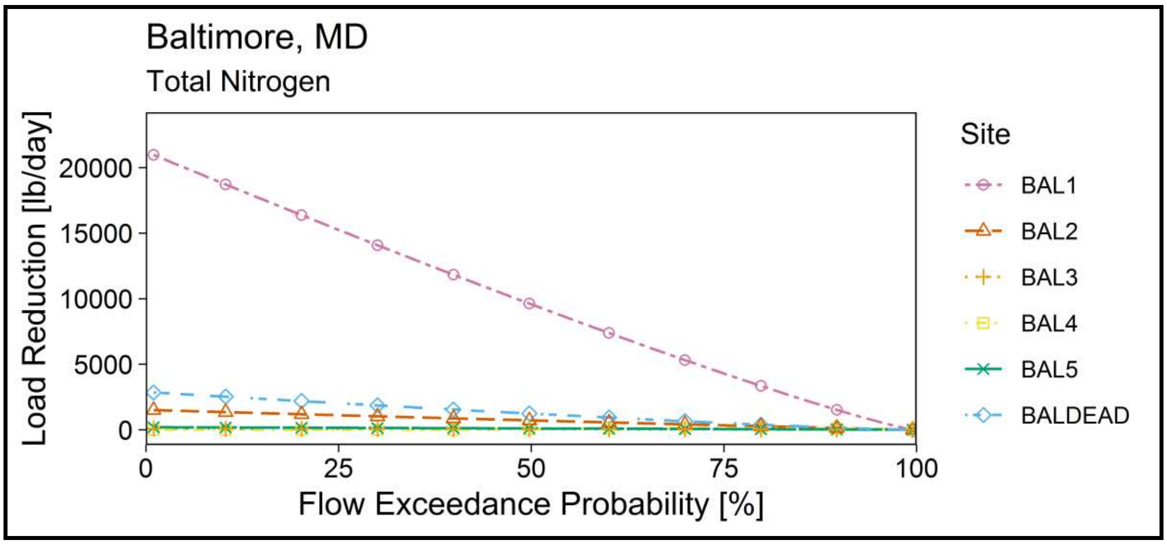

Phoenix, AZ
Total Nitrogen
Concentration Reduction [mg/L]
0.9
0.6
0.3
0.0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
PHO2
PHO3
PHOSALT

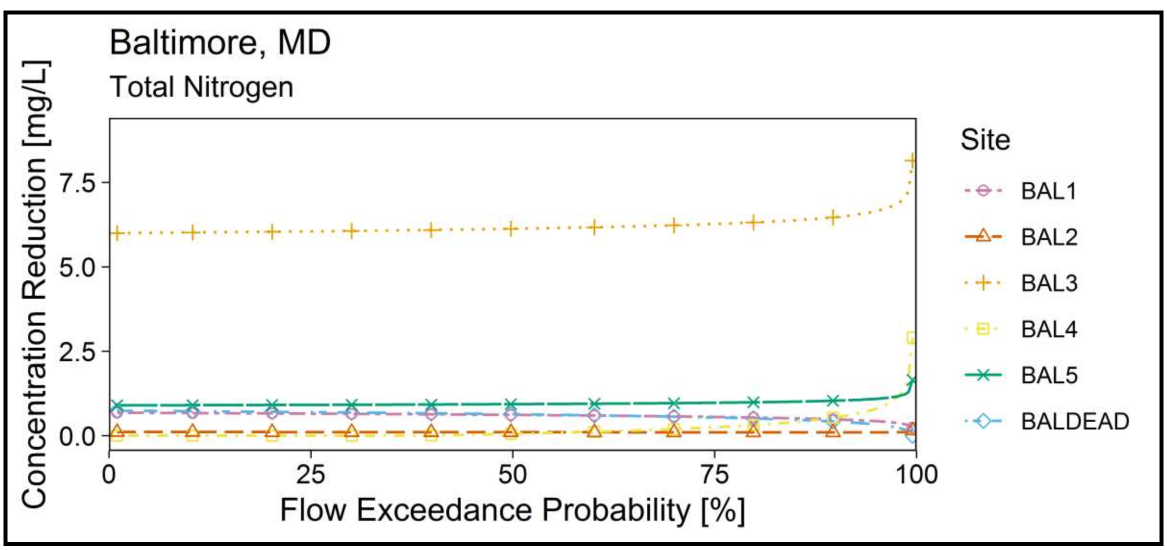

Baltimore, MD
Total Phosphorus
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
BAL1
BAL2
BAL3
BAL4
BAL5
BALDEAD


Baltimore, MD
Total Phosphorus
Load Reduction [lb/day]
40000
20000
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
BAL1
BAL2
BAL3
BAL4
BAL5
BALDEAD


Baltimore, MD
Total Phosphorus
Concentration Reduction [mg/L]
4
3
2
1
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
BAL1
BAL2
BAL3
BAL4
BAL5
BALDEAD


Baltimore, MD
Total Nitrogen
Vulnerability
1.00
0.75
0.50
0.25
0.00
0
25
50
75
100
Flow Exceedance Probability [%]
Site
BAL1
BAL2
BAL3
BAL4
BAL5
BALDEAD


Baltimore, MD
Total Nitrogen
Load Reduction [lb/day]
20000
15000
10000
5000
0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
BAL1
BAL2
BAL3
BAL4
BAL5
BALDEAD


Baltimore, MD
Total Nitrogen
Concentration Reduction [mg/L]
7.5
5.0
2.5
0.0
0
25
50
75
100
Flow Exceedance Probability [%]
Site
BAL1
BAL2
BAL3
BAL4
BAL5
BALDEAD