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Riparian Impacts to Stream Water Quality across Spatial Scales

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Riparian Impacts to Stream Water Quality across Spatial Scales

David John Rosa, PhD

University of Connecticut, 2017

This research contributes new knowledge to two major challenges: 1) up-scaling water quality results from riparian treatment plots to larger watersheds and 2) determining if a short-rotation woody crop (SRWC) can be an effective riparian buffer for treating agricultural nonpoint source pollution. An exhaustive literature review was conducted to provide detailed insight into the methods of scaling, the associated mathematical equations, and their application to the problem of predicting water quality. Dimensional analysis was identified as an underutilized but promising technique for water quality scaling. Dimensional analysis was used to predict total phosphorus (TP) concentrations across heterogeneous watersheds ranging from ~ 200 to 3,400 km². Variables describing attenuated point (kW_p) and nonpoint (W_{np}) sources of pollution, discharge for rivers (Q_s) and treatment plants (Q_w), longitudinal distance of watershed river networks (S) and the cross-sectional area at outlets (A) were transformed into dimensionless groups and a power law equation was derived using multiple linear regression. The scale invariant equation resulted in an R^2 of 0.931 between observed and predicted TP concentrations. The results improve our understanding of spatial scaling methodologies and provide a guide for future work aimed at scaling water quality. A randomized complete block design was used to determine water quality changes resulting from converting plots previously cultivated in corn to SRWC willow (*Salix. spp*) adjacent to a stream in Storrs, CT. Overland flow and ground water samples were analyzed for total nitrogen (TN) and total phosphorus (TP). Additionally, overland flow was analyzed for suspended solids concentration (SSC) and ground water samples were analyzed for nitrate + nitrite (NO^2+NO^3-N). Lower ($p = 0.05$)

concentrations of TN (41%) and TP (53%) were observed in overland flow from willow plots than from corn plots. Shallow ground water concentrations at the edge of willow plots were lower in TN (56%) and $\text{NO}^3 + \text{NO}^2\text{-N}$ (64%), but 35% higher in TP, than at the edge of corn plots. Overland flow associated with willow was also lower in SSC (71%) compared to corn. Changes in water quality from a riparian buffer of willow was found to be similar to those found in restored and established buffers.

Riparian Impacts to Stream Water Quality across Spatial Scales

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B.S., University of Vermont, 2006

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A Dissertation

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2017

APPROVAL PAGE

Doctor of Philosophy Dissertation

Riparian Impacts to Stream Water Quality across Spatial Scales

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Literature review: Scaling methods for water quality predictions, with an emphasis on dimensional analysis

Abstract

Several approaches to transferring information across temporal or spatial resolutions exist, but scaling water quality remains a challenge. This review summarizes the approaches to scaling, the associated mathematical equations, and their application to the problem of predicting water quality. Two general approaches to water quality scaling are Lagrangian-Eulerian, which track changes in particles or volumes of water, and similarity methods, which use a conversion factor to relate characteristics of one system to corresponding characteristics of another. Dimensional analysis, a method founded on the concepts of similarity, addresses several of the limitations of other scaling approaches. While dimensional analysis has been applied to a broad range of physical, chemical, and biological processes, it has remained underutilized in its application to water quality. Dimensional analysis can provide a relatively simplified approach to understanding the dominant processes affecting water quality across watersheds. Furthermore, the method provides a framework for watershed classification based on characterizing similarity among watersheds using dimensionless variables. The successful application of dimensional analysis to a range of complex scaling problems suggest that the method may also be efficacious for scaling water quality. A method for dimensional analysis is presented, and opportunities, advantages, and limitations are discussed.

Introduction

Much of scientific research involves gaining an understanding of a particular process or system, then transferring that understanding to new or different circumstances. For example, Darcy (1856) performed laboratory experiments using packed columns and then transferred that information to groundwater aquifers in order to better understand hydrogeological processes. Like Darcy, Reynolds (1883) also derived a scaling equation concerning the flow of fluids based on laboratory experiments. Two systems with the same Reynolds number, a dimensionless ratio of inertial to viscous forces, have similar flow conditions (laminar versus turbulent), regardless of spatial scale. This transfer of information, termed scaling, can be applied to both spatial and temporal resolutions (Blöschl and Sivapalan, 1995; Wu and Li, 2006a). Scaling has been identified as a fundamental challenge in the natural sciences (Blöschl, 2001; Levin, 1995; Lohrer et al., 2015; Marceau, 1999; Wiens, 1989). Water resources management relies heavily on the concept of scaling. Information obtained from plot or field scale experiments has demonstrated that several best management practices (BMPs) improve water quality in overland flow and ground water (Hoffmann et al., 2009; Jordan et al., 2000; Liu et al., 2008; Mayer et al., 2007; Parkyn, 2004; Penn and Bryant, 2006). These findings have been applied to water quality management at the watershed scale (Mander et al., 2017; U.S. EPA, 2010; UMRSHNC, 2005). However, assessing the impacts of watershed scale management on stream water quality has been difficult (Sharpley et al., 2009; Sutton et al., 2010). The theory and application of scaling in hydrology attempts to close the gaps between observations and predictions (Blöschl et al., 1995). An improved understanding of watershed response to management across spatial and temporal scales is critical to improving water quality (Sharpley et al., 2009, 2014).

Blöschl and Sivapalan (1995) distinguished two general approaches to scaling: those based on modeling and those based on similiarity. The two approaches are not mutually exclusive, and should be considered complementary (Wu and Li, 2006b). In hydrological systems, Eulerian, Lagrangian, and mixed Eulerian-Lagrangian modeling frameworks are used to scale the transport and conservation of mass, momentum and energy (Kavvas et al., 2007). Compared to this process-based modeling approach, similiarity-based methods characterize complex relationships using relatively simple mathematical or statistical scaling functions (Wu and Li, 2006b).

Water quality models which employ Lagrangian-Eulerian stream transport frameworks are often presented as the most rational and economic approach to predicting the outcomes of management practices at the watershed scale (Chapra, 1997). Such models are typically parameterized and many are calibrated to represent the unique characteristics of specific watersheds, but the resulting predictions are often difficult to apply to new settings (McDonnell et al., 2007). The simulated advective and dispersive transport processes are assumed to be additive (Fischer, 1966, 1972). Model errors in general are treated as additive measurement errors, or multiplicative if log transformed (Beven, 2006).

The equations and theories used in models are often developed at small-scales, but are regularly used to simulate large-scale processes (Blöschl and Sivapalan, 1995). Lagrangian-Eulerian methods apply the point-scale conservation of mass equation (Table1) to the scale of the frame of reference (Kavvas et al., 2007). However, as scales change, the processes and patterns controlling phenomena may also change (Wu and Li, 2006a). Additionally, the application of equations which assume homogeneity, uniformity, and time invariance to heterogeneous, dynamic watersheds can result in an increase in the uncertainty of predictions (Kavvas et al., 2007). Researchers attempt to address this issue by modeling watersheds as small, separate units

that are assumed to be homogenous enough that the process equations and theories are applicable (Sivapalan, 2005).

Alternatively, similarity-based approaches establish a simplified relationship between systems based on shared properties (Blöschl and Sivapalan, 1995). In geometry, similar triangles are those in which the values of the lengths of the sides are different, but the dimensionless values of the angles are identical, and therefore the shape of the triangles are the same.

Likewise, physically similar phenomenon are those in which the numerical values of parameters may differ, but the values of dimensionless ratios are identical (Barenblatt, 1996). Compared to highly parameterized, process-based modeling approaches, similarity-based methods characterize complex processes using relatively simple mathematical or statistical scaling functions (Wu and Li, 2006b). Scaling methods and their basic equations are presented in Table 1. Areal extrapolation, power laws, and fractals are similarity-based methods which have previously been applied to water quality scaling (Beaulac and Reckhow, 1982; Kirchner and Neal, 2013; Leopold and Maddock, 1953). Dimensional analysis, also a similarity-based approach, has received relatively little consideration.

Dooge (1986) noted that efforts to scale watershed processes would benefit from a review of scaling laws. While model-based approaches to water quality continue to become more sophisticated and complex, improved understanding of the scaling of watershed behavior is likely to come from the analysis of differences and similarities among catchments (Dooge, 1986; McDonnell et al., 2007; Sivapalan, 2005). Several researchers have called for a transition from attempting to capture detailed features of individual watersheds to identifying dominant hydrological processes applicable across different environments and scales (Blöschl, 2001; Dooge, 1986; Wagener et al., 2007). As an example of this latter approach, Dooge (1986) noted

Table 1. Water quality scaling methods

Methods	Basic equation form	Variables	Assumptions	References
Lagrangian-Eulerian	$\Delta S = M_{in} - M_{out}$	S = storage M = mass	Calculations of point-scale changes can be applied to large networks	Dingman, 2002
Areal extrapolation	$L = CA$	L = mass loading C = export coefficient A = area	No temporal variability	Johnes, 1996
Power laws	$L = \alpha Q^\beta$	L = mass loading Q = discharge	Scale invariance of relationships	Leopold and Maddock, 1953
Fractals				
Temporal (1/f scaling)	$h(\tau) \sim \tau^{-0.5}$	$h(\tau)$ = travel time distribution	Observations reflect both short-term response and long-term memory of past inputs	Kirchner et al., 2000
Spatial (Koch snowflake)	$P_n = 3 S \frac{4^n}{3}$	P_n = length of perimeter at iteration n S = length of side	Patterns repeat at all scales	Mandelbrot, 1982
Dimensional analysis	$\frac{A}{B} = \alpha \left(\frac{B}{C}\right)^\beta$	$\frac{A}{B}$ = dependent ratio $\frac{B}{C}$ = independent ratio	All relevant variables are included	Ipsen, 1960

the successful application of dimensional analysis in the study of hydraulics and suggested that a similar organization of information could improve understanding of hydrologic systems.

Dimensional analysis is a mathematical method for reducing a dimensionally homogenous equation with fundamental dimensions (i.e., mass, length, and time) to a new relation between dimensionless quantities (Taylor, 1974; Langhaar, 1951; Buckingham 1914). The result is a reduction in the number of variables in a problem (Langhaar, 1951), and the elimination of extraneous information (Taylor, 1974). There has been relatively few studies applying the method to predicting water quality, and no application to the spatial scaling of water quality. Dimensional analysis is a promising method for scaling water quality as it can define the similarity between systems (i.e., watersheds), establish relationships that are valid over a range of scales, and characterize dominant hydrological processes and their associated physical, chemical, and biological mechanisms based on dimensionless classifications.

Objectives

The objective of this review was to summarize and evaluate the current state of knowledge pertaining to the scaling of stream water quality, with an emphasis on dimensional analysis. Approaches to scaling water quality predictions were classified as either Lagrangian-Eulerian, areal extrapolation, power law, fractal, or dimensional analysis. The review summarizes the theory and methodology of dimensional analysis and examines dimensional analysis applications across five environmental spheres: the hydrosphere, biosphere, lithosphere, atmosphere, and anthroposphere. The potential for dimensional analysis to scale water quality prediction is evaluated; weaknesses and gaps in existing hydrologic scaling knowledge are identified.

Approaches to scaling

Scaling water quality entails either solving conservation equations using Lagrangian or Eulerian frameworks (Kavvas et al., 2007) or similarity approaches which use a conversion factor to relate characteristics of one system to corresponding characteristics of another (Blöschl and Sivapalan, 1995).

Lagrangian-Eulerian

Eulerian models divide a system into a series of fixed, interconnected volumes, and changes within these volumes or at their boundaries are determined as water flows through them. Lagrangian models track discrete parcels of water or particles as they travel through space and time and record their changes (Rossman and Boulos, 1996). The numerical accuracy between Lagrangian and Eulerian methods is mostly the same and both are capable of predicting observed water quality (Rossman and Boulos, 1996). However, selecting a suitable modeling approach is a highly specialized task that requires a detailed understanding of model features and limitations (Chau, 2006).

Numerous studies have used Eulerian and Lagrangian methods separately and combined to predict water quality (Baker et al., 2014; Baptista et al., 1984; Bella and Dobbins, 1968; Devkota and Imberger, 2009; Fischer, 1972; Helton et al., 2012; Holzbecher, 2012; Linker et al., 2013; Orlob et al., 1967; Torres-bejarano et al., 2013; Waldon et al., 1999). Eulerian approaches included tracking discharge and concentration along stream reaches to model nutrient uptake (Mulholland et al., 2008; Wollheim et al., 2001). Wollheim (2016) presents the following as the most fundamental representation of the proportional removal (R) of a nutrient based on a Eulerian mass balance approach and stream spiraling metrics

$$R = 1 - \exp \frac{U \times W \times L}{Q \times C} \quad (1)$$

where U = areal uptake [$M L^{-2} T$], W is mean stream width [L], L is longitudinal stream length [L], Q = discharge [$L^3 T^{-1}$] and C = concentration [$M L^{-3}$] (Wollheim, 2016).

Detailed representation of transport and biogeochemical processes at the catchment scale can be problematic (Hrachowitz et al., 2016). Difficulties can arise when trying to identify an appropriate and satisfactory scale to represent the variables and processes of interest (Walters and Korman, 1999). The Enhanced Stream Water Quality Model (QUAL2E) is a water quality model that can be applied to dendritic stream systems and uses an Eulerian approach to scaling (USEPA, 1995). Ryu et al., (2016) used the QUAL2E model to scale pollutant loads from fields to watersheds. Agreement between observed and predicted loads were assessed, R^2 ranged from 0.66 to 0.81 and Nash-Sutcliffe efficiency ranged from 0.64 to 0.74. Applications of the Lagrangian framework has included simulating riparian hydrology dynamics using particle tracking (Cloke et al., 2006). Limitations of the this approach included algorithm instability and non-convergence, model uncertainty, and data requirements (Cloke et al., 2006).

Areal Extrapolation

Areal extrapolation is the process of making per unit area measurements on representative plots of land and upscaling predictions based on the areal extent of similar land classes at larger scales. Areal extrapolation equations generally take the form:

$$L = C A \quad (2)$$

where L is a mass or volume conveyed from a land surface, C is a coefficient established for a specific land use, and A is the area of land use. Kuichling (1889) developed the rational method, the now ubiquitous equation used by engineers and planners to upscale predictions of peak discharges. The method uses a modified Equation 2 which includes a rainfall intensity (i) on the right hand side and treats (C) is a dimensionless variable approximating the ratio of peak runoff rate to rainfall rate (Chow et al., 1988). Areal extrapolation methods are often used to predict water quality (Beaulac and Reckhow, 1982; Jones et al., 2001; Soranno et al., 1996). Examples of areal extrapolation applied to water quality prediction include nutrient export coefficients (Beaulac and Reckhow, 1982), the Universal Soil Loss Equation (USLE) (Wischmeier, 1965; Wischmeier and Smith, 1978) and urban buildup/washoff functions (Sartor et al., 1974).

Early water quality studies demonstrated the relationship between the trophic state of lakes and the amount of nutrients added per unit lake area per unit time (Sawyer, 1947; Vollenweider, 1968). In order to quantify the loading from land use, and therefore predict trophic state, export coefficients have been estimated by monitoring plots or watersheds of specific land uses and dividing the observed mass export by the area drained (Dillon and Kirchner, 1975; Reckhow et al., 1980; Soranno et al., 1996). These coefficients can then be included in a scaling equation for predicting loading from watersheds:

$$L = \sum_{i=1}^n C_i A_i \quad (3)$$

where L is total loading from land [M/T], n is the number of land-use types, C_i is the export coefficient for the land use type [$M/L^2/T$] and A_i is the area of land use i [L^2]. Soranno (1996) modified Equation 3 to account for attenuation. Reckhow et al. (1980) suggested annual export coefficients as a method for extrapolating watershed impact assessments on lake quality across similar watersheds. Beaulac and Reckhow (1982) reviewed, screened and compiled results from

several nutrient export studies and presented a range of export values in kg/ha/yr that may be used to estimate loading from various land uses. Export coefficients have been shown to be an effective method of scaling in watersheds where nutrient loading is assumed to be dominated by land use in the catchment, rather than the proximity and connectivity of nutrient sources to the drainage network (Johnes, 1996). Export coefficients have been used to predict observed loadings within 0.5% to 2.5% for two watersheds in the United Kingdom and to evaluate the water quality impact of proposed best management practices (Johnes, 1996). However, the predictive power of export coefficients can be limited by basin heterogeneity (Smith et al., 1997). Wickham et al. (2006) found that scaling nutrient exports introduced two sources of uncertainty: the estimations of in-stream decay rates and the assumption of similarity, or lack thereof, in export behavior among neighboring watersheds.

Streams draining urban areas have been consistently found to be degraded (Walsh et al., 2015). Buildup and washoff functions (Sartor et al., 1974) can be used to simulate the accumulation and removal of a pollutant per area of urban land or length of curb. The Storm Water Management Model (Rossman, 2015) can simulate exponential, power, or linear buildup of pollutants. The following equation simulates areal pollutant accumulation [$M L^{-2}$] proportional to time raised to a power up to a user defined maximum value:

$$B = \text{Min}(C_1, C_2 t^{C_3}) \quad (4)$$

where C_1 = maximum buildup possible [$M L^{-2}$], C_2 = buildup rate constant [$M L^{-2}$], and C_3 = time exponent. Pollutant washoff load [$M T^{-1}$] may be simulated using:

$$W = (C_1 q^{C_2} B) \quad (5)$$

where C_1 = washoff coefficient, C_2 = washoff exponent, q = runoff rate [$L\ T^{-1}\ L^{-2}$] and B = pollutant buildup [M] (Rossman, 2015). Models use areal extrapolation to scale up buildup and washoff predictions to the total length of curbs or area of land in a watershed. These equations are often applied at some aggregated, or lumped watershed approach, implicitly assuming that these functions behave similarly at much larger scales (Bonhomme and Petrucci, 2017).

Areal extrapolation has also been applied to biogeochemical processes. Dodds et al. (2002) used field experiments to estimate process rates per unit area of stream benthos, thus allowing for those processes to be extrapolated based on area. Duncan et al. (2013) applied areal extrapolation to measurements of denitrification rates. Denitrification measurements from soil cores were spatially and temporally extrapolated using data collected from in situ oxygen and soil moisture probes to extrapolate daily N_2 fluxes to the watershed scale (Duncan et al., 2013).

Areal extrapolation can produce good estimates at the scale for which the coefficients were developed (Wischmeier and Smith, 1978). However, when extrapolated to whole watersheds, the equations can result in overestimation of loads by several orders of magnitude (Trimble and Crosson, 2000). Process complexity and heterogeneous watershed characteristics can limit the development of generalized prediction equations (Walling, 1983). Scaling the USLE from the plot to the watershed scale requires a dimensionless sediment delivery ratio to represent the amount delivered to the outlet of a watershed compared to the amount of gross erosion within that watershed (Almendinger et al., 2014; Walling, 1983). Sediment delivery has been demonstrated to decrease as watershed area increases, a result of decreasing land slopes and lower probability of intense rainstorms over an entire watershed (Dendy and Bolton, 1976).

Power Laws

Similarity-based scaling approaches, including fractals and dimensional analysis, are established on the concept of power laws. A power law is a functional relationship in which a relative change in one quantity results in a proportional relative change in another. A power law relation between two quantities does not change with the scale of measurement, a quality known as scale invariance (Frank, 2009). Power laws, also called scaling laws, are the only mathematical function to possess scale invariance (Newman, 2005). Power laws are different than exponential functions; in a power law, a variable is raised to a constant, in an exponential function, a constant is raised to a variable exponent. Power laws can be identified by plotting two variables on a log-log graph, if a power law exists, the resulting relationship will be a straight line whose slope is the value of the power law exponent. Log-normal distributions cannot be considered power laws although they appear as straight lines on a log-normal graph. While they may also appear as straight lines on small portions of log-log graphs, at larger scales they produce quadratic curves (Newman, 2005). Care should be taken when attempting to establish power laws, as relationships may in fact be log-normal when considered at a large enough scale.

Power laws are common in nature, famously describing a range of biological phenomena. Arrhenius (1921) demonstrated the power law relationship between area and number of species. Kleiber found that mammalian metabolism scales to the $\frac{3}{4}$ power of animal mass (1932). West (1997) concluded that power law scaling is perhaps the most prevalent theme describing biological diversity. Power laws are also ubiquitous in hydrology and can integrate complex information about the processes within a watershed (Sivapalan, 2005). Some of the earliest and continued work in scaling water quality has investigated the linear relationship between the

logarithms of sediment loading and stream discharge (Campbell and Bauder, 1940; Crawford, 1991; Dendy and Bolton, 1976; Leopold and Maddock, 1953; Nash, 1994). The resulting rating curves are power law functions in the form:

$$L = \alpha Q^\beta \quad (6)$$

where L is suspended sediment load, Q = stream discharge, α and β are empirically derived coefficient and exponent, respectively.

Several researchers have identified the power law as the most appropriate function for preserving hydrological relationships across scales (Gupta, 2004; Mendez and Ordoñez, 2005; Newman, 2005; Rigon et al., 1996; Rodríguez-Iturbe et al., 1995). Power law relationships have been used to describe scaling of hydrologic and geomorphic variables (Leopold and Miller, 1962; Maritan et al., 1996; Wolman, 1955), including the relationship between drainage area and the length of streams (Hack, 1957; Rigon et al., 1996), river discharge (Rodríguez-Iturbe et al., 1992; Rodríguez-Iturbe and Rinaldo, 1997), flow processes through wetlands (Kadlec, 1990), and flood exceedance probabilities (Kroll et al., 2017; Medhi and Tripathi, 2015). Several hydrologic scaling power laws and their associated variables are presented in Table 2. Power laws are commonly used to describe the relationship between reaction rates (kinetics) and the concentration of one or more reactants (Schnoor, 1996). Additionally power laws can be used to scale chemical reaction rates effected by transport processes (Hunt et al., 2015) and the distribution of dissolved oxygen at the sediment-water interface (Hondzo et al., 2005).

Table 2. Hydrologic power laws

Power law	Variables	Source
$p(a, L)$ $= \pi a^{-r} f(\frac{a}{a_c(L)})$	a = watershed area L = length of river network	Maritan et al., 1996
$L = 1.4A^{0.6}$	L = stream length A = watershed area	Hack, 1957
$W = aQ^b$ $D = cQ^f$ $V = kQ^m$ $L = pQ^i$	W = width D = mean depth V = mean velocity L = suspended sediment load Q = discharge	Leopold and Maddock, 1953
$P_i = kQ_i^{0.5}L_i$	P = energy expenditure rate Q = discharge L = length	Rodríguez-Iturbe and Rinaldo, 1997
$\frac{Q}{W} = Kd^\beta S^\alpha$	Q = discharge W = wetland width d = depth S = slope	Kadlec, 1990
$Q_T = \alpha_T A^{\beta_T}$	Q_T = flood quantile T = year of return period flood A = watershed area	Medhi and Tripathi, 2015
$\frac{dc}{dt} = -kc^n$	c = concentration of reactant n = order of reaction rate	Chapra, 1997

Fractals

Fractals have been suggested as a tool to overcome scale problems in hydrology (Hubert, 2001; Rodríguez-Iturbe and Rinaldo, 1997). While terms such as fractal and multifractal lack an agreed upon mathematical definition (Wu and Li, 2006a), a fractal can generally be described as a mathematical set with a repeating pattern occurring at all scales (Mandelbrot, 1967, 1982;

Wiens, 1989). Fractals are scale invariant and can therefore be represented with a power law (Barenblatt, 1996; Peitgen et al., 2006; Rodríguez-Iturbe and Rinaldo, 1997). Fractal patterns are characterized by their fractal dimension, a ratio representing the change in detail to the change in scale (Mandelbrot, 1982). The classic example is a Koch snowflake, after Koch (1904). The length of the perimeter of a Koch snowflake is

$$P_n = 3 S \frac{4^n}{3} \quad (7)$$

where P_n is the perimeter at iteration n , where an iteration is analogous to a change in scale and S = the length of each side of the snowflake. As a visual example, Figure 1 presents an equilateral triangle with sides whose length = S and each is divided into three equal lengths. In the first iteration of the snowflake, an equilateral triangle with sides = $\frac{S}{3}$ is added into the center third of each original side (Figure 2). The length of each side of the original triangle is now equal to $4(\frac{S}{3})$. A second iteration again adds an equilateral triangle into the center third of each side of the snowflake (Figure 3). With subsequent iterations, additional triangles are added to the center third of each side of the existing triangles. The limit of the perimeter of the Koch snowflake = ∞ . Each edge, which consisted of three units of length $\frac{S}{3}$, becomes four units long. The fractal dimension, or the ratio between the scale of the object and the observable detail is:

$$\frac{\log 4}{\log 3} = 1.2618 \quad (8)$$

Describing the perimeter of a Koch snowflake as a one dimensional length [L^1] is insufficient. The detail of a regular geometric line, divided into three units, remains three units ($3^1 = 3$). The fractional dimension of the Koch snowflake reveals additional, repeating patterns ($3^{1.2618} \approx 4$).

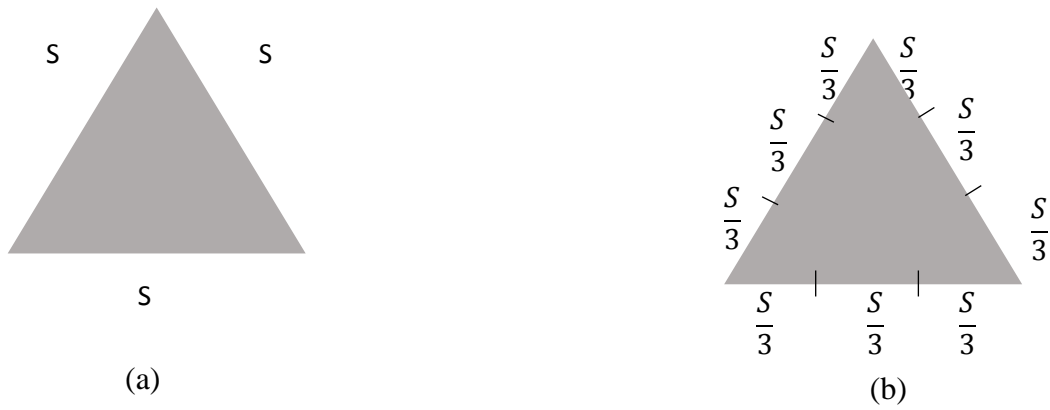


Figure 1. Equilateral triangle (a) with side lengths = S . Each side is divided into three equal parts (b). Adapted from Mandelbrot (1982).

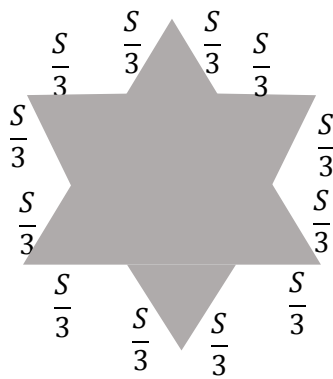


Figure 2. First iteration of a Koch snowflake

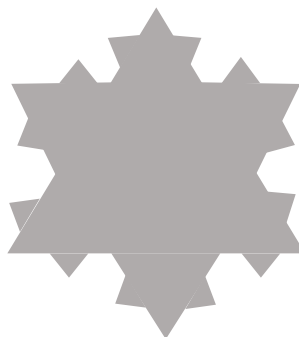


Figure 3. Second iteration of Koch snowflake

Mandelbrot (1967) introduced the concept of fractals in nature by demonstrating that Britain's seacoast was not well-defined but instead was related to the method used to measure it. Measuring the seacoast of Britain using a set unit (i.e km) results in a perimeter of some finite length. However, like a Koch snowflake, a coastline has features (i.e bays and headlands) at all scales. Measuring with increasingly smaller line lengths continuously increases the measured perimeter length. Transport systems, such as plant vascular systems, vertebrate circulatory and respiratory systems, have been described as fractal networks (West et al., 1997). The spatial organization of river networks have been found to resemble fractals (Nikora et al., 1996). Spatial application of fractal geometry has also been used to describe the change in spatial patterns of stream habitat due to impoundment (Nestler and Sutton, 2000).

Fractals not only describe spatial complexity, but temporal complexity as well. Temporal fractal patterns have been identified in rainfall (Douglas et al., 2003; Lovejoy and Mandelbrot, 1985; Olsson, 1996; Schertzer et al., 2010; Schertzer and Lovejoy, 1987) and groundwater flow (Molz et al., 2004; Painter, 1996). Fractals have also been used to develop a scale invariant advection-dispersion governing equation to spatially and temporally scale ground water contamination in an aquifer (Benson et al., 2001). Fractal temporal scale invariance is identified through analysis of the frequency spectrum of a signal, i.e. how its amplitude varies in time (Kirchner et al., 2000; Scher et al., 2002). Fractal scaling of stream water quality exists if the spectral density at frequency f is in the form $\frac{1}{f^\alpha}$ with α being a positive exponent (Gisiger, 2001; Kirchner et al., 2001; Mandelbrot, 1982; Schroeder, 1991). If α is close enough to 1, the temporal scaling is termed $\frac{1}{f}$ (one-over-f) noise. Data with $\frac{1}{f}$ scaling, sometimes called pink noise or flicker noise, is an intermediate function between completely uncorrelated white noise and highly correlated brown noise (termed after Brownian motion) (Schroeder, 1991). Studies of

transport in dynamic systems, ranging from resistors to rivers, have identified the ubiquitous occurrence of $\frac{1}{f}$ noise (Bak et al., 1987).

As near continuous, in-situ water quality monitoring data sets become more available, the use of spectral analysis to identify fractal scaling in river chemistry has increased (Aubert et al., 2014; Godsey et al., 2010; Shaw et al., 2008). Chemical fluctuations in stream water can follow a distinctive fractal pattern that is valid over a range of time scales, from hours to decades (Kirchner and Neal, 2013). Kirchner et al. (2000) investigated the fractal nature of stream water quality by applying spectral methods (Duffy and Gelhar, 1985) to water quality time series. Kirchner and Neal (2013) concluded that watersheds can act as fractal filters, in which storage, transport and mixing processes convert white noise rainfall chemistry into fractal $\frac{1}{f}$ streamflow outputs. The results suggest watershed chemistry travel-time distributions are inherently long-tailed, and may support monitoring studies that have found long lag times in water quality improvement after the implementation of BMPs (Clausen et al., 1992; Meals et al., 2010; Scher et al., 2002). Catchments in England, Scandinavia, and North America have been found to exhibit fractal scaling of water quality (Kirchner and Neal, 2013), suggesting fractal scaling is a ubiquitously occurring signal in stream chemistry. However, Hrachowitz et al. (2015) argue that although $\frac{1}{f}$ scaling can occur in streams, modeled intra- and inter-watershed variations in power law exponents do not support the hypothesis of fractal scaling as a universal characteristic of water quality.

Dimensional analysis

Theory

Dimensional analysis is based on the premise that physical quantities can be expressed as power laws. For example, velocity [V] is expressed as length [L] over time [T], or LT^{-1} , which is a power law monomial (Barenblatt, 1996). Dimensional analysis reduces a dimensionally homogenous equation with fundamental dimensions (i.e., mass, length, and time) to a new relation between dimensionless groups (Buckingham, 1914; Dingman, 2009; Langhaar, 1951; Taylor, 1974). The result is a ratio-based, power law equation that describes the relationship between dimensionless variables using experimental data and regression analysis (Canterbury and Lowther, 1976). The equation can then be used to predict phenomena across scales (Wu and Li, 2006b). In addition to scaling predictions, dimensional analysis can be used to derive theoretical equations, check the plausibility of formulae, and design experiments (Gibbings, 2011; Haynes, 2010). Dimensional analysis was notably used in the field of fluid mechanics to derive the dimensionless Reynolds number (Reynolds, 1883).

Natural phenomena are conceptualized using physical variables with numeric magnitude. Physical variables can be divided into two categories: those which are expressed in terms of dimensions (i.e length, mass, time) and units (i.e feet, kilogram, second), and dimensionless numbers (Barenblatt, 1996; Ipsen, 1960). Dimensionless numbers, such as ratios, describe a physical relation without reference to a unit of measure (Ipsen, 1960). Any equation used to describe or predict a situation must have equal dimensions and units on either side of the equality sign, or be dimensionless. Just as dimensional physical quantities can be related by power law exponents, so too can dimensionless quantities (Langhaar, 1951). A common demonstration of dimensional analysis is the prediction of tree volume (v) given height (h) and diameter (d) (Shen

et al., 2014; Vignaux and Scott, 1999). Dimensional analysis of the variables, all having dimension [L], results in:

$$\frac{v}{h^3} = \alpha \left(\frac{d}{h}\right)^\beta \quad (9)$$

where α and β are an unknown coefficient and exponent, respectively. Observed data, such as for black cherry trees in Allegheny National Park (Vignaux and Scott, 1999), can be used in a regression equation to estimate α and β . Solving for v results in a predictive equation for volume based on height and diameter:

$$v = \alpha d^\beta h^{3-\beta} \quad (10)$$

For dimensional analysis to be successfully applied to a physical problem, a phenomena must be sufficiently understood so that no pertinent quantities are omitted and no extraneous quantities are included in the analysis (Gibbings, 2011; Taylor, 1974). The method is especially useful when mathematical analysis of the problem is too complex or when experiments may be impractical (Huntley, 1967). Dimensional analysis relies on the analyst's knowledge of a problem (Langhaar, 1951), which can range from a basic theory to detailed understanding. The predictive power of dimensional analysis is derived from the concept of similarity. Two systems which share the same value for a dimensionless variable, such as two hydraulic systems with the same Reynolds number, can be assumed to be similar (Barenblatt, 1996).

As a rule, the number of dimensionless groups that can be expected from dimensional analysis can be calculated using the Buckingham π theorem (Buckingham, 1914). Buckingham, a soil physicist, found that the number of dimensional groups (π groups) resulting from dimensional analysis is equal to the number of variables in a problem minus the number of fundamental dimensions (e.g. mass, length, and time) that describe those variables. A rigorous

proof of the π theorem is presented by Gibbings (2011). One limitation of the theorem is that it assumes that the dimensions used are the minimal number required to describe the necessary variables (Ipsen, 1960; Taylor, 1974). If the result of dimensional analysis yields more dimensionless groups than predicted from Buckingham's theorem, it is likely that the original variables could have been described using a smaller number of dimensions (Ipsen, 1960).

The predictive π groups resulting from dimensional analysis should be independent from each other so that the value of a π group can be experimentally varied without changing the value of the other groups (Langhaar, 1951). Furthermore, care should be taken in interpreting seemingly statistically significant results that are in fact due to spurious correlation. Analytical methods, including dimensional analysis, can produce correlation that is an artefact of the analysis itself. For example, researchers should avoid dimensional analysis in situations where observational error may be large, such as measurements of wind shear during times of high atmospheric instability (Hicks, 1978). After dimensionless groups have been derived, a functional scaling relationship among the dimensionless products can be determined using experimental data and regression analysis (Canterbury and Lowther, 1976). There also can be dimensionless values such as ratios included later into the regression (Taylor, 1974; Vignaux and Scott, 1999; Wong, 1979). For example, dimensionless variables such as land use ratios and channel slope may not be involved in dimensional analysis, but may be relevant and therefore included when establishing a functional scaling relationship.

Methods for dimensional analysis

Good description of the methods for performing dimensional analysis are found in Langhaar (1951), Ipsen (1960), Taylor (1974), Vignaux and Scott (1999), and Gibbings (2011). Generally, analysts may use the matrix approach presented by Langhaar (1951) or Ipsen's step-by-step method (1960). The step-by-step method, adapted from Ipsen's (1960) example of fluid force on a cylinder, is demonstrated below.

The amount of drag force (F) on a sphere by a fluid can be assumed to be a function of the density (ρ), viscosity (μ), and mean velocity (V) of the fluid, and the diameter (D) of the sphere. The dimensions involved in this relationship are length [L], mass [M], and time [T] (Table 3). The problem may be conceptualized as:

$$F = f(\rho, \mu, V, D) \quad (11)$$

where (f) is some unknown function. The step-by-step method systematically cancels each dimension in the equation. In each step, a dimension is chosen to be cancelled from the given variables. A variable containing that dimension is then selected and used to multiply or divide the remaining variables which also include that dimension. Given that there are three original dimensions in this example (Table 3), three steps will be required to derive the dimensionless equation. However, it is sometimes possible to eliminate two dimensions at once (Ipsen, 1960).

Step1. From inspection of Table 3, the dimension [L] is included in the variables ρ , μ , D , and V . For simplicity, D was selected to create products or quotients of the remaining variables containing [L] in a manner so that [L] is cancelled from each those variables (Table 3). When a dimension is cancelled from a variable, the operation is reflected in the symbol and respective dimensions.

Table 3. Dimensional analysis of variables for the drag force F on a sphere by a fluid using the step-by-step method (Ipsen, 1960)

Original variables and dimensions			Step 1: Cancel [L] using D		Step 2: Cancel [M] using ρD3		Step 3: Cancel [T] using $\frac{V}{D}$	
Variable	Dimensions	Symbol	Dimension Calculation	Symbol	Dimension Calculation	Symbol	Dimension Calculation	Symbol
Force	$\frac{ML}{T^2}$	F	$\frac{ML}{T^2} \cdot \frac{1}{L} = \frac{M}{T^2}$	$\frac{F}{D}$	$\frac{M}{T^2} = \frac{1}{T^2}$	$\frac{F}{\frac{D}{\rho D^3}} = \frac{F}{\rho D^4}$	$\frac{1}{T^2} = 1$	$\frac{F}{\frac{\rho D^4}{(\frac{V}{D})^2}} = \frac{F}{\rho D^2 V^2}$
Density	$\frac{M}{L^3}$	ρ	$\frac{M}{L^3} * L^3 = M$	ρD ³	_____		_____	
Viscosity	$\frac{M}{LT}$	μ	$\frac{M}{LT} * L = \frac{M}{T}$	μD	$\frac{M}{T} = \frac{1}{T}$	$\frac{\mu D}{\rho D^3} = \frac{\mu}{\rho D^2}$	$\frac{1}{T} = 1$	$\frac{\mu}{\frac{\rho D^2}{\frac{V}{D}}} = \frac{\mu}{\rho V D}$
Diameter	L	D	_____		_____		_____	
Mean velocity	$\frac{L}{T}$	V	$\frac{L}{T} = \frac{1}{T}$	$\frac{V}{D}$	$\frac{1}{T}$	$\frac{V}{D}$	_____	

Step 2. The dimension [M] is chosen next to eliminate. Any of the three terms involving [M] may be used to eliminate the mass dimension. Inspection of Table 3 suggests that the term ρD^3 can be used to cancel the remaining occurrences of [M].

Step 3. The remaining dimension [T] was canceled using $\frac{V}{D}$. The two remaining variables are dimensionless, denoted with a dimension of 1. As expected from Buckingham's π theorem, application of dimensional analysis to five variables (F , ρ , μ , V , and D) with three dimensions ([L], [M], and [T]) resulted in two dimensionless π groups:

$$\pi_1 = \left(\frac{F}{\rho D^2 V^2} \right) \quad (3)$$

$$\pi_2 = \left(\frac{\mu}{\rho D V} \right) \quad (4)$$

The π_1 group was interpreted as a drag coefficient and π_2 is the inverse of the Reynolds number. Dimensional analysis has reduced Equation 1, which required finding a function for four variables, to Equation 5, which only requires finding the function of one variable:

$$\pi_1 = f(\pi_2) \quad (5)$$

Experimental measurements of drag for a wide range of F , D , ρ , and V have demonstrated the power law relationship (Figure 4) between the drag coefficient and the Reynolds number, whereby $\frac{F}{\rho D^2 V^2}$ is a function of $\frac{24}{\frac{\mu}{\rho D V}}$ for fluids with Reynolds numbers < 1 (Dingman, 2009). The relation depicted in Figure 4 has one coefficient (24) and one exponent (-1), and results in:

$$\frac{F}{\rho D^2 V^2} = 24 \left(\frac{\mu}{\rho D V} \right)^{-1} \quad (6)$$

Equation 6 represents a power law scaling equation valid for Reynold's numbers ranging from 0.01 to 1. If dimensional analysis had resulted in more than two π groups, multiple linear regression could be used to derive the coefficient and the exponents for the additional π groups. Several authors have used logarithms of π groups in regressions

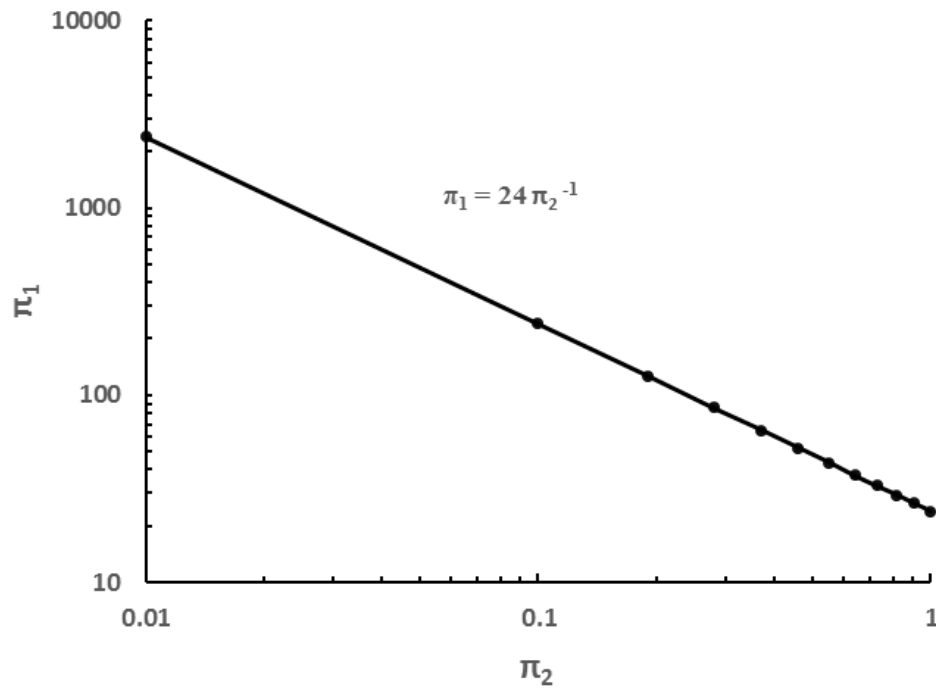


Figure 4. Relationship between drag coefficient (π_1) and the Reynold's number (π_2) (adapted from Dingman (2002))

(Barnes et al., 2007; Canterbury and Lowther, 1976; Carnogurska et al., 2011; Vignaux and Scott, 1999; Warnars et al., 2007). The log-log regression may then reveal power law scaling relationships among the dimensionless groups.

Applications of dimensional analysis

While the fluid mechanics example presented above is perhaps one of the best known applications of dimensional analysis, the method has been used across the five environmental

spheres (hydrosphere, biosphere, lithosphere, atmosphere, and anthroposphere) to better understand natural and anthropogenic processes (Table 4). The application of dimensional analysis has been encouraged in the biological (Stahl, 1962a, 1962b) and ecological sciences (Legendre and Legendre, 1998; Petersen and Hastings, 2001). Hydrological studies have included predicting runoff from watersheds (Langhaar, 1951; Wong, 1979), infiltration along a wetting front (Glass et al., 1989), periphyton biomass (Barnes et al., 2007; Warnars et al., 2007), hyporheic biogeochemical reactions (O'Connor and Harvey, 2008), and evaluating the role of seasonal climatic variability on the water balance (Feng et al., 2012). Dimensional analysis has resulted in dependent π_1 variables associated with the spatial and temporal scaling of phenomena ranging from traffic density to crater ejecta (Table 4).

The application of dimensional analysis to a broad range of environmental problems has resulted in a generalizing of complex processes and the establishment of spatial and temporal scaling relationships. Haynes (1982) suggests the advantages of dimensional analysis are similar to factor or principal component analysis; similar variables are clustered together and an initially large number of variables is replaced with smaller composite quantities. However, this simplification can result in limited predictive ability. Warnars et al. (2007) used dimensional analysis to develop a scaling relationship for stream periphyton. However, their equation did not account for losses from grazing, and therefore likely underpredicted biomass since only abiotic factors were assumed to be limiting. Zeleňáková et al (2013) used dimensional analysis to predict changes in nitrogen and phosphorus concentrations over time in a stream in Slovakia. This approach, did not account for the potential sources of observed nutrients concentrations (Neverova-Dziopak, 2013), and is therefore limited in its applicability to ascertain cause and effect, a prime concern in water quality management.

Table 4. Dimensional analysis applications across environmental fields

Dependent variable	Spatial vs Temporal		
	π_1	Scaling	Reference
<u>Hydrosphere</u>			
Runoff	$\frac{Q\sqrt{g}}{A^{0.75}H}$	Spatial	Langhaar, 1951; Wong, 1979
Subsurface flow in hillslopes	$(\frac{L}{2})^{-3}\tilde{Q}$	Temporal	Berne et al., 2005
Soil water balance	$\frac{\overline{ET}^{yr}}{\alpha\lambda^W}$	Temporal	Feng et al., 2012
Fluvial sedimentation	$\frac{Z_c u_*}{\mu}$	Spatial	Huston and Fox, 2014
Nitrogen concentrations	$\frac{Q_m}{F v C_i}$	Temporal	Zeleňáková and Čarnogurská, 2013
Hyporheic chemical reactions	$\frac{D_e}{D'_m}$	Spatial	O'Connor and Harvey, 2008
Pollutant dispersion in natural streams	$\frac{K_f}{hU_g}, \frac{T}{h/U_*}, \varepsilon$	Temporal	Cheong et al., 2007
<u>Biosphere</u>			
Stream periphyton biomass	$\frac{P B^2}{CU}$	Temporal	Warnaars et al., 2007
Denitrification	$\frac{J_{NO_3}}{u_* C_{NO_3}}$	Spatial	O'Connor et al., 2006
Forest fires	$\frac{r\rho_o c_p T_o}{I_a}$	Temporal	Nelson Jr and Adkins, 1988
Tree growth	$\frac{v}{h^3}$	Spatial	Shen et al., 2014
Population growth in aquatic systems	$\left[\frac{x_*^2}{Dt_*}\right]\frac{\partial C}{\partial T}$	Spatial	Legendre and Legendre, 1998
Seagrass canopy fragmentation	$\frac{TKE_5}{U_{w,5}^2}$	Spatial	El Allaoui et al., 2016
Prey encounter, Animal territoriality	$\frac{ps\sqrt{A}}{\lambda}, hps\sqrt{A}$	Spatial	Stephens and Dunbar, 1993

Table 4 continued. Dimensional analysis applications across environmental fields

Dependent variable	π_1	Spatial vs	
		Temporal	
		Scaling	Reference
<u>Lithosphere</u>			
Crater ejecta	$\frac{C}{x^\psi(\rho x^3)^\phi x/v}$	Spatial	Housen et al., 1983
Fluvial eroded landforms	$\frac{1}{HD}$	Spatial	Strahler, 1958
Marsh erosion	$\frac{Rhc}{\bar{P}_i}$	Spatial	Marani et al., 2011
<u>Atmosphere</u>			
Boundary layer height	$\frac{ B_s }{hf u_*}$	Spatial and Temporal	Steenefeld et al., 2007
Urban heat island effect	$\frac{UHI_{max}}{DTR}$	Temporal	Theeuwes et al., 2016
Ozone in a forest canopy	$\frac{C}{C_{top}}$	Spatial	Krzyzanowski, 2004
Lake breeze	$\frac{h}{t}$	Temporal	Biggs and Graves, 1962
<u>Anthroposphere</u>			
Traffic density	$\frac{\rho}{O} \frac{L_s}{q}$	Spatial	Amritha et al., 2015
Profit from hydropower	$\frac{Z_{t,i}H_{t,i}}{C_{pe}\rho Q_{V,t,i}^2}$	Temporal	Carnogurska et al., 2016
Mechanical reliability of involute splines	FN	Temporal	Canterbury and Lowther, 1976
Screw conveyor performance	$\frac{Q}{\frac{\pi}{4}(d_t^2 - d_{ss}^2)1_p n}$	Spatial	Degirmencioglu and Srivastava, 1996
Friction loss in drip irrigation	$\frac{\Delta H_s}{S}$	Spatial	Demir et al., 2007
Economics	$\frac{MV}{PT}$	Temporal	Jong, 1967

Potential for Water Quality Scaling

Dimensional analysis provides a promising technique for scaling water quality. The greatest challenge in the application of dimensional analysis is identifying all the variables which are relevant. A number of watershed and channel variables have been identified that influence stream water quality. Foremost, water quality is influenced by streamflow (Langbein and Dawdy, 1964; Smith et al., 1982). Classical approaches have described land-phase and channel-phase effects on streamflow (Chapra, 1997; Dingman, 2002, 2009). Common relational variables have included discharge (Lewis, 2002; Zeleňáková et al., 2013), stream velocity (Zeleňáková and Čarnogurská, 2013), channel depth (Alexander et al., 2000), watershed area (Brezonik and Stadelmann, 2002; T.-Prairie and Kalff, 1986; Zeleňáková et al., 2013), watershed slope (Sliva and Williams, 2001), soils (erodability, permeability, clay content) and/or geology (examples include alluvium and bedrock (Skoulikidis et al., 2006)) (Sliva and Williams, 2001), land use/cover (particularly agriculture in Skoulikidis et al. (2006) and urban) (Brezonik and Stadelmann, 2002; Klein, 1979) and point sources such as municipal wastewater (Moore et al., 2004; Skoulikidis et al., 2006). These watershed and channel variables serve as prime candidates for developing dimensionless relationships with stream concentrations. Several of these variables influencing stream water quality are presented in Table 5. The majority of variables consist of some combination of [M], [L], and [T]. Temperature may be included in dimensional analysis, but it must be thermodynamic temperature [K] since values in C and F do not represent numerical values of a physical quantity (Sonin, 1992). Variables that represent ratios, such as the slope of a stream, or with no applicable physical dimension, such as the number of impoundments, are dimensionless and represented with a dimension of 1 (Table 5). Such variables are not involved in dimensional analysis but may be included as additional π groups

when establishing a functional scaling equation. Information for many of the variables is readily available online in GIS layers, federal and state databases, and scientific reports. The effort of data collection and experimentation may be substantially reduced by first applying dimensional analysis to the dimensional variables, thereby reducing the number of variables to be considered.

Application of dimensional analysis to water quality variables may help address the need for a watershed classification system. Wagener et al. (2007) argue that hydrology is currently in a preclassification phase, similar to the biological sciences before taxonomic classification of organisms. While several scientific fields have established classification schemes (Table 6), the science of hydrology lags behind in forming an agreed upon system for classifying watersheds (Wagener et al., 2007). Classification allows for entities or processes with similar properties to be grouped together, such as the periodic table for chemical properties, the Reynolds number for flow regimes, or trophic status for lakes (McDonnell and Woods, 2004). While each class may contain a large amount of complexity, classification into similar groups limits internal variability within classes (McDonnell and Woods, 2004). In order to take hydrological data gained from monitoring or field experiments and transfer that information to new circumstances (and watersheds), a classification system that facilitates the identification of patterns and similarities would be useful (Sivapalan, 2005). In the same way that different hydraulic systems may be classified as having either laminar or turbulent flow based on their Reynolds number, so too may watersheds be classified based on π groups. The establishment of dimensionless, ratio-based variables for watersheds, governed by similar patterns and processes, may enable the prediction

Table 5. Dimensional variables affecting water quality

Variable	Dimension
Nutrient Concentration	$\frac{M}{L^3}$
<u>Nutrient Sources</u>	
Land use/land cover (agriculture, urban, etc) area	L^2
Area of soil type	L^2
Nonpoint source loading	$\frac{M}{T}$
Point source loading	$\frac{M}{T}$
Atmospheric deposition	$\frac{M}{L^2 T}$
<u>Nutrient Cycling</u>	
Number of impoundments	1
Areal uptake rate	$\frac{M}{L^2 T}$
Decay coefficients	$\frac{1}{T}$
Watershed and stream characteristics	
Watershed area	L^2
Length of streams	L
Stream depth	L
Stream width	L
Riparian buffers	L
<u>Watershed and stream characteristics</u>	
Stream discharge	$\frac{L^3}{T}$
Drainage density	$\frac{1}{L}$
Stream velocity	$\frac{L}{T}$
Stream/watershed slope	1
Wastewater treatment plant discharge	$\frac{L^3}{T}$
Ground water flow	$\frac{L^3}{T}$
Rainfall rate	$\frac{L}{T}$
Temperature/Season	K

Table 6. Classification schemes across scientific fields

Subject	Classification scheme
Organisms	Taxonomic
Lakes	Mixing regime, trophic level
Fluid mechanics	Dimensionless numbers (e.g. Froude, Reynolds)
Wetlands	Cowardin
Soils	Order
Elements	Periodic table, valency
Climate	Köppen

of water quality across scales. Furthermore, opportunities may exist in conceptualizing governing equations such as advective-dispersive transport using dimensional analysis.

Advection-dispersion processes have previously been incorporated into other scaling methods including Lagrangian-Eulerian (Neuman, 1984; Rossman and Boulos, 1996) and fractal (Benson et al., 2001; Kirchner et al., 2001; Scher et al., 2002) approaches.

Conclusions

Dimensional analysis has resulted in admirably simple relationships that have proven to be instrumental in improving our understanding and prediction of natural phenomenon. However, dimensional analysis should not be viewed as a panacea for all water quality scaling problems. The approach is limited by the assumption that all relevant variables have been included in the formation of π groups. The complex processes governing watershed hydrology and biogeochemistry are often difficult to measure empirically, but dimensional analysis relies

on the accurate measurement of variables expressed in fundamental units. Furthermore, stochastic and deterministic modeling approaches that explore the exchanges between terrestrial and aquatic systems continue to improve our understanding of how biological, physical, and chemical watershed characteristics impact water quality. Dimensional analysis and modeling approaches are complimentary to each other. The opportunity may exist to establish scaling relationships for water quality through dimensional analysis that may then be incorporated into models.

Dimensional analysis has been demonstrated to successfully scale predictions across several disciplines, and should be more widely considered as a method for water quality prediction. Application of dimensional analysis to variables which have been shown to impact water quality is needed. Future research may elucidate similarities and differences between watersheds at local, regional and continental scales. While current research continues to improve our understanding of the processes governing water quality in individual watersheds, applying this understanding to different scales and watersheds remains a challenge. An improved understanding of the scaling of water quality predictions should lead to more effective and parsimonious management of our water resources.

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Spatial scaling of stream phosphorus concentrations using dimensional analysis

Abstract

We describe a spatial scaling method using dimensional analysis to predict total phosphorus (TP) concentrations across heterogeneous watersheds ranging from ~ 200 to 3,400 km². Variables describing attenuated point (kW) and nonpoint (Wnp) sources of pollution, volumetric flow rates for rivers (Qs) and treatment plants (Qw), longitudinal distance of watershed river networks (S) and the cross-sectional area (A) at stream gages were transformed into dimensionless ratios. These ratios defined fluvial features, sources of nutrient loading, and stream discharge. A relationship among these dimensionless groups in the form of a scaling power law equation was derived using multiple linear regression. Average annual TP concentrations were predicted by \sqrt{kW} , \sqrt{kWnp} , $Qw^{\frac{2}{5}}$, $Qs^{-\frac{7}{5}}$, and $\frac{S^{\frac{1}{10}}}{\sqrt{A}}$. The resulting predictive equation explained 93% of the variability observed in TP concentrations across watersheds. This study further advances the application of dimensional analysis to the spatial scaling of stream water quality.

Introduction

After decades of agricultural best management practice (BMP) implementation, a majority of U.S. rivers remain impaired due to nonpoint source pollution (U.S. EPA, 2014). High levels of phosphorus and riparian zone disturbances have been identified as the major chemical and physical stressors, respectively, to rivers in the U.S. (U.S. EPA, 2016). The physical, chemical, and biological processes affecting water quality have been well documented in plot and field scale experiments that assess agricultural best management practices (Jordan et al., 2000; Penn and Bryant, 2006; Sharpley et al., 2014, 2009) including riparian buffers (Hoffmann et al., 2009; Lowrance et al., 1985; Mayer et al., 2007; Parkyn, 2004). Results from these studies have been incorporated into water quality models in order to predict watershed scale responses to changes in land use and management. Familiar examples include the Universal Soil Loss Equation

(Wischmeier and Smith, 1958), Erosion-Productivity Impact Calculator (Williams, 1990), Chemicals, Runoff and Erosion from Agricultural Management Systems (Knisel, 1980), Groundwater Loading Effects of Agricultural Management Systems (Leonard et al., 1987), Soil and Water Assessment Tool (Arnold et al., 2012), and the Riparian Ecosystem Management Model (Lowrance et al., 2000). Despite their popularity, current modeling approaches have several limitations for predicting water quality, especially across watersheds:

- 1) Models rely on governing equations (e.g. Darcy's law, Richard's equation) which were developed at small-scales but are used to simulate watershed responses at large scales (Beven, 1993; Blöschl and Sivapalan, 1995; Kirchner, 2006). However, as scales change, the processes and patterns controlling phenomena may also change (Wu and Li, 2006a), limiting the efficacy of these equations.
- 2) Models can include a few dozen (Roman et al., 2012; White and Chaubey, 2005) to several thousand (Whittaker et al., 2010) variables which:
 - a. require information that is difficult to obtain, such as antecedent moisture conditions, hydraulic conductivities, and nutrient soil pools (Beven, 1993; Y. Liu et al., 2008; Lowrance et al., 2000; Tilak et al., 2014).
 - b. need to be adjusted during calibration to some observed data (Alexander et al., 2013; James, 1982; Rosa et al., 2015). Calibration of several variables can lead to overparameterization and overfitting. The former occurs when redundant information is nevertheless included in a model. A model may be overfitted if errors in the calibration dataset are reduced but large errors result when the model is applied to other circumstances (Jakeman and Hornberger, 1993; Whittaker et al., 2010)

- c. can result in large prediction errors (Beck, 1987; Grayson et al., 1992; Kirchner, 2006).
- 3) Many models require researchers to explicitly represent the complexity of processes, spatial heterogeneity, and variability within a watershed (Alexander et al., 2013; Blöschl and Sivapalan, 1995; Dooge, 1986).
- 4) Models may produce equally satisfactory predictions from combinations of different sets of realistic variable values (Arhonditsis et al., 2008; Bathurst and Cooley, 1996; Beven, 2006, 1993; Franks et al., 1997).
- 5) Experience and detailed knowledge (Shanahan et al., 1998) or extensive training (Friedman et al., 1984) is typically required in order to use individual models.
- 6) Models are often designed for a specific watershed composition, such as urban (Gironás et al., 2010) or agricultural (Lowrance et al., 2000), although some models can represent complex land uses (Douglas-Mankin et al., 2010; Smith et al., 1997).

Scaling is the transfer of information from one temporal or spatial scale to another (Blöschl and Sivapalan, 1995). The above limitations make scaling water quality problematic.

Dimensional analysis is a common scaling method, but few studies have applied it to water quality, and none to the spatial scaling of water quality.

Dimensional analysis

Dimensional analysis is the reduction of a dimensionally homogenous equation with fundamental dimensions (i.e., mass, length, and time) to a new relationship between dimensionless groups (Buckingham, 1914; Langhaar, 1951; Taylor, 1974). Dimensional analysis can address the challenge of scaling water quality by establishing a power law relationship that is dimensionless and therefore invariant to changes in scale (Shen et al., 2014; Wu and Li, 2006b). Several researchers have identified the power law as the most appropriate function for describing

similarity and preserving hydrological relationships across scales (Gupta, 2004; Mendez and Ordoñez, 2005; Newman, 2005; Rigon et al., 1996; Rodriguez-Iturbe et al., 1995). A power law, also called a scaling law, is an equation in which a relative change in one quantity results in a proportional relative change in another. Power laws are the only mathematical function in which the relationship between two variables does not change with the scale of measurement, a quality known as scale invariance (Frank, 2009; Newman, 2005).

Dimensional analysis of watershed characteristics may help researchers understand and scale hydrological processes (Blöschl, 2001; Dooge, 1986; Wagener et al., 2007). In fluid dynamics, the Reynolds and Froude numbers are common dimensionless ratios derived from dimensional analysis and used to define hydraulically similar systems and predict their responses (Strahler, 1958). Dimensional analysis reduces the number of variables in a problem (Langhaar, 1951), and the elimination of extraneous information (Taylor, 1974). The method is useful when mathematical analysis of the problem is too complex or when experiments may be impractical (Huntley, 1967). Dimensional analysis relies on the analyst's knowledge of a problem (Langhaar, 1951), which can range from a basic theory to detailed understanding.

After dimensionless groups have been derived, a functional relationship among the independent groups can be determined using experimental data and regression analysis. Variables that can be easily manipulated experimentally should occur in at least one of the dimensionless groups (Canterbury and Lowther, 1976). The application of dimensional analysis is best known in the field of fluid mechanics. However, over several decades, dimensional analysis has been employed in a range of diverse fields, including marsh erosion (Karimpour et al., 2016), forest fires (Byram and Nelson, 1970; Martini et al., 1991), and animal territoriality (Stephens and Dunbar, 1993). Hydrological applications of dimensional analysis have included

scaling runoff from a watershed (Langhaar, 1951), infiltration along a wetting front (Glass et al., 1989), periphyton biomass in streams (Barnes et al., 2007; Warnars et al., 2007), hyporheic biogeochemical reactions (O'Connor and Harvey, 2008), and evaluating the role of seasonal climatic variability on the water balance of soil (Feng et al., 2012). Dimensional analysis has also been used to predict monthly changes in nitrogen (Zeleňáková and Čarnogurská, 2013) and phosphorus (Zeleňáková et al., 2013) concentrations in a single stream. However, no study to date has applied dimensional analysis to the spatial scaling of water quality.

Objectives

The objective of this study was to use dimensional analysis for the spatial scaling of TP concentrations across nested and separated watersheds which varied in area, land cover, stream network characteristics, and nutrient loading. Two approaches to variable selection were examined: stepwise regression and dimensional analysis of variables based on the advection-dispersion equation. The predictive power of the dimensionally homogenous scaling equation, in which variables were in the form of ratios, was compared to stepwise regression of dimensional variables. The scaling equation resulting from dimensional analysis was used to assess the water quality impacts of three management scenarios aimed at improving water quality across watershed scales.

Materials and Methods

Study Sites and Characteristics

Dimensional analysis was applied to watershed variables hypothesized to impact the average TP concentrations observed at the outlets of eleven nested and separated watersheds in Connecticut and Massachusetts (Figure 1). Watersheds were selected based on availability of discharge and water quality data from 2001-2007, a period of time matching available point

source loading and land cover data. The contributing watersheds for the gages were delineated using StreamStats (<http://water.usgs.gov/osw/streamstats/>).

A review of the literature resulted in identification of several watershed characteristics shown to impact stream phosphorus concentrations. These characteristics (Table 1) included point source loading (Chapra, 1997), stream and ground water discharge (Novotny, 2003), location of sampling within the stream network (McGuire et al., 2014), soil (Abrams and Jarrell, 1995), impoundments (Smith et al., 1997), and watershed and riparian land use characteristics (Allan et al., 1997; Jones et al., 2001; Sliva and Williams, 2001). Data sources for watershed and channel characteristics and water quality included the National Land Cover Dataset (NLCD), the Natural Resources Conservation Service (NRCS) Soil Survey Geographic Database (SSURGO), the United States Geological Survey (USGS) National Hydrography Dataset, and the USGS National Water Information System (NWIS).

Total phosphorus (TP) loading (mg/yr) was calculated for both point and nonpoint sources. Mass loading and volumetric discharge from point sources were obtained from National Pollutant Discharge Elimination System (NPDES) permit data available from the Connecticut Department of Energy and Environmental Protection (CT DEEP) from April through October, 2001 – 2007 (Becker, 2014). We relied on NPDES facility data compiled by the state of Connecticut, however databases including the United States Environmental Protection Agency (EPA) Enforcement and Compliance History Online (ECHO) (<http://echo.epa.gov/>), Permit Compliance System (PCS), and the Integrated Compliance System (ICIS) (<http://www.epa.gov/enviro/facts/pcs-icis/search.html>) contain comparable information.

Attenuated point source loading (kW) was calculated using coefficients accounting for in-stream decay processes determined by Smith et al. (1997) and based on stream size, average velocity,

and upstream distance to facility (Table 1). Nonpoint source loading was calculated using the 2006 National Land Cover Dataset (NLCD) (http://www.mrlc.gov/nlcd06_data.php) and phosphorus export coefficients for urban, agricultural, and forest land cover classifications obtained from Becker and Dunbar (2009). Frink (1991) and Beaulac and Reckhow (1982) also provide export coefficients calculated from Connecticut and national studies, respectively. However, the coefficients calculated by Becker and Dunbar (2009) were based on stream water quality data, as opposed to sampling lakes or overland flow from study plots, and were therefore assumed to be most appropriate for this study. The export coefficients calculated from Becker and Dunbar (2009) were assumed to account for in-stream attenuation.

The bankfull stream width at the gage was estimated based on watershed area using an equation developed for the northeastern United States by Bent (2006). Stream depth was obtained using USGS stage-discharge ratings (USGS, 2017a). The average annual discharge was calculated from instantaneous measurements taken during sample collection (USGS, 2017b). Average stream velocity was obtained by dividing the average annual discharge (m^3/s) by stream width (m) and stream depth (m). Total stream length and distance from each WWTP to the downstream gage determined using the National Hydrography Dataset (NHD) high resolution dataset (<http://nhd.usgs.gov/>).

Dimensional Analysis of Water Quality Variables

We used the advection-dispersion transport equation for streams (Schnoor, 1996) as the underlying basis for identifying relevant variables to include in dimensional analysis. Therefore stream phosphorus concentrations are a function of initial concentration, discharge, distance, cross-sectional area, external loads, and reactions. In order to apply dimensional analysis to watershed variables, total phosphorus concentration (C) was assumed to be dependent on point-

source loading (kW_p), nonpoint source loading (W_{np}), average stream discharge (Q_s), average annual point-source discharge (Q_w), total length of streams (S), and cross-sectional area at the gage (X -sect):

$$C = f_1 (kW_p, W_{np}, Q_s, Q_w, S, X - sect) \quad (1)$$

where f_1 is an unknown function. Equation (1) comprises three dimensions, mass [M], length [L], and time [T] (Table 1). Following Ipsen (1960), the step-by-step approach was used to eliminate each dimension in turn (Table 2). Dimensionless groups were denoted as having a dimension of 1. In the first step, the length dimension [L] was chosen as the first to eliminate using the variable S . All variables with dimension [L] were divided or multiplied by S , raised to a power if needed, in order to eliminate [L] from equation (1). In the second step, the dimensions [M] was eliminated using kW . The dimension T was eliminated in the third steps using $\frac{Q_s}{s^3}$ to divide $\frac{Q_w}{s^3}$ and multiply $\frac{C S^3}{kW}$. After eliminating all dimensions, equation (1) was then represented in the following dimensionless form:

$$\frac{C Q_s}{kW_p} = f\left(\frac{S}{\sqrt{X-sect}}, \frac{W_{np}}{kW_p}, \frac{Q_w}{Q_s}\right) \quad (2)$$

The seven original variables (Equation 1) were reduced to four dimensionless π groups identified as follows:

$$\pi_1 = \frac{C Q_s}{kW_p} \quad \text{stream mass to point source load ratio} \quad (3)$$

$$\pi_2 = \frac{S}{\sqrt{X-sect}} \quad \text{stream length-area ratio} \quad (4)$$

$$\pi_3 = \frac{W_{np}}{kW_p} \quad \text{pollutant source ratio} \quad (5)$$

$$\pi_4 = \frac{Q_w}{Q_s} \quad \text{point source discharge to stream discharge ratio} \quad (6)$$

As expected from Buckingham's theorem (Buckingham, 1914), the number of π groups resulting from dimensional analysis (four) is equal to the number of variables in the problem (seven) minus the number of dimensions that describe those variables (three). Equation (3) suggests that TP concentration can be expressed as a dimensionless ratio of TP mass exported from a watershed (CQ_s), normalized by the attenuated TP mass loading from point sources (kW_p). Therefore the stream mass to point source load ratio, π_1 , describes the amount of TP exported from a watershed that is attributable to point sources.

Equation (2) defined in terms of the π groups is:

$$\pi_1 = f_1(\pi_2, \pi_3, \pi_4) \quad (7)$$

Power laws appear as straight lines on log-log scales (Newman, 2005), therefore in order to establish a scaling power law, the π groups were log-transformed:

$$\log(\pi_1) = f(\log(\pi_2), \log(\pi_3), \log(\pi_4)) \quad (8)$$

A solution for equation (8) was obtained through multiple linear least squares regression with the general form

$$\pi_1 = \alpha + \beta_1\pi_2 + \beta_2\pi_3 + \beta_3\pi_4 \quad (9)$$

where α and β_{1-3} are an empirically derived constant and coefficients, respectively. A power law equation was derived by taking the antilog of equation (9)

$$\pi_1 = 10^\alpha * \pi_2^{\beta_1} * \pi_3^{\beta_2} * \pi_4^{\beta_3} \quad (10)$$

The Variance Inflation Factor (VIF), which quantifies the severity of multicollinearity for the independent variables, was used to assess the impact of existing correlations between π_2 , π_3 , and π_4 . Marquardt (1970) suggests VIF values between 1 and 10 indicates sufficiently low multicollinearity.

Scenario-testing

The predictive equation resulting from dimensional analysis of variables based on the advection-dispersion equation was further investigated using three scenarios. Scenarios adjusted variables related to the loading and transport of point and nonpoint source pollution. Scenario testing served to evaluate whether the functional scaling equation produced logical results as well as to assess the impact of the scenarios on predicted TP at different scales. The Riparian Restoration Scenario converted 10% of each watershed's agricultural land into forest, reflecting changes in land management such as the restoration of riparian buffers. The WWTP Improvement Scenario simulated adoption of improved treatment practices in all WWTPs in the study watersheds to meet Connecticut's minimum performance concentration of 0.1 mg/l TP (Becker, 2014). Improved practices may include tertiary treatment using filtration aided by chemical addition (USEPA, 2007). The In-Stream Decay Scenario increased coefficients to the upper limits of ranges provided by Smith et al. (1997). Uptake of phosphorus in streams can be highly variable (Mulholland et al., 1985) and may increase with restoration of stream conditions such as improved habitat heterogeneity (Doyle et al., 2003).

Statistical Analysis

Prior to dimensional analysis, associations between TP and the other variables in Table 1 were assessed using a correlation matrix and step-wise multiple linear regression using SAS

statistical software (SAS Institute, 2012). All variables, excluding ratios describing land use, ground water input, and hydric soils, were log transformed prior to analysis. Stepwise regression was also applied to log-transformed variables derived from dimensional analysis following Canterbury and Lowther (1976) and Demir et al (2007). However our final scaling equation relied on a multiple linear regression of log-transformed variables resulting from dimensional analysis of variables based on the advection-dispersion equation (Schnoor, 1996). The Pearson correlation coefficient (r) was used to assess linear correlations among dimensionless groupings. We compared the methodological and conceptual benefit of multiple linear regression of dimensionless variables versus step-wise regression of dimensional variables, a traditional approach in water quality studies. The coefficient of determination (R^2) and root mean square error (RSME) were used to assess predictions of annual average TP.

Results

Correlations and stepwise regression of original variables

Average TP concentrations were above the EPA reference criterion of 31.25 mg m^{-3} (U.S. EPA, 2000) for all rivers except the Housatonic River at Stevenson and the Farmington River at Unionville (Table 1). Pearson correlation coefficients for TP and all independent variables are presented in Table 3. Total phosphorus concentrations were significantly correlated ($p < 0.05$) with ratios of urban, agriculture + urban, and forest/wetland land use to total watershed area. Additionally, stream order, length, depth, and cross-sectional area at the gaging station, and point source loading were significantly correlated to TP concentrations. Step-wise multiple linear regression identified the percent of urban land use, stream depth, and attenuated point source loading as significant ($\alpha = 0.15$) predictive variables for TP. The resulting linear equation ($F = 20.28$, $p < 0.001$, $R^2 = 0.897$):

$$\log \text{TP} = -1.513 + \text{AgUrb}(1.617) + \log \text{Depth}(-1.093) + \log kW_p(0.303) \quad (11)$$

Figure 2 presents observed versus predicted concentrations using equation (11), the RMSE was 100 mg m^{-3} .

Dimensional Analysis

Two approaches were used to perform dimensional analysis for stream TP concentrations. The first approach used concentration, discharge, point source loading, land use, and stream geomorphic variables in dimensional analysis. This approach identified two π groups, the stream mass to point source load ratio ($\frac{CQ}{kW_p}$) and a ratio of stream width to depth ($\frac{D}{Z}$). These π groups were not correlated to each other ($r = 0.095$). Stepwise regression was performed using the two π groups and several other dimensionless variables representing riparian and watershed land use, soils, and ground water discharge ratios. Significant ($\alpha = 0.15$) variables which entered the regression were base flow index (BFI) and the ratio of stream length in urban areas to total stream length ($F = 4.57$, $p = 0.045$, $R^2 = 0.662$). However, this approach was deemed unsatisfactory because of illogical results. Watershed urbanization has long been associated with higher levels of stream phosphorus (Brett et al., 2005; Omernik, 1976; Osborne and Wiley, 1988; Paul and Meyer, 2001). The equation resulting from stepwise regression of dimensionless variables established a negatively correlated relationship between urban land use in riparian areas and TP concentrations which is contrary to observations.

The second approach used the advective-dispersive transport equation as the underlying theory for dimensional analysis. In order to better quantify nutrient loading, export coefficients were used to calculate nonpoint sources of TP (W_{np}). Log values of π groups $\frac{W_{np}}{kW_p}$ and $\frac{Q_w}{Q_s}$ were significantly correlated ($p < 0.01$) with logTP (Table 4). The independent π group $\frac{W_{np}}{kW_p}$ was significantly ($p < 0.01$) correlated with the dependent π group $\frac{CQ_s}{kW_p}$. Log values for $\frac{Q_w}{Q_s}$ and $\frac{W_{np}}{kW_p}$

were significantly ($p = 0.05$) correlated with each other. The multiple linear regression using the four log transformed π groups resulted in an improvement ($F = 10.60$, $p = 0.005$, $R^2 = 0.819$) over the stepwise regression of dimensionless variables.

The antilog form of the regression is the following power law equation:

$$\frac{CQ_s}{kW_p} = 10^{0.583} * \frac{S}{\sqrt{X-sec}}^{0.103} * \frac{W_{np}}{kW_p}^{0.519} * \frac{Q_w}{Q_s}^{0.387} \quad (12)$$

The VIF for the independent variables were between 1 and 3. The low VIF values suggest that the correlation between π_3 and π_4 did not sufficiently effect the estimated impact of the variables on π_1 . The functional relationship between $\frac{CQ_s}{kW}$ and $\frac{W_{np}}{kW_p}$, $\frac{Q_w}{Q_s}$, and $\frac{S}{\sqrt{X-sec}}$ is depicted in Figure

3. In order to compare the predictive ability of dimensional analysis to stepwise regression of original variables (equation 11), equation (12) was solved for concentration (C) yielding:

$$C = 3.83 * W_{np}^{0.519} * kW_p^{0.481} * Q_w^{0.387} * \frac{1}{Q_s^{1.387}} * \frac{S}{\sqrt{X-sec}}^{0.103} \quad (13)$$

The relationship between observed TP concentrations and those predicted by equation (13) had an R^2 of 0.931 (Figure 4), a slight improvement in the amount of total variance of observed concentrations explained by stepwise regression of original variables (Figure 2). Dimensional analysis resulted in a RMSE of 71 mg m^{-3} , and was lower than the RMSE of 100 mg m^{-3} from stepwise regression of the original variables.

Scenario Testing

Management scenarios aimed at reducing TP concentrations were evaluated across watersheds by adjusting variables in equation 13. The Riparian Restoration Scenario, which

converted 10% of each watershed's agricultural land to forest, resulted in reduced TP exported from nonpoint sources. The TP concentration response ranged from no change to a 3% reduction depending on the watershed (Table 5). The WWTP Improvement Scenario lowered the average annual TP concentration of the effluent from the 48 WWTPs in the eleven watersheds, reductions in point source mass loading ranging from 77% and 93% for individual watersheds. As a result, average TP concentrations at the outlet of the watersheds were reduced by 47% to 81%, varying by watershed (Table 5). The In-Stream Decay Scenario resulted in reductions in TP ranging from 2% to 10%.

Discussion

Dimensional analysis of variables impacting TP concentrations, based on the advection-dispersion equation, resulted in three independent π groups that resemble dimensionless numbers previously identified in the literature. The stream length-area ratio (π_2) is similar to one of the several dimensionless groups Wong (1979) derived when the author applied dimensional analysis to the prediction of mean annual flood in New England watersheds. The pollutant source ratio (π_3) is comparable to a variable identified as an adaptive management screening tool for reducing phosphorus loads, although π_3 accounts for attenuation while the point to nonpoint ratio presented in Diebel et al. (2013) does not. The $Q_w:Q_s$ ratio (π_4) represents a watershed scale quantification of how much of a stream's discharge can be attributed to point-source effluent. A similar assessment is used to measure how much of a NPDES facility's discharge contributes to the total flow of a receiving stream (U.S. EPA, 1980).

The power law relationship presented in Figure 3 describes a dimensionally homogenous scaling equation for predicting stream TP concentrations across a range of watershed sizes and characteristics. Equation 11, based on stepwise regression, is not dimensionally homogenous

and therefore the constant and coefficients of the predictive equation will change with the scale of the variables (Legendre and Legendre, 1998). Based on stepwise regression, nonpoint source loading (W_{np}) was not a significant variable affecting TP concentrations. However, the inclusion of the fraction of agriculture and urban land use in the watershed (AgUrb, equation 11) may be a proxy for nutrient loading from nonpoint sources. Alternatively, equation (12), based on dimensionless variables, is dimensionally homogenous and scale invariant. Equation (12) used W_{np} for loading estimates of nonpoint sources. The inclusion of W_{np} allows for better quantification of loading per the advective-dispersive equation. Additionally, since equation (12) is ratio based and dimensionally homogenous, the values for the exponents remain the same no matter what units are chosen for measurement (i.e. lengths measured as cm, m, or km). Dimensional analysis offers a simplified method for spatially scaling water quality with similar predictive ability as commonly used methods (Douglas-Mankin et al., 2010; Moore et al., 2004; Smith et al., 1997). Comparing observed to predicted TP loading using the Spatially Referenced Regressions On Watershed attributes (SPARROW) at regional (Moore et al., 2004) and national scales (Smith et al., 1997) resulted in an R^2 of 0.81 and 0.94, respectively. Equation (13) resulted in an $R^2 = 0.931$ for predicted versus observed TP concentrations (Figure 4). While our study used published decay coefficients from Smith et al. (1997), our method offers a simplified approach to scaling, including using fewer variables than SPARROW and no need to spatially reference land characteristics. An alternative approach to incorporating attenuation is presented by Wollheim et al. (2006) and uses both biological and hydrological variables to calculate a proportional of in-stream removal of nutrient inputs to a waterbody. If nonpoint loading estimates do not account for in-stream attenuation, then calculating a proportional removal may be appropriate. Equation (13) provides a single power law equation for predicting TP

concentration across multiple watersheds. Equation (13) underestimated the highest average TP concentration, observed at Beacon Falls, by 226 mg m^{-3} . Hockanum River at East Hartford had the next highest concentrations of TP after Beacon Falls (Table 1), although it was almost half that observed at Beacon Falls. Additional observed TP concentrations in the 300 to 600 mg m^{-3} range may have improved estimation at higher values.

Douglas-Mankin et al. (2010) reviewed several studies which calibrated and validated The Soil and Water Assessment Tool (SWAT) for individual watersheds. Predictive capabilities for daily and monthly TP concentrations ranged from R^2 0.22 to 0.85 (Douglas-Mankin et al., 2010). Similarly, Bosch (2008) found that predicted versus observed monthly TP concentrations from a Michigan watershed resulted in R^2 of 0.78 and 0.62 for calibration and validation datasets, respectively. The SWAT model can use several thousand variables in simulations (Whittaker et al., 2010) and annual predicted versus observed TP loading for single watersheds range from R^2 of 0.83 (Chu et al., 2004) to 0.95 (Kirsch et al., 2002). Predictions are scaled using areal extrapolation and nutrient decay is simulated using first order reaction rates similar to our dimensional analysis approach (Arnold et al., 2012; Neitsch et al., 2011).

This study applied dimensional analysis to address the challenge of spatially scaling water quality predictions. Previous applications of dimensional analysis to water quality only assessed temporal scaling and did not account for any loading from point or non-point sources (Carnogurska et al., 2016; Zelenáková et al., 2015, 2013). We present a method for the spatial scaling of TP that accounts for nonpoint and point sources, including attenuation. Few studies using dimensional analysis give detailed statistical assessments, and no studies compare results to the more common stepwise regression of dimensional variables. While some dimensional analysis studies exclude π groups that are not significantly correlated with the dependent group

(Warnaars et al., 2007), others do not (Zeleňáková et al., 2015; Zeleňáková and Čarnogurská, 2013). Logged values for $\frac{S}{\sqrt{X}-Sec}$ and $\frac{Q_w}{Q_s}$ were not significantly correlated with the dependent variable $\frac{CQ_s}{kW_p}$. Two independent variables $\frac{W_{np}}{kW_p}$ and $\frac{Q_w}{Q_s}$ were significantly ($p < 0.05$) correlated. Warnaars et al. (2007) excluded independent π groups that were significantly correlated from regression. Several others (Biggs and Graves, 1962; Huston and Fox, 2014; Karimpour et al., 2016; O'Connor et al., 2006) present multiple independent π groups without assessing correlations. Given that all variables in Table 2 were necessary to form a dimensionally homogenous equation in accordance to Buckingham's theorem (Buckingham, 1914), all resulting π groups were included in the analysis. The resulting R^2 for predicted versus observed TP concentrations across heterogeneous watersheds of varying sizes was 0.931 compared to 0.897 from stepwise regression of dimensional variables. Unlike the regression equation based on stepwise regression (equation 11), equation (12) will not change with scale.

The results of scenario testing demonstrated that the predictive equation (13) can be used to assess the impact of watershed management. The three scenarios predicted reductions in TP concentrations as a result of changes in land cover, improvements to WWTPS, and increased stream uptake. The Riparian Reduction Scenario reduced the total nonpoint loading from the landscape by replacing agriculture with forest but did not account for the spatial location of the restored forested land in each watershed. Previous studies have found mixed results when assessing the relationship between water quality and land use patterns in riparian buffers versus whole watersheds (Baker et al., 2006; Hunsaker and Levine, 1995; Osborne and Wiley, 1988; Sliva and Williams, 2001). While some researchers have used land use close to streams to effectively predict water quality (Baker et al., 2006; Wilkin and Jackson, 1983) others have

found total watershed land use to be a better predictor (Hunsaker and Levine, 1995; Sliva and Williams, 2001). Land use proportions in riparian buffers have been found to be correlated to watershed-wide ratios (Baker et al., 2006). Converting agriculture to forest had the largest impact on TP concentrations in the Housatonic River at New Milford, and the smallest impact on Quinnipiac River at Wallingford. These watersheds have the largest (12.9%) and smallest (1.4%) percentages of agricultural land compared to total watershed area, respectively. The scenario only assessed BMP implementation on agricultural land. Our analysis did not address the impact of urban BMPs at the watershed scale. Riparian buffers are predominantly an agricultural BMP, replacing watershed scale agriculture with forest was used as a proxy for riparian restoration. While research suggests that this approach is appropriate (Baker et al., 2006; Hunsaker and Levine, 1995; Sliva and Williams, 2001), it is unclear the level of spatial detail required to predict the effects of urban BMPs. The effect of urban BMPs may be assessed by adjusting export coefficients or land use ratios.

The WWTP Improvement Scenario addressed the effect of upgrading wastewater treatment practices. Improvements to WWTPs resulted in the largest reductions in predicted TP concentrations. Bowes et al. (2005) assessed P loading in watersheds in southern England and arrived at a similar conclusion; sites with the highest proportion of P attributed to WWTPs had the highest P concentrations. Similarly, Bowes et al. (2005) also used observed stream and WWTP nutrient data and relied on export coefficients to estimate nonpoint source loading. For watersheds like the Quinnipiac River at Wallingford whose TP loading is dominated by WWTPs, management strategies aimed at upgrading NPDES facilities or restoring stream function may be more successful at improving water quality than changes in land management.

The coefficients used in the In-Stream Decay Scenario are assumed to be a conservative estimates of TP removal since they are based on the discharge at the outlet of the watershed, and do not account for possibly higher removal rates in smaller upstream tributaries. Watershed management strategies which increase retention times, transient storage and food web interactions may reduce P delivery to downstream waters (Jarvie et al., 2013; Withers and Jarvie, 2008).

This research applied dimensional analysis to water quality predictions in the Northeastern U.S. Future work should assess the predictive ability of the scaling equation on TP concentrations in watersheds which were not used to establish the regression equation. Future research may also assess and compare functional scaling relationships in other regions. Expanded application of dimensional analysis may further elucidate similarities and differences among watersheds varying in hydrology and anthropogenic impacts, and help to inform and implement management decisions. Our predictions are limited to long term (7 year) average concentrations. The scaling equation presented in this study does not address temporal scaling. Temporal scaling may help address management objectives aimed at predicting the frequency of water quality standards violations. Furthermore, our approach relies on runoff coefficients which assume steady and uniform export of TP from land cover classifications. Export coefficients cannot account for the temporal variability of nutrient export which may exist in a single watershed (Beaulac and Reckhow, 1982). The method is also insensitive to spatial variability of nutrient export due to heterogeneous distribution of nonpoint sources in a watershed.

Conclusions

Dimensional analysis was used to establish a functional scaling relationship between stream TP concentrations, point and nonpoint source P loading, and channel characteristics. The analysis produced four dimensionless ratios: the stream mass to point source load ratio, the stream length-area ratio, the pollutant source ratio, and the point source to stream discharge ratio. A scaling power law was established between the groups using available data and multiple linear regression. The resulting equation predicted average annual TP concentrations over a range of watershed scales and did not require a detailed mechanistic representation or extensive empirical data. While stepwise regression of dimensional variables yielded similar predictive power, dimensional analysis resulted in a scale invariant equation. Additionally, dimensional analysis required data for four dimensionless ratios versus the 23 variables used in stepwise regression.

The study improves upon our understanding of spatial scaling methodologies in general and further deepens our understanding of the utility of dimensional analysis in hydrological science. Furthermore, this study provides a guide for future work aimed at simplifying complex phenomena and establishing scaling relationships for water quality predictions.

TABLES

Table 1. Variables associated with TP concentrations in streams

	Average annual TP(USGS, 2017b)	Total watershed area(USGS, 2012)	Average annual discharge (USGS, 2017b)	agriculture ratio (Fry et al., 2011)	Urban ratio (Fry et al., 2011)	Agriculture + urban ratio (Fry et al., 2011)	Forest/wetland ratio (Fry et al., 2011)	Hydric soil ratio (USDA-NRCS, 2016)	Base flow Index at gage (Wolock, 2003)	Average Velocity (calculated)	Strahler Order (USGS, 2017c)	Number of Impoundments (USGS, 2017c)
Unit	mg m ⁻³	m ² *10 ⁵	m ² yr ⁻¹ *10 ⁵	L ² L ⁻²	L ² L ⁻²	L ² L ⁻²	L ² L ⁻²	L ² L ⁻²	L ³ L ⁻³	(m s ⁻¹)	-	-
Symbol	C	A	Q	Ag	Urb	AgUrb	ForW	Hyd	BFI	V	Order	Imp
Dimension	M L ⁻³	L ²	L ² T ⁻¹	1	1	1	1	1	1	L T ⁻¹	1	1
<u>River station</u>												
Housatonic at Ashley Falls, MA	54	12076.07	6444	0.096	0.099	0.195	0.766	0.625	48	48	5	54
Housatonic at New Milford, CT	44	26465.87	20855	0.129	0.080	0.209	0.755	0.577	51	51	6	105
Housatonic at Stevenson, CT	30	39920.97	26742	0.120	0.109	0.228	0.726	0.550	47	47	6	154
Quinebaug at Jewett City, CT	58	26465.87	9454	0.086	0.118	0.204	0.751	0.314	55	55	5	143
Quinebaug at Quinebaug, CT	37	3923.497	2251	0.052	0.121	0.173	0.787	0.557	52	52	4	35
Shetucket at Taftville, CT	33	13322.22	7939	0.074	0.098	0.172	0.791	0.462	52	52	5	76
Naugatuck at Beacon Falls, CT	624	6714.785	4249	0.073	0.268	0.341	0.623	0.452	49	49	4	63
Farmington at Unionville, CT	18	9778.326	5890	0.030	0.075	0.105	0.844	0.561	56	56	5	54
Farmington at Tarrifville, CT	137	14927.22	7872	0.047	0.144	0.192	0.763	0.512	54	54	5	73
Quinnipiac at Wallingford, CT	298	2871.423	1750	0.014	0.537	0.550	0.401	0.408	52	52	4	17
Hockanum at East Hartford, CT	338	1907.71	1064	0.067	0.443	0.510	0.461	0.212	52	52	3	13

Table 1. Continued

	Average WWTP discharge (Becker, 2014)	Total length of streams (USGS, 2017c)	Length of riparian buffers with agriculture (Fry et al., 2011; USGS, 2017c)	Length of urbanized riparian buffers (Fry et al., 2011; USGS, 2017c)	Length of vegetated riparian buffers (Fry et al., 2011; USGS, 2017c)	Main branch length (USGS, 2017c)	Bankfull stream width (Bent, 2006)	Stream depth (USGS, 2017a)	Cross sectional Area (calculated)	Attenuated point-source loading (Becker, 2014)	Nonpoint source loading (Becker and Dunbar, 2009)
Unit	$\text{m}^3 \text{yr}^{-1} * 10^3$	$\text{m} * 10^3$	$\text{m} * 10^3$	$\text{m} * 10^3$	$\text{m} * 10^3$	m	m	m	m	$\text{mg year}^{-1} * 10^6$	$\text{mg year}^{-1} * 10^6$
Symbol	WQ	S	StreamAg	StreamU rb	StreamVeg	MB	D	Z	XSect	kW_p	W_{np}
Dimension	$\text{L}^3 \text{T}^{-1}$	L	L	L	L	L	L	L	L	M T^{-1}	M T^{-1}
River station	313	1256	65	103	992	224	62.6	1.2	73.7	5892	15404
Housatonic at Ashley Falls, MA	322	3145	244	224	2457	224	88.8	1.5	129.8	9341	39780
Housatonic at New Milford, CT	512	5278	393	495	3967	224	106.7	1.7	186.3	23911	58660
Housatonic at Stevenson, CT	253	3082	108	231	2493	112	88.8	2.0	177.6	15587	32432
Quinebaug at Jewett City, CT	69	777	18	67	625	112	37.9	0.9	35.8	1137	3803
Quinebaug at Quinebaug, CT	74	2431	109	154	2052	32	65.4	1.9	127.4	5249	14739
Shetucket at Taftville, CT	436	1032	47	200	709	64	48.2	0.8	39.2	117044	8915
Naugatuck at Beacon Falls, CT	33	1263	27	100	979	75	57.0	1.8	102.8	6670	7177
Farmington at Unionville, CT	289	2048	63	244	1542	75	68.8	0.7	45.5	76348	14390
Farmington at Tarrifville, CT	240	338	4	113	201	73	33.0	1.0	33.4	39014	3534
Quinnipiac at Wallingford, CT	87	262	20	62	165	36	27.5	0.8	23.2	25177	2903
Hockanum at East Hartford, CT	313	1256	65	103	992	224	62.6	1.2	73.7	5892	15404

Table 2. Dimensional analysis of variables for predicting TP in streams using Ipsen's (1960) step-by-step method. Π groups in bold

Original variables and dimensions			Step 1: Cancel [L] using S		Step 2: Cancel [M] using kW		Step 3: Cancel [T] using $\frac{Q_s}{S^3}$	
Variable	Dimensions	Symbol	Dimension Calculation	Symbol	Dimension Calculation	Symbol	Dimension Calculation	Symbol
TP concentration	$\frac{M}{L^3}$	C	$\frac{M}{L^3} * L^3 = M$	CS^3	$\frac{M}{M} = T$	$\frac{CS^3}{kW_p}$	$T * \frac{1}{T} = 1$	$\frac{CS^3}{kW_p} * \frac{Q_s}{S^3} = \frac{CQ_s}{kW_p}$
Attenuated point source loading	$\frac{M}{T}$	kW_p	$\frac{M}{T}$	kW_p	--	--		
Attenuated nonpoint source loading	$\frac{M}{T}$	W_{np}	$\frac{M}{T}$	W_{np}	$\frac{M}{M} = 1$	$\frac{W_{np}}{kW_p}$		
Stream Discharge	$\frac{L^3}{T}$	Q_s	$\frac{L^3}{T} = \frac{1}{T}$	$\frac{Q_s}{S^3}$	$\frac{L^3}{T} = \frac{1}{T}$	$\frac{Q_s}{S^3}$	--	--
WWTP discharge	$\frac{L^3}{T}$	Q_w	$\frac{L^3}{T} = \frac{1}{T}$	$\frac{Q_w}{S^3}$	$\frac{L^3}{T} = \frac{1}{T}$	$\frac{Q_w}{S^3}$	$\frac{1}{T} = 1$	$\frac{Q_w}{\frac{Q_s}{S^3}} = \frac{Q_w}{Q_s}$
Stream network length	L	S	--	--	--	--		
Cross-sectional area of stream	L^2	X-Sec	$\frac{L}{\sqrt{L^2}} = 1$	$\frac{S}{\sqrt{X - Sec}}$				

Table 3. Covariance matrix for variables influencing average annual TP. All variables except for ratios were log transformed in order to improve normality.

	TP	Area	Q	AG	Urb	AgUrb	ForW	Hyd	BFI	V	Order	Imp	WQ	S	SAG	SUrb	SVeg	MB
TP	1.000																	
Area		1.000																
Q			1.000															
AG				1.000														
Urb					1.000													
AgUrb						1.000												
ForW							1.000											
Hyd								1.000										
BFI									1.000									
V										1.000								
Order											1.000							
Imp												1.000						
WQ													1.000					
S														1.000				
SAG															1.000			
SUrb																1.000		
SVeg																	1.000	
MB																		1.000
D																		
Z																		
Xsec																		
kW																		
K'Wnp																		

*Significant at the 0.05 Level

** Significant at the 0.01 Level

*** Significant at the <0.001 level

Table 3. Continued.

	D	Z	X-Sec	kW_p	W_{np}
TP	-0.571	-0.729**	-0.724**	0.736**	-0.456
Area	1.000	0.593*	0.903***	-0.003	0.975***
Q	0.980***	0.566	0.877**	-0.003	0.965***
Ag	0.672*	0.364	0.588	-0.084	0.789**
Urb	-0.759*	-0.50	-0.71*	0.48	-0.65*
AgUrb	-0.669*	-0.463	-0.639*	0.506	-0.525
ForW	0.663*	0.454	0.631*	-0.513	0.524
Hyd	0.444	0.129	0.329	-0.371	0.355
BFI	-0.141	0.110	-0.024	-0.113	-0.282
V	0.611	-0.189	0.257	0.335	0.632
Order	0.933***	0.594	0.864**	-0.138	0.878**
Imp	0.966***	0.558	0.864**	-0.005	0.930***
WQ	0.437	-0.182	0.159	0.584	0.563
S	0.980***	0.585	0.886**	-0.068	0.943***
SAg	0.772**	0.481	0.710*	0.039	0.844**
SUrb	0.833**	0.304	0.651*	0.453	0.862**
SVeg	0.971***	0.596	0.887**	-0.127	0.926***
MB	0.585	0.217	0.459	-0.202	0.613
D	1.000	0.593	0.903***	-0.003	0.975***
Z		1.000	0.882**	-0.421	0.555
Xsec			1.000	-0.227	0.868**
kW_p				1.000	0.068
W_{np}					1.000

*Significant at the 0.05 Level

** Significant at the 0.01 Level

*** Significant at the <0.001 level

Table 4. Correlation Matrix for TP and π groups

	LogTP	$\text{Log} \frac{CQ_s}{kW}$	$\text{Log} \frac{Wnp}{kW}$	$\text{Log} \frac{Q_w}{Q_s}$	$\text{Log} \frac{s}{\sqrt{X-Sec}}$
Log TP	1	-0.52	-0.89 **	0.89**	-0.47
$\text{Log} \frac{CQ_s}{kW}$		1	0.83**	-0.34	0.43
$\text{Log} \frac{Wnp}{kW}$			1	-0.72 *	0.53
$\text{Log} \frac{Q_w}{Q_s}$				1	-0.51
$\text{Log} \frac{s}{\sqrt{X-Sec}}$					1

*Significant at the 0.05 Level

** Significant at the 0.01 Level

Table 5. Scenario testing results and percent change from predicted average annual TP (mg m^{-3}) based on existing conditions

			Scenarios					
Existing Conditions			<u>Riparian Restoration</u>		<u>Improved Treatment</u>		<u>In-stream Decay</u>	
Predicted TP			TP	% Change	TP	% Change	TP	% Change
Housatonic	Ashley, MA	61	59	-3.0	23	-47.1	57	-6.9
Housatonic	New Milford, CT	26	26	-3.5	10	-47.7	24	-9.7
Housatonic	Stevenson, CT	45	43	-3.3	13	-58.7	41	-8.4
Quinebaug	Jewett City, CT	82	79	-2.8	20	-65.2	74	-9.6
Quinebaug	Quinebaug, CT	32	31	-2.1	17	-27.1	31	-2.4
Shetucket	Taftville, CT	25	25	-2.7	5	-70.3	23	-8.2
Naugatuck	Beacon Falls, CT	398	389	-2.2	55	-80.7	391	-1.7
Farmington	Unionville, CT	20	20	-1.6	3	-80.8	19	-5.0
Farmington	Tariffville, CT	160	157	-2.0	22	-81.3	155	-3.2
Quinnipiac	Wallingford, CT	354	353	-0.4	59	-76.8	338	-4.5
Housatonic	Ashley, CT	347	341	-1.8	57	-77.1	337	-2.9
Housatonic	New Milford, CT	61	59	-3.0	23	-47.1	57	-6.9
Hockanum	East Hartford, CT	26	26	-3.5	10	-47.7	24	-9.7

FIGURES

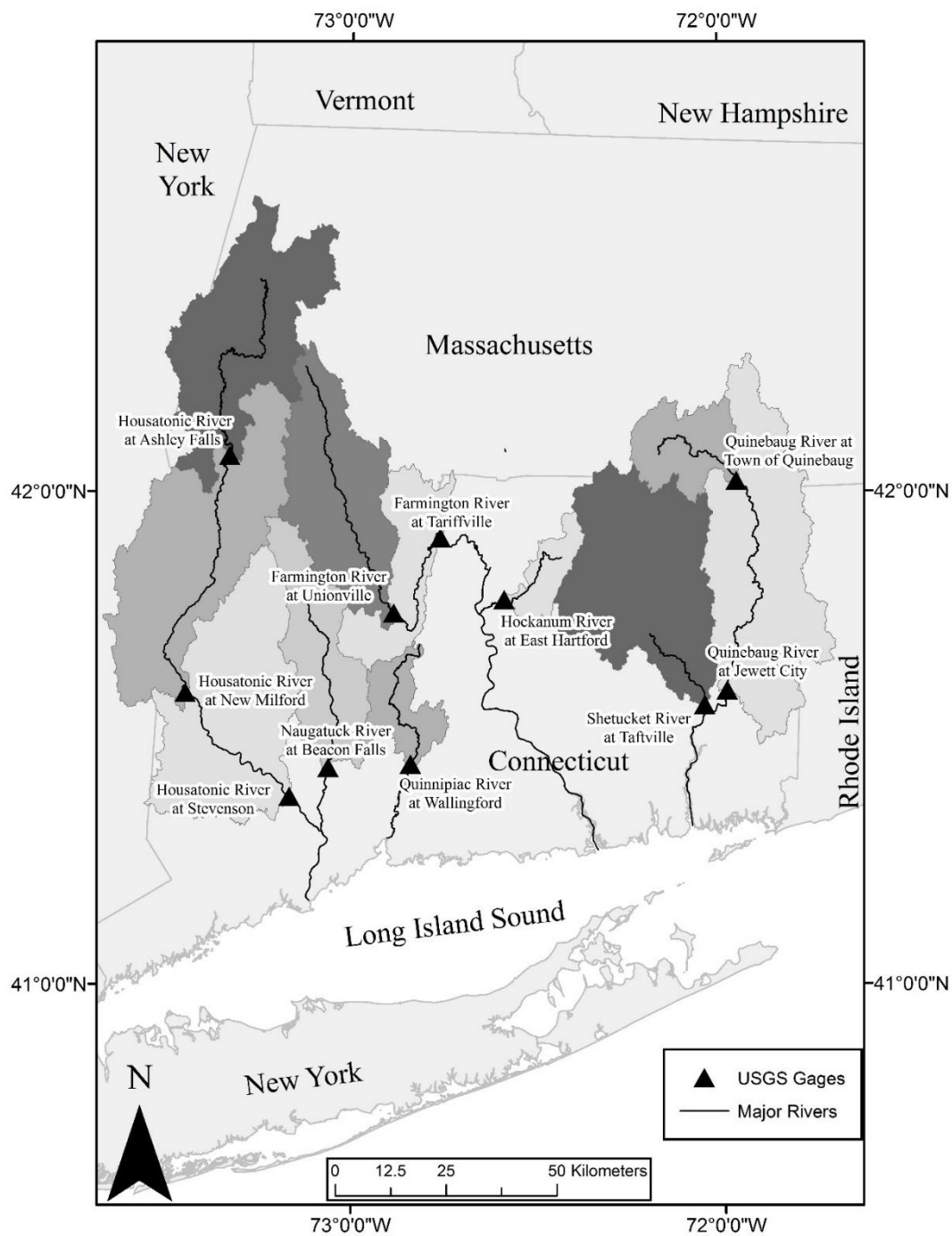


Figure 1. Map of Connecticut and part of Massachusetts (41.748 N, 72.717 W), showing USGS gage stations and associated watersheds.

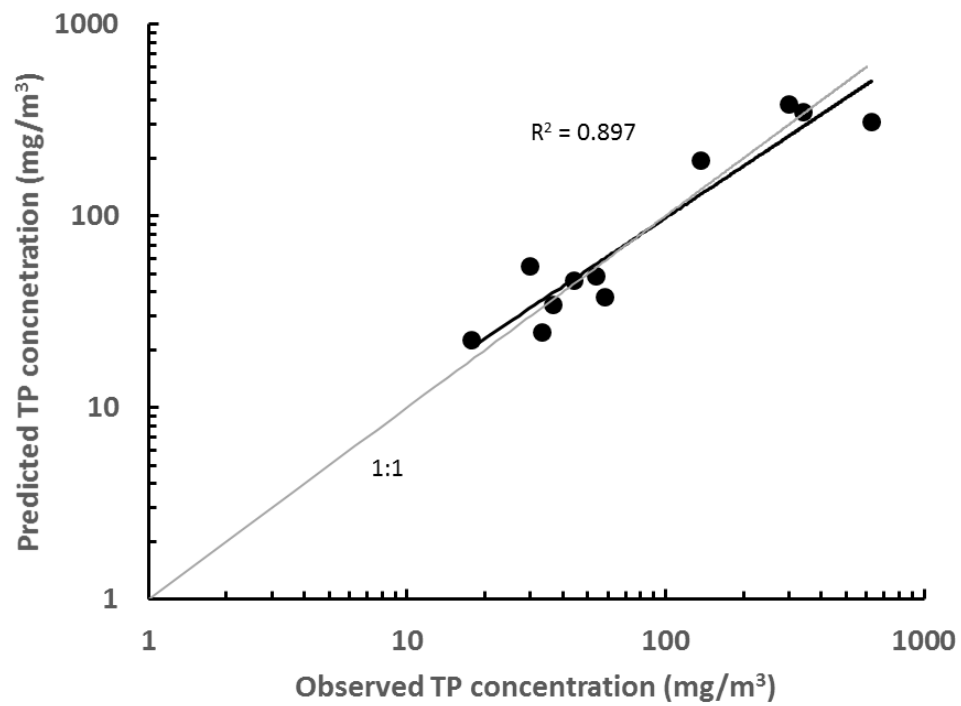


Figure 2. Comparison of observed and predicted TP concentrations for 11 watersheds in Northeast US using stepwise regression of original variables (Equation 11).

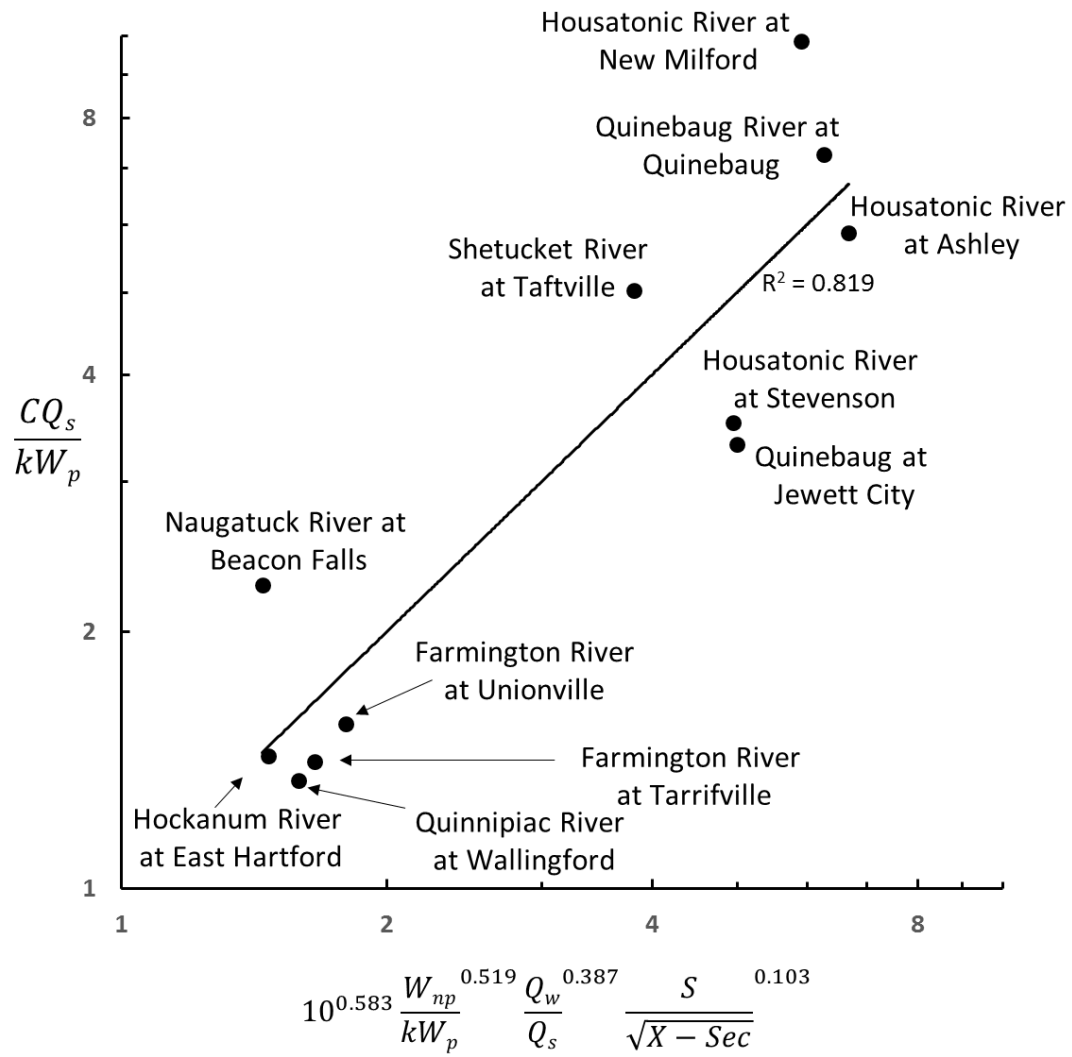


Figure 3. Dimensionless scaling relationship for average annual total phosphorus concentrations

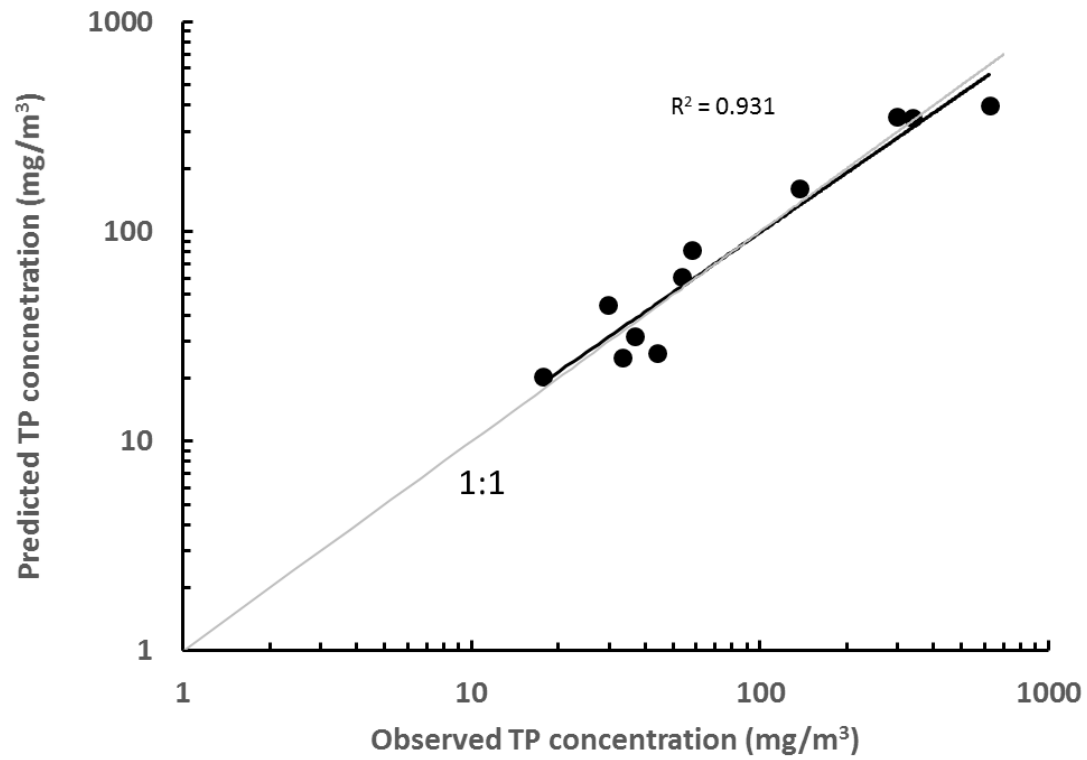


Figure 4. Comparison of observed and predicted TP concentrations for 11 watersheds in Northeast US using dimensional analysis based on the advection-dispersion equation

(Equation 13)

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Water quality changes in a short-rotation woody crop riparian buffer

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Abstract

Converting riparian buffers in agricultural areas from annual row crops to short rotation woody crops (SRWCs) grown for biofuel can provide both water quality benefits and a financial incentive for buffer adoption among agricultural producers. A randomized complete block design was used to determine water quality changes resulting from converting plots previously cultivated in corn to SRWC willow (*Salix. spp*) adjacent to a stream in Storrs, CT. Both overland flow and ground water samples were analyzed for total nitrogen (TN) and total phosphorus (TP). Additionally, overland flow was analyzed for suspended solids concentration (SSC) and ground water samples were analyzed for nitrate + nitrite (NO₂+NO₃-N). Lower ($p = 0.05$) concentrations of TN (41%) and TP (53%) were observed in overland flow from willow plots than from corn plots. Shallow ground water concentrations at the edge of willow plots were lower in TN (56%) and NO₃+NO₂-N (64%), but 35% higher in TP, than at the edge of corn plots. SSC was also lower (71%) in overland flow associated with willow compared to corn. The treatment had no effect on discharge or mass export. These results suggest conversion from corn to a SRWC in a riparian area can provide water quality benefits similar to those observed in restored and established buffers.

Introduction

Riparian buffers have been widely shown to improve water quality associated with agricultural nonpoint source pollution (Clausen et al., 2000; Cooper and Gilliam, 1987; Gold et

al., 2002; Lowrance et al., 1995, 1984; Lowrance and Sheridan, 2005; Peterjohn and Correll, 1984; Schoonover et al., 2005; Vellidis et al., 2003). Buffers improve water quality through several physical and biological mechanisms including infiltration (Gharabaghi et al., 2002; Schoonover et al., 2006), deposition of sediment (Daniels and Gilliam, 1996), adsorption (Cooper and Gilliam, 1987), nutrient uptake (Peterjohn and Correll, 1984), and denitrification (Hill et al., 2000; Lowrance, 1992). The United States Department of Agriculture (USDA) Forest Service has specified a three-zone buffer composed of undisturbed forest, managed forest, and grasses and forbs (Welsch, 1991). Under the Conservation Reserve Program (CRP), administered through the U.S. Department of Agriculture's Farm Service Agency (USDA-FSA), an enrollment-eligible riparian forest buffer (Code 391) must have a minimum width of 10.7 m (USDA-NRCS, 2010). State width guidelines range from 15.5 to 24.2 m (Mayer et al., 2005). Sweeney and Newbold (Sweeney and Newbold, 2014) concluded widths ≥ 30 m are needed to protect the physical, chemical, and biological integrity of small streams. However, fixed width recommendations can be problematic due to high variability in riparian ecological responses (Hansen et al., 2015) and optimal buffer widths may vary site to site (Sweeney and Newbold, 2014). The effectiveness of a buffer is more closely associated with site characteristics, including soil type, hydrology and biogeochemistry (Mayer et al., 2005). Nutrient and sediment retention in riparian buffers has been summarized in several reviews [19, 21–26]. Liu et al. (X. Liu et al., 2008) reviewed over 80 riparian experiments and found buffers reduced sediment concentration or mass in overland flow by 45 – 100%. In a review of ten phosphorus retention studies, Hoffman et al. (Hoffmann et al., 2009) found a median 67% reduction of TP concentration or mass in overland flow from buffers. Removal of particulate P in overland flow through riparian buffers is most likely due to sedimentation processes (Hoffmann et al., 2009).

others have suggested preferential pathways such as macropores can play a role in Retention of dissolved reactive P (DRP) in overland flow is more variable and has been found to range from - 71 to 95% (Hoffmann et al., 2009), while increases in ground water concentrations of TP (Clausen et al., 2000; Osborne and Kovacic, 1993; Peterjohn and Correll, 1984) and DRP (Osborne and Kovacic, 1993) through riparian buffers have been observed. The variable retention and mobility of DRP observed in buffers may result from the relatively high biological activity found in riparian zones compared to agricultural areas (Roberts et al., 2012); transporting P to ground water (Simard et al., 2000). Mayer et al. (Mayer et al., 2007) reviewed results from 88 individual riparian buffers for nitrogen removal efficiency in overland (n = 22) and subsurface (n = 65) flow conditions and calculated mean concentration reductions of 42% and 77%, respectively. Subsurface removal of nitrogen in riparian buffers has been found to be associated with localized denitrification and dilution from upwelling (Clausen et al., 2000; Hill, 1996).

Despite demonstrated benefits of riparian buffer systems, adoption usually requires financial incentives or regulations (Rhodes et al., 2002). Among CRP participants surveyed in 2001, only 1.2% of farms had installed riparian buffers, filter strips, grass waterways or contour strips (Lambert et al., 2007). Other studies of conservation practices adoption in select watersheds in Michigan and Oregon have found from 15% to 26% of producers use some shrub or tree buffer along their streams (Habron, 2004; Ryan et al., 2003). As the demand for renewable energy production has increased, so has interest in short-rotation willow as a bioenergy crop. The Northeast Woody/Warm-season Biomass Consortium (NEWBio) regional network is composed of power corporations, universities, government agencies and the U.S. Departments of Agriculture (USDA) and Energy and has been formed to promote the commercialization of willow biomass crops. Commercial willow biomass production has been shown to reduce fossil

fuel consumption and net greenhouse gas emissions (Heller et al., 2004). In the northeastern U.S. short-rotation willow is harvested at 3-5 yr cycles for 4 to 5 rotations, followed by replanting. Recent trials of willow clones developed for commercial harvest have resulted in a mean yield of 11.5 odt ha⁻¹, with increased yields expected for subsequent harvests (Volk et al., 2011). As of 2015, central and northern New York State had 480 ha of land in commercial biomass production, supported by the USDA's Biomass Crop Assistance Program (Heavey et al., 2015).

Willow characteristics include an extensive fine root system and abundant and diverse microbial rhizosphere communities, suggesting potential as an effective riparian buffer (Volk et al., 2006). In Canada, short-rotation poplar planted in 5.5 m riparian buffers strips has been found to produce above-average biomass yields (Fortier et al., 2010). Also in Canada, short-rotation willow used as a managed riparian buffer accumulated more N than P in biomass, with most P sequestered in the root system (Schroeder et al., 2013). SRWCs are generally considered to improve water quality (Dworak et al., 2008; U.S. Congress, 1993), however, most studies have been limited to non-riparian European sites that are typically irrigated and used to treat wastewater (Aronsson et al., 2010; Aronsson and Bergström, 2001; Dimitriou et al., 2012). Thornton et al. (Thornton et al., 1998) converted cropland to SRWC in the Tennessee Valley and found significantly greater export of nutrients from crop plots, including corn, than from SRWC plots. Densely planted poplar (*Populus* spp.) trees grown for nonpoint source control and biomass production were shown to remove about 95% of NO₃-N from near-surface ground water in annual row-cropped fields (Licht and Schnoor, 1993).

The regional short-rotation willow industry is expected to expand and become more profitable (Heavey et al., 2015) and research has demonstrated water quality benefits associated

with SRWCs as well as their use in riparian buffers. SRWCs riparian buffers in agricultural areas may be increasingly adopted due to their potential profitability, however, the water quality impacts of converting a buffer from an annual row crop to a SRWC has not been demonstrated. In this study, we assess overland flow and ground water quality changes from converting a riparian area cropped in corn to short-rotation willow.

Materials and methods

Study site

The riparian buffer was located along a 180 m reach of Robert's Brook on the University of Connecticut campus in Storrs, CT (Figure 1). Robert's Brook is a first order stream that drains a 194-ha watershed at the downstream end of the study area. Soils were classified as Woodbridge fine sandy loam (coarse-loamy, mixed, active, mesic Aquic Dystrudepts) sloped at 5% with a restrictive layer of densic glacial till occurring at 0.5-1.0 m depth (USDA-NRCS, 2016). After precipitation events, a temporary perched water table would form above this restrictive layer and move laterally as either sub-surface flow or as overland flow towards Robert's Brook. Lateral sub-surface flow created hillslope seeps on the field and riparian area.

The 2.4 ha field was originally cropped in continuous corn. In May, 2013, the field was topdressed with urea to supply 50 kg $-N\ ha^{-1}$ and herbicide was applied in the form of atrazine and glyphosate. In late May and early June, 2013, three control plots and three treatment plots, each measuring 30 m x 10 m, were planted in corn and short-rotation willow, respectively (Figure 1). Control and treatment plots were randomly assigned within blocks based on observed differences in elevation and soil moisture in the riparian area. After installation of the SRWC, no fertilizer or herbicides were applied to the willow plots. Corn plots continued to receive the same management as the field, including seasonal fertilization, herbicide, tillage, harvest, and a cover crop of winter rye. The willow plots were manually weeded once a season.

High-yielding *Salix* spp. cultivars were planted as 25 cm hardwood cuttings at a density of 10,000 plants ha⁻¹. Four willow varieties, 'SX61' (*Salix sachalinensis*), 'SX67' (*S. miyabeana*), 'Millbrook' (*S. purpurea* x *S. miyabeana*), and 'Fabius' (*S. viminalis* x *S. miyabeana*) (Double A Willow, New York), were randomly assigned to each treatment plot. The establishment of the willow treatment followed Cameron et al. (Cameron et al., 2008). Willow plots contained five sets of double row plantings with individual plants spaced 0.61 m in a row, 0.76 m between rows and 1.50 m between double rows, following Zalesny et al. (2011). Willows were coppiced in April 2014 after one growing season.

Experimental Design and Statistical Analysis

The experiment was a randomized complete block design consisting of three blocks (replicates) and two treatments, willow or corn, for a total of six experimental plots. The MIXED procedure within the SAS statistical software (SAS Institute, 2012) was used to conduct an analysis of variance (ANOVA) in order to determine if significant differences in the means for corn and willow treatments existed for all variables measured. The effects of treatment were considered fixed, while those of block were considered random. Type III sum of squares and least square means were used in all interpretations. Differences among blocks were determined using one-way ANOVA and Fisher's Least Significant Difference test ($\alpha = 0.05$). Normality of observations was analyzed using the Shapiro Wilk test; data found to be log-normally distributed was log-transformed. Standard errors were calculated on untransformed data.

Sample collection and analyses

Overland flow was collected near the downslope edge of each plot, approximately 4 m from the top of the stream bank. Fabricated sheet metal walls were installed to create runoff plots open to the upslope corn field with watershed areas ranging from 8.4 m² to 47.8 m² due to microtopographic features of the field. Surface water was conveyed from runoff plot outlets

along a 2.5 cm PVC pipe to a tipping bucket recorder and passive splitter to collect a water sample.

Ground water was sampled using 5 cm ID, 10 slot, screened PVC wells installed to the depth of the existing restrictive soil layer in each plot, approximately 0.6 m below the surface. The annular space between PVC screens and was packed with sand (1.0 mm grain size) and sealed at the surface with packed soil. Wells were sampled weekly and after rain events. Wells remained dry until sufficient rainfall created a temporary perched water table and samples were obtained by purging the total well volume using a peristaltic pump. Precipitation at the site was measured using a standard non-recording rain gage. Beginning in April 2015, soil volumetric water content ($\text{cm}^3 \text{H}_2\text{O cm}^{-3} \text{soil}$) was measured weekly using a portable meter which integrated over the upper 12 cm of soil (Campbell Scientific, Logan, UT, USA).

Surface and ground water samples were collected within 12 h of the end of a precipitation event during April through November of each year; samples were also obtained during the winter of the first growing season (2013-2014). Sample bottles were transported to the lab in a cooler with ice and refrigerated at 4° C. Sample concentrations of TP and TN were determined by colorimetry using a SmartChem ® discrete wet chemistry analyzer according to EPA Methods 365.4, 351.2 (USEPA, 1983), and 353.2 (USEPA, 1993), respectively. Subsamples of overland flow were obtained by means of a churn splitter and analyzed for suspended sediment concentrations using the American Society for Testing and Materials (ASTM) method D 3977-97 (American Society for Testing and and Materials (ASTM), 1997).

Results and Discussion

Precipitation and overland flow

Precipitation at the site during the sampling period (June, 2013 to November, 2016) was 34% below normal based on the National Weather Service National Climatic Data Center station in Storrs, CT, located 2.2 km from the study site. During this time, the site also produced less overland flow than expected; plot runoff coefficients ranged from 0.001 to 0.022. Cultivated, sandy soil with 3 - 6% slopes would be expected to have a runoff coefficient of 0.4 (Novotny, 2003). Runoff depth from block one was significantly ($p < 0.05$) higher than from blocks two and three (Table 1). There was no treatment effect on the volume or depth of overland flow (Table 2). Variability in overland flow (Figure 2) may have contributed to a lack of difference. Similarly, Thornton et al. (Thornton et al., 1998) found that the variance associated with runoff from row crops and those converted to SRWC was such that statistical significance could not be detected.

Concentration

Overland Flow

Conversion to SRWC within the riparian zone significantly decreased concentrations of TN (41%), TP (53%), and SSC (71%) in overland flow compared to corn (Table 2). Concentrations of TN were higher in runoff from block three than from block one (Table 1). The corn plot in block three had significantly higher discharge compared to the willow plot (Figure 2). The higher discharge resulted in 3x as many samples collected from the corn plot, which may explain the higher TN attributed to block 3. A separate study in Connecticut found slightly greater reductions in TKN (70%), $\text{NO}_3\text{-N}$ (83%), TP (73%), and TSS (92%) in runoff from a 35 m wide restored riparian buffer initially seeded with fine leaf fescue (*Festuca* spp.) and allowed to revegetate naturally (Clausen et al., 2000). Total nitrogen removal in overland flow from the SRWC buffer was above the mean 33% ($n = 18$) that Mayer et al. (Mayer et al., 2007) calculated

in their review of nitrogen removal effectiveness for riparian buffers. Removal of TP was within the reported range ($n = 10$) of 32 to 93% that Hoffman et al. (2009) reported in a review of TP retention in overland flow from vegetated buffers. The percent reduction in suspended sediment from the SRWC buffer was below the 90% predicted for a 10 m wide buffer with a 5% slope calculated by Liu et al. (X. Liu et al., 2008) using data from over 80 riparian studies. The observed reductions in TN and TP from the SRWC buffer also are similar to those observed for a three-zone buffer, which reduced concentrations by 37% and 56%, respectively (Lowrance and Sheridan, 2005). Reductions in SSC in our study were an improvement over the 43% decrease Newbold et al. (Newbold et al., 2010) observed in a 15-year old three-zone buffer.

Ground water

Short-rotation willow significantly decreased the concentrations of TN by 41% in ground water at the edge of the plots (Table 2), $\text{NO}_3+\text{NO}_2\text{-N}$ was also reduced ($p=0.051$) by 41%. The observed reduction of N in ground water was somewhat less than the mean subsurface removal effectiveness of 77% N calculated for riparian buffers by Mayer et al. (Mayer et al., 2007). Treatment effects on ground water concentrations of TN and $\text{NO}_3+\text{NO}_2\text{-N}$ were confounded by the interaction between blocks and treatments. Conversion to short-rotation willow lowered ground water concentrations of TN in blocks two and three but had no effect in block one (Table 3). No difference in TN and $\text{NO}_3+\text{NO}_2\text{-N}$ concentrations were observed between blocks one and three. Block one had the lowest mean $\text{NO}_3+\text{NO}_2\text{-N}$ concentration and was the wettest, demonstrated by significantly higher runoff depth and volumetric water content (Table 1), while block three had the highest $\text{NO}_3+\text{NO}_2\text{-N}$ concentrations, suggesting blocking was appropriate. Concentrations of $\text{NO}_3+\text{NO}_2\text{-N}$ in ground water can be reduced by high denitrification rates in wetter parts of buffers (Lowrance et al., 1995). Therefore, the lack of treatment effect in block

one may be due to increased denitrification in both corn and willow plots in this portion of the riparian area. However, denitrification was not measured as part of this study.

Total P concentrations in ground water associated with the willow plots increased by 31% compared to the corn plots (Table 2). Although riparian buffers have been shown to be effective in retaining TP in overland flow, there is less certainty regarding their impact on ground water TP concentrations (Hoffmann et al., 2009). Vellidis et al. (2003) found a 40% reduction in TP mass in ground water from a restored forested wetland, while others have found concentration increases ranging from 52% to 122% in revegetated and mature forests (Clausen et al., 2000; Osborne and Kovacic, 1993; Peterjohn and Correll, 1984). Vellidis et al. (2003) did not report concentrations in ground water, however, reductions in TP mass may have been associated with observed reductions in ground water discharge at the site.

Decades of work has assessed the nutrient use efficiency of crops, including corn (Mengel and Barber, 1974; Schlegel and Havlin, 2017) and SRWC willow (Hangs et al., 2014; Weih and Nordh, 2002). Approaches range from ecological based assessment of accumulation and losses, agronomic valuation of harvested products, and analysis of nutrient use of various physiological processes (Weih et al., 2011). However, it is often not possible to compare the results from these different approaches, especially when assessing different crops and production systems (Weih et al., 2011). Kuzovkina and Volk (2009) characterized willow as a relatively nutrient demanding crop (Kuzovkina and Volk, 2009), while Hangs et al. (2014) concluded that the nutrient demand by willow is low. Several studies have assessed the nitrogen requirements of willow (Ericsson, 1994; Ferrarini et al., 2016; Weih et al., 2011; Weih and Nordh, 2002), which can be highly variable among clones (Weih and Nordh, 2002). However, less is known about phosphorus uptake. While willow has been estimated to leach less phosphorus than corn (Börjesson and

Tufvesson, 2011), Dimitriou et al. (2012) found increased phosphorus in ground water monitored in willow fields compared to reference fields that grew grass or cereal crops. The authors suggest preferential flow of phosphorus bound to soil particles along willow root channels and elevated soil organic matter as potential causes for higher phosphorus in ground water.

Roberts et al. (2012) identified the need for additional research in phosphorus retention and remobilization in riparian buffers, including identifying plant traits that enhance biological retention and the role microbial activity has on elevated phosphorus concentrations observed in some riparian buffers. Similarly, our results reinforce this need for a better understanding of the mechanisms involved in phosphorus export in ground water from riparian buffers including from SRWCs.

Mass

There was no treatment effect on the mass export of TN, TP, or SSC in overland flow (Table 2). The lack of difference may be due to the flow variability and lack of treatment effects on overland flow (Figure 2).

Conclusions

The SRWC willow buffer significantly reduced concentrations of TP, TN, and SSC in overland flow compared to corn. Ground water at the edge of willow plots had lower concentrations of TN and $\text{NO}_3\text{+NO}_2\text{-N}$, but significantly higher concentrations of TP than corn plots. Overland flow from the riparian area was less than expected and no differences were detected between corn and willow treatments. Our results show that converting corn to a SRWC buffer can result in improvements to water quality similar to other studied mature and restored buffers.

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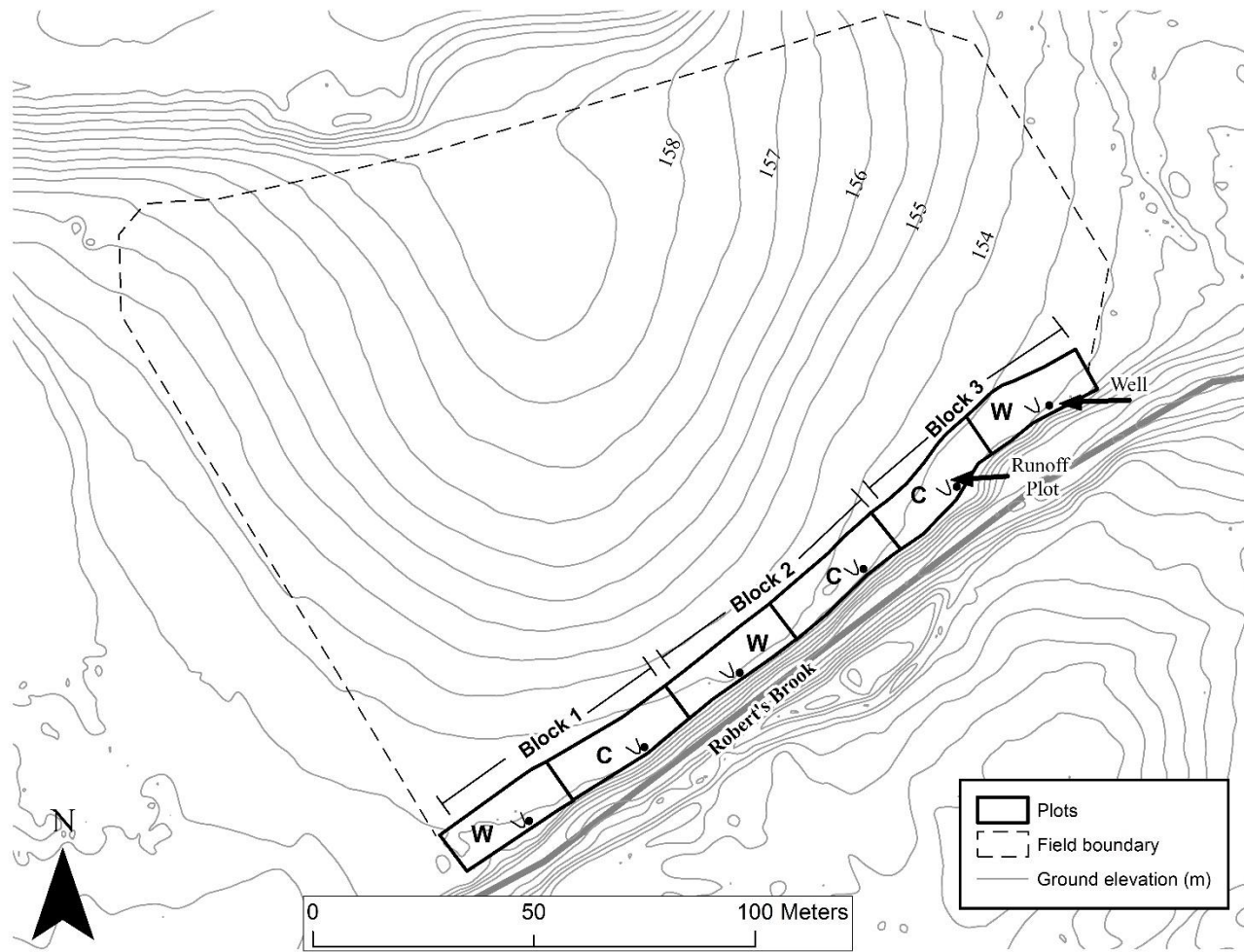


Figure 1. Plan view of the SRWC riparian study. Plots are annotated W for willow and C for corn. Sampling locations and surface elevations are also shown.

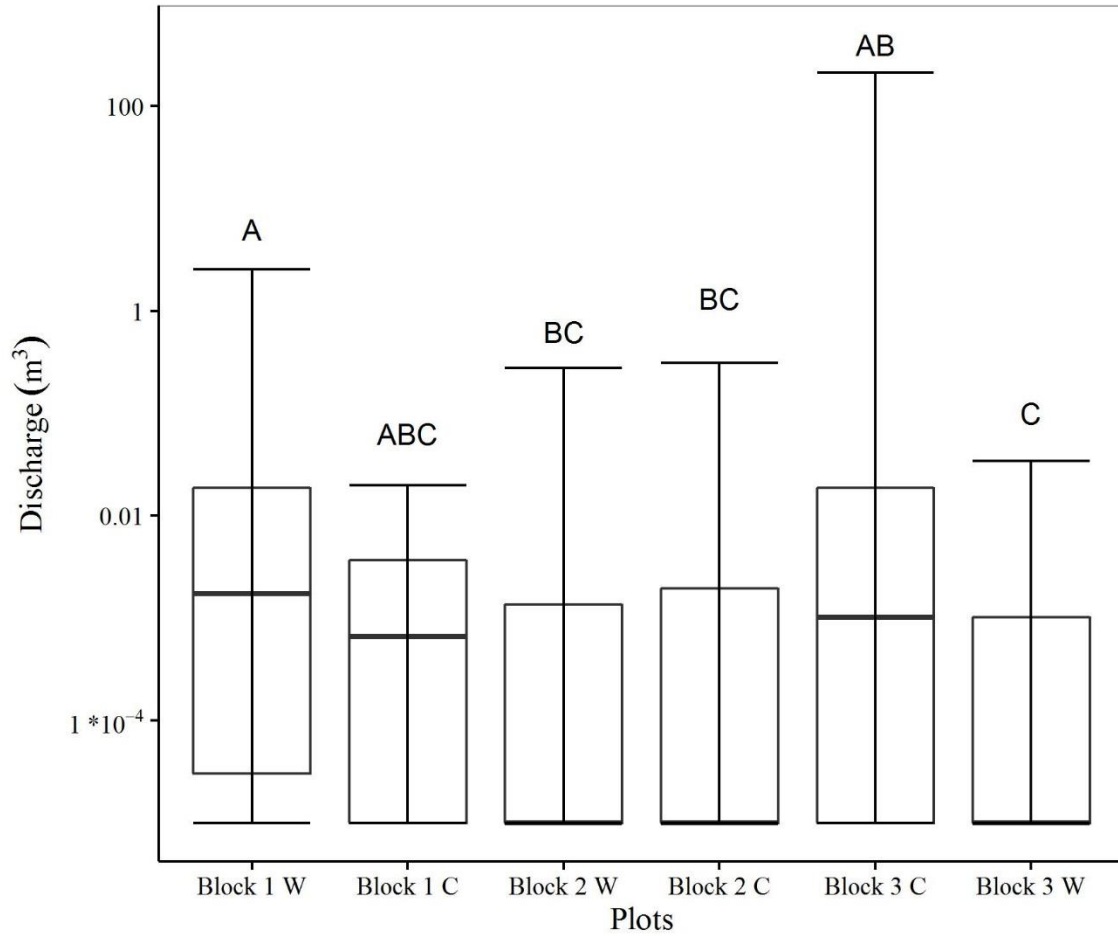


Figure 1. Box plots of overland flow at Storrs, CT. W = willow, C = corn. Boxplots topped by the same letters are not significantly different ($\alpha = 0.05$).

Table 1. Geometric means \pm standard errors of runoff volume, depth, and concentrations and arithmetic means and standard errors of volumetric water content. Thirty events produced runoff samples and 43 produced ground water samples. Block means followed by the same letters are not significantly different for a variable ($\alpha = 0.05$).

Overland Flow	Block One	Block Two	Block Three
Volume ($\text{m}^3 \cdot 10^3$)	0.516 ± 12.50 A	0.523 ± 12.40 A	0.192 ± 12.40 A
Depth (cm)	0.0156 ± 0.3024 A	0.0025 ± 0.3003 B	0.0026 ± 0.3003 B
SSC (mg L^{-1})	25.7 ± 337.1 A	66.1 ± 422.6 A	32.4 ± 456.4 A
TN (mg L^{-1})	2.26 ± 0.40 B	2.94 ± 0.51 AB	3.87 ± 0.56 A
TP (mg L^{-1})	1.251 ± 0.345 A	1.461 ± 0.435 A	1.682 ± 0.481 A
Ground water			
TN (mg L^{-1})	2.12 ± 1.0 B	3.35 ± 1.64 B	10.60 ± 1.28 A
TP (mg L^{-1})	1.169 ± 0.143 A	1.06 ± 0.238 A	1.191 ± 0.179 A
NO ₃ +NO ₂ -N (mg L^{-1})	0.61 ± 0.90 B	1.11 ± 1.49 B	6.44 ± 1.88 A
Volumetric water content (%)	24.6 ± 0.5 A	20.73 ± 0.5 C	23.2 ± 0.5 B

Table 2. Geometric means, standard errors and ANOVA results for overland flow volume, depth, concentrations, mass export and ground water concentrations associated with willow and corn plots, Storrs, CT.

Overland Flow	Treatment		<i>F</i> value	<i>P</i> value
	Corn	Willow		
Volume (m ³ *10 ³)	0.286 ± 11.64	0.216 ± 11.60	0.53	0.594
Depth (mm)	0.0042 ± 0.2460	0.0052 ± 0.2448	0.13	0.721
TN (mg L ⁻¹)	3.78 ± 0.45	2.22 ± 0.46	13.54	< 0.001
TP (mg L ⁻¹)	2.056 ± 0.317	1.008 ± 0.297	21.34	< 0.001
SSC (mg L ⁻¹)	54.82 ± 328.49	25.01 ± 319.49	4.14	0.046
TN (kg ha ⁻¹)	0.014 ± 0.025	0.001 ± 0.026	0.58	0.451
TP (kg ha ⁻¹)	0.008 ± 0.011	0.005 ± 0.012	0.91	0.364
SSC (kg ha ⁻¹)	0.216 ± 0.7786	0.1372 ± 0.8276	0.65	0.423
Ground water	Corn	Willow	<i>F</i> value	<i>P</i> value
TN (mg L ⁻¹)	5.629 ± 3.512	3.345 ± 3.506	5.86	0.017
TP (mg L ⁻¹)	0.964 ± 0.155	1.392 ± 1.082	10.97	0.001
NO ₃ +NO ₂ (mg L ⁻¹)	2.13 ± 3.41	1.25 ± 3.41	3.88	0.051

Table 3. Geometric means \pm standard errors for TN and NO₃+NO₂-N by treatment and block in ground water. Means followed by the same letters are not significantly different ($\alpha = 0.05$) across all plots.

	Block One		Block Two		Block Three	
	Corn	Willow	Corn	Willow	Corn	Willow
TN (mg L ⁻¹)	2.23 \pm 3.67 B	2.02 \pm 3.93 B	7.93 \pm 2.38 A	1.78 \pm 2.04 B	13.22 \pm 1.64 A	8.224 \pm 1.76 A
NO ₃ +NO ₂ -N (mg L ⁻¹)	0.56 \pm 1.17 B	0.674 \pm 1.294 B	3.784 \pm 2.11 A	0.45 \pm 1.81 B	9.1 \pm 1.46 A	4.147 \pm 1.65 A

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