

Modelling of Phosphorus Retention Dynamics in Freshwater Ecosystem

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Abstract—The present paper describes the impacts of hydrology, biogeochemistry and bathymetry on phosphorus dynamics in freshwater ecosystem. Various methods for quantifying phosphorus retention have been discussed, including the phosphorus spiraling concept and the advection-dispersion-reaction equation as well as its associated forms. The various parameters typically measured during field or experimental studies that are used in these models. Finally, we compare the similarities and differences in methodologies used to model phosphorus retention in freshwater ecosystems and the need to frame phosphorus processing freshwater ecosystems.

1. INTRODUCTION

Freshwater bodies receive large quantities of excess nutrients generated from terrestrial ecosystems, and both lentic systems (slow-moving water bodies such as lakes, reservoirs, and wetlands) and lotic systems (fast-moving water bodies such as streams and rivers) function as key reactive interfaces for phosphorus removal from the water column [1]. Additionally, phosphorus typically exists in two major forms: sediment bound phosphorus and dissolved phosphorus [2]. Phosphorus typically enters the terrestrial ecosystem through physical or chemical erosion of phosphorus-bearing minerals (such as apatite) or anthropogenic inputs such as fertilizer [3]. Once in the soils, phosphorus may be used by plants if bio-available, stored as sediment-bound phosphorus until eroded by overland flow, or leached into groundwater [4, 5]. Phosphorus is only retained in the ecosystem via storage (whether in biomass or sediments). These storage pools can be temporary in nature, as biomass will eventually die and become active in the cycle again, and sediment phosphorus can be re-released under reducing conditions and high pH [6]. The settling of particulate phosphorus in aquatic ecosystems, however, serves as an important sink of phosphorus in ecosystem. Retention processes for phosphorus are typically modeled as first-order reactions, although more complex process-based models that consider saturation kinetics and second-order dependencies do exist [7-10]. First-order fluxes are characterized by a rate constant (k) multiplied by the mass or concentration of a chemical constituent. While first-order equations allow for simple analytical solutions of models and thus less computation time, they may be only applicable under certain

conditions. Consequently, models of these first-order processes can be modified to accommodate different biogeochemical factors. Over fifty models that quantified and found that approximately 65% of them followed first-order kinetics. Amongst these models, additional modifiers such as soil saturation, temperature, pH level, and phosphorus availability have been formulated. Similarly, the settling and sorption of phosphorus is not truly linear in the environment. Linear settling rates are based on the assumption that lakes are dilute and that the sediment particles do not interact with each other [11]. While the kinetics of phosphorus sorption can be modelled using a linear isotherm, they can also be modelled using Michaelis-Menten type functions, or dependencies on iron concentrations, pH, etc. [12]. The explicitly of model sorption does not depend on sorption, but treat settling as a dominant, first-order process, which implicitly assumes that phosphorus will be adsorbed onto sediment. Accordingly, our focus herein is on literature that employs first-order modeling approaches to simulate phosphorus retention processes in different freshwater ecosystems. While freshwater ecosystems are often thought of as net phosphorus sinks in the landscape, there are instances in which these systems act as net phosphorus sources. Net source dynamics may manifest seasonally and be caused by the dominance of certain internal processes or the reduction of the main removal processes [13]. Net export of reactive phosphorus in water bodies across long time scales tend to be uncommon, as described by the meta-analysis performed by [14] and the work by [15]. The present paper describes the impacts of hydrology, biogeochemistry and bathymetry on phosphorus dynamics in freshwater ecosystem. Various methods for quantifying phosphorus retention have been discussed, including the phosphorus spiraling concept and the advection-dispersion-reaction equation as well as its associated forms.

2. METHODS OF MODELLING

The phosphorus spiraling model can be summarized using several simple metrics. [16] presented the concept of the spiraling length, S , which is the characteristic length that a

phosphorus particle must travel to complete one spiral (from dissolved form in water to particulate phase to organic phase and back to aqueous phase). This spiraling length, S , can be quantified by using the uptake rate constant, k , and the stream velocity, u , where $S = u/k$. Thus systems with a low spiraling length are considered to be more efficient in using nutrients.

A process-based model that is commonly used to characterize phosphorus retention in the advection-dispersion-reaction equation (ADRE) [17]. This model provides three modes of transport for a contaminant: advective transport with the flow of water, dispersion or diffusive transport due to concentration gradients, and a reactive pathway due to a general biogeochemical reaction. As described below, there have been two common modifications to the ADRE are: (1) the addition of the hyporheic exchange and (2) the simplified plug flow reactor model (PFR). More complex nutrient spiraling models that explicitly account for biological uptake in the channel and hyporheic zone do exist, but it has been demonstrated that at long-term scales (at annual or greater time scales) settling (for P) are the dominant retention processes. Furthermore, while more complex models provide more flexibility and fewer assumptions, the number of parameters may lead to issues of equifinality and difficulties in isolating the interactions between state variables and outputs [18].

The ADRE with hyporheic exchange, also known as the One-Dimensional Transport with Inflow and Storage model (OTIS) model was originally developed to model the tracers under the influence of surface and groundwater interactions on water quality [19]. This modeling framework has been widely used in stream systems where the groundwater-surface water exchange constitutes an important component of nitrogen cycling [20] and can be used to link the physical geometry to phosphorus retention in a parsimonious manner. This model can be written as:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - kC - \alpha(C - C_{HZ}) \quad (1a)$$

$$\frac{\partial C_{HZ}}{\partial t} = R\alpha(C - C_{HZ}) - k_s C_{HZ} \quad (1b)$$

where C is the concentration of the contaminant in the channel (M/L^3), t and x are time (T) and space (L), v is the mean velocity of the advective flow (L/T), D is the dispersion coefficient (L^2/T), k is a biogeochemical reaction in the channel ($1/T$), C_{HZ} is the concentration in the hyporheic zone (M/L^3), R is the ratio of the cross-sectional area of the main channel to the hyporheic zone (-), and k_s is the biogeochemical reaction rate constant in the hyporheic zone ($1/T$).

The PFR model is a simplification of the ADRE model in that it removes the dispersive term and assumes that the contaminant moves as a 'plug' through the system. In this model, it is common to use the apparent uptake velocity v_f

(L/T) to quantify nutrient uptake in streams assuming first-order kinetics. This parameter also spatially and temporally averages the phosphorus spiraling mechanisms into a constant. The PFR equation and its associated analytical solution are:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} - \frac{v_f}{h} C \quad (2a)$$

$$C = C_0 e^{-\frac{v_f}{h} \tau} \quad (2b)$$

Where v_f is the nutrient uptake velocity (L/T) and h is the mean depth of the channel (L), C_0 is the initial concentration at the inlet (M/L^3), and τ is the mean water residence time (T).

The PFR model has been used extensively in freshwater ecosystem and continental scales due to its simplicity and its spatiotemporal averaging of the fine-scale processes. SPARROW, the commonly used PFR approach, as have studies [21-24]. In addition, [25] used the PFR model as the basis for a river network model to determine the relative roles of stream order on phosphorus removal. They found that small streams remove more phosphorus mass on a per length basis while larger streams remove more total phosphorus mass due to longer residence times and because most of the land (and nutrient mass) will eventually drain through the large streams.

3. PHOSPHORUS RETENTION RATES IN FRESHWATER ECOSYSTEM

Numerous studies have focused on phosphorus processing and removal in freshwater bodies [26-32]. For phosphorus, the mass flux of particulate phosphorus into long term sediment storage has also been widely recognized as a dominant process for phosphorus removal [33]. Wetlands, and especially constructed wetlands, have also been a subject of interest as sites for removing phosphorus from runoff or wastewater [34].

Limnological research was initially more strongly focused on phosphorus removal, stemming from the seminal work of who observed the limiting effects of phosphorus from a lake-scale experiment, and the early work by [35] observing N:P ratios on lake ecosystem health. [36] using a regression based model, did not focus on the results pertaining to small lakes and reservoirs nor postulate a mechanistic reason for this phenomena. This modelling result was treated as a curiosity and also speaks to the need of furthering our understanding of these systems.

Early models of wetlands stem from the constructed wetland use the PFR formulation to describe phosphorus retention [37-41]. More complex models that consider the wetland to be comprised of different compartments like the surface water, littoral zone, macro fauna, top and deep soil exist as well. Those using the simpler input-output model such as the PFR

formulation typically are interested in the overall behavior and the influence of relatively few controlling factors; conversely, complex models are able to quantify the interaction of multiple processes and the presence of feedback loops at the cost of needing many parameters or constraints.

Similar to modelling phosphorus in stream, there are many levels of complexity that can be added to a model to capture more complex interactions among the biophysical and ecosystem controls on phosphorus removal. In their simpler forms, models can simulate water column dynamics alone, while more complex approaches can extend to additional compartments such as sediments, macrophytes and periphyton [42].

The most basic models focus on the water column, with the sediment being treated as a boundary. Limnologists studying phosphorus retention commonly use the [43] methods, which conceptualizes the lake as a continuously stirred tank reactor (CSTR) with an effective removal rate constant σ (also referred to as the volumetric rate constant $k_{v,C}$, (T^{-1})) that can be estimated based on the percent removal R and the mean water residence time τ (Table 1). In its most basic form, the CSTR equation can be written as:

$$V \frac{dC}{dt} = QC_0 - QC - k_{v,C}CV \quad (3)$$

where V is the volume of the water column (L^3), C_0 is the concentration in the inflow (ML^{-3}), C is the nitrogen concentration in the water column and outflow (ML^{-3}), and Q is the flow (L^3T^{-1}).

CSTRs, or well-mixed reactors, are diffusion-dominated systems, with any mass entering the system being assumed to be instantaneously mixed within the water body, such that the concentration within the water body and the outflow are the same. Modeling as a CSTR is a widely accepted practice in the limnologic literature. [44] conducted a review and found hundreds of studies citing the original Vollenweider model or some variant of the CSTR model to describe phosphorus retention. By adding other mass fluxes such as a sedimentation term, other studies such as those by [45-46] used the CSTR formulation for phosphorus in lakes and reservoirs.

Another group of models focus only on the sediment, with the water column providing a boundary condition to the sediment model. Commercial models such as the HYDRUS Wetland Module and COMSOL operate in a similar manner [47]. HYDRUS and COMSOL solve the Richard's equation for water flow and couple advective-dispersive transport processes to contaminant flow [48]; however these models are highly parameterized and are more tailored to subsurface systems, with the surface water being treated as a boundary condition.

There are also more complex limnologic models such as Minlake [49], the wetland model by [50] and eutrophication models [51] that couple nutrient processes in the water column to the sediment zone, but these models have the added complexity of hydrodynamics, spatial dimensions, or ecological feedbacks that are beyond the scope of what can be parameterized from a data synthesis.

4. PHOSPHORUS RETENTION RATE CONSTANTS IN FRESHWATER ECOSYSTEMS

Modelling studies attempting to replicate field studies or predict future behavior of a specific water body or its internal processes at small scales tend to require more precise spatiotemporal resolution and may necessitate additional parameters to account for effects of temperature, pH, etc. On the other hand, studies quantifying the behavior of systems at larger scales such as watersheds or even continents will encounter issues of expensive computational simulations because of model complexity [52]. In the case of larger scales, the first-order rate constant approach is often considered sufficient to describe the behavior of water bodies as many processes may be averaged spatially or temporally – thus organization from complexity may emerge so that dominant behaviours may be quantified at these scales with simple rate constants [53].

The original phosphorus spiraling model for streams by [16] presents a rate constant k_a (LT^{-1}) in the form of uptake velocity, there is also a large body of work that uses the volumetric constant $k_{v,P}$ (T^{-1}) (Table 1). The relation between the two rate constants can be expressed as $k_{a,i} = k_{v,i}h$ where h (L) is the depth of the water body, $i = c$ or p for CSTR and PFR formulations [37]. The areal rate constant $k_{a,i}$ or $v_{f,i}$ is a biological measure of removal that is independent of the surface water hydrology, while spatiotemporal variations in hydrology are considered in the volumetric rate constant [54]. The areal rate constant is mainly affected by biogeochemical controls such as dissolved oxygen, redox potential, organic content and microbial activity [55], and has been shown to be relatively independent of stream order. The independence of the areal rate constant with respect to the depth and volume of a system makes it a weaker choice when comparing the effects of system size on its nutrient processing and points to the choice of the volumetric rate constant within our work to explore the controls of system size. Interestingly, tracer tests on a number of treatment wetlands have shown that the flow regimes actually lie between the extremes of a PFR and a CSTR [56], and thus studying these two end-member systems enable us to constrain the system response. The simplicity of the equations allows us to calculate these rate constants as a function of R (for the volumetric rate constant) or R and hydraulic loading rate q (for the areal rate constant).

Table 1. Comparison of commonly used first-order removal rate constants

Removal Rate Constant Name	Units	Steady State Removal/Retention Equation	Example Usage in Papers in Different Disciplines
CSTR Model			
Apparent removal velocity ($v_{f,c}$)	[LT ⁻¹]	$k_{a,c} = v_{f,c} = \left(\frac{R}{1-R}\right)q$	Lakes and reservoirs: Sonzogni et al. [1982], Dillon and Molot [1996] for P; Kelly et al. [1987] for N
Volumetric rate constant ($k_{v,c}$), Vollenweider rate constant (σ)	[T ⁻¹]	$k_{v,c} = \left(\frac{R}{1-R}\right)\frac{1}{\tau}$	Lakes and reservoirs: Hejzlar et al. [2006] for P, Vollenweider [1975] for P;
PFR Model			
Areal rate constant ($k_{a,p}$), Uptake velocity ($v_{f,p}$)	[LT ⁻¹]	$k_{a,p} = v_{f,p} = -\ln(1-R)q$	Lakes and reservoirs: Harrison et al. [2009] for N, Knight et al. [2003] for P, Wollheim et al. [2008] and Beusen et al. [2015] for N and P; Constructed wetlands: Kadlec and Wallace [2009] for N and P; Rivers: Wollheim et al. [2006] for N
Volumetric rate constant ($k_{v,p}$), time specific uptake rate	[T ⁻¹]	$k_{v,p} = \ln(1-R)\frac{1}{\tau}$	Constructed wetlands: Carleton et al. [2007] for N and P; Rivers: Alexander et al. [2009] for N

where R is the fraction of nutrient retained [-], q is the hydraulic loading rate [LT⁻¹] and τ is the mean water residence time [T]. The subscripts a and v indicate the areal and volumetric rate constants, the p and c refer to the PFR and CSTR models.

5. DAMKOHLE NUMBER: A RATIO TO UNITE HYDROLOGY WITH BIOGEOCHEMISTRY

The Damkohler number, Da , is a dimensionless ratio between a hydrological time scale (for example the water residence time τ_w (T)) and a reaction time scale (for example the inverse of the volumetric rate constant $\tau_{rxn} = 1/k$ (T)); the ratio can be generally written as τ_w / τ_{rxn} . A Damkohler number equal to 1 indicates that the transport and reaction timescales are balanced, while $Da < 1$ indicates transport limitation, and $Da > 1$ implies reaction rate limitation where biophysical conditions are limiting for the reaction [57]. In other words, the reaction times are much smaller than transport or exposure times, and thus the nutrient will be removed fully from the water column under reaction rate limiting conditions. Conversely, if reaction times are larger than transport times, there is insufficient time for reactions to occur (and often assumptions of equilibrium are not met) in transport limiting conditions. [58] sampled a transverse cross-section of a streambed and found that deep locations characterized by hyporheic exchange flows had a Da greater than 1 (i.e. reaction rate limited). These hotspots had more reducing conditions and lower oxygen levels [59], similarly found that the hyporheic zone was largely reaction limited in their study site. [60] applied the Da framework to hillslopes and riparian zones and found that the slope of the system acted as a major control on nutrient attenuation. The flatter hillslope, which had longer transport times, would consequently be reaction limited. The use of the Damkohler number provides a concise way to summarize a system's behavior in a non-dimensional

manner and thus allows one to compare different types of water bodies that span multiple orders of magnitude in size.

6. CONCLUSION

The clear relationships seen between the biogeochemical functions of the water body and the size of the system. A process-based model that is commonly used to characterize phosphorus retention in the advection-dispersion-reaction equation (ADRE) which provides three modes of transport for a contaminant: advective transport with the flow of water, dispersion or diffusive transport due to concentration gradients, and a reactive pathway due to a general biogeochemical reaction. The PFR model has been used extensively in freshwater ecosystem and continentals scales due to its simplicity and its spatiotemporal averaging of the fine-scale processes. The Damkohler number provides a concise way to summarize a system's behavior in a non-dimensional manner and thus allows one to compare different types of water bodies that span multiple orders of magnitude in size.

REFERENCES

- [1] McClain, M. E. et al. (2003) Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems, *Ecosystems*, 6(4), 301–312, doi:10.1007/s10021-0030161-9.
- [2] Pierrou, U. (1976) The global phosphorus cycle, *Ecol. Bull.*, 75–88.
- [3] Ruttenger, K. C. (2014), The Global Phosphorus Cycle, in *Treatise on Geochemistry*, pp. 499– 558, Elsevier.

- [4] Follmi, K. (1996), The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits, *Earth-Sci. Rev.*, 40(1–2), 55–124, doi:10.1016/0012-8252(95)00049-6.
- [5] Filippelli, G. M. (2008), The global phosphorus cycle: past, present, and future, *Elements*, 4(2), 89–95, doi:10.2113/GSELEMENTS.4.2.89
- [6] Christophoridis, C., and K. Fytianos (2006), Conditions affecting the release of phosphorus from surface lake sediments, *J. Environ. Qual.*, 35(4), 1181, doi:10.2134/jeq2005.0213.
- [7] Hamilton, D. P., and S. G. Schladow (1997), Prediction of water quality in lakes and reservoirs. Part I — Model description, *Ecol. Model.*, 96(1–3), 91–110, doi: 10.1016/S03043800(96)00062-2.
- [8] Bicknell, B. R., J. C. Imhoff, J. L. Kittle Jr, T. H. Jobes, A. S. Donigan Jr, and R. Johanson (2001), Hydrological simulation program-Fortran: HSPF version 12 user's manual, AQUA TERRA Consultants, Mountain View, California
- [9] Wade, A. J., P. Durand, V. Beaujouan, W. W. Wessel, K. J. Raat, P. G. Whitehead, D. Butterfield, K. Rankinen, and A. Lepisto (2002), A nitrogen model for European catchments: INCA, new model structure and equations, *Hydrol. Earth Syst. Sci.*, 6(3), 559–582, doi: 10.5194/hess-6-559-2002.
- [10] Gu, C., G. M. Hornberger, A. L. Mills, J. S. Herman, and S. A. Flewelling (2007), Nitrate reduction in streambed sediments: Effects of flow and biogeochemical kinetics, *Water Resour. Res.*, 43(12), doi: 10.1029/2007WR006027.
- [11] Di Toro, D. M. (2001), *Sediment flux modeling*, Wiley-Interscience, New York.
- [12] Song, K.-Y., K.-D. Zoh, and H. Kang (2007), Release of phosphate in a wetland by changes in hydrological regime, *Sci. Total Environ.*, 380(1–3), 13–18, doi:10.1016/j.scitotenv.2006.11.035
- [13] Morris, J. T. (1991), Effects of Nitrogen Loading on Wetland Ecosystems with Particular Reference to Atmospheric Deposition, *Annu. Rev. Ecol. Syst.*, 22(1), 257–279, doi:10.1146/annurev.es.22.110191.001353
- [14] Jordan, S. J., J. Stoffer, and J. A. Nestlerode (2011), Wetlands as sinks for reactive nitrogen at continental and global scales: A meta-analysis, *Ecosystems*, 14(1), 144–155, doi:10.1007/s10021-010-9400-z.
- [15] Seitzinger, S., J. A. Harrison, J. K. Böhlke, A. F. Bouwman, R. Lowrance, B. Peterson, C. Tobias, and G. V. Drecht (2006), Denitrification across landscapes and waterscapes: A synthesis, *Ecol. Appl.*, 16(6), 2064–2090, doi:10.1890/10510761(2006)016[2064:DALAWA]2.0.CO;2
- [16] Newbold, J. D., R. V. O'Neill, J. W. Elwood, and W. Van Winkle (1982), Nutrient spiralling in streams: implications for nutrient limitation and invertebrate activity, *Am. Nat.*, 120(5), 628–652.
- [17] Jones, J. B., and P. J. Mulholland (Eds.) (2000), *Streams and ground waters*, Aquatic ecology series, Academic, San Diego, Calif.
- [18] Robson, B., D. Hamilton, I. Webster, and T. Chan (2008), Ten steps applied to development and evaluation of process-based biogeochemical models of estuaries, *Environ. Model. Softw.* 23(4), 369–384, doi:10.1016/j.envsoft.2007.05.019.
- [19] Harvey, J. W., B. J. Wagner, and K. E. Bencala (1996b), Evaluating the Reliability of the Stream Tracer Approach to Characterize Stream-Subsurface Water Exchange, *Water Resour. Res.*, 32(8), 2441–2451, doi: 10.1029/96WR01268.
- [20] Stewart, R. J., W. M. Wollheim, M. N. Gooseff, M. A. Briggs, J. M. Jacobs, B. J. Peterson, and C. S. Hopkins (2011), Separation of river network-scale nitrogen removal among the main channel and two transient storage compartments, *Water Resour. Res.*, 47(10), doi: 10.1029/2010WR009896
- [21] Chapra, S. C. (1975), Comment on “An empirical method of estimating the retention of phosphorus in lakes” by W. B. Kirchner and P. J. Dillon, *Water Resour. Res.*, 11(6), 1033–1034, doi: 10.1029/WR011i006p01033.
- [22] Boyer, E. W., R. B. Alexander, W. J. Parton, C. Li, K. Butterbach-Bahl, S. D. Donner, R. W. Skaggs, and S. J. D. Grosso (2006), Modeling denitrification in terrestrial and aquatic ecosystems at regional scales, *Ecol. Appl.*, 16(6), 2123–2142, doi:10.1890/10510761(2006)016[2123:MDITAA]2.0.CO;2
- [23] Wollheim, W. M., C. J. Vörösmarty, A. F. Bouwman, P. Green, J. Harrison, E. Linder, B. J. Peterson, S. P. Seitzinger, and J. P. M. Syvitski (2008), Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach, *Glob. Biogeochem. Cycles*, 22(2), GB2026, doi: 10.1029/2007GB002963
- [24] Basu, N. B., P. S. C. Rao, S. E. Thompson, N. V. Loukinova, S. D. Donner, S. Ye, and M. Sivapalan (2011), Spatiotemporal averaging of in-stream solute removal dynamics, *Water Resour. Res.*, 47(10), doi: 10.1029/2010WR010196
- [25] Wollheim, W. M., C. J. Vörösmarty, B. J. Peterson, S. P. Seitzinger, and C. S. Hopkins (2006), Relationship between river size and nutrient removal, *Geophys. Res. Lett.*, 33(6), L06410, doi: 10.1029/2006GL025845.
- [26] Nichols, D. S. (1983), Capacity of natural wetlands to remove nutrients from wastewater, *J. Water Pollut. Control Fed.*, 495–505.
- [27] Dillon, P. J., and L. A. Molot (1990), The role of ammonium and nitrate retention in the acidification of lakes and forested catchments, *Biogeochemistry*, 11(1), 23–43
- [28] Saunders, D. L., and J. Kalff (2001), Nitrogen retention in wetlands, lakes and rivers, *Hydrobiologia*, 443(1–3), 205–212, doi: 10.1023/A: 1017506914063
- [29] Jeppesen, E. et al. (2005), Lake responses to reduced nutrient loading - an analysis of contemporary long-term data from 35 case studies, *Freshw. Biol.*, 50(10), 1747–1771, doi:10.1111/j.1365-2427.2005.01415.x.
- [30] Brett, M. T., and M. M. Benjamin (2007), A review and reassessment of lake phosphorus retention and the nutrient loading concept, *Freshw. Biol.*, 53(1), 194–211, doi:10.1111/j.13652427.2007.01862.x.
- [31] Downing, J. A. (2010), Emerging global role of small lakes and ponds: little things mean a lot, *Limnetica*, 29(1), 0009–24.
- [32] Maavara, T., C. T. Parsons, C. Ridenour, S. Stojanovic, H. H. Dürr, H. R. Powley, and P. Van Cappellen (2015), Global phosphorus retention by river damming, *Proc. Natl. Acad. Sci.*, 201511797, doi:10.1073/pnas.1511797112.
- [33] Chapra, S. C. (1975), Comment on “An empirical method of estimating the retention of phosphorus in lakes” by W. B. Kirchner and P. J. Dillon, *Water Resour. Res.*, 11(6), 1033–1034, doi: 10.1029/WR011i006p01033.
- [34] Nichols, D. S. (1983), Capacity of natural wetlands to remove nutrients from wastewater, *J. Water Pollut. Control Fed.*, 495–505
- [35] Smith, V. H. (1983), Low nitrogen to phosphorus ratios favor dominance by blue-green algae in lake phytoplankton, *Science*, 221(4611), 669–671.
- [36] Harrison, J. A., P. J. Frings, A. H. W. Beusen, D. J. Conley, and M. L. McCrackin (2012), Global importance, patterns, and

- controls of dissolved silica retention in lakes and reservoirs; *Glob. Biogeochem. Cycles*, 26(2), doi: 10.1029/2011GB004228.
- [37] Kadlec, R. H., and S. D. Wallace (2009), *Treatment wetlands*, 2nd ed., CRC Press, Boca Raton, FL.
- [38] Mitsch, W. J., and J. W. Day (2006), Restoration of wetlands in the Mississippi–Ohio–Missouri (MOM) River Basin: Experience and needed research, *Ecol. Eng.*, 26(1), 55–69, doi:10.1016/j.ecoleng.2005.09.005.
- [39] Griffin, D. M., R. R. Bhattarai, and H. Xiang (1999), The Effect of Temperature on Biochemical Oxygen Demand Removal in a Subsurface Flow Wetland, *Water Environ. Res.*, 71(4), 475–482, doi: 10.2175/106143097X122185.
- [40] Arheimer, B., and H. B. Wittgren (2002), Modelling nitrogen removal in potential wetlands at the catchment scale, *Ecol. Eng.*, 19(1), 63–80.
- [41] Carleton, J. N., and H. J. Montas (2010), An analysis of performance models for free water surface wetlands, *Water Res.*, 44(12), 3595–3606, doi:10.1016/j.watres.2010.04.008.
- [42] Paudel, R., and J. W. Jawitz (2012), Does increased model complexity improve description of phosphorus dynamics in a large treatment wetland? *Ecol. Eng.*, 42, 283–294, doi:10.1016/j.ecoleng.2012.02.014.
- [43] Vollenweider, R. A. (1975), Input-output models: With special reference to the phosphorus loading concept in limnology, *Schweiz. Z. Für Hydrol.*, 37(1), 53–84, doi: 10.1007/BF02505178.
- [44] Brett, M. T., and M. M. Benjamin (2007), A review and reassessment of lake phosphorus retention and the nutrient loading concept, *Freshw. Biol.*, 53(1), 194–211, doi:10.1111/j.13652427.2007.01862.x.
- [45] Sonzogni, W. C., S. C. Chapra, D. E. Armstrong, and T. J. Logan (1982), Bioavailability of phosphorus inputs to lakes, *J. Environ. Qual.*, 11(4), 555–563.
- [46] Maavara, T., C. T. Parsons, C. Ridenour, S. Stojanovic, H. H. Dürr, H. R. Powley, and P. Van Cappellen (2015), Global phosphorus retention by river damming, *Proc. Natl. Acad. Sci.*, 201511797, doi:10.1073/pnas.1511797112.
- [47] Orellana, F., P. Verma, S. P. Loheide, and E. Daly (2012), Monitoring and modeling water vegetation interactions in groundwater-dependent ecosystems, *Rev. Geophys.*, 50(3), doi: 10.1029/2011RG000383.
- [48] Langergraber, G. (2016), Applying process-based models for subsurface flow treatment wetlands: Recent developments and challenges, *Water*, 9(1), 5, doi: 10.3390/w9010005.
- [49] Riley, M. J., and H. G. Stefan (1988), Minlake: A dynamic lake water quality simulation model, *Ecol. Model.*, 43(3–4), 155–182, doi: 10.1016/0304-3800(88)90002-6.
- [50] Kadlec, R. H., and D. E. Hammer (1988), Modeling nutrient behavior in wetlands, *Ecol. Model.*, 40(1), 37–66.
- [51] Arhonditsis, G. B., and M. T. Brett (2005), Eutrophication model for Lake Washington (USA), *Ecol. Model.*, 187(2–3), 140–178, doi:10.1016/j.ecolmodel.2005.01.040.
- [52] Beven, K., and J. Freer (2001), Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE methodology, *J. Hydrol.*, 249(1–4), 11–29, doi: 10.1016/S0022-1694(01)00421-8.
- [53] Bras, R. L. (2015), Complexity and organization in hydrology: A personal view, *Water Resour. Res.*, 51(8), 6532–6548.
- [54] Marcé, R., and J. Armengol (2009), Modeling nutrient in-stream processes at the watershed scale using Nutrient Spiralling metrics, *Hydrol. Earth Syst. Sci.*, 13(7), 953–967, doi: 10.5194/hess-13-953-2009.
- [55] Boyer, E. W., R. B. Alexander, W. J. Parton, C. Li, K. Butterbach-Bahl, S. D. Donner, R. W. Skaggs, and S. J. D. Grosso (2006), Modeling denitrification in terrestrial and aquatic ecosystems at regional scales, *Ecol. Appl.*, 16(6), 2123–2142.
- [56] Kadlec, R. H. (1994), Detention and mixing in free water wetlands, *Ecol. Eng.*, 3(4), 345–380, doi:10.1016/0925-8574(94)00007-7.
- [57] Harvey, J. W., J. K. Böhlke, M. A. Voytek, D. Scott, and C. R. Tobias (2013), Hyporheic zone denitrification: Controls on effective reaction depth and contribution to whole-stream mass balance: Scaling hyporheic flow controls on stream denitrification, *Water Resour. Res.*, 49(10), 6298–6316, doi:10.1002/wrcr.20492.
- [58] Lansdown, K., C. M. Heppell, M. Trimmer, A. Binley, A. L. Heathwaite, P. Byrne, and H. Zhang (2015), The interplay between transport and reaction rates as controls on nitrate attenuation in permeable, streambed sediments, *J. Geophys. Res. Biogeosciences*, 120(6), 1093–1109, doi:10.1002/2014JG002874.
- [59] Harvey, J. W., J. K. Böhlke, M. A. Voytek, D. Scott, and C. R. Tobias (2013), Hyporheic zone denitrification: Controls on effective reaction depth and contribution to whole-stream mass balance: Scaling hyporheic flow controls on stream denitrification, *Water Resour. Res.*, 49(10), 6298–6316, doi:10.1002/wrcr.20492.
- [60] Ocampo, C. J., C. E. Oldham, and M. Sivapalan (2006), Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction, *Water Resour. Res.*, 42(1).