Nutrient Dynamics in Flooded Wetlands. II: Model Application

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Abstract: In this paper, the authors applied and evaluated the wetland nutrient model that was described in Paper I. Hydrologic and water quality data from a small restored wetland located on Kent Island, Maryland, which is part of the Delmarva Peninsula on the eastern shores of the Chesapeake Bay, was used for this purpose. The model was assessed through various methods against the observed data in simulating nitrogen (N), phosphorus (P), and total suspended sediment (TSS) dynamics. Time series plots of observed and simulated concentrations and loads generally compared well; better performance was demonstrated with dissolved forms of nitrogen, i.e., ammonia and nitrate. Through qualitative and quantitative sensitivity analysis, dominant processes in the study wetland were scrutinized. Nitrification, plant uptake, and mineralization were the most important processes affecting ammonia. Denitrification in the sediment layer and diffusion to bottom sediments were identified as key processes for nitrate. Settling and resuspension were the most important processes for particulate matter (organic N, sediment) and sediment-bound phosphate (inorganic P). Order of parameter sensitivities and dominant processes exhibited seasonality. Uncertainty bands created from Monte Carlo simulations showed that parameter uncertainty is relatively small; however, uncertainty in the wetland inflow rates and loading concentrations have much more bearing on model predictive uncertainty. N, P, and TSS mass balance analysis showed that the wetland removed approximately 23, 33, and 46%, respectively, of the incoming load (runoff + atmospheric deposition) over the two-year period, with more removal in year 1 (34, 43, and 55%, respectively), which had a long stretch of a dry period. The developed model can be employed for exploring wetland response to various climatic and input conditions, and for deeper understanding of key processes in wetlands. **DOI: 10.1061/(ASCE)HE.1943-5584.0000750.**

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Introduction

Wetlands are an effective way to treat point and nonpoint sources of nutrients and to improve water quality in downstream lakes and rivers (USEPA 2007). The ability of operating under a wide range of hydraulic loads, providing internal water storage capacities, and removal or transformation of contaminants are among the benefits that wetlands provide for treatment of pollutants (Dierberg et al. 2002). Therefore, use of natural and constructed wetlands for removal of pollutants has gained considerable interest recently, particularly nutrients from point sources (Godfrey et al. 1985; Hammer 1989; Richardson 1985; Howard-Williams 1985; Richardson and Davis 1987). Sedimentation, plant uptake, adsorption, precipitation, and burial are primary phosphorus (P) removal/retention mechanisms in wetlands. Similarly, filtration, sedimentation, uptake by plants and microorganisms, adsorption, denitrification, and volatilization are nitrogen (N) removal/retention mechanisms in wetlands. In general, the most significant N removal mechanism in natural and constructed freshwater wetlands is reported to be gaseous losses of N through denitrification (DeBusk 1999; Bowden 1987; Faulkner and Richardson 1989).

The function of wetlands as sinks, transformers, and sources of nutrients depends on the wetland type, hydrologic condition, and the length of time the wetland is subjected to nutrient loading. Wetlands have been shown to be sinks or storage places for N and P, although not all wetlands exhibit this trait (USEPA 2007). Using data from 57 wetlands from around the world, Fisher and Acreman (2004) concluded that 80% of studied wetlands exhibited nutrient retention, whereas Jordan et al. (2011) found a near-linear relationship between N removal and loading from published wetland studies worldwide. Nutrient removal in wetlands has also been shown to exhibit seasonal variations (USEPA 1999; Tanner 2001; Kuschk et al. 2003; Szabó et al. 2001; García-García et al. 2009).

Modeling is a practical tool that can be used in exploring how wetlands perform under varying physical and climatic conditions. Models of varying levels of complexity have been developed and applied to field data to gain insight into important processes

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taking place and to perform scenario analyses to find answers to various what-if questions. For example, Son et al. (2010) developed regression and wetland design models to determine treatment performance using data from a free-surface-flow constructed wetland system receiving agricultural runoff. Sonavane and Munavalli (2009) incorporated distributed parameter models with various reaction kinetics to study N removal from wastewater in a constructed wetland treatment system. Laboratory/pilot-scale field experiments were carried out and used for model verification. Model results showed that the plant uptake rate was higher than denitrification for nitrate removal. For ammonia removal, nitrification and plant uptake were equally dominant. Chavan and Dennett (2008) developed a simulation model to evaluate N, P, and sediment retention from a constructed wetland system. Through the model they predicted that wetlands along a major creek would remove N, P, and sediments by 62, 38, and 84%, respectively, which would help to reduce eutrophication in the lower Truckee River in Nevada.

Cohen and Brown (2007) developed a dynamic systems model to compare stormwater management using a hierarchical network of treatment wetlands with the standard incremental approach wherein treatment systems were designed considering only site-level effluent criteria. The model was able to simulate watershed hydrology, total suspended sediment (TSS) transport, and P removal and transformation. They showed that hierarchical networks could greatly enhance overall effectiveness (annual retention improvements of 31% for flow, 36% for TSS, and 27% for P) with respect to an equal area of uniformly sized wetlands.

Hattermann et al. (2006), by integrating riparian zones and wetlands into an eco-hydrological river basin model, tried to quantify the effects of riparian wetland processes on water and nutrient fluxes in a meso-scale catchment located in the northeastern German lowland. Although they represent relatively small portions of the total catchment area, simulation results indicated that wetlands might have a significant effect on the overall water and nutrient balances of the catchment. On the contrary, through mathematical modeling in a 224 km^2 watershed in southern Sweden, Arheimer and Wittgren (2002) showed that wetland creation must cover fairly large areas and be combined with other measures to achieve substantial reduction of N fluxes to coastal waters. Their scenario was based on topographically realistic siting of 40 potential wetlands with a total area of 0.92 km^2 (0.4% of the catchment area).

Wang and Mitsch (2000) used a calibrated and validated wetland ecosystem model at four similarly constructed wetlands in northeastern Illinois to explore the role of different wetland structure and function in relation to P retention. They concluded that manipulating the hydrologic regime might be a desirable strategy to increase P removal efficiency for constructed wetlands. Similarly, Martin and Reddy (1997), through a spatially explicit, two-dimensional model, found a significant increase in denitrification rates in response to augmented vertical flux of soluble N.

In this paper a process-based N and P wetland model (Hantush et al. 2013) was applied to a restored wetland in the Eastern shores of Maryland, and its performance was evaluated. Sensitivity of the developed model to various parameters was investigated through dotty plots and global sensitivity analysis. Sensitivity analysis of a model can reveal the important processes taking place in the study area. Therefore, quite commonly the order of sensitive parameters could change with the study area and data set used. As a matter of fact, for the same study area parameter sensitivities could show variations from year to year. For example, different processes could dominate the systems in a dry and a wet year. To gain insight into dominant processes, it is crucial to have such a detailed sensitivity analysis. Model performance and model predictive uncertainty were also investigated to evaluate the reliability of the model. Estimating model predictive uncertainty provides environmental managers a basis for selecting among alternative actions and for deciding whether or not additional experimental/field data are needed (Reckhow 1994). The generalized sensitivity analysis (GSA) (Spear and Hornberger 1980) was applied to identify the most sensitive parameters. The generalized likelihood uncertainty estimation (GLUE) (Beven and Freer 2001) was used to estimate the predictive uncertainty of the wetland nutrient cycling model described in Paper I (Hantush et al. 2013). The paper concludes with N, P, and TSS budgets for major retention, removal, and loss pathways in the study wetland.

Study Area

The wetland model described in Paper I was applied to data collected during a two-year study in a restored wetland called "Barnstable 1," as described in detail by Jordan et al. (2003) and Whigham et al. (2002). The study wetland is on Kent Island, Maryland, which is part of the Delmarva Peninsula on the eastern shore of Chesapeake Bay (Fig. 1). Much of the surrounding land was farmlands, cultivated primarily for corn and soybean production. The 14-ha watershed draining to the wetland was 18% forest and 82% cropland with an average slope of 1%. It was planted with corn in 1995 and 1997, and with soybean in 1996. Soils of the area have a silt loam texture with a moderate or moderately slow permeability. Because of the low permeability of the soils and the low topographic relief, most croplands in the study area are drained by ditches or by plowed channels that discharge water into wetlands, streams, riparian forests, or directly into the Chesapeake Bay. Artificial drainage has converted some wetlands to croplands (Jordan et al. 2003).

Before being restored to wetland in 1986 by the Chesapeake Wildlife Heritage, as part of their program to provide wildlife habitat and to improve the quality of runoff from agricultural fields, the study wetland had been an artificially drained cropland. During the restoration, a 1-m-deep depression was created by removing a layer of soil, some of which was later used to create a low dike to retain water. Topsoil was returned to the surface after excavation and wetland vegetation was established by natural succession.

Drainage carrying surface runoff from the surrounding watershed and precipitation falling directly on the wetland surface were the only sources of water entering the wetland. Loss of water from the wetland was through a standpipe drain installed in the dike and evapotranspiration. When the water was deep enough to flow out of the drain, the entire 1.3-ha area of the wetland was submerged and lacked well-defined flow channels. Jordan et al. (2003) reported negligible groundwater exchanges resulting from the impermeable layer of clay within 0.5 m of the soil surface. Clay sampled from beneath inundated areas was dry (Jordan et al. 2003).

Removal of nutrients and suspended solids from this restored wetland, which received unregulated inflows from the 14-ha agricultural watershed, were monitored through automated flow-proportional sampling. Water entered the wetland primarily in brief pulses of runoff, which sometimes exceeded the 2,500-m^3 water holding capacity of the wetland.

Model Application

A list of the input parameters along with their definitions required to run the model are provided at the end of the manuscript. Some of these parameters are measurable in the field such as ϕ, ρ_s, υ_s, etc. Those that are not measurable should be treated as calibration

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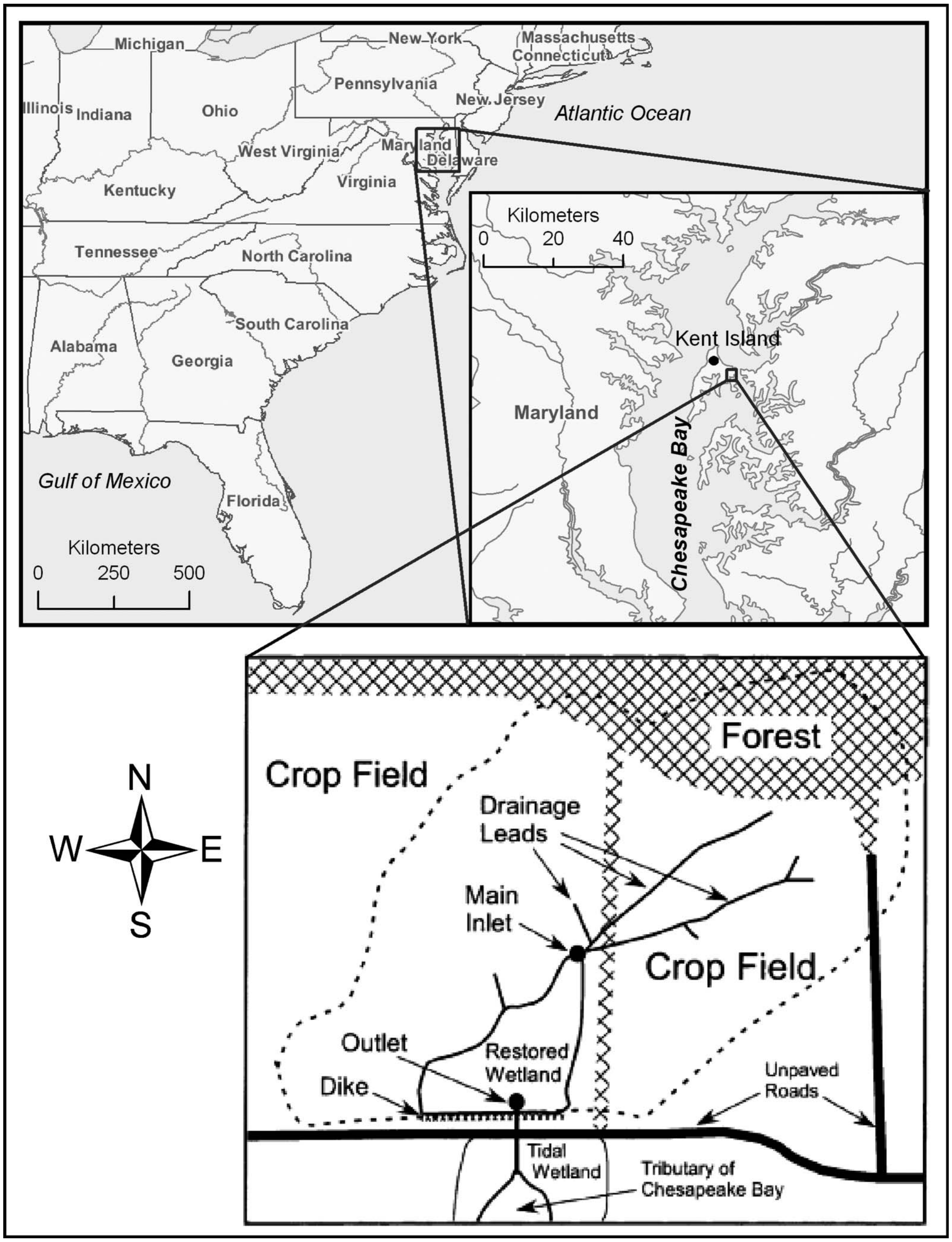

Fig. 1. Study wetland and the watershed (dashed lines) draining into wetland; automated samplers were located at outlet and main inlet points

parameters. Sensitivity analysis can reveal the most sensitive parameters, the order of which is specific to the wetland system being studied. This paper focuses only on those sensitive parameters during calibration. For this study wetland, no measured parameter values were available. Thus, all of the listed parameters were treated as calibration parameters. 100,000 independent parameter sets were generated from the model parameters. Table 1 shows the underlying distributions and statistics used in parameter generation, essentially obtained from soft information (literature and expert judgment). By feeding the model with input forcing data, i.e., runoff from the watershed to the wetland, concentrations of organic-N, total ammonia-N, (nitrate + nitrite)-N, TSS and total inorganic-P in runoff, precipitation, temperature, atmospheric deposition, and hydrography of the wetland (time series of storage, surface area, and depth of water in the wetland), Monte Carlo (MC) simulations were performed by running the model one parameter set at a time to yield 100,000 simulated output time series for each constituent. Short descriptions of input data used in the study are provided next.

Input Data

Jordan et al. (2003) measured water flow and sampled water entering and leaving the wetland from May 8, 1995, through May 12, 1997. Details of the data collection and analysis can be found in Jordan et al. (2003). The water input from precipitation directly on the wetland was calculated from the surveyed wetland area (1.3 ha) and the precipitation volume measured with standard rain gauges at the wetland and at the Wye Research Center (WRC), 13 km from the wetland. The WRC precipitation was obtained from the

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Table 1. Model Parameters Considered Random and Their Best Estimates Based on Loadings

Parameters	Distributed	Min[a]	Max[a]	N_{ow}	N_{aw}	N_{nw}	P_w	m_w
l_2 (cm)	U	5	50	21.2	19.3	20.0	27.9	29.8
θ	U	1	1.2	1.10	1.11	1.16	1.06	—
K_d (mL/g)	log-N	0.075	19.3	1.80	0.99	1.73	—	—
k_{ga} (d^{-1})	log-N	0.01	0.2	0.0014	0.0014	0.0014	0.0014	—
k_{gb} (d^{-1})	log-N	0.01	0.2	0.0014	0.0015	0.0015	0.0014	—
k_{ms} (d^{-1})	log-N	0.000001	0.001	0.000058	0.000020	0.000052	0.000063	—
k_{nw} (d^{-1})	log-N	0.0001	0.1	—	0.0129	0.0051	—	—
k_{mw} (d^{-1})	log-N	0.000001	0.001	0.000065	0.000047	0.000055	0.000062	—
k_{ns} (d^{-1})	log-N	0.01	10	—	0.601	0.571	—	—
k_{dn} (d^{-1})	U	0.004	2.6	—	1.511	0.277	—	—
ρ_s (g/cm^3)	U	1.5	2.2	2.01	1.98	2.01	2.01	2.06
v_s (cm/d)	log-N	0.025	25	2.34	1.38	1.45	1.25	25.6
v_b (cm/d)	U	0.000274	0.006575	0.0035	0.0034	0.0033	0.0034	0.0033
a_{na} (gN/gChl)	U	3.5	17.6	10.9	14.7	12.7	—	—
$r_{c,chl}$ (gN/gChl)	U	20	100	59.0	59.9	59.4	59.4	—
S_s (g/L/d)	U	0.022	0.065	—	0.042	0.044	0.043	—
f_r	U	0.5	1	0.753	0.733	0.754	0.744	—
S ($mg/m^2/d$)	log-N	0.0004	0.4	0.175	0.179	0.169	—	—
K_w (cm^3/g)	log-N	10	100	—	—	—	97,627	—
a_{pa} (gP/gChl)	U	0.4	2	—	—	—	1.196	—
K_{sa} (cm^3/g)	log-N	10	100	—	—	—	97,627	—
K_{sb} (cm^3/g)	log-N	100	1,000	—	—	—	523,686	—
ϕ	U	0.5	0.9	0.684	0.680	0.686	0.662	0.620
f_{Sw}	U	0.5	1	0.753	0.748	0.752	—	—
v_r (mm/yr)	log-N	0.0146	8.74	0.0235	0.0092	0.0066	0.0002	0.0011
K_0 (cm/d)	U	25.6	102.02	—	68.32	63.81	64.06	—
k_v (cm/d)	U	14.64	23.1	—	20.55	—	—	—
f_N	U	0.00024	1	—	0.998	—	—	—
β_{a1} (cm/d)	U	2.34	114.1	—	22.9	—	—	—
β_{n1} (cm/d)	U	2.28	111.1	—	—	21.322	—	—
β_{p1} (cm/d)	U	1.08	54.1	—	—	—	4.310	—
ϕ_w	U	0.65	0.95	0.865	0.821	0.811	0.785	0.840

Note: U, uniform distribution; log-N, log-normal distribution; lower and upper bounds in log-N distributions refer to values corresponding to probabilities of 0.1% and 99.9%.

[a]The selected ranges of values for the listed parameters/coefficients are from soft information (i.e., literature tabulation and expert knowledge). Refer to Hantush et al. (2013) and references therein for more detail.

Maryland State Climatologist. The amount of water that the wetland received from watershed runoff was calculated by subtracting the direct precipitation input from the total water input, which was calculated by summing the rate of outflow and the rate of increase in wetland water volume. Outflow was measured with a 120° V-notch weir every 15 min. Evapotranspiration from the wetland was estimated using data from a standard weather-bureau evaporation pan at the Smithsonian Environmental Research Center (SERC), 25 km from the wetland (Jordan et al. 2003). Evaporation was assumed to be negligible during periods of precipitation and runoff input.

The developed wetland model, which was described in Paper I (Hantush et al. 2013), runs on a daily time scale. Simulations started on May 9, 1995, and ended on May 12, 1997. Therefore, all of the input data are required on a daily time scale. The model internally divides the one-day time interval into a smaller time interval (in this case, 0.01 day) for numerical integration. Daily data are interpolated to generate inputs at higher than daily time resolution. Initial concentrations required to initiate the model were taken from the values of day one, which was May 9, 1995. Temperature data were obtained from Annapolis Brks NCDC Station (COOP ID:180193). Wind speed values were taken from Baltimore-Washington International Airport (COOP ID:180465) NCDC station. Atmospheric deposition data were obtained from the National Oceanic and Atmospheric Administration Station (Lewes-DE02) in Sussex County, Delaware (http://nadp.sws.uiuc.edu). Fig. 2 shows the hydrology of the wetland and the nutrient and TSS input concentrations.

Weekly (typically 5–8 days) flow averaged nitrate N, total ammonia N, organic N, inorganic P, and TSS concentrations in runoff were available from Jordan et al. (2003). To convert them into daily values the concentrations were assumed to be constant over the given period. There were missing data, sometimes up to 5 months. Records were reconstructed during time periods of missing data so that the model could be run in continuous mode. Missing data were filled by taking averages of the last available measurement before the gap and the first available measurement at the end of the gap. However, these periods were excluded at the model validation stage. Finally, when comparing the model results with observed data, the model-generated daily outputs were flow averaged to the original input/output data periods (5–8 days) and comparisons were carried out at that scale.

Model Assessment

The wetland model was evaluated both qualitatively and quantitatively. In Paper I (Hantush et al. 2013) dotty plots were used to gain a general understanding of sensitive model parameters and to assess the model for consistency (e.g., an increase in settling velocity should result in a reduction of TSS concentration). Model-generated concentrations in the water column averaged over the simulation period were plotted for organic N (N_{ow}), total ammonia

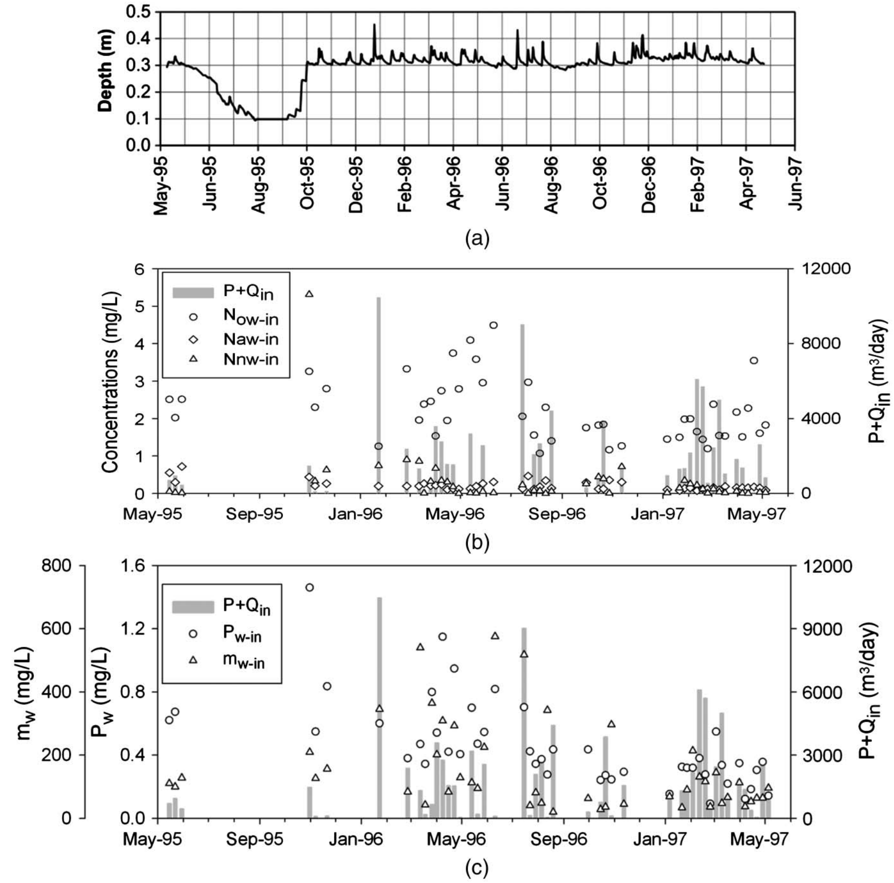

Fig. 2. (a) Average water depth (volume/area) in study wetland over the study period; (b) concentrations of N_{ow}, N_{aw}, and N_{nw}; (c) P_w and m_w in inflowing runoff. $P + Q_{in}$ indicate total water input to wetland (precipitation directly onto wetland and watershed runoff)

N (N_{aw}), nitrate + nitrite N (N_{nw}), TSS (m_w), and inorganic P (P_w) against individual parameter values for each MC simulation. When observed data are available, model performance can be calculated for each MC simulation. Replacing average concentrations with a quantitative measure of model performance in the dotty plots could reveal more insight. Such dotty plots not only provide information about sensitive parameters, but also depict the range in which the model is most sensitive to a given parameter. Model sensitivity to a parameter could vary depending on where the parameter is perturbed, which is why global sensitivity analysis is highly recommended over local sensitivity analysis (Saltelli and Sobol 1995). Furthermore, such dotty plots also disclose the optimal ranges or the values of each parameter where the model performs best. In other words, they can be helpful during model calibration. We used the Nash Sutcliffe coefficient E_N (Nash and Sutcliffe 1970) as the model performance measure.

One of the main functions of wetlands is the pollutant reduction. Whether concentrations or loads (concentration multiplied with discharge) should be used as the metric in measuring pollutant reductions or BMP effectiveness has been debated (Strecker et al. 2001). In a recent study, Lenhart and Hunt (2011) showed in a North Carolina constructed wetland that it is possible to observe an increase in effluent concentrations, yet reduction in loading. They discourage sole reliance on concentration reduction as a performance evaluation metric. Because point concentration data are generally sparse and less reflective of average waterbody conditions, model performance evaluation will be better served by comparing predicted loads with observed loads.

Dotty plots provide only qualitative measures for model sensitivity. Although the scientific literature is replete with approaches and methods for estimating predictive uncertainty, careful examination of the hydrologic and environmental modeling literature reveals four dominant approaches including Bayesian uncertainty estimation, sampling-based methods, Pareto optimality, and stochastic analysis of model residual errors (Hantush and Kalin 2008). The GSA method (Spear and Hornberger 1980), which is applicable only when observed data are available, is a quantitative approach for performing sensitivity analysis. The data described previously were used to fulfill this purpose. The GLUE (e.g., Beven and Binley 1992) and GSA approaches were combined and applied to the wetland model to simultaneously perform sensitivity and uncertainty analysis. The GLUE methodology fundamentally rejects the "optimum parameter set or a model" concept and instead promotes the notion of "equifinality" of different parameter sets and/or model structures (Beven and Binley 1992). The fact that all model structures are necessarily subject to errors and the measurements from which model calibration is based are also prone to error, it is not realistic to seek for "a true parameter set" by calibrating a particular model structure. Parameter sets for the particular model structure that pass a threshold criterion are considered equally likely or likely modeled system simulators. The GSA procedure can be summarized as follows:

1. Model parameter sampling: Randomly sample model parameter values from their respective previous distributions to form a matrix $\boldsymbol{A}$, whose rows correspond to the randomly generated parameter sets. Each column of matrix $\boldsymbol{A}$ corresponds to a particular model parameter. Soft information was relied upon for prior parameter distributions (see Hantush et al. 2013). For example, when no information was available on a particular parameter other than minimum and maximum values, a uniform distribution was assumed.

2. Monte Carlo (MC) simulation: Run the model for each parameter set (i.e., one row of $\boldsymbol{A}$ at a time) to obtain the ensemble of model-predicted time series for each of the modeled constituents. Each model simulation corresponds to one parameter set (or row of $\boldsymbol{A}$).
3. Performance evaluations: Evaluate the model performance for each of the MC-simulated model outputs by using a performance criterion, such as the Nash-Sutcliffe coefficient E_N.
4. Behavioral and nonbehavioral sets: Select a threshold value, E'_N. Divide the parameter matrix $\boldsymbol{A}$ into behavioral, $\boldsymbol{B}$, and nonbehavioral, $\boldsymbol{B}'$, matrices of parameter sets such that for a specific parameter set (or matrix row), if $E_N > E'_N$, it falls in $\boldsymbol{B}$, otherwise in $\boldsymbol{B}'$. A behavioral set is the one that represents the system and provides a valid simulation according to the selected threshold criterion. There is a level of subjectivity in the selection of E'_N. A new approach was implemented here by partitioning the data set into behavioral and nonbehavioral sets by selecting the m set of parameters that have higher E_N values than the remainder of parameter sets. This approach is helpful when one deals with multiple model output variables. Similar to E'_N, selection of m is also subjective. In this study m was set to 1,000 to form the $\boldsymbol{B}$ parameter sets, which corresponds to 1% of the total number of datasets generated. The remaining parameter sets that fail the criterion form the $\boldsymbol{B}'$ set and are thus discarded from further model evaluation.
5. Kolmogorov-Smirnov (K-S) test: Construct two cumulative distribution functions for each parameter, one from $\boldsymbol{B}$ and another from $\boldsymbol{B}'$, namely CDF_B and $\mathrm{CDF}_{B'}$. Then, for each parameter, determine the maximum deviation ($D_{\max}$) between the two CDFs:

$$D_{\max} = \max |\mathrm{CDF}_B(x) - \mathrm{CDF}_{B'}(x)| \tag{1}$$

   For a predetermined significance level of α, if $D_{\max}$ is smaller than the K-S statistic, D_α, or the $p-$ value that corresponds to $D_{\max}$ is larger than α, then separation is not achieved and the two distributions are statistically similar; consequently, the model is not sensitive to that parameter. Conversely, $p < \alpha$ indicates a sensitive parameter. The confidence level, α was set to 5% in this study.
6. Order of sensitivity: Rank the $D_{\max}$ values from largest to smallest. Larger $D_{\max}$ values are associated with higher sensitivities and vice versa.

The initial model uncertainty bounds were obtained from the entire parameter sets, i.e., ($\boldsymbol{A} = \boldsymbol{B} \bigcup \boldsymbol{B}'$), which is the a priori uncertainty. This uncertainty may be improved (reduced uncertainty) by using the behavioral parameter sets, $\boldsymbol{B}$, to yield the posterior uncertainty.

The best estimate of each parameter for each constituent was calculated through weighted averaging using the likelihood values as the weight. The best estimate of the parameter x was calculated as

$$x' = \sum_{i=1}^{n} (e^{E_{N,i}-1} x_i) / \sum_{i=1}^{n} e^{E_{N,i}-1} \tag{2}$$

where $E_{N,i}$ = Nash-Sutcliffe efficiency from the ith model run of the MC simulation, n = total number of MC simulations, and x_i = generated value of parameter x at ith parameter set. The weight allocated to each parameter $e^{E_{N,i}-1}$ varies from 0 for $E_{NS} = -\infty$ to 1 for $E_{NS} = 1$. Therefore, parameters contributing to higher model performances are assigned higher weights and vice versa.

Finally, the N, P, and TSS budgets were computed over the two-year simulation period, as well as for year 1 (May 15, 1995 to May 13, 1996) and year 2 (May 14, 1996 to May 12, 1997). The authors looked into individual pathways of losses (sinks) and sources to gain an appreciation of important processes taking place in the study wetland. For N, annual and two-year budgets were computed for total nitrogen (TN) loading by runoff, atmospheric deposition, deposition to wetland bottom (settling-resuspension), denitrification, volatilization, and N_{Tw} export as outflow. In P budget annual and the whole period deposition and diffusion amounts were computed to comprehend the differences in loading to and export out of the wetland. TSS budget was simply dictated by loading, deposition, and outflow from the wetland.

Results and Discussion

Dotty Plots

Fig. 3 shows the dotty plots of N_{ow}, N_{aw}, N_{nw}, P_w, and m_w loads for parameters that visually appear to be among the most sensitive parameters. Only four parameters are shown for the purposes of brevity. Less sensitive and insensitive parameters were not included. On the vertical axes are the E_N values, whereas horizontal axes show the model parameters. Table 1 shows the parameter ranges and units. The resuspension rate, v_r, and the settling velocity, v_s, appear to be the most sensitive parameters for N_{ow} and m_w. Because most of the TN is in organic form, the dotty plots for TN in the water column (N_{Tw}) resemble the ones for N_{ow}. Therefore, to conserve space, dotty plots for N_{Tw} are not shown in Fig. 3. The optimal range of v_r for TSS is approximately an order of magnitude smaller than the one for organic matter. Conversely, based on the range in which model performance is superior, v_s for organic matter is about one to two orders of magnitude smaller than v_s for TSS. These are consistent with the physically based nature of the model, because TSS, which is mostly silty soil in this case (see study area description), is much denser than the organic matter.

In natural wetlands, most particulate matters settle down once they flow into the wetland because of reduced flow velocity caused by increased vegetation resistance. In contrast, resuspension might play a very little role, and therefore could be deemed as a trivial process. The wetland system studied in this paper exhibits characteristics different than most natural wetlands. It receives pulses of inflow through runoff from an agricultural field, sometimes as high as 2 m^3/s (not shown in figures). When the water level in the wetland is low, such strong runoff events can easily stir the wetland bottom and resuspend some of the deposited particulate matter.

Fig. 4 provides further evidence that resuspension is an important process in the study wetland, which shows net removals (inflow-outflow) at roughly weekly time intervals. Only periods with complete inflow and outflow data are shown (i.e., no data filling). In Fig. 4, positive removal indicates that wetland acts as a sink, whereas negative removal represents net export of material from the wetland (wetland acts as a source). There are periods with both positive and negative TSS and org-N removals. This illustrates that both settling and resuspension are important processes for TSS and org-N. For example, over the two-year study period, the biggest runoff event occurred on January 19, 1996. The resulting effect of this big runoff event is clearly seen during the week of January 16–23, 1996, during which over 2 t of sediment was exported out of the system. A similar significant net org-N export is observed in February 1997.

The effect of vegetation is clearly seen through the parameter ϕ_w, which is a surrogate parameter used to emulate reduction in flow-accessible space in the water column resulting from vegetation, similar to porosity in the soil media. Both TSS and organic N

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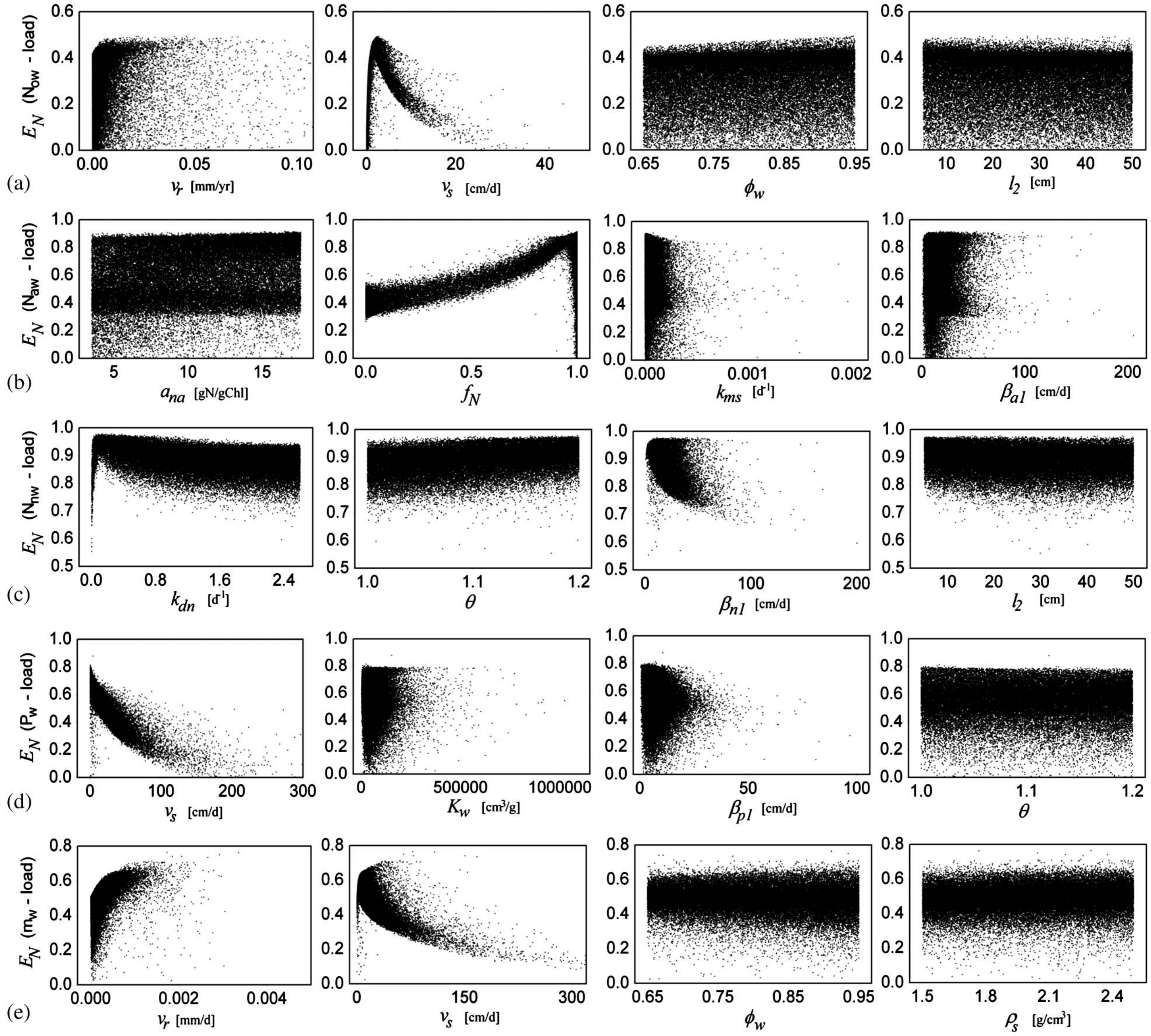

Fig. 3. Dotty plots of E_N values for (a) N_{ow}; (b) N_{aw}; (c) N_{nw}; (d) P_w; (e) m_w loads versus some selected model parameters

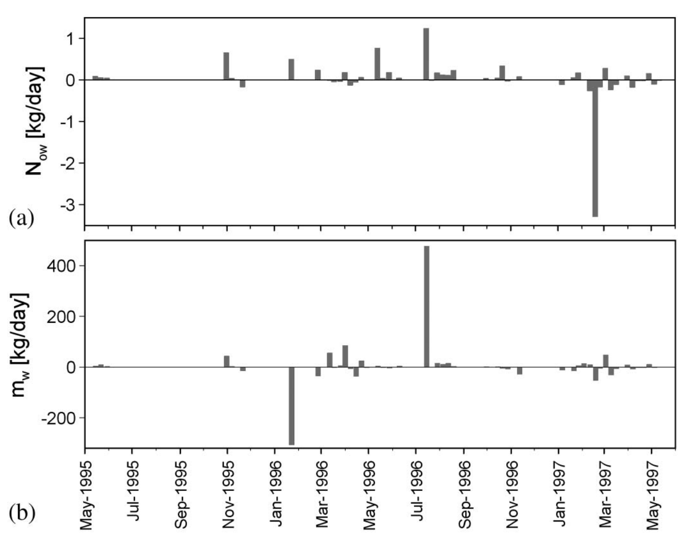

Fig. 4. Net removal of (a) N_{nw}; (b) m_w by study wetland (inflow-outflow) at roughly weekly time intervals; negative removal indicates a net export of material from wetland

appear to be highly sensitive to this parameter. Although not very clear, the optimal value for ϕ_w seems to be in the [0.75, 0.85] range for TSS. For organic N there is a clear positive trend: The higher the ϕ_w values, the higher the model performance, with the best model performance achieved near the higher ends of ϕ_w values. Based on the dotty plots of N_{ow} and N_{nw}, the anaerobic soil thickness, l_2, which is approximately equal to the active sediment layer depth, exhibits a negative correlation with the model performance. This does not necessarily mean any reduction or increase in organic N loads; it only shows that the optimal range is closer to the lower end of the parameter range. Nevertheless, the difference in E_N values from left to right is not considerable. This was also the case with ϕ_w.

The inorganic form of P, P_w shows a high degree of sensitivity to v_s because of its association with sediment particles and organic matter as a source (through mineralization). Interestingly, the resuspension rate, v_r, which was the most sensitive parameter for both organic N and TSS, did not visually emerge as one of the sensitive parameters for P. Close inspection of the dotty plot for v_s reveals that model performance for P_w is best for small values, almost close to zero, which is in contradiction to optimal v_s values observed with TSS. This could potentially be explained as follows.

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P is adsorbed to the surfaces of particles. Therefore, smaller particles having a higher surface to volume ratio will hold more adsorbed P per weight of particle than will larger particles. Thus, particles that settle rapidly are apt to include less adsorbed P per weight than particles that settle slowly. The sorption coefficient K_w also shows a high degree of sensitivity to P_w. Small K_w values are associated with higher E_N values in general. Although not very clear from the figure, diffusion-related parameter β_{p1} also shows up as a significant parameter. The implication of all these values is that P settling, adsorption to sediment particles, desorption, and release back to water column are all key processes in this study wetland.

The last of Fig. 3 for P_w suggests that the Arrhenius temperature coefficient may be less than 1. This is rather unintuitive, because θ is generally greater than 1. Larger previous mineralization rates (k_{mw}, k_{ms}) than site-specific values and/or model structural and data errors might have contributed to such discrepancy. For example, overestimating the site-specific mineralization rates could potentially lead to artificially lower than 1 as the optimal θ values. Nonetheless, the difference of likelihood-weighted value of θ from 1 (minimal temperature effect) for P_w appears to be statistically insignificant.

Like TN, total phosphorus (TP) in water (P_{Tw}) is also dominated by organic P, which is calculated simply as a fraction of organic N in the model [see the term $a_{pn}N_{ow}$ in Eq. (25) of Hantush et al. (2013)]. Although not shown in a figure, the dotty plots of P_{Tw} are quite similar to those for N_{Tw} or N_{ow}.

Nitrate, as expected, is very sensitive to the denitrification parameter, k_{dn}. This indicates that denitrification is a major N loss pathway in this study wetland. Nitrate also exhibits a high degree of sensitivity to the Arrhenius coefficient, with higher temperatures stimulating the nitrate reactions and diffusion. Likewise, diffusion of nitrate to sediment layer is another important process in the study wetland.

For total ammonium, the model seems to perform better for higher a_{na} (gram of N per gram of chlorophyll-a in algae/plants) and f_N (fraction of total ammonia N as ammonium N) values. The parameter a_{na} is linked to plant uptake of ammonia, whereas f_N indicates that the system is low in NH_4 and low in NH_3 (high *pH*). Dotty plots further reveal that mineralization of organic matter into ammonia and diffusion of ammonia from bottom sediments to the water column are the other likely key processes in the study site. Surprisingly, nitrification does not seem to play a major role. Neither nitrate nor ammonia showed much sensitivity to the nitrification parameter.

These inferences are based on visual observations and therefore offer only qualitative judgments. As shown subsequently, the statistically based quantitative approach could provide more insight into some of the nuances that may not be detectable in dotty plots. Comparison of these dotty plots and the qualitatively obtained sensitivities to the ones presented in Paper I, where no data were used, reaffirms that the order of sensitive parameters is not stationary, and rather changes from site to site. Moreover, as will be shown later, it can also vary in time depending on climatic and other conditions.

K-S Test and Sensitivity

The Kolmogorov-Smirnov (K-S) test was applied to the behavioral ($\boldsymbol{B}$) and nonbehavioral ($\boldsymbol{B}'$) data sets to statistically quantify the sensitive and insensitive parameters at a 5% confidence level. Results of the K-S test for N_{ow}, N_{aw}, N_{nw}, P_w, and m_w loads are shown in Fig. 5. In the figures, the horizontal axes rank the parameters according to their sensitivities. Each parameter has a $D_{\max}$ and p-value associated with it, shown on the left and right vertical axes,

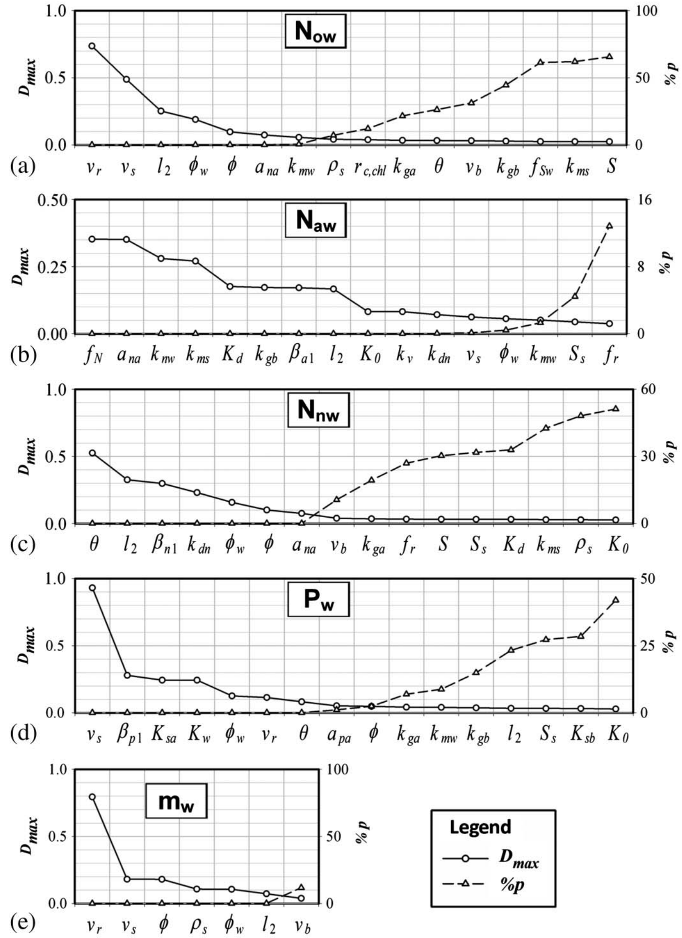

Fig. 5. Summary of Kolmogorov-Smirnov tests and order of sensitivities based on loads (years 1 and 2)

respectively. If a parameter has a p-value larger than α (=5% in this study), it is deemed not a sensitive parameter. The very first observation is the variation in number of sensitive parameters with each constituent. By far, total ammonia has the most number of sensitive parameters at a 5% confidence level with 15. TSS has the least number of parameters with 6. There is an apparent parallel between the number of sensitive parameters and the number of processes by which each constituent is affected. Only three processes affect TSS: settling, resuspension, and burial. However, the total ammonia is affected by multiple processes such as mineralization, nitrification, adsorption, volatilization, plant uptake, and diffusion.

The most sensitive parameters for organic N, in order, are v_r, v_s, l_2, ϕ_w, ϕ, a_{na}, and k_{mw}. Obviously, the orders of the sensitive parameters demonstrate that settling and resuspension are the two dominant processes in the study wetland. Plant death (through parameter a_{na}) and mineralization in the water column have secondary effects. Results also show that N fixation is not a significant process as predicted by the model in this study wetland ($p > 5\%$ for f_{Sw}).

In the parameter representing the fraction of total ammonia as ammonium ions (NH_4^+), f_N is the most sensitive parameter along with a_{na}. The former captures the effects of *pH* and temperature [see Hantush et al. 2013, Eq. (47)]. Nitrification of ammonia to nitrate in the water column and ammonification seem to be equally important processes. Ammonia uptake by plants was an important loss pathway for ammonia in the study wetland, as shown through parameters a_{na} and k_{gb}. Diffusion of ammonia from the sediment layer to the water column appears to be a significant source of ammonia (see parameters β_{a1} and l_2). The relatively high sensitivity of partition coefficient, K_d, indicates the importance of adsorption of ammonium ions onto negatively charged particles.

The Arrhenius coefficient for temperature adjustment was surprisingly the mostly sensitive parameter for nitrate. As discussed in the appendix of Hantush et al. (2013), many reaction rates and physiological parameters vary with temperature. Diffusion of nitrate from the water column to bottom sediments (β_{n1} and l_2) and denitrification therein are the two most important processes affecting nitrate. Results show that plants prefer ammonia over nitrate for uptake as evidenced by their sensitivities. The water and soil porosity parameters, ϕ_w and ϕ, are two other important parameters as they dictate flow-accessible volumes in water and soil, respectively, and affect dissolved constituent concentrations.

TN behavior was similar to the organic N (not shown in figure). This was again the result of N_{Tw} being mostly composed of N_{ow}. The first four most sensitive parameters of N_{TW} were also the most sensitive parameters in N_{ow} (v_r, v_s, l_2, ϕ_w). Next in the list of sensitive parameters for N_{Tw} were the most sensitive parameters for the N_{aw} and N_{nw} (f_N, a_{na}, ϕ, k_{dn}). Hence, the order of sensitivity for TN is determined by its composition of N_{ow}, N_{aw}, and N_{nw}. The prevailing form dictates the order of sensitive parameters.

Most of the model parameters pertinent to TSS transport ended up being sensitive parameters at a 5% significance level. The only parameter that the model was insensitive to was the burial rate, v_b. Burial did not show up as a critical process in any of the constituents; thus, it could be ignored. However, this could be a result of the relatively short period of data record. Burial is a slow process that takes place over decades. Thus, for studies looking into long-term effects, the burial process may require special attention. Among the sensitive parameters, the model was by far most sensitive to the resuspension rate, v_r, followed by the settling velocity, v_s. In the model, resuspension was related to runoff discharge into the wetland. Using an analogy similar to the modified universal soil loss equation (Williams 1995), where sediment yield, Q_s, is related to runoff volume, Q, and peak runoff rate q_p through $Q_s = \alpha(Qq_p)^{0.56}$, it was assumed that $v_r = \alpha_{v_r} Q^{1.12}$, in which α_{v_r} is a calibration parameter. Hence, large runoff volumes cause higher resuspension rates.

Similar to TSS, total inorganic P is sensitive to most model parameters relevant to P processes. Settling and diffusion are the two most important processes for P_w. Plant uptake seems to be a relatively negligible loss pathway for P_w. Like TN, TP is also dominated by organic form; thus the K-S test results are quite similar to N_{ow}. The most dominant processes affecting the TP cycle in the study wetland, in order, are settling/resuspension and adsorption/desorption.

Interannual Variation

Although the total precipitation in years 1 and 2 were comparable, the first year had a three-month period of decreasing water level in the wetland (Fig. 2). Therefore, differences in removal rates of nutrients and TSS in years 1 and 2 are assumed. To scrutinize this the K-S test was performed separately for years 1 and 2. To do this the two-year data was split into years 1 and 2 and the model performances were calculated for each year. Hence, for each MC simulation, the behavioral and nonbehavioral sets were determined twice.

Figs. 6 and 7 show the order of sensitivities for each constituent for years 1 and 2, respectively. In general, not many differences exist between years 1 and 2. The most notable was N_{aw}. The parameter a_{na} was not among the sensitive parameters in year 1, yet it is the most sensitive parameter in year 2. The interpretation of this is that ammonia uptake by plants is more prominent in year 2 than in year 1. Another difference in sensitivities between the two years

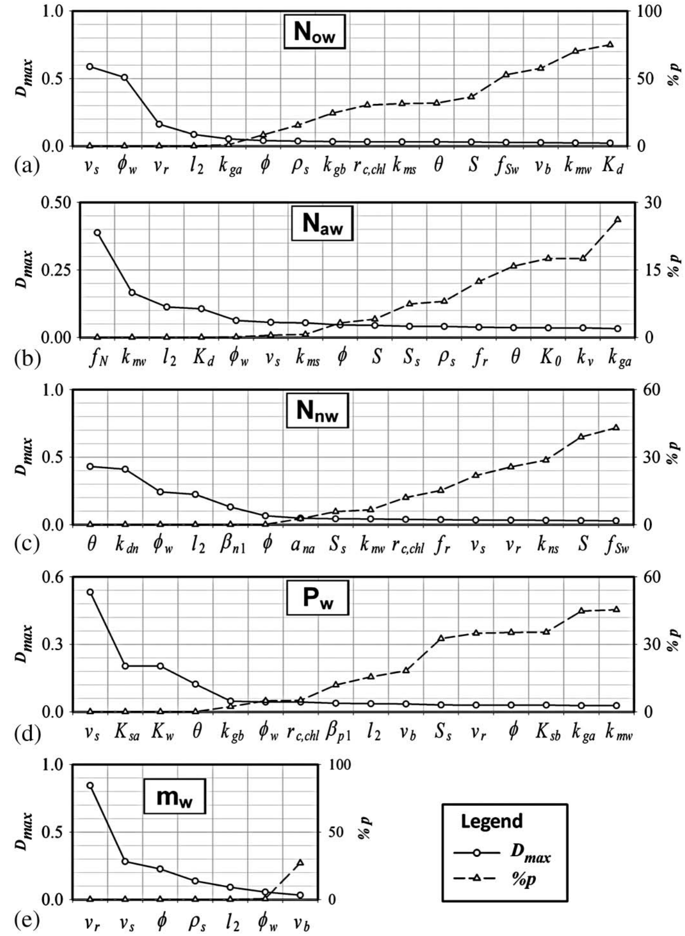

Fig. 6. Summary of Kolmogorov-Smirnov tests and order of sensitivities based on loads (year 1)

is observed with N_{nw}. Diffusion of nitrate to sediment layer is a key process in year 2, as evidenced by parameter β_{n1}'s number-one ranking. Although in year 1 denitrification is the more important process, nitrate diffusion across the soil-water interface and denitrification are two interacting processes. Diffusive mass transfer is driven by concentration gradients from higher concentrations in the overlying water to lower concentrations in bottom sediments where nitrate is depleted under anaerobic conditions. P exhibits a similar characteristic with respect to the diffusion process. Like nitrate, diffusion of inorganic P from the sediment layer to the water column is a significant process in year 2, but not in year 1. As a matter of fact, the number of sensitive parameters and consequently dominant processes in year 2 is almost twice of that found in year 1. Another interesting observation is with TSS. The year 1 model appears to be more sensitive to the resuspension of sediment particles and secondarily to settling. In year 2 the order reverses, and settling is more dominant than resuspension. In year 1 the average depth in the wetland was significantly lower than in year 2 (Fig. 2); this might have contributed to greater stirring of the bottom and resuspension of sediment particles by incoming runoff during the first year. In contrast, the increased water depth in year 2 implied smaller shear forces on the bottom, hence diminishing the role of resuspension. Furthermore, deeper water meant more time for sediment settling.

Model Performance and Uncertainties

Although the focus of this paper is more on pollutant loads than concentrations, model performance for both concentrations and

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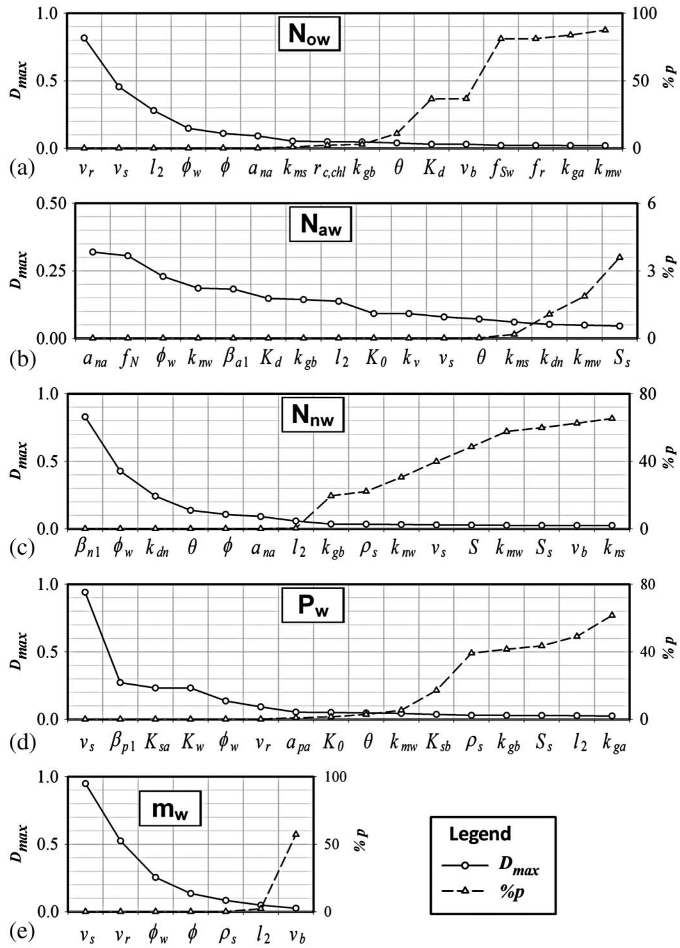

Fig. 7. Summary of Kolmogorov-Smirnov tests and order of sensitivities based on loads (year 2)

loads were evaluated. Fig. 8 compares the observed flow-averaged concentrations with the model results generated from the behavioral data set and the 95% prediction interval (the band where 95% of simulated values fall within) of the MC simulations. Fig. 9 shows simulation results for loads. The top panels in each figure show the weekly cumulative precipitations as a reference. (The horizontal axes in the figures do not necessarily correspond to consecutive weeks.) As mentioned previously, there are periods of missing data. In plotting the results in the figures, those missing weeks were ignored, which did not leave any gaps. Hence, the last data point on the plots, week 47, actually corresponds to the last week of the two-year simulation period.

The model appears to be doing a decent job in predicting nitrate, ammonia, and TN concentrations. The average E_N values for the behavioral set simulations for N_{aw}, N_{nw}, and N_{Tw} concentrations are 0.51, 0.85, and 0.65, respectively. Mass balance errors are all less than 6%. The fact that the bands formed from behavioral data set simulations are relatively narrow indicates small uncertainty. Model performance for organic N concentration is at an acceptable level based on visual comparison and mass balance error (5%). However, average E_N for the behavioral set was -0.18. Inorganic P, P_w, generally looks good except for the period from week 21 through week 26. The model significantly underestimates P_w concentrations during that period. The average mass balance error over the two-year period is approximately -30%. Inorganic P can exist either in dissolved form or as attached to sediments. The input data received from the agricultural runoff to the wetland was total inorganic P. Having data for dissolved and sediment bound fractions of P_w in runoff would have improved the model performance for P_w. The model performs better when predicting TP, P_{Tw} concentrations with an average $E_N = 0.22$ and a mass balance error of <10%. The model does not perform as well when predicting TSS concentrations, although it performs relatively better in the first year than the second year. The overall average mass balance error is -34% when behavioral set model simulations are considered. Fig. 9 compares the observed and the model generated loads. Model performances are much better for loads than for concentrations. The average E_N values from the behavioral set simulations for N_{ow}, N_{aw}, N_{nw}, N_{Tw}, P_w, P_{Tw}, and m_w loads are 0.47, 0.90, 0.97, 0.64, 0.78, 0.71, and 0.66, respectively. Mass balance errors are less than 20%.

Using Eq. (2) the best estimates of each parameter are calculated. This is not to suggest a single set of calibrated parameters for future use, but rather to provide a general sense of representative parameter values. The authors nevertheless embrace the equifinality concept and use of behavioral parameter sets to obtain the ensemble of model predictions. Table 1 summarizes the likelihood-weighted values for each parameter and constituent. In general there is very little difference between the values obtained from concentrations and loads. Results presented in the table are based on loads. There is also only small variations in the likelihood-weighted parameter values obtained using different constituents as the base of evaluation. The biggest variation was with the parameters v_s and v_r. The optimal value of v_s for organic N is 2.34 cm/day, whereas it is 1.25 cm/day for P; for TSS it is 25.6 cm/day. A reverse trend is observed with v_r, that is, higher values were obtained for N_{ow} and lower values for P_w and m_w.

N, P, and TSS Budgets and Major Retention and Removal Pathways

Tables 2 and 3 summarize the N, P, and TSS budgets and the major retention and removal pathways for years 1 and 2 and the whole period. In addition to their absolute values, all of the numbers in the table are also normalized with the incoming load (shown in parentheses) to have a better understanding of all sources and sinks relative to loading. The values shown are the mean +/− one standard deviation obtained from the behavioral set simulations.

Over the two-year period, approximately 77% of the incoming TN load through runoff and atmospheric deposition left the wetland (hydrologic export). Thus, TN removal was approximately 23%. Breaking this into years, there was more removal in year 1 than in year 2 (34% to 13%). This was likely the result of the prolonged dry period in year 1. Further scrutinizing of the major processes responsible for the retention/removal of N reveals that deposition of organic N retained approximately 19% of the incoming TN load through runoff over the two-year period. Denitrification of nitrate in the bottom sediments was responsible for approximately 8% removal of TN loading. Volatilization was a relatively small loss pathway when TN is considered, but was significant when considered with respect to ammonia loading (30%). Denitrification played a more dominant role in year 1 than it did in year 2 in removing nitrate out of the system. More nitrates were produced during periods of shallow water depth in year 1 because of greater oxygen concentrations and thicker aerobic layer. A thicker aerobic layer results in more production of nitrate by nitrification of ammonia. Consequently, greater amount of nitrate was available for transport to the lower anaerobic layer, where it was removed by denitrification. High N loss resulting from denitrification in the sediment layer in year 1 also created a higher concentration gradient, and therefore, greater mass of nitrate diffused from the water column

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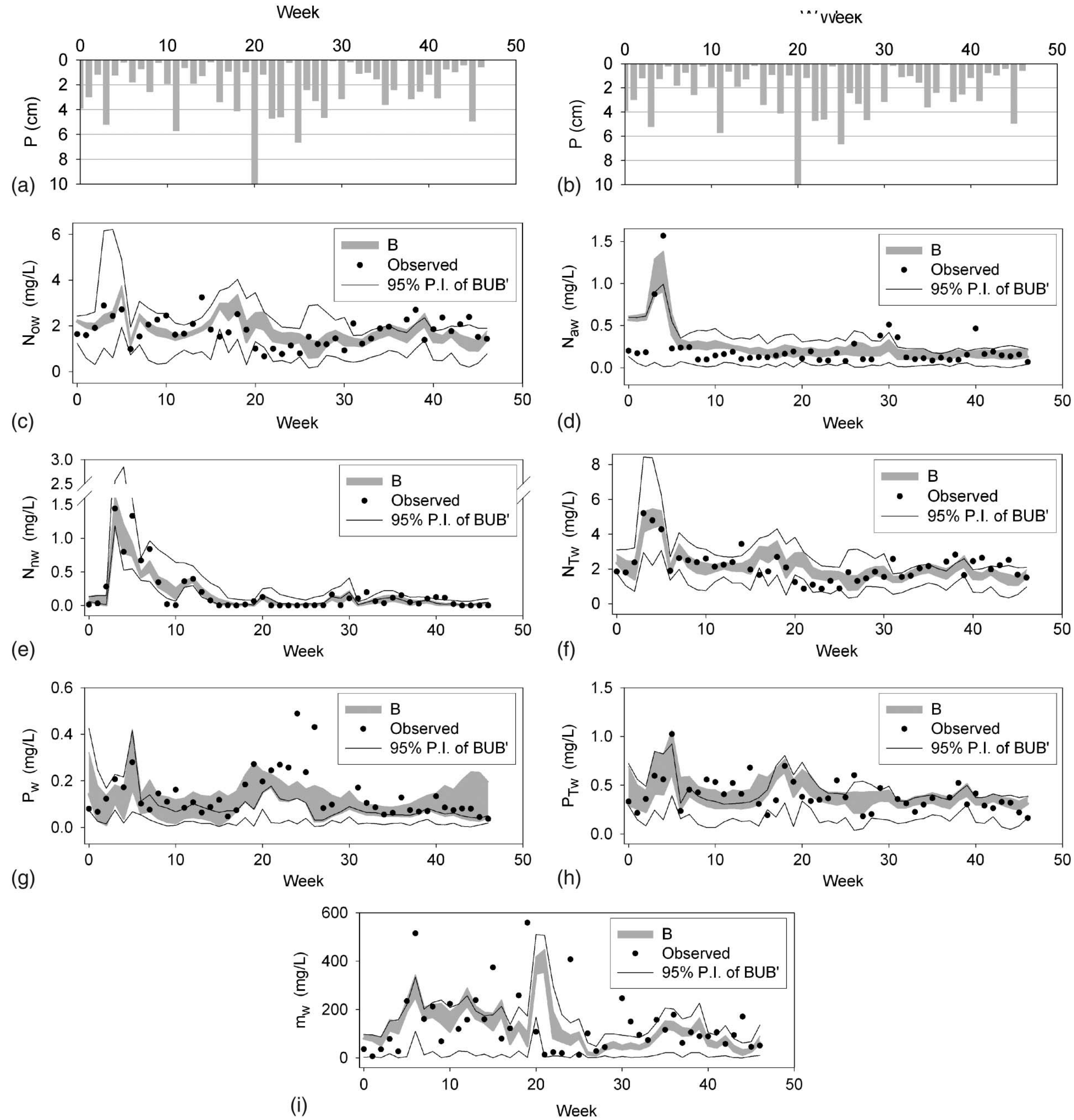

Fig. 8. (a and b) Cumulative weekly precipitations over the observation periods; (c–i) model-generated 95% prediction intervals (P.I.) from 100,000 MC simulations versus observed concentrations; B = behavior set; B′ = nonbehavior set

to the sediment layer in year 1 than it did in year 2. Diffusion is an internal exchange pathway; therefore, it is a temporary retention process, not a system loss pathway.

The summarized N budget in Table 2 is not exactly a closed budget, and the difference between sources and removal + retention is approximately 5.3% over the two-year period. Plant uptake is a temporary retention pathway. After plants die or shed their leaves, the nutrients taken in are released back to the system. Elucidating various retention and removal processes is further confounded by complex interactions among various physical and biogeochemical processes and different forms of N. The moderately high uncertainty in outflow (s.d. = 10.5%) and net deposition (s.d. = 8.9%) should be taken into consideration.

TP and TSS budgets are relatively easy because of the smaller number of processes affecting their cycle. Net deposition is the primary retention process for P and TSS. This is more so in year 1 than in year 2, again likely the result of the longer residence time in year 1 because of the prolonged dry period. Over the two-year period, there was approximately 44% and 33% net TSS and P removal, respectively. Diffusion of inorganic P to bottom sediments accounts for approximately 7% of the TP retained in the wetland soil over the two-year period.

Comparison to a Simpler Model

The model described in Hantush et al. (2013) was simplified by eliminating some of the processes that are intuitively believed to be minor, and the model results were compared to that of the complete model to see whether a simpler model can produce comparable results. The sensitivity rankings in Fig. 5 were intentionally

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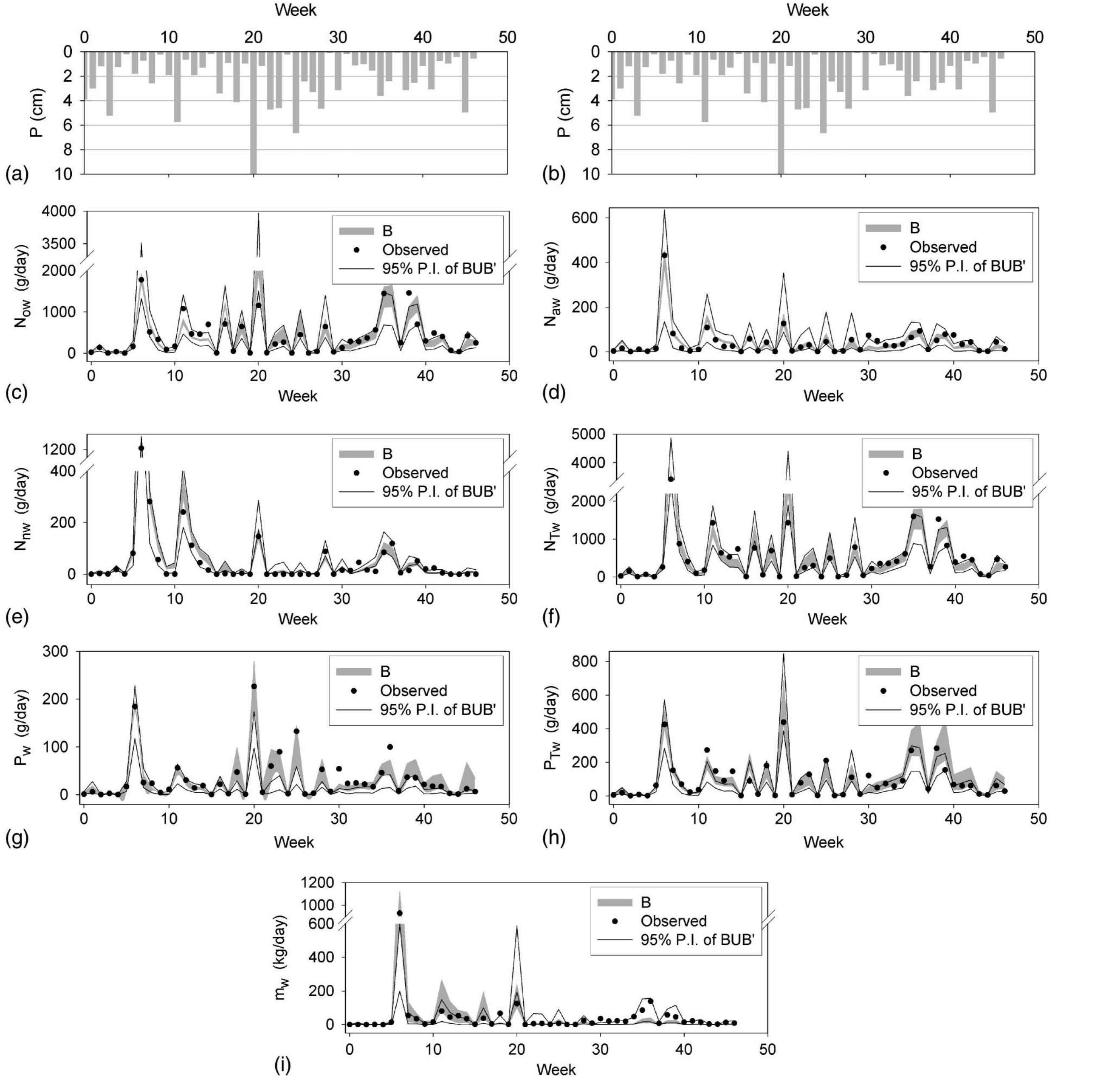

Fig. 9. (a and b) Cumulative weekly precipitations over the observation periods; (c–i) model-generated 95% prediction intervals (P.I.) from 100,000 MC simulations versus observed loadings; B = behavior set; B′ = nonbehavior set

Table 2. Nitrogen Budget in Study Wetland

	Nitrogen budget							
Year	Runoff	Atmospheric deposition	Outflow	Net deposition	Volatatilization	Denitrification	NH_4 diffusion[a]	NO_3 diffusion[a]
1	166.5	6.7	114.5 ± 22.5	36.6 ± 19.7[b]	4.7 ± 5.3	22 ± 5.4	−0.9 ± 1.7	24.1 ± 4.7
	(96.1)	(3.9)	(66.1 ± 13)	(21.2 ± 11.4)[c]	(2.7 ± 3.0)	(12.7 ± 3.1)	(−0.5 ± 1.0)	(13.9 ± 2.7)
2	169.8	7.9	154.7 ± 28.2	28.0 ± 23.9	3.5 ± 4.2	5.8 ± 2.0	−0.12 ± 2.2	7.4 ± 1.6
	(95.6)	(4.4)	(87 ± 15.9)	(15.7 ± 13.4)	(1.9 ± 2.4)	(3.3 ± 1.1)	(−0.07 ± 1.2)	(4.2 ± 0.9)
Total	336.3	14.6	269.2 ± 36.7	64.6 ± 31.3	8.1 ± 6.8	27.9 ± 5.8	−1.1 ± 2.8	31.6 ± 5.0
	(95.8)	(4.2)	(76.7 ± 10.5)	(18.4 ± 8.9)	(2.3 ± 1.9)	(7.9 ± 1.6)	(−0.3 ± 0.8)	(9 ± 1.4)

Numbers in parentheses are values normalized with runoff + atmospheric deposition loading.
[a](+) from water column to sediment layer.
[b]Mean+Std (kg).
[c]Mean+Std (%).

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Table 3. Phosphorous and Sediment Budgets in Study Wetland

Year	Phosphorous budget				Sediment budget		
	Net deposition	Diffusion	Outflow	Input loading	Net deposition	Outflow	Input loading
Year 1	11.2 ± 3.4	2.4 ± 1.2	15.8 ± 3.1	27.6	6.4 ± -2.3	5.2 ± 2.2	11.6
	(40.7 ± 12.2)	(8.7 ± 4.4)	(57.4 ± 11.4)	(100)	(54.7 ± -19.7)	(44.5 ± 18.6)	(100)
Year 2	7.6 ± 3.7	1.6 ± 1	23.4 ± 4	30.7	4.1 ± 3.4	7.3 ± 3.4	11.5
	(24.7 ± 12)	(5.2 ± 3.3)	(76.3 ± 13.1)	(100)	(35.6 ± 29.1)	(63.3 ± 29.4)	(100)
Total	18.8 ± 5	4 ± 1.6	39.3 ± 5.1	58.3	10.5 ± 3.9	12.5 ± 4	23.2
	(32.3 ± 8.6)	(6.9 ± 2.7)	(67.4 ± 8.8)	(100)	(45.2 ± 16.9)	(53.8 ± 17.1)	(100)

Note: Numbers in parentheses are values normalized with input loading.

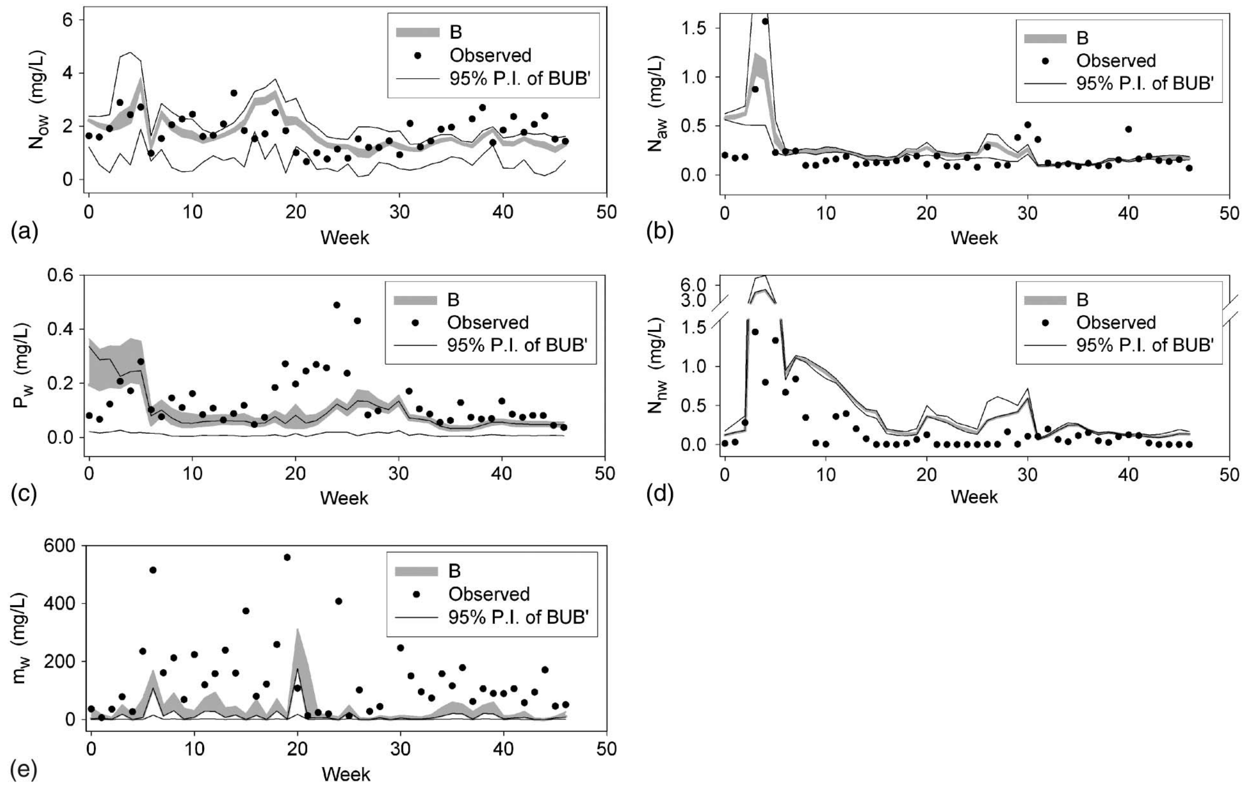

Fig. 10. Model-generated 95% prediction intervals (P.I.) from 100,000 MC simulations versus observed concentrations for the simplified model; B = behavior set; B′ = nonbehavior set

not followed when deciding which processes to eliminate. Those sensitivity results reflect the conditions of this study wetland. The intention was to develop a generic model that is applicable to wetland systems with varying characteristics. The following processes were removed: resuspension of sediment and organic nitrogen, diffusion of NH_4, NO_3 and mineral P between the sediment/water interface, groundwater flux (or infiltration), and ammonia volatilization. The retained processes were settling, mineralization, nitrification, denitrification, and plant uptake. Fig. 10 shows the observed flow-averaged concentrations and the simplified model results generated from the behavioral data set and the 95% prediction interval of the MC simulations. Compared to Fig. 8, model performances deteriorated in all, some more than others. On average, E_N values dropped by −1.2. Sediment appears to be affected the most. The drop in model performance is a clear indication of the role that resuspension plays in this wetland system. Nitrate also shows a significant drop in model performance. The simplified model substantially overestimates observed concentrations. This is likely the result of the exclusion of the diffusion process. The difference between the results from simulations with the simplified and original model is least with organic nitrogen. The only eliminated process in that case was resuspension. Organic nitrogen was sensitive to resuspension more in year 2 than in year 1 (Figs. 6 and 7), as evidenced by the results.

Summary and Conclusions

Wetlands are an effective way to treat pollutants and improve water quality in downstream waters. Wetland modeling can help in studying processes that are not easily observable or measurable at field or laboratory scale. In this paper the wetland nutrient cycling model described in the first part of this sequel was evaluated by using a restored wetland on the Delmarva Peninsula in Maryland as a case study. The model was assessed through varies ways against observed data in simulating N, TSS, and P dynamics. Time series plots of roughly weekly averages of observed and simulated concentrations and loads generally compared well. Model results were

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much better for dissolved forms of N, i.e., ammonia and nitrate. The reason for not getting relatively as good results for the particulate forms is likely linked to input data. Input concentrations from runoff were available only as flow-weighted weekly averages. This hinders the modeling of high flows, which carry most of particulate forms.

Sensitivity analysis through qualitative and quantitative approaches revealed important insight into dominant processes in the study wetland. Nitrification, plant uptake, and mineralization were the most important processes affecting ammonia. Denitrification in bottom sediments was a key loss pathway for nitrate. Settling and resuspension were the most important processes for particulate matters (organic N, TSS) and ions attached to sediment particles (inorganic P).

Breaking up the analysis into years revealed that ranking of sensitive parameters, and thus the order of dominant processes, could vary with years. Settling appeared more important than resuspension in year 1 for organic N. In year 2 it was the opposite. TSS exhibited a reverse trend with resuspension dominating settling in year 1 and settling dominating resuspension in year 2. Sensitivity analysis also revealed that plant uptake was much more prominent in year 2 than in year 1. Diffusion of mineral P from the water column to bottom wetland soil was more significant in year 2 compared to other processes.

N, P, and TSS mass balance analysis showed that the wetland removed approximately 23, 33, and 46%, respectively, of the incoming load (runoff + atmospheric deposition) over the two-year period, with more removal in year 1. Year 1 had a long dry period, resulting in longer residence times, which created ideal conditions for removal. Approximately 53% of nitrate and 24% of ammonia loading was removed over the two-year period.

In spite of all of the limitations in the input data set, results presented in this application paper show the potential in the developed wetland nutrient and sediment model for design and management of constructed and natural wetlands. The developed model can be employed for exploring wetland response to various climatic and input conditions, and for deeper understanding of chief processes that play a role in the fate and transport of nutrients and sediments.

Acknowledgments

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Notation

The following symbols are used in this paper:

a_{na} = gram of nitrogen per gram of Chlorophyll-a in algae/plants;
a_{pa} = gram of phosphorus per gram of Chlorophyll-a in algae/plants;
f_N = fraction of total ammonia nitrogen ($[NH_4^+] + [NH_3]$) as NH_4^+;
f_r = fraction of rapidly mineralizing particulate organic matter;
f_{Sw} = fraction of nitrogen fixation in water;
K_d = ammonium ion distribution coefficient [$L^3\,M^{-1}$];
K_o = oxygen reaeration mass-transfer velocity [LT^{-1}];
K_{sa}, K_{sb} = partitions of phosphorus distribution coefficient in sediment layer [$L^3\,M^{-1}$];
K_w = phosphorus distribution coefficient in water column [$L^3\,M^{-1}$];
k_{dn} = denitrification rate in anaerobic soil layer [T^{-1}];
k_{ga} = growth rate of free-floating plant [T^{-1}];
k_{gb} = growth rate of benthic and rooted plant [T^{-1}];
k_{ms} = first-order slow mineralization rate in wetland soil [T^{-1}];
k_{mw} = first-order mineralization rate in wetland free water [T^{-1}];
k_{ns} = first-order nitrification rate in aerobic soil layer [T^{-1}];
k_{nw} = first-order nitrification rate in wetland free water [T^{-1}];
k_v = volatilization mass transfer velocity [LT^{-1}];
l_2 = thickness of anaerobic layer [L];
$r_{c,chl}$ = carbon mass ration in Chlorophyll-a;
S = rate of nitrogen fixation by microorganisms [$ML^{-2}\,T^{-1}$];
S_s = oxygen removal rate per unit volume of aerobic layer [$ML^{-3}\,T^{-1}$];
v_b = burial velocity [LT^{-1}];
v_s = effective settling velocity [LT^{-1}];
v_r = resuspension rate [LT^{-1}];
β_{a1}, β_{n1} = diffusive mass-transfer rates, respectively, of total ammonia and nitrate between wetland water and aerobic soil layer [LT^{-1}];
β_{p1} = diffusive mass-transfer rate of dissolved phosphorus between wetland water and aerobic soil layer [LT^{-1}];
ϕ = porosity of sediment layer;
ϕ_w = effective porosity of wetland surface water;
ρ_s = soil particle density [ML^{-3}]; and
θ = temperature coefficient in Arrhenius equation.

References

Arheimer, B., and Wittgren, H. (2002). "Modelling nitrogen removal in potential wetlands at the catchment scale." *Ecol. Eng.*, 19(1), 63–80.

Beven, K., and Binley, A. (1992). "The future of distributed models: Model calibration and uncertainty prediction." *Hydrol. Processes*, 6(3), 279–298.

Beven, K., and Freer, J. (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.

Bowden, W. (1987). "The biogeochemistry of nitrogen in fresh-water wetlands." *Biogeochemistry*, 4(3), 313–348.

Chavan, P., and Dennett, K. (2008). "Wetland simulation model for nitrogen, phosphorus, and sediments retention in constructed wetlands." *Water Air Soil Pollut.*, 187(1–4), 109–118.

Cohen, M., and Brown, M. (2007). "A model examining hierarchical wetland networks for watershed stormwater management." *Ecol. Modell.*, 201(2), 179–193.

DeBusk, W. F. (1999). *Nitrogen cycling in wetlands*, Univ. of Florida, Institute of Food and Agricultural Science, Gainesville, FL.

Dierberg, F. E., DeBusk, T. A., Jackson, S. D., Chimney, M. J., and Pietro, K. (2002). "Submerged aquatic vegetation-based treatment wetlands for removing phosphorus from agricultural runoff: Response to hydraulic and nutrient loading." *Water Res.*, 36(6), 1409–1422.

Faulkner, S. P., and Richardson, C. J. (1989). "Physical and chemical characteristics of freshwater wetland soils." *Constructed wetlands for wastewater treatment: Municipal, industrial, and agricultural*, Lewis Publishers, Chelsea, MI.

Fisher, J., and Acreman, M. (2004). "Wetland nutrient removal: A review of the evidence." *Hydrol. Earth System Sci.*, 8(4), 673–685.

Garcia-Garcia, V., Gomez, R., Vidal-Abarca, M. R., and Suarez, M. L. (2009). "Nitrogen retention in natural Mediterranean wetland-streams affected by agricultural runoff." *Hydrol. Earth Syst. Sci.*, 13(12), 2359–2371.

Godfrey, P. J., Kaynor, E. R., Pelczarski, S., and Benforado, J. (1985). *Ecological considerations in wetlands treatment of municipal wastewaters*, Van Nostrand Reinhold, New York.

Hammer, D. A. (1989). "Wetland ecosystems: Natural water purifiers?" *Constructed wetlands for wastewater treatment, municipal, industrial and agricultural*, D. A. Hammer, ed., CRC Press, Boca Raton, FL, 5–19.

Hammer, D., and Kadlec, R. (1989). "A model for wetland surface-water dynamics—reply." *Water Resour. Res.*, 25(5), 1063–1065.

Hantush, M. M., and Kalin, L. (2008). "Stochastic residual-error analysis for estimating hydrologic model predictive uncertainty." *J. Hydrol. Eng.*, 10.1061/(ASCE)1084-0699(2008)13:7(585), 585–596.

Hantush, M. M., Kalin, L., Isik, S., and Yucekaya, A. (2013). "Nutrient dynamics in flooded wetlands. I: Model development." *J. Hydrol. Eng.*, 10.1061/(ASCE)HE.1943-5584.0000741, 1709–1723.

Hattermann, F. F., Krysanova, V., Habeck, A., and Bronstert, A. (2006). "Integrating wetlands and riparian zones in river basin modelling." *Ecol. Modell.*, 199(4), 379–392.

Howard-Williams, C. (1985). "Cycling and retention of nitrogen and phosphorus in wetlands: A theoretical and applied perspective." *Freshwater Biol.*, 15(4), 391–431.

Jordan, S. J., Stoffer, J., and Nestlerode, J. (2011). "Wetlands as sinks for reactive nitrogen at continental and global scales: A meta-analysis." *Ecosystems*, 14(1), 144–155.

Jordan, T. E., Whigham, D. F., Hofmockel, K. H., and Pittek, M. A. (2003). "Nutrient and sediment removal by a restored wetland receiving agricultural runoff." *J. Environ. Qual.*, 32(4), 1534–1547.

Kuschk, P., Wiessner, A., Kappelmeyer, U., Weissbrodt, E., Kästner, M., and Stottmeister, U. (2003). "Annual cycle of nitrogen removal by a pilot-scale subsurface horizontal flow in a constructed wetland under moderate climate." *Water Res.*, 37(17), 4236–4242.

Lenhart, H. A., and Hunt, W. F. (2011). "Evaluating four storm-water performance metrics with a North Carolina coastal plain storm-water wetland." *J. Environ. Eng.*, 10.1061/(ASCE)EE.1943-7870.0000307, 155–162.

Martin, J., and Reddy, K. (1997). "Interaction and spatial distribution of wetland nitrogen processes." *Ecol. Modell.*, 105(1), 1–21.

Nash, J. E., and Sutcliffe, J. V. (1970). "River flow forecasting through conceptual models part I—A discussion of principles." *J. Hydrol.*, 10(3), 282–290.

Reckhow, K., and Qian, S. (1994). "Modeling phosphorus trapping in wetlands using generalized additive-models." *Water Resour. Res.*, 30(11), 3105–3114.

Richardson, C. (1985). "Mechanisms controlling phosphorus retention capacity in fresh-water wetlands." *Science*, 228(4706), 1424–1427.

Richardson, C. J., and Davis, J. A. (1987). "Natural and artificial wetland ecosystems: Ecological opportunities and limitations." *Aquatic plants for water treatment and resource recovery*, K. R. Reddy, and W. H. Smith, eds., Magnolia Publishing, Orlando, FL, 819–854.

Saltelli, A., and Sobol, I. M. (1995). "About the use of rank transformation in sensitivity analysis of model output." *Reliab. Eng. Sys. Safety*, 50(3), 225–239.

Son, Y. K., Yoon, C. G., Kim, H. C., Jang, J. H., and Lee, S. B. (2010). "Determination of regression model parameter for constructed wetland using operating data." *Paddy Water Environ.*, 8(4), 325–332.

Sonavane, P., and Munavalli, G. (2009). "Modeling nitrogen removal in a constructed wetland treatment system." *Water Sci. Technol.*, 60(2), 301–309.

Spear, R., and Hornberger, G. (1980). "Eutrophication in peel inlet—II. Identification of critical uncertainties via generalized sensitivity analysis." *Water Res.*, 14(1), 43–49.

Strecker, E. W., Quigley, M. M., Urbonas, B. R., Jones, J. E., and Clary, J. K. (2001). "Determining urban storm water BMP effectiveness." *J. Water Resour. Plng. and Mgmt. Div.*, 10.1061/(ASCE)0733-9496(2001)127:3(144), 144–149.

Szabo, A., Osztoics, A., and Szilagyi, F. (2001). "Natural wastewater treatment in Hungary." *Water Sci. Technol.*, 44(11–12), 331–338.

Tanner, C. C. (2001). "Growth and nutrient dynamics of soft-stem bulrush in constructed wetlands treating nutrient-rich wastewaters." *Wetlands Ecol. Manage.*, 9(1), 49–73.

U.S. Environmental Protection Agency (USEPA). (1999). "Free water surface wetlands for wastewater treatment technology: A technology assessment." *EPA Rep. 832-S-99-002*, Office of Water, Washington, DC, 165.

U.S. Environmental Protection Agency (USEPA). (2007). "Wetlands and water quality trading: Review of current science and economic practices with selected case studies." *EPA/600/R-06/155*, Ground Water and Ecosystems Restoration Division, Ada, OK, 195.

Wang, N., and Mitsch, W. (2000). "A detailed ecosystem model of phosphorus dynamics in created riparian wetlands." *Ecol. Modell.*, 126(2–3), 101–130.

Whigham, D., Pittek, M., Hofmockel, K. H., Jordan, T., and Pepin, A. L. (2002). "Biomass and nutrient dynamics in restored wetlands on the outer coastal plain of Maryland, USA." *Wetlands*, 22(3), 562–574.

Williams, J. R. (1995). "The EPIC model." *Computer models of watershed hydrology*, V. P. Singh, ed., Water Resources Publications, USGS, Reston, VA, 909–1000.