# Comparison of the Monod and Droop Methods for Dynamic Water Quality Simulations

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**Abstract:** The Monod method is widely used to model nutrient limitation and primary productivity in water bodies. It offers a straightforward approach to simulate the main processes governing eutrophication and it allows the proper representation of many aquatic systems. The Monod method is not able to represent the nutrient luxury uptake by algae, which consists of the excess nutrient uptake during times of high nutrient availability in the water column. The Droop method, which is also used to model nutrient limitation and primary productivity, takes into account the luxury uptake of nutrients. Because of the relative complexity of the Droop method, it has not been systematically adopted for the simulation of large stream networks. The Water Quality Analysis Simulation Program (WASP) version 7.1 was updated to include nutrient luxury uptake for periphyton growth. The objective of this paper is to present the new nutrient limitation processes simulated by WASP 7.1 and to compare the performance of the Droop and the Monod methods for a complex stream network where periphyton is the main organism responsible for primary productivity. Two applications of WASP 7.1 with the Droop and Monod methods were developed for the Raritan River Basin in New Jersey. Water quality parameters affecting the transport and fate of nutrients were calibrated based on observed data collected for the Raritan River total maximum daily load. The dissolved oxygen and nutrients simulated with WASP 7.1, obtained with the Droop and Monod methods, were compared at selected monitoring stations under different flows and nutrient availability conditions. The comparison of the WASP 7.1 applications showed the importance of using the Droop method when periphyton was the main organism responsible for primary productivity. The data simulated with the Droop method resulted in good agreement with the observed data for dissolved oxygen, ammonia-nitrogen, nitrate-nitrogen, and dissolved orthophosphate at the selected stations. The Monod method was not able to capture the diel dissolved oxygen variation when nutrients were scarce, and it resulted in unrealistic diel variations of nutrients at times of strong primary productivity at some locations.

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## Introduction

The relationship between nutrient availability and primary productivity is an important ecological process in aquatic systems. Phosphorus and nitrogen are nutrients necessary to support algae and aquatic plant growth. The excess of these nutrients in water contributes to eutrophication and associated water quality problems, such as low dissolved oxygen levels. The role of nutrients in fresh waters and their effects on dissolved oxygen and aquatic ecosystems can be evaluated using mechanistic water quality models.

Phosphorus is generally considered to be the primary nutrient limiting algal and plant growth in fresh waters. Due to its importance, phosphorus is often listed as an impairment parameter for rivers and streams throughout the United States. The nutrient limitation for algae growth is simulated in water quality models according to the Monod method and the Droop method (Sommer 1991). The Monod method (Monod 1949) relates aquatic plants and algae growth rates with available nitrogen and phosphorus dissolved in the water column. The Droop method (Droop 1974) relates algae and plant growth with their internal nutrient levels. The Monod method provides a simple and effective approach to represent many aquatic systems. However, it may not provide realistic simulations when internal nutrient levels of algae and aquatic plants support primary productivity during periods of low water column nutrient levels. Algae and aquatic plants are known to take up and store nutrients at higher rates than those necessary for growth at times of excess nutrient availability in the water column. This phenomenon is called nutrient luxury uptake (Droop 1973, 1983). The stored nutrients can be used to support primary productivity at times of low nutrient availability in the water column.

While the Monod method has been applied for a variety of lakes, streams, and rivers, the majority of the applications of the Droop method have been focused on the simulation of phytoplankton growth in lakes (Jørgensen et al. 1978; Jørgensen et al. 1986; Riley and Stefan 1988; Matsuoka et al. 1986; Rossi et al. 1986; Hamilton and Schaldow 1997). The simulation of the internal nutrient pools with the Droop method is complex and involves

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more computational effort. Mass balances for the internal nutrient pools in the organisms are driven by available nutrient concentrations in the water column and internal nutrient concentrations in the algae, along with uptake and growth rates that vary with these concentrations. The applications of the Droop method for lakes generally involve one-dimensional schematizations with few computational elements. However, the complexity of the simulation increases considerably for dynamic models with multiple simulation elements representing complex river networks. Cerco et al. (2004) developed a three-dimensional water quality model for an estuary in Florida that incorporated the Droop method for phosphorus kinetics within a dynamic and finite-volume framework.

Although periphyton and aquatic plants are responsible for primary productivity in many fresh water streams (Azim et al. 2005), most of the applications of the Droop method assume that phytoplankton is the main organism responsible for primary productivity. Periphyton is a variety of algae that is attached to the stream bottom, stream walls, and debris. Periphyton growth depends on water column and internal nutrient levels. Aquatic plants are macrophytes that can be attached to the stream bed or free floating. They may obtain nutrients from the water column or from the bottom sediment depending on the species and environmental conditions (Thiebaut and Muller 2003). Son and Fujino (2003) applied the Droop method to simulate periphyton growth and nutrient uptake in a fresh water channel. However, this application did not cover an extensive and complex stream network.

The Water Quality Analysis Simulation Program (WASP 7.1) (Wool et al. 2001) was updated for this study to include the Droop method for nutrient limitation and periphyton growth. WASP 7.1 allows the dynamic simulation of attached algae with the luxury uptake of nutrients for large and complex stream networks. The objective of this paper is to demonstrate the importance of adopting the Droop method for dynamic water quality models when attached algae is the main organism responsible for primary productivity and the supply of nutrients, dissolved orthophosphate in particular, is limited in the water column.

In order to demonstrate the relevance of luxury uptake for water quality simulations, two one-dimensional applications of WASP 7.1 with the Droop method and Monod methods for nutrient limitation were developed for the Raritan River Basin in New Jersey. Several streams in the Raritan River basin were characterized by high diel DO variation, undetectable levels of dissolved orthophosphate, low concentrations of chlorophyll-a, and the abundance of periphyton and rooted macrophytes. The state variables simulated with WASP 7.1 were dissolved oxygen, organic phosphorus, orthophosphate, ammonia, nitrate, organic nitrogen, carbonaceous biochemical oxygen demand, phytoplankton, and periphyton. The model was prepared for a total of 307 km (191 miles) of streams and rivers within the Raritan River Basin. Water quality parameters affecting periphyton growth, transport, and fate of nutrients were calibrated in order to capture the observed diel pattern of dissolved oxygen and the uptake of nutrients by periphyton for the entire watershed. The results of the simulations obtained with the Droop method and the Monod method were compared at three selected sampling stations and different time periods, which provide a range of conditions to assess the relevance of the nutrient limitation methods.

## Modeling of Nutrient Limitation and Growth

### Monod and Droop Methods

Nutrient luxury uptake is critical to sustain the growth of algae when the available nutrients in the water column are scarce (Wetzel 2001; Effler 1996; Sigee 2005). The most common approaches to quantify the interplay of nutrient availability and the growth of algae and aquatic plants are the Monod method and the Droop method (Droop 1974). The Monod method, also known as the Michaelis-Menten model (Chapra 1997), is the simpler approach of the two. It consists of calculating the maximum specific growth rate $G$ that can be achieved, according to the water column concentration of inorganic phosphorus [P] or inorganic nitrogen [N] and their respective half saturation constant $K_p$ or $K_n$ [Eqs. (1) and (2)]

$$G = \frac{[\mathrm{P}]}{K_p + [\mathrm{P}]} \tag{1}$$

$$G = \frac{[\mathrm{N}]}{K_n + [\mathrm{N}]} \tag{2}$$

The Monod approach is simpler because it directly relates growth with available nitrogen and phosphorus in the water column. However, it ignores the phenomenon of luxury uptake, where nutrients are acquired and stored at levels well beyond the immediate demand for growth. By drawing on internal nutrient reserves, algae can grow at nearly maximum rates during periods of water column nutrient depletion (Effler 1996).

The Droop method relates algae and plant growth to their internal nutrient levels, or cell quotas, and the minimum cell quotas, which are the internal nutrient concentrations below which growth ceases. This method allows nutrient luxury uptake to be taken into account, but it is more complex from a computational standpoint. The Droop method requires the mass balance of the internal nutrient pool to be calculated, considering the contributions from nutrient uptake from the water column, and the losses through demand and growth (Effler 1996). The relative computational complexity required by the Droop method delayed its implementation in compartmented and dynamic water quality models such as WASP.

### WASP

WASP is a compartmental model that uses finite-difference methods to simulate the transport and fate of pollutants in surface water bodies. Supported by the U.S. Environmental Protection Agency, WASP includes a selection of water quality submodels, or modules, that can be used to simulate a variety of conventional and toxicant water quality problems. The EUTRO module is used to simulate conventional pollution problems involving dissolved oxygen, biochemical oxygen demand, nutrients, and eutrophication (Ambrose et al. 1993). At the time of this study, the latest version (WASP 7.1) included a version of EUTRO that simulated phytoplankton and periphyton growth according to the Monod method. During this study, the Periphyton module (PERI) was developed as an alternative to EUTRO to allow the simulation of benthic algae with the Droop method (Ambrose et al. 2006). In this module, benthic algal nutrient uptake and growth algorithms were adapted from a formulation developed for the River and Stream Water Quality Model (QUAL2K 2.04), a steady-state model that simulates conventional water quality in branching one-





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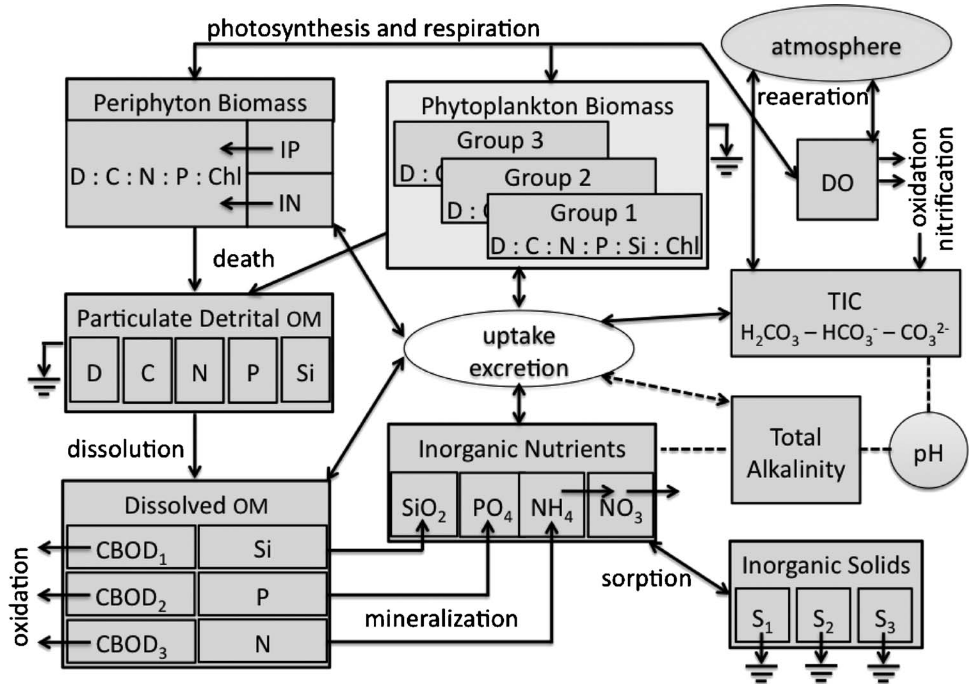


**Fig. 1.** WASP 7.1 eutrophication kinetics

dimensional stream networks (Chapra et al. 2006). Following this study, subsequent releases of WASP dropped the Monod-based periphyton routines from the EUTRO module. Simulation of periphyton using the Droop uptake and growth kinetics became standard in the PERI module and, later, in the advanced eutrophication module.

The WASP 7.1 periphyton module includes the standard WASP 7 eutrophication algorithms and incorporates bottom algae using three additional state variables: bottom algal biomass, bottom algal cell nitrogen, and bottom algal cell phosphorus, as illustrated in Fig. 1. Bottom algae are not subject to advective and dispersive transport. Sources and sinks include nutrient uptake, growth, nutrient excretion, death, and respiration.

Nutrient uptake rates are driven by concentrations of inorganic nitrogen and phosphorus in the water column and within algal cells and are controlled by cell minimum and half-saturation parameters as in Rhee (1973)

$$F_{UNb} = 10^{-3}\rho_{mN}\left(\frac{NH_4 + NO_3}{K_{sNb} + NH_4 + NO_3}\right)\left(\frac{K_{qN}}{K_{qN} + (q_N - q_{0N})}\right)a_b \quad (3)$$

$$F_{UPb} = 10^{-3}\rho_{mP}\left(\frac{PO_4}{K_{sPb} + PO_4}\right)\left(\frac{K_{qP}}{K_{qP} + (q_P - q_{0P})}\right)a_b \quad (4)$$

where $NH_4$, $NO_3$, and $PO_4$=external water concentrations of ammonium N, nitrate N, and phosphate P (mgN/L and mgP/L); $\rho_{mN}$ and $\rho_{mP}$=maximum uptake rates for nitrogen and phosphorus (mgN/gD d and mgP/gD d); $K_{sNb}$ and $K_{sPb}$=half-saturation constants for external nitrogen and phosphorus (mgN/L and mgP/L); $K_{qN}$ and $K_{qP}$=half-saturation constants for intracellular nitrogen and phosphorus (mgN/gD and mgP/gD); and $10^{-3}$ is a units conversion factor (g/mg). Note that nutrient uptake rates fall to half of their maximum values when external nutrient concentrations decline to the half-saturation constants or when excess internal nutrient concentrations rise to the internal half-saturation constants. The internal N and P excretion rates are represented using first-order, temperature-corrected kinetics. The internal N and P loss rates from benthic algal death are the product of the algal death rate and the cell nutrient quotas.

Biomass growth is computed from a maximum zero or first-order rate constant that is adjusted internally by water temperature, bottom light intensity, internal nutrient concentrations, and maximum carrying capacity. Nutrient limitation of the photosynthesis rate is dependent on intracellular nutrient concentrations using a formulation originally developed by Droop (1974)

$$\phi_{Nb} = \min\left[\left(1 - \frac{q_{0N}}{q_N}\right), \left(1 - \frac{q_{0P}}{q_P}\right)\right] \quad (5)$$

where $q_N$ and $q_P$=cell quotas of nitrogen (mgN/gD) and phosphorus (mgP/gD), respectively; and $q_{0N}$ and $q_{0P}$=minimum cell quotas of nitrogen (mgN/gD) and phosphorus (mgP/gD), respectively. The minimum cell quotas are the levels of intracellular nutrient at which growth ceases. Light limitation is determined by the amount of photosynthetically active radiation reaching the bottom of the water column. This quantity is computed with the Beer-Lambert law evaluated at the bottom of the river. Three formulations are available to characterize the impact of light on bottom algae photosynthesis—half saturation, Smith, and Steele. Bottom algal densities are limited by their carrying capacity or maximum density. Space limitation of the first-order growth rate is modeled as a logistic function. More details on the Periphyton equations and their implementation can be found in Ambrose et al. (2006).

## Application of WASP 7.1 for the Raritan River Watershed

As a part of the Raritan River total maximum daily load (TMDL), Omni Environmental LLC prepared an application of the PERI submodel for the Raritan River Watershed in New Jersey. This



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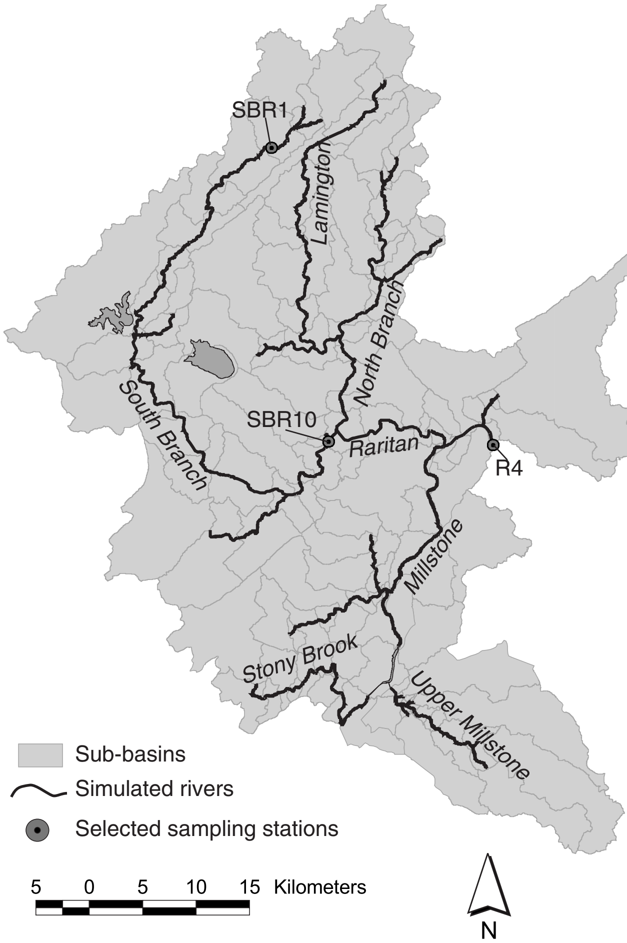


**Fig. 2.** Raritan River Basin

was the first application of WASP 7.1 for a complex stream network using the Droop method and probably the first dynamic application of the Droop method to a stream network with multiple branches and segments. An application of EUTRO was also prepared in order to compare the results of simulations according to the Monod and Droop methods.

The Raritan River Basin encompasses approximately 2,850 $km^2$ (1,100 sq miles) in the central portion of New Jersey that drain to the Raritan Bay. Major tributaries to the Raritan River are the North Branch Raritan River, South Branch Raritan River, and the Millstone River (Fig. 2). The model inputs include a five-minute time-step hydrodynamic file with continuous flows, a nonpoint source loads' file, point source loads from dischargers, time series of stream temperature, and solar radiation derived from local measurements and several kinetic parameters. The hydrodynamic and nonpoint source inputs were obtained with the Hydrologic and Water Quality integration Tool (HYDROWAMIT) (Cerucci and Jaligama 2008), which is a hydrologic model developed especially to provide input parameters for WASP 7.1. Stream flow data from 17 gauge stations maintained by the U.S. Geological Survey were used for the hydrologic model calibration (Omni Environmental LLC 2008). The water quality model was calibrated based on data collected during sampling programs performed in 2003, 2004, and 2005 for the TMDL study. The overall calibration of the hydrologic and water quality model for the TMDL involved 75 stations distributed over the watershed (Omni Environmental LLC 2008). The water quality calibration consisted of adjusting kinetic parameters such as periphyton growth rates, phosphorus cell quotas, and maximum phosphorus uptake by periphyton. The calibration of the model developed for the Raritan River Basin TMDL is not the scope of this paper. However, the model results at selected stations chosen to evaluate the relevance of the Droop and the Monod methods are presented and discussed.

Three stations with different flow characteristics and nutrient availability were selected to evaluate the nutrient limitation methods: South Branch Raritan 1 (SBR1), South Branch Raritan 10 (SBR10), and Raritan River 4 (R4). The locations of the selected stations are shown on Fig. 2. The selected monitoring stations contain measurements of nutrient and diel dissolved-oxygen (DO) concentrations. The sites differ in terms of average flows, concentration of dissolved orthophosphate ($PO_4$), total phosphorus (TP), ammonia ($NH_3$), nitrate ($NO_3$), and diel DO variation.

Station SBR1 is located at the headwaters of the South Branch Raritan River. This site presents very low $PO_4$ and $NH_3$ concentrations and the average flows are in the order of 1.5 $m^3/s$ (52 cfs). Station SBR10 is located near the mouth of the South Branch Raritan River. The nutrient concentrations measured at SBR10 are higher than those observed at SBR1 and the average flow is 12.5 $m^3/s$ (450 cfs). Station R4 is located at the main steam of the Raritan River, downstream of the confluence with Green Brook. R4 is the most downstream station of the model and is characterized by higher nutrient concentrations and an average flow of 36.8 $m^3/s$ (1,300 cfs). The average chlorophyll-a (Chl-a) measured at the sampling stations during the summer is 3 $\mu g/l$. This level of Chl-a is an indication that phytoplankton is not the main organism responsible for the primary productivity. Instead, periphyton and aquatic plants play a major role in the Raritan Basin.

The PERI submodel was calibrated to capture the nutrient concentrations and the diel DO variations observed at the monitoring stations for multiple sampling events. Initially, the same set of common parameters was adopted for the EUTRO submodel. The reaeration methods, hydrodynamic inputs, temperature, solar radiation, and concentration boundary conditions were identical for both submodels. Because of the relative simplicity of the Monod method, EUTRO requires fewer parameters than PERI. Periphyton maximum growth rate, death rate, and half-saturation concentrations for water column nutrients are present in both algorithms. In addition to these parameters, PERI requires values for maximum and minimum nutrient cell quotas, internal nutrient half-saturation concentrations, and nutrient excretion rates. Table 1 contains the calibrated periphyton global kinetic parameters for PERI and EUTRO. In addition to these global kinetic parameters, which affect all model segments, the segment-specific bottom fractions available to benthic algae (PERIFRAC) assigned to individual segments in PERI and EUTRO are also presented in Table 1.

Table 2 contains a summary of the statistics derived with predicted and observed data obtained with PERI and EUTRO. Overall, both PERI and EUTRO provided a good representation of $NO_3$, $PO_4$, and TP at SBR1. PERI results for TP and $NO_3$ at SBR10 are representative of the observed data. However, PERI underpredicted $PO_4$ at SBR10 during certain time periods. In terms of statistics, EUTRO seems to provide a better simulation of $PO_4$ at SBR10. The $NH_3$ simulation was less representative for both submodels at SBR1 and SBR10. PERI provided a good representation of $PO_4$, $NO_3$, and TP at station R4. However, PERI's $NH_3$ simulation at R4 was less representative than the other parameters. EUTRO's simulations at R4 were not representative for all forms of nutrients. Figs. 3–5 show the time series plots of



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**Table 1.** Periphyton Global Kinetic Parameters Adopted for PERI and EUTRO

| Parameter | PERI | EUTRO |
|---|---|---|
| Benthic algae D:C ratio (mg dry weight/mg C) | 2.5 | 2.5 |
| Benthic algae N:C ratio (mg N/mg C) | 0.18 | 0.18 |
| Benthic algae P:C ratio (mg P/mg C) | 0.025 | 0.025 |
| Benthic algae Chl a:C ratio (mg chlorophyll a/mg C) | 0.025 | 0.025 |
| Benthic algae O2:C production (mg O2/mg C) | 2.69 | 2.69 |
| Benthic algae max growth rate (gD/m2/d) | 25 | 25 |
| Temp coefficient for benthic algal growth | 1.07 | 1.07 |
| Respiration rate (1/day) | 0.1 | 0.1 |
| Temperature coefficient for benthic algal respiration | 1.07 | 1.07 |
| Internal nutrient excretion rate for benthic algae (1/day) | 0.01 | — |
| Temperature coefficient for benthic algal nutrient excretion | 1.07 | — |
| Death rate (1/day) | 0.01 | 0.01 |
| Temperature coefficient for benthic algal death | 1.07 | 1.07 |
| Half saturation uptake constant for extracellular N (mg N/L) | 0.02 | 0.02 |
| Half saturation uptake constant for extracellular P (mg P/L) | 0.005 | 0.005 |
| Light constant for growth (langleys/day) | 100 | 100 |
| Benthic algae ammonia preference (mg N/L) | 0.025 | 0.025 |
| Minimum cell quota of internal nitrogen for growth (mgN/gDW) | 26.6 | — |
| Minimum cell quota of internal P for growth (mgP/gDW) | 3.7 | — |
| Maximum N uptake rate for benthic algae (mgN/gDW-day) | 38.3 | — |
| Maximum P uptake rate for benthic algae (mgP/gDW-day) | 1.86 | — |
| Half saturation uptake constant for intracellular N (mgN/gDW) | 44.4 | — |
| Half saturation uptake constant for intracellular P (mgP/gDW) | 7.4 | — |
| PERIFRAC SBR1 | 0.60 | 0.60 |
| PERIFRAC SBR10 | 0.74 | 0.74 |
| PERIFRAC R4 | 0.65 | 0.65 |

EUTRO's and PERI's outputs at the selected stations. The nutrient simulations at stations SBR10 and R4 were influenced by existing upstream wastewater treatment plants (WWTPs), whereas the nutrient concentrations at station SBR1 were influenced by nonpoint source loads. The point source loads from the majority of WWTPs were derived based on available discharge monitoring reports (DMRs) since few WWTPs keep daily records of effluent nutrient concentrations. Given the uncertainties associated with the boundary conditions and their influence on simulated nutrient concentrations, the predictions of PERI were considered reasonable and representative for all stations. The predictions of EUTRO were representative only for SBR1 and SBR10. The mean errors for the EUTRO nutrient predictions were considerably larger than those for PERI at R4, suggesting the model's processes, and not the boundary condition uncertainties, were responsible for the large percent mean error at R4.

Four diel DO events were also used to compare the relevance of the Monod and Droop methods at the selected stations. Three continuous DO monitoring events occurred in the summer during low flow periods. One event occurred in the fall and was representative of average flow conditions. The main calibration objective for diel DO was to minimize the mean error and to maximize the coefficient of determination ($R^2$). Table 3 contains the diel DO calibration statistics obtained with PERI and EUTRO. Because DO was not strongly dependent on boundary conditions and the trend of diel DO variation was an important aspect to assess the effectiveness of the Monod and Droop methods, the $R^2$ was adopted to quantify the diel DO goodness of fit. The DO statistics suggested that simulations with PERI were a good representation of the average and the diel DO variation for all stations and time periods. The statistics also suggested that DO simulations with EUTRO were not representative at SBR1, acceptable at SBR10, and good at R4.

## Discussion of WASP Applications with Droop and Monod Methods

The results of the simulations obtained with PERI and EUTRO were compared to evaluate the performances of the Droop and Monod methods. Since phosphorus was the nutrient of concern and the limiting factor for periphyton growth in the Raritan River basin, the analysis of nutrient limitation was focused on $PO_4$ and diel DO for the selected sampling stations.

The nutrient simulations with PERI and EUTRO do not show relevant differences between the methods at SBR1 and SBR10. Both methods resulted in good to acceptable representations of the overall trends and the daily average concentrations for these stations. The processes affecting the nutrient cycling, such as mineralization, settling, and the influence of boundary conditions,

**Table 2.** Calibration Statistics for Nutrients Obtained with PERI and EUTRO

| | SBR1 | | | | SBR10 | | | | R4 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $NH_3$ | $NO_3$ | $PO_4$ | TP | $NH_3$ | $NO_3$ | $PO_4$ | TP | $NH_3$ | $NO_3$ | $PO_4$ | TP |
| Number of samples | 20 | 20 | 20 | 20 | 18 | 18 | 21 | 21 | 22 | 22 | 22 | 22 |
| Mean predicted PERI | 0.05 | 1.50 | 0.01 | 0.05 | 0.02 | 1.28 | 0.02 | 0.08 | 0.06 | 1.95 | 0.21 | 0.29 |
| Mean predicted EUTRO | 0.05 | 1.52 | 0.02 | 0.05 | 0.02 | 1.31 | 0.05 | 0.06 | 0.27 | 2.09 | 0.32 | 1.49 |
| Mean observed | 0.04 | 1.49 | 0.02 | 0.04 | 0.04 | 1.19 | 0.05 | 0.09 | 0.15 | 1.66 | 0.18 | 0.24 |
| Mean error PERI | −0.01 | −0.01 | 0.00 | −0.01 | 0.02 | −0.09 | 0.02 | 0.02 | 0.09 | −0.29 | −0.03 | −0.05 |
| Mean error EUTRO | −0.02 | −0.03 | 0.00 | 0.00 | 0.02 | −0.12 | 0.00 | 0.03 | 0.17 | 2.38 | 0.26 | 0.36 |
| Root-mean-square error PERI | 0.04 | 0.19 | 0.03 | 0.04 | 0.03 | 0.24 | 0.03 | 0.05 | 0.19 | 0.53 | 0.22 | 0.12 |
| Root-mean-square error EUTRO | 0.02 | 0.19 | 0.02 | 0.02 | 0.03 | 0.28 | 0.02 | 0.05 | 0.23 | 0.66 | 0.34 | 0.15 |
| % mean error PERI | −24% | −1% | 7% | −17% | 50% | −7% | 50% | 16% | 60% | −17% | −17% | −20% |
| % mean error EUTRO | −50% | −2% | −8% | −11% | 40% | −10% | −3% | 32% | 116% | 143% | 144% | 148% |



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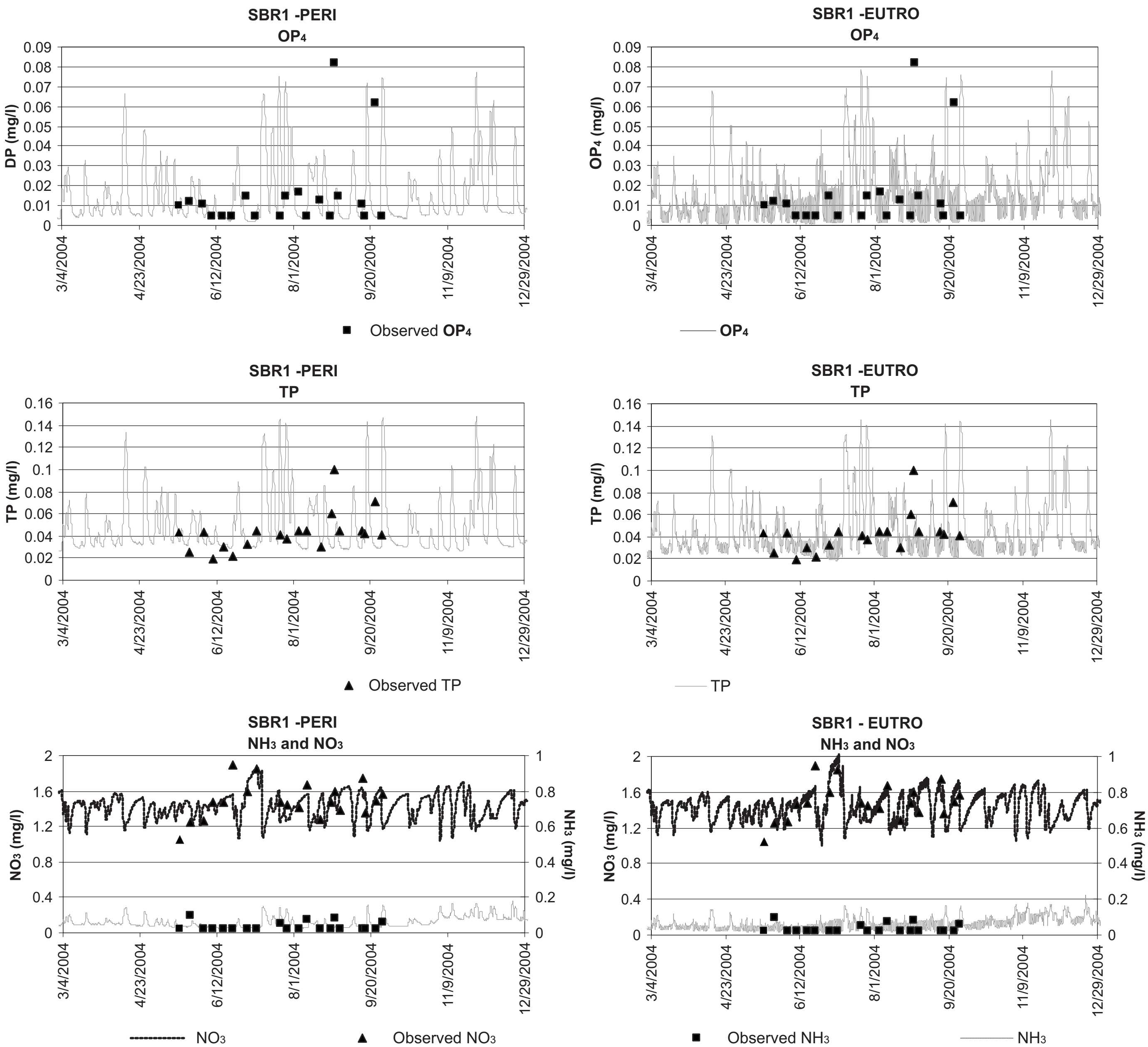


**Fig. 3.** SBR1 nutrient time series with PERI and EUTRO

were the same for both EUTRO and PERI submodels. One aspect that distinguishes the submodels is the uptake and release of nutrients by periphyton. When higher growth rates of periphyton are necessary to capture the amplitude of diel DO variation, the Monod method results in simulations with strong diel variation of nutrients. The relatively high mean percent errors observed for EUTRO simulations at R4 are explained in part by the diel variation of nutrients. The hourly variation of nutrients is not a realistic representation of the processes occurring in the water column. The effects of the diel variation are more noticeable in $PO_4$ and $NH_3$, which sustain plant growth when they are present in smaller concentrations in the water column. The diel variations of $NH_3$, $PO_4$, TP, and $NO_3$ simulated with EUTRO can be seen on Figs. 3–5. A closer look at the diel variation of $PO_4$ and the calibration data are available in Figs. 6–9.

Station SBR1 is a critical location for the use of the Droop method. The average concentration of $PO_4$ at SBR1 is 0.02 mg/L, which is at the detection limit of the samples. The average concentration of $NH_3$ is 0.036 mg/L and the detection limit for $NH_3$ is 0.025 mg/L. Fig. 6 shows the diel DO simulations for SBR1 with Droop and Monod methods during a steady low flow period (0.63 $m^3/s$). The $PO_4$ concentrations predicted with PERI were below the detection limit during the time of the diel sampling and were in agreement with the observed data. PERI was able to capture the extent of diel DO variation during the three day continuous sampling event. EUTRO captured approximately half of the diel dissolved oxygen variation measured at SBR1 and it did not present the typical sinusoidal shape of diel DO obtained with the Droop method. This indicates that phosphate concentration in the water column was not enough to support growth during times of nutrient depletion with EUTRO. The same values for half-saturation concentrations of extracellular $PO_4$ and $NH_3$ were adopted in EUTRO and PERI. The excessive diel variation of $PO_4$ simulated with EUTRO can be seen in Fig. 6. The diel variation



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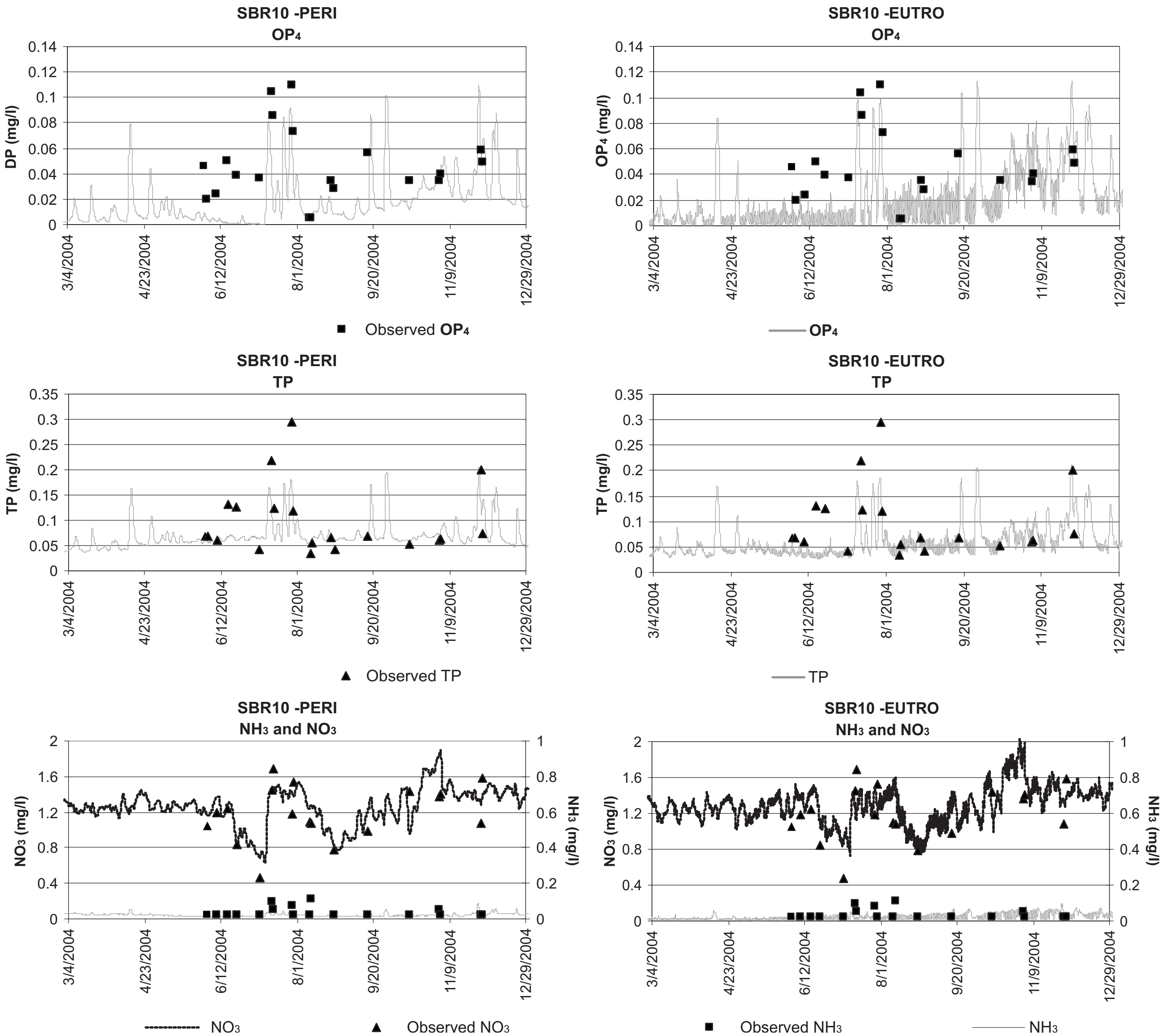


**Fig. 4.** SBR10 nutrient time series with PERI and EUTRO

of $PO_4$ simulated with EUTRO was around 0.02 mg/L, whereas PERI did not result in noticeable diel variation of $PO_4$.

Fig. 7 shows the comparison of diel DO and $PO_4$ obtained with PERI and EUTRO at SBR10 during a continuous 10-day sampling event performed in August of 2004. This event was representative of a recession period after a moderate storm followed by a steady low flow period ($4.81\ m^3/s$). Both submodels accurately captured the observed $PO_4$ concentrations during the recession and the steady low flow periods. The observations made in July of 2004 at SBR10 allowed a comparison during times of different phosphorus availability and flow conditions. During the time of flow recession and higher nutrient availability in the water column, the diel DO variation was on the order of 2 mg/L. The $PO_4$ concentration decreased after the flow recession period and the diel DO variation increased to 4.5 mg/L. The diel DO variation was accurately captured by PERI during times of high and low phosphorus availabilities. The simulations obtained with EUTRO provided a less accurate representation of diel DO for this event. The Monod method overpredicted the average DO concentration at times of excess $PO_4$ availability and low productivity and it did not capture the entire extent of the diel variation when the observed $PO_4$ was below the detection limit. Therefore, when $PO_4$ concentrations dropped under 0.025 mg/L, the Monod method was not able to sustain the same growth levels as the Droop method. As at the other stations, EUTRO predicted a diel oscillation of $PO_4$ concentrations at times of low $PO_4$ availability.

The results obtained with the Droop and Monod methods at SBR10 were also evaluated for a three-day diel event performed during the month of November of 2004. The November event consisted of steady flow conditions and an average $PO_4$ concentration of 0.05 mg/L. The results of the simulations with PERI and EUTRO are shown in Fig. 8. The Droop method was able to capture the average DO concentrations and the DO minima. However, it underpredicted most of the DO peaks. The opposite effect was observed with the Monod method, which overpredicted the maximum and minimum diel DO concentrations. The underpre-



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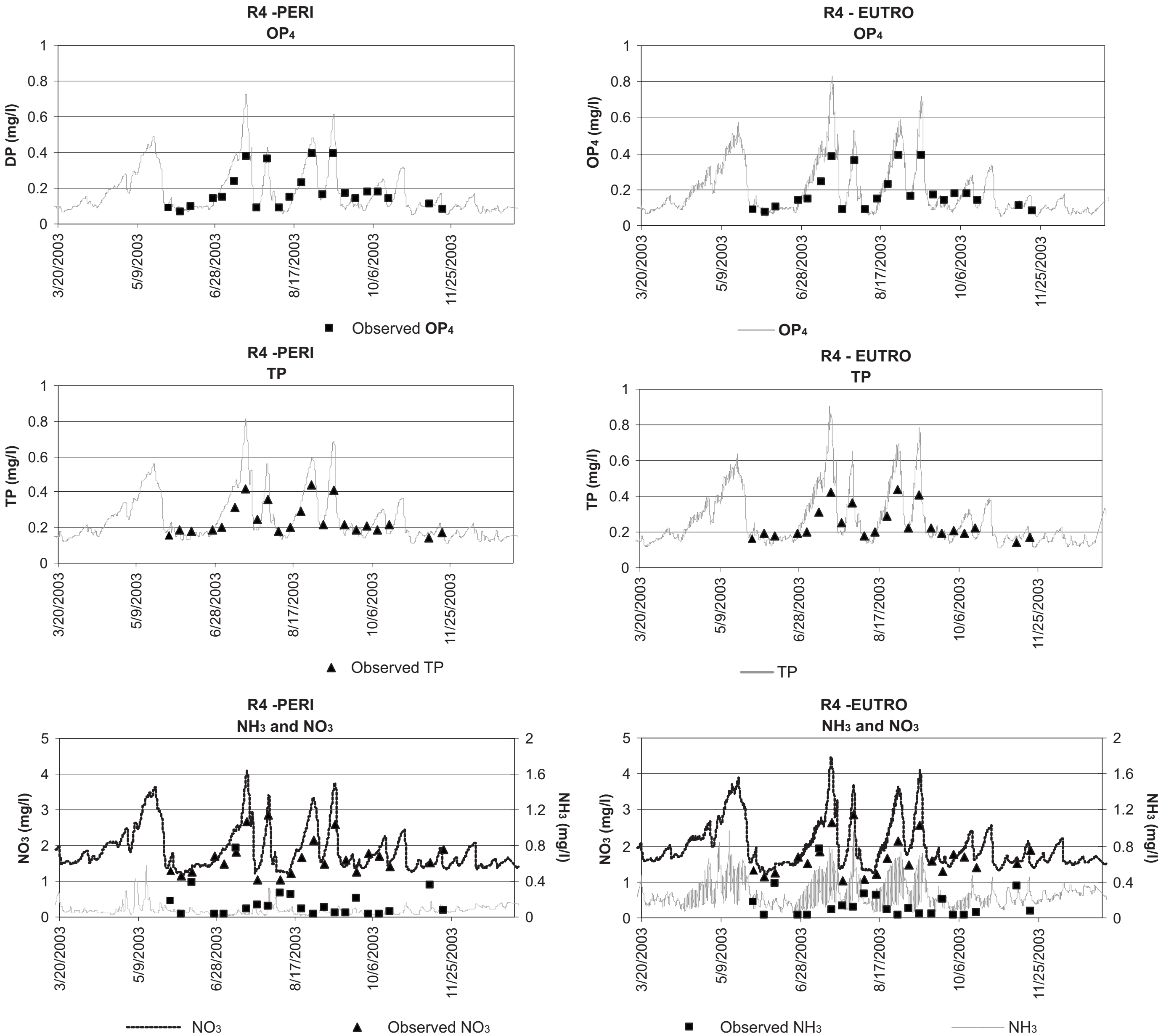


**Fig. 5.** R4 nutrient time series with PERI and EUTRO

diction of the DO maxima by the Droop method was not a result of the nutrient availability. Both EUTRO and PERI simulated a similar level of diel DO variation (3.5 mg/L) and there was no shortage of $PO_4$ during the November diel DO event (average $PO_4$ concentration$=0.05$ mg/L). During the November event at SBR10, the Monod and the Droop methods resulted in a different average DO and a similar degree of diel variation.

The comparison of Droop and Monod methods at station R4 was performed during a 2-week continuous diel DO sampling event in August 2004. The flow conditions were mostly steady,

**Table 3.** Calibration Statistics for DO Obtained with PERI and EUTRO

| | SBR1—June | SBR10—July | SBR10—November | R4—August |
|---|---|---|---|---|
| DO mean predicted PERI | 9.04 | 8.79 | 10.64 | 8.76 |
| DO mean predicted EUTRO | 9.25 | 9.05 | 12.37 | 7.83 |
| DO mean observed | 8.53 | 8.40 | 10.92 | 8.07 |
| Mean error PERI | 0.52 | 0.39 | −0.28 | 0.69 |
| Mean error EUTRO | 0.72 | 0.65 | 1.45 | −0.24 |
| R2 PERI | 0.74 | 0.74 | 0.78 | 0.77 |
| R2 EUTRO | 0.17 | 0.40 | 0.65 | 0.73 |



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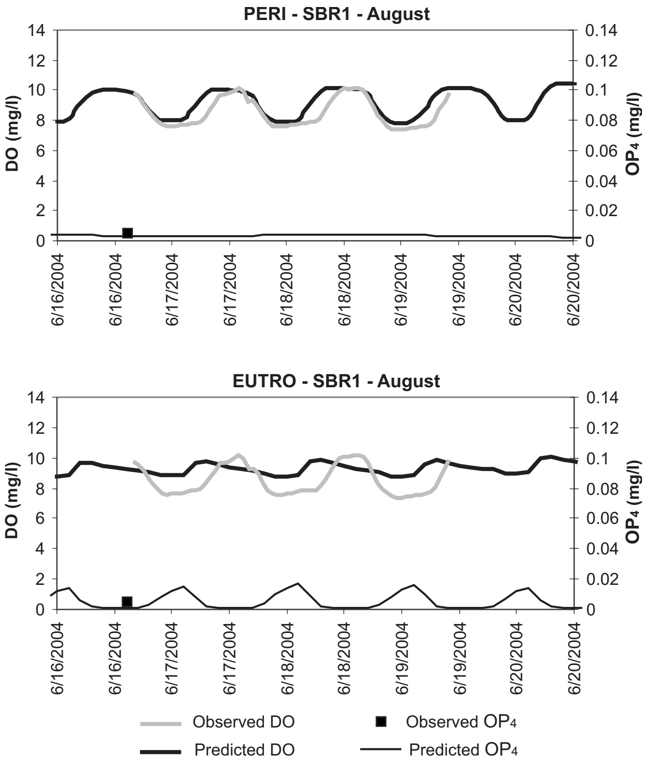


**Fig. 6.** Summer event: diel DO and $PO_4$ with PERI and EUTRO at SBR1

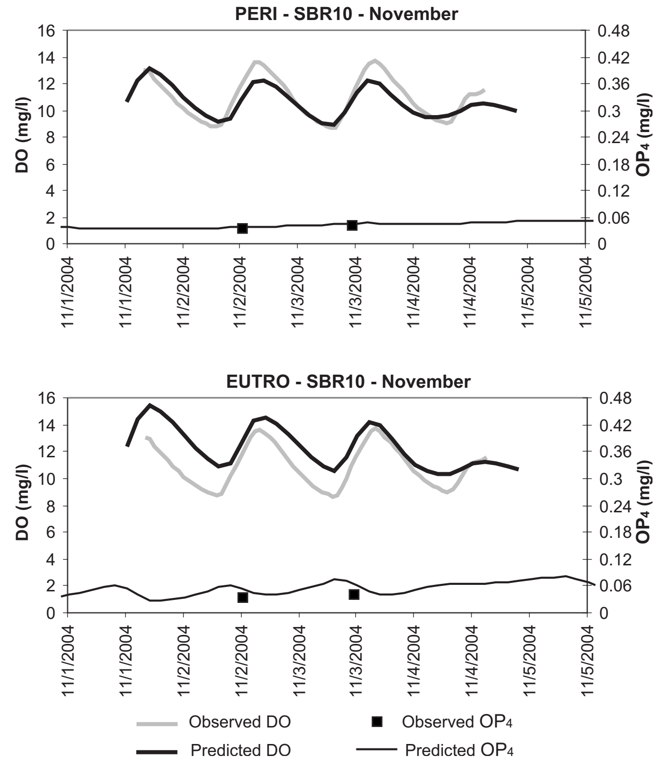


**Fig. 8.** Fall event: diel DO and $PO_4$ with PERI and EUTRO at SBR10

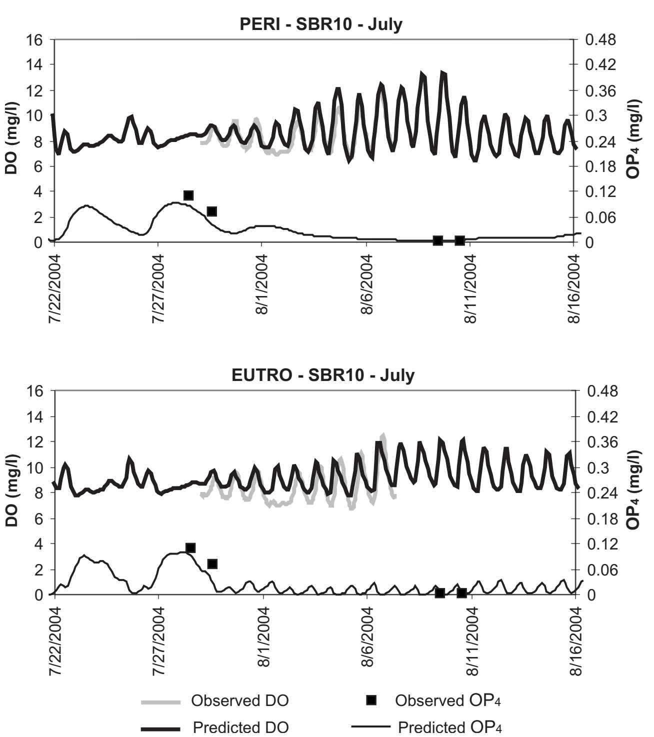


**Fig. 7.** Summer event: diel DO and $PO_4$ with PERI and EUTRO at SBR10

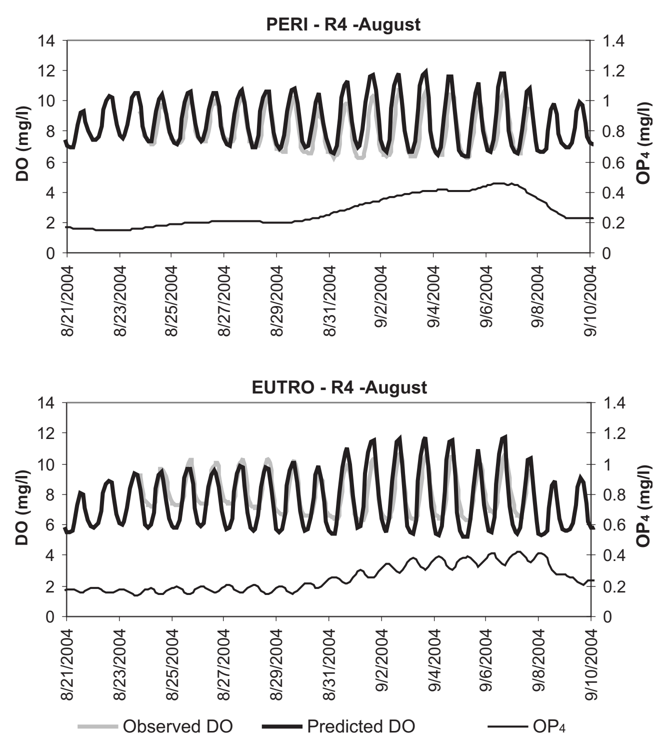


**Fig. 9.** Summer event: diel DO and $PO_4$ with PERI and EUTRO at R4

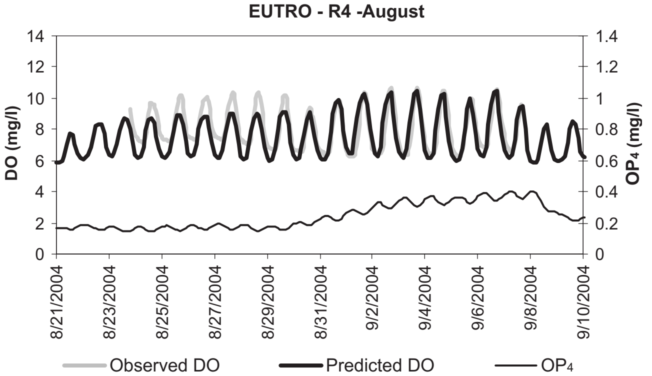


**Fig. 10.** EUTRO sensitivity analysis—summer diel DO and $PO_4$ at R4

with average flow of approximately 9.9 $m^3/s$ (350 cfs). The average simulated $PO_4$ concentrations were approximately 0.35 mg/L for the period. Observed $PO_4$ was not available during the 2004 diel events performed at station R4. However, the PERI calibration results obtained in 2003 showed a good representation of the average $PO_4$ at R4 (Fig. 5). Fig. 9 shows the comparison of the methods at R4. The Droop method captured the diel variation very well in the first week of the event and it seemed to overpredict the DO peaks on the second week. The Monod method overpredicted the diel DO variation during the entire event. The results of simulations at R4 suggested that the Droop method required higher growth rates or a larger PERIFRAC in order to replicate the diel DO variation when nutrients are not scarce.

Limited sensitivity analysis was performed with EUTRO at station R4 to determine if different values of PERIFRAC would result in a better representation of diel DO and nutrient concentrations. PERIFRAC was selected because it was a local parameter and it did not affect the results of upstream segments. An increase or decrease in PERIFRAC was proportional to an increase or decrease of the periphyton growth rates. Periphyton maximum growth rate is a global parameter, meaning it affected all model segments. Fig. 10 shows the results obtained after a 25% reduction of PERIFRAC at R4. After the primary productivity levels at R4 were reduced, EUTRO was able to capture the diel DO swing during the second week of the sampling event very well. However, the minimum diel DO concentrations were underpredicted by EUTRO during the first week of the event, when observed diel DO variation was less intense. Therefore, PERI would still provide a better representation of the long-term diel DO trends at R4, even after the EUTRO parameters were subject to adjustments.

Changes in PERIFRAC did not improve the diel DO representation at locations with lower $PO_4$ supply, such as SBR1 and SBR10. In the case of SBR1, the lack of $PO_4$ was clearly reflected in the shape of the diel DO time series. Increasing PERIFRAC or the maximum periphyton growth rates in EUTRO did not improve the model performance at this location. In the case of SBR10, higher PERIFRAC or growth rates improve the model performance under low flow conditions. However, at times of less primary productivity, the average DO concentrations were still overpredicted.

## Conclusions

The WASP 7.1 PERI module with the Droop method for nutrient limitation was developed as an alternative to EUTRO and the Monod method. Applications of WASP's EUTRO and PERI modules were developed and calibrated for the Raritan River Basin in New Jersey. The model results were compared and limited sensitivity analysis was performed to evaluate the methods' performance at locations with different characteristics. The comparison of the Droop and Monod methods at three stations in the Raritan Basin indicated that the Droop method provided more realistic simulations of diel DO and nutrients at all locations.

The Monod method did not capture the intensity of the diel DO variation at sites characterized by high primary productivity and undetectable nutrient levels during the summer months. The modeling of nutrient limitation with the Droop method at sites such as SBR1 was critical to capture primary productivity and diel DO variation. The Monod method provided acceptable representations of diel DO when nutrients were not scarce. However, the results obtained at SBR10 and the sensitivity analysis performed at R4 indicated that, even though the diel DO variation could be represented with the Monod method at times of high productivity in the summer, the average DO during times of lower productivity was underpredicted. Conversely, the analysis of the results performed during the fall at SBR10 indicated the Monod method overpredicted the average diel DO concentrations. The Droop method also provided a more realistic representation of nutrient concentrations at all sites. During times of intense periphyton growth, the Monod method resulted in a strong and unrealistic diel variation of nutrient levels in the water column, which was caused by the daily uptake and release of nutrients in the water column.

The comparison of the results obtained with the Droop and Monod methods demonstrates that nutrient luxury uptake is a critical component of water quality modeling when strong primary productivity of periphyton is observed regardless of the limitation of nutrient availability. As a result of this study, subsequent releases of WASP dropped the Monod based periphyton routines from the EUTRO module. Simulation of periphyton using the Droop uptake and growth kinetics became standard in the advanced eutrophication module.

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