

Using Geographically Isolated Loading Scenarios to Analyze Nitrogen and Phosphorus Exchanges and Explore Tailored Nutrient Control Strategies for Efficient Management

Ping Wang¹ · Lewis C. Linker² · Gary W. Shenk²

Received: 5 February 2014 / Accepted: 4 October 2015 / Published online: 10 October 2015
© Springer International Publishing Switzerland 2015

Abstract A set of geographically isolated differential nitrogen (N) and phosphorus (P) load model scenarios from major Chesapeake basins provides information on the relative impact of nutrient loads on primary production and dissolved oxygen in the Chesapeake Bay. Model results show the relationships of deep water dissolved oxygen with nutrient limitation-related algal blooms, organic carbon loads from the watershed, estuarine circulation, nutrient cycling, and nutrient diagenesis. The combined effect of changes in load from multiple basins is additive for changes in both chlorophyll-*a* and deep water dissolved oxygen concentrations. Management of both N and P are required in the Chesapeake watershed and tidal waters to achieve water quality standards, but overall efficiencies could be gained with strategies that place greater emphasis on P control in the upper Bay and greater emphasis on N control in the lower Bay. The areas of the Bay with the highest degree of dissolved oxygen degradation that generally drive management decisions are mostly P-limited and are significantly influenced by the load from the upper Bay's basins. Reducing P from the upper Bay's basins will intensify P limitation and would allow an increase in N of about six times the weight of P reduction. Combining the relative nutrient reduction effectiveness with the relative control cost information could improve management efficiency and provide benefits at a lower cost. This article describes initial steps that can be taken to examine the benefits from N-P exchanges.

Keywords Nutrient exchange · Nitrogen · Phosphorus · Dissolved oxygen · Geo-loading model

1 Introduction

Controlling Chesapeake nitrogen (N) and phosphorus (P) loads is required to achieve the water quality dissolved oxygen (DO) standards of the Chesapeake Total Maximum Daily Load (TMDL) [1–3]. In the Chesapeake TMDL, the estuary (Fig. 1) is divided into 92 CB segments based on salinity, geographic location, and state boundaries [4]. Based on the depths of the upper and lower mixed layers, each CB segment is further divided into as many as three vertical layers by the designated-uses of open water (OW), deep water (DW), and deep channel (DC), which have separate DO water quality criteria based on living resource needs [2]. The name of a CB segment designated-use is made of two parts separated by a dash. The first part is the segment name, and the second part is a two-digit of depth/layer category. For example, designated-use CB4MH-DW is the deep water of CB segment CB4MH (Fig. 1). The degree that nutrient and sediment loads need to be reduced to attain water quality standards in the Chesapeake TMDL is assessed in all of the individual designated-uses of CB segments [3,5]. The CB segments that required the greatest nutrient reductions in order to achieve the DO water quality standards were the deep water contiguous CB segments in the center of the mainstem Bay including the deep water and deep channel designated uses of CB3MH, CB4MH, and CB5MH.

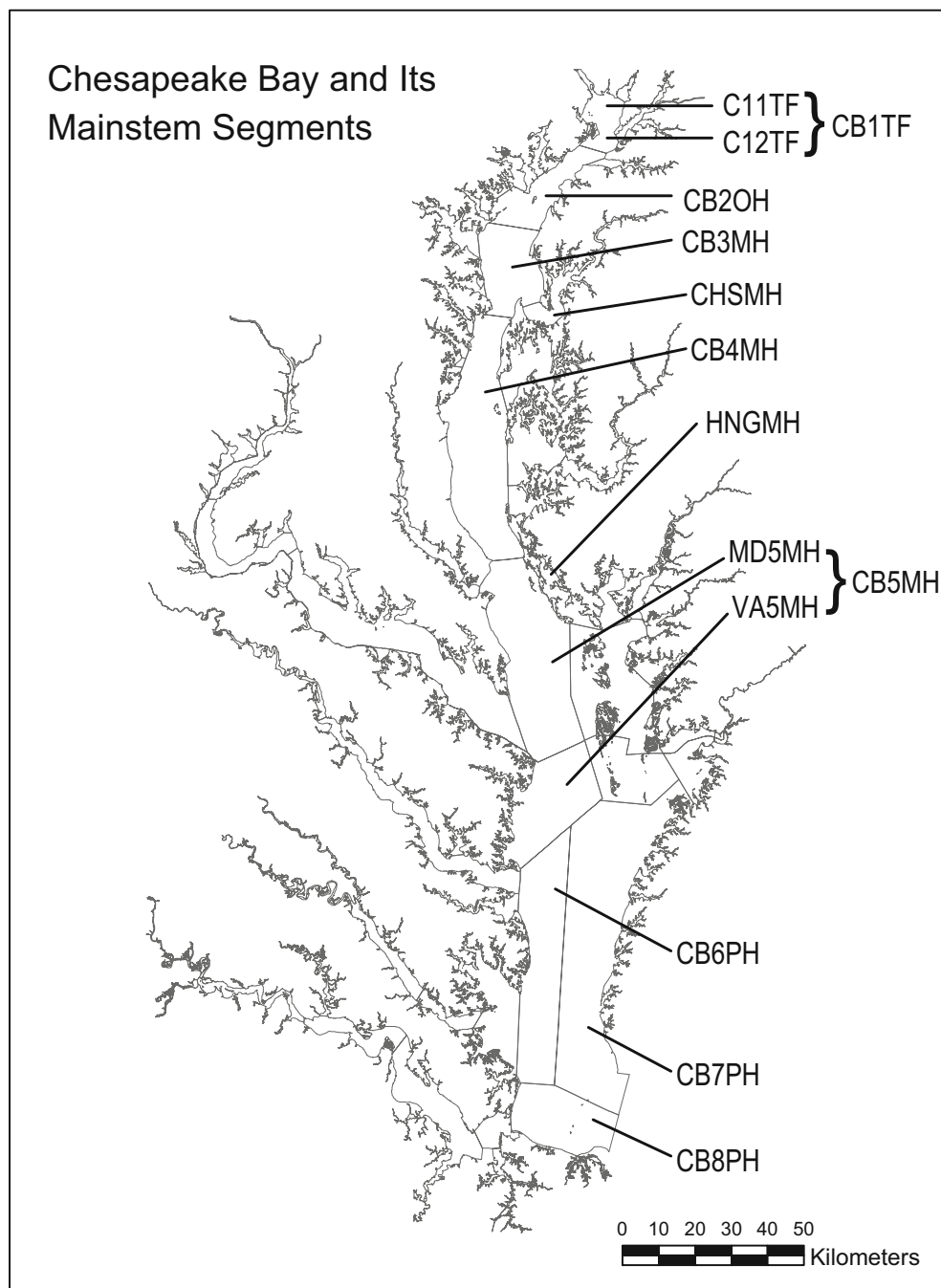
Achievement of the DO and other water quality standards in the Bay will require a reduction in N and P loads from its watershed by about half from the levels estimated for the 1985 conditions. The advantages of dual control of both N and P in watersheds have been described for the

✉ Ping Wang
pwang@chesapeakebay.net

¹ Virginia Institute of Marine Science, Chesapeake Bay Office, 410 Severn Avenue, Annapolis, MD 21403, USA

² U.S. Environmental Protection Agency Chesapeake Bay Program, Annapolis, MD, USA

Fig. 1 Chesapeake Bay mainstem CB segments



management of eutrophic rivers and lakes [6]. Dual nutrient control of N and P has long been an established pillar of the Chesapeake restoration. Nevertheless, there is utility to examine alternative N and P reduction approaches that can achieve the same water quality end point more efficiently, and at less cost, within the overall dual nutrient approach. Provisions of the Chesapeake TMDL provide flexibility in achieving the water quality standards in a more efficient and most cost-effective manner, while providing equally environmentally protective solutions. The provisions allow

exchanges of N and P loads within each basin and exchanges of nutrient loads between basins. A necessary condition for either exchange is that the exchanges do not cause a violation of water quality standards anywhere in the tidal Chesapeake or watershed. Both exchange approaches require a robust model to assess the influence on DO and chlorophyll-*a* water quality in different regions of the Bay and to insure the water quality standards are met. A number of Bay jurisdictions were already implementing separate water quality trading programs

using either a trading approach between point sources or by allowing trades between point source and nonpoint source nutrient loads [7].

In some basins, the operational costs of point source or nonpoint source nutrient reduction practices can be lowered by emphasizing either P or N load reductions. In many of the Watershed Implementation Plans (WIPs), which are the multiyear plans of implementation of the TMDL allocation's nutrient and sediment reductions, the N and P exchanges within a basin were done at the end of the WIP development as a standard practice. This is because the WIPs often have a number of practices that are added up in a watershed in order to reach the N and P load targets required under the TMDL. The N and P load reductions from the sum of these practices rarely hit both the N and P targets exactly. Usually, either the N or P target is reached first, generating an overshoot in the nutrient load as practices continue to be added in order to meet both nutrient targets. While an overshoot in a nitrogen or phosphorus nutrient target is not a problem per se, it does lead to excessive cost. To avoid excessive cost from nutrient overshoots, N and P exchanges are commonly used, ensuring that all Chesapeake water quality standards are achieved in a most efficient manner.

The relative importance of N or P limitation on primary production in the Chesapeake has been well studied by foundational work by a number of researchers [8–13]. D'Elia et al. [9] used bioassays to analyze seasonal and spatial differences in nutrient limitation in the Chesapeake. Boynton et al. [14, 15] described the process of benthic pelagic nutrient coupling in the Chesapeake which formed the basis for observed seasonal differences in nutrient limitation. Fisher et al. [10] described seasonal shifts from P in the spring to N in the summer as the nutrient limiting the accumulation of algal biomass in the Chesapeake Bay, and established that nutrient limitation of phytoplankton growth rates exert primary control over biomass accumulation. Kemp et al. [13] in a seminal synthesis examined Chesapeake nutrient limitation within the context of a wide sweep of ecological history.

Extending this work with model estimates of Chesapeake nutrient limitation, Wang and Linker [16, 17] analyzed P and N limitations with respect to algal growth in the Chesapeake estuary and analyzed the feasibility of exchanges in N versus P load reductions showing that in some regions of the upper Bay, one mass unit of P reduction can be compensated with five mass units of N increase and still achieve the same model estimated DO concentration response. As suggested by Wang et al. [16], separate N or P loads of geographically isolated scenarios can be useful for analyzing the relative influence of N versus P controls from different load sources and basins on Chesapeake water quality standards. This article analyzes the relative influences of N and P loads from 16 major basins (Fig. 2)

on dissolved oxygen to examine alternative N and P reduction approaches. Geographically isolated loading scenarios of N or P load change were used to assess relative strengths in N versus P limitation to algal growth and the subsequent influence on dissolved oxygen in the Bay's critical designated-uses, and to provide suggestions on the relative emphasis of N versus P control to achieve a cost-effective nutrient management strategy.

2 Method

2.1 The Estuarine Water Quality Model

2.1.1 Model Description

The relative impacts of N and P loads on DO were estimated using an estuarine water quality model, called the Chesapeake Bay Water Quality and Sediment Transport Model (WQSTM). The WQSTM is a coupled CH3D hydrodynamic model and ICM water quality model [18]. The 2010 version of the model consists of 56,920 model cells with 11,064 surface cells and up to 19 vertical layers. The average cell dimension is about 1 km by 1 km by 1.5 m in depth. The cell compartments are the control volumes in the algorithms. The hydrodynamic model simulates transport processes in 90-s intervals and provides hydrodynamic forcing for the ICM water quality model.

The WQSTM simulates 36 state variables including various nutrient species and three generalized groups of algae to develop a full carbon-based simulation of DO [18]. The WQSTM simulates nutrient transport and dynamics in the estuary in variable time steps of about 2–5 min. For each control volume, i , and for each state variable, transport and kinetics are calculated based on the mass-conservation equation:

$$\frac{C_i \cdot \delta V_i}{\delta t} = \sum_{k=1}^n Q_k C_k + \sum_{k=1}^n A_k D_k \frac{\delta C_k}{\delta x_k} + S_i \quad (1)$$

in which

V_i =volume of i th control volume (m^3),

C_i =concentration in i th control volume ($g\ m^{-3}$),

t, x =temporal and spatial coordinates,

n =number of flow faces attached to i th control volume,

Q_k =volumetric flow across flow face k of i th control volume ($m^3\ s^{-1}$),

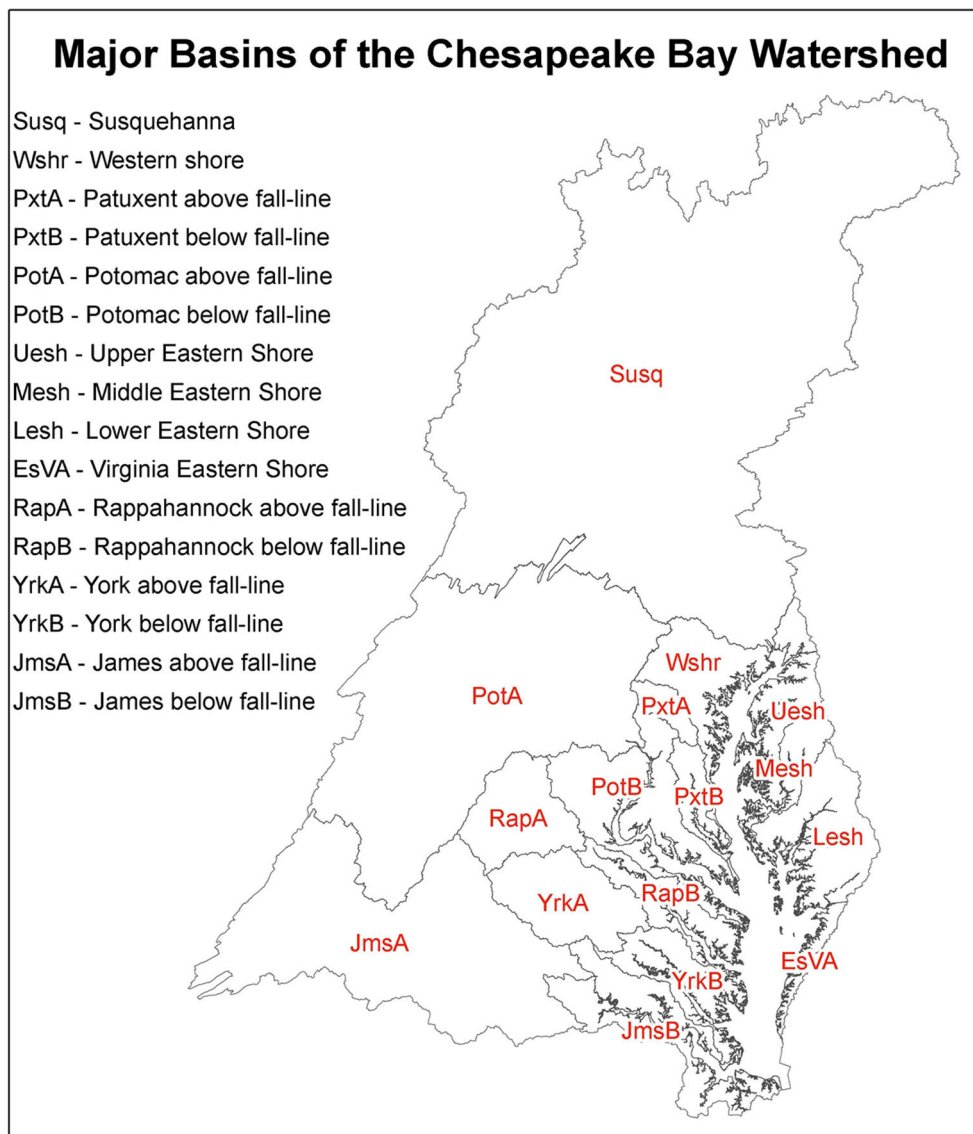
C_k =concentration in flow across face k ($g\ m^{-3}$),

A_k =area of flow face k (m^2),

D_k =diffusion coefficient at flow face k ($m^2\ s^{-1}$),

S_i =summation of external loads and kinetic sources and sinks in i th control volume ($g\ s^{-1}$).

Fig. 2 Chesapeake Bay watershed and major basins



2.1.2 Dissolved Oxygen Simulation

Sources and sinks of dissolved oxygen in the water column considers algal photosynthesis and respiration, heterotrophic respiration, nitrification, chemical oxygen demand, and atmospheric reaeration, as described in the following equation:

$$\frac{\delta DO}{\delta t} = Aocr \cdot [(1.3 - 0.3PN)P - (1 - FCD)BM] \cdot B - Aont \cdot Nt - \frac{DO}{KHodoc + DO} Aocr \cdot Kdoc \cdot DOC - \frac{DO}{KHocod + DO} Kcod \cdot CDO + \frac{Kr}{\Delta z} (DOs - DO) \tag{2}$$

in which
Aocr=dissolved oxygen-to-carbon ratio in respiration (2.67 g O₂ g⁻¹ C),
PN=algal preference for ammonium uptake (0 ≤ *PN* ≤ 1),
P=algal production rate (day⁻¹),

FCD=fraction dissolved organic carbon produced by algal metabolism (0.0),

BM=basal metabolism rate of algae at reference temperature (day⁻¹),

B=algal biomass, expressed as carbon (g C m⁻³),

Aont=mass dissolved oxygen consumed per mass ammonium-nitrogen nitrified (4.33 g O₂ g⁻¹ N),

Nt=nitrification rate (g N m⁻³ day⁻¹),

KHodoc=half-saturation concentration of DO required for oxalic respiration (g O₂ m⁻³),

Kdoc=respiration rate of dissolved organic carbon (day⁻¹),

DOC=dissolved organic carbon concentration (g C m⁻³),

KHocod=half-saturation concentration of DO required for exertion of chemical oxygen demand (g O₂ m⁻³),

Kcod=oxidation rate of chemical oxygen demand (day⁻¹),

COD=chemical oxygen demand concentration (g O₂-equivalents m⁻³),

Kr =reaeration coefficient ($m\ day^{-1}$),
 DOs =dissolved oxygen saturation concentration ($g\ O_2\ m^{-3}$),
 z =vertical coordinate (m).

2.1.3 Algal Simulation and Analysis of Nutrient Limitation

Algal sources and sinks in the conservation equation include production, metabolism, predation, and settling.

$$\frac{\delta B}{\delta t} = \left(G - BM - WS \frac{\delta}{\delta z} \right) B - PR \quad (3)$$

in which

B =algal biomass, expressed as carbon ($g\ C\ m^{-3}$),
 G =growth (day^{-1}), which depends on light, and nutrient of N-P and/or silica (for diatom) are simulated,
 BM =basal metabolism (day^{-1}),
 WS =algal settling velocity ($m\ day^{-1}$),
 PR =predation ($g\ C\ m^{-3}\ day^{-1}$),
 z =vertical coordinate (m).

The three algal groups simulated by the WQSTM are based upon the distinctive characteristics of each group and their role in the ecosystem [19]. The three groups are (1) cyanobacteria, characterized by their ability to fix atmospheric nitrogen and their bloom-forming potential in fresh water; (2) spring diatoms, represented as large phytoplankton that produce an annual bloom in saline portions of the Chesapeake; and (3) green algae, a lumped group representing the general algal community that characterizes saline waters during summer and autumn, and fresh waters year round. The parameter of metabolism at the reference temperature (i.e., 20 °C) for cyanobacteria, diatoms, and green algae were set, respectively, at 0.03, 0.01, and 0.02 day^{-1} . Key parameters used in algal simulations are listed in Table 1. Chlorophyll concentration is used in this article to represent algal populations.

Carbon, nitrogen, and phosphorus are the primary nutrients required for algal growth. Silica is required as well for diatoms. Inorganic carbon is usually available in excess and silica is usually sufficient in the modeled system; therefore, they are not analyzed in this article. The primary limiting nutrients for algal growth in the Chesapeake are N and P. Other than nutrients, light is also a limiting factor of algal growth, and plays an important role in limitation particularly in the tidal fresh and oligohaline regions and is also fully simulated in the model. In low nutrient load conditions such as in the TMDL conditions explored in this article, light limitation is less important and the light condition does not significantly influence the relative strength of N versus P limitations [17]. Thus, light limitation is not further discussed.

The effects of N and P nutrients on growth are described by the formulation commonly referred to as the Monod Equation [20] or the Michaelis-Menten kinetics [21]:

$$G = \frac{D}{KHd + D} G_{max} \quad (4)$$

in which G and G_{max} are the algal growth rate and maximum growth rate, respectively, D =concentration of dissolved nutrient ($g\ m^{-3}$), and KHd =half-saturation constant for nutrient uptake ($g\ m^{-3}$).

In the model, dissolved inorganic nitrogen (DIN) consists of ammonium and nitrate, and dissolved inorganic phosphorus (DIP) consists of orthophosphate. The half-saturation concentration is the key parameter: the growth rate is half the maximum when the available nutrient concentration equals the half-saturation concentration. The KHd has been assessed through various experiments for various environments by researchers [22]. The half-saturation constants for DIN and DIP uptake by algae, i.e., K_{DIN} and K_{DIP} , set in the WQSTM (Table 1) are consistent with the requirements of the calibration to observed algal biomass and nutrients, and to the range of literature values [19,22].

Based on modeled DIN and DIP concentrations and their half-saturation constants, ratios of $DIN/(K_{DIN} + DIN)$ and $DIP/(K_{DIP} + DIP)$ were calculated. According to Liebig's "law of the minimum" [23], algal growth is controlled by the nutrient in the least supply:

$$\min \left(\frac{DIN}{K_{DIN} + DIN}, \frac{DIP}{K_{DIP} + DIP} \right).$$

A nutrient limitation was considered to be at the point of a 50 % reduction in algal growth. Based on modeled daily average DIN and DIP concentrations, a limitation is counted for N if:

$$\frac{DIN}{K_{DIN} + DIN} < \frac{DIP}{K_{DIP} + DIP} \text{ and } \frac{DIN}{K_{DIN} + DIN} < 0.5, \text{ or, for P if:}$$

$$\frac{DIP}{K_{DIP} + DIP} < \frac{DIN}{K_{DIN} + DIN} \text{ and } \frac{DIP}{K_{DIP} + DIP} < 0.5.$$

2.1.4 Nutrient Simulation

The WQSTM simulates nutrient cycles for various N and P species, e.g., ammonium, nitrate, phosphate, and organic nitrogen and phosphorus, in forms of dissolved and particulate, labile, and refractory. The processes of algae and DO described in the previous sections involve reactions with nutrients. The processes of conversion among nutrient species are not further described in this article. The related reactions and parameters can be obtained [18].

Table 1 Key parameters in the simulation of three groups of algae

Key parameters in algal simulation	Algal species		
	Cyanobacteria	Diatom	Green
BM: basal metabolism rate at referred T (day^{-1})	0.03	0.01	0.02
Optimal temperature of algal growth ($^{\circ}\text{C}$)	29	16	30
K_{DIN} : half-saturation concentration (mg l^{-1}) for dissolved inorganic nitrogen (DIN) uptake	0.010	0.025	0.020
K_{DIP} : half-saturation concentration (mg l^{-1}) for dissolved inorganic phosphorus (DIP) uptake	0.0025	0.0025	0.0025
K_{Si} : half-saturation concentration (mg l^{-1}) for Si uptake	0.00	0.03	0.001
Maximum photosynthesis rate ($\text{g C g}^{-1} \text{ Chl day}^{-1}$)	200	300	450
Carbon-to-chlorophyll ratio ($\text{g C g}^{-1} \text{ Chl}$)	37	75	60
Nitrogen-to-carbon ratio ($\text{g N g}^{-1} \text{ C}$)	0.167	0.167	0.167
Phosphorus-to-carbon ratio ($\text{g P g}^{-1} \text{ C}$)	0.0125	0.0125	0.0220
Silica-to-carbon ratio ($\text{g Si g}^{-1} \text{ C}$)	0.0	0.3	0.1
PR: predation rate on algae ($\text{g C m}^{-3} \text{ day}^{-1}$)	0.0	0.01	0.2–0.3
WS: settling velocity (m day^{-1})	0.5	0.0	0.5

2.1.5 Model Skills in Simulations of DO and Chlorophyll-*a*

This work uses modeled chlorophyll-*a* concentration to represent the algal population. The model was calibrated with observed data for 10 years using a 1991–2000 hydrology and loads from the watershed. In the mainstem Bay, in chlorophyll-*a* estimates, the model mean error (ME) and relative error (RE) are $-0.34 \mu\text{g m}^{-3}$ and 53.6 %, respectively. In DO estimates, at depths greater than 6.7 m, the ME and RE are 0.14 g m^{-3} and 11.2 %; at depths between 6.7 and 12.8 m, the ME and RE are 0.30 g m^{-3} and 19.4 %; and at depths greater than 12.8 m, the ME and RE are -0.45 g m^{-3} and 28.7 % [18]. Model simulations in 1985–1990 and 2001–2005 hydrology were also conducted and compared with observations for model verification. The model mean error and relative error in chlorophyll-*a* and DO simulations in the verification periods are similar to those in the calibration period, and even have slightly smaller errors in the verification periods. This may partly be due to less frequent extreme storm events in the verification periods.

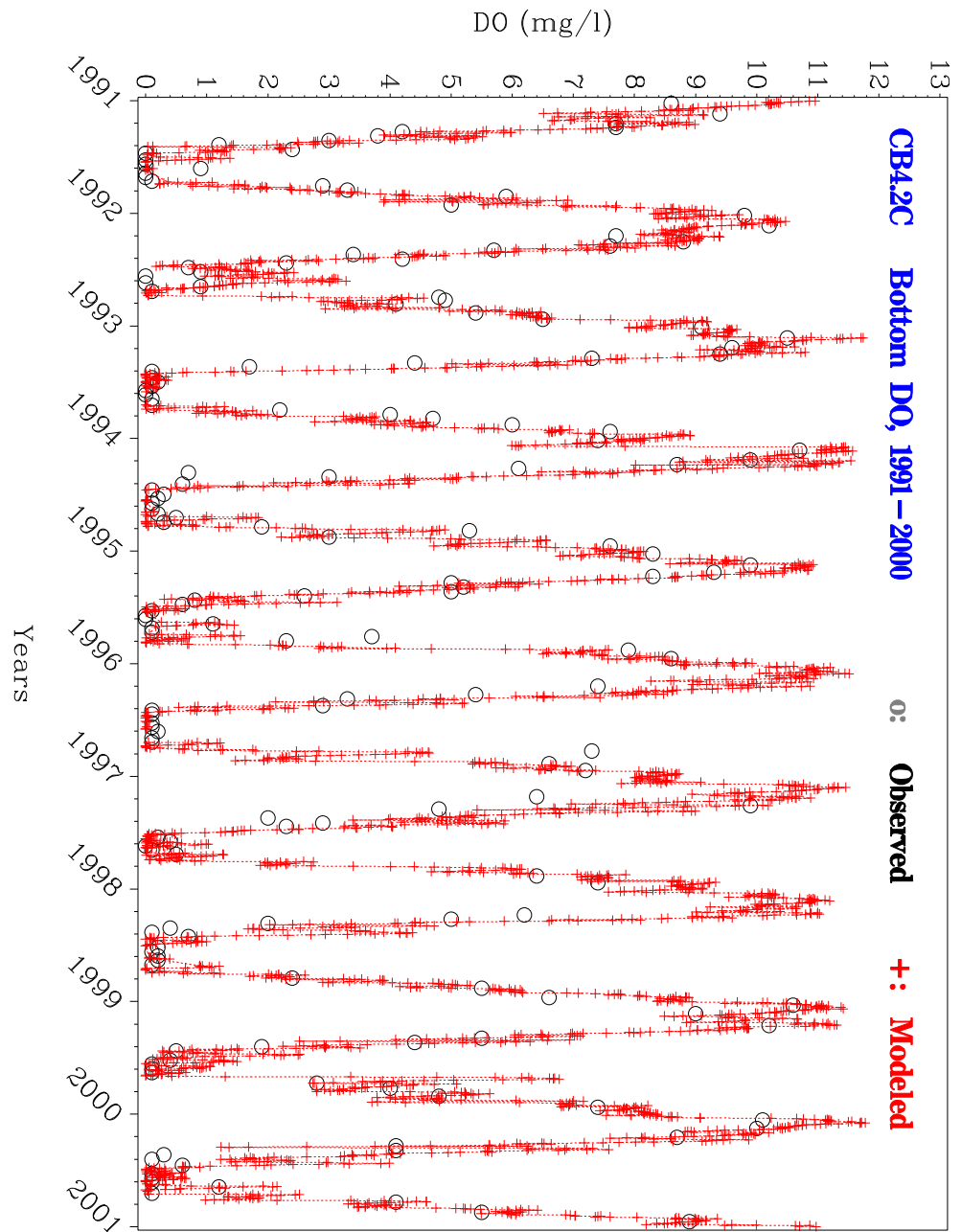
In the statistical assessment of model errors, the comparisons of modeled and observed paired data were selected at the same time and location. The observations used were called the instantaneous samples, which were assumed to represent the conditions at the entire day (or hour) to compare with model averaged daily (or hourly) values. Spatially, a sampling location of a monitoring station was considered to represent the condition in the 1 km^2 approximate area of a model cell. Errors in transport simulation also caused time mismatches between the modeled and observed data. Because of the above factors, the uncertainty in parameter estimates, and other factors, the deviation of the modeled and observed paired was a

20–30 % relative error in DO estimates. Nevertheless, the model estimates were close to the observed values in the one-to-one comparison as an example shown in Fig. 3 for station CB4.2C, which is one of the monitoring stations at the Bay's anoxic center in segment CB4MH—a key segment in the Chesapeake Bay TMDL.

2.2 Model Input of Nutrient Load and Geographic Divisions of Watershed Basins

Distributed daily nutrient and sediment inputs to the WQSTM are estimated from the Chesapeake Bay Watershed Model Phase 5.3 [24–26]. The 2010 Chesapeake Bay TMDL set nutrient reduction goals for major basin-jurisdictions [1,3]. The watershed (Fig. 2) is divided into eight major river or coastal plain basins. Five of the major river basins, the Potomac, Patuxent, Rappahannock, York, and James, are divided by a fall line between the upland Piedmont region and the coastal plain. The portion of the watershed above and including the Piedmont region was designated as the *above-fall-line* (AFL) subbasin, which is characterized by a free flowing river. The *below-fall-line* (BFL) subbasin of the coastal plain is characterized by low-slope rivers and direct drainage to tidal waters. The Susquehanna River basin is only assigned the above-fall-line. Adjacent to the Susquehanna are the below-fall-line area and coastal plain basin of the West Shore and East Shore. The coastal plain of East Shore is divided into four subbasins. This results in the 16 basins shown in Fig. 3. They are Susquehanna (Susq), West Shore (Wshr), Patuxent AFL (PxtA), Patuxent BFL (PxtB), Potomac AFL (PotA), Potomac BFL (PxtB), Upper East Shore (Uesh), Middle East Shore (Mesh), Lower East Shore (Lesh), Virginia East Shore (VaEs), Rappahannock AFL (RapA), Rappahannock BFL (RapB),

Fig. 3 Model simulated versus observed bottom dissolved oxygen at Chesapeake Bay monitoring station CB4.2C from 1991 to 2000. The observations were conducted bi-monthly from March through November and monthly in the winter. The model simulated estimates were daily



York AFL (YrkA), York BFL (YrkB), James AFL (JmsA), and James BFL (JmsB). The nutrient loads from the above-fall-line and below-fall-line of a major basin have different impacts on the estuary. These 16 basins have been used in the development of the Watershed Implementation Plans for the Chesapeake Bay TMDL to assess the relative effectiveness of various management strategies [1,27].

2.3 Model Scenarios

Geographically isolated load scenarios were designed to analyze the impact of the nutrient load on the Bay from each of the 16 basins. A change of nutrient load from a

basin causes changes of chlorophyll-*a* and DO in the Bay's critical designated uses the areas of the Bay that are most prone to anoxia. The geographical relationships of the 16 basins with the Bay's anoxic regions determine the extent of their impacts on Bay's water quality. Analyzing their impacts provides information on the recommendation of allocating nutrient reductions for basin-jurisdictions in the Bay TMDL. The nutrient sources of the major land uses and the management actions available to control the nutrients is a key determinant of the degree of flexibility available for examining more efficient lower cost implementation plans. The basin areas and percent cover of the major land uses are listed in Table 2, columns 2–6.

Table 2 Percent cover of major land use types and annual average N and P loads (tons year⁻¹) for the base scenario and the TMDL Scoping Scenario

Basins	Total area (km ²)	Wood/open (%)	Agricultural (%)	Urban (%)	Water (%)	Base scenario (tons year ⁻¹)		TMDL Scoping Scenario (tons year ⁻¹)	
						N	P	N	P
Susquehanna (Susq)	71,223	73.04	21.19	4.67	1.10	61,608	2,198	36,843	1,303
West Shore (Wshr)	4,120	51.56	17.43	30.07	0.94	8,051	394	4,281	228
Patuxent AFL (PxtA)	910	51.72	20.49	27.16	0.64	651	50	473	36
Patuxent BFL (PxtB)	1,384	64.40	17.58	17.44	0.58	1,101	112	802	72
Upper East Shore (Uesh)	2,809	42.88	50.55	5.89	0.68	3,175	251	1,995	181
Middle East Shore (Mesh)	1,952	42.69	52.06	4.30	0.95	2,094	238	1,311	143
Lower East Shore (Lesh)	5,222	60.39	33.63	3.65	2.33	4,539	411	2,790	261
Potomac AFL (PotA)	29,963	63.35	29.65	6.32	0.68	21,774	1,794	14,793	1,250
Potomac BFL (PotB)	6,786	59.47	15.34	24.51	0.68	12,406	421	5,746	391
Virginia East Shore (EsVA)	840	53.95	41.25	3.08	1.72	1,018	115	580	76
Rappahannock AFL (RapA)	4,134	61.21	35.11	3.27	0.40	2,052	385	1,426	284
Rappahannock BFL (RapB)	2,781	72.50	21.20	5.46	0.84	1,733	178	1,200	119
York AFL (YrkA)	4,859	78.11	17.76	2.67	1.46	1,387	129	1,097	93
York BFL (YrkB)	3,092	76.62	14.93	7.29	1.16	1,961	217	1,317	147
James AFL (JmsA)	21,054	79.49	16.15	3.55	0.81	6,243	1,045	5,731	647
James BFL (JmsB)	5,189	60.95	11.81	25.52	1.72	10,438	917	4,848	416
Total load						140,230	8,860	85,230	5,650

2.3.1 The Reference Scenario

The average annual N and P loads in 1991–2000 for the 16 basins are estimated from the Phase 5.3 Watershed Model calibration base scenario condition (Table 2, columns 7 and 8). Table 2 also has the 2010 Chesapeake Bay TMDL Scoping Scenario which is the “reference scenario,” from which individual geographically isolated scenarios were derived [3]. The reference TMDL Scoping Scenario was one of the early tested scenario loads that achieved Chesapeake DO criteria, but was not the final TMDL load allocation, which was ultimately determined after the work described in this article was completed. This paper uses the model calibration runs, i.e., the base scenario and the reference TMDL Scoping Scenario to analyze nutrient limitation in the mainstem Bay. The geographically isolated loading scenarios are set by changing the N or P load in one of the 16 basins from the reference TMDL Scoping Scenario condition and are used to estimate the response of water quality in the Bay’s CB segments to geographic changes in loading. The reference scenario was the TMDL Scoping Scenario because it is a nutrient load scenario close to the final TMDL loads and is an estimated nutrient load to the Bay where all tidal water quality standards are met [1].

2.3.2 Geographically Isolated Loading Scenarios

A geographically isolated N loading scenario is designed to increase N loads by a relatively small amount called a “standard

weight N-unit” which is 453,600 kg year⁻¹ from the reference TMDL Scoping Scenario condition of one basin, while phosphorus loads from that basin and all N and P loads from other basins are unchanged. The “standard weight N-unit” is about 0.7 % of the total N loads in the TMDL Scoping Scenario (Table 2). Similarly, a geographically isolated phosphorus loading scenario is to increase phosphorus in one basin by a standard weight P-unit of 45,360 kg year⁻¹ from the reference scenario while all other loads are kept at the reference scenario. The P load increase is equivalent to about 0.8 % of the total P loads in the reference scenario. The small amount N or P was added to the reference scenario because the aim of the study was to estimate the DO response to the relatively small amounts of nutrient exchange at the TMDL loading level that would be consistent with the size of nutrient exchanges expected in the WIPs. For each of the 16 major basins, geographically isolated N or P load-increment scenarios were run.

The 10:1 weight ratio of N to P (453,600 kg year⁻¹ for N and 45,360 kg year⁻¹ for P) was chosen as the nutrient increment in the scenarios because it was between the Redfield ratio of 7.2:1 in N to P weight ratio (which is 16:1 for the stoichiometric N to P ratio) [28] and the TMDL load ratio of roughly 15:1 in N to P weight ratio [29].

Three types of geographically isolated scenarios were designed.

Single nutrient geographically isolated scenarios are an increase only in N or P for a specified basin in one standard weight N- or P-unit which is symbolized as N \uparrow or P \uparrow ,

respectively. Single nutrient scenarios are used to analyze relative effects on the critical designated-uses by N versus P load from a basin, and relative impacts on the critical area by different basins under a same amount change in N or P load. The scenario name is composed of two parts, basin's name and symbol of nutrient change, which are separated by a dash. For example, for a single nutrient scenario, Susq-N↑ is a scenario that the N load from the Susquehanna Basin increases one standard weight N-unit beyond the reference TMDL Scoping Scenario. The same way in scenario naming is applied to other types of geo-scenarios. Table 3 lists and describes the scenario names that appear in the presented figures.

In an *N-P exchange* scenario, one nutrient is decreased by one standard weight while the other is increased by one standard weight. We use symbol of N↑P↓ if load from the source basin increases in N and decreases in P, and use symbol of N↓P↑ if load from the source basin decreases in N and increases in P. The N-P exchange scenarios are used to analyze which direction of N and P exchanges, i.e., N versus P in decrease or increase, from a basin would result in water quality improvement.

Single nutrient and N-P exchange scenarios reduce or increase nutrient species by the same fraction for all constituent species, but these fractions vary across basins according to the physical and anthropogenic characteristics. For a standard weight unit of N or P load increment, the amounts of changes in organic nutrient loads are thus different in different basins. The organic carbon (OrC) is also changed proportionally to the organic nitrogen load change. Changes in organic carbon load have an effect on sediment oxygen demand which in turn affects DO. In order to isolate the effect on DO brought about by dead

algae via utilization of inorganic nutrient loads from the effect on DO by the oxygen demand due to organic load, *inorganic exchange* scenarios were developed. Inorganic exchange scenarios are similar to N-P exchange scenarios in that the one nutrient is increased by a standard weight while the other is decreased, but for inorganic exchanges scenarios, these changes are applied to dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) loads only with no change in the organic nutrient load. An "O" is used as an additional suffix to N-P exchange scenario name for an inorganic exchange scenario. For example, inorganic exchange scenario Susq-N↑P↓_O is modified from a N-P exchange scenario Susq-N↑P↓ by keeping organic material loads at the reference TMDL Scoping Scenario while increasing DIN and decreasing DIP loads from the Susquehanna basin.

2.4 Data Treatment on Model Results of Chlorophyll-*a* and DO to Analyze the Impact of Load

An average summer DO in a designated-use was calculated based on the average of the lower 25th percentiles of the simulated hourly DO concentrations in individual cells. The 25th percentile was used as the metric of relative change to avoid influences with supersaturation or oxygen demand below 0 mg l⁻¹ DO. The change of modeled DO in a loading scenario versus a reference scenario was symbolized as dDO. A similar approach was used for chlorophyll-*a*. An average spring and summer chlorophyll-*a* concentration for surface waters of a CB segment was calculated based on the average of the lower 75th percentiles of the model simulated daily chlorophyll-*a* in the surface cells of the CB segment.

Table 3 Descriptions of scenario names used in the figures

Basin scenario	Description for basin-scenario names	Note
Susq-N↑	Increase N load in 1 s.w.N from the Susquehanna Basin (Susq)	Single nutrient.
Susq-P↑	Increase P load in 1 s.w.P from the Susquehanna Basin (Susq)	Similarly is for other basins in Fig. 5
Susq-N↑P↓	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the Susquehanna Basin (Susq)	N-P exchange
Susq-N↑P↓_O	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the Susquehanna Basin, while organic nutrient load unchanged	Inorganic exchange
Mesh-N↑P↓	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the Middle Eastern Shore Basin (Mesh)	N-P exchange
Mesh-N↑P↓_O	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the Middle Eastern Shore Basin (Mesh), while organic nutrient load unchanged	Inorganic exchange
Wshr-N↑P↓	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the Western Shore Basin (Wshr)	N-P exchange
YrkB-N↑P↓	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the York below-fall-line basin (YrkB)	N-P exchange
YrkB-N↑P↓_O	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the York below-fall-line basin (YrkB), while organic nutrient load unchanged	Inorganic exchange
JmsB-N↑P↓	Increase N load in 1 s.w.N, and decrease P load in 1 s.w.P from the James below-fall-line basin (JmsB)	N-P exchange

s.w.N is the "standard weight N-unit," i.e., 543,600 kg year⁻¹; s.w.P is the "standard weight P-unit," i.e., 54,360 kg year⁻¹ from a specific basin

The 75th percentile of chlorophyll-*a* was used as the metric of relative change to avoid the confounding influences of occasional extreme chlorophyll-*a* peaks due to algal blooms. The change of modeled chlorophyll-*a* in a loading scenario versus the reference scenario was symbolized as dChl.

3 Results and Discussion

3.1 Nutrient Limitation on Algal Growth

Based on results from the Model Calibration and Reference TMDL Scoping Scenario, nutrient limitations on algal growth were investigated. Table 4 lists the extent of simulated nutrient limitation in spring and summer for the loads in model calibration of 1991–2000 and under the reference TMDL Scoping Scenario condition, respectively. They are based on WQSTM estimated DIN and DIP concentrations in the CB segments for the months of March through September. The spring and summer months were chosen because they cover the period of Chesapeake deep water hypoxia and are the period covered by the TMDL DO water quality standard. Limitation by light and silica are unquantified in Table 4.

The counts of nitrogen (N) limitation and phosphorus (P) limitation are for euphotic model cells in the top three layers (representing the water that is within 4.5 m of the surface) for each CB segment in the spring (March to May) and summer (June to September) months in the 1991–2000 simulation period (Table 4). The extent of limitation in Table 4 is expressed as a percentage which is equal to the counts of cells–days limitation divided by 2140 days and the number of cells in the CB segment. Figure 4 is a plot of

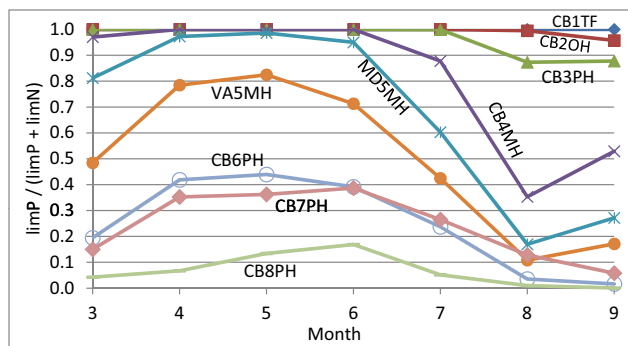


Fig. 4 Spring and summer monthly variation in relative P limitation (limP) versus N limitation (limN) in the mainstem CB segments

$P_{limitation} / (P_{limitation} + N_{limitation})$ based on monthly $P_{limitation}$ and $N_{limitation}$ counts from the model calibration. A value greater than 0.5 is taken as an indication that the CB segment in the month is predominantly P limited; otherwise, it is predominantly N limited. It is interesting to note in Table 4 that in all cases, the extent of limitation is increased by the TMDL Scoping Scenario as compared to the calibration condition, and in almost all cases, the direction of the limitation (N or P limited) is reinforced by the reduced nutrient loads of the TMDL Scoping Scenario. That is to say, the TMDL nutrient reduction reinforced the estimated existing nutrient limitations in all mainstem CB segments. The upper Bay is generally P limited in the calibration conditions and remains so in the TMDL Scoping Scenario, only more so. Likewise, the prevailing N limitation in the lower Bay is only reinforced and made deeper by the TMDL Scoping Scenario's load reductions.

The majority of land-source nutrients from the Chesapeake watershed have an N/P ratio greater than Redfield, while the

Table 4 Percent N or P limitations in mainstem CB segments

Mainstem segment	Average condition in 1991–2000				TMDL Scoping Scenario			
	Limit counts		Percent limited		Limit counts		Percent limited	
	N	P	N	P	N	P	N	P
C11TF	0	980	0.0	46	0	1715	0.0	80
C12TF	0	1245	0.0	58	0	1655	0.0	77
CB2OH	0	333	0.0	16	0	1282	0.0	60
CB3MH	3	280	0.1	13	14	959	0.7	45
CB4MH	81	745	3.8	35	145	1528	6.8	71
MD5MH	318	849	15	40	695	1219	32	57
VA5MH	734	746	34	35	1271	754	59	35
CB6PH	1204	390	56	18	1606	444	75	21
CB7PH	1259	404	59	19	1680	377	79	18
CB8PH	1590	108	74	5.1	1981	60	93	2.8

The total counts (after normalized by cell numbers of CB segment) for each case are 2140, equivalent to total 2140 days in March through September of 1991–2000

ocean source has a lower N/P ratio. From the upper Bay to the lower Bay, the mainstem CB segments (in the order from CB1TF to CB8PH) change from predominantly being P limited to predominantly being N limited (Fig. 4). Segment CB4MH in the mid-upper Bay is predominantly P limited for much of the year. Despite the dominant P limitation in CB4MH, there are still widespread occurrences of N limitation in CB4MH which are mainly in the cells of the southern portion of the CB segment, where saline water intrusion from the lower Bay plays a larger role, as well as the segment-wide N limitation in August (Fig. 4). On the other hand, CB6PH in the lower Bay is consistently N limited. The overall spatial and seasonal pattern of nutrient limitation estimated by the model is comparable to that from observations and literature [9–13], providing additional confidence in the model analysis. Nevertheless, the model features of limitation may fail to match the cited research in all details perhaps because of different metrics of limitation as well as differences in where and when nutrient limitation was measured.

3.2 DO Responses in Single Nutrient Geographically Isolated N- or P-Increment Scenarios and Potential Implications for Water Quality Management

The designated-use of CB segment CB4MH deep water requires the largest nutrient reduction in order to attain the DO criteria among the mainstem Bay CB segments, and because of this, it is the focus of this study in DO responses to nutrient loads. Figure 5 illustrates changes of DO (dDO) versus the reference scenario in deep water of CB4MH due to either increasing N at one standard weight N-unit (N↑) or increasing P at one standard weight P-unit (P↑) from the 16 basin sources. Figure 5 shows that the relative effects on CB segment CH4MH by N and P loads among basins are high variability. Generally, load changes from the northern basins, e.g., Susq and Wshr (Fig. 2), are more effective than those from the southern basins. This is because the southern basins are closer to the ocean boundary; therefore, the N and P from the southern basins have shorter residence time in the Bay and, thus,

have a weaker influence on the Bay's eutrophication processes.

The results in Table 5 show similar relative effects on DO by nutrient loads from the major basins as described in Wang et al. [30]. In the analysis by Wang et al. [30], N and P loads were integrated as a single weight nutrient load $((N+10 P)/2)$ [29] and showed relative impacts of DO in deep water of CB4MH by the change in the integrated nutrient load from basins. The work described in this article further analyzes DO effects by differentiating N and P loads. Columns 2 and 3 of Table 5 tabulate the DO change in the deep water of CB segment CB4MH shown in Fig. 5 for the N or P geo-scenarios there were added one standard weight N-unit of N-load or P-unit of P-load into a specific basin's load. Table 5 can be a useful guide to approximate DO improvements in segment CB4MH at the overall nutrient load inputs to the Chesapeake with changes in either N or P loads from a particular basin, as described in the following.

Column 4 of Table 5 is calculated by 10 times column 3 then divided by column 2, which is unitless, representing the ratio of DO changes by a same mass of total nitrogen (TN) versus total phosphorus (TP) load changes. The factor 10 is used because a standard weight N-unit is 10 times the standard weight P-unit, which is the added load respectively in the paired single nutrient N↑ and P↑ geographic scenarios from each individual basin (Fig. 5). The fractions of DIN/TN or DIP/TP in the load are different among the basins (Table 5, columns 5 and 6), which are based on the nutrient compositions in the reference TMDL Scoping Scenario. Although in the single nutrient geographic scenarios set, the same amount of TN (or TP) load was changed for all basins, the changes in inorganic nutrient loads are different. In order to analyze the impact of changes in inorganic N versus inorganic P on algal growth and DO, column 7 is derived:

$$\text{Column 7} = 10 \frac{\text{column 3} / \text{column 2}}{\text{column 6} / \text{column 5}}$$

Fig. 5 Effects on DO in CB4MH-Deep Water due to load increment in one standard weight N-unit or one standard weight P-unit from individual basins

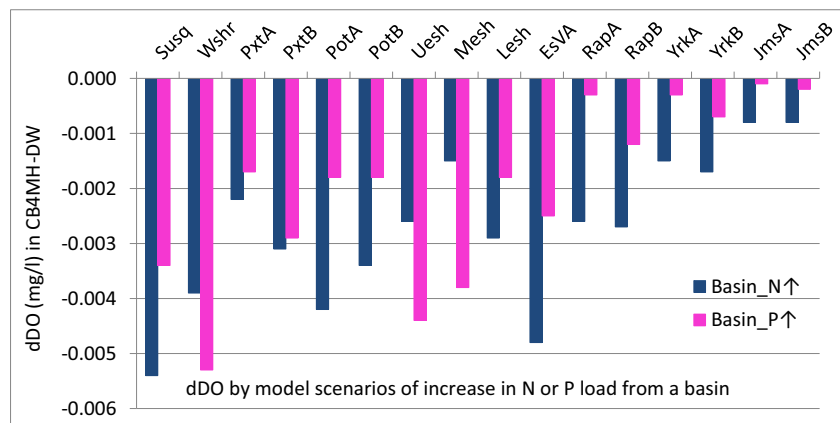


Table 5 Effect of DO change (dDO) in CB4MH-DW by N and P changes from sources

Basins	dDO (mg l ⁻¹)		dDO ratio by weight unit dTP/dTN	Percent DIN in the added 1 s.w.N	Percent DIP in the added 1 s.w.P	dDO ratio by weight unit dDIP/dDIN
	After adding 1 s.w.N	After adding 1 s.w.P				
Susquehanna (Susq)	-0.0054	-0.0034	6.30	55.99	25.70	13.72
West Shore (Wshr)	-0.0039	-0.0053	13.59	67.37	53.61	17.08
Patuxent AFL (PxtA)	-0.0022	-0.0017	7.73	54.32	29.82	14.08
Patuxent BFL (PxtB)	-0.0031	-0.0029	9.35	62.75	56.69	10.35
Upper East Shore (Uesh)	-0.0026	-0.0044	16.92	60.39	62.95	16.23
Middle East Shore (Mesh)	-0.0015	-0.0038	25.33	59.86	65.54	23.14
Lower East Shore (Lesh)	-0.0029	-0.0018	6.21	59.23	64.34	5.71
Potomac AFL (PotA)	-0.0042	-0.0018	4.29	69.32	36.90	8.05
Potomac BFL (PotB)	-0.0034	-0.0018	5.29	68.16	56.10	6.43
Virginia East Shore (EsVA)	-0.0048	-0.0025	5.21	66.37	80.53	4.29
Rappahannock AFL (RapA)	-0.0026	-0.0003	1.15	49.73	87.60	6.55
Rappahannock BFL (RapB)	-0.0027	-0.0012	4.44	60.31	70.66	3.79
York AFL (YrkA)	-0.0015	-0.0003	2.00	50.23	26.64	3.77
York BFL (YrkB)	-0.0017	-0.0007	4.12	64.82	64.58	4.13
James AFL (JmsA)	-0.0008	-0.0001	1.25	39.74	22.26	2.23
James BFL (JmsB)	-0.0008	-0.0002	2.50	71.03	60.44	2.94

s.w.N is the “standard weight N-unit,” i.e., 543,600 kg year⁻¹; s.w.P is the “standard weight P-unit,” i.e., 54,360 kg year⁻¹ from a specific basin

in which columns 5 and 6 are the percent DIN and DIP in the added standard weight N-unit of N and P-unit of P, respectively; the inorganic portion of the nutrient load is based on the average nutrient composition of each individual basin's annual average load in the reference TMDL Scoping Scenario in its 1991–2000 hydrology. Column 7 is non-unit and is the ratio of DO changes by any weigh-unit (kilogram or ton or pound, etc.) load changes in DIN versus DIP. The value, for example 8.05, in column 7 for Basin PotA indicates that the change of DO in deep water of CB4MH would be the same by reducing either 1 weight of DIP or 8.05 weight of DIN from the source-basin PotA. Because DIN and DIP are the active nutrient components in algal utilization, and, subsequently, the algal metabolism impact DO, the change in algae and DO is highly related to dissolved inorganic nutrient load. The weight ratio of DIN/DIP taken up by algae can be assumed in the Redfield weight ratio of 7.2:1 [28]. Thus, *the basin having a value of DIN/DIP greater than 7.2 in column 7 indicates that the nutrient supplying to algae from the basin is in short of DIP, thus is likely to cause P limitation to algal growth. This suggests that controlling DIP load could be more effective than controlling DIN load for the basin.* Therefore, column 7 is also called the DO-effectiveness ratio by DIP versus DIN load reduction.

In addition, the effects of the geographically isolated scenarios have been demonstrated to be additive, but these results are not shown in this article due to space

limitations. The additive effects can be generalized as (1) if N and P load changes in two basins cause similar effects, i.e., both increase or both decrease DO, the load changes from the two basins would increase the relative effect in a predictable additive manner; and (2) conversely, if changes in two basins' N and P loads result in antagonistic effects, the load changes from two basins would tend to cancel their influence on DO concentrations. Similar effects are in chlorophyll-*a* responses to two basins' N/P load changes: to be either intensified or canceled each other out. The additive feature allows an exchange of a specified amount of required reduction for a nutrient component (e.g., N) from one basin with a certain amount of reduction for the same nutrient component from another basin. The calculation of the exchange rate is based on the ratio values in column 3 (for P) or column 2 (for N) of Table 5 for the two basins. For example, the PxtA (Patuxent AFL) basin could exchange 1 ton of P reduction with the Susquehanna basin (Susq) if the Susquehanna basin reduced an additional 0.5 ton of P load. The exchange between the two basins would have no estimated impact on DO hypoxia in the deep water of CB4MH. The calculation is based on column 3 of Table 5: the DO decreases in CB4MH-DW are -0.0034 and -0.0017 mg l⁻¹, respectively, after adding 1 standard-weight-P of P load from the Susquehanna basin and the Patuxent AFL basin. In other words, the DO increments in CB4MH-DW are 0.0034 and 0.0017 mg l⁻¹,

respectively, after reducing 1 standard-weight-P of P load from the Susquehanna basin and the Patuxent AFL basin. The exchange for 1 ton less P reduction from the Patuxent AFL basin needs the Susquehanna to have more P reduction by $1 \text{ ton} \times (0.0017/0.0034) = 0.5 \text{ ton}$.

3.3 Chlorophyll Responses in N-P Exchange and Inorganic Exchange Geo-scenarios for N-P Load Exchange with a Single Basin

The results from the pair scenarios “N↑P↓” and “N↓P↑” for a specific basin’s load are essentially mirror images. For example, if a N↑P↓ scenario causes chlorophyll-*a* to increase, its counterpart N↓P↑ scenario would likely cause chlorophyll-*a* to decrease by a similar amount. The same effect occurs for DO. Therefore, the following discussion using the N↑P↓ scenarios will be applicable to both “N↑P↓” and “N↓P↑” cases. The responses of spring and summer chlorophyll-*a* concentrations in a CB segments to N-P load changes are almost the same in their change trends. Only spring chlorophyll-*a* is presented in the following.

Figures 6 and 7 are estimated spring chlorophyll-*a* changes in surface water of mainstem CB segments by nutrient loading change from the source basins in the upper and lower Bay, respectively. Increasing one standard weight N-unit (453, 600 kg year⁻¹) and decreasing one standard weight P-unit (45,360 kg year⁻¹) from either an upper or lower Bay’s source, i.e., N↑P↓, causes the P-limited upper Bay’s CB segments (CB1TF–CB4MH) to decrease chlorophyll-*a* and the N-limited lower Bay’s CB segments (CB6PH–CB8PH) to increase chlorophyll-*a*. This provides two insights for water quality management. (1) The existing nutrient limitation of a CB segment is the intrinsic factor governing the primary production to increase or decrease. If a CB segment is predominantly P limited, in these N↑P↓ scenarios the decreased P load becomes more important than the increased N load to influence the CB segment’s primary production, thus reducing

primary production; if a CB segment is predominantly N limited, in these N↑P↓ scenarios the increased N load becomes more important than the decreased P load to influence the CB segment’s primary production, thus increasing the primary production. This is because in these N↑P↓ scenarios, the weight ratio of the increased N and decrease P is close to the system’s N/P ratio and the Redfield ratio. Thus, in the actual management, it will be more effective to decrease the limiting nutrient component more from the target segment. (2) The geographic location of the sources relative to the CB segment determines the relative intensity of the effect. For example, the upper Bay’s basins influence segment CB4MH more than the lower Bay’s basins, which is due in part to the longer transit and residence time of nutrients in the estuary for loads from the upper Bay’s basins.

The chlorophyll-*a* concentrations in the paired scenarios with and without changes in the organic matter load (e.g., scenarios Mesh-N↑P↓ and Mesh-N↑P↓_O, respectively) are similar due to the same amount of DIN and DIP loads. The slight difference in chlorophyll-*a* concentrations is due to the difference in organic nutrient loads, a portion of which is converted into inorganic nutrients.

3.4 DO Responses to Changes of Nutrient Load and Primary Production—Based on N-P Exchange and Inorganic Exchange Geo-scenarios for N-P Exchange with a Single Basin

Figures 8 and 9 are DO changes in deep water of mainstem CB segments, responding to nutrient load changes from source basins in the upper Bay and the lower Bay, respectively. The deep water designated-use is absent in CB1TF, CB2OH, and CB8PH and so are not shown in Figs. 8 and 9.

Examining first the response of DO in segment CB4MH from the inorganic exchange scenarios, i.e., increasing DIN and decreasing DIP without changing the organic load,

Fig. 6 Chlorophyll-*a* concentration changes in mainstem CB segments by nutrient load changes from the Upper Bay’s basins. The counterpart scenarios, with or without ending “_O,” have the same change in dissolved inorganic nutrients, while the former also changes in organic load from the reference scenario

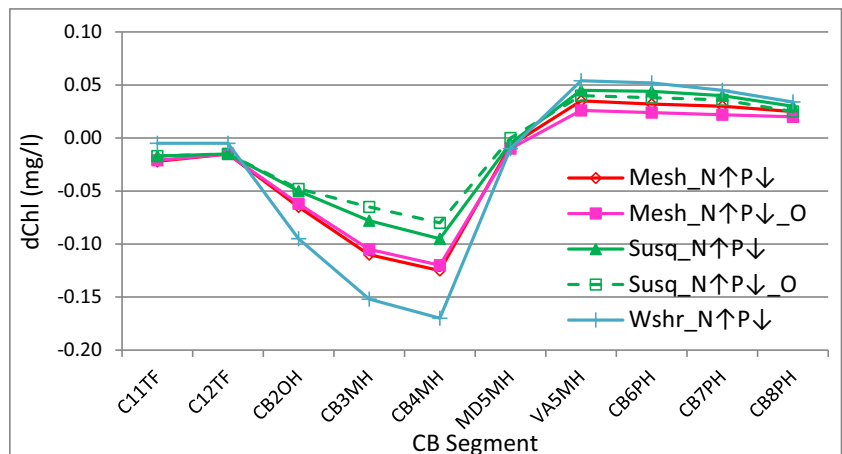
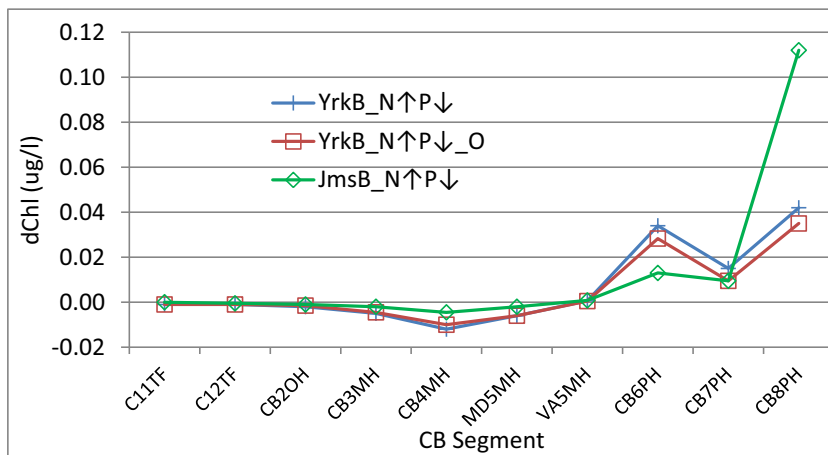


Fig. 7 Chlorophyll-*a* concentration changes in mainstem CB segments by nutrient load changes from the lower Bay's basins sources. The counterpart scenarios, with or without ending “_O,” have the same change in dissolved inorganic nutrients, while the former also changes in organic load from the reference scenario



N↑P↓_O, finds that increasing DIN and decreasing DIP without changing the organic load from the Susquehanna basin or Middle East Shore, i.e., scenario Susq-N↑P↓_O or Mesh-N↑P↓_O, intensifies P limitation in the upper Bay. This is seen as reduced algae as measured by chlorophyll-*a* concentrations from the reference TMDL Scoping Scenario, i.e., the distance from zero (Fig. 6) as well as higher summer DO (Fig. 8) in CB4MH deep water. Their counterpart N-P exchange scenarios with increasing organic N and decreasing organic P loads besides increasing DIN and decreasing DIP, i.e., scenario Susq-N↑P↓ or Mesh-N↑P↓, reduce slightly less algae, i.e., have slightly more chlorophyll-*a* than scenario SuN↑P↓_O or MeN↑P↓_O (Fig. 6), because less DIP was converted from the reduced organic P load. This indicates that for the simulated results, the inorganic nutrient for algae growth is mainly from the watershed load, while its conversion from organic nutrient is less important in CB4MH. The Susquehanna scenario Susq-N↑P↓ has more organic matter load associating the increase in organic N load, causing decreased DO in deep water of CB4MH (Fig. 8). This indicates that the model calculates organic matter loads from the Susquehanna basin which plays an important role in exhausting CB4MH deep water hypoxia.

Increasing DIN and decreasing DIP without changing organic loads from the lower Bay's basin York BFL, i.e., scenario YrkB-N↑P↓_O, also intensifies estimated P limitation in CB4MH, causing fewer algae (i.e., chlorophyll-*a*, distance from zero) in CB4MH (Fig. 7). However, it yields lower summer DO (Fig. 9), which is not related to algal production in the CB segment itself but is influenced by the higher algal production in the lower Bay's CB segments. Decreasing P and increasing N from basins in the lower Bay causes more algal biomass in the N-limited lower Bay's CB segments of CB6PH and CB7PH (Fig. 7). The transport of organic oxygen demand up-estuary-ward in bottom currents [31,32] increases bottom oxygen demand in CB segment CB4MH, causing lower DO in scenario YrkB-N↑P↓_O. Its counterpart scenarios with increased organic matter loads, i.e., scenario YrkB-N↑P↓, causes similar levels of changes in algae, but reduces more DO due to the oxidation of organics in segment CB4MH.

The close relationship between DO responses with N or P load change and with the algal responses can also be observed in the lower Bay's segment. Segment CB6PH is in the lower Bay, where it is predominantly N limited. Increasing N and decreasing P without or with changing organic load from the lower Bay's basin York BFL or James BFL (i.e., scenario

Fig. 8 DO changes in deep water mainstem CB segments by nutrient load changes from the Upper Bay's basins. The counterpart scenarios, with or without ending “_O,” have the same change in dissolved inorganic nutrients, while the former also changes in organic load from the reference scenario

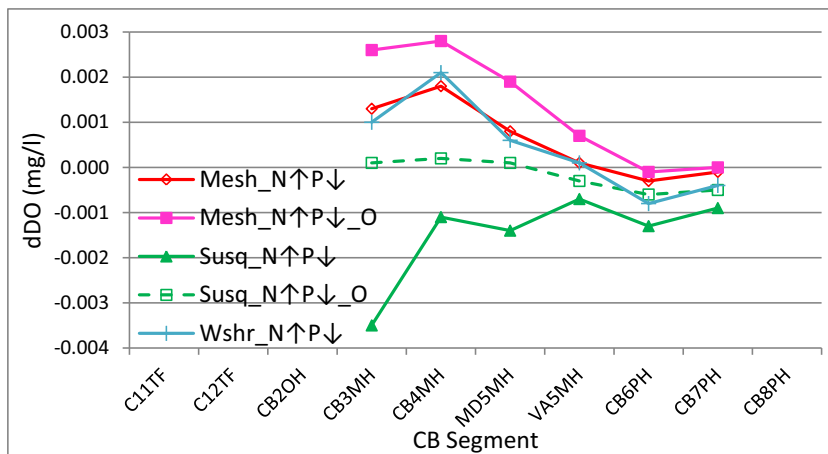
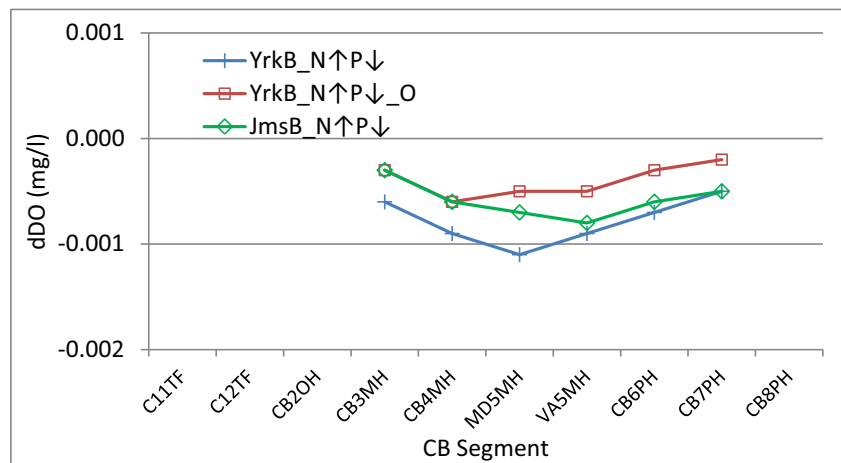


Fig. 9 DO changes in deep water mainstem CB segments by nutrient load changes from the Lower Bay's Basins. The counterpart scenarios, with or without ending “_O,” have the same change in dissolved inorganic nutrients, while the former also changes in organic load from the reference scenario



Yrkb-N↑P↓_O or Yrkb-N↑P↓ or Jmsb-N↑P↓) reduces the N limitation in deep water of CB6PH, causing more algae in the spring (Fig. 7) and summer and lower summer DO (Fig. 9).

Similarly, increasing DIN and decreasing DIP with or without changing the organic load from most upper Bay's basins, e.g., the Susquehanna basin (scenarios Susq-N↑P↓_O and Susq-N↑P↓), Middle Eastern Shore (scenarios Mesh-N↑P↓_O and Mesh-N↑P↓), and the Western Shore (scenario WsN↑P↓), also reduces estimated N limitation in CB6PH and increases algae in the spring (Fig. 6) and in the summer, and lowers summer DO (Fig. 8) in CB6PH deep water. The increase of DO in deep water of segment CB4MH by about 0.002 mg l⁻¹ by scenario Wshr_N↑P↓ (Fig. 8) suggests that a proper N-P load exchange will not degrade DO water quality and may reduce cost. The application to management will be further discussed in later sections.

3.5 DIN and DIP Controls Versus TN and TP Controls

The decay of organic material generates oxygen demand and depletes DO, especially in summer deep waters. Reducing DIP or DIN loads could intensify nutrient limitation and reduce primary production in the Bay. Consequently, the reduction of algal biomass and oxygen demand will improve DO. The effects on DO are different among individual CB segments and are more complicated than the algal responses to inorganic nutrient loads. The bottom organic matter impact DO in a CB segment can come from autochthonous primary production in the CB segment, or can be allochthonous organic material imported from other CB segments or from the watershed. In addition, the DO of a CB segment designated-use can be influenced by the DO conditions of adjacent CB segments due to wind mixing and estuarine circulation. Considering biochemical reactions in daily or monthly or seasonal time frame, we may need to pay more attention to DIN and DIP components in the watershed loads. However, considering the relatively long residence time (e.g., about 6 months,

with longer times for particulate organic matter than dissolved components) in the Chesapeake estuary [33] and conversions between organic and inorganic components, total nitrogen (TN) and total phosphorus (TP) loads have been used to allocate N and P loads among basins and states in Chesapeake Bay management [34]. This article quantifies the contribution to hypoxia in the Chesapeake from both inorganic nutrient and oxygen demanding organic loads. Analyzing the roles by individual organic and inorganic nutrient components in the simulation and their conversions could provide a more accurate assessment of their influence on Chesapeake hypoxia, and detailed analysis of simulated primary production, respiration, or oxygen release via photosynthesis, and estuarine circulation would improve understanding; however, these topics are beyond the scope of this work as is associated data mining of the observed data that could potentially corroborate the model analysis of nutrient limitation and Chesapeake deep water hypoxia.

3.6 Challenges of N-P Exchanges in Estuaries

In the Chesapeake, the upper Bay is usually P limited (Table 4, Fig. 4), while the southern Bay is usually N limited. This observation provides an opportunity to examine potential alternatives to attaining the water quality standards of the TMDL through strategic nutrient control on multiple sources, i.e., from the 16 major basins. Three alternatives in N and P control are considered.

1. Alternative 1 keeps the current nutrient reduction plans. The 2010 Chesapeake Bay TMDL Scoping Scenario loads have about 60 % nutrient reduction from the 1985 level targeting attainment of DO standard in critical zones of the Bay [3]. This nutrient control strategy keeps the ongoing practice [34] that pays similar attention to both N and P reductions. The advantages to this approach are that provisions have already been made for N and P

exchanges which already lead to more efficient WIPs through N to P exchanges within a basin and N to P exchanges between basins.

2. Alternative 2 would be to focus on a single nutrient such as increasing N limitation throughout the Bay, concordant to the water from the ocean to have N/P weight ratio less than 7. But success with this strategy is likely to be elusive because this is in conflict to the need for P control in large areas of the watershed and in the tidal fresh and oligohaline regions of the Bay and runs counter to the established advantages of dual nutrient control in the Chesapeake [35].
3. Alternative 3 is to systematically and strategically reduce P in the upper Bay and N in the lower Bay. Much work would be needed to develop this strategy. The feasibility of an upper Bay and lower Bay N-P load exchange is dependent on the relative costs in reducing DIN and DIP loads, and the N/P exchange ratio. Wang and Linker [17] demonstrated a case where a particular exchange with reducing P and increasing N at 1:5 ratio from some upper Bay's basins results in no DO degradation in most CB segments.

Alternative 3 could be feasible and reduce cost through N-P exchange controls. The first six basins in Table 5 are in the upper Bay, and the last six basins are in the lower Bay, while basins Potomac AFL, Potomac BFL, Lower East Shore, and Virginia East Shore are a transitional group between them. The CB segments that have a deep water designated use including the upper Bay CB segments of CB3MH, CB4MH, and MD5MH are primarily P limited, and the lower Bay CB segments CB6PH and CB7PH are predominantly N limited (Table 4). Concordantly, the upper Bay's basins have DO effectiveness ratio greater than 7.2:1 by DIP versus DIN reductions (Table 5, last column). The ratio is less than 7.2:1 for the lower Bay's basins. Therefore, it could be feasible and of benefit to make an N-P exchange with P decreasing for the six basins at the upper Bay. The exchange by emphasizing N decreasing is feasible to the six basins in the lower Bay.

For individual basins, for example, the Western Shore (Wshr) load, according to the DO effectiveness ratio of 17 by DIP versus DIN reductions, there could be an increase of 17 units of N by reducing 1 unit of P. However, a conservative management approach would exchange less N load increase for the relative P load decrease. This is because, in addition to the consideration of model uncertainties, one type of N-P exchange in a basin may improve DO in a CB segment, but could cause adverse effects on other CB segments. An N-P exchange with P reduction in the upper Bay can generate an adverse effect by causing excess N not taken up by primary production in the upper Bay to be transported down-estuary to stimulate Bay algal growth in more N-limited waters [13,36,37]. The situation gets more complex due to seasonal variations of P or N release from sediments [8,17]. Thus, a safety factor is needed to

acquire lower N and/or P load than the calculated. And any potential strategic approaches to estuarine nutrient management would need to be thoroughly tested.

Certain reverse N-P exchanges may be allowable between two upper Bay's basins. For example, an N-P exchange scenario involving two basins was conducted: basin Upper East Shore increases N and decreases P (i.e., Uesh-N↑P↓), while basin West Shore decreases N and increases P (i.e., Wshr-N↓P↑). They partly canceled out the opposite effects on DO in deep water of CB4MH, with slightly positive improvement (no figure provided). This was because the intensities of DO effect on CB segment CB4MH by basins Upper East Shore and West Shore are similar. However, we saw DO decreases in deep water of a tributary CB segment in the western upper Bay because the CB segment is affected more by basin West Shore (that increases P) than by the Upper East Shore basin (that decreases P). Using a safety factor, to decrease more on the decreasing nutrient component or increase less on the compensated increasing component would be needed to avoid degradation from the counter-effects between two basin nutrient exchanges. Note that the reference condition in this exploration of N-P exchange is the 2010 TMDL, which reduces nutrient loads to achieve all water quality standards. Under the TMDL Scenario's relatively low level of nutrient loads, an N-P load exchange to increase one component (e.g., N) load without violating DO standard by further reducing another component (e.g., P) could be allowed. In the nutrient control management, the "load increment" for N in the above example means to have a higher allowable N load or to allow a lesser N reduction when P is reduced more.

Model errors could limit the application. Although the statistics showed the model had 20–30 % errors, in many cases the deviation from a one-to-one match between the modeled and the observed was due to their differences in temporal and spatial scales, and the constraint of parameter adjustment as addressed in the "Method" section. Detailed analysis of model uncertainty was not conducted. About 10–20 % differences were found when varying key parameter values in their applicable ranges [22]. These errors or uncertainties may not inhibit applications of the model. On the other hand, the model considered most important physical, chemical, and biological processes in algae and dissolved oxygen simulations, and the model parameters were optimized to reduce errors. After obtaining acceptable calibration, the model estimated chlorophyll-*a* and DO was close to the observed (Fig. 3). From dozens of sensitivity analyses, the response of simulated algae and DO was monotonic to the nutrient load changes, and the monotonic relationship was nearly linear in the range of the modeled conditions. When adding a certain amount of a nutrient, either N or P on a basin, the spring and summer algae in CB4MH increased, and DO decreased as can be referred partly from Fig. 5. The response was more sensitive if the changed nutrient is a strong limiting element. The absolute errors or

relative errors of the model will not lead to a reverse conclusion. Nevertheless, the 20–30 % model errors in DO calls for the application of a safety factor in these calculations. The model experiments suggested that it is well protective for the water quality when using a factor of 1.5 for the nutrient of load reduction or a factor of 0.5 for the allowable load increment of the compensate nutrient. Prior to finalization of an N-P exchange plan, a computer simulation is needed to confirm that all water quality standards continue to be met with the proposed exchange. For the combined upper Bay basins, it is estimated to allow about six times less reduction in N loads with respect to the reduction of one additional equivalent weight of P load. Strategic nutrient control considering the N-P tradeoff and nutrient limitation in the Chesapeake could improve management efficiencies and provide benefits at a lower cost.

4 Future Work

The current work does not quantify the conversion between organic nitrogen and dissolved inorganic nitrogen. Refined geographic scenario sets further isolating nutrient species would be helpful to understand the relative effect of dissolved inorganic nutrient load versus organic nutrient load. Analyzing primary production, respiration, oxidation, and transport flux of nutrient species, algae, and dissolved oxygen would help understand some complicated phenomena.

The relative N versus P limitation in the Bay tends to vary seasonally [9,13]. Observations [12] and model simulations show that P limitation is generally stronger in the spring, while N limitation is dominant in the critical summer period when the Chesapeake DO water quality standard is most difficult to achieve. The analysis of algae and DO response to nutrient loads at a temporarily finer scale would help. Detailed simulation of water quality attainment through trading between N and P associated with regional and local nutrient management practices would be important.

The whole premise of exchanging N and P nutrients will depend on there being significant cost savings for the exchange to proceed, and the economics of the exchange may not align with the exchanges that would be suggested by nutrient limitation patterns in the Chesapeake. Future work should examine the economic factors that come into play in any exchange.

5 Conclusions

The geographically isolated, separate N and P increment scenarios (Fig. 5) show relative effects of N and P from the basins of the Chesapeake on DO and chlorophyll-*a*. These effects can inform management decisions on exchanges between N and P

reduction and between reductions occurring in different basins.

In spring to mid-summer, the Chesapeake estuary is estimated to be predominantly P limited in the upper Bay (CB1–CB4) and N limited in the lower Bay from CB6 to CB8. The nutrient limitation of a CB segment is an important factor governing the primary production to be intensified or weakened in responding to DIN or DIP load change from sources.

While chlorophyll-*a* responds strongly to local loads of dissolved inorganic nutrients, DO has a more complex response. The algae formed in surface water of a CB segment may sink down to the bottom resulting in local and far-field oxygen demand through estuarine circulations. The bottom organic matter can come from either the algae formed in the local or from far-field CB segment or from the organic load from the watershed. The above processes determine the bottom organic matter pool in a CB segment, consequently impacting DO. An increase of algal production generally causes the CB segment to have lower summer DO; however, due to complex circulation in the Chesapeake Bay, the movement of organic matter and dissolved inorganic nutrients may behave differently. The geographic location and hydrodynamic relationship between CB segment and source may influence DO response in certain CB segments to nutrient load changes. Hence, the response of DO to nutrient load change in the mainstem CB segments is more complicated than the response of algae to nutrient changes.

The combined effect in chlorophyll-*a* and DO in a segment-designated-use by multiple basins' loads are generally the summation of the effects in the segment-designated-use by individual basin's load. In the nutrient control with N-P exchange involving multiple basins, coordination among managers in different basins is necessary to achieve common benefits.

Since the costs in controlling N versus P are different, and because most nonpoint source management practices control both nitrogen and phosphorus, strategic load reduction planning that considers N-P exchanges could be theoretically appealing but in practice infeasible because of inadequate economic benefits. Nevertheless, nutrient control considering strategic N-P exchanges could improve management efficiencies and provide benefits at a lower cost.

References

1. Linker, L. C., Batiuk, R. A., Shenk, G. W., & Cerco, C. F. (2013). Development of Chesapeake Bay TMDL Allocations. *J Am Water Resour Assoc*, 49, 986–1006.
2. USEPA. (2003). *Ambient water quality criteria for dissolved oxygen, water clarity and chlorophyll-a for the Chesapeake Bay and its tidal tributaries*. Annapolis, MD, USA: USEPA CBPO. EPA903-R-03-002, pp 170.

3. USEPA (U.S. Environmental Protection Agency). (2010). *Chesapeake Bay total maximum daily load for nitrogen, phosphorus and sediment*. Annapolis MD: USEPA Chesapeake Bay Program Office.
4. USEPA (U.S. Environmental Protection Agency). (2004). *Technical support document for identification of Chesapeake Bay designated uses and attainability, 2004 addendum. EPA 903-R-04-008*. Annapolis, MD: USEPA, Region 3, Chesapeake Bay Program Office.
5. Tango, P., & Batiuk, R. (2013). Development of Chesapeake Bay water quality standards. *J Am Water Resour Assoc*, *49*, 1007–1024.
6. Lewis, W. M., Jr., Wurtsbaugh, W. A., & Paerl, H. W. (2011). Rationale for control of anthropogenic nitrogen and phosphorus to reduce eutrophication of inland waters. *Environ Sci Tech*, *2011*(45), 10300–10305.
7. USEPA (U.S. Environmental Protection Agency). (2003). *Water quality trading policy*. Washington, DC: Environmental Protection Agency, Office of Water.
8. Boynton, W. R., Garber, J. H., Summers, R., & Kemp, W. M. (1995). Input, transformations and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries*, *18*(1B), 285–314.
9. D'Elia, C. F., Sanders, J. G., & Boynton, W. R. (1986). Nutrient enrichment studies in a coastal plain estuary: phytoplankton growth in large-scale, continuous cultures. *Can J Fish Aquat Sci*, *43*, 397–406.
10. Fisher, T. R., Peele, E. R., Ammerman, J. A., & Harding, L. W. (1992). Nutrient limitation of phytoplankton in Chesapeake Bay. *Mar Ecol Prog Ser*, *82*, 51–63.
11. Fisher, T. R., Gustafson, A. B., Sellner, K., Lacature, R., Haas, L. W., Magnien, R., Karrh, R., & Michael, B. (1999). Spatial and temporal variation in resource limitation in Chesapeake Bay. *Mar Biol*, *133*, 763–778.
12. Fisher, T. R., Gustafson, A. B., Radcliffe, G. R., Sundberg, K. L., & Stevenson, J. C. (2003). A long-term record of photosynthetically active radiation (PAR) and total solar energy at 38.6°N, 78.2°W. *Estuaries*, *26*, 1450–1460.
13. Kemp, W. M., Boynton, W., Adolf, J., Boesch, D., Boicourt, W., Brush, G., Cornwell, J., Fisher, T., Glibert, P., Hagy, J., Harding, L., Houde, E., Kimmel, D., Miller, W. D., Newell, R. I. E., Roman, M., Smith, E., & Stevenson, J. C. (2005). Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Mar Ecol Prog Ser*, *303*, 1–29.
14. Boynton, W. R., Kemp, M. W., & Keete, C. W. (1982). A comparative analysis of nutrients and other factors influencing estuarine phytoplankton production. In V. S. Kennedy (Ed.), *Estuarine comparisons* (pp. 69–90). New York: Academic.
15. Boynton, W. R., & Kemp, W. M. (1985). Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. *Mar Ecol Prog Ser*, *23*, 45–55.
16. Wang, P., Linker, L., & Shenk, G. (2004). Assessment of relative effect of nutrient loads from different sub-watershed to a specific water-body. In *Proceedings of 8th International Conference on Diffuse/Nonpoint Pollution, October 2004. Kyoto, Japan. PII* (pp. 9–16).
17. Wang, P., & Linker, L. (2009). Assessment of nitrogen and phosphorus control trade-offs using a water quality model with a response surface method. *J Water Resour Plan Manag*, *135*(3), 171–177.
18. Cerco, C. F., Kim, S. C., & Noel, M. R. (2010). *The 2010 Chesapeake Bay eutrophication model. A report to the USEPA and to the US Army Corps of Engineer Baltimore District*. Vicksburg, MD: US Army Engineer Research and Development Center.
19. Cerco, C. F., & Noel, M. R. (2004). *The 2002 Chesapeake Bay eutrophication model* (EPA 903-R-04-004). Annapolis, MD: USEPA, Chesapeake Bay Program Office.
20. Monod, J. (1949). The growth of bacterial cultures. *Annu Rev Microbiol*, *3*, 371–394.
21. Likens, G. E. (1972). Eutrophication and aquatic ecosystems. In G. E. Likens (Ed.), *Nutrients and eutrophication: the limiting nutrient controversy* (pp. 3–13). Lawrence, KS: Allen Press.
22. USEPA. (1985). *Rates, constants, and kinetics formulations in surface water quality modeling. EPA/600/3-85/040* (2nd ed., p. 456). Athens, GA, USA: USEPA Office of Res. and Development.
23. Odum, E. (1971). *Fundamentals of ecology* (3rd ed., pp. 106–7). Philadelphia, PA: W.B. Saunders.
24. Linker, L. C., Shenk, G. W., Wang, P., & Batiuk, R. (2008). Chapter 3: integration of modeling, research, and monitoring in the Chesapeake Bay program. In A. Jose & D. Ariel (Eds.), *Management of water quality and irrigation techniques*. London, UK: Earthscan.
25. Shenk, G. W., & Linker, L. C. (2013). Development and Application of the 2010 Chesapeake TMDL watershed model. *J Am Water Res Assoc*, *49*, 1042–1056.
26. USEPA (U.S. Environmental Protection Agency). (2010). *EPA 903-S-10-002—CBP/TRS-303-10*. Annapolis MD: Chesapeake Bay Program Office. Chesapeake Bay Phase 5 Community Watershed Model: Section 12, Key Scenarios and Findings.
27. Wu, J., Wang, P., Shenk, G., & Linker, L. (2009). *Geographic region isolation runs for developing nutrient load allocations for the Chesapeake Bay restoration*. Portland, OR: Proc. Coastal and Estuarine Research Federation Biannual Conference.
28. Redfield, A., Ketchum, B., & Richards, F. (1966). The influence of organism on the composition of sea-water. In *The sea* (IIth ed., pp. 26–48). New York, NY: Interscience.
29. Wang, P., Linker, L., & Batiuk, R. A. (2013). Monitored and modeled correlations of sediment and nutrients with Chesapeake Bay water clarity. *J Am Water Res Assoc*, *49*, 1103–1118.
30. Wang, P., & Linker, L. (2004). *Nutrient equivalence for water quality management. Proc. of 8th International Conf. on Diffuse/Nonpoint Pollution* (pp. 1–8). Kyoto, Japan: ICIII. October 2004.
31. Pritchard, D. W. (1967). Observations of circulation in coastal plain estuaries. In G. H. Lauff (Ed.), *Estuaries, AS Publ. 83* (pp. 37–44). Washington DC: Am Acad Sci.
32. Wang, P., Linker, L., Batiuk, R., & Lung, W. (2008). *Tracer simulation to analyze channel effect on particle transport in the Chesapeake estuary, Estuarine and Coastal Modeling: Proc Tenth Intern'l Conf* (pp. 744–763). USA: Newport, RI. Nov 5–7, 2007. ISBN 978-0-7844-0990-9.
33. Boicourt, W. C. (1992). Influences of circulation processes on dissolved oxygen in the Chesapeake Bay. In D. E. Smith (Ed.), *Oxygen dynamics in the Chesapeake Bay: a synthesis of recent research* (pp. 7–59). College Park, Maryland: Maryland Sea Grant Publication.
34. CEC. (2000). *Chesapeake Bay Agreement, 2000 Amendments*. Annapolis, MD, USA: Chesapeake Executive Council.
35. Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Lancelot, C., & Likens, G. E. (2009). Controlling eutrophication: nitrogen and phosphorus. *Science*, *232*, February 20, 2009.
36. Graneli, E., Wallström, K., Larsson, U., Graneli, W., & Elmgren, R. (1990). Nutrient limitation of primary production in the Baltic Sea area. *Ambio*, *19*, 142–151.
37. Paerl, H. W., Bales, L. M., Joyner, A. R., & Piehler, M. F. (2004). Solving problems resulting from solutions: evolution of a dual nutrient management strategy for the eutrophying Neuse River estuary, North Carolina. *Environ Sci Tech*, *2004*(38), 3068–3073.