RESEARCH ARTICLE





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# Interactions of warming and altered nutrient load timing on the phenology of oxygen dynamics in Chesapeake Bay

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#### **Abstract**

The effects of nutrient loading on estuaries are well studied, given the multitude of negative water quality and ecosystem effects that have been attributed to excess nitrogen and phosphorus. A current gap in this knowledge involves the sensitivity of seasonal cycles of estuarine biogeochemical processes to direct (warming) and indirect influences (nutrient load timing) of climate change. We used a coupled hydrologic-biogeochemical model to investigate changes in the phenology of hypoxia and related biogeochemical processes in Chesapeake Bay under three different hydrologic regimes. Shifts to earlier nutrient load timing during idealized simulations reduced the overall annual hypoxic volume, resulting from discernable, but relatively small reductions in phytoplankton biomass and both sediment and water-column respiration. Simulated increases in water temperature caused an increase in spring/ early summer hypoxic volume associated with elevated respiration rates, but an associated exhaustion of organic matter in the early summer caused a decrease in late summer/fall hypoxic volume due to lowered respiration. Warming effects on hypoxia were larger than nutrient timing effects in scenarios where warming was restricted to spring and when it was applied to all months of the year. These idealized simulations begin the process of understanding the potential impacts of future climatic changes in the seasonal timing of key biogeochemical processes associated with eutrophication.

#### KEYWORDS

eutrophication < ECOLOGY, total maximum daily loading (TMDL) < WATER QUALITY, estuaries < GEOGRAPHY, Chesapeake Bay, climate variability/change < CLIMATE, metabolism, biogeochemical model

## **INTRODUCTION**

The impacts of nutrient loading on estuaries have been well studied over the past several decades (Boynton et al., 1982; Riemann et al., 2015; Scavia et al., 2004), due to the multitude of negative water quality, ecosystem, and economic impacts that have been attributed to excess nitrogen and phosphorus concentrations. The extent and duration of low dissolved oxygen waters are increasing in frequency and scale worldwide (Breitburg et al., 2018), in part because high rates of microbial respiration result from elevated phytoplankton production, fueled by these excess nutrients, and consume oxygen (Chen et al., 2007; Kemp et al., 1987). Low dissolved oxygen conditions impart physiological stress on many mobile and sessile aquatic organisms and can influence behavior (Brady et al., 2009; Breitburg, 1994; Díaz & Rosenberg, 1995),

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#### Research Impact Statement

Climate change impacts on agriculture, watershed processes, and estuarine biogeochemistry interact to potentially drive a seasonal shift in the consumption of oxygen and associated hypoxia.

motivating many large-scale, expensive socioeconomic commitments to reduce the extent and duration of hypoxia. Although modest reductions in nutrient loads have occurred in Chesapeake Bay and other estuaries worldwide (Kubo et al., 2019; Murphy et al., 2011; Riemann et al., 2015), many hypoxic volumes remain stable or are increasing (Turner et al., 2008; Wang et al., 2018).

Climate change is expected to alter precipitation and temperature patterns that are expected to influence hypoxia via changes in nutrient inputs, metabolic rates, stratification, and oxygen solubility (Irby et al., 2018; Laurent et al., 2018; Meier et al., 2011; Ni et al., 2019). Chesapeake Bay is expected to have larger hypoxic volumes in the future associated with climate change, given that contemporary warming has already compensated for expected improvements from nutrient loading (Ni et al., 2020) and that warmer temperatures are expected to reduce oxygen concentrations through many pathways (Irby et al., 2018; Ni et al., 2019; Testa et al., 2021). Climate change impacts on precipitation will also influence hypoxia, as interannual variations in river flow are a key driver of hypoxia through stratification enhancement and elevated nutrient inputs (Hagy et al., 2004; Li et al., 2016). Restoration efforts to reduce nutrient loads are expected to interact with these climate-induced changes in hypoxia.

Climate change also has the potential to alter myriad watershed processes. Agricultural activities that influence nutrient inputs (irrigation and fertilization) and water and soil temperatures that impact crop uptake and nutrient transformations in soils are sensitive to temperature and precipitation changes (Wagena et al., 2018). For example, warmer spring temperatures have allowed for agricultural activities across much of the Midwest and Mid-Atlantic regions to begin earlier in recent years, where for example, corn planting occurred 6 days earlier from 1996–2012 compared to 1979–1995 in Pennsylvania (U.S. Department of Agriculture, 2010). Given that the agriculture sector has been identified as a considerable source of nutrient pollution to the Chesapeake Bay estuary (Boesch et al., 2001), alterations to agricultural nutrient loads will have a significant effect on land-water nutrients fluxes. Fluctuations in climate can also mediate the seasonality in nutrient inputs because periods of high precipitation, when following several years of dry conditions, have the potential to flush high loads of dissolved nitrogen into the estuary (Lee et al., 2016). In forested parts of the Chesapeake Bay watershed, climate change has been linked to reduced nitrogen availability associated with earlier leaf-out during spring in temperate forests (Elmore et al., 2016), which will likely alter the timing and magnitude of nutrient export. Despite widespread evidence for seasonal changes to watershed processes, there remains a limited understanding of how these potential seasonal changes to nutrient loading will impact eutrophication and hypoxia in Chesapeake Bay.

While the impacts of climate variability on eutrophication and hypoxia have been well studied, most prior analyses have focused on annual-scale ecosystem changes. However, many key biogeochemical processes associated with oxygen have distinct annual cycles, and may be characterized as having a phenology (Testa et al., 2018). For example, the timing of hypoxia initiation correlates strongly with winter-spring freshwater flow and the associated accumulation of chlorophyll-a in bottom water (Lee et al., 2013; Testa & Kemp, 2014), both of which are strongly seasonally dependent. Testa et al. (2018) observed a shift in hypoxic volume phenology between the time periods 1985–1999 and 2000–2015, with the latter years experiencing a lower peak volume and slightly earlier cycle that corresponded to a pattern of warming and a muted spring bloom. Examples in other estuaries have suggested phenological changes in estuarine biogeochemistry associated with climatic change, altering metabolism rates and the timing and magnitude of plankton production (Jahan & Choi, 2014; Nixon et al., 2009; Stæhr et al., 2017). Given the complexity of relevant processes driving phenology and the subtle changes in timing (e.g., days) associated with phenological shifts, there is a clear need to use tools with high spatial and temporal frequency to understand long-term changes to seasonal timing.

Thus, the purpose of this paper was to use a numerical modeling framework to understand the potential changes in Chesapeake Bay hypoxia associated with altered seasonal timing of nutrient inputs and increased water temperature. The Chesapeake Bay estuary is an ideal study system for such an analysis given its strong response to external forces, characteristic seasonal cycles, and hypoxia vulnerability to future climate. We used idealized numerical model simulations to understand how changes in the seasonal timing of nutrient inputs and elevated water temperatures affect the seasonality and spatial response of hypoxia in the Chesapeake Bay.

#### 2 | METHODS

To quantify the biogeochemical response of Chesapeake Bay hypoxia to altered timing of nutrient inputs and temperature, we conducted several idealized sensitivity simulations using a coupled, three-dimensional hydrodynamic-biogeochemical model (Regional Ocean Modeling System and Row-Column Aesop [ROMS-RCA]). Model scenarios included changes in the timing of riverine nutrient concentrations that attempt

to reflect expected changes in farmer behavior and watershed processes resulting from climate change, as well as seasonally specific and annual-scale increases in water temperature that are consistent with observed temperature increases over the past 30 years. We investigated the seasonal biogeochemical response to altered external forcing by examining the volume of hypoxic water in the mainstem of Chesapeake Bay, chlorophyll-a accumulation during spring, and the associated respiratory processes in the water-column and sediments.

#### 2.1 | Numerical model

A coupled hydrodynamic-biogeochemical model (ROMS-RCA) was used to simulate and analyze estuarine biogeochemical responses to simulated changes in temperature and nutrient input timing. The application of ROMS has been validated against a wide range of observational data (Li et al., 2005, 2007) and this application used a 80×120 grid points in the horizontal direction (about ~1 km grid size) and 20 layers in the vertical dimension (Figure 1) as reported previously (Li et al., 2016). Freshwater inputs for ROMS-RCA are based on gauged inputs measured at the eight major Bay tributaries: including the Susquehanna, Patuxent, Patapsco, Potomac, Choptank, Rappahannock, York, and James Rivers. Further details of the ROMS configuration are reported elsewhere (Li et al., 2016; Testa et al., 2014). ROMS-generated salinity, water temperature, advective, and diffusive transport fields are passed to the biogeochemical model (RCA) offline (i.e., soft coupling). RCA is a biogeochemical model that simulates water column and sediment (aerobic and anaerobic layers) biogeochemical processes by simulating the cycling of phytoplankton growth (two different groups) using light, temperature, and nutrient availability. Simulations were run using previously used temperature optima for the growth of both phytoplankton groups (Testa et al., 2014), and we tested these formulations against simulations where elevated temperature would not limit phytoplankton growth (see Supporting Information). RCA simulates oxygen, carbon, nitrogen, phosphorus, silica, and sulfur dynamics, and we used initial sediment porewater and solid concentrations that were generated from a 5-year "warm-up" (see Testa et al., 2014). Detailed descriptions of ROMS-RCA and the sediment biogeochemical model (SFM) and their parameters can be found in recent publications (Brady et al., 2013; Li et al., 2016; Ni et al., 2019; Shen et al., 2019; Testa et al., 2014) and we report mean concentrations of relevant model state variables in the Supporting Information from our baseli

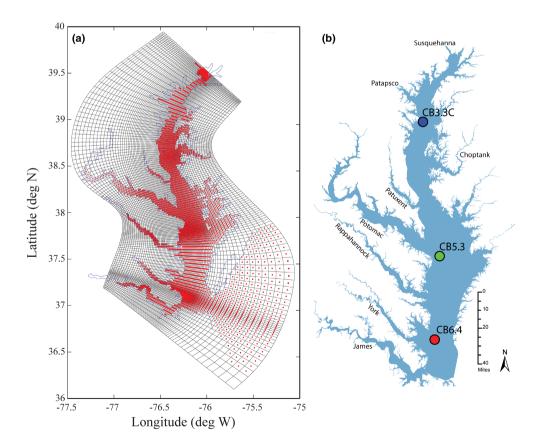


FIGURE 1 (a) Chesapeake Bay Regional Ocean Modeling System and Row-Column Aesop model grid (water cells = red) and (b) map of Chesapeake Bay's major tributaries and the Chesapeake Bay Program long-term water quality monitoring stations (CB3.3C, CB5.3, and CB6.4) that correspond to example locations for analysis in the upper, middle, and lower Bay, respectively.

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# Sensitivity simulations

Sensitivity simulations were performed using 3 years with different hydrologic regimes to allow for the quantification of the impacts of different physical regimes on the estuary's sensitivity to altered temperature and nutrient load timing. The years include an above-average river flow year (2004), a below-average river flow year (2002), and a moderate, or average flow year (2000; Figure 2). For warming simulations, we only elevated temperature in the biogeochemical model to isolate the biogeochemical effects of the warming on hypoxia.

#### 2.3 **Nutrient timing scenarios**

For each of the three hydrologic conditions (2000, 2002, and 2004), the average of all major tributary NO<sub>23</sub> concentrations (i.e., concentrations in the river load) was used to generate an idealized annual cycle. We focused on  $NO_{23}$  because it is typically >70% of the TN load (Zhang et al., 2015) and is the dominant source of nitrogen that reaches downstream areas to support algal growth Chesapeake Bay (Palinkas et al., 2019). This annual cycle was then scaled to match the nutrient concentration and load magnitude in each individual tributary by multiplying the cross-tributary average annual loading cycle by a tributary-specific factor (i.e., the ratio of the tributary concentration to the watershed-mean concentration). This approach maintained the relative load magnitude from each tributary, but removed tributary-specific seasonal variability in concentrations to establish an identical seasonal variation in concentration for each tributary to allow for the isolation and simplification of the timing effect. This approach comprised the "idealized Base" (no change) scenario for comparison to a suite of altered nutrient concentration timing simulations. For each hydrologic year, two additional model scenarios were performed that consisted of shifting the idealized tributary (riverine) nitrate + nitrite concentration earlier in the year (1 and 2 months earlier), for each of the major tributaries modeled. Thus, the NO23 timing scenarios consisted of three different model simulations: (1) an idealized "Base" scenario where no changes in  $NO_{23}$  were applied, and two "shift" scenarios where the peak  $NO_{23}$  concentration is shifted (2) one and (3) 2 months early (Figure 3). Although the potential for this particular type of shift in nitrogen concentration to be realized in Chesapeake Bay watershed is unclear, numerous studies

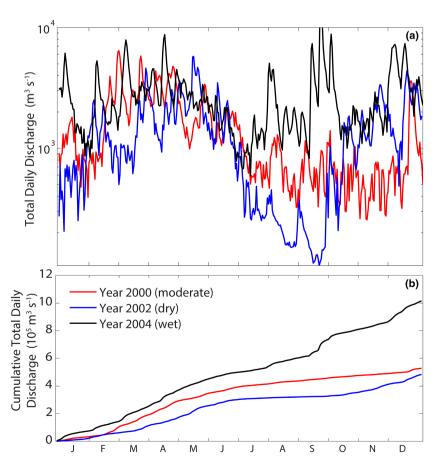
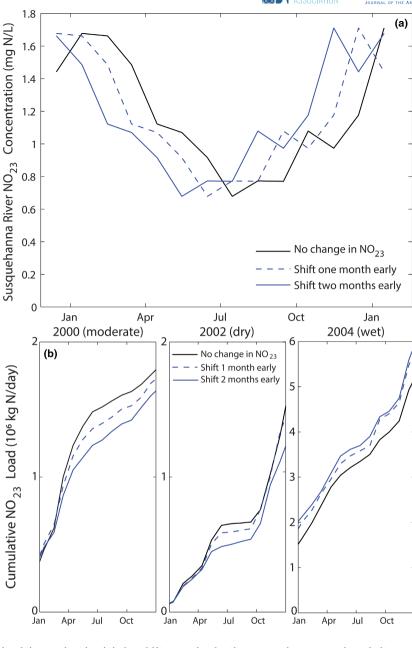


FIGURE 2 Comparison of the daily total riverine flow (a) and cumulative daily riverine flow (b) of all major Chesapeake Bay tributaries (Susquehanna, Patuxent, Patapsco, Potomac, Choptank, Rappahannock, York, and James Rivers) to highlight that the years 2000 (moderate flow), 2002 (dry), and 2004 (wet) are hydrologically different.



**FIGURE 3** (a) An example of the nutrient load timing shift scenarios for the seasonal concentration of nitrate and nitrite ( $NO_{23}$ ) shifted to a peak 1-month early (dashed) and 2-month early (blue) for the Susquehanna River in 2000. This process was repeated for each hydrological year (2000, 2002, and 2004) and tributary. (b) The resulting cumulative  $NO_{23}$  load of all tributaries combined, for each year and scenario.

in other regions have projected that future climates will alter the seasonality of nutrient loads (Bouraoui et al., 2004), including shifts to larger winter loading proportions (Marshall & Randhir, 2008; Verma et al., 2015).

## 2.4 | Summer water temperature increase scenario

We performed sensitivity simulations to understand the seasonally specific response of Bay biogeochemistry to elevated temperatures. While climate projections typically predict that water temperature increases will occur across all months of the year (Ni et al., 2019), recent analyses have suggested that late spring and summer temperatures have warmed faster than fall or winter (Hinson et al., 2021; Testa et al., 2018). Therefore, warming was applied by increasing the water temperature by 1.5°C during the period spanning May 1–July 31 for each hydrologic year (2000, 2002, and 2004). The temperature increase scenarios were compared to a Base (no change) scenario that included observed nutrient concentrations in riverine inflows.

#### 2.5 Nutrient shift and summer water temperature increase combination scenarios

The effects of earlier nutrient load timing and elevated summer water temperatures are likely to occur simultaneously. Therefore, we conducted simulations of summer water temperature increases of  $1.5^{\circ}$ C Bay-wide from May 1 to July 31 combined with shifting the NO<sub>23</sub> timing 1 and 2 months early, respectively, for each hydrologic year. These simulations allow for an analysis of interactions between the two climate change-induced alterations of external forcing with reference to the impacts in isolation.

#### 2.6 | Year-round water temperature increase scenario

In contrast to the observation of the largest deviations in long-term averages of water temperature occurring in the summer (Testa et al., 2018), other studies have projected year-round water temperature increases in the Chesapeake Bay region (Ding & Elmore, 2015; Ni et al., 2019). To evaluate estuarine sensitivity to potential year-round water temperature increases, we performed a simulation by increasing the water temperature by 1.5°C, Bay-wide, for the entire year, under the Base loading scenario. This simulation was repeated for each hydrologic year (i.e., 2000, 2002, and 2004). These year-round temperature increases were directly compared to the early summer increases.

#### 3 | RESULTS

#### 3.1 | Nutrient timing scenarios

At the Bay-wide scale, idealized simulations of earlier nutrient loads resulted in lower annual hypoxic volumes for all hydrologic regimes (Figure 4). This occurred even as the cumulative NO<sub>23</sub> load was higher in the nutrient shift scenarios for the wet year, resulting from an alignment of the shift with high January flow in 2004 (Figures 2 and 3). The simulated reductions in hypoxic volume were comparable across years, with a maximal reduction between 1.2 and 1.6 km³, equating to a 5%–10% reduction relative to base conditions (Figure 4). For all years, the scenario that shifted NO<sub>23</sub> 2 months earlier saw a larger reduction in annual hypoxic volume than the 1-month early shift. We also computed hypoxic volume days (HVD) as an integrated measure of annual hypoxic volume, where HVD =  $\sum_{d=1}^{365}$  HV<sub>d</sub> and d = day of the year and HV = the daily hypoxic volume in the mainstem Bay and its tributaries (km³). At the hypoxia threshold of 2 mg O<sub>2</sub>/L, the 2-month earlier shift during the moderately wet year (2000) had the largest decrease in HVD with a change of 117.4 km³-day, followed by 106.4 km³-day in 2004 (wet), and 75.4 km³-day in the 2002 (dry) scenario. Although there was no change in the timing of the peak hypoxic volume for any of the scenarios, the reductions were consistent from June to October in the moderate (2000) flow year, between June and September in the dry year, and larger in May to July in the wet (2004) year (Figure 4). The timing of hypoxia initiation was not heavily influenced by the shift in nitrate load timing, and only changed by 1 or 2 days for a region or two in each of the hydrologic years.

The fact that earlier nitrate load timing initiated a decrease in Bay-wide hypoxic volume indicates that these scenarios included an increase in bottom-water dissolved oxygen. We computed the difference in modeled dissolved oxygen, chlorophyll-a, and respiration during the spring (January–May) and summer (June–August) in model cells corresponding to three Chesapeake Bay Program monitoring stations along the Bay

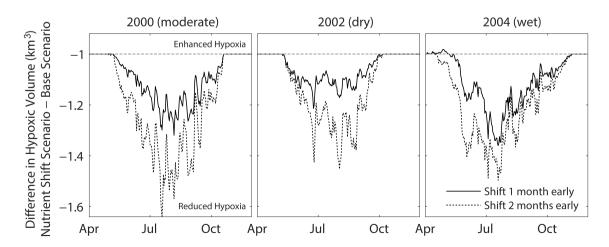


FIGURE 4 Comparison of the difference between modeled mainstem Chesapeake Bay hypoxic volumes ( $<2 \text{ mg O}_2/L$ ) in the nutrient load ( $NO_{23}$ ) shift scenarios and the baseline simulation (nutrient shift-base) in each year 2000, 2002, and 2004.

mainstem including: CB3.3C (Bay Bridge) in the upper Bay, CB5.3 (Smith Point) mid-Bay, and CB6.4 in the lower Bay (Figure 1). Both the 1- and 2-month shifts in nitrate concentration caused an increase in water column dissolved oxygen that correlated to a decrease in chlorophyll-a (see Supporting Information) and total respiration (DOC oxidation + sulfide oxidation + phytoplankton respiration) during both the spring and summer seasons (Figure 5). For the moderately wet (2000) and wet (2004) years, the middle and lower-Bay stations saw a larger increase in dissolved oxygen in both seasons compared to the upper-Bay station (Figure 5). During the driest year (2002), the upper-Bay station showed the largest change in dissolved oxygen during the spring season. In general, the 2-month earlier nutrient shift had a larger effect on the dissolved oxygen linkage with chlorophyll-a and respiration during both seasons than the 1-month early scenario. The 2-month earlier nutrient shift increased the dissolved oxygen as much as 3 mg  $O_2/L$  at the mid-Bay station in the summer, whereas the 1-month early nutrient shift scenario generated about a  $0.5-1 \text{ mg O}_2/L$  at the same station and season.

Remineralization processes in sediments and associated sediment-water fluxes also varied seasonally in response the simulated shift in NO23 concentration and load. Comparisons of the NO23 shift 1-month early scenario in all regions showed that modeled sediment oxygen demand (SOD), sediment-water  $NH_4$  flux, and sediment nitrogen content all deviated from the "Base" case beginning in May, continuing through the summer, and then returned to "Base" case values between October and November (Figures 6 and 7). The 1-month early nutrient shift scenario actually resulted in enhanced SOD in the two upper CBP stations (CB3.3C and CB5.3), and slightly reduced SOD at the lower Bay station (CB6.4) (Figure 6). Sediment-water NH $_4$  fluxes peaked during late summer through early fall (July-October), and during this period, the shift  $NO_{23}$  1-month early scenario shows a reduction in  $NH_4$  release from the sediments of 1%-5% except for the wet year (2004) in the upper bay (Figure 7). Particulate organic nitrogen (PON) in the sediment was also reduced in the nutrient shift scenarios (Figure 7). For the upper-Bay stations (CB3.3C and CB5.3), this reduction in PON initiated around March, but was delayed until May in the lower-Bay station (CB6.4; Figure 7).

# Seasonal water temperature increase scenario

The idealized early summer warming scenarios resulted in an altered annual cycle of dissolved oxygen. Hypoxic volume increased up to  $3 \text{ km}^3$ during the period of increased water temperature (May-July), but once warming subsided after July 31, model simulations revealed a slight reduction in hypoxic volume in all hydrologic years (Figure 8). The associated largest overall (delta) change in HVD occurred during the 2004

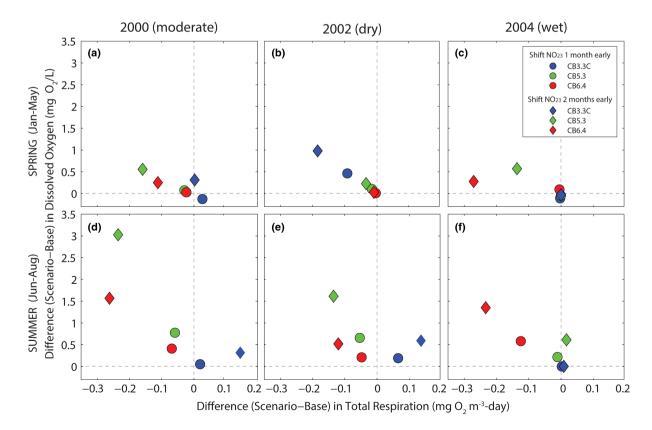


FIGURE 5 Comparison of the difference in bottom layer dissolved oxygen (O2) and total respiration respectively, between nutrient timing shift scenarios during the spring (January-May; a-c) and summer (June-August; d-f) seasons at three locations that represent the upper Bay (CB3.3C), the middle bay (CB5.3), and the lower Bay (CB6.4).

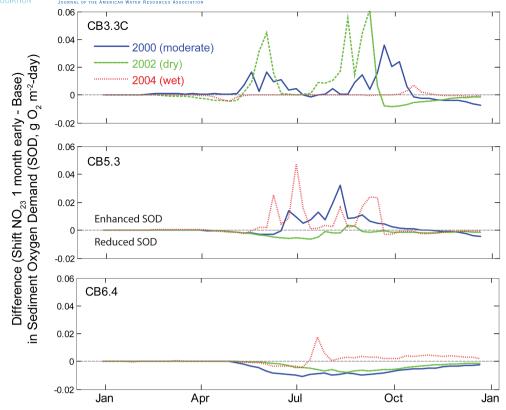


FIGURE 6 Model-simulated differences (nutrient shift scenario-base scenario) in sediment oxygen demand (SOD) for the 1-month shift in NO<sub>23</sub> concentration at three locations that represent the upper Bay (CB3.3C), the middle bay (CB5.3), and the lower Bay (CB6.4). Each of the three hydrologically unique years are included (2000, 2002, and 2004).

scenario with an increase of 108.6 km<sup>3</sup>-day, where this year had the largest increase in hypoxia during the temperature increase period and the largest reduction after July 31 time period with a change in HVD of 146.3 and –37.6 km<sup>3</sup>-day, respectively (Figure 8). The moderately wet year (2000) had the largest lag after July 31 for hypoxia to decrease below the Base scenario at 10 days, whereas the dry and wet years responded in 7 and 4 days, respectively (Figure 8).

The seasonal response of hypoxia to temperature increases was driven by changes in water-column and sediment respiration. SOD and water-column respiration uniformly increased under warming in the middle and lower Bay, except for the wet year, 2004, when both rates declined with elevated temperature in the middle Bay (Figure 9). In contrast, SOD and water-column respiration were reduced or changed minimally under warming in the upper Bay (Figure 9). In the week leading up to the end of the warming on July 31 and in the month after, sediment respiration (SOD) declined in the middle and lower Bay, which corresponded to the reduction in available sediment organic carbon (SOC), which never recovered to levels from the Base case within the remainder of the year (Figure 10). The upper-Bay station (CB3.3C) saw the largest reduction in SOC (up to  $\sim 0.15 \, \text{mg C/m}^3$  in moderate and dry year; Figure 7) relative the middle and lower Bay, but SOD reductions in the mid-late summer were larger in the middle and lower Bay (Figure 9a). We compared the relative contribution of sediment and water column respiration to total respiration in middle and lower Bay regions when both rates were enhanced under warming (May-July in Figure 9), where we assumed a 10-meter sub-pycnocline water-column. If we consider an enhancement of water-column respiration by 0.01  $\, \text{mg} \, \text{O}_2/\text{m}^3$ -day, which is at the low end of the May-July increases in the middle and lower Bay (Figure 9b), sub-pycnocline respiration would equal 0.1  $\, \text{mg} \, \text{O}_2/\text{m}^2$ -day, which is comparable to the enhancement in SOD (Figure 9). Consequently, a reduced SOC pool following summer warming was associated with reduced water-column and sediment respiration in the fall, which was consistent with the Bay-wide decrease in fall hypoxic volume in the warming scenario.

#### 3.3 | Nutrient shift and water temperature increase combination scenarios

The combined scenario of earlier nutrient input timing and summer temperature increases resulted in an increase in hypoxic volume (at threshold of 2 mg  $O_2/L$ ) during the first half of the year (before July 31) and decrease in hypoxic volume in the second half of the year (after July 31) for both scenarios and for all hydrologic years (Figure 11). The summer temperature increase only scenario had the largest hypoxic volume

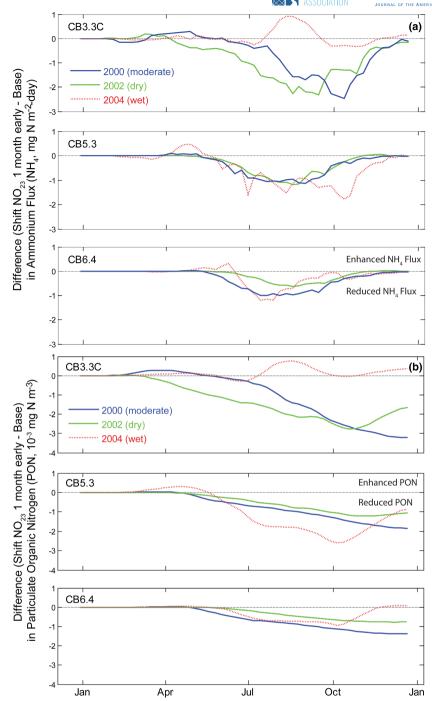


FIGURE 7 Model-simulated differences (nutrient shift scenario-base scenario) in sediment water  $NH_4$  flux (a) and sediment particulate organic nitrogen concentration (PON, b) for the 1-month shift in  $NO_{23}$  concentration at three locations that represent the upper Bay (CB3.3C), the middle bay (CB5.3), and the lower Bay (CB6.4). Each of the three hydrologically unique years are included (200, 2002, and 2004).

increase (11%–25%) in the first half of the year and smallest (reduced volume) change (–1% to –4%) in the second half of the year. The combined nutrient shift + summer temperature increase scenarios had smaller increases (shift 1-month early = 8%–18%, shift 2-month early = 5%–13%) than the temperature-only increase, and larger decreases in hypoxic volume in the latter half of the year relative to temperature increases only (shift 1-month early = -3% to -7%, shift 2-month early = -8% to -12%; Figure 11). Separate computations of HVD indicated that summer temperature increases had a sufficient stimulatory effect on hypoxia to overcome reductions resulting from an earlier NO<sub>23</sub> load. The shift NO<sub>23</sub> 1-month early scenario had a reduction of 3%–6% across all three hydrologic years, whereas the combined warming and NO<sub>23</sub> 1-month early shift scenario had a 2%–10% increase. The shift NO<sub>23</sub> 2-month early scenario had larger reductions in volume of 5%–12% across all three

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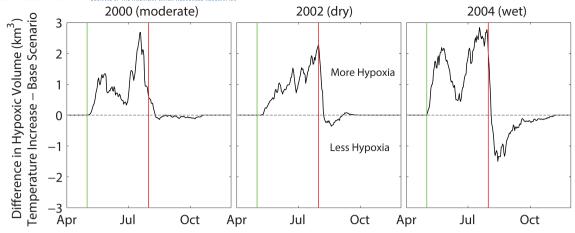


FIGURE 8 Seasonal difference (warming-base) in modeled mainstem hypoxia (<2.0 mg O<sub>2</sub>/L) in each of three hydrologic years in response to idealized, seasonally distinct water temperature increase (warming) scenario, where water temperature was increased Bay-wide by 1.5°C from May 1 (start, green line) to July 31 (stop, red line).

hydrologic years, while the comparable combined scenario had a 3% reduction in 2000, 3% increase in 2002, and negligible change (0.05%) in 2004.

#### Year-round water temperature increase scenario

The year-round temperature increase scenario caused elevated hypoxic volumes (at threshold of 2 mg O<sub>2</sub>/L) in comparison to the Base (no change) scenario throughout the year. These increases were comparable in 2000 (by 18%) and 2002 (by 17%) and somewhat smaller for 2004 (by 8%; Figure 11). This increase in hypoxic volume was larger than the summer temperature increase scenario, which had a 10%, 15%, and 5% increase for 2000, 2002, and 2004, respectively. In the year-round increase scenarios, both 2002 and 2004 showed a slight decline in hypoxic volume around October, but it was relatively small in comparison to the overall increase. The late fall decrease in the two warming scenarios was of similar magnitude, but is shifted about a month later in the year-round warming scenario. Across all years, the early summer (before July 31) increase in volume was comparable to the summer water temperature increase only scenario. One difference observed was during 2004, when the increase in hypoxic volume occurred much earlier in the year than all other temperature scenarios (Figure 11).

#### **DISCUSSION** 4

The phenological response of estuaries to changes in climate and watershed nutrient loading is complex and can be subtle, but model simulations (e.g., ROMS-RCA) were able to quantify the effects of seasonal changes to external forcing on oxygen depletion. Here, we documented responses of Chesapeake Bay hypoxia to two distinct changes in the seasonal timing of physical forcing. Shifts in nutrient load timing had the effect of reducing the overall annual hypoxic volume in response to declines in phytoplankton biomass and both sediment and water-column respiration in three regions of the Bay. Seasonally specific and annual-scale water temperature increase scenarios indicated an increase in the spring/early summer hypoxic volume, but a decrease in late summer/fall hypoxic volume. In combined load timing-warming simulations, warming outweighed load timing in its effect of increasing hypoxic volume. Each of these idealized simulations represents a potential future change to Chesapeake Bay associated with either a direct (temperature) or indirect (nutrient load timing) response to future climate warming, and the simulations highlight the complex metabolic response to external forcing that drives responses in hypoxic volume.

Previous studies have shown how annual or long-term scale reductions in nutrient load are linked to reductions in stream nutrient concentrations (Ator et al., 2020; Eshleman et al., 2013) and lead to improvements in dissolved oxygen (Fisher et al., 2021), the recovery of submerged aquatic vegetation (Greening & Janicki, 2006; Lefcheck et al., 2018), the reduction in sediment nutrient cycling (Taylor et al., 2020), and other ecosystem responses (Fulweiler et al., 2007; Riemann et al., 2015). This study suggests that reductions in hypoxia might also occur as a result of seasonal shifts in nutrient load timing (Figure 4). Although the idealized shifts in nutrient timing we simulated may be more extreme (e.g., 2-month shift) than changes resulting from fertilizer application or forest phenology (Elmore et al., 2016), the oxygen response we found may be an overlooked potential effect of changes in watershed nitrogen export on estuarine biogeochemistry. A large portion of the Chesapeake Bay watershed is occupied by agricultural landscapes, contributing a large source of estimated nutrient load (42% nitrogen, 55% phosphorus;

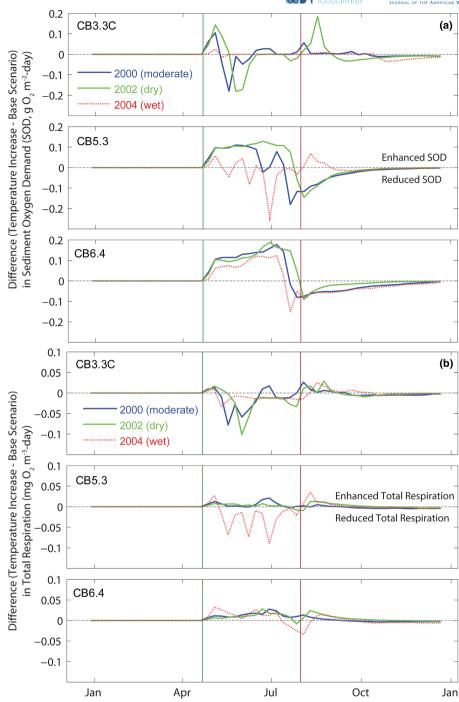


FIGURE 9 The difference in (a) SOD and (b) total respiration between the seasonally distinct temperature increase scenario and the base scenario in the upper Bay (CB3.3C), the middle bay (CB5.3), and the lower Bay (CB6.4). The water temperature was increased Bay-wide by 1.5°C from May 1 (start, green line) to July 31 (stop, red line).

Chesapeake Bay Program, 2022). Thus, farmer adaptations to changing climate conditions by adjusting agricultural practices to maintain crop yield (Ortiz-Bobea et al., 2019) is worth considering in future climate scenarios, because it is estimated to lead to earlier nitrate ( $NO_3$ ) loading (kg/ha) to waterbodies (Chang et al., 2018). By shifting nutrient load timing earlier,  $NO_{23}$  availability is reduced during a key period of phytoplankton production (e.g., winter-spring), which means that there would be less organic material available for hypoxia generation later in the year (Boynton & Kemp, 2008; Testa & Kemp, 2014).

Freshwater flow is a strong driver of nutrient loading to estuaries and river flow moderated the spatial response of hypoxia and metabolism to idealized changes in load timing. The Susquehanna River is the dominant source of freshwater and nutrients to the mainstem Chesapeake Bay, correlating strongly with the magnitude of annual hypoxia in estuaries (Li et al., 2016; Scavia et al., 2006) and water-column chlorophyll-a

-0.2

Jan

FIGURE 10 The difference in sediment organic carbon (mg C/m³) between the seasonally distinct temperature increase scenario and Base scenario at three locations in upper Bay (CB3.3C), the middle bay (CB5.3), and the lower Bay (CB6.4). The water temperature was increased Bay-wide by 1.5°C from May 1 (start, green line) to July 31 (stop, red line).

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accumulation (Miller & Harding, 2007). Model scenario results highlight this flow effect regardless of the nutrient timing or temperature scenario, where the relative change in Bay-wide hypoxic volume was largest in the highest flow (and hypoxic volume) year for the 1-month shift (2004) and highest in the moderate flow year (2000) for the 2-month shift (Figure 4). The spatially specific responses of other variables were distinct, including a larger reduction in NH<sub>4</sub> fluxes and sediment PN and PC during the moderate and low flow years in the upper Bay. This high sensitivity of the upper Bay is consistent with high flow conditions that push the spring bloom and associated organic matter deposition seaward (Testa et al., 2014) and thus the upper-Bay had little biogeochemical production and sensitivity to load changes in the wet year of 2004. The lower Bay, in contrast, had the strongest metabolic response to nutrient load timing changes, revealing the dependence of primary production and associated metabolism to Susquehanna River nutrient inputs in this region (Miller & Harding, 2007; Testa et al., 2018).

An unexpected result of the simulations was the apparent stimulation of SOD and water-column respiration with altered nutrient input timing and reduced hypoxia. This feature was especially evident in the upper Bay in the moderate and dry year, the middle Bay in the moderate and high flow year, and the lower Bay during the wet year (Figure 6). This result reflects the fact that respiration (and associated oxygen uptake) can be limited by oxygen availability (Cowan & Boynton, 1996; Sampou & Kemp, 1994). Thus, in the upper and middle-Bay, where oxygen concentrations in bottom waters under the base scenario are anoxic or severely hypoxic, SOD and water-column respiration are oxygen limited. Therefore, when the nutrient shifts reduced oxygen consumption and increased oxygen concentration due to reduction of chlorophyll-a and total respiration (Figures 5 and 6; Figure S1), oxygen limitation was relieved and SOD increased. The fact that respiration increased when oxygen was made available, but not to an extent to elicit a feedback that would generate the same volume hypoxia for a lower nutrient load, underscores the fact that nutrient reductions, independent of their timing, serve to limit consumption of oxygen.

Many previous studies have examined long-term changes in hypoxic volume in estuaries (Carstensen et al., 2014; Hagy et al., 2004; Murphy et al., 2011; Scavia et al., 2006), including simulated responses to future climate change (Cai et al., 2021; Irby et al., 2018; Laurent et al., 2018; Meier et al., 2011; Ni et al., 2020). Fewer studies, however, have examined detailed metabolic responses that exert influences on changes in hypoxic volume (Li et al., 2016; Testa et al., 2021). Murphy et al. (2011) reported significant increases in early summer hypoxia and a slight decrease in late summer hypoxia in Chesapeake Bay over a 60-year period, where climate-related variables (e.g., elevated stratification) were one explanation for the early-summer increase. Other studies have shown how increases in water temperature are likely to increase the annual hypoxic volume in the Bay (Irby et al., 2018; Ni et al., 2019), or have already mitigated nutrient reduction (Frankel et al., 2022; Ni et al., 2020) through warming enhancements of respiration and/or reductions in oxygen solubility. In contrast, this study suggests that increases in hypoxic volume in the early part of the year can result from an increase in the early summer temperature, which can be followed by a subsequent

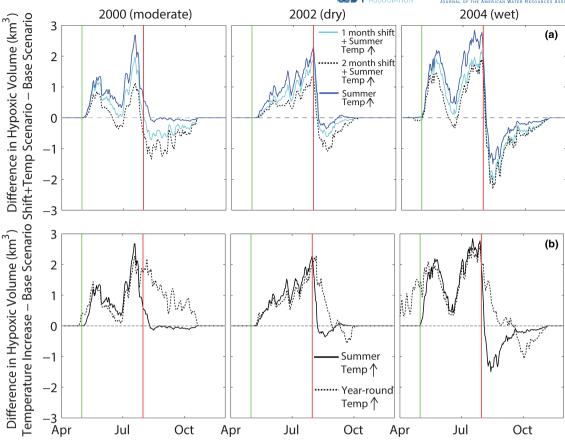


FIGURE 11 (a) Comparison of the hypoxic volumes resulting from combined scenarios of nutrient shifts and water temperature increases in comparison to the Base scenario (no changes to nutrients or water temperature), at a hypoxia threshold of 2.0 mg  $O_2/L$ . The water temperature was increased Bay-wide by 1.5°C from May 1 (start, green line) to July 31 (stop, red line), and the riverine  $NO_{23}$  was shifted 1 and 2 months early, respectively. (b) Comparison of the hypoxic volumes resulting from the water temperature increase scenarios (seasonally distinct [summer only] and year-round) in comparison to the Base scenario (no changes to nutrients or water temperature), at a hypoxia threshold of 2.0 mg  $O_2/L$ . For both scenarios the water temperature was increased Bay-wide by 1.5°C. For the summer scenario this increase occurred from May 1 (start, green line) to July 31 (stop, red line), and for the year-round scenario, from January 1 to December 31.

decrease in later summer/early fall hypoxic volume (Figure 11). Testa et al. (2018) hypothesized that warmer early summer temperatures would stimulate the respiration of the spring bloom to generate early summer hypoxia increases, but also exhaust organic matter earlier in the year and allow for late-season relief from hypoxia due to lower late summer respiration rates. The model simulations we performed are consistent with that hypothesis, where the seasonal temperature change leads to a faster rate of sediment and water-column respiration in the early summer, and when temperature returned to observed levels, there was less sediment organic matter to support respiration and nutrient fluxes (Figure 11). Thus, the impacts of future climate changes may not simply lead to higher hypoxia, but rather increase hypoxia in early summer and decrease it in later summer, as has been previously documented (Murphy et al., 2011; Testa et al., 2018; Zhou et al., 2014). The fact that the year-round warming scenario generated a smaller late summer hypoxia decline than the summer-only temperature increase scenario (except 2002 with a 15%–17% increase; Figure 11) reinforces that the extent and seasonality of warming will modulate the realization of any proposed alteration of seasonal hypoxia cycles. Thus, although temperature increases may indeed lead to a more rapid respiration of labile organic material in the early part of the annual cycle, temperature increases across all times of year will extend a larger hypoxic volume into the mid to late fall in Chesapeake Bay.

These idealized simulations appear to support the hypothesis that temperature increases can have complex, spatially and seasonally dependent effects on hypoxia. Some of these effects may be realized through recycling-associated feedbacks (Savchuk, 2018; Testa & Kemp, 2012), which we did not fully explore here. For example, warming-induced increases in respiration (Yvon-Durocher et al., 2010) would allow for elevated regeneration of nutrients in the water-column and sediments (Lake & Brush, 2015), which could stimulate additional phytoplankton production during summer and add additional organic material later in summer to compensate for the material exhausted by warming. Indeed, a 10%–20% increase in water column NH<sub>4</sub> in both the surface and bottom waters occurred under warming in our simulations, which could

support additional phytoplankton growth. Although this regeneration of nitrogen is relatively strong during the summer temperature increase, the effect did not persist long into the fall, and therefore was unable to sustain further phytoplankton production in the model simulations.

The combined scenarios of earlier nutrient load timing and warmer water temperature showed that the reduction in hypoxic volume generated by the shift in nutrient load timing is overcome by the increase in summer water temperature. This result indicates that although organic matter reductions through lowered primary production under earlier nutrient inputs will reduce the respiration that generates hypoxia, elevated respiration rates of the existing organic material, and reduced oxygen solubility will increase hypoxia. This is consistent with simulations that have shown that temperature effects will limit the oxygen improvements expected from nutrient load reductions in Chesapeake Bay (Du et al., 2018; Irby et al., 2018; Ni et al., 2020) and other estuaries (Meier et al., 2011; Whitney & Vlahos, 2021). However, the reduction in later summer hypoxia associated with warmer summer temperatures persists with the addition of earlier nutrient inputs, and the reduction in hypoxic volume was larger in the combined nutrient shift+ warming scenarios for 2000 and 2002 than the summer temperature increase scenario alone (and was comparable across years; 4%–8%). Thus, the combination of these two likely climate change effects on external forcing could lead to an altered seasonality of hypoxic volume. These seasonal alterations are potentially relevant for mobile and sessile organisms that have seasonally-specific recruitment and migration patterns, and whose habitat may be limited by reduced dissolved oxygen (O<sub>2</sub>) levels more than high temperature during summer months (Kraus et al., 2015).

The model simulations presented here provide new insights into the potential alteration of biogeochemical phenology in Chesapeake Bay and other estuaries, but the idealized simulations do have limitations. First, future simulations could include more realistic temperature changes from downscaled model simulations and account for other effects of climate change, including changes in the timing and variability of freshwater discharge. Our application of three different hydrologic years in our simulations was advantageous because it allowed for the simulation of changes only in nutrient concentration under natural hydrological conditions. The disadvantage of this approach is that future climate in this region is expected to include both warming and elevated flow, and also that differences in flow seasonality within the years we simulated caused an increase in nitrogen load in some scenarios (Figure 3), but even in this case the phenology shift appeared to persist (e.g., Figure 5). Furthermore, the 2-month shift in nutrient concentration scenario is likely an extreme case, but we included this run to provide an upper bound to the potential effect of altered load timing. We also did not explore potentially co-occurring impacts on phosphorus, which is a key limiting nutrient in spring (Zhang et al., 2021), and future efforts could consider changes in the N:P ratio. Finally, the scenarios including warming combined with nutrient load timing changes represent perhaps the most realistic case of future conditions, as future warming is the presumed cause of any shifts in nutrient load timing.

#### 5 | CONCLUSION AND FUTURE RECOMMENDATIONS

Targets for watershed nutrient load reductions are typically evaluated on an annual basis, but the results of idealized model simulations presented here indicate that even when the annual load remains stable, intra-seasonal dynamics in loading may also impact hypoxic volumes. Future changes in the timing of agricultural activity and associated stream nutrient concentrations—including changes in practices that occur in response to climate changes—will have cascading effects on the estuary. These idealized seasonal simulations and the hypoxia responses displayed that earlier nutrient timing can limit the extent of hypoxic volume, but that warming can overwhelm these effects. The reduction in hypoxic volume due to the decoupling of nutrient load and seasonal water temperature would not be as strong if water temperatures continue to warm earlier in the spring, expanding the seasonal overlap of high nutrient loading and high metabolic rates. These outcomes would be further modulated by other future climatic changes, including altered wind patterns, sea level rise, and changes in the biological communities within the plankton.

Making future projections with a biogeochemical model can be challenging, because the model kinetic formations are inflexible and are limited by the science available to inform model development, parameterization, and the inclusion of all relevant biological and biogeochemical interactions. For example, future climate changes will likely alter phytoplankton species abundance and distribution, but the current biogeochemical model only represents two idealized functional types (a summer group and a winter diatom group). Given that these models do not represent a dynamic and flexible community of different phytoplankton types and metabolic modes, the model will have a limited capability to accurately predict the varied potential outcomes for phytoplankton metabolism. Phytoplankton kinetics, including nutrient uptake and respiration could play a large role in ecosystem nutrient cycling under climate change. Overall, this study illustrates how alterations in the phenology of human behavior, physical forcing, and biogeochemistry can potentially be important when studying climate change effects on Chesapeake Bay and other estuaries. Future simulations with more comprehensive watershed-estuarine model coupling are necessary to more confidently evaluate the potential for these altered realizations of hypoxia to occur. For examples, the effects of warming and altered precipitation patters on watershed nitrogen cycling (Wagena et al., 2018), nitrogen speciation (Bertani et al., 2021), and estuarine nutrient cycling will impact any future estuarine responses in terms of nutrient loading and its impacts on oxygen depletion, phytoplankton growth, and nutrient cycling. While the scenarios presented here are simplistic and somewhat hypothetical, they lend insights into the potential cascading effects of phenological changes within the watershed and estuary and warrant further study.

#### **AUTHOR CONTRIBUTIONS**

Nicole Basenback: Conceptualization; formal analysis; validation; visualization; writing - original draft. Jeremy M. Testa: Conceptualization; formal analysis; funding acquisition; investigation; methodology; project administration; software; supervision; writing - review and editing. Chunqi Shen: Conceptualization; formal analysis; methodology; software; writing - review and editing.

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#### CONFLICT OF INTEREST

We have no conflicts of interest to report.

#### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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#### SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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