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Key Points:

- Based on the CMIP5 models, this article systematically diagnosed the global oceanic oxygen budget and its response to climate change
- The ocean deoxygenation was the direct consequence of the escape of oxygen from the ocean, tightly associated with marine warming
- Due to continued warming, oxygen outgassing from ocean may increase in the next few decades, leading to a more hypoxic ocean in the future

Supporting Information:

- Supporting Information S1

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Increasing Escape of Oxygen From Oceans Under Climate Change

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Abstract The global oxygen cycle is one of the most important cycles on Earth for all aerobic organisms, and it is a basic constraint sustaining aerobic life. As a major component of the cycle, oceans are now experiencing widespread declines in oxygen concentrations. Here, based on model simulations we found that ocean deoxygenation occurs as a result of oceanic oxygen outgassing, which is tightly related with the marine warming. Although the O₂ flux from the ocean to atmosphere is quite small compared with that of oceanic oxygen production, this outgassing accounts for almost all of the decline in marine oxygen and even exceeds the amount of the loss. The model projections indicate accelerated oxygen escape from the ocean under climate change. The oceanic outgassing will increase from 1.6 to 4.3 Gt/yr over the 21st century due to solubility and circulation changes related with warming, which may eventually lead to a more hypoxic ocean in the future.

Plain Language Summary It is well-known that O₂ is fundamental for all aerobic life. However, the oxygen content of the ocean has been declining during the past few decades. This phenomenon, known as the “ocean deoxygenation,” will have widespread consequences, which could eventually threaten the marine ecosystems. In this study, we systematically diagnosed the global oceanic oxygen budget on the basis of earth system models and found enhanced O₂ escape from the ocean to atmosphere. The O₂ outgassing is directly responsible for ongoing deoxygenation, and it will continue to increase in the future. A shift in the oceanic oxygen cycle characterized by increasing oxygen escape has been occurring as a consequence of human-induced climate change, followed by intensified ocean deoxygenation and resulting in severe damage to marine biota.

1. Introduction

Oxygen is one of the most crucial and fundamental components for aerobic life on Earth. This key element, which is influenced by multiprocesses (e.g., photosynthesis, redox reactions, and air-sea transfer), defines the features of Earth as a planet housing active and diverse biology (Petsch, 2003). Current oxygen in the atmosphere and ocean accumulated over billions of years during Earth's evolution (Canfield, 2016), and the ocean is thought to be an important contributor of oxygen due to the high production of this element by marine plant photosynthesis. Currently, evidence has shown that the balance between the production and consumption of oxygen in the Earth system is undergoing an irreversible shift and becoming increasingly fragile due to the interference of human activities. The oxygen concentration on Earth is now undergoing non-negligible depletion, especially in the ocean (Cocco et al., 2013; Long et al., 2016). Decreases in dissolved oxygen in the ocean interior, the “ocean deoxygenation” phenomenon, have occurred since the mid-twentieth century (Breitburg et al., 2018). The observations showed that the open ocean has lost approximately 2% of the oxygen content over the past 50 years (Schmidtko et al., 2017), and subsequent rapid expansions of oxygen-minimum zones have crucial implications for marine productivity, biodiversity, and ecosystem services, threatening survival of marine biota (Diaz & Rosenberg, 2008; Doney et al., 2012; Mora et al., 2013). The changes in the ocean O₂ inventory are tightly associated with the features of the air-sea O₂ flux, which works as a connector between the ocean and atmosphere in the oxygen cycle (Bopp et al., 2002; Gruber et al., 2001; Manning & Keeling, 2006; Najjar & Keeling, 2000; Plattner et al., 2002). The variability of the flux is influenced by ocean circulation, productivity, and other processes that could affect the concentration of dissolved oxygen in the ocean and is thus of vital importance (Deutsch et al., 2005). Wind and sea-ice

coverage could also affect the oxygen exchange between atmosphere and ocean. In this study, based on a suite of Coupled Model Intercomparison Project phase 5 (CMIP5) simulations (Taylor et al., 2011), we investigate the spatiotemporal characteristics of the air-sea O₂ flux and oceanic dissolved oxygen, as well as the mechanism of their changes under anthropogenic forcing. We expect to provide a clear understanding of oceanic oxygen budget and the attribution of air-sea oxygen exchange to ocean deoxygenation under climate change.

2. Materials and Methods

The analysis in the study builds on the recent ocean physical and biochemical projections developed as part of CMIP5. Table S1 in the supporting information summarizes the models used in this study. Aside from the air-sea O₂ flux and oceanic O₂ concentration, nitrogen fixation and denitrification products are used to analyze changes in the oceanic oxygen budget under warming scenarios. The unit of the CMIP5 products is mol m⁻² s⁻¹, which in this study we convert to g m⁻² yr⁻¹ for the sake of comparison. In addition, the variables in these models were all interpolated to a common 1° by 1° grid. The in situ dissolved O₂ concentration data from World Ocean Atlas 2013 (WOA13, Garcia et al., 2014) is used to make comparisons with simulated O₂ concentration from CMIP5.

3. Results

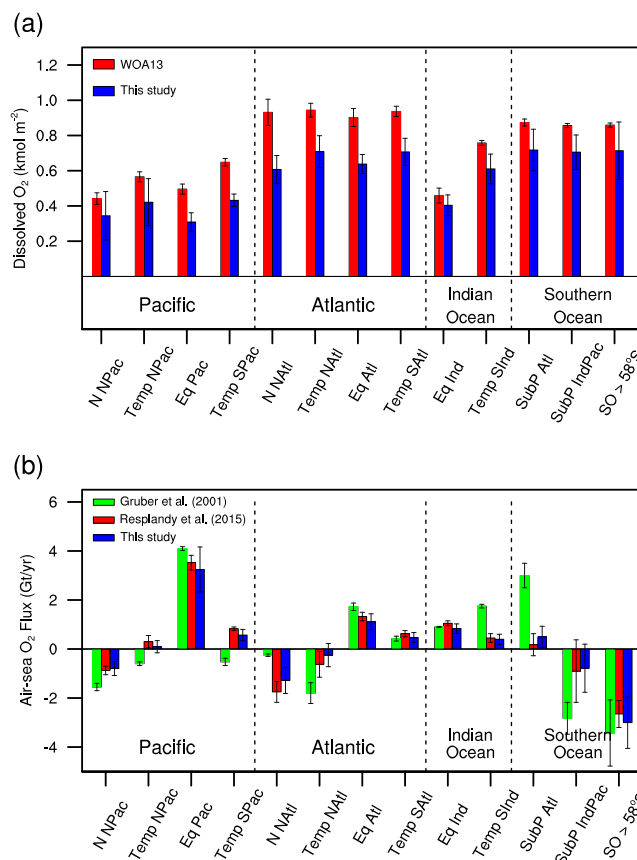


Figure 1. The distributions of ocean dissolved O₂ inventory (a) and air-sea O₂ flux (b) for 13 regions. Positive flux numbers indicate oxygen outgassing to the atmosphere, and the division of the ocean regions is shown in Figure S1. Error bars indicate the uncertainty in each region. The World Ocean Atlas (WOA13) is a data set of climatological mean, gridded fields of oceanographic variables based on in situ measurements from a wide variety of sources (Garcia et al., 2014).

3.1. Spatial Patterns of Air-Sea O₂ Flux and Evaluation Against Available Estimates

Figures 1a and 1b show the spatial distributions of the air-sea O₂ flux and dissolved O₂ inventory averaged from 1975 to 2005 in CMIP5 historical experiments. The global ocean was partitioned into 13 regions (Figure S1) to explore the regional features of the variable. We evaluated the simulated oceanic dissolved oxygen inventory against the in situ data from the World Ocean Atlas 2013 (WOA13) (Garcia et al., 2014). The models underestimate O₂ content among these regions (Figures 1a and S2). It shows a global averaged O₂ content about 0.52 kmol m⁻² in the simulations, which is generally less than WOA13 (~0.69 kmol m⁻²). The largest difference between simulations and WOA13 exists in North Atlantic; the former is approximately 34% lower (~0.32 kmol m⁻²) than the latter. While in other regions such as Equatorial Indian Ocean, the difference can be relatively small (~0.06 kmol m⁻²). Although the simulations are systematically less than the observed marine O₂ content overall, the ensemble mean of models can reproduce spatial distributions of ocean

dissolved oxygen similar to those derived by WOA13 which reflect different bathymetries and ventilation rates across the ocean.

However, the air-sea O₂ flux, different from the dissolved O₂ concentration, has not been observed sufficiently at the global scale. Thus, we evaluated the simulated flux against the results of two previous studies (Gruber et al., 2001; Resplandy et al., 2015). The flux in Gruber et al. (2001) was based on assimilations of oceanic observations with inverse methods, whereas Resplandy et al. (2015) used model simulations. The simulated O₂ flux in this study is generally consistent with the flux derived by Resplandy et al. (2015), with maximum differences (less than 0.47 Gt/yr) existing in North Atlantic. Although the simulated O₂ fluxes in

these regions are slightly different in magnitude from the O₂ flux derived by Gruber et al. (2001), the patterns of the fluxes correspond well in almost all of the regions. The largest differences in O₂ fluxes exist in the Southern Ocean region. In Subpolar South Atlantic, the flux in Gruber et al. shows a much larger outgassing (~3.0 Gt/yr), compared with 0.49 Gt/yr in our study. There is also a stronger influx of oxygen in Subpolar Indian-Pacific Ocean, which is about 2.0 Gt/yr larger than our study. These differences, however, are related to differences in the spatial distribution of the fluxes and could cancel out when averaged over several regions. The results show that all of the models produce similar patterns of air-sea O₂ exchanges, with a net outflux from the oceans to the atmosphere at low latitudes and a net influx to the oceans from the atmosphere at high latitudes (Figures 1b and S3). For all models, the maximum O₂ flux values occur in the same region, with the most outgassing of oxygen to the atmosphere in the Equatorial Pacific and most uptake of oxygen by the ocean in the Southern Ocean (>58S). This pattern is dominated primarily by the characteristics of O₂ solubility, which decreases with increasing temperature, as well as biological O₂ production, which exhibits a surplus in low latitudes and the opposite in high latitudes (Bopp et al., 2002).

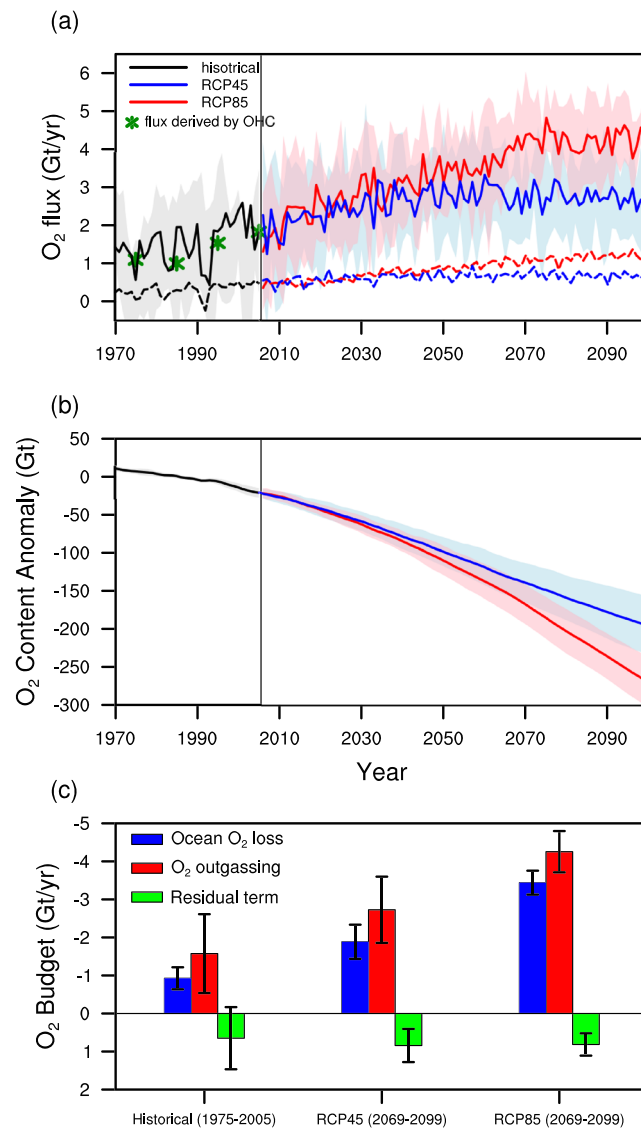


Figure 2. Characteristics of the ocean O₂ budget. (a, b) The temporal variation in the air-sea O₂ flux (a) and dissolved O₂ inventory (b). The black, blue, and red solid lines represent the total air-sea O₂ flux under the historical, RCP4.5, and RCP8.5 scenarios, respectively. The green asterisk indicates the flux derived by linear regression between observed ocean heat content and the oxygen flux, and the dashed lines represent the thermal components of the total flux. (c) The ocean O₂ budget under different scenarios and periods. The shadings in (a) and (b) and error bars in (c) indicate the standard deviation between the CMIP5 models.

3.2. The Global Oceanic Oxygen Budgets

Figure 2 shows the characteristics of the ocean O₂ budget. Observations have already provided sufficient

evidence of a decline in oceanic oxygen concentrations under climate change (Schmidtko et al., 2017). However, the long-term variability of the air-sea O₂ flux, which occurs simultaneously with marine oxygen loss, is severely understudied due to a lack of observations and the relatively large uncertainty of this flux. Thus, we explore their responses to different representative concentration pathway (RCP) scenarios based on a suite of CMIP5 models. From our results, we found a notable variability in air-sea O₂ exchange at the global scale (Figure 2a). Overall, the results show that the ocean released oxygen in the historical period, with a total net O₂ outgassing approximately 1.6 Gt/yr to the atmosphere. This simulated global air-sea O₂ flux also shows remarkable consistency with the results based on the observational ocean heat content (Cheng et al., 2017), which were derived from the tight relationship between the two parameters, assuming that the flux is linearly proportional to ocean heat content (Bopp et al., 2002; Manning & Keeling, 2006). Compared with the historical period, the projected O₂ flux will significantly increase under both RCP scenarios, indicating that more oxygen will escape from the ocean in the future. Ocean deoxygenation can also be detected in the model results (Figure 2b). Simulations reveal an overall decrease in the marine oxygen content under climate change and, more strikingly, an acceleration of this deoxygenation in the future, which will eventually lead to an approximate 2% reduction of the marine oxygen content by the end of the 21st century. The changes of global mean ocean O₂ concentration can be found in Figure S4.

To further understand changes in the oceanic oxygen budget under anthropogenic forcing, we use the oxygen conservation equation derived by Palter and Trossman (2018). Here, we eliminate lateral and vertical transport and treat the ocean as an entirety:

$$\frac{\partial O_2}{\partial t} = F_{air-sea} + J_{residual},$$

where $\frac{\partial O_2}{\partial t}$ is the change of oceanic O₂ inventory, $F_{air-sea}$ is the air-sea O₂ exchanges, and $J_{residual}$ is the residual term (equivalent to the difference between oxygen change and air-sea O₂ flux), which may represent some other processes that could affect the budget, such as organic carbon burial and denitrification. We estimate the contributions of each term under different scenarios (Figure 2c). During the historical period, there was already oxygen escape from the ocean to the atmosphere, with a speed of approximately 1.6 Gt/yr. The residual term compensated for part of the loss, adding ~0.6 Gt O₂ per year to the ocean, although there is large uncertainty. The ocean O₂ content thus decreased by approximately 1.0 Gt/yr in this period. Near the end of the century, the results show that there will be no significant increase in the residual term but an upward trend of oxygen outgassing from the ocean, giving rise to a net loss. Compared with the historical period, models show an increase in outgassing of 1.2 Gt/yr in RCP4.5 and 2.7 Gt/yr in RCP8.5 averaged from year 2069 to 2099, leading to an accelerated decline in the dissolved O₂ content. According to the estimates, marine O₂ loss could grow to approximately 1.9 Gt/yr under the RCP4.5 scenario and could increase to 3.4 Gt/yr under the RCP8.5 scenario. Ocean deoxygenation will become more severe in the future as a consequence of increased oceanic oxygen escape.

Figure 3 presents the spatial distributions of the air-sea O₂ flux trend and ocean O₂ content changes under the RCP8.5 scenario. Strong positive trend of the flux, which indicates more O₂ outgassing or less O₂ uptake by ocean, is primarily found in the high latitudes. The O₂ flux per unit area increases most in the North Atlantic, with an upward trend for over 1.8 gm⁻² yr⁻¹ per year in RCP8.5 (Figure 3a). The magnitudes of the negative changes in the O₂ flux are less than those of the positive changes, leading to a total increased outgassing at the global scale. We can also see the close change between the two variables (Figure 3b). In the low latitudes, there is a net negative change in the air-sea O₂ flux corresponding to an increase of the oceanic O₂ content in the upper layer, while in the high latitudes, the largest positive changes in the O₂ flux occur in the areas with the maximum O₂ loss. Ocean deoxygenation is largely influenced by changes in the air-sea O₂ flux, which describes the characteristics of oxygen escape from the ocean. It should be noted that the spatial distributions of the O₂ inventory are also influenced by the O₂ transport in the ocean, which leads to differences in the spatial pattern of ocean O₂ loss (Figure S5). The changes in the air-sea O₂ flux and oceanic O₂ concentration under the RCP4.5 scenario follow remarkably similar trends as those under the RCP8.5 scenario, although the magnitude of change in RCP8.5 is larger than that in RCP4.5 (Figure S6).

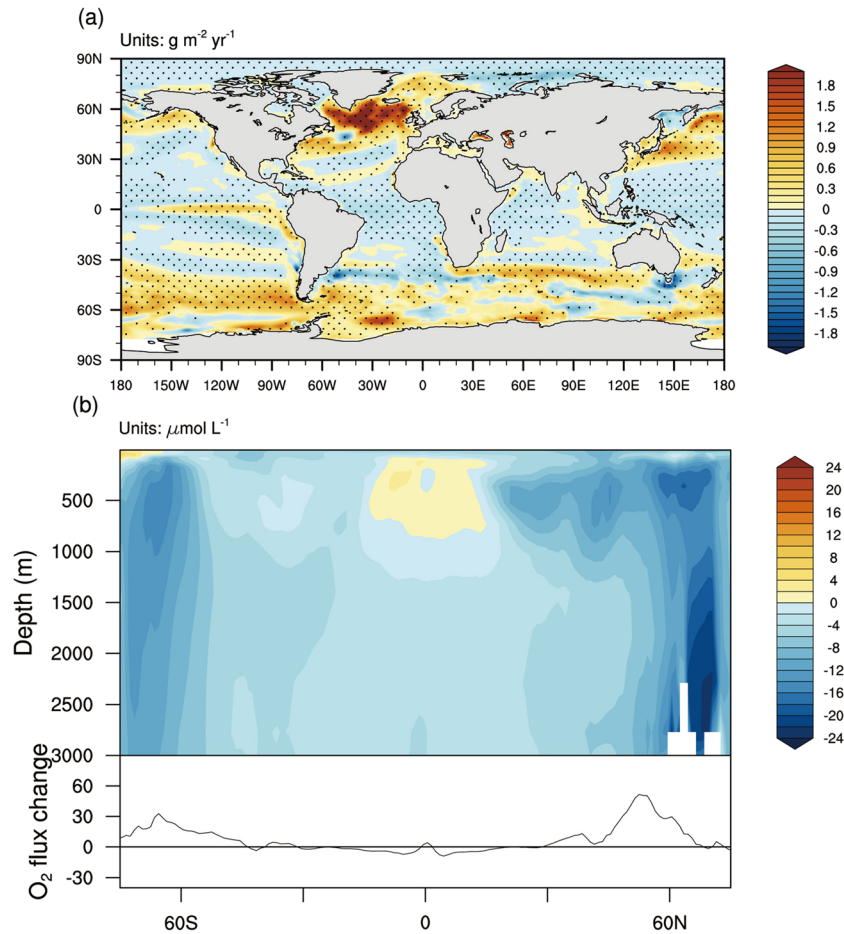


Figure 3. Spatial distributions of the air-sea O₂ flux trend and ocean O₂ concentration changes under the RCP8.5 scenario. (a) Linear tendency of air-sea O₂ flux during 1975–2099. The dotted zones are statistically significant at the 0.01 level. (b) The zonal mean of changes in the O₂ content (color coded) and O₂ flux (line). Change is calculated as the difference between future (i.e., average values from 2069 to 2099) and historical values (i.e., average values from 1975 to 2005).

3.3. Mechanisms of the Increasing Oxygen Escape

This increased oceanic oxygen escape indicates that the physical and biological processes in marine systems may vary in the future due to the interference of human activities, which ultimately lead to more severe ocean deoxygenation. Here, we investigated the mechanisms of this outgassing qualitatively by analyzing other related variables in CMIP5 simulations.

The increase of oceanic temperature can directly influence air-sea O₂ flux as the solubility decreases along with oceanic warming. This thermal effect on O₂ outgassing can be estimated by the following equation (Bopp et al., 2002; Palter & Trossman, 2018):

$$F_{O_2}^{them} = -\frac{Q \partial O_2}{C_p \partial T},$$

where Q is the total downward heat flux at the sea surface; C_p is the capacity of sea water; and $\partial O_2 / \partial T$ represents the temperature dependence of O₂ solubility, which can be derived from Garcia and Gordon (1992). The calculations show that, under the background of ocean warming (Chen & Tung, 2016; Keeling et al., 2010; Levitus et al., 2000; Oliver et al., 2018), the thermal effect contributes approximately one quarter of the total outgassing overall, and this percentage seems to be constant throughout all of the simulated period (Figure 2, dashed lines), which is consistent with previous study

(Bopp et al., 2002). At the end of this century, the thermal effect will account for approximately 0.7 Gt/yr of outgassing in RCP4.5 and 1.2 Gt/yr in RCP8.5.

The air-sea O₂ flux can also be influenced by changes in ocean circulation and mixing, which is called the dynamic effect. There is now evidence on the variability of ocean circulation under marine warming (Chen & Tung, 2018; Morison et al., 2012). Studies have shown that increase of oceanic temperature could lead to enhanced near-surface stratification and shallower mixed layers (Capotondi et al., 2012; Tyrrell, 2011), which finally reduces oxygen supply to the deeper ocean and increases O₂ outgassing. Although quantifying the contribution of these dynamic processes is quite difficult due to their complicated mechanisms, it can be concluded that this dynamic effect is the major contributor to the increased O₂ outgassing according to the features of the thermal components, and the effect due to mixing can be roughly represented by the variability of the mixed layer depth. The simulations show that regions of strong shoaling of the mixed layer correspond well with regions with increasing O₂ outgassing, which is especially apparent in the North Atlantic and in widespread areas in the Southern Ocean (Figure 4a). Other warming-caused dynamic processes, such as slowdown of the Atlantic Meridional Overturning Circulation, which may result in decreased formation of intermediate and deep waters (Krasting et al., 2016), could also prevent oxygen supply from reaching the deeper layers.

It is interesting that the residual term shown in Figure 2c indicates an oxygen gain in the ocean (~0.6 Gt/yr), which makes up for the difference between O₂ outgassing and oceanic O₂ decline. Considering that the differences between oxygenic photosynthesis and respiration are negligible if we integrate the whole ocean, this oxygen source in the ocean could be due to process like denitrification that saves oxygen by utilization of oxidants other than O₂ (Oschlies et al., 2019). The ensemble-mean of models show decreases of the global oceanic nitrate inventory under warming scenarios, revealing nitrogen imbalances (Figure 4b, Figure S7). The tendency of denitrification exceeds the rate of nitrogen fixation, resulting in a net loss of nitrate (Figure S7). Based on the relation that about 1.4 moles of oxygen are gained for every 1 mole of nitrate lost during denitrification (Paulmier et al., 2009), this process on average contributes about 4.1 Tmol/yr of nitrate loss, equivalent to a net gain of ~0.2 Gt of oxygen per year, which could account for more than 30% of the residual term. The remaining part, with a relatively large uncertainty, may be related to some other processes such as the sulfate reduction or the model internal error.

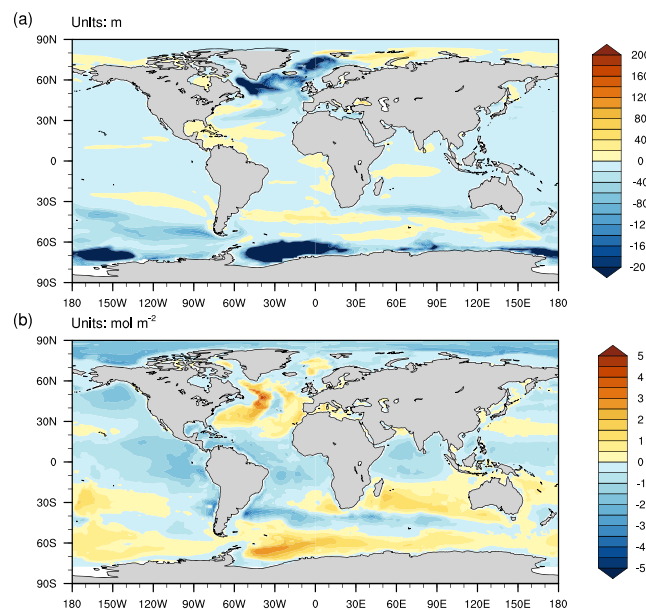


Figure 4. Spatial differences in mixed layer depth and nitrate inventory between future and historical periods under the RCP8.5 scenario. The units in (a) and (b) are m and mol m⁻², respectively. Change is calculated as the difference between future (i.e., average values from 2069 to 2099) and historical values (i.e., average values from 1975 to 2005).

4. Conclusions

Since the air-sea O₂ flux acts as a bridge between the ocean and atmosphere in the oxygen cycle, changes in this flux will directly reflect the status of oceanic oxygen inventory. Based on the CMIP5 models, this study highlights the modification of the oceanic oxygen budget under global warming and the vital importance of changes in air-sea O₂ flux to ocean deoxygenation. The projected increase in the flux indicates that there will be an inevitable shift in the oceanic oxygen cycle under climate change. The ocean is at the risk of accelerated deoxygenation as well as other deleterious biogeochemical changes in the future. It is interesting that our study also shows an oceanic oxygen gain, which could be partly attributed to the nitrate loss due to

denitrification, could compensate for part of the oxygen decrease. However, the magnitude of the oxygen gain is relatively small compared with the magnitude of outgassing. It should also be emphasized that the increased oceanic oxygen outgassing to the atmosphere cannot compensate for the rapid decline in atmospheric O₂ due to human activities, which was approximately 21 Gt/yr in the historical period and may reach 100 Gt/yr by the end of the century (Huang et al., 2018).

Although there are some differences among models in the strength and features of the natural variability of the air-sea O₂ flux, the ensemble-mean of the model results shows remarkable consistency with fluxes derived by observational ocean heat content data. The models provide us with an alternative method to explore the future characteristics of the air-sea O₂ flux under oceanic warming. But it is now still difficult to obtain observed long-term changes in the global air-sea O₂ flux due to the insufficient spatiotemporal coverage of observations and relatively large uncertainty (Bushinsky et al., 2017). Studies have shown that current models may underestimate decline in ocean oxygen inventory because of unresolved transport processes or some missing biogeochemical feedback (Oschlies et al., 2018; Schmidtke et al., 2017). The underestimation by models indicates that the future deoxygenation may be more substantial than the projected scenario shown in this study. Thus, further explorations, especially dedicated observations of air-sea O₂ fluxes, are still needed to improve our understanding and predictions of future changes in the oxygen cycle.

Data Availability Statement

The CMIP5 data set can be downloaded from the website (<https://esgf-node.llnl.gov/search/esgf-llnl/>), and The WOA13 data set is available at the NOAA/NCEI website (<https://www.nodc.noaa.gov/OC5/woa13/>).

Acknowledgments

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