Denitrification under glacial and interglacial conditions: A physical approach

Katrin J. Meissner
School of Earth and Ocean Sciences, University of Victoria, Victoria, British Columbia, Canada

Eric D. Galbraith
Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada

Christoph Völker
Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

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[1] Recent analysis of sedimentary δ15N records over the last 200,000 years has shown an expansion of water column denitrification zones during warmer periods and a shrinkage of these oxygen-poor regions during glacial periods. Two different mechanisms could be responsible for driving the changes in the denitrification records: variations in local productivity leading to a change in remineralization rates and/or changes in the ocean circulation and ocean temperature resulting in variations of the physical supply of dissolved oxygen. Here we focus on the “supply” mechanism by using a fully coupled atmosphere-ocean-land surface scheme model (the University of Victoria Earth System Climate Model) to examine oxygen supply under varying physical conditions while maintaining an invariant biological oxygen utilization scheme. We show that circulation changes can be the cause for the observed changes in dissolved oxygen in the glacial oceans. Lower temperatures and enhanced formation of Antarctic Intermediate Water and North Pacific Intermediate Water during glacial periods increase the physical supply of oxygen and therefore decrease water column denitrification. In our Last Glacial Maximum simulations the change in water characteristics in the eastern tropical Pacific is important enough to reduce denitrification by 46% to 65% compared to present-day conditions, depending on the wind fields used as boundary conditions. The consequences of our findings could be substantial for the near future. With a warming climate, denitrification zones could expand, leading to changes in the biological pump and the flux of N2O into the atmosphere.

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1. Introduction

[2] Biological activity in the marine environment transforms nitrogen between a range of redox states and chemical forms, such as dissolved molecular nitrogen (N2), ionic forms of ammonia (NH4+), nitrite (NO2-) and nitrate (NO3-), as well as organic compounds (e.g., amino acids). Although N2 is very abundant in the oceans, it is biologically unavailable unless “fixed” to an accessible useful form by specialized species of bacteria and archaea (see Karl et al. [2002] for a review). Fixed nitrogen is therefore one of the growth-limiting nutrients in the ocean and has a direct control on the biological pump of carbon [Volk and Hoffert, 1985]. For example, strengthening the biological pump by increasing the oceanic nitrate inventory and biological production is one mechanism that could explain the drawdown of glacial CO2 levels [McElroy, 1983; Falkowski, 1997]. It is therefore necessary to study possible changes in the oceanic nitrogen cycle during glacial and interglacial periods.

[3] Denitrification and N fixation are two important processes related to sources and sinks in the budget of fixed nitrogen. Denitrification occurs when, in the absence or near absence of oxygen, nitrate is used as an electron acceptor in the remineralization of organic matter. This process results in a net loss of fixed nitrogen from the ocean, as the products of denitrification (N2O and N2) are to a large extent lost to the atmosphere [Codispoti and Richards, 1976]. On the other hand, the main source of fixed nitrogen to the ocean is by in situ N fixation by cyanobacteria [Codispoti and Christensen, 1985].

[4] Both denitrification and N fixation leave isotopic imprints in marine sediments. During denitrification, nitrate containing the light isotope of nitrogen (14N) is preferentially reduced, causing the remaining nitrate in the region to become progressively enriched in 15N [Liu and Kaplan, 1989]. Conversely, N fixation contributes low δ15N (close to the atmospheric ratio of zero) where it occurs [Minagawa and Wada, 1986]. The δ15N of organic matter ultimately depends on the isotopic character of the regional nitrogen...
pool; thus, when organic matter sinks and is buried in sediment, it can record the relative influences of denitrification and N fixation [Altabet et al., 1995; Rau et al., 1987].

Recent analysis of sedimentary $^{15}$N records has led to the suggestion that global aggregate rates of N fixation have responded to climatically driven changes in global aggregate water column denitrification rates over the past 200,000 years [Haug et al., 1998; Ganeshram et al., 2002; Galbraith et al., 2004]. Both processes appear to be less active during cold periods and more active during warm periods, suggesting a relative decrease in the extent of water column suboxia during cold periods.

Changes in water column denitrification could be driven by two mechanisms: variations in local productivity leading to a change in remineralization rates and oxygen drawdown, and/or changes in ocean circulation and ocean temperature resulting in variations of the physical supply of dissolved oxygen. Several studies have emphasized the importance of the first mechanism, i.e., variations in biological productivity [Altabet et al., 1995; Ganeshram et al., 2000; Altabet et al., 2002]. However, other studies emphasize the role of variable oxygen supply due to changes in upper ocean ventilation [e.g., Behl and Kennett, 1996; Kienast et al., 2002; Nameroff et al., 2004; Galbraith et al., 2004]. Possible causes include colder water temperatures in the subduction areas, a greater volume production of Antarctic Intermediate Water (AAIW) and/or Subantarctic Mode Water (SAMW), a shorter flow path to the Eastern Tropical Pacific because of an equatorward shift of subduction zones and an increased subsurface current speed. Although both mechanisms are certainly relevant on various temporal and spatial scales, here we will focus on the “supply” mechanism by testing the degree to which purely physical changes are expected to have altered the delivery of dissolved oxygen in the glacial oceans according to a fully coupled atmosphere-ocean-sea ice-land surface scheme model (the University of Victoria (UVic) Earth System Climate Model). We approach this problem by modeling the extent and location of oxygen-depleted zones in the ocean under glacial and interglacial climatic conditions with constant biological oxygen demand.

The experimental setup is described in section 2 and the present-day simulations are discussed in section 3. In section 4 Last Glacial Maximum (LGM) simulations are compared to the present-day control run and changes in the physical supply of dissolved oxygen due to temperature and ventilation changes are analyzed. Conclusions are given in section 5.

2. Experimental Setting

We use the UVic Earth System Climate Model (ESCM, Version 2.6) which consists of an ocean general circulation model (Modular Ocean Model, Version 2 [Pacanowski, 1995]) coupled to a vertically integrated two dimensional energy-moisture balance model of the atmosphere, a dynamic-thermodynamic sea ice model [Bits et al., 2001] and a land surface scheme [Matthews et al., 2003]. The model version including the atmospheric, ocean and sea ice model is described by Weaver et al. [2001]. It is driven by seasonal variations in solar insolation at the top of the atmosphere and seasonally varying wind stress at the ocean surface [Kalnay et al., 1996].

To model the concentration of dissolved oxygen in the ocean, monthly averages of the vertical flux of particulate organic phosphorus at 75 m depth are used (please refer to Appendix A for a detailed description of the parameterizations used to implement oxygen as a tracer in the model). Fields of vertical fluxes of particulate organic phosphorus were generated by five different models, all members of OCMIP-2 (the Ocean Carbon-Cycle Model Intercomparison Project). The vertical fluxes were interpolated linearly to construct a field which varies smoothly over time. Biological utilization of dissolved oxygen was then calculated with a depth-dependent remineralization rate. As the model used in this study does not incorporate a biogeochemical cycle, the biology in the ocean has only a fixed seasonal variability and does not depend on the climate state. All simulations presented in this study are in statistical equilibrium.

3. Present-Day Simulations

Since the sensitivity of the model climate ultimately depends on the model’s climate state itself, the present day simulation must be reasonably accurate. We therefore begin our discussion with the model’s simulated dissolved oxygen concentrations in the ocean under present-day climatological wind fields and solar radiation.

3.1. Choosing an Adequate Biological Productivity Field

Five control experiments were carried out, forced with five different fields of vertical fluxes of particulate organic phosphorus obtained with the following models: LLNL (Lawrence Livermore National Laboratory, USA), NCAR (National Center for Atmospheric Research, USA), PRINCETON (Princeton University, USA), SOC (Southampton Oceanography Centre, UK) and MIT (Massachusetts Institute of Technology, USA); all data are available at the DODS-IPSL server (http://dods.ipsl.jussieu.fr). These five control experiments are characterized by the same circulation and climate; only the biological productivity (i.e., the export of particulate organic phosphorus) is changed. The simulated apparent oxygen utilization (AOU) at 300 m depth for these five simulations are compared to observations [Conkright et al., 2002] in Figure 1. All simulations capture the high AOU on the eastern side of the tropical oceans, as well as low AOU in the subtropics and in the North Atlantic Ocean. The extent of the high-AOU tongue in the tropical eastern Pacific is exaggerated in all simulations except for PRINCETON (Figure 1d) and LLNL (Figure 1e). This is due to the relatively high productivity in the central eastern equatorial Pacific simulated by the MIT, NCAR and SOC models combined with a relatively broad and weak equatorial undercurrent (compared to observations) in global ocean general circulation models. Forcing the model with the productivity from MIT, NCAR and SOC also leads to an overestimation of AOU in the subtropical gyres and in the Southern Ocean.

Overall, we find that the simulated concentration of dissolved oxygen in our model is in best agreement with
observations when forced with the vertical flux of particulate organic phosphorus from the PRINCETON or LLNL models. Our goal is to test the extent to which circulation changes can impact the distribution of suboxia, irrespective of changes in biological export production: We will thus compare the concentrations of dissolved O$_2$ under present-day and Last Glacial Maximum climate states without changing the biological productivity. Therefore the absolute values of productivity are only of importance for illustrative purposes and can be adjusted in order to simulate a distribution of dissolved oxygen under present-day conditions in best agreement with observations. For this purpose,

Figure 1. Annually averaged apparent oxygen utilization (AOU) at 300 m depth under present-day conditions for experiments run with data from (a) MIT, (b) NCAR, (c) SOC, (d) PRINCETON, (e) LLNL, and (f) observations [Conkright et al., 2002]. Units are in mol m$^{-3}$. See color version of this figure at back of this issue.
we reduced the simulated productivity by the LLNL and PRINCETON model by a factor of 20 west of South Africa and increased the productivity by a factor of 10 in the Arabian Sea. The resulting simulated AOU is shown in Figures 1d and 1e (Figures 1a–1c show simulations with the unmodified productivity fields from MIT, NCAR and SOC, whereas Figures 1d and 1e have been simulated with the modified fields in the Arabian Sea and west of South Africa from PRINCETON and LLNL). The AOU west of South Africa is smaller in the LLNL and PRINCETON simulations and in better agreement with observations than the other present-day simulations; By increasing the productivity in the Arabian Sea, the simulated AOU is higher there than in the three other simulations; however, it is still lower than observational data.

The PRINCETON and LLNL simulations are very similar; the model run forced with LLNL productivity shows a slightly better representation of dissolved oxygen in the deep ocean than the PRINCETON simulation (not shown). We finally chose the biological productivity simulated by the LLNL model [Caldeira and Duffy, 2000] to force our ocean model for the simulations described in this study. To test the impact of the changed productivities in the Arabian Sea and west of South Africa, a control run forced with unchanged LLNL productivity has also been carried out. The results (not shown) indicate that the triggered productivities introduce a discrepancy in oxygen concentrations of the order of magnitude of $10^{-5} \text{ mol m}^{-3}$ in the simulated eastern tropical Pacific denitrification zones. Compared to the critical oxygen concentration of $5 \times 10^{-3} \text{ mol m}^{-3}$, below which denitrification takes place, this difference is negligible.

### 3.2. LLNL Present-Day Control Run

It is apparent through comparison of Figures 1e and 1f, that there are four regions where the simulated AOU is in poor agreement with observations. The first two have already been discussed in section 3.1: AOU is still underestimated in the Arabian Sea and overestimated west of South Africa despite the changes applied to the productivity forcing field. This points to deficiencies either in the physical flow field (Arabian Sea) and/or the parameterization of the vertical flux of organic matter (Namibia). West of West Africa (Cape Verde Islands), the simulated AOU is underestimated because of an underestimate of the high biological productivity in this region due to coastal upwelling. The last region with a larger discrepancy is situated in the North Pacific, where the simulated AOU is weaker than in the observational data. This discrepancy is also due to our forcing field and is not unique: model simulations with coupled biological-physical models consistently underpredict biological productivity in the North Pacific relative to observations [Gnanadesikan et al., 2002; Sarmento et al., 2003].

Coarse-resolution ocean general circulation models (OGCMs) generally overestimate equatorial upwelling [Toggweiler et al., 1991; Doney et al., 2004] and simulate a too diffuse and weak equatorial upwelling [Doney et al., 2004]. These dynamical flaws have been related in the past to the phenomenon of “nutrient trapping” in the equatorial zones (excess of subsurface nutrient concentrations relative to observations which occurs principally in the eastern equatorial Pacific [Najjar et al., 1992]. Aumont et al. [1999] and Oschlies [2000] describe how model resolution and the numerical treatment of advection can lead to an overestimation of subsurface nutrients in the tropical oceans. The fields of particulate organic phosphorus used in this study have been generated by coarse-resolution OGCMs, which are prone to such problems [Doney et al., 2004] and result in an enhanced flux of particulate organic phosphorus in equatorial regions which leads to a high AOU in our simulations. On the other hand, the UVic ESCM is also a coarse-resolution model and is therefore unable to simulate a strong and narrow equatorial upwelling current that brings in low-nutrient water from the western basins, potentially counteracting the overestimation of particulate organic phosphorus. The difficulty in modeling equatorial dynamics and biology explains why the two lobes of the most oxygen-depleted water masses in the subtropical Pacific centered between 15° and 20°N and S, respectively, are not as precisely defined in our simulation as in the observations. However, the comparison between Figures 1e and 1f shows that the modeled AOU at 300 m depth in the eastern tropical Pacific is very close to observations in concentration as well as distribution.

The annual and zonal means of dissolved oxygen over the Atlantic, Pacific and Indian oceans are shown in Figure 2. In all three ocean basins the distinctive oxygen-rich tongue of Antarctic Intermediate Water (AAIW) agrees well with observations. North Pacific Intermediate water is also well represented. The oxygen signature of Antarctic Bottom Water (AABW) can be seen in the Pacific Ocean, but oxygen concentrations are slightly too low for AABW in the Atlantic and Indian Ocean. The oxygen-poor zone in the Pacific northern subtropics reaches too far south, but the overall structure of these suboxic zones in the Pacific and Indian Ocean is similar to observations. The largest discrepancy between modeled results and observations occurs in the North Atlantic ocean, where the simulated North Atlantic Deep Water (NADW) is too enriched in dissolved oxygen. A possible explanation for this discrepancy is the fact that simulated sea surface temperatures (SSTs) are too cold in the Greenland, Iceland, and Norwegian seas in our present-day control run [Weaver et al., 2001]. This surface water anomaly leads to the formation of NADW which is cooler than observed and therefore too enriched in dissolved oxygen. However, since we concentrate our analysis on the eastern tropical Pacific oxygen minimum zones, we conclude that our implementation of oxygen as a new tracer in the UVic ESCM with “constant” biology has been successful and adequately simulates the present-day concentrations.

### 4. Last Glacial Maximum Experiments

To test the hypothesis that physical circulation changes in the glacial ocean may impact water column suboxia and, hence, sedimentary nitrogen isotopic records, we integrate the coupled system under 20 ka BP conditions, with an atmospheric CO$_2$ concentration equal to 200 ppm and orbital parameters corresponding to 20 ka BP [Berger,
1978]. We use elevated topography based on a reconstruction of Northern Hemisphere ice sheets [Peltier, 1993]. As the atmospheric model consists of an energy and moisture balance model, atmospheric dynamics are poorly represented. At the same time, prevailing winds during glacial times are not very well constrained. For this reason, we carry out three different LGM simulations, each forced with a different wind field. The first simulation is run with

**Figure 2.** Annually and zonally averaged concentration of dissolved oxygen (in mol m$^{-3}$). (left) LLNL present-day control run and (right) observations [Conkright et al., 2002] for the (a and b) Atlantic, (c and d) Pacific, and (e and f) Indian oceans. See color version of this figure at back of this issue.
Table 1. Description of the Simulations

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Boundary Condition</th>
<th>Wind Stress</th>
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<tbody>
<tr>
<td>PD</td>
<td>PD</td>
<td>pp</td>
</tr>
<tr>
<td>LGM_PD</td>
<td>LGM</td>
<td>pp</td>
</tr>
<tr>
<td>LGM_SOUTH</td>
<td>LGM</td>
<td>PD</td>
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<tr>
<td>LGM_HIGH_LAT</td>
<td>LGM</td>
<td>PD plus increased wind stress in southern high latitudes</td>
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*Present-day orbital parameters, atmospheric CO$_2$ = 365 ppm.

1. Kalnay et al. [1996].

2. Last Glacial Maximum orbital parameters, atmospheric CO$_2$ = 200 ppm, prescribed continental ice sheets.

4.1. Eastern Tropical Pacific Oxygen Minimum Zones

One method to quantify denitrification in our model is to compute the virtual amount of dissolved oxygen which would have been used by remineralization in suboxic regions (here defined as O$_2$ $< 5 \times 10^{-3}$ mol m$^{-3}$) if enough oxygen was available (called “O$_2$ deficit” hereinafter). It has been suggested that oxidation of organic matter is less effective under suboxic conditions [e.g., Hartnett and Devol (1993); hence the rate of denitrification may be less than implied by the O$_2$ deficit. However, the importance of this discrepancy is debatable [e.g., Ganeshram et al., 1999] and, more importantly, would be unlikely to change the relative glacial-interglacial changes upon which we focus, impacting only the absolute rates. Thus it bears little importance on our investigation. Given the stoichiometry (1 mol of O$_2$ can accept 4 mol of electrons, whereas 1 mol of NO$_3^-$ can accept 5 mol of electrons), we can assume that 1.25 mol s$^{-1}$ of O$_2$ deficit is equivalent to an NO$_3^-$ reduction rate of approximately 1 mol s$^{-1}$.

Integrated over the eastern tropical Pacific (ETP) oxygen minimum zones the annual mean of this O$_2$ deficit amounts to 0.5524 $\times 10^4$ mol s$^{-1}$ for our present-day equilibrium run. This is equivalent to 195 Tg N yr$^{-1}$, 4 times higher than many estimates based on observations [Deutsch et al., 2001; Gruber and Sarmiento, 1997]. Such a discrepancy may appear significant but is in fact unimportant when reasoned as follows: The amount of “denitrification” is quantified as the oxidant demand which exceeds the total supply of oxygen. This could be written as $D = U - S$, where D is denitrification, U is oxygen utilization, and S is oxygen supply. Because D is small ($\sim 10$ $\mu$M) compared to U and S ($\sim 320$ $\mu$M), small errors in the size of U and S can produce large errors in D. Hence a factor of 4 error in D would be equivalent to an error of only 12% in the relative sizes of U and S. Since our goal is not to quantify denitrification rates but to examine the degree by which S varies between glacial and interglacial conditions, the large error in D is unimportant.

In addition to the argument above we note that modern day water column denitrification rates remain poorly quantified because of the fact that rates can only be measured indirectly. Estimates of denitrification rates have increased drastically over the past decades, illustrated by the decrease in estimated turnover time from as much as 26,000 years [Tsunogai, 1971] through 8000 [Liu, 1979] and 3500 [Gruber and Sarmiento, 1997] to 1500 years [Codispoti et al., 2001], more than a full order of magnitude in thirty years. Hence the model value is in fact closer to current estimates than are most historical estimates. Furthermore, currently accepted denitrification rates, which are based on limited observations, may still be underestimated to some degree. This is suggested by the observations of high N$_2$/Ar in denitrification zones discussed by Codispoti et al. [2001], which at face value would suggest that denitrification rates are close to 100 Tg N yr$^{-1}$ in the ETP, which is half the value generated by our model.

An important uncertainty in our simulations is the definition of the critical oxygen concentration below which denitrification takes place (here defined as $5 \times 10^{-3}$ mol m$^{-3}$). Codispoti et al. [2005] state in a review of suboxic processes: “Due primarily to analytical difficulties, working definitions of suboxic conditions vary with upper limit dissolved oxygen concentrations ranging from $\sim 2$ to 10 $\mu$M [e.g., Codispoti et al., 1991, 2001; Murray et al., 1995]. The best available data suggest that suboxic respiration does not become prominent until oxygen concentrations fall below $\sim 2-4$ $\mu$M.” To examine the impact that this span of critical oxygen concentration has on denitrification rates in our model, two additional present-day equilibrium runs were conducted (one with $2 \times 10^{-3}$ mol m$^{-3}$, the other with $10 \times 10^{-3}$ mol m$^{-3}$ as cutoff values). The simulated denitrification rates in the eastern tropical Pacific amount to 179 Tg N yr$^{-1}$ and 209 Tg N yr$^{-1}$ for critical oxygen concentrations of $2 \times 10^{-3}$ mol m$^{-3}$ and $10 \times 10^{-3}$ mol m$^{-3}$, respectively, indicating that the integrated rate of denitrification is relatively insensitive to the O$_2$ threshold.

Comparing our present-day control run to LGM simulations, the annual mean of O$_2$ deficit integrated over the eastern tropical Pacific oxygen minimum zones amounts to 0.30 $\times 10^6$ mol s$^{-1}$ (106 Tg N yr$^{-1}$) for LGM_PD, 0.22 $\times 10^6$ mol s$^{-1}$ (77 Tg N yr$^{-1}$) for LGM_SOUTH and 0.19 $\times 10^6$ mol s$^{-1}$ (69 Tg N yr$^{-1}$) in the case of LGM_HIGH_LAT (Table 2). By only changing the orbital parameters, atmospheric CO$_2$ concentrations and topography/albedo over
Figure 3. Annually averaged concentration of “deficit” dissolved oxygen (see text, $O_2$ deficit in mmol m$^{-3}$ yr$^{-1}$), present-day (PD) control run at depth (a) 177 m, (b) 292 m, and (c) 433 m; LGM_PD at (d) 177 m, (e) 292 m, and (f) 433 m; LGM_SOUTH at (g) 177 m, (h) 292 m, and (i) 433 m; and LGM_HIGH_LAT at (j) 177 m, (k) 292 m, and (l) 433 m. See color version of this figure at back of this issue.
areas of continental ice sheets, the change in water characteristics in the eastern tropical Pacific is large enough to reduce denitrification by almost 50% compared to present-day conditions (106 Tg N yr⁻¹ versus 195 Tg N yr⁻¹). The two other experiments illustrate that an enhanced circulation due to higher wind speeds reinforce this trend. The spatial distribution of O₂ deficit and the volume of suboxic zones are shown in Figure 3 and Table 2, respectively. In our simulations, denitrification in the eastern tropical Pacific occurs in three model layers, the maximum occurring at the shallowest of the three at 177 m depth. Size and intensity of denitrification zones decreases significantly between the present-day control run and the LGM run with present-day wind fields (LGM_PD).

[23] To quantify ventilation changes, we introduce an artificial passive tracer. The concentration of this tracer is held at one in the top layer over a period of 100 years, enabling an investigation of the extent to which water masses in deeper layers are replaced by surface waters during the last 100 years of model integration (e.g., if the concentration of this tracer in a given grid box equals 0.3, 30% of the water has been “ventilated” during the last 100 years). Table 2 shows weighted averages, calculated by two different methods, of temperature, salinity and “age” or “ventilation” of the eastern tropical Pacific integrated over the volume in which denitrification occurs. The first group of averages reflects differences in the denitrifying water masses and are computed as follows:

\[
X_{\text{weighted average}} = \frac{\int X \cdot O_2(\text{deficit}) \, dV}{\int O_2(\text{deficit}) \, dV} \quad (1)
\]

where X stands for the variable to be averaged and \(O_2(\text{deficit})\) is the amount of oxygen which would have been used by remineralization if enough oxygen was available. The volume over which the average is calculated changes in each simulation with the volume of oxygen-poor zones, so that the weighted average gives an indication of the average water characteristics in which denitrification occurs in that simulation. However, the comparison of these values between different simulations has to be interpreted with care, as the weighted integral depends on the varying size of oxygen-poor zones as well as the amount of O₂ deficit. Furthermore, as the denitrification zones shoul under LGM conditions, part of the weighted average reflects a shift in the locus of denitrification to shallower, warmer, better ventilated waters rather than a temporal change in regional water mass characteristics.

[24] Also shown in Table 2 are the weighted averages of temperature, salinity and “age” calculated using a spatially constant volume of ocean, defined as the region in which denitrification takes place in our present-day simulation. Because this volume includes parts of the ocean in which denitrification is attenuated by physical changes under LGM scenarios, these values reflect the physical changes that drive the decrease in oxygen deficiency. The weighted averages over present-day denitrification regions are computed as in equation (1) but using \(O_2(\text{deficit,FD})\), the amount of oxygen in our present-day simulation which would have been used by remineralization if enough oxygen was available.

[25] The following discussion of temperature and salinity in the suboxic zone is based on the assumption that potential temperature and salinity are conserved quantities. Therefore the characteristics of the water masses in suboxic zones depend on the characteristics that the source water masses had at the surface in the subduction zones.

[26] The change in mean temperature of denitrifying water masses between PD and LGM simulations exceeds 1°C (10.5°C versus 9.2°C), whereas the temperature change averaged over PD denitrification zones changes by almost 2°C (10.5°C versus 8.7°C). Changing surface wind speeds affects the temperatures only slightly. The rise in global salinity due to freshwater storage on land in the form of continental ice sheets has not been taken into account in the LGM simulations presented here. Salinity changes between different experiments are therefore solely due to circulation changes. According to Table 2, the average salinity in denitrification zones remains almost unchanged during the 4 simulations (change of less than 0.21 psu). The mean water characteristics in oxygen-poor zones are cooler and saltier during the LGM simulations than during the present-day control run. Whereas cooler temperatures increase the solubility of oxygen, higher salinities reduce the solubility of oxygen and counteract the total effect of reduced denitrification. The effect of temperature changes on oxygen solubility is greater by an order of magnitude, than the counter effect due to salinity changes (\(O_2(\text{sat},10^\circ C) = 10.52\) psu; \(O_2(\text{sat},10^\circ C) = 8.2 \times 10^{-3}\) mol m⁻³), whereas \(O_2(\text{sat},9.2^\circ C) = 4.26\) psu; \(O_2(\text{sat},10.5^\circ C) = 3.4 \times 10^{-3}\) mol m⁻³) [Garcia and Gordon, 1992].

[27] Another important factor is the age of the water mass in denitrification zones. The weighted average concentration of our artificial tracer amounts to 0.74 in the present-day simulation, and to 0.81, 0.84, 0.85 in LGM_PD, respectively.
Figure 4. Annual and zonal mean between 75°W and 145°W: (left) artificial "ventilation" tracer (after 100 years of integration, see text) and (right) temperature (°C) for (a and b) LGM_PD minus PD, (c and d) LGM_SOUTH minus LGM_PD, and (e and f) LGM_HIGH_LAT minus LGM_SOUTH. The annual and zonal mean concentration of "deficit" dissolved oxygen (O₂ deficit in mmol m⁻² yr⁻¹) is also plotted in contour lines (PD in black, LGM_PD in cyan, LGM_SOUTH in blue, and LGM_HIGH_LAT in green). See color version of this figure at back of this issue.
LGM_SOUTH and LGM_HIGH_LAT experiments, respectively. Seventy-four percent of the water mass in which denitrification occurs has been in contact with surface waters over the last 100 years during the present-day simulation. The ventilation of these water masses increases under LGM conditions and with increasing wind speeds. The water masses in the eastern tropical Pacific low-oxygen zones are therefore better ventilated during the LGM runs, especially when wind speeds in the southern and northern high latitudes are increased. This trend is partly due to the fact that the denitrification zones shoal under LGM conditions. Averaged over the PD suboxic zones, the weighted average concentration of our artificial tracer amounts to 0.74 in the present-day simulation, and to 0.75, 0.78, 0.79 in LGM_PD, LGM_SOUTH and LGM_HIGH_LAT experiments, respectively.

Figure 4 shows the zonal average of temperature and ventilation changes between 75°W and 145°W in the Pacific Ocean (same region as shown in Figure 3). Water masses in which denitrification takes place are both better ventilated and cooler during the LGM_PD run compared to the PD control run (Figures 4a and 4b). However, by increasing the wind stress in the Southern Hemisphere, suboxic zones shrink even more although the temperature increases in the suboxic zones. In this case, the increase in dissolved oxygen is therefore due to better ventilation of AAIW and not to temperature change (Figures 4c and 4d). Increased wind stresses in the Northern Hemisphere have only a very small effect on suboxic zones in the eastern tropical Pacific, water temperatures decrease and the ventilation increases slightly because of more vigorous formation of North Pacific Intermediate Water (NPIW). The effect on the size of suboxic zones is negligible.

Finally, Figure 5 shows differences in zonal average ventilation tracer concentration over the whole Pacific Ocean. Running the model with LGM boundary conditions (orbital parameters, atmospheric CO$_2$ and topography/albedo changes over land) results in an enhanced formation of AABW and AAIW. Increasing the wind speeds in the Southern Hemisphere increases the ventilation of AAIW and AABW even further, whereas increasing wind speeds in the Northern Hemisphere creates a well-defined tongue of better ventilated NPIW.

4.2. Discussion

By comparing model simulations of glacial versus interglacial circulation with unchanged export production, we have shown that changes in physical characteristics of water masses can be important enough to significantly change the supply of oxygen to suboxic zones and therefore denitrification rates. Changes in local productivity and remineralization rates do not seem to be needed to trigger an important change in the suboxic zones. We realize, however, that the biological activity would at least react to changes in the nitrogen cycle, oxygen concentrations, temperature and salinity. We have neglected this potentially important feedback in our study by using a climate-
independent biological activity to investigate the physical mechanism in isolation first. It would be interesting to repeat the simulations with a fully coupled biogeochemistry ocean model.

[31] The reconstruction of wind patterns during glacial periods is still a topic of ongoing research. Owing to stronger temperature gradients, wind speeds were probably higher during glacial periods than under interglacial conditions [COHMAP Members, 1988]. Higher wind speeds in high latitudes increase intermediate water formation and therefore the physical supply of dissolved oxygen to oxygen-poor zones. To address this point, we carried out several LGM simulations with different wind forcings. Our approach to increase wind stresses linearly in high latitudes to a maximum of 1.5 times the present-day values is very simple and highly unrealistic. However, it shows that increased wind speeds indeed increase the oxygen supply and therefore reduce denitrification in the eastern tropical Pacific. Our results are not quantitative, but the qualitative finding is important: Our LGM_PD simulation which has been integrated with present-day wind speeds and therefore simulates the lowest possible intermediate water ventilation rates due to wind speeds under glacial conditions, shows an important reduction in the O$_2$ deficit which is a measure for the strength of denitrification (by almost 50%).

[32] Another important shortcoming in our simulations is related to the global salinity in the ocean. During the LGM when large amounts of freshwater were stored on continents in form of continental ice sheets, the world ocean was about 1 psu saltier than today. The global increase in salinity and its spatial redistribution affects the oceanic circulation as well as the solubility of dissolved oxygen [Meissner and Gerdes, 2002]. An increase in salinity decreases the solubility of oxygen and counters the changes in temperature and ventilation. In our simulations, we find a decrease of 1°–2°C averaged over oxygen-depleted zones in the eastern tropical Pacific. With a potential increase in salinity of 1 psu, the solubility of oxygen in glacial water masses would still be higher than during interglacial periods (O$_{2\text{sat}}$(10°C, 34 psu) = 0.2838 mol m$^{-3}$ whereas O$_{2\text{sat}}$(9°C, 35 psu) = 0.2883 mol m$^{-3}$ [Garcia and Gordon, 1992]). This simplified calculation does not take into account the fact that the increase in salinity did not occur uniformly and that it would have affected the circulation.

[33] Finally, our simulation of oxygen distribution relies on two assumptions on the vertical flux and remineralization of organic matter, namely a constant ratio between oxygen and phosphate consumption [Anderson and Sarmiento, 1994], and a uniform vertical dependency of the organic matter flux following a power law [Martin et al., 1987]. Both assumptions have long been suspected to be oversimplifications. Only recently are we beginning to get an understanding of the extent and mechanisms behind deviations from Redfield scaling and power law flux distributions [e.g., Li and Peng, 2002; Schneider et al., 2004; Francois et al., 2002; Armstrong et al., 2002; Klaas and Archer, 2002]. Incorporation of these variations, however, only makes sense in a fully coupled physical-biological model of primary production and nutrient cycling, which is beyond the scope of our present study.

5. Conclusions

[34] We have shown in the present study that, by changing dissolved oxygen in the glacial ocean, circulation changes can be the cause for the changes in denitrification rates that have been inferred from proxy data. Lower temperatures and enhanced formation of Antarctic Intermediate Water and North Pacific Intermediate Water during glacial periods increase the physical supply of oxygen and therefore decrease water column denitrification. As wind patterns during glacial periods are not very well defined, several experiments with different wind fields have been performed. All simulations show an increase in dissolved oxygen in the eastern tropical Pacific suboxic zones compared to a present-day control simulation. As wind speeds were probably higher in most regions during glacial times, we can define our simulation LGM_PD using present-day wind stresses as the “worst” possible scenario. This simulation shows that by only changing the orbital parameters, atmospheric CO$_2$ concentrations and topography/albedo over areas of continental ice sheets, the change in water characteristics in the eastern tropical Pacific is important enough to reduce denitrification by almost 50% compared to present-day conditions. An enhanced circulation due to higher wind speeds even reinforces this trend. Future improvements to model physics should hopefully better resolve the geometry of the ETP denitrification zones. We therefore agree with the recent findings of Nameroff et al. [2004] and suggestion of Galbraith et al. [2004] that changes in ventilation and water characteristics were a very important factor in the variability of water column denitrification, potentially outweighing changes in regional export productivity. The consequences of our findings could be substantial for the near future. With a warming climate, denitrification zones could expand leading to changes in the amount of available fixed nitrogen in the ocean, and thus in marine productivity, the biological pump, and the flux of N$_2$O into the atmosphere. Nitrous oxide is a 275 times more powerful greenhouse gas than carbon dioxide and is also involved in the destruction of stratospheric ozone.

Appendix A: Implementing Oxygen

[35] The balance equations for dissolved oxygen and dissolved organic phosphorus (DOP) can be written as

$$\frac{\partial}{\partial t}O_2 = \mathcal{L}(O_2) + J_{O_2}$$

$$\frac{\partial}{\partial t}DOP = \mathcal{L}(DOP) + J_{DOP}$$

where $\mathcal{L}$ is the advection-diffusion operator, and $J$ stands for sources minus sinks due to biological activity. In the
first layer, dissolved oxygen is set to the saturation concentration.

[36] As the model version used for this study does not have a biology component, the sources minus sinks due to biological activity are calculated from the vertical flux of particulate organic phosphorus (POP) at 75 m ($F_{\text{POP}}(z = 75 \text{ m})$).

[37] Following Anderson and Sarmiento [1995] and R. Najjar and J. Orr (Design of OCMIP-2 simulations of chlorofluorocarbons, the solubility pump and common biogeochemistry, 1998, available at http://www.ipsl. jussieu.fr/OCMIP/, hereinafter referred to as Najjar and Orr, OCMIP-2 protocol, 1998), the decrease of the downward flux of POP with depth due to remineralization is assumed to follow a power law relationship proposed by Martin et al. [1987] for vertical carbon flux:

$$F_{\text{POP}}(z) = F_{\text{POP}}(z = 75 \text{m}) \cdot \left(\frac{75}{z}\right)^{-a}$$

where $a = 0.9$. To compute $J_{\text{DOP}}$ two regions are defined, separated by the compensation depth at which photosynthesis equals respiration [Smetacek and Passow, 1990; Najjar and Orr, OCMIP-2 protocol, 1998]. In the present study the first region is restricted to the first layer in the ocean model, whereas the second region covers the rest of the ocean.

[38] Taking the assumption that a fixed fraction, $\sigma$, of the phosphate uptake in the first layer is converted into DOP (Najjar and Orr, OCMIP-2 protocol, 1998):

$$J_{\text{DOP}} = \begin{cases} \frac{\sigma}{1 - \sigma} \frac{\partial F_{\text{POP}}}{\partial z} - \kappa [\text{DOP}] & \text{first layer} \\ -\kappa [\text{DOP}] & \text{below} \end{cases}$$

where $\sigma = 0.67$ and $\kappa$ is the semilabile DOP consumption rate constant (set to 1/0.5 yr [Najjar and Orr, OCMIP-2 protocol, 1998]).

[39] Finally

$$J_{\text{O}_2} = \begin{cases} R_{\text{O}_2, \text{P}} \cdot \left( J_{\text{DOP}} + \frac{\partial F_{\text{POP}}}{\partial z} \right) & \text{if } \text{O}_2 > O_2^{\text{crit}} \\ 0 & \text{otherwise} \end{cases}$$

where $R_{\text{O}_2, \text{P}}$ is the Redfield Ratio (set to 170 [Anderson and Sarmiento, 1994]) and $O_2^{\text{crit}}$ is set equal to $5 \times 10^{-3}$ mol m$^{-3}$.

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E. D. Galbraith, Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, Vancouver, B. C., Canada V6T 1Z4.

K. J. Meissner, School of Earth and Ocean Sciences, University of Victoria, P.O. Box 3055, Stn CSC, Victoria, B. C., Canada V8W 3P6. (katrin@ocean.uvic.ca)

C. Völker, Alfred Wegener Institute for Polar and Marine Research, D-27568 Bremerhaven, Germany.
Figure 1. Annually averaged apparent oxygen utilization (AOU) at 300 m depth under present-day conditions for experiments run with data from (a) MIT, (b) NCAR, (c) SOC, (d) PRINCETON, (e) LLNL, and (f) observations [Conkright et al., 2002]. Units are in mol m$^{-3}$. 
Figure 2. Annually and zonally averaged concentration of dissolved oxygen (in mol m$^{-3}$). (left) LLNL present-day control run and (right) observations [Conkright et al., 2002] for the (a and b) Atlantic, (c and d) Pacific, and (e and f) Indian oceans.
Figure 3. Annually averaged concentration of “deficit” dissolved oxygen (see text, $O_2$ deficit in mmol m\(^{-3}\) yr\(^{-1}\)), present-day (PD) control run at depth (a) 177 m, (b) 292 m, and (c) 433 m; LGM_PD at (d) 177 m, (e) 292 m, and (f) 433 m; LGM_SOUTH at (g) 177 m, (h) 292 m, and (i) 433 m; and LGM_HIGH_LAT at (j) 177 m, (k) 292 m, and (l) 433 m.
Figure 4. Annual and zonal mean between 75°W and 145°W: (left) artificial “ventilation” tracer (after 100 years of integration, see text) and (right) temperature (°C) for (a and b) LGM_PD minus PD, (c and d) LGM_SOUTH minus LGM_PD, and (e and f) LGM_HIGH_LAT minus LGM_SOUTH. The annual and zonal mean concentration of “deficit” dissolved oxygen (O₂ deficit in mmol m⁻² yr⁻¹) is also plotted in contour lines (PD in black, LGM_PD in cyan, LGM_SOUTH in blue, and LGM_HIGH_LAT in green).
Figure 5. Annual and zonal mean over the Pacific Ocean. Artificial “ventilation” tracer (after 100 years of integration, see text) for (a) LGM_PD minus PD, (b) LGM_SOUTH minus LGM_PD, (c) and LGM_HIGH_LAT minus LGM_SOUTH. The annual and zonal mean concentration of “deficit” dissolved oxygen (in mmol m$^{-2}$ yr$^{-1}$) is also plotted in contour lines for the PD simulation.