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Nutrient enrichment of the subarctic Pacific Ocean pycnocline

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[1] At the end of the global thermohaline circulation, the subarctic Pacific is the richest nutrient repository in the world oceans. Trends towards lower oxygen and higher nutrients in waters below the surface layer (the pycnocline) have been observed in recent decades. We assess these trends using data from four programs and suggest the enrichment of pycnocline nitrate (200 Gmol y^{-1}) is essential in keeping supply to the surface ocean constant, despite increasing upper ocean stratification. A nitrate budget helps identify possible vertical processes that could account for nutrient redistribution. We hypothesize that warming and oxygen loss in the deeper pycnocline, arising from ice loss in the Okhotsk Sea, have initiated a largely vertical redistribution of nutrients due to compression of vertical migrator habitat and/or changes in dissolution of sinking particulates. Coupled climate-ecosystem models will need to incorporate these processes to more fully understand projected changes in the subarctic Pacific.
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1. Introduction

[2] The most persistent loss of oxygen from world oceans is being observed in pycnocline waters of the subarctic Pacific (SAP) [*Keeling et al.*, 2010] where loss rates as high as 4–6 μM y^{-1} have been reported from repeat surveys between the mid 1980s and the end of the 1990s [*Watanabe et al.*, 2001; *Kumamoto et al.*, 2004; *Mecking et al.*, 2006]. However, many time-series measurements identify an oscillation with an amplitude of 30 to 50 μM O_2 throughout the Okhotsk Sea, Oyashio region, Western Subarctic Gyre, and Alaska Gyre which makes assessments of climate change impossible over periods of >20 years [*Whitney*, 2011]. The best current estimates of climate induced oxygen change come from time-series measurements extending over periods of 30 to 60 years, where rates of −0.5 to −1.0 μM y^{-1} are common on density surfaces in the pycnocline [*Ono et al.*, 2001; *Whitney et al.*, 2007; *Nakanowatari et al.*, 2007; *Watanabe et al.*, 2008].

[3] Some of these studies also note that nutrients vary inversely with oxygen, as would be expected from the remineralization of marine detritus. No comprehensive assessment of nutrient change has been undertaken to date; therefore, we use time-series data from three programs in the subarctic Pacific (SAP) and one in the subtropical Pacific to assess the impacts of climate change on oxygen and nutrient distribution. Based on the widespread findings of oxygen loss, our analysis can be extrapolated throughout the SAP and suggests vertical processes such as habitat compression or increased remineralization rates account for changes within the pycnocline waters of this region. These changes could impact productivity and habitat throughout the subtropical Pacific and into the Indian Ocean [*Sarmiento et al.*, 2004b].

2. Methods and Data Sources

2.1. Trend Analyses

[4] To assess nutrient trends, we rely on programs with internally consistent methodologies. The time-series sites included in this study (Figure 1) make most data available online (Oyashio: hnf.fra.affrc.go.jp; OSP, P16, P4 and HG: www.pac.dfo-mpo.gc.ca; C_{in} and C_{off}: calcofi.org; HOT: hahana.soest.hawaii.edu). In all instances throughout this paper, nitrate (NO_3) refers to $NO_3 + NO_2$. Linear trends were computed at fixed depths, with ~60% of these trends being significant at $p < 0.05$ in the SAP. Non-significant trends were common at HOT (weak slopes) and P16 (transition region between oceanic and coastal waters), whereas Ocean Station P (OSP), Oy, C_{off}, and P4 were uniformly significant throughout the pycnocline.

[5] Except for Oy, all data from 1983 to 2011 for California Cooperative Oceanic Fisheries Investigations (an extension of a previous analysis; *Bograd et al.*, [2008]), 1988 to 2010 for HOT, and 1987 to 2011 for Institute of Ocean Sciences (IOS) (OSP, P16, P4, HG) were used in trend analysis. In the Oy region, the influence of the 18.6 years lunar nodal cycle is strong; therefore, trends between cycle maxima of 1986–1990 and 2004–2008 were assessed. Oxygen losses from the mid 1980s to 2008/11 were somewhat larger than those obtained over longer time-series at Oy [*Ono et al.*, 2001] and OSP [*Whitney et al.*, 2007]. The consistency of weaker trends found in, e.g., the deeper coastal waters along North America gives us increased confidence in their validity. For example, silicate losses between 300 and 500 m at C_{in} are similar to those found at HOT (a possible upstream source) and at P4 (a known downstream site).

[6] The bottom of the mixed layer (BML) is assessed as the minimum depth at which surface variability does not contaminate trend analyses, varying between 50 m near the California coast and 150 m in the more strongly mixed waters of the Alaska Gyre. Integrated rates of change were calculated by multiplying the average trend at two adjacent standard depths by the depth interval between them.

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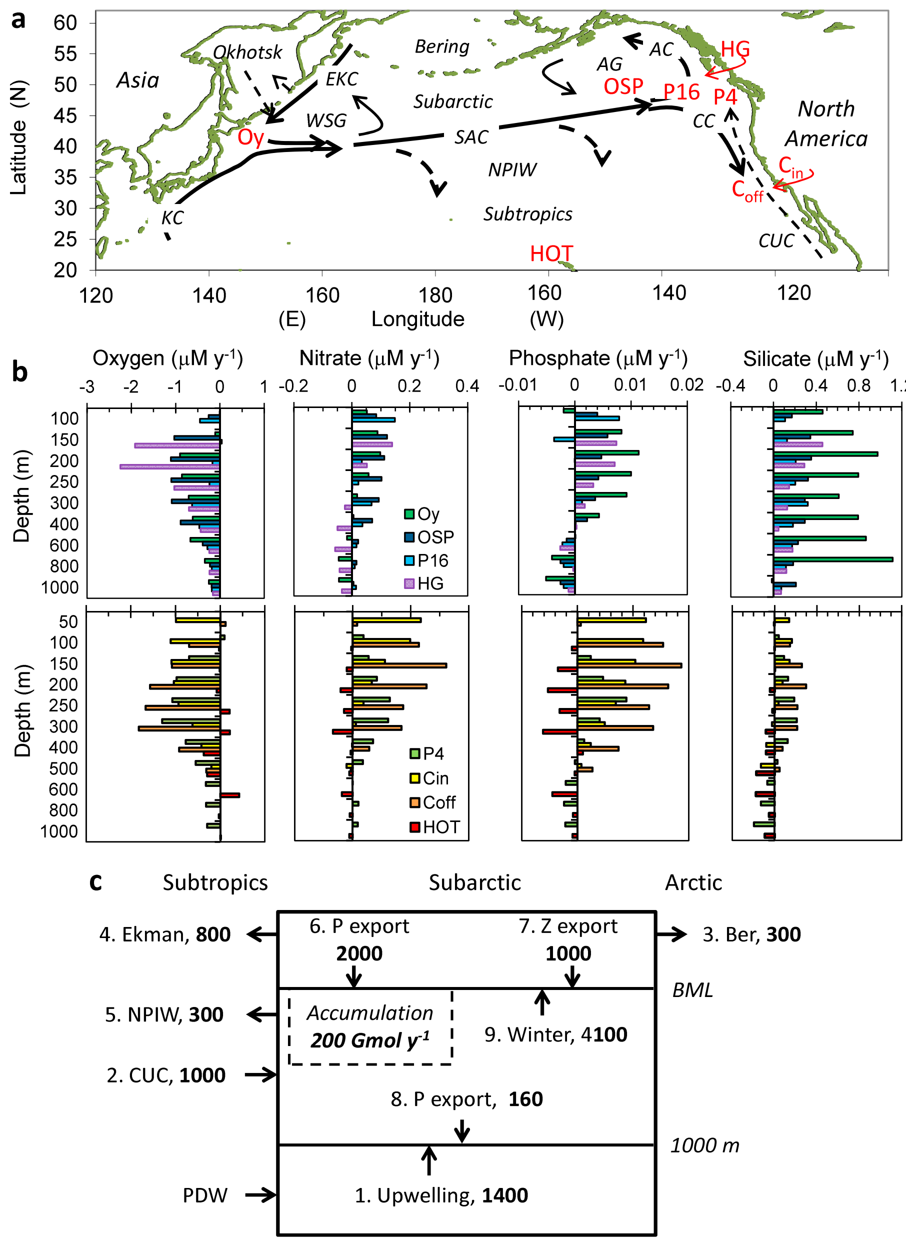

Figure 1. (a) Map of the North Pacific Ocean, its major circulation patterns (arrowed lines) and locations of eight time-series sampling locations (red). Solid black lines show surface currents important in transporting nutrient across the North Pacific, including the East Kamchatka (EKC), Kuroshio (KC), Subarctic (SAC), Alaska (AC), and California Currents (CC). Subsurface flows (dashed lines) include the California Undercurrent (CUC), North Pacific Intermediate Water (NPIW), and exchanges between Okhotsk Sea and the NW Pacific. The Western Subarctic Gyre (WSG) and Alaska Gyres (AG) are also identified. (b) Linear trends at standard depths over a 23–25 year period (mid 1980s to 2008–2011) for oxygen, nitrate, phosphate, and silicate at time-series sites. Trends are significant ($p < 0.05$) for 60% of the depth intervals, becoming not significant as the slope approaches zero. (c) A nitrate budget (in Gmol y^{-1}) for the upper 1000 m of the SAP, identifying the major source of import (CUC and upwelling of Pacific Deep Water, PDW) and export (NPIW, Arctic through the Bering Strait, Ekman transport to the subtropics in winter and particle flux deeper than 1000 m). Exchanges between the surface layer (BML, bottom of the mixed layer) and pycnocline include winter resupply of the mixed layer, annual removal by sinking particles (P export), and zooplankton export (Z export).

[7] World Ocean Circulation Experiment (WOCE) data (http://cchdo.ucsd.edu/) were used whenever nutrient or oxygen concentrations were needed beyond those available from time-series programs. When the density of seawater is discussed, units are sigma-theta (σ_θ = seawater density − 1) *1000.

2.2. Nitrate Budget

[8] A simple nitrate budget of the SAP is used in section 4 to help identify which processes could account for nutrient accumulation in the pycnocline. The SAP includes waters north of the axis of the Subarctic Current (clearly delineated

Table 1. Nutrient and Oxygen Trends Integrated Between the Bottom of the Winter Mixed Layer (BML) to 500 and 1000 m Depths[a]

	O_2	NO_3	PO_4	Si	O/N	O_2	NO_3	PO_4	Si	26.5	27.0
Site (BML, m)	BML to 500 m, mmol m^{-2} y^{-1}					BML to 1000 m, mmol m^{-2} y^{-1}				Av. depth ± SD (m)	
Oy (100)	−240	15	2.7	300	16	−470	−1.2	1.5	700	69 ± 48	466 ± 108
OSP (100)	−360	34	1.3	120	11	−530	45	0.4	230	137 ± 14	370 ± 44
P16 (100)	−140	16	0.0	81	8.7	−260	24	−0.9	150	155 ± 18	473 ± 49
P4 (50)	−330	30	1.1	46	11	−510	40	0.2	−4	173 ± 25	519 ± 50
HG (150)	−310	−4.2	0.7	49	-	−420	−28	0.0	110	170 ± 29	510 ± 43
C_{off} (100)	−480	61	4.7	68	7.8		no deep data			276 ± 19	519 ± 16
C_{in} (50)	−340	27	2.9	9	13		no deep data			232 ± 29	518 ± 20
HOT (100)	−30	−11	−1.0	−26	-	−60	−25	−2.4	−98	468 ± 31	662 ± 27

[a]Depths with standard deviations of two isopycnal surfaces are also noted.

by nitrate on density surfaces) but not those of marginal seas (Bering and Okhotsk). We use an area of 6 million km^2, although 10 million km^2 is found in *Harrison et al*. [2004] who include a region between the subarctic and subtropical fronts. Estimates of fluxes in Figure 1 were made as follows:

[9] 1. upwelling across the 1000 m depth boundary [*Kawabe and Fujio*, 2010] = 1 Sv × the average NO_3 concentration for the SAP from WOCE data. We assume the quoted flux of 1 Sv covers a range from 0.5 to 1.5 Sv, thus nitrate transport falls between 700 and 2000 Gmol y^{-1};

[10] 2. California Undercurrent (CUC) transport of 0.9 Sv [*Thomson and Krassovski*, 2010] × the average NO_3 concentration in the 200–275 m depth range (32–37 μM) from IOS data off the southern coast of British Columbia. Uncertainty is estimated at 30% based on CUC uncertainties, giving a range of 700 to 1300 Gmol y^{-1};

[11] 3. Bering Strait export is based on 0.8 Sv transport and historical nitrate [*Deutsch et al*., 2001]. The largest uncertainty here may be in the removal of nitrate by phytoplankton before water passes through Bering Strait, although most of this loss may still be exported to the Arctic as biomass. Since flow measurements are robust in this region [*Woodgate and Aargaard*, 2005], we estimate an uncertainty of no more than 20%, resulting in a range of 230–350 Gmol y^{-1};

[12] 4. Mixed layer export: two estimates are averaged, (a) the area impacted by SAP nutrients from satellite chlorophyll (140°E to 130°W, 30°N to 40°N; *Ayers and Lozier*, [2010]) × the seasonal difference in surface nitrate (*Whitney*, [2011]; varying from 7.5 μM between 39°N and 40°N to zero at 30°N to 31°N) × the depth of the mixed layer (40 m) ~1100 Gmol y^{-1}; or (b) area as above × Ekman transport estimate of 0.06 mol N m^{-2} y^{-1} ~500 Gmol y^{-1} [*Ayers and Lozier*, 2010]. The potential error in this transport estimate is at least the difference between our two calculations of 500 and 1100 Gmol y^{-1} (40%);

[13] 5. *You* [2003] describes cabbeling (mixing of two water masses of different density to produce a water of slightly greater density) as the dominant process forming North Pacific Intermediate Water (NPIW) along the Subarctic Current. We therefore assess nitrate export based on the enrichment of subtropical waters arising from mixing with the SAP. Export into the subtropics over the isopycnal layer 26.5–27.2 (layer thickness ~350 m in the subarctic) is estimated by assuming the NPIW (~3 Sv; *You*, [2003]) is formed when equal volumes of its two component members are mixed. Nitrate gradients between the SAP and the subtropics vary between 5 and 10 μM in the density range of NPIW, with higher gradients observed at shallower depth. A weighted average (accounting for thicknesses of isopycnal layers) of 7 μM nitrate difference results in an export of 300 ± 100 Gmol y^{-1} nitrate to the south. Other mixing processes not considered here will increase this export term;

[14] 6 and 8. Particle export at 100 and 1000 m from free drifting sediment traps at OSP [*Wong et al*., 1999]. Using these data to calculate SAP fluxes may result in estimates that are 30% low because primary production is higher in the Western Subarctic Gyre, compared with the central and eastern SAP [*Harrison et al*., 2004; *Whitney*, 2011]. We use drifting trap rather than moored data due to the extreme under trapping that may occur with shallow moored traps [*Yu et al*., 2001]. These flux rates are estimated to fall between 2000–2600 Gmol y^{-1} at 100 m and 160–210 Gmol y^{-1} at 1000 m;

[15] 7. Carbon export via migrating zooplankton is missed by sediment traps (zooplanktons commonly swim into traps during diurnal migration and are therefore removed from flux estimates) and has been shown to be significant in the SAP (6.4×10^{12} mol C y^{-1}; *Harrison et al*., [2004]). Nitrogen fluxes are estimated to be 15% of carbon (Redfield ratio). Transport by migrating biota may be underestimated since excretion by diel migrators including myctophids (midwater fish) has yet to be assessed (range from ~1000 to 1500 Gmol y^{-1}); and

[16] 9. Winter supply to the mixed layer must balance export fluxes (4100 Gmol y^{-1}), and is in reasonable agreement with winter enrichment of 12 μM y^{-1} [*Whitney*, 2011] × a seasonal depletion depth of 50 to 60 m × area of SAP = 3600 to 4300 Gmol y^{-1}. Uncertainties in the depth of summer nitrate uptake across the SAP introduce ~20% uncertainty, giving a range of 3300 to 4900 Gmol y^{-1}.

[17] Pycnocline accumulation of 200 ± 50 Gmol y^{-1} nitrate for the open SAP is based on a rate of 40 ± 10 mmol m^{-2} y^{-1} (Table 1, an average of 36 mmol m^{-2} y^{-1} for sites P4, OSP, Oy, and C_{off} between BML and 500 m or P4, 16, and OSP to 1000 m) over an area of 5 million km^2 (excluding continental margins where denitrification tends to dominate).

3. North Pacific Nutrient and Oxygen Trends

[18] A consistent pattern of oxygen loss and nutrient gain over the past couple of decades is found in waters below the winter mixed layer (Figure 1). Peak oxygen losses often exceed 1 μM y^{-1}, with integrated loss rates ranging from 140 to 480 mmol m^{-2} y^{-1} to a depth of 500 m (Table 1). At OSP, it has been estimated that 22% of the

oxygen inventory was lost from the pycnocline (100–400 m) between 1956 and 2006 [*Whitney et al.*, 2007]. Below ~300 m, contact with organic rich sediments in Okhotsk Sea and along the North American coast results in the loss of nitrate (denitrification) as microbes run out of oxygen to carry out metabolic processes [*Castro et al.*, 2001; *Yoshikawa et al.*, 2006]. Consequently, oxygen consumption to nitrate production ratios increase from 8 to 11 in oceanic waters to 13–16 off the California (C_{in}) and Japanese (Oy) coasts. Along the North American coast (HG), other organic materials such as methane may contribute to oxygen consumption, since neither phosphate nor nitrate is increasing as oxygen levels decline. Methane seeps are common along continental margins, yet are rarely thought of as a significant sink for oxygen [*Reeburg*, 2007].

[19] A remarkable exception to general nutrient trends is the 700 $mmol\,m^{-2}\,y^{-1}$ silicate enrichment of Oy waters (Table 1). This signal is observed to a lesser degree at OSP and P16 but is lacking in waters influenced by the subtropics. The Oyashio region receives the Okhotsk Sea outflow that modifies most of the water flowing south from the Bering Sea in winter [*Overlander et al.*, 1994; *Katsumata and Yasuda*, 2010]. We speculate that warming and a reduction of dense water formation [*Nakanowatari et al.*, 2007] are causes of this enrichment (i.e., increased dissolution rate for Si in warmer waters and a reduced flux of low Si water to depth). The lack of Si enrichment along the North American coast is attributed to influences of subtropical waters that are losing Si over time (HOT, Figure 1).

[20] California surveys only sample the upper 500 m of the ocean, which adequately covers the pycnocline where nutrient enrichment is strongest. In the Oy region, oxygen losses are detectable to at least 800 m. Integrated trends to 1000 m show a fairly consistent rate of oxygen loss (from 530 to 470 $mmol\,m^{-2}\,y^{-1}$; Table 1) from Oy to OSP, 5000 km downstream. Oxygen losses are similarly high in the California Current (C_{off}), the southern branch of the Subarctic Current. Consistent oxygen loss across the Subarctic Current (Oy, OSP, C_{off}) is perhaps a surprising finding, since subarctic waters mix with the subtropics as they flow away from the major sources of ventilation along the Asian coast [*Whitney et al.*, 2007], and suggests local processes are contributing to observed changes.

[21] Oxygen and nutrient variability in the pycnocline is caused by changes in supply, consumption, and regeneration. Oxygen supply is controlled largely by winter mixing and ice formation along the Asian margin coupled with horizontal transport of these waters along isopycnal (density) surfaces into the ocean interior, whereas consumption depends on levels of primary production and the ensuing export of organic matter to the intermediate ocean by sinking particles and migrating biota. Despite suggestions that upper ocean stratification may be decreasing nutrient supply and therefore primary productivity in surface waters [*Watanabe et al.*, 2008; *Freeland et al.*, 1997; *Ono et al.*, 2008], a recent analysis of nutrient variability which included adequate coverage of the SAP in winter concluded surface nutrient supply and seasonal drawdown have remained quite stable over at least the past 24 years [*Whitney*, 2011]. *Freeland et al.* [1997] modeled the impact of upper ocean stratification on nutrient supply, suggesting that at observed rates of change, summer nitrate could be depleted within 100 years. However, their model also implies that if the nutricline shoals such that nutrient concentrations remain constant at the base of the mixed layer, nutrient supply to the mixed layer will also remain constant. At OSP, for example, nitrate levels at 125 m are currently similar to those observed at 150 m 25 years ago.

[22] To help identify processes accounting for an overall increase in nutrients in the upper 400 to 800 m of the subarctic Pacific (pycnocline and mixed layer, ML), we develop a nitrate budget. Many of the flux rates are approximate due to the poorly constrained estimates of, e.g., upwelling or export to the subtropics. However, the budget identifies dominant processes controlling nutrient distribution within the SAP as well as major export pathways into other ocean basins.

4. Nitrate Budget for the Subarctic Pacific

[23] Fluxes into upper 1000 m of the water column (Figure 1) include a 1 Sv upward transport ([*Kawabe and Fujio*, 2010]; 1 Sv = $10^6\,m^3\,s^{-1}$, equivalent to the discharge rate of all global rivers into our oceans), a consequence of global thermohaline circulation, and a 0.9 Sv subsurface flow along the coast of North America in the California Undercurrent [CUC; *Thomson and Krassovski*, 2010]. Nutrients are exported into the western Arctic via the Bering Strait (0.8 Sv; *Deutsch et al.*, [2001]; *Woodgate and Aargaard*, [2005]), the interior of the subtropical Pacific via NPIW (by mixing of low nutrient Kuroshio with the high nutrient Oyashio waters along the Subarctic Current, but with little volume exchange between basins; [*You*, 2003; *Ueno and Yasuda*, 2003]) and the winter mixed layer of the subtropics due mainly to wind driven Ekman transport [*Ayers and Lozier*, 2010]. Volume transports (1.9 Sv in, 0.8 Sv out) require a southward export that is poorly defined at present, but which will be associated with wind forcing in the surface layer (accounting for freshening in the subtropics), the bifurcation of the Subarctic Current as it approaches North America, and density driven flow in the NPIW. Nitrate imports (2400 $Gmol\,y^{-1}$) and exports (1600 $Gmol\,y^{-1}$) allow for losses within the SAP due to denitrification and burial, but may also indicate our estimates of export to the subtropics are low.

[24] Using OSP data from free-drifting sediment traps [*Wong et al.*, 1999], annual fluxes of particulate N are estimated at 2000 $Gmol\,y^{-1}$ across the base of the ML (~100 m) and 160 $Gmol\,y^{-1}$ at 1000 m. In addition, migrating biota that are commonly excluded from vertical flux estimates account for at least 1000 $Gmol\,y^{-1}$ N export out of the ML [*Harrison et al.*, 2004]. Via metabolic processes and predation, this biomass is largely remineralized in the mid-ocean. An annual resupply of the ML due to winter storms must equal export fluxes (4100 $Gmol\,y^{-1}$), an estimate that is in agreement with observed seasonal change (average resupply of 12 μM nitrate in a 50 to 60 m deep surface layer [*Whitney*, 2011] over 6 million km^2 ~3600 to 4300 $Gmol\,y^{-1}$). Finally, we estimate a nitrate accumulation rate of 200 $Gmol\,y^{-1}$ in the pycnocline of the SAP.

[25] Pycnocline enrichment requires depletion in some other water masses. Horizontal transports include exports to the Arctic and NPIW that are small enough that they could not account for the SAP accumulation. A weakened surface layer export to the subtropics might be a contributor to nutrient redistribution within the SAP since satellite data suggest low chlorophyll waters are expanding northward [*Polovina et al.*, 2008]. However, this analysis is not long enough to

span bidecadal variability that is common in North Pacific time-series studies. Ekman pumping and coastal upwelling tend to follow bidecadal changes in atmospheric forcing rather than long-term climate trends [*Di Lorenzo et al.*, 2009; *Cummins and Masson*, 2012]. We consider what changes could occur in large vertical terms that would explain our observations.

[26] First, an increase in nitrate of 200 Gmol y^{-1} over 25 years (5000 Gmol) would require a surface ocean depletion (upper 100 m) of 10 μM nitrate, whereas a loss of 0.3 μM nitrate over 3000 m of deep ocean could account for pycnocline enrichment. Since the surface ocean shows little change over time, and weak declining trends in phosphate and nitrate at depth are seen at several time-series sites (Figure 1), nutrient redistribution is likely occurring between the pycnocline and deep ocean.

[27] We envisage a two step process whereby the winter oxygenation of dense waters is weakening in the Okhotsk Sea due to Siberian warming and reduced ice cover, leading to weaker oxygen transport into the SAP and a loss of deep habitat mid-water biota. Evidence of the importance of this community on respiration and nitrate remineralization rates is observed on the 26.9–27.0 isopycnal surfaces (approximate depth range of 300–400 m) across the Central SAP [*Aydin et al.*, 2004]. If they are unable to tolerate oxygen levels below ~60 μM, their habitat would have shoaled by 100 m at OSP between 1956 and 2006 [*Whitney et al.*, 2007].

[28] In addition, if the ballasting of detrital material (increased density due to carbonates and silicates) were to decrease due to the increased acidity of the pycnocline (declining oxygen producing higher carbon dioxide levels) and a faster dissolution of carbonates, a slower sinking rate would allow greater bacterial remineralization at shallower depth. We cannot exclude the effects of changes to the grazing community on remineralization. Changes in abundance or shifts from migrating to more sedentary grazers (e.g., medusae) may result in more effective recycling of nutrients at shallow depths. Also, the 0.5 to 0.9°C warming occurring in subsurface waters of the Okhotsk Sea and both SAP gyres [*Whitney et al.*, 2007; *Nakanowatari et al.*, 2007] may be increasing the remineralization rate of detritus by microbes, an anticipated outcome of global warming [*Denman and Pena*, 2002].

5. Implications

[29] To date, predictive models have tended to conclude temperate oceans will become more productive as a result of increased light levels or less productive as a result of reduced nutrient supply [e.g., *Sarmiento et al.*, 2004a; *Steinacher et al.*, 2010; *Polovina et al.*, 2011]. Both are a consequence of increased thermal stratification of the upper ocean. However, the surface layer of the SAP has become more buoyant largely due to freshening, whereas the pycnocline has warmed, resulting in both an increased buoyancy of the ML and a deepening of subsurface isopycnal surfaces [*Whitney et al.*, 2007; *Nakanowatari et al.*, 2007; *Watanabe et al.*, 2008; *Cummins and Masson*, 2012]. Because of this, increased stability of the upper water column may not develop as rapidly as many models predict. The effect of increased ML buoyancy is being countered by nutrient enrichment of the pycnocline with the result that nutrient supply and seasonal uptake are remaining stable. A recent global Earth Systems Model focusing on the California Current ecosystem captures some of these changes, predicting an increase in nitrate supply to surface waters in coming decades as nitrate enrichment of the pycnocline overcomes the effects of enhanced upper ocean stratification [*Rykaczewski and Dunne*, 2010]. Further analyses of this type are needed to better quantify some of the changes we observe in the North Pacific.

[30] Global warming will likely increase ice losses from the Okhotsk Sea over the next few decades, exacerbating trends toward lower oxygen and warmer waters in the SAP pycnocline and the NPIW. Predictive models will need to resolve both physical changes (e.g., ice formation, dense water production, heat, and fresh water transport) and ecosystem responses (habitat compression, possible community changes toward subtropical species, and remineralization in a more acidic ocean) to understand how the productivity of the SAP may change with warming. On regional scales, the processes we describe (oxygen loss and nutrient enrichment) will impact mid-water fisheries [*Koslow et al.*, 2011] and have the potential to exacerbate upwelling-driven hypoxia [*Chan et al.*, 2008].

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