

Sensitivity of the North Pacific oxygen minimum zone to changes in ocean circulation: A simple model calibrated by chlorofluorocarbons

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[1] Chlorofluorocarbon (CFC) data collected in 1999 at 11 stations along the western margin of Baja California indicate that the oxygen-minimum zone (OMZ) of the area is ventilated from the far North Pacific on decadal timescales. The new data are combined with existing CFC data to constrain a one-dimensional advection-diffusion model that simulates changes in water column properties on the $\sigma_{\Theta} = 26.80$ density surface along the path of ventilation. The results show that the penetration of CFCs into the OMZ off Baja California can be explained by slow advection and rapid isopycnal mixing from the southern margin of the Alaskan Gyre. The deficit in dissolved oxygen along the same path relative to conservative behavior is modeled with a consumption term that is the product of a single rate constant and the dissolved oxygen concentration. The model is used to show that very different oceanographic conditions must have prevailed in the North Pacific between 15 and 13 kyr ago, when water containing less than $5 \mu\text{mol kg}^{-1}$ oxygen impinged on a portion of the western margin of North America that was considerably expanded compared to today. To match the distribution of oxygen from the presence of laminations in a series of sediment cores, the least extreme scenario combines a 2.5-fold decrease in advection and diffusion along the current flow path, a 2.5-fold reduction in the oxygen content of ventilated waters of the central North Pacific, and a 2.5-fold increase in the rate constant for oxygen consumption rate, presumably linked to a proportional increase in surface productivity.

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1. Introduction

[2] As Wyrtki [1961] pointed out, oceanographers of the first half of the 20th century puzzled over the relative importance of circulation, or more precisely the lack thereof, versus biology in maintaining pronounced oxygen-minimum zones (OMZ) at intermediate depth of several ocean basins. The notion of a delicate balance between oxygen supply to the deep ocean along density surfaces that outcrop at high latitudes and the countering effect of a supply of mineralizable plankton matter through the water column was already recognized at the time. However, since the prevailing view was that OMZs represented regions of the ocean where lateral advection is inhibited, the founders of oceanography might have been surprised to learn that man-made chlorofluorocarbons (CFCs) were detected within the North Pacific OMZ only four decades after CFCs concentrations began to increase in the atmosphere [Warner *et al.*, 1996]. Such a dynamic perspective of the OMZ, reinforced by geological evidence of a greatly expanded

OMZ in the past, provided the motivation for the present study of the penetration of CFCs in some of the most oxygen-depleted waters of the North Pacific located off Baja California, Mexico.

[3] The formation of intermediate waters in the North Pacific is a complex process that occurs during winter in the far northwestern Pacific, specifically the Sea of Okhotsk, and perhaps occasionally also in the Gulf of Alaska [Reid, 1965; Talley, 1991; Van Scoy *et al.*, 1991]. There is evidence that formation of North Pacific Intermediate Water (NPIW) in these areas, traceable as a salinity minimum across much of the basin, is sensitive to interannual climate variability such as the El Niño–Southern Oscillation [Van Scoy and Druffel, 1993]. Collection of hydrographic data over time has demonstrated that the formation of NPIW also varies over longer timescales and that this variability causes widespread changes in salinity and dissolved oxygen (DO) concentrations at intermediate depths. Wong *et al.* [1999] report, for instance, a large-scale freshening of intermediate waters of the North Pacific in recent decades that appears to be linked to changes in conditions in areas of formation at higher latitudes. Andreev and Watanabe [2002], Emerson *et al.* [2004], and Mecking *et al.* [2006] found evidence of freshening and warming in surface waters of the far North Pacific and attributed a decrease in DO

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concentrations in intermediate waters of the region to a decline in ventilation caused by increased stratification.

[4] Over even longer timescales, there is evidence of considerably more pronounced variations in DO concentrations in the intermediate waters of the northeast Pacific based on sediment cores raised from the western margin of North America [Keigwin and Jones, 1990; Behl and Kennett, 1996; Zheng et al., 2000; Stott et al., 2000]. Variations in bottom water DO concentrations across a threshold of 2–5 $\mu\text{mol kg}^{-1}$ are fairly unambiguous because that is the level below which benthic organisms no longer bioturbate the sediment. The resulting signature in a number of locations is the preservation of fine-scaled laminations recording variations in the nature of sediment input over seasonal or longer timescales. On the basis of this signature, it appears that bottom water DO concentrations were well above their present level in the core of the OMZ off Baja California 22 kyr ago during the Last Glacial Maximum (LGM) [e.g., van Geen et al., 2003]. In contrast, patterns of laminations indicate that the OMZ was considerably more intense than it is today on the open margin off central California during a warm climate interval that lasted from 15 to 13 kyr ago. This specific event has variously been attributed to a change in ventilation at middepths of the North Pacific [Zheng et al., 2000; Ahagon et al., 2003] or a reduction of DO concentrations in intermediate waters driven by higher productivity in the northwest Pacific [Crusius et al., 2004]. To complicate matters, there is also evidence that preservation of laminations off Baja California over the past 52 kyr may have been driven in large part by changes in productivity [Ortiz et al., 2004].

[5] The purpose of this contribution is to quantify the sensitivity of the northeast Pacific OMZ to changes in circulation and productivity with a one-dimensional (1-D) advection-diffusion model calibrated with new and existing CFC data. The model is then used to simulate the conditions that could have led to changes in bottom water DO concentrations of the magnitude that have been recorded by sediment cores along the margin of North America. Section 2 of the paper describes the procedures that were followed to collect new CFC data along the western margin of Baja California in 1999. The selection of existing hydrographic and CFC data that encompass the likely path of ventilation that leads to Baja California is also described, followed by an overview of the numerical methods that were used to solve the model. In section 3, the main features of the distribution of CFCs along the Baja California margin are described, with a focus on the $\sigma_{\Theta} = 26.8$ isopycnal. The new observations are combined with previous CFC data to simulate DO consumption along the same density surface with the advection/diffusion model. In Section 4, model parameters are varied by prescribed values, in isolation and simultaneously, over a period of 200 years to model the distribution of DO at two locations along the transect. The paper concludes by reviewing the potential implications of the study for our understanding of climate variability.

2. Methods

2.1. Data Collection

[6] The data were collected on board R/V *Melville* between October 29 and November 22, 1999, during a

core cruise along the western margin of North America [van Geen and Scientific Party R/V *Melville*, 2001; van Geen et al., 2003]. Hydrographic data were collected with a SeaBird 911+ instrument, calibrated with discrete salinity samples from 10-L Niskin bottles mounted on a rosette system. Niskin samples were analyzed for DO by standard Winkler titration and by micro-Winkler titration [van Geen et al., 2003].

[7] CFC data were obtained at 11 hydrographic stations distributed between 23.1°N off the southern tip of Baja California and 34.3°N off southern California. Samples were collected for CFC analysis from each Niskin bottle in glass ampoules that were flame sealed with a small headspace of CFC-free nitrogen [Busenberg and Plummer, 1992]. After collection, the samples were stored in the dark and trucked to Lamont-Doherty Earth Observatory, where they were refrigerated. The samples were analyzed for CFC-11, CFC-12, and CFC-113 over a period of 2 weeks, approximately 1 month after collection, with a purge-trap gas system equipped with an electron-capture detector [Smethie et al., 2000]. Blank corrections of the samples were based on stripper blanks measured every 10 water samples. A standard gas sample was also analyzed every 10 samples for drift correction. The detection limit for CFC-11 and CFC-12 is estimated to be $\sim 0.01 \text{ pmol kg}^{-1}$, based on the variability of the blanks. Of the total of 192 samples that were analyzed, results for 20 were rejected because of a bad flame seal or contamination (see auxiliary material for data listing).¹

2.2. Selection of Additional Data

[8] To expand the spatial and temporal coverage of this analysis, CFC and hydrographic data were selected from an additional 20 stations sampled between 1985 and 1994 on seven separate cruises of the World Ocean Circulation Experiment (Table 1). The stations are distributed along the paths of geostrophic flow at 200 and 500 dB calculated by Reid [1997] that start in the western North Pacific and reach southern Baja California (Figure 1). Nine of the selected profiles were collected in 1985, mostly across the North Pacific along $\sim 47^{\circ}\text{N}$, and another two in 1991. CFC data are also available at four stations visited in 1993, including again one overlapping with the 1985 data, and five profiles collected in 1994, primarily south of Baja California. Along this flow path, the depth of the $\sigma_{\Theta} = 26.8$ density surface which, according to climatology, is the least dense isopycnal that typically doesn't outcrop in the far North Pacific, deepens from 200 m at 47°N to 400 m at 23°N . At each of the 31 hydrographic stations distributed over the $\sim 8000 \text{ km}$ distance separating the first profile off Kamchatka from the southern tip of Baja California, potential temperature and concentrations of DO, CFC-11 and CFC-12 along the $\sigma_{\Theta} = 26.8$ isopycnal were estimated by linear interpolation (Table 2).

2.3. Modeling

[9] To model the distribution of potential temperature, DO, CFC-11, and CFC-12 along the $\sigma_{\Theta} = 26.8$ isopycnal, the standard advection-diffusion equation

¹Auxiliary materials are available at <ftp://ftp.agu.org/pend/jc/2005jc003192>.

Table 1. Hydrographic Stations With CFC Data Selected for This Study

WOCE Section	Date	Expedition	Number of Stations	Laboratory ^a	Reference
P03	Mar 1985	31TTTPS24/1	1	SIO	Warner et al. [1996]
P01	Aug 1985	31TTTPS47	8	SIO	Warner et al. [1996]
P16N	Mar 1991	31DICGC91_2	1	PMEL	
P17C	Jun 1991	31WTTUNES/1	1	PMEL	Fine et al. [2001]
P17N	May 1993	325021_1	4	RSMAS	Fine et al. [2001]
P18	Apr 1994	31DSCG94_3	4	PMEL	
P15N	Sep 1994	18DD9403_1	1	IOS	
	Nov 1999	OXMZ01MV	11	LDEO	this study

^aSIO, Scripps Institution of Oceanography; PMEL, Pacific Marine Environmental Laboratory; RSMAS, Rosenstiel School of Marine and Atmospheric Science; IOS, Institute of Ocean Sciences (Sydney, Canada); LDEO, Lamont-Doherty Earth Observatory.

$$\frac{dC}{dt} = v \frac{dC}{dx} + K \frac{d^2C}{dx^2} - JC$$

where C represents concentrations of CFCs, DO, or potential temperature, K is the horizontal eddy diffusivity, V is the southerly advective term along the transect, J is the first-order DO consumption constant, t is time and x is distance along the transect, was solved by finite differences using a leapfrog scheme centered in time and space for the advective terms, and a Dufort-Frankel scheme for the diffusive terms [Sonnerup et al., 1999]. The sink term, JC, for modeling the distribution of DO, was time-split equally for both present and forward time steps. The model uses a 100 km grid spacing over a total distance 4300 km and a half-month time step from January 1940 to December 1999. Potential temperature was assumed to be in steady state and

the northern and southern boundary values were determined by averaging the values interpolated to the $\sigma_\Theta = 26.8$ potential density surface over two stations sampled at $\sim 47^\circ\text{N}$, 195°E (4.9°C at 4155 km) and four stations collected south of Baja California near 22°N , 250°E (9.0°C at 8455 km).

[10] An iterative approach was used to set the time-varying boundary condition for CFC concentrations in the northern end-member. Using the increase in atmospheric CFC concentrations and the solubilities of CFC-11 and CFC-12, which are known [Warner and Weiss, 1985], apparent ages for intermediate water at $\sigma_\Theta = 26.8$ were calculated for 1985 and 1993 assuming a range of effective saturations (Figure 2 and Table 3). An effective saturation of 55% was selected because it maintains a constant apparent

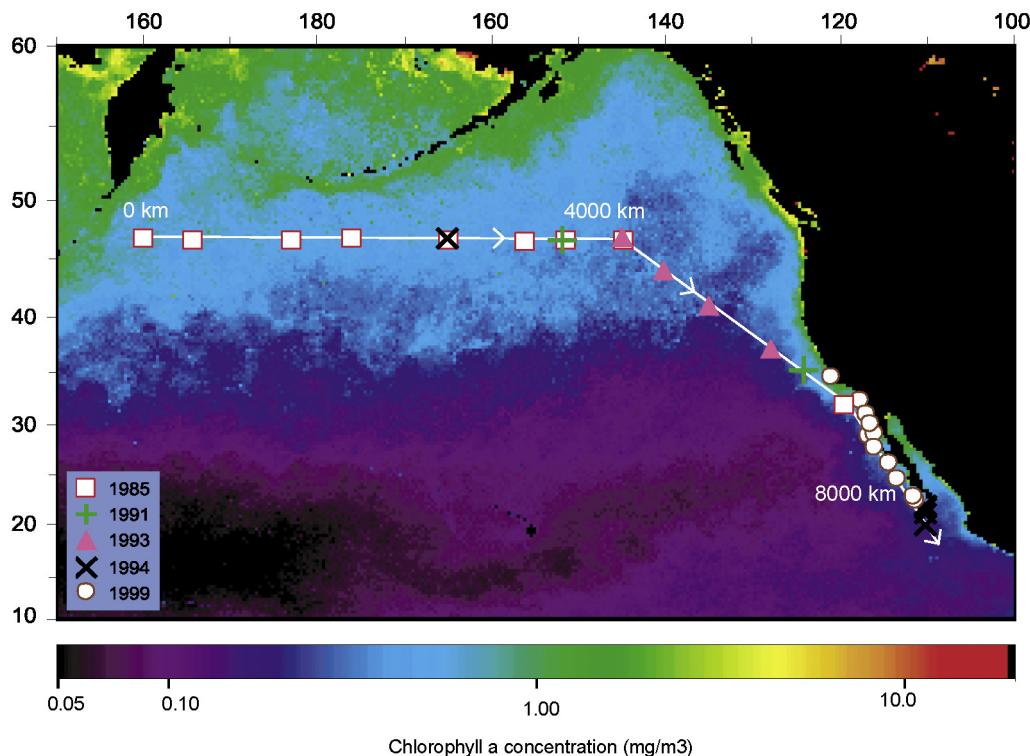


Figure 1. Annually averaged distribution of chlorophyll in North Pacific surface waters based on SeaWiFS observations during 1999. Also shown are the locations of CFC profiles used to constrain the advection-diffusion model.

Table 2. Interpolated Water Column Properties at 31 Stations in the North Pacific Along the $\sigma_\Theta = 26.80$ Isopycnal

Distance, km	Latitude, °N	Longitude, °W	Cruise	Station	Date	Potential		Oxygen, $\mu\text{mol kg}^{-1}$	CFC-11, pmol kg^{-1}	CFC-12, pmol kg^{-1}
						Depth, m	Temperature, °C			
0	47.02	199.98	31TTTPS47	38	15 Aug 1985	145	2.75	33.6161	122	2.28
429	46.99	194.37	31TTTPS47	43	17 Aug 1985	188	2.70	33.6074	149	2.50
1302	47.01	182.81	31TTTPS47	59	22 Aug 1985	213	3.07	33.6489	141	2.30
1814	47.01	176.04	31TTTPS47	65	24 Aug 1985	192	3.85	33.7410	138	2.01
2658	47.00	164.87	31TTTPS47	75	27 Aug 1985	249	4.37	33.8083	140	1.82
2721	47.08	165.00	18DD9403_1	18	22 Sep 1994	267	4.76	33.8636	149	2.77
3336	46.99	155.86	31TTTPS47	83	29 Aug 1985	280	4.63	33.8445	135	1.65
3663	47.00	152.00	31DICGC91_2	55	26 Mar 1991	286	4.83	33.8724	148	2.33
3681	47.00	151.42	31TTTPS47	87	31 Aug 1985	289	4.23	33.7900	135	1.80
4155	47.23	145.00	325021_1	65	2 Jun 1993	320	4.98	33.8948	133	2.25
4182	46.99	144.67	31TTTPS47	93	1 Sep 1985	319	4.77	33.8638	130	1.44
4673	44.28	140.13	325021_1	56	30 May 1993	375	5.16	33.9199	103	1.62
5225	41.00	135.00	325021_1	46	28 May 1993	422	5.47	33.9654	91	1.14
5992	37.03	127.71	325021_1	15	19 May 1993	459	6.36	34.1070	53	0.57
6386	35.08	124.02	31WTTUNES/1	7	3 Jun 1991	396	6.51	34.1313	50	0.43
6673	34.37	120.73	OXMZ01MV	2	30 Oct 1999	387	6.82	34.1843	39	0.92
6965	31.91	119.26	31TTTPS24/1	12	31 Mar 1985	362	7.18	34.2465	36	0.11
7035	32.18	117.27	OXMZ01MV	20	21 Nov 1999	375	7.14	34.2397	36	0.53
7181	31.02	116.62	OXMZ01MV	19	21 Nov 1999	402	7.37	34.2805	30	0.47
7294	30.07	116.18	OXMZ01MV	18	21 Nov 1999	358	7.49	34.3015	29	0.47
7386	29.00	116.32	OXMZ01MV	4	2 Nov 1999	395	7.19	34.2492	34	0.53
7413	29.10	115.58	OXMZ01MV	5	2 Nov 1999	386	7.68	34.3370	23	0.38
7510	28.00	115.72	OXMZ01MV	6	3 Nov 1999	376	7.73	34.3493	22	0.36
7737	26.53	114.03	OXMZ01MV	7	3 Nov 1999	387	8.17	34.4329	11	0.24
7932	25.08	112.95	OXMZ01MV	8	4 Nov 1999	395	8.52	34.4987	5	0.13
8186	23.42	111.23	OXMZ01MV	15	11 Nov 1999	400	8.70	34.5339	3	0.10
8224	23.16	110.95	OXMZ01MV	10	6 Nov 1999	401	8.68	34.5300	4	0.14
8308	22.80	110.00	31DSCG94_3	193	25 Apr 1994	402	8.90	34.5740	1	0.09
8337	22.50	110.00	31DSCG94_3	191	25 Apr 1994	376	8.89	34.5730	2	0.10
8385	22.00	110.00	31DSCG94_3	190	25 Apr 1994	389	8.66	34.5261	5	0.05
8480	20.99	110.00	31DSCG94_3	188	24 Apr 1994	402	8.89	34.5715	1	0.06

age at this location in 1985 and 1993. This apparent age is 9 years, as indicated independently by CFC-11 and CFC-12. To set the northern boundary condition of the model, a 55% saturation was applied to the entire time series of atmospheric CFC-11 and CFC-12 concentrations between 1940 and 1999 and lagged by 9 years to account for the 9 year apparent age at the northern boundary. The CFC concentrations at the southern boundary were held constant at zero in agreement with the observations.

3. Results

3.1. Distribution of Oxygen and CFCs Along Baja California

[11] The OMZ intensifies considerably along the margin of Baja California, with the lowest DO concentrations measured at the core decreasing from $10 \mu\text{mol kg}^{-1}$ at 32°N to $1 \mu\text{mol kg}^{-1}$ at 23°N (Figure 3). In 1999, CFC-11 and CFC-12 concentrations in samples collected in the same area ranged between 3.3 and 1.9 pmol kg^{-1} in shallow waters, respectively, to $\leq 0.01 \text{ pmol kg}^{-1}$ in the deepest water that was sampled. Between the $\sigma_\Theta = 26.8$ isopycnal at ~ 400 m and the core of the OMZ at 500 m, concentrations of both CFC-11 and CFC-12 are clearly detectable (Figure 4). This includes several suboxic samples, defined as those containing $< 5 \mu\text{mol kg}^{-1}$ DO, at the southern end of the transect. Below a depth of 500 m, CFC-11 concentrations are $< 0.1 \text{ pmol kg}^{-1}$ in all but four samples along the margin of Baja California, one of which contains a little over 0.1 pmol kg^{-1} CFC-12 as well (Figure 4).

3.2. Comparison of the Distributions of DO and CFCs in the Northeast Pacific

[12] Interpolation of water column properties off Baja California along the $\sigma_\Theta = 26.8$ isopycnal facilitates comparison with the composition of NPIW upstream in the North Pacific. The curvature of the potential temperature–DO relation extending to the overlapping profiles collected in 1985 and 1993 at 47°N , 145°W indicates significant oxygen consumption (Figure 5a). From Kamchatka to this location at the southern margin of the Gulf of Alaska, DO concentrations interpolated to the $\sigma_\Theta = 26.8$ isopycnal are elevated and variable (130 – $150 \mu\text{mol kg}^{-1}$), potential temperature increases, and CFC concentrations decrease. However, at this location potential temperature, DO and CFC concentrations begin to decrease more rapidly with distance along the flow path (Figure 6). This change in slope appears to be caused by mixing between well-ventilated water from the Bering Sea and the Alaska Gyre with NPIW advecting eastward in the Subarctic Current (see circulation pattern in Figure 1 of Andreev and Watanabe [2002]). Once the flow path turns southward, this input of well ventilated water ceases and potential temperatures and DO concentrations indicate that two end-member advection-diffusion could potentially reproduce the distribution of these properties between the southern margin of the Gulf of Alaska and the southern tip of Baja California.

[13] Whereas the close-to-linear relationship between potential temperature and interpolated CFC-11 and CFC-12 concentrations off Baja California serendipitously extrapolates to the composition of NPIW in the north-

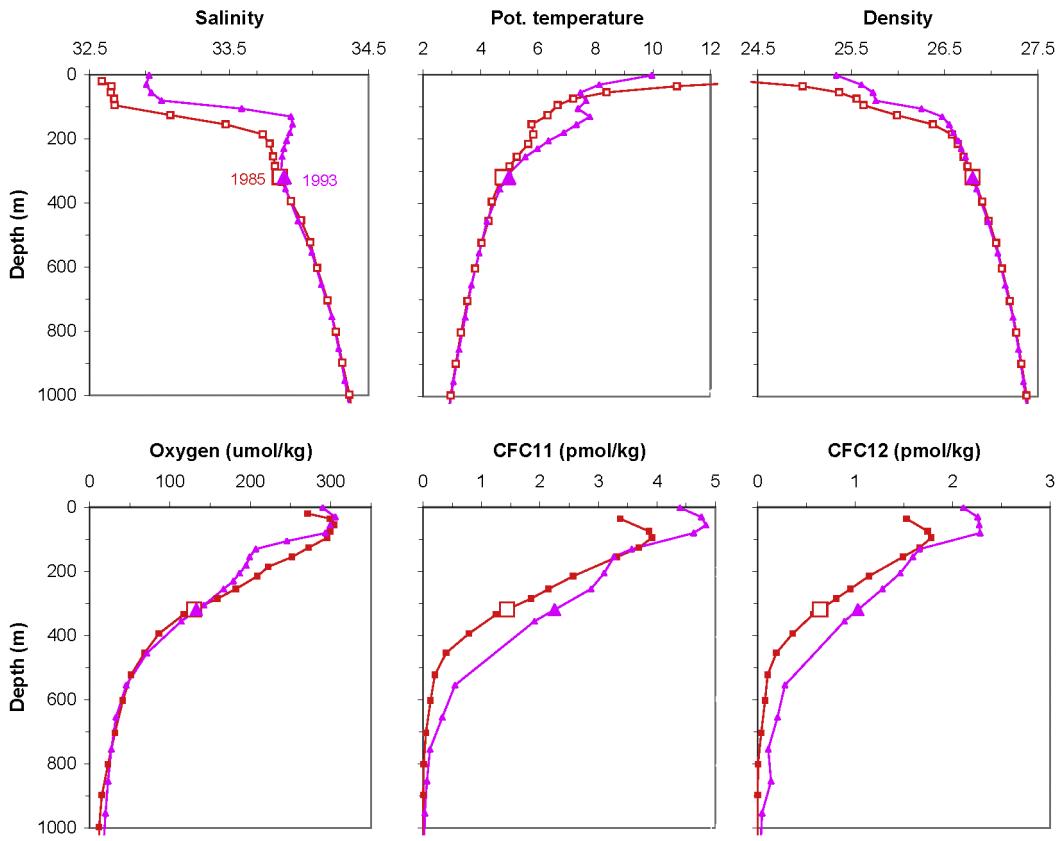


Figure 2. Water column profiles in 1985 and 1993 at 47°N, 215°E (~4100 km), the starting point of the portion of the modeled transect. The open square and pink triangle indicate interpolated properties on the $\sigma_\Theta = 26.80$ isopycnal surface.

western Pacific in 1985, the evolution of atmospheric CFC concentrations clearly had an imprint on the composition of intermediate waters during intervening years (Figures 5b and 5c). A steady rise in CFC concentrations between 1985 and 1999 along the $\sigma_\Theta = 26.8$ isopycnal is evident at several locations along the transect that were sampled repeatedly (Figure 6). At distances of ~2700 and 4200 km, for instance, concentrations of CFC-11 and CFC-12 rose by a factor of 1.5–1.6 between 1985 and 1993–1994 (Table 2). Further downstream, offshore of the U.S.–Mexican border at ~7000 km, concentrations of CFC-11 rose from 0.11 to 0.53 pmol kg⁻¹ (a factor of about 5) and concentrations of CFC-12 rose from 0.06 to 0.26 (a factor of about 4) between 1985 and 1999. The more rapid rate of increase further downstream reflects the fact that CFCs entered this water at an earlier time when the atmospheric CFC concentration was increasing more rapidly.

3.3. Model of Ventilation Along the $\sigma_\Theta = 26.8$ Isopycnal

[14] We model the distribution of potential temperature, DO, and CFC on the $\sigma_\Theta = 26.8$ isopycnal along the second half of the ~8000 km transect that separates Kamchatka from the southern tip of Baja California (Figure 1). The first half is not modeled because of apparent lateral mixing with well ventilated waters north of the flow path as discussed above. First the potential temperature data are fitted to set the ratio of diffusion to advection (K/V). The solution that minimizes the sum of squared residuals between model and

interpolated potential temperatures is shown, together with two scenarios corresponding to half and double the optimized K/V ratio, respectively (Figure 6a). A K/V ratio of 465,000 m provides the best fit. We did a similar calculation for salinity, which is nearly linearly correlated with potential temperature on a constant density surface, and obtained a ratio within 5% of the value derived from potential temperature. The absolute value of V, and therefore also K, is determined by minimizing the squared residuals between interpolated and modeled CFC-11 concentrations along the transect, yielding $V = 1.1 \times 10^{-3}$ m s⁻¹ and $K = 5100 \text{ m}^2 \text{ s}^{-1}$. Despite its simplicity, the model rather successfully reproduces the penetration of CFC-11 over a distance of 4000 km

Table 3. Comparison of Interpolated CFC-11 and CFC-12 Concentrations^a

Ventilation Year	Atmospheric, ppt	At 55%, pmol kg ⁻¹	Interpolated, pmol kg ⁻¹	Age, years
<i>CFC-11</i>				
1976	134	1.44	1.44	9
1984	205	2.25	2.25	9
<i>CFC-12</i>				
1976	249	0.68	0.64	9
1984	382	1.04	1.03	9

^aFor $\sigma_\Theta = 26.8$; at 47°N, 215°E in 1985 and 1993. Prediction assumes a saturation of 55% and a solubility F at 5°C and 34 psu of 1.958×10^{-2} and 4.957×10^{-3} mol kg⁻¹ atm⁻¹ for CFC-11 and CFC-12, respectively [Warner and Weiss, 1985]. Atmospheric values are from Walker *et al.* [2000].

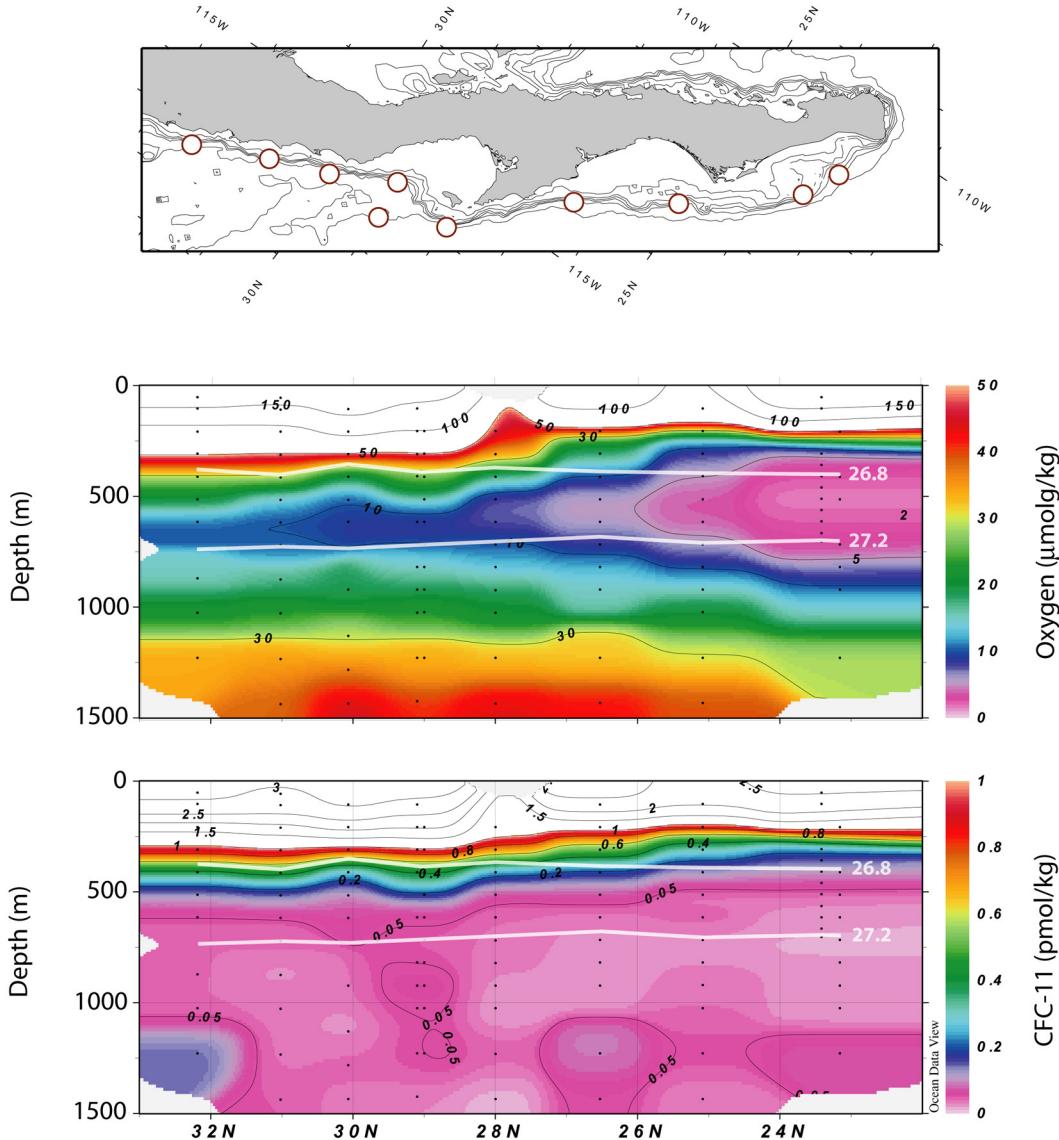


Figure 3. (a) Map of Baja California margin showing bathymetry and location of hydrographic data collected in 1999. Contour plots of (b) DO and (c) CFC-11 concentrations along the Baja California margin based on the 1999 data.

into the thermocline of the North Pacific between 1985 and 1999 (Figure 6c). Without additional tuning, the same model also reproduces the evolution of CFC-12 along the transect (Figure 6d).

[15] Finally, the DO concentrations along the transect are fitted using K and V obtained from potential temperature and CFCs and assuming that the rate constant J does not vary. The underlying assumption is that the rain of planktonic matter reaching NPIW is relatively uniform along the transect. Whereas this is clearly a simplification, Seaviewing Wide Field-of-view Sensor (SeaWiFS) data indicate that annually averaged chlorophyll concentrations range only fourfold from the southern margin of the Gulf of Alaska to southern Baja California, with a local maximum off northern California (Figure 1). The DO concentrations of the northern and southern end-member were set to 134 and $0 \mu\text{mol kg}^{-1}$ at 4155 and 8455 km, respectively.

The best fit obtained by minimizing the sum of squared residuals between interpolated and model DO concentrations is compared with two scenarios: conservative mixing ($J = 0$) and $J = 2X$ the best fit value (Figure 6b). The value of J providing the best fit is $1.3 \times 10^{-9} \text{ s}^{-1}$ or 0.041 yr^{-1} , which yields oxygen consumption rates ranging from about $5.5 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ at the northern end of the section to essentially zero at the southern end of the section. Such values span the range of independently calculated oxygen consumption rates [Warner et al., 1996; Feely et al., 2004].

4. Discussion

4.1. Timescale and Depth of Ventilation

[16] Min et al. [2000] first showed that CFC data collected off southern California over six cruises between 1982 and 1994 could be reduced to a single consistent profile

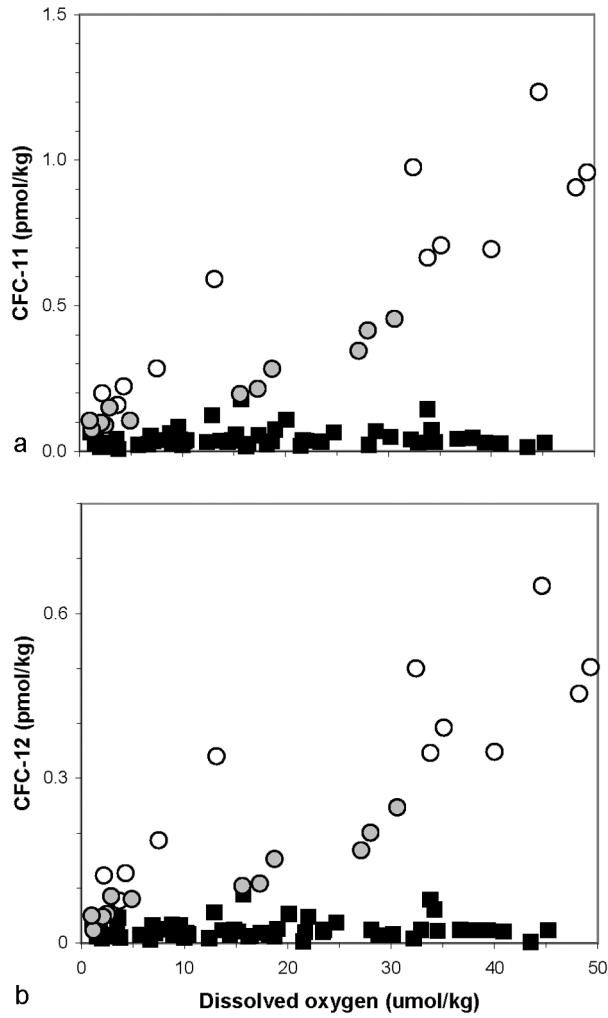


Figure 4. Comparison of DO concentrations with (a) CFC-11 and (b) CFC-12 concentrations along Baja California margin in 1999 in Niskin samples from depths <400 m (open circles), 400–500 m (grey circles), and 500–1500 m (solid squares).

when converted to ventilation ages. This indicated that the propagation of ventilated water was relatively steady over this period. The present study focused on the $\sigma_{\Theta} = 26.8$ isopycnal builds on this interpretation, while broadening the analysis to include existing data upstream of the same area and new data further downstream. Whereas the OMZ certainly intensifies along the Baja California margin, the CFC data indicate this is not because of an appreciable reduction in the rate of ventilation, or an increase in the oxygen consumption rate, but rather because of eddy mixing with water particularly low in DO from the south.

[17] It is worth pointing out that our model-derived advective term is a factor of 5–8 lower, and the diffusive term a factor of 7–10 higher, compared to the values obtained by Sonnerup *et al.* [1999] and Min *et al.* [2000] by modeling the penetration of CFC into North Pacific along somewhat different pathways. In both these studies, however, the distribution of a conservative tracer was not taken into account as an additional constraint on the model.

To compare our results more closely to those of Min *et al.* [2000], whose flow path for the $26.8 \sigma_{\Theta}$ surface is close to the flow path we used, we performed our model calculation with their parameters ($K = 500 \text{ m}^2 \text{ s}^{-1}$, $V = 8.5 \times 10^{-3} \text{ m s}^{-1}$), distance and boundary conditions and reproduced their fits to their CFC data. Then we performed the calculation for potential temperature, taking the end point values from the World Ocean Circulation Experiment (WOCE) stations located at their endpoints. The model run with their parameters was much too advective to fit the potential temperature data (i.e., too much curvature as a function of distance) even though it does fit the CFC data. The combination of a low-velocity and high horizontal mixing rate that we obtained by fitting both CFCs and a conservative property may be the result of the circulation pattern of water between 200 and 500 dB along the west coast of North America depicted by Reid [1997]. In addition to the broad south-easterly flow of the subtropical gyre that roughly parallels

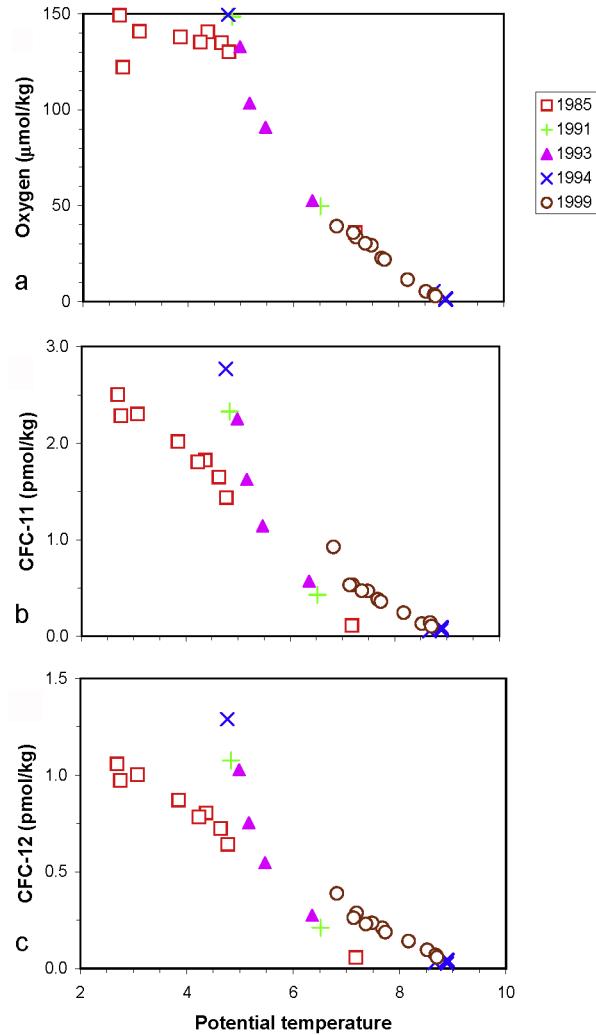


Figure 5. Comparison of potential temperature with (a) DO, (b) CFC-11, and (c) CFC-12 concentrations interpolated along the path of geostrophic flow on the $\sigma_{\Theta} = 26.80$ isopycnal surface between 1985 and 1999.

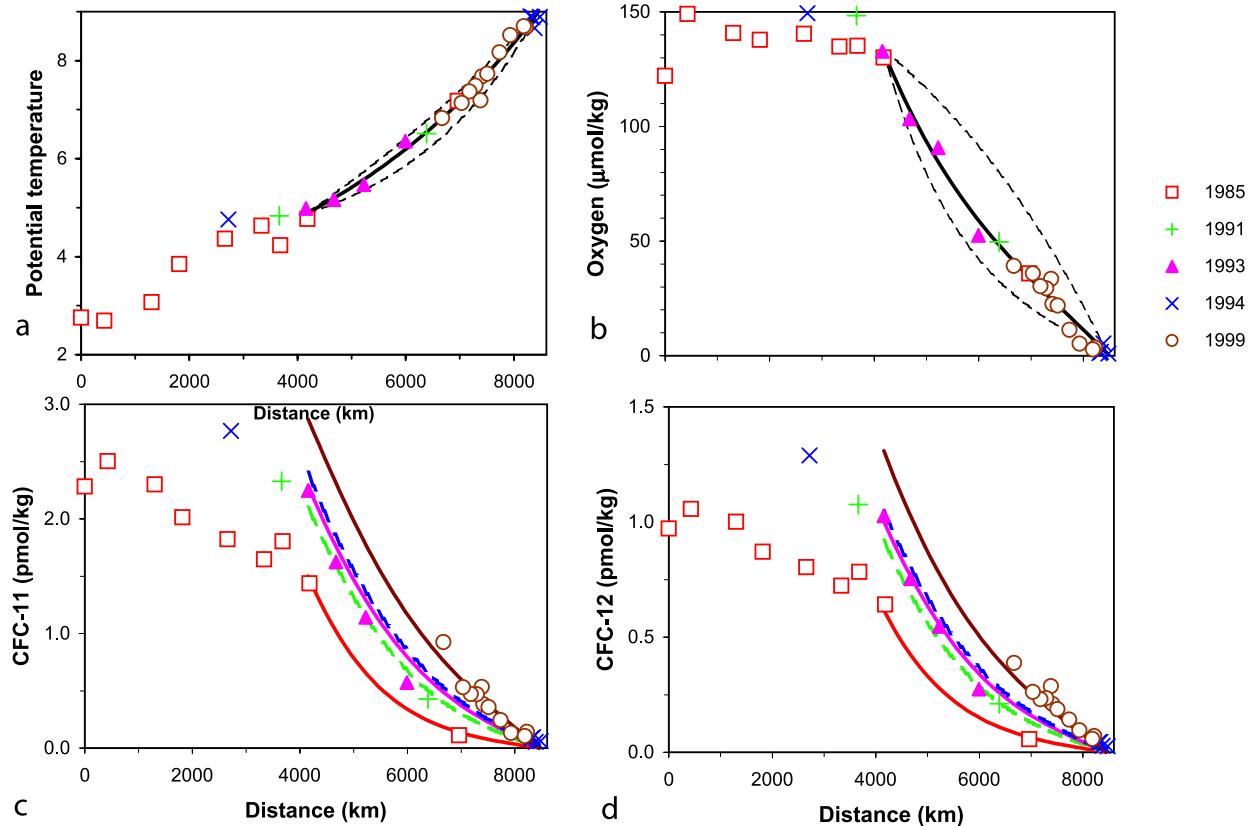


Figure 6. Variations in (a) potential temperature, (b) DO, (c) CFC-11, and (d) CFC-12 concentrations as a function of distance along the path of geostrophic flow on the $\sigma_\Theta = 26.80$ isopycnal surface between 1985 and 1999. Black lines in Figure 6a show potential temperatures corresponding to the best fit K/V values, as well as double and half this value. Black lines in Figure 6b show DO corresponding to the best fit constant, conservative mixing, and twice the best fit constant. Colored lines in Figures 6c and 6d show the predicted evolution of CFC-11 and CFC-12 concentrations, respectively, during 1985–1999.

the North American coast, there is a northward flow very close to the coast line. Northerly transport to a depth of 600 m along the coast accompanied by eddies has been confirmed by numerous float deployments [Collins *et al.*, 2004]. The mean pattern reflected in the tracer and hydrographic data could be the combination of these two flows, resulting in relatively small southward component and large meridional mixing in the 1-D model.

[18] The new data also suggest that ventilation from the north extends beyond the core of the OMZ at 500 m depth. When the CFC-11 data are interpolated on the $\sigma_\Theta = 27.2$ isopycnal, which averages a depth of 700 m along Baja California, there is a clear decline in concentrations as a function of distance along the margin, leading to the even lower values observed off Mazatlan in 1994 (Figure 7). The CFC-12 results on the $\sigma_\Theta = 27.2$ isopycnal are consistent, though more scattered because the roughly twofold lower concentrations (auxiliary material). A tube-flow model was not applied to this deeper layer because a flow path that is consistent with geostrophic flow and two end-member mixing could not be identified.

[19] There are two alternative explanations for the presence of CFC-11 and CFC-12 at 700 m that cannot be ruled out. Min *et al.* [2002] observed unexpectedly high CFC concentrations in bottom waters of the southern California Basins that were attributed to scavenging by particles in surface waters followed by regeneration at depth. Since productivity is considerably higher to the north, such a vertical conveyor might have enriched the OMZ in accordance with the observed pattern instead of ventilation from the north. The other possibility is that CFC levels observed along the $\sigma_\Theta = 27.2$ isopycnal off Baja California reflect advection from the more vigorously ventilated western and South Pacific [Fine *et al.*, 2001].

4.2. Paleoceanographic Application

[20] The penetration of CFCS into the OMZ suggests that changes in circulation and/or productivity linked to climate change on interannual to interdecadal timescales could affect oxygen levels in the NPIW. This section examines what plausible combination of conditions could have caused prolonged periods of a significantly expanded OMZ in the past. During the Bolling-Allerod warm interval (15–13 ka)

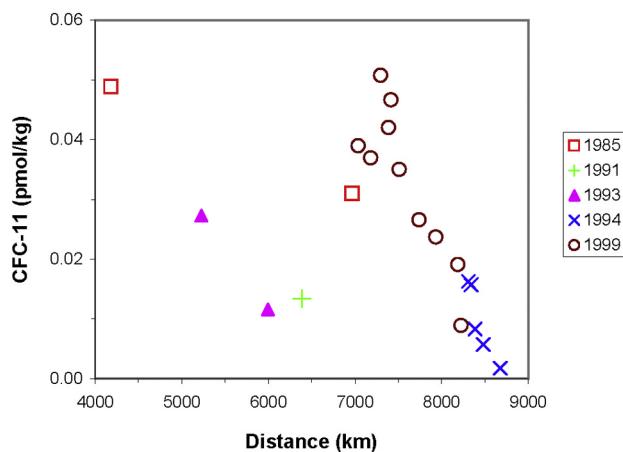


Figure 7. Interpolated concentrations of CFC-11 off Baja California along the $\sigma_\Theta = 27.2$ isopycnal as a function of distance along the transect.

that punctuated the last deglaciation, packets of laminated sediment were preserved within today's OMZ along the open margin of North America at a number of locations between 35 and 42°N [Lyle *et al.*, 1997; Gardner *et al.*, 1997]. Further south where the OMZ is more intense today, laminated sediments of the same age have been documented in the Gulf of California [Keigwin and Jones, 1990] and off the Mexican coast near Mazatlan [Ganeshram and Pedersen, 1998]. For reasons that are not entirely clear, laminated sediments were not preserved off southern Baja California during the Bolling-Allerod even if other proxies suggest increased accumulation of various biogenic proxies during this period [van Geen *et al.*, 2003; Ortiz *et al.*, 2004]. The undoubtedly most famous record of alternating packets of laminated and bioturbated sediment in the region, including a laminated interval corresponding to the Bolling-Allerod, was retrieved from the silled Santa Barbara Basin at 34°N [Behl and Kennett, 1996]. However, the hydrographic setting of this record, including elevated productivity in overlying waters, has complicated its interpretation [Cannariato *et al.*, 1999; van Geen *et al.*, 2003; Ivanochko and Pedersen, 2004]. Despite the inconsistencies, there is overall convincing evidence that the portion of the OMZ where laminated sediments are preserved today repeatedly expanded in the past well beyond its current boundaries.

[21] Under what conditions could the OMZ have expanded to the point where DO concentrations off central California dropped to $5 \mu\text{mol kg}^{-1}$? A preliminary sensitivity analysis using the CFC-calibrated model suggests that such conditions could be reached by modifying individual parameters under rather extreme conditions: (1) reducing the rate of advection of NPIW by an order of magnitude to $1.1 \times 10^{-4} \text{ m s}^{-1}$, (2) reducing the DO content of the high-latitude end-member by an order of magnitude to $13 \mu\text{mol kg}^{-1}$, or (3) increasing the constant defining the rate of consumption of oxygen at depth by an order of magnitude to 0.41 yr^{-1} , which would presumably be indicative of an order of magnitude higher productivity in overlying waters. Ahagon *et al.* [2003] document an increase in ventilation ages at 1400 m depth in the northwestern Pacific from

~1500 to ~2300 years based on radiocarbon age differences between benthic and planktonic foraminifera, but this observation is not necessarily related to a possibly sharper decline in ventilation at shallower depths. Increased stratification of the North Pacific between 15 and 13 ka, on the other hand, has been documented and could have drastically reduced ventilation of the OMZ [Zheng *et al.*, 2000]. Finally, as an alternative explanation that is consistent with the model, Crusius *et al.* [2004] proposed an order of magnitude increase in productivity in the western North Pacific that caused a drastic decline in the DO content of ventilating waters advected toward the western margin of North America.

[22] Less drastic, and perhaps more plausible, changes in a combination of model parameters can also reproduce the expanded OMZ indicated by the geologic record. The model is most sensitive to a change in the DO content of the high-latitude end-member: A 2.5-fold reduction results in a proportional decline in DO from 44 to $18 \mu\text{mol kg}^{-1}$ at 6600 km within a few decades (Figure 8a). A 2.5-fold increase in the oxygen consumption rate constant from 0.041 to 0.102 yr^{-1} is accompanied by a comparable decline in DO to $24 \mu\text{mol kg}^{-1}$. In comparison, the impacts of 2.5-fold reductions in diffusion (from 5100 to $2040 \text{ m}^2 \text{ s}^{-1}$) or advection (1.1×10^{-3} to $4.4 \times 10^{-4} \text{ m s}^{-1}$) are individually relatively mild, with predicted DO concentrations of 33 and $38 \mu\text{mol kg}^{-1}$ at 6600 km, respectively. None of the individual changes in parameters reproduce the conditions documented for the Bolling-Allerod warm period. On the other hand, DO concentrations drop below $5 \mu\text{mol kg}^{-1}$ at 6600 km within a few decades when all parameters are modified at the same time (Figure 8b). It is worth noting that the model reaches a new steady state in response to a sudden change in forcing within only a few decades. This is entirely consistent with the documented timescale of variability in hydrography and oxygen utilization of intermediate waters of the North Pacific [Van Scoy and Druffel, 1993; Wong *et al.*, 1999; Andreev and Watanabe, 2002; Emerson *et al.*, 2004; Mecking *et al.*, 2006].

[23] There are reasons to believe that the effect of changes in ventilation on the intensity of the OMZ could be reinforced by changes in productivity. Ventilation of intermediate waters in the North Pacific today prevents the nutrient content of subsurface waters to increase to the level observed in the more intense portion of the OMZ off Baja California. A reduction in ventilation could therefore lead to an increase in subsurface nutrient levels and, therefore, productivity. This is one reason why attempts to separate the effects of productivity and ventilation on the intensity of the OMZ may remain fruitless. By design, the model does not address conditions prevailing during the LGM when laminations were not preserved anywhere along the western margin of North America.

5. Conclusion

[24] Our new CFC data from the margin of Baja California are consistent with previous observations indicating ventilation of the OMZ throughout the North Pacific. A simple advection-diffusion model that is consistent with the distribution of conservative properties as well as DO indicates that propagation from a southern end-member that is

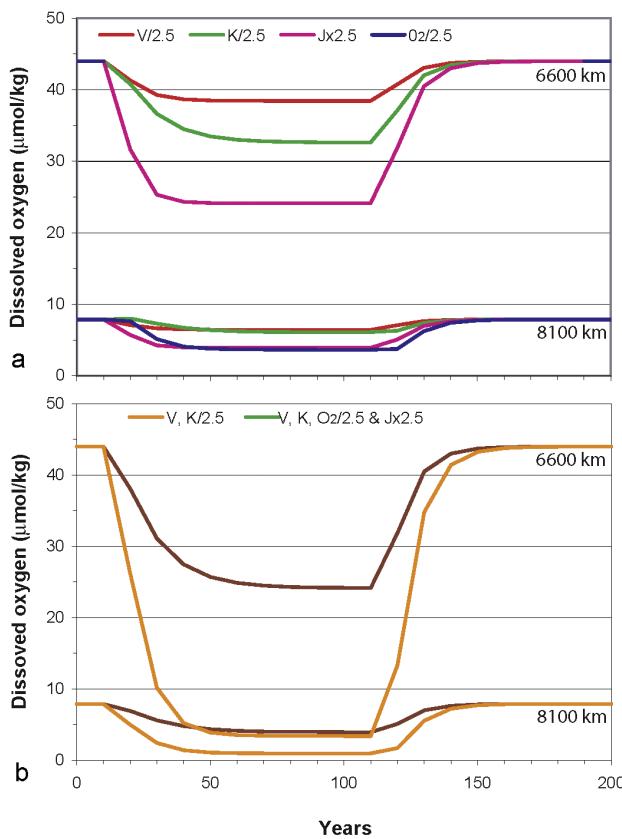


Figure 8. Modeled response of DO concentrations on the $\sigma_\Theta = 26.80$ isopycnal surface at distances of 6600 and 8100 km along the transect after changing model parameters from best fit values corresponding to present conditions: $V = 1.1 \times 10^{-3} \text{ m s}^{-1}$; $K = 5100 \text{ m}^2 \text{ s}^{-1}$; $J = 0.041 \text{ yr}^{-1}$; and initial DO concentration at high latitudes of $134 \mu\text{mol kg}^{-1}$. The changes in model parameters and/or boundary condition indicated in the legends are imposed (a) individually and (b) in combination as a step function starting at year 10 and ending at year 110.

particularly low in DO, rather than sluggish circulation or elevated productivity, drives the northward extent of the OMZ into the subtropics. The model also suggests that using suitable proxies, records of changes in ventilation or productivity on decadal timescales could potentially both be retrieved from rapidly accumulating sediment deposits along the west coast of North America.

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References

- Ahagon, N., K. Ohkushi, M. Uchida, and T. Mishima (2003), Mid-depth circulation in the northwest Pacific during the last deglaciation: Evidence from foraminiferal radiocarbon ages, *Geophys. Res. Lett.*, 30(21), 2097, doi:10.1029/2003GL018287.
- Andreev, A., and S. Watanabe (2002), Temporal changes in dissolved oxygen of the intermediate water in the subarctic North Pacific, *Geophys. Res. Lett.*, 29(14), 1680, doi:10.1029/2002GL015021.
- Behl, R. J., and J. P. Kennett (1996), Brief interstadial events in the Santa Barbara Basin, NE Pacific, during the past 60 kyr, *Nature*, 379, 243–246.
- Busenberg, E., and L. N. Plummer (1992), Use of chlorofluorocarbons (CCl3F and CCl2F2) as hydrologic tracers and age-dating tools—The alluvium and terrace system of central Oklahoma, *Water Resour. Res.*, 28, 2257–2283.
- Cannariato, K. K., J. P. Kennett, and R. J. Behl (1999), Biotic response to late Quaternary rapid climate switches in Santa Barbara Basin: Ecological and evolutionary implications, *Geology*, 27, 63–66.
- Collins, C. A., L. M. Ivanov, O. V. Melnichenko, and N. Garfield (2004), California Undercurrent variability and eddy transport estimated from RAFOS float observations, *J. Geophys. Res.*, 109, C05028, doi:10.1029/2003JC002191.
- Crusius, J., T. F. Pedersen, S. Kienast, L. Keigwin, and L. Labeyrie (2004), Influence of northwest Pacific productivity on North Pacific intermediate water oxygen concentrations during the Bolling-Allerod interval (14.7–12.9 ka), *Geology*, 32, 633–636.
- Emerson, S., Y. W. Watanabe, T. Ono, and S. Mecking (2004), Temporal trends in apparent oxygen utilization in the upper pycnocline of the North Pacific: 1980–2000, *J. Oceanogr.*, 60, 139–147.
- Feely, R. A., C. L. Sabine, R. Schlitzer, J. L. Bullister, S. Mecking, and D. Greeley (2004), Oxygen utilization and organic carbon remineralization in the upper water column of the Pacific Ocean, *J. Oceanogr.*, 60, 45–52.
- Fine, R. A., K. A. Maillet, K. F. Sullivan, and D. Willey (2001), Circulation and ventilation flux of the Pacific Ocean, *J. Geophys. Res.*, 106, 22,159–22,178.
- Ganeshram, R. S., and T. F. Pedersen (1998), Glacial-interglacial variability in upwelling and bioproductivity off NW Mexico: Implications for Quaternary paleoclimate, *Paleoceanography*, 13, 634–645.
- Gardner, J. V., W. E. Dean, and P. Dartnell (1997), Biogenic sedimentation beneath the California Current system for the past 30 kyr and its paleoceanographic significance, *Paleoceanography*, 12, 207–225.
- Ivanochko, T. S., and T. F. Pedersen (2004), Determining the influences of Late Quaternary ventilation and productivity variations on Santa Barbara Basin sedimentary oxygenation: A multi-proxy approach, *Quat. Sci. Rev.*, 23, 467–480.
- Keigwin, L. D., and G. Jones (1990), Deglacial climatic oscillations in the Gulf of California, *Paleoceanography*, 5, 1009–1023.
- Lyle, M., et al. (1997), *Proceedings of the Ocean Drilling Program Initial Reports*, vol. 167, 1376 pp., Ocean Drill. Program, College Station, Tex.
- Mecking, S., M. J. Warner, and J. L. Bullister (2006), Temporal changes in pCFC-12 ages and AOU along two hydrographic sections in the eastern subtropical North Pacific, *Deep Sea Res., Part I*, 53, 169–187.
- Min, D.-H., J. L. Bullister, and R. F. Weiss (2000), Constant ventilation age of thermocline water in the eastern subtropical North Pacific Ocean from chlorofluorocarbon measurements over a 12-year period, *Geophys. Res. Lett.*, 27, 3909–3912.
- Min, D.-H., J. L. Bullister, and R. F. Weiss (2002), Anomalous chlorofluorocarbons in the Southern California Borderland Basins, *Geophys. Res. Lett.*, 29(20), 1955, doi:10.1029/2002GL015408.
- Ortiz, J. D., S. E. O'Connell, J. DelViscio, W. Dean, J. D. Carriquiry, T. Marchitto, Y. Zheng, and A. van Geen (2004), Enhanced marine productivity off western North America during warm climate intervals of the past 52 kyr, *Geology*, 32, 521–524.
- Reid, J. L. (1965), Intermediate waters of the Pacific Ocean, *Johns Hopkins Oceanogr. Stud.*, 2, 85 pp.
- Reid, J. L. (1997), On the total geostrophic circulation of the Pacific Ocean: Flow patterns, tracers, and transports, *Prog. Oceanogr.*, 39, 263–352.
- Smethie, W. M., Jr., P. Schlosser, T. S. Hopkins, and G. Boenisch (2000), Renewal and circulation of intermediate waters in the Canadian Basin observed on the SCICEX-96 cruise, *J. Geophys. Res.*, 105, 1105–1121.
- Sonnerup, R. E., P. D. Quay, and J. L. Bullister (1999), Thermocline ventilation and oxygen utilization rates in the subtropical North Pacific based on CFC distributions during WOCE, *Deep Sea Res., Part I*, 46, 777–805.
- Stott, L. D., M. Neumann, and D. Hammond (2000), Intermediate water ventilation on the northeastern Pacific margin during the late Pleistocene inferred from benthic foraminiferal $\delta^{13}\text{C}$, *Paleoceanography*, 15, 161–169.
- Talley, L. D. (1991), An Okhotsk Sea water anomaly: Implications for ventilation in the North Pacific, *Deep Sea Res., Part A*, 38, suppl., S171–S190.
- van Geen, A., and Scientific Party R/V *Melville* (2001), Baja California coring cruise OXMZ01MV: Core descriptions and CTD/Rosette data, *Tech. Rep. LDEO 2001-01*, Lamont-Doherty Earth Obs., Columbia Univ., Palisades, N. Y.

- van Geen, A., Y. Zheng, J. M. Bernhard, K. G. Cannariato, J. Carriquiry, W. E. Dean, B. W. Eakins, J. D. Ortiz, and J. Pike (2003), On the preservation of laminated sediments along the western margin of North America, *Paleoceanography*, 18(4), 1098, doi:10.1029/2003PA000911.
- Van Scoy, K. A., and E. R. M. Druffel (1993), Ventilation and transport of thermocline and intermediate waters in the northeast Pacific during recent El Niños, *J. Geophys. Res.*, 98, 18,083–18,088.
- Van Scoy, K. A., D. B. Olson, and R. A. Fine (1991), Ventilation of North Pacific intermediate waters: The role of the Alaskan gyre, *J. Geophys. Res.*, 96, 16,801–16,810.
- Walker, S. J., R. F. Weiss, and P. K. Salameh (2000), Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113, and carbon tetrachloride, *J. Geophys. Res.*, 105, 14,285–14,296.
- Warner, M. J., and R. F. Weiss (1985), Solubilities of chlorofluorocarbons 11 and 12 in water and seawater, *Deep Sea Res., Part A*, 32, 1485–1497.
- Warner, M. J., J. L. Bullister, D. P. Wisegarver, R. H. Gammon, and R. F. Weiss (1996), Basin-wide distributions of chlorofluorocarbons CFC-11 and CFC-12 in the North Pacific: 1985–1989, *J. Geophys. Res.*, 101, 20,525–20,542.
- Willey, D. A., R. A. Fine, J. L. Bullister, W. M. Smethie, and M. K. Warner (2004), Global ocean chlorofluorocarbon inventory, *Geophys. Res. Lett.*, 31, L01303, doi:10.1029/2003GL018816.
- Wong, A. P. S., N. L. Bindoff, and J. A. Church (1999), Large-scale freshening of intermediate waters in the Pacific and Indian oceans, *Nature*, 400, 440–443.
- Wyrtki, K. (1961), The oxygen minima in relation to ocean circulation, *Deep Sea Res.*, 9, 11–12.
- Zheng, Y., A. van Geen, R. F. Anderson, J. V. Gardner, and W. E. Dean (2000), Intensification of the northeast Pacific oxygen minimum zone during the Bolling/Allerod warm period, *Paleoceanography*, 15, 528–536.

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