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Possible biological or physical explanations for decadal scale trends in North Pacific nutrient concentrations and oxygen utilization

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Abstract

We analyze North Pacific GEOSECS (1970s) and WOCE (1990s) observations to examine potential decadal trends of the marine biological carbon pump. Nitrate concentrations ($[NO_3^-]$) and apparent oxygen utilization (AOU) decreased significantly in intermediate waters (by -0.6 and -2.9 μmol kg^{-1}, respectively, at $\sigma_\theta = 27.4$ kg m^{-3}, corresponding to ≈ 1050 m). In shallow waters (above roughly 750 m) $[NO_3^-]$ and AOU increased, though the changes were not statistically significant. A sensitivity study with an ocean general circulation model indicates that reasonable perturbations of the biological carbon pump due to changes in export production or remineralization efficiency are insufficient to account for the intermediate water tracer trends. However, changes in water ventilation rates could explain the intermediate water tracer trends and would be consistent with trends of water age derived from radiocarbon. Trends in AOU and $[NO_3^-]$ provide relatively poor constraints on decadal scale trends in the marine biological carbon pump for two reasons. First, most of the expected changes due to decadal scale perturbations of the marine biota occur in shallow waters, where the available data are typically too sparse to account for the strong spatial and temporal variability. Second, alternative explanations for the observed tracer trends (e.g., changes in the water ventilation rates) cannot be firmly rejected. Our data analysis does not disprove the null-hypothesis of an unchanged biological carbon pump in the North Pacific. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

Understanding global carbon sinks is crucial for understanding past and future climatic change. The deep oceans are the largest carbon reservoir relevant for century scale perturbations, and most anthropogenic carbon dioxide (CO_2) will ultimately end up in this reservoir. One potential pathway for CO_2 to the deep oceans is the "biological carbon pump", i.e. the export of organic matter from the surface oceans (Volk and Hoffert, 1985). For a steady-state marine biota, the net carbon flux due to the biological carbon pump is negligible because the downward flux of organic carbon is closely balanced by the upwards flux of remineralized carbon — an assumption adopted by many studies (Toggweiler, 1994; Keeling et al., 1996). If the marine biota is indeed in steady state, the oceans act as a carbon sink mostly through the "solubility pump", i.e. chemical absorption and physical transport. However, this steady-state assumption is problematic, as numerous studies demonstrate significant long-term trends of the marine biota (Venrick et al., 1987; Karl et al., 1995; McGowan et al., 1998), potentially driven by changes in trace metal supply (Jickells et al., 1998; Chavez et al., 1999), changes in nitrogen fixation (Karl et al., 1995), or changes in mixed-layer depth (Freeland et al., 1997). The uncertainty about the biological carbon pump translates into an uncertainty about the carbon sinks. Quantifying the uncertainties about global carbon sinks is an essential step towards improved CO_2 budgets and climate policy (Edmonds, 1992; Sarmiento and Wofsy, 1999).

Studies that test whether the marine biota has changed over long spatial and temporal scales [and would hence be important for global CO_2 budgets] face a daunting task and have come to contradicting conclusions. The majority of studies do not find a significant CO_2 uptake due to a changing marine biota (Peng and Broecker, 1984; Falkowski and Wilson, 1992). In contrast, Pahlow and Riebesell (2000) suggest a significant increase in export production for the North Pacific. The different results might be explained by differences in the analyzed data sets, the analysis methods or the interpretation of the estimated trends.

The hypothesis of an unperturbed marine biota can be tested by analyzing trends in oceanic apparent oxygen utilization (AOU) and nutrient concentrations. This indirect approach of studying the marine biota by looking at the affected tracers has previously been used to analyze nutrient and oxygen/AOU data (for example, Redfield et al., 1963; Peng and Broecker, 1984; Garcia et al., 1998; Emerson et al., 2001; Pahlow and Riebesell, 2000). Here, we focus on the North Pacific, and refine the analysis methods. Specifically, we analyze differences in the distribution of apparent oxygen utilization and nitrate concentrations ($[NO_3^-]$) between the Geochemical Ocean Sections Study (GEOSECS) and the World Ocean Circulation Experiment (WOCE), which yields an average time difference of roughly 20 years.

This study differs from studies on the strength of the solubility pump, which typically analyze the concentration or isotopic composition of dissolved inorganic carbon that change directly because of the anthropogenic CO_2 transient (Wanninkhof et al., 1999; Quay et al., 1992; Ortiz et al., 2000). Our analysis focuses on the North Pacific, where previous studies showed considerable trends on a local scale (e.g., Karl et al., 1997). To test whether the observed trends could be explained by a changing marine biota, we perturb export production and remineralization efficiency in an ocean general circulation model and compare the simulated and estimated trends.

Our results indicate that North Pacific AOU and $[NO_3^-]$ increased in shallow waters and decreased in intermediate waters (between roughly 1000–1600 m) over the approximately 20 year period between GEOSECS and WOCE. Because the observed intermediate water trends are much larger than simulated perturbations for reasonable changes of the biological carbon pump, changes in the marine biota alone are unlikely the sole explanation for the observed trends. The interpretation of AOU and $[NO_3^-]$ trends as indicators for a changing marine biota can be confounded by a variety of other mechanisms. One important mechanism is a change in water ventilation rates. Water ventilation rates show a considerable decadal variability and are expected to change in response to global warming (Manabe et al., 1991; Sarmiento et al., 1998). Variable water ventilation rates may partially explain the observations, and would be consistent with the available radiocarbon age constraints.

2. Methods

Because the expected AOU and $[NO_3^-]$ trends are likely to be small relative to the natural spatial and temporal variability (Peng and Broecker, 1984), great care has to be taken to effectively exclude sources of variability other than temporal trends. For intermediate and deep waters, the main problems arise from biases in sampling location and water masses. One approach is to correct for these biases by analyzing nearby stations with similar water mass properties (typically the crossovers between two cruises; Peng and Broecker, 1984). This approach is relatively simple, but subject to numerous caveats (discussed below). Here, we start with this crossover method and extend it by various interpolation and correction steps.

2.1. Crossover analysis

The crossover method is applied to the intersections between the WOCE and GEOSECS cruises (Fig. 1). We analyze GEOSECS and WOCE stations with reasonable proximity and exclude locations where water density and salinity differences on isopycnal and isobaric interpolations indicate a significant change in water masses. Specifically, we analyze waters between 1000 and 1750 m (to exclude the more variable shallower waters) with average salinity and σ_θ differences below 0.01 (on the PSS-78 scale) and 0.05 kg m^{-3}, respectively. This step in the crossover analysis is intended to minimize possible artifacts due to changes in preformed nutrients or vertical motion of isopycnals.

As a further precaution, we consider offsets in deep-water concentrations to reflect analytical artifacts and exclude tracers with deep-water offsets and intermediate water trends of similar magnitude. This criterion excludes, for example, the phosphate data. To minimize potential biases by changing water masses and the averaging process, we perform the analysis on isopycnal surfaces (Lozier et al., 1994; Gouretski and Jancke, 1999). We analyze apparent oxygen utilization to minimize the effects of the observed changes in water temperatures and salinities in the North Pacific (Levitus et al., 2000). AOU measures primarily biological oxygen utilization and is defined as the saturated oxygen concentration at the potential water temperature and salinity minus the observed oxygen concentration.

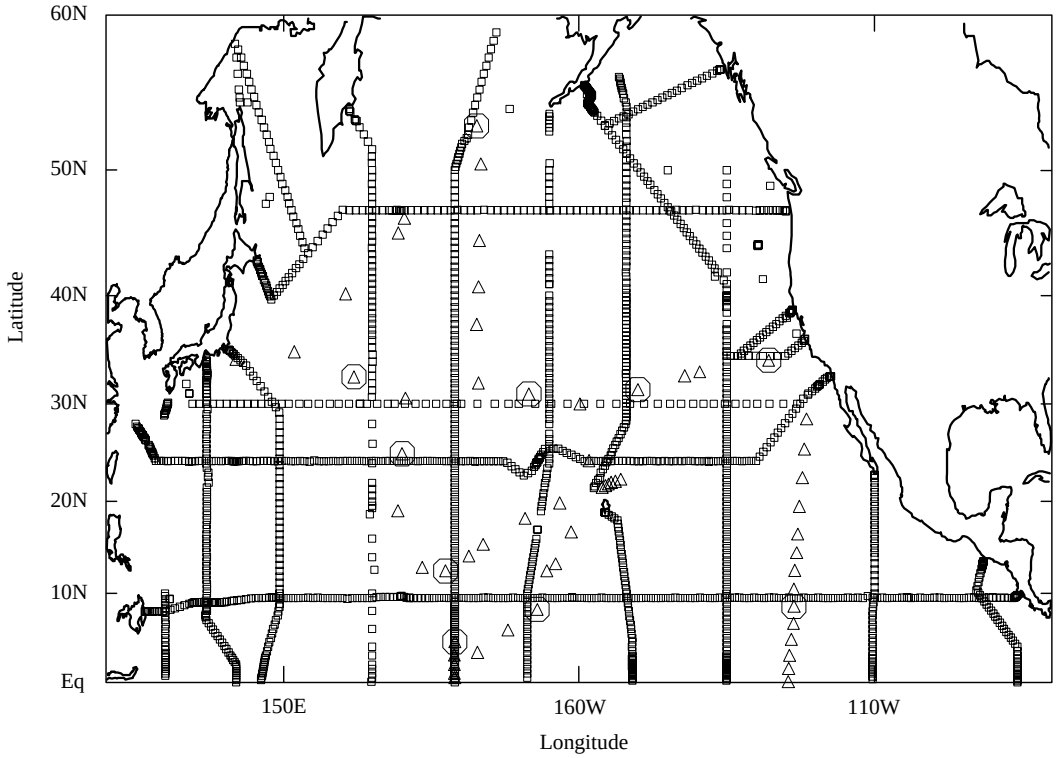

Fig. 1. Map of the analyzed WOCE (squares) and GEOSECS (triangles) stations in the North Pacific. We analyzed all North Pacific GEOSECS stations (Broecker et al., 1982) and the WOCE cruises P1W, P2, P8S, P9, P10, P15N, P16N, P16S, P17S, P17N, and P17C (WOCE Hydrographic Program Office, 2000; JODC Japan Oceanographic Data Center, 2000). The circles denote the GEOSECS locations for the crossover analysis detailed in Table 1.

2.2. Isopycnal interpolations

While the crossover analysis yields valuable insights into possible temporal trends, the results are based on only a small number of stations and might still be affected by biases due to (i) different vertical and horizontal sampling locations, (ii) different sampling season, (iii) different analysis methods, or (iv) data interpolation. We address these potential problems by applying various correction steps.

First, to correct for the sampling location bias, we interpolate the WOCE observations (squares in Fig. 1) on various isopycnal surfaces to the GEOSECS sampling locations (technical details are given in Keller, 2000, p. 57). Second, to minimize seasonal biases, we analyze only water masses below $\sigma_\theta = 26.9\ \mathrm{kg\ m^{-3}}$ (average depth roughly 500 m). Water masses above 500 m show significant seasonal variability (Najjar and Keeling, 1997), and a basin-wide analysis furthermore would be biased by the outcropping of more shallow isopycnals. We hence show the results for waters shallower than $\sigma_\theta = 26.9\ \mathrm{kg\ m^{-3}}$ for illustrative purposes only. Third, we correct for analytical offsets by subtracting the trends of waters with $\sigma_\theta = 27.77\ \mathrm{kg\ m^{-3}}$ (average depth roughly 3500 m). This constant deep water correction has been applied in numerous studies (e.g., Saunders, 1996; Mantyla, 1994). It assumes that the temporal trend in deep waters are negligible

and that the complex combination of sampling and analytical errors can be corrected by a constant offset. We shall return to these assumptions in the discussion. Finally, we investigate whether the data interpolation methods bias the results by using two different interpolation methods (either a locally weighted regression (Cleveland and Devlin, 1988) or an objective mapping procedure (Bretherton et al., 1976; Sarmiento et al., 1982)).

3. Observations

3.1. Crossover analysis

The crossover analysis (Fig. 2) suggests that AOU generally (in 8 out of 10 locations) decreased between 1000 and 1750 m (Fig. 2, Table 1). Given the assumptions of the crossover analysis, the

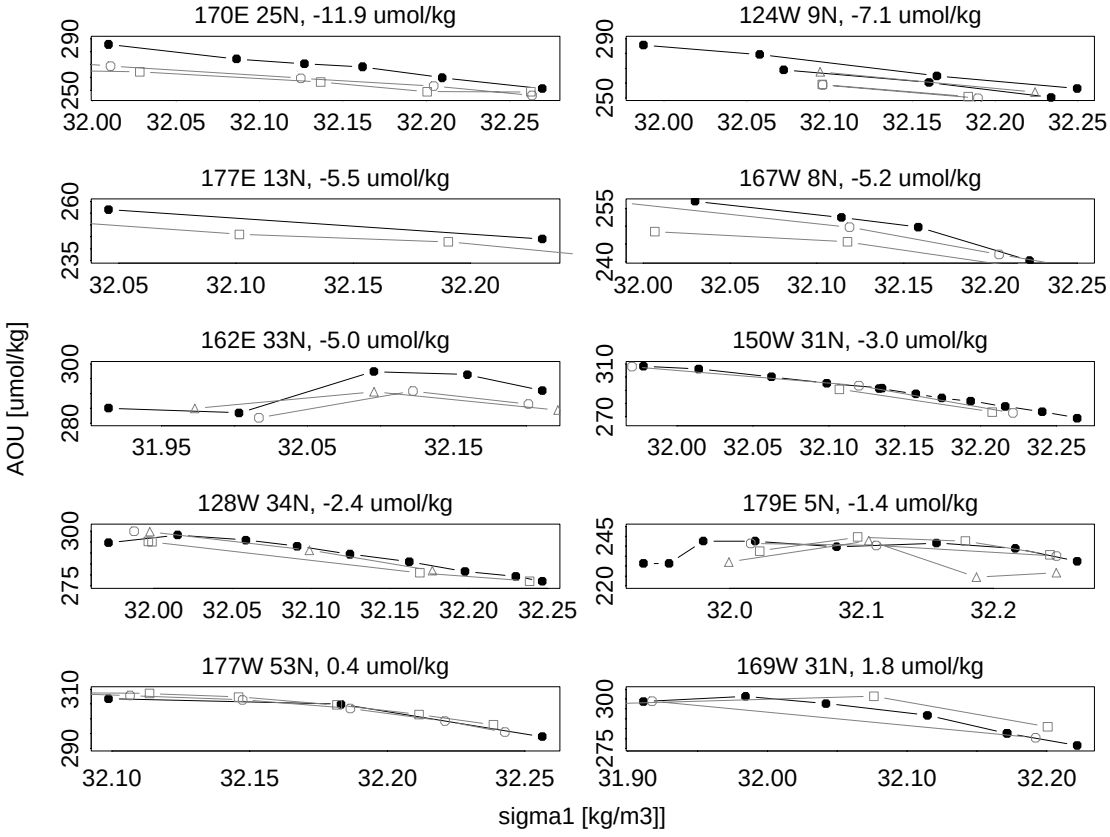

Fig. 2. Crossover analysis of WOCE (open symbols) and GEOSECS (closed symbols) observations for selected crossovers on isopycnal surfaces between 1000 and 1750 m. The number after the location coordinates in each panel title is the AOU trend (i.e., WOCE–GEOSECS) between two regression fits to the observations. The crossover locations are plotted in Fig. 1, the results are detailed in Table 1. Potential densities are calculated using the reported temperatures and following Fofonoff (1977), Millero et al. (1980), and Millero and Poisson (1981). AOU is calculated from θ, salinity, the oxygen concentration and the oxygen solubility (Garcia and Gordon, 1992).

Table 1
Estimation of mean AOU and nitrate ($[NO_3^-]$) differences between WOCE and GEOSECS at selected crossovers on isopycnal surfaces between 1000 and 1750 m depth[a]

Latitude	Longitude	GEOSECS stations	WOCE stations	Δ AOU	Δ $[NO_3^-]$
170°E	25°N	227	TPS24(221:223)	−11.9	−0.8
124°W	9°N	339,340	TPS10(165,167)	−7.1	−0.2
167°W	8°N	238	P15N(95:96)	−5.2	−0.9
162°E	33°N	225	P13N(51:53)	−5.0	−1.8
177°E	13°N	230	P14N(100)	−5.5	+0.2
179°E	5°N	241	P14N(124:126)	−1.4	−0.7
150°W	31°N	204	P2(70:71)	−3.0	+0.3
128°W	34°N	201	P17C(10:12)	−2.4	+0.8
177°W	53°N	219	P14N(12,13)	+0.4	−0.8
169°W	31°N	213	P2(63,64)	+1.8	+0.5
Mean of all trends				−3.9	−0.34
Standard deviation of all trends				3.9	0.80
Standard error of mean trend				1.25	0.25

[a] Values are in μmol kg^{-1}. The trends are the differences between linear (for less than 8 data points per station depth interval) or locally weighted interpolations (Cleveland and Devlin, 1988) (for more than 8 data points per station and depth interval). For each tracer, the standard deviation of the mean trend is the standard deviations of the n trend observations divided by $\sqrt{n}$. The station locations are shown in Fig. 1. The analyzed nitrate concentrations are corrected for nitrite whenever possible. For intermediate and deep water the nitrite is negligible relative to nitrate (Dore and Karl, 1996).

mean AOU decreased by 3.9 μmol kg^{-1} (marginally significant at $p \leqslant 0.05$, with a standard error of the mean of 1.25 μmol kg^{-1}). The mean $[NO_3^-]$ decreased by 0.34 μmol kg^{-1}, but not significantly (standard error of the mean 0.25 μmol kg^{-1}, $p \geqslant 0.05$). The analytical uncertainty is of comparable magnitude as the estimated standard errors (WHPO, 1994). However, the analytical uncertainty probably does not contribute considerably to the standard errors for two reasons. First, the standard error of the mean is the standard deviations of the n trend observations divided by $\sqrt{n}$. Second, we use deep waters to correct for possible offsets. This simple crossover analysis suggests that there has been a significant change in AOU. However, to estimate the AOU and $[NO_3^-]$ trends with more confidence requires a more refined data analysis method.

3.2. Interpolation along isopycnal surfaces

Correcting for the station location bias by interpolating all WOCE observations to the GEOSECS stations (exemplified for AOU on the $\sigma_\theta = 27.4$ kg m^{-3} isopycnal surface in Fig. 3) allows more GEOSECS stations to be used.

The calculated trends between the considered GEOSECS station (numbers in Fig. 3) and the interpolated WOCE values are analyzed for various isopycnal surfaces (Fig. 4). Using more stations and interpolating the signal to various isopycnal surfaces results in smaller error bars and

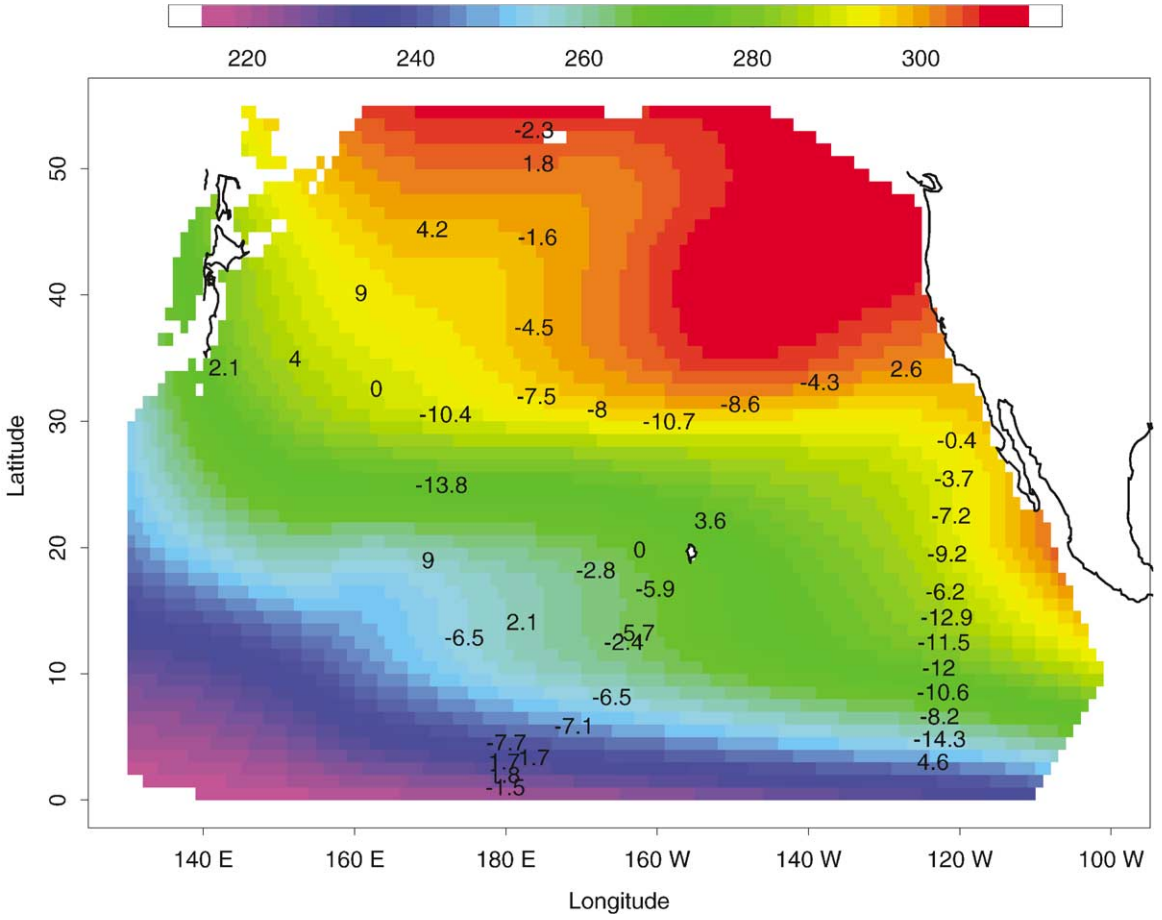

Fig. 3. Example interpolation of the WOCE AOU observations (in μmol kg^{-1}) on the $\sigma_\theta = 27.4$ kg m^{-3} isopycnal surface (approximate depth of 1050 m) using locally weighted regression. The numbers indicate the estimated changes between the GEOSECS and WOCE observations.

illustrates the variability of the trends with depth (Fig. 4). In shallow waters (roughly above 750 m) AOU and $[NO_3^-]$ increase (though not significantly), while AOU and $[NO_3^-]$ decrease below. Between roughly 1000 and 1600 m, the AOU and $[NO_3^-]$ decreases are highly significant ($p \leqslant 0.01$).

Two observations argue against the possibility that the estimated trends are artifacts of analytical errors or sparse sampling. First, the trends are similar for three different analytical methods. For example, using an objective analysis instead of the locally weighted regression for $\sigma_\theta = 27.4$ kg m^{-3} results in similar AOU and $[NO_3^-]$ trends (crosses, Fig. 4). Second, the ratio between the estimated AOU and $[NO_3^-]$ changes are consistent with previous estimates. For example, the estimated AOU to $[NO_3^-]$ ratio for the crossover analysis is 12 ± 4.2, statistically indistinguishable from the 9.1 estimate of Minster and Boulahdid (1987). Random errors probably would not lead to a reasonable tracer ratio.

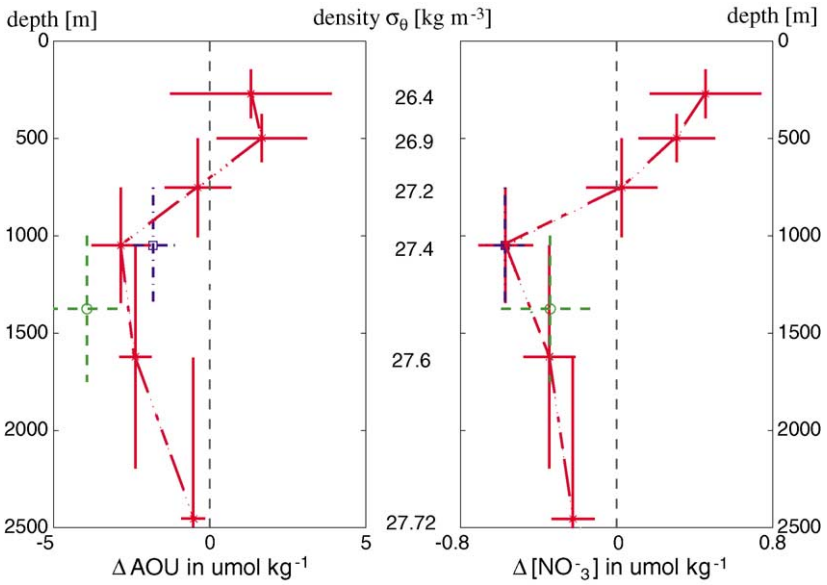

Fig. 4. Estimated changes in AOU and $[NO_3^-]$ for various isopycnal surfaces and average depths. Shown are the result of the locally weighted regression using the full data set (red crosses), the objective analysis on $\sigma_\theta = 27.4$ kg m^{-3} (blue squares), and the results of the crossover analysis between 1000 and 1750 m depth detailed in Table 1 (green circles). The horizontal error bars represent one standard error of the estimated mean. The vertical error bars indicate one standard deviation of the depth range for the isopycnal surface and the entire depth range for the crossover analysis. The results for the isopycnal interpolations are corrected using AOU and $[NO_3^-]$ deep water ($\sigma_\theta = 27.77$ kg m^{-3}, average depth roughly 3500 m) trends of -0.84 ± 0.29 and -0.15 ± 0.08 μmol kg^{-1}, respectively. The uncertainty due to the deep water corrections is propagated to the signal uncertainties assuming uncorrelated errors.

4. Discussion

Given our assumptions, the significant changes in intermediate water AOU and $[NO_3^-]$ are inconsistent with a steady-state system. These AOU and $[NO_3^-]$ changes can be caused by (at least) two mechanisms: (i) changes in the remineralization fluxes driven by changes in the biological carbon pump, and (ii) changes in the water ventilation rates. In the following section, we use two model sensitivity studies to explore whether the observed trends are consistent with these biological and physical changes.

4.1. Possible changes of the biological carbon pump

To test whether changes in the biological carbon pump might explain the observed trends, we perturb the biological carbon pump in an ocean general circulation model for a period of 20 years (see Toggweiler et al., 1989; Najjar and Orr, 1998, for a detailed model description). Biological production in the model (J_p) is parameterized in terms of phosphate and determined by the difference between the surface phosphate ($[PO_4^{3-}]_m$) and a restoring value ($[PO_4^{3-}]_r$) as well as a

time constant (τ) according to

$$J_p = \begin{cases} \frac{1}{\tau}([PO_4^{3-}]_m - [PO_4^{3-}]_r) & \text{for } [PO_4^{3-}]_m \geqslant [PO_4^{3-}]_r, \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

Biologically mediated fluxes of tracers such as oxygen or carbon are linked to the phosphate fluxes by Redfield ratios. The biological production is partitioned in the model into particulate organic matter (POM) and dissolved organic matter (DOM) with a constant proportion. DOM is advected and diffused with the circulation and is remineralized following first order kinetics. POM is sinking and the remineralization is parameterized following Martin et al. (1987), with the remineralization flux ($F(z)$) of particulate organic matter being a function of depth (z), the flux at the compensation depth (F_c), the compensation depth (z_c), and a slope parameter (a) as a measure of the remineralization efficiency:

$$F(z) = F_c \left[\frac{z}{z_c}\right]^{-a}. \quad (2)$$

For the model spin-up and the control run, the restoring values are a compilation of annual mean surface layer observations (Najjar and Orr, 1998). To simulate the AOU and $[NO_3^-]$ changes due to changes in the biological carbon pump, we perturb export production and remineralization efficiency in the Northern Hemisphere for 20 years to approximate the time interval between GEOSECS and WOCE. Changes in export production are simulated by increasing or decreasing $[PO_4^{3-}]_r$ by a factor of two. Changes in the remineralization efficiency are simulated by increasing or decreasing the parameter a by a factor of two. Much larger perturbations would arguably contradict local observations of macro-nutrients and remineralization fluxes (Karl et al., 1997; Wong et al., 1998; Whitney and Freeland, 1999; Martin et al., 1987; Christian et al., 1997).

The model sensitivity study (Fig. 5) suggests that significant perturbations of the marine biological pump could cause considerable changes in shallow water AOU but would keep intermediate water AOU virtually unchanged. For example, a simulated increase in nutrient-use efficiency by a shift to $\frac{1}{2}[PO_4^{3-}]_r$ causes an increase in particulate organic matter production of roughly 0.5 Gt C year^{-1} after 20 years in the considered region. The increase in export production drives an increase in remineralization fluxes. Because remineralization fluxes decrease with depth (Eq. (2)), the concomitant changes in AOU tend to decrease with depth (Fig. 5A). As a result, the maximum AOU increase occurs around 300 m, and the observed changes in intermediate water AOU cannot be explained by this scenario. Reversing the scenario by decreasing the nutrient use efficiency reverses the AOU trends but leaves the magnitude roughly constant (Fig. 5B). The modeled changes in nutrient use efficiency cannot explain the observed intermediate water signal.

The assumption of constant remineralization efficiency is problematic, as some observations hint at a shift towards shallower remineralization (Karl et al., 1995). Shallower remineralization shifts the AOU source towards shallower waters. As a result, shallow water AOU increases and intermediate water AOU decreases, as illustrated by the model sensitivity study (Fig. 5D, for a shift towards $\frac{1}{2}a$). However, as most carbon is remineralized in shallow waters, the largest AOU changes occur in shallow waters and intermediate water AOU is virtually unaffected. Assuming a shift towards deeper remineralization (Fig. 5C, with a shift towards $2a$) tends to decrease AOU in shallow waters and increase AOU in intermediate waters. Because the modeled intermediate water

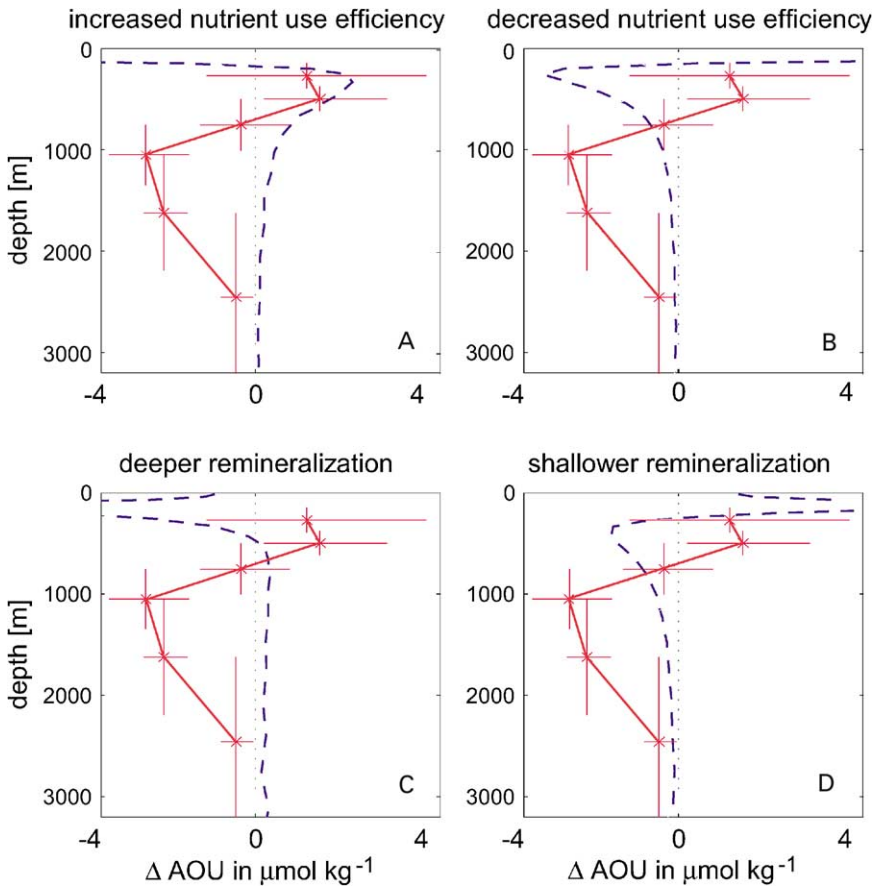

Fig. 5. Estimated AOU changes as a function of depth for the GCM perturbation analyses (blue dashed lines) compared to the estimated trends (red crosses, same as in Fig. 4). The model changes are calculated from the phosphate perturbations scaled by an AOU to $[PO_4^{3-}]$ ratio of 170 (Anderson and Sarmiento, 1994). The GCM data are analyzed for the region 125°E−110°W and 0−60°N, because the GEOSECS stations sample only a subregion of the North Pacific. Increased and decreased nutrient use efficiency (cases A and B) refers to the model scenarios of $\frac{1}{2}$ and 2 times the restoring surface phosphate concentrations in Eq. (1). Deeper and shallower remineralization denote the model scenarios of increasing and decreasing the slope parameter in Eq. (2) by a factor of 2, respectively.

AOU trends are much smaller than the observed trends, changes in remineralization efficiency cannot explain the observed AOU trends.

This model sensitivity study with respect to changes in the marine biological carbon pump supports two conclusions. First, significant changes in the marine biota cannot be rejected for shallow waters (roughly above 500 m) due to the large uncertainty of our data-analysis method. In other words, changes in export production and/or remineralization depth could very likely explain the shallow water trends within their uncertainties. Second, changes in the North Pacific biota between GEOSECS and WOCE are unlikely the only explanation for the observed intermediate water AOU trends. Other mechanisms, such as changes in the water ventilation rates, are thus expected to be important, at least for intermediate waters.

4.2. Possible changes of water ventilation rates

The interplay between remineralization and ventilation rates can be illustrated by the changes of AOU along the $\sigma_\theta = 27.4$ kg m^{-3} isopycnal surface (mean depth roughly 1050 m) in the North Pacific (Fig. 6). In this example, waters flow along the isopycnal surface towards higher latitudes. Along the flow path, organic matter is remineralized and AOU increases. The slope of the AOU vs. latitude relationship depends on the oxygen utilization rate (OUR) as well as the water ventilation rate (v) (illustrated by the vector diagram in Fig. 6). For example, increasing the ventilation rate would decrease the slope of the AOU vs. latitude relationship. At a given location, increasing ventilation rates would cause AOU to decrease.

To test whether this ventilation mechanisms can explain the observed AOU trends, we first evaluate the magnitude of the implied changes in ventilation rate and water ages. The changes in ventilation rates and water ages are then compared to available observations and constraints. We shall argue that the necessary changes are well within the available constraints, hence a simple order of magnitude analysis seems sufficient.

The change in AOU for a step change in ventilation rate can be approximated by a simple plug-flow model as

$$\Delta\,\mathrm{AOU} = \Delta t\,\mathrm{OUR}\left[1 - \frac{v_2}{v_1}\right], \tag{3}$$

where Δ AOU is the observed change in AOU, Δt denotes the time since the step change, and the subscripts identify the values before (1) and after (2) the step change. Eq. (3) is valid only for Δt

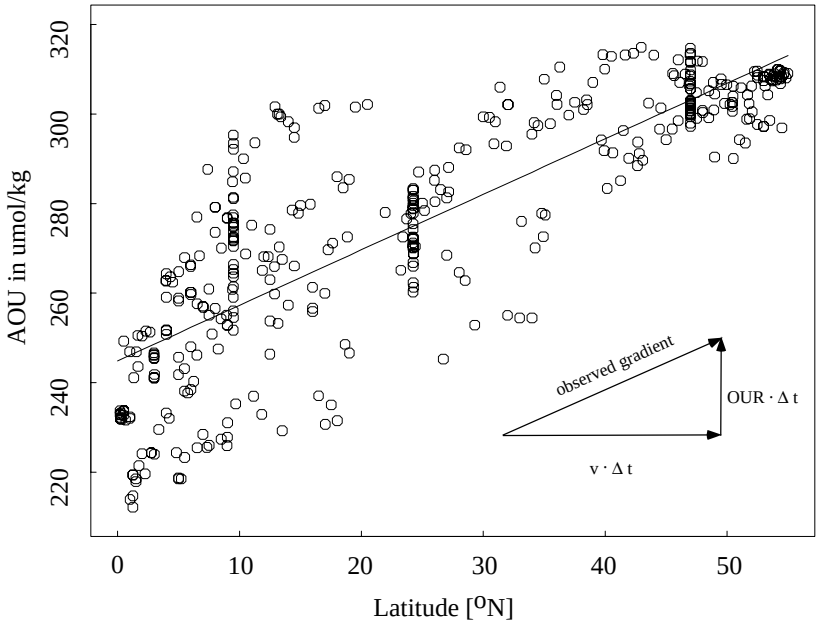

Fig. 6. AOU as a function of latitude for North Pacific WOCE and GEOSECS observations with $\sigma_\theta = 27.4 \pm 0.01$ kg m^{-3}. The line is the least square fit. The vector diagram illustrates the relationship between OUR, ventilation rate and the observed AOU gradient.

values much smaller than the flushing time of water on the isopycnal surface. In this framework, the ventilation rate (v) is represented by the average flow velocity along the isopycnal surface. Changes in ventilation rates, furthermore, affect water ages with the age trend approximately equal to

$$\Delta \text{ age} = \Delta t \left[\frac{v_1}{v_2} - 1 \right]. \tag{4}$$

Note that this simple model is only a rough approximation, as it neglects, for example, the effects of diapycnal mixing and the surface boundary condition.

Adopting an average flushing time of roughly 250 years for the North Pacific (Stuiver et al., 1983; England and Rahmstorf, 1997) results in an OUR of 0.27 μmol kg^{-1} a^{-1}, consistent with reported OUR values for this depth range (Tseytlin, 1992). According to our model defined in Eq. (3) and illustrated in Fig. 6, an increase in ventilation rates on the order of 50% would explain the observed 2.85 μmol kg^{-1} decrease in AOU for the considered isopycnal surface (Eq. (3)). This 50% increase in ventilation rate translates to an observed age decrease over the roughly 20 years between GEOSECS and WOCE of roughly 7 years (Eq. (4)). As we shall argue below, these changes in ventilation rate and water age are well within the reported range of variability given data presently available.

There exist to our knowledge no direct observations of changes in ventilation rates for the considered water masses. Perhaps, the most relevant results are reported by Johnson et al. (1994), indicating a roughly five-fold increase in water flow across the Samoa passage between 1968 and 1992. However, the Samoa passage is deeper than the $\approx$1000 m depth of the isopycnal surface we consider. Thus it remains an open question whether the magnitude of the observed variability for the Samoa passage is relevant here. The available radiocarbon data are insufficient for detecting decadal-scale shifts in ventilation rate of the required levels to produce the observed changes in AOU and nitrate (Keller, 2000, pp. 52–54).

4.3. Caveats

The scarcity of the available data and analyzed mechanisms argues for a cautious interpretation of our results. For example, changes in the thermohaline structure of intermediate water masses affect our analysis. Changes in the thermohaline structure are caused, for example, by El Niño events (Jacobs et al., 1994; Chavez et al., 1999), or by the warming of the North Pacific (Levitus et al., 2000). However, the artifacts introduced by such changes are arguably small because the observed signals occur in intermediate waters away from the more shallow perturbations caused by El Niño events and the warming of the North Pacific. Further, changing from isopycnal to depth space in the crossover analysis does not change the results very much.

This study examines changes in carbon cycling that influence the distribution of AOU and $[NO_3^-]$. It does not address another mechanism by which a changing marine biota can influence the atmospheric CO_2 budget: a change in the rain ratio (the ratio of calcite to organic matter export) (Deuser et al., 1995). Changes in the rain ratio would keep AOU and $[NO_3^-]$ approximately constant, while changing oceanic carbon uptake via changing the efficiency of the biological carbon pump (Volk and Hoffert, 1985). Changes in the rain ratio also would affect the ratio of dissolved inorganic carbon to alkalinity. However, the interpretation of this signal

would be confounded by the increasing DIC levels due to the abiotic absorption of CO_2 (''the solubility pump''). Unfortunately, the available data set seems too sparse to estimate these change with sufficient confidence on a basin scale. Further analyses are likely to yield more precise and detailed answers as the necessary data become available.

Clearly, our ocean model considers only a much simplified representation of the biogeochemical processes, and the modeled tracer distributions should be taken with a grain of salt. Nonetheless, ocean models have been shown to reproduce the general features of observed tracer distributions with some confidence (Najjar et al., 1992; Anderson and Sarmiento, 1995; Orr et al., 2001). For example, our model reproduces the average depth profile of phosphate in the considered region reasonably well with a root mean square error of 0.3 μmol kg^{-1} (equivalent to 13% of the mean concentration). The model underpredicts [PO_4^{3-}] in shallow and intermediate waters (depths less than 1250 m) and overpredicts the observed phosphate in deeper waters — similar to the model behaviors shown in Anderson and Sarmiento (1995, Fig. 3d) or Najjar et al. (1992, Fig. 16). A second example involves the capability of our model to reproduce the estimated export production in the subtropical North Pacific. Emerson et al. (1997) estimate the export production at station ALOHA (22°45″N, 150°W) between 19 and 32 gC m^{-2} a^{-1}. Our model estimate of 22 gC m^{-2} a^{-1} (assuming that 30% of the downward flux of organic carbon is in the form of dissolved organic carbon (Yamanaka and Tajika, 1996)) is within the observed range. The available ocean biogeochemical models still face major challenges (Doney, 1999). Nonetheless, we believe that the small calculated changes in AOU and [NO_3^-] below 1000 m are robust.

Finally, our results depend on the method used to improve the data base consistency. For example, we do not adjust the WOCE data for internal consistency as proposed by Johnson et al. (2001). This is a challenging task, as there are no certified reference materials for the tracer measurements in question. One problematic issue is the question whether the deep water correction should be applied as a constant or proportional offset (Zhang et al., 2000). However, in our analysis this effect seems not very important because the analyzed intermediate water masses show relatively small changes in tracer concentration. For example, the average [NO_3^-] decreases from the isopycnal surface with the maximal signal ($\sigma_\theta = 27.4$ kg m^{-3}) to the isopycnal surface used for the deep water correction ($\sigma_\theta = 27.77$ kg m^{-3}) by approximately 13%. Applying a proportional instead of a constant deep water correction very slightly decreases the magnitude of the estimated [NO_3^-] trend from -0.57 to -0.55 μmol kg^{-1} at $\sigma_\theta = 27.4$ kg m^{-3}. More refined methods to improving the data base consistency than applied in our study are presently developed (Ross et al., 1999; Johnson et al., 2001; Gouretski and Jancke, 2001), and our analysis can certainly be refined, once an accepted database of corrected GEOSECS and WOCE observations becomes available.

4.4. *Implications for the net oceanic* CO_2 *uptake due to changes in the biological carbon pump*

As discussed above, the inferred AOU and [NO_3^-] trends do not allow us to exclude the possibility that the export production has changed in the North Pacific. One can ask how much the export production would have changed, if the tracer trends were caused solely by changes in the marine biota. The answer is a decrease in export production of approximately 0.1 Gt C a^{-1}, or 2.5 Gt C over the 20 years. This estimate is derived from the -0.1 Gt C a^{-1} change in carbon inventory, calculated from the average AOU trend in the isopycnal interpolation (Fig. 4), a

surface area of 1.1×10^{14} m^2, and an AOU to carbon ratio of 1.4. Note that the change in oceanic carbon uptake would be less than the change in export production (e.g., Sarmiento and Orr, 1991). The magnitude of the decrease in export production is roughly a factor of twenty smaller than estimates of the global oceanic carbon uptake (1.85 ± 0.35 Gt; Orr et al., 2001), and roughly a factor of 100 smaller than typical estimates of global oceanic export production (around 10 Gt C a^{-1} with a large uncertainty; Ducklow, 1995). One also can ask how much error the estimated change in the oceanic oxygen inventory would introduce to values of land and ocean uptake of anthropogenic CO_2 calculated from the atmospheric balance assuming no change in the oceanic oxygen content (Keeling and Shertz, 1992; Bender et al., 1996)? The answer is the same: about 0.1 Gt C a^{-1}. Oxygen balance calculations would underestimate land sequestration by 0.1 Gt C a^{-1}, and overestimate ocean sequestration by the same amount.

4.5. Comparison with previous studies

Our findings of increased AOU and [NO_3^-] concentrations in shallow waters (above roughly 750 m) are consistent with the study of Emerson et al. (2001), who report increasing AOU and [NO_3^-] for shallow waters (above roughly 700 m) in the northeast subtropical Pacific. On the other hand, our results of a decrease in intermediate water AOU are in contrast to the study of Pahlow and Riebesell (2000), who report a significant increase in intermediate water AOU. This discrepancy in the estimated magnitude of changes might be explained by differences in data selection and analysis. First, we analyze only data between the 1970s and the 1990s, while Pahlow and Riebesell (2000) analyze data between the 1940s and the 1990s. Because we analyze a shorter time period, our results do not bear on the possibility that much of the AOU trend reported by Pahlow and Riebesell (2000) occurred between the 1940s and the 1970s. Second, Pahlow and Riebesell (2000) correct for potential analytical offsets using water masses as shallow as 2100 m (their Fig. 1). Using such shallow waters for the correction step would shift our estimated AOU trends towards more positive values and decrease the discrepancy between the AOU trends estimated by Pahlow and Riebesell (2000) and our results. However, this approach would be at variance with the assumption of negligible decadal scale trends in the water masses used for the correction step. Third, Pahlow and Riebesell (2000) analyze changes in tracer ratios while we investigate changes in tracer concentrations.

The conclusions of Pahlow and Riebesell (2000) differ from our study also in the interpretation of the estimated trends. Pahlow and Riebesell (2000) note that AOU inventory changes imply CO_2 sequestration. In contrast, Gruber et al. (2000), Emerson et al. (2001), and our analysis show that AOU inventory changes may reflect changes in ventilation rates as well as changes in export production. The calculated change in export production generally will depend on which of the two possibilities is assumed to cause the AOU inventory change.

5. Conclusions

We analyze the changes in AOU and [NO_3^-] between GEOSECS and WOCE in the North Pacific. Given our assumptions, the observed significant decrease in intermediate water AOU and [NO_3^-] are inconsistent with a steady-state system. A model sensitivity study shows that

considerable perturbations of the marine biota over 20 years would cause only small changes in intermediate water AOU and $[NO_3^-]$, close to the uncertainties of our analysis method. The observed trends are consistent with changing ventilation rates, but seem unlikely the sole result of changes in the North Pacific marine biota. However, the observed trends cannot exclude a changing marine biota. As a result, estimates of oceanic carbon uptake due to decadal scale trends in the marine biota are uncertain.

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