

Silicon-nitrogen coupling in the equatorial Pacific upwelling zone

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Abstract. We describe the role of diatoms on nitrogen and silicon cycling in the equatorial Pacific upwelling zone (EUZ) using water column nutrient data from 19 equatorial cruises and particle concentration, new production, and sediment trap data from the U.S. Joint Global Ocean Flux Study (JGOFS) equatorial Pacific (EqPac), France JGOFS fluxes in the Pacific (FLUPAC), and U.S. Zonal Flux cruises. Our results suggest that production and sinking of diatoms dominate particulate nitrogen export at silicate concentrations above 4 μM . Below this level, silicate is preferentially retained; while inorganic nitrogen is completely utilized, silicate remains at concentrations of 1-2 μM and is completely exhausted only under nonsteady state conditions. This lower nutrient condition accounts for a majority of particulate nitrogen export in the EUZ with minor loss of particulate silicon. Retention of silicon relative to nitrogen appears due to a combination of new production by nondiatoms, dissolution of silica frustules after grazing, iron limitation, and steady state upwelling. This synthesis supports the argument that diatom production was tightly coupled to new production during the U.S. JGOFS EqPac survey II cruise [Dugdale and Wilkerson, 1998]. However, this compilation suggests EqPac survey II cruise took place during a period of atypically high subsurface nutrients. We conclude that silicon and nitrogen are tightly coupled only at periods of very high nutrient concentration and nonsteady state. In addition, nutrient cycling in the EUZ is consistent at all times with a mechanism of combined iron and grazing control of phytoplankton size classes [Landry et al., 1997].

1. Introduction

Diatoms are phytoplankton which utilize silicate to form siliceous frustules. These frustules have a high excess density and are often large in size and thus prone to rapid sinking [Smith et al., 1996]. Diatoms utilize nitrate readily and sometimes preferentially [Dugdale et al., 1995; Lomas and Glibert, 1998], thus feeding the ammonium-based microbial loop with new nitrogen. Their high growth rates, resistance to grazing, and readiness to sink make them an important part of the sinking particle flux in open ocean [e.g., Billet et al., 1983], coastal upwelling [e.g., Nelson and Goering, 1978], and high-nitrate low-chlorophyll (HNLC) waters [e.g., Gersonde and Wefer, 1987].

The central equatorial Pacific upwelling zone (EUZ) [Murray et al., 1994] is an HNLC regime in which diatoms

have been implicated to play an important role [Chavez et al., 1990] and is of considerable interest to biogeochemists. The U. S. Joint Global Ocean Flux Study (JGOFS) surveyed this region in a process study of the central equatorial Pacific (EqPac) [Murray et al., 1994] to characterize carbon fluxes and better understand the mechanism of the HNLC food web [Barber and Chavez, 1991]. Previous work suggested that the HNLC condition was due to iron limitation [Martin, 1990], grazing control [Frost and Franzen, 1992], or a combination of both [Chavez et al., 1991]. Landry et al. [1997] synthesized EqPac data and concluded that the presence of the HNLC condition in the region was due to a combination of microzooplankton grazing control on picoplankton and limitation of larger phytoplankton because of lack of iron. In the absence of significant eolian iron inputs to this region [Duce and Tindale, 1991; Donaghay et al., 1991], the equatorial undercurrent may be the dominant, though low level, source of iron [Gordon et al., 1997].

Availability of silicate has also been invoked as a regulating force for the HNLC condition. Bender and McPhaden [1990] found a silicate minimum at the equator,

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Paper number 1999GB900031
0886-6236/99/1999GB900031\$12.00

135°W during 1988. They inferred this was the signature of a recent diatom bloom. *Ku et al.* [1995] recognized that the silicate to nitrate disappearance ratio in EqPac data was much lower than in other ocean areas. They suggested this was due to dominance of local recycling relative to eolian input of nutrients and further hypothesized that particle export might be regulated by input of "new" silicate.

Dugdale and Wilkerson [1998] expanded this argument using two additional pieces of information: 1) The regression between silicate and nitrate between 1°S and 1°N in the upper 200 m during U.S. JGOFS EqPac survey II (see methods) suggested that nitrate and silicate were taken up in a 1:1 ratio consistent with diatom growth requirements and 2) average euphotic zone silicate concentrations during *R/V Wecoma* 1988 (WEC 88), EqPac survey I, and EqPac survey II showed that silicate varied little between seasons relative to nitrate, consistent with the chemostat concept wherein only the limiting nutrient is drawn down to a constant, low level while other nutrients are more variable depending on their input concentrations. *Dugdale and Wilkerson* [1998] then used a food web model of silicon and nitrogen cycling based on the work of *Dugdale et al.* [1995] to illustrate agreement between this hypothesis and estimates of nitrogen cycling during EqPac survey II.

In this paper we provide a comprehensive assessment of silicon-nitrogen coupling in the equatorial upwelling zone to investigate the role of diatoms in new production and particle export. We include water column nutrient data from 19

equatorial cruises and particulate silica and organic nitrogen measurements in sediment traps and the water column and ¹⁵N new production from the U.S. JGOFS EqPac surveys, the France JGOFS fluxes in the Pacific transect (FLUPAC), and the U.S. Zonal Flux transect. We show that silicon and nitrogen are sometimes tightly coupled in the central equatorial Pacific euphotic zone but that there is, in general, preferential export of nitrogen over silicon. We suggest that the occurrence of diatom dominance of new production and particle export is controlled by grazing selectivity and iron limitation and stimulated by nonsteady state conditions, such as those occurring during propagation of Kelvin waves and tropical instability waves.

2. Data

Water column nutrient data from the upper 120 m from 2°N to 2°S were obtained from 19 equatorial cruises (Table 1): 8 Hawaii-Tahiti Shuttle Experiment (HTSE) meridional transects along 150°-158°W in 1979 and 1980 [D. Archer, personal communication, 1998; T. Takahashi, personal communication, 1998]; 3 National Oceanographic and Atmospheric Administration (NOAA) National Marine Fisheries Service cruises along 81°-129°W from August to September of 1986, 1987 and 1989 [*Fiedler et al.*, 1991]; World Ocean Circulation Experiment (WOCE) cruise P16C along 150°W in September of 1991 and P17C along 120°W in June of 1991 (<ftp://nemo.ucsd.edu/woce/Data/Pacific/>); 2

Table 1. Summary of cruise data

Cruise	Date	Longitude, deg	SOI	Niño 3.5 Anomaly	Slope	Intercept	r^2
HTSE 1	Feb. 1979	150-153 W	-0.07	0.08	0.33	1.67	0.84
HTSE 3	April 1979	150-158 W	-0.03	0.31	0.86	-1.50	0.80
HTSE 5	June 1979	150-158 W	0.67	0.36	0.62	-0.33	0.69
HTSE 7	Aug. 1979	150-158 W	0.37	0.05	0.21	1.25	0.32
HTSE 9	Nov. 1979	150-158 W	-0.30	0.53	0.22	1.66	0.50
HTSE 11	Jan. 1980	150-158 W	-0.43	0.79	0.20	1.44	0.42
HTSE 13	March 1980	150-158 W	-0.30	0.2	0.51	0.47	0.72
HTSE 15	May, 1980	150-158 W	-0.83	0.43	0.35	1.31	0.69
NOAA-86	Oct. 1986	87-113 W	-0.37	1.13	0.69	1.01	0.96
NOAA-87	Oct. 1987	85-129 W	-0.67	1.73	0.62	1.01	0.94
NOAA-88	Sept.-Oct. 1988	81-128 W	1.50	-1.58	0.70	-0.28	0.96
WOCE P17	June 1991	120 W	-1.0	0.98	0.70	-0.96	0.68
WOCE P16	Sept. 1991	150 W	-1.0	0.64	0.42	1.65	0.74
Survey I	Feb. 1992	140 W	-2.6	1.99	0.27	1.63	0.37
Time series I	March-April 1992	140 W	-1.9	1.66	0.49	0.21	0.34
Survey II	Aug. 1992	140 W	-0.3	0.07	0.76	-2.49	0.93
Time series II	Oct. 1992	140 W	-0.6	-0.05	0.83	-1.63	0.81
FLUPAC	Oct. 1994	163W- 150W	-1.7	0.93	0.40	0.75	0.71
Zonal Flux	April-May 1996	165E- 150W	0.5	-0.20	0.41	0.63	0.66
Average		142 W	-0.48	0.53	0.50	+0.39	0.69
Sum N ≤ 7.62		-	-		0.28	+1.54	0.29
Sum N > 7.62		-	-		0.85	-2.83	0.90

Summary of data from the HTSE, NOAA, WOCE P16 and P17, JGOFS EqPac, France JGOFS FLUPAC, and Zonal Flux cruises between 2°N and 2°S showing the date and longitude of study, Southern Oscillation Index (SOI), Niño 3.5 sea surface temperature anomaly, the slope and intercept of the model II least squares regression of silicate versus dissolved inorganic nitrogen as well as the squared Pearson product-moment coefficient (r^2). The longitude (-), SOI (+), and Niño 3.5 sea surface temperature anomaly (-) are indicators of the strength of upwelling. The slope is an indicator of the relative consumption of silicate and nitrogen. The intercept is an indicator of the extent of nitrogen limitation relative to silicate. The r^2 is an indicator of the percent of the variability accounted for in the correlation.

U.S. JGOFS EqPac surveys along 140°W in February-March (survey I) and August-September (survey II) of 1992; 2 U.S. JGOFS EqPac time series at the equator 140°W in March-April (time series I) and October (time series II) of 1992 (<http://www1.whoi.edu/jgofs.html>); France JGOFS FLUPAC transect along the equator between 165°E and 150°W in October of 1994 aboard the *N/O l'Atalante* [LeBorgne et al., 1995]; and the U.S. Zonal Flux transect along the equator between 165°E and 150°W in April-May of 1996 aboard the *R/V Thomas G. Thompson*. For HTSE cruises, nitrite and ammonia data were not available. For WOCE and NOAA cruises, ammonia data were not available.

Survey I took place in boreal spring during the passage of a series of Kelvin waves associated with El Niño conditions, while survey II took place in the fall during a temporary abatement of El Niño [Kessler and McPhaden, 1995]. Carbon fluxes (e.g., new production, primary production, and particle export) all increased dramatically from survey I to survey II [Murray et al., 1994] as a consequence of this physical forcing. Survey II encountered a convergent front associated with a tropical instability wave (TIW) [Yoder et al., 1994], which resulted in an intense accumulation of *Rhizosolenia* at this "Great Front" and dramatic changes in the biogeochemistry of the euphotic zone [Archer et al., 1997]. During the France JGOFS FLUPAC cruise a boreal fall El Niño condition displaced the warm pool east of the date line to 170°W. Because the warm pool is a water mass distinct from the EUZ, only FLUPAC nutrient data taken east of the western Pacific warm pool were considered in this analysis. During the Zonal Flux cruise a boreal spring La Niña displaced the warm pool over 25° westward, past 165°E. Consequently, equatorial nutrient data along the entire Zonal Flux transect were considered in this analysis. Southern Oscillation Indices (SOI), shown in Table 1, are averages for the three months before each cruise, while temperature anomalies in the Niño 3.5 region of 5°N-5°S, 170°W-120°W (Table 1) are monthly averages for each cruise (<http://www.pmel.noaa.gov/toga-tao/el-nino/home.html>). All regressions between nutrients were made using model II (principal axis or major axis from Sokal and Rohlf [1995]) which treats both variables as being subject to error and thus avoids biasing the regression toward the x axis.

Particulate silica was measured as both water column concentrations and sinking fluxes during EqPac. Silica flux samples were collected on 0.4 μm Nuclepore filters in drifting sediment traps of the particle interceptor trap (PIT) design [Murray et al., 1996] during survey I between 12°N and 1°N (until the array was lost at the equator) and survey II between 12°N and 12°S. Samples for water column particulate silica concentration were collected during survey II between 9°N and 5°S by filtration of 2.36 L samples from 10 L Niskin bottles onto 1 μm Nuclepore filters. All EqPac silica samples were processed in Seattle using the soda-hydrolysis method of Paasche [1980] and measured spectrophotometrically using a Bausch and Lomb spectronic 100. All Zonal Flux and FLUPAC silica samples were processed in Brest, France, using the method of Paasche [1973] [Blain et al., 1997].

We utilize data for on-deck $^{15}\text{NO}_3$ new production [McCarthy et al., 1996] and drifting sediment trap nitrogen fluxes from EqPac surveys I and II (available at

<http://www1.whoi.edu/jgofs.html>); water column particulate silica concentrations [Blain et al., 1997], in-situ $^{15}\text{NO}_3$ new production [Navarette, 1998; Rodier and LeBorgne, 1997], drifting sediment trap nitrogen [Rodier and LeBorgne, 1997], and silica fluxes from FLUPAC; in situ $^{15}\text{NO}_3$ new production (A. K. Aufdenkampe et al., manuscript in preparation, 1999a), drifting sediment trap nitrogen and silica fluxes from Zonal Flux.

All sediment trap fluxes for EqPac [Murray et al., 1996] and for FLUPAC and Zonal Flux ("Export production in the western and central equatorial Pacific: zonal and temporal variability", J. P. Dunne et al., submitted to *Deep-Sea Research, Part I*, 1998) were calibrated by comparing ^{234}Th fluxes in traps with advection-corrected ^{234}Th deficiency fluxes. Sediment trap nitrogen and silica estimates for all cruises shown here are averages of all trap samples collected between 100 and 150 m. As eolian inputs are thought to be extremely low in this region [Donaghay et al., 1991; Duce and Tindale, 1991], particulate silica is assumed to be 100% biogenic.

3. Results

We first consider the relationship between dissolved silicate and dissolved inorganic nitrogen (DIN), defined as the sum of NO_3^- , NO_2^- , and NH_4^+ , in the upper 120 m of the water column. Nutrient data are presented in Figure 1 for the EUZ between 2°N and 2°S for cruises from which we have particulate silica data. We chose the 2°N-2°S interval to be consistent with the EqPac designation of the equatorial upwelling zone [Murray et al., 1996] and with model results for the meridional extent of equatorial upwelling [e.g., Liu et al., 1994]. We limited our analysis to the upper 120 m in order to focus on only the zone where new production takes place, using the EqPac designation of the euphotic zone's 0.1% light level at 120 m [Murray et al., 1994]. Restricting the vertical analysis to the euphotic zone minimized complications due to (1) differential remineralization of organic nitrogen and dissolution of particulate silica beneath the euphotic zone and (2) complexities of equatorial circulation, specifically the combination of the shallowness of equatorial upwelling and the strength of the equatorial undercurrent, both tending to decouple processes from distributions in the vertical extent. We chose to include NO_2^- and NH_4^+ in our analysis to enable comparison of nutrient mass balances with sediment trap fluxes.

Our analysis for survey II (Figure 1b) gave a significantly lower slope (0.76, see Table 1) than the value of 1.00 in Dugdale and Wilkerson [1998]. The difference in slope was due to a combination of factors. Model II regression of nitrate in the 0-200 m, 1°N-1°S domain of Dugdale and Wilkerson [1998] gave a slope of 0.923. Increasing the latitudinal extent of the domain to 2°N-2°S decreased the slope to 0.865. Decreasing the vertical extent of the domain to 0-120 m further decreased the slope to 0.763. Adding NO_2^- and NH_3 into the analysis decreased the slope only slightly, to 0.759. These differences, however, are small relative to the differences observed between cruises which deviate considerably (± 0.22) from the mean (0.50, see Table 1).

In addition to the slopes, the y intercepts of the nutrient

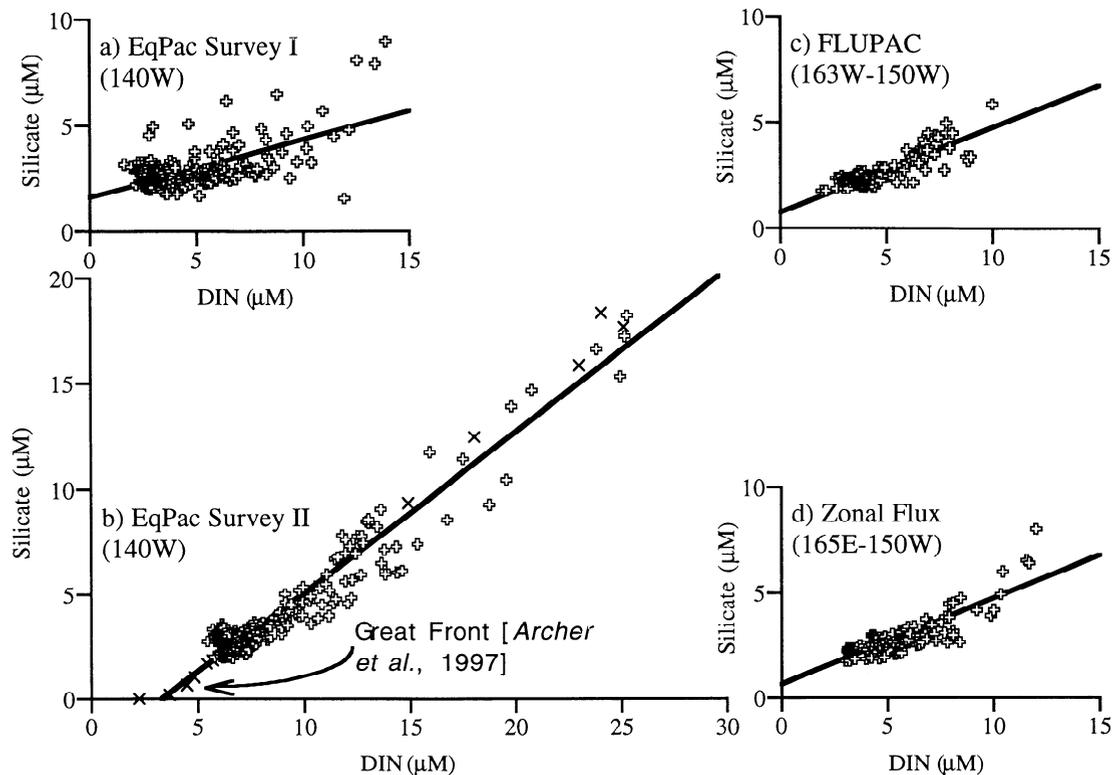


Figure 1. Dissolved inorganic nitrogen ($\text{NO}_3 + \text{NO}_2 + \text{NH}_4$; μM) versus silicate (μM) in the upper 120 m between 2°N and 2°S for four cruises: (a) U.S. Joint Global Ocean Flux Study (JGOFS) EqPac survey cruises along 140°W in February-March and (b) August-September 1992, (c) the France JGOFS FLUPAC cruise along the equator between 163°W and 150°W in October 1994 and (d) the Zonal Flux cruise along the equator between 165°E and 150°W in April-May 1996. Also shown are model II least squares regressions for each cruise given in Table 1. Data from the Great Front (crosses) are distinguished from the rest of EqPac survey II to highlight that this highly nonsteady state feature caused severe changes in nutrient utilization [Archer *et al.*, 1997].

regressions provide useful information. The negative y intercept of the regression for survey II (-2.5 , see Table 1 and Figure 1b) implies that if the observed trend in silicate and DIN continued, silicate would be exhausted before DIN. However, neither nutrient decreased below $2 \mu\text{M}$ (except at the Great Front), prohibiting the general conclusion that either nutrient was absolutely limiting. At the predicted rate of uptake, silicate would be exhausted when DIN reached about $3.3 \mu\text{M}$. In this entire analysis the only instance where silicate was reduced to zero coincided with the surface biomass accumulation that was associated with the passage of the instability wave at 2°N (the Great Front [Archer *et al.*, 1997]). This is the only station among the 19 cruises analyzed in which diatoms were apparently able to completely remove silicate.

The silicate-DIN regressions from survey I, FLUPAC and Zonal Flux are shown in Figures 1a, 1c, and 1d. Maximum silicate and nitrate concentrations during these cruises reached only half those found during survey II. The slopes of these regressions (see Table 1) range between 0.27 and 0.41. All the y intercepts of these regressions are positive, implying that DIN would be exhausted first, while silicate remained at 0.6– $1.6 \mu\text{M}$. Clearly, either the ocean biogeochemistry or physics or both was unique during survey II.

More comprehensive analysis of all available cruise data showed the wide range of conditions which exist in the EUZ. Characterizations by longitude $^\circ\text{W}$, SOI, Niño 3.5 sea surface temperature (SST) anomaly, and model II (principal axis) least squares regression are shown for all 19 cruises in Table 1. Silicate-DIN slopes range between 0.20 and 0.83. The slopes in Table 1 are highly correlated (probability that they are uncorrelated ($P \leq 0.01$, Pearson product-moment correlation ($r \geq 0.56$, number of samples ($n = 19$ [Sokal and Rohlf, 1995]) with the mean DIN and silicate concentrations as well as the maximum DIN and silicate concentrations for each cruise (Table 2). Because nutrient concentrations tend to increase with the strength of upwelling, one might expect the slopes to increase seasonally toward the months of maximum trade winds (positive at maximum winds in July [Philander, 1990]), geographically toward the eastern Pacific (negative with longitude $^\circ\text{W}$) and climatologically with the Niño 3.5 SST anomaly (negative with temperature) and SOI (positive). Though the correlations of these four parameters with the silicate-DIN slope were all in the correct direction, only the longitude correlation was significant at the 95% confidence level (Table 2).

To describe the overall relationship between DIN and silicate in the euphotic zone of the equatorial upwelling zone,

Table 2. Summary of Pearson Product-Moment Coefficients

Parameter Correlated With Slope	<i>r</i>
Mean DIN concentration	0.72
Mean silicate concentration	0.66
Maximum DIN concentration	0.80
Maximum silicate concentration	0.91
Longitude ^o W	-0.49
Month ^a	0.30
SOI	0.23
Niño 3.5 SST anomaly	-0.21

Only values of $r \geq 0.43$ are significant at the $P = 0.05$ level (Sokal and Rohlf, 1995).

^aAway from January (maximum is July).

we show data from all 19 equatorial cruises in Figure 2. The data in Figure 2 are distributed such that the slope is low (0.28) at low-DIN and low-silicate concentrations and high (0.85) at high-DIN and high-silicate concentrations, with an inflection near $7.6 \mu\text{M}$ DIN and $3.7 \mu\text{M}$ silicate. At high-DIN and high-silicate concentrations, changes in DIN are accompanied by approximately equal changes in silicate. However, the data from the euphotic zone predominantly occupy the region of lower slope. Of the 2313 data points in Figure 2, 1534 (66%) have $\text{DIN} \leq 7.62 \mu\text{M}$, with DIN concentrations in the upper 120 m averaging $6.9 \pm 3.4 \mu\text{M}$.

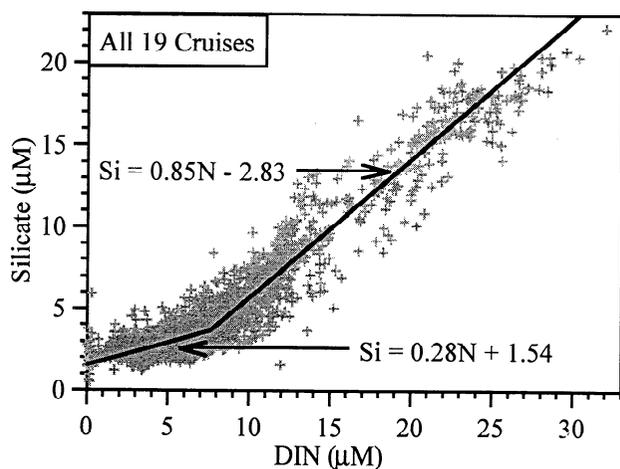


Figure 2. The composite relationship between dissolved inorganic nitrogen ($\text{NO}_3 + \text{NO}_2 + \text{NH}_4$; μM) and silicate (μM) in the upper 120 m between 2°N and 2°S for the Hawaii-Tahiti Shuttle Experiment (HTSE), National Oceanic and Atmospheric Administration (NOAA), World Ocean Circulation Experiment (WOCE) P16C and P17C, JGOFS EqPac, FLUPAC, and Zonal Flux cruises in Table 1. The data were ranked by nitrogen and fitted using least squares regressions from each end. The break in slope was determined as the point where each of the two regressions predicted the same silicate value at the nitrogen midpoint (fixed nitrogen is $7.26 \mu\text{M}$, silicate is $3.32 \mu\text{M}$). Data from the Great Front were omitted to focus only on the two major modes of nutrient utilization.

These data imply that the low-slope signature dominated the euphotic zone during these cruises.

The important role of diatoms is clearly evident in our water column particulate silica results for survey II (Figure 3). The distribution of water column particulate silica shows strong maxima north and (less so) south of the equator. The intense northern maximum coincides with the location of the Great Front at 2°N [Archer *et al.*, 1997]. The maximum value of 413 nM at the equator, 140°W during non-El Niño survey II is approximately twice the maximum value of 201 nM at 155°W observed during El Niño FLUPAC [Blain *et al.*, 1997] and 4 times the maximum value of 102 nM at 155°W during the La Niña Zonal Flux cruise. The Si:N mole ratio in bottle-filtered particulate matter was 0.2 at 150°W on the equator during both FLUPAC and Zonal Flux. During survey II at 140°W this ratio was much higher, at 0.8, both on the equator and on average between 9°N and 5°S .

Comparisons between ^{15}N new production and sediment trap nitrogen and silica fluxes corroborate the differential elemental cycling suggested in the nutrient data. ^{15}N new production [McCarthy *et al.*, 1996; Navarette, 1998; A. K. Aufdenkampe *et al.*, manuscript in preparation, 1999a] and ^{234}Th -calibrated sediment trap nitrogen and silica fluxes are shown for surveys I and II, FLUPAC, and Zonal Flux in Figure 4. EqPac nitrogen uptake and sediment flux data were discussed by McCarthy *et al.* [1996] and Murray *et al.* [1996]. FLUPAC nitrogen uptake and sediment flux data were discussed by Rodier and LeBorgne [1997]. FLUPAC silica data were discussed in Blain *et al.* [1999]. Values of all three parameters were uniformly low during survey I but relatively high between 5°N and 5°S during survey II. Highly significant correlations ($P < 0.1$) exist between sediment trap fluxes of nitrogen and silica ($r^2 = 0.88$) and between each of these and new production ($r^2 = 0.51$ and 0.73 , respectively) for the EqPac surveys. Sediment trap data during the FLUPAC short time series at 150°W show similar magnitude and variability as the Zonal Flux transect between 165°E and 150°W . The FLUPAC and Zonal Flux cruises alone give only weak correlations ($0.02 < P < 0.05$) between nitrogen and silica fluxes ($r^2 = 0.44$). No correlation was observed between new production and either nitrogen or silica sediment trap fluxes during these cruises. The range of new production and particulate organic nitrogen sinking flux during the FLUPAC site at 150°W and Zonal Flux ($0.5\text{--}4.8 \text{ mmol N m}^{-2} \text{ d}^{-1}$) were of similar magnitude to survey II between 2°N and 2°S ($0.6\text{--}4.7 \text{ mmol N m}^{-2} \text{ d}^{-1}$). While silicon fluxes are only

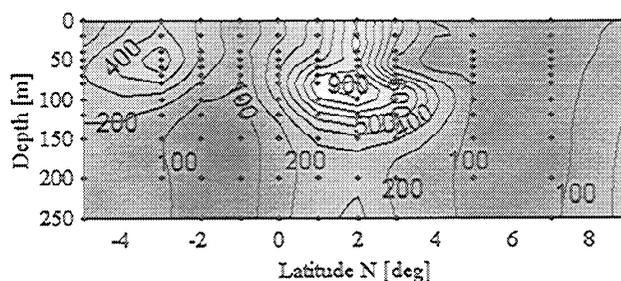


Figure 3. Latitude-depth section of water column particulate silica concentration (nM) during U.S. JGOFS EqPac survey II.

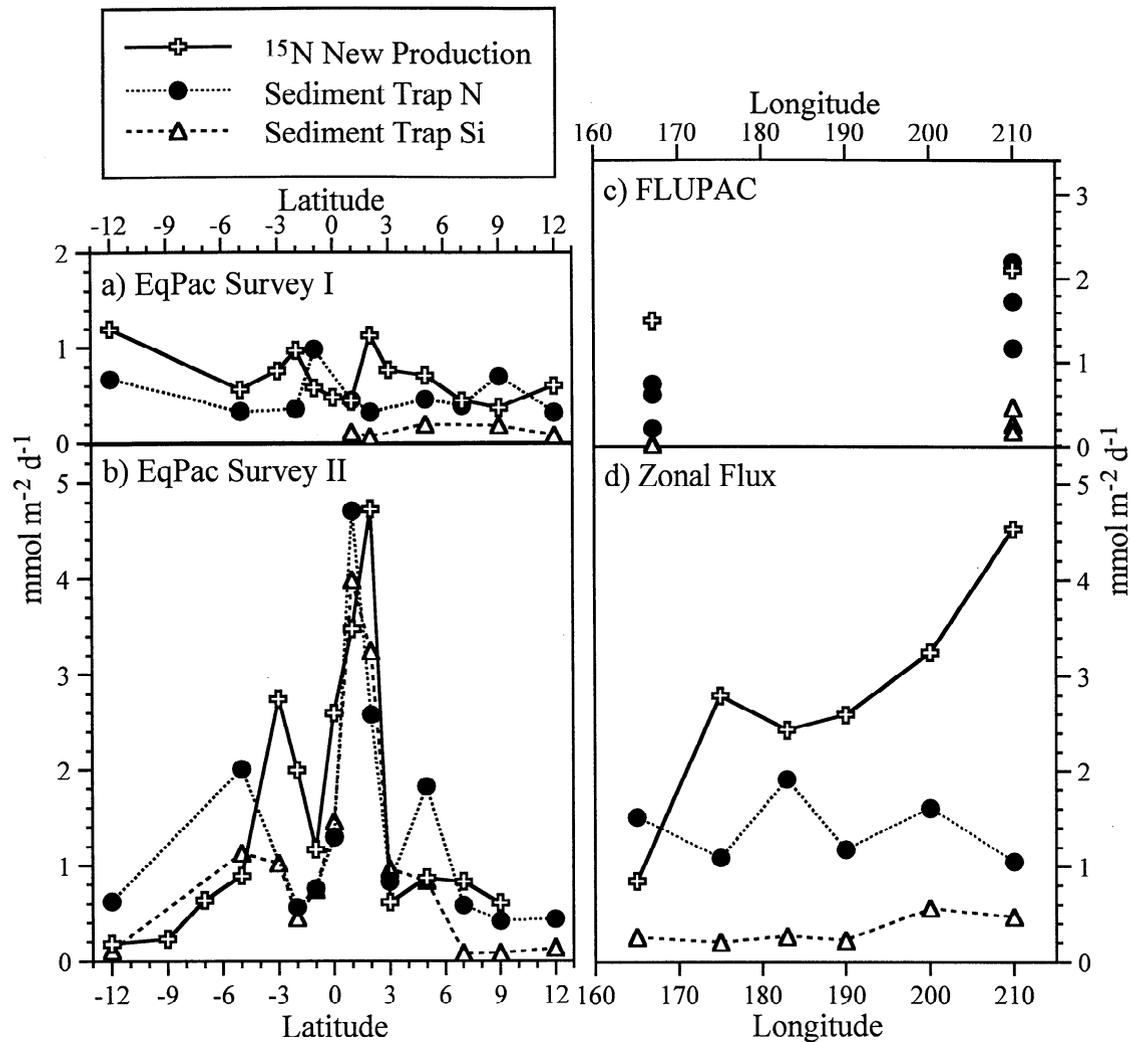


Figure 4. Integrated ^{15}N new production [McCarthy *et al.*, 1995] and sediment trap fluxes of nitrogen and silicon versus latitude for (a) EqPac survey I, (b) EqPac survey II, (c) FLUPAC, and (d) Zonal Flux cruises, all in $\text{mmol m}^{-2} \text{d}^{-1}$. All sediment trap fluxes were corrected using ^{234}Th as described by Murray *et al.* [1996].

high during survey II, nitrogen fluxes are only low during EqPac survey II. Silicon fluxes appear tightly coupled to nitrogen fluxes during EqPac survey II but not during the other three cruises.

4. Discussion

4.1 Observed coupling between silicon and nitrogen

The silicate-DIN slope gives an indication of net Si:N uptake by biota in the euphotic zone. As illustrated in our data compilation (Figure 2), the silicate-DIN nutrient slope depends on nutrient concentration. Specifically, two modes of nutrient utilization exist in the EUZ: In the first mode, which is characteristic of El Niño/warm conditions, nutrients are low ($\text{NO}_3 < 7.6 \mu\text{M}$), silicate levels are maintained at 1 - 2 μM levels, and diatoms contribute only a fraction of new production. In the second mode, which is characteristic of strong cold tongue conditions, nutrients are high ($\text{NO}_3 > 7.6$

μM) and diatom new production is an efficient particle export mechanism.

Silicon to nitrogen ratios in nutrients compare well with sediment trap ratios near the equator. Assuming that (1) particle concentration is at steady state, (2) production of dissolved organic nitrogen is negligible, and (3) nutrients are predominantly supplied vertically, then the Si:N ratio of vertical disappearance from the nutrient pool ($\Delta\text{Si}:\Delta\text{DIN}$ ratio) should equal the Si:N ratio in sinking particles. The Si:N ratio of vertical disappearance, expressed as the mole ratio of $\Delta\text{Si}:\Delta\text{DIN}$ between the surface and 120 m ($[\text{SiO}_3]_{120} - [\text{SiO}_3]_0)/([\text{N}]_{120} - [\text{N}]_0)$, is compared with the Si:N ratio in sediment trap material in meridional sections for surveys I and II (Figure 5a and 5c) and in zonal sections for FLUPAC and Zonal Flux (Figure 5b and 5d). Off the equator the Si:N ratio of vertical disappearance was higher than the sediment trap Si:N ratio. This difference may reflect meridional or zonal differences in $\Delta\text{Si}:\Delta\text{DIN}$ ratios combined dominance of horizontal processes off the equator. Near the equator,

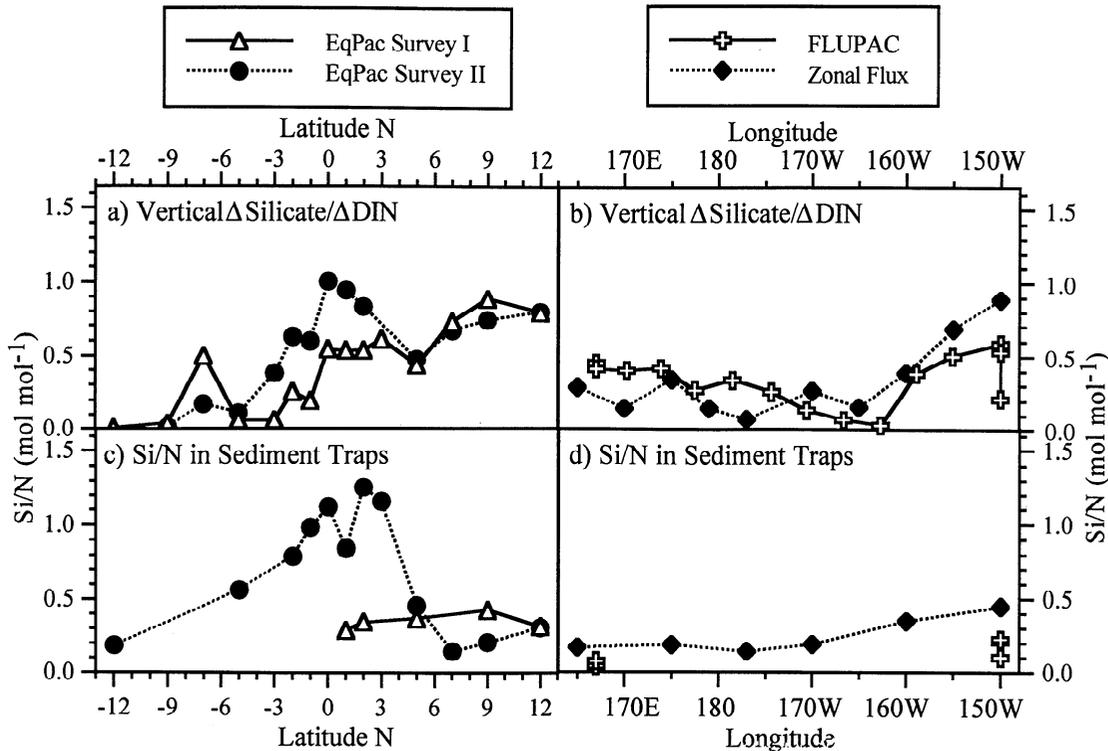


Figure 5. (a and b) The disappearance ratio of silicate over dissolved inorganic nitrogen between 120 m and the surface ($[\text{SiO}_3]_{120} - [\text{SiO}_3]_0 / ([\text{N}]_{120} - [\text{N}]_0)$) and (c and d) the average ratio of silicon to nitrogen in sediment traps between 100 and 150 m both mol mol^{-1} versus latitude for EqPac survey I (open triangles) and EqPac survey II (solid circles) cruises (Figures 5a and 5c) and versus longitude for the FLUPAC (open crosses) and Zonal Flux (solid diamonds) cruises (Figures 5b and 5d).

however, there was good intra-cruise agreement between the Si:N ratio of vertical disappearance and the sinking flux, giving us confidence in the validity of the assumptions of particle steady state, vertical particle export, and vertical nutrient supply during these cruises.

Si:N ratios in sediment trap material, the ratio of vertical disappearance and the silicate-DIN slope in the 2°N - 2°S band were all high during survey II and low during the other three studies (Table 3). During surveys I and II between 2°N and 2°S the ranges in the Si:N ratio in trap material agreed well with the disappearance ratio of $\Delta\text{Si}:\Delta\text{DIN}$ in the water column and the slope of the silicate-DIN regression from Table 1. During FLUPAC the range of Si:N ratio in trap material was at the low end of the disappearance ratio of $\Delta\text{Si}:\Delta\text{DIN}$ in the water column and the slope of the silicate-DIN regression from Table 1. During Zonal Flux the range in Si:N ratios in trap material spanned the range in the disappearance ratio of Si:N in the water column. On the whole, all three parameters suggest that relative utilization of silicate was much higher during survey II than during the other three cruises.

Taken alone, the high silicate-DIN regression slope from survey II could be interpreted as an artifact of horizontal advection or of recent upwelling of waters characterized by remineralization/dissolution processes. Results from sediment traps corroborate the apparent nutrient uptake, however, suggesting that the nutrient disappearance is indeed a signature of biological removal from the euphotic zone.

The low utilization and export of silicon relative to nitrogen during survey I, FLUPAC, and Zonal Flux suggest that the coupling between nitrogen and silicon in the equatorial upwelling zone is variable. Particulate silica is apparently only exported from the EUZ euphotic layer during high-nutrient and high-flux periods of very strong nutrient upwelling such as occurred during survey II.

Comparison of particulate fluxes with the water column inventory of particulate silica suggests two things (1) the biomass and sinking flux of diatoms are tightly coupled, but (2) the role of diatoms in the coupling of silicon to nitrogen is variable. Average sediment trap silica flux between 100 and

Table 3. Summary of Mole Ratios of Silicon to Nitrogen Utilization Using Three Methods

Cruise	Sediment Trap Si/N ^a	Vertical $\Delta\text{Silicate}/\Delta\text{DIN}$ ^b	Silicate-DIN slope ^c
Survey I	0.29 - 0.34	0.19 - 0.54	0.27
Survey II	0.79 - 1.25	0.60 - 1.00	0.76
FLUPAC	0.10 - 0.23	0.03 - 0.59	0.40
Zonal Flux	0.14 - 0.45	0.07 - 0.89	0.41

^aRange of 100-150 m vertical averages.

^bRange between the surface and 120 m.

^cModel II regression slope from Table 1.

150 m and integrated ^{15}N new production in the euphotic zone are both highly correlated ($P < 0.005$) with the particulate silica inventory in the upper 120 m during survey II (12°N – 12°S , see Figures 6a and 6b). Variability in the inventory of particulate silica can explain 71% of the variability in silica flux (Figure 6a) and 77% of the variability in new production (Figure 6b) during survey II. The regression with silica trap flux for survey II has a slope corresponding to a residence time (τ_{Si}) of 30 ± 7 days for particulate silica sinking out of the upper 120 m. The regression for new production during survey II has a positive intercept, suggesting either that a small amount of new production occurs independent of the particulate silica inventory (i.e. by non-Si-requiring phytoplankton) or that diatoms were more efficient under conditions of low abundance.

Data from FLUPAC and Zonal Flux have a different relationship between new production and particulate silica concentration than observed during survey II (Figure 6b). During these cruises, particulate silica concentrations and silica fluxes were low, while new production remained high. This implies that diatoms were either extremely efficient at utilizing nitrate or that another phytoplankton group was dominating new production. Particulate silica residence times from FLUPAC at 150°W ($\tau_{\text{Si}} = 31 \pm 13$ days) and Zonal Flux ($\tau_{\text{Si}} = 18 \pm 5$ days), however, compare well with survey II (Figure 6a). While particulate silica concentration has a relatively direct link with sinking flux (Figure 6a), its link with new production is variable (Figure 6b).

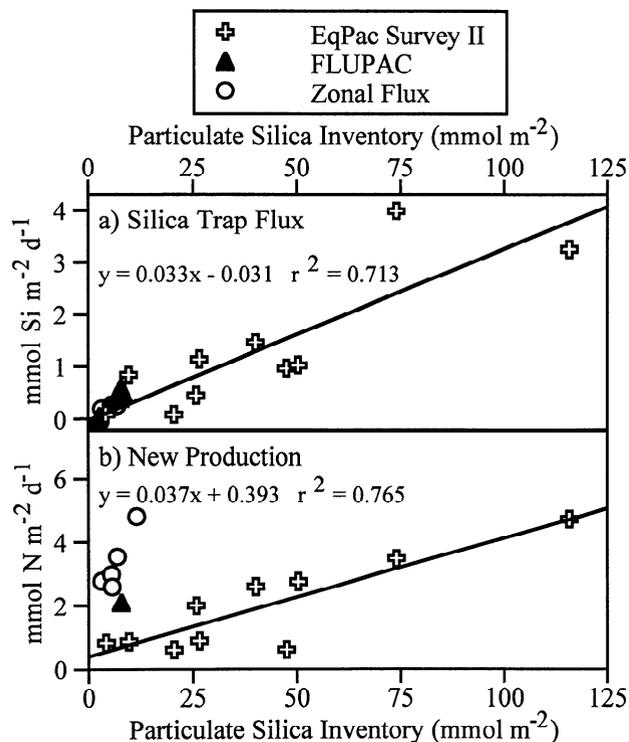


Figure 6. (a) ^{234}Th -corrected silica flux in sediment traps and (b) ^{15}N new production versus the inventory of particulate silica in the upper 120 m for the EqPac survey II (open crosses), FLUPAC (solid triangles), and Zonal Flux (open circles) cruises.

4.2 Implications for a silicate-regulated chemostat

Dugdale and Wilkerson [1998] modeled the equatorial Pacific as a chemostat in which nutrients input from below were consumed internally by biological uptake in a constant ratio. With surface concentration of the most limiting nutrient fixed at its limiting value, less limiting nutrients could vary as a function of input concentration. In this application of the chemostat model, nitrate was utilized only with equivalent utilization of silicate. Within the euphotic zone, silicate was observed at a constant, low level while nitrate varied. They interpreted this as a consequence of constant relative nitrate and silicate utilization combined with variable nitrate input. The chemostat model thus predicts that the range of waters of the first observed mode ($\text{NO}_3 < 7.6 \mu\text{M}$) is produced by a family of water masses with different silicate-nitrate signatures. This interpretation is not supported by the data, however, as only a single family of silicate-nitrate signatures was observed (Figure 2). Given the very limited range of silicate-nitrate signatures in upwelled water, mixing is the only mechanism consistent with both the chemostat model and observed distributions. For new production to be regulated by silicate in these two modes, new production would have to occur only in the second mode ($\text{NO}_3 > 7.6 \mu\text{M}$) such that the first mode ($\text{NO}_3 < 7.6 \mu\text{M}$) is a result of mixing between waters of variable nitrate and constant silicate. Given that high new production was measured during cruises characteristic of the first, low nutrient mode, nitrogen utilization must be prevalent in the first mode. The silicate-based chemostat explanation must therefore be rejected.

A key assumption in the interpretation of silicon-nitrogen coupling is the Si:N ratio for nutrient uptake by diatoms. Brzezinski [1985] found the Si:N ratio to be $1.05 \text{ mol mol}^{-1}$ (total range: 0.41 – $4.38 \text{ mol mol}^{-1}$) in laboratory experiments with 27 species of coastal and open ocean diatoms. This ratio has been shown to vary considerably when diatom growth is limited by light, temperature, and other nutrients [Paasche, 1980; Brzezinski, 1985]. Recent work suggests that the diatom Si:N uptake ratio increases to approximately 2.0 (mol Si) (mol N) $^{-1}$ under iron limitation [Hutchins and Bruland, 1998; Takeda, 1998]. Since the equatorial Pacific is known to have extremely low iron levels [e.g., Johnson et al., 1997] (see Figure 8), it is likely that the Si:N ratio of diatom uptake is high (i.e. 2.0) in this region. We thus interpret silicon cycling by considering the Brzezinski [1985] value of 1.05 (mol Si) (mol N) $^{-1}$ as providing an upper bound for diatom-based nitrogen cycling.

4.3 Mechanisms of decoupling between nitrogen and silicon

To understand the source of variability in new and export production in this region, it is crucial to understand the nature of the coupling between the particulate nitrogen and silicon mass balances. We utilize the following conceptual model to synthesize constraints on nitrogen and silicon uptake and removal processes in the equatorial Pacific upwelling zone. In this model (Figure 7), nitrate upwells and is taken up by phytoplankton which convert it to particulate organic nitrogen (PON). PON is subject to conversion to dissolved organic nitrogen (DON), remineralization to ammonium and nitrite

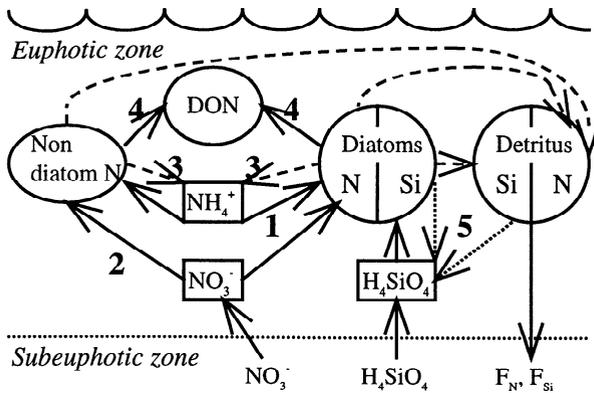


Figure 7. Flow diagram of the conceptual model. Boxes represent nutrient reservoirs, and circles represent particle reservoirs. Arrows represent fluxes due to: grazing (long dash), dissolution (short dash), upwelling, uptake, removal to DON, and sinking (solid). Numbers refer to (1) diatom regenerated production, (2) nondiatom new production, (3) remineralization of PON, (4) removal to DON, and (5) silica dissolution.

(which are subsequently reincorporated into diatom and nondiatom PON), and loss through a pool of sinking detritus. Silicate also upwells into the euphotic zone and is taken up by a subset of phytoplankton, diatoms, which convert it to silica. Silica is subject to dissolution back to silicate and loss through a pool of sinking detritus. In this model the nitrogen and silicon cycles can be decoupled in five ways (Figure 7): (1) Silicate can be taken up both during new (nitrate) and regenerated (ammonia and nitrite) diatom production. (2) Nondiatom phytoplankton may utilize nitrate. (3) PON and DON can be remineralized (either to the relatively utilizable forms of ammonium and nitrite or to nitrate), while silica cannot. (4) Organic nitrogen can cycle biologically between PON and DON phases, providing for significant horizontal export of a large refractory nitrogen pool (DON), while silica cannot. (5) Diatom silica is subject to chemical dissolution, while PON is not.

Analysis of survey II suggests that nitrogen and silicon were tightly coupled because regenerated diatom production, new production by other phytoplankton, DON production, and silica dissolution were negligible. Evidence from the other cruises suggests that at least some of these decoupling processes are important. Here we discuss each of these processes in the context of the conceptual model.

4.3.1. Diatom regenerated production and nondiatom new production. The link between diatoms and new production in the equatorial Pacific is variable. Silicate uptake rates from ^{32}Si incubations [Blain *et al.*, 1997] during FLUPAC were approximately equal to rates of ^{15}N new production [Navarette; 1998]. If diatoms were incorporating silicon and nitrogen in a 1:1 ratio (mol mol^{-1}), then diatom silica production would have been high enough to accommodate all new production during FLUPAC. Evidence from Price *et al.* [1994], however, suggests that phytoplankton other than diatoms take up nitrate in this region. They performed experiments on nitrate and ammonia uptake near 140°W at the equator during August of 1991 and

found that the $<3 \mu\text{m}$ size class was responsible for 85% of the nitrate uptake and that even the $<1 \mu\text{m}$ size class took up significant levels of nitrate. Since the $<3 \mu\text{m}$ size class excludes diatoms [e.g., Blain *et al.*, 1997; Chavez *et al.*, 1990], it appears that significant amounts of nitrate can be taken up by phytoplankton other than diatoms.

4.3.2. PON remineralization. PON removal may be another significant source of decoupling between the nitrogen and silicon cycles. Diatom specific mortality rates due to microzooplankton grazing were estimated to be high during EqPac, $0.53 \pm 0.21 \text{ d}^{-1}$ during survey I and $0.44 \pm 0.13 \text{ d}^{-1}$ during survey II [Latasa *et al.*, 1997]. These high specific mortality rates imply that diatom PON is recycled on the timescale of 2 days. Specific mortality rates for nondiatoms were estimated to be higher than for diatoms [Landry *et al.*, 1995; Latasa *et al.*, 1997], suggesting that recycling of diatom PON was less efficient than for nondiatom PON. PON remineralization to DIN serves to increase the slope of the silicate-DIN regression over the uptake ratio because DIN is preferentially retained relative to silicate. The observed high loss of DIN relative to silicate under the low-nutrient condition (Table 1) thus implies a dominant role of nondiatoms.

4.3.3. DON removal. Another potential mechanism of PON removal is accumulation and horizontal advective export of total organic nitrogen ($\text{TON} = \text{PON} + \text{DON}$). Hansell *et al.* [1997] presented TON results from the NOAA ocean-atmosphere carbon exchange study (OACES) cruises along 110°W , 125°W , and 140°W . They estimated that 27% of the total draw down of DIN either accumulated as TON or was transported away by horizontal advection. This extra loss term for nitrogen would lead to a lower disappearance ratio of Si:N relative to the sediment trap ratio.

4.3.4. Silica dissolution. Similarity in the rates of diatom production based on fucoxanthin and silica export in ^{234}Th -calibrated sediment traps leaves little room for particulate silica dissolution during survey II. Average growth rates of diatoms estimated from fucoxanthin changes in dilution experiments of $0.89 \pm 0.05 \text{ d}^{-1}$ [Latasa *et al.*, 1997] combined with the Si:N ratio of Brzezinski [1985] give total diatom nitrogen and silica production rates of $1.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ for survey II. These diatom production estimates are similar in magnitude to estimates of ^{15}N new production ($2.6 \text{ mmol N m}^{-2} \text{ d}^{-1}$ from McCarthy *et al.*, [1996]) and ^{234}Th -calibrated sediment trap fluxes ($1.8 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and $1.7 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ from this study) for this latitude band during survey II.

Measurements of particulate silica dissolution in surface waters available from other studies, however, attest to the importance of dissolution in the silica balance at the high temperatures of the EUZ. It has been well documented that living diatoms are resistant to dissolution, while deceased forms readily dissolve [e.g., Lewin, 1961; Paasche, 1973]. Silica in small, centric diatoms can dissolve with specific rates of $0.05\text{--}0.2 \text{ d}^{-1}$ at 20°C [Nelson *et al.*, 1976]. Kamatani [1982] measured particulate silica dissolution for a variety of diatom species. He found a strong species effect on the absolute rate and a strong temperature effect such that the rate constant increased by a factor of 2.3 for each 10°C rise in temperature independent of the species studied. He also found that the rate constant increased by a factor of 4 to 5

after acid cleaning, simulating passage through a gut. *Nelson and Goering* [1978] found dissolution rates equal to diatom growth rates in the Baja California and northwest African upwelling systems. *Brzezinski and Nelson* [1995] measured specific rates of $0.07 \pm 0.03 \text{ d}^{-1}$ for particulate silica dissolution in sediment traps ($\sim 19^\circ\text{C}$) at the Bermuda Atlantic Time-Series Site (BATS). *Blain et al.* [1999] estimated a specific rate of particulate silica dissolution of 0.4 d^{-1} ($\sim 27^\circ\text{C}$) during the FLUPAC cruise from the mass balance between ^{32}Si silicate uptake and the flux of silica in sediment traps, suggesting that 92% of biogenic silica produced in the euphotic zone re-dissolved. These studies suggest that dissolution can be a major part of the silica cycle in the euphotic zone and imply that diatom growth rates had to exceed $0.2\text{--}0.4 \text{ d}^{-1}$ in the equatorial Pacific upwelling zone during FLUPAC solely to overcome losses by dissolution before silica can be exported vertically. Dissolution, the potentially dominant loss term for particulate silica [*Brzezinski and Nelson*, 1995; *Blain et al.*, 1997], may be the source of the large observed variability between cruises. Based on the larger diatom assemblage, the high particulate silica concentrations and high Si:N utilization ratios during survey II, we suggest that relatively dissolution-resistant diatoms were responsible for nitrate-based production at that time.

4.4 Role of iron and a non-steady state food web

In the chemostat regulation hypothesis, the limiting nutrient is drawn down to a consistently low level while all other nutrients vary. Comparison of dissolved iron distributions in the central and eastern equatorial Pacific presents a strong case for chemostat regulation by iron. While the relationship between silicate and nitrate is identical in the eastern and central Pacific (Figure 8a), the relationship between dissolved iron and nitrate is quite different between these two regions (Figure 8b). Dissolved iron is lowered to the detection limit at $10 \mu\text{M}$ nitrate in the central Pacific and at $17 \mu\text{M}$ nitrate in the eastern Pacific, while having similar subsurface slopes between these nutrients ($0.022 \text{ mmol Fe (mol NO}_3\text{)}^{-1}$). Isopycnals and isopleths of the major nutrients (nitrate, silicate) shoal toward the eastern Pacific, while dissolved iron is drawn down to the detection limit near the base of the euphotic zone (120 m) in both the central and eastern Pacific. This shift in the iron-nitrate relationship is consistent with chemostat regulation by iron as dissolved iron appears to be fixed by the depth of the euphotic zone rather than by the nitrate concentration.

One critical factor in nitrogen-silicon coupling is net specific growth of diatoms. The relationship between new production and water column and sediment trap silica (Figures 5 and 7) suggests that in situations where specific growth rates of diatom populations are much greater than loss by grazing, new production by diatoms rises dramatically. The change in nutrient utilization ratio inferred from Figure 2 implies a change in food web dynamics due to depletion of one of the two macronutrients (DIN or silicate) or a third nutrient, such as iron. Results from *Blain et al.* [1997] from FLUPAC showed that diatom uptake was independent of silicate concentration and significantly depressed, suggesting that silicate uptake limitation is not the crucial factor in the

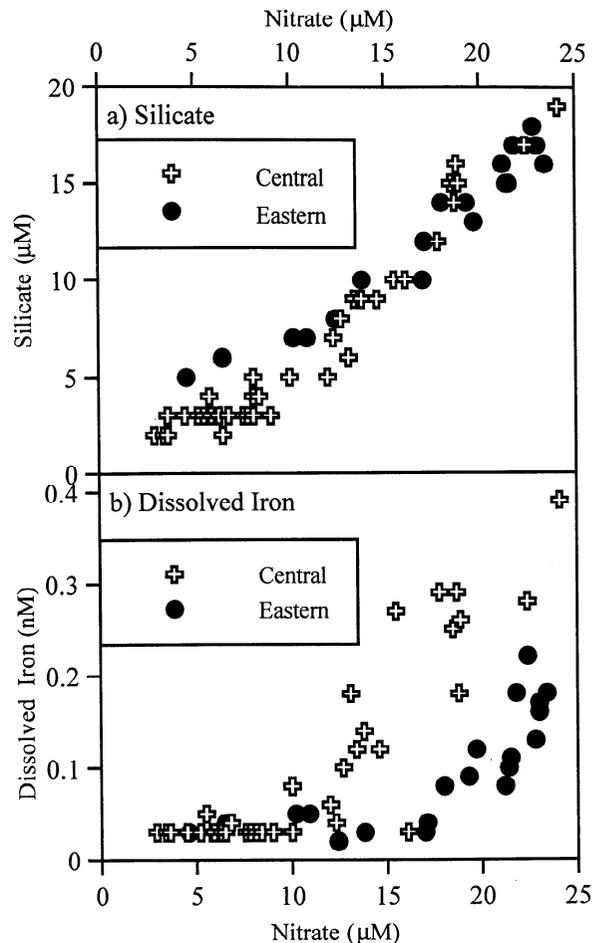


Figure 8. (a) Silicate (μM) and (b) dissolved iron (nM) versus nitrate (μM) from the central equatorial Pacific (Feline and EqPac time series cruises at the equator, 140°W) in the upper 200 m and from the eastern equatorial Pacific (PlumEx cruise at the 1°N , 92°W and the equator, 93°W) in the upper 150 m. Data from *Johnson et al.* [1997].

equatorial Pacific. This was further illustrated during survey II at the Great Front in which diatoms were able to draw down silicate completely, arguing against a high-silicate concentration threshold for uptake. More recently, A. K. Aufdenkampe et al. (Manuscript in preparation, 1999b) used a multilinear regression to show that new production could be predicted from the combination of nitrate, ammonia, and primary production (or chlorophyll), while the predictive capacity of silicate for new production was insignificant. While evidence supporting silicate limitation is inconclusive, evidence supporting iron limitation in this region is overwhelming [e.g., *Duce and Tindale*, 1991; *DiTullio et al.*, 1993; *Martin et al.*, 1994; *Coale et al.*, 1996; *Johnson et al.*, 1997; *Landry et al.*, 1997].

Iron control may be exerted through a shift in the size spectrum of phytoplankton rather than through a shift in phytoplankton specific growth rate. While diatom community specific growth rates did not change significantly between surveys I and II [*Latasa et al.*, 1997], the species composition

and size distributions changed dramatically between these time periods [Iriarte and Fryxell, 1995]. Landry *et al.* [1997] provide the convincing argument that differences observed between the two EqPac surveys were due to the combination of selective increase in growth rates of large phytoplankton (including diatoms) through selective grazing control of smaller phytoplankton (including diatoms). In this scenario, small diatoms grow at their maximum growth rates at all times, but large diatoms only match these rates during periods of increased iron input. This hypothesis is consistent with the high particulate silica concentrations observed during the survey II cruise. If this hypothesis is correct, then variability in the ratio of Si:N utilization and particle export in the equatorial Pacific is controlled by variability in food web structure induced by changes in the intensity of iron limitation.

Two forms of variable physical forcing, tropical instability waves (TIW) and Kelvin waves, appear capable of inducing changes in iron limitation and ecosystem structure. During the nonsteady state event associated with the passage of a TIW called the Great Front [Archer *et al.*, 1997], diatom production increased so much as to drive silicate to zero. TIWs lift normally deep (and presumably iron-rich) isopycnals into the euphotic layer for a short period [Flament *et al.*, 1996], allowing large diatoms to flourish temporarily. The very nature of variable nutrient upwelling may exert a strong influence on the observed variability in production. An ensemble of data types from both EqPac time series II and survey II point to the potentially large role of TIWs in changing food web structure in the EUZ. Kelvin waves depress the thermocline [Kessler and McPhaden, 1995], decreasing the subsurface inputs of iron. During survey I the euphotic zone was only beginning to rebound from the passage of a series of Kelvin waves which had depressed the 20°C isotherm from 120 to 200 m [Kessler and McPhaden, 1995]. Consequently, survey I had the lowest levels of new production and particle export observed in this synthesis.

The role of nonsteady state has long been considered an important factor for polar to subtropical regions but has previously been thought to be unimportant for the EUZ. Observation of the Great Front and comparisons between cruises illustrated the potential role of Kelvin waves and TIWs in driving diatom control of production and variability in equatorial biogeochemistry. While the frequency, geographical extent, and total impact of Kelvin waves and TIWs remains uncertain, the concept of nonsteady state is an important area for future efforts in understanding equatorial biogeochemical cycles.

5. Conclusions

In summary, evidence in nutrients and sediment traps suggests that two modes of relative nitrogen and silicon cycling occur in the equatorial Pacific. In the primary mode the role of diatoms in particle export is limited. In a second mode, however, diatoms appear to dominate new production and particle export for episodes of intense nutrient upwelling such as during EqPac survey II. This analysis of the EUZ supports the Dugdale and Wilkerson [1998] conclusion that diatoms can dominate nutrient utilization and export during

conditions of vigorous nutrient upwelling such as EqPac survey II but also suggests that non-diatom production may account for the majority of nitrate disappearance (Table 1 and Figure 2).

We suggest that the conditions that determine diatom control of the biological pump are the combination of size selectivity in iron, grazing [Landry *et al.*, 1997] and dissolution limitation of diatom abundance. Thus, the small varieties of diatoms which are able to grow under the lowest silicate and iron concentrations are only partial contributors to total new production, and their frustules (after grazing) are subject to intense silica dissolution. Nonsteady state conditions such as tropical instability waves bring high-nitrate, high-silicate, and high-iron waters from depth on short time scales. We suspect that these events are the major mechanisms that allow the flourishing of larger diatoms, which utilize nitrate, resist dissolution, and subsequently sink.

Acknowledgments. We thank Barbara Paul for help with sample collection and analysis during EqPac. New production estimates were provided by Claudie Navarette for the FLUPAC cruise. James McCarthy assisted in ¹⁵N determinations for the Zonal Flux cruise. The manuscript benefited highly from discussion with Bob Bidigare, Francisco Chavez, Bruce Frost, Richard Dugdale, and Karl Banse and two anonymous reviewers. Ricardo Letelier provided the model II regression routine. This research was supported by NASA Earth System Science Fellowship 1995-GlobalCh00307 and NSF grant 9504202. School of Oceanography Contribution Number 2213. US JGOFS Contribution Number 514.

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(received June 1, 1998; revised April 29, 1999; accepted May 28, 1999.)