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Effects of the 1997–98 El Nino on seasonal variations in suspended and sinking particles in the Santa Barbara basin

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53 Abstract

5 84 The relationship between water column processes and sedimentation was investigated using a five year time series of bi-weekly water column measurements and continuous sediment trap collections in the Santa Barbara Basin, California. 55 Conditions during the strong El Niño period of 1997-98 were compared to those during the previous years and the 56 post El Niño period. Suspended particulate concentrations of chlorophyll a (chl a), particulate organic carbon (POC), 57 particulate organic nitrogen (PON) and biogenic silica (bSi) normally underwent a seasonal cycle characterized by high 58 phytoplankton abundance in the spring, dominated by diatoms, followed by lower concentrations of biogenic particles 59 throughout the rest of the year. Maxima in sinking fluxes of POC, PON, bSi and lithogenic silica (ISi) generally 60 occurred during the summer. Prior to the El Niño period, molar ratios of C/N, Si/C and Si/N were all higher in sinking 61 particulate material relative to particulate material suspended in the upper 75 m. Si/N and Si/C ratios were highest in 62 the spring and summer in both surface and sinking pools. 63

During the 1997-98 El Niño, the seasonal evolution of the density structure of surface waters was altered by the 64 presence of a water mass high in temperature and low in salinity. The depression of the thermocline resulted in concen-65 trations of nitrate, phosphate and silicic acid in the upper 75 m becoming lower that those measured in other years. 66 Mean chl a and bSi concentrations integrated from the surface to 75 m were low on an annual basis, but there were 67 no clear changes in the seasonality of suspended particle concentrations. Perhaps unexpectedly, fluxes of POC, PON 68 and ISi at 470 m increased during the El Niño period. Lower C/N ratios and shorter turnover times suggest increases 69 in the export ratios of POC and PON at that time. We hypothesize that the increase in ISi flux, despite the absence of 70 elevated concentrations of ISi in the upper 75 m, resulted from the lateral advection of particles into the region from 71 the increased riverine discharges at the margins of the basin and subsequent scavenging of the small particles by organic 72 material. Decreases in ratios of C/N, Si/C and Si/N in sinking particles that occurred during the El Niño were sustained 73 until the end of the time series in June 1999, and may have resulted from a shift toward a less diatom dominated pool 74 of sinking particles. © 2002 Published by Elsevier Science Ltd. 76

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1. Introduction

The El Niño mode of the El Niño–Southern Oscillation (ENSO) phenomenon is associated with changes in global climate and anomalous warming in the eastern equatorial Pacific Ocean. During El Niño conditions, dramatic changes in water column structure occur in the productive eastern boundary upwelling regions of North and South America (e.g., Lynn et al., 1998; Guilderson & Schrag, 1998). Associated changes in chemical conditions of the upper water column cascade to the biology. Biological impacts include: (1) Reductions in oxygen consumption rates of microplankton (Eissler & Quiñones, 1999); (2) Reductions in phytoplankton nitrogen uptake rates (Wilkerson, Dugdale, & Barber, 1987); (3) Low gonad production and low annual somatic production per biomass in bivalves (Urban & Tarazona, 1996); (4) A shift towards smaller classes in crustacean zooplankton (González, Sobarzo, Figueroa, & Nöthig, 2000); and (5) Minimum abundances of both macrozooplankton and seabirds (Lynn et al., 1998).

Changes in phytoplankton processes brought on by El Niño can affect global as well as local biogeochem-90 ical cycles. For example, a phytoplankton bloom of exceptionally large spatial extent developed in the 91 equatorial Pacific after the 1997-98 El Niño event (Chavez et al., 1999). This bloom was associated with 92 low nutrient and CO₂ concentrations for this region, which is normally the largest oceanic source of CO₂ 93 to the atmosphere. Wilkerson, Dugdale and Barber (1987) documented the dramatic effect of the 1976 El 94 Niño conditions had on nitrate and ammonium concentrations and uptake rates by the phytoplankton assem-95 blage in the Peru upwelling system. They indicated that suppression of N uptake may have been a wide-96 spread phenomenon in both the California and Peru upwelling systems. Since nitrate uptake is a measure 97 of new production, which is the maximum amount of material that can be exported from a steady-state 98 system (Dugdale & Goering, 1967), El Niño conditions can clearly have effects on the biological pump, 90 or the ability of biological activity to transport C from the atmosphere to the seafloor. 5 \$00

Diatoms are a common component of the phytoplankton assemblages in coastal upwelling areas 101 (Guillard & Kilham, 1978). Unusual among phytoplankton, diatoms have an obligate requirement for Si, 102 which they use to construct their siliceous cell walls. Thus, potentially the availability of silicon can limit 103 the productivity of the phytoplankton assemblage. In addition, diatom blooms have been observed to floc-104 culate and sink rapidly to the seafloor (Smetacek, 1985; Alldredge & Gotschalk, 1989), potentially trans-105 porting large amounts of organic material as well as opaline silica. Despite these potential links between 106 the cycling of Si, C and N, neither the seasonal trends in the coupling between C, N and Si nor the effect 107 of climatic events on this coupling have been described. 108

The data presented here were collected in the Santa Barbara Basin (SBB), a basin containing sediments 109 of paleoceanographic importance, which clearly record strong El Niño signatures (Lange et al., 1987; 110 Kennedy & Brassell, 1992). Surface conditions in the SBB are influenced by the upwelling off Point 111 Conception at its northwestern margin and the warmer, more saline waters of the Southern California 112 Countercurrent that entering the basin from the south. The center of the basin is ~600 m deep and the sills 113 at its western and eastern boundaries are at 475 and 230 m, respectively. Low-oxygen East Pacific inter-114 mediate water bisects the basin between the two sills and is further depleted of oxygen by the decomposition 115 of sedimenting organic material. Despite occasional flushing of the basin (e.g., Sholkovitz & Gieskes, 116 1971), the sediments are preserved in laminated sequences (review by Schimmelmann & Lange, 1996). 117 These laminae consist mainly of terrigenous detritus and biogenic silica (Grimm, Lange, & Gill, 1996), 118 and form a continuous, high resolution record of recent climatic fluctuations over much of the Holocene 119 (Kennett & Ingram, 1995). 120

The objective of this study is to document the effects of particularly strong El Niño conditions on the cycling of C, N and Si in surface waters and their consequent effects on vertical export in the Santa Barbara Basin (SBB). The 1997–98 El Niño serendipitously developed during an ongoing long-term study, providing a time series, which depicted biogeochemical cycling under 'normal' conditions prior to the evolution of this climatic event. We will first describe the variability inherent in the water column and sedimentation

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processes between 1994 and 1997, prior to the El Niño conditions. Our dataset is unique because surface 126 measurements have been conducted at the same temporal resolution as particle flux measurements (twicemonthly) over several years. Thus, we will address the relationship between surface processes and sedimentation before, during and after the 1997-98 El Niño at a high resolution.

Past and ongoing interest in the characterization of the physical aspects of the water column and circu-130 lation (e.g. Harms & Winant, 1998; Dever & Winant, this issue) and the sedimentary history and processes 131 in the SBB form a well-developed context for the analysis of biological processes in the water column. It 132 has been suggested that variability in signals recorded in the sediments of the SBB may reflect climate 133 changes over larger scales (Behl & Kennett, 1996; Berger & Lange, 1998; Lange, Burke, & Berger, 1990). 134 An implicit assumption of these studies, which we will test, is that climatic conditions affects export 135 processes in this basin. 136

2. Methods 137

2.1. Station locations 138

Physical, chemical and biological properties were measured twice monthly in the vicinity of a station 139 20 km offshore in the Santa Barbara Basin (SBB). Sampling of the upper 75 m of the water column was 140 carried out at 34°17'30" N, 120°00'30"W before June 1995. After June 1995, when a subsurface sediment-141 trap mooring was deployed 10 km to the southeast at 34°15'00"N, 119°54'30"W, the water column sampling 142 was shifted to this new location (Fig. 1). Sediment trap and water column collections were continued until 143 August 1999. The water masses at the two water column stations were biologically similar; the chlorophyll 5 k44 a concentrations (level 2 SeaWiFS data) at the two sites were indistinguishable (Shipe & Brzezinski, 2000). 145 In order to assess cross-channel variability, surface samples were also collected along a 7-station transect 146 at stations located 3, 9, 14, 20, 26, 32 and 43 km offshore (Fig. 1). 147



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Fig. 1. Sampling stations and bathymetry of the Santa Barbara Basin. The seven cross-channel stations are indicated by diamonds, 712 and are sequentially numbered (1-7) from the mainland to the Channel Islands. The sampling site before June 1995 (34°17'30"N, 713 120°00'30"W) is indicated by a circle the sampling site after June 1995 is indicated by a diamond with a cross-hair (station 4 and 714 subsurface mooring site; 34°15'00"N, 119°54'30"W). The small box in the inset map indicates the area portrayed in the larger map. 716

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2.2. Upper water column sampling

Water samples were collected at seven discrete depths (0, 5, 10, 20, 30, 50 and 75 m) for particulate 149 and nutrient analyses. Prior to August 1997, samples were collected using a 10L Niskin bottle and were 150 drained into darkened 20L carboys. These carboys were transported to the laboratory within an hour in 151 insulated containers and were inverted several times to resuspend any material that had settled before 152 draining subsamples. After August 1997 the water samples were collected using a Seabird compact rosette 153 with 5L Niskin bottles and all filtrations were done at sea. Throughout the time series, approximately 30 154 ml of sample water was filtered through 0.2 µm filters before being frozen in small vials for nutrient 155 analyses. Nitrate and phosphate concentrations were determined using a Zelweger Analytics, Inc. flow 156 injection analyzer, model QuikChem 8000, resulting in precisions of $\pm 0.1 \ \mu\text{M}$ and $\pm 0.05 \ \mu\text{M}$ (or 5%) for 157 nitrate and phosphate concentrations, respectively. Determinations of particulate organic carbon (POC) and 158 particulate organic nitrogen (PON) were performed as described by Sharp (1992) using a CHN analyzer 159 (Leeman Labs Inc., CE Model 440) on three replicate 500 ml samples filtered onto combusted GF/F filters 160 (Whatman brand). POC and PON concentrations were not measured at the six lower depths after August 161 1997, and only surface concentrations were measured between August 1997 and October 1998. Two repli-162 cate 200 ml samples were filtered onto GF/F filters and chlorophyll a (chl a) concentrations were determined 163 using a Turner Model 111 fluorometer according to the technique of Parsons, Maita and Lalli (1984). 164 Dissolved silicon, biogenic silica and lithogenic silica concentrations were measured as described by Shipe 165 and Brzezinski (2000). 166

After August 1996, a Sea-Bird Electronics 911plus CTD was deployed with a Sea-Tech 660 nm beam transmissometer on a SBE 32C compact carousel with the intent of sampling to within 5 m of the bottom at each station. We report temperature and beam attenuation during the downcast.

The temporal resolution of sampling was lower during the El Niño period because of the poor weather conditions and equipment failures. It was only possible to profile the water column properties at the mooring site (station 4) on four dates between September 1997 and March 1998. However, surface measurements at the seven cross-channel stations were collected on these four dates, and also on 2 March 1998.

174 2.3. Sediment trap samples

A Mark 7GW-13 PARFLUX rotating time-series sediment trap (McLane Research Laboratories, Inc.) 175 with 12 500 ml collecting bottles was deployed at the mooring site (34°15′00″N, 119°54′30″W) at a depth 176 of 470 m, approximately 50 m above the seafloor, as previously described by Passow et al. (2002) and 177 Shipe and Brzezinski (2000). The collecting bottles were filled with brine solution poisoned with 4% 178 formalin, and a new bottle rotated into the collection position every two weeks. Between January and June 179 1999, the frequency of sampling was increased to every week. The sediment trap was serviced every six 180 months. Upon retrieval the pH of the samples was adjusted to 8.0 and the fixative concentration to 4%, 181 and refrigerated at ~4°C. Each sample was divided into 16ths in a rotary plankton splitter using distilled 182 water for rinses. One 1/16th split was picked for swimmers under a dissecting microscope before being 183 passed through a 1 mm Nitex screen. This material was diluted to 250 ml with distilled water and six 20 184 ml aliquots were removed by pipette while mixing. Each aliquot was filtered onto combusted GF/F filters, 185 and three of them were decalcified with 8N HCL. The filters were dried at 60°C and particulate C and N 186 contents were measured using an automated organic elemental analyzer (Dumas combustion method). A 187 separate 1/16th split was used to determine the biogenic and lithogenic silica concentrations, which were 188 subsequently corrected assuming that the dissolution of lithogenic silica during alkaline digestion led to a 189 factor of 1.6 increase in the biogenic silica concentration as discussed by Shipe and Brzezinski (2000). As 190 a result of this correction, the biogenic silica fluxes reported here should be considered lower estimates. 191

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3. Results

3.1. Physical setting

The surface waters of the SBB consist of a seasonally varying combination of cool waters upwelled 194 offshore of Point Conception and warmer, more saline waters advected in by the Southern California 195 Countercurrent. The contributions of the two water masses vary seasonally in response to local wind stress 196 and basin-scale pressure gradients (Harms & Winant, 1998). Changes in local circulation and water masses 197 occur on the order of days in the SBB. For example, Harms and Winant (1998) show that four distinct 198 states of circulation are traversed approximately every 16 days during the summer and fall. Thus, we 199 suspect there is a great deal of temporal variability in both water column and deep-basin processes that 200 may lead to series of discrete sedimentary events in the upper 75 m of the water column that will not have 201 been discriminated in the sediment trap flux measurements at 470 m.

Time series of temperature, salinity and density from the surface to 75 m at the mooring site during the 203 1997–98 El Niño show there were dramatic changes in the physical structure of the water column (Shipe & 2.04 Brzezinski, 2000). There was an abrupt decrease in density throughout the upper 75 m in early June 1997, 205 and an unusually low density and low salinity water mass remained in the channel until the spring of 1998. 206 The extent of the warming of the upper water column and the depression of the thermocline is exemplified 207 by the depth of the 10° C isotherm, which plunged from <100 m and remained >140 m from August 1997 208 through April 1998 (Fig. 2a). Dever and Winant (this issue) report temperature anomalies at the western 209 and eastern entrances to the SBB of up to $+4^{\circ}$ C in two pulses. The first pulse occurred in the upper 50 210 m in May and June, 1997, and the second, stronger and deeper pulse occurred from the end of September 211 1997 to February 1998. 212

In the SBB, the relatively weak El Niño conditions in the equatorial Pacific in the winter of 1994–95 (McPhaden, Kessler, & Soreide, 2000) were accompanied by a brief period (November 1994–March, 1995) of low density as a result of low salinities and high temperatures (>13°C to 70 m depth) in the upper 75 m of the water column (data presented by Shipe & Brzezinski, 2000). However, these anomalies were neither as large, nor as prolonged, as those observed during 1997–98, which was one of the most intense and prolonged El Niño events that have been observed in the past ~120 years (Wolter & Timlin, 1988).

3.2. Nutrient concentrations

Nutrient levels during the 1997–98 El Niño were unusually low (Fig. 3). Nitrate concentrations from 220 the surface to 75 m depth at the mooring station fell to $<2.0 \,\mu$ M during November 1997. Normally under 221 non El Niño conditions nitrate concentrations at 50-75 m water depths during late fall/early winter range 222 between 10 and 20 µM. Whereas during the El Niño between October 1997 and January 1998 dissolved 223 silicon and phosphate concentrations in the upper 75 m both fell to $<5 \,\mu\text{M}$ and $<0.45 \,\mu\text{M}$, respectively. 224 Inspection of contour plots of nutrient concentrations over time and latitude suggest that events across 225 the channel were observable at the mooring site in nearly every instance (Fig. 4). However, during spring 226 and summer when nutrient concentrations are normally high, the highest surface concentrations were at 227 times localized, either at offshore stations (e.g. April 1997 and May, 1999), or onshore stations (spring 228 1998) or in the center of the basin (May, 1998). In a more rigorous analysis, correlation coefficients were 229 calculated between surface nutrient concentrations at the mooring site (station 4) and those at the other 230 six cross-channel stations (Table 1). Statistically significant correlations existed between nitrate and dis-231 solved silicon concentrations at Station 4 and at all the other stations except at the innermost station (station 232 1). Phosphate concentrations at station 4 were only significantly correlated with the concentrations at the 233 onshore stations 5, 6 and 7. This analysis suggests that nutrient concentrations at the mooring site are fairly 234



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Fig. 2. Time series of (a) the 10°C isotherm depth and concentrations of (b) chlorophyll a (c) biogenic silica (d) particulate organic 723 724 carbon (POC) (e) particulate organic nitrogen (PON) and (f) lithogenic silica at the mooring station in the SBB, integrated from the surface to 75 m water depth. 725

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Fig. 3. Time series contour plots of (a) nitrate concentrations (μ M) (b) dissolved silicon concentrations (μ M) and (c) phosphate concentrations (μ M) from the surface to 75 m water depth at the mooring station in the SBB.

representative of those present across the channel, but that inshore nutrient concentrations are somewhat variable.

237 3.3. Suspended particle concentrations

The seasonal cycles of particulate organic nitrogen (PON), particulate organic carbon (POC), chlorophyll 238 a (chl a) and biogenic silica (bSi) concentrations were each characterized by maxima in late spring each 239 year with smaller pulses occurring throughout the rest of the year (Fig. 2). During the 1997-98 El Niño, 240 chl a concentrations in the upper 75 m underwent their typical annual cycle, but the peak concentrations 241 were the lowest we observed (Fig. 2b). The maximum integrated concentration of chl a during the El Niño 242 was 134 mg m⁻², compared to the maxima of 319-1220 mg m⁻² observed in 1994-1996. At the surface 243 chl a concentrations were fairly similar at the seven cross-channel stations. Most of the maxima observed 244 at the mooring site (20 km offshore) were accompanied by high concentrations across the channel (data 245 not shown). Despite low chl a concentrations observed during the 1997-98 El Niño conditions, neither the 246

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Fig. 4. Time series contour plots of surface (a) nitrate concentrations (μ M) (b) dissolved silicon concentrations (μ M) and (c) phosphate concentrations (μ M) at 7 transect stations across the Santa Barbara Channel.

seasonality of spring maxima nor the maximum concentrations of bSi clearly altered during that time
(Fig. 2c).

Although POC and PON concentrations were not measured at subsurface depths after August 1997, 249 surface concentrations at the mooring site indicated there were consistently low values through out the fall 250 and winter of 1997-98. Maximum surface concentrations of POC and PON during that period were 44 251 and 5.5 μ mol 1⁻¹, respectively, as compared to 76–310 μ mol POC 1⁻¹ and 8.7–14 μ mol PON 1⁻¹ in the 252 previous years. Surface data have to be interpreted with some caution given that there is a poor relationship 253 between surface and integrated concentrations of POC, PON and chl a. Regressions between the concen-254 trations at the surface and those integrated to 75 m produce r² values of 0.36, 0.49 and 0.51 for POC, 255 PON and chl a, respectively. Thus, despite low surface concentrations after August 1997, we cannot rule 256 out the possibility of subsurface maxima. Although no measurements of POC or PON were made during 257

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Table 1

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Correlation coefficients for surface nutrient and particulate silicon concentrations between the mooring site (station 4) and each of the cross-channel stations. Autocorrelations were performed for each time series with two week lags in order to determine decorrelation time scales and the appropriate degrees of freedom for the correlation analysis. The statistical significance of correlation coefficients was determined at α =0.05, using both a conservative test for significance in which the decorrelation time is taken as the number of lags before which the correlation coefficient went to zero (+ denotes significance) and a less conservative test for significance, in which the decorrelation time is taken as the number of lags before which the correlation coefficient dropped to the e-folding time (* denotes significance). Concentrations at station 4 are perfectly correlated with themselves, hence a correlation coefficient of 1.0 for all parameters

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840	Station	Distance offshore (km)	nitrate	silicate	phosphate	biogenic silica	lithogenic silica	
856 864		-	_	-				
872	1	3	0.29	0.34	0.20	0.66*+	0.22	
880	2	9	0.53*	0.56*	0.61	0.66*+	0.31	
888	3	14	0.83*+	0.83*+	0.47	0.79*+	0.56*	
896	4	20	$1.0*^{+}$	$1.0*^{+}$	$1.0*^{+}$	1.0*+	1.0*+	
904	5	26	0.69*	0.67*	0.71*	0.94*+	0.73*	
912	6	32	0.74*	0.75*	$0.82*^{+}$	$0.84*^{+}$	0.56*	
920 928	7	43	0.76*	0.74*	0.80*	0.55*	0.28	

the post El Niño period, an integrated chl concentration of 357 mg m⁻² was observed on 10 April 1998 258 (Fig. 2b). Biogenic silica concentrations of 302 mmol m^{-2} indicate that siliceous organisms were abundant 259 during this bloom (Fig. 2c). 260

The annual cycle of lithogenic silica (ISi) suspended in the upper 75 m was also altered during the El 5 261 Niño (Fig. 2f). The annual winter maxima we measured in 1994–1995 and 1995–1996 were 140 and 310 262 mmol m⁻² respectively. The annual maximum measured in 1997 was not unusual in magnitude (192 mmol 263 m^{-2}), but was delayed until June. In addition, there was no clear maximum at the mooring station in the 264 winter of 1997–1998, during the El Niño. Although sampling was sparse in winter 1997–98, the observed 265 concentrations of 1Si remained consistently <80 mmol m⁻² after the El Niño until the time series ended 266 in August 1999. 267

Surface bSi concentrations at the mooring site were highly correlated with those at all of the cross-268 channel stations. Surface ISi concentrations were only significantly correlated with those at stations 3, 5, 269 6 and 7 (Table 1). This is probably because lithogenic material of terrestrial origin derived from the plumes 270 of riverine discharges was sinking out of surface waters in nearshore waters (see Warrick et al., 2000; 271 Shipe & Brzezinski, 2000). It was not possible to undertake a similar analysis of the surface concentrations 272 of POC and PON because of the limited number of observations. 273

Peaks in beam attenuation at a wavelength of 660 nm occurred at many of the stations on several 274 occasions throughout the year. Representative examples of profiles of beam attenuation show maxima 275 occurred at ~180-260 in January 1997, ~70-100 m in August 1999 and ~90-105 m in September 1997 276 (Fig. 5). These maxima indicate the presence of increased concentrations of particulate material at depth, 277 but since they were not associated with maxima in fluorescence (data not shown), these particles were 278 unlikely to be of biogenic origin, since rapidly sinking aggregates normally contain chlorophyll 279 (Alldredge & Gotschalk, 1990). 280

The C/N ratio of suspended particulate material in the upper 75 m varied between 4.5 and 12.3, with 281 a mean and standard deviation of 7.3±1.4 (Fig. 6, Table 2). A mean C/N ratio of 7.3 is slightly enriched 282 in carbon relative to 6.6, the Redfield ratio for marine plankton (Table 1) (Redfield, Ketchum & Richards, 283 1963). This enrichment of C over expected values for living plankton is partially a result of our method-284 ology, which included carbonate from calcified plankton in POC concentrations. There may also be a 285 detrital component to the suspended organic material. The mean suspended C/N ratio implies that the 286









Fig. 6. Time series of elemental ratios of suspended particulate organic carbon, particulate organic nitrogen and biogenic silica.
Concentrations were integrated from the surface to 75 m water depth and subsequently divided to provide (a) C/N, (b) Si/N and (c)
Si/C ratios. Dashed lines indicate the expected ratios for plankton (Redfield, Ketchum & Richards, 1963) and diatoms (Brzezinski, 1985); C/N=6.6, Si/N=0.95, Si/C=0.12.

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Table 2

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Elemental ratios of carbon, nitrogen and silicon in the Santa Barbara Basin. Expected ratios of C/N are from Redfield, Ketchum and Richards (1963) and ratios including Si are mean values for diatoms in laboratory culture (Brzezinski, 1985). Mean ratios and standard deviations are given for suspended particulates integrated over the upper 75 m and sinking particulates collected in a sediment trap at 470 m. Ratios for sinking particulates are further divided into ratios before, during and after the 1997–98 El Niño. Since bSi fluxes are minimum estimates (see methods), all sinking Si/N and Si/ratios are also minimum estimates. The number of observations is given in parentheses

	C/N	Si/N	Si/C
Expected	6.6	0.95	0.12
Suspended particles	7.3±1.4 (88)	0.43±0.29 (85)	0.06±0.04 (85)
Sinking particles	8.9±1.6 (89)	3.2±2.0 (89)	0.36±0.21 (89)
pre-El Niño	10.3±0.7 (41)	4.3±2.3 (41)	0.43±0.24 (41)
El Niño	10.0±0.9 (9)	1.7±0.7 (9)	0.17±0.08 (9)
La Niña	7.3±0.8 (39)	2.4±1.0 (39)	0.33±0.14 (39)

maximum contribution of carbonate to our POC concentrations would be only 10%, averaged over the time series. There was greater variability in C/N ratios during the winter of 1994–95 and the following spring, but no seasonal trends were apparent. Although the Si/N and Si/C ratios of the suspended material did not show strong seasonal trends, they did approach or even exceeded those of diatoms grown in laboratory culture (Si/N=0.95, Si/C=0.12; Brzezinski, 1985) both during late spring of each year, and in the fall of 1994 (Fig. 5).

Ratios of C/N, Si/N and Si/C in surface particulates (Fig. 7) are included in addition to the integrated ratios because surface measurements were continued throughout the El Niño period, ending in September 1998. Surface ratios and integrated ratios exhibit similar trends, although C/N ratios tended to be >6.6, and a few values were >15 in the spring of 1995. During and after the El Niño, surface ratios of C/N increased slightly but surface Si/N and Si/C ratios were generally low.

298 3.4. Sinking particulate flux

Prior to the 1997-98 El Niño, the sinking fluxes of POC, PON, bSi and lSi at 470 m water depth were 299 highest during spring and summer, whereas the flux of $CaCO_3$ was highest in the summer and fall (Fig. 300 8). The highest sinking fluxes of POC, PON and ISi were observed in the summer of 1997 and early in 301 1998 during the 1997-98 El Niño. Maximum fluxes of POC, PON and lSi occurred simultaneously, between 302 31 January 1998 and 4 February 1998, reaching concentrations of 24, 2.5 and 61 mmol $m^{-2} d^{-1}$, respect-303 ively. Despite the high fluxes of organic and inorganic material during the El Niño period, the sinking 304 fluxes of bSi were consistently low with values <9.0 mmol m⁻² d⁻¹ throughout 1997 and 1998. CaCO₃ 305 fluxes fluctuated around the time series mean of 2.2 mmol $m^{-2} d^{-1}$. There are gaps of 89, 175 and 77 306 days in the observational time series during 1997 and 1998 as a result of clogging of the collecting cone 307 in March 1997, a mechanical failure in August 1997 and again in May 1998, clogging of the trap, this 308 time by an excess of material. 309

The 1997–98 El Niño conditions were accompanied by changes in the ratios of C, N and Si in sinking particles. The mean ratio of C/N of sinking particles during the entire time series was 8.9 ± 1.6 (Table 2). However, there was a significant decrease in the C/N ratios between the pre-El Niño period and the La Niña period (*t*-test: α =0.95, *p*=<0.01). The mean C/N ratio was 10.3 prior to April 1997, 10.0 during the El Niño conditions (April 1997–March, 1998) and 7.3 after March 1998 (Fig. 9, Table 2). The flux of Si relative to C and N was also altered during the 1997–98 El Niño (Table 2, Fig. 9). The seasonal cycles of Si/N and Si/C ratios in the sinking particulate material were similar prior to the El Niño, with highest



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Fig. 7. Time series of elemental ratios of (a) C/N, (b) Si/N and (c) Si/C in suspended particulate material at the surface. Dashed
lines indicate the expected ratios for plankton (Redfield, Ketchum & Richards, 1963) and diatoms (Brzezinski, 1985); C/N=6.6,
Si/N=0.95, Si/C=0.12.

values in the spring/summer and the lowest values in the winters. The mean values of the Si/N and Si/C ratios of the trap material for the entire time series were 3.2 and 0.36, respectively. The expected ratios for live diatoms (Si/N=0.95 and Si/C=0.12) indicate that these samples were enriched in Si over C and N by a factor of ~3. During the El Niño, mean ratios of Si/N and Si/C were 1.7 and 0.17, respectively, consistently lower than the long-term mean and more similar to those of live diatoms. Post El Niño ratios did not recover to the same magnitude as pre-El Niño values.

323 **4. Discussion**

4.1. Typical seasonal cycle of suspended particles

Prior to the 1997–98 El Niño, the Santa Barbara Basin was characterized by a clear seasonal cycle in concentration of suspended particulate material, with the highest concentration of biogenic particles occurring in the spring of each year (Fig. 2). The likely dominance of diatoms was indicated by the association of most of the chl a, POC and PON maxima with high bSi concentrations. The presence of a diatom dominated planktonic assemblage in the Santa Barbara Channel was demonstrated by Venrick (1998).

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Fig. 8. Time series of flux of (a) biogenic silica (b) POC (c.) PON (d) lithogenic silica and (e) C in $CaCO_3$ into a sediment trap at 470 m located at station 4 in the Santa Barbara Basin. Points are plotted on the date that the trap began collecting.

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Fig. 9. Time series of elemental ratios of (a) C/N, (b) Si/N and (c) Si/C in particulate material sinking into a trap at 470 m in the
Santa Barbara Basin. Dashed lines indicate the expected ratios for plankton (Redfield, Ketchum & Richards, 1963) and diatoms
(Brzezinski, 1985); C/N=6.6, Si/N=0.95, Si/C=0.12.

Microscope counts of phytoplankton sampled during the seasonal chlorophyll maximum in 1995 and 1996 revealed that the assemblages were either dominated by *Chaetoceros sp.* or consisted of mixed diatom assemblage (Passow, Shipe, Pak, Brzezinski, & Alldredge, 2000).

The summation of all of the biological processes (including nutrient uptake and the recycling and grazing 333 of particulate material) affecting the C/N ratios of suspended particles resulted in the rations being consistent 334 throughout the time series. The ratios of Si/N and Si/C in the suspended particulate material peaked in the 335 springs of 1994, 1995 and 1996 (Fig. 6), and there were concomitant high concentrations of biogenic silica 336 (Fig. 2) many of which were diatom-derived (Passow, Shipe, Pak, Brzezinski & Alldredge, 2000). Based 337 on past studies of the siliceous phytoplankton flora of the SBB (Lange, Weinheimer, Reid, & Thunell, 338 1997; Venrick, 1998), we have assumed that the bulk of the biogenic silica is in the form of diatom 339 frustules. High Si/N and Si/C ratios suggest that diatoms dominated the suspended particulate material. 340 However, observations of Si/N and Si/C ratios exceeding 0.95 and 0.12, respectively, indicated that there 341 was probably a detrital component to the bSi on two occasions in the fall of 1994 (31 August and 28 342 September). Mean ratios of Si/N and Si/C for the entire time series were 0.43 and 0.06, respectively (Table 343 2). Thus, healthy diatoms could have contributed a maximum of approximately half of the POC and PON, 344 by atoms. 345

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Prior to the 1997–98 El Niño, maximum concentrations of suspended lithogenic silica (ISi) occurred in the late winter (Fig. 2f). This timing is consistent with the observations of Gorsline et al. (1984) who established that the coastal watersheds of the California Borderland deposit terrigenous material during winter runoff events. More specifically, the winter ISi maxima are consistent with the timing of the runoff from the Santa Clara River, which provides the majority of recent sediments accumulating in the SBB (Fleischer, 1972).

4.2. Typical seasonal cycle of sinking particle fluxes

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The sinking flux of particulate material in the SBB is highly seasonal, with the highest fluxes of all 353 measured components occurring in the spring and summer and the lowest fluxes occurring in the winter 354 (Fig. 8). We did not detect any distinct surface events being transmitted to depth, probably because the 354 time scales of such events in the surface waters are less than a week, so would not be picked up by the 356 trap sampling, which was twice monthly. However, seasonality in sinking fluxes is related to the seasonal 357 appearance of particles in the euphotic zone. Prior to the El Niño of 1997-98, there were no seasonal 358 variations in sinking C/N ratios. The mean sinking C/N ratio, 10.3, was higher relative to the mean sus-359 pended C/N (7.3). There is a higher rate of remineralization of N relative to C, assuming that either the 360 biogenic particles observed in surface waters are the same as those that sink within the basin, or that were 361 additions of small amounts of terrestrially derived material, which would have a higher C/N ratio, or some 362 combination of the two processes. 363

The seasonal cycles of Si/N and Si/C ratios in the sinking particulate material were similar. The highest values occurred in the spring and summer of 1996 and the lowest values in the winters of 1995–96 and 1996–97. On average, the sinking ratios were seven and six times higher than mean suspended ratios of Si/N and Si/C, respectively indicating the preferential recycling of organic matter over silica below 75 m. However, in April and June 1996 the highest Si/N and Si/C ratios were >40 and >30 times greater than suspended Si/N and Si/C ratios, respectively.

The sinking flux of both organic and inorganic material in the SBB appears to have been driven at least in part by the presence of transparent exopolymer particles (TEP) (Passow, Shipe, Pak, Brzezinski & Alldredge, 2000). They conclude that TEP appears to be required for the export of bSi through the formation of marine snow. Although the relationship between the fluxes of POC and TEP is not as strong as that between bSi and TEP, TEP will also drive the flux of POC at times. The sinking flux of lSi may result from the scavenging of these small particles from the water column onto marine snow although the source of the lSi varies between direct riverine inputs in the spring and resuspended material in the summer.

Thunell (1998) reported sinking fluxes during a three year period between August 1993 and August 377 1996 into a trap identical to ours, which was also located in the SBB (34°14.033'N, 120°02.856'W). Direct 378 comparisons of the fluxes measured by our trap at 470 m depth and Thunell's trap at 540 m during June 379 1995–August 1996 indicate that our trap tended to collect higher quantities of opal, POC, and CaCO₃, 380 especially during periods of high sedimentation in the spring and summer of 1996. The seasonal periodicity 381 of the fluxes of organic carbon and biogenic silica we observed agrees with Thunell's (1998) who also 382 reported minima in sinking fluxes during the autumn and winter, but maxima in fluxes of lithogenic material 383 in late fall/early winter and spring. 384

³⁸⁵ Differences in magnitude of flux and the presence of brief flux events in only one of the two sediment ³⁸⁶ traps may reflect genuine within-basin variability. Although both traps were deployed within the 500 m ³⁸⁷ isobath and both were 50 m above the seafloor, they were approximately 13 km apart horizontally. Kolpack ³⁸⁸ and Drake (1985) observed a seasonal redistribution of sediments within the basin resulting from winter ³⁸⁹ events transporting sediments to deeper waters. This is supported by the observation of turbid plumes ³⁹⁰ below sill depths in the SBB (Gorsline et al., 1984). The presence of particulate lithogenic plumes within ³⁹¹ the SBB is supported by the maxima in beam attenuation observed at depths below 75 m during the winter,

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summer and fall which were not associated with fluorescence maxima (Fig. 5). Sediments also accumulate 392 at shallow depths before being redistributed within the basin during large flux events (Drake, Kolpack, & 393 Fischer, 1972). The redistribution of material within the basin may account for the maxima of mass flux and lithogenic material observed by Thunell (1998) in his deeper trap in the late fall-early winter. It might be expected that the two traps would have shown differences in sedimentation rates during the high flux conditions of the 1997-98 El Niño as well. 397

Hebbeln, Marchant and Wefer (2000) reported a somewhat different pattern of seasonality in sinking 398 flux in the Peru-Chile current. They found that the highest export rates offshore of Chile are confined to 399 the month of September. However the peaks in fluxes of biogenic and lithogenic material were synchronous, 400 as in the SBB. They suggested that biogenic particles remain in the deep chlorophyll maximum for up to 401 two months before they sink out. In a six-month study in the San Pedro Basin off southern California 402 Thunell (1998) revealed that pulses of particulate organic carbon, bSi and lithogenic material occurred 403 synchronously in the late winter. Although these pulses coincided with high stream discharge in the winter, 404 it remains possible that the flux of lithogenic material may be dependent on the presence of high sinking fluxes of organic material, as in the SBB. It is possible that a similar mechanism is responsible for particle 406 export in all three of these coastal regions, export being triggered by some event, which takes place when 407 both biogenic and lithogenic particles are present in high concentrations in the water column. 408

One difference between our observations and those of both Thunell, Pilskaln, Tappa and Sautter (1994) 409 and Hebbeln et al. (2000) is that there is a decrease in the C/N ratios of the sinking particulate material 410 in both the San Pedro Basin and the Peru-Chile current between January and July. These decreases are 411 interpreted as resulting from changes in the proportions of terrigenous and marine organic material. The 412 lack of a similar seasonal change in C/N ratios of sinking particulate material in the SBB may be because 413 there the terrigenous inputs remain relatively small during normal years compared to those in the other 5 #14 coastal regions. 415

4.3. Relationship between surface and sinking particle pools 416

Turnover times for POC, PON, total particulate carbon (POC+calcium carbonate=TPC), bSi and lSi were 417 calculated for summer/fall and winter/spring periods of each year by dividing the mean concentration 418 integrated to 75 m by the mean sinking flux of each particle constituent (Table 3). POC turnover times 419 were estimated by assuming that 10% of the TPC is carbonate. Although sinking fluxes were measured 420 continuously, turnover times may be misleading if events were missed during the twice-monthly sampling 421 of the upper 75 m. Prior to the 1997-98 El Niño, turnover times of all four particulate pools tended to be 422 faster in summer/fall than in winter/spring. Thus, a larger proportion of the particles in the upper 75 m is 423 exported during the summer/fall. 424

Turnover times for pools of POC, TPC, PON and bSi followed the order: PON > POC > TPC > bSi425 (Table 3). Within carbon pools, POC is turned over more slowly than the TPC pool suggesting the export 426 of carbonate is faster. In addition, a greater proportion of the bSi pool suspended in the upper 75 m is 427 exported to 470 m depth compared to POC, TPC and PON. Slow remineralization rates of bSi relative to 428 POC and PON and the greatest remineralization of PON is consistent with the differences in mean elemental 429 ratios between suspended and sinking material (Table 2) and is likely a function of deeper remineralization 430 of bSi relative to organic material (Dugdale, 1972). DeMaster, Nelson, Haden and Nittrouer (1991) also 431 documented the enhanced preservation of bSi relative to POC during sinking in the Ross Sea. However, 432 the C/N ratios in the Ross sea sediments indicated that was very little difference in remineralization rates 433 between organic C and N in that water column, which contrasts to the 40% enrichment in C relative to 434 N in the SBB during normal conditions prior to the 1997–98 El Niño. 435

It is widely believed that net phytoplankton (>20 μ m) constitutes the largest fraction of sinking material 436 (Michaels & Silver, 1988), which is consistent with high rates of sedimentation associated with spring 437

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Table 3

Turnover times of pools of biogenic silica (bSi), lithogenic silica (lSi), particulate organic nitrogen (PON), particulate organic carbon (POC) and total particulate carbon (TPC) during summer/fall and winter/spring periods and the 1997–98 El Niño. Turnover times are based on the mean concentration integrated over the upper 75 m and the mean flux into a sediment trap at 470 m in the Santa Barbara Basin. POC turnover times were estimated by assuming that integrated POC concentrations suspended in the upper 75 m were 90% of integrated TPC concentrations

	Dates		Turnov	ver time (days)		
Period	Profile	Flux	bSi	lSi	PON	POC	TPC
Summer/fall 1995	27 Jun 95–18 Oct 95	28 Jun 95–1 Nov 95	8.3	4.5	93	65	27
Winter/spring 1995– 1996	1 Nov 95–19 Mar 95	1 Nov 95–1 Apr 96	18	13	140	98	44
Summer/fall 1996	4 Apr 96-8 Oct 96	1 Apr 96—8 Nov 96	7.4	1.3	98	65	26
Winter/spring 1996– 1997	6 Nov 96–26 Mar 97	8 Nov 96–14 Mar 97	12	1.6	130	74	27
El Niño 1997–1998	9 Apr 97–22 Jan 98	13 Jun–8 Aug 97; 31 Jan–11 Apr 98	12	1.4	79	53	19
Summer/fall 1998	10 Apr 98-5 Oct 98	11 Apr 98–3 Nov 98	11	2.0		-	_
Winter/spring 1998– 1999	17 Nov 98–17 Mar 99	3 Nov 98–4 Apr 99	21	1.7	-1	5	-
Summer 1999	6 Apr 99–14 Jun 99	4 Apr 99–20 Jun 99	15	2.2		/ <u>-</u>	_

blooms (e.g. Smetacek, Broekel, Zeitzchel, & Zenk, 1978). An abundance of diatoms would result in large 438 fluxes of carbon and nitrogen, especially in a shallow coastal basin such as the SBB where sinking material **4**39 can quickly reach the sediments. In fact, diatom blooms have been observed to aggregate and sink quickly 440 within the SBB (Alldredge & Gotschalk, 1989). A comparison of bSi/chl a in the upper 75 m and the 441 sinking fluxes of bSi, POC and PON at time lags of 0, 2 and 4 weeks showed no clear relationships 442 $(r^2 < 0.03 \text{ for all analyses})$. Thus, surface conditions during twice-monthly suspended particle profiles and 443 continuous sediment trap measurements were sufficiently decoupled for the signals from the diatom blooms, 444 which we sampled, not to produce discrete increases in particle flux, at these scales. 445

446 4.4. El Niño effects on surface processes

The presence of warm, nutrient-poor waters during the 1997–98 El Niño resulted in exceptionally low mean concentrations of chl a and bSi (Table 4). For the purpose of interannual comparisons, we have defined the El Niño year as the period between 1 April 1997 and 31 March 1998, based on the high SST anomalies observed in the equatorial Pacific in April 1997 (McPhaden, 1999). During 1997–1998, chl a

Mean annual particulate concentrations integrated to 75 m at station 4 (April 1 to March 30). The average concentrations from subsequent sampling dates were used, and each day is equally weighted

1200				
1205	Year	chl a	biogenic silica	lithogenic silica
1213		$(mg m^{-2})$	$(\text{mmol } \text{m}^{-2})$	(mmol m^{-2})
1228		-		
1233	1994–1995	120	67	47
1238	1995–1996	140	70	85
1243	1996–1997	68	47	35
1248	1997–1998	29	27	46
1253	1998–1999	75	58	37
1258				

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and bSi concentrations integrated over the upper 75 m were 29 mg m⁻² and 27 mmol m⁻², respectively. During non-El Niño years, chl a and bSi concentrations were 68–146 mg m⁻² and 47–70 mmol m⁻², respectively.

The low phytoplankton biomass observed in the SBB during the 1997-98 El Niño is consistent with the reductions in chlorophyll concentrations and primary productivity in the California Current observed 455 during the 1992 El Niño (Chavez, Buck, Service, Newton & Barber, 1996). However, the effects of the 456 1997-98 El Niño on phytoplankton biomass within surface waters along the California coast have not been 457 completely consistent. Lynn et al. (1998) reported that the vertically integrated chlorophyll concentrations 458 in the California Current were similar to those of the previous 13 years. However, they did indicate that 459 the El Niño conditions had effects on higher trophic levels; the lowest macrozooplankton abundance in 460 their 50-year time series was measured during 1997–98. Wilkerson et al. (this issue) reports that despite 461 lower nutrient concentrations, chlorophyll concentrations in the San Francisco Bay were higher during the 462 1997-98 El Niño than during the following 1999 La Niña. 463

This paper has been the first to address the effect of El Niño conditions on suspended elemental ratios. Our data show there were little changes in suspended elemental ratios during the 1997–98 El Niño, although Si/N and Si/C ratios were slightly depressed between May and July, 1996. The mean Si/N and Si/C ratios of 0.22 and 0.30, respectively, observed during this period reflect a small contribution of diatoms to phytoplankton biomass. Thus, if the assemblage was in balanced growth based on stoichiometric relationships between Si, N and C, less than 25% of the suspended concentrations of POC and PON could be attributed to diatoms.

The mean concentration of lithogenic silica integrated over the upper 75 m increased during the El Niño 471 year (1997-98) relative to mean concentrations in the years both before and after the El Niño, but it was 472 not as high as the mean concentration during 1995–96 (Table 3). We suspect that seasonal changes in the 473 suspended pool of lithogenic material in the basin may not be well represented by profiles at the mooring 474 site (station 4) because of the within-basin variability (Table 1; Shipe & Brzezinski, 2000). The delay in 475 the appearance of the lSi maximum at the mooring site in the spring of 1997 (Fig. 2) may have been 476 caused by this heterogeneous cross-shelf distribution of lithogenic material. Based on cross-channel surveys, 477 the increases in surface ISi concentrations between December 1997 and January 1998 were confined to 478 the basin margins (stations 1,7) (Shipe & Brzezinski, 2000). The absence of a pulse of lithogenic material 479 in the winter of the El Niño was enigmatic, considering the high discharges from the Santa Clara River 480 that began in November 1997 (USGS, 2000). Cross-channel ISi concentrations resolve this inconsistency 481 as well; some of the highest lSi concentrations (up to 4.4 μ mol l⁻¹) were observed between November 482 1997 and March 1998 at the onshore stations 1 and 2. We believe that the particles were present in the 483 basin, but had been subducted below 75 m by the time they reached the mooring site at the center of the 484 basin. This scenario is supported by the results of satellite remote sensing and shipboard measurements 485 by Warrick, Mertes, Neumann, Siegel and Washburn (2000) who suggested that <1% of the particles 486 discharged into the SBB were present in the buoyant surface plume during a large event in February 1998. 487

488 4.5. El Niño effects on sinking particle fluxes

The central region of the Santa Barbara Basin contains laminated sediments that have accumulated over 489 the past ~20kyr (Kennett & Ingram, 1995). Previous studies of sediment cores from the SBB indicate that 490 El Niño events are associated with changes in microfossil abundances and organic biomarker concentrations 491 (Kennedy & Brassell, 1992). During El Niño incidents, sediment records of microfossils indicate that there 492 are shifts toward plankton assemblages associated with warm waters (Lange et al., 1987) and decreases in 493 fluxes of diatoms were associated with the El Niño events of the 1960s–1980s (Lange, Burke & Berger, 494 1990). Particle fluxes during this time series study provide further evidence that climatic events such as 495 the El Niño phase of ENSO may be recorded in the sedimentary record. The varved layers found in the 496

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SBB are commonly considered to be deposited with a seasonality whereby dark lithogenic material accumulates in the winter and deposition of paler biogenic material occurs in the spring. The observed changes in the seasonality of sinking fluxes imply that sediments were not be accumulating according to this model during the 1997–98 El Niño, as discussed in greater detail by Shipe and Brzezinski (2000).

The increases in sinking fluxes of POC and PON, and the possibility of higher C sequestration during the 1997–98 El Niño are not intuitive. Low suspended concentrations of bSi and chl a observed during the El Niño would not seemingly result in high flux. We believe that the increased sinking flux of POC, PON and ISi during the 1997–98 El Niño (summer 1997, later winter 1998) may be explained by changes in the proportion of particulate material being exported to 470 m depth.

Turnover times of POC and PON averaged over the El Niño period (Table 3) are 53 and 79 days, 506 respectively. The mean sinking velocity of marine snow in coastal California waters measured in situ 507 (Alldredge & Gotschalk, 1989) and in settling chambers (Shanks & Trent, 1980) is approximately 70 m 508 d^{-1} . Thus, the sinking flux of POC and PON at 470 m could easily have been supported by the particulate 50 material present in the overlying waters. An increase in the export ratio of this material could easily account 510 for the increased sinking concentrations at depth. POC and PON turnover times during the El Niño period 511 were the fastest during the time series, implying that the largest percentage of the suspended POC and 512 PON pools was exported at this time. However, Thunell (1998) reported a decrease in flux of organic 513 carbon concentrations during the 1994 El Niño. The effects of El Niño conditions on the export of organic 514 material within the SBB may either be variable or this may be yet another example of within-basin varia-515 bility, as discussed above. 516

C/N ratios of sinking particulate material were lower and more similar to those of suspended material
in the latter half of the El Niño, between January and April 1998. This shift of C/N ratios was even more
exaggerated during the post-El Nino period, resulting in the same mean ratio as in suspended material. Thus,
sedimentation rates may have been faster at this time, causing a decreased opportunity for the recycling of
the PON. This does not, however, explain the high fluxes of organic material in the summer of 1997.

A terrestrial source of sinking organic material during the winter of the El Niño period in the SBB is 522 supported by observations of an increase in detritus, clay minerals, pollen grains, plant debris, and benthic 523 plankton in the sediment trap material during December 1997 to February 1998 (Lange, Weinheimer, Reid, 524 Tappa, & Thunell, 2000). We cannot exclude the possibility that additional terrestrial sources of C and N 525 caused the high sinking fluxes of PON and POC in the late winter. However, C/N ratios did not increase 526 in our trap material at that time. In general, C/N ratios of terrestrial particulate organic material are higher 527 than those of marine organic material. Unfortunately, it was impossible to use stable isotopic analysis, 528 which could have indicated a terrigenous source of organic material, because of the use of formalin as a 529 trap poison. 530

The 1997-98 El Niño seems to be associated with a change in community composition of sinking 531 particulate material in the SBB. The decrease in the bSi flux throughout the El Niño period may have been 532 in part because of low suspended bSi concentrations on an annual basis suggesting a decline in the biomass 533 of diatoms. Another indication of the change in community composition of the sinking particles was the 534 dramatic decrease observed in Si/N and Si/C ratios. Ratios of Si/N and Si/C are more similar to those of 535 live diatoms (Table 2), however, low annual silica production rates in the spring/summer of 1997 lead us 536 to believe that the bulk of the organic C and N sinking at this time had been derived from a marine source 537 other than diatoms. Mean Si production rates between April and August in the upper 75 m during 1996 538 and 1997 were 20 and 12 mmol m⁻² d⁻¹, respectively (Shipe & Brzezinski, 2000). A change in the sinking 539 assemblage to one less dominated by diatoms would have resulted in the low bSi fluxes to 470 m as well 54(as lower apparent preservation of Si relative to C and N. A decrease in the contribution of diatoms to flux 541 in the SBB has been documented during previous El Niño periods of 1972 and 1994 (Lange, Burke & 542 Berger, 1990; Thunell, 1998). Chavez (1996) also observed a shift from a diatom-dominated phytoplankton 543 community in the spring of 1990 to a picoplankton-sized community during the El Niño of 1992 in the 544

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Monterey Bay. The ecological consequences of a shift away from a diatom-dominated plankton community must depend on the trophic position of the organisms that newly dominate the replacement assemblage. A shift from a net phytoplankton community (such as diatoms) to one dominated by picoplankton might be expected to lead to a decrease in sinking fluxes (Michaels & Silver, 1988). However, a bloom of generalist grazers might cause increases in sinking fluxes. Passow, Shipe, Pak, Brzezinski and Alldredge (2000) reported a dramatic increase in larvacean abundances in the water column at the mooring site in February–March 1997. Similar events during the 1997–98 El Nino could have caused the increases in organic and inorganic sinking fluxes associated with this event.

The turnover time for lithogenic silica in surface waters during the El Niño period was 1.4 days (Table 553 3). Since this turnover time was calculated using concentrations integrated over the upper 75 m, it implies 554 a sinking rate of approximately 50 m d^{-1} . Lithogenic material in the SBB is fine-grained (Fleischer, 1972) 555 and is unlikely to sink at this rate as individual particles. Thus, the lithogenic material may either have 556 been scavenged by other particulates (Passow et al., 2000) or been advected laterally into the region at 557 depths below 75 m. A combination of these two mechanisms seems likely since ISi tends to be exported 558 at the same time as organic material and elevated ISi concentrations at the basin margins can serve as a 559 source of sinking ISi. We believe that during the 1997-98 El Niño, elevated ISi concentrations derived 560 from the basin's margins became associated with particulate organic material and sank, causing the observed 561 increases in POC, PON and ISi flux. Lithogenic silica turnover times of approximately two days were not 562 unusual during the time series (Table 3), suggesting that there is a consistent lateral input of lithogenic 563 material and/or scavenging by other sinking particles, regardless of the presence or absence of ENSO 564 conditions. These low turnover times are consistent with observations of increases in beam attenuation at 565 depths greater than 75 m throughout the year (Fig. 5). 566

567 4.6. Post El Niño conditions

By 10 April 1998, there was a dramatic increase in both density and salinity in the upper 75 m of the 568 water column and the concentrations of nitrate, dissolved silicon and phosphate recovered to the levels 569 observed during the previous spring. A maximum in chl a and bSi concentrations both at the mooring site 570 and at the seven cross-channel stations on April 1998 and a smaller bloom on 29 May 1998 marked the 571 return of the seasonal cycle of biogenic particulates to pre-El Niño conditions (Fig. 2). Mean annual concen-572 trations of chl a and bSi integrated to 75 m in 1998–99 increased by a factor of ~2 relative to 1997–98 573 (Table 4). There were no remarkable changes in the ratios of Si/N and Si/C in surface waters at this time. 574 However, C/N ratios in surface waters were elevated in the fall of 1998, presumably because of an increase 575 in the detrital content of the material, which was high in POC and low in PON and chl a (surface data 576 not shown). 577

During the post-El Niño period, the export flux remained less diatom-dominated than during normal 578 conditions prior to the spring of 1997. The export flux of bSi was consistently low (Fig. 8a) and Si/N and 579 Si/C ratios did not recover to their former high values (Fig. 9, Table 2). C/N ratios in sinking material 580 were consistently low until the time series ended in June 1999. The sinking ratio of C/N was 7.3, which 581 was significantly lower than ratios prior to the El Niño (two-tailed *t*-test; $\alpha = 0.05$, p < 0.01), was identical 582 to the mean ratio of particulates suspended in the upper 75 m. These shifts in the relationship between 583 surface processes and export may be further expression of a regime shift along the eastern margin of the 584 North Pacific Ocean, as postulated by Schwing and Moore (2000). Their 54-year upwelling index showed 585 the strongest upwelling conditions in 1999 and they report observations of ecological shifts at all trophic 586 levels. This is consistent with the influence of strong upwelling in the SBB in the spring of 1999, when 587 the highest nutrient concentrations and lowest temperatures ($<11.5^{\circ}$ C) were recorded in the upper 75 m 588 of the water column. 589

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