

## A time series investigation of the oxygen isotopic composition of dissolved inorganic phosphate in Monterey Bay, California

Karen McLaughlin<sup>1</sup>

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115

Francisco Chavez and J. Timothy Pennington

MBARI, 7700 Sandholdt Rd., Moss Landing, California 95039-9644

Adina Paytan

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115

### Abstract

We present a 2-yr time series of the oxygen isotopic composition of dissolved inorganic phosphate ( $\delta^{18}\text{O}_p$ ) in Monterey Bay, California.  $\delta^{18}\text{O}_p$  can serve as a proxy for phosphate utilization because its approach toward isotopic equilibrium is a function of the degree of biological phosphate cycling. When phosphate is extensively cycled by the biological community in the euphotic zone, the  $\delta^{18}\text{O}_p$  approaches isotopic equilibrium with surrounding water. Our results indicate that  $\delta^{18}\text{O}_p$  in the upper water column is consistently out of isotopic equilibrium with respect to seawater and fluctuates between the equilibrium value and the isotopic signatures of phosphate sources. This suggests that either phosphate is not extensively utilized or that the input of new phosphate to the bay exceeds the requirements of the biological community.  $\delta^{18}\text{O}_p$  is variable and linked to episodic upwelling events and the biotic response to these events. The greatest percent of phosphate oxygen exchange, and thus the greatest phosphate utilization relative to input, occurs at the locus of upwelling (Sta. M1), followed by the offshore (M2) and nearshore (C1) stations, respectively. During the highly productive upwelling season, phosphate turnover is greater than in the winter. Episodes of higher phosphate turnover, as indicated by peaks in  $\delta^{18}\text{O}_p$ , occur simultaneously throughout the upper 200 m of the water column and at all three stations, indicating that these events affect the bay on a large scale.  $\delta^{18}\text{O}_p$  data also suggest that deep water (>500 m) may be a source of phosphate to the euphotic zone in Monterey Bay.

Eastern-boundary upwelling systems, like that of the California coast, represent a small percentage of the world ocean surface area but possess the highest levels of primary production (Chavez and Toggweiler 1995; Toggweiler and Carson 1995). Primary production rates in these systems are typically 3–5 times greater per unit area than in open ocean systems (Berger et al. 1989) and are fueled by upwelling events that supply nutrients to the euphotic zone

(Pennington and Chavez 2000). Because phosphorus (P) is a required element for life, its availability can impact primary production rates as well as species distribution and ecosystem structure (Smith 1984; Sharp 1991; Benitez-Nelson 2000). Accordingly, studies of P turnover in coastal upwelling regions are necessary to increase understanding of the biogeochemical cycling of this important nutrient as well as the coupling of the P cycle with biological productivity.

<sup>1</sup> Corresponding author (karenm@uci.edu). Present address: Department of Chemical Engineering and Materials Science, University of California–Irvine, California 92697-2575.

### Acknowledgments

We thank Carol Kendall, Steven Silva, and Mark Rollog from the U.S. Geological Survey in Menlo Park, California, for running the silver phosphate samples for phosphate oxygen isotopes and Scott Wankel for his intellectual input. Reiko Michisaki from the Monterey Bay Aquarium Research Institute compiled the Monterey Bay Time Series Cruise data for us, and Peter Walz provided the soluble reactive phosphorus concentration data. We also thank the crew of the *R/V Point Lobos*. Special thanks to Jim O'Neil for inspiration. This manuscript was greatly improved from comments from Albert Coleman and an anonymous reviewer.

This work was supported by a NSF-OCE grant 0354319-002 to A.P., the David and Lucille Packard Foundation for funding the Monterey Bay Time Series Project, on which this work was piggy-backed, and a Schlanger graduate fellowship and a Stanford-USGS fellowship to K.M.

Previous workers have used cosmogenic isotopes ( $^{33}\text{P}$  and  $^{32}\text{P}$ ) to study P turnover in the coastal ocean (Lal and Lee 1988; Benitez-Nelson and Buesseler 1999). Their results indicate that P recycling rates are rapid (less than a day to two weeks) and seasonally variable, which suggests that low P concentrations can support relatively high primary production. There is also evidence that P can be preferentially remineralized from both particulate and dissolved organic matter in the water column (Clark et al. 1998; Loh and Bauer 2000; Paytan et al. 2003). More specifically, certain organic P compounds are preferentially remineralized in sinking particulate matter and the hydrolysis of organic P occurs throughout the water column, although more prevalently in shallow depths (Paytan et al. 2003; Faul et al. 2005).

Because P has only one stable isotope, P stable isotope ratios cannot be used for studies of nutrient sources, cycling, and utilization. However, most of the P found in nature is strongly bound to oxygen (O), which has three

stable isotopes; hence, phosphate ( $\text{PO}_4^{3-}$ ) can be analyzed for  $\delta^{18}\text{O}$ . The P–O bond in phosphate is resistant to inorganic hydrolysis and, at the temperature and pH of most ecosystems, phosphate does not exchange oxygen with water without biological mediation (Longinelli et al. 1976; Blake et al. 1997; O'Neil et al. 2003). Thus, any observed variability in the oxygen isotopic composition of phosphate will either reflect mixing of isotopically distinct sources of phosphate or the alteration of the phosphate  $\delta^{18}\text{O}$  as the result of the exchange of oxygen during the cycling of phosphate through living cells (i.e., biological uptake, utilization, and subsequent release). In the latter case, each time a phosphate molecule is cycled (processed by enzymes), phosphate oxygen will be replaced from water, ultimately resulting in isotopic equilibrium with the surrounding water at the temperature of reaction.

The equilibrium  $\delta^{18}\text{O}_p$  resulting from the biological cycling of phosphate can be calculated from the temperature and the oxygen isotopic composition of the environmental water using the empirically derived fractionation equation between phosphate and water developed by Longinelli and Nuti (1973):

$$T(^{\circ}\text{C}) = 111.4 - 4.3(\delta^{18}\text{O}_p - \delta^{18}\text{O}_w) \quad (1)$$

where  $T$  is the environmental temperature,  $\delta^{18}\text{O}_p$  is the isotopic composition of the phosphate, and  $\delta^{18}\text{O}_w$  is the isotopic composition of the environmental water. A similar equation was derived by Blake et al. [1997] for phosphate extracted from microbial cultures.

$$T(^{\circ}\text{C}) = 155.8 - 6.4(\delta^{18}\text{O}_p - \delta^{18}\text{O}_w) \quad (2)$$

The deviation from the isotopic composition of the source value (riverine phosphate or deep-water phosphate in the case of Monterey Bay) toward the expected equilibrium value (calculated from Eq. 1 or 2) can be used to determine the extent of phosphate cycling in the system. Greater cycling compared to new phosphate input will result in a  $\delta^{18}\text{O}_p$  closer to the equilibrium value, whereas less cycling will result in a value closer to the source  $\delta^{18}\text{O}_p$ .

Results of several laboratory studies characterizing the exchange and fractionation of phosphate oxygen isotopes suggest that the  $\delta^{18}\text{O}_p$  of dissolved inorganic phosphate (DIP) could be used to evaluate the degree of cycling of the DIP pool (Blake et al. 1997; Blake et al. 1998; Paytan et al. 2002; Blake et al. 2005). Enzyme-mediated turnover of phosphate and the microbially mediated degradation of organic matter demonstrated that a significant exchange of oxygen isotopes between phosphate and water accompanies the hydrolytic cleavage and metabolism of both organically bound phosphate and inorganic orthophosphate (Blake et al. 1997). Bacterial metabolic processes have also been found to significantly alter the  $\delta^{18}\text{O}_p$  of DIP in laboratory culture experiments, even when phosphate concentrations were high (Blake et al. 1998). Furthermore, results of an algae culture experiment indicate that intracellular oxygen

isotope exchange between phosphorus compounds and water is very rapid (Paytan et al. 2002).

Phosphate oxygen isotope fractionation has been observed, in both microbial culture experiments and in cell-free systems, where specific enzymes were used (Blake et al. 2005). Intracellular phosphate cycling by inorganic pyrophosphatase results in the temperature-dependent, equilibrium oxygen isotope fractionation (Eq. 1), which imparts the equilibrium  $\delta^{18}\text{O}_p$  on phosphate cycled within cells. In contrast, extracellular phosphate regeneration by alkaline phosphatase (e.g., conversion of organic phosphate-monoester to inorganic phosphate) is accompanied by disequilibrium isotope effects (both kinetic effects and inheritance of phosphate oxygen from hydrolyzed phosphomonoesters) in the inorganic phosphate released into the system (Blake et al. 2005). However, the equilibrium isotope effects associated with intracellular phosphate cycling are expected to dominate in natural systems, particularly those that are not phosphate limited (Blake et al. 2005).

There are relatively few studies assessing the  $\delta^{18}\text{O}_p$  in aquatic ecosystems. Pioneering work by Longinelli et al. (1976) found no variation in the  $\delta^{18}\text{O}_p$  of DIP in seawater or of marine organism soft tissue with either depth or latitude in the Atlantic and Pacific Oceans, although there was a significant difference between the two ocean basins. The  $\delta^{18}\text{O}_p$  values were thought to reflect kinetic–biological isotopic fractionation. However, Longinelli et al. (1976) extracted P from seawater without prefiltration and used iron-coated fibers that absorb inorganic and organic P, and such complications may confound interpretation of their results (Blake et al. 2005). More recently, Colman (2002) concluded that the large deviations in  $\delta^{18}\text{O}_p$  between riverine and coastal waters in the Long Island Sound reflected equilibration with local water and indicated that rapid microbial cycling overprints source  $\delta^{18}\text{O}_p$  values on a timescale of weeks. Finally, Colman et al. (2005) found that  $\delta^{18}\text{O}_p$  in open ocean waters is a function of DIP transport and biological turnover in both the Atlantic and the Pacific Oceans and highlighted the importance of cell lysis in the regeneration of DIP in the euphotic zone. They also found that depth profiles of  $\delta^{18}\text{O}_p$  are near the temperature-dependent equilibrium (Eq. 1), suggestive of extensive turnover of DIP in open ocean seawater (Colman et al. 2005).

In this study, we used the oxygen isotopic composition of  $\delta^{18}\text{O}_p$  in seawater as a tracer for identifying phosphate sources and estimating phosphate biological turnover (cycling) within the Monterey Bay. The deviation of  $\delta^{18}\text{O}_p$  in the euphotic zone from the source  $\delta^{18}\text{O}_p$  (riverine phosphate or upwelled phosphate) toward the expected isotopic equilibrium (calculated from Eq. 1) can be used as a measure of the extent of biological phosphate cycling (e.g., phosphate utilization, also defined as biological uptake relative to input of new phosphate). By measuring spatial and temporal variations in the  $\delta^{18}\text{O}_p$  in Monterey Bay, we gain a better understanding of both the temporal and spatial scales of the biogeochemical cycling of phosphate within coastal upwelling systems and learn how it compares to the open ocean.

## Site description

Monterey Bay is a deep (>1,000 m), non-estuarine embayment that is broadly open to the coastal ocean (Fig. 1). Monterey Bay experiences seasonally high primary productivity associated with upwelling during the spring and summer months ("upwelling season"), transitioning toward lower levels of primary productivity during the fall/winter months ("winter season") when upwelling-favorable winds relax (Rosenfeld et al. 1994; Chavez 1996). However, upwelling events are not continuous throughout the spring and summer, and consequently the ecosystem experiences intercalated events of upwelling and relaxation that can last up to 3 weeks (Dugdale and Wilkerson 1989).

High primary production and chlorophyll concentrations are observed during episodic phytoplankton blooms within the bay, typically during the spring and summer and occasionally in the fall when nutrient concentrations are highest (Pennington and Chavez 2000). Phytoplankton communities in the bay are dominated by larger cell-sized species (>5  $\mu\text{m}$ ), particularly during periods of high productivity (Wilkerson et al. 2000). A model of plankton dynamics of the bay suggests that a large proportion of the daily phytoplankton growth is ungrazed in the mixed layer and is advected downstream and offshore away from the production site (Olivieri and Chavez 2000). Nutrient enrichment (grow-out experiments) conducted within the Monterey Bay indicated that additions of nitrate provided the most potential for growth and biomass accumulation and although silica did not limit biomass accumulation, silica additions did modify the uptake rates of nitrogen (Kudela and Dugdale 2000). Furthermore, P addition did not have significant effects. These experiments suggest that the phytoplankton population as a whole is largely not P-limited although certain species in the Monterey Bay phytoplankton community may be (Nicholson et al. 2006).

Phosphate in the euphotic zone in Monterey Bay has two primary sources: terrestrial phosphate, from surface-water runoff and dust deposition, and oceanic phosphate, from advection, eddy diffusion, and seasonal upwelling (Olivieri and Chavez 2000) (Fig. 2). The  $\delta^{18}\text{O}_\text{p}$  observed in Monterey Bay at any given time will represent the balance between the input flux from the various phosphate sources and the degree of cycling (biological turnover and reuse of phosphate) within the euphotic zone (e.g., phosphate utilization rate).

## Materials and methods

A  $\delta^{18}\text{O}_\text{p}$  time series investigation was conducted in Monterey Bay from May 2002 through August 2004 (18 cruises). Samples were collected aboard the *R/V Point Lobos* on single-day cruises along an onshore/offshore transect consisting of three stations: C1 (latitude: 36.797, longitude: -121.847), M1 (latitude: 36.747, longitude: -122.022), and M2 (latitude: 36.697, longitude: -122.378) (Fig. 1). The temporal distribution of sampling was skewed toward the summer months as a result of inclement weather in the winter and scheduling conflicts. The measurements made at each station are the same as

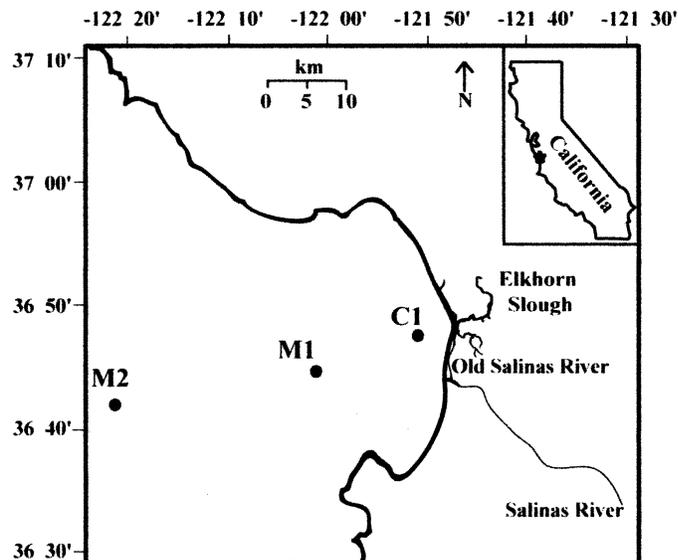


Fig. 1. Map of Monterey Bay and Sta. C1, M1, and M2.

those described by Pennington and Chavez (2000) and consisted of conductivity, temperature, and depth (CTD) casts made to 200 m with a Sea-Bird 911 CTD mounted on a General Oceanics 12-place rosette with 5-liter Niskin bottles. Conductivity and temperature sensors are calibrated annually.

Chlorophyll *a* (Chl *a*) concentration ( $\text{mg chl m}^{-3}$ ) was measured by a modified fluorometric procedure in which plant pigments were filtered onto 25-mm Whatmann GF/F filters, extracted in acetone in a freezer overnight, and measured on a Turner Designs Model-10 fluorometer calibrated with a commercial Chl *a* standard (Pennington and Chavez 2000). Approximately 10 mL of water was collected for dissolved nutrient concentrations from each depth, frozen, and analyzed on an Alpkem autoanalyzer (Pennington and Chavez 2000). Water samples for isotope analysis were collected from four depths (10 m, 40 m, 100 m, and 200 m) at each station, although on occasion

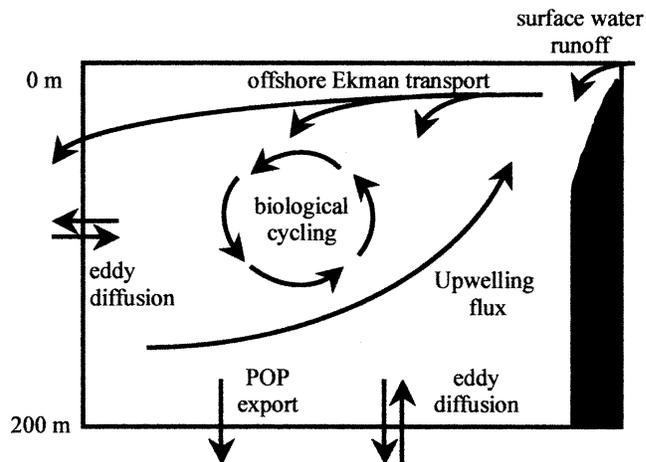


Fig. 2. Schematic diagram of the Monterey Bay system and parameters affecting the oxygen isotopic composition of  $\delta^{18}\text{O}_\text{p}$ .

the shallower depths did not contain enough phosphate for analyses in the volume collected. In addition, water samples were collected on separate sampling trips to Moss Landing Harbor and from depths of 500 m and 800 m in the bay at Sta. M1. For each sample, 8 liters of water were collected in high-density polyethylene (HDPE) bottles and processed for  $\delta^{18}\text{O}_p$  analysis. DIP was stripped from seawater by adding 1 mol L<sup>-1</sup> sodium hydroxide to each sample immediately after collection and rigorously shaking (Karl and Tien 1992; Thomson-Bulldis and Karl 1998). Magnesium hydroxide floc was allowed to settle for 1 h before supernatant was siphoned off, leaving approximately 1–2 liters of floc in seawater. Post cruise, magnesium hydroxide floc was stored in a cold room (4°C) overnight before being processed to silver phosphate according to the method of McLaughlin et al. (2004) and analyzed for phosphate  $\delta^{18}\text{O}$ . Duplicates processed immediately or after overnight storage yielded identical  $\delta^{18}\text{O}_p$  (within analytical error, 0.3‰), indicating that the up-to-15-h storage in the cold room did not affect the data. Isotopic analyses were conducted on a Eurovector elemental analyzer coupled to a Micromass (now GVI) IsoPrime mass spectrometer at the U.S. Geological Survey in Menlo Park, California. Two internal silver phosphate standards, sodium phosphate ([STDH]  $\delta^{18}\text{O}_p = 20.0\text{‰}$ ) and potassium phosphate ([STDL]  $\delta^{18}\text{O}_p = 11.3\text{‰}$ ), were analyzed throughout each mass spectrometer run for calibration and drift correction. Water samples were collected in 20-mL HDPE-depressed cap scintillation vials with no headspace for  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_w$ ) analysis.  $\delta^{18}\text{O}_w$  was determined using a Finnigan MAT 251 mass spectrometer also at the U.S. Geological Survey in Menlo Park. All oxygen isotopic composition measurements are reported in standard delta notation ( $\delta^{18}\text{O}$ ), which is calculated using the following equation:

$$\delta^{18}\text{O} = \left[ \frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right] \cdot 1000 \quad (3)$$

where  $R_{\text{sample}}$  is the ratio of  $^{18}\text{O}/^{16}\text{O}$  in our sample, and  $R_{\text{VSMOW}}$  is the ratio of  $^{18}\text{O}/^{16}\text{O}$  in the isotopic standard for oxygen, Vienna standard mean ocean water (VSMOW).

The upwelling index used is a 10-d running mean of the daily upwelling index recorded in the National Oceanic and Atmospheric Administration (NOAA) Pacific Fisheries Environmental Laboratory data set (available at <ftp://Orpheus.pfeg.noaa.gov/outgoing/upwell/daily/p10dayac.all>). Upwelling index values are daily averages of Ekman wind-driven, cross-shore, mass transport computed from the U.S. Navy Fleet Numerical Meteorological and Oceanographic Center six-hourly surface pressure analyses recorded at 36°N and 122°W by the NOAA/National Marine Fisheries Service/Pacific Fisheries Environmental Laboratory buoy. Indices are in units of cubic meters per second along each 100 m of coastline.

## Results

The oxygen isotopic composition of DIP in Monterey Bay ranged between 16.5‰ and 21.6‰ at Sta. C1, 17.9‰ and 22.3‰ at Sta. M1, and 17.0‰ and 22.1‰ at Sta. M2.

The full data set is available in Web Appendix 1 ([http://www.aslo.org/lo/toc/vol\\_51/issue\\_5/2370a.pdf](http://www.aslo.org/lo/toc/vol_51/issue_5/2370a.pdf)). Relatively large fluctuations in the  $\delta^{18}\text{O}_p$  (up to 6‰) occurred episodically and, in many cases, simultaneously throughout the bay over the course of the time series (Fig. 3, Table 1). Whereas the standard deviations of average values for each station were large (e.g., temporal variability), Student's  $t$ -tests indicated that during the time series M1 had significantly higher  $\delta^{18}\text{O}_p$  values than either C1 or M2 at the 95% confidence interval and that C1 and M2 were not significantly different. Furthermore,  $\delta^{18}\text{O}_p$  values for the spring–summer upwelling season were significantly higher than those observed during the winter season at the 95% confidence interval. Whereas the average  $\delta^{18}\text{O}_p$  typically increased with depth (between 10 m and 200 m),  $t$ -tests indicated that this trend was not statistically significant at any station.

The  $\delta^{18}\text{O}_p$  expected if phosphate had reached isotopic equilibrium with seawater through the biological cycling of phosphate can be calculated from the Longinelli and Nuti (1973) equilibrium expression (Eq. 1) using the temperature and  $\delta^{18}\text{O}_w$  at each station and depth. The  $\delta^{18}\text{O}_w$  was measured at each station and depth on 27 March 2003 and again on 14 April 2003 and ranged from  $-0.4\text{‰}$  to  $-1.0\text{‰}$ , with lower values at the surface and higher values at depth. Because of the small variability in water temperature and  $\delta^{18}\text{O}_w$ , there is not much variability in the expected equilibrium  $\delta^{18}\text{O}_p$  through the course of the time series or with depth, and the average equilibrium value is  $23.1\text{‰} \pm 0.6\text{‰}$ , where the standard deviation predominantly represents the variability in the  $\delta^{18}\text{O}_w$ .

The highest  $\delta^{18}\text{O}_p$  values in the upper water column occurred during the upwelling season in distinct episodes of short duration, lasting not more than 2 months (Fig. 3). The highest  $\delta^{18}\text{O}_p$  values approached but were always less than the predicted equilibrium value (Fig. 3). In fact, the  $\delta^{18}\text{O}_p$  values measured in the bay throughout this study were consistently lower than values expected from equilibrium (Fig. 3). The lowest values in  $\delta^{18}\text{O}_p$  throughout the time series (approximately 17‰) occurred as distinct minima during the upwelling season and were similar to  $\delta^{18}\text{O}_p$  of samples collected in the bay at depths of 500–800 m and were also similar to  $\delta^{18}\text{O}_p$  of the Moss Landing Harbor samples taken at low tide, when the terrestrial signature is most pronounced (Fig. 3, Table 2). The  $\delta^{18}\text{O}_p$  of the harbor sample at low tide and the 500–800-m samples were analytically indistinguishable, although they are produced independently (e.g., do not represent the same water mass or phosphate source). Most of the observed  $\delta^{18}\text{O}_p$  values during the time series fall between the source (e.g., terrestrial/deep water) value and the equilibrium value (Fig. 3). Maxima and minima in the  $\delta^{18}\text{O}_p$  time series usually appeared simultaneously at all depths and at all stations (Fig. 3), indicating that the processes affecting the  $\delta^{18}\text{O}_p$  operate broadly throughout the bay across a broad depth range.

Phosphate oxygen isotope values were not linearly correlated with phosphate concentration, temperature, or Chl *a* concentration at the depths sampled (Web Appendix 1). However, the temporal fluctuations in  $\delta^{18}\text{O}_p$  generally

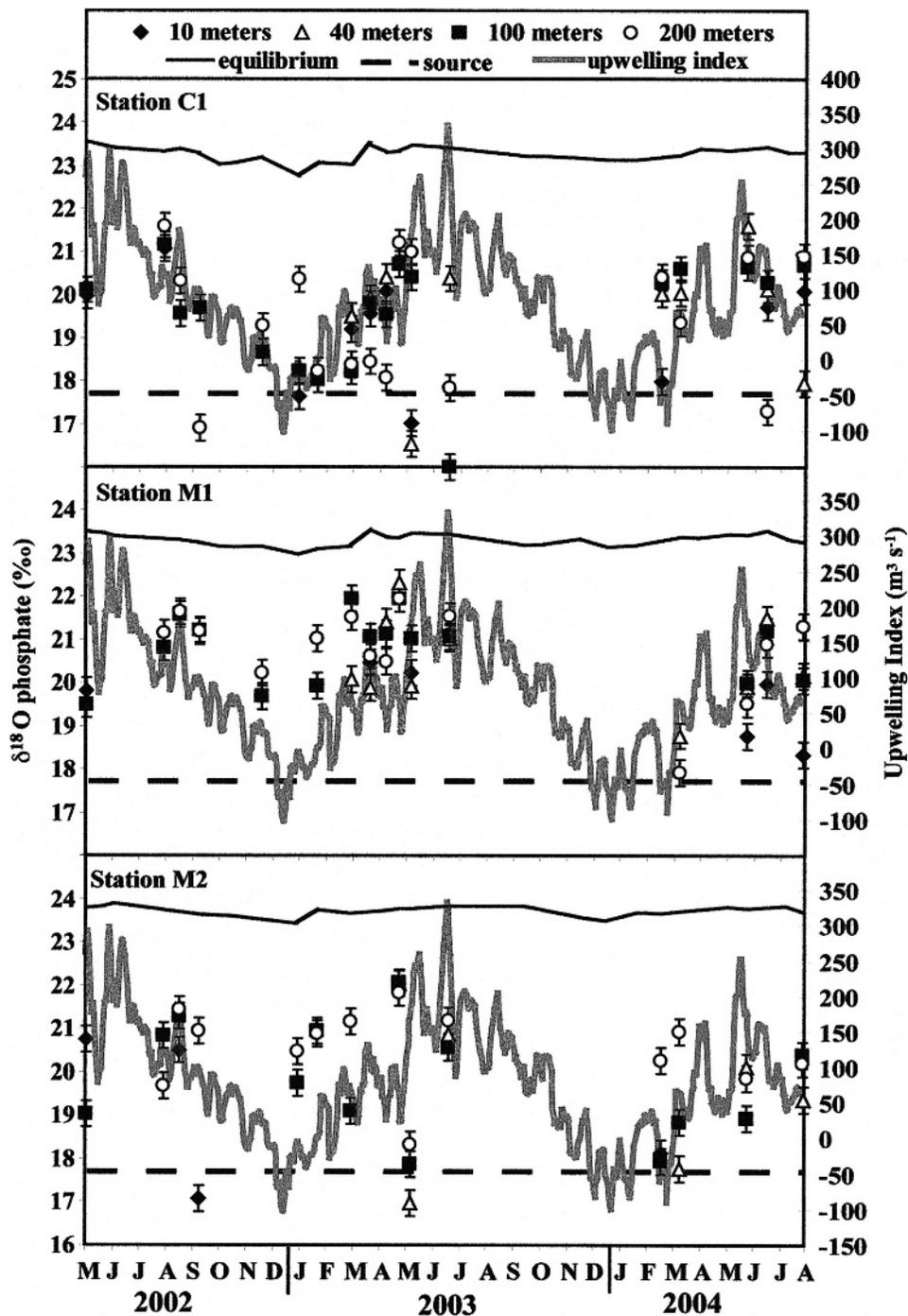


Fig. 3. Observed phosphate  $\delta^{18}\text{O}$  variability relative to VSMOW during the course of the time series from May 2002 through August 2004. All panels indicate 10-d running mean of the NOAA upwelling index as a function of time;  $\delta^{18}\text{O}_p$  as a function of time for 10-m depth, 40-m depth, 100-m depth, and 200-m depth; expected equilibrium phosphate  $\delta^{18}\text{O}$ ; and the  $\delta^{18}\text{O}$  of the phosphate source. The top panel is for the nearshore Sta. C1, the middle panel is for the bay mouth Sta. M1, and the lower panel is for the offshore Sta. M2. Equilibrium phosphate  $\delta^{18}\text{O}$  is the isotopic composition that would be expected if phosphate had been completely recycled and reached equilibrium with the seawater  $\delta^{18}\text{O}$  at the environmental temperature and was calculated from Eq. 1 from the temperature at each depth. Error bars indicate analytical error (0.4%), one  $\sigma$  standard deviation between replicates falls within this range for all samples.

Table 1. Average phosphate  $\delta^{18}\text{O}$  values relative to VSMOW for each station (all depths combined) and for each depth (at all stations combined). Averages were calculated for the entire time series and for each season (upwelling and winter).

	Annual average (‰)	Standard deviation	Upwelling average (‰)	Upwelling standard deviation	Winter average (‰)	Winter standard deviation
Sta. C1	19.5	1.4	19.7	1.5	19.1	1.1
Sta. M1	20.6	1.0	20.7	1.0	20.3	1.2
Sta. M2	20.0	1.4	20.1	1.3	19.6	1.4
10 m	19.3	1.2	19.8	1.0	18.0	0.8
40 m	19.9	1.5	20.1	1.5	19.2	1.0
100 m	20.1	1.3	20.3	1.2	19.6	1.2
200 m	20.1	1.3	20.2	1.4	19.8	1.3

followed a pattern similar to that of the smoothed upwelling index for Monterey Bay (Fig. 3), particularly at Sta. C1 within the bay. Surface-water Chl *a* concentrations at each of the stations also traced a pattern similar to the Monterey Bay upwelling index (Fig. 4). Chl *a* and the  $\delta^{18}\text{O}_p$  varied similarly in time for most of the record (both tracing the upwelling index); however, they did not correspond in magnitude and consequently were not linearly correlated. The amount of total variability at each station differed, with C1 and M2 having similar average variability ( $\pm 1.4\text{‰}$ ) in  $\delta^{18}\text{O}_p$  values across the depth and time interval samples and M1 having less variability ( $\pm 1.0\text{‰}$ ) than the other stations (Table 1).

## Discussion

*Phosphate sources*—The net rate of phosphate input into the euphotic zone relative to biological demand (thus uptake and metabolism) plays a role in the oxygen isotopic composition of DIP ( $\delta^{18}\text{O}_p$ ). At any given time the  $\delta^{18}\text{O}_p$  within Monterey Bay represents the balance between the input of new phosphate, with a low  $\delta^{18}\text{O}_p$  relative to equilibrium, and the amount of biological turnover of phosphate in the system, which results in isotopic signatures approaching the equilibrium value. Excess input of new phosphate into the upper 200 m of Monterey Bay relative to demand (i.e., phosphate that has not yet been biologically cycled within that water mass) will lower the measured  $\delta^{18}\text{O}_p$  such that it more closely reflects the source value. Alternatively, extensive biological demand and turnover relative to input will shift the source values toward the expected equilibrium value. The parameters that affect  $\delta^{18}\text{O}_p$  in the Monterey Bay include upwelling, terrestrial runoff, advection, utilization by organisms, and sinking of particulate matter (Fig. 2). The phosphate

sources from outside the upper 200 m in Monterey Bay include terrestrial runoff and deeper water (from 500–800 m), which have lower  $\delta^{18}\text{O}_p$  relative to values within the upper 200 m. The terrestrial source of phosphate as indicated by the  $\delta^{18}\text{O}_p$  measurement at low tide in the Moss Landing Harbor (the discharge site for the Salinas River), when freshwater infiltrates the harbor, is 17.8‰. This value is consistent with results from San Francisco Bay, which show that the  $\delta^{18}\text{O}_p$  from riverine inputs is isotopically lower than seawater (e.g., Sacramento River range is 11‰ to 15‰) (McLaughlin et al. 2006). However, we do not expect to see the terrestrial freshwater  $\delta^{18}\text{O}_p$  signature maintained far from shore (unless accompanied by a salinity anomaly) because of extensive dilution of the terrestrial signal by seawater  $\delta^{18}\text{O}_p$ . Discharge from the Salinas River, a major river discharging into Monterey Bay through the Moss Landing Harbor, is greatest in the winter months ( $30\text{ m}^3\text{ s}^{-1}$ ), dropping to an average of  $1\text{ m}^3\text{ s}^{-1}$  for the remainder of the year (<http://nwis.waterdata.usgs.gov>). Thus, if any terrestrial influence on  $\delta^{18}\text{O}_p$  occurs, we would expect it to be greatest at Sta. C1 (8 km from shore) and during the winter months when discharge is highest. Although this may account for the lower  $\delta^{18}\text{O}_p$  at C1 during the winter months, it is unlikely to account for the low  $\delta^{18}\text{O}_p$  values observed at M1 and M2, which are too far from shore to be affected by the terrestrial runoff (as evident by salinity measurements that would indicate a freshwater signature on the surface waters).

Based on our analyses, deep-water (500–800 m) phosphate in Monterey Bay also has a relatively low ( $\sim 17.7\text{‰}$ )  $\delta^{18}\text{O}_p$  value compared to values within the upper 200 m. Thus, inputs of new phosphate to the euphotic zone from these depths will also lower the  $\delta^{18}\text{O}_p$ . In contrast, cycling within the biomass will tend to increase the observed  $\delta^{18}\text{O}_p$  toward the expected equilibrium value (23.1‰ on average). Recirculation of upwelled water originating from 60–100-m depth (Pennington and Chavez 2000) will also tend to increase the observed  $\delta^{18}\text{O}_p$  because this will bring remineralized phosphate back to the surface for additional cycling within the euphotic zone. A loss of phosphate from the surface waters through packaging as particulate organic phosphate or through advection/diffusion of dissolved P out of the system will tend to lower the  $\delta^{18}\text{O}_p$  of the surface waters by removing phosphate before it has been extensively and repeatedly cycled. Our results indicate that the  $\delta^{18}\text{O}_p$  within the upper 200 m always lies between the source values and the expected equilibrium value. These

Table 2.  $\delta^{18}\text{O}_p$  values relative to VSMOW of potential phosphate sources to the upper water column in Monterey Bay.

Date	Depth (m)	$\delta^{18}\text{O}_p$ (‰)
Sta. M1, 15 May 2003	500	17.6
Sta. M1, 13 May 2004	500	17.5
Sta. M1, 13 May 2004	800	17.8
Moss Landing Harbor		
low tide, 1 Feb 2003	surface	17.8
high tide, 1 Feb 2003	surface	19.7

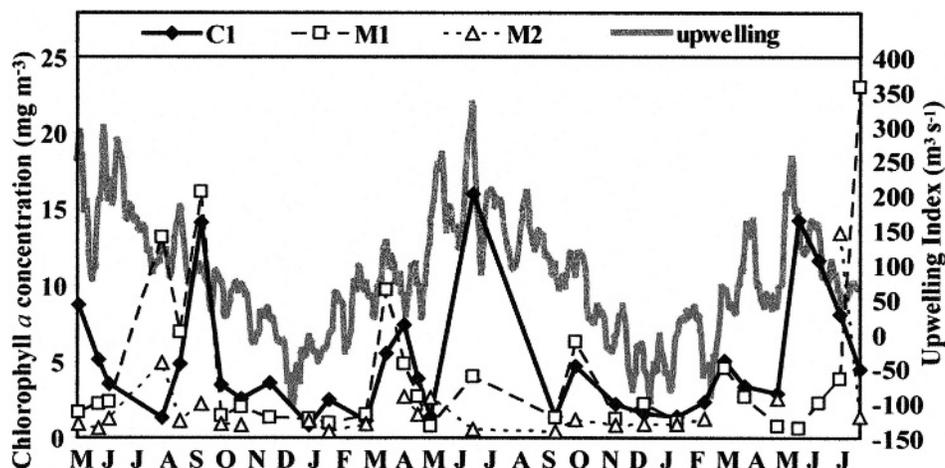


Fig. 4. Surface-water Chl *a* concentration for Stations C1, M1, and M2 plotted with the 10-d running mean of upwelling index during the time series from May 2002 through August 2004.

results suggest that phosphate is cycled to some extent in surface waters but is not extensively cycled such that isotopic equilibrium is achieved. Some phosphate source signature is retained by the  $\delta^{18}\text{O}_p$ .

**Phosphate utilization**—The observed  $\delta^{18}\text{O}_p$  values in Monterey Bay are bracketed by the  $\delta^{18}\text{O}_p$  values for the potential sources of phosphate to the bay (deep water and terrestrial phosphate) and the equilibrium  $\delta^{18}\text{O}_p$  value. Thus, the  $\delta^{18}\text{O}_p$  represents deviations from the source signal toward equilibrium via phosphate utilization and cycling. In a system that is not phosphate limited and where phosphorus in the surface waters is never depleted, phosphate may not be extensively cycled (e.g., repeatedly utilized by the biomass) resulting in variability in the isotopic ratios because of different degrees of approach toward isotopic equilibrium. In other words, the observed  $\delta^{18}\text{O}_p$  values at any time represents the balance between the input flux from the various sources and the degree of cycling (turnover and reuse of phosphate) within the euphotic zone (e.g., phosphate utilization rate). The deviations of  $\delta^{18}\text{O}_p$  in Monterey Bay from isotopic equilibrium is in contrast to  $\delta^{18}\text{O}_p$  measured in low-nutrient open ocean sites where P is more extensively cycled within the euphotic zone, and the values are higher and much closer to those expected from isotopic equilibrium with seawater (Colman et al. 2005). This indicates that coastal ocean phosphate cycling (utilization) is typically lower and more variable both spatially and temporally than in the open ocean.

If phosphate is heavily utilized in the euphotic zone it will be extensively cycled intracellularly and the  $\delta^{18}\text{O}_p$  will achieve isotopic equilibrium. This will result in a correlation between  $\delta^{18}\text{O}_p$  and temperature (and  $\delta^{18}\text{O}_w$ ) according to Eq. 1. The relatively large differences between the observed  $\delta^{18}\text{O}_p$  and the expected equilibrium  $\delta^{18}\text{O}_p$  are indicative of incomplete cycling of phosphate (Fig. 3). The closest that the observed  $\delta^{18}\text{O}_p$  approaches the equilibrium value is still lower than the expected equilibrium value, suggesting that even during the maximum cycling and utilization of

phosphate in the Monterey Bay, the complete exchange of oxygen isotopes of phosphate is not obtained.

We would expect that when or where phosphate concentrations are low compared to demand phosphate cycling will be the most extensive and  $\delta^{18}\text{O}_p$  will be closer to equilibrium (in this case higher relative to the source). In such cases, a negative correlation between  $\delta^{18}\text{O}_p$  and phosphate concentration and possibly a positive correlation with Chl *a* concentration may be expected. Although the  $\delta^{18}\text{O}_p$  values closest to equilibrium were associated with periods of high productivity, consistent correlations between Chl *a* or phosphate concentrations and  $\delta^{18}\text{O}_p$  were not observed. This indicates that phosphate is not heavily cycled through the biomass in the euphotic zone (e.g., phosphate is not limiting). In this case, the DIP retains some residual signature of the isotopic composition of its source, which is independent of phosphate and chlorophyll concentrations in the euphotic zone.

Assuming that the source signal is approximately 17.7‰ (the average of the harbor-water DIP and deep-water DIP signatures) and that phosphate that has been extensively cycled will approach the expected equilibrium value (23.1‰  $\pm$  0.6‰ on average), the degree of oxygen isotopic exchange can be calculated by mass balance using the following equation.

$$\begin{aligned} \text{Percent Phosphate Oxygen Exchange} \\ = \frac{(\delta^{18}\text{O}_{\text{observed}} - 17.7)}{(23.1 - 17.7)} \cdot 100 \end{aligned}$$

Using this equation, we determined that Sta. M1 had the greatest average annual percent oxygen exchange (58%) followed by M2 (47%) and C1 (40%) (Fig. 5). In addition, we observed that phosphate turnover and cycling is greater during the upwelling season relative to the winter season, as indicated by an increase in the percent oxygen exchange of 15% at C1, 8% at M1, and 9% at M2 from the winter season to the upwelling season. This suggests that, although there is more phosphate input to the system during the upwelling season, there is even more phosphate demand.

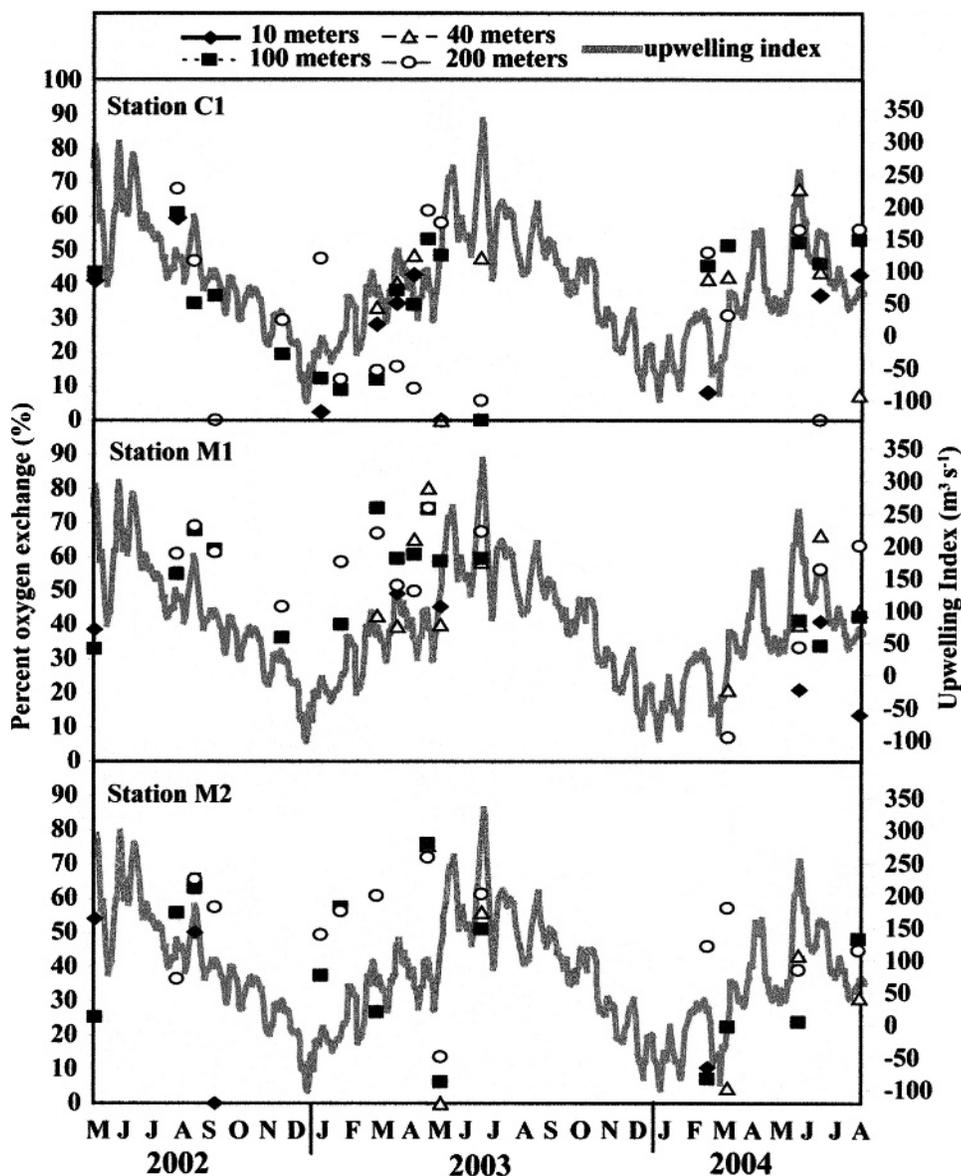


Fig. 5. Percent phosphate oxygen isotope exchange during the course of the time series from May 2002 through August 2004. All panels indicate 10-d running mean of the NOAA upwelling index as a function of time; percent oxygen isotope exchange at 10-m depth, 40-m depth, 100-m depth, and 200-m depth for Sta. C1 (top panel), Sta. M1 (middle panel), and Sta. M2 (lower panel). The percent oxygen isotope exchange was calculated for each station and each depth using Eq. 4. For phosphate  $\delta^{18}\text{O}$  that falls below 17.7‰, percent oxygen exchange was set to zero rather than a negative percentage.

Consequently, phosphate is more extensively cycled within the biological community than during the winter period, and the percent oxygen exchange values increase accordingly. It is also possible that the nutritional phosphate demand and/or phosphate uptake and storage of the resident phytoplankton changes seasonally because of changes in species distribution or physiology, resulting in variable phosphate cycling rates. Interestingly, although the greatest percent exchange occurs during the upwelling season (up to 90% phosphate oxygen exchange at times), there are also events of near zero percent exchange during this same season (Fig. 5). This implies a lag in the response

of the biomass to the onset of phosphate influx, resulting in periods of relatively low phosphate utilization.

*Temporal and spatial variability*— $\delta^{18}\text{O}_p$  varies seasonally, approaching isotopic equilibrium episodically particularly during the upwelling period. Although data from the winter months are sparse, if we assume the winter data are representative, we can make some generalizations about temporal variability in phosphate cycling in Monterey Bay. Phosphate  $\delta^{18}\text{O}$  is lower than the expected equilibrium values and somewhat less variable during the winter months. This is when net productivity in the bay is

depressed because of increased mixing and light limitation (Pennington and Chavez 2000). The decrease in demand for phosphate relative to phosphate input, primarily riverine during the winter, results in reduced phosphate turnover relative to input within the upper 200 m during this period (e.g., lower phosphate utilization rates).

In contrast, the upwelling season is marked by episodic maxima and minima in the  $\delta^{18}\text{O}_p$  within the bay. Increased nutrients, sunlight, and some degree of water column stratification result in higher primary productivity during the upwelling season (Pennington and Chavez 2000). Service et al. (1998) found that the upwelling plume reaches M1 approximately 3 d after the winds in the Monterey Bay start to blow from the northwest and photosynthetically available radiation increases. Four days after the upwelling plume reaches M1, productivity peaks (Service et al. 1998). Because of the lag between the onset of upwelling-favorable winds and the peak in productivity at M1 and because Monterey Bay is not a phosphate-limited system (Kudela and Dugdale 2000), we did not expect to see a strong linear correlation between the upwelling index and  $\delta^{18}\text{O}_p$ . However, the observed phosphate  $\delta^{18}\text{O}$  does show a pattern similar to that of the upwelling index (Fig. 3).  $\delta^{18}\text{O}_p$  approaches, but is still lower than the value expected from equilibrium during periods of increased upwelling and productivity (thus increased P demand) and tends to decrease (i.e., less demand relative to input) when productivity-associated P demand is lower.

Pennington and Chavez (2000) note that phytoplankton blooms within the bay are episodic, thus the observed pattern of phosphate  $\delta^{18}\text{O}$  is most likely linked to periods of increased phosphate turnover related to these episodic blooms. Increases in chlorophyll concentration and productivity are tied to upwelling events (Fig. 4), and maxima in  $\delta^{18}\text{O}_p$  occur concurrently with increases in chlorophyll concentration following the onset of upwelling (Figs. 3, 4). Minima in the phosphate  $\delta^{18}\text{O}$  seem to correspond to decreases in surface-water chlorophyll concentration and lag the decreases in the upwelling index. These minima in the  $\delta^{18}\text{O}_p$  may be associated with an influx of phosphate to the system from deeper waters (500–800 m) not accounted for in the upwelling index, which corresponds to wind-driven upwelling from Ekman transport from ~100-m depth (Rosenfeld et al. 1994). Thus, we speculate that increased P input from deep water relative to demand during the relatively lower productivity periods is the cause for the episodic low  $\delta^{18}\text{O}_p$  values. This may also suggest that the biotic response via increased productivity at times lags the upwelling of nutrients to the euphotic zone.

Sta. M1, which lies directly within the upwelling plume (Service et al. 1998; Pennington and Chavez 2000), has a slightly but significantly higher  $\delta^{18}\text{O}_p$  than either C1 or M2, both of which are away from the upwelling center (Table 1). During an upwelling event, water from approximately 100 m is brought to the surface (Rosenfeld et al. 1994). The DIP at 100 m has been remineralized from surface-water particulate phosphate and re-enters the system to be cycled again in the surface waters. This would explain the somewhat higher phosphate  $\delta^{18}\text{O}$  values within

the upwelling plume. However, the surface-water circulation in Monterey Bay does move water away from M1 toward both C1 and M2 (Breaker and Broenkow 1994). Thus, one might expect both C1 and M2 to have higher  $\delta^{18}\text{O}_p$  values relative to M1 because phosphate advected from M1 toward C1 and M2 would have more time to be utilized and turned over by the biomass and thus shift further toward equilibrium. However, this is not observed, and we offer several possible explanations for this pattern. The first possibility is that phosphate utilization relative to deep-water phosphate input (with a lower  $\delta^{18}\text{O}_p$ ) is slightly greater at M1 relative to C1 and M2. It is also possible that C1 and M2 receive more deep-water phosphate (via advection and eddy diffusion), whereas M1 receives more of its phosphate from waters upwelled from 100 m (with higher  $\delta^{18}\text{O}_p$ ). Alternatively, or in addition to the above possibilities, the export flux of phosphate as particulate organic phosphate may be slightly larger at C1 and M2 relative to M1, which would remove a greater amount of phosphate from surface waters before it can be more completely cycled. The stronger upwelling jet operating at M1 may weaken the export flux at this station relative to C1 or M2 (Rosenfeld et al. 1994; Olivieri and Chavez 2000), lending credibility to this last option. On average C1 has the greatest Chl *a* concentrations and M2 has the lowest concentration of phosphate, both of which would be predicted to result in increased phosphate turnover and increase  $\delta^{18}\text{O}_p$  (which is not supported by the data). Thus, the cause of the slightly lower  $\delta^{18}\text{O}_p$  values at C1 and M2 may result from a combination of the latter two possibilities.

In summary, the oxygen isotopic composition of phosphate within the upper 200 m of the water column in Monterey Bay is consistently out of isotopic equilibrium with respect to seawater at the measured water temperature and fluctuates between the equilibrium value and the isotopic signatures of the DIP sources. During the upwelling season, the  $\delta^{18}\text{O}_p$  is slightly higher (closer to equilibrium) than the non-upwelling season. This is a result of one or a combination of three mechanisms: (1) rapid and extensive phosphate cycling during the productive upwelling season resulting in an approach toward the equilibrium value, (2) less input of phosphate with a lower  $\delta^{18}\text{O}_p$  from either terrestrial or deep-water phosphate sources, and (3) lower phosphate export from surface waters resulting in a longer residence time in the euphotic zone and allowing more time for phosphate turnover to occur. Based on our understanding of the oceanography in Monterey Bay, the first of these explanations is most likely. None of the stations at any point during the time series reached isotopic equilibrium with surrounding water. Thus, there is generally less phosphate turnover relative to input in these coastal waters compared to low-nutrient open ocean sites where phosphate is approximately in equilibrium with the surrounding water (Colman et al. 2005).

## References

- BENITEZ-NELSON, C. R. 2000. The biogeochemical cycling of phosphorus in marine systems. *Earth Sci. Rev.* **51**: 109–135.

- , AND K. O. BUESSELER. 1999. Variability of inorganic and organic phosphorus turnover rates in the coastal ocean. *Nature* **398**: 502–505.
- BERGER, W. H., V. S. SMETACEK, AND G. WEFER. 1989. Ocean productivity and paleoproductivity—an overview, p. 1–34. *In* W. H. Berger, V. S. Smetacek and G. Wefer [eds.], *Productivity of the oceans: Present and past*. Wiley.
- BLAKE, R. E., J. R. O'NEIL, AND G. A. GARCIA. 1997. Oxygen isotope systematics of biologically mediated reactions of phosphate: I. Microbial degradation of organophosphorus compounds. *Geochim. Cosmochim. Acta* **61**: 4411–4422.
- , ———, AND ———. 1998. Effects of microbial activity on the  $\delta^{18}\text{O}$  of dissolved inorganic phosphate and textural features of synthetic apatites. *Am. Mineral.* **83**: 1516–1531.
- , ———, AND A. V. SURKOV. 2005. Biogeochemical cycling of phosphorus: Insights from oxygen isotope effects of phosphoenzymes. *Am. J. Sci.* **305**: 596–620.
- BREAKER, L. C., AND W. W. BROENKOW. 1994. The circulation of Monterey Bay and related processes. *Oceanogr. Mar. Biol.* **32**: 1–64.
- CHAVEZ, F. P. 1996. Forcing and biological impact of onset of the 1992 El Niño in central California. *Geophys. Res. Lett.* **23**: 265–268.
- , AND J. R. TOGGWEILER. 1995. Physical estimates of global new production: The upwelling contribution, p. 149–169. *In* C. P. Summerhayes, K. C. Emeis, M. V. Angel, R. L. Smith and B. Zeitzschel [eds.], *Upwelling in the oceans: Modern processes and ancient records*. Wiley.
- CLARK, L. L., E. D. INGALL, AND R. BENNER. 1998. Marine phosphorus is selectively remineralized. *Nature* **393**: 426.
- COLMAN, A. 2002. The oxygen isotope composition of dissolved inorganic phosphate and the marine phosphorus cycle. PhD thesis. Yale Univ.
- , R. E. BLAKE, D. M. KARL, M. L. FOGEL, AND K. K. TUREKIAN. 2005. Marine phosphate oxygen isotopes and organic matter remineralization in the oceans. *Proc. Natl. Acad. Sci. USA* **102**: 13023–13028.
- DUGDALE, R. C., AND F. P. WILKERSON. 1989. New production in the upwelling center at Point Conception, California: Temporal and spatial patterns. *Deep-Sea Res.* **36**: 985–1007.
- FAUL, K., A. PAYTAN, AND M. L. DELANEY. 2005. Phosphorus distribution in sinking oceanic particulate matter. *Mar. Chem.* **97**: 307–333.
- KARL, D. M., AND G. TIEN. 1992. MAGIC: A sensitive and precise method for measuring dissolved phosphorus in aquatic environments. *Limnol. Oceanogr.* **37**: 105–116.
- KOLODNY, Y., B. LUZ, AND O. NAVON. 1983. Oxygen isotope variations in phosphate of biogenic apatites, I. Fish bone apatite—rechecking the rules of the game. *Earth Planet. Sci. Lett.* **64**: 398–404.
- KUDELA, R. M., AND R. C. DUGDALE. 2000. Nutrient regulation of phytoplankton productivity in Monterey Bay, California. *Deep-Sea Res. II* **47**: 1023–1053.
- LAL, D., AND T. LEE. 1988. Cosmogenic  $^{32}\text{P}$  and  $^{33}\text{P}$  uses as tracers to study phosphorus recycling in the upper ocean. *Nature* **333**: 752–754.
- LOH, A. N., AND J. E. BAUER. 2000. Distribution, partitioning and fluxes of dissolved and particulate organic C, N and P in the eastern North Pacific and Southern Oceans. *Deep-Sea Res. I* **47**: 2287–2316.
- LONGINELLI, A., M. BARTELLONI, AND G. CORTECCI. 1976. The isotopic cycle of oceanic phosphate, I. *Earth Planet. Sci. Lett.* **32**: 389–392.
- , AND S. NUTI. 1973. Revised phosphate-water isotopic temperature scale. *Earth Planet. Sci. Lett.* **19**: 373–376.
- MCLAUGHLIN, K., C. KENDALL, S. SILVA, H. STUART-WILLIAMS, AND A. PAYTAN. 2004. A precise method for the analysis of  $\text{d}^{18}\text{O}$  of dissolved inorganic phosphate in seawater. *Limnol. Oceanogr. Method.* **2**: 202–212.
- , A. PAYTAN, C. KENDALL, AND S. R. SILVA. 2006. Phosphate oxygen isotopes as a tracer for sources and cycling of phosphate in North San Francisco Bay. *JGR-Biogeosciences* **111**, G03003, doi: 10.1029/2005JG000079.
- NICHOLSON, D., S. DYHRMAN, F. CHAVEZ, AND A. PAYTAN. 2006. Alkaline phosphatase activity in the phytoplankton communities of Monterey Bay and San Francisco Bay. *Limnol. Oceanogr.* **51**: 874–883.
- OLIVIERI, R. A., AND F. P. CHAVEZ. 2000. A model of plankton dynamics for the coastal upwelling system of Monterey Bay, California. *Deep-Sea Res. II* **47**: 1077–1106.
- O'NEIL, J. R., T. W. VENNEMANN, AND W. F. MCKENZIE. 2003. Effects of speciation on equilibrium fractionations and rates of oxygen isotope exchange between  $(\text{PO}_4)_{\text{aq}}$  and  $\text{H}_2\text{O}$ . *Geochim. Cosmochim. Acta* **67**: 3135–3144.
- PAYTAN, A., B. J. CADE-MENUN, K. MCLAUGHLIN, AND K. L. FAUL. 2003. Selective phosphorus regeneration of sinking marine particles: Evidence from  $^{31}\text{P}$ -NMR. *Mar. Chem.* **82**: 55–70.
- , Y. KOLODNY, A. NEORI, AND B. LUZ. 2002. Rapid biologically mediated oxygen isotope exchange between water and phosphate. *Global Biogeochem. Cycles* **16**: 1013.
- PENNINGTON, J. T., AND F. P. CHAVEZ. 2000. Seasonal fluctuations of temperature, salinity, nitrate, chlorophyll, and primary production at station H3/M1 over 1989–1996 in Monterey Bay, California. *Deep-Sea Res. II* **47**: 947–973.
- ROSENFELD, L. K., F. B. SCHWING, N. GARFIELD, AND D. E. TRACY. 1994. Bifurcated flow from an upwelling center: A cold water source for Monterey Bay. *Cont. Shelf Res.* **14**: 931–964.
- SERVICE, S. K., J. A. RICE, AND F. P. CHAVEZ. 1998. Relationship between physical and biological variables during the upwelling period in Monterey Bay, CA. *Deep-Sea Res. II* **45**: 1669–1685.
- SHARP, J. H. 1991. Review of carbon, nitrogen, and phosphorus biogeochemistry. *Rev. of Geophys. Supplement* **29**: 648–657.
- SMITH, S. V. 1984. Phosphorus versus nitrogen limitation in the marine environment. *Limnol. Oceanogr.* **29**: 1149–1160.
- THOMSON-BULLDIS, A., AND D. KARL. 1998. Application of a novel method for phosphorus determinations in the oligotrophic North Pacific Ocean. *Limnol. Oceanogr.* **43**: 1565–1577.
- TOGGWEILER, J. R., AND S. CARSON. 1995. What are upwelling systems contributing to the ocean's carbon and nutrient budgets? p. 337–360. *In* C. P. Summerhayes, K. C. Emeis, M. V. Angel, R. L. Smith and B. Zeitzschel [eds.], *Upwelling in the ocean: Modern processes and ancient records*. Wiley.
- WILKERSON, F. P., R. C. DUGDALE, R. M. KUDELA, AND F. P. CHAVEZ. 2000. Biomass and productivity in Monterey Bay, California: Contribution of the large phytoplankton. *Deep-Sea Res. II* **47**: 1003–1022.

Received: 13 October 2005  
Accepted: 25 April 2006  
Amended: 23 May 2006