Phosphorus composition of sinking particles in the Guaymas Basin, Gulf of California

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Abstract

Phosphorus (P) composition and fluxes were measured in samples collected using a moored sediment trap located at 500 m in depth in the center of Guaymas Basin, Gulf of California, from February 1991 through September 1997. P composition was measured using a sequential extraction technique that chemically separates the particulate inorganic P (PIP) pool into exchangeable, oxide-bound, authigenic, and detrital phases. PIP comprised 69% ± 15% of the total particulate P pool, with significantly higher concentrations during the rainy summer. Strong relationships between authigenic and detrital P fluxes with lithogenic material ($r^2 = 0.85$) indicate that a significant component of PIP is terrestrially derived and varies with large-scale changes in regional climate. Particulate organic P (POP) fluxes were significantly higher during the winter as a result of stimulation of biological production during upwelling. Average particulate organic carbon (POC): POP ratios also varied seasonally, with higher ratios in the summer (221) vs. the winter (138). The fact that POC fluxes remained relatively constant throughout the year indicates that in winter, fresher, less degraded organic material was more effectively transported to depth. Strong correlations between POP and opal fluxes ($r^2 = 0.63$) further support a ballast mechanism, whereby enhanced sinking rates reduce the time during which organic matter is subjected to water column degradation. Compared to trap concentrations, POP is preferentially remineralized over PIP, in concert with an increase in the authigenic P pool; this signifies rapid diagenetic transformations of sedimentary P between the sediment trap and underlying sediments.

Of all of the macronutrients in marine systems, phosphorus (P) continues to remain one of the least studied (Hecky and Kilham 1988; Karl and Björkman 2002; Paytan and Mclaughlin 2007). Yet P is a key element necessary for biological growth and can greatly influence marine primary production as well as biological community structure (Benitez-Nelson 2000; Ruttenberg 2005; Paytan and Mclaughlin 2007). In marine systems, the majority of P within the water column exists in the dissolved inorganic form as HPO$_4^{2-}$ or as dissolved organic P, as more than 90% of sinking particulate P is regenerated into dissolved phases (Benitez-Nelson 2000; Paytan and Mclaughlin 2007). Unfortunately, relatively little is known regarding the distribution of P within marine dissolved and particulate matter, its spatial and temporal variability, and its transformation as particles sink through the water column and into underlying marine sediments (Faul et al. 2005). Until recently, most of the particulate P measured in marine systems was thought to be dominated by the organic P pool; however, several studies (Loh and Bauer 2000; Paytan et al. 2003; Benitez-Nelson et al. 2007) now indicate that inorganic P forms may be a major fraction in both coastal and open ocean environments. As P compounds may differ in their chemical or biological lability, it is essential that researchers understand the source, magnitude, and composition of sinking particles within the water column.

P enters the ocean via erosional runoff from rivers, the atmosphere (both wet and dry fallout), and anthropogenic sources, including certain industrial effluents, urban sewage, and leaching from agricultural areas (Benitez-Nelson 2000). The major removal pathway is sedimentation, as P does not exist in a stable gaseous phase in oxic environments (Delaney 1998). The amount of P available for uptake by organisms is not necessarily the equivalent of the total P (TP) measured in dissolved and particulate forms, as TP includes fractions such as apatite, occluded (adsorbed) P, detrital P, particulate organic P (POP), soluble organic P, and inorganic P.

In the ocean, P is generally considered to limit production over geologic timescales (> 1000 yr) (Broecker 1982; Delaney 1998; Benitez-Nelson 2000), but a number of recent studies (Pahlow and Riebesell 2000; Wu et al. 2000; Yoshimura et al. 2007) indicate that P may limit production in the modern ocean as well. This is of particular interest because many of these studies link increasing P limitation to changes in climate (e.g., increasing di-nitrogen fixation) and anthropogenic effects (increase in nitrogen [N] inputs relative to P) (Karl et al. 1997; Tyrrell and Law 1997). For example, Sylvan et al. (2006) found that P limitation may sometimes occur in the Gulf of Mexico near the Mississippi River as a result of agricultural loading of N. Such nutrient loading, or coastal eutrophication, has been shown to contribute to estuarine and coastal algal blooms, which may subsequently lead to hypoxic (< 2 mg L$^{-1}$ O$_2$) or anoxic conditions. These changes in oxygen conditions may further influence the remineralization of particulate P, as bulk POP appears to be more efficiently remineralized under oxic conditions (Paytan et al. 2003; Faul et al. 2005; Benitez-Nelson et al. 2007), while particulate inorganic P (PIP) is more easily remineralized under anoxic conditions (Benitez-Nelson et al. 2007), relative to particulate organic carbon (POC). As such, understanding P transformations within coastal ecosystems, as well as those with suboxic and
anoxic waters, provides insight into the mechanisms that may control particulate P availability during ancient, modern, and future regimes.

The goal of this study was to examine P sources and particle fluxes to the low-oxygen (0.2–2 mg L\(^{-1}\)) deep waters (500 m) of the Guaymas Basin, Gulf of California (Thunell 1998), by specifically measuring the P composition and fluxes of sinking particles collected using a moored sediment trap, as well as in the underlying sediments. The Gulf of California is of particular interest because it maintains one of the most diverse biological communities in the world and supports an active and large fishing industry (Lluch-Cota et al. 2007). Recent studies, however, indicate that long-term changes in climate, coupled with increasing anthropogenic activities that include deforestation and agricultural runoff, are greatly reducing ecosystem health, as evidenced by increasing harmful algal blooms, declining oxygen concentrations at depth, and decreasing fish catch (Lluch-Cota et al. 2010). P composition is therefore also examined relative to the regional hydrography and climatology (e.g., the El Niño–Southern Oscillation [ENSO]) that occurred within the Gulf of California over the 6-yr time period (1991–1997) during which the sediment traps were deployed.

**Methods**

**Study area:** The Guaymas Basin, Gulf of California—The Gulf of California is an elongate marginal sea that exists between the mainland of Mexico and the Baja California peninsula (Fig. 1). Guaymas Basin is located within the central Gulf, a tectonically active region formed by seafloor spreading. On average, 70% of the annual precipitation occurs between August and September, coincident with a maximum in riverine discharge. The Gulf of California’s circulation is driven by a combination of sea surface winds, tides, and air–sea heat exchange. In general, strong winds from the northwest drive winter intensification of surface currents and cause upwelling along the eastern coast, increasing nutrient concentrations and, thus, biological production (Lavín et al. 2009). During this period, phytoplankton are dominated by diatoms and silicoflagellates that result in an increase in opal (bSi) fluxes to depth. During the summer, reversing winds increase regional precipitation and warmer waters enhance planktonic foraminifera and coccolithophores, which contribute to enhanced terrestrial and carbonate fluxes (Thunell et al. 1996). These seasonal cycles are in turn modified by episodic, mesoscale phenomena, such as eddies, jets, and meanders, and large-scale changes in regional climate modes, such as ENSO (Lavín et al. 2009; Lluch-Cota et al. 2010).

An intrusion of low-oxygen Pacific Intermediate Water into the Gulf of California between 500-m and 1000-m water depths (Bray and Robles 1991) moves northward into the Guaymas Basin and becomes even more depleted in oxygen with the oxidation of sinking organic material. As such, at this depth interval hypoxic to anoxic conditions exist that reduce bioturbation and facilitate the formation of laminated sediments, comprising alternating coccoliths (white bands) and lithogenic material (dark bands) (Thunell 1998).

**Sample collection and measurement**—Sinking particulate samples from the center of the Guaymas Basin (27° 53′ N, 111° 40′ W) were collected using a bottom-tethered and automated conical (area: 0.5 m\(^2\)) PARFLUX Mark 7G, 13-cup, time-series sediment trap from McLane Research Labs deployed at 500 m in depth. The sediment trap was covered by a polycarbonate baffle (2.5-cm diameter) to minimize swimmers and hydrodynamic effects. Two-week–long samples were continuously collected from February 1991 through September 1997, with trap deployment and recovery occurring every 6 months. As a result of trap malfunction, there exists a sampling gap between November 1992 and March 1993. Sediment traps were poisoned with a buffered 10 g L\(^{-1}\) sodium azide solution (for preservation of organic material). Samples were split using a precision rotary splitter, rinsed, and examined under a microscope to remove obvious swimming organisms not considered to be part of the particle flux. Samples were then freeze-dried and ground to grain sizes of less than 250 \(\mu m\) prior to analysis. Surface sediment samples were collected from four stations in the Gulf of California using a Mark IV box corer (BC) (Fig. 1). A subcore (10.2 cm in diameter, 50–65 cm in length) from each station was sliced into 0.2-cm (BC-50) or 0.5-cm (BC-43, BC-57, BC-10) sections, freeze-dried, and ground.

Each trap and sediment sample was subjected to a five-step sediment sequential extraction (SEDEX) procedure (Ruttenberg 1992; Anderson and Delaney 2000) that targets specific P pools: exchangeable P (step 1), oxide-
bound P (step 2), authigenic P (step 3), detrital P (step 4), and organic P (step 5). The sum of the P extracted during steps 1 through 4 is considered equivalent to the PIP pool. Step 2 extractants were analyzed for soluble reactive P (SRP) on a Lachat Quickchem 8000 Automated Ion Analyzer using Quickchem Method 31-115-01-4-A. Extracted solutions from the other steps were analyzed for SRP using the phosphomolybdate method described by Koroleff (1983). Each sample was run in duplicate through the SEDEX method, while blanks and a standard reference material (National Institute of Standards and Technology 1646a; estuarine sediment) were run in quadruplicate with each sample set in order to evaluate recovery and run-to-run variability. Samples were also analyzed using the acid-hydrolysis, high-temperature combustion method of Aspila et al. (1976) to quantify total particulate P (TPP) and PIP, with POP quantified by difference. This enables comparison with previous studies that have used this simpler procedure.

Samples have been previously analyzed for a range of other geochemical parameters, such as POC, particulate nitrogen (PN), calcium carbonate (CaCO₃), and bSi (opal) (Thunell 1998). POC and PN were measured using a Perkin-Elmer 2400 Elemental Analyzer following the procedure of Froelich (1980). Carbonate was determined using an automated, computer-controlled system in which samples are reacted under vacuum in 100% phosphoric acid and the resultant carbon dioxide is measured by a pressure transducer (Osterman et al. 1990). The wet chemical leaching techniques described by Mortloch and Froelich (1989) were used to determine opal or biogenic silica (bSi) concentrations. Total mass flux is a measure of the total sediment mass per sediment trap opening area per time in days that the trap remained open. Terrigenous content was estimated by subtraction of the biogenic components’ weights (carbonate, opal, and organic matter [2.5 × OC]) from the total sample weight.

**Results**

**Concentrations**—Average TPP, PIP, and POP concentrations measured using the method of Aspila et al. (1976) were not significantly different from those determined using SEDEX (Table 1). However, a more detailed methods comparison showed some distinct trends. SEDEX PIP concentrations were on average 11.8 ± 22.3% greater (and, hence, resulted in lower POP) than those determined using the method of Aspila et al. (1976). It is hypothesized that some organic P compounds are hydrolyzed during the earlier chemical extractions conducted in steps 1 through 4 of the SEDEX procedure. While SEDEX and Aspila TPP and PIP generally fall on a 1:1 line, POP is more variable,
likely as a result of the fact that POP is the difference between two large numbers (TPP and PIP). Given the additional information provided by the SEDEX method, the remaining results and discussion are focused on the SEDEX data.

SEDEX sediment trap results showed that TPP is comprised of 70% PIP, equally portioned among the exchangeable, oxide-bound, and authigenic fractions (Table 1). Core top TPP concentrations and compositions were similar, with only the cores' authigenic and organic P concentrations being significantly higher ($p < 0.005$) and lower ($p < 0.0005$), respectively, than those determined in sinking particles (Table 2). POC and PN concentrations also decreased significantly between the sediment trap and cores ($p < 0.05$). Average POC : POP ratios, however, were not significantly different between the sediment trap and underlying sediments, indicating that no preferential elemental remineralization of organic matter occurs at the seafloor. Once within the sediments, concentrations of POC, PN, and the various P fractions showed no significant changes with depth.

Two different seasons were defined in a manner similar to that described by Thunell (1998). The winter season was defined as November to March, coincident with periods of high surface chlorophyll $a$ concentrations and, presumably, higher rates of primary production. The summer season was defined as April to October and encompasses the period of highest precipitation. There were significant seasonal differences in the concentration of each component of the PIP pool ($p < 0.05$), with higher concentrations of all PIP components during the summer (Fig. 2). In contrast, there were no significant seasonal differences in POP concentrations ($p = 0.22$). There were also significant seasonal differences in concentrations of the other trap constituents, with higher concentrations of POC, carbonate, and terrigenous material in the summer and higher concentrations of opal in the winter ($p < 0.01$) (Fig. 2).

During May 1994, an anomalously high peak in TPP concentration occurred (244.8 $\mu$mol g$^{-1}$), with SEDEX concentrations significantly different from the summer seasonal average. Specifically, higher concentrations were observed in the exchangeable (42%), oxide-bound (47%), and organic (7%) P fractions. The %PIP composition (93%) was well above the time-series average (69% ± 15%). Of the other measured components, POC concentrations and fluxes were also elevated (10,500 $\mu$mol g$^{-1}$, 3078 $\mu$mol m$^{-2}$ d$^{-1}$) relative to the summer average (4841 $\mu$mol g$^{-1}$, 1903 $\mu$mol m$^{-2}$ d$^{-1}$).

**Fluxes**—Sediment trap fluxes were determined by multiplying individual constituent concentrations by the total mass flux. There were large-scale fluctuations in TPP fluxes, with higher fluxes driven in large part by higher mass fluxes (Table 2). Surprisingly high TPP and PIP fluxes were observed in the spring of 1992, the winter of 1993, and throughout the spring and summer of 1994 (Fig. 3). Most of these anomalous events are also driven almost entirely by high mass fluxes rather than by higher P concentrations. Authigenic and detrital P pools were strongly correlated with terrigenous fluxes (Fig. 4). No similar relationships

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### Table 2. Sediment core POC, PN, and SEDEX-derived particulate P concentrations, nd = no data.

<table>
<thead>
<tr>
<th>Station ID</th>
<th>Core depth (cm)</th>
<th>OC ((\mu)mol g$^{-1}$)</th>
<th>TPP</th>
<th>PIP</th>
<th>Exchangeable</th>
<th>Oxide-bound</th>
<th>Authigenic</th>
<th>Organic</th>
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<td>BC-10: 2644.98 N, 110°14.31 W</td>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<tr>
<td></td>
<td>0.5–1</td>
<td>3400</td>
<td>29.8</td>
<td>22.9</td>
<td>2.2</td>
<td>1.2</td>
<td>15.6</td>
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<td>30.2</td>
<td>22.7</td>
<td>2.7</td>
<td>1.4</td>
<td>17.1</td>
<td>7.5</td>
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<td></td>
<td>1.5–2.0</td>
<td>3517</td>
<td>29.8</td>
<td>23.5</td>
<td>2.9</td>
<td>1.7</td>
<td>17.5</td>
<td>6.3</td>
</tr>
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<td></td>
<td>Average</td>
<td>3486</td>
<td>30.1</td>
<td>23.5</td>
<td>2.6</td>
<td>1.6</td>
<td>17.9</td>
<td>7.0</td>
</tr>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>18.8</td>
<td>2.3</td>
<td>1.7</td>
<td>13.7</td>
<td>6.9</td>
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<td></td>
<td>Average</td>
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<td>27.7</td>
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<td>2.4</td>
<td>1.8</td>
<td>14.4</td>
<td>7.0</td>
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<tr>
<td>BC-50: 27.14 N, 112°42.51 W</td>
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<td>3242</td>
<td>27.5</td>
<td>21.2</td>
<td>2.5</td>
<td>1.5</td>
<td>13.8</td>
<td>7.3</td>
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<tr>
<td></td>
<td>0.5–1</td>
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<td>21.2</td>
<td>2.5</td>
<td>1.7</td>
<td>12.9</td>
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<td>20.2</td>
<td>2.4</td>
<td>1.8</td>
<td>14.4</td>
<td>7.0</td>
</tr>
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</table>

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were observed for the other PIP components (e.g., exchangeable \( r^2 = 0.02 \) and oxide-bound P \( r^2 = 0.10 \)). Of the other constituents measured in the basin, only opal fluxes showed significant seasonal differences, with higher fluxes in the winter \( (p < 0.001) \).

POC, POC:PN, and carbonate fluxes also showed no significant seasonal differences \( (p = 0.13, 0.76, \) and 0.07, respectively). POP fluxes, in contrast, were significantly higher during the winter \( (p < 0.01, 6.2 \pm 4.7 \mu \text{mol m}^{-2} \text{d}^{-1} \) vs. \( 4.4 \pm 2.9 \mu \text{mol m}^{-2} \text{d}^{-1} \)) as a result of a combination of slightly higher POP concentrations and mass flux. These higher POP fluxes were also associated with higher fluxes of bSi \( (p > 0.001, 0.28 \pm 0.18 \text{ g m}^{-2} \text{d}^{-1} \) vs. \( 0.14 \pm 0.08 \text{ g m}^{-2} \text{d}^{-1} \)). Note that these trends were examined over all winter and summer months combined rather than within each year.

Average POC:POP ratios were slightly higher than expected from traditional Redfield values of 106C:1P (POC:POP \( \sim 172, r^2 = 0.59 \)), with strong seasonal oscillations. During the summer, POC:POP ratios were \( \sim 221 (r^2 = 0.72) \) and decreased during the winter bloom months to \( \sim 158 (r^2 = 0.62) \) (Fig. 5). A logarithmic relationship between POC:POP ratios and opal fluxes was also observed, with POC:POP ratios decreasing during the winter, as opal fluxes significantly increased (Fig. 6). This resulted in a strong correlation between opal and POP fluxes throughout the year, with a better correlation during the winter. POP fluxes were also correlated with carbonate, but only during the summer months \( (r^2 = 0.52) \). An inverse exponential relationship between POC:POP ratios and mass fluxes was also observed \( (r^2 = 0.42) \).

In order to examine the role of large-scale climate modes such as ENSO, we compared P fluxes and other trap components measured during two El Niño periods, as defined by the National Weather Surface Climate Prediction Center (http://www.cpc.ncep.noaa.gov/products/analysis_monitoring/ensostuff/ensoyears.shtml), that lasted from April 1991 to June 1992 and from April 1994 to February 1995, relative to the rest of the time series. El Niño influenced sediment trap bulk PIP fluxes, and, specifically, exchangeable and authigenic P fluxes were significantly higher than non-El Niño influenced samples (Table 3). In contrast, POP fluxes showed no significant differences.

Discussion

Most studies of sinking particulate P in marine systems assume that the majority of the material is composed of organic P derived from biological production in surface waters (Benitez-Nelson 2000). However, recent evidence indicates that a significant fraction of the sinking TPP, at least in coastal regions, consists of several inorganic phases, potentially derived from other sources. These various components are in turn likely affected in very different ways by changes in water column biogeochemistry (Paytan et al. 2003; Benitez-Nelson et al. 2007). In the following sections we discuss sources, composition, and fluxes of the various P pools over seasonal and annual timescales within the Gulf of California.

\( P \) concentration and composition—Several studies have shown that sinking particulate matter captured within
moored sediment traps may be compromised by the loss of material to the dissolved phase (supernatants), but the magnitude of that loss can be highly variable depending on environmental conditions, poison used, and length of trap deployment (Buesseler et al. 2007). Unfortunately, no supernatant samples were available for the sediment traps analyzed in this study, a common occurrence for most sediment trap sampling programs. While it is tempting to correct our sediment trap analyses for these losses, the high variability and potential for changes in speciation during particle dissolution (e.g., conversion of organic to inorganic phases) make such corrections difficult at best. As such, all concentrations and fluxes reported here should be viewed as minimum estimates.

There have been very few studies that have examined the relative bioavailability or solubility of P within sinking particles. Yet sinking particulate P likely comprises a continuum of P phases with very different bioavailabilities that may change both temporally and spatially in response to the surrounding biogeochemical environment. We have therefore used the SEDEX approach to define the relative chemical reactivity of various P pools as an analog of particulate P lability within the water column. Using the SEDEX technique, the exchangeable P pool is simply that...
P which is easily released into the dissolved phase after agitation. As such, one might expect that this pool is the most bioavailable to marine organisms. Oxide-associated P is that P which is associated with iron and manganese oxides and can be formed in situ or transported into marine systems from surrounding soils. While this pool may also be bioavailable, it has distinct redox chemistry, such that with decreasing O$_2$ levels, this P may be released to the dissolved phase upon oxide reduction. Authigenic P is distinct from more relict detrital P phases in that authigenic P may be formed in situ, whereas detrital P is less reactive, likely derived from continental sources, and therefore remains uninvolved in the cycling of marine P. Finally, the organic P pool, which is often thought to dominate the sinking particle flux, may be more or less labile than the inorganic P pools depending on composition and biological community structure (e.g., simple sugars vs. lipids).

In general, P fluxes decrease exponentially with depth, and several studies (Paytan et al. 2003; Faul et al. 2005; Benitez-Nelson et al. 2007) have shown that the bulk POP appears to be more efficiently remineralized relative to POC under oxic conditions. Preferential remineralization of specific POP compounds under typical marine conditions appears to be the result of enzymatic hydrolysis of phosphate-esters, which dominates the particulate P pool, leaving behind more recalcitrant non–P containing compounds, such as carbohydrates (Paytan et al. 2003; Paytan and Mclaughlin 2007).

In order to assess if preferential remineralization of POP over POC was occurring in this study, we examined POC : POP ratios. On average, POC : POP ratios were substantially higher than those expected from traditional Redfield values of 106C : 1P, indicating preferential remineralization of POP relative to POC within the water column above 500 m. These results were similar to those found by Benitez-Nelson et al. (2007) in the Cariaco Basin, where the POC : POP molar ratio was 193 ($r^2 = 0.69$), with PIP fluxes averaging $52\% \pm 19\%$ of the TPP. Loh and Bauer (2000) also measured significantly higher POC : POP ratios (205–1099) in traps located at 3450 m, 3500 m, and 4050 m in the Eastern North Pacific, with comparable PIP fluxes (36–60% of the TPP flux).

This preferential remineralization of POP likely continues into the bottom. Sediments in close proximity to the Guaymas Basin sediment trap showed a higher %PIP composition of the TPP pool (74% ± 4%), even though overall TPP concentrations decreased with depth. This indicates (1) preferential loss of POP over PIP via biologically mediated remineralization or degradation to soluble P forms, (2) transformation of organic P into inorganic phases, and/or (3) an external source of PIP at depths below the sediment trap, perhaps from the lateral advection of reworked material from the sides of the basin.

Filippelli and Delaney (1995), Delaney and Anderson (1997), and Faul et al. (2005) all suggest that POP may be transformed into inorganic P phases, specifically authigenic P (e.g., sink-switching), within sediments or terrestrial soils. This occurs when authigenic carbonate fluorapatite is formed after P is released into pore waters as a result of remineralization of organic matter and/or reduction of iron by microbes (Ruttenberg and Berner 1993; Faul et al. 2005). Faul et al. (2005) and, more recently, Diaz et al. (2008) further suggest that this transformation occurs as particles sink throughout the water column. Our results indicate that this is indeed possible in Guaymas Basin, as well as between the sediment trap and underlying
sediiments; POP concentrations decrease by \( \sim 4 \mu \text{mol g}^{-1} \), while sedimentary authigenic P concentrations increase by \( \sim 5.2 \mu \text{mol g}^{-1} \) (Tables 1, 2).

The bioavailability of the PIP pool in Guaymas Basin is also difficult to assess. Both sediment traps and underlying sediments are dominated by a PIP pool that is composed of significant inorganic P components that are considered to be less available for direct biological uptake: oxide-associated, authigenic, and detrital P (Table 1). These results are similar to those of Paytan et al. (2003), who examined PIP concentrations in various sediment traps of varying designs and poisons located in open-ocean and coastal regions, and those of Faul et al. (2005), who examined sediment trap samples measured along the California coast over similar depth horizons (note that no corrections for particle dissolution were included in the Paytan et al. [2003] or Faul et al. [2005] studies). Closer inspection of the specific PIP pools shows a strong correlation between the terrigenous sediment trap fluxes and the authigenic and detrital P fluxes (Fig. 4). This indicates that aeolian deposition derived from increased precipitation, as well as river runoff, is a substantial source of authigenic and detrital P to the basin. The Guaymas Basin results therefore have important ramifications for our understanding of P export. For example, estimates of the potential effects of upwelling on particulate P export and dissolved nutrient chemistry may be significantly lower than expected based on measurements of TPP alone. These results may further influence our current understanding of nutrient sources in Gulf coastal regions, and, therefore, remediation as P derived from sewage outfalls is compositionally very different from P derived from agriculture or used in pesticides. Management efforts to reduce coastal eutrophication may be further influenced by changes in coastal hydrography, as anoxic waters may facilitate release of P associated with oxides as opposed to P associated with apatite or detrital material (Benitez-Nelson et al. 2007).

**Seasonal trends**—In the summer (August and September), \( \sim 70\% \) of the annual precipitation to the Guaymas Basin watershed occurs, resulting in a maximum in riverine discharge, although riverine flow has been substantially reduced and modified as a result of the building of dams along the rivers since 1940 (Baumgartner et al. 1991). Thus, much of the terrestrial material that reaches the basin during the summer may be from the atmosphere, either through dust or precipitation. In contrast, primary production tends to be significantly higher during the winter as a result of increased upwelling. The strong seasonal cycle in precipitation and mixing drives significant changes in P composition, concentration, and flux. Total PIP concentrations, as well as concentrations of the specific PIP components—exchangeable, oxide, authigenic, and detrital P—were all significantly higher during the summer relative to the winter seasons \( (p < 0.005; \text{Fig. 2}) \). Other components also showed this summer–winter trend, with higher summer concentrations of terrigenous material, carbonate, POC, and PN. Interestingly, neither POC/PN ratios or POP concentrations showed a significant difference between winter and summer months, although opal concentrations were significantly higher in the winter as a result of increased diatom production in surface waters (Thunell 1998). This again indicates that a large portion of the POP pool is rapidly remineralized in the upper 500 m. Other sources of POP to the basin during the summer cannot be ruled out, however. While river damming may

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**Fig. 6.** Logarithmic relationship between POC:POP sediment trap ratios and opal flux. The solid line represents a regression of the combined summer (black diamonds) and winter (open squares) data.
Table 3. Mean concentrations and fluxes of sediment trap constituents and relative %P during ENSO (1991–1994) and non-ENSO (1995–1997) years. All p values are derived using the SEDEX method. Significance (p values) was determined using a two-tailed, unpaired t-test assuming equal variance. Bolded numbers indicate a significant difference with p ≤ 0.05.

<table>
<thead>
<tr>
<th></th>
<th>ENSO (average ± SD)</th>
<th>Non-ENSO (average ± SD)</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (μmol g⁻¹)</td>
<td></td>
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<tr>
<td>POC</td>
<td>4900±1900</td>
<td>4100±900</td>
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</tr>
<tr>
<td>PN</td>
<td>650±220</td>
<td>570±130</td>
<td>0.009</td>
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<tr>
<td>CaCO₃*</td>
<td>13±4</td>
<td>13±5</td>
<td>0.99</td>
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<tr>
<td>Opal*</td>
<td>42±18</td>
<td>43±16</td>
<td>0.64</td>
</tr>
<tr>
<td>Terrigenous*</td>
<td>32±16</td>
<td>31±15</td>
<td>0.59</td>
</tr>
<tr>
<td>TPP</td>
<td>51±40</td>
<td>36±13</td>
<td>0.002</td>
</tr>
<tr>
<td>PIP</td>
<td>51±39</td>
<td>36±13</td>
<td>0.002</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>13.4±19.2</td>
<td>6.3±5.5</td>
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</tr>
<tr>
<td>Oxide bound</td>
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<td>8.6±7.4</td>
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</tr>
<tr>
<td>Authigenic</td>
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<tr>
<td>Detrital</td>
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<td>0.59</td>
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<tr>
<td>POP</td>
<td>11±3.1</td>
<td>11±3.2</td>
<td>0.92</td>
</tr>
<tr>
<td>Flux (μmol m⁻² d⁻¹)</td>
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<td></td>
</tr>
<tr>
<td>Mass flux*</td>
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<td>0.45±0.23</td>
<td>0.81</td>
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<tr>
<td>POC</td>
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<td>1750±800</td>
<td>0.33</td>
</tr>
<tr>
<td>PN</td>
<td>250±140</td>
<td>240±110</td>
<td>0.50</td>
</tr>
<tr>
<td>POC:PN</td>
<td>7.5±1</td>
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<tr>
<td>CaCO₃†</td>
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<td>0.052±0.023</td>
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<tr>
<td>Opal†</td>
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<tr>
<td>Terrigenous†</td>
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<tr>
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<tr>
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<td>0.02</td>
</tr>
<tr>
<td>Detrital</td>
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<td>1.0±0.9</td>
<td>0.08</td>
</tr>
<tr>
<td>POP</td>
<td>5.4±4.5</td>
<td>4.8±3.4</td>
<td>0.40</td>
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</table>

* wt%.
† g m⁻² d⁻¹.

decrease anthropogenic effects such as nutrient inputs from agriculture, aquaculture is becoming an increasingly important source of nutrients to coastal systems. Within the past two decades, shrimp aquaculture has rapidly increased in Mexico, with coastal lagoons along the Mexican Northwestern coast serving as major nursery grounds (Paez-Osuna et al. 1999). The organic matter produced in these shrimp lagoons results in the accumulation of a significant amount of nutrients, specifically P, within the underlying sediments in the nearshore (Paez-Osuna et al. 1999). This enriched sediment may subsequently be discharged into adjacent waterways or may remain in the lagoon system, where a portion is recycled back into the dissolved nutrient pool (Paez-Osuna et al. 1999). During high precipitation events, a portion of this coastal shallow sediment may be swept into the basin, depending upon the distance between the adjacent receiving waterways and other removal processes, such as sedimentation and biological uptake during transit.

In order to examine POP availability and the relative freshness of material, we examined POC:POP ratios on a seasonal basis. During the summer months, POC:POP ratios were ~ 221, and these ratios decreased during the winter bloom periods to ~ 158, mainly as a result of an increase in POP fluxes to depth (Fig. 5). By the same token, POC:POP ratios were logarithmically related to opal fluxes, such that POC:POP ratios decreased and approached Redfield proportions during bloom periods (Fig. 6). These lower POC:POP ratios during the winter again indicate that sinking organic material may be fresher, or less biodegraded, than that associated with non-bloom summer periods, during which POP may be preferentially remineralized relative to POC. A strong correlation exists between biogenic opal fluxes and POP fluxes ($r^2 = 0.63$). This observation, along with the strong inverse relationship between POC:POP ratios and opal and mass flux, implies that this may be due to ballast, by which higher opal and mass fluxes increase the rate at which organic matter is transported to depth (Hedges et al. 2001; Thunell et al. 2007, 2008). Thus, despite the fact that neither mass fluxes nor POP concentrations showed significant seasonal differences, the product of these two constituents, from which POP fluxes are derived, proved to be significantly different depending on the season. POP fluxes were also correlated with carbonate during the summer months ($r^2 = 0.52$). This indicates that carbonate, likely derived from a combination of both terrestrial material and coccoliths, is also an important transporter of POP to depth, but it is not as efficient in exporting fresher, undegraded material. Preferential remineralization of POP relative to POC ceases
once in the sediments, as indicated by the lack of any observable change in the POC : POP ratio between the sediment trap and core samples.

Interannual to decadal variability—Over the past century, sea surface temperatures within the Gulf of California have varied significantly, with a positive long-term warming trend (Lluch-Cota et al. 2010). Whether or not this is due to anthropogenic influences is unclear, but there does appear to be a periodicity in climate fluctuations that are related to both the Pacific Decadal Oscillation (PDO) and ENSO (Lluch-Cota et al. 2010). The Gulf of California experienced a prolonged, but relatively weak, El Niño period that lasted from April 1991 to June 1992 and again from April 1994 to February 1995. During El Niño conditions, strong winds that blow from the northwest during the winter are reduced as a result of changes in mid-latitude circulation. ENSO-related internal waves also enter the Gulf, but they are weakened by friction and dispersion as they travel northwest. Combined, these processes warm the Gulf by reducing upwelling along the eastern boundary and have been cited as causing decreased sea surface chlorophyll, collapse of the squid fishery, and failure of sardine reproduction (Lluch-Cota et al. 2010). Warming sea surface temperatures in the Gulf of California further increase evaporation and act as the primary source of moisture for the Mexican monsoon. As such, El Niño conditions also increase precipitation and riverine discharge and, thus, sedimentation in the region (Thunell 1998; Lluch-Cota et al. 2010).

In order to examine the effects of El Niño on our time series, we split the data set into El Niño— and non–El Niño— influenced periods (Table 3). During El Niño, POC, PN, and PIP concentrations and PIP fluxes were significantly higher, while POP, terrigenous, carbonate, and opal concentrations and fluxes remained unchanged. This indicates that while the composition of sinking particles became enriched in OC, N, and inorganic P phases, this enrichment was unlikely to be due to an increase in marine biological production at the surface. Rather, significant increases in PIP fluxes and elevated POC : PN ratios indicate a terrestrial origin and one that may differ from more typical terrestrial inputs. Strong relationships between terrestrial fluxes and authigenic and detrital P phases are apparent throughout the time series (Fig. 5). However, El Niño— influenced periods have significantly higher exchangeable and authigenic P fluxes and, to a lesser extent, oxide-associated P. Detrital P fluxes, like terrigenous fluxes, showed no significant differences. We therefore hypothesize that increases in wind, riverine discharge, and precipitation that occur in the region during El Niño are transporting more labile forms of inorganic P into the basin and that these P forms are perhaps associated with material from wider or different geographic areas. This hypothesis is consistent with century-long records of sediments from the Guaymas Basin, in which increases in terrestrial material are in good agreement with warm phases of the PDO and during a period of increased El Niños (Dean et al. 2004).

An alternative hypothesis is that reduced primary production in the Guaymas Basin results in less efficient uptake and transformation of inorganic P forms.

It is important to note here that there were also a number of episodic flux events recorded throughout the time series (Fig. 3). Most of these high flux events occurred during the El Niño periods, particularly in the spring of 1992 and throughout the spring and summer of 1994. One exception is the high flux event that occurred during a non–El Niño period in December 1993. Lack of hydrographic data precludes us from examining the causes of these high flux events in detail. However, they are likely due to a combination of mesoscale features, such as eddies and filaments, that enhance biological production of P at the surface vs. increased river runoff due to high-precipitation events and possible deep-water advection of material from the sides of the basin due to turbidity currents that enhance PIP (Lluch-Cota et al. 2007, 2010; Lavín et al. 2009). High POP, POC, PN, and opal fluxes and a close-to-Redfield POC : POP ratio in conjunction with high PIP and mass fluxes in December 1993 indicate a combination of terrestrial and biological sources. In contrast, low opal fluxes and high PIP fluxes and %PIP observed within the sediment trap samples in the summer of 1994 (Fig. 3) indicate terrestrial sources and are consistent with episodically large rainfall events that occurred throughout the region during that time period, as measured in the nearby city of Hermosillo, Mexico (Hermosillo International Airport, 29°5′N, 110°58′W).

The implications of higher PIP inputs into the Gulf of California during El Niño are difficult to assess as a result of the complex interplay between biological activity, physical mixing, and terrestrial inputs. One might expect that increasing terrestrial inputs of biologically available P forms, such as exchangeable P, promote phytoplankton production in surface waters or influence the composition of the biological community. Yet such effects are difficult to deduce with our limited data. While El Niño was prolonged during the early 1990s, it is not considered one of the stronger El Niño periods of the last 50 yr. During the more intense El Niños of 1982–1983 and 1997–1998, sea surface temperatures associated with increasing stratification and decreased surface pigment concentrations in the Gulf of California were observed (Lluch-Cota et al. 2010). There was also significant spatial variability in phytoplankton biomass in the southern Gulf, and while primary production in the central and northern Gulf remained relatively stable, diatom biomass decreased and the occurrence of harmful algal blooms diminished (Lluch-Cota et al. 2010). Another potential outcome of increasing stratification during prolonged El Niño conditions is an increase in N2 fixation and expansion of the oxygen minimum zone. Both directly influence the P cycle, as N2-fixing organisms are more likely to be P limited and decreasing oxygen levels in the subsurface are more likely to reduce oxide-associated particulate P into more bioavailable dissolved P forms.

In summary, analyses of sediment trap samples for P composition and flux in the Guaymas Basin provides significant insight into the physical and biogeochemical dynamics of P in this marine system. Our results indicate that PIP is a substantial fraction of the TPP pool, which compares well with the results of previous, albeit limited,
studies (Loh and Bauer 2000; Paytan et al. 2003; Benitez-Nelson et al. 2007). The general increases in PIP during the summer months throughout the study indicate that increased winds and precipitation and, hence, terrestrial input increases TPP fluxes, specifically detrital and authigenic phases. Furthermore, large-scale increases in TPP fluxes during El Niño years indicate a complex interplay between riverine or aeolian inputs and increases in primary production, as indicated by changes in elemental ratios and PIP and POP concentrations and fluxes. While higher PIP concentrations during El Niño are likely associated with an increase in terrestrial material from storm or wind events, enhanced POP fluxes are likely due to a combination of terrrestrially derived nutrients and episodic storm-induced upwelling.

A closer examination of the POP pool shows increased fluxes during winter bloom months (decreased POC:POP ratios between November and March), strongly correlated with increased fluxes of opal and coincident with an inverse relationship between POC:POP ratios and opal flux. This indicates rapid transport of organic material to depth, perhaps as a result of increased ballasting (Hedges et al. 2001; Armstrong et al. 2002; Thunell et al. 2008) or other protective measures that are minimized in the summer because of a lack of diatom blooms. Thus, phytoplankton blooms dominated by diatoms may play an important role in the transport of fresher or more labile POP compounds to depth. Closer inspection of specific POP compounds (Miyata and Hattori 1986) would help decipher some of this complexity, providing much needed insight into sources of P to sediments and potential P sequestration mechanisms involved in the conversion of more labile forms into less bioavailable P species (Filippelli and Delaney 1995; Delaney and Anderson 1997; Diaz et al. 2008).

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