

# Importance of Terrestrially-Derived, Particulate Phosphorus to Phosphorus Dynamics in a West Coast Estuary

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**ABSTRACT:** Allochthonous inputs of suspended particulate matter from freshwater environments to estuaries influence nutrient cycling and ecosystem metabolism. Contributions of different biogeochemical reactions to phosphorus dynamics in Tomales Bay, California, were determined by measuring dissolved inorganic phosphorus exchange between water and suspended particulate matter in response to changes in salinity, pH, and sediment redox. In serum bottle incubations of suspended particulate matter collected from the major tributary to the bay, dissolved inorganic phosphorus release increased with salinity during the initial 8 h; between 1-3 d, however, rates of release were similar among treatments of 0 psu, 16 psu, 24 psu, and 32 psu. Release was variable over the pH range 4-8.5, but dissolved inorganic phosphorus releases from sediments incubated for 24 h at the pH of fresh water (7.3) and seawater (8.1) were similarly small. Under oxidizing conditions, dissolved inorganic phosphorus release was small or dissolved inorganic phosphorus was taken up by particulate matter with total P content  $<50 \mu\text{moles P g}^{-1}$ ; release was greater from suspended particulate matter with total phosphorus content  $>50 \mu\text{moles P g}^{-1}$ . In contrast, under reducing conditions maintained by addition of free sulfide ( $\text{HS}^-$ ), dissolved inorganic phosphorus was released from particles at all concentrations of total phosphorus in suspended particulate matter, presumably from the reduction of iron oxides. Since extrapolated dissolved inorganic phosphorus release from this abiotic source can account for only 12.5% of the total dissolved inorganic phosphorus flux from Tomales Bay sediments, we conclude most release from particles is due to organic matter oxidation that occurs after estuarine deposition. The abiotic, sedimentary flux of dissolved inorganic phosphorus, however, could contribute up to 30% of the observed net export of dissolved inorganic phosphorus from the entire estuary.

## Introduction

The timing, magnitude, and degradability of particulate carbon, nitrogen, and phosphorus inputs to estuaries may be significant forcing functions for ecosystem metabolism (Hopkinson in press). Interactions among different biogeochemical processes influencing the fate of nutrients input to estuaries as suspended particulate matter (SPM), however, are not understood clearly. For example, particulate forms of phosphorus (P), a major limiting nutrient in freshwater ecosystems,

are delivered to coastal marine environments primarily from terrigenous sources (Froelich 1988). Upon delivery to estuaries from watershed streams and rivers, SPM and associated P experience large changes in salinity, pH, and sometimes redox potential. Changes in these environmental variables influence the exchange of inorganic phosphorus (IP) between water and inorganic and organic particulate matter (Carpenter and Smith 1984; Eastman and Church 1984; Kunishi and Glotfelty 1985; Fox 1989; Lebo 1991). Because the amount of IP taken up and released by biotic reactions is relatively small in estuarine environments with high seston concentrations, nonconservative behavior of IP is attributed exclusively to abiotic changes in P sorption (Pomeroy et al. 1965; Fox et al. 1985,

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1986). A phosphate buffer mechanism is hypothesized to maintain dissolved inorganic phosphorus (DIP) concentrations in equilibrium with P sorbed onto inorganic surfaces (Barrow 1983; summarized by Froehlich 1988).

In other estuarine environments, however, where both biotic and abiotic processes strongly influence inorganic phosphorus exchange with particulates (Lucotte and d'Anglejan 1983; Sharp et al. 1984; Lebo and Sharp 1992; Conley et al. in press), the phosphate buffer is less apparent. Potential P sinks in SPM that could depress DIP concentrations include biological uptake (primary production) and chemical removal (sorption, mineral precipitation). Sources of P in SPM that could elevate DIP concentrations include biological generation (decomposition of allochthonous organic matter, internal cycling of autochthonous production) and geochemical release (desorption, mineral dissolution). With so many reaction pathways involving DIP in these estuaries, the potential importance of abiotic P exchange is difficult to determine.

When the magnitude of abiotic or geochemical reactions involving SPM is small relative to biological activity, nonconservative changes in DIP concentration may be attributed to biotic processes (Nixon and Pilson 1984; Smith et al. 1987, 1991). Under these circumstances, some estuaries that generate DIP in excess of amounts predicted by seawater dilution are considered net heterotrophic, because the excess DIP is assumed generated by biotic processes: more organic matter is consumed in the system (releasing DIP) than is produced (removing DIP). Smith et al. (1991) have used an analysis based on DIP and carbon budgets to infer net heterotrophy in Tomales Bay, a small estuary in California; carbon-budget analysis of the metabolism of many other coastal ocean systems indicates net heterotrophy is common (Smith and Hollibaugh 1993).

Use of nonconservative DIP flux as a measurement of system metabolism is attractive because, unlike other nutrients important to biological production and respiration (C, O, N), the P cycle has no major gaseous component. Thus, exchanges of inorganic phosphorus are limited to those between water and dissolved and particulate reservoirs. One limitation of using P (or nitrogen) as a unit of metabolic currency is that quantifying inputs and outputs of water and constituents is not always possible for estuarine systems. Perhaps more importantly, even in hydrologically simple systems where this problem can be solved, there remains the additional problem of testing the assumption that abiotic contributions to nonconservative DIP flux are insignificant. Often, budgets of other constituents

must be used to test indirectly the validity of assuming that P exchanges mediated by inorganic reactions are small relative to organic reactions (Smith et al. 1991).

With these considerations in mind, an experimental study was initiated to determine the behavior of P in terrestrially-derived particulate matter under conditions of estuarine mixing. We chose the Tomales Bay estuary as the site for the study, where the contribution of abiotic exchange reactions to the DIP budget of the ecosystem is believed to be small (Smith et al. 1987, 1991; Dollar et al. 1991). We measured DIP exchange between water and allochthonous SPM exposed to gradients in pH and salinity. Since most SPM derived from the watershed is eventually buried in the sediments of the bay, we also measured the exchange of DIP with particles under oxidized and reduced conditions. Our experiments were designed to measure biotic and abiotic reactions influencing inorganic P dynamics in a United States West Coast estuary, toward the goal of determining the importance of terrestrially-derived, particulate phosphorus to estuarine metabolism.

## Materials and Methods

### STUDY SITE

We completed our study in Tomales Bay, California (Fig. 1); an 8-yr time series of data on total particulate phosphorus loading, water budgets, and water-column and benthic metabolism has been collected as part of Land Margin Ecosystems Research (LMER). The inner portion of Tomales Bay (Fig. 1) is net heterotrophic, demonstrated by nonconservative, net DIP and DIC fluxes from the estuary from 1987 to 1994 inclusive (Smith et al. 1991; S. V. Smith personal communication). Supporting information on particulate loading and sedimentation in the bay indicates the primary allochthonous source of particulate phosphorus is terrigenous organic matter, the oxidation of which supports community respiration rates in excess of primary production rates (Smith et al. 1991).

A single, gauged stream flowing year-round (Lagunitas Creek, Fig. 1) drains 52% of the Tomales Bay watershed, and is the source of about 75% of the sediment input to the inner bay (Oberdorfer et al. 1990). Many ungauged, ephemeral streams, which flow during the rainy wet season—November to May—contribute roughly 25% of the annual surface water runoff and sediment budgets for the inner bay. As part of the sampling program for the LMER project, suspended particulate material in Lagunitas Creek was sampled at regular bimonthly intervals year-round, and during storms and runoff events, for determinations of SPM, and C, N, and P content of SPM.

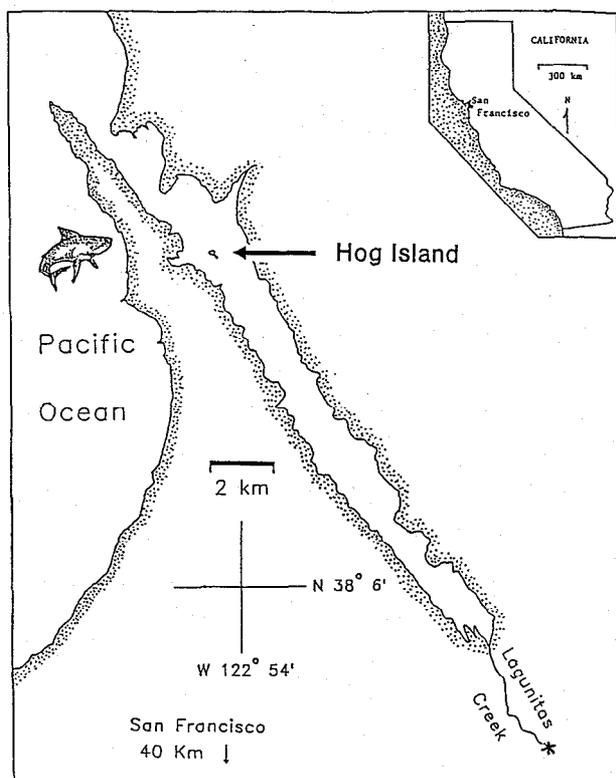


Fig. 1. Tomales Bay site map (after Hopkins 1993). Suspended particulate material and "resuspended" sediment samples were collected from Lagunitas Creek (\*), the major source of freshwater runoff to the inner portion of the bay (southeast of Hog Island).

#### Particulate Samples Collection and Phosphorus Analysis

Samples of Lagunitas Creek SPM were obtained during wet and dry seasons in 1992–1993 by filtration onto glass-fiber (Whatman GF/F) filters. To characterize SPM used for each batch incubation experiment, 12 tared filters and collected sediments were freeze-dried, then weighed, ashed at 500°C and reweighed for determinations of total SPM and organic matter content. Total particulate phosphorus was determined from six of these samples using the ashing-acid hydrolysis extraction technique of Solorzano and Sharp (1980).

The composition of SPM in Lagunitas Creek varies seasonally, and is more inorganic during the wet season (November–May; Table 1). During the dry season we also collected "resuspended" sediments from the creek, to examine the behavior of sediments with a lower organic content more typical of SPM collected during the wet season. We stirred sediments off the creek bottom and collected water plus resuspended sediments carried downstream by creek flow (Fig. 1). Samples of these "resuspended" sediments were processed

TABLE 1. Seasonal variation in organic and P content (% dry weight) of sediments in Lagunitas Creek, the main tributary to inner Tomales Bay.

Sediment Type	Month	% Organic	% Phosphorus
Suspended	July	53	0.35
	September	68	0.36
	November–May <sup>a</sup>	≈15	≈0.10
Resuspended	May	10	0.03
	July	12	0.08
	September	13	0.05

<sup>a</sup> Summary data, averaged throughout the rainy season, for suspended sediment load from Lagunitas Creek, from LMER research (S. V. Smith personal communication).

and analyzed as for suspended sediments. Our intent was to measure IP exchange of "resuspended" sediments for comparison with SPM collected during periods of high and low water flow. We suspect, however, that most SPM transported by creeks during the rainy season is derived from erosion in the watershed and not directly from resuspension of creekbed sediments.

#### Incubation Experiments

The general experimental protocol was to perform batch incubations of SPM and "resuspended" sediments collected on filters (Table 2). Capped serum bottles containing filters plus fresh SPM or "resuspended" sediments (5–25 mg dry wgt) were filled with 20 ml of filtered water of different chemical compositions, depending on treatment group, then incubated on a shaker table in the dark. Incubation temperatures were 15–20°C, higher than field temperatures of 5–15°C. At each sampling time, three bottles per treatment group were removed, and the water was filtered and analyzed for DIP.

We examined the effect of increasing salinity on IP release by incubating SPM samples for up to 3 d, using salinity treatments of 0 psu (deionized water, DIW), 0 psu (ambient creek water), 16 psu, 24 psu, and 32 psu (seawater diluted with creek water). The effect of pH on IP release was determined by completing 24-h incubations of fresh SPM in filtered seawater from pH 4 to pH 8.5, at 0.5 pH unit increments. Seawater pH in each treatment group initially was adjusted upward or downward using NaOH or HCl, but no attempt was made to adjust pH during the incubations. Finally, the effect of redox on IP exchange was determined by incubating SPM or "resuspended" sediment samples in 32 psu seawater (pH 8.1) under oxic or anoxic conditions. Anoxic conditions were obtained by purging the treatment water with N<sub>2</sub> gas, then adding hydrogen sulfide (HS<sup>-</sup>) to a final concentration of 0.5 mM. This treatment was designed to facilitate the reaction of reducible iron oxy-hy-

TABLE 2. Experimental conditions for sediment incubations. SPM = Suspended Particulate Matter.

Environmental Variable	Incubation Conditions			Sediment Types	Incubation Times
	Salinity	pH	Redox		
Salinity	0–32 psu	7.3–8.1	Oxic	SPM	0–72 h
pH	32 psu	4–8.5	Oxic	SPM	24 h
Redox	32 psu	8.1	Oxic, Anoxic	SPM and “Resuspended”	0–144 h

dioxides in the sediments with sulfide. Most particulate matter delivered from the watershed and buried in Tomales Bay spends several years in the upper bioturbated zone, where rates of sulfate reduction (and sulfide production) are highest (Chambers et al. 1994). Reduction of iron hydroxides can lead to release of inorganically bound P (Callender 1982; Strom and Biggs 1982; J. C. Cornwell unpublished data).

Water samples from anoxic treatment groups were filtered, acidified, bubbled with  $N_2$ , and adjusted to pH  $\approx 7$  to remove possible sulfide interference with the colorimetric analyses of DIP and ammonium,  $NH_4^+$  (Parsons et al. 1984). Analytical precision for dissolved nutrient analyses was better than  $\pm 5\%$ . Because DIP can be generated or taken up by both biotic and abiotic reactions, we used  $NH_4^+$  production as a measure of biotic decomposition of organic matter. With this method, we made the assumption that changes in  $NH_4^+$  concentrations due to nitrification were small relative

to ammonification (see Results and Discussion); we also determined that ammonium sorption to the acid-washed, glass walls of the serum bottles was negligible. Based on 16:1 stoichiometry of N:P in suspended organic matter (Vink 1994), we calculated the amount of DIP generated by the decomposition of organic matter.

Time-course changes in IP release to or removal from the incubation water were determined by subtracting the initial concentration of DIP in that water from concentrations measured at each incubation time. IP fluxes from SPM and “resuspended” sediments were plotted with respect to weight and total P content of the SPM or “resuspended” sediments.

## Results and Discussion

### EFFECT OF SALINITY ON RELEASE OF INORGANIC PHOSPHORUS

For 3-d incubations of suspended sediments, IP release from SPM increased with increasing salinity (Fig. 2). The smallest releases were seen for SPM resuspended in ambient creek water, which initially took up IP from solution. For all other treatments, including deionized water, large IP releases were observed after just 8 h. From 8 h to 72 h, the rates of IP release were similar among creek water and higher salinity treatments (Fig. 2).

Both inorganic and organic reactions could contribute to the observed release of IP from SPM incubated in solutions of different salinities. We interpret the initial, 8-h release of P from SPM as an abiotic effect possibly involving three factors: the phosphate buffer mechanism—desorption of P because of exposure to lower concentrations of DIP in seawater and deionized water (ambient creek-water, seawater, and deionized water DIP concentrations of  $3.4 \mu M$ ,  $1.1 \mu M$ , and  $0 \mu M$ , respectively); desorption of P from clay minerals, displaced by high concentrations of anions ( $SO_4^{2-}$ ,  $OH^-$ ,  $F^-$ ,  $B(OH)_4^-$ ) competing for sorption sites (Froelich 1988; Caraco et al. 1989); or lysis of cells and release of DIP (Callender 1982; Lucotte and d'Anglejan 1983). Although slower, long-term abiotic release is possible (Froelich 1988), the continued release of IP over 8–72 h that was observed for all salinity treatments could also reflect biotic miner-

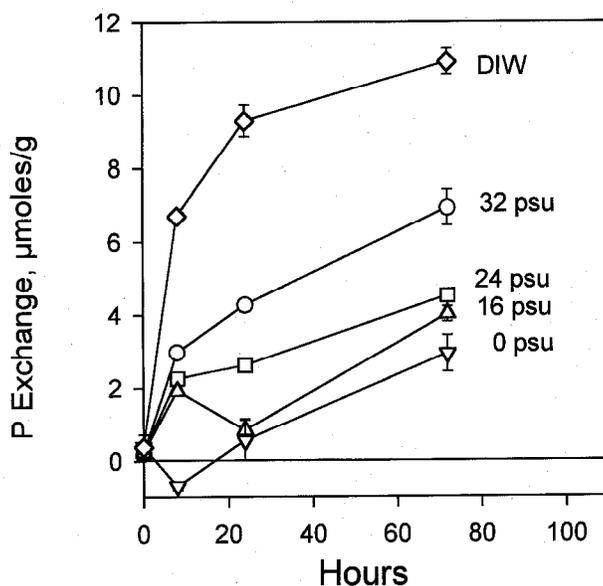


Fig. 2. Effect of salinity (psu = practical salinity units) on average IP release ( $\pm$ SE) from suspended particulate material collected during the rainy season and incubated up to 72 h ( $n = 3$ ). Effect of incubation in deionized water (DIW) is also shown. Error bars where not evident are smaller than the symbols.

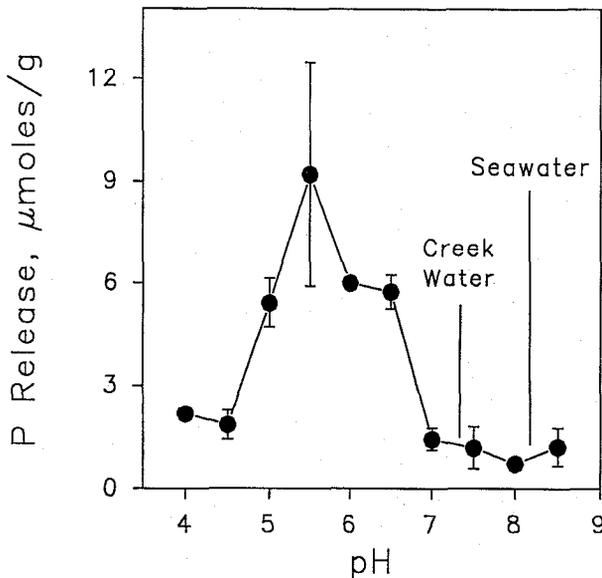


Fig. 3. Effect of pH on average inorganic phosphorus release ( $\pm$  SE) from suspended particulate material incubated for 24 h ( $n = 3$ ). Error bars where not shown are smaller than the symbols. The difference in inorganic phosphorus release from sediments incubated at the pH of seawater and creek water (highlighted on graph) is small relative to the difference throughout the pH range 4 to 8.5.

alization of organic matter and gradual release of DIP. An increase in ammonium concentrations would have supported this explanation but was not measured.

#### EFFECT OF pH ON RELEASE OF INORGANIC PHOSPHORUS

For the completed 24-h incubations of SPM in seawater solutions of pH 4–8.5, IP release was variable; most IP was released from SPM within the pH range of 5–6.5 (Fig. 3). At lower and higher pH, the releases were smaller. Increasing release of P from different mineral phases with increasing pH would be expected if at low pH, mineral surfaces were positively charged; increasing pH would reverse the positive charges on mineral surfaces, leading to phosphate release (White and Taylor 1977; Carpenter and Smith 1984; Lebo and Sharp 1993). In our experiment, however, IP release was less at pH > 6, indicating processes other than simple sorption-desorption reactions were affecting IP release. Lucotte and d'Anglejan (1988) found little effect of pH on phosphate adsorption onto SPM throughout the St. Lawrence estuary, and Seitzinger (1991) found significant IP release from incubated estuarine sediments of the Potomac River did not occur below pH 9.5. These observations highlight the complexities in determining specific biotic and abiotic components of SPM most influ-

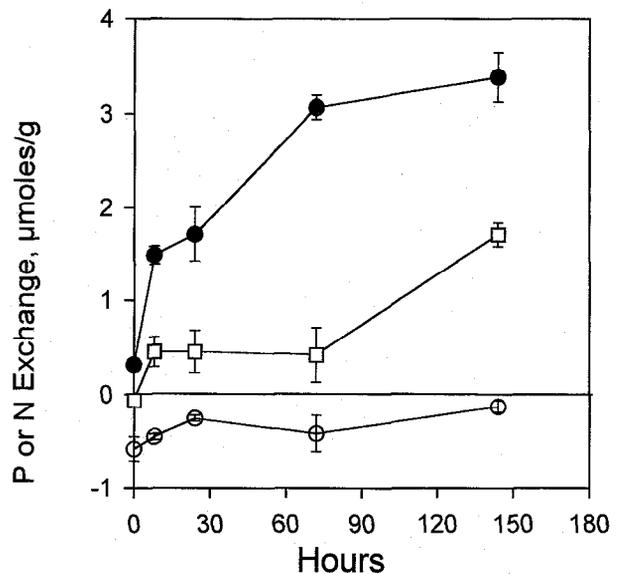


Fig. 4. Average inorganic phosphorus release ( $\pm$  SE) from "resuspended" sediments incubated in seawater under oxic (open circles) and anoxic (filled circles) conditions, May 1993. Under anoxic conditions, inorganic phosphorus release should reflect contributions from both degradation of organic matter and reduction of iron oxides. Average ammonium release ( $\pm$  SE) measured under oxic conditions (open squares), was used to estimate oxidation of organic matter.

enced by solution pH. In our experiments, the observed difference in IP release between sediments incubated at the pH of creek water (7.3) and seawater (8.1) was quite small (Fig. 3). At least within the range of natural environmental conditions, pH did not appear to influence strongly the release of IP from suspended sediments.

#### EFFECT OF OXIDATION STATE ON RELEASE OF INORGANIC PHOSPHORUS

Anoxic incubation of "resuspended" sediments in the presence of sulfides led to release of IP, much of the release occurring within the first 24 h (Fig. 4). In contrast, IP was not released from sediments under oxic conditions, even after 144 h. We suspect the observed production of black iron monosulfides in anoxic incubations was due to reduction of iron oxides in the resuspended sediments, with a concomitant release of sorbed IP. Likewise, we attribute IP uptake in oxic incubations primarily to sorption onto iron oxides.

We measured the production of  $\text{NH}_4^+$  in oxic incubations, as a proxy for organic matter mineralization, to determine the extent to which biotic reactions were contributing to the observed release of IP in anoxic incubations. Anoxic incubations were not used, since sulfide poisoning probably inhibits bacterial decomposition of organic matter. The potential loss of  $\text{NH}_4^+$  by nitrification is clim-



son when freshwater runoff is low, SPM transported into Tomales Bay from Lagunitas Creek is composed primarily of organic matter with high %P (>0.2%, Table 1), probably freshwater phytoplankton and other labile material. In addition to cell lysis due to the salinity effect (Fig. 2), oxidation of this material contributes substantially to IP release from SPM during the dry season.

Most sediment inputs to Tomales Bay, however, occur during the rainy season and include a higher percentage of inorganic matter, with a lower %P (Table 1). During winter runoff, organic matter may be more refractory, since presumably much labile material has decomposed on land. Inorganic phosphorus produced under oxic conditions by organic matter oxidation may be sorbed to iron oxides and other inorganic substances which make up the bulk of the suspended sediments. Under anoxic conditions, then, more IP release occurs due to abiotic release from inorganic sediments. At sediment P concentrations less than 32  $\mu\text{moles g}^{-1}$  (0.1% P), an average of 3.2  $\mu\text{moles P}$  is released per gram of sediment after 6 days (Fig. 6). This estimate is calculated from anoxic releases of IP measured from both suspended and resuspended sediments, which may not be analagous (see Methods). The estimate in fact may be conservative, since in many experiments abiotic IP release was larger for suspended sediments with higher %P.

#### FATE OF PARTICULATE PHOSPHORUS TRANSPORTED TO TOMALES BAY

Suspended particulate material and "resuspended" sediments transported to Tomales Bay are exposed to changes in salinity and pH, which may lead to release of IP (Figs. 2 and 3). Since most sediment transport to the estuary occurs during winter runoff when water residence time in the bay is low, however (Smith et al. 1991), any changes in DIP in the estuary due to changes in salinity and pH would be a transient phenomenon, that is, IP would be released and exported rapidly from the estuary. Biological activities are low at this time of year, so the influence of winter IP release would not be substantial. Further, nonconservative increases in DIP concentrations in Tomales Bay are most evident during the dry summer season when particulate phosphorus runoff is negligible (Smith et al. 1991). Neither salinity nor pH changes are important environmental factors influencing the summer, net export of DIP from Tomales Bay.

Suspended particulate material and "resuspended" sediments transported to Tomales Bay are not exported to the coastal ocean but eventually are deposited in the estuary (Plant et al. 1994). Organic matter in these sediments can be decom-

posed via oxic and anoxic respiration, leading to net DIP production throughout the year. Studies have shown or modelled this long-term oxidation process as a function of organic matter lability (Westrich and Berner 1984; Burdige 1991), and nearly 50% of the total sediment P is bound to organic phases (Vink 1994). Organic matter oxidation obviously continues beyond the incubation times used in the present experiments, so the long-term release of P from organic sediment sources could be substantial. Further, in anoxic zones of sulfate reduction and iron-sulfide mineral formation, iron oxides derived from the watershed and deposited in bay sediments can be reduced and release IP. The average P content in SPM delivered to Tomales Bay is 0.1% P, or 32  $\mu\text{moles P g}^{-1}$  sediment, and the annual, baywide phosphorus load calculated from rating curves for Lagunitas Creek, is 0.5  $\text{mmol P m}^{-2} \text{d}^{-1}$  (15 year average, S. V. Smith personal communication). Although the total amount of IP release from oxidation of organic matter in sediments cannot be addressed with short-term incubations, we have shown that under anoxic conditions, abiotic IP release from sediments with total P content less than 32  $\mu\text{moles P g}^{-1}$  averages about 3.2  $\mu\text{moles P g}^{-1}$  sediment (Fig. 6). This release, which we attribute to P desorption from reduced iron oxides, is 10% of the average P content in SPM delivered to Tomales Bay. Using a multiple P extraction technique (Ruttenberg 1992), Vink (1994) similarly determined that 5–12% of total P in Lagunitas Creek SPM was composed of Fe-bound, exchangeable P. If we assume 10% of the total P load can be released from sediments by iron reduction and P desorption (i.e., P is not resorbed), this amounts to potential DIP flux from inorganic sediments to the water column of about 0.05  $\text{mmol m}^{-2} \text{d}^{-1}$  (Table 3).

Are rates of sulfide-driven iron reduction in Tomales Bay sediments sufficient to realize the full potential abiotic generation of IP? Although gross rates of sulfate reduction are high, most of the sulfide produced in the sediments is reoxidized before burial, a consequence of extensive bioturbation to depths of 30 cm or more (Joye and Paerl 1993; Chambers et al. 1994). Net reduction of iron oxides in Tomales Bay sediments, however, is recorded by accumulation with depth of reduced iron minerals, primarily pyrite (Chambers et al. 1994). IP from abiotic generation (P desorption from reduced iron) may be released concomitantly with organic matter oxidation (i.e., gross sulfate reduction mobilizes DIP directly from organic matter and indirectly from sulfide reaction with iron).

We use the net reduction of iron oxides in the sediments to estimate the relative contributions of abiotic and biotic reactions to DIP flux from the

TABLE 3. Contribution of inorganic exchange reactions to the observed net flux of DIP from Tomales Bay.

Sediment P-load to Tomales Bay <sup>a</sup>	32.3 $\mu\text{moles P g}^{-1}$ sediment
DIP release due to iron reduction and desorption reactions <sup>b</sup>	3.2 $\mu\text{moles P g}^{-1}$ sediment
Percentage of P-load which can be released by abiotic exchange	10%
Watershed input of particulate P <sup>c</sup>	200 $\text{mmol m}^{-2} \text{yr}^{-1}$
Potential P desorption and release of DIP by abiotic exchange	20 $\text{mmol m}^{-2} \text{yr}^{-1} \approx 0.05 \text{mmol m}^{-2} \text{d}^{-1}$
Estimated P desorption by net iron reduction <sup>d</sup>	0.03 $\text{mmol m}^{-2} \text{d}^{-1}$
Net DIP flux from Tomales Bay <sup>e</sup>	$\approx 0.1 \text{mmol m}^{-2} \text{d}^{-1}$
Estimated contribution of abiotic P exchange to net DIP flux	30%

<sup>a</sup> Weighted-average concentration of P in SPM is 0.1%.

<sup>b</sup> This study.

<sup>c</sup> 15-yr average P load from watershed.

<sup>d</sup> See Discussion.

<sup>e</sup> Smith et al. 1991.

sediments of Tomales Bay. Total DIP release from the sediments is on average  $0.24 \text{mmol P m}^{-2} \text{d}^{-1}$ , and represents DIP released from both biotic and abiotic reactions (Dollar et al. 1991). Pyrite formation associated with organic matter oxidation by net sulfate reduction reduces  $1.5 \text{mmol Fe m}^{-2} \text{d}^{-1}$  (Chambers et al. 1994). From 1N HCl extractions, the Fe:P ratio in Tomales Bay sediments is roughly 50:1 (R. M. Chambers unpublished data), so that abiotic DIP production in the sediments could contribute about  $0.03 \text{mmol P m}^{-2} \text{d}^{-1}$  to the total DIP flux (less than the full abiotic potential, Table 3). We estimate abiotic P release is only 12.5% of the total DIP flux from the sediments; most of the DIP flux from the sediments is from direct oxidation of organic matter.

Finally, Smith et al. (1991) calculate a net DIP flux from inner Tomales Bay of about  $0.1 \text{mmol P m}^{-2} \text{d}^{-1}$ , which they interpret as due solely to organic matter oxidation (Table 3). Our estimate of abiotic DIP release from the sediments ( $0.03 \text{mmol P m}^{-2} \text{d}^{-1}$ ) is 30% of the observed net DIP flux from Tomales Bay. With our estimate, the amount by which community metabolism exceeds primary production in Tomales Bay is about two-thirds as large as has been reported (Smith et al. 1991). Our results support the contention that Tomales Bay is a net heterotrophic estuary. The ecosystem, however may not be as strongly heterotrophic because almost one-third of the net DIP flux, assumed a valid proxy for net organic matter oxidation, is account-

ed for by abiotic release of DIP from inorganic sediments (Table 3).

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