



Phosphorus distribution in sinking oceanic particulate matter

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Abstract

Despite the recognition of the importance of phosphorus (P) in regulating marine productivity in some modern oceanic systems and over long timescales, the nature of particulate P within the ocean is not well understood. We analyzed P concentration in particulate matter from sediment traps and selected core tops from a wide range of oceanic regimes: open ocean environments (Equatorial Pacific, North Central Pacific), polar environments (Ross Sea, Palmer Deep), and coastal environments (Northern California Coast, Monterey Bay, Point Conception). These sites represent a range of productivity levels, temporal (seasonal to annual) distributions, and trap depths (200–4400 m). P associations were identified using an operationally defined sequential extraction procedure. We found that P in the sediment traps is typically composed of reactive P components including acid-insoluble organic P (~40%), authigenic P (~25%), and oxide associated and/or labile P (~21%), with lesser proportions of non-reactive detrital P depending on location (~13%). The concentrations and fluxes of all particulate P components except detrital P decrease or remain constant with depth between the shallowest and the deepest sediment traps, indicating some regeneration of reactive P components. Transformation from more labile forms of P to authigenic P is evident between the deepest traps and core top sediments. Although for most sites the magnitudes of reactive P fluxes are seasonally variable and productivity dependent, the fractional associations of reactive P are independent of season. We conclude that P is transported from the upper water column to the sediments in various forms previously considered unimportant. Thus, acid-insoluble organic P measurements (typically reported as particulate organic P) likely underestimate biologically related particulate P, because they do not include the labile, oxide-associated, or authigenic P fractions that often are or recently were biologically related. Organic C to reactive P ratios are typically higher than Redfield Ratio and are relatively constant with depth below ~300 m suggesting that preferential regeneration of P relative to C occurs predominantly at shallow depths in the water column, but not deeper in the water column (>300 m). The view of P cycling in the oceans should be revised (1) to include P fractions other than acid-soluble organic P as important carriers of reactive P in rapidly sinking particles, (2) to include the efficient transformation of labile forms of P

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to authigenic P in the water column as well as in sediments, and (3) to consider the occurrence of preferential P regeneration at very shallow depths.

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1. Introduction

Despite the recognition of the importance of P in regulating marine productivity in some modern oceanic systems (e.g., Karl et al., 1995; Wu et al., 2000) and over long timescales (e.g., Tyrrell, 1999), P cycling within the ocean is not well understood (e.g., Delaney, 1998; Benitez-Nelson, 2000). The major carrier phase of P to marine sediments is thought to be particulate organic matter, although few direct measurements of particulate P flux in the oceans have been made and even fewer measurements have determined the organic P fraction (Benitez-Nelson, 2000). Little is known about the distribution of P within different fractions in marine particulate matter, about the temporal or spatial variability in this distribution, or about the differences in P distribution in marine particulate matter compared to marine sediments.

Mass balance studies of the P cycle indicate that the primary input of P to the oceans is the dissolved P flux from rivers (Froelich et al., 1982; Delaney, 1998, and references therein). This P is utilized by organisms and transformed into the particulate fraction. Particulate P is recycled in the water column as manifested by the “nutrient type” distribution of dissolved P in the water column; however, the processes of recycling are poorly understood (Benitez-Nelson, 2000). A few recent studies have pioneered the exploration of the nature of particulate P in the water column (e.g., Clark et al., 1998, 1999; Loh and Bauer, 2000; Paytan et al., 2003; Benitez-Nelson et al., 2004), but much remains to be determined regarding the distribution, composition, and spatial and temporal variability of particulate P. A small fraction (~1%) of the reactive particulate P escapes regeneration in the water column and is buried in the sediments (e.g., see discussion in Delaney, 1998). In open ocean sites, it is thought that much of the P is delivered to the sedi-

ment–water interface primarily in association with organic material and secondarily with oxyhydroxides (e.g., Delaney, 1998). Through the process of sink switching, these phases are transformed to authigenic P in the sediments with increasing age and depth (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1995, 1996; Slomp et al., 1996; Delaney and Anderson, 1997, 2000; Anderson et al., 2001; Faul et al., 2003). A fraction of this P may also diffuse out of the sediments (e.g., McManus et al., 1997).

In sediments, sink switching occurs when P is liberated into porewaters as a result of microbial remineralization of organic matter and/or microbial iron reduction of organic P and/or oxide-associated P. Authigenic carbonate fluorapatite (CFA) is formed as a result (Ruttenberg and Berner, 1993). When the ion activity product is equal to or exceeds the solubility product for authigenic CFA, precipitation of this mineral within the sediment is favored (Ruttenberg and Berner, 1993). Ruttenberg and Berner (1993) suggested that when the decrease in organic P in sediments mirrors the increase in authigenic P in sediments, with little change in total P, formation of CFA is implied. Therefore, they argue, this authigenic P constitutes a component of the oceanic reactive P sink (Ruttenberg and Berner, 1993). Reactive P in this context refers to any P that is or has been associated at some point with living (or dead) organisms and thus consists of labile P, organic P, P adsorbed onto or associated with oxide particles, and authigenic P (CFA), and does not necessarily imply bioavailability.

To address questions about the nature of oceanic sinking particulate P, we present the concentrations and association of different, operationally defined, components of particulate P in various sediment trap and core top sediment samples. Our objectives are to characterize the nature of particulate P, its transformations through the water column, and any spatial or temporal trends in distribution. This is important for

understanding the modern P cycle, for defining processes of P regeneration in the water column, and for better interpretation of sedimentary P burial as a proxy for past nutrient burial and as a paleoproductivity indicator.

2. Methods

2.1. Definitions

We use the following definitions pertaining to particulate P. Reactive P is defined as the sum of labile (water soluble) and oxide-associated (sorbed to or incorporated in oxyhydroxides) P (P_{1-0a}), authigenic P (CFA formed by in situ precipitation and biogenic apatite, e.g., fish debris), and organic (acid-insoluble) P. Detrital P is from apatite of igneous or metamorphic origin (Ruttenberg, 1992). Total P is defined here as the sum of reactive P and detrital P. Note that, by these definitions, the reactive P compo-

nent includes P which at some point was most likely associated with the biomass, but not necessarily the fraction immediately available to the biota, and that our definition of acid-insoluble organic P is what is classically referred to as particulate organic phosphorus, or POP. Total P and acid-insoluble organic P concentrations for many, but not all, of these samples are also given in Paytan et al. (2003).

2.2. Site characteristics

Samples used in this study represent three different oceanic regimes: open ocean settings (Equatorial Pacific: EP-2, MPC-3; North Central Pacific: M-T4), Southern Ocean coastal environments (Ross Sea: A/Adelie, Chinstrap, Gentoo; Palmer Deep) and an eastern boundary current coastal environment (Northern California Coast: NS-1; Monterey Bay: S-2, S-3; and Point Conception: Station M) (Fig. 1). These samples cover a range of productivity regimes (approximately two orders of magnitude), a range of depths (300–

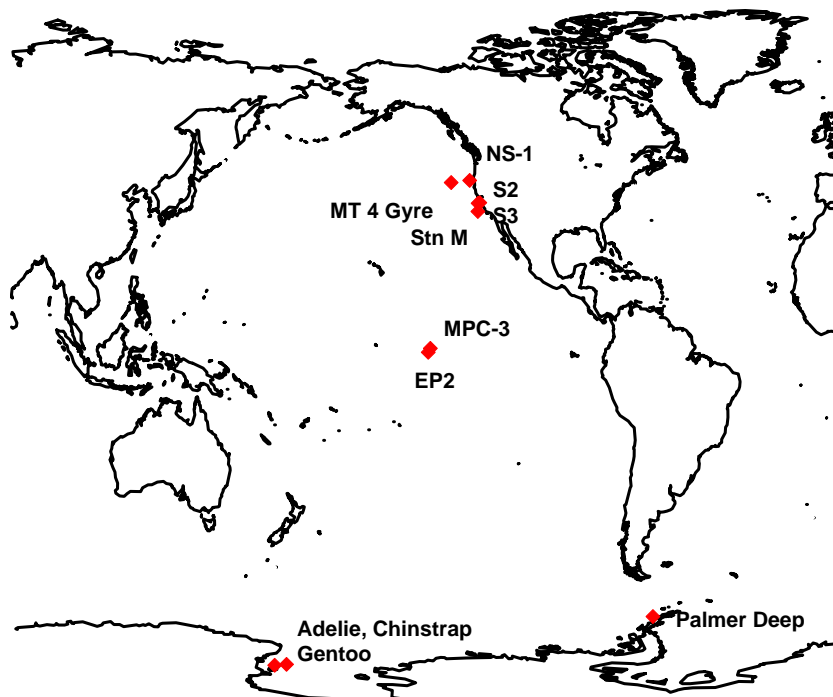


Fig. 1. Sites used in this study. Sites are grouped into three general categories based on location (Table 1): Equatorial Pacific (EP2 and MPC-3), Southern Ocean (Ross Sea sites, A/Adelie, Chinstrap, and Gentoo; and Palmer Deep sites), and California Coast (Northern California, NS 1; Monterey Bay, S2 and S3; and Point Conception, Station M). MT Gyre 4 has productivity values approximately the same as the Equatorial Pacific category, but was not grouped with these sites because of its different geographic location.

Table 1
Sample location, depth, sampling time, organic C, organic N, mass flux, chlorophyll, and sampling protocol

Sample name	Lat	Long	Water depth (m)	Trap depth (m)	Sampling dates	Organic C (wt.%)	Organic N (wt.%)	Total mass flux (mg/m ² /day)	Organic C flux (mmol C/m ² /day)	SeaWiFS average chlorophyll 1997–2003 (mg/m ³)	Poison, storage temperature	Contact and references
<i>Equatorial Pacific sites</i>												
EP2 1–14	0.09°N	139.7°W	4360	1042	2/1/93–9/27/93	6.68	0.95	8.14	0.045	0.3	3% formalin; 4 °C	R. Collier, 1
EP2 1–21	0.09°N	139.7°W	4360	1926	2/1/93–1/24/94	5.26	0.77	4.66	0.020	0.3	3% formalin; 4 °C	
EP2 1–21	0.09°N	139.7°W	4360	3650	2/1/93–1/24/94	4.58	0.67	9.97	0.038	0.3	3% formalin; 4 °C	
MP C3 1–3	1.06°N	139.0°W	4450	1083	2/24/80–7/9/80, 2/21/81–5/3/81	5.61	NA	9.53	0.045	0.3	0.3% Na azide; 4 °C	R. Collier, 2, 3
MP C3 4–5	1.06°N	139.0°W	4450	1083	7/9/80–2/21/81	4.92	NA	10.30	0.042	0.3	0.3% Na azide; 4 °C	
MP C3 1–3	1.06°N	139.0°W	4450	2908	2/24/80–7/9/80, 2/21/81–5/3/81	4.47	NA	10.67	0.040	0.3	0.3% Na azide; 4 °C	
MP C3 4–5	1.06°N	139.0°W	4450	2908	7/9/80–2/21/81	4.17	NA	13.50	0.047	0.3	0.3% Na azide; 4 °C	
MP C3 annual	1.06°N	139.0°W	4450	4220	2/21/80–4/30/81	4.21	NA	11.35	0.040	0.3	0.3% Na azide; 4 °C	
MP C3 annual	1.06°N	139.0°W	4450	4390	2/24/80–4/30/81	4.03	NA	11.46	0.039	0.3	0.3% Na azide; 4 °C	
MP C3 3	1.06°N	139.0°W	4450	1883	4/1/84–7/10/84	5.73	NA	21.67	0.103	0.3	0.3% Na azide; 4 °C	
MP C3 4	1.06°N	139.0°W	4450	1883	7/10/84–10/20/84	3.97	NA	13.58	0.045	0.3	0.3% Na azide; 4 °C	
MP C3 5	1.06°N	139.0°W	4450	1883	10/18/84–2/21/85	3.30	NA	13.93	0.038	0.3	0.3% Na azide; 4 °C	
<i>North Central Pacific site</i>												
M T4	41.56°N	132.0°W	3718	1500	9/21/89–9/25/90	NA	NA	NA	NA	0.2	0.3% Na azide; 4 °C	R. Collier
<i>Southern Ocean sites</i>												
Ross Sea												
A-T1	76.07°S	169.0°W	817	228	1/22/95–1/19/96	8.31	1.04	82	0.57	4	3% formalin, 0 °C	R. Dunbar, 4, 5, 6, 7
A-B2	76.07°S	169.0°W	817	775	2/1/95–2/15/95	6.40	0.81	1297	6.91	4	3% formalin, 0 °C	
A-B4	76.07°S	169.0°W	817	775	3/1/95–4/1/95	3.38	0.50	846	2.38	4	3% formalin, 0 °C	
A-B5	76.07°S	169.0°W	817	775	4/1/95–6/1/95	3.15	0.44	440	1.16	4	3% formalin, 0 °C	
A'-B 6–7	76.07°S	169.0°W	827	775	4/1/96–6/1/96	3.91	0.57	422	1.37	4	3% formalin, 0 °C	
Adelie98-T2-4	76.07°S	169.0°W	822	203	1/3/98–2/15/98	7.98	1.12	699	4.65	4	3% formalin, 0 °C	
Adelie97-B8	76.07°S	169.1°W	819	768	5/15/97–7/15/97	3.97	0.66	449	1.48	4	3% formalin, 0 °C	
Adelie98-B3	76.07°S	169.0°W	822	771	1/16/98–2/01/98	5.27	0.78	1319	5.79	4	3% formalin, 0 °C	
Adelie98-B4	76.07°S	169.0°W	822	771	2/1/98–2/15/98	6.43	0.96	1098	5.88	4	3% formalin, 0 °C	
Chin97-B8–11	76.03°S	165.1°E	825	777	5/15/97–11/15/97	NA	NA	NA	NA	4	3% formalin, 0 °C	
Chin98-B6–7	76.03°S	165.0°E	827	775	3/01/98–4/01/98	3.91	0.63	1949	6.35	4	3% formalin, 0 °C	
Gentoo B 1–2	76.03°S	172.1°E	621	571	1/5/98–2/1/98	5.42	0.74	1160	5.24	4	3% formalin, 0 °C	

Palmer Deep												
PD 99-B3	64.08°S	64.0°W	1040 m	1010	6/1/99–8/1/99	1.36	0.19	2500	2.84	4	3% formalin, 0 °C	R. Dunbar
PD 99-B4	64.08°S	64.0°W	1040 m	1010	8/1/99–10/1/99	1.18	0.16	1999	1.97	4	3% formalin, 0 °C	
<i>Eastern boundary current sites</i>												
Northern California Coast												
NS1 1–2	42.08°N	125.8°W	2829	500	9/21/83–12/23/83	4.68	0.92	26.64	0.104	1	15 g/l Na azide; 4 °C	R. Collier, 3
NS1 3	42.08°N	125.8°W	2829	500	12/23/83–9/15/84	5.07	0.77	25.78	0.109	1	15 g/l Na azide; 4 °C	
NS 1 500 m Ave	42.08°N	125.8°W	2829	500	9/21/83–9/15/84	4.98	0.81	26	0.108	1	15 g/l Na azide; 4 °C	
NS1 1–3	42.08°N	125.8°W	2829	1000	9/21/83–2/21/84	3.00	0.77	44.30	0.111	1	15 g/l Na azide; 4 °C	
NS1 4–6	42.08°N	125.8°W	2829	1000	2/21/84–9/15/84	4.47	1.02	28.12	0.105	1	15 g/l Na azide; 4 °C	
NS 1 1000 m Ave	42.08°N	125.8°W	2829	1000	9/21/83–9/15/84	3.86	0.92	35	0.107	1	15 g/l Na azide; 4 °C	
NS1 1–3	42.08°N	125.8°W	2829	1500	9/21/83–11/23/83	2.88	0.90	113.03	0.271	1	15 g/l Na azide; 4 °C	
NS1 4–5	42.08°N	125.8°W	2829	1500	11/23/83–1/22/84	3.40	0.98	63.58	0.180	1	15 g/l Na azide; 4 °C	
NS1 6	42.08°N	125.8°W	2829	1500	1/22/84–9/15/84	4.21	0.68	19.46	0.068	1	15 g/l Na azide; 4 °C	
NS 1 1500 m Ave	42.08°N	125.8°W	2829	1500	9/21/83–9/15/84	3.85	0.77	42	0.121	1	15 g/l Na azide; 4 °C	
NS1 1–3	42.08°N	125.8°W	2829	1750	9/21/83–2/21/84	2.82	0.63	45.84	0.108	1	15 g/l Na azide; 4 °C	
NS1 4–6	42.08°N	125.8°W	2829	1750	2/21/84–9/15/84	3.87	0.76	32.98	0.106	1	15 g/l Na azide; 4 °C	
NS1 1750 m Ave	42.08°N	125.8°W	2829	1750	9/21/83–9/15/84	3.43	0.70	38	0.107	1	15 g/l Na azide; 4 °C	
NS1 1–6	42.08°N	125.8°W	2829	2329	9/21/83–9/15/84	3.09	0.67	44.05	0.114	1	15 g/l Na azide; 4 °C	
Monterey Bay												
S2HJ-FA98 2	36.66°N	122.4°W	1800	1200	4/8/98–4/22/98	4.39	0.55	971	3.56	10	3 mM HgCl ₂ ; frozen	F. Chavez, 8
S2HJ-FA98 3	36.66°N	122.4°W	1800	1200	4/22/98–5/6/98	6.14	0.63	1154	5.90	10	3 mM HgCl ₂ ; frozen	
S2HJ-FA98 9	36.66°N	122.4°W	1800	1200	7/15/98–7/29/98	3.96	0.56	2021	6.67	10	3 mM HgCl ₂ ; frozen	
S2HJ-A98-F99 9	36.66°N	122.4°W	1800	1200	12/16/98–2/30/98	3.68	0.52	2053	6.30	10	3 mM HgCl ₂ ; frozen	
S2HJ-FA98 1–3	36.66°N	122.4°W	1800	1200	3/25/98–5/6/98	5.00	0.58	963	4.01	10	3 mM HgCl ₂ ; frozen	
S2HJ-FA98 4–6	36.66°N	122.4°W	1800	1200	5/6/98–6/17/98	4.22	0.63	753	2.65	10	3 mM HgCl ₂ ; frozen	
S2HJ-FA98 7–9	36.66°N	122.4°W	1800	1200	6/17/98–7/29/98	4.00	0.57	1490	4.97	10	3 mM HgCl ₂ ; frozen	
S2 HJ-FA98 Ave	36.66°N	122.4°W	1800	1200	3/25/98–7/29/98	4.41	0.59	1069	3.88	10	3 mM HgCl ₂ ; frozen	
S2IRS-FA98	36.66°N	122.4°W	1800	300	3/25/98–8/21/98	6.27	0.78	919	4.80	10	3 mM HgCl ₂ ; frozen	
S2HJ-FA00 1–2	36.66°N	122.4°W	1800	1200	2/9/00–3/8/00	4.15	0.80	395	1.36	10	3 mM HgCl ₂ ; frozen	
S2HJ-FA00 3–5	36.66°N	122.4°W	1800	1200	3/8/00–4/19/00	3.92	0.61	617	2.01	10	3 mM HgCl ₂ ; frozen	
S2IRS-FA00	36.66°N	122.4°W	1800	300	2/9/00–7/12/00	7.29	1.10	1437	8.73	10	3 mM HgCl ₂ ; frozen	
S3HJ-FA98 1–2	36.50°N	122.9°W	3000	2400	3/25/98–4/22/98	5.82	0.66	146	0.71	10	3 mM HgCl ₂ ; frozen	
S3HJ-FA98 3–	36.50°N	122.9°W	3000	2400	4/22/98–5/6/98	NA	NA	NA	NA	10	3 mM HgCl ₂ ; frozen	
S3HJ-FA00 1–4	36.50°N	122.9°W	3000	2400	2/9/00–4/5/00	NA	0.67	317	NA	10	3 mM HgCl ₂ ; frozen	
S3IRS-FA00	36.50°N	122.9°W	3000	300	2/8/00–7/12/00	11.06	1.42	628	5.78	10	3 mM HgCl ₂ ; frozen	
Point Conception												
Stn. M-118	34.83°N	123.0°W	4100	4050	6/23/89–10/22/89	5.89	NA	219	1.08	3	3 mM HgCl ₂ ; frozen	K. Smith, 9
Stn. M-208	34.83°N	123.0°W	4100	4050	11/23/89–2/15/90	7.18	NA	130	0.78	3	3 mM HgCl ₂ ; frozen	
Stn. M-327	34.83°N	123.0°W	4100	4050	2/15/90–6/15/90	5.71	NA	137	0.65	3	3 mM HgCl ₂ ; frozen	

(continued on next page)

Table 1 (continued)

Sample name	Lat	Long	Water depth (m)	Trap depth (m)	Sampling dates	Organic C (wt.%)	Organic N (wt.%)	Total mass flux (mg/m ² /day)	Organic C flux (mmol C/m ² /day)	SeaWiFS average chlorophyll 1997–2003 (mg/m ³)	Poison, storage temperature	Contact and references
<i>Point Conception</i>												
Stn. M-439	34.83°N	123.0°W	4100	4050	6/27/90–8/26/90	6.90	NA	205	1.18	3	3 mM HgCl ₂ ; frozen	
Stn. M-513	34.83°N	123.0°W	4100	4050	10/26/90–2/24/91	6.84	NA	48	0.27	3	3 mM HgCl ₂ ; frozen	
Stn. M-621	34.83°N	123.0°W	4100	4050	2/25/91–6/25/91	5.26	NA	418	1.83	3	3 mM HgCl ₂ ; frozen	
Stn. M-725	34.83°N	123.0°W	4100	4050	6/26/91–10/24/91	5.55	NA	181	0.84	3	3 mM HgCl ₂ ; frozen	
<i>Plankton</i>												
MBARI—75 μm	36.41°N	121.6°W		Surface	5/9/02	NA	NA	NA	NA	10	Filtered, dry 50 °C	A. Paytan
<i>Coretops</i>												
TTN013-69 MC	0.11°N	139.7°W	4307	1–3 cm	Holocene	NA	NA	NA	NA		4 °C	B. Conard
W8709-10BC	42.08°N	125.8°W	2778	0–2 cm	Holocene	NA	NA	NA	NA		4 °C	
W8709-01BC	41.54°N	132.0°W	3680	1–3 cm	Holocene	0.58	0.12	NA	NA		4 °C	
BNTH II-08	1.06°N	139.0°W	4435	1–3 cm	Holocene	NA	NA	NA	NA		4 °C	

1: Honjo et al. (1995), 2: Dymond and Collier (1988); 3: Dymond and Lyle (1994); 4: Collier et al. (2000); 5: Dunbar et al. (1998); 6: Dunbar et al. (2003); 7: Langone et al. (2003), 8: Pilskaln et al. (1996); 9: Baldwin et al. (1998).

4000 m), and a range of temporal (seasonal to annual) distributions (Table 1). Since these samples were previously used to study carbon fluxes (Dymond and Collier, 1988; Dymond and Lyle, 1994; Honjo et al., 1995; Pilskaln et al., 1996; Dunbar et al., 1998; Baldwin et al., 1998), we used total mass flux and organic C concentration and flux information from previous studies for comparison to particulate P concentrations and fluxes presented here (Table 1).

2.3. Procedure

We used a four-step operationally defined sequential extraction (Anderson and Delaney, 2000) modified from a five-step P extraction procedure (SEDEX, Ruttenberg, 1992) to determine P concentrations in four components: labile and oxide-associated P (P removed by reduction with dithionite and complexation with citrate, pH 7.6), authigenic P (P extracted with 1 M sodium acetate buffered to pH 4; includes authigenic CFA), detrital P (P extracted with 1 N hydrochloric acid; includes detrital apatite), and organic P (extracted by adding 50% magnesium nitrate to sediments, drying in oven at 80 °C, and ashing at 550 °C; this is the acid-insoluble organic fraction). This four-step leaching protocol combines the oxide-associated P fraction and P associated with very labile particulate matter that decomposes or dissolves in water since both fractions will be leached in the dithionite–citrate extraction. We therefore identify this fraction as labile and oxide-associated P (P_{l-oa}). After extracting the four components of P into known volumes of extractants from replicate samples (~0.1 g), we used a LaChat Quick Chem 8000 automated

spectrophotometric flow injection analysis system to measure P concentrations. Results are reported as the means $\pm 1\sigma$ (σ , sample standard deviation) of duplicate runs of sample replicates. Reactive P is calculated as the sum of P_{l-oa} , authigenic P, and acid-insoluble organic P, with errors propagated from errors on individual components. Water rinseable P is also included in this total when it was determined separately using an additional first step extraction (note that this water rinse is not the same as the first step in the original SEDEX procedure (Ruttenberg, 1992) which is a magnesium chloride rinse to release loosely sorbed P). Total P is the sum of reactive P and detrital P.

The long-term analytical reproducibility was assessed by calculation of the mean P concentrations $\pm 1\sigma$ for two sedimentary consistency standards (Table 2). Consistency standards were made of sedimentary samples from the Ocean Drilling Program (ODP) since sediment trap material was of extremely limited quantity. Consistency standards are similar in composition to core top samples used in this study, but generally contain more authigenic P and less organic P than sediment trap samples. One consistency standard was made of a mixture of subtropical North Atlantic sedimentary samples (ODP Sites 1050–1052) and one was made of a mixture of Southern Ocean samples (ODP Sites 689, 690, and 738). One of the two standards was processed and measured with each run as a sample. Consistency standard relative errors are similar to those from other sedimentary P studies (e.g., Filippelli and Delaney, 1996; Anderson and Delaney, 2000; Faul et al., 2003).

The relative errors on the long-term means of the consistency standard were higher for components that were close to detection limits and that constitute small

Table 2
Analytical figures of merit

	Phosphorus concentration ($\mu\text{mol g}^{-1}$ sediment)						
	Water rinseable	L-OA ^a	Authigenic	Organic	Detrital	Reactive	Total
Detection limits ^b	0.03	0.30	0.41	0.05	0.06	NA	NA
Reproducibility of consistency standards ^c							
North Atlantic	NA	0.83 ± 0.66	9.39 ± 0.87	0.60 ± 0.17	0.38 ± 0.20	10.30 ± 1.02	10.66 ± 1.07
Southern Ocean	NA	0.47 ± 0.16	11.12 ± 0.65	0.40 ± 0.14	1.08 ± 0.41	11.60 ± 0.59	12.67 ± 0.51

^a Labile and oxide associated.

^b Detection limits are defined as three times the standard deviation of replicate measures of a low concentration solution standard and expressed in equivalent concentration for a sediment sample.

^c Long-term analytical reproducibility was assessed by calculation of the mean P concentrations $\pm 1\sigma$ for two sedimentary consistency standards.

fractions of total P for the standards (Table 2). Therefore the reproducibility for P_{1-0a} , organic, and detrital components for the sediment trap samples should be better than for these fractions in the sedimentary consistency standards because the sediment trap samples contain higher proportions of these forms of P than the sediment samples. Typical sample concentrations compared to detection limits (Table 2) were ~30 times higher for water rinseable P, ~17 times higher for P_{1-0a} and authigenic P, ~50 times higher for detrital P, and ~180 times higher for organic P.

The operationally defined technique we use (Anderson and Delaney, 2000, modified from Ruttenberg, 1992) was optimized for sedimentary material, where little highly labile (water rinseable) P is present. Fine-tuning of the sedimentary extraction procedure for sediment trap analyses requires consideration of a very labile water-soluble fraction. Ruttenberg (1992) showed that 80% of P in fresh plankton material is readily extracted in distilled water, likely due to cell lysing. This release of P is likely not due to changes in ionic strength or pH as this fraction is observed even in cell cultures grown in freshwater (e.g., the distilled water has about the same ionic strength and pH as the culture media). Using our four-step extraction procedure this component will be extracted together with the oxide-associated fraction (P_{1-0a}).

The P in the fresh plankton tow sample (Monterey Bay, 2002) was mainly composed of P_{1-0a} ($18.2 \mu\text{mol P g}^{-1}$, or 88% of $20.6 \mu\text{mol P g}^{-1}$ total P, Table 4). The vast majority of plankton P is indeed extracted in the first step. Ruttenberg (1992) states that this very labile water-soluble P would be lost from sinking particulate matter before it reaches the sediments. Accordingly, we expect P in sediment traps to have an intermediate distribution between phytoplankton and sediments. Moreover it is likely that much of this labile P is lost from the particulate matter into the sediment trap cup solutions (B. Collier personal communication, 2004), thus will no longer be detected in our sediment trap samples which were mostly dry solid fractions.

To determine how much of the P_{1-0a} fraction might be associated with the very labile (water soluble) P within the sediment trap and core top samples, we added a water rinse step to the processing of six samples that had been run using the four-step method, including one core top sample (Table 3). We carried out this experiment on a small number of samples

because of the limited availability of sediment trap material. When included, the water rinse step constituted between 2% (for a core top sample at the Northern California Coast site, NS-1) and 10% (for a Ross Sea site, Adelie) of total P measured. The concentration of P associated with the P_{1-0a} fraction decreased by 5–51% when the water rinse preceded the reductive extraction (Table 3). Although the glass distilled water used in this procedure was slightly acidic (pH 6), it is unlikely that the pH was low enough to desorb much P from inorganic mineral or oxide coatings of sinking particles. However, these are operationally defined distinctions and confirming that this is not P associated with iron oxides would require more detailed solid phase measurements. Thus, we interpret this water-soluble component to be associated with the labile component, concluding that a significant portion of the P in the operationally defined, P_{1-0a} step could be water-soluble labile P when the water rinse step is not applied.

Because the samples were collected previously for other research, a wide range of sample treatment protocols was used (Table 1). Issues with sample treatment and storage and their possible effects on P were addressed in detail in Paytan et al. (2003) and Cade-Menun et al. (2005). In this study, we find no systematic correlation between P concentrations or associations and sample treatment. In fact, despite a wide range of sample treatment protocols, we see consistent trends in the data, indicating that these trends are not artifacts of sample processing or storage after collection.

Previous studies have shown that significant fractions of total P are found in the cup solutions of shallow traps (<1000 m); however, the fraction is very much less (<10%) in the cup solutions of deep traps (>1000 m, Paytan et al., 2003, citing personal communication with R. Collier). It is likely that the P in cup solutions is associated with the very labile fraction (which would be water soluble) and that this fraction would have been released to the seawater during particle sinking. As most of our sediment trap samples are from below the annual mixed layer, this may not be an important part of the particulate matter that this work is characterizing. In the future, it would be interesting to determine the amount and fractions of P (dissolved organic and dissolved inorganic) found in sediment trap cup solutions and the effect that this partitioning has on the nature of particulate P in the cups.

Table 3
Comparison of sample treatments

Sample name	Phosphorus concentrations ($\mu\text{mol P g}^{-1}$ sediment)																			
	Water rinseable			L-OA ^a			Authigenic			Organic			Detrital			Reactive			Total	
	Mean	S.D. ^b	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.
<i>Equatorial Pacific</i>																				
MP C3 3	1.25	0.09	9.5	7.79	0.26	43	2.98	0.27	16	7.18	0.33	40	0.22	0.03	1.0	17.95	0.50	99	18.17	0.50
				3.68	0.24	28	2.85	0.01	22	5.28	0.13	40	BDL	BDL	0	13.06	0.29	100	13.06	0.29
<i>Southern Ocean</i>																				
Ross Sea																				
Adelie98-B3	1.43	0.17	10	2.09	0.56	14	1.31	0.06	9.1	2.09	0.24	62	8.97	0.65	14	12.36	0.86	86	14.45	0.90
				1.30	0.05	9	1.18	0.08	8.5	1.58	0.04	60	8.40	0.17	11	12.30	0.26	89	13.89	0.27
<i>Eastern boundary current sites</i>																				
Northern California Coast																				
NS1 1–6	0.61	0.09	2.3	3.11	0.18	12	6.70	0.58	26	7.01	0.33	36	9.35	0.54	27	19.16	0.81	73	26.17	0.88
				2.30	0.22	8.7	8.48	0.10	32	6.55	0.29	32	8.39	0.17	25	19.79	0.31	75	26.34	0.42
Monterey Bay																				
S2HJ-FA98 7–9	1.18	0.03	2.4	4.87	0.26	14	13.27	0.53	38	5.83	0.26	31	10.83	0.45	17	28.98	0.74	83	34.80	0.79
				4.53	0.22	12	12.11	0.11	33	7.91	0.93	29	10.52	0.26	22	28.33	0.36	78	36.25	1.00
Point Conception																				
Stn. M-118	0.47	0.03	2.9	7.03	0.50	34	3.35	0.15	16	1.01	0.03	46	9.56	0.35	4.8	19.94	0.63	95	20.95	0.63
				4.83	0.04	30	2.58	0.07	16	0.88	0.04	46	7.52	0.23	5.4	15.40	0.25	95	16.28	0.25
<i>Coretop</i>																				
W8709–10BC	0.38	0.03	1.9	1.06	0.05	5.4	6.76	0.05	34	6.83	0.41	25	4.99	0.25	35	12.81	0.26	65	19.64	0.48
				0.75	0.14	3.8	5.99	0.14	30	8.56	0.28	21	4.23	0.15	43	11.34	0.25	57	19.90	0.38

^a Labile and oxide associated.

^b S.D.=standard deviation.

Table 4
Concentrations and percentages of phosphorus components in sediment trap samples

Sample name	Phosphorus concentrations ($\mu\text{mol P g}^{-1}$ sediment)																	
	L-OA ^a			Authigenic			Organic			Detrital			Reactive			Total		
	Mean	S.D. ^b	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	
<i>Equatorial Pacific sites</i>																		
EP2 1–14	7.40	1.00	24	13.85	1.43	45	8.94	0.38	29	0.31	0.08	1.0	30.18	1.78	99	30.50	1.79	
EP2 1–21 1926 m	2.80	0.34	22	3.37	0.79	26	6.50	0.35	51	0.17	0.02	1.3	12.67	0.93	99	12.84	0.93	
EP2 1–21 3650 m	1.92	0.24	17	2.99	0.07	27	6.03	0.05	54	0.19	0.01	1.7	10.95	0.25	98	11.14	0.25	
MP C3 1–3 1083 m	6.69	0.13	37	5.05	0.06	28	5.86	0.06	33	0.35	0.05	1.9	17.60	0.16	98	17.95	0.17	
MP C3 4–5 1083 m	6.71	0.69	36	5.50	0.95	30	6.14	0.34	33	0.26	0.07	1.4	18.35	1.22	98	18.61	1.22	
MP C3 1–3 2908 m	3.59	0.12	34	2.53	0.16	24	4.46	0.51	42	0.10	0.03	1.0	10.58	0.55	99	10.68	0.55	
MP C3 4–5 2908 m	3.37	0.06	33	1.96	0.27	19	4.77	0.24	47	0.15	0.00	1.5	10.09	0.37	99	10.24	0.37	
MP C3 annual 4220 m	2.31	0.09	23	2.18	0.13	21	5.42	0.11	53	0.26	0.06	2.6	9.91	0.19	97	10.17	0.20	
MP C3 annual 4390 m	3.97	0.24	32	3.63	0.16	29	4.74	0.12	38	0.25	0.03	2.0	12.34	0.31	98	12.59	0.31	
MP C3 3	7.79	0.26	43	2.98	0.27	16	7.18	0.33	40	0.22	0.03	1.2	17.95	0.50	99	18.17	0.50	
MP C3 4	5.57	0.38	43	2.24	0.42	17	4.99	0.23	38	0.16	0.01	1.3	12.79	0.61	99	12.96	0.61	
MP C3 5	2.89	0.34	34	2.15	0.05	25	3.34	0.10	40	0.06	0.01	0.8	8.38	0.36	99	8.44	0.36	
Average	4.58	0.32	31	4.04	0.40	26	5.70	0.23	41	0.21	0.03	1.5	14.32	0.60	99	14.52	0.61	
<i>North Central Pacific site</i>																		
M T4 bulk	13.73	1.08	54	3.33	0.52	13	7.69	0.40	30	0.53	0.02	2.1	24.75	1.26	98	25.28	1.26	
<i>Southern Ocean sites</i>																		
<i>Ross Sea</i>																		
A-T1	9.48	0.14	44	0.74	0.09	3	10.94	0.10	51	0.49	0.01	2.3	21.16	0.19	98	21.66	0.19	
A-B2	1.79	0.28	13	0.71	0.04	5	10.14	0.21	72	1.45	0.05	10	12.64	0.35	90	14.09	0.35	
A-B4	1.82	0.01	15	1.68	0.02	14	6.62	0.52	54	2.09	0.22	17	10.11	0.52	83	12.20	0.57	
A-B5	2.42	0.51	16	2.09	0.07	14	7.80	0.24	51	3.00	0.28	20	12.31	0.56	80	15.31	0.63	
A'-B 6–7	2.22	0.02	18	0.93	0.07	8	6.67	0.04	56	2.19	0.20	18	9.82	0.09	82	12.01	0.21	
Adelie98-T2–4	4.71	0.66	29	0.89	0.01	5.5	10.18	0.22	63	0.34	0.02	2.1	15.77	0.70	98	16.11	0.70	
Adelie97-B8	3.55	0.49	17	3.24	0.02	16	9.43	0.10	46	4.43	0.06	21	16.23	0.50	79	20.66	0.50	
Adelie98-B3	2.09	0.56	14	1.31	0.06	9.1	8.97	0.65	62	2.09	0.24	14	12.36	0.86	86	14.45	0.90	
Adelie98-B4	2.29	0.32	12	1.72	0.07	9.2	12.28	0.23	66	2.43	0.21	13	16.30	0.40	87	18.73	0.45	
Chin97-B8–11	2.10	0.54	12	2.84	0.22	17	7.78	0.55	46	4.24	0.41	25	12.72	0.80	75	16.96	0.90	
Chin98-B6–7	1.40	0.20	12	1.76	0.06	15	6.71	0.13	56	2.01	0.08	17	9.87	0.25	83	11.89	0.26	
Gentoo B 1–2	2.27	0.19	4.3	41.46	2.38	78	8.49	0.19	16	0.65	0.02	1.2	52.23	2.40	99	52.87	2.40	
Average	3.01	0.33	17	4.95	0.26	16	8.84	0.26	53	2.12	0.15	13	16.80	0.63	87	18.91	0.67	
<i>Palmer Deep</i>																		
PD 99-B3	3.15	0.06	13	7.44	0.12	30	4.82	0.05	20	9.07	0.12	37	15.41	0.15	63	24.48	0.19	
PD 99-B4	2.19	0.01	10	7.02	0.21	31	3.85	0.14	17	9.45	0.11	42	13.06	0.25	58	22.51	0.27	
Average	2.67	0.04	11	7.23	0.16	31	4.33	0.10	18	9.26	0.11	40	14.23	0.20	60	23.49	0.23	
<i>Eastern boundary current sites</i>																		
<i>Northern California Coast</i>																		
NS1 1–2 500 m	10.41	0.16	27	10.93	0.56	28	11.28	0.16	29	6.30	0.17	16	32.63	0.60	84	38.93	0.63	
NS1 3 500 m	13.05	1.28	31	11.60	0.57	28	10.91	0.13	26	6.11	0.03	15	35.57	1.41	85	41.68	1.41	

Table 4 (continued)

Sample name	Phosphorus concentrations ($\mu\text{mol P g}^{-1}$ sediment)																	
	L-OA ^a			Authigenic			Organic			Detrital			Reactive			Total		
	Mean	S.D. ^b	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	
<i>Eastern boundary current sites</i>																		
<i>Northern California Coast</i>																		
NS 1 500 m	12.39	1.00	30	11.43	0.57	28	11.01	0.14	27	6.16	0.06	15	34.83	1.21	85	40.99	1.21	
Annual ^c																		
NS1 1–3 1000 m	3.91	0.53	13	8.52	0.33	29	9.35	0.22	31	7.91	0.04	27	21.79	0.66	73	29.70	0.66	
NS1 4–6 1000 m	3.44	0.52	13	5.42	0.28	21	11.47	1.45	44	5.74	0.89	22	20.33	1.57	78	26.07	1.80	
NS 1 1000 m	3.64	0.53	13	6.72	0.30	24	10.59	0.94	39	6.65	0.53	24	20.94	1.19	76	27.58	1.33	
Annual ^c																		
NS1 1–3 1500 m	2.19	0.00	8.0	7.80	0.25	29	8.96	0.27	33	8.43	0.87	31	18.95	0.37	69	27.38	0.94	
NS1 4–5 1500 m	3.74	1.66	13	7.64	1.28	26	10.91	0.26	37	7.13	0.35	24	22.28	2.11	76	29.42	2.14	
NS1 6 1500 m	1.54	0.50	2.7	41.46	2.38	72	11.38	0.17	20	3.47	0.20	6.0	54.38	2.44	94	57.84	2.45	
NS 1 1500 m	2.02	0.61	5	30.21	1.84	57	10.89	0.20	25	4.90	0.34	13	43.12	2.04	87	48.03	2.15	
Annual ^c																		
NS1 1–3 1750 m	1.63	0.78	6.3	6.84	0.27	26	8.99	0.08	35	8.46	0.06	33	17.46	0.83	67	25.93	0.83	
NS1 4–6 1750 m	1.53	0.20	6.1	6.22	0.12	25	11.40	0.03	46	5.82	0.13	23	19.15	0.23	77	24.96	0.27	
NS1 1750 m	1.57	0.44	6	6.48	0.18	26	10.40	0.05	41	6.92	0.10	27	18.45	0.48	73	25.37	0.50	
Annual ^c																		
NS1 1–6 2329 m	3.11	0.18	12	6.70	0.58	26	9.35	0.54	36	7.01	0.33	27	19.16	0.81	73	26.17	0.88	
Average ^d	4.45	0.58	13	11.31	0.66	31	10.40	0.33	34	6.64	0.31	22	26.17	1.10	78	32.81	1.20	
<i>Monterey Bay</i>																		
S2HJ-FA98 2	10.77	0.68	25	13.08	1.30	31	12.67	0.20	30	5.78	0.46	14	36.51	1.48	86	42.29	1.55	
S2HJ-FA98 3	9.43	0.22	23	8.95	0.51	22	17.07	0.50	42	5.10	0.18	13	35.44	0.75	87	40.55	0.77	
S2HJ-FA98 9	6.77	0.33	20	8.70	0.41	25	10.30	0.57	30	8.64	0.72	25	25.77	0.77	75	34.41	1.06	
S2HJ-A98-F99 9	8.13	0.23	22	8.88	0.50	24	11.77	0.28	32	8.08	0.33	22	28.78	0.62	78	36.86	0.70	
S2HJ-FA98 1–3	4.88	0.13	16	8.36	0.23	28	12.42	1.03	42	4.16	0.21	14	25.66	1.06	86	29.82	1.08	
S2HJ-FA98 4–6	5.76	2.98	14	16.73	0.60	40	13.30	0.11	31	6.54	0.37	15	35.79	3.04	85	42.33	3.06	
S2HJ-FA98 7–9	4.87	0.26	14	13.27	0.53	38	10.83	0.45	31	5.83	0.26	17	28.98	0.74	83	34.80	0.79	
S2HJ-FA98 Ave	5.17	1.12	14.65	12.79	0.46	35.23	12.18	0.53	34.74	5.51	0.28	15.38	30.14	1.61	84.62	35.65	1.64	
S2IRS-FA98	1.92	0.03	5.6	10.51	1.03	31	16.01	4.01	47	5.72	0.56	17	28.44	4.14	83	34.17	4.18	
S2HJ-FA00 1–2	2.21	1.38	5.7	18.29	2.45	47	11.76	1.11	30	6.88	0.18	18	32.27	3.02	82	39.15	3.03	
S2HJ-FA00 3–5	5.89	0.18	18	11.07	0.31	33	11.77	0.40	35	4.71	0.14	14	28.73	0.54	86	33.44	0.56	
S2IRS-FA00	6.42	0.95	18	6.66	0.40	18	19.07	0.58	52	4.53	0.32	12	32.15	1.18	88	36.68	1.23	
S3HJ-FA98 1–2	2.64	0.36	8.7	9.19	0.07	30	14.15	0.76	46	4.45	0.63	15	25.98	0.84	85	30.43	1.05	
S3HJ-FA98 3–	2.72	0.10	8.4	10.87	0.10	33	14.47	0.43	44	4.53	0.12	14	28.06	0.46	86	32.59	0.47	
S3HJ-FA00 1–4	4.54	1.67	14	8.86	0.51	28	15.01	0.83	47	3.57	0.06	11	28.41	1.93	89	31.99	1.94	
S3IRS-FA00	2.39	0.08	7.2	2.52	0.17	7.5	26.40	6.22	79	2.09	0.01	6.3	31.31	6.22	94	33.40	6.22	
Average	5.29	0.64	15	10.40	0.61	29	14.47	1.16	41	5.38	0.30	15	30.15	1.79	85	35.53	1.85	
<i>Point Conception</i>																		
Stn. M-118	7.03	0.50	34	3.35	0.15	16	9.56	0.35	46	1.01	0.03	4.8	19.94	0.63	95	20.95	0.63	
Stn. M-208	9.29	0.96	34	7.04	0.29	26	8.58	0.46	32	2.29	0.22	8.4	24.91	1.10	92	27.19	1.12	
Stn. M-327	7.04	0.10	28	6.92	0.15	28	8.77	0.52	35	2.19	0.16	8.8	22.72	0.55	91	24.91	0.57	
Stn. M-439	7.12	0.20	27	7.01	0.12	26	10.00	0.92	38	2.41	0.16	9.1	24.14	0.95	91	26.55	0.96	
Stn. M-513	4.51	0.33	27	5.83	0.35	35	5.01	0.84	30	1.30	0.09	7.8	15.35	0.96	92	16.64	0.97	
Stn. M-621	6.95	0.45	27	4.83	0.23	19	12.57	0.40	48	1.74	0.04	6.7	24.36	0.65	93	26.10	0.65	
Stn. M-725	6.90	0.07	28	6.01	0.44	24	9.99	0.12	40	1.85	0.01	7.5	22.90	0.47	93	24.75	0.47	
Average	6.98	0.37	29	5.86	0.25	25	9.21	0.52	38	1.83	0.10	7.6	22.04	0.76	92	23.87	0.77	
<i>Plankton</i>																		
MBARI 75 μm	18.20	1.02	88	0.84	0.14	4.1	1.41	0.07	6.8	0.17	0.02	0.8	20.45	1.03	99	20.61	1.03	

(continued on next page)

Table 4 (continued)

Sample name	Phosphorus concentrations ($\mu\text{mol P g}^{-1}$ sediment)																
	L-OA ^a			Authigenic			Organic			Detrital			Reactive			Total	
	Mean	S.D. ^b	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.	% of Total	Mean	S.D.
<i>Coretops</i>																	
TTN013-69 MC	0.67	0.03	8.0	6.62	0.07	79	0.95	0.21	11	0.13	0.01	1.5	8.24	0.22	98	8.37	0.22
W8709-10BC	1.06	0.05	5.4	6.76	0.05	34	4.99	0.25	25	6.83	0.41	35	12.81	0.26	65	19.64	0.48
W8709-01BC	2.76	0.08	12	6.88	0.19	29	6.66	0.14	28	7.42	0.24	31	16.29	0.25	69	23.71	0.34
BNTN II-08	0.88	0.07	8.0	8.37	0.38	77	1.36	0.06	12	0.32	0.10	2.9	10.61	0.39	97	10.93	0.40

^a Labile and oxide associated.

^b S.D.=standard deviation.

^c Weighted averages of preceding samples to calculate an annual average value.

^d Average of preceding individual samples.

Fluxes of P components were calculated from their respective concentrations and existing mass flux measurements for traps for which this information was available. In addition, organic C to total P, organic C to reactive P, and organic C to organic P molar ratios were calculated using previously reported organic C concentration data.

Reported total mass fluxes at some traps that are close to the seafloor increase significantly with depth (e.g., Adelie trap depth 775 m, water depth 817 m; S2 trap depth 1200 m, water depth 1800 m; R. Dunbar, personal communication; F. Chavez, personal communication). It is likely that these traps are experiencing some horizontal advection of material and or resuspension of material from the seafloor. Indeed, Collier et al. (2000) report significantly higher fluxes into the deep traps at several Ross Sea sites, indicating horizontal transport of particulate matter. We comment on these samples for completeness, but because of the possibility of advected or resuspended material from the seafloor in these traps, we do not include these samples (the Adelie deep traps (~775 m) or the S2 Monterey Bay deep traps (~1200 m)) in our assessment of depth trends or in our assessment of C to P ratios of suspended material.

3. Results

Total P concentrations and fluxes in sediment trap particles varied considerably between sites, ranging from 7 to 58 $\mu\text{mol P g}^{-1}$ and from less than 1 to 76 $\mu\text{mol P m}^{-2} \text{day}^{-1}$, respectively (Tables 4 and 5). The reactive P fraction of particulate P was also variable

ranging from 6 to 54 $\mu\text{mol P g}^{-1}$, which corresponds to 58% and to 100% of the total P in the various traps (Table 4). Detrital P concentrations were typically lower, but also spanned a wide range from 0.1 to 9 $\mu\text{mol P g}^{-1}$, which consists of between 0 and 42% of the total P in the trap samples (Table 4). The major component of the P in all sediment trap samples is the acid-insoluble organic P (on average 42% of total P), with about equal proportions of authigenic P (~25%), labile and oxide-associated P (~21%), and lesser proportions of detrital P (~13%) (Fig. 2).

3.1. Regional trends

Total particulate P concentrations and the P concentrations associated with each of the operationally defined fractions are in general higher in coastal ocean sites (e.g., Ross Sea, Palmer Deep, Northern California, Monterey Bay, Pt. Conception) than in open ocean sites (e.g., Equatorial Pacific) (Fig. 2a). Average reactive P (30 $\mu\text{mol P g}^{-1}$) and acid-insoluble organic P (14 $\mu\text{mol P g}^{-1}$) concentrations are highest in Monterey Bay and are lowest in the equatorial Pacific sites (14 and 6 $\mu\text{mol P g}^{-1}$, respectively, Fig. 2a). NS1, a northern California coastal site, has both the highest average authigenic P (11 $\mu\text{mol P g}^{-1}$) and highest detrital P concentrations (Fig. 2a). At this near shore site, the aluminosilicate rain rates are approximately 50 times higher than in the open ocean, indicating input from continental sources (Dymond and Lyle, 1994). The highest P_{1-0a} concentrations are found in the Point Conception samples (Fig. 2a).

The distribution of P in the different fractions varies by region (Fig. 2a). The relative contribution

Table 5
P component fluxes and C to P ratios

Sample name	L-OA ^a P flux ($\mu\text{mol}/\text{m}^2/\text{day}$)	Authigenic P flux ($\mu\text{mol}/\text{m}^2/\text{day}$)	Organic P flux ($\mu\text{mol}/\text{m}^2/\text{day}$)	Detrital P flux ($\mu\text{mol}/\text{m}^2/\text{day}$)	Reactive P flux ($\mu\text{mol}/\text{m}^2/\text{day}$)	Total P flux ($\mu\text{mol}/\text{m}^2/\text{day}$)	C/Organic P (M)	C/Reactive P (M)	C/Total P (M)
<i>Equatorial Pacific sites</i>									
EP2 1–14	0.060	0.113	0.073	0.003	0.246	0.25	623	184	182
EP2 1–21 1926 m	0.013	0.016	0.030	0.001	0.059	0.06	674	346	341
EP2 1–21 3650 m	0.019	0.030	0.060	0.002	0.109	0.11	632	348	343
MP C3 1–3 1083 m	0.064	0.048	0.056	0.003	0.168	0.17	797	266	260
MP C3 4–5 1083 m	0.069	0.057	0.063	0.003	0.189	0.19	668	223	220
MP C3 1–3 2908 m	0.038	0.027	0.048	0.001	0.113	0.11	836	352	349
MP C3 4–5 2908 m	0.046	0.026	0.064	0.002	0.136	0.14	729	344	339
MP C3 annual 4220 m	0.026	0.025	0.061	0.003	0.112	0.12	647	354	345
MP C3 annual 4390 m	0.045	0.042	0.054	0.003	0.141	0.14	709	272	267
MP C3 3	0.169	0.065	0.156	0.005	0.389	0.39	665	266	263
MP C3 4	0.076	0.030	0.068	0.002	0.174	0.18	664	259	255
MP C3 5	0.040	0.030	0.047	0.001	0.117	0.12	823	328	326
Average	0.055	0.042	0.065	0.002	0.163	0.165	706	295	291
<i>Southern Ocean sites</i>									
<i>Ross Sea</i>									
A-T1	0.774	0.060	0.893	0.040	1.727	1.77	633	327	320
A-B2	2.319	0.921	13.16	1.878	16.40	18.27	525	422	378
A-B4	1.535	1.418	5.599	1.764	8.552	10.32	425	278	231
A-B5	1.067	0.921	3.431	1.321	5.419	6.74	337	213	171
A'-B 6–7	0.934	0.393	2.814	0.924	4.141	5.06	488	332	271
Adelie98-T2–4	3.288	0.619	7.115	0.234	11.02	11.26	653	422	413
Adelie97-B8	1.595	1.456	4.233	1.989	7.285	9.27	351	204	160
Adelie98-B3	2.750	1.733	11.82	2.758	16.31	19.06	490	355	304
Adelie98-B4	2.517	1.890	13.49	2.664	17.89	20.56	436	329	286
Chin97-B8–11	NA	NA	NA	NA	NA	NA	NA	NA	NA
Chin98-B6–7	2.729	3.437	13.08	3.928	19.25	23.17	485	330	274
Gentoo B 1–2	2.635	48.09	9.853	0.749	60.57	61.32	531	86	85
Average	2.013	5.539	7.771	1.659	15.32	16.98	487	300	263
<i>Palmer Deep</i>									
PD 99-B3	7.877	18.59	12.05	22.67	38.52	61.19	235	74	46
PD 99-B4	4.383	14.03	7.697	18.88	26.11	44.99	256	75	44
Average	6.130	16.31	9.873	20.78	32.31	53.09	246	75	45
<i>Eastern boundary current sites</i>									
<i>Northern California Coast</i>									
NS1 1–2 500 m	0.277	0.291	0.301	0.168	0.869	1.04	346	120	100
NS1 3 500 m	0.336	0.299	0.281	0.158	0.917	1.07	387	119	101
NS 1 500 m Annual ^b	0.322	0.297	0.286	0.160	0.905	1.06	377	119	101
NS1 1–3 1000 m	0.173	0.378	0.414	0.351	0.965	1.32	268	115	84
NS1 4–6 1000 m	0.097	0.152	0.322	0.161	0.572	0.73	325	183	143
NS 1 1000 m Annual ^b	0.129	0.246	0.361	0.240	0.736	0.98	301	155	119
NS1 1–3 1500 m	0.247	0.882	1.012	0.953	2.142	3.09	268	127	88
NS1 4–5 1500 m	0.238	0.485	0.693	0.453	1.417	1.87	260	127	96
NS1 6 1500 m	0.030	0.807	0.221	0.067	1.058	1.13	308	65	61
NS 1 1500 m Annual ^b	0.101	0.766	0.432	0.279	1.298	1.58	293	85	71
NS1 1–3	0.075	0.314	0.412	0.388	0.801	1.19	261	135	91
NS1 4–6	0.050	0.205	0.376	0.192	0.631	0.82	283	168	129

(continued on next page)

Table 5 (continued)

Sample name	L-OA ^a P flux ($\mu\text{mol}/$ m^2/day)	Authigenic P flux ($\mu\text{mol}/$ m^2/day)	Organic P flux ($\mu\text{mol}/$ m^2/day)	Detrital P flux ($\mu\text{mol}/$ m^2/day)	Reactive P flux ($\mu\text{mol}/$ m^2/day)	Total P flux ($\mu\text{mol}/$ m^2/day)	C/Organic P (M)	C/Reactive P (M)	C/Total P (M)
<i>Eastern boundary current sites</i>									
NS1 1750 m Annual ^b	0.060	0.250	0.391	0.274	0.702	0.98	274	154	113
NS1 1–6	0.137	0.295	0.412	0.309	0.844	1.15	276	135	99
Average ^c	0.166	0.411	0.445	0.320	1.022	1.341	298	129	99
<i>Monterey Bay</i>									
S2HJ-FA98 2	10.46	12.70	12.30	5.615	35.46	41.08	289	100	87
S2HJ-FA98 3	10.89	10.32	19.69	5.887	40.89	46.78	300	144	126
S2HJ-FA98 9	13.68	17.59	20.82	17.46	52.09	69.55	320	128	96
S2HJ-A98-F99 9	16.69	18.24	24.16	16.59	59.09	75.69	261	107	83
S2HJ-FA98 1–3	4.697	8.048	11.96	4.003	24.71	28.71	335	162	140
S2HJ-FA98 4–6	4.336	12.60	10.02	4.930	26.96	31.89	265	98	83
S2HJ-FA98 7–9	7.256	19.78	16.15	8.686	43.18	51.87	308	115	96
S2HJ-FA98 Ave	5.43	13.48	12.71	5.87	31.62	37.49	303	125	106
S2IRS-FA98	1.763	9.665	14.72	5.263	26.15	31.41	326	184	153
S2HJ-FA00 1–2	0.872	7.219	4.642	2.716	12.73	15.45	294	107	88
S2HJ-FA00 3–5	3.635	6.826	7.261	2.905	17.72	20.63	277	114	98
S2IRS-FA00	9.223	9.564	27.39	6.509	46.18	52.69	319	189	166
S3HJ-FA98 1–2	0.384	1.341	2.064	0.650	3.789	4.44	343	187	159
S3HJ-FA98 3	NA	NA	NA	NA	NA	NA	NA	NA	NA
S3HJ-FA00 1–4	1.442	2.812	4.766	1.135	9.020	10.15	NA	NA	NA
S3IRS-FA00	1.502	1.581	16.57	1.310	19.65	20.96	349	294	276
Average	6.201	9.878	13.75	5.976	29.83	35.81	307	148	127
<i>Point Conception</i>									
Stn. M-118	1.540	0.734	2.095	0.221	4.369	4.59	513	246	234
Stn. M-208	1.207	0.914	1.114	0.297	3.236	3.53	698	240	220
Stn. M-327	0.963	0.947	1.200	0.300	3.110	3.41	543	209	191
Stn. M-439	1.463	1.440	2.053	0.495	4.956	5.45	575	238	217
Stn. M-513	0.216	0.279	0.240	0.062	0.736	0.80	1138	372	343
Stn. M-621	2.903	2.019	5.251	0.728	10.17	10.90	349	180	168
Stn. M-725	1.250	1.089	1.811	0.335	4.150	4.49	463	202	187
Average	1.363	1.060	1.966	0.348	4.390	4.738	611	241	223

^a Labile and oxide associated.

^b Weighted averages of preceding samples to calculate an annual average value.

^c Average of preceding individual samples.

of reactive P to total P in the different regions increases in the following order: equatorial Pacific, Ross Sea, Point Conception, Palmer Deep, Northern California Coast, and Monterey Bay (Fig. 2a). Organic P is almost always the single largest contributor to total P, especially in the Ross Sea (average 53% of total P, Fig. 2a). Detrital P is a more significant contributor to total P on the California Coast (Monterey Bay, average 16% of total P; Northern California Coast, average 22% of total P), where lithogenic contributions, presumably from riverine, or at least continental, sources, are known to be significant (Pilskaln et al., 1996; Dymond and

Lyle, 1994), and in the Palmer Deep (average 40% of total P). The lowest detrital contribution is, unsurprisingly, in the open ocean site from the high nutrient low chlorophyll (HNLC) region of the equatorial Pacific (average 1%) where almost all the P is reactive P (99% of total P) (Table 4; Fig. 2a). P_{10-0a} is a significant contributor to total P in the equatorial Pacific (31% of total P) and in Point Conception samples (29% of total P). Authigenic P is an especially significant contributor to total P in the northern California coastal sites (NS 1 and Monterey Bay) and in the Palmer Deep, comprising about 30% of total P.

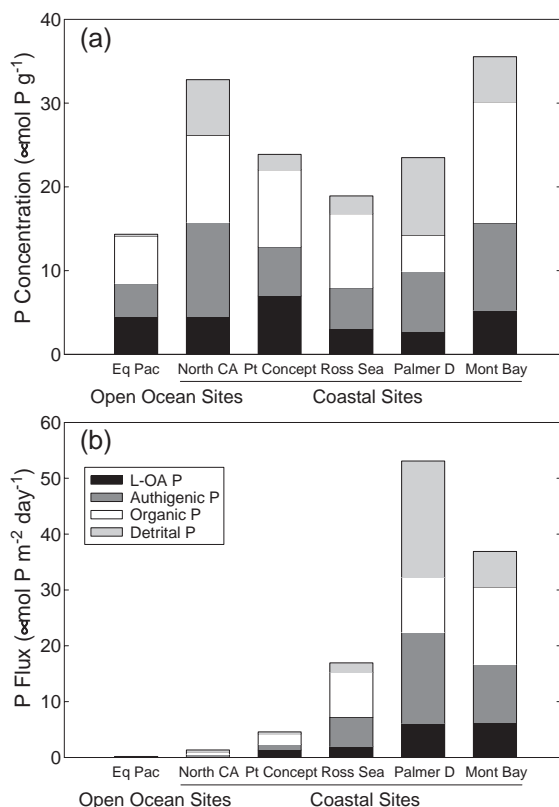


Fig. 2. (a) Variation of average P concentration ($\mu\text{mol P g}^{-1}$) in sediment trap particles with region. Each stacked bar includes the concentration, from the bottom up, of P_{l-oa} (labile and oxide-associated P), authigenic P, organic P, and detrital P. Averages from the Ross Sea and Palmer Deep sites are shown for the Southern Ocean, and the Northern California, Monterey Bay, and Point Conception site averages are shown for the California Coastal sites. Sites are listed in order from lowest to highest productivity, based on SeaWiFS Average Chlorophyll values provided in Table 1. All samples (listed in Table 3) from each region are included in the averages. (b) Variation of average P fluxes ($\mu\text{mol P m}^{-2} \text{ day}^{-1}$) in sediment trap particles with region. Concentration and flux averages in this figure include sites that may be affected by advection.

Reactive P fluxes in the sediment traps range from 0.06 to 61 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$, organic P fluxes range from 0.03 to 27 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$, authigenic fluxes range from 0.02 to 48 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$, P_{l-oa} fluxes range from 0.01 to 17, and detrital P fluxes range from 0 to 23 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$ (Fig. 2b). Average reactive P fluxes are highest in coastal areas (e.g., Monterey Bay, 31 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$ and Ross Sea, 15 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$) and lowest in the open ocean (0.17 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$, Fig. 2b). Although the NS 1 and Point Conception sites have relatively

high P concentrations, they have relatively low reactive P fluxes because of the low total rain flux reported for these sites (Fig. 2b). In contrast, the Ross Sea has relatively low reactive P concentrations, but the reactive P fluxes are high because the total particulate flux is high (Fig. 2b). Palmer Deep P fluxes are very high as well, but this is likely due to advection and/or resuspension of sediment. In general, P flux at each site is proportional to the site's productivity and total mass flux (Fig. 2b).

3.2. Depth trends

Reactive P component concentrations (P_{l-oa} , authigenic and organic) typically decrease with depth, consistent with loss of reactive P between the shallower sediment traps and the deeper traps (Fig. 3). Detrital P concentrations remain relatively constant with depth, indicating that this phase of P is not being recycled in the water column (Fig. 3d). Exceptions to this trend are the sites experiencing advection and or resuspension, as seen for example at the Adelie site in the Ross Sea where authigenic P concentrations remain constant with depth (Fig. 3b) or for the S2 Monterey Bay site where P_{l-oa} and authigenic P (thus the reactive P concentrations) increase with depth (Fig. 3a, b, and e). Although the sample at 1500 m for NS1 has a very high authigenic P and thus reactive P concentration, this is not seen when concentrations are converted to P fluxes (Figs. 3b,e and Fig. 4).

Reactive P fluxes generally decrease or remain constant with depth (Fig. 4) except for sites experiencing resuspension (Adelie and S2 in Monterey Bay, not included in Fig. 4). Based on the depth trends observed in other sites we suspect that the P fluxes associated with the Chinstrap, Gentoo, and Palmer Deep traps in the Southern Ocean may also include resuspended particulate P from the seafloor. The locations of the Chinstrap and Gentoo traps are near the location of the Adelie sediment trap and other traps known to contain resuspended matter (Collier et al., 2000; Dunbar et al., 1998, 2003; Langone et al., 2003). Both the Gentoo and Palmer Deep sites have relatively high proportions of authigenic P (78% and 31% of total P, respectively) (Table 4). Although samples containing resuspended material would be enriched in all P components, the observed proportions (e.g., highly enriched in authigenic P) are more

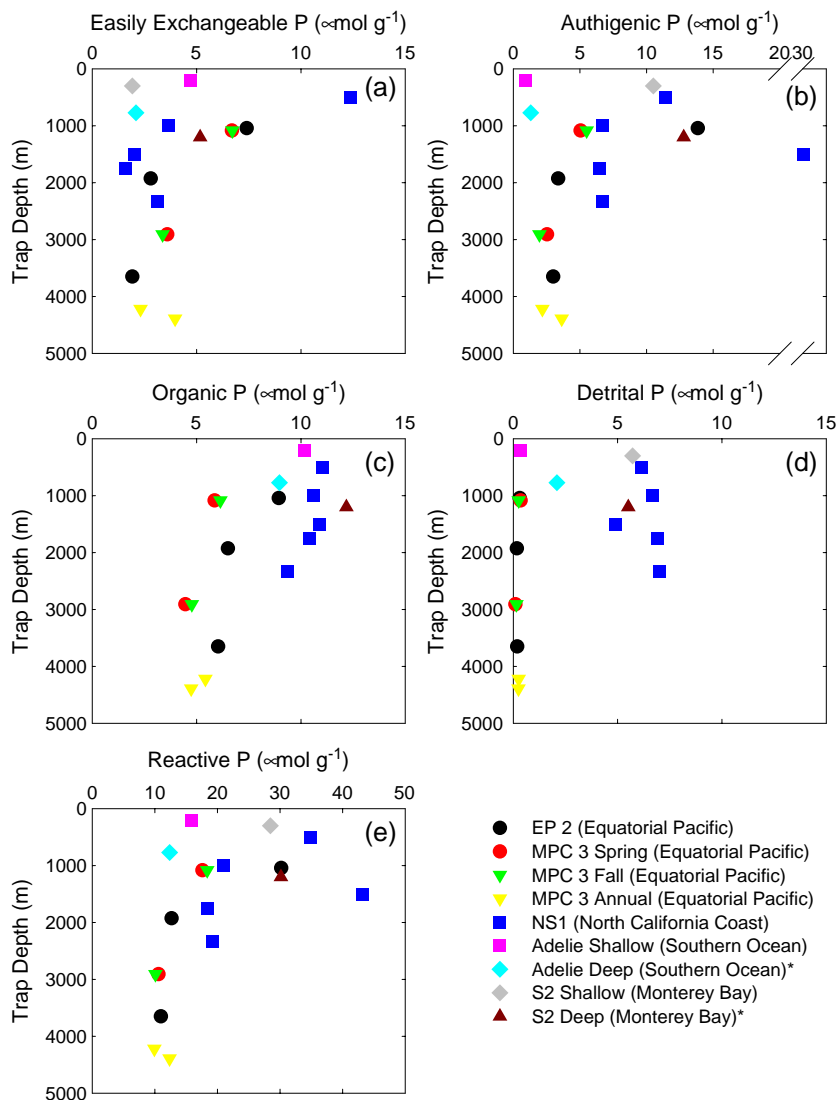


Fig. 3. Particulate phosphorus (P) concentrations ($\mu\text{mol P g}^{-1}$) vs. sediment trap depth (m) for selected samples in this study. Samples represent different regions and time intervals as well as varying depths. Symbols identify samples from each region as shown in the legend. For a given site, the samples cover approximately the same sampling time interval. See Table 1 for exact sampling time intervals. See Methods for typical analytical errors. Values below detection limit ($<0.4 \mu\text{mol g}^{-1}$ for labile and oxide-associated P, $<0.3 \mu\text{mol g}^{-1}$ for authigenic P, $<0.1 \mu\text{mol g}^{-1}$ for detrital P, and $<0.1 \mu\text{mol g}^{-1}$ for organic P) are not plotted. Sites that may be affected by advection or resuspension, the Adelie and Monterey Bay deep traps, are plotted separately and are starred on the legend. All component concentrations decrease with depth. (a) P_{1-0a} . (b) Authigenic P. (c) Organic P. (d) Detrital P. (e) Reactive P, the sum of labile/oxide-associated, authigenic, and organic P.

similar to coretops than to sinking particulate matter. It is possible that the Palmer Deep trap is receiving detrital P flux ($\sim 40\%$ of total P) associated with falling particulate matter because it is so close to the coast. However, for the preceding reasons, we do not include samples from Chinstrap, Gentoo, or Palmer

Deep in further discussions of depth trends or C to P ratios.

In this study, the range of reactive P concentrations in the deepest sediment traps (10 to $25 \mu\text{mol P g}^{-1}$, at ~ 4000 m) is similar to or slightly higher than the range of reactive P values in the sediments (8 to $20 \mu\text{mol P}$

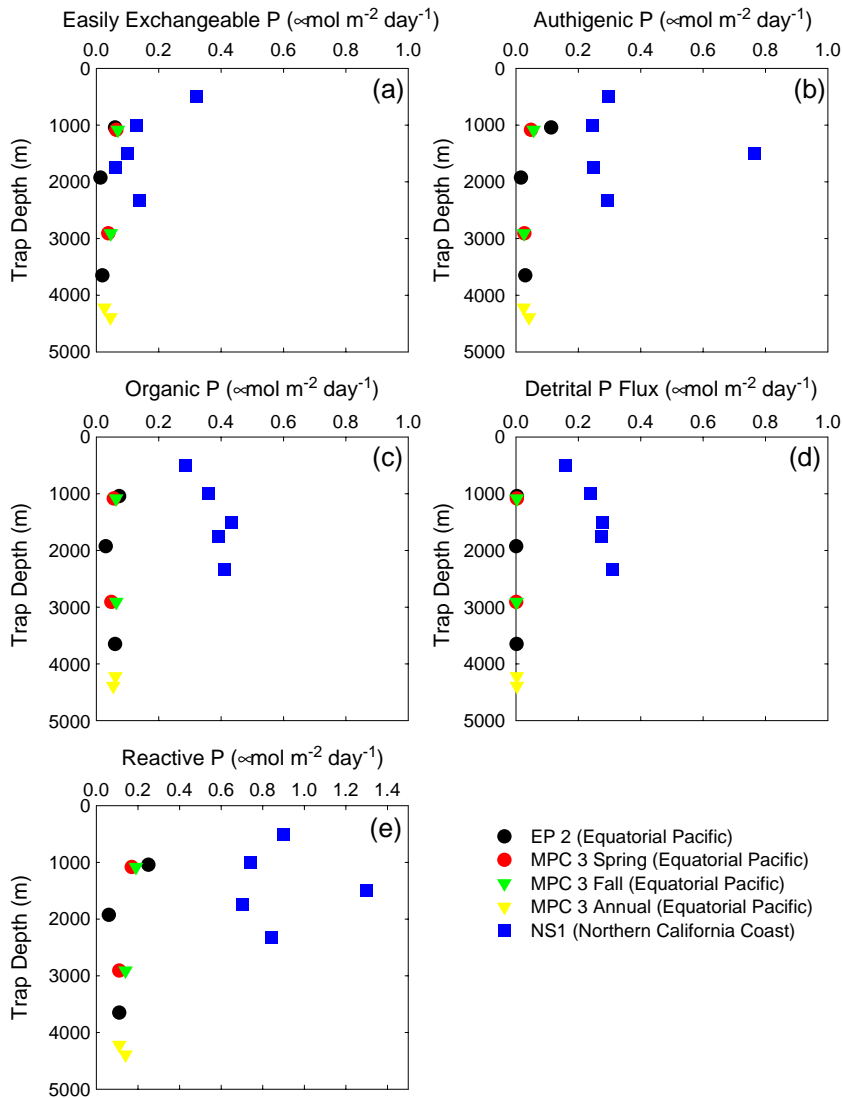


Fig. 4. Particulate phosphorus (P) fluxes ($\mu\text{mol P m}^{-2} \text{ day}^{-1}$) vs. sediment trap depth (m) for selected samples in this study. Samples represent different regions and time intervals as well as varying depths. Symbols identify samples from each region as shown in the legend. For a given site, the samples cover approximately the same sampling time interval. See Table 1 for exact sampling time intervals. See Methods for typical analytical errors. Sites that may be affected by advection or resuspension, the Adelle and Monterey Bay deep traps, are not plotted. (a) $P_{1-\text{oa}}$. (b) Authigenic P. (c) Organic P. (d) Detrital P. (e) Reactive P, sum of labile/oxide-associated, authigenic, and organic P.

g^{-1}) (Table 4). Generally, when core top samples are compared to the deep traps at the respective sites, reactive P concentrations are similar, indicating little loss of total P from deep sediment traps to core top sediments (Fig. 5a–c). This is true for all sites including those not “suffering” from input from resuspension or lateral advection. Although reactive P concentrations in deep traps and core tops are similar, the organic and

$P_{1-\text{oa}}$ fractions’ contributions decrease. The proportion of authigenic P, on the other hand, increases dramatically from the deepest sediment traps to the core tops (Fig. 5a–c). These changes indicate that we are observing “sink switching,” as defined by Ruttenberg and Berner (1993), occurring between the deepest sediment trap samples and the core top samples as $P_{1-\text{oa}}$ and organic P are transformed to authigenic P.

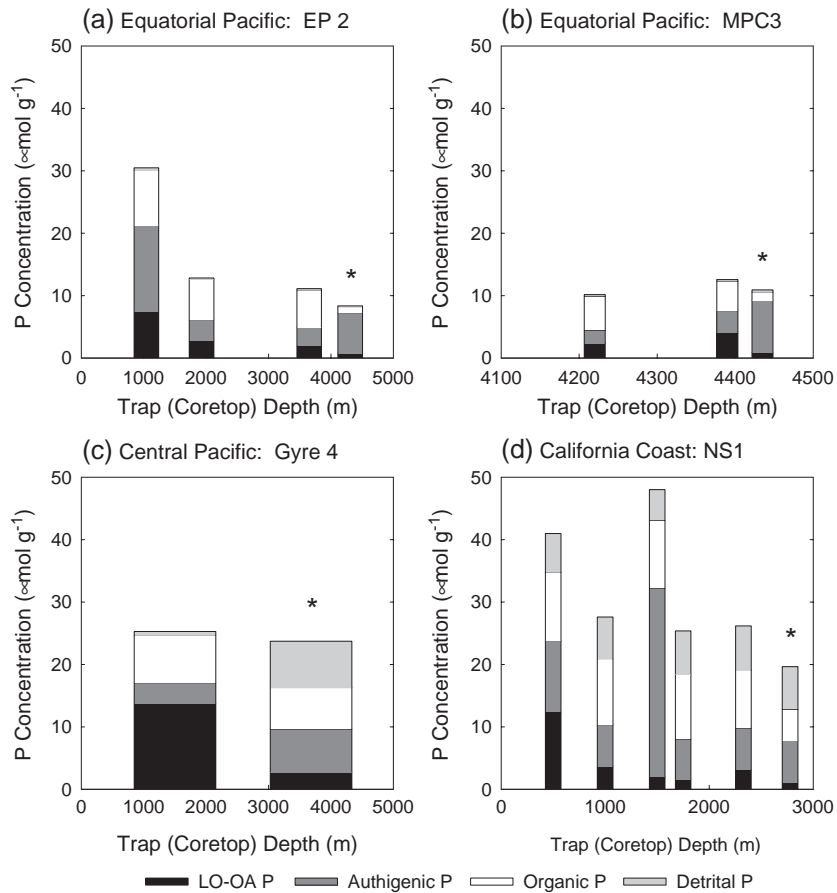
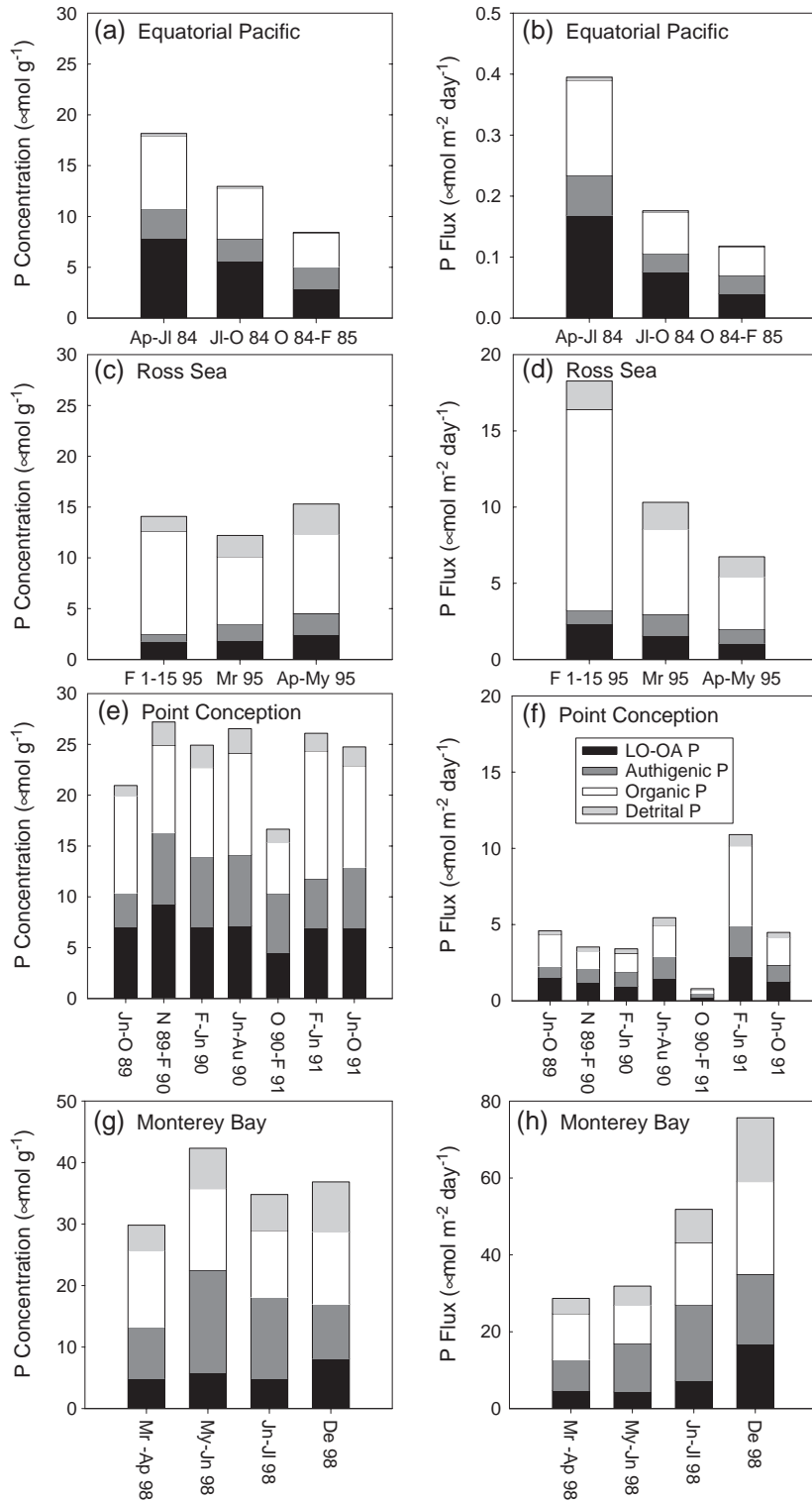


Fig. 5. Particulate phosphorus (P) concentrations ($\mu\text{mol P g}^{-1}$) vs. sediment trap or core top depth (m) for selected individual sites. Each stacked bar includes the concentration, from the bottom up, of $P_{\text{lo-oa}}$, authigenic P, organic P, and detrital P. For each site, each vertical bar represents a sediment trap, except the last vertical bar in each group, which represents a core top sediment sample (denoted by *). Note the sink switching apparent at each site (except the California Coast site) from the deepest sediment trap to the core top: the relative amount of $P_{\text{lo-oa}}$ and organic P decreases as the relative amount of authigenic P increases. (a) Equatorial Pacific site EP2, water depth 4360 m. The sediment trap at 1042 m represents a time interval from February–September 1993. The deeper traps represent a yearlong interval from February 1993 to 1994. (b) Equatorial Pacific site MPC3, water depth 4450 m. Each sediment trap represents approximately a yearlong time interval from February 1980 to April 1981. (c) Central Pacific site MT 4 Gyre, water depth 3718 m. This sediment trap covers an annual interval from September 1989 to 1980. (d) Northern California Coast site NS-1, water depth 2829 m. These sediment trap samples represent annual averages from September 1983 to 1984 calculated as a weighted average from individual samples covering shorter time intervals within the year.

Sink switching was observed for every sediment trap-core top set we examined except the Northern California Coastal site (NS 1). Although reactive P, $P_{\text{lo-oa}}$, and organic P all decrease with depth for NS 1,

their proportions generally remain the same throughout the water column and the core top (Fig. 5d). This site is much shallower (2778 m) compared to the other sites that show sink switching, so perhaps there is a

Fig. 6. Particulate phosphorus (P) concentrations ($\mu\text{mol P g}^{-1}$) and fluxes ($\mu\text{mol P m}^{-2} \text{ day}^{-1}$) vs. season for selected individual sediment traps in this study. Each stacked bar includes, from the bottom up, $P_{\text{lo-oa}}$, authigenic P, organic P, and detrital P. Note that concentrations do not systematically vary with season, but fluxes for each site (except Monterey Bay) decrease from spring to summer to fall to winter. (a and b) Equatorial Pacific site MPC 3, water depth 4450 m, trap depth 1883 m. (c and d) Ross Sea site A, water depth 817 m, trap depth 775 m. (e and f) Point Conception site Station M, water depth 4100 m, trap depth 4050 m. (g and h) Monterey Bay site S2, water depth 1800 m, trap depth 1200 m.



minimum depth or time needed for significant sink switching to occur.

3.3. Seasonal trends

Particulate P fluxes vary temporally at all sites (Fig. 6). However, the proportions of fractions of P in the sinking particulate matter remain relatively constant

over time (Fig. 6). While at the Equatorial Pacific and Ross Sea the highest fluxes correspond to the seasons with maximum productivity (spring and austral summer, respectively), samples from the Point Conception do not show consistent seasonal trends, and traps from Monterey Bay from 1998 show a maximum flux in December (Fig. 6h). A possible cause for the trend in the latter trap is that advected or resuspended material,

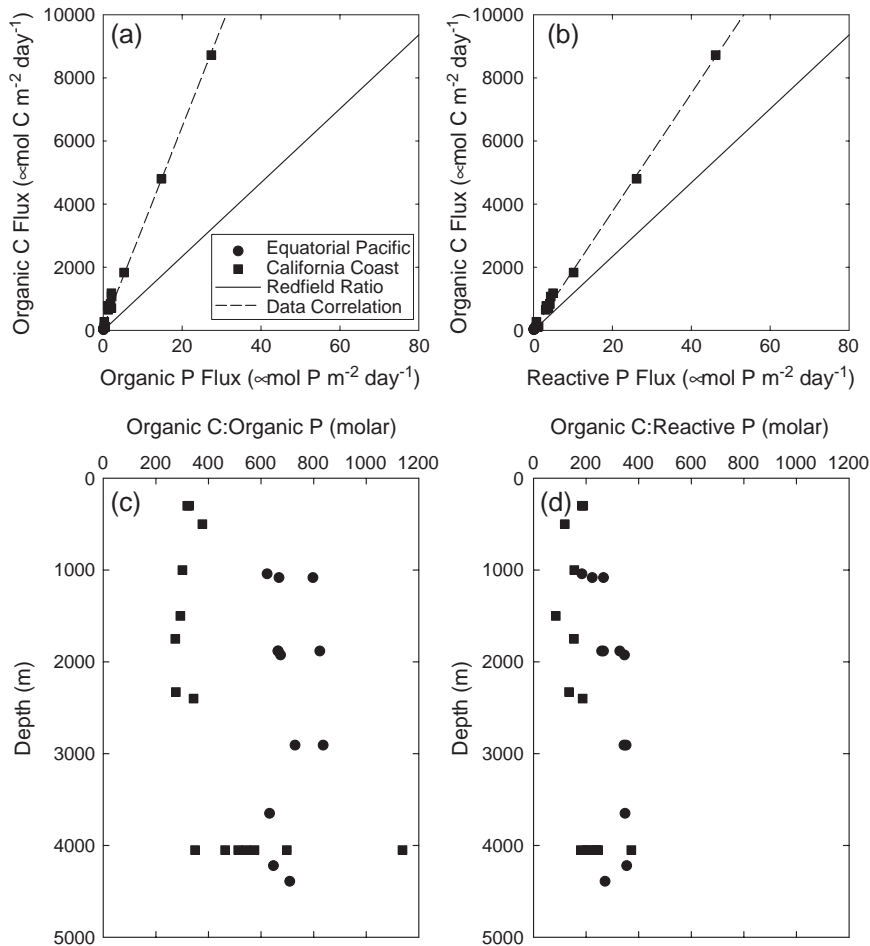


Fig. 7. (a) Organic C flux ($\mu\text{mol C m}^{-2} \text{ day}^{-1}$) vs. organic P flux ($\mu\text{mol P m}^{-2} \text{ day}^{-1}$). Note that values are much higher than the Redfield Ratio (117:1, Anderson and Sarmiento, 1994). Organic C and organic P fluxes are correlated (overall, slope=318, y-intercept=99, $r^2=0.99$, $n=28$; Equatorial Pacific, slope=622, y-intercept=4.8, $r^2=0.96$, $n=12$; California Coast, slope=314, y-intercept=176, $r^2=0.99$, $n=16$) within a 95% confidence interval. (b) Organic C flux ($\mu\text{mol C m}^{-2} \text{ day}^{-1}$) vs. reactive P flux ($\mu\text{mol P m}^{-2} \text{ day}^{-1}$). Organic C and reactive P fluxes are also correlated (overall, slope=187, y-intercept=27, $r^2=0.99$, $n=28$; Equatorial Pacific, slope=209, y-intercept=11, $r^2=0.84$, $n=12$; California Coast, slope=187, y-intercept=41, $r^2=0.99$, $n=16$) within a 95% confidence interval. (c) Organic C: organic P molar ratio vs. depth. (d) Organic C/ reactive P molar ratio vs. depth. The slope between the organic C/ reactive P and depth is indistinguishable from zero (slope=0.02, y-intercept=176, $r^2=0.18$, $n=28$) within a 95% confidence interval. Samples represent different regions, time intervals, and depths. Symbols identify samples from each region as shown in the legend.

which contributes to all the P component fluxes and total flux in the Monterey Bay S2 trap, is most common during winter storms (Pilska et al., 1996).

3.4. C/P ratios

Particulate organic C and organic P (acid-insoluble) are highly correlated within each region (e.g., Equatorial Pacific, $r^2=0.96$, $n=12$; California Coast, $r^2=0.99$, $n=16$; Fig. 7a) and overall ($r^2=0.99$, $n=28$; Fig. 7a), implying that this operationally defined organic P is associated with organic C. However, these correlations do not yield the Redfield Ratio (117:1, Anderson and Sarmiento, 1994). The slopes for the equations relating organic C and organic P are significantly higher than the Redfield Ratio: 622 for the Equatorial Pacific, 314 for the California coastal sites, and 318 overall (Fig. 7a). The range of ratios is very large (between 276 to 1138) and could be as much as eight times higher than the Redfield ratio (Fig. 7c).

Organic C and reactive P are also positively correlated (overall, $r^2=0.99$, $n=28$; Equatorial Pacific $r^2=0.84$, $n=12$; California Coast $r^2=0.99$, $n=16$, Fig. 7b). Notably, the slope between organic C and reactive P is much closer to, but still higher than the Redfield Ratio: 209 for the Equatorial Pacific, 187 for the California Coastal sites, and 187 overall (Fig. 7b). Individual sample ratios range from 85 to 354 (Fig. 7d). Including some of the reactive P fractions and not others in the correlations with organic C results in slopes much higher than Redfield Ratio. These higher slopes indicate that a significant amount of reactive P is missing relative to Redfield ratio prediction (e.g., 318 for organic C to organic P, $r^2=0.99$; $n=28$; 463 for organic C to reactive minus organic P, $r^2=0.83$, $n=28$ [note that when a Monterey Bay sample with an unusually high proportion of organic P is removed, the slope becomes 452, $r^2=0.99$, $n=27$]; and 256 for organic C to reactive minus authigenic P, $r^2=0.98$, $n=28$). However, for each of these fractions, the strong correlation remains, indicating that all forms of reactive P are associated with organic C in the water column. In contrast, there is no correlation between organic C and detrital P. Within the Coastal California region and the Equatorial Pacific region, at all sites, the organic C to reactive P ratios are relatively constant with depth and have a slope indistinguishable from zero (slope=0.02, y-intercept=176,

$r^2=0.18$, $n=28$). Samples from Southern Ocean sites are mostly suspected of suffering from resuspension or advection of P and thus are not included in these correlations.

4. Discussion

4.1. The nature of particulate P

It has been widely assumed that much of the sinking particulate P that leaves the upper ocean and arrives at the sediment is associated with organic compounds from biological production (e.g., organic P), but this material has not been well characterized. Indeed, classically defined (acid-insoluble) organic P comprises the largest portion (40% on average) of total P in sinking particulate matter relative to other fractions at all sites. However, in addition to acid-insoluble P, we identify several previously unrecognized pools of P in the sinking particulate matter. P_{l-oa} in rapidly sinking particles which may be largely labile P that is released by degradation of biological particulate matter or is associated with oxide particles comprises another ~21% (ranging from 3% to 54%) of total P. This labile P should be included in the sinking particulate P previously associated with living organisms (as is the organic P). Together these fractions comprise up to ~60% of total P in particulate matter (e.g., very labile P, oxide-associated P and acid-insoluble P). In some coastal and Southern Ocean sites detrital P is also quite significant. For example, it comprises up to ~25% of total P in NS1, and up to ~40% of total P in Palmer Deep (although it is likely this site has resuspended or advected material). This detrital P is not part of the reactive P fraction and is not related to biogenic material.

Even more surprising is that a significant fraction of total P (~25%, ranging from 3–78%) is carried from the upper ocean to the sediments as authigenic P. The importance of authigenic P (not always biogenic debris like fish teeth) in sediment traps shows that regeneration of organic P and exchange with other forms of P may begin in the water column, and continues in the sediments. Paytan et al. (2003) also found ^{31}P NMR evidence that there is considerable transformation from the organic to the inorganic P pool in the water column. Authigenic P, or CFA formation, as detailed in Ruttenberg and Berner (1993), is an abiotic process where

precipitation occurs chemically, not biologically, when the ion activity product is equal to or exceeds the solubility product for authigenic CFA. However, the necessary phosphorus for authigenic P precipitation most likely comes from a biological source. Authigenic P does not form from detrital phosphorus.

Carbonate fluorapatite could form in the water column in microenvironments in large sinking particles. Perhaps there are microenvironments in the water column that allow the concentration of P and precipitation of authigenic CFA. There is a possibility that the authigenic P is forming only in the sediment trap cups, in which case the authigenic P would be a sampling artifact. For example, it is possible that in sinking particulate matter the P released from the remineralization of biological material is mostly dissolved and dispersed into the water column and conditions that promote CFA formation do not exist. If indeed authigenic P formation is an artifact of cup sampling we would expect that there would be a relationship between the length of time the cup was out and the amount or percentage of authigenic P in the cup. Neither relationship exists in this data set. In terms of total reactive P, if authigenic P formation were only occurring in the traps, it would be no more a sampling artifact than the high concentrations of organic P found in the traps, in the sense that authigenic P almost always forms at the expense of organic P or intermediaries in its transformation. Additionally, the strong correlations ($r^2=0.98-0.99$) between organic C and reactive P (with or without either organic P or authigenic P) in this data set implies that all of these forms of P are strongly associated with organic C and are not sampling artifacts. However, we acknowledge that tests need to be designed and carried out in order to confirm that the presence of authigenic P is not a sampling artifact.

It is important to note that the SEDEX extraction was extremely well designed and tested (Ruttenberg, 1990, 1992) to target specific fractions, thus we do not think that the any other phase is incorporated in the authigenic P extraction step. Ruttenberg tested both phytoplankton and zooplankton samples, closely analogous to sinking particulate matter in the ocean. For the phytoplankton, 80% of the P was removed in SEDEX step 1 (a magnesium chloride rinse, representing loosely sorbed or exchangeable P), about 10% was removed in step 5 (organic P), and less than 5% was extracted in

the authigenic P phase. Likewise, 90% of the P in the zooplankton sample was extracted in step 1, almost 10% in step 5, and a negligible amount in the authigenic phase. Specificity experiments for CFA show that greater than 95% of the P in CFA is extracted in the authigenic step, with the remaining 5% extracted in the previous steps. The only other possibility for the authigenic P step is that we are extracting P from fish teeth (none were observed in any samples upon visual inspection), which should obviously be included in biogenic related P. As a result, we are confident that the authigenic P phase is well targeted.

All forms of reactive P (labile P, oxide-associated P, acid-insoluble P, and authigenic P) in oceanic particulate matter together make up about 90% of total P. Since a significant fraction (~60%) of P is delivered to the sediment water interface in phases other than acid-insoluble organic P, the internal oceanic particulate P cycle should be revised. P associated with the labile, oxide, and authigenic fractions should be included as components of reactive P in discussions of the export of P from the photic zone and delivery of P to the sediments from a sedimentary perspective (Fig. 8). By “reactive” P, we mean any kind of P that was at some point part of the biomass and therefore should be included in the “flux” budget of P within the ocean, and particularly when regeneration, export of P relative to C to the ocean floor, and C/P ratios are discussed.

The concentrations and fluxes of all components of P but detrital P decrease or remain relatively constant with depth greater than 300 m in the water column, therefore, we can conclude that these fractions are being remineralized with depth to some degree, although not necessarily by biological processes (Fig. 4). For example, the decrease of authigenic P concentration and flux with depth observed at some sites may be due to increasing acidity in the water column, an abiotic process, rather than remineralization by the biota. However, this increase in acidity is very small and is unlikely to cause a significant loss in authigenic P with depth. At greater depths and in the sediments, P_{1-0a} and organic P undergo additional significant transformations to authigenic P, therefore justifying the inclusion of authigenic P in the reactive P fraction, but not necessarily in the “bio-available” fraction.

Other workers have identified the importance of P fractions other than classically defined organic P in the rapidly sinking particulate P pool. Loh and Bauer

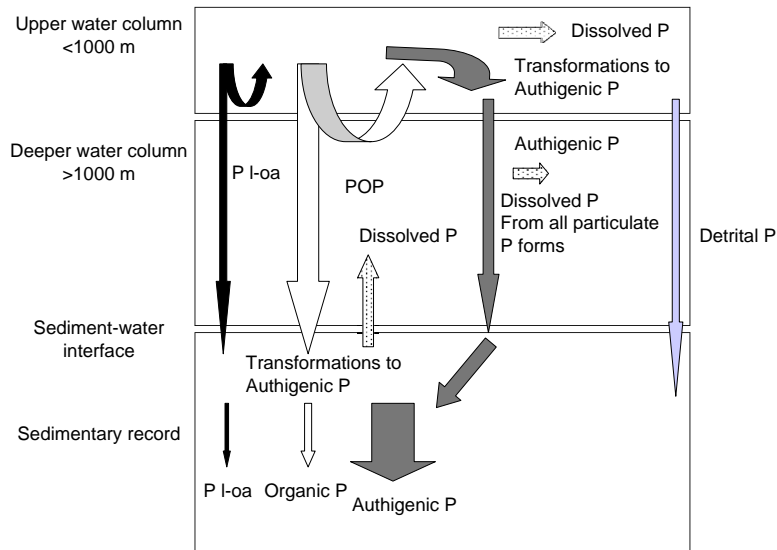


Fig. 8. This figure shows the current state of knowledge of the particulate P cycle in the oceans and sediments (modified from figures in Filippelli and Delaney, 1996; Delaney, 1998; Benitez-Nelson, 2000), updated with results from this work. Particulate P is recycled in the water column before a fraction of P is delivered to the deep ocean, primarily associated with organic matter. Based on this work, we indicate in the figure that a significant fraction of P is also delivered to the deep ocean associated with authigenic, labile, and oxide-associated P phases. A small amount of detrital P is also delivered to the deep ocean. In the surface sediments, particulate P delivered with organic matter and/or oxide associated is regenerated to dissolved P and precipitated as oxyhydroxide-associated P or authigenic P which is then preserved in the sedimentary record (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996). Ultimately, a small fraction of P produced as organic P in the upper water column is buried (Delaney, 1998). Colors used for labile/oxide-associated, authigenic, organic, and detrital P arrows are the same as those used in previous figures.

(2000) measured particulate inorganic P (PIP) and particulate organic P (POP) in sediment traps from Station M (Point Conception). Their sinking particulate organic P (POP) fraction should correspond to our acid-insoluble organic P fraction, and their sinking PIP fraction should correspond to our total P minus acid-insoluble organic P. They found that a significant fraction, up to 80% of total particulate P in sinking particulate matter consisted of particulate inorganic P (Loh and Bauer, 2000). Similarly, we found that for Station M, P_{I-oa} , authigenic P, and detrital P together comprised about 60% of the total P but only about 7% of this P was detrital P. Therefore, much of the P commonly characterized as PIP may have previously been biologically associated (e.g., reactive P such as P_{I-oa} or authigenic P).

Reactive P concentrations and fluxes are highest in areas of high primary productivity, such as coastal sites (Fig. 2). Indeed, the highest reactive P fluxes are associated with areas characterized by the highest productivity (Monterey Bay, Ross Sea, and Palmer Deep, Table 1; Fig. 2). However, this may be confounded

by the resuspension and horizontal advection occurring at these sites. Likewise, total particulate P concentrations are also higher in coastal ocean sites than in open ocean sites (Fig. 2), with a significant contribution of detrital P to coastal sites (e.g., 22% in the northern California coast site (NS1) to 40% in the Palmer Deep sites). This detrital P is undoubtedly from continental sources. For NS1, lithogenic flux rates have been documented as approximately 50 times higher than in the open ocean (Dymond and Lyle, 1994).

4.2. Core top sink switching

For almost all sites examined, sink switching occurs between the deepest sediment trap and the core top sample (Fig. 5). The proportions of P_{I-oa} and organic P decrease while proportions of authigenic P increase between the deepest trap and core top (Fig. 5). This, combined with the fact that the total reactive P concentrations remain relatively constant during this switch (e.g., do not change between the deepest trap and the sediment), implies

that the organic P signal has been retained as authigenic P, via sink switching, or the formation of carbonate fluorapatite at the expense of organic P or intermediaries in its transformation. This is the same indirect evidence that [Ruttenberg and Berner \(1993\)](#) identify as indicative of sink switching in the sediments, and implies that some precipitation of authigenic P occurs early after deposition in the upper sediments and does not require burial. This observation has significant implications for paleo studies of nutrient burial in the form of sedimentary P, as it suggests a close correspondence between the sinking particles and the sedimentary record. We recognize however that these core top and sediment trap samples are from oxygenated environments and thus may not capture processes that are specific to lower oxygen conditions. Other sedimentary studies of P have shown that this transformation continues with depth/age in the sediment column ([Ruttenberg and Berner, 1993](#); [Filippelli and Delaney, 1995, 1996](#); [Slomp et al., 1996](#); [Delaney and Anderson, 1997, 2000](#); [Anderson et al., 2001](#); [Faul et al., 2003](#)).

4.3. Seasonality of particulate P

In most cases, the magnitude of P flux at a given site and depth depends strongly on season, with the season where biological productivity is highest corresponding to the highest reactive P (and organic C) export fluxes ([Fig. 6a–f](#)). For most sites studied, detrital fluxes remain relatively constant throughout the year ([Fig. 6a–f](#)). The relative distribution of P within the total particulate P pool (e.g., association with specific fractions) is also relatively constant throughout the year ([Fig. 6a–f](#)). This implies that the overall composition and the relative regeneration processes of particulate P at depth are independent of season.

The Monterey Bay S2 site does not follow the seasonal trends observed for the other regions and expected from the seasonality of biological production ([Fig. 6g–h](#)). The highest P fluxes of all components (including detrital P) during 1998 are occurring in the winter. Indeed, [Pilskaln et al. \(1996\)](#) observed that in winter the lithogenic fluxes in Monterey Bay sediment trap samples, albeit in different years at slightly different locations, were

high, generally over 50% of the material collected. This was attributed to periodic resuspension and lateral advection of sediments from the slope during winter storms resulting in fluxes greater than those expected from vertical particle sinking for all P carrying components ([Pilskaln et al., 1996](#)). This process explains the deviation of samples from this site from the expected trend and should be considered as a process that could influence studies based on sediment traps.

4.4. Organic C to organic P and organic C to reactive P ratios

Organic C to organic P ratios in large, rapidly sinking particles yield values much higher than the Redfield Ratio, whereas organic C to reactive P ratios are closer to, but still generally higher than, Redfield ratio ([Table 5](#); [Fig. 7](#)). These data imply that P in sinking particulate matter has been preferentially regenerated relative to C when compared to C/P ratios in the living biomass. Considerable scatter is seen in the organic C to organic P ratios at different depths in the water column and no obvious trend is detected. Similarly the organic C to reactive P ratios do not have a slope distinguishable from zero at depth below ~300 m within each region ([Fig. 7](#), slope=0.02, y-intercept=176, $r^2=0.18$, $n=28$). This observation suggests that preferential regeneration of labile P compounds occurs at very shallow depths in the water column and little or no preferential regeneration of P relative to C occurs at depths below ~300 m. This is important in considering processes of carbon sequestration since the depth based decoupling of C and P regeneration may enable easier re-supply of P to the euphotic zone (higher recycling to support C fixation) while C is exported to depth. The closer to Redfield C/P ratios calculated using reactive rather than organic P indicates that at least some of the regenerated biological P at depth remain in the particulate pool rather than being transferred into the dissolved P pool.

When using total particulate P to estimate regeneration rates of P relative to organic C, including the detrital P fraction will result in overestimation of the actual organic P or even biologically related P in the sample. This would result in lower C/P ratios relative to those calculated from the organic P fraction or the

reactive P fraction and underestimating of the degree of preferential regeneration of P in sinking particles. On the other hand, if only acid-insoluble organic P is considered, this will result in the opposite effect (e.g., overestimating the degree of preferential regeneration) because the labile particulate P and authigenic P components, which have been part of the particulate matter, are not being included. Underestimates of organic C/organic P ratios using previously reported total P and organic C measurements are more pronounced in coastal sites where the detrital P comprise large fractions of total P. Likewise, overestimates of organic C/organic P ratios using acid-insoluble organic P are most pronounced in the equatorial Pacific, where a significant fraction of the organic P is P_{1-0a} , which includes the very labile P fraction that was part of the biological pool (thus included in the Redfield ratio of the biomass) and which is not included in the acid-insoluble organic P pool. Additionally, studies that have reported preferential remineralization of organic P relative to organic C with depth and assumed that all of the regenerated P moves into the dissolved pool may not be taking into account the sink switching effect, which results in authigenic P being an important carrier of P in particulate matter. The sites least affected by miscalculations of organic C to organic P and relative regeneration are sites where the vast majority of total P is acid-insoluble organic P. As we have shown, this is often not the case.

5. Conclusions

We analyzed particulate matter from sediment traps and selected coretops from a wide range of oceanic regimes for their P concentration and association. P in the sediment traps is primarily composed of acid-insoluble organic P (~40%), with significant proportions of authigenic P (~25%) and P_{1-0a} (~21%), and lesser proportions of detrital P (~13%). Previously unappreciated associations of P in sinking particulate matter change views about P delivery and recycling in the oceans. Authigenic P, and to some degree labile and oxide-associated P, should be included as additional shuttles of P from the upper ocean to the sediments (Fig. 8). Previous estimates of P regeneration using total P likely overestimate the

organic and even the biologically related (e.g., reactive) P in particulate matter by including detrital P. Acid-insoluble organic P measurements likely underestimate biogenic particulate P, because they do not include the P_{1-0a} or authigenic P fractions that undoubtedly are or were biologically related. Much of the organic P regeneration occurs at very shallow depths, however, remineralization of all reactive P phases persists in the water column at depths >300 m, implying that all of these P components are involved in biogeochemical cycling.

Sink switching occurs between the deepest sediment trap and the core top sample from P_{1-0a} and organic P to authigenic P. In most cases, although the magnitude of P flux at a given site decreases with depth and fluctuates seasonally, the relative association of P with different components of the sinking particulate matter is constant with depth (below ~300 m) and throughout the year, implying no seasonal or depth control on these associations.

Organic C to reactive P ratios are closer to Redfield ratio than organic C to organic P implying that reactive P may be more representative of the P in the original organic matter and possibly a more accurate measure of paleo P concentrations and paleo productivity. Additionally, organic C/reactive P values remain relatively constant with depth (>300 m) within different regions, showing that no preferential release of P relative to C into the dissolved pool takes place deeper in the water column. These factors should be considered when interpreting P cycling in the oceans and burial in the sediments.

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