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# Phosphorus-cadmium cycling in northeast Pacific waters

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## ABSTRACT

The vertical distributions of dissolved and particulate Cd and  $PO_4$  were determined in water samples collected off the central California coast. The same elements, plus carbon, were also measured in passively sinking particulates that were caught in particle interceptor traps set at depths of 35, 65, 150, 500, 750, and 1500 m. As expected, close relationships were observed between these elements; Cd and  $PO_4$  concentrations in the suspended and trapped particulates decreased markedly with depth, suggesting that these elements are released as their organic carriers are destroyed. This, in turn, leads to maxima for soluble Cd and  $PO_4$  regularly observed at mid-depths.

The dissolved Cd and  $PO_4$  concentrations observed in water, together with the flux data for these elements, were used to calculate residence times for various segments of the water column. Residence times of one year were found for the upper 65 m in comparison to ~ 250 years for the upper 750 m for both Cd and  $PO_4$ . Various components of the  $PO_4$  cycle actually measured in this study, together with estimates from the literature, were combined in a schematic drawing in an attempt to depict the  $PO_4$  cycle occurring in the upper waters of the ocean.

## 1. Introduction

The cycling and vertical transport of major and minor elements in the sea involve the uptake and release of elements from two classes of particles, those formed in the ocean (biogenous particulates), and those not formed in the ocean but rather introduced via riverine and atmospheric input (largely lithogenous). Although many elements can be associated with both classes of particles, some cycles appear to be dominated by one class of particles and not the other. For example, the similarity between the vertical distributions of Cd and the plant nutrients, phosphate and nitrate, suggests that the biogeochemistry of this element is strongly dominated by the cycling of organic matter (Martin *et al.*, 1976; Boyle *et al.*, 1976; Bender and Gagner, 1976; Bruland *et al.*, 1978). Cadmium levels are depleted near the surface and enriched in deep waters. This distribution and the Cd-plant-nutrient relationships suggest that Cd is taken up by the phytoplankton in the surface waters and is transported to depth in association with the organic remains of these organisms. As

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the sinking organic detritus is destroyed, Cd is released in concert with  $\text{PO}_4$  and various organo-N compounds which are eventually oxidized to nitrate.

In order to gain understanding of Cd and  $\text{PO}_4$  cycling in relation to organic matter, we set a series of particle interceptor traps (MULTITRAPS) off central California in December of 1978. The traps enabled us to catch passively sinking particles at several depths and, after appropriate analyses, calculate the vertical fluxes of Cd,  $\text{PO}_4$  and C. In this paper, we report these data and relate them to the vertical distributions of particulate and soluble Cd and  $\text{PO}_4$  existing in the water column at the time of this study. The relationships between these elements and residence times for Cd and  $\text{PO}_4$  are presented and discussed. An attempt is also made to inter-relate the major components of the  $\text{PO}_4$  cycle using the actual measurements mentioned above in conjunction with estimates for zooplankton standing crop, soluble  $\text{PO}_4$  excretion and growth.

## 2. Methods

In order to measure the vertical fluxes of C, P and Cd in association with passively sinking particles, free-floating MULTITRAPS were set 100 km off the California coast ( $\sim 36^\circ 50'N$ ;  $123W$ ) at depths of 35, 65, 150, 500, 750, and 1500 m during a six-day, four-hour period in December of 1978. Basically, the traps consist of PVC cross frames fitted with eight identical lucite cylinders that are filled with a high-density NaCl solution ( $\rho = 1.07 \text{ g cm}^{-3}$ ) containing 5% buffered formalin. All internal parts of the traps were thoroughly cleaned with Micro and dilute quartz-distilled  $\text{HNO}_3$ . Contaminant Cd was removed from the NaCl-formalin solution by passing it through Chelex resin prior to loading. All handling procedures were carried out in shore-based or shipboard filtered-air clean laboratories. Further details about the traps, including a discussion of their accuracy based on  $^{210}\text{Pb}$  data, have been published elsewhere (Knauer *et al.*, 1979). Sediment traps of different design were recently tested in the Sediment Trap Intercalibration Experiment (STIE); the MULTITRAPS yielded fluxes similar to those reported by Honjo, Gardner and Soutar (Spencer, WHOI, pers. comm.).

The trapped particulates from three of the eight trap cylinders at each depth were analyzed for Cd using flameless atomic absorption after digestion with  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  (Martin and Knauer, 1973). A fraction of the digest was diluted and analyzed for  $\text{PO}_4$  colorimetrically (Murphy and Riley, 1962). Aliquots of trapped particulates were also analyzed for organic C using a CHN analyzer after treatment with dilute HCl to remove carbonates (Knauer *et al.*, 1979). The high density NaCl solutions in the trap cylinders were filtered through acid-washed 0.4  $\mu\text{m}$  Nuclepore filters and, after preconcentration on Chelex, analyzed for Cd by flameless atomic absorption. The filters were also digested and analyzed, and the amounts of Cd found in this fraction (usually  $< 1\%$  of the total Cd) were added in with the trapped partic-



ulate fraction. Additional portions of the salt solution were evaporated to dryness, combusted, diluted and analyzed for  $\text{PO}_4$  (Murphy and Riley, 1962).

In order to accurately estimate Cd and  $\text{PO}_4$  blanks, sealed trap cylinders containing the NaCl-formalin solution were deployed at 35, 500 and 1500 m for the duration of the experiment. These blanks, processed in the same manner as the experimental solutions, contained less than 0.022 nmol Cd and 0.01  $\mu\text{mol PO}_4$ , liter<sup>-1</sup>.

Water samples were collected in Teflon coated 30-liter Go-Flo bottles that were suspended on non-metallic Kevlar line. Immediately after collection, the samples were filtered through tared acid-washed 142 mm 0.4  $\mu\text{m}$  Nuclepore filters, mounted in Teflon sandwiches. Cadmium in the filtered water was then preconcentrated by passage through Chelex-100 ion exchange resin. After elution with 2 N  $\text{HNO}_3$ , the samples were analyzed for their Cd content by flameless atomic absorption. After washing off sea salts with pH adjusted Milli-Q water, drying and reweighing, the filters and residues were digested in Teflon bombs (Eggiman and Betzer, 1976) and analyzed for Cd and  $\text{PO}_4$  as described above. All of these procedures were carried out using stringent anticontamination techniques that have been described elsewhere (Martin *et al.*, 1976; Bruland *et al.*, 1978, 1979).

### 3. Results and discussion

Amounts of dissolved Cd at the study site (Table 1, Fig. 1) were very similar to those observed on previous cruises (Bruland, *et al.*, 1978). Once again, Cd levels were lowest at the surface (0.25 nmol liter<sup>-1</sup>) and greatest at mid-depth (940 m = 1.09 nmol liter<sup>-1</sup>). A similar Cd: $\text{PO}_4$  correlation was also observed. The slope of the resulting equation (nmol Cd =  $-0.037 + 0.36 [\mu\text{mol PO}_4]$ ) was somewhat higher than that previously reported (nmol Cd =  $-0.032 + 0.31 [\mu\text{mol PO}_4]$ ; Bruland *et al.*, 1978); but this difference is within experimental error.

In addition to the dissolved fractions, we also analyzed suspended particulates for their Cd and  $\text{PO}_4$  content (Table 1, Fig. 1). Amounts of particulate Cd and  $\text{PO}_4$  were highest near the surface (15 pmol Cd, 41 nmol  $\text{PO}_4$  liter<sup>-1</sup>) and lowest in the deepest samples (0.6 pmol Cd, 2.2 nmol  $\text{PO}_4$  liter<sup>-1</sup>). The amounts of Cd and  $\text{PO}_4$  per gram dry suspended particulates showed a similar decrease with depth, from near-surface maxima of 49 nmol Cd; 120  $\mu\text{mol PO}_4$  g dry wt<sup>-1</sup> to minima of 2.1 nmol Cd; 7.1  $\mu\text{mol PO}_4$  g dry wt<sup>-1</sup> at depth (Table 1). Thus, the vertical distribution of particulate Cd and  $\text{PO}_4$  mirrors that of dissolved Cd and  $\text{PO}_4$  (Fig. 1). It is also apparent that the amounts of suspended particulate Cd and  $\text{PO}_4$  are negligible in comparison to the dissolved fraction; i.e., of the total Cd and  $\text{PO}_4$  in the water column, the maximum percentages of particulate Cd and  $\text{PO}_4$  were only 5.2 and 4.4, respectively, while in the deeper samples, particulate Cd and  $\text{PO}_4$  were consistently < 0.1% of the total quantities observed (Table 1).

Table 1. Amounts of particulate and dissolved Cd and PO<sub>4</sub> observed in the water column at the time of this study. Particulate Cd and PO<sub>4</sub> as % of total Cd and PO<sub>4</sub> in water samples and Cd and PO<sub>4</sub> concentrations in the suspended particulates are also shown.

Depth (m)	Part. Cd pmol Liter <sup>-1</sup>	Diss. Cd nmol Liter <sup>-1</sup>	Part. Cd %	Cd Conc. in Part. nmol g <sup>-1</sup>	Part. PO <sub>4</sub> nmol Liter <sup>-1</sup>	Diss. PO <sub>4</sub> umol Liter <sup>-1</sup>	Part. PO <sub>4</sub> %	Part. PO <sub>4</sub> Conc. in Part. umol g <sup>-1</sup>
0.5	7	0.25	2.6	19	34	0.91	3.6	94
10	14	0.26	5.2	39	41	0.89	4.4	120
35	15	0.36	4.1	47	34	0.97	3.4	110
65	10	0.44	2.2	49	21	1.35	1.5	100
150	4	0.70	0.5	9.8	20	2.02	1.0	51
350	2	1.01	0.2	20	6.4	2.63	0.2	57
500	1	1.08	0.1	12	2.4	2.98	0.08	23
750	1	1.08	0.09	2.8	2.4	3.31	0.07	7.1
940	0.4	1.09	0.04	2.7	3.1	3.17	0.09	21
1500	0.6	1.08	0.06	2.1	2.2	3.02	0.07	7.9
1940	0.6	1.06	0.06	6.1	2.2	2.96	0.07	21

Similar trends with depth were also observed in the amounts of C, PO<sub>4</sub> and Cd measured in the trapped particulates (Table 2). For example, an average of 630 umol of trapped particulate organic carbon (TPOC) was found at 35 m in comparison to an average of 47 umol TPOC observed at 750 m. An increase in TPOC was noted at the 1500 m depth. The possible reasons for the increase are discussed elsewhere (Knauer and Martin, 1981). Identical patterns were also observed for trapped particulate PO<sub>4</sub> and Cd.

In order to check for possible solubilization, the salt solutions from the trap collectors (and appropriate trap blanks) were also analyzed for dissolved PO<sub>4</sub> and Cd; significant amounts were found at all depths (Table 2). In fact, the quantities in the salt gradients exceeded that associated with the trapped particles. About 80% of the total trapped Cd and about 65% of the PO<sub>4</sub> were found in the trap solutions.

The occurrence of major amounts of trapped soluble Cd and PO<sub>4</sub> raises two questions. What caused the solubilization and with which class of particles were solubilized Cd and PO<sub>4</sub> originally associated? We don't have a definitive answer to the first question; we can only offer the following possibilities. Cadmium was originally adsorbed on the surfaces of the sinking particles and when the particles entered the salt solution, the adsorbed Cd was displaced by the excess Na<sup>+</sup> ions or pulled off after complexation with the excess chloride ions. Phosphate may also have been desorbed from the particles or may have been released via cell lysing. In any event, it would appear that the NaCl solution led to the release of this PO<sub>4</sub> fraction.

In order to determine whether the trapped solubilized elements were originally

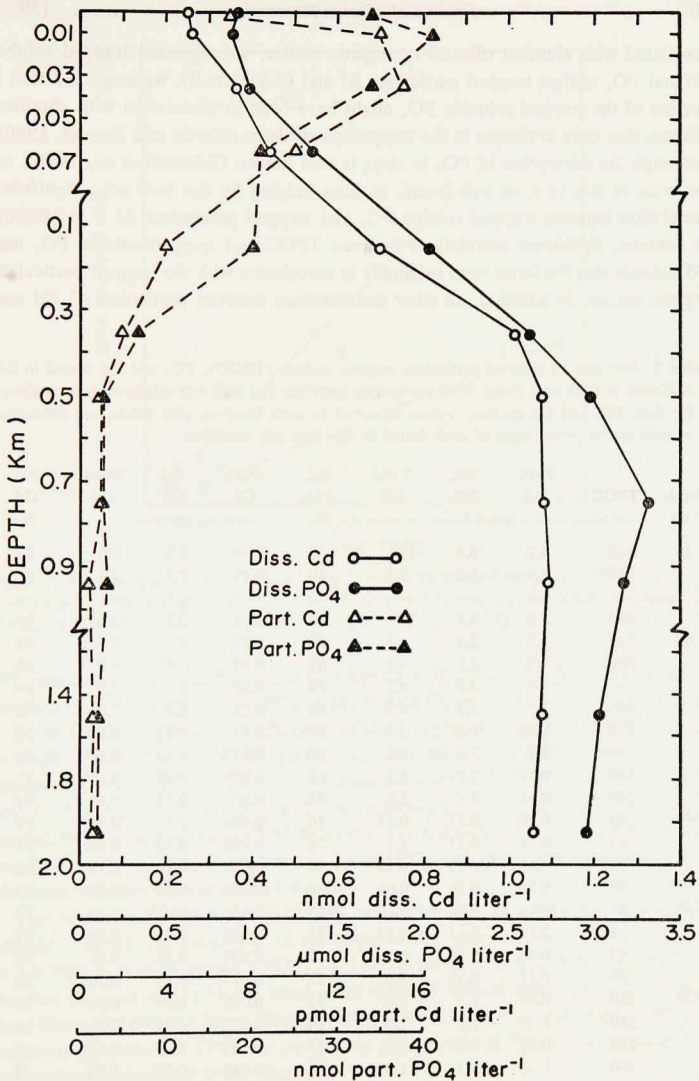


Figure 1. Vertical distributions of dissolved and particulate Cd and PO<sub>4</sub>.

associated with aluminosilicates or organic matter, we regressed trapped soluble Cd and  $\text{PO}_4$  against trapped particulate Al and C. Originally, we suspected that a portion of the trapped soluble  $\text{PO}_4$  might have been in association with aluminosilicates that were abundant in the trapped particulates (Martin and Knauer, 1980). Although the adsorption of  $\text{PO}_4$  to clays is well known (Edzwald *et al.*, 1976), no evidence of this process was found, at least judging by the lack of a significant correlation between trapped soluble  $\text{PO}_4$  and trapped particulate Al ( $r = 0.0280$ ). In contrast, significant correlations between TPOC and trapped soluble  $\text{PO}_4$  and Cd indicate that the latter were originally in association with the trapped particulate organic matter. In addition, all other combinations between particulate C, Cd and

Table 2. Amounts of trapped particulate organic carbon (TPOC),  $\text{PO}_4$  and Cd found in 2-3 replicates at each trap depth. Both particulate fractions and trap salt solutions were analyzed for their  $\text{PO}_4$  and Cd content. Values observed in each fraction, plus totals, are presented, as well as the percentages of each found in the trap salt solutions.

Depth (m)	TPOC	Part.	Sol.	Total	Sol.	Part.	Sol.	Total	Sol.
		$\text{PO}_4$	$\text{PO}_4$	$\text{PO}_4$	$\text{PO}_4$	Cd	Cd	Cd	Cd
		-----umol-----			%	-----nmol-----			%
35	680	4.2	6.8	11	62	0.49	2.8	3.3	85
	580	3.9	5.8	9.7	60	0.28	2.1	2.4	88
	—	—	—	—	—	—	1.7	—	—
$\bar{X}$	630	4.0	6.3	10	63	0.38	2.2	2.6	85
65	320	1.7	2.4	4.1	58	0.27	1.1	1.4	79
	280	1.7	2.9	4.6	63	0.20	0.98	1.2	82
	—	1.6	2.7	4.3	63	0.20	1.7	1.9	89
$\bar{X}$	300	1.7	2.7	4.4	61	0.22	1.2	1.4	86
150	190	0.81	1.8	2.6	69	0.12	0.77	0.89	86
	150	1.0	2.2	3.2	69	0.098	0.42	0.52	81
	140	0.74	1.2	1.9	63	0.089	0.40	0.49	82
$\bar{X}$	160	0.85	1.7	2.6	65	0.098	0.53	0.63	84
500	40	0.20	0.17	0.37	46	0.026	0.11	0.14	79
	55	0.32	0.77	1.1	70	0.056	0.30	0.36	83
	53	0.18	0.21	0.39	54	0.028	0.14	0.17	82
$\bar{X}$	49	0.23	0.38	0.61	62	0.036	0.19	0.23	83
750	39	0.16	0.30	0.46	65	0.021	0.089	0.11	81
	58	0.16	0.45	0.61	74	0.040	0.15	0.19	79
	44	0.18	0.55	0.73	75	0.020	0.19	0.21	90
$\bar{X}$	47	0.17	0.43	0.60	72	0.027	0.14	0.17	82
1500	110	0.55	1.5	2.0	75	0.068	0.18	0.24	71
	220*	0.26	1.2	1.5	80	0.023	0.19	0.21	90
	100	0.42	0.87	1.3	67	0.044	0.18	0.22	82
$\bar{X}$	100	0.41	1.2	1.6	75	0.045	0.18	0.22	82

\* Not included in mean.



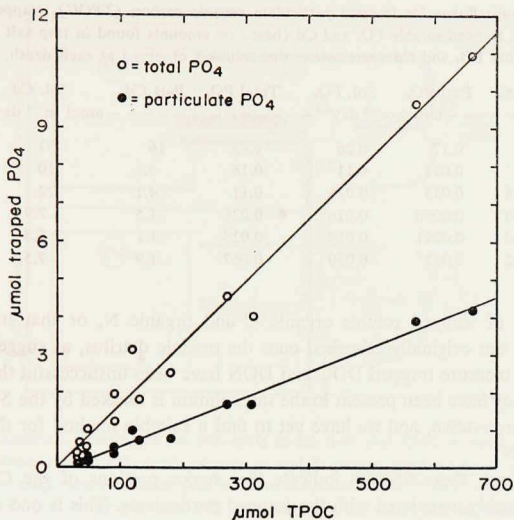


Figure 2. Trapped particulate organic carbon (TPOC) vs trapped particulate  $\text{PO}_4$  ( $\text{umol PO}_4 = -0.089 + 0.0066 [\text{umol TPOC}]; r = .9932; n = 15$ ) and TPOC vs total trapped  $\text{PO}_4$  ( $\text{umol PO}_4 = 0.0020 + 0.0165 [\text{umol TPOC}]; r = .9889; n = 15$ ).

$\text{PO}_4$  and soluble Cd and  $\text{PO}_4$  were also significantly correlated (lowest correlation coefficient = .9365 for soluble  $\text{PO}_4$  vs particulate Cd;  $n = 17$ ).

Several of the equations resulting from these regressions deserve comment. For example, the slope for total trapped Cd versus total trapped  $\text{PO}_4$  is 0.29, a value similar to the slopes for sea water Cd versus sea water  $\text{PO}_4$  (e.g., 0.36 in this study and 0.31 reported previously by us [with Bruland]). This similarity would, of course, be expected if the vertical distribution of Cd and  $\text{PO}_4$  in the water column results from the sinking of particulate Cd and  $\text{PO}_4$  and subsequent release of these elements with destruction of the carriers.

The relationships between TPOC and particulate  $\text{PO}_4$  and total  $\text{PO}_4$  are also of interest (Fig. 2). The reciprocal of the slope of the equation,  $\text{umol particulate PO}_4 = -0.089 + 0.0066 (\text{umol TPOC})$ , is 152, a value that would be expected for detritus (Knauer *et al.*, 1979), since such material should have higher C:P ratios than those reported for living phytoplankton (103 C:1 P; Redfield *et al.*, 1963). In contrast, the ratio for TPOC to particulate plus dissolved  $\text{PO}_4$  is 61, a value well below that observed for living plankton.

The low TPOC to total  $\text{PO}_4$  ratio of 61 suggests that either we are missing a



Table 3. Average fluxes for trapped particulate organic carbon (TPOC), trapped particulate  $\text{PO}_4$  and Cd, trapped soluble  $\text{PO}_4$  and Cd (based on amounts found in trap salt solutions; see text) and total  $\text{PO}_4$  and Cd (particulate plus soluble) observed at each depth.

Depth (m)	TPOC -----	Part $\text{PO}_4$ mmol $\text{m}^{-2}$	Sol. $\text{PO}_4$ $\text{day}^{-1}$ -----	Total $\text{PO}_4$ -----	Part Cd -----	Sol. Cd $\text{nmol m}^{-2}$	Total Cd $\text{day}^{-1}$ -----
35	26	0.17	0.26	0.43	16	91	110
65	12	0.071	0.11	0.18	9.1	50	59
150	6.6	0.035	0.071	0.11	4.1	22	26
500	2.0	0.0096	0.016	0.026	1.5	7.9	9.4
750	2.0	0.0071	0.018	0.025	1.1	5.8	6.9
1500	4.2	0.017	0.050	0.067	1.9	7.5	9.4

similar pool of trapped soluble organic C and organic N, or that much of the soluble  $\text{PO}_4$  was originally adsorbed onto the organic detritus, as suggested above. Attempts to measure trapped DOC and DON have been unsuccessful thus far. The DOC that may have been present in the salt solution is masked by the 5% formalin used as a preservative, and we have yet to find a suitable method for the measurement of DON.

In any event, these findings indicate that major portions of the Cd and  $\text{PO}_4$  were very weakly associated with the trapped particulates. This is one of the more important findings of this study. It indicates that significant portions of elements and compounds associated with sinking particles may be lost after the particles enter the traps. Although such solubilization may occur only in traps with NaCl density gradients and formalin solutions such as those we use, similar losses may also occur in traps of other designs, and the phenomenon represents a potential problem that must be assessed for other collecting devices.

Fluxes for C,  $\text{PO}_4$  and Cd at each depth (Table 3) were calculated by dividing the average amounts trapped (Table 2) by the mouth area of each cylinder ( $0.0039 \text{ m}^2$ ) and by the number of days that the traps were set (6.17). The surface TPOC and  $\text{PO}_4$  flux values fell in between those observed by us in a previous study; e.g.,  $12 \text{ mmol C m}^{-2} \text{ day}^{-1}$  at 65 m in comparison to 36 and  $7.6 \text{ mmol C m}^{-2} \text{ day}^{-1}$  at 50 m under upwelling and nonupwelling conditions (Knauer *et al.*, 1979). Fluxes decreased rapidly with depth. For example, the C flux observed at 150 m ( $6.6 \text{ mmol m}^{-2} \text{ day}^{-1}$ ) was a factor of 4 lower than that at 35 m ( $26 \text{ mmol m}^{-2} \text{ day}^{-1}$ ). This pattern suggests that large amounts of organic matter were being consumed and recycled in the upper water column, and relatively small amounts were being injected into the deep water column (see Knauer and Martin, 1981).

Since we had both "standing crop" (dissolved water Cd and  $\text{PO}_4$ ; Table 1) estimates together with fluxes for these elements (Table 3), we were able to calculate residence times for various portions of the water column (Table 4). Residence times of less than a year were measured for the 0-35 and 0-65 m depth intervals.

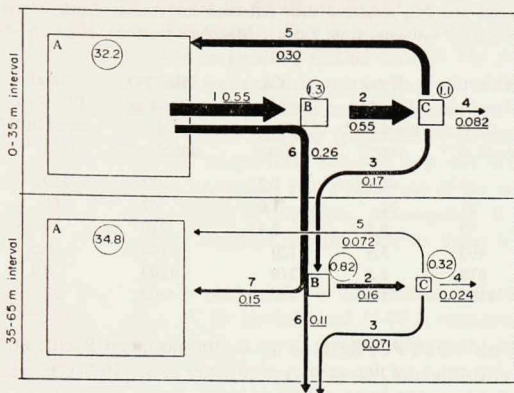


Figure 3. A schematic drawing of the PO<sub>4</sub> cycle in the 0-35 and 35-65 m depth segments. The boxes represent various PO<sub>4</sub> pools (drawn to scale); circled numbers in or near the boxes are standing crop values for each pool in units of mmol PO<sub>4</sub> m<sup>-2</sup>; A = dissolved PO<sub>4</sub>; B = particulate PO<sub>4</sub>; C = zooplankton PO<sub>4</sub>. Arrows represent rates (arrow width = scale) at which PO<sub>4</sub> is being cycled between pools and/or depth intervals. Underlined numbers are rates in units of mmol PO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>; 1 = primary production; 2 = zooplankton ingestion; 3 = zooplankton particulate excretion; 4 = zooplankton growth; 5 = zooplankton soluble excretion; 6 = flux of trapped soluble PO<sub>4</sub> in association with sinking particles (data from table 3); 7 = associated soluble PO<sub>4</sub> returned to dissolved pool ("flux in" minus "flux out" of 35-65 m depth interval for associated soluble PO<sub>4</sub>).

Probably, most of this material is recycled in the upper layers; however, Cd and PO<sub>4</sub> leaving the 150 m depth interval would not be returned to the surface except under intensive upwelling conditions. Thus, reasonable estimates for surface residence times for PO<sub>4</sub> and Cd are five and seven years, respectively. The former is in remarkable agreement with the four-year estimate calculated by Broecker using box models (see p. 18, 1974).

With the increases in Cd and PO<sub>4</sub> "standing crops" with depth, together with decreases in vertical transport rates, residence times become longer in the midwater column; e.g., 210 and 270 years at 750 m for PO<sub>4</sub> and Cd. Because of the increased PO<sub>4</sub> flux observed at 1500 m, the residence time for the 0-1500 m interval was about the same as that observed for the 750 m interval. The increase in the Cd flux at 1500 m was much less than that observed for PO<sub>4</sub> and as a result, the residence time nearly doubled (440 years) for this element.

Because of relatively high surface productivity rates in the nearshore environment, these deep residence times are shorter than those occurring in the open ocean.

Table 4. Cadmium and  $\text{PO}_4$  residence time estimates for various depth intervals calculated using "standing crop" estimates from Table 1 (dissolved fractions only) and flux data from Table 3.

Depth (m)	Diss. Cd Standing Crop $\mu\text{mol m}^{-2}$	Total Cd Flux $\mu\text{mol m}^{-2}$ $\text{year}^{-1}$	Cd Residence Time Years	Diss. $\text{PO}_4$ Standing Crop $\text{mmol m}^{-2}$	Total $\text{PO}_4$ Flux $\text{mmol m}^{-2}$ $\text{year}^{-1}$	$\text{PO}_4$ Residence Time Years
0- 35	10	40	0.25	32	160	0.20
0- 65	22	22	1.0	67	66	1.0
0- 150	70	9.5	7.4	210	40	5.2
0- 500	400	3.4	120	1100	9.5	120
0- 750	670	2.5	270	1900	9.1	210
0-1500	1500	3.4	440	4200	24	180

For example, particulate  $\text{PO}_4$  fluxes in the central northeast Pacific at 1050 m are on the order of  $0.40 \text{ mmol } \text{PO}_4 \text{ m}^{-2} \text{ yr}^{-1}$  (Knauer *et al.*, 1979). If we assume that this particulate flux was about one third of the total  $\text{PO}_4$  flux (soluble trapped  $\text{PO}_4$  was not measured in that study), and that the  $\text{PO}_4$  "standing crop" was  $2200 \text{ mmol m}^{-2}$  (Station 17, Bruland, 1980), a formal (ignoring lateral advection/diffusion) residence time of 1800 years ( $2200 \text{ mmol m}^{-2} \div 1.2 \text{ mmol m}^{-2} \text{ yr}^{-1}$ ) is obtained for the upper 1050 m. Because of the close relationship between Cd and  $\text{PO}_4$ , it is probable that Cd also has a similar residence time.

The data presented above represent several important components of the marine  $\text{PO}_4$  cycle: particulate and dissolved standing crop estimates in the water column; estimates of the vertical fluxes of particulate  $\text{PO}_4$  and associated trapped soluble  $\text{PO}_4$  throughout the upper 1500 m; and good estimates of the rate of  $\text{PO}_4$  fixation by the phytoplankton using the primary production data presented in Knauer and Martin (1981). However, we lack important data for the zooplankton component; i.e., standing crop, soluble  $\text{PO}_4$  excretion and the amounts of  $\text{PO}_4$  used by the zooplankton for growth.

Nevertheless, we believed that it was important that we try to summarize our findings in a schematic diagram showing the various components and rates for  $\text{PO}_4$  cycling in the upper water column. In order to include the zooplankton, we used the data of Butler *et al.* (1970) to make the following estimates: (1) We assume steady-state conditions under which the zooplankton are consuming all of the phytoplankton produced each day. (The zooplankton ingestion rate in terms of  $\text{PO}_4$  is equal to the  $\text{PO}_4$  fixation rate by the phytoplankton.) (2) The zooplankton are eating an equivalent of half of their body weight each day. (Zooplankton  $\text{PO}_4$  standing crop is equal to twice the amount of phytoplankton  $\text{PO}_4$  ingested each day.) (3) The particulate  $\text{PO}_4$  caught in the traps is equal to the amounts of particulate  $\text{PO}_4$  excreted by the zooplankton in their feces. (4) The amount of phytoplankton  $\text{PO}_4$  ingested by the zooplankton minus the particulate  $\text{PO}_4$  excreted in the feces repre-



sents the  $\text{PO}_4$  used in growth, together with that excreted in soluble form by the zooplankton. Based on the findings of Butler, *et al.* (1970), we estimate that the ratio of "growth"  $\text{PO}_4$  to soluble excreted  $\text{PO}_4$  is 1:3. (5) Zooplankton living beneath the photic zone are feeding on passively sinking detritus. The particulate  $\text{PO}_4$  entering a selected segment of the water column represents the food ingested by the zooplankton in that segment. The zooplankton in sub-surface segments are again consuming one half their body weight each day (particulate  $\text{PO}_4$  flux into a given segment is equivalent to one half zooplankton standing crop and amount ingested each day by zooplankton.) The particulate  $\text{PO}_4$  sinking out of the segment represents their particulate  $\text{PO}_4$  excretion in the feces. Assumptions for growth and soluble excretion in sub-surface segments are the same as those for the surface segment.

The measurements from this study and the zooplankton estimates described above are summarized in Figure 3 for the 0-35 and 35-65 m segments of the water column. Whether the depicted cycle is at all realistic remains to be determined. However, if nothing else, Figure 3 serves as a model for future investigations. It shouldn't be difficult to obtain good values for zooplankton standing crops and methods for the measurement of zooplankton soluble  $\text{PO}_4$  excretion are well established. These additional data, together with future primary production and flux observations, could enable actual field estimates for zooplankton secondary productivity rates. However, this assumption would prove invalid if micro-organisms play a large role in  $\text{PO}_4$  cycling. Obviously, we have left this important component out of our cycling scheme. If the particles we trapped had undergone extensive microbial decomposition,  $\text{PO}_4$  amounts would be lower than in freshly excreted zooplankton feces. This would, of course, lead to overestimates for secondary productivity.

Nevertheless, the suggested method for the measurement of secondary production is, perhaps, the most interesting aspect of this study. In contrast, the Cd results yielded few surprises. Once again, the biogeochemistry of this element is shown to be closely inter-related with the cycling of organic matter. The finding of significant amounts of  $\text{PO}_4$  in the trap salt solutions is also noteworthy. This suggests that either we are missing similar pools of dissolved organic C and N and thus underestimating vertical fluxes for these elements, or that large pools of weakly sorbed  $\text{PO}_4$  are associated with suspended organic detritus. The latter would seem to be a likely possibility in view of the reports of elevated  $\text{PO}_4$  amounts in association with marine snow particles (Shanks and Trent, 1979). In any event, excess  $\text{PO}_4$  should be studied further because of the importance of this element in oceanic cycling processes.

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