

## Phosphonates and particulate organic phosphorus cycling in an anoxic marine basin

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### Abstract

Total particulate phosphorus (TPP), particulate inorganic P (PIP), and particulate organic P (POP) concentrations were measured in a year-long series of sediment trap samples collected throughout the oxic–anoxic water column (275 m, 455 m, 930 m, and 1,255 m) of the Cariaco Basin. TPP, PIP, and POP fluxes varied seasonally and decreased significantly with depth, from 65 to 19  $\mu\text{mol TPP m}^{-2} \text{ d}^{-1}$ , 43 to 8  $\mu\text{mol PIP m}^{-2} \text{ d}^{-1}$ , and 22 to 11  $\mu\text{mol POP m}^{-2} \text{ d}^{-1}$ . Significant flux relationships ( $p < 0.001$ ) were found between POP and particulate organic carbon (POC) and particulate organic nitrogen (PON). The lack of a relationship between POC and PIP fluxes and the large fraction of TPP associated with the PIP pool in both oxic and anoxic traps suggests that future analyses must separate PIP and POP when evaluating biological relationships between C, N, and P. The strong relationships between POC, PON, and POP also suggest that POP is not preferentially remineralized relative to PON and POC with increasing depth in this anoxic environment. P composition was also determined using solid state  $^{31}\text{P}$  nuclear magnetic resonance (NMR), and it was found that phosphonates, chemically and thermally inert compounds, are a significant fraction of the TPP pool. Furthermore, these compounds were preferentially removed relative to more bioavailable P esters during a low flux event. Their selective removal suggests that these compounds may be an unrecognized source of bioavailable P under anoxic conditions.

Phosphorus (P) is an essential element used by all living organisms. In the modern ocean, a number of recent studies have suggested that plankton production may become increasingly P limited because of anthropogenic and naturally induced climate fluctuations (Fanning 1989; Wu et al. 2000; Karl et al. 2001). In the open ocean, dissolved P concentrations are so low that upwelling of deep waters becomes increasingly important for regulating dissolved P availability (e.g., see reviews by Delaney 1998; Benitez-Nelson 2000). Therefore, measuring midwater P sources is essential for determining new sources of P to the upper water column. Particulate P concentrations can vary from less than 10 nmol  $\text{L}^{-1}$  to as high as 0.3  $\mu\text{mol L}^{-1}$  (see review by Romankovich

1984). Sinking particulate P is one of the major transport mechanisms of P to the deep ocean (e.g., Delaney 1998). Yet greater than 90% of P exported from the euphotic zone as sinking particles is regenerated directly into dissolved forms. Anthropogenic and natural tracer studies support this finding and directly indicate that at least a fraction of sinking particles is comprised of highly bioavailable P compounds (Benitez-Nelson and Buesseler 1999; Benitez-Nelson and Karl 2002; Björkman and Karl 2003). Thus, remineralization of P occurs quickly and is an important process for the regeneration of particulate inorganic and organic P compounds to the dissolved phase.

Because rock weathering is the ultimate source of P to the oceans, P is often suggested to limit marine primary productivity over geologic time scales (Broecker 1982; Codispoti 1989; Tyrrell 1999). Several studies have further suggested that alternating periods of oxic and anoxic conditions have greatly impacted the efficiency of P remineralization over the geologic past (Van Capellen and Ingall 1996). For example, under anoxic conditions, positive feedbacks exist between enhanced regeneration of particulate P and increased production via upwelling of P-rich waters (Van Capellen and Ingall 1996; Ingall and Jahnke 1997). This hypothesis remains controversial, however, since new investigations into sediment P geochemistry using sequential

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extraction methods and additional sediment cores suggest otherwise (Anderson et al. 2001).

One of the major limitations to our understanding of the role of P in primary production over modern and geological timescales is that there have been relatively few studies that examine sinking particles for P composition or even inorganic versus organic concentration (Loh and Bauer 2000; Paytan et al. 2003). There is virtually nothing known about water column organic P cycling in anoxic environments. As a result, particulate P has remained an enigmatic player in the biogeochemical cycling of P. In this study, we examined the phosphorus geochemistry of sinking particles collected in sediment traps and surface sediments across the oxic–anoxic boundary of the Cariaco Basin. Our results suggest that there is no preferential remineralization of sinking particulate organic P over organic C and N and that phosphonates are a significant fraction of the marine particulate P pool in these settings.

## Methods

*Study area and sample collection*—The Cariaco Basin is presently anoxic below ~275 m and is therefore an ideal location for tracking the chemical transformations of marine particulate P across a redox boundary and into anoxic sediments. Sinking particles were collected from a vertical array of four sediment traps deployed from November 1997 through September 1998 (water depths of 275, 455, 930, and 1,255 m; 10°30'N, 64°40'W). The uppermost trap is positioned near the oxic–anoxic interface, with the three deeper traps located within the anoxic zone.

The Cariaco sediment traps are cone shaped with a 0.5-m<sup>2</sup> opening that is covered with a baffle top to reduce turbulence. The mooring is typically deployed for 6-month intervals. Each trap contains 13 cups, which collect falling particulate matter for 2-week intervals before rotating to allow the next cup to collect particles (begins at cup 1 and ends at cup 13). The cups contain a buffered 3.2% formalin solution as a preservative for the accumulating organic matter (Thunell et al. 2000). The samples are sealed and refrigerated before processing begins, usually within 1–3 weeks after recovery. Most of the supernatant from each cup is discarded, along with all obvious swimming organisms, which are not considered part of the particle flux. During sample processing for some of the cruises, aliquots of the trap cup supernatants were saved and stored frozen. Trap samples are then split into quarters using a precision rotary splitter. The quarter sample used for analysis is rinsed a total of three times, freeze dried, and ground. (Thunell et al. 2000).

A sediment core was collected in June 2002 at a water depth of ~245 m, directly north of the sediment trap site on the northern slope of Cariaco Basin in anoxic waters (10°51'N, 64°40'W). Integrated 0–200-m plankton tows (>200 μm) were collected monthly from October 2001 to August 2002. Each tow was deployed for ~15 min. Once collected, samples were transported back to the laboratory and preserved in a 5% formalin solution. Subsamples of each plankton tow were freeze dried and ground prior to P anal-

ysis. Total mass flux, as well as carbon and nitrogen data for the sediment trap samples, was determined according to the methods described in Thunell et al. (2000).

*Elemental analyses*—Particulate inorganic P (PIP) and total particulate P (TPP) concentrations were determined using the Aspila method (Aspila et al. 1976). Particulate organic P (POP) was found by difference (TPP – PIP = POP). A standard reference material, NIST 1573a (tomato leaves), was run with each sample set to evaluate total P recovery and the reproducibility of the analyses. Approximately 20% of the samples were run in duplicate. It is important to note that the distinction between PIP and POP concentrations is operationally defined, since the Aspila method was originally developed for use on sediment samples. As such, it is likely that our inorganic particulate P fraction contains labile organic P compounds as well. Soluble reactive P (SRP) and total dissolved P (TDP) concentrations in sediment trap cup solutions were determined using the methods described by Monaghan and Ruttenberg (1999). Dissolved organic P (DOP) was determined by difference (TDP – SRP = DOP). Again it should be noted that SRP and DOP are operationally defined terms, presumed to be dominated by inorganic and organic P, respectively. Furthermore, supernatant solutions were stored frozen for approximately 6 yr prior to analysis. It is possible that P scavenging onto the walls of the container and/or abiotic repartitioning among P phases may have occurred.

*Solid state <sup>31</sup>P nuclear magnetic resonance (NMR)*—Solid state <sup>31</sup>P NMR was used to determine the chemical structure of P (1) in sinking particles during low (13 November 1997, collected over 7 d, cup 1) and high mass flux periods (12 March 1998, collected over 14 d, cup 10), and (2) in a sediment core at different depths. <sup>31</sup>P spectra were recorded on a Varian Inova 500 spectrometer operating at 202.489 MHz using a Doty Scientific 4 mm/XC magic angle spinning (MAS) probe. Bloch decays of 50 ms were collected with a 200% window after 30 degree excitation pulses. Continuous wave proton dipolar decoupling with a field strength of 45 kHz was applied during acquisition. A MAS speed of 15 kHz was used, and 8,000 to 81,000 scans were collected for each run.

Bloch decays were chosen over the traditionally used cross-polarization (CP) method (Clark et al. 1999; Kolowitz et al. 2001) for two fundamental reasons. First, Bloch decay pulses excite all spins (signals) in the sample uniformly. The same cannot be said for CP, where the proximity of protons dictates the intensity and even the detectability of P signals. The second factor that makes Bloch decays the preferred method of data collection is the loss of CP efficiency at high spinning frequencies (Stejskal et al. 1977; Raya and Hirshinger 1998). At the relatively high field strength used in this study, it was necessary to spin the samples at 15 kHz to position the spinning sidebands outside the chemical shift window of interest. This spinning frequency is approaching the dipolar coupling magnitude between protons and P and, as predicted by NMR theory, the CP intensity decreases and the Hartmann-Hahn matching splits into sidebands (Stejskal et al. 1977; Raya and Hirshinger 1998). This behavior was

confirmed by comparing the signal intensity of a  $\text{KH}_2\text{PO}_4$  sample taken with Bloch decays versus CP at varying spinning frequencies. At frequencies below 10 kHz there was an enhancement of signal intensity with CP. However, at 15 kHz the CP signal (run using the same parameters described in Kolowitz et al. 2001) was actually weaker than the Bloch decay spectrum. Further testing using a 13 November 1997 (at 930 m) sediment trap sample demonstrated that the CP spectrum required over four times more transients to achieve a comparable signal-to-noise ratio than the Bloch decay result. Furthermore, the detectable signal in the phosphonate region was significantly reduced. Based on this evidence and the support of theory, we concluded that Bloch decays were the most efficient way to obtain data that fully represented the chemical species present in the sediment samples.

Peaks were identified using chemical shifts of anoxic Cariaco sediment core samples spiked with phosphate, phytic acid, and 2-aminoethylphosphonic acid. These spiked standards further confirmed that a relaxation delay of 1 s yielded quantitative results. The  $T_1$  relaxation times of the pure standards were measured at 26 s and 9 s. However, when these standards were mixed into the sediment matrix, both relaxation times were reduced to 0.5 s and peaks broadened. We attribute this reduction in relaxation time to the presence of paramagnetic species (such as Fe and Mn).

The energy associated with excited P nuclei is easily transferred to the unpaired electrons of paramagnetic ions. In essence, during spin-spin relaxation, nuclei will exchange energy with neighboring nuclei of different excitation states. Thus, higher energy nuclei transfer their energy to nuclei in a lower energy level and this decreases the average time that all nuclei remain in the excited state (Cade-Menun 2004). This results in the line broadening that is apparent in our samples and decreases the accuracy to which individual peaks may be quantified as well as reduces the sensitivity since the signal-to-noise ratio decreases as the peak broadens. This is true for both Bloch decay and CP. In the future, it may be possible to reduce line broadening by pretreating our samples with dithionite or oxalate (Cade-Menun 2004).

Peak deconvolution using the routine present in the standard instrument software (Varian VNMR 6.1C) was used to estimate the relative contributions of phosphonates versus other P compounds. Each spectrum was processed with the deconvolution program using the same starting chemical shift positions that were determined from the pure and spiked sediment standards and one of our sediment trap samples that contained a clear phosphonate peak (13 November 1997 at 455 m). Each result was visually inspected to determine that the deconvolution result was valid. Estimated uncertainties with repeated deconvolution analyses on a single spectrum are  $\pm 5\%$ . However, some of the data sets have poor signal-to-noise ratios, and we estimate that the error associated with these spectra is on the order of 10%. Even with this conservative treatment, the trends displayed by our data are significant. Note that for the sediment samples, the solid state  $^{31}\text{P}$  NMR peak centered around 0 ppm was broad, which suggests the presence of two different components: (1) orthophosphate and P monoesters and (2) P diesters. Given the significant overlap of these two deconvolution peaks, the data should be interpreted with caution.

## Results

TPP concentrations in the sediment trap samples ranged from 32 to 270  $\mu\text{mol P g}^{-1}$  dry weight of sediment, PIP from 5 to 213  $\mu\text{mol P g}^{-1}$  dry weight of sediment, and POP from 8 to 88  $\mu\text{mol P g}^{-1}$  dry weight of sediment (Fig. 1). Annual fluxes of TPP, PIP, and POP varied seasonally and all decreased significantly with depth over the course of the 298-d deployment, from 65 to 19  $\mu\text{mol TPP m}^{-2} \text{d}^{-1}$ , 43 to 8  $\mu\text{mol PIP m}^{-2} \text{d}^{-1}$ , and 22 to 11  $\mu\text{mol POP m}^{-2} \text{d}^{-1}$  (Table 1). PIP concentrations decreased by  $\sim 40\%$  between the upper two traps (275 and 455 m) and the two deeper traps ( $p \leq 0.001$ ). POP concentrations, however, increased by  $\sim 20\%$  between the upper two traps and the two deeper traps ( $p < 0.01$ ), following similar trends in POC and PON (Fig. 1). Standard deviations for replicate TPP and PIP analyses were less than 5%. Standard reference material recoveries ranged from 98% to 108%, with a median of 101%.

While correlations between TPP and PIP fluxes with fluxes of POC, and hence PON, were weak to poor ( $r^2$  ranged from 0.00 to 0.41,  $p > 0.05$  in almost all cases), correlations between POP and POC fluxes were significant ( $r^2$  ranged from 0.61 to 0.74,  $p < 0.001$ ). POC:POP, PON:POP, and POC:PON molar ratios did not show consistent seasonal or depth trends and had average values of POC:POP =  $295 \pm 140$  ( $r^2 = 0.73$ ), PON:POP =  $37 \pm 18$  ( $r^2 = 0.73$ ), and POC:PON =  $8.9 \pm 2.1$  ( $r^2 = 0.96$ ) (Fig. 2). POC:POP and PON:POP were significantly greater than classic Redfield ratios of C:N:P of 106:16:1 (Redfield et al. 1963). Elemental analysis of the plankton tow samples ( $n = 10$ ) collected during 2001 and 2002 reveals POC:POP ratios of  $294 \pm 38$ , PON:POP ratios of  $53 \pm 9$ , and POC:PON molar ratios of  $5.6 \pm 0.5$ .

We analyzed the supernatant of the 275-, 455-, and 930-m sediment trap samples for SRP (assumed to be inorganic P for this discussion) and TDP (Table 1). Supernatants for the deepest trap, 1,255 m, were unavailable. Supernatant concentrations ranged from 12% to 65% of the total P measured within the sediment trap, 14% to 82% of the total inorganic P, and 0% to 33% of the total organic P (Table 2). There was no evidence that the loss of either inorganic or organic P to the supernatant increased with deployment period. However, there does appear to be a significant difference in the relative percentage (10–20%) of the inorganic P (as SRP) released to the supernatant in the 455- and 930-m traps located in the anoxic portion of the water column, relative to the 275-m oxic trap (Table 2;  $p \leq 0.01$ ). In contrast, the release of organic P (as DOP) appears to decrease between the oxic and anoxic waters (Table 2;  $p \leq 0.05$ ). Analyses of water used to process recent sediment trap samples from the Cariaco Basin suggest that an additional 10–30% of total P (mostly as inorganic P) may be lost during sediment trap processing and preservation (O'Neill 2004). Inclusion of supernatant SRP and DOP concentrations into the measured PIP and POP fluxes increased the TPP flux by  $\sim 32\%$  for the 275-m trap (from 65 to 86  $\mu\text{mol TPP m}^{-2} \text{d}^{-1}$ ), by  $\sim 53\%$  for the 455-m trap (from 36 to 55  $\mu\text{mol TPP m}^{-2} \text{d}^{-1}$ ), and by  $\sim 76\%$  for the 930-m trap (from 21 to 37  $\mu\text{mol TPP m}^{-2} \text{d}^{-1}$ ). Inclusion of the supernatant DOP into

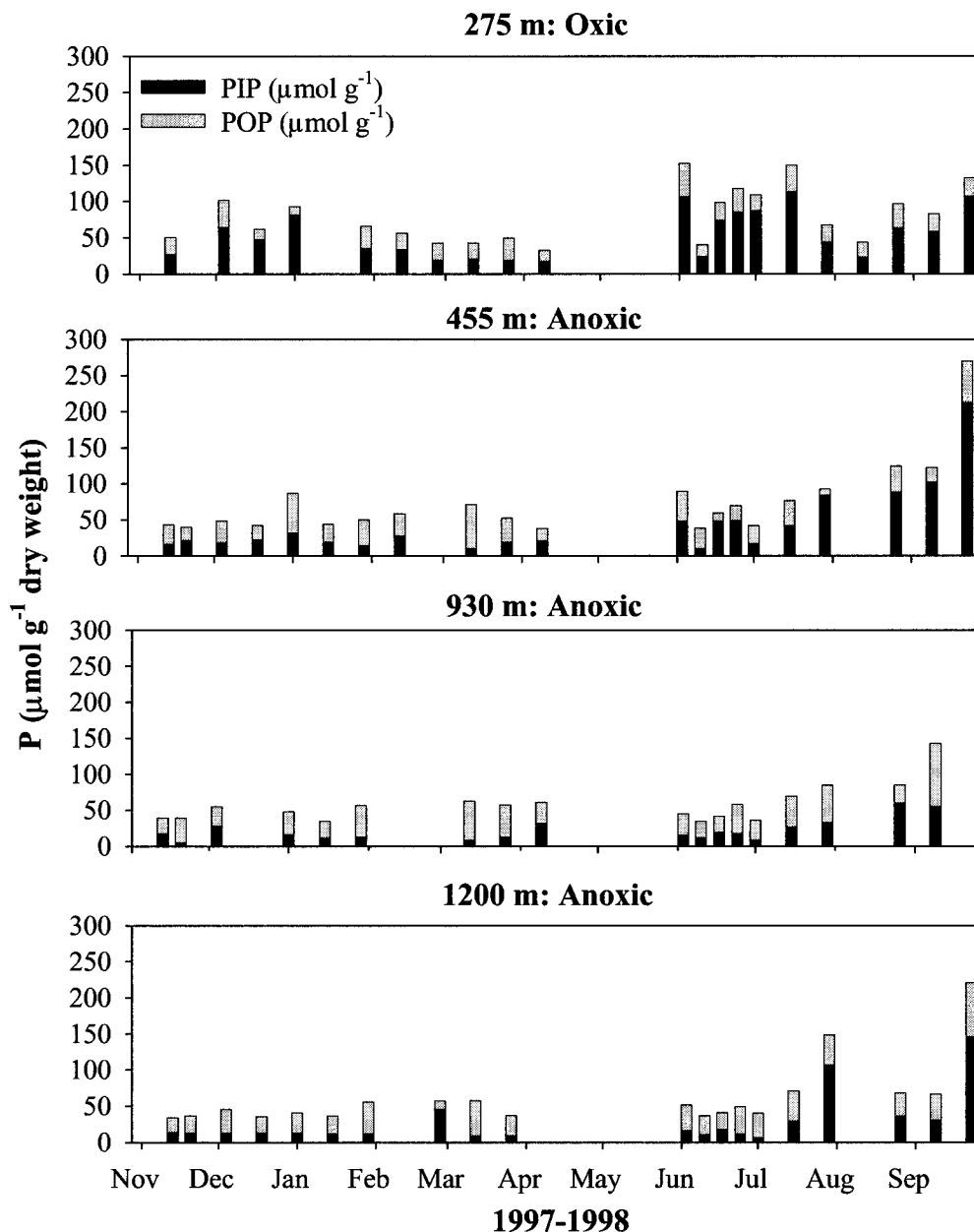


Fig. 1. TPP normalized to total mass flux ( $\mu\text{mol P g}^{-1}$  dry weight) versus time for each sediment trap. Black bars represent PIP concentrations and the gray bars represent POP concentrations (TPP - PIP).

the POP fluxes measured in the 275- to 930-m traps brings the POC:POP molar ratio closer to that of Redfield (from  $295 \pm 140$  to  $259 \pm 107$ ), but this difference is not significant ( $p > 0.05$ ). Although inclusion of supernatant TDP into the POP fluxes (again 275 to 930 m only) decreases the POC:POP molar ratio to  $122 \pm 55$ , this substantially decreased the relationship with either POC or PON fluxes ( $r^2$  ranged from 0.1 to 0.6).

The solid state  $^{31}\text{P}$  NMR spectra of our sediment trap and sediment core samples show a clear signal of phosphonates, phosphate, and phosphorus esters at all depths (Figs. 3 and 4 and Table 3). Sediment trap samples collected on 13 November 1997, a relatively low mass flux period, showed a

significant decrease in the percentage of phosphonates with depth, 18% to 3%, relative to orthophosphate and P esters. Sediment trap samples, collected on 12 March 1998, a relatively high flux period, however, showed little change in the relative percentage of phosphonates with depth,  $9 \pm 2\%$ . Solid state  $^{31}\text{P}$  NMR analysis of phytoplankton tow samples collected during seasonally similar high and low flux events, albeit in different years from the trap samples, reveals no evidence of a phosphonate peak (Fig. 3). Sediment core samples collected during 2002 from a water column depth of 245 m also demonstrate a clear phosphonate signal that decreases relative to orthophosphate and P esters with depth in the core (Fig. 4 and Table 3).

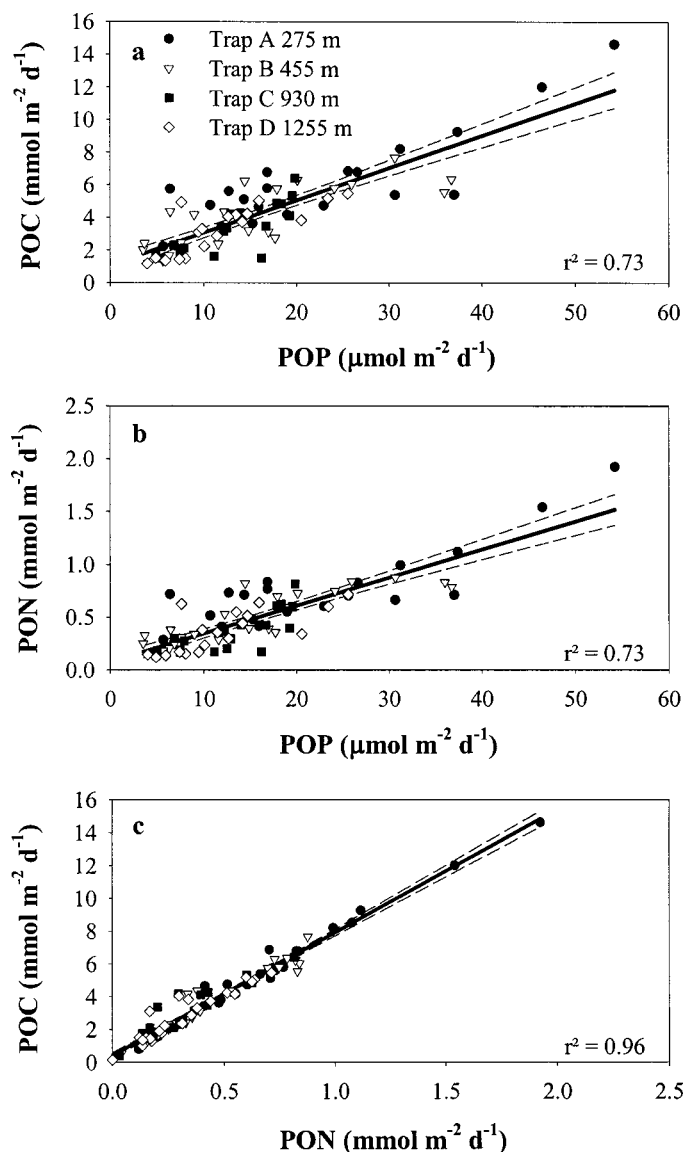


Fig. 2. Sediment trap fluxes. (a) POP versus POC, (b) POP versus PON, and (c) PON versus POC for each sediment trap collected from November 1997 to September 1998. Trap A, 275 m, is denoted by the black circles; Trap B, 455 m, by the inverted white triangles; Trap C, 930 m, by the black squares; and Trap D, 1,250 m, by the white diamonds. The black line represents the best fit through all of the data, and the dashed lines represent the 95% confidence interval of the fit.

## Discussion

*Elemental fluxes and concentrations*—One of the major difficulties in evaluating the role of P in primary production is a lack of knowledge regarding the sinking TPP pool. Currently, there are debates in the literature concerning the relative remineralization rates of sinking TPP, POC, and PON in the water column. The widely held view is that TPP is preferentially remineralized relative to POC and PON in the upper water column (Knauer et al. 1979; Martin et al. 1987). This is based on sediment trap and hydrographic studies that

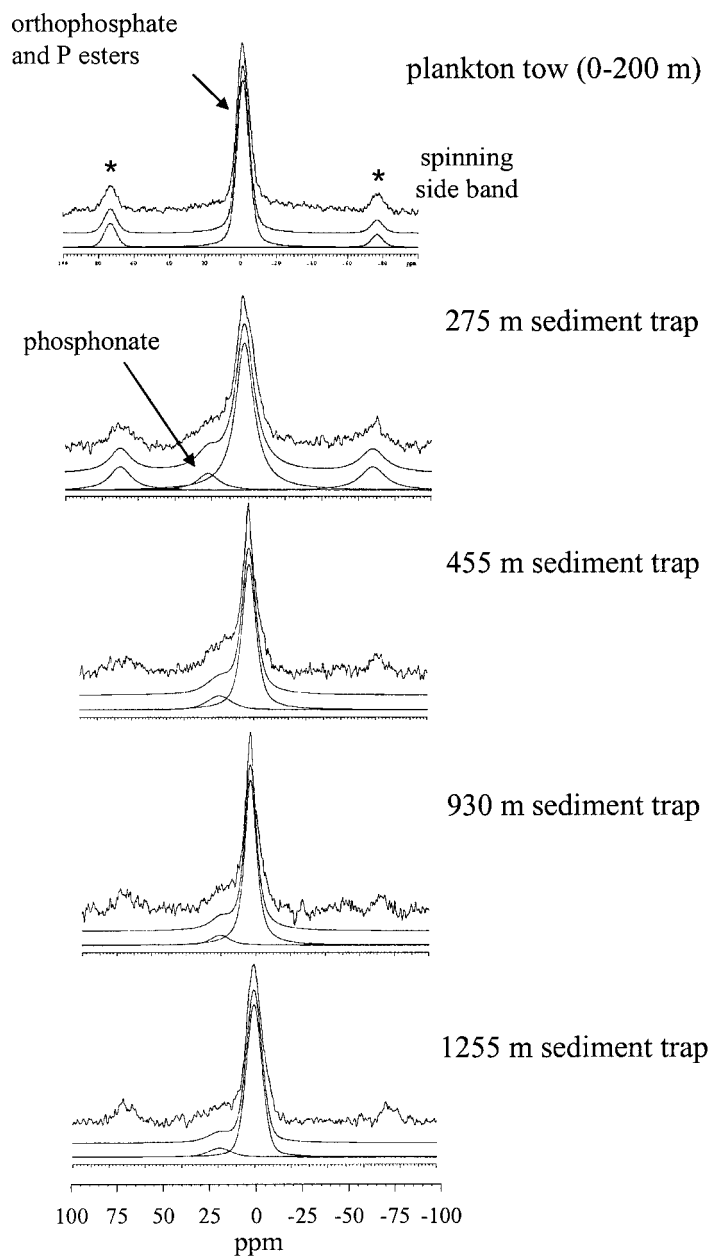


Fig. 3.  $^{31}\text{P}$  solid state spectra of sediment trap samples collected during a low flux event, 13 November 1997. The plankton tow sample (integrated from 0–200 m) was collected in November 2001.

depict differential decreases in TPP, PON, and POC and shallower maxima in phosphate concentrations relative to C and N. It is important to note here that these studies did not distinguish between TPP, POP, and PIP. Anderson and Sarmiento (1994) and Tyrell and Law (1997), however, suggest that shallower maxima in dissolved inorganic P concentrations, when compared to N, are due to the removal of nitrate via denitrification in low-oxygen waters and subsequent horizontal water mass advection. They suggested that C:P ratios at depths greater than 400 m are similar to those found in fresh organic matter and are constant with both depth and oceanic regime.

The debate over preferential remineralization of POP ver-

Table 1. TPP, PIP, POP (TPP – PIP) fluxes and TDP, SRP, and DOP fluxes found in the overlying supernatant for each trap. No supernatant samples were collected for the 1,255 m, D trap.

| Date                  | Total mass flux<br>(g m <sup>-2</sup> d <sup>-1</sup> ) | Whole sample<br>(g) | TPP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | PIP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | POP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | Supernatant TDP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | Supernatant SRP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | Supernatant DOP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) |
|-----------------------|---|---------------------|--|--|--|--|--|--|
| Trap A: 275 m, oxic   |   |                     |  |  |  |  |  |  |
| 13 Nov 1997           | 0.73  | 2.57                | 36.6   | 19.7   | 16.9   | 34.1   | 25.7   | 8.4  |
| 20 Nov 1997           | 1.38  | 9.64                | ND*  | ND   | ND   | 23.6   | 20.2   | 3.4  |
| 4 Dec 1997            | 1.01  | 7.09                | 102.9  | 65.5   | 37.4   | 26.8   | 20.6   | 6.2  |
| 18 Dec 1997           | 1.02  | 7.12                | 63.0   | 48.7   | 14.3   | 27.4   | 24.5   | 2.9  |
| 1 Jan 1998            | 0.58  | 4.07                | 54.0   | 47.6   | 6.4  | 22.5   | 19.3   | 3.2  |
| 15 Jan 1998           | 0.08  | 0.55                | ND   | ND   | ND   | ND   | ND   | ND   |
| 29 Jan 1998           | 0.19  | 1.31                | 12.3   | 6.6  | 5.7  | 14.5   | 12.7   | 1.8  |
| 12 Feb 1998           | 0.27  | 1.86                | 14.8   | 8.9  | 5.9  | 15.5   | 13.6   | 1.9  |
| 26 Feb 1998           | 0.81  | 5.64                | 34.3   | 15.4   | 19.0   | 10.6   | 9.1  | 1.5  |
| 12 Mar 1998           | 2.48  | 17.35               | 105.0  | 50.8   | 54.2   | 20.1   | 18.9   | 1.2  |
| 26 Mar 1998           | 1.54  | 10.76               | 75.7   | 29.2   | 46.5   | 14.8   | 13.8   | 1.0  |
| 9 Apr 1998            | 0.88  | 6.14                | 28.3   | 15.6   | 12.7   | 12.2   | 10.2   | 1.9  |
| 23 Apr 1998           | 0.63  | 3.45                | ND   | ND   | ND   | ND   | ND   | ND   |
| 3 Jun 1998            | 0.67  | 2.35                | 102.2  | 71.6   | 30.7   | 37.6   | 28.7   | 8.9  |
| 10 Jun 1998           | 1.97  | 6.88                | 79.0   | 47.7   | 31.2   | 36.0   | 32.9   | 3.1  |
| 17 Jun 1998           | 1.07  | 3.75                | 105.3  | 79.7   | 25.6   | 37.5   | 36.6   | 0.9  |
| 24 Jun 1998           | 0.49  | 1.73                | 58.2   | 42.2   | 15.9   | 35.0   | 32.3   | 2.7  |
| 1 Jul 1998            | 0.49  | 3.42                | 53.5   | 42.8   | 10.7   | 23.9   | 21.5   | 2.4  |
| 15 Jul 1998           | 0.47  | 3.28                | 70.1   | 53.3   | 16.9   | 22.1   | 21.2   | 0.9  |
| 29 Jul 1998           | 0.66  | 4.62                | 44.4   | 29.2   | 15.2   | 18.4   | 18.2   | 0.2  |
| 12 Aug 1998           | 0.60  | 4.20                | 26.0   | 14.0   | 11.9   | 16.4   | 15.7   | 0.7  |
| 26 Aug 1998           | 1.13  | 7.92                | 109.1  | 72.0   | 37.0   | 20.3   | 20.0   | 0.3  |
| 9 Sep 1998            | 0.94  | 6.57                | 77.9   | 55.0   | 22.9   | 18.8   | 18.4   | 0.4  |
| 23 Sep 1998           | 1.05  | 7.34                | 138.9  | 112.3  | 26.6   | 18.6   | 18.1   | 0.6  |
| Trap B: 455 m, anoxic |   |                     |  |  |  |  |  |  |
| 13 Nov 1997           | 0.565   | 1.98                | 24.30  | 9.46   | 14.83  | 10.87  | 9.86   | 1.01   |
| 20 Nov 1997           | 0.683   | 4.78                | 27.04  | 14.82  | 12.22  | 11.58  | 10.86  | 0.72   |
| 4 Dec 1997            | 1.019   | 7.13                | 49.23  | 18.56  | 30.67  | 23.22  | 21.18  | 2.04   |
| 18 Dec 1997           | 1.327   | 9.29                | 55.78  | 29.81  | 25.98  | 27.61  | 27.56  | 0.05   |
| 1 Jan 1998            | 0.671   | 4.70                | 58.12  | 21.37  | 36.75  | 27.52  | 24.50  | 3.02   |
| 15 Jan 1998           | 0.259   | 1.81                | 11.34  | 5.05   | 6.29   | 11.51  | 10.74  | 0.77   |
| 29 Jan 1998           | 0.505   | 3.54                | 25.29  | 7.38   | 17.91  | 13.68  | 11.41  | 2.27   |
| 12 Feb 1998           | 0.185   | 1.30                | 10.80  | 5.17   | 5.63   | 19.88  | 19.00  | 0.88   |
| 26 Feb 1998           | 0.139   | 0.97                | ND   | ND   | ND   | ND   | ND   | ND   |
| 12 Mar 1998           | 0.397   | 2.78                | 28.28  | 4.15   | 24.13  | 12.89  | 12.03  | 0.86   |
| 26 Mar 1998           | 0.435   | 3.04                | 22.80  | 8.37   | 14.43  | 10.21  | 8.64   | 1.56   |
| 9 Apr 1998            | 0.210   | 1.47                | 7.93   | 4.43   | 3.50   | 2.88   | 1.74   | 1.14   |
| 23 Apr 1998           | 0.157   | 0.86                | ND   | ND   | ND   | ND   | ND   | ND   |
| 3 Jun 1998            | 0.286   | 1.00                | 25.45  | 13.88  | 11.57  | 32.00  | 29.89  | 2.11   |
| 10 Jun 1998           | 1.302   | 4.56                | 49.50  | 13.50  | 36.00  | 12.75  | 10.97  | 1.78   |
| 17 Jun 1998           | 0.643   | 2.25                | 37.98  | 31.55  | 6.43   | 27.91  | 27.25  | 0.66   |
| 24 Jun 1998           | 0.453   | 1.58                | 31.40  | 22.40  | 9.00   | 31.95  | 31.13  | 0.82   |
| 1 Jul 1998            | 0.279   | 1.96                | 11.64  | 4.80   | 6.84   | 11.28  | 10.55  | 0.72   |
| 15 Jul 1998           | 0.591   | 4.14                | 45.08  | 24.99  | 20.10  | 21.49  | 21.28  | 0.20   |
| 29 Jul 1998           | 0.473   | 3.31                | 43.64  | 39.97  | 3.67   | 18.77  | 18.77  | 0.00   |
| 12 Aug 1998           | 0.041   | 0.28                | ND   | ND   | ND   | ND   | ND   | ND   |
| 26 Aug 1998           | 0.497   | 3.48                | 61.77  | 44.08  | 17.69  | 26.76  | 26.76  | 0.00   |
| 9 Sep 1998            | 0.378   | 2.64                | 46.16  | 38.58  | 7.57   | 26.71  | 26.71  | 0.00   |
| 23 Sep 1998           | 0.295   | 2.07                | 79.78  | 62.80  | 16.98  | 20.97  | 20.52  | 0.45   |

sus POC and PON is further complicated by the presence or absence of dissolved oxygen. There is increasing evidence that large areas of the world's ocean were subjected to low or no oxygen environments at various times in the geologic past (Handoh and Lenton 2003; Shen et al. 2003). Further-

more, a number of studies have documented recent trends of decreasing O<sub>2</sub> concentrations in the oceanic water column, possibly because of anthropogenic induced forcing mechanisms (Joos et al. 2003). A controversial hypothesis suggests that sedimentary POP is preferentially released from sedi-

Table 1. Continued.

| Date                    | Total mass flux<br>(g m <sup>-2</sup> d <sup>-1</sup> ) | Whole sample<br>(g) | TPP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | PIP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | POP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | Supernatant TDP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | Supernatant SRP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) | Supernatant DOP<br>(μmol m <sup>-2</sup> d <sup>-1</sup> ) |
|-------------------------|---|---------------------|--|--|--|--|--|--|
| Trap C: 930 m, anoxic   |   |                     |  |  |  |  |  |  |
| 13 Nov 1997             | 0.371   | 2.25                | 14.6   | 6.7  | 7.9  | ND   | ND   | ND   |
| 20 Nov 1997             | 0.489   | 7.30                | 19.2   | 2.5  | 16.7   | ND   | ND   | ND   |
| 4 Dec 1997              | 0.731   | 1.32                | 40.5   | 20.9   | 19.5   | ND   | ND   | ND   |
| 18 Dec 1997             | 0.515   | 0.48                | ND   | ND   | ND   | ND   | ND   | ND   |
| 1 Jan 1998              | 0.558   | 1.17                | 27.0   | 9.1  | 17.9   | ND   | ND   | ND   |
| 15 Jan 1998             | 0.224   | 0.50                | 7.7  | 2.7  | 5.0  | ND   | ND   | ND   |
| 29 Jan 1998             | 0.279   | 1.13                | 15.9   | 3.7  | 12.2   | ND   | ND   | ND   |
| 12 Feb 1998             | 0.105   | 0.24                | ND   | ND   | ND   | ND   | ND   | ND   |
| 26 Feb 1998             | 0.109   | 0.49                | ND   | ND   | ND   | ND   | ND   | ND   |
| 12 Mar 1998             | 0.339   | 0.42                | 21.3   | 2.9  | 18.4   | ND   | ND   | ND   |
| 26 Mar 1998             | 0.451   | 0.16                | 25.8   | 5.9  | 19.9   | ND   | ND   | ND   |
| 9 Apr 1998              | 0.234   | 0.35                | 14.3   | 7.5  | 6.8  | ND   | ND   | ND   |
| 23 Apr 1998             | 0.108   | 0.26                | ND   | ND   | ND   | ND   | ND   | ND   |
| 3 Jun 1998              | 0.255   | 0.89                | 11.5   | 4.0  | 7.5  | 18.7   | 18.6   | 0.2  |
| 10 Jun 1998             | 0.866   | 3.03                | 29.9   | 10.6   | 19.2   | 5.9  | 5.5  | 0.4  |
| 17 Jun 1998             | 0.574   | 2.01                | 24.1   | 11.2   | 12.9   | 26.2   | 24.4   | 1.8  |
| 24 Jun 1998             | 0.312   | 1.09                | 18.1   | 5.6  | 12.5   | 20.0   | 19.3   | 0.7  |
| 1 Jul 1998              | 0.181   | 1.27                | 6.5  | 1.6  | 4.9  | 5.1  | 4.7  | 0.4  |
| 15 Jul 1998             | 0.333   | 2.33                | 23.1   | 9.1  | 14.0   | 17.7   | 17.5   | 0.2  |
| 29 Jul 1998             | 0.215   | 1.51                | 18.2   | 7.1  | 11.1   | 17.3   | 17.3   | 0.0  |
| 12 Aug 1998             | 0.033   | 0.23                | ND   | ND   | ND   | ND   | ND   | ND   |
| 26 Aug 1998             | 0.297   | 2.08                | 25.3   | 17.8   | 7.4  | 22.2   | 22.2   | 0.0  |
| 9 Sep 1998              | 0.185   | 1.29                | 26.3   | 10.1   | 16.2   | 18.6   | 18.6   | 0.0  |
| 23 Sep 1998             | 0.154   | 1.08                | ND   | ND   | ND   | ND   | ND   | ND   |
| Trap D: 1,255 m, anoxic |   |                     |  |  |  |  |  |  |
| 13 Nov 1997             | 0.568   | 1.99                | 19.3   | 7.9  | 11.4   | ND   | ND   | ND   |
| 20 Nov 1997             | 0.633   | 4.43                | 22.9   | 8.3  | 14.7   | ND   | ND   | ND   |
| 4 Dec 1997              | 0.726   | 5.08                | 32.9   | 9.5  | 23.4   | ND   | ND   | ND   |
| 18 Dec 1997             | 1.161   | 8.13                | 41.1   | 15.5   | 25.6   | ND   | ND   | ND   |
| 1 Jan 1998              | 0.579   | 4.05                | 23.7   | 7.8  | 15.9   | ND   | ND   | ND   |
| 15 Jan 1998             | 0.163   | 1.14                | 5.9  | 1.9  | 4.0  | ND   | ND   | ND   |
| 29 Jan 1998             | 0.325   | 2.27                | 18.1   | 3.9  | 14.1   | ND   | ND   | ND   |
| 12 Feb 1998             | 0.146   | 1.02                | ND   | ND   | ND   | ND   | ND   | ND   |
| 26 Feb 1998             | 0.115   | 0.81                | ND   | ND   | ND   | ND   | ND   | ND   |
| 12 Mar 1998             | 0.276   | 1.93                | 15.9   | 2.5  | 13.5   | ND   | ND   | ND   |
| 26 Mar 1998             | 0.271   | 1.90                | 10.1   | 2.5  | 7.6  | ND   | ND   | ND   |
| 9 Apr 1998              | 0.267   | 1.87                | ND   | ND   | ND   | ND   | ND   | ND   |
| 23 Apr 1998             | 0.202   | 1.11                | ND   | ND   | ND   | ND   | ND   | ND   |
| 3 Jun 1998              | 0.288   | 1.01                | 14.8   | 4.7  | 10.1   | ND   | ND   | ND   |
| 10 Jun 1998             | 0.794   | 2.78                | 29.3   | 8.7  | 20.5   | ND   | ND   | ND   |
| 17 Jun 1998             | 0.550   | 1.92                | 22.6   | 9.9  | 12.6   | ND   | ND   | ND   |
| 24 Jun 1998             | 0.250   | 0.88                | 12.3   | 2.9  | 9.4  | ND   | ND   | ND   |
| 1 Jul 1998              | 0.146   | 1.02                | 5.8  | 0.9  | 4.9  | ND   | ND   | ND   |
| 15 Jul 1998             | 0.239   | 1.68                | 16.9   | 7.1  | 9.8  | ND   | ND   | ND   |
| 29 Jul 1998             | 0.194   | 1.36                | 28.8   | 20.7   | 8.0  | ND   | ND   | ND   |
| 12 Aug 1998             | 0.013   | 0.09                | ND   | ND   | ND   | ND   | ND   | ND   |
| 26 Aug 1998             | 0.236   | 1.65                | 16.1   | 8.7  | 7.4  | ND   | ND   | ND   |
| 9 Sep 1998              | 0.166   | 1.16                | 11.0   | 5.1  | 5.9  | ND   | ND   | ND   |
| 23 Sep 1998             | 0.145   | 1.02                | ND   | ND   | ND   | ND   | ND   | ND   |

\* ND = no data.

ments under anoxic conditions, thus increasing the concentrations of P in the water column and enhancing surface water production (Van Capellen and Ingall 1996; Anderson et al. 2001). Much of this controversy stems from the analytic methods used to distinguish sedimentary POP versus

TPP and the fact that there have been few studies of P composition in marine sediments. If anoxic sediments do regenerate POP more effectively relative to POC and PON, one might also expect this phenomena to occur in the overlying anoxic water column.

Table 2. Percentage of the total P, inorganic P, and organic P measured in each trap that was found in the supernatant (i.e.,  $TDP_{\text{supernatant}} / [PP_{\text{solid}} + TDP_{\text{supernatant}}]$ ). Note that SRP was considered to be completely composed of inorganic P for this analysis.

| Trap           | % total P in supernatant | % inorganic P in supernatant | % organic P in supernatant |
|----------------|--------------------------|------------------------------|----------------------------|
| Trap A (275 m) |                          |                              |                            |
| Min            | 11.8                     | 13.9                         | 0.8                        |
| Max            | 54.2                     | 65.8                         | 33.3                       |
| Mean           | 29.1                     | 36.3                         | 12.2                       |
| Median         | 29.3                     | 33.4                         | 9.0                        |
| Trap B (455 m) |                          |                              |                            |
| Min            | 20.5                     | 24.6                         | 0.0                        |
| Max            | 64.8                     | 78.6                         | 24.6                       |
| Mean           | 36.5                     | 51.3                         | 7.2                        |
| Median         | 32.1                     | 50.8                         | 6.4                        |
| Trap C (930 m) |                          |                              |                            |
| Min            | 16.4                     | 34.0                         | 0.0                        |
| Max            | 61.9                     | 82.1                         | 12.2                       |
| Mean           | 45.2                     | 65.9                         | 3.4                        |
| Median         | 46.8                     | 68.5                         | 2.0                        |

In this study, we compared POC, PON, TPP, PIP, and POP fluxes with depth. POC, PON, and POP fluxes are well correlated in the Cariaco Basin, which suggests that there is no preferential remineralization of POP relative to POC or PON throughout this oxic–anoxic water column (Fig. 2). Thus, if POP is preferentially released relative to POC and PON, it must occur on timescales longer than those represented by sinking particles. Our study also suggests that PIP and POP must be distinguished when comparing P with POC and PON fluxes.

POC:POP, PON:POP, and POC:PON did not vary systematically during different seasons or depth, with POC:POP =  $295 \pm 140$  ( $r^2 = 0.73$ ), PON:POP =  $37 \pm 18$  ( $r^2 = 0.73$ ), and POC:PON =  $8.9 \pm 2.1$  ( $r^2 = 0.96$ ) (Fig. 2). POC:POP and PON:POP were significantly greater than classical Redfield ratios of C:N:P of 106:16:1 (Redfield et al. 1963). Elemental analysis of the plankton tow samples ( $n = 10$ ) collected during 2001 and 2002 reveals molar ratios similar to those of the sediment traps, POC:PON ratios of  $5.6 \pm 0.5$ , POC:POP ratios of  $294 \pm 38$ , and PON:POP ratios of  $53 \pm 9$ . Although the plankton tow and sediment trap samples were collected from different years, these results imply that there is little preferential remineralization of P between particle production and the particulate samples collected in the 275-m trap. Low plankton C:N and high C:P ratios may suggest P limitation or stress in this ecosystem, lower P demand by the organisms, faster P regeneration in the euphotic zone, or sample processing artifacts.

Nutrient limitation of primary production in the Cariaco Basin remains virtually unexplored. Cariaco Basin primary production is characterized by a strong main upwelling period caused by increased local winds that typically occurs from December to May (Astor et al. 2003). Elevated chlorophyll and primary production rates are usually confined to the top 25 m of the water column, although subsurface maxima may occur during periods of stratification in the summer

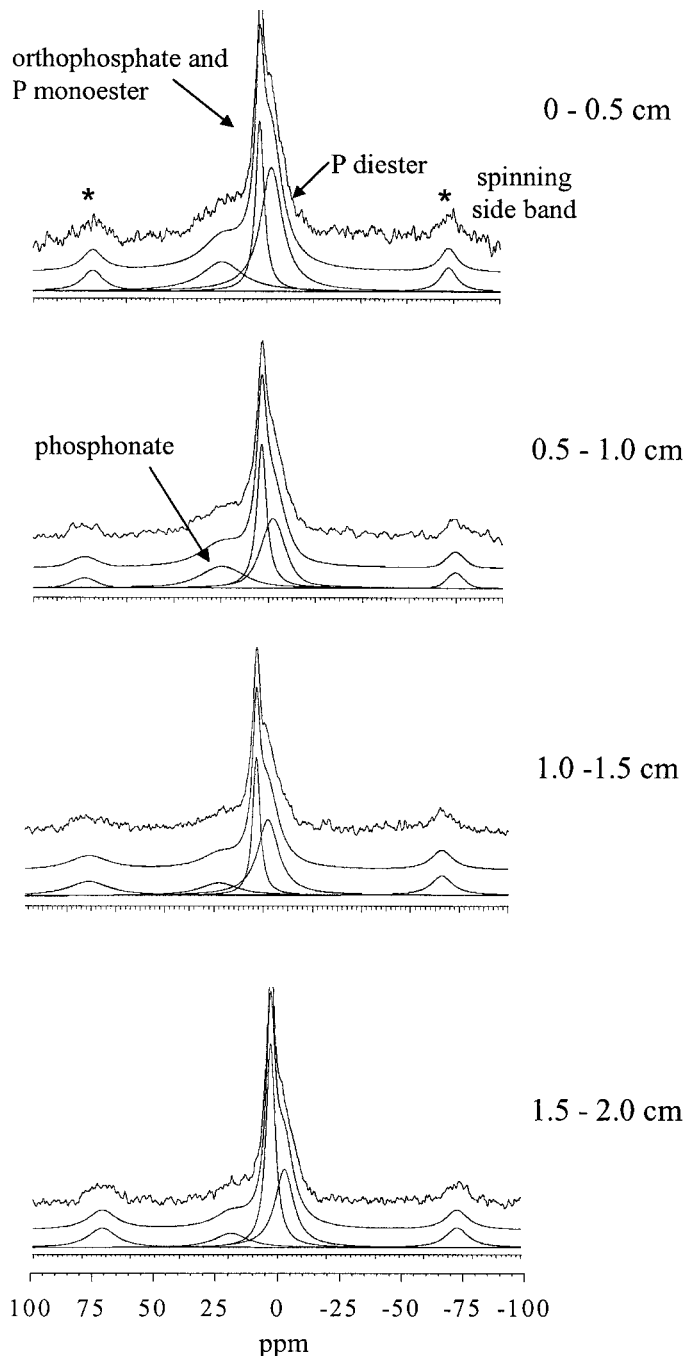


Fig. 4.  $^{31}\text{P}$  solid state spectra of an anoxic sediment core from a water depth of 245 m. Broader peaks enabled deconvolution of phosphate and P monoester peaks from P diesters.

and early fall. As a result, most of the annual export production is supported by the entrainment of nutrient-rich waters from the thermocline during upwelling (Goñi et al. 2003). During the collection period presented in this study, rapid warming and thermal stratification of the upper water column from December 1997 to February of 1998 was caused by the lateral intrusion of a massive anticyclonic eddy from the Caribbean (Astor et al. 2003) that temporarily suppressed upwelling. Upwelling resumed in February and

Table 3. TPP, PIP, and POP concentrations ( $\mu\text{mol P g}^{-1}$  dry weight) and NMR based P speciation (%).

| Sample                                   | TPP<br>( $\mu\text{mol g}^{-1}$ ) | PIP<br>( $\mu\text{mol g}^{-1}$ ) | POP<br>( $\mu\text{mol g}^{-1}$ ) | Phosphonates<br>(%) | Orthophosphate<br>+ P-esters<br>(%) | P diester<br>(%) |
|--|-----------------------------------|-----------------------------------|-----------------------------------|---------------------|-------------------------------------|------------------|
| Plankton tow (>200 $\mu\text{m}$ )       | 134.9                             | 3.4                               | 131.5                             | 0                   | 100                                 | NA*              |
| 13 Nov 1997 (cup 1)                      |                                   |                                   |                                   |                     |                                     |                  |
| Trap A (275 m)                           | 49.7                              | 26.8                              | 22.9                              | 18                  | 82                                  | NA               |
| Trap B (455 m)                           | 43.0                              | 16.8                              | 26.3                              | 14                  | 86                                  | NA               |
| Trap C (930 m)                           | 39.4                              | 18.1                              | 21.3                              | 9                   | 91                                  | NA               |
| Trap D (1,255 m)                         | 34.0                              | 13.9                              | 20.1                              | 3                   | 97                                  | NA               |
| 12 Mar 1998 (cup 10)                     |                                   |                                   |                                   |                     |                                     |                  |
| Trap A (275 m)                           | 42.4                              | 20.5                              | 21.9                              | 12                  | 88                                  | NA               |
| Trap B (455 m)                           | 71.3                              | 10.5                              | 60.8                              | 7                   | 93                                  | NA               |
| Trap C (930 m)                           | 62.8                              | 8.6                               | 54.2                              | 10                  | 90                                  | NA               |
| Trap D (1,255 m)                         | 57.7                              | 8.9                               | 48.8                              | 9                   | 91                                  | NA               |
| Sediment core (water depth $\sim$ 245 m) |                                   |                                   |                                   |                     |                                     |                  |
| 0–0.5 cm                                 | 19.3                              | 6.0                               | 13.3                              | 23                  | 27                                  | 50               |
| 0.5–1.0 cm                               | 30.1                              | 8.3                               | 21.8                              | 23                  | 38                                  | 39               |
| 1.0–1.5 cm                               | 24.8                              | 10.8                              | 14.1                              | 15                  | 33                                  | 52               |
| 1.5–2.0 cm                               | 34.2                              | 10.9                              | 23.3                              | 13                  | 49                                  | 39               |

\* NA = not applicable.

March 1998, during which two relatively large sized cyclonic eddies passed through the area (Astor et al. 2003). Although no direct analyses of phytoplankton and zooplankton speciation have been conducted in the Cariaco Basin, the close correlation between opal and POC in the traps suggests that most of the particle flux is driven by diatoms, with additional export from coccolithophore species such as *E. huxleyi* (Thunell et al. 2000; Goñi et al. 2003). Recent studies of particulate and dissolved N species and  $\delta^{15}\text{N}$ , however, also suggest that  $\text{N}_2$  fixation may be significant in the Cariaco Basin (Thunell et al. 2004). Water column measurements of dissolved inorganic nutrients demonstrate an excess of nitrate relative to phosphate, when compared to the global mean nitrate:phosphate relationships. Thus, it is feasible that the higher POC:POP and PON:POP ratios observed during this study are indicative of P limitation due, at least in part, to increased  $\text{N}_2$  fixation.

Another potential cause of the high POC:POP and PON:POP ratios is analytical. Measurements of PP in sediment trap samples have been hindered by the possibility that P is released from the particulate phase into the overlying trap solution (supernatant) during sediment trap deployment and processing (Bodungen et al. 1991; Paytan et al. 2003). In this study, SRP and DOP concentrations within the supernatant were significant and variable (Table 2). However, there was no evidence that either inorganic or organic P loss to the supernatant increased with deployment time (Table 1). The addition of supernatant DOP to the POP pool brings the C:N:P closer to Redfield, but this is not a significant change. Addition of supernatant TDP to the POP pool also brings the C:N:P ratios closer to Redfield, but this significantly reduced the correlations between POP and POC and PON fluxes. The significant reduction in the relationship between POP and POC and PON fluxes with the addition of supernatant TDP may be attributed to incomplete and variable conversion of some of the supernatant DOP to SRP

during trap deployment. It may also be due to our inability to quantify POC and PON supernatant losses, which have also been well documented to occur in formalin-poisoned sediment traps of similar design (Knauer et al. 1984; Bodungen et al. 1991; Lee et al. 1992). Alternatively, it has been shown that 50–100% of the dissolved P present in sediment trap solutions may be from swimmers, i.e., leaching of their tissues after they have entered the sediment trap (Bodungen et al. 1991). The addition of either DOP or TDP to the POP pool decreased the POC:POP ratio to  $259 \pm 107$  and  $122 \pm 55$ , respectively, and the PON:POP ratio to  $33 \pm 14$  and  $15 \pm 7$ , respectively. Although these ratios are significantly lower than those measured in the plankton tows (POC:POP =  $294 \pm 38$ , PON:POP =  $53 \pm 9$ ), it should be noted that the plankton tow samples were also preserved in formalin (albeit for less than 72 h) prior to processing. If such studies are to be conducted in the future, the regeneration of P, N, and C into the cup solution should be calculated and the effect of formalin should be evaluated.

While fluxes of POC, PON, and POP decrease substantially with depth, the specific concentrations (i.e., per gram of dried sediment trap material) do not (Fig. 1). Only PIP concentrations decrease significantly across the oxic–anoxic interface, and this is likely due to the release of PIP to the dissolved phase in association with the reduction of metal oxides as they fall through the anoxic water column of the Cariaco Basin (Lucotte and D'Anglejan 1988) and bacterial remineralization (Shapiro 1967). POC, PON, and POP concentrations actually increase slightly in the anoxic 455-m trap before achieving a relatively constant concentration with depth. One possibility is that the upper sediment traps may have been affected by partial clogging during high flux events (Goñi et al. 2003) because of enhanced horizontal shear associated with lateral subsurface intrusions from the Caribbean Sea observed from December 1997 to February 1998 (Astor et al. 2003). A second possibility is midwater

production of POP, POC, and PON. There is growing evidence of a large chemoautotrophic community at the oxic-anoxic interface in the Cariaco Basin that rivals the magnitude of surface primary production (0–100 m) and supports an active microbial loop between 250 and 455 m (Taylor et al. 2001). Heterotrophic carbon demand between 250 and 455 m frequently exceeds sinking POC, which suggests that these organisms are subsisting on in situ production and/or horizontal advection of organic carbon.

*Particulate phosphorus speciation*—Solid state  $^{31}\text{P}$  NMR analysis reveals that phosphonates are a significant component of the TPP pool (3–23%; Table 3). Phosphonates are characterized by strong C-P bonds that are resistant to chemical, thermal, and photolytic degradation (Ternan et al. 1998; Kononova and Nesmeyanova 2002). Reactive phosphonic acids are the only organic P containing compounds documented in meteorites and have been proposed as the first prebiotic organic P containing compounds during the early stages of Earth's evolution (Degraaf et al. 1997). Although they are in the lipids, proteins, and polysaccharides of many organisms and are anthropogenically produced as xenobiotics (Ternan et al. 1998; Kononova and Nesmeyanova 2002), until now they have not been found to any significant extent in sinking marine particulate matter. They comprise 25% of the high molecular weight (HMW: 0.001–0.1  $\mu\text{m}$ ) ultrafiltered DOP throughout the world ocean (Clark et al. 1999; Kolowitz et al. 2001). If HMW DOP comprises 25% of total DOP as shown for HMW DOC (i.e., 25%, Benner 2002), then phosphonates may compose approximately 6% of the total DOP pool. Phosphonates have yet to be identified in particulate material (0.1–60  $\mu\text{m}$ ) collected using large volume ultrafiltration (Clark et al. 1999; Kolowitz et al. 2001). Recent work using solution  $^{31}\text{P}$  NMR has shown phosphonates to comprise only a minor fraction (<6%) of sinking particulate organic matter in seawater (Paytan et al. 2003). In contrast to our results are a clear indication that phosphonates are produced and incorporated in substantial amounts into sinking organic material in oxic and possibly anoxic environments. According to our NMR data, phosphonates may comprise up to 20% of surface sinking POP in the Cariaco Basin. The difference between our results and those of Paytan et al. (2003) may represent different P cycling processes in anoxic basins, or it may stem from differences in sample processing and NMR methodologies.

In the Cariaco Basin, the source of the phosphonates remains enigmatic. The lack of phosphonate signal in our plankton tow samples suggests that these compounds are (1) produced by organisms able to pass through the plankton net mesh, <200  $\mu\text{m}$  (e.g., smaller microplankton and nanoplankton in this ecosystem), and/or (2) synthesized by the plankton captured by the plankton net but are present in concentrations too low to be detected by solid state  $^{31}\text{P}$  NMR. The ubiquity of phosphonates in marine systems, the presence of phosphonates in bacteria (Ternan et al. 1998), and previous research demonstrating that bacteria are an important source of dissolved organic N (McCarthy et al. 1998) in marine systems are several lines of evidence that suggest that bacteria could be the main producers of both dissolved

and particulate phosphonates in marine ecosystems (Kolowitz et al. 2001).

Another surprising feature of the TPP pool is that we see significant removal of phosphonates with depth relative to theoretically more bioavailable P esters in sinking organic matter, decreasing from 18% to 3% of total particulate P during the low flux period of November 1997 in the Cariaco Basin. The value for the deeper traps is consistent with the data collected by Paytan et al. (2003), which analyzed samples from predominantly deep sediment traps. The decrease in phosphonates with depth is probably due to rapid release from particles and/or preferential remineralization in anoxic environments. It is unlikely that this release occurred in the sediment trap cups during the deployment period, since most P in trap supernatants is probably from the more labile cellular components, such as DNA and RNA (Elser et al. 1996), whereas phosphonates are mostly found in cell walls (Ternan et al. 1998). If the released phosphonates become incorporated into the DOP pool, then processes occurring in anoxic environments may represent a significant source of phosphonates to the dissolved organic matter pool. If phosphonates are hydrolyzed, our results provide some of the first evidence of this phenomenon in marine anoxic waters. Both pathways suggest that while bulk POP is not selectively removed relative to POC below the euphotic zone, phosphonates *within* the POP pool are preferentially remineralized in this environment. This is surprising since dissolved P uptake experiments suggest that P esters should be more bioavailable than phosphonates (Karl and Björkman 2002).

Mechanisms of phosphonate degradation in marine systems are poorly constrained, but almost all are linked to bacterial activity (Ternan et al. 1998; Kononova and Nesmeyanova 2002). The rapid decrease of phosphonates may be further related to the unique chemosynthetic community documented by Taylor et al. (2001). Phosphonate degradation may occur via several enzymatic pathways (Kononova and Nesmeyanova 2002). Genetic studies indicate that reductive cleavage of the C-P bond by one enzyme, C-P lyase, is a two-step process in which phosphite is produced as an intermediary (Ternan et al. 1998). This information, coupled with recent studies revealing that phosphite is directly oxidized to phosphate in anaerobic sediments by sulphate-reducing bacteria (Schink and Friedrich 2000), suggests that bacterial phosphonate reduction may be favorable in the anoxic waters of Cariaco Basin. Furthermore, it is interesting that phosphonate degradation occurred in waters containing  $>0.5 \mu\text{mol L}^{-1}$  of SRP. This suggests that synthesis and activity of the enzyme responsible for phosphonate degradation may not require the presence of low inorganic P concentrations. The lack of a phosphonate decrease during the high mass flux period of March 1998 (averages  $9 \pm 2\%$  of total P over all depths) may be due to increased sinking rates for particulate organic matter that do not allow bacteria sufficient time for phosphonate degradation (Kononova and Nesmeyanova 2002) or due to the abundance of other forms of P.

It has been suggested that organic matter degradation is a nonselective process due to physical protection by the inorganic matrix of sinking organic matter (Hedges et al. 2001). In other words, labile organic matter is trapped within

the interstitial spaces of particles, effectively protecting it from efficient biological degradation. We do not believe this is the case for phosphonates, possibly because bacteria adhere to particle surfaces (Azam 1998). As particles sink through the water column, bacteria may preferentially release particulate phosphonates to the dissolved phase or use it directly to satisfy their own P requirements, and potentially for their C and N metabolic needs (Ternan et al. 1998).

Analysis of a sediment core taken during 2002 at 245 m in the Cariaco Basin also demonstrates a clear phosphonate signal (Fig. 4) that decreases relative to orthophosphate and P esters with depth in the core. This again suggests preferential removal of phosphonates relative to P esters. A similar decrease in phosphonates relative to orthophosphate and P esters has been documented in anoxic cores collected in the Santa Barbara Basin (Laarkamp 2000), which suggests that the dominant mechanism for remineralization of organic P compounds to the dissolved phase in anoxic environments is not directly related to chemical bond lability. It is possible however, that degradation of P esters is restricted by chemical bonding during humification or metal bridging, as suggested by Laarkamp (2000). It should be noted that the Santa Barbara cores had pore water SRP concentrations that exceeded  $20 \mu\text{mol L}^{-1}$ , which suggests that low SRP concentrations are not a requirement for sedimentary phosphonate degradation to occur as observed in traps from the anoxic basin of Cariaco.

Analysis and separation of TPP, PIP, and POP in sediment traps across an oxic–anoxic interface has provided powerful insight into the relationships between the biogeochemical cycling of C, N, and P. Although TPP concentrations may be affected by artifacts associated with loss to supernatants, the strong relationship between POC, PON, and POP suggests that supernatant losses must affect POC and PON fluxes to a significant extent as well in both oxic and anoxic waters. The strong relationship further argues against preferential remineralization of bulk water column POP in anoxic environments. As a result, those studies that focus solely on TPP include a significant portion of PIP that may not be representative of the sinking biogenic pool. Furthermore, if preferential remineralization of POP relative to POC and PON does occur, it must occur on timescales on the order of weeks to months and in the sediments.

Our results also provide evidence of a potentially significant particulate source of phosphonates to the dissolved organic matter pool. In addition, these inert compounds are being preferentially removed within the TPP pool relative to biologically more labile P esters in both the sinking particles and underlying sediments. If phosphonates are produced mainly by bacteria, as suggested by previous research, then the preferential removal of bacterial byproducts from sinking TPP in anoxic environments may help to explain the surprisingly uniform composition of ultrafiltered dissolved organic matter throughout the world's oceans. It also implies that although bulk POP is not preferentially removed in anoxic environments, specific compounds thought to be relatively biologically unavailable (i.e., phosphonates), may be preferentially regenerated. This may provide an additional source of SRP for enhanced production in overlying surface waters. Finally, the selective removal of phosphonates in an

anoxic water column supports previous research that suggests that these compounds may have been a source of P in prebiotic Earth when anoxic conditions were prevalent.

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