Inorganic and organic sinking particulate phosphorus fluxes across the oxic/anoxic water column of Cariaco Basin, Venezuela

Claudia R. Benitez-Nelson a,b,⁎, Lauren P. O’Neill Madden b, Renée M. Styles a, Robert C. Thunell a,b, Yrene Astor c

a Department of Geological Sciences, University of South Carolina, Columbia, SC 29208, USA
b Marine Science Program, University of South Carolina, Columbia, SC 29208, USA
c Fundacion La Salle de Ciencias Naturales, Estacion de Investigaciones Marinas de Margarita, Isla de Margarita, Venezuela

Received 28 March 2006; received in revised form 20 December 2006; accepted 5 January 2007
Available online 26 January 2007

Abstract

Phosphorus (P) is a vital nutrient that is essential for all organisms and may limit growth on both modern and geologic timescales. The major removal mechanism of P from marine systems is via the transformation of dissolved P into sinking particulate P pools. Although most particulate P is remineralized before it reaches the seafloor, little is known about the processes that control its breakdown into dissolved phases. In this study, the P composition of sinking particles captured by five sediment traps distributed through the oxic and anoxic water column of the Cariaco Basin, Venezuela is examined. Samples were collected from January 1996 to December 2004. Total particulate P (TPP), particulate inorganic P (PIP), and particulate organic P (POP) fluxes varied considerably over the course of the nine year study, yet there were no significant seasonal differences in the overall flux of POP. In contrast, PIP, which comprises a major portion of TPP (averaging 52±19% across all depths) had fluxes that were 30% higher during non-upwelling periods. Poor relationships between PIP and biologically derived constituents, e.g. particulate organic carbon (POC), suggest that most of this material was derived from non-biological sources, namely terrestrial runoff from rivers. Rapid remineralization of POP occurred relative to POC and PIP in oxic surface waters, whereas PIP was quickly remineralized relative to POC and POP in subsurface anoxic waters. This suggests a significant and alternating source of particulate P to the dissolved P pool that depends on oxygen availability. Thus, particulate P release to the dissolved phase and the upwelling of dissolved P into the euphotic zone is a potentially important positive feedback mechanism for enhanced primary production and carbon sequestration in continental margin sediments regardless of oxic versus anoxic conditions.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Particulate flux; Particulate organic phosphorus; Particulate inorganic phosphorus; Continental margins; Sediment traps; Cariaco Basin

1. Introduction

Phosphorus (P) is one of the major nutrients utilized by all organisms. In the open ocean, regeneration of dissolved P compounds from sinking particles and the upwelling of these products to the euphotic zone is a critical step regulating P availability and biological production in surface waters (Thomson-Bulldis and Karl, 1998; Benitez-Nelson, 2000; Karl and Bjorkman, 2002; Paytan et al., 2003). Yet, little is known about the particulate P pool with regard to its composition and spatial and temporal variability. A major topic of debate
is whether or not there is preferential remineralization of sinking particulate P relative to particulate organic carbon and nitrogen and whether this changes under oxic versus anoxic conditions (Knauer et al., 1979; Martin et al., 1987; Minster and Boulahhid, 1987; Anderson and Sarmiento, 1994; Benitez-Nelson, 2000; Karl and Bjorkman, 2002; Paytan et al., 2003). This debate is further confounded by increasing evidence that not all of the particulate P measured in sinking particles is organic in nature (Loh and Bauer, 2000; Benitez-Nelson et al., 2004; Faul et al., 2005). Rather, there appears to be a significant fraction that is inorganic, associated with non-biological sources, and potentially less bioavailable (Paytan et al., 2003; Faul et al., 2005).

The Cariaco Basin, located along the northern margin of Venezuela, is anoxic below ~275 m. Primary production occurs mainly within the upper 20–40 m of the mixed layer and most particle production occurs in the oxic zone (Thunell et al., 2000; Scranton et al., 2006). Therefore, it is an excellent place to examine particle regeneration in both oxic and anoxic waters. In this study, P concentrations and organic versus inorganic P speciation in sinking particles collected from five different depths in the water column between January 1996 and December 2004 are examined as part of the Cariaco Time Series Program (Müller-Karger et al., 2005).

2. Methods

The Cariaco Basin is a 1400-m-deep depression approximately 160 km long by 70 km wide located off the central Venezuelan coast (Fig. 1). It is connected to the Atlantic Ocean by a sill ~100-m-deep, and two slightly deeper channels that breech it; Canal Centinela (146-m-deep) and Canal de la Tortuga (135-m-deep). High surface production rates and restricted circulation result in anoxic waters below ~275 m. The depth of the oxycline varies between 250 and 320 m and is independent of density. Rather, fluctuations in oxycline depth appear to be due to lateral intrusions of Caribbean Sea water that are linked to eddies along the continental shelf (Astor et al., 2003).

Primary production in the Cariaco Basin varies seasonally and is driven by wind-induced coastal upwelling. As the Intertropical Conversion Zone (ITCZ) moves to its southern-most position, strong easterly/northeasterly trade winds develop between December and April (Thunell et al., 1999; Müller-Karger et al., 2000; Thunell et al., 2000; Müller-Karger...
et al., 2001; Taylor et al., 2001; Goñi et al., 2003). This leads to shoaling of the nutricline, bringing nutrients to the surface and increasing biological production in the upper 50 m (Scranton et al., 2006). During the summer and fall, the winds weaken causing cessation of upwelling and decreased primary production (Thunell et al., 1999; Müller-Karger et al., 2000; Thunell et al., 2000; Müller-Karger et al., 2001; Taylor et al., 2001; Goñi et al., 2003). Most of the biological particle flux appears to be driven by diatoms, with additional export from coccolithophore species such as Emiliania huxleyi and fecal pellets (Thunell et al., 2000; Goñi et al., 2003). A secondary source of biologically derived particulate matter may be due to chemoeautotrophic microbial production at the oxic/anoxic boundary at ∼ 275 m (Taylor et al., 2001).

Non-upwelling time periods are characterized by maxima in rainfall (June–August) as the Atlantic ITCZ moves to its most northern position over the Venezuelan coast (Peterson and Haug, 2006). This causes an increase in discharge rates from rivers draining South America and it is likely that this increase also occurs in the four local rivers that drain directly into the Cariaco Basin, the Tuy, Unare, Neveri, and Manzanares, though direct evidence is limited (Milliman and Syvitski, 1992). The input of terrigenous material to Cariaco Basin is generally enhanced during and following the regional rainy season (Peterson and Haug, 2006).

A mooring with five sediment traps (Z, A–D) is located in the eastern Cariaco Basin at 10°30′N and 64°40′W (Fig. 1). Traps A–D have been in place since November 1995. Trap A is located in oxic waters at 226 ± 6 m. Trap B is located at 407 ± 3 m and Trap D is located at 1205 ± 3 m. Trap C was located at a depth of 880 ± 2 m from Jan. 1996 to Nov. 2000, and was moved to 807 ± 2 m in Nov. 2000. A fifth trap, Z, was added in November 2003 at 110 m for the first 6 months, and at 880 ± 2 m from Jan. 1996 to Nov. 2000, and was moved to its most northern position over the Venezeulan coast (Peterson and Haug, 2006). This causes an increase in discharge rates from rivers draining South America and it is likely that this increase also occurs in the four local rivers that drain directly into the Cariaco Basin, the Tuy, Unare, Neveri, and Manzanares, though direct evidence is limited (Milliman and Syvitski, 1992). The input of terrigenous material to Cariaco Basin is generally enhanced during and following the regional rainy season (Peterson and Haug, 2006).

Sediment trap samples were sealed and refrigerated before processing began, usually 1–3 weeks after recovery. Most of the supernatant from each cup was discarded, along with all obvious swimming organisms not considered part of the particle flux. Samples were then split into quarters using a precision rotary splitter. The quarter sample used for analysis was rinsed with deionized water a total of three times, frozen, dried, and ground (Thunell et al., 2000; Goñi et al., 2003).

Total particulate P (TPP) and particulate inorganic P (PIP) were measured using an adaptation of the Aspila method (Aspila et al., 1976). Particulate organic P (POP) is estimated by difference (TPP – PIP). As such, each fraction is analytically defined and the PIP fraction may contain some acid-labile organic P-containing molecules, such as simple sugars, whereas the POP may contain inorganic compounds, such as pyrophosphates (Benitez-Nelson, 2000). To check analytical accuracy and to monitor potential variability from run to run, a standard reference material (SRM), NIST # 1573a (Tomato leaves) was analyzed with each run. This SRM was chosen for its similarity in P content relative to the samples (0.216%) and because it is comprised of fresh organic material.

Particulate organic carbon (POC) and particulate nitrogen (PN) analyses were conducted according to the methods described in Thunell et al. (2000). Briefly, ∼ 25 mg of dried, ground sample was treated with a 10% solution of phosphoric acid to remove all carbonate. Samples were rinsed with deionized water and then dried in a tin capsule prior to analysis using a Perkin Elmer 2400 elemental analyzer.

3. Results

All significant (p) values were determined using a two-tailed t-test unless otherwise noted. TPP, PIP (and therefore POP) were measured in all of the sediment trap samples available from January 1996–December 2004 (Table 1, n=623). Approximately 5% of the samples were run in duplicate and SRM recovery was 101 ± 3%. TPP and PIP measurements have a standard error of 6%. POP, found by difference, has a standard error of 8.5%. Recently, O’Neill et al. (2005) examined possible diagenetic artifacts associated with sediment trap collections of particulate P in samples retrieved from Cariaco Basin. They determined that on average, ∼ 30% of the total P within trap cups is within the supernatants with an additional 10% of total P lost during sediment trap processing. Most of this lost material (> 80%) was in the form of inorganic P. No temporal or depth trends (e.g. oxic versus anoxic waters) were found in the release of P to the supernatants, implying that seasonal and depth trends

92 C.R. Benitez-Nelson et al. / Marine Chemistry 105 (2007) 90–100
in particle phases should be maintained. Given the lack of supernatant information for many of the samples analyzed, and the inability to distinguish the source of the inorganic P to the dissolved phase (e.g. hydrolyzed from PIP or POP), supernatant concentrations were not added to the measured particle concentrations or fluxes discussed below.

PIP comprises a significant part of the TPP pool, 52±19%. PIP concentrations decrease from an average of 0.066 mmol g⁻¹ in Z trap samples to 0.026 mmol g⁻¹ in samples from the D trap. In contrast, POP concentrations decrease only within the oxic waters (0.045 mmol g⁻¹ in Trap Z to 0.030 mmol g⁻¹ in Trap A, p<0.01) and remain constant, ~0.029 mmol g⁻¹ in the samples collected from the anoxic portion of the basin (p>0.1). These changes in trap concentration are also reflected in the percentage of PIP within the trap samples. For example, with the exception of the shallow Z trap (n=14), the percentage of PIP decreases significantly between oxic and anoxic waters (p<0.001) and more rapidly during upwelling. The percentage of PIP is also lower during upwelling (48±18%) versus non-upwelling conditions (56±19%).

TPP, PIP, and POP fluxes vary substantially (Fig. 2, Table 1). Annual fluxes of TPP, PIP, and POP fluctuate by as much as 40% depending on the depth. Annual fluxes were divided into two periods, upwelling and non-upwelling, where upwelling is defined by an average temperature over the upper 25 m of less than 24.5 °C (Goñi et al., 2003). Additional upwelling time periods were identified based on continuity of primary production. While average primary production rates (as measured by ¹⁴C uptake over the upper 100 m, (Müller-Karger et al., 2001) are a factor of two higher during upwelling (163 mg C m⁻² h⁻¹) versus non-upwelling (77 mg C m⁻² h⁻¹) conditions, average POP fluxes between seasons are similar (not including the relatively few samples available from trap Z, n=14). In contrast, PIP fluxes are on average 30% higher during non-upwelling (again not including the Z trap), which

---

**Table 1**

Summary of average particle fluxes and elemental ratios from 1996 to 2004

<table>
<thead>
<tr>
<th>Trap</th>
<th>Depth (m)</th>
<th>POC Flux</th>
<th>PN Flux</th>
<th>TPP Flux</th>
<th>PIP Flux</th>
<th>POP Flux</th>
<th>% IP</th>
<th>POC:POP</th>
<th>POC:TPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>130</td>
<td>6</td>
<td>7.61</td>
<td>4.29</td>
<td>1.09</td>
<td>0.58</td>
<td>0.062</td>
<td>0.038</td>
<td>0.023</td>
</tr>
<tr>
<td>A</td>
<td>226</td>
<td>72</td>
<td>6.68</td>
<td>4.38</td>
<td>0.83</td>
<td>0.55</td>
<td>0.053</td>
<td>0.035</td>
<td>0.031</td>
</tr>
<tr>
<td>B</td>
<td>407</td>
<td>72</td>
<td>6.47</td>
<td>3.74</td>
<td>0.78</td>
<td>0.44</td>
<td>0.041</td>
<td>0.024</td>
<td>0.019</td>
</tr>
<tr>
<td>C</td>
<td>844</td>
<td>71</td>
<td>4.28</td>
<td>2.83</td>
<td>0.50</td>
<td>0.34</td>
<td>0.024</td>
<td>0.020</td>
<td>0.012</td>
</tr>
<tr>
<td>D</td>
<td>1205</td>
<td>62</td>
<td>3.79</td>
<td>2.68</td>
<td>0.45</td>
<td>0.31</td>
<td>0.019</td>
<td>0.018</td>
<td>0.008</td>
</tr>
<tr>
<td>All</td>
<td></td>
<td>283</td>
<td>5.41</td>
<td>3.73</td>
<td>0.65</td>
<td>0.45</td>
<td>0.035</td>
<td>0.029</td>
<td>0.018</td>
</tr>
</tbody>
</table>

**Non-upwelling (77 mg C m⁻² h⁻¹)**

<table>
<thead>
<tr>
<th>Trap</th>
<th>Depth (m)</th>
<th>POC Flux</th>
<th>PN Flux</th>
<th>TPP Flux</th>
<th>PIP Flux</th>
<th>POP Flux</th>
<th>% IP</th>
<th>POC:POP</th>
<th>POC:TPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>130</td>
<td>8</td>
<td>5.34</td>
<td>3.38</td>
<td>0.78</td>
<td>0.49</td>
<td>0.046</td>
<td>0.025</td>
<td>0.023</td>
</tr>
<tr>
<td>A</td>
<td>226</td>
<td>99</td>
<td>6.11</td>
<td>3.53</td>
<td>0.77</td>
<td>0.44</td>
<td>0.073</td>
<td>0.051</td>
<td>0.047</td>
</tr>
<tr>
<td>B</td>
<td>407</td>
<td>90</td>
<td>3.78</td>
<td>2.48</td>
<td>0.47</td>
<td>0.32</td>
<td>0.041</td>
<td>0.032</td>
<td>0.026</td>
</tr>
<tr>
<td>C</td>
<td>844</td>
<td>74</td>
<td>3.11</td>
<td>2.54</td>
<td>0.37</td>
<td>0.30</td>
<td>0.029</td>
<td>0.026</td>
<td>0.018</td>
</tr>
<tr>
<td>D</td>
<td>1205</td>
<td>69</td>
<td>2.81</td>
<td>1.99</td>
<td>0.33</td>
<td>0.25</td>
<td>0.021</td>
<td>0.017</td>
<td>0.010</td>
</tr>
<tr>
<td>All</td>
<td></td>
<td>340</td>
<td>4.15</td>
<td>3.07</td>
<td>0.51</td>
<td>0.39</td>
<td>0.044</td>
<td>0.041</td>
<td>0.027</td>
</tr>
</tbody>
</table>

**All periods (116 mg C m⁻² h⁻¹)**

<table>
<thead>
<tr>
<th>Trap</th>
<th>Depth (m)</th>
<th>POC Flux</th>
<th>PN Flux</th>
<th>TPP Flux</th>
<th>PIP Flux</th>
<th>POP Flux</th>
<th>% IP</th>
<th>POC:POP</th>
<th>POC:TPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>130</td>
<td>14</td>
<td>5.09</td>
<td>2.81</td>
<td>0.91</td>
<td>0.53</td>
<td>0.053</td>
<td>0.031</td>
<td>0.023</td>
</tr>
<tr>
<td>A</td>
<td>226</td>
<td>171</td>
<td>6.35</td>
<td>3.91</td>
<td>0.79</td>
<td>0.49</td>
<td>0.064</td>
<td>0.046</td>
<td>0.040</td>
</tr>
<tr>
<td>B</td>
<td>407</td>
<td>160</td>
<td>5.02</td>
<td>3.37</td>
<td>0.61</td>
<td>0.41</td>
<td>0.041</td>
<td>0.029</td>
<td>0.022</td>
</tr>
<tr>
<td>C</td>
<td>844</td>
<td>145</td>
<td>3.68</td>
<td>2.74</td>
<td>0.44</td>
<td>0.32</td>
<td>0.027</td>
<td>0.023</td>
<td>0.015</td>
</tr>
<tr>
<td>D</td>
<td>1205</td>
<td>131</td>
<td>3.27</td>
<td>2.38</td>
<td>0.39</td>
<td>0.28</td>
<td>0.020</td>
<td>0.018</td>
<td>0.009</td>
</tr>
<tr>
<td>All</td>
<td></td>
<td>623</td>
<td>4.72</td>
<td>4.34</td>
<td>0.58</td>
<td>0.43</td>
<td>0.040</td>
<td>0.036</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Average primary production rates are shown in parentheses for the time period specified.

a See Methods for details on trap depths.
corresponds to time periods of increased rainfall and river discharge (Peterson and Haug, 2006). PIP fluxes decrease on average by \(\sim 78\%\) from Trap A to D, while POP fluxes decrease by only \(\sim 58\%\).

The molar ratio of POC and PN to TPP, PIP, and POP was determined using a linear fit to all available data (Table 1, Fig. 3). The molar ratio of POC:POP and PN: POP across all depths and years is 193 \((r^2=0.69, p<0.0001)\) and 24.3 \((r^2=0.71, p<0.0001)\), respectively. In contrast, the molar ratio of POC:PIP is 68 and POC and PIP are not well-correlated \((r^2=0.27)\). Further analysis with depth shows a decrease in the POC:POP ratio from 147 in the surface Z trap, to a constant value of \~190 at 226 m and below. POC:POP ratios at these depths also changes between upwelling and non-upwelling periods (Fig. 4), with POC:POP ratios of 223 and 173, respectively (ANOVA, \(p<0.001\)). Similar relationships between POC:PN ratios are also observed, with a POC:PN ratio of 6.4 \((n=14, r^2=0.89)\) in the surface Z trap, increasing to a near constant value of 8.1 at 226 m and below \((r^2=0.99, p<0.001)\). POC:PN ratios, however, are only slightly elevated during upwelling (all data=8.1, A–D traps only=8.2) versus non-upwelling periods (all data=7.8, A–D traps only=7.9; \(p_{A-D}<0.01\)). PN:POP had no observable trends with depth, but did have significant differences in PN:POP between upwelling (27.6) and non-upwelling (21.8, \(p<0.01\)) seasons.

In addition to sinking particulate organic matter, trap samples were measured for CaCO₃, opal, and terrestrial material, where the terrestrial fraction is defined as that portion remaining after subtraction of particulate organic matter, CaCO₃, and opal (Thunell et al. 2000). Similar to POC, POP fluxes are significantly correlated to terrestrial fluxes \((r^2=0.48, p<0.01)\), and the other biologically derived minerals of CaCO₃ \((r^2=0.65, p<0.01)\) and opal \((r^2=0.44, p<0.01)\), with slightly elevated terrigenous, opal, and CaCO₃ to POP ratios during upwelling versus non-upwelling periods \((p<0.01)\).

The relationship between PIP and terrigenous, CaCO₃ and opal fluxes is more complicated. During upwelling, overall relationships between PIP and opal and CaCO₃ are insignificant \((r^2<0.21)\), but the significance does increase with depth, with an \(r^2\) of \(<0.1\) for both CaCO₃ and opal at the surface, increasing to 0.34 and 0.44 at 1250 m for CaCO₃ and opal, respectively. PIP is well-correlated to terrestrial material at almost all depths during upwelling, with an overall \(r^2=0.43\) \((p<0.001)\). During non-upwelling, PIP is only well-correlated to opal in the upper 150 m \((r^2=0.79)\), but is significantly correlated to CaCO₃ above 226 m \((r^2=0.69\) in Trap Z and 0.47 in Trap A) and at 1205 m \((r^2=0.53)\). PIP is significantly correlated to terrestrial fluxes only in the two deeper traps located at \~900 m \((r^2=0.40)\) and 1205 m \((r^2=0.48)\). Closer examination of the associations between PIP and terrestrial material during non-upwelling periods reveals two distinct relationships. During high terrestrial flux periods \((>1.3\ g\ m^{-2}\ d^{-1})\), also associated with high mass flux events of \(>2\ g\ m^{-2}\ d^{-1}\), there is a significant and different correlation between PIP and terrestrial fluxes \((r^2=0.74)\) not evident throughout the rest of the year (Fig. 5).
4. Discussion

Cariaco Basin is a dynamic upwelling system that results in strong phytoplankton blooms that typically occur from December to April (Thunell et al., 1999; Müller-Karger et al., 2000; Thunell et al., 2000; Müller-Karger et al., 2001; Taylor et al., 2001; Goñi et al., 2003). Although Cariaco Basin phytoplankton production currently appears to be nitrate limited (Scranton et al., 2006), a number of studies in other areas have suggested that phytoplankton production may become increasingly P stressed due to anthropogenic inputs of excess nitrogen and naturally induced climate fluctuations (Fanning, 1989; Wu et al., 2000; Karl et al., 2001). In many systems, dissolved P availability is regulated by the upwelling of P-rich deep waters (e.g. see reviews by Benitez-Nelson 2000; Delaney 1998). Thus, the remineralization of sinking particles is a key parameter in understanding the source of nutrients to the euphotic zone. Unfortunately, there is a distinct lack of knowledge regarding the composition and magnitude of sinking TPP.

Within the 9-year period studied, TPP, PIP, and POP fluxes in Cariaco Basin fluctuate by as much as 40% and decrease with increasing depth. We consider these fluxes to be minimum estimates as none of the P lost to supernatants are included in these or the following calculations (see above). There is no clear relationship between primary production and particle flux, and POP fluxes are indistinguishable between upwelling and non-upwelling seasons (Table 1, Fig. 2). In fact, PIP fluxes actually increase by 50% during non-upwelling periods. POC fluxes are only slightly elevated (~25%) during upwelling versus non-upwelling seasons, even though primary production rates differ by a factor of two. Rather, POC fluxes tend to covary with total mass fluxes (Thunell et al., 2000; Thunell et al., in press). Although terrestrially derived POC is difficult to pinpoint, particularly if from erosion of marine sedimentary rocks (Petsch et al., 2006), there is surprisingly no

Fig. 3. POC versus TPP, PIP, and POP fluxes with depth in oxic (top panel, A–C) and anoxic (bottom panel, D–E) waters from 1996 to 2004.
evidence of terrestrial POC within the sediment traps. Almost all of the POC within the traps has classic marine indices (Hedges et al., 1997); δ^{13}C values range from −17.6 to −22.6‰ (Woodworth et al., 2004), POC: PN molar ratios are ∼8.0 (Thunell et al., submitted for publication), and there is a strong odd C preference of short chained n-alkanes (Thunell et al., 2000). Other evidence includes the presence of only a very small amount of lignin phenols, a tracer of terrestrial organic matter input (Woodworth et al., 2004). Thunell et al. (in press) conclude that Cariaco Basin organic matter fluxes are driven by association with higher density material, or “mineral ballast” that may be derived from both marine and terrestrial sources. This interaction enables organic matter, which is typically neutrally buoyant in seawater, to sink rapidly out of the upper ocean regardless of overlying primary production rates. Mineral ballast may further hamper degradation, causing preferential loss of labile material not associated with minerals (e.g. fecal pellets), and thereby explain large scale differences in the composition of sinking organic matter as evidenced by changes in POC:POP and POC:PN ratios within oxic waters (Fig. 3) (Hedges et al., 2001; Armstrong et al., 2002).

There are significant decreases in the flux of material with depth between the A and D traps. It is interesting to note that fluxes actually increase slightly between the Z and A traps for all constituents (Fig. 3). One possibility is that the upper two sediment traps may have been affected by either partial clogging during high flux events (Goñi et al., 2003) or enhanced horizontal shear associated with lateral subsurface intrusions from the Caribbean Sea (Astor et al., 2003). It may also be due to zooplankton feeding in surface waters and fecal pellet production at depths below the Z trap.

PIP is consistently a major component of the TPP pool (52±19%) at all depths and seasons. It is likely that this percentage is a minimal estimate as most of the P loss to supernatants is inorganic in nature (O’Neill et al., 2005). This high percentage is similar to that found in several previous, albeit limited studies (Loh and Bauer, 2000; Paytan et al., 2003; Faul et al., 2005). PIP fluxes also decrease rapidly with depth in anoxic waters suggesting that PIP is an important source of dissolved P.

Fig. 4. Elemental relationships of organic constituents in upwelling (filled squares) versus non-upwelling periods (open squares). All data from 1996 to 2004 is shown. A) POC versus POP, B) PN versus POP, C) POC versus PN. Linear regressions are shown for upwelling (solid lines) and non-upwelling (dashed lines) periods. Upwelling and non-upwelling slopes are significantly different at p<0.01 except for POC versus PN when Z trap data are included (e.g. when Z trap data are removed, p<0.01).

Fig. 5. Terrigenous versus PIP fluxes from 1996 to 2004. Data within the dashed box is shown in the inset and contains only those points with terrigenous fluxes >1.3 g m^{-2} d^{-1}.
to marine systems. The source of this PIP, however, remains enigmatic.

Most studies that examine the sinking P pool measure TPP with the assumption that most of the PIP captured within the traps is either derived from in situ cellular release or remineralization of biologically derived organic material (Knauer et al., 1979; Minster and Boulaahdid, 1987). Thus, it is often considered a bioavailable component of the TPP pool. If PIP is derived from biogenic matter, there should be excellent relationships between TPP, PIP and POC, as POC is derived from marine biological production (Werne et al., 2000; Goñi et al., 2003; Woodworth et al., 2004). This is not the case (Table 1, Fig. 3). In fact the molar ratio of POC:TPP ranges from a low of 56 in the A trap to 107 at depth (average=69, \( r^2 = 0.53 \)). This is significantly lower than that expected for an upwelling system based on canonical Redfield ratios (Redfield et al., 1963). In contrast, the ratio of POC:POP ranges from 147 in the Z trap to a maximum of 205 in the C Trap (average=193, \( r^2 = 0.69 \)). Hence, organic matter ratios in surface waters are closer to Redfield ratios. Furthermore, the rapid increase in the POC:POP ratio with depth (relative to POC:TPP) suggests rapid and preferential remineralization of POP relative to PIP in oxic waters (% TPP that is IP increases by \( \sim 11\% \) from the Z to A traps). In anoxic waters, POP, POC, and PN are degraded at the same rate (constant ratios with depth), whereas PIP continues to decrease significantly.

Additional evidence that the sinking POP pool is preferentially remineralized in oxic waters stems from the contemporaneously collected monthly nutrient data. Scranton et al. (2006) compiled dissolved nutrient concentrations and determined that the dissolved N:P ratio within the upper 100 m rarely falls below 14:1, but decreases immediately below this depth. This decrease occurs simultaneously with an increase in POC:POP and PN:POC ratios, whereas the POC:PIP and PN:PIP ratios actually decrease.

Although organic matter fluxes do not vary with season, the ratio of POC:POP in the A–D traps does (Fig. 4), with POC:POP ratios significantly higher during upwelling (\( \sim 223 \)) versus non-upwelling (\( \sim 173, p < 0.001 \)). Similar patterns between upwelling and non-upwelling are observed with PN:POP ratios (27.6 versus 21.8, \( p < 0.001 \)) and to a much lesser extent, POC:PN (8.1 versus 7.8). Given that the ratios of POC:POP in the upper 100-m trap are within error, the same between seasons, this implies more rapid remineralization of POP relative to POC in the underlying oxic waters during upwelling periods. The cause of this more rapid remineralization during upwelling is unclear, but may be due to: 1) higher bacterial concentrations which facilitate this remineralization, or 2) differences in the bioavailability of the sinking organic matter (e.g. a higher fraction of more labile material during upwelling). Relationships between POP, POC, and PN are discussed in more detail in Thunell et al. (submitted for publication).

PIP fluxes are higher during non-upwelling periods (when primary production is relatively low and rainfall high, Table 1). This higher flux and the weak relationship between PIP and POC suggest that a large fraction of the PIP pool is not derived from marine produced sinking organic matter (Fig. 3). Instead, the timing suggests that the most likely source of PIP is from terrestrially derived material that likely enters Cariaco Basin from rivers (Fig. 5). During the non-upwelling season, increased rainfall from June through August drives increased riverine discharge from June through November from four local rivers: Tuy, Unare, Neveri, and Manzanares (Peterson and Haug, 2006). The Tuy River has by far the highest discharge rate, contributing \( 12 \times 10^6 \) tons of sediment \( y^{-1} \) into the western end of Cariaco Basin (Milliman and Syvitski, 1992). The Unare, Neveri, and Manzanares Rivers, while closer in proximity to the sediment trap site, contribute only \( \sim 0.5 \times 10^6 \) tons of sediment \( y^{-1} \) (Milliman and Syvitski, 1992). Only the Manzanares River discharges directly into the Cariaco Basin, while the Tuy, Unare, and Neveri discharge onto the Unare Platform. The rivers drain the Araya Peninsula, to the east of Cariaco Basin, and the Coastal Range of the Cabo Codera to the west, which are predominantly comprised of Mesozoic metamorphic and igneous rocks (Peterson and Haug, 2006). Mountains (Cordillera de la Costa and the Serrania del Interior) and the Maturin and Guarico Sub-basins to the south are comprised of Cretaceous and Tertiary sedimentary rocks characterized by organic carbon (and presumably P) rich limestones, cherts, and shales (Macsotay et al., 2003; Peterson and Haug, 2006). Although information is limited, phosphate deposits have been found in northwestern Venezuela adjacent to the western Cariaco Basin in the Falcón region (Rodriguez, 1981) and further west in the Barinas/Anare Basins (La Luna and Navay Formations) (Macsotay et al., 2003).

Closer examination of the relationship between PIP and terrestrial material during non-upwelling suggests that there are two distinct relationships between PIP and terrestrial organic matter that is directly related to total mass and terrigenous fluxes (Fig. 5). When mass fluxes exceed \( 2 \) g m\(^{-2}\) d\(^{-1}\), and hence terrigenous fluxes exceed \( 1.3 \) g m\(^{-2}\) d\(^{-1}\), PIP and terrestrial fluxes are
highly correlated \((r^2 = 0.74)\). Most of these high mass flux events are associated with high rainfall events and in one case, an earthquake (Thunell et al., 1999).

The composition of the terrestrially derived PIP fractions remains ambiguous, but it is likely associated with detrital, authigenic and oxide-associated materials commonly found in rivers and continental margin sediments (Froelich et al., 1982; Ruttenberg and Berner, 1993; Berner and Rao, 1994; Vink et al., 1997). In the Cariaco Basin, much of the PIP released to the dissolved phase occurs within anoxic waters between the A and C traps (226–844 m, Table 1). This coincides with a peak in dissolved iron and an increase in dissolved phosphate that are consistent with the reduction of PIP associated metal oxides and possible consumption by chemosynthetic bacteria at the oxic/anoxic interface (Ho et al., 2004). The weak relationships that exist between PIP and carbonate and opal, are likely related to PIP adsorption via metal oxides to shell surfaces. Studies of other South American watersheds support the hypothesis of terrestrially derived oxide-associated P. For example, Berner and Rao (1994) determined that \(\sim 30\%\) of the P within suspended particles of the Amazon River was associated with oxides and transported onto the shelf. Tropical soils are further typically characterized by low P concentrations that are mobilized with changes in iron and aluminum biogeochemistry. For example, Chacon et al. (2005) recently provided evidence that soils located in the flood plain of the Mapire River in southeastern Venezuela, seasonally release P under anoxic conditions due to oxide dissolution.

5. Conclusions and implications

A major topic of debate regarding the sinking particulate fraction of the marine P cycle is whether or not there is preferential remineralization of organic P relative to organic C and N (Knauer et al., 1990). Here, POP is shown to be preferentially remineralized in oxic versus anoxic waters. Although pore water processes are much more complicated, our results are in direct contrast to studies which have found that in anoxic sediments, P is preferentially released relative to C (Van Capellen and Ingall, 1994; Wallman, 2003). These results also demonstrate that PIP is a substantial fraction of the TPP pool and appears to be largely terrestrially derived. In contrast to POP, PIP fluxes appear to decrease significantly in anoxic waters, likely due to dissolution of metal oxides.

Combined, this study suggests that PIP and POP contribute significantly to the dissolved P pool depending on the available oxygen concentrations. This finding has important implications for understanding feedback mechanisms of nutrient availability and carbon sequestration on continental margins under oxic versus anoxic conditions. Oxygen is important for not only understanding nutrient regimes in the geologic past, but also in the present day. For example, recent evidence suggests that there is a decreasing trend in dissolved oxygen concentrations in the world’s oceans (Emerson et al., 2002; Joos et al., 2003). Here, evidence is provided that it is the PIP pool (as opposed to bulk TPP) which needs to be considered under anoxic conditions.

In other words, under anoxic conditions, preferential remineralization of PIP relative to POC creates a direct decoupling of the P and C cycles, where P that is released into the water column may enhance primary production and facilitate continued C export. This is particularly important in highly productive continental margin systems like the Cariaco Basin, which often have suboxic waters at depth and large terrestrial inputs. Such continental margins are hypothesized to be responsible for more than 40% of global C sequestration in modern times (Müller-Karger et al., 2005). We must note that this hypothesis is dependent on the magnitude of the PIP flux to other continental margins. The lack of information regarding riverine P geochemistry and PIP composition and fluxes in marine systems in general makes it difficult to assess how Cariaco Basin differs from other continental margins around the world.

This study has focused on the bulk characteristics of the sinking organic and inorganic P pools. Recent evidence has shown that preferential remineralization of specific organic compounds, such as phosphonates, may occur under anoxic conditions (Benitez-Nelson et al., 2004) and it is likely that other organic compounds are also affected. The composition of the analytically defined PIP pool is probably equally complex and also needs to be studied in much more detail. Thus, additional analysis and characterization of specific compounds within the P pool is necessary to better understand dissolution and degradation processes with depth. This information will help develop a more complete understanding of P cycling in anoxic systems, and the global P cycle in general.

Acknowledgements

We thank E. Tappa and M. Luc for the help with sample analyses. Estacion de Investigaciones Marinas de Fundacion La Salle provided logistical support and we thank the crew of the R/V Hermano Gines for their assistance at sea. The manuscript was greatly improved
by the insightful comments of two anonymous reviewers. This work was partially supported by a grant from the University of South Carolina Research and Productive Scholarship Fund and NSF Grants OCE-0118349, OCE-0326313, and OCE-0432616.

References


