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Cycling of suspended particulate phosphorus in the redoxcline of the Cariaco Basin

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Abstract

The Cariaco Basin, located off the coast of Venezuela, is anoxic below ~250 m and has a productive redoxcline where several chemical gradients support multiple biogeochemical reactions. Thus, the Cariaco Basin is an ideal study site for investigating how redox chemistry influences phosphorus (P) biogeochemistry, especially in oxygen-depleted waters. While sinking particles in the Cariaco Basin have been investigated previously for P composition and flux, this is the first study to describe P within suspended particulate particles, a key phase connecting biogeochemical cycling of elements: oxygen minimum zones, euxinic basins and seas, eutrophic estuaries and fjords (Spencer and Brewer, 1971; Emerson et al., 1983; Stramma et al., 2010; Lam and Kuypers, 2011; Kalvelage et al., 2013).

Oxygen minimum zones (OMZs) occur along major ocean basin boundaries, typically at water depths that range from 100–1000 m, and emanate from regions characterized by highly productive surface waters (Wyrtki, 1962). Limited mixing, coupled with oxygen consumption during remineralization of sinking organic matter, reduces oxygen concentrations far below equilibrated surface water concentrations (Codispoti et al., 2005; Karstensen et al., 2008; Paulmier and Ruiz-Pino, 2009). Over the past several decades, open ocean systems have experienced a significant decline in dissolved oxygen concentrations, resulting in the expansion of OMZs worldwide (Stramma et al., 2008; Deutsch et al., 2011, 2014). Such expansions are expected to continue in response to climate induced changes in ocean temperature and circulation, which result in decreased oxygen solubility, a decline in vertical mixing, and reduced subduction and advection of deep waters (Matear and Hirst, 2003; Stramma et al., 2008). In coastal marine systems, increased fertilizer runoff from rivers and atmospheric nitrogen deposition from fossil fuel burning have also contributed to the global expansion of OMZs via intensified eutrophication, which results in large-scale increases in organic matter export that significantly stimulates microbial respiration in the subsurface (Jahnke, 1992; Paerl, 1997; Correll, 1998; Bennett et al., 2001; Doney, 2010).

Indeed, coastal OMZs have spread exponentially since the 1960’s (Diaz and Rosenberg, 2008).
Euxinic basins, while less prevalent than OMZs, provide invaluable test beds for examination of redox chemistry and include three major sites: the Cariaco Basin, the Black Sea and the Baltic Deeps. Euxinic basins are characterized by minimal mixing with the upper ocean and shallow sills that restrict vertical circulation below the surface waters, creating anoxic, sulfidic bottom waters (Diaz et al., 2012). Transition zones between oxygen and anoxic waters are usually characterized by large hydrographic and chemical gradients due to large scale changes in density structure, intense elemental cycling, and elevated microbial activity (e.g., Taylor et al., 2001; Murray and Yakshe, 2006; Wakeham et al., 2012; Li et al., 2012). Stratified waters create multiple layers of biological activity fueled by a variety of redox reactions that rely on specific elements, such as sulfur, nitrogen, iron and manganese (Carl, 1978; Madrid et al., 2001; Taylor et al., 2006). These redox reactions are similar to those found in marine sediments, except that they tend to occur over scales of tens of meters, rather than centimeters, enabling redox processes to be studied in more detail. Finally, these basins are relatively small, and their enclosed nature is such that climate forcing tends to be more evident in basin-wide physical, chemical and biological processes (Murray and Yakshe, 2006).

The majority of research in these oxygen-depleted environments has understandably focused on the biogeochemical cycling of elements with clear redox chemistry, such as nitrogen, carbon, sulfur and trace elements (Spencer and Brewer, 1971; Emerson et al., 1983; Stramma et al., 2010; Lam and Kuppers, 2011; Kalvelage et al., 2013). Less attention has been given to the macronutrient phosphorus (P). P is a vital nutrient utilized by all marine organisms in essential biomolecules, including nucleic acids, phospholipids, ATP and other energy-conserving compounds (Benitez-Nelson et al., 2007; Diaz et al., 2012). While P is often thought to limit global primary production over geologic timescales, recent evidence suggests that P availability may also influence phytoplankton cellular composition, community structure, growth and production in the modern ocean (Benitez-Nelson, 2000; Paytan and McLaughlin, 2007; Karl, 2014; Stilkin et al., 2014). This has led to more focused investigations regarding P speciation and cycling over short time scales (e.g., Diaz et al., 2012; Martin et al., 2014). As natural and anthropogenically-induced climatic changes occur, biological production has been hypothesized to become increasingly P limited (Fanning, 1989; Wu et al., 2000; Karl et al., 2001; Benitez-Nelson et al., 2004; Karl, 2014).

Until recently, P was not considered to have extensive reduced forms in natural environments, with the exception of phosphine gas (PH₃) potentially produced via microbial activity under strongly reducing conditions (Pasek et al., 2013). Newer studies, however, have now shown that P exists in a variety of reduced P phases (phosphonates, phosphite, and hypophosphite) that are cycled rapidly in both marine and freshwater regimes (Pasek et al., 2014; Van Mooy et al., 2015). Thus P biogeochemistry may be significantly influenced by redox chemistry in unanticipated ways.

Many studies focusing on marine sediments and sinking particles argue for enhanced regeneration of dissolved P forms from particulate matter under anoxic conditions, mainly as a result of inorganic P release via metal oxide reduction (Dellwig et al., 2010); although the magnitude of P regeneration, particularly in comparison to carbon, continues to be debated (e.g., Anderson and Delaney, 2001). Other studies suggest that under reducing conditions, microbial activity is instrumental in controlling P biogeochemistry by either preferentially releasing P storage compounds (e.g., polyphosphate), or by converting soluble P into insoluble apatite forms (Samrinahgi and Inglall, 2005; Goldhammer et al., 2010). Again, the magnitude of this release may vary given the rapid transformation of polyphosphate into apatite, e.g., sink switching (Diaz et al., 2008; Goldhammer et al., 2010). Observations of enhanced P remobilization across oxic/anoxic boundaries in both lacustrine and marine environments imply that over geologic timescales, P remobilization has contributed to redox stabilization of the atmosphere and oceans (Van Cappelen and Inglall, 1994). On shorter timescales, enhanced P regeneration in oxygen deficient zones perturbs ecosystems via increasing eutrophication, or by changing relative nutrient availability (Diaz and Rosenberg, 2008). Despite increasing evidence that P biogeochemistry is significantly influenced by changing oxygen conditions, mechanisms of these processes and their participants remain poorly understood (Diaz et al., 2008).

Continental shelves may only occupy a small area of the oceans, but they are responsible for 15–30% of global marine production and more than 40% of seabed carbon sequestration; hence, climate-induced changes in these marginal seas are likely to be more readily apparent than in their more open ocean counterparts (Yool and Fashman, 2001; Mulker-Karger et al., 2005; Taylor et al., 2012). The Cariaco Basin, located on the northern continental margin of Venezuela, is a euxinic basin having remained anoxic below 250–350 m over the past millennia (Black et al., 2004; Muller-Karger et al., 2010; Scraton et al., 2014). Cariaco Basin surface waters also experience wind-induced seasonal upwelling, a characteristic similar to that of many OMZs (Helly and Levin, 2004; Karstensen et al., 2008). Within the Cariaco Basin, water density is relatively homogenous below 200 m and thus has little influence on structuring the geochemical and biological properties or vertical particle transport through the redoxcline and below (Taylor et al., 2001). Rather, distributions of elemental species and transitions between particulate and dissolved phases within the redoxcline result from an array of reactions catalyzed by a diverse community of heterotrophic and chemosynthetic microorganisms (Taylor et al., 2001, 2006; Edgcomb et al., 2011). Previous research has shown that a chemosynthetic community residing within the Cariaco redoxcline assimilates dissolved organic carbon on the same order of magnitude as surface photoautotrophic production (Taylor et al., 2001; Wakeham et al., 2012).

Similar to the observed expansion of OMZs in marine systems associated with rising global temperatures (Oschlies et al., 2008; Stramma et al., 2010), a number of changes have been observed in the Cariaco Basin over the past two decades. Intrusions of dense, deep water from the Caribbean Sea have declined, causing a decrease in density and a reduction in the width of the suboxic zone (Scraton et al., 2014). At the same time, as the density in the Cariaco Basin is strongly controlled by temperature, continued increases in surface temperature (Astor et al., 2013) have the potential to enhance stratification and decrease exchange between surface and deep waters. This is further exacerbated by declining surface wind strength caused by climatic shifts in the Intertropical Convergence Zone (ITCZ), which has increased water stratification over time (Taylor et al., 2012). As a result, a large scale shift in the biological community structure from larger to smaller taxa, including nitrogen fixing organisms that have moved deeper into the water column, has also occurred in the basin (Taylor et al., 2012; Montes et al., 2013; Pinckney et al., 2015).

Investigations of P geochemistry within sinking particles in the Cariaco Basin suggest that preferential remineralization of particulate P to the dissolved pool alternates between inorganic and organic P phases, depending on oxygen availability (Benitez-Nelson et al., 2007). Furthermore, a large fraction of the sinking particulate P pool appears to be comprised of phosphonates that are also preferentially remineralized with increasing depth in the water column (Benitez-Nelson et al., 2004). The source of the phosphonates remains ambiguous, but may be due to the presence of cyanobacteria in Cariaco Basin surface waters, which have recently become more abundant (Dyrhm et al., 2009; Montes et al., 2013; Pinckney et al., 2015).

Suspended particulate P may serve as an important link between sinking particulate P and dissolved P phases, especially across the redoxcline where an active microbial community has been consistently observed. This study is the first to investigate the composition and transformation of suspended particulate P across the Cariaco Basin redoxcline. The results suggest that suspended particulate P composition is also significantly influenced by oxygen availability and is likely controlled by both abiotic and biotic processes.
2. Methodology

2.1. Sample site and collection

The Cariaco Basin is the largest, truly marine, semi-permanent anoxic basin in the world (Scranton et al., 2001). Located off the north coast of Venezuela, it is surrounded by a relatively undeveloped coastline that includes several major rivers: the Unari, Tuy, and Neveri. Water exchange with the Caribbean Sea is restricted to the upper 90–140 m by a sill and is focused through the Tortuga and Centinela channels (Percy et al., 2008; Lorenzoni et al., 2009). The eastern Cariaco Basin is the site of the joint Venezuela–United States CARIACO Ocean Time Series Program, which has collected monthly data on hydrography, primary production, nutrient and carbonate chemistry, sinking flux of particulate matter and many other biogeochemical variables since November 1995 (Thunell et al., 2007; Muller-Karger et al., 2010; Taylor et al., 2012). Enhanced seasonal primary production over the Cariaco Basin is driven by wind-induced coastal upwelling. From December to May, the annual southern migration of the ITZC causes Trade Winds in the southeastern Caribbean to intensify (Benitez-Nelson et al., 2007; Muller-Karger et al., 2010; Taylor et al., 2012). During this period of coastal upwelling, surface productivity averages ~1.7 g C m⁻² d⁻¹ in contrast to less than ~0.99 g C m⁻² d⁻¹ during non-upwelling months (Muller-Karger et al., 2001). High surface productivity combined with restricted water exchange results in anoxic waters below ~250 m. The oxic/anoxic interface fluctuates between 250 and 320 m of depth due to both lateral intrusions of oxygenated waters from the Caribbean Sea and variations in upwelling intensity (Astor et al., 2003, 2013; Li et al., 2012; Scranton et al., 2014). Recent data suggest that the depth of the oxic/anoxic interface has shoaled over the 19 years of the CARIACO Ocean Time Series (Scranton et al., 2014). In this study we define the redoxcline to be the depth range starting from where oxygen begins to exponentially decline to where oxygen concentrations fall below detection.

As part of the CARIACO Ocean Time Series Program, microbial abundance and suspended particulate matter samples were collected monthly from April 2006 to April 2012 at 19 different depths from 1–1310 m (Table 1). Heterotrophic bacterial net production and dark dissolved inorganic carbon (DIC) assimilation rates were evaluated semi-annually during the same time period and over the same depth range.

2.2. Microbial abundance, bacterial net production, dark dissolved inorganic carbon assimilation

For microbial abundance, whole-water samples (200 mL) were preserved with 2% (final concentration) borate-buffered formaldehyde and stored at 5 °C. Bacteria were enumerated with epifluorescence microscopy using standard acridine orange-stained slides prepared on dark 0.2 Nuclepore polycarbonate membranes (Taylor et al., 2006).

Heterotrophic bacterial net production (BNP) was estimated by 3H-leucine incorporation into protein following the methods of Kirchman (1993) and Taylor et al. (2001). Using a gas-tight syringe, triplicate samples in 40 mL Pierce septa vials with no headspace were immediately preserved with 2% (final concentration) borate-buffered formaldehyde and stored at 5 °C. Samples were incubated in on-deck water baths for 6–8 h at ambient temperature in darkness. Following incubation, samples were fixed with cold trichloroacetic acid (TCA; 5% final concentration) and refrigerated until processing immediately after the cruise. Filter blanks from samples fixed with 5% TCA immediately after 3H-leucine addition were used to correct for 3H-leucine incorporation into protein over time. In the lab, samples were processed according to Kirchman (1993) and 3H-protein precipitates were captured on 0.22 µm cellulose filters (Osmonics). Filters were then dissolved in 0.5 ml ethyl acetate, suspended in Hionic-Fluor scintillation cocktail and radioassayed. BNP was calculated using a conversion factor of 3.1 kg C mole⁻¹ of leucine incorporation (Kirchman, 1993).

Chemoautotrophic assimilation of dark DIC was measured by 14C-bicarbonate incorporation into particles. Triplicate samples were dispensed into 40 mL ground glass stoppered bottles and injected with 200 µl of chilled N₂-purged 14C-bicarbonate in an alkaline brine (pH 9.5; S = 60 on practical salinity scale) at the bottom before sealing without a headspace (Tuttle and Jannasch, 1973). 14C-bicarbonate samples were incubated in parallel with BNP samples for 14–20 h under conditions minimizing potential oxygen contamination and light exposure. After incubation, particles were collected on 0.22 µm cellulose filters (Osmonics) and then rinsed twice with 5 ml of filtered seawater adjusted to pH 3.5. Unassimilated 14C was further purged from filters in a saturated HCl atmosphere for >1 h. Filters were then dried and suspended in Hionic-Fluor scintillation cocktail and radioassayed. Non-biological sorption was corrected for by samples processed immediately after introduction of the radiotracer. Rates of dark dissolved inorganic carbon (DIC) assimilation were normalized to µM C d⁻¹ with values of total DIC derived from pH, temperature and alkalinity (Taylor et al., 2001).

2.3. Suspended particulate matter

Water samples for suspended particulate matter analysis were collected in 2 L opaque polyethylene bottles, immediately filtered through acid-cleaned and pre-combusted (450 °C at 3 h) Whatman glass fiber filters (0.7 µm nominal pore size), and frozen in the dark until analysis. Total suspended particulate P (TSPP) and suspended particulate inorganic P were determined on all samples using a modification of the Aspila phosphomolybdate method (Aspila et al., 1976; Benitez-Nelson et al., 2007). Briefly, samples for suspended particulate inorganic P were extracted using weak hydrochloric acid, while samples for TSPP were combusted at 550 °C to convert any organic P to inorganic P prior to extraction (Aspila et al., 1976). Suspended particulate organic P was determined as the difference between TSPP and suspended particulate inorganic P. To monitor run to run variability and validate analytical accuracy, standard reference materials of tomato leaves (NIST# 1573a) and estuarine sediment (NIST# 1646a) were analyzed with each run (Benitez-Nelson et al., 2007). During analysis of suspended particulate inorganic P, it is possible for some organic P compounds, e.g., simple sugars, to be hydrolyzed during analysis, thus inflating suspended particulate inorganic P concentration estimates. We have therefore more appropriately termed this pool suspended soluble reactive P (SSRP). It is also possible that suspended particulate organic P concentrations may contain non-reactive inorganic compounds, such as inorganic phosphopolysaccharides, and we have therefore termed this pool as suspended soluble non-reactive P (SSNP) (Benitez-Nelson, 2000). Rather than deciphering the difference between inorganic and organic P, these methods separate P into pools of different chemical reactivity. The more reactive pool, SSP, is presumably more widely bioavailable than SSNP (Benitez-Nelson, 2000). SSP and TSPP were measured with 3% precision and SSNP, with 5% precision.

In all water column profiles, results from the Aspila TSPP measurements show a large peak in suspended particulate P within the redoxcline, usually located directly below the depth where oxygen began to decrease exponentially. These peaks equaled or surpassed the suspended P concentrations within the upper 100 m. A subset of these samples was selected from within, above and below the redoxcline TSPP peak for additional sequential extraction analyses. “Within the redoxcline” refers to samples collected between the depths of 230 and 300 m, depending on the depth profile of oxygen concentrations measured for a given month. These samples contained the highest TSPP concentrations. “Above redoxcline” and “Below redoxcline” samples ranged between depths of 160–230 m and 260–350 m, depending on the given month’s redoxcline depth range. TSPP concentrations within these zones dropped by > 30% from the within redoxcline concentrations. Due to limited sample material availability, filters were combined across monthly cruises to ensure adequate material for
analysis. “Within redoxcline” samples contained at most two samples from different cruises, whereas “Above redoxcline” and “Below redoxcline” samples could contain up to five samples from different cruises. Samples were combined across similar depths, years and hydrographic conditions (e.g., upwelling versus non-upwelling periods as defined by Astor et al., 2003). Table S1 catalogues the individual filters combined and used for the analyses described below.

A sequential extraction method, SEDEX, was performed on these selected sub-samples from April 2009 to June 2011 to quantify five different inorganic forms of P: 1) loosely-bound P, 2) oxide-bound P, 3) authigenic P, 4) detrital P, and 5) organic P (Ruttenberg, 1992). Due to small sample sizes and high run to run variability, we report the first two steps as a combined fraction, loosely/oxide-bound P. SEDEX TSP refers to the sum of both inorganic and organic P fractions (Steps 1–5), SEDEX SSRP refers to the sum of inorganic P fractions (Steps 1–4; loosely/oxide-bound, authigenic and detrital P) and SEDEX SSNP refers to only the organic P fraction (Step 5; organic P). A standard reference material of tomato leaves (NIST# 1646a) and estuarine sediment (NIST# 1573a) were analyzed with each run (Benitez-Nelson et al., 1976; Benitez-Nelson et al., 2007). The extractions were analyzed for P concentrations using a mod-

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Suspended particulate organic carbon (SPOC) and suspended particulate nitrogen (SPN) concentrations were determined on the same filters as the P analyses following the procedures outlined in Froelich (1980). Briefly, approximately 1/4 to 1/2 of the filter was acidified (1 M H3PO4) to remove the particulate inorganic carbon (i.e., carbonates) and then combusted at 100 °C in a Perkin Elmer 2400 elemental analyzer (Thunnell et al., 2007).

3. Results

3.1. Bacteria

From April 2008 to April 2012, average prokaryoplankton concentrations tended to follow a bimodal pattern with depth across all seasons (described previously by Taylor et al., 2006), but were highly variable (Fig. 1A, B and C). The median surface prokaryote peak from 0–100 m was 1 μM C (25th percentile = 0.7 μM C and 75th percentile = 2 μM C) and the median in redoxcline depths (230–290 m) was 0.7 μM C (25th percentile = 0.6 μM C and 75th percentile = 0.9 μM C) (Fig. 1A). Bacterial net production in the surface peaked at 35 ± 38 m and dark DIC assimilation rates peaked within the redoxcline at 268 ± 26 m. The median dark DIC assimilation rate was 0.2 μM C · day⁻¹ (25th percentile = 0.02 μM C · day⁻¹ and 75th percentile = 0.5 μM C · day⁻¹) within the redoxcline (Fig. 1).

For the most part, prokaryoplankton depth profiles complement dissolved oxygen and TSPP profiles, similar to those depicted in the example provided from December 2010: as oxygen becomes depleted, TSPP concentrations increase to form a secondary peak, prokaryotic biomass forms one or more slightly shallower peaks (Fig. 2A), while peaks in dark DIC assimilation and BNP are nearly coincident with that of TSPP (Fig. 2B). Incongruities between peak positions for prokaryoplankton biomass and chemoautotrophic and heterotrophic production (Fig. 2A) are interpreted as evidence for higher mortality rates within the most productive layer. Enhancements in dark DIC assimilation in the upper ~100 m likely are caused by anaerobic reactions occurring in the tricarboxylic acid cycle, a pathway present in all non-fermenting organisms (Taylor et al., 2001). As the euphotic zone
contains the greatest biomass, contributions of anaplerotic reactions are expected to dominate dark carbon fixation in this layer. The majority of TSPP peaks (93%, n = 44) occurred between 240 and 270 m, as did 70% of the peaks in prokaryotic biomass (n = 43) (Fig. 2A) and 75% of the peaks in dark DIC assimilation rates (n = 8) (Fig. 2B).

3.2. Suspended particulate P

Suspended P concentrations in the upper 100 m (n = 44) were highest at 25 ± 17 m (average ± 1 standard deviation) and averaged 84 ± 77 nM TSPP, 17 ± 23 nM SSRP and 68 ± 57 nM SSNP (Fig. 3A).

Fig. 1. Box and whisker plot of A) prokaryoplankton, B) bacterial net production, and C) dark DIC assimilation rate weighted means binned from 1–100, 101–229, 230–290 and > 300 m. Weighted means were computed from the layer’s integral divided by the layer’s depth interval (n represents the number of weighted means represented in each box). Boxes, internal lines, error bars and circles represent the 25th to 75th (= interquartile range), medians, 10th to 90th, and 5th to 95th percentiles of all observations, respectively.

Fig. 2. Prokaryote distributions and production with depth relative to P and DO. A) Example profile from December 2010 showing prokaryoplankton concentration (μM C), TSPP (nM) and DO (μM). Frequency of TSPP maximum peaks (black bars) and prokaryoplankton maximum peaks (gray bars) at each depth within the redoxcline from April 2008 to April 2012. B) Example profile from December 2010 showing heterotrophic bacterial net production, dark DIC assimilation rate, TSPP (nM) and DO (μM). Frequency of TSPP maximum peaks (black bars) and dark DIC assimilation rate maximum peaks (gray bars) at each depth within the redoxcline from April 2008 to April 2012.
Below the upper 100 m, concentrations steadily decreased until reaching the redoxcline. Secondary peaks were always observed between 230 and 290 m (mean depth = 256 ± 13 m) and TSPP, SSRP, and SSNP averaged 88 ± 60, 54 ± 53 and 34 ± 23 nM, respectively. Suspended P declined throughout the deeper anoxic waters (>300 m).

The magnitude of the redoxcline P peaks was not significantly different between upwelling and non-upwelling seasons (Student t-test, p > 0.05). However, the composition of the TSPP maximum in the upper 100 m and the redoxcline was significantly different (Fig. 3A and B). Average SSRP peak concentrations in the redoxcline (54 ± 53 nM) were as much as 5 (3 ± 2) times greater than those associated with the peak in surface waters (17 ± 23 nM) (Student t-test, p < 0.00006). In contrast, upper 100 m SSNP peak concentrations (68 ± 57 nM) were as much as 4.5 (2 ± 2.5) times greater than in the redoxcline peaks (34 ± 23 nM) (Student t-test, p < 0.0007). Thus, SSNP dominated in the surface, while SSRP dominated in the redoxcline.

3.3. SEDEX speciation

From April 2008 to June 2011, TSPP concentrations were measured in a subset of samples from above, within and below the redoxcline using SEDEX (n = 24). As SEDEX samples were analyzed for a shorter time period, average P concentrations differ from those averaged over the entire dataset. SEDEX TSPP concentrations were significantly higher within the redoxcline (143 ± 26 nM) than those above and below the redoxcline (81 ± 22 and 71 ± 57 nM, respectively) (Student t-test, p < 0.002). Loosely/oxide-bound P dominated SEDEX TSPP pools within the redoxcline, averaging 111 ± 24 nM (79 ± 12% of SEDEX TSPP) for all observations, and were significantly different from those above and below the redoxcline (Student t-test, p < 0.002; Fig. 4A and B). In contrast, SEDEX TSPP pools above and below the redoxcline were almost equally comprised of loosely/oxide-bound P, 39 ± 7 nM (49 ± 6% of SEDEX TSPP) above and 43 ± 39 nM (52 ± 23% of SEDEX TSPP) below, and organic bound P, 35 ± 7 nM (44 ± 8% of SEDEX TSPP) above and 19 ± 8 nM (34 ± 18% of SEDEX TSPP) below (Fig. 4A and B). Authigenic P concentrations did not vary significantly with depth, contributing only 13 ± 14 nM (9 ± 10% of SEDEX TSPP) within the redoxcline, 5 ± 6 nM (6 ± 7% of SEDEX TSPP) above, and 9 ± 19 nM (13 ± 8% of SEDEX TSPP) below the redoxcline. Detrital P was almost undetectable, accounting for 0.5 ± 1.5 nM (0.3 ± 1% of SEDEX TSPP)

![Fig. 3. Suspended particulate P concentrations with depth. A) Depth profile of SSRP (nM). Gray dots represent individual samples measured for SSRP, while black solid line represents average SSRP. Dashed line represents average TSPP to illustrate contribution of SSRP to TSPP. B) Depth profile of SSNP (nM). Gray dots represent individual samples measured for SSNP, while black solid line represents average SSNP. Dashed line represents TSPP to illustrate contribution of SSNP to TSPP.](image1)

![Fig. 4. Phosphorus composition across the redoxcline. A) Average concentrations of loosely/oxide-bound P, authigenic P, detrital P and organic P (nM) within the redoxcline (light gray bars), above the redoxcline (black bars) and below the redoxcline (dark gray bars). Error bars represent the standard deviation. B) Percent average concentrations of loosely/oxide-bound P, authigenic P, detrital P and organic P (nM) within the redoxcline (light gray bars), above the redoxcline (black bars) and below the redoxcline (dark gray bars). Error bars represent the standard deviation.](image2)
within the redoxcline, 1 ± 2 nM (1.5 ± 2% of SEDEX TSPP) above, and 0.2 ± 0.4 nM (0.3 ± 0.6% of SEDEX TSPP) below the redoxcline. Although SEDEX data is limited, depth-dependent trends in P composition were similar during upwelling (December to April) and non-upwelling seasons, with no significant difference in P speciation.

### 3.4. C:N:P ratios

From April 2008 to April 2012, average concentrations of suspended particulate organic carbon (SPOC) and suspended particulate nitrogen (SPN) in the upper 100 m (n = 44) were highest at 25 ± 17 m and averaged 10 ± 9 μM and 1.0 ± 0.9 μM, respectively (Table 1). Average concentrations of SPOC and SPN within the redoxcline maximum (256 ± 12 m) were 5 ± 2 μM and 0.7 ± 0.3 μM, respectively. Both SPOC and SPN were significantly lower within the redoxcline compared to the upper 100 m (Student t-test, p < 0.002 and p < 0.0005, respectively).

With the exception of the upper 100 m and redoxcline, SPOC:TSPP and SPN:TSPP ratios were much higher than Redfield (106 C: 16N: 1P) and increased slowly with depth to ~400 m, consistent with preferential remineralization of P (Fig. 5). Within the redoxcline, however, suspended SPOC:TSPP and SPN:TSPP ratios declined sharply, with significantly lower SPOC:TSPP and SPN:SSNP ratios averaging 52 ± 50 and 208 ± 221, respectively, before increasing back to near surface values (Student t-test, P < 0.005). SPOC:SPN ratios were not significantly different within the redoxcline (7.5 ± 4), as compared to above (8.3 ± 4) and below (6.3 ± 4). The dramatic depth-dependent decreases in SPOC:TSPP and SPN:SSNP ratios are mainly due to the abrupt increase in suspended P across the redox boundary.

### 4. Discussion

Large scale variability in dissolved and particulate P concentrations has been observed in other redoxclines similar to that of the Cariaco Basin (e.g., Black Sea and Baltic Sea) and attributed to: 1) microbial activity, which converts dissolved into particulate P during biological growth and vice versa during decomposition (Taylor et al., 2001, 2009) and 2) delivery of iron and manganese, whose colloidal and particulate oxides adsorb and co-precipitate P or remobilize P into the dissolved phase upon oxide reduction (Dellwig et al., 2010; Diaz et al., 2009) and 2) delivery of iron and manganese, whose colloidal and particulate oxides adsorb and co-precipitate P or remobilize P into the dissolved phase upon oxide reduction (Dellwig et al., 2010; Diaz et al., 2009). The lack of an observable redoxcline SPOC or SPN peak is at odds with the clear 1–2 μM increase in SPOC concentrations observed within the Cariaco Basin redoxcline in November 2007 (Wakeham et al., 2012) and other studies reporting enriched SPOC and SPN concentrations across redox boundaries in other euxinic basins and OMZs (e.g., Wishner et al., 1995; Coban-Yildiz et al., 2006; Pitcher et al., 2011; Diaz et al., 2012). Closer examination of individual profiles for SPOC and SPN suggests that redoxcline peaks in SPOC and SPN concentrations do exist in the Cariaco Basin, but are obscured by high cruise to cruise variability in P dynamics. While a significant factor of two enrichment is observed in the redoxcline’s SSNP pool relative to that measured immediately above and below, the same is not observed for SPOC or SPN, which results in a sharp decline in suspended SPOC:TSPP ratios within the redoxcline (Fig. 5A, B and C). The lack of an observable redoxcline SPOC or SPN peak is at odds with the clear 1–2 μM increase in SPOC concentrations observed within the Cariaco Basin redoxcline in November 2007 (Wakeham et al., 2012) and other studies reporting enriched SPOC and SPN concentrations across redox boundaries in other euxinic basins and OMZs (e.g., Wishner et al., 1995; Coban-Yildiz et al., 2006; Pitcher et al., 2011; Diaz et al., 2012). Closer examination of individual profiles for SPOC and SPN suggests that redoxcline peaks in SPOC and SPN concentrations do exist in the Cariaco Basin, but are obscured by high cruise to cruise variability in P dynamics. While a significant factor of two enrichment is observed in the redoxcline’s SSNP pool relative to that measured immediately above and below, the same is not observed for SPOC or SPN, which results in a sharp decline in suspended SPOC:TSPP ratios within the redoxcline (Fig. 5A, B and C). The lack of an observable redoxcline SPOC or SPN peak is at odds with the clear 1–2 μM increase in SPOC concentrations observed within the Cariaco Basin redoxcline in November 2007 (Wakeham et al., 2012) and other studies reporting enriched SPOC and SPN concentrations across redox boundaries in other euxinic basins and OMZs (e.g., Wishner et al., 1995; Coban-Yildiz et al., 2006; Pitcher et al., 2011; Diaz et al., 2012). Closer examination of individual profiles for SPOC and SPN suggests that redoxcline peaks in SPOC and SPN concentrations do exist in the Cariaco Basin, but are obscured by high cruise to cruise variability in P dynamics. While a significant factor of two enrichment is observed in the redoxcline’s SSNP pool relative to that measured immediately above and below, the same is not observed for SPOC or SPN, which results in a sharp decline in suspended SPOC:TSPP ratios within the redoxcline (Fig. 5A, B and C). The lack of an observable redoxcline SPOC or SPN peak is at odds with the clear 1–2 μM increase in SPOC concentrations observed within the Cariaco Basin redoxcline in November 2007 (Wakeham et al., 2012) and other studies reporting enriched SPOC and SPN concentrations across redox boundaries in other euxinic basins and OMZs (e.g., Wishner et al., 1995; Coban-Yildiz et al., 2006; Pitcher et al., 2011; Diaz et al., 2012). Closer examination of individual profiles for SPOC and SPN suggests that redoxcline peaks in SPOC and SPN concentrations do exist in the Cariaco Basin, but are obscured by high cruise to cruise variability in P dynamics. While a significant factor of two enrichment is observed in the redoxcline’s SSNP pool relative to that measured immediately above and below, the same is not observed for SPOC or SPN, which results in a sharp decline in suspended SPOC:TSPP ratios within the redoxcline (Fig. 5A, B and C).

Microbial biosynthesis is likely a major factor in DOP, SSRP, and SSNP enrichment within the redoxcline. Dark DIC assimilation rates within the redoxcline are often of the same order of magnitude as primary production in the euphotic zone (Taylor et al., 2001), suggesting that microbial production in this layer plays a critical role in P dynamics. While a significant factor of two enrichment is observed in the redoxcline’s SSNP pool relative to that measured immediately above and below, the same is not observed for SPOC or SPN, which results in a sharp decline in suspended SPOC:TSPP ratios within the redoxcline (Fig. 5A, B and C).

### 4.1. Biotic transformations of suspended P

TSPP concentrations within the Cariaco Basin redoxcline on average were similar or slightly greater than those measured in the upper 100 m (Fig. 3A and B). For one cruise (December 2008), TSPP was observed to be almost five times higher in the redoxcline than in the upper 100 m. These large scale enrichments in the redoxcline are similar to patterns observed in other systems, e.g., Effingham Inlet (Diaz et al., 2012). Lorenzoni et al. (2013) showed that while DOC concentrations remain relatively constant across the Cariaco Basin redoxcline, dissolved organic P (DOP) concentrations are elevated, exceeding waters immediately above and below the redoxcline by ~20–40 nM. In contrast, dissolved inorganic P concentrations, or phosphate, steadily increase below the mixed layer and across the redox transition, with no obvious peak in phosphate concentrations observed at the redoxcline (Scantlon et al., 2014).

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The decoupling of SSNP from SPOC and SPN may be due to the presence of inorganic polyphosphate. Inorganic polyphosphate is formed
during microbial growth within both P-rich and poor environments primarily as intracellular P storage, but it also has been shown to be involved in gene regulation and can serve as ballast material in *Trichodesmium* (Romans et al., 2004; Brown and Kornberg, 2004; Orchard et al., 2010). Only recently has polyphosphate been emphasized as a critical player in the marine P cycle (Diaz et al., 2008; Bjorkman, 2014; Martin et al., 2014). Genes encoding for enzymes critical for polyphosphate metabolism (ppk1, ppk2, and ppkx) commonly occur in the Global Ocean Sampling (GOS) metagenomic database, suggesting broad geographic distribution of polyphosphate utilization (Temperton et al., 2011). Furthermore, prevalence of ppk1 and ppkx genes in the GOS database appear to be inversely proportional to phosphate (P) concentrations in surrounding waters, suggesting that microbial communities subjected to low or intermittent P supply are more reliant on polyphosphate sequestration strategies than communities in P-replete environments (Temperton et al., 2011).

Compared to the oxygenated surface ocean, very little is known about redox-sensitive mobilization of inorganic polyphosphate. In anoxic sediments, however, intracellular polyphosphate has been shown to be hydrolyzed and released back into the dissolved phase (Gächter and Meyer, 1993; Sammigrahi and Ingall, 2005; Schulz and Schulz, 2005; Hупfer et al., 2007), although some sulfide-oxidizing bacteria have been shown to convert this released phosphate into apatite (Goldhammer et al., 2010). In Effingham Inlet, concentrations of total particulate phosphorus per bacterial cell increased up to five fold in the redoxcline and polyphosphate was shown to compose a substantial amount of this pool despite high phosphate concentrations (Diaz et al., 2012).

We do not have direct evidence of polyphosphate in our samples. Polyphosphate is normally described as a part of the operationally defined organic P fraction in Aspila SSNP and in the SEDEX analysis (Diaz et al., 2012). However, based on the chemical structure and reactivity of polyphosphate, we argue that some of the shorter chain polyphosphate compounds are likely to be observed in the loosely/oxide-bound P fractions as well, given their reaction with citrate bicarbonate solution. Thus, the observed increase in the loosely/oxide-bound P and within the SSNP pool in the redoxcline is consistent with the presence of a polyphosphate pool (Figs. 3 and 4).

Furthermore, if we assume an average cellular C:P atomic ratio of 41 ± 16 for prokaryotes not producing polyphosphate (Vrede et al., 2002), then prokaryotic P-biomass (nucleic acids, phospholipids, etc.) accounts for 77% ± 44, 136% ± 135, 54% ± 42, and 102% ± 107 of TSP in the eugenic, diaphotic, redoxcline and eucric layers, respectively. Prokaryotic P-biomass accounts for a significantly smaller proportion of the TSP inventory (p < 0.001, ANOVA, n = 47) in the redoxcline than in other layers. In the diaphotic and eucric layers, prokaryotic P-biomass essentially accounts for all TSP, while phytoplankton in the eutrophic layer easily account for the residual 23% of the TSP inventory not attributable to prokaryotes. Thiotropic chemoautotrophic c- proteobacteria dominate in the Cariaco Basin redoxcline and are known from the GOS database to carry polyphosphate metabolizing genes (Lin et al., 2006, 2008; Temperton et al., 2011). These results are supported further by a recent study of intact polar lipids (IPLs) within the Cariaco Basin, which found that phospholipids, although less than 1 nM of the TSP pool, accounted for up to 90% of IPLs measured within the redoxcline, and are typically associated with a suite of organisms capable of polyphosphate synthesis and remineralization (Wakeham et al., 2012). These facts, coupled with the 46% shortfall between P-biomass and TSP inventories in the Cariaco Basin redoxcline, are suggestive of chemoautotrophic community residing in this layer that likely relies, at least in part, on polyphosphate. It is unclear why else polyphosphate would reside in the redoxcline despite high concentrations of phosphate and DOP (Lorenzoni et al., 2013), but it may be associated with “luxury” uptake and storage (Diaz et al., 2008, 2012; Crocetti et al., 2000; Orchard et al., 2010; Goldhammer et al., 2010).

### 4.2. Abiotic transformation of P

Trace metal redox reactions are also likely to play an important role in the enrichment of TSP through the redoxcline of the Cariaco Basin, particularly with regard to the SSDP pool (Dellwig et al., 2010; Li et al., 2012). The “redox shuttle” refers to the formation of P-associated colloids and particulates when reduced metals, particularly manganese and iron, diffuse upward through the redoxcline and rapidly oxidize and scavange both phosphate and organic P compounds (Dellwig et al., 2010; Ruttenberg and Sulak, 2011). As these oxidized particles sink back through the redoxcline, they are reduced abiotically thereby releasing the associated P (Dellwig et al., 2010). Recent evidence suggests that microbial activity may also enhance these oxidation/reduction reactions (Cosmidis et al., 2014). Closer examination of the TSP pool reveals that a switch occurs from SSDP dominated waters (81%) at the surface to SSRP dominated waters (61%) within the redoxcline (Fig. 3A). The majority of the SSRP enrichment is attributable to loosely/oxide-bound P, which comprises ~80% of the SSRP pool in the redoxcline compared to ≤50% above and below (Fig. 4B). Comparing average concentrations of loosely/oxide-bound P above and below the redoxcline (39 ± 7 nM and 43 ± 39 nM, respectively) with the much higher average concentrations of loosely/oxide-bound P within the redoxcline of 111 ± 24 nM indicates potential in situ production and subsequent loss of ~70 nM of this highly labile redoxcline P pool (Fig. 4A). Such contrasts in P speciation and large enrichments in loosely/oxide-bound P, suggest that redox reactions play a significant role in inorganic P accumulation in the redoxcline.

It is possible that some of the measured increase in redoxcline TSP pools is due to remineralization of sinking particles and lateral transport from the nearshore rather than due to in situ formation. However, we argue that this is unlikely. For example, Lorenzoni et al. (2009) measured the composition of several intermediate and bottom nepheloid layers derived from the near shore across the continental shelf of the Cariaco Basin. They found a significant enrichment in SSRP with SSDP concentrations similar to that measured in the overlying water column. At the same time, however, SPOC concentrations were also higher, resulting in elevated SPOC/SSNP ratios within the nepheloid plumes. This is the opposite of that observed within the redoxcline in our study (Fig. 5).

Disaggregation and dissolution of large sinking particles from the euphotic zone could also play a role in the observed increase in TSP concentrations within the redoxcline. Indeed, attenuated particulate P fluxes within the Cariaco Basin below the redoxcline have been described previously for sinking particles (Benitez-Nelson et al., 2004, 2007). However, disaggregation processes would also significantly increase redoxcline SPOC and SPN pools as well, and this is not observed in our dataset. Furthermore, surface suspended P concentrations in the Cariaco Basin have been shown to vary considerably through time, with higher surface water concentrations occurring during upwelling versus non-upwelling periods coincident with higher rates of primary production (Benitez-Nelson et al., 2015). Within the redoxcline, however, suspended P did not significantly vary with time, confirming a decoupling of the surface and redoxcline particles.

### 4.3. The fate of suspended P

While much of the TSP formed within the redoxcline is likely recycled there, it is quite possible that at least a fraction of the redoxcline TSP escapes to deeper depths. Taylor et al. (2001) found that the flux of sinking particulate organic carbon captured in sediment traps below the redoxcline frequently exceeded that measured in waters from above and argued that mid-water chemoautotrophic production was an important secondary source of sinking organic carbon in the water column. Other research using a variety of biomarkers suggests that sinking particles and sediments commonly contain organic matter derived from mid-water chemoautotrophic processes in OMs and
euxinic basins, such as the Arabian and Black Seas and the Peru upwelling zone (Wakeham et al., 2007; Saenz et al., 2011).

While absolute fluxes of sinking inorganic and organic P decline with increasing depth in the water column in the Cariaco Basin (Benitez-Nelson et al., 2007), there are a number of instances when sediment trap P fluxes below the redoxcline (~400 m) also exceed those measured directly above (~225 m) during our study period (~40% of samples, data not shown). While these differences in sediment trap fluxes could be due to hydrodynamic issues associated with sediment trap collections (e.g., Buesseler et al., 2007), the enclosed nature of the Cariaco Basin produces a relatively quiescent setting that minimizes those effects. Therefore, it is quite possible that biologically mediated coagulation of suspended particles within the redoxcline enhances the observed “excess” sinking particulate P fluxes measured at depth. Diverse protist communities, now recognized to play major roles in particle coagulation (Sherr and Sherr, 1987; Richardson and Jackson, 2007), are known to exist within the redoxcline of the Cariaco Basin (Edgcomb et al., 2011) and zooplankton migration and repackaging of material has been observed within the redoxcline of other OMZs (Wishner et al., 2008).

Further evidence for an additional redoxcline source of sinking particulate P at depth is derived from comparison of nutrient ratios. Scanton et al. (2014) noted a dichotomy between the dissolved inorganic N:P ratios measured in Cariaco Basin deep waters (approximately 16:1) relative to the rate of nutrient accumulation (11:1) and the overall ratio of total N:P in the sinking particulate flux (approximately 5:1 to 12.5:1). These authors hypothesized that the ratio difference was due to changes in the relative proportions of sinking particulate source material enriched in P relative to C and N and argued that both terrestrial and redoxcline sources were the likely culprits. Our relatively low C/P ratios within the redoxcline suspended pool support the potential for a redoxcline P source to depth.

5. Conclusions

While there are a number of studies that have focused on the role of anoxia on the sinking particulate and sedimentary P pools, few have focused on P biogeochemistry within water column redoxclines (Ingall et al., 1993; Benitez-Nelson et al., 2007; Gilbert and Slomp, 2013). In this study, suspended particulate P and its composition within the redoxcline of the Cariaco Basin was examined for the first time. A lack of seasonal variation in redoxcline TSPP dynamics indicates a decoupling from surface processes and in situ production. The significant shift from biologically less available (SSNP) to more labile P forms (SSRP) within the redoxcline suggests suspended P cycling in the Cariaco Basin is redox sensitive and is cycled through a combination of both a trace metal redox shuttle and polyphosphate accumulation/remobilization. Furthermore, combined with sediment trap data above and below the redoxcline, our results indicate a mid-water redoxcline source of particulate P (Scanton et al., 2014).

The Cariaco Basin has undergone a number of physical and biogeochemical changes over the past two decades that have been assessed through the Cariaco Time-Series (Scanton et al., 2014; Astor et al., 2013; Taylor et al., 2012). It is unclear whether the changes in surface processes (e.g., plankton community structure) influence suspended P cycling within the redoxcline (Scanton et al., 2014). However, the processes of suspended P transformation presented here suggest independent in situ production of suspended P and contribution by coagulation of suspended P to sinking P particles. The reduction in oxygen intrusions and size of the redox zone within the Cariaco Basin, however, may influence the magnitude of suspended P cycling within the redoxcline by changing the bacterial community structure and lowering the concentrations of trace elements available for redox scavenging. As such, mid-water cycling of suspended P and contributions to the sinking particle phase may be reduced, removing an important sink of P within the system. This would create a positive feedback to eutrophication via the diffusion of P enriched waters back to the surface and contribute to the expansion of OMZs in the future.

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