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INTERANNUAL AND SUBDECADAL VARIABILITY IN
THE NUTRIENT GEOCHEMISTRY OF THE CARIACO BASIN

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The conductivity, temperature, depth (CTD) rosette package being deployed at the CARIACO station. *Photo credit: Jaimie Rojas*

ABSTRACT. The CARIACO Ocean Time Series program has made monthly measurements of oxygen, nutrients, and carbon system parameters (ΣCO_2, alkalinity, pH) in the Cariaco Basin since 1996. At the same time, sediment traps have collected settling particles at four to five depths ranging from 150 to 1,200 m. The depth of the transition from oxic to anoxic conditions has fluctuated dramatically over the time series due to changes in the occurrence of Caribbean water intrusions into the deep basin. Nutrient concentrations in the deep basin have increased steadily with time in a proportion reflective of the elemental ratios in the settling organic matter, although N:P ratios in the water column (approximately 16:1) differ from ratios in the accumulating nutrients (11:1) and the settling flux (ranging between 5:1 and 12.5:1). This difference is likely due to changes in the source material for remineralization, either because of sizeable ecosystem changes or changes in the relative importance of the terrestrial input of inorganic P or scavenging of P by mineral precipitation near the oxic/anoxic interface. Alternatively, there may have been changes in the degree of preferential remineralization of P.

INTRODUCTION

The Cariaco Basin, located on Venezuela's continental margin, is the site of one of the longest geochemical time series in the ocean. Primary productivity there is dominated by strong seasonal upwelling that is driven largely by trade-wind variations (Muller-Karger et al., 1989, 2001, 2010). Redox chemistry and transition-zone microbiology in the Cariaco Basin respond to large-scale processes and ecosystem state changes in both the upper water column and in the twilight zone. Although it is known that changes in oxygen levels in offshore water masses coupled with changes in circulation patterns strongly affect coastal hypoxia in many systems (Monteiro et al 2011), it has not been well understood what factors are most important in controlling the depth or character of the oxic/anoxic transition or how fluctuations in these processes might influence nutrient cycling in the basin overall. In addition, basin sediments are deposited at very high rates (> 100 cm per thousand years) and are annually varved (undisturbed by bioturbation), indicating that the bottom waters have remained anoxic for centuries to millennia (Black et al., 2004). For this reason, the paleoceanographic research community has used the record of surface processes stored in Cariaco Basin sediments as a tool for examining tropical climate variability over long time scales (e.g., Peterson et al., 1991; Hughen et al., 2000; Haug et al., 2001; Black et al., 2004, 2007; Goni et al., 2004; Tedesco et al., 2007).

According to Richards (1975), Alfred Redfield initially suggested the possibility that the Cariaco Basin was anoxic, arguing that, due to bathymetry, it was likely that its deep waters would be depleted in oxygen; to confirm his hypothesis, Redfield arranged for Valentine Worthington to sample the system in 1954. Soon afterward, Richards and Vaccaro (1956) made the first chemical observations (other than salinity, oxygen, and phosphorus), setting the stage for a number of expeditions examining various aspects of the water column geochemistry (e.g., Richards and Benson, 1961; Fanning and Pilson, 1972; Deuser, 1973; Reeburgh, 1976; Bacon et al., 1980; Hashimoto et al., 1983; Scranton et al., 1987; Jacobs et al., 1987; Scranton, 1988; deBaar et al., 1988; Hastings and Emerson, 1988; Zhang and Millero, 1993). Studies in the Cariaco Basin were central to the development of stoichiometric models for organic carbon remineralization, including what is now familiarly called the "Redfield ratio," which describes the elemental composition of organic matter and its decomposition products (Redfield et al., 1963; Richards, 1975), as well as to the development of vertical advection/diffusion models to explain geochemical distributions (Fanning and Pilson, 1972). Since 1995, the internationally funded Venezuela-US CARIACO Ocean Time Series program has recorded roughly monthly measurements of a variety of parameters, including hydrography, nutrients, and those related to the carbon system (alkalinity, ΣCO_2, pH, dissolved organic carbon [DOC]), obtained biweekly samples of settling particulates at four to five depths, and conducted semi-annual cruises to study water column (and particularly oxic/anoxic interface) biogeochemistry and microbial ecology. Data, methods, and publication lists are available on the CARIACO website (http://www.imars.usf.edu/CAR) or from the authors of this article. A methods manual, describing in detail the procedures used to analyze samples for the CARIACO program, is available in Spanish and English (Astor et al., 2011).
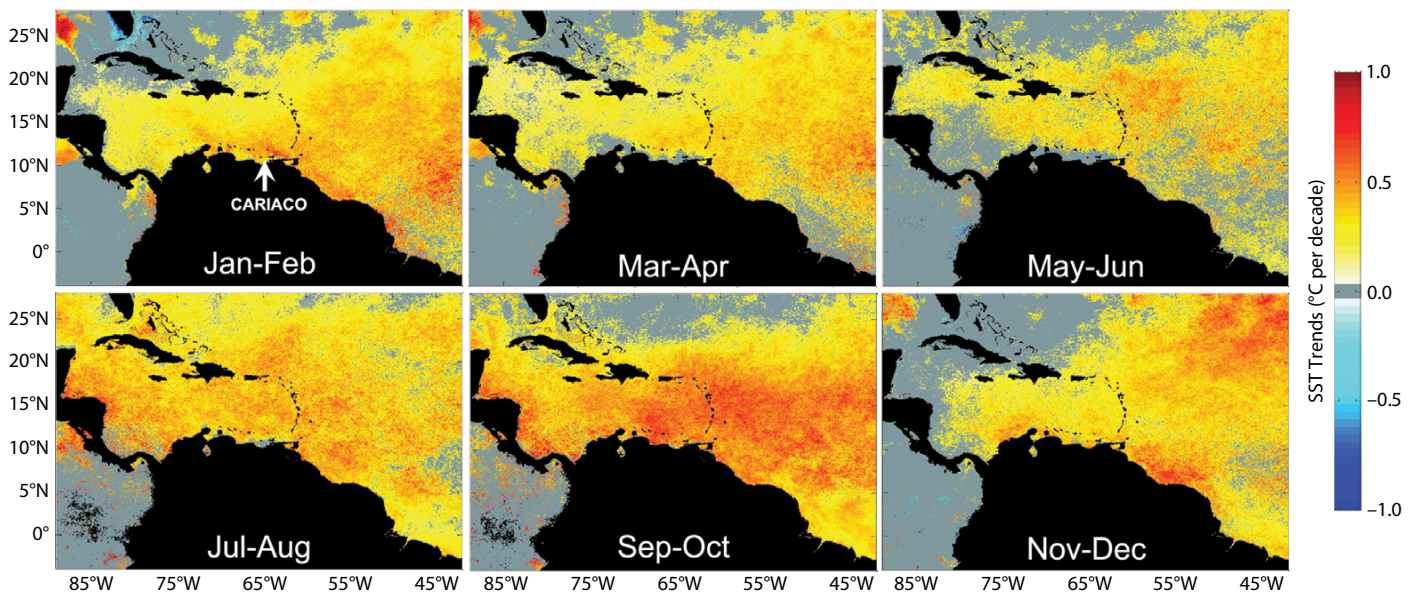
Figure 1. Satellite-derived Sea Surface Temperature (SST) trends [°C per decade] for the period January 1985 to December 2009 in the tropical Atlantic and Caribbean Sea. Trends were computed using monthly long-term SST anomalies derived from satellite images collected with the NOAA Advanced Very High Resolution Radiometer (AVHRR; Pathfinder 4 km resolution, Version 5.0; for a description of the data set, see Casey et al., 2010). Positive or negative values indicate long-term SST warming or cooling trends, respectively. The panels only show SST trend values with 95% of statistical significance (p < 0.05); values not significant are masked in gray. The figure shows that the Caribbean Sea and much of the tropical western North Atlantic have experienced a warming trend in SST (Chollett et al., 2012; Ruiz-Ochoa et al., 2012). In the CARIACO Ocean Time Series area, positive SST trends are observed during January and February, which is the beginning of the upwelling season. This is suggestive of weaker—and possibly shorter—upwelling events. The warming trend was stronger and affected a larger area during August and October than during May and June. The fastest warming trend (~ 0.5°C per decade) was observed in September. Consecutive years of weak upwelling starting in 2004–2005 likely have contributed to a collapse in the Venezuelan Spanish sardine fishery, which as of 2012 had not recovered to previous yields. The approximate location of the CARIACO Ocean Time Series is shown with a white arrow in the upper left hand panel.

Although the deeper waters of the Cariaco Basin have typically been characterized as a stable or slowly changing system, higher-frequency sampling has provided evidence that the system is considerably more dynamic than previously thought. Observations show periods of relatively intense deep injections of water from outside the basin as well as stable periods when the dominant process below 200 m is more passive and dominated by vertical mixing. At the same time, Cariaco Basin surface waters are clearly warming (Figure 1) and pCO$_2$ increasing, and changes are evident in the ecosystem at all trophic levels (Taylor et al., 2012; Astor et al., 2013). While changes in wind patterns resulted in reduced primary production and chlorophyll a concentrations between 1995 and 2010, zooplankton biomass and sinking flux paradoxically increased (Taylor et al., 2012). Studies by Lorenzoni et al. (2012) and Montes et al. (2012) link trends in upper water column biogeochemistry and physics to the concentration and composition of sinking

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particles. The goal of this paper is to explore what we have learned about the interplay among physics, particles, and changes in water column nutrient concentrations as they influence the deeper anoxic waters of the Cariaco Basin.

PHYSICAL SETTING

The deep waters of the Cariaco Basin are usually considered to be relatively quiescent, with a residence time of 100 (Deuser, 1973) to several hundred years (Fanning and Pilson, 1972). Because the Cariaco Basin is separated from the rest of the Caribbean by a 100 m deep sill broken by two channels extending to around 150 m, only the upper portions of the Cariaco Basin water column are strongly influenced by regional circulation. Surface waters in the area are warm and salty, and the density structure is controlled by temperature. This contrasts with the situation in the world's largest anoxic marine basin, the Black Sea, where the primary density control is salinity (Richards, 1975). Nutrients are supplied to the Cariaco Basin largely as a result of the advection of 100–200 m Caribbean water onto the shelf. With upwelling, these waters are injected into the euphotic zone during favorable winds.

Richards (1975), Scranton et al. (1987), and Zhang and Millero (1993) all noted long-term, gradual trends in potential temperature, salinity, and nutrients in the deep parts of the Cariaco Basin. Based on the limited data available, they concluded that change was both unidirectional and steady over many decades, and envisioned the basin as a passive trap for organic material sinking from above. Zhang and Millero (1993) extrapolated the trends to predict that the basin had been fully oxic in ~ 1916, due possibly to an earthquake.

However, Holmen and Rooth (1990) reported tritium in basin bottom waters, consistent with at least some injection of surface waters to the bottom on a time scale of decades. The CARIACO Ocean Time Series has now clearly shown that the basin's hydrography is more variable than the early simple model would have predicted and that some parameters can respond very rapidly to forcing from outside. Indeed, geochemical signatures, observed in the water column and in the sediments of the Cariaco Basin, reflect large-scale and long-term changes occurring over the Atlantic Ocean (Peterson et al., 1991).

TEMPORAL VARIABILITY IN SUBSURFACE WATERS

Prior to the CARIACO Ocean Time Series, most studies of the anoxic portions of the Cariaco Basin had used Nansen or Niskin bottles to collect water samples, so sampling depths were mostly chosen without detailed knowledge of the physical regime, and sampling resolution tended to be relatively coarse except during a few cruises where multiple casts were conducted at a single station. Most prior studies found the oxic/anoxic interface (usually defined by the appearance of sulfide) to be between 250 m and 300 m water depth. However, Richard and Vaccaro (1956) and Richards and Benson (1961) reported the depth of the oxic/anoxic interface to be 375 and 340 m, respectively, and Zhang and Millero (1993) interpolated their data to locate the interface at 330 m.

As mentioned earlier, previous discussions assumed a unidirectional and constant rate of change of potential temperature and salinity, which can be explained conceptually by downward mixing of warm surface water (Scranton et al., 1987). Although CARIACO Ocean Time Series bottom water data confirm that long-term trends reported for bottom water (> 1,200 m) for both temperature (increase of 0.00906°C yr^{-1} for waters below 1,200 m since 1995) and salinity (increase of 0.00157 yr^{-1}) continue, a
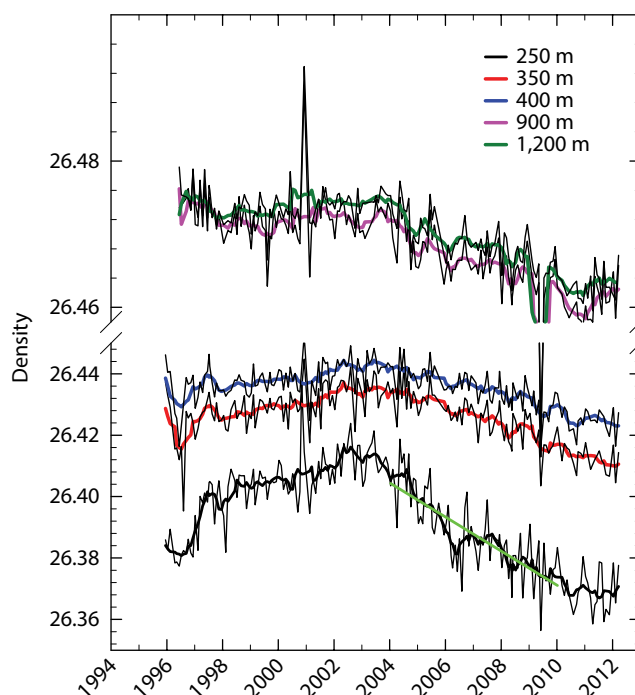

Figure 2. Trends in density between 1995 and 2013 are given for five depths in the Cariaco Basin. Between 1995 and 2004, densities at all depths increased with time or remained approximately constant. Density increases can only be caused by advection of denser water from the Caribbean into the basin. The solid green line is the linear regression for the trend between 2004 and 2011 for 250 m water depth, which represents a period when densities at all depths decreased with time. Downward mixing of warm surface water largely drives the density decreases.

more detailed examination shows that the situation is not straightforward. Figure 2 plots the densities taken from conductivity-temperature-depth (CTD) profiles collected monthly since November 1995 at three depths bracketing the oxic/anoxic interface as well as two depths from the deep waters. At all depths, potential density either increased or remained roughly constant from 1995 to sometime in mid-2002 or 2003. After 2004, density linearly decreased with time at all depths (p < 0.001), a pattern also reported by Samodurov et al. (2013) using a shorter data set.

The only mechanism for density to increase at depth in a closed basin is by intrusion of denser water from outside. The density gradient in Cariaco Basin waters is very weak (density increases by only 0.1 between 250 and 1,200 m), and previous studies have shown that such intrusions likely originate below 150 m in the Caribbean Sea (Astor et al., 2003). This water is relatively high in oxygen compared to depths within the basin with similar density, and will contain different concentrations of nutrients and CO_2. During the early years of the CARIACO Ocean Time Series program, we observed periodic intrusions of oxygen-containing water at depths of at least 400 m (Astor et al., 2003). The depth where oxygen became undetectable by the Winkler method (2 µM) ranged from 250 to 310 m (Figure 3). During this period, the suboxic zone (defined as the layer where oxygen and sulfide concentrations were both less than 1–2 µM) extended as deep as 370 m and ranged in thickness from < 10 to almost 100 m (Samurodov et al., 2013; Figure 3). At times of intrusions, although oxygen may have been undetectable or extremely low in the suboxic zone at the CARIACO Ocean Time Series station (about 50 km from the eastern channel), we assume that the water initially contained oxygen, and that this oxygen was removed during transit, both by reaction with reduced chemical species, forming iron and manganese oxides, elemental sulfur, and other oxidized species, and by microbial respiration. Large excursions of the 5 µM oxygen contour estimated from the Winkler measurements (Figure 4; deepest contour line) to greater depths were seen frequently until mid-2003. There have been a few similar excursions in more recent years, but they are less pronounced.

Beginning in 2004 and extending through at least 2011, the suboxic zone became relatively thin, with measurable oxygen and sulfide values detected in close vertical proximity (samples spaced 10–25 m apart). This timing coincides
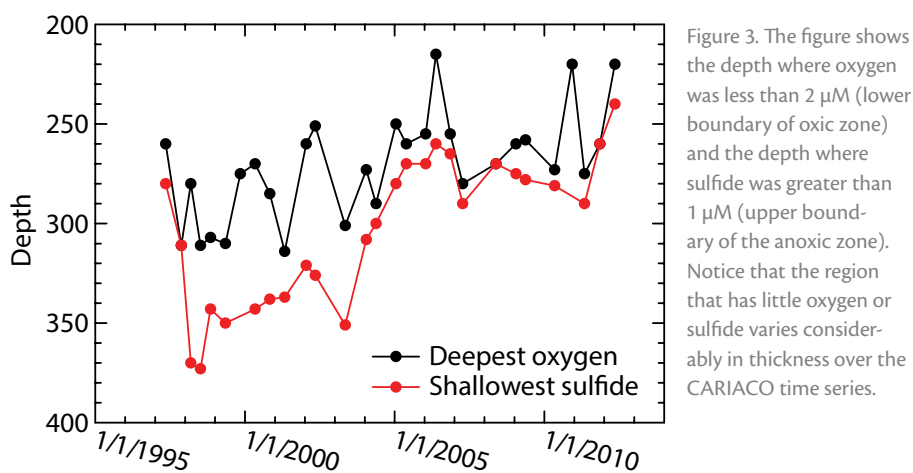

Figure 3. The figure shows the depth where oxygen was less than 2 µM (lower boundary of oxic zone) and the depth where sulfide was greater than 1 µM (upper boundary of the anoxic zone). Notice that the region that has little oxygen or sulfide varies considerably in thickness over the CARIACO time series.
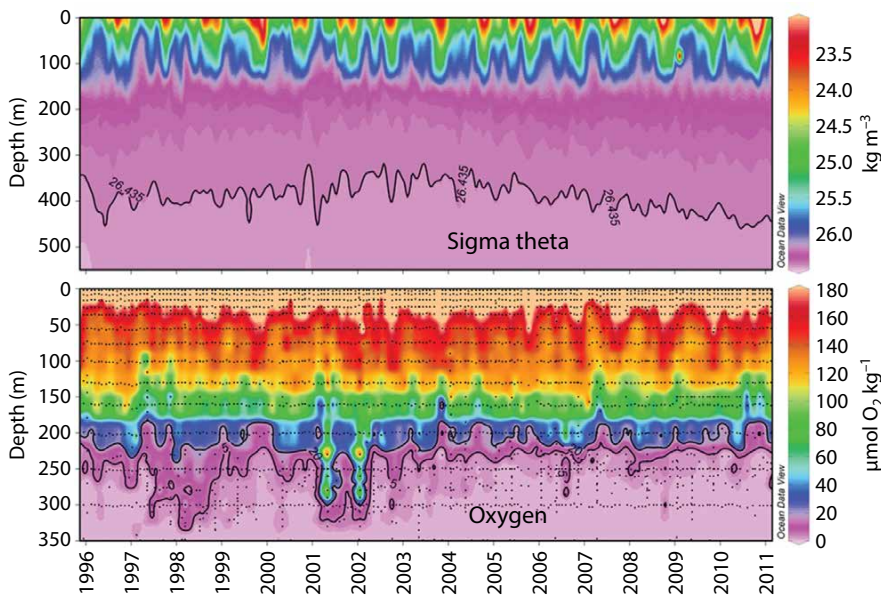

Figure 4. Density and oxygen contours for the CARIACO time series. The two deepest dark contour lines on the oxygen plot represent depths of 20 µM and 5 µM interpolated from Winkler oxygen data. This figure shows both seasonal upwelling of denser water to near the surface in winter and the fluctuations in penetration of oxygen over the time series.

with temporal changes in the variation of water density versus time (Figure 2) from increasing density (implying the dominant importance of intrusions) to decreasing density (implying dominance of vertical mixing). The cause of intrusions is still not fully understood, although Astor et al. (2003) noted that eddies within the westward-moving Caribbean Sea Current near the continental shelf are associated with some (but not all) deep oxygen maxima.

Intrusions have important impacts on nutrient concentrations (Figure 5a–d) and on the ecology of the microbial populations in the upper 500 m of the basin (Taylor et al., 2012). Because the interface gradients are very steep and our monthly sampling depths are relatively coarse, we cannot define the depth of the interface precisely. However, due to the oxidation of ammonium by aerobic microbial nitrifiers, we never observe ammonium concentrations above trace levels near the oxic/anoxic interface if oxygen is present. Therefore, the depth at which ammonium appears is approximately the depth of the top of the sulfidic zone. From Figure 5c, it is evident that this depth has shoaled over the 16 years of the CARIACO Ocean Time Series. A deep secondary nitrite maximum is periodically seen just above the depth where ammonium appears (Figure 5b). This maximum is expected to be quite thin, and, thus, we may have missed it in a number of cases due to coarse sample spacing. The deep nitrite maxima are more intense since 2004, coinciding with fewer intrusions into the basin and the greater relative importance of vertical mixing compared to advection (Figure 5b).

On a number of occasions, the ammonium and phosphate (Figure 5c and d) contours exhibited relatively large excursions near the oxic/anoxic interface (around 250 m), and we have observed dissolved phosphate minima in profiles that are poorly resolved in contour plots. These excursions likely reflect more subtle effects of intrusions. Ammonium is most likely removed by nitrification or anammox reactions. Phosphate is likely removed by reactions near the interface caused by oxidation of reduced iron (Percy et al., 2008). Iron oxides will be precipitated if oxygen is added to sulfidic water in sufficient quantities to remove the sulfide. Both sulfide and iron
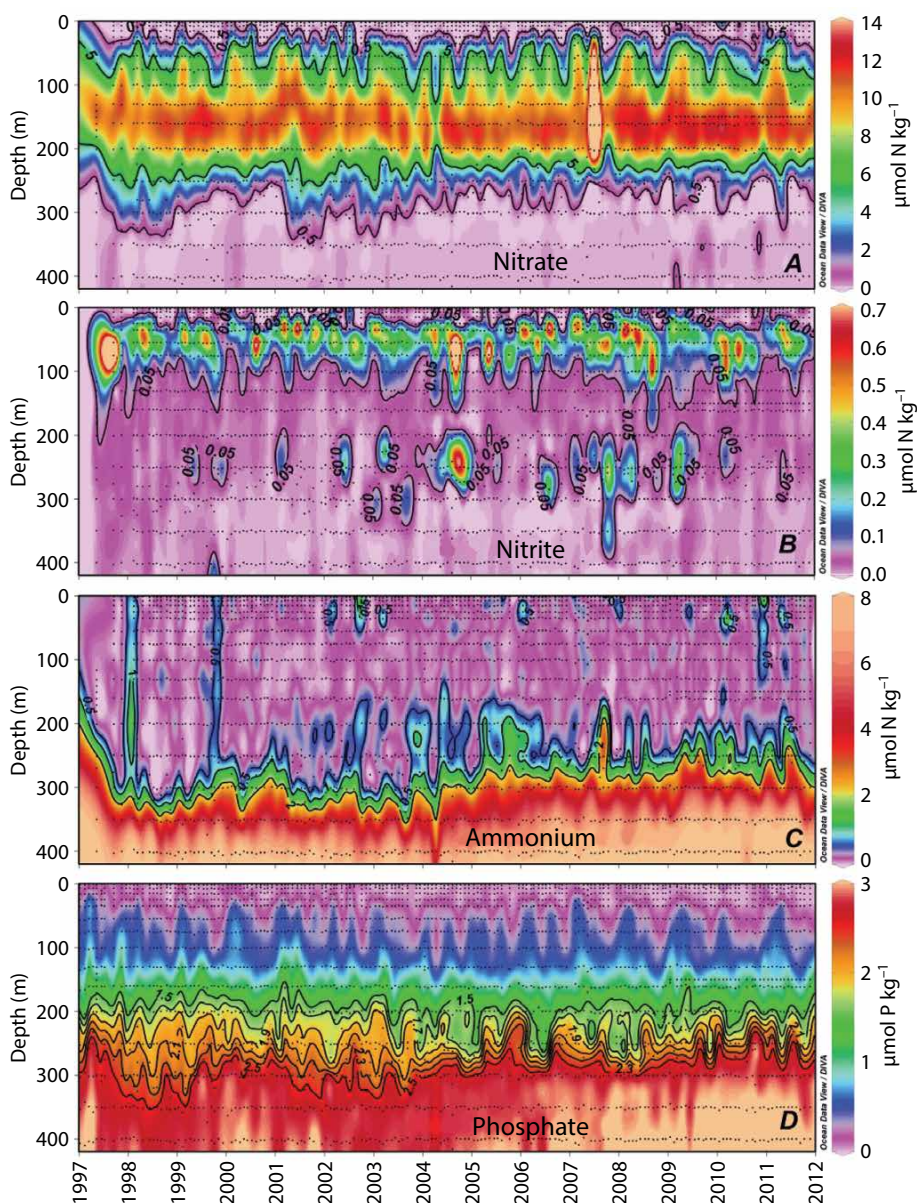

Figure 5. (A) Nitrate, (B) nitrite, (C) ammonium, and (D) phosphate concentrations are plotted for upper waters during the CARIACO Ocean Time Series. Note that the depths at which nitrate disappears and ammonium appears seem to be shoaling with time, while the deep nitrite maximum may become more prominent. Phosphate and ammonium concentrations increase with depth, but near the oxic/anoxic interface, there are a number of periods when there are large depth excursions in these contours. These may represent periods when intrusions of oxidant-containing water resulted in scavenging of phosphate on iron minerals, and ammonium was lost due to denitrification or anammox reactions.

oxidation will remove oxygen, and the iron oxides may persist and could scavenge phosphate (Spencer and Brewer, 1971; Dellwig et al., 2010).

NUTRIENT RATIOS

Observations from the Cariaco Basin were among those used by Richards and colleagues to develop the idea of the Redfield ratio model of organic-matter remineralization (Redfield et al., 1963). It is of interest to examine that central concept in terms of measurements from the Cariaco Basin now that we have considerably more detailed data. Total dissolved inorganic nitrogen ($DIN = NH_4^+ + NO_3^- + NO_2^-$) is plotted versus phosphate for all monthly cruises and all depths at the CARIACO Ocean Time Series station in Figure 6. At low DIN and low phosphate, the two

parameters are strongly correlated. These samples are from the upper water column where oxygen is present and nitrification rates are high. The blue line in Figure 6 represents the linear regression of all depths where phosphate concentrations were less than 0.5 µM (arbitrarily chosen to represent early, oxic diagenesis). The N:P ratio in these waters is 18.0 ± 0.2 (p < 0.001), very close to that reported for mixed phytoplankton communities by Redfield et al. (1963).

As DIN approaches 10–12 µM, measured oxygen concentrations decrease dramatically (typically ≤ 50 µM). Denitrification dominates in this depth range as nitrate is converted to N_2 (Thunell et al., 2004; Montes et al., 2013). Phosphate values in this region are more variable than in overlying and underlying waters, possibly because of

phosphate removal by minerals precipitating just above the sulfidic zone (McParland et al., 2012).

At depths where phosphate concentrations exceed about 2.5 µM, the plot of DIN (now almost all in the form of NH_4^+) versus phosphate returns to linearity with a slope of 16.2 ± 0.2 (p < 0.001). This slope is close to the slope for the shallow water data and agrees well with the original Redfield-Ketchum-Richards model (Redfield et al., 1963). In this case, examining the water column nutrient pools results in an integrated picture of nutrient accumulation in the basin over time scales comparable to water column residence times (decades to centuries).

We can obtain an independent estimate of the elemental ratio for remineralization over shorter time scales by examining nutrient concentration changes with time and by comparing these to material flux into the deep basin. Figure 7 shows the long-term trends for ammonium and phosphate in waters below 1,200 m, the depth for which there is the best long-term data set for the Cariaco Basin, going back to the early work of Richards and colleagues (Richards and Vaccaro, 1956; Richards, 1975). We have also included data for ΣCO_2 from the CARIACO program, as there are few older points for this parameter. Confidence intervals for the regressions are plotted as dotted lines. Based on these plots, ΣCO_2 has been increasing at about 3.2 µmol L^{-1} yr^{-1}, ammonium at a rate of 0.34 µmol L^{-1} yr^{-1}, and phosphate at 0.0315 µmol L^{-1} yr^{-1} (all slopes significant at the p < 0.001 level; Scranton et al., 2001). CARIACO data dominate the regression line slopes, but the overall trends seem consistent over the more than 50 years that the basin has been sampled. These data yield a
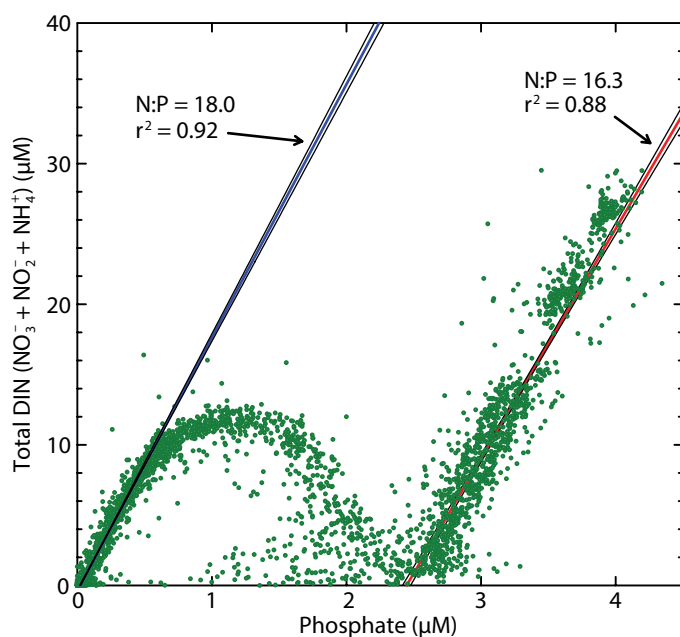

Figure 6. Water column nitrate and phosphate data plotted against each other for the entire CARIACO Ocean Time Series. The cycling of nitrogen in oxic, suboxic, and anoxic waters can clearly be seen. In shallow water below the euphotic zone, nitrate and phosphate are remineralized in constant ratio. Once oxygen concentrations fall below about 50 µM, denitrification and anammox take place, removing nitrogen from the DIN pool. As the water becomes sulfidic (at phosphate ~ 2.5 µM), nitrogen and phosphorus again accumulate in constant ratios (and at a ratio very similar to that seen just below the euphotic zone).

$\Delta\Sigma CO_2:\Delta NH_4^+:\Delta PO_4^{-3}$ production ratio of approximately 101:11:1, compared with a water column concentration ratio of 16:1 for N:P.

For comparison, we can calculate the accumulation of nutrients in the mid-water column (800–1,200 m) that can be supported by the amount of sinking material that is remineralized (disappears) between these two depths. Because the long-term trends of nutrient accumulation mentioned above were determined over 15 years of the time series, Table 1 presents the average annual particulate organic C, total particulate nitrogen (TPN), and total particulate phosphorus (TPP) fluxes at 800 m and 1,200 m for the full CARIACO Ocean Time Series calculated from the average daily fluxes for this period. The difference between the flux to 800 m and the flux to 1,200 m represents the amount of material that is remineralized between 800 and 1,200 m. If we assume that material is decomposed evenly over the 400 m between 800 and 1,200 m, we can estimate the amount of C, N, and P added to the water on average. We conclude that the sinking flux is supplying the equivalent of 0.88 µmol L^{-1} yr^{-1} of ΣCO_2, 0.055 µmol L^{-1} yr^{-1} ammonium, and 0.009 µmol L^{-1} yr^{-1} phosphate (98:6.1:1). The average fluxes calculated from sediment traps are consistently lower than we would predict from the water column increases. However, there are large uncertainties in this calculation due to (1) averaging fluxes that are highly variable both in time and in space (Muller-Karger et al., 2004), and (2) the fact that the periods of highest flux may have been missed due to sediment trap clogs. Also, trapping efficiency has yet to be determined for any of the traps (Buesseler, 1991). Finally, in this estimate, we also have ignored the flux

of C, N, and P from bottom sediments as well as the effect of lateral advection of organic material in sediment plumes from the coast (Lorenzoni et al., 2012). Nonetheless, it is encouraging that the concentration increases for C and P calculated from the trap data are within a factor of three or four of the measured increases. The increase of nitrogen predicted from trap data is somewhat lower, with the predicted concentration increases about a factor of 6 lower than observed.

Finally, we can compare the ratio of TPN to TPP in the sinking flux with the ratio of the measured concentration increases. TPN:TPP ratios in the sinking flux range from around 5 at 150 m to between 9.2 and 12.5 in the deeper traps (Figure 8; data for 1,200 m trap not shown). The dotted lines represent the 95% confidence limits for each regression. The solid red line in each panel in Figure 8 is for an N:P molar ratio of 16:1.
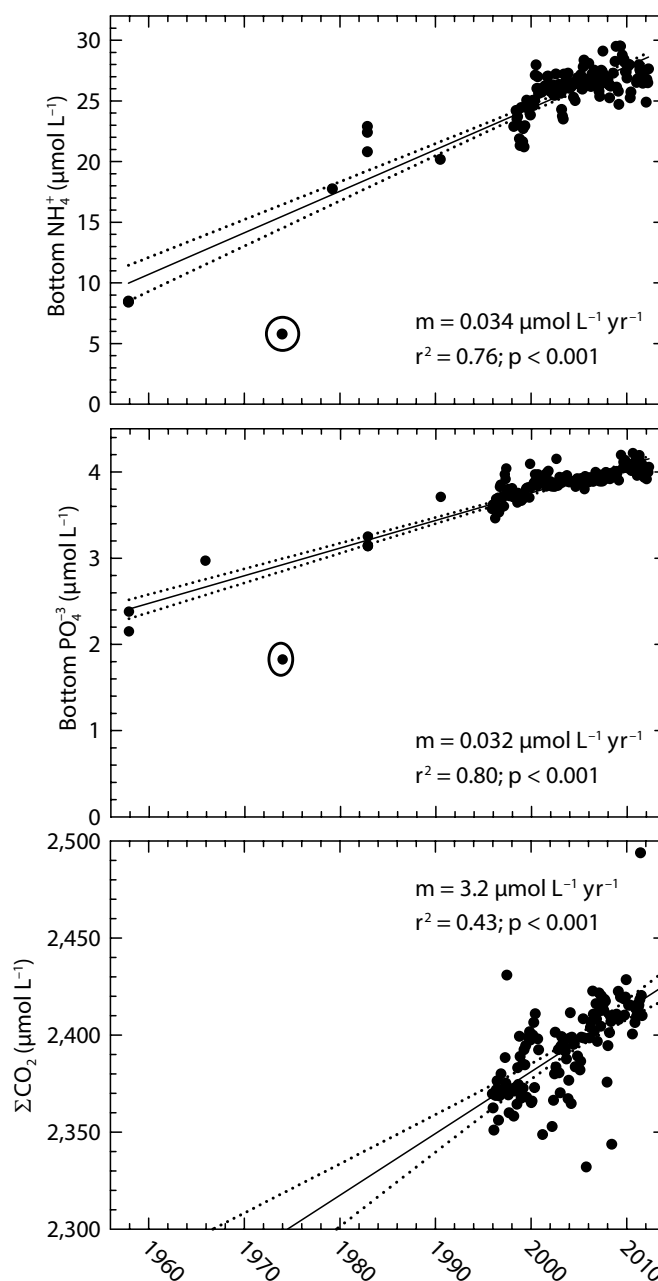

Figure 7. Long-term trends in ΣCO_2, ammonium, and phosphate for waters deeper than 1,200 m. Trends for the CARIACO time series are consistent with older data. The dotted lines represent 95% confidence intervals for the regressions. Only CARIACO data are plotted for ΣCO_2.

Top panel: m = 0.034 µmol L^{-1} yr^{-1}; r^2 = 0.76; p < 0.001

Middle panel: m = 0.032 µmol L^{-1} yr^{-1}; r^2 = 0.80; p < 0.001

Bottom panel: m = 3.2 µmol L^{-1} yr^{-1}; r^2 = 0.43; p < 0.001

Points that deviate to the right (higher P flux than expected for a given N flux) generally represent samples with high levels of inorganic P, potentially derived from terrestrial sources (Benitez-Nelson et al., 2007) or from water column scavenging during precipitation of iron or manganese above the interface. The increase in the elemental ratio with depth suggests preferential release of P, which is consistent with the longer-term trends observed within the water column (recent work of author Benitez-Nelson and colleagues).

Table 1. Calculation of nutrient supply to the 400–800 m depth layer in the Cariaco Basin.

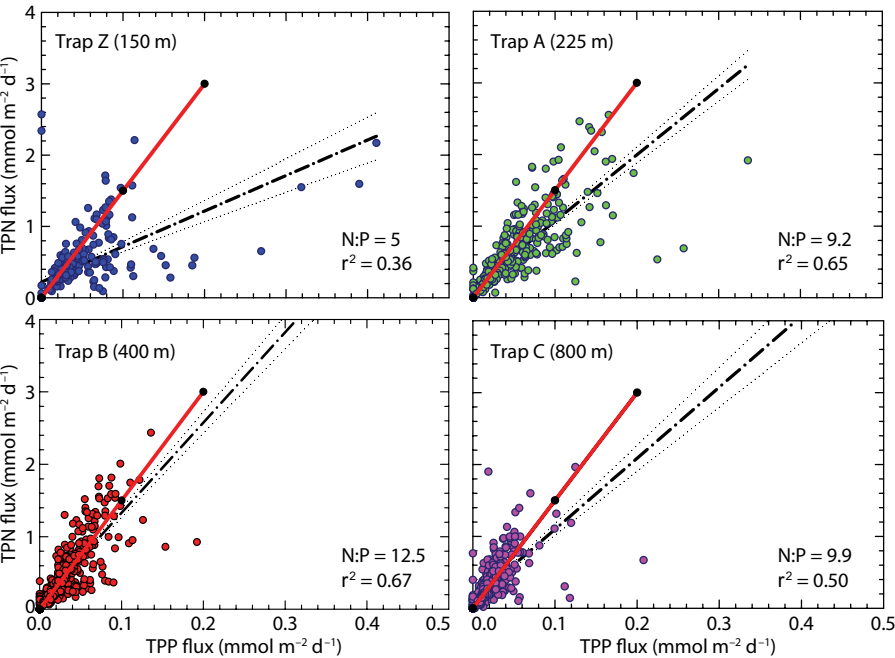|	Average Organic Carbon Flux (μmol m^{-2} d^{-1})	Average Nitrogen Flux (μmol m^{-2} d^{-1})	Average Phosphorus Flux (μmol m^{-2} d^{-1})
800 m	3.42 ± 4.91	0.41 ± 0.59	0.03 ± 0.03
1,200 m	2.45 ± 2.2	0.35 ± 0.43	0.02 ± 0.02
Change in flux	0.97 ± 5.38	0.06 ± 0.53	0.01 ± 0.036
Predicted concentration increase in element in 400 m thick layer	0.88 ± 4.91	0.055 ± 0.48	0.0091 ± 0.03
Average annual concentration change 1998–2013	3.2	0.34	0.032

Figure 8. Total particulate N (TPN) and total particulate P (TPP) fluxes are plotted for sediment traps from four depths (150, 225, 400, and 800 m). The black lines are fits through the data; all slopes are highly significant (p < 0.001). The dotted lines show 95% confidence intervals for the regressions. The red lines in each panel represent a Redfield ratio slope of 16:1. The calculated slopes for the various trap data are all somewhat below the Redfield ratio, but visual inspection shows two populations of points: one lying on the Redfield ratio line and the other with more phosphate than predicted from the nitrogen flux values.

It is intriguing that nutrient concentrations in the deep basin have increased steadily with time in proportion to the elemental ratios in the settling organic matter, although N:P ratios in the water column (approximately 16:1) are quite different from ratios in the accumulating nutrients (11:1) and the overall settling flux (approximately 5:1 to 12.5:1). It seems likely that this difference is due to changes in the relative proportions of source material for remineralization. The current sediment trap material appears to consist of two groups of particles: one group with an N:P close to 16:1 and a second group with much higher P for a given N (Figure 8). This is particularly obvious for the 150 m trap where the regression visually appears to be strongly influenced by only a few points (although the same features can be seen in the other traps as well). The two groups of particles likely make up the primary sources of sinking flux: biogenic material produced in Cariaco Basin surface water and particles enriched in inorganic P by an abiotic process. There can be significant terrigenous input from the nearby coast of both dissolved iron and particles (Percy et al., 2008; Lorenzoni et al., 2009), so our results suggest sizeable ecosystem changes or changes in the relative importance of terrestrial input. Phosphorus adsorption by minerals precipitated near the oxic/anoxic interface (Spencer and Brewer, 1971; Percy et al., 2008) may also result in particles enriched in P under some conditions. Present data are inadequate to decide between these possibilities, but long-term monitoring offers the possibility of separating these important processes.

One important question we are yet unable to answer is whether changes in the surface water ecosystem (from lower relative abundance of diatoms,

dinoflagellates, and coccolithophorids and increasing importance of smaller taxa; Taylor et al., 2012) may have resulted in the observed differences between the recent sinking flux and the ratios of nutrients in the water column that have built up over many decades (Martiny et al., 2013). Previous studies show that changes in upwelling intensity, and surface conditions in general resulting from varying trade wind intensity, are recorded in the basin's sediments in the form of geochemical proxies (e.g., δ^{18}O, δ^{13}C, trace elements, and organic biomarkers; e.g., Goni et al., 2009; McConnell et al., 2009; Romero et al., 2009; Martinez et al., 2010; Black et al., 2011).

CONCLUSIONS

Long-term trends in the nutrient chemistry of the Cariaco Basin are consistent with the biogeochemical picture originally developed by Richards (1975). Temperature and salinity of deep waters have continued to increase

of increase observed in dissolved pools. However, ratios of the elements present in Cariaco Basin deep waters are not quite the same as the ratios of elemental increase, suggesting a change in the elemental input over the residence time of the water. We also have improved evidence of how deep intrusions and fluctuations in deep and shallow oceanographic processes can affect water chemistry and the ecology of anoxic environments, even if the waters are not fully oxygenated by these processes.

> **"…RATIOS OF THE ELEMENTS PRESENT IN CARIACO BASIN DEEP WATERS ARE NOT QUITE THE SAME AS THE RATIOS OF ELEMENTAL INCREASE, SUGGESTING A CHANGE IN THE ELEMENTAL INPUT OVER THE RESIDENCE TIME OF THE WATER."**

with time, although the decrease in density experienced a lull in the early years of the CARIACO Ocean Time Series (1995–2004). Deep-basin nutrient concentrations increased at relatively constant rates, with fluxes of C, N, and P in sediment traps consistent with rates

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