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Vertical fluxes of particulate biogenic material through the euphotic and twilight zones in the Cariaco Basin, Venezuela

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ABSTRACT

Surface-tethered particle interceptor traps (PITs) were deployed at 50 and 100 m (1–3 days) on ten occasions in the Cariaco Basin between March 2007 and November 2009 to measure the settling fluxes of biogenic particles at 50 m (the base of the euphotic zone—Ez) and 100 m. Fluxes at these two depths were compared to concurrent fluxes estimated with moored sediment traps at 150, 225 and 410 m from the CARIACO Ocean Time-Series program. We measured particulate organic carbon (POC), particulate organic nitrogen (PON), calcium carbonate, biogenic silica and terrigenous material concentrations in samples collected with both the drifting and moored traps. We also estimated the fluxes of foraminifera shells and coccolithophore cells at 50 and 100 m using drifting traps samples. Surface chlorophyll *a* and primary production observations during each sampling period were examined to quantify the relationship between the magnitude and geochemical composition of the vertical flux and overlying production. Surface chlorophyll *a* concentrations and primary production rates were highest during months of upwelling ($2.58-1.35\ \mathrm{mg\ m^{-3}}$ and $3.6-1.4\ \mathrm{g\ C\ m^{-2}\ d^{-1}}$, respectively). The fluxes of POC, PON, calcite and silica measured during the upwelling season (December–May) were typically higher than during the period of non-upwelling (August–November), when surface waters are more strongly stratified. POC fluxes measured with the drifting traps (50 and 100 m) varied between 0.95 (upwelling) and $0.14\ \mathrm{g\ m^{-2}\ d^{-1}}$ (non-upwelling), compared with those from the moored traps (150, 225 and 410 m) which ranged from 0.21 to $0.01\ \mathrm{g\ m^{-2}\ d^{-1}}$. Similarly, the fluxes of biogenic opal in the upper 100 m ranged from 1.12 and $0.18\ \mathrm{g\ m^{-2}\ d^{-1}}$, and those at greater depths varied from $0.27\ \mathrm{g\ m^{-2}\ d^{-1}}$ during upwelling to values near zero during stratification periods. The fluxes of POC, PON, calcite and silica in the upper 100 m decreased by an order of magnitude at the depth of the oxic–anoxic interface (>200 m). The sinking organic matter collected with the floating traps within the upper 100 m was significantly correlated with surface chlorophyll *a* concentrations ($r=0.68$, $p<0.05$) as a result of close coupling between the flux of biogenic particles and primary production. In contrast, there was no clear relationship between surface chlorophyll/primary production and fluxes measured below 150 m depth.

1. Introduction

Among the most challenging problems in oceanography has been estimating the magnitude and variability of the vertical export of particulate organic material from sunlit surface waters and the rates of transfer of this material to the underlying 1000 m of water, or the so-called twilight zone (Eppley and Peterson, 1979; Knauer et al., 1979; Martin et al., 1987; Pace et al., 1987; Karl et al., 1996; Buesseler et al., 2007). In the open ocean, only a small fraction of the particulate organic carbon (POC) generated by photosynthetic plankton exits the base of the euphotic zone. Most of this export production is then grazed and remineralized within the twilight zone. To a first order, the magnitude of the sinking POC flux in the ocean decreases exponentially with depth (Suess, 1980; Betzer et al., 1984; Pace et al., 1987; Martin et al., 1987), although the efficiency of this transfer varies regionally (Buesseler et al., 2007). On average, 1–2% of the carbon fixed at the surface reaches the bottom of the global ocean (Muller-Karger et al., 2005). Since most particulate organic matter (POM) is nearly neutrally buoyant in seawater, mineral ballast provides a mechanism for the rapid delivery of POM to the deep ocean (Archer et al., 2002; Armstrong et al., 2002, 2009; Francois et al.,

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2002; Thunell et al., 2007). This process reduces exposure of POM to dissolution and consumption, and enhances CO_2 sequestration (Honjo, 1980; Deuser et al., 1981; Volk and Liu, 1988; Armstrong et al., 2002; Francois et al., 2002).

We studied the link between the processes modulating the vertical flux of particulate organic material in the Cariaco Basin, off the coast of Venezuela. Specifically, we examined the relationship between near-surface oceanographic processes, export production at the base of the euphotic zone (~50 m; Ez) and sediment flux at 100 m, and below 150 m. The CARIACO Ocean Time-Series program (CArbon Retention In A Colored Ocean; Muller-Karger et al., 2000, 2001) has been collecting particle flux measurements using moored sediment traps for over 15 years at 10° 30′N, 64°40′W in the Cariaco Basin. Five traps collect sinking material at depths from ~200 to ~1300 m on biweekly intervals (Thunell et al., 2000, 2004, 2007; Benitez-Nelson et al., 2007). CARIACO also conducts monthly (or more frequent) oceanographic cruises to collect hydrographic and biogeochemical observations. One of the main objectives of the program is to decipher the impact of changing hydrographic/environmental conditions in the Cariaco Basin on the production and geochemical composition of sinking particulate material, to help interpret the tropical paleoclimatic record preserved in Cariaco Basin sediments (Peterson et al., 1991; Hughen et al., 1996, 2004; Black et al., 1999, 2004, 2007; Haug et al., 2001). While the first two years of CARIACO sediment trap data (1995–1996) showed some coupling between the annual cycles of primary production (PP) and the settling flux of POC (Thunell et al., 2000; Muller-Karger et al., 2001; Goñi et al., 2003), a subsequent analysis of observations spanning ten years of data showed that the POC flux and PP were not closely coupled (Thunell et al., 2004, 2007). Rather, these results indicate that ballasting plays an important role in controlling the flux of POC to the deeper parts of the basin.

The objective of this study was to test the hypothesis that the magnitude and variability of the POC escaping the base of the euphotic zone responds directly to changes in surface processes, while the POC flux within the 'twilight zone' becomes uncoupled. We also wanted to further understand the relationship between the flux of organic matter and ballasting by minerals within the Ez at different times of the year.

2. Study area

The Cariaco Basin is a tectonic depression approximately 160 km in length, 70 km in width, and 1400 m deep on the continental shelf of Venezuela (Fig. 1). It is bound to the north and west by a sill (< 150 m) that prevents deeper waters from the adjacent Atlantic Ocean and the Caribbean Sea from entering the basin. Surface waters from the Cariaco Basin and the Caribbean Sea exchange through two channels, La Tortuga (135 m) and Centinela (145 m), located in the northeast and northwest of the basin, respectively (Fig. 1; Lidz et al., 1969; Richards, 1975). The sinking flux of organic matter generated by highly productive surface waters (300 to 600 g $C\,m^{-2}\,y^{-1}$) and the restricted ventilation of deep waters lead to anoxia below ~275 m depth (Richards, 1975; Hastings and Emerson, 1988; Zhang and Millero, 1993; Muller-Karger et al., 2001, 2010; Scranton et al., 2001; Astor et al., 2003). This condition allows the accumulation of varved sediments which have been extensively used to study past climate variability in the tropics with high temporal resolution (Peterson et al., 1991; Black et al., 1999, 2007; Haug et al., 2001; Hughen et al., 2004)

The Cariaco Basin is subject to a strong seasonal cycle driven by the migration of the Inter-Tropical Convergence Zone (ITCZ). During boreal winter and spring the ITCZ shifts to its southernmost position, resulting in strong easterly Trade Winds that cause upwelling along the Venezuelan coast; primary productivity is highest during this period (Muller-Karger et al., 2001, 2004). During boreal summer and early fall, the Trade Winds weaken as the ITCZ migrates northward. This leads to stratification of the basin, decreased primary production, and increased precipitation

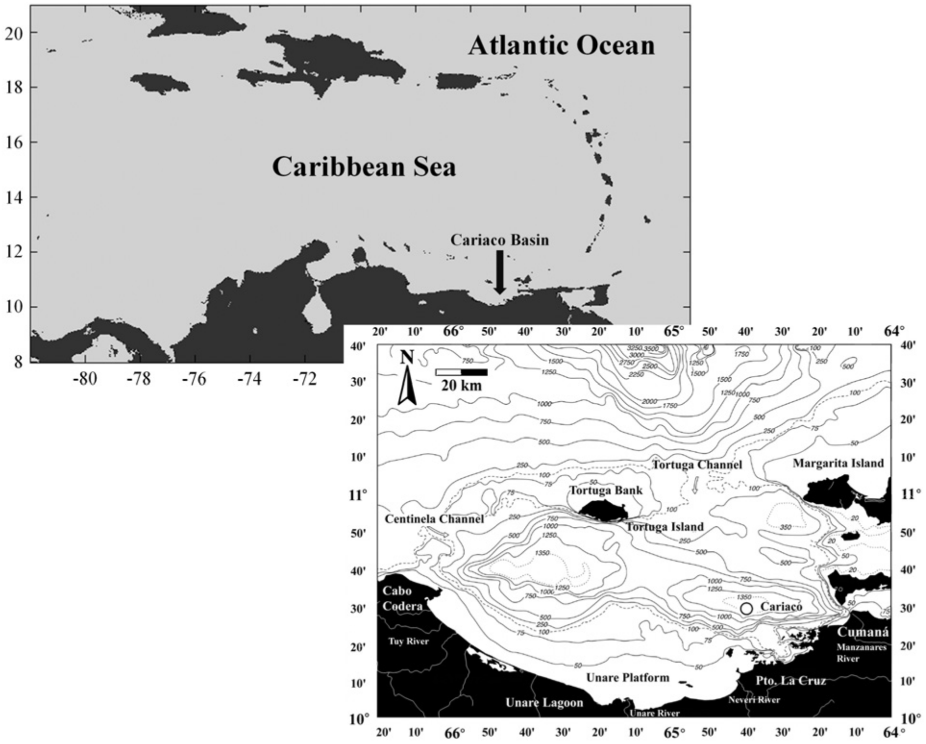

Fig. 1. Location of the Cariaco Basin. The circle indicates the location of the CARIACO Station (10.5°N, 64.4°W).

over northern South America (Muller-Karger et al., 2001; Peterson and Haug, 2006). During these months, the discharge of continental material into the basin by local rivers is highest (Astor et al., 1998; Muller-Karger et al., 2001; Martinez et al., 2007; Elmore et al., 2009; Lorenzoni et al., 2009).

3. Materials and methods

3.1. Hydrography, surface chlorophyll a and primary production

Conductivity, temperature and density (CTD) data from the CARIACO time series were used to detect seasonal variations in the hydrography of the basin during the study period. We estimated the depth of the mixed layer (MLD) using a change of water column temperature of 0.2 °C (de Boyer-Montégut et al., 2004). Near-surface chlorophyll *a* concentration estimates were derived from weekly and monthly composites of satellite-derived ocean color products, constructed using daily images collected by the Sea-viewing Wide Field of View Sensor (SeaWiFS) and the Moderate Resolution Imaging Spectroradiometer (MODIS) sensor on the Aqua satellite. The processed images were downloaded from NASA's Ocean Color website (http://oceancolor.gsfc.nasa.gov/), and mapped to 1 km^2 pixel resolution using a cylindrical equidistant projection. Values of chlorophyll *a* concentration were extracted from weekly and monthly composites corresponding to each sampling period at pixels along the track followed by the drifting traps during each of the deployments. The values along each track were averaged to obtain a single value of chlorophyll *a* concentration for each sampling period. Satellite estimates were compared to *in situ* measurements of chlorophyll *a* from the CARIACO time series to assess the accuracy of the remote sensing estimates. Profiles of conductivity, temperature, depth (CTD), and chlorophyll *a* fluorescence were also carried out in conjunction with each of the drifting traps deployments in order to determine the depth of the deep chlorophyll maximum (DCM).

Primary production measurements were obtained from *in situ* incubations from the CARIACO Ocean Time-Series program. Monthly measurements followed a modified method by Steeman-Nielsen (1952), consisting of determining the rate of $NaH^{14}CO_3$ uptake in seawater samples from several depths between the surface and 100 m during a 6 h incubation at those same depths (see Muller-Karger et al., 2001).

3.2. Drifting sediment traps

Ten deployments of drifting surface-tethered particle interceptor traps (PITs; BATS Method Manual, 1997) were carried out between March 2007 and November 2009 at the CARIACO time-series site (Table 1). Deployments were carried out from the *R/V Hermano Ginés*, operated by Fundación La Salle de Ciencias Naturales (FLASA, Venezuela).

The mean depth of the euphotic zone (where downwelling irradiance was 1% of surface photosynthetically active radiation) in the Cariaco Basin was 42.2 ± 13.2 m between 1997 and 2006 (Lorenzoni et al., 2011). Hence, flux measurements at 50 m from this study were used to estimate the export production, or the amount of particulate organic carbon that rains out of the base of the euphotic zone. The mixed layer depth in the Cariaco Basin during our study period was typically shallower than the mean Ez by 15–25 m (see the "Results" section). Therefore, traps were deployed to float at 50 and 100 m, i.e., approximately at the base of the Ez and 50 m below that.

Two sets of six acrylic tubes, each mounted on a PVC rack, were attached to a line, which was in turn tethered to a surface buoy. Sinking material was collected at both 50 and 100 m simultaneously. Each cylinder had a cross-sectional collection area of 0.00456 m^2. A grid constructed of short acrylic cylinders, each 1.5 cm in diameter, open to the top and bottom, was placed side by side across the mouth of the trap cylinders to function as a baffle to help reduce turbulence across the top of the trap. Each cylinder contained a density gradient solution (brine solution plus formalin). This solution was used to reduce advective-diffusive exchange of the trap content with ambient seawater, to reduce decomposition of the organic matter during the deployment, and to minimize the consumption of materials by any larger organism entering the trap. A 76 mm Poretics GE polycarbonate membrane filter was positioned at the base of each tube to collect all of the particulate material upon draining the sample through a valve at the bottom of the cylinder. Upon retrieval of the traps, the brine solution was drained from each cylinder through the bottom-mounted valve, allowing the sample material to be retained on the membrane filters. Each membrane filter was then removed from the cylinder, wrapped in pre-combusted aluminum foil paper, and kept frozen for 5–7 days until analysis.

Table 1
Dates of deployment of PITs during the study period and corresponding moored traps sampling dates. Each of the sampling dates of the moored traps indicates the date the cup starts collecting material; the collection period of each cup is 14 days.

Year	PITs (date of deployment)	Moored traps (date cup opens)
2007	Mar 13–15	28-Feb 14-Mar
	May 10–11	25-Apr 16-May
	Jul 4–6	27-Jun 11-Jul
	Oct 3–5	3-Oct 17-Oct
	Nov 28–29	30-Nov 13-Dec
2008	Jan 29–30	21-Jan 3-Feb
	May 27–28	4-May 28-May
	Nov 13–14	22-Oct

The PITs were deployed for periods of 19–56 h, during which they drifted as much as 16 km per day. The traps always remained on the deeper side of the 1000 m isobath of the eastern Cariaco Sub-Basin (Fig. 1). An Argos unit installed on the surface buoy was used to track the drifting array.

Each sample was examined under a microscope to remove swimmers using established protocols for sediment traps (BATS Method Manual, 1997; Thunell et al., 2000; Goñi et al., 2003). Foraminifera, bivalve and gastropods shells, and any other identifiable organism remains were identified and counted. After removing the swimmers, samples were dried in an oven at 65 °C for 24 h, weighed to estimate total mass, pulverized, and placed into vials that were then kept in a desiccator until further analysis.

3.3. Moored sediment traps

The CARIACO Ocean Time-Series program has systematically measured the sinking flux of particles using moored conical sediment traps since November 1995. Traps are located at five depths: 150, 220, 440, 800, and 1300 m. Each trap collected settling material falling into the cone across a 1 m^2 aperture, integrating flux samples in a cup for periods of two weeks before rotating a new cup under the trap. Each cup was filled with 2% formalin to avoid microbial degradation of the material. After collection, all samples were analyzed for bulk geochemical properties including

POC, PON, calcite, opal, and lithogenic material as described by Thunell et al. (2004, 2007).

For this study we used moored trap data for the period January 2007 to October 2008. Flux measurements from the moored traps were not available for comparisons with those collected with the drifting traps during 2009 because of a mooring malfunction. To compare the data to the floating sediment trap observations, we averaged observations from the moored traps over the two consecutive collection periods closest to the dates of the drifting trap deployments (Table 1). Thus, moored trap measurements correspond approximately to the period spanning a week before and a week after the deployment of the drifting traps.

3.4. Analytical methods

The weight percent of total carbon (%TC), organic carbon (%OC) and organic nitrogen (%ON) were measured for two or three of the six drifting traps samples collected at each depth. Measurements were done using a Carlo-Erba NA2500 Elemental Analyzer (EA) in continuous-flow configuration. The standard deviation of particulate organic carbon (POC) and particulate organic nitrogen (PON) measurements was better than 0.08% and 0.01%, respectively. For organic carbon content analyses, two aliquots of ~1000 μg were taken from each sample, placed into silver cups and exposed to 12 N HCL vapor in a fuming chamber for 36 h to remove the carbonate component. Other two similar aliquots were placed into tin cups without exposure to acid fumes for total carbon determinations. The fraction of particulate inorganic carbon ($CaCO_3$) was obtained as the difference between the amount of carbon in the acidified samples versus non-acidified samples. Biogenic silica ($bSiO_2$) in traps was determined using the wet chemical leaching technique outlined by Mortlock and Froelich (1989). The lithogenic flux was determined by subtracting the fluxes of POC, PON, $CaCO_3$ and $bSiO_2$ from the total mass flux.

3.5. Coccolithophore and foraminifera flux estimates

Coccolithophore cells were counted in samples collected with the drifting traps from March 2007 to January 2008. One of the six samples collected at both 50 and 100 m during each deployment was preserved in a Nalgene amber rectangular HDPE bottle (125 ml) containing filtered seawater with formalin neutralized with sodium tetraborate. After homogenizing by shaking, an aliquot of each sample was analyzed in the laboratory with the Utermöhl technique (Hasle, 1978) to estimate flux of cells from each phytoplankton group. Foraminifera shells were counted in each of the PIT's samples under a microscope during the process to remove swimmers and were left in the samples.

4. Results

4.1. Hydrography, surface chlorophyll a and primary production

Water column temperature, surface chlorophyll *a* concentrations, and primary production followed a seasonal pattern associated with the upwelling cycle of the basin (Fig. 2). High primary production and surface chlorophyll *a* concentrations coincided with periods in which the 21 °C isotherm was near the surface as a result of the upwelling. *In situ* and remotely sensed chlorophyll *a* concentrations were significantly correlated ($r=0.55$, $p<0.01$) within the time frame of this study. Both chlorophyll *a* concentrations and primary production were higher during upwelling (December to May) than those during the period of thermal stratification (September to November). A secondary peak in these parameters, associated with a weaker annual upwelling event (Muller-Karger et al., 2001; Astor et al., 2003), was observed between July and August during 2007 and 2008 (Fig. 2).

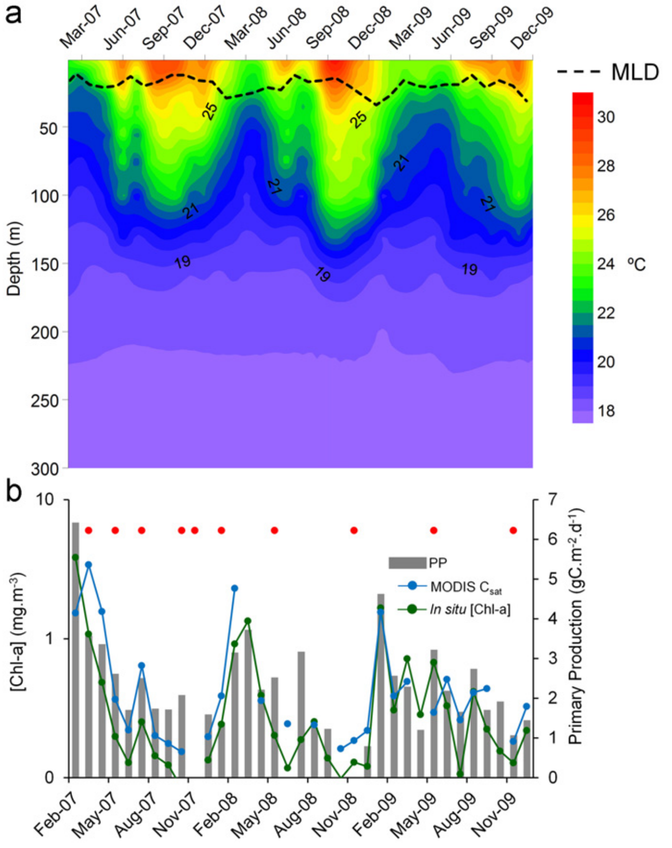

Fig. 2. Water column temperature profiles, *in situ* and satellite chlorophyll *a* concentrations, and primary production measurements from the CARIACO Ocean Time-Series program. (a) Temperature profiles and mixed layer depth (MLD) during the study period. (b) Satellite chlorophyll *a* (C_{sat}) measurement at the CARIACO station (10.5°N, 64.4°W) extracted from MODIS weekly mean composites, average *in situ* chlorophyll *a* concentrations within the upper 15 m and *in situ* integrated primary production (0–100 m) at the CARIACO station. Red dots indicate months in which the drifting sediment traps were deployed.

During the upwelling period, the average mixed layer depth (MLD) was 21 ± 3 m, while during the non-upwelling season the MLD was significantly shallower (15 ± 3 m). The maximum MLD (33 m) was observed in January 2009 (Fig. 2).

4.2. POC and PON fluxes

The POC and PON flux data for the drifting and moored sediment traps samples are presented in Table 2 and Fig. 3. Particulate organic matter (POM), which comprises both POC and PON (POM:POC=1.87; from Anderson, 1995), within the upper 100 m was 15–46% of the total mass flux. High POC and PON fluxes routinely occurred during upwelling months (March 2007, January 2008) and all May months, which are considered the end of the upwelling period or transition to the non-upwelling regime. POC and PON fluxes were lower during months of thermal stratification (October and November 2007, November 2008, and November 2009). For example, POC fluxes were higher in May compared to November 2008 (0.95 ± 0.01 and 0.20 ± 0.01 g m^{-2} d^{-1} at 50 m; 0.83 ± 0.02 and 0.14 ± 0.00 g m^{-2} d^{-1} at 100 m, respectively). PON fluxes at 50 and 100 m were also higher in May compared to November 2008 (0.18 ± 0.01 and 0.04 ± 0.00 g m^{-2} d^{-1} at 50 m; 0.13 ± 0.01 and 0.03 ± 0.00 g m^{-2} d^{-1} at 100 m, respectively). The fluxes of POC and PON captured at 50 m were generally higher than those at 100 m.

Table 2
Integrated primary production within the upper 100 m of the water column (PP_{100}) during the study period, with the corresponding export production and rates measured at multiple depths with the drifting traps (50 and 100 m) and the moored traps (150, 225 and 410 m).

	PP_{100} (mgC.m^{-2} d^{-1})	Average export production (POC flux in g m^{-2} d^{-1})					Export ratios			
		50 m	100 m	150 m	225 m	410 m	100/50	150/50	225/50	410/50
Mar-07	3577	0.62 ± 0.11	0.57 ± 0.13	0.05 ± 0.03	0.05 ± 0.02	0.04 ± 0.01	0.91	0.08	0.08	0.07
May-07	2624	0.55 ± 0.02	0.39 ± 0.04	0.10 ± 0.04	0.21	0.04 ± 0.02	0.71	0.17	0.38	0.08
Jul-07	2513	0.39 ± 0.04	0.25 ± 0.03	0.07 ± 0.01	0.11 ± 0.03	0.05 ± 0.00	0.65	0.18	0.27	0.13
Oct-07	2087	0.43 ± 0.01	0.27 ± 0.08		0.03 ± 0.03		0.62		0.06	
Nov-07		0.49 ± 0.13	0.21 ± 0.07	0.04 ± 0.00	0.08 ± 0.00	0.06 ± 0.02	0.44	0.09	0.17	0.13
2007 annual mean ± SD	**2700 ± 629**	**0.49 ± 0.09**	**0.34 ± 0.14**	**0.06 ± 0.02**	**0.10 ± 0.07**	**0.05 ± 0.01**	**0.67 ± 0.17**	**0.13 ± 0.06**	**0.19 ± 0.14**	**0.10 ± 0.03**
Jan-08	1400	0.60 ± 0.08	0.42 ± 0.13	0.05	0.08	0.10 ± 0.03	0.70	0.08	0.13	0.17
May-08	2533	0.95 ± 0.01	0.83 ± 0.02	0.14 ± 0.05		0.07 ± 0.03	0.87	0.14		0.08
Nov-08	1446	0.20 ± 0.01	0.14 ± 0.00	0.01		0.01	0.70	0.07		0.06
2008 annual mean ± SD	**1793 ± 641**	**0.59 ± 0.37**	**0.46 ± 0.34**	**0.07 ± 0.06**	**0.08**	**0.06 ± 0.05**	**0.76 ± 0.10**	**0.10 ± 0.04**	**0.13**	**0.10 ± 0.06**
May-09	3229		0.65 ± 0.01							
Nov-09	1078	0.46 ± 0.13	0.30 ± 0.04				0.64			
2009 annual mean ± SD	**2154 ± 1521**	**0.46**	**0.47 ± 0.25**				**0.64**			
Mean ± SD	**2019 ± 945**	**0.48 ± 0.21**	**0.38 ± 0.20**	**0.06 ± 0.03**	**0.09 ± 0.05**	**0.05 ± 0.03**	**0.61 ± 0.24**	**0.10 ± 0.05**	**0.17 ± 0.10**	**0.09 ± 0.04**

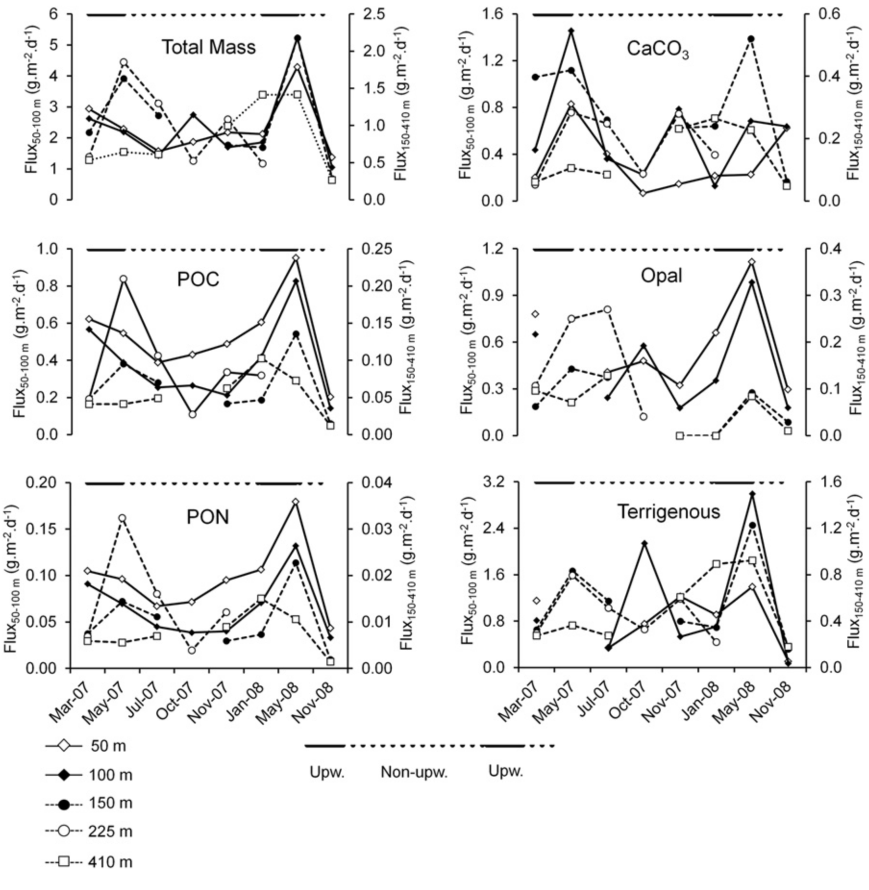

Fig. 3. Shallow (50–100 m) and deep (150–410 m) fluxes of total mass, POC, PON, calcite, opal and lithogenic material in the Cariaco Basin during each deployment of the drifting sediment trap array. The continuous and dotted horizontal lines at the top of each plot indicate periods of upwelling and non-upwelling, respectively.

POM accounted for 9–21% of the total mass flux at 150, 225 and 410 m. The settling flux of POC estimated at these horizons decreased rapidly with depth, and ranged between 0.21 g m^{-2} d^{-1} at 150 m and 0.01 g m^{-2} d^{-1} at 410 m. PON flux also decreased with depth, from 0.032 to 0.001 g m^{-2} d^{-1}. POC and PON fluxes peaked in May and were lowest in November.

4.3. *Mineral fluxes*

The average flux of $CaCO_3$ at 50 and 100 m fluctuated between 0.14 ± 0.11 g m^{-2} d^{-1} (October 2007) and 1.82 g m^{-2} d^{-1} (only one measurement, May 2009), (Table 3). Carbonate fluxes at 100 m were typically higher than or equal to those measured at 50 m (Fig. 3). In the deeper traps, the flux of carbonate oscillated between 0.52 ± 0.10 g m^{-2} d^{-1} (May 08 at 150 m) and 0.05 ± 0.00 g m^{-2} d^{-1} (November 08 at 410 m) (Fig. 3).

The fluxes of biogenic opal at 50 m were higher than or similar to those at 100 m throughout the study period except in October 2007, when the opal flux at 100 m was significantly higher than that at 50 m (Fig. 3). Opal fluxes measured at 50 and 100 m were highest in May 2008 (1.12 ± 0.17 g m^{-2} d^{-1}) and lowest in November 2007 and 2008 (0.18 ± 0.01 g m^{-2} d^{-1}, both months).

Table 3
Average fluxes (50–100 m) of calcite, foraminifera shells and coccolithophores during the study period, and the associated contributions from these organisms to the total $CaCO_3$ flux. The foraminiferal $CaCO_3$ flux was calculated by averaging the products of the foraminifera fluxes (shells.m^{-2} d^{-1}) times the approximate weights of *G. bulloides* (5 μg per shell within the 212–250 μm size fraction) and *G. ruber* (12 μg per shell within the 212–250 μm size fraction) (David Black, personal communication). The coccolithophores $CaCO_3$ flux was calculated by averaging the products of the coccolithophores fluxes (cells.m^{-2} d^{-1}) times the approximate weights of *Emiliania spp* and *Gephyrocapsa spp* (5.3 and 53 pg per cell, respectively) (Beaufort, 2005).

	Total $CaCO_3$ flux (g m^{-2} d^{-1})	**Foraminifera flux (shells.m^{-2} d^{-1})**	**Foraminiferal $CaCO_3$ flux (g m^{-2} d^{-1})**	**Foraminiferal contribution to the total $CaCO_3$ flux**	**Coccolithophores flux (cells.m^{-2} d^{-1})**	**Coccolithophores $CaCO_3$ flux (g m^{-2} d^{-1})**	**Coccolithophores contribution to the total $CaCO_3$ flux**
13–15 Mar 07	0.32 ± 0.17	388 ± 282	0.003 ± 0.002	1%	$4 \times 10^6 \pm 1 \times 10^6$	$1 \times 10^{-4} \pm 1 \times 10^{-4}$	0.037%
10–11 May 07	1.14 ± 0.44	9,661 ± 2987	0.082 ± 0.048	7%	$1 \times 10^6 \pm 7 \times 10^6$	$4 \times 10^{-5} \pm 4 \times 10^{-5}$	0.003%
4–6 Jul 07	0.38 ± 0.03	1,895 ± 213	0.016 ± 0.009	4%	$2 \times 10^5 \pm 4 \times 10^4$	$6 \times 10^{-6} \pm 7 \times 10^{-6}$	0.002%
3–5 Oct 07	0.14 ± 0.11	1,040 ± 523	0.009 ± 0.005	6%	$2 \times 10^5 \pm 5 \times 10^4$	$5 \times 10^{-6} \pm 6 \times 10^{-6}$	0.003%
28–29 Nov 07	0.46 ± 0.45	1,392 ± 1056	0.012 ± 0.007	3%	$1 \times 10^6 \pm 2 \times 10^6$	$4 \times 10^{-5} \pm 5 \times 10^{-5}$	0.009%
29–30 Jan 08	0.17 ± 0.06	1,612 ± 94	0.014 ± 0.008	8%	$7 \times 10^4 \pm 3 \times 10^4$	$2 \times 10^{-6} \pm 2 \times 10^{-6}$	0.001%
27–28 May 08	0.45 ± 0.32	16,741 ± 2,033	0.142 ± 0.083	31%	N/A	N/A	N/A
13–14 Nov 08	0.63 ± 0.01	1,589 ± 281	0.014 ± 0.008	2%	N/A	N/A	N/A
12–13 May 09	1.82	3,257	0.028 ± 0.016	2%	N/A	N/A	N/A
2–4 Nov 09	0.76 ± 0.10	3,091 ± 749	0.026 ± 0.015	3%	N/A	N/A	N/A

Already at 150 m, opal fluxes captured in the moored traps were about a factor of two or more lower than those in the upper 100 m (Fig. 3). The deeper opal fluxes were highest during June 07 (at 225 m; 0.27 ± 0.01 g m^{-2} d^{-1}) but were undetectable in November and January 2007 (at 150 and 410 m; opal estimates at 225 m were not available for this period).

The terrigenous fraction of the settling flux was often an important component of the total mass flux in the samples collected at 50 and 100 m (Fig. 3), contributing up to 54% to the total mass flux at 50 m and 66% at 100 m. The settling flux of lithogenic particles at 100 m was frequently similar to that at 50 m, with some occasions when the flux at 100 m was higher than at 50 m (October 2007, May 2008 and November 2009). Maximum and minimum fluxes of lithogenic material measured at the base of Ez (50 m) were observed in May and November 2008, respectively (ranges were from 0.11 ± 0.06 to 1.39 ± 0.13 g m^{-2} d^{-1} at 50 m, and from 0.07 ± 0.04 to 2.99 ± 0.51 g m^{-2} d^{-1} at 100 m). A similar pattern was observed in the moored trap samples (Fig. 3), where terrigenous material contributed 33–67% to the total mass flux. Fluxes of lithogenic material at depths >150 m also peaked in May 2008 (1.23 ± 0.03 g m^{-2} d^{-1}), and were lowest in November 2008 (0.16 g m^{-2} d^{-1}).

4.4. *Coccolithophore cells and foraminifera fluxes, and associated $CaCO_3$ flux estimates*

Between March 2007 and January 2008, the mean flux of coccolithophore cells, calculated from fluxes at 50 and 100 m, varied between $7 \times 10^4 \pm 3 \times 10^4$ (January 2008) and $4 \times 10^6 \pm 1 \times 10^6$ cells.m^{-2} d^{-1} (March 2007) (Table 3). In order to estimate the coccolithophore $CaCO_3$ flux, we averaged the products of the settling fluxes of coccolithophores (cells.m^{-2} d^{-1}) times the weights of *Emiliania spp* and *Gephyrocapsa spp* (5.3 and 53 pg per cell, respectively; Beaufort, 2005). These genera were chosen as they represented ~99% of the coccolithophores assemblage in the drifting sediment traps samples. The coccolithophores contribution to the total vertical transport of calcite varied from 0.001 and 0.037%, and was two to three orders of magnitude lower than that of foraminifera.

The flux of planktonic foraminifera showed minima in January–March, and maxima in May (Table 3). The average settling fluxes of foraminifera shells in the upper 100 m varied from 16,741 ± 2033 shells.m^{-2} d^{-1} (May 2008) to 388 ± 282 shells.m^{-2} d^{-1} (March 2007, Table 3). The average foraminiferal contribution to the total calcite flux in the upper 100 m (mean foraminiferal $CaCO_3$ contribution at 50 and 100 m) ranged from 1% (March 2007) and 31% (May 2008) (Table 3). The foraminiferal $CaCO_3$ flux was estimated by averaging the products of the foraminifera fluxes (shells m^{-2} d^{-1}) times the weights of *G. bulloides* (5 μg per shell within the 212–250 μm size fraction) and *G. ruber* (12 μg per shell within the 212–250 μm size fraction; David Black, personal communication).

5. Discussion

5.1. *POC fluxes, hydrography, primary production and surface chlorophyll a*

The magnitude of the POC flux escaping the Ez was controlled by hydrographic variability in the Cariaco Basin. Average POC fluxes at 50 and 100 m were typically higher during upwelling periods (0.62 ± 0.16 g m^{-2} d^{-1}; January to May) than during thermal stratification (POC flux = 0.31 ± 0.09 g m^{-2} d^{-1}; September to November). However, we observed only a very weak (not significant) negative relationship between POC flux and sea surface temperature (SST) at either depth. Maximum fluxes of sinking organic carbon occurred at the end of the upwelling period (i.e., May months; Fig. 3), when surface temperatures had already risen 3–4 °C above the seasonal SST minima associated with the strongest upwelling (i.e., February and March months, Fig. 2). This lag weakens the correlation.

Historically, studies have attempted to model POC flux within the twilight zone based on primary production estimates (Suess, 1980; Martin et al., 1987; Pace et al., 1987). Subsequent studies concluded that the vertical transport of organic carbon below the euphotic zone is uncoupled from primary production or export production, and that this POC flux responds instead to multiple physical and biological processes (Karl et al., 1996; Conte et al., 2001; Armstrong et al., 2002, 2009). In the Cariaco Basin, Thunell et al. (2007) found no statistically significant relationship between primary production and POC fluxes using observations at four different depths between about 200 and 1300 m. They suggested that the "ballast model" proposed by Armstrong et al. (2002) explains this uncoupling. The vertical transport of organic matter is proportional to the mineral fraction of the flux, while "excess" organic matter in sinking particles is quickly remineralized in the upper layers of the water column. We also found that there was a weak correlation ($r=0.41$, $p>0.3$) between the average of the POC flux measured at 50 m and 100 m by the drifting traps during their 1–3 day deployments and the punctual primary production observations made during the CARIACO cruises conducted 1–2 weeks before or after the trap deployments (shown in Fig. 2). We saw a similar weak statistical relationship ($r=0.39$, $p>0.29$) between these average POC fluxes and the punctual *in situ* chlorophyll *a* estimates from the monthly CARIACO cruises. However, these POC fluxes showed a better correlation ($r=0.68$, $p<0.05$) with the concurrent weekly mean satellite-derived surface chlorophyll *a* concentrations averaged along the track followed by the drifting trap array (Fig. 4). This supports previous studies showing that the export of POC out of the Ez is affected by changes in surface phytoplankton biomass within narrow spatial (few km) and temporal (days to weeks) scales (Perry et al., 2008; Collins et al., 2011). These observations provide confidence that there is a direct link between near surface biomass and POC flux exiting the euphotic zone, and that satellite chlorophyll observations can be used to derive export production in tropical coastal systems. If this relationship applies elsewhere, it has implications for developing a better understanding of the global carbon balance in shelf systems, where >40% of the carbon burial in the global ocean occurs (Muller-Karger et al., 2005).

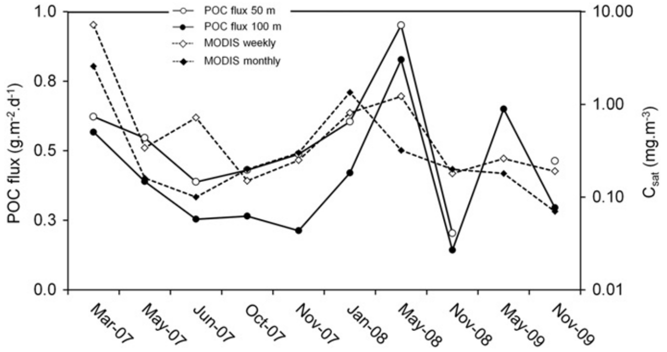

Fig. 4. Average satellite chlorophyll *a* (C_{sat}) along the track of the drifting sediment traps for each sampling period (using weekly and monthly composites from MODIS) and the corresponding POC flux measurements at 50 and 100 m.

5.2. Fluxes of organic matter at the base of the Ez and at 225 and 410 m depth

The fluxes of POC and PON measured at the oxic–anoxic interface and deeper (225 and 410 m) were typically an order of magnitude lower than those observed within the upper 100 m. We attribute the ten-fold difference between the shallow (50 and 100 m) and deep (225 and 410 m) fluxes of organic matter mainly to remineralization in Cariaco. However, sampling biases in the collection methods could contribute to amplifying this difference. For example, hydrodynamic biases associated with horizontal flow across the mouth of the trap and trap tilt can lead to oversampling of sinking material in surface-tethered drifting traps and undersampling in moored traps (Murray et al., 1996; Gardner, 2000; Hernes et al., 2001; Buesseler et al., 2007). We believe that flux measurements from the moored traps in Cariaco do not suffer from these biases since the horizontal flows at depths below the sill (~100–140 m) are almost zero (Alvera-Azcárate et al., 2009). Stanley et al. (2004) found that POC and PON fluxes collected with surface-tethered drifting traps were comparable to those estimated with neutrally buoyant drifting traps, indicating that, specifically for these two components, hydrodynamic biases are not significantly higher in surface-tethered traps than in neutrally buoyant drifting traps.

The average C:N ratio (atom) of the organic matter collected at 50 and 100 m was 7.31 ± 0.9 and was generally lower than that in the deeper moored traps (8.06 ± 0.7). Sinking organic matter undergoes high degradation rates over short depth intervals, with preferential removal of nitrogen over carbon by bacterial decomposition (Redfield, 1934; Knauer et al., 1979). For example, Martin et al. (1987) found that C:N ratios increased from ~6 at 100 m depth to over 10 at 5000 m depth in the northeast Pacific. This is also consistent with observations throughout the global ocean (Schneider et al., 2003).

The POC fluxes measured at 225 and 410 m did not co-vary with those at 50 and 100 m. The decoupling between the shallow and deep POC fluxes can be partly attributed to lateral advection, since the depth of the sill is ~140 m and strong currents ($>20\ \mathrm{cm\ s^{-1}}$) observed in the 120–140 m depth interval (Alvera-Azcárate et al., 2009) can affect the settling flux of particles (Thunell et al., 2007). Recent work by Burd et al. (2010) suggests that, in general, lateral advection can be an important factor contributing to the decoupling between carbon fluxes in surface layers and those below the Ez. Also, the diel vertical migration by zooplankton can decouple fluxes between shallow and deep traps, since zooplankton release fecal pellets and dissolved organic and inorganic carbon and nitrogen several hundred meters below the euphotic zone during daylight hours (Fowler and Knauer, 1986; Longhurst and Harrison, 1988; Small et al., 1989; Altabet and Small, 1990; Steinberg et al., 2000, 2002). Similar to observations reported by Wishner et al. (2008) in the Arabian Sea oxygen minimum zone, vertical migrators in Cariaco can penetrate low oxygen layers, thus bypassing the deep traps and transferring organic matter to the anoxic layer.

Rapid degradation rates of organic carbon and nitrogen with depth in the Cariaco Basin, especially in the upper 100 m of the water column, are consistent with models of exponential decay of organic matter with depth in the open ocean (Suess, 1980; Betzer et al., 1984; Martin et al., 1987; Pace et al., 1987; Thunell et al., 2000; Buesseler et al., 2007). Although these models are based on flux attenuation measurements in oxygenated open ocean systems, they can be applied in the sub-oxic and anoxic waters of the Cariaco Basin; previous studies have shown that respiration rates of organic carbon under low oxygen and anoxic conditions in Cariaco are as efficient as within oxygenated waters (Thunell et al., 2000; Taylor et al., 2009). POC fluxes measured at 50 and 100 m were in good agreement with predicted fluxes using the models by Martin et al. (1987); Pace et al. (1987) (Fig. 5), while deeper fluxes often deviated from the models. Observations during March 2007, October 2007, November 2007 and November 2008 had POC fluxes much lower than those predicted by such models both within the oxic–anoxic interface (225 m) and in anoxic waters (410 m). These results are consistent with previous findings in which models are good predictors of export production (e-ratios) but not of deeper fluxes in coastal systems like the Cariaco Basin (Thunell et al., 2000).

5.3. *Ez-ratios and transfer efficiency (T_{100})*

Buesseler and Boyd (2009) introduced the concepts of the “Ez-ratio” (POC flux at the base of the euphotic zone relative to net primary production [NPP]) and “T_{100}” (the ratio of POC flux 100 m below the base of the Ez to POC flux at the base of the Ez). Their aim was to improve estimates of new and export production and to be able to compare regions with contrasting primary production regimes by normalizing POC fluxes to the depth of the euphotic zone.

The mean depth of the Ez in the Cariaco Basin varied from 37.6 ± 12.3 m during upwelling months to 47.9 ± 13.5 m during non-upwelling months between 1997 and 2006 (Lorenzoni et al., 2011). Ez-ratios were therefore calculated using the flux measurements made at 50 m with the drifting traps. In this study, we defined T_{100} as the ratio of POC flux at 150 m to flux at 50 m.

Ez-ratios in the Cariaco Basin varied between 16% and 44% (Fig. 6a). Ez-ratios were higher (> 40%) in 2008 relative to 2007 (< 20%). During the upwelling season of 2007, PP rates were higher than in 2008 and POC fluxes at the base of Ez were similar or lower than those measured during 2008, yielding a higher Ez ratio for 2008. All Cariaco Basin Ez-ratio estimates were higher than values estimated for the tropical Pacific Ocean (2–7% at ALOHA and EQPAC stations), but similar to those measured in more productive systems like the North Atlantic (45% at NABE station), the North Pacific (3–25% at OSP and K2-D1/K2-D2 stations), and the Southern Ocean (29–34% at KIWI-7/KIWI-8 stations) (Buesseler and Boyd, 2009). The similarity of the Cariaco Ez-ratios to those in these systems is in part due to the high primary production by phytoplankton assemblages dominated by diatoms. These form rapidly-sinking particles (~200–300 m d^{-1}) that are rich in organic matter (Armstrong et al., 2002, 2009; Thunell et al., 2007). The Ez in each of these systems (typically 30–60 m Ez) is shallower than at the ALOHA and EQPAC stations

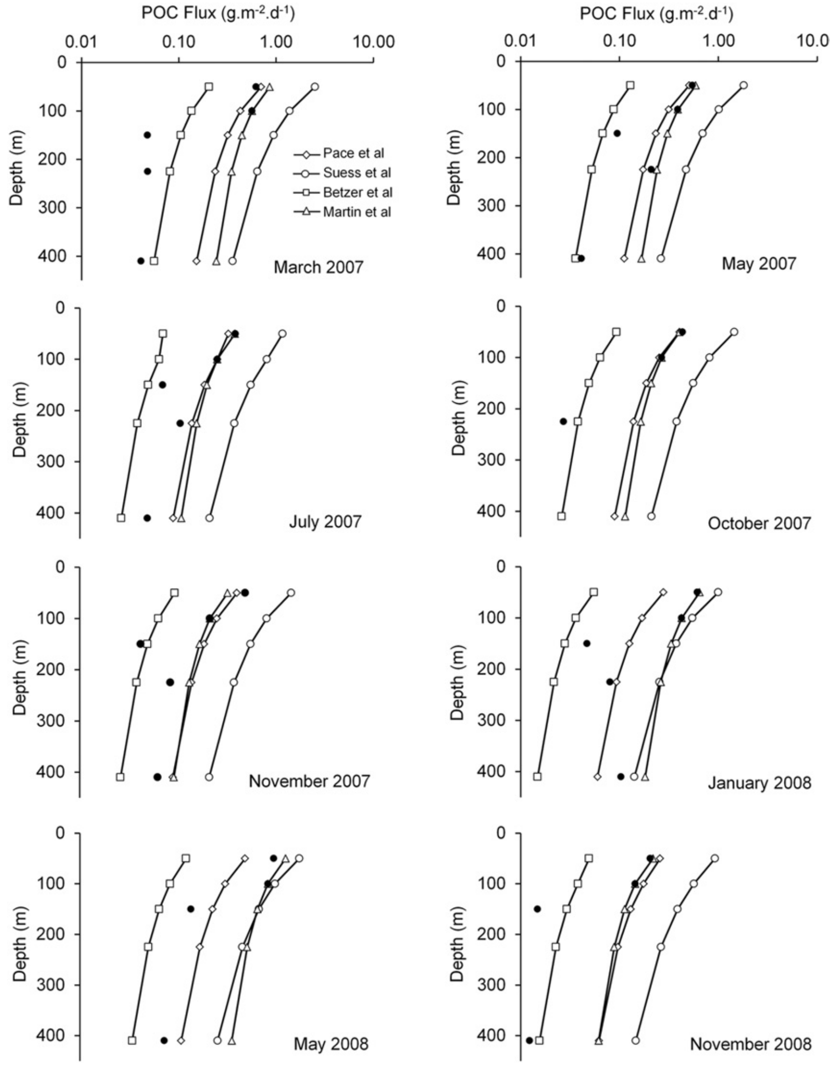

Fig. 5. Measured and modeled POC fluxes in the Cariaco Basin. Black circles indicate fluxes measured with the drifting (50 and 100 m) and moored (150, 225 and 410 m) traps. *In situ* measurements of integrated primary production (IPP) in the upper 100 m of the water column from each sampling period were used to predict POC fluxes for each corresponding model. Modeled POC fluxes in November 2007 were based on IPP from October 2007 since there were no IPP measurements available for November 2007.

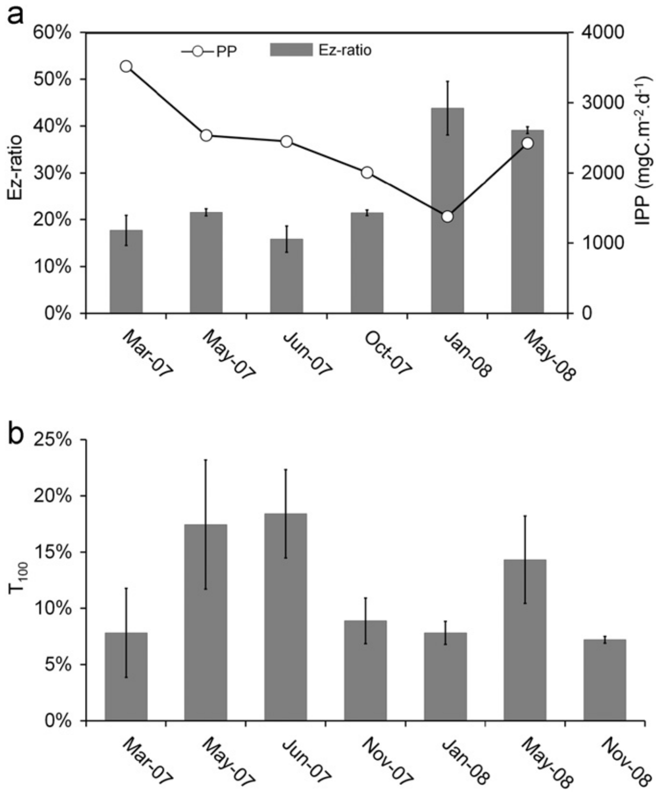

Fig. 6. Ez-ratios and T_{100}. (a) Ez-ratios (ratio of the POC flux at the base of Ez to the integrated PP-bars) and primary productivity (line); (b) T_{100} (ratio of the POC flux at 150 m to POC flux at 50 m or the base of Ez). The *X* axis of the Ez-ratios are different from those of the T_{100}, as they were calculated based on different data availability.

(> 120 m Ez), which exposes particles in the ALOHA and EQPAC settings to more degradation within the Ez.

While we often found a 10-fold or higher difference between the magnitude of the fluxes at 50 and 100 m and those at greater depths (> 200 m), the temporal patterns of POC and PON fluxes at 150 m (the shallowest moored trap) were similar to those observed at 50 and 100 m (Fig. 3; $r = 0.78$ and 0.82, respectively, with a confidence interval of 95%). This relationship weakens at deeper depths; most of the organic matter produced at the surface does not reach depths of > 200 m. Thus, the POC flux observed at the 150 m trap (100 m below the base of the Ez) reflected seasonal variations in the export production, suggesting that the T_{100} in Cariaco is responsive to surface conditions.

T_{100} estimates for the Cariaco Basin (Fig. 6b) were between 7 and 20%, with higher values of 15–20% typically observed during upwelling. This is a factor of two to three lower than those observed at deep ocean locations (T_{100} was 61–67% at ALOHA and EQPAC stations, > 100% at the NABE station, 31–54% at the OSP and K2-D1/K2-D2 stations, and 32–80% at the KIWI-7/KIWI-8 stations; Buesseler and Boyd, 2009). Low T_{100} values in Cariaco can possibly be a result of undersampling by the conical traps, particularly at shallow depths like 150 m, and oversampling by the PITs (Hernes et al., 2001; Murray et al., 1996; Buesseler et al., 2007). High POC flux attenuation rates (as low T_{100} values) can also result from overestimation of the flux near the surface due to turbulence if drifting traps are collecting settling material within the mixed layer. Turbulence within the mixed layer depth (MLD) can increase the suspension time of particles in the upper part of the water column (Lande and Wood, 1987), amplifying thus the collection of sinking particles near the surface (Gardner and Richardson, 1992; Kerr and Kuiper, 1997; Gardner, 2000).

However, we think that the low transfer efficiency (T_{100}) in the Cariaco Basin is a realistic observation, as we discuss below. Our flux measurements at 50 and 100 m were not influenced by the mixed layer; in Cariaco the MLD never exceeded 30 m during the PIT's deployments. During this study, the MLD (calculated using a water column temperature threshold of 0.2 °C; from de Boyer-Montégut et al., 2004) varied between 10 m (March 2007) and 33 m (January 2009), so the drifting traps were always below the MLD (Fig. 2). Instead, high 'excess' POC flux relative to POC 'quantitatively associated' with the particle flux (F_{OC}^{E} and F_{OC}^{QA}, respectively; from Armstrong et al., 2002) explains the elevated attenuation rate in the settling flux of organic matter (or low T_{100}). Excess organic carbon in sinking particles can be readily consumed and respired by bacteria, while ballasting materials such as opal, calcium carbonate and clays, which we find in abundance, may dissolve, but are generally not consumed or respired. Elevated excess POC flux can be expected in sinking particles in Cariaco since PP rates are several times higher in this location than in the open ocean. During this study, the excess POC flux (calculated using a POC/ballast ratio [ρ] of 0.05; from Armstrong et al., 2002) was on average 87 ± 5% at 50 m, and 77 ± 10% at 100 m. Finally, Cariaco's PP rates are higher than those in open ocean waters by factors of three or more. Hence, higher rates of consumption of the POC are expected (Suess, 1980; Betzer et al., 1984; Pace et al., 1987). As a result of all these factors, our measured T_{100} values should be considered minimum estimates.

5.4. Mineral fluxes

The vertical flux of particulate inorganic carbon in the Cariaco Basin was coupled to the settling flux of foraminifera shells (Fig. 7). The foraminiferal contribution to the total $CaCO_3$ flux was two to four orders of magnitude greater than that of coccolithophores (Table 3). This is consistent with findings by Goñi et al. (2003), in which they demonstrated that variations in the flux of carbonate in the basin were mainly regulated by the abundance of planktonic foraminifera rather than that of coccolithophores. Both carbonate and foraminifera fluxes varied in response to the seasonal upwelling cycle in Cariaco Basin. However, maxima in carbonate and foraminifera fluxes did not coincide with periods of highest primary production or chlorophyll *a* concentrations. Rather, the highest fluxes occur toward the end of the upwelling period (May). At this time, surface waters have become nutrient-depleted and primary production has declined.

Some species of foraminifera live below 50 m in the Cariaco Basin (Tedesco et al., 2003), explaining why carbonate fluxes at 100 m were often greater than those at 50 m (Fig. 7). The 100 m trap captured the production of both surface and sub-surface dwelling species. Seasonal changes in the relative abundance of

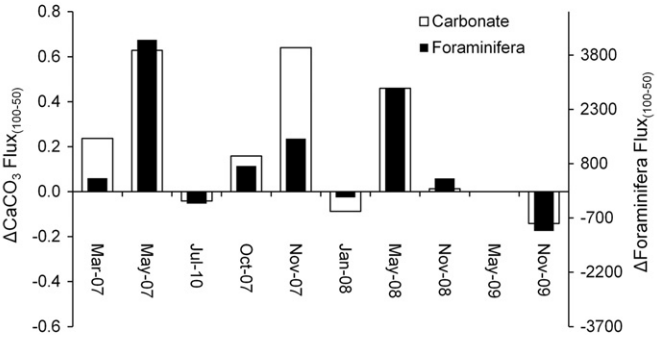

Fig. 7. Difference in the settling $CaCO_3$ flux (in g m^{-2} d^{-1}) and in the settling flux of foraminifera shells (in shells.m^{-2} d^{-1}) between 100 and 50 m. Positive values indicate higher fluxes at 100 than at 50 m.

foraminifera shells of surface and sub-surface dwelling species in samples from the moored traps have been observed in Cariaco, and have been attributed to variability in the hydrographic conditions associated with the upwelling cycle of the basin (Tedesco et al., 2003, 2007).

The particulate carbonate flux at the depths of the moored traps was within the range of the fluxes observed at 50 and 100 m. $CaCO_3$ particles are more resilient to degradation and dissolution than sinking organic matter. Unfortunately, we did not have sufficient samples to examine the relationship between the shallow (50 and 100 m) and deep fluxes (150, 225 and 410 m) of $CaCO_3$. However, fluxes of carbonate peaked in May 2007 and 2008 in the deep traps, similar to what we observed in the drifting traps. This suggests that the deep fluxes of $CaCO_3$ are more directly linked to those in the upper 100 m than POC, and that they are also in part connected to the abundance of foraminifera in the euphotic zone.

The vertical transport of $bSiO_2$ within the upper 100 m in Cariaco was directly linked to the upwelling cycle. The fluxes of opal at both drifting trap depths were higher during upwelling (January to May) than during the relaxation period (September to November). During upwelling, near surface diatom blooms result in enhanced opal fluxes (Thunell et al., 2007, 2008). Fluxes of $bSiO_2$ decrease significantly during the non-upwelling period as the abundance of diatoms declines as well (Troccoli, unpublished data).

The fluxes of $bSiO_2$ in the upper 100 m appeared to be related to the depth of the deep chlorophyll maximum (DCM). For most of the trap deployment periods, the depth of the DCM varied between 1 and 35 m, with high fluxes of $bSiO_2$ at 50 m relative to those at 100 m. Conversely, $bSiO_2$ fluxes were higher at 100 m in October 2007 when the depth of the DCM was at 75 m (Fig. 3).

The historical (1995–2008) time series of moored trap measurements shows that, on average, lithogenic fluxes are highest in May at all depths. Our working hypothesis for CARIACO (Lorenzoni et al., 2009) is that this terrigenous material moves across the southern margin of the Cariaco Basin as bottom and intermediate-depth nepheloid layers, which become detached from the shelf and extend offshore towards the end of the upwelling period. Unfortunately, as mentioned above, because of the very small sample size obtained in May 2007 and May 2009 due to short deployments of the drifting traps, it was not possible to estimate opal fluxes with sufficient precision. Therefore, we could not estimate lithogenic fluxes at 50 and 100 m for these deployments. This diminished the number of samples that we could use to compare lithogenic and POC fluxes simultaneously in the upper 100 m and at 150, 225 and 410 m. The few paired measurements available of shallow and deep traps showed that the average flux of lithogenic particles collected in the drifting traps was well correlated with that at 150 m ($r=0.85$, $p<0.05$) but not with those at greater depths (i.e., 225 and 410 m; Fig. 3).

The question that remains is then whether POC fluxes are affected significantly by mineral ballasting materials. Fig. 8 shows scatter plots of POC flux versus opal, lithogenic, calcium carbonate and total mineral fluxes in the upper 100 m in the Cariaco Basin. Most mineral flux measurements derived from the drifting traps showed a statistically significant relationship with POC flux both at 50 and 100 m. However, the fluxes of POC and $CaCO_3$ at both 50 and 100 m did not exhibit a clear statistical relationship probably because of the complex vertical distribution of the foraminiferal assemblage discussed in the previous section. We found a weak correlation between POC and lithogenic fluxes at 100 m, likely because of the smaller sample size related to the shorter deployments of May 2007 and May 2009.

In general, our results were consistent with those of Thunell et al. (2007), who concluded that the vertical flux of organic carbon in the moored traps is coupled to the flux of minerals following the "ballast hypothesis" (Armstrong et al., 2002). These observations therefore confirm that mineral ballasting of organic matter controls the transfer of carbon from the Ez to the twilight zone in the Cariaco Basin.

6. Summary and conclusions

This study was aimed at understanding the relationships between biogenic fluxes exported from the base of the euphotic zone (Ez) and seasonal environmental variability in the Cariaco Basin. We also investigated the transfer rates of organic matter from the base of the Ez to the oxic–anoxic interface and deeper (>200 m). Export production in the upper 100 m responded to changes in phytoplankton biomass estimated using concurrent satellite-derived surface chlorophyll *a* concentrations. This relationship was weaker when POC fluxes within the upper 100 m were compared with either primary production or *in situ* chlorophyll *a* measurements from CARIACO's observations carried out

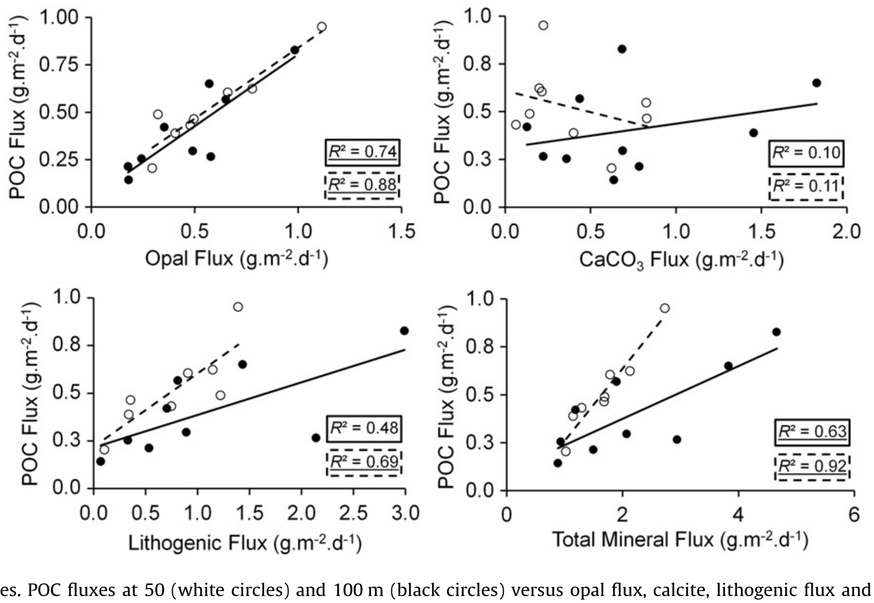

Fig. 8. POC versus mineral fluxes. POC fluxes at 50 (white circles) and 100 m (black circles) versus opal flux, calcite, lithogenic flux and total mineral flux at the same depths. Best fit linear regression parameter and coefficients of determination (R^2) are shown. Underlined R^2 values are statistically significant ($p<0.01$).

a week or two before or after our drifting traps deployments. This result suggests that the export production responds to surface chlorophyll (and possibly to PP as well) variations within small temporal and spatial scales. This finding supports the use of surface chlorophyll concentration to estimate export production in marine systems. The relationship between sea surface temperature (SST) and POC vertical fluxes escaping the Ez was weak because the highest POC fluxes occurred toward the end of the upwelling period (May), when SST's are >3 °C higher than those at the peak of the upwelling ($\sim$22 °C; January to March).

Average POC fluxes measured with drifting sediment traps at the base of the Ez in Cariaco (0.52 ± 0.20 g C m^{-2} d^{-1} at 50 m) decreased by an order of magnitude in the following 100 m (i.e., fluxes at 150 to 225 m were 0.08 ± 0.05 g C m^{-2} d^{-1}). This is the result of high remineralization rates within the upper 200 m. Ez-ratios in the Cariaco Basin varied between $\sim$20–50%, comparable to those in other highly productive open ocean regions such as the North Atlantic, North Pacific and Southern Ocean. However, the estimated transfer efficiency (T_{100}) in the Cariaco Basin was $<25\%$, or lower than values reported for the open ocean (31 to $>100\%$). We believe that this is due to high remineralization rates associated with excess organic matter relative to ballasting minerals in sinking particles in Cariaco in the upper 200 m. Our observations confirm that mineral ballasting controls the transfer of organic carbon from the Ez to the twilight zone in the Cariaco Basin.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dsr.2012.05.005.

References

Alvera-Azcárate, A., Barth, A., Weisberg, R., 2009. A nested model of the Cariaco Basin (Venezuela): description of the basin's interior hydrography and interactions with the open ocean. Ocean Dyn. 59, 97–120, http://dx.doi.org/10.1007/s10236-008-0169-y.

Altabet, M.A., Small, L.F., 1990. Nitrogen isotopic ratios in fecal pellets produced by marine zooplankton. Geochim. Cosmochim. Acta 54, 155–163.

Anderson, L.A., 1995. On the hydrogen and oxygen content of marine phytoplankton. Deep-Sea Res. I 42, 1675–1680.

Archer, D.E., Morford, J.L., Emerson, S.R., 2002. A model of suboxic sedimentary diagenesis suitable for automatic tuning and gridded global domains. Global Biogeochem. Cycles, 16, Doi:0.1029/2000GB001288.

Armstrong, R.A., Lee, C., Hedges, J.I., Honjo, S., Wakeham, S.G., 2002. A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep-Sea Res. II 49, 219–236.

Armstrong, R.A., Peterson, M.L., Lee, C., Wakeham, S.G., 2009. Settling velocity spectra and the ballast ratio hypothesis. Deep-Sea Res. II 56, 1470–1478.

Astor, Y., Meri, J., Muller-Karger, F., 1998. Variabilidad estacional hidrográfica en la Fosa de Cariaco. Mem. Soc. Cienc. Nat. "La Salle" 63, 61–72.

Astor, Y., Muller-Karger, F., Scranton, M.I., 2003. Seasonal and interannual variation in the hydrography of the Cariaco Basin: implications for basin ventilation. Cont. Shelf Res. 23, 125–144.

B.A.T.S. Method Manual, 1997. US Joint Global Ocean Flux Study. Bermuda Atlantic Time-Series Study. BATS Method Manual Version 4, US JGOFS Planning and Coordination Office, Woods Hole, pp. 136.

Beaufort, L., 2005. Weight estimates of coccoliths using the optical properties (birefringence) of calcite. Micropaleontology 51, 289–297.

Benitez-Nelson, C., O'Neill, L.P., Styles, R.M., Thunell, R.C., Astor, Y., 2007. Inorganic and organic sinking particulate phosphorus fluxes across the oxic/anoxic water column of Cariaco Basin, Venezuela. Mar. Chem. 105, 90–100.

Betzer, P., Showers, W., Laws, E., Winn, C., DiTullio, G., Krooponik, P., 1984. Primary production and particle fluxes on a transect of the equator at 153°W in the Pacific Ocean. Deep-Sea Res. 31, 1–11.

Black, D.E., Peterson, L.C., Overpeck, J.T., Kaplan, A., Evans, M.N., Kashgarian, M., 1999. Eight centuries of North Atlantic Ocean atmosphere variability. Science 286, 1709–1713, http://dx.doi.org/10.1126/science.286.5445.1709.

Black, D.E., Thunell, R.C., Kaplan, A., Peterson, L.C., Tappa, E.J., 2004. A 2000-year record of Caribbean and tropical North Atlantic hydrographic variability. Paleoceanography 19, PA2022, http://dx.doi.org/10.1029/2003PA000982.

Black, D.E., Abahazi, M.A., Thunell, R.C., Kaplan, A., Tappa, E.J., Peterson, L.C., 2007. An 8-century tropical Atlantic SST record from the Cariaco Basin: baseline variability, twentieth-century warming, and Atlantic hurricane frequency. Paleoceanography 22, PA4204, http://dx.doi.org/10.1029/2007PA001427.

Buesseler, K.O., Lamborg, C.H., Boyd, P.W., Lam, P.J., Trull, T.W., Bidigare, R.R., Bishop, J.K.B., Casciotti, K.L., Dehairs, F., Elskens, M., Honda, M., Karl, D.M., Siegel, D.A., Silver, M.W., Steinberg, D.K., Valdes, J., Van Mooy, B., Wilson, S., 2007. Revisiting carbon flux through the ocean's twilight zone. Science 316, 567, http://dx.doi.org/10.1126/science.1137959.

Buesseler, K.O., Boyd, P.W., 2009. Shedding light on processes that control particle export and flux attenuation in the twilight zone of the open ocean. Limnol. Oceanogr. 54, 1210–1232.

Burd, A.B., Hansell, D.A., Steinberg, D.K., Anderson, T.R., Arístegie, J., Baltar, F., Beaupré, S.R., Buesseler, K.O., DeHairs, F., Jackson, G.A., Kadko, D.C., Koppelmann, R., Lampitt, R.S., Nagata, T., Reithaler, T., Robinson, C., Robinson, B.H., Tamburini, C., Tanaka, T., 2010. Assessing the apparent imbalance between geochemical and biochemical indicators of meso- and bathypelagic biological activity: what the @$#! is wrong with present calculations of carbon budgets? Deep-Sea Res. II 57, 1557–1571.

Collins, L.E., Berelson, W., Hammond, D.E., Knapp, A., Schwartz, R., Capone, D., 2011. Particle fluxes in San Pedro Basin, California: a four-year record of sedimentation and physical forcing. Deep Sea Res. I 58, 898–914.

Conte, M.H., Ralph, N., Ross, E.H., 2001. Seasonal and interannual variability in deep ocean particle fluxes at the Oceanic Flux Program (OFP)/Bermuda Atlantic Times-Series (BATS) site in the western Sargasson Sea near Bermuda. Deep-Sea Res. II 48, 1471–1505.

Deuser, W.G., Ross, E.H., Anderson, R.F., 1981. Seasonality in the supply of sediment to the deep Sargasso Sea and implications for the rapid transfer of matter to the deep ocean. Deep-Sea Res. 28, 495–505.

de Boyer Montégut, C., Madec, G., Fischer, A.S., Lazar, A., Iudicone, D., 2004. Mixed layer depth over the global ocean: an examination of profile data and a profile-based climatology. J. Geophys. Res. 109, C12003.

Elmore, A.C., Thunell, R.C., Styles, R., Black, D., Murray, R.W., Martinez, N., Astor, Y., 2009. Quantifying the seasonal variations in fluvial and eolian sources of terrigenous material to Cariaco Basin, Venezuela. J. South Amer. Earth Sci. 27, 197–210, http://dx.doi.org/10.1016/j.jsames.2008.11.002.

Eppley, R.W., Peterson, B., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. Nature 282, 677–680.

Fowler, S.W., Knauer, G.A., 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Prog. Oceanogr. 16, 147–194.

Francois, R., Honjo, S., Krishfield, R., Manganini, S., 2002. Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean. Global Biogeochem. Cycles 16, 1087, http://dx.doi.org/10.1029/2001GB001722.

Gardner, W.D., Richardson, M.J., 1992. Particle export and resuspension fluxes in The Western North Atlantic. In: Rowe, G.T., Pariente, V. (Eds.), Deep-Sea Food Chains and the Global Carbon Cycle. Springer, Netherlands, pp. 339–364.

Gardner, W.D., 2000. Sediment trap technology and sampling in surface waters. In: Hanson, R.B., Ducklow, H.W., Field, J.G. (Eds.), The Changing Ocean Carbon Cycle: Midterm Synthesis of the Joint Global Ocean Flux Study. Cambridge University Press, Cambridge, pp. 240–281.

Goñi, M.A., Aceves, H.L., Thunell, R., Tappa, E., Black, D., Astor, Y., Varela, R., Muller-Karger, F., 2003. Biogenic Fluxes in the Cariaco Basin: a combined study of sinking particulates and underlying sediments. Deep-Sea Res. I 50, 781–807.

Hasle, S., 1978. The inverted microscope method. In: Sournia, A. (Ed.), Phytoplankton Manual. SCOR-UNESCO, pp. 337.

Hastings, D., Emerson, S., 1988. Sulfate reduction in the presence of low oxygen levels in the water column of the Cariaco Trench. Limnol. Oceanogr. 33, 391–396.

Haug, G.H., Hughen, K.A., Sigman, D.M., Peterson, L.C., Rohl, U., 2001. Southward migration of the intertropical convergence zone through the Holocene. Science 293, 1304–1308.

Hernes, P.J., Peterson, M.L., Murray, J.W., Wakeham, S.G., Lee, C., Hedges, J., 2001. Particulate carbon and nitrogen fluxes and compositions in the central equatorial Pacific. Deep-Sea Res. I 48, 1023–1999.

Honjo, S., Connell, J.F., Sachs, P.L., 1980. Deep-ocean sediment trap: design and function of PARFLUX Mark II. Deep-Sea Res. 27, 745–753.

Hughen, K.A., Overpeck, J.T., Peterson, L.C., Trumbore, S., 1996. Rapid climate changes in the tropical Atlantic region during the last deglaciation. Nature 380, 51–54.

Hughen, K.A., Eglinton, T.I., Xu, L., Makou, M., 2004. Abrupt tropical vegetation response to rapid climate changes. Science 304, 1955–1958.

Karl, D.M., Christian, J.R., Dore, J.E., Hebel, D.V., Letelier, R.M., Tupas, L.M., Winn, C.D., 1996. Seasonal and interannual variability in primary production and particle flux at Station ALOHA. Deep-Sea Res. II 43, 539–568.

Kerr, R.C., Kuiper, G.S., 1997. Particle settling through a diffusive-type thermohaline staircase in the ocean. Deep Sea Res. I 44, 399–412.

Knauer, G.A., Martin, J.H., Bruland, K.W., 1979. Fluxes of particulate carbon, nitrogen, and phosphorus in the upper water column of the northeast Pacific. Deep-Sea Res. 26A, 97–108.

Lande, R., Wood, A.M., 1987. Suspension times of particles in the upper ocean. Deep Sea Res. 34, 61–72.

Lidz, L., Charm, W.B., Ball, M.M., Valdes, S., 1969. Marine Basin off the coast of Venezuela. Bull. Mar. Sci. 19, 1–17.

Longhurst, A.R., Harrison, W.G., 1988. Vertical nitrogen flux from the oceanic photic zone by diel migrant zooplankton and nekton. Deep-Sea Res. 35, 881–889.

Lorenzoni, L., Thunell, R.C., Benitez-Nelson, C.R., Hollander, D., Martinez, N., Tappa, E., Varela, R., Astor, Y., Muller-Karger, F.E., 2009. The importance of subsurface nepheloid layers in transport and delivery of sediments to the eastern Cariaco Basin, Venezuela. Deep-Sea Res. I 56, 2249–2262.

Lorenzoni, L., Hu, C., Varela, R., Arias, G., Guzman, L., Muller-Karger, F., 2011. Bio-optical characteristics of Cariaco Basin (Caribbean Sea) waters. Cont. Shelf Res. 31, 582–593.

Martin, J., Knauer, G., Karl, D., Broenkow, W., 1987. VERTEX: carbon cycling in the northeast Pacific. Deep-Sea Res. 34, 267–286.

Martinez, N.C., Murray, R.W., Thunell, R.C., Peterson, L.C., Muller-Karger, F., Astor, Y., Varela, R., 2007. Modern climate forcing of terrigenous deposition in the tropics (Cariaco Basin, Venezuela). Earth Planet. Sci. Lett. 264, 438–451, http://dx.doi.org/10.1016/j.epsl.2007.10.002.

Mortlock, R., Froelich, P., 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep-Sea Res. 36, 1415–1426.

Muller-Karger, F.E., Varela, R., Thunell, R., Scranton, M., Bohrer, R., Taylor, G., Capelo, J., Astor, Y., Tappa, E., Ho, T.Y., Labichella, M., Walsh, J.J., Diaz, J.R., 2000. The CARIACO Project: understanding the link between the ocean surface and the sinking flux of particulate carbon in the Cariaco Basin. EOS. AGU Trans. 81, 529–535.

Muller-Karger, F., Varela, R., Thunell, R., Scranton, M., Bohrer, R., Taylor, G., Capelo, J., Astor, Y., Tappa, E., Ho, T.Y., Walsh, J.J., 2001. Annual cycle of primary production in the Cariaco Basin: response to upwelling and implications for vertical export. J. Geophys. Res. 106, 4527–4542.

Muller-Karger, F., Varela, R., Thunell, R., Astor, Y., Zhang, H., Luerssen, R., Hu, C., 2004. Processes of coastal upwelling and carbon flux in the Cariaco Basin. Deep-Sea Res. II 51, 927–943.

Muller-Karger, F.E., Varela, R., Thunell, R., Zhang, H., Hu, C., Walsh, J., 2005. The importance of continental margins in the global carbon cycle. Geophys. Res. Lett. 32, LO1602, http://dx.doi.org/10.1029/2004GL021346.

Muller-Karger, F.E., Varela, R., Thunell, R.C., Scranton, M.I., Taylor, G.T., Astor, Y., Benitez-Nelson, C.R., Lorenzoni, L., Tappa, E., Goñi, M.A., Rueda, D., Hu, C., 2010. The CARIACO oceanographic Time-Series. In: Liu, K.K., Atkinson, L., Quinones, R., Talaue-McManus, L. (Eds.), Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis. JGOFS Continental Margins Task Team (CMTT). Springer-Verlag, Berlin/Heidelberg.

Murray, J.W., Young, J., Newton, J., Dunne, J., Chapin, T., Paul, B., McCarthy, J., 1996. Export flux of particulate organic carbon from the central equatorial Pacific determined using a combined drifting trap-^{234}Th approach. Deep Sea Res. II 43, 1095–1132.

Pace, M., Knauer, G., Karl, D., Martin, J., 1987. Primary production, new production and vertical flux in the eastern Pacific Ocean. Nature 325, 803–804.

Perry, M.J., Sackmann, B.S., Eriksen, C.C., Lee, C.M., 2008. Seaglider observations of blooms and subsurface chlorophyll maxima off the Washington coast. Limnol. Oceanogr. 53, 2169–2179, http://dx.doi.org/10.4319/lo.2008.53.5_part_2.2169.

Peterson, L.C., Overpeck, J.T., Kipp, N.G., Imbrie, J., 1991. A high-resolution late quaternary upwelling record from the anoxic Cariaco Basin, Venezuela. Paleoceanography 6, 99–119.

Peterson, L.C., Haug, G.H., 2006. Variability in the mean latitude of the Atlantic Intertropical Convergence Zone as recorded by riverine input of sediments to the Cariaco Basin (Venezuela). Palaeogeogr. Palaeoclimatol. Palaeoecol. 234, 97–113.

Redfield, A.C., 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In: Daniel, R.J. (Ed.), James Johnstone Memorial Volume. University Press of Liverpool, pp. 177–192.

Richards, F.A., 1975. The Cariaco Basin (Trench). Oceanogr. Mar. Biol. Ann. Rev. 13, 11–67.

Schneider, B., Schlitzer, R., Fischer, G., Nothig, E.M., 2003. Depth dependent elemental compositions of particulate organic matter (POM) in the ocean. Global Biogeochem. Cycles 17, 1032, http://dx.doi.org/10.1029/2002GB001871.

Scranton, M.I., Astor, Y., Bohrer, R., Ho, T.Y., Muller-Karger, F.E., 2001. The effect of subsurface water mass intrusions on the geochemistry of the Cariaco Basin. Deep-Sea Res. 48, 1605–1625.

Small, L.F., Landry, M.R., Eppley, R.W., Azam, F., Carlucci, A.F., 1989. Role of plankton in the carbon and nitrogen budgets of the Santa Monica Basin, California. Mar. Ecol. Prog. Ser. 56, 57–73.

Stanley, R., Buesseler, K., Manganini, S., Steinberg, D., Valdes, J., 2004. A comparison of major and minor elemental fluxes collected in neutrally buoyant and surface-tethered sediment traps. Deep Sea Res. I 51, 1387–1395.

Steeman-Nielsen, E., 1952. The use of radio-active carbon (C^{14}) for measuring organic production in the sea. ICES J. Mar. Sci. 18, 117–140.

Steinberg, D.K., Carlson, C.A., Bates, N.R., Goldthwait, S.A., Madin, L.P., Michaels, A.F., 2000. Zooplankton vertical migration and the active transport of dissolved organic and inorganic carbon in the Sargasso Sea. Deep-Sea Res. I 47, 137–158.

Steinberg, D.K., Goldthwait, S.A., Hansell, D.A., 2002. Zooplankton vertical migration and the active transport of dissolved organic and inorganic nitrogen in the Sargasso Sea. Deep Sea Res. I 49, 1445–1461.

Suess, E., 1980. Particulate organic carbon flux in the oceans-surface productivity and oxygen utilization. Nature 228, 260–263.

Taylor, G.T., Thunell, R., Varela, R., Benitez-Nelson, C., Scranton, M.I., 2009. Hydrolytic ectoenzyme activity associated with suspended and sinking organic particles within the anoxic Cariaco Basin. Deep-Sea Res. I 56, 1266–1283.

Tedesco, K.A., Thunell, R.C., 2003. Seasonal and interannual variations in planktonic foraminiferal flux and assemblage composition in the Cariaco Basin, Venezuela. J. Foraminiferal Res. 33, 192–210.

Tedesco, K.A., Thunell, R., Astor, Y., Muller-Karger, F.E., 2007. The oxygen isotope composition of planktonic foraminifera from the Cariaco Basin, Venezuela: seasonal and interannual variations. Mar. Micropaleontol. 62, 180–193.

Thunell, R., Varela, R., Llano, M., Collister, J., Muller-Karger, F.E., Bohrer, R., 2000. Organic carbon fluxes, degradation, and accumulation in an anoxic basin: sediment trap results from the Cariaco Basin. Limnol. Oceanogr. 45, 300–308.

Thunell, R., Sigman, D., Muller-Karger, F., Astor, Y., Varela, R., 2004. Nitrogen isotopes dynamics of the Cariaco Basin, Venezuela. Global Biogeochem. Cycles 18, GB3001, http://dx.doi.org/10.1029/2003GB002185.

Thunell, R., Benitez-Nelson, C., Varela, R., Astor, Y., Muller-Karger, F., 2007. Particulate organic carbon fluxes along upwelling-dominated continental margins: rates and mechanisms. Global Biogeochem. Cycles 21, GB1022, http://dx.doi.org/10.1029/2006GB002793.

Thunell, R., Benitez-Nelson, C., Muller-Karger, F., Lorenzoni, L., Fanning, K., Scranton, M., Varela, R., Astor, Y., 2008. Si cycle in the Cariaco Basin, Venezuela: seasonal variability in silicate availability and the Si:C:N composition of sinking particles. Global Biogeochem. Cycles 22, GB4001, http://dx.doi.org/10.1029/2007GB003096.

Volk, T., Liu, Z., 1988. Controls of CO_2 sources and sinks in the Earth scale surface ocean: temperature and nutrients. Global Biogeochem. Cycles 2, 73–89.

Wishner, K.F., Gelfman, C., Gowing, M.M., Outram, D.M., Rapien, M., Williams, R.L., 2008. Vertical zonation and distributions of calanoid copepods through the lower oxycline of the Arabian Sea oxygen minimum zone. Prog. Oceanogr. 78, 163–191.

Zhang, J.Z., Millero, J.J., 1993. The chemistry of anoxic waters in the Cariaco Trench. Deep Sea Res. I 40, 1023–1041.