



Radionuclide fluxes and particle scavenging in Cariaco Basin

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Abstract

²³⁴Th, ²²⁸Th and ²¹⁰Pb fluxes were measured in a series of sediment trap samples in Cariaco Basin from November 1995 to 8 May 1996. Sediment traps were located at 275, 455, 930 and 1255 m depth, with the 275 m trap just above the oxic/anoxic interface. Total mass, organic carbon, carbonate, biogenic opal, and lithogenic fluxes were also determined. Our results found that ²³⁴Th, ²²⁸Th and ²¹⁰Pb fluxes are highly correlated with total mass ($r^2 = 0.92 - 0.94$), major sediment component fluxes ($r^2 = 0.82 - 0.93$), and one another ($r^2 = 0.94 - 0.99$). Decreases in radionuclide, total mass and major sediment component fluxes with depth were attributed to physical disaggregation and remineralization. While the ²¹⁰Pb specific activity loss from settling particles is the same as the bulk specific activity of the trapped particles between 455 and 930 m, the ²¹⁰Pb specific activity loss is substantially higher than the bulk specific activity of the trapped particles between 930 and 1255 m. We attributed this fractionation to a loss of minor components from settling particles. This suggests that minor components are responsible for the initial water column scavenging of ²¹⁰Pb in the Cariaco Basin. Steady state release of ²¹⁰Pb from settling particles would produce an anoxic water column activity an order of magnitude greater than previously reported. Therefore, a non-steady state removal mechanism must exist and is potentially caused by high sediment flux events from earthquake triggered turbidity currents or major plankton blooms.

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1. Introduction

The oceans play a major role in the removal and sequestration of atmospheric CO₂. The magnitude of this uptake is partially influenced by the

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biological ‘pump’, i.e. the uptake of atmospheric CO₂ by phytoplankton during primary production and its subsequent removal to depth via sinking particles. Only a small fraction of these sinking particles reach the seafloor and are buried, thereby storing carbon over geologic time scales. The Cariaco Basin remains permanently anoxic below 275 m. This has made it an almost perfect setting for understanding organic carbon (OC) preservation over the last 12,000 years and for understanding how modern processes are reflected and preserved in the underlying sediments (Hughen et al., 1996a,b; Black et al., 1999; Peterson et al., 1991; Werne et al., 2000; Muller-Karger et al., 2001). One of the key missing parameters in linking modern day processes to the geologic sedimentary record is the alteration that occurs to particles as they sink through the water column (e.g. Goni et al., 2003). Although the anoxic conditions of Cariaco Basin enhance preservation, there are still a number of important reaction mechanisms that occur as particles sink through the oxic/anoxic interface, such as the redox cycling of Mn and Fe, and the precipitation of metallic sulfides.

The goal of the present study is to use a suite of radioisotopes to understand particle scavenging throughout the water column of the Cariaco Basin. The three naturally occurring particle-reactive radionuclides ²³⁴Th, ²²⁸Th, and ²¹⁰Pb are particularly useful because they allow for the investigation of particle sources, formation, and sinking over a range of time periods. ²³⁴Th ($t_{1/2} = 24.1$ d) is produced from the radioactive decay of ²³⁸U, a conservative element in seawater (Chen et al., 1986). The combination of its short half-life and high particle reactivity has made ²³⁴Th an excellent tracer of water column particle formation and export on biologically driven time scales (e.g. Buesseler, 1998). ²²⁸Th (produced via ²²⁸Ra decay, $t_{1/2} = 1.91$ yr) and ²¹⁰Pb (produced via water column ²²⁶Ra decay and atmospheric deposition, $t_{1/2} = 22.3$ yr) have also been used to trace particle export, but over annual to decadal timescales (Moore and Dymond, 1988; Luo et al., 1995).

There have been only a few radionuclide studies within anoxic systems (Bacon et al., 1980; Todd et

al., 1986; Wei and Murray, 1991, 1994; Sarin et al., 1994a,b; Swarzenski et al., 1999). Nonetheless, they have provided vital information regarding particle scavenging across the oxic/anoxic interface and the role of metal oxides. In this study, we analyzed a series of sediment traps for ²³⁴Th, ²²⁸Th, and ²¹⁰Pb in order to evaluate the processes that control the removal of particle reactive elements.

2. Study area and methods

The Cariaco Basin is currently the focus of the CARbon Retention In A Colored Ocean (CAR-IACO) time series program, a cooperative United States-Venezuelan research project (Muller-Karger et al., 2001). Located on the Venezuelan continental shelf (Fig. 1a), the Cariaco Basin spans 160 km × 40 km and has a maximum depth of about 1400 m. It is divided into two sub-basins by a saddle at about 900 m. The basin is isolated from the rest of the Caribbean by a 150 m deep sill connecting Isla Margarita to Cabo Codera on the Venezuelan mainland. Vertical mixing within this isolated basin is prevented by a strong pycnocline that inhibits exchange of deep water. Decomposition of sinking organic material has led to permanent anoxia below about 275 m (Richards, 1975).

Sinking particles were collected using four automated sediment traps placed on a single mooring (10° 30' N and 64° 40' W), with each collecting 13 sequential two-week long samples (Honjo and Doherty, 1988). The traps have a 0.5 m² collection area covered with a baffle to reduce turbulence over the trap. Trap cups were poisoned with a buffered formalin solution prior to deployment. The sediment traps were placed at 275 (Trap A), 455 (Trap B), 930 (Trap C) and 1255 m (Trap D) in a water depth of approximately 1400 m (Fig. 1b). The uppermost trap is positioned just above the oxic/anoxic interface. Radionuclide data for a 6-month deployment from 8 November 1995 to 8 May 1996 are presented here.

A quarter split of each sample was used for radionuclide analysis. Samples were rinsed with

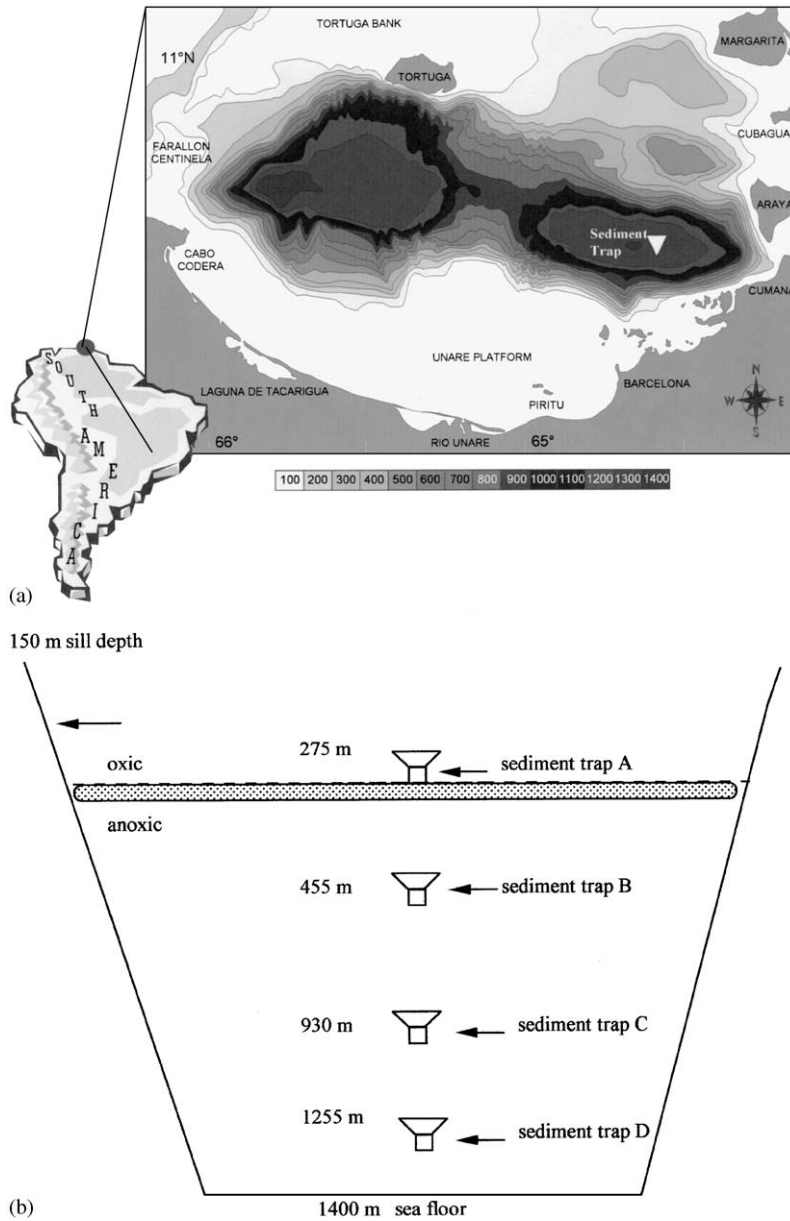


Fig. 1. (a) Map of the Cariaco Basin with sediment trap mooring site shown. (b) Cross section of basin with traps and oxic/anoxic boundary shown.

deionized water to remove salts, centrifuged, and the supernatant discarded. The remaining particles were then dried in an oven at 60 °C. After drying, samples were weighed to determine total particulate flux and ground to a fine powder. A portion of each ground sample was packed into a reprodu-

cible sample geometry within a 3-dram (20 ml) vial.

^{234}Th , ^{228}Th and ^{210}Pb activities were measured with an intrinsic well germanium detector. ^{234}Th and ^{210}Pb were determined from direct photopeaks at 63.3, and 46.5 keV, respectively. ^{228}Th was

Table 1

Radionuclide, total mass and individual major component flux data for the Cariaco Basin. Missing data points are due to low mass in some samples and/or decay of ^{234}Th between collection and gamma counting

Mid point	^{234}Th flux (dpm m ⁻² d ⁻¹)	^{228}Th flux (dpm m ⁻² d ⁻¹)	^{210}Pb flux (dpm m ⁻² d ⁻¹)	Total mass flux (g m ⁻² d ⁻¹)	Org. carbon flux (g m ⁻² d ⁻¹)	Carbonate flux (g m ⁻² d ⁻¹)	Opal flux (g m ⁻² d ⁻¹)	Lithogenic flux (g m ⁻² d ⁻¹)
(a) Trap A (275m)								
15-Nov-95	1623 ± 139	4.37 ± 0.12	34.6 ± 0.69	0.478	0.04	0.067	0.072	0.239
29-Nov-95	1015 ± 107	2.26 ± 0.12	18.7 ± 0.48	0.318	0.038	0.045	0.063	0.115
13-Dec-95	718 ± 77	2.10 ± 0.17	20.4 ± 0.84	0.316	0.037	0.078	0.049	0.097
27-Dec-95		0.50 ± 0.06	5.5 ± 0.61	0.078	0.012	0.017	0.013	0.018
10-Jan-96	265 ± 23	0.99 ± 0.12	7.5 ± 0.55	0.124	0.024	0.017	0.014	0.033
24-Jan-96	754 ± 39	2.02 ± 0.14	16.8 ± 0.79	0.303	0.031	0.032	0.04	0.154
7-Feb-96	2969 ± 135	11.09 ± 0.73	90.2 ± 3.27	1.645	0.114	0.147	0.192	1.021
21-Feb-96	1313 ± 29	3.13 ± 0.24	27.2 ± 0.95	0.599	0.059	0.043	0.104	0.305
6-Mar-96				1.122	0.113	0.072	0.219	0.549
20-Mar-96	4101 ± 66	20.72 ± 0.94	142.6 ± 3.71	1.749	0.168	0.17	0.231	0.928
3-Apr-96	783 ± 18	2.25 ± 0.30	21.1 ± 1.35	0.435	0.062	0.041	0.057	0.182
17-Apr-96	640 ± 11	1.74 ± 0.15	17.0 ± 0.87	0.387	0.045	0.046	0.065	0.164
30-Apr-96								
(b) Trap B (455 m)								
15-Nov-95	1431 ± 219	3.95 ± 0.15	33.2 ± 0.89	0.475	0.039	0.067	0.058	0.253
29-Nov-95	707 ± 98	2.49 ± 0.12	19.5 ± 0.54	0.344	0.037	0.048	0.063	0.141
13-Dec-95		1.73 ± 0.15	17.1 ± 0.65	0.266	0.029	0.06	0.037	0.097
27-Dec-95		1.39 ± 0.17	7.9 ± 0.74	0.097	0.012	0.023	0.013	0.031
10-Jan-96		1.30 ± 0.19	10.7 ± 0.75	0.121	0.014	0.024	0.014	0.048
24-Jan-96	961 ± 65	3.72 ± 0.21	26.6 ± 1.21	0.387	0.037	0.062	0.055	0.178
7-Feb-96	3347 ± 65	12.97 ± 0.27	98.0 ± 1.69	1.543	0.104	0.16	0.172	0.951
21-Feb-96	1795 ± 71	6.08 ± 0.41	43.1 ± 2.95	0.693	0.074	0.067	0.128	0.313
6-Mar-96				1.309	0.149	0.122	0.28	0.535
20-Mar-96	3048 ± 66	13.04 ± 0.47	90.1 ± 2.46	1.166	0.138	0.126	0.0189	0.506
3-Apr-96	1147 ± 29	5.01 ± 0.28	40.2 ± 1.76	0.55	0.075	0.057	0.069	0.237
17-Apr-96	950 ± 21	3.01 ± 0.38	19.7 ± 2.43	0.447	0.077	0.041	0.093	0.121
30-Apr-96	179 ± 15			0.157	0.032	0.005	0.028	0.044

(c) Trap C (930 m)								
15-Nov-95		2.97 ± 0.16	27.1 ± 0.79	0.422	0.035	0.045	0.054	0.236
29-Nov-95		2.26 ± 0.17	17.8 ± 0.63	0.283	0.03	0.037	0.05	0.121
13-Dec-95		1.31 ± 0.16	7.4 ± 0.73	0.133	0.017	0.028	0.019	0.044
27-Dec-95			2.8 ± 0.29	0.04	0.008	0.007	0.004	0.009
10-Jan-96			2.9 ± 0.47	0.042	0.009	0.005	0.003	0.012
24-Jan-96	152 ± 33	0.76 ± 0.08	7.6 ± 0.49	0.097	0.015	0.011	0.013	0.036
7-Feb-96	1120 ± 115	4.87 ± 0.29	36.8 ± 1.87	0.664	0.053	0.042	0.078	0.412
21-Feb-96	395 ± 34	1.31 ± 0.12	10.9 ± 0.54	0.196	0.026	0.012	0.039	0.08
6-Mar-96	1184 ± 50	4.20 ± 0.19	31.9 ± 1.17	0.455	0.063	0.019	0.094	0.185
20-Mar-96	808 ± 37	3.17 ± 0.22	23.8 ± 0.87	0.302	0.044	0.006	0.061	0.125
3-Apr-96	377 ± 17	1.75 ± 0.15	14.8 ± 0.77	0.172	0.027	0.002	0.024	0.079
17-Apr-96	394 ± 16	1.23 ± 0.12	9.8 ± 1.06	0.169	0.032	0.002	0.033	0.054
30-Apr-96	325 ± 14	1.92 ± 0.21	14.3 ± 1.14	0.191	0.026	0.011	0.023	0.092
(d) Trap D (1255 m)								
15-Nov-95		1.87 ± 0.14	16.6 ± 1.17	0.39	0.032	0.045	0.051	0.214
29-Nov-95		0.74 ± 0.10	6.3 ± 0.40	0.238	0.028	0.029	0.045	0.094
13-Dec-95		1.14 ± 0.13	9.1 ± 0.79	0.117	0.014	0.024	0.015	0.043
27-Dec-95		0.10 ± 0.02	0.3 ± 0.05	0.029	0.006	0.004	0.002	0.008
10-Jan-96				0.019	0.004	0.002		0.007
24-Jan-96		0.12 ± 0.02	0.9 ± 0.07	0.04	0.008	0.003	0.003	0.014
7-Feb-96	254 ± 28	1.10 ± 0.06	8.8 ± 0.30	0.354	0.029	0.026	0.038	0.218
21-Feb-96		0.29 ± 0.05	2.9 ± 0.22	0.114	0.015	0.007	0.022	0.048
6-Mar-96	252 ± 24	1.10 ± 0.07	6.9 ± 0.37	0.262	0.034	0.013	0.049	0.115
20-Mar-96	122 ± 13	0.58 ± 0.06	4.2 ± 0.36	0.165	0.023	0.007	0.031	0.07
3-Apr-96	27 ± 5		0.9 ± 0.10	0.096	0.017	0.003	0.011	0.04
17-Apr-96	183 ± 15	0.51 ± 0.07	4.6 ± 0.41	0.11	0.02	0.007	0.02	0.033
30-Apr-96	65 ± 10	0.50 ± 0.11		0.097	0.014	0.007	0.011	0.044

determined using its radioactive daughter ^{212}Pb , which has a photopeak at 238.6 keV. Measured counts per minute were converted to disintegrations per minute (dpm) using standards of known activities packed in similar geometry (Moore, 1984; Thunell et al., 1994; Smoak et al., 1999; Smoak et al., 2000). ^{234}Th and ^{228}Th activities were corrected for decay to the midpoint of sample collection. Specific activities (dpm g^{-1}) measured in the vials were multiplied by the mass fluxes ($\text{g m}^{-2}\text{d}^{-1}$) to yield the radionuclide fluxes ($\text{dpm m}^{-2}\text{d}^{-1}$). All errors were determined from counting statistics.

After non-destructive gamma counting, samples were analyzed for OC, carbonate, biogenic opal, and lithogenic content. OC content was determined with a Perkin–Elmer 2400 CHN Elemental Analyzer by the Froelich (1980) procedure. Carbonate content was measured with an automated computer-controlled system in which samples are reacted under vacuum in 100% phosphoric acid and the resultant CO_2 is measured by a pressure transducer (Osterman et al., 1990). Opaline silica analyses were determined using a wet chemical leaching technique (Mortlock and Froelich, 1989). Lithogenic content was estimated by subtracting the weights of the biogenic components (carbonate, opal, and organic matter) from the total mass. Organic matter was estimated to be 2.5 times the OC content (Thunell, 1998). The percent determinations of OC, carbonate, and biogenic opal were approximately 5%. Percentages of the individual components were multiplied by the mass flux to calculate the component flux.

3. Results and discussion

Radionuclide, total mass and individual major component fluxes are shown in Table 1. Correlations (r^2) among all three radionuclide fluxes and all of the major sediment component fluxes, including total mass, were always high ranging from 0.82 to 0.99 (Table 2). In contrast, there was no significant correlation ($r^2 < 0.1$) between specific activity and the major component fluxes, including mass. The strong correlations among all three radionuclide fluxes indicate similar mechanisms of

Table 2
Cariaco Basin flux correlation coefficients (r^2)

	^{234}Th	^{228}Th	^{210}Pb
^{234}Th	1	0.94	0.96
^{228}Th	0.94	1	0.99
^{210}Pb	0.96	0.99	1
Total mass	0.93	0.92	0.94
Organic carbon	0.90	0.90	0.89
Carbonate	0.89	0.84	0.86
Opal	0.93	0.86	0.89
Lithogenic	0.82	0.83	0.88

All values are significant ($P < 0.05$).

removal from the water column. The excellent correlation between radionuclide fluxes and major sediment trap component fluxes further suggests that the flux of these components controls the temporal variability in the radionuclide flux. The radionuclide flux increase is due to increased particle export caused by enhanced primary production during the upwelling season. Interannual variability has been shown previously by Thunell et al. (2000) and Goni et al. (2003).

The traps for each collection period have a general trend of decreasing radionuclide flux, total mass flux, and major component fluxes with depth (Table 3a–c; Figs. 2a–c). The reduction in total mass flux and major sediment component fluxes may occur by either physical disaggregation (abiotic) or remineralization (biotic) of the settling particles. These two processes may also occur in concert where remineralization of biogenic components, that are important in the aggregation of settling particles (Alldredge and Jackson, 1995), results in the disaggregation of particles to the suspended phase. This provides a mechanism for the decrease in the lithogenic flux, as the lithogenic material would not easily be remineralized.

During several sampling periods, the radionuclide flux measured at 455 m exceeded the flux from the 275 m trap. This typically occurred with an increase in the mass flux. The two deeper traps always had lower fluxes than the upper traps and the deepest trap, 1250 m, always had the lowest flux except for a single ^{210}Pb flux during the first collection period of December, when the flux at 930 m was slightly lower. The mismatch between

Table 3

(a) Average radionuclide flux and specific activity data

Trap (depth)	^{234}Th flux ($\text{dpm m}^{-2} \text{d}^{-1}$)	^{228}Th flux ($\text{dpm m}^{-2} \text{d}^{-1}$)	^{210}Pb flux ($\text{dpm m}^{-2} \text{d}^{-1}$)	^{234}Th (dpm g^{-1})	^{228}Th (dpm g^{-1})	^{210}Pb (dpm g^{-1})
Trap A (275 m)	1418	4.65	36.5	2251	7.38	57.9
Trap B (455 m)	1338	4.97	36.9	2307	8.57	63.6
Trap C (930 m)	595	2.34	16.0	2479	9.75	66.7
Trap D (1255 m)	151	0.73	5.6	944	4.56	35.0

(b) Average total mass, organic carbon, carbonate, opal and lithogenic flux data

Trap (depth)	Total mass ($\text{g m}^{-2} \text{d}^{-1}$)	Org. carbon ($\text{g m}^{-2} \text{d}^{-1}$)	Carbonate ($\text{g m}^{-2} \text{d}^{-1}$)	Opal ($\text{g m}^{-2} \text{d}^{-1}$)	Lithogenic ($\text{g m}^{-2} \text{d}^{-1}$)
Trap A (275 m)	0.63	0.06	0.07	0.09	0.32
Trap B (455 m)	0.58	0.06	0.07	0.09	0.27
Trap C (930 m)	0.24	0.03	0.02	0.04	0.11
Trap D (1255 m)	0.16	0.02	0.01	0.03	0.07

(c) Loss of total mass and individual major sediment components between sediment traps.

Trap	Total mass ($\text{mg m}^{-3} \text{d}^{-1}$)	Org. carbon ($\text{mg m}^{-3} \text{d}^{-1}$)	Carbonate ($\text{mg m}^{-3} \text{d}^{-1}$)	Opal ($\text{mg m}^{-3} \text{d}^{-1}$)	Lithogenic ($\text{mg m}^{-3} \text{d}^{-1}$)
A to B	0.28	0.00	0.00	0.00	0.28
B to C	0.72	0.06	0.11	0.11	0.34
C to D	0.25	0.03	0.03	0.03	0.12

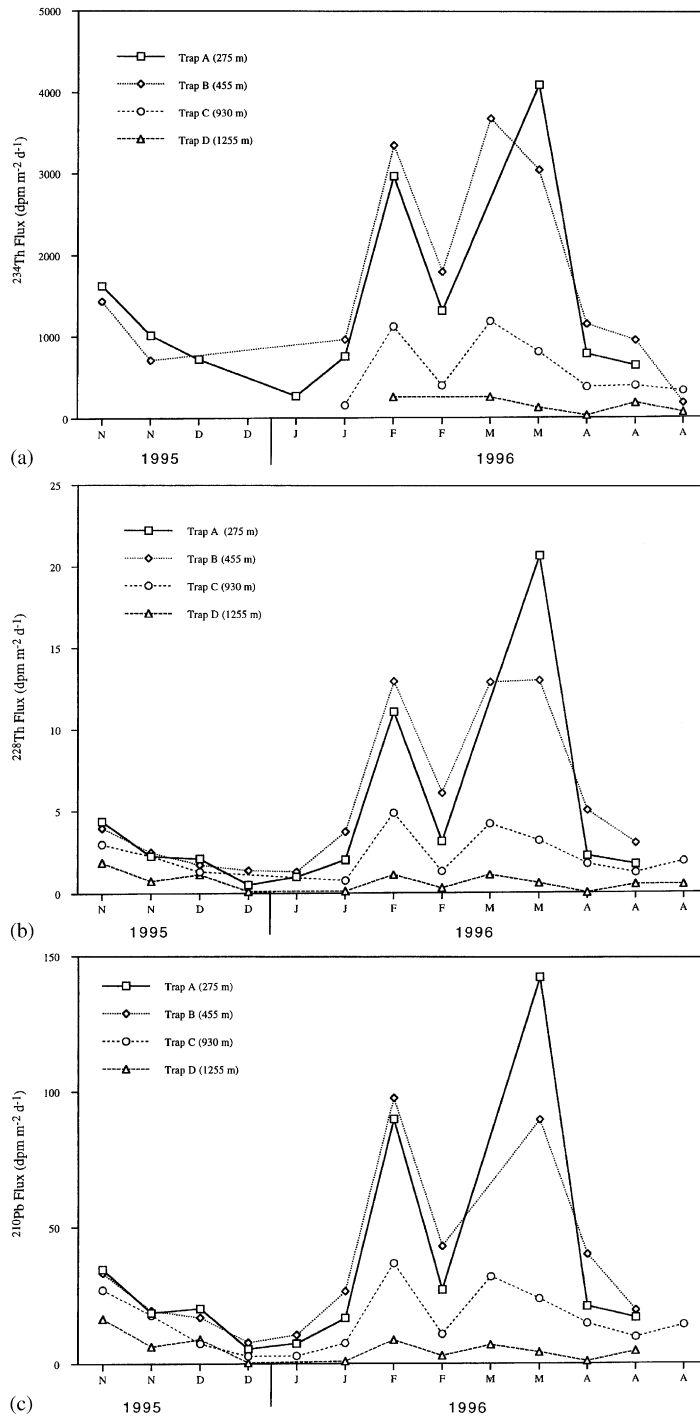


Fig. 2. Time-series records of (a) ²³⁴Th, (b) ²²⁸Th and (c) ²¹⁰Pb flux for the period November 1995 to May 1996.

the 275 m and the 455 m sediment traps has also been observed in organic carbon, opal and carbonate in ~30% of the sediment trap samples that have been collected in Cariaco Basin since 1995 (Goni et al., 2003). This mismatch may be due to lateral advection of oxygenated waters (Astor et al., 2003), in situ production by chemoautotrophic bacteria at the oxic/anoxic interface (Taylor et al., 2001), potential analytical issues associated with upper-ocean (<1500 m) sediment traps (Baker et al., 1988; Buesseler, 1991; Scholten et al., 2001; Yu et al., 2001), production via migrating zooplankton (Wilson, 1972; Baird et al., 1973) or sediment focusing associated with lateral advection (Smoak et al., 2000). Unfortunately, the lack of water column radionuclide measurements does not allow us to distinguish between the possibilities.

Closer examination of the relationship among mass and radionuclide flux with depth shows that while the overall correlations are strong, the slope decreases substantially between the upper three traps and the deepest trap (Table 4). This indicates a change in the removal efficiency of the particles and possible fractionation between the radionuclide material lost and the radionuclide material remaining as part of the flux. To examine this loss further, we calculated the amount of sinking particulate ^{210}Pb activity lost between the three deepest traps. ^{210}Pb is used in this comparison because the best data record exists for ^{210}Pb , and decay is not a factor. Although Pb and Th are different chemically, because of the strong correlations among the radionuclides, we hypothesize that the trends observed for ^{210}Pb are also applicable to ^{234}Th and ^{228}Th .

In order to determine the magnitude of the ^{210}Pb lost between each trap we calculated an average

^{210}Pb flux over the six-month collection period (Table 3a) and used the gradient to determine the average ^{210}Pb lost. We use the average because it represents the sum of ^{210}Pb loss on a per day basis over the study period. Our results show that $20.9 \text{ dpm m}^{-2} \text{ d}^{-1}$ is lost from the flux between 455 and 930 m. Dividing $20.9 \text{ dpm m}^{-2} \text{ d}^{-1}$ by the change in depth between the two traps (475 m) results in an activity loss of $0.044 \text{ dpm m}^{-3} \text{ d}^{-1}$. A similar calculation for the total mass loss yields $0.72 \text{ mg m}^{-3} \text{ d}^{-1}$ (Table 3c). The specific activity loss of ^{210}Pb from sinking particles of 61 dpm g^{-1} was calculated by dividing the ^{210}Pb activity loss by the total mass loss. Our results are similar to the average specific activity of the trapped particles (64 dpm g^{-1} at 455 m and 67 dpm g^{-1} at 930 m) and implies that above 930 m, the specific activity loss is simply a portion of the bulk specific activity of the settling particles or very close to the bulk specific activity. This suggests that there is little or no fractionation in ^{210}Pb particle remineralization above 930 m.

Using the same calculation as above, the activity loss between 930 and 1250 m was $0.032 \text{ dpm m}^{-3} \text{ d}^{-1}$ with a mass loss of $0.25 \text{ mg m}^{-3} \text{ d}^{-1}$ (Table 3c). The specific activity ^{210}Pb loss of 128 dpm g^{-1} is twice that between 455 and 930 m, and is much higher than the specific activity of the particles caught in either trap of the 930 and 1250 m traps (67 dpm g^{-1} and 35 dpm g^{-1} , respectively). This suggests that a portion of the sinking particles remineralized or disaggregated between the two traps is fundamentally different from the bulk specific activity that was lost and that this fraction has a substantially higher specific activity than bulk settling particles. Therefore, between 930 and 1255 m substantial fractionation does occur. This fractionation occurs between 930 and 1255 m despite the greater loss of total mass,

Table 4
Linear curve fit slope of ^{210}Pb flux versus total mass, organic carbon, carbonate, opal and lithogenic flux

Trap (depth)	Total mass	Org. carbon	Carbonate	Opal	Lithogenic
Trap A (275 m)	71 (0.93)	900 (0.95)	792 (0.91)	580 (0.92)	113 (0.87)
Trap B (455 m)	68 (0.97)	682 (0.78)	710 (0.93)	475 (0.85)	108 (0.89)
Trap C (930 m)	59 (0.95)	621 (0.86)	422 (0.36)	364 (0.88)	90 (0.85)
Trap D (1255 m)	33 (0.72)	352 (0.50)	322 (0.87)	199 (0.56)	53 (0.67)

Correlation coefficients (r^2) shown in parentheses.

organic carbon, carbonate, opal and lithogenic components happening between 455 and 930 m (Table 3c). Use of median ^{210}Pb flux and mass flux, instead of average flux, increases the observed fractionation slightly. Our results suggest that minor components are thus responsible for the greater release of ^{210}Pb between 930 and 1255 m and for the initial scavenging of ^{210}Pb from the water column. A similar change in removal efficiency that was unrelated to either total mass or major component fluxes was also observed by Smoak et al. (1999) in Guaymas Basin, Gulf of California.

One possible explanation for the observed fractionation is the highly efficient removal of particle-reactive radionuclides by minor biogenically derived compounds. Several studies have shown a strong correlation with the concentrations of particle-reactive species and organic matter in coastal marine sediments (Calvert and Price, 1970; Bruland et al., 1974) and open ocean sediment traps (Moore and Dymond, 1988). Still, other studies indicate the ubiquitous presence of organic films on marine particles (Neihof and Loeb, 1972, 1974; Loeb and Neihof, 1977; Hunter and Liss, 1979, 1982; Hunter, 1980) whose surface functional groups provide sites with a high binding efficiency for particle-reactive radionuclides. Recently, exopolymers released by certain phytoplankton have been shown to have high removal efficiencies of ^{234}Th (Niven et al., 1995; Guo et al., 2002; Quigley et al., 2002). Therefore, sinking particles may scavenge radionuclides by binding with surface functional groups of the biogenic components, organic coatings and exopolymers. Preferential remineralization of this material would release the particle-reactive radionuclides without a corresponding loss in total mass or individual major components.

Another possible, but unlikely explanation for the ^{210}Pb fractionation, is preferential associations with specific mineral phases, such as Fe and Mn oxides. Although there have been only a few radionuclide studies within anoxic systems, several attribute low activities just above the oxic/anoxic interface followed by high radionuclide activities below, to the formation and remineralization of Mn and Fe oxides. These features have been found

in Cariaco Basin (Bacon et al., 1980), the Black Sea (Wei, 1990; Wei and Murray, 1991), and the Orca Basin, Gulf of Mexico (Todd et al., 1986). Therefore, fractionation may be the result of sinking Mn and Fe oxides that have high capacities to adsorb ^{210}Pb . This scavenging would increase the bulk ^{210}Pb activity of the settling particles. As the particles sink through the water column, Mn and Fe are reduced, releasing the high activity particulate portion into the dissolved phase. Although possible, we hypothesize that this mechanism of ^{210}Pb remineralization at depth is minor given that it occurs well below the oxic/anoxic interface where such processes are thought to occur. If Mn and Fe oxides are important, we would expect to find large dissolution and release of ^{210}Pb activity between 275 and 450 m, and not between 450 and 930 m. Dissolved and particulate profiles of Mn and Fe from Cariaco Basin further demonstrate that the major zone of oxide dissolution is above 455 m (Bacon et al., 1980).

Regardless, neither of the above explanations explains why the release of high activity material is delayed (i.e., occurs between 930 and 1255 m and not between 455 and 930 m). One explanation for the delay in apparent fractionation is the simultaneous loss of minor components with total mass and individual major components between 455 and 930 m, i.e. the fractionation effect is masked. As particles sink further in the water column, the minor components that contain higher radionuclide activities are lost, but relatively less total mass and the major individual components (Table 3c), thus making fractionation more easily observed.

A mechanism of particle-reactive radionuclide removal that may be eliminated as a factor in this environment is the removal by sulfides. Bacon et al. (1980) suggested that formation of sulfides in the anoxic waters of the Cariaco Basin was a carrier phase for ^{210}Pb . If correct, sulfides should be more important for Pb than Th due to their respective reactivity. However, there is a strong correlation among all the radionuclide fluxes, Pb and Th alike. Furthermore, the specific activity of particulate ^{210}Pb does not show an increase in the anoxic region where the sulfides would form and

finally, sulfides would not be released at depth. While we agree that sulfides may remove ^{210}Pb from the dissolved phase, they are not responsible for the flux during the course of this study, and are therefore, not responsible for the observed fractionation.

We can determine the total release of particulate ^{210}Pb to the anoxic waters of Cariaco Basin by determining the ^{210}Pb activity loss between traps 455 and 1255 m as calculated above. The ^{210}Pb flux loss between 455 and 1255 m is $30.9 \text{ dpm m}^{-2} \text{ d}^{-1}$ or $0.039 \text{ dpm m}^{-3} \text{ d}^{-1}$. This is equivalent to the addition of $1.4 \text{ dpm } ^{210}\text{Pb } 100 \text{ L}^{-1} \text{ yr}^{-1}$ to the anoxic waters of Cariaco Basin in the form of suspended and/or dissolved ^{210}Pb activity. Several studies have determined deep water residence times in Cariaco Basin of 70–800 years (e.g. Richards 1975). Zhang and Millero (1993) suggested that the last major flushing event of deep waters had occurred in 1915. Combining the water column addition of $1.4 \text{ dpm } 100 \text{ L}^{-1} \text{ yr}^{-1}$ and the removal of ^{210}Pb via radioactive decay between 1915 and 1971, the year Bacon et al. (1980) first collected ^{210}Pb water column samples, leads to a total suspended and dissolved ^{210}Pb activity of approximately $35 \text{ dpm } 100 \text{ L}^{-1}$. This is an order of magnitude higher than the $2.3 \text{ dpm } 100 \text{ L}^{-1}$ measured by Bacon et al. (1980) in the anoxic waters.

It is possible that some of the order of magnitude difference between the Bacon et al. (1980) value and that determined here is due to periodic intrusions of water masses from outside the basin (Astor et al., 2003; Scranton et al., 2001; Holmen and Rooth, 1990). However, it is unlikely that these intrusions are large enough in scale to completely account for the difference. Furthermore, there was no evidence that such intrusions occurred during the course of our study (Astor et al., 2003). Another possibility is that the cycling of ^{210}Pb is not in steady state. One scenario for non steady state is that the addition of ^{210}Pb during the months sampled in this study is balanced by the large scale removal during the remainder of the year (i.e., seasonal timescale differences). The removal also might occur during higher sediment flux events. Although not observed during this study, an extremely high flux event occurred in July 1997 due to an earthquake

triggered turbidity current (Thunell et al., 1999). The sediment flux increased by greater than 50 fold during the earthquake event. Therefore, the ^{210}Pb in the anoxic waters of Cariaco Basin may not be in steady state, but rather maintained by periodic high sediment flux events.

4. Conclusion

There is no observed difference between the initial removal of Pb and Th in the Cariaco Basin. The radionuclide fluxes determined for all four depths in the basin correlate well with each other and with the total mass and major sediment component fluxes. The strong correlations among the radionuclides and the major sediment components prevent the relative importance of each major component from being distinguished in surface waters.

A decrease in radionuclide, total mass and major sediment component fluxes with depth was observed. The decrease in flux is caused by physical disaggregation and remineralization of the sinking particles. The ^{210}Pb activity loss from the flux between 455 and 930 m may be explained by a simple decrease in the mass flux. However, between 930 and 1255 m the ^{210}Pb activity loss is substantially higher than the bulk activity of these particles. This fractionation of ^{210}Pb results from the loss of minor components, most likely associated with biological activity. The loss of these minor components represents a very small decrease in mass but a high specific activity loss, resulting in large changes in the bulk activity that reaches the seafloor. These results have important repercussions for those trying to use specific compounds in sediments as tracers of upper ocean chemistry.

The ^{210}Pb loss from settling particles supplies substantial activity to the anoxic waters during the six month period of this study. A steady state ^{210}Pb addition would have produced an anoxic water column activity an order of magnitude greater than previously observed by Bacon et al. (1980). Therefore there must be a mechanism other than decay to remove ^{210}Pb from the anoxic waters during other time periods. This mechanism is

possibly due to the occurrence of higher sediment flux events such as earthquake triggered turbidity currents and further indicates that ^{210}Pb in the anoxic waters is not in steady state.

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