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^{228}Th - ^{228}Ra RADIOACTIVE DISEQUILIBRIUM IN THE NEW YORK BIGHT AND ITS IMPLICATIONS FOR COASTAL POLLUTION

YUAN-HUI LI, HERBERT W. FEELY¹ and PETER H. SANTSCHI

Lamont-Doherty Geological Observatory of Columbia University, Palisades, NY 10964 (U.S.A.)

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In the summer of 1975, the half removal time of ^{228}Th by settling particles, t_c , was about 11 ± 4 , 29 ± 8 and 70 ± 10 days in the shelf surface water, the shelf winter water and the slope surface water of the New York Bight, respectively. In the fall of 1974, t_c was about 17 ± 1 to 28 ± 2 days from the inner shelf to the outer shelf surface waters and about 70 ± 10 days in the slope surface water. A simple box model of the shelf water in the Middle Atlantic Bight shows that (1) the exchange rate between the shelf and the slope waters is about $2500 \pm 800 \text{ km}^3/\text{yr}$, (2) the mean residence time of the shelf water is only about 132 ± 36 days, and (3) the average ^{226}Ra and ^{228}Ra fluxes per unit area of the coastal sediments are about $0.05 \text{ dpm } ^{226}\text{Ra}/\text{cm}^2 \text{ yr}$ and $0.37 \text{ dpm } ^{228}\text{Ra}/\text{cm}^2 \text{ yr}$. These rates are consistent with previously reported results. The implication of these rates to pollutants in the coastal environment is discussed.

1. Introduction

^{228}Th ($t_{1/2} = 1.91$ years) is continuously produced by the decay of the dissolved ^{228}Ra ($t_{1/2} = 5.75$ years) in seawater. The extent of the radioactive disequilibrium between ^{228}Th and ^{228}Ra in seawater has been utilized to estimate the removal rate of ^{228}Th from surface ocean water by settling particles [1]. It was found that the removal rate of ^{228}Th from surface water increases from the open ocean toward the shore, probably due to the general increase of settling particles (both organic and inorganic) toward the coastal environment, and partly to the direct uptake of ^{228}Th by coastal sediments at the water-sediment interface [1]. A similar increasing trend of removal rate was also observed for ^{234}Th using ^{234}Th - ^{238}U data [2,3].

In order to predict semi-quantitatively how fast

many highly reactive pollutants, which may geochemically behave similarly to ^{228}Th , will be removed from a coastal water once they are introduced, we have undertaken a detailed seasonal study of ^{228}Th - ^{228}Ra radioactive disequilibrium in the New York Bight.

This work presents the results from two seasons, i.e., the summer of 1975 and fall of 1974, representing periods of high-density stratification in the water column. We also present here (see section 4) a simple box model of the shelf water in the Middle Atlantic Bight. It illustrates the importance of water exchange along the shelf-slope boundary in understanding the overall budgets of radium isotopes and ^{228}Th in the shelf water.

The ^{228}Th and ^{228}Ra concentrated fractions from each water sample (~800 liters) were obtained on shipboard during the cruises of R/V "Vema" 32-01 (October 18–30, 1974) and R/V "Conrad" 19-01 (July 19–August 3, 1975). The details of the sample processing procedure and the analytical methods for the determination of ^{228}Ra and ^{228}Th are given elsewhere [1]. In brief, a large volume of water (~800

liters) is pumped into a nalgene tank. After adding ^{230}Th spike and, through several chemical steps, thorium and radium isotopes in the water are scavenged down by $\text{Fe}(\text{OH})_3$ and BaSO_4 precipitates, respectively.

Once in the laboratory, thorium isotopes in the $\text{Fe}(\text{OH})_3$ fraction are separated, purified and mounted on a stainless steel disc for α counting. The ^{228}Th concentration in the water sample can be calculated from the $^{228}\text{Th}/^{230}\text{Th}$ ratio obtained from the α counting, since the amount of ^{230}Th spike added to the sample is known. The BaSO_4 fraction is converted to a solution (the radium fraction) and is rid of ^{228}Th . As a natural yield tracer for ^{228}Ra , ^{226}Ra in the radium solution is measured by the standard Rn technique [1]. The ^{230}Th spike is added to the radium solution. After a known period of time (several months), the daughter products ^{228}Th and ^{230}Th are milked and counted. From the above the measurements the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio in the radium solution is obtained. Since the ^{226}Ra concentration in the water sample is known independently, the ^{228}Ra concentration in the water sample can be calculated.

2. Brief description of hydrography in the New York Bight during the two cruises

The mean advective transport of the shelf water in the Middle Atlantic Bight (including the New York Bight) is from north to south along the shore [4]. The shelf water is eventually entrained in the Gulf Stream at Cape Hatteras (e.g. [5–8]), but it also mixes with the slope water either by diffusive mixing or as “calved parcels” along the length of the shelf [6,9]. The mean residence time of the shelf water in the Middle Atlantic Bight has been estimated by Beardsley et al. [4] to be about 0.75 year.

Fig. 1 shows the T - S diagrams of water columns at stations taken more or less along the Hudson Canyon during the summer of 1975 (bottom) and the fall of 1974 (top). There are at least six identifiable water types: shelf surface water, shelf winter water (at bottom), slope surface water, top of the slope water, slope oxygen minimum and deep slope water. During the winter season, the thermocline disappears and the shelf and slope surface waters merge into the mixing line between the shelf winter water and the top of

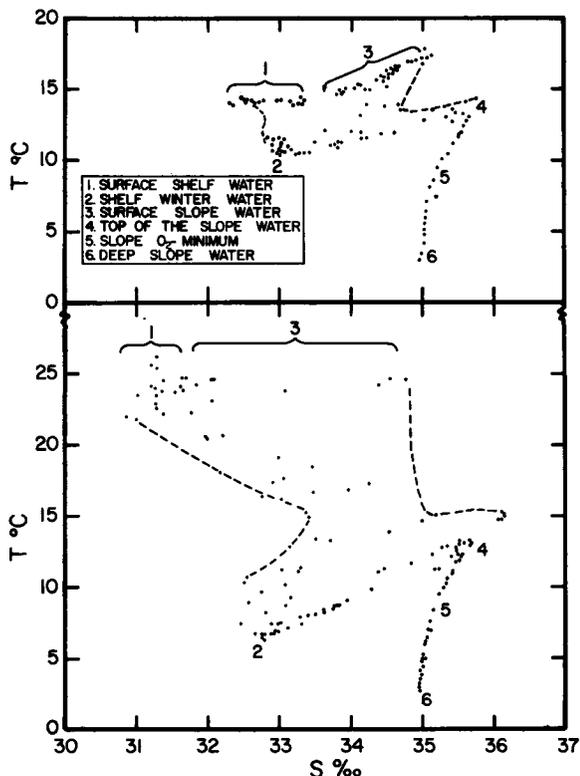


Fig. 1. The T - S diagrams of water columns at stations taken roughly along the Hudson Canyon during October 1974 (top) and July–August 1975 (bottom).

the slope water [10]. The thickness of the vertically well-mixed surface layer (i.e., the shelf and slope surface waters) was only about 10 m in the summer of 1975, but was as deep as 30 m near shore and 50 m off shore in the fall of 1974.

Since the surface mixed layer is relatively thin in the summer, temperature is not a good conservative tracer for delineating the mixing of surface water masses; for example, the boundary between the shelf and the slope-surface waters in the summer is not clear cut in the T - S diagram (Fig. 1). Fortunately, the boundary is still identifiable as a front in the surface salinity contour lines, as shown in Fig. 2 (at $S \sim 31.5\text{‰}$). It is also apparent from the salinity contour lines in Fig. 2 that there were two types of slope surface waters separated roughly by the Hudson Canyon. At identical salinity, the northern slope surface water was about 1° to 2°C cooler (see Fig. 5) and higher in phosphate content ($0.1 \sim 0.2$ vs. $0.05 \mu\text{mole/l}$, un-

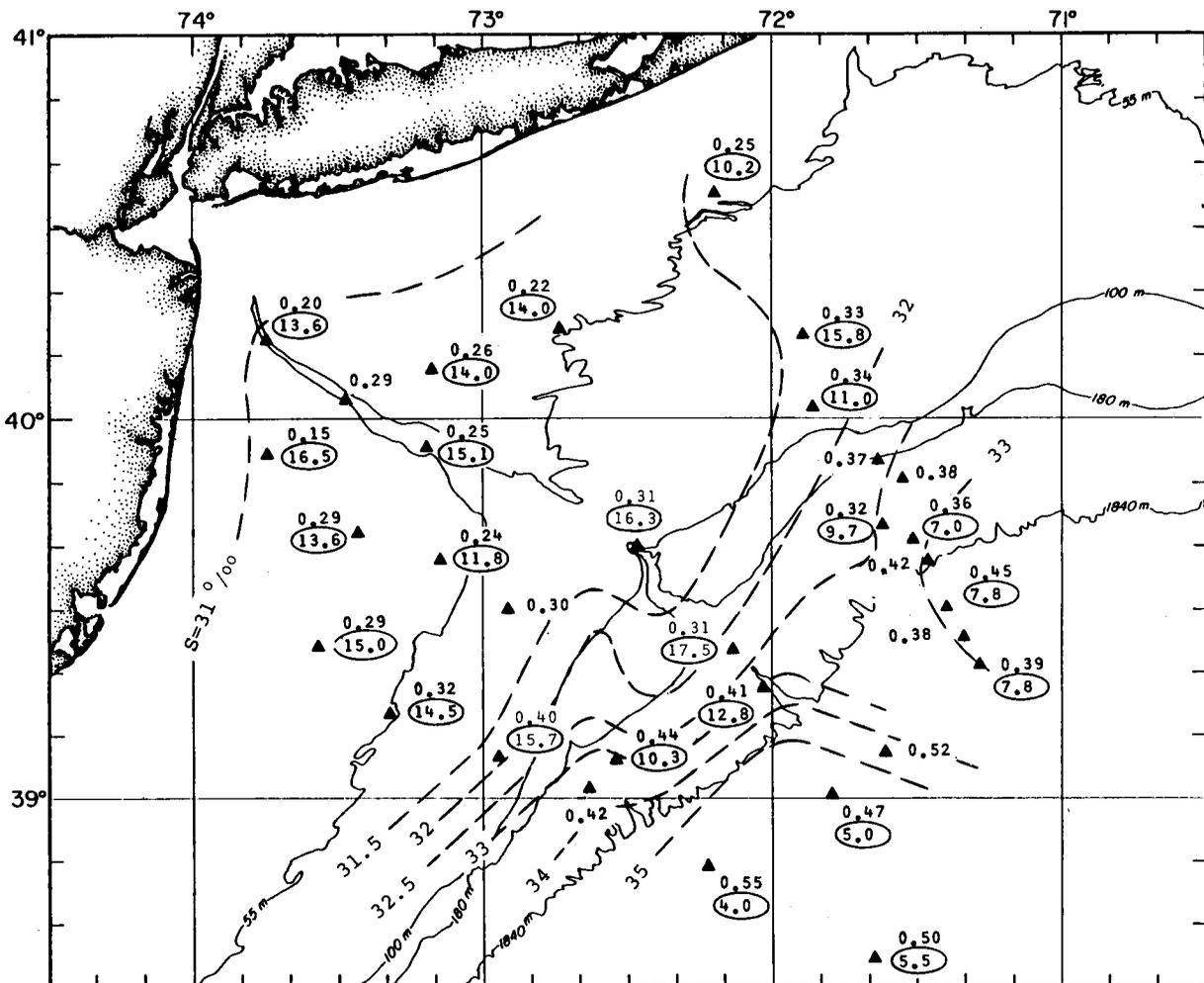


Fig. 2. ^{228}Th and ^{228}Ra (within the ovals) concentration (dpm/100 kg) of the unfiltered surface water samples, July-August 1975. The contour lines are the isohaline.

published data) than the southern one.

In the fall of 1974 the boundary between the shelf- and slope-surface waters was at a salinity (S) of about 33.6‰ (Fig. 1). The hydrological details have been discussed by Gordon et al. [11].

3. Results and discussion

The ^{228}Ra and ^{228}Th concentrations of unfiltered water samples from two cruises are summarized in Tables 1 and 2 along with other pertinent information. ^{226}Ra , as a natural yield tracer for ^{228}Ra analysis, was

estimated by the salinity vs. ^{226}Ra relationship in the New York Bight area ([12], and our unpublished data).

3.1. Summer season

As shown in Fig. 2, the ^{228}Ra concentration in the shelf surface water ($S < 31.6$ ‰) is uniformly high ($\sim 15 \pm 1$ dpm/100 kg) as compared to the slope surface water, indicating that coastal sediments (including estuarine and shelf sediments) are the source of ^{228}Ra . On the other hand, ^{228}Th (Fig. 2) and the $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio (Fig. 3), are uniformly

TABLE I
 ^{228}Th and ^{226}Ra concentration of water samples from the New York Bight area (R/V "Conrad" cruise 19-01, July-August, 1975)

Sample No.	Lat. N	Long. W	S (%)	T (°C)	^{228}Th		^{226}Ra		$^{228}\text{Th}/^{226}\text{Ra}$
					dpm 100 kg	^{228}Ra	dpm 100 kg	^{226}Ra	
2254	40°11.8'	73°44.5'	30.89	22.1	0.20 ± 0.02	1.36 ± 0.22	10.0	13.6 ± 2.2	0.015 ± 0.003
2257	39°55.1'	73°44.6'	31.14	21.69	0.15 ± 0.06	1.65 ± 0.19	10.0	16.5 ± 1.9	0.009 ± 0.004
2258 (31 m) **	39°55.1'	73°44.6'	32.52	7.75		1.34 ± 0.21	10.0	13.4 ± 2.1	
2259	39°23.9'	73°34.6'	(31.3)	(24.0)	0.29 ± 0.04	1.50 ± 0.23	10.0	15.0 ± 2.3	0.019 ± 0.004
2261	39°07.3'	72°57.1'	31.85	24.58	0.40 ± 0.04	1.78 ± 0.34	10.0	15.7 ± 3.4	0.025 ± 0.005
2263 (37 m)	39°08.2'	72°57.1'	32.89	7.4	0.46 ± 0.05	1.99 ± 0.27	10.0	19.9 ± 2.7	0.023 ± 0.004
2264	39°01.7'	72°37.4'	33.65	25.02	0.42 ± 0.04				
2265	38°33.8'	71°38.8'	35.79	23.30	0.50 ± 0.05	0.60 ± 0.10	9.2	5.5 ± 0.9	0.091 ± 0.017
2268 (37 m)	38°33.3'	71°39.3'	-	-	0.43 ± 0.04	0.56 ± 0.14	9.2	5.6 ± 1.4	0.077 ± 0.021
2269	38°50.4'	72°13.5'	35.60	23.18	0.55 ± 0.08	0.45 ± 0.06	9.2	4.1 ± 0.6	0.110 ± 0.031
2272	39°00.9'	71°49.0'	(35.5)	(25.2)	0.47 ± 0.06	0.55 ± 0.10	9.2	5.0 ± 0.9	0.094 ± 0.020
2283	39°17.3'	72°00.6'	33.0	24.5	0.41 ± 0.04	1.28 ± 0.13	10.0	12.8 ± 1.3	0.032 ± 0.004
2286	39°07.6'	71°37.7'	34.75	24.57	0.52 ± 0.05				
2290	39°20.6'	71°17.8'	33.03	23.79	0.39 ± 0.05	0.78 ± 0.12	10.0	7.8 ± 1.2	0.051 ± 0.010
2292	39°24.5'	71°21.3'	33.10	23.00	0.38 ± 0.05	1.22 ± 0.71	10.0	(12.2 ± 7.1) ***	
2293	39°31.3'	71°24.5'	33.2	23.0	0.45 ± 0.05	0.78 ± 0.11	10.0	7.8 ± 1.1	0.058 ± 0.010
2296	39°37.4'	71°29.0'	33.23	23.08	0.42 ± 0.05	0.78 ± 0.36	10.0	(7.8 ± 3.6)	
2298	39°41.3'	71°31.7'	32.63	22.63	0.36 ± 0.04	0.70 ± 0.13	10.0	7.0 ± 1.3	0.053 ± 0.011
2299	39°43.4'	71°37.1'	32.55	22.69	0.32 ± 0.04	0.97 ± 0.23	10.0	9.7 ± 2.3	0.034 ± 0.006
2301	39°50.3'	71°34.7'	32.66	23.02	0.38 ± 0.04	1.98 ± 0.46	10.0	(19.8 ± 4.6)	
2304	39°53.3'	71°39.0'	32.33	23.09	0.37 ± 0.04	1.11 ± 0.65	10.0	(11.1 ± 6.5)	

2305 (55 m)	39°52.1'	71°38.7'	33.19	7.5	0.48 ± 0.05	1.10 ± 0.23	10.0	11.0 ± 2.3	0.031 ± 0.007
2306	40°02.5'	71°50.9'	31.86	22.67	0.34 ± 0.04	0.80 ± 0.47	10.0	(8.0 ± 4.7)	
2307 (55 m)	40°13.4'	71°53.7'	32.86	6.90	0.47 ± 0.06	1.58 ± 0.25	10.0	15.8 ± 2.5	0.021 ± 0.004
2308	40°13.2'	71°53.6'	31.68	22.58	0.33 ± 0.04				
2312 (37 m)	40°36.7'	72°13.4'	32.71	7.15	0.42 ± 0.05				
2313	40°36.6'	72°13.0'	31.76	21.26	0.25 ± 0.03	1.02 ± 0.24	10.0	10.2 ± 2.4	0.025 ± 0.007
2317 (37 m)	40°14.5'	72°44.8'	32.62	7.13	0.47 ± 0.06	0.96 ± 0.22	10.0	9.6 ± 2.2	0.049 ± 0.013
2318	40°14.6'	72°44.8'	31.52	21.77	0.22 ± 0.04	1.40 ± 0.27	10.0	14.0 ± 2.7	0.016 ± 0.004
2321 (27 m)	40°08.5'	73°10.4'	32.67	6.94	0.52 ± 0.05	1.17 ± 0.25	10.0	11.7 ± 2.5	0.044 ± 0.010
2322	40°08.5'	73°10.4'	31.32	23.34	0.26 ± 0.04	1.40 ± 0.21	10.0	14.0 ± 2.1	0.018 ± 0.004
2324	40°03.6'	73°28.3'	31.26	23.46	0.29 ± 0.05				
2325	39°55.9'	73°11.5'	31.26	22.88	0.25 ± 0.03	1.51 ± 0.30	10.0	15.1 ± 3.0	0.017 ± 0.004
2327	39°41.9'	73°27.1'	31.26	23.97	0.29 ± 0.03	1.36 ± 0.25	10.0	13.6 ± 2.5	0.021 ± 0.005
2328	39°38.0'	73°08.7'	31.36	23.79	0.24 ± 0.04	1.18 ± 0.29	10.0	11.8 ± 2.9	0.020 ± 0.006
2329 (37 m)	39°30.9'	72°55.4'	32.87	7.4	0.47 ± 0.05	1.37 ± 1.11	10.0	(13.7 ± 11.1)	
2330	39°30.7'	72°55.2'	31.20	24.19	0.30 ± 0.04	1.99 ± 0.68	10.0	(19.9 ± 6.8)	
2333 (37 m)	39°42.7'	73°21.6'	33.05	6.31	0.60 ± 0.07	1.74 ± 0.40	10.0	17.4 ± 4.0	0.034 ± 0.009
2334	39°13.0'	73°21.6'	31.14	24.30	0.32 ± 0.04	1.45 ± 0.33	10.0	14.5 ± 3.3	0.022 ± 0.006
2344 (55 m)	39°05.6'	72°33.3'	(35.85)		0.60 ± 0.08				
2345	39°05.6'	72°33.7'	33.65	25.0	0.44 ± 0.04	1.03 ± 0.15	10.0	10.3 ± 1.5	0.042 ± 0.007
2355	39°24.0'	72°08.3'	31.82	24.23	0.31 ± 0.04	1.76 ± 0.27	10.0	17.5 ± 2.7	0.018 ± 0.004
2356 (55 m)	39°24.7'	72°08.6'	33.28	7.98	0.48 ± 0.05	0.81 ± 0.07	10.0	8.1 ± 0.7	0.060 ± 0.007
2370	39°40.2'	72°27.3'	31.19	25.6	0.31 ± 0.03	1.63 ± 0.22	10.0	16.3 ± 2.2	0.019 ± 0.003

* ^{226}Ra is estimated from the salinity- ^{226}Ra relationship in the New York Bight area.

** (- m) = sample depth, otherwise all are unfiltered surface water samples.

*** The parentheses represents ^{228}Ra value with a high counting uncertainty (>20%).

TABLE 2

^{228}Th and ^{228}Ra concentration of water samples from the New York Bight area (R/V "Vema" cruise 32-01, October, 1974)

Sample No.	Lat. N	Long. W	S (%)	T (°C)	dpm ^{228}Th 100 kg	^{228}Ra		dpm ^{226}Ra * 100 kg	dpm ^{228}Ra 100 kg	$^{228}\text{Th}/^{228}\text{Ra}$
						^{228}Ra	^{226}Ra			
2061 (91 m) **	39°07.9'	71°43.0'	35.640	14.0	0.50 ± 0.05	0.55 ± 0.07	9.3	5.2 ± 0.6	0.125 ± 0.022	
2062	39°07.9'	71°43.0'	35.024	17.10	0.73 ± 0.06	0.66 ± 0.07	9.7	6.4 ± 0.7	0.114 ± 0.016	
2063	39°38.8'	72°29.4'	33.967	15.03	0.45 ± 0.06	0.92 ± 0.10	10.0	9.2 ± 1.0	0.049 ± 0.009	
2064 (37 m)	39°38.8'	72°29.4'	34.234	15.53	0.34 ± 0.08	0.68 ± 0.08	10.0	6.8 ± 0.8	0.050 ± 0.013	
2065 (60 m)	39°38.8'	72°29.4'	34.196	14.35	0.28 ± 0.05	1.01 ± 0.11	10.0	10.1 ± 1.1	0.028 ± 0.006	
2070	40°06.3'	73°45.6'	32.379	13.97	0.34 ± 0.06	1.43 ± 0.16	10.0	14.3 ± 1.6	0.024 ± 0.005	
2076	40°00.0'	73°01.0'	32.932	14.40	0.40 ± 0.07	1.24 ± 0.13	10.0	12.4 ± 1.3	0.032 ± 0.007	
2069	39°52.7'	72°56.8'	33.273	14.03	(0.10 ± 0.16)	1.26 ± 0.13	10.0	12.6 ± 1.3		
2071 (82 m)	39°29.7'	72°04.0'	35.462	14.18	0.38 ± 0.06	0.60 ± 0.06	9.5	5.7 ± 0.6	0.067 ± 0.013	
2072	39°29.7'	72°04.0'	34.282	15.81	0.50 ± 0.05	0.69 ± 0.07	10.0	6.9 ± 0.7	0.073 ± 0.011	
2074 (47 m)	38°55.0'	72°07.0'	35.296	16.06	0.67 ± 0.07	0.51 ± 0.06	9.8	5.0 ± 0.5	0.133 ± 0.020	
2075	39°19.3'	72°19.7'	34.336	15.50	0.46 ± 0.04	0.72 ± 0.12	10.0	7.2 ± 1.2	0.064 ± 0.012	
2077	40°09.5'	72°08.7'	33.624	14.90	0.43 ± 0.05	0.86 ± 0.08	10.0	8.6 ± 0.8	0.050 ± 0.008	
2078 (77 m)	39°34.8'	72°18.5'	35.101	13.92	0.40 ± 0.04	0.39 ± 0.05	9.7	3.8 ± 0.4	0.106 ± 0.016	
2083	39°34.8'	72°18.5'	34.541	16.38	0.46 ± 0.05	0.62 ± 0.07	10.0	6.2 ± 0.6	0.074 ± 0.012	
2079	39°30.2'	71°48.3'	34.429	15.95	0.54 ± 0.06	0.60 ± 0.07	10.0	6.0 ± 0.7	0.090 ± 0.010	
2080	39°29.9'	72°17.8'	34.308	15.84	0.39 ± 0.05	0.71 ± 0.09	10.0	7.1 ± 0.9	0.055 ± 0.010	
2082	38°49.2'	72°01.3'	34.8	16.4	0.64 ± 0.06	0.65 ± 0.07	10.0	6.5 ± 0.7	0.099 ± 0.013	
2084	39°18.0'	72°00.5'	34.492	16.11	0.51 ± 0.05	0.56 ± 0.06	10.0	5.6 ± 0.6	0.092 ± 0.013	
2085	39°15.3'	74°12.2'	32.232	16.83	0.32 ± 0.04	1.34 ± 0.16	10.0	13.4 ± 1.6	0.024 ± 0.004	
2086	39°24.9'	72°09.3'	34.468	16.32	0.52 ± 0.05	0.60 ± 0.06	10.0	6.0 ± 0.6	0.087 ± 0.012	
2112	40°14.4'	73°46.2'	31.890	13.6	0.38 ± 0.05	1.44 ± 0.15	10.0	14.4 ± 1.5	0.026 ± 0.004	
2089 (64 m)	39°07.5'	72°56.2'	34.107	11.52		0.79 ± 0.09	10.0	7.9 ± 0.9		
2113	30°0.75'	72°56.2'	33.510	15.83	0.49 ± 0.06	1.23 ± 0.13	10.0	12.3 ± 1.3	0.040 ± 0.006	
2090	39°16.1'	73°24.0'	32.525	16.25	0.31 ± 0.07	1.25 ± 0.13	10.0	12.5 ± 1.3	0.025 ± 0.006	

* ^{226}Ra is estimated by salinity- ^{226}Ra relationship in the New York Bight area.

** (- m) = sample depth, otherwise all are unfiltered surface water samples.

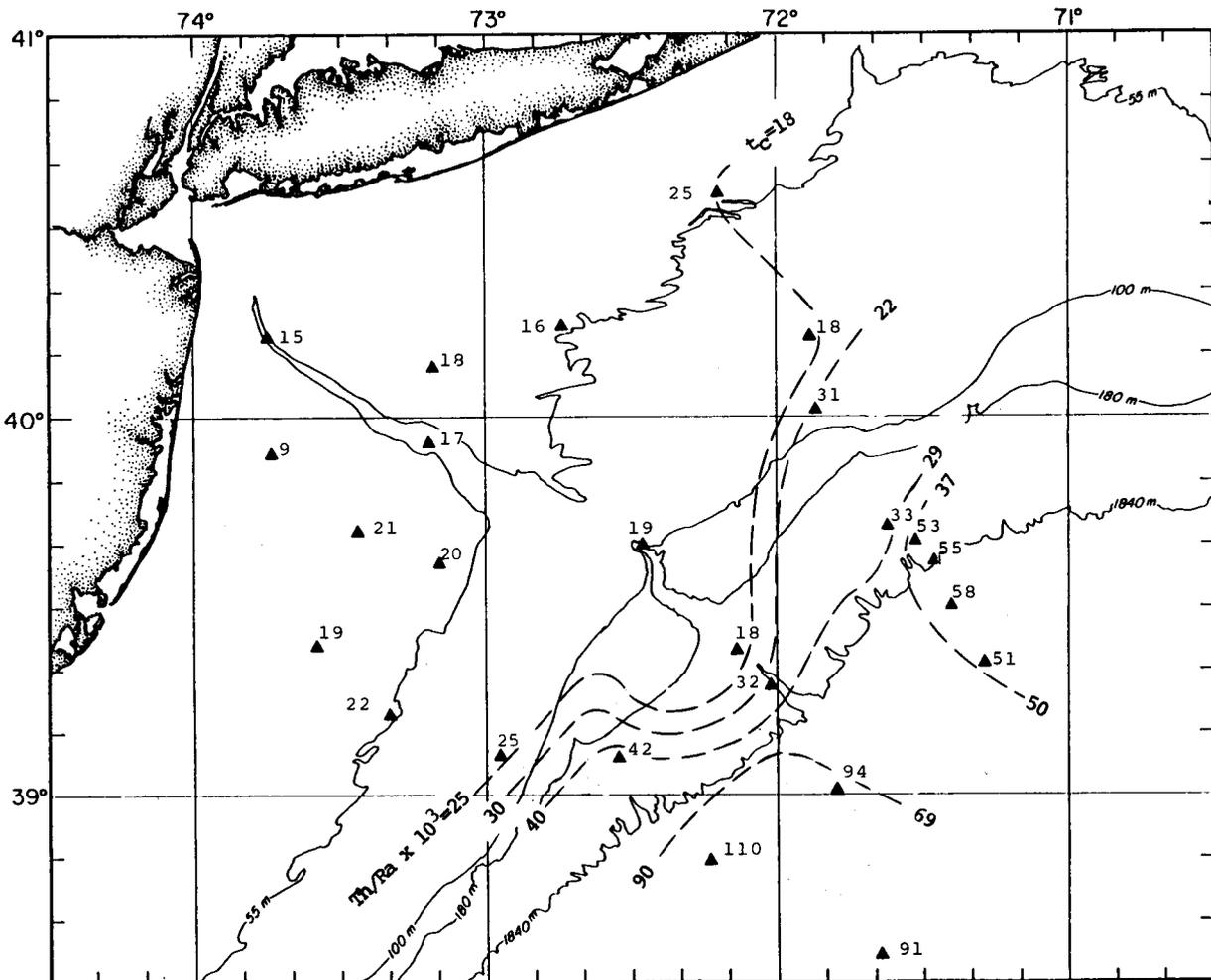


Fig. 3. $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio multiplied by 1000 from Fig. 2. Notice the similarity between the contours of $^{228}\text{Th}/^{228}\text{Ra}$ (the corresponding half removal time of ^{228}Th is also given) and salinity (Fig. 2).

low in the shelf surface water, indicating a high removal rate of ^{228}Th from the shelf surface water. According to the simple model of Broecker et al. [1], it is assumed as a first approximation that in a well-mixed water parcel the production rate of ^{228}Th from the decay of ^{228}Ra ($\lambda_{\text{Ra}} \cdot N_{\text{Ra}}$) is just balanced by the decay rate of ^{228}Th ($\lambda_{\text{Th}} \cdot N_{\text{Th}}$) and the removal rate of ^{228}Th by settling particles ($\lambda_{\text{c}} \cdot N_{\text{Th}}$), neglecting mixing effects with other surrounding water parcels. Thus:

$$\lambda_{\text{Ra}} \cdot N_{\text{Ra}} = \lambda_{\text{Th}} \cdot N_{\text{Th}} + \lambda_{\text{c}} N_{\text{Th}} \quad (1a)$$

or:

$$A_{\text{Ra}} = A_{\text{Th}} + \lambda_{\text{c}} A_{\text{Th}} / \lambda_{\text{Th}} \quad (1b)$$

where λ_{Ra} , N_{Ra} and $A_{\text{Ra}} (= \lambda_{\text{Ra}} \cdot N_{\text{Ra}})$ are the radioactive decay constant, the number of atoms and the activity per unit volume of water for ^{228}Ra , respectively; λ_{Th} , N_{Th} and $A_{\text{Th}} (= \lambda_{\text{Th}} \cdot N_{\text{Th}})$ are the same as above, but for ^{228}Th ; and λ_{c} is the first-order removal rate constant of ^{228}Th by settling particles.

By rearranging equation (1b), one obtains:

$$\lambda_{\text{c}} = (1 - R) / R \cdot \lambda_{\text{Th}}$$

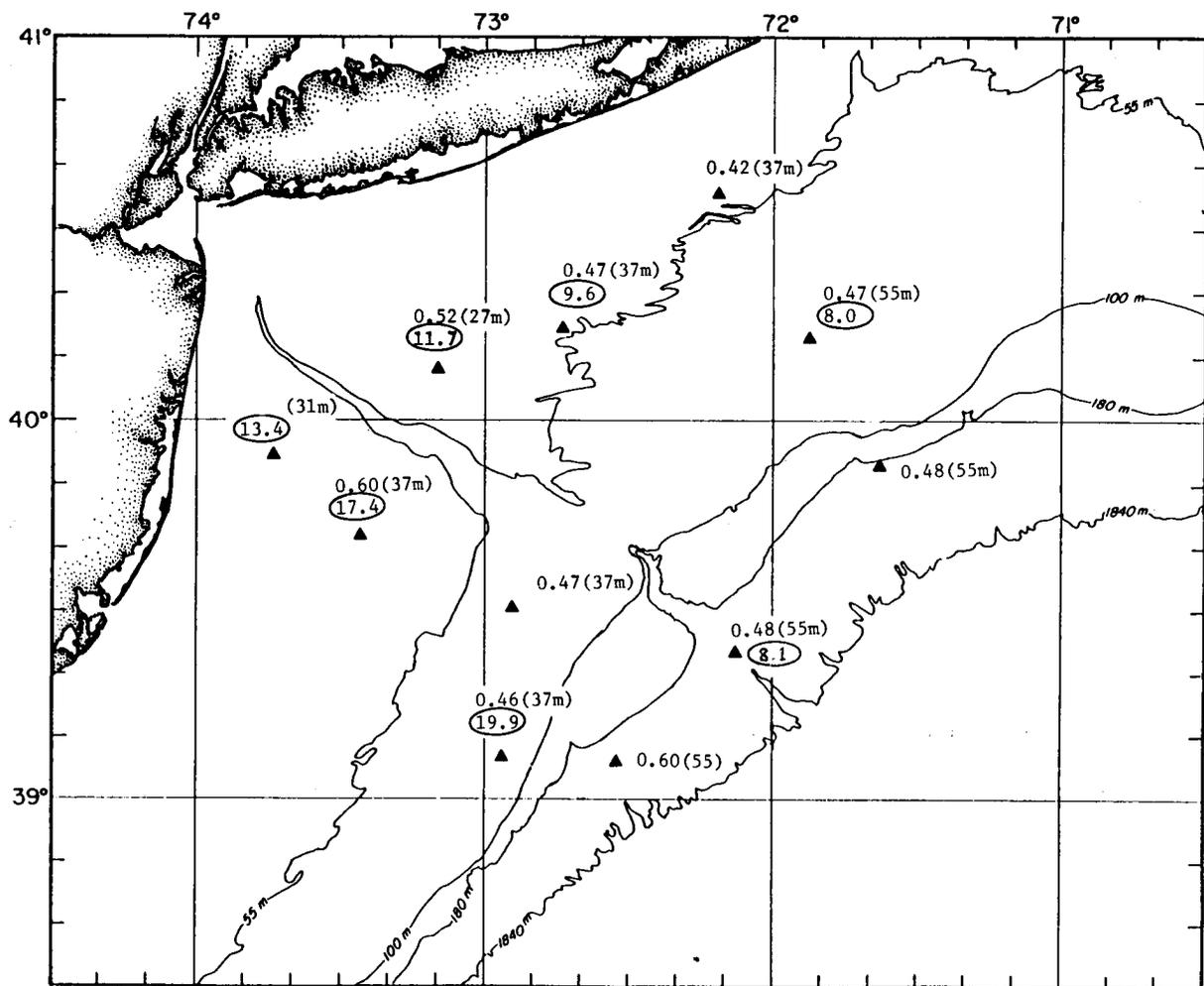
where

$$R = {}^{228}\text{Th}/{}^{228}\text{Ra} \text{ activity ratio.}$$

The removal rate constant λ_c is the fraction removed per unit time. The other convenient ways of expressing the removal rate by settling particles are the "half removal time", $t_c (= \ln 2 / \lambda_c)$, and the "removal residence time", $\tau_c (= 1 / \lambda_c)$. The former can be visualized as the time span required for the initial activity in the water column to be reduced to one half by settling of particles, and the latter as the average time span that a radionuclide atom remains in the water column before it is removed by settling par-

ticles. Throughout this paper we use mainly the t_c , but one should keep in mind that λ_c , t_c and τ_c refer to the same process, but expressed in different ways. The average ${}^{228}\text{Th}/{}^{228}\text{Ra}$ activity ratio of 0.016 ± 0.006 in the shelf surface water (Fig. 3) gives a half removal time of ${}^{228}\text{Th}$, t_c , equal to about 11 ± 4 days (or $\lambda_c = 0.063 \text{ day}^{-1}$, $\tau_c = 16$ days). For comparison, t_c in the slope surface water is about 40 days (north) and 70 days (south) (Fig. 3) and about 185 days in the surface layer of the open ocean [1].

All our subsurface samples are characterized by their T - S data as being from the shelf winter water (compare Fig. 1 and crosses in Fig. 5). ${}^{228}\text{Ra}$ concen-



trations in the shelf winter water are quite variable, ranging from 8 dpm/100 kg north of the Hudson Canyon to about 20 dpm/100 kg south of the Hudson Canyon (Fig. 4). But it is clear from the ^{228}Ra vs. salinity plot of all our data (excluding the few ^{228}Ra data with high uncertainty as indicated by parentheses in Table 1) that all ^{228}Ra data points can be obtained by the mixing of four end members (Fig. 5, top), i.e., shelf surface water ($^{228}\text{Ra} \sim 15$ dpm/100 kg, $S \sim 31\text{‰}$), the northern slope surface water ($^{228}\text{Ra} \sim 7.8$ dpm/100 kg, $S \sim 33\text{‰}$), the southern slope surface water ($^{228}\text{Ra} \sim 5$ dpm/100 kg, $S \sim 35.5\text{‰}$) and the shelf winter water south of the Hudson Canyon ($^{228}\text{Ra} \sim 19$ dpm/100 kg, $S \sim 33\text{‰}$, the high ^{228}Ra concentration here indicates again the source of ^{228}Ra from the shelf sediments).

The ^{228}Th concentration in the shelf winter water

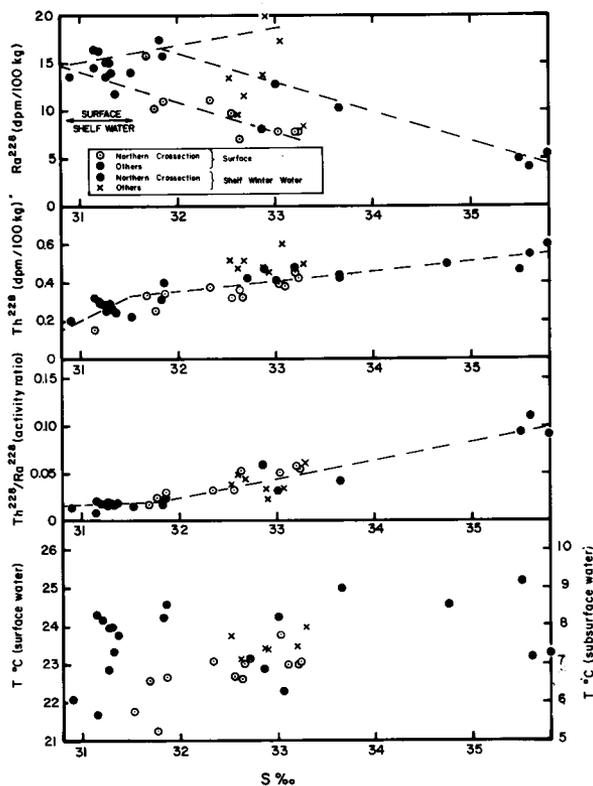


Fig. 5. Plots of salinity vs. various parameters, July-August 1975. The northern cross section represents the slope water ($S > 31.6\text{‰}$) north of the Hudson Canyon. The first and third diagrams do not include the highly uncertain points (parentheses in Table 1).

is quite uniform (0.5 ± 0.1 dpm/100 kg). The average $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio of 0.04 ± 0.01 gives t_c in the shelf winter water equal to about 29 ± 8 days. The longer t_c in the shelf winter water than in the shelf surface water is probably due to the lack of phytoplanktonic uptake of ^{228}Th and/or release of ^{228}Th by oxidation of organic matter in the shelf winter water.

We have also collected a series of filtered surface water samples in addition to the unfiltered samples. The ^{228}Ra concentration in the filtered and the unfiltered sample pair agrees very well within our experimental uncertainty. On the other hand the ^{228}Th concentration in the filtered samples appears to be systematically about 0.1 dpm/100 kg lower than in the unfiltered counterparts, though the suspended particulates concentration varies greatly from sample to sample (varying from $12 \mu\text{g/l}$ to $270 \mu\text{g/l}$). We suspect that the systematic lowering of 0.1 dpm $^{228}\text{Th}/100$ kg was caused by the adsorption of ^{228}Th in our filtration system. The real ^{228}Th contribution from the suspended particles should be less than 0.1 dpm/100 kg. A strong acid leachate of suspended particles collected by centrifugation in the inner shelf of New York Bight during the winter of 1976 gave $^{232}\text{Th} = 1.1 \pm 0.1$ dpm/g and $^{228}\text{Th}/^{232}\text{Th} = 2.0 \pm 0.1$. Therefore, the suspended particulates concentration of less than 0.027 g/100 l in the surface water (mostly less than 0.010 g/100 l [13]) will contribute no more than 0.06 dpm ^{228}Th or 0.03 dpm $^{232}\text{Th}/100$ l. Our measured ^{232}Th concentration in unfiltered surface waters is usually less than 0.04 dpm/100 l and the most likely value is 0.02 ± 0.02 dpm/100 l, in good agreement with our prediction.

The suspended particulate concentration in our inner shelf winter water samples is about $0.04 \sim 0.03$ g/100 l and in the outer shelf samples about $0.02 \sim 0.005$ g/100 l [13]. Therefore the ^{228}Th contribution from suspended particulates in the near shore zone is usually not greater than 0.09 dpm/100 l. Additional measurement of the ^{228}Th content of suspended particulate matter will be performed in the future.

3.2. Fall season

The ^{228}Ra concentration of the surface waters increases steadily from the slope (6.5 ± 0.5 dpm/100 kg) to the inner shelf (14.4 dpm/100 kg) while the

^{228}Th concentration and $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio show the reverse of this trend (Figs. 6 and 7). We calculate t_c in the shelf surface water ($S < 33.6\text{‰}$) to be about 28 ± 2 days in the outer shelf, and 17 ± 1 days in the inner shelf (Fig. 7). In the slope surface water t_c is again about 70 days (Fig. 7).

Of the shelf surface water data (Fig. 8), the high ^{228}Ra concentration of the inner shelf waters and the non-linearity in the ^{228}Ra vs. salinity plot again indicate that the ^{228}Ra is supplied from the coastal sediments.

4. A box model of the shelf water in the Middle Atlantic Bight

One can regard the shelf water within the 100-m isobath and between Cape Cod and Norfolk as a big box. In order to keep the mass balance of water and salt within the box at a steady state, the sum of input fluxes should be equal to that of output fluxes, i.e.:

$$Q_R + Q_1 = Q_2 + Q_V \quad (2)$$

for water balance ,

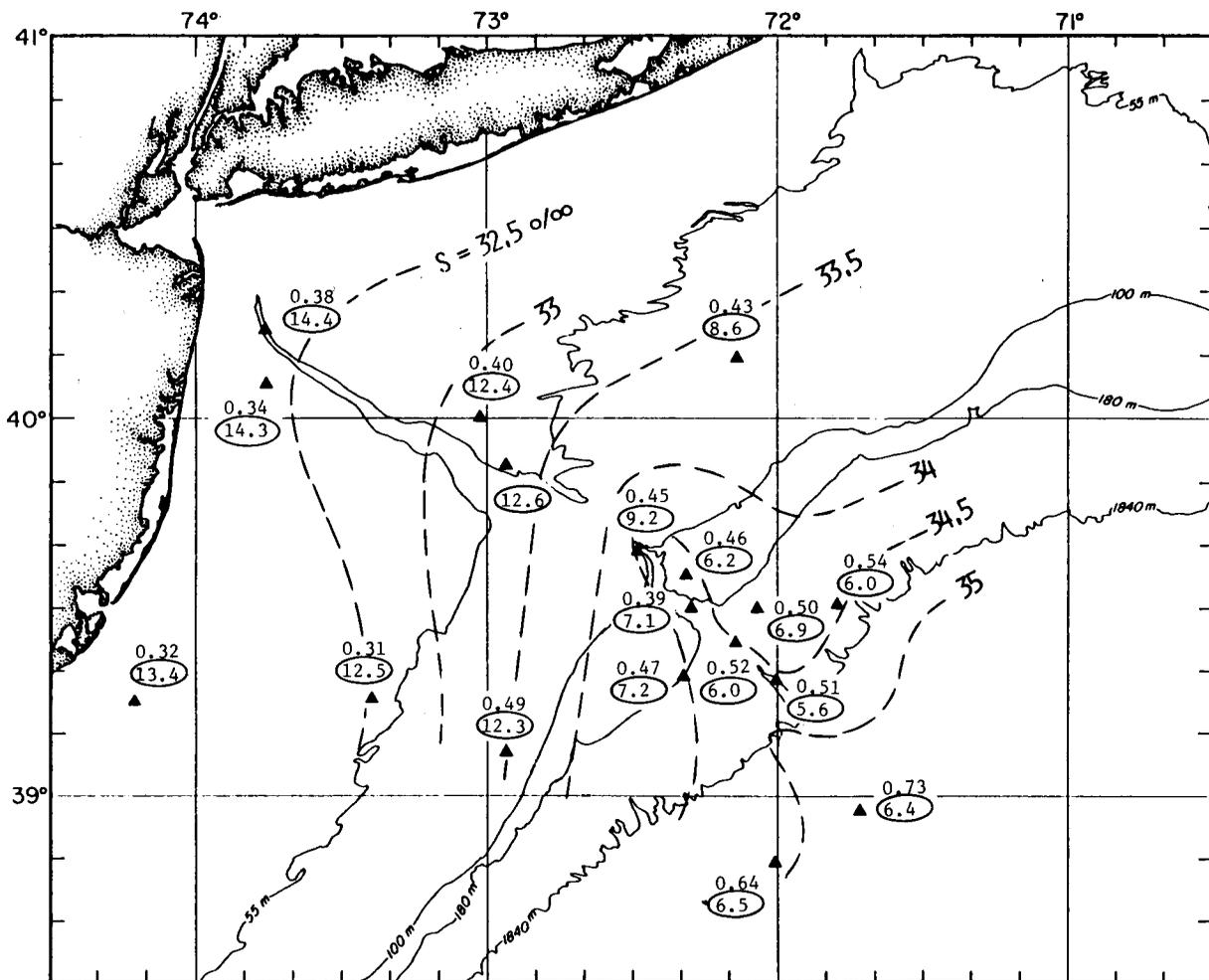


Fig. 6. ^{228}Th and ^{228}Ra (in ovals) concentration of the unfiltered surface water samples, October 1974.

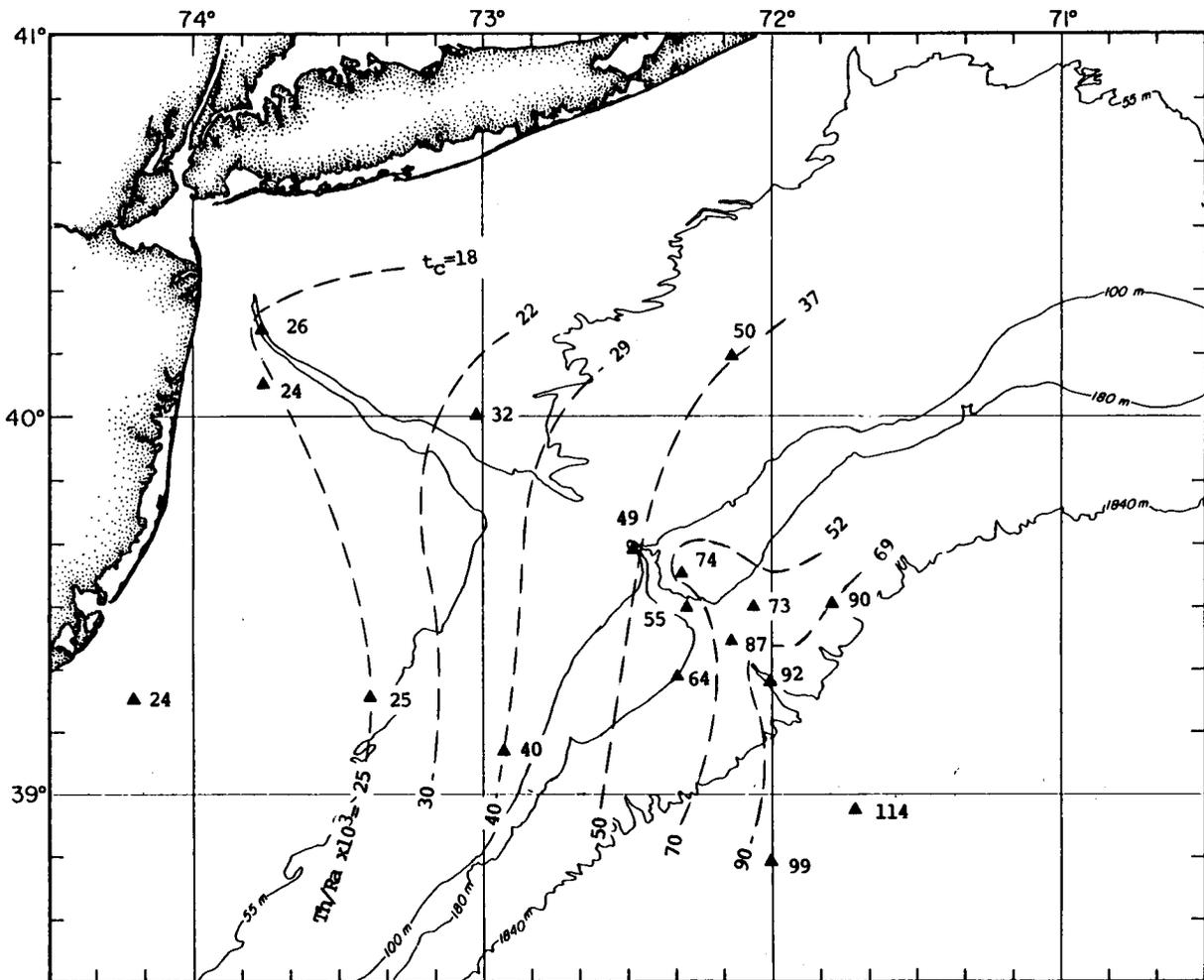


Fig. 7. $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio multiplied by 1000 from Fig. 6.

and:

$$Q_R \cdot S_R + S_1 + Q_x \cdot S_{sl} = Q_2 \cdot S_2 + Q_x \cdot S_{sh} \quad (3)$$

for salt balance,

where:

- Q_R = the total river discharge along the coast to the box $\sim 150 \text{ km}^3/\text{yr}$ [9] to $157 \text{ km}^3/\text{yr}$ [14];
- Q_v = the excess of evaporation over precipitation on the box $\sim 0.2 Q_R$ [9] or near zero [15];
- Q_1 = the along shore mean influx of shelf water within the 100-m isobath through a transect south of Cape Cod $\sim 7000 \pm 1800 \text{ km}^3/\text{yr}$ [4];
- Q_2 = the along shore mean outflux of shelf water

within the 100-m isobath through a transect east of Norfolk;

Q_x = the exchange rate of shelf and slope waters across the shelf-slope boundary by horizontal eddy diffusion normal to the coast (including calved parcels);

- S_R = the mean salinity of river water $\sim 0.1\text{‰}$;
- S_1 = the annual mean salinity of $Q_1 \sim 32.96 \pm 0.02\text{‰}$ (estimated from fig. 2 of Ketchum and Keen [9] down to 50 fathoms);
- S_2 = the annual mean salinity of $Q_2 \sim 33.19 \pm 0.02\text{‰}$ [9];
- S_{sh} = the annual mean salinity of shelf water within the box $\sim 32.93 \pm 0.02\text{‰}$ [9];

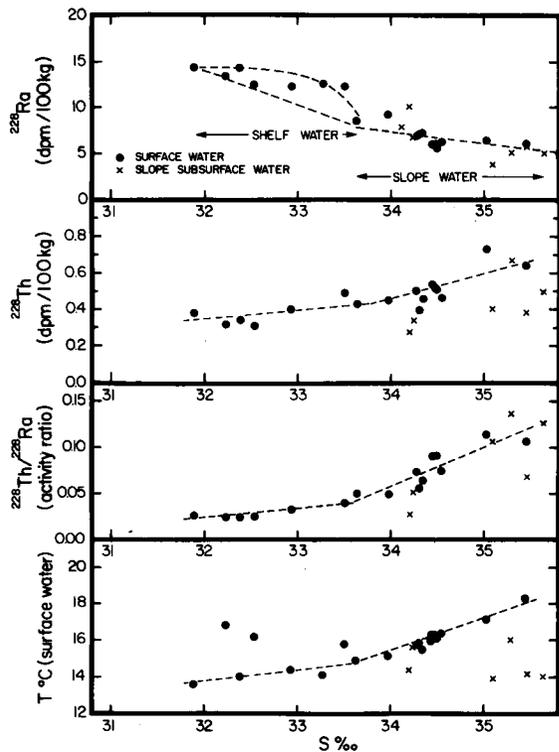


Fig. 8. Plots of salinity vs. various parameters, October 1974. Two high-temperature points stick out in the T - S diagram (bottom) represent the most southern stations of the shelf water (Fig. 6). The dashed lines in various diagrams are drawn to show the difference in slopes between the shelf and slope waters.

S_{sl} = representative average salinity of the slope surface water $\sim 35.2\%$ [15].

By solving equations (2) and (3) with the values given above, one obtains:

$$Q_x = \frac{Q_1(S_2 - S_1) + Q_R(S_2 - S_R) - Q_v \cdot S_2}{(S_{sl} - S_{sh})}$$

$$= 2500 \pm 800 \text{ km}^3/\text{yr}$$

The uncertainty here is largely due to the uncertainty in Q_1 , Q_v and Q_R , but the uncertainty in Q_1 is not so critical in estimating Q_x as long as $(S_2 - S_1)$ is small. Our model is essentially similar to Wright's model [15] except that he implicitly assumed $S_1 = S_2 = S_{sh}$, and $(Q_2 - Q_1) = 300 \text{ km}^3/\text{yr}$. The latter assumption is not correct, as has recently been pointed out by Kupferman and Garfield [8].

The mean residence time of shelf water, τ_w , in the box is defined as:

$$\tau_w = \frac{V_{sh}}{Q_1 + Q_R + Q_x} = \frac{V_{sh}}{Q_2 + Q_x + Q_v} \quad (4)$$

$$= 0.36 \pm 0.10 \text{ year}$$

$$= 132 \pm 36 \text{ days}$$

(or t_w = the half replacement time of water in the box

$$= \ln 2 \times \tau_w = 91 \text{ days}$$

λ_w = the fraction of water in the box replaced per unit time = $1/\tau_w = 0.0076 \text{ day}^{-1}$)

where $V_{sh} = 3500 \text{ km}^3$ = the volume of the box, estimated from table 1 of Ketchum and Keen [9]:

Beardsley et al. [4] give $\tau_w = 0.75 \text{ year}$, using $V_{sh} = 6000 \text{ km}^3$. We consider this to be an over-estimate, even though the volume which they use includes the entire shelf area between Nantucket Shoals and Cape Hatteras. Moreover, they neglected the important Q_x term in equation (4).

For a mass balance of radium isotopes within the shelf water box, the following relationship should hold at a steady state:

$$Q_R \cdot C_R + Q_1 \cdot C_1 + Q_x \cdot C_{sl} + I$$

$$= Q_2 \cdot C_2 + Q_x \cdot C_{sh} + \lambda \cdot C_{sh} \cdot V_{sh} \quad (5)$$

where C_i = mean radium concentration in Q_i or a water mass V_i ; and I = total radium influx from the coastal sediments under the box. For ^{226}Ra , $C_R \sim 1 \text{ dpm}/100 \text{ l}$ and $C_{sl} \sim 9 \text{ dpm}/100 \text{ l}$ [12]. Assuming $C_1 \sim C_2 \sim C_{sh} \sim 10 \text{ dpm}/100 \text{ l}$ (New York Bight value [12]), we obtain from equation (5):

$$I = (36 \pm 8) \times 10^{12} \text{ dpm } ^{226}\text{Ra}/\text{yr}.$$

Since the bottom area of our box is about $730 \times 10^{12} \text{ cm}^2$ [9], the ^{226}Ra flux per unit area of the coastal sediments is about $0.05 \pm 0.01 \text{ dpm}/\text{cm}^2 \text{ yr}$ or $(2.3 \pm 0.5) \times 10^{-14} \text{ g}/\text{cm}^2 \text{ yr}$, which is comparable to the estimate of Li et al. [16] of $\sim 4.6 \times 10^{-14} \text{ g}/\text{cm}^2 \text{ yr}$ through the mass balance of ^{226}Ra in the oceans. For ^{228}Ra , $C_R \sim 1.4 \pm 0.2 \text{ dpm}/100 \text{ l}$ (unpublished data from Hudson River); and $C_{sl} \sim 6 \pm 0.5 \text{ dpm}/100 \text{ l}$ (present work). Again assuming $C_1 \sim C_2 \sim C_{sh} \sim$

14 ± 1 dpm/100 l (New York Bight data from the present work), we obtain:

$$I = (270 \pm 40) \times 10^{12} \text{ dpm } ^{228}\text{Ra/yr}$$

$$\text{or } 0.37 \pm 0.06 \text{ dpm } ^{228}\text{Ra/cm}^2 \text{ yr.}$$

According to our unpublished Atlantic GEOSECS ^{228}Ra data, the total ^{228}Ra in the surface layer of the Atlantic Ocean is about $(30 \pm 10) \times 10^{16}$ dpm. Since the shelf area within the 200-m isobath in the Atlantic Ocean is about 14×10^{16} cm² [17], the average ^{228}Ra flux per unit area of the coastal sediment should be:

$$\frac{0.693}{5.75 \text{ yr}} \times \frac{30 \times 10^{16} \text{ dpm}}{14 \times 10^{16} \text{ cm}^2}$$

$$= 0.26 \pm 0.09 \text{ dpm } ^{228}\text{Ra/cm}^2 \text{ yr,}$$

again in general agreement with our box model calculations.

5. Conclusions

It has been shown that minor alkali and alkaline-earth elements (e.g., ^{137}Cs [18], Ba [19,20] and Ra [12]) are desorbed from river-borne sediments by ion exchange as soon as the river sediments contact with the high ionic strength waters of estuaries and the continental shelf. Therefore, the newly deposited estuarine and shelf sediments often become the sources of minor alkaline and alkaline-earth elements instead of the sinks. As shown in this work, the shelf sediments are the sources of radium isotopes for the coastal and open ocean waters.

If non-reactive pollutants (alkaline and alkaline-earth elements or halides) which are soluble in seawater and do not react significantly with any solid phases are introduced into the shelf water of the Middle Atlantic Bight, they will on average reside in the shelf water for about 132 ± 36 days (i.e., for the mean residence time of the shelf water). About $3/4$ ($Q_2/[Q_2 + Q_x]$) of the pollutant will be entrained into the landward-side of the Gulf Stream and the other $1/4$ ($Q_x/[Q_2 + Q_x]$) will be dissipated into the slope water by the water exchange processes through the shelf-slope water boundary.

If any highly reactive pollutant (e.g., heavy metals,

Pu, DDT, PCB, etc.) which adheres to particles as rapidly as ^{228}Th is introduced into the shelf water during a summer or fall season, the mean residence time of that pollutant in the shelf water τ_Σ , would be (neglecting the spontaneous decomposition or decay of the pollutant):

$$\tau_\Sigma = \frac{1}{\lambda_{c'} + \lambda_w} = \frac{1}{(1/t_{c'} + 1/t_w) \cdot \ln 2} \quad (6)$$

where $\lambda_{c'}$ and $t_{c'}$ are the removal rate constant and the half removal time of the reactive pollutant in the shelf water.

For $t_{c'} = 11$ days (i.e., equal to the half removal time of ^{228}Th in the shelf surface water during the summer) and $t_w = 91$ days (the half replacement time of the shelf water), τ_Σ is about 14 days. About 90% ($=[\lambda_{c'}/(\lambda_{c'} + \lambda_w)] \times 100\%$) of the pollutant will be deposited on the continental shelf sediments (within the 100-m isobath), and 10% will be exported to the Gulf Stream and the slope water.

For $t_{c'} = 29$ days (i.e., equal to the half removal time of ^{228}Th in the shelf winter water during the summer) and $t_w = 91$ days, τ_Σ is about 32 days. About 76% of the pollutant will end up on the shelf sediments and the rest (24%) will be transported to the Gulf Stream and the slope water.

There is no reliable estimate of the mean residence time of the slope surface water. If the reactive pollutant is introduced into the slope surface water, we still can estimate a maximum mean residence time of the pollutant in the slope surface water by ignoring the λ_w term in equation (6), i.e.:

$$\tau_\Sigma < 1/\lambda_{c'} = 100 \text{ days for } t_{c'} = 70 \text{ days,}$$

which is still smaller than in the surface open ocean (~ 270 days [1]).

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