[4]

THE FLUX OF ^{226}Ra FROM ESTUARINE AND CONTINENTAL SHELF SEDIMENTS

YUAN-HUI LI, GUY MATHIEU, PIERRE BISCAYE and H. JAMES SIMPSON

Lamont-Doherty Geological Observatory of Columbia University, Palisades, N.Y. 10964 (USA)

A pronounced desorption phenomenon of ^{226}Ra from sediment was observed in the Hudson River estuary. Mass balance calculations indicate that the desorption of ^{226}Ra from the river-borne sediment in estuarine environment is an important source of ^{226}Ra to the oceans.

1. Introduction

In order to explain the observed high concentration of both ^{226}Ra and ^{228}Ra in coastal waters as compared to either surface ocean water or river waters, Blanchard and Oakes [1] and Moore [2] proposed that ^{226}Ra and ^{228}Ra diffuse out of coastal sediments to the overlying coastal waters at a rate sufficient to significantly increase the water column concentration. Based on the geochemical similarity between barium and radium in the oceans and their mass balance in a two-box model of oceans (i.e., warm surface ocean and cold deep ocean), Li et al. [3] also concluded that, besides deep-sea sediments, coastal sediments (estuarine and continental shelf sediments) are a significant ^{226}Ra source for the oceans. They predicted a total ^{226}Ra flux of about 17×10^3 g ^{226}Ra/yr from the coastal sediments to the warm surface ocean as comparing to a total net flux of about 46×10^3 g ^{226}Ra/yr from the deep sea sediments to the cold deep ocean [3].

To estimate the flux of ^{226}Ra from the coastal sediments, we collected a series of surface seawater samples (~20 liters) off the coastal area of the eastern United States during May 8–17, 1976, and another series of filtered water samples (~20 liters) from the

Hudson estuary during October 27–28, 1976 (Fig. 1). Analysis of ^{226}Ra was made by extraction and scintillation counting of ^{222}Rn in radioactive equilibrium
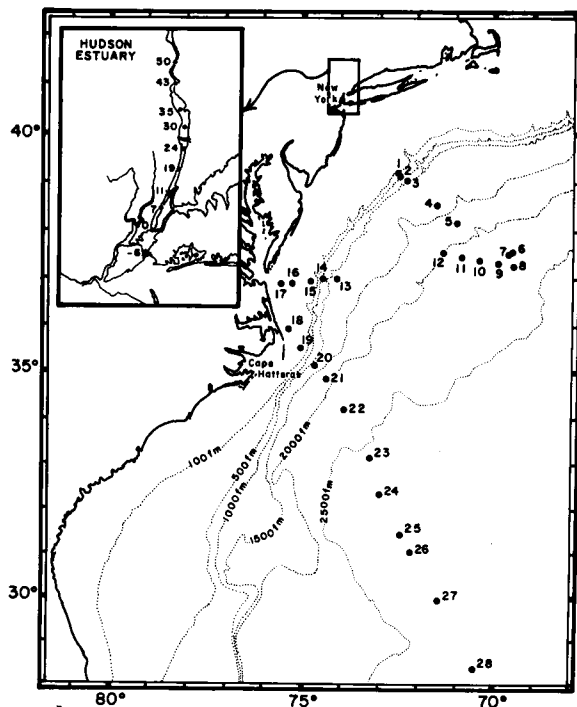

Fig. 1. The sample localities in the coastal area of eastern U.S.A. and in the Hudson river.

with ^{226}Ra [4]. Minor modifications are that ^{222}Rn is absorbed on a charcoal trap instead of a liquid nitrogen trap, and is de-emanated and transferred into a counting chamber made of quartz material instead of plexy glass to improve the reproducibility.

2. Results and discussion

The analytical results are summarized in Tables 1 and 2 and plotted in Fig. 2.

From Fig. 2 it is clear that all data points fall above a mixing line connecting the Hudson fresh water ($S < 0.2‰$, ^{226}Ra ≈ 1 dpm/100 l) and the surface ocean water (S 36.7‰, ^{226}Ra = 8.0 dpm/100 l =

7.4 dpm/100 kg, taken from Table 1) indicating a local supply of excess ^{226}Ra. The excess ^{226}Ra has apparently been derived from Hudson estaurine ($S > 0.4‰$, i.e., mile point less than ~20, Table 2), and continental shelf sediments. It appears that whenever sediments on the estuary floor or the suspended particles in the water are in contact with water of high ionic strength, exchangeable radium on the particles will be replaced by major cations of the contacting solution. Similar desorption phenomena were also observed in estuarine environ for ^{137}Cs [5], Ba [6], Zn [7], ^{65}Zn and ^{54}Mn [8] and Ag, Co and Ni [9]. In the fresh-water section of the Hudson River, the concentration of ^{226}Ra is correlated to that of silica (Table 2). Probably the blooming fresh-water diatoms take up both silica and ^{226}Ra from the water. The cor-

TABLE 1

^{226}Ra concentration of the surface coastal waters off the eastern U.S.A. (R/V "Conrad cruise" 20-01, May 8–17, 1976)

Sample No.	Date (May, 1976)	Lat. N.	Long. W	Temperature (°C)	Salinity (‰)	^{226}Ra * (dpm/100 l)
1	8	39°14'	72°32'	9.6	32.509	10.5
2	8	39°12'	72°29'	9.5	32.768	9.8
3	8	39°05'	72°19'	10.7	33.309	9.8
4	8	38°33'	71°31'	15.6	35.339	9.3
5	9	38°12'	70°60'	15.8	35.519	9.2
6	9	37°35'	69°36'	19.2	35.495	9.4
7	10	37°35'	69°39'	22.6	35.267	9.1
8	10	37°21'	69°33'	24.2	36.049	8.3
9	10	37°21'	69°56'	24.5	36.087	9.3
10	11	37°25'	70°25'	24.2	36.084	8.6
11	11	37°29'	70°51'	24.7	36.031	8.8
12	11	37°35'	71°22'	17.9	34.544	9.8
13	12	37°02'	74°09'	14.9	34.440	9.8
14	12	37°03'	74°30'	14.1	33.796	9.8
15	12	37°00'	74°47'	14.6	32.445	9.7
16	12	36°56'	75°17'	15.2	31.262	8.3
17	12	36°55'	75°36'	15.8	29.216	7.9
18	14	35°56'	75°23'	20.1	34.855	9.4
19	14	35°35'	75°03'	23.0	35.655	9.8
20	14	35°10'	74°40'	24.4	35.948	8.8
21	14	34°51'	74°22'	22.3	36.165	8.2
22	14	34°13'	73°56'	23.4	36.208	8.8
23	15	33°07'	73°15'	21.7	36.420	8.1
24	15	32°21'	72°57'	–	36.540	8.3
25	15	31°25'	72°26'	23.0	36.570	8.0
26	15	31°02'	72°10'	23.3	36.533	8.7
27	16	29°54'	71°27'	23.8	36.702	8.1
28	17	28°23'	70°31'	24.4	36.761	7.9

* The analytical reproducibility is about 4%.

TABLE 2

[226]Ra concentration of the Hudson estuary waters (October 27–28, 1976)

Sample No. mile point *	Date (October, 1976)	Depth (m)	Temperature (°C)	Salinity (‰)	SiO_2 (μm/l)	[226]Ra ** (dpm/100 l)
50s	27	0	9.8	<0.2	68	2.3
50b	27	9	9.8	<0.2	69	2.9
43s	27	0	11.0	<0.2	52	2.4
43b	27	9	11.1	<0.2	53	2.5
35s	27	0	10.8	<0.2	24	1.5
35b	27	8	10.7	<0.2	24	1.3
30s	27	0	10.9	<0.2	14	1.4
30b	27	10	11.0	<0.2	–	1.9
24s	28	0	10.4	<0.2	17	1.3
24b	28	14	10.7	<0.2	19	0.9
19s	28	0	10.3	0.4	14	1.2
19b	28	10	10.8	2.8	15	4.3
11s	28	0	10.5	3.8	17	5.4
11b	28	16	11.7	13.7	20	8.1
7s	28	0	11.0	4.8	15	4.0
7b	28	16	11.5	21.1	22	10.7
0s	28	0	11.0	12.5	20	7.7
0b	28	16	10.5	25.4	17	9.8
−6s	28	0	10.8	18.3	24	8.5
−6b	28	21	9.9	28.6	15	10.5

* s = surface; b = about 1 m above bottom.
** The analytical uncertainty is about 10%.

relation plot of Si vs. [226]Ra in the fresh-water section gives a slope of about 0.46×10^{-11} g Ra/g Si as compared to a slope of 1.2×10^{-11} g Ra/g Si in the Antarctic Ocean south of the Convergence [10]. The low silica concentration in the Hudson estuary indicates that [226]Ra input from the dissolution of silica is negligible.

The daily water flow rate of the Hudson River at the last gauging station (Green Island, mile point 154) during October 12 ~ 28, 1976, though varied from 410 m^3/s to 1170 m^3/s but their mean is about 730 m^3/s with a standard deviation of only ±60 m^3/s (U.S. Geological Survey preliminary report). Therefore, one can expect a semi-steady state distribution of salinity along the Hudson estuary at the end of this period. On the other hand, the estuarine circulation of the Hudson, driven by the horizontal density gradient, is characterized by a dense salty water flowing upstream at depth under a less dense surface water flowing seaward [11,12]. With the above two conditions in mind, one can calculate the flux of [226]Ra from sediments between mile points 24 and −6

(Fig. 3) as follows:

$$Q_U = Q_F + Q_L \text{ for water mass balance}$$

$$Q_U \cdot S_U = Q_F \cdot S_F + Q_L \cdot S_L \text{ for salt mass balance}$$

and

$$Q_U[Ra]_U = Q_F \cdot [Ra]_F + Q_L[Ra]_L + I_{Ra}$$

for [226]Ra mass balance (radioactive decay term is neglected)

where Q = water flow rate, S = salinity, [Ra] = [226]Ra, and I_{Ra} = total [226]Ra flux from sediments between mile points 24 and −6. The subscripts F, U, L represent river inflow, upper non-tidal net outflow, and lower non-tidal net inflow of bay water respectively.

By solving the above equations, one obtains:

$$I_{Ra} = Q_F\left[\frac{S_L - S_F}{S_L - S_U}[Ra]_U - [Ra]_F - \frac{S_U - S_F}{S_L - S_U}[Ra]_L\right]$$

Since at mile point −6:

$$S_U = 18.3‰ \qquad [Ra]_U = 9.3 \text{ dpm/100 l}$$

$S_L = 28.6\%o$ $[Ra]_L = 10.7$ dpm/100 l

($[Ra]_U$ and $[Ra]_L$ values were read off from the best fit curve in Fig. 2) and at mile point 24:

$S_F = 0.2\%o$ $[Ra]_F = 1.1$ dpm/100 l

$Q_F = 1140 \pm 90$ m^3/s

(the mean of daily flow rate at Green Island during October 12–28, 1976, multiplied by a factor of 1.56 to include the water contribution of tributaries downstream of Green Island [13]), therefore:

$I_{Ra} = 2.1 \times 10^{12}$ dpm ^{226}Ra/yr

$= 0.97$ g ^{226}Ra/yr (where 1 dpm ^{226}Ra = 0.461×10^{-12} g ^{226}Ra)

The area of the sediments of Hudson between mile points 24 and −6 is about 87 km^2; thus, the average ^{226}Ra flux from a unit area of Hudson estuarine sedi-
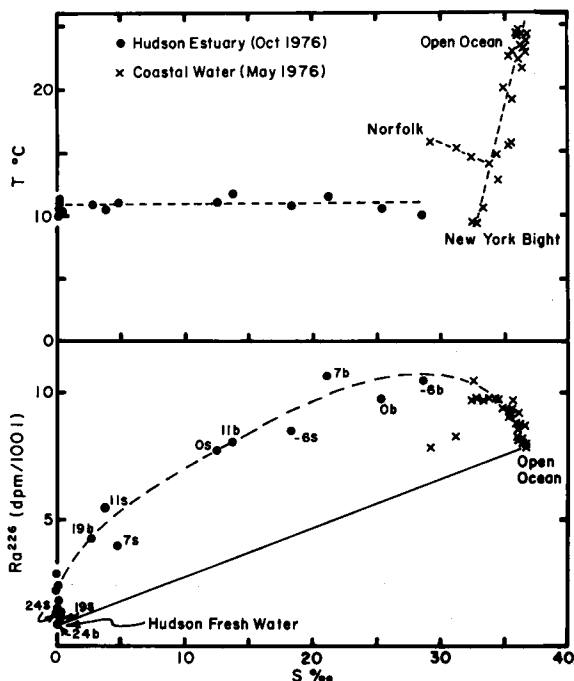

Fig. 3. The mile point vs. $S\%o$ (top) of the Hudson river samples, and the salinity distribution along the Hudson estuary (bottom).

Fig. 2. The temperature vs. $S\%o$ (top) and the ^{226}Ra vs. $S\%o$ (bottom) plots of water samples from the Hudson river and the coastal area of eastern U.S.A. The mile point and the depth (s = surface, b = bottom) of the Hudson ^{226}Ra samples between mile points 24 and −6, are indicated in the bottom figure.
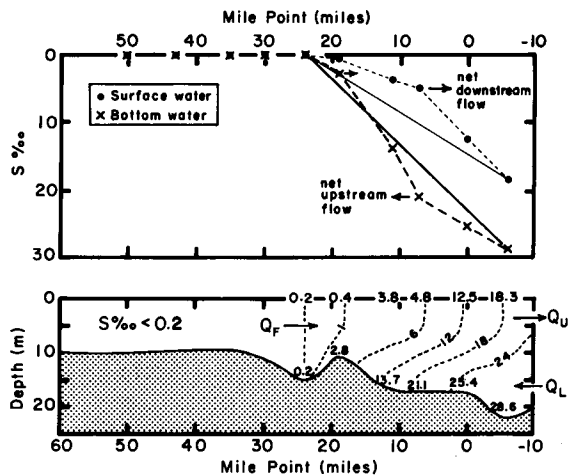
ments is about 110×10^{-14} g ^{226}Ra cm^{-2} yr^{-1}, which is much higher than the flux from deep-sea sediments, i.e., about 1.7×10^{-14} g cm^{-2} yr^{-1} [3]. With such a high radium flux, we expect a big deficiency of ^{226}Ra with respect to its parent ^{230}Th in the sediments. Indeed, a strong acid (6N HCl + 6N HNO$_3$) leachate of the surface sediment from the New York Harbor gives ^{230}Th = 1.2 ± 0.1 dpm per gram of dry sediment with ^{226}Ra/^{230}Th activity ratio of 0.19 ± 0.02 (our unpublished data), i.e., about 1 dpm ^{226}Ra deficiency per gram of the Harbor sediment. Thomson et al. [14] also found ^{230}Th $\approx 1.5 \pm 0.2$ dpm/g and ^{226}Ra/^{230}Th ≈ 0.35 from the leachates of a Long Island Sound sediment core (0 to 18 cm). Another interesting observation is that an unfiltered surface water at mile point 35 ($S < 0.2\%o$), after being acidified to pH ~ 2, gives ^{226}Ra concentration of 5.1 dpm ^{226}Ra/100 l as compared to 1.5 dpm ^{226}Ra/100 l of a filtered sample. Since the concentration of suspended particles is about 2.0 g/100 l, one gram of dry suspended particles gives off about 1.8 dpm ^{226}Ra. On the other hand, at mile point 11 ($S = 3.8\%o$), the concentration of ^{226}Ra for filtered and unfiltered surface water (3.0 g suspended matters/100 l) is respectively 5.4 and 6.4 dpm/100 l. Therefore, the suspended particles give off at most only about 0.3 dpm ^{226}Ra/g, indicating a big loss (≈ 1.5 dpm ^{226}Ra/g) of ^{226}Ra from suspended particles by desorption in the Hudson estuarine environment.

The sedimentation rate in the New York Harbor is about 5 g cm^{-2} yr^{-1} and the total area of the New York Harbor is about 30 km^2 [15]. Therefore, the total sediment deposited in the Harbor annually is about 1.5×10^{12} g/yr, which should be close to the total sediments that have passed through the Hudson estuary every year since most of the sediments from the Hudson River have been deposited in the New York Harbor [15]. If the deficiency of ^{226}Ra with respect to ^{230}Th in the Harbor sediments is due to the desorption of ^{226}Ra in the estuarine environment, then from the total sedimentation rate of the harbor one can predict a desorption rate of at least about 1.5×10^{12} dpm ^{226}Ra/yr in the Hudson estuary, which is comparable to our model calculation (i.e., $I_{Ra} = 2.1 \times 10^{12}$ dpm ^{226}Ra/yr).

The worldwide estimate of suspended sediment carried to the oceans by the rivers ranges from 13×10^{14} to 33×10^{14} g/yr, as summarized by Garrels and Mackenzie [16]. If the radium deficiency of 1 dpm ^{226}Ra/g from the New York Harbor is assumed to be typical of all other estuaries, the total ^{226}Ra flux from the estuaries by desorption would be about 13×10^{14} to 33×10^{14} dpm ^{226}Ra/yr or 6×10^3 to 15×10^3 g ^{226}Ra/yr, which is again comparable to the total flux of 17×10^3 g ^{226}Ra/yr from the coastal sediments as estimated by Li et al. [3].

Of course, our calculations involve a lot of assumptions and uncertainties, but they indicate, at least, that the amount of ^{226}Ra desorbed from the river-borne sediments in the estuarine environment are a significant source of ^{226}Ra to the surface ocean.

Acknowledgements

References

1 R.L. Blanchard and D. Oakes, Relationships between uranium and radium in coastal marine shells and their environment, J. Geophys. Res. 70 (1965) 2911–2921.
2 W.S. Moore, The measurement of ^{228}Ra and ^{228}Th in sea-water, J. Geophys. Res. 74 (1969) 694–704.
3 Y.H. Li, T.L. Ku, G.G. Mathieu and K. Wolgemuth, Barium in the Antarctic Ocean and implications regarding the marine geochemistry of Ba and ^{226}Ra, Earth Planet. Sci. Lett. 19 (1973) 352–358.
4 W.S. Broecker, An application of natural radon to problems in ocean circulation, in: Symposium on Diffusion in Oceans and Fresh Waters, T. Ichiye, ed. (Lamont Geological Observatory, Palisades, N.Y., 1965) 116–145.
5 S.M. Jinks and M.E. Wrenn, Radio cesium transport in the Hudson River estuary, in: environmental Toxicity of Aquatic Radionuclides. Models Mechanisms, M.W. Miller and J.N. Stannard, eds. (Ann Arbor Science, Ann Arbor, Mich., 1975) 207–227.
6 J.S. Hanor and L.H. Chan, Non-conservative behavior of barium during mixing of Mississippi River and Gulf of Mexico waters. Earth Planet. Sci. Lett. 37 (1977) in press.
7 B.N. Troup and O.P. Bricker, Processes affecting the transport of materials from continents to oceans, in: Marine Chemistry in the Coastal Environment, T.M. Church, ed., Am. Chem. Soc. Symp. Ser. 18 (1975) 133–151.
8 D.W. Evans and N.H. Cutshall, Effects of ocean water on the soluble-suspended distribution of Columbia River radionuclides, in: Radioactive Contamination of the Marine Environment (International Atomic Energy Agency, Vienna, 1973) 125–140.
9 K.K. Turekian, Rivers, tributaries and estuaries, in: Impingement of Man on the Oceans, D.W. Hood, ed. (John Wiley and Sons, New York, N.Y., 9–73.
10 T.L. Ku and M.C. Lin, ^{226}Ra distribution in the Antarctic Ocean, Earth Planet. Sci. Lett. 32 (1976) 236–248.
11 H.B. Stewart, Upstream bottom currents in New York Harbor, Science 127 (1958) 1113–1114.
12 A.F. Kao, A study of the current structure in the Sandy Hook–Rockaway Point transect, MS Res. Paper, Stony Brook Marine Sci., Res. Center, State Univ. of New York (1975) unpublished.
13 H.J. Simpson and D.E. Hammond, Application of one-dimensional models to the Hudson river estuary (in press).
14 J. Thomson, K.K. Turekian and R.J. McCaffrey, The accumulation of metals in and release from sediments of Long Island Sound, Estuarine Res. 1 (1975) 28–43.
15 H.J. Simpson, C.R. Olsen, R.M. Trier and S.C. Williams, Man-made radionuclides and sedimentation in the Hudson River estuary, Science 194 (1976) 179–183.
16 R.M. Garrels and F.T. Mackenzie, Evolution of Sedimentary Rocks (Norton and Co., 1971) 397 pp.