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DESORPTION OF Ba AND ^{226}Ra FROM RIVER-BORNE SEDIMENTS IN THE HUDSON ESTUARY

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The pronounced desorption of Ba and ^{226}Ra from river-borne sediments in the Hudson estuary can be explained quantitatively by the drastic decrease in the distribution coefficients of both elements from a fresh to a salty water medium. The desorption in estuaries can augment, at least, the total global river fluxes of dissolved Ba and ^{226}Ra by one and nine times, respectively. The desorptive flux of ^{226}Ra from estuaries accounts for 17–43% of the total ^{226}Ra flux from coastal sediments. Two mass balance models depicting mixing and adsorption-desorption processes in estuaries are discussed.

1. Introduction

The general linear correlation between Ba and ^{226}Ra concentrations in the oceans [1,2] indicates that both alkaline-earth elements are influenced by the same processes in the oceans, i.e., particulate uptake at the surface oceans, gravitational settling, and release in the deep ocean. From the linear correlation between ^{226}Ra and Si [3,4] or Ba and Si [5–7], it has been further suggested that tests of siliceous plankton may act as a major carrier for both Ba and ^{226}Ra in the ocean.

The pronounced desorption phenomena of ^{226}Ra in the Hudson estuary [8] and of Ba in the Amazon [9], Mississippi [10] and Zaire [11] river estuaries, again point to a very similar geochemical behavior of both elements in estuarine environments. In order to compare the geochemical behavior of Ba and ^{226}Ra directly within one estuary at the same time, we

report here the dissolved Ba concentration data from the Hudson estuary samples (filtered through 0.45 μm millipore filter) of which ^{226}Ra and Si concentration data have already been published elsewhere [8].

Furthermore, to test the extent of the desorption of Ba and ^{226}Ra when river-borne sediments contact with the salt-wedge of an estuary, we performed desorption experiments in laboratory using soupy surface sediments obtained from the upstream Hudson. Dissolved Ba was determined by a high-precision isotope dilution technique [6] and dissolved ^{226}Ra by scintillation counting of ^{222}Rn [8].

2. Results and discussion

2.1. The dissolved Ba, ^{226}Ra and Si concentration data from the Hudson estuary and the New York Bight

The results are summarized in Table 1 and Table 2. The data from the fresh water section (salinity <0.2 ,

TABLE 1

Barium and ^{226}Ra concentration of the Hudson estuary waters (October 27–28, 1976)

Sample No. * Mile point	Depth (m)	Temperature (°C)	Salinity (‰)	SiO ₂ (μmole/l)	^{226}Ra ** (dpm/100 l)	Ba *** (nmole/l)
50s	0	9.8	<0.2	68	2.3	366
50b	9	9.8	<0.2	69	2.9	—
43s	0	11.0	<0.2	52	2.4	366
43b	9	11.1	<0.2	53	2.5	—
35s	0	10.8	<0.2	24	1.5	244
35b	8	10.7	<0.2	24	1.3	—
30s	0	10.9	<0.2	14	1.4	222
30b	10	11.0	<0.2	—	1.9	—
24s	0	10.4	<0.2	17	1.3	221
24b	14	10.7	<0.2	19	0.9	—
19s	0	10.3	0.4	14	1.2	237
19b	10	10.8	2.8	15	4.3	266
11s	0	10.5	3.8	17	5.4	—
11b	16	11.7	13.7	20	8.1	207
7s	0	11.0	4.8	15	4.0	250
7b	16	11.5	21.1	22	10.7	210
0s	0	11.0	12.5	20	7.7	224
0b	16	10.5	25.4	17	9.8	145
-6s	0	10.8	18.3	24	8.5	161
-6b	21	9.9	28.6	15	10.5	131

* s = surface; b = about 1 m above bottom.

** The analytical uncertainty is about 5%.

*** The analytical uncertainty is about 1%.

between mile point (m.p.) 50 to 24) are plotted in Fig. 1. The linear correlation among Ba, ^{226}Ra and Si is evident from Fig. 1. The drastic decrease of Si as well as Ba and ^{226}Ra concentrations from m.p. 50 to m.p. 24 (Table 1) is best explained by the uptake of those elements by blooming fresh water diatoms as suggested earlier by Simpson et al. [12] for Si in the Hudson estuary. The significant spread of Ba con-

centration values in the fresh water section of the Amazon, Mississippi and Zaire Rivers [11] may be also caused by the various degree of uptake of Ba by diatoms. Further studies are needed.

The general characteristic of the Ba vs. salinity plot of the Hudson estuary (Fig. 2) is very similar to that of other estuaries [9–11]; the Ba concentration increases from a minimum at m.p. 24 up to a maxi-

TABLE 2

Barium and ^{226}Ra concentrations of surface coastal waters from the New York Bight (May 8–10, 1976)

Sample No.	Latitude (N)	Longitude (W)	Temperature (°C)	Salinity (‰)	^{226}Ra (dpm/100 l)	Ba (nmole/l)
1	39° 14'	72° 32'	9.6	32.509	10.5	63.1
2	30° 12'	72° 29'	9.5	32.768	9.8	67.5
4	38° 33'	71° 31'	15.6	35.339	9.3	57.6
5	38° 12'	70° 60'	15.8	35.519	9.2	56.4
8	37° 21'	69° 33'	24.2	36.049	8.3	55.4

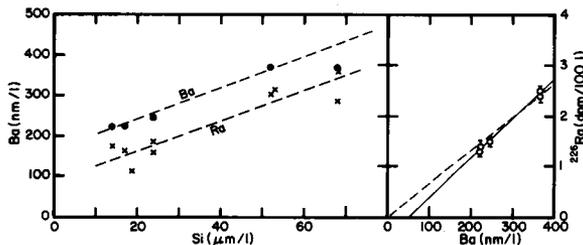


Fig. 1. The correlation plots among the dissolved Si, Ba and ^{226}Ra concentration data in the fresh water section of the Hudson River (m.p. 50 to 24).

mum at m.p. 19 ($S \sim 3\text{‰}$) due to the desorptive input from the suspended particles and sediments, then decrease linearly with increasing salinity. The linear section in the Ba vs. S plot represents the region of pure two end member mixing without desorptive input [9,11]. For comparison, the ^{226}Ra concentration increases non-linearly from m.p. 24 to m.p. 11 indicating the desorptive input of ^{226}Ra in this region. The linear increment of ^{226}Ra with salinity between m.p. 11 to m.p. -6 again represents the region of pure two end member mixing (Fig. 2). The surface and bottom waters appear to be indistinguishable in their mixing trend (Fig. 2). However, anomalously high concentrations of both Ba and ^{226}Ra in the bottom water sample at m.p. 7 (Fig. 2) are probably caused by local input from the river bed sediments. This particular sample has abnormally high particulate matter concentration (89 mg/l). We suspect that the water sampler might have hit the bottom sediment. There is no apparent correlation between Si and ^{226}Ra or Si and Ba within the Hudson estuary (m.p. 24 to -6). Barium concentrations of the New York Bight surface waters are much lower than that of Hudson estuary (Table 2; and Fig. 2). In contrast, ^{226}Ra concentrations increase toward the shore and reach a maximum (Fig. 2), indicating coastal shelf sediments as an important source of ^{226}Ra to the overlying shelf water [8].

2.2. Mass balance models

In any estuary the spacial distribution of sea salts is never in a steady state. The overall spacing of isosaline contours is controlled by the water discharge

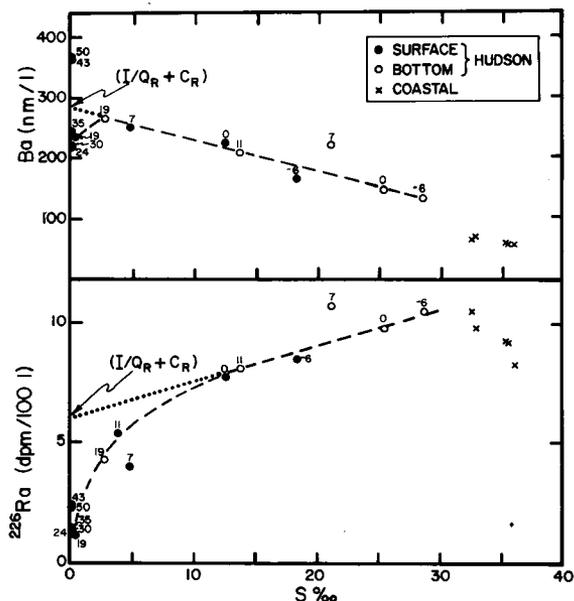


Fig. 2. The plots of Ba vs. S (top) and ^{226}Ra vs. S (bottom) for the Hudson estuarine and some coastal water samples. The numbers beside each data point represent the mile point.

rate of rivers and their minor fluctuation by the tidal cycle. Only under a special condition i.e., after a long period of relatively steady water discharge rate (about 2 to 3 times of water residence time in an estuary), the distribution of sea salts in an estuary may approach to a semi-steady state. As discussed in the earlier paper [8], the salt distribution in the Hudson estuary was probably in a semi-steady state when we took our water samples. The Hudson estuary (between m.p. 24 and -6 for the present case) can be considered as a box consisting of a less dense surface water flowing seaward and a dense salty water flowing upstream at depth (Fig. 3, top). Assuming a steady state, the following relationships should hold for the box:

$$Q_U = Q_R + Q_L \quad (1)$$

for the water balance,

$$Q_U \cdot S_U = Q_R \cdot S_R + Q_L \cdot S_L \quad (2)$$

for the mass balance of salts,

$$Q_U \cdot C_U = Q_R \cdot C_R + Q_L \cdot C_L + I_c \quad (3)$$

for the mass balance of non-conservative element;

where Q = water flow rate, S = salinity, C = concentration of non-conservative element, and I_c = the total flux of non-conservative element from (positive) or to (negative) suspended particles and sediments within the box. The subscripts R, U, and L represent the river inflow at the upstream boundary of the box (m.p. 24), upper non-tidal net outflow and lower non-tidal net inflow at the downstream boundary of the box (m.p. -6), respectively (Fig. 3, top). By solving the above three equations, one obtains:

$$C_R + \frac{I_c}{Q_R} = \frac{S_L - S_R}{S_L - S_U} C_U - \frac{S_U - S_R}{S_L - S_U} C_L \quad (4)$$

In a concentration vs. salinity plot (Fig. 2) it can be easily shown geometrically that the interception of a line connecting points (S_U, C_U) and (S_L, C_L) on C -axis at $S = S_R$ is $(C_R + I_c/Q_R)$. The $(C_R + I_c/Q_R)$ term is called the "effective river end member concentration" [9,11]. From Fig. 2, $C_R + I_c/Q_R$ for Ba and ^{226}Ra are about 284 nm Ba/1 and 5.9 dpm $^{226}\text{Ra}/100$ l. If the Ba and ^{226}Ra concentration values at m.p. 24 and $Q_R = 1140 \pm 90 \text{ m}^3/\text{s}$ [8] are chosen, I_c for Ba and ^{226}Ra would be $(2.3 \pm 0.2) \times 10^6$ mole Ba/yr and $(1.7 \pm 0.2) \times 10^{12}$ dpm $^{226}\text{Ra}/\text{yr}$. In the same model calculation, Li et al. [8] gave $I_{\text{Ra}} = 2.1 \times 10^{12}$ dpm $^{226}\text{Ra}/\text{yr}$, which is a slight over-estimation caused by the different way of choosing C_U and C_L values for ^{226}Ra .

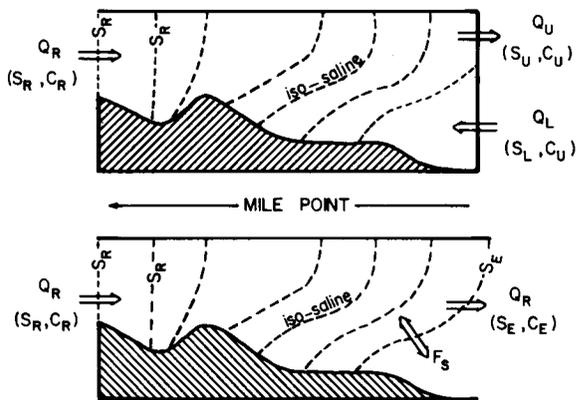


Fig. 3. The Hudson estuary between an upstream mile point and a downstream mile point (top) and between iso-saline surfaces of S_R (riverine end member) and S_E (estuarine end member) (bottom) is isolated as an enclosed box for mass balance consideration of water, salt and non-conservative element at a steady state.

Re-arranging equation (4), one obtains:

$$\begin{aligned} C_R + I_c/Q_R &= C_U - (S_U - S_R) \frac{C_U - C_L}{S_U - S_L} \\ &= C_U - (S_U - S_R) \left(\frac{dC}{dS} \right)_{\text{at m.p. } -6} \end{aligned} \quad (5)$$

Equation (5) is very similar in form to the chemical mass balance equation derived by Boyle et al. [13] for non-conservative element in estuaries. We present here an alternate and much simpler way of deriving their equation: we consider an estuary between two iso-saline surfaces of salinity S_R (riverine end member) and S_E (estuarine end member) as a box (Fig. 3, bottom). The total advective flux of water across any iso-saline surface is assumed to be Q_R (= the total water flow rate across S_R iso-saline surface). The S_R iso-saline surface can be chosen such that the diffusive flux of salt across this surface is near zero (due to near zero salinity gradient). On the other hand, the integrated diffusive flux of salt across the iso-saline surface of salinity S_E , F_s , is defined by:

$$F_s = - \int_a K_n \left(\frac{dS}{d\gamma_n} \right)_{S=S_E} da \quad (6)$$

where a = the area of iso-saline surface of salinity S_E , K_n = eddy diffusion coefficient normal to the iso-saline surface, and γ_n = distance normal to the iso-saline surface, positive in direction of decreasing salinity.

Similarly, the total diffusive flux of non-conservative elements across the iso-saline surface of salinity S_E , F_c , can be defined by:

$$\begin{aligned} F_c &= - \int_a K_n \left(\frac{dC}{d\gamma_n} \right)_{S=S_E} da \\ &= - \int_a K_n \left(\frac{dC}{dS} \cdot \frac{dS}{d\gamma_n} \right)_{S=S_E} da \\ &= F_s \left(\frac{dC}{dS} \right)_{S=S_E} \end{aligned} \quad (7)$$

but only if $(dC/dS)_{S=S_E}$ or the concentration of non-conservative element along the S_E iso-saline surface, C_E , is constant, in other words, S_E and C_E surfaces never cross over. Boyle et al. [13] assumed implicitly

this condition. Again only at a steady state condition, the following relationships hold:

$$Q_R \cdot S_R + F_s \cdot S_E = Q_R \cdot S_E \quad (8)$$

for the salt mass balance, and:

$$Q_R \cdot C_R + I_c + F_c = Q_R \cdot C_E \quad (9)$$

for the mass balance of non-conservative element in the box. Solving equations (7), (8) and (9), one obtains:

$$C_R + \frac{I_c}{Q_R} = C_E - (S_E - S_R) \left(\frac{dC}{dS} \right)_{S=S_E} \quad (10)$$

Equation (10) is equivalent to the equation derived by Boyle et al. [13]. The assumption by Boyle et al. [13] that sea salts does not accumulate in the mixing zone of an estuary is equivalent to assume a steady state as we have done here.

Differentiating equation (10) with salinity, one obtains:

$$\frac{dI_c}{dS} = -Q_R(S_E - S_R) \left(\frac{d^2C}{dS^2} \right)_{S=S_E} \quad (11)$$

Since d^2C/dS^2 is equal to zero in the linear section of the C vs. S plot, there is no material transport between suspended particle + sediments and water column (i.e., $dI_c/dS = 0$).

In summary one should keep in mind that the mass balance models derived by Boyle et al. [13] and by us here assume a steady state condition of an estuary, which may not be always true.

2.3. Desorption experiment

In our desorption experiment we dispersed two known different amounts of wet surface sediments (20.7 g and 4.1 g dry weight obtained from the upstream Hudson) separately into two vessels containing known amount of seawater (1540 g each). The sediments are 83% fine ($<63 \mu\text{m}$). The sediments were resuspended twice a day. After about 10 days of equilibration time, the supernates were filtered through a $0.45\text{-}\mu\text{m}$ millipore filter and were analyzed for Ba and ^{226}Ra contents. Thus we obtain two equations defining the distribution coefficient and two mass balance equations for exchangeable ion, i.e.:

$$k = X_1/C_1 \quad (12a)$$

$$k = X_2/C_2 \quad (12b)$$

$$V_1 C_1 + m_1 X_1 = V_1 C_0 + m_1 X_0 \quad (12c)$$

$$V_2 C_2 + m_2 X_2 = V_2 C_0 + m_2 X_0 \quad (12d)$$

where k = distribution coefficient (g water/g dry sediment), X = concentration of an exchangeable ion per gram of sediment, C = concentration of an exchangeable ion per gram of supernate, V = weight of seawater in a vessel (grams), and m = weight of sediment added to the vessel (in dry weight, grams); the subscripts 0, 1 and 2 represent initial, first vessel and second vessel, respectively.

In the above equations V_1 , V_2 , m_1 , m_2 , C_0 , C_1 and C_2 are known parameters.

Solving equations (12a) to (12d), one obtains k and X_0 (initial concentration of exchangeable ion per gram of upstream Hudson sediments), i.e.:

$$k = \frac{V_2}{m_2} \left(\frac{C_2}{C_1} - \frac{C_0}{C_1} \right) - \frac{V_1}{m_1} \left(1 - \frac{C_0}{C_1} \right) \left/ \left(1 - \frac{C_2}{C_1} \right) \right. \quad (13)$$

and:

$$X_0 = \frac{V_1}{m_1} (C_1 - C_0) + k C_1 \quad (14)$$

Substituting the following known and measured values in equations (13) and (14):

$$V_1 = V_2 = 1540 \text{ g}, \quad m_1 = 20.7 \text{ g}, \quad m_2 = 4.1 \text{ g}$$

and:

$$C_0 = 0.10 \pm 0.01, \quad C_1 = 1.60 \pm 0.10,$$

$$C_2 = 0.86 \pm 0.05 \text{ dpm } ^{226}\text{Ra/kg for } ^{226}\text{Ra},$$

$$C_1 = 0.070 \pm 0.001, \quad C_1 = 1.73 \pm 0.02,$$

$$C_2 = 1.18 \pm 0.02 \text{ }\mu\text{mole Ba/kg for Ba},$$

one obtains:

$$k_{\text{Ba}} = 532 \pm 10 \text{ and } X_0 = 1.04 \pm 0.02 \text{ }\mu\text{mole Ba/g}$$

and:

$$k_{\text{Ra}} = 235 \pm 20 \text{ and } X_0 = 0.49 \pm 0.05 \text{ dpm } ^{226}\text{Ra/g}.$$

We note that C_1 and C_2 of Ba represents values several times the saturation level with respect to barite. Should precipitation of barite occur, k_{Ba} and k_{Ra} determined would be erroneously low. However, it has been found that ion activity product many

times the thermodynamic equilibrium value is required for heterogeneous or homogeneous nucleation [14,15]. Hence it is most likely that barite precipitation did not occur in our experimental systems and calculations of k_{Ba} and k_{Ra} are not affected.

If we assume that the concentrations of Ba and ^{226}Ra at m.p. 50 represent the values in rough ion exchange equilibrium with river sediments before the drastic diatom uptake, the distribution coefficients of Ba and ^{226}Ra in the fresh river water would be about:

$$k_{\text{Ba}} = \frac{X_0}{C_{\text{R}}} = \frac{1.04 \mu\text{mole/g}}{0.366 \text{ nmole/g}} = 2800$$

and

$$k_{\text{Ra}} = \frac{0.41 \text{ dpm/g}}{2.3 \times 10^{-5} \text{ dpm/g}} = 21,000$$

which are much higher than that in seawater.

If the sediments at m.p. -6 is again in rough equilibrium with the overlying water, the exchangeable Ba and ^{226}Ra in the sediments there would be:

$$\begin{aligned} X_{\text{Ba}} &= k_{\text{Ba}} \cdot C_{\text{Ba}} = 532 \times 131 \times 10^{-12} \text{ mole Ba/g} \\ &= 70 \text{ nmole Ba/g} \end{aligned}$$

$$\begin{aligned} X_{\text{Ra}} &= k_{\text{Ra}} \cdot C_{\text{Ra}} = 235 \times 10.5 \text{ dpm } ^{226}\text{Ra}/100 \text{ kg} \\ &= 0.024 \text{ dpm } ^{226}\text{Ra/g} \end{aligned}$$

Comparing to $X_0 \approx 1040 \text{ nmole Ba/g}$ and $X_0 \approx 0.49 \text{ dpm } ^{226}\text{Ra/g}$, more than 93% of exchangeable Ba and ^{226}Ra should have been desorbed from the upstream river-borne sediment within the estuary.

The total flux of suspended particles across m.p. 24 was estimated about $2.9 \pm 0.3 \times 10^{12} \text{ g/yr}$ on October 25, 1976 (two days before our water sampling) [16]. Therefore the desorption of Ba and ^{226}Ra from this suspended particle flux in the estuary are roughly:

$$\begin{aligned} I_{\text{Ba}} &= (1040 - 70) \times 10^{-9} \text{ mole Ba/g} \times 2.9 \times 10^{12} \text{ g/yr} \\ &= (2.8 \pm 0.3) \times 10^6 \text{ mole Ba/yr} \end{aligned}$$

and:

$$\begin{aligned} I_{\text{Ra}} &= (0.49 - 0.02) \text{ dpm } ^{226}\text{Ra/g} \times 2.9 \times 10^{12} \text{ g/yr} \\ &= (1.4 \pm 0.2) \times 10^{12} \text{ dpm } ^{226}\text{Ra/yr} . \end{aligned}$$

Comparing with $I_{\text{Ba}} = (2.3 \pm 0.2) \times 10^6 \text{ mole Ba/yr}$ and $I_{\text{Ra}} = 1.7 \pm 0.2 \times 10^{12} \text{ dpm } ^{226}\text{Ra/yr}$ obtained from the mass balance model, the agreement is remarkable.

The worldwide estimate of total suspended sediment flux from rivers to oceans ranges from 13×10^{15} to $33 \times 10^{15} \text{ g/yr}$ [17]. Therefore, if the Hudson River sediments are assumed to be typical of all other river sediments with regard to the characteristics of desorption, the total dissolved Ba and ^{226}Ra fluxes from the estuaries by desorption would be about $(13 \sim 32) \times 10^9 \text{ mole Ba/yr}$ and $(6.1 \sim 15.5) \times 10^{15} \text{ dpm } ^{226}\text{Ra/yr}$. Comparing to the fluxes of $14.5 \times 10^9 \text{ mole Ba/yr}$ and $0.7 \times 10^{15} \text{ dpm } ^{226}\text{Ra/yr}$ from the fresh water parts of rivers (assuming the global flux of river waters = $3.33 \times 10^{19} \text{ g/yr}$ [18], and average concentration of Ba and ^{226}Ra in rivers $\bar{C}_{\text{Ba}} = 0.44 \times 10^{-9} \text{ mole Ba/g}$ [18], and $\bar{C}_{\text{Ra}} = 0.02 \times 10^{-3} \text{ dpm/g}$ [8,19]), the desorption of Ba in estuaries can easily increase the continental flux of dissolved Ba one to three times. This value is compared to an increase of 30% for the Zaire [11], 90% for the Amazon [9] and 75–130% for the Mississippi [10] by desorption. On the other hand, the desorption of ^{226}Ra in estuaries can increase the continental ^{226}Ra flux 9 to 22 times. Compared to the total ^{226}Ra flux from coastal sediments (including estuaries and shelves) to the surface oceans ($\sim 36 \times 10^{15} \text{ dpm/yr}$) [1], the desorptive ^{226}Ra fluxes from estuaries can account for 17 to 43%. (Note: the worldwide estimate of total suspended sediment flux from rivers to oceans was misprinted as 13×10^{14} to $33 \times 10^{14} \text{ g/yr}$ instead of 13×10^{15} to $33 \times 10^{15} \text{ g/yr}$ at the end of Li et al.'s paper [8].)

The ion exchange experiments between fluvial clays and seawater [20] also shows that an appreciable amount of exchangeable Ca^{2+} in the fluvial clays are replaced out mainly by Na^+ and slightly by K^+ and Mg^{2+} ions of seawater when fluvial clays and seawater was mixed together. Ca^{2+} released through ion exchange may increase the total river flux of Ca^{2+} by about 10% [20]. The distribution coefficients of Cs [21] and Sr [22] decrease about one to two orders of magnitude from 0.01*N* to 0.2*N* NaCl solution for various clay minerals. Therefore, one would also expect significant desorptive inputs of Sr and Cs (and probably Rb) from sediment particles in estuaries. Indeed, the desorption of reactor released ^{137}Cs and

^{134}Cs from sediment particles was observed in the Hudson estuary [23] and in the Bombay harbor [24].

3. Summary

(1) The linear correlation among Si, Ba and ^{226}Ra in the fresh water section of the Hudson River is plausibly explained by their uptake by fresh water diatoms.

(2) The desorptive fluxes of Ba and ^{226}Ra in the Hudson estuary as estimated from a simple mass balance model is consistent with the estimation based on the distribution coefficient of Ba and ^{226}Ra , exchangeable Ba and ^{226}Ra on particles and the total suspended particle flux.

(3) The desorption of Ba and ^{226}Ra in estuaries augment at least the global river flux of dissolved Ba about one time and of dissolved ^{226}Ra about nine times.

(4) The desorptive flux of ^{226}Ra from estuaries to the surface oceans account for 17–43% of the total flux from the coastal sediments.

(5) The desorptive input of other alkali (Rb and Cs) and alkaline earth elements (Ca, Sr) in estuaries should be appreciable. Further studies are needed.

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