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Distribution and Flux of ^{226}Ra and ^{228}Ra in the Amazon River Estuary

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Measurements of ^{226}Ra and ^{228}Ra in the Amazon River estuary show that desorption from riverborne suspended particulate matter in the estuary increases the riverine flux of both isotopes to the ocean by a factor of approximately 5 over the flux attributable to radium dissolved in the river water alone. The total Amazon flux supplies approximately 0.20% of the ^{226}Ra and approximately 2.6% of the ^{228}Ra standing crops in the near-surface Atlantic (0–200 m). Diffusive flux from estuarine and shelf sediments and desorption from resuspended sediments in the region of the estuary approximately double the estuarine ^{226}Ra concentration and quadruple the estuarine ^{228}Ra concentration above that caused by the dissolved and desorbed river components alone.

INTRODUCTION

The mixing between low ionic strength river water and high ionic strength seawater in an estuary is associated with numerous chemical and biological processes that can significantly modify the flux of chemical species to the ocean. Iron, other trace metals, and organics are removed by condensation and flocculation reactions; sodium and magnesium are removed and minor ions added by ion exchange on clays and organics; and nutrients are removed by organisms. If an element is either released to or removed from solution during mixing of river water and seawater, the measured river concentration multiplied by the water flow rate will not give a reliable estimate of the total dissolved flux of that element to the ocean. Such is the case for radium.

Previous authors [*Koczy et al.*, 1957; *Blanchard and Oakes*, 1965; *Moore*, 1969] proposed a large flux of radium from coastal sediments to explain the high concentrations of radium measured in coastal waters relative to river water and open ocean surface waters. More recent estuarine studies on the behavior of radium [e.g., *Li et al.*, 1977, 1979; *Elsinger and Moore*, 1980, 1983; *Elsinger et al.*, 1981] and its chemical analog, barium [*Hanor and Chan*, 1977; *Edmond et al.*, 1978], have demonstrated that desorption during mixing can strongly influence the estuarine concentration and net riverine flux of these elements. Similar desorption phenomena have been observed for several other cations [e.g., *Kharkar et al.*, 1968; *Thomson et al.*, 1975]. In this paper, dissolved ^{228}Ra and ^{226}Ra concentrations from the Amazon River estuary are reported, and estimates are made for their fluxes. The Amazon is an important case study, since it is the major riverine source of water and particulate matter to the Atlantic Ocean.

SAMPLE COLLECTION AND ANALYSIS

All of the samples reported here were collected from the R/V *Knorr* during leg 1 of the Transient Tracers in the Ocean–Tropical Atlantic Study (TTO–TAS) on December 19–20, 1982. The station locations are shown in Figure 1. Data were obtained by a number of investigative groups for salinity, temperature, nutrients, alkalinity, pCO_2, tritium, freon, total suspended matter, trace metals, and major cations, as well as ^{226}Ra and ^{228}Ra.

A detailed description of the ^{228}Ra and ^{226}Ra collection and analysis procedures used during TTO has been given by *Key* [1983] and *Moore et al.* [1985]. The standard TTO collection procedures were modified slightly to accommodate the high estuarine levels of suspended matter and the fact that stations were closely spaced in time. Briefly, water for all ^{226}Ra samples, and all except three ^{228}Ra samples, was collected by lowering a plastic hose over the side and pumping from just below the surface. The large volume (250 L) ^{228}Ra samples were collected in plastic barrels and the small volume (20–28 liter) ^{226}Ra samples in plastic carboys. The samples stood for approximately 4 days to allow suspended matter to settle out. The water was then filtered through a plug of raw acrylic fiber before extracting the radium by gravity draining through manganese-dioxide-coated acrylic fiber. Three ^{228}Ra samples were collected by hanging a nylon mesh bag filled with manganese fiber over the fantail and allowing it to soak while the boat was on station. It was difficult to assign a precise salinity value to the surface soak samples because of the salinity variations experienced while on station. The value assigned was that measured on the small volume sample collected at the same station.

Radium was extracted from the large volume ^{228}Ra fiber samples in the lab. Any sediment that passed through the raw fiber filter and was trapped on the manganese fiber was removed by thorough rinsing with deionized water. The ^{228}Ra/^{226}Ra ratio was determined by counting with a germanium well detector. ^{226}Ra in the small volume samples was determined by ^{222}Rn ingrowth. Errors reported with the ^{228}Ra/^{226}Ra ratio are 1 standard deviation and include counting, blank, background, and calibration errors for three gamma peaks for each isotope [*Moore et al.*, 1985]. The ^{226}Ra concentration errors are an error-weighted standard deviation of the mean of multiple analyses and include contributions from counting, efficiency determination, volume, background, and blank [*Key*, 1983]. These uncertainties were propagated to give the ^{228}Ra concentration error.

RESULTS

The results are presented in Tables 1 and 2. The average uncertainties are 6.2% for the ^{228}Ra/^{226}Ra ratio, 2.4% for the ^{226}Ra concentration, and 7.1% for the ^{228}Ra concentration. No correction was made for radium released from any particulate matter that remained on the manganese fiber after rinsing. *Moore and Edmond* [1983], who used similar procedures, estimated that the particulate contribution to the measured radium concentration was less than 10%, based on measurements of aluminum and iron concentrations on the residue from fiber leaches and washes. Careful examination of the sample leachates and knowledge of the radium concentration

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of the suspended matter indicate that particulate radium contamination is much less than 10% and well within the analytical precision.

The suspended solids and radium data from station 38 are somewhat questionable. The water was extremely shallow, and it is possible that the high suspended solids were due to turbulent resuspension caused by the ship's cycloids (Note: the depth contours shown in Figure 1 are only approximate). Cycloid usage was limited as much as possible at subsequent stations. Since the samples were allowed to settle before the radium was extracted, there was ample time to come to exchange equilibrium. Any artificially induced suspended matter in the sample would result in an increased dissolved radium concentration.

The suspended particulate matter, ^{226}Ra, ^{228}Ra, and ^{228}Ra/^{226}Ra data are plotted against salinity in Figures 2–4. Both ^{226}Ra and ^{228}Ra concentrations increase with salinity from the river end-member (station 44) to a maximum value near 20‰ salinity. Both concentrations then decrease to the ocean end-member value (station 33). The ^{228}Ra/^{226}Ra activity ratio also increases with salinity from the river end-member. The ratio levels off through the mid-salinity range then finally drops to the ocean ratio above a salinity of 32.5‰. Although the near-surface suspended particulate matter data exhibit more scatter than the radium data, a broad maximum in the mid-salinity region of the estuary is still prominent. The maximum in suspended matter coincides with the radium isotope maxima.

DISCUSSION

Hydrography

Samples were collected at the end of the dry season, which is the time of lowest river discharge. On December 13, just prior to sampling, the river discharge measured at Obidos was 123,000 m^3/s (J. Richey, personal communication, 1983). The mean annual discharge is 175,000 m^3/s [*Oltman*, 1968]. The general hydrographic state of the estuary during the December sampling period can best be described by contrasting it to the detailed data of *Edmond et al.* [1981], which were taken in May 1976 during high discharge (230,000 m^3/s at Obidos). The spatial variation of surface salinity at low discharge closely resembled the data collected at high discharge. However, the salt wedge was not nearly as well developed at low discharge. The difference between surface and bottom salinity never exceeded 13‰, and strong stratification was seen only for surface salinities greater than 21‰. At high discharge the maximum surface-to-bottom difference approached 30‰. This contrast in salt wedge development in the estuary is suggestive of "river dominated" conditions at high discharge and "tidally dominated" conditions at low discharge.

On the same day that the discharge was measured the total suspended load of particles (less than 63 μm) at Obidos was 238 mg/kg (R. Meade, personal communication, 1983), which is considerably higher than the annual mean of 163 mg/kg [*Meade et al.*, 1979]. The total suspended load at the river end-member during our investigation was 114 mg/kg near the surface and 127 mg/kg near the bottom. The large difference between the suspended load we measured at station 44 and that measured by Meade et al. at Obidos is probably due to different sampling methods. His value is an integrated average across the entire channel, an average obtained by using equipment designed to collect suspended matter, while ours is a spot sample taken from a Niskin bottle.

During this work, at low discharge, suspended matter concentrations peaked at intermediate salinities with values significantly above 100 mg/kg and remained elevated until salinities reached 21–22‰ (Figure 2). The very high suspended matter concentrations may be the result of resuspension of bottom sediments in the estuary. In addition the near-bottom to near-surface suspended sediment concentration differences were significantly greater than at high river discharge. For salinities less than 20‰ the suspended sediment concentrations given here are much higher than reported by *DeMaster et al.* [1983] for October 1979. Their data decreased rapidly from about 40 mg/L at the river end-member to less than 10 mg/L at a salinity of 7–8‰, and it decreased gradually from that value throughout the rest of the estuary. Their data is similar to that presented by *Edmond et al.* [1981] during high river discharge (see Figure 2), but the values are lower at very low salinities.

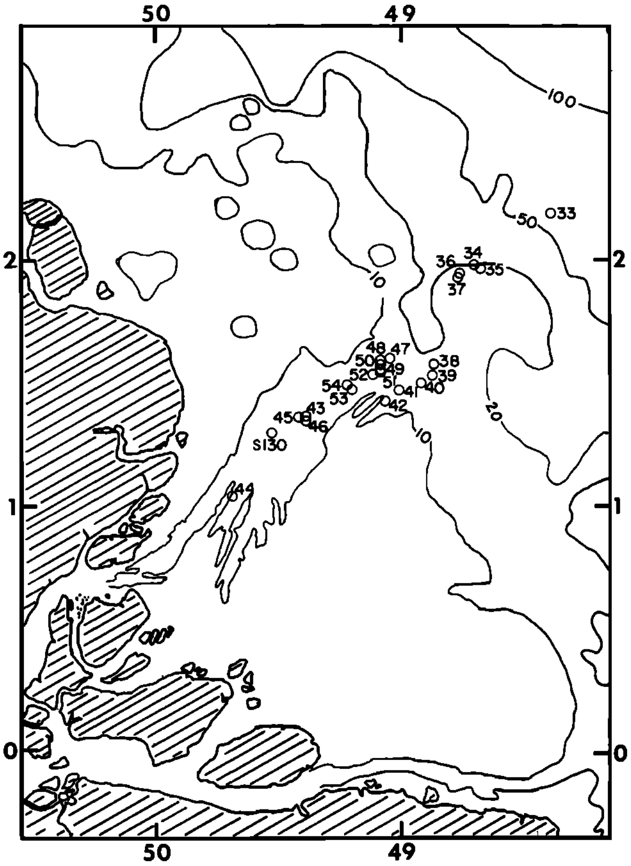

Fig. 1. Station locations in the Amazon River estuary during leg 1 of the Transient Tracers in the Ocean–Tropical Atlantic Study.

The low concentration of near-surface suspended matter at salinities greater than 22‰ may be due to the plume of the Para River. This plume is often evident on GOES satellite photographs of the estuary [see, for example, *Szekielda*, 1982]. The silicate data are consistent with this interpretation. Silicate data for salinities less that 22‰ plot on a straight line connecting the points (S = 0‰, Si = 143 μm/kg) and (S = 36.5‰, Si = 4 μm/kg). The silicate concentration is discontinuous at approximately 22‰ salinity, falling from 58 μm/kg to 6–10 μm/kg and remains low through the rest of the estuary (see Figure 5). Other nutrients show similar features. If the drop in nutrients and suspended particulate matter are a result of the Para River plume, then this water must have been subjected to fairly extensive biological activity at some point. D. J. DeMaster (personal communication, 1984) measured a silica concentration of 48 μm/kg for the Para River in October

TABLE 1. Amazon River Estuary Hydrography

Station*	Latitude (N), deg, min	Longitude (W), deg, min	Date	Time +3	Temperature, °C	Salinity, ‰	Suspended Matter, mg/kg
33 S	2 11.6	48 24.0	December 9, 1982	1117	27.364	36.356	0.82
B					26.988	36.326	0.74
34 S	1 59.2	48 42.4	December 9, 1982	1438	28.378	32.353	
B					27.890	36.543	4.64
35 S	1 58.7	48 41.2	December 9, 1982	1542	28.497	29.670	4.40
B					27.870	36.535	8.97
36 S	1 57.3	48 46.0	December 9, 1982	1703	28.459	25.478	5.66
B					27.857	36.317	21.8
37 S	1 55.5	48 47.0	December 9, 1982	1800	28.432	22.909	6.06
B					27.907	35.749	17.5
38 S	1 33.8	48 48.3	December 9, 1982	2100	27.899	21.006	†319.
B					27.943	22.442	†453.
39 S	1 31.4	48 53.3	December 9, 1982	2208	27.928	14.556	54.2
B					27.954	18.743	485.
40 S	1 29.8	48 56.1	December 9, 1982	2300	27.837	12.182	45.6
B					27.932	17.479	870.
41 S	1 27.9	49 00.9	December 9, 1982	2344		10.324	166.
B					27.941	12.524	754.
42 S	1 25.9	49 03.7	December 10, 1982	0045	27.654	6.680	95.3
B					27.818	8.052	541.
43 S	1 21.5	49 23.4	December 10, 1982	0223	27.792	2.307	37.9
B					27.875	3.316	461.
44 S	1 02.8	49 41.7	December 10, 1982	0731	28.478	0.043	114.
B					28.471	0.046	127.
45 S	1 21.7	49 24.9	December 10, 1982	1136	28.188	0.653	185.
B					27.885	1.437	182.
46 S	1 21.9	49 23.6	December 10, 1982	1230	28.161	1.649	134.
47 S	1 35.6	49 02.8	December 10, 1982	1612	28.210	19.479	529.
48 S	1 35.5	49 03.3	December 10, 1982	1650	28.290	17.338	349.
49 S	1 33.4	49 04.9	December 10, 1982	1812	28.120	14.384	571.
50 S	1 34.2	49 05.0	December 10, 1982	1843	27.850	9.320	173.
51 S	1 33.9	49 05.3	December 10, 1982	1906	28.000	8.034	128.
52 S	1 32.2	49 07.1	December 10, 1982	1948	28.100	5.723	125.
53 S	1 28.6	49 12.4	December 10, 1982	2051	27.920	3.106	153.
54 S	1 29.2	49 13.5	December 10, 1982	2129	28.100	4.234	125.

*S, surface sample; B, near-bottom sample.

†Very shallow water; possible resuspension by ship's cycloids.

1979. If this water were mixed with enough surface seawater to produce a salinity of 22‰, the silica would be about 21 μm/kg. The difference between this calculated value and the measured value (6–10 μm/kg) implies a silicate loss of 10–15 μm/kg, which agrees with *DeMaster et al.*'s [1983] biological uptake estimates for the region. The Para River explanation for the silicate discontinuity is also consistent with the surface salinity distribution. There was a very broad band (31 km) of water with salinities between 21 and 25‰. More than half the width of this band had a salinity between 21 and 22‰. This relatively isohaline band was followed by a strong salinity gradient from 21 to 15‰ in a distance of only 9 km. Surface nutrients and suspended solids increased dramatically in the strong gradient zone. These distributions are consistent with what one might expect in the shear zone between two major river plumes.

An alternative explanation for the decrease in nutrients and particulate matter at 22‰ is that this water is a remnant of another circulation regime or that biological activity was high in that area. The biological explanation is unlikely, since very few tests were observed in any of the suspended matter collected during this study.

Radium Distribution

Radium and barium are generally considered to be chemical analogs. *Boyle* [1976] reported barium data for the Amazon estuary during high discharge (June 1974). He found a sharp increase in barium concentrations from 0 to 5‰ salinity. Above 5‰ salinity the barium concentration decreased linearly to the ocean end-member value. The sharp increase was attributed to desorption from suspended particulate matter. This is consistent with the suspended solids distribution with salinity mentioned above, i.e., rapidly decreasing particle concentration with increasing salinity in the low-salinity region of the estuary during the high-flow regime.

Three previous studies that included radium measurements have been made in the Amazon. *Moore* [1967, 1969] measured one ^{226}Ra water sample from the river and used the ^{228}Ra/^{226}Ra measured in carbonate shells to calculate the ^{228}Ra concentration in the river. *Dion* [1983] made a series of ^{226}Ra and ^{228}Ra measurements in the Amazon estuary during October 1979. *Moore and Edmond* [1983] measured ^{226}Ra and ^{228}Ra throughout the river system during high river discharge in June and July 1976. Based on *Stallard*'s [1980] mass balance model, Moore and Edmond concluded that ^{226}Ra behaved conservatively upriver of the estuary.

The river and ocean end-member radium measurements are summarized in Table 3. The range of concentrations for ^{228}Ra and ^{226}Ra in the river end-member samples shows considerably more variability than the precision of the individual measurements. The variability may be due to seasonal changes in concentration, sampling location, and/or different sampling and analysis techniques. Variability with location is illustrated by *Moore and Edmond*'s [1983] ^{226}Ra data. They found a

TABLE 2. Amazon River Estuary Surface Samples

Station	Salinity	Silicate	^{228}Ra/^{226}Ra	^{226}Ra, dpm/100 *L*	^{228}Ra, dpm/100 *L*
33	36.4	1.6	0.39 ± .05	7.4 ± .2	2.9 ± 0.4
34	31.8	6.0	*3.19 ± .09	14.2 ± .3	*45. ± 2.
35	29.5	9.0	3.2 ± .2	15.1 ± .3	49. ± 3.
36	25.3	13.9	*3.0 ± .2	15.2 ± .3	*46. ± 3.
37	22.7	25.	3.4 ± .2	16.6 ± .3	57. ± 3.
38†	21.5	60.	*3.39 ± .07	21.7 ± .4	*74. ± 2.
47	18.9	69.	3.24 ± .08	20.2 ± .4	66. ± 2.
48	17.2	76.	3.1 ± .2	lost	
49	14.3	95.	3.1 ± .1	18.0 ± .3	56. ± 3.
39	13.7	87.	3.13 ± .09	18.8 ± .3	59. ± 2.
40	13.2	94.	3.1 ± .1	16.8 ± .4	52. ± 2.
50	8.91	106.	2.7 ± .2	12.5 ± .4	34. ± 3.
41	8.71	108.	2.7 ± .1	13.0 ± .3	36. ± 2.
51	7.87	110.	2.6 ± .1	12.3 ± .3	31. ± 2.
42	6.64	113.	2.7 ± .2	11.0 ± .2	29. ± 3.
52	5.59	120.	2.5 ± .3	9.5 ± .3	24. ± 2.
54	4.86	126.	2.3 ± .2	7.7 ± .3	18. ± 2.
53	3.10	130.	2.19 ± .09	—	—
43	2.34	131.	1.9 ± .2	7.6 ± .2	15. ± 1.
46	1.69	136.	2.0 ± .1	5.5 ± .1	10.8 ± 0.8
45	0.913	137.	1.9 ± .3	6.4 ± .2	12. ± 2.
44	0.043	142.	1.5 ± .2	5.0 ± .2	7.4 ± 1.

*Sample taken as surface soak rather than being pumped aboard.

†Radium values may be high. Very shallow water; possible resuspension of sediment by ship's cycloids.

^{226}Ra concentration of 4.7 dpm/100 L at station S130 (0‰ salinity), which was approximately halfway between our stations 44 and 45 (see Figure 1), and a concentration of 7.3 dpm/100 L at station S202 at Urutai (0‰ salinity; 200 km upstream of the mouth but downstream of all major tributaries). Similar differences were measured for barium. Seasonal variability can be crudely estimated by comparing Moore and Edmond's ^{226}Ra data from station S130 to our data from stations 44 and 45. Their samples were collected near maximum river discharge, while ours were taken near minimum discharge, yet the ^{226}Ra results agree within experimental error. The sampling and analysis techniques were very similar for the two studies. This comparison indicates that seasonal variability of the dissolved radium concentration may be minimal in spite of the large difference in the river transport. *Dion*'s [1983] river end-member concentrations are lower than Moore and Edmond's and this study, even though his samples were collected at midseason. Insufficient data exist to resolve definitively the cause for this difference. His river end-member ^{226}Ra value falls considerably below the general trend of his data in the low-salinity region of the estuary. If a straight line is fit to his data in the low- to mid-salinity region of the estuary (excluding those data he has noted as biogenic), the river end-member intercept is 6.3 dpm/100 L, which is in the middle of the recent data by Moore and Edmond and our data.

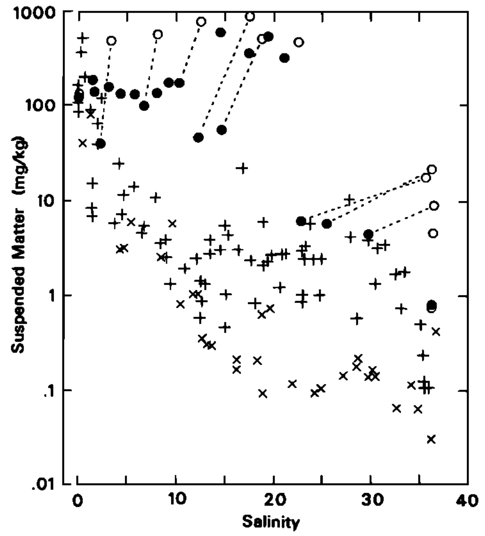

Fig. 2. Suspended matter in the Amazon River estuary. Data are adapted from *Edmond et al.* [1981] (plus), *Milliman and Boyle* [1975] (cross), and this work (dots—near surface; circles—near bottom). Previous data were collected at high discharge and are all near-surface. Note the mid-salinity maximum observed in samples collected at low discharge during this work. Surface and bottom data from each station are connected by a dotted line.

The only previous radium data in high-salinity water for this area are *Dion*'s [1983]. His values for ^{228}Ra and ^{226}Ra at high salinity fall on the trends of our data indicating that his highest-salinity stations included a shelf/estuary component.

For salinities between the freshwater and oceanic components the data presented here are generally comparable to *Dion*'s [1983]. Both isotope concentrations increase to a broad maximum in the mid-salinity range of the estuary. One important difference in the two data sets is that no compelling evidence of biological radium removal was found during this study. Plankton blooms are common in the Amazon estuary, but none were observed during the December 1982 sampling. Diatoms were very rare on filters, in contrast to high-flow-regime sampling when filters are often clogged by diatoms (R. Stallard, unpublished data, 1983). As pointed out earlier, the silica-salinity trend is linear. If biological removal was important in estuarine waters with salinities less than 20‰ during December, it would have been reflected in the silica data.

The fact that the ^{228}Ra/^{226}Ra ratio is higher in the mid-salinity region of the estuary than at the end-members indicates that there is an additional source to the estuary besides the ocean and river end-members. The only reasonable source is sediments within the estuary and along the adjacent shelf.

One of the more distinctive features of the radium data is

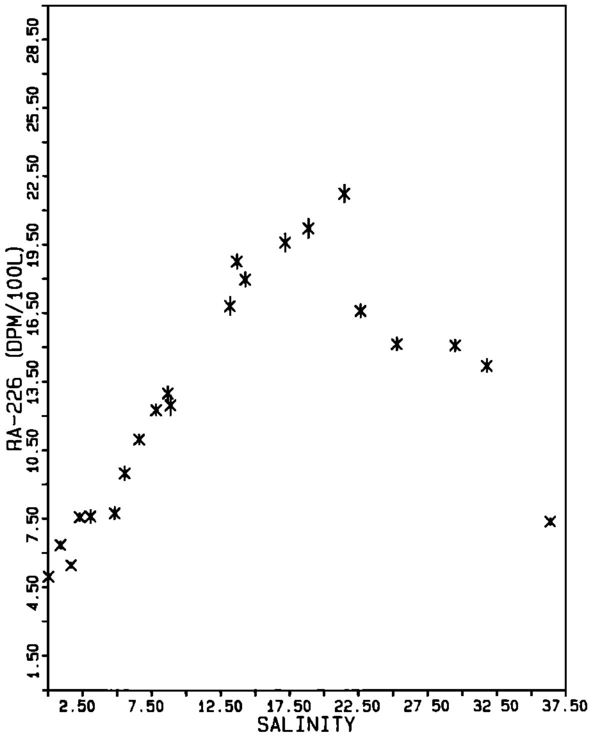

Fig. 3*a*

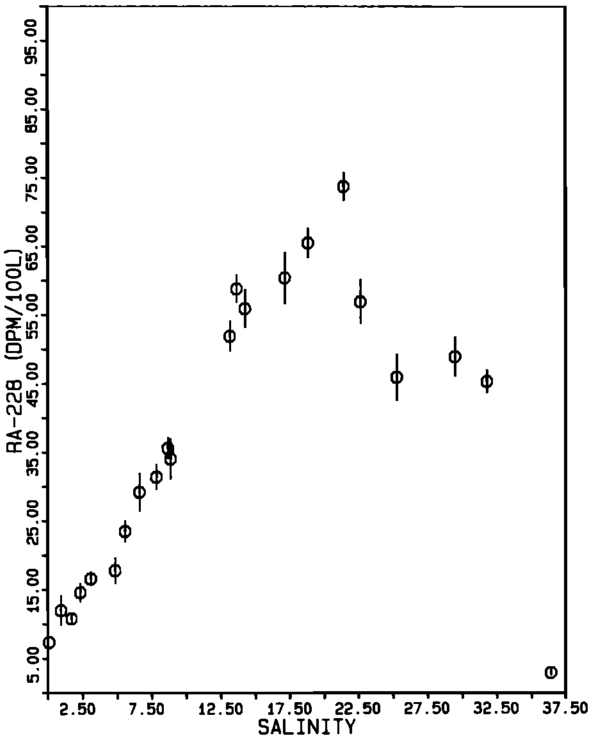

Fig. 3*b*

Fig. 3. (*a*) ^{226}Ra and (*b*) ^{228}Ra as a function of salinity in the Amazon estuary at a time of low discharge. The error bars are 1 standard deviation, as described in *Moore et al.* [1985].

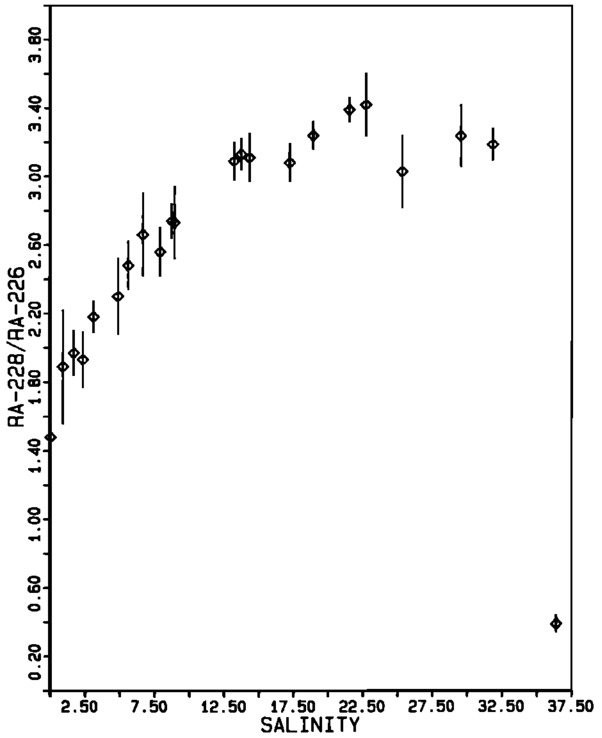

Fig. 4. ^{228}Ra/^{226}Ra activity ratio as a function of salinity in the Amazon estuary. The error bars are 1 standard deviation, as described in *Moore et al.* [1985]. The fact that the ratio is higher at mid-salinity than at either end-member indicates an additional source with a ratio higher than either end-member.

the approximate linearity of radium versus salinity between 0 and 21‰ salinity. A linear trend is generally taken as indicative of conservative mixing of two end-members. The two end-members in this case would presumably be river water and a homogeneous body of water that has properties falling somewhere along an extension of the linear salinity-radium line at a salinity greater than 21‰. This radium-enriched water could be interpreted as water that has had extensive exposure to shelf sediments. The problem with this interpretation is that it fails to account for the nonconservative desorption of radium in the estuary from river borne sediments and the addition of radium from estuarine sediments. Furthermore, no evidence was found of the large water mass of salinity greater than 21‰ with appropriate radium isotope concentrations that would be required for the conservative mixing scenario. The linear trend is probably due to the intensity of mixing in the 0–21‰ salinity zone.

MASS BALANCE CALCULATIONS

The mid-salinity maxima in dissolved ^{226}Ra and ^{228}Ra are caused by mixing Amazon River water and surface ocean water with a significant additional radium input into the estuary. In order to describe the mass balance of radium throughout the estuary, the individual sources and sinks must be quantified. Previous investigations of radium in estuaries did not have the benefit of sufficient high-precision ^{228}Ra and ^{226}Ra data to differentiate addition via desorption from riverborne suspended matter and addition by diffusive flux from bottom sediments and desorption from resuspended bottom sediments. This data set is still insufficient to absolutely separate all the different processes. However, the model used below is based on a minimum number of assumptions, which are no more restrictive than necessary.

River Flux

The flux of labile radium into the estuary can be calculated for December 1982 by using estimates of the dissolved radium

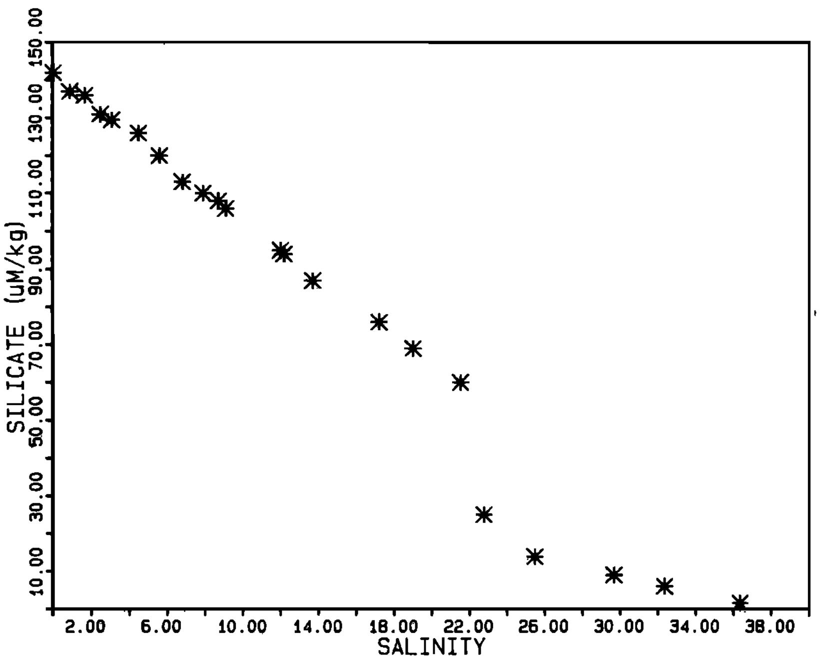

Fig. 5. Distribution of silicate as a function of salinity in the Amazon River estuary. The discontinuity at a salinity of approximately 22‰ is attributed to the Para River plume (see text).

concentration in the river and river discharge along with estimates of exchangeable radium on the river-borne sediments and the total river sediment transport. Probably the best method for estimating exchangeable radium would be to perform a series of desorption experiments (similar to those reported by *Li and Chan* [1979] for the Hudson estuary) on samples of total suspended solids taken from river water upstream of the estuary. The only assumptions needed with this approach are that the samples are representative and that estuarine conditions causing desorption can be duplicated in the laboratory. Time and equipment constraints precluded this type of sampling during this expedition. We have begun a set of desorption experiments using bottom sediment from the river; however, these results may be biased because of size differences between bottom sediments and suspended solids. On a mass basis the fine fraction of the particulate matter carries a disproportionate amount of the adsorbed material because of the higher surface-area-to-volume ratio [*Sayles and Mangelsdorf*, 1979].

TABLE 3. Comparison of River and Ocean End-Member Radium Results

^{226}Ra, dpm/100 *L*		^{228}Ra, dpm/100 *L*		Sampling Time	Reference
River	Ocean	River	Ocean		
4.7[a]	—	—	—	Jun.-Jul.	*Moore and Edmond* [1983]
7.3[b]	—	6.4[b]	—	Jun.-Jul.	*Moore and Edmond* [1983]
2.	(10.)[c]	3.2	(20.)[d]	Oct.	*Dion* [1983]
5.0[e]	7.4[f]	7.4[e]	2.9[f]	Dec.	this paper

[a] Station S130 approximately halfway between our stations 44 and 45 but with a zero salinity.

[b] Station S202 at Urutai, 20 km upriver from the mouth.

[c] Station 64 at salinity of 35.8‰. Open ocean salinity for this area is usually greater than 36‰, indicating that these values are probably elevated in radium activity by a shelf component. See text for more information.

[d] Station 63 at salinity of 34.8‰. See text and note *c* above.

[e] Station 44.

[f] Station 33.

An estimate of the radium desorbed from river-borne suspended matter was obtained by considering the decrease in total ^{226}Ra measured on suspended solids that settled from the water samples prior to radium extraction. If we assume that the decrease in ^{226}Ra concentration on the suspended material is representative of desorption, then we can calculate the ^{226}Ra source caused by desorption. Results of a few analyses are presented in Table 4. The difference in the total ^{226}Ra concentration of the solids between station 44 ($S = 0.04‰$) and station 38 ($S = 21.5‰$) was 0.93 ± 0.24 dpm/g dry weight. Using this value for the desorption and Meade's value of 238 mg/kg for the total suspended load of the river, the desorbed ^{226}Ra, expressed in terms of water concentration, is 22.1 ± 5.7 dpm/100 L.

Dion [1983] made six measurements of particulate ^{226}Ra concentration. He found 1.71 ± 0.03 dpm/g in the river. The value dropped to 0.73 ± 0.01 dpm/g by the time salinity had reached 1.3‰, and it remained at about that level through the estuary to the highest salinity he reported of 21.3‰. The

TABLE 4. Preliminary Suspended Solids Results

		Total Activity by Gamma Counting, dpm/g dry weight		
Station	Salinity, ‰	^{226}Ra	^{228}Ra	^{228}Ra/^{226}Ra
44	0.043	2.59 ± 0.21	2.59 ± 0.20	1.00 ± 0.11
46	1.69	2.16 ± 0.08	2.64 ± 0.18	1.22 ± 0.09
50	8.91	2.11 ± 0.23	2.47 ± 0.27	1.17 ± 0.18
38	21.5	1.66 ± 0.11	1.79 ± 0.20	1.08 ± 0.14

average of his values for samples with a salinity greater than or equal to 5‰ was 0.60 ± 0.07 dpm/g. Assuming these data are representative, one obtains an ^{226}Ra loss of 1.1 ± 0.1 dpm/g, which is very close to our estimate of 0.93 dpm/g.

These calculations are somewhat biased, since the suspended material collected in the estuary must be a mixture of resuspended bottom sediments derived from both the shelf and the river as well as newly supplied river-borne suspended solids. The situation is complicated further by the fact that the sediments in the estuary are continually reequilibrating with the dissolved radium in the estuary. The magnitude of this bias can be estimated by further examination of *Dion*'s [1983] data. He presented aluminum concentrations on the same samples analyzed for particulate radium. If his radium data are normalized to his zero-salinity aluminum value and then the radium loss calculated as above, the result is 0.58 ± 0.07 dpm/g or only about half of the original estimate from his data (1.1 ± 0.1 dpm/L). The normalized estimate agrees rather well, however, with the desorption experiment value of 0.49 ± 0.05 dpm/g obtained by *Li and Chan* [1979] for the Hudson estuary.

An extreme upper limit for the desorption can be obtained by assuming that all of the particulate radium at the river end-member is adsorbed and that all of it is released in the estuary. This would result in a desorptive ^{226}Ra addition to the estuary of 2.59 ± 0.21 dpm/g. The point of this discussion is that, even though our estimate of 0.9 dpm/g is tenuous, it should be good to a factor of approximately 2 (i.e., the desorbed ^{226}Ra is between 0.6 and 2.6 dpm/g) and is probably quite a bit better than that.

Since the chemistry of the two radium isotopes is identical, the comparable ^{228}Ra source term can be calculated from the desorbed ^{226}Ra value and ^{228}Ra/^{226}Ra in the river, assuming, as before, that the radium dissolved in the river and adsorbed on the river-borne suspended matter is in ion exchange equilibrium. The resulting desorbed ^{228}Ra source is 1.4 dpm/g. We feel that it is better to use this method for ^{228}Ra than to utilize the method just used for ^{226}Ra. The reequilibration problem mentioned above for ^{226}Ra would be much more severe for ^{228}Ra because of the very large fraction of the total estuarine concentration of ^{228}Ra derived from the sedimentary source term (see below). These data and the resulting river flux values are summarized in Table 5.

TABLE 5. Model Results

	December 1982	Units
River discharge	123,000 (38.8e)	m^3/s (L/yr)
Suspended load	238*	mg/kg
	(120)†	(mg/kg)
	^{226}Ra	
River discharge	5.0 ± 0.2	dpm/100 L
River adsorbency	0.93 ± 0.24 (22.1 ± 5.7)	dpm/g (dpm/100 L)
	(11.2 ± 2.9)†	(dpm/100 L)
Ocean discharge	7.4 ± 0.2	dpm/100 L
	^{228}Ra	
River discharge	7.4 ± 1.0	dpm/100 L
River adsorbency	1.4 ± 0.4 (32.7 ± 9.6)	dpm/g (dpm/100 L)
	(16.8 ± 4.3)†	(dpm/100 L)
Ocean discharge	2.9 ± 0.4	dpm/100 L
	^{228}Ra/^{226}Ra	
River discharge and absorbency	1.5 ± 0.2	activity ratio
Sediment component	11.2 ± 6.3	activity ratio
	River Flux Calculations	
Dissolved ^{226}Ra	1.94 ± 0.08 *e*	dpm/yr
^{228}Ra	2.9 ± 0.4 *e*	dpm/yr
Desorbed ^{226}Ra	8.6 ± 2.2 *e*	dpm/yr
	(4.3 ± 1.1 *e*)	(dpm/yr)†
^{228}Ra	12.9 ± 3.8 *e*	dpm/yr
	(6.5 ± 1.9 *e*)	(dpm/yr)†
Total river		
^{226}Ra	10.5 ± 2.2 *e*	dpm/yr
^{228}Ra	15.8 ± 3.8 *e*	dpm/yr
Apparent total‡		
^{226}Ra	14.4 ± 0.8 *e*	dpm/yr
^{228}Ra	62. ± 5. *e*	dpm/yr

$e = (\times 10^{14})$.

*At Obidos [from *Meade et al.*, 1979].

†Using average measured suspended solids data from station 44.

‡Resulting total if flux from estuarine and adjacent continental shelf sediments (as reflected in dissolved radium in the plume) are included in the river flux.

Estuarine Radium Distribution

The four components used to describe the chemical mass balance of total radium in the Amazon estuary are

(1) $\mathrm{Ra_O}$, radium dissolved in ocean water that mixes conservatively into the estuary;

(2) $\mathrm{Ra_D}$, radium dissolved in river water that mixes conservatively into the estuary.

(3) $\mathrm{Ra_A}$, adsorbed radium that desorbs from suspended matter being newly supplied to the estuary by the river; and

(4) $\mathrm{Ra_X}$, the net addition of radium resulting from diffusive flux from the sediments, desorption from particles resuspended from the bottom sediments, resorption of radium at estuarine ratios onto particles, and radium removed from solution in the estuary by biological activities.

The distribution with salinity for each of the four components for both ^{226}Ra and ^{228}Ra is to be estimated. This gives eight unknowns, thus requiring eight equations. The four sources can be expressed as two mass balance equations—one for ^{226}Ra and one for ^{228}Ra—of the following form

$$ {}^i\mathrm{Ra_E} = {}^i\mathrm{Ra_O} + {}^i\mathrm{Ra_D} + {}^i\mathrm{Ra_A} + {}^i\mathrm{Ra_X} \qquad (1, 2)$$

where E refers to the dissolved estuarine concentration at salinity S, and each of the terms is the concentration at S that can be attributed to that component, and i is the isotope in question, i.e., 226 or 228.

The value for the dissolved ocean ($\mathrm{Ra_O}$) and dissolved river ($\mathrm{Ra_D}$) components for each isotope can be directly calculated at any point in the estuary from the measured concentrations at the river of ocean end-member stations and the salinity. For any salinity S,

$$ {}^i\mathrm{Ra_O} = {}^i\mathrm{Ra_O}{}^e\left(\frac{S}{S_\mathrm{O}}\right) = {}^i\mathrm{Ra_O}{}^e * f \qquad (3, 4)$$

$$ {}^i\mathrm{Ra_D} = {}^i\mathrm{Ra_D}{}^e * (1 - f) \qquad (5, 6)$$

where S is the salinity at the point in question, S_O is the salinity at the ocean end-member, f is the fraction of ocean water in the sample, and superscript e refers to the concentration of the component at the end member.

This gives six equations. Two additional equations are necessary to complete the calculations. One equation is obtained

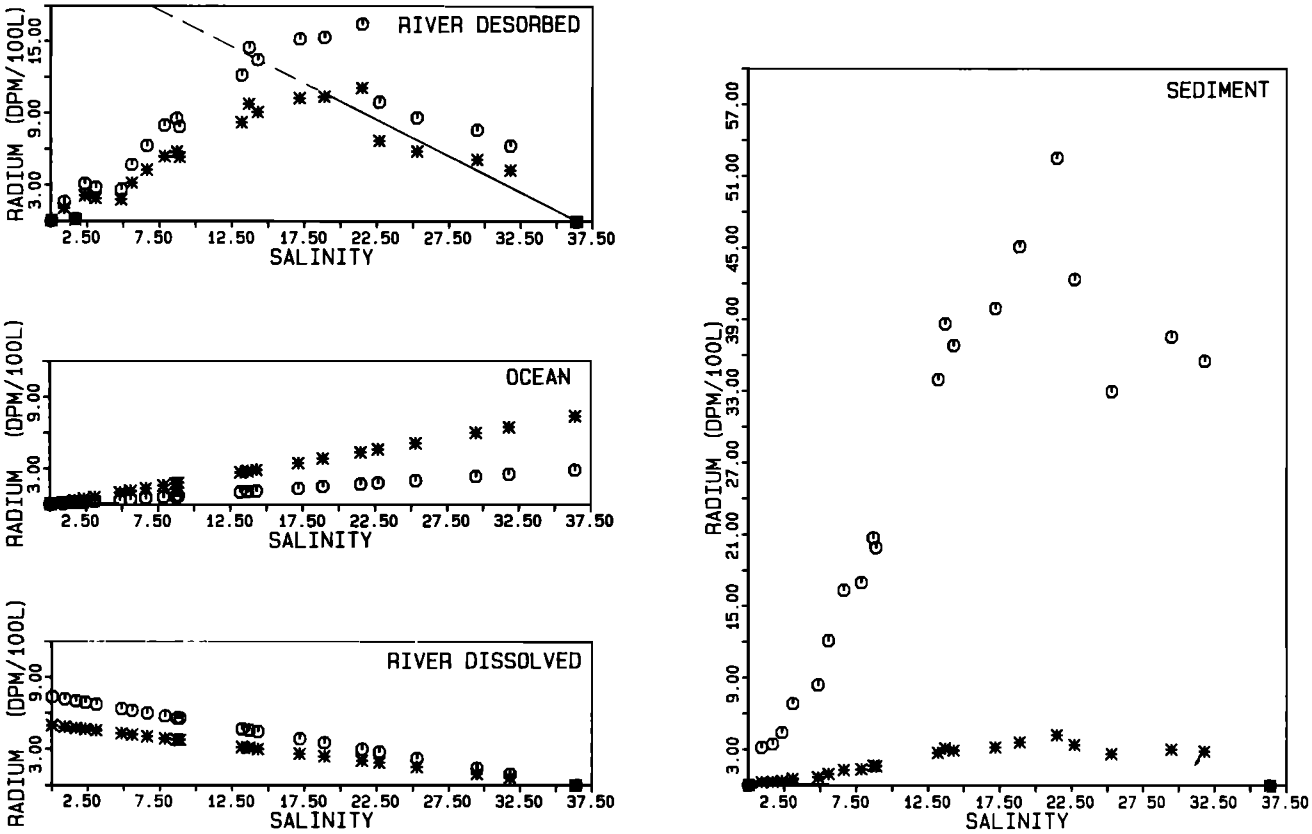

Fig. 6. Distribution of the four components comprising the total ^{226}Ra (asterisks) and ^{228}Ra (circles) concentration in the Amazon estuary as a function of salinity. The fractions derived from radium dissolved in seawater and in river water mix conservatively in the estuary. Radium desorption from river-borne particulate matter and the "sedimentary" source are both calculated from equations (1), (2), (7), and (8). The lines used to obtain the preliminary estimate of the desorbed radium that was necessary to obtain (8) are shown on the river desorption figure. The fourth source includes radium diffusing from estuarine and coastal sediments, radium desorbing from resuspended sediments, and radium scavenged by biological activity. The sedimentary flux source was assumed to have a constant ^{228}Ra/^{226}Ra ratio throughout the estuary. The sum of the four terms is the value measured in the estuary and is shown in Figure 3.

by assuming that the isotopic ratio $^{228}\mathrm{Ra}/^{226}\mathrm{Ra}_A$ is constant throughout the estuary. It was previously assumed that river-borne particulate matter is at exchange equilibrium when it enters the estuary. The radium that desorbs from river-borne particulate matter in the estuary will thus have the same ^{228}Ra/^{226}Ra ratio as the river end-member, i.e. (from Table 5),

$$^{228}\mathrm{Ra}/^{226}\mathrm{Ra}_A = 1.5 \pm 0.2 \qquad (7)$$

Actually there is a continuous reequilibration of particulate radium with dissolved radium as sediment moves through the estuary. As a result the data in Table 4 cannot be used to check the validity of this assumption.

The final equation is obtained by assuming that $^{228}\mathrm{Ra}/^{226}\mathrm{Ra}_X$ is constant throughout the estuary. There is no simple way to measure this ratio. Its value is estimated by using equations (1) and (2) to calculate $^{226}\mathrm{Ra}_X$ and $^{228}\mathrm{Ra}_X$. Ra_E is measured for both isotopes, and Ra_O and Ra_D can be obtained from equations (3), (4), (5), and (6). Therefore, only an estimate of Ra_A is needed in order to calculate Ra_X. This estimate is made as follows. First, it is assumed that all radium desorption from river-borne particles (the Ra_A component) has occurred by the time the particles have reached water with a salinity of 20‰ and that the desorbed radium will behave conservatively at salinities greater than 20‰. Existing data on the behavior of radium and barium in estuaries [e.g., *Elsinger and Moore*, 1980; *Edmond et al.*, 1978] and theoretical calculations made by R. Stallard (unpublished data, 1984) on the behavior of other alkaline earths indicate that this assumption is quite conservative. Desorption is generally complete by a salinity of 5‰. The assumption is further supported by *Dion*'s [1983] suspended solid measurements mentioned above.

One can now obtain an estimate of $^{226}\mathrm{Ra}_A$ for salinities greater than 20‰ by using an equation defining the line connecting the points (S = 0‰, ^{226}Ra = 22.1 dpm/100 L) and (S = 36.4‰, ^{226}Ra = 0 dpm/100 L), where the value 22.1 dpm/100 L is the total ^{226}Ra concentration resulting from desorption from river-borne particulate matter (Table 5). The comparable $^{228}\mathrm{Ra}_A$ estimate is then simply $^{226}\mathrm{Ra}_A$ multiplied by $^{228}\mathrm{Ra}/^{226}\mathrm{Ra}_A$ (= 1.5).

For the five samples between a salinity of 20‰ and the ocean end-member an estimate of the sedimentary radium component in the estuary (Ra_X) can now be calculated by subtracting Ra_O, Ra_D, and Ra_A from the measured radium concentration Ra_E.

The estimates for Ra_X and their ratios are listed below.

Salinity	$^{226}\mathrm{Ra}_X$	$^{228}\mathrm{Ra}_X$	$^{228}\mathrm{Ra}/^{226}\mathrm{Ra}_X$
31.8	4.33	37.7	8.71
29.5	3.98	39.0	9.80
25.3	1.76	31.7	17.9
22.7	1.81	40.0	22.1
21.5	6.30	55.6	8.82

Due to the small denominator effect, two of the samples have a rather high ratio. In order to avoid giving undue weight to these numbers, the geometric mean rather than the arithmetic mean is used to obtain a "best estimate" of the ratio. This defines the final equation:

$$^{228}\text{Ra}/^{226}\text{Ra}_x = 12.4^{+3.0}_{-2.0} \qquad (8)$$

There are now eight equations in eight unknowns, therefore the concentration of each component can be calculated at any salinity in the estuary where a sample was collected. The results are summarized in Figure 6.

Apparent Radium Flux

In the past the standard procedure for estimating the riverine flux of a particle reactive species has been to (1) fit a straight line to the "linear" portion of the concentration vs. salinity plot, (2) extrapolate this line to the intercept at zero salinity, and (3) multiply this value by the river discharge to get an apparent river-estuary flux. Using this procedure, the intercept values for ^{226}Ra and ^{228}Ra are 37.2 ± 2 dpm/100 L and 100 ± 13 dpm/100 L, respectively, and the resulting apparent fluxes are 14×10^{14} dpm/yr and 62×10^{14} dpm/yr. Comparing these apparent fluxes to the total river fluxes from Table 5 (10.5×10^{14} dpm/yr and 15.8×10^{14} dpm/yr), one concludes that diffusion of radium from estuarine and adjacent shelf sediments is approximately half as important as the river flux (dissolved + desorbed from river-borne particulate matter) for ^{226}Ra but much more important for ^{228}Ra.

Significance of the Amazon Flux to the Atlantic Standing Crop

One final point that can be addressed using this data is the importance of the river flux of radium to the standing crop of radium in the near-surface ocean. The mean lives of ^{226}Ra and ^{228}Ra are 2300 and 8.3 years, respectively. Taking 7.5 dpm/100 L [*Broecker et al.*, 1976] as an average ^{226}Ra concentration for the upper 200 m of the Atlantic Ocean gives a standing crop of 1.2×10^{21} dpm, of which 5.2×10^{17} dpm/yr are lost by decay. Of this loss only 10.5×10^{14} dpm/yr, or 0.20%, is supplied by the Amazon River. If the apparent estuary flux is used, the result is still only 0.27%. *Li et al.* [1980] estimated the integrated standing crop of ^{228}Ra for the near-surface Atlantic to be 5×10^{17} dpm. Of this 6×10^{16} dpm/yr are lost by decay. The Amazon River thus supplies approximately 2.6%. If the apparent estuary flux is used, the result is 10.3%!

CONCLUSIONS

The radium flux of the Amazon River is increased by a factor of approximately 5 for both ^{226}Ra and ^{228}Ra when radium desorption from river-borne suspended particulate matter is included with the dissolved river water component. Even when desorption is included, the Amazon River flux is an insignificant source to the near-surface Atlantic for ^{226}Ra and relatively minor for ^{228}Ra. If the Amazon can be considered typical of all rivers emptying into the Atlantic, then approximately 1.1% of the ^{226}Ra and 14% of the ^{228}Ra standing crops in the near-surface Atlantic are supported by rivers. If one is attempting to model radium, these data imply that rivers can be ignored as a source for ^{226}Ra but that river sources probably should be included for ^{228}Ra in detailed models on a basin-wide scale and must be included in smaller-scale regional models.

By measuring the concentration of both ^{226}Ra and ^{228}Ra throughout the estuary and having an estimate of the radium added to the estuary by desorption from river-borne particles, it is possible to separate and quantify the input from four sources: (1) radium dissolved in river water, (2) radium dissolved in ocean water, (3) radium desorbed from river-borne particles, and (4) a "sedimentary flux" source, which includes diffusion from coastal and estuarine sediments, desorption from resuspended particles, and biological removal. It remains to be established what role the Amazon River has in maintaining or changing the "sedimentary flux." Finally, it must be reemphasized that the data and calculations presented here represent only two sampling days. Yearly, seasonal, and shorter time scale changes may be significant.

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