

Desorption and coagulation of trace elements during estuarine mixing

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Abstract—Mixing experiments of seawater and the Hudson and Mississippi riverwaters with radiotracer spikes show that Co, Mn, Cs, Cd, Zn and Ba will be desorbed from river suspended particles, while significant fractions of “dissolved” Fe, Sn, Bi, Ce and Hg will be coagulated during estuarine mixing.

INTRODUCTION

THE PARTITION of many elements between solution and suspended particles (the operational boundary is set at 0.4 μm) in rivers undergoes drastic changes during estuarine mixing in response to the changes in pH, ionic strength, solution composition etc. The field observations indicate that ⁶⁵Zn and ⁵⁴Mn (EVANS and CUTSHALL, 1973), Ba (BOYLE, 1976; HANOR and CHAN, 1977), Ra isotopes (Li *et al.*, 1977; Li and CHAN 1979; ELSINGER and MOORE, 1980, 1983), ¹³⁴Cs and ¹³⁷Cs (JINKS and WRENN, 1975; PATEL *et al.*, 1978; OLSEN *et al.*, 1981) are all desorbed from the riverine suspended particles during estuarine mixing. The mixing experiment of the suspended particles from the Rhine River with seawater (VAN DER WEIJDEN *et al.*, 1977) showed that Mn, Co, Ni, Cu, Zn and Cd were desorbed from the particles. The desorption phenomena can be represented by the drastic decrease in the distribution coefficients for many elements from a fresh to a salty water medium (LI and CHAN, 1979).

In contrast, SHOLKOVITZ (1978) demonstrated, both in the field and the laboratory, that the dissolved iron and humic acid were coagulated into particles during estuarine mixing of the Amazon River. The mixing experiments of filtered riverwater of the Water of Luce (Scotland) and seawater further demonstrated that the metals which form strong complexes with humic acids (e.g., Al, Cu, Ni, Cd and rare earth elements) were also precipitated along with humic acids and iron hydrous oxides (SHOLKOVITZ, 1978; SHOLKOVITZ and COPLAND, 1981; HOYLE *et al.*, 1984).

In short, the desorption of metals from suspended particles and the flocculation of metal-humates from solution are the two most important counteractive, non-biological processes which affect the partition of metals between solution and suspended particles dur-

ing estuarine mixing. However, the relative importance of the desorption and flocculation processes, and their net effect during estuarine mixing needs to be investigated. Since the regular riverwaters contain much less humic acids than the Water of Luce, the flocculation of metal-humates may not be important as already indicated by the behavior of rare earth elements in estuarine mixing experiments (HOYLE *et al.*, 1984). To avoid the ambiguities of interpretation inherent in many field observations, we performed the mixing experiments of seawater and riverwater from the Hudson and Mississippi Rivers with and without riverine suspended particles, and measured the distribution coefficients (K_d = activity of radiotracer per gram of suspended particles/activity of radiotracer per ml of filtered solution) for 13 radiotracers having widely different chemical properties.

EXPERIMENTAL MATERIALS AND METHODS

About 20 liters of Hudson riverwater (salinity < 0.1‰, conductivity \approx 150 μmhos) were collected at the Bear Mountain Inn Pier, one day before the experiments in April of 1983. The suspended particle concentration (C_p) was about 22.5 mg/l. About 3 liters of Mississippi riverwater were provided by Dr. E. Boyle (collected in November of 1982). The C_p was about 12.5 mg/l. The salinity was unfortunately about 1.4‰, therefore the Mississippi riverwater sample was not a real freshwater end member. A few milligrams of filtered suspended particles for each river (through 0.4 μm Nuclepore filter) were ignited at 450°C to estimate roughly the organic matter content. The ashes were analyzed for 19 elements by an emission spectrographic method (TERAOKA, 1982). USGS standards PCC-1, GSP-1 and BCR-1 were used as references. The seawater sample was collected from the New York Bight ($S = 29\%$). All the water samples, which contained the original suspended particles, were kept in a cold darkroom ($2 \pm 1^\circ\text{C}$) before and during the experiments.

The 13 radiotracers are ¹³³Ba ($t_{1/2} = 10.8$ y), ²⁰⁷Pb (38 y), ¹³⁹Ce (138 d), ¹⁰⁹Cd (1.24 y), ⁶⁰Co (5.27 y), ¹³⁴Cs (2.06 y), ⁵⁶Fe (45 d), ²⁰³Hg (46.6 d), ¹⁹²Ir (74 d), ⁵⁴Mn (313 d), ¹²⁵Sb (2.77 y), ¹¹³Sn (115 d) and ⁶⁵Zn (244 d). These radiotracers were in HCl solution and hence, cationic. Our spikes did not greatly change the natural concentration of various trace elements in river and seawater, as most radiotracers were carrier free and the amounts of spikes added were small (\approx 100 to 500 cpm/100 ml for each radiotracer).

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For the Hudson River mixing experiments the radiotracer spikes were added to the following four Nalgene plastic bottles right after the mixing of:

- 400 ml filtered riverwater and 100 ml filtered seawater,
- 400 ml unfiltered and 100 ml filtered riverwater,
- 400 ml unfiltered riverwater and 100 ml filtered seawater.
- 500 ml filtered seawater and suspended particles obtained from 400 ml riverwater.

Except for bottle *a*, all bottles contained about 9 mg of Hudson River suspended particles. For Mississippi River experiments, bottle *d* was omitted, and bottles *b* and *c* contained about 5 mg of Mississippi suspended particles. The pH was maintained at 7.5 ± 0.1 and 7.8 ± 0.1 for the Hudson River and the Mississippi River mixing experiments respectively.

Once the spikes were added, the plastic bottles were shaken constantly but gently by a wrist action shaker to keep particles in suspension in a dark cold room ($2 \pm 1^\circ\text{C}$). At predetermined time intervals, 100 ml of solution were removed and filtered through two 0.4 μm Nuclepore filters. The activities of the radiotracers in the filter, the filter blank (the second filter in-line behind the top filter) and the filtrate (in a 100 ml plastic bottle) were γ -counted by a Ge(Li) detector with a multichannel analyzer of 4096 channels. K_d 's were calculated using the following relationship:

$$K_d = \frac{A_{\text{filter}} - A_{\text{filter blank}}}{A_{\text{water}}} \cdot \frac{10^5}{m \cdot f} \quad (\text{ml/g}) \quad (1)$$

where

A = activity of a radiotracer

m = dry weight of solid particles on the filter (mg)

f = factor to convert filter geometry to 100 ml plastic bottle geometry.

A similar method was used originally by DUURSMA and BOSCH (1970). In our experiments, the filter blank corrections turned out to be negligible, therefore in the latter experiments the second filter was omitted. From the mass balance we can also easily estimate the loss of radiotracer on the container wall. At the end of the Hudson River mixing experiments the pH of the solutions were increased by a pH unit of 0.2 through adding NaOH solution. After another 7 days of equilibration, the samples were filtered and the K_d 's calculated.

RESULTS AND DISCUSSION

The elemental compositions of suspended particles from the two rivers are given in Table 1 along with the world's average compositions of river suspended particles (MARTIN and MEYBECK, 1979) and soils (BOWEN, 1979). Zr and Be data for the world's average river suspended particles are adopted from the Yellow and Yangtze rivers (LI *et al.*, 1984a). The compositions of suspended particles from the Hudson and Mississippi rivers are very similar to the world's average (Table 1). Therefore our suspended particles are representative of normal rivers. The contents of Zn, V, Cr, Cu, Ni, Co, and Pb in river suspended particles are all much higher than that of the world's average soils, indicating appreciable pollution inputs (LI, 1981).

In the Hudson River mixing experiments of filtered riverwater and filtered seawater (bottle *a*), only 0.5% Fe, 1.5% Bi, 0.8% Sn, 5.3% Hg and 1% Ce of the

TABLE 1. Elemental compositions of suspended particles (S.P.) from rivers and soils (ppm in ash)

	HUDSON RIVER	MISSISSIPPI RIVER	AVERAGE * AVERAGE ** S.P.	AVERAGE ** SOILS
Si	270k±30k	280k±30k	285k	330k
Al	91k±9k	91k±9k	94k	71k
Fe	59k±6k	57k±6k	48k	40k
Ca	13k±1k	15k±1k	21.5k	15k
Mg	10k±0.5k	11k±0.6k	11.8k	5k
Na	7k±0.7k	6.2k±0.7k	7.1k	5k
Ti	4.6k±0.5k	4.2k±0.4k	5.6k	5k
Mn	1400±150k	1300±140k	1050	1000
Ba	680±100	700±100	600	500
Zn	400±40	110±10	350	90
Sr	150±13	220±20	150	250
Zr	14±14	190±20	175*	400(?)
V	15±15	180±18	170	100
Cr	200±20	120±10	100	70
Cu	97±9	61±6	100	30
Ni	91±5	88±5	90	50
Co	26±2	31±3	20	8
Pb	66±9	48±7	150	12
Be	2.3±0.3	2.2±0.3	1.8*	0.3(?)
LOI**	≈10%	≈10%		

* $k = 10^3$. ** lost weight on ignition

* Martin and Meybeck (1979). ** Bowen (1979),

x Li *et al.* (1984a)

total radiotracer spikes were coagulated after one hour of mixing and these amounts were nearly doubled after one day. After one week, the wall adsorption of these radiotracers became appreciable and the extent of coagulation could not be estimated reliably. However, there was neither coagulation nor wall adsorption for Ba, Cd, Co, Cs, Ir, Sb, Mn and Zn during the three week experiment. There was some particle contamination in bottle *a* for the Mississippi River mixing experiment, therefore, the extent of coagulation could not be estimated accurately, but the results were similar to those of the Hudson River experiment. Apparently, both in the Hudson River and the Mississippi River, there were not enough humic acids to form the coagulates of metal-humates for Ba, Cd, Co, Cs, Ir, Sb, Mn and Zn during estuarine mixing.

The K_d 's for radiotracers as a function of equilibration time in the Hudson River mixing experiments *b*, *c* and *d* are summarized in Fig. 1. The K_d 's after 20 days of equilibration as a function of salinity are shown in Fig. 2. Missing data for some radiotracers in Fig. 1 as well as other figures are caused by their activities being below the detection limit either in solution (e.g. Bi, Sn, Fe and Hg) or in the filter (e.g. Ba, Cs, Ir and Sb). In bottle *a*, the wall adsorption of Fe, Bi, Sn and Hg was appreciable, but in bottles *b*, *c* and *d*, the wall adsorption became much smaller ($\approx 10\%$ of Fe, Bi, Sn and Ce spikes, and $\approx 20\%$ Hg at the end of the experiments). Apparently, there were enough suspended particles in these bottles to compete efficiently for the adsorption of radiotracers against the wall surface. Even though there is some extent of wall adsorption, it does not affect the K_d calculations according to Eqn. (1).

The differences in K_d 's for Ir, Ba, Zn, Sb, Cd and Ce between one hour and one day of equilibration

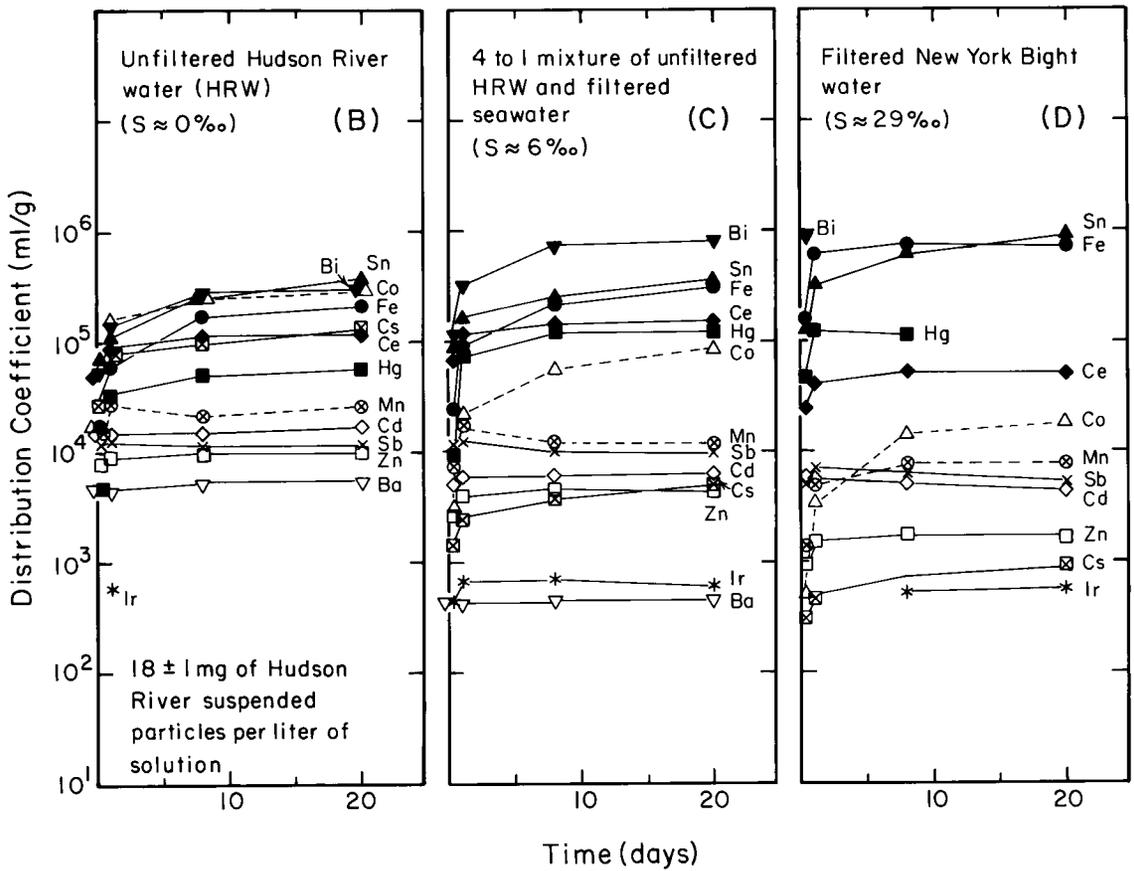


FIG. 1. The distribution coefficients (K_d) for radiotracers as functions of equilibration time and salinity in the Hudson River mixing experiments.

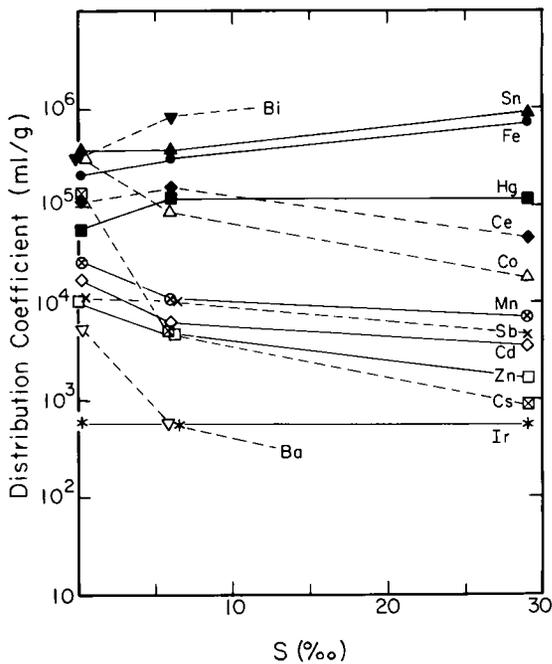


FIG. 2. The K_d 's for radiotracers, after 20 days of equilibration time, as a function of salinity for the Hudson River mixing experiments.

we were small and those K_d 's reached almost constant values after one day (Fig. 1), regardless of salinity. While the K_d 's for Bi, Sn, Fe, Hg, Co and Cs increased drastically from 1 hour to 1 day and kept increasing with time. NYFFELER *et al.* (1984) and LI *et al.* (1984b) also observed a similar pattern for these radiotracers in ocean sediment-seawater systems. The slow increase of K_d 's with time may indicate the relatively slow processes of oxidation (Co), and aggregation of "radiocolloids" (e.g. Fe, Bi, Sn, Ce and Hg) onto suspended particles (NYFFELER *et al.*, 1984; LI *et al.*, 1984b). The K_d 's for Bi, Sn, Fe, Hg and Ce increased with salinity from near zero to 6‰ (Fig. 2), suggesting the coagulation of these radiotracers in addition to the normal direct absorption onto larger particles. The radiotracers with a high hydrolysis constant such as Bi, Sn, Fe, Hg and Ce (BAES and MESMER, 1981) may first form hydroxide colloids through hydrolysis and/or adsorb onto pre-existing colloids (including humate colloids), then these "radiocolloids" coagulate into or onto larger filterable particles (LI *et al.*, 1984b). A further increase in salinity (to 29‰) enhanced the coagulation of Bi, Fe and Sn but caused no effect on the K_d for Hg and caused the decrease in the K_d for Ce, probably indicating the counteractive processes of desorption.

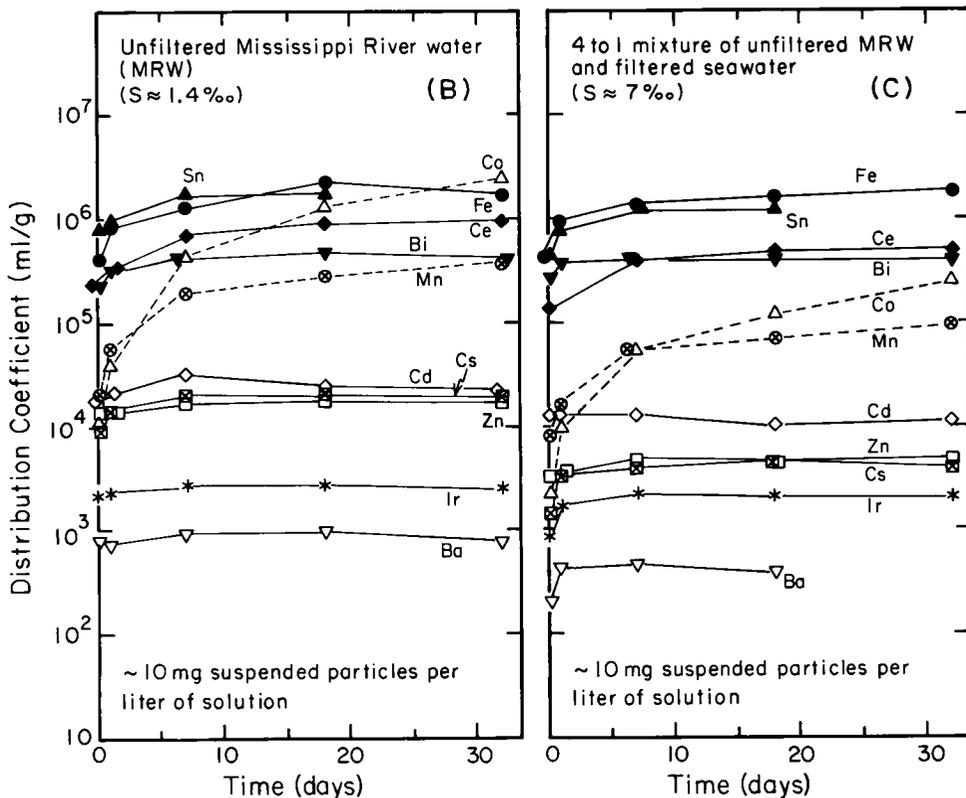


FIG. 4. The K_d 's for radiotracers as a function of equilibration time at two different salinity in the Mississippi River mixing experiments.

The results of the Mississippi River mixing experiments *b* and *c* (Fig. 4) are very similar to that of Hudson River mixing experiments. The K_d 's for Co, Ce, Mn, Cd, Cs, Zn and Ba decreased with salinity. However, the decrease in the K_d 's for Cs and Ba was not as drastic as in the Hudson River, because the Mississippi River water already has a salinity of $\approx 1.4\text{‰}$. In other words, the drastic decrease in the K_d 's for Cs and Ba already occurred at a salinity lower than 1.4‰ . The K_d 's for Fe, Sn and Bi did not show changes with salinity, probably indicating the lack of further coagulation of these radiotracers at a salinity higher than 1.4‰ .

CONCLUSIONS

- 1) The K_d 's for Co, Mn, Cs, Cd, Zn and Ba decrease with salinity, suggesting the desorption of these cations from the river suspended particles during estuarine mixing. The coagulation of the metal-humates of these cations are negligible during the estuarine mixing of the Hudson and Mississippi rivers.
- 2) The increase of K_d 's for Fe, Sn and Bi, Ce and Hg with salinity suggests that a significant fraction of Fe, Sn, Bi, Ce and Hg coagulate during estuarine mixing.
- 3) The K_d for Ir is independent of salinity and the K_d for Sb decreases only slightly with increasing salinity and pH. Both elements may exist as anions

in natural aquatic environments. The decrease in K_d for Hg with slight increase in pH may indicate the existence of anionic Hg-organic matter complexes in natural aquatic environments.

4) The extent of desorption of Co, Mn, Cs, Cd, Zn and Ba from suspended particles during estuarine mixing depends more on salinity than on pH changes.

5) In a normal natural estuarine environment, the increase in both pH and seasalts and the existence of suspended particles all enhance the coagulation of metals with high hydrolysis constant such as Fe, Sn, Bi and rare earths etc.

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