



The Behaviour of Dissolved Barium in Estuaries

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Estuarine profiles of dissolved barium are reported from six estuarine systems in the U.S.A. and Europe. All show clear evidence of mid-estuarine barium concentration maxima, although the location and scale of these maxima vary. These differences are rationalized in terms of low-salinity desorption of particulate barium, estuarine particle dynamics, riverine sediment supply and barium storage and subsequent slow release in salt marshes. Low-salinity removal of barium also occurs in some estuaries, apparently related to dissolved iron and manganese removal. © 1997 Academic Press Limited

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Introduction

Estuaries¹ are important environments in the geochemical cycling of many elements. Steep gradients in ionic strength and composition, pH and Eh, and suspended particulate matter (SPM) concentration occurring in estuaries can cause elements/ions to change phase, and alter their mass transport to the ocean.

The presence and extent of reactivity of a chemical constituent in the estuarine mixing zone (i.e. conservative or non-conservative behaviour) is typically shown using a dissolved constituent:salinity plot (Boyle *et al.*, 1974). Release of dissolved barium has always been reported in the mixing zone (e.g. Hanor & Chan, 1977; Edmond *et al.*, 1978; Li & Chan, 1979), in contrast to the removal of dissolved aluminium, iron and manganese (e.g. Burton & Liss, 1976), although only a few of the world's very large estuaries have been studied.

A variety of mechanisms have been proposed to explain estuarine trace element removal and release. Removal mechanisms include sorption to particles, colloid destabilization and precipitation, biological uptake and co-precipitation with iron/manganese phases; suggested release mechanisms have included the reverse of these removal processes and also ionic exchange from particle surfaces. Barium is considered to be released by ion-exchange processes with particu-

late matter, a process modelled successfully in the Hudson River (Hanor & Chan, 1979).

This paper investigates the estuarine behaviour of dissolved barium by comparing results from several very different estuaries, using data collected by three research groups.

Methods

The general characteristics of the estuaries investigated here are given in Table 1, together with survey dates in the period 1982–92. Dissolved barium was measured by ICP-OES using either the method of standard additions (Dehairs *et al.*, 1989), or using a (scandium) internal standard to correct for nebulization variations resulting from viscosity differences between the water samples (Coffey, 1994). Dissolved barium data are summarized in Table 2, together with other published data. Suspended particulate matter and particulate barium data (where available) are presented in Table 3. Salinities are reported using the Practical Salinity Scale.

Discussion

Dissolved barium exhibits estuarine release in all studies (examples shown in Figure 1), although the magnitude of release and the salinity of the dissolved barium concentration maximum varies, both between estuaries and between surveys on the same estuary

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TABLE 1. Study sites

Estuary	Location of estuary mouth	Annual average flow ($\text{m}^3 \text{s}^{-1}$)	Sampling dates	Character
Humber	53.5°N0°	250	J3 11/90 J4 1/91 J5 4/91 J6 9/91 J7 1/92 J8 6/92	Large industrialized shallow coastal plain estuary with low-oxygen region frequently present.
Schelde	50.5°N1.5°W	120	5/82 3/83 1/91 6/92	Large industrialized shallow coastal plain estuary with substantial permanently anoxic region.
Chesapeake Bay	37°N76°W	990	8/85	Large deep drained river system with seasonal anoxia in deep basin.
Delaware Bay	39°N75°W	330	5/84 7/84	Large industrialized shallow coastal plain estuary, well-oxygenated throughout.
Maurice River	39°N75°W	5	8/90	Organic rich river draining peat bog and salt marshes to Delaware Bay.
Canary Creek	39°N75°W	<1	6/85 7/90	Saltmarsh creek system draining to Delaware Bay.

TABLE 2. Dissolved barium characteristics

Estuary	Cruise	Salinity of peak dissolved Ba concs	Riverine dissolved Ba (nM) [REM]	EZSEMC (nM)	Estuarine Ba release (nM)	Reference
Zaire	-	2.5	68	176	108	Edmond <i>et al.</i> (1978)
Amazon	-	6	150	270	120	Dion (1983)
Ganges	-	2.5	155	385	230	Carroll <i>et al.</i> (1993)
Chesapeake	CDR-1	6	280	600	320	Present study
Delaware	YABLEDXV	4	168	240	72	Present study
	YADBLEDXVI	7	182	192	10	Present study
Maurice	BAN-1	5	290	420	130	Present study
	BAN-2	6	350	365	15	Present study
Canary Creek	-	9	634	760	126	Present study
Schelde	May 1982	10.1	320	540	220	Present study
	March 1983	13	100	450	350	Present study
	January 1991	10.4	170	240	70	Present study
	June 1992	11	420	790	370	Present study
Humber	J3	14-16	186	505	319	Present study
	J4	4-5	219	325	106	Present study
	J5	6-7	206	595	389	Present study
	J6	18-20	120	1178	1058	Present study
	J7	11-12	190	450	260	Present study

TABLE 3. Particulate barium characteristics

Estuary		Riverine particulate Ba ($\mu\text{g g}^{-1}$)	Riverine suspended load (mg l^{-1})	Riverine particulate Ba ($\mu\text{g l}^{-1}$)	Riverine particulate Ba available for release (nM)
Zaire		500 ^a	51	25.5	186
Amazon		500 ^a	66–265	33–132	240–961
Ganges		500 ^a	3400	1700	12 380
Chesapeake		500 ^a	3.6	1.8	13
Delaware	YABLEOXV	500 ^a	9.3	4.6	33
	YABLEOXVI	500 ^a	10.4	5.2	38
Maurice ^b	BAN-1	54.5	370	9.8	71
	BAN-2	671	1.42	0.95	7
Schelde ^b					
May 1982		94	60	5.6	41
June 1992		55	73	4	29
Humber ^c	J3	95	500	47.5	346
	J4	200	250	50	364
	J5	105	300	31.5	229
	J6	210	250	52.5	382
	J7	230	150	34.5	251

^aCrustal Ba value (Bowen, 1979).

^bDetermined after HF/HNO₃ digestion.

^cDetermined after 0.1 M HNO₃ digestion; this recovered 50–100% of the total Ba (Coffey, 1994).

There are no suspended particulate matter load data for Canary Creek.

(Figure 2). Similar variability has also been reported in the Amazon (Dion, 1983). The factors controlling this variability are considered below.

Location of the barium release in the estuarine mixing zone

Peak dissolved barium concentrations occur at salinities <3 in the Ganges, Mississippi, Zaire (Table 2) and Hudson (Hanor & Chan, 1977; Li & Chan, 1979), at around 6 in the Amazon, 5–10 in the Maurice, Delaware, Chesapeake and Canary Creek system, and at 10–15 in the Schelde and Humber.

Hanor and Chan (1977) modelled barium release from clay particles, assuming a rapid ion exchange with Mg²⁺ as a representative seawater ion. Assuming suspended particles are the only source of the released barium, the differences between the estuaries in dissolved barium maxima locations must be attributed to hydrodynamic processes, since rapid ion exchange from river-borne particles would occur globally in the low-salinity region. Dion (1983) suggested that, in the Amazon, under high flow conditions, a given suspended particle travels across a relatively small salinity range as compared to the salinity range covered in the same distance or time under low flow conditions. Thus, given constant barium desorption kinetics, the barium is released at higher salinity under

low flow conditions. This theory demands that barium desorbs strongly under relatively low-salinity conditions. This is supported by laboratory experiments with riverine SPM from the Humber (Coffey, 1994) and Maurice River (Dehairs, unpubl.), in which much of the particulate barium is desorbed within 60 min at salinity >1.7.

This theory involving salinity, hydrodynamics and SPM transport is consistent with data presented here, and with that published previously. Large discharge rivers (e.g. Zaire, Ganges-Brahmaputra, Amazon) desorb barium within the 0–6 salinity range. The Schelde, however, with a smaller discharge, has a relatively compressed salinity gradient with distance, and the dissolved barium peak is observed at a higher salinity. The Humber desorbs barium in regions of lower salinities during winter higher discharge conditions, whilst in low-flow summer conditions, the peak is observed at higher salinity. The Delaware, Chesapeake and Maurice rivers fall between these two extremes.

Barium budgets for the studied estuaries

Riverine dissolved barium concentrations vary between estuaries (Table 2). This variability is not likely to be anthropogenic in origin, since the more

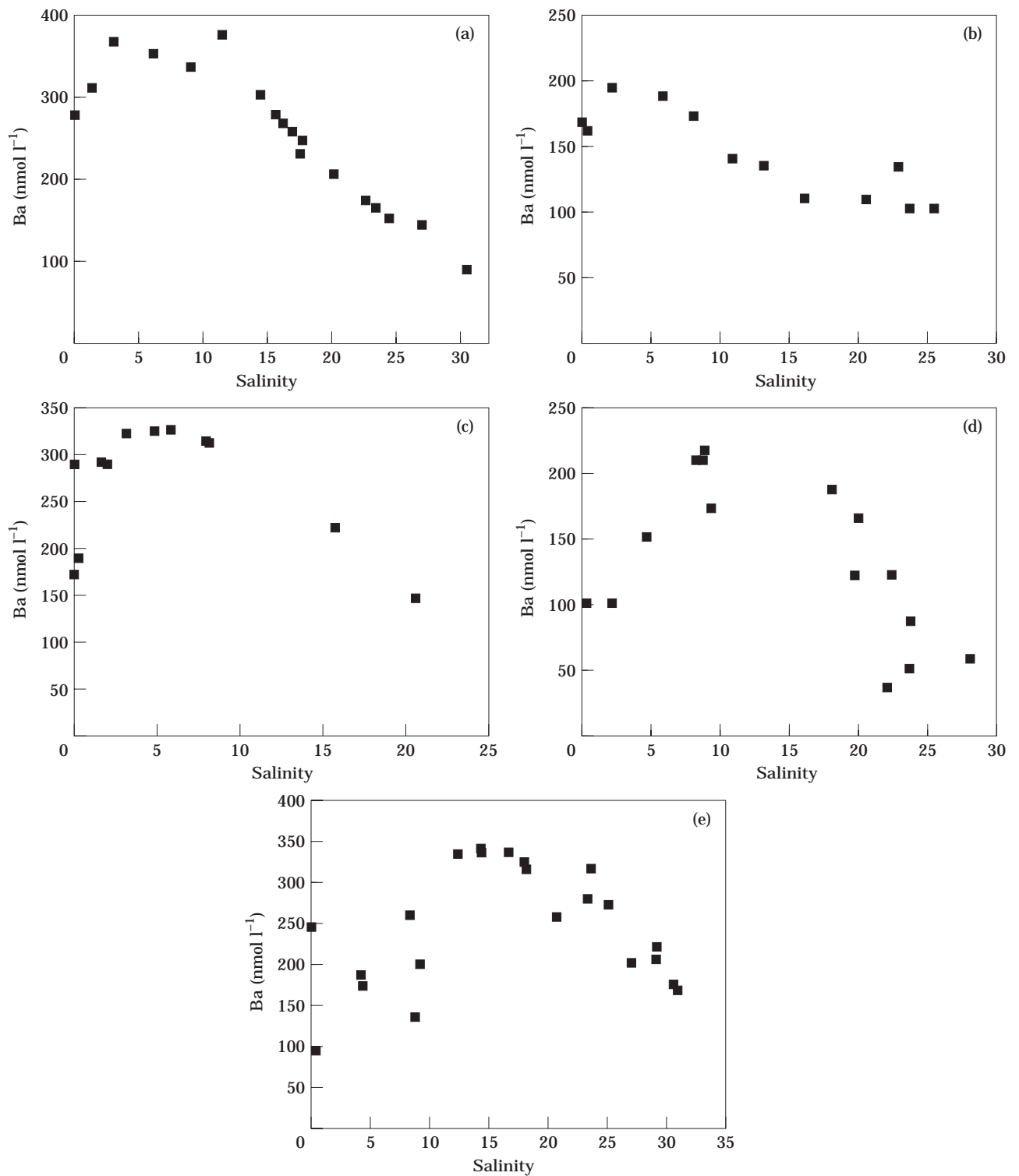


FIGURE 1. Estuarine profile of dissolved barium. (a) Chesapeake; (b) Delaware, YABLED-XV; (c) Maurice, BAN-1; (d) Schelde, March 1983; (3) Humber, J3.

industrialized estuaries (e.g. Humber and Schelde) do not necessarily have the highest dissolved barium concentrations. Differences in catchment rock type,

weathering rates and river flow are a more likely explanation. The release of dissolved barium in the mixing zone is calculated (Table 2) as being the

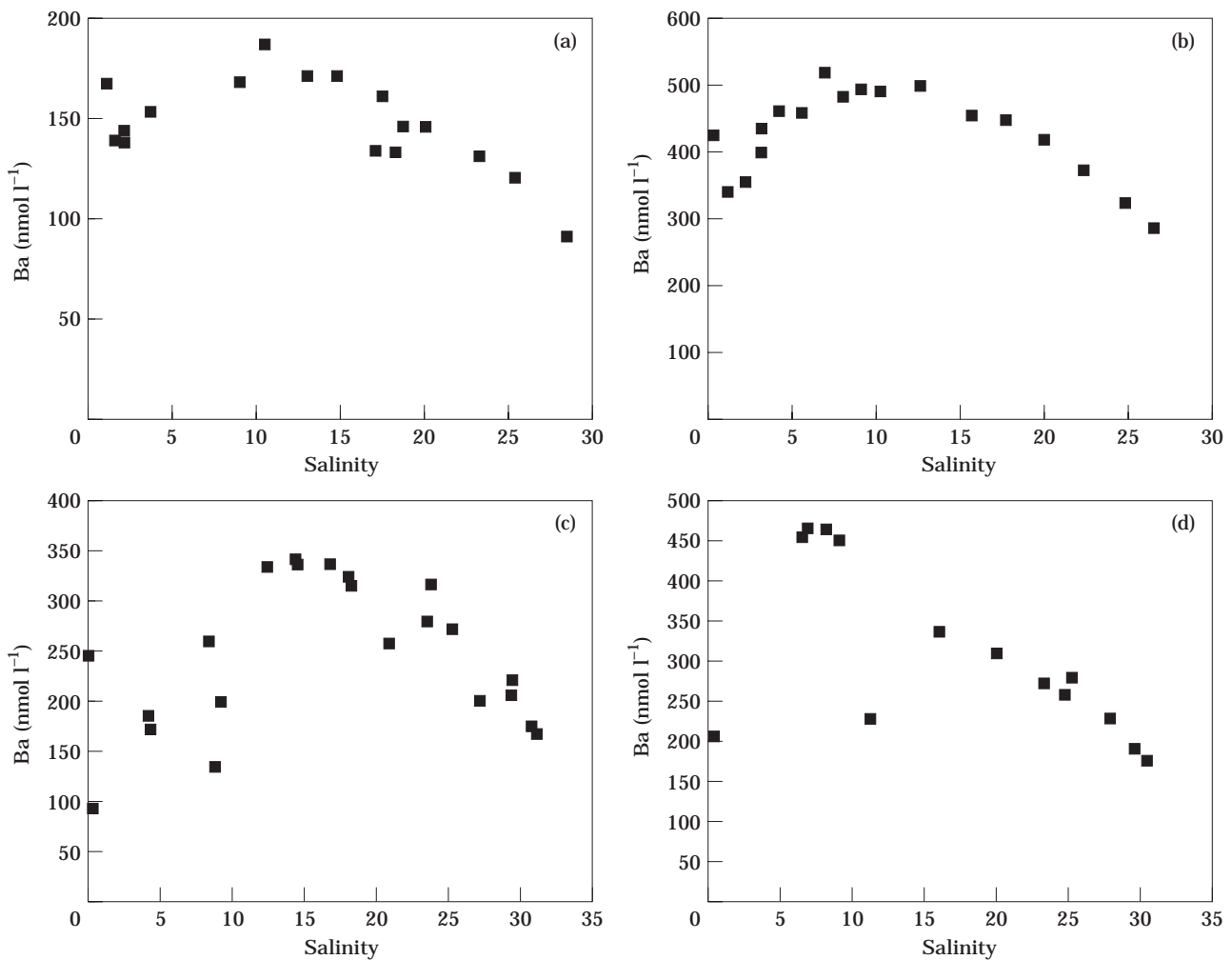


FIGURE 2. Intra-estuary variability in the magnitude and location of dissolved barium release. (a) Schelde January 1991; (b) Schelde June 1992; (c) Humber J3, (d) Humber J5.

difference between the effective zero salinity end-member concentration (EZSEMC, see Figure 3) and the measured zero salinity dissolved barium concentration (Boyle *et al.*, 1974). Notably, high EZSEMC values (i.e. >300 nM) are calculated for the Schelde, Humber, Chesapeake, Maurice and Canary Creek, all low flow rivers (Table 1).

Potential sources of the barium released within the estuaries are discussed below. The maximum available desorbable barium has been estimated (Table 3) as the measured SPM load of the furthest upstream sample multiplied by the barium content of that SPM [where measured, otherwise assuming a crustal barium average of $500 \mu\text{g g}^{-1}$ (Bowen, 1979); the riverine particulate barium concentrations are, in reality, rather variable]. In the Schelde, higher particulate barium concentrations (250 nM) have been measured on surveys other than those discussed here,

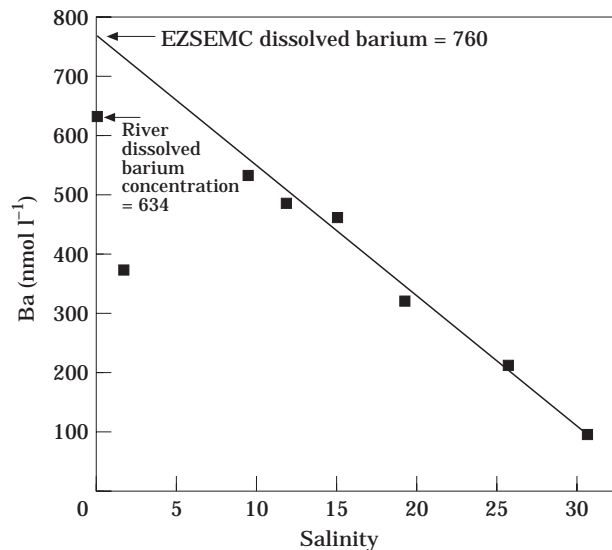


FIGURE 3. Calculation of EZSEMC (Canary Creek).

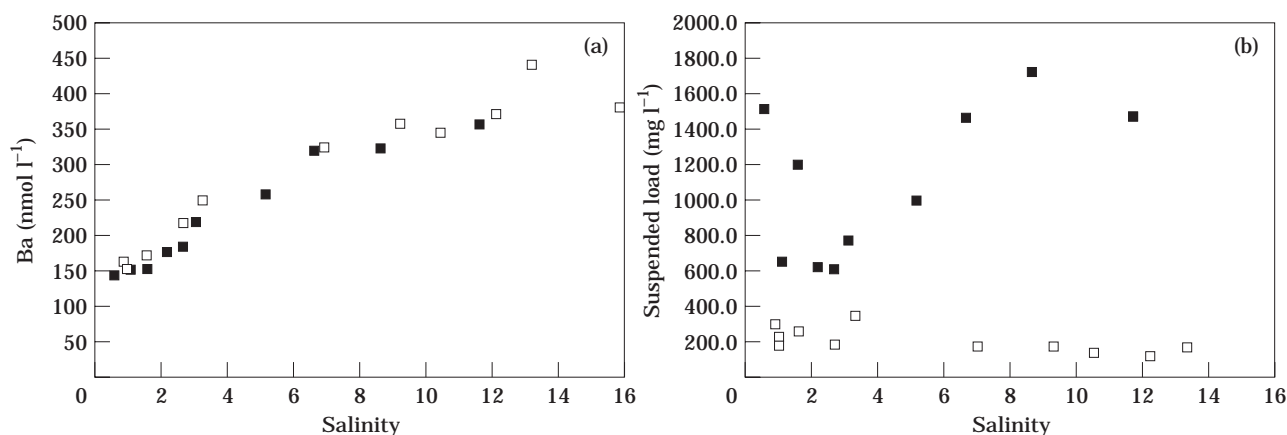


FIGURE 4. Riverine profiles of (a) dissolved barium and (b) suspended solids at high (□) and low (■) tide in the Humber during J8.

but corresponding dissolved barium data are not available. These calculations yield an upper limit to the supply of available barium for desorption, since some lattice-bound particulate barium will not be released. For example, in laboratory experiments involving mixing of riverine SPM and estuarine water, 20–100% of the barium was released from Humber particles (Coffey, 1994).

Comparison of the estuarine barium release (Table 2) with the available riverine particulate barium (Table 3) shows there is generally sufficient supply of particulate barium to account for the release in the large estuaries such as the Amazon, Ganges-Brahmaputra and Zaire, but not in the other estuaries. An exception is the Humber estuary, where the very high riverine SPM loads usually supply sufficient particulate barium.

Two major uncertainties may render these budget calculations inaccurate. Firstly, representative estimates of SPM load are difficult to make in dynamic fluvial environments, and the single values used in Table 3 may be inappropriate. Furthermore, two dissolved barium profiles from the Humber estuary (Figure 4), one taken at low tide (when tidal stirring produced very high SPM loads), the other at the immediately preceding high tide (when SPM loads were lower), are nearly identical, despite the 2–3 fold difference in SPM load. This implies that the extra SPM at low tide is not a source of desorbable barium, assuming desorption kinetics to be fast (as implied by laboratory experiments described above). This additional SPM is predominantly re-suspended estuarine sediment, whilst the source of desorbable barium in estuaries is likely to be fresh riverine SPM. Thus, SPM loads in an estuary are not necessarily a useful indicator of desorbable particulate barium. The

relatively large discrepancy between calculated riverine particulate barium supply and estuarine dissolved barium release argues that the problem is not simply related to short-term variations in riverine SPM loads.

The second uncertainty for this budget calculation is in establishing the riverine particulate barium concentration. Calculations were made using barium concentrations measured in particles collected furthest upstream, usually close to the salt mixing zone. Figure 5 shows an example of the particulate Ba/Fe relationship with salinity in the Humber, together with the crustal ratio (Bowen, 1979); this pattern was seen in all of the present Humber studies. The Ba/Fe ratio falls rapidly with increasing salinity, reflecting a combination of desorption of barium from the particles and the ‘dilution’ of high Ba/Fe riverine particles by

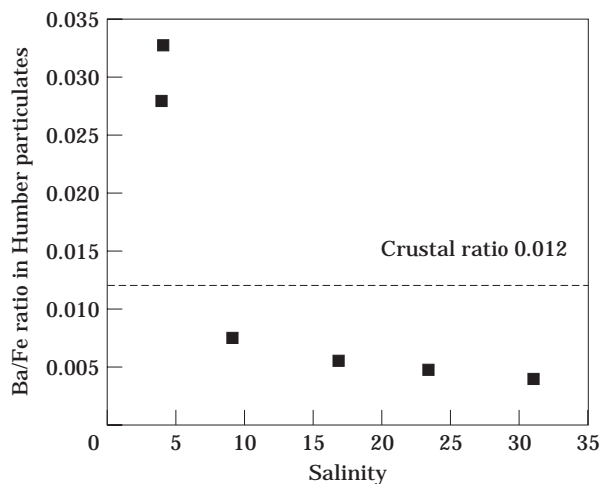


FIGURE 5. Total Ba/Fe (concentrated nitric acid digest) against salinity for suspended particulate matter in the Humber.

low Ba/Fe marine particles. The estimates of particulate barium supply in Table 3, thus, may be erroneously low.

Despite these caveats, assuming the calculations in Table 3 are (to a first approximation) accurate, sources of barium additional to the riverine particulate supply are required for some of the estuaries studied.

Carroll *et al.* (1993) suggested that in the Ganges-Brahmaputra system, particulate material deposited in the lower reaches of the system during high flow (winter) subsequently released barium as saline water moved upstream under low flow (summer) conditions. A similar mechanism may be invoked for the estuaries studied here, with freshwater sediment, deposited to the estuarine region during storm events or high flow winter conditions, slowly releasing barium by diffusion as salinities rise under lower flow conditions. This may be particularly important in the Chesapeake, where large releases of dissolved barium occur within the estuary, despite a very low riverine SPM barium supply; the extensive salt marshes of Chesapeake Bay may act as the storage site for storm event pulses of particulate barium. Sediment budgets for the Chesapeake (Biggs, 1970) emphasize the importance of storm event transport of SPM, where 57% of the annual flux is reported in just 42 days during the late winter of the year studied, and average SPM concentrations were almost eight times those measured in the present authors' surveys. Canary Creek, which drains a salt marsh, has higher freshwater dissolved barium concentrations than the other rivers (Table 2), further implying the potential importance of salt marshes as a source of dissolved barium. Moore (1981) and Elsinger and Moore (1983) were unable to balance budgets in the Chesapeake and Delaware estuaries for radium, an element exhibiting estuarine release apparently analogous to that of barium, and concluded that salt marshes were an important source of radium.

A further source of dissolved barium in some estuaries may be desorption from iron and manganese oxyhydroxides (see below).

Low-salinity removal of dissolved barium

Removal of dissolved barium at low salinities, yielding a concentration minimum at a salinity of about 2 (Figure 6), is seen in the Schelde, Delaware and Maurice river estuaries as well as Canary Creek (in all surveys), and is also seen in some, but not all, of the Humber surveys. Barium removal is not seen in the Chesapeake, nor is there clear evidence of removal in the Zaire, the Amazon (Edmond *et al.*, 1978) or Ganges-Brahmaputra (Carroll *et al.*, 1993) estuaries.

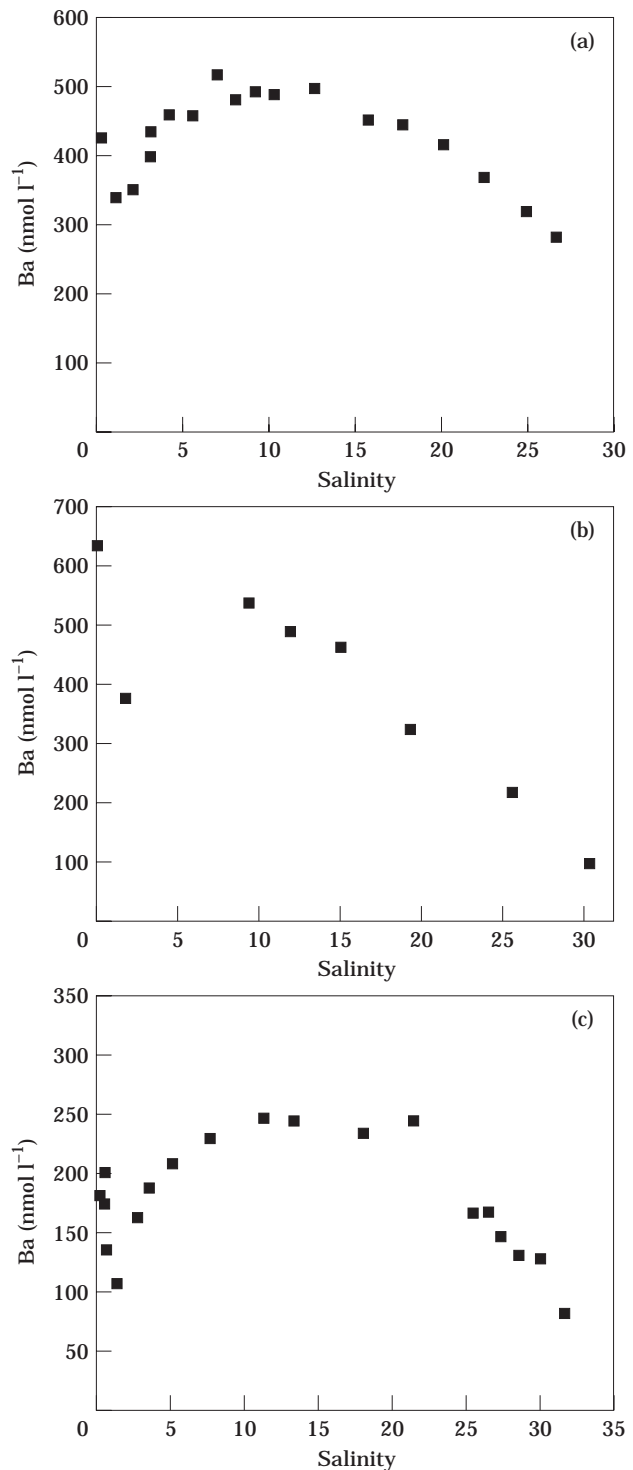


FIGURE 6. Estuarine profiles of dissolved barium illustrating low-salinity removal. (a) Schelde June 1992, (b) Canary Creek, (c) Humber J7.

However, Yan *et al.* (1990) reported low-salinity removal for ²²⁶Ra (apparently analogous to barium) under certain conditions in the Mullica river.

TABLE 4. Extent of low-salinity removal of dissolved barium

River estuary	Low-salinity removal of dissolved Ba (%)	Riverine dissolved Fe (μM)
Chesapeake Bay	0	0.2
Delaware Bay	5	0.4
Schelde	12–28	1.2
Humber	0–50	3.6
Canary Creek	37	0.9
Maurice River	26–45	9.5

Quantification of such dissolved barium removal is difficult because of overlapping release at higher salinities. However, in several of these systems, the process is clearly quantitatively significant. Based on deviations from conservative mixing (i.e. the minimum concentration in the low-salinity region compared to the observed riverine dissolved barium concentration), the extent of barium removal ranges from 5% (in the Delaware) to about 50% (in the Humber and Maurice systems, Table 4).

The existence of such low-salinity removal of Ba has not been reported previously. This may be because studies to date have focused on the large estuaries (e.g. Amazon, Zaire) where the release of barium by desorption occurs at low salinities, which would mask removal. The chemistry of the river systems may also contribute to dissolved barium removal, and the estuaries will be compared below to infer possible removal mechanisms.

Low-salinity removal processes for trace metals in estuaries have been ascribed to several related processes involving the flocculation of colloidal material, rich in iron and organic matter, in the steep gradients of pH and ionic strength and composition which occur during the early stages of estuarine mixing. The extent of low-salinity barium removal appears to be a function of riverine organic matter and dissolved iron concentrations (Table 4). Dissolved iron concentrations in the Amazon and Zaire, where dissolved barium removal has not been observed, are uncertain, but are likely to be low (Stallard & Edmond, 1983), whilst in the Mullica river estuary, where dissolved ^{226}Ra removal has been reported (Yan *et al.*, 1990), dissolved riverine iron concentrations are higher (c. 2 μM).

The relationship implied in Table 4 is not proof that iron hydroxide co-precipitation is necessarily the direct mechanism for low-salinity barium removal. High dissolved iron concentrations in river systems are invariably associated either with low pH, and/or

low oxygen levels and/or high dissolved organic matter content [the latter is assumed to complex and stabilize the iron in dissolved or colloidal form (Moore *et al.*, 1979)]. However, the addition of large amounts (mM concentrations) of dissolved iron to an acidified river-water sample from the Humber system, followed by neutralization, resulted in the visible precipitation of brown iron oxyhydroxides and removal of 40% of the dissolved barium within 30 min (Coffey, 1994). Thus, removal of barium by iron oxyhydroxide co-precipitation is a plausible mechanism for low-salinity removal. Observed recycling of barium at oxic/anoxic interfaces in the Chesapeake Bay (Dehairs, unpubl.), in the Mediterranean (de Lange *et al.*, 1990) and in the Black Sea (Falkner *et al.*, 1993) also suggest Fe/Mn oxyhydroxides may play a role in barium cycling (although in the Black Sea, microbial cycling may also be important).

The subsequent fate of barium removed at low salinity is uncertain, but is important for estuarine barium budgets, since calculations of barium release during estuarine mixing depend on the baseline value used (either the river concentration, as used here, or the lowest concentration observed during low-salinity removal). If barium is co-precipitated within Fe/Mn oxyhydroxide solid phases, it might be expected to be relatively immobile, but if sorbed to colloidal phases, barium may be available for subsequent desorption at higher salinities.

Barium is less sensitive to low-salinity removal processes than some other elements, as would be expected for a simple alkaline earth cation. This contrasts with, for example, dissolved rare earth elements, which are removed extensively at low salinities in the Chesapeake (Sholkovitz & Elderfield, 1988). Despite the apparent absence of extensive low-salinity barium removal in the Delaware, dissolved iron is rapidly scavenged (Sharp *et al.*, 1982), although barium removal might not be observed because of simultaneous desorptive barium release.

In the Hudson, Amazon, Mississippi and Zaire, variable dissolved barium concentrations in low-salinity waters were observed (Li & Chan, 1979 and references therein). This variability was ascribed to uptake by diatoms, although the possibility of abio-genic removal was not rejected. While biological uptake may indeed be responsible for some barium removal, this process is unlikely to be important for low-salinity removal in some systems reported here, since the removal is too localized. In the Humber (Malcolm, in prep.) and Delaware (Sharp *et al.*, 1982), primary production in the low-salinity region has been demonstrated to be negligible due to high turbidity.

Conclusions

Barium is released from river-borne suspended matter during estuarine mixing in all estuaries studied. The primary source of the released barium seems to be fresh riverine SPM; re-suspended estuarine particles appear not to contribute desorbable barium. Thus, the magnitude of barium release is strongly dependent upon the riverine supply of particulate matter. Hydrodynamic conditions affect the location of peak dissolved barium concentrations. The release appears to occur at higher salinities in rivers of lower flows because the releasing particles travel further along the salinity gradient before desorbing the barium. Laboratory experiments imply that barium desorbs from the particles in suspension strongly and rapidly at salinities 1–2, whilst at very low salinities (<1), the extent of desorption is small. The physical location of secondary barium sources, such as intertidal sediments, may also affect the location of the dissolved barium maximum along the salinity gradient.

Budgets for released barium and riverine SPM barium supply only balance for the large estuaries of the world (e.g. Amazon, Mississippi), and for estuaries of high SPM load (Humber). In other estuaries, there appears to be insufficient riverine particulate barium to supply the observed release. Although uncertainties in the calculation may explain this deficit, it is possible that fluvial particulate barium delivered under high flow events is stored in mud flats and salt marshes after the storm events, and is subsequently desorbed, as suggested in the Ganges-Brahmaputra system (Carroll *et al.*, 1993).

There is evidence of low-salinity removal of dissolved barium, possibly associated with co-precipitation with iron and manganese oxyhydroxides.

Estuarine cycling of barium appears to be particularly complex. While general patterns seen in individual estuaries have some similarities, the details are quite different. This illustrates the value of comparing the behaviour of trace metals in contrasting estuarine environments.

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