

TRACE ELEMENT COMPOSITION OF ZAIRE SUSPENDED SEDIMENTS

by

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I. INTRODUCTION

The major input of material to the oceans arises from the supply of dissolved and suspended matter by rivers. While the yearly input of dissolved major elements is rather well-documented (ALEKIN & BRAZHNKOVA, 1960; LIVINGSTONE, 1963; MEYBECK, 1977), dissolved trace elements and nutrients are badly known (TUREKIAN, 1969; MOROZOV, 1969; KONOVALOV, 1970; GIBBS, 1977). Data on major and trace elements of river suspended matter have been summarized by MARTIN & MEYBECK (1978, 1979). A compilation of data on dissolved elements in the Zaire river is presented by MEYBECK (1978). In the estuarine zone, various geochemical and mixing processes can affect the concentrations of chemical elements (MÜLLER & FÖRSTNER, 1975; DUINKER & NOLTING, 1976). The present preliminary study concerns the trace element composition of the suspended matter in the Zaire river and estuary.

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II. SAMPLING AND ANALYTICAL PROCEDURES

Suspended sediment samples have been collected in November 1975, in the Zaire river at stations 22 and 23, in the estuarine mixing zone at the surface at stations 24, 25, 27, 28, 29 and 33, in the halocline at stations 25 and 27 and in the marine waters below the halocline at station 27. Near-bottom samples were taken at stations 25, 28 and 31.

The water samples collected with Niskin bottles, were filtered on board within 1 to 12 hours after sampling, either on 0.45 μm Millipore (INAA) or 0.4 μm Nuclepore (XRF) filters.

Cu, Ni, Pb, Zn and Rb have been analyzed in all samples (Table I)

TABLE

Elemental content of suspended sediments of Zaire river and mixing zone; X-ray fluorescence analysis (concentrations in ppm on a 105° C dry weight basis). The Zaire river value is the average of 4 samples taken at stations 22 and 23, at surface and at depth; the near-bottom values are the average of 3 bottom water particulate samples at stations 25, 28 and 31. For comparison also the average of 2 previous determinations of the Zaire river and averages for the world major rivers are given; these values are after MARTIN & MEYBECK (1979). Values in brackets have an analysis inaccuracy larger than 25%.

Station	Depth	Salinity (‰)	Concentration (ppm)				
			Cu	Ni	Pb	Rb	Zn
river (4)	s + b	0.00	(100)	(54)	220	82	350
24	surf.	<0.1	170	<29	570	64	1200
25	surf.	<0.1	(31)	(20)	230	51	850
27	surf.	<0.1	(36)	(45)	250	72	590
28	surf.	0.20	87	<40	270	80	290
25	10 m	0.56	57	(24)	160	70	250
24	depth	2.1	(54)	(46)	260	96	420
33	surf.	5.6	75	(67)	380	68	340
27	halo.	10.6	(80)	<60		(65)	850
25	halo.	11.1	(40)	50	150	81	430
29	surf.	25	(200)	(110)	1200	(75)	1800
27	20 m	35	(150)	(150)	(510)	<85	2000
bottom (3)		35	(74)	<60	440	76	560
Zaire (2 previous)		0.00	144	74	455	60	400
world rivers		0.00	100	90	150	100	350

by the energy dispersive X-ray fluorescence method (XRF). The Nuclepore filters were dried at 105° C. A single 3000 seconds analysis was made of each sample and corrected for Nuclepore blank and Nuclepore X-ray absorption. Several concentrations were measured close to the detection limits, especially for Cu and Ni and, therefore,

errors of 25% or more can be expected for part of the measurements. Four samples taken in the 0 to 12‰ salinity range (Table II) have been analyzed by instrumental neutron activation analysis (INAA) for Zn and other elements.

The 100 mg sediment samples, after ashing at 600° C, and geochemical standards (USGS W1 and G2) were irradiated 90 min in a flux of $1.08 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and counted by GeLi spectrometry.

Two suspended sediment samples collected in the Parana river (Santo Dome, Argentina, December 1975) and the Magdalena river (upstream Barranquilla, Colombia, July 1973), respectively, have also been analyzed by INAA.

III. RESULTS

The concentrations of the various elements in the Zaire, Parana and Magdalena suspended sediments are given in Tables I and II. For comparison a previous estimate for the Zaire river (average of two surface samples taken at Brazzaville, July 1969 and July 1970) and a world-average of the concentrations in the river suspended sediments (MARTIN & MEYBECK, 1979) are also presented.

IV. DISCUSSION

1. RIVER SUSPENDED SEDIMENTS

The comparison of elemental concentrations with our former estimates shows on the whole a good agreement. Comparison of the Zaire river with other large rivers in different morphoclimatic environments, Parana and Magdalena, confirms our assessment about the constancy of some trace element concentrations, especially lanthanides, Sc, Th, Hf, Ta, in large river suspended sediment (MARTIN & MEYBECK, 1979). This may be related primarily to the fact that large drainage areas integrate various morphological and geological characteristics, thus averaging local variations in concentration of these elements.

The comparison of Zaire data with the world average of river suspended sediments obviously shows good agreement, except for Cr and Sb, the ratios between Zaire and world average concentrations ranging from 0.5 to 1.5.

2. THE MIXING ZONE

All the elements measured in the river samples were also analyzed in the 0 to 12‰ salinity range; they can be classified according to their

TABLE II

Elemental content of suspended sediments of Zaire river and mixing zone. Data for Magdalena and Parana rivers and for an average of the world major rivers are given for comparison (after MARTIN & MEYBECK, 1979). Neutron activation analysis (concentrations in ppm on a 600° C dry weight basis).

	Rivers					Zaire mixing zone		
	World	Magdalena	Parana	Zaire		Stations:		
	average	(Barran-	(Santo	Previous	This	24 depth	33 surf.	27 halo
		quilla)	Dome)	estimate	study			
					22 surf.			
Salinity (‰)						2.1	5.4	11.6
Ag	—	—	—	—	35	—	7.4	—
As	5	6.6	3.6	3.8	—	—	—	—
Au	—	—	0.07	0.04	0.05	—	0.13	0.47
Br	5	1.9	4.6	10	6.4	—	37	152
Ce	95	—	—	90	74	97	76	64
Co	20.0	18.9	23.4	25	29.6	33.4	16.6	17.0
Cr	100	136	90	175	211	137	158	106
Cs	6	6	11	6.0	5.3	4.5	3.7	3.5
Eu	1.5	1.4	2.0	1.6	1.7	2.1	1.9	1.9
Hf	6	6.9	7.4	5.1	5.4	—	4.3	3.7
La	45	37	50	50	53	51	40	46
Lu	0.5	—	0.57	0.37	0.36	0.43	0.31	0.34
Na	7100	7700	5600	2100	—	3800	20000	70000
Sb	2.5	2.4	3	1.0	(0.5)	1.4	0.6	—
Sc	18	21	25.4	12	18.4	17.7	16.2	15.6
Sm	7	6.7	9.1	—	7.7	7.7	6.6	7.7
Ta	1.25	—	1.0	1.1	0.87	0.88	—	—
Tb	1.0	0.27	0.89	1.6	0.56	0.55	0.79	0.52
Th	14	12.6	15.7	16.2	16.2	17.2	16.0	13.5
Yb	3.5	3.7	3.5	2.6	2.8	3.6	2.7	2.8
Zn	350	—	—	400	300	345	280	312

behaviour in this mixing zone (Tables I and II; Fig. 1). Most of the concentrations (lanthanides, Th, Sc, Hf and also Cs, Rb) show an overall constancy (within about 30%) versus salinity, up to 12‰ S, and possibly to 35‰ S as can be seen for Rb. This constancy already observed in numerous estuaries (MARTIN, KULBICKI & DE GROOT, 1973; DE GROOT & ALLERSMA, 1975; MARTIN, HØGDAHL & PHILIPPOT, 1976; MARTIN & MEYBECK, 1978) shows that these elements remain strongly bound to the suspended sediment in estuaries.

Only Br, Au and Na concentrations sharply increase with salinity (10 to 35 times the river value). Sea salts trapping onto the unwashed filters easily accounts for the noticeable seaward increase of Na and probably Br, but cannot explain the Au enrichment.

Lead and transitional elements (Cr, Co, Ni, Cu, Zn) concentrations

are much more variable (between 40 and 200% of the river value) and do not show any clear trend.

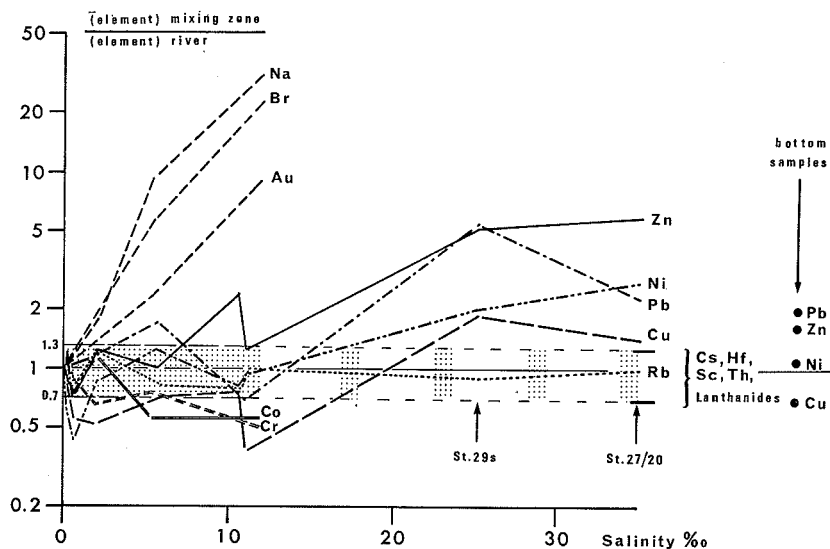


Fig. 1. Element content of suspended sediments of the Zaire mixing zone normalized to the river concentration; data of Tables I and II (sodium mean concentration in the river is assumed to be identical to the previous estimate in Table II; the "bottom samples" are suspended sediment samples from deep marine waters).

When the whole mixing zone is considered (Table I), the same scattered distribution is observed for Pb, Zn, Cu and Ni. This is obvious in the estuarine fresh waters ($<0.1\text{‰}$ S), whereas a possible seaward increase trend is foreseen in the salinity range from 12 to 35‰ S. However, the marine near-bottom samples present lower concentrations, rather similar to the river values. Contrary to these trace metals, Rb concentrations remain constant within the analytical error in the whole mixing zone. Some difficulties arise in defining an appropriate marine end-member. We can first consider that the surprisingly high concentrations found in samples 29 (surface) and 27 (20 m) are representative for the natural "marine" suspended matter ($\geq 25\text{‰}$ S). Similar high concentrations for trace metals have actually been found in oceanic suspended matter (BUAT-MÉNARD & CHESSELET, 1979). In the Zaire estuary preferential settling of coarse quartz particles and increased mixing with marine particles enriched in trace metals may account for both the concentration increase of these trace metals in the surface waters and just beneath the halocline, and their decrease in the bottom water particulate samples. However, contamination of the samples 24 (surface), 27 (20 m) and 29 (surface) cannot

be ruled out. If these samples are discarded, no general trend is observed in the mixing zone for trace metals, and differential settling is not seen to affect the trace metal concentrations significantly. Anyhow the metal distributions do not correspond to the general seaward concentration decrease often observed in European, partially mixed, estuaries (MARTIN, KULBICKI & DE GROOT, 1973; DE GROOT & ALLERSMA, 1975; MÜLLER & FÖRSTNER, 1975; DUINKER & NOLTING, 1976). The distributions are much more similar to the overall constancy of particulate trace metal concentrations already observed in other stratified (salt wedge) estuaries (TREFRY, 1977; MARTIN, SALVADORI & THOMAS, 1978; EISMA, VAN DER GAAST, MARTIN & THOMAS, 1978).

V. SUMMARY

The results of a preliminary study of trace element concentrations in the Zaire river and estuary suspended sediments are presented. Zaire river concentrations show a close agreement with those observed in other rivers of the world (including Magdalena and Parana). Within the mixing zone, lanthanides, Th, Sc, Hf and Rb remain nearly constant, whereas Cr, Co, Ni, Cu, Zn and Pb concentrations show much more scattering and are either constant or increasing. This last distributions differ significantly from the results of studies conducted in partially mixed estuaries.

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