

GEOCHEMICAL STUDIES OF THE RIVER-ESTUARINE SYSTEMS OF KRISHNA AND GODAVARI

M.M. SARIN, K.S. RAO*, S.K. BHATTACHARYA, R. RAMESH
AND B.L.K. SOMAYAJULU.

Physical Research Laboratory, Ahmedabad 380 009, Gujarat.

ABSTRACT

During summer season, the Krishna river waters are enriched in major cations Na, K, Mg, Ca and Si by a factor of 1.2-1.9, in U by a factor of 3 and in δ D by 14.2% compared to those of Godavari. The high δ D of Krishna river waters (+ 1.6%) over those of Godavari (- 12.6%) indicate relatively more evaporation of the former by 15%.

The Uranium concentrations of Krishna waters at Vijayawada is 2.6 $\mu\text{g/l}$ which decreases to 1.6 $\mu\text{g/l}$ at Puligadda which is ~ 100 km downstream, whereas the $^{234}\text{U}/^{238}\text{U}$ activity ratio at both places is identical, 1.65 ± 0.03 suggesting authigenic removal of U in regions downstream of Vijayawada. Also, U does not appear to behave conservatively in the Krishna estuary as has been its behaviour in other Indian and some world rivers; there is removal of U from the Krishna estuarine waters.

The major cations and δ D behave conservatively in both Krishna and Godavari estuaries. Si behaves almost conservatively in the Krishna estuary whereas in the Godavari estuary there is about 15% Si removal. The fluxes of all the measured constituents from Krishna and Godavari to the Bay of Bengal during the non-monsoon period are calculated.

The clay, silt and sand fractions as well as the Al, Fe, Mn, Cr and Ni concentrations of the clay fractions were determined in eight Krishna estuarine sediments and the results are discussed. The non-monsoonal clay, Al, Fe, Mn, Cr and Ni fluxes from Krishna river to the Bay of Bengal are also estimated.

Key-words: Estuaries, major cations, dissolved Si, Hydrogen isotopes, Uranium isotopes.

INTRODUCTION

Geochemical studies of river estuarine systems are very important towards understanding the mechanism of weathering processes, water quality, the study of physico-chemical and sorption reactions that take place in the estuarine regime and for estimating the ultimate input of continental material to the oceans and their mass balance (Fukai, Murray & Huygh-Nogoc 1973; Boyle, Collier, Dengler, Edmond, Ng and Stanillard, 1974; Burton & Liss, 1976; Turekian, 1977; Borole, Krishnaswami & Somayajulu, 1977; Morris, Mantoura, Bale & Howland, 1978; Martin & Meybeck, 1979; Borole, 1980; Borole, Sarin & Somayajulu 1982; Milliman & Meade, 1983; Sarin, 1983;

*Address: Geology Department, Andhra University, Waltair 530 003, Andhra Pradesh.

Sarin & Krishnaswami, 1984). More recently, due to introduction of man-made pollutants to the river-estuarine systems, the study becomes even more important from the point of view of understanding the ultimate fate of the pollutants and the associated hazards (Turekian 1971; 1974; Elbaz — Pouliche, Huang, Jednack — Biscan, Martin & Thomas, 1982).

Several rivers drain the Indian sub-continent into the Bay of Bengal and the Arabian sea and these have to be studied in detail to estimate the total fluvial input to the Indian ocean and adjacent seas. As a part of the programme to study river input to oceans, we have taken up a preliminary investigation of the Krishna and Godavari rivers. Godavari was studied earlier in detail (Borole, Eisma, Martin, Rao, Somayajulu and Thomas, in preparation). In addition to the measurement of U, Si and major cations and particulate concentrations in both rivers, Krishna river sediments were also analyzed for some major and trace elements. Martin & Letolle (1979) measured stable isotopes of oxygen to characterise estuarine mixing. We have measured for the first time hydrogen isotope ratio D/H in both estuaries; these are best suited for studying mixing between seawater and freshwater in estuaries.

MATERIALS AND METHODS

Geology of the drainage basins

The Krishna river starts in the Western ghats near Mahabaleshwar and traverses across the peninsular shield. The north western part of its drainage basin is occupied by the Deccan traps of Upper Cretaceous to Eocene age whereas the lower south eastern part is occupied by Precambrian formations (Cuddapahs and Kurnools) and the Dharwar formations of Archean age. The entire drainage basin occupies an area of 2.6×10^5 km² and the mean annual discharge of Krishna at Vijayawada (Fig. 1) is 6.0×10^{13} l (Unesco 1971). For further geological details of the Krishna drainage basin adjacent coastal sediments reference is made to Swamy (1970), Siddiquie (1967) and Rao (1975).

Godavari river starts from Nasik district near the Western ghats and traverses across the Indian peninsular shield a little north of Krishna river and the main geological units of its drainage basin are similar to that of Krishna river. Reference is made to Naidu (1966), Siddiquie (1967) and Rao (1975) for further details. For Godavari river, the area of drainage basin is 3.1×10^5 km² and the mean annual discharge into the bay of Bengal as measured at Dowlaishwaram near Rajahmundry (Fig. 2) is 1.05×10^{14} l (Unesco, 1971).

During May-June 1981 a field trip was undertaken to the Krishna and Godavari river — estuarine regions. Sampling of Krishna river started from Vijayawada to almost the river-mouth via the Nadimi Eru channel and most sample locations are indicated in Fig. 1. In the case of Godavari sample collections were made between Rajahmundry and the confluence of the Gautami Godavari channel (Fig. 2).

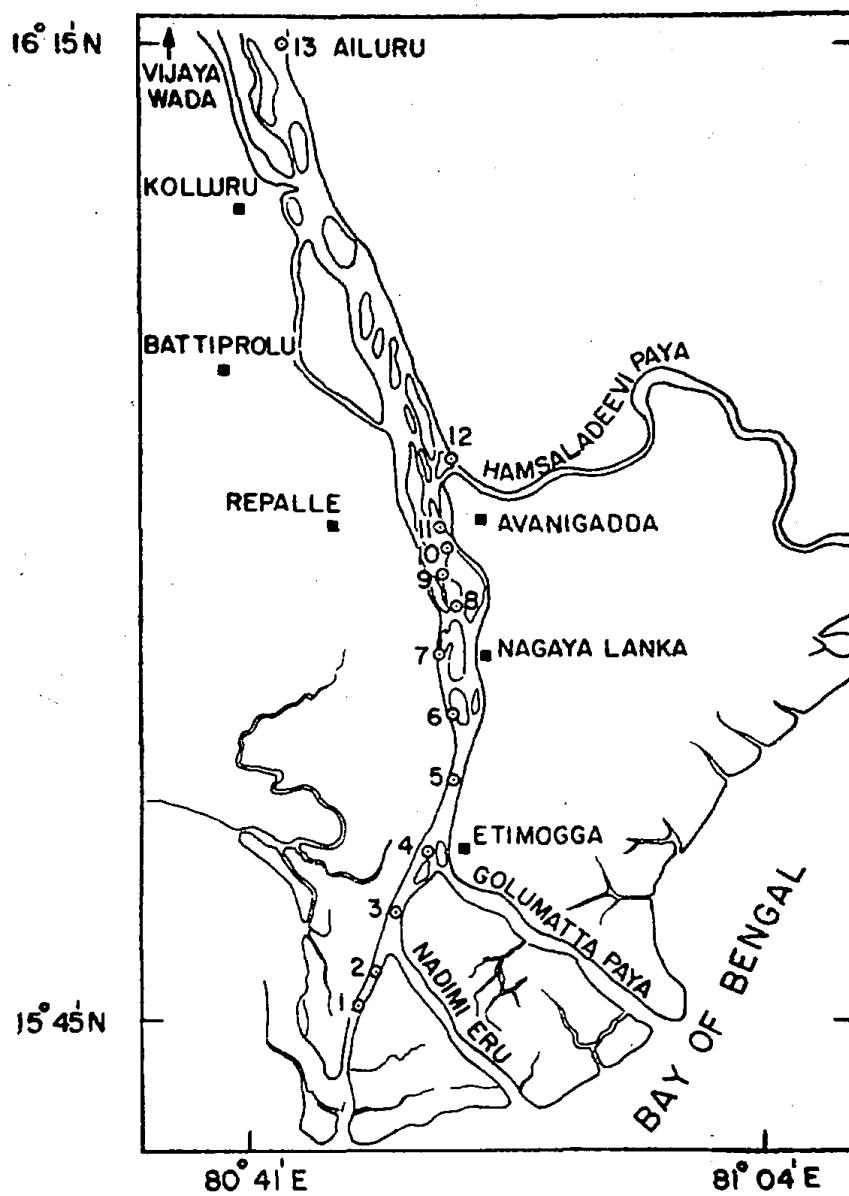


Fig. 1. Map of the Krishna estuary. Numbers indicate sampling locations.

One 20 l and two 500 ml water samples were collected from depths ≥ 1 m in clean plastic bottles onboard country boats. At some freshwater regions where boats were not available, samples were collected as far away from the banks as possible. Sediment samples from the Krishna river bed were also collected using a Van Veen type grab sampler.

At site, chlorosity was determined to a precision of $\pm 3\%$ by Ag NO₃ titration method. Scavenging of uranium from the 20 l water sample

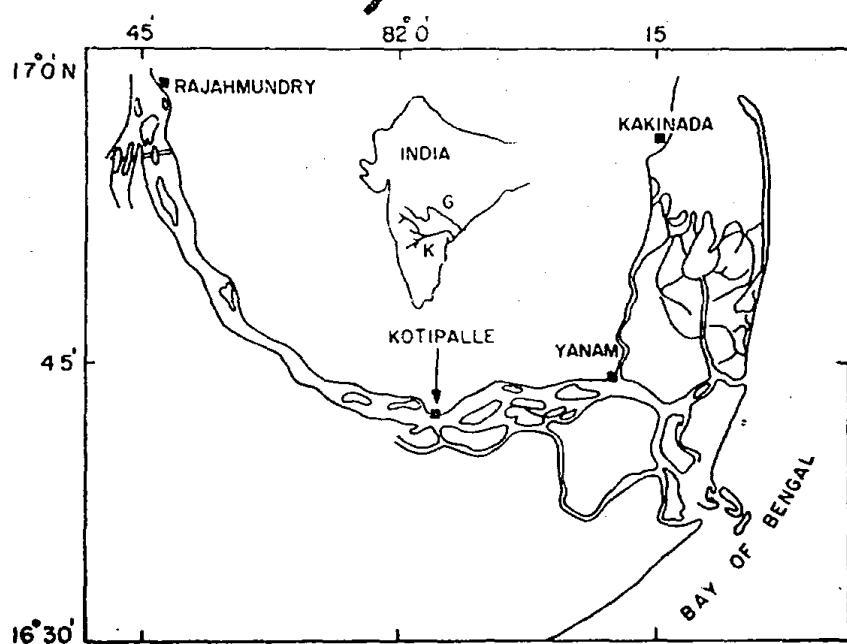


Fig. 2. Map of the Godavari estuary sampling was done between Rajahmundry and the river mouth via Yanam. The freshwater end-member of the estuary resides between Kotipalle and Rajahmundry.

was done according to the procedure described by Borole (1980). Rest of the analyses were carried out in the laboratory.

Particulate concentrations were determined by filtering the entire contents of one 500 ml bottle through a $0.45\text{ }\mu$ weighed Millipore filter, drying the filter and weighing again (Ray, Mohanti and Somayajulu, 1984). From the second 500 ml bottle 20 ml were first removed in a small plastic bottle for hydrogen isotope measurement. The remainder was used for major cations. Na, K, Mg, Ca (reproducibility = $\pm 5\%$) and Si (reproducibility = $\pm 3\%$) determinations (Borole, 1980; Strickland and Parsons, 1972, Ray, Mohanti and Somayajulu, 1984).

For hydrogen isotope measurements, $10\text{ }\mu\text{l}$ of water was reduced to hydrogen by passing its vapour over uranium filings at 800°C . This hydrogen was quantitatively collected and analyzed for D/H ratio in a VG Micromass 602 D mass spectrometer with an overall precision of $\pm 2\%$ (Bigeleisen, Perlmutter and Prosser, 1952; Krishnamurthy, 1984). The D/H values are reported with respect to standard mean ocean water (Craig, 1961).

Sedimentological studies were carried out on the Krishna sediments following the procedures given by Galchouse (1971). Known amounts of the clay fractions ($< 2\text{ }\mu\text{m}$) of the sediments were brought into solution by HF, H_2SO_4 , HNO_3 , HCl treatments and Al, Fe, Mn, Cr and Ni concentrations in them were measured by atomic absorption spectrophotometry (Bas-

karan, Sarin and Somayajulu, 1984). Heavy mineral identification was done on the thin sections of the + 200 size fractions.

RESULTS AND DISCUSSION

The concentrations of Na, K, Mg, Ca, Si suspended matter, the δD and chlorosity data are given in Table I for both Krishna and Godavari

Table I. Suspended matter, major cations and δD in Krishna and Godavari estuarine waters.

Sample Code	Chloro-sity (g/l)	Suspend-ed matter (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	Si (μ mol/l)	D^* (%)
KRISHNA								
KR-18	0	3.1	134	2.98	12.4	24.2	322	—
KR-17	0	3.3	133	2.97	12.0	24.0	316	—
KR-16	0	1.1	129	3.0	12.4	24.0	319	1.6
KR-15	0	11.5	125	3.0	12.6	22.5	321	—
KR-14	0	50.8	121	3.0	12.6	22.5	315	—
KR-11	1.3	9.4	888	30	91	52	308	2.5
KR-12	3.5	3.8	2185	78	221	101	255	—
KR-10	3.8	1.5	2375	82	247	108	247	—
KR-9	3.8	3.7	2375	89	247	108	248	—
KR-8	5.3	13.5	3225	113	347	139	222	1.5
KR-7	8.0	7.0	4950	167	516	197	177	—
KR-13	9.6	4.9	5780	205	607	225	154	—
KR-6	10.5	7.1	5950	235	633	221	145	—2.4
KR-5	11.9	0.5	6900	250	753	255	130	—
KR-4	13.8	0.4	7440	290	752	288	102	—
KR-3	14.5	2.5	8800	300	912	388	92	—3.5
KR-2	17.5	0.3	10,300	400	1067	374	50.3	—
KR-1	19.3	3.5	10,900	400	1120	380	24.1	—2.4
GODAVARI								
GD3-1	0	0	68	2.30	7.9	14.0	271	—
GD3-2	0	3.3	70	2.47	8.1	16.0	265	—12.6
GD3-4	4.15	1.9	2550	93	260	113	179	—9.8
GD3-3	6.1	1.5	3800	125	367	154	140	—8.4
GD3-5	11.1	3.6	6350	230	667	230	78.7	—4.8
GD3-6	13.0	6.1	8340	290	840	300	60.2	—
GD3-7	14.4	6.1	8900	330	899	304	49.0	—
GD3-8	14.9	4.4	9000	350	936	310	43.4	—
GD3-10	15.4	3.6	8900	344	912	300	39.1	—
GD3-17	15.4	10.6	9380	300	960	318	40.0	—
GD3-9	15.45	5.3	9080	340	933	300	39.6	—3.1
GD3-11	16.9	2.3	9900	360	1021	320	29.2	—
GD3-16	17.6	8.5	10,400	376	1080	330	26.7	—
GD3-12	18.4	11.3	11,200	380	1173	350	25.0	—
GD3-14	19.6	20.5	11,560	400	1205	360	26.2	—2.7
GD3-13	19.7	15.0	11,780	420	1251	376	24.1	—
GD3-15	19.7	21.1	11,400	420	1226	368	28.4	—

$$* \delta D = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{SMOW}}}{(D/H)_{\text{SMOW}}} \times 1000 \text{ per mil} (\%)$$

systems. The uranium concentrations and the $^{234}\text{U}/^{238}\text{U}$ activity ratios in Krishna and Godavari estuarine waters are given in Table II. The sedimentological data and the Al, Fe, Mn, Cr, Ni concentrations of the Krishna river — estuarine sediments are presented in Tables III and IV respectively.

Table II. U isotopes in Krishna and Godavari estuarine waters.

Sample Code	Chlorosity (g/l)	^{234}U (dpm/l)	^{238}U (dpm/l)	$^{234}\text{U}/^{238}\text{U}$ (Activity Ratio)
KR-16	0*	3.16 ± 0.06	1.93 ± 0.05	1.64 ± 0.02
KR-15	0*	2.40 ± 0.04	1.43 ± 0.04	1.67 ± 0.03
KR-14	0*	2.00 ± 0.04	1.23 ± 0.03	1.63 ± 0.03
KR-11	1.3	1.44 ± 0.03	0.9 ± 0.02	1.49 ± 0.03
KR-8	5.3	1.78 ± 0.04	1.25 ± 0.03	1.42 ± 0.02
KR-6	10.5	1.54 ± 0.02	1.20 ± 0.02	1.28 ± 0.02
KR-3	14.5	2.39 ± 0.05	1.85 ± 0.05	1.29 ± 0.04
WR-1	19.3	2.59 ± 0.06	2.27 ± 0.06	1.14 ± 0.02
KR-1	19.3	2.34 ± 0.03	2.02 ± 0.03	1.16 ± 0.02
GODAVARI				
GD3-1	0*	0.37 ± 0.04	0.27 ± 0.03	1.37 ± 0.15
GD3-5	11.1	1.79 ± 0.05	1.52 ± 0.05	1.18 ± 0.03

*Fresh water.

Table III. Sand Silt and clay contents of Krishna estuarine sediments.

Sample No.	Sand (%)	Silt (%)	Clay (%)
KR 1	77.1	11.2	11.7
KR 2	48.5	24.0	27.5
KR 3	49.5	33.0	17.5
KR 4	92.6	6.0	1.4
KR 5	68.0	19.5	12.5
KR 7	85.0	12.0	3.0
KR 9	88.2	10.2	1.6
KR 15	5.3	69.7	25.0

Major cations

The Na, K, and Mg, Ca variations as a function of chlorosity in the Krishna and Godavari estuaries are shown in Figs. 3 and 4 respectively. Na, K and Mg Ca behave conservatively in both estuaries — a behaviour similar to that in Narbada Tapati (Borole, 1980) and in Mahanadi (Ray, Mohanti and Somayajulu, 1984).

The concentrations of Na, K, Mg and Ca are enriched in the freshwater-end-member of Krishna by a factor of 1.9, 1.6, 1.6 and 1.3 respectively over those of Godavari. However, the Mg/Ca ratios in both these end-members are identical, 0.53. The Na/K ratio of Krishna freshwaters is 42.7

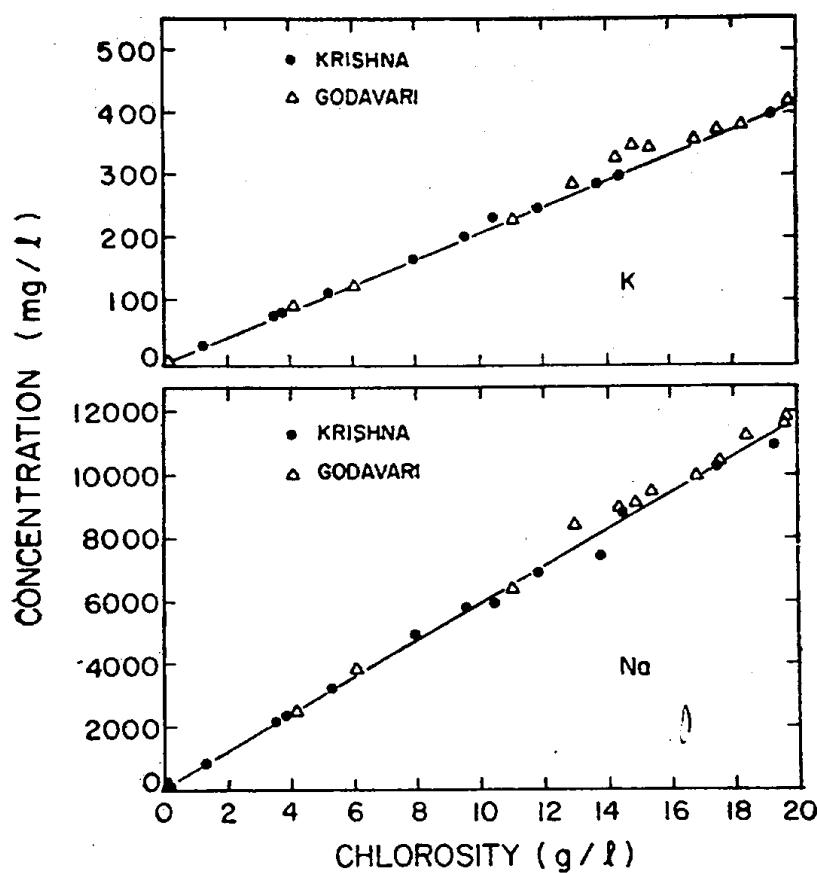


Fig. 3. Na and K concentrations of Krishna and Godavari estuarine waters as a function of chlorosity.

compared to 28.8 of Godavari freshwaters. The higher concentrations of major cations in the Krishna freshwaters is due to more intense weathering of its drainage basin and more evaporation of its water relative to that of Godavari. The relative enrichment of Na over K in the Krishna freshwaters is most likely due to drainage basin chemistry. A salt deposit area was also reported in the Krishna drainage basin. Because of the conservative behaviour of the major cations, we can calculate their fluxes to the Bay of Bengal by multiplying their lowest concentrations measured in the freshwater-end-member ($\text{c } 1 \ll 0.1 \text{ g/l}$) with the discharge. Even the lowest concentrations can be upper limits as sea salts can reach the freshwater regions via atmospheric transport. Since the months May–June comprise non-monsoon period (which can be defined as mid-October to mid-June), we use the data to evaluate the annual non-monsoonal fluxes to the Bay of Bengal. Using the past 14 year monthly discharge data of Krishna and Godavari (UNESCO, 1971) we have estimated that the annual discharges are $6.0 \times 10^{13} \text{ l}$ for Krishna and $1.05 \times 10^{14} \text{ l}$ for Godavari out of which 16.5 and 12.3% are their non-monsoonal discharges viz. $1.0 \times 10^{13} \text{ l/yr}$ from Krishna and $1.3 \times 10^{13} \text{ l/yr}$ from Godavari. The fluxes to the Bay of Bengal from Krishna and Godavari

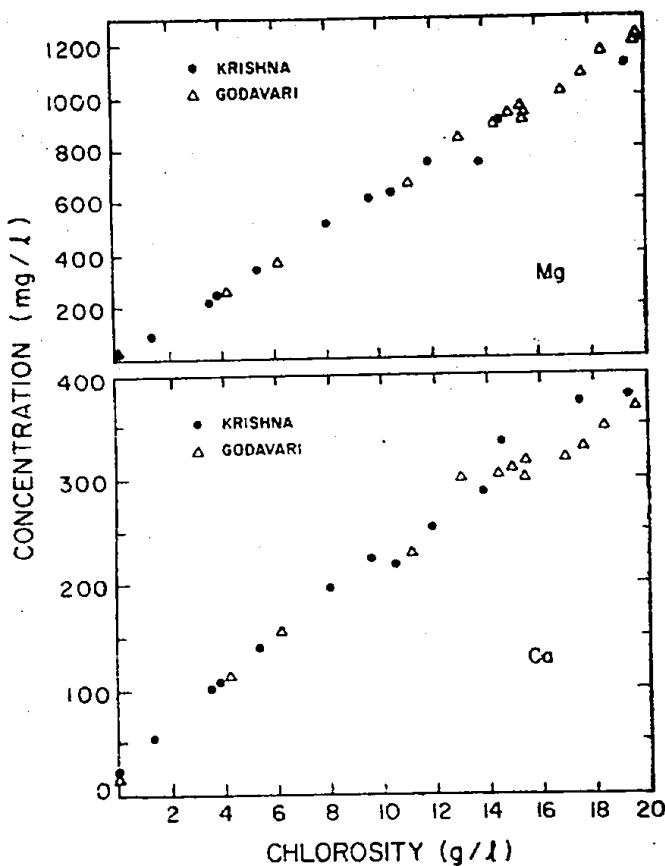


Fig. 4. Mg and Ca concentrations of estuarine waters versus chlorosity.

rivers respectively are 7.4×10^{10} and 8.8×10^{11} g Na/yr, 1.4×10^{10} and 3.0×10^{10} g K/yr, 7.3×10^{11} and 1.0×10^{10} g Mg/yr and 1.4×10^{10} and 1.8×10^{11} g Ca/yr. Though Subramanian (1979) reported major cation concentrations in "Wet monsoon" period of 1977, we could not use them as his K values are high compared to his Na values and his Ca concentrations are also higher than his Mg concentrations — as compared to our data. Our data agrees very well with that compiled by the Central Water and Power Commission which compiled the chemical characteristics of Krishna and Godavari besides several other Indian rivers (CWPC, 1973). More extensive major ion measurements during different months (especially during the monsoon months) are required in the freshwater-end-members of Krishna and Godavari to compute precise annual fluxes from these rivers to the Bay of Bengal.

Silicon

Dissolved Si has been reported to behave both conservatively and otherwise in estuaries (Burton and Liss, 1976). Earlier work on the Godavari (Borole, Krishnaswami and Somayajulu, 1977) and on Mahanadi (Ray Mohanti

and Somayajulu, 1984) showed that Si behaves non-conservatively in these estuaries due to its removal through biological productivity in the form of diatoms. Si versus chlorosity plots for Krishna and Godavari estuaries are shown in Fig. 5. In Krishna Si behaves almost conservatively whereas in Godavari there is 15% removal in the estuary. The reason for Si depletion in Godavari should be, most likely due to diatom formation. Based on the mean-freshwater concentrations and the discharge during non-monsoon season,

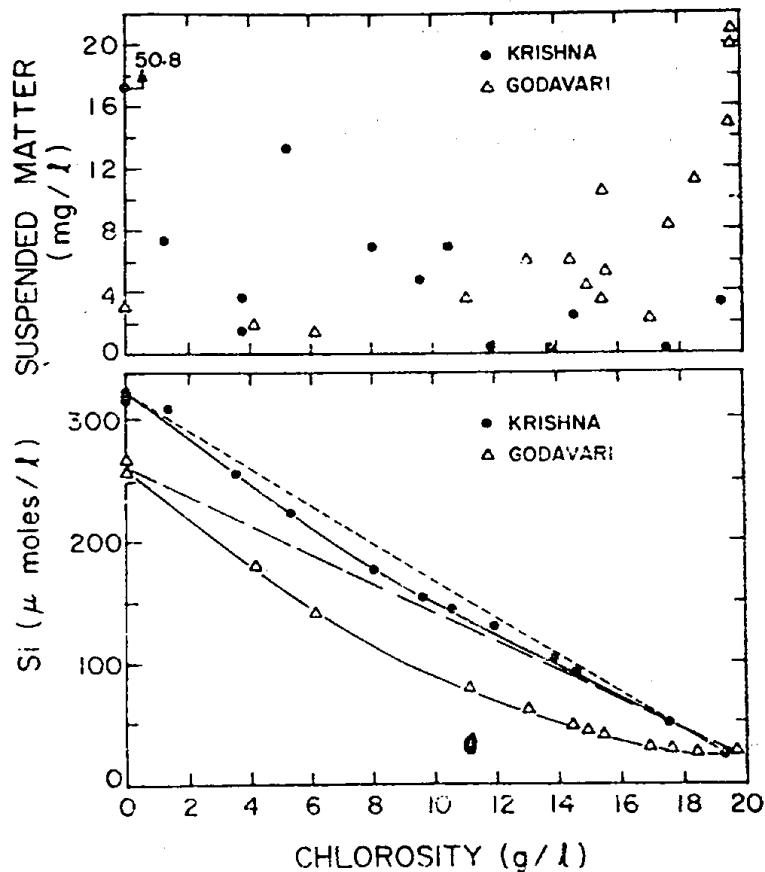


Fig. 5. Suspended matter and dissolved Si concentrations in Krishna and Godavari estuarine waters.

and following the procedure given for major cations, we calculate the non-monsoonal Si flux to the Bay of Bengal to be 5.5×10^{10} g/yr from Krishna and 9.8×10^{10} g/yr from Godavari. There is a 15% removal of dissolved Si in the Godavari estuary which reduces its Si flux to 8.3×10^{10} g/yr. Here again more extensive data during the monsoon period are required. The few Si concentrations reported by Subramanian (1979) for the fresh water-end-member regions of Krishna and Godavari are even higher than our measurements made in summer months which again is unlikely. It should be mentioned here that in general the major ion concentrations in Indian river waters

are low during the monsoon period (Borole, 1980; Ray, Mohanti and Somayajulu, 1984).

Uranium isotopes

The ^{238}U and ^{234}U concentrations as a function of chlorosity in the Krishna estuary are plotted in Fig. 6. In most estuaries so far studied U isotopes behaved conservatively (Borole, Krishnaswami and Somayajulu, 1977, 1982; Martin, Meybeck and Pusset, 1978) except in the highly polluted ones like the Charante estuary in France (Martin, Nijampurkar and Salvadori, 1978). Deviation from conservative behaviour was observed in the very low chlorosity regions ($\leq 1 \text{ g Cl/l}$). In Krishna estuary, even between the region of 1.3 to 19.3 g Cl/l there is a deviation from the conservative behaviour. At the region of 10.5 g Cl/l , the U isotope concentrations are lower

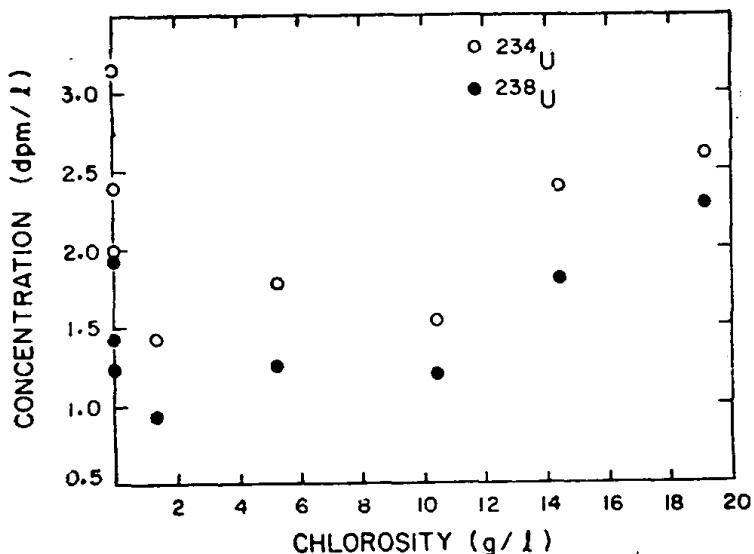


Fig. 6. ^{234}U and ^{238}U concentrations in the Krishna estuarine waters.

than what is predicted by the theoretical mixing line which can be obtained by joining the data points at chlorosites 1.3 and 19.3 g/l . We do not have a satisfactory explanation for the U depletion. In the freshwater regions the U isotope concentrations decreased from 3.16 dpm $^{234}\text{U/l}$ and 1.93 dpm $^{238}\text{U/l}$ at Vijayawada to 2.00 and 1.23 dpm/l at Puligadda without a change in the $^{234}\text{U}/^{238}\text{U}$ activity ratio viz 1.65 ± 0.03 . This means that U is getting authigenically removed from the river water which is due to the presence of reducing environment in the region interspacing the sampling stations Vijayawada and Puligadda. The $^{234}\text{U}/^{238}\text{U}$ activity ratio in fact decreases from 1.63 ± 0.03 in the freshwater region (sample KR-14) to 1.16 ± 0.02 the seawater-end member. The $^{234}\text{U}/^{238}\text{U}$ activity ratio of

1.64 ± 0.02 measured at Vijayawada is identical to that (1.58 ± 0.04 , measured almost 14 years ago at the same location by Bhat and Krishnaswami (1969) who were one of the earliest teams to measure U in river waters. Only their ^{238}U concentration was 0.81 dpm/l which is about a factor of three lower than ours. In the Godavari freshwater region also the present $^{234}\text{U}/^{238}\text{U}$ ratio 1.37 ± 0.15 is identical to the one measured by Bhat and Krishnaswami (1969) viz 1.35 ± 0.03 . Their samples collected in October at the fag end of the SW monsoon showed U concentrations of 0.81 dpm/l in Krishna at Vijayawada compared to our 1.93 dpm/l which is a factor of two higher and 0.51 dpm/l in Godavari at Rajahmundry (compared to our $0.27 \pm 0.03 \text{ dpm/l}$ which is about a factor of two lower).

Taking ^{238}U concentrations of 1.64 mg/l and 0.36 mg/l respectively for the freshwater-end-members of Krishna and Godavari estuaries, we estimate the non-monsoonal U flux to the Bay of Bengal to be 1.6×10^7 and $4.7 \times 10^6 \text{ g/yr}$.

Hydrogen isotopes

The δD values for Krishna and Godavari estuaries (Table I) are plotted as a function of chlorosity in Fig. 7. It is clearly seen that in both these estuaries the δD behaves conservatively. As a matter of fact one should expect δD to be the best index of mixing in estuaries as the stable hydrogen isotopes do not get involved in biogeochemical processes. The δD values essentially depend on the end-member values and on evaporation. Here again evaporation does not significantly affect the running water of the estuary or ocean waters. Freshwater-end-member is the only water body that can get seriously effected evaporation. This can be clearly seen from the data (Fig. 7, Table I). The freshwaters of Godavari at Rajahmundry have a δD of $\sim -12.6\text{\textperthousand}$ whereas those of Krishna at Vijayawada have a δD of $\sim +1.6\text{\textperthousand}$. Since both rivers start at about the same

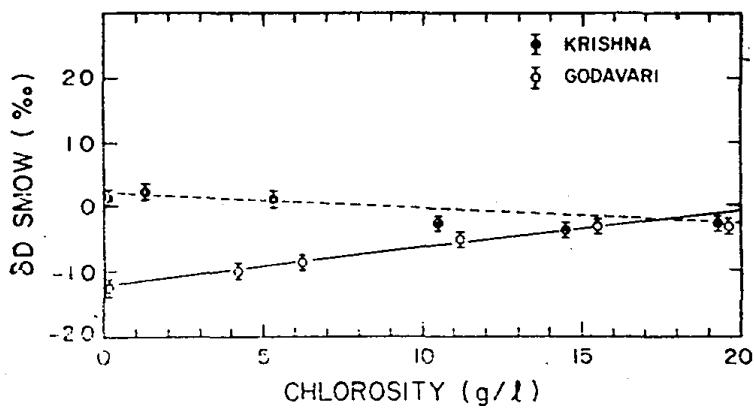


Fig. 7. δD variation with chlorosity in Krishna and Godavari estuarine waters.

region where south-west monsoon dominates with about similar annual rainfall, one can assume that the source waters of Krishna and Godavari rivers to have about the same δD . The increase in Krishna freshwaters by 14.2% over their counter part in Godavari indicates about 15% higher evaporation in the former compared to the latter. The most likely region where this evaporation could have taken place is the Nagarjunasagar dam on Krishna river. As has been mentioned earlier, this higher evaporation of Krishna fresh waters can also account upto 15% enrichment (relative to Godavari freshwaters) of major cations, Si and U in them.

Suspended matter

The suspended matter concentrations ranged from 0.3 to 50.8 mg/l in Krishna waters and 1.5–21.1 mg/l in Godavari waters. Plot of particulate concentrations as a function of chlorosity (Fig. 5) shows in general a decreasing trend with chlorosity in the case of Krishna and the opposite for Godavari. We do not wish to dwell too much on this data except to mention the encountered variations. Using the suspended matter concentrations of 2.5 and 3.3 mg/l respectively for Krishna and Godavari and taking their non-monsoonal discharges the suspended fluxes during the non-monsoon period to the Bay of Bengal are calculated to be 2.5×10^{10} g/yr from Krishna and 4.3×10^{10} g/yr from Godavari. These should be insignificant compared to the monsoonal fluxes of 3×10^{13} g/yr from Krishna and 2.1×10^{14} g/yr from Godavari. The monsoonal suspended fluxes are calculated from the monsoonal discharges (mentioned earlier) and suspended matter concentrations of 600 mg/l for Krishna and 2000 mg/l for Godavari (Subramanian, 1979).

Sediments

As has been mentioned earlier, we have investigated only the Krishna river-estuarine sediments. The sand, silt and clay contents of the sediments are given in Table III. There is no dependence of any of these fractions on the chlorosity of the water from which the sediments are collected, which is as expected. The clay contents vary from 1.4% to as much as 27.5% with a geometric mean of 7.7%.

Based on the thin section studies, heavy minerals amphiboles pyroxenes, garnet, epidote, tourmaline, Sillimanite, biotite, chlorite, Zircon and iron ore are observed. These are expected from the parent rocks of the Krishna drainage basin (Swamy, 1970).

Geochemistry of sediments:

Since clays represent the ultimate river input to the deep sea, besides being the fraction most-suitable for studying sorption reactions, we analyzed Al, Fe, Mn, Cr and Ni concentrations of the clay fractions (Table IV). The Al and Fe concentrations varied from 5.59 to 7.0% and 6.60 to 7.44%

Table IV. Composition of clays separated from Krishna estuarine region.

Sample code.	Concentration						Metal/Al ratio			
	Cl (g/l)	Al (%)	Fe (%)	Mn (ppm)	Cr (ppm)	Ni (ppm)	Fe/Al	Mn/Al x 10 ⁻²	Cr/Al x 10 ⁻³	Ni/Al x 10 ⁻³
KR-1	19.6	6.66	7.25	1036	152.7	103.6	1.09	1.56	2.29	1.65
KR-2	17.64	6.44	7.00	1342	146.3	86.8	1.09	2.08	2.27	1.35
KR-3	15.5	6.61	7.31	994	147.4	98.6	1.11	1.50	2.23	1.49
KR-4	14.35	6.47	7.10	1891	150.3	88.8	1.10	2.92	2.32	1.37
KR-5	11.9	6.76	7.44	1213	160.5	97.0	1.10	1.79	2.37	1.43
KR-7	8.05	6.02	6.60	2114	150.1	102.0	1.10	3.51	2.49	1.69
KR-9	3.67	5.59	6.64	772	126.0	109.2	1.19	1.38	2.25	1.95
KR-15	0	7.00	6.70	718	180.0	86.2	0.96	1.03	2.57	1.23

respectively and show no trends with chlorosity. Ni and Cr are relatively more constant compared to Mn which shows a factor of 3 variations. The metal/Al ratios show more constancy compared to individual concentrations the mean Fe/Al, Cr/Al and Ni/Al ratios are (1.09 ± 0.03) , $(2.35 \pm 0.05) \times 10^{-3}$ and $(1.51 \pm 0.09) \times 10^{-3}$ respectively meaning that whatever sorption reactions are present in the estuary are insignificant ($> 5\%$). Only the mean Mn/Al ratio is $(1.97 \pm 0.32) \times 10^{-2}$ which accounts for the high variation. Mn freshwater sediments get leached by seawater but the irregular distribution of both Mn concentrations as well as the Mn/Al ratios show the complexity of the estuarine basin.

Assuming that the suspended matter in the freshwater-end-member has on an average the same clay content as the estuarine sediments viz 7.7% and that the concentrations of the measured metals in suspended clays are identical to those of the underlying sediments, the metal flux to the deep sea regions of the Bay of Bengal during the non-monsoon period are calculated from the relation.

$$F_m = M_c \cdot F_c \cdot P \cdot D_{n-m}$$

where M_c = metal concentration of clay (g/g)

f_c = fraction of clay in the sediment = 0.077

P = Mean particulate concentration in the freshwater-end-member (g/l)

D_{n-m} = Discharge during the non-monsoon period

$(1.0 \times 10^{13} \text{ l/yr})$.

The annual non-monsoon fluxes are: 1.9×10^9 g clay, 1.4×10^8 g Al, 1.3×10^8 g Fe, 1.4×10^6 g Mn, 3.5×10^5 g Cr and 1.7×10^5 g Ni.

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REFERENCES

Baskaran, M., M.M. Sarin & B.L.K. Somayajulu, 1984. Composition of mineral fractions of the Narbada and Tapti estuarine particles and the adjacent Arabian Sea sediments of Western India, *Chemical Geology*, **45** : 33-51.

Bhat, S.G. & S. Krishnaswami, 1969. Isotopes of uranium and radium in Indian rivers, *Proceedings of the Indian Academy of Sciences*, **70** : 1-17.

Bigeleisen, J., M.L. Periman & H.C. Prosser, 1952. Conversion of hydrogenic materials to hydrogen for isotopic analysis, *Analtical Chemistry*, **24** : 1356-1357.

Borole, D.V. 1980. Radiometric and trace elemental investigations on Indian estuaries and adjacent seas. *Ph.D. thesis*, Gujarat University, 155 pp.

Borole, D.V., S. Krishnaswami and B.L.K. Somayajulu, 1977. Investigations on dissolved uranium, silicon and particulate trace elements in estuaries. *Estuarine & Costal Marine Science*, **5** : 743-754.

Borole, D.V., S. Krishnaswami and B.L.K. Somayajulu, 1982. Uranium isotopes in rivers, estuaries and adjacent coastal sediments of Western India: their weathering, transportation and oceanic budget, *Geochimica et Cosmochimica Acta*, **46** : 125-137.

Borole, D.V., M.M. Sarin and B.L.K. Somayajulu, 1982. Composition of of Narbada and Tapti estuarine particles and adjacent Arabian Sea sediments, *Indian Journal of Marine Sciences*, **11** : 51-62.

Boyle, E., E. Collier, A.T. Dengler, J.M. Edmond, A.C. Ng and R.F. Stallard, 1974. On the chemical mass balance in estuaries, *Geochimica et Cosmochimica Acta*, **38** : 1719-1728.

Burton, J.D. and P.S. Liss, 1976. Estuarine Chemistry, Academic Press, London, 229 pp.

CWPC, 1973. Geochemical investigations of River waters of India. CWPC Press, New Delhi, 85 pp.

Craig, H., 1961. Standard for reporting concentrations of deuterium and oxygen — 18 in natural waters, *Science*, **133** : 1833-1834.

Elbaz — Pouliche, F., W.W. Huang, J. Jednacak-Biscan, J.M. Martin and A.J. Thomas, 1982. Trace metal behaviour in the Gironde estuary: the problem revisited, *Thalassia Jugoslavica*, **18** : 61-95.

Fukai, R., C.N. Murray and L. Huygh — Nogoc, 1973. Interaction between suspension and seawater as a possible regulating mechanism for trace elemental concentration in near shore water — A Preliminary Report, *Thalassia Jugoslavica* **9** : 33-37.

Galehouse, J.S., 1971. Sedimentation analysis, In : *Procedures in sedimentary petrology*, Ed. by R.E. Carver, Wiley Interscience, New York pp. 69-94.

Krishnamurthy, R.V., 1984. Stable isotope studies on sedimentary deposits and groundwaters and their climatic implications. *Ph.D. thesis*, Gujarat University 127 pp.

Martin, J.M., V.N. Nijampurkar and F. Salvadori, 1978. Uranium and thorium isotopes behaviour in estuarine systems, In: *Biogeochemistry of Estuarine sediments* Ed. E.D. Goldberg, UNESCO Publication, Paris. 111-127.

Martin, J.M., M. Meybeck and M. Pusset, 1978. Uranium behaviour in Zaire estuary, *Netherlands Journal of sea Research* **12**: 338-344.

Martin, J.M. and M. Meybeck, 1979. Elemental mass balance of material carried by World major rivers, *Marine Chemistry*, **7**: 173-206.

Martin, J.M. & R. Letolle, 1979. Oxygen 18 in estuaries, *Nature* **282**: 292-294.

Martin, J.M. and M. Whitfield, 1983. The significance of the river input of chemical elements to the ocean, In: *Trace Metals in seawater*, Ed. C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg, Plenum Publishing corporation, New York p. 265-196.

Milliman, J.D. and R.H. Meade, 1983. World-wide delivery of river sediment to the oceans, *Journal of Geology* **91**: 1-21.

Morris, A.W., R.F.C. Mantoura, A.J. Bale and R.J.M. Howland, 1978. Very low salinity regions of estuaries: important sites for chemical and biological reactions, *Nature*, **274**: 678-679.

Naidu, A.S., 1966. Lithological and chemical facies changes in the recent deltaic sediments of the Godavari river, India. In: *Deltas in their geological frame work*, Ed. M.L. Shirley, Houston Geological Society Publication, USA p. 125-157.

Rao, K.L., 1975. Indias water wealth, Orient Longman, New Dehi, 255 pp.

Ray, S.B., M. Mohanti & B.L.K. Somayajulu, 1984. Suspended matter, major cations and dissolved silicon in the estuarine waters of the Mahanadi River, India, *Journal of Hydrology*, **69**: 183-196.

Sarin, M.M., 1983. Chemistry of major elements and U-Th series nuclides in Indian rivers. *Ph.D. thesis*, Gujarat University, 183. pp.

Sarin, M.M. and S. Krishnaswami, 1984. Major ion chemistry of the Ganga-Brahmaputra river systems, *Nature*, **312**: 312-315.

Siddiquie, H.N., 1967. Recent sediments of the Bay of Bengal, *Marine Geology*, **5**: 249-291.

Strickland, J.D.H. & T.R. Parsons, 1972. A practical handbook of seawater analysis, Fisheries Research Board of Canada Bulletin No. 161.

Subramanian, V., 1979. Chemical and suspended sediment characteristics of Rivers of India, *Journal of Hydrology*, **44**: 37-55.

Swami, A.S.R., 1970. Studies on some aspects of the modern deltaic sediments of the Krishna River, India, *Ph.D. thesis*, Andhra University.

Turekian, K.K., 1971. Rivers, tributaries and estuaries, In: *Impingment of Man on oceans*, Ed. D.W. Hood, Wiley Interscience, New York, 9-73.

Turekian, K.K., 1974. Heavy metals in estuarine systems, *Oceanus*, **18**: 32-33.

Turekian, K.K., 1977. The fate of metals in estuaries, In: *Estuaries Geophysics and the environment*, National Academy of Sciences, Washington DC, 127 pp.

Unesco Paris, 1971. Discharge of selected rivers of the world Vols. II and III.

