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GEOCHEMICAL DISPERSION OF URANIUM IN THE SEDIMENTS OF KRISHNA DELTA AND ITS OFFSHORE REGION, EAST COAST OF INDIA*

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ABSTRACT

The uranium content is estimated in the clay fraction ($<4\mu$) of the sediments of river channel (fresh water), estuary, tidal creek and marine environments of the Krishna Delta. Its dispersion pattern in various environments and sub-environments is discussed in relation to montmorillonite, organic matter, phosphate and copper contents of the sediments. Physico-chemical conditions of the environments and organic matter appear to play a greater role in the fixation of uranium than montmorillonite.

INTRODUCTION

THE study of modern deltaic sediments is in its infancy in India. The distribution pattern of sedmiments in the Godavari Delta has been studied by Naidu (1968). Swamy (1970) has taken up the study of various aspects of the modern deltaic sediments of the Krishna River. In continuation of the above study and with a view to understand and establish reliable physico-chemical and biological factors that operate and control the concentrations of various elements, the present work on the Krishna Delta has been undertaken by the authors.

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The Krishna River is one of the largest rivers in India with a drainage area of 2,52,500 sq. km. The maximum discharge of the river at Vijayawada is estimated to be about 1,19,390 sec^3 (Khosla, 1951). The major geological formations drained by the river and its tributaries are the Deccan Traps, unclassified Crystallines and Cuddapahs. A low dam (anicut) was constructed at Vijayawada. The present investigation covers the river bed from a point 15 km upstream from the anicut to the river-confluence (115 km) and offshore region of the Krishna Delta (Fig. 1).

METHODS

A number of sediment samples were collected using La Fond-Dietz snapper from the river channel and the tidal creek during the pre-flood season (March to May). The core samples (about one metre in length) from the offshore region were obtained during the 18th scientific cruise aboard the "INS Kistna" during the International Indian Ocean Expedition programme in the year 1964.

Clay fractions of less than 4 microns in size were separated from 48 sediment samples by the standard sedimentation techniques (Krumbien and Pettijohn, 1938)

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and were analysed for uranium, copper, phosphate and organic matter. The methods of analyses are given in Table 1.

TABLE 1. *Methods of Analyses*

Constituents	Analytical Technique	Method of analysis followed (Ref.)
Uranium	Flurometer (Jarrel-Ash, G. M. Type) Mark V	Geier and Holland (1957)
Copper	Colorimeter	Sandell (1950)
Total phosphate	Klett-Summerson photoelectric colorimeter	Rochford (1951)
Organic matter	Volumetric	Allison (1935)

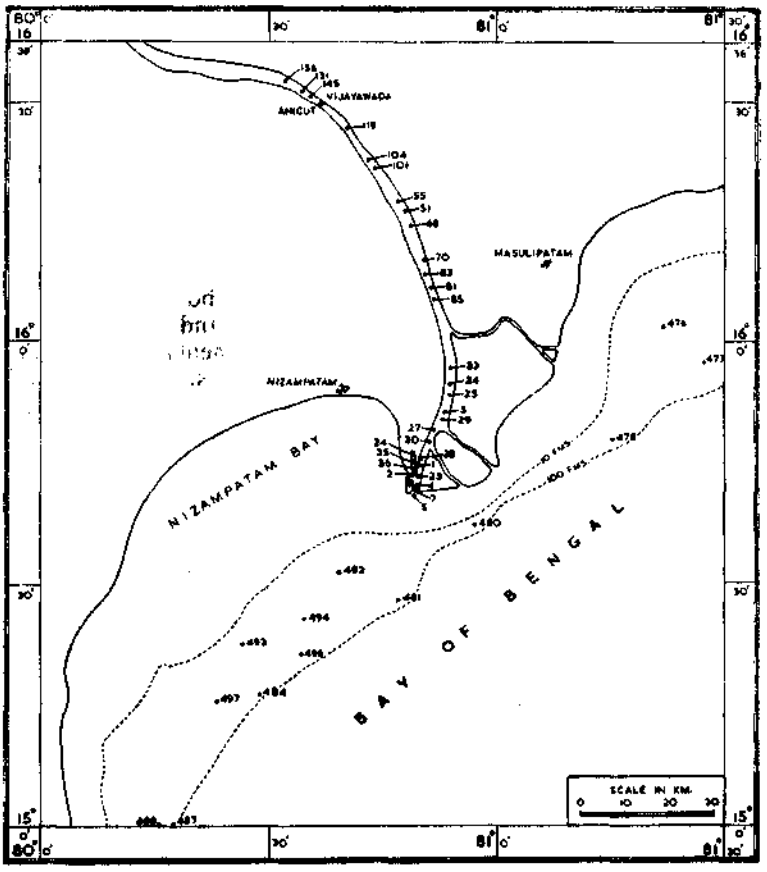

Fig. 1. Location of samples in different environments of the Krishna delta.

RESULTS

The results of the analyses are presented in Table 2. The uranium content averages 1.8 ppm in the fresh water sediments above the anicut and increases downstream upto a distance of 25 km. On an average, the concentration of uranium is 1.2 ppm in fresh water sediments downstream (0-65 km) from anicut and 0.76 ppm

TABLE 2. *Concentrations of Uranium, Copper, Phosphate and organic matter*

Sample No.	Uranium ppm	Copper ppm	Phosphate %	Organic matter %
River channel (above anicut)				
156	2.0	428	0.022	0.240
145	1.7	342	0.029	0.669
131	1.8	464	0.041	0.712
River channel (Below anicut)				
119	0.3	338	0.044	0.887
104	0.7	374	0.031	0.620
101	0.9	590	0.048	1.008
55	1.8	386	0.042	1.242
51	0.3	448	0.040	1.081
48	1.8	484	0.035	0.618
70	0.6	428	0.035	1.124
83	2.4	424	0.041	1.379
81	2.4	360	0.044	0.742
85	0.8	644	0.047	0.707
Estuary				
33	0.6	560	0.038	0.831
26	0.3	382	0.033	1.008
25	0.5	334	0.042	0.926
3	0.3	334	0.045	0.804
29	1.0	528	0.038	1.008
27	1.5	432	0.033	0.646
30	1.4	430	0.033	1.230
38	0.9	334	0.033	0.617
1	1.7	462	0.037	0.920
23	0.3	422	0.024	0.710
4	0.6	320	0.051	0.455
7	0.3	534	0.038	0.543
5	0.5	374	0.044	0.331
Tidal creek				
24	1.8	416	0.049	1.285
35	2.3	428	0.039	0.728
36	3.9	392	0.041	0.764
2	1.4	372	0.055	0.694
Marine				
476 T	2.1	210	0.043	1.395
B	0.3	300	0.027	1.101
477 T	0.9	250	0.045	1.637
B	0.9	276	0.034	1.450
478 T	0.6	236	0.033	1.016
480 T	0.3	386	0.035	1.114
B	1.2	400	0.042	0.847
481 T	0.9	448	0.042	0.847
B	1.8	62	0.035	0.727
482 T	1.7	248	0.038	1.041
494 T	0.6	250	0.052	0.896
B	0.6	316	0.038	0.950
496 T	0.9	278	0.043	1.041
493 T	0.3	604	0.035	1.040
484 T	3.6	574	0.031	1.428
497 T	4.8	202	0.026	0.910
488 T	1.4	224	0.021	1.403
487 T	0.3	284	0.055	1.692

T - top, B - bottom.

in the estuary. The average concentration in the regions of head (9 km), middle (12 km) and mouth (5 km) of the estuary are 0.42, 1.30 and 0.37 ppm respectively. The variation of uranium with distance in the estuary is shown in Fig. 2. The highest concentration of uranium averaging 2.33 ppm is observed in the tidal creek sediments. In the marine environment, the content of uranium on an average is 1.5 ppm, in the top and 0.96 ppm in the bottom portions of the cores. There seems to be on systematic and significant variation of uranium either with the length of the core or with the depth of collection. There appears to be some amount of lateral variation in the marine environment lower at the mouth of the river and higher on either side of the mouth. Scatterplots of uranium versus organic matter, phosphate and copper are shown in Fig. 3.

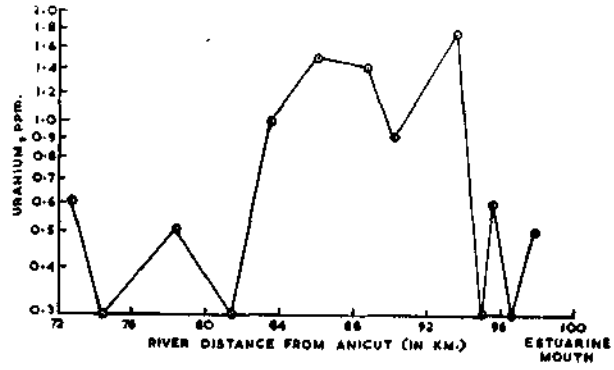

Fig. 2. Variation in the concentration of uranium with distance in the Krishna Estuary.

The uranium content in the offshore region of the Krishna Delta is lower in comparison with its counter-part, the Godavari Delta (2.0 to 6.1 ppm; Naidu, 1968). It is to be noted that the values of uranium (1.3 ppm) in the clays of the Indian Ocean obtained by Starik *et al.* (1958) are comparable to those from the offshore region. There is no significant variation in the montmorillonite distribution in the various environments of the Krishna Delta.

DISCUSSION

The distribution of uranium during transport and sedimentation is related to the processes of oxidation and reduction, cation exchange, solubility of the salts, coprecipitation, presence of humic acids, aqueous regime (in relation to time) and finally the water exchange environment (Ginzburg, 1960).

The dispersion of uranium in relation to the other constituents of the sediments of the various sub-environments *viz.*, the impounded water sediments, the zone just below the anicut, estuary (head, middle and mouth), tidal creek and marine environments of the delta are discussed.

The concentrations of uranium (1.8 ppm) and copper (412 ppm) in the sediments of the impounded water upstream are slightly higher in comparison with those in the areas downstream of the anicut and estuary. This may be due to the selective assimilation and adsorption of uranium and copper on the clays. This is promoted further by the pH (neutral to slightly acidic) of the waters and longer contact of the water with the sediments (large aqueous regime). This pH condition of water

prevents the phosphate from settling, as is indicated by the low phosphate content. This is in agreement with the observation of Ronov and Korzina (1960) in their studies on phosphorus in sedimentary rocks.

The variation of phosphate concentration in the river channel is not significant. Its behaviour is more similar to uranium in the tidal creek though no relationship is evident between them (Fig. 3). On the otherhand, iron and phosphate seem to be related perhaps forming ferriphosphate (Swamy, 1970).

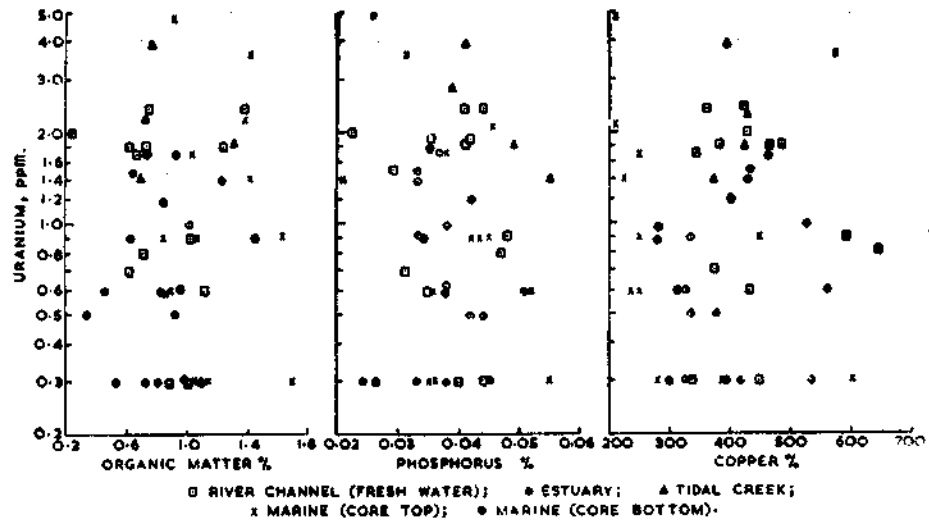

Fig. 3. Scatter plots of uranium vs organic matter, phosphorus and copper.

The uranium, in the clay fraction, immediately downstream of the anicut is affected by the rapidity of the flow of water which in turn affects the aqueous regime, resulting in the lesser adsorption by the clays. There is a gradual increase of uranium and organic matter contents in the estuary from head to middle portions and a decrease towards the mouth (Fig. 2). This may be attributed to the more stabilised conditions in the flow of water at the head and middle portions. The decrease towards the mouth may be due to the relative disturbance at the mouth, eventhough there is no significant change in the organic matter. The covariation of organic matter with uranium (Fig. 3) suggests that uranium in this zone is being fixed in the sediments by the organic matter and not so much by the clay minerals.

The relationship between uranium and copper in the estuarine zone, tidal creek and marine environments is not significant. Uranium, organic matter and phosphate are high and copper low in the tidal creek, compared to the upper reaches of the estuary. This indicates that uranium is increasingly being adsorbed by organic matter in preference to copper. This is so because the greater amount of indigenous humic matter derived from micro and macro organisms and plant material fixes uranium by a process of cation exchange (Szalay, 1958; Vine *et al.*, 1958). This fact is further supported by a covariation of organic matter with uranium and a corresponding negative relation with copper. This observation of a negative relationship of copper with organic matter is contrary to the observed data

elsewhere (Goldberg and Arrehenius, 1958; La Riche, 1959). On the other hand, copper seems to be associated with hydroxides of manganese and iron (Swamy,1970). The low content of uranium opposite to the river mouth is attributable to the higher rate of sedimentation which interferes with the process of adsorption. In the region to the south of the mouth, the uranium content is high although the organic matter content is about the same. This is surmised to be due to the area having a lower rate of sedimentation, in general, the transportation of the river sediments in this area is towards northeast (Sewell, 1925).

Fixation of uranium in the sediments is mainly due to the physico-chemical factors like adsorption, pH, aqueous regime and organic matter. The role of montmorillonite does not seem to be significant.

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DISCUSSION

V. CHALAPATHI RAO: What is the nature of relationship between dissolved organic matter and Uranium concentration in waters?

A. S. R. SWAMY: The relationship of dissolved organic matter and Uranium has not been brought out. The estimation of Uranium was carried out in the clay fraction ($< 4\mu$) of the sediments.

K. C. PILLAI: I like to know what is the method used for Uranium estimation? I feel it is necessary to decompose the sample completely. Nitric acid extraction alone may not be sufficient.

A. S. R. SWAMY: Sample ($<4\mu$) was separated from the bulk sediment by settling sedimentation method (Knubiam and Pettijohn, 1938). The clay sample was digested in the HF (48%) with phosphoric acid. After complete digestion the sample is brought into the 1.3 H NO_3 medium. The 5 ml sample ('B' solution) was taken and Uranium is extracted with Aluminium Nitrate and ethyl acetate. 'U' was estimated by Flurometer (Janet Ash, G. M. type, Mark V, by the method given by Geier and Holland, 1957).

B. L. K. SOMAYAJULU: I have a comment to make and that is regarding the state of Uranium in water. It exists in both + 4 and + 6 value states; in sea water especially in the + 6 state as Uranyl carbonate complex. When there is organic matter, it is found in the reduced state in which state it gets quickly removed to the sediments. Hence one should expect high concentrations of Uranium in sediments having large amounts of organic matter.

A. K. DATTA: Whether any correlation has been attempted between organic matter distribution and dispersion of Uranium.

A. S. R. SWAMY: There is covariance between organic matter and Uranium in the deltaic sediments of the Krishna River. Uranium is high in the tidal creek sediments where organic matter is also high. They are positively related.

B. L. K. SOMAYAJULU: A second comment I would like to make. This concerns with the measurement of Uranium activity ratio i. e. $\frac{U^{234}}{U^{238}}$. As shown by Bhat and Krishnaswami $\frac{U^{234}}{U^{238}}$ activity ratio varies significantly in river waters and river mouths. Along with U the $\frac{U^{234}}{U^{238}}$ activity ratio should be measured to have better understanding of the problem.

K. C. PILLAI: I want to add one more thing to what Dr. Somayajulu said. It also depends on the carbonate content in waters.

S. N. SENGUPTA: In Petroleum exploration, the problem of source rocks remains unsolved as yet. Abundance of Uranium in the sediments, its correlation with fossil organic matter and also with distribution of oil or gas accumulation, may be of interest.

D. LAL: Why did you choose Uranium as an indicator trace element? It would be better if you would also include salinity measurements in your interesting studies.

A. S. R. Swamy: I have determined the elements Fe, Mn, Ti, P, Na, K, Ca, Mg, Cu, Ni, B, and U in the clay fraction of the Krishna delta sediments. There is no special reason in choosing this element as a trace element indicator, but we have tried to find an anology between U content and environment of deposition.