

**RADIOCHEMICAL DETERMINATION OF URANIUM
AND STUDIES OF
 $^{234}\text{U}/^{238}\text{U}$ AND $^{235}\text{U}/^{238}\text{U}$ ACTIVITY RATIOS
IN ESTUARINE SEDIMENTS OF MINDOLA RIVER**

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Measurements carried out recently with surface labile layers of the estuarine sediments have indicated remarkable dis-equilibrium between ^{234}U and ^{238}U activities. The $^{234}\text{U}/^{238}\text{U}$ activity ratios on the surface of the sediments collected from Mindola estuary of Gujarat State in India have been found to vary in the range of 1.12 to 1.43 while $^{235}\text{U}/^{238}\text{U}$ activity ratios lie in the range of 0.045. On removing the labile layers and leaching uranium from the core of the sediment particles gave an equilibrium ratio of 1.00 for $^{234}\text{U}/^{238}\text{U}$. There is however no change in the activity ratios of $^{235}\text{U}/^{238}\text{U}$.

Introduction

The increasing concern in recent years about the pollution of the aquatic environment by radio-nuclides has resulted in extensive studies of naturally occurring radio-isotopes in sediments.

During the last few years, workers have studied the anomalous behaviour of uranium isotopes in sea water,¹ fossil corals,^{2,3} deep sea sediments,⁴ and coastal sediments⁵ but there is not much information available on the ratio of activities of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ on surface labile layers of estuarine sediments. Earlier workers had used chemical methods which involved chemical attack on the mineral body of the sediments. However, it is difficult to explain the ratios of activities in sea water and the ratios obtained with the sediments by earlier workers on the basis of the geochemical equilibrium processes between the estuarine sediments and the ambient water.

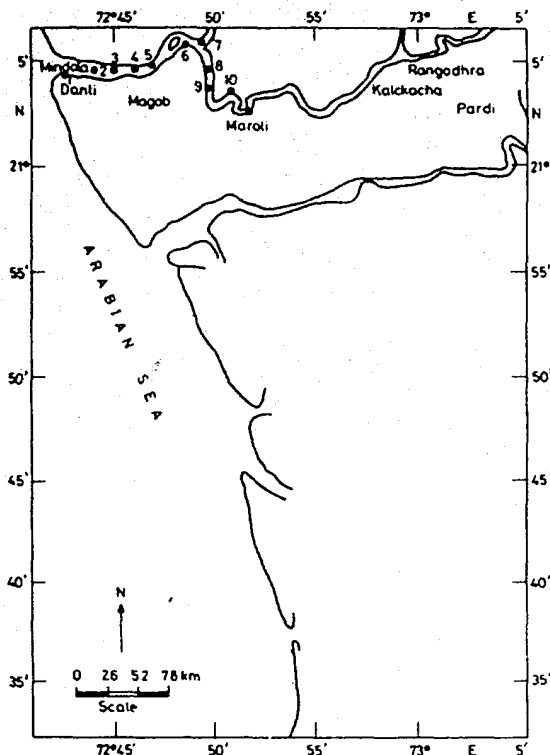


Fig. 1. Sampling locations in Mindola River (Gujarat State)

Mindola river is narrow in fresh water zone and broadens appreciably in the mouth region. Its course through south Gujarat State of India is in east-west direction until it joins the Arabian Sea. The rapid industrialization of Surat city and adjoining areas has resulted in the disposal of wastes from various industrial units into Mindola river either directly or through creeks which join the river in the estuarine and fresh water regions. This has given rise to a large variations in the suspended load from 10 mg/l to 1000 mg/l. Most of the added radioisotopes to the sediment surface lie on the surface labile layers of the sediments.

Sample collection

The sediment samples from Mindola river are collected from top surface layers at each sampling location. A number of samples are collected from nearby regions of

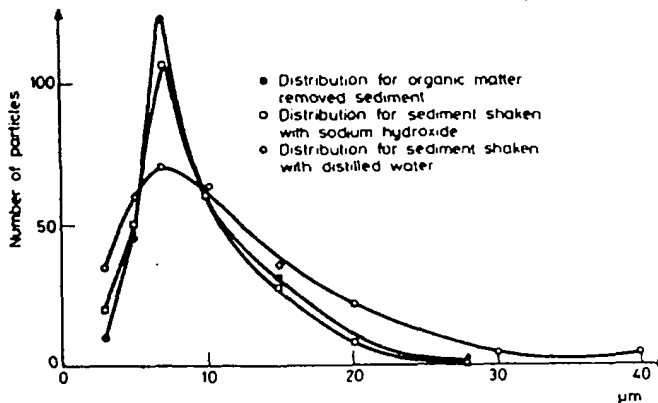


Fig. 2. Particle size distribution for sediments from Mindola

each sampling station. These sediment samples are pooled together and used as a representative sample of the respective station. These samples are air-dried. Fig. 1 gives the sampling locations at the Mindola river.

Experimental

Particle size determination of the sediment particles

The sediment samples collected from Mindola river are suspended in de-ionized water. The pH of the solution is adjusted to 9.0 by dropwise addition of sodium hydroxide. The solution is then shaken for 4 hours. The particle suspension is transferred to a 0.22 μm membrane filter. The filter paper is dried in air and a drop of emulsion oil is added to the filter paper. The size of the sediment particles and the number frequency are determined microscopically. Fig. 2 gives particle size distribution for the estuarine sediments collected from Mindola River.

The difference in the distribution indicates the agglomerates that are present in the particles, which do not get dispersed in neutral medium.

Leaching of surface labile layer of the sediment particles:

The dried sediment samples (150 g each) are leached with 400 ml saturated ammonium carbonate solution for 8 hours. The sediment particles are allowed to settle overnight. The solution is filtered through a 0.22 μm membrane filter. The sediment is

again leached with another aliquot of 400 ml saturated ammonium carbonate solution. The procedure is repeated four times. The filtrates are pooled together and evaporated to dryness. The residue is gently heated with 5 ml aliquots of concentrated hydrochloric acid to drive off ammonia. The residue is finally heated in a muffle furnace at 450 °C. It is then dissolved in 10 ml of 8 N hydrochloric acid.

Removal of iron from the solution

The solution in 8N hydrochloric acid containing iron is shaken with 10 ml of di-isopropyl ether for five minutes in a separating funnel. The organic and inorganic layers are allowed to separate in the funnel. The organic layer containing iron is removed. The procedure is repeated three times to remove the last traces of iron. The aqueous layer is evaporated to dryness and again dissolved in 10 ml of 8N hydrochloric acid.

Ion-exchange separation of uranium

The anion-exchange resin, Bio-rad AG-1 X 8 (100–200 mesh) is washed with distilled water to remove the fine particles. 10 g of the resin is then loaded in pyrex glass columns (1X25 cm).

Column operations

(a) The anion-exchange resin is pretreated with 50 ml of 8N hydrochloric acid passing at a flow rate of 0.5 ml/min.

(b) The sample containing uranium is passed through the resin at a flow rate of 0.5 ml/min. Uranium is sorbed on the resin and the effluent is rejected.

(c) The resin is washed with 30 ml of 8N hydrochloric acid at a flow rate of 1.0 ml/min and the effluent is rejected.

(d) Uranium is eluted from the resin by passing 100 ml of 0.5 N hydrochloric acid at a flow rate of 0.5 ml/min. The effluent is evaporated to dryness.

The purified uranium obtained in chloride form is converted to nitrate form by heating the dried mass with 1.0 ml portions of concentrated nitric acid. Uranium is electro-deposited on a stainless steel disc one inch in diameter.

Alpha counting of uranium isotopes:

The plated uranium samples are counted for alphas in a silicon surface barrier detector (active area 200 mm², depletion depth 700 μm) coupled to a low noise amplifier, a pre-amplifier and 256 channel analyser.⁶ The alpha particle background is

negligible over long periods of time. The counting efficiency is 24% for weightless samples plated on stainless steel discs. The resolution of the detector is 4.3 keV full width at halfmaximum (FWHM) at 5.108 MeV alphas of ^{208}Po . The uranium samples are counted for 1000 min in order to get satisfactory counting statistics.

Results and discussion

Table 1 gives the activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ on the surface labile layers of the estuarine sediment samples collected from Mindola river. Fig. 3 gives disequilibrium between ^{238}U and ^{234}U in the estuarine sediment sample collected from Mindola river. The activity ratios of $^{234}\text{U}/^{238}\text{U}$ are obtained in the range of 1.12 to 1.43 while the activity ratio of $^{235}\text{U}/^{238}\text{U}$ is close to 0.045, which is the same as that for natural uranium.

Significant variations in the activity ratios of $^{234}\text{U}/^{238}\text{U}$ are observed from the samples collected from different sampling locations in Mindola River. However, these variations in the activity ratios existing on the surface labile layers of the sediments get masked when special care is not taken in analytical chemical procedure to avoid attacking the mineral core of the sediment particles.

Estuaries are the most important regions to mankind. The use and production of radio-nuclides will continue to increase. Some of these isotopes will never reach the open sea but will accumulate instead in estuaries. The estuarine organisms play the dominant role in transporting the radioactive contaminants from shallow water areas to man since these regions are important to commercial fisheries because they serve as nursery areas for larval and immature forms. It is therefore necessary to understand the geochemical processes occurring in these regions.

Table 1
Activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in estuarine sediments of Mindola river

Place of collection	^{238}U , dpm	^{235}U , dpm	^{234}U , dpm	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$
Mindola (1)	0.94	0.04	1.05	1.12	0.04
Mindola (2)	0.86	0.04	0.98	1.14	0.04
Mindola (3)	0.87	0.04	1.01	1.16	0.04
Mindola (4)	0.80	0.03	1.02	1.28	0.04
Mindola (5)	0.77	0.03	0.97	1.26	0.04
Mindola (6)	0.75	0.03	0.90	1.20	0.04
Mindola (7)	0.83	0.03	1.13	1.36	0.04
Mindola (8)	0.78	0.03	0.95	1.22	0.04
Mindola (9)	0.76	0.03	0.99	1.30	0.04
Mindola (10)	0.82	0.03	1.17	1.43	0.04

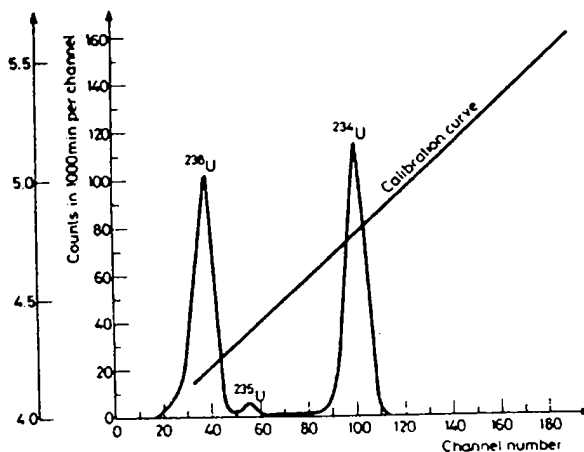


Fig. 3. Disequilibrium between ^{238}U and ^{234}U in estuarine sediment from Mindola river

The radioisotopes reach the rivers through land run-offs. Some of these radio-nuclides are picked up by organisms and finally get deposited in estuaries. The variations in the activity ratios of $^{234}\text{U}/^{238}\text{U}$ in estuarine region indicate that there is fractionation between ^{238}U and ^{234}U . However, there is no fractionation between ^{238}U and ^{235}U .

In the weathering processes, ^{234}U atoms are more likely to be oxidized to hexavalent state forming more soluble uranyl ions. It is assumed that uranyl ions are loosely bound in structure than U(IV) , the former being able to exchange with dissolved form in water. Two recoil mechanisms have also been suggested for this type of exchange,^{7,8} thereby explaining the dis-equilibrium between ^{238}U and ^{234}U .

Destruction of surface organic layer of sediment particle:

150 g Mindola estuarine sediment is treated with 400 ml of 0.05 N hydrochloric acid. A few drops of phosphate-free hydrogen peroxide are added to it and the solution is gently stirred for eight hours to destroy the surface organic matter from the sediment particles. The hydrochloric acid extract after this treatment is filtered through a $0.22\ \mu\text{m}$ membrane filter and the filtrate is used for the radiochemical analysis of uranium isotopes. The core of the sediment particles thus obtained after destruction of organic matter, is leached with a saturated solution of ammonium carbonate to extract uranium isotopes. Uranium is chemically separated using an anion-exchange resin and then counted for alphas of uranium isotopes as detailed

Table 2
Activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in the surface organic
layers and in the core of the particles
after 0.05 N HCl + H₂O₂ treatment

Sample, No.	Place of collection	Sample	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$
1.	Mindola (1)	Surface organic layer	1.12	0.04
2.	Mindola (1)	Core of the particles	1.00	0.04
3.	Mindola (2)	Surface organic layer	1.14	0.04
4.	Mindola (2)	Core of the particles	0.99	0.04
5.	Mindola (6)	Surface organic layer	1.20	0.04
6.	Mindola (6)	Core of the particles	1.01	0.04

earlier. Table 2 gives the ratios of activities of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in the surface organic layers and in the core of the sediment particles from Mindola estuary.

The activity ratio of $^{235}\text{U}/^{238}\text{U}$ in the surface organic layer and in the core of the particles is 0.045, which is the same as the theoretical value of this ratio, indicating thereby that there is no fractionation between ^{235}U and ^{238}U . However, the $^{234}\text{U}/^{238}\text{U}$ activity ratio is greater than 1.0 in the organic layer while it is close to 1.0 in the core of the particles. It can be stated from the results of these measurements that uranium present in the estuarine regions exhibits disequilibrium between ^{238}U and ^{234}U only on the surface of the particles and as surface organic matter from the particles is removed, the core of the particles shows equilibrium activity. This behaviour of uranium isotopes is the same as that observed in the coastal sediments.

This work has been found to be useful in understanding the geochemical behaviour of uranium isotopes in the estuarine regions. Since, estuarine regions accumulate both radioactive and stable isotopes, they become nursery grounds for contamination of living resources of the region. These isotopes also enter into the Arabian Sea. A detailed study of the geochemical processes has to be undertaken in different regions of the Indian subcontinent particularly those areas of the Marine environment which are close to highly industrialized cities.

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