

Nuclear Methods in Environmental Science

ANOMALOUS BEHAVIOUR OF URANIUM ISOTOPES
IN BACKWATER SEDIMENTS OF ZUARI RIVER

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The surface leaching of the labile component of uranium has been carried out in estuarine sediments of Zuari river in Goa. The measurements of alpha activities of ^{238}U , ^{235}U and ^{234}U in the leachates indicated a remarkable anomaly between the activities of ^{238}U and ^{234}U . The activity ratios of $^{234}\text{U}/^{238}\text{U}$ in these leachates have been found to be in the range of 1.10 to 1.14. However, the activity ratios of $^{235}\text{U}/^{238}\text{U}$ have been found to be 0.045 which is close to that in natural uranium. It has also been observed that the anomaly between ^{238}U and ^{234}U exists only on the surface organic layers of the backwater sediments of the Zuari river.

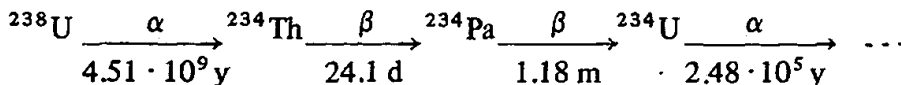
Introduction

During the past few years increasing interest has been shown in the studies of pollution of the marine environment due to the addition of naturally occurring radioisotopes by land runoff and by atmospheric fallout.

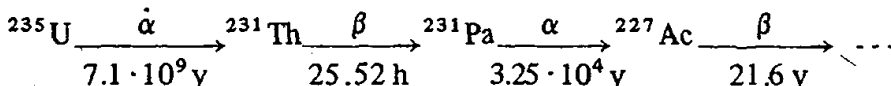
The long-lived, naturally occurring isotopes of uranium, e.g., ^{238}U , and ^{234}U belong to the uranium series and ^{235}U belongs to actinium series.

The parts of the two decay chains of uranium and actinium series are as given below:

Uranium series:



Actinium series:



Recently, several workers have studied disequilibrium between ^{238}U and ^{234}U in sea water, deep sea sediments etc. but very little information is available on the activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in backwater sediments, particularly from the backwater regions of India. THURBER¹ determined activity ratios of $^{234}\text{U}/^{238}\text{U}$ in Pacific waters as 1.15 while UMEMOTO² determined the activity ratios of $^{234}\text{U}/^{238}\text{U}$ in the range of 1.17–1.18 in Sagami Bay Pacific water. KU³ had observed the activity ratios of $^{234}\text{U}/^{238}\text{U}$ in the range of 0.95–1.04 in the deep sea sediments of Atlantic and Pacific oceans. JOSHI and GANGULY⁴ determined activity ratios of $^{234}\text{U}/^{238}\text{U}$ in coastal sediments of the west coast of India. The chemical methods used by earlier workers involved total destruction of the sediment particles by acid digestion. It is therefore difficult to explain the activity ratios of $^{234}\text{U}/^{238}\text{U}$ in the sediments on the basis of geochemical equilibrium processes between the sediments and water. In the present work, the backwater sediments have been leached with saturated ammonium carbonate solution for the extraction of the surface labile uranium present on the sediment particles.

Zuari river is one of the important rivers in the region for transportation of ores from the inland mines to the Marmagoa harbour. It is comparatively narrow in the fresh water zone and is sufficiently broad in the mouth region which connects to the Arabian sea on the west coast of India. Extensive mining for iron and manganese ores in the catchment areas has resulted in heavy land runoff in the estuarine and fresh water regions of the river. In the present study the trapped organic matter has all been assumed as deposited on the surface layers of the mineral core of the sediments. The total calcareous matter determined by CO_2 evolution on treatment with 0.05N hydrochloric acid has been observed to be <5% by weight. On dissolution of the calcareous matter, the organic matter released is extracted with dilute ammonium hydroxide. The extract is observed to be <5% of the total organic matter present in the sediments. Most of the radioisotopes present in the marine environment are added to the surface organic layers of the sediments and get concentrated on the surface of the ocean floor.

Sample collection

The backwater sediment samples are collected from top surface layers at each sampling station marked in Fig. 1. A number of samples from nearby areas are collected from each sampling station. These sediment samples are pooled together and then used as a representative sample of each sampling station. The samples are air-dried in aluminium trays.

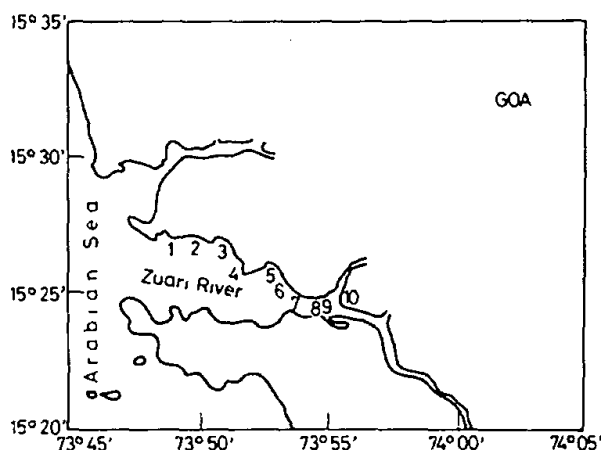


Fig. 1. Map showing locations of sampling stations on Zuari river (Goa)

Experimental

Surface leaching of uranium

Uranium has a great tendency to form two stable anionic complexes with carbonate ions, the dicarbonate, $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$ and the tricarbonate, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. The tricarbonate complex of uranium is more stable in presence of excess of carbonate ions.

300 g of air-dried sediments are shaken with 4 instalments of 800 ml of saturated solution of ammonium carbonate for 8 hrs, using a mechanical shaker. The sediment particles are allowed to settle overnight. The supernate is filtered through $0.22 \mu\text{m}$ membrane filter. The filtrate is evaporated to dryness.

Destruction of ammonium carbonate

The dried mass is treated with 5 ml of concentrated hydrochloric acid and 10 ml of distilled water and the mass is gently heated to drive off ammonium salts. The residue is cooled and then treated with 2 ml portions of concentrated hydrochloric acid and evaporated to dryness. The procedure is repeated four times. The residue is then heated in a muffle furnace at 450°C . It is then dissolved in 10 ml of 10% nitric acid.

Uranium separation by column chromatography

- (1) Pyrex glass column (2x40 cm) is filled with a 3% ether-nitric acid mixture.
- (2) Cellulose powder is added to this column so that the cellulose powder height in the column is 8 cm.

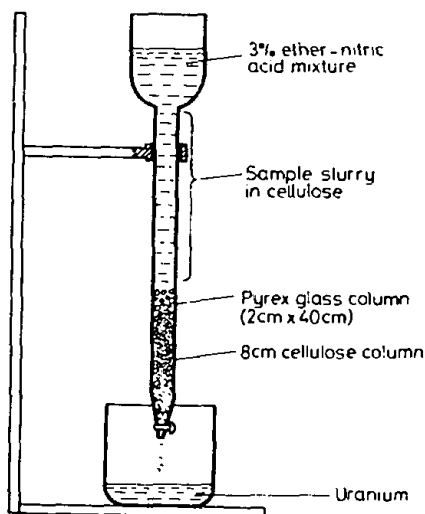


Fig. 2. Cellulose column for the separation of uranium

(3) Cellulose powder is added to 10 ml of 10% nitric acid solution containing uranium. The powder is thoroughly mixed with the sample solution and the slurry is added to the cellulose column, above 8 cm layer of the cellulose powder.

(4) 250 ml of a 3% ether – nitric acid mixture is passed through the column at a flow rate of 2 ml/min. Uranium passes through the column and is collected in the effluent.

Ether in the effluent is carefully evaporated and uranium is further purified. Fig. 2 gives the diagrammatic representation of the cellulose column for the separation of uranium.

Purification of uranium

The residue containing uranium is dissolved in 2 ml of 8% nitric acid. 10 ml of saturated solution of aluminium nitrate is added to it and equilibrated with 10 ml of ethyl acetate for 2 min. The organic layer containing uranium is separated from the aqueous layer. Uranium is then stripped with water. The water extract is finally evaporated to dryness.

Electrodeposition of uranium

The dried residue containing uranium is dissolved in 1.2 ml of 0.001M nitric acid and transferred to a plating cell. To this solution, 1.2 ml of saturated ammonium oxalate solution and 2.6 ml of double distilled water are added and after stirring the solution with platinum anode rod, a current of 150 mA is passed at 6 volts for about an hour at 78 °C. The plating efficiency obtained by this method is about 70%.

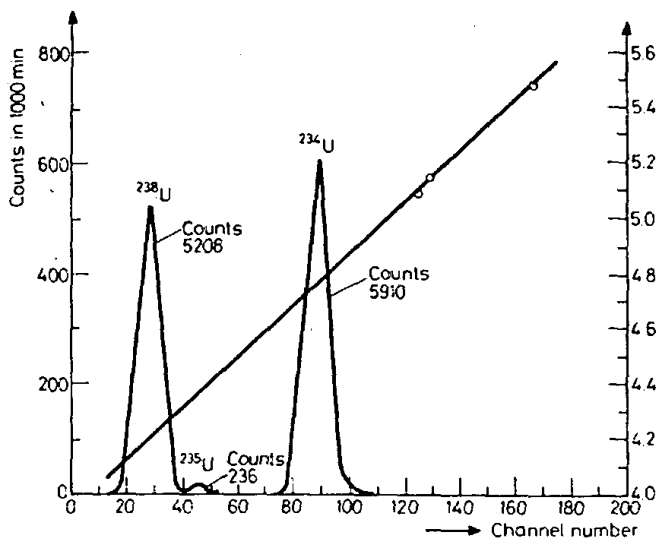


Fig. 3. Disequilibrium between ^{238}U and ^{234}U in sediment sample from Zuari river (Goa)

Counting of uranium

The electrodeposited samples of uranium are counted in a partially depleted silicon surface barrier detector (active area 200 mm^2 and a depletion depth of $700\ \mu$) coupled to a low noise amplifier, a pre-amplifier and 400 channel analyser. The diameter of the detector is 15.96 mm and it is mounted inside a brass vacuum chamber. The resolution of the detector is 43.4 keV full width at half-maximum (FWHM) at 5.108 MeV and 5.477 MeV alphas of ^{208}Po and ^{241}Am , respectively. The counting efficiency is 24%. The counting time is set at 1000 min for each of the samples in order to obtain satisfactory counting statistics. The samples usually accumulate $3 \cdot 10^3$ to $10 \cdot 10^3$ counts under the ^{238}U and ^{234}U peaks giving a standard deviation of 1–2%. However, the counts in ^{235}U peak gives a standard deviation of 5–7%. Fig. 3 gives alpha spectrum of uranium indicating disequilibrium between ^{238}U and ^{234}U in a backwater sediment sample collected from Zuari river.

Results and discussion

Zuari river in Goa is the major waterway for transportation of mined ores from its interland of Goa to Marmagao harbour. Due to accidental spillage during loading and unloading of ores and also because of the land runoffs, the riverine and estuarine sediments are contaminated. Besides the mixing of the waters of the Arabian Sea with the waters of the Zuari river which has a wide mouth near Marmagao Port results in the mixing of the sediments even in the backwater areas. The sampling was carried out in such way that these represent broadly in the backwater region but at the same

Table 1
 $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ activity ratios in the backwater
 sediment surface of Zuari river

Place of collection	^{238}U dpm	^{235}U , dpm	^{234}U , dpm	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$
Zuari (1)	18.38	0.84	20.62	1.12	0.046
Zuari (2)	13.78	0.62	15.56	1.13	0.045
Zuari (3)	18.06	0.82	20.41	1.13	0.045
Zuari (4)	17.41	0.79	19.81	1.14	0.045
Zuari (5)	19.70	0.89	22.36	1.13	0.045
Zuari (6)	18.01	0.83	20.16	1.12	0.046
Zuari (7)	16.58	0.75	18.24	1.10	0.045
Zuari (8)	17.85	0.81	19.81	1.11	0.045
Zuari (9)	17.87	0.81	19.66	1.10	0.045
Zuari (10)	19.94	0.91	22.72	1.14	0.046

time they represent the areas of mixing of waters of the Zuari river with that of the Arabian sea.

Table 1 gives the activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ on the surface organic layers of the sediment particles. The activity ratios of $^{234}\text{U}/^{238}\text{U}$ are found to vary in the range of 1.10 to 1.14 indicating that there is disequilibrium between ^{238}U and ^{234}U on the surface layers of the particles. This increase of 10 to 14% in ^{234}U over ^{238}U is close to the increase obtained in sea water by several investigators in different sea water samples of the world. Although, there is mixing of waters of Zuari river and that of Arabian Sea, the ratios of the activities of $^{234}\text{U}/^{238}\text{U}$ in the backwater regions of Zuari river are close to those obtained in the coastal sediments of the west coast of India (JOSHI, GANGULY⁵).

This increase in activity ratios of $^{234}\text{U}/^{238}\text{U}$ may be attributed to recoil mechanisms suggested for the exchange between ^{238}U and ^{234}U . During the decay of ^{238}U , the daughter ^{234}U atoms are more likely to be oxidized to hexavalent state forming more soluble uranyl ions than the parent ^{238}U . CHERDYNTSEV⁶ suggested that ^{234}U is relocated by recoil at crystal defects, where it becomes more labile. ROSHOLT et al.⁷ and DOOLEY et al.⁸ pointed out that recoil energy during radioactive transformation is sufficient to break the chemical bonds and ^{234}U is stripped of two of its electrons as a result of the recoil. Thus, ^{234}U ends up preferentially as hexavalent uranium.

Removal of the organic layer on the surface of the sediments

In order to obtain the sediment particles free from organic matter present on their surface, 300 g of each of the sediment sample is treated with 800 ml of 0.05N hydrochloric acid and phosphate-free hydrogen peroxide. The acid extract is filtered through 0.22 μ membrane filter and the filtrate is used for the separation of uranium by cellulose column chromatography. The sediment remained behind after removal of

Table 2
 $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in surface organic layers
 and in organic matter free sediments

Sample No.	Place of collection	Sample	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$
1.	Zuari (4)	Surface organic layer	1.14	0.045
2.	Zuari (4)	Organic matter free sediment	1.00	0.045
3.	Zuari (5)	Surface organic layer	1.13	0.046
4.	Zuari (5)	Organic matter free sediment	0.99	0.045
5.	Zuari (8)	Surface organic layer	1.11	0.046
6.	Zuari (8)	Organic matter free sediment	1.01	0.046

surface organic matter is leached with saturated solution of ammonium carbonate for the extraction of uranium. It is then separated by cellulose column chromatographic method.

Table 2 gives the activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in the surface organic layers and in organic matter free sediments.

It has been observed from the results of the experiment that there is disequilibrium between ^{238}U and ^{234}U in the acid-hydrogen peroxide extract of the sediment, while equilibrium is obtained between ^{238}U and ^{234}U in the organic matter free sediment. It can therefore be said that disequilibrium exists only on the surface of the sediment particles and have the same ratio as in the ambient sea water. However, the ratio of $^{235}\text{U}/^{238}\text{U}$ is 0.046 in the acid-hydrogen peroxide extract as well as in the organic matter free residue indicating that there is no disequilibrium between ^{238}U and ^{235}U .

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